

**SYNTHESIS, CHARACTERIZATION AND REACTIVITY OF IMIDO
CHROMIUM(VI) COMPLEXES**

by

Pengcheng Wu

A dissertation submitted to the Faculty of the University of Delaware in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Chemistry and Biochemistry

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ABSTRACT

This dissertation describes research on imido chromium(VI) complexes. The relative instability of the highest oxidation state and the weaker metal-bonds of the first-row metal generally make for sparse organometallic chemistry of hexavalent chromium. The motivation of my research is to make high valent chromium complexes supported by imido ligands and explore their reactivity in C-H activation, olefin metathesis and the activation of other small molecules (e.g. PhNCO, CO₂).

Chapter 1 describes the syntheses of bis(arylimido) chromium(VI) complexes, (ArN)₂CrR₂ (Ar = 2,6-diisopropylphenyl, R = CH₂SiMe₃, Ph, 4-tolyl, 2,6-dimethylphenyl, 3,5-dimethylphenyl and 2,4,6-trimethylphenyl, aka mesityl). The corresponding Grignard reagents were employed in alkylations or arylations of the starting material (ArN)₂CrCl₂ to make each complex. Bis(imido) bis(phenyl) chromium was prepared through arylation by triphenylaluminum, AlPh₃. The thermostability of these chromium(VI) dialkyls and diaryls has been studied.

Chapter 2 describes the synthesis and reactivity of chromium(VI) alkylidenes. Three of them, namely (ArN)₂Cr(=CHCMe₃)(PPh₃), (ArN)₂Cr(=CHSiMe₃)(PPh₃) and (Et₄N)[(ArN)₂Cr(=CHSiMe₃)(CH₂SiMe₃)] have been structurally characterized. Transient neopentylidene [(ArN)₂Cr(=CHCMe₃)], which is generated by α -hydrogen abstraction, is able to do C-H bond activation of alkanes, [2+2] cycloaddition with alkenes, and N-H activation of *tert*-butylamine. Unusual chromium(IV) complexes were formed via C-H bond activation of cyclohexane. These results are attributed to β -hydrogen elimination of intermediate (ArN)Cr(CH₂CMe₃)(Cy). [2+2] cycloaddition

with alkenes afforded chromacyclobutanes, which are key intermediates in olefin metathesis. Trimethylsilylmethylidene THF adduct $(\text{ArN})_2\text{Cr}(=\text{CHSiMe}_3)(\text{THF-d}_8)$ also shows reactivity in C-H bond activation of alkanes.

Chapter 3 describes the synthesis and reactivity of tris(imido) chromium(VI) complexes, including both neutral and ionic compounds. $\text{K}[(^t\text{BuN})_3\text{CrCl}]$ was prepared by deprotonation of $(^t\text{BuN})_2\text{Cr}(\text{NH}^t\text{Bu})\text{Cl}$ by $\text{KN}(\text{SiMe}_3)_2$. The tris(imido) anion undergoes nucleophilic substitution by PPh_3 and $^t\text{BuNH}_2$ to form $(^t\text{BuN})_3\text{Cr}(\text{PPh}_3)$ and $(^t\text{BuN})_2\text{Cr}(\text{NH}^t\text{Bu})_2$, respectively. $(^t\text{BuN})_2\text{Cr}(\text{NH}^t\text{Bu})_2$ loses one amido hydrogen to form $\text{K}[(^t\text{BuN})_3\text{Cr}(\text{NH}^t\text{Bu})]$ when it is treated with $\text{KN}(\text{SiMe}_3)_2$. The imido ligands of $\text{K}[(^t\text{BuN})_3\text{CrCl}]$ as well as $(^t\text{BuN})_3\text{Cr}(\text{PPh}_3)$ are attacked by electrophile MeI to produce $(^t\text{BuN})_2\text{Cr}(\text{NMe}^t\text{Bu})\text{Cl}$ and $(^t\text{BuN})_2\text{Cr}(\text{NMe}^t\text{Bu})\text{I}$, respectively. An alternate way to make tris(imido) anion is deprotonation of $(^t\text{BuN})_2\text{Cr}(\text{NH}^t\text{Bu})\text{Cl}$ by alkyl lithium reagent, $\text{Me}_3\text{SiCH}_2\text{Li}$. The corresponding product $\text{Li}[(^t\text{BuN})_3\text{CrCl}]$ can be alkylated by a second equiv. of $\text{Me}_3\text{SiCH}_2\text{Li}$ to form $\text{Li}[(^t\text{BuN})_3\text{Cr}(\text{CH}_2\text{SiMe}_3)]$. Reactivity studies of tris(imido) complexes show cycloaddition with PhNCO or CO_2 to form metallacycles.

Chapter 1

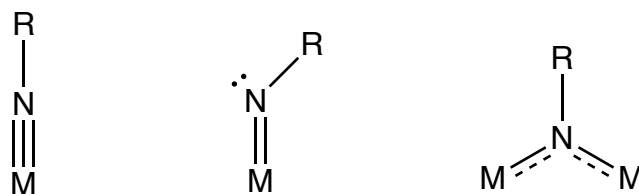
SYNTHESIS AND CHARACTERIZATION OF BIS(ARYLIMIDO) CHROMIUM(VI) COMPLEXES

1.1 Introduction

Imido ligands (RN^{2-}) are widely used as spectator (or ancillary) ligands in high valent transition metal chemistry.¹⁻³ The formal charge of this type of ligand is -2. When the lone-pair electrons on nitrogen are donated to a metal center, the imido ligand is considered a $1\sigma, 2\pi$ donor. As a result, the M-N-C linkage is close to linear in crystal structures and linearity is generally considered a reflection of triple bond character of the M-N bond. For example, structural characterization of $\text{OsO}_3(\text{NAd})$ showed a linear imido bond ($171.4(4)^\circ$).⁴ However, a linear M-N-C linkage is not always an indication of a triple bond between the metal center and the imido ligand. (e.g. it seems unlikely for a “20-electron” osmium complex, namely $\text{Os}(\text{NAr})_3$ ($\text{Ar} = 2,6\text{-diisopropylphenyl}$), while all three imido ligands are actually in linear configuration based on the structural parameters.⁵ When the lone pair of electrons remains localized on N, the imido ligand behaves as a $1\sigma, 1\pi$ donor. A few $1\sigma, 1\pi$ -donor examples of bent imido ligands are known. The classic one is found in the structure of $(\text{PhN})_2\text{Mo}(\text{S}_2\text{CNEt}_2)_2$, which has one bent ($\text{Mo-N-C}: 139.4(4)^\circ$) and one linear ($\text{Mo-N-C}: 169.4(4)^\circ$) imido ligand.⁶

Generally, the coordination geometry of an imido ligand is classified as linear when the M-N-C angle is between 180° and 150° and bent when between 150° and 130° .⁷ In addition to terminal binding, imido could also be a bridging ligand in

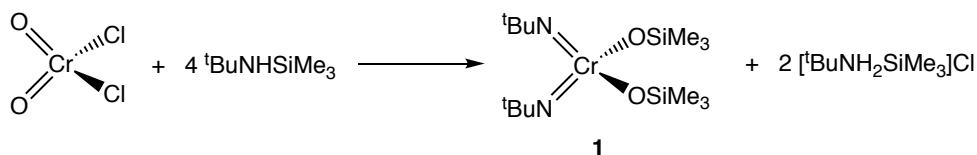
inorganic chemistry.⁸ Scheme 1.1 shows these three different coordination modes of imido ligand.



Scheme 1.1 The coordination modes of imido ligands in metal complexes

1.1.1 Development of Bis(imido) Chromium(VI) Chemistry

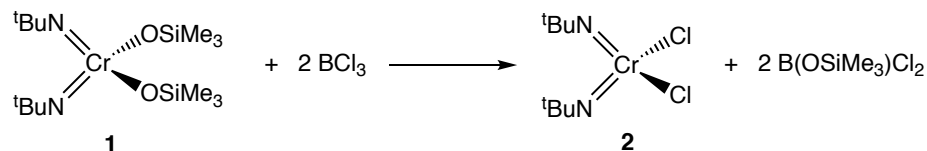
The first transition metal imido complex, namely (^tBuN)OsO₃, was made by Milas et al in 1959.⁹ 20 years later, its structure was determined by X-ray crystallography.¹⁰ In 1980, Nugent introduced the *tert*-butylimido ligand to chromium(VI) chemistry. The first bis(imido) chromium(VI) complex, (^tBuN)₂Cr(OSiMe₃)₂ (**1**), was prepared by adding *tert*-butyl(trimethylsilyl)amine to chromyl chloride (CrO₂Cl₂) in hexane solution. (Scheme 1.2)¹¹



Scheme 1.2 Synthesis of bis(imido) chromium(VI) siloxide (**1**)

Arylation of **1** was reported by Wilkinson et al in 1988. **1** reacted with Grignard reagent mesMgCl (mes = 2,4,6-trimethylphenyl, aka mesityl) to form

chromium diaryl complex (^tBuN) $_2\text{Cr}(\text{mes})_2$.¹² However, alkylation of **1** was unsuccessful. Reaction of **1** with alkyl Grignard reagents or alkyl lithium reagents gave mixtures of reduced products. Both Schaverien and Wilkinson explored synthesis of bis(imido) chromium halides (^tBuN) $_2\text{CrX}_2$ ($\text{X} = \text{Cl}, \text{Br}$), which are suitable for alkylation.¹³⁻¹⁴ Wilkinson's procedure was applied in the preparation of starting material (^tBuN) $_2\text{CrCl}_2$ (**2**) for the research presented in this dissertation, because the product from this procedure is easier to isolate and purify than the product from Schaverien's procedure. (Scheme 1.3)

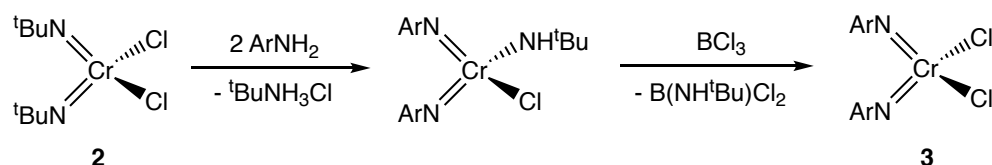


Scheme 1.3 Wilkinson's procedure to make (^tBuN) $_2\text{CrCl}_2$ (**2**)

A number of bis(imido) bis(alkyl) chromium complexes of the type (^tBuN) $_2\text{CrR}_2$ ($\text{R} = \text{CH}_2\text{CMe}_3$, CH_2SiMe_3 , $\text{CH}_2\text{CMe}_2\text{Ph}$, $o\text{-(CHSiMe}_3)_2\text{C}_6\text{H}_4$) lacking β -hydrogen were prepared by Schaverien from (^tBuN) $_2\text{CrX}_2$ ($\text{X} = \text{Cl}, \text{Br}$).¹³ Another bis(alkyl) complex, namely (^tBuN) $_2\text{Cr}(\text{CH}_2\text{Ph})_2$, was reported by Gibson via alkylation of **2**. Due to the better crystallinity of (^tBuN) $_2\text{Cr}(\text{CH}_2\text{Ph})_2$ than that of other dialkyls, the first crystal structure of a bis(imido) chromium dialkyl was published as well. (^tBuN) $_2\text{Cr}(\text{CH}_2\text{Ph})_2$ features both η^1 and η^2 coordination modes of the benzyl ligands.¹⁵

Most chromium dialkyls with *tert*-butylimido ligand are reported to be oils, which makes structural characterization and further study difficult.¹³ In general,

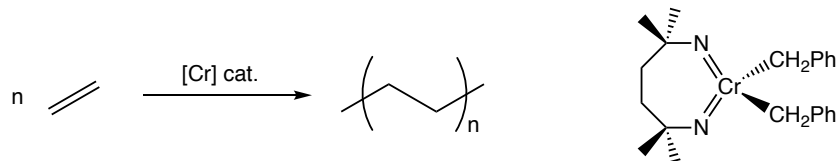
arylimido ligands are helpful to improve crystallinity of organometallic complex. Accordingly, Gibson brought this type of ligand to chromium(VI) chemistry. The synthesis of $(\text{ArN})_2\text{CrCl}_2$ (**3**) is shown in Scheme 1.4.¹⁶ Three dialkyls, namely $(\text{ArN})_2\text{CrR}_2$ ($\text{R} = \text{CH}_3$ (**4**), CH_2Ph (**5**), CH_2CMe_3 (**6**)), were made from **3** reacting with the corresponding Grignard reagents.¹⁷⁻¹⁸ **6** was unstable in solution. It underwent α -H abstraction to form the first Cr(VI) alkylidene moiety $(\text{ArN})_2\text{Cr}(=\text{CHCMe}_3)\text{L}$ ($\text{L} = \text{THF}, \text{PMe}_3$).¹⁷ This reaction will be discussed in more details in **Chapter 2**.



Scheme 1.4 Synthesis of $(\text{ArN})_2\text{CrCl}_2$ (**3**), reported by Gibson in 1995

1.1.2 Applications of Bis(imido) Chromium Complexes

In recent years there has been increasing interest in the search for new-generation olefin polymerization catalyst.¹⁹ Gibson found that $(\text{tBuN})_2\text{Cr}(\text{CH}_2\text{Ph})_2$ is a catalyst precursor for ethylene polymerization. Upon abstracting one benzyl ligand from the chromium center by $(\text{Ph}_3\text{C})[\text{B}(\text{C}_6\text{F}_5)_4]$, the corresponding cationic alkyl complex $[(\text{tBuN})_2\text{Cr}(\text{CH}_2\text{Ph})]^+$ is able to catalytically polymerize ethylene (ca. 2 – 3 atm).^{15,18} Siemeling reported that a chromium dibenzyl complex chelated by a di(organoimido) ligand, namely $(\text{NCMe}_2\text{CH}_2\text{CH}_2\text{CMe}_2\text{N})\text{Cr}(\text{CH}_2\text{Ph})_2$, is also able to serve as a catalyst precursor for the polymerization of ethylene as well as its derivative acrylonitrile.²⁰⁻²¹



Scheme 1.5 Left: ethylene polymerization catalyzed by the bis(imido) chromium catalyst; Right: the structure of $(\text{NCMe}_2\text{CH}_2\text{CH}_2\text{CMe}_2\text{N})\text{Cr}(\text{CH}_2\text{Ph})_2$.

Based on prior work, this chapter focuses on the synthesis of new chromium dialkyls and diaryls supported by two 2,6-diisopropylphenyl imido ligands.

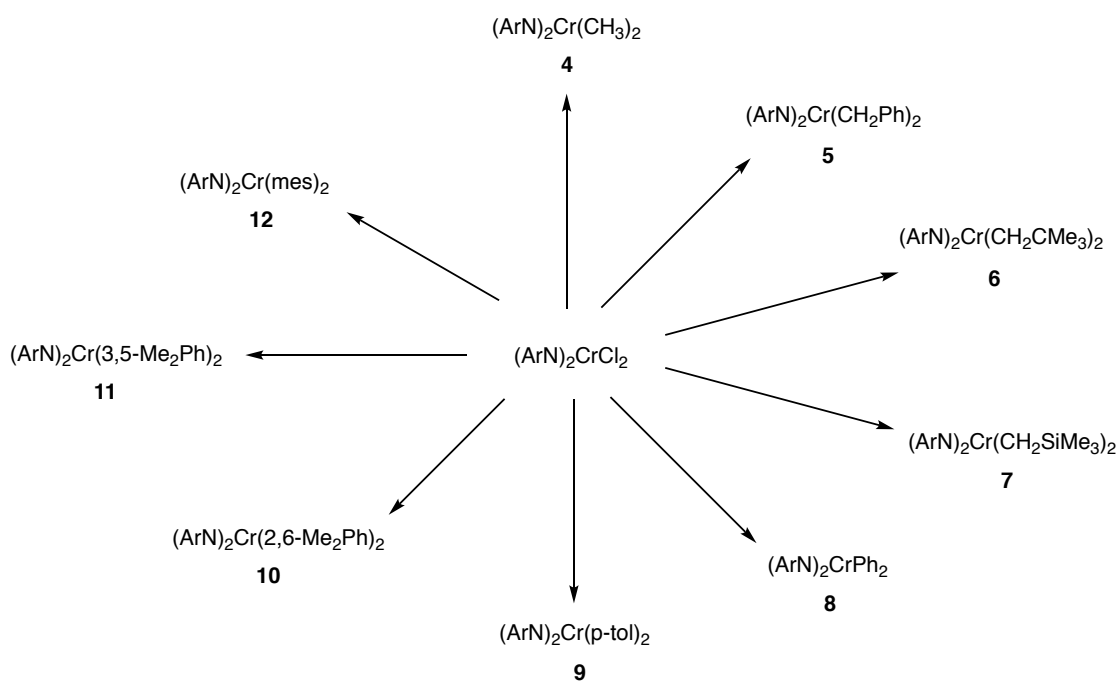
1.2 Results and Discussion

1.2.1 Synthesis and Characterization

Three chromium(VI) dialkyls of the type $(\text{ArN})_2\text{CrR}_2$ (Ar = 2,6-diisopropylphenyl, R = CH_3 (**4**), CH_2Ph (**5**), CH_2CMe_3 (**6**)) had been synthesized by Gibson through alkylation of **3** with the corresponding Grignard reagents.¹⁷⁻¹⁸ Following Gibson's procedure, one new chromium(VI) dialkyl and five diaryls, namely $(\text{ArN})_2\text{CrR}_2$ (Ar = 2,6-diisopropylphenyl, R = CH_2SiMe_3 (**7**), 4-tolyl (**9**), 2,6-dimethylphenyl (**10**), 3,5-dimethylphenyl (**11**) and mesityl (**12**)), were synthesized by alkylation or arylation of **3**, except $(\text{ArN})_2\text{CrPh}_2$ (**8**), which was made from **3** with AlPh_3 (Scheme 1.6). All these complexes have similar green colors in solution. Considering that hexavalent chromium does not have d-electrons, the green color cannot be a result of d-d transitions or metal to ligand charge transfer (MLCT). Accordingly, this green color is attributed to ligand to metal charge transfer (LMCT).

The aforementioned preparations of chromium dialkyls are limited to hydrocarbyl ligands lacking β -hydrogens, due to facile β -hydrogen elimination of hexavalent chromium alkyls.^{22,30} In contrast, molybdenum and tungsten provide some

complexes with β -hydrogens, namely $\text{Mo}(=\text{O})_2(\text{CH}_2\text{CH}_3)_2(\text{bpy})$ and $\text{W}(=\text{O})_2(\text{CH}_2\text{CH}_3)_2(\text{bpy})$, which were structurally characterized.²³⁻²⁴ Alkylation of $(\text{mesN})_2\text{CrCl}_2$ with EtMgBr to make $(\text{mesN})_2\text{Cr}(\text{CH}_2\text{CH}_3)_2$ yielded reduced product $(\text{mesN})\text{BrCr}(\mu\text{-Nmes})_2\text{CrBr}(\text{Nmes})(\text{PMe}_3)$ in the presence of PMe_3 .²⁵ My attempt at making bis(2,6-diisopropylphenylimido) chromium(VI) diethyl was also unsuccessful. After addition of EtMgCl into the solution of **3** at $-78\text{ }^\circ\text{C}$, the color slowly changed from red to green, which is the expected color. However, the green color changed to brown upon warming the reaction mixture to room temperature. The product of this reaction was intractable in my hands. Attempts at crystallization of crude product did not generate any crystal that could be used for structural characterization.



Scheme 1.6 Alkylation and arylation of **3**. See details in the Experimental section.

Among previously prepared **4**, **5** and **6**, only **6** had been structurally characterized. Crystallization of **4** was unsuccessful due to its high solubility in pentane. However, a single crystal of **5** that was suitable for X-ray diffraction was grown from pentane solution at -30 °C over a couple of days. The crystal structure of **5** is depicted in Figure 1.1 and the corresponding interatomic distances and angles are listed in Table 1.1. **5** features pseudo-tetrahedral coordination geometry with two short Cr-N bonds (1.644(3) and 1.653(3) Å), which are close to reported Cr^{VI}-N imido bond lengths (1.61–1.65 Å).^{15,17,26-28} Cr-C_α distances (2.044(4) and 2.078(4) Å) are consistent with those of reported Cr-C single bonds.^{15,17,26} A detailed statistical analysis of imido bond lengths and bond angles for terminal imido chromium complexes is shown in **Appendix D**. An interesting feature of this crystal structure is the presence of η^1 and η^2 coordination modes of the two benzyl ligands. The distance between Cr1 and C38 (2.517 Å) is much shorter than the distance between Cr1 and C31 (3.063 Å). Besides, the bond angle Cr1-C32-C38 (90.4(3)°) is obviously smaller than the bond angle Cr1-C25-C31 (117.0(2)°). These structural parameters suggest that the benzyl ligand containing C32 to C38 is coordinated to chromium center in a η^2 mode. This feature cannot be observed in solution NMR spectroscopy because of rapid averaging of η^1 and η^2 ligands. As mentioned above, this feature was also observed in the structure of (tBuN)₂Cr(CH₂Ph)₂, which resulted in two different peaks assigned for C_{ipso} of the benzyl ligands in the solid state ¹³C NMR spectrum.¹⁵

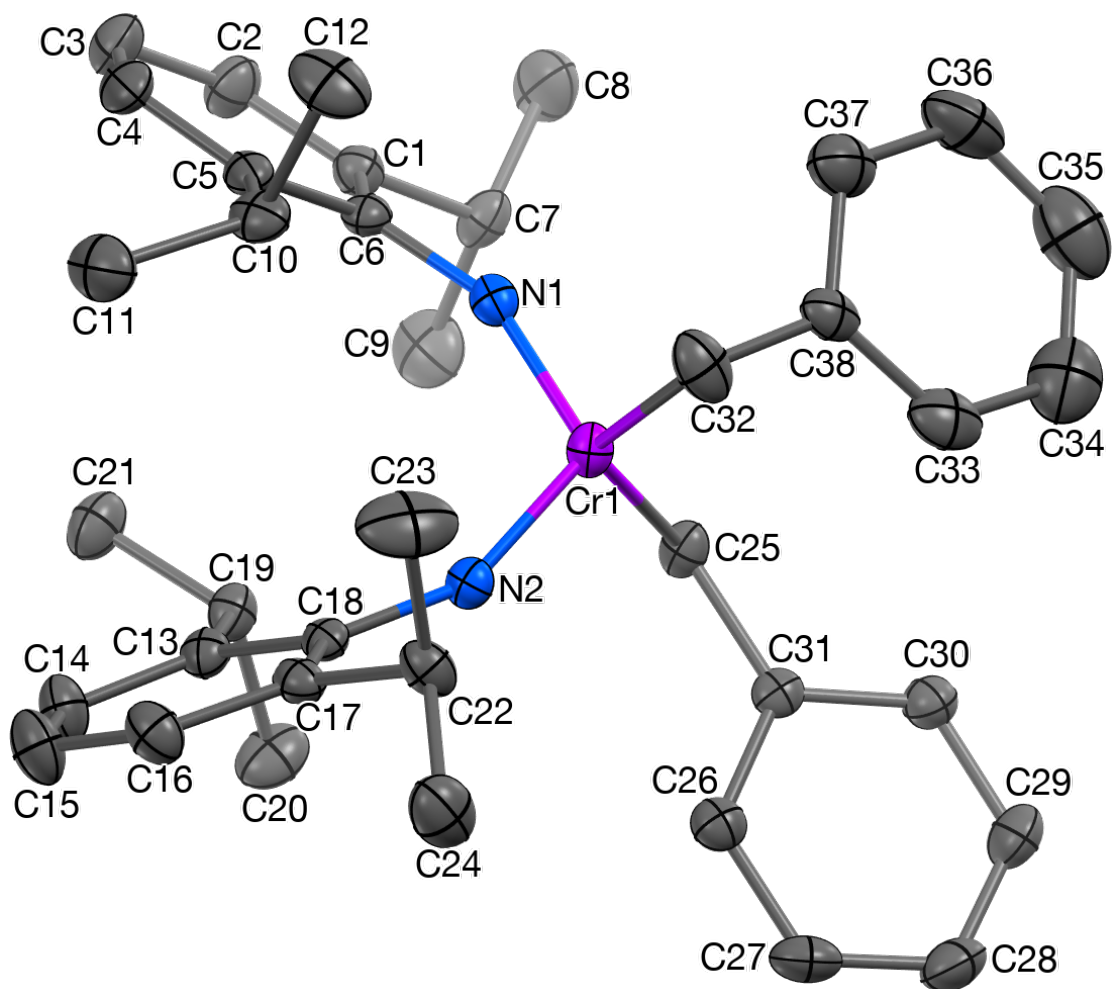


Figure 1.1 Molecular structure of $(\text{ArN})_2\text{Cr}(\text{CH}_2\text{Ph})_2$ (**5**). Ellipsoids are drawn at the 30% probability level. Hydrogen atoms have been omitted for clarity.

Table 1.1 Interatomic distances (Å) and angles (°) for (ArN)₂Cr(CH₂Ph)₂ (**5**)

Distances (Å)			
Cr(1)-N(1)	1.644(3)	C(14)-C(15)	1.367(6)
Cr(1)-N(2)	1.653(3)	C(15)-C(16)	1.379(6)
Cr(1)-C(32)	2.044(4)	C(16)-C(17)	1.378(5)
Cr(1)-C(25)	2.078(4)	C(17)-C(18)	1.413(5)
N(1)-C(6)	1.393(4)	C(17)-C(22)	1.525(5)
N(2)-C(18)	1.391(4)	C(19)-C(21)	1.527(5)
C(1)-C(2)	1.377(5)	C(19)-C(20)	1.529(6)
C(1)-C(6)	1.412(5)	C(22)-C(23)	1.510(7)
C(1)-C(7')	1.514(6)	C(22)-C(24)	1.517(6)
C(1)-C(7)	1.514(6)	C(25)-C(31)	1.497(5)
C(2)-C(3)	1.387(6)	C(26)-C(31)	1.383(5)
C(3)-C(4)	1.372(6)	C(26)-C(27)	1.392(6)
C(4)-C(5)	1.387(5)	C(27)-C(28)	1.363(6)
C(5)-C(6)	1.425(5)	C(28)-C(29)	1.364(6)
C(5)-C(10)	1.504(6)	C(29)-C(30)	1.378(6)
C(7)-C(9)	1.527(7)	C(30)-C(31)	1.402(5)
C(7)-C(8)	1.529(7)	C(32)-C(38)	1.455(6)
C(7')-C(9') ^a	1.501(15)	C(33)-C(34)	1.367(7)
C(7')-C(8') ^a	1.525(15)	C(33)-C(38)	1.399(7)
C(10)-C(12)	1.528(6)	C(34)-C(35)	1.367(9)
C(10)-C(11)	1.545(6)	C(35)-C(36)	1.365(9)
C(13)-C(14)	1.388(5)	C(36)-C(37)	1.401(7)
C(13)-C(18)	1.426(5)	C(37)-C(38)	1.395(6)

^a One isopropyl group with labeling C7 to C9 was found disordered in two positions with a refined site occupancy ratio of 77/23.

Angles (°)			
N(1)-Cr(1)-N(2)	110.51(14)	C(15)-C(14)-C(13)	122.4(4)
N(1)-Cr(1)-C(32)	104.32(18)	C(14)-C(15)-C(16)	120.0(4)
N(2)-Cr(1)-C(32)	105.54(16)	C(15)-C(16)-C(17)	121.4(4)
N(1)-Cr(1)-C(25)	103.47(15)	C(16)-C(17)-C(18)	118.3(3)

N(2)-Cr(1)-C(25)	103.99(16)	C(16)-C(17)-C(22)	120.5(4)
C(32)-Cr(1)-C(25)	128.51(17)	C(18)-C(17)-C(22)	121.1(3)
C(6)-N(1)-Cr(1)	157.7(3)	N(2)-C(18)-C(17)	118.8(3)
C(18)-N(2)-Cr(1)	154.3(3)	N(2)-C(18)-C(13)	120.3(3)
C(2)-C(1)-C(6)	118.3(4)	C(17)-C(18)-C(13)	121.0(3)
C(2)-C(1)-C(7')	121.3(4)	C(13)-C(19)-C(21)	112.9(3)
C(6)-C(1)-C(7')	120.4(3)	C(13)-C(19)-C(20)	110.9(4)
C(2)-C(1)-C(7)	121.3(4)	C(21)-C(19)-C(20)	110.6(3)
C(6)-C(1)-C(7)	120.4(3)	C(23)-C(22)-C(24)	110.8(4)
C(1)-C(2)-C(3)	121.3(4)	C(23)-C(22)-C(17)	110.6(4)
C(4)-C(3)-C(2)	119.8(4)	C(24)-C(22)-C(17)	113.1(3)
C(3)-C(4)-C(5)	122.5(4)	C(31)-C(25)-Cr(1)	117.0(2)
C(4)-C(5)-C(6)	116.8(4)	C(31)-C(26)-C(27)	121.1(4)
C(4)-C(5)-C(10)	121.9(4)	C(28)-C(27)-C(26)	120.7(4)
C(6)-C(5)-C(10)	121.3(3)	C(27)-C(28)-C(29)	119.4(4)
N(1)-C(6)-C(1)	118.7(3)	C(28)-C(29)-C(30)	120.6(4)
N(1)-C(6)-C(5)	119.9(3)	C(29)-C(30)-C(31)	121.5(4)
C(1)-C(6)-C(5)	121.4(3)	C(26)-C(31)-C(30)	116.7(4)
C(1)-C(7)-C(9)	111.2(4)	C(26)-C(31)-C(25)	122.3(4)
C(1)-C(7)-C(8)	113.7(4)	C(30)-C(31)-C(25)	120.9(4)
C(9)-C(7)-C(8)	109.3(5)	C(38)-C(32)-Cr(1)	90.4(3)
C(9')-C(7')-C(1)	113.3(9)	C(34)-C(33)-C(38)	123.4(5)
C(9')-C(7')-C(8')	111.2(13)	C(35)-C(34)-C(33)	118.3(6)
C(1)-C(7')-C(8')	108.4(10)	C(36)-C(35)-C(34)	122.0(6)
C(5)-C(10)-C(12)	110.5(4)	C(35)-C(36)-C(37)	118.9(6)
C(5)-C(10)-C(11)	112.2(4)	C(38)-C(37)-C(36)	121.3(5)
C(12)-C(10)-C(11)	111.6(4)	C(37)-C(38)-C(33)	116.1(4)
C(14)-C(13)-C(18)	116.9(4)	C(37)-C(38)-C(32)	123.6(4)
C(14)-C(13)-C(19)	121.7(3)	C(33)-C(38)-C(32)	120.2(4)
C(18)-C(13)-C(19)	121.4(3)		

(ArN)₂Cr(CH₂SiMe₃)₂ (**7**) had not been reported before. Its preparation procedure was adapted from the preparation of **6**, which was reported by Gibson et al. After workup, a concentrated pentane solution was cooled to -30 °C overnight to afford crystals suitable for structural characterization. The crystal structure is depicted in Figure 1.2 and the corresponding interatomic distances and angles are listed in Table 1.2. This molecule features pseudo-tetrahedral coordination geometry with a N-Cr-N angle of 113.85(7)°. The distances between Cr and N (1.6496(15) and 1.6522(15) Å) are consistent with imido bond length. The bond distances of Cr-C_α (2.0113(19) and 2.0182(18) Å) are slightly shorter than reported Cr-C single bonds (2.03–2.09 Å) of Cr^{VI} complexes.^{15,17,26} In NMR spectroscopy, the two trimethylsilylmethyl ligands are equivalent due to effective C_{2v} symmetry of the molecule in solution. ¹J_{CH} (118.1 Hz) for C_α and H_α indicates no agostic interaction between the Cr center and H_α in solution of **7**. If there was such an agostic interaction, a coupling constant ¹J_{CH} lower than 100 Hz would be expected.²⁹ The work about **7** has been communicated in Journal of the American Chemical Society.³⁰

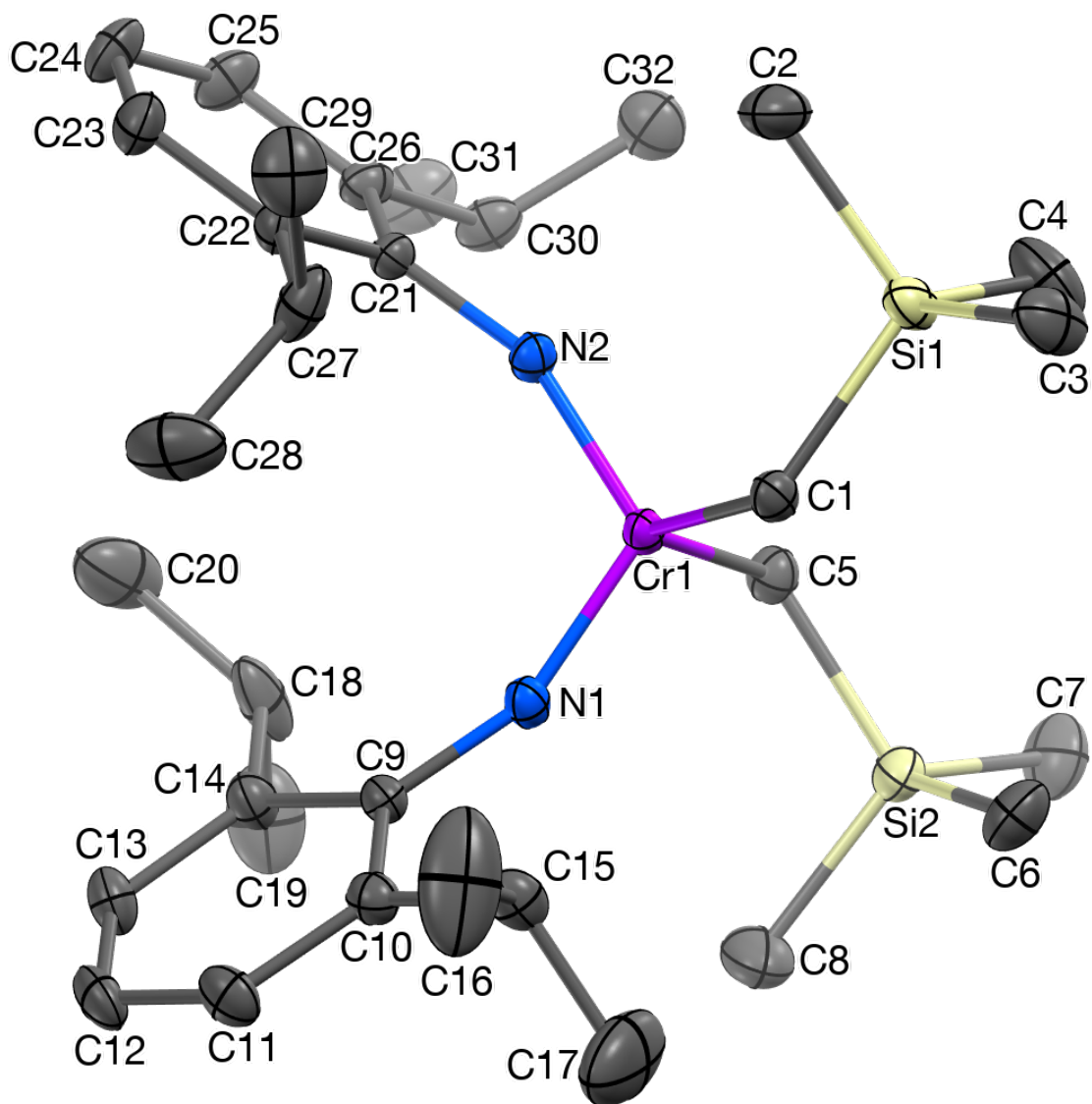


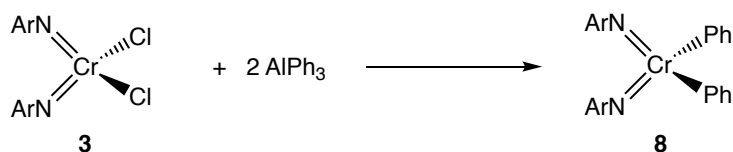
Figure 1.2 Molecular structure of $(\text{ArN})_2\text{Cr}(\text{CH}_2\text{SiMe}_3)_2$ (7). Ellipsoids are drawn at the 30% probability level. Hydrogen atoms have been omitted for clarity.

Table 1.2 Interatomic distances (Å) and angles (°) for (ArN)₂Cr(CH₂SiMe₃)₂ (7)

Distances (Å)			
Cr(1)-N(1)	1.6496(15)	C(12)-C(13)	1.377(3)
Cr(1)-N(2)	1.6522(15)	C(13)-C(14)	1.386(3)
Cr(1)-C(5)	2.0113(19)	C(14)-C(18)	1.519(3)
Cr(1)-C(1)	2.0182(18)	C(15)-C(16)	1.495(4)
Si(1)-C(4)	1.861(3)	C(15)-C(17)	1.512(4)
Si(1)-C(2)	1.867(3)	C(18)-C(20)	1.520(4)
Si(1)-C(1)	1.8683(18)	C(18)-C(19)	1.543(4)
Si(1)-C(3)	1.870(2)	C(21)-C(22)	1.410(3)
Si(2)-C(8)	1.862(3)	C(21)-C(26)	1.419(2)
Si(2)-C(6)	1.863(3)	C(22)-C(23)	1.392(3)
Si(2)-C(5)	1.866(2)	C(22)-C(27)	1.516(3)
Si(2)-C(7)	1.868(2)	C(23)-C(24)	1.378(3)
N(1)-C(9)	1.382(2)	C(24)-C(25)	1.385(3)
N(2)-C(21)	1.384(2)	C(25)-C(26)	1.387(3)
C(9)-C(14)	1.415(3)	C(26)-C(30)	1.517(3)
C(9)-C(10)	1.416(3)	C(27)-C(29)	1.528(4)
C(10)-C(11)	1.388(3)	C(27)-C(28)	1.529(4)
C(10)-C(15)	1.516(3)	C(30)-C(32)	1.517(3)
C(11)-C(12)	1.383(3)	C(30)-C(31)	1.534(3)
Angles (°)			
N(1)-Cr(1)-N(2)	113.85(7)	C(13)-C(12)-C(11)	119.97(18)
N(1)-Cr(1)-C(5)	104.84(8)	C(12)-C(13)-C(14)	121.58(19)
N(2)-Cr(1)-C(5)	106.89(8)	C(13)-C(14)-C(9)	118.09(18)
N(1)-Cr(1)-C(1)	106.74(7)	C(13)-C(14)-C(18)	119.78(18)
N(2)-Cr(1)-C(1)	106.03(8)	C(9)-C(14)-C(18)	122.12(17)
C(5)-Cr(1)-C(1)	118.82(8)	C(16)-C(15)-C(17)	111.3(3)
C(4)-Si(1)-C(2)	109.42(15)	C(16)-C(15)-C(10)	113.4(2)
C(4)-Si(1)-C(1)	112.75(11)	C(17)-C(15)-C(10)	109.5(2)
C(2)-Si(1)-C(1)	109.56(10)	C(14)-C(18)-C(20)	112.1(2)
C(4)-Si(1)-C(3)	108.37(14)	C(14)-C(18)-C(19)	110.2(2)

C(2)-Si(1)-C(3)	108.40(13)	C(20)-C(18)-C(19)	110.7(2)
C(1)-Si(1)-C(3)	108.24(10)	N(2)-C(21)-C(22)	120.58(16)
C(8)-Si(2)-C(6)	108.69(14)	N(2)-C(21)-C(26)	118.34(16)
C(8)-Si(2)-C(5)	110.03(11)	C(22)-C(21)-C(26)	121.08(16)
C(6)-Si(2)-C(5)	112.71(10)	C(23)-C(22)-C(21)	118.15(18)
C(8)-Si(2)-C(7)	108.71(14)	C(23)-C(22)-C(27)	119.79(18)
C(6)-Si(2)-C(7)	108.06(13)	C(21)-C(22)-C(27)	122.05(17)
C(5)-Si(2)-C(7)	108.56(11)	C(24)-C(23)-C(22)	121.14(19)
C(9)-N(1)-Cr(1)	158.57(13)	C(23)-C(24)-C(25)	120.40(19)
C(21)-N(2)-Cr(1)	158.45(13)	C(24)-C(25)-C(26)	121.15(19)
Si(1)-C(1)-Cr(1)	116.38(9)	C(25)-C(26)-C(21)	118.05(18)
Si(2)-C(5)-Cr(1)	116.26(10)	C(25)-C(26)-C(30)	122.44(18)
N(1)-C(9)-C(14)	121.23(16)	C(21)-C(26)-C(30)	119.51(16)
N(1)-C(9)-C(10)	117.80(16)	C(22)-C(27)-C(29)	112.2(2)
C(14)-C(9)-C(10)	120.97(16)	C(22)-C(27)-C(28)	110.5(2)
C(11)-C(10)-C(9)	117.89(18)	C(29)-C(27)-C(28)	110.6(2)
C(11)-C(10)-C(15)	121.66(18)	C(32)-C(30)-C(26)	111.14(18)
C(9)-C(10)-C(15)	120.44(16)	C(32)-C(30)-C(31)	110.03(19)
C(12)-C(11)-C(10)	121.49(19)	C(26)-C(30)-C(31)	113.74(18)

Chromium(VI) dialkyls supported by 2,6-diisopropylphenyl imido or *tert*-butyl imido ligands have been investigated for more than two decades.¹⁷⁻¹⁸ However, studies of chromium(VI) diaryls are still limited to (^tBuN)₂Cr(2,6-Me₂Ph)₂ and (^tBuN)₂Cr(mes)₂, which were reported 30 years ago.¹² Besides, prior to this work there were no σ-aryl chromium(VI) complex supported by two arylimido ligands. The rarity of this type of complex is partially due to the relative instability of the highest oxidation state of chromium.³⁰ The motivation of making chromium diaryls was to study their reactivity and thermostability, which were unexplored to date.



Scheme 1.7 Synthesis of (ArN)₂CrPh₂ (**8**) using AlPh₃

Phenylation of **3** with PhMgCl was unsuccessful. This reaction generated biphenyl and unidentified paramagnetic compounds instead of the expected product **8**. This observation suggests that the starting material is more likely to be reduced than to be arylated by PhMgCl. However, **8** could be synthesized successfully when **3** was treated with the less reducing arylation reagent AlPh₃, (Scheme 1.6). Single crystals suitable for X-ray diffraction study were obtained from concentrated pentane solution at -30 °C. The molecular structure of **8** is depicted in Figure 1.3 and the corresponding interatomic distances and angles are listed in Table 1.3. The structure of **8** features pseudo-tetrahedral coordination geometry. One imido is linear with angle 172.1(3)° (Cr1-N1-C6). The other one has a bond angle of 156.0(3)° (Cr1-N2-C18). Besides, the

Cr1-N1 bond (1.637(4) Å) is slightly shorter than Cr-N2 (1.653(3) Å). These structural parameters suggest that N1 is more π -electron donating than N2. In both ^1H NMR and ^{13}C NMR spectra, the two imido ligands are magnetically equivalent. One doublet peak at 1.07 ppm attributed to CHMe_2 and one septet peak at 4.05 ppm attributed to CHMe_2 were observed in ^1H NMR spectrum. I believe that this is a result of rapid averaging of linear imido and bent imido in solution at room temperature.

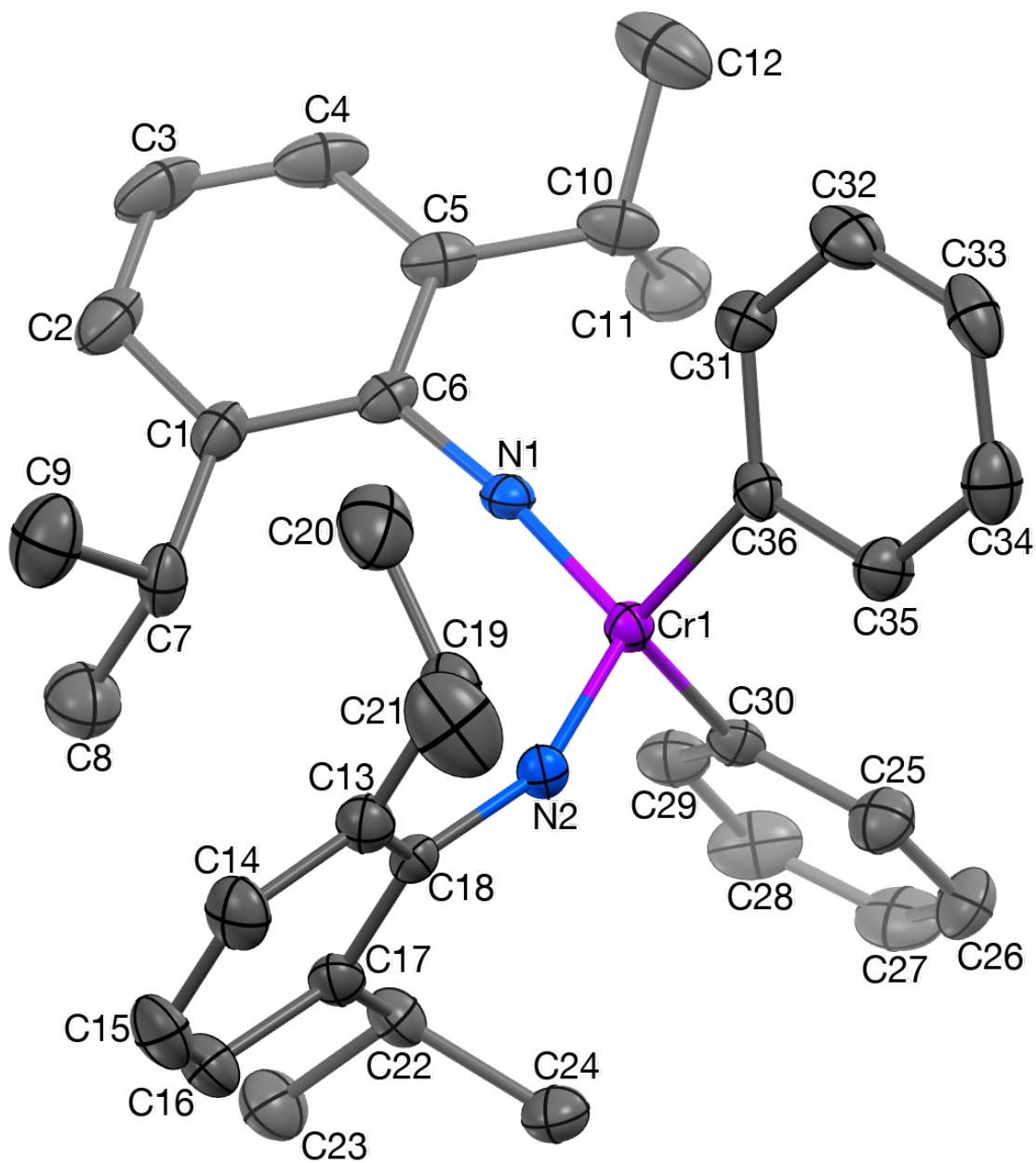


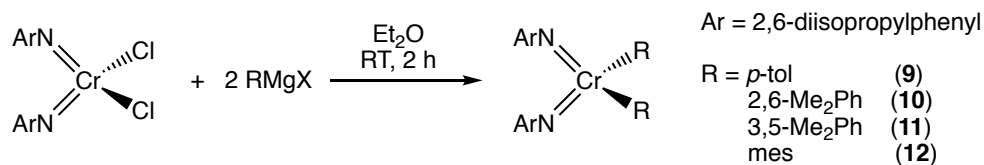
Figure 1.3 Molecular structure of $(\text{ArN})_2\text{CrPh}_2$ (**8**). Ellipsoids are drawn at the 30% probability level. Hydrogen atoms have been omitted for clarity.

Table 1.3 Interatomic distances (Å) and angles (°) for (ArN)₂CrPh₂ (**8**)

Distances (Å)			
Cr(1)-N(1)	1.637(4)	C(14)-C(15)	1.373(10)
Cr(1)-N(2)	1.653(3)	C(15)-C(16)	1.364(10)
Cr(1)-C(36)	1.996(6)	C(16)-C(17)	1.394(10)
Cr(1)-C(30)	2.004(7)	C(17)-C(18)	1.405(9)
N(1)-C(6)	1.389(5)	C(17)-C(22)	1.514(9)
N(2)-C(18)	1.390(5)	C(19)-C(20)	1.483(11)
C(1)-C(2)	1.391(7)	C(19)-C(21)	1.535(10)
C(1)-C(6)	1.422(6)	C(22)-C(24)	1.527(9)
C(1)-C(7)	1.501(7)	C(22)-C(23)	1.542(9)
C(2)-C(3)	1.364(8)	C(25)-C(30)	1.380(10)
C(3)-C(4)	1.377(9)	C(25)-C(26)	1.385(9)
C(4)-C(5)	1.377(8)	C(26)-C(27)	1.366(12)
C(5)-C(6)	1.416(7)	C(27)-C(28)	1.364(11)
C(5)-C(10)	1.508(8)	C(28)-C(29)	1.367(9)
C(7)-C(9)	1.519(8)	C(29)-C(30)	1.394(9)
C(7)-C(8)	1.545(9)	C(31)-C(32)	1.363(9)
C(10)-C(12)	1.518(9)	C(31)-C(36)	1.401(9)
C(10)-C(11)	1.527(9)	C(32)-C(33)	1.386(11)
C(13)-C(14)	1.379(9)	C(33)-C(34)	1.385(11)
C(13)-C(18)	1.415(9)	C(34)-C(35)	1.391(9)
C(13)-C(19)	1.519(9)	C(35)-C(36)	1.400(10)

Angles (°)			
N(1)-Cr(1)-N(2)	116.92(17)	C(16)-C(15)-C(14)	121.1(5)
N(1)-Cr(1)-C(36)	104.1(3)	C(15)-C(16)-C(17)	120.8(7)
N(2)-Cr(1)-C(36)	106.3(3)	C(16)-C(17)-C(18)	117.6(7)
N(1)-Cr(1)-C(30)	103.7(3)	C(16)-C(17)-C(22)	122.4(7)
N(2)-Cr(1)-C(30)	105.3(3)	C(18)-C(17)-C(22)	119.9(6)
C(36)-Cr(1)-C(30)	121.43(19)	N(2)-C(18)-C(17)	119.4(7)
C(6)-N(1)-Cr(1)	172.1(3)	N(2)-C(18)-C(13)	118.7(7)
C(18)-N(2)-Cr(1)	156.0(3)	C(17)-C(18)-C(13)	121.8(4)

C(2)-C(1)-C(6)	116.4(5)	C(20)-C(19)-C(13)	112.1(7)
C(2)-C(1)-C(7)	121.4(5)	C(20)-C(19)-C(21)	109.8(7)
C(6)-C(1)-C(7)	122.2(4)	C(13)-C(19)-C(21)	111.6(7)
C(3)-C(2)-C(1)	122.5(5)	C(17)-C(22)-C(24)	110.5(6)
C(2)-C(3)-C(4)	119.9(5)	C(17)-C(22)-C(23)	115.3(6)
C(5)-C(4)-C(3)	122.0(6)	C(24)-C(22)-C(23)	109.8(6)
C(4)-C(5)-C(6)	117.4(5)	C(30)-C(25)-C(26)	121.2(7)
C(4)-C(5)-C(10)	121.8(5)	C(27)-C(26)-C(25)	120.7(9)
C(6)-C(5)-C(10)	120.8(5)	C(28)-C(27)-C(26)	118.5(8)
N(1)-C(6)-C(5)	117.0(4)	C(27)-C(28)-C(29)	121.6(8)
N(1)-C(6)-C(1)	121.2(4)	C(28)-C(29)-C(30)	120.9(8)
C(5)-C(6)-C(1)	121.8(4)	C(25)-C(30)-C(29)	117.0(7)
C(1)-C(7)-C(9)	113.3(6)	C(25)-C(30)-Cr(1)	117.0(5)
C(1)-C(7)-C(8)	109.5(6)	C(29)-C(30)-Cr(1)	125.9(6)
C(9)-C(7)-C(8)	110.2(6)	C(32)-C(31)-C(36)	121.9(7)
C(5)-C(10)-C(12)	112.9(6)	C(31)-C(32)-C(33)	120.7(8)
C(5)-C(10)-C(11)	110.4(6)	C(34)-C(33)-C(32)	119.2(7)
C(12)-C(10)-C(11)	110.9(5)	C(33)-C(34)-C(35)	119.9(8)
C(14)-C(13)-C(18)	117.2(6)	C(34)-C(35)-C(36)	121.5(7)
C(14)-C(13)-C(19)	123.0(7)	C(35)-C(36)-C(31)	116.7(6)
C(18)-C(13)-C(19)	119.8(6)	C(35)-C(36)-Cr(1)	116.7(5)
C(15)-C(14)-C(13)	121.5(7)	C(31)-C(36)-Cr(1)	126.2(6)



Scheme 1.8 Synthesis of **9** to **12** from corresponding Grignard reagents

Syntheses of (ArN)₂Cr(*p*-tol)₂ (**9**), (ArN)₂Cr(2,6-Me₂Ph)₂ (**10**), (ArN)₂Cr(3,5-Me₂Ph)₂ (**11**) and (ArN)₂Cr(mes)₂ (**12**) were straightforward. They were made from **3** reacting with the corresponding Grignard reagents. Crystal structures of these four new complexes are depicted in Figure 1.4–1.7 respectively. The corresponding interatomic distances and angles of **9**, **10**, **11** and **12** are listed in Tables 1.4–1.7. All of them have pseudo-tetrahedral coordination geometry. In solution ¹H NMR spectroscopy, the two aryl ligands are equivalent and the two arylimido ligands are also equivalent. The peaks of C_{ipso} of the aryl ligands are found in the very downfield with chemical shift around 200 ppm (193.68–203.09 ppm) in ¹³C NMR spectra. This extreme deshielding is likely caused by the strongly electron-withdrawing metal center Cr(VI).

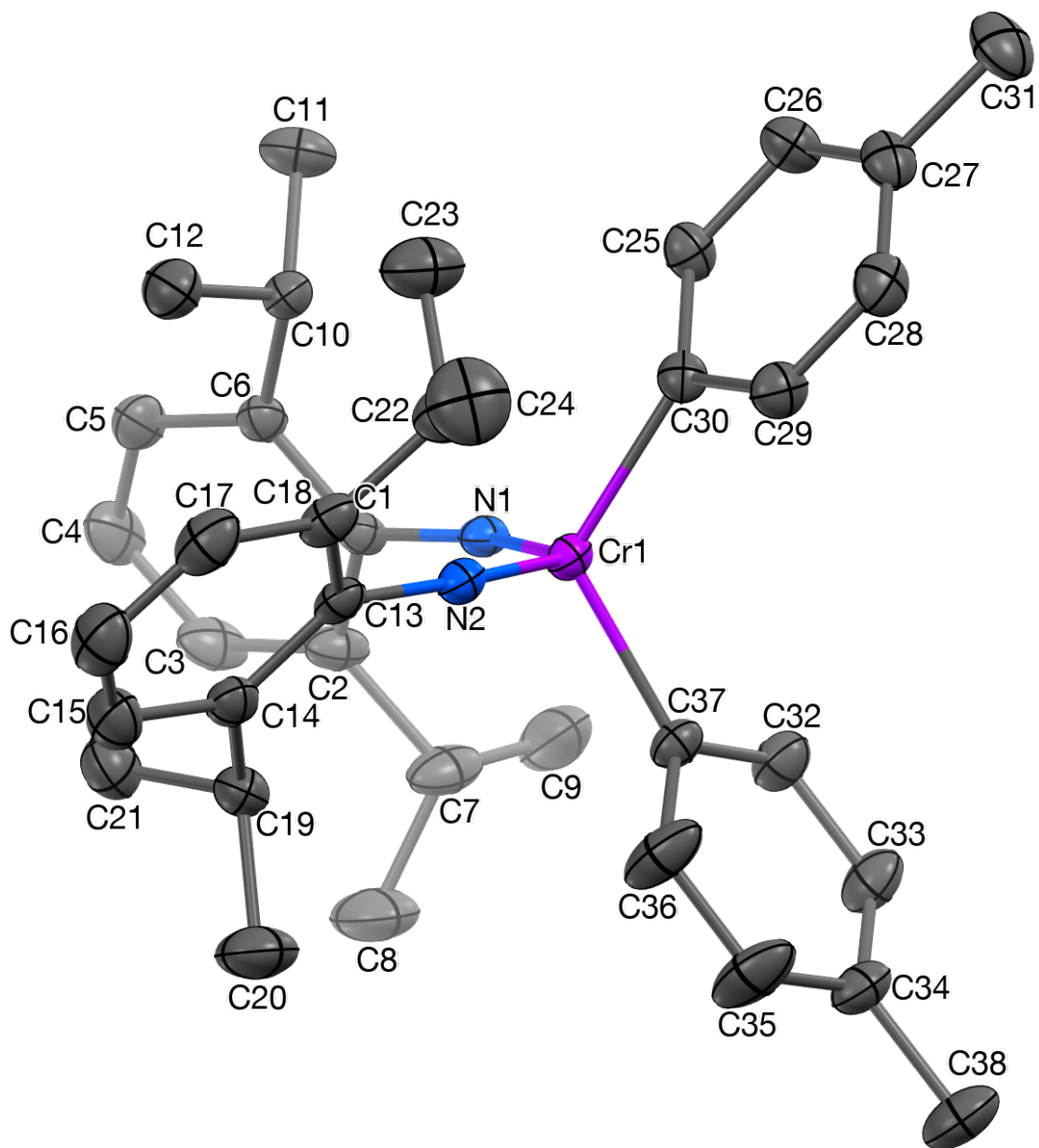


Figure 1.4 Molecular structure of $(\text{ArN})_2\text{Cr}(p\text{-tol})_2$ (**9**). Ellipsoids are drawn at the 30% probability level. Hydrogen atoms have been omitted for clarity.

Table 1.4 Interatomic distances (Å) and angles (°) for (ArN)₂Cr(*p*-tol)₂ (**9**)

Distances (Å)			
Cr(1)-N(2)	1.6461(19)	C(15)-C(16)	1.378(5)
Cr(1)-N(1)	1.6523(17)	C(16)-C(17)	1.380(5)
Cr(1)-C(37)	1.996(2)	C(17)-C(18)	1.388(4)
Cr(1)-C(30)	1.996(2)	C(18)-C(22)	1.518(4)
N(1)-C(1)	1.382(3)	C(19)-C(21)	1.524(4)
N(2)-C(13)	1.383(3)	C(19)-C(20)	1.534(4)
C(1)-C(6)	1.410(3)	C(22)-C(23)	1.509(4)
C(1)-C(2)	1.417(3)	C(22)-C(24)	1.533(4)
C(2)-C(3)	1.387(4)	C(25)-C(26)	1.393(3)
C(2)-C(7)	1.513(4)	C(25)-C(30)	1.393(3)
C(3)-C(4)	1.374(4)	C(26)-C(27)	1.384(4)
C(4)-C(5)	1.375(4)	C(27)-C(28)	1.380(4)
C(5)-C(6)	1.392(3)	C(27)-C(31)	1.511(4)
C(6)-C(10)	1.513(3)	C(28)-C(29)	1.385(4)
C(7)-C(9)	1.435(6)	C(29)-C(30)	1.393(3)
C(7)-C(8)	1.519(5)	C(32)-C(37)	1.376(3)
C(10)-C(11)	1.522(4)	C(32)-C(33)	1.394(4)
C(10)-C(12)	1.528(4)	C(33)-C(34)	1.364(4)
C(13)-C(14)	1.413(4)	C(34)-C(35)	1.364(4)
C(13)-C(18)	1.422(3)	C(34)-C(38)	1.515(4)
C(14)-C(15)	1.391(4)	C(35)-C(36)	1.389(4)
C(14)-C(19)	1.511(4)	C(36)-C(37)	1.384(4)

Angles (°)			
N(2)-Cr(1)-N(1)	113.70(9)	C(16)-C(15)-C(14)	121.4(3)
N(2)-Cr(1)-C(37)	103.09(9)	C(15)-C(16)-C(17)	120.3(3)
N(1)-Cr(1)-C(37)	106.97(9)	C(16)-C(17)-C(18)	121.5(3)
N(2)-Cr(1)-C(30)	107.06(9)	C(17)-C(18)-C(13)	117.7(3)
N(1)-Cr(1)-C(30)	108.10(9)	C(17)-C(18)-C(22)	122.1(2)
C(37)-Cr(1)-C(30)	118.11(9)	C(13)-C(18)-C(22)	120.2(2)
C(1)-N(1)-Cr(1)	153.25(16)	C(14)-C(19)-C(21)	111.7(2)

C(13)-N(2)-Cr(1)	162.94(16)	C(14)-C(19)-C(20)	111.3(3)
N(1)-C(1)-C(6)	119.98(19)	C(21)-C(19)-C(20)	110.1(3)
N(1)-C(1)-C(2)	119.2(2)	C(23)-C(22)-C(18)	111.5(3)
C(6)-C(1)-C(2)	120.8(2)	C(23)-C(22)-C(24)	111.8(3)
C(3)-C(2)-C(1)	118.2(2)	C(18)-C(22)-C(24)	113.0(3)
C(3)-C(2)-C(7)	121.9(2)	C(26)-C(25)-C(30)	120.6(2)
C(1)-C(2)-C(7)	119.9(2)	C(27)-C(26)-C(25)	121.5(2)
C(4)-C(3)-C(2)	121.2(2)	C(28)-C(27)-C(26)	117.8(2)
C(3)-C(4)-C(5)	120.4(2)	C(28)-C(27)-C(31)	121.3(3)
C(4)-C(5)-C(6)	121.3(3)	C(26)-C(27)-C(31)	120.9(3)
C(5)-C(6)-C(1)	118.0(2)	C(27)-C(28)-C(29)	121.4(2)
C(5)-C(6)-C(10)	120.4(2)	C(28)-C(29)-C(30)	121.2(2)
C(1)-C(6)-C(10)	121.56(19)	C(29)-C(30)-C(25)	117.5(2)
C(9)-C(7)-C(2)	111.4(3)	C(29)-C(30)-Cr(1)	113.53(17)
C(9)-C(7)-C(8)	110.2(4)	C(25)-C(30)-Cr(1)	128.40(16)
C(2)-C(7)-C(8)	113.1(3)	C(37)-C(32)-C(33)	121.5(2)
C(6)-C(10)-C(11)	110.9(2)	C(34)-C(33)-C(32)	121.7(3)
C(6)-C(10)-C(12)	111.6(2)	C(35)-C(34)-C(33)	116.9(2)
C(11)-C(10)-C(12)	111.3(2)	C(35)-C(34)-C(38)	120.8(3)
N(2)-C(13)-C(14)	120.8(2)	C(33)-C(34)-C(38)	122.3(3)
N(2)-C(13)-C(18)	118.0(2)	C(34)-C(35)-C(36)	122.3(3)
C(14)-C(13)-C(18)	121.2(2)	C(37)-C(36)-C(35)	120.9(3)
C(15)-C(14)-C(13)	117.9(2)	C(32)-C(37)-C(36)	116.5(2)
C(15)-C(14)-C(19)	119.3(2)	C(32)-C(37)-Cr(1)	119.20(18)
C(13)-C(14)-C(19)	122.8(2)	C(36)-C(37)-Cr(1)	123.96(18)

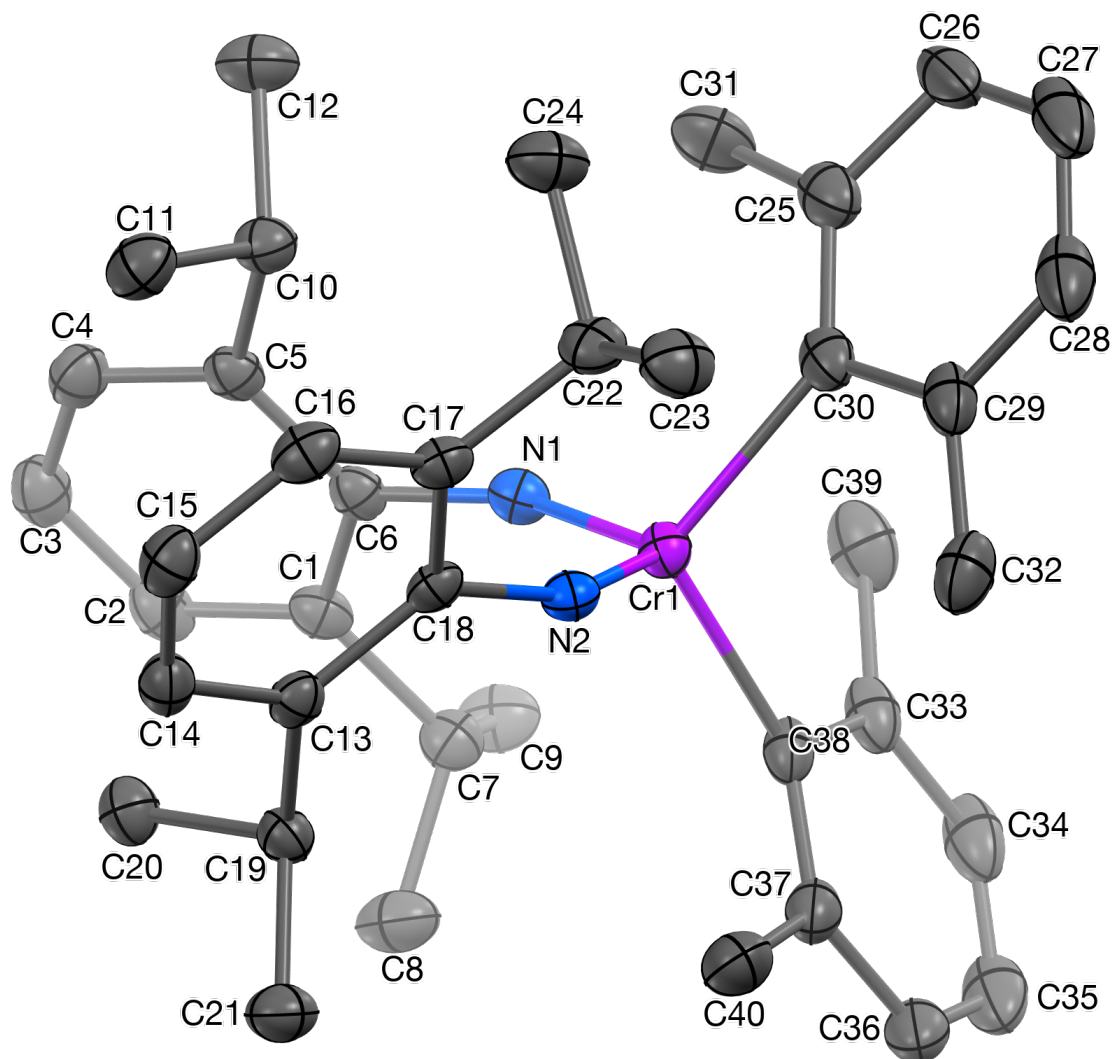


Figure 1.5 Molecular structure of $(\text{ArN})_2\text{Cr}(2,6\text{-Me}_2\text{Ph})_2$ (**10**). Ellipsoids are drawn at the 30% probability level. Hydrogen atoms have been omitted for clarity.

Table 1.5 Interatomic distances (Å) and angles (°) for (ArN)₂Cr(2,6-Me₂Ph)₂ (**10**)

Distances (Å)			
Cr(1)-N(2)	1.647(3)	C(16)-C(17)	1.388(5)
Cr(1)-N(1)	1.653(3)	C(17)-C(18)	1.423(4)
Cr(1)-C(38)	2.025(3)	C(17)-C(22)	1.514(5)
Cr(1)-C(30)	2.033(3)	C(19)-C(20)	1.526(5)
N(1)-C(6)	1.396(4)	C(19)-C(21)	1.532(5)
N(2)-C(18)	1.393(4)	C(22)-C(24)	1.518(5)
C(1)-C(2)	1.386(5)	C(22)-C(23)	1.525(5)
C(1)-C(6)	1.421(4)	C(25)-C(30)	1.409(5)
C(1)-C(7)	1.514(5)	C(25)-C(26)	1.411(6)
C(2)-C(3)	1.386(5)	C(25)-C(31)	1.491(6)
C(3)-C(4)	1.380(5)	C(26)-C(27)	1.363(7)
C(4)-C(5)	1.387(5)	C(27)-C(28)	1.363(7)
C(5)-C(6)	1.422(5)	C(28)-C(29)	1.392(5)
C(5)-C(10)	1.512(5)	C(29)-C(30)	1.414(5)
C(7)-C(8)	1.517(5)	C(29)-C(32)	1.502(6)
C(7)-C(9)	1.521(5)	C(33)-C(34)	1.393(6)
C(10)-C(11)	1.527(5)	C(33)-C(38)	1.427(5)
C(10)-C(12)	1.533(5)	C(33)-C(39)	1.499(6)
C(13)-C(14)	1.393(5)	C(34)-C(35)	1.369(7)
C(13)-C(18)	1.411(5)	C(35)-C(36)	1.372(7)
C(13)-C(19)	1.520(4)	C(36)-C(37)	1.401(5)
C(14)-C(15)	1.378(5)	C(37)-C(38)	1.412(5)
C(15)-C(16)	1.376(5)	C(37)-C(40)	1.497(6)

Angles (°)			
N(2)-Cr(1)-N(1)	108.74(13)	C(18)-C(17)-C(22)	121.6(3)
N(2)-Cr(1)-C(38)	112.61(14)	N(2)-C(18)-C(13)	121.0(3)
N(1)-Cr(1)-C(38)	106.01(13)	N(2)-C(18)-C(17)	117.8(3)
N(2)-Cr(1)-C(30)	104.29(13)	C(13)-C(18)-C(17)	121.2(3)
N(1)-Cr(1)-C(30)	113.80(15)	C(13)-C(19)-C(20)	111.2(3)
C(38)-Cr(1)-C(30)	111.52(13)	C(13)-C(19)-C(21)	111.2(3)

C(6)-N(1)-Cr(1)	156.0(2)	C(20)-C(19)-C(21)	109.4(3)
C(18)-N(2)-Cr(1)	152.7(2)	C(17)-C(22)-C(24)	112.4(3)
C(2)-C(1)-C(6)	118.4(3)	C(17)-C(22)-C(23)	112.0(3)
C(2)-C(1)-C(7)	120.3(3)	C(24)-C(22)-C(23)	110.8(3)
C(6)-C(1)-C(7)	121.4(3)	C(30)-C(25)-C(26)	119.0(4)
C(3)-C(2)-C(1)	121.2(3)	C(30)-C(25)-C(31)	124.0(4)
C(4)-C(3)-C(2)	119.9(3)	C(26)-C(25)-C(31)	117.1(4)
C(3)-C(4)-C(5)	122.2(3)	C(27)-C(26)-C(25)	121.4(5)
C(4)-C(5)-C(6)	117.5(3)	C(28)-C(27)-C(26)	120.1(4)
C(4)-C(5)-C(10)	119.3(3)	C(27)-C(28)-C(29)	121.1(5)
C(6)-C(5)-C(10)	123.2(3)	C(28)-C(29)-C(30)	120.0(4)
N(1)-C(6)-C(1)	117.9(3)	C(28)-C(29)-C(32)	117.0(4)
N(1)-C(6)-C(5)	121.2(3)	C(30)-C(29)-C(32)	123.0(3)
C(1)-C(6)-C(5)	120.9(3)	C(25)-C(30)-C(29)	118.4(3)
C(1)-C(7)-C(8)	112.5(3)	C(25)-C(30)-Cr(1)	126.4(3)
C(1)-C(7)-C(9)	112.3(3)	C(29)-C(30)-Cr(1)	115.1(3)
C(8)-C(7)-C(9)	110.4(3)	C(34)-C(33)-C(38)	119.1(4)
C(5)-C(10)-C(11)	111.9(3)	C(34)-C(33)-C(39)	117.5(4)
C(5)-C(10)-C(12)	111.3(3)	C(38)-C(33)-C(39)	123.3(3)
C(11)-C(10)-C(12)	110.2(3)	C(35)-C(34)-C(33)	121.5(4)
C(14)-C(13)-C(18)	117.5(3)	C(34)-C(35)-C(36)	120.1(4)
C(14)-C(13)-C(19)	119.6(3)	C(35)-C(36)-C(37)	121.2(5)
C(18)-C(13)-C(19)	122.9(3)	C(36)-C(37)-C(38)	119.4(4)
C(15)-C(14)-C(13)	121.9(3)	C(36)-C(37)-C(40)	116.6(4)
C(16)-C(15)-C(14)	119.9(3)	C(38)-C(37)-C(40)	124.0(3)
C(15)-C(16)-C(17)	121.7(3)	C(37)-C(38)-C(33)	118.7(3)
C(16)-C(17)-C(18)	117.7(3)	C(37)-C(38)-Cr(1)	127.1(3)
C(16)-C(17)-C(22)	120.7(3)	C(33)-C(38)-Cr(1)	113.8(3)

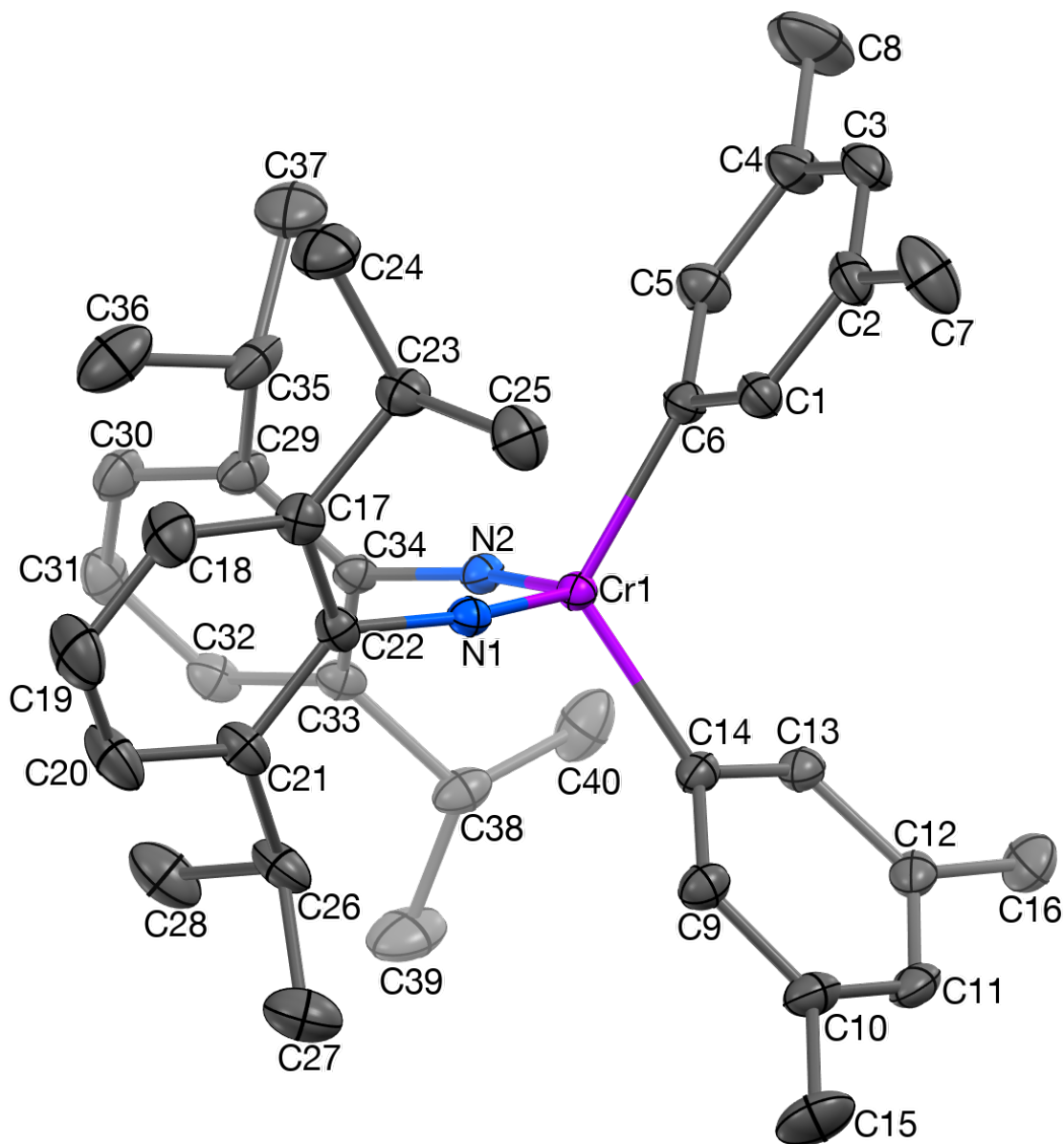


Figure 1.6 Molecular structure of $(\text{ArN})_2\text{Cr}(3,5\text{-Me}_2\text{Ph})_2$ (**11**). Ellipsoids are drawn at the 30% probability level. Hydrogen atoms have been omitted for clarity.

Table 1.6 Interatomic distances (Å) and angles (°) for (ArN)₂Cr(3,5-Me₂Ph)₂ (**11**)

Distances (Å)			
Cr(1)-N(2)	1.6491(14)	C(17)-C(22)	1.420(2)
Cr(1)-N(1)	1.6507(14)	C(17)-C(23)	1.511(3)
Cr(1)-C(14)	1.9955(17)	C(18)-C(19)	1.379(3)
Cr(1)-C(6)	2.0002(16)	C(19)-C(20)	1.378(3)
N(1)-C(22)	1.380(2)	C(20)-C(21)	1.385(3)
N(2)-C(34)	1.384(2)	C(21)-C(22)	1.412(2)
C(1)-C(2)	1.389(2)	C(21)-C(26)	1.517(3)
C(1)-C(6)	1.394(2)	C(23)-C(25)	1.525(3)
C(2)-C(3)	1.380(3)	C(23)-C(24)	1.536(3)
C(2)-C(7)	1.515(3)	C(26)-C(27)	1.529(3)
C(3)-C(4)	1.387(3)	C(26)-C(28)	1.530(3)
C(4)-C(5)	1.393(3)	C(29)-C(30)	1.393(3)
C(4)-C(8)	1.513(3)	C(29)-C(34)	1.410(2)
C(5)-C(6)	1.388(3)	C(29)-C(35)	1.518(3)
C(9)-C(10)	1.391(3)	C(30)-C(31)	1.378(3)
C(9)-C(14)	1.395(2)	C(31)-C(32)	1.379(3)
C(10)-C(11)	1.388(3)	C(32)-C(33)	1.387(2)
C(10)-C(15)	1.514(3)	C(33)-C(34)	1.416(2)
C(11)-C(12)	1.380(3)	C(33)-C(38)	1.513(3)
C(12)-C(13)	1.400(2)	C(35)-C(36)	1.525(3)
C(12)-C(16)	1.504(3)	C(35)-C(37)	1.529(4)
C(13)-C(14)	1.392(2)	C(38)-C(40)	1.520(3)
C(17)-C(18)	1.384(3)	C(38)-C(39)	1.534(3)

Angles (°)			
N(2)-Cr(1)-N(1)	111.84(7)	C(22)-C(17)-C(23)	120.33(16)
N(2)-Cr(1)-C(14)	107.02(7)	C(19)-C(18)-C(17)	121.2(2)
N(1)-Cr(1)-C(14)	106.36(7)	C(20)-C(19)-C(18)	120.3(2)
N(2)-Cr(1)-C(6)	107.86(7)	C(19)-C(20)-C(21)	121.6(2)
N(1)-Cr(1)-C(6)	106.87(7)	C(20)-C(21)-C(22)	117.69(19)
C(14)-Cr(1)-C(6)	116.98(7)	C(20)-C(21)-C(26)	120.52(18)

C(22)-N(1)-Cr(1)	156.17(12)	C(22)-C(21)-C(26)	121.79(17)
C(34)-N(2)-Cr(1)	154.43(12)	N(1)-C(22)-C(21)	120.22(16)
C(2)-C(1)-C(6)	122.14(18)	N(1)-C(22)-C(17)	118.50(15)
C(3)-C(2)-C(1)	118.03(19)	C(21)-C(22)-C(17)	121.28(16)
C(3)-C(2)-C(7)	121.93(19)	C(17)-C(23)-C(25)	109.77(16)
C(1)-C(2)-C(7)	120.0(2)	C(17)-C(23)-C(24)	113.90(17)
C(2)-C(3)-C(4)	121.99(18)	C(25)-C(23)-C(24)	110.03(18)
C(3)-C(4)-C(5)	118.46(19)	C(21)-C(26)-C(27)	110.71(19)
C(3)-C(4)-C(8)	120.6(2)	C(21)-C(26)-C(28)	111.2(2)
C(5)-C(4)-C(8)	120.9(2)	C(27)-C(26)-C(28)	111.11(18)
C(6)-C(5)-C(4)	121.49(19)	C(30)-C(29)-C(34)	117.85(17)
C(5)-C(6)-C(1)	117.88(16)	C(30)-C(29)-C(35)	120.02(17)
C(5)-C(6)-Cr(1)	127.18(14)	C(34)-C(29)-C(35)	122.12(16)
C(1)-C(6)-Cr(1)	114.61(13)	C(31)-C(30)-C(29)	121.04(18)
C(10)-C(9)-C(14)	121.07(18)	C(30)-C(31)-C(32)	120.46(17)
C(11)-C(10)-C(9)	118.52(18)	C(31)-C(32)-C(33)	121.51(17)
C(11)-C(10)-C(15)	121.20(18)	C(32)-C(33)-C(34)	117.53(16)
C(9)-C(10)-C(15)	120.3(2)	C(32)-C(33)-C(38)	122.20(16)
C(12)-C(11)-C(10)	122.27(17)	C(34)-C(33)-C(38)	120.27(15)
C(11)-C(12)-C(13)	118.10(18)	N(2)-C(34)-C(29)	120.00(15)
C(11)-C(12)-C(16)	121.59(18)	N(2)-C(34)-C(33)	118.43(15)
C(13)-C(12)-C(16)	120.30(19)	C(29)-C(34)-C(33)	121.57(15)
C(14)-C(13)-C(12)	121.34(17)	C(29)-C(35)-C(36)	112.33(19)
C(13)-C(14)-C(9)	118.65(16)	C(29)-C(35)-C(37)	110.60(19)
C(13)-C(14)-Cr(1)	114.92(13)	C(36)-C(35)-C(37)	110.97(19)
C(9)-C(14)-Cr(1)	125.41(13)	C(33)-C(38)-C(40)	110.90(17)
C(18)-C(17)-C(22)	117.84(18)	C(33)-C(38)-C(39)	113.10(18)
C(18)-C(17)-C(23)	121.81(17)	C(40)-C(38)-C(39)	110.4(2)

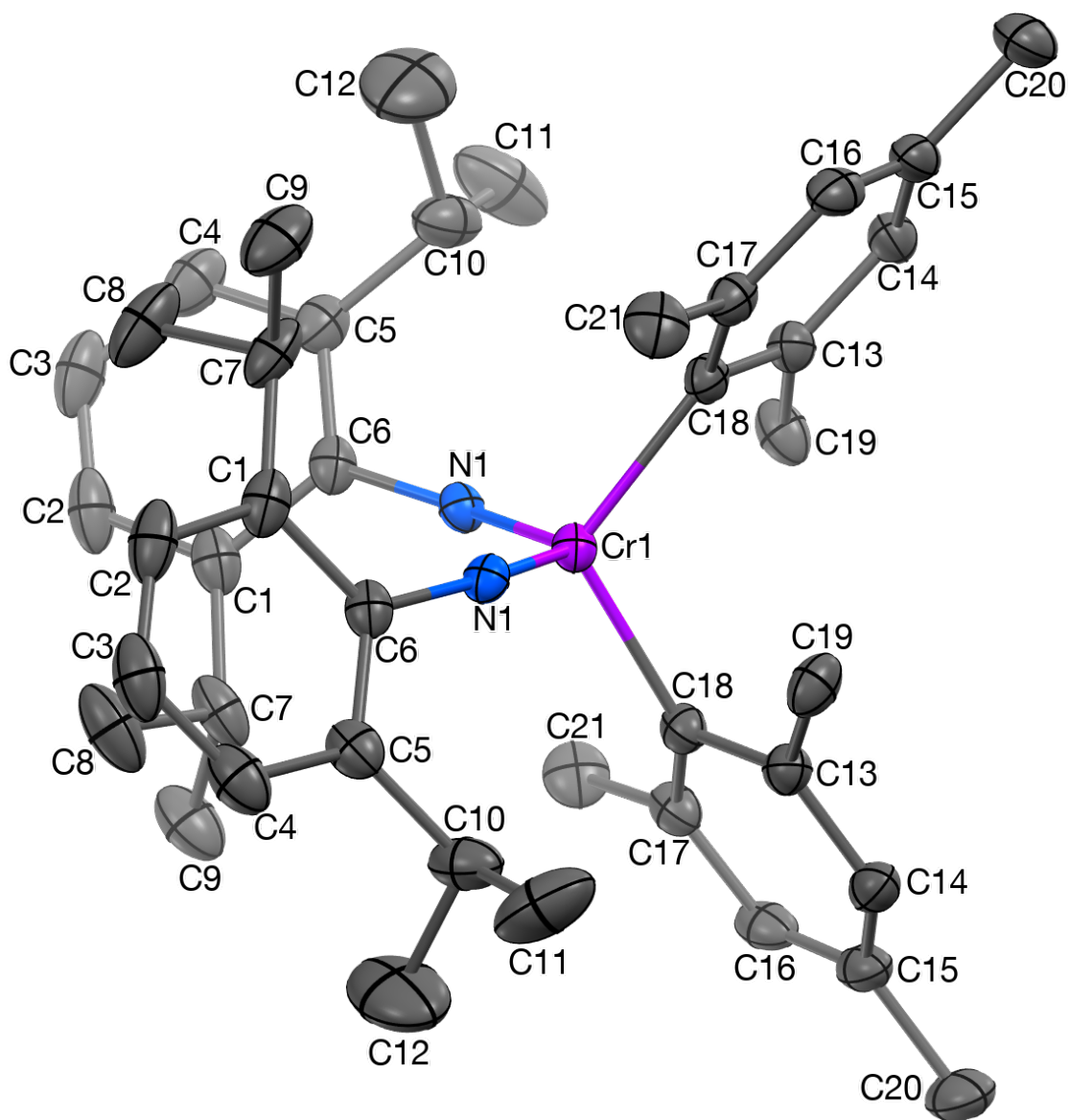


Figure 1.7 Molecular structure of $(\text{ArN})_2\text{Cr}(\text{mes})_2$ (**12**). Ellipsoids are drawn at the 30% probability level. Hydrogen atoms have been omitted for clarity.

Table 1.7 Interatomic distances (Å) and angles (°) for (ArN)₂Cr(mes)₂ (**12**)

Distances (Å)			
Cr(1)-N(1)	1.6549(16)	C(7)-C(9)	1.527(4)
Cr(1)-N(1)	1.6549(16)	C(7)-C(8)	1.539(4)
Cr(1)-C(18)	2.023(2)	C(10)-C(11)	1.521(5)
Cr(1)-C(18)	2.023(2)	C(10)-C(12)	1.529(5)
N(1)-C(6)	1.390(3)	C(13)-C(14)	1.393(3)
C(1)-C(2)	1.394(4)	C(13)-C(18)	1.421(3)
C(1)-C(6)	1.419(3)	C(13)-C(19)	1.514(3)
C(1)-C(7)	1.516(4)	C(14)-C(15)	1.381(3)
C(2)-C(3)	1.374(4)	C(15)-C(16)	1.377(4)
C(3)-C(4)	1.371(4)	C(15)-C(20)	1.512(3)
C(4)-C(5)	1.388(3)	C(16)-C(17)	1.396(3)
C(5)-C(6)	1.412(3)	C(17)-C(18)	1.416(3)
C(5)-C(10)	1.523(4)	C(17)-C(21)	1.505(3)
Angles (°)			
N(1)-Cr(1)-N(1)	110.20(12)	C(1)-C(7)-C(8)	110.3(2)
N(1)-Cr(1)-C(18)	111.08(8)	C(9)-C(7)-C(8)	109.4(2)
N(1)-Cr(1)-C(18)	106.53(8)	C(11)-C(10)-C(5)	110.3(2)
N(1)-Cr(1)-C(18)	106.52(8)	C(11)-C(10)-C(12)	111.2(3)
N(1)-Cr(1)-C(18)	111.09(8)	C(5)-C(10)-C(12)	111.6(3)
C(18)-Cr(1)-C(18)	111.49(12)	C(14)-C(13)-C(18)	120.3(2)
C(6)-N(1)-Cr(1)	156.72(14)	C(14)-C(13)-C(19)	116.9(2)
C(2)-C(1)-C(6)	117.5(2)	C(18)-C(13)-C(19)	122.73(19)
C(2)-C(1)-C(7)	119.6(2)	C(15)-C(14)-C(13)	122.0(2)
C(6)-C(1)-C(7)	122.9(2)	C(16)-C(15)-C(14)	117.5(2)
C(3)-C(2)-C(1)	122.0(3)	C(16)-C(15)-C(20)	121.2(2)
C(4)-C(3)-C(2)	119.8(3)	C(14)-C(15)-C(20)	121.2(3)
C(3)-C(4)-C(5)	121.7(3)	C(15)-C(16)-C(17)	123.3(2)
C(4)-C(5)-C(6)	118.4(2)	C(16)-C(17)-C(18)	119.1(2)
C(4)-C(5)-C(10)	120.5(2)	C(16)-C(17)-C(21)	116.9(2)
C(6)-C(5)-C(10)	121.1(2)	C(18)-C(17)-C(21)	123.9(2)

N(1)-C(6)-C(5)	118.38(19)	C(17)-C(18)-C(13)	117.70(19)
N(1)-C(6)-C(1)	121.0(2)	C(17)-C(18)-Cr(1)	126.58(17)
C(5)-C(6)-C(1)	120.6(2)	C(13)-C(18)-Cr(1)	115.42(15)
C(1)-C(7)-C(9)	111.9(2)		

Table 1.8 shows a comparison of Cr-N and Cr-C_α bond lengths of the new organometallic compounds. Table 1.9 summarizes bond angles of Cr-N-C and N-Cr-N. Imido bonds of all complexes have Cr-N distances in the range found for bis(imido) chromium(VI) molecules (typically 1.61–1.65 Å).^{15,17,26-28} Cr-C_α bond lengths are consistent with Cr-C single bond.^{15,17,26} Imido bond angles Cr-N-C indicate that the geometries of imido ligands are at the low end of linear coordination except one imido of **8**.⁷ Substitutions in the 2,6-positions of the aromatic ring make the Cr-C_α bonds of **10** and **12** longer than those of the other three chromium diaryls.

Table 1.8 Cr-N bond length and Cr-C_{ipso} bond length for **5** and **7-12**

Complex	Cr-N (Å)		Cr-C _α (Å)	
(ArN) ₂ Cr(CH ₂ Ph) ₂ (5)	1.644(3)	1.653(3)	2.044(4)	2.078(4)
(ArN) ₂ Cr(CH ₂ SiMe ₃) ₂ (7)	1.6496(15)	1.6522(15)	2.0113(19)	2.0182(18)
(ArN) ₂ CrPh ₂ (8)	1.637(4)	1.653(3)	1.996(6)	2.004(7)
(ArN) ₂ Cr(<i>p</i> -tol) ₂ (9)	1.6461(19)	1.6523(17)	1.996(2)	1.996(2)
(ArN) ₂ Cr(2,6-Me ₂ Ph) ₂ (10)	1.647(3)	1.653(3)	2.025(3)	2.033(3)
(ArN) ₂ Cr(3,5-Me ₂ Ph) ₂ (11)	1.6491(14)	1.6507(14)	1.9955(17)	2.0002(16)
(ArN) ₂ Cr(mes) ₂ (12)	1.6549(16)	1.6549(16)	2.023(2)	2.023(2)

Table 1.9 Bond angles Cr-N-C and N-Cr-N for **5** and **7-12**

Complex	Cr-N-C (°)		N-Cr-N (°)
(ArN) ₂ Cr(CH ₂ Ph) ₂ (5)	157.7(3)	154.3(3)	110.51(14)
(ArN) ₂ Cr(CH ₂ SiMe ₃) ₂ (7)	158.57(13)	158.45(13)	113.85(7)
(ArN) ₂ CrPh ₂ (8)	172.1(3)	156.0(3)	116.92(17)
(ArN) ₂ Cr(<i>p</i> -tol) ₂ (9)	153.25(16)	162.94(16)	113.70(9)
(ArN) ₂ Cr(2,6-Me ₂ Ph) ₂ (10)	156.0(2)	152.7(2)	108.74(13)
(ArN) ₂ Cr(3,5-Me ₂ Ph) ₂ (11)	156.17(12)	154.43(12)	111.84(7)
(ArN) ₂ Cr(mes) ₂ (12)	156.72(14)	156.72(14)	110.20(12)

Table 1.10 shows the chemical shifts of the C_{ipso} of each chromium diaryl complex in the ¹³C NMR spectra and the lowest-energy absorption band in the UV-vis spectra. An interesting correlation was found between the chemical shifts of C_{ipso} and the lowest-energy absorption band. The lowest-energy absorption bands for **8-12** in the UV-vis spectra show that the energy of ligand to metal charge transfer transitions of **10** and **12** is less than those of **8**, **9** and **11**. The more downfield shift of the C_{ipso} of **10** and **12** than the C_{ipso} of **8**, **9** and **11** might be a result of the paramagnetic contribution (σ_P), which is one component of the molecular shielding (σ , $\sigma = \sigma_D + \sigma_P$). In NMR spectroscopy, the diamagnetic contribution (σ_D) causes an upfield shift whereas the paramagnetic contribution causes a downfield shift. The

$$\sigma_P = \frac{e^2 h}{8\pi^2 M_e^2 c^2 \Delta E} \langle 1/r^3 \rangle_{2p} \left[Q_N + \sum Q_{ND} \right]$$

paramagnetic contribution is inversely proportional to the average excitation energy (ΔE).³¹ Based on the aforementioned result from the UV-vis spectra, σ_P in **10** and **12** is more than that in **8**, **9** and **11**. Thus, the C_{ipso} of **10** and **12** have more downfield shift than the C_{ipso} of **8**, **9** and **11**. It is notable, that **10** and **12** are also the most thermally stable diaryls in this group. However, I believe this is coincidental.

Table 1.10 Chemical shift of C_{ipso} and the lowest-energy absorption band in UV-vis for **8–12**

Complex	δ (C_{ipso}) (ppm)	Lowest-energy Absorption Band in UV-vis (nm)
(ArN) ₂ CrPh ₂ (8)	194.28	603
(ArN) ₂ Cr(<i>p</i> -tol) ₂ (9)	193.68	608
(ArN) ₂ Cr(2,6-Me ₂ Ph) ₂ (10)	203.09	624
(ArN) ₂ Cr(3,5-Me ₂ Ph) ₂ (11)	195.44	610
(ArN) ₂ Cr(mes) ₂ (12)	202.92	625

1.2.2 Thermostability study

A thermostability study of the five chromium(IV) diaryls was conducted by monitoring their decomposition reactions by ¹H NMR spectroscopy. Decompositions of **8**, **9**, **11** were observed at 50 °C. **10** and **12** were both stable at this temperature. After increasing the temperature to 80 °C, decompositions of **10**, **12** were observed. Here are some observations about the relative decomposition rates:

- **8**: No decomposition was observed at 50 °C after 1 hour and decomposition was complete after one day at 50 °C.
- **9**: 45 % decomposition was observed after one day at 50 °C.

- **10**: No decomposition was observed at 50 °C after one day. 25 % decomposition was observed after one day at 80 °C.
- **11**: 12 % decomposition was observed after one hour at 50 °C and decomposition was complete after one day at 50 °C.
- **12**: 14 % decomposition was observed after one day at 80 °C.

Based on the relative decomposition rate, the thermostability of these five chromium diaryls ranks as: **11** < **8** < **9** << **10** < **12**. **10** and **12** are significantly more stable than **8**, **9** and **11** at elevated temperature. To understand the reason why there is a significant difference in stability of **8** to **12**, the decomposition mechanism should be addressed.

These decompositions generated unidentified black particles and organic products. Table 1.11 lists the organic decomposition product of each diaryl complex.

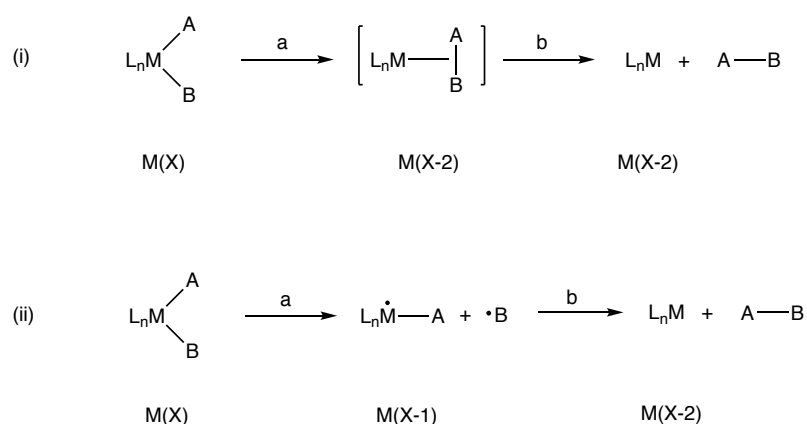
Table 1.11 Chromium(VI) diaryls and the corresponding organic decomposition products

Cr(VI) diaryl	Organic decomposition product
(ArN) ₂ CrPh ₂ (8)	biphenyl
(ArN) ₂ Cr(<i>p</i> -tol) ₂ (9)	4,4'-dimethylbiphenyl
(ArN) ₂ Cr(2,6-Me ₂ Ph) ₂ (10)	<i>m</i> -xylene
(ArN) ₂ Cr(3,5-Me ₂ Ph) ₂ (11)	3,3',5,5'-tetramethylbiphenyl
(ArN) ₂ Cr(mes) ₂ (12)	mesitylene

Curiously, *m*-xylene and mesitylene were formed exclusively from decomposition of **10** and **12**, respectively, instead of the corresponding biaryl. The integration of the peaks of mesitylene from the decomposition of **12** in the ¹H NMR

spectrum shows a ratio of 2.98:1 between the methyl hydrogen and the aromatic hydrogen. This suggests the hydrogen source is not solvent (C_6D_6). My guess is that the hydrogen is probably from the methyl group in the *ortho* positions of the aryl ligand or the isopropyl group of the imido ligand. However, I do not have any experimental data to support it.

Based on the organic decomposition products of **8–12**, the thermolysis of complexes should follow the mechanism of reductive elimination. Reductive elimination, the reverse of oxidative addition, is often seen in high oxidation states because the formal oxidation state of the metal is reduced by two units in the reaction. Generally, a concerted pathway and a radical mechanism are both possible with reductive



Scheme 1.9 Two possible mechanisms for reductive elimination: (i) concerted reductive elimination; (ii) radical mechanism

elimination. In a concerted mechanism, step a (the reductive step) in (i) of Scheme 1.9 involves formation of a σ -complex during which the formal oxidation of the metal

changed from X to X-2. Step b is dissociation of A-B from the metal center. In a radical pathway, step a in (ii) of Scheme 1.9 is the homolysis of the bond M-B to form L_nMA and radical B during which the formal oxidation of the metal changed from X to X-1. Step b is abstraction of A by radical B to form A-B.³² Obviously, one major difference between these two pathways is the formation of an intermediate radical. To distinguish which pathway is involved in a reductive elimination, a radical trap (e.g. 9,10-dihydroanthracene, as known as DHA) can be added to a reaction of reductive elimination. The formation of HB might be evidence of the radical pathway that the reductive elimination follows.

Accordingly, to figure out the mechanism of the decompositions of these chromium diaryl complexes, the following experiments were carried out. Heating **11** with 2.8 equivalents of 9,10-dihydroanthracene (DHA) in C_6D_6 at 50 °C for 16 hours still yielded 3,3',5,5'-tetramethylbiphenyl instead of *m*-xylene, suggesting the absence of free radicals. Besides, the thermostability rank of **8–12** argues against homolysis of Cr- C_{ipso} . If these decompositions follow a radical pathway, **10** and **12** are expected to be less stable because they have weaker bonds of Cr- C_{ipso} than those bonds of **8**, **9** and **11** according to the longer bond lengths of Cr- C_{ipso} . Thus, I postulate that the decompositions of these chromium diaryl complexes (**8**, **9**, **11**) follow the concerted reductive elimination pathway, involving a three-centered (Cr, 2 C_{ipso}) transition state. Due to the substituents in the *ortho* positions, the decompositions of **10** and **12** are more sterically hindered than the decompositions of **8**, **9** and **11** following the concerted reductive elimination pathway. Thus, **10** and **12** are significantly more stable than **8**, **9** and **11** at elevated temperature.

Interestingly, heating a mixture of **8** and **11** in C₆D₆ at 50 °C for one day not only yielded biphenyl and 3,3',5,5'-tetramethylbiphenyl but also gave 3,5-dimethylbiphenyl. Based on the integration of the characteristic methyl peaks of 3,3',5,5'-tetramethylbiphenyl and 3,5-dimethylbiphenyl in the ¹H NMR spectrum, the ratio between 3,3',5,5'-tetramethylbiphenyl and 3,5-dimethylbiphenyl is about 1.56:1. The formation of the mixed biaryl could be an indicator of decomposition via the radical pathway, i.e. **8** and **11** underwent homolysis and generated phenyl radical and 3,5-dimethylphenyl radical, respectively. However, the formation of the mixed biaryl did not rule out the possibility of the concerted pathway because the mixed biaryl could be formed from the decomposition of (ArN)₂Cr(Ph)(3,5-Me₂Ph), which might result from the transmetalation of **8** and **11** during the reaction. To figure out if (ArN)₂Cr(Ph)(3,5-Me₂Ph) was formed or not, the following experiment was done. Heating a mixture of **8** and **11** (ratio = 1:1.06, based on the integration) in C₆D₆ at 50 °C for one hour, resulted in some new peaks in the ¹H NMR spectrum. Some of these new peaks were assigned to 3,3',5,5'-tetramethylbiphenyl. The other new peaks were assigned to the mixed diaryl chromium complex. Based on the integration of the characteristic peaks of **8** (*H_{ortho}* of Ph), **11** (*H_{ortho}* of 3,5-Me₂Ph) and (ArN)₂Cr(Ph)(3,5-Me₂Ph) (*H_{ortho}* of Ph), the ratio between **8**, **11** and (ArN)₂Cr(Ph)(3,5-Me₂Ph) is about 1:0.99:1.8. After one day of heating, peaks that belong to (ArN)₂Cr(Ph)(3,5-Me₂Ph) were gone and the peaks of 3,5-dimethylbiphenyl showed up in the ¹H NMR spectrum. Thus, the formation of the mixed biaryl is not evidence for the radical reductive elimination mechanism. 3,5-dimethylbiphenyl was presumably generated from the decomposition of the mixed diaryl chromium complex (ArN)₂Cr(Ph)(3,5-Me₂Ph).

1.3 Experimental

1.3.1 General Considerations

All manipulations were carried out with standard Schlenk, vacuum line, and glovebox techniques. Pentane, diethyl ether, toluene and tetrahydrofuran were dried by passing through activated alumina and were degassed prior to use. THF- d_8 and C_6D_6 were purchased from Cambridge Isotopes Laboratory, dried with sodium and stored under vacuum over Na/K alloy. Grignard reagents and $AlPh_3$ were purchased from Sigma Aldrich. $(^tBuN)_2Cr(OSiMe_3)_2$,¹¹ $(^tBuN)_2CrCl_2$,¹⁴ $(ArN)_2CrCl_2$ ($Ar = 2,6$ -diisopropylphenyl)¹⁶, $(ArN)_2Cr(CH_2CMe_3)_2$,¹⁷ $(ArN)_2Cr(CH_3)_2$ and $(ArN)_2Cr(CH_2Ph)_2$ ¹⁸ were prepared according to literature procedures.

1H NMR spectra were taken on a Bruker AVIII-400 spectrometer and were referenced to the residual protons of the solvent ($C_6D_6 = 7.16$ ppm, THF- $d_8 = 3.58$ ppm and 1.72 ppm). ^{13}C NMR spectra were taken on a Bruker AVIII-400 or a Bruker AVIII-600 spectrometer and were referenced to the ^{13}C of the solvent ($C_6D_6 = 128.06$ ppm, THF- $d_8 = 67.21$ ppm and 25.31 ppm).³³ FT-IR spectra were obtained using a Nicolet Magna-IR 560 spectrometer with a resolution of 4 cm^{-1} . UV-vis spectra were obtained using a SILVER-Nova-TEC-X2 equipped with SL1-LED, which was purchased from StellarNet Inc. X-ray crystallographic studies were conducted in the X-ray Crystallographic Laboratory at the University of Delaware. Elemental analyses were obtained from Robertson Microlit, Ledgewood, NJ. LIFDI-MS were obtained using a Waters GCT Premier high-resolution time-of-flight mass spectrometer by liquid injection field desorption ionization (LIFDI-MS).

1.3.2 X-ray Crystallography

Unless specified otherwise, single crystal X-ray diffraction studies were performed under the following conditions. Crystals were selected, sectioned as required, and mounted onto MiTeGenTM plastic mesh with viscous oil and flash-cooled to the data collection temperature. Diffraction data were collected on a Bruker-AXS APEX II Duo CCD diffractometer with graphite-monochromated Mo-K α radiation ($\lambda=0.71073$ Å). The data-sets were treated with absorption corrections based on redundant multi-scan data.³⁴ The structures were solved using intrinsic phasing and refined with full-matrix, least-squares procedures on F^2 .³⁵⁻³⁶ Unit cell parameters were determined by sampling three different sections of the Ewald sphere. Nonhydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were treated as idealized contributions with geometrically calculated positions. Structure factors and anomalous dispersion coefficients are contained in the SHELXTL program library.

The unit cell parameters and systematic absences in the diffraction data were consistent for space group $P 2_12_12_1$ for **5**, $P 2_1/n$ for **7**, $P 2_12_12_1$ for **8**, $P 2_1/n$ for **11**, $C 2/c$ for **12**. No symmetry higher than triclinic was observed in the diffraction data for **9**, **10**. Structural solution in the centrosymmetric space group option, $P \bar{1}$, yielded chemically reasonable and computationally stable results of refinement. One isopropyl group on arylimido ligand in **5** was found disordered in two positions with a refined site occupancy ratio of 77/23. One pentane molecule in the diffraction data of **11** was squeezed in PLATON.

Some CIFs have been deposited with the Cambridge Crystallographic Database Centre under depositary numbers **5**: 1831800; **7**: 1831801.

1.3.3 Preparation of (ArN)₂Cr(CH₂SiMe₃)₂ (7)

(ArN)₂CrCl₂ (0.220 g, 0.465 mmol) was dissolved in 50 mL Et₂O, giving a red solution. The solution was stored at -30 °C for 15 min before adding the Grignard reagent. 2 equiv. of (Me₃SiCH₂)MgCl (0.72 mL, 1.3 M in THF, 0.930 mmol) were added dropwise into the pre-chilled (-30 °C) solution. The solution was stirred at room temperature for 2 hours during which time the color changed to green. The solvent was then removed in vacuum and the residue was extracted with pentane and the extract was filtered through Celite. The filtrate was concentrated to 4 mL and then cooled to -30 °C overnight to yield green crystals. Yield: 0.166 g, 62%. ¹H NMR (400 MHz, C₆D₆): δ 6.89 (m, 6 H, ArN), 3.79 (sept, 4 H, CHMe₂), 1.96 (s, 4 H, CH₂SiMe₃), 1.12(d, 24 H, CHMe₂), 0.35 (s, 18 H, CH₂SiMe₃) ppm. ¹³C {¹H} NMR (150 MHz, C₆D₆): δ 157.86 (C_{ipso} of ArN), 145.69 (C_{ortho} of ArN), 128.35 (C_{para} of ArN), 123.06 (C_{para} of ArN), 65.13 (CH₂SiMe₃), 28.60 (CHMe₂), 23.85 (CHMe₂), 1.97 (CH₂SiMe₃) ppm. Anal. Calcd. for C₃₂H₅₆CrN₂Si₂: C, 66.61; H, 9.78; N, 4.86. Found: C, 66.57; H, 9.70; N, 4.80. MS(LIFDI) m/z: 576.3293 [M⁺]. Calcd. m/z: 576.3387 [M⁺]. IR (KBr, cm⁻¹): 3054 (w), 2962 (s), 2866 (m), 1455 (w), 1381 (w), 1359 (w), 1321 (w), 1272 (w), 1243 (m), 930 (w), 875 (m), 845 (s), 829 (s), 797 (w), 756 (m), 737 (w), 724 (w), 704 (w), 679 (w). UV-vis (pentane): λ_{max} (ε) = 263 (4.9*10⁴), 296 (4.3*10⁴), 436 (8.5*10³), 629 (6.8*10³) nm (M⁻¹cm⁻¹). M.p.: 154 °C.

1.3.4 Preparation of (ArN)₂CrPh₂ (8)

(ArN)₂CrCl₂ (0.220g, 0.465 mmol) was dissolved in 60 mL diethyl ether and cooled in a freezer (-30 °C). To this red solution was added 0.31 mL AlPh₃ (2/3 equiv., 1.0 M in Bu₂O, 0.310 mmol) dropwise. The solution was allowed to warm to room temperature and stirred for 1 day. On the second day, an additional 0.31 mL AlPh₃

(2/3 equiv., 1.0 M in Et₂O, 0.310 mmol) was added to the solution. On the third day, a third aliquot of 0.31 mL AlPh₃ (2/3 equiv., 1.0 M in Et₂O, 0.310 mmol) was added into solution. On the fourth day, all volatiles were removed from the green solution in vacuum. The residue was extracted with pentane and filtered through Celite. Crystallization from concentrated pentane solution at -30 °C afforded green crystals. Yield: 0.164 g, 63 %. This procedure gave a higher yield than the procedure of adding 2 equiv. of AlPh₃ all at once. ¹H NMR (400 MHz, C₆D₆): δ 8.28 (dd, 4 H, H_{meta}), 7.09 (m, 6 H, H_{ortho} and H_{para} of Ph), 6.95 (m, 6 H, H_{meta} and H_{para} of ArN), 4.05 (sept, 4 H, CHMe₂), 1.07 (d, 24 H, CHMe₂) ppm. ¹³C{¹H} NMR (150 MHz, C₆D₆): δ 194.28 (C_{ipso} of Ph), 158.21 (C_{ipso} of ArN), 146.43 (C_{ortho} of ArN), 135.00 (C_{meta} of Ph), 129.70 (C_{para} of Ph), 128.47 (C_{para} of ArN), 127.62 (C_{ortho} of Ph), 123.13 (C_{meta} of ArN), 28.69 (CHMe₂), 23.94 (CHMe₂) ppm. Anal. Calcd. for C₃₆H₄₄CrN₂: C, 77.66; H, 7.97; N, 5.03. Found: C, 77.66; H, 7.97; N, 5.05. IR (KBr, cm⁻¹): 3051 (w), 2962 (s), 2924 (m), 2867 (m), 1582 (w), 1558 (w), 1464 (m), 1419 (w), 1382 (w), 1360 (w), 1320 (w), 1249 (w), 1058 (w), 1015 (w), 990 (m), 935 (w), 801 (w), 767 (m), 725 (s), 690 (s), 464 (w). UV-vis (pentane): λ_{max} (ε) = 257 (3.7*10⁴), 295.5 (3.3*10⁴), 603 (5.1*10³) nm (M⁻¹cm⁻¹). M.p.: 130 °C.

1.3.5 Preparation of (ArN)₂Cr(*p*-tol)₂ (9)

(ArN)₂CrCl₂ (0.220 g, 0.465 mmol) was dissolved in 50 mL Et₂O, giving a red solution. The solution was stored in freezer for 15 min before adding Grignard reagent. 2 equiv. of (*p*-tol)MgCl (1.96 mL, 0.5 M in Et₂O, 0.930 mmol) were added dropwise into the pre-chilled (-30 °C) solution. The solution was stirred at room temperature for 2 hours during which time the color changed to green-brown. The solvent was then removed in vacuum. The residue was extracted with pentane and the extract was

filtered through Celite. The filtrate was concentrated to 4 mL and then cooled to -30 °C overnight to yield green crystals. Yield: 0.117 g, 43 %. ^1H NMR (400 MHz, C_6D_6): δ 8.30 (d, 4 H, H_{meta}), 6.97 (m, 6 H, ArN), 6.92 (d, 4 H, H_{ortho}), 4.12 (sept, 4 H, CHMe_2), 2.03 (s, 6H, *para*- CH_3), 1.11 (d, 24 H, CHMe_2) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, C_6D_6): δ 193.68 (C_{ipso} of *p*-tol), 158.23 (C_{ipso} of ArN), 146.25 (C_{ortho} of ArN), 139.57 (C_{para} of *p*-tol), 135.46 (C_{meta} of *p*-tol), 127.90 (C_{para} of ArN), 127.80 (C_{ortho} of *p*-tol), 123.11 (C_{meta} of ArN), 28.67 (CHMe_2), 24.00 (CHMe_2), 21.68 (*p*-tol) ppm. Anal. Calcd. for $\text{C}_{38}\text{H}_{48}\text{CrN}_2$: C, 78.05; H, 8.27; N, 4.79. Found: C, 77.85; H, 8.55; N, 4.73. IR (KBr, cm^{-1}): 3050 (w), 2962 (s), 2924 (m), 2867 (m), 1577 (w), 1458 (m), 1382 (w), 1361 (w), 1262 (w), 1208 (w), 1181 (w), 1100 (w), 1049 (w), 1012 (w), 792 (s), 754 (s), 486 (w). UV-vis (pentane): λ_{max} (ϵ) = 248 (1.1×10^5), 279.5 (7.5×10^4), 353 (4.7×10^4), 408.5 (3.3×10^4), 608 (8.5×10^3) nm ($\text{M}^{-1}\text{cm}^{-1}$). M.p.: 117 °C.

1.3.6 Preparation of $(\text{ArN})_2\text{Cr}(\text{2,6-Me}_2\text{Ph})_2$ (10)

$(\text{ArN})_2\text{CrCl}_2$ (0.142 g, 0.300 mmol) was dissolved in 40 mL Et_2O , giving a red solution. The solution was stored in the glove box freezer (-30 °C) for 15 min before adding Grignard reagent. 2 equiv. of $(\text{2,6-Me}_2\text{Ph})\text{MgCl}$ (0.60 mL, 1.0 M in THF, 0.600 mmol) were added dropwise into the pre-chilled (-30 °C) solution. The solution was stirred at room temperature for 2 hours during which time the color changed to green-brown. The solvent was then removed in vacuum. The residue was extracted with pentane and the extract filtered through Celite. The filtrate was concentrated to 3 mL and then cooled to -30 °C overnight to yield green crystals. Yield: 0.076 g, 41 %. ^1H NMR (400 MHz, C_6D_6): δ 7.05 (t, 2 H, H_{para} of 2,6- Me_2Ph), 6.94 (d, 4 H, H_{meta} of 2,6- Me_2Ph), 6.88 (s, 6 H, ArN), 3.86 (sept, 4 H, CHMe_2), 2.93 (s, 12 H, Me_2Ph), 0.89 (d, 24 H, CHMe_2) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, C_6D_6): δ 203.09 (C_{ipso} of 2,6-

Me₂Ph), 159.70 (*C_{ipso}* of ArN), 145.92 (*C_{ortho}* of ArN), 140.44 (*C_{ortho}* of 2,6-Me₂Ph), 130.06 (*C_{para}* of 2,6-Me₂Ph), 128.61 (*C_{para}* of ArN), 127.33 (*C_{meta}* of 2,6-Me₂Ph), 123.88 (*C_{meta}* of ArN), 28.03 (CHMe₂), 27.79 (2,6-Me₂Ph), 24.21 (CHMe₂) ppm. Anal. Calcd. for C₄₀H₅₂CrN₂: C, 78.39; H, 8.55; N, 4.57. Found: C, 79.06; H, 8.71; N, 4.53. IR (KBr, cm⁻¹): 3040 (w), 2962 (s), 2924 (s), 2866 (m), 1457 (s), 1435 (m), 1382 (w), 1360 (w), 1315 (w), 1253 (w), 1226 (w), 1103 (w), 1055 (w), 979 (w), 933 (w), 798 (w), 766 (s), 754 (s), 705 (w). UV-vis (pentane): λ_{max} (ε) = 245.5 (1.1*10⁵), 286 (9.0*10⁴), 379 (3.8*10⁴), 422 (3.3*10⁴), 624 (8.4*10³) nm (M⁻¹cm⁻¹). M.p.: 166 °C.

1.3.7 Preparation of (ArN)₂Cr(3,5-Me₂Ph)₂ (11)

(ArN)₂CrCl₂ (0.100 g, 0.211 mmol) was dissolved in 30 mL Et₂O, giving a red solution. The solution was stored in the glove box freezer (-30 °C) for 15 min before adding Grignard reagent. 2 equiv. of (3,5-Me₂Ph)MgBr (0.85 mL, 0.5 M in 2-MeTHF, 0.425 mmol) were added dropwise into the pre-chilled (-30 °C) solution. The solution was stirred at room temperature for 2 hours during which time the color changed to green. The solvent was then removed in vacuum. The residue was extracted with pentane and the extract was filtered through Celite. The filtrate was concentrated to 3 mL and then cooled to -30 °C overnight to yield green crystals. Yield: 0.068 g, 53%. ¹H NMR (400 MHz, C₆D₆): δ 8.10 (s, 4 H, *H_{ortho}* of 3,5-Me₂Ph), 6.98 (m, 6 H, ArN), 6.76 (s, 2 H, *H_{para}* of 3,5-Me₂Ph), 4.15 (sept, 4 H, CHMe₂), 2.11 (s, 12 H, 3,5-Me₂Ph), 1.12 (d, 24 H, CHMe₂) ppm. ¹³C {¹H} NMR (150 MHz, C₆D₆): δ 195.44 (*C_{ipso}* of 3,5-Me₂Ph), 158.19 (*C_{ipso}* of ArN), 146.30 (*C_{ortho}* of ArN), 136.41 (*C_{meta}* of 3,5-Me₂Ph), 132.82 (*C_{ortho}* of 3,5-Me₂Ph), 131.52 (*C_{para}* of 3,5-Me₂Ph), 127.82 (*C_{para}* of ArN) (assigned based on HSQC due to overlap with C₆D₆ peak), 123.16 (*C_{meta}* of ArN), 28.64 (CHMe₂), 24.09 (CHMe₂), 21.45 (3,5-Me₂Ph) ppm. Anal. Calcd. for

C₄₀H₅₂CrN₂: C, 78.39; H, 8.55; N, 4.57. Found: C, 77.48; H, 8.84; N, 4.30. IR (KBr, cm⁻¹): 3018 (w), 2963 (s), 2923 (m), 2867 (w), 1585 (w), 1552 (w), 1458 (m), 1381 (w), 1358 (w), 1321 (w), 1262 (w), 1109 (w), 1058 (w), 987 (w), 932 (w), 841 (m), 802 (w), 754 (m), 686 (w). UV-vis (pentane): λ_{max} (ϵ) = 250 (7.6*10⁴), 275 (5.9*10⁴), 610 (5.9*10³) nm (M⁻¹cm⁻¹). M.p.: 110 °C.

1.3.8 Preparation of (ArN)₂Cr(mes)₂ (12)

(ArN)₂CrCl₂ (0.220 g, 0.465 mmol) was dissolved in 50 mL Et₂O, giving a red solution. The solution was stored in the glove box freezer (-30 °C) for 15 min before adding Grignard reagent. 2 equiv. of (2,4,6-Me₃Ph)MgCl (0.93 mL, 1.0 M in THF, 0.930 mmol) were added dropwise into the pre-chilled (-30 °C) solution. The solution was stirred at room temperature for 2 hours during which time the color changed to green-brown. The solvent was then removed in vacuum. The residue was extracted with pentane and the extract was filtered through Celite. The filtrate was concentrated to 4 mL and then cooled to -30 °C overnight to yield green crystals. Yield: 0.140 g, 51 %. ¹H NMR (400 MHz, C₆D₆): δ 6.90 (m, 6 H, ArN), 6.75 (s, 4 H, mesityl), 3.92 (sept, 4 H, CHMe₂), 2.97 (s, 12 H, *ortho*-CH₃ of mesityl), 2.09 (s, 6 H, *para*-CH₃ of mesityl), 0.92 (d, 24 H, CHMe₂) ppm. ¹³C{¹H} NMR (150 MHz, C₆D₆): δ 202.92 (C_{ipso} of mesityl), 159.70 (C_{ipso} of ArN), 145.73 (C_{ortho} of ArN), 140.56 (C_{ortho} of mesityl), 139.57 (C_{para} of mesityl), 128.41 (C_{para} of ArN), 127.80 (C_{meta} of mesityl), 123.90 (C_{meta} of ArN), 28.00 (mesityl, overlapped with CHMe₂, assigned by HSQC), 27.95 (CHMe₂), 24.27 (CHMe₂), 21.34 (*para*-CH₃ of mesityl) ppm. Anal. Calcd. for C₄₂H₅₆CrN₂: C, 78.71; H, 8.81; N, 4.37. Found: C, 76.94; H, 7.97; N, 3.58. IR (KBr, cm⁻¹): 3008 (w), 2959 (s), 2923 (m), 2867 (m), 1587 (w), 1459 (m), 1383 (w), 1360 (w), 1316 (w), 1279 (m), 1263 (w), 1223 (w), 1176 (w), 1105 (w), 1055 (w), 982 (w),

932 (w), 846 (w), 798 (w), 754 (s), 702 (w). UV-vis (pentane): λ_{max} (ϵ) = 250
($3.1 \cdot 10^4$), 435 ($1.2 \cdot 10^4$), 625 ($2.9 \cdot 10^3$) nm ($\text{M}^{-1}\text{cm}^{-1}$). M.p.: 185 °C.

Table 1.12 Crystallographic data for complexes **5** and **7-12**

	5 (kla0708)	7 (kla0695)	8 (kla0728)
Formula	C ₃₈ H ₄₇ CrN ₂	C ₃₂ H ₅₆ CrN ₂ Si ₂	C ₃₆ H ₄₄ CrN ₂
Formula Wt.	583.77	576.96	556.73
Space group	<i>P</i> 2 ₁ 2 ₁ 2 ₁	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ 2 ₁ 2 ₁
Color	brown	green	brown
a, Å	9.8933(15)	11.0281(6)	10.3776(10)
b, Å	17.768(3)	16.9697(10)	15.7518(15)
c, Å	19.173(3)	19.3066(11)	19.3244(19)
α, deg	90	90	90
β, deg	90	101.4220(10)	90
γ, deg	90	90	90
V, Å ³	3370.3(9)	3541.5(3)	3158.9(5)
Z	4	4	4
D(calcd), g/cm ³	1.150	1.082	1.171
μ, mm ⁻¹	0.366	0.411	0.388
Temp, K	200	200	200
T _{max} /T _{min}	0.7456/0.6007	0.7456/0.6767	0.7456/0.6410
No. data/params	7746/386	8225/348	7254/361
GOF on F ²	1.010	1.014	0.952
R1(F), % ^a	5.15	4.22	6.40
wR ² (F ²), % ^a	10.59	10.80	10.87

^a Quantity minimized: $wR^2(F^2) = \sum[w(F_o^2 - F_c^2)^2] / \sum[(wF_o^2)^2]^{1/2}$; $R1 = \sum \Delta / \sum (F_o)$, $\Delta = |(F_o - F_c)|$.

Table 1.12 Crystallographic data for complexes **5** and **7-12** (continued)

	9 (kla0714)	10 (kla0741)	11 (kla0705)
Formula	C ₃₈ H ₄₈ CrN ₂	C ₄₀ H ₅₂ CrN ₂	C ₄₀ H ₅₂ CrN ₂
Formula Wt.	584.78	612.83	612.83
Space group	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>P</i> 2 ₁ / <i>n</i>
Color	brown	black	brown
a, Å	10.3322(6)	11.5342(3)	12.7658(9)
b, Å	10.6394(6)	15.7841(5)	18.9424(13)
c, Å	16.1943(9)	19.6623(6)	16.1524(11)
α, deg	97.1300(10)	99.9570(10)	90
β, deg	92.5670(10)	97.1800(10)	91.6720(10)
γ, deg	102.7770(10)	90.2580(10)	90
V, Å ³	1717.90(17)	3496.84(18)	3904.2(5)
Z	2	4	4
D(calcd), g/cm ³	1.131	1.164	1.043
μ, mm ⁻¹	0.359	0.356	0.319
Temp, K	200	200	200
T _{max} /T _{min}	0.7456/0.6965	0.7456/0.7087	0.7456/0.6549
No. data/params	7806/380	16193/798	9083/400
GOF on F ²	1.060	1.043	1.049
R1(F), % ^a	5.26	7.48	4.32
wR ² (F ²), % ^a	13.97	13.50	11.04

^a Quantity minimized: $wR^2(F^2) = \sum[w(F_o^2 - F_c^2)^2] / \sum[(wF_o^2)^2]^{1/2}$; $R1 = \sum \Delta / \sum (F_o)$, $\Delta = |F_o - F_c|$.

Table 1.12 Crystallographic data for complexes **5** and **7-12** (continued)

12 (kla0753)	
Formula	C ₄₂ H ₅₆ CrN ₂
Formula Wt.	640.88
Space group	<i>C</i> 2/ <i>c</i>
Color	red
a, Å	22.883(3)
b, Å	10.1896(12)
c, Å	17.573(2)
α, deg	90
β, deg	110.730(2)
γ, deg	90
V, Å ³	3832.4(8)
Z	4
D(calcd), g/cm ³	1.111
μ, mm ⁻¹	0.327
Temp, K	200
T _{max} /T _{min}	0.7456/0.6730
No. data/params	4405/211
GOF on F ²	1.044
R1(F), % ^a	5.39
wR ² (F ²), % ^a	13.26

^a Quantity minimized: $wR^2(F^2) = \sum[w(F_o^2 - F_c^2)^2] / \sum[(wF_o^2)^2]^{1/2}$; $R1 = \sum \Delta / \sum (F_o)$, $\Delta = |F_o - F_c|$.

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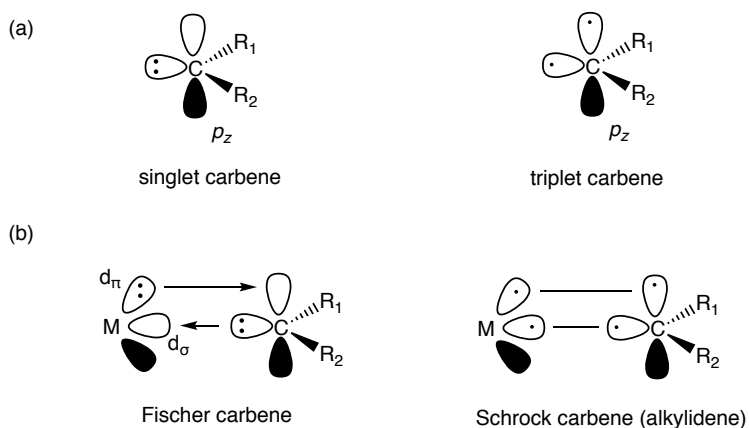
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Chapter 2

SYNTHESIS AND REACTIVITY OF CHROMIUM(VI) ALKYLIDENES

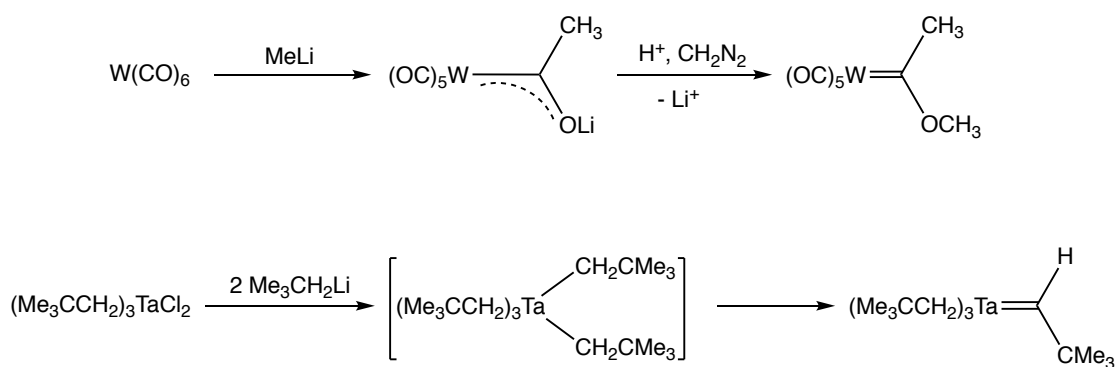
2.1 Introduction

Transition metals can be bonded to carbon through M-C single bonds, as in the complexes introduced in **Chapter 1**. It is also possible for a metal to form a M=C double bond. The corresponding type of complex is called Fischer carbene or Schrock carbene, also known as alkylidene. These two types of transition metal carbene complexes can be identified and distinguished as illustrated in Scheme 2.1. Generally, a Fischer carbene has a low oxidation state metal center, whereas a Schrock carbene has a high oxidation state metal center. Besides, Fischer carbene ligands are π -acceptors and electrophilic at the α -carbon while Schrock carbene ligands are π -donors and nucleophilic at the α -carbon.¹



Scheme 2.1 (a) singlet and triplet forms of a carbene; (b) Fischer carbene and Schrock carbene complexes

The first transition metal carbene, namely $(\text{OC})_5\text{W}[\text{=C}(\text{OCH}_3)(\text{CH}_3)]$ was reported by Fischer et al. in 1964.² Ten years later, the first alkylidene was reported by Schrock. Tris(neopentyl) tantalum dichloride can be further alkylated with neopentyllithium. However, the product penta(neopentyl) tantalum is unstable and undergoes intramolecular α -hydrogen abstraction to afford a new class of complex, namely an alkylidene.³ (Scheme 2.2)



Scheme 2.2 Synthesis of Fischer carbene and Schrock carbene complexes

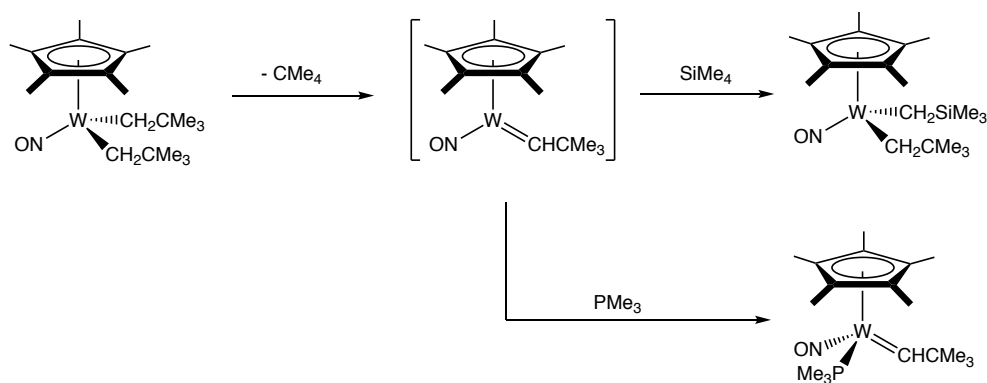
NMR spectroscopy and X-ray diffraction are two common ways to characterize transition metal alkylidenes. Due to short data collection time and easy sample preparation, NMR spectroscopy is considered an invaluable characterization method for diamagnetic high valent metal alkylidenes. In ^1H NMR spectra, the alkylidene hydrogen resonance is usually found downfield (10–15 ppm).⁴⁻⁶ Large chemical shifts (200–300 ppm) of the alkylidene carbon are also a feature of metal alkylidenes in ^{13}C NMR spectroscopy.^{4,6-7} Based on structural parameters, the $\text{M}=\text{C}$ double bond in an alkylidene complex is obviously shorter than $\text{M}-\text{C}$ single bond.

Besides, the alkylidene bond angle $M-C_{\alpha}-C_{\beta}$ is found to be larger than the alkyl bond angle $M-C_{\alpha}-C_{\beta}$ due to sp^2 hybridization of C_{α} in alkylidene complexes.

Since the discovery of $Np_3Ta=CHCMe_3$ by Schrock, transition metal alkylidenes have become an iconic class of organometallic compounds with increasing significance in C-H bond activation and olefin metathesis.

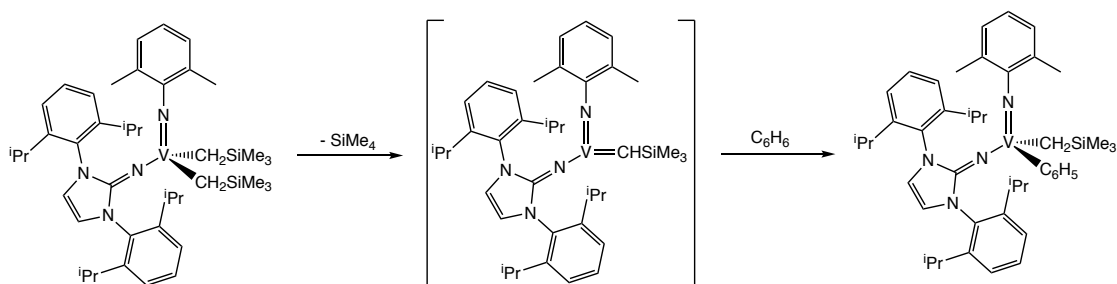
2.1.1 C-H Bond Activation by Alkylidenes

Intramolecular α -hydrogen abstraction from dialkyl precursors, which are not subject to the more facile β -hydrogen elimination, is the simplest synthetic approach to alkylidenes. The reverse of such a reaction is intermolecular C-H bond activation. For example, Legzdins et al. reported a thermally unstable dialkyl, namely $Cp^*Mo(NO)(CH_2CMe_3)_2$, which is able to undergo α -hydrogen abstraction to form a transient coordinatively unsaturated alkylidene. The alkylidene can react with $SiMe_4$ to produce a stable compound $Cp^*Mo(NO)(CH_2CMe_3)(CH_2SiMe_3)$ (Scheme 2.3). The transient alkylidene can be trapped by PMe_3 to form a stable alkylidene complex.⁸



Scheme 2.3 C-H bond activation of $SiMe_4$ initiated by $Cp^*Mo(NO)(CH_2CMe_3)_2$

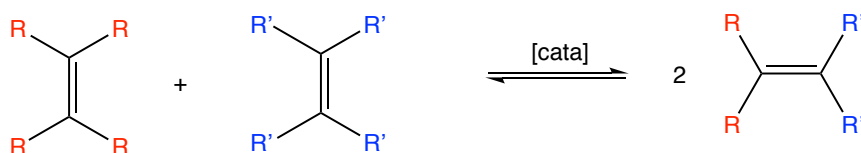
An imido vanadium dialkyl complex, namely $(\text{ArN})[1,3\text{-Ar}'_2(\text{CHN})_2\text{C=N}]\text{V}(\text{CH}_2\text{SiMe}_3)_2$ reported by Nomura et al., loses SiMe_4 to form an alkylidene. The latter is able to react with benzene to generate trimethylsilylmethyl phenyl vanadium complex (Scheme 2.4).⁹



Scheme 2.4 C-H bond activation of benzene initiated by vanadium dialkyl complex

2.1.2 Olefin Metathesis by Alkylidenes

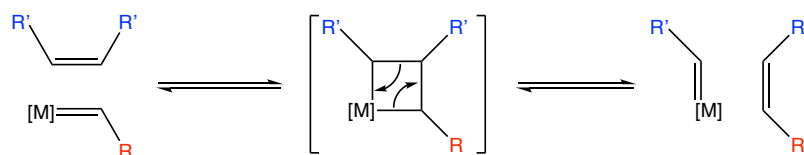
Olefin metathesis is a valuable synthetic tool for the construction of carbon-carbon bonds. As shown in Scheme 2.5, C-C double bonds of $\text{R}_2\text{C}=\text{CR}_2$ and $\text{R}'_2\text{C}=\text{CR}'_2$ can be cleaved and reformed to produce a new olefin $\text{R}_2\text{C}=\text{CR}'_2$ in the presence of alkylidene catalyst.¹⁰



Scheme 2.5 Olefin metathesis

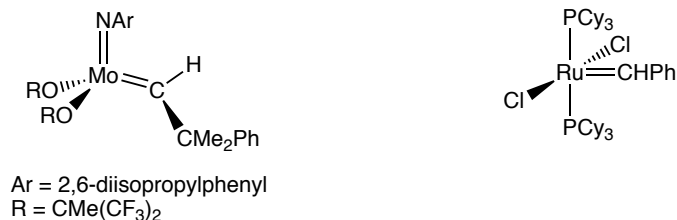
One important application of olefin metathesis is ring-opening metathesis polymerization, as known as ROMP. For example, norbornene is able to undergo ROMP to form polynorbornene, which have been used in a range of applications that include rubber industry, photoresists, and adhesives.¹¹⁻¹²

The non-pairwise mechanism of olefin metathesis was first postulated by Yves Chauvin in 1971. The alkylidene undergoes [2+2] cycloaddition with an olefin to form a metallacyclobutane, which then transforms to a new alkylidene and a new olefin (Scheme 2.6).¹³ This mechanism was verified by Grubbs and Schrock in the late 1970s. Since then, it has been universally recognized and accepted.¹⁴⁻¹⁵



Scheme 2.6 Non-pairwise mechanism of olefin metathesis

The catalysts used for olefin metathesis are of two types, i.e. Schrock catalysts and Grubbs catalysts (Scheme 2.7). Schrock catalysts are high valent metal (Mo^{VI} and W^{VI}) alkylidenes.^{4,16-17} Grubbs catalysts are ruthenium complexes with metal-carbon double bonds.^{11,18-19}

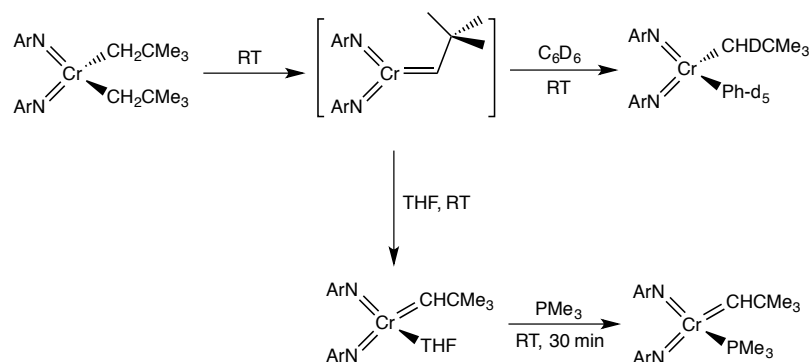


Scheme 2.7 Left: Schrock catalyst. Right: Grubbs catalyst

The Nobel Prize in chemistry 2005 was awarded jointly to Yves Chauvin, Robert H. Grubbs and Richard R. Schrock for the development of the metathesis method in organic synthesis.

2.1.3 Chromium(VI) Alkylidenes

Most alkylidenes contain the heavier group 6 elements (Mo and W), predominantly in their highest oxidation state (VI).²⁰⁻²¹ However, chromium, as a group 6 element in first row, does not have any structurally characterized Cr(VI) alkylidene. The strongest claim for such a complex came from Gibson in 1996. (ArN)₂Cr(CH₂CMe₃)₂ (**6**) is unstable in THF solution at room temperature. It undergoes α -hydrogen abstraction to generate transient neopentylidene [(ArN)₂Cr(=CHCMe₃)], which can be trapped with σ -donors like THF or PMe₃ to form the corresponding product (ArN)₂Cr(=CHCMe₃)L (L = THF, PMe₃). The transient neopentylidene shows ability in C-H bond activation of benzene, as introduced in section 2.1.1 (Scheme 2.8). Due to high solubility of those adducts in common organic solvent (pentane, diethyl ether and THF), they cannot be crystallized for further characterization, like X-ray crystallographic analysis. Thus, no structural parameters of Cr(VI) alkylidene existed before this work.



Scheme 2.8 Chromium(VI) alkylidene species reported by Gibson et al.

As part of an extended survey of organochromium chemistry, I am interested in exploring the chemistry of chromium(VI) alkylidenes. The second chapter of this dissertation focuses on the synthesis, characterization and reactivity study of chromium(VI) alkylidenes.

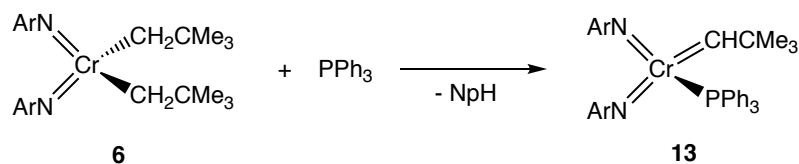
2.2 Results and Discussion

Most alkylidenes are generated by α -hydrogen abstraction of transition metal dialkyls. Alkylidenes in this chapter were made from three dialkyl precursors, namely $(\text{ArN})_2\text{Cr}(\text{CH}_2\text{Ph})_2$ (**5**), $(\text{ArN})_2\text{Cr}(\text{CH}_2\text{CMe}_3)_2$ (**6**) and $(\text{ArN})_2\text{Cr}(\text{CH}_2\text{SiMe}_3)_2$ (**7**). The synthesis and characterization of **5** and **6** have been reported by Gibson before.^{6,22} **7** has been introduced in **Chapter 1**.

2.2.1 Synthesis and Characterization of Chromium(VI) Alkylidenes

As described by Gibson et al., the first chromium(VI) alkylidene, which is generated from **6** by elimination of neopentane, can be trapped by THF and PMe_3 .⁶ I found that an alkylidene triphenylphosphine adduct, namely $(\text{ArN})_2\text{Cr}(=\text{CHCMe}_3)(\text{PPh}_3)$ (**13**), can be produced through the reaction of **6** with PPh_3

in THF (Scheme 2.9). A color change from green to red was observed during the reaction at room temperature for three days.



Scheme 2.9 Synthesis of $(\text{ArN})_2\text{Cr}(=\text{CHCMe}_3)(\text{PPh}_3)$ (**13**)

Due to the better crystallinity of **13**, red crystals suitable for a structure determination by X-ray diffraction were grown from concentrated pentane solution at $-30\text{ }^\circ\text{C}$. The first crystal structure of a chromium(VI) alkylidene is depicted in Figure 2.1. This compound features pseudo-tetrahedral coordination geometry with a large N-Cr-N bond angle $124.26(18)^\circ$, being significantly opened up compared to the dialkyl **6** ($111.71(8)^\circ$). The two imido ligands are both linear with bond angles of Cr-N-C_{ipso} $166.3(3)^\circ$ and $168.5(3)^\circ$ respectively. The most interesting feature of this complex is the short bond length of Cr-C _{α} ($1.848(5)\text{ \AA}$). This bond is considerably shorter than the Cr-C _{α} bonds ($2.030(2)$ and $2.042(2)\text{ \AA}$) that were found in the structure of **6**. The alkylidene hydrogen H1 was located on a difference map and its location was refined. The resulting sum of the bond angles about the alkylidene carbon C1 (357.1°) suggests sp^2 hybridization. The torsion angle of N2-Cr1-C1-C2 (3.59°) indicates that the *tert*-butyl group of the alkylidene ligand is *syn* to one imido ligand. No agostic interaction of Cr1 $\cdots$ H1 $\cdots$ C1 was observed in the structure of **13** based on the bond angle Cr1-C1-C2 ($137.4(4)^\circ$).²³

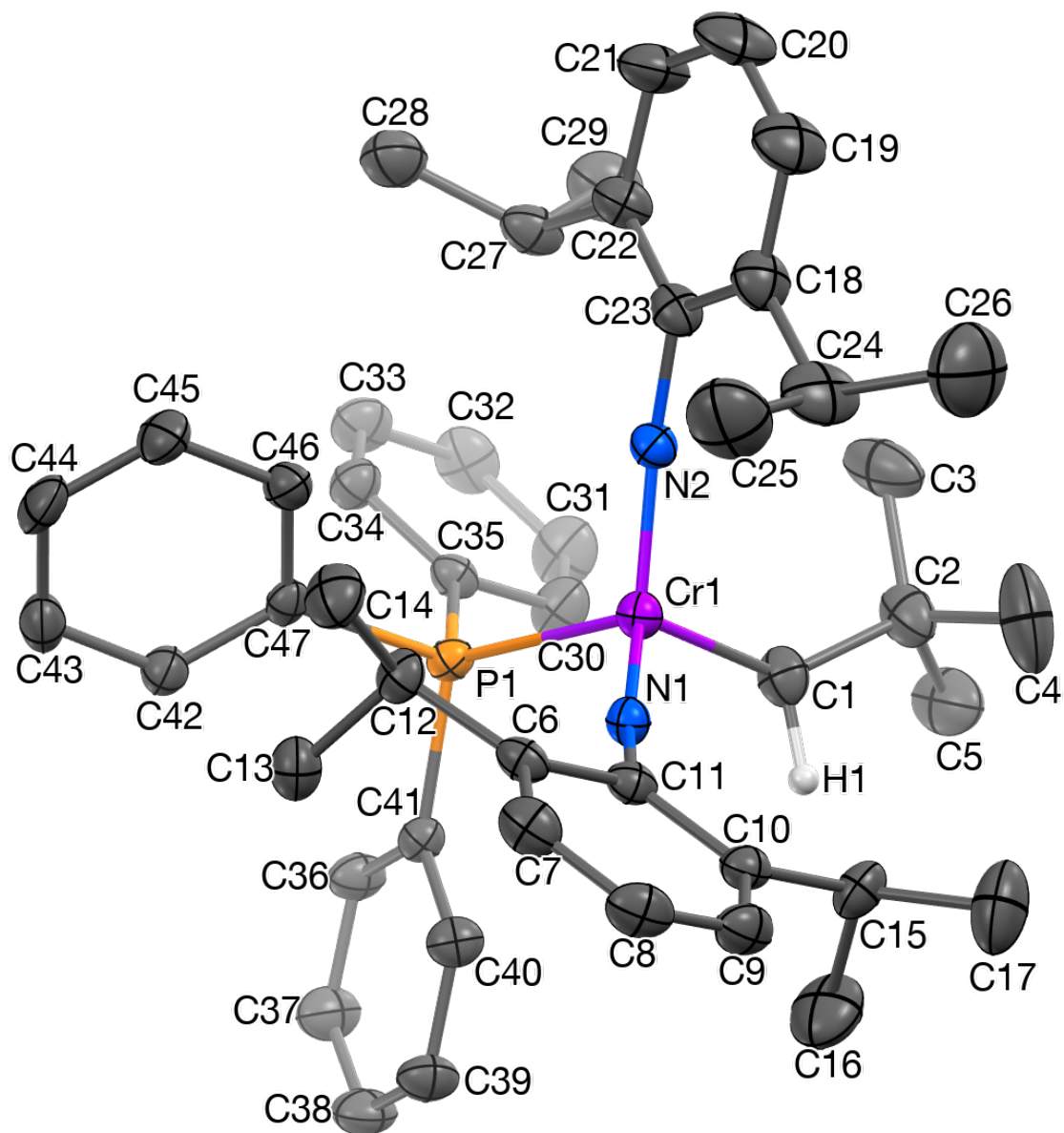


Figure 2.1 Molecular structure of $(\text{ArN})_2\text{Cr}(=\text{CHCMe}_3)(\text{PPh}_3)$ (**13**). Ellipsoids are drawn at the 30% probability level. Hydrogen atoms excluding the alkylidene hydrogen have been omitted for clarity.

Table 2.1 Interatomic distances (Å) and angles (°) for (ArN)₂Cr(=CHCMe₃)(PPh₃)
(13)

Distances (Å)			
Cr(1)-N(2)	1.656(4)	C(18)-C(24)	1.499(8)
Cr(1)-N(1)	1.675(3)	C(19)-C(20)	1.370(8)
Cr(1)-C(1)	1.848(5)	C(20)-C(21)	1.372(8)
Cr(1)-P(1)	2.3647(13)	C(21)-C(22)	1.385(7)
P(1)-C(41)	1.818(4)	C(22)-C(23)	1.403(7)
P(1)-C(35)	1.824(4)	C(22)-C(27)	1.519(7)
P(1)-C(47)	1.829(4)	C(24)-C(25)	1.509(8)
N(1)-C(11)	1.394(5)	C(24)-C(26)	1.520(9)
N(2)-C(23)	1.380(6)	C(27)-C(28)	1.518(7)
C(1)-C(2)	1.516(7)	C(27)-C(29)	1.530(7)
C(1)-H(1)	1.03(4)	C(30)-C(35)	1.378(6)
C(2)-C(5)	1.515(7)	C(30)-C(31)	1.389(7)
C(2)-C(3)	1.523(8)	C(31)-C(32)	1.362(7)
C(2)-C(4)	1.539(9)	C(32)-C(33)	1.372(7)
C(6)-C(7)	1.395(6)	C(33)-C(34)	1.394(6)
C(6)-C(11)	1.423(6)	C(34)-C(35)	1.381(6)
C(6)-C(12)	1.501(6)	C(36)-C(37)	1.385(6)
C(7)-C(8)	1.379(7)	C(36)-C(41)	1.389(6)
C(8)-C(9)	1.364(7)	C(37)-C(38)	1.357(7)
C(9)-C(10)	1.386(6)	C(38)-C(39)	1.372(7)
C(10)-C(11)	1.420(6)	C(39)-C(40)	1.380(6)
C(10)-C(15)	1.505(6)	C(40)-C(41)	1.389(6)
C(12)-C(13)	1.516(7)	C(42)-C(47)	1.384(6)
C(12)-C(14)	1.533(6)	C(42)-C(43)	1.390(6)
C(15)-C(16)	1.504(8)	C(43)-C(44)	1.384(7)
C(15)-C(17)	1.521(7)	C(44)-C(45)	1.367(7)
C(18)-C(19)	1.390(7)	C(45)-C(46)	1.396(6)
C(18)-C(23)	1.424(6)	C(46)-C(47)	1.390(6)

Angles (°)

N(2)-Cr(1)-N(1)	124.26(18)	C(19)-C(18)-C(24)	120.3(5)
N(2)-Cr(1)-C(1)	107.4(2)	C(23)-C(18)-C(24)	121.2(5)
N(1)-Cr(1)-C(1)	107.2(2)	C(20)-C(19)-C(18)	121.0(6)
N(2)-Cr(1)-P(1)	106.83(13)	C(19)-C(20)-C(21)	120.2(6)
N(1)-Cr(1)-P(1)	107.81(13)	C(20)-C(21)-C(22)	121.7(6)
C(1)-Cr(1)-P(1)	100.91(16)	C(21)-C(22)-C(23)	118.5(5)
C(41)-P(1)-C(35)	102.8(2)	C(21)-C(22)-C(27)	119.9(5)
C(41)-P(1)-C(47)	104.3(2)	C(23)-C(22)-C(27)	121.6(4)
C(35)-P(1)-C(47)	103.65(19)	N(2)-C(23)-C(22)	121.0(4)
C(41)-P(1)-Cr(1)	115.83(14)	N(2)-C(23)-C(18)	118.9(5)
C(35)-P(1)-Cr(1)	116.00(15)	C(22)-C(23)-C(18)	120.1(5)
C(47)-P(1)-Cr(1)	112.69(15)	C(18)-C(24)-C(25)	110.0(6)
C(11)-N(1)-Cr(1)	166.3(3)	C(18)-C(24)-C(26)	114.6(6)
C(23)-N(2)-Cr(1)	168.5(3)	C(25)-C(24)-C(26)	109.8(6)
C(2)-C(1)-Cr(1)	137.4(4)	C(28)-C(27)-C(22)	112.3(5)
C(2)-C(1)-H(1)	107(2)	C(28)-C(27)-C(29)	110.0(5)
Cr(1)-C(1)-H(1)	112(2)	C(22)-C(27)-C(29)	110.6(5)
C(5)-C(2)-C(1)	110.5(5)	C(35)-C(30)-C(31)	120.6(5)
C(5)-C(2)-C(3)	108.6(5)	C(32)-C(31)-C(30)	119.9(5)
C(1)-C(2)-C(3)	112.4(5)	C(31)-C(32)-C(33)	120.5(5)
C(5)-C(2)-C(4)	108.9(5)	C(32)-C(33)-C(34)	119.6(5)
C(1)-C(2)-C(4)	106.8(5)	C(35)-C(34)-C(33)	120.5(4)
C(3)-C(2)-C(4)	109.6(6)	C(30)-C(35)-C(34)	118.8(4)
C(7)-C(6)-C(11)	117.4(5)	C(30)-C(35)-P(1)	118.6(3)
C(7)-C(6)-C(12)	122.4(4)	C(34)-C(35)-P(1)	122.6(3)
C(11)-C(6)-C(12)	119.9(4)	C(37)-C(36)-C(41)	120.6(4)
C(8)-C(7)-C(6)	121.7(5)	C(38)-C(37)-C(36)	119.6(5)
C(9)-C(8)-C(7)	119.7(5)	C(37)-C(38)-C(39)	121.1(5)
C(8)-C(9)-C(10)	122.8(5)	C(38)-C(39)-C(40)	119.7(5)
C(9)-C(10)-C(11)	117.3(4)	C(39)-C(40)-C(41)	120.4(4)
C(9)-C(10)-C(15)	122.7(4)	C(36)-C(41)-C(40)	118.5(4)
C(11)-C(10)-C(15)	120.0(4)	C(36)-C(41)-P(1)	121.2(3)
N(1)-C(11)-C(10)	119.0(4)	C(40)-C(41)-P(1)	120.1(3)
N(1)-C(11)-C(6)	120.0(4)	C(47)-C(42)-C(43)	120.3(5)

C(10)-C(11)-C(6)	121.0(4)	C(44)-C(43)-C(42)	119.9(5)
C(6)-C(12)-C(13)	109.4(4)	C(45)-C(44)-C(43)	119.9(4)
C(6)-C(12)-C(14)	113.5(4)	C(44)-C(45)-C(46)	120.9(5)
C(13)-C(12)-C(14)	110.8(4)	C(47)-C(46)-C(45)	119.2(5)
C(10)-C(15)-C(16)	110.0(5)	C(42)-C(47)-C(46)	119.8(4)
C(10)-C(15)-C(17)	113.4(4)	C(42)-C(47)-P(1)	122.2(4)
C(16)-C(15)-C(17)	110.6(5)	C(46)-C(47)-P(1)	118.0(3)
C(19)-C(18)-C(23)	118.4(5)		

NMR spectroscopy showed a downfield doublet peak with two satellite peaks (δ 14.97 ppm, $^1J_{\text{CH}} = 126.1$ Hz, $^3J_{\text{PH}} = 5.6$ Hz) in the ^1H NMR spectrum and a downfield doublet peak (δ 341.73 ppm, $^2J_{\text{PC}} = 21.4$ Hz) in the ^{13}C NMR spectrum. These numbers are similar to those reported by Gibson et al. and consistent with an alkylidene complex. The coupling constant $^1J_{\text{CH}}$ (126.1 Hz) is similar to those of reported alkylidenes.^{8,24-26} A clear correlation between H_α and C_α was found in the 2D-NMR HMQC spectrum (Figure 2.2).

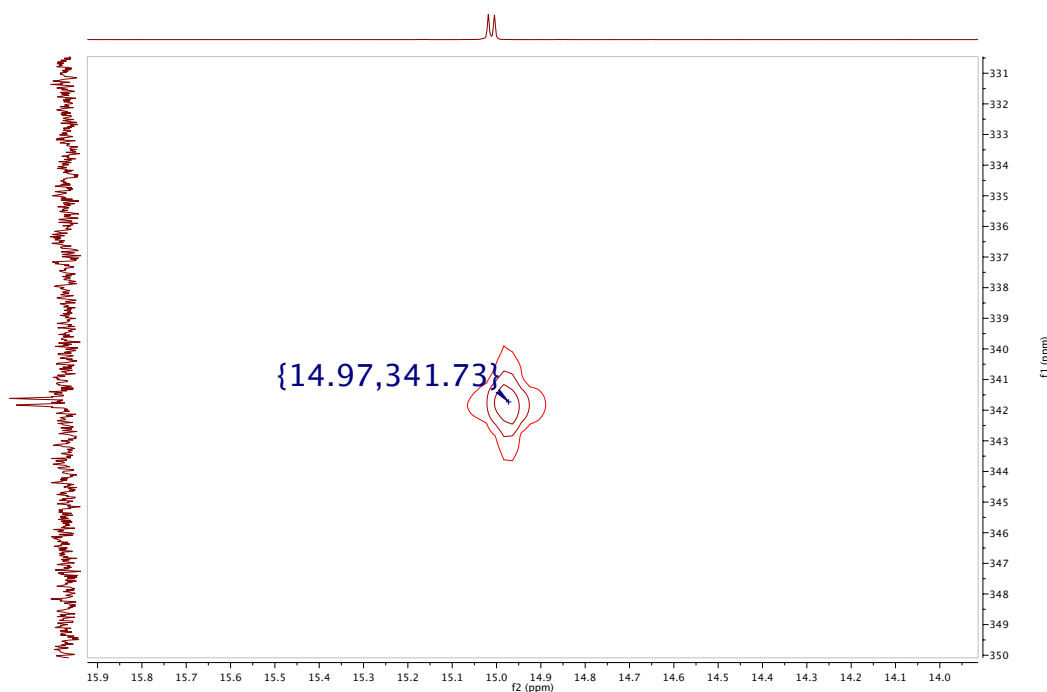
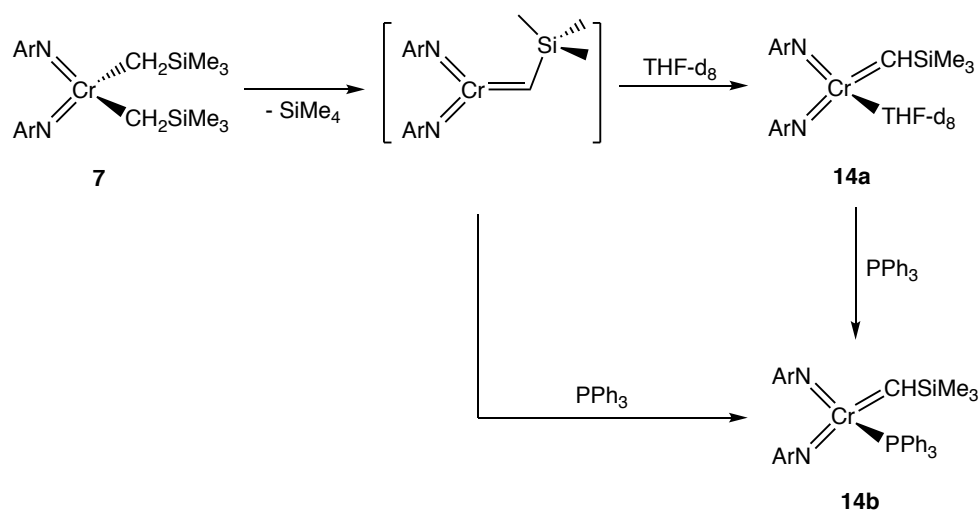


Figure 2.2 2D-NMR HMQC of **13** in the alkylidene region

Since the generation of neopentylidene was successful through α -hydrogen abstraction, it was of interest to know if $(\text{ArN})_2\text{Cr}(\text{CH}_3)_2$ (**4**), $(\text{ArN})_2\text{Cr}(\text{CH}_2\text{Ph})_2$ (**5**) and $(\text{ArN})_2\text{Cr}(\text{CH}_2\text{SiMe}_3)_2$ (**7**) would undergo similar reactions to form the corresponding alkylidenes. **7** is stable in THF- d_8 at room temperature. However, upon heating at 80 °C, **7** starts to lose SiMe_4 to form alkylidene complex $(\text{ArN})_2\text{Cr}(\text{=CHSiMe}_3)(\text{THF-}\text{d}_8)$ (**14a**). Characteristic alkylidene resonances of **14a** are found at 17.22 ppm ($^1J_{\text{CH}} = 124.4$ Hz, CHSiMe_3) in the ^1H NMR spectrum and at 326.78 ppm (CHSiMe_3) in the ^{13}C NMR spectrum.

During the formation of **14a**, C-D activation of THF- d_8 was not observed based on the ^1H NMR spectrum. Gibson and coworkers did not observe C-D activation of THF- d_8 in the report of neopentylidene THF- d_8 adduct in 1996⁶ either. In the presence of one equivalent of PPh_3 , transient $[(\text{ArN})_2\text{Cr}(\text{=CHSiMe}_3)]$ can be trapped as a phosphine adduct, namely $(\text{ArN})_2\text{Cr}(\text{=CHSiMe}_3)(\text{PPh}_3)$ (**14b**) (Scheme 2.10).



Scheme 2.10 Synthesis of trimethylsilylmethylidene **14a** and **14b**

Being only the second example of an isolable chromium(VI) alkylidene, the structure of **14b** has been determined by X-ray diffraction. The structure is depicted in Figure 2.3. Like **13**, **14b** also features pseudo-tetrahedral coordination geometry with a large bond angle of N1-Cr1-N2 ($122.60(14)^\circ$). The alkylidene bond Cr=C is short with length $1.843(4) \text{ \AA}$, which is pretty close to the bond length that is found in the neopentylidene. Besides, the bond angle Cr-C $_{\alpha}$ -Si ($133.1(2)^\circ$) is consistent with sp² hybridization of the alkylidene carbon. The torsion angle N1-Cr1-C25-Si1 ($-3.2(3)^\circ$) indicates that the *tert*-butyl group of the alkylidene ligand is *syn* to one imido ligand.

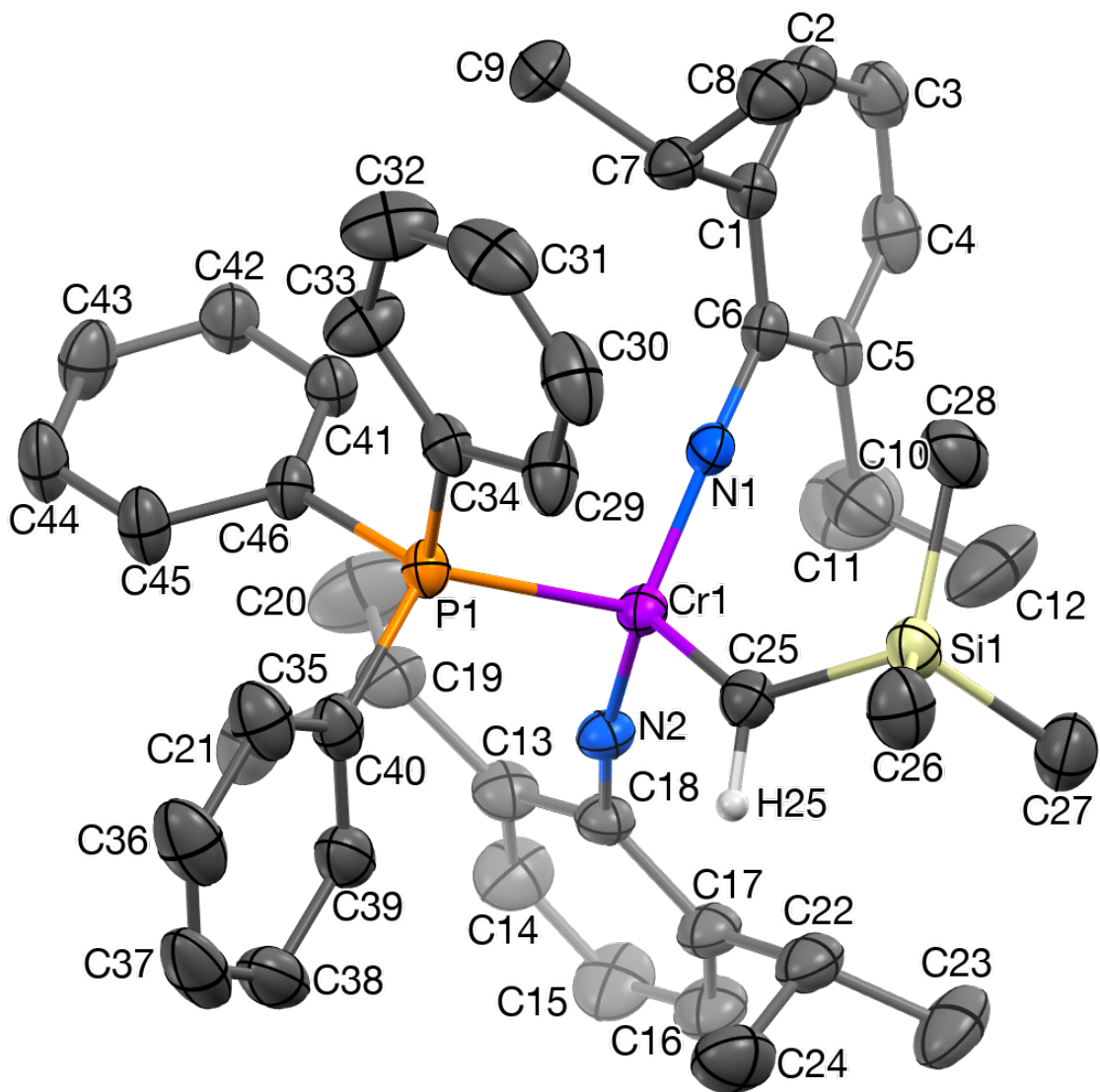


Figure 2.3 Molecular structure of $(\text{ArN})_2\text{Cr}(=\text{CHSiMe}_3)(\text{PPh}_3)$ (**14b**). Ellipsoids are drawn at the 30% probability level. Hydrogen atoms excluding the alkylidene hydrogen have been omitted for clarity.

Table 2.2 Interatomic distances (Å) and angles (°) for (ArN)₂Cr(=CHSiMe₃)(PPh₃)
(**14b**)

Distances (Å)			
Cr(1)-N(1)	1.668(3)	C(13)-C(18)	1.408(5)
Cr(1)-N(2)	1.668(3)	C(13)-C(19)	1.504(6)
Cr(1)-C(25)	1.843(4)	C(14)-C(15)	1.378(7)
Cr(1)-P(1)	2.3503(10)	C(15)-C(16)	1.374(7)
P(1)-C(46)	1.818(3)	C(16)-C(17)	1.391(6)
P(1)-C(34)	1.821(4)	C(17)-C(18)	1.419(5)
P(1)-C(40)	1.824(4)	C(17)-C(22)	1.508(6)
Si(1)-C(28)	1.849(5)	C(19)-C(21)	1.495(8)
Si(1)-C(25)	1.854(4)	C(19)-C(20)	1.505(8)
Si(1)-C(27)	1.872(5)	C(22)-C(23)	1.507(7)
Si(1)-C(26)	1.877(5)	C(22)-C(24)	1.537(7)
N(1)-C(6)	1.391(5)	C(25)-H(25)	1.01(5)
N(2)-C(18)	1.398(4)	C(29)-C(34)	1.377(6)
C(1)-C(2)	1.388(5)	C(29)-C(30)	1.390(6)
C(1)-C(6)	1.412(5)	C(30)-C(31)	1.353(8)
C(1)-C(7)	1.528(5)	C(31)-C(32)	1.359(8)
C(2)-C(3)	1.376(6)	C(32)-C(33)	1.414(7)
C(3)-C(4)	1.395(7)	C(33)-C(34)	1.376(6)
C(4)-C(5)	1.370(6)	C(35)-C(36)	1.385(7)
C(5)-C(6)	1.426(5)	C(35)-C(40)	1.387(6)
C(5)-C(10)	1.518(6)	C(36)-C(37)	1.353(9)
C(7)-C(8)	1.521(6)	C(37)-C(38)	1.381(9)
C(7)-C(9)	1.525(5)	C(38)-C(39)	1.390(7)
C(46)-C(41)	1.377(5)	C(39)-C(40)	1.383(7)
C(46)-C(45)	1.400(5)	C(41)-C(42)	1.409(6)
C(10)-C(12)	1.458(9)	C(42)-C(43)	1.375(6)
C(10)-C(11)	1.535(8)	C(43)-C(44)	1.364(7)
C(13)-C(14)	1.394(5)	C(44)-C(45)	1.394(6)

Angles (°)

N(1)-Cr(1)-N(2)	122.60(14)	C(14)-C(13)-C(19)	120.4(4)
N(1)-Cr(1)-C(25)	111.40(16)	C(18)-C(13)-C(19)	121.5(3)
N(2)-Cr(1)-C(25)	107.29(16)	C(15)-C(14)-C(13)	121.3(4)
N(1)-Cr(1)-P(1)	106.92(9)	C(16)-C(15)-C(14)	119.9(4)
N(2)-Cr(1)-P(1)	106.46(11)	C(15)-C(16)-C(17)	122.3(4)
C(25)-Cr(1)-P(1)	99.64(12)	C(16)-C(17)-C(18)	117.0(4)
C(46)-P(1)-C(34)	105.28(17)	C(16)-C(17)-C(22)	122.8(4)
C(46)-P(1)-C(40)	104.44(16)	C(18)-C(17)-C(22)	120.2(3)
C(34)-P(1)-C(40)	104.87(18)	N(2)-C(18)-C(13)	120.1(3)
C(46)-P(1)-Cr(1)	111.70(11)	N(2)-C(18)-C(17)	118.3(3)
C(34)-P(1)-Cr(1)	113.19(11)	C(13)-C(18)-C(17)	121.5(3)
C(40)-P(1)-Cr(1)	116.35(14)	C(21)-C(19)-C(13)	111.2(4)
C(28)-Si(1)-C(25)	113.2(2)	C(21)-C(19)-C(20)	108.3(6)
C(28)-Si(1)-C(27)	109.4(3)	C(13)-C(19)-C(20)	113.0(5)
C(25)-Si(1)-C(27)	107.4(2)	C(23)-C(22)-C(17)	114.1(4)
C(28)-Si(1)-C(26)	109.5(3)	C(23)-C(22)-C(24)	111.1(4)
C(25)-Si(1)-C(26)	110.1(2)	C(17)-C(22)-C(24)	109.9(4)
C(27)-Si(1)-C(26)	107.1(2)	Cr(1)-C(25)-Si(1)	133.1(2)
C(6)-N(1)-Cr(1)	163.4(2)	Cr(1)-C(25)-H(25)	119(3)
C(18)-N(2)-Cr(1)	164.5(3)	Si(1)-C(25)-H(25)	106(3)
C(2)-C(1)-C(6)	119.1(4)	C(34)-C(29)-C(30)	120.2(5)
C(2)-C(1)-C(7)	119.4(3)	C(31)-C(30)-C(29)	120.9(5)
C(6)-C(1)-C(7)	121.5(3)	C(30)-C(31)-C(32)	120.2(5)
C(3)-C(2)-C(1)	121.4(4)	C(31)-C(32)-C(33)	119.8(5)
C(2)-C(3)-C(4)	119.3(4)	C(34)-C(33)-C(32)	119.9(5)
C(5)-C(4)-C(3)	121.7(4)	C(33)-C(34)-C(29)	119.0(4)
C(4)-C(5)-C(6)	118.9(4)	C(33)-C(34)-P(1)	122.2(3)
C(4)-C(5)-C(10)	121.0(4)	C(29)-C(34)-P(1)	118.8(3)
C(6)-C(5)-C(10)	120.1(4)	C(36)-C(35)-C(40)	119.6(5)
N(1)-C(6)-C(1)	120.5(3)	C(37)-C(36)-C(35)	121.0(6)
N(1)-C(6)-C(5)	119.9(3)	C(36)-C(37)-C(38)	120.3(5)
C(1)-C(6)-C(5)	119.6(3)	C(37)-C(38)-C(39)	119.4(6)
C(8)-C(7)-C(9)	109.8(3)	C(40)-C(39)-C(38)	120.4(5)
C(8)-C(7)-C(1)	112.0(3)	C(39)-C(40)-C(35)	119.2(4)

C(9)-C(7)-C(1)	110.9(3)	C(39)-C(40)-P(1)	118.9(3)
C(41)-C(46)-C(45)	118.9(3)	C(35)-C(40)-P(1)	121.9(4)
C(41)-C(46)-P(1)	119.1(3)	C(46)-C(41)-C(42)	121.1(3)
C(45)-C(46)-P(1)	122.0(3)	C(43)-C(42)-C(41)	118.4(4)
C(12)-C(10)-C(5)	110.9(5)	C(44)-C(43)-C(42)	121.7(4)
C(12)-C(10)-C(11)	111.4(5)	C(43)-C(44)-C(45)	119.8(4)
C(5)-C(10)-C(11)	112.2(5)	C(44)-C(45)-C(46)	120.0(4)
C(14)-C(13)-C(18)	118.0(4)		

NMR spectroscopy showed a downfield doublet peak at 17.60 ppm ($^1J_{\text{CH}} = 119.9$ Hz, $^3J_{\text{PH}} = 7.6$ Hz) assigned to the alkylidene hydrogen in the ^1H NMR and a downfield doublet peak at 340.63 ppm ($^2J_{\text{PC}} = 21.0$ Hz) assigned to the alkylidene carbon in the ^{13}C NMR spectrum. These NMR characters are very similar to those of **13**, save for the rather more downfield shift of the alkylidene hydrogen in the ^1H NMR spectrum. A clear correlation between H_α and C_α was found in the 2D-NMR HSQC spectrum (Figure 2.4).

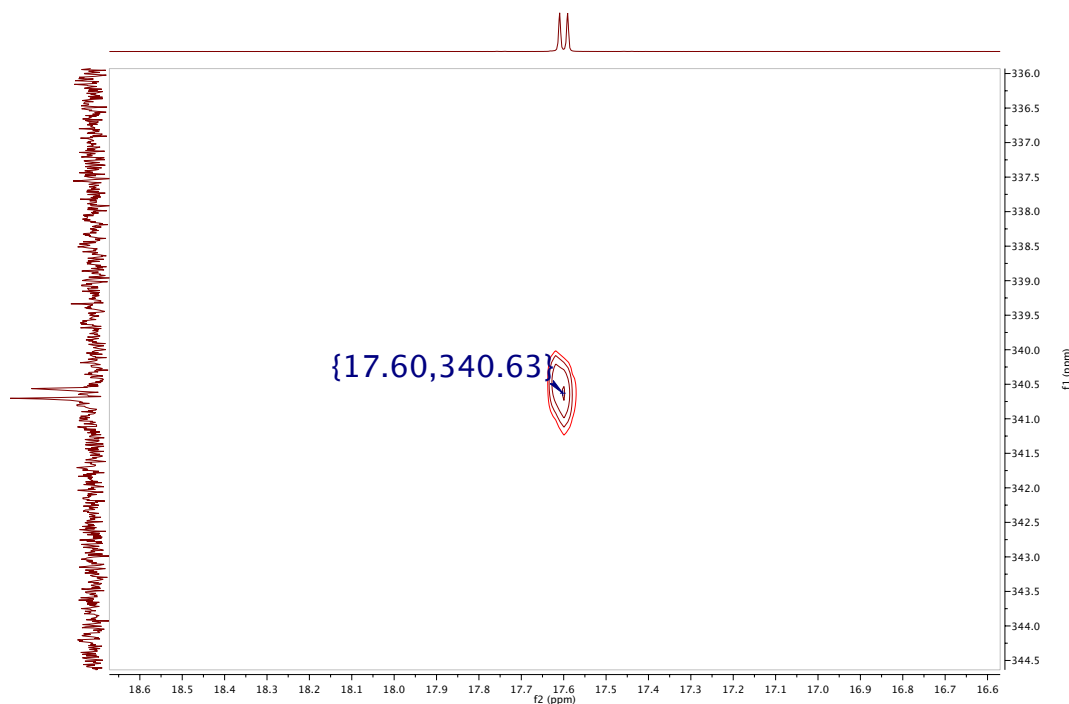
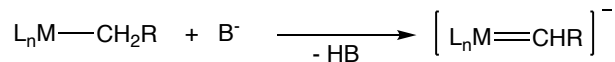


Figure 2.4 2D-NMR HSQC of **14b** in the alkylidene region

The α -hydrogen abstraction of **6** took place at room temperature but α -hydrogen abstraction of **7** required heating to 80 °C. The more facile formation of **13** is attributed to greater steric repulsions in **6**, which result from the shorter distances between the chromium center and the terminal carbons of the alkyl ligand. The average distance between chromium and the terminal carbons in **6** is 3.818 Å, whereas the average distance between chromium and the terminal carbons in **7** is 4.221 Å. This relative stability is similar to the relative stability of TaNp₅ and Ta(CH₂SiMe₃)₅.²⁷ To better understand the process of α -hydrogen abstraction of **7**, a kinetic study was performed. The conversion of **7** to **14a** in THF-d₈ at 80 °C clearly revealed first order behavior with a rate constant of 3.14(9)×10⁻⁵ s⁻¹. The reaction rate was not affected by the concentration of PPh₃, according to rate constants 3.32(8)×10⁻⁵ s⁻¹ (1 PPh₃, 0.038 M in d₈-THF) and 3.47(6)×10⁻⁵ s⁻¹ (10 PPh₃, 0.37 M in d₈-THF). The result of the kinetic study suggested that α -hydrogen abstraction is the rate-determining step of formation of **14a** and no order in [PPh₃] was observed.

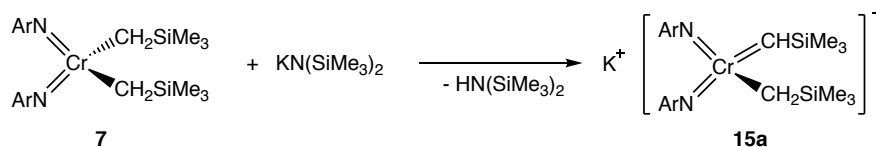
Despite several attempts, neither **4** nor **5** have yielded isolable alkylidene phosphine adduct in my hands. Upon heating **4** or **5** with PPh₃ in THF-d₈, methane or toluene was found in each J-Young tube but no alkylidene resonance was found downfield in either ¹H NMR spectrum.

13 and **14b** are both generated through α -hydrogen abstraction of the corresponding chromium dialkyls. Removal of α -hydrogen to form an alkylidene can also be achieved by deprotonation of an alkyl ligand by Bronsted base, as illustrated in Scheme 2.11.



Scheme 2.11 Formation of an alkylidene anion by deprotonation

To carry out this kind of reaction, ⁿBuLi, KH and KN(SiMe₃)₂ were employed to deprotonate **7**. All three bases can deprotonate **7** to produce the alkylidene anion, namely [(ArN)₂Cr(=CHSiMe₃)(CH₂SiMe₃)]⁻. The deprotonation by the weak base KN(SiMe₃)₂ (pK_a = 26 in THF)²⁸ has the best performance based on the yield (91%) of K[(ArN)₂Cr(=CHSiMe₃)(CH₂SiMe₃)]⁻ (**15a**) (Scheme 2.12).



Scheme 2.12 Synthesis of K[(ArN)₂Cr(=CHSiMe₃)(CH₂SiMe₃)] (**15a**)

Multinuclear NMR spectroscopy of **15a** showed a downfield singlet peak at 15.15 ppm (¹J_{CH} = 127.5 Hz) assigned to the alkylidene hydrogen in the ¹H NMR spectrum and a downfield singlet peak at 295.24 ppm assigned to the alkylidene carbon in the ¹³C NMR spectrum. **15a** can be isolated as powder, but it is hard to obtain good crystals. To improve the crystallinity of the anionic alkylidene, cation-exchange was performed to yield Et₄N[(ArN)₂Cr(=CHSiMe₃)(CH₂SiMe₃)] (**15b**). Dissolving **15a** in THF gave a red solution and then one equivalent of Et₄NCl was added into this solution. After four hours, THF solvent was removed in vacuum. The residue was extracted with the minimum amount of THF and the extract was filtered through Celite to remove the precipitate (KCl). Crystallization of **15b** in a saturated

THF solution at -30 °C was not successful. Slow evaporation of the THF solution of **15b** at room temperature did not form any crystal either. Finally, single crystals suitable for X-ray diffraction were grown by layering the THF solution of **15b** with pentane after one day at -30 °C. The structure of **15b** is depicted in Figure 2.5. The alkylidene anion has pseudo-tetrahedral coordination geometry with a short Cr=C bond (1.791(7) Å), which is similar to the bond lengths of alkylidenes in **13** and **14b**.

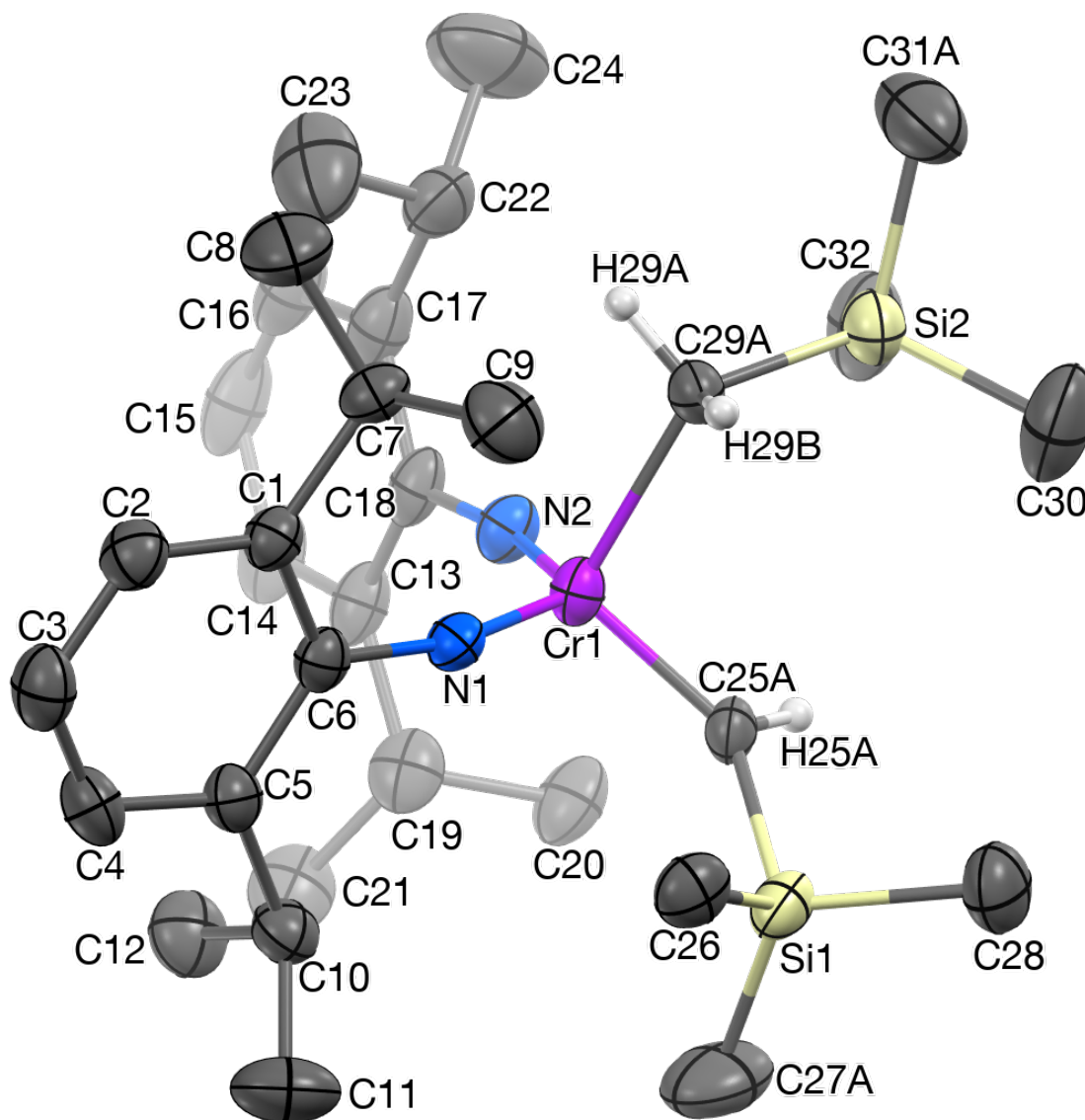


Figure 2.5 Molecular structure of $\text{Et}_4\text{N}[(\text{ArN})_2\text{Cr}(=\text{CHSiMe}_3)(\text{CH}_2\text{SiMe}_3)]$ (**15b**). Ellipsoids are drawn at the 30% probability level. The Et_4N^+ cation and any hydrogen atoms besides the alkylidene hydrogen and the α -hydrogens of the alkyl ligand have been omitted for clarity.

Table 2.3 Interatomic distances (Å) and angles (°) for
Et₄N[(ArN)₂Cr(=CHSiMe₃)(CH₂SiMe₃)] (**15b**)

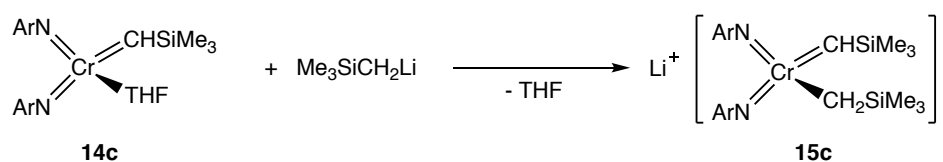
Distances (Å)			
Cr(1)-N(2)	1.670(4)	C(1)-C(7)	1.527(8)
Cr(1)-N(1)	1.675(4)	C(2)-C(3)	1.382(9)
Cr(1)-C(29B) ^a	1.777(12)	C(3)-C(4)	1.364(9)
Cr(1)-C(25A) ^a	1.791(7)	C(4)-C(5)	1.402(7)
Cr(1)-C(29A) ^a	2.131(8)	C(5)-C(6)	1.415(7)
Cr(1)-C(25B) ^a	2.186(12)	C(5)-C(10)	1.515(7)
N(1)-C(6)	1.369(6)	C(7)-C(8)	1.490(9)
N(2)-C(18)	1.375(6)	C(7)-C(9)	1.517(9)
N(3)-C(37)	1.486(8)	C(10)-C(11)	1.522(9)
N(3)-C(35)	1.522(8)	C(10)-C(12)	1.541(8)
N(3)-C(39)	1.547(8)	C(13)-C(14)	1.394(7)
N(3)-C(33)	1.548(7)	C(13)-C(18)	1.434(8)
Si(1)-C(25B) ^a	1.762(12)	C(13)-C(19)	1.508(8)
Si(1)-C(27A) ^a	1.858(13)	C(14)-C(15)	1.357(10)
Si(1)-C(28)	1.859(6)	C(15)-C(16)	1.372(10)
Si(1)-C(26)	1.871(6)	C(16)-C(17)	1.384(8)
Si(1)-C(25A) ^a	1.909(8)	C(17)-C(18)	1.433(8)
Si(1)-C(27B) ^a	1.941(14)	C(17)-C(22)	1.517(10)
Si(2)-C(29A) ^a	1.812(7)	C(19)-C(20)	1.520(8)
Si(2)-C(32)	1.847(8)	C(19)-C(21)	1.544(9)
Si(2)-C(31B) ^a	1.847(17)	C(22)-C(24)	1.495(10)
Si(2)-C(30)	1.853(8)	C(22)-C(23)	1.533(11)
Si(2)-C(31A) ^a	1.901(13)	C(33)-C(34)	1.480(9)
Si(2)-C(29B) ^a	1.946(12)	C(35)-C(36)	1.522(10)
C(1)-C(2)	1.391(7)	C(37)-C(38)	1.509(12)
C(1)-C(6)	1.415(7)	C(39)-C(40)	1.538(10)

^a The alkyl ligand and the alkylidene ligand have position disorder in **15b** with a site occupancy ration of 62/38.

Angles (°)			
N(2)-Cr(1)-N(1)	120.3(2)	C(6)-C(1)-C(7)	119.0(4)
N(2)-Cr(1)-C(29B)	117.3(5)	C(3)-C(2)-C(1)	121.1(5)
N(1)-Cr(1)-C(29B)	109.5(5)	C(4)-C(3)-C(2)	119.9(5)
N(2)-Cr(1)-C(25A)	111.8(3)	C(3)-C(4)-C(5)	121.9(6)
N(1)-Cr(1)-C(25A)	112.1(3)	C(4)-C(5)-C(6)	118.2(5)
N(2)-Cr(1)-C(29A)	103.2(3)	C(4)-C(5)-C(10)	121.1(5)
N(1)-Cr(1)-C(29A)	104.0(3)	C(6)-C(5)-C(10)	120.6(5)
C(25A)-Cr(1)-C(29A)	103.0(4)	N(1)-C(6)-C(1)	119.5(4)
N(2)-Cr(1)-C(25B)	104.2(4)	N(1)-C(6)-C(5)	120.8(4)
N(1)-Cr(1)-C(25B)	100.2(4)	C(1)-C(6)-C(5)	119.7(5)
C(29B)-Cr(1)-C(25B)	101.7(6)	C(8)-C(7)-C(9)	110.3(6)
C(6)-N(1)-Cr(1)	161.2(4)	C(8)-C(7)-C(1)	114.2(5)
C(18)-N(2)-Cr(1)	166.0(4)	C(9)-C(7)-C(1)	109.8(5)
C(37)-N(3)-C(35)	110.7(6)	C(5)-C(10)-C(11)	114.3(5)
C(37)-N(3)-C(39)	107.8(5)	C(5)-C(10)-C(12)	110.1(5)
C(35)-N(3)-C(39)	111.3(5)	C(11)-C(10)-C(12)	111.3(5)
C(37)-N(3)-C(33)	111.0(5)	C(14)-C(13)-C(18)	117.8(5)
C(35)-N(3)-C(33)	107.4(4)	C(14)-C(13)-C(19)	123.4(5)
C(39)-N(3)-C(33)	108.7(5)	C(18)-C(13)-C(19)	118.7(4)
C(25B)-Si(1)-C(28)	121.3(6)	C(15)-C(14)-C(13)	122.3(6)
C(27A)-Si(1)-C(28)	114.1(7)	C(14)-C(15)-C(16)	119.8(6)
C(25B)-Si(1)-C(26)	117.0(5)	C(15)-C(16)-C(17)	122.8(6)
C(27A)-Si(1)-C(26)	113.5(8)	C(16)-C(17)-C(18)	117.5(6)
C(28)-Si(1)-C(26)	109.2(3)	C(16)-C(17)-C(22)	122.4(6)
C(27A)-Si(1)-C(25A)	105.4(6)	C(18)-C(17)-C(22)	120.1(5)
C(28)-Si(1)-C(25A)	102.2(3)	N(2)-C(18)-C(17)	120.2(5)
C(26)-Si(1)-C(25A)	111.8(3)	N(2)-C(18)-C(13)	120.0(5)
C(25B)-Si(1)-C(27B)	104.6(8)	C(17)-C(18)-C(13)	119.8(5)
C(28)-Si(1)-C(27B)	100.9(6)	C(13)-C(19)-C(20)	110.9(5)
C(26)-Si(1)-C(27B)	99.8(6)	C(13)-C(19)-C(21)	113.6(5)
C(29A)-Si(2)-C(32)	114.6(4)	C(20)-C(19)-C(21)	110.5(5)
C(32)-Si(2)-C(31B)	112.1(10)	C(24)-C(22)-C(17)	112.7(7)
C(29A)-Si(2)-C(30)	117.2(4)	C(24)-C(22)-C(23)	111.5(7)
C(32)-Si(2)-C(30)	108.2(4)	C(17)-C(22)-C(23)	110.6(6)

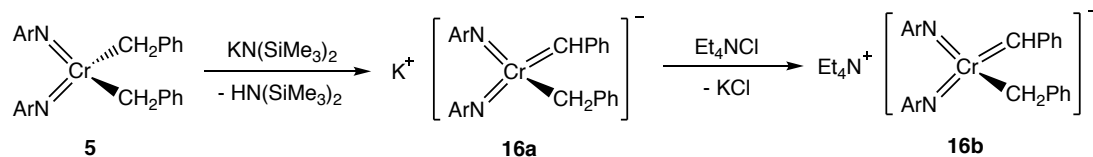
C(31B)-Si(2)-C(30)	125.0(10)	Cr(1)-C(25A)-Si(1)	128.6(5)
C(29A)-Si(2)-C(31A)	110.7(6)	Si(1)-C(25B)-Cr(1)	114.8(7)
C(32)-Si(2)-C(31A)	105.1(7)	Si(2)-C(29A)-Cr(1)	119.1(4)
C(30)-Si(2)-C(31A)	99.2(7)	Cr(1)-C(29B)-Si(2)	132.1(8)
C(32)-Si(2)-C(29B)	110.9(5)	C(34)-C(33)-N(3)	115.3(5)
C(31B)-Si(2)-C(29B)	103.8(12)	C(36)-C(35)-N(3)	112.7(6)
C(30)-Si(2)-C(29B)	94.9(5)	N(3)-C(37)-C(38)	114.1(6)
C(2)-C(1)-C(6)	119.1(5)	C(40)-C(39)-N(3)	112.6(5)
C(2)-C(1)-C(7)	121.9(5)		

Alkylidene anion $[(\text{ArN})_2\text{Cr}(=\text{CHSiMe}_3)(\text{CH}_2\text{SiMe}_3)]^-$ can also be made independently by treating $(\text{ArN})_2\text{Cr}(=\text{CHSiMe}_3)(\text{THF})$ (**14c**) with $\text{Me}_3\text{SiCH}_2\text{Li}$ in THF (Scheme 2.13). The corresponding product $\text{Li}[(\text{ArN})_2\text{Cr}(=\text{CHSiMe}_3)(\text{CH}_2\text{SiMe}_3)]$ (**15c**) has a ^1H NMR spectrum that is identical to that of **15a**.



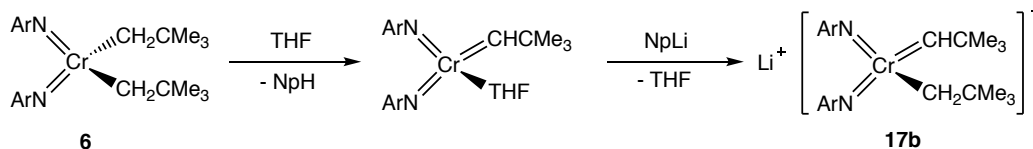
Scheme 2.13 Alternative way to make $\text{Li}[(\text{ArN})_2\text{Cr}(=\text{CHSiMe}_3)(\text{CH}_2\text{SiMe}_3)]$ (**15c**)

The success in making alkylidene complex **15a** by deprotonating α -hydrogen of the dialkyl **7** gave me a new way to generate alkylidenes. Then this approach was applied to dibenzyl complex **5**. **5** was also deprotonated successfully by $\text{KN}(\text{SiMe}_3)_2$, to make anionic benzylidene compound $\text{K}[(\text{ArN})_2\text{Cr}(=\text{CHPh})(\text{CH}_2\text{Ph})]$ (**16a**). After ion-exchange with Et_4NCl , $\text{Et}_4\text{N}[(\text{ArN})_2\text{Cr}(=\text{CHPh})(\text{CH}_2\text{Ph})]$ (**16b**) can be crystallized out by layering a THF solution with pentane (Scheme 2.14). However, these crystals were too small to be structurally characterized with X-ray diffraction. NMR spectra including ^1H NMR and ^{13}C NMR were consistent with the formation of a benzylidene. The peak of the benzylidene hydrogen was found at 13.92 ppm in the ^1H NMR spectrum and the peak at 291.74 ppm in the ^{13}C NMR spectrum was assigned to the benzylidene carbon.



Scheme 2.14 Synthesis of ionic benzylidene complexes **16a** and **16b**

Curiously, and despite the successful deprotonation of **5** and **7**, deprotonation of **6** with $\text{KN}(\text{SiMe}_3)_2$ afforded intractable species instead of forming the desired product $\text{K}[(\text{ArN})_2\text{Cr}(=\text{CHCMe}_3)(\text{CH}_2\text{CMe}_3)]$ (**17a**). Then I switched to the alternative way of making neopentylidene anion. $\text{Li}[(\text{ArN})_2\text{Cr}(=\text{CHCMe}_3)(\text{CH}_2\text{CMe}_3)]$ (**17b**) was generated successfully by adding NpLi to a THF solution of $(\text{ArN})_2\text{Cr}(=\text{CHCMe}_3)(\text{THF})$ (Scheme 2.15). The peak of alkylidene hydrogen was found at 13.41 ppm ($^1J_{\text{CH}} = 128.0$ Hz) in the ^1H NMR spectrum. The alkylidene carbon has a resonance at 306.91 ppm in the ^{13}C NMR spectrum.



Scheme 2.15 Synthesis of ionic neopentylidene **17b**

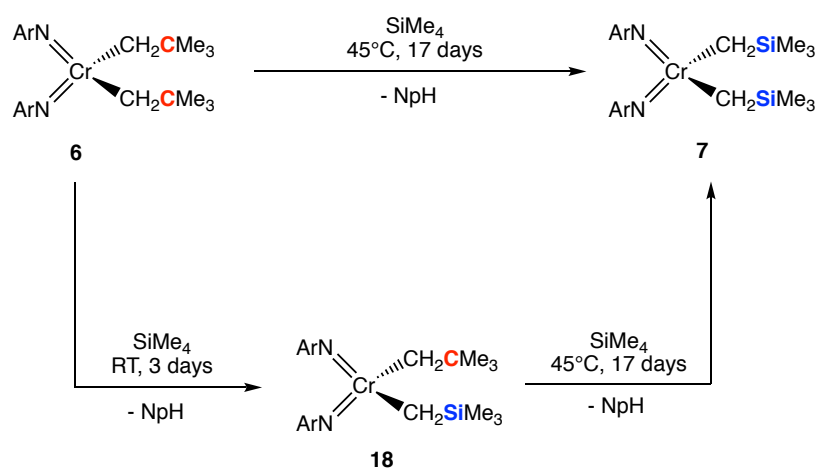
With these anionic alkylidenes in hand, I tried to make neutral alkylidenes by abstracting the alkyl ligand from an alkylidene anion. However, my attempts were not successful. The reactions of **15a** with $\text{Ph}_3\text{C}[\text{B}(\text{C}_6\text{F}_5)_4]$ and **16a** with $\text{Ph}_3\text{C}[\text{B}(\text{C}_6\text{F}_5)_4]$ both gave intractable brown oily products even in the presence of PPh_3 . The alkylidene resonance was not observed downfield in the ^1H NMR spectra of these oily

products. The other idea was oxidation of alkylidene anions to generate neutral alkylidene with organic byproducts $\text{Me}_3\text{SiCH}_2\text{CH}_2\text{SiMe}_3$ or $\text{PhCH}_2\text{CH}_2\text{Ph}$. The reactions of **15a** with AgOTf and **16a** with AgOTf both caused the formation of black particles (Ag) on the inner wall of the reaction flask. However, no alkylidene peak was found downfield in the ^1H NMR spectra of the crude products. Thus, the oxidation of alkylidene anions by AgOTf to make neutral alkylidenes was not successful either.

2.2.2 Reactivity of the Transient Neopentylidene

One important reactivity of alkylidenes is C-H bond activation. Gibson et al. found that when **6** is dissolved in C_6D_6 , it slowly converts to $(\text{ArN})_2\text{Cr}(\text{CHDCMe}_3)(\text{C}_6\text{D}_5)$. The mechanism of this reaction presumably involves transient neopentylidene, which is generated from the precursor dialkyl **6** through α -hydrogen abstraction. This result raises the question whether transient neopentylidene might activate unactivated C-H bonds of alkanes. To answer this question, **6** was dissolved in pure SiMe_4 . After stirring at room temperature for three days, no color change was observed, but NMR spectroscopy and LIFDI-MS both indicate that **6** has been quantitatively transformed into the mixed alkyl complex $(\text{ArN})_2\text{Cr}(\text{CH}_2\text{CMe}_3)(\text{CH}_2\text{SiMe}_3)$ (**18**). Exchange of the second neopentyl ligand was much slower, presumably due to less steric repulsions in **18**. However, after heating at $45\text{ }^\circ\text{C}$ for 17 days, all starting material had been cleanly converted to **7** according to ^1H NMR (Scheme 2.16). Though the mechanism of σ -bond metathesis cannot presently be ruled out, both reactions, formation of **13** and C-H bond activation of SiMe_4 to make **18**, qualitatively have the same reaction rate. This suggests a common rate-determining step and intermediate in both reactions. Besides, the reaction of $(\text{ArN})_2\text{Cr}(=\text{CHCMe}_3)(\text{THF})$ with pure SiMe_4 was completed in one hour, which is

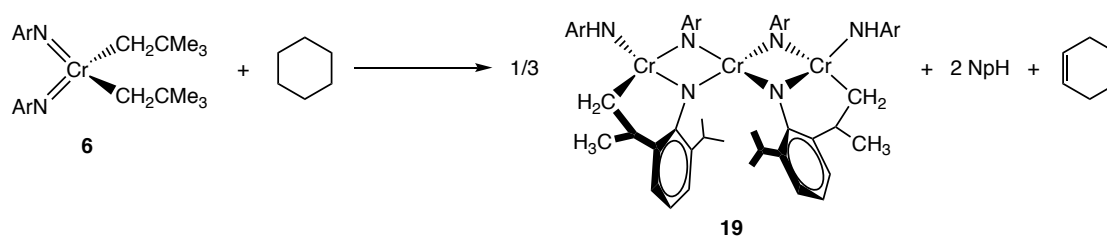
much faster than the reaction of **6** with SiMe₄. So, the proposed mechanism is that the alkyl ligand exchange goes via α -hydrogen abstraction, which is presumably the rate-determining step, followed by C-H bond activation of SiMe₄ by transient neopentylidene [(ArN)₂Cr(=CHCMe₃)], yielding **18**. The second exchange of neopentyl to trimethylsilylmethyl involves transient [(ArN)₂Cr(=CHSiMe₃)], generated from **18** by eliminating neopentane, then yielding **7**.



Scheme 2.16 C-H bond activation of SiMe₄ initiated by (ArN)₂Cr(CH₂CMe₃)₂ (**6**)

Cyclohexane is usually considered an inert solvent because its secondary C-H bonds are relatively sterically congested and weakly acidic. Therefore, it is a common solvent employed in C-H bond activation reactions.²⁹ For instance, cyclohexane was used as a solvent for intramolecular C-H bond activation of L^{Me}Cr(CH₂SiMe₃)(THF) (L^{Me} = 2,4 Pentane-N,N'-bis(2,6-dimethylphenyl) ketiminato).³⁰ However, I found that **6** reacted with cyclohexane at room temperature (Scheme 2.17). A color change was observed from green to brown when stirring a cyclohexane solution of **6** at room

temperature for three days. After work up, an organometallic product can be crystallized from concentrated pentane solution at -30 °C. Structure determination was achieved by X-ray diffraction of a single crystal. The structure is depicted in Figure 2.6 and the corresponding interatomic distances and angles are listed in Table 2.4. All three chromium centers of this trinuclear complex have pseudo-tetrahedral coordination geometry. This organometallic product is formally a trimer of $\text{Cr}(\text{NAr})_2$ with molecular formula $\text{Cr}_3\text{C}_{72}\text{H}_{102}\text{N}_6$ (**19**). Amido hydrogen H3N was assigned on N3 due to a long distance between Cr1A and N3 (1.836(2) Å), which is obviously longer than an $\text{Cr}=\text{N}$ imido bond (around 1.64 Å). The relatively small angle of Cr1A-N3-C30 (139.1(2)°) is consistent with this amido ligand assignment. An absorption band at 3340 cm^{-1} in the infrared spectrum was assigned as N-H stretching vibration. Besides, LIFDI-MS data also agreed with the formula of **19**. The ^1H NMR spectrum and the ^{13}C NMR spectrum both suggest **19** is diamagnetic.



Scheme 2.17 C-H bond activation of cyclohexane initiated by $(\text{ArN})_2\text{Cr}(\text{CH}_2\text{CMe}_3)_2$

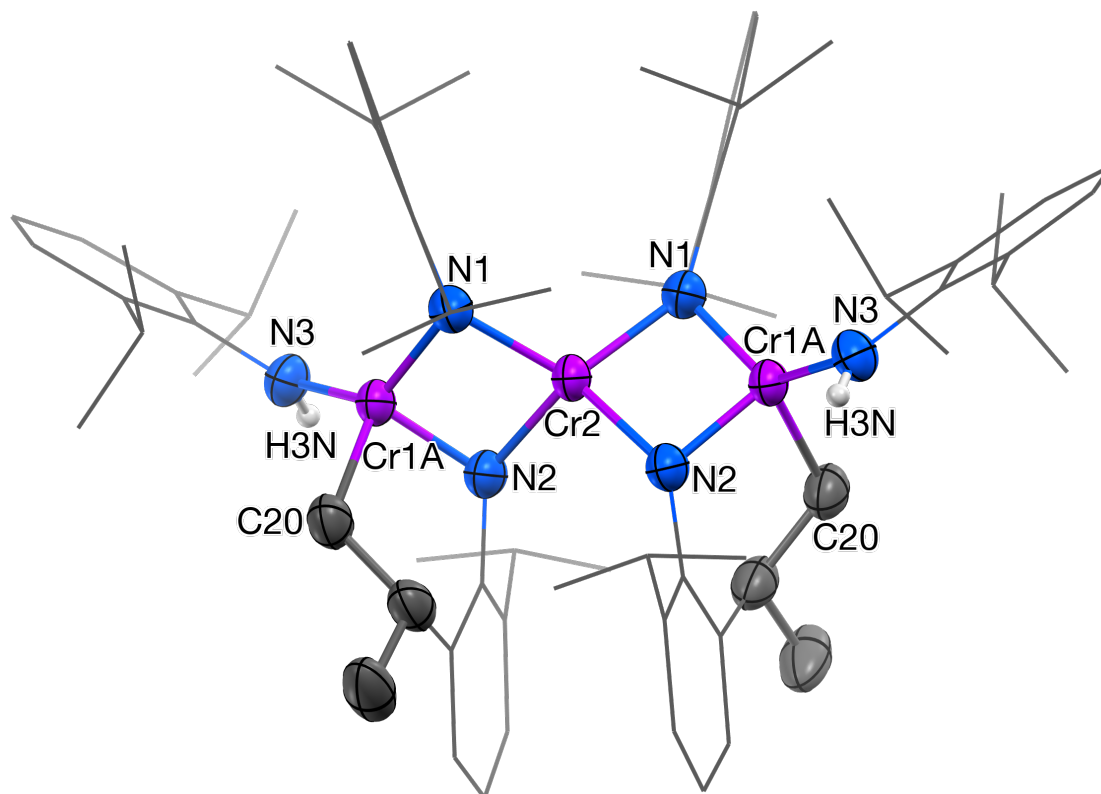


Figure 2.6 Molecular structure of trinuclear Cr(IV) complex $\text{Cr}_3\text{C}_{72}\text{H}_{102}\text{N}_6$ (**19**). Ellipsoids are drawn at the 30% probability level. Hydrogen atoms excluding amido hydrogen have been omitted for clarity. Aromatic rings and isopropyl groups are drawn in wireframe for clarity.

Table 2.4 Interatomic distances (Å) and angles (°) for Cr₃C₇₂H₁₀₂N₆ (**19**)

Distances (Å)			
Cr(1A)-N(2) ^a	1.763(2)	C(10)-C(11)	1.540(5)
Cr(1A)-N(1) ^a	1.792(2)	C(13)-C(14)	1.389(5)
Cr(1A)-N(3) ^a	1.836(2)	C(13)-C(18)	1.396(6)
Cr(1A)-C(20) ^a	2.040(3)	C(13)-C(19)	1.497(6)
Cr(1A)-Cr(2) ^a	2.5440(4)	C(14)-C(15)	1.344(9)
Cr(1B)-N(1) ^a	2.323(6)	C(15)-C(16)	1.388(9)
Cr(1B)-Cr(2) ^a	2.545(4)	C(16)-C(17)	1.429(6)
Cr(2)-N(1)	1.862(2)	C(17)-C(18)	1.406(6)
Cr(2)-N(1)	1.862(2)	C(17)-C(22)	1.497(7)
Cr(2)-N(2)	1.889(2)	C(19)-C(20)	1.507(4)
Cr(2)-N(2)	1.889(2)	C(19)-C(21)	1.529(5)
N(1)-C(6)	1.433(4)	C(22)-C(24)	1.532(7)
N(2)-C(18)	1.428(4)	C(22)-C(23)	1.534(6)
N(3)-C(30)	1.416(3)	C(25)-C(26)	1.385(4)
C(1)-C(2)	1.403(6)	C(25)-C(30)	1.402(5)
C(1)-C(6)	1.415(6)	C(25)-C(31)	1.513(5)
C(1)-C(7)	1.485(7)	C(26)-C(27)	1.371(6)
C(2)-C(3)	1.361(9)	C(27)-C(28)	1.377(6)
C(3)-C(4)	1.357(9)	C(28)-C(29)	1.407(4)
C(4)-C(5)	1.406(6)	C(29)-C(30)	1.412(5)
C(5)-C(6)	1.428(6)	C(29)-C(34)	1.528(6)
C(5)-C(10)	1.502(7)	C(31)-C(32)	1.513(5)
C(7)-C(9)	1.510(6)	C(31)-C(33)	1.531(5)
C(7)-C(8)	1.556(8)	C(34)-C(35)	1.530(9)
C(10)-C(12)	1.516(7)	C(34)-C(36)	1.580(9)

^a Cr1 in **19** was found disordered in two positions with a refined site occupancy ratio of 91/9. With such occupancy ratio, the structure of the minor component cannot be modeled due to a very low electron density.

Angles (°)			
N(2)-Cr(1A)-N(1)	94.92(10)	C(4)-C(5)-C(6)	115.7(5)
N(2)-Cr(1A)-N(3)	109.03(12)	C(4)-C(5)-C(10)	120.2(4)
N(1)-Cr(1A)-N(3)	128.78(11)	C(6)-C(5)-C(10)	124.1(3)
N(2)-Cr(1A)-C(20)	91.96(13)	C(1)-C(6)-C(5)	120.8(4)
N(1)-Cr(1A)-C(20)	109.54(13)	C(1)-C(6)-N(1)	119.3(4)
N(3)-Cr(1A)-C(20)	113.95(12)	C(5)-C(6)-N(1)	119.8(4)
N(2)-Cr(1A)-Cr(2)	47.92(7)	C(1)-C(7)-C(9)	112.0(5)
N(1)-Cr(1A)-Cr(2)	47.00(8)	C(1)-C(7)-C(8)	110.9(4)
N(3)-Cr(1A)-Cr(2)	134.19(9)	C(9)-C(7)-C(8)	112.8(5)
C(20)-Cr(1A)-Cr(2)	106.65(8)	C(5)-C(10)-C(12)	112.9(4)
N(1)-Cr(1B)-Cr(2)	44.67(10)	C(5)-C(10)-C(11)	114.6(4)
N(1)-Cr(2)-N(1)	117.12(14)	C(12)-C(10)-C(11)	108.2(4)
N(1)-Cr(2)-N(2)	132.89(12)	C(14)-C(13)-C(18)	118.2(5)
N(1)-Cr(2)-N(2)	88.59(10)	C(14)-C(13)-C(19)	121.7(4)
N(1)-Cr(2)-N(2)	88.59(10)	C(18)-C(13)-C(19)	120.0(3)
N(1)-Cr(2)-N(2)	132.89(12)	C(15)-C(14)-C(13)	121.8(6)
N(2)-Cr(2)-N(2)	102.08(13)	C(14)-C(15)-C(16)	120.1(4)
N(1)-Cr(2)-Cr(1B)	61.33(14)	C(15)-C(16)-C(17)	121.6(5)
N(1)-Cr(2)-Cr(1B)	116.90(14)	C(18)-C(17)-C(16)	115.3(5)
N(2)-Cr(2)-Cr(1B)	142.53(13)	C(18)-C(17)-C(22)	123.7(4)
N(2)-Cr(2)-Cr(1B)	40.48(12)	C(16)-C(17)-C(22)	120.7(5)
N(1)-Cr(2)-Cr(1B)	116.90(14)	C(13)-C(18)-C(17)	122.5(3)
N(1)-Cr(2)-Cr(1B)	61.33(14)	C(13)-C(18)-N(2)	116.7(3)
N(2)-Cr(2)-Cr(1B)	40.47(12)	C(17)-C(18)-N(2)	120.8(4)
N(2)-Cr(2)-Cr(1B)	142.53(13)	C(13)-C(19)-C(20)	111.9(3)
N(1)-Cr(2)-Cr(1A)	44.74(7)	C(13)-C(19)-C(21)	112.8(4)
N(1)-Cr(2)-Cr(1A)	142.02(7)	C(20)-C(19)-C(21)	110.4(3)
N(2)-Cr(2)-Cr(1A)	128.84(7)	C(19)-C(20)-Cr(1A)	115.1(2)
N(2)-Cr(2)-Cr(1A)	43.85(7)	C(17)-C(22)-C(24)	115.4(5)
N(1)-Cr(2)-Cr(1A)	142.02(7)	C(17)-C(22)-C(23)	109.8(5)
N(1)-Cr(2)-Cr(1A)	44.75(7)	C(24)-C(22)-C(23)	108.2(4)
N(2)-Cr(2)-Cr(1A)	43.85(7)	C(26)-C(25)-C(30)	118.3(3)
N(2)-Cr(2)-Cr(1A)	128.84(7)	C(26)-C(25)-C(31)	120.7(3)
Cr(1A)-Cr(2)-Cr(1A)	171.43(3)	C(30)-C(25)-C(31)	121.0(3)

C(6)-N(1)-Cr(1A)	128.10(18)	C(27)-C(26)-C(25)	122.0(4)
C(6)-N(1)-Cr(2)	143.43(18)	C(26)-C(27)-C(28)	120.3(3)
Cr(1A)-N(1)-Cr(2)	88.25(11)	C(27)-C(28)-C(29)	120.1(4)
C(6)-N(1)-Cr(1B)	133.2(2)	C(28)-C(29)-C(30)	118.8(4)
Cr(2)-N(1)-Cr(1B)	74.00(14)	C(28)-C(29)-C(34)	117.3(4)
C(18)-N(2)-Cr(1A)	123.10(19)	C(30)-C(29)-C(34)	123.9(3)
C(18)-N(2)-Cr(2)	139.27(17)	C(25)-C(30)-C(29)	120.5(3)
Cr(1A)-N(2)-Cr(2)	88.22(11)	C(25)-C(30)-N(3)	120.3(3)
C(30)-N(3)-Cr(1A)	139.1(2)	C(29)-C(30)-N(3)	119.3(3)
C(2)-C(1)-C(6)	118.2(5)	C(25)-C(31)-C(32)	110.8(3)
C(2)-C(1)-C(7)	119.1(5)	C(25)-C(31)-C(33)	113.5(3)
C(6)-C(1)-C(7)	122.7(4)	C(32)-C(31)-C(33)	110.5(3)
C(3)-C(2)-C(1)	121.9(6)	C(35)-C(34)-C(29)	111.9(5)
C(4)-C(3)-C(2)	119.2(5)	C(35)-C(34)-C(36)	109.6(5)
C(3)-C(4)-C(5)	124.2(6)	C(29)-C(34)-C(36)	109.9(5)

An interesting feature of intramolecular π -stacking was found between two aromatic rings in the crystal structure of **19** (Figure 2.7). Typical distances between the centroids of two aromatic rings for parallel π -stacking are in the range of 3.3–4.6 Å and typical dihedral angles are in the range of 0–20°. The distance between the centroids of two rings of **19** is 3.853 Å and their dihedral angle is 7.72°. Considering the two aromatic rings are not perfectly aligned, the interaction between the two rings is described as an intramolecular parallel offset π -stacking.³¹⁻³²

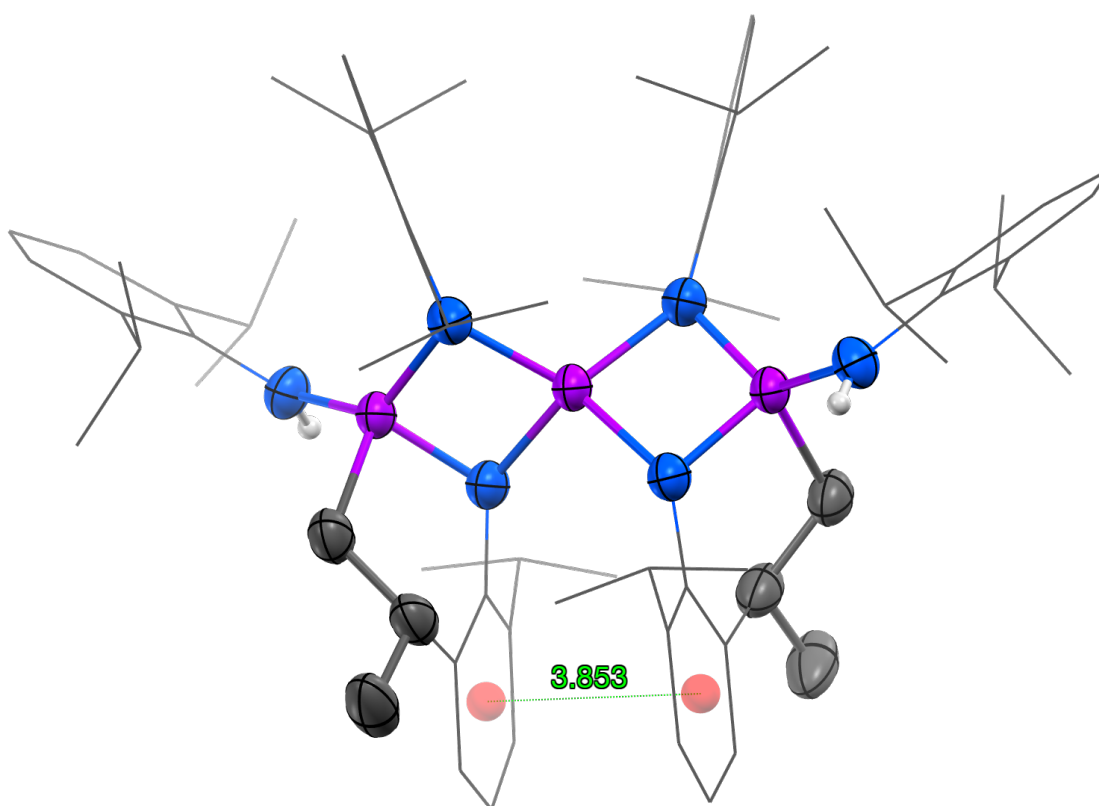
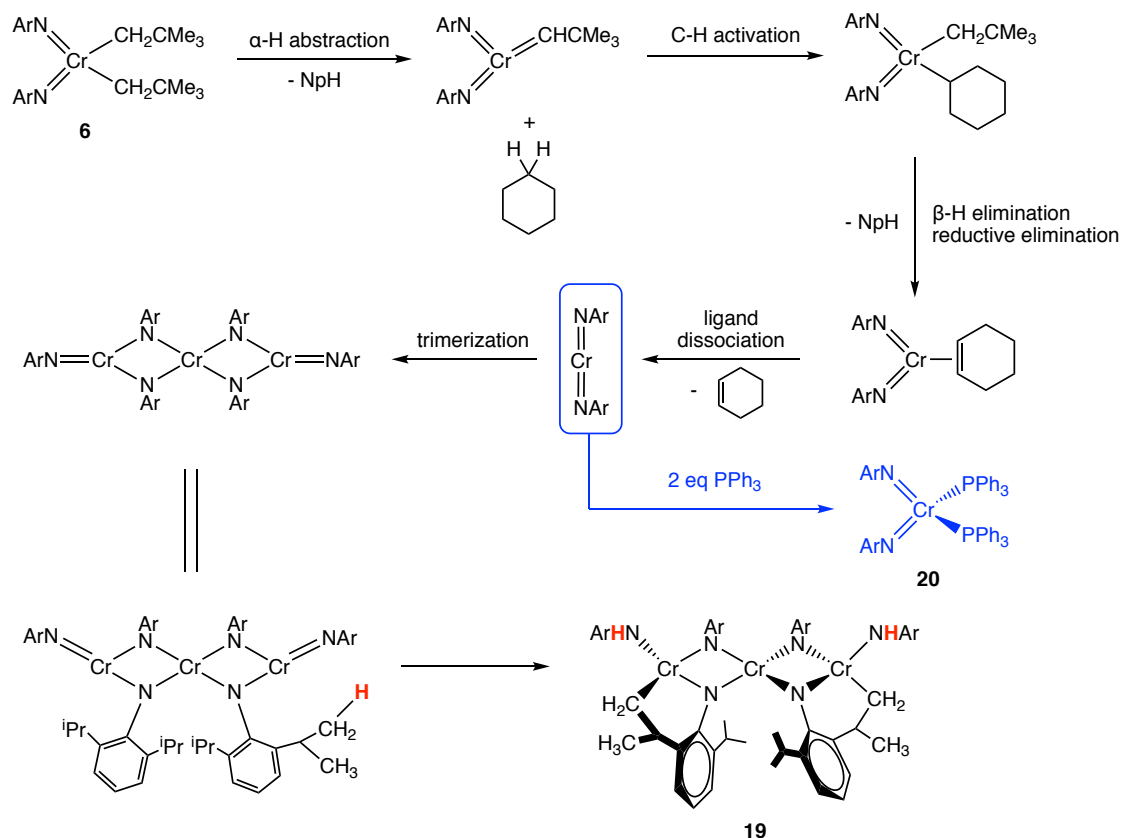


Figure 2.7 Intramolecular π -stacking interaction in the structure of **19**. Each red dot is the centroid of an aromatic ring.

To understand the mechanism of formation of **19**, the organic byproducts of this reaction needed to be identified. The same reaction was set up in a sealed and degassed ampule. After stirring for three days, a small amount of organic volatiles was vacuum transferred into a J-Young tube. Then C₆D₆ was transferred into the same tube. The ¹H NMR spectrum clearly showed the formation of neopentane and cyclohexene by comparing the ¹H NMR spectrum of the reaction sample in the J-Young tube with the ¹H NMR spectra of authentic neopentane and cyclohexene. The ratio between neopentane and cyclohexene was confirmed by an experiment that was done in a sealed J-Young tube. 5 mg of **6** as well as three drops of cyclohexane were added into a J-Young tube. After three days, C₆D₆ was transferred to the same tube. Integrating the peak of neopentane and the olefinic peak of cyclohexene gave the ratio 2.06:1 between neopentane and cyclohexene. Based on the information that I collected from these experiments, Scheme 2.18 shows a proposed mechanism for C-H bond activation of cyclohexane by transient neopentylidene. Chromium dialkyl **6** undergoes α-hydrogen abstraction to yield coordinatively unsaturated neopentylidene, which is able to react with cyclohexane to produce neopentyl cyclohexyl chromium. Due to the β-hydrogen on the cyclohexyl group, this mixed alkyl intermediate is unstable and decomposes via β-hydrogen elimination followed by reductive elimination of neopentane to form a Cr(IV) intermediate. Then the labile cyclohexene ligand dissociates from the chromium center to generate a two-coordinate bis(imido) Cr(IV) intermediate. Due to its coordinative unsaturation, the two-coordinate intermediate is likely to oligomerize. Indeed, it apparently trimerizes. In the last step, the terminal imido reacts rapidly with a C-H bond of isopropyl methyl, yielding the final product **19**.



Scheme 2.18 A possible mechanism for the formation of **19**

In support of this proposed mechanism, one intermediate of this reaction sequence, namely $[(\text{ArN})_2\text{Cr}^{\text{IV}}]$, can be trapped by PPh_3 to form a stable complex, i.e. $(\text{ArN})_2\text{Cr}(\text{PPh}_3)_2$ (**20**). Thus, **6** and two equivalents of PPh_3 were dissolved in cyclohexane. After stirring at room temperature for three days, the color changed from green to brown. The product was crystallized out from concentrated Et_2O solution at room temperature. Curiously, **13** was not observed by NMR spectroscopy which might be a result of relative high concentration of cyclohexane and the low energy barrier for C-H activation of cyclohexane. The structure of **20** has been determined by X-ray diffraction and it is depicted in Figure 2.8. **20** features pseudo-tetrahedral coordination

geometry and C_{2v} symmetry with the largest bond angle, i.e. N1-Cr1-N1, $133.66(7)^\circ$, being significantly opened up compared to dialkyls as well as diaryls in **Chapter 1** and alkylidenes in this chapter. The imido bond of **20** (Cr1-N1, $1.6934(10)$ Å) is slightly longer than those of bis(imido) chromium(VI) complexes, probably due to the lower formal oxidation state of chromium of **20**. In the ^1H NMR spectrum, a broad peak caused by coupling with PPh_3 is assigned to isopropyl methine and a doublet peak is assigned to isopropyl methyl. As indicated by the NMR spectra (^1H NMR, ^{13}C NMR, and ^{31}P NMR), the Cr(IV) complex **20** is diamagnetic.

Imido ligands have the isolobal relationship with cyclopentadienyl ligands.³³ Thus, **20** shares the similar d-orbital splitting diagram of a bent metallocene complex Cp_2ML_2 . One bent metallocene chromium(IV) complex, namely $[\text{Me}_4\text{C}_2(\eta^5\text{-C}_5\text{H}_4)\{\eta^5\text{-C}_5\text{H}_3\text{B}(\text{C}_6\text{F}_5)_3\}]\text{Cr}(\text{CN})\text{CNXyl}$, is diamagnetic because its HOMO is a single non-degenerate d-orbital and the two d-electrons occupy this orbital.³⁴⁻³⁵ Accordingly, **20** is also diamagnetic.

20 can also be synthesized independently by reduction of $(\text{ArN})_2\text{CrCl}_2$ (**3**) with Mg in the presence of PPh_3 . (See details in the Experimental section). One phosphine ligand of **20** can be replaced by other ligands, like ethylene and carbon monoxide. These observations are discussed in **Appendix B**.

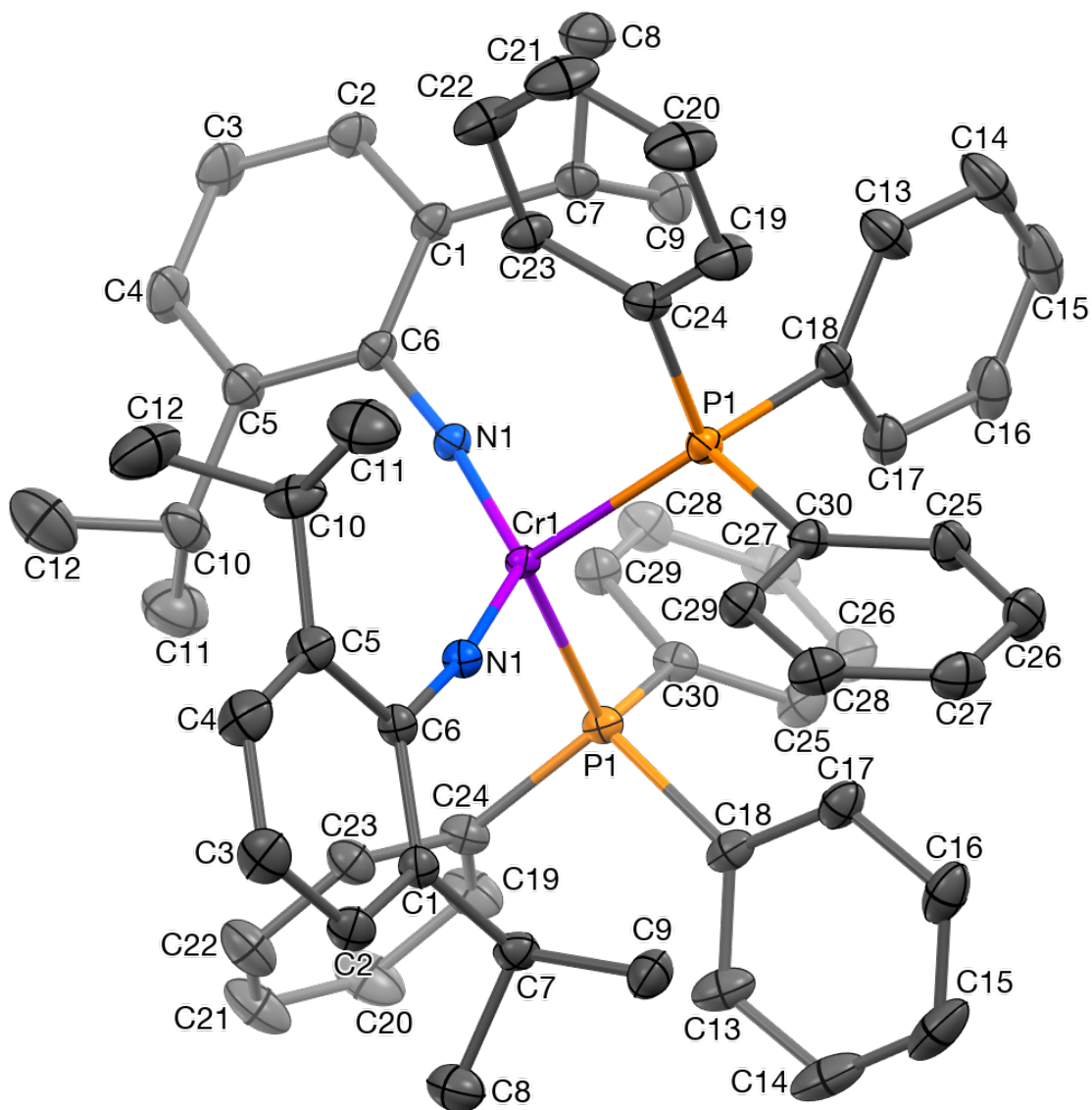


Figure 2.8 Molecular structure of $(\text{ArN})_2\text{Cr}(\text{PPh}_3)_2$ (**20**). Ellipsoids are drawn at the 30% probability level. Hydrogen atoms have been omitted for clarity.

Table 2.5 Interatomic distances (Å) and angles (°) for (ArN)₂Cr(PPh₃)₂ (**20**)

Distances (Å)			
Cr(1)-N(1)	1.6934(10)	C(10)-C(12)	1.541(3)
Cr(1)-N(1)	1.6934(10)	C(13)-C(18)	1.394(2)
Cr(1)-P(1)	2.3210(3)	C(13)-C(14)	1.396(2)
Cr(1)-P(1)	2.3210(3)	C(14)-C(15)	1.368(3)
P(1)-C(30)	1.8330(12)	C(15)-C(16)	1.381(3)
P(1)-C(18)	1.8403(13)	C(16)-C(17)	1.391(2)
P(1)-C(24)	1.8475(14)	C(17)-C(18)	1.392(2)
N(1)-C(6)	1.3852(14)	C(19)-C(20)	1.386(2)
C(1)-C(2)	1.3976(17)	C(19)-C(24)	1.4010(19)
C(1)-C(6)	1.4210(17)	C(20)-C(21)	1.384(3)
C(1)-C(7)	1.5145(18)	C(21)-C(22)	1.381(3)
C(2)-C(3)	1.379(2)	C(22)-C(23)	1.392(2)
C(3)-C(4)	1.381(2)	C(23)-C(24)	1.3928(19)
C(4)-C(5)	1.3941(19)	C(25)-C(30)	1.3918(19)
C(5)-C(6)	1.4214(18)	C(25)-C(26)	1.3955(19)
C(5)-C(10)	1.512(2)	C(26)-C(27)	1.375(2)
C(7)-C(9)	1.526(2)	C(27)-C(28)	1.382(2)
C(7)-C(8)	1.530(2)	C(28)-C(29)	1.3883(19)
C(10)-C(11)	1.514(3)	C(29)-C(30)	1.3975(18)
Angles (°)			
N(1)-Cr(1)-N(1)	133.66(7)	C(5)-C(10)-C(11)	109.74(15)
N(1)-Cr(1)-P(1)	102.60(3)	C(5)-C(10)-C(12)	112.54(15)
N(1)-Cr(1)-P(1)	103.42(3)	C(11)-C(10)-C(12)	109.26(16)
N(1)-Cr(1)-P(1)	103.42(3)	C(18)-C(13)-C(14)	119.57(17)
N(1)-Cr(1)-P(1)	102.60(3)	C(15)-C(14)-C(13)	121.39(17)
P(1)-Cr(1)-P(1)	110.217(18)	C(14)-C(15)-C(16)	119.58(15)
C(30)-P(1)-C(18)	102.47(6)	C(15)-C(16)-C(17)	119.76(18)
C(30)-P(1)-C(24)	100.00(6)	C(16)-C(17)-C(18)	121.17(15)
C(18)-P(1)-C(24)	102.30(6)	C(17)-C(18)-C(13)	118.49(13)
C(30)-P(1)-Cr(1)	117.04(4)	C(17)-C(18)-P(1)	118.10(10)

C(18)-P(1)-Cr(1)	119.91(4)	C(13)-C(18)-P(1)	123.39(12)
C(24)-P(1)-Cr(1)	112.35(5)	C(20)-C(19)-C(24)	120.76(15)
C(6)-N(1)-Cr(1)	172.01(9)	C(21)-C(20)-C(19)	120.13(16)
C(2)-C(1)-C(6)	119.01(12)	C(22)-C(21)-C(20)	119.76(15)
C(2)-C(1)-C(7)	118.97(12)	C(21)-C(22)-C(23)	120.47(16)
C(6)-C(1)-C(7)	121.97(11)	C(22)-C(23)-C(24)	120.42(14)
C(3)-C(2)-C(1)	121.37(13)	C(23)-C(24)-C(19)	118.46(13)
C(2)-C(3)-C(4)	119.69(13)	C(23)-C(24)-P(1)	119.85(10)
C(3)-C(4)-C(5)	121.68(14)	C(19)-C(24)-P(1)	121.68(11)
C(4)-C(5)-C(6)	118.81(13)	C(30)-C(25)-C(26)	120.33(14)
C(4)-C(5)-C(10)	119.64(13)	C(27)-C(26)-C(25)	120.40(14)
C(6)-C(5)-C(10)	121.43(12)	C(26)-C(27)-C(28)	119.82(13)
N(1)-C(6)-C(1)	121.38(11)	C(27)-C(28)-C(29)	120.31(14)
N(1)-C(6)-C(5)	119.20(11)	C(28)-C(29)-C(30)	120.45(13)
C(1)-C(6)-C(5)	119.40(11)	C(25)-C(30)-C(29)	118.65(12)
C(1)-C(7)-C(9)	110.50(12)	C(25)-C(30)-P(1)	123.16(10)
C(1)-C(7)-C(8)	113.14(12)	C(29)-C(30)-P(1)	118.17(10)
C(9)-C(7)-C(8)	110.30(12)		

The most prominent application of metal alkylidenes is the catalysis of olefin metathesis. Molybdenum alkylidenes, tungsten alkylidenes and ruthenium alkylidenes are widely used in this type of reaction. Accordingly, it is interesting to explore the reactivity of chromium(VI) alkylidenes with olefins. Neither **13** nor **14b** reacted with alkenes (e.g. ethylene, norbornene, cyclopentene), suggesting that tight binding of phosphine prevents coordination of potential substrate. However, a color change from green to red was observed when stirring a cyclopentene solution of **6** at room temperature over three days. Standard workup gave a new organometallic compound $(\text{ArN})_2\text{Cr}(\text{C}_{10}\text{H}_{18})$ (**21**), which was characterized by spectroscopy and X-ray diffraction. The molecular structure is depicted in Figure 2.9. The compound **21** features pseudo-tetrahedral coordination geometry. The four atoms (CrA, C25A, C26A, C30A) of the chromacyclobutane are almost in the same plane according to the short distance (0.013 Å) between C26A and the plane C25A-CrA-C30A. The two Cr-C $_{\alpha}$ bonds (1.932(4) and 1.965(4) Å) are short compared to other Cr^{VI}-C single bonds, but longer than Cr-C double bonds that are found in the structures of chromium alkylidenes. The cyclopentyl ring and *tert*-butyl group are in trans positions to minimize steric repulsions. NMR spectra showed both α -hydrogens and both α -carbons of chromacyclobutane shifted downfield (6.98 ppm for α -hydrogen of cyclopentyl, 5.81 ppm ($^3J_{\text{HH}} = 6.08$ Hz) for α -hydrogen of CHCMe_3 and 148.09 ppm for CHCMe_3 , 143.81 ppm for α -carbon of cyclopentyl). Full assignment of ¹H NMR and ¹³C NMR can be found in the Experimental section and is supported by the 2D-NMR HSQC spectrum.

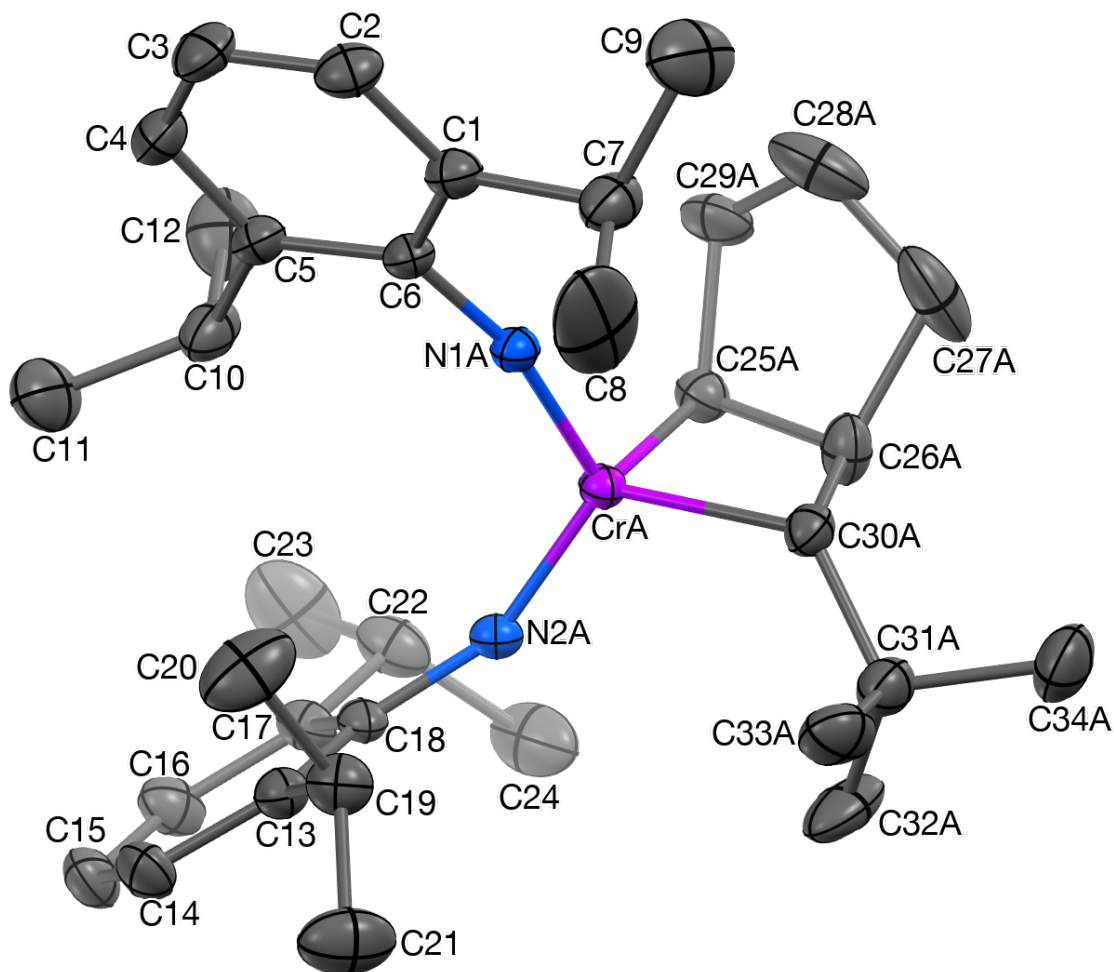


Figure 2.9 Molecular structure of $(\text{ArN})_2\text{Cr}(\text{C}_{10}\text{H}_{18})$ (**21**). Ellipsoids are drawn at the 30% probability level. Hydrogen atoms have been omitted for clarity.

Table 2.6 Interatomic distances (Å) and angles (°) for (ArN)₂Cr(C₁₀H₁₈) (**21**)

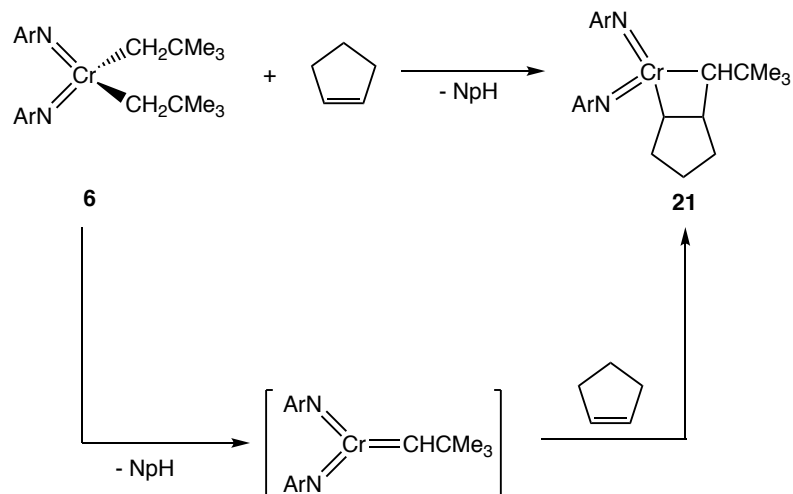
Distances (Å)			
CrA-N(1A) ^a	1.656(4)	C(14)-C(15)	1.369(6)
CrA-N(2A) ^a	1.662(3)	C(15)-C(16)	1.380(5)
CrA-C(25A) ^a	1.932(4)	C(16)-C(17)	1.384(5)
CrA-C(30A) ^a	1.965(4)	C(17)-C(18)	1.410(5)
CrA-C(26A) ^a	2.245(5)	C(17)-C(22)	1.517(5)
N(1A)-C(6) ^a	1.393(5)	C(19)-C(20)	1.508(6)
N(2A)-C(18) ^a	1.385(5)	C(19)-C(21)	1.515(6)
CrB-N(1B) ^a	1.636(15)	C(22)-C(24)	1.517(6)
CrB-N(2B) ^a	1.657(15)	C(22)-C(23)	1.535(6)
CrB-C(25B) ^a	1.939(13)	C(25A)-C(29A) ^a	1.543(6)
CrB-C(30B) ^a	1.968(14)	C(25A)-C(26A) ^a	1.582(6)
CrB-C(26B) ^a	2.23(2)	C(26A)-C(27A) ^a	1.554(8)
N(1B)-C(6) ^a	1.373(16)	C(26A)-C(30A) ^a	1.595(6)
N(2B)-C(18) ^a	1.448(17)	C(27A)-C(28A) ^a	1.494(10)
C(1)-C(2)	1.388(5)	C(28A)-C(29A) ^a	1.482(8)
C(1)-C(6)	1.417(4)	C(30A)-C(31A) ^a	1.535(6)
C(1)-C(7)	1.512(5)	C(31A)-C(33A) ^a	1.502(8)
C(2)-C(3)	1.371(5)	C(31A)-C(32A) ^a	1.504(7)
C(3)-C(4)	1.380(6)	C(31A)-C(34A) ^a	1.557(7)
C(4)-C(5)	1.387(5)	C(25B)-C(26B) ^a	1.560(17)
C(5)-C(6)	1.413(4)	C(25B)-C(29B) ^a	1.566(17)
C(5)-C(10)	1.514(5)	C(26B)-C(27B) ^a	1.555(19)
C(7)-C(8)	1.490(7)	C(26B)-C(30B) ^a	1.578(16)
C(7)-C(9)	1.510(6)	C(27B)-C(28B) ^a	1.487(19)
C(10)-C(12)	1.515(7)	C(28B)-C(29B) ^a	1.493(19)
C(10)-C(11)	1.533(6)	C(30B)-C(31B) ^a	1.531(16)
C(13)-C(14)	1.391(5)	C(31B)-C(32B) ^a	1.484(18)
C(13)-C(18)	1.418(4)	C(31B)-C(33B) ^a	1.487(17)
C(13)-C(19)	1.509(5)	C(31B)-C(34B) ^a	1.553(17)

^a The chromium, nitrogen atoms and metallacyclobutane ligand in **21** were found disordered in two positions with a refined site occupancy ratio of 81/19.

Angles (°)			
N(1A)-CrA-N(2A)	117.2(2)	N(2A)-C(18)-C(17)	116.4(3)
N(1A)-CrA-C(25A)	109.42(18)	N(2A)-C(18)-C(13)	122.5(3)
N(2A)-CrA-C(25A)	109.69(17)	C(17)-C(18)-C(13)	121.1(3)
N(1A)-CrA-C(30A)	111.4(2)	C(17)-C(18)-N(2B)	134.5(8)
N(2A)-CrA-C(30A)	117.31(19)	C(13)-C(18)-N(2B)	104.3(8)
C(25A)-CrA-C(30A)	87.61(18)	C(20)-C(19)-C(13)	111.2(3)
N(1A)-CrA-C(26A)	119.3(2)	C(20)-C(19)-C(21)	111.7(4)
N(2A)-CrA-C(26A)	123.1(2)	C(13)-C(19)-C(21)	112.7(3)
C(25A)-CrA-C(26A)	43.71(17)	C(24)-C(22)-C(17)	110.4(4)
C(30A)-CrA-C(26A)	43.90(16)	C(24)-C(22)-C(23)	111.3(4)
C(6)-N(1A)-CrA	165.6(4)	C(17)-C(22)-C(23)	113.7(4)
C(18)-N(2A)-CrA	156.6(3)	C(29A)-C(25A)-C(26A)	107.5(4)
N(1B)-CrB-N(2B)	119.0(13)	C(29A)-C(25A)-CrA	123.5(3)
N(1B)-CrB-C(25B)	110.4(9)	C(26A)-C(25A)-CrA	78.7(2)
N(2B)-CrB-C(25B)	112.4(8)	C(27A)-C(26A)-C(25A)	100.9(4)
N(1B)-CrB-C(30B)	110.7(10)	C(27A)-C(26A)-C(30A)	112.8(4)
N(2B)-CrB-C(30B)	113.0(9)	C(25A)-C(26A)-C(30A)	116.2(3)
C(25B)-CrB-C(30B)	86.9(6)	C(27A)-C(26A)-CrA	123.6(4)
N(1B)-CrB-C(26B)	118.5(12)	C(25A)-C(26A)-CrA	57.6(2)
N(2B)-CrB-C(26B)	122.5(10)	C(30A)-C(26A)-CrA	58.66(19)
C(25B)-CrB-C(26B)	43.3(5)	C(28A)-C(27A)-C(26A)	107.4(5)
C(30B)-CrB-C(26B)	43.6(5)	C(29A)-C(28A)-C(27A)	103.8(5)
C(6)-N(1B)-CrB	165(2)	C(28A)-C(29A)-C(25A)	104.3(4)
C(18)-N(2B)-CrB	152.5(16)	C(31A)-C(30A)-C(26A)	117.5(4)
C(2)-C(1)-C(6)	118.0(3)	C(31A)-C(30A)-CrA	128.8(3)
C(2)-C(1)-C(7)	122.2(3)	C(26A)-C(30A)-CrA	77.4(2)
C(6)-C(1)-C(7)	119.8(3)	C(33A)-C(31A)-C(32A)	110.9(5)
C(3)-C(2)-C(1)	121.6(3)	C(33A)-C(31A)-C(30A)	106.7(4)
C(2)-C(3)-C(4)	120.0(3)	C(32A)-C(31A)-C(30A)	113.3(4)
C(3)-C(4)-C(5)	121.7(3)	C(33A)-C(31A)-C(34A)	107.8(4)
C(4)-C(5)-C(6)	117.8(3)	C(32A)-C(31A)-C(34A)	109.9(5)
C(4)-C(5)-C(10)	121.3(3)	C(30A)-C(31A)-C(34A)	108.1(4)
C(6)-C(5)-C(10)	120.9(3)	C(26B)-C(25B)-C(29B)	108.7(12)
N(1B)-C(6)-C(5)	127.1(11)	C(26B)-C(25B)-CrB	78.3(9)

N(1A)-C(6)-C(5)	119.0(3)	C(29B)-C(25B)-CrB	124.7(14)
N(1B)-C(6)-C(1)	110.1(10)	C(27B)-C(26B)-C(25B)	100.1(13)
N(1A)-C(6)-C(1)	120.1(3)	C(27B)-C(26B)-C(30B)	114.6(18)
C(5)-C(6)-C(1)	120.9(3)	C(25B)-C(26B)-C(30B)	117.8(14)
C(8)-C(7)-C(9)	111.5(5)	C(27B)-C(26B)-CrB	125.5(15)
C(8)-C(7)-C(1)	109.0(4)	C(25B)-C(26B)-CrB	58.4(8)
C(9)-C(7)-C(1)	114.1(3)	C(30B)-C(26B)-CrB	59.4(8)
C(5)-C(10)-C(12)	111.2(3)	C(28B)-C(27B)-C(26B)	106.1(16)
C(5)-C(10)-C(11)	112.3(4)	C(27B)-C(28B)-C(29B)	103.2(16)
C(12)-C(10)-C(11)	110.6(4)	C(28B)-C(29B)-C(25B)	101.1(14)
C(14)-C(13)-C(18)	117.3(3)	C(31B)-C(30B)-C(26B)	121.6(14)
C(14)-C(13)-C(19)	121.6(3)	C(31B)-C(30B)-CrB	128.9(12)
C(18)-C(13)-C(19)	121.1(3)	C(26B)-C(30B)-CrB	77.0(9)
C(15)-C(14)-C(13)	122.1(3)	C(32B)-C(31B)-C(33B)	114.5(16)
C(14)-C(15)-C(16)	119.9(3)	C(32B)-C(31B)-C(30B)	105.9(16)
C(15)-C(16)-C(17)	121.4(3)	C(33B)-C(31B)-C(30B)	111.5(15)
C(16)-C(17)-C(18)	118.3(3)	C(32B)-C(31B)-C(34B)	110.5(18)
C(16)-C(17)-C(22)	121.3(3)	C(33B)-C(31B)-C(34B)	107.8(16)
C(18)-C(17)-C(22)	120.5(3)	C(30B)-C(31B)-C(34B)	106.5(15)

The reaction of preformed neopentylidene THF adduct $(\text{ArN})_2\text{Cr}(=\text{CHCMe}_3)(\text{THF})$ with pure cyclopentene also gave **21**. The color change associated with this reaction was observed in one hour, which means the dissociation of THF from the chromium center and the [2+2] cycloaddition are both pretty fast. Thus, α -hydrogen abstraction is presumably the rate-determining step in the reaction of **6** with cyclopentene (Scheme 2.19). This metallacyclobutane is a result of a [2+2] cycloaddition of transient neopentylidene $[(\text{ArN})_2\text{Cr}(=\text{CHCMe}_3)]$ with one molecule of cyclopentene. ROMP of cyclopentene was not observed when stirring cyclopentene solution of **6** at room temperature. Heating cyclopentene solution of **21** at a higher temperature only resulted in decomposition of **21** to black particles and intractable product. The ^1H NMR spectrum of the crude product did not give valuable information for identification of the product.

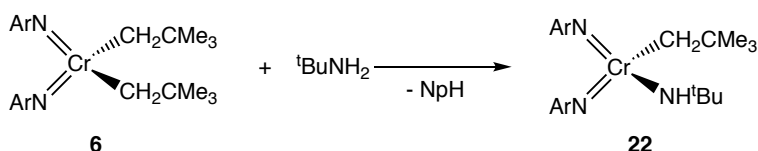


Scheme 2.19 [2+2] cycloaddition of neopentylidene with alkene

Dissolving **6** in liquid norbornene (M.p. 42–46 °C) at 60 °C yielded a red product. LIFDI-MS data suggest that the formula of the product should be $\text{CrC}_{36}\text{H}_{56}\text{N}_2$, which is consistent with the product, namely $(\text{ArN})_2\text{Cr}(\text{C}_{12}\text{H}_{20})$, from [2+2] cycloaddition of the transient neopentylidene and norbornene. Dissolving **6** in pure acyclic olefin *tert*-butyl ethylene also yielded the cycloaddition product $(\text{ArN})_2\text{Cr}(\text{C}_{11}\text{H}_{22})$, which is supported by LIFDI-MS. Accordingly, olefin metathesis catalysis was not observed when treating **6** with cyclopentene, norbornene or *tert*-butyl ethylene. So, it appears that the transformation of neopentylidene with olefin into chromacyclobutane is irreversible, presumably due to significantly greater thermodynamic stability of the cycloaddition product.

In addition to the reactivity of C-H bond activation and cycloaddition with olefins, **6** shows capability of N-H activation of $^t\text{BuNH}_2$. Dissolving **6** in neat $^t\text{BuNH}_2$ and stirring for three days caused a color change from green to red. (Scheme 2.20) The product $(\text{ArN})_2\text{Cr}(\text{CH}_2\text{CMe}_3)(\text{NH}^t\text{Bu})$ (**22**) was characterized spectroscopically. Structural characterization by X-ray diffraction showed a strong disorder between Np and NH^tBu , which results from similar electron density of carbon and nitrogen. Even without structural characterization, the formula of **22** is supported by LIFDI-MS (m/z : 545.3776 [M^+]. Calcd. m/z : 545.3801 [M^+]) and elemental analysis. The peak at 10.24 ppm in ^1H NMR is assigned to the amido hydrogen (NH^tBu) and the N-H bond has an absorption band at 3287 cm^{-1} in the infrared spectrum. Though the mechanism of simple protonolysis of an alkyl ligand by *tert*-butylamine cannot presently be ruled out, both reactions, i.e. formation of **13** and N-H bond activation of $^t\text{BuNH}_2$ to make **22**, have qualitatively the same reaction rate. This suggests a common rate-determining step and intermediate in both reactions. So, the proposed mechanism is that the ligand

exchange goes via α -hydrogen abstraction, followed by N-H bond activation of $^t\text{BuNH}_2$ by transient neopentylidene $[(\text{ArN})_2\text{Cr}(=\text{CHCMe}_3)]$, yielding **22**.



Scheme 2.20 Synthesis of $(\text{ArN})_2\text{Cr}(\text{CH}_2\text{CMe}_3)(\text{NH}^t\text{Bu})$ (**22**)

In summary, neopentylidene phosphine adduct **13** is not reactive towards alkane or alkene. This can be ascribed to the absence of empty coordination site due to the strong binding of phosphine to the chromium center. The transient neopentylidene, which is generated from α -hydrogen abstraction of **6**, shows C-H bond activation of alkanes, [2+2] cycloaddition with alkenes, and N-H activation of *tert*-butylamine.

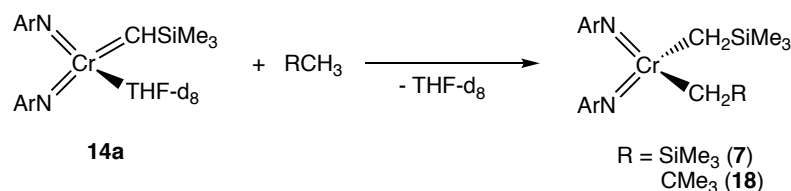
2.2.3 Reactivity of Trimethylsilylmethylidene

Trimethylsilylmethylidene $[(\text{ArN})_2\text{Cr}(=\text{CHSiMe}_3)]$ is analogous to neopentylidene. It is reasonable to expect that it should show similar reactivity, like C-H bond activation. The study of C-H bond activation was performed with $(\text{ArN})_2\text{Cr}(=\text{CHSiMe}_3)(\text{THF-d}_8)$ (**14a**) instead of the precursor $(\text{ArN})_2\text{Cr}(\text{CH}_2\text{SiMe}_3)_2$ (**7**) because α -hydrogen abstraction of **7** proceeds at 80 °C and C-H bond activation product may not survive at such high temperature as well as for reasons of safety (vapor pressure at 80 °C: SiMe_4 (4.90 atm), NpH (7.26 atm)).

Dissolving **14a** in SiMe_4 and waiting for 2 days at room temperature caused a color change from brown to green. NMR spectrum indicated the formation of

(ArN)₂Cr(CH₂SiMe₃)₂ (**7**) by comparing the ¹H NMR spectrum of crude product and ¹H NMR spectrum of authentic **7** (Scheme 2.21).

Studying the reaction of **14a** with NpH is slightly different from the aforementioned reaction of **14a** with SiMe₄ because NpH is a gas at room temperature. **14a** was prepared in an ampule first and then THF was removed in vacuum. NpH was added into the ampule through vacuum transfer. A color change was observed from brown to green after 2 days at room temperature. NMR spectrum indicated the formation of (ArN)₂Cr(CH₂CMe₃)(CH₂SiMe₃) (**18**) by comparing the ¹H NMR spectrum of crude product and the ¹H NMR spectrum of authentic **18** (Scheme 2.21).



Scheme 2.21 C-H bond activation of alkane by trimethylsilylmethyldene **14a**

2.3 Summary

Multiple chromium(VI) alkylidenes, including (ArN)₂Cr(=CHCMe₃)(PPh₃) (**13**), (ArN)₂Cr(=CHSiMe₃)(PPh₃) (**14b**), K[(ArN)₂Cr(=CHSiMe₃)(CH₂SiMe₃)] (**15a**), Et₄N[(ArN)₂Cr(=CHPh)(CH₂Ph)] (**16b**) and Li[(ArN)₂Cr(=CHCMe₃)(CH₂CMe₃)] (**17b**), have been synthesized and characterized. Structures of **13**, **14b** and **15b** have been determined by X-ray diffraction.

Transient neopentylidene shows C-H bond activation of alkanes, [2+2] cycloaddition with alkenes and N-H activation of *tert*-butylamine. No ROMP catalysis

was observed when treating either **13** or neopentylidene precursor **6** with cyclopentene or norbornene, even when heated to 60 °C.

Trimethylsilylmethylidene **14a** shows similar C-H bond activation reactivity as transient neopentylidene.

Some results in this chapter have been communicated in Journal of the American Chemical Society.³⁶

2.4 Experimental

2.4.1 General Considerations

All manipulations were carried out with standard Schlenk, vacuum line, and glovebox techniques. Pentane, diethyl ether, toluene and tetrahydrofuran were dried by passing through activated alumina and were degassed prior to use. THF- d_8 and C_6D_6 were purchased from Cambridge Isotopes Laboratory, dried with sodium and stored under vacuum over Na/K alloy. Grignard reagents, PPh_3 , $SiMe_4$ and cyclopentene were purchased from Sigma Aldrich. $SiMe_4$ and cyclopentene were dried with molecular sieves and stored in an inert atmosphere glove box. $(ArN)_2CrCl_2$ ³⁷ and $(ArN)_2Cr(CH_2CMe_3)_2$ ⁶ (Ar = 2,6-diisopropylphenyl) were prepared according to the literature procedures.

1H NMR spectra were taken on a Bruker AVIII-400 spectrometer and were referenced to the residual protons of the solvent (C_6D_6 = 7.16 ppm, THF- d_8 = 3.58 ppm and 1.72 ppm). ^{13}C NMR spectra were taken on a Bruker AVIII-400 spectrometer or a Bruker AVIII-600 spectrometer and were referenced to the ^{13}C of the solvent (C_6D_6 = 128.06 ppm, THF- d_8 = 67.21 ppm and 25.31 ppm).³⁸ FT-IR spectra were obtained using a Nicolet Magna-IR 560 spectrometer with a resolution of 4 cm^{-1} . UV-

vis spectra were obtained using a SILVER-Nova-TEC-X2 equipped with SL1-LED, which was purchased from StellarNet Inc. X-ray crystallographic studies were conducted in the X-ray Crystallographic Laboratory at the University of Delaware. Elemental analyses were obtained from Robertson Microlit, Ledgewood, NJ. LIFDI-MS were obtained using a Waters GCT Premier high-resolution time-of-flight mass spectrometer by liquid injection field desorption ionization (LIFDI-MS).

2.4.2 X-ray Crystallography

Crystals of **13**, **14b**, **15b**, **19**, **20** and **21** were mounted onto plastic mesh using viscous oil and flash-cooled to the data collection temperature. Data were collected on a Bruker-AXS APEX II Duo CCD diffractometer with graphite-monochromated Mo-K α radiation ($\lambda=0.71073$ Å) for **13**, **14b**, **15b**; and with Cu-K α radiation ($\lambda = 1.54178$ Å) focused with Goebel mirrors for **19**, **20**, **21**. Unit cell parameters were determined by sampling three different sections of the Ewald sphere. The systematic absences in the diffraction data were uniquely consistent with $P 2_12_12_1$ for **13**. The systematic absences in the diffraction data were consistent with $P bcm$ or $P ca2_1$ for **14b**. Only the non-centrosymmetric space group option, $P ca2_1$, yielded chemically reasonable and computationally stable results of refinement for **14b**. The unit cell parameters and systematic absences in the diffraction data were consistent for space group $P \bar{4}2_1c$ for **15b**, $R \bar{3}c$ for **19**, $P bcn$ for **20**. No symmetry higher than triclinic was observed for **21** and solution in the centrosymmetric space group option, $P \bar{1}$, yielded chemically reasonable and computationally stable results of refinement. The data sets were treated with absorption corrections based on redundant multi-scan data.³⁹ The structures were solved using intrinsic phasing and refined with full-matrix, least-squares procedures on F^2 .⁴⁰⁻⁴¹

One pentane molecule of solvation was found disordered in the asymmetric unit of **13**, which was treated as diffused contributions but was included in the sum formula.

A severely disordered solvent molecule, found in the asymmetric unit of **14b** that was treated as diffused contributions, could not be assigned a reasonable identity and was ignored.

Alkyl ligand and alkylidene ligand have position disorder in **15b** with a site occupancy ratio of 62/38. The minor component was treated with similar 1,2 and 1,3 atom distance restraints based on the major component geometry.

Cr1 in **19** was found disordered in two positions with a refined site occupancy ratio of 91/9. With such occupancy ratio, the structure of the minor component cannot be modeled due to a very low electron density. Amido hydrogen H3N was assigned on N3 because of long bond length of Cr1-N3. Besides, this assignment was supported by LIFDI-MS and infrared spectroscopy.

The chromium, nitrogen atoms and metallacyclobutane ligand in **21** were found disordered in two positions with a refined site occupancy ratio of 81/19. The chemically analogous atoms between the disordered contributions were treated with equal atomic displacement parameters. The minor component was treated with similar 1,2 and 1,3 atom distance restraints based on the major component geometry.

All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were treated as idealized contributions. Atomic scattering factors are contained in the SHELXTL program library.

Some CIFs have been deposited with the Cambridge Crystallographic Database Centre under depositary numbers **13**: 1831804; **14b**: 1831802; and **21**: 1831803.

2.4.3 Preparation of (ArN)₂Cr(=CHCMe₃)(PPh₃) (**13**)

(ArN)₂Cr(CH₂CMe₃)₂ (**6**) (0.200 g, 0.367 mmol) was dissolved in 40 mL THF, giving a green solution. 1 equiv. of PPh₃ (0.096 g, 0.367 mmol) was added. The solution was stirred for 3 days at room temperature during which time the color changed to red. The solvent was then removed in vacuum and the residue was extracted with pentane and the extract was filtered through Celite. The filtrate was concentrated to 3 mL then cooled to -30 °C overnight to yield red crystals. Yield: 0.226 g, 84%. ¹H NMR (400 MHz, THF-d₈): δ 14.97 (d, 1 H, CHCMe₃), 7.59 (m, 6 H, PPh₃), 7.42 (m, 9 H, PPh₃), 6.89 (m, 6 H, ArN), 3.88 (sept, 2 H, CHMe₂), 3.66 (sept, 2 H, CHMe₂), 1.18 (s, 9 H, CHCMe₃), 1.00 (d, 6 H, CHMe₂), 0.88 (d, 6 H, CHMe₂), 0.81 (d, 6 H, CHMe₂), 0.74 (d, 6 H, CHMe₂) ppm. ¹³C{¹H} NMR (100 MHz, THF-d₈): δ 341.73 (CHCMe₃), 158.64 (C_{ipso} of ArN), 157.51 (C_{ipso} of ArN), 144.90 (C_{ortho} of ArN), 143.93 (C_{ortho} of ArN), 135.26 (C_{ortho} of PPh₃), 133.35 (C_{ipso} of PPh₃), 131.41 (C_{para} of PPh₃), 129.43 (C_{meta} of PPh₃), 124.63 (C_{para} of ArN), 124.13 (C_{para} of ArN), 123.00 (C_{meta} of ArN), 122.58 (C_{meta} of ArN), 50.84 (CHCMe₃), 32.32 (CHCMe₃), 28.45 (CHMe₂), 28.04 (CHMe₂), 24.62 (CHMe₂), 24.22 (CHMe₂), 24.16 (CHMe₂), 23.41 (CHMe₂) ppm. ³¹P{¹H} NMR (162 MHz, THF-d₈): δ 65.95 ppm. Anal. Calcd. for C₄₇H₅₉CrN₂P: C, 76.81; H, 8.09; N, 3.81. Found: C, 77.30; H, 8.63; N, 4.21. MS(LIFDI) m/z: 734.3871 [M⁺]. Calcd. m/z: 734.3821 [M⁺]. IR (KBr, cm⁻¹): 3050 (w), 2959 (s), 2864 (m), 1480 (w), 1458 (w), 1435 (m), 1418 (w), 1379 (w), 1357 (w), 1324 (m), 1276 (m), 1257 (w), 1095 (m), 989 (w), 796 (w), 751 (m), 694 (m), 526 (m),

506 (w). UV-vis (pentane): λ_{max} (ϵ) = 260 (4.3×10^4), 324 (2.1×10^4), 430 (7.6×10^3) nm ($\text{M}^{-1}\text{cm}^{-1}$). M.p.: 222 °C.

2.4.4 Preparation of $(\text{ArN})_2\text{Cr}(=\text{CHSiMe}_3)(\text{THF-d}_8)$ (14a)

$(\text{ArN})_2\text{Cr}(\text{CH}_2\text{SiMe}_3)_2$ (**7**) (0.010 g, 0.017 mmol) was added into a J-Young NMR tube. About 0.5 mL THF-d₈ was added into the tube through vacuum transfer. The tube was heated at 80 °C for 24 hours, yielding $(\text{ArN})_2\text{Cr}(=\text{CHSiMe}_3)(\text{THF-d}_8)$. ¹H NMR (400 MHz, d8-THF): δ 17.22 (s, 1 H, *CHSiMe*₃; ¹J_{CH} = 124.4 Hz), 6.97 (d, 2 H, *H*_{meta} of ArN), 6.92 (d, 2 H, *H*_{meta} of ArN), 6.85 (t, 1 H, *H*_{para} of ArN), 6.78 (t, 1 H, *H*_{para} of ArN), 4.13 (sept, 2 H, *CHMe*₂), 3.46 (sept, 2 H, *CHMe*₂), 1.20 (d, 6 H, *CHMe*₂), 1.17 (d, 6 H, *CHMe*₂), 1.05 (d, 6 H, *CHMe*₂), 0.89 (d, 6 H, *CHMe*₂), 0.18 (s, 9 H, *CHSiMe*₃) ppm. ¹³C {¹H} NMR (100 MHz, d8-THF): δ 326.78 (*CHSiMe*₃), 160.64 (*C*_{ipso}), 159.40 (*C*_{ipso}), 143.74 (*C*_{ortho}), 140.72 (*C*_{ortho}), 125.24 (*C*_{para}), 123.33 (*C*_{para}), 122.37 (*C*_{meta}), 122.25 (*C*_{meta}), 28.86 (*CHMe*₂), 28.32 (*CHMe*₂), 23.96 (*CHMe*₂), 23.76 (*CHMe*₂), 23.61 (*CHMe*₂), 23.57 (*CHMe*₂), 1.75 (=CH*SiMe*₃) ppm.

2.4.5 Preparation of $(\text{ArN})_2\text{Cr}(=\text{CHSiMe}_3)(\text{PPh}_3)$ (14b)

$(\text{ArN})_2\text{Cr}(\text{CH}_2\text{SiMe}_3)_2$ (**7**) (0.174 g, 0.302 mmol) was dissolved in 20 mL THF, giving a green solution. 1 equiv. of PPh₃ (0.079 g, 0.302 mmol) was added. The solution was transferred into an ampule, which then was degassed. The solution was stirred for 10 days at 80 °C during which time the color changed to red. The solvent was then removed in vacuum and the residue was extracted with pentane and the extract was filtered through Celite. The filtrate was concentrated to 2 mL then cooled to -30 °C overnight to yield red crystals. Yield: 0.194 g, 86%. ¹H NMR (400 MHz, C₆D₆): δ 17.60 (d, 1 H, *CHSiMe*₃), 7.59 (m, 6 H, PPh₃), 7.08 (m, 9 H, PPh₃), 6.97 (m,

6 H, ArN), 4.09 (sept, 2 H, CHMe₂), 3.87 (sept, 2 H, CHMe₂), 1.22 (d, 6 H, CHMe₂), 1.11 (d, 6 H, CHMe₂), 1.10 (d, 6 H, CHMe₂), 1.04 (d, 6 H, CHMe₂), 0.33 (s, 9 H, CHSiMe₃) ppm. ¹³C{¹H} NMR (150 MHz for alkylidene carbon, 100 Hz for the rest, C₆D₆): δ 340.63 (d, ²J_{PC} = 21.0 Hz, CHSiMe₃), 158.43 (C_{ipso} of ArN), 157.85 (C_{ipso} of ArN), 145.19 (C_{ortho} of ArN), 142.15 (C_{ortho} of ArN), 134.64 (C_{ortho} of PPh₃), 132.30 (C_{ipso} of PPh₃), 130.79 (C_{para} of PPh₃), 128.86 (C_{meta} of PPh₃), 125.27 (C_{para} of ArN), 124.18 (C_{para} of ArN), 122.90 (C_{meta} of ArN), 122.62 (C_{meta} of ArN), 28.28 (CHMe₂), 27.96 (CHMe₂), 24.52 (CHMe₂), 24.29 (CHMe₂), 24.17 (CHMe₂), 23.59 (CHMe₂), 1.65 (CHSiMe₃) ppm. ³¹P{¹H} NMR (162 MHz, C₆D₆): δ 65.23 ppm. ²⁹Si{¹H} NMR (120 MHz, C₆D₆): δ -4.59 (³J_{SiP} = 3.24 Hz) ppm. Anal. Calcd. for C₄₆H₅₉CrN₂PSi: C, 73.56; H, 7.92; N, 3.73. Found: C, 73.94; H, 7.94; N, 3.71. MS(LIFDI) m/z: 750.3654 [M⁺]. Calcd. m/z: 750.3590 [M⁺]. IR (KBr, cm⁻¹): 3050 (w), 2958 (s), 2866 (w), 1480 (w), 1458 (w), 1435 (m), 1417 (w), 1380 (w), 1358 (w), 1324 (m), 1274 (m), 1239 (w), 1096 (m), 999 (w), 971 (w), 855 (s), 830 (m), 794 (w), 748 (m), 706 (w), 694 (m), 527 (m), 503 (w). UV-vis (pentane): λ_{max} (ε) = 253 (7.4*10⁴), 336.5 (2.6*10⁴), 421 (8.3*10³) nm (M⁻¹cm⁻¹). M.p.: 204 °C.

2.4.6 Preparation of K[(ArN)₂Cr(=CHSiMe₃)(CH₂SiMe₃)] (15a) and Et₄N[(ArN)₂Cr(=CHSiMe₃)(CH₂SiMe₃)] (15b)

(ArN)₂Cr(CH₂SiMe₃)₂ (7) (0.230 g, 0.400 mmol) was dissolved in 50 mL THF, giving a green solution. 1 equiv. of KN(SiMe₃)₂ (0.080 g, 0.400 mmol) was added into the green solution at room temperature. The solution was stirred for 1 hour during which time the color changed to brown and then finally to red. All volatile solvents were removed in vacuum. The residue was washed with pentane and filtered to give the product as powder, which is pure enough for characterization and reactivity study.

Yield: 0.222 g, 91%. It was then dissolved in THF, giving a bright red solution. 1 equiv. of Et₄NCl (0.060 g, 0.361 mmol) was added to the red solution at room temperature. The solution was stirred for 4 hours during which time no color change was observed. The solvent was removed in vacuum and the residue was re-dissolved in a small amount of THF. KCl was removed by filtering the THF solution. Crystalline product was obtained from recrystallization by layering the THF solution with pentane (volume ratio = 1 : 2) at -30 °C. Characterization for **15a**: ¹H NMR (400 MHz, THF-d₈): δ 15.15 (s, ¹J_{CH} = 127.5 Hz, 1 H, CHSiMe₃), 6.73 (d, 2 H, H_{meta} of ArN), 6.67 (d, 2 H, H_{meta} of ArN), 6.48 (t, 1 H, H_{para} of ArN), 6.39 (t, 1 H, H_{para} of ArN), 4.13 (sept, 2 H, CHMe₂), 3.88 (sept, 2 H, CHMe₂), 1.15 (d, 6H, CHMe₂), 1.13 (d, 6H, CHMe₂), 1.01 (d, 6 H, CHMe₂), 0.84 (d, 6 H, CHMe₂), 0.18 (s, 2 H, CH₂SiMe₃), 0.03 (s, 9 H, =CHSiMe₃), -0.09 (s, 9 H, CH₂SiMe₃) ppm. ¹³C{¹H} NMR (150 MHz, THF-d₈) δ 295.24 (CHSiMe₃), 158.66 (C_{ipso}), 158.55 (C_{ipso}), 140.88 (C_{ortho}), 139.65 (C_{ortho}), 120.44 (C_{para}), 120.33 (C_{para}), 118.36 (C_{meta}), 117.24 (C_{meta}), 27.58 (CHMe₂), 27.07 (CHMe₂), 23.71 (CHMe₂), 23.54 (CHMe₂), 22.83 (CHMe₂), 22.43 (CHMe₂), 14.11 (CH₂SiMe₃), 2.28 (=CHSiMe₃), 2.13 (CH₂SiMe₃) ppm. Anal. Calcd. for C₃₂H₅₅CrN₂Si₂K: C, 62.49; H, 9.01; N, 4.55. Found: C, 59.14; H, 8.72; N, 4.24. IR (KBr, cm⁻¹): 3052 (w), 2959 (s), 2866 (w), 1576 (w), 1460 (w), 1413 (m), 1381 (w), 1359 (w), 1331 (s), 1282 (s), 1244 (m), 1216 (w), 1096 (w), 991 (w), 942 (w), 906 (w), 847 (s), 795 (w), 754 (m), 718 (w), 680 (w). UV-vis (THF): λ_{max} (ε) = 250 (2.3*10⁵), 311 (1.1*10⁵), 430 (3.9*10⁴) nm (M⁻¹cm⁻¹). M.p.: 235 °C. Characterization for **15b**: ¹H NMR (400 MHz, THF-d₈): δ 15.17 (s, ¹J_{CH} = 126.5 Hz, 1 H, CHSiMe₃), 6.75 (d, 2 H, H_{meta} of ArN), 6.69 (d, 2 H, H_{meta} of ArN), 6.49 (t, 1 H, H_{para} of ArN), 6.40 (t, 1 H, H_{para} of ArN), 4.13 (sept, 2 H, CHMe₂), 3.89 (sept, 2 H, CHMe₂), 3.24 (q, 8 H,

CH_2CH_3), 1.25 (br, 12 H, CH_2CH_3), 1.16 (d, 6H, CHMe_2), 1.15 (d, 6H, CHMe_2), 1.03 (d, 6 H, CHMe_2), 0.85 (d, 6 H, CHMe_2), 0.19 (s, 2 H, CH_2SiMe_3), 0.05 (s, 9 H, $=\text{CHSiMe}_3$), -0.08 (s, 9 H, CH_2SiMe_3) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, THF-d_8) δ 296.17 (CHSiMe_3), 159.50 (C_{ipso}), 159.39 (C_{ipso}), 141.68 (C_{ortho}), 140.49 (C_{ortho}), 121.28 (C_{para}), 121.17 (C_{para}), 119.14 (C_{meta}), 118.04 (C_{meta}), 52.76 (CH_2CH_3), 28.37 (CHMe_2), 27.85 (CHMe_2), 24.53 (CHMe_2), 24.30 (CHMe_2), 23.64 (CHMe_2), 23.19 (CHMe_2), 14.98 (CH_2SiMe_3), 7.33 (CH_2CH_3), 3.06 ($=\text{CHSiMe}_3$), 2.91 (CH_2SiMe_3) ppm.

2.4.7 Preparation of $(\text{Et}_4\text{N})[(\text{ArN})_2\text{Cr}(=\text{CHPh})(\text{CH}_2\text{Ph})]$ (**16b**)

$(\text{ArN})_2\text{Cr}(\text{CH}_2\text{Ph})_2$ (**5**) (0.168 g, 0.288 mmol) was dissolved in 50 mL THF, giving a green brown solution. 1 equiv. of $\text{KN}(\text{SiMe}_3)_2$ (0.058 g, 0.288 mmol) was added into the solution at room temperature. The solution was stirred for 45 minutes during which time the color changed to red. Then all volatile solvents were removed in vacuum. The residue was washed with pentane and filtered to give the product $\text{K}[(\text{ArN})_2\text{Cr}(=\text{CHPh})(\text{CH}_2\text{Ph})]$ (**16a**) as powder (0.144 g, 80 %). It was then dissolved in THF, giving a bright red solution. 1 equiv. of Et_4NCl (0.039 g, 0.232 mmol) was added to the red solution at room temperature. The solution was stirred for 4 hours during which time no color change was observed. The solvent was removed in vacuum and the residue was re-dissolved in a small amount of THF. KCl was removed by filtering the THF solution. Crystalline product was obtained from recrystallization by layering the THF solution with pentane (volume ratio = 1 : 2) at $-30\text{ }^\circ\text{C}$. Yield: 0.150 g, 73 %. ^1H NMR (400 MHz, THF-d_8): δ 13.92 (s, 1 H, CHPh), 7.38 (d, 2 H, Ar), 6.96 (t, 2 H, Ar), 6.86 (d, 2 H, Ar), 6.79 (d, 2 H, Ar), 6.76 (d, 2 H, Ar), 6.70 (t, 2 H, Ar), 6.53 (quintet, 3 H, Ar), 6.40 (t, 1 H, Ar), 4.03 (sept, 2 H, CHMe_2), 3.88 (sept,

2 H, CHMe_2), 3.08 (broad, 8 H, CH_2CH_3 of Et_4N), 2.80 (d, 1 H, CH_2Ph), 2.64 (d, 1 H, CH_2Ph), 1.15 (broad, 18 H, CH_2CH_3 of Et_4N and CHMe_2), 1.05 (d, 6 H, CHMe_2), 1.01 (d, 6 H, CHMe_2), 0.97 (d, 6 H, CHMe_2) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, THF-d_8) δ 291.74 (CHPh), 159.66 (Ar), 158.93 (Ar), 158.36 (Ar), 150.59 (Ar), 142.27 (Ar), 141.48 (Ar), 128.56 (Ar), 127.26 (Ar), 126.86 (Ar), 126.52 (Ar), 122.10 (Ar), 121.54 (Ar), 121.39 (Ar), 119.93 (Ar), 119.06 (Ar), 119.01 (Ar), 52.86 (CH_2CH_3 of Et_4N), 41.19 (CH_2Ph), 28.46 (CHMe_2), 28.11 (CHMe_2), 24.11 (CHMe_2), 24.03 (CHMe_2), 24.00 (CHMe_2), 23.80 (CHMe_2), 7.39 (CH_2CH_3 of Et_4N) ppm. Anal. Calcd. for $\text{C}_{46}\text{H}_{67}\text{CrN}_3$: C, 77.38; H, 9.46; N, 5.88. Found: C, 76.59; H, 9.37; N, 5.71. IR (KBr, cm^{-1}): 3045 (w), 2957 (m), 2865 (w), 1576 (w), 1483 (m), 1461 (w), 1413 (s), 1392 (w), 1355 (w), 1327 (s), 1279 (s), 1208 (w), 1171 (w), 1096 (w), 980 (w), 769 (w), 753 (m), 698 (w), 691 (w). UV-vis (THF): λ_{max} (ϵ) = 289 (1.0×10^5), 412.5 (3.9×10^4), 509.5 (2.1×10^4) nm ($\text{M}^{-1}\text{cm}^{-1}$). M.p.: 132 °C.

2.4.8 Preparation of $\text{Li}[(\text{ArN})_2\text{Cr}(=\text{CHCMe}_3)(\text{CH}_2\text{CMe}_3)]$ (17b)

$(\text{ArN})_2\text{Cr}(\text{CH}_2\text{CMe}_3)_2$ (**6**) (0.050 g, 0.091 mmol) was dissolved in 10 mL THF, giving a green solution. The solution was stirred at room temperature for 3 days, during which time the color changed from green to red. Then 1 equiv. of NpLi (0.18 mL, 0.5 M in pentane) was added to the THF solution. The solution was stirred at room temperature for 1 hour. All volatile solvents were removed in vacuum. The residue was washed with pentane and filtered to give the product (0.037 g, 73%). ^1H NMR (400 MHz, THF-d_8): δ 13.41 (s, 1 H, CHCMe_3), 6.72 (d, 2 H, H_{meta} of ArN), 6.63 (d, 2 H, H_{meta} of ArN), 6.43 (t, 1 H, H_{para} of ArN), 6.35 (t, 1 H, H_{para} of ArN), 4.29 (sept, 2 H, CHMe_2), 3.91 (sept, 2 H, CHMe_2), 1.83 (d, 1 H, CH_2CMe_3), 1.58 (d, 1 H, CH_2CMe_3), 1.22 (s, 9 H, CHCMe_3), 1.18 (d, 6H, CHMe_2), 1.12 (d, 6H, CHMe_2),

1.02 (d, 6 H, CHMe_2), 0.99 (s, 9 H, CH_2CMe_3), 0.84 (d, 6 H, CHMe_2) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, THF-d_8) δ 306.91 (CHCMe_3) 159.56 (C_{ipso}), 158.98 (C_{ipso}), 141.33 (C_{ortho}), 141.31 (C_{ortho}), 121.14 (C_{para}), 121.04 (C_{para}), 118.15 (C_{meta}), 117.33 (C_{meta}), 51.84 (CH_2CMe_3), 45.58 (CHCMe_3), 35.71 (CHCMe_3), 33.95 (CH_2CMe_3), 32.84 (CH_2CMe_3), 28.40 (CHMe_2), 27.81 (CHMe_2), 24.47 (CHMe_2), 24.19 (CHMe_2), 23.70 (CHMe_2), 23.28 (CHMe_2) ppm. IR (KBr, cm^{-1}): 2960 (s), 2868 (m), 1539 (s), 1461 (w), 1323 (w), 1264 (m), 1207 (m), 1174 (m), 1045 (m), 1014 (w), 987 (w), 830 (w), 753 (w), 513 (m). M.p.: 115 °C.

2.4.9 Preparation of $(\text{ArN})_2\text{Cr}(\text{CH}_2\text{CMe}_3)(\text{CH}_2\text{SiMe}_3)$ (18)

$(\text{ArN})_2\text{Cr}(\text{CH}_2\text{CMe}_3)_2$ (**6**) (0.123 g, 0.226 mmol) was dissolved in 20 mL SiMe_4 , giving a green solution. The solution was stirred for 3 days at room temperature during which time no color change was observed. SiMe_4 was then removed in vacuum and the residue was extracted with pentane and the extract was filtered through Celite. The filtrate was concentrated to 2 mL and then cooled to -30 °C overnight to yield green crystals. Yield: 0.051 g, 40%. ^1H NMR (400 MHz, C_6D_6): δ 6.90 (m, 6 H, ArN), 3.81 (sept, 4 H, CHMe_2), 2.59 (s, 2 H, CH_2CMe_3), 1.78 (s, 2 H, CH_2SiMe_3), 1.33 (s, 9 H, CH_2CMe_3), 1.14 (d, 12 H, CHMe_2), 1.12 (d, 12 H, CHMe_2), 0.36 (s, 9H, CH_2SiMe_3) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, C_6D_6): δ 157.87 (C_{ipso}), 145.50 (C_{ortho}), 127.63 (C_{para}), 123.10 (C_{meta}), 100.62 (CH_2CMe_3), 58.75 (CH_2SiMe_3), 35.73 (CH_2CMe_3), 32.92 (CH_2CMe_3), 28.60 (CHMe_2), 23.91 (CHMe_2), 23.85 (CHMe_2), 2.18 (CH_2SiMe_3) ppm. Anal. Calcd. for $\text{C}_{33}\text{H}_{56}\text{CrN}_2\text{Si}$: C, 70.66; H, 10.06; N, 4.99. Found: C, 71.34; H, 10.45; N, 4.96. MS(LIFDI) m/z : 560.3584 [M^+]. Calcd. m/z : 560.3618 [M^+]. IR (KBr, cm^{-1}): 3054 (w), 2956 (s), 2865 (m), 1460 (m), 1382 (w), 1358 (w), 1320 (w), 1273 (w), 1242 (m), 1231 (w), 1069 (m), 929 (w), 881

(w), 844 (m), 829 (m), 795 (w), 755 (m), 704 (w), 680 (w). UV-vis (pentane): λ_{max} (ϵ) = 252.5 (3.7×10^4), 284 (2.5×10^4), 434 (4.9×10^3), 616 (3.9×10^3) nm ($\text{M}^{-1}\text{cm}^{-1}$). M.p.: 133 °C.

2.4.10 Preparation of $\text{Cr}_3\text{C}_{72}\text{H}_{102}\text{N}_6$ (19)

$(\text{ArN})_2\text{Cr}(\text{CH}_2\text{CMe}_3)_2$ (**6**) (0.100 g, 0.184 mmol) was dissolved in 10 mL cyclohexane, giving a green solution. The solution was stirred for 3 days at room temperature during which time the color changed to red purple. Cyclohexane was then removed in vacuum and the residue was extracted with pentane. The extract was filtered through Celite. The filtrate was concentrated to 1 mL and then cooled to -30 °C overnight to yield red purple crystals. Yield: 0.056 g, 76 %. ^1H NMR (400 MHz, C_6D_6): δ 7.67 (broad, 2 H, NHAr), 7.13–6.77 (Ar), 3.23 (broad, 4 H, $\text{CH}(\text{CH}_2)\text{Me}$), 2.62 (sept, 4 H, CHMe_2), 2.32 (sept, 4 H, CHMe_2), 1.87 (broad, 2 H, $\text{CH}(\text{CH}_2)\text{Me}$), 1.65 (sept, 4 H, CHMe_2), 1.16 (d, 6 H, $\text{CH}(\text{CH}_2)(\text{CH}_3)$), 1.09 (d, 12 H, CHMe_2), 1.08 (d, 12 H, CHMe_2), 0.61 (d, 12 H, CHMe_2), 0.49 (d, 12 H, CHMe_2), 0.37 (d, 12 H, CHMe_2) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, C_6D_6): δ 169.62 (C_{ipso}), 165.10 (C_{ipso}), 152.90 (C_{ipso}), 138.53 (Ar), 137.32 (Ar), 137.07 (Ar), 134.81 (Ar), 126.07 (Ar), 125.84 (Ar), 124.89 (Ar), 124.22 (Ar), 123.92 (Ar), 123.55 (Ar), 122.11 (Ar), 40.61 ($\text{CH}(\text{CH}_2)\text{Me}$), 29.03 (CHMe_2), 28.35 (CHMe_2), 28.11 (CHMe_2), 27.69 (CHMe_2), 24.49 (CHMe_2), 24.38 (CHMe_2), 24.10 ($\text{CH}(\text{CH}_2)\text{Me}$), 23.94 (CHMe_2), 23.53 (CHMe_2), 22.43 (CHMe_2) ppm. MS(LIFDI) m/z : 1207.5747 [M^+]. Calcd. m/z : 1207.6407 [M^+]. IR (KBr, cm^{-1}): 3340 (w), 3055 (w), 2960 (s), 2927 (m), 2868 (m), 2795 (w), 1460 (m), 1427 (w), 1383 (w), 1361 (w), 1314 (w), 1244 (w), 1200 (w), 1111 (w), 1045 (w), 1006 (w), 930 (w), 886 (w), 858 (w), 798 (w), 750 (m), 658 (w). M.p.: 176 °C.

2.4.11 Preparation of (ArN)₂Cr(PPh₃)₂ (**20**)

Method A: (ArN)₂Cr(CH₂CMe₃)₂ (**6**) (0.100 g, 0.184 mmol) was dissolved in 10 mL cyclohexane, giving a green solution. 2 equivalents of PPh₃ (0.096 g, 0.368 mmol) were added into solution. The solution was stirred for 3 days at room temperature during which time the color changed to brown. Cyclohexane was then removed in vacuum and the residue was washed with pentane and filtered. The filter cake was dissolved in Et₂O and then concentrated to 1 mL. Yellow brown crystals were formed at room temperature in one day. Yield: 0.094 g, 55 %. Method B: (ArN)₂CrCl₂ (**3**) (0.200 g, 0.423 mmol) was dissolved in 20 mL THF, giving a red solution. 20 equivalents of magnesium chips (0.205 g, 8.439 mmol) and 2 equivalents of PPh₃ (0.222 g, 0.846 mmol) were added into solution. The solution was stirred for 2 days at room temperature during which time the color changed to brown. THF was then removed in vacuum and the residue was washed with pentane and filtered. The filter cake was dissolved in Et₂O and then concentrated to 1 mL. Yellow brown crystals were formed at room temperature in one day. This synthesis method is modified from a procedure for making (ArN)₂Cr(PMe₃)₂, which was reported by Gibson.⁴² ¹H NMR (400 MHz, C₆D₆): δ 7.48 (m, 12 H, H_{ortho} of PPh₃), 7.16 (H_{para} of PPh₃, overlap with C₆D₆, ppm), 6.87 (m, 18 H, H_{meta} of PPh₃ and H of ArN), 3.98 (br, 4 H, CHMe₂), 0.93 (d, 24 H, CHMe₂) ppm. ¹³C {¹H} NMR (150 MHz, C₆D₆): δ 160.49 (C_{ipso} of ArN), 144.66 (C_{ortho} of ArN), 137.39 (C_{ipso} of PPh₃), 134.60 (C_{ortho} of PPh₃), 129.32 (C_{meta} of PPh₃), 128.06 (C_{meta} of ArN and C_{para} of ArN, overlap with C₆D₆), 123.51 (C_{para} of PPh₃), 28.21 (CHMe₂), 24.70 (CHMe₂) ppm. ³¹P {¹H} NMR (162 MHz, C₆D₆): δ 102.87 ppm. Anal. Calcd. for C₆₀H₆₄CrN₂P₂: C, 77.73; H, 6.96; N, 3.02. Found: C, 77.72; H, 6.92; N, 2.97. IR (KBr, cm⁻¹): 3048 (w), 2960 (m), 2924 (w), 2865 (w), 1478 (w), 1458 (w), 1434 (s), 1416 (w), 1380 (w), 1319 (w), 1264 (s), 1086

(w), 975 (w), 796 (w), 747 (m), 695 (s), 527 (m), 517 (s), 507 (s). UV-vis (THF): λ_{max} (ϵ) = 258 (6.6×10^4), 421 (1.1×10^4) nm ($\text{M}^{-1}\text{cm}^{-1}$). M.p.: 175 °C.

2.4.12 Preparation of $(\text{ArN})_2\text{Cr}(\text{C}_{10}\text{H}_{18})$ (21)

$(\text{ArN})_2\text{Cr}(\text{CH}_2\text{CMe}_3)_2$ (6) (0.132 g, 0.242 mmol) was dissolved in 20 mL cyclopentene, giving a green solution. The solution was stirred for 3 days at room temperature during which time the color changed to red. Cyclopentene was then removed in vacuum and the residue was extracted with pentane and the extract was filtered through Celite. The filtrate was concentrated to 2 mL then cooled to -30 °C overnight to yield red crystals. Yield: 0.84 g, 64%. ^1H NMR (400 MHz, C_6D_6): δ 6.98 (m, 6 H, Ar), 6.98 (m, 1 H, α -CH of cyclobutane), 5.81 (d, 1 H, CHCMe_3), 4.08 (sept, 2 H, CHMe_2), 4.02 (sept, 2 H, CHMe_2), 2.83 (m, 1 H, β -CH₂), 2.50 (m, 1 H, β -CH₂), 1.88 (m, 2 H, CH₂, CH₂), 1.58 (m, 1 H, CH₂), 1.47 (m, 1 H, CH₂), 1.33 (d, 12 H, CHMe_2), 1.17 (d, 6 H, CHMe_2), 1.16 (s, 9H, CMe_3), 1.09 (d, 6 H, CHMe_2), 0.72 (m, 1 H, β -CH) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, C_6D_6): δ 157.33 (C_{ipso}), 157.21 (C_{ipso}), 148.09 (CHCMe_3), 144.55 (C_{ortho}), 144.44 (C_{ortho}), 143.81 (α -C of cyclobutane, not CHCMe_3), 125.86 (C_{para}), 125.71 (C_{para}), 122.66 (C_{meta}), 122.46 (C_{meta}), 39.77 (CH₂), 39.00 (CMe_3), 37.13 (CH₂), 31.59 (CMe_3), 28.79 (CHMe_2), 28.57 (CHMe_2 overlapped with CH₂), 24.11 (CHMe_2), 23.91 (CHMe_2), 23.47 (CHMe_2), 23.33 (CHMe_2), 21.91 (β -CH) ppm. Anal. Calcd. for $\text{C}_{34}\text{H}_{52}\text{CrN}_2$: C, 75.51; H, 9.69; N, 5.18. Found: C, 75.33; H, 9.59; N, 5.13. MS(LIFDI) m/z : 540.3514 [M^+]. Calcd. m/z : 540.3536 [M^+]. IR (KBr, cm^{-1}): 3051 (w), 2960 (s), 2865 (m), 1459 (w), 1418 (w), 1380 (w), 1358 (w), 1325 (m), 1280 (m), 1261 (w), 1098 (w), 1051 (w), 796 (w), 752 (m). UV-vis (pentane): λ_{max} (ϵ) = 253 (8.4×10^4), 306.5 (4.8×10^4), 486 (1.1×10^4) nm ($\text{M}^{-1}\text{cm}^{-1}$). M.p.: 133 °C.

2.4.13 Preparation of (ArN)₂Cr(C₁₂H₂₀)

(ArN)₂Cr(CH₂CMe₃)₂ (**6**) (0.050 g, 0.092 mmol) was mixed with 2 g norbornene in a sealed ampule. The ampule was heated at 60 °C for one day. Color change was observed from green to reddish brown. Then the crude product was dissolved in toluene to give a red solution. This solution was used to prepare LIFDI sample. MS(LIFDI) m/z: 566.3719 [M⁺]. Calcd. m/z: 566.3692 [M⁺].

2.4.14 Preparation of (ArN)₂Cr(C₁₁H₂₂)

(ArN)₂Cr(CH₂CMe₃)₂ (**6**) (0.143 g, 0.263 mmol) was dissolved in 5 mL *tert*-butylethylene, giving a green solution. The solution was stirred at room temperature for 3 days, during which time the color changed to red. Extra *tert*-butylethylene was removed in vacuum and the residue was extracted with pentane. The pentane solution was filtered through Celite and concentrated. NMR sample and LIFDI sample were both prepared from this crude product. Two characteristic peaks of the corresponding isomeric chromacyclobutanes, which was a result of two ways of cycloaddition, were found in the ¹H NMR (400 MHz, C₆D₆) spectrum: δ 6.04 (t, 2 H, β-H of metallacyclobutane), 5.79 (t, 2 H, β-H of metallacyclobutane) ppm. MS(LIFDI) m/z: 556.3823 [M⁺]. Calcd. m/z: 556.3849 [M⁺].

2.4.15 Preparation of (ArN)₂Cr(CH₂CMe₃)(NH^tBu) (**22**)

(ArN)₂Cr(CH₂CMe₃)₂ (**6**) (0.120 g, 0.220 mmol) was dissolved in 10 mL ^tBuNH₂, giving a green solution. The solution was stirred at room temperature for 3 days, during which time the color changed to red. Extra ^tBuNH₂ was removed in vacuum and the residue was extracted with pentane. The pentane solution was filtered through Celite. The filtrate was concentrated to 2 mL then cooled to -30 °C overnight to yield red crystals. Yield: 0.112 g, 93%. ¹H NMR (400 MHz, C₆D₆): δ 10.24 (s, 1 H,

NH^tBu), 6.95 (m, 6 H, ArN), 3.88 (m, 4 H, CHMe_2), 2.96 (d, 1 H, CH_2CMe_3), 2.82 (d, 1 H, CH_2CMe_3), 1.36 (s, 9 H, ^tBu), 1.34 (s, 9 H, ^tBu), 1.28 (d, 6 H, CHMe_2), 1.23 (d, 6 H, CHMe_2), 1.14 (d, 6 H, CHMe_2), 1.06 (d, 6 H, CHMe_2) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, C_6D_6): δ 158.44 (C_{ipso}), 158.29 (C_{ipso}), 144.60 (C_{ortho}), 143.82 (C_{ortho}), 126.85 (C_{para}), 126.26 (C_{para}), 122.83 (C_{meta} , 2 peaks merge together, confirmed by HSQC), 72.03 (CH_2CMe_3), 61.17 (CMe_3 of NH^tBu), 34.08 (^tBu), 33.52 (CH_2CMe_3), 33.26 (^tBu), 28.83 (CHMe_2), 28.58 (CHMe_2), 24.53 (CHMe_2), 23.52 (CHMe_2), 23.44 (CHMe_2), 23.40 (CHMe_2) ppm. Anal. Calcd. for $\text{C}_{33}\text{H}_{55}\text{CrN}_3$: C, 72.62; H, 10.16; N, 7.70. Found: C, 72.93; H, 10.43; N, 7.63. MS(LIFDI) m/z : 545.3776 [M^+]. Calcd. m/z : 545.3801 [M^+]. IR (KBr, cm^{-1}): 3287 (w), 3053 (w), 2956 (s), 2866 (m), 1459 (w), 1420 (w), 1301 (w), 1359 (w), 1322 (w), 1279 (m), 1234 (w), 1205 (m), 1100 (w), 1078 (w), 1058 (w), 1021 (w), 988 (w), 961 (w), 932 (w), 796 (w), 787 (w), 759 (w), 752 (m). UV-vis (pentane): λ_{max} (ϵ) = 245.5 (1.2×10^5), 294.5 (7.9×10^4), 338 (6.1×10^4), 388.5 (3.7×10^4) nm ($\text{M}^{-1}\text{cm}^{-1}$). M.p.: 130 °C (dec, red to black).

2.4.16 Kinetic study of α -hydrogen abstraction of $(\text{ArN})_2\text{Cr}(\text{CH}_2\text{SiMe}_3)_2$ (**7**)

No PPh_3 . 0.010 g $(\text{ArN})_2\text{Cr}(\text{CH}_2\text{SiMe}_3)_2$ (**7**) was added into a J-Young tube and then about 0.5 mL d_8 -THF was transferred into the tube. The NMR tube was heated at 80 °C in an oil bath. According to the integration of the alkylidene peak and the peak of CH_2SiMe_3 in the ^1H NMR spectrum, the percentage of **7** (i.e. 100 % in the beginning of the reaction, 0 % when **7** is out) can be calculated. This percentage is proportional to the concentration of **7** in d_8 -THF. Based on the plot in Figure 2.10, the rate constant of α -hydrogen abstraction of **7** is $3.14(9) \times 10^{-5} \text{ s}^{-1}$ at 80 °C.

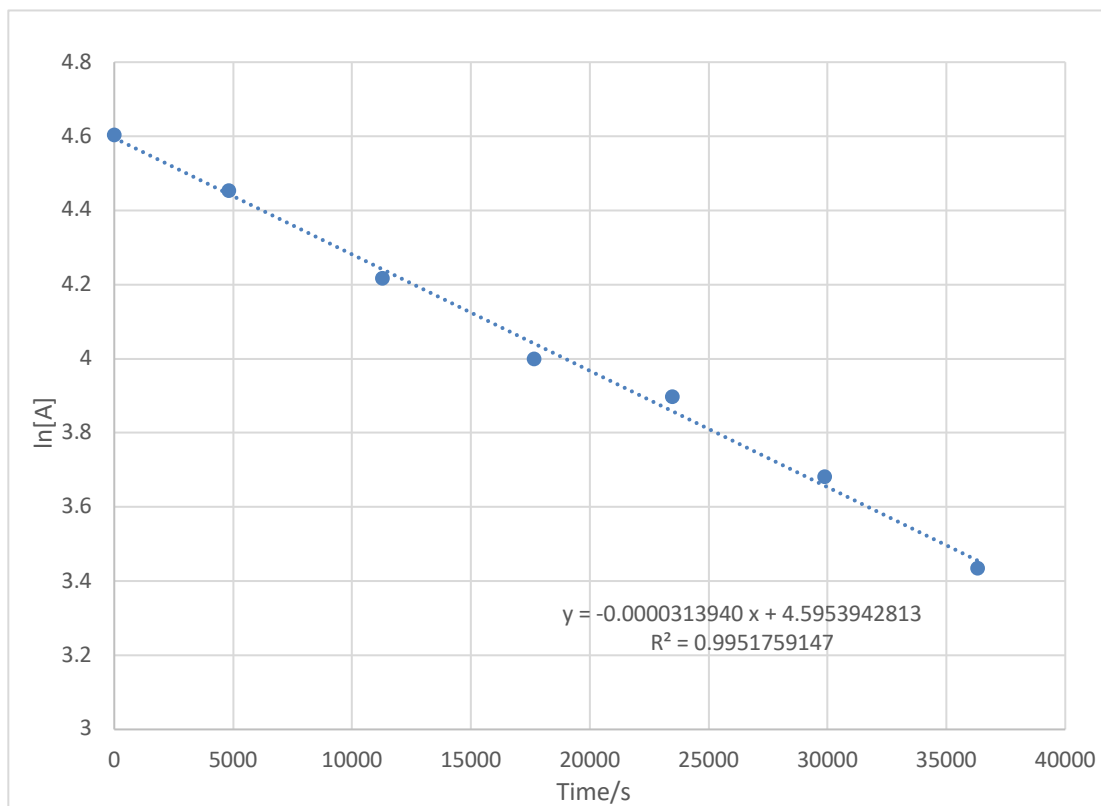


Figure 2.10 The plot of $\ln[A]$ versus time (s). $[A]$ = % of $(\text{ArN})_2\text{Cr}(\text{CH}_2\text{SiMe}_3)_2$

1 equiv. of PPh₃. (ArN)₂Cr(CH₂SiMe₃)₂ (**7**) (0.010 g) and PPh₃ (0.005 g) were added into a J-Young tube and then about 0.5 mL d₈-THF was transferred into the tube. The same procedure in the previous experiment was followed. Based on the plot in Figure 2.11, the rate constant of α -hydrogen abstraction of **7** in the presence of one equivalent of PPh₃ is $3.32(8) \times 10^{-5} \text{ s}^{-1}$ at 80 °C.

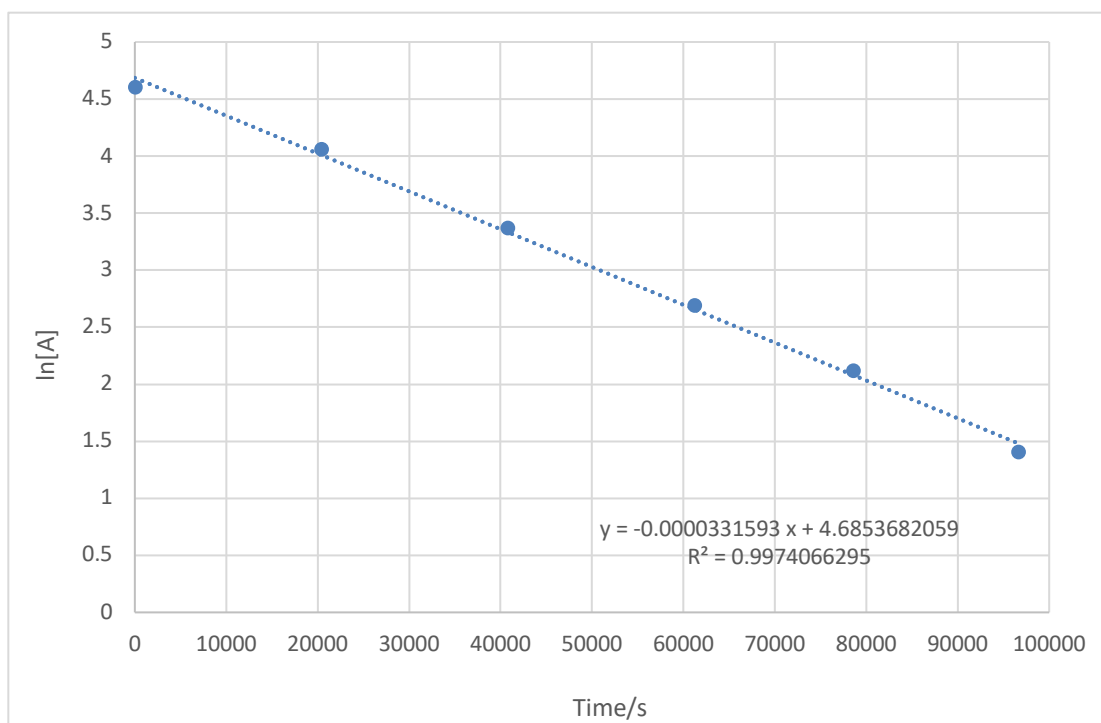


Figure 2.11 The plot of $\ln[A]$ versus time (s). $[A]$ = % of (ArN)₂Cr(CH₂SiMe₃)₂

10 equiv. of PPh₃. (ArN)₂Cr(CH₂SiMe₃)₂ (**7**) (0.010 g) and PPh₃ (0.049 g) were added into a J-Young tube and then about 0.5 mL d₈-THF was transferred into the tube. The same procedure in the previous experiment was followed. Based on the

plot in Figure 2.12, the rate constant of α -hydrogen abstraction of **7** in the presence of ten equivalents of PPh_3 is $3.47(6) \times 10^{-5} \text{ s}^{-1}$ at 80°C .

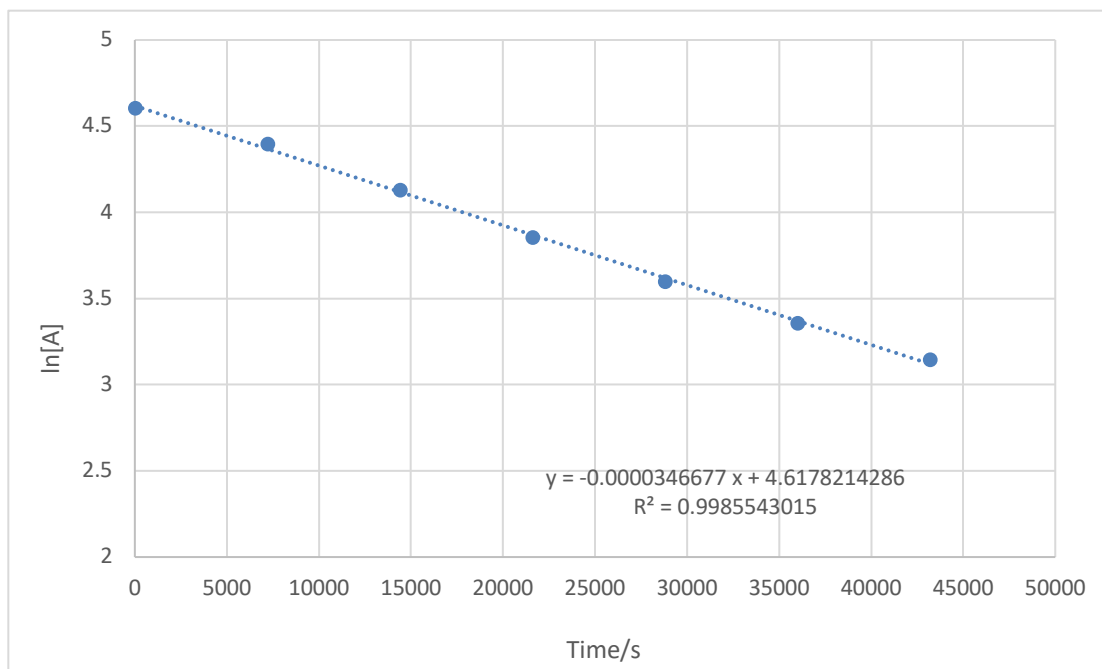


Figure 2.12 The plot of $\ln[A]$ versus time (s). $[A] = \%$ of $(\text{ArN})_2\text{Cr}(\text{CH}_2\text{SiMe}_3)_2$

Table 2.7 Crystallographic data for complexes **13**, **14b**, **15b** and **19** to **21**

	13 (kla0756)	14b (kla0941)	15b (kla0813)
Formula	C ₅₂ H ₇₁ CrN ₂ P	C ₄₆ H ₅₉ CrN ₂ PSi	C ₄₀ H ₇₅ CrN ₃ Si ₂
Formula Wt.	807.07	751.01	706.21
Space group	<i>P</i> 2 ₁ 2 ₁ 2 ₁	<i>P</i> <i>ca</i> 2 ₁	<i>P</i> $\bar{4}$ ₂ 1 <i>c</i>
Color	orange	orange	red
a, Å	12.4593(4)	17.0985(11)	21.9368(13)
b, Å	12.8057(4)	13.5512(9)	21.9368(13)
c, Å	30.8680(10)	21.4178(14)	19.1573(11)
α, deg	90	90	90
β, deg	90	90	90
γ, deg	90	90	90
V, Å ³	4925.0(3)	4962.6(6)	9218.9(12)
Z	4	4	8
D(calcd), g/cm ³	1.088	1.005	1.018
μ, mm ⁻¹	0.298	0.315	0.327
Temp, K	200	200	200
T _{max} /T _{min}	0.7456/0.6605	0.7456/0.6853	0.7456/0.6758
No. data/params	11229/475	11366/475	10454/448
GOF on F ²	0.969	1.035	1.027
R1(F), % ^a	6.42	4.24	6.49
wR ² (F ²), % ^a	11.81	10.53	15.65

^a Quantity minimized: $wR^2(F^2) = \sum[w(F_o^2 - F_c^2)^2] / \sum[(wF_o^2)^2]^{1/2}$; $R1 = \sum \Delta / \sum (F_o)$, $\Delta = |(F_o - F_c)|$.

Table 2.7 Crystallographic data for complexes **13**, **14b**, **15b** and **19** to **21**
(continued)

	19 (kla0956)	20 (kla0958)	21 (kla0951)
Formula	C ₇₂ H ₁₀₂ Cr ₃ N ₆	C ₆₀ H ₆₄ CrN ₂ P ₂	C ₃₄ H ₅₂ CrN ₂
Formula Wt.	1207.59	927.07	540.77
Space group	<i>R</i> $\bar{3}c$	<i>P</i> <i>bcn</i>	<i>P</i> $\bar{1}$
Color	brown	brown	red
a, Å	26.3427(6)	13.9462(5)	9.9722(3)
b, Å	26.3427(6)	17.9775(6)	11.1746(3)
c, Å	71.6398(17)	20.6293(7)	17.0474(4)
α, deg	90	90	72.2270(10)
β, deg	90	90	74.053(2)
γ, deg	120	90	65.5810(10)
V, Å ³	43053(2)	5172.1(3)	1622.84(8)
Z	18	4	2
D(calcd), g/cm ³	0.838	1.191	1.107
μ, mm ⁻¹	2.988	2.695	3.049
Temp, K	200	200	200
T _{max} /T _{min}	0.7539/0.6068	0.7539/0.5552	0.7539/0.5623
No. data/params	9830/381	5323/298	6448/388
GOF on F ²	1.056	1.044	1.208
R1(F), % ^a	6.47	3.30	7.14
wR ² (F ²), % ^a	19.32	8.95	16.84

^a Quantity minimized: $wR^2(F^2) = \sum[w(F_o^2 - F_c^2)^2] / \sum[(wF_o^2)^2]^{1/2}$; $R1 = \sum \Delta / \sum (F_o)$, $\Delta = |F_o - F_c|$.

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Chapter 3

SYNTHESIS AND REACTIVITY OF TRIS(IMIDO) CHROMIUM(VI) COMPLEXES

3.1 Introduction

Since Nugent introduced imido ligands to chromium(VI) to make the first bis(imido) chromium complex, namely $(^t\text{BuN})_2\text{Cr}(\text{OSiMe}_3)_2$, in 1980 and Wilkinson reported the first tetrakis(imido) chromium complex, namely $\text{Li}_2\text{Cr}(\text{N}^t\text{Bu})_4$, in 1990, people have been interested in making tris(imido) chromium(VI) complexes.¹⁻³ Both Wilkinson and Gibson were involved in the exploration of this chemistry.⁴ However, complexes with the $\text{Cr}(\text{NR})_3$ fragment are still extremely rare.

$[\text{Li}(\text{Et}_2\text{O})_2][(\text{mesN})_3\text{Cr}(\text{NHmes})]$ remains the unique example before the work presented in this dissertation.⁵ Surprisingly, the heavier elements in group 6, molybdenum and tungsten, have abundant tris(imido) chemistry contributed by Wigley and co-workers.⁶⁻⁷

3.1.1 Attempted Synthesis of a Molecule Featuring the $\text{Cr}(\text{NR})_3$ Fragment

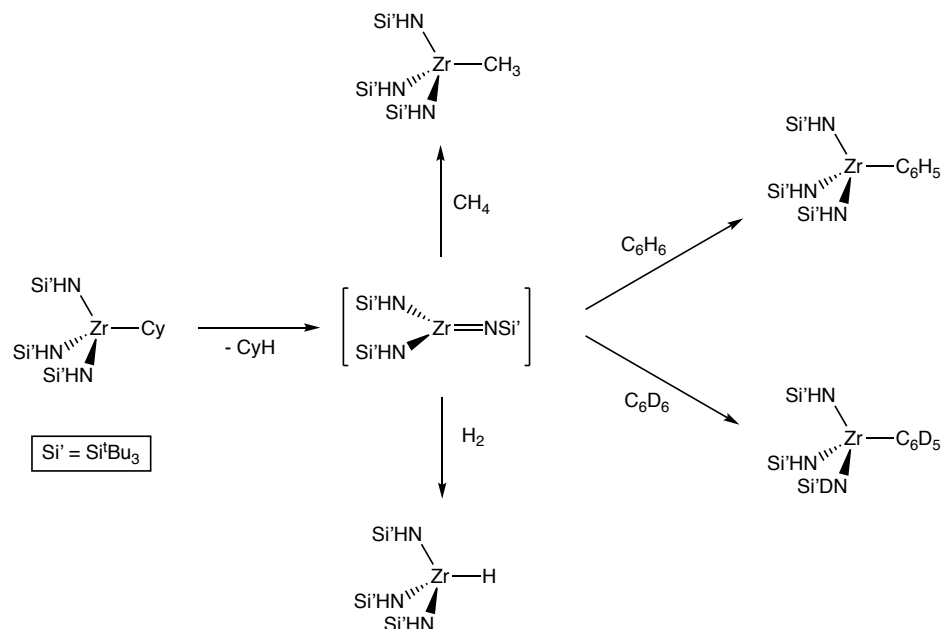
Wilkinson and co-workers described attempts of preparing complexes that contain the $\text{Cr}(\text{N}^t\text{Bu})_3$ moiety from $(^t\text{BuN})_2\text{Cr}(\text{NH}^t\text{Bu})_2$, $(^t\text{BuN})_2\text{Cr}(\text{NH}^t\text{Bu})\text{Cl}$, and $(^t\text{BuN})_2\text{Cr}[\text{N}(\text{SiMe}_3)^t\text{Bu}]\text{Cl}$, but none of these complexes are viable precursors to $\text{Cr}(\text{N}^t\text{Bu})_3$. For example, inducing HCl elimination from $(^t\text{BuN})_2\text{Cr}(\text{NH}^t\text{Bu})\text{Cl}$ in the presence of base gave intractable products.²

Although preparation of complexes containing the $\text{Cr}(\text{N}^t\text{Bu})_3$ moiety was not successful, the first example that contains the $\text{Cr}(\text{NR})_3$ fragment, namely $[\text{Li}(\text{Et}_2\text{O})_2][(\text{mesN})_3\text{Cr}(\text{NHmes})]$, was generated from the interaction of the arylimido complex $(\text{mesN})_2\text{CrCl}_2$ ($\text{mes} = 2,4,6\text{-trimethylphenyl}$, aka mesityl) with mesNHLi .⁵

Gibson and co-workers also attempted to synthesize $\text{Cr}(\text{NR})_3$ derivatives by using $(\text{ArN})_2\text{Cr}(\text{NH}^t\text{Bu})\text{Cl}$ ($\text{Ar} = 2,6\text{-diisopropylphenyl}$) as a starting material. Heating a sample in the presence of NEt_3 at 60°C did not help elimination of HCl . Their attempts at deprotonating $(\text{ArN})_2\text{Cr}(\text{NH}^t\text{Bu})\text{Cl}$ with $^t\text{BuLi}$ to make a mixed tris(imido) chromium complex were also unsuccessful.⁴

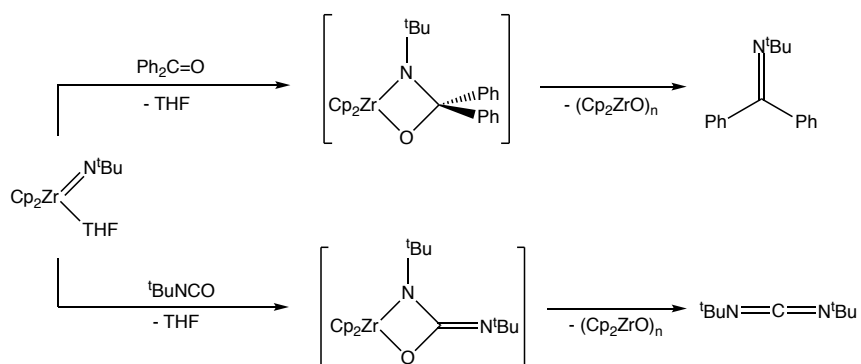
3.1.2 Reactions Involving Imido Ligand

Traditionally, imido ligands are considered as ancillary ligands to support high oxidation state metal centers.⁸⁻¹⁰ However, recently transition metal imido complexes have attracted attention due to their reactive $\text{L}_n\text{M}=\text{NR}$ ligands that can activate C-H bonds or engage in imido metathesis chemistry followed by cycloaddition. Wolczanski and co-workers reported methane and benzene activation via transient $[(^t\text{Bu}_3\text{SiNH})_2\text{Zr}(=\text{NSi}^t\text{Bu})]$, as illustrated in Scheme 3.1. Heating $(^t\text{Bu}_3\text{SiNH})_3\text{Zr}(\text{Cy})$ caused elimination of cyclohexane through $\alpha\text{-H}$ abstraction and gave a coordinatively unsaturated zirconium imido intermediate, which could activate the C-H bonds of methane and benzene. Hydrogenation of this intermediate with hydrogen gas generated a terminal hydride complex.¹¹



Scheme 3.1 Methane and benzene activation via transient $[(^t\text{Bu}_3\text{SiNH})_2\text{Zr}(=\text{NSi}^t\text{Bu})]$

Bergman and co-workers found that imido bonds could be involved in metathesis with benzophenone and isocyanate followed by cycloaddition (Scheme 3.2).¹²



Scheme 3.2 Imido metathesis initiated by $\text{Cp}_2\text{Zr}(\text{N}^t\text{Bu})(\text{THF})$

Considering the rarity of tris(imido) chromium and the interesting reactivity of imido complexes, I was attracted by this project in 2016. This chapter describes the synthesis and characterization of five tris(imido) chromium(VI) complexes featuring $\text{Cr}(=\text{N}^t\text{Bu})_3$ as well as their reactivity studies, like nucleophilic substitution, 1,2-insertion to $\text{Cr}=\text{N}$, and cycloaddition with small molecules to generate metallacycles.

3.2 Results and Discussion

A precursor to tris(imido) chromium, namely $(^t\text{BuN})_2\text{Cr}(\text{NH}^t\text{Bu})\text{Cl}$ (**23**), was reported by Wilkinson before. In this reported procedure, $^t\text{BuNHSiMe}_3$ was employed as an amido source to react with $(^t\text{BuN})_2\text{CrCl}_2$ (**2**), yielding **23** after 12-hour reflux.² I used a new procedure that involved transmetalation of **2** with 1 equivalent of $^t\text{BuNHLi}$. Compared to Wilkinson's procedure, my synthesis method does not need reflux and saves time. Full characterization of **23** can be found in Wilkinson's paper. When treating **2** with 1.1 equivalent of $^t\text{BuNHLi}$, a minor product with dark red color was formed, namely $(^t\text{BuN})\text{CrCl}(\mu\text{-}^t\text{BuN})_2\text{Cr}(\text{N}^t\text{Bu})_2\text{Cl}$. Its ^1H NMR spectrum clearly shows three singlet peaks with 1:2:2 of integration ratio in diamagnetic region. The structure of this minor product was determined by X-ray diffraction. (Structure in **Appendix C**)

3.2.1 Approaching $\text{Cr}(\text{N}^t\text{Bu})_3$ by Deprotonation with $\text{KN}(\text{SiMe}_3)_2$

In **Chapter 2**, $\text{KN}(\text{SiMe}_3)_2$ ($\text{pK}_a = 26$ in THF) was employed to deprotonate a chromium dialkyl to generate an alkylidene anion. **23** was deprotonated by $\text{KN}(\text{SiMe}_3)_2$, too. The corresponding product $\text{K}[(^t\text{BuN})_3\text{CrCl}]$ (**24a**) features the $\text{Cr}(\text{N}^t\text{Bu})_3$ moiety. Three *tert*-butylimido groups are magnetically equivalent in solution because only one singlet peak was observed in the ^1H NMR spectrum. The

success of preparing **24a** opened the gate to study tris(imido) chromium(VI) complexes. After the third imido ligand is introduced to the chromium center, imido ligands become reactive. This enhanced reactivity of imido may be attributed to ‘ π -loading’, which was addressed by Wigley.¹³ Multiple coordination of strongly π -bonding ligand such as RN^{2-} will increase competition for metal $d_{\pi}\text{-N}_{\text{imido}} p_{\pi}$ bonding, which will cause weakened π bonding. Since many reactions involving imido ligands proceed through cleavage of the $\pi_{\text{M-N}}$ bond, it is reasonable to expect that π -loaded tris(imido) complexes may have greater potential reactivity compared to mono(imido) or bis(imido) analogues.¹⁴

The bonding description of $(^t\text{BuN})_3\text{CrL}$ ($\text{L} = \sigma$ donor only, like PPh_3 , Cl^- , CH_2SiMe_3) in C_{3v} symmetry is depicted in Figure 3.1 by considering the symmetries of the ligand and metal orbitals of such a complex: ligand σ ($2a_1 + e$), ligand π ($a_1 + 2e + a_2$), metal $s + p$ ($2a_1 + e$), metal d ($a_1 + 2e$).¹⁵ Under 3-fold symmetry, one combination of the imido nitrogen p_{π} orbitals has a_2 symmetry. However, there is no corresponding metal orbital that can match this symmetry. Therefore, two electrons are consigned to occupy a ligand-based, nonbonding a_2 molecular orbital comprised of $\text{N}(2p)$ orbitals lying perpendicular to the C_3 axis in the orbital interaction diagram for $(^t\text{BuN})_3\text{CrL}$. Thus, the imido nitrogen of a π -loaded complex like **24a** is subject to be attacked by an electrophile (e.g. MeI).

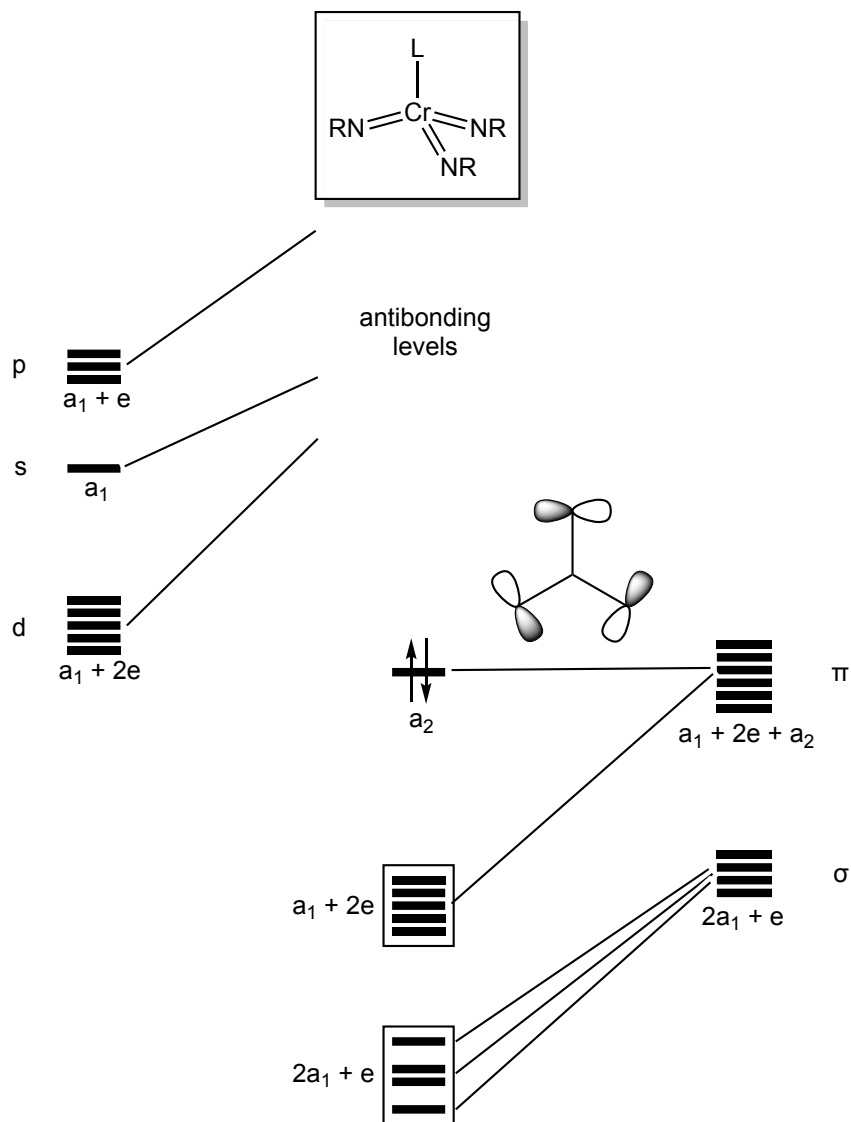
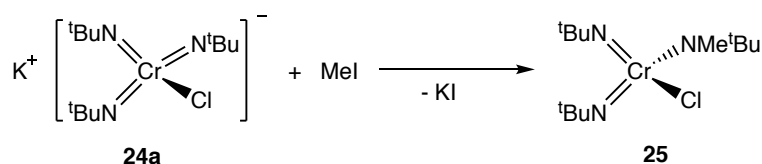


Figure 3.1 Orbital interaction diagram for C_{3v} , d^0 tris(imido) chromium complex $(^t\text{BuN})_3\text{CrL}$ and an illustration of the nonbonding a_2 molecular orbital

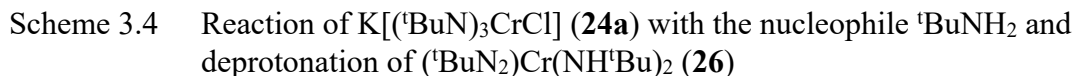
24a reacts with the electrophile MeI to generate $(^t\text{BuN})_2\text{Cr}(\text{NMe}^t\text{Bu})\text{Cl}$ (**25**). (Scheme 3.3) The electron-rich nitrogen is subject to attack by MeI and then iodide falls off to associate with potassium cation to precipitate out. **25** is too soluble in

organic solvents to be characterized with crystallography. NMR spectra and LIFDI-MS are both consistent with the structure of **25**.



Scheme 3.3 Reaction of $K[(tBuN)_3CrCl]$ (**24a**) with electrophile MeI

Due to the high oxidation state of chromium, the chromium center of **24a** is subject to be attacked by nucleophiles. **24a** reacts with $tBuNH_2$ to yield $(tBuN)_2Cr(NH^tBu)_2$ (**26**). **26** was reported by Wilkinson before through a route of **2** with two equivalents of $tBuNHLi$. The reported procedure gave a 40% yield of **26**, probably due to the formation of side product $(tBuN)CrCl(\mu-tBuN)_2Cr(N^tBu)_2Cl$. The two amido ligands can both be deprotonated by the strong base $nBuLi$ to form the known tetrakis(imido) chromium complex $Li_2Cr(N^tBu)_4$.² To generate tris(imido) chromium, only one amido hydrogen needs to be deprotonated. The same mild base $KN(SiMe_3)_2$ was employed to achieve this goal, as illustrated in Scheme 3.4. The



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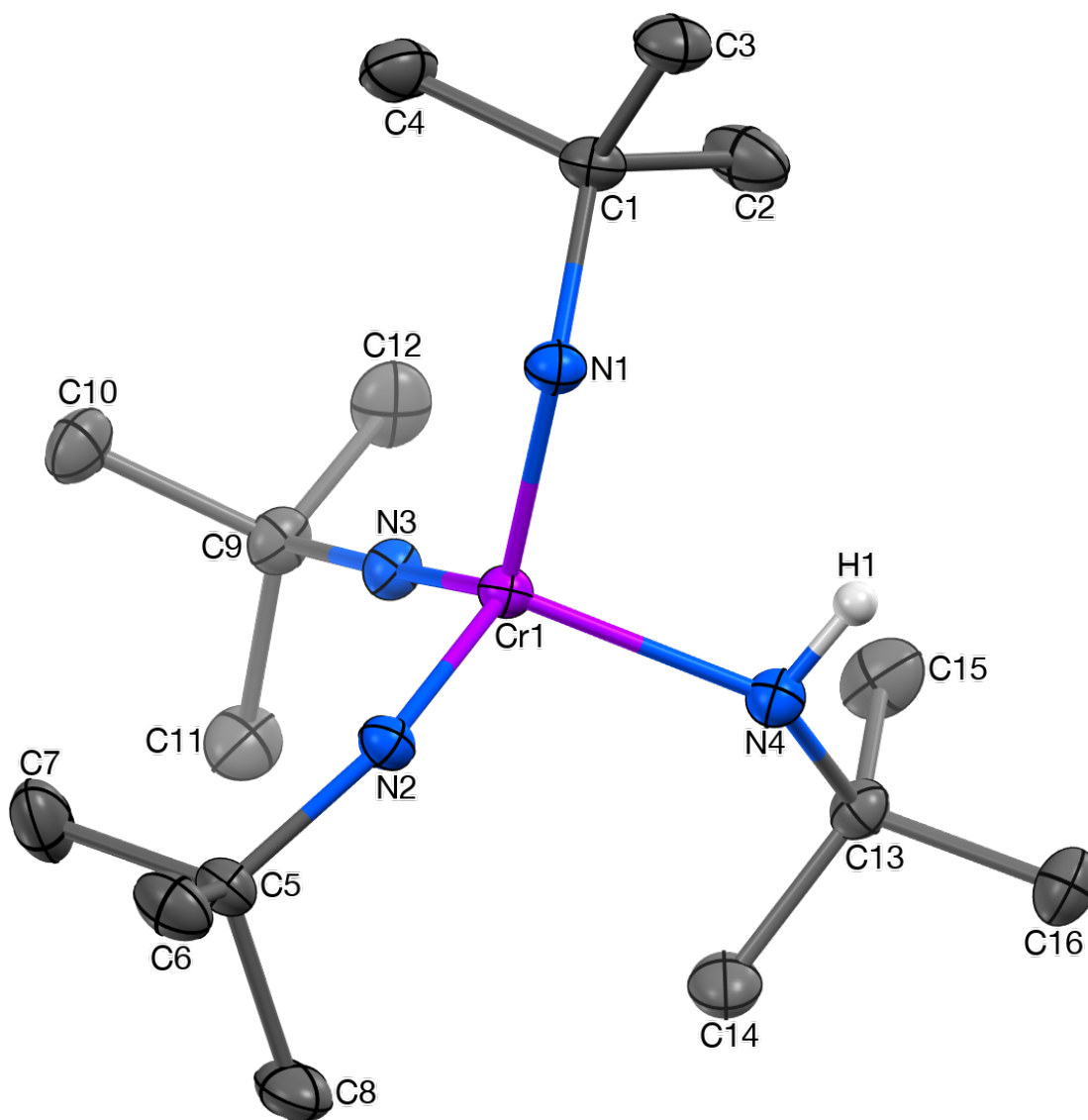


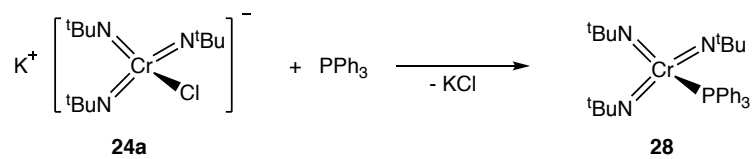
Figure 3.2 Molecular structure of K[(^tBuN)₃Cr(NH⁺tBu)] (**27**). Ellipsoids are drawn at the 30% probability level. The potassium cation and hydrogen atoms excluding the amido hydrogen have been omitted for clarity.

Table 3.1 Interatomic distances (Å) and angles (°) for K[(^tBuN)₃Cr(NH^tBu)] (**27**)

Distances (Å)			
Cr(1)-N(3)	1.6500(11)	C(5)-C(7)	1.523(2)
Cr(1)-N(2)	1.7236(11)	C(5)-C(8)	1.534(2)
Cr(1)-N(1)	1.7384(11)	C(5)-C(6)	1.537(2)
Cr(1)-N(4)	1.9656(12)	C(9)-N(3)	1.4525(17)
K(1)-N(1)	2.7573(12)	C(9)-C(12)	1.535(2)
K(1)-N(4)	2.7827(12)	C(9)-C(11)	1.535(2)
K(1)-N(2)	2.8358(11)	C(9)-C(10)	1.535(2)
C(1)-N(1)	1.4619(17)	C(13)-N(4)	1.4734(17)
C(1)-C(4)	1.528(2)	C(13)-C(14)	1.525(2)
C(1)-C(3)	1.534(2)	C(13)-C(15)	1.530(2)
C(1)-C(2)	1.535(2)	C(13)-C(16)	1.535(2)
C(5)-N(2)	1.4590(17)		
Angles (°)			
N(3)-Cr(1)-N(2)	114.83(6)	C(4)-C(1)-C(2)	109.86(14)
N(3)-Cr(1)-N(1)	114.34(6)	C(3)-C(1)-C(2)	108.76(13)
N(2)-Cr(1)-N(1)	107.62(5)	C(1)-C(4)-K(1)	170.61(12)
N(3)-Cr(1)-N(4)	111.68(5)	N(2)-C(5)-C(7)	111.35(12)
N(2)-Cr(1)-N(4)	106.50(5)	N(2)-C(5)-C(8)	110.09(12)
N(1)-Cr(1)-N(4)	100.69(5)	C(7)-C(5)-C(8)	109.35(14)
N(3)-Cr(1)-K(1)	145.70(4)	N(2)-C(5)-C(6)	108.28(12)
N(2)-Cr(1)-K(1)	57.17(4)	C(7)-C(5)-C(6)	108.90(14)
N(1)-Cr(1)-K(1)	99.23(4)	C(8)-C(5)-C(6)	108.81(13)
N(4)-Cr(1)-K(1)	52.10(4)	N(3)-C(9)-C(12)	110.67(12)
N(1)-K(1)-N(4)	161.48(4)	N(3)-C(9)-C(11)	109.26(12)
N(1)-K(1)-N(2)	59.92(3)	C(12)-C(9)-C(11)	109.62(14)
N(4)-K(1)-N(2)	109.84(4)	N(3)-C(9)-C(10)	108.78(12)
N(1)-K(1)-N(2)	102.98(3)	C(12)-C(9)-C(10)	109.17(13)
N(4)-K(1)-N(2)	61.93(3)	C(11)-C(9)-C(10)	109.31(13)
N(2)-K(1)-N(2)	99.90(3)	N(4)-C(13)-C(14)	109.08(12)
N(1)-K(1)-C(4)	87.74(4)	N(4)-C(13)-C(15)	111.84(12)

N(4)-K(1)-C(4)	108.31(4)	C(14)-C(13)-C(15)	109.68(14)
N(2)-K(1)-C(4)	89.16(4)	N(4)-C(13)-C(16)	108.35(12)
N(2)-K(1)-C(4)	168.44(4)	C(14)-C(13)-C(16)	109.21(13)
N(1)-K(1)-Cr(1)	128.92(3)	C(15)-C(13)-C(16)	108.63(13)
N(4)-K(1)-Cr(1)	33.87(2)	C(1)-N(1)-Cr(1)	135.23(9)
N(2)-K(1)-Cr(1)	100.54(2)	C(1)-N(1)-K(1)	126.55(8)
N(2)-K(1)-Cr(1)	29.28(2)	Cr(1)-N(1)-K(1)	96.90(5)
C(4)-K(1)-Cr(1)	141.99(3)	C(5)-N(2)-Cr(1)	142.78(10)
N(1)-K(1)-K(1)	78.31(3)	C(5)-N(2)-K(1)	117.03(8)
N(4)-K(1)-K(1)	83.37(3)	Cr(1)-N(2)-K(1)	94.48(4)
N(2)-K(1)-K(1)	51.43(2)	C(5)-N(2)-K(1)	110.15(8)
N(2)-K(1)-K(1)	48.47(2)	Cr(1)-N(2)-K(1)	93.55(5)
C(4)-K(1)-K(1)	140.03(3)	K(1)-N(2)-K(1)	80.10(3)
Cr(1)-K(1)-K(1)	56.410(9)	C(9)-N(3)-Cr(1)	175.17(10)
N(1)-C(1)-C(4)	109.41(12)	C(13)-N(4)-Cr(1)	128.46(9)
N(1)-C(1)-C(3)	108.66(12)	C(13)-N(4)-K(1)	113.81(8)
C(4)-C(1)-C(3)	108.89(12)	Cr(1)-N(4)-K(1)	94.03(4)
N(1)-C(1)-C(2)	111.21(12)		

24a also reacts with the nucleophile PPh_3 to extrude KCl , yielding the first neutral tris(imido) chromium(VI) complex, namely $(^t\text{BuN})_3\text{Cr}(\text{PPh}_3)$ (**28**) (Scheme 3.5). The structure of **28** was determined by X-ray crystallography and it is depicted in Figure 3.3. The geometry of **28** is better described as a trigonal pyramid than a pseudo-tetrahedral configuration for the following reasons. Firstly, the sum of three N-Cr-N bond angles (347.79°) is close to 360° . Secondly, the chromium center is situated only slightly above the N1-N2-N3 plane ($0.343 \text{ \AA}$). **28** has C_{3v} symmetry. All three Cr-N bonds ($\text{Cr1-N1} = 1.6822(17)$, $\text{Cr1-N2} = 1.6788(16)$, $\text{Cr1-N3} = 1.6710(17) \text{ \AA}$) are slightly longer than those bonds of bis(imido) chromium(VI) complexes. The Cr-N-C angles ($\text{Cr1-N1-C1} = 148.18(16)$, $\text{Cr1-N2-C5} = 144.84(14)$, $\text{Cr1-N3-C9} = 150.11(16)^\circ$) fall in the category of bent imido ligands ($130\text{--}150^\circ$). These observations can be attributed to strong π -loading on the chromium center. In the ^1H NMR spectrum, the three *tert*-butyl groups are equivalent due to C_{3v} symmetry. Based on the reported *tert*-butylimido complexes, Nugent found that increasing electron donation from nitrogen to the metal center causes a downfield shift for the α -carbon and an upfield shift for the β -carbon. Thus, he defined the Δ parameter, which is the difference between the chemical shifts of C_α and C_β of a *tert*-butyl group of an imido ligand in the ^{13}C NMR spectrum, to approximately indicate bent coordination or linear coordination of an imido ligand. The range of Δ was found to be $16\text{--}55$ in Nugent's paper.¹⁶ The Δ parameter of **28** (37.25 ppm) is smaller than that of reported bis(*tert*-butylimido) chromium(VI) complexes, suggesting that **28** has a smaller bond angle of the Cr-N-C linkage than the Cr-N-C linkage of bis(*tert*-butylimido) chromium(VI) complexes. This suggestion is consistent with the structural parameters of **28**.



Scheme 3.5 Reaction of K[(^tBuN)₃CrCl] (**24a**) with nucleophile PPh₃

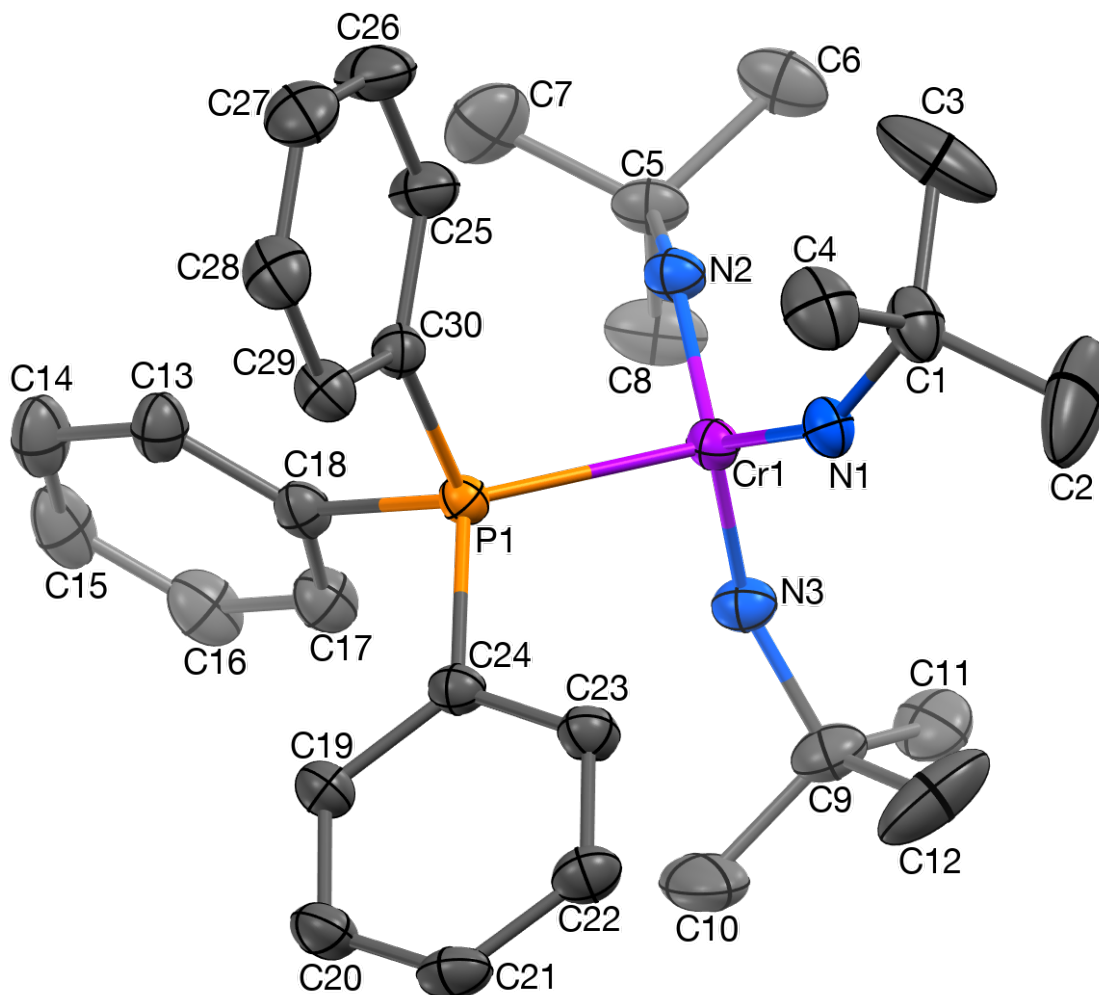


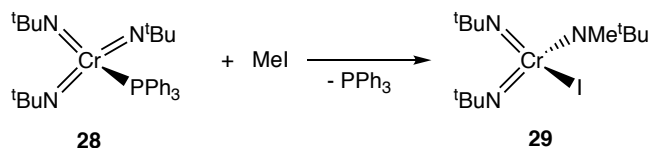
Figure 3.3 Molecular structure of $(t\text{-BuN})_3\text{Cr}(\text{PPh}_3)$ (**28**). Ellipsoids are drawn at the 30% probability level. Hydrogen atoms have been omitted for clarity.

Table 3.2 Interatomic distances (Å) and angles (°) for (tBuN)₃Cr(PPh₃) (**28**)

Distances (Å)			
Cr(1)-N(3)	1.6710(17)	C(13)-C(14)	1.385(3)
Cr(1)-N(2)	1.6788(16)	C(13)-C(18)	1.392(3)
Cr(1)-N(1)	1.6822(17)	C(14)-C(15)	1.371(4)
Cr(1)-P(1)	2.3341(6)	C(15)-C(16)	1.379(4)
P(1)-C(30)	1.820(2)	C(16)-C(17)	1.385(3)
P(1)-C(18)	1.819(2)	C(17)-C(18)	1.391(3)
P(1)-C(24)	1.8244(19)	C(19)-C(24)	1.388(3)
C(1)-N(1)	1.447(3)	C(19)-C(20)	1.391(3)
C(1)-C(2)	1.508(4)	C(20)-C(21)	1.380(3)
C(1)-C(4)	1.524(3)	C(21)-C(22)	1.374(3)
C(1)-C(3)	1.531(4)	C(22)-C(23)	1.388(3)
C(5)-N(2)	1.459(3)	C(23)-C(24)	1.389(3)
C(5)-C(8)	1.522(3)	C(25)-C(26)	1.382(3)
C(5)-C(7)	1.530(4)	C(25)-C(30)	1.393(3)
C(5)-C(6)	1.533(3)	C(26)-C(27)	1.378(4)
C(9)-N(3)	1.453(3)	C(27)-C(28)	1.374(4)
C(9)-C(12)	1.508(4)	C(28)-C(29)	1.381(3)
C(9)-C(11)	1.529(4)	C(29)-C(30)	1.384(3)
C(9)-C(10)	1.533(4)		
Angles (°)			
N(3)-Cr(1)-N(2)	114.65(8)	C(11)-C(9)-C(10)	109.8(2)
N(3)-Cr(1)-N(1)	116.57(9)	C(14)-C(13)-C(18)	120.2(2)
N(2)-Cr(1)-N(1)	116.57(8)	C(15)-C(14)-C(13)	120.2(2)
N(3)-Cr(1)-P(1)	102.35(6)	C(14)-C(15)-C(16)	120.1(2)
N(2)-Cr(1)-P(1)	101.64(6)	C(15)-C(16)-C(17)	120.5(2)
N(1)-Cr(1)-P(1)	101.40(6)	C(16)-C(17)-C(18)	119.8(2)
C(30)-P(1)-C(18)	104.56(9)	C(17)-C(18)-C(13)	119.2(2)
C(30)-P(1)-C(24)	104.89(9)	C(17)-C(18)-P(1)	118.60(16)
C(18)-P(1)-C(24)	105.37(9)	C(13)-C(18)-P(1)	122.13(16)
C(30)-P(1)-Cr(1)	113.74(6)	C(24)-C(19)-C(20)	120.1(2)

C(18)-P(1)-Cr(1)	113.70(6)	C(21)-C(20)-C(19)	120.2(2)
C(24)-P(1)-Cr(1)	113.63(6)	C(22)-C(21)-C(20)	120.0(2)
N(1)-C(1)-C(2)	107.6(2)	C(21)-C(22)-C(23)	120.3(2)
N(1)-C(1)-C(4)	108.53(19)	C(22)-C(23)-C(24)	120.2(2)
C(2)-C(1)-C(4)	110.5(3)	C(19)-C(24)-C(23)	119.23(18)
N(1)-C(1)-C(3)	109.9(2)	C(19)-C(24)-P(1)	122.31(16)
C(2)-C(1)-C(3)	111.1(3)	C(23)-C(24)-P(1)	118.46(15)
C(4)-C(1)-C(3)	109.1(3)	C(26)-C(25)-C(30)	120.1(2)
N(2)-C(5)-C(8)	111.92(18)	C(27)-C(26)-C(25)	120.4(2)
N(2)-C(5)-C(7)	107.29(19)	C(28)-C(27)-C(26)	119.7(2)
C(8)-C(5)-C(7)	110.5(2)	C(27)-C(28)-C(29)	120.5(2)
N(2)-C(5)-C(6)	106.60(19)	C(28)-C(29)-C(30)	120.4(2)
C(8)-C(5)-C(6)	110.2(2)	C(29)-C(30)-C(25)	118.95(19)
C(7)-C(5)-C(6)	110.2(2)	C(29)-C(30)-P(1)	122.94(16)
N(3)-C(9)-C(12)	110.4(2)	C(25)-C(30)-P(1)	118.10(15)
N(3)-C(9)-C(11)	107.3(2)	C(1)-N(1)-Cr(1)	148.18(16)
C(12)-C(9)-C(11)	109.6(3)	C(5)-N(2)-Cr(1)	144.84(14)
N(3)-C(9)-C(10)	107.7(2)	C(9)-N(3)-Cr(1)	150.11(16)
C(12)-C(9)-C(10)	111.8(3)		

Like the nucleophilic nature of **24a**, the imido ligands of **28** are also nucleophilic, rendering them subject to reaction with MeI. Dissolving **28** in pentane with 60 equivalents of MeI gave a purple solution. A color change was observed from purple to deep red after three days at room temperature. This reaction gave an alkylation product, namely (^tBuN)₂Cr(NMe^tBu)I (**29**). (Scheme 3.6) The structure of **29** was determined by X-ray diffraction and it is depicted in Figure 3.4. **29** features pseudo-tetrahedral coordination geometry. The Cr1-N3A (1.846(9) Å) bond of the amido ligand is obviously longer than the Cr-N bonds (Cr1-N1 = 1.636(9), Cr1-N2 = 1.644(9) Å) of the two imido ligands. As one original imido π -bonding was broken by alkylation, π -loading is weakened in the structure of **29** compared to that in the structure of **28**. Thus, the two imido Cr-N-C angles (Cr1-N1-C1 = 166.0(9), Cr1-N2-C5 = 159.9(8)°) are in the range of linear configuration.



Scheme 3.6 Reaction of (^tBuN)₃Cr(PPh₃) (**28**) with electrophile MeI

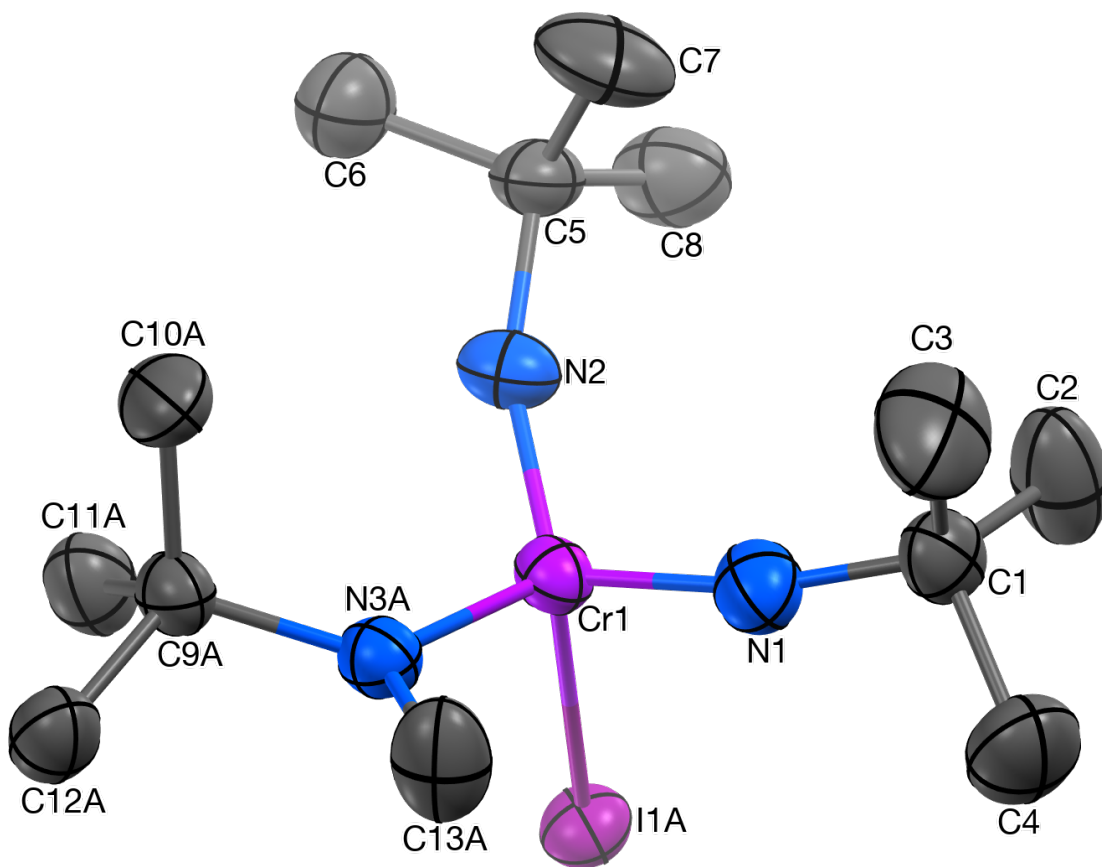


Figure 3.4 Molecular structure of (t-BuN)₂Cr(NMeⁱBu)I (**29**). Ellipsoids are drawn at the 30% probability level. Hydrogen atoms have been omitted for clarity.

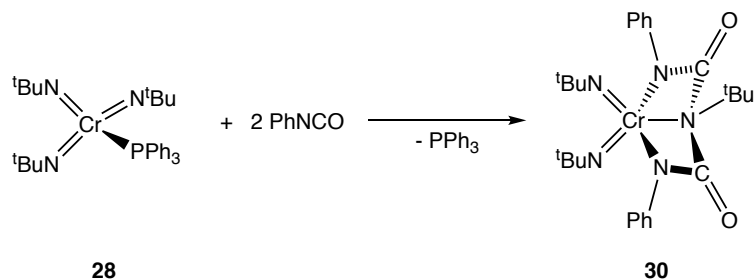
Table 3.3 Interatomic distances (Å) and angles (°) for (tBuN)₂Cr(NMe^tBu)I (**29**)

Distances (Å)			
Cr(1)-N(1)	1.636(9)	C(5)-C(6)	1.521(17)
Cr(1)-N(2)	1.644(9)	C(5)-C(7)	1.533(17)
Cr(1)-N(3B) ^a	1.83(2)	N(3A)-C(13A) ^a	1.47(2)
Cr(1)-N(3A) ^a	1.846(9)	N(3A)-C(9A) ^a	1.522(14)
Cr(1)-I(1B) ^a	2.513(7)	C(9A)-C(10A) ^a	1.519(19)
Cr(1)-I(1A) ^a	2.623(2)	C(9A)-C(12A) ^a	1.530(17)
C(1)-N(1)	1.410(12)	C(9A)-C(11A) ^a	1.53(2)
C(1)-C(3)	1.487(19)	N(3B)-C(13B) ^a	1.49(3)
C(1)-C(2)	1.516(18)	N(3B)-C(9B) ^a	1.54(3)
C(1)-C(4)	1.533(18)	C(9B)-C(11B) ^a	1.52(3)
C(5)-N(2)	1.451(13)	C(9B)-C(10B) ^a	1.53(3)
C(5)-C(8)	1.502(19)	C(9B)-C(12B) ^a	1.53(3)

^a The iodide ligand with labeling I1 and one amido ligand were found disordered in two positions with a refined site occupancy ratio of 80/20.

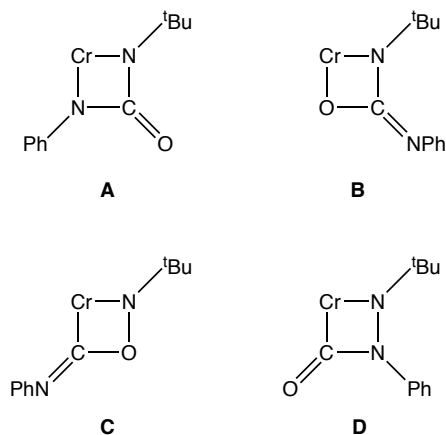
Angles (°)			
N(1)-Cr(1)-N(2)	114.3(5)	C(6)-C(5)-C(7)	108.8(12)
N(1)-Cr(1)-N(3B)	131.1(11)	C(1)-N(1)-Cr(1)	166.0(9)
N(2)-Cr(1)-N(3B)	90.8(11)	C(5)-N(2)-Cr(1)	159.9(8)
N(1)-Cr(1)-N(3A)	105.4(5)	C(13A)-N(3A)-C(9A)	113.4(12)
N(2)-Cr(1)-N(3A)	115.9(5)	C(13A)-N(3A)-Cr(1)	120.5(11)
N(1)-Cr(1)-I(1B)	110.2(4)	C(9A)-N(3A)-Cr(1)	124.8(8)
N(2)-Cr(1)-I(1B)	107.0(4)	C(10A)-C(9A)-N(3A)	109.3(10)
N(3B)-Cr(1)-I(1B)	100.3(12)	C(10A)-C(9A)-C(12A)	110.1(12)
N(1)-Cr(1)-I(1A)	102.9(3)	N(3A)-C(9A)-C(12A)	111.1(10)
N(2)-Cr(1)-I(1A)	108.0(3)	C(10A)-C(9A)-C(11A)	110.1(13)
N(3A)-Cr(1)-I(1A)	109.6(3)	N(3A)-C(9A)-C(11A)	110.3(12)
N(1)-C(1)-C(3)	108.5(11)	C(12A)-C(9A)-C(11A)	105.8(12)
N(1)-C(1)-C(2)	108.4(10)	C(13B)-N(3B)-C(9B)	106(3)
C(3)-C(1)-C(2)	113.6(16)	C(13B)-N(3B)-Cr(1)	132(3)
N(1)-C(1)-C(4)	107.2(12)	C(9B)-N(3B)-Cr(1)	122(2)
C(3)-C(1)-C(4)	109.9(16)	C(11B)-C(9B)-C(10B)	112(3)

C(2)-C(1)-C(4)	109.0(13)	C(11B)-C(9B)-C(12B)	109(3)
N(2)-C(5)-C(8)	109.7(10)	C(10B)-C(9B)-C(12B)	106(3)
N(2)-C(5)-C(6)	106.8(10)	C(11B)-C(9B)-N(3B)	110(3)
C(8)-C(5)-C(6)	110.1(12)	C(10B)-C(9B)-N(3B)	109(3)
N(2)-C(5)-C(7)	107.8(10)	C(12B)-C(9B)-N(3B)	109(3)
C(8)-C(5)-C(7)	113.5(14)		



Scheme 3.7 Reaction of $(^t\text{BuN})_3\text{Cr}(\text{PPh}_3)$ (**28**) with isocyanate PhNCO

In addition to electrophile MeI , **28** shows cycloaddition with isocyanate PhNCO or CO_2 to generate metallacycles. The cycloaddition of **28** with PhNCO gave the chromacyclic complex $(^t\text{BuN})_2\text{Cr}\{[\text{PhNC}(\text{O})]_2\text{N}^t\text{Bu}\}$ (**30**). (Scheme 3.7) The ^1H NMR spectrum of **30**, according to the integration of aromatic peaks and the peak of *tert*-butyl group, indicates that two equivalents of PhNCO have reacted with **28**. Of the



Scheme 3.8 The four possible cycloaddition configurations for **28** with PhNCO

four possible cycloaddition configurations for **28** with PhNCO illustrated in Scheme 3.8, only configurations **A** and **B** are consistent with the cycloaddition expected from

the polarity of the $\text{Cr}^{\delta+}\text{-N}^{\delta-}$ bond and the highly electropositive carbon in PhNCO . The proposed structure of **30** arises from configuration **A**, as indicated by a strong absorption band at 1720 cm^{-1} in the infrared spectrum of **30**, which is assigned to the C=O double bond. The structure of this biuret complex was confirmed by X-ray diffraction and it is depicted in Figure 3.5. This five-coordinate complex has a coordination geometry half-way between square pyramid and trigonal bipyramid ($\tau = 0.49$)¹⁷. In its ^1H NMR spectrum, two *tert*-butyl groups of imido ligands are inequivalent. This difference might be resulted from non-flexibility of the ring, which makes the $\text{Cr=N}^t\text{Bu}$ imido ligands *cis* and *trans* to the biuret $\text{Cr-N}^t\text{Bu}$ inequivalent. The difference was also observed in the ^1H NMR spectrum of $(^t\text{BuN})_2\text{Cr}\{[^t\text{BuNC(O)}]_2\text{N}^t\text{Bu}\}$, which was synthesized by the reaction of $(^t\text{BuN})_2\text{Cr}(\text{NH}^t\text{Bu})_2$ with 15 equivalents of $^t\text{BuNCO}$ by Wilkinson.¹⁸ In the ^{13}C NMR spectrum of **30**, the peak at 152.30 ppm is assigned to carbonyl carbon. The C=O double bond causes a strong absorption band at 1720 cm^{-1} in the infrared spectrum of **30**. Adding only one equivalent of isocyanate to the solution of **28** also gave **30** instead of yielding urea complex $(^t\text{BuN})_2\text{Cr}\{[\text{PhNC(O)}]\text{N}^t\text{Bu}\}$. As a chromium bis(imido) biuret complex, **30** has three different types of Cr-N bonding, namely imido bonds ($\text{Cr1-N4} = 1.6558(13)$, $\text{Cr1-N5} = 1.6439(13)\text{ \AA}$), amido bonds ($\text{Cr1-N1} = 1.9841(13)$, $\text{Cr1-N3} = 1.9877(13)\text{ \AA}$), and an amine bond ($\text{Cr1-N2} = 2.1262(12)\text{ \AA}$). Another example that has three different types of Cr-N bonding is the nitrido-imido-amido chromium anion $[\text{Cr}(\equiv\text{N})(=\text{NPh})(\text{N}^i\text{Pr}_2)_2]^-$, which was reported by Odom in 2016.¹⁹

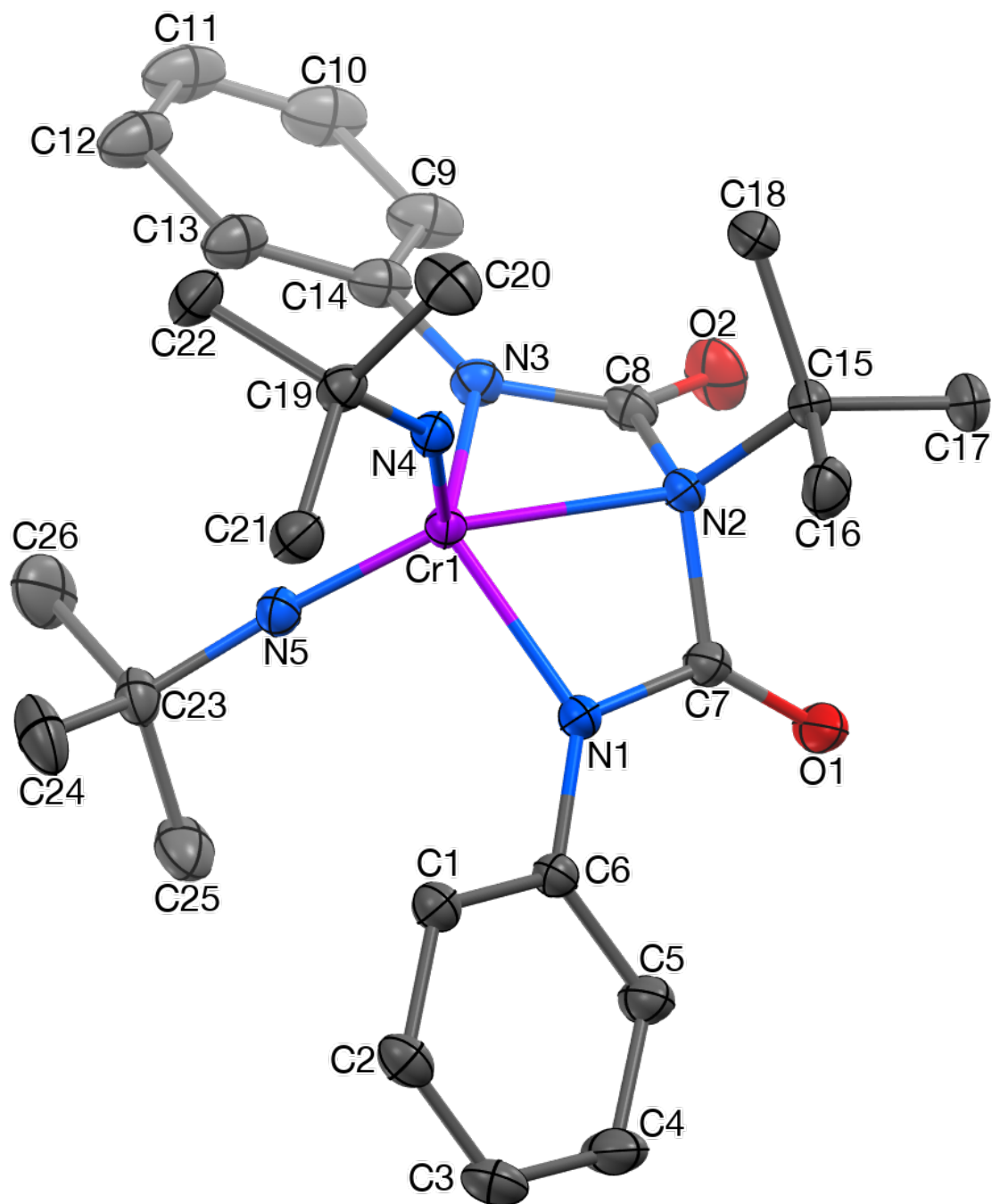
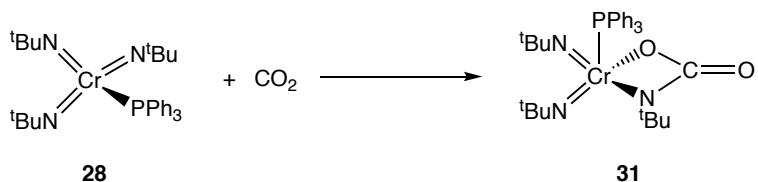


Figure 3.5 Molecular structure of $(t\text{BuN})_2\text{Cr}\{[\text{PhNC}(\text{O})]_2\text{N}^t\text{Bu}\}$ (**30**). Ellipsoids are drawn at the 30% probability level. Hydrogen atoms have been omitted for clarity.

Table 3.4 Interatomic distances (Å) and angles (°) for (tBuN)₂Cr{[PhNC(O)]₂N^tBu}
(**30**)

Distances (Å)			
Cr(1)-N(5)	1.6439(13)	C(3)-C(4)	1.377(3)
Cr(1)-N(4)	1.6558(13)	C(4)-C(5)	1.388(2)
Cr(1)-N(1)	1.9841(13)	C(5)-C(6)	1.395(2)
Cr(1)-N(3)	1.9877(13)	C(9)-C(10)	1.400(3)
Cr(1)-N(2)	2.1262(12)	C(9)-C(14)	1.402(3)
O(1)-C(7)	1.209(2)	C(10)-C(11)	1.356(4)
O(2)-C(8)	1.212(2)	C(11)-C(12)	1.398(4)
N(1)-C(7)	1.3412(19)	C(12)-C(13)	1.390(2)
N(1)-C(6)	1.4149(18)	C(13)-C(14)	1.392(3)
N(2)-C(8)	1.483(2)	C(15)-C(16)	1.523(2)
N(2)-C(7)	1.4872(18)	C(15)-C(18)	1.527(2)
N(2)-C(15)	1.5308(19)	C(15)-C(17)	1.534(2)
N(3)-C(8)	1.344(2)	C(19)-C(22)	1.528(2)
N(3)-C(14)	1.417(2)	C(19)-C(21)	1.531(2)
N(4)-C(19)	1.4577(19)	C(19)-C(20)	1.536(2)
N(5)-C(23)	1.4536(19)	C(23)-C(25)	1.525(3)
C(1)-C(6)	1.392(2)	C(23)-C(24)	1.526(3)
C(1)-C(2)	1.394(2)	C(23)-C(26)	1.527(3)
C(2)-C(3)	1.371(3)		
Angles (°)			
N(5)-Cr(1)-N(4)	111.03(6)	O(1)-C(7)-N(1)	133.21(15)
N(5)-Cr(1)-N(1)	98.10(6)	O(1)-C(7)-N(2)	124.32(13)
N(4)-Cr(1)-N(1)	114.20(6)	N(1)-C(7)-N(2)	102.44(12)
N(5)-Cr(1)-N(3)	101.71(6)	O(2)-C(8)-N(3)	133.29(16)
N(4)-Cr(1)-N(3)	113.44(6)	O(2)-C(8)-N(2)	123.72(15)
N(1)-Cr(1)-N(3)	116.29(5)	N(3)-C(8)-N(2)	102.99(12)
N(5)-Cr(1)-N(2)	145.56(6)	C(10)-C(9)-C(14)	118.7(2)
N(4)-Cr(1)-N(2)	103.34(6)	C(11)-C(10)-C(9)	121.8(2)
N(1)-Cr(1)-N(2)	64.83(5)	C(10)-C(11)-C(12)	120.00(19)

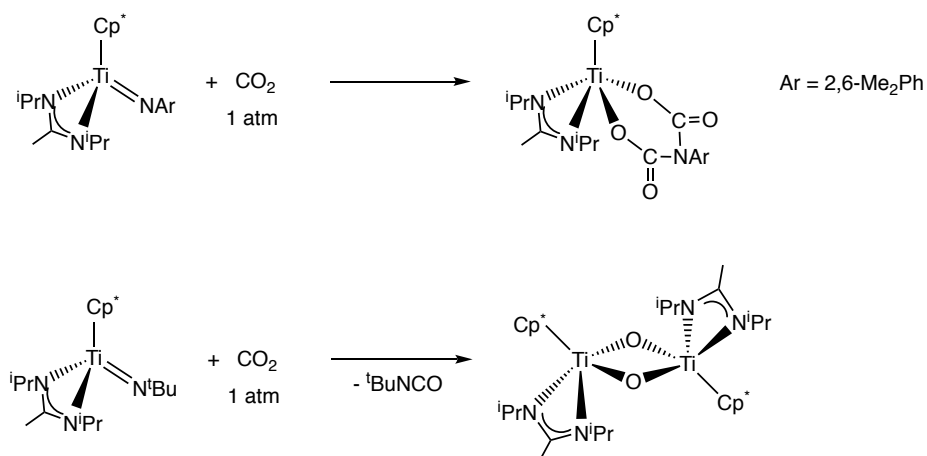
N(3)-Cr(1)-N(2)	65.03(5)	C(13)-C(12)-C(11)	119.2(2)
C(7)-N(1)-C(6)	124.70(13)	C(12)-C(13)-C(14)	120.9(2)
C(7)-N(1)-Cr(1)	100.27(9)	C(13)-C(14)-C(9)	119.35(17)
C(6)-N(1)-Cr(1)	134.51(10)	C(13)-C(14)-N(3)	117.50(15)
C(8)-N(2)-C(7)	119.61(12)	C(9)-C(14)-N(3)	123.10(18)
C(8)-N(2)-C(15)	114.84(12)	C(16)-C(15)-C(18)	110.58(15)
C(7)-N(2)-C(15)	113.34(12)	C(16)-C(15)-N(2)	107.73(13)
C(8)-N(2)-Cr(1)	89.68(9)	C(18)-C(15)-N(2)	107.90(12)
C(7)-N(2)-Cr(1)	89.56(8)	C(16)-C(15)-C(17)	110.21(14)
C(15)-N(2)-Cr(1)	126.49(9)	C(18)-C(15)-C(17)	109.26(13)
C(8)-N(3)-C(14)	124.41(14)	N(2)-C(15)-C(17)	111.13(14)
C(8)-N(3)-Cr(1)	99.98(10)	N(4)-C(19)-C(22)	109.05(13)
C(14)-N(3)-Cr(1)	135.53(12)	N(4)-C(19)-C(21)	108.61(12)
C(19)-N(4)-Cr(1)	150.49(11)	C(22)-C(19)-C(21)	111.18(14)
C(23)-N(5)-Cr(1)	175.65(12)	N(4)-C(19)-C(20)	107.30(13)
C(6)-C(1)-C(2)	120.55(15)	C(22)-C(19)-C(20)	110.75(15)
C(3)-C(2)-C(1)	120.35(16)	C(21)-C(19)-C(20)	109.84(14)
C(2)-C(3)-C(4)	119.25(16)	N(5)-C(23)-C(25)	109.44(14)
C(3)-C(4)-C(5)	121.56(17)	N(5)-C(23)-C(24)	109.43(14)
C(4)-C(5)-C(6)	119.45(16)	C(25)-C(23)-C(24)	109.73(17)
C(1)-C(6)-C(5)	118.81(14)	N(5)-C(23)-C(26)	107.59(15)
C(1)-C(6)-N(1)	117.81(14)	C(25)-C(23)-C(26)	110.39(18)
C(5)-C(6)-N(1)	123.37(14)	C(24)-C(23)-C(26)	110.22(19)



Scheme 3.9 Reaction of $(^t\text{BuN})_3\text{Cr}(\text{PPh}_3)$ (**28**) with CO_2

The reaction of **28** with CO_2 gave the chromacyclic complex $(^t\text{BuN})_2\text{Cr}[\text{OC}(\text{O})\text{N}^t\text{Bu}](\text{PPh}_3)$ (**31**). After one atmosphere of CO_2 was charged into the reaction ampule, the pentane solution of **28** changed color from purple to orange immediately at room temperature. The solution also became cloudy due to the low solubility of **31** in pentane. The structure of **31** was determined by X-ray diffraction and it is depicted in Figure 3.6. This molecule features distorted square pyramidal coordination geometry ($\tau = 0.25$)¹⁷ with an axis of Cr1-N2. Cr1-N3 (1.9768(14) Å) is obviously longer than the two imido bonds (Cr1-N1 = 1.6497(14), Cr1-N2 = 1.6387(14) Å) because it participated in the [2+2] cycloaddition with C=O double bond. The two imido angles Cr-N-C (Cr1-N1-C1 = 162.95(13), Cr1-N2-C5 = 171.49(13)°) are larger than those in the structure of **28**. This might be attributed to less π -loading in **30**. In the ^1H NMR spectrum, two imido ligands are magnetically equivalent due to a mirror plane of O1-Cr1-N3. The C=O double bond causes a strong absorption band at 1649 cm^{-1} in the infrared spectrum. Mountford and co-workers reported a titanium imido complex $\text{Cp}^*\text{Ti}(\text{NAr})[\text{MeC}(\text{N}^i\text{Pr})_2]$ (Ar = 2,6-Me₂Ph), which can do cycloaddition with two equivalents of CO_2 to form $\text{Cp}^*\text{Ti}[\text{OC}(\text{O})\text{NArC}(\text{O})\text{O}][\text{MeC}(\text{N}^i\text{Pr})_2]$. Another titanium imido complex $\text{Cp}^*\text{Ti}(\text{N}^t\text{Bu})[\text{MeC}(\text{N}^i\text{Pr})_2]$ can react with CO_2 to extrude $^t\text{BuNCO}$ to form bridging

oxo complex *trans*-{Cp*Ti(μ-O)[MeC(NⁱPr)₂]}₂ (Scheme 3.10).²⁰ However, such kinds of reactivities were not observed when treating **28** with CO₂. The interesting



Scheme 3.10 Reactions of titanium imido complexes with CO₂

thing is that **31** can lose CO₂ upon heating at 80°C in a degassed ampule to go back to **28**. This observation is consistent with LIFDI-MS data of **31** (MS(LIFDI) *m/z*: 527.2534 [M⁺-CO₂]. Calcd. *m/z*: 527.2521 [M⁺-CO₂]).

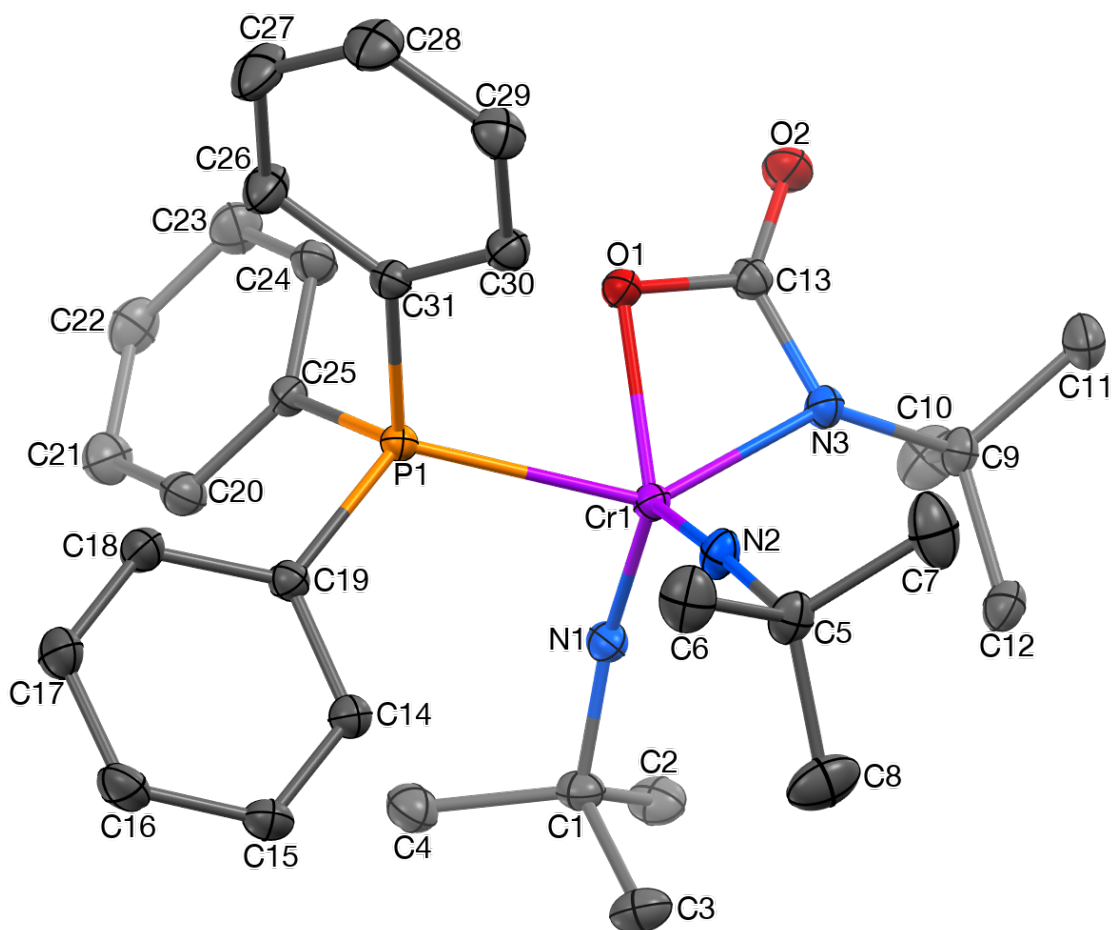
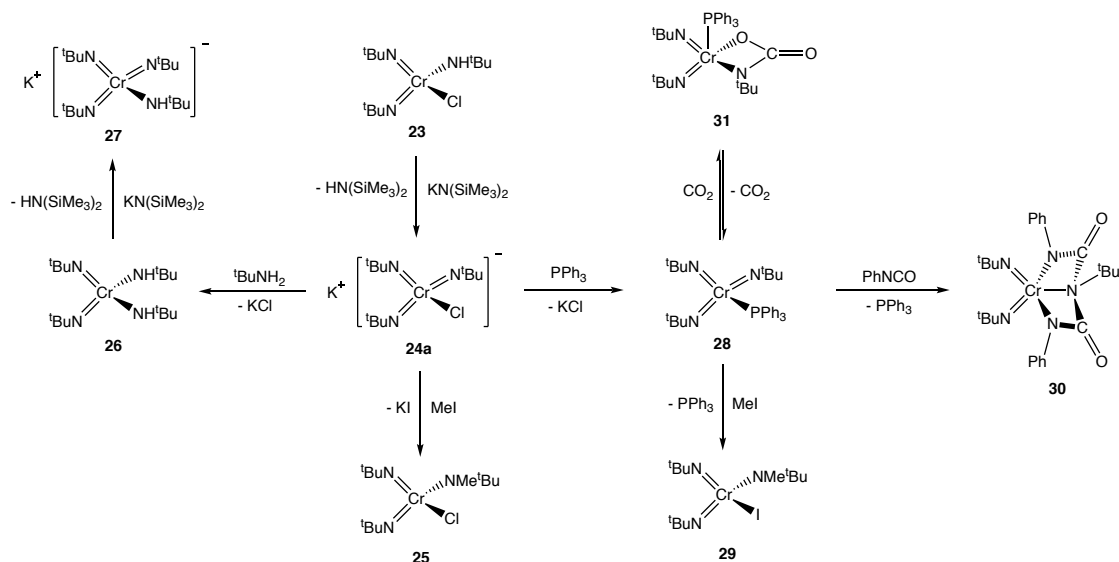


Figure 3.6 Molecular structure of $(t\text{BuN})_2\text{Cr}[\text{OC}(\text{O})\text{N}^t\text{Bu}](\text{PPh}_3)$ (**31**). Ellipsoids are drawn at the 30% probability level. Hydrogen atoms have been omitted for clarity.

Table 3.5 Interatomic distances (Å) and angles (°) for (tBuN)₂Cr[OC(O)N^tBu](PPh₃)
(**31**)

Distances (Å)			
Cr(1)-N(2)	1.6387(14)	C(14)-C(15)	1.386(2)
Cr(1)-N(1)	1.6497(14)	C(14)-C(19)	1.387(2)
Cr(1)-N(3)	1.9768(14)	C(15)-C(16)	1.379(3)
Cr(1)-O(1)	1.9898(11)	C(16)-C(17)	1.378(3)
Cr(1)-P(1)	2.4154(5)	C(17)-C(18)	1.382(3)
Cr(1)-C(13)	2.4641(16)	C(18)-C(19)	1.398(2)
C(1)-N(1)	1.457(2)	C(19)-P(1)	1.8198(16)
C(1)-C(3)	1.524(2)	C(20)-C(25)	1.389(2)
C(1)-C(4)	1.531(3)	C(20)-C(21)	1.394(3)
C(1)-C(2)	1.534(2)	C(21)-C(22)	1.372(3)
C(5)-N(2)	1.457(2)	C(22)-C(23)	1.377(3)
C(5)-C(7)	1.521(3)	C(23)-C(24)	1.387(2)
C(5)-C(8)	1.525(3)	C(24)-C(25)	1.390(2)
C(5)-C(6)	1.530(3)	C(25)-P(1)	1.8228(16)
C(9)-N(3)	1.470(2)	C(26)-C(27)	1.387(3)
C(9)-C(10)	1.523(2)	C(26)-C(31)	1.389(2)
C(9)-C(11)	1.524(3)	C(27)-C(28)	1.375(3)
C(9)-C(12)	1.526(2)	C(28)-C(29)	1.375(3)
C(13)-O(2)	1.224(2)	C(29)-C(30)	1.387(2)
C(13)-O(1)	1.3432(19)	C(30)-C(31)	1.388(2)
C(13)-N(3)	1.347(2)	C(31)-P(1)	1.8221(16)
Angles (°)			
N(2)-Cr(1)-N(1)	114.01(7)	N(3)-C(13)-Cr(1)	53.18(8)
N(2)-Cr(1)-N(3)	102.92(6)	C(15)-C(14)-C(19)	120.84(16)
N(1)-Cr(1)-N(3)	104.54(6)	C(16)-C(15)-C(14)	119.78(17)
N(2)-Cr(1)-O(1)	121.72(6)	C(17)-C(16)-C(15)	120.17(17)
N(1)-Cr(1)-O(1)	124.24(6)	C(16)-C(17)-C(18)	120.28(18)
N(3)-Cr(1)-O(1)	65.70(5)	C(17)-C(18)-C(19)	120.30(17)
N(2)-Cr(1)-P(1)	100.69(5)	C(14)-C(19)-C(18)	118.63(15)

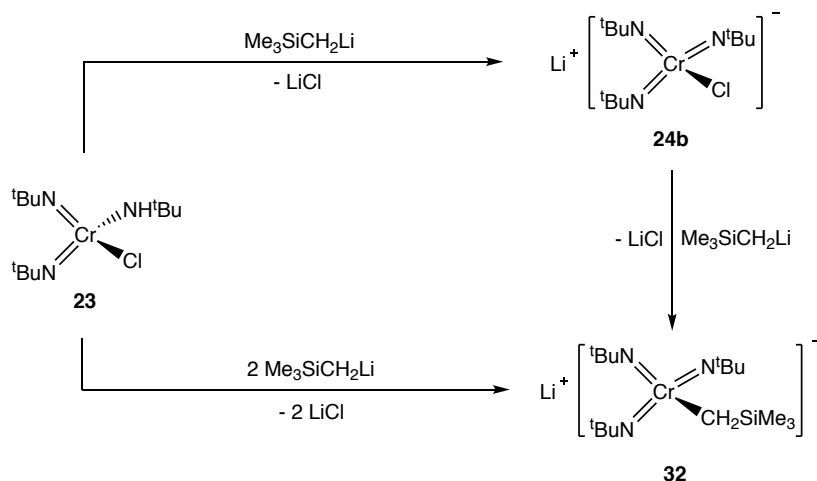
N(1)-Cr(1)-P(1)	95.45(5)	C(14)-C(19)-P(1)	120.74(12)
N(3)-Cr(1)-P(1)	139.18(4)	C(18)-C(19)-P(1)	120.60(13)
O(1)-Cr(1)-P(1)	73.60(3)	C(25)-C(20)-C(21)	120.28(17)
N(2)-Cr(1)-C(13)	119.79(7)	C(22)-C(21)-C(20)	120.44(18)
N(1)-Cr(1)-C(13)	115.70(6)	C(21)-C(22)-C(23)	119.60(17)
N(3)-Cr(1)-C(13)	33.06(5)	C(22)-C(23)-C(24)	120.55(18)
O(1)-Cr(1)-C(13)	32.97(5)	C(23)-C(24)-C(25)	120.36(17)
P(1)-Cr(1)-C(13)	106.14(4)	C(20)-C(25)-C(24)	118.75(15)
N(1)-C(1)-C(3)	111.67(15)	C(20)-C(25)-P(1)	121.75(13)
N(1)-C(1)-C(4)	107.60(14)	C(24)-C(25)-P(1)	119.43(12)
C(3)-C(1)-C(4)	110.73(16)	C(27)-C(26)-C(31)	120.10(18)
N(1)-C(1)-C(2)	107.77(14)	C(28)-C(27)-C(26)	120.73(19)
C(3)-C(1)-C(2)	109.85(15)	C(27)-C(28)-C(29)	119.53(18)
C(4)-C(1)-C(2)	109.12(15)	C(28)-C(29)-C(30)	120.29(17)
N(2)-C(5)-C(7)	106.67(15)	C(29)-C(30)-C(31)	120.57(16)
N(2)-C(5)-C(8)	110.23(15)	C(30)-C(31)-C(26)	118.77(15)
C(7)-C(5)-C(8)	111.20(19)	C(30)-C(31)-P(1)	119.56(12)
N(2)-C(5)-C(6)	109.04(14)	C(26)-C(31)-P(1)	121.54(13)
C(7)-C(5)-C(6)	109.76(17)	C(1)-N(1)-Cr(1)	162.95(13)
C(8)-C(5)-C(6)	109.86(18)	C(5)-N(2)-Cr(1)	171.49(13)
N(3)-C(9)-C(10)	110.29(14)	C(13)-N(3)-C(9)	123.13(14)
N(3)-C(9)-C(11)	109.71(14)	C(13)-N(3)-Cr(1)	93.77(10)
C(10)-C(9)-C(11)	110.15(17)	C(9)-N(3)-Cr(1)	138.61(11)
N(3)-C(9)-C(12)	108.17(13)	C(13)-O(1)-Cr(1)	93.31(9)
C(10)-C(9)-C(12)	109.02(16)	C(19)-P(1)-C(31)	103.64(7)
C(11)-C(9)-C(12)	109.46(15)	C(19)-P(1)-C(25)	104.68(7)
O(2)-C(13)-O(1)	123.44(15)	C(31)-P(1)-C(25)	105.59(7)
O(2)-C(13)-N(3)	130.32(16)	C(19)-P(1)-Cr(1)	119.22(5)
O(1)-C(13)-N(3)	106.23(13)	C(31)-P(1)-Cr(1)	111.67(5)
O(2)-C(13)-Cr(1)	172.79(13)	C(25)-P(1)-Cr(1)	110.91(5)
O(1)-C(13)-Cr(1)	53.72(7)		



Scheme 3.11 Preparation of molecules featuring $\text{Cr}(\text{N}^t\text{Bu})_3$ from deprotonation of $(t\text{BuN})_2\text{Cr}(\text{NH}^t\text{Bu})\text{Cl}$ (**23**) by $\text{KN}(\text{SiMe}_3)_2$ and reactivity studies of tris(imido) chromium complexes

In summary, ionic tris(imido) chromium complexes can be made from deprotonation of **23** or **26** by $\text{KN}(\text{SiMe}_3)_2$. **24a** undergoes nucleophilic substitution by PPh_3 to form the first neutral tris(imido) chromium complex **28**. The imido ligands of **24a** and **28** are both subject to be attacked by the electrophile MeI to afford the alkylation products **25** and **29** respectively. In addition, **28** shows reactivity with PhNCO or CO_2 to generate metallacycles.

3.2.2 Approaching Cr(N^tBu)₃ by Deprotonation with Me₃SiCH₂Li



Scheme 3.12 Approaching the Cr(N^tBu)₃ moiety by deprotonating **23**

Now that the amido hydrogen of **23** can be abstracted by the weak base KN(SiMe₃)₂, it should also be able to be removed by strong bases, such as alkyl lithium reagents. Me₃SiCH₂Li was employed to deprotonate **23**, yielding Li[(^tBuN)₃CrCl] (**24b**) (Scheme 3.12). The three imido ligands of **24b** are magnetically equivalent in solution, as only one singlet peak was observed at 1.43 ppm in the ¹H NMR spectrum. **24b** can be alkylated by a second equivalent of Me₃SiCH₂Li, yielding Li[(^tBuN)₃Cr(CH₂SiMe₃)] (**32**). Treating **23** with two equivalents of Me₃SiCH₂Li produced **32** directly. (Scheme 3.12) A color change was observed from red orange to orange during the first hour and then slowly to yellow green. Based on this observation and the reactions of making **24b** and **32**, **23** was deprotonated first and was then alkylated when reacting with two equivalents of Me₃SiCH₂Li. **32** was characterized in multiple ways. Based on its ¹H NMR spectrum,

it initially seemed that all three imido groups are magnetically equivalent because only one peak was observed. However, two sets of peaks were assigned to the imido groups in the ^{13}C NMR spectrum. The 2D-NMR HSQC spectrum indicates that the imido groups of **32** are accidentally degenerate in the ^1H NMR spectrum. In other words, **32** has two different types of imido groups. This difference compared to other chromium complexes featuring the $\text{Cr}(\text{N}^i\text{Bu})_3$ moiety (i.e. **24a**, **24b**, **27** and **28**) might be attributed to the coordination of imido nitrogen atoms to the lithium cation. An upfield shift of CH_2SiMe_3 (0.24 ppm, compared to 1.96 ppm of CH_2SiMe_3 in **7**) was attributed to a shielding effect, resulting from the negative charge of organometallic species **32**. According to the integrations of each peak, one equivalent of diethyl ether was also observed. All of these observations are consistent with the result of X-ray diffraction. The structure of **32** is depicted in Figure 3.7 and the corresponding interatomic distances and angles are listed in Table 3.6. The lithium cation is coordinated by two imido nitrogen atoms and one molecule of diethyl ether. The chromium center of **32** features pseudo-tetrahedral coordination geometry. The two imido bonds Cr1-N2 (1.7182(16) Å) and Cr1-N3 (1.7205(16) Å), whose nitrogen atoms are coordinated to lithium cation, are both slightly longer than Cr1-N1 (1.6336(16) Å). The angle of Cr1-N1-C1 (174.13(15)°) falls in the category of linear imido ligands.²¹

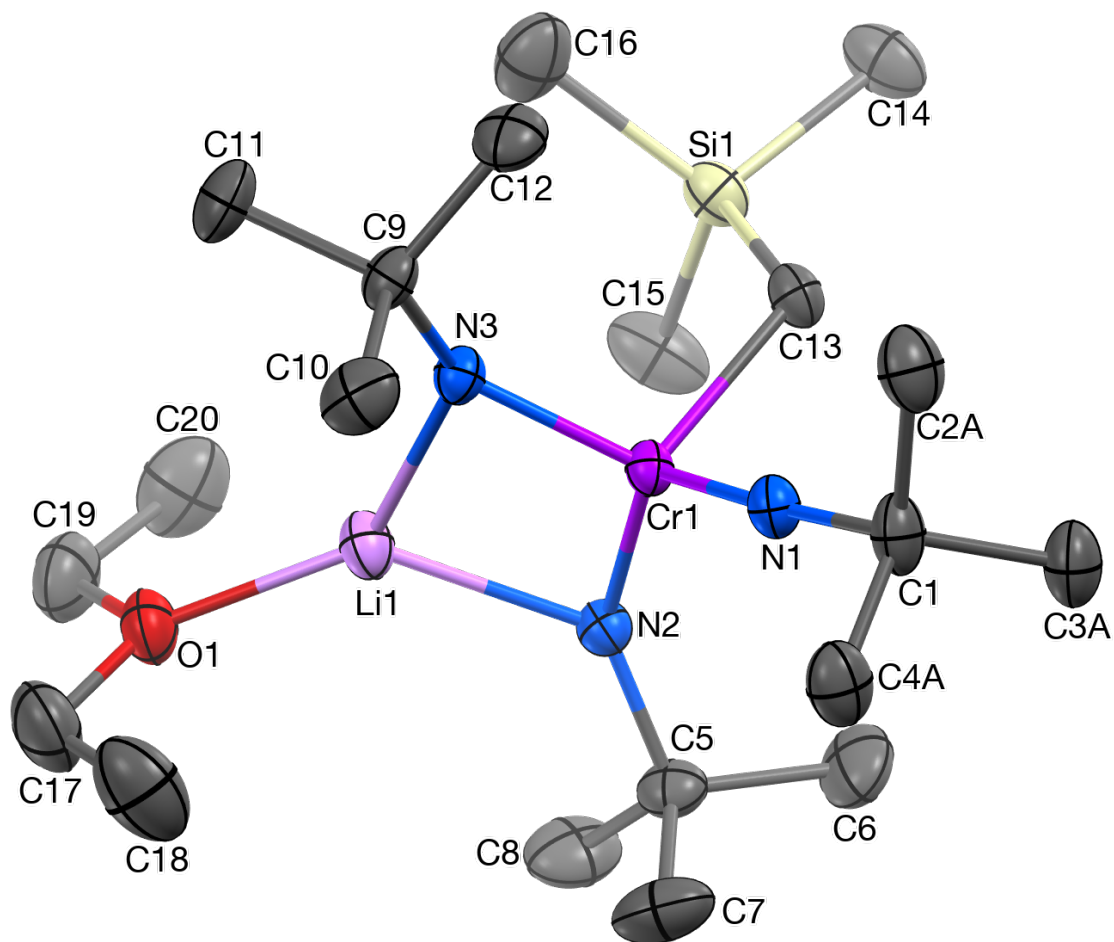


Figure 3.7 Molecular structure of $\text{Li}[(^t\text{BuN})_3\text{Cr}(\text{CH}_2\text{SiMe}_3)]$ (**32**). Ellipsoids are drawn at the 30% probability level. Hydrogen atoms have been omitted for clarity.

Table 3.6 Interatomic distances (Å) and angles (°) for Li[(^tBuN)₃Cr(CH₂SiMe₃)]
(32)

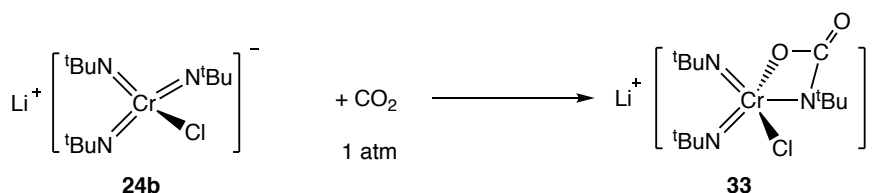
Distances (Å)			
Cr(1)-N(1)	1.6336(16)	C(5)-C(7)	1.510(4)
Cr(1)-N(2)	1.7182(16)	C(5)-C(8)	1.515(4)
Cr(1)-N(3)	1.7205(16)	C(5)-C(6)	1.535(4)
Cr(1)-C(13)	2.076(2)	C(9)-C(11)	1.527(3)
Cr(1)-Li(1)	2.521(3)	C(9)-C(12)	1.532(3)
N(1)-C(1)	1.450(2)	C(9)-C(10)	1.534(3)
N(2)-C(5)	1.458(3)	Si(1)-C(13)	1.848(2)
N(2)-Li(1)	2.015(4)	Si(1)-C(16)	1.865(3)
N(3)-C(9)	1.461(2)	Si(1)-C(15)	1.873(3)
N(3)-Li(1)	2.008(4)	Si(1)-C(14)	1.882(3)
C(1)-C(2B) ^a	1.431(13)	C(17)-O(1)	1.418(4)
C(1)-C(4A) ^a	1.479(4)	C(17)-C(18)	1.468(6)
C(1)-C(4B) ^a	1.492(13)	C(19)-O(1)	1.421(4)
C(1)-C(3A) ^a	1.501(4)	C(19)-C(20)	1.481(5)
C(1)-C(2A) ^a	1.546(5)	O(1)-Li(1)	1.930(4)
C(1)-C(3B) ^a	1.549(12)		

^a The *tert*-butyl group of one imido ligand with labeling C2 to C4 was found disordered in two positions with a refined site occupancy ratio of 81/19.

Angles (°)			
N(1)-Cr(1)-N(2)	118.87(8)	N(2)-C(5)-C(8)	108.9(2)
N(1)-Cr(1)-N(3)	117.24(8)	C(7)-C(5)-C(8)	110.9(2)
N(2)-Cr(1)-N(3)	105.18(8)	N(2)-C(5)-C(6)	109.4(2)
N(1)-Cr(1)-C(13)	99.09(8)	C(7)-C(5)-C(6)	109.0(3)
N(2)-Cr(1)-C(13)	107.26(8)	C(8)-C(5)-C(6)	109.6(2)
N(3)-Cr(1)-C(13)	108.31(8)	N(3)-C(9)-C(11)	108.90(17)
N(1)-Cr(1)-Li(1)	141.70(11)	N(3)-C(9)-C(12)	110.56(17)
N(2)-Cr(1)-Li(1)	52.72(10)	C(11)-C(9)-C(12)	109.2(2)
N(3)-Cr(1)-Li(1)	52.47(10)	N(3)-C(9)-C(10)	108.69(17)
C(13)-Cr(1)-Li(1)	119.21(10)	C(11)-C(9)-C(10)	109.7(2)
C(1)-N(1)-Cr(1)	174.13(15)	C(12)-C(9)-C(10)	109.8(2)

C(5)-N(2)-Cr(1)	139.21(14)	C(13)-Si(1)-C(16)	111.67(12)
C(5)-N(2)-Li(1)	131.44(17)	C(13)-Si(1)-C(15)	111.27(13)
Cr(1)-N(2)-Li(1)	84.55(12)	C(16)-Si(1)-C(15)	110.04(18)
C(9)-N(3)-Cr(1)	135.91(13)	C(13)-Si(1)-C(14)	110.01(12)
C(9)-N(3)-Li(1)	134.30(17)	C(16)-Si(1)-C(14)	107.66(15)
Cr(1)-N(3)-Li(1)	84.72(12)	C(15)-Si(1)-C(14)	105.98(13)
C(2B)-C(1)-N(1)	111.3(8)	O(1)-C(17)-C(18)	110.9(3)
N(1)-C(1)-C(4A)	109.6(2)	O(1)-C(19)-C(20)	110.0(3)
C(2B)-C(1)-C(4B)	113.2(9)	C(17)-O(1)-C(19)	112.8(2)
N(1)-C(1)-C(4B)	109.5(9)	C(17)-O(1)-Li(1)	122.6(2)
N(1)-C(1)-C(3A)	109.5(2)	C(19)-O(1)-Li(1)	124.1(2)
C(4A)-C(1)-C(3A)	113.3(3)	Si(1)-C(13)-Cr(1)	120.04(10)
N(1)-C(1)-C(2A)	107.6(2)	O(1)-Li(1)-N(3)	137.8(2)
C(4A)-C(1)-C(2A)	110.8(4)	O(1)-Li(1)-N(2)	135.5(2)
C(3A)-C(1)-C(2A)	105.8(3)	N(3)-Li(1)-N(2)	85.52(14)
C(2B)-C(1)-C(3B)	109.5(8)	O(1)-Li(1)-Cr(1)	172.8(2)
N(1)-C(1)-C(3B)	108.4(6)	N(3)-Li(1)-Cr(1)	42.81(8)
C(4B)-C(1)-C(3B)	104.6(8)	N(2)-Li(1)-Cr(1)	42.72(8)
N(2)-C(5)-C(7)	109.01(18)		

Since **28** undergoes cycloaddition with CO₂, tris(imido) anions (i.e. **24b** and **32**) might react with CO₂ following the same route. First, **24b** was treated with one atmosphere of CO₂ at room temperature, yielding Li{('BuN)₂Cr[OC(O)N^tBu]Cl} (**33**) with a slight color change from orange to light orange immediately. (Scheme 3.13) Unlike the starting material **24b**, **33** is soluble in pentane. A single crystal grown from



Scheme 3.13 Reaction of Li[(^tBuN)₃CrCl] (**24b**) with CO₂

pentane was not suitable for X-ray diffraction because the crystal cracked during cooling. After several attempts at growing a crystal that would survive in the dry cold nitrogen gas, I found that a single crystal grown from a concentrated toluene solution met this requirement. The structure of **33** is depicted in Figure 3.8 and the corresponding interatomic distances and angles are listed in Table 3.7. **33** has a distorted square pyramidal geometry ($\tau = 0.39$)¹⁷. The bond of Cr1-N3, part of the metallacycle, is longer than the imido bonds (Cr1-N1, 1.611(5); Cr1-N2 1.640(5) Å). The two imido groups of **33** were found to be magnetically equivalent in the ¹H NMR spectrum, which can be attributed to the approximate mirror plane containing the metallacycle. In the ¹³C NMR spectrum, the carbonyl carbon was found at 165.82 ppm. The carbonyl group has a strong absorption band in the infrared spectrum at 1578 cm⁻¹. Like the reaction of **28** with CO₂, a longer exposure time in CO₂ did not result in a

second addition of CO₂ to the chromium species nor to extrusion of ^tBuNCO to yield an oxo complex.

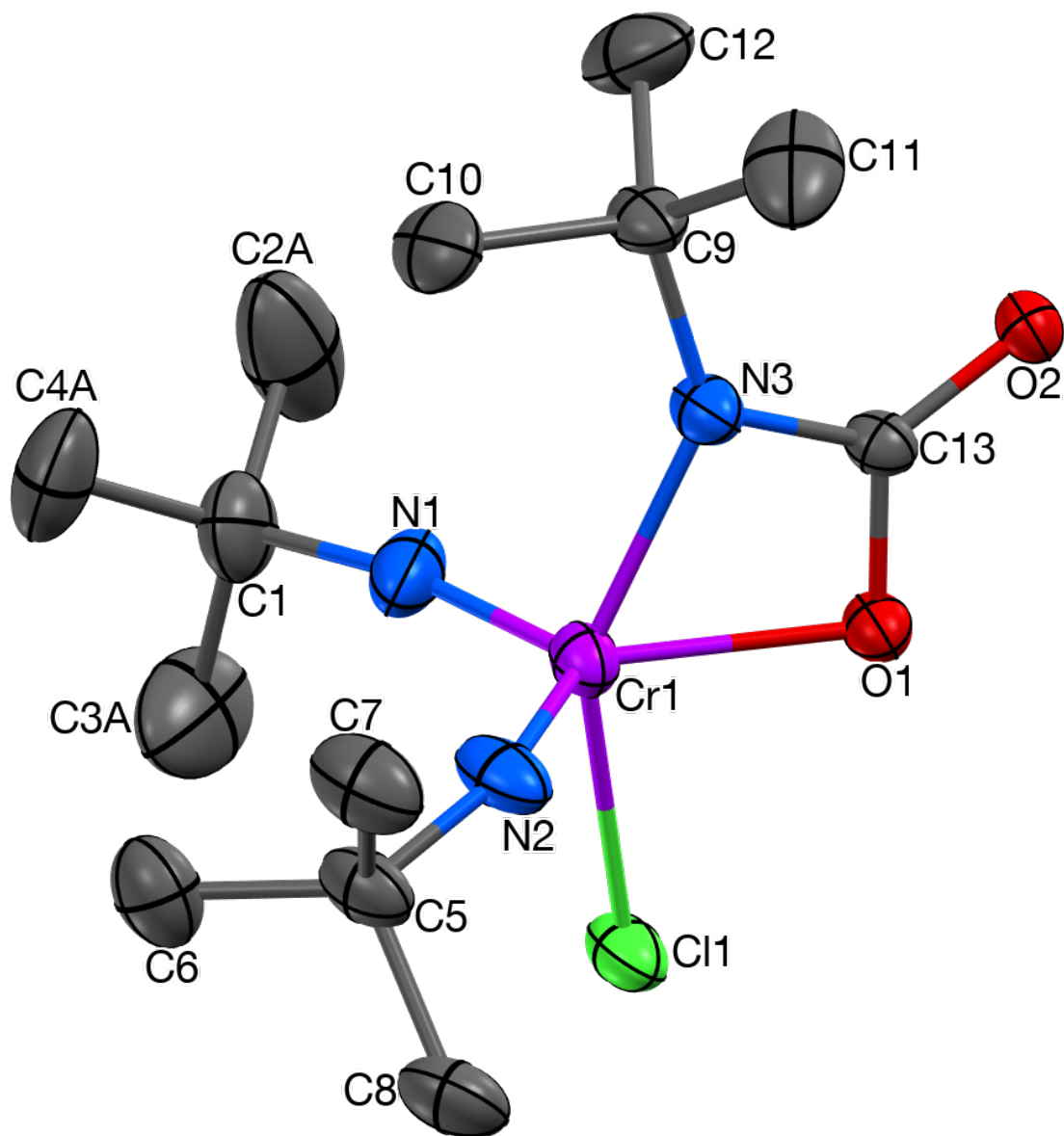


Figure 3.8 Molecular structure of $\text{Li}\{(^t\text{BuN})_2\text{Cr}[\text{OC}(\text{O})\text{N}^t\text{Bu}]\text{Cl}\}$ (**33**). Ellipsoids are drawn at the 30% probability level. Hydrogen atoms and lithium cation have been omitted for clarity. The crystal structure contains four molecules of **33** due to the linkage of lithium cation. The lithium cation is coordinated to two oxygen atoms and the chloride atom.

Table 3.7 Interatomic distances (Å) and angles (°) for Li{(^tBuN)₂Cr[OC(O)N^tBu]Cl}
(33)

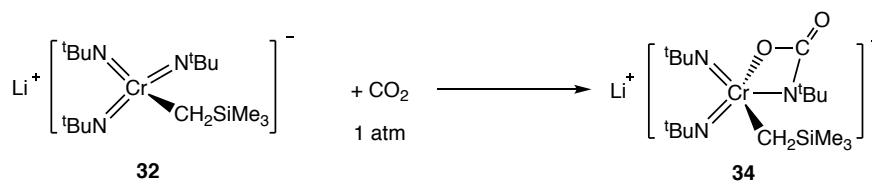
Distances (Å)			
C(1)-N(1)	1.451(7)	C(26)-O(3)	1.319(5)
C(1)-C(4B)	1.496(16)	C(26)-N(6)	1.331(6)
C(1)-C(2B)	1.508(16)	C(26)-Cr(2)	2.442(4)
C(1)-C(3A)	1.513(10)	C(26)-Li(1)	2.775(9)
C(1)-C(3B)	1.514(16)	C(34)-C(35)	1.388(12)
C(1)-C(2A)	1.526(10)	C(34)-C(35)	1.388(12)
C(1)-C(4A)	1.533(9)	C(35)-C(36)	1.367(12)
C(5)-N(2)	1.456(6)	C(36)-C(37)	1.368(9)
C(5)-C(8)	1.519(9)	C(37)-C(38)	1.522(14)
C(5)-C(6)	1.525(9)	Cl(1)-Cr(1)	2.3549(14)
C(5)-C(7)	1.534(8)	Cl(1)-Li(1)	2.399(8)
C(9)-N(3)	1.463(6)	Cl(2)-Cr(2)	2.3493(14)
C(9)-C(12)	1.515(9)	Cl(2)-Li(2)	2.413(8)
C(9)-C(11)	1.517(9)	Cr(1)-N(1)	1.611(5)
C(9)-C(10)	1.524(7)	Cr(1)-N(2)	1.640(5)
C(13)-O(2)	1.264(5)	Cr(1)-N(3)	1.986(4)
C(13)-O(1)	1.320(5)	Cr(1)-O(1)	2.002(3)
C(13)-N(3)	1.330(5)	Cr(1)-Li(1)	3.113(7)
C(13)-Cr(1)	2.443(4)	Cr(2)-N(4)	1.623(4)
C(14)-N(4)	1.450(7)	Cr(2)-N(5)	1.627(5)
C(14)-C(15)	1.519(11)	Cr(2)-N(6)	1.989(4)
C(14)-C(16)	1.523(9)	Cr(2)-O(3)	2.023(3)
C(14)-C(17)	1.534(9)	Cr(2)-Li(2)	3.170(8)
C(18)-N(5)	1.461(8)	Li(1)-O(1)	1.881(9)
C(18)-C(21)	1.520(12)	Li(1)-O(4)	1.933(9)
C(18)-C(19)	1.529(12)	Li(1)-O(4)	1.951(8)
C(18)-C(20)	1.532(12)	Li(1)-Li(1)	2.609(15)
C(22)-N(6)	1.466(6)	Li(2)-O(3)	1.904(8)
C(22)-C(24)	1.512(8)	Li(2)-O(2)	1.911(8)
C(22)-C(25)	1.534(8)	Li(2)-O(2)	1.960(8)
C(22)-C(23)	1.538(7)	Li(2)-Li(2)	2.597(16)

C(26)-O(4) 1.266(5)

Angles (°)			
N(1)-C(1)-C(4B)	115(3)	N(3)-Cr(1)-Li(1)	98.00(19)
N(1)-C(1)-C(2B)	97(3)	O(1)-Cr(1)-Li(1)	35.40(18)
C(4B)-C(1)-C(2B)	113.9(15)	Cl(1)-Cr(1)-Li(1)	49.71(16)
N(1)-C(1)-C(3A)	107.4(6)	C(13)-Cr(1)-Li(1)	65.34(19)
N(1)-C(1)-C(3B)	104(3)	N(4)-Cr(2)-N(5)	111.6(3)
C(4B)-C(1)-C(3B)	113.2(15)	N(4)-Cr(2)-N(6)	102.5(2)
C(2B)-C(1)-C(3B)	112.2(15)	N(5)-Cr(2)-N(6)	104.9(2)
N(1)-C(1)-C(2A)	108.8(6)	N(4)-Cr(2)-O(3)	123.4(2)
C(3A)-C(1)-C(2A)	112.4(7)	N(5)-Cr(2)-O(3)	125.0(2)
N(1)-C(1)-C(4A)	109.4(6)	N(6)-Cr(2)-O(3)	65.08(14)
C(3A)-C(1)-C(4A)	109.9(7)	N(4)-Cr(2)-Cl(2)	92.91(16)
C(2A)-C(1)-C(4A)	109.0(7)	N(5)-Cr(2)-Cl(2)	96.17(18)
N(2)-C(5)-C(8)	105.8(5)	N(6)-Cr(2)-Cl(2)	146.80(12)
N(2)-C(5)-C(6)	110.3(5)	O(3)-Cr(2)-Cl(2)	81.86(9)
C(8)-C(5)-C(6)	111.1(5)	N(4)-Cr(2)-C(26)	112.6(2)
N(2)-C(5)-C(7)	107.1(4)	N(5)-Cr(2)-C(26)	124.1(2)
C(8)-C(5)-C(7)	110.7(6)	N(6)-Cr(2)-C(26)	33.00(15)
C(6)-C(5)-C(7)	111.7(6)	O(3)-Cr(2)-C(26)	32.70(13)
N(3)-C(9)-C(12)	110.7(5)	Cl(2)-Cr(2)-C(26)	113.82(11)
N(3)-C(9)-C(11)	108.8(5)	N(4)-Cr(2)-Li(2)	106.7(2)
C(12)-C(9)-C(11)	111.5(6)	N(5)-Cr(2)-Li(2)	129.1(2)
N(3)-C(9)-C(10)	107.9(4)	N(6)-Cr(2)-Li(2)	97.93(18)
C(12)-C(9)-C(10)	108.7(5)	O(3)-Cr(2)-Li(2)	34.91(17)
C(11)-C(9)-C(10)	109.2(5)	Cl(2)-Cr(2)-Li(2)	49.13(15)
O(2)-C(13)-O(1)	122.6(4)	C(26)-Cr(2)-Li(2)	64.99(18)
O(2)-C(13)-N(3)	128.9(4)	O(1)-Li(1)-O(4)	120.6(5)
O(1)-C(13)-N(3)	108.5(4)	O(1)-Li(1)-O(4)	113.4(4)
O(2)-C(13)-Cr(1)	171.4(3)	O(4)-Li(1)-O(4)	94.4(3)
O(1)-C(13)-Cr(1)	55.0(2)	O(1)-Li(1)-Cl(1)	83.4(3)
N(3)-C(13)-Cr(1)	54.3(2)	O(4)-Li(1)-Cl(1)	118.3(4)
N(4)-C(14)-C(15)	107.8(5)	O(4)-Li(1)-Cl(1)	129.5(4)

N(4)-C(14)-C(16)	108.0(5)	O(1)-Li(1)-Li(1)	123.2(3)
C(15)-C(14)-C(16)	109.8(6)	O(4)-Li(1)-Li(1)	48.1(3)
N(4)-C(14)-C(17)	108.6(5)	O(4)-Li(1)-Li(1)	47.5(3)
C(15)-C(14)-C(17)	112.6(7)	Cl(1)-Li(1)-Li(1)	153.3(2)
C(16)-C(14)-C(17)	110.0(6)	O(1)-Li(1)-C(26)	90.1(3)
N(5)-C(18)-C(21)	107.4(7)	O(4)-Li(1)-C(26)	112.0(3)
N(5)-C(18)-C(19)	107.6(6)	O(4)-Li(1)-C(26)	23.81(17)
C(21)-C(18)-C(19)	113.3(9)	Cl(1)-Li(1)-C(26)	124.8(3)
N(5)-C(18)-C(20)	109.9(6)	Li(1)-Li(1)-C(26)	64.0(3)
C(21)-C(18)-C(20)	109.4(8)	O(1)-Li(1)-Cr(1)	38.06(17)
C(19)-C(18)-C(20)	109.1(8)	O(4)-Li(1)-Cr(1)	118.4(3)
N(6)-C(22)-C(24)	111.3(4)	O(4)-Li(1)-Cr(1)	144.0(4)
N(6)-C(22)-C(25)	106.0(4)	Cl(1)-Li(1)-Cr(1)	48.48(14)
C(24)-C(22)-C(25)	110.7(5)	Li(1)-Li(1)-Cr(1)	154.1(3)
N(6)-C(22)-C(23)	109.3(4)	C(26)-Li(1)-Cr(1)	120.9(3)
C(24)-C(22)-C(23)	110.9(5)	O(3)-Li(2)-O(2)	125.3(4)
C(25)-C(22)-C(23)	108.5(5)	O(3)-Li(2)-O(2)	109.6(4)
O(4)-C(26)-O(3)	121.6(4)	O(2)-Li(2)-O(2)	94.3(4)
O(4)-C(26)-N(6)	129.3(4)	O(3)-Li(2)-Cl(2)	82.6(3)
O(3)-C(26)-N(6)	109.0(4)	O(2)-Li(2)-Cl(2)	117.1(4)
O(4)-C(26)-Cr(2)	167.8(3)	O(2)-Li(2)-Cl(2)	131.4(4)
O(3)-C(26)-Cr(2)	55.9(2)	O(3)-Li(2)-Li(2)	122.9(3)
N(6)-C(26)-Cr(2)	54.5(2)	O(2)-Li(2)-Li(2)	48.7(3)
O(4)-C(26)-Li(1)	38.5(3)	O(2)-Li(2)-Li(2)	47.1(3)
O(3)-C(26)-Li(1)	102.9(3)	Cl(2)-Li(2)-Li(2)	154.4(2)
N(6)-C(26)-Li(1)	130.7(4)	O(3)-Li(2)-Cr(2)	37.46(18)
Cr(2)-C(26)-Li(1)	129.4(2)	O(2)-Li(2)-Cr(2)	123.3(3)
C(35)-C(34)-C(35)	117.6(12)	O(2)-Li(2)-Cr(2)	139.2(3)
C(36)-C(35)-C(34)	120.7(9)	Cl(2)-Li(2)-Cr(2)	47.41(14)
C(35)-C(36)-C(37)	121.2(8)	Li(2)-Li(2)-Cr(2)	155.7(2)
C(36)-C(37)-C(36)	118.5(10)	C(1)-N(1)-Cr(1)	171.1(5)
C(36)-C(37)-C(38)	120.7(5)	C(5)-N(2)-Cr(1)	157.8(5)
C(36)-C(37)-C(38)	120.7(5)	C(13)-N(3)-C(9)	125.3(4)
Cr(1)-Cl(1)-Li(1)	81.8(2)	C(13)-N(3)-Cr(1)	92.8(3)
Cr(2)-Cl(2)-Li(2)	83.46(19)	C(9)-N(3)-Cr(1)	139.8(3)

N(1)-Cr(1)-N(2)	114.1(3)	C(14)-N(4)-Cr(2)	166.6(4)
N(1)-Cr(1)-N(3)	102.2(2)	C(18)-N(5)-Cr(2)	156.1(5)
N(2)-Cr(1)-N(3)	103.27(19)	C(26)-N(6)-C(22)	124.1(4)
N(1)-Cr(1)-O(1)	123.6(2)	C(26)-N(6)-Cr(2)	92.5(3)
N(2)-Cr(1)-O(1)	122.3(2)	C(22)-N(6)-Cr(2)	138.5(3)
N(3)-Cr(1)-O(1)	65.25(14)	C(13)-O(1)-Li(1)	144.3(4)
N(1)-Cr(1)-Cl(1)	93.60(18)	C(13)-O(1)-Cr(1)	92.4(2)
N(2)-Cr(1)-Cl(1)	96.01(16)	Li(1)-O(1)-Cr(1)	106.5(3)
N(3)-Cr(1)-Cl(1)	147.21(12)	C(13)-O(2)-Li(2)	122.3(4)
O(1)-Cr(1)-Cl(1)	82.06(9)	C(13)-O(2)-Li(2)	118.2(3)
N(1)-Cr(1)-C(13)	113.7(2)	Li(2)-O(2)-Li(2)	84.3(4)
N(2)-Cr(1)-C(13)	120.4(2)	C(26)-O(3)-Li(2)	144.7(4)
N(3)-Cr(1)-C(13)	32.93(14)	C(26)-O(3)-Cr(2)	91.4(2)
O(1)-Cr(1)-C(13)	32.67(13)	Li(2)-O(3)-Cr(2)	107.6(3)
Cl(1)-Cr(1)-C(13)	114.29(11)	C(26)-O(4)-Li(1)	125.4(4)
N(1)-Cr(1)-Li(1)	105.5(2)	C(26)-O(4)-Li(1)	117.7(4)
N(2)-Cr(1)-Li(1)	129.1(2)	Li(1)-O(4)-Li(1)	84.4(4)



Scheme 3.14 Reaction of $\text{Li}[(^t\text{BuN})_3\text{Cr}(\text{CH}_2\text{SiMe}_3)]$ (**32**) with CO_2

The reaction of the tris(imido) alkyl complex **32** with CO_2 yielded $\text{Li}\{(^t\text{BuN})_2\text{Cr}[\text{OC}(\text{O})\text{N}^t\text{Bu}](\text{CH}_2\text{SiMe}_3)\}$ (**34**) (Scheme 3.14) instead of the carboxylate complex $\text{Li}[(^t\text{BuN})_3\text{Cr}(\text{O}_2\text{CCH}_2\text{SiMe}_3)]$, which might have resulted from the nucleophilic addition of chromium alkyl to CO_2 . The formation of **32** is consistent with the more nucleophilic nature of the imido nitrogen of π -loaded tris(imido) chromium complex than that of the monoanionic alkyl carbon, commensurate with the orbital interaction diagram depicted in Figure 3.1, showing that the HOMO of $(^t\text{BuN})_3\text{CrL}$ is an imido nitrogen based p_π orbital. The reaction of **32** with CO_2 in THF was also very fast at room temperature, as an immediate color change was observed from deep yellow to light yellow as soon as **32** was exposed to one atmosphere of CO_2 . In the ^1H NMR spectrum of **34**, the remaining two imido ligands are magnetically equivalent with a singlet peak of *tert*-butyl at 1.40 ppm. In the infrared spectrum, the carbonyl group exhibits a strong absorption band at 1560 cm^{-1} . Like the reactions of **28** and **33** with CO_2 , a longer exposure time of **32** in CO_2 did not result in a second addition of CO_2 to the chromium species. This observation might be attributed to the coordinatively crowded chromium center.

3.2.3 Attempted Synthesis of a Molecule Featuring the $\text{Cr}(\text{NAr})_3$ Fragment

My attempt to synthesize a tris(arylimido) chromium(VI) complex started from preparing the analogue of $(^t\text{BuN})_2\text{Cr}(\text{NH}^t\text{Bu})\text{Cl}$, namely $(\text{ArN})_2\text{Cr}(\text{NHAr})\text{Cl}$ ($\text{Ar} =$

2,6-diisopropylphenyl). The synthesis of $(\text{ArN})_2\text{Cr}(\text{NHA}r)\text{Cl}$ was reported by Gibson in 1999.⁴ It was made from the reaction of $(\text{ArN})_2\text{CrCl}_2$ with one equivalent of ArNHLi . The next step was the deprotonation of $(\text{ArN})_2\text{Cr}(\text{NHA}r)\text{Cl}$ by $\text{KN}(\text{SiMe}_3)_2$. However, the desired tris(arylimido) chromium complex, namely $\text{K}[(\text{ArN})_3\text{CrCl}]$, was not observed in the ^1H NMR spectrum after the deprotonation.

3.3 Summary

Multiple chromium complexes featuring the $\text{Cr}(\text{N}^t\text{Bu})_3$ moiety have been made by deprotonation of $(^t\text{BuN})_2\text{Cr}(\text{NH}^t\text{Bu})\text{Cl}$ (**23**), including the first neutral tris(imido) chromium complex $(^t\text{BuN})_3\text{Cr}(\text{PPh}_3)$ (**28**). The imido ligands of these tris(imido) complexes are subject to be attacked by electrophiles (i.e. MeI , PhNCO , CO_2). With carbonyl containing electrophiles, tris(imido) complexes undergo $[2+2]$ cycloaddition to form metallacycles.

3.4 Experimental

3.4.1 General Considerations

All manipulations were carried out with standard Schlenk, vacuum line, and glovebox techniques. Pentane, diethyl ether, toluene and tetrahydrofuran were dried by passing through activated alumina and were degassed prior to use. THF-d_8 and C_6D_6 were purchased from Cambridge Isotopes Laboratory, dried with sodium and stored under vacuum over Na/K alloy. CO_2 gas was purchased from Keen Compressed Gas Co. and dried with an inline moisture trap. *tert*-butylisocyanate, lithium reagents, $\text{KN}(\text{SiMe}_3)_2$, MeI , PPh_3 and $^t\text{BuNH}_2$ were purchased from Sigma Aldrich. $^t\text{BuNH}_2$ was dried with molecular sieves. $^t\text{BuNHLi}$ was prepared by deprotonation of $^t\text{BuNH}_2$

with $n\text{BuLi}$ in Et_2O . $(^t\text{BuN})_2\text{Cr}(\text{OSiMe}_3)_2$ ¹ and $(^t\text{BuN})_2\text{CrCl}_2$ ² were prepared according to the literature procedures.

^1H NMR spectra were taken on a Bruker AVIII-400 spectrometer and were referenced to the residual protons of the solvent ($\text{C}_6\text{D}_6 = 7.16$ ppm, $\text{THF-d}_8 = 3.58$ ppm and 1.72 ppm). ^{13}C NMR spectra were taken on a Bruker AVIII-400 spectrometer or a Bruker AVIII-600 spectrometer and were referenced to the ^{13}C of the solvent ($\text{C}_6\text{D}_6 = 128.06$ ppm, $\text{THF-d}_8 = 67.21$ ppm and 25.31 ppm).²² FT-IR spectra were obtained using a Nicolet Magna-IR 560 spectrometer with a resolution of 4 cm^{-1} . UV-vis spectra were obtained using a SILVER-Nova-TEC-X2 equipped with SL1-LED, which was purchased from StellarNet Inc. X-ray crystallographic studies were conducted in the X-ray Crystallographic Laboratory at the University of Delaware. Elemental analyses were obtained from Robertson Microlit, Ledgewood, NJ. LIFDI-MS were obtained using a Waters GCT Premier high-resolution time-of-flight mass spectrometer by liquid injection field desorption ionization (LIFDI-MS).

3.4.2 X-ray Crystallography

Crystals of **27**, **28**, **29**, **30**, **31**, **32** and **33** were mounted onto plastic mesh using viscous oil and flash-cooled to the data collection temperature. Data were collected on a Bruker-AXS APEX II Duo CCD diffractometer with graphite-monochromated $\text{Mo-K}\alpha$ radiation ($\lambda=0.71073\text{ \AA}$) for **27**, **28**, **30**, **31**, **32**; and with $\text{Cu-K}\alpha$ radiation ($\lambda = 1.54178\text{ \AA}$) focused with Goebel mirrors for **29**, **33**. Unit cell parameters were determined by sampling three different sections of the Ewald sphere. No symmetry higher than triclinic was observed for **27** and solution in the centrosymmetric space group option, $P\bar{1}$, yielded chemically reasonable and computationally stable results of refinement. The systematic absences in the diffraction data are uniquely consistent

with $C 2/c$ for **28** and **33**. The unit cell parameters and systematic absences in the diffraction data were consistent for space group $P na2_1$ for **29**, $P 2_1/n$ for **30** and **32**. No symmetry higher than triclinic was observed for **31** and solution in the centrosymmetric space group option, $P \bar{1}$, yielded chemically reasonable and computationally stable results of refinement. The data sets were treated with absorption corrections based on redundant multi-scan data.²³ The structures were solved using intrinsic phasing and refined with full-matrix, least-squares procedures on F^2 .²⁴⁻²⁵

Two molecules of **27** were found in the crystal structure with an inversion center. Potassium cations behave as bridges between two chromium centers. The amido hydrogen was located on a difference map and its location was refined.

The iodide ligand and one amido ligand in **29** were found disordered in two positions with a refined site occupancy ratio of 80/20.

The *tert*-butyl group of one imido ligand in **32** was found disordered in two positions with a refined site occupancy ratio of 81/19. Two imido ligands and one molecule of diethyl ether are coordinated to the lithium cation.

Four molecules of **33** were found in one structure due to the linkage of lithium cation. Three molecules of toluene were also found in this crystal structure.

All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were treated as idealized contributions. Atomic scattering factors are contained in the SHELXTL program library.

3.4.3 Preparation of (^tBuN)₂Cr(NH^tBu)Cl (**23**)

(^tBuN)₂CrCl₂ (0.500 g, 1.887 mmol) was dissolved in 80 mL Et₂O, giving a brown solution. The solution was stored at -30 °C for 15 min before adding ^tBuNHLi,

which is prepared from deprotonation of $t\text{BuNH}_2$ by $n\text{BuLi}$. 1 equiv. of $t\text{BuNHLi}$ (0.149 g, 1.886 mmol, dissolved in 15 mL Et_2O) was added into the pre-chilled ($-30\text{ }^\circ\text{C}$) solution. After addition, solvent was removed in vacuum immediately. The residue was extracted with pentane and the extract was filtered without Celite. The filtrate was concentrated to 20 mL then cooled to $-30\text{ }^\circ\text{C}$ overnight to yield orange crystals. Yield: 0.378 g, 66%. ^1H NMR (400 MHz, C_6D_6): δ 11.49 (s, 1 H, NH^tBu), 1.34 (s, 18 H, $t\text{Bu}$), 1.23 (s, 9 H, $t\text{Bu}$) ppm. Full characterization has been reported by Wilkinson.

3.4.4 Preparation of $\text{K}[(t\text{BuN})_3\text{CrCl}]$ (24a)

$(t\text{BuN})_2\text{Cr}(\text{NH}^t\text{Bu})\text{Cl}$ (0.200g, 0.663 mmol) was dissolved in 50 mL THF, giving a red orange solution. 1 equiv. of $\text{KN}(\text{SiMe}_3)_2$ (0.132 g, 0.663 mmol) was added into the THF solution. The solution was stirred at room temperature for 15 minutes, during which time the color changed from red orange to red purple. Then all volatile solvents were removed in vacuum. The residue was washed with chilled pentane and filtered to give the product as red powder, which needs to be washed again with 10 mL chilled Et_2O . The powder left in the frit is pure enough for characterization and synthesis. Yield: 0.171 g, 76%. ^1H NMR (400 MHz, $d_8\text{-THF}$): δ 1.39 (s, 18 H, $t\text{Bu}$) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, $d_8\text{-THF}$) δ 69.12 (CMe_3 of $t\text{Bu}$), 33.00 (CMe_3 of $t\text{Bu}$) ppm. IR (KBr, cm^{-1}): 2969 (s), 2921 (m), 2860 (w), 1452 (w), 1352 (m), 1234 (m), 1201 (s), 1026 (w), 804 (w), 793 (w), 618 (w), 597 (w). M.p.: $172\text{ }^\circ\text{C}$. Anal. Calc. for $\text{C}_{12}\text{H}_{27}\text{CrN}_3\text{KCl}$: C, 42.40; H, 8.01; N, 12.36. Found: C, 41.18; H, 7.86; N, 11.87. UV-vis (THF): λ_{max} (ϵ) = 260.5 (5.311×10^4), 508 (1.986×10^3) nm ($\text{M}^{-1}\text{cm}^{-1}$).

3.4.5 Preparation of (^tBuN)₂Cr(NMe^tBu)Cl (25)

K[(^tBuN)₃CrCl] (0.114 g, 0.336 mmol) was dissolved in 30 mL THF, giving a red purple solution. 20 equiv. of MeI (0.418 mL, 6.716 mmol) The solution was stirred at room temperature for 1 day during which time the color changed to deep red. The solvent and excess MeI was then removed in vacuum. The residue was extracted with pentane and the extract was filtered through Celite. Pentane was removed in vacuum to afford the product as a red oil. Yield: 0.087 g, 82 %. ¹H NMR (400 MHz, C₆D₆): δ 4.16 (s, 3 H, NMe^tBu), 1.38 (s, 9 H, NMe^tBu), 1.32 (s, 18 H, N^tBu) ppm. ¹³C{¹H} NMR (100 MHz, C₆D₆): δ 75.82 (CMe₃ of N^tBu), 75.36 (CMe₃ of N^tBu), 65.39 (CMe₃ of NMe^tBu), 55.41 (NMe^tBu), 31.27 (CMe₃ of NMe^tBu), 30.96 (CMe₃ of N^tBu), 30.90 (CMe₃ of N^tBu) ppm. IR (KBr, cm⁻¹): 2972 (s), 2924 (m), 2861 (w), 1471 (w), 1451 (w), 1387 (w), 1357 (m), 1202 (s), 1155 (w), 880 (w), 804 (w), 772 (w). MS(LIFDI) m/z: 315.1667 [M⁺]. Calcd. m/z: 315.1534 [M⁺]. UV-vis (pentane): λ_{max} (ε) = 245 (1.749*10⁴), 298 (1.345*10⁴), 347 (9.255*10³), 486 (5.249*10³), 685 (1.035*10³) nm (M⁻¹cm⁻¹).

3.4.6 Preparation of (^tBuN)₂Cr(NH^tBu)₂ (26)

(^tBuN)₂Cr(NH^tBu)Cl (0.100g, 0.332 mmol) was dissolved in 40 mL THF, giving a red orange solution. 1 equiv. of KN(SiMe₃)₂ (0.066 g, 0.332 mmol) were added into the THF solution. The solution was stirred at room temperature for 15 minutes. Then all volatile solvents were removed in vacuum. The residue was washed with chilled pentane and filtered to give product K[(^tBuN)₃CrCl] as powder, which needs to be washed again with chilled Et₂O. K[(^tBuN)₃CrCl] was dissolved in 40 mL THF, giving a red purple solution. 10 equiv. of ^tBuNH₂ (0.35 mL, 3.317 mmol) was added into solution. The solution was stirred at room temperature overnight, during

which time the color changed to purple. The solvent and excess $t\text{BuNH}_2$ were then removed in vacuum. The residue was extracted with pentane and the extract was filtered through Celite. Pentane was removed in vacuum and the leftover is a red oily product, which is pure enough for characterization and synthesis. Yield: 0.100 g, 89%. Alternative procedure and full characterization have been reported by Wilkinson and co-workers.

3.4.7 Preparation of $\text{K}[(t\text{BuN})_3\text{Cr}(\text{NH}^i\text{Bu})]$ (27)

$(t\text{BuN})_2\text{Cr}(\text{NH}^i\text{Bu})_2$ (0.111 g, 0.328 mmol) was dissolved in 50 mL THF, giving a purple solution. 1 equiv. of $\text{KN}(\text{SiMe}_3)_2$ (0.065 g, 0.328 mmol) was added into the solution at room temperature. The solution was stirred for 15 minutes during which time no color change was observed. Then all volatile solvents were removed in vacuum. The residue was washed with pentane and filtered to give product as powder. The product was then dissolved in a minimum amount of Et_2O for the purpose of recrystallization. Red crystals with clear edges were grown from saturated Et_2O solution at $-30\text{ }^\circ\text{C}$. Yield: 0.105 g, 85%. ^1H NMR (400 MHz, d_8 -THF): δ 7.15 (broad, 1 H, NH^iBu), 1.33 (s, 27 H, N^iBu), 1.02 (s, 9 H, NH^iBu) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, d_8 -THF): δ 66.48 (CMe_3 of N^iBu), 50.46 (CMe_3 of NH^iBu), 35.11 (CMe_3 of NH^iBu), 33.30 (CMe_3 of N^iBu) ppm. IR (KBr, cm^{-1}): 3354 (w), 2967 (s), 2949 (s), 2921 (m), 2857 (w), 1454 (w), 1382 (w), 1350 (m), 1231 (m), 1201 (s), 1039 (w), 1021 (w), 954 (w), 804 (w), 791 (w), 652 (w), 609 (w), 555 (w). M.p.: $203\text{ }^\circ\text{C}$. Anal. Calc. for $\text{C}_{16}\text{H}_{37}\text{CrN}_4\text{K}$: C, 51.03; H, 9.90; N, 14.88. Found: C, 45.19; H, 8.96; N, 13.26. UV-vis (THF): λ_{max} (ϵ) = 279 (5.046×10^3), 367 (1.713×10^3), 532.5 (8.444×10^2) nm ($\text{M}^{-1}\text{cm}^{-1}$).

3.4.8 Preparation of (^tBuN)₃CrPPh₃ (28)

(^tBuN)₂Cr(NH^tBu)Cl (0.100 g, 0.332 mmol) was dissolved in 40 mL THF, giving a red orange solution. 1 equiv. of KN(SiMe₃)₂ (0.066 g, 0.332 mmol) were added into the THF solution. The solution was stirred at room temperature for 15 minutes. Then all volatile solvents were removed in vacuum. The residue was washed with pentane and filtered to give product K[(^tBuN)₃CrCl] as powder, which needs to be washed again with chilled Et₂O. K[(^tBuN)₃CrCl] was dissolved in 40 mL THF, giving a red purple solution. 0.8 equiv. of PPh₃ (0.070 g, 0.266 mmol) was added into solution. The solution was stirred at room temperature for 2 days, during which time the color changed to purple. The solvent was then removed in vacuum. The residue was extracted with pentane and the extract was filtered through Celite. The filtrate was concentrated to 3 mL then cooled to -30 °C overnight to yield purple crystals. Yield: 0.130 g, 74%. ¹H NMR (400 MHz, C₆D₆): δ 7.87 (m, 6 H, PPh₃), 7.07 (m, 9 H, PPh₃), 1.52 (s, 27 H, ^tBu) ppm. ¹³C{¹H} NMR (100 MHz, C₆D₆): δ 135.04 (*C_{ortho}*), 131.96 (*C_{ipso}*), 130.61 (*C_{para}*), 128.54 (*C_{meta}*), 69.71 (^tBu), 32.46 (^tBu) ppm. ³¹P{¹H} NMR (162 MHz, C₆D₆): δ 56.19 ppm. IR (KBr, cm⁻¹): 3047 (w), 2962 (s), 2934 (w), 2914 (w), 2854 (w), 1481 (w), 1436 (m), 1351 (w), 1199 (s), 1099 (m), 1028 (w), 800 (w), 747 (w), 709 (w), 694 (m), 622 (w), 528 (m), 503 (w), 441 (w). M.p.: 211 °C. MS(LIFDI) m/z: 527.2533 [M⁺]. Calcd. m/z: 527.2521 [M⁺]. Anal. Calc. for C₃₀H₄₂CrN₃P: C, 68.29; H, 8.02; N, 7.96. Found: C, 67.04; H, 8.01; N, 7.45. UV-vis (pentane): λ_{max} (ε) = 269.5 (1.114*10⁴), 294.5 (1.030*10⁴), 518 (1.462*10³) nm (M⁻¹cm⁻¹).

3.4.9 Preparation of (^tBuN)₂Cr(NMe^tBu)I (29)

(^tBuN)₃CrPPh₃ (0.060 g, 0.114 mmol) was added into 6 mL MeI, giving a red purple solution. The solution was stirred at room temperature for 1 day, during which time the color of solution changed to deep red. MeI was then removed in vacuum and the residue was extracted with pentane. Insoluble white precipitate Ph₃PCH₃I was removed by filtration. The filtrate was concentrated to 1 mL then cooled to -30 °C overnight to yield red crystals. Yield: 0.040 g, 86 %. ¹H NMR (400 MHz, C₆D₆): δ 3.70 (s, 3 H, NMe^tBu), 1.40 (s, 9 H, NMe^tBu), 1.36 (s, 9 H, N^tBu), 1.31 (s, 9 H, N^tBu) ppm. ¹³C{¹H} NMR (150 MHz, C₆D₆): δ 76.21 (CMe₃ of N^tBu), 75.73 (CMe₃ of N^tBu), 67.01 (CMe₃ of NMe^tBu), 56.41 (NMe^tBu), 31.44 (CMe₃ of NMe^tBu), 31.08 (CMe₃ of N^tBu), 31.04 (CMe₃ of N^tBu) ppm. IR (KBr, cm⁻¹): 2972 (s), 2924 (m), 2863 (w), 1451 (w), 1387 (w), 1357 (m), 1202 (s), 1155 (w), 883 (w), 805 (w), 772 (w). M.p.: 75 °C. MS(LIFDI) m/z: 407.0887 [M⁺]. Calcd. m/z: 407.0890 [M⁺]. Anal. Calc. for C₁₃H₃₀CrN₃I: C, 38.34; H, 7.42; N, 10.32. Found: C, 37.82; H, 7.45; N, 9.95. UV-vis (pentane): λ_{max} (ε) = 244 (1.653*10⁴), 277 (7.175*10³), 356 (3.581*10³), 468 (2.593*10³) nm (M⁻¹cm⁻¹).

3.4.10 Preparation of (^tBuN)₂Cr{[PhNC(O)]₂N^tBu} (30)

(^tBuN)₃CrPPh₃ (0.154 g, 0.292 mmol) was dissolved in 50 mL pentane, giving a purple solution. 10 equiv. of PhNCO (0.32 mL, 2.931 mmol) was added into solution. The solution was stirred at room temperature for 30 minutes during which time the color changed to orange. The solvent was then removed in vacuum. The residue was washed with chilled pentane and filtered to remove excess PhNCO. Leftover in the frit was dissolved in large amount of pentane due to low solubility in pentane. Recrystallization through slow evaporation of pentane solution gave red

crystals. Yield: 0.042 g, 29 %. ^1H NMR (400 MHz, C_6D_6): δ 7.52 (d, 4 H, H_{ortho}), 7.08 (t, 4 H, H_{meta}), 6.87 (t, 2 H, H_{para}), 1.87 (s, 9 H, ^tBu), 1.46 (s, 9 H, ^tBu), 0.67 (s, 9 H, ^tBu) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, C_6D_6): δ 152.30 (C=O), 148.12 (C_{ipso}), 128.49 (C_{ortho}), 124.85 (C_{para}), 124.36 (C_{meta}), 81.30 (CMe_3 of ^tBu), 76.16 (CMe_3 of ^tBu), 61.67 (CMe_3 of ^tBu), 31.47 (CMe_3 of ^tBu), 30.31 (CMe_3 of ^tBu), 28.33 (CMe_3 of ^tBu) ppm. IR (KBr, cm^{-1}): 2976 (w), 2926 (w), 1720 (s), 1595 (w), 1489 (w), 1451 (w), 1394 (w), 1347 (w), 1329 (w), 1319 (w), 1194 (w), 1061 (w), 973 (w), 756 (w), 694 (w). M.p.: 170 °C. MS(LIFDI) m/z : 503.2365 [M^+]. Calcd. m/z : 503.2352 [M^+]. Anal. Calc. for $\text{C}_{26}\text{H}_{37}\text{CrN}_5\text{O}_2$: C, 62.01; H, 7.41; N, 13.91. Found: C, 63.72; H, 7.23; N, 13.40. UV-vis (pentane): λ_{max} (ϵ) = 256 (9.892×10^4), 343.5 (1.441×10^4), 487 (4.452×10^3) nm ($\text{M}^{-1}\text{cm}^{-1}$).

3.4.11 Preparation of $(^t\text{BuN})_2\text{Cr}[\text{OC}(\text{O})\text{N}^t\text{Bu}](\text{PPh}_3)$ (31)

$(^t\text{BuN})_3\text{CrPPh}_3$ (0.100 g, 0.190 mmol) was dissolved in 20 mL pentane, giving a purple solution. The ampule was degassed by doing freeze-pump-thaw three times. Then 1 atmosphere of CO_2 was charged to the ampule. Upon addition of CO_2 , solution changed to orange cloudy immediately due to product with low solubility in pentane. Then the solvent and CO_2 were removed in vacuum. The residue was washed with chilled pentane and filtered to give product as powder. Yield: 0.088 g, 81 %. Recrystallization would afford red crystals by slow evaporation of THF solution. ^1H NMR (400 MHz, $\text{d}_8\text{-THF}$): δ 7.81 (m, 6 H, PPh_3), 7.00 (m, 9 H, PPh_3), 1.80 (s, 9 H, ^tBu), 1.15 (s, 18 H, ^tBu) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, $\text{d}_8\text{-THF}$) δ 163.93 (C=O), 135.24 (C_{ortho}), 132.17 (C_{ipso}), 131.53 (C_{para}), 129.10 (C_{meta}), 76.94 (CMe_3 of ^tBu), 76.89 (CMe_3 of ^tBu), 53.05 (CMe_3 of carbamate ^tBu), 31.75 (CMe_3 of ^tBu), 31.70 (CMe_3 of ^tBu), 31.49 (CMe_3 of carbamate ^tBu) ppm. IR (KBr, cm^{-1}): 3046 (w), 2978

(w), 2923 (w), 1649 (s), 1583 (w), 1570 (w), 1480 (w), 1435 (w), 1353 (w), 1281 (w), 1223 (w), 1190 (w), 1096 (w), 1064 (w), 942 (w), 800 (w), 792 (w), 751 (w), 710 (w), 693 (w), 525 (w), 509 (w), 496 (w). M.p.: 90 °C (dec). MS(LIFDI) m/z: 527.2534 [M⁺-CO₂]. Calcd. m/z: 527.2521 [M⁺-CO₂]. Anal. Calc. for C₃₁H₄₂CrN₃O₂P: C, 65.13; H, 7.41; N, 7.35. Found: C, 63.76; H, 7.42; N, 6.85. UV-vis (pentane): λ_{max} (ε) = 272 (1.216*10⁴), 368.5 (2.500*10³), 494 (769.3) nm (M⁻¹cm⁻¹).

3.4.12 Preparation of Li[(^tBuN)₃CrCl] (24b)

(^tBuN)₂Cr(NH^tBu)Cl (0.150 g, 0.498 mmol) was dissolved in 50 mL Et₂O, giving a red orange solution. 1 equiv. of Me₃SiCH₂Li (0.50 mL, 1.0 M, 0.50 mmol) were added into the Et₂O solution. The solution was stirred at room temperature for 1 hour, during which time the color changed from red orange to orange. All volatile solvents were removed in vacuum. The residue was washed with chilled pentane and filtered to give product **24b** as orange powder, which is pure enough for characterization and synthesis. Yield: 0.135 g, 88%. ¹H NMR (400 MHz, d₈-THF): δ 1.43 (s, 18 H, ^tBu) ppm. ¹³C{¹H} NMR (150 MHz, d₈-THF) δ 70.31 (CMe₃ of ^tBu), 33.08 (CMe₃ of ^tBu) ppm. IR (KBr, cm⁻¹): 2972 (s), 2924 (m), 1472 (w), 1455 (w), 1356 (m), 1210 (s), 925 (w), 823 (m), 805 (m). M.p.: 130 °C (dec). Anal. Calc. for C₁₆H₃₅CrON₃ClLi (with one coordinated THF): C, 50.59; H, 9.29; N, 11.06. Found: C, 51.31; H, 10.27; N, 10.74. UV-vis (THF): λ_{max} (ε) = 275 (6.121*10³), 324 (3.720*10³), 468.5 (1.181*10³) nm (M⁻¹cm⁻¹).

3.4.13 Preparation of Li[(^tBuN)₃Cr(CH₂SiMe₃)] (32)

(^tBuN)₂Cr(NH^tBu)Cl (0.100 g, 0.332 mmol) was dissolved in 40 mL Et₂O, giving a red orange solution. 2 equiv. of Me₃SiCH₂Li (0.67 mL, 1.0 M, 0.67 mmol)

were added into the Et₂O solution. The solution was stirred at room temperature for 4 hours, during which time the color changed from red orange to brown upon addition finished and then slowly to green. The solvent was then removed in vacuum and the residue was extracted with pentane, giving an orange brown solution. Pentane solution was filtered through frit. Then the filtrate was concentrated to 2 mL and stored at -30 °C overnight to yield yellow crystals. Yield: 0.070 g, 59%. ¹H NMR (400 MHz, C₆D₆): δ 3.05 (q, 4 H, CH₂ of coordinated Et₂O), 1.56(s, 27 H, ^tBu), 0.93 (t, 6 H, CH₃ of coordinated Et₂O), 0.34 (s, 9 H, CH₂SiMe₃), 0.24 (s, 2 H, CH₂SiMe₃) ppm. ¹³C{¹H} NMR (100 MHz, C₆D₆): δ 71.23 (CMe₃ of linear CrN^tBu), 66.49 (CH₂ of coordinated Et₂O), 65.87 (CMe₃ of bent CrN^tBu), 35.10 (CMe₃ of bent CrN^tBu), 32.49 (CMe₃ of linear CrN^tBu), 14.70 (CH₃ of coordinated Et₂O), 9.42 (CH₂SiMe₃), 2.96 (CH₂SiMe₃) ppm. IR (KBr, cm⁻¹): 2970 (s), 2922 (m), 2896 (w), 1453 (w), 1386 (w), 1354 (m), 1239 (s), 1208 (s), 966 (w), 933 (w), 905 (w), 852 (m), 826 (m), 787 (w), 714 (w), 675 (w), 458 (w). M.p.: 81 °C. UV-vis (THF): λ_{max} (ε) = 247.5 (3.003*10⁴), 273 (2.826*10⁴), 358.5 (1.205*10⁴), 448 (3.318*10³) nm (M⁻¹cm⁻¹).

3.4.14 Preparation of Li{(^tBuN)₂Cr[OC(O)N^tBu]Cl} (33)

Li[(^tBuN)₃CrCl] (0.050 g, 0.162 mmol) was dissolved in 10 mL THF, giving an orange solution. The ampule was degassed by doing freeze-pump-thaw three times. Then 1 atmosphere of CO₂ was charged to the ampule. Upon addition of CO₂, solution color changed to light orange. After 30 minutes at room temperature, the solvent and CO₂ were removed in vacuum. The residue was extracted with pentane and filtered to give light orange solution. The solution was concentrated to 5 mL and stored at -30 °C overnight to give red crystals. Yield: 0.050 g, 87 %. ¹H NMR (400 MHz, C₆D₆): δ 1.51 (s, 18 H, ^tBu), 1.44 (s, 9 H, carbamate ^tBu) ppm. ¹³C{¹H} NMR (150 MHz, C₆D₆):

δ 165.82 (C=O), 78.15 (CMe₃ of imido ^tBu), 52.00 (CMe₃ of carbamate ^tBu), 31.17 (CMe₃ of carbamate ^tBu), 30.90 (CMe₃ of imido ^tBu) ppm. IR (KBr, cm⁻¹): 2974 (m), 2925 (w), 2863 (w), 1620 (m), 1578 (s), 1470 (w), 1454 (w), 1357 (s), 1217 (m), 1198 (m), 1113 (w), 804 (w), 620 (w), 583 (w), 455 (w). M.p.: 195 °C (dec, red to black). Anal. Calc. for C₁₃H₂₇CrN₃O₂ClLi: C, 44.39; H, 7.74; N, 11.95. Found: C, 43.31; H, 7.93; N, 11.09. UV-vis (THF): λ_{max} (ϵ) = 259 (2.211*10⁴), 412 (2.857*10³) nm (M⁻¹cm⁻¹).

3.4.15 Preparation of Li{(^tBuN)₂Cr[OC(O)N^tBu](CH₂SiMe₃)} (34)

Li[(^tBuN)₃Cr(CH₂SiMe₃)] (0.050 g, 0.139 mmol) was dissolved in 10 mL THF, giving a yellow solution. The ampule was degassed by doing freeze-pump-thaw three times. Then 1 atmosphere of CO₂ was charged to the ampule. Upon addition of CO₂, solution color changed to light yellow. After 30 minutes at room temperature, the solvent and CO₂ were removed in vacuum. The residue was washed with chilled pentane and filtered to give yellow powder. Yield: 0.036 g, 64 %. ¹H NMR (400 MHz, d₈-THF): δ 1.40 (s, 18 H, ^tBu), 1.26 (s, 9 H, carbamate ^tBu), 0.92 (s, 2 H, CH₂SiMe₃), 0.03 (s, 9 H, CH₂SiMe₃) ppm. ¹³C NMR (150 MHz, d₈-THF): δ 168.71 (C=O), 71.69 (CMe₃ of imido ^tBu), 50.41 (CMe₃ of carbamate ^tBu), 31.69 (CMe₃ of imido ^tBu), 31.31 (CMe₃ of carbamate ^tBu), 26.19 (CH₂SiMe₃), 3.54 (CH₂SiMe₃) ppm. IR (KBr, cm⁻¹): 2972 (s), 2925 (m), 2896 (w), 1560 (s), 1473 (w), 1453 (m), 1393 (m), 1376 (s), 1355 (s), 1239 (s), 1218 (s), 1203 (s), 1105 (w), 940 (w), 851 (s), 825 (m), 806 (w), 680 (w), 468 (w). M.p.: 150 °C (dec, yellow to black). UV-vis (THF): λ_{max} (ϵ) = 264.5 (3.832*10⁴), 387 (7.043*10³) nm (M⁻¹cm⁻¹).

Table 3.8 Crystallographic data for complexes **27** to **33**

	27 (kla0911)	28 (kla0841)	29 (kla0889)
Formula	C ₁₆ H ₃₇ CrKN ₄	C ₃₀ H ₄₂ CrN ₃ P	C ₁₃ H ₃₀ CrIN ₃
Formula Wt.	376.59	527.63	401.30
Space group	<i>P</i> $\bar{1}$	<i>C</i> 2/ <i>c</i>	<i>P</i> <i>na</i> 2 ₁
Color	red	red	red
a, Å	9.3756(3)	22.9096(15)	12.9687(5)
b, Å	10.4258(4)	17.1035(11)	10.1027(5)
c, Å	11.2630(4)	19.5779(13)	14.8888(6)
α, deg	81.4960(10)	90	90
β, deg	88.4080(10)	125.4502(10)	90
γ, deg	80.3100(10)	90	90
V, Å ³	1073.29(7)	6249.2(7)	1950.71(15)
Z	2	8	4
D(calcd), g/cm ³	1.165	1.122	1.387
μ, mm ⁻¹	0.730	0.438	17.164
Temp, K	200	200	200
T _{max} /T _{min}	0.7456/0.6902	0.7456/0.6690	0.7539/0.4757
No. data/params	5009/226	7343/325	3510/199
GOF on F ²	1.048	1.069	1.007
R1(F), % ^a	2.97	4.41	4.80
wR ² (F ²), % ^a	7.86	11.96	12.97

^a Quantity minimized: $wR^2(F^2) = \sum[w(F_o^2 - F_c^2)^2] / \sum[(wF_o^2)^2]^{1/2}$; $R1 = \sum \Delta / \sum (F_o)$, $\Delta = |(F_o - F_c)|$.

Table 3.8 Crystallographic data for complexes **27** to **33** (continued)

	30 (kla0885)	31 (kla0891)	32 (kla0920)
Formula	C ₂₆ H ₃₇ CrN ₅ O ₂	C ₃₁ H ₄₂ CrN ₃ O ₂ P	C ₂₀ H ₄₈ CrLiN ₃ OSi
Formula Wt.	503.60	571.64	433.64
Space group	<i>P</i> 21/ <i>n</i>	<i>P</i> $\bar{1}$	<i>P</i> 21/ <i>n</i>
Color	red	orange	yellow
<i>a</i> , Å	9.4986(4)	9.4534(4)	10.2601(17)
<i>b</i> , Å	11.4306(5)	10.8633(5)	18.153(3)
<i>c</i> , Å	24.3356(12)	14.9190(7)	15.166(3)
α , deg	90	82.7080(10)	90
β , deg	90.6287(9)	87.0810(10)	95.535(3)
γ , deg	90	89.1490(10)	90
<i>V</i> , Å ³	2642.1(2)	1517.69(12)	2811.4(8)
<i>Z</i>	4	2	4
<i>D</i> (calcd), g/cm ³	1.266	1.251	1.025
μ , mm ⁻¹	0.464	0.461	0.461
Temp, K	200	200	200
<i>T</i> _{max} / <i>T</i> _{min}	0.7456/0.6931	0.7456/0.7041	0.6826/0.4914
No. data/params	6182/316	7145/352	6462/265
GOF on <i>F</i> ²	1.005	1.033	1.063
<i>R</i> 1(<i>F</i>), % ^a	3.73	3.74	6.18
<i>wR</i> ² (<i>F</i> ²), % ^a	10.33	9.98	18.05

^a Quantity minimized: $wR^2(F^2) = \sum[w(F_o^2 - F_c^2)^2] / \sum[(wF_o^2)^2]^{1/2}$; $R1 = \sum \Delta / \sum (F_o)$, $\Delta = |(F_o - F_c)|$.

Table 3.8 Crystallographic data for complexes **27** to **33** (continued)

33 (kla0934)	
Formula	C ₅₂ H ₁₀₈ Cr ₄ Li ₄ N ₁₂ O ₈ , 3 (C ₇ H ₈)
Formula Wt.	1683.47
Space group	<i>C2/c</i>
Color	orange
a, Å	22.3193(7)
b, Å	15.0752(5)
c, Å	29.8393(11)
α, deg	90
β, deg	110.258(2)
γ, deg	90
V, Å ³	9418.9(6)
Z	16
D(calcd), g/cm ³	1.187
μ, mm ⁻¹	5.153
Temp, K	200
T _{max} /T _{min}	0.7539/0.5069
No. data/params	9671/486
GOF on F ²	1.033
R1(F), % ^a	7.88
wR ² (F ²), % ^a	19.90

^a Quantity minimized: $wR^2(F^2) = \sum[w(F_o^2 - F_c^2)^2] / \sum[(wF_o^2)^2]^{1/2}$; $R1 = \sum \Delta / \sum(F_o)$, $\Delta = |(F_o - F_c)|$.

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Appendix A

¹H AND ¹³C NMR SPECTRA OF ALL COMPLEXES

General considerations: ¹H NMR spectra were taken on a Bruker AVIII-400 spectrometer and were referenced to the residual protons of the solvent (C₆D₆ = 7.16 ppm, THF-d₈ = 3.58 ppm and 1.72 ppm). ¹³C NMR spectra were taken on a Bruker AVIII-400 spectrometer or Bruker AVIII600 spectrometer and were referenced to the ¹³C of the solvent (C₆D₆ = 128.06 ppm, THF-d₈ = 67.21 ppm and 25.31 ppm).

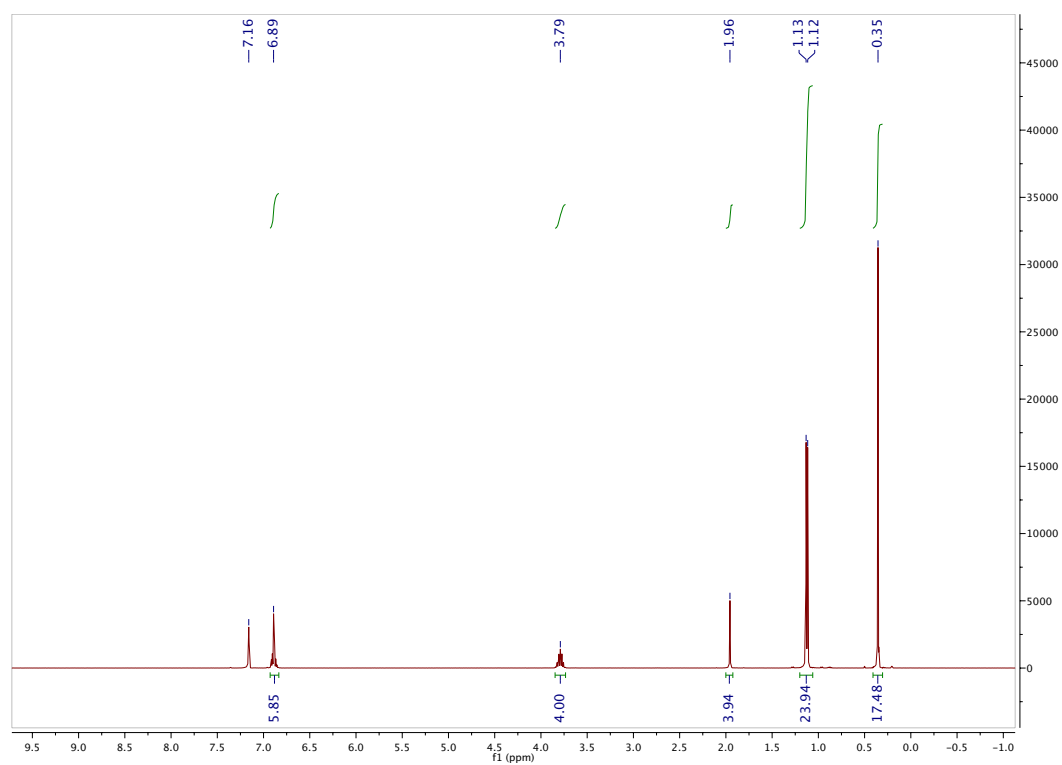


Figure A.1 ^1H NMR spectrum of **7** in C_6D_6 (400 MHz): δ 6.89 (m, 6 H, ArN), 3.79 (sept, 4 H, CHMe_2), 1.96 (s, 4 H, CH_2SiMe_3), 1.12(d, 24 H, CHMe_2), 0.35 (s, 18 H, CH_2SiMe_3) ppm.

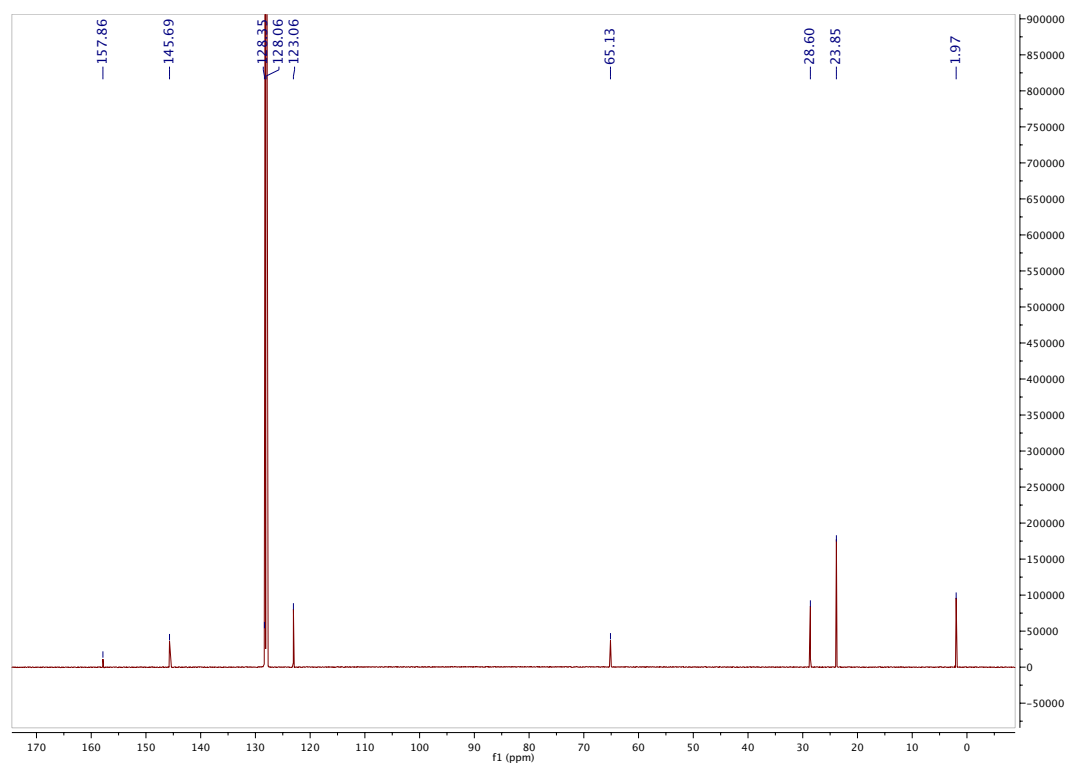


Figure A.2 $^{13}C\{^1H\}$ NMR spectrum of **7** in C_6D_6 (150 MHz): δ 157.86 (C_{ipso} of ArN), 145.69 (C_{ortho} of ArN), 128.35 (C_{para} of ArN), 123.06 (C_{para} of ArN), 65.13 (CH_2SiMe_3), 28.60 ($CHMe_2$), 23.85 ($CHMe_2$), 1.97 (CH_2SiMe_3) ppm.

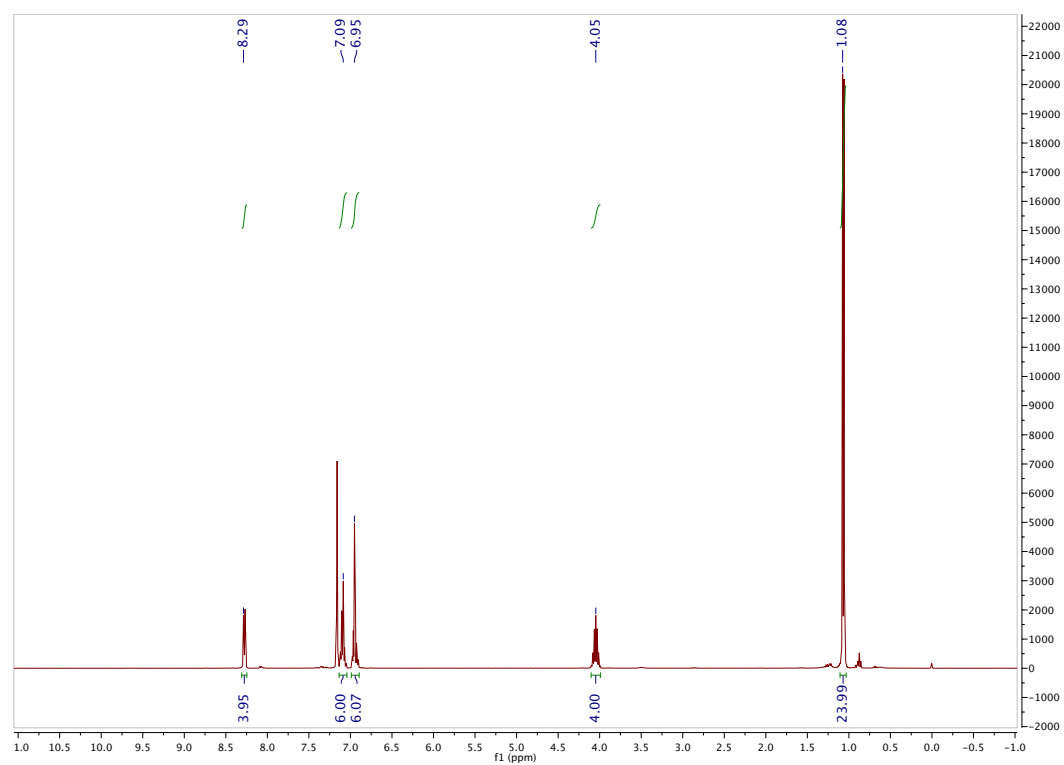


Figure A.3 ^1H NMR spectrum of **8** in C_6D_6 (400 MHz): δ 8.28 (dd, 4 H, H_{meta}), 7.09 (m, 6 H, H_{ortho} and H_{para} of Ph), 6.95 (m, 6 H, H_{meta} and H_{para} of ArN), 4.05 (sept, 4 H, CHMe_2), 1.07 (d, 24 H, CHMe_2) ppm.

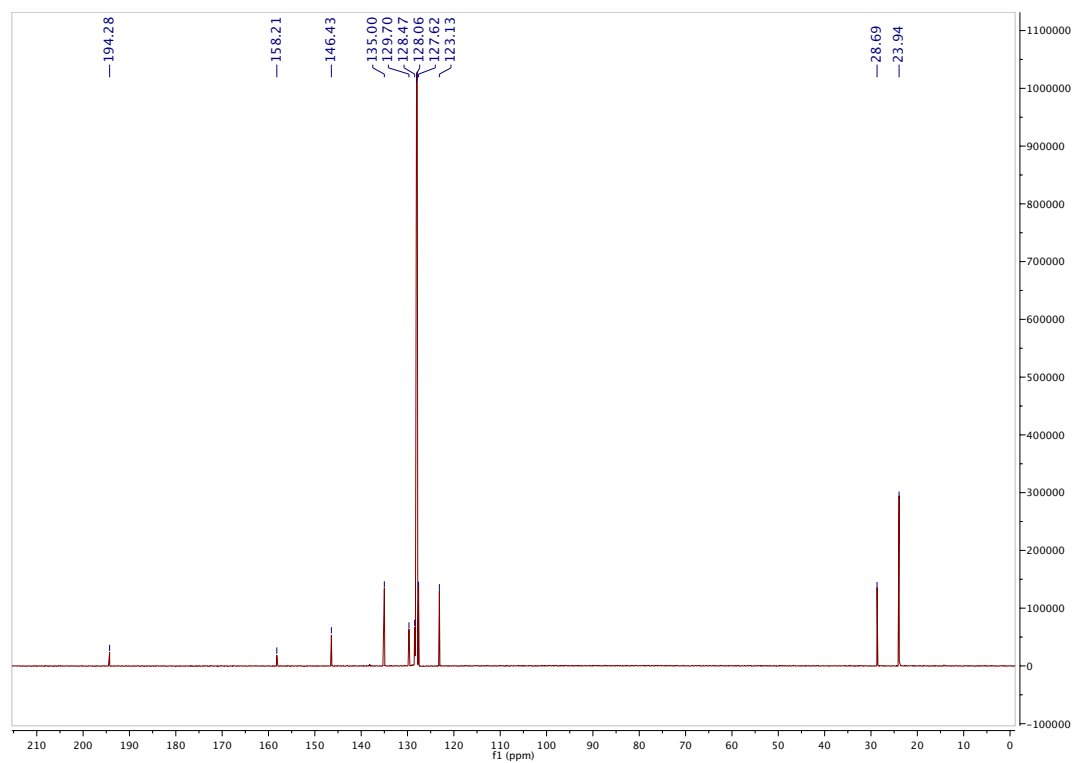


Figure A.4 $^{13}C\{^1H\}$ NMR spectrum of **8** in C_6D_6 (150 MHz): δ 194.28 (C_{ipso} of Ph), 158.21 (C_{ipso} of ArN), 146.43 (C_{ortho} of ArN), 135.00 (C_{meta} of Ph), 129.70 (C_{para} of Ph), 128.47 (C_{para} of ArN), 127.62 (C_{ortho} of Ph), 123.13 (C_{meta} of ArN), 28.69 ($CHMe_2$), 23.94 ($CHMe_2$) ppm.

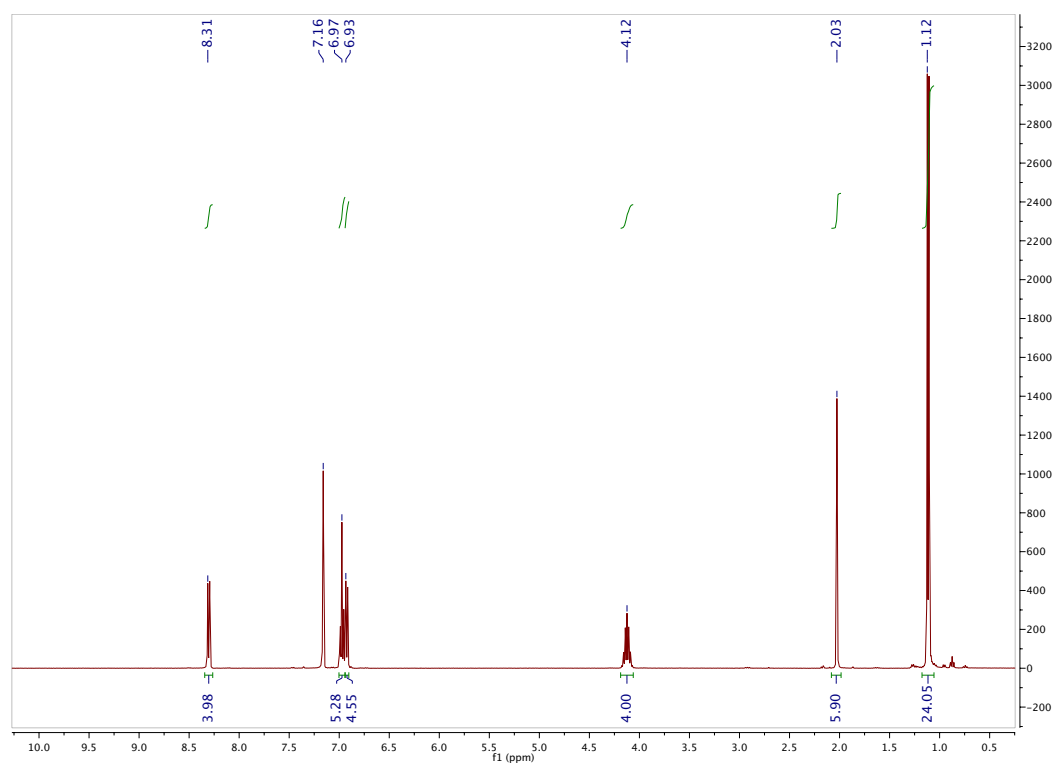


Figure A.5 ^1H NMR spectrum of **9** in C_6D_6 (400 MHz): δ 8.30 (d, 4 H, H_{meta}), 6.97 (m, 6 H, ArN), 6.92 (d, 4 H, H_{ortho}), 4.12 (sept, 4 H, CHMe_2), 2.03 (s, 6H, para-CH_3), 1.11 (d, 24 H, CHMe_2) ppm.

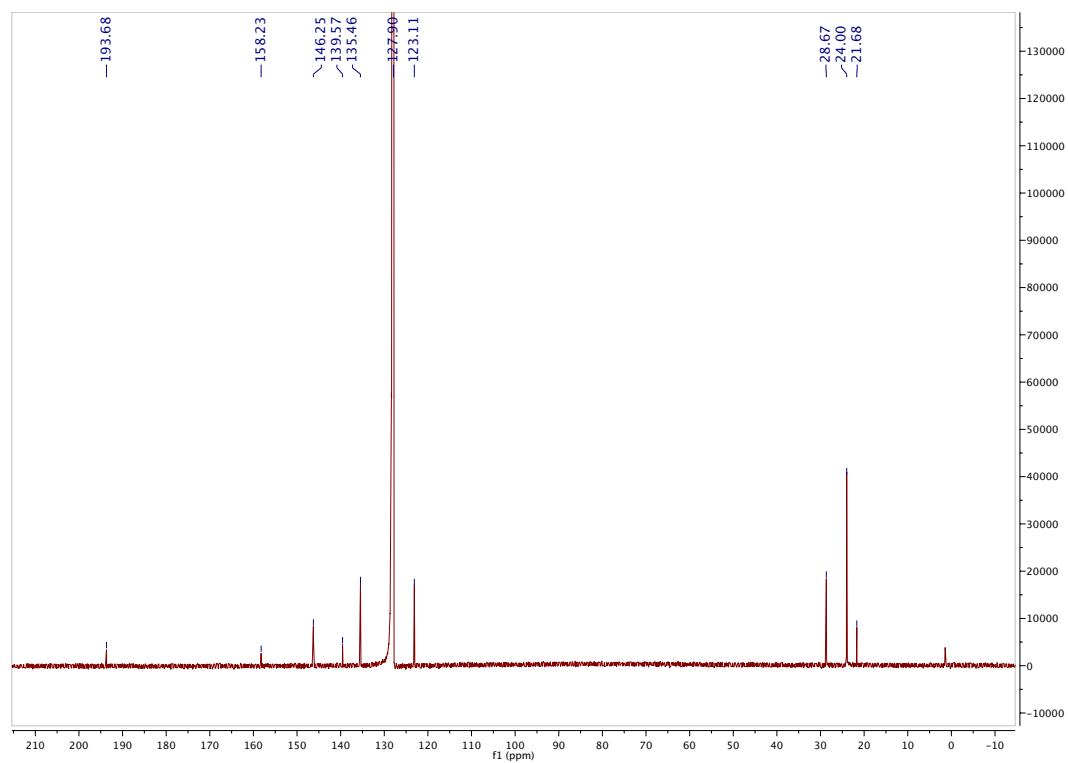


Figure A.6 $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **9** in C_6D_6 (150 MHz): δ 193.68 (C_{ipso} of *p*-tol), 158.23 (C_{ipso} of ArN), 146.25 (C_{ortho} of ArN), 139.57 (C_{para} of *p*-tol), 135.46 (C_{meta} of *p*-tol), 127.90 (C_{para} of ArN), 127.80 (C_{ortho} of *p*-tol), 123.11 (C_{meta} of ArN), 28.67 (CHMe_2), 24.00 (CHMe_2), 21.68 (*p*-tol) ppm.

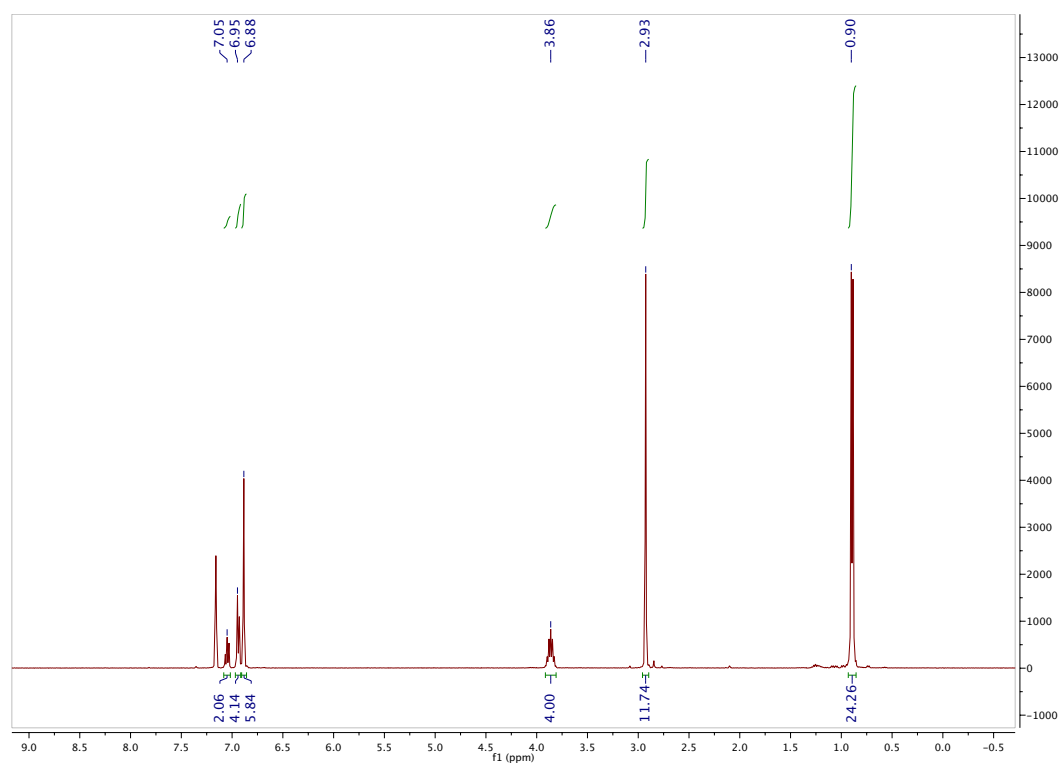


Figure A.7 ^1H NMR spectrum of **10** in C_6D_6 (400 MHz): δ 7.05 (t, 2 H, H_{para} of 2,6- Me_2Ph), 6.94 (d, 4 H, H_{meta} of 2,6- Me_2Ph), 6.88 (s, 6 H, ArN), 3.86 (sept, 4 H, CHMe_2), 2.93 (s, 12 H, Me_2Ph), 0.89 (d, 24 H, CHMe_2) ppm.

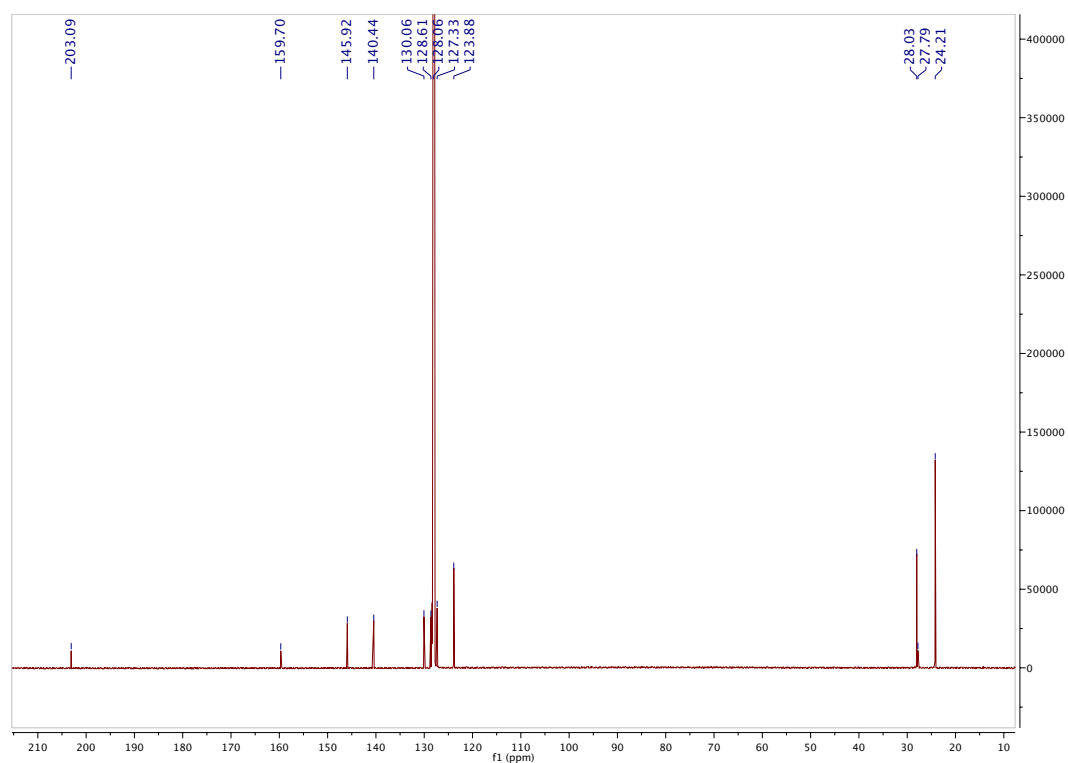


Figure A.8 $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **10** in C_6D_6 (150 MHz): δ 203.09 (C_{ipso} of 2,6-Me₂Ph), 159.70 (C_{ipso} of ArN), 145.92 (C_{ortho} of ArN), 140.44 (C_{ortho} of 2,6-Me₂Ph), 130.06 (C_{para} of 2,6-Me₂Ph), 128.61 (C_{para} of ArN), 127.33 (C_{meta} of 2,6-Me₂Ph), 123.88 (C_{meta} of ArN), 28.03 (CHMe₂), 27.79 (2,6-Me₂Ph), 24.21 (CHMe₂) ppm.

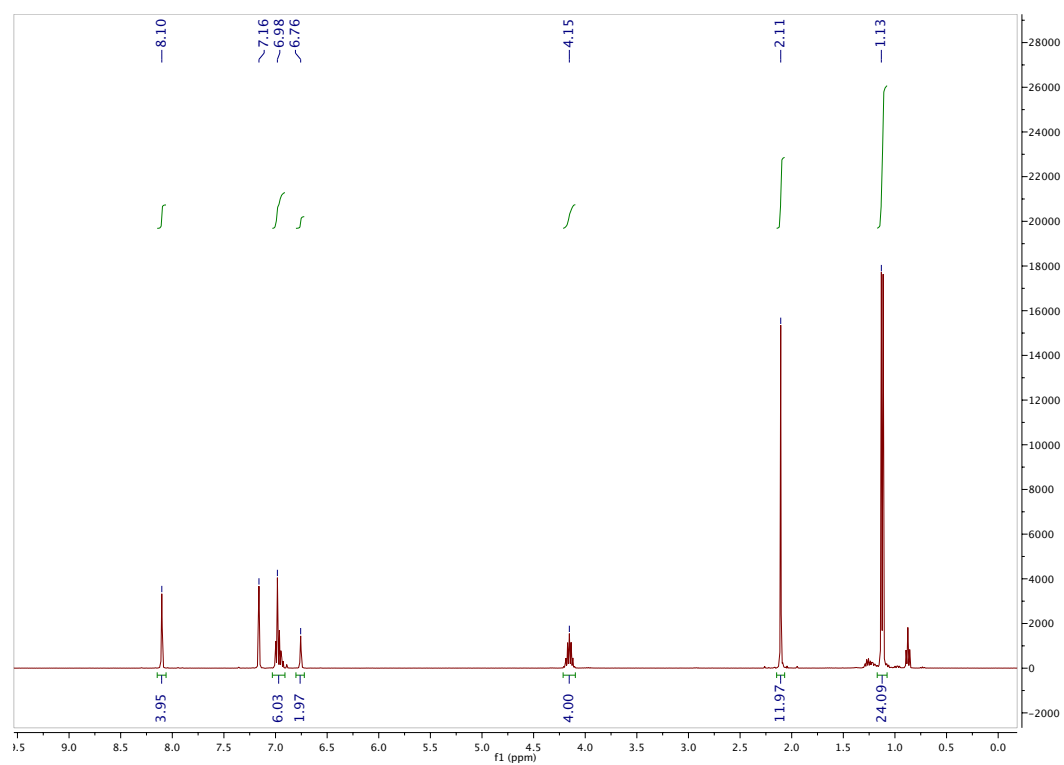


Figure A.9 ^1H NMR spectrum of **11** in C_6D_6 (400 MHz): δ 8.10 (s, 4 H, H_{ortho} of 3,5- Me_2Ph), 6.98 (m, 6 H, ArN), 6.76 (s, 2 H, H_{para} of 3,5- Me_2Ph), 4.15 (sept, 4 H, CHMe_2), 2.11 (s, 12 H, 3,5- Me_2Ph), 1.12 (d, 24 H, CHMe_2) ppm.

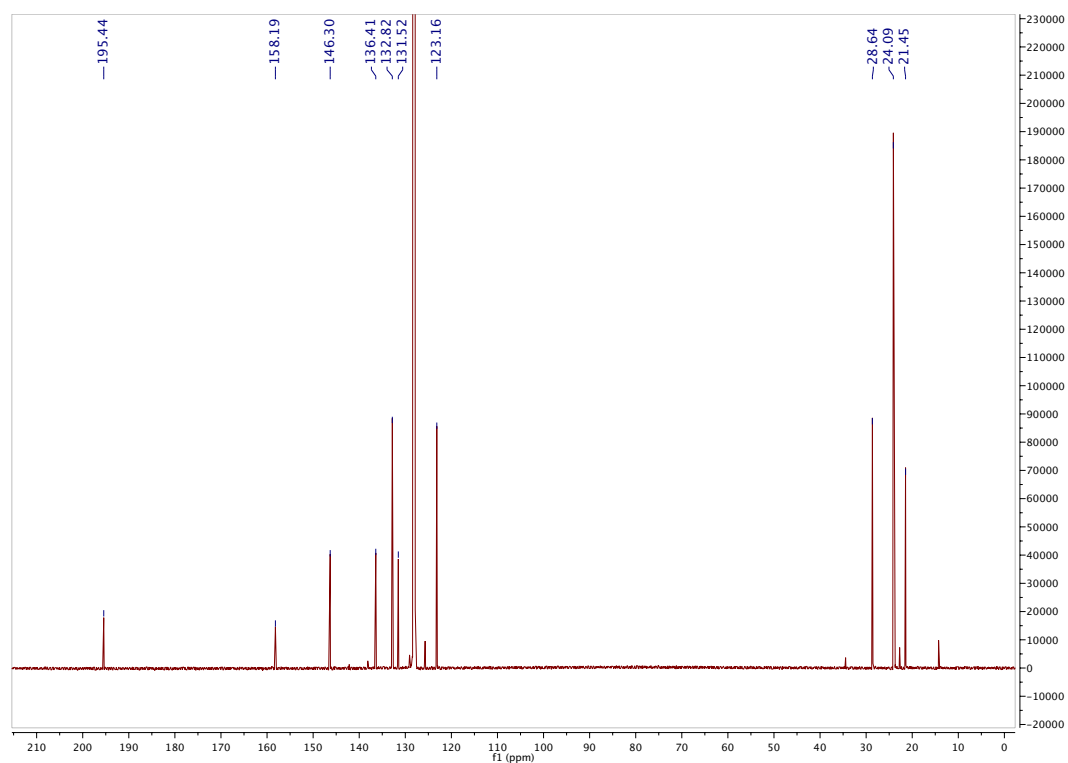


Figure A.10 $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **11** in C_6D_6 (150 MHz): δ 195.44 (C_{ipso} of 3,5- Me_2Ph), 158.19 (C_{ipso} of ArN), 146.30 (C_{ortho} of ArN), 136.41 (C_{meta} of 3,5- Me_2Ph), 132.82 (C_{ortho} of 3,5- Me_2Ph), 131.52 (C_{para} of 3,5- Me_2Ph), 127.82 (C_{para} of ArN) (assigned based on HSQC due to merge with C_6D_6 peak), 123.16 (C_{meta} of ArN), 28.64 (CHMe_2), 24.09 (CHMe_2), 21.45 (3,5- Me_2Ph) ppm.

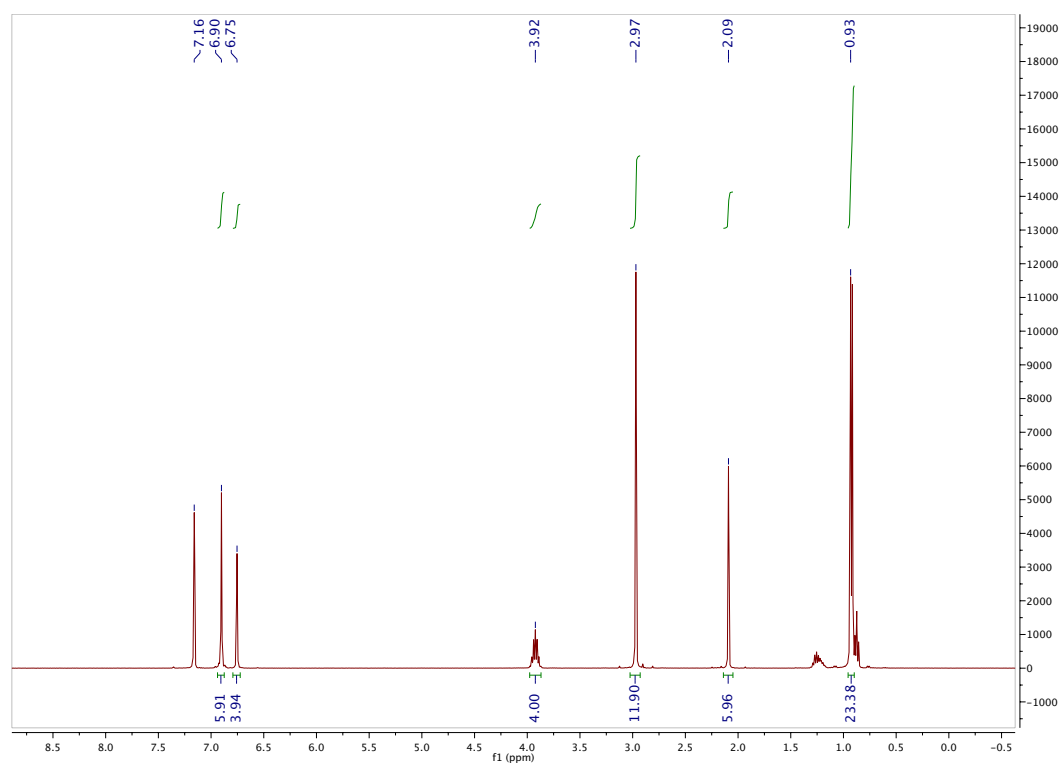


Figure A.11 ^1H NMR spectrum of **12** in C_6D_6 (400 MHz): δ 6.90 (m, 6 H, ArN), 6.75 (s, 4 H, mesityl), 3.92 (sept, 4 H, CHMe₂), 2.97 (s, 12 H, *ortho*-CH₃ of mesityl), 2.09 (s, 6 H, *para*-CH₃ of mesityl), 0.92 (d, 24 H, CHMe₂) ppm.

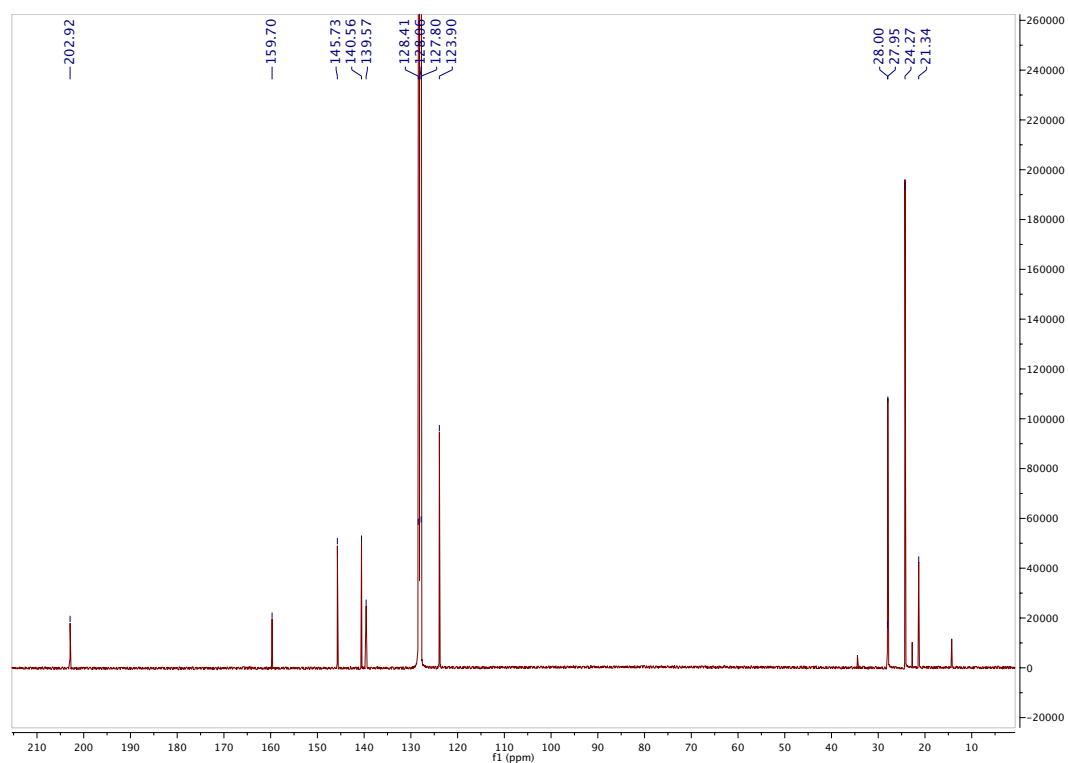


Figure A.12 $^{13}C\{^1H\}$ NMR spectrum of **12** in C_6D_6 (150 MHz: δ 202.92 (C_{ipso} of mesityl), 159.70(C_{ipso} of ArN), 145.73 (C_{ortho} of ArN), 140.56 (C_{ortho} of mesityl), 139.57 (C_{para} of mesityl), 128.41 (C_{para} of ArN), 127.80 (C_{meta} of mesityl), 123.90 (C_{meta} of ArN), 28.00 (mesityl, overlapped with $CHMe_2$, assigned by HSQC), 27.95 ($CHMe_2$), 24.27 ($CHMe_2$), 21.34 ($para-CH_3$ of mesityl) ppm.

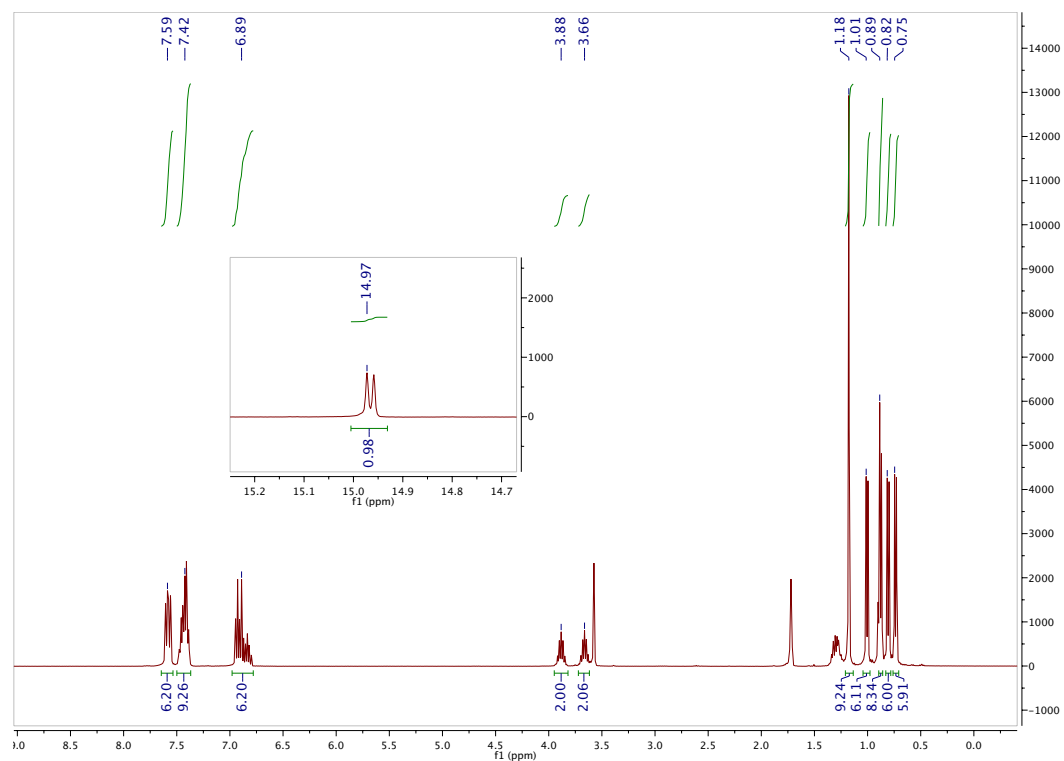


Figure A.13 ^1H NMR spectrum of **13** in THF-d_8 (400 MHz): δ 14.97 (d, 1 H, CHCMe_3), 7.59 (m, 6 H, PPh_3), 7.42 (m, 9 H, PPh_3), 6.89 (m, 6 H, ArN), 3.88 (sept, 2 H, CHMe_2), 3.66 (sept, 2 H, CHMe_2), 1.18 (s, 9 H, CHCMe_3), 1.00 (d, 6 H, CHMe_2), 0.88 (d, 6 H, CHMe_2), 0.81 (d, 6 H, CHMe_2), 0.74 (d, 6 H, CHMe_2) ppm.

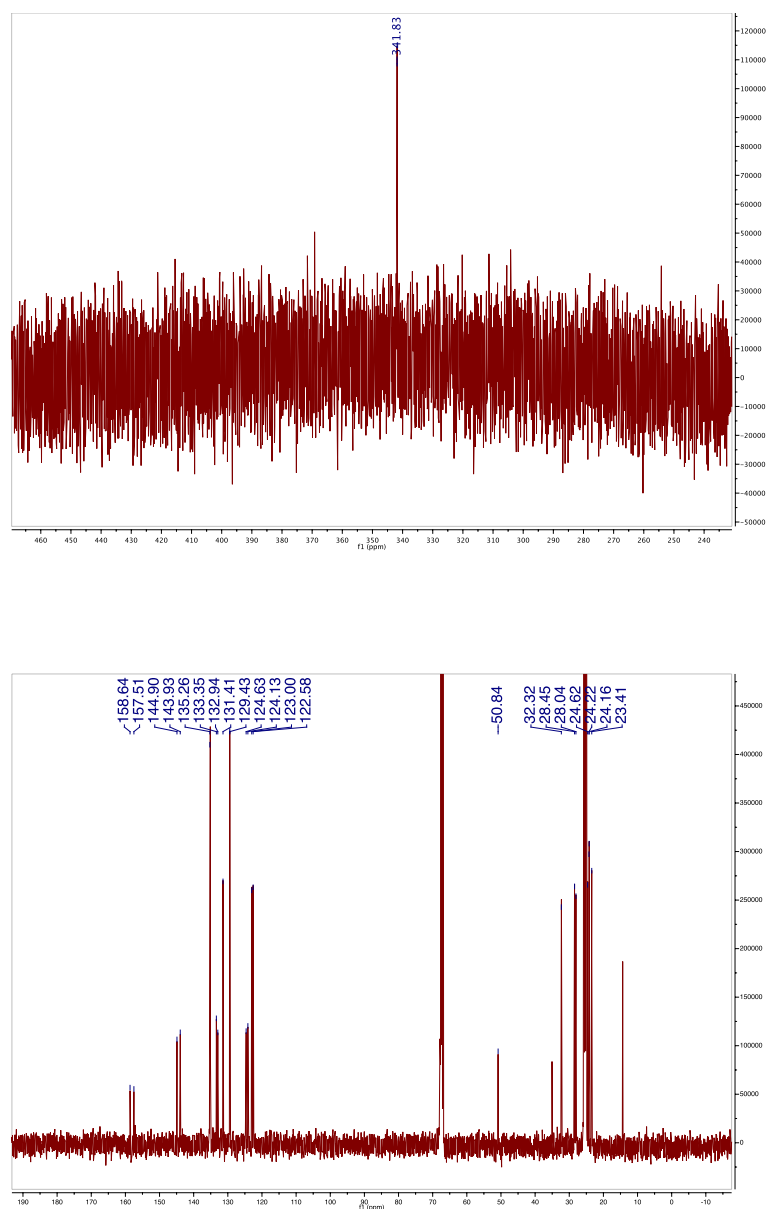


Figure A.14 $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **13** in THF- d_8 (100 MHz): δ 341.73 (CHCMe₃), 158.64 (*C*_{ipso} of ArN), 157.51 (*C*_{ipso} of ArN), 144.90 (*C*_{ortho} of ArN), 143.93 (*C*_{ortho} of ArN), 135.26 (*C*_{ortho} of PPh₃), 133.35 (*C*_{ipso} of PPh₃), 131.41 (*C*_{para} of PPh₃), 129.43 (*C*_{meta} of PPh₃), 124.63 (*C*_{para} of ArN), 124.13 (*C*_{para} of ArN), 123.00 (*C*_{meta} of ArN), 122.58 (*C*_{meta} of ArN), 50.84 (CHCMe₃), 32.32 (CHCMe₃), 28.45 (CHMe₂), 28.04 (CHMe₂), 24.62 (CHMe₂), 24.22 (CHMe₂), 24.16 (CHMe₂), 23.41 (CHMe₂) ppm.

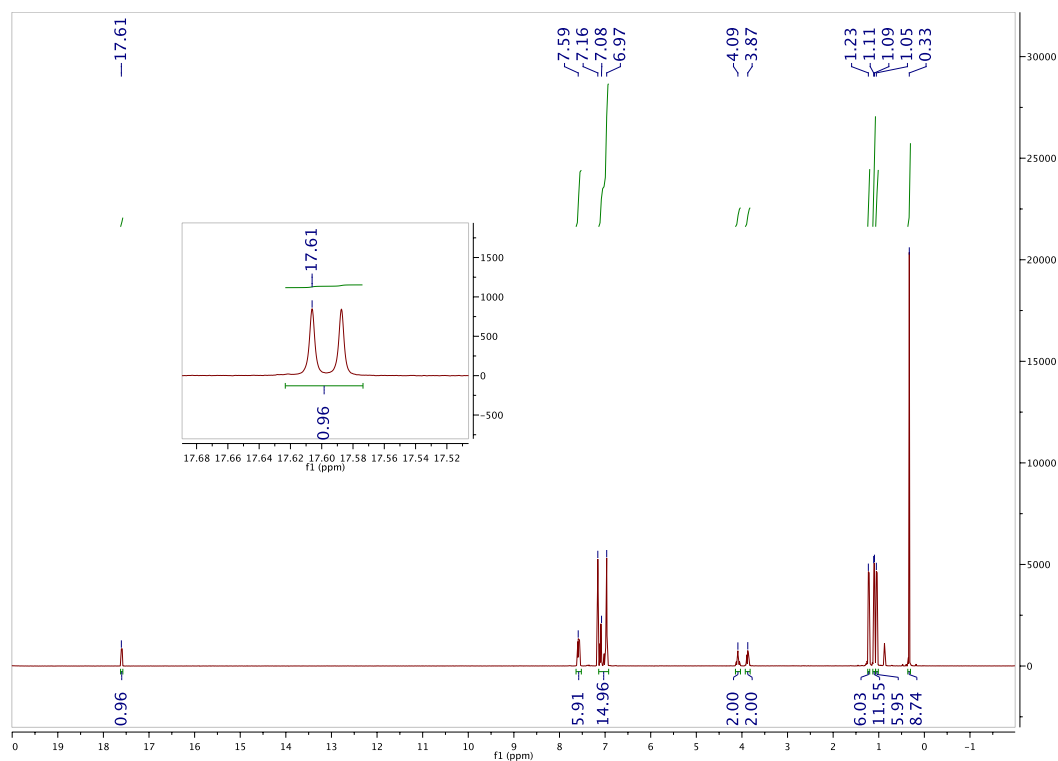


Figure A.15 ^1H NMR spectrum of **14b** in C_6D_6 (400 MHz): δ 17.60 (d, 1 H, CHSiMe_3), 7.59 (m, 6 H, PPh_3), 7.08 (m, 9 H, PPh_3), 6.97 (m, 6 H, ArN), 4.09 (sept, 2 H, CHMe_2), 3.87 (sept, 2 H, CHMe_2), 1.22 (d, 6 H, CHMe_2), 1.11 (d, 6 H, CHMe_2), 1.10 (d, 6 H, CHMe_2), 1.04 (d, 6 H, CHMe_2), 0.33 (s, 9 H, CHSiMe_3) ppm.

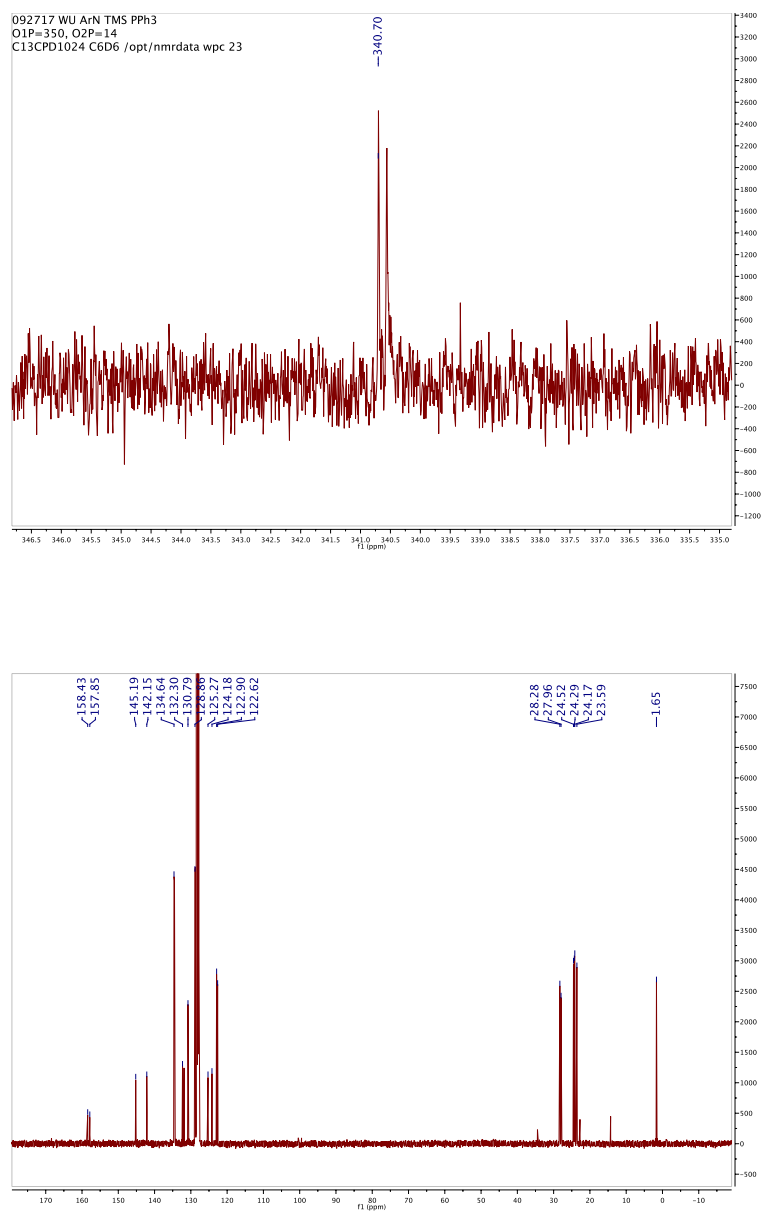


Figure A.16 $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (150 MHz for alkylidene carbon, 100 Hz for the rest) of **14b** in C_6D_6 : δ 340.63 (d, $^2J_{\text{PC}} = 21.0$ Hz, CHSiMe_3), 158.43 (C_{ipso} of ArN), 157.85 (C_{ipso} of ArN), 145.19 (C_{ortho} of ArN), 142.15 (C_{ortho} of ArN), 134.64 (C_{ortho} of PPh_3), 132.30 (C_{ipso} of PPh_3), 130.79 (C_{para} of PPh_3), 128.86 (C_{meta} of PPh_3), 125.27 (C_{para} of ArN), 124.18 (C_{para} of ArN), 122.90 (C_{meta} of ArN), 122.62 (C_{meta} of ArN), 28.28 (CHMe_2), 27.96 (CHMe_2), 24.52 (CHMe_2), 24.29 (CHMe_2), 24.17 (CHMe_2), 23.59 (CHMe_2), 1.65 (CHSiMe_3) ppm.

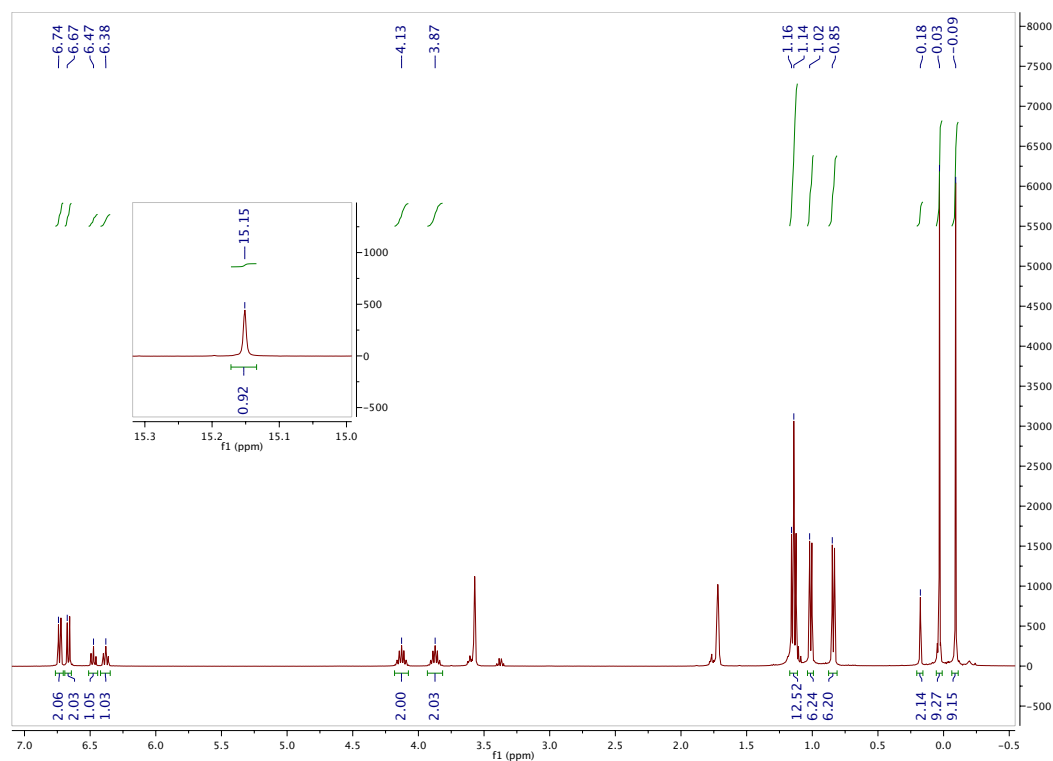


Figure A.17 ^1H NMR spectrum of **15a** in THF-d_8 (400 MHz): δ 15.15 (s, 1 H, CHSiMe_3), 6.73 (d, 2 H, H_{meta} of ArN), 6.67 (d, 2 H, H_{meta} of ArN), 6.48 (t, 1 H, H_{para} of ArN), 6.39 (t, 1 H, H_{para} of ArN), 4.13 (sept, 2 H, CHMe_2), 3.88 (sept, 2 H, CHMe_2), 1.15 (d, 6H, CHMe_2), 1.13 (d, 6H, CHMe_2), 1.01 (d, 6 H, CHMe_2), 0.84 (d, 6 H, CHMe_2), 0.18 (s, 2 H, CH_2SiMe_3), 0.03 (s, 9 H, $=\text{CHSiMe}_3$), -0.09 (s, 9 H, CH_2SiMe_3) ppm.

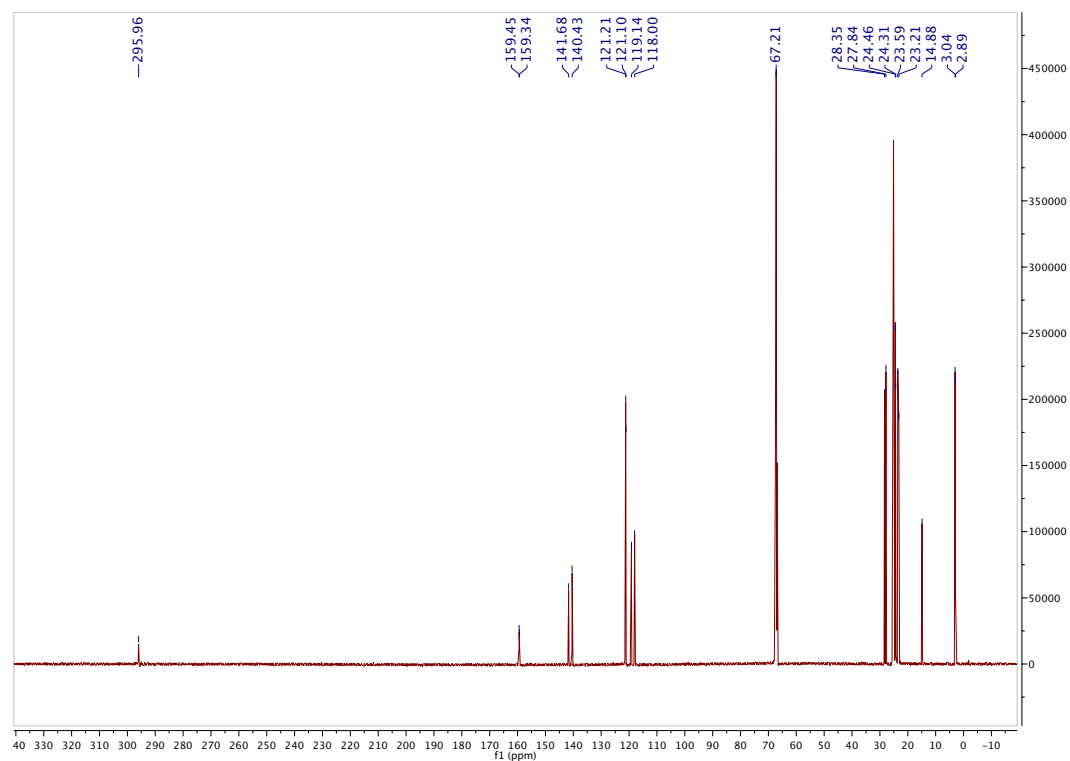


Figure A.18 $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **15a** in THF- d_8 (100 MHz): δ 295.96 (CHSiMe₃), 159.45 (*C*_{ipso}), 159.34 (*C*_{ipso}), 141.68 (*C*_{ortho}), 140.43 (*C*_{ortho}), 121.21 (*C*_{para}), 121.10 (*C*_{para}), 119.14 (*C*_{meta}), 118.00 (*C*_{meta}), 28.35 (CHMe₂), 27.84 (CHMe₂), 24.46 (CHMe₂), 24.31 (CHMe₂), 23.59 (CHMe₂), 23.21 (CHMe₂), 14.88 (CH₂SiMe₃), 3.04 (=CHSiMe₃), 2.89 (CH₂SiMe₃) ppm.

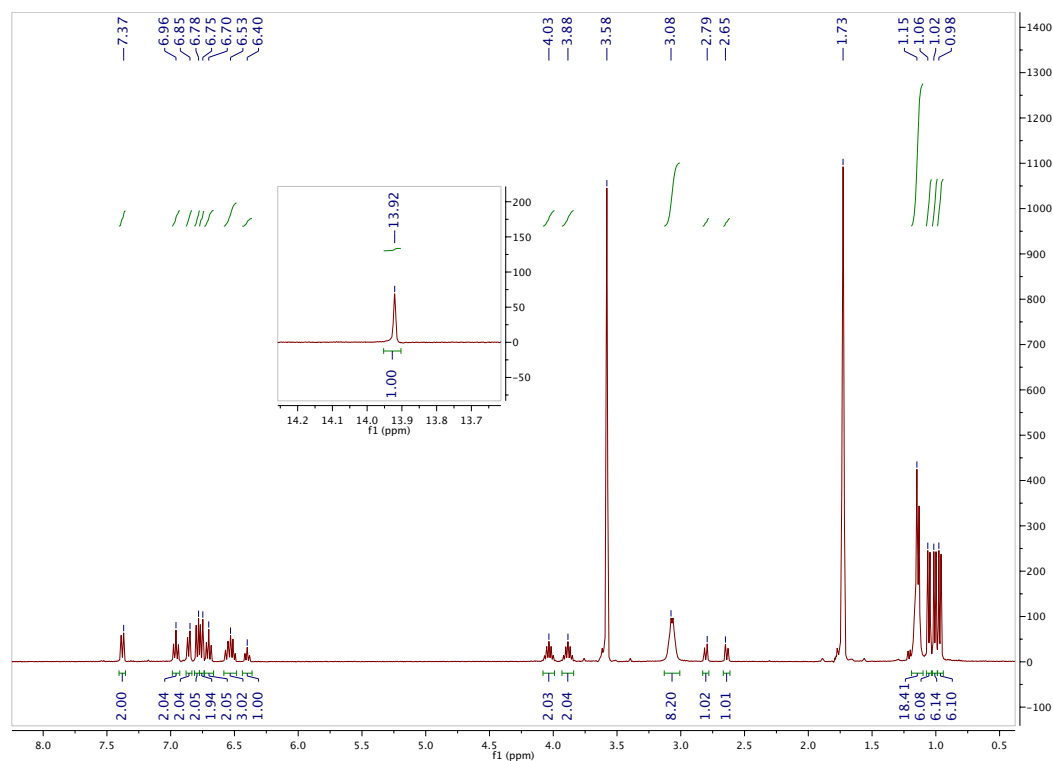


Figure A.19 ^1H NMR spectrum of **16b** in THF-d_8 (400 MHz): δ 13.92 (s, 1 H, CHPh), 7.38 (d, 2 H, Ar), 6.96, (t, 2 H, Ar), 6.86 (d, 2 H, Ar), 6.79 (d, 2 H, Ar), 6.76 (d, 2 H, Ar), 6.70 (t, 2 H, Ar), 6.53 (quintet, 3 H, Ar), 6.40 (t, 1 H, Ar), 4.03 (sept, 2 H, CHMe_2), 3.88 (sept, 2 H, CHMe_2), 3.08 (broad, 8 H, CH_2CH_3 of Et_4N), 2.80 (d, 1 H, CH_2Ph), 2.64 (d, 1 H, CH_2Ph), 1.15 (broad, 18 H, CH_2CH_3 of Et_4N and CHMe_2), 1.05 (d, 6 H, CHMe_2), 1.01 (d, 6 H, CHMe_2), 0.97 (d, 6 H, CHMe_2) ppm.

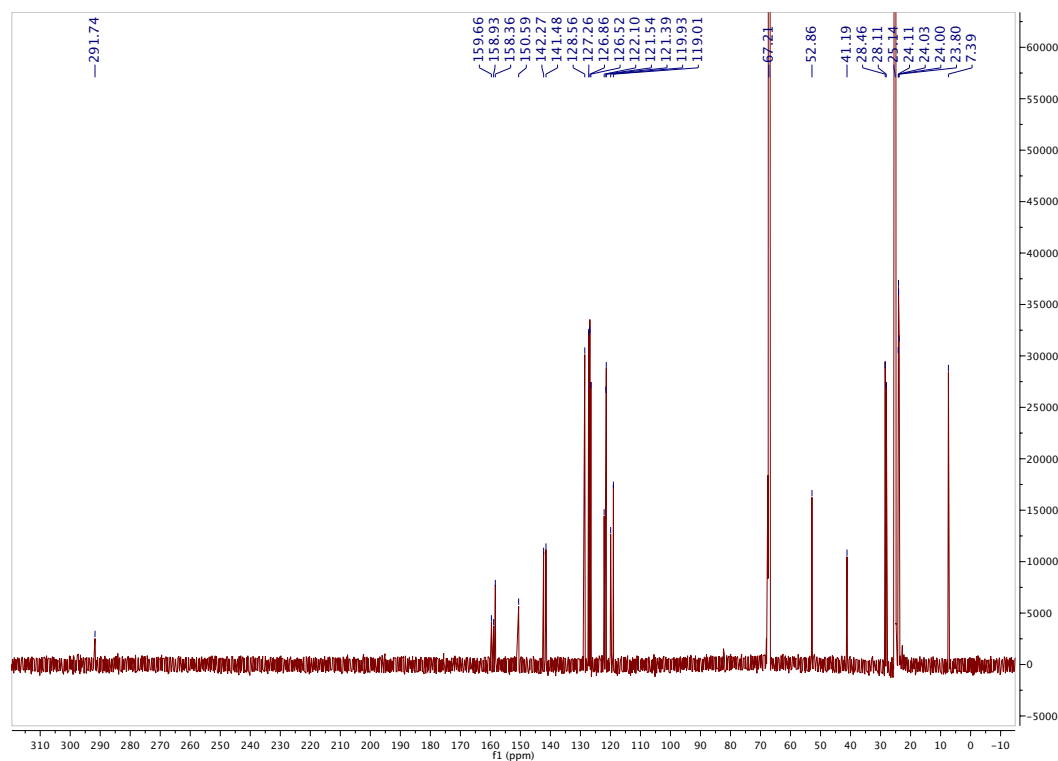


Figure A.20 $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **16b** in THF- d_8 (150 MHz): δ 291.74 (CHPh), 159.66 (Ar), 158.93 (Ar), 158.36 (Ar), 150.59 (Ar), 142.27 (Ar), 141.48 (Ar), 128.56 (Ar), 127.26 (Ar), 126.86 (Ar), 126.52 (Ar), 122.10 (Ar), 121.54 (Ar), 121.39 (Ar), 119.93 (Ar), 119.06 (Ar), 119.01 (Ar), 52.86 (CH_2CH_3 of Et_4N), 41.19 (CH_2Ph), 28.46 (CHMe_2), 28.11 (CHMe_2), 24.11 (CHMe_2), 24.03 (CHMe_2), 24.00 (CHMe_2), 23.80 (CHMe_2), 7.39 (CH_2CH_3 of Et_4N) ppm.

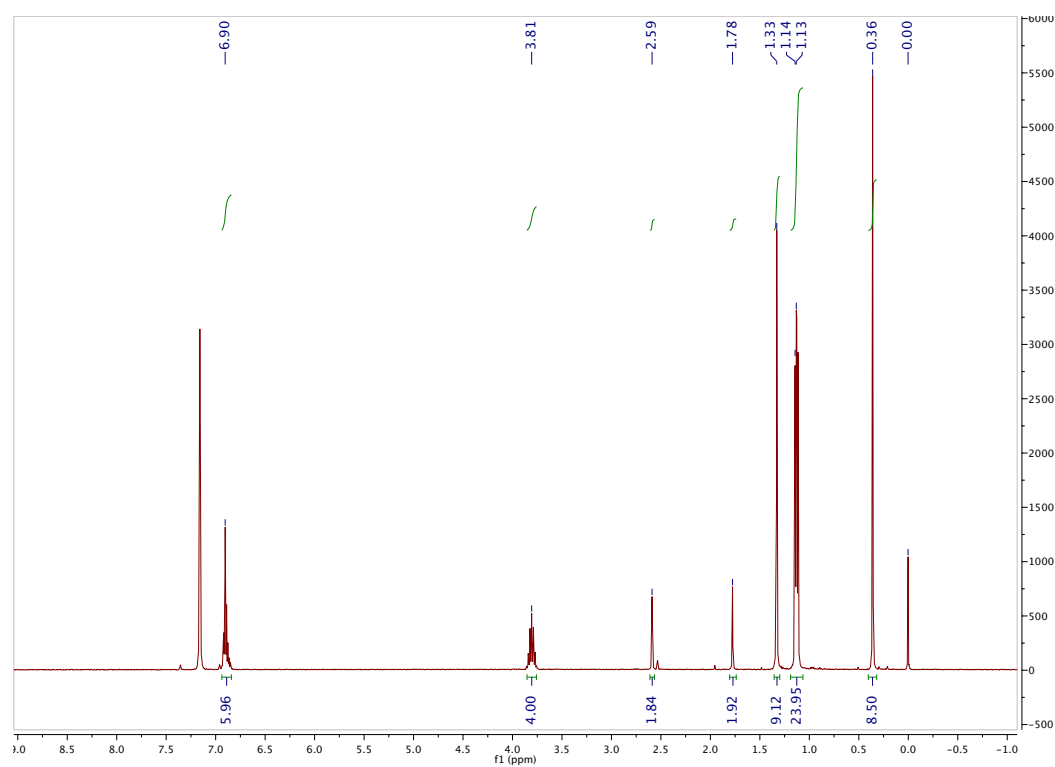


Figure A.21 ^1H NMR spectrum of **18** in C_6D_6 (400 MHz): δ 6.90 (m, 6 H, ArN), 3.81 (sept, 4 H, CHMe_2), 2.59 (s, 2 H, CH_2CMe_3), 1.78 (s, 2 H, CH_2SiMe_3), 1.33 (s, 9 H, CH_2CMe_3), 1.14 (d, 12 H, CHMe_2), 1.12 (d, 12 H, CHMe_2), 0.36 (s, 9H, CH_2SiMe_3) ppm.

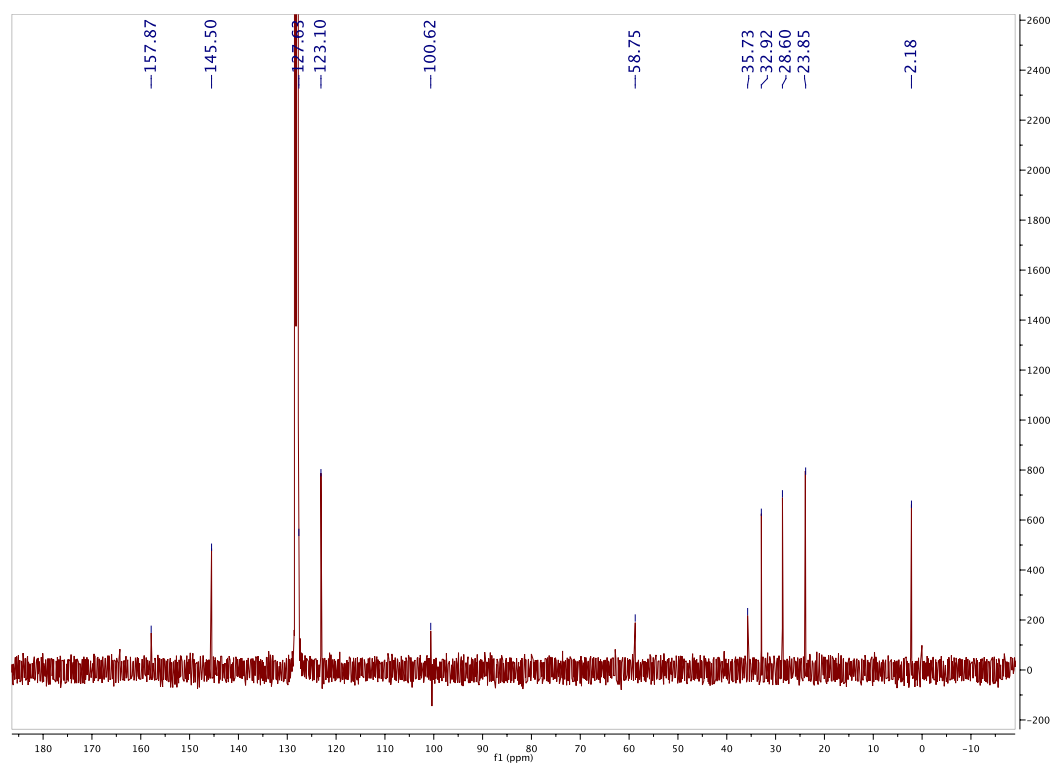


Figure A.22 $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **18** in C_6D_6 (100 MHz): δ 157.87 (C_{ipso}), 145.50 (C_{ortho}), 127.63 (C_{para}), 123.10 (C_{meta}), 100.62 (CH_2CMe_3), 58.75 (CH_2SiMe_3), 35.73 (CH_2CMe_3), 32.92 (CH_2CMe_3), 28.60 (CHMe_2), 23.91 (CHMe_2), 23.85 (CHMe_2), 2.18 (CH_2SiMe_3) ppm.

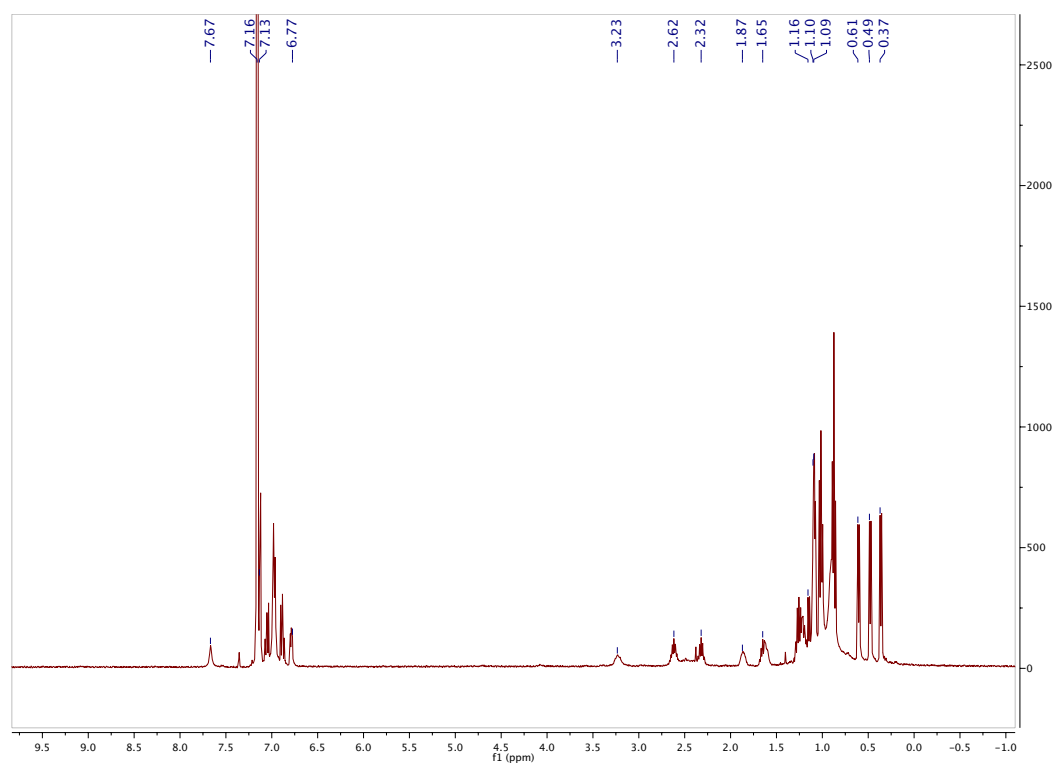


Figure A.23 ^1H NMR spectrum of **19** in C_6D_6 (400 MHz): δ 7.67 (broad, 2 H, NHAr), 7.13–6.77 (Ar), 3.23 (broad, 4 H, $\text{CH}(\text{CH}_2)\text{Me}$), 2.62 (sept, 4 H, CHMe_2), 2.32 (sept, 4 H, CHMe_2), 1.87 (broad, 2 H, $\text{CH}(\text{CH}_2)\text{Me}$), 1.65 (sept, 4 H, CHMe_2), 1.16 (d, 6 H, $\text{CH}(\text{CH}_2)(\text{CH}_3)$), 1.09 (d, 12 H, CHMe_2), 1.08 (d, 12 H, CHMe_2), 0.61 (d, 12 H, CHMe_2), 0.49 (d, 12 H, CHMe_2), 0.37 (d, 12 H, CHMe_2) ppm.

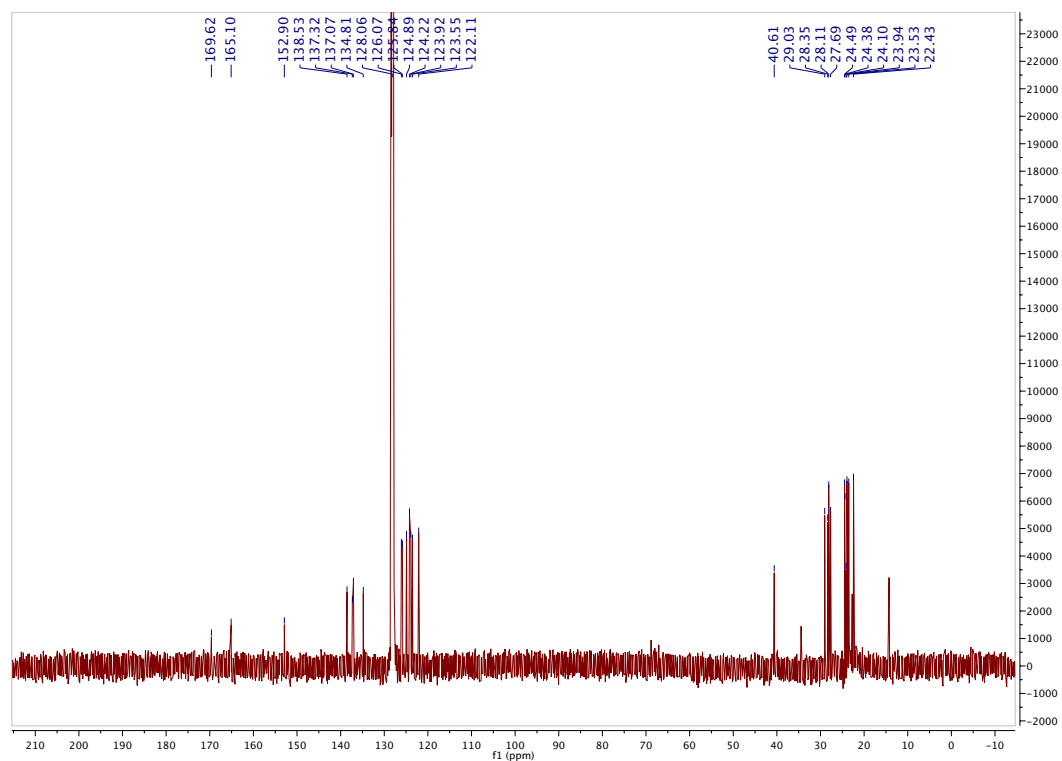


Figure A.24 $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **19** in C_6D_6 (150 MHz): δ 169.62 (C_{ipso}), 165.10 (C_{ipso}), 152.90 (C_{ipso}), 138.53 (Ar), 137.32 (Ar), 137.07 (Ar), 134.81 (Ar), 126.07 (Ar), 125.84 (Ar), 124.89 (Ar), 124.22 (Ar), 123.92 (Ar), 123.55 (Ar), 122.11 (Ar), 40.61 ($\text{CH}(\text{CH}_2)\text{Me}$), 29.03 (CHMe_2), 28.35 (CHMe_2), 28.11 (CHMe_2), 27.69 (CHMe_2), 24.49 (CHMe_2), 24.38 (CHMe_2), 24.10 ($\text{CH}(\text{CH}_2)\text{Me}$), 23.94 (CHMe_2), 23.53 (CHMe_2), 22.43 (CHMe_2) ppm.

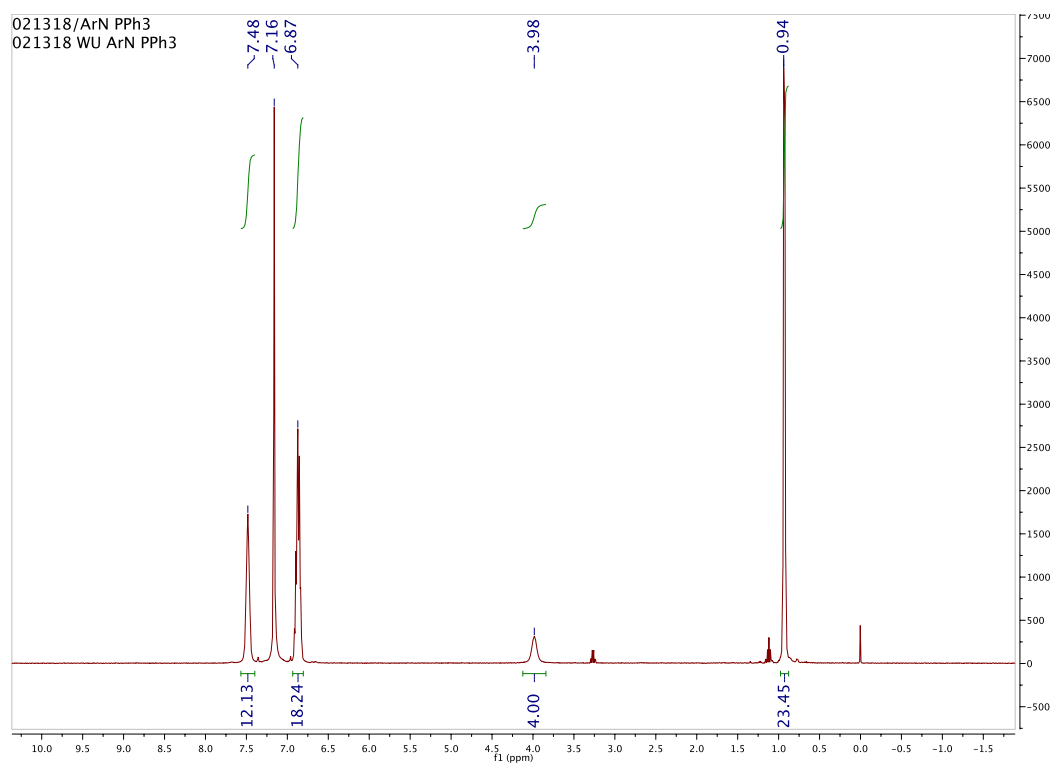


Figure A.25 ^1H NMR spectrum of **20** in C_6D_6 (400 MHz): δ 7.48 (m, 12 H, H_{ortho} of PPh_3), 7.16 (H_{para} of PPh_3 , overlap with C_6D_6), 6.87 (m, 18 H, H_{meta} of PPh_3 and H of ArN), 3.98 (br, 4 H, CHMe_2), 0.93 (d, 24 H, CHMe_2) ppm.

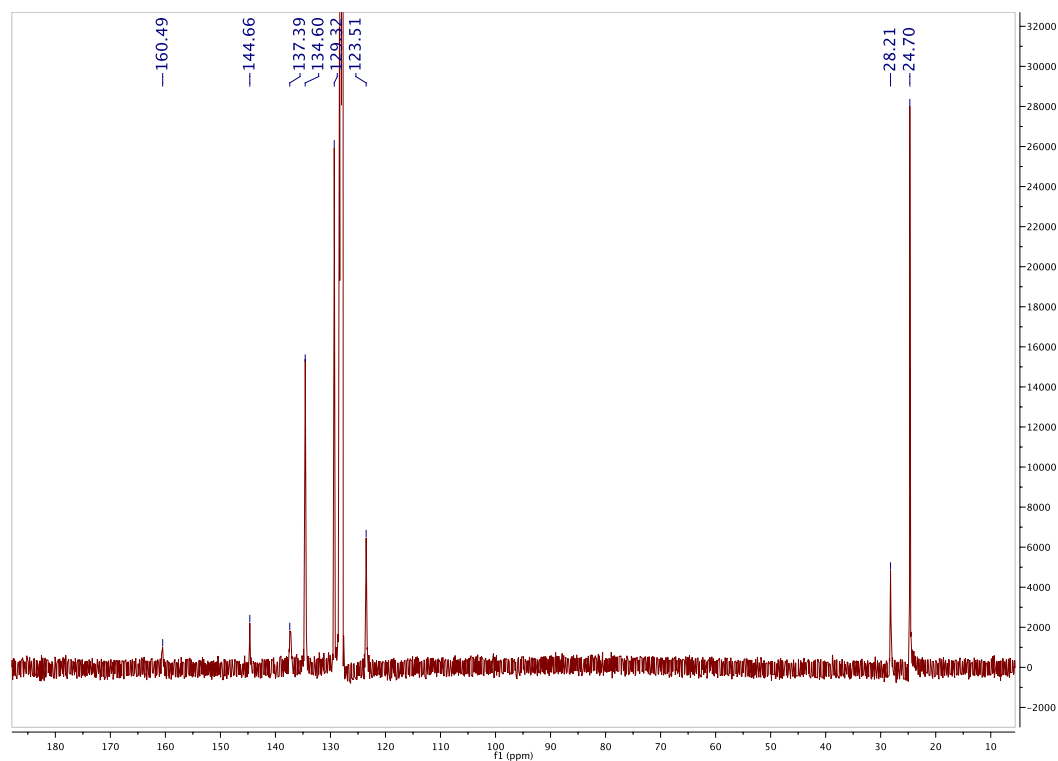


Figure A.26 $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **20** in C_6D_6 (150 MHz): δ 160.49 (C_{ipso} of ArN), 144.66 (C_{ortho} of ArN), 137.39 (C_{ipso} of PPh_3), 134.60 (C_{ortho} of PPh_3), 129.32 (C_{meta} of PPh_3), 128.06 (C_{meta} of ArN and C_{para} of ArN, overlap with C_6D_6), 123.51 (C_{para} of PPh_3), 28.21 (CHMe_2), 24.70 (CHMe_2) ppm.

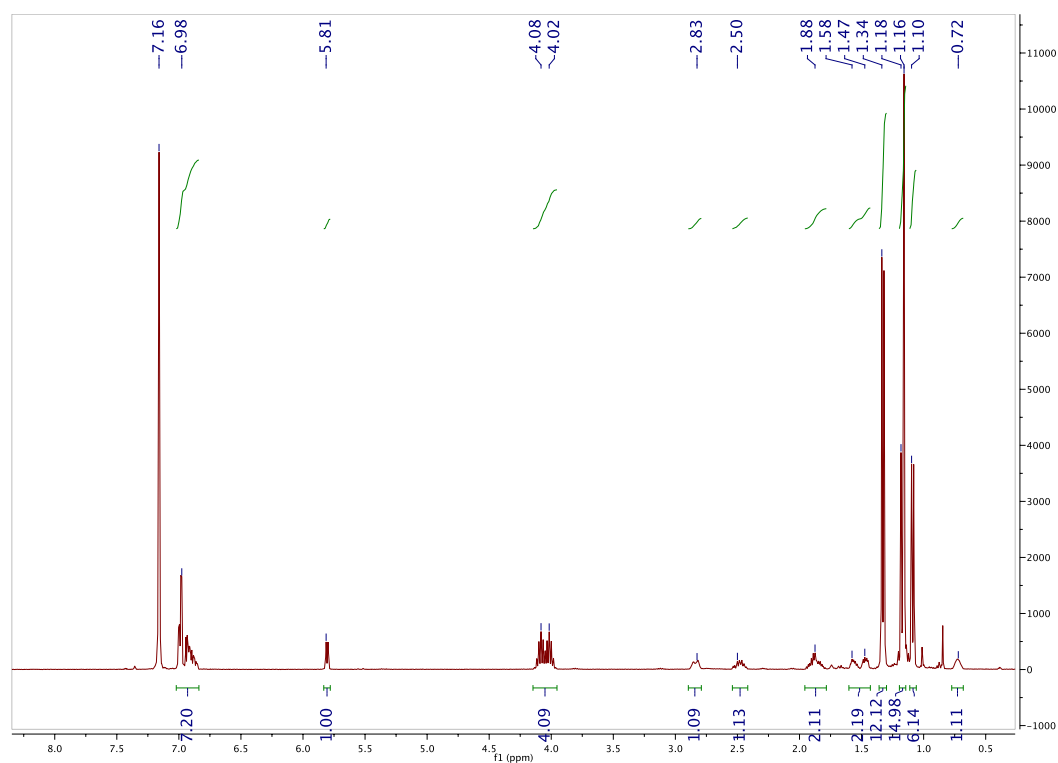


Figure A.27 ^1H NMR spectrum of **21** in C_6D_6 (400 MHz): δ 6.98 (m, 6 H, Ar), 6.98 (m, 1 H, α -CH of cyclobutane), 5.81 (d, 1 H, CHCMe_3), 4.08 (sept, 2 H, CHMe_2), 4.02 (sept, 2 H, CHMe_2), 2.83 (m, 1 H, β - CH_2), 2.50 (m, 1 H, β - CH_2), 1.88 (m, 2 H, CH_2 , CH_2), 1.58 (m, 1 H, CH_2), 1.47 (m, 1 H, CH_2), 1.33 (d, 12 H, CHMe_2), 1.17 (d, 6 H, CHMe_2), 1.16 (s, 9H, CMe_3), 1.09 (d, 6 H, CHMe_2), 0.72 (m, 1 H, β -CH) ppm.

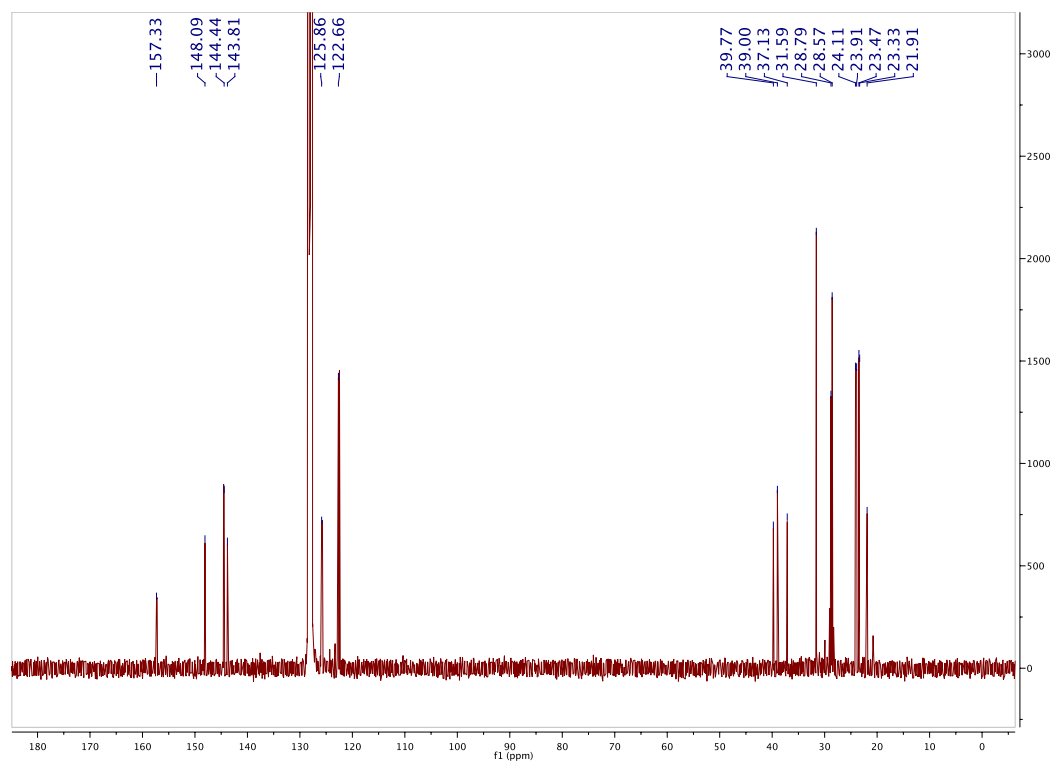


Figure A.28 $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **21** in C_6D_6 (100 MHz): δ 157.33 (C_{ipso}), 157.21 (C_{ipso}), 148.09 (CHCMe_3), 144.55 (C_{ortho}), 144.44 (C_{ortho}), 143.81 ($\alpha\text{-C}$ of cyclobutane, not CHCMe_3), 125.86 (C_{para}), 125.71 (C_{para}), 122.66 (C_{meta}), 122.46 (C_{meta}), 39.77 (CH_2), 39.00 (CMe_3), 37.13 (CH_2), 31.59 (CMe_3), 28.79 (CHMe_2), 28.57 (CHMe_2 overlapped with CH_2), 24.11 (CHMe_2), 23.91 (CHMe_2), 23.47 (CHMe_2), 23.33 (CHMe_2), 21.91 ($\beta\text{-CH}$) ppm.

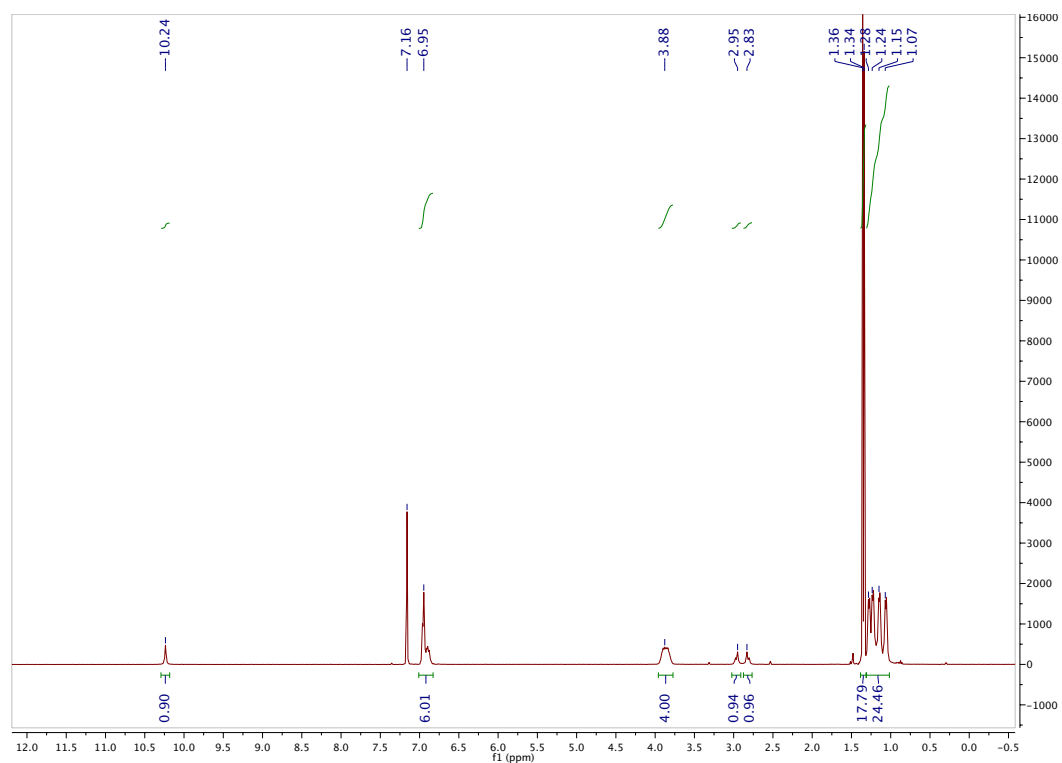


Figure A.29 ^1H NMR spectrum of **22** in C_6D_6 (400 MHz): δ 10.24 (s, 1 H, NH^tBu), 6.95 (m, 6 H, ArN), 3.88 (m, 4 H, CHMe_2), 2.96 (d, 1 H, CH_2CMe_3), 2.82 (d, 1 H, CH_2CMe_3), 1.36 (s, 9 H, ^tBu), 1.34 (s, 9 H, ^tBu), 1.28 (d, 6 H, CHMe_2), 1.23 (d, 6 H, CHMe_2), 1.14 (d, 6 H, CHMe_2), 1.06 (d, 6 H, CHMe_2) ppm.

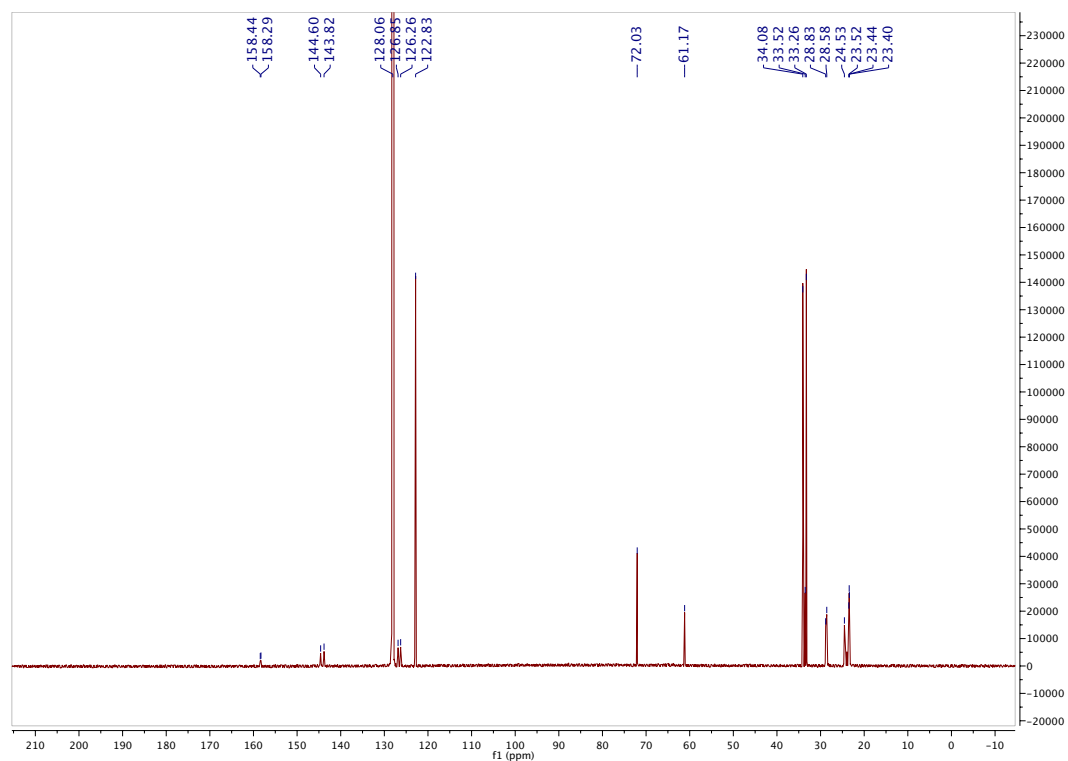


Figure A.30 $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **22** in C_6D_6 (150 MHz): δ 158.44 (C_{ipso}), 158.29 (C_{ipso}), 144.60 (C_{ortho}), 143.82 (C_{ortho}), 126.85 (C_{para}), 126.26 (C_{para}), 122.83 (C_{meta} , 2 peaks merge together, confirmed by HSQC), 72.03 (CH_2CMe_3), 61.17 (CMe_3 of NH^tBu), 34.08 (^tBu), 33.52 (CH_2CMe_3), 33.26 (^tBu), 28.83 (CHMe_2), 28.58 (CHMe_2), 24.53 (CHMe_2), 23.52 (CHMe_2), 23.44 (CHMe_2), 23.40 (CHMe_2) ppm.

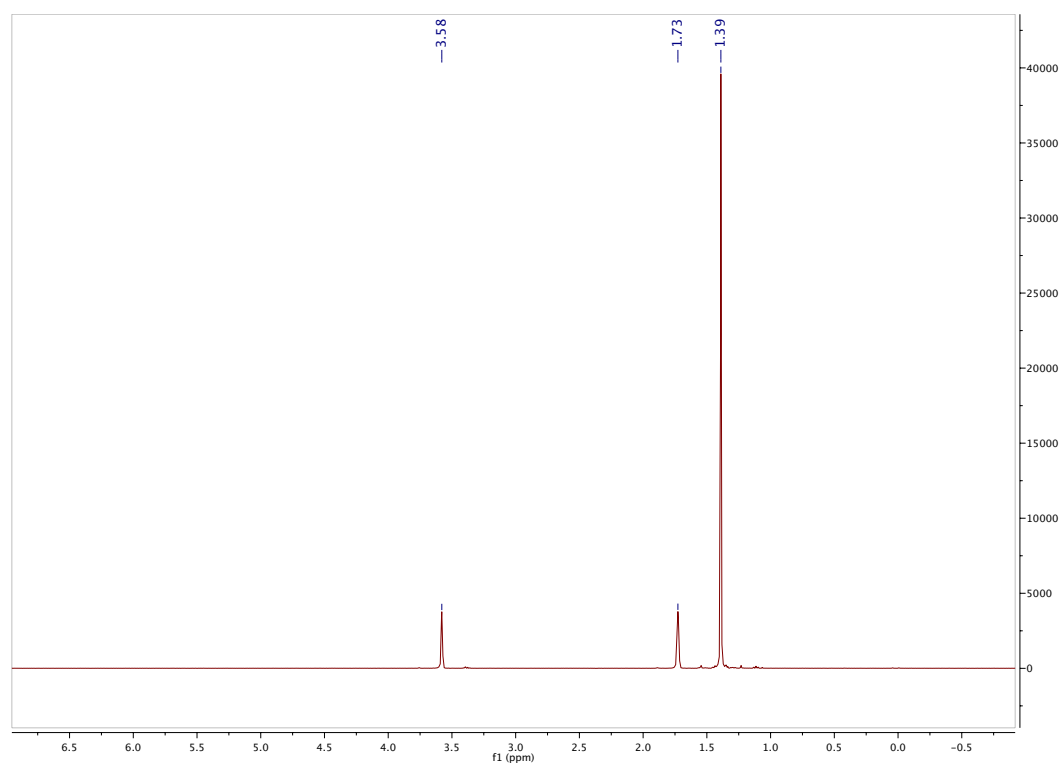


Figure A.31 ^1H NMR spectrum of **24a** in THF- d_8 (400 MHz): δ 1.39 (s, 18 H, ^tBu) ppm.

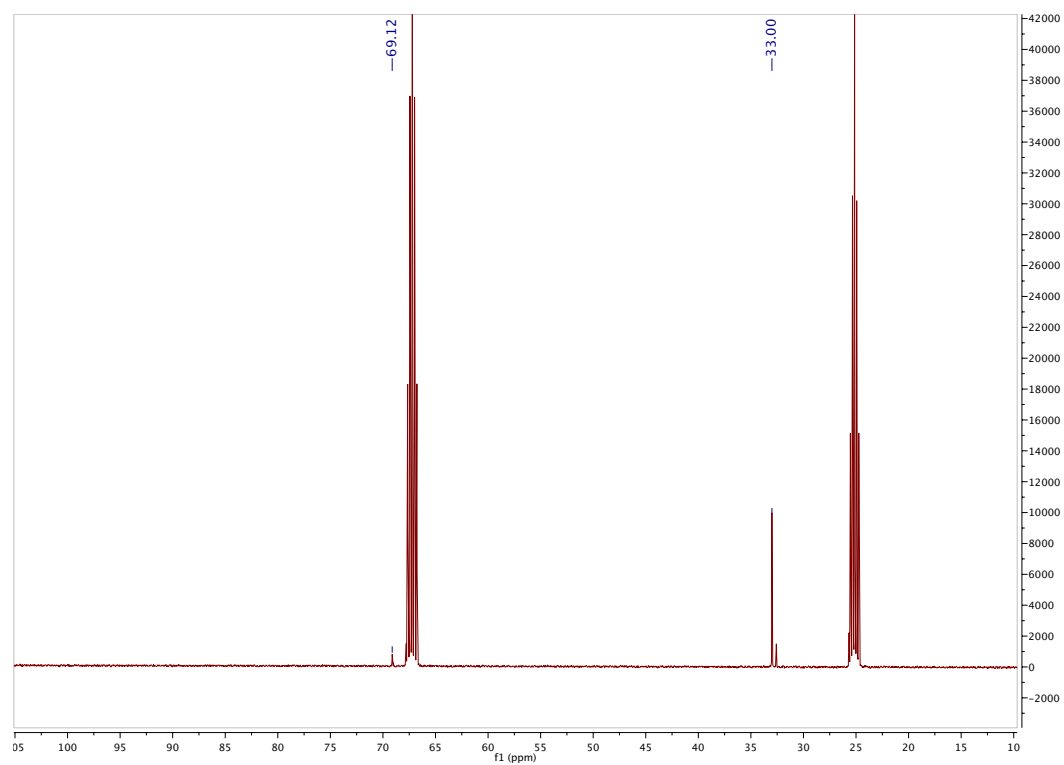


Figure A.32 $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **24a** in THF-d_8 (100 MHz): δ 69.12 (CMe_3 of ^tBu), 33.00 (CMe_3 of ^tBu) ppm.

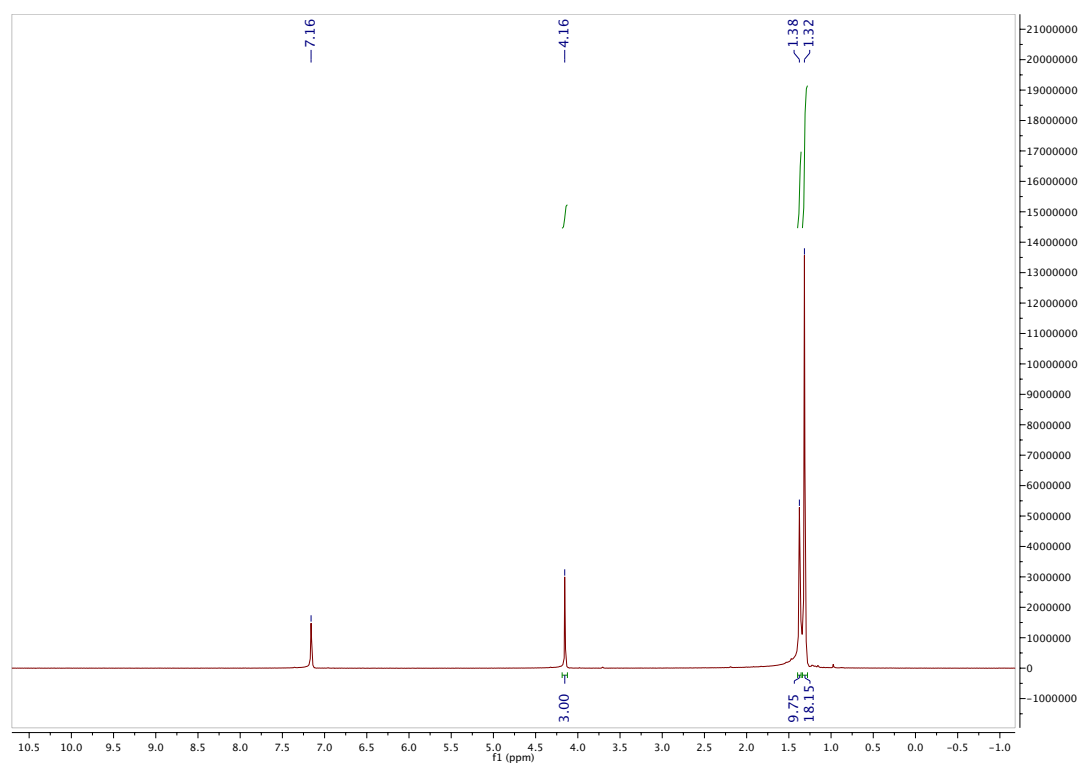


Figure A.33 ^1H NMR spectrum of **25** in C_6D_6 (400 MHz): δ 4.16 (s, 3 H, NMe^tBu), 1.38 (s, 9 H, NMe^tBu), 1.32 (s, 18 H, N^tBu) ppm.

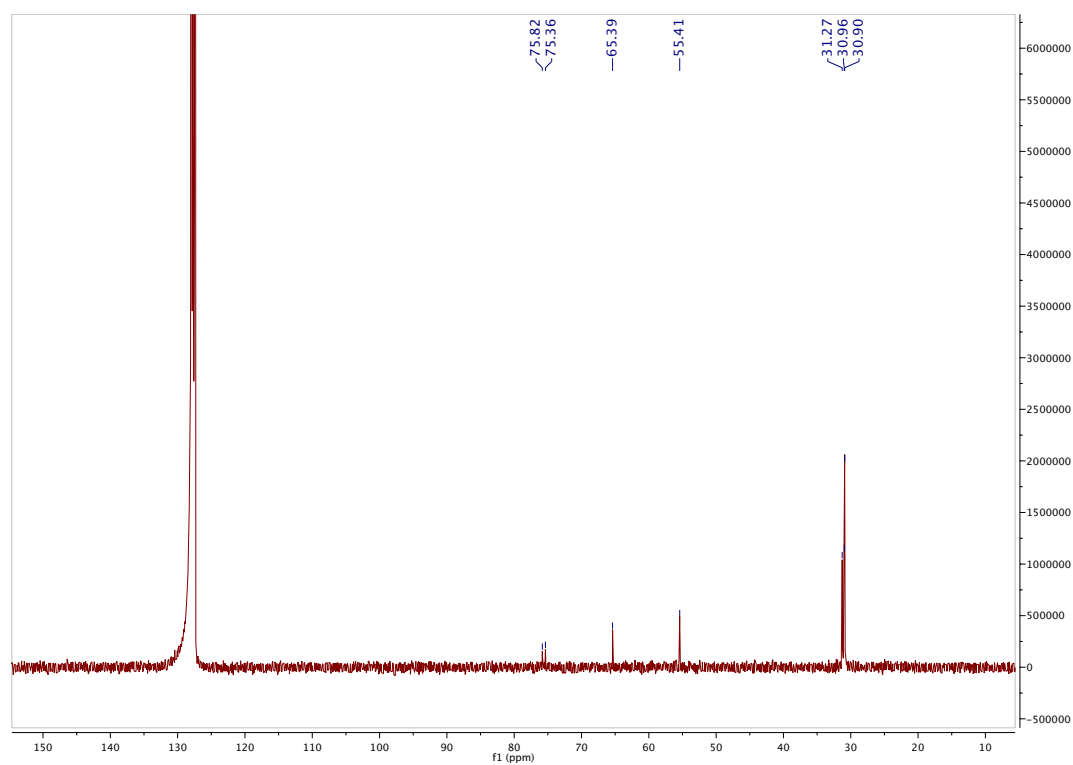


Figure A.34 $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **25** in C_6D_6 (100 MHz): δ 75.82 (CMe_3 of N^tBu), 75.36 (CMe_3 of N^tBu), 65.39 (CMe_3 of NMe^tBu), 55.41 (NMe^tBu), 31.27 (CMe_3 of NMe^tBu), 30.96 (CMe_3 of N^tBu), 30.90 (CMe_3 of N^tBu) ppm.

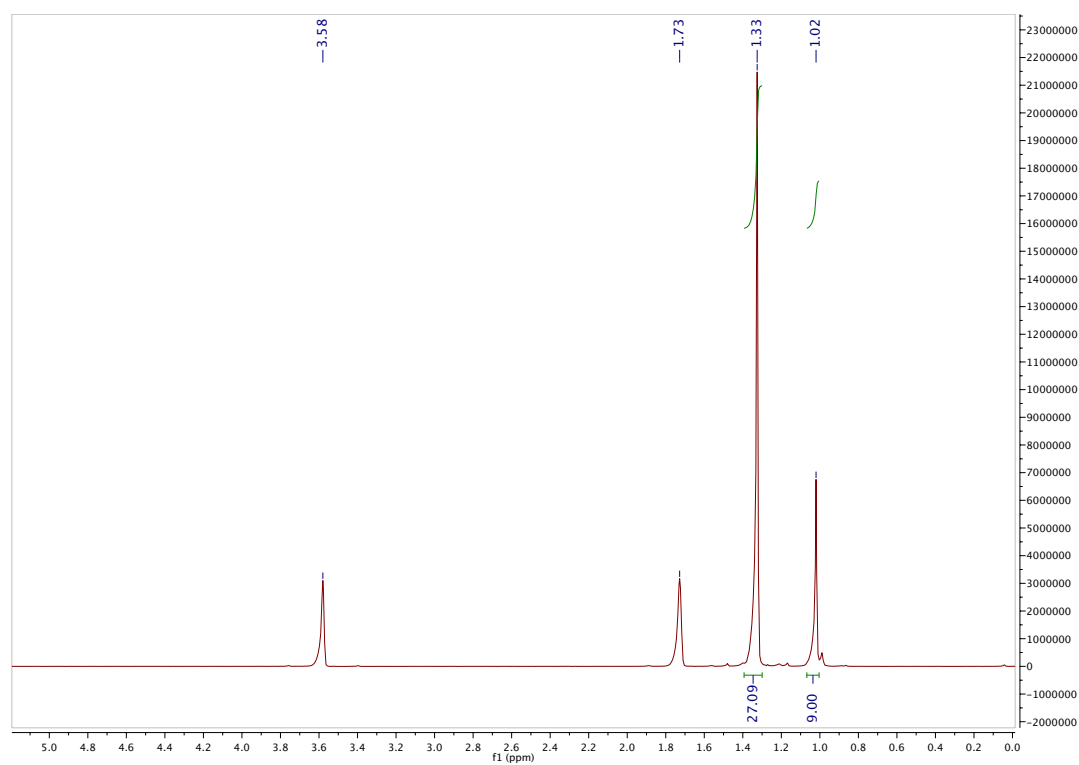


Figure A.35 ^1H NMR spectrum of **27** in THF-d_8 (400 MHz): δ 7.15 (broad, 1 H, $\text{NH}'\text{Bu}$, assigned in NOESY), 1.33 (s, 27 H, $\text{N}'\text{Bu}$), 1.02 (s, 9 H, $\text{NH}'\text{Bu}$) ppm.

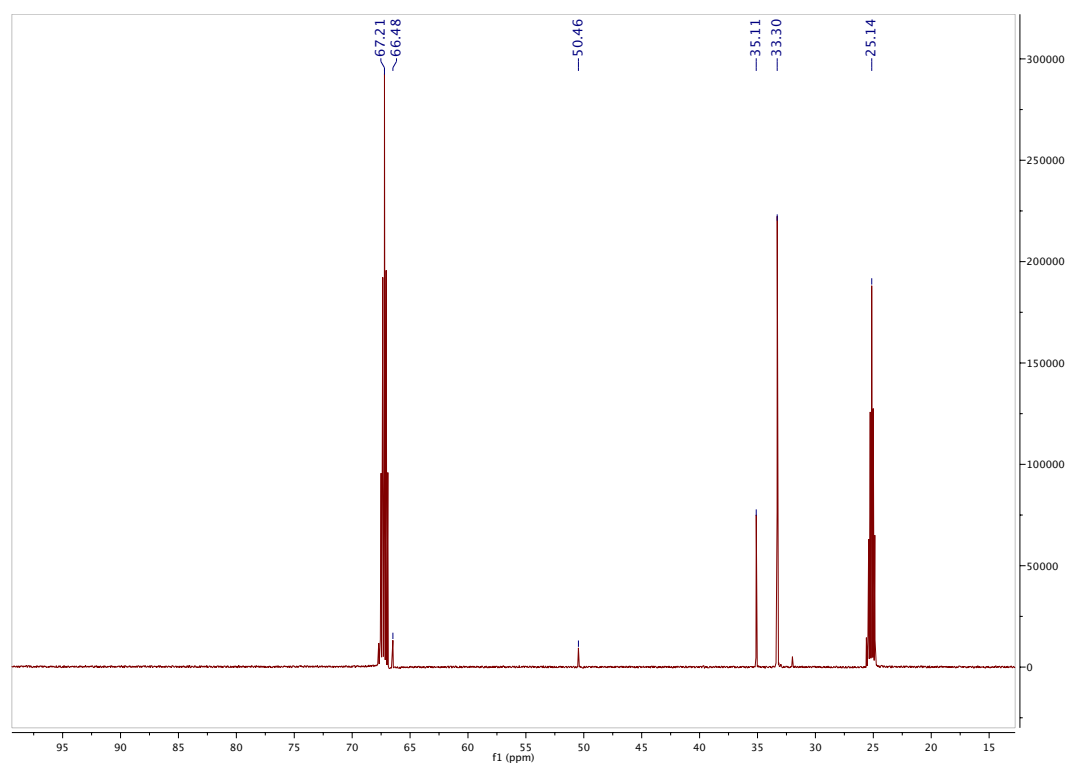


Figure A.36 $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **27** in THF-d_8 (150 MHz): δ 66.48 (CMe_3 of N^tBu), 50.46 (CMe_3 of NH^tBu), 35.11 (CMe_3 of NH^tBu), 33.30 (CMe_3 of N^tBu) ppm.

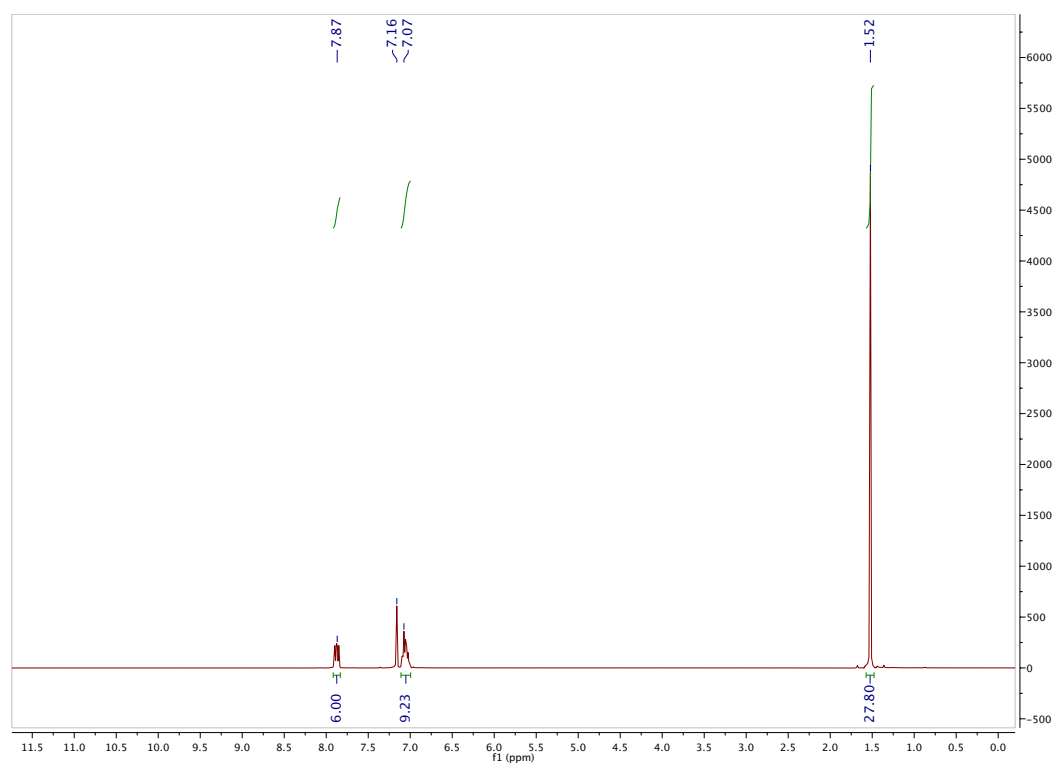


Figure A.37 ^1H NMR spectrum of **28** in C_6D_6 (400 MHz): δ 7.87 (m, 6 H, PPh_3), 7.07 (m, 9 H, PPh_3), 1.52 (s, 27 H, ^tBu) ppm.

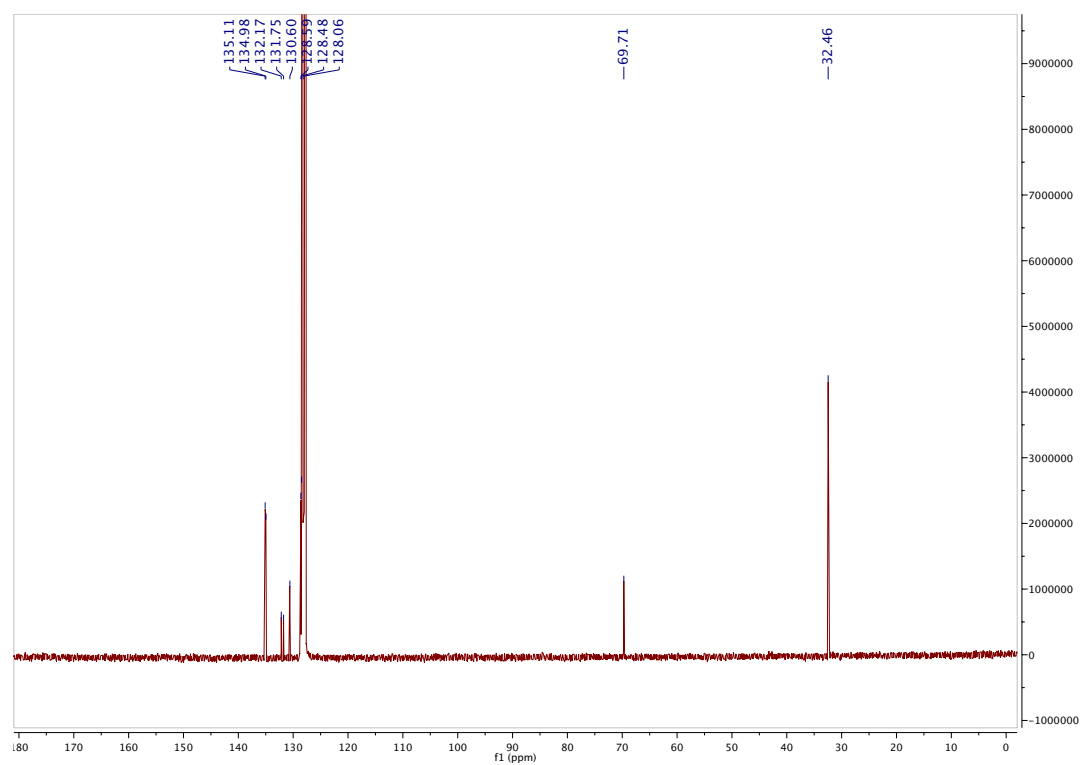


Figure A.38 $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **28** in C_6D_6 (150 MHz): δ 135.04 (C_{ortho}), 131.96 (C_{ipso}), 130.61 (C_{para}), 128.54 (C_{meta}), 69.71 (^tBu), 32.46 (^tBu) ppm.

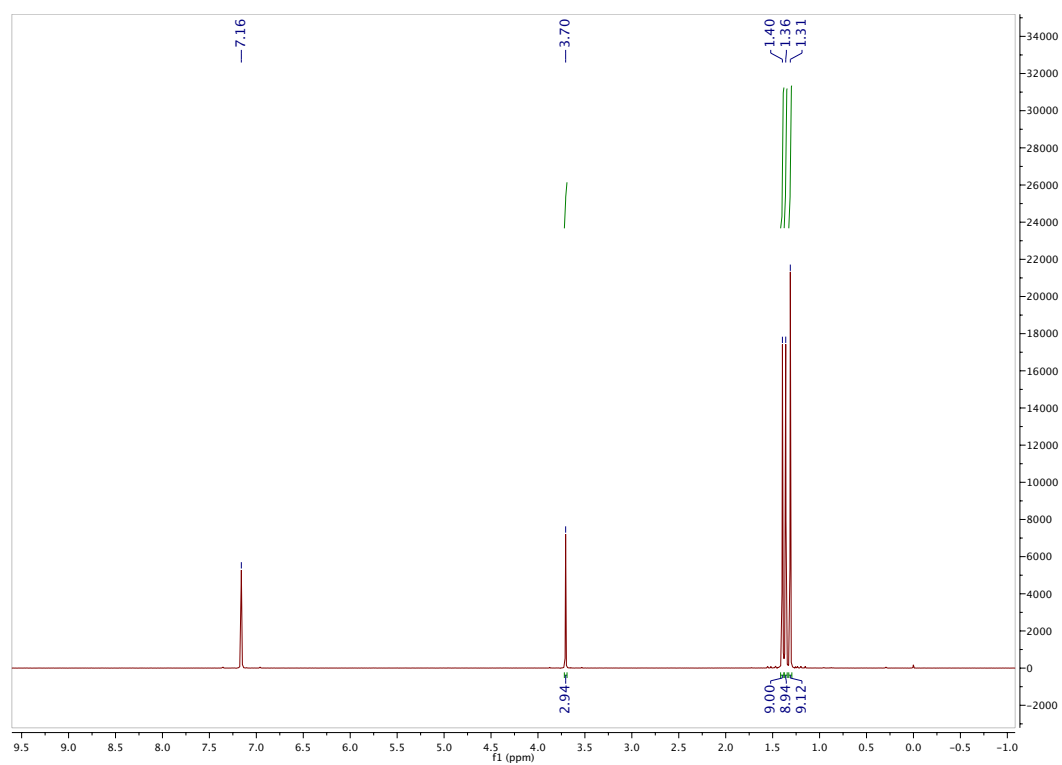


Figure A.39 ^1H NMR spectrum of **29** in C_6D_6 (400 MHz): δ 3.70 (s, 3 H, NMe^tBu), 1.40 (s, 9 H, NMe^tBu), 1.36 (s, 9 H, N^tBu), 1.31 (s, 9 H, N^tBu) ppm.

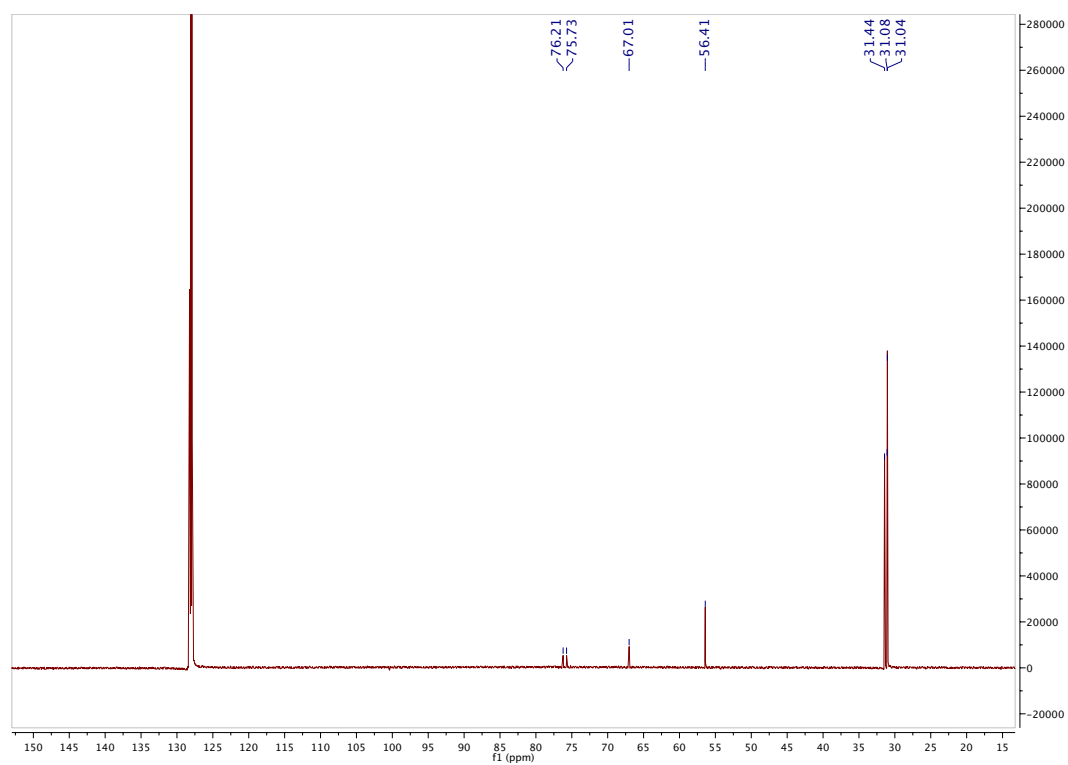


Figure A.40 $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **29** in C_6D_6 (150 MHz): δ 76.21 CMe_3 of N^tBu , 75.73 (CMe_3 of N^tBu), 67.01 (CMe_3 of NMe^tBu), 56.41 (NMe^tBu), 31.44 (CMe_3 of NMe^tBu), 31.08 (CMe_3 of N^tBu), 31.04 (CMe_3 of N^tBu) ppm.

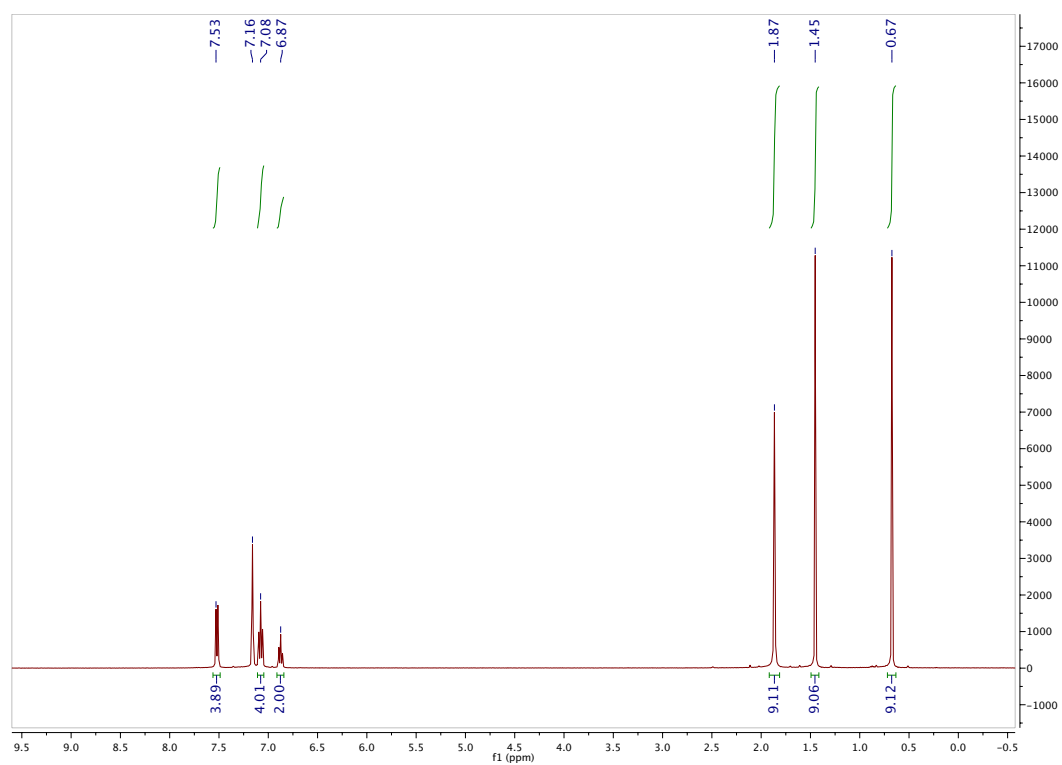


Figure A.41 ^1H NMR spectrum of **30** in C_6D_6 (400 MHz): δ 7.52 (d, 4 H, H_{ortho}), 7.08 (t, 4 H, H_{meta}), 6.87 (t, 2 H, H_{para}), 1.87 (s, 9 H, tBu), 1.46 (s, 9 H, tBu), 0.67 (s, 9 H, tBu) ppm.

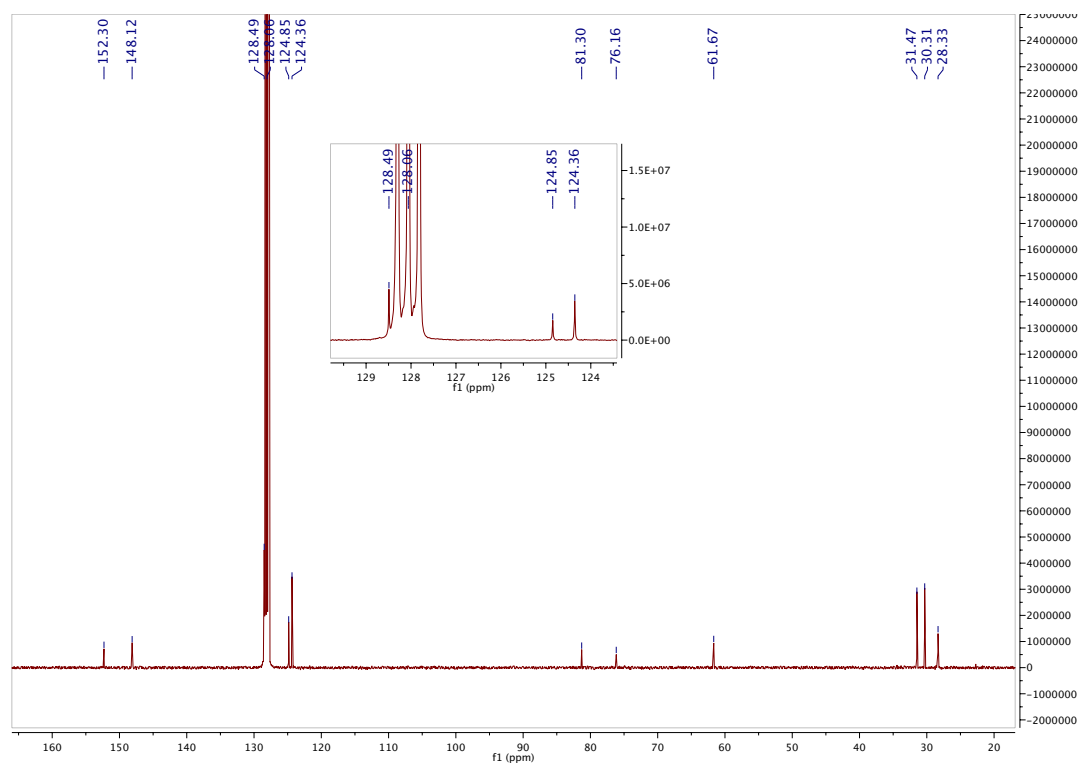


Figure A.42 $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **30** in C_6D_6 (100 MHz): δ 152.30 ($\text{C}=\text{O}$), 148.12 (C_{ipso}), 128.49 (C_{ortho}), 124.85 (C_{para}), 124.36 (C_{meta}), 81.30 (CMe_3 of ^tBu), 76.16 (CMe_3 of ^tBu), 61.67 (CMe_3 of ^tBu), 31.47 (CMe_3 of ^tBu), 30.31 (CMe_3 of ^tBu), 28.33 (CMe_3 of ^tBu) ppm.

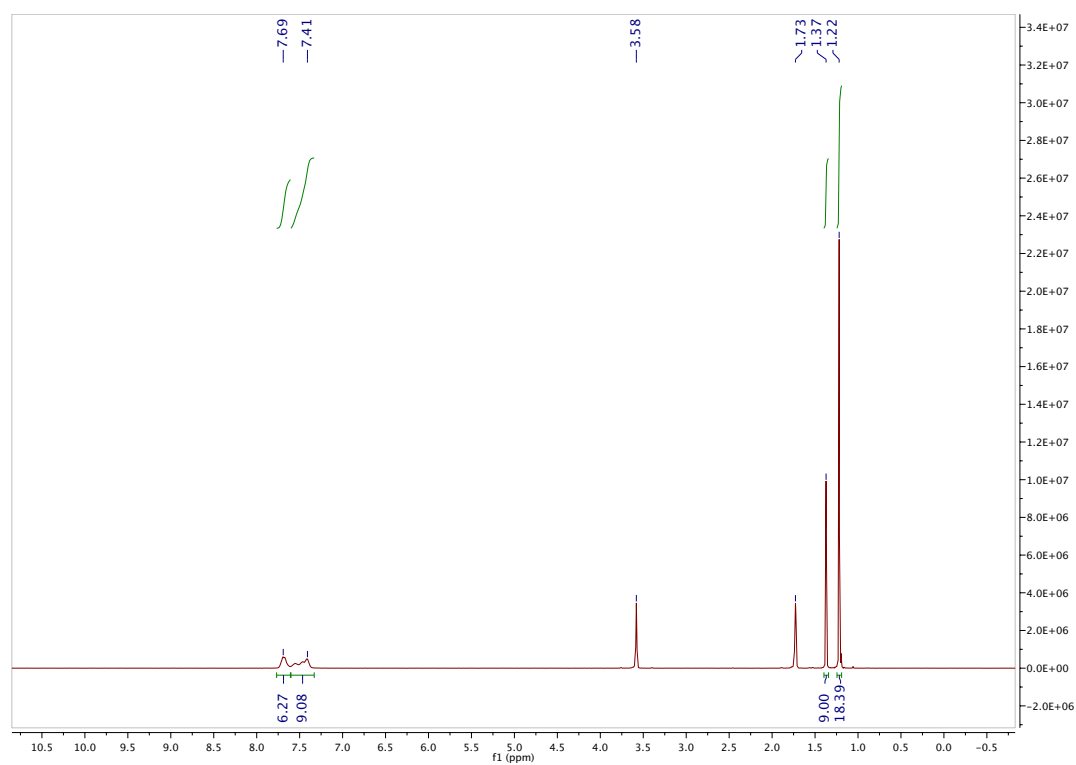


Figure A.43 ^1H NMR spectrum of **31** in THF-d_8 (400 MHz): δ 7.69 (m, 6 H, PPh_3), 7.41 (m, 9 H, PPh_3), 1.37 (s, 9 H, tBu), 1.22 (s, 18 H, tBu) ppm.

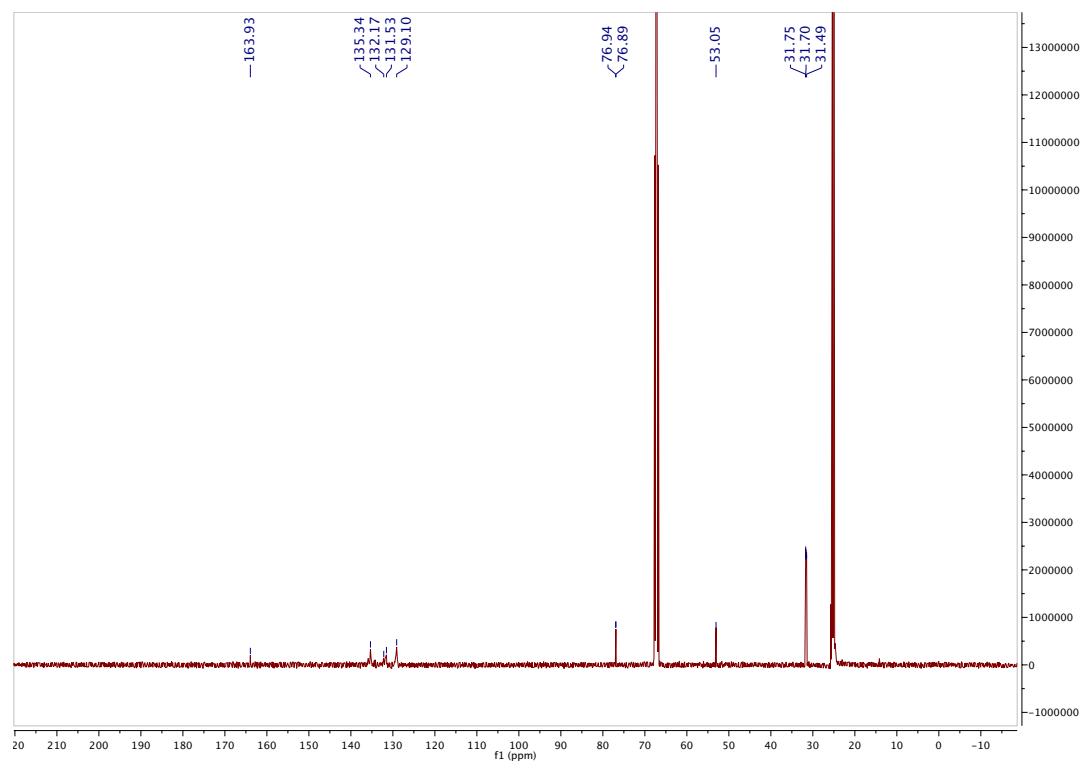


Figure A.44 $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **31** in THF- d_8 (100 MHz): δ 163.93 (C=O), 135.24 (C_{ortho}), 132.17 (C_{ipso}), 131.53 (C_{para}), 129.10 (C_{meta}), 76.94 (CMe_3 of 'Bu), 76.89 (CMe_3 of 'Bu), 53.05 (CMe_3 of carbamate 'Bu), 31.75 (CMe_3 of 'Bu), 31.70 (CMe_3 of 'Bu), 31.49 (CMe_3 of carbamate 'Bu) ppm.

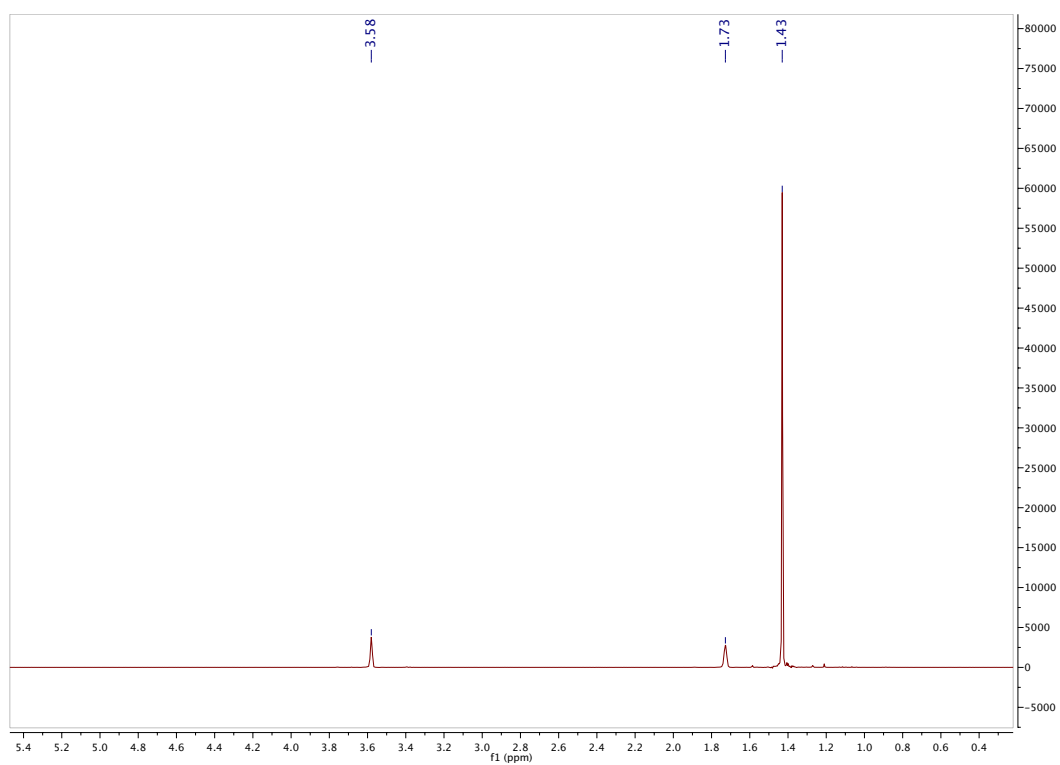


Figure A.45 ^1H NMR spectrum of **24b** in THF-d_8 (400 MHz): δ 1.43 (s, 18 H, ^tBu) ppm.

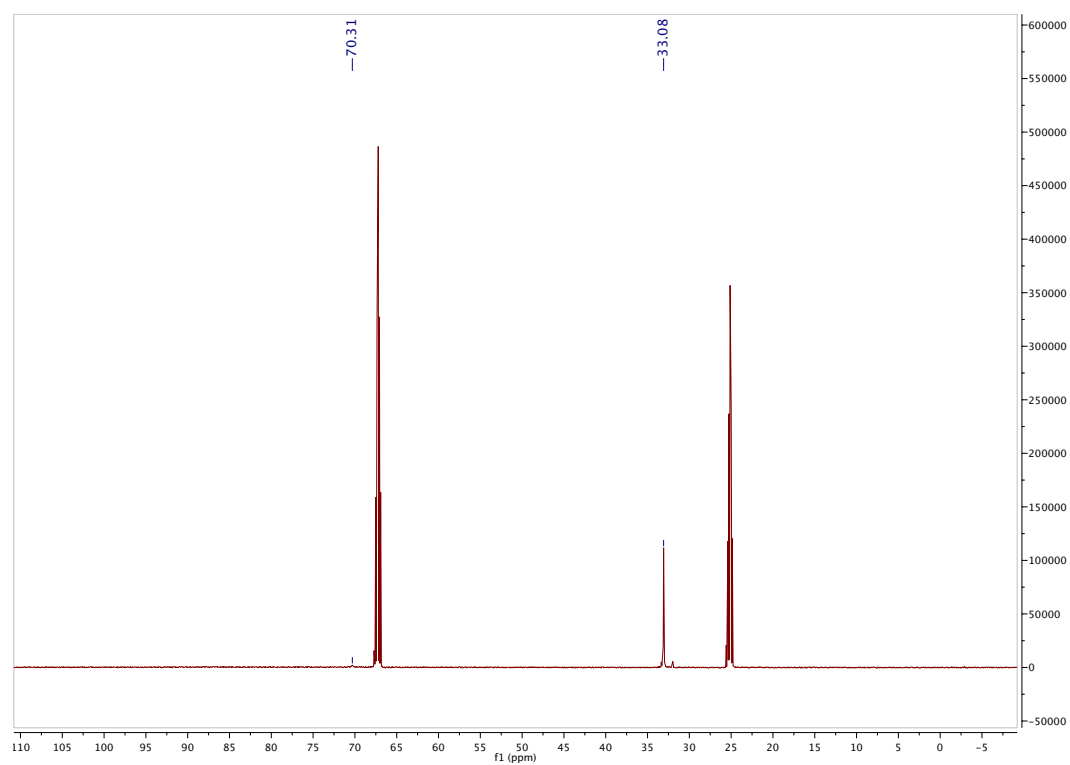


Figure A.46 $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **24b** in THF- d_8 (150 MHz): δ 70.31 (CMe_3 of ^tBu), 33.08 (CMe_3 of ^tBu) ppm.

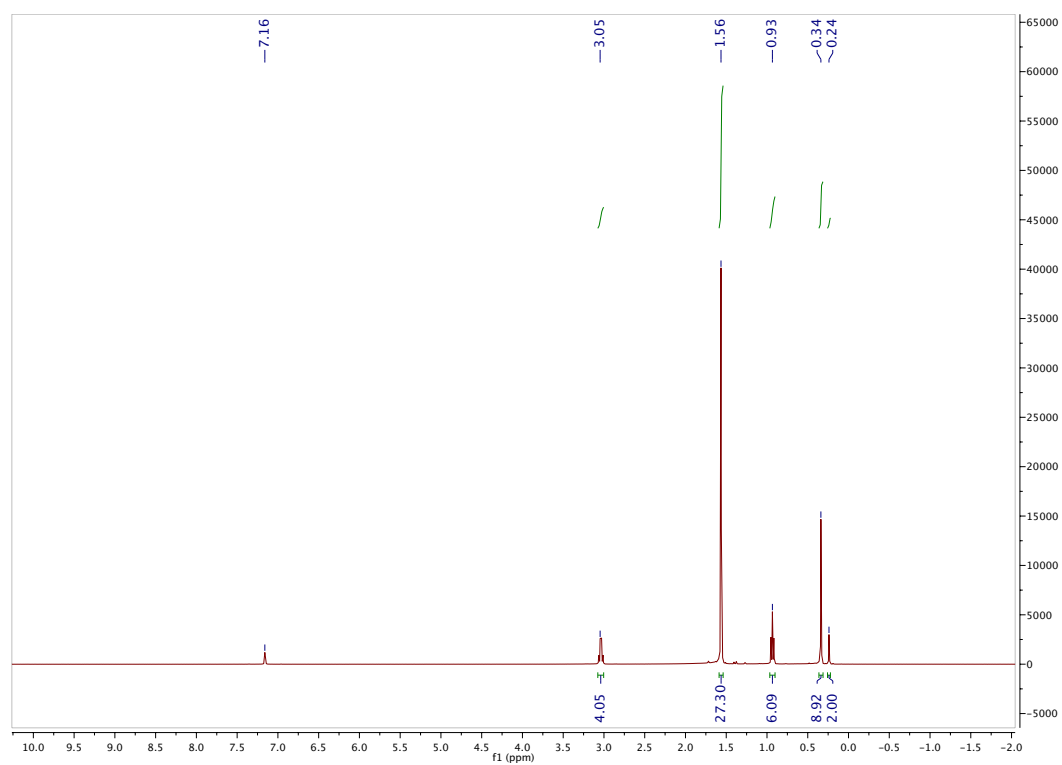


Figure A.47 ^1H NMR spectrum of **32** in C_6D_6 (400 MHz): δ 3.05 (q, 4 H, CH_2 of coordinated Et_2O), 1.56(s, 27 H, ^tBu), 0.93 (t, 6 H, CH_3 of coordinated Et_2O), 0.34 (s, 9 H, CH_2SiMe_3), 0.24 (s, 2 H, CH_2SiMe_3) ppm.

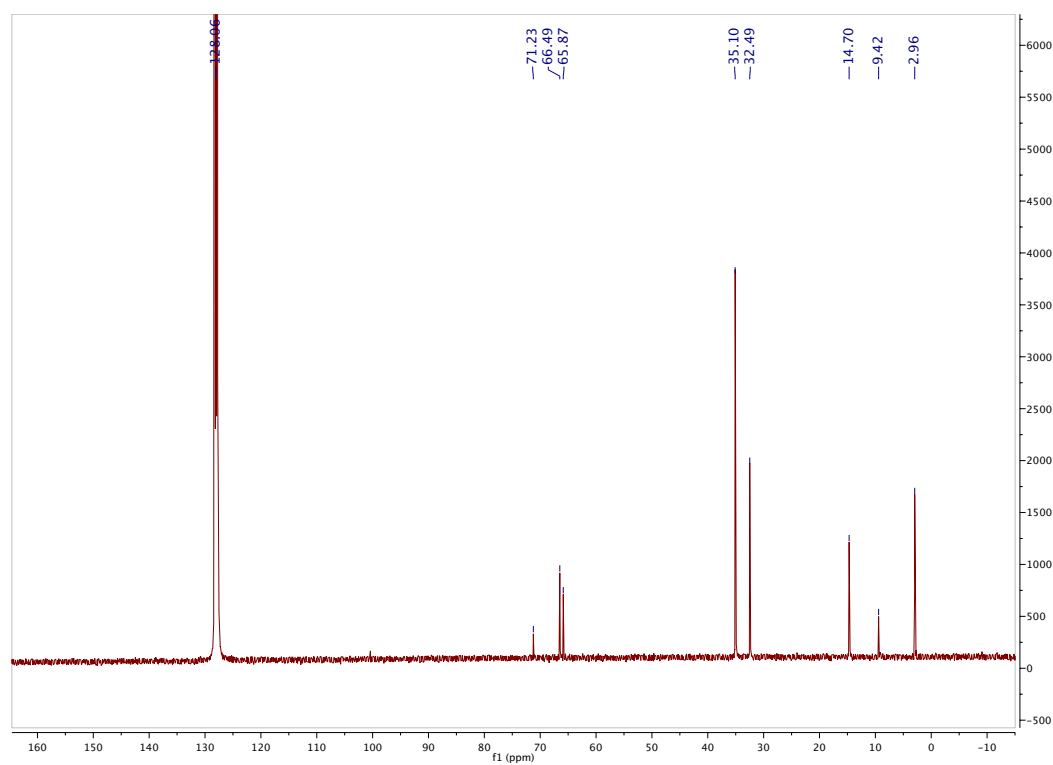


Figure A.48 $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **32** in C_6D_6 (100 MHz): δ 71.23 (CMe_3 of linear CrN^tBu), 66.49 (CH_2 of coordinated Et_2O), 65.87 (CMe_3 of bent CrN^tBu), 35.10 (CMe_3 of bent CrN^tBu), 32.49 (CMe_3 of linear CrN^tBu), 14.70 (CH_3 of coordinated Et_2O), 9.42 (CH_2SiMe_3), 2.96 (CH_2SiMe_3) ppm.

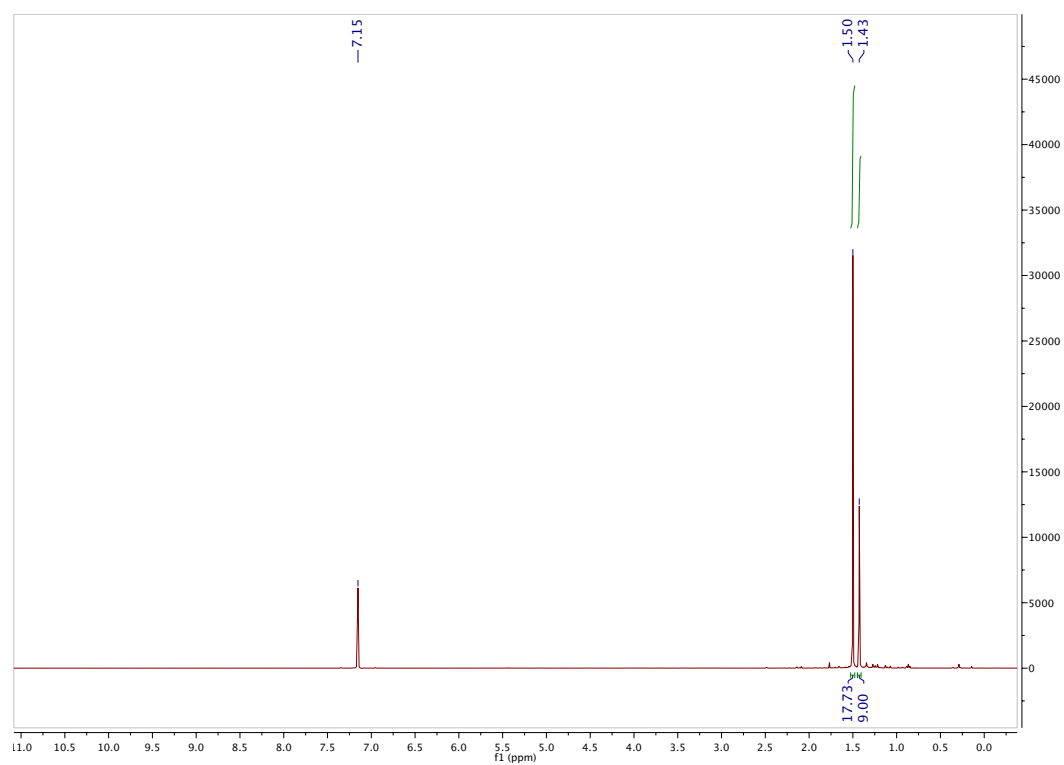


Figure A.49 ^1H NMR spectrum of **33** in C_6D_6 (400 MHz): δ 1.51 (s, 18 H, ^tBu), 1.44 (s, 9 H, carbamate ^tBu) ppm.

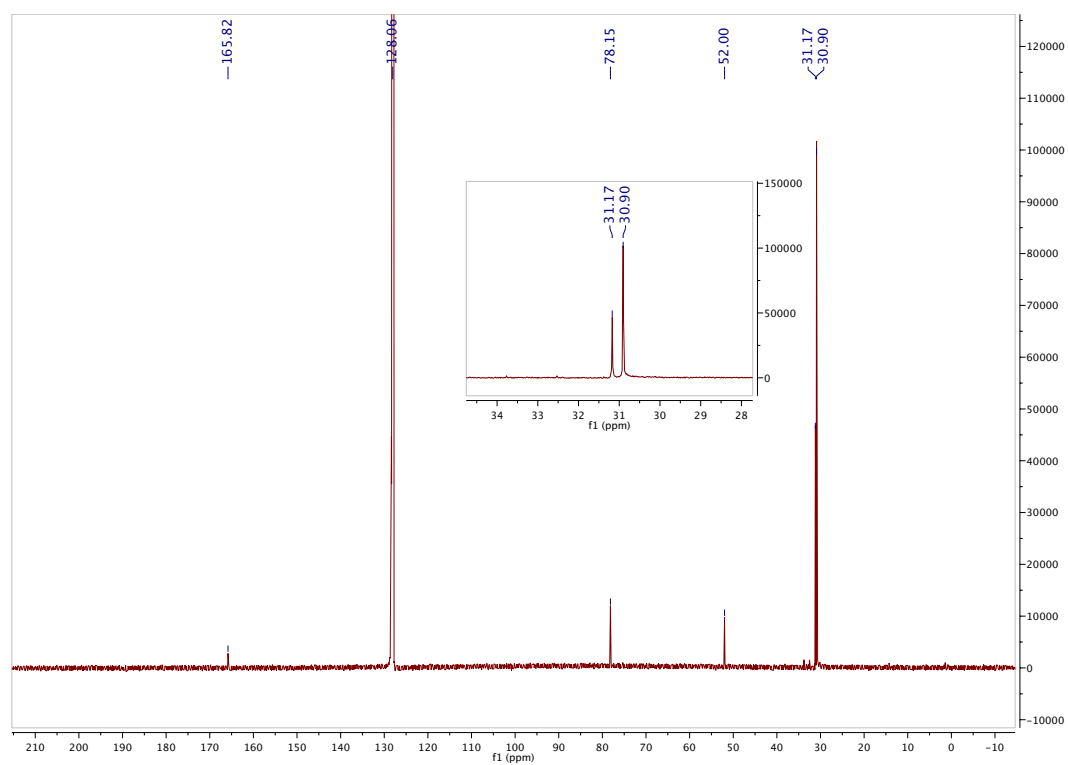


Figure A.50 $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **33** in C_6D_6 (150 MHz): δ 165.82 (C=O), 78.15 (CMe_3 of imido ^tBu), 52.00 (CMe_3 of carbamate ^tBu), 31.17 (CMe_3 of carbamate ^tBu), 30.90 (CMe_3 of imido ^tBu) ppm.

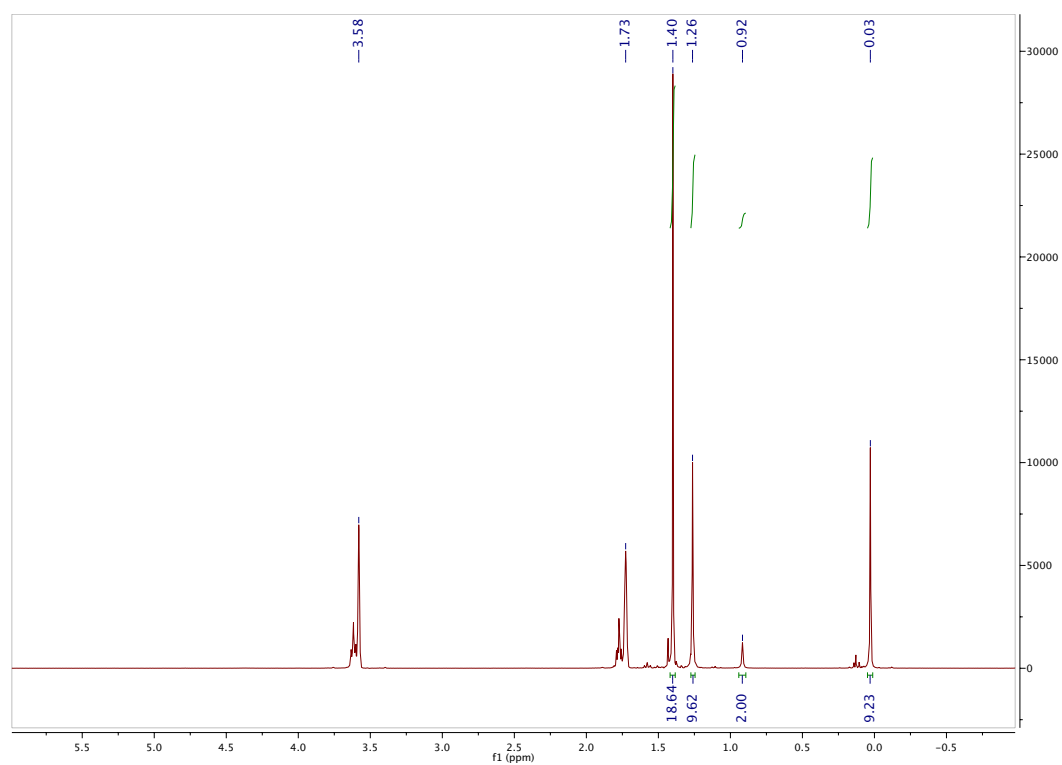


Figure A.51 ^1H NMR spectrum of **34** in THF-d_8 (400 MHz): δ 1.40 (s, 18 H, ^tBu), 1.26 (s, 9 H, carbamate ^tBu), 0.92 (s, 2 H, CH_2SiMe_3), 0.03 (s, 9 H, CH_2SiMe_3) ppm.

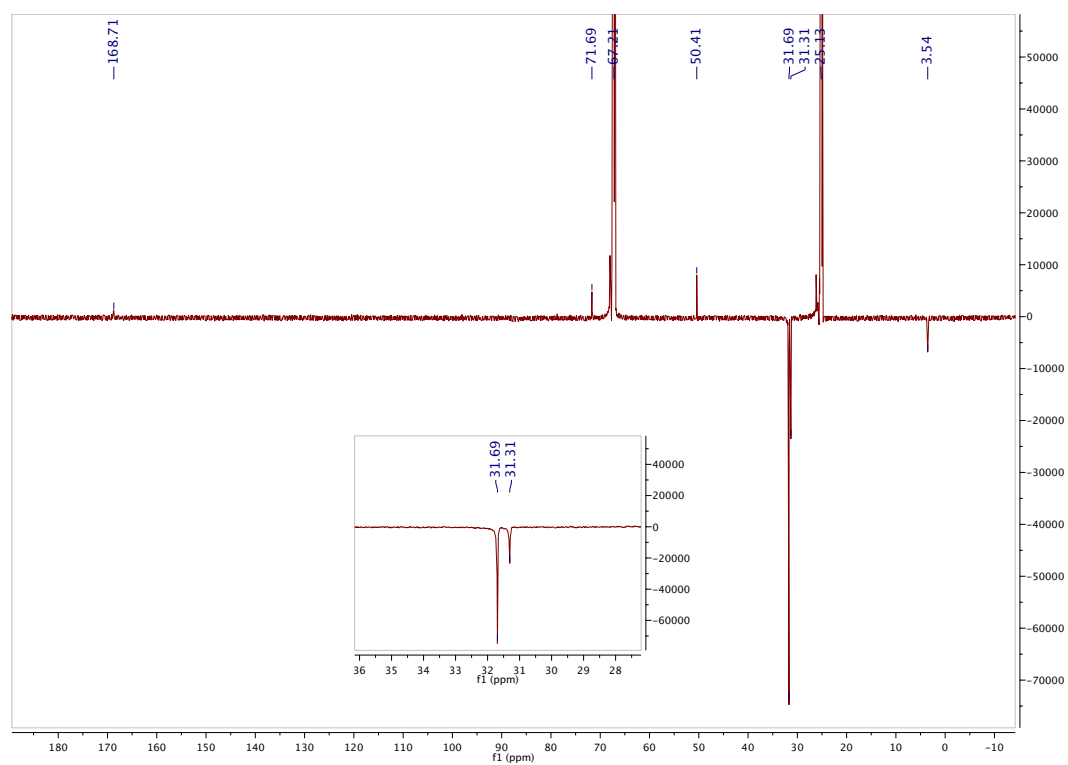


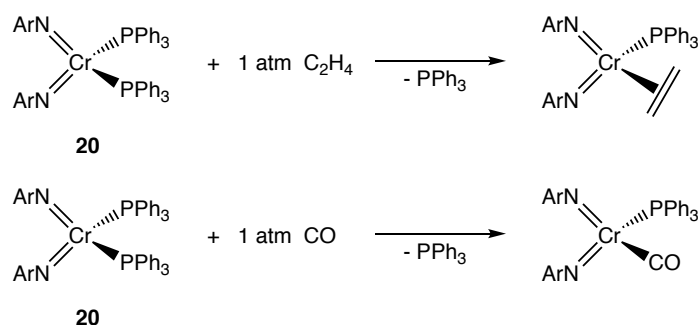
Figure A.52 $^{13}\text{C}\{^1\text{H}\}$ APT NMR spectrum of **34** in THF-d_8 (150 MHz): δ 168.71 (C=O), 71.69 (CMe_3 of imido ^tBu), 50.41 (CMe_3 of carbamate ^tBu), 31.69 (CMe_3 of imido ^tBu), 31.31 (CMe_3 of carbamate ^tBu), 26.19 (CH_2SiMe_3), 3.54 (CH_2SiMe_3) ppm.

Appendix B

LIGAND SUBSTITUTION OF $(\text{ArN})_2\text{Cr}(\text{PPh}_3)_2$ (**20**)

B.1 Ligand substitutions with ethylene and CO

One phosphine ligand of **20** could be substituted by ethylene or CO, yielding $(\text{ArN})_2\text{Cr}(\text{PPh}_3)(\text{C}_2\text{H}_4)$ and $(\text{ArN})_2\text{Cr}(\text{PPh}_3)(\text{CO})$ respectively (Scheme B.1).



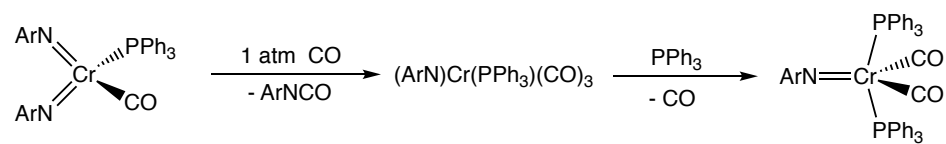
Scheme B.1 Ligand substitutions of **20** with ethylene and CO

The ethylene adduct was characterized with multi-nuclear NMR spectra, 2D-NMR HSQC, and LIFDI-MS. After removal of ethylene atmosphere, the ethylene adduct went back to **20** in pentane solution due to the presence of free phosphine.

Chromium(IV) carbonyl complexes are not common. The Cr^{IV} center has less d-electrons than the metal center of low-valent chromium carbonyl complexes. Thus, π -back donation from Cr^{IV} center is weaker than that from low-valent chromium center. However, in the presence of a strong π -donating ligand, Cr^{IV} carbonyls can

exist. The notable chromium(IV) carbonyl complex in the literature was reported by Mayr in 1986, namely $\text{Br}(\text{CO})[\text{P}(\text{OMe})_3]_3\text{Cr}\equiv\text{CPh}$ ($\nu_{\text{CO}} = 1954 \text{ cm}^{-1}$).

The CO adduct $(\text{ArN})_2\text{Cr}(\text{PPh}_3)(\text{CO})$ is unstable at room temperature. It slowly decomposed to $(\text{ArN})\text{Cr}(\text{PPh}_3)(\text{CO})_3$ and the byproduct isocyanate ArNCO . The formation of $(\text{ArN})\text{Cr}(\text{PPh}_3)(\text{CO})_3$ was supported by ^{31}P NMR and LIFDI-MS. The production of ArNCO was confirmed by comparing the NMR spectra (^1H NMR and ^{13}C NMR) of products and the NMR spectra (^1H NMR and ^{13}C NMR) of authentic ArNCO . Even under one atmosphere of CO, $(\text{ArN})\text{Cr}(\text{PPh}_3)(\text{CO})_3$ is still not stable due to the existence of free phosphine. $(\text{ArN})\text{Cr}(\text{PPh}_3)(\text{CO})_3$ was slowly transformed to $(\text{ArN})\text{Cr}(\text{PPh}_3)_2(\text{CO})_2$, which has been structurally characterized. (Scheme B.2) The structure of $(\text{ArN})\text{Cr}(\text{PPh}_3)_2(\text{CO})_2$ is depicted in Figure B.1 and the corresponding interatomic distances and angles are listed in Table B.1. The geometry of this five-coordinated complex is half-way between square pyramid and trigonal bipyramid with τ value equal to 0.47. The structure features C_{2v} symmetry with axial Cr1-N1. The Cr1-N1 imido bond ($1.696(2) \text{ \AA}$) is slightly longer than imido bonds of those bis(imido) chromium(VI) complexes that have been discussed in **Chapter 1** and **Chapter 2**. This might be a result of the lower oxidation state (Cr(II)) of chromium in $(\text{ArN})\text{Cr}(\text{PPh}_3)_2(\text{CO})_2$. The geometry of the imido group is close to linear with a bond angle of Cr1-N1-C6 ($169.2(1)^\circ$). In ^{13}C NMR, a downfield triplet peak (261.91 ppm , $^2J_{\text{PC}} = 34.0 \text{ Hz}$) was assigned to carbonyl carbon. The two carbonyl ligands of $(\text{ArN})\text{Cr}(\text{PPh}_3)_2(\text{CO})_2$ cause two strong absorption bands (symmetric vibration and asymmetric vibration) in the infrared spectrum. The calculation result based on group theory gave the irreducible representation Γ ($\text{A}_1 + \text{B}_2$, both are active in infrared spectroscopy), which is consistent with two peaks in the infrared spectrum.



Scheme B.2 Decomposition of $(\text{ArN})_2\text{Cr}(\text{PPh}_3)(\text{CO})$

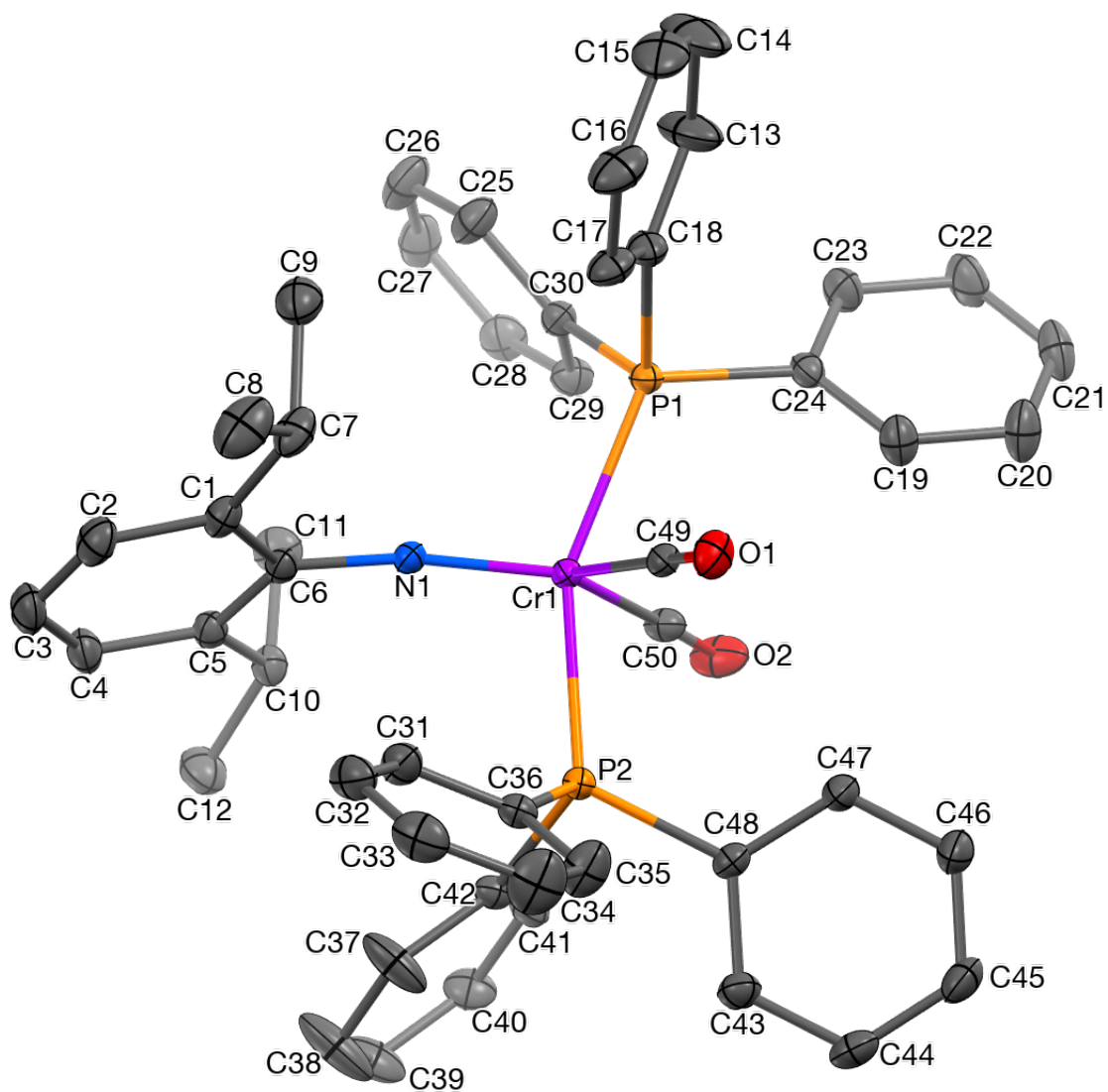


Figure B.1 Molecular structure of $(\text{ArN})\text{Cr}(\text{PPh}_3)_2(\text{CO})_2$. Ellipsoids are drawn at the 30% probability level. Hydrogen atoms have been omitted for clarity.

Table B.1 Interatomic distances (Å) and angles (°) for (ArN)Cr(PPh₃)₂(CO)₂

Distances (Å)			
Cr(1)-N(1)	1.6957(16)	C(19)-C(24)	1.384(3)
Cr(1)-C(49)	1.849(2)	C(19)-C(20)	1.391(3)
Cr(1)-C(50)	1.867(2)	C(20)-C(21)	1.376(4)
Cr(1)-P(2)	2.3344(6)	C(21)-C(22)	1.367(4)
Cr(1)-P(1)	2.3570(6)	C(22)-C(23)	1.394(3)
P(1)-C(30)	1.824(2)	C(23)-C(24)	1.394(3)
P(1)-C(24)	1.834(2)	C(25)-C(26)	1.391(4)
P(1)-C(18)	1.837(2)	C(25)-C(30)	1.395(3)
P(2)-C(42)	1.833(2)	C(26)-C(27)	1.368(4)
P(2)-C(48)	1.837(2)	C(27)-C(28)	1.384(4)
P(2)-C(36)	1.839(2)	C(28)-C(29)	1.380(3)
O(1)-C(49)	1.164(3)	C(29)-C(30)	1.398(3)
O(2)-C(50)	1.157(3)	C(31)-C(36)	1.384(3)
N(1)-C(6)	1.387(2)	C(31)-C(32)	1.388(3)
C(1)-C(2)	1.396(3)	C(32)-C(33)	1.371(4)
C(1)-C(6)	1.423(3)	C(33)-C(34)	1.372(4)
C(1)-C(7)	1.514(3)	C(34)-C(35)	1.387(4)
C(2)-C(3)	1.382(4)	C(35)-C(36)	1.386(3)
C(3)-C(4)	1.384(4)	C(37)-C(42)	1.380(3)
C(4)-C(5)	1.391(3)	C(37)-C(38)	1.395(4)
C(5)-C(6)	1.424(3)	C(38)-C(39)	1.367(4)
C(5)-C(10)	1.514(3)	C(39)-C(40)	1.367(4)
C(7)-C(9)	1.530(4)	C(40)-C(41)	1.383(3)
C(7)-C(8)	1.532(4)	C(41)-C(42)	1.388(3)
C(10)-C(12)	1.521(3)	C(43)-C(44)	1.390(3)
C(10)-C(11)	1.527(3)	C(43)-C(48)	1.401(3)
C(13)-C(14)	1.380(4)	C(44)-C(45)	1.378(4)
C(13)-C(18)	1.392(4)	C(45)-C(46)	1.382(4)
C(14)-C(15)	1.361(5)	C(46)-C(47)	1.389(3)
C(15)-C(16)	1.376(5)	C(47)-C(48)	1.384(3)
C(16)-C(17)	1.397(3)	C(19)-C(24)	1.384(3)
C(17)-C(18)	1.379(3)	C(19)-C(20)	1.391(3)

Angles (°)

N(1)-Cr(1)-C(49)	122.93(8)	C(17)-C(18)-C(13)	118.5(2)
N(1)-Cr(1)-C(50)	126.92(9)	C(17)-C(18)-P(1)	120.88(17)
C(49)-Cr(1)-C(50)	109.75(9)	C(13)-C(18)-P(1)	120.5(2)
N(1)-Cr(1)-P(2)	98.73(6)	C(24)-C(19)-C(20)	120.8(2)
C(49)-Cr(1)-P(2)	80.32(6)	C(21)-C(20)-C(19)	120.3(2)
C(50)-Cr(1)-P(2)	83.12(6)	C(22)-C(21)-C(20)	119.8(2)
N(1)-Cr(1)-P(1)	105.88(6)	C(21)-C(22)-C(23)	120.3(2)
C(49)-Cr(1)-P(1)	87.12(6)	C(24)-C(23)-C(22)	120.6(2)
C(50)-Cr(1)-P(1)	81.32(6)	C(19)-C(24)-C(23)	118.2(2)
P(2)-Cr(1)-P(1)	155.37(2)	C(19)-C(24)-P(1)	120.04(17)
C(30)-P(1)-C(24)	102.55(10)	C(23)-C(24)-P(1)	121.66(17)
C(30)-P(1)-C(18)	104.47(11)	C(26)-C(25)-C(30)	120.1(3)
C(24)-P(1)-C(18)	100.02(10)	C(27)-C(26)-C(25)	120.8(2)
C(30)-P(1)-Cr(1)	109.71(7)	C(26)-C(27)-C(28)	119.8(2)
C(24)-P(1)-Cr(1)	118.10(7)	C(29)-C(28)-C(27)	120.1(3)
C(18)-P(1)-Cr(1)	119.87(8)	C(28)-C(29)-C(30)	120.9(2)
C(42)-P(2)-C(48)	100.19(9)	C(25)-C(30)-C(29)	118.3(2)
C(42)-P(2)-C(36)	104.60(9)	C(25)-C(30)-P(1)	122.42(19)
C(48)-P(2)-C(36)	102.75(9)	C(29)-C(30)-P(1)	119.21(16)
C(42)-P(2)-Cr(1)	115.93(6)	C(36)-C(31)-C(32)	120.8(2)
C(48)-P(2)-Cr(1)	119.63(7)	C(33)-C(32)-C(31)	120.8(2)
C(36)-P(2)-Cr(1)	111.80(7)	C(32)-C(33)-C(34)	118.8(2)
C(6)-N(1)-Cr(1)	169.21(15)	C(33)-C(34)-C(35)	121.1(3)
C(2)-C(1)-C(6)	118.1(2)	C(36)-C(35)-C(34)	120.4(3)
C(2)-C(1)-C(7)	121.8(2)	C(31)-C(36)-C(35)	118.1(2)
C(6)-C(1)-C(7)	119.9(2)	C(31)-C(36)-P(2)	118.65(16)
C(3)-C(2)-C(1)	121.7(2)	C(35)-C(36)-P(2)	123.07(17)
C(2)-C(3)-C(4)	119.9(2)	C(42)-C(37)-C(38)	120.0(3)
C(3)-C(4)-C(5)	121.6(2)	C(39)-C(38)-C(37)	121.0(3)
C(4)-C(5)-C(6)	118.4(2)	C(40)-C(39)-C(38)	119.5(2)
C(4)-C(5)-C(10)	121.8(2)	C(39)-C(40)-C(41)	120.1(2)
C(6)-C(5)-C(10)	119.78(18)	C(40)-C(41)-C(42)	121.2(2)
N(1)-C(6)-C(1)	120.07(19)	C(37)-C(42)-C(41)	118.2(2)
N(1)-C(6)-C(5)	119.57(18)	C(37)-C(42)-P(2)	123.01(17)

C(1)-C(6)-C(5)	120.26(19)	C(41)-C(42)-P(2)	118.80(16)
C(1)-C(7)-C(9)	108.7(2)	C(44)-C(43)-C(48)	120.5(2)
C(1)-C(7)-C(8)	114.3(2)	C(45)-C(44)-C(43)	120.5(2)
C(9)-C(7)-C(8)	110.6(2)	C(44)-C(45)-C(46)	119.4(2)
C(5)-C(10)-C(12)	114.09(19)	C(45)-C(46)-C(47)	120.5(2)
C(5)-C(10)-C(11)	108.78(18)	C(48)-C(47)-C(46)	120.8(2)
C(12)-C(10)-C(11)	110.5(2)	C(47)-C(48)-C(43)	118.3(2)
C(14)-C(13)-C(18)	120.6(3)	C(47)-C(48)-P(2)	121.27(16)
C(15)-C(14)-C(13)	120.5(3)	C(43)-C(48)-P(2)	120.34(16)
C(14)-C(15)-C(16)	120.3(3)	O(1)-C(49)-Cr(1)	172.96(19)
C(15)-C(16)-C(17)	119.5(3)	O(2)-C(50)-Cr(1)	175.7(2)
C(18)-C(17)-C(16)	120.7(3)		

B.2 EXPERIMENTAL

B.2.1 General Considerations

All manipulations were carried out with standard Schlenk, vacuum line, and glovebox techniques. Pentane, diethyl ether, toluene and tetrahydrofuran were dried by passing through activated alumina and were degassed prior to use. C₆D₆ was purchased from Cambridge Isotopes Laboratory, dried with sodium and stored under vacuum over Na/K alloy. (ArN)₂Cr(PPh₃)₂ (**20**) was prepared according to the procedure in **Chapter 2**.

¹H NMR spectra were taken on a Bruker AVIII-400 spectrometer and were referenced to the residual protons of the solvent (C₆D₆ = 7.16 ppm, THF-d₈ = 3.58 ppm and 1.72 ppm). ¹³C NMR spectra were taken on a Bruker AVIII600 spectrometer and were referenced to the ¹³C of the solvent (C₆D₆ = 128.06 ppm). FT-IR spectra were obtained using a Nicolet Magna-IR 560 spectrometer with a resolution of 4 cm⁻¹. X-ray crystallographic studies were conducted in the X-ray Crystallographic Laboratory at the University of Delaware. LIFDI-MS were obtained using a Waters GCT Premier high-resolution time-of-flight mass spectrometer by liquid injection field desorption ionization (LIFDI-MS).

B.2.2 X-ray Crystallography

Crystal of (ArN)Cr(PPh₃)₂(CO)₂ was mounted onto plastic mesh using viscous oil and cooled to the data collection temperature. Data were collected on a Bruker-AXS APEX II Duo CCD diffractometer with Cu-K α radiation (λ = 1.54178 Å). Unit cell parameters were determined by sampling three different sections of the Ewald sphere. The systematic absences in the diffraction data are uniquely consistent with

$P2_1/c$. The data sets were treated with absorption corrections based on redundant multi-scan data. The structures were solved using intrinsic phasing and refined with full-matrix, least-squares procedures on F^2 .

B.2.3 Preparation of $(\text{ArN})_2\text{Cr}(\text{PPh}_3)(\text{C}_2\text{H}_4)$

$(\text{ArN})_2\text{Cr}(\text{PPh}_3)_2$ (**20**) (10 mg) was added into a J-Young tube. Then approximate 0.5 mL of C_6D_6 was added into the tube through vacuum transfer. One atmosphere of ethylene was charged into the tube. A color change from dark brown to light brown was observed immediately. This ethylene adduct was characterized with NMR spectroscopy and LIFDI-MS. ^1H NMR (400 MHz, C_6D_6): δ 7.71 (m, 6 H, H_{ortho} of PPh_3), 7.05 (m, 13 H, 3 H from H_{para} of free PPh_3 , 6 H from H_{meta} of free PPh_3 and 4 H from H_{meta} of ArN), 7.01 (m, 2 H, H_{para} of ArN), 6.96 (m, 9 H, H_{para} of PPh_3 and H_{meta} of PPh_3), 3.88 (sept, 4 H, CHMe_2), 3.12 (t, 2 H, C_2H_4 , *trans* to PPh_3), 2.35 (dt, 2 H, *cis* to PPh_3), 1.09 (d, 12 H, CHMe_2), 0.98 (d, 12 H, CHMe_2) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, C_6D_6): δ 158.24 (C_{ipso} of ArN), 145.19 (C_{ortho} of ArN), 134.70 (C_{ortho} of PPh_3), 133.73 (C_{ipso} of PPh_3), 130.20 (C_{para} of PPh_3), 128.56 (C_{meta} of PPh_3), 124.73 (C_{para} of ArN), 122.75 (C_{meta} of ArN), 58.18 (d, $J_{\text{PC}} = 8.8$ Hz, coordinated C_2H_4 , *cis* to PPh_3), 46.98 (s, coordinated C_2H_4 , *trans* to PPh_3), 28.38 (CHMe_2), 24.12 (CHMe_2), 23.86 (CHMe_2) ppm. $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, C_6D_6): δ 81.82 ppm. MS(LIFDI) m/z : 692.3369 [M^+]. Calcd. m/z : 692.3351 [M^+].

B.2.4 Preparation of $(\text{ArN})_2\text{Cr}(\text{PPh}_3)(\text{CO})$

$(\text{ArN})_2\text{Cr}(\text{PPh}_3)_2$ (**20**) (18 mg) was added into a J-Young tube. Then approximate 0.5 mL of C_6D_6 was added into the tube through vacuum transfer. One atmosphere of CO was charged into the tube. A color change from dark brown to light

brown was observed immediately. This carbonyl complex was characterized with NMR spectroscopy and IR spectroscopy. ^1H NMR (400 MHz, C_6D_6): δ 7.62 (m, 6 H, H_{ortho} of PPh_3), 7.05 (m, 6 H, H_{meta} of PPh_3), 6.94 (m, 9 H, H_{para} of PPh_3 and ArN), 3.99 (sept, 4 H, CHMe_2), 1.13 (d, 12 H, CHMe_2), 1.08 (d, 12 H, CHMe_2) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, C_6D_6): δ 158.41 (C_{ipso} of ArN), 144.93 (C_{ortho} of ArN), 134.08 (d, $^2J_{\text{PC}} = 12.5$ Hz, C_{ortho} of PPh_3), 134.08 (d, $^1J_{\text{PC}} = 40.0$ Hz, C_{ipso} of PPh_3 , different coupling constant so it can be assigned), 130.42 (C_{para} of PPh_3), 128.82 (C_{meta} of PPh_3), 125.30 (C_{para} of ArN), 122.74 (C_{meta} of ArN), 28.60 (CHMe_2), 23.68 (CHMe_2), 23.32 (CHMe_2) ppm. $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, C_6D_6): δ 84.38 ppm. IR (KBr, cm^{-1}): 3052(w), 2961 (m), 2922 (w), 2867 (w), 1932 (s), 1479 (w), 1458 (w), 1435 (m), 1377 (w), 1361 (w), 1326 (w), 1279 (w), 1182 (w), 1094 (w), 797 (w), 745 (m), 695 (m), 529 (w), 503 (w).

B.2.5 Preparation of $(\text{ArN})\text{Cr}(\text{PPh}_3)(\text{CO})_3$

Let the NMR tube from **B.2.4** stand at room temperature for 7 days. Solution color changed from light brown to yellow-brown slowly. NMR showed that most $(\text{ArN})_2\text{Cr}(\text{PPh}_3)(\text{CO})$ decomposed to $(\text{ArN})\text{Cr}(\text{PPh}_3)(\text{CO})_3$ and small amount of $(\text{ArN})\text{Cr}(\text{PPh}_3)_2(\text{CO})_2$. Small amount of $(\text{ArN})\text{Cr}(\text{PPh}_3)_2(\text{CO})_2$ was confirmed by NMR and LIFDI-MS. ^1H NMR (400 MHz, C_6D_6): δ 7.82 (m, 6 H, PPh_3), 7.05-6.89 (m, 12 H, PPh_3 and ArN, overlapped with ArNCO , PPh_3), 4.06 (sept, 2 H, CHMe_2), 1.17 (d, 12 H, CHMe_2) ppm. $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, C_6D_6): δ 72.65 ppm. MS(LIFDI) m/z : 573.1534 [M^+]. Calcd. m/z : 573.1525 [M^+].

B.2.6 Preparation of $(\text{ArN})\text{Cr}(\text{PPh}_3)_2(\text{CO})_2$

Let the NMR tube from **B.2.4** stand at room temperature for 18 days. Solution color changed from light brown to yellow-green slowly. The solvent was then removed in vacuum and the residue was washed with pentane and then extracted with Et₂O. The extract was filtered through Celite and the filtrate was concentrated to 0.5 mL then cooled to -30 °C overnight to yield yellow-green crystals. Single crystals for structural characterization was grown from slow evaporation of ether solution at room temperature. ¹H NMR (400 MHz, C₆D₆): δ 7.82 (m, 12 H, PPh₃), 7.03 (m, 18H, PPh₃), 6.93 (m, 3 H, ArN), 4.21 (sept, 2 H, CHMe₂), 0.99 (d, 12 H, CHMe₂) ppm. ¹³C {¹H} NMR (150 MHz, C₆D₆): δ 261.91 (t, ²J_{PC} = 34.0 Hz, CO), 155.19 (C_{ipso} of ArN), 150.23 (C_{ortho} of ArN), 137.50 (C_{ipso} of PPh₃), 134.18 (C_{ortho} of PPh₃), 129.77 (C_{para} of PPh₃), 128.39 (C_{meta} of PPh₃), 27.47 (CHMe₂), 24.41 (CHMe₂) ppm. ³¹P {¹H} NMR (162 MHz, C₆D₆): δ 89.73 ppm. MS(LIFDI) m/z: 807.2549 [M⁺]. Calcd. m/z: 807.2487 [M⁺]. IR (KBr, cm⁻¹): 3052 (w), 2961 (w), 2866 (w), 1900 (s), 1800 (s), 1480 (w), 1434 (m), 1089 (w), 743 (w), 695 (m), 642 (w), 619 (w), 572 (w), 541 (w), 515 (m).

Table B.2 Crystallographic data for (ArN)Cr(PPh₃)₂(CO)₂

	(ArN)Cr(PPh ₃) ₂ (CO) ₂ (kla0966)
Formula	C ₅₀ H ₄₇ CrNO ₂ P ₂
Formula Wt.	807.82
Space group	<i>P</i> 2 ₁ / <i>c</i>
Color	green
<i>a</i> , Å	41.8349(12)
<i>b</i> , Å	12.7298(4)
<i>c</i> , Å	16.4140(5)
α , deg	90
β , deg	100.7140(10)
γ , deg	90
<i>V</i> , Å ³	8588.9(5)
<i>Z</i>	8
<i>D</i> (calcd), g/cm ³	1.249
μ , mm ⁻¹	3.201
Temp, K	200
<i>T</i> _{max} / <i>T</i> _{min}	0.7539/0.4688
No. data/params	17696/1017
GOF on <i>F</i> ²	1.058
<i>R</i> 1(<i>F</i>), % ^a	4.58
<i>wR</i> ² (<i>F</i> ²), % ^a	12.29

^a Quantity minimized: $wR^2(F^2) = \sum[w(F_o^2 - F_c^2)^2] / \sum[(wF_o^2)^2]^{1/2}$; $R1 = \sum \Delta / \sum(F_o)$, $\Delta = |F_o - F_c|$.

Appendix C

CRYSTAL STRUCTURE OF (^tBuN)CrCl(μ-^tBuN)₂Cr(N^tBu)₂Cl

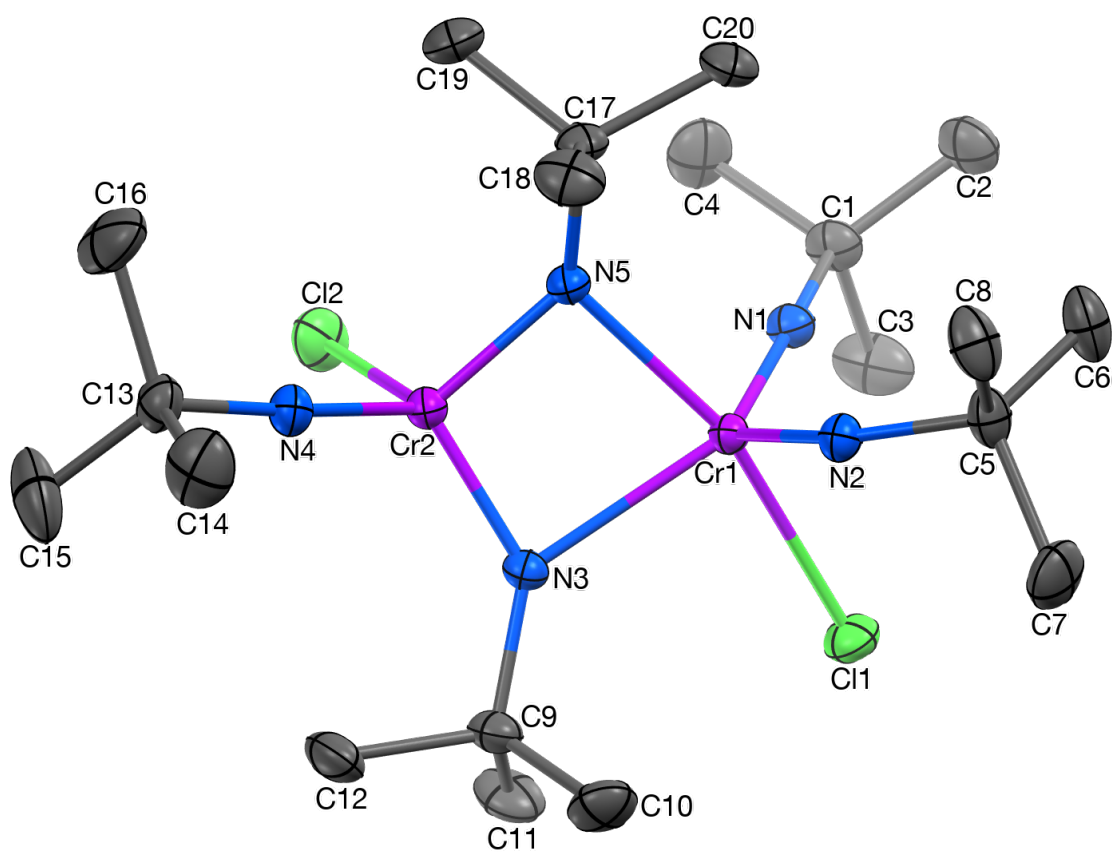


Figure C.1 Molecular structure of (^tBuN)CrCl(μ-^tBuN)₂Cr(N^tBu)₂Cl. Ellipsoids are drawn at the 30% probability level. Hydrogen atoms have been omitted for clarity.

Table C.1 Interatomic distances (Å) and angles (°) for (tBuN)CrCl(μ-tBuN)₂Cr(N^tBu)₂Cl

Distances (Å)			
Cr(1)-N(1)	1.6333(14)	C(5)-C(8)	1.531(3)
Cr(1)-N(2)	1.6613(14)	C(5)-C(7)	1.535(3)
Cr(1)-N(5)	2.0590(13)	C(9)-N(3)	1.478(2)
Cr(1)-N(3)	2.1908(13)	C(9)-C(12)	1.528(3)
Cr(1)-Cl(1)	2.3616(5)	C(9)-C(10)	1.529(3)
Cr(2)-N(4)	1.6303(15)	C(9)-C(11)	1.535(3)
Cr(2)-N(3)	1.7156(13)	C(13)-N(4)	1.454(2)
Cr(2)-N(5)	1.7211(13)	C(13)-C(14)	1.515(3)
Cr(2)-Cl(2)	2.2407(5)	C(13)-C(15)	1.517(3)
C(1)-N(1)	1.449(2)	C(13)-C(16)	1.520(3)
C(1)-C(2)	1.525(3)	C(17)-N(5)	1.476(2)
C(1)-C(4)	1.528(3)	C(17)-C(18)	1.524(3)
C(1)-C(3)	1.534(3)	C(17)-C(20)	1.528(3)
C(5)-N(2)	1.461(2)	C(17)-C(19)	1.534(3)
C(5)-C(6)	1.525(3)		

Angles (°)			
N(1)-Cr(1)-N(2)	113.22(7)	N(3)-C(9)-C(12)	109.58(15)
N(1)-Cr(1)-N(5)	93.74(6)	N(3)-C(9)-C(10)	110.15(15)
N(2)-Cr(1)-N(5)	101.32(6)	C(12)-C(9)-C(10)	109.08(17)
N(1)-Cr(1)-N(3)	128.16(6)	N(3)-C(9)-C(11)	107.32(15)
N(2)-Cr(1)-N(3)	118.62(6)	C(12)-C(9)-C(11)	107.89(17)
N(5)-Cr(1)-N(3)	77.17(5)	C(10)-C(9)-C(11)	112.75(18)
N(1)-Cr(1)-Cl(1)	89.42(5)	N(4)-C(13)-C(14)	108.35(17)
N(2)-Cr(1)-Cl(1)	92.76(5)	N(4)-C(13)-C(15)	108.35(17)
N(5)-Cr(1)-Cl(1)	162.96(4)	C(14)-C(13)-C(15)	110.1(2)
N(3)-Cr(1)-Cl(1)	87.71(4)	N(4)-C(13)-C(16)	108.61(17)
N(4)-Cr(2)-N(3)	117.81(7)	C(14)-C(13)-C(16)	110.7(2)
N(4)-Cr(2)-N(5)	115.22(7)	C(15)-C(13)-C(16)	110.7(2)
N(3)-Cr(2)-N(5)	101.04(6)	N(5)-C(17)-C(18)	108.39(14)

N(4)-Cr(2)-Cl(2)	105.06(6)	N(5)-C(17)-C(20)	110.99(14)
N(3)-Cr(2)-Cl(2)	109.30(5)	C(18)-C(17)-C(20)	110.91(17)
N(5)-Cr(2)-Cl(2)	108.13(5)	N(5)-C(17)-C(19)	107.49(15)
N(1)-C(1)-C(2)	111.24(15)	C(18)-C(17)-C(19)	110.76(17)
N(1)-C(1)-C(4)	107.43(15)	C(20)-C(17)-C(19)	108.25(16)
C(2)-C(1)-C(4)	110.91(17)	C(1)-N(1)-Cr(1)	171.22(13)
N(1)-C(1)-C(3)	106.61(15)	C(5)-N(2)-Cr(1)	148.70(12)
C(2)-C(1)-C(3)	109.91(18)	C(9)-N(3)-Cr(2)	136.55(12)
C(4)-C(1)-C(3)	110.63(19)	C(9)-N(3)-Cr(1)	134.35(11)
N(2)-C(5)-C(6)	110.82(15)	Cr(2)-N(3)-Cr(1)	87.82(5)
N(2)-C(5)-C(8)	108.79(15)	C(13)-N(4)-Cr(2)	173.54(14)
C(6)-C(5)-C(8)	111.21(18)	C(17)-N(5)-Cr(2)	135.51(11)
N(2)-C(5)-C(7)	105.83(16)	C(17)-N(5)-Cr(1)	130.74(11)
C(6)-C(5)-C(7)	110.20(18)	Cr(2)-N(5)-Cr(1)	92.06(6)
C(8)-C(5)-C(7)	109.84(18)		

Appendix D

STATISTICAL ANALYSIS OF IMIDO BOND LENGTHS AND BOND ANGLES

Methodology. The structural data used in this statistical analysis derive from the Cambridge Structural Database, based on the search result on October 16, 2018. Only terminal imido chromium complexes are considered. Bridging imido chromium complexes are not included.

Table D.1 Query setting and search result

Query Setting	Search Result
$\text{Cr}=\text{N}-\text{C}$	60 terminal imido chromium complexes were found in CSD. These complexes contain 103 imido ligands totally.

Table D.2 Statistical analysis result

Name	Minimum	Maximum	Mean	Std. Dev	Mean. Dev	Median
ANG (°)	139.03	178.825	163.591	9.86	8.305	163.624
DIST (Å)	1.55	1.736	1.645	0.026	0.019	1.647

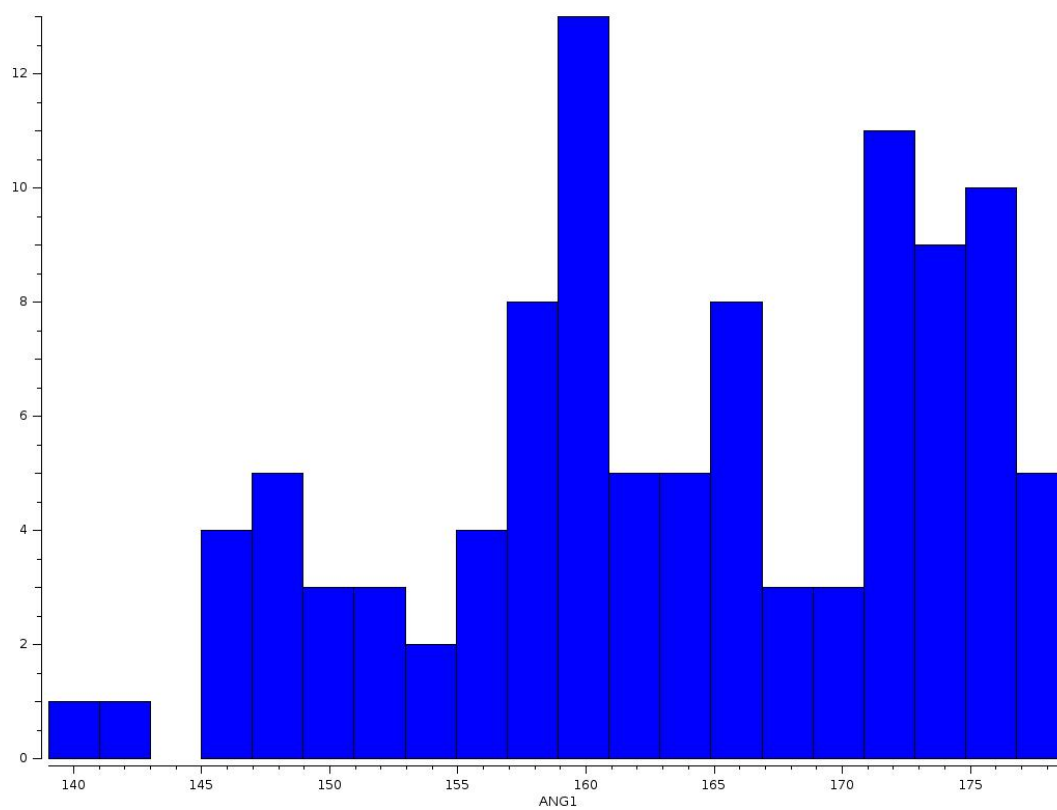


Figure D.1 Distribution of Cr-N-C imido bond angles (°) for terminal imido chromium complexes

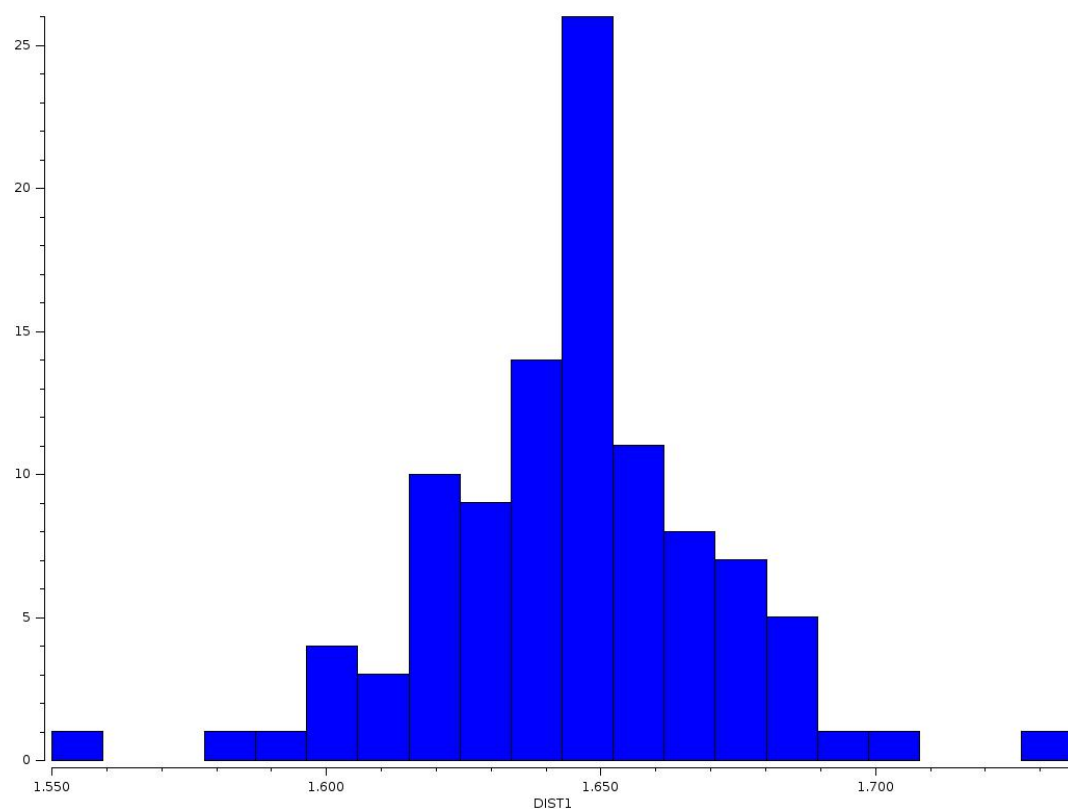


Figure D.2 Distribution of Cr-N imido bond lengths (Å) for terminal imido chromium complexes

Appendix E

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