

**STERIC MODIFICATION OF BETA-DIKETIMINATO LIGANDS ON LOW
VALENT CHROMIUM TOWARDS A BETTER MODEL OF ETHYLENE
TRIMERIZATION**

by

Anthony James Doellman

A thesis submitted to the Faculty of the University of Delaware in partial fulfillment of the requirements for the degree of Master of Science in Chemistry and Biochemistry

Summer 2012

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LIST OF ABBREVIATIONS

BTMSA	Bis-trimethylsilyl acetylene
Dipp-NacNac	2,4 Pentane-N,N ² -bis(2,6-diisopropylphenyl) ketiminato
HDPE	High-Density Polyethylene
GC	Gas Chromatography
IR	Infrared Spectrum
KHMDS	Potassium Hexamethyl DiSilazide
LAO	Linear Alpha Olefin
LLDPE	Linear Low-Density Polyethylene
L ^{DiprTrit}	2,4 Pentane-N,N ² -bis(2,6-diisopropyl-4-tritylphenyl) ketiminato
L ^{iPr}	2,4 Pentane-N,N ² -bis(2,6-diisopropylphenyl) ketiminato
L ^{tipr}	2,4 Pentane-N,N ² -tris(2,4,6-diisopropylphenyl) ketiminato
MeLi	Methyl Lithium
M.P.	Melting Point
NacNac	2,4 Pentane-N,N ² - ketiminato
NMR	Nuclear Magnetic Resonance
PE	Polyethylene
TMS	Trimethylsilyl
Trit	Trityl (triphenylmethyl)
UV/Vis	Ultraviolet/Visible Spectrum

ABSTRACT

This thesis describes an extension of the research conducted on low valent β -diketiminato chromium compounds. The main thrust of this work is the significant increase of steric bulk on the known 2,4 Pentane- N,N' -bis(2,6-diisopropylphenyl) ketiminato (Dipp-NacNac) ligand by the addition of a triphenylmethyl substituent at the 4- position of the phenyl rings. This has the effect of nearly doubling the ligand's mass and significantly increasing its size, with the result that the metal complexes with this ligand show signs of steric effects seeming to play a more significant role in their formation than in complexes of the parent system. Unfortunately, complexes of this ligand tend to suffer from solubility issues, making them somewhat difficult to work with. Although the goal of ethylene trimerization with a monomeric Cr (I) ethylene complex has not been achieved, this work points to possible promising lines of inquiry in the form of easily modified trityl derivatives.

INTRODUCTION

Since their discovery in 1933, polyethylene plastics have become a ubiquitous part of everyday life. For over fifty years, various types of polyethylenes have been the material of choice to make products ranging from disposable packaging to artificial joints to electrical insulation¹. Its tunable properties, chemical resistance, lightness and low expense relative to many traditional materials have made polyethylene extremely attractive for a great many applications in very diverse fields.

Chapter 1

ETHYLENE OLIGOMERIZATION AND POLYMERIZATION

1.1 Catalytic Polyethylene Production

Perhaps the most important advance in the field of ethylene polymerization was the discovery by Banks and Hogan in 1951² of a chromium trioxide/silicon dioxide catalyst system that could polymerize ethylene at moderate temperatures (79-177 °C) and pressures (100-700 p.s.i.). Previous processes³ used pressures of over to 1000 atm. (14,700 p.s.i.) and temperatures of 150-250 °C. The Phillips system therefore represented a significant improvement in terms of both capital and operating costs for production, while maintaining slightly better yields.

Even though the Phillips catalyst system has been known for over sixty years, there is still debate as to its mechanism of polymerization. The best supported at the time of writing⁴ is the Cossee-Arlman mechanism, proposed by Cossee and Arlman⁵ during their study of the class of compounds known as Ziegler-Natta⁶ catalysts. (See Figure 1.1). In it, a metal with an alkyl chain and a vacant coordination site binds a molecule of ethylene. Migratory insertion gives a new vacant site and an alkyl chain lengthened by two carbons. Repeating this process thousands of times gives polyethylene.

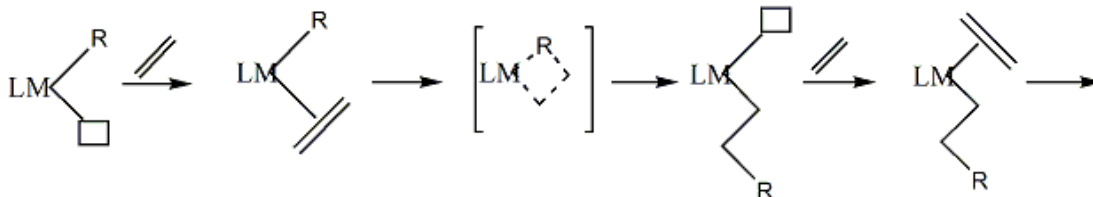


Figure 1.1: Cossee-Arlman Mechanism

While polyethylene has many uses, plastics with different thermal and mechanical properties can be made by copolymerization of ethylene with other small molecules. The most important of these are Linear Low Density Polyethylene (LLDPE), which had a market value of almost \$24 billion in 2010, and High Density Polyethylene (HDPE), with a market volume of over 30 million tons⁷. LLDPE is typically made by copolymerization of ethylene with short chain α -olefins, usually 1-butene, 1-hexene and/or 1-octene.⁸

The high demand for LLDPE leads to a high demand for linear α -olefins. These can be made by dehydration of the corresponding alcohols, but industrially they are more often supplied as part of a range of products made by the thermal cracking of waxes⁹, by the Fischer-Tropsch process¹⁰, by the Shell Higher Olefins Process¹¹, or by some combination of the these (e.g. thermal cracking of waxes generated by Fischer-Tropsch.) The products often follow a Schulz-Flory distribution¹², described by the equation:

$$W_n = n(1-\alpha)^2\alpha^{n-1}$$

where W_n is the weight fraction of the product which contains n monomeric units and α is the probability of chain growth. This is useful because it allows conditions to be tuned to favor a particular fraction, but the only fraction that can be made theoretically pure is $n=1$. All other fractions must be separated, costing time and energy.

1.2 Selective Production of 1-Hexene From Ethylene

Industry has thus naturally been attracted to the development of selective trimerization catalysts with very high activities. The field of “on purpose” ethylene trimerization began as an observation of a side pathway during a process for continuous production of polyethylene (PE), as described in a patent by Manyik, Walker and Wilson at the Union Carbide Corporation¹³. They found that though the main product is PE, the catalyst(s) generated by Cr(III) 2-ethylhexanoate activated by partially hydrolysed tri-isobutylaluminium, also trimerizes some of the ethylene to produce 1-hexene. This 1-hexene then co-polymerizes with ethylene to form a polymer with butyl side chains.

Ten years later, the same team published what they had learned about the mechanism of this side reaction¹⁴. Gas chromatography showed the ethylene oligomers 1-butene, 1-hexene, 1-octene, and various terminal and branched decenes present in the solvent, with a 1-hexene:1-butene ratio of 25:1. They found that the rate of 1-hexene formation showed a second order dependence on the ethylene pressure, consistent with two ethylene molecules involved in the rate limiting step, and that the reaction was significantly inhibited by dienes. The authors interpreted this data to mean that the rate limiting step was the oxidative (with respect to the metal) coupling of two coordinated ethylenes to give a metallacyclopentane. They then proposed that a third molecule of ethylene could then react with this metallacycle to split off 1-hexene and regenerate the original catalytically active compound, giving the scheme shown in Figure 1.2.

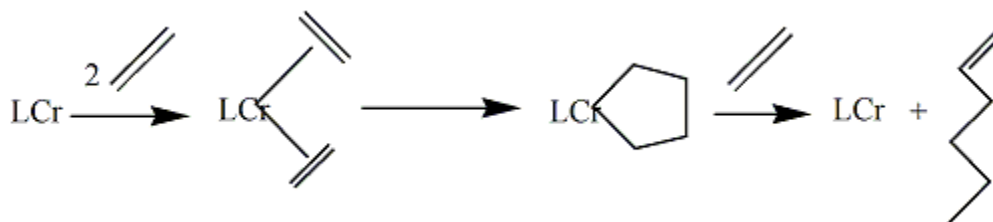


Figure 1.2 Metallacycle Mechanism Proposed by Manyik *et al.*

This metallacyclic intermediate has remained the most popular mechanistic hypothesis for selective ethylene oligomerization as the field has advanced¹⁵. High hexene selectivities, such as the 98 wt% seen in by McGuiness, *et al.*¹⁶ are difficult to explain via linear chain growth mechanisms, but can be rationalized by the observation of McDermott *et al.*¹⁷ that, at least in the case of platinum, decomposition of the metallacycloheptane to 1-hexene occurred much more readily than the corresponding decomposition of the metallacyclopentane or metallacyclohexane (Figure 1.3).

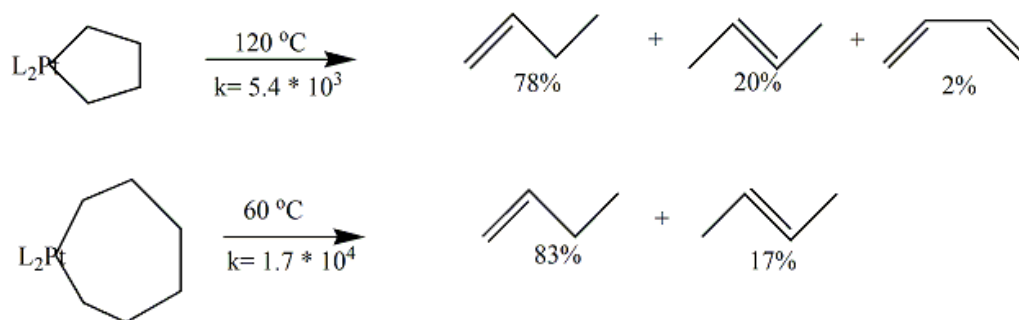


Figure 1.3 Rates and Products of Platinacycle Decomposition. L = PPh₃

Essentially, the argument is that if decomposition of the metallacyclopentane into 1-butene is more difficult than insertion of ethylene to make a metallacycloheptane, and if decomposition of the metallacycloheptane to 1-hexene is more facile than a second ethylene insertion to form a metallacyclononane, then decomposition of the metallacycloheptane to 1-hexene will be the predominant pathway (Figure 1.4). The result of such a system would necessarily be a preponderance of 1-hexene.

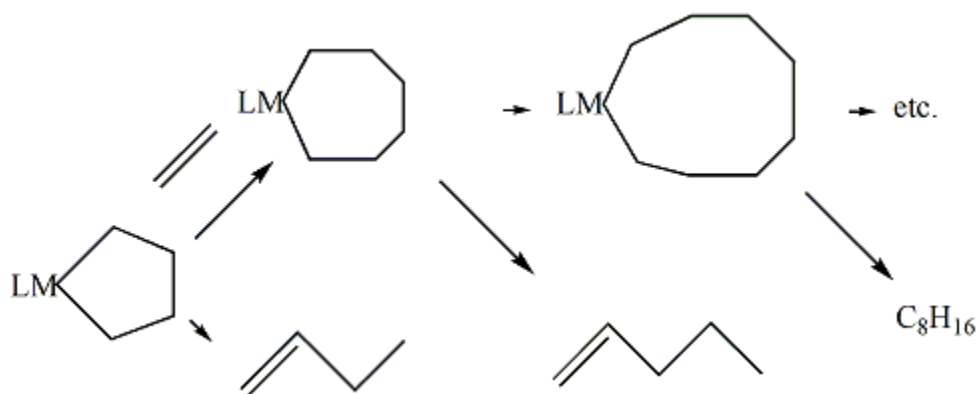


Figure 1.4 Proposed Metallacycle Mechanism to Explain 1-Hexene Selectivity, with Reaction Likelihood Indicated by Arrow Length

Furthermore, several deuterium labeling studies¹⁸ using both a 1:1 mix of C_2H_4 and C_2D_4 and gem- $C_2H_2D_2$ both gave results consistent with what would be expected from a metallacycle mechanism versus a Cossee type chain growth mechanism.

Studies using various N,N,N and N,P,N Cr (II) and Cr (III) precatalysts activated with MAO or other alkylaluminum compounds have shown very high activity and selectivity for 1-hexene. Chevron-Phillips has reported and commercialized a

system with an activity of 156,666 g 1-hexene/g Cr per hr with a 93% selectivity for 1-hexene¹⁹ (Figure 1.5). British Petroleum has reported a catalyst with an unprecedented activity of 1,033,200 g/g Cr per hr with an 89.9% selectivity for 1-hexene²⁰ (Figure 1.6). Compared to the Chevron-Phillips catalyst, Sasol Technology achieved slightly higher selectivity at the cost of catalyst activity, reporting a catalyst with an activity of 37,400 g/g Cr per hr with a 93.2% selectivity for 1-hexene²¹ (Figure 1.7).

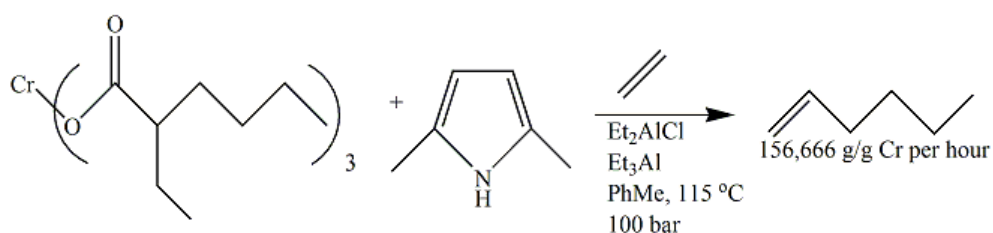


Figure 1.5 Chevron-Phillips Selective Ethylene Trimerization

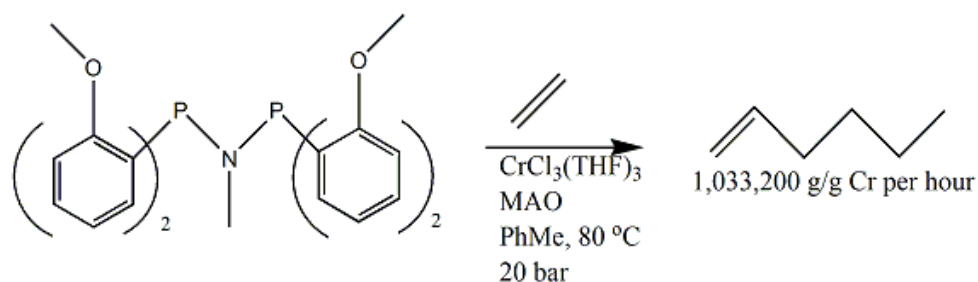


Figure 1.6 British Petroleum Selective Ethylene Trimerization

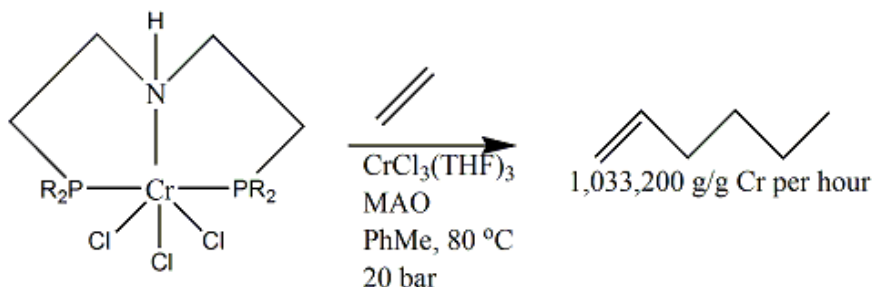


Figure 1.7 Sasol Technology Ethylene Trimerization

All require significant amounts of alkylaluminum activators, thus obscuring the active species and making mechanistic investigations somewhat more difficult. There is thus still a great deal of speculation as to the nature of the mechanism of ethylene oligomerization, including the above mentioned metallacycle vs Cossee mechanism, the initial oxidation state of the chromium and how it changes during the catalytic cycle (e.g. Cr (I)/(III) vs Cr (II)/(IV) etc.), and even whether multiple chromium atoms might be involved¹⁸. A homogenous model which trimerized ethylene without the need for activators would eliminate some of these ambiguities in the mechanism(s) of the industrial 1-hexene systems. The mechanistic understanding derived from the model could then lead to rational design of new catalysts.

1.3 Investigations Into A Homogenous Trimerization Catalyst

Some previous work to develop a heterogenous model of ethylene trimerization has been done by Drs. Monillas and Young in this lab. Monillas²² found that upon exposure to ethylene, the Cr (I) compound $[L^{iPr}Cr]_2[\mu-N_2]$ (where L^{iPr} represents Dipp NacNac) generates 1-hexene and a smaller amount of 1-butene. So long as a constant pressure of ethylene is maintained, there is no observed decrease in trimerization activity over 72 hours. After workup, the observed product is

$[L^{iPr}Cr]_2[\mu-\eta^2=\eta^2-C_2H_4]$ (Figure 1.8). This compound does not react further with ethylene, suggesting it is a decomposition product of the active catalyst.

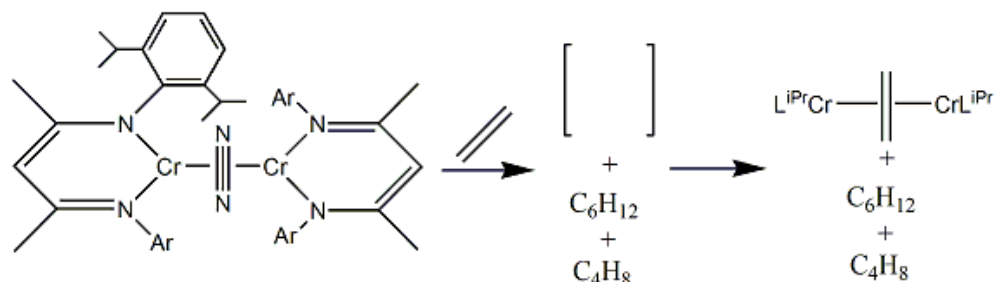


Figure 1.8 Trimerization of Ethylene from a Homogenous Cr(I) Complex

During the period of active trimerization, there is an observable peak at 7.07 ppm in the 1H NMR which disappears once the ethylene is depleted and may correspond to an active intermediate. There is some tentative evidence that this is a metallacycle, notably that the reaction is first-order in catalyst and second order in ethylene, and that quenching the reaction with Br_2 in CH_2Cl_2 gave 1,4-dibromobutane and $[L^{iPr}Cr-\mu-Br]_2$ as products (Figure 1.9). All attempts to directly trap the intermediate failed.

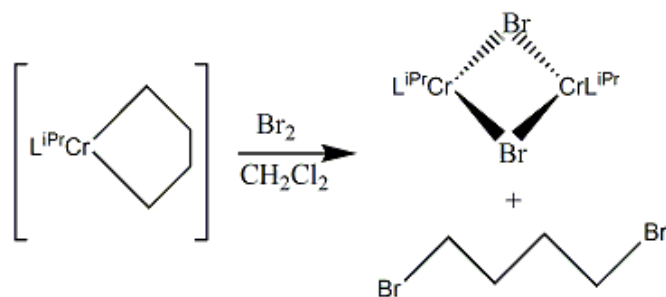


Figure 1.9 Products from Quenching Monillas' Intermediate with Br_2 . Metallacycle structure was not directly observed, but proposed based on trimerization kinetics and observation of 1,4-Bromobutane

Young²³ noted that a previous attempt to synthesize a metallacyclopentane by reacting 1,4-dilithiobutane with $L^{\text{Me}}\text{CrCl}_2\text{THF}_2$ did not give the desired product but instead a bridging bimetallacycle, as shown in Figure 1.10. He hypothesized that since the starting material $[\text{L}^{\text{iPr}}\text{Cr}]_2[\mu\text{-N}_2]$ and final product $[\text{L}^{\text{iPr}}\text{Cr}]_2[\mu\text{-}\eta^2\text{-}\eta^2\text{-C}_2\text{H}_4]$ in Monillas's trimerization were both dinuclear, perhaps something similar to the previously observed bridging bimetallacycle was Monillas's mystery intermediate. He proposed the Cr(I/II) bimetallic pathway seen in Figure 1.11, which could be conveniently tested by synthesizing the intermediate bimetallacycle.

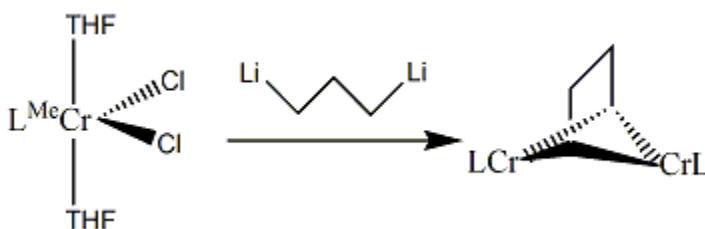


Figure 1.10 Synthesis of a Bridging Bimetallic. $L^{\text{Me}} = 2,6\text{-dimethylphenyl NacNac}$

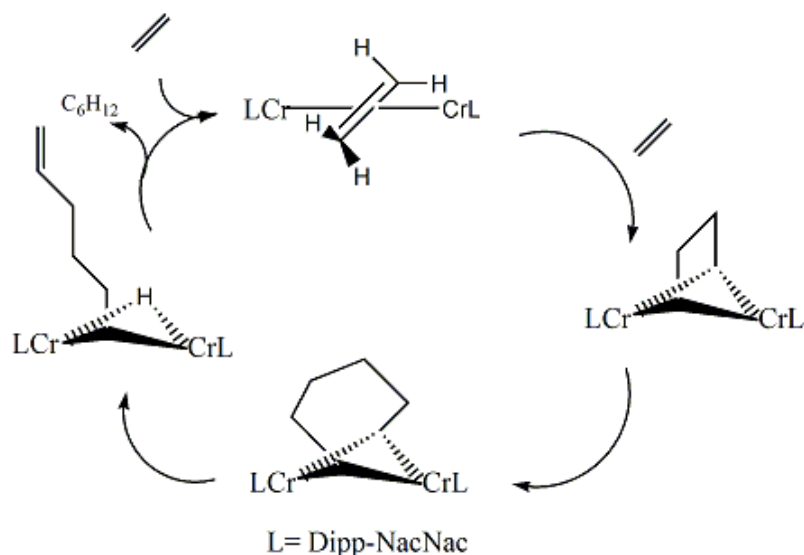


Figure 1.11 Proposed Bimetallic Pathway

The dinuclear complex $[L^{iPr}Cr]_2[(\mu-CH_2)_2(CH_2)_2]$ was synthesized and reacted with ethylene. While this complex did slowly produce a small amount of 1-hexene, it failed to reach even a single turnover even after two weeks. The drastic difference in rates of trimerization affirm that this compound is not an intermediate in the ethylene trimerization that Monillas observed.

Even though the bridging six membered dimetallacycle was determined not to be an intermediate in the trimerization seen when $[L^{iPr}Cr]_2[\mu-N_2]$ was exposed to ethylene, the possibility still remained that the bridging bimetallacycles could insert a molecule of ethylene and then reductively eliminate to form the α -olefin. To test this, Young took the next carbon homologue, $[L^{iPr}Cr]_2[(\mu-CH_2)_2(CH_2)_3]$, having 5-carbons, and reacted it with ethylene. The expectation was to see 1-heptene produced by ethylene insertion followed by reductive elimination, followed by the production of

even numbered olefins. Instead, he saw no 1-heptene but the production of a small amount of 1-pentene.

Given the absence of heptene, the insertion of ethylene into the binuclear metallacycle could be eliminated. Therefore, some other mechanism must be responsible for the trimerization. The observation of 1-pentene suggests that the first step toward generating the active species is the decomposition of the bridging bimetallacycles, Young decided to study their decomposition in the absence of ethylene. Heating the 4-carbon bridging bimetallacycle at 65 °C for 2 hours and following by NMR resulted in the complete decomposition of the bimetallacycles, giving the known $[L^{iPr}Cr-\mu-H]_2$ and unassigned resonances later determined by independent synthesis to be a $cis-\eta^4$ butadiene complex (Figure 1.12).

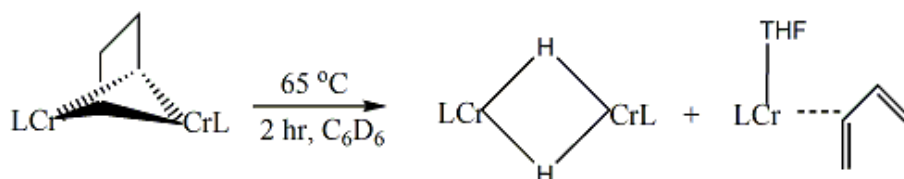


Figure 1.12 Decomposition of a Bimetallacycle as Observed by Young

Upon exposing this butadiene complex to an atmosphere of ethylene, 1-hexene and lesser amounts of 1-butene are produced. Given the already low rate of trimerization seen in the bridging bimetallacycle system, the ability of one of its decomposition products to trimerize ethylene makes the bimetallic pathway very unlikely. Young points out that these observations are consistent with a mechanism in which the butadiene dissociates from the metal, allowing ethylene to bind and trimerize as shown above in Figure 1.2. Afterwards, ethylene could bind again and trimerization could continue, or butadiene could rebind.

In Monillas's case, a Cr (I) starting material exposed to ethylene continuously catalyzes trimerization as long as the ethylene pressure is maintained. In Young's system, decomposition of the starting material gives a product which catalyzes trimerization of ethylene, and which could quite possibly dissociate to become a Cr (I) species in situ. Both of these observations are mechanistically consistent with a monomeric chromium (I) species. Given this, and given the difficulty Monillas had in trapping the intermediate, an interesting question is – what would happen if the ligand were to prevent the formation of dinuclear complexes? The work in the remainder of this thesis represents attempts to reach that goal.

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Chapter 2

EFFECTS OF ADDING STERIC BULK TO THE β -DIKETIMINATE LIGAND

2.1 Attempts to Add Steric Bulk to the Aniline 4-Position

It was hoped that by increasing the steric bulk of the β -diketiminato ligand, it would be possible to prevent the formation of dinuclear complexes. The obvious spot for easy steric modification, without making large alterations to the binding site of the metal, was the 4- position of the phenyl rings. Initially, attempts were focused on 2,4,6-tri-isopropylaniline, made by the route in Figure 2.1.

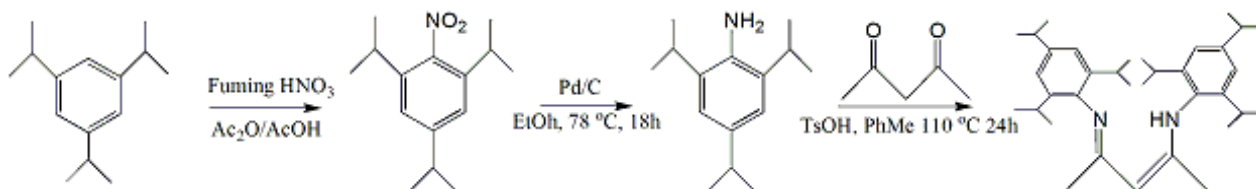


Figure 2.1 2,4,6-Tri-isopropyl NacNac (L^{tiprH}) Synthesis

Unfortunately, once this ligand was bound chromium, it behaved in largely the same ways as the parent system, with the drawback of having worse solubility. Examination of the crystal structures of $[L^{\text{tipr}}\text{CrCl}]_2$ and $[L^{\text{tipr}}\text{CrI}]_2$ shows that the 4-position of the phenyl rings is positioned in such a way that there is ample room for the tri-isopropyl NacNac to adopt the same configuration as the parent, without the additional isopropyl groups interacting with each other.

Another substitution that was contemplated was a tert-butyl group at the 4-position. 4-tert-butyl-2,6-diisopropylaniline is a known compound¹, but its synthesis

requires maintaining propylene at a high pressure that is kept constant, necessitating specialized equipment beyond the Parr bombs available in this department at the time of this writing. Instead, various tert-butyl alternatives were considered, such as 4-trimethylsilyl and 4-triphenylmethyl (4-trityl). 2,6-di-isopropyl-4-(triphenylmethyl)-aniline was not reported in the literature, but some references suggested it could be made².

Initial attempts focused on the reaction of N-protected anilines and substituted triphenylmethanes, similar to the synthesis of the 4-(tert-ButylDiphenylSilyl) aniline³. Trityl lithium was prepared via lithiating trityl chloride to give a bright red solution, which was then reacted with the N-protected 4-bromo anilines. These were, in turn, made by N-protection of the product from brominating 2,6-di-isopropylanilinium hydrochloride⁴. See Figure 2.2.

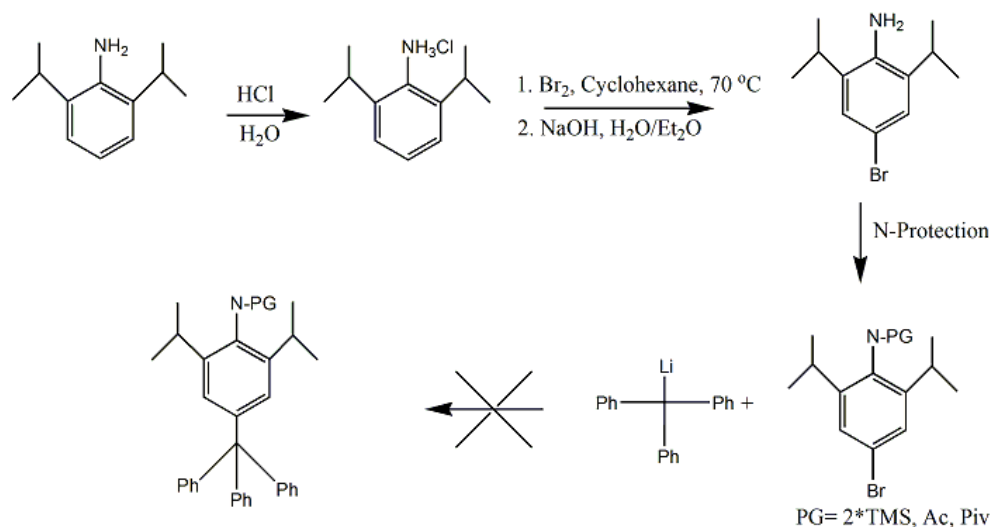


Figure 2.2 Attempted Tritylations on N-protected 4-Bromo-2,6-di-isopropyl Anilines

These reactions generally did not give the desired product in any appreciable yield. However, an older paper suggested an intriguing alternative synthesis⁵. In it, 4-(triphenylmethyl) aniline can be made in high yield via an uncatalyzed Friedel-Crafts reaction between triphenylmethanol and anilinium hydrochloride in either sulfuric or acetic acids as solvent. It was reasoned that since the 4-position of 2,6-diisopropyl aniline should be electronically and sterically similar to unsubstituted aniline, it would likely behave the same way. Gratifyingly, this turned out to be true, and 2,6-diisopropyl-4-trityl-aniline could be made in good yield (74%). This success suggested the synthetic scheme shown in scheme 2.3.

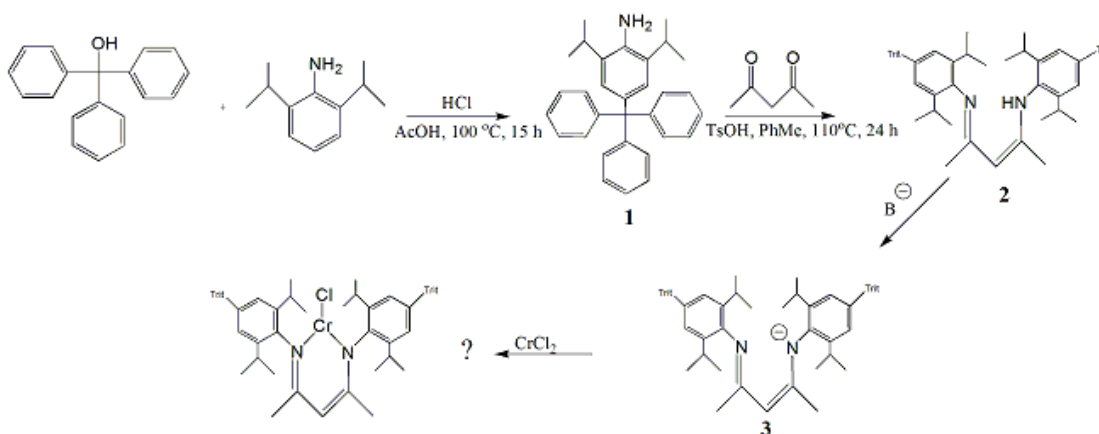


Figure 2.3. Synthesis of 4-Trityl-2,6-diisopropyl NacNac Ligand and Hypothesized Chromium Complex

In a sense, the trityl substituent can be thought of as a tert-butyl group with each methyl replaced by a phenyl ring. It certainly accomplished the goal of putting a large substituent into the 4-position, and even better, the reaction is very amenable to large scale-up (it has been run up to one mole). This aniline is a solid easily

crystallized by slow evaporation of chloroform, and the crystal structure is shown in Figure 2.4 below.

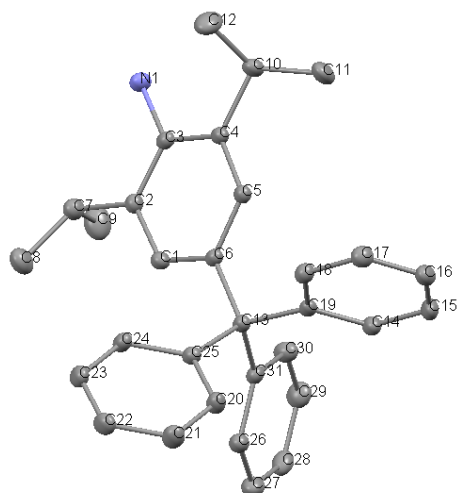


Figure 2.4 Crystal Structure of 2,6-Di-isopropyl-4-trityl Aniline (1). Hydrogen atoms are omitted for clarity. Ellipsoids are depicted at the 30% probability level.

Table 2.1: Interatomic Distances and Angles for 2,6-di-isopropyl-4-trityl aniline (1)

Distances (Å)

C1 C2	1.3902(19)	C5 C6	1.3922(19)
C1 C6	1.3935(19)	C6 C13	1.5519(18)
C2 C3	1.4060(19)	C7 C9	1.513(2)
C2 C7	1.5230(19)	C7 C8	1.527(2)
C3 N1	1.4053(17)	C10 C11	1.526(2)
C3 C4	1.4063(19)	C10 C12	1.531(2)
C4 C5	1.3935(18)	C13 C19	1.5482(19)
C4 C10	1.5178(19)	C13 C25	1.5498(18)
C13 C31	1.5543(19)	C14 C19	1.391(2)

C14 C15	1.395(2)	C15 C16	1.374(3)
C16 C17	1.387(2)	C17 C18	1.385(2)
C18 C19	1.397(2)	C20 C21	1.384(2)
C20 C25	1.3991(19)	C21 C22	1.385(2)
C22 C23	1.381(2)	C23 C24	1.396(2)
C24 C25	1.392(2)	C26 C31	1.386(2)
C26 C27	1.394(2)	C27 C28	1.376(3)
C28 C29	1.382(3)	C29 C30	1.378(2)
C30 C31	1.395(2)		

Angles (deg)

C2 C1 C6	122.83(13)	C1 C2 C3	118.85(12)
C1 C2 C7	120.60(13)	C3 C2 C7	120.53(12)
N1 C3 C2	119.85(12)	N1 C3 C4	120.28(13)
C2 C3 C4	119.81(12)	C5 C4 C3	118.78(12)
C5 C4 C10	120.61(12)	C3 C4 C10	120.61(12)
C4 C5 C6	122.82(12)	C5 C6 C1	116.81(12)
C5 C6 C13	122.92(12)	C1 C6 C13	120.20(12)
C9 C7 C8	111.80(15)	C9 C7 C2	110.33(14)
C8 C7 C2	113.41(13)	C4 C10 C11	114.10(13)
C4 C10 C12	110.95(13)	C11 C10 C12	109.01(15)
C19 C13 C25	107.65(10)	C19 C13 C6	109.63(10)
C25 C13 C6	112.50(11)	C19 C13 C31	110.47(11)
C25 C13 C31	109.20(11)	C6 C13 C31	107.40(10)
C19 C14 C15	120.98(15)	C16 C15 C14	120.60(15)
C15 C16 C17	119.28(15)	C16 C17 C18	120.19(15)
C17 C18 C19	121.39(14)	C14 C19 C18	117.55(13)
C14 C19 C13	123.49(13)	C18 C19 C13	118.95(12)
C21 C20 C25	121.67(14)	C22 C21 C20	120.28(14)
C23 C22 C21	119.10(14)	C22 C23 C24	120.55(14)
C25 C24 C23	121.13(13)	C24 C25 C20	117.25(13)
C24 C25 C13	124.19(12)	C20 C25 C13	118.48(12)
C31 C26 C27	120.99(14)	C28 C27 C26	120.92(15)
C27 C28 C29	118.64(15)	C30 C29 C28	120.49(16)
C29 C30 C31	121.81(15)	C26 C31 C30	117.15(13)
C26 C31 C13	123.82(12)	C30 C31 C13	119.03(12)

Since substitution at the 4-position doesn't significantly alter the environment of the aniline nitrogen, the additional steric bulk should not alter the ability of the

aniline to form the NacNac ligand. This is true of the method using 4-toluenesulfonic acid (TsOH), refluxing toluene, and a Dean-Stark trap to form the NacNac ligand, which goes in high yield (84%). Using $\text{HCl}_{(\text{aq})}$ in refluxing ethanol results in much lower yields, but that is likely due to the low solubility of both the starting aniline and the product NacNac ligand in ethanol. Once again, slow evaporation of chloroform produces good sized crystals, and the crystal structure is shown in Figure 2.5.

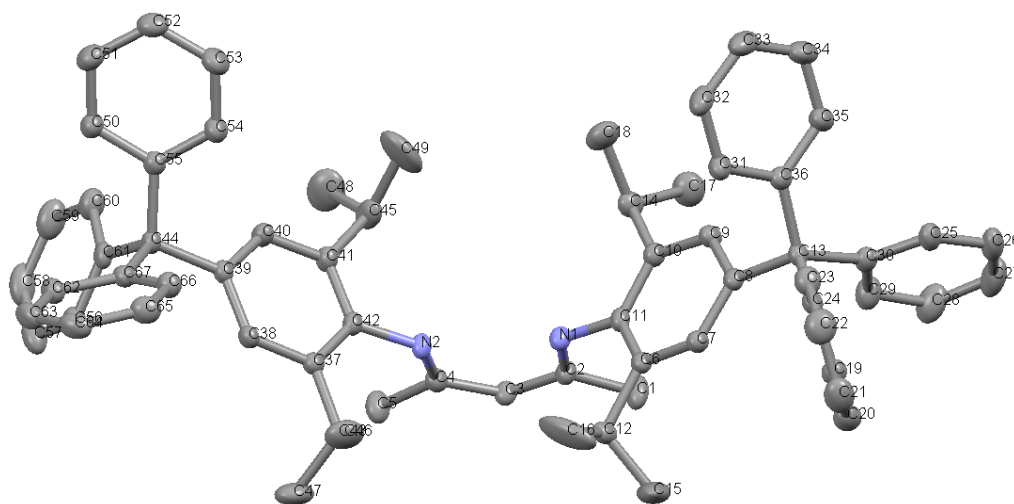


Figure 2.5 Crystal Structure of $\text{L}^{\text{DippTrit}}\text{H}$ (2) Hydrogen atoms are omitted for clarity. Ellipsoids are depicted at the 30% probability level.

Table 2.2: Interatomic Distances and Angles for $\text{L}^{\text{DippTrit}}\text{H}$ (2)

Distances (Å)			
N1 C2	1.312(3)	N1 C11	1.429(3)
N2 C4	1.328(3)	N2 C42	1.428(3)
C1 C2	1.509(3)	C2 C3	1.414(3)
C3 C4	1.395(3)	C4 C5	1.501(3)
C6 C7	1.396(3)	C6 C11	1.395(3)
C6 C12	1.524(3)	C7 C8	1.383(3)

C8 C9	1.398(3)	C8 C13	1.556(3)
C9 C10	1.388(3)	C10 C11	1.407(3)
C10 C14	1.521(3)	C12 C16	1.472(5)
C12 C15	1.480(5)	C13 C30	1.549(3)
C13 C36	1.549(3)	C13 C24	1.547(3)
C14 C17	1.516(4)	C14 C18	1.533(4)
C19 C20	1.377(4)	C19 C24	1.394(3)
C20 C21	1.380(4)	C21 C22	1.370(5)
C22 C23	1.388(4)	C23 C24	1.389(3)
C25 C26	1.380(4)	C25 C30	1.403(3)
C26 C27	1.377(5)	C27 C28	1.382(5)
C28 C29	1.392(4)	C29 C30	1.383(4)
C31 C32	1.389(4)	C31 C36	1.396(4)
C32 C33	1.373(5)	C33 C34	1.372(5)
C34 C35	1.396(4)	C35 C36	1.391(4)
C37 C42	1.395(3)	C37 C38	1.402(3)
C37 C43	1.521(3)	C38 C39	1.386(3)
C39 C40	1.393(3)	C39 C44	1.553(3)
C40 C41	1.388(3)	C41 C42	1.404(3)
C41 C45	1.520(3)	C43 C47	1.510(4)
C43 C46	1.529(4)	C44 C67	1.543(3)
C44 C55	1.546(3)	C44 C61	1.549(3)
C45 C49	1.517(5)	C45 C48	1.516(5)
C50 C51	1.382(4)	C50 C55	1.393(3)
C51 C52	1.386(4)	C52 C53	1.379(4)
C53 C54	1.393(4)	C54 C55	1.384(3)
C56 C61	1.384(4)	C56 C57	1.388(4)
C57 C58	1.365(5)	C58 C59	1.368(5)
C59 C60	1.403(4)	C60 C61	1.389(4)
C62 C63	1.389(4)	C62 C67	1.396(3)
C63 C64	1.364(4)	C64 C65	1.386(4)
C65 C66	1.380(3)	C66 C67	1.392(3)

Angles (deg)

C2 N1 C11	122.30(19)	C4 N2 C42	124.74(19)
N1 C2 C3	121.1(2)	N1 C2 C1	121.0(2)
C3 C2 C1	117.9(2)	C4 C3 C2	125.3(2)
N2 C4 C3	121.2(2)	N2 C4 C5	119.6(2)
C3 C4 C5	119.2(2)	C7 C6 C11	119.1(2)
C7 C6 C12	120.0(2)	C11 C6 C12	120.85(19)
C8 C7 C6	122.2(2)	C7 C8 C9	117.4(2)
C7 C8 C13	124.6(2)	C9 C8 C13	118.04(19)

C10 C9 C8	122.6(2)	C9 C10 C11	118.5(2)
C9 C10 C14	119.6(2)	C11 C10 C14	121.9(2)
C6 C11 C10	120.20(19)	C6 C11 N1	119.6(2)
C10 C11 N1	120.1(2)	C16 C12 C15	112.1(4)
C16 C12 C6	112.1(2)	C15 C12 C6	111.5(2)
C30 C13 C36	113.00(19)	C30 C13 C24	104.65(17)
C36 C13 C24	111.53(18)	C30 C13 C8	110.21(18)
C36 C13 C8	105.54(17)	C24 C13 C8	112.06(18)
C17 C14 C10	112.2(2)	C17 C14 C18	110.5(2)
C10 C14 C18	110.4(2)	C20 C19 C24	121.9(3)
C21 C20 C19	120.0(3)	C22 C21 C20	119.3(3)
C21 C22 C23	120.6(3)	C22 C23 C24	121.2(3)
C23 C24 C19	116.9(2)	C23 C24 C13	123.9(2)
C19 C24 C13	119.2(2)	C26 C25 C30	121.5(3)
C27 C26 C25	120.2(3)	C26 C27 C28	119.5(3)
C27 C28 C29	120.0(3)	C30 C29 C28	121.5(3)
C29 C30 C25	117.2(2)	C29 C30 C13	123.2(2)
C25 C30 C13	119.2(2)	C32 C31 C36	121.5(3)
C33 C32 C31	120.0(3)	C34 C33 C32	119.8(3)
C33 C34 C35	120.5(3)	C36 C35 C34	120.9(3)
C35 C36 C31	117.3(2)	C35 C36 C13	124.7(2)
C31 C36 C13	118.0(2)	C42 C37 C38	118.6(2)
C42 C37 C43	121.7(2)	C38 C37 C43	119.6(2)
C39 C38 C37	122.3(2)	C38 C39 C40	117.3(2)
C38 C39 C44	123.12(19)	C40 C39 C44	119.39(19)
C41 C40 C39	122.5(2)	C40 C41 C42	118.7(2)
C40 C41 C45	119.7(2)	C42 C41 C45	121.5(2)
C37 C42 C41	120.4(2)	C37 C42 N2	120.2(2)
C41 C42 N2	119.3(2)	C47 C43 C37	111.6(2)
C47 C43 C46	110.6(3)	C37 C43 C46	C67 C44 C55
C67 C44 C55	102.22(17)	C67 C44 C61	113.12(17)
C55 C44 C61	112.29(18)	C67 C44 C39	113.12(18)
C55 C44 C39	113.16(17)	C61 C44 C39	103.31(17)
C49 C45 C48	111.4(3)	C49 C45 C41	110.2(3)
C48 C45 C41	112.8(3)	C51 C50 C55	121.6(2)
C50 C51 C52	120.1(2)	C53 C52 C51	119.1(2)
C52 C53 C54	120.3(3)	C55 C54 C53	121.4(2)
C54 C55 C50	117.5(2)	C54 C55 C44	123.1(2)
C50 C55 C44	119.0(2)	C61 C56 C57	121.4(3)
C58 C57 C56	120.4(3)	C57 C58 C59	119.6(3)
C58 C59 C60	120.4(3)	C61 C60 C59	120.5(3)

C56 C61 C60	117.7(2)	C56 C61 C44	120.5(2)
C60 C61 C44	121.6(2)	C63 C62 C67	120.7(2)
C64 C63 C62	121.0(3)	C63 C64 C65	119.3(2)
C66 C65 C64	119.9(3)	C65 C66 C67	121.8(2)
C66 C67 C62	117.1(2)	C66 C67 C44	119.9(2)
C62 C67 C44	122.4(2)		

This is indeed a very large ligand, as was desired. The next challenge was to put it onto a metal. Patrick Holland of the University of Rochester had presented this same ligand system on iron at the Boston ACS meeting in 2010, though nothing about it had been published at the time of this writing. The student who worked on the project, Tom Dugan, suggested deprotonation with potassium hexamethyldisilazane (KHMDS, potassium salt of bis-trimethylsilylamine) in refluxing THF, followed by removing the THF and heating in vacuo to drive off the formed bis-TMS amine⁶. This is an effective method of deprotonation, but it requires exactly one equivalent of base, and the product was often found to contain some free ligand. Instead, since KHMDS is soluble in toluene and the NacNac is soluble in hot toluene, using 1.1-1.2 equivalents of KHMDS and deprotonating for 12-24 hours in refluxing toluene followed by cooling the toluene solution to -30 °C, filtering and washing with a small amount of cold toluene gave a more pure product. The bright yellow TritylNacNac K can easily be made on a scale of tens of grams, and stored at r.t. under nitrogen for months without any apparent decomposition.

2.2 Behavior of Ligand L^{DippTrit}Cr Complexes

Up to this point, all materials had consistently been soluble in THF, CH₂Cl₂, and hot toluene, and insoluble in pentanes, hexanes, Et₂O, and cold toluene. As in the synthesis of previous NacNac Cr(II) complexes, CrCl₂ was slurried in THF and a solution of ligand salt in THF slowly added with stirring. Unlike other NacNac

chromium complexes, this did not turn dark green, but brown-black and eventually became an insoluble gray-brown substance which presented several difficulties in characterization. It was mostly insoluble in the common glovebox solvents – pentanes, diethyl ether, toluene, and THF, making purification difficult. Since this material was filtered off, it had to contain formed KCl, and since it was the majority product and showed a paramagnetic peak in the NMR in THF- d_8 , it had to contain a ligated chromium species. The paramagnetic peak in THF- d_8 appears at 117 ppm, similar to the value of the peak for $[L^{iPr}Cr-\mu-Cl]_2^6$, implying that the material contained ligated chromium chloride. Accordingly, the material was used for some further reactions, and found to react in THF to form new complexes with ligated chromium, as in the initial synthesis of the allyl complex [*vide infra*].

Several attempts were made to purify this gray-brown solid. The first successful attempt was a Soxhlet extraction under nitrogen using hot toluene. While this method is effective, leaving a brown residue in the extractor and producing a concentrated yellow-green solution, it takes on the order of a week to finish. Since the material is air-sensitive, this is very inconvenient. Fortunately, a much easier purification route was found during attempts to grow crystals for diffraction. Dissolving this substance in methylene chloride and stirring results in a green solution with white particles suspended. Cooling this solution as-is results in the gray-brown solid crashing back out, but filtering gives a dark green solution, similar to that of the parent ligand chromium chloride complexes and a white powder remaining on the frit.

Since KCl had not been removed from the original gray-brown solid, it was suspected to be the white substance which had been filtered off. Several qualitative analyses were therefore run on the powder. It was brought outside the glovebox and

dissolved in water, in which it was highly soluble. This aqueous solution was then split into two portions. To the first portion, an aqueous solution of NaBPh₄ was added. NaBPh₄ is very soluble in water, while KBPh₄ is very insoluble⁸, causing it to precipitate out in mixed ion solutions due to LeChatelier's principle. The appearance of a white precipitate therefore confirmed the presence of potassium in the solution. To the second portion, an aqueous solution of AgNO₃ was added. The appearance of a white precipitate of AgCl confirmed the presence of chloride in the solution. It is therefore reasonable to conclude that the white material is KCl. Since the gray-brown material contains KCl and ligated chromium, and since it turns green upon liberating KCl, it is likely to be a different species from the green material identified below. Based on the species observed by Monillas *et al.*⁹, it is most likely the structure shown in Figure 2.6.

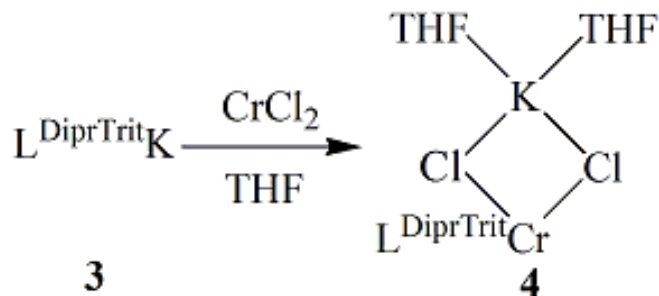


Figure 2.6 Synthesis of Gray-brown $L^{\text{DiprTrit}}\text{CrCl}_2\text{K}(\text{THF})_2$ (4)

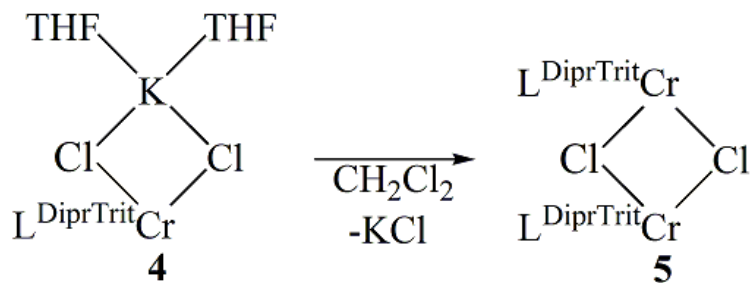


Figure 2.7 Synthesis of Green Dinuclear $[\text{L}^{\text{DippTrit}}\text{Cr}\mu\text{-Cl}]_2$ (**5**) from Gray-brown Material (**4**)

Cooling the green methylene chloride solution gave a small number of green crystals. Single crystal X-ray diffraction analysis gave the structure shown in Figures 2.7 and 2.8.

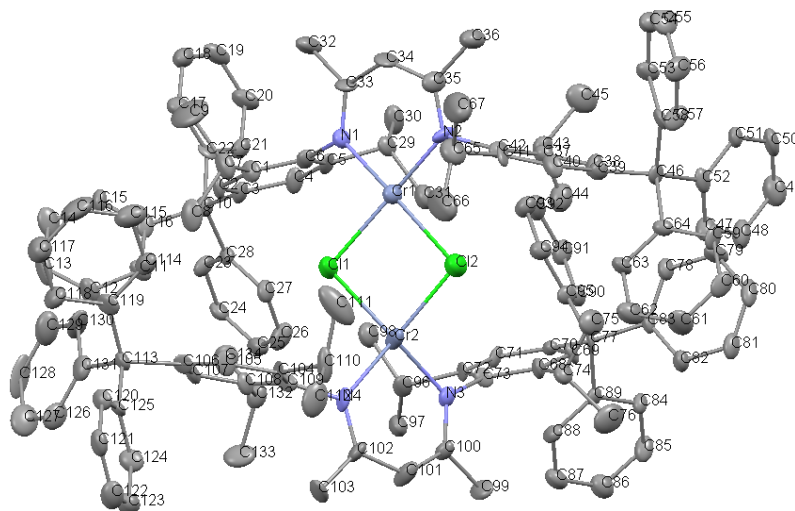


Figure 2.8 Crystal structure of $[\text{L}^{\text{DippTrit}}\text{Cr}\mu\text{-Cl}]_2$ (**5**). Hydrogen atoms are omitted for clarity. Ellipsoids are depicted at the 30% probability level.

Table 2.3 Interatomic Distances and Angles for [L^{DippTrit}Cr- μ -Cl]₂ (5)

Distances (Å)

Cr1 N2	2.017(7)	Cr1 N1	2.080(6)
Cr1 Cl2	2.371(3)	Cr1 Cl1	2.410(3)
Cr2 N4	2.065(7)	Cr2 N3	2.083(6)
Cr2 Cl2	2.364(3)	Cr2 Cl1	2.413(3)
N1 C33	1.321(9)	N1 C6	1.500(7)
N2 C35	1.328(11)	N2 C42	1.512(7)
N3 C100	1.354(10)	N3 C73	1.473(7)
N4 C102	1.341(10)	N4 C109	1.489(7)
C1 C2	1.3900	C1 C6	1.3900
C1 C7	1.556(10)	C2 C3	1.3900
C3 C4	1.3900	C3 C10	1.589(9)
C4 C5	1.3900	C5 C6	1.3900
C5 C29	1.578(9)	C7 C9	1.537(13)
C7 C8	1.546(12)	C10 C16	1.581(9)
C10 C28	1.585(9)	C10 C22	1.587(9)
C11 C12	1.3900	C11 C16	1.3900
C12 C13	1.3900	C13 C14	1.3900
C14 C15	1.3900	C15 C16	1.3900
C17 C18	1.3900	C17 C22	1.3900
C18 C19	1.3900	C19 C20	1.3900
C20 C21	1.3900	C21 C22	1.3900
C23 C24	1.3900	C23 C28	1.3900
C24 C25	1.3900	C25 C26	1.3900
C26 C27	1.3900	C27 C28	1.3900
C29 C30	1.521(11)	C29 C31	1.546(11)
C32 C33	1.592(12)	C33 C34	1.426(11)
C34 C35	1.402(12)	C35 C36	1.543(12)
C37 C38	1.3900	C37 C42	1.3900
C37 C43	1.555(10)	C38 C39	1.3900
C39 C40	1.3900	C39 C46	1.594(8)
C40 C41	1.3900	C41 C42	1.3900
C41 C65	1.555(11)	C43 C44	1.521(12)
C43 C45	1.577(12)	C46 C58	1.593(9)
C46 C52	1.611(9)	C46 C64	1.611(9)
C47 C48	1.3900	C47 C52	1.3900
C48 C49	1.3900	C49 C50	1.3900
C50 C51	1.3900	C51 C52	1.3900
C53 C54	1.3900	C53 C58	1.3900

C54 C55	1.3900	C55 C56	1.3900
C56 C57	1.3900	C57 C58	1.3900
C59 C60	1.3900	C59 C64	1.3900
C60 C61	1.3900	C61 C62	1.3900
C62 C63	1.3900	C63 C64	1.3900
C65 C66	1.478(14)	C65 C67	1.547(14)
C68 C69	1.3900	C68 C73	1.3900
C68 C74	1.567(9)	C69 C70	1.3900
C70 C71	1.3900	C70 C77	1.618(8)
C71 C72	1.3900	C72 C73	1.3900
C72 C96	1.550(9)	C74 C75	1.519(11)
C74 C76	1.587(12)	C77 C83	1.573(8)
C77 C89	1.596(9)	C77 C95	1.617(9)
C78 C79	1.3900	C78 C83	1.3900
C79 C80	1.3900	C80 C81	1.3900
C81 C82	1.3900	C82 C83	1.3900
C84 C85	1.3900	C84 C89	1.3900
C85 C86	1.3900	C86 C87	1.3900
C87 C88	1.3900	C88 C89	1.3900
C90 C91	1.3900	C90 C95	1.3900
C91 C92	1.3900	C92 C93	1.3900
C93 C94	1.3900	C94 C95	1.3900
C96 C98	1.536(11)	C96 C97	1.575(12)
C99 C100	1.493(11)	C100 C101	1.425(11)
C101 C102	1.415(11)	C102 C103	1.530(11)
C104 C105	1.3900	C104 C109	1.3900
C104 C110	1.572(10)	C105 C106	1.3900
C106 C107	1.3900	C106 C113	1.594(9)
C107 C108	1.3900	C108 C109	1.3900
C108 C132	1.546(9)	C110 C111	1.526(15)
C110 C112	1.556(13)	C113 C125	1.585(9)
C113 C119	1.593(10)	C113 C131	1.600(9)
C114 C115	1.3900	C114 C119	1.3900
C115 C116	1.3900	C116 C117	1.3900
C117 C118	1.3900	C118 C119	1.3900
C120 C121	1.3900	C120 C125	1.3900
C121 C122	1.3900	C122 C123	1.3900
C123 C124	1.3900	C124 C125	1.3900
C126 C127	1.3900	C126 C131	1.3900
C127 C128	1.3900	C128 C129	1.3900
C129 C130	1.3900	C130 C131	1.3900

C132 C134	1.549(11)	C132 C133	1.577(12)
Angles (deg)]			
N2 Cr1 N1	91.8(3)	N2 Cr1 Cl2	95.0(2)
N1 Cr1 Cl2	160.5(2)	N2 Cr1 Cl1	162.1(2)
N1 Cr1 Cl1	96.0(2)	Cl2 Cr1 Cl1	82.91(10)
N4 Cr2 N3	90.7(3)	N4 Cr2 Cl2	160.4(2)
N3 Cr2 Cl2	97.5(2)	N4 Cr2 Cl1	97.8(2)
N3 Cr2 Cl1	152.66(19)	Cl2 Cr2 Cl1	82.99(10)
Cr1 Cl1 Cr2	95.81(10)	Cr2 Cl2 Cr1	98.18(11)
C33 N1 C6	116.5(6)	C33 N1 Cr1	124.3(6)
C6 N1 Cr1	117.6(4)	C35 N2 C42	114.1(7)
C35 N2 Cr1	126.0(6)	C42 N2 Cr1	119.9(4)
C100 N3 C73	117.1(6)	C100 N3 Cr2	125.6(5)
C73 N3 Cr2	116.5(4)	C102 N4 C109	118.0(6)
C102 N4 Cr2	125.1(6)	C109 N4 Cr2	116.9(5)
C2 C1 C6	120.0	C2 C1 C7	118.8(5)
C6 C1 C7	121.2(5)	C3 C2 C1	120.0
C2 C3 C4	120.0	C2 C3 C10	122.5(5)
C4 C3 C10	117.3(5)	C3 C4 C5	120.0
C6 C5 C4	120.0	C6 C5 C29	121.1(5)
C4 C5 C29	118.8(5)	C5 C6 C1	120.0
C5 C6 N1	117.7(5)	C1 C6 N1	122.2(5)
C9 C7 C8	109.9(8)	C9 C7 C1	111.8(8)
C8 C7 C1	112.2(8)	C16 C10 C28	102.6(6)
C16 C10 C22	114.8(6)	C28 C10 C22	111.1(6)
C16 C10 C3	112.9(6)	C28 C10 C3	113.1(6)
C22 C10 C3	102.7(6)	C12 C11 C16	120.0
C11 C12 C13	120.0	C14 C13 C12	120.0
C13 C14 C15	120.0	C16 C15 C14	120.0
C15 C16 C11	120.0	C15 C16 C10	122.4(5)
C11 C16 C10	117.4(5)	C18 C17 C22	120.0
C19 C18 C17	120.0	C18 C19 C20	120.0
C19 C20 C21	120.0	C22 C21 C20	120.0
C21 C22 C17	120.0	C21 C22 C10	120.2(5)
C17 C22 C10	119.7(5)	C24 C23 C28	120.0
C25 C24 C23	120.0	C26 C25 C24	120.0
C25 C26 C27	120.0	C28 C27 C26	120.0
C27 C28 C23	120.0	C27 C28 C10	122.2(5)
C23 C28 C10	117.7(5)	C30 C29 C31	108.7(8)
C30 C29 C5	113.3(6)	C31 C29 C5	109.1(6)
N1 C33 C34	122.9(9)	N1 C33 C32	121.5(8)

C34 C33 C32	115.5(8)	C35 C34 C33	129.4(9)
N2 C35 C34	123.0(9)	N2 C35 C36	123.3(8)
C34 C35 C36	113.7(8)	C38 C37 C42	120.0
C38 C37 C43	116.7(5)	C42 C37 C43	123.2(5)
C39 C38 C37	120.0	C40 C39 C38	120.0
C40 C39 C46	118.6(5)	C38 C39 C46	120.8(5)
C39 C40 C41	120.0	C42 C41 C40	120.0
C42 C41 C65	122.4(6)	C40 C41 C65	117.5(6)
C41 C42 C37	120.0	C41 C42 N2	117.8(5)
C37 C42 N2	122.1(5)	C44 C43 C37	111.8(7)
C44 C43 C45	109.1(9)	C37 C43 C45	108.4(7)
C58 C46 C39	104.5(6)	C58 C46 C52	112.7(6)
C39 C46 C52	109.9(6)	C58 C46 C64	113.6(6)
C39 C46 C64	112.8(6)	C52 C46 C64	103.6(6)
C48 C47 C52	120.0	C47 C48 C49	120.0
C50 C49 C48	120.0	C49 C50 C51	120.0
C52 C51 C50	120.0	C51 C52 C47	120.0
C51 C52 C46	121.5(5)	C47 C52 C46	118.2(5)
C54 C53 C58	120.0	C55 C54 C53	120.0
C56 C55 C54	120.0	C57 C56 C55	120.0
C56 C57 C58	120.0	C57 C58 C53	120.0
C57 C58 C46	122.8(5)	C53 C58 C46	117.1(5)
C60 C59 C64	120.0	C59 C60 C61	120.0
C62 C61 C60	120.0	C63 C62 C61	120.0
C64 C63 C62	120.0	C63 C64 C59	120.0
C63 C64 C46	121.8(5)	C59 C64 C46	118.1(5)
C66 C65 C67	108.9(10)	C66 C65 C41	111.3(9)
C67 C65 C41	113.9(9)	C69 C68 C73	120.0
C69 C68 C74	119.3(5)	C73 C68 C74	120.7(5)
C68 C69 C70	120.0	C71 C70 C69	120.0
C71 C70 C77	119.8(4)	C69 C70 C77	119.3(4)
C72 C71 C70	120.0	C71 C72 C73	120.0
C71 C72 C96	117.5(5)	C73 C72 C96	122.3(5)
C72 C73 C68	120.0	C72 C73 N3	117.3(4)
C68 C73 N3	122.6(4)	C75 C74 C68	113.3(7)
C75 C74 C76	104.4(8)	C68 C74 C76	110.4(7)
C83 C77 C89	111.0(6)	C83 C77 C95	108.7(6)
C89 C77 C95	107.7(6)	C83 C77 C70	110.4(5)
C89 C77 C70	110.7(6)	C95 C77 C70	108.2(5)
C79 C78 C83	120.0	C80 C79 C78	120.0
C79 C80 C81	120.0	C82 C81 C80	120.0

C81 C82 C83	120.0	C82 C83 C78	120.0
C82 C83 C77	117.8(5)	C78 C83 C77	122.1(5)
C85 C84 C89	120.0	C84 C85 C86	120.0
C87 C86 C85	120.0	C88 C87 C86	120.0
C87 C88 C89	120.0	C88 C89 C84	120.0
C88 C89 C77	122.7(5)	C84 C89 C77	117.1(5)
C91 C90 C95	120.0	C90 C91 C92	120.0
C93 C92 C91	120.0	C92 C93 C94	120.0
C95 C94 C93	120.0	C94 C95 C90	120.0
C94 C95 C77	118.8(5)	C90 C95 C77	120.6(5)
C98 C96 C72	111.2(7)	C98 C96 C97	111.9(7)
C72 C96 C97	112.4(7)	N3 C100 C101	121.9(8)
N3 C100 C99	122.7(8)	C101 C100 C99	115.4(8)
C102 C101 C100	129.4(9)	N4 C102 C101	123.3(8)
N4 C102 C103	120.2(8)	C101 C102 C103	116.5(8)
C105 C104 C109	120.0	C105 C104 C110	117.2(5)
C109 C104 C110	122.4(5)	C104 C105 C106	120.0
C107 C106 C105	120.0	C107 C106 C113	120.4(5)
C105 C106 C113	119.0(5)	C106 C107 C108	120.0
C107 C108 C109	120.0	C107 C108 C132	120.7(5)
C109 C108 C132	119.2(5)	C108 C109 C104	120.0
C108 C109 N4	121.4(5)	C104 C109 N4	118.2(5)
C111 C110 C112	112.7(9)	C111 C110 C104	113.4(9)
C112 C110 C104	110.9(8)	C125 C113 C119	110.6(6)
C125 C113 C106	105.4(6)	C119 C113 C106	113.0(6)
C125 C113 C131	113.4(6)	C119 C113 C131	105.6(6)
C106 C113 C131	109.0(6)	C115 C114 C119	120.0
C116 C115 C114	120.0	C115 C116 C117	120.0
C116 C117 C118	120.0	C117 C118 C119	120.0
C118 C119 C114	120.0	C118 C119 C113	116.3(6)
C114 C119 C113	123.6(6)	C121 C120 C125	120.0
C120 C121 C122	120.0	C123 C122 C121	120.0
C124 C123 C122	120.0	C123 C124 C125	120.0
C124 C125 C120	120.0	C124 C125 C113	117.1(5)
C120 C125 C113	122.9(5)	C127 C126 C131	120.0
C126 C127 C128	120.0	C129 C128 C127	120.0
C128 C129 C130	120.0	C131 C130 C129	120.0
C130 C131 C126	120.0	C130 C131 C113	116.1(6)
C126 C131 C113	123.6(6)	C108 C132 C134	111.5(7)
C108 C132 C133	112.6(7)	C134 C132 C133	106.9(7)

Since one of the goals of adding steric bulk to the ligand was to prevent the ability to form a dinuclear complex, it is somewhat disappointing that this compound still does so. However, closer inspection of the crystal structure does give reason for hope in that the planes defined by the N-C-C-C-N atoms of the ligand are canted with respect to one another, and the geometry of the chromium atoms is distorted from square planar. This is unlike the dinuclear chloride complex in the parent system⁷, which have the ligands, chromium atoms, and chlorides all in the same plane – an arrangement that requires both chromium atoms be square planar.

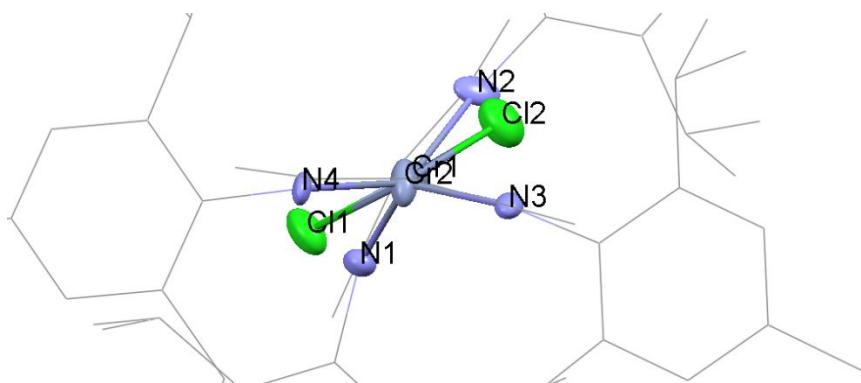


Figure 2.9 View of the Metal Core of $[L^{\text{DippTrit}}-\mu\text{-Cl}]_2$ (5) N1 and N2 are ligated to Cr1, N3 and N4 to Cr2. Torsion angles: N1-N4= -57° , N2-N3= -63° , N1-Cl1= -31° , and N2-Cl2= -22°

The canted ligands suggest that the steric bulk is indeed affecting the ability of the dimeric complex to come together. Further, it suggests that a chromium (I) ethylene complex with this ligand might be monomeric, since the bridging ethylene between two chromium atoms seen in the parent system requires coplanarity for the

necessary π -backbonding. Since one of the goals of this line of investigation was to produce a monomeric ethylene complex, the potential was encouraging.

Based on previous experience with the triisopropyl system, it was suspected that an allyl complex would be more soluble than the chloride and therefore easier to work with and crystallize. The synthesis of the allyl complex is shown in Figure 2.10

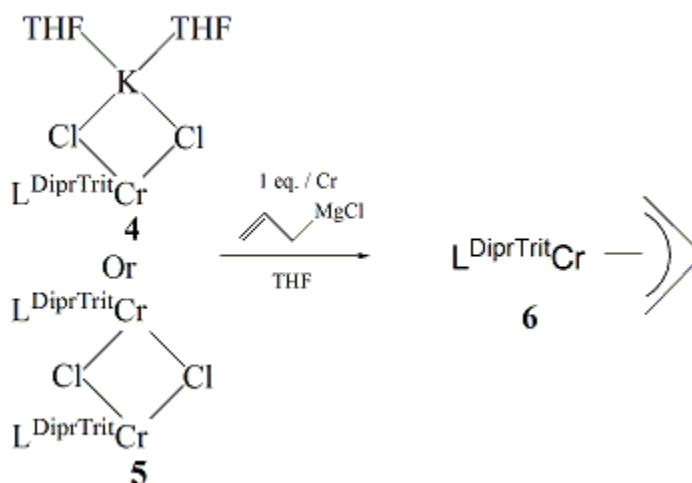


Figure 2.10 Synthesis of $L^{\text{DippTrit}}\text{Cr}-\eta^3\text{-C}_3\text{H}_5$ (6) from the Chloride.

Treating the chloride (either as the gray-brown solid **4** or the green powder **5**) with one equivalent of allylmagnesium chloride in THF gave a homogenous brown solution, thus the allyl derivative is indeed more soluble. Cooling a THF solution of this substance produced orange crystals, which were found to have the molecular structure shown in Figure 2.11. This crystal structure proved that the gray-brown material described above did indeed contain a ligated chromium species. As in the parent system, the allyl complex is a monomer.

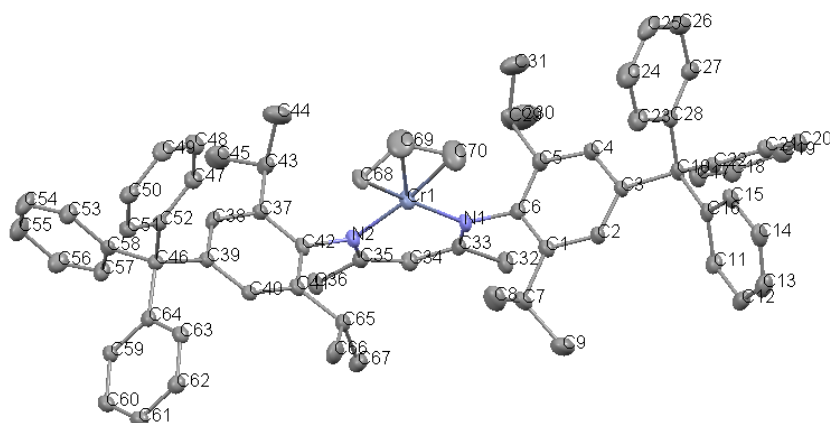


Figure 2.11 Crystal structure of $L^{\text{DippTrit}}\text{Cr-}\eta^3\text{-C}_3\text{H}_5$ (**6**). Hydrogen atoms are omitted for clarity. Ellipsoids are depicted at the 30% probability level.

Table 2.4: Interatomic Distances and Angles for $L^{\text{DippTrit}}\text{Cr-}\eta^3\text{-C}_3\text{H}_5$ (**6**)

Distances (Å)			
Cr1 N1	2.032(4)	Cr1 N2	2.038(4)
Cr1 C69	2.208(6)	Cr1 C68	2.254(4)
Cr1 C70	2.267(7)	N1 C33	1.329(6)
N1 C6	1.435(6)	N2 C35	1.341(6)
N2 C42	1.442(6)	C1 C2	1.402(6)
C1 C6	1.413(7)	C1 C7	1.513(7)
C2 C3	1.374(6)	C3 C4	1.396(7)
C3 C10	1.553(6)	C4 C5	1.391(7)
C5 C6	1.408(7)	C5 C29	1.525(7)
C7 C8	1.523(8)	C7 C9	1.533(8)
C10 C22	1.553(7)	C10 C16	1.553(7)
C10 C28	1.559(7)	C11 C16	1.390(7)
C11 C12	1.396(7)	C12 C13	1.385(8)
C13 C14	1.359(8)	C14 C15	1.392(7)
C15 C16	1.400(7)	C17 C18	1.383(7)

C17 C22	1.389(7)	C18 C19	1.375(7)
C19 C20	1.378(7)	C20 C21	1.389(7)
C21 C22	1.394(6)	C23 C24	1.373(8)
C23 C28	1.402(7)	C24 C25	1.373(9)
C25 C26	1.379(9)	C26 C27	1.395(8)
C27 C28	1.364(7)	C29 C30	1.497(9)
C29 C31	1.515(9)	C32 C33	1.503(6)
C33 C34	1.410(7)	C34 C35	1.387(6)
C35 C36	1.506(7)	C37 C42	1.405(7)
C37 C38	1.403(6)	C37 C43	1.524(7)
C38 C39	1.392(7)	C39 C40	1.389(6)
C39 C46	1.553(6)	C40 C41	1.387(6)
C41 C42	1.401(7)	C41 C65	1.522(7)
C43 C44	1.524(8)	C43 C45	1.528(8)
C46 C58	1.541(6)	C46 C52	1.549(7)
C46 C64	1.561(7)	C47 C48	1.376(7)
C47 C52	1.385(7)	C48 C49	1.392(7)
C49 C50	1.386(7)	C50 C51	1.388(7)
C51 C52	1.394(7)	C53 C58	1.381(7)
C53 C54	1.387(7)	C54 C55	1.370(8)
C55 C56	1.372(8)	C56 C57	1.382(7)
C57 C58	1.393(7)	C59 C60	1.386(7)
C59 C64	1.391(6)	C60 C61	1.369(7)
C61 C62	1.378(7)	C62 C63	1.381(7)
C63 C64	1.394(7)	C65 C66	1.525(8)
C65 C67	1.531(7)	C68 C69	1.381(8)
C69 C70	1.393(9)		

Angles (deg)

N1 Cr1 N2	90.19(16)	N1 Cr1 C69	135.9(2)
N2 Cr1 C69	132.9(2)	N1 Cr1 C68	164.51(18)
N2 Cr1 C68	101.59(17)	C69 Cr1 C68	36.0(2)
N1 Cr1 C70	101.5(2)	N2 Cr1 C70	168.1(2)
C69 Cr1 C70	36.3(2)	C68 Cr1 C70	66.5(2)
C33 N1 C6	116.7(4)	C33 N1 Cr1	127.0(3)
C6 N1 Cr1	116.3(3)	C35 N2 C42	118.0(4)
C35 N2 Cr1	126.4(3)	C42 N2 Cr1	115.5(3)
C2 C1 C6	118.4(4)	C2 C1 C7	120.4(4)
C6 C1 C7	121.2(4)	C3 C2 C1	122.1(5)
C2 C3 C4	118.4(4)	C2 C3 C10	125.2(4)
C4 C3 C10	116.4(4)	C5 C4 C3	122.2(5)
C4 C5 C6	118.4(5)	C4 C5 C29	119.7(5)

C6 C5 C29	121.9(4)	C5 C6 C1	120.3(4)
C5 C6 N1	119.6(4)	C1 C6 N1	120.0(4)
C1 C7 C8	111.5(5)	C1 C7 C9	114.4(4)
C8 C7 C9	108.6(5)	C22 C10 C16	104.1(4)
C22 C10 C3	111.6(4)	C16 C10 C3	113.7(4)
C22 C10 C28	112.0(4)	C16 C10 C28	111.0(4)
C3 C10 C28	104.7(4)	C16 C11 C12	120.6(5)
C13 C12 C11	120.1(5)	C14 C13 C12	120.1(5)
C13 C14 C15	120.2(5)	C14 C15 C16	121.1(5)
C11 C16 C15	117.7(5)	C11 C16 C10	120.3(5)
C15 C16 C10	121.8(5)	C18 C17 C22	120.9(5)
C19 C18 C17	121.2(5)	C18 C19 C20	118.7(5)
C19 C20 C21	120.5(5)	C20 C21 C22	121.2(5)
C17 C22 C21	117.4(5)	C17 C22 C10	123.7(4)
C21 C22 C10	118.8(4)	C24 C23 C28	120.9(6)
C25 C24 C23	120.3(6)	C24 C25 C26	119.7(6)
C25 C26 C27	119.7(6)	C28 C27 C26	121.3(6)
C27 C28 C23	118.1(5)	C27 C28 C23	118.1(5)
C27 C28 C10	125.1(5)	C23 C28 C10	116.7(5)
C30 C29 C31	111.1(6)	C30 C29 C5	112.2(5)
C31 C29 C5	112.8(5)	N1 C33 C34	123.1(4)
N1 C33 C32	121.1(4)	C34 C33 C32	115.7(5)
C35 C34 C33	128.8(5)	N2 C35 C34	123.3(5)
N2 C35 C36	119.9(4)	C34 C35 C36	116.8(5)
C42 C37 C38	118.6(4)	C42 C37 C43	121.7(4)
C38 C37 C43	119.5(4)	C39 C38 C37	122.2(4)
C40 C39 C38	116.9(4)	C40 C39 C46	123.0(4)
C38 C39 C46	119.7(4)	C41 C40 C39	123.5(4)
C40 C41 C42	118.2(4)	C40 C41 C65	119.6(4)
C42 C41 C65	122.1(4)	C41 C42 C37	120.5(4)
C41 C42 N2	118.5(4)	C37 C42 N2	121.0(4)
C37 C43 C44	110.8(5)	C37 C43 C45	113.5(4)
C44 C43 C45	109.7(5)	C58 C46 C52	109.4(4)
C58 C46 C39	109.4(4)	C52 C46 C39	109.9(4)
C58 C46 C64	110.0(4)	C52 C46 C64	108.1(4)
C39 C46 C64	110.1(4)	C48 C47 C52	121.4(5)
C47 C48 C49	121.0(5)	C50 C49 C48	118.6(5)
C49 C50 C51	119.9(5)	C50 C51 C52	121.8(5)
C47 C52 C51	117.4(5)	C47 C52 C46	123.0(4)
C51 C52 C46	119.6(4)	C58 C53 C54	121.8(5)
C55 C54 C53	120.3(5)	C54 C55 C56	119.4(5)

C55 C56 C57	119.8(5)	C56 C57 C58	122.2(5)
C53 C58 C57	116.3(4)	C53 C58 C46	123.7(4)
C57 C58 C46	119.9(4)	C60 C59 C64	120.6(5)
C61 C60 C59	121.3(5)	C60 C61 C62	119.0(5)
C61 C62 C63	120.2(5)	C62 C63 C64	121.6(5)
C59 C64 C63	117.2(4)	C59 C64 C46	123.4(4)
C63 C64 C46	119.4(4)	C41 C65 C66	113.6(4)
C41 C65 C67	114.1(4)	C66 C65 C67	108.5(5)
C69 C68 Cr1	70.2(3)	C68 C69 C70	126.8(8)
C68 C69 Cr1	73.8(3)	C70 C69 Cr1	74.2(4)
FC69 C70 Cr1	69.6(4)		

As a control in the attempts to synthesize the ethylene complex [*vide infra*], the chloride was first reduced with KC_8 in THF with no trapping ligands around. This caused the solution to turn black, and after filtering off the graphite and removing the THF, gave a shiny black solid with a paramagnetic NMR having a peak at 102.4 ppm. At first, this was exciting, since it suggested a possible dinitrogen complex, but a further control experiment where the chloride was reduced with potassium graphite in THF under vacuum in a J Young tube showed the same peak. The solid is soluble in pentane, and is quite pure, having a melting point of 120-124 °C. 68% of the total mass that goes into the reaction becomes this product. Since the identity of the species was unknown, taking a magnetic moment was not possible, but the solution did bubble and turn red when adamantyl azide was added, suggesting a low-valent chromium species. As is typical of low valent Dipp-NacNac Cr compounds, exposure to air caused the immediate formation of a peak at 88 ppm in the NMR, most likely an oxo or hydroxo species. Refluxing the product with bis-TMS-acetylene in THF did not give the bis-TMS-acetylene complex [*vide infra*], so this compound is not an intermediate on the way to the formation of the BTMSA complex. IR did not reveal any obvious new features, and attempts to grow crystals for diffraction did not succeed, so this is as far as the compound was characterized.

Several attempts were made to synthesize the hypothetical ethylene complex by direct reduction of the chloride under ethylene, using various reducing agents such as KC_8 and Na/Naphthalenide, in THF. Unfortunately, these showed the formation of the mystery product at 102.4 ppm. For the reaction with KC_8 under ethylene, the solvent was vacuum transferred to a second ampoule. A GC of it showed that a very small amount of butene had been formed, though it was less than the small amount of residual pentane the THF solvent had picked up from the glovebox atmosphere. Whether this is indicative of some transient species capable of dimerizing ethylene or of something else entirely is impossible to say.

Since direct reduction to the ethylene complex was unsuccessful, an alternate Cr (I) synthon was sought for possible synthesis via an alternate route. In the parent system, alkyne complexes have been shown to give the metallacyclopentadienes, which then form the bridging ethylene complex upon exposure to ethylene¹¹. Initially, the trityl ligand chromium chloride complex was reduced in the presence of diphenylacetylene as in the parent case, but this gave a difficult to separate mixture of products. A colleague was successful in using the bis-(trimethylsilyl) acetylene complex of the parent system¹⁰ for his purposes, so the synthesis of the bis-TMS acetylene complex was pursued instead. Reduction of the ligand chromium chloride complex in the presence of one equivalent of bis-TMS acetylene with KC_8 in THF gave the BTMSA complex as a brown solid in 62% yield (Figure 2.12).

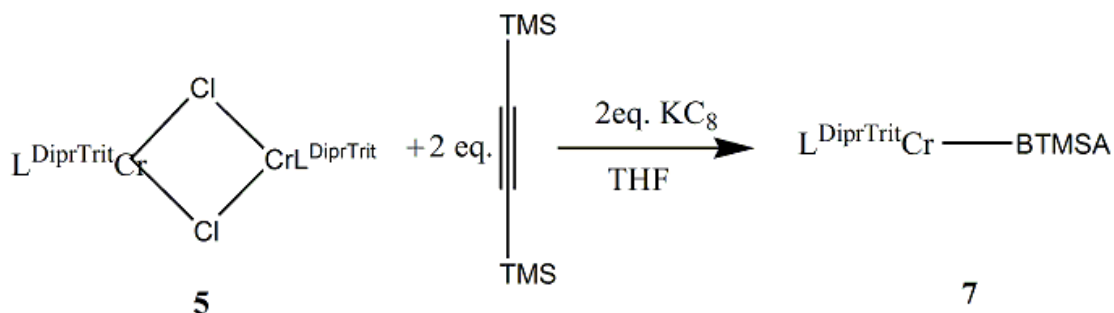


Figure 2.12 Synthesis of Bis-TMS Acetylene Complex (7)

Similar to the mysterious reduction product described above, purification of the BTMSA complex is convenient because dissolving in pentane and filtering removes most of the impurities. Cooling a pentane or ether solution gave crystals, but all were too multiple to get meaningful diffraction data. Exposure of this complex to ethylene gave a new product, as judged by NMR, and this did not react further with the ethylene. This may be similar to the metallacyclopentene product described by Monillas¹¹ (Figure 2.13), but was not characterized any further.

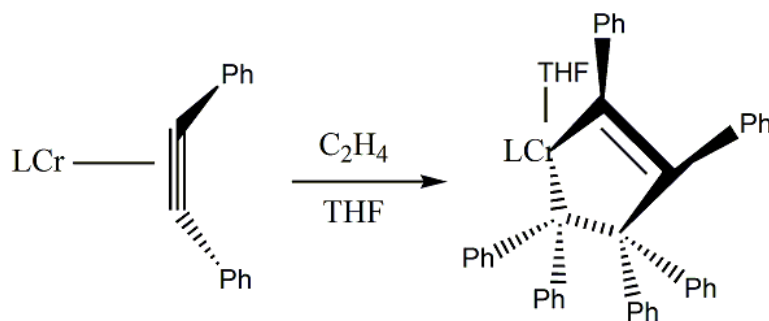


Figure 2.13 Metallacyclopentene Product from Exposing Diphenylacetylene Complex to Ethylene. L = DippNacnac.

2.3 Attempted Further Ligand Modifications

It had been hoped that the trityl substituent would aid in crystallizations for single crystal x-ray diffraction, which turned out to be true in the case of the organic molecules, but less so for the metal complexes for reasons of solubility. In a private communication, Holland mentioned having the same problem, and suggested using modified trityl substituents with methyls or tert-butyls in the 4- position of the trityl phenyl rings¹², as in Figure 2.14.

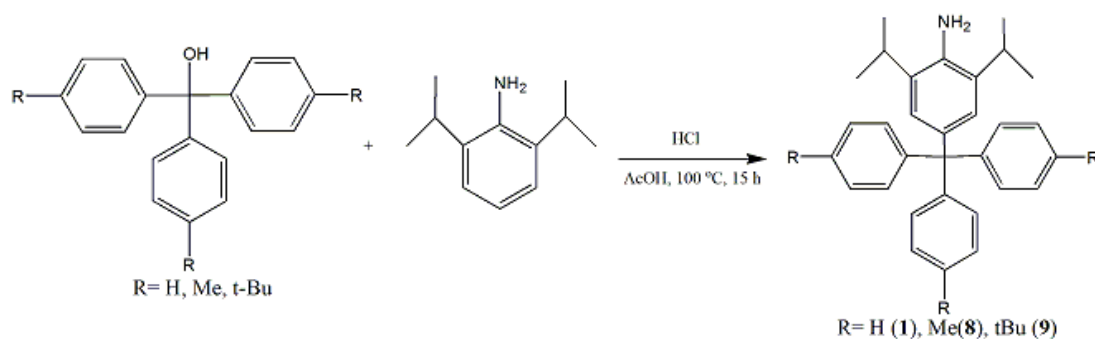


Figure 2.14 Synthesis of Anilines with Substituted Trityl Groups

The synthesis of the requisite trityl alcohols was described in the literature¹³, and the substituted anilines can be made from these alcohols via the same procedure as for the unsubstituted system. The synthesis is described in the experimental section. Attempts to make these NacNac ligands showed the appearance of a NacNac peak in the NMR, but it was often not the major product. Any further inquiries into these ligands would need to address this.

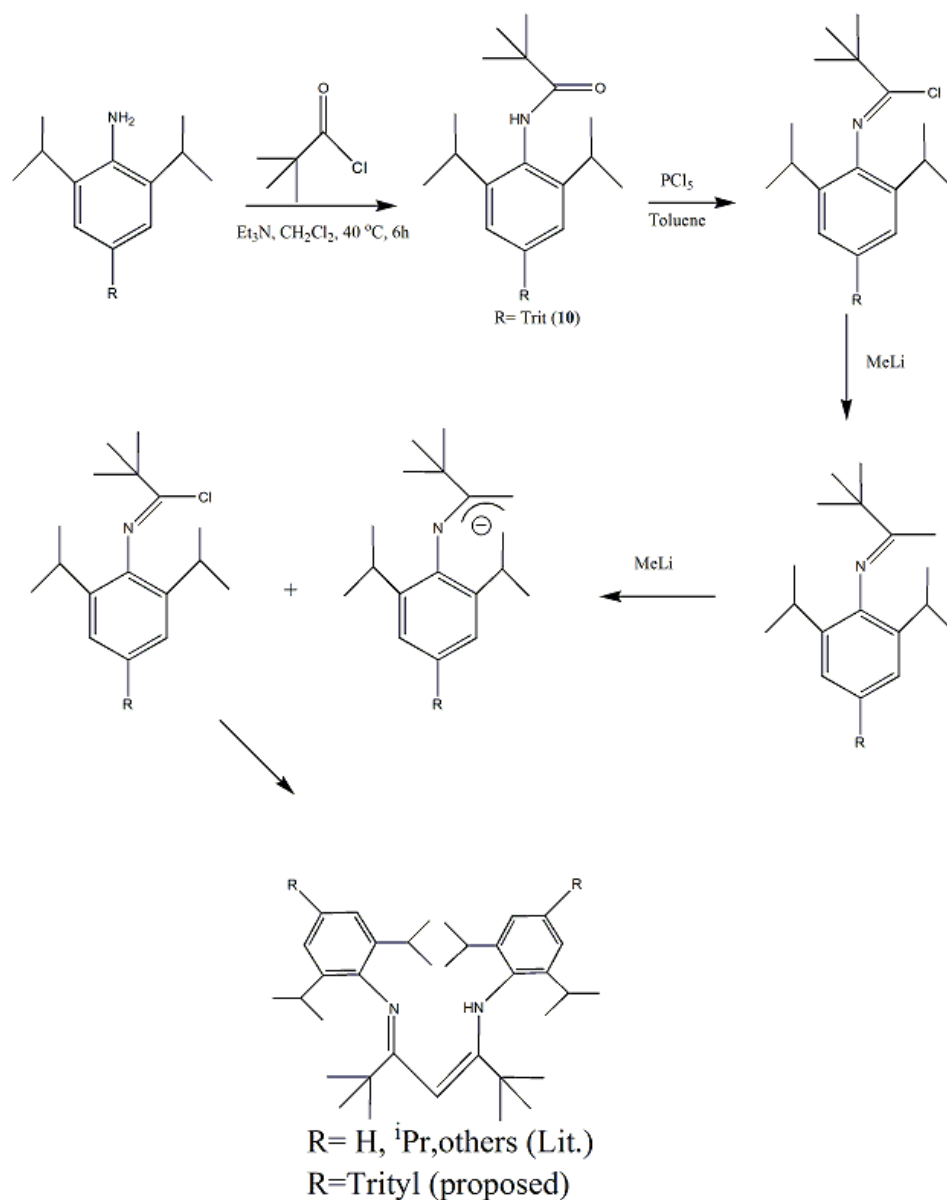


Figure 2.15 Adding t-Butyl Groups to the Ligand Backbone

In addition to altering the trityl substituents for solubility, an attempt was made to modify the backbone of the NacNac ligand as per Budzelaar *et al.*¹⁴. Adding tert-butyl substituents to the backbone of the ligand often has the effect of adding a steric ‘push’ on the phenyl rings¹⁵. Budzelaar’s synthetic scheme and the proposed route for the trityl aniline is shown in Figure 2.15. Refluxing the aniline in CH_2Cl_2 with

pivaloyl chloride and triethylamine gave the amide as a white fluffy solid in 83% yield.

A convenient way to follow these reactions was the NMR septet of the isopropyl group, which sits in an uncluttered region and shifts with each new complex. Unfortunately, the next step in the series could not be made to go cleanly, always giving a mix of product and starting material by NMR. Many attempts were made with different ratios of PCl_5 , SOCl_2 , Oxalyl Chloride, and Lawesson's Reagent to get something that contained no starting material, but none succeeded¹⁶. The best ratios came with a slight excess of PCl_5 , refluxed in toluene for 12 or more hours, but even then 8-10% starting material remained as judged by NMR in CDCl_3 . An NMR taken before running a solution of the compound through a pipette full of silica gel versus and NMR taken after indicated the imidoyl chloride begins to decompose to the starting material on silica, making purification difficult. Instead, if the toluene was removed under nitrogen, dry THF cannula transferred into the reaction flask and the white solid dissolved, then the solution was cooled to 0 °C, and approximately two equivalents MeLi added, a third species would appear in the NMR after quench. This canary yellow solid is presumably the methyl imine, but as with the previous reactions, there was significant amount of amide remaining by NMR. Attempts to lithiate this and add it to the imidoyl chloride to make the NacNac all failed, but the cause is difficult to discern. It is likely that a significant amount of the lithiating reagent was consumed by unreacted amide in the imine, and unreacted or excess PCl_5 in the imidoyl chloride. It is also possible that even if the materials were completely clean, the steric bulk of the trityl and tert-butyl groups would not allow the reactive

species to approach each other. Without a good way of cleaning up the imidoyl chloride, this scheme turned out to be unworkable.

2.4 Suggested Future Directions

The trityl substituent allows a lot of flexibility for increasing steric bulk, since it is relatively easily substituted at the 3, 4, or 5 positions of its phenyl rings. The 4,4',4''-methyl and tert-Butyl derivatives are the obvious place to start, since they have anecdotally been useful to another researcher [*vide supra*]. Examination of the chloride crystal structure suggests that the main steric interaction between the trityl substituents of the two ligands may be between one of the 3 and 5 positions of the trityl phenyl rings. Adding steric bulk there such as 3,5-trifluoromethyl may be the extra push the ligand needs to prevent dimer formation. 3,5-trifluoromethyl is suggested because 3,5-trifluoromethyl bromobenzene is commercially available, while 3,5-tert-butyl bromobenzene is not. Further, after the anilines are made, it may be possible to make the anilinium hydrochloride and brominate the 4 positions, as in the parent di-isopropyl aniline⁴. This would open up a vast world of synthetic derivatives, including anything that can be made by Pd cross-coupling – alkenes, alkynes, biphenyls, other aromatics such as ferrocene, etc.¹⁷ Though, care would have to be taken that these derivatives will remain soluble, or they will not be of much use.

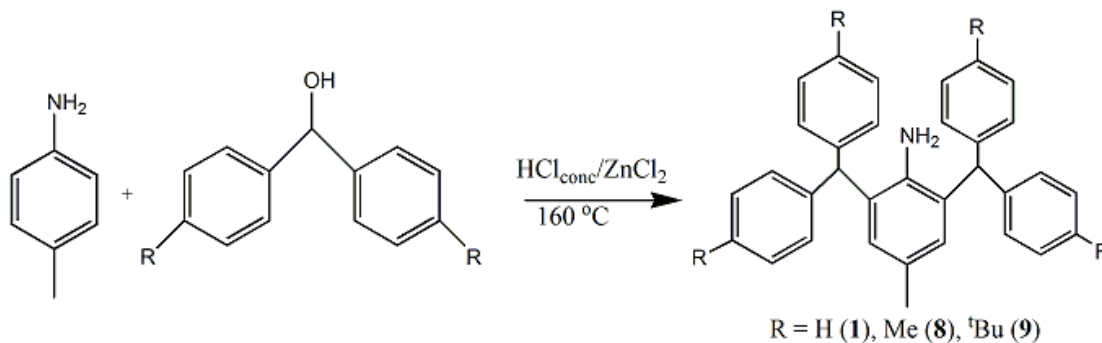


Figure 2.16 Synthesis of iPr* Anilines

Another possible interesting direction would be the so called iPr* ligands¹⁸ (Figure 2.16). Essentially, these take the isopropyl group and replace each methyl with a phenyl. The NacNac using one of these anilines with R=H was made, but had even worse solubility issues than the trityl NacNac, so it was abandoned. However, the benzhydrols needed to make 4-substituted derivatives are no more difficult to make than the substituted trityl alcohols, and this would greatly increase the bulk around the metal center. If this did not change the reactivity too much, it might be useful in preventing dimerization as well.

2.5 Experimental:

All experimental manipulations of compounds were carried out using standard techniques for reflux, extraction, washing and other workup, filtration, trituration, recrystallization, etc. Where applicable, manipulations under inert atmosphere were carried out using standard Schlenk, high vacuum, and/or glovebox techniques under an atmosphere of N₂. In the case of Schlenk manipulation, transfers between airfree glassware setups were accomplished using syringe or cannula techniques. Air sensitive NMRs were taken in J. Young tubes filled under inert atmosphere with the NMR sample and then evacuated on a high vacuum line before vacuum transferring NMR solvent. IRs were prepared by grinding 1-2 mg of sample mixed with 120-130

mg KBr in a small mortar until the mixture was homogenous, then pressed into a pellet. UV/vis samples were made by dissolving a known mass of compound in a known amount of solvent, and were run against a blank of the solvent. Magnetic susceptibility samples were prepared by grinding the sample into a fine powder and filling 9-16 mm of a magnetic susceptibility tube, capped with a small septum. Melting point samples were taken by collecting the material in a melting point capillary, and adding grease to seal the top of the capillary in the case of air-sensitive samples.

^1H NMR spectra were taken on Bruker DRX-400 or Bruker AV-300 spectrometers and were referenced to residual protons of the solvent. ^{13}C NMR spectra were taken on a Bruker AV-300 spectrometer and referenced to the residual signals from the solvent. FTIR spectra were taken on Nicolet Magna-IR S60 ESP or Mattson Genesis series spectrometers. UV/Vis spectra were taken on a Thermo Electron Co. UV1 1002E spectrophotometer. Solid state room temperature magnetic susceptibilities (χ_m) were measured with a Johnson Matthey magnetic susceptibility balance. After correcting for diamagnetism using Pascal constants¹⁹, they were converted in to effective magnetic moments (μ_{eff}). Melting points were determined on a Mel-Temp apparatus.

With the exception of Diethyl Ether, which was purchased from Honeywell, Burdick and Jackson, all solvents were purchased from Fisher Scientific. Solvents used in inert atmosphere were degassed and dried by passage through activated alumina before use. THF- d_8 and C_6D_6 were purchased from Cambridge Isotope Labs, degassed and stored under vacuum over Na/K alloy until use. Ethylene was purchased from Matheson and dried with an inline Model 127 oxygen trap purchased from Keen

Compressed Gas Co. Triphenylmethyl alcohol was purchased from TCI America, CrCl_2 was purchased from Strem Chemical Co., and all other reagents were purchased from Sigma-Aldrich or Acros and dried or purified using standard procedures when necessary.

2.5.1 Preparation of 2,6-di-isopropyl-4-trityl aniline (1): To a dry 500 mL Schlenk flask with a stir bar was added 130 g (500 mmol) of triphenylmethanol, 104 mL of 2,6-di-isopropylaniline (97.51 g, 550 mmol), and 100 mL acetic acid to give a slurry. With stirring, 42 mL conc. HCl was added (12M, 504 mmol). This addition often causes anilinium chloride to crash out as a white solid; this is not a problem as long as all solid remains in the AcOH slurry. More AcOH may be added if necessary. The flask was fitted with a reflux condenser with an outlet to an oil bubbler, the Schlenk flask stopcock closed, and the mix was heated with stirring to 100 °C for 15 hr. At the end of 15 hr, the mix had become a solid mass in the bottom of the flask. The flask was allowed to cool to r.t. and the mass was dissolved in CH_2Cl_2 , approx. 600 mL. 250 mL water was added, stirred briefly, then decanted to remove most of the AcOH. After repeating this procedure with another 250 mL water, 600 mL Sat. $\text{NaHCO}_{3(\text{aq})}$ was added to the CH_2Cl_2 and stirred for 30 min. The layers were then separated, the aqueous layer extracted 3x with CH_2Cl_2 (50 mL), and the organic layers combined, dried over Na_2SO_4 , and filtered. The solvent was removed in vacuo to give 194.6 g of a light brown solid. Recrystallization from 400 mL toluene gave 155.3 g of an off white solid after drying at 90 °C overnight. (370 mmol, 74% yield) ^1H NMR (CDCl_3): 7.25-7.20 (*m*, 15H), 6.92 (*s*, 2H), 3.71 (*br s*, 2H), 2.97-2.90 (*sept.*, 2H), 1.16 (*d*, 12H) ppm. ^{13}C NMR (CDCl_3): 147.6, 137.7, 135.5, 131.2, 127.2, 126.1, 125.6, 64.9, 28.0, 22.5 ppm. IR (KBr): 3471 (*m*), 3402 (*m*), 2961 (*s*), 2922 (*m*), 2867 (*m*),

1959 (w), 1619 (s), 1594 (s), 1491 (m), 1472 (s), 1441 (s), 1384 (s), 1355 (m), 1263 (m), 1169 (m), 1121 (w), 1036 (s), 873 (m), 758 (s), 710 (s), 659 (m) cm^{-1} . M.P. 236 $^{\circ}\text{C}$

2.5.2 Preparation of $\text{L}^{\text{DippTrit}}\text{H}$ (2): To a 500 ml round bottom flask was added 12.6 g of 2,6-di-isopropyl-4-trityl aniline (**1**) (30.0 mmol, 2.3 eq), 2.36 g toluene sulfonic acid monohydrate (12.4 mmol, 0.95 eq), 200 mL of toluene, and 1.33 mL of acetylacetone (1.294 g, 13.0 mmol, 1.0 eq). A Dean-Stark reflux apparatus was fitted on the flask, the setup was protected from atmosphere with an oil bubbler, and the mix refluxed for 48 hr. The mix was then cooled and the toluene removed in vacuo. The resulting brown solid was redissolved in CH_2Cl_2 and stirred with sat. $\text{NaHCO}_3(\text{aq})$ for 2 hr until bubbles stopped. The layers were separated and the aqueous layer extracted with 50 mL CH_2Cl_2 . The organic layers were combined, dried over Na_2SO_4 , filtered, and the solvent removed in vacuo to give a golden-brown solid. This was recrystallized from 200 mL of toluene to give 9.94 g of off-white solid. (84% yield) ^1H NMR (CDCl_3): 12.26 (*br s*, 1H), 7.33-7.20 (*m*, 30H), 6.97 (*s*, 4H), 4.91 (*s*, 1H), 3.07 (*sept.*, 4H), 1.79 (*s*, 6H), 1.15 (*d*, 12H), 0.99 (*d*, 12H) ppm. ^{13}C NMR (CDCl_3): 161.3, 147.2, 143.0, 140.9, 138.2, 131.2, 131.1, 129.1, 128.3, 127.3, 127.2, 126.3, 126.1, 125.8, 125.6, 125.7, 93.0, 65.1, 28.2, 24.0, 23.3, 20.8 ppm. IR (KBr): 3423 (w), 3054 (m), 2958 (s), 2925 (m), 2867 (m), 1943 (w), 1620 (s), 1551 (s), 1491 (s), 1442 (m), 1383 (m), 1327 (m), 1264 (m), 1114 (m), 1035 (m), 872 (m), 790 (m), 731 (s) cm^{-1} . M.P. 118-122 $^{\circ}\text{C}$.

2.5.3 Preparation of $\text{L}^{\text{DippTrit}}\text{K}$ (3): In the inert atmosphere box, 9.42 g (10.4 mmol) $\text{L}^{\text{DippTrit}}\text{H}$ (**2**), 2.28 g Potassium Hexamethyldisilazane (KHMDs, 11.4 mmol) and 100 mL toluene were added to give a light brown slurry. Under N_2 , the solution

was gently refluxed for 24 hr, the NacNac dissolving upon heating. After 24 hr, the mix was cooled to -30 °C for 14 hr, causing bright yellow solid to crash out. This was filtered under N₂, washed with a small amount of cold toluene, and dried to give 7.2 g (76% yield) of L^{DippTrit}K (**3**). Concentrating the mother liquor and repeating the cooling and filtering process yields more salt, but also may include residual KHMDs. ¹H NMR (THF-d₈): 7.19 (*m*, 30 H), 6.78 (*s*, 4H), 4.22 (*s*, 1H), 3.23 (*m*, 4H), 1.65 (*s*, 6H), 1.03 (*d*, 12H), 0.94 (*d*, 12H) ppm. IR(KBr): 3058 (*m*), 2946 (*s*), 2924 (*m*), 2869 (*m*), 1957 (*w*), 1620 (*s*), 1550 (*s*), 1492 (*s*), 1460 (*m*), 1442 (*s*), 1382 (*m*), 1363 (*m*), 1326 (*m*), 1261 (*s*), 1190 (*m*), 1160 (*m*), 1108 (*s*), 1035 (*s*), 873 (*m*), 799 (*s*), 748 (*m*), 682 (*s*) cm⁻¹. M.P.: 212-216 °C dec.

2.5.4 Preparation of L^{DippTrit}CrCl₂K(THF)₂ (4**):** To a 500 mL flask in the N₂ box, 1.24 g CrCl₂ (10.1 mmol) and 50 mL THF were added. In a separate flask, 9.42 L^{DippTrit}K (**3**) (10.0 mmol) was dissolved in 200 mL THF. The L^{DippTrit}K (**3**) solution was slowly added to the CrCl₂ solution, causing it to go from light green to brown. The mix was then stirred overnight (16 hr). About two hours after the addition, the mix had turned black, and about 6 hours after the addition, brown. Finally, after stirring overnight, the mix had formed a distinctive insoluble gray-brown. Filtering gave a light yellow-green supernatant, and 8.7 g of gray-brown solid. (70% yield) ¹H NMR: same as the green [L^{DippTrit}Cr-μ-Cl]₂ (**5**) below, due to slight interconversion and the greater solubility of the green compound. IR: 3056 (*m*), 2957 (*s*), 2922 (*m*), 2870 (*m*), 1953 (*w*), 1814 (*w*), 1597 (*m*), 1527 (*m*), 1465 (*s*), 1443 (*s*), 1383 (*w*), 1321 (*s*), 1186 (*w*), 1099 (*m*), 1034 (*s*), 967 (*w*), 874 (*m*), 802 (*m*), 750 (*m*), 702 (*s*) cm⁻¹. μ_{eff}(298 K): 3.0 μ_B.

2.5.5 Preparation of $[L^{\text{DippTrit}}\text{Cr}-\mu\text{-Cl}]_2$ (5): In the inert atmosphere box, 150 mL CH_2Cl_2 was added to the 8.7 g gray-brown solid (4) from above and stirred for 30 min to give a green solution with a small amount of solid remaining. Filtering to remove KCl and removing the CH_2Cl_2 *in vacuo* gave $[L^{\text{DippTrit}}\text{Cr}-\mu\text{-Cl}]_2$ (5) in quantitative yield. M.P.: ^1H NMR (C_6D_6): 116.7 (br), 8.67 (br), 2.35 (br) ppm. IR (KBr): 3057 (m), 3027 (m), 2960 (s), 2963 (m), 2867 (m), 1953 (w), 1815 (w), 1620 (m), 1529 (m), 1492 (s), 1444 (s), 1391 (s), 1320 (s), 1261 (s), 1188 (m), 1111 (m) 1034 (s), 874 (m), 800 (m), 750 (m), 701 (s) cm^{-1} . UV/vis (CH_2Cl_2): λ_{max} (ϵ)= 524 (306 $\text{M}^{-1}\text{cm}^{-1}$), 553 (310 $\text{M}^{-1}\text{cm}^{-1}$), 591 (319 $\text{M}^{-1}\text{cm}^{-1}$) nm. μ_{eff} (298 K): 2.7 μ_{B} / Cr. 248-252 °C dec.

2.5.6 Preparation of $L^{\text{DippTrit}}\text{Cr}-\eta^3\text{-C}_3\text{H}_5$ (6): In the inert atmosphere box, 20 mL of THF was added to 715 mg $[L^{\text{DippTrit}}\text{Cr}-\mu\text{-Cl}]_2$ (5) (0.72 mmol, 1 eq). 1.35 mL of 1.88 M allylmagnesium chloride (0.72 mmol, 1 eq) was added dropwise via syringe, and the reaction allowed to stir for two hours. After filtering, THF was removed and the residue was redissolved in toluene. The solution was filtered again, toluene removed, and repeated cooling of a THF solution gave 630 mg (87 %) of orange-brown crystals. ^1H NMR (THF- d_8): 142.16 (br), 10.05 (br), 7.16, 6.87, 4.82, 3.06, 0.95 ppm. IR (KBr): 3066 (m), 2960 (m), 2921 (s), 2853 (s), 2778 (m), 1932 (w), 1655 (m), 1618 (m), 1560 (m), 1459 (m), 1261 (s), 1097 (s), 1031 (s), 801 (s), 702 (m) cm^{-1} . UV/vis (CH_2Cl_2): λ_{max} (ϵ) = 409 (525 $\text{M}^{-1}\text{cm}^{-1}$), 503 (739 $\text{M}^{-1}\text{cm}^{-1}$), 666 (824 $\text{M}^{-1}\text{cm}^{-1}$), 705 (750 $\text{M}^{-1}\text{cm}^{-1}$) nm. μ_{eff} (298 K): 2.8 μ_{B} .

2.5.7 Preparation of $L^{\text{DippTrit}}\text{Cr}-\text{BTMSA}$ (7): In the inert atmosphere box, 126 mg $[L^{\text{DippTrit}}\text{Cr}-\mu\text{-Cl}]_2$ (5) (0.063 mmol, 1 eq) and 22 mg bis-TMS acetylene (0.129 mmol, 2.04 eq) were added to a 25 mL round bottom flask. 10 mL THF was

added, and, slowly, with stirring, was added 18 mg KC_8 (0.133 mmol, 2.1 eq). The mix immediately turned black, and was left to stir overnight. It was then filtered through celite to remove the graphite and give a black solution. THF was removed in vacuo, the residue taken up in pentane, and filtered again. Repeated cooling of a saturated pentane solution gave 90 mg brown crystals. (61%) ^1H NMR (THF- d_8): 137.3 (br), 32.0 (br), 8.7 (br), 7.2, 2.4, 1.0, -7.2 (br) ppm. IR (KBr): 3057 (m), 3028 (m), 2960 (s), 2925 (m), 2868 (m), 2283 (w), 1953 (w), 1813 (w), 1620 (m), 1596 (m), 1528 (s), 1492 (s), 1443 (s), 1390 (s), 1320 (s), 1261 (s), 1188 (m), 1103 (s), 1034 (s), 844 (s), 751 (s), 702 (s) cm^{-1} . UV/vis (CH_2Cl_2): λ_{max} (ϵ) = 560 ($210 \text{ M}^{-1}\text{cm}^{-1}$), 603 ($220 \text{ M}^{-1}\text{cm}^{-1}$) μ_{eff} (298 K): $2.78 \mu_{\text{B}}$. M.P.: 98-102 $^\circ\text{C}$ dec.

2.5.8 Preparation of 2,6-di-isopropyl-4-(4,4',4''-trimethyl)trityl aniline (8):

4,4',4''-trimethyl-triphenylmethanol was prepared via the method of Horn and Mayr²⁰, with the exception that the gummy crude was recrystallized from hexanes rather than a mixed system to give an off-white solid with a distinctive sour smell. 3.02 g (10 mmol) of 4,4',4''-trimethyl-triphenylmethanol, 1.98 mL (1.861 g, 10.5 mmol) of 2,6-diisopropylaniline, and 20 mL of glacial acetic acid were stirred in a 50 mL flask to give a slurry. 0.83 mL of 12M HCl (10 mmol) was added with stirring, the flask fitted with a reflux condenser and an outlet to an oil bubbler, and heated at 100 $^\circ\text{C}$ for 15 hr. After 15 hr, the mix had become a purple cake. This was worked up as above for the unsubstituted trityl alcohol, with the addition that after the organic layers were combined, the purple solution was filtered through a plug of silica gel to give a yellow filtrate. This was dried and concentrated to give a light yellow solid.

Recrystallization from hexanes gave 3.81 g (83% yield) of an off-white solid. ^1H NMR: 7.16 (*d*, 6H), 7.06 (*d*, 6H), 6.92 (*s*, 2H), 3.68 (*br s*, 2H), 2.91 (*sept.*, 2H), 2.35

(s, 9H), 1.15 (d, 12H) ppm. ^{13}C NMR: 145.0, 137.5, 136.9, 134.7, 131.1, 130.9, 127.9, 125.9, 63.9, 28.0, 22.5, 21.0 ppm. IR(KBr): 3484 (m), 3401 (s), 3018 (m), 3009 (s), 2922 (m), 2867 (m), 1917 (w), 1622 (s), 1507 (s), 1443 (s), 1384 (s), 1354 (m), 1265 (m), 1191 (m), 1122 (m), 1021 (m), 873 (m), 810 (s), 783 (m), 734 (m) cm^{-1} . M.P.: 168-170 $^{\circ}\text{C}$.

2.5.9 Preparation of 2,6-di-isopropyl-4-(4,4',4''-tri-t-butyl)trityl aniline (9):

As with compound (8) above. 4,4',4''-tri-tert-Butyl-triphenylmethanol was prepared via the method of Gibson *et al*¹³. 22.8 g (53.3 mmol) of 4,4',4''-tert-Butyl-triphenylmethanol, 10.5 mL (9.91 g, 55.9 mmol) of 2,6-diisopropyl aniline, and 37 mL of glacial AcOH were stirred in a 100 mL flask to give a slurry. With stirring, 4.44 mL of 12 M HCl (53.3 mmol) were added, the flask fitted with a reflux condenser and an outlet to an oil bubbler, and heated at 100 $^{\circ}\text{C}$ for 15 hr. After 15 hr, the mix had become a purple cake, worked up identical to compound 8. Recrystallization from hexanes gave 27.3 g (87% yield) of an off-white solid. ^1H NMR: (CDCl_3) 7.24 (d, 6H), 7.14 (d, 6H), 6.78 (s, 2H), 3.65 (br s, 2H), 2.89 (sept., 2H), 1.32 (s, 27H), 1.10 (d, 12H) ppm. ^{13}C NMR (CDCl_3): 144.6, 137.2, 130.9, 130.8, 127.5, 126.2, 124.7, 123.7, 63.6, 34.3, 31.4, 28.0, 22.4 ppm. IR (KBr): 3469 (m), 3380 (m), 3028 (m), 3001 (s), 2902 (m), 2866 (m), 1921 (w), 1621 (s), 1507 (s), 1400 (s), 1267 (s), 1201 (m), 1109 (m), 1018 (s), 822 (s), 730 (m) cm^{-1} . M.P: 224-228 $^{\circ}\text{C}$.

2.5.10 Preparation of 2,6-di-isopropyl-4-trityl pivalanilide (10): To a dry 2-neck 25 mL flask was added 2.484 g (6 mmol) 2,6-di-isopropyl-4-trityl aniline (1) under blowing N_2 . 12 mL CH_2Cl_2 was added, followed by 597 mg Et_3N (5.9 mmol) and 711 mg 2,2,2-Trimethylacetyl (Pivaloyl) Chloride (5.85 mmol), both slowly via 1 mL syringe. Mix was refluxed under N_2 for 6 hr, then allowed to cool to RT. 10 mL

H₂O was added, and the contents of the flask were transferred to a separatory funnel. The organic layer was separated, and the aqueous layer extracted twice with 10 mL CH₂Cl₂. The organic layers were combined, dried over Na₂SO₄, filtered, and concentrated in vacuo to give a light brown solid smelling of rancid cheese from residual pivalic acid. This solid was recrystallized from toluene to give 2.4 g (83% yield) of fluffy white powder. ¹H NMR (CDCl₃): 7.25-7.17 (*m*, 15H); 7.02 ppm (*s*, 2H); 6.84 (*s*, 1H); 2.97-2.92 (*sept.*, 2H); 1.37 (*s*, 9H); 1.05 (*d*, 12H) ppm. ¹³C NMR (CDCl₃): 177.3, 146.9, 146.0, 131.1, 129.0, 127.4, 126.5, 125.8, 65.2, 28.7, 27.8, 23.4 ppm. IR (KBr): 3420 (*m*), 2960 (*s*), 2920 (*m*), 2868 (*m*), 1920 (*w*), 1658 (*s*), 1510 (*s*) 1492 (*s*), 1441 (*m*), 1384 (*s*), 1366 (*m*), 1262 (*s*), 1226 (*m*), 1184 (*m*), 1109 (*s*), 1036 (*s*), 873 (*m*), 803 (*m*), 767 (*m*), 743 (*m*), 701 (*s*) cm⁻¹. M.P.: 286-88 °C.

X-ray Crystallography

General considerations. Unless specified otherwise, single crystal X-ray diffraction studies were performed under the following conditions. Crystals were selected, sectioned as required, and mounted on glass fibers or MiTeGen™ plastic mesh with viscous oil and flash-cooled to the data collection temperature. Diffraction data were collected on a Brüker-AXS APEX CCD diffractometer with graphite-monochromated Mo-K α radiation ($\lambda=0.71073$ Å). The data-sets were treated with SADABS absorption corrections based on redundant multiscan data.²¹ The structures were solved using direct methods and refined with full-matrix, least-squares procedures on *F*². Unit cell parameters were determined by sampling three different sections of the Ewald sphere. Non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were treated as idealized contributions.

Structure factors and anomalous dispersion coefficients are contained in the SHELXTL 6.12 program library.²²

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CONCLUSION

Steric modification of the known ligand Dipp-NacNac was accomplished by substituting the 4-position of 2,6-di-isopropyl aniline with a triphenylmethyl group, then condensing the modified aniline with acetyl acetone to give 2,4 Pentane-N,N'-bis(2,6-diisopropyl-4-tritylphenyl) ketimine. Deprotonation with KHMDS gives the potassium salt of the ligand, which can then be added to a slurry of CrCl₂ to give ligated chromium chloride complexes. The dinuclear green [L^{DiprTrit}Cr-μ-Cl]₂ shows signs of steric strain, in that the geometry of both of its chromium atom deviates from square planar and in that the two ligands are canted with respect to one another. Reaction of the chloride complexes with allylmagnesium chloride gives the monomeric allyl complex, as is typical of Dipp-NacNac derivatives. Reduction of the chloride complexes with potassium graphite in THF with no trapping ligand gives an unidentified, but apparently pure, product having a peak of 102 ppm in the NMR in THF-d₈. If bis-TMS acetylene is added to the potassium graphite reductions as a trapping ligand, the product is a bis-TMS acetylened complex.

Further modification of the ligand can be achieved through modification of the aniline, for example putting methyl groups on the four positions of the trityl phenyl rings. Speculatively, the ligand could also be modified by replacing the isopropyl methyl groups with phenyl rings, as with the so called iPr* anilines, or by adding tert-butyl groups to the methyls on the NacNac backbone. The iPr* aniline using the unsubstituted benzhydrol was made and suffered from significant solubility issues, suggesting the use of substituted benzhydrols for iPr* anilines may be more useful.

Adding t-butyl groups to the NacNac backbone was attempted using the series of reactions shown in Figure 2.15, but was abandoned due to purification difficulties.

Overall, adding a trityl group to the 4-position of the aniline did not have as strong an effect as hoped, since the chloride is still dinuclear, but its distorted geometry suggests that the trityl group is sterically significant. This is somewhat encouraging, because the conformation adopted by the bridging chloride is unfavorable for a bridging ethylene complex, since it would hinder π -backbonding. Therefore, if the solubility issues this ligand presents can be worked around, and/or the steric interaction between the ligands can be increased, it may be possible to make a monomeric ethylene complex, which may function as a homogenous model for ethylene trimerization.