# ORGANOMETALLICS

## Trianionic NCN<sup>3-</sup> Pincer Complexes of Chromium in Four Oxidation States (Cr<sup>II</sup>, Cr<sup>III</sup>, Cr<sup>IV</sup>, Cr<sup>V</sup>): Determination of the Active Catalyst in Selective 1-Alkene to 2-Alkene Isomerization

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Supporting Information

ABSTRACT: The synthesis and characterization of a series of four Cr complexes in the +2, +3, +4, and +5 oxidation states supported by an NCN trianionic pincer ligand are reported. Treating CrMeCl<sub>2</sub>(THF)<sub>3</sub> with the dilithio salt pincer ligand precursor {[2,6-<sup>*i*</sup>PrNCHN]Li<sub>2</sub>}<sub>2</sub> provides the Cr<sup>III</sup> complex [2,6-<sup>*i*</sup>PrNCN]Cr<sup>III</sup>(THF)<sub>3</sub> (1), Cr<sup>IV</sup> complex [2,6-<sup>*i*</sup>PrNCN]-Cr<sup>IV</sup>Me(THF) (2), and Cr<sup>II</sup> complex [2,6-<sup>*i*</sup>PrNHCN]Cr<sup>II</sup>- $(THF)_2$  (3). Complexes 2 and 3 are the result of disproportionation. Treating 1 with 1 equiv of styrene oxide in THF converts the Cr<sup>III</sup> complex to the Cr<sup>V</sup>(O) species [2,6-<sup>i</sup>PrNCN]Cr<sup>V</sup>-(O)(THF) (4). Complex 2, characterized by single-crystal X-ray diffraction, is a rare  $Cr^{IV}$  methyl complex that is kinetically stable at 25 °C; at 85 °C, Cr–Me bond homolysis occurs. The



homolytic cleavage results in CH<sub>4</sub> formation and biphenyl via a radical mechanism. The metal-containing product from thermolysis is the same  $Cr^{II}$  species formed during metalation, except one of the protons is substituted for a deuterium from  $C_6D_6$  (3-d). Complex 2 is a precatalyst for the selective isomerization of 1-hexene and 1-octene to the corresponding 2-alkenes. An induction period occurs during the catalytic isomerization, and the active catalyst was determined to be the Cr<sup>II</sup> complex 3, not 2.

### ■ INTRODUCTION

In comparison to  $\mathrm{Cr}^{\mathrm{II}}$  and  $\mathrm{Cr}^{\mathrm{III}}$  alkyl complexes,  $^{1-4}$   $\mathrm{Cr}^{\mathrm{IV}}$ alkyls,  $^{5-19}$  including silica-supported species,  $^{20-23}$  are uncommon. Of the few homogeneous Cr<sup>IV</sup> alkyl species reported, only one Cr<sup>IV</sup> monomethyl and one Cr<sup>IV</sup> monobutyl complex have been structurally characterized;<sup>5</sup> the others comprise the class of homoleptic  $CrR_4$  species.<sup>6–19</sup> The applications of  $Cr^{IV}$  alkyl complexes are scarce due to the greater oxidizing potential of chromium in the +4 oxidation state and their proclivity to decompose via bond homolysis, valence disproportionation, and reductive elimination.<sup>24–29</sup> Despite their instability, silica-supported  $Cr^{IV}$  alkyls polymerize  $\alpha$ -olefins.<sup>20–23,30</sup> Additionally, theoretical studies predict that cationic Cr<sup>IV</sup> alkyl model ally, theoretical studies predict that cationic Cr<sup>--</sup> any model complexes  $[Cr^{IV}(NR_2)_2R']^+$  (R = H, Me, SiH<sub>3</sub>: R' = Me, Et) should polymerize ethylene.<sup>31</sup> Employed extensively in the polymerization of  $\alpha$ -olefins,<sup>32–35</sup> homogeneous Cr<sup>II</sup> and Cr<sup>III</sup> complexes<sup>36–50</sup> are informative models of the heterogeneous Phillips<sup>51–53</sup> catalyst, which is responsible for the mass produc-tion of high-density polyethylene.<sup>32</sup> A common feature among the model complexes is the presence of a Cr-alkyl bond or a Cr complex capable of accessing such a structure upon activation. Ongoing debate exists regarding the oxidation state and identity of the active chromium species in the Phillips catalyst.<sup>51</sup> Therefore, the development of homogeneous molecular chromium catalysts is an important objective, particularly the development

of comparatively difficult to access Cr<sup>IV</sup> alkyl models, which may illuminate what, if any, function these elusive species serve in  $\alpha$ -olefin polymerization.

One approach to understanding the potential participation of Cr<sup>IV</sup> is to develop new ligands capable of stabilizing chromium complexes in the +4 oxidation state. In this study we explore the use of a NCN<sup>3-</sup> trianionic pincer ligand<sup>54,55</sup> to stabilize a  $Cr^{IV}$  alkyl. Trianionic pincer ligands<sup>54-65</sup> are capable of supporting reactive metal species, since they occupy three coordination sites but can only contribute a maximum of 10-12 electrons. Additionally, trianionic pincer ligands (such as the NCN ligand utilized in this research) feature a strong M-C<sub>pincer</sub> bond that promotes an open or labile trans coordination site.55-57,59 Consequently, metal ions bound by trianionic pincer ligands should be electrophilic and capable of binding substrates, 1-hexene and 1-octene being the focus of this study. In particular, the strongly  $\pi$ -electron donating NCN versions were prognosticated to be well-suited to stabilize a neutral Cr<sup>IV</sup> alkyl.55 Indeed, accomplishing this goal, we now report the synthesis, properties, and structural characterization of the Cr<sup>fV</sup> methyl complex  $[2,6^{-i}PrNCN]Cr^{1V}Me(THF)$  (2; 2,6 $^{-i}PrNCN = 2,6-bis({[2,6-i]PrNCN = 2,6-bis([2,6-i]PrNCN = 2$ bis(1-methylethyl)phenyl]azanidyl}methyl)phenyl). To exemplify

Received: June 24, 2011 Published: August 29, 2011



the versatility of trianionic pincer ligands to support Cr ions in various oxidation states, we also report the synthesis and characterization of NCN  $Cr^{II}$ ,  $Cr^{III}$ ,  $Cr^{IV}$ , and  $Cr^{V}$  complexes.

#### RESULTS AND DISCUSSION

Synthesis and Characterization of  $[2,6^{-i}PrNCN]Cr^{II}(THF)_3$ (1),  $[2,6^{-i}PrNCN]Cr^{IV}Me(THF)$  (2), and  $[2,6^{-i}PrNHCN]Cr^{II}(THF)_2$ (3). Three chromium NCN pincer complexes form by treating  $CrMeCl_2(THF)_3^{66}$  with  $\{[2,6^{-i}PrNCHN]Li_2\}_2^{67}$  in diethyl ether at -80 °C (eq 1). The major product of the reaction is the  $Cr^{III}$  complex  $[2,6^{-i}PrNCN]Cr^{III}(THF)_3$  (1). During the reaction, disproportionation<sup>68</sup> also provides the  $Cr^{IV}$ complex  $[2,6^{-i}PrNCN]Cr^{IV}Me(THF)$  (2) and  $Cr^{II}$  complex  $[2,6^{-i}PrNHCN]Cr^{II}(THF)_2$  (3). Adding pentane to the mixture of Cr ions dissolves the  $Cr^{IV}$  (2) and  $Cr^{II}$  (3) complexes, and filtering



results in the segregation of pentane-insoluble  $Cr^{III}$  (1) and LiCl. Dissolving 1 in benzene and removing insoluble LiCl provides analytically pure [2,6-<sup>i</sup>PrNCN]Cr<sup>III</sup>(THF)<sub>3</sub> (1). Cooling a pentane solution of the  $Cr^{IV}/Cr^{II}$  (2/3) mixture to -35 °C results in the precipitation of the purple  $Cr^{IV}$  complex 2 in 10% yield. Repeated (3×) precipitation of 2 from the 2/3 mixture results in a supernatant containing mostly the  $Cr^{II}$  complex 3, though some 2 and free ligand [2,6-<sup>i</sup>PrNCN]H<sub>3</sub> always remain. Thus, an alternative synthesis of 3 was sought (vide infra).

Exemplifying the need to explore various metalation conditions, conducting the reaction in THF suppresses disproportionation and provides the Cr<sup>III</sup> complex 1 exclusively (eq 2). The Cr<sup>III</sup> complexes produced in either Et<sub>2</sub>O or THF exhibit identical paramagnetic <sup>1</sup>H NMR spectral signatures in C<sub>6</sub>D<sub>6</sub>. Interpretation of the spectrum does not permit structural assignment. Broad resonances appear at 5.84 ( $\nu_{1/2}$  = 270 Hz), 1.95 ( $\nu_{1/2}$  = 420 Hz), and -5.01 ppm ( $\nu_{1/2}$  = 390 Hz). No resonances are detectable in the <sup>13</sup>C{<sup>1</sup>H} NMR spectrum. The Evans method<sup>69</sup> conclusively establishes  $\mathbf{1}$  as a d<sup>3</sup>  $\mathbf{Cr}^{III}$  ion with an experimentally determined magnetic moment of 3.99  $\mu_{\rm B}$  (3.87  $\mu_{\rm B}$  theoretical). Combustion analysis of a sample of 1 fits an empirical formula that includes three coordinated THF ligands. The analogous  $OCO^{3-}$  trianionic pincer complex [<sup>t</sup>BuOCO]Cr<sup>III</sup>(THF)<sub>3</sub> also contains three bound THF ligands with a distorted-octahedral Cr<sup>III</sup> metal center.<sup>59</sup> To confirm the pincer ligand is bound in the tridentate trianionic form, a C<sub>6</sub>D<sub>6</sub> solution of 1 was quenched with  $D_2O$  to provide the deuterated free ligand [2,6-'PrNCN] $D_3$ . Absent from the <sup>1</sup>H NMR spectrum of the quenched material is a resonance at the conspicuous location of 7.57 ppm for the  $C_{ipso}-H$ proton of the parent protio ligand [2,6-<sup>*i*</sup>PrNCN]H<sub>3</sub>.



Characterization of the Cr<sup>IV</sup> complex **2** includes a <sup>1</sup>H NMR spectrum that exhibits broadened paramagnetic spectral signatures not suitable for structural assignment. Broad resonances appear at 25.53 ( $\nu_{1/2} = 360$  Hz), 10.33 ( $\nu_{1/2} = 90$  Hz), 4.23 ( $\nu_{1/2} = 300$  Hz), -0.75 ( $\nu_{1/2} = 300$  Hz), and -7.23 ( $\nu_{1/2} = 165$  Hz) ppm. The Evans method<sup>69</sup> provides a magnetic moment of 2.68  $\mu_{\rm B}$  (2.83  $\mu_{\rm B}$  theoretical) consistent with a d<sup>2</sup> Cr<sup>IV</sup> ion. Combustion analysis and X-ray diffraction data support an empirical formula that includes one THF ligand. Single crystals suitable for interrogation by X-ray diffraction deposit from a concentrated solution of **2** in diethyl ether at -35 °C. Figure 1 depicts the molecular structure of **2**, and the caption of this figure gives selected bond lengths and bond angles.



**Figure 1.** Molecular structure of  $[2,6^{-P}\text{PNCN}]\text{Cr}^{IV}\text{Me}(\text{THF})$  (2) with ellipsoids presented at the 50% probability level and hydrogen atoms removed for clarity. Selected bond lengths (Å) and angles (deg): Cr-(1)-N(1) = 1.9048(19), Cr(1)-N(2) = 1.8870(19), Cr(1)-C(13) = 1.953(2), Cr(1)-O(1) = 2.1878(15); N(2)-Cr(1)-N(1) = 152.00(8), C(13)-Cr(1)-O(1) = 165.78(7), C(13)-Cr(1)-C(33) = 96.34(9), C(33)-Cr(1)-O(1) = 97.85(8).

Complex 2 is pseudo  $C_s$  symmetric and contains a  $Cr^{IV}$  ion in a distorted-square-pyramidal coordination geometry. Found in its trianionic form, the NCN pincer ligand occupies three of the basal sites, with a THF molecule residing in the fourth and the methyl group in the apical position. Much of the distortion arises from the NCN<sup>3-</sup> pincer arms, which cannot span the trans position by 180°; instead, the N1-Cr1-N2 angle is 152°. The THF ligand binds opposite to the strong-trans-influence Cr-C<sub>pincer</sub> bond of the pincer ligand. The Cr-O<sub>THF</sub> bond length is 2.1878(15) Å. For comparison, the related OCO<sup>3-</sup> trianionic  $Cr^{III}$  complex [<sup>t</sup>BuOCO] $Cr^{III}$ (THF)<sub>3</sub> and  $Cr^{V}$  complex [<sup>t</sup>BuOCO]Cr<sup>V</sup>(O)(THF) have Cr $-O_{THF}$  bond lengths of 2.1938(18) and 2.1781(17) Å.59 Disregarding possible steric influences of the different ligands, the Cr-O bond lengths vary according to the ionic radius of the Cr ion  $(Cr^{III} > Cr^{V})$ . In both  $[^{t}BuOCO]^{3-}$  Cr pincer complexes the THF ligand is labile,

and thus **2** should also exhibit similar substitution chemistry. The Cr1–C33 bond distance for the methyl group is 2.057(2) Å, which is consistent with the few crystallographically characterized Cr<sup>IV</sup> complexes that possess a Cr–C(sp<sup>3</sup>) bond. For example, in [Cr<sup>IV</sup>(N<sub>3</sub>N)Me] and [Cr<sup>IV</sup>(N<sub>3</sub>N)("Bu)], where N<sub>3</sub>N<sup>3-</sup> = ((SiMe<sub>3</sub>NCH<sub>2</sub>CH<sub>2</sub>)<sub>3</sub>N)<sup>3-</sup>, the Cr–C(sp<sup>3</sup>) bond lengths are 2.078(2) and 2.074(4) Å, respectively.<sup>5</sup> The 0.021(2) Å longer distances in N<sub>3</sub>N<sup>3-</sup> complexes is most likely due to the trans influence of the amine ligand opposite the methyl group. In **2**, no ligands oppose the methyl, thus permitting maximum  $\sigma$  overlap. Significant N<sub>amido</sub>  $\rightarrow$  Cr p $\pi$ –d $\pi$  bonding occurs and is manifested in short Cr–N<sub>amido</sub> bonds with an average length of 1.896(2) Å. Similarly, [Cr<sup>IV</sup>(N<sub>3</sub>N)Me] and [Cr<sup>IV</sup>(N<sub>3</sub>N)("Bu)], which also contain significant  $\pi$  bonding, possess a Cr–N<sub>amido</sub> average bond length of 1.879 Å.<sup>70</sup> In contrast, a recently reported pincer dimine Cr(III) complex contains N<sub>imine</sub>–Cr bonds not capable of  $\pi$  interactions. Consequently, the Cr–N bond lengths are significantly longer than in **2** by 0.28 Å.<sup>71</sup>

To balance redox equivalents, an equal amount of the  $Cr^{II}(3)$ complex must form by disproportionation during the reaction of  $\{[2,6-PrNCHN]Li_2\}_2$  with  $CrMeCl_2(THF)_3$  in diethyl ether. Indeed, 3 comprises 12% of the total isolated mixture. Unable to obtain pure 3 from the disproportionation, an alternative synthesis of 3 was sought. Treating anhydrous CrCl<sub>2</sub> with  $\{[2,6-^{i}PrNCHN]Li_{2}\}_{2}$  in THF at -80 °C provides the Cr<sup>II</sup> complex 3 (eq 3). The Cr<sup>II</sup> complexes isolated by the reaction of  $\{[2,6-PrNCHN]Li_2\}_2$  with either CrMeCl<sub>2</sub>(THF)<sub>3</sub> or CrCl<sub>2</sub> exhibit identical paramagnetic <sup>1</sup>H NMR spectral signatures in  $C_6D_6$ . Broad resonances appear at 21.71 ( $\nu_{1/2}$  = 330 Hz), 7.96  $(\nu_{1/2} = 150 \text{ Hz}), 6.42 (\nu_{1/2} = 330 \text{ Hz}), 3.54 (\nu_{1/2} = 685 \text{ Hz}), \text{ and}$  $-6.88 \text{ ppm} (\nu_{1/2} = 240 \text{ Hz})$ . The Evans method<sup>69</sup> establishes 3 as a d<sup>4</sup> Cr<sup>II</sup> ion with an experimentally determined magnetic moment of 4.42  $\mu_{\rm B}$  (4.90  $\mu_{\rm B}$  theoretical). Combustion analysis is consistent with the empirical formula that comprises one NCN ligand in the dianionic form, the Cr ion, and two coordinated THF ligands. Evidence for the assignment of the proton attached to one N atom, as an aniline, comes from quenching studies. Quenching a solution of 3 with D<sub>2</sub>O provides a <sup>1</sup>H NMR spectrum  $(C_6D_6)$  in which the resonance for the  $C_{ipso}$ -H proton is absent at the conspicuous location of 7.57 ppm for the parent protio ligand [2,6-'PrNCN]H<sub>3</sub>. Therefore, the metal-carbon bond must be present in 3, as well as one amide and one aniline attachment. Indeed, the IR spectrum of 3 contains a weak NH stretch at 3274  $\text{cm}^{-1}$ .



Synthesis and Characterization of  $[2,6^{-i}PrNCN]Cr^{V}(O)(THF)$ (4). Treating 1 with styrene oxide in THF at -35 °C provides the pentane-insoluble Cr<sup>V</sup>(O) complex  $[2,6^{-i}PrNCN]Cr^{V}(O)(THF)$ (4) (eq 4).<sup>8,59,72-80</sup> <sup>1</sup>H NMR resonances are paramagnetically broadened beyond interpretation, though sharp <sup>1</sup>H NMR spectral signatures at 6.57, 5.63, and 5.09 ppm are consistent with the vinyl protons of styrene. The Evans method<sup>69</sup> conclusively establishes 4 as a d<sup>1</sup> Cr<sup>V</sup> ion with an experimentally determined magnetic moment of 1.67  $\mu_{\rm B}$  (1.73  $\mu_{\rm B}$  theoretical). An EPR spectrum of a 2.5 mmol solution of [2,6-<sup>*i*</sup>PrNCN]Cr<sup>V</sup>(O)(THF) exhibits a strong resonance at  $g_{\rm iso} = 1.9876$  with a 19 G line width (Figure 2). The central line corresponds to the allowed ( $\Delta M_S = \pm 1$ ) electron spin transition from the ( $S = {}^{1}/_{2}$ , I = 0) <sup>52</sup>Cr isotope, consistent with a Cr<sup>V</sup> ion.<sup>81</sup> Combustion analysis of a sample of 4 fits an empirical formula that includes one coordinated THF molecule, analogous to the OCO<sup>3-</sup> trianionic pincer complex [<sup>*t*</sup>BuOCO]Cr<sup>V</sup>(O)(THF) in which the Cr ion has a distorted-trigonal-bipyramidal geometry.<sup>59</sup>





**Figure 2.** EPR spectrum of  $[2,6^{-i}PrNCN]Cr^{V}(O)(THF)$  (2.5 mM solution, toluene) at T = 20 K.

In the solid state, the  $Cr^{V}\equiv O$  stretch appears as a strong absorption at 975 cm<sup>-1</sup>. In comparison, the analogous  $OCO^{3-}$ complex  $Cr^{V}\equiv O$  stretch appears as a strong absorption at 988 cm<sup>-1.59</sup> On the basis of the IR stretching frequency, the  $Cr^{V}\equiv O$  bond in 4 is weaker. However, unlike the analogous  $OCO^{3-}$  complex, which catalytically oxidizes PPh<sub>3</sub> to  $O=PPh_3$ via O-atom transfer,<sup>59,82</sup> 4 is unable to oxidize PPh<sub>3</sub> at 25 °C. The reason for this lack of reactivity is potentially due to the difference in  $\pi$ -donor ability of the nitrogen on the NCN ligand in comparison to the oxygen on the OCO ligand. The amido nitrogens are stronger  $\pi$ -donors and therefore stabilize the  $Cr^{V}$ oxidation state.

**Isomerization of 1-Hexene and 1-Octene.** Developed over many decades,<sup>83</sup> homogeneous transition-metal-catalyzed isomerization of alkenes is an important synthetic tool,<sup>84</sup> especially for selective isomerization applications in organic synthesis.<sup>85</sup> However, scarcely employed are catalysts featuring chromium.<sup>86–90</sup> One example is the class of in situ generated precatalysts  $R_3Cr^{III}(THF)_3$  (R = methyl, ethyl, *n*-butyl, decyl), which degrade to form a Cr–H species capable of the isomerization. The isomerization occurs within 5 h at 20 °C to provide mainly *cis*- and *trans*-2-alkenes.<sup>89,90</sup>

Initially [2,6-<sup>*i*</sup>PrNCN]Cr<sup>IV</sup>Me(THF) (2) was screened as a potential catalyst for the polymerization of  $\alpha$ -olefins. However, the discovery of selective isomerization of 1-alkenes to internal olefins by catalytic amounts of 2 was studied with respect to

activity and selectivity. Tables 1 and 2 give the percent conversion and product distribution for 1-hexene and 1-octene isomerization reactions, respectively.

Table 1. Isomerization of 1-Hexene Using 2 as thePrecatalyst<sup>a</sup>

reacn time (h)	conversn (%) <sup>b</sup>	<i>trans</i> -2-hexene/ <i>cis</i> -2- hexene (%) <sup>b</sup>	<i>trans</i> -3-hexene/ <i>cis</i> -3-hexene (%) <sup>b</sup>
48	90 (±5)	95 (±2)	5 (±2)
60	$95(\pm 1)$	92 (±2)	8 (±2)
72	$96(\pm 0)$	87 (±3)	13 (±3)

<sup>*a*</sup> Isomerization was carried out with [2,6-<sup>*i*</sup>PrNCN]Cr<sup>IV</sup>Me(THF) (2; 10 mg, 0.017 mmol), C<sub>6</sub>D<sub>6</sub> (0.5 mL), and 1-hexene (20.5  $\mu$ L, 0.170 mmol) in a sealed NMR tube at 80 °C. <sup>*b*</sup> Percent conversion and product composition measured by <sup>1</sup>H NMR (500 MHz).

 Table 2. Isomerization of 1-Octene Using 2 as the Precatalyst<sup>a</sup>

reacn time (h)	conversn (%) <sup>b</sup>	<i>trans</i> -2-octene/ <i>cis</i> octene (%) <sup>b</sup>	-2- <i>trans</i> -3-octene/ <i>cis</i> -3-octene (%) <sup>b</sup>
48	90 (±3)	88 (±2)	12 (±2)
60	95 (±2)	86 (±3)	14 (±3)
72	$97(\pm 0)$	82 (±3)	18 (±3)
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<sup>*a*</sup> Isomerization was carried out with [2,6-<sup>1</sup>PrNCN]Cr<sup>1</sup>VMe(THF) (2; 10 mg, 0.017 mmol), C<sub>6</sub>D<sub>6</sub> (0.5 mL), and 1-octene (26.5  $\mu$ L, 0.170 mmol) in a sealed NMR tube at 80 °C. <sup>*b*</sup> Percent conversion and product composition measured by <sup>1</sup>H NMR (500 MHz).

The catalytic isomerization of 1-hexene and 1-octene to internal olefins with **2** as the precatalyst occurs nearly quantitatively with 95 ( $\pm$ 1) and 95 ( $\pm$ 2)% conversion, respectively, after 60 h. Alkene isomerization from a terminal to internal olefin is favorable thermodynamically. Additionally, equilibration of alkenes based on standard enthalpies of formation typically favors structures with the double bond farther from the end of the carbon chain.<sup>91</sup> However, **2** is a highly selective precatalyst for the transformation of 1-alkenes to 2-alkenes. For the isomerization of 1-hexene, 95% of the converted product consists of *cis-/trans*-2-hexene after 48 h; for 1-octene, 88% of the converted product consists of *cis-/trans*-2-octene after 48 h. Notably, during the isomerization of 1-octene, no *cis*-4-octene or *trans*-4-octene is detectable by <sup>1</sup>H NMR spectroscopy.

Figure 3 indicates that percent conversion versus time for both substrates follows a sigmoidal curve. A clear induction period



exists, after which the reaction accelerates and maximum turnover occurs at approximately 16 h. The presence of an induction period signals that 2 is likely not the active catalyst. Rather, 2 is a precatalyst which transforms to the active catalyst. Heating a solution of 2 in  $C_6D_6$  for 24 h in the absence of 1-alkene forms the active catalyst. To confirm the active catalyst forms, subsequent substrate addition and continued heating does not exhibit an induction period, and the reaction achieves maximum turnover at the outset (Figure 4).



Figure 4. Catalytic percent conversion of 1-hexene upon preheating 2 to 85  $^{\circ}$ C for 24 h, followed by substrate addition.

Studying the thermolysis of  $Cr^{IV}$  complex 2 ( $C_6D_6$ ) in the absence of substrate elucidates the identity of the active catalyst. Thermolysis of 2 at 85 °C in  $C_6D_6$  produces paramagnetically broadened resonances at 21.62, 7.94, 6.45, and -7.01 ppm, identical with those for the  $Cr^{II}$  complex 3. Concurrently, paramagnetically broadened resonances at 25.77, 10.40, 4.25, and -7.30 ppm of the  $Cr^{IV}$  precatalyst 2 disappear. The metal-containing product from the thermolysis is the same  $Cr^{II}$  complex 3 that forms during metalation of {[2,6-<sup>i</sup>PrNCHN]Li<sub>2</sub>} with CrMeCl<sub>2</sub>(THF)<sub>3</sub> or CrCl<sub>2</sub>, except the aniline proton is substituted for a deuterium, presumably acquired from  $C_6D_6$ . This gives a molecular formula of [2,6-<sup>i</sup>PrNDCN]Cr<sup>II</sup>(THF)<sub>2</sub> (3-*d*) for the active catalyst (Scheme 1).

On the basis of this conclusion, the  $Cr^{II}$  complex 3 formed exclusively by treating anhydrous  $CrCl_2$  with {[2,6-PrNCHN]Li<sub>2</sub>}<sub>2</sub> in THF should catalyze the isomerization of 1-alkenes with no induction period. Indeed, no induction period occurs for the 1-hexene isomerization reaction with 3 (Figure 5).



Figure 5. Catalytic percent conversion of 1-hexene by 3 in  $C_6D_6$  at 85 °C.

Scheme 1. Proposed Conversion of Precatalyst Cr<sup>IV</sup> 2 to the Active Catalyst Cr<sup>II</sup> 3-d



Additional support for the formation of **3** upon heating **2** in benzene comes from quenching studies. Quenching a solution of **3**-*d* with D<sub>2</sub>O provides the deuterated free ligand  $[2,6^{-i}PrNCN]D_3$ . ESI-TOF mass spectrometry supports the formula  $[2,6^{-i}PrNCN]DH_2$ , in which the N-D deuterium atoms are exchanged with protons from methanol (Figure 6, top). However, ESI-TOF mass spectrometry of a methanol solution of **3**-*d* quenched with H<sub>2</sub>O supports the formula  $[2,6^{-i}PrNCN]H_3$ , in which the N-D deuterium atom is exchanged with protons from methanol (Figure 6, bottom). Therefore, on the basis of these results the Cr-C<sub>pincer</sub> bond must be intact.



**Figure 6.** ESI-TOF mass spectra of (top)  $[2,6^{-i}PrNCN]Cr^{IV}Me(THF)$ (2) heated for 48 h at 85 °C and then quenched with D<sub>2</sub>O and (bottom)  $[2,6^{-i}PrNCN]Cr^{IV}Me(THF)$  (2) heated for 48 h at 85 °C and then quenched with H<sub>2</sub>O.

Mechanistic Details for the Thermolysis of  $[2,6^{-i}$ PrNCN]Cr<sup>IV</sup>Me(THF) (2) to  $[2,6^{-i}$ PrNDCN]Cr<sup>II</sup>(THF)<sub>2</sub> (3-*d*). During the thermolysis of 2 in C<sub>6</sub>D<sub>6</sub>, a <sup>1</sup>H NMR spectrum of the reaction mixture indicates the formation of  $CH_4$  as a singlet at 0.16 ppm. Sampling the headspace of the reaction vessel by GC also indicated the presence of  $CH_4$ . Additionally, gas chromatography of the reaction solution indicates the presence of deuterated biphenyl ( $C_6D_5$ )<sub>2</sub> (Figure 7). Cr–R complexes are



**Figure 7.** Gas chromatography spectra of a standard solution of biphenyl and of the reaction mixture after heating **2** for 48 h at 85 °C: (blue line) 5 mM biphenyl standard; (red line) reaction mixture.

known to decompose via bond homolysis; thus, one possible mechanism involves radical intermediates. Adding (2,2,6,6-tetramethylpiperidin-1-yl)oxyl (TEMPO), as a radical trap, results in the formation of TEMPO-Me, indicating that a  $CH_3$  radical is an intermediate. Therefore, the thermolysis reaction likely occurs through a radical mechanism (Scheme 2).

Scheme 2. Proposed Mechanism for Thermolysis of 2, 3-*d*,  $CH_4$ , and  $(C_6D_5)_2$ 



Initially, the  $Cr^{IV}$ -methyl bond homolytically cleaves to produce a  $Cr^{III}$  intermediate and a methyl radical. The methyl radical forms  $CH_4$  via hydrogen atom abstraction. The  $Cr^{III}$ abstracts a deuterium atom from  $C_6D_6$ , forming a  $Cr^{IV}$ -D



#### Scheme 3. Formation of 3 (3-d) via Salt Metathesis or Thermolysis of 2 Featuring the Common Intermediate B

intermediate (not shown) and a deuterated phenyl radical. The  $Cr^{IV}-D$  species subsequently undergoes conversion via reductive elimination to provide 3-*d*. To test the capacity of  $Cr^{III}$  to abstract a deuterium atom from  $C_6D_6$ , authentic  $Cr^{III}$  (1) was heated at 85 °C in  $C_6D_6$ . Indeed,  $Cr^{III}$  can abstract a deuterium atom, as the product mixture contains  $(C_6D_5)_2$  (determined by GC). Finally, the deuterated phenyl radical can add to  $C_6D_6$  with concomitant loss of a deuterium atom to form  $(C_6D_5)_2$ . Phenyl radical addition to benzene to form biphenyl is documented.<sup>92</sup>

#### CONCLUSIONS

Trianionic pincer ligands offer an opportunity to access and study chromium complexes in high oxidation states. For instance, NCN trianionic pincer ligands provide a combination of strong  $\sigma$ donation from the pincer arylide and two  $\pi$ -donating anilides to stabilize electronically deficient chromium ions in high oxidation states and low d-electron counts. Illustrating this concept, treating  $CrMeCl_2(THF)_3$  with {[2,6-<sup>*i*</sup>PrNCHN]Li<sub>2</sub>}<sub>2</sub> in Et<sub>2</sub>O results in disproportionation to provide chromium complexes in the  $Cr^{II}(3)$ ,  $Cr^{III}(1)$ , and  $Cr^{IV}(2)$  oxidation states. Subsequent oxidation of 1 with styrene oxide yields the Cr<sup>V</sup> trianionic pincer oxo complex  $[2,6^{-i}PrNCN]Cr^{V}(O)(THF)$  (4). For the  $Cr^{V}$  oxo species, it appears the NCN trianionic pincer ligand stabilizes the  $Cr^{v}$  oxidation state to such an extent that 4 is unwilling to relinquish the O atom even to PPh<sub>3</sub>. This is in contrast with the reactivity of the analogous OCO<sup>3-</sup> trianionic pincer complex [<sup>t</sup>BuOCO]Cr<sup>V</sup>(O)(THF) (where <sup>t</sup>BuOCO = [2,6-C<sub>6</sub>H<sub>3</sub>-(6-<sup>t</sup>BuC<sub>6</sub>H<sub>3</sub>O)<sub>2</sub>]<sup>3-</sup>), which readily oxidizes PPh<sub>3</sub>.<sup>59,93</sup> Provided no insurmountable kinetic barrier exists for the OAT with 4, NCN<sup>3-</sup> trianionic pincer ligands are thus more strongly donating than  $OCO^{3-}$  ligands.

The major disproportionation product is the Cr<sup>III</sup> complex 1, which can also be synthesized exclusively by conducting the metalation in THF, instead of Et<sub>2</sub>O. The minor disproportionation product **2** is a rare example of a stable chromium(IV) monoalkyl. Short Cr $-N_{\text{amido}}$  bonds suggest significant N $\rightarrow$ Cr p $\pi$  $-d\pi$  bonding, thus enabling access to chromium in the unusual Cr<sup>IV</sup> oxidation state.

The third product from disproportionation is the Cr<sup>II</sup> species 3. Complex 3 contains the pincer ligand as a dianion, in which one arm of the ligand binds as an aniline. However, precedent suggests that treating  $CrCl_2$  with the dilithio salt {[2,6-i]  $PrNCHN Li_{2}_{2}$  would provide a complex in which the pincer aryl C-H bond would remain intact and the ligand would be bound instead via two amido linkages.<sup>54</sup> Insight into why the observed  $Cr^{II}$  species exhibits the unexpected conformation comes from thermolysis of the  $Cr^{IV}$  complex in  $C_6D_6$ . The products from thermolysis indicate the unstable Cr<sup>IV</sup> deuteride  $[2,6^{-i}PrNCN]Cr^{IV}(D)(THF)_2$  forms as an intermediate; subsequent N–D reductive elimination provides  $Cr^{II}$  (3-*d*). The fact that complexes 3 and 3-d form from salt metathesis between  $CrCl_2$  and  $\{[2,6-'PrNCHN]Li_2\}_2$  and thermolysis, respectively, suggests both reactions share a common intermediate. Scheme 3 depicts the proposed pathway for the formation of 3 from salt metalation and 3-d via thermolysis of 2. During metalation in THF, it is reasonable to expect the amido linkages to attach first and eliminate LiCl, forming intermediate A. Held in close proximity to the low-oxidation-state Cr<sup>II</sup> ion, the pincer aryl C–H bond oxidatively adds (OA) to provide a  $Cr^{IV}$  hydride<sup>94</sup> (B). During thermolysis of 2 in  $C_6D_6$ ,  $Cr^{IV}$ –Me bond homolysis and deuterium atom abstraction from  $C_6D_6$  provides again the corresponding Cr<sup>IV</sup> deuteride B and biphenyl (detected by GC). The  $\hat{Cr}^{IV}$  oxidation state in **B** is unstable relative to  $Cr^{II}$ , but rather than reductively eliminate to form an aryl C-H bond, N-H reductive elimination provides either 3 or 3-d.

The transformation of 2 to 3 is kinetically relevant during the selective isomerization of 1-alkenes to 2-alkenes. Starting with complex 2, an induction period occurs during the isomerization at 85 °C. The induction period involves the thermal conversion of 2 to 3. Preheating complex 2 to form 3 in situ, followed by addition of 1-alkene substrates, results in the immediate onset of isomerization (85 °C). Also, employing authentic 3 provides a percent conversion profile identical with that of the in situ catalysis. The selectivity (95:5, 48 h, 1-hexene; 88:12, 48 h, 1-octene) exhibited for 2-alkenes versus 3-alkenes and 4-alkenes

is kinetically controlled. Prolonged heating (2 weeks) ultimately results in the thermodynamically expected ratios.

The important findings of this study are that, indeed, NCN<sup>3–</sup> ligands support chromium in high oxidation states, including  $Cr^{IV}$ , though only below 85 °C and it appears trianionic pincer  $Cr^{IV}$  hydride complexes are inherently unstable relative to  $Cr^{II}$ . The implication of the latter finding is broad, in that any catalytic application of the  $Cr^{IV}$ –Me complex that results in the formation of a  $Cr^{IV}$ –hydride bond will result in rapid reductive elimination. The task remaining is to exploit this property in catalytic transformations.

#### EXPERIMENTAL SECTION

General Considerations. Unless specified otherwise, all manipulations were performed under an inert atmosphere using standard Schlenk or glovebox techniques. Pentane, toluene, diethyl ether  $(Et_2O)$ , and tetrahydrofuran (THF) were dried using a GlassContour drying column. C<sub>6</sub>D<sub>6</sub> (Cambridge Isotopes) was dried over sodium benzophenone ketyl, distilled or vacuum-transferred, and stored over 4 Å molecular sieves. Anhydrous CrCl<sub>2</sub>, 1-hexene, 1-octene, and styrene oxide were purchased from Sigma-Aldrich and used as received. CrMeCl<sub>2</sub>(THF)<sub>3</sub><sup>66</sup> and {[2,6-<sup>*i*</sup>PrNCHN]Li<sub>2</sub>}<sub>2</sub><sup>67</sup> were prepared according to literature procedures. NMR spectra were obtained on Varian Gemini 300 MHz, Varian VXR 300 MHz, Varian Mercury 300 MHz, Varian Mercury Broad Band 300 MHz, Varian INOVA 500 MHz, and Varian INOVA2 500 MHz spectrometers. Chemical shifts are reported in  $\delta$  (ppm). For <sup>1</sup>H and <sup>13</sup>C NMR spectra, the residual solvent peak was used as an internal reference. Infrared spectra were obtained on a Thermo Scientific Nicolet 6700 FT-IR instrument. Spectra of solids were measured as KBr disks. UV-visible spectra were recorded on a Cary 50 instrument with scan software version 3.00(182). Gas chromatography was performed on a Varian CP-3800 gas chromatograph using an intermediate polarity column. EPR measurements were conducted using a Bruker Elexsys-500 spectrometer at the X-band microwave frequency ~9.4 GHz at 20 K. The microwave frequency was measured with a built-in digital counter, and the magnetic field was calibrated using 2,2-diphenyl-1-picrylhydrazyl (DPPH; g = 2.0037). The temperature was controlled using an Oxford Instruments cryostat, to accuracy within  $\pm 0.1$  K. Modulation amplitude and microwave power were optimized for high signal-to-noise ratio and narrow peaks. Mass spectrometry was performed at the in-house facility of the Department of Chemistry at the University of Florida. Accurate mass was determined by the electrospray ionization time-of-flight mass spectrometric (ESI-TOF) method in methanol. Combustion analyses were performed at Complete Analysis Laboratory Inc., Parsippany, NJ.

Synthesis of [2,6-<sup>*i*</sup>PrNCN]Cr<sup>III</sup>(THF)<sub>3</sub> (1). CrMeCl<sub>2</sub>(THF)<sub>3</sub> (1.000 g, 2.84 mmol) was added to a solution of { $[2,6-^{$ *i* $</sup>PrNCHN]Li<sub>2</sub>}<sub>2</sub> (1.333 g, 1.42 mmol) in tetrahydrofuran (50 mL) with stirring at -80 °C. The reaction mixture was warmed to room temperature and stirred for 1 h, and then all volatiles were removed in vacuo. Nonvolatile products were dissolved in pentane (50 mL) and filtered to collect an orange solid, which was evaporated in vacuo to remove all volatiles. The solid was redissolved in benzene (25 mL) and the solution was filtered, reduced under vacuum, and added to a stirred solution of pentane (50 mL) to precipitate 1 as a black crystalline solid. Yield: 1.291 g, 63.0%. <sup>1</sup>H NMR (300 MHz, C<sub>6</sub>D<sub>6</sub>; <math>\delta$  (ppm)): 5.84 (bs,  $v_{1/2} = 270$  Hz), 1.95 (br s,  $v_{1/2} = 420$  Hz), -5.01 (bs,  $v_{1/2} = 390$  Hz).  $\mu_{eff} = 3.99 \,\mu_{B}$ . Anal. Calcd for C<sub>44</sub>H<sub>62</sub>CrN<sub>2</sub>O<sub>3</sub>: C, 73.50; H, 8.69; N, 3.90. Found: C, 73.39; H, 8.51; N, 4.02.

Synthesis of  $[2,6^{-i}PrNCN]Cr^{IV}Me(THF)$  (2). CrMeCl<sub>2</sub>(THF)<sub>3</sub> (1.000 g, 2.84 mmol) was added to a solution of  $\{[2,6^{-i}PrNCHN]Li_2\}_2$ (1.333 g, 1.42 mmol) in diethyl ether (50 mL) with stirring at -80 °C. The reaction mixture was warmed to ambient temperature and stirred for 1 h, and then the solution was filtered and the filtrate was evaporated in vacuo to produce a dark solid. Pentane was added (50 mL), the resulting slurry was filtered, and the filtrate again was evaporated in vacuo to remove volatiles. The resulting purple-red oil was dissolved in a minimum amount of pentane and cooled to -35 °C to yield a purple precipitate. The product was isolated and purified by filtering the solution and washing with cold pentanes. X-ray-quality single crystals were obtained by dissolving **2** in a minimum amount of diethyl ether and cooling to -35 °C. Yield: 185 mg, 10%. <sup>1</sup>H NMR (300 MHz, C<sub>6</sub>D<sub>6</sub>;  $\delta$ (ppm)): 25.53 (bs,  $v_{1/2} = 360$  Hz), 10.33 (bs,  $v_{1/2} = 90$  Hz), 4.23 (bs,  $v_{1/2} = 300$  Hz), -0.75 (bs,  $v_{1/2} = 300$  Hz), -7.23 (bs,  $v_{1/2} = 165$  Hz).  $\mu_{eff} = 2.68 \mu_{\rm B}$ . Anal. Calcd for C<sub>37</sub>H<sub>52</sub>CrN<sub>2</sub>O: C, 74.96; H, 8.84; N, 4.73. Found: C, 74.92; H, 8.96; N, 4.72.

Synthesis of [2,6-<sup>*i*</sup>PrNHCN]Cr<sup>II</sup>(THF)<sub>2</sub> (3). Anhydrous CrCl<sub>2</sub> (524 mg, 4.268 mmol) was added to a solution of {[2,6-<sup>*i*</sup>PrNCHN]Li<sub>2</sub>}<sub>2</sub> (2.00 g, 2.13 mmol) in THF (50 mL) with stirring at -80 °C. The reaction mixture was warmed to ambient temperature and stirred for 1 h, and then all volatiles were removed in vacuo to provide a solid. The solid was dissolved in pentane (50 mL), the solution was filtered, and the filtrate was evaporated in vacuo. The resulting purple-red oil was dissolved in a minimum amount of ether and cooled to -35 °C to yield 3 as a purple precipitate. Yield: 287 mg, 10%. <sup>1</sup>H NMR (300 MHz, C<sub>6</sub>D<sub>6</sub>;  $\delta$  (ppm)): 21.71 (bs,  $\nu_{1/2} = 330$  Hz), 7.96 (bs,  $\nu_{1/2} = 150$  Hz), 6.42 (bs,  $\nu_{1/2} = 330$  Hz), 3.54 (bs,  $\nu_{1/2} = 685$  Hz), -6.88 (bs,  $\nu_{1/2} = 240$  Hz).  $\mu_{\text{eff}} = 4.42 \,\mu_{\text{B}}$ . Anal. Calcd for C<sub>40</sub>H<sub>58</sub>CrN<sub>2</sub>O<sub>2</sub>: C, 73.81; H, 8.98; N, 4.30. Found: C, 73.72; H, 8.85; N, 4.27.

Synthesis of  $[2,6^{-i}PrNCN]Cr^{V}(O)(THF)$  (4). The complex  $[2,6^{-i}PrNCN]Cr^{III}(THF)_3$  (500 mg, 0.693 mmol) was treated with styrene oxide (80  $\mu$ L, 0.693 mmol) in THF (15 mL) with stirring at -35 °C. The reaction mixture was warmed to ambient temperature and stirred for 30 min, and then all volatiles were removed in vacuo. Nonvolatile products were dissolved in pentane (10 mL) and filtered to collect the product as a black solid. Yield: 407 mg, 99%.  $\mu_{eff} = 1.67$   $\mu_{B}$ . Anal. Calcd for C<sub>36</sub>H<sub>49</sub>CrN<sub>2</sub>O<sub>2</sub>: C, 72.82; H, 8.32; N, 4.72. Found: C, 72.76; H, 8.41; N, 4.58.

Isomerization of 1-Hexene and 1-Octene Using [2,6-<sup>*i*</sup>PrNCN]Cr<sup>IV</sup>Me(THF) (2). A mixture of [2,6-<sup>*i*</sup>PrNCN]Cr<sup>IV</sup>Me(THF) (2; 10 mg, 0.017 mmol), 1-hexene (20.5  $\mu$ L, 0.170 mmol), and benzene- $d_6$  (0.5 mL) were added to a sealable NMR tube under a nitrogen atmosphere. The reaction mixture was heated in an oil bath thermostated at 80 °C (±1 °C) for 72 h. The reaction progress was monitored by <sup>1</sup>H NMR spectroscopy at 48, 60, and 72 h. The reaction mixture was analyzed by <sup>1</sup>H NMR spectroscopy to identify and quantify the organic products.

*Kinetic Measurements.* For kinetic measurements the reaction was set up using the method above and the reaction progress was monitored by <sup>1</sup>H NMR spectroscopy at 4, 8, 12, 16, 20, 24, 28, 32, and 36 h. The percent conversion of 1-hexene to 2-hexene was determined by <sup>1</sup>H NMR spectroscopy. The above procedure was adopted for the isomerization of 1-octene.

Preheating (24 h, 85 °C). The sample setup was the same as above, with the exception that alkene substrate was not added initially. The sealable reaction mixture was heated in an oil bath thermostated at 85 °C ( $\pm 1$  °C) for 24 h. After heating, 1-hexene (52  $\mu$ L, 0.422 mmol) was added to the NMR tube under a nitrogen atmosphere and returned to the oil bath. The reaction progress was monitored by <sup>1</sup>H NMR spectroscopy at 4, 8, 12, 16, 20, 24, 28, 32, and 36 h. The above procedures were adopted for the isomerization of 1-octene.

**TEMPO Procedures.** A mixture of 2,2,6,6-tetramethylpiperidine (TEMPO; 0.017 mmol),  $[2,6^{-i}$ PrNCN]Cr<sup>IV</sup>Me(THF) (2; 10 mg, 0.017 mmol), and benzene- $d_6$  (0.5 mL) were added to a sealable NMR tube under a nitrogen atmosphere. The reaction mixture was heated in an oil bath thermostated at 85 °C ( $\pm$ 1 °C) for 24 h. The reaction progress was monitored by <sup>1</sup>H NMR spectroscopy at 4, 12, and 24 h. The reaction

mixture was analyzed by gas chromatography to identify and quantify the organic products using an internal standard (hexamethyldisiloxane).

#### ASSOCIATED CONTENT

**Supporting Information.** Text, tables, and figures giving details of the syntheses and characterization data for all compounds and a CIF file giving crystallographic data for **2**. This material is available free of charge via the Internet at http://pubs. acs.org.

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