

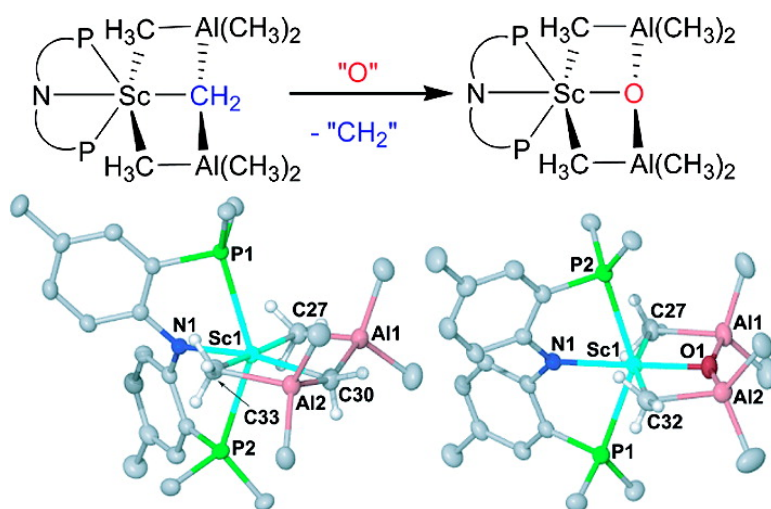
Communication

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## Lewis Acid Stabilized Methylidene and Oxoscandium Complexes

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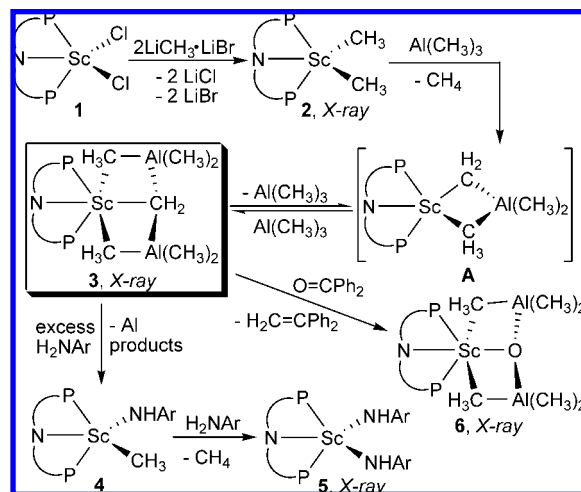
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Tebbe's reagent,  $\text{Cp}_2\text{Ti}[\mu_2\text{-CH}_2](\mu_2\text{-Cl})\text{Al}(\text{CH}_3)_2$ , can be categorized as a quintessential organometallic reagent due to its role in catalytic olefin metathesis<sup>1</sup> and stoichiometric methylidene group-transfer processes.<sup>2</sup> It has been instrumental in the design of more efficient catalysts as well as the synthesis of natural products and commodity chemicals and materials.<sup>3</sup> The preparation of Tebbe's reagent involves treatment of  $\text{Cp}_2\text{TiCl}_2$  with 2 equiv of  $\text{Al}(\text{CH}_3)_3$ , resulting in the elimination of  $\text{CH}_4$  and  $\text{AlCl}(\text{CH}_3)_2$ .<sup>2a</sup> Likewise, the analogue  $\text{Cp}_2\text{Ti}[\mu_2\text{-CH}_2](\mu_2\text{-CH}_3)\text{Al}(\text{CH}_3)_2$  is prepared by addition of  $\text{Al}(\text{CH}_3)_3$  to  $\text{Cp}_2\text{Ti}(\text{CH}_3)_2$ .<sup>2a</sup> Although originally speculated by Tebbe,<sup>2a</sup> the role of  $\text{Al}(\text{CH}_3)_3$  along the deprotonation step has been addressed by Grubbs (Ti)<sup>4</sup> and Schrock (Ta).<sup>5</sup> Surprisingly, for over 30 years the report of a scandium (or lanthanide) methylidene complex analogous to Tebbe's reagent has not been realized.<sup>6</sup> In fact, scandium alkylidene complexes are unknown to date, while their lanthanide relatives have been scarcely documented.<sup>6–8</sup> We were curious as to whether  $\text{Al}(\text{CH}_3)_3$  could stabilize a highly polarized  $\text{Sc}=\text{CH}_2$  ligand as it does in the case of Ti. Here, we describe the preparation of such a ligand, its isolation, and use as a Brønsted base or as a group 3 Wittig reagent.<sup>7a,b</sup>

When  $(\text{PNP})\text{ScCl}_2$  (**1**,  $\text{PNP}^- = \text{N}[2\text{-P}(\text{CHMe}_2)_2\text{-4-methylphenyl}]_2$ )<sup>9,10</sup> is treated with 2 equiv of  $\text{LiCH}_3 \cdot \text{LiBr}$  complex, the dimethyl  $(\text{PNP})\text{Sc}(\text{CH}_3)_2$  (**2**) is isolated in 58% yield after workup of the reaction mixture (Scheme 1).<sup>10,11</sup> Although the <sup>31</sup>P NMR spectrum of **2** is rather featureless (0.4 ppm,  $\Delta\nu_{1/2} = 80$  Hz), the <sup>1</sup>H NMR spectrum clearly reveals the resonance for the equivalent dimethyl ligands (0.51 ppm). The solid state structure collected on a single crystal of **2** portrays a highly skewed  $(\text{PNP})\text{Sc}$  scaffold ( $\text{P}-\text{Sc}-\text{P}$ ,  $146.58(3)^\circ$ ) with a  $\text{Sc}-\text{CH}_3$  distance of  $2.207(3)$  Å.<sup>11</sup> Treating **2** with 2 equiv or an excess of  $\text{Al}(\text{CH}_3)_3$  in benzene at 25 °C resulted in the clean, gradual formation of a new product along with methane extrusion, as inferred by <sup>1</sup>H NMR spectroscopy. The new resonance in the <sup>31</sup>P NMR spectrum of this complex was uninformative due to the broad line widths.<sup>11</sup> The <sup>1</sup>H NMR spectrum was also rather uninformative at room temperature, revealing a very broad peak centered at  $-0.20$  ppm. However, the notable presence of a singlet at 0.69 ppm integrating to two protons suggested the formation of a methylidene unit. The latter  $\text{CH}_2$  resonance was unambiguously correlated to the <sup>13</sup>C NMR resonance at 28.8 ppm by HMQC NMR experiments. Cooling the NMR solution of this newly isolated product to  $-50$  °C shifted the  $\text{CH}_2$  resonance to 0.75 ppm in the <sup>1</sup>H NMR spectrum and also resolved the resonance at  $-0.20$  ppm to suggest the formation of an organometallic complex having three inequivalent  $-\text{CH}_3$  environments with the same ratio of hydrogens (6:6:6). Due to these interesting spectroscopic signatures, the structural connectivity of this new scandium complex was elucidated by single crystal X-ray diffraction studies.

Figure 1 depicts the molecular structure of the first mononuclear scandium methylidene,  $(\text{PNP})\text{Sc}(\mu_3\text{-CH}_2)(\mu_2\text{-CH}_3)_2[\text{Al}(\text{CH}_3)_2]_2$  (**3**), stabilized by two  $\text{Al}(\text{CH}_3)_3$  ligands in a pseudo transoid fashion ( $\text{Al}-\text{CH}_2-\text{Al}$ ,  $152.77(11)^\circ$ ).<sup>11,12</sup> The Sc atom in the structure of **3** is confined in an octahedral geometry due to bridging of two  $\text{CH}_3$  and

Scheme 1. Synthesis of Complexes 1–6<sup>a</sup>



<sup>a</sup> For simplicity, the PNP cartoon represents  $\text{N}[2\text{-P}(\text{CHMe}_2)_2\text{-4-methylphenyl}]_2^-$ .

one  $\text{CH}_2$  ligands between Sc and two Al atoms to form a  $\text{ScC}_3\text{Al}_2$  set of planar rings. Overall, the gross features of the two fused four-atom planar rings resembles Cavell's lanthanide complex having a formal  $\text{Sm}=\text{C}$  bond.<sup>8,12a</sup> The  $\text{Sc}-\text{CH}_2$  distance ( $2.3167(17)$  Å) is slightly longer than the average  $\text{Sc}-\text{CH}_3$  bond length ( $\sim 2.2$  Å)<sup>13a–d</sup> but much shorter than methide abstracted  $\text{Sc}\cdots\text{CH}_3$  distances ( $\sim 2.7$  Å).<sup>13b–d</sup> The methylidene hydrogens, as well as the bridging and terminal methyl hydrogens of this complex, were also located and refined isotropically. The methylidene hydrogens are not equivalent in the solid state, with one of them pointing more toward Sc, whereas one of the bridging methyls suggests an  $\alpha$ -hydrogen agostic interaction taking place with the metal center ( $2.33(2)$  Å, Figure 1).<sup>11</sup> Whether or not  $\text{Al}(\text{CH}_3)_3$  abstracts the methyl in **2** to promote deprotonation is speculative at present, but we favor the formation of an intermediate  $(\text{PNP})\text{Sc}[\mu_2\text{-CH}_2](\mu_2\text{-CH}_3)\text{Al}(\text{CH}_3)_2$  (**A**) based on our variable temperature <sup>27</sup>Al NMR spectra. The room temperature <sup>27</sup>Al NMR spectra

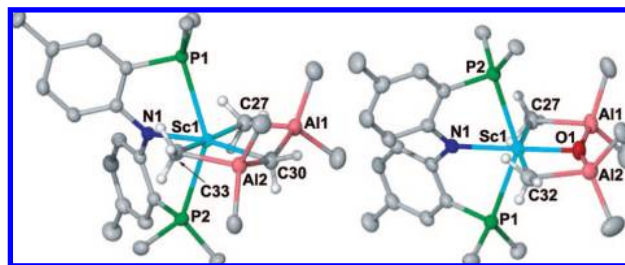
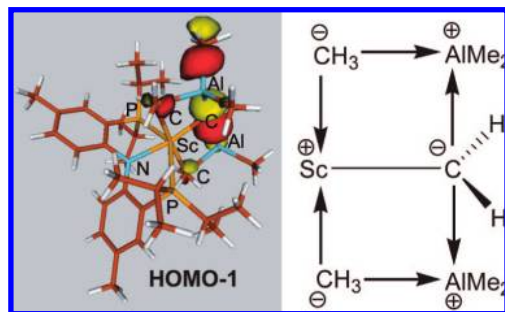


Figure 1. Molecular structures of complexes **3** (left) and **6** (right) with thermal ellipsoid at the 50% probability level. Pr methyls on P, solvent, and H-atoms (with the exception of  $\alpha$ -hydrogens) have been excluded for clarity.



**Figure 2.** (Left) HOMO-1 orbital for the optimized structure of complex **3** with isodensity at 0.05 au. (Right) Most plausible resonance structure for the Sc( $\mu_3$ -CH<sub>2</sub>)( $\mu_2$ -CH<sub>3</sub>)<sub>2</sub>Al<sub>2</sub> motif.

of **3** display two broad Al environments (154 and 50 ppm), where the former resonance is virtually identical to that of free Al(CH<sub>3</sub>)<sub>3</sub>.<sup>11</sup> Upon cooling to  $-30$  °C, the two resonances coalesce into one broad signal at 57 ppm ( $\Delta\nu_{1/2} = 4900$  Hz), consistent with the resting state of **3** having equivalent Al environments. Therefore, we propose that **3** is most likely undergoing dissociation into putative **A** and free Al(CH<sub>3</sub>)<sub>3</sub> in solution state at room temperature.

To address the bonding scheme in complex **3**, DFT methods were relied upon to compute the frontier orbitals and natural bond order about the Sc( $\mu_3$ -CH<sub>2</sub>)( $\mu_2$ -CH<sub>3</sub>)<sub>2</sub>Al<sub>2</sub> scaffold.<sup>11,14</sup> The HOMO-1 stipulates that the *p* orbital on the methylidene carbon does not form a  $\pi$  interaction with Sc (Figure 2). Likewise, the computed Mayer bond order of 0.83 is too small to suggest a strong interaction and formally assign it as a Sc=CH<sub>2</sub> ligand (X-ray: 2.317 Å, calcd: 2.284 Å). In addition, HOMO-6 and HOMO-7 present highly ionic bridging methyl groups confined between Sc and Al.<sup>11</sup> The computed Mayer bond orders of 0.54 for both Sc- $\mu_2$ -C-Al units and 0.42 and 0.44 for each Al- $\mu_2$ -C-Sc further corroborate this proposition. Based on these data, we propose that the two fused four-membered rings in **3** adopt a canonical structure depicted in Figure 2. To account for this type of geometry, the bridging methyls and methylene groups must all be involved in 3-centered-2-electron bonding (Figure 2).<sup>14</sup>

Given our proposal that **3** equilibrates to **A** and Al(CH<sub>3</sub>)<sub>3</sub>, we inquired whether such a system would be amenable to reactivity similar to Tebbe's reagent. Complex **3** can be protonated with an excess of H<sub>2</sub>NAr (Ar = 2,6-*i*-Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>) to quickly form the anilide-methyl (PNP)Sc(NHAr)(CH<sub>3</sub>) (**4**) intermediate<sup>9</sup> and after 12 h ultimately produce the bis-anilide (PNP)Sc(NHAr)<sub>2</sub> (**5**) quantitatively (Scheme 1).<sup>11</sup> The connectivity of complex **5** has been inferred by single crystal X-ray diffraction analysis and NMR spectral data and can be prepared independently by the reaction of (PNP)ScCl<sub>2</sub> with 2 equiv of LiNHAr.<sup>11</sup> When a solution of **3** was added to OCPH<sub>2</sub> in benzene, an immediate reaction occurred. Examination of the mixture by <sup>31</sup>P and <sup>1</sup>H NMR evinced clean formation of a new C<sub>2</sub> symmetric Sc complex. Notably, the methylidene resonance originally present in **3** was absent, suggesting that this ligand has been transformed or replaced. However, the resonances corresponding to the bridging and terminal methyl moieties in the two Al(CH<sub>3</sub>)<sub>3</sub> groups were fluxional even to  $-50$  °C, unlike those observed for complex **3**. Based on this evidence and the formation of the terminal olefin, H<sub>2</sub>C=CPh<sub>2</sub><sup>15</sup> (verified by <sup>1</sup>H NMR spectroscopy), we propose the new product to be the Lewis acid stabilized scandium oxo complex (PNP)Sc( $\mu_3$ -O)( $\mu_2$ -CH<sub>3</sub>)<sub>2</sub>[Al(CH<sub>3</sub>)<sub>2</sub>]<sub>2</sub> (**6**), depicted in Scheme 1. The solid state structure of **6** further supports our proposed connectivity, revealing a three-coordinate oxo-ligand bridged by one Sc and two Al atoms (Figure 2). The metrical parameters of **6** closely resemble those for **3**, with the only significant

exception being the shorter Sc-O bond length 2.008(2) Å, thus leading to a tucked-in appearance of the ScOC<sub>2</sub>Al<sub>2</sub> skeleton. The latter distance is longer than scandium alkoxide distances ( $\sim 1.9$  Å) but shorter than dative Sc $\leftarrow$ :OR<sub>2</sub> resulting from a coordinating ether ( $\sim 2.2$  Å).<sup>16</sup>

Herein, credible evidence for formation of a scandium methylidene is presented. The nucleophilic nature of the methylidene carbon, coupled with the large ionic radius of the Sc(III) ion, allows for this rare motif to coordinate two Al(CH<sub>3</sub>)<sub>3</sub> ligands, one of which appears to be dissociating to permit interesting reactivity. We have also demonstrated that the methylidene ligand can be smoothly protonated with a weak acid such as H<sub>2</sub>NAr or transferred to an organic group such as a ketone, to yield the corresponding olefin and novel scandium oxo ligand (also stabilized by two Al(CH<sub>3</sub>)<sub>3</sub>). Therefore, Tebbe's original strategy to trap group 4 alkylidene compounds can now be expanded to the earliest of the transition metals.

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**Supporting Information Available:** Experimental preparation and reactivity (all compounds), computational studies, and crystallographic details for compounds **2**, **3**, **5**, and **6**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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