

## Isolation and Characterization of a Monomeric Cationic Titanium Hydride

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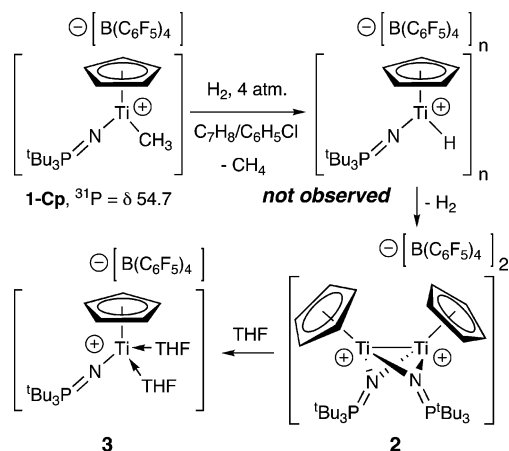
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Organotitanium hydrides<sup>1</sup> are a highly reactive class of compounds that have been implicated in a variety of catalytic processes, including olefin hydrogenation and hydrosilation and silane dehydrocoupling.<sup>2</sup> Despite their importance, isolated, terminal titanium hydrido compounds are restricted to a few Ti(III) examples<sup>3,4</sup> or highly sterically protected neutral Ti(IV) derivatives.<sup>5</sup> Cationic variants are even more rare,<sup>6</sup> but presumably play a critical role in olefin polymerization<sup>7</sup> and oligomerization<sup>8</sup> reactions, especially where H<sub>2</sub> is used as a polymer MW controlling agent. Given the tendency of Ti(IV) hydrides to undergo reduction to Ti(III) via loss of H<sub>2</sub>,<sup>9</sup> it is of interest to probe the behavior of cationic titanium hydrides in ligand environments relevant to olefin polymerization, because reductive side reactions might be expected to impact overall catalyst performance. Here, we report reactions of the catalysts [Cp(<sup>t</sup>Bu<sub>3</sub>PN)TiCH<sub>3</sub>]<sup>+</sup>[B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>]<sup>-</sup> (Cp = C<sub>5</sub>H<sub>5</sub>, **1-Cp**; C<sub>5</sub>Me<sub>5</sub>, **1-Cp\***) with H<sub>2</sub> and detail the complete characterization of a monomeric cationic organotitanium hydride.

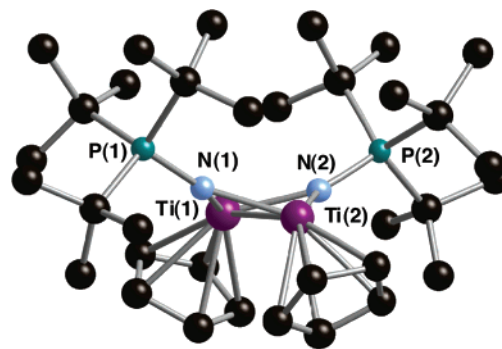
Triptyl borate activation of the neutral dimethyl derivatives Cp-(<sup>t</sup>Bu<sub>3</sub>P=N)Ti(CH<sub>3</sub>)<sub>2</sub><sup>10</sup> proceeds cleanly in toluene. To solubilize the resultant liquid clathrate-like oils, haloarene solvents such as chloro- or bromobenzene are required. The cations **1-Cp** and **1-Cp\*** were characterized completely using NMR spectroscopy.<sup>11</sup> Although analogous cations incorporating [H<sub>3</sub>CB(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>]<sup>-</sup> counteranions via B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> activation have been reported,<sup>12</sup> and are somewhat more well-behaved than the [B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>]<sup>-</sup> partnered cations, their reactions with H<sub>2</sub> are complicated by the slower conversion of the [H<sub>3</sub>CB(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>]<sup>-</sup> counteranions to [HB(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>]<sup>-</sup>.<sup>13</sup> To preclude this complication, we have focused on the [B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>]<sup>-</sup> salts.

A toluene solution of in situ generated cation **1-Cp** reacts rapidly with H<sub>2</sub>, producing a green precipitate and CH<sub>4</sub> (Scheme 1). The

### Scheme 1



putative cationic hydride produced upon treatment of **1-Cp** with H<sub>2</sub> was not observed and must be unstable toward loss of H<sub>2</sub>, producing **2**. The green microcrystalline product **2** is sparingly soluble even in CD<sub>2</sub>Cl<sub>2</sub>, preventing the acquisition of NMR data,

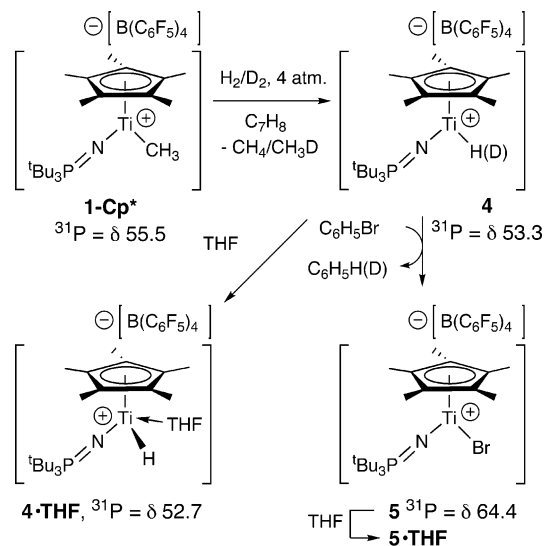


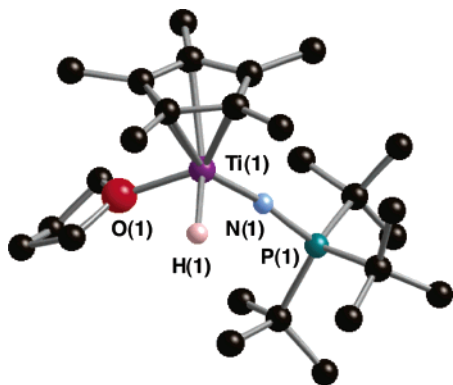
**Figure 1.** Crystalmaker depiction of the molecular structure of the dication in **2**. Selected bond distances (Å): Ti(1)-N(1), 1.997(2); Ti(1)-N(2), 1.979(2); P(1)-N(1), 1.631(2); Ti(1)-Ti(2), 2.5966(7). Selected bond angles (deg): N(1)-Ti(1)-N(2), 91.21(9); Ti(1)-N(1)-Ti(2), 81.21(8); Ti(1)-N(1)-P(1), 137.83(13); Ti(2)-N(1)-P(1), 139.74(13).

but X-ray crystallographic analysis revealed it to be a dicationic Ti<sup>III</sup>-Ti<sup>III</sup> dimer (Figure 1) in which the Ti<sub>2</sub>N<sub>2</sub> core exists in a butterfly conformation (Figure 1) in which the Ti-Ti distance of 2.5966(7) Å. A related neutral dimer, also formed via loss of D<sub>2</sub>, has a Ti-Ti distance of 2.442(1) Å.<sup>14</sup> Dilute CD<sub>2</sub>Cl<sub>2</sub> solutions of **2** are ESR silent, but, upon addition of donor solvents such as THF, the dimer is broken up into the yellow, paramagnetic d<sup>1</sup> bis-THF Ti(III) cation **3**, which was also characterized crystallographically<sup>15</sup> and via ESR spectroscopy (toluene, 294 K, *g* = 1.9675).

The tendency of [Cp(<sup>t</sup>Bu<sub>3</sub>P=N)TiH]<sub>n</sub><sup>+</sup> to undergo reductive loss of H<sub>2</sub> may be due to a combination of the lack of steric protection and relatively poor electron donation afforded by the C<sub>5</sub>H<sub>5</sub> ligand. Indeed, for the cation **1-Cp\***, incorporating the more highly donating and sterically demanding Cp\* donor, reaction with H<sub>2</sub> leads rapidly to a cationic titanium(IV) hydride (Scheme 2). The reaction must

### Scheme 2





**Figure 2.** Crystallmaker depiction of the molecular structure of the cationic portion of **4·THF**. Selected bond distances (Å): Ti(1)–H(1), 1.84(2); Ti(1)–N(1), 1.781(2); Ti(1)–O(1), 2.075(2); P(1)–N(1), 1.613(2). Selected bond angles (deg): N(1)–Ti(1)–O(1), 104.33(8); N(1)–Ti(1)–H(1), 98.6(7); O(1)–Ti(1)–H(1), 94.4(7); N(1)–Ti(1)–Cp\*<sub>cent</sub>, 131.66(6); O(1)–Ti(1)–Cp\*<sub>cent</sub>, 115.78(5); Ti(1)–N(1)–P(1), 168.39(12).

be carried out in toluene in the absence of haloarene solvents for hydride **4** to be generated cleanly. Toluene solutions of **4** in the presence of H<sub>2</sub> are spectroscopically well behaved, and a broad signal at 7.80 ppm is tentatively assigned to the Ti–H moiety, although this is likely an averaged position due to exchange with dissolved H<sub>2</sub>. A corresponding resonance appears in the <sup>2</sup>H NMR spectrum for *d*<sub>1</sub>-**4**. While **4** is stable for a couple of hours at room temperature, eventually the yellow solutions decolorized and decomposition of the sample was spectroscopically evident after 16 h. Attempts to isolate **4** were unsuccessful because removal of H<sub>2</sub> led to accelerated decomposition.

When dissolved in bromobenzene, base free **4** undergoes conversion to the cationic bromide **5**, with loss of benzene, via formal  $\sigma$  bond metathesis.<sup>16</sup> Compound **5** was characterized spectroscopically in solution and also crystallographically as its THF adduct **5·THF**.<sup>11</sup> When this reaction was done with *d*<sub>1</sub>-**4**, C<sub>6</sub>H<sub>5</sub>D was detected spectroscopically and via mass spectrometry, further implicating the hydride moiety in **4**. Furthermore, addition of a slight excess of THF to toluene solutions of **4** gave a diamagnetic mono-THF adduct, **4·THF**, which could be isolated as a crystalline solid in 87% yield upon precipitation with hexanes. A signal at 7.25 ppm in the <sup>1</sup>H NMR spectrum integrating to one proton was assigned to the Ti–H moiety and confirmed by <sup>2</sup>H NMR spectroscopy on *d*<sub>1</sub>-**4·THF**.<sup>17</sup> The nature of **4·THF** was also established via an X-ray crystallographic analysis (Figure 2).

The hydride ligand in **4·THF** was located and refined, giving a Ti–H distance of 1.84(2) Å, somewhat longer than the distances found in other monomeric titanium hydrides (1.64–1.77 Å<sup>3–5</sup>). The Ti center is of distorted tetrahedral geometry, and no contacts with the [B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>]<sup>–</sup> counteranion under 3.2 Å are evident. The Ti–N(1) distance of 1.781(2) Å is consistent with a cationic Ti(IV) center (cf. the distance of 1.780(2) Å in **5·THF**) rather than cationic Ti(III) (cf. the distances of ~1.98 Å in **2**).

The fact that cationic hydride **4·THF** can be obtained preparatively offers an unprecedented opportunity to examine the reactivity of such a species in detail. Studies aimed at mapping out this reactivity, including the  $\sigma$ -bond metathesis chemistry mentioned above, are ongoing. Although the long Ti–H distance suggests that homolytic cleavage of this bond may be facile, the tendency to undergo reduction via loss of H<sub>2</sub> is diminished in the Cp\* system as opposed to the Cp stabilized cations, partially accounting for the higher olefin polymerization activities observed in the former catalyst.

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**Supporting Information Available:** Experimental details, tables of crystal data, atomic coordinates, bond lengths and angles, ORTEP diagrams, and anisotropic displacement parameters for **2**, **4·THF**, and **5·THF** (PDF and CIF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- IR spectroscopy was ineffective because the phosphinimide ligand exhibits several strong bands around 1500–1600 cm<sup>–1</sup>, the region expected for Ti–H stretches (see ref 5).

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