Stabilization of a Cationic Ti Center by a Ferrocene Moiety: A Remarkably Short Ti−Fe Interaction in the Diamide $\{[(\eta^5\text{-}C_5H_4NSiMe_3)_2Fe]TiCl\}_2^{2+}$

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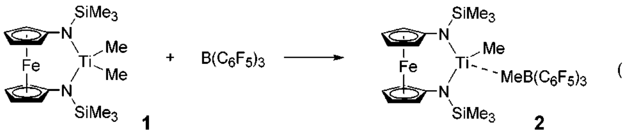
Incorporation of electron-rich transition metals is known to stabilize carbocations and other positively charged organic fragments.[1] For example, incorporation of a ferrocenyl substituent allowed for the first observation of an otherwise highly unstable cyclopropyl cation.[2] Extending this concept to stabilization of electron deficient and cationic early transition metal complexes is an interesting possibility in the context of Ziegler−Natta olefin polymerization. Coordinatively unsaturated cationic Ti and Zr complexes have been established as active species in this process, but their high reactivity often renders them unstable and difficult to characterize.[3]

We recently reported a series of Ti complexes[4] supported by a ligand based on 1,1′-diaminoferrocene,[5] in particular $[(\eta^5\text{-}C_5H_4NSiMe_3)_2Fe]TiMe_2$ ($LTiMe_2$ **1)**. In addition to the bis-amido donor set found to be effective in a number of olefin polymerization catalysts,[6] these complexes incorporate a ferrocene group as an integral part of the ligand backbone.[7] We therefore felt that the system was well suited for the study of the interaction between an electron-rich ferrocene group and an electron-deficient Ti center. In the solid state, the dimethyl complex features a pseudo-tetrahedral Ti, although the N−Ti−N angle of 135° is somewhat larger than the tetrahedral angles normally found in Ti bis-amido complexes.[8] While in **1** the Fe−Ti distance of 3.32 Å precludes any significant direct metal−metal interaction, our study of the activation of $LTiMe_2$ with $B(C_6F_5)_3$ and $[Ph_3C][B(C_6F_5)_4]$ shows that the resulting cationic species are stabilized through a direct Fe−Ti interaction. Here we present the results of this study.



Catalytic activation of Ti dialkyl complexes is frequently accomplished by the abstraction of an alkide group with a strong Lewis acid, e.g., $B(C_6F_5)_3$ or $[Ph_3C][B(C_6F_5)_4]$ (**TB**), resulting in a Ti−alkyl cation.[3] Generally, $B(C_6F_5)_3$ affords a more stable species due to the better coordinating ability of $MeB(C_6F_5)^-$ compared to that of $B(C_6F_5)_4^-$. On the other hand, the TB-activated species tend to have higher catalytic activity.

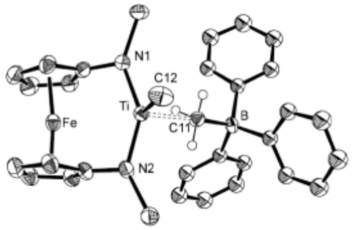
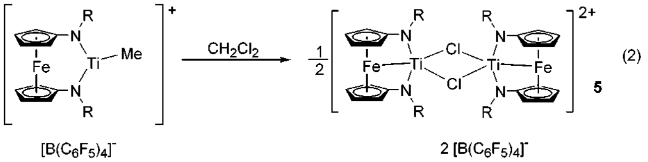


Figure 1. ORTEP (50%) plot of **2**. Fluorine and hydrogen atoms (except H1, H2, and H3) and the silicon-bound methyl group have been omitted.

Reaction of **1** with $B(C_6F_5)_3$ in toluene-d_8 resulted in the immediate formation of a dark-purple solution. The resulting material is highly fluxional in solution even at 205 K, as gauged by ^1H NMR. Nonetheless, the ^{11}B NMR spectrum showed a sharp resonance at −11.0 ppm consistent with the formation of a tetrahedral borate $[CH_3B(C_6F_5)_3]^-$ anion (eq 1). In pentane, the same reaction gave a dark, cloudy solution, which yielded dark-red crystals of **2** (64%) on standing. Elemental analysis and X-ray crystallography confirms the formulation of **2** as $[LTiMe][CH_3B(C_6F_5)_3]$ (Figure 1).[9] As found in related species,[10] the borate methyl group interacts with the Ti. Nevertheless, the Ti−C(11) bond distance (2.297(4) Å) for the borate methyl group is significantly longer than the Ti−C(12) distance (2.081(5) Å) for the terminal methyl group. The dihedral angle between the two Cp rings is 7.64°, almost twice that in (neutral) **1,** and the N−Ti−N angle has opened up to 145.2(2) °. Importantly, the resulting Fe−Ti distance in **2** is 3.07 Å, some 0.25 Å shorter than in **1**. These changes are consistent with the formation of a weak Fe−Ti donor bond stabilizing the cationic Ti center.



On the basis of the structure of $[LTiMe][MeB(C_6F_5)_3]$ we expected that activation with TB, which tends to produce even more electronically unsaturated metal centers, would lead to an increased electron donation from iron to titanium. Compound **1** reacted with $[Ph_3C][B(C_6F_5)_4]$ in chlorobenzene-d_5 at room temperature (Scheme 1) to produce a dark solution. The ^1H NMR shows the formation of CH_3CPh_3, confirming the abstraction of a methyl group. The spectrum of **3** consists of a silyl resonance at 0.21 ppm, a TiMe resonance at 0.55 ppm, and two ferrocenyl resonances at 4.46 (a pseudo-triplet) and 4.50 (very broad) ppm. Mixing the reagents in benzene resulted in a dark oil, which upon washing with additional portions of benzene and drying under vacuum resulted an analytically pure **3** as brown powder. Crystals

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[9] Crystal data for **2**: $C_{36}H_{32}N_2BF_{15}FeTiSi_2$, FW = 948.37, monoclinic, space group $P2_1/n$, $Z = 4$, $a = 11.25520(10)$ Å, $b = 16.4336(3)$ Å, $c = 21.55350(10)$ Å, $\beta = 92.698(1)^o$, $V = 3982.19(6)$ Å^3, $\rho_{calcd} = 1.582$ g/cm^3, $\mu = 7.25$ cm^{-1}, $R_1(I > 3.00\sigma(I)) = 0.041$, wR_2(all data) = 0.060 for 4156 observations and 457 parameters.

[10] Stephan, D. W.; Stewart, J. C.; Guerin, F.; Spence, R. E. v. H.; Xu, W.; Harrison, D. G. *Organometallics* **1999**, *18*, 1116.

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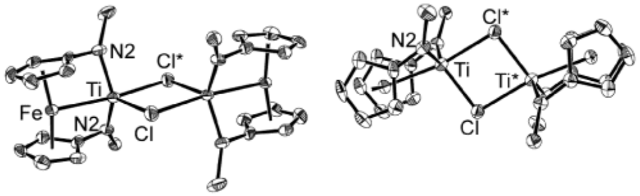
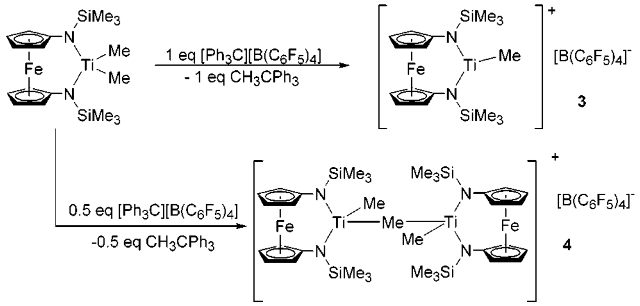


Figure 2. ORTEP plot of **5** showing side and top views of the dication. Hydrogen atoms and silicon-bound methyls have been omitted.

Scheme 1



suitable for X-ray diffraction have not yet been obtained and the exact coordination geometry at Ti remains uncertain.

Using 0.5 equiv of TB in chlorobenzene-d_5 resulted in formation of the methyl-bridged, dinuclear **4**. Its ^{1}H NMR spectrum shows a silyl resonance at 0.34 ppm, a TiMe resonance at 0.87 ppm, and two ferrocenyl pseudo-triplets at 4.40 and 3.02 ppm. The presence of a single TiMe resonance integrating to 9 H indicates rapid exchange between bridging/terminal methyl groups. The compound can be thought of as a $LTiMe^+$ cation coordinated by a neutral $LTiMe_2$ molecule.[11]

The polymerization activity of **2** and **3** was tested with 1-hexene. Both compounds are active at producing short-chain oligomers of 5−6 monomer units. As expected, **3** is a more active catalyst than **2**, producing 102 g (oligomer)/(mmol catalyst)·(h). The ^{1}H NMR spectrum of the oligomer shows a characteristic olefinic resonance at 5.3−5.4 ppm, indicating an internal double bond. Therefore, we postulate that β-H elimination is the chain-termination mechanism and that a new chain can then be initiated by the resulting Ti−hydride cation.

Despite the fact that **3** can be generated in CD_2Cl_2 and is stable in this solvent for several hours, crystallization from this solvent afforded dark-purple crystals shown by elemental analysis to be $[LTiCl][B(C_6F_5)_4]$ (**5**), i.e., the result of CH_2Cl_2 activation by **3** (eq 2). The X-ray crystal structure of **5** revealed its dimeric nature (Figure 2).[12] The dicationic dimer resides on a crystallographic inversion center and contains a planar Ti_2Cl_2 core. Analogous transformations leading to a dimeric dication have been reported for Zr[13] and very recently for Ti.[14] In our system, **5** is the major product and was isolated in 69% yield. The most notable feature of the solid-state structure is an extremely short Fe−Ti distance (2.49 Å), which is 0.58 Å shorter than the Fe−Ti distance in **2** and 0.83 Å shorter than in **1**. This distance is equal to the sum of covalent radii[15] for Fe and Ti and is well within the range reported by Selegue et al. and Gade and co-workers for Fe−Ti single bonds in $(Cp)Fe(CO)_2^-$-coordinated titanium complexes.[16]

Such close approach of Ti to Fe results in the distortion of the complex compared to **1** and **2**. The dihedral angle between the Cp rings has increased to 12.87° and, unlike in **1** and **2,** Ti is found out of the plane formed by Fe, N1, and N2. The geometry around Ti is best described as trigonal bipyramidal with N1, N2, and Cl residing in the equatorial plane while Fe and Cl* are in the axial positions.[17] The Ti−Cl bond (2.505(2) Å) for the chloride trans to Fe is longer than the Ti−Cl* bond (2.377(2) Å)).

An Fe−M dative bond in ferrocene-containing complexes was first reported by Seyferth and co-workers in 1983 for the palladium complex $[(C_5H_4S)_2Fe]Pd(PPh_3)$,[18] where a weak Fe−Pd dative bond stabilizes an otherwise three-coordinate Pd center. Despite the fact that a number of related systems containing late metals have been reported since,[19] to the best of our knowledge (a) **2** and **5** (and possibly **3** and **4**) represent the first examples of a ferrocene group stabilizing an electron-deficient early transition metal center through an Fe−M dative bond and (b) **5** contains the shortest Fe−M bond for a ferrocene-containing bimetallic compound.

The Fe−Ti dative interaction in the cationic Ti complexes exemplifies the Lewis-basic behavior of ferrocene. Although not a strong base in solution, gas-phase measurements show that its proton affinity lies between that of NH_3 and $MeNH_2$.[20] In solution, protonation of ferrocene has been shown to occur at iron;[21] furthermore, in many cases electrophilic substitution reactions proceed through initial formation of an Fe−E dative bond, followed by transfer of the electrophile to the Cp.[22] Understanding the interaction between Fe and strong Lewis acids has, therefore, attracted much interest. Compounds **2** and **5** may serve as constrained models for such interactions.

Work in progress aims to more fully understand the nature of the Fe−Ti interaction by using spectroscopic and electrochemical techniques, and to extend this chemistry to other metals.

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Supporting Information Available: Details of synthetic work, characterization data, polymerization tests, and tables of crystallographic data for **2** and **5** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(11) For recent examples see: Zhang, S.; Piers, W. E. *Organometallics* **2001**, *20*, 2088 and theferences therein.

(12) Crystal data for **5**: $C_{40}H_{26}N_2Si_2FeTiF_{20}BCl$, FW = 1120.81, monoclinic, space group $P2_1/c$, $Z = 4$, $a = 13.711(1)$ Å, $b = 12.699(1)$ Å, $c = 24.453(2)$ Å, $\beta = 94.329(1)^\circ$, $V = 4245.5(5)$ Å^3, $\rho_{calcd} = 1.753$ g/cm^3, $\mu = 7.72$ cm^{-1}, $R_1(I > 3.00\sigma(I)) = 0.047$, wR_2(all data) = 0.084 for 3353 observations and 493 parameters.

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(17) Ti complexes with phenylenediamide ligands (ref 8a) undergo what may be a related distortion, presumably to facilitate a donor interaction between the phenyl π-system and the metal.

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