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Stabilizing Zr and Ti Cations by Interaction With a Ferrocenyl Fragment

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The discovery of Sinn and Kaminsky[1] that active olefin polymerization catalysts are generated by the treatment of zirconocenes with methylalumoxane initiated exploration of the chemistry of electrophilic group 4 metal cations. Subsequent work by Jordan et al. resulted in the structural characterization of the THF stabilized zirconocene cation $[Cp_2ZrMe(THF)][BPh_4]$,[2] which in the absence of excess THF or donor solvent is an active olefin polymerization catalyst. Attempts by Turner's research group to isolate 'base-free' cationic compounds afforded the species $[Cp^*_2Zr(C_6H_3R)B(C_6H_4R)_3]$ (R = H, Me, Et) and $[Cp'_2ZrMe(C_2B_9H_{12})]$ (Cp′ = Cp*, C_5Me_4Et).[3] Horton and Orpen described closely related 'base-free' zirconocene cations derived from the insertion of alkyne into the Zr−C bond of $[Cp'_2ZrMe(NMe_2Ph)_n][B(4\text{-}C_6H_4F)_4)]$.[4] Marks and co-workers[5] pioneered and continue to exploit the use of electrophilic boranes as activators, describing the single component catalysts $[Cp_2ZrMe(\mu\text{-}MeB(C_6F_5)_3)]$ and $[Cp_2ZrH(\mu\text{-}HB(C_6F_5)_3)]$ in which the anion is bound to the metal center. A variety of classical Lewis bases have been employed to stabilize group 4 metal cations,[2,6] but catalytic activity for the resulting species is greatly diminished. More recently the research groups of Casey, Jordan, and others have prepared zirconocene cations with a weakly basic alkene or alkyne group.[7] Although these serve as models for polymerization catalysts in action, the weak donor ability of alkene/alkyne and the low insertion barrier requires special precautions for their successful synthesis. Recently, compounds exhibiting unusual dative interactions of electron-rich metal fragments with Lewis acidic centers have attracted attention.[8] Compounds containing group 13 Lewis acids (e.g., BR_3) have received the most attention.[9] A few examples are known in which 'metalloligands' with $M_1 \rightarrow M_2$ dative interactions modulate the redox chemistry or reactivity of the metal complex.[10] Surprisingly, the ability of electron-rich metal centers to act as dative donors to electrophilic early transition metals has drawn only limited attention.[11] In this communication, we describe the reaction of early metal cations with ferrocene. The facile CH-activation of ferrocene results in remarkably stable yet active polymerization catalysts, in which cationic metal centers are stabilized by interaction with the ferrocenyl moiety.

Treatment of $[Cp_2ZrMe(\mu\text{-}MeB(C_6F_5)_3)]$ **1**[5c] with ferrocene in bromobenzene solution resulted in the clean formation of a new cationic zirconocene species **2a**, which was isolated as an orange solid in 93% yield upon precipitation with pentane. Loss of CH_4 was evident by ^1H NMR spectroscopy. ^1H and ^{13}C NMR spectral data for **2a** show resonances attributable to the Cp_2Zr moiety at 5.92 and 111.2 ppm, respectively; ^1H NMR signals at 4.28, 4.20, and 2.44 ppm in a 2:2:5 ratio indicated C−H-activation of one of the ferrocene Cp-rings. The most downfield resonance of the corresponding ^{13}C NMR signals for the metalated ring (171.0, 85.5, and 74.7 ppm) is consistent with a $Zr-C(sp^2)$ bond. These data support the formulation of **2a** as $[Cp_2Zr(\mu\text{-}C_5H_4)FeCp][MeB(C_6F_5)_3]$. The ^1H NMR resonance of the CpFe fragment (2.44 ppm) is significantly upfield of typical ferrocene signals (3.5−4.5 ppm). The variable temperature ^1H NMR spectra of **2a** in CD_2Cl_2 show considerable broadening of this resonance at temperatures below −25 °C, while other resonances are not affected. The signal broadens into the baseline upon cooling to −90 °C, but a limiting spectrum was not accessible. Nonetheless, these data imply a dynamic exchange process involving an agostic interaction of a Cp C−H bond with the cationic Zr center. To probe this, the 1,1′-dimethylferrocenyl analog $[Cp_2Zr(\mu\text{-}C_5H_3Me)Fe(C_5H_4Me)]$ $[MeB(C_6F_5)_3]$ **2b** was prepared. The ^1H NMR spectrum of **2b** at 25 °C shows seven inequivalent CH resonances due to the 1,1′-dimethylferrocenyl fragment. Two of these are observed at relatively high field (−1.29 and 0.85 ppm). Both signals broaden into the baseline upon cooling to −80 °C, inferring that the observed shifts are the average of agostic and nonagostic contributions arising from exchange between two conformers with an eclipsed 1,1′-dimethylferrocenyl geometry (Figure S1). X-ray crystallographic studies confirmed the nature of these compounds **2** (Figure 1).[12] The anions of **2** were unexceptional. The cations of **2a** and **2b** are comprised of a Cp_2Zr fragment which is σ-bound to the C_5H_4 or C_5H_3Me unit of a ferrocenyl fragment, respectively. In **2a**, the Zr− and Fe−Cp(centroid) bonds are typical in length averaging 2.207 and 1.660 Å, respectively. The Zr−C σ-bond distance to the C_5H_4 fragment is 2.2894(15) Å. The electron deficient nature of the Zr cation results in a close approach of the Fe center to Zr at a distance of 2.8910(3) Å, shorter than that in the related neutral [1]-ferrocenophane $(tBuC_5H_4)_2Zr(C_5H_4)_2Fe$ (2.9621(5) Å).[13] This results in a slight deformation of the ferrocenyl fragment, with a Cp(centroid)−Fe−Cp(centroid) angle of 172.01(4)° and interplanar angle between the two C_5 rings of 4.72(9)°. In agreement with the NMR data, the structure shows an agostic interaction, which is characterized by short Zr−C (2.6151(15) Å) and Zr−H (2.38(2) Å) distances, and the H atom (which was located in the difference Fourier map) is out of the C_5 plane by 16.7°. The metrical parameters for **2b** are similar, but the slightly more electron-rich 1,1′-dimethylferrocenyl group results in a marginally shorter Zr−Fe distance of 2.8825(7) Å. The Fe−Zr distances in **2** are significantly longer than the Fe−Ti distance (2.4907(18) Å) reported by Arnold and co-workers for $[LTi(\mu\text{-}Cl)]_2^{2+}$ (L = 1,1′-diamidoferrocene).[11a] It is also noteworthy that arylzirconocene cations are known to be stabilized by an agostic interaction with an aryl β-CH bond.[14] The cationic zirconocene ferrocenyl complexes **2** presented herein combine both a Zr−Fe interaction and

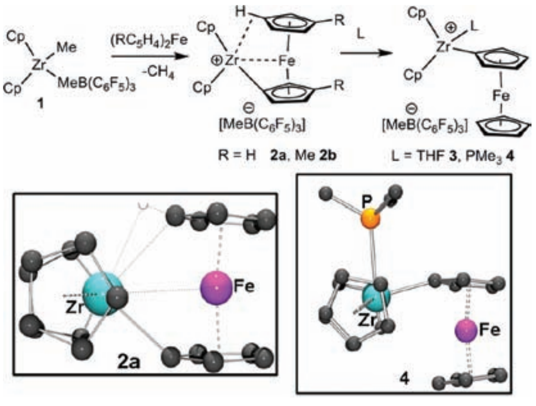

Figure 1. Synthesis and POV-ray depiction of cations of **2a** and **4**.

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agostic CH bond, imparting remarkable stability to these compounds. For example, samples **2a** and **2b** remained unchanged on storage for a week in C_6D_5Br solution at room temperature.

To probe the generality of this approach, the metallocene-cation analogue $[CpTi(NPtBu_3)Me(\mu\text{-}MeB(C_6F_5)_3)]$[15] **5** was prepared and treated with ferrocene to give $[CpTi(NPtBu_3)(C_5H_4)FeCp][MeB(C_6F_5)_3]$ **6**. NMR and crystallographic data were consistent with a Ti−ferrocenyl interaction similar to that described for the Zr compounds **2** (Figure 2). In **6**, the Ti−Fe distance is 2.7112(4) Å, while the agostic interaction with the Cp CH fragment gives rise to Ti−C and Ti−H distances of 2.337(2) and 2.051 Å, respectively.

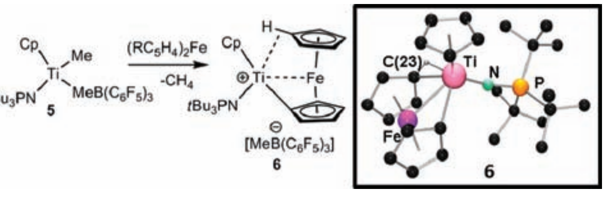

Figure 2. Synthesis and POV-ray depiction of cation of **6**.

Despite the stability of these compounds, they remain highly reactive. For example, **2a** acts as a single component catalyst for the polymerization of ethylene at 25 °C and 1 atm, with an activity similar to that observed for **1** (**2a**: 3000, **1**; 2800 g/mmol/atm/h). As this reactivity implies, the dative Zr−ferrocenyl interaction is readily displaced. Treatment of a C_6H_5Br solution of **2a** with a stoichiometric amount of a Lewis base such as THF or PMe_3 results in formation of deep blue or purple solutions of the adducts $[Cp_2Zr(L)(\mu\text{-}C_5H_4)FeCp][MeB(C_6F_5)_3]$ (L = THF **3**; PMe_3 **4**) in 90 and 91% yield, respectively. NMR spectroscopy is consistent with the proposed formulation of **3**, although attempts to isolate **3** in pure form were unsuccessful. The PMe_3 adduct **4**, obtained as purple crystals, showed ^1H NMR spectroscopic data similar to **3** as well as a ^{31}P NMR signal at −7.8 ppm, consistent with the Zr-bound PMe_3 fragment. A crystal structure determination of **4** (Figure 1) confirmed displacement of the Zr−Fe interaction by PMe_3, resulting in crystallographically independent Zr−Fe distances of 3.5146(4) and 3.5981(3) Å.[12]

DFT optimization (B3LYP/6-31G(d)) of the structure of the cation **2a** gave $\mathbf{2a_{calc}}$, which exhibits metric parameters similar to those obtained experimentally, with a Zr−Fe contact of 2.955 Å and a Zr−CH agostic interaction with one of the C_5H_4 CH bonds (Zr−C: 2.795 Å, Zr−H: 2.510 Å). These latter bond lengths are slightly longer than the crystallographic values; however, the B3LYP functional is known to underestimate noncovalent interactions.[16] Examination of the bonding orbitals involving an interaction between Zr and Fe revealed that primarily the HOMO-3, HOMO-10, and HOMO-11 orbitals are derived from a combination of Zr and Fe d-orbitals, although in all cases there is considerable mixing with cyclopentadienyl-based orbitals (Figure S2). The calculations infer a Wiberg bond order between Zr and Fe of 0.2540. The decreased positive NBO charge on the Zr center in $\mathbf{2a_{calc}}$ (+1.10) compared to Cp_2ZrMe^+ (+1.56) or Cp_2ZrPh^+ (+1.54) establishes that there is net CpFe→Zr electron transfer in the cations **2**, albeit small.

In summary, the present compounds demonstrate the ability of electron-rich metallocenes to stabilize electrophilic Zr cations by a combination of dative Fe→Zr interactions and agostic CH bonds. Despite this stabilization, these donor interactions are readily displaced for subsequent derivatization and reactivity and, thus, provide a strategy to 'tame' highly reactive early transition metal cations. The cooperation of such Lewis acidic and Lewis basic metal centers in subsequent chemistry is being explored.

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Supporting Information Available: Experimental procedures and X-ray crystallographic details of **2a**, **2b**, **4**, and **6**. This material is available free of charge via the Internet at http://pubs.acs.org.

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