Stabilizing Zr and Ti Cations by Interaction With a Ferrocenyl Fragment

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The discovery of Sinn and Kaminsky 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 [Cp2ZrMe(THF)][BPH4],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 [Cp2TaR2] and [Cp2ZrR2] (R = H, Me, Et).4 Horton and Orpen described closely related ‘base-free’ zirconocene cations derived from the insertion of alkyl into the Zr-C bond of [Cp2ZrMe(NMe2Ph)2] and [Cp2ZrMe(THF)].4 Marks and co-workers5 pioneered and continue to exploit the use of electrophilic boranes as activators, describing the single component catalysts [Cp2ZrMe(µ- MeB(C6F5)3)] and [Cp2ZrMe(µ- HB(C6F5)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,6,7 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., AlMe3) have received the most attention.9 A few examples are known in which ‘metalloligands’ with M3-M3 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 [Cp2ZrMe(µ-MeB(C6F5)3)] 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 CH4 was evident by 1H NMR spectroscopy. 1H and 13C NMR spectral data for 2a show resonances attributable to the Cp2Zr 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 13C NMR signals for the metalted ring (171.0, 85.5, and 74.7 ppm) is consistent with a Zr—C(sp2) bond. These data support the formulation of 2a as [Cp2Zr(µ-C5H3Me)FeCP][MeB(C6F5)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 CD2Cl2 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 [Cp2Zr(µ-C5H3Me)Fe(C5H4Me)][MeB(C6F5)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 exceptional. The cations of 2a and 2b are comprised of a Cp2Zr fragment which is α-bound to the C5H4 or C5H3Me unit of a ferrocenyl fragment, respectively. In 2a, the Zr—Fe distance of 2.7319(7) Å was evident by 1H NMR data, the structure shows an agostic interaction, which is characterized by short Zr—C₂(1.194(1) Å) and Zr—H (2.6894(9) Å). The electron deficient nature of the Zr cation results in a close approach of the Fe center to Zr at a distance of 2.6910(3) Å, shorter than that in the related neutral [1]-ferrocenophane ([Buc(H2)2]2Zr(C5H5)2Fe (2.9621(5) Å).13 This results in a slight deformation of the ferrocenyl fragment, with a Cp(centroid)—C—Zr angle of 172.04(4)° and interplanar angle between the two C₅ rings of 4.72(9)°. In agreement with the NMR data, the structure shows an agostic interaction, which is characterized by short Zr—C₂(2.6151(15) Å) and Zr—H (2.332(2) Å) distances, and the H atom (which was located in the difference Fourier map) is out of the C₅ 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 of 2.4907(18) Å reported by Arnold and co-workers for [L3Ti(µCl)2] (L = 1,1′-diamidoferrocene). It is also noteworthy that alkylzirconocene cations are known to be stabilized by an agostic interaction with an alkyl β-CH bond.14 The cationic zirconocene ferrocenyl complexes 2 presented herein combine both a Zr—Fe interaction and...
Despite the stability of these compounds, they remain highly reactive. For example, sample 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 interactions and agostic CH bonds.

To probe the generality of this approach, the metallocene-cation analogue [CpTi(NP Bu3)(μ-MeB(C6F5)3)]15 5 was prepared and treated with ferrocene to give [CpTi(NP Bu3)(C5H4)FeCp] [MeB(C6F5)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.

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.

**Acknowledgment.** D.W.S. gratefully acknowledges the financial support of NSERC of Canada. E.O. is grateful for the support of a Rubicon postdoctoral fellowship from The Netherlands Organization for Scientific Research (NWO).

**Supporting Information:** Experimental procedures and X-ray crystallographic details of 2a, 2b, 4, and 6.

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