Disproportionation of Cationic Zirconium Complexes: A Possible Pathway to the Deactivation of Catalytic Cationic Systems

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Protonolysis of the zirconium borohydride $[(C_5H_4R)_2Zr(BH_4)_2]$ (R = H, Me, $SiMe_3$) with $NHMe_2PhBPh_4$ in THF leads to the corresponding cationic zirconium complex $[(C_5H_4R)_2Zr(BH_4)(THF)]BPh_4$, and the structure of $[(C_5H_4Me)_2Zr(BH_4)(THF)]BPh_4$ was determined. In the presence of phosphine, PMe_2Ph, the formation of the cationic hydride $[(C_5H_4R)_2ZrH(PMe_2Ph)_2]BPh_4$ is observed by ^1H and ^{31}P NMR followed by a disproportionation and a redox reaction with $[BPh_4]^-$, giving the neutral $[(C_5H_4R)_2ZrH(\mu\text{-}H)]_2$ and the cationic Zr^{III} species $[(C_5H_4R)_2Zr(PMe_2Ph)_2]BPh_4$ characterized by EPR spectroscopy and suggesting a probable pathway in the deactivation of cationic catalyst systems.

Introduction

There is great current interest in the chemistry of cationic d^0 complexes $[Cp_2MR]^+$ (M = Ti, Zr), due to their implication as the active species in Ziegler−Natta olefin polymerization. Several reports have dealt with the bis(cyclopentadienyl)metal alkyl series $[Cp_2MR]^+$, which are efficient systems for modeling polymerization catalysis but show a rapid decay in activity for olefin polymerization.[1,2] As part of our contribution in this area, we have investigated new types of cationic zirconium borohydride complexes, $[(C_5H_4R)_2Zr(BH_4)]^+$ (R = H, Me, $SiMe_3$), which should provide other insights into the zirconium cationic chemistry, due to the presence of a Zr−H−B bond. It is well-known that the zirconium hydride complex $[Cp_2ZrH_2]_n$ can be prepared from the corresponding borohydride complex $[Cp_2Zr(BH_4)_2]$ in the presence of a base such as NEt_3.[3] We are able to take advantage of this effective chemical method to produce and generate hydride cationic species from $[(C_5H_4R)_2Zr(BH_4)]^+$ (R = H, Me, $SiMe_3$).

Results and Discussion

Organometallic zirconium derivatives of tetrahydroborates have received much attention.[4] Our research has been centered upon the synthesis of new substituted cyclopentadienyl borohydrides of zirconium complexes. The reaction in toluene of $(C_5H_4R)_2ZrCl_2$ (R = H, Me, $SiMe_3$) and $Cp_2ZrClMe$ with $LiBH_4$, a standard methodology in the synthesis of the borohydride complexes, enables us to easily obtain respectively the compounds $[(C_5H_4R)_2Zr(BH_4)_2]$ (**1**, R = H; **2**, R = Me; **3**, R = $SiMe_3$) and $[Cp_2Zr(CH_3)(BH_4)]$ (**4**).[4b] The ^1H and ^{13}C NMR spectra of **1**−**4** show typical resonances for the C_5H_4R ring (a typical AA′BB′ pattern is observed in the ^1H NMR spectra of **2** and **3**, respectively). The BH_4 ligands are observed as a well-resolved 1:1:1:1 quadruplet in the ^1H NMR spectra. The infrared pattern spectra of the B−H−Zr bridge and the B−H terminal vibration are characteristic of the $Zr(\mu\text{-}H)_2BH_2$ interaction.[4d]

The reaction of $[(C_5H_4R)_2Zr(BH_4)_2]$ (**1**−**3**) or $[Cp_2Zr(BH_4)Me]$ (**4**) with the ammonium salt $NHMe_2PhBPh_4$ proceeds rapidly when a THF solution of the reactants is warmed from −78 °C to room temperature to yield $[(C_5H_4R)_2Zr(BH_4)(THF)]BPh_4$ (Scheme 1: **5,** R = H; **6**, R = Me; **7**, R = $SiMe_3$). Only **5** and **6** have been isolated as white crystalline solids. We have been unable to isolate **7**, due to its higher solubility in the presence of the trimethylsilyl group on the Cp ring, but **7** was characterized in situ, via its reaction with phosphine (see below). Complexes **5** and **6** have been characterized by ^1H and ^{13}C NMR spectroscopy, infrared spectroscopy, and elemental analysis. ^1H NMR spectra were measured in THF-d_8 and CD_3CN, although their solubilities are extremely low in these solvents (the presence of a Me-substituted cyclopentadienyl ring does not increase the solubility of **6**). The products **5** and **6** decompose rapidly in chlorinated solvents. Characteristic resonances of the C_5H_4R ligand are observed (THF-d_8: **5**, δ(Cp) 6.59 ppm; **6**, $\delta(C_5H_4Me)$ 6.42, 6.25 ppm; **7**, $\delta(C_5H_4SiMe_3)$ 6.40, 6.21, 6.18, 5.74 ppm). The borohydride peaks, which are well-resolved quadruplets in **1**−**3**, appear as broad unresolved quadruplet signals for **5**−**7** (**5**, 0.45 ppm, J_{BH} = 92 Hz; **6**, 0.40 ppm, J_{BH} = 84 Hz; **7**, −0.16 ppm, J_{BH} = 90 Hz). When ^1H NMR of **5** or **6** is

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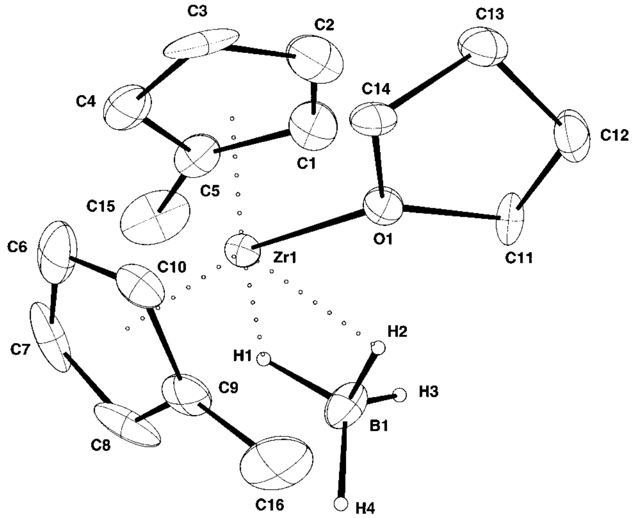

Figure 1. View of the molecular structure of the $[(C_5H_4Me)_2Zr(BH_4)(THF)]^+$ cation. The BPh_4^- structure is normal.

registered in CD_3CN, the presence of 1 equiv of free THF is observed, suggesting that dissociation of THF occurs and that **5** or **6** exists as the adduct $[(C_5H_4R)_2Zr(BH_4)(CH_3CN)_n]^+$ ($n = 1, 2$).[7] The IR spectra show the characteristic bands of μ_2-bonded (via two hydrogen bridges) BH_4 to the metal atom in compounds **5** and **6**.

Scheme 1

$$[(C_5H_4R)_2Zr(BH_4)_2] + [NHMe_2Ph][BPh_4] \rightarrow \underset{\mathbf{1-3}}{[(C_5H_4R)_2Zr(BH_4)(THF)][BPh_4]} + {}^{1}/_{2}H_2 + Me_2PhN\cdot BH_3$$

1, R = H; **2**, R = CH_3; **3**, R = $SiMe_3$

$$[Cp_2Zr(CH_3)(BH_4)] + [NHMe_2Ph][BPh_4] \rightarrow \underset{\mathbf{4}}{[Cp_2Zr(BH_4)(THF)][BPh_4]} + NMe_2Ph + CH_4$$

The solid-state structure of **6** was determined by single-crystal X-ray diffraction and consists of discrete $(C_5H_4Me)_2Zr(\mu\text{-}H_2BH_2)(THF)^+$ and BPh_4^- ions. The molecular structure of **6** shows two independent but very similar molecules in the unit cell, and Figure 1 is a perspective view of a single molecule. Selected bond distances and bond angles are listed in Table 1. The zirconium atom is at the center of a distorted tetrahedron consisting of the centers of two cyclopentadienyl rings, an oxygen atom, and the boron atom. An additional structural feature is the Zr(1)B(1)H(1)H(2) plane, which nearly includes the O(1) atom (distance of O(1) to this plane 0.110 Å) and is almost perpendicular to the Cp(1)−Zr−Cp(2) plane. The structure establishes the presence of a μ_2-bonded BH_4 group,[4g,h] in agreement with the Zr···B distance,[5] and confirms the analysis of the IR data. The THF ligand is oriented almost in the plane defined by boron, zirconium, and THF oxygen atoms (dihedral angle C(11)−O(1)−C(14)/O(1)−Zr(1)−B(1) = 24°) with a Zr−O bond length longer than in the THF ligand of $[Cp_2Zr(CH_3)(THF)]^+$ (d(Zr−O) = 2.122(14) Å) which is oriented nearly perpendicular to the plane defined by the methyl carbon, zirconium, and THF oxygen atoms.[6]

Table 1. Bond Lengths (Å) and Angles (deg)[a]

molecule 1		molecule 2	
Zr(1)−O(1)	2.239(5)	Zr(2)−O(2)	2.231(6)
Zr(1)−B(1)	2.54(1)	Zr(2)−B(4)	2.55(1)
Zr(1)−H(1)	1.87(9)	Zr(2)−H(5)	1.98(9)
Zr(1)−H(2)	1.93(9)	Zr(2)−H(6)	1.92(8)
B(1)−H(1)	1.10(9)	B(4)−H(5)	1.24(8)
B(1)−H(2)	1.30(9)	B(4)−H(6)	1.27(9)
Cp−Zr (av)	2.18	Cp−Zr (av)	2.19
O(1)−Zr(1)−B(1)	99.6(3)	O(2)−Zr(2)−B(4)	103.5(3)
O(1)−Zr(1)−H(1)	122.6(29)	O(2)−Zr(2)−H(5)	131.8(24)
O(1)−Zr(1)−H(2)	69.8(28)	O(2)−Zr(2)−H(6)	74.6(26)
B(1)−Zr(1)−H(1)	23.1(29)	B(4)−Zr(2)−H(5)	28.6(24)
B(1)−Zr(1)−H(2)	29.9(28)	B(4)−Zr(2)−H(6)	28.8(26)
H(1)−Zr(1)−H(2)	52.9 (38)	H(5)−Zr(2)−H(6)	57.3(34)
C(11)−O(1)−C(14)	107.7(6)	C(29)−O(2)−C(32)	105.1(7)
H(1)−B(1)−H(2)	89.5(61)	H(5)−B(4)−H(6)	96.2(53)
Zr(1)−H(1)−B(1)	115.4(67)	Zr(2)−H(5)−B(4)	101.7(51)
Zr(1)−H(2)−B(1)	102.2(54)	Zr(2)−H(6)−B(4)	104.5(50)
Cp(1)−Zr(1)−Cp(2)	131.6	Cp(3)−Zr(2)−Cp(4)	132.3

[a] Cp(1), Cp(2), Cp(3), and Cp(4) are the centroids of the C_5H_4 rings C(1)−C(5), C(9)−C(13), C(17)−C(21), and C(22)−C(26).

Attempts to react **5** and **6** with triethylamine or tetramethylethylenediamine (TMEDA) do not lead to the zirconium hydride cationic species, and unchanged ^1H NMR spectra of **5** and **6** are observed. Since the cleavage of BH_3 from tetrahydroborate complexes by suitable σ donors is a common route to transition-metal hydride species,[4g] **5** and **6** were treated in THF-d_8 or C_6D_6 with an excess of the phosphine PMe_2Ph. The formation of the cationic hydrides $[(C_5H_4R)_2ZrH(PMe_2Ph)_2]^+$ (**8**, R = H; **9**, R = Me) is observed. The same behavior was observed for the reaction of **7** with phosphine (prepared in situ from **3** and $NHMePh_2BPh_4$ in THF-d_8) to give **10** (R = $SiMe_3$). Their identification as a cationic hydride diphosphine arose from ^1H and ^{31}P NMR and from comparison with the data of the same cationic hydride species obtained from hydrogenolysis of $[(C_5H_5)_2ZrMe]^+$.[7] The BH_3-PMe_2Ph adduct can be recognized by ^{31}P NMR (q, δ 9 ppm, $J_{PB} = 56$ Hz). No reaction was observed with other bulky phosphines such as PPh_2Me, PPh_3, and P(cyclohexyl)$_3$.

Reduction occurs during the course of the reaction. This slow process can be detected by the complete disappearance of $[(C_5H_4R)_2ZrH(PMe_2Ph)_2]^+$ in 1−2 days. At this stage, $[(C_5H_4R)_2ZrH(PMe_2Ph)_2]^+$ is entirely consumed and the complex is not at this point detected by ^1H NMR, but the formation of the well-known dihydride $[(C_5H_4R)_2ZrH(\mu\text{-}H)]_2$ is observed[8,9] (R = Me, $SiMe_3$; for R = H, the corresponding insoluble dihydride is characterized by chemical derivatization with acetone as $Cp_2Zr(O\text{-}i\text{-}Pr)_2$). The decay of **6** in the presence of 5 equiv of PMe_2Ph and the formation of the dimeric dihydride Zr complex were monitored by ^1H NMR in THF-d_8 in a sealed tube. An approximate mole ratio of 4:1 is observed at the end of the reaction between the starting complex **6** and $[(C_5H_4Me)_2ZrH(\mu\text{-}H)]_2$. At the same time, the reaction was monitored by EPR spectroscopy and a stable EPR 1:2:1 triplet signal was observed with a characteristic coupling constant to two

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equivalent phosphorus nuclei, suggesting the formation of $[(C_5H_4R)_2Zr(PMe_2Ph)_2]^+$ (**11**) ($g = 1.986$, $a(^{31}P) = 32.4$ G, $a(^{91}Zr) = 23$ G). The observation that the cationic Ti^{III} species $[(C_5H_5)_2Ti(THF)_2]^+$ gives in the presence of PMe_3 a similar EPR 1:2:1 triplet signal with the same hyperfine coupling constant to two equivalent phosphorus atoms ($a(^{31}P) = 30.2$ G) provides support for the proposal of species **11**.[10] Further support for this redistribution and redox reaction was independently provided by reacting $[Cp_2ZrH(THF)]^+$ (synthesized by hydrogenation of $[Cp_2Zr(CH_3)(THF)]^+$ in THF[7]) for 1 day with PMe_2Ph. The product **11** can be easily identified by EPR spectroscopy, whereas the presence of polymeric $[Cp_2ZrH_2]_n$ was identified by chemical derivatization with acetone as $Cp_2Zr(O\text{-}i\text{-}Pr)_2$. The amount of Zr^{III}, directly measured by comparison of EPR integration with the area of a standard of TEMPO in THF, accounts for about 40−45% yield from the starting complex **6**, **7**, or $[Cp_2Zr(CH_3)(THF)]^+$. The presence of the dihydride species $[(C_5H_4R)_2ZrH(\mu\text{-}H)]_2$ and the formation of a Zr^{III} species is reminiscent of a disproportionation reaction followed by a redox reaction with $[BPh_4]^-$ recently observed by us in the case of the cationic vanadium(IV) $[Cp_2V(CH_3)(CH_3CN)][BPh_4]$[11] (see Scheme 2). Effectively, we observed the formation of PhPh (identified by GC/MS; the quantification of liberated PhPh was impossible, attributable to the presence of other unidentified boron species[12,13] which leads us to underestimate PhPh) and BPh_3 in the solution (identified by ^{11}B NMR and by comparison with an authentic sample). The mechanism of the reaction, namely a disproportionation and a redox reaction between Zr^{IV} and $[BPh_4]^-$ in the presence of phosphine, cannot be stopped at its early stage by adding ethylene to $[(C_5H_4R)_2ZrH(PMe_2Ph)_2]^+$. The expected ethyl complex $[(C_5H_4R)_2Zr(C_2H_5)(PMe_2Ph)]^+$ is not observed by ^1H NMR and ^{31}P NMR and the disproportionation/redox reaction still occurs, although this reaction was already observed in the case of $[Cp_2Zr(H)(PMe_3)_2][BPh_4]$ with ethylene.[7,14] The presence of the bulkier and less basic phosphine PMe_2Ph, instead of PMe_3, seems responsible for the lack of reactivity of ethylene observed in our case. We suggest the formation of the monophosphine $[(C_5H_4R)_2Zr(H)(PMe_2Ph)]^+$ as an intermediate to describe the formation of both the hydride dimer complex $[(C_5H_4R)_2ZrH(\mu\text{-}H)]_2$ via a four-center mechanism and the transient dicationic species $[(C_5H_4R)_2Zr(PMe_2Ph)_2]^{2+}$.[15] The presence of a dicationic zirconocene species was already suggested by Jordan *et al.*[1,16] along with the disproportionation reaction observed with the cationic zirconium and hafnium complexes $[Cp_2MCH_3]^+$ in the presence of NMe_3 or CH_3CN, respectively, and with $[(C_5Me_5)Zr(CH_2Ph)_2]^+$. Also, the exchange reaction of ligands between $[Cp_2Zr(CH_3CN)_3]^{2+}$ and PMe_3 in CD_3CN was identified by NMR to be consistent with an equilibrium of $[Cp_2Zr(CH_3CN)_x(PMe_3)_{3-x}]^{2+}$ species.[15] Such an equilibrium in our case with THF and PMe_2Ph ligand substitution could drive the dicationic species to undergo a redox reaction with the $[BPh_4]^-$ anion and lead to paramagnetic **11**. In order to clarify this point, the dicationic species $[Cp_2Zr(CH_3CN)_3][BPh_4]_2$ was monitored by EPR spectroscopy in presence of 5 equiv of PMe_2Ph in THF-d_8. Although the dicationic species is insoluble in THF, after 5 days, $[Cp_2Zr(PMe_2Ph)_2][BPh_4]$ (**11**) is formed in low yield (3−5%, depending on the experiments).[17] This seems to demonstrate the puzzling accessibility of the dicationic species $[Cp_2Zr(PMe_2Ph)_2]^{2+}$ (or $[Cp_2Zr(THF)(PMe_2Ph)]^{2+}$). The contribution of the σ−donor ability of THF and various phosphines, which explains the different hydrogenation rates of cationic $[Cp_2ZrCH_3(THF)][BPh_4]$ in the presence of phosphine,[18] could be connected to the disproportionation redox reaction of $[Cp_2ZrH(PMe_2Ph)_2][BPh_4]$ in the presence of THF and phosphine. On the other hand, the observation that $[Cp_2ZrH(PMe_3)_2]^+$ reacts with ethylene and not $[Cp_2ZrH(PMe_2Ph)_2]^+$ seems to indicate that the contribution of the steric effect of the phosphine ligand could not be eliminated.

The presence of paramagnetic species in cationic polymerization was observed by others.[19] Reductive decomposition of the catalytic system $(C_5Me_5)TiMe_3/B(C_6F_5)_3$ was recently studied by Grassi *et al.*,[20] and an

Scheme 2

$$[(C_5H_4R)_2Zr(BH_4)(THF)][BPh_4] + 3\ PMe_2Ph \rightarrow [(C_5H_4R)_2ZrH(PMe_2Ph)_2][BPh_4] + Me_2PhP{\cdot}BH_3$$

5−**7**

5, R = H; **6**, R = CH_3; **7**, R = $SiMe_3$

$$[(C_5H_4R)_2ZrH(PMe_2Ph)_2][BPh_4] \rightarrow {}^1/_4[(C_5H_4R)_2ZrH(\mu\text{-}H)]_2 + {}^1/_2[(C_5H_4R)_2Zr(PMe_2Ph)_2][BPh_4]_2$$

$${}^1/_2[(C_5H_4R)_2Zr(PMe_2Ph)_2][BPh_4]_2 \rightarrow {}^1/_2[(C_5H_4R)_2Zr(PMe_2Ph)_2][BPh_4] + {}^1/_2BPh_3 + {}^1/_4PhPh$$

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[10] (a) The cationic species $[Cp_2Ti(THF)_2][BPh_4]$ was isolated and fully characterized by an X-ray structure determination. Its EPR signal in the presence of PMe_3 gives the expected triplet for $[Cp_2Ti(PMe_3)_2]^+$ ($g = 1.989$; $a(^{31}P) = 30.2$ G), whereas in the presence of PMe_2Ph, an EPR doublet is observed for the monophosphine adduct $[Cp_2Ti(PMe_2Ph)]^+$ ($g = 1.986$; $a(^{31}P) = 26.7$ G), probably due to the steric effect of the phosphine and the size of the titanium radius. In both cases, a large $a(^{31}P)$ is observed: Choukroun, R.; Douziech, B. Unpublished results. For other $a(^{31}P)$ values: (b) Choukroun, R.; Gervais, D. *J. Chem. Soc., Chem. Commun.* **1985**, 224. (c) Williams, G. M.; Schwartz, J. *J. Am. Chem. Soc.* **1982**, *104*, 1122. (d) Dioumaev, V. K.; Harrod, J. F. *Organometallics* **1997**, *16*, 2798.

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[17] The amount of Zr^{III} (three experiments) was directly measured by comparison of EPR integration with the area of a standard amount of TEMPO in THF. ^1H NMR of a THF-d_8 solution[10] shows three Cp resonances at 6.29 (broad s, 20%), 6.25 (d, $J(^{31}P-^1H) = 0.4$ Hz, 30%), and 6.16 ppm (d, $J(^{31}P-^1H) = 0.4$ Hz, 50%), free CH_3CN (1.97 ppm, 3 equiv), and PMe_2Ph (broad s, 1.42 ppm). The unreacted dicationic acetonitrile adduct is still present in the NMR tube.

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ESR spectroscopy study suggests the formation of the cationic Ti^{III} complex $[(C_5Me_5)TiMe]^+$. With the group 4 dicyclopentadienyl complex, the redistribution reaction leads to a cationic Zr^{III} species in which there is no metal−carbon bond left to produce the catalytic polymerization of olefins. Although this disproportionation process is quite slow and requires donor ligands, a pathway for the deactivation of cationic catalyst species may be suggested to take into account our findings, which can be mainly regarded as studies on the reactivity of cationic metallocenes (see Scheme 3). At present, the mechanism of the disproportionation/redox reaction observed in vanadium chemistry and in this work needs further investigation with other cationic systems to support a relationship with the deactivation of the catalyst in the olefin polymerization.[21]

Scheme 3

$$[Cp_2MR]^+ + \text{excess } L \rightarrow {}^1/_2Cp_2MR_2 + {}^1/_2[Cp_2M(L)_n]^{2+}$$

$$L = \text{donor ligands}$$

Experimental Section

General Procedure. All manipulations were performed either on a high-vacuum line or in a glovebox under a purified argon atmosphere. Solvents were distilled from Na/benzophenone for THF and Et_2O and from Na/K alloy for pentane and toluene. $Cp_2Zr(BH_4)_2$,[4a] $(C_5H_4Me)_2ZrCl_2$,[7] $(C_5H_4SiMe_3)_2ZrCl_2$,[22] and $NHMe_2PhBPh_4$[23] were synthesized by the literature methods. NMR spectra were recorded on Bruker WM 80, 200, and 250 MHz instruments. EPR spectra were recorded on a Bruker ER 200T spectrometer. Quantitative EPR measurements were performed with an external standard of TEMPO of known concentration, and the acquisition parameters were kept constant for both the unknown and the standard sample measurements. Chemical analyses were performed by either the Service Central de Microanalyse du CNRS or by our laboratory services.

$(C_5H_4Me)_2Zr(BH_4)_2$ (2). A toluene solution of $(C_5H_4Me)_2ZrCl_2$ (2.0 g, 6.2 mmol) was stirred with an excess of $LiBH_4$ (0.68 g, 31.2 mmol) for 48 h, at room temperature. The mixture was filtered on Celite to remove the excess unreacted $LiBH_4$ and LiCl and the filtrate concentrated to a small volume and left overnight at −30 °C. A white solid product was collected by filtration, washed with pentane, and dried under vacuum, giving 1.3 g of product (yield 75%). Anal. Calcd for $C_{12}H_{22}B_2Zr$: C, 51.63; H, 7.94. Found: C, 51.46; H, 7.91. ^{1}H NMR (C_6D_6, 293 K, ppm): 5.60 (t, J_{CH} = 2,7 Hz, 4 H, C_5H_4), 5.44 (t, J_{CH} = 2,6 Hz, 4 H, C_5H_4), 1.92 (s, 6 H, Me), 0.80 (q, J_{BH} = 85 Hz, H, BH_4).

$(C_5H_4SiMe_3)_2Zr(BH_4)_2$ (3). An Et_2O solution of $(C_5H_4SiMe_3)_2ZrCl_2$ (1 g, 2.3 mmol) was stirred with an excess of $LiBH_4$ (0.4 g, 18 mmol) for 48 h, at room temperature. The mixture was evaporated to dryness; then toluene was added. The mixture was filtered on Celite to remove the excess unreacted $LiBH_4$ and LiCl and the filtrate evaporated to dryness, giving a white powder (0.860 g; yield 95%). Anal. Calcd for $C_{16}H_{34}B_2Si_2Zr$: C, 48.6; H, 8.6; Zr, 23.08. Found: C, 48.63; H, 8.88; Zr, 23.05. ^{1}H NMR (C_6D_6, 293 K, ppm): 6.24 (t, J_{CH} = 2,5 Hz, 4H, C_5H_4), 5.71 (t, J_{CH} = 2,5 Hz, 4H, C_5H_4), 0.27 (s, 18H, $SiMe_3$), 0.75 (q, J_{BH} = 85 Hz, 8H, BH_4). ^{13}C NMR (C_6D_6, 293 K, ppm): 125.8 (dq, $^1J_{CH}$ = 174 Hz, $^2J_{CH}$ = 6.8 Hz, C_5H_4), 120.5 (s, C_5H_4), 111.7 (dq, $^1J_{CH}$ = 174 Hz, $^2J_{CH}$ = 7.5 Hz, C_5H_4), 0.83 (q, J_{CH} = 122 Hz, $SiMe_3$).

$Cp_2Zr(BH_4)(Me)$ (4). A toluene solution of $(C_5H_5)_2Zr(CH_3)Cl$ (1.06 g, 3.9 mmol) was stirred with $LiBH_4$ (0.085 g, 3.9 mmol) for 72 h, at room temperature. The mixture was filtered on Celite to remove the excess unreacted $LiBH_4$ and LiCl, and the filtrate was then concentrated to a small volume. A yellow solid was observed during diffusion with hexane, which was filtered and dried under vacuum, giving 0.47 g of product (yield 48%). Anal. Calcd for $C_{11}H_{17}BZr$: C, 52.58; H, 6.82. Found: C, 53.0; H, 6.60. ^{1}H NMR (toluene-d_8, 293 K, ppm): 5.83 (s, 10H, C_5H_5), 0.36 (s, 3H, CH_3), 0.32 (q, J_{BH} = 85 Hz, 4 H, BH_4). ^{1}H NMR (toluene-d_8, 373 K, ppm): 5.89 (s, 10H, C_5H_5), 0.31 (s, 3H, CH_3), 0.26 (q, J_{BH} = 86 Hz, 4 H, BH_4). ^{13}C{^{1}H} NMR (THF-d_8, 293 K, ppm): 111.4 (d, J_{CH} = 180 Hz, C_5H_5), 21.6 (q, J_{CH} = 120 Hz, CH_3).

$[(C_5H_5)_2Zr(BH_4)(THF)][BPh_4]$ (5). To a stirred THF solution of $Cp_2Zr(BH_4)_2$ (0.4 g, 1.6 mmol) at −78 °C was slowly added a THF solution of $NHMe_2PhBPh_4$ (0.685 g, 1.55 mmol) cooled to −78 °C. After 5 min of stirring, a white crystalline precipitate was obtained when the solution was slowly warmed to room temperature. The solid was filtered, washed with cold THF, and dried under vacuum, giving 0.5 g of product (yield 50%). Anal. Calcd for $C_{38}H_{42}B_2OZr$: C, 72.73; H, 6.75; B, 3.45; Zr, 14.53. Found: C, 72.19; H, 6.92; B, 3.40; Zr, 13.75. ^{1}H NMR (THF-d_8, 326 K, ppm): 7.45 (br m, 8 H), 7.01 (t, J_{CH} = 7.3 Hz, 8 H), 6.86 (t, J_{CH} = 7.1 Hz, 4 H) ($B(C_6H_5)_4$); 6.58 (s, 10 H, C_5H_5); 3.74, 1.90 (m, 8 H, THF); 0.45 (q, J_{BH} = 92 Hz, 4 H, BH_4). ^{1}H NMR (CD_3CN, 298 K, ppm): 7.28 (br m, 8 H), 7.00 (t, J_{CH} = 7.3 Hz, 8 H), 6.85 (t, J_{CH} = 7.2 Hz, 4 H) ($B(C_6H_5)_4$); 6.25 (s, 10 H, C_5H_5); 3.65 (4H), 1.80 (4 H) (free THF); 1.53 (q, J_{BH} = 96 Hz, 4 H, BH_4). ^{13}C{^{1}H} NMR (CD_3CN, 293 K, ppm): 164.8, 136.8, 126.7, 122.8, ($B(C_6H_5)_4$); 113.3 (C_5H_5); 68.3, 26.3 (free THF). ^{11}B{^{1}H} NMR (C_6D_6/THF, 293 K, ppm): −6.2 ($B(C_6H_5)_4$), BH_4 not observed. IR: 2467−2415 cm^{-1}, B−H$_t$ str; 2121 cm^{-1}, B−H$_b$ str.

$[(C_5H_4Me)_2Zr(BH_4)(THF)][BPh_4]$ (6). To a stirred THF solution of $(C_5H_4Me)_2Zr(BH_4)_2$ (0.445 g, 1.6 mmol) at −78 °C was slowly added a THF solution of $NHPhMe_2BPh_4$ (0.685 g, 1.55 mmol) cooled to −78 °C. After 5 min of stirring, a white crystalline precipitate was observed when the solution was warmed to room temperature. The solid was then filtered, washed with cold THF, and dried under vacuum, giving 0.565 g of product (yield 54%). Anal. Calcd for $C_{40}H_{46}B_2OZr$: C, 73.28; H, 7.07; Zr, 13.91. Found: C, 72.04; H, 7.09; Zr, 13.23. $_1$H NMR (THF-d_8, 293 K, ppm): 7.40 (br m, 8 H), 6.99 (t, J_{CH} = 7.2 Hz, 8 H), 6.84 (t, J_{CH} = 7.1 Hz, 4 H) ($B(C_6H_5)_4$); 6.42 (4 H), 6.25 (4 H) (C_5H_4Me); 3.74, 1.89 (m, 8 H, THF); 2.34 (s, 6H, Me); 0.40 (q, J_{BH} = 84 Hz, 4 H, BH_4). ^{13}C{^{1}H} NMR (THF-d_8, 293 K, ppm): 137.7, 126.3, 122.4 ($B(C_6H_5)_4$); 138.4, 130.8, 128.5 (C_5H_4Me); 16.2 (CH_3). ^{11}B{^{1}H} NMR (C_6D_6/THF, 293 K, ppm): −6.4 ($B(C_6H_5)_4$); BH_4 not observed. IR: 2472−2429 cm^{-1}, B−H$_t$ str; 2119 cm^{-1}, B−H$_b$ str.

$[(C_5H_4SiMe_3)_2Zr(BH_4)(THF)][BPh_4]$ (7). An NMR sample was prepared as follows: $NHMe_2PhBPh_4$ (0.156 g, 0.35 mmol) was added to a THF-d_8 solution of **3** (0.140 g,; 0.35 mmol). Evolution of B_2H_6 occurred, which was characterized by MS. ^{1}H NMR (THF-d_8, 293 K, ppm): 7.8−6.5 (m, $B(C_6H_5)_4$, NMe_2Ph); 6.40, 6.21, 6.08, 5.74 (pseudo q, 8 H, J_{CH} = 3 Hz, C_5H_4); 0.38 (s, 18 H, $SiMe_3$); −0.16 (br q, J_{BH} = 90 Hz, 4 H, BH_4). ^{11}B{^{1}H} NMR (C_6D_6/THF, 293 K, ppm): −6.2 ($B(C_6H_5)_4$); BH_4 not observed.

Preparation in Situ of 8 and 9. : In an NMR tube, excess PMe_2Ph (at least 5 equiv) is added to a THF-d_8 suspension of **5** (0.120 g, 0.19 mmol) or **6** (0.10 g, 0.15 mmol). Immediate

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[20] Grassi, A.; Zambelli, A.; Laschi, F. *Organometallics* **1996**, *15*, 480. We reason that a $[CpMR_2]^+$ complex provides access to a $[CpMR]^+$ species (and other unidentified complexes) via a redistribution reaction (the presence of a metal−carbon bond in the coordination sphere of the cationic $[CpMR]^+$ reflects the possibility of having access to a new catalytic cationic system).

[21] Other proposed deactivation pathways are (i) the formation of dinuclear species by α- or β-CH activation and (ii) aryl or fluoride transfer from the counteranion to the cationic complex.

[22] Lappert, M. F.; Pickett, C. J.; Riley, P. I.; Yarrow, P. I. W. *J. Chem. Soc., Dalton Trans.* **1981**, 805.

[23] (a) Bochmann, M.; Wilson, L. *J. Chem. Soc., Chem. Commun.* **1986**, 1610. (b) Crane, F. E., Jr. *Anal. Chem.* **1956**, *28*, 1794.

solubilization occurs, giving the cationic hydride complex $[(C_5H_4R)_2ZrH(PMe_2Ph)_2]BPh_4$ (R = H (**8**), Me (**9**)). **8**: ^{1}H NMR (THF-d_8, 293 K, ppm) 8−6.9 (m, $B(C_6H_5)_4$, Ph), 5.68 (t, J_{HP} = 3 Hz, 10 H, (C_5H_5)), 2.17 (t, J_{HP} = 103 Hz, 1 H, Zr−H), 1.7 (pseudo t, J_{HP} = 3.5 Hz, 12 H, $Zr(PMe_2Ph)_2$), 1.6 (d, J_{HP} = 10.4 Hz, 6 H, $PMe_2Ph{\cdot}BH_3$), 1.4 (free PMe_2Ph); $^{31}P\{^1H\}$ NMR (THF-d_8, ppm) 21.0 ($ZrH(PMe_2Ph)_2$), 9.4 (q, J_{BP} = 56 Hz, $PMe_2Ph{\cdot}BH_3$), −40 (free PMe_2Ph). **9**: ^{1}H NMR (THF-d_8, 293 K, ppm) 7.9−6.8 (m, $B(C_6H_5)_4$, Ph), 5.6−5.2 (quint, J_{HP} = 2,6 Hz, 8H, C_5H_4), 2.24 (s, 6H, CH_3), 2.23 (t, J_{HP} = 104 Hz, 1H, ZrH), 1.97 (pseudo t, J_{HP} =3, 6 Hz, 12H, $Zr(PMe_2Ph)_2$), 1.71 (d, J_{HP} = 10,4 Hz, 6 H, $PMe_2Ph{\cdot}BH_3$), 1.5 (free PMe_2Ph); ^{31}P (THF-d_8, ppm) 22.6 (d, J_{HP} = 102 Hz, $ZrH(PMe_2Ph)_2$), 9 (m, $PMe_2Ph{\cdot}BH_3$), −40 (free PMe_2Ph); ^{11}B (THF-d_8, ppm) −6.4 (s, $B(C_6H_5)_4$), −38 (d, J_{BP} = 56 Hz, $PMe_2Ph{-}BH_3$).

Preparation in Situ of 10. In an NMR tube, $NHMe_2PhBPh_4$ (44 mg, 0.15 mmol) was added to a THF-d_8 solution of **3** (60 mg, 0.15 mmol); then 5 equiv of PMe_2Ph was added, which gave $[(C_5H_4SiMe_3)_2ZrH(PMe_2Ph)_2]BPh_4$ (**10**). ^{1}H NMR (THF-d_8, 293 K, ppm): 7.82−6.82 (m, $B(C_6H_5)_4$, Ph), 6.10 (s, 4H, C_5H_4), 5.49 (s, 4H, C_5H_4), 1.9 (t, J_{HP} = 3.2 Hz, 12H, $Zr(PMe_2Ph)_2$), 1.6 (d, J_{HP} = 10.4 Hz, 6 H, $PMe_2Ph{\cdot}BH_3$), 1.4 (free PMe_2Ph), 0.32 (s, 18 H, $SiMe_3$). ^{31}P NMR (THF-d_8, ppm): 19.9 (d, J_{HP} = 113 Hz, $ZrH(PMe_2Ph)_2$), 9 (q, J_{BP} = 56 Hz, $PMe_2Ph{\cdot}BH_3$), −40 (free PMe_2Ph).

Crystallography Study for the Compound $[(C_5H_4Me)Zr(BH_4)(THF)]BPh_4$ (6). Data collection was performed at low temperature (T = 180 K) on a IPDS STOE diffractometer using graphite-monochromatized Mo Kα radiation equipped with Oxford Cryostream cooling device. Details on data collection, crystal parameters, and refinements are summarized in Table 2. Corrections were made for Lorentz and polarization effects on the data. Computations were performed by using the CRYSTALS package[24] adapted for a PC. The atomic scattering factors for all atoms were taken from the literature.[25] The structure was solved by direct methods using SIR92[26] and subsequent difference Fourier maps. All hydrogen atoms were located by difference Fourier maps, but their coordinates were introduced in processes of refinement as fixed contributors in calculated positions (C−H = 0.96 Å) and recalculated after each cycle of refinement. Their U(iso) values were fixed 20% higher than those of the carbon atoms to which they were attached, except for the hydrogen atoms of BH_4, which were refined isotropically. All non-hydrogen atoms were anisotropically refined; full-matrix least-squares refinements were carried out by minimizing the function $\sum w(||F_o| - |F_c||)^2$, where F_o and F_c are the observed and calculated structure factors. Models reached convergence with the formulas $R = \sum(||F_o| - |F_c||)/\sum|F_o|$ and $R_w = [\sum w(||F_o| - |F_c||)^2/\sum w(|F_o|)^2]^{1/2}$. A diagram was produced by using the program CAMERON.[27]

Table 2. Crystal Data and Data Collection and Refinement Details for Compound 6

Crystal Data and Data Collection	
chem formula	$[(C_5H_4Me)Zr(BH_4)(THF)]BPh_4$
fw	655.65
cryst syst	monoclinic
space group	$P2_1/n$
a (Å)	26.405(2)
b (Å)	9.5866(8)
c (Å)	28.473(2)
β (deg)	110.275(6)
cell vol (Å^3)	6761
Z; D (g cm^{-3})	8; 3.48
μ (cm^{-1})	1.29
cryst color	colorless
cryst size (mm)	0.50 × 0.30 × 0.10
cryst form	block
radiation type	Mo Kα
temp (K)	180
no. of reflns collected	43329
no. of reflns merged	9305
R_{av}	0.052
θ_{max} (deg)	24.2
Refinement	
refinement on	F
R^a	0.056
$R_w{}^b$	0.068
abs cor	none
weighting scheme	1
goodness of fit^c	1.07
no. of rflns used	6261
observn criterion	$I > \sigma(I)$
no. of params refined	826

[a] $R = \sum(||F_o| - |F_c||)/\sum|F_o|$. [b] $R_w = [\sum w(||F_o| - |F_c||)^2/\sum w(|F_o|)^2]^{1/2}$. [c] Goodness of fit $= [\sum(|F_o - F_c|)^2/(N_{observns} - N_{params})]^{1/2}$.

Supporting Information Available: Tables giving crystal data and data collection and structure refinement details, bond distances and angles, and positional and thermal parameters for **6** (14 pages). Ordering information is given on any current masthead page.

OM9701736

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