eters for Ir, P, and Cl, and isotropic thermal parameters were used for all remaining atoms. Hydrogen atoms were refined by using a riding model in which an idealized C–H vector of 0.96 Å length is recalculated with each cycle of refinement. Isotropic hydrogen thermal parameters were fixed at 1.2 times the equivalent isotropic thermal parameter of the bonded carbon. In the last cycle of refinement the mean shift/esd was 0.008. The largest feature on the final difference map was 1.35 e Å^{-3}, located near the center of one phenyl ring.

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Supplementary Material Available: ORTEP drawing of **4** and listings of anisotropic thermal parameters, hydrogen atom positions, and additional bond lengths and bond angles (11 pages); listings of structure factor amplitudes (50 pages). Ordering information is given on any current masthead page.

Contribution from the Department of Chemistry, Washington State University, Pullman, Washington 99164

Synthesis and Chemistry of $[Cp_2Zr(CH_3CN)_3][BPh_4]_2$: A Five-Coordinate, Dicationic Zirconocene Complex

Richard F. Jordan* and Scott F. Echols

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The five-coordinate, dicationic complex $[Cp_2Zr(CH_3CN)_3][BPh_4]_2$ (**2**) is formed by reaction of Cp_2ZrI_2 and 2 equiv of $Ag[BPh_4]$ in CH_3CN. A stable derivative of complex **2**, $[Cp_2Zr(4,4'\text{-dimethylbipyridine})(CH_3CN)][BPh_4]_2$ (**11**), has been synthesized and fully characterized. Reaction of complex **2** with PMe_3 produces a complex mixture of Cp_2Zr^{IV}–PMe_3 products. Complex **2** reacts rapidly with $Cp_2Zr(CH_3)_2$ to form $[Cp_2Zr(CH_3)(CH_3CN)_2][BPh_4]$ (**10**) but reacts only slowly with $Cp_2Zr(CH_2Ph)_2$ to form $[Cp_2Zr(\eta^n\text{-}CH_2Ph)(CH_3CN)][BPh_4]$ (**3**). The relevance of these results to the synthesis of $Cp_2Zr(R)(L)_n^+$ complexes is discussed. Halide complexes Cp_2ZrX_2 react with complex **2** to form the monohalide cations $Cp_2Zr(X)(L)_n^+$, which are unstable with respect to disproportionation to Cp_2ZrX_2 and **2** in CH_3CN.

Introduction

Cationic Cp_2Zr^{IV} alkyl complexes $Cp_2Zr(R)(L)_n^+$ (L = THF, CH_3CN) are highly reactive as a result of the charge at the metal center and the lability of the ligand L.[1] We recently reported the synthesis and structure of $[Cp_2Zr(CH_3)(THF)][BPh_4]$ (**1**) formed by reaction of $Ag[BPh_4]$ and $Cp_2Zr(CH_3)_2$ (eq 1).

$$Cp_2Zr(CH_3)_2 + Ag[BPh_4] \xrightarrow[2.\ THF]{1.\ CH_3CN} \underset{\mathbf{1}}{[Cp_2Zr(CH_3)(THF)][BPh_4]} + Ag^0 + {}^1/_2CH_3CH_3 \quad (1)$$

Complex **1** polymerizes ethylene in CH_2Cl_2 solution and alkylates polar substrates, including ketones and nitriles.[1,2] Tetraphenylborate, BPh_4^-, is the anion of choice for these cationic complexes as it is apparently nonreactive and noncoordinating.

We were interested in the related dicationic species $[Cp_2Zr(CH_3CN)_3][BPh_4]_2$ (**2**) and its THF analogue $Cp_2Zr(THF)_n^{2+}$ for use as synthetic intermediates and mechanistic probes[3] in support of this work. Reaction of $Cp_2ZrL_n^{2+}$ complexes with Cp_2ZrR_2 provides a potential route to $Cp_2Zr(R)(L)_n^+$ complexes (eq 2) which may be useful in certain cases. For example, the

$$Cp_2ZrL_n^{2+} + Cp_2ZrR_2 \rightarrow 2Cp_2Zr(R)(L)_n^+ \quad (2)$$

$$Cp_2Zr(CH_2Ph)_2 \xrightarrow[-Ag^0,\ -{}^1/_2PhCH_2CH_2Ph]{Ag[BPh_4],\ CH_3CN} \underset{\mathbf{3}^+}{Cp_2Zr(\eta^n\text{-}CH_2Ph)(CH_3CN)^+} \xrightarrow[reflux]{THF} \text{no reaction} \quad (3)$$

cationic benzyl complex $[Cp_2Zr(\eta^n\text{-}CH_2Ph)(CH_3CN)][BPh_4]$ (**3**)[4] has been synthesized with use of $Ag[BPh_4]$ as shown in eq 3; however, attempts to replace the CH_3CN with THF by a simple ligand-exchange reaction have proven unsuccessful. We reasoned that it might be possible to synthesize $Cp_2Zr(\eta^n\text{-}CH_2Ph)(THF)_n^+$ via comproportionation of $Cp_2Zr(THF)_n^{2+}$ and $Cp_2Zr(CH_2Ph)_2$ in THF. Also, reaction of the dication of **2** with Cp_2ZrX_2 provides a potential route to the monohalide cations $Cp_2Zr(X)(L)_n^+$, which were previously reported but not well characterized.[5]

The best characterized examples of dicationic Cp_2M^{IV} (M = Ti, Zr) complexes are $[Cp_2Ti(H_2O)_2][ClO_4]_2$ (**4**) and $[Cp_2Zr(H_2O)_3][CF_3SO_3]_2 \cdot THF$ (**5**), for which X-ray structures have been reported by Thewalt.[6] However, ligands such as H_2O are incompatible with many organometallic applications. The dicationic Ti species $[Cp_2Ti(CH_3CN)_2][PF_6]$ (**6**) has been partially characterized by ^1H NMR and IR spectroscopy though its reactivity has not been explored.[7] The chloro cations $[(Cp_2ZrCl)_2(\mu$-

(1) (a) Jordan, R. F.; Dasher, W. E.; Echols, S. F. *J. Am. Chem. Soc.* **1986**, *108*, 1718. (b) Jordan, R. F.; Bajgur, C. S.; Willett, R.; Scott, B. *J. Am. Chem. Soc.* **1986**, *108*, 7410.

(2) Jordan, R. F.; Bajgur, C. S.; Dasher, W. E.; Scott, B.; Rheingold, A. L. *Organometallics*, in press.

(3) One possible mechanism for the formation of the cationic complexes **1** and **3** in eq 1 and 3 involves a $Cp_2Zr(CH_3CN)_n^{2+}$ intermediate formed from Cp_2ZrR_2 and 2 equiv of Ag^+ (e.g. via oxidatively induced R–R elimination). Comproportionation of this intermediate and Cp_2ZrR_2 would produce the $Cp_2Zr(R)(L)_n^+$ product.

$$Cp_2ZrR_2 + 2Ag^+ \xrightarrow{CH_3CN} Cp_2Zr(CH_3CN)_n^{2+} + R\text{–}R + 2Ag^0$$

$$Cp_2Zr(CH_3CN)_n^{2+} + Cp_2ZrR_2 \rightarrow 2Cp_2ZrR(CH_3CN)_n^+$$

(4) Compound **3** has been fully characterized by spectroscopy and X-ray diffraction: Jordan, R. F.; Willett, R., manuscript in preparation.

(5) Cuenca, T.; Royo, P. *J. Organomet. Chem.* **1985**, *293*, 61.

(6) (a) Thewalt, U.; Klein, H. P. *J. Organomet. Chem.* **1980**, *194*, 297. (b) Thewalt, U.; Lasser, W. *J. Organomet. Chem.* **1984**, *276*, 341. (c) Related complexes include $Cp_2Zr(THF)(CF_3SO_3)_2$ (Thewalt, U.; Klein, H. P. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1983**, *38B*(11), 1501) and $[\{Cp_2Ti(H_2O)\}_2O][ClO_4]_2 \cdot 2H_2O$ (Thewalt, U.; Kebbel, B. *J. Organomet. Chem.* **1978**, *150*, 59).

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bpy)][ClO_4]$_2$ (**7**, bpy = bipyridine), [$Cp_2Zr(Cl)(OPPh_3)$][ClO_4] (**8**), and [Cp_2ZrCl]$_2$[BF_4]$_2$ (**9**) were reported to exist on the basis of ^{1}H NMR, IR, and conductivity studies, but full details were not published.[5] In this paper we report on the synthesis and reactivity of [$Cp_2Zr(CH_3CN)_3$][BPh_4]$_2$ (**2**) and its 4,4′-dimethylbipyridine (4,4′-Me_2-2,2′-bpy) and PMe_3 derivatives.

Results and Discussion

1. Synthesis of [$Cp_2Zr(CH_3CN)_3$][BPh_4]$_2$ (2). Reaction of Cp_2ZrI_2 with 2 equiv of (insoluble) Ag[BPh_4] in CH_3CN followed by filtration and concentration of the filtrate produces white, crystalline [$Cp_2Zr(CH_3CN)_3$][BPh_4]$_2$ (**2**) (eq 4), which may be purified by recrystallization from CH_3CN/Et_2O. Complex **2** has

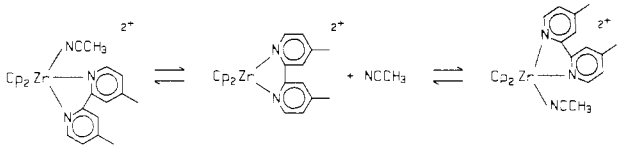
$$Cp_2ZrI_2 + 2Ag[BPh_4] \xrightarrow{CH_3CN} \underset{\mathbf{2}}{[Cp_2Zr(CH_3CN)_3][BPh_4]_2} + 2AgI \quad (4)$$

been characterized by spectroscopy and elemental analysis. The presence of coordinated CH_3CN is confirmed by the IR spectrum of **2**, in which ν(CN) bands are observed at 2295 and 2270 cm^{-1} shifted from 2287 and 2251 cm^{-1} for free CH_3CN.[8] The room-temperature ^{1}H NMR spectrum of a CD_3CN solution of **2** shows a singlet at δ 1.95 integrating for 9 H, corresponding to 3 equiv of CH_3CN liberated per Cp_2Zr unit, as well as a singlet due to the Cp ligands at δ 6.48 and characteristic BPh_4^- absorbances. The Cp resonance is 0.41 ppm downfield of the Cp resonance in [$Cp_2Zr(CH_3)(CH_3CN)_2$][BPh_4] (**10**)[2] and is in the range observed for **5**.[6] Complex **2** is extremely soluble in CH_3CN but is insoluble in THF and CH_2Cl_2. Repetitive washing of **2** with THF results in some exchange of coordinated CH_3CN with THF; however, the insolubility of the product has prevented adequate characterization, and a well-defined $Cp_2Zr(THF)_n^{2+}$ complex has not been isolated.

Complex **2** remains five-coordinate[9] as a solid even after 18 h under high vacuum. In contrast, the five-coordinate complex [$Cp_2Zr(CH_3)(CH_3CN)_2$][BPh_4] (**10**) loses 1 equiv of CH_3CN under high vacuum to become four-coordinate.[1,2] This indicates that the CH_3CN ligands are bonded more strongly in **2** than in **10**. Consistent with this proposal, in contrast to the ν(CN) bands for **2**, the ν(CN) bands for **10** are virtually unshifted from those of free CH_3CN.[2] In contrast to the case for **2**, the Ti complex **6** is reported to undergo partial dissociation of a CH_3CN ligand in CD_2Cl_2 solution.[7]

2. Synthesis of [Cp_2Zr(4,4′-Me_2-2,2′-bpy)(CH_3CN)][BPh_4]$_2$ (11). The reactions of **2** with several potential ligands were investigated with the aim of generating a dicationic complex with better solubility properties than **2**.

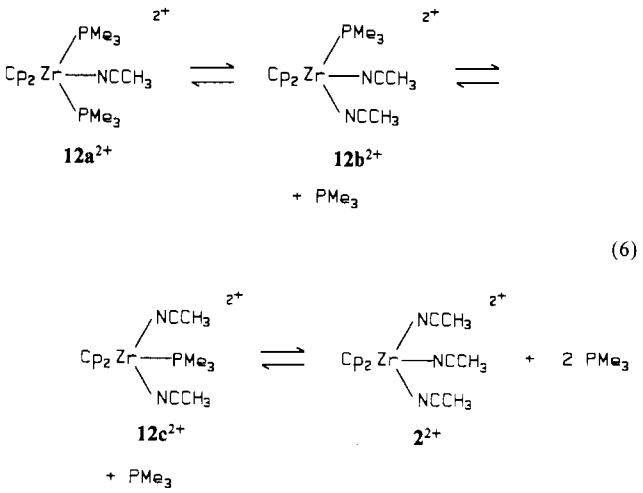
The light green solid **11** is obtained from the reaction of **2** and 1 equiv of 4,4′-dimethylbipyridine in CH_3CN. On the basis of spectroscopy and elemental analysis **11** is formulated as the Me_2bpy adduct [Cp_2Zr(4,4′-Me_2-2,2′-bpy)(CH_3CN)][BPh_4]$_2$. The IR spectrum of this compound exhibits ν(CN) for coordinated CH_3CN at 2295 and 2262 cm^{-1}.[8] The room-temperature ^{1}H NMR spectrum of a CD_3CN solution of **11** features BPh_4^- absorbances (δ 7.5–6.8, 40 H), a singlet at δ 1.95 (3 H, for 1 CH_3CN liberated per Cp_2Zr^{IV} unit), and a singlet at δ 6.40 (10 H), similar to that observed for the Cp^- ligands of **2**. These data imply that **11** contains a dication incorporating 1 equiv of CH_3CN per Zr center. The Me_2bpy resonances are shifted from those of the free ligand; in the room-temperature ^{1}H NMR spectrum the halves of the Me_2bpy ligand are equivalent while in the low-temperature spectrum they are inequivalent. As **11** incorporates only one CH_3CN ligand, and at low T the resonances for both halves of the Me_2bpy ligand are shifted from those for free Me_2bpy, it is likely that the Me_2bpy ligand is coordinated in a bidentate fashion.[10] At room temperature an exchange process of the sort shown in eq 5 is probably responsible for the apparent equivalence of the halves of the bpy ligand in the NMR spectrum.



$\mathbf{11}^{2+}$ $\mathbf{11}^{2+}$ (5)

Unfortunately, the solubility properties of **11** are very similar to those of **2**; **11** is soluble in CH_3CN but insoluble in THF.

3. Reaction of 2 with PMe_3. Addition of 3 equiv of PMe_3 to a concentrated solution of **2** in CH_3CN results in the rapid precipitation of a white, crystalline solid whose IR spectrum includes ν(CN) bands at 2300 and 2270 cm^{-1} assigned to coordinated CH_3CN.[8] The ^{1}H NMR spectrum of a CD_3CN solution of this material indicates that there is a total of ca. 1 PMe_3 ligand and ca. 2 CH_3CN ligands per Cp_2Zr unit.[11] Recrystallization from CH_3CN results in loss of some PMe_3 and a corresponding increase in CH_3CN content; the total number of ligands per Cp_2Zr unit remains constant at 3. Low-temperature ^{1}H and ^{31}P{^{1}H} NMR spectra of this material show that there are four Cp_2Zr^{IV} species in solution. In the −25 °C ^{1}H NMR spectrum, resonances assigned to the dication of **2**, two mono(trimethylphosphine) dications (δ 6.43 (d, $J_{^{31}P-^1H}$ = 0.6 Hz, Cp), 1.51 (d, $J_{^{31}P-^1H}$ = 8.4 Hz, Me); δ 6.33 (d, $J_{^{31}P-^1H}$ = 2.4 Hz, Cp), 1.53 (d, $J_{^{31}P-^1H}$ = 8.8 Hz, Me)), and a bis(trimethylphosphine) dication (δ 6.16 (t, $J_{^{31}H-^1H}$ = 2.2 Hz, Cp), 1.43 (d, $J_{^{31}P-^1H}$ = 9.0 Hz, Me)) present in the relative amounts 7:2:5:1 are observed. The −25 °C ^{31}P{^{1}H} NMR spectrum confirms the existence of three phosphine-containing products, exhibiting peaks at δ −3.5 and −4.3 assigned to PMe_3 monoadducts and a peak at δ −24.7 assigned to a PMe_3 bisadduct in the appropriate relative intensities. For comparison, ^{31}P chemical shifts for $Cp_2Zr(CH_3)(PMe_3)_2^+$ and $Cp_2Zr(H)(PMe_3)_2^+$ are δ 6.2 and 3.1, respectively.[2] Resonances for free PMe_3 are also present in the ^{1}H and ^{31}P{^{1}H} NMR spectra.[12] These data are consistent with equilibrium 6.[13]



$\mathbf{12a}^{2+}$ $\mathbf{12b}^{2+}$ (6)

$\mathbf{12c}^{2+}$ $\mathbf{2}^{2+}$

(7) (a) Bruce, M. R. M.; Tyler, D. R. *Organometallics* **1985**, *4*, 528. (b) The ^{1}H NMR spectrum of a CD_2Cl_2 solution of this complex exhibited three Cp resonances, two of which were assigned to mono CH_3CN species formed by ligand dissociation. However, the formation of Ti–F complexes in solution by F^- transfer from PF_6^- apparently was not ruled out; cf. ref 1 and: Thomas, R. R.; Chebolu, V.; Sen, A. *J. Am. Chem. Soc.* **1986**, *108*, 4096.

(8) See footnote 11 in ref 7a for a discussion of the IR spectrum of CH_3CN.

(9) The coordination number is defined as the number of ligands around the metal center. Complex **2** is nine-coordinate if the Cp^- ligands are considered tridentate.

(10) Compare to the structure claimed for [$(Cp_2ZrCl)_2(\mu$-bpy)][ClO_4]$_2$ in ref 5.

(11) ^{1}H NMR (CD_3CN, room temperature): δ 7.3–6.8 (m, BPh_4^-), 6.48 (s, $\mathbf{2}^{2+}$, 62%), (6.37 (broad s, PMe_3 monoadducts, 34%), 6.18 (t, $J_{^{31}P-^1H}$ = 2.2 Hz, PMe_3 bisadduct, 4%), 1.95 (s, CH_3CN), 1.54 (broad d, $J_{^{31}P-^1H}$ = 8.4 Hz, Zr–PMe_3), 0.98 (broad s, PMe_3).

(12) (a) ^{1}H NMR: δ 0.98 (broad s). ^{31}P{^{1}H}: δ −60.0 (s). (b) Tolman, C. A. *Chem. Rev.* **1977**, *77*, 313.

(13) Exchange between **12b** and **12c** is fast on the NMR time scale at room temperature, while exchange between **12a,b** and **12c** or **2** is slow.

The PMe_3 complexes are less soluble in CH_3CN than the parent dication $\mathbf{2}^{2+}$ and are insoluble in THF and CH_2Cl_2. This limited solubility prevented separation and precluded ^{13}C NMR analysis.

4. Reaction of 2 with Cp_2ZrR_2 Complexes. Complex **2** rapidly reacts with 1 equiv of $Cp_2Zr(CH_3)_2$ in CH_3CN at room temperature to produce $[Cp_2Zr(CH_3)(CH_3CN)_2][BPh_4]$ (**10**,[2] $t_{1/2}$ < 3 min, 100% by ^1H NMR; eq 7). In contrast, reaction between

$$\underset{\mathbf{2}}{[Cp_2Zr(CH_3CN)_3][BPh_4]_2} + Cp_2Zr(CH_3)_2 \xrightarrow[\text{room temp}]{\text{fast}} 2\underset{\mathbf{10}}{[Cp_2Zr(CH_3)(CH_3CN)_2][BPh_4]} \quad (7)$$

$$\underset{\mathbf{2}}{[Cp_2Zr(CH_3CN)_3][BPh_4]_2} + Cp_2Zr(CH_2Ph)_2 \xrightarrow[60\ ^\circ C]{\text{slow}} 2\underset{\mathbf{3}}{[Cp_2Zr(\eta^n\text{-}CH_2Ph)(CH_3CN)][BPh_4]} \quad (8)$$

complex **2** and $Cp_2Zr(CH_2Ph)_2$ in CH_3CN to form $[Cp_2Zr(\eta^n\text{-}CH_2Ph)(CH_3CN)][BPh_4]$ (**3**)[4] is relatively slow (40% by ^1H NMR, 4 h, 60 °C, CD_3CN, sealed tube). Further heating of the reaction mixture results in decomposition of the starting material. While $Cp_2Zr(CH_2Ph)_2$ is only slightly soluble in CH_3CN, experiments with $Cp_2Zr(CH_3)_2$ at dilute concentration show that this is not the origin of the rate difference and that the reaction of $Cp_2Zr(CH_3)_2$ with **2** is inherently faster than that of $Cp_2Zr(CH_2Ph)_2$. The use of THF (in which **2** is insoluble) as the solvent for the $Cp_2Zr(CH_2Ph)_2$ reaction results in about the same reaction rate (45%, 5 h, 50 °C, sealed tube, THF-d_8); however, only the CH_3CN adduct **3** is formed along with small amounts of other unidentified Cp_2Zr products. Since neither the dication of **2** nor $Cp_2Zr(\eta^n\text{-}CH_2Ph)(CH_3CN)^+$ ($\mathbf{3}^+$) undergo THF substitution at an appreciable rate, this result is not surprising.

The trend in rate of comproportionation with **2**, $Cp_2Zr(CH_3)_2 >> Cp_2Zr(CH_2Ph)_2$, reflects the facility with which $^-CH_3$ and $^-CH_2Ph$ ligands are transferred between Cp_2Zr^{IV} centers. For example, in CH_3CN, comproportionation of $Cp_2Zr(CH_3)_2$ and Cp_2ZrI_2 (to produce $Cp_2Zr(R)(I)$) is fast (room temperature, 5 min) and that of $Cp_2Zr(CH_2Ph)_2$ and Cp_2ZrI_2 is relatively slow (room temperature, days). The relative importance of steric and electronic contributions to this trend is not yet clear.[14,15]

5. Reaction of 2 with Cp_2ZrX_2 Complexes. Mixture of $[Cp_2Zr(CH_3CN)_3][BPh_4]_2$ (**2**) and Cp_2ZrCl_2 in CD_3CN at room temperature results in the formation of an equilibrium mixture whose ^1H NMR spectrum consists of sharp absorbances at δ 6.52, 6.45, and 6.37. The two downfield peaks are assigned to Cp_2ZrCl_2 and the dication of **2**, respectively, by comparison to the peaks of actual samples; the upfield peak is assigned to $Cp_2ZrCl(CH_3CN)_n^+$. The results are consistent with the equilibrium shown in (9) with exchange slow on the NMR time scale. Reaction 9

$$Cp_2ZrX_2 + \underset{\mathbf{2}}{[Cp_2Zr(CH_3CN)_3][BPh_4]_2} \rightleftharpoons 2[Cp_2ZrX(CH_3CN)_n][BPh_4] \quad (9)$$

reaches equilibrium within 2 h (K_{eq} = 1.0 ± 0.1). This equilibrium may also be reached from the opposite direction by mixture of **2** with 1 equiv of $[R_4N]Cl$, but not by mixture of Cp_2ZrCl_2 with 1 equiv of $Ag[BPh_4]$ as there is no reaction between the latter two compounds in CH_3CN. $[Cp_2ZrCl(CH_3CN)_n^+][BPh_4]$ could not be isolated.

The reaction of **2** with Cp_2ZrBr_2 in CH_3CN is similar; an equilibrium mixture of **2**, Cp_2ZrBr_2 (s, δ 6.56), and $Cp_2ZrBr(CH_3CN)_n^+$ (s, δ 6.43) is produced (K_{eq} = 2.5 ± 0.3). In this case the equilibrium may be approached from the opposite direction by reaction of $Ag[BPh_4]$ with Cp_2ZrBr_2 in CH_3CN.

^1H NMR spectra of CD_3CN solutions containing the dication of **2** and Cp_2ZrI_2 or Cp_2ZrF_2 exhibit only broad Cp resonances typical of chemically exchanging systems over the temperature range +25 to −35 °C. As the dication of **2** is only soluble in CH_3CN (mp −44 °C), the useful temperature range for study is limited. However, it is certain that both halides react with **2** and it is likely that equilibria of the sort shown in eq 9 result from these reactions. Cp_2ZrI_2 reacts with $Ag[BPh_4]$ to form a mixture, the ^1H NMR spectrum of which is similar to that obtained when it is reacted with **2**, while Cp_2ZrF_2 is unreactive with $Ag[BPh_4]$. The increased lability of the F^- and I^- systems vs. that of the Cl^- and Br^- systems is consistent with previous results.[15a]

The facile disproportionation of $Cp_2ZrX(CH_3CN)_n^+$ complexes is surprising in view of the relative stability of $Cp_2Zr(R)(L)_n^+$ complexes[1,2] and the reported properties of $Cp_2Zr(X)(L)^+$ complexes **7** and **8**.[5]

Conclusion

The five-coordinate dicationic complex $[Cp_2Zr(CH_3CN)_3][BPh_4]_2$ (**2**) has been prepared and fully characterized. Complex **2** forms a stable 4,4′-dimethylbipyridine derivative, $[Cp_2Zr(4,4'\text{-}Me_2\text{-}2,2'\text{-}bpy)(CH_3CN)][BPh_4]_2$ (**11**), while reaction with PMe_3 produces a complex mixture of Cp_2Zr^{IV}–PMe_3 products. All of these complexes are soluble in CH_3CN but not THF or CH_2Cl_2; it is likely that substituted Cp^- ligands will be required for more soluble $Cp_2ZrL_n^{2+}$ complexes. The dication of **2** does not form a soluble THF derivative, and the goal of preparing $Cp_2Zr(\eta^n\text{-}CH_2Ph)(THF)_n^+$ by comproportionation of $Cp_2Zr(CH_2Ph)_2$ and $Cp_2Zr(THF)_n^{2+}$ was not realized. The observation that $Cp_2Zr(CH_2Ph)_2$ reacts much more slowly with **2** (eq 8) than with $Ag[BPh_4]$ (eq 3) rules out mechanisms for the latter reaction that involve the intermediacy of the dication of **2**.[3,16] The trend in reactivity with complex **2**, $Cp_2Zr(CH_3)_2 >> Cp_2Zr(CH_2Ph)_2$, is similar to that with Cp_2ZrI_2. Apparently redistribution of $^-CH_2Ph$ ligands between Cp_2Zr^{IV} centers is inherently slow vs. that of $^-CH_3$. Halide cations $Cp_2ZrX(CH_3CN)_n^+$ are unstable toward disproportionation in CH_3CN in contrast to the case for the alkyl cations $Cp_2Zr(R)(L)_n^+$, which are stable.[1-3] The origin of this difference is not yet understood.

Experimental Section

All manipulations were performend under an inert atmosphere or under vacuum with use of a Vacuum Atmospheres drybox or high-vacuum line. Solvents were purified by using appropriate procedures[17] prior to use, stored in evacuated bulbs, and vacuum-transferred into reactions flasks or NMR tubes. NMR spectra were recorded on JEOL FX-90Q or Nicolet 200 instruments in sealed tubes. ^1H and ^{13}C shifts are reported in ppm downfield from Me_4Si with residual solvent protons used as an internal reference. ^{31}P shifts are reported in ppm downfield from 85% H_3PO_4. IR spectra were recorded on a Perkin-Elmer 283 spectrometer. Elemental analyses were performed by Schwarzkopf Analytical Laboratories.

Cp_2ZrCl_2 was purchased from Alfa. $Cp_2Zr(CH_3)_2$,[18] $Cp_2Zr(CH_2Ph)_2$,[19] Cp_2ZrI_2,[20] Cp_2ZrBr_2,[20] and Cp_2ZrF_2[20] were prepared by using previously published procedures. PMe_3 was vacuum-distilled and degassed by three freeze–pump–thaw cycles prior to use. 4,4′-Dimethylbipyridine was purchased and used without further purification. $[(CH_2Ph)(Et)_3N]Cl$ was dried at 100 °C in vacuo for 12 h prior to use. $Ag[BPh_4]$ was prepared by metathesis of $Na[BPh_4]$ and $Ag[NO_3]$ followed by extensive washing with hot distilled H_2O to remove NO_3^- impurities.

Reported K_{eq} values were calculated from ^1H NMR peak integrals; the reported values are averaged from two to three experiments.

$[Cp_2Zr(CH_3CN)_3][BPh_4]_2$ (2). A 5.55-g (12.6-mmol) amount of $Ag[BPh_4]$ was added in small portions to a slurry of 3.00 g (6.31 mmol) of Cp_2ZrI_2 in 125 mL of CH_3CN at −40 °C. The reaction mixture was warmed to 0 °C, at which time a light tan precipitate was observed.

(14) (a) Weak η^n interactions in the benzyl case may slow the transmetalation as suggested by a reviewer. Note that the Zr–CH_3 bond is probably ca. 10 kcal stronger than the Zr–CH_2Ph bond. (b) Lappert, M. F.; Patil, D. S.; Pedley, J. B. *J. Chem. Soc., Chem. Commun.* **1975**, 830. (c) Bruno, J. W.; Marks, T. J.; Morss, L. R. *J. Am. Chem. Soc.* **1983**, *105*, 6824. (d) Conner, J. A. *Top. Curr. Chem.* **1977**, *71*, 71.

(15) For related ligand redistribution reactions see: (a) Jordan, R. F. *J. Organomet. Chem.* **1985**, *294*, 321. (b) Puddephatt, R. J.; Stalteri, M. A. *Organometallics* **1983**, *3*, 1716.

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After the mixture was stirred for 1 h at 0 °C and 2 h at room temperature, it was filtered, giving a light yellow filtrate and a tan solid. The solid was extracted until the extracts were colorless, and the filtrate and extracts were combined. The solvent was removed under vacuum and the white, highly air-sensitive product recrystallized from CH_3CN/Et_2O and dried under vacuum for 12 h; yield 4.45 g (72%). ^1H NMR (CD_3CN): δ 7.50–6.70 (m, 40 H), 6.49 (s, 10 H), 1.95 (s, 9 H). $^{13}C\{^1H\}$ NMR (CD_3CN): δ 165 (q, $J_{^{13}C-^{11}B}$ = 49 Hz), 136.7, 126.5, 122.8, 116.6 (Cp_2Zr^{2+}). IR (KBr): ν(CN) 2295, 2270 cm^{-1}. Anal. Calcd: C, 78.20; H, 6.05; N, 4.27; Zr, 9.28. Found: C, 78.43; H, 6.19; N, 4.12; Zr, 9.46.

$[Cp_2Zr(4,4'\text{-}Me_2\text{-}2,2'\text{-}bpy)(CH_3CN)][BPh_4]_2$ (11). A 1.00-g (1.02-mmol) amount of **2** was dissolved in 30 mL of CH_3CN. A 0.188-g (1.02-mmol) amount of 4,4'-dimethylbipyridine was added and the reaction mixture stirred for 21 h at room temperature with the mixture gradually turning a dark green. A light green powder was isolated by removing the solvent and washing the product several times with THF; yield 0.74 g (67%). ^1H NMR (CD_3CN): δ 8.64 (d, J_{HH} = 6 Hz, 2 H), 8.33 (broad s, 2 H), 7.62 (d, J_{HH} = 6 Hz, 2 H), 7.5–6.8 (m, 40 H, BPh_4^-), 6.40 (s, 10 H), 2.60 (s, 6 H), 1.95 (s, 3 H). ^1H NMR (CD_3CN, −27 °C): δ 8.81 (d, J_{HH} = 6 Hz, 1 H), 8.40 (d, J_{HH} = 6 Hz, 1 H), 8.32 (broad s, 2 H), 7.59 (d, J_{HH} = 6 Hz, 1 H), 7.58 (d, J_{HH} = 6 Hz, 1 H), 7.5–6.8 (m, 40 H, BPh_4^-), 6.33 (s, 10 H), 2.56 (s, 6 H), 1.95 (s, 3 H). $^{13}C\{^1H\}$ NMR (CD_3CN): δ 165 (q, $J_{^{13}C-^{11}B}$ = 48 Hz), 157.0, 154.0, 152.9, 136.7, 129.0, 126.4, 122.0, 117.4 (Cp_2Zr), 21.7 (Me_2bpy). IR (KBr): ν(CN) 2295, 2262 cm^{-1}. Anal. Calcd: C, 79.69; H, 6.04; N, 3.87; Zr, 8.41. Found: C, 79.73; H, 6.29; N, 3.68; Zr, 8.14.

Reaction of 2 with PMe_3. A 0.45-g (5.90-mmol) amount of PMe_3 was vacuum-distilled into a solution of 1.90 g (1.93 mmol) of **2** in 30 mL of CH_3CN at −40 °C. After 1 min of stirring, a large amount of white solid precipitated. The reaction mixture was warmed to room temperature and stirred for 1.5 h. The white solid was collected by filtration (crude yield 1.73 g) and recrystallized from CH_3CN. The ^1H and $^{31}P\{^1H\}$ NMR spectra are described in the text. IR (KBr): ν(CN) 2300, 2270 cm^{-1}.

Reaction of 2 with $Cp_2Zr(CH_3)_2$. A 0.5-mL amount of CD_3CN was added to 39 mg (0.04 mmol) of **2** and 10 mg (0.04 mmol) of $Cp_2Zr(CH_3)_2$ in an NMR tube. The tube was flame-sealed and the reaction progress followed by ^1H NMR.

In a preparative-scale experiment 2.25 g (2.29 mmol) of **2** and 0.60 g (2.38 mmol) of $Cp_2Zr(CH_3)_2$ were stirred together in 30 mL of CH_3CN. After 10 min white, crystalline $[Cp_2Zr(CH_3)(CH_3CN)_2][BPh_4]$ precipitated,[2] from which was isolated $[Cp_2Zr(CH_3)(THF)][BPh_4]$ as previously described;[1] yield 2.40 g (84%).

Reaction of 2 with $Cp_2Zr(CH_2Ph)_2$. A 0.5-mL amount of CD_3CN was added to 24 mg (0.02 mmol) of **2** and 10 mg (0.02 mmol) of $Cp_2Zr(CH_2Ph)_2$ in an NMR tube. The tube was flame-sealed and heated to 60 °C in an oil bath and the reaction progress monitored by ^1H NMR. After 4 h peaks corresponding to starting materials and a 40% yield of $Cp_2Zr(\eta^n\text{-}CH_2Ph)(CH_3CN)^+$ (s, δ 6.00; s, δ 2.74)[4] were observed. Further heating resulted in decomposition of the starting materials to unidentified Cp_2Zr products. In a similar manner 0.5 mL of THF was added to **2** and $Cp_2Zr(CH_2Ph)_2$ in an NMR tube, which was sealed and heated at 50 °C. After 5 h peaks corresponding to starting materials and a 45% yield of $Cp_2Zr(\eta^n\text{-}CH_2Ph)(CH_3CN)^+$ (s, δ 5.98; s, δ 2.75) were observed. Further heating resulted in decomposition of the starting materials. The presence of coordinated CH_3CN was confirmed by the position of its absorbance at δ 1.73 shifted upfield from that of free CH_3CN (δ 1.89).

Reaction of 2 with Cp_2ZrX_2. A 1.0-mL amount of CD_3CN was added to 34 mg (0.034 mmol) of **2** and 10 mg (0.034 mmol) of Cp_2ZrCl_2 in an NMR tube, giving a light yellow solution. The tube was sealed and the reaction monitored by ^1H NMR. The same method was used in the reactions of **2** with Cp_2ZrBr_2, Cp_2ZrI_2, and Cp_2ZrF_2. The ^1H NMR data for the Cp_2ZrCl_2 and Cp_2ZrBr_2 reactions are given in the text. ^1H NMR (Cp_2ZrI_2 reaction, CD_3CN): broad singlets for Cp at δ 6.50 and 6.46, and a sharp singlet at δ 6.41. ^1H NMR (Cp_2ZrF_2 reaction, CD_3CN): broad singlets for Cp at δ 6.42 and 6.32.

Reaction of 2 with $[(CH_2Ph)Et_3N]Cl$. A 43-mg (0.044-mmol) amount of **2** was added to a solution of 10 mg (0.044 mmol) of $[(CH_2Ph)Et_3N]Cl$ in 0.5 mL of CD_3CN. The ^1H NMR spectrum of this mixture revealed an equilibrium mixture of **2**, Cp_2ZrCl_2, and $Cp_2ZrCl(CH_3CN)_n^+$ with K_{eq} = 1.0 ± 0.1.

Reaction of $Ag[BPh_4]$ with Cp_2ZrBr_2. A 0.5-mL amount of CD_3CN was added to an NMR tube containing 10 mg (0.026 mmol) of Cp_2ZrBr_2 and 11 mg (0.026 mmol) of $Ag[BPh_4]$. The tube was sealed and centrifuged upside down to remove AgBr and the reaction monitored by ^1H NMR. ^1H NMR (CD_3CN): δ 7.5–6.8 (BPh_4^-), 6.56 (s, Cp_2ZrBr_2), 6.49 (s, $[Cp_2Zr(CH_3CN)_3]^{2+}$), 6.43 (s, $Cp_2ZrBr(CH_3CN)_n^+$).

The reactions of $Ag[BPh_4]$ with the other halides were performed in a similar manner. ^1H NMR (Cp_2ZrCl_2 reaction, CD_3CN): only starting Cp_2ZrCl_2 was observed (s, δ 6.51) even after 1 week at room temperature. ^1H NMR (Cp_2ZrF_2 reaction, CD_3CN): only starting Cp_2ZrF_2 was observed (s, δ 6.43). ^1H NMR (Cp_2ZrI_2 reaction, CD_3CN): broad singlets for Cp at δ 6.48 and 6.47 and a sharp singlet at δ 6.41.

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