

tailed chemical investigation of the resulting dodecahedranes.

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Reactive Cationic Dicyclopentadienylzirconium(IV) Complexes

Richard F. Jordan,* William E. Dasher,[†] and Scott F. Echols

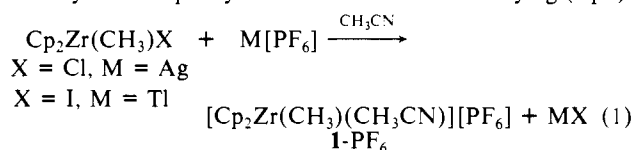
Department of Chemistry, Washington State University
Pullman, Washington 99164

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Electron deficient early-transition-metal complexes are highly reactive with a variety of small molecules and organic substrates as exemplified by the now classic studies of dicyclopentadienylzirconium(IV) and -titanium(IV) compounds.¹ Attempts to extend this chemistry by increasing the electrophilicity of the metal center have involved replacement of (6-e⁻ donor) cyclopentadienyl ligands with 2-e⁻ donor ligands as well as investigation of related dicyclopentadienyl compounds of group III (3),²⁵ lanthanide, and actinide metals.¹¹ Notable recent work includes the alkylation of carbonyl compounds by TiR_mX_{4-m},² the complete scission of CO by CpZrCl(diene),³ intramolecular oxygen transfer in [(Me₃C)₃CO]₂ZrR₂,⁴ and olefin polymerization and C-H activation by (C₅Me₅)₂LuR.⁵ In an alternate approach to this problem we began an investigation of cationic dicyclopentadienyl Zr(IV) complexes of the type Cp₂ZrR⁺. Previously the 14-electron fragment Cp₂ZrCH₃⁺ had been incorporated in a variety of heterobimetallic compounds of both metal-metal bonded and iso-carbonyl structures.⁶ As initial observations indicate that reactions involving both metal centers will play a major role in the chemistry of such bimetallic compounds,⁷ we sought simpler monometallic systems incorporating unreactive noncoordinating anions.⁸ We report here the preparation of Cp₂ZrR⁺ complexes via X⁻ or R⁻

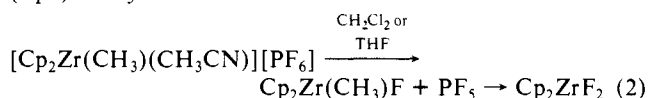
abstraction from Zr(IV) by Ag⁺ and several reactions which demonstrate the high electrophilicity of these complexes.

Reaction of Cp₂Zr(CH₃)Cl with AgPF₆ or of Cp₂Zr(CH₃)I with TlPF₆ in CH₃CN followed by filtration and concentration of the filtrate produced [Cp₂Zr(CH₃)(CH₃CN)][PF₆] (1-PF₆) in 75% yield as a pale yellow solid after vacuum drying (eq 1).



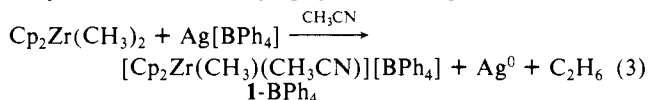
This compound was characterized spectroscopically,⁹ in particular a singlet in the ¹H NMR (CD₃CN) spectrum at δ 1.95 integrating for 3 H and IR ν_{CN} bands at 2310 and 2283 cm⁻¹ shifted from 2287 and 2251 cm⁻¹ for free CH₃CN indicate the presence of a coordinated CH₃CN ligand.¹⁰ In CD₃CN the ¹H NMR resonances for the Cp and Zr-CH₃ groups of 1-PF₆ appear at δ 6.11 and 0.09, values that are nearly identical with those observed for the heterobimetallic compounds Cp₂ZrCH₃(μ-OC)M(CO)₂Cp (M = Cr, Mo, W) which exhibit substantial conductivity in this solvent.^{6b}

While stable as a solid, 1-PF₆ decomposed instantaneously in THF and in CH₂Cl₂ to Cp₂Zr(CH₃)F via F⁻ abstraction from PF₆⁻ (eq 2). PF₅ was not detected in this reaction but its formation



was implicated by the observed polymerization of the solvent in the THF experiment. Cp₂ZrF₂, presumably formed by CH₃/F exchange between Cp₂Zr(CH₃)F and PF₅,¹¹ was observed as a secondary reaction product. A similar but much slower (days) decomposition was observed in CH₃CN.¹²

Previously we had observed that while CH₃/F exchange between Cp₂Zr(CH₃)₂ and Cp₂ZrF₂ was fast, phenyl/F exchange between Cp₂ZrPh₂ and Cp₂ZrF₂ was extremely slow.¹¹ This suggested that use of BPh₄⁻ as a counterion might provide a more stable compound for study. [Cp₂Zr(CH₃)(CH₃CN)][BPh₄] (1-BPh₄) was prepared most conveniently by reaction of Cp₂Zr(CH₃)₂ with AgBPh₄ in CH₃CN followed by filtration, recrystallization from CH₃CN, and vacuum drying (yield 80%, eq 3).¹³ The ¹H and



¹³C NMR and IR spectra of 1-BPh₄ are nearly identical with those of 1-PF₆ except for characteristic BPh₄⁻ absorbances.¹⁴ The other products of this reaction, Ag⁰ and ethane (which was identified by its characteristic ¹H NMR signal at δ 0.86 but was not quantified), are those expected from the thermal decomposition of AgCH₃, a possible intermediate in this reaction.¹⁵ In contrast to its PF₆⁻ analogue, 1-BPh₄ is stable in THF solution. In this

[†] Visiting summer fellow from University of Puget Sound, Tacoma, WA.

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(8) Several cationic Cp₂M (M = Ti, Zr) complexes have been reported.

(a) [(Cp₂Ti(H₂O))₂O][S₂O₈]; Thewalt, U.; Schleussner, G. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 531. (b) [Cp₂Ti(H₂O)₂][ClO₄]₂; Thewalt, U.; Klein, H.-P. *J. Organomet. Chem.* **1980**, *194*, 297. (c) [(Cp₂Ti(H₂O))₂O][ClO₄]₂; Thewalt, U.; Keibel, B. *J. Organomet. Chem.* **1978**, *150*, 59. (d) [Cp₂ZrCH₂CH(AlEt₂)₂][Cp]; Kaminsky, W.; Kopf, J.; Sinn, H.; Vollmer, J. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 629. (e) [Cp₂Ti(CH₃CN)₂][PF₆]₂; Bruce, M. R. M.; Tyler, D. R. *Organometallics* **1985**, *4*, 528.

(9) 1-PF₆ ¹H NMR (CD₃CN) δ 6.11 (s, 10 H), 1.95 (s, 3 H), 0.09 (s, 3 H, ZrCH₃); ¹³C{¹H} NMR (CD₃CN) δ 112.6, 28.0 (J_{13C-1H} = 121 Hz); ³¹P NMR (CD₃CN) δ -143.4 (septet, J_{1P-19F} = 707 Hz); IR (KBr) ν_{CN} 2310, 2283 cm⁻¹, ν_{PF₆} 835, 561 cm⁻¹.

(10) For a discussion of the IR spectrum of CH₃CN see footnote 11 in ref 8e.

(11) Jordan, R. F. *J. Organomet. Chem.* **1985**, *294*, 321.

(12) (a) 1-BF₄, prepared from Cp₂Zr(CH₃)₂ and HBF₄·Et₂O, decomposes similarly. (b) For a review of F⁻ transfer reactions, see: Reedijk, J. *Comments Inorg. Chem.* **1982**, *24*, 379.

(13) This reaction was suggested by the observation of minor amounts of ethane product in the reaction of Cp₂Zr(CH₃)Cl with AgNO₃. Jordan, R. F., unpublished work.

(14) 1-BPh₄ ¹H NMR (CD₃CN) δ 7.4-6.7 (m, 20 H, BPh₄⁻) 6.07 (s, 10 H), 1.95 (s, 3 H), 0.079 (s, 3 H, ZrCH₃); ¹¹B NMR (THF) δ -6.31 s; ¹³C NMR (CD₃CN) δ 165 (q, J_{13C-11B} = 50 Hz), 136.6, 126.4, 122.6, 112.1 (Cp₂Zr), 30.8 (ZrCH₃); IR (KBr) ν_{CN} 2303, 2273 cm⁻¹.

(15) (a) Beverwijk, C. D. M.; van der Kerck, G. J. M.; Leusink, A. G.; Noltes, J. G. *Organometallic Chem. Rev. Sect. A*, **1970**, *5*, 215. (b) Experiments designed to probe the mechanism of this reaction are under way. (c) Reaction of boron alkyls with Ag⁺ also gives alkyl coupling products. Brown, H. C.; Snyder, C. H. *J. Am. Chem. Soc.* **1961**, *83*, 1002.

solvent coordinated CH_3CN was displaced yielding the THF adduct $[\text{Cp}_2\text{Zr}(\text{CH}_3)(\text{THF})][\text{BPh}_4^-]$ (**2-BPh₄**) which was isolated as a pale yellow crystalline solid.¹⁶ **1-BPh₄** also formed stable complexes with the hard unhindered Lewis bases 4,4'-dimethylbipyridine and 4-(dimethylamino)pyridine in CH_3CN but not with PF_3 or diphos.¹⁷

As expected for $\text{Cp}_2\text{Zr}^{\text{IV}}$ complexes lacking π donor ligands,¹⁸ **1** and **2** reacted rapidly with CO in CH_3CN to produce (in the BPh_4^- cases) $[\text{Cp}_2\text{Zr}(\text{COCH}_3)(\text{CH}_3\text{CN})][\text{BPh}_4^-]$ (**3-BPh₄**) isolated (70%) as a yellow solid.¹⁹ Unlike neutral $\text{Cp}_2\text{Zr}^{\text{IV}}$ acyl complexes, **3-BPh₄** and its THF and PF_6^- analogues did not release CO under vacuum.²⁰ Also, unlike neutral $\text{Cp}_2\text{Zr}^{\text{IV}}$ alkyl complexes,^{21,22} the cationic zirconium alkyls **1** and **2** add rapidly to ketones under mild conditions. For example, **1-BPh₄** reacted with benzophenone at room temperature in THF (ca. 1 h) to produce $[\text{Cp}_2\text{Zr}(\text{OCPh}_2\text{CH}_3)(\text{THF})][\text{BPh}_4^-]$ (**4**) (100% by ¹H NMR).²³ When this reaction was monitored by ¹H NMR spectroscopy, transient signals (δ 6.22 (s, 10 H), 0.47 (s, 3 H)) presumably due to an intermediate adduct $[\text{Cp}_2\text{Zr}(\text{CH}_3)(\text{OCPh}_2)]^+[\text{BPh}_4^-]$ were observed. In contrast, $\text{Cp}_2\text{Zr}(\text{CH}_3)_2$ reacted only extremely slowly with benzophenone (30% complete after 70 h, 110 °C, sealed tube) to produce $\text{Cp}_2\text{Zr}(\text{CH}_3)(\text{OCPh}_2\text{CH}_3)$.

The observed F^- abstraction from PF_6^- , the selectivity for adduct formation with Lewis bases, and the reactivity with CO and carbonyl compounds characterize the fragment $\text{Cp}_2\text{ZrCH}_3^+$ as a highly electrophilic hard Lewis acid. We are currently exploring the reactivity of **1-3**, and other cationic $\text{Cp}_2\text{Zr}^{\text{IV}}$ complexes, with olefins, acetylenes, and other substrates.²⁴

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American Chemical Society, and the Washington State University Research and Arts Committee is gratefully acknowledged.

Registry No. **1-PF₆**, 100909-46-4; **1-BPh₄**, 100909-48-6; **2-BPh₄**, 100909-50-0; **3-BPh₄**, 100909-54-4; **4**, 100909-56-6; $\text{Cp}_2\text{Zr}(\text{CH}_3)\text{Cl}$, 1291-45-8; $\text{Cp}_2\text{Zr}(\text{CH}_3)\text{I}$, 63643-49-2; $\text{Cp}_2\text{Zr}(\text{CH}_3)\text{F}$, 100909-47-5; Cp_2ZrF_2 , 11090-85-0; $\text{Cp}_2\text{Zr}(\text{CH}_3)_2$, 12636-72-5; $\text{Cp}_2\text{Zr}(\text{CH}_3)(\text{OCPh}_2\text{CH}_3)$, 100909-57-7; $[\text{Cp}_2\text{Zr}(\text{CH}_3)(4,4'\text{-dimethylbipyridine})][\text{BPh}_4^-]$, 100909-52-2; benzophenone, 119-61-9.

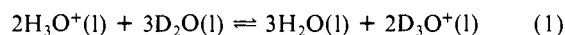
Deuterium Fractionation Factor for the Gas-Phase Hydronium Ion

J. W. Larson and T. B. McMahon*

Department of Chemistry, University of Waterloo
Waterloo, Ontario, Canada N2L 3G1

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The hydronium ion, L_3O^+ where $\text{L} = \text{D}$ or H , plays a central role in the interpretation of isotope effects in aqueous solutions. Several workers¹⁻⁵ have measured the isotope effect for the hydronium ion in deuterated aqueous solutions which may be expressed in terms of the equilibrium constant for reaction 1, K_1



= 0.11. More commonly, however, the isotope effect is reported in terms of a fractionation factor,^{6,7} ϕ_1 , that expresses, on a per hydrogen basis with statistical effects removed, the effect of the change in environment in proceeding from bulk solvent to solvated solute. The fractionation factor for the hydronium ion is equal to $(K_1)^{1/6}$ and has a value of 0.69 ± 0.02 . This value indicates that, relative to water protium is accumulating in the hydronium ion and therefore the force field for O-H bonds in the hydronium ion is weaker than in water. Both the positive charge and the hydrogen bonding of the hydronium ion to solvent water, as indicated in the formula $\text{O}(\text{L} \cdots \text{OL}_2)_3^+$, could contribute to this weakening of the proton bond.⁷⁻⁹ Recently, Kurz et al.¹⁰ have investigated the relative importance of these two factors by measuring the fractionation factor of hydronium ion in acetonitrile. They obtained a fractionation factor of 0.79 for this *unhydrated hydronium ion* and concluded that either hydrogen bonding is of secondary importance in influencing the fractionation factor or that the hydrogen bonding from L_3O^+ to NCCH_3 is almost as effective in weakening the force field as is the hydrogen bonding in the aqueous system. The value of the fractionation factor for the completely unsolvated, gaseous hydronium ion should provide considerable insight into this question. The statistical mechanical calculations of Henchman, Smith, and Adams¹¹ contain estimates that lead to a fractionation factor for gaseous L_3O^+ with a large uncertainty. In the present paper we report the first accurate experimental determination of the fractionation factor for the hydronium ion in the gas phase.

A mixture of $\text{H}_2\text{O}(\text{l})$ and $\text{D}_2\text{O}(\text{l})$ was made up by weight and placed in a large glass bulb. The partial pressures of $\text{H}_2\text{O}(\text{g})$,

(16) **2-BPh₄**: ¹H NMR (CD_2Cl_2) δ 7.6-6.7 (m, 20 H, BPh_4^-) 6.31 (s, 10 H), 3.44 (m, 4 H, THF), 1.80 (m, 4 H, THF), 0.74 (s, 3 H). The absorbances due to coordinated THF are shifted 0.23 and 0.01 δ upfield from those of free THF (3.67, 1.81) in this solvent. Anal. Calcd: C, 74.62; H, 6.58, Zr, 14.53. Found: C, 74.51, H, 6.63, Zr, 14.52.

(17) $[\text{Cp}_2\text{Zr}(\text{CH}_3)(4,4'\text{-dimethylbipyridine})][\text{BPh}_4^-]$: Isolated as the toluene solvate by recrystallization from $\text{CH}_3\text{CN}/\text{toluene}$. Anal. Calcd for $\text{C}_{54}\text{H}_{53}\text{N}_3\text{Bzr}$: C, 77.95; H, 6.42; N, 3.37. Found C, 77.75; H, 6.34; N, 3.56. ¹H NMR (CD_3CN) δ 8.70 (d, 7 Hz, 1 H), 8.49 (d, 6 Hz, 1 H), 8.19 (s, br, 2 H), 7.54 (d, 7 Hz, 1 H), 7.4-6.6 (m, 21 H, BPh_4^- and bpy) 5.93 (s, 10 H), 2.56 (s, 3 H), 2.51 (s, 3 H), 0.43 (s, 3 H, ZrCH_3); ¹³C{¹H} NMR (THF-*d*₆) δ 165 (q, $J_{13\text{C}-11\text{B}} = 49.5$ Hz), 156.0, 155.1, 154.4, 152.9, 152.8, 152.0, 137.0, 128.0, 125.9, 122.0, 112.4, (Cp_2Zr), 35.9 (ZrCH_3 , $J_{13\text{C}-1\text{H}} = 121$ Hz from gated decoupled spectrum), 21.7.

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(19) **3-BPh₄**: ¹H NMR (CD_3CN) δ 7.4-6.7 (m, 20 H, BPh_4^-) 6.00 (s, 10 H), 3.06 (s, 3 H), 1.95 (s, 3 H); ¹³C{¹H} NMR (CD_3CN) δ 315.0 (ZrCOCH_3), 164.6 (q, $J_{13\text{C}-11\text{B}} = 49.5$ Hz), 136.6, 126.5, 122.6, 110.6 (Cp_2Zr), 33.8 (CH_3); IR ν_{CN} 2304, 2276 cm^{-1} , ν_{CO} 1563 cm^{-1} . Anal. Calcd: C, 73.06; H, 5.81; N, 2.24; B, 1.73; Zr, 14.60. Found: C, 72.78; H, 5.98; N, 2.49; B, 1.90; Zr, 14.36.

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(21) Cp_2ZrR_2 and Cp_2ZrRX complexes are reported to be unreactive with ketones.^{16,2} However, $\text{Cp}_2\text{Zr}^{\text{IV}}$ allyl and enolate complexes react with a variety of carbonyl substrates²² as do $\text{R}_n\text{MX}_{4-n}$ ($\text{M} = \text{Ti}, \text{Zr}$).²

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(23) **4**: ¹H NMR (CD_3CN) δ 7.5-6.7 (m, 30 H), 6.32 (s, 10 H), 3.65 (m, 4 H), 1.95 (OCCH_3 , masked by solvent peak), 1.80 (m, 4 H); ¹H NMR (THF-*d*₆) δ 7.5-6.7 (m, 30 H), 6.28 (s, 10 H), 1.93 (s, 3 H); ¹³C{¹H} NMR (CD_3CN) δ 164 (q, $J_{13\text{C}-11\text{B}} = 50$ Hz), 148.5, 136.4, 128.8, 127.7, 126.3, 122.4, 115.4, 88.4 ($\text{ZrOCPh}_2\text{CH}_3$), 68.1 (THF), 31.5, 26.1 (THF).

(24) Eisch and co-workers recently reported evidence implicating $\text{Cp}_2\text{TiCH}_3^+$ as the active species in the $\text{Cp}_2\text{TiCl}_2/\text{CH}_3\text{AlCl}_2$ Ziegler-Natta ethylene polymerization model system. Eisch, J. J.; Piotrowski, A. M.; Brownstein, S. K.; Gabe, E. J.; Lee, F. L. *J. Am. Chem. Soc.* **1985**, *107*, 7219.

(25) In this paper the periodic group notation in parentheses is in accord with recent reactions by IUPAC and ACS nomenclature committees. A and B notation is eliminated because of wide confusion. Groups 1A and 11A become groups 1 and 2. The d-transition elements comprise groups 3 through 12, and the p-block elements comprise groups 13 through 18. (Note that the former Roman number designation is preserved in the last digit of the new numbering: e.g., 111 \rightarrow 3 and 13.)

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