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Hydrogenation of Cationic Dicyclopentadienyl Zirconium(IV) Alkyl Complexes. Characterization of Cationic Zirconium(IV) Hydrides

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The cationic Zr(IV) alkyl complex $[Cp_2Zr(CH_3)(THF)][BPh_4]$ (1) undergoes hydrogenation to the insoluble hydride complex $[Cp_2Zr(H)(THF)][BPh_4]$ (6) under mild conditions (23 °C, 1 atm of H_2). This reaction is faster in CH_2Cl_2 ($t_{1/2}$ = 5 h) than in THF ($t_{1/2}$ = 21 h) and in the latter solvent is ca. 5 times faster than hydrogenation of $Cp_2Zr(CH_3)_2$ (2) to $[Cp_2Zr(CH_3)(\mu\text{-}H)]_2$ (8). In CH_3CN, 1 forms the 18-electron complex $[Cp_2Zr(CH_3)(CH_3CN)_2][BPh_4]$ (3) which does not undergo significant reaction with H_2. Reaction of 1 with PMe_3 yields $[Cp_2Zr(CH_3)(PMe_3)_2][BPh_4]$ (10) which undergoes rapid PMe_3 exchange at 23 °C in THF and CH_2Cl_2 and very rapid ($t_{1/2}$ < 2 min) hydrogenation to the nonlabile hydride complex $[Cp_2Zr(H)(PMe_3)_2][BPh_4]$ (13). Complex **13** crystallizes in the monoclinic space group $P2_1/c$ with a = 11.249 (4) Å, b = 19.082 (6) Å, c = 17.391 (5) Å, β = 99.57 (3)°, Z = 4, and R_{wF} = 6.53%. **13** exhibits a normal bent metallocene structure with the hydride ligand in the central position in the plane between the two Cp^- ligands. PMe_2Ph coordinates weakly to 1; in the presence of 17 equiv of PMe_2Ph, 1 undergoes rapid ($t_{1/2}$ = ca. 8 min) hydrogenation to the nonlabile hydride complex $[Cp_2Zr(H)(PMe_2Ph)_2][BPh_4]$ (15) which by NMR is isostructural with **13**. Neither $PMePh_2$ nor PPh_3 react with 1 to form detectable phosphine complexes. The presence of 17 equiv of $PMePh_2$ produces a minor acceleration of the hydrogenation of 1 ($t_{1/2}$ = 5 h, THF) and results in the formation of $[Cp_2Zr(H)(PMePh_2)_2][BPh_4]$ (16) which by NMR is isostructural with **13** and **15**. PPh_3 does not accelerate the hydrogenation of 1 and does not produce a phosphine hydride product. The 18-electron complex $[Cp_2Zr(CH_3)(dmpe)][BPh_4]$ (11) does not react with H_2 even at elevated temperatures. As for neutral $Cp_2Zr(R)(X)$ complexes, the hydrogenation reactivity of $Cp_2Zr(CH_3)^+$ complexes depends strongly upon the availability of a low-energy Zr LUMO for interaction with H_2. The acceleration of the hydrogenation of 1 by PMe_3 and PMe_2Ph is ascribed to the removal of Zr–O π-bonding upon substitution of THF by phosphine.

Introduction

The hydrogenation of d^0 metal alkyl complexes (eq 1) provides a general synthesis of metal hydride complexes,[1] is a key step in metal catalyzed alkene and alkyne hydrogenations,[2] and provides a means of molecular weight control in metal-catalyzed alkene polymerizations.[3] The scope and mechanisms of this process are thus of considerable interest.[4] The fundamental features of this H–H activation reaction also may be relevant to the understanding of C–H activation by d^0 complexes.[1m,5]

$$L_nM\text{–}R + H_2 \rightarrow L_nM\text{–}H + R\text{–}H \qquad (1)$$

Cationic dicyclopentadienyl Zr(IV) alkyl complexes $Cp_2Zr(R)(L)^+$ (L = THF, CH_3CN, etc.) have been prepared as the BPh_4^- salts and are highly reactive as a result of the high electrophilicity of the metal center and the lability of the ligand L.[6] The Zr–R bonds of these compounds undergo rapid insertion of polar substrates such as ketones and nitriles, and, in CH_2Cl_2 solvent, $Cp_2Zr(R)(THF)^+$ (R = CH_3, CH_2Ph) complexes polymerize ethylene.[7] This reactivity greatly exceeds that of neutral $Cp_2Zr(R)_2$ and $Cp_2Zr(R)(X)$ compounds and in some cases rivals that of the metallocene alkyls of group III (3[53]), lanthanide, and actinide metals.[1k–q] We were interested in the reactions of $Cp_2Zr(R)(L)^+$ complexes with H_2 as a possible route to cationic hydride complexes $Cp_2Zr(H)(L)^+$ and for comparison to the H_2 reactions of other d^0 alkyls.[1] We also anticipated that the reactivity of the cationic complexes with H_2 would provide a chemical probe of their solution structures (e.g. coordination number) that would complement spectroscopic studies. In this paper the reactions with H_2 of $[Cp_2Zr(CH_3)(THF)][BPh_4]$ (1) and several phosphine derivatives are reported. Qualitative rate data

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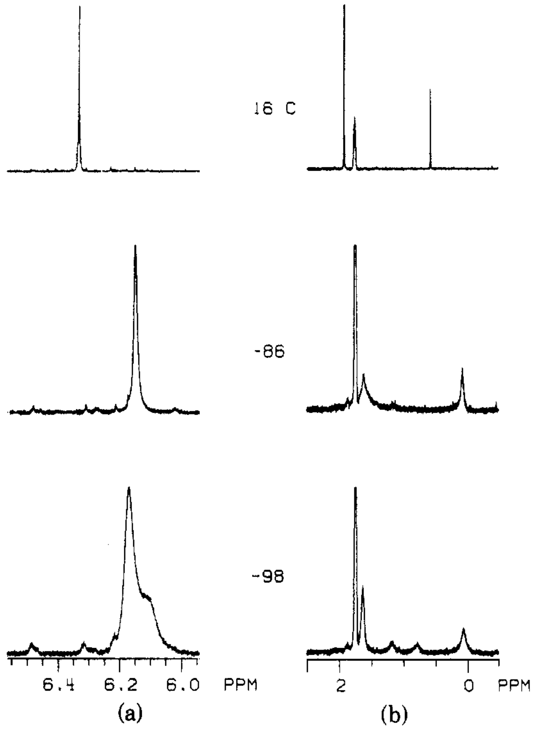

Figure 1. Variable-temperature ^1H NMR spectra of $[Cp_2Zr(CH_3)(CH_3CN)_2][BPh_4]$ (**3**) in THF-d_8 solution: (a) $C_5H_5^-$ region; (b) CH_3CN and Zr–CH_3 region. The peak at δ 1.73 is due to residual H's of the solvent. The chemical shift scale is the same for all three temperatures while the vertical expansion is variable for clarity. The spectral changes are reversible.

for these reactions and the characterization of cationic Zr hydride products are discussed.

Scheme I

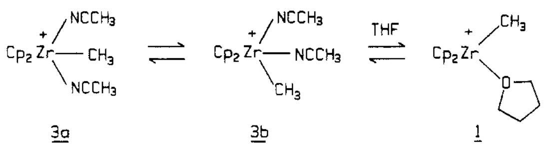

Table I. Hydrogenation of $Cp_2Zr(CH_3)^+$ Complexes[a]

complex[b]	solv	$t_{1/2}$	product[b]
$Cp_2Zr(CH_3)(THF)^+$ (**1**)	THF	21 h	$Cp_2Zr(H)(THF)^+$ (**6**)
1	CH_2Cl_2	5 h	**6**
$Cp_2Zr(CH_3)(CH_3CN)_2^+$ (**3**)	CH_3CN	very slow[c]	
$Cp_2Zr(CH_3)(PMe_3)_2^+$ (**10**)	THF or CH_2Cl_2	<2 min	$Cp_2Zr(H)(PMe_3)_2^+$ (**13**)
1 + PMe_2Ph[d]	THF	8 min	$Cp_2Zr(H)(PMe_2Ph)_2^+$ (**15**)[e]
1 + $PMePh_2$[d]	THF	5 h	$Cp_2Zr(H)(PMePh_2)_2^+$ (**16**)[e]
$Cp_2Zr(CH_3)_2$ (**2**)	THF	>86 h[f]	$[Cp_2Zr(CH_3)(H)]_2$ (**8**)

[a] 1 atm of H_2; 23 °C. [b] BPh_4^- salts. [c] Only trace hydrogenation observed after 24 h. Major product $Cp_2Zr(NCMe_2)(CH_3CN)^+$. [d] 17 equiv/Cp_2Zr. [e] Characterized by ^1H and ^{31}P NMR. [f] Estimated from NMR tube reaction. 38% isolated yield after 5 days.

Results

1. Synthesis and Solution Structures of $Cp_2Zr(R)^+$ Complexes. $[Cp_2Zr(CH_3)(THF)][BPh_4]$ (**1**) is prepared by reaction of $Cp_2Zr(CH_3)_2$ (**2**) with $Ag[BPh_4]$ in CH_3CN followed by filtration, evaporation of filtrate, and recrystallization of the product from THF as previously described (eq 2).[6] The ^1H NMR spectrum of **1** in CD_2Cl_2

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

features a Cp resonance at δ 6.31 and a Zr–CH_3 resonance at δ 0.73 along with absorbances for BPh_4^- and coordinated THF. This spectrum is insensitive to the concentration of **1** and to the addition of excess (e.g. >25 equiv) THF, suggesting that dissociation of THF or coordination of a second equivalent occur to only a minor extent. Several lines of evidence suggest that **1** also exists as the mono(tetrahydrofuran) complex in THF solution. Only the mono adduct **1** crystallizes from THF solution, and the ^1H NMR spectrum of **1** in THF-d_8 (δ 6.32 (Cp), 0.60 (Zr–CH_3)) is nearly identical with that in CD_2Cl_2. Also, low-temperature (−90 °C) ^1H NMR spectra of CD_2Cl_2 solutions (under conditions where exchange of coordinated and free THF is slow) show that **1** exists as the mono adduct even in the presence of excess THF.

In contrast, available evidence indicates that $Cp_2Zr(CH_3)^+$ exists as the bis(acetonitrile) complex $[Cp_2Zr(CH_3)(CH_3CN)_2][BPh_4]$ (**3**) in CH_3CN solvent. Complex **3** is isolated as a white solid from eq 2 when the crude product is recrystallized from CH_3CN. Characterization of 18-electron complex **3** has been difficult as it loses CH_3CN slowly (days) under an inert atmosphere and rapidly (hours) under vacuum affording the previously reported, yellow, 16-electron complex $[Cp_2Zr(CH_3)(CH_3CN)][BPh_4]$ (**4**)[6] and in solution irreversibly rearranges (1 day) to the CH_3CN insertion product $[Cp_2Zr(NCMe_2)(CH_3CN)][BPh_4]$ (**5**).[8] However, ^1H NMR spectra (Figure 1) clearly show that the white material **3** is a bis(acetonitrile) adduct.[9] The 16 °C ^1H NMR spectrum of a THF-d_8 solution of **3** exhibits a resonance at δ 1.90 corresponding to 2 equiv of *free* CH_3CN as well as resonances due to $Cp_2Zr(CH_3)(THF)^+$ (**1**).[6] *This indicates that complex 2 contains 2 equiv of CH_3CN/Cp_2Zr unit* and that at room temperature these are essentially completely displaced by THF solvent. As the temperature is lowered, the CH_3CN resonance shifts upfield, indicating an increase in the extent of CH_3CN coordination (Figure 1).[10] At −98 °C the CH_3CN resonance is split into a singlet at δ 1.62 (relative intensity 4) and two singlets (each of relative intensity 1) at δ 1.16 and 0.76 that may be assigned to the symmetric **3a** and nonsymmetric **3b** isomers of **3** present in a 2/1 ratio (Scheme I). Consistent with this interpretation, the Cp resonance, a sharp singlet (δ 6.32) at 25 °C, shifts upfield and at −98 °C appears as an asymmetric peak which may be deconvoluted into two singlets (δ 6.16, 6.10) of approximately 2/1 relative intensity. The Zr–CH_3 resonance also shifts upfield from δ 0.60 to 0.05 when the temperature is lowered from 25 to

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(8) (a) ^1H NMR (CD_3CN); δ 6.23 (s, 10 H), 1.95 (s, 3 H, liberated CH_3CN), 1.88 (s, 6 H); IR $\nu_{C{=}N}$ 1680 cm^{-1}. Jordan, R. F.; Echols, S. F., unpublished work. (b) $(C_5Me_5)_2ScCH_3$ also inserts nitriles. Bercaw, J. E.; Davies, D. L.; Wolczanski, P. T. *Organometallics* **1986**, *5*, 443.

(9) (a) Low solubility has precluded low-temperature ^{13}C NMR analysis of THF-d_8 solutions of **3**. Complex **3** is nearly insoluble in and rearranges rapidly to **5** in CD_2Cl_2, precluding ^1H NMR analysis in this solvent. (b) The IR spectrum of **3** (KBr) shows CH_3CN bands at 2287 and 2251 cm^{-1}, virtually unshifted from the bands for free CH_3CN.[9c] In contrast, for **4**, in which perturbation of the coordinated CH_3CN should be greater, the CH_3CN bands are shifted to 2310 and 2283 cm^{-1}. A similar effect is observed for the corresponding PF_6^- salts. We are currently investigating the synthesis of analogous RCN complexes with simpler IR spectra. (c) For a discussion of the IR spectrum of CH_3CN see footnote 11 in: Bruce, M. R. M.; Tyler, D. R. *Organometallics* **1985**, *4*, 528.

(10) The chemical shift for free CH_3CN in THF-d_8 shifts slightly downfield between 25 (δ 1.95) and −98 °C (δ 2.09).

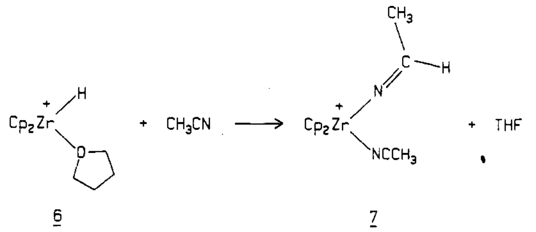
−98 °C and broadens but does not split. The similarity of the Cp and Zr–CH_3 shifts for **3a** and **3b** in THF at −98 °C to those for **1**, **3**, and **4** in CD_3CN solvent (δ 6.07, 0.08)[6] and the observation that **3** crystallizes from CH_3CN provide strong support for the proposal that $Cp_2ZrCH_3^+$ exists as the bis(acetonitrile) adduct **3** in this solvent.[11]

2. Reaction of $Cp_2Zr(CH_3)(THF)^+$ (1) with H_2. Complex **1** reacts rather slowly with H_2 (1 atm) in THF ($t_{1/2}$ = 21 h, 23 °C, Table I; $t_{1/2}$ < 1 h, 50 °C) to produce CH_4 and white, insoluble $[Cp_2Zr(H)(THF)][BPh_4]$ (**6**) (eq 3). The CH_4 was identified by its characteristic ^1H NMR

$$\underset{\mathbf{1}}{Cp_2Zr(CH_3)(THF)^+} + H_2 \rightarrow \underset{\mathbf{6}}{Cp_2Zr(H)(THF)^+} + CH_4 \quad (3)$$

shift (δ 0.18) in NMR tube reactions but was not quantified. The cationic hydride complex **6** was identified by IR, elemental analysis, and chemical derivatization. The IR spectrum of **6** exhibits a broad M–H band centered at 1450 cm^{-1}, which shifts to ca. 1050 cm^{-1} in the corresponding deuteride (prepared from **1** and D_2, coproduct CH_3D, δ 0.18 (t, J_{D-H} = 1.9 Hz)). This ν_{M-H} is somewhat lower than that reported for the terminal Zr–H ligands of $[Cp_2Zr(H)(\mu\text{-}H)]_2$ (1520 cm^{-1}),[12] [(tetrahydroindenyl)$_2$Zr(H)(μ-H)]$_2$ (1545 cm^{-1}),[1c] $[(C_5H_4Me)_2Zr(H)(\mu\text{-}H)]_2$ (1565 cm^{-1}),[13] and $(C_5Me_5)_2ZrH_2$ (1555 cm^{-1})[14] but is similar to values reported for the terminal hydrides of the actinide complexes $[(C_5Me_5)_2Th(H)(\mu\text{-}H)]_2$ (1401, 1370 cm^{-1})[1q] and $M[N(SiMe_3)_2]_3H$ (M = Th, 1480 cm^{-1}; M = U, 1430 cm^{-1}).[15] Bridging hydrides in d^0 metallocene systems typically exhibit ν_{M-H} at lower energy, as in $[Cp_2Zr(\mu\text{-}H)(CH_2C_6H_{11})]_2$ (1380 cm^{-1}),[1a] $[Cp_2Zr(H)(\mu\text{-}H)]_2$ and analogues (ca. 1300 cm^{-1}),[1c,11,13] $[(C_5Me_5)_2Th(H)(\mu\text{-}H)]_2$ (1215, 1114 cm^{-1}),[1q] and $[Cp'_2M(\mu\text{-}H)(THF)]_2$ (1240–1350 cm^{-1}, Cp′ = C_5H_5 or C_5H_4Me; M = Lu, Er, Y).[1o] On the basis of these data the 1450 cm^{-1} IR band of **6** is assigned to a terminal Zr–H stretch and **6** is assigned a monomeric structure. However, as deviations from these trends have been observed,[16] these assignments are tentative. The insolubility of **6** does not necessarily imply a dimeric or polymeric structure since $[Cp_2Zr(CH_2Ph)(THF)][BPh_4]$ is also only sparingly soluble.[7b]

As expected for a hydridic hydride complex, **6** reacts upon dissolution in CH_3CN to produce pale yellow $[Cp_2Zr(NCHCH_3)(CH_3CN)][BPh_4]$ (**7**) with the liberation of 1 quiv of THF/Cp_2Zr unit (eq 4). Diagnostic spectral parameters for **7** include a low-field quartet (δ 8.49 (J = 4.9 Hz)) and a doublet (δ 1.83) in the ^1H NMR spectrum for the $NCHCH_3$ ligand, bands at 2310 and 2282 cm^{-1} and at 1696 cm^{-1} in the IR spectrum assignable to ν_{CN} for the CH_3CN and $NCHCH_3$ ligands, respectively,[8,9b,c] and a ^{13}C NMR signal at δ 173 for the imine carbon.[17] Hydride **6** also reacts slowly (days at room temperature) with PMe_3 to produce $[Cp_2Zr(H)(PMe_3)_2][BPh_4]$ (vide infra).



(4)

In CH_3CN solution, the THF adduct **1** forms $Cp_2Zr(CH_3)(CH_3CN)_2^+$ (**3**), which undergoes only very slow reaction with H_2. Hydrogenation of **3** in CD_3CN (1 atm, 23 °C, 20 h, NMR scale) produces only traces of $Cp_2Zr[(NCH(CD_3)](CD_3CN)^+$ (**7**-d_6), the expected product of the reaction of the hydride $Cp_2Zr(H)(CD_3CN)_n^+$ with solvent. Instead, only $Cp_2Zr[NC(CH_3)(CD_3)](CD_3CN)^+$ (**5**-d_6) (60%), resulting from insertion of CD_3CN into the Zr–CH_3 bond,[8] and starting bis(trideuterioacetonitrile) complex **3**-d_6 (30%) are observed at the end of the reaction.

In contrast, hydrogenation of **1** in CH_2Cl_2 is faster than in THF and proceeds with a $t_{1/2}$ of ca. 5 h at 23 °C (1 atm of H_2), yielding **6**.

3. Reaction of $Cp_2Zr(CH_3)_2$ (2) with H_2. The reaction of $Cp_2Zr(CH_3)_2$ (**2**) with H_2 was originally reported to give an uncharacterized crimson product[18] and more recently was reported to yield (polymeric or dimeric[13]) Cp_2ZrH_2.[1b,c] Related complexes $(C_5H_4R)_2Zr(CH_3)_2$ (R = Me, $CHMe_2$, CMe_3, etc) and (tetrahydroindenyl)$_2$Zr(CH_3)$_2$ also reportedly yield the corresponding dihydrides upon hydrogenation at elevated H_2 pressure and temperature.[1b,c] To provide a direct comparison for **1**, the hydrogenation of **2** was studied in THF under the conditions described above.

Hydrogenation of **2** proceeds slowly (Table I) at 23 °C in THF (1 atm of H_2) to yield white, insoluble $[Cp_2Zr(CH_3)(\mu\text{-}H)]_2$ (**8**) (38%, 5 days) and CH_4 (eq 5).[19] Unreacted **2** is the only other Zr compound present in significant amount at the end of the reaction. Hydride complex **8** was characterized by IR, elemental analysis, and chemical derivatization. The IR spectrum of **8** includes strong aliphatic C–H stretching bands indicative of a Zr–CH_3 group and a broad band at ca. 1390 cm^{-1} assignable to a bridging hydride by reference to related systems.[1a,c,12,13,19] Complex **8** reacts upon dissolution in acetone to produce $Cp_2Zr(CH_3)(OCH(CH_3)_2)$ (**9**) (eq 6) for which the important spectral features are a septet (δ 3.99 (J = 6.1 Hz) and a doublet (δ 0.96) for the isopropoxide ligand in the ^1H NMR and a ^{13}C NMR signal at δ 73.8 for the alkoxy carbon. An identical product results from the reaction of **2** with 1 equiv of 2-propanol.

$$\underset{\mathbf{2}}{2Cp_2Zr(CH_3)_2} \xrightarrow{H_2} \underset{\mathbf{8}}{[Cp_2Zr(CH_3)(\mu\text{-}H)]_2} + 2CH_4 \quad (5)$$

$$\underset{\mathbf{8}}{[Cp_2Zr(CH_3)(\mu\text{-}H)]_2} + 2(CH_3)_2CO \rightarrow \underset{\mathbf{9}}{2Cp_2Zr(CH_3)(OCH(CH_3)_2)} \quad (6)$$

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[11] (a) At −86 °C singlets are observed for the Cp (δ 6.14), CH_3CN (δ 1.61), and $ZrCH_3$ (δ 0.06) resonances, indicating rapid (NMR time scale) interconversion of **3a** and **3b** and significant substitution of coordinated CH_3CN by solvent at this temperature. (b) Recrystallization of **3** by evaporation of solvent from a THF solution yields the THF adduct $[Cp_2Zr(CH_3)(THF)][BPh_4]$ (**1**). However, recrystallization by chilling a concentrated THF solution to 0 °C yields material that retains significant (ca. 1.5 equiv/Zr) CH_3CN.

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[17] The dimeric yttrium hydride $[(C_5H_4R)_2Y(\mu\text{-}H)(THF)]_2$ (R = H, CH_3) adds to nitriles to give dimeric products $[(C_5H_4R)_2Y(\mu\text{-}NCHR)]_2$. Evans, W. J.; Meadows, J. H.; Hunter, W. E.; Atwood, J. L. *J. Am. Chem. Soc.* **1984**, *106*, 1291.

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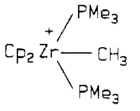
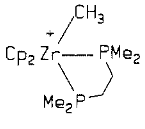
[19] A report describing the preparation of $Cp_2Zr(CH_3)(H)$ by reaction of $Cp_2Zr(CH_3)Cl$ and $Li[AlH_4]$, and its decomposition to a red-purple product has appeared. The reported ν_{Zr-H} are 1500 and 1310 br cm^{-1}, values which are in fact almost identical with those reported for Cp_2ZrH_2. By comparison the ν_{Zr-H} for $Cp_2Zr(H)Cl$ is 1390 br cm^{-1}. Wailes, P. C.; Weigold, H. *J. Organomet. Chem.* **1970**, *24*, 405.

4. Reaction of 1 with PMe_3. Structure of $[Cp_2Zr(CH_3)(PMe_3)_2][BPh_4]$ (10). Reaction of 1 with excess PMe_3 in THF followed by removal of the volatiles yields the bis(trimethylphosphine) complex $[Cp_2Zr(CH_3)(PMe_3)_2][BPh_4]$ (**10**) as a white crystalline solid.[20,21] Low-temperature ^1H, ^{13}C, and ^{31}P NMR spectra indicate that **10** adopts the symmetric structure shown with the PMe_3 ligands in the lateral positions. The -85 °C ^1H NMR spectrum of **10** consists of binomial triplets for the Cp (δ 5.96 (J_{P-H} = 2.1 Hz) and $Zr-CH_3$ (δ -0.99 (J_{P-H} = 16.0 Hz)) ligands which are shifted upfield by δ 0.4 and 1.7 from the corresponding resonances for **1**, a pseudotriplet for the PMe_3 ligands at δ 1.36 (vs. δ 0.97 for free PMe_3), and characteristic BPh_4^- absorbances. The -90 °C ^{13}C NMR spectrum of **10** contains a relatively high-field Cp resonance (δ 104.8 vs. 112.1 for $Cp_2Zr(CH_3)(CH_3CN)_2^+$ (**3**)),[6] a binomial triplet for the $Zr-CH_3$ carbon (δ -0.10 (J_{P-C} = 14.2 Hz)), and resonances for coordinated PMe_3 (δ 12.9 vs. δ 14.3 for free PMe_3) and BPh_4^-. The -90 °C ^{31}P NMR consists of a singlet at δ -6.2 shifted from δ -62 for free PMe_3.[22] In contrast, for $Cp_2Zr(CH_3)(PMe_2CH_2CH_2PMe_2)^+$ (**11**) (vide infra), which has a nonsymmetric structure with the $Zr-CH_3$ group in a lateral position, ABX multiplets are observed for the $Zr-CH_3$ resonances in the ^1H and ^{13}C NMR spectra and the inequivalent P atoms produce an AB quartet in the ^{31}P NMR spectrum.


10


11

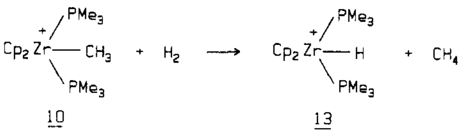
PMe_3 is not released when **10** is heated under vacuum in the solid state (70 °C, 3 h). However, in THF and CH_2Cl_2 solutions the PMe_3 ligands are labile (i.e. exchange rapid on the NMR time scale) and partial dissociation occurs as evidenced by NMR spectroscopy. Above ca. -60 °C ^{31}P coupling is lost in the ^1H and ^{13}C NMR spectra of THF solutions of **10**, and the Cp and $Zr-CH_3$ resonances shift toward those of **1**. Also, the ^{31}P NMR signal shifts toward that of free PMe_3. For example, for a THF solution of **10** at 20 °C, the $Zr-CH_3$ ^1H NMR signal appears at δ -0.14 and the ^{31}P NMR signal appears at δ -24.8, values which are shifted ca. 50% and 34% toward the values for **1** and free PMe_3 from the low T values noted above. The ^1H NMR $Zr-CH_3$ shift varies slightly with the concentration of **10** and significantly with the concentration of added PMe_3; at 23 °C addition of 6 equiv of PMe_3 to a solution of **10** produces a ^1H NMR $Zr-CH_3$ chemical shift of δ -0.90, nearly the limiting low T value (δ -0.99). These observations are consistent with the equilibrium shown in eq 7.

$$\underset{\mathbf{10}}{Cp_2Zr(CH_3)(PMe_3)_2^+} \overset{THF}{\rightleftharpoons} \underset{\mathbf{12}}{Cp_2Zr(CH_3)(PMe_3)^+} + PMe_3 \qquad (7)$$

The room-temperature ^1H NMR spectrum of a CD_2Cl_2 solution of **10** contains, in addition to PMe_3 and BPh_4^- absorbances, singlets for the Cp ligands (δ 5.85) and the $Zr-CH_3$ ligand (δ -0.70). The latter values are very similar to the limiting low T values for **10** listed above, indicating less extensive PMe_3 dissociation than in THF. However, the lack of ^{31}P coupling indicates that PMe_3 exchange is rapid on the NMR time scale in this solvent.

Precise determination of the equilibrium constants awaits more detailed studies. For the present work the important point is that a significant degree of PMe_3 coordination to **1** occurs in THF and CH_2Cl_2 as evidenced by the drastically shifted NMR signals.

5. Hydrogenation of 10. Synthesis of $[Cp_2Zr(H)(PMe_3)_2][BPh_4]$ (13). In THF or CH_2Cl_2 the bis(trimethylphosphine) complex **10** reacts very rapidly with H_2 ($t_{1/2}$ < 2 min, 23 °C, 1 atm, Table I) to produce the soluble hydride complex $[Cp_2Zr(H)(PMe_3)_2][BPh_4]$ (**13**) and CH_4 (eq 8). Reaction with D_2 produces the corresponding deuteride complex and CH_3D.


(8)

Complex **13** has been fully characterized by spectroscopy and X-ray diffraction and adopts the symmetric structure analogous to that of **10** both in solution and in the solid state. The IR spectrum of **13** contains a band at 1498 cm^{-1} that shifts to ca. 1080 cm^{-1} in the deuteride complex and is assigned to ν_{Zr-H} for the terminal hydride ligand. The room temperature ^1H spectrum of a THF-d_8 solution of **13** contains, in addition to absorbances for BPh_4^- and coordinated PMe_3, binomial triplets for the Cp(δ 5.72 (J_{P-H} = 2.1 Hz)) and Zr–H ligands (δ 1.40 (J_{P-H} = 104 Hz)). The $^{31}P\{^1H\}$ spectrum of **13** consists of a singlet at δ 3.1 and is temperature-independent; in the ^1H-coupled ^{31}P spectrum this resonance splits to a doublet with J_{P-H} = 104 Hz. These data imply the symmetric structure for **13** shown and indicate that PMe_3 exchange is slow on the NMR scale. The lower lability of the PMe_3 ligands in **13** vs. the CH_3 analogue **10** may be steric in origin: in **10** relief of steric crowding provides a driving force for PMe_3 dissociation.

Hydride complex **13** is stable and rather unreactive due to the presence of the two nonlabile PMe_3 ligands. It survives heating to 80 °C in THF (sealed tube) for 30 min and does not undergo H/D exchange (1 atm of D_2, 23 °C, 18 h). Complex **13** reacts slowly with CH_3CN at 23 °C (50%, 24 h, 50% unreacted **13** remaining) to produce azomethine complex **7** and with ethylene at 50 °C in THF (1 atm, 6 h) to produce a labile ethyl complex $Cp_2Zr(CH_2CH_3)(PMe_3)_n^+$ that will be described fully elsewhere.[23]

When the reaction of complex **10** with H_2 in CD_2Cl_2 or THF is monitored by ^1H NMR spectroscopy, transient Cp signals (δ 5.62 (d, J_{P-H} = 2 Hz), δ 5.71 (d, J_{P-H} = 2.0 Hz) tentatively assigned to the mono(phosphine) hydride complex $Cp_2Zr(H)(PMe_3)^+$ or its solvates can be observed. PMe_3 and Zr–H resonances for this species have not yet

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[20] For representative Zr(IV) phosphine complexes incorporating other ligand systems see: (a) Gordon, D.; Wallbridge, M. G. H. *Inorg. Chim. Acta* **1986**, *111*, 77. (b) Girolami, G. S.; Wilkinson, G.; Thornton-Pett, M.; Hursthouse, M. B. *J. Chem. Soc., Dalton Trans.* **1984**, 2789. (c) Planalp, R. P.; Anderson, R. A. *Organometallics* **1983**, *2*, 1675. (d) Fryzuk, M. D.; Williams, H. D.; Rettig, S. J. *Inorg. Chem.* **1983**, *22*, 863. (e) Wengrovious, J. H.; Schrock, R. R. *J. Organomet. Chem.* **1981**, *205*, 319. (f) Datta, S.; Wreford, S. S.; Beatty, R. P.; McNeese, T. J.; *J. Am. Chem. Soc.* **1979**, *101*, 1053.

[21] Cp_2Zr^{II},[1c] dimeric Cp_2Zr^{III}, and Cp_2Zr(alkylidene) phosphine complexes are known. (a) Sikora, D.; Rausch, M. D. *J. Organomet. Chem.* **1984**, *276*, 21. (b) Kool, L. B.; Rausch, M. D.; Alt, H. G.; Herberhold, M.; Wolf, B.; Thewalt, U. *J. Organomet. Chem.* **1985**, *297*, 159. (c) Demerseman, B.; Bouquet, G.; Bigorgne, M. *J. Organomet. Chem.* **1977**, *132*, 223. (d) Gell, K. I.; Harris, T. V.; Schwartz, J. *Inorg. Chem.* **1981**, *20*, 481. (e) Hartner, F. W.; Schwartz, J.; Clift, S. M. *J. Am. Chem. Soc.* **1983**, *105*, 640. (f) Barger, P. T.; Santarsiero, B. D.; Armantrout, J.; Bercaw, J. E. *J. Am. Chem. Soc.* **1984**, *106*, 5178.

[22] Crutchfield, M. M.; Dungan, C. H.; Van Wazer, J. R. *Top. Phosphorus Chem.* **1967**, *5*, 19.

[23] $[Cp_2Zr(CH_2CH_3)(PMe_3)_n][BPh_4]$: ^1H NMR (THF-d_8) δ 7.5–6.5 (m, BPh_4^-), 5.84 (s, 10 H, Cp), 1.10 (d, J = 2.9 Hz, ca. 18 H, PMe_3), 0.96 (q, J = 8.7 Hz, $Zr-CH_2CH_3$, integration not possible due to overlap with PMe_3 signal), -1.19 (t, J = 8.7 Hz, 2 H, $ZrCH_2CH_3$); Jordan, R. F.; Bajgur, C. S., unpublished work.

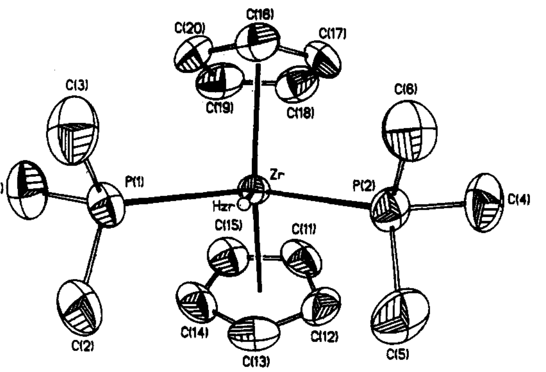

Figure 2. Labeling scheme and cation structure for $[Cp_2Zr(H)(PMe_3)_2][BPh_4]$ (13). Hydrogen atom Zr–H is shown with an arbitrary radius. Other hydrogen atoms are removed for clarity.

Table II. Selected Bond Lengths and Angles for $[(C_5H_5)_2Zr(H)(PMe_3)_2][BPh_4]$ (13)

(a) Bond Lengths (Å)			
Zr–P(1)	2.684 (3)	Zr–C(17)	2.508 (9)
Zr–P(2)	2.676 (3)	Zr–C(18)	2.483 (10)
Zr–HZr	1.97 (8)	Zr–C(19)	2.497 (11)
Zr–C(11)	2.488 (9)	Zr–C(20)	2.529 (10)
Zr–C(12)	2.509 (9)	Zr–CNT(1)[a]	2.195 (9)
Zr–C(13)	2.479 (9)	Zr–CNT(2)[a]	2.207 (10)
Zr–C(14)	2.496 (8)	⟨av⟩Cp(C)–Cp(C)	1.38 (1)
Zr–C(15)	2.480 (9)	⟨av⟩P–C	1.82 (1)
Zr–C(16)	2.498 (9)		
(b) Bond Angles (deg)			
HZr–Zr–P(1)	60.4 (23)	P(1)–Zr–CNT(1)	101.6 (2)
HZr–Zr–P(2)	59.6 (23)	P(1)–Zr–CNT(2)	102.5 (2)
P(1)–Zr–P(2)	119.7 (1)	P(2)–Zr–CNT(1)	100.8 (2)
HZr–Zr–CNT(1)	118.3 (23)	P(2)–Zr–CNT(2)	102.2 (2)
HZr–Zr–CNT(2)	109.6 (23)	CNT(1)–Zr–CNT(2)	132.0 (3)

[a] CNT(1) and CNT(2) are the centroids of the C(11)–C(15) and C(16)–C(20) rings, respectively.

been unambiguously assigned due to interference of resonances of 10 and 13.

6. X-ray Structure of $[Cp_2Zr(H)(PMe_3)_2][BPh_4]$ (13). The molecular structure of complex 13 was confirmed by X-ray diffraction and consists of discrete $Cp_2Zr(H)(PMe_3)_2^+$ and BPh_4^- ions. The structure of the cation is shown in Figure 2, and bond lengths and bond angles are summarized in Table II. Atomic coordinates are listed in Table III. The cation adopts the normal bent metallocene structure with the PMe_3 and hydride ligands arrayed in the plane between the two Cp ligands. The Zr–H ligand, which was located by difference Fourier syntheses, is located in the central position consistent with the solution structure implied by the NMR spectra. The Zr–H bond distance (1.97 (8) Å) is at the long end of the range spanned by the few other Zr(IV)–H distances available by X-ray diffraction. This distance is considerably longer than the Zr–H distance for the terminal hydrides $[(C_5H_4Me)_2Zr(\mu\text{-}H)(H)]_2$ (1.78 (2) Å)[13] but similar to that for the terminal hydride in one of the two crystallographically independent molecules of $Cp_2Zr(\mu\text{-}CH_3C(O)H)(\mu\text{-}H)Zr(H)Cp_2$ (1.95 (5) Å).[24] M–H distances for several bis(pentamethylcyclopentadienyl) Zr and Hf hydrides are in the rage of 1.86–1.93 Å.[25,26]

Table III. Atomic Coordinates (×10⁴) and Isotropic Thermal Parameters (Å² × 10³) for 13

	x	y	z	U
Zr	1683.8 (6)	9728.3 (4)	2693.8 (4)	33.0 (2)[a]
B	4932 (8)	7571 (4)	275 (5)	35 (3)[a]
P(1)	1998 (2)	10642 (1)	1571 (2)	54 (1)[a]
P(2)	945 (2)	8423 (1)	2307 (1)	52 (1)[a]
C(1)	2488 (11)	11533 (5)	1854 (7)	91 (5)[a]
C(2)	3085 (10)	10387 (6)	975 (6)	89 (5)[a]
C(3)	675 (10)	10812 (6)	851 (6)	92 (5)[a]
C(4)	784 (10)	7793 (5)	3067 (6)	83 (5)[a]
C(5)	1909 (11)	7957 (5)	1733 (7)	93 (5)[a]
C(6)	−528 (9)	8357 (5)	1686 (6)	79 (5)[a]
C(11)	3208 (7)	9383 (5)	3837 (6)	62 (4)[a]
C(12)	3376 (8)	8922 (5)	3242 (7)	67 (4)[a]
C(13)	3763 (7)	9312 (5)	2661 (6)	66 (4)[a]
C(14)	3884 (7)	10001 (5)	2906 (6)	63 (4)[a]
C(15)	3522 (8)	10045 (6)	3625 (6)	59 (4)[a]
C(16)	−496 (8)	10049 (5)	2536 (5)	54 (3)[a]
C(17)	−288 (7)	9606 (5)	3175 (5)	53 (4)[a]
C(18)	501 (8)	9931 (5)	3758 (5)	58 (4)[a]
C(19)	759 (8)	10600 (5)	3488 (6)	63 (4)[a]
C(20)	114 (9)	10669 (5)	2739 (6)	62 (4)[a]
C(21)	7254 (4)	7485 (2)	164 (3)	45 (3)[a]
C(22)	8258	7151	−43	58 (4)[a]
C(23)	8146	6479	−364	54 (4)[a]
C(24)	7031	6142	−478	50 (3)[a]
C(25)	6027	6476	−271	43 (3)[a]
C(26)	6139	7147	50	32 (3)[a]
C(31)	5703 (5)	7837 (2)	1786 (3)	45 (3)[a]
C(32)	6246	8260	2399	48 (3)[a]
C(33)	6512	8958	2261	50 (3)[a]
C(34)	6236	9233	1510	55 (4)[a]
C(35)	5693	8810	896	43 (3)[a]
C(36)	5427	8112	1034	32 (3)[a]
C(41)	4521 (4)	7913 (2)	−1243 (3)	38 (3)[a]
C(42)	3921	8287	−1881	48 (3)[a]
C(43)	3079	8798	−1773	54 (4)[a]
C(44)	2836	8936	−1026	48 (3)[a]
C(45)	3436	8562	−389	45 (3)[a]
C(46)	4278	8050	−497	34 (3)[a]
C(51)	2673 (4)	7057 (2)	191 (3)	40 (3)[a]
C(52)	1848	6560	365	45 (3)[a]
C(53)	2245	5992	845	53 (4)[a]
C(54)	3466	5921	1151	50 (3)[a]
C(55)	4291	6418	977	36 (3)[a]
C(56)	3895	6986	497	36 (3)[a]
HZr	1206 (68)	9463 (42)	1589 (46)	71 (26)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalised U_{ij} tensor.

The angle between the two lateral PMe_3 ligands of 13 (<P1–Zr–P2 = 119.7°) is considerably smaller than the corresponding angle in other five-coordinate zirconocene complexes such as $[Cp_2Zr(H_2O)_3][CF_3SO_3]_2$ (145.2)[27] and $Cp_2Zr(\eta^1\text{-}CF_3SO_3)_2(THF)$(140.9°).[28] This difference may be ascribed to the small cone angle of the H ligand. The Zr–P distances in 13 (2.676, 2.684 Å) are ca. 0.1–0.2 Å shorter than those observed for other Zr(IV) phosphine complexes, though comparison is complicated by differences in ligand array, phosphine cone angle, and possible ring strain due to chelation.[29] As for other cationic zir-

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(24) The Zr–terminal H distance for the other crystallographically independent molecule of $Cp_2Zr(\mu\text{-}CH_3C(O)H)(\mu\text{-}H)Zr(H)Cp_2$ is 1.733 (39) Å. Erker, G.; Kropp, K.; Kruger, C.; Chiang, A.-P. *Chem. Ber.* **1982**, *115*, 2447.

(25) For example: $Cp_2WC(H)OZr(H)(C_5Me_5)_2$, 1.93 Å; $(C_5Me_5)_2Hf(H)(allyl)$, 1.86 Å. Wolczanski, P. T.; Threlkel, R. S.; Santarsiero, B. D. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1983**, *39C*, 1330.

(26) The Zr(II) hydride complex $(H)Zr(\eta^5\text{-}C_8H_{11})(dmpe)_2$ has been structurally characterized: Zr–H distance = 1.67 Å. Fischer, M. B.; James, E. J.; McNeese, T. J.; Nyburg, S. C.; Posin, B.; Wong-Ng, W.; Wreford, S. S. *J. Am. Chem. Soc.* **1980**, *102*, 4941.

(27) Thewalt, U.; Lasser, W. *J. Organomet. Chem.* **1984**, *276*, 341.

(28) Thewalt, U.; Lasser, W. *Z. Naturforsch., B*: **1983**, *38*, 1501.

(29) For example; (a) $ZrMe_4(dmpe)_2$ (2.812, 2.815 Å): ref 20b. (b) $Zr[(C,N)\text{-}CH_2SiMe_2NSiMe_3]_2(dmpe)$ (2.848, 2.855 Å): ref 20c. (c) $Zr[(N,P)\text{-}N(SiMe_2CH_2PMe_2)_2]_2Cl_2$ (2.794, 2.803 Å): ref 20d. Compare also: (d) $(H)Zr(\eta^5\text{-}C_8H_{11})(dmpe)_2$ (2.73–2.80) Å): ref 26. (e) $[ZrCl_3(PBu_3)_2]_2$ (2.839, 2.830) Å): Wengrovious, J. H.; Schrock, R. R.; Day, C. S. *Inorg. Chem.* 1981, *20*, 1844. (f) $(\eta\text{-}C_4H_6)_2Hf(dmpe)$ (2.685, 2.675 Å): Wreford, S. S.; Whitney, J. F. *Inorg. Chem.* **1981**, *20*, 3918.

conocene complexes, little distortion of the Cp_2Zr framework from that of neutral complexes is observed.[7,27,28,30,31]

7. Hydrogenation of 1 in the Presence of Other Ligands. The dramatic influence of PMe_3 on the hydrogenation of 1 prompted us to examine the effects of other potential ligands on this reaction. We were particularly interested in a possible correlation of the ability of the ligand to coordinate to 1 and its effect on the hydrogenation.

PMe_2Ph forms a weak labile complex, $[Cp_2Zr(CH_3)(THF)(PMe_2Ph)][BPh_4]$ (**14**), that precipitates from concentrated THF solutions of **1** containing a large excess of PMe_2Ph. The ^1H NMR spectra of CD_2Cl_2 and THF solutions of isolated **14** show no ^{31}P coupling and only minor shifts from the spectra of **1**, indicating rapid exchange and significant dissociation of PMe_2Ph in these solvents. This is confirmed by the $^{31}P\{^1H\}$ spectrum (CH_2Cl_2 solution) that consists of a singlet at δ -9.3, shifted considerably less from the resonance for free PMe_2Ph (δ -47) than the signal for the nonlabile complex $Cp_2Zr(H)(PMe_2Ph)_2^+$ (δ 16.5) (vide infra). However, addition of a large excess of PMe_2Ph (33 equiv/Zr) to a THF solution of **1** causes a shift of the $Zr-CH_3$ resonance from δ 0.67 to 0.35, indicating a significant degree of PMe_2Ph coordination as a result of mass action.

Hydrogenation of a THF solution of **1** containing excess PMe_2Ph (1 atm, 23 °C) is complete within minutes (Table I), producing $[Cp_2Zr(H)(PMe_2Ph)_2][BPh_4]$ (**15**) and CH_4 (eq 9). Complex **15** was characterized by ^1H and ^{31}P NMR (but was not isolated in pure form) and has a structure analogous to that of the bis(trimethylphosphine) hydride complex **13**; as for **13** the phosphine ligands of **15** do not exchange on the room-temperature NMR time scale. Key spectroscopic parameters for **15** (CD_2Cl_2 solution) include triplets for the Cp (δ 5.56 (J_{P-H} = 2.0 Hz) and Zr-H (δ 2.14 (J_{P-H} = 102 Hz)) ligands in the ^1H NMR spectrum and a doublet (δ 16.5 (J_{H-P} = 102 Hz)) in the ^{31}P NMR spectrum.

The larger phosphine ligands $PMePh_2$ and PPh_3 do not coordinate to **1** to a significant extent and exert only minor effects on the hydrogenation. Addition of a large excess of $PMePh_2$ (>60 equiv) to a THF-d_8 solution of **1** does not result in perturbation of the ^1H NMR shifts of **1**, indicating the absence of significant $PMePh_2$ coordination. Hydrogenation of a THF solution of **1** and excess $PMePh_2$ (1 atm of H_2, 23 °C) proceeds slowly ($t_{1/2}$ = 5 h), yielding CH_4 and the nonlabile $PMePh_2$ hydride complex $[Cp_2Zr(H)(PMePh_2)_2][BPh_4]$ (**16**), which was characterized by ^1H and ^{31}P NMR and is isostructural with **13** and **15** (eq 9).

$$\begin{array}{ccl} Cp_2Zr(CH_3)(THF)^+ & \xrightarrow{H_2,\ \text{excess L}} & Cp_2Zr(H)(L)_2^+ + CH_4 \\ \mathbf{1} & & \mathbf{15}, L = PMe_2Ph \\ & & \mathbf{16}, L = PMePh_2 \end{array} \qquad (9)$$

Similarly, addition of PPh_3 (to produce a saturated solution, 5.1 equiv in solution/Zr), 1,8-bis(dimethylamino)naphthalene (proton sponge, 13 equiv/equiv Zr), or NPh_3 (13 equiv/Zr) to a THF-d_8 solution of **1** does not result in observable shifts in the NMR signals, indicating the absence of significant complexation of these ligands to $Cp_2Zr(CH_3)^+$. No significant enhancement in the rate of hydrogenation of **1** in the presence of these ligands is observed. In these cases hydrogenation yields **6**.

8. Synthesis and Attempted Hydrogenation of $[Cp_2Zr(CH_3)(dmpe)][BPh_4]$ (11). To provide a point of reference for studies of $Cp_2Zr(R)^+$ phosphine complexes, the 18-electron, nonlabile complex $[Cp_2Zr(CH_3)(PMe_2CH_2CH_2PMe_2)][BPh_4]$ (**11**) was prepared by addition of the chelating diphosphine $PMe_2CH_2CH_2PMe_2$ (dmpe) to **1**. The ^1H NMR spectrum of **11** consists of, in addition to characteristic BPh_4^- absorbances, a triplet for the Cp ligands (δ 5.68), a pseudotriplet for the $Zr-CH_3$ group (δ -0.12), and a complex pattern for the dmpe ligand similar to that observed in other dmpe complexes.[32] The $^{31}P\{^1H\}$ NMR spectrum consists of an AB pattern as expected for two inequivalent P atoms (δ 7.8, 4.9 (J_{P-P} = 53 Hz) shifted from δ -49 for free dmpe), and the $^{13}C\{^1H\}$ spectrum features BPh_4^- resonances, a singlet for the Cp ligands, and multiplets for the $Zr-CH_3$ (δ 14.7) and dmpe carbons.[33] The dmpe complex **11** does not undergo detectable reaction with H_2 (1 atm) in 24 h at 60 °C in THF.

9. Hydrogenation of $Cp_2Zr(CH_3)_2$ (2) in the Presence of PMe_3. Addition of PMe_3 (2 equiv/Zr) to a THF solution of $Cp_2Zr(CH_3)_2$ (**2**) does not perturb the ^1H NMR spectrum of **2** and does not accelerate the reaction with H_2. After 18 h the reaction solution turns dark red; however, no new resonances are detected in the ^1H NMR spectrum.

Discussion

Five-Coordinate Cp_2Zr^{IV} Complexes. While five-coordinate, 18-electron $Cp_2M(R)(X)(L)$ species (M = Ti, Zr, Hf; X = H, R, halide, etc.; L = neutral 2e donor) are important intermediates or transition states for many reactions,[34] *neutral* Cp_2M^{IV} complexes typically exist as four-coordinate, 16-electron, unsaturated $Cp_2M(R)(X)$ species in the ground state. The bond energy gained by complexation of a fifth ligand is less than the loss in stability resulting from increased steric crowding.[35] However,

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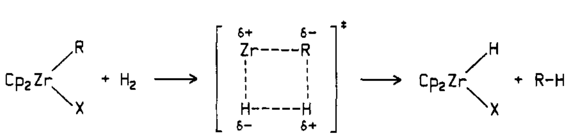
(35) However M^{IV} metallocene compounds incorporating potentially bidentate ligands such as ketenes and related ligands,[35a-f] acyls,[35g] iminoacyls,[35h] mono- and dithiocarbamates,[35i,j] hydrazonato, formamido, and related ligands,[35k,l] etc. are 18-electron species as are, arguably, some bimetallic compounds.[35m-o] M^{IV} metallocene complexes incorporating π-donor ligands are effectively saturated.[1a,35p] Five-coordinate, dicationic Zr(IV) complexes are also known.[27,28,35q] (a) Waymouth, R. M.; Santarsiero, B. D.; Coots, R. J.; Bronikowski, M. J.; Grubbs, R. H. *J. Am. Chem. Soc.* **1986**, *108*, 1427. (b) Ho, S. C. H.; Straus, D. A.; Armantrout; J. Schaefer, W. P.; Grubbs, R. H. *J. Am. Chem. Soc.* **1984**, *106*, 2210. (c) Moore, E. J.; Straus, D. A.; Armantrout, J. Santarsiero, B. D.; Grubbs, R. H.; Bercaw, J. E. *J. Am. Chem. Soc.* **1983**, *105*, 2068. (d) Erker, G.; Dorf, U.; Atwood, J. L.; Hunter, W. E. *J. Am. Chem. Soc.* **1986**, *108*, 2251. (e) Erker, G. *Acc. Chem. Res.* **1984**, *17*, 103. (f) Gambarotta, S.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *J. Am. Chem. Soc.* **1983**, *105*, 1690. (g) Fachinetti, G.; Fochi, G.; Floriani, C. *J. Chem. Soc., Dalton Trans.* **1977**, 1946. (h) Lappert, M. F.; Luong-Thi, N. T.; Milne, C. R. C. *J. Organomet. Chem.* **1979**, *174*, C35. (i) Silver, M. E.; Fay, R. C. *Organometallics* **1983**, *2*, 44. (j) Silver, M. E.; Eisenstein, O.; Fay, R. C. *Inorg. Chem.* **1983**, 22, 759. (k) Gambarotta, S.; Strologo, S.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *J. Am. Chem. Soc.* **1985**, *107*, 6278. (l) Gambarotta, S.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *Inorg. Chem.* **1983**, *22*, 2029. (m) Marsella, J. A.; Huffman, J. C.; Caulton, K. G.; Longato, B.; Norton, J. R. *J. Am. Chem. Soc.* **1982**, *104*, 6360. (n) Casey, C. P.; Palermo, R. E.; Jordan, R. F.; Rheingold, A. L. *J. Am. Chem. Soc.* **1985**, *107*, 4597. (o) Choukroun, R.; Gervais, D.; Jud, J.; Kalck, P.; Senocq, F. *Organometallics* **1985**, *5*, 67. (p) Marsella, J. A.; Moloy, K. G.; Caulton, K. G. *J. Organomet. Chem.* **1980**, *201*, 389. (q) Jordan, R. F.; Echols, S. F. *Inorg. Chem.* **1987**, *26*, 383.

the charge and concomitant high electrophilicity of the metal center in cationic $Cp_2Zr(R)^+$ complexes results in a pronounced tendency for the formation of five-coordinate, 18-electron complexes. A variety of such complexes (**3**, **10**, **11**, and **13–16**) incorporating CH_3CN and phosphine ligands have been characterized in solution and/or the solid state.

Hydrogenation Reactions. Sequential H_2 oxidative addition/R–H reductive elimination is not a reasonable mechanism for the hydrogenation of d^0, early-transition-metal alkyl complexes and other systems lacking easily accessible higher oxidation states (e.g. lanthanide and actinide complexes). Alternative mechanisms include (1) a direct interaction between H_2 and L_nMR not involving formal oxidation of M and (2) an initial formal reduction at the metal center (e.g. via an intramolecular rearrangement)[14,36] followed by H_2 oxidative addition.[37] On the basis of kinetics, labeling studies and structure-reactivity relationships, Schwartz and co-workers proposed that hydrogenation of $Cp_2Zr(R)(X)$ (X = H, R, Cl) (eq 10) complexes proceeds thru a mechanism of type 1 involving a four-center/four-electron transition state in which H_2 is polarized by the Zr(IV) center, one terminus ultimately becoming the Zr–H ligand and the other a proton trapped by R^-.[1a] The susceptibility of 16-electron $Cp_2Zr(R)X$ complexes to hydrogenation depends strongly on the availability of the low-lying, metal-based LUMO[34e] for interaction with the incoming H_2 reactant: if X is an effective π-donor (e.g. Cl), the LUMO energy is raised, interaction with H_2 is inhibited, and hydrogenation is slow. Studies by Evans and co-workers on the hydrogenation of Y and lanthanide metallocene alkyl complexes have shown that the required low-lying empty orbital must be centered at a sterically accessible metal center for effective hydrogenation.[1k,o,2d]



(10)

A somewhat different picture for the "direct" hydrogenation process of type 1 was proposed by Brintzinger on the basis of an extended Hückel analysis of H/D exchange and hydrogenation of $Cp_2Zr(R)_2$ (R = H, CH_3).[38] The calculations suggested that the transition state is a Zr–H_2 "adduct" and that back-donation of Zr–R bonding electron density to the H_2 σ^* orbital is significant.[39] Similar back-bonding has been invoked to explain the lowering of ν_{CO} upon coordination of CO to $(C_5Me_5)_2ZrH_2$.[34a] However, H_2 is a much weaker π acceptor than is CO. If back-bonding is important in the interaction of H_2 with d^0 zirconocene alkyl complexes, the hydrogenation reactivity might be sensitive to the σ-donor ability of the ligand complement on Zr. However, definitive experimental data relevant to this point is lacking.[37b,40,41]

On the basis of Schwartz's conclusions, we anticipated that the cationic methyl complex **1** would undergo facile hydrogenation as a result of the charge at the metal center and the resulting low-lying LUMO. In fact, **1** reacts with H_2 in THF only ca. 5 times faster than does the related neutral complex $Cp_2Zr(CH_3)_2$ (**2**) (Table I). In contrast, **1** reacts many orders of magnitude faster than does **2** with other substrates such as ketones, nitriles, and ethylene.[6,7]

The surprisingly slow hydrogenation of **1** in THF appears to be due to π donation by the THF ligand which effectively ties up the Zr LUMO and hinders interaction with H_2. The X-ray structure of **1** shows that in the solid state the THF ligand is oriented nearly perpendicular to the "equatorial" plane between the Cp ligands in a conformation that allows overlap of the Zr LUMO and the O p orbital.[7,34e,35j] In contrast, in the solid-state structure of the isoelectronic (neglecting f electrons) lanthanide complex $Cp_2Yb(CH_3)(THF)$, the THF ligand lies nearly parallel to this plane.[1k] As lanthanide structures are determined primarily by steric factors, this difference suggests that the origin of the conformational preference of **1** is electronic, i.e. that the energy of the Zr–O π bond in **1** is significant and comparable to the steric preference for the parallel orientation of THF.[42] The more rapid hydrogenation of **1** in CH_2Cl_2 may result from a very rapid reaction of the 14-electron cation $Cp_2Zr(CH_3)^+$, formed by a thermodynamically unfavorable but fast dissociation of THF.[43]

Formation of an unreactive, 18-electron, bis(tetrahydrofuran) adduct in THF would also produce a slow rate of hydrogenation. However, the observation that mono(tetrahydrofuran) complex **1** crystallizes from THF, the similarity of the ^1H NMR spectra of CD_2Cl_2 and THF-d_8 solutions of **1**, and the observation of the mono(tetrahydrofuran) complex **1** by low temperature NMR in CD_2Cl_2 in the presence of excess THF, all suggest that **1** does not coordinate a second THF ligand in THF.

Several lines of evidence suggest that $Cp_2Zr(CH_3)^+$ exists as the bis(acetonitrile) adduct $Cp_2Zr(CH_3)(CH_3CN)_2^+$ (**3**) in CH_3CN solvent. A product of this stoichiometry (by ^1H NMR) crystallizes from CH_3CN solution; low-temperature ^1H NMR spectra of THF solutions of this product exhibit Cp and Zr–CH_3 shifts nearly identical with those observed for CD_3CN solutions of **1**, **3**, or **4**. The tendency of CH_3CN to form a bis(acetonitrile) adduct with $Cp_2Zr(CH_3)^+$, rather than a π-bonded mono adduct as observed for THF, reflects the small cone angle of the CH_3CN ligand and the relatively low energy of its filled π orbitals.[44,45]

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[36] McAlister, D. R.; Erwin, D. K.; Bercaw, J. E. *J. Am. Chem. Soc.* **1978**, *100*, 5966.

[37] (a) In an extended Hückel analysis of H/H exchange of Cp_2LuH and H_2, a mechanism involving oxidative addition of H_2, with the required two electrons coming from Cp orbitals, was considered and rejected. Rabaa, H.; Saillard, J.-Y.; Hoffmann, R. *J. Am. Chem. Soc.* **1986**, *108*, 4327. (b) See also: Wochner, F.; Brintzinger, H. H. *J. Organomet. Chem.* **1986**, *309*, 65.

[38] Brintzinger, H. H. *J. Organomet. Chem.* **1979**, *171*, 337.

[39] Back-bonding from metal-based d orbitals is believed to be important in bonding of H_2 to low-valent transition-metal centers. In the extreme this corresponds to oxidative addition. See ref 5d and: Hay, P. J. *Chem. Phys. Lett.* **1984**, *103*, 466.

[40] The decrease in M core binding energies resulting from replacement of the two $C_5H_5^-$ ligands of a Cp_2MX_2 complex with $C_5Me_5^-$ ligands approaches that expected for a 1e reduction.[41] Oxidation potentials are consistent with this trend.[41] Analysis of reported data on hydrogenolysis reactions of group IV (4), lanthanide, and actinide metallocene alkyl complexes[1] reveals that often complexes incorporating $C_5Me_5^-$ ligands react considerably faster (minutes at room temperature, 1 atm) than do complexes incorporating $C_5H_5^-$ ligands (hours–days). More effective back-bonding of the type proposed by Brintzinger in the relatively electron-rich $C_5Me_5^-$ systems may contribute to this difference. However, other factors, such as relief of steric crowding, differences in monomer/dimer equilibria, and in particular the availability of alternative mechanisms,[14,36,37] clearly are of major significance.

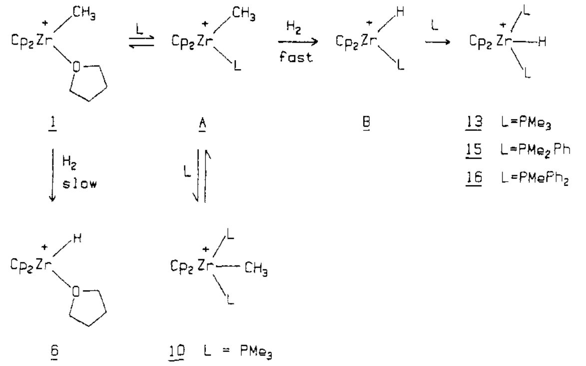
[41] Gassman, P. G.; Macomber, D. W.; Hershberger, J. W. *Organometallics* **1983**, *2*, 1470.

[42] THF is not an effective π-donor ligand in metal carbonyl complexes. Cotton, F. A. *J. Am. Chem. Soc.* **1964**, *5*, 702.

[43] Exchange of free and coordinated THF is rapid for **1** in CD_2Cl_2 above ca. −85 °C (second-order rate constant ca. 2×10^4 M^{-1} s^{-1} at −85 °C). $Cp_2Zr(CH_3)^+$ can be generated in CH_2Cl_2 by reaction of **2** with $[Cp_2Fe][BPh_4]$ and trapped with THF to yield **1**. In the absence of a potential ligand, $Cp_2Zr(CH_3)Cl$ is obtained as the major product.

[44] The PES-derived ionization potential (IP) for the CN π-bonding orbital of CH_3CN is 12.1 eV,[45a] whereas the IP for the O-centered b_1 π-donor orbital of THF is 9.6 eV.[45b,c]

Scheme II



The slow hydrogenation of 3 (and its precursors 1 and 4) in CH_3CN is attributed to the absence of a vacant orbital for interaction with H_2. The 18-electron, nonlabile dmpe complex 11 is also completely unreactive with H_2, even at elevated temperatures.

Small basic phosphines form labile complexes with $Cp_2Zr(CH_3)^+$ in THF and CH_2Cl_2 as evidenced by significant shifts in the NMR spectra of solutions of 1 upon addition of phosphine. Two such complexes, $Cp_2Zr(CH_3)(PMe_3)_2^+$ (10) and $Cp_2Zr(CH_3)(THF)(PMe_2Ph)^+$ (14) have been isolated. *Small phosphines that coordinate to a spectroscopically observable extent greatly accelerate the rate of hydrogenation of 1.* In the presence of PMe_3 or PMe_2Ph, which clearly coordinate to a significant extent, 1 reacts with H_2 in THF or CH_2Cl_2 within min at 23 °C to yield bis(phosphine) hydride complexes $Cp_2Zr(H)L_2^+$, one of which, 13, has been characterized by X-ray diffraction. In contrast, $PMePh_2$ does not perturb the NMR spectra of 1 and produces a comparatively minor acceleration of the hydrogenation of 1 ($t_{1/2}$ = 5 h); the product in this case is also a bis(phosphine) hydride complex 16. PPh_3 has no effect on the NMR spectra of 1 nor on the rate of hydrogenation; in this case 6 rather than a PPh_3 hydride complex is obtained.

This trend suggests that the active species in the rapid hydrogenations of 1 in the presence of small phosphines are Zr–phosphine complexes which are far more reactive than the THF complex 1. Consistent with this proposal, PMe_3 does not accelerate the hydrogenation of $Cp_2Zr(CH_3)_2$ (2), to which it does not coordinate. Also, the absence of any effect of 1,8-bis(dimethylamino)naphthalene (proton sponge) on the hydrogenation of 1 argues against acceleration by base catalysis.[46]

The isolated phosphine complexes 10 and 14 are 18-electron species and therefore are poor candidates for rapid hydrogenation. Rather, the active species in the rapid hydrogenations are almost certainly the mono(phosphine) adducts $Cp_2Zr(CH_3)(L)^+$ (A). Scheme II summarizes a proposed mechanism for these reactions. For PMe_3 and PMe_2Ph, significant concentrations of A are present and reaction with H_2 is fast. For the bulkier phosphines $PMePh_2$ and PPh_3, only minor (if any) concentrations of A are present and reaction with H_2 is slow. In the case of PPh_3, 1 is probably the active species. Mono(phosphine) complexes A are likely in equilibrium with $Cp_2Zr(CH_3)(L)_2^+$ complexes such as 10 and, in THF, $Cp_2Zr(CH_3)(THF)(L)^+$ complexes such as 14. Transient ^1H NMR resonances attributable to the mono(phosphine) intermediates B were observed.

The difference in the hydrogenation reactivity of THF complex 1 and phosphine complexes A is electronic in origin. On the basis of the Schwartz picture of the hydrogenation reaction,[1a] the acceleration by PMe_3 and PMe_2Ph is ascribed to the removal of Zr–O π-bonding upon substitution of the THF ligand of 1 by phosphine. While PMe_3 and PMe_2Ph are stronger σ donors than is THF, these ligands are not π donors, and the LUMO of A is thus relatively unperturbed and available for interaction with H_2. Consequently, in these cases the high reactivity anticipated for cationic complexes is observed.

PMe_3 and especially PMe_2Ph are considerably larger than THF, and the Zr center of A is more crowded than that of 1. On the basis of the results of Evans and coworkers this should produce a rate profile opposite from that observed.[1k] Thus steric effects are comparatively minor.

It is possible that the difference in σ-donor ability of THF and the phosphine ligands contributes to the observed reactivity in a manner predicted by the Brintzinger analysis.[38] The stronger donor ability of PMe_3 and PMe_2Ph could result in more effective back-bonding to H_2 in the transition state and a lower activation energy. We are reluctant to ignore this possibility until a better estimate of the Zr–THF π-bond strength is available. To probe the relative importance of σ- and π-bonding effects, we are investigating the H_2 reactions of other cationic zirconocene alkyl complexes $Cp_2Zr(R)L^+$ in which the σ- and π-donor ability of the spectator ligand L is systematically varied. Further studies of the solution behavior and ligand exchange equilibria of these systems as well as detailed kinetic studies are in progress.[47]

The dramatic effects produced by phosphines on the hydrogenation of 1 are surprising in view of results for other systems. The hydrogenation of main-group-metal alkyls is favored by high M–R bond polarity.[1j] The opposite trend appears to be observed here. The presence of the soft phosphine ligand in A should render the metal center softer, and the Zr–C bond less polar, than in THF complex 1.[48] Phosphines retard the hydrogenation of WMe_6 by coordinating to and decreasing the effective coordinative unsaturation of the metal center.[1g,49] On the other hand, PMe_3 has essentially no effect on the H_2 reactions of $(C_5Me_5)HfMeCl_2$[1d] and $(C_5Me_5)ZrMe_3$ though a bis(trimethylphosphine) complex is formed in the latter case.[50] PMe_3 does promote the hydrogenation of the Hf–P bond of $(C_5Me_5)HfCl_2[P(CMe_3)_2]$. In this case initial coordination of PMe_3 may weaken the Zr–phosphide π bond, facilitating cleavage by H_2.[1d]

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(45) (a) Frost, D. C.; Herring, F. G.; McDowell, C. A.; Stenhouse, I. A. *Chem. Phys. Lett.* **1970**, *4*, 533. (b) Schmidt, H.; Schweig, A. *Chem. Ber.* **1974**, *107*, 725. (c) Pignataro, S.; Distefano, G. *Chem. Phys. Lett.* **1974**, *26*, 356.

(46) James, B. R.; Rattray, A. D.; Wang, D. K. W. *J. Chem. Soc., Chem. Commun.* 1976, 792.

(47) Hydrogenation of 1 in THF is first order in Zr over >4 half-lives. A reviewer has suggested that the rapid hydrogenations of 1 in the presence of PMe_3 and PMe_2Ph (to soluble $Cp_2Zr(H)(L)_2^+$ products) may be autocatalytic. Due to the rapidity of these reactions we have not yet studied their kinetics in detail. However, we observe that hydrogenation of 1 in the presence of 1 equiv of PMe_3 results in rapid (minutes) formation of $^1/_2$ equiv of 13, and slow hydrogenation of the remaining 1 to 6, at a rate ($t^1/_2$ = ca. 16 h) which is only slightly faster than in the absence of 13. This minor increase may be due to a minor amount of free PMe_3 in equilibrium with 13.

(48) The higher ν_{Zr-H} in 13 (1498 cm^{-1}) vs. 6 (1450) supports this argument.

(49) (a) Chiu, K. W.; Jones, R. A.; Wilkinson, G.; Galas, A. M. R.; Hursthouse, M. B.; Malik, M. A. *J. Chem. Soc., Dalton Trans.* 1981, 1204. (b) Gregson, D.; Howard, J. A. K.; Nicholls, J. N.; Spencer, J. L.; Turner, D. G. *J. Chem. Soc., Chem. Commun.* **1980**, 572.

(50) Wolczanski, P. T.; Bercaw, J. E. *Organometallics* **1982**, *1*, 793.

Conclusion

Cationic zirconocene alkyl complexes $Cp_2Zr(R)^+$ exhibit a pronounced tendency to form 18-electron, five-coordinate $Cp_2Zr(R)(L)_2^+$ complexes, a variety of which have been isolated and characterized. In cases where ligand dissociation from the five-coordinate complex is inhibited by mass action (**3** in CH_3CN) or precluded by chelation (**11**), no reaction with H_2 occurs. The 16-electron complex $Cp_2Zr(CH_3)(THF)^+$ (**1**) undergoes hydrogenation under mild conditions in THF or CH_2Cl_2 to the corresponding cationic hydride complex $Cp_2Zr(H)(THF)^+$ (**6**). The hydrogenation is faster in CH_2Cl_2 than in THF; as **1** does not appear to form a bis(tetrahydrofuran) adduct, this rate enhancement probably results from the intermediacy of a highly reactive 14-electron species $Cp_2Zr(CH_3)^+$ formed by THF dissociation. In the presence of the small basic phosphines PMe_3 and PMe_2Ph, the rate of hydrogenation of **1** is greatly enhanced and bis(phosphine) hydride complexes $Cp_2Zr(H)(L)_2^+$ are produced. The active species in these rapid hydrogenations are probably mono(phosphine) complexes $Cp_2Zr(CH_3)(L)^+$ (A). The rate enhancements likely result from the removal of Zr–THF π-bonding and the corresponding increased availability of an empty orbital for interaction with H_2 upon substitution of THF by phosphine. However, the possibility that the difference in σ-donor ability of THF and the phosphine ligands contributes to the hydrogenation rate profile cannot be ruled out at present. Due to insolubility and the presence of two nonlabile phosphine ligands, respectively, neither **6** nor the bis(phosphine) complexes **13**, **15**, and **16** are exceptionally reactive. While no C–H activation reactions have been detected yet for $Cp_2Zr(R)(L)^+$ complexes, the H–H activation results here suggest that the 14-electron species $Cp_2Zr(R)^+$ as well as phosphine complexes $Cp_2Zr(R)(PR_3)^+$ might be good candidates for such reactivity.

Experimental Section

All manipulations were performed under an inert atmosphere or under vacuum using a Vacuum Atmospheres drybox or a high vacuum line. Solvents were purified by using appropriate drying/deoxygenating agents or procedures[51] prior to use, stored in evacuated bulbs, and vacuum transferred into reaction flasks or NMR tubes. NMR spectra were obtained on JEOL FX-90Q or Nicolet 200 instruments. ^1H and ^{13}C chemical shifts are reported vs. Me_4Si and were determined by reference to the residual ^1H or ^{13}C solvent peaks. ^{31}P shifts are vs. 85% H_3PO_4. Peak deconvolutions were performed with the curve analysis program available with the Nicolet 200 software. IR spectra were obtained on a Perkin-Elmer 283 instrument. Microanalyses were performed by Schwarzkopf Microanalytical Laboratory and/or Galbraith Laboratories. Suitable C analyses could not be obtained for the cationic Zr–CH_3 phosphine complexes **10** and **11** despite several attempts on spectroscopically pure samples. However, H, P, and Zr analyses for these compounds were acceptable, and no problems were encountered with other cationic Zr alkyl[6] and hydride complexes. The insoluble salt $Ag[BPh_4]$ was prepared from $Ag[NO_3]$ and $Na[BPh_4]$ in distilled H_2O, washed several times with hot H_2O, to remove residual NO_3^-, and dried under vacuum.

NMR Scale Reactions. An NMR tube attached to a valved adapter was charged with solid reactants in the drybox and then attached to a vacuum line and evacuated. Volatile reactants and solvent were vacuum transferred into the tube. If necessary the tube was charged with H_2. The tube was sealed with a torch. Alternatively, reactions were performed in valved NMR tubes available from R. J. Brunfeldt Co, Bartlesville, OK.

$[Cp_2Zr(CH_3)(CH_3CN)_2][BPh_4]$ (3). $Ag[BPh_4]$ (5.86 g, 13.7 mmol) was added in portions (via a solid addition tube) over 20 min to a slurry of 3.46 g (13.8 mmol) of $Cp_2Zr(CH_3)_2$[52] in 50 mL of CH_3CN at 0 °C. Gas evolution was observed, and a dark gray solid formed. The reaction mixture was warmed to room temperature after $Ag[BPh_4]$ addition was complete and stirred for 1 h. The mixture was filtered, yielding a yellow filtrate and a gray solid. The solid was extracted with CH_3CN until the extracts were colorless. The filtrate and extracts were combined, the volume was reduced under vacuum to ca. 40 mL, and a white solid began to precipitate from solution. The slurry was cooled to −35 °C and filtered, yielding a white crystalline product that was washed with cold CH_3CN and dried 8–12 h under vacuum. Yield of **3** after a second recrystallization from CH_3CN: 6.10 g (70%). **3** turned yellow over several days in the drybox as CH_3CN was lost: IR (KBr) 2287, 2251 cm^{-1}; ^1H NMR see text.

$[Cp_2Zr(CH_3)(CH_3CN)][BPh_4]$ (4).[6] **4** was obtained as a yellow solid when the white product from above was dried under high vacuum for 48 h. (Note—the vacuum drying times required to obtain **3** and **4** vary somewhat with sample size and pressure. However, no problems with ligand stoichiometry are experienced with **1**.)

$[Cp_2Zr(CH_3)(THF)][BPh_4]$ (1).[6,7] Complex **3** was recrystallized twice from THF. Alternatively complex **3** was slurried in THF, and the solvent was removed under vacuum. This process was repeated several times, and the yellow product was washed with cold THF and dried under vacuum.

$[Cp_2Zr(H)(THF)][BPh_4]$ (6). In an NMR tube reaction **1** was dissolved in THF-d_8 and charged with 1 atm of H_2 at 23 °C. The reaction was monitored by ^1H NMR. **1** disappeared with a $t_{1/2}$ of 21 h and white **6** precipitated from solution. Prep scale: a pale yellow slurry of 1.00 g (1.59 mmol) of **1** in 30 mL of THF under 1 atm of H_2 was heated to 50 °C for 12 h to produce a white slurry. Filtration gave a white solid that was washed with 3 × 10 mL of THF and dried under vacuum, yielding analytically pure **6** (0.73 g, 75%): IR (KBr) 3105 (m), 3060 (a), 2985 (m), 2896 (m), 1960 (w), 1887 (w), 1830 (w), 1770 (w), 1580 (s), 1480 (m), 1450 (vs, br), 1265 (m), 1250 (m), 1175 (m), 1125 (m), 1060 (m), 1000 (s), 965 (m), 817 (vs), 745 (m), 730 (vs), 701 (vs), 603 (s) cm^{-1}. Anal. Calcd: C, 74.36; H, 6.40; Zr, 14.86. Found: C, 74.23; H, 6.53; Zr, 15.18.

$[Cp_2Zr(NCHCH_3)(CH_3CN)][BPh_4]$ (7). A slurry of 0.52 g (0.85 mmol) of **6** in 20 mL of CH_3CN was stirred for 1 h. Insoluble **6** gradually dissolved to give an orange solution that was filtered. Concentration and cooling the filtrate to −20 °C produced a yellow precipitate **7**, that was collected by filtration, washed with Et_2O, and vacuum dried (yield 0.30 g, 57%): ^1H NMR (THF-d_8) δ 8.49 (q, J = 4.9 Hz, 1 H), 7.5–6.5 (m, 20 H, BPh_4^-), 6.21 (s, 10 H), 1.92 (s, 3 H), 1.83 (d, J = 4.9 Hz, 3 H); $^{13}C\{^1H\}$ NMR (THF-d_8) δ 173.4 (J_{C-H} = 186 Hz from gated-decoupled spectrum, N*C*HCH$_3$), 165.1 (q, J_{B-C} = 49 Hz), 137.1, 125.8, 122.0, BPh_4^-, 118, 112.2 (Cp), 27.6 (NCH*C*H$_3$), 1.0; IR (KBr) 3100 (m), 3050 (s), 3021 (s), 3000 (m), 2979 (m), 2910 (s), 2310 (m), 2282 (m), 1696 (s) (ν(NCHMe)), 1580 (m), 1480 (m), 1425 (s), 1350 (w), 1269 (m), 1180 (w), 1150 (m), 1068 (m), 1010 (s), 803 (vs), 730 (s), 696 (vs), 600 (m) cm^{-1}.

$[Cp_2Zr(CH_3)(\mu\text{-}H)]_2$ (8). In an NMR tube experiment **2** was dissolved in THF-d_8 and charged with 1 atm of H_2 and the reaction monitored by ^1H NMR. After 48 h at 23 °C the ^1H NMR resonances for **2** had decreased by ca. 30%, a new minor resonance at δ 5.82 was observed, and a white precipitate, **8**, had formed. Prep scale: a solution of 0.87 g (3.5 mmol) of **2** in 20 mL of THF was stirred under 1 atm of H_2 at room temperature for 5 days. A pink slurry was obtained. Filtration yielded a pink filtrate that contained **2** as the only significant Zr species (^1H NMR) and a white solid. The solid was washed with THF and dried under vacuum to yield 0.31 g (38%) of analytically pure **8**: IR (KBr) 3110 (m), 3090 (m), 2920 (vs), 2880 (s), 2840 (m) 2803 (s), 1815

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(53) In this paper the periodic group notation in parentheses is in accord with recent actions by IUPAC and ACS nomenclature committees. A and B notation is eliminated because of wide confusion. Groups IA and IIA 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 presented in the last digit of the new numbering: e.g., III → 3 and 13.)

(w, br), 1709 (w, br), 1440 (w), 1390 (vs, br), 1063 (s), 1018 (vs), 960 (vs), 903 (m), 800 (vs) cm^{-1}; Anal. Calcd: C, 55.64; H, 5.94; Zr, 38.42. Found: C, 55.76; H, 6.00; Zr, 38.35.

$Cp_2Zr(CH_3)(OCH(CH_3)_2)$ (9). A slurry of 0.2 g (0.4 mmol) of **8** in 10 mL of acetone was stirred at room temperature for 3 h. **8** gradually dissolved, yielding a clear colorless solution. The solvent was removed under vacuum to give a colorless oil. Attempted recrystallization from hexane gave **9** as an oil that even after overnight vacuum drying contained minor amounts of acetone and hexane. An identical (by ^1H NMR) product was obtained by treatment of **2** with 1 equiv of 2-propanol: ^1H NMR (benzene-d_6) δ 5.77 (s, 10 H), 3.99 (septet, J = 6.1 Hz, 1 H), 0.96 (d, J = 6.1 Hz, 6 H), 0.30 (s, 3 H); $^{13}C\{^1H\}$ NMR (benzene-d_6) δ 110.1, 73.8 (J_{C-H} = 145 Hz from gated decoupled spectrum, $OCH(CH_3)_2$), 30.4, 26.4 ($OCH(CH_3)_2$).

$[Cp_2Zr(CH_3)(PMe_3)_2][BPh_4]$ (10). PMe_3 (0.60 g, 7.9 mmol) was added to a slurry of 1.5 g (2.4 mmol) of **1** in 25 mL of THF. The reaction mixture was stirred for 30 min, and the solvent and volatiles were removed under vacuum, leaving a white solid, **10** (1.6 g, 94%). **10** was recrystallized from THF: ^1H NMR (200 MHz, THF-d_8, −85 °C) δ 7.3 (m, 8 H), 6.88 (t, J = 7.3 Hz, 8 H), 6.73 (t, J = 7.3 Hz, 4 H), BPh_4^-; 5.96 (t, J_{P-H} = 2.1 Hz, 10 H, Cp), 1.36 (pseudotriplet, $J_{apparent}$ = 3.2 Hz, 18 H, PMe_3), −0.99 (t, J_{P-H} = 16.0 Hz, 3 H, Zr–CH_3); ^1H NMR (90 MHz, CD_2Cl_2, 23 °C) δ 7.5–6.7 (m, 20 H), 5.85 (s, 10 H), 1.30 (d, J = 6.1 Hz, 18 H), −0.70 (s, 3 H); $^{13}C\{^1H\}$ NMR (50.3 MHz, CD_2Cl_2, −90 °C) δ 162.4 (q, J_{B-C} = 49 Hz), 134.3, 124.9, 120.9, BPh_4^-, 104.8 (Cp), 12.9 (pseudotriplet, $J_{apparent}$ = 8.2 Hz, PMe_3), −0.10 (t, J_{P-C} = 14.2 Hz, Zr–CH_3); $^{31}P\{^1H\}$NMR (THF-d_8, −90 °C) δ −6.2 (s). Anal. Calcd: C, 69.57; H, 7.26; P, 8.75; Zr, 12.89. Found: C, 71.77; H, 7.53; P, 8.64; Zr, 12.97.

$[Cp_2Zr(H)(PMe_3)_2][BPh_4]$ (13). In NMR tube experiments solutions of **10** in THF-d_8 or CD_2Cl_2 were charged with 1 atm of H_2 at 23 °C and the reactions monitored by ^1H NMR. Conversion to **13** was complete within 5 min in both cases. Prep scale: a slurry of 0.90 g (1.3 mmol) of **10** in 30 mL of THF was charged with 1 atm of H_2 and stirred at room temperature for 1 h, yielding a colorless solution. The solution was filtered, and the solvent and volatiles were removed under vacuum from the filtrate to yield **13** as a white solid that was vacuum dried. **13** was recrystallized from THF or CH_2Cl_2/Et_2O: yield 0.80 g, 91%; ^1H NMR (THF-d_8, 23 °C, 90 MHz) δ 7.5–6.5 (m, 20 H, BPh_4^-), 5.72 (t, J_{P-H} = 2.1 Hz, 10 H, Cp), 1.40 (t, J_{P-H} = 104 Hz, 1 H, Zr–H, center line obscured by PMe_3 resonance), 1.37 (pseudotriplet, $|J_{P-H} - J_{P'-H}|$ = 7.8 Hz, 18 H, PMe_3); ^1H NMR (THF-d_8, −90 °C, 200 MHz) δ 7.24 (s, br, 8 H), 6.89 (t, J = 7.0 Hz, 8 H), 6.75 (t, J = 7.0 Hz, 4 H), 5.86 (s, br, 10 H), 1.41 (s, br, 18 H), 1.13 (t, J_{P-H} = 104 Hz); $^{13}C\{^1H\}$ NMR (THF-d_8) δ 136.4, 124.9, 121.0, BPh_4^- (δ 165 quartet not observed due to limited signal/noise), 102.8 (Cp_2Zr), 18.4 (t, J_{P-C} = 14 Hz); IR (KBr) ν_{Zr-H} 1498 cm^{-1} (ν_{Zr-D} ca. 1080 (br) cm^{-1}). Anal. Calcd: C, 69.24; H, 7.01; P, 8.79; Zr, 12.94. Found: C, 69.42; H, 7.08; P, 8.85; Zr, 12.69.

X-ray Diffraction Study of 13. Collection of Diffraction Data. The parameters used during the collection of diffraction data are summarized in Table IV. A colorless cubic crystal of $C_{40}H_{49}P_2BZr$ (**13**) was enclosed in a sealed capillary under drybox conditions. **13** was found to crystallize in the monoclinic space group $P2_1/c$. Unit cell dimensions were derived from the least-squares fit of the angular settings of 25 reflections with 17° ≤ 2θ ≤ 20°. An absorption correction was not needed due to low absorption coefficient (μ = 4.20 cm^{-1}) and uniform crystal shape.

Solution and Refinement of Structure. The structure was solved with the direct methods program SOLV that located the Zr atom. The remaining non-hydrogen atoms as well as Zr–H were located from subsequent difference Fourier syntheses. The other hydrogen atoms were calculated in idealized updated positions (d(C–H) = 0.96 Å: thermal parameters equal 1.2 times the isotropic equivalent for the carbon to which it was attached). The anion phenyl rings were constrained to rigid hexagonal groups (d(C–C) = 1.395 Å). All *non*-hydrogen atoms were refined anisotropically. The final difference Fourier synthesis showed only a diffuse background (maximum 0.54 e/Å^3). An inspection of F_o vs. F_c values and trends based upon sin θ, Miller index, and parity group failed to reveal any systematic error. All computer programs used in the data collection and refinement are contained in the Nicolet program packages P3 and SHELXTL (version 4.1) (Nicolet Corp., Madison, WI).

Table IV. Crystal, Data Collection, and Refinement Parameters for 13

	(a) Crystal Parameters		
formula	$C_{40}H_{49}P_2BZr$	V, Å^3	3681 (2)
cryst system	monoclinic	Z	4
space group	$P2_1/c$	cryst size, mm	0.34 × 0.34 × 0.34
a, Å	11.249 (4)	color	colorless
b, Å	19.082 (6)	ρ(calcd), g cm^{-3}	1.25
c, Å	17.391 (5)	temp, °C	24
β, deg	99.57 (3)	μ, cm^{-1}	4.10
	(b) Data Collection		
diffractometer	Nicolet R3m/μ	rflns collected	5649
radiation	Mo K$_\alpha$ (λ = 0.71073 Å)	unique data	5445
		R(int), %	3.23
monochromator	graphite	unique data, $4\sigma(F_o)$	3266
scan technique	Wyckoff	std rflns	3 std/197 rflns
2θ limits, deg	4° ≤ 2θ ≤ 47°	decay	<1%
data collected	$\pm h,+k,+l$		
scan speed, deg min^{-1}	variable, 5-20		
	(c) Refinement		
R_F, %	6.36	data/parameter	9.25
R_{wF}, %	6.53	mean shift/esd max	0.040
GOF	1.099	g, $w^{-1} = \sigma^2(F_o) + gF_o^2$	0.001

Bond lengths and angles are given in Table II, and atomic coordinates are given in Table III. Additional crystallographic data are available as supplementary material.

$[Cp_2Zr(CH_3)(THF)(PMe_2Ph)][BPh_4]$ (14). A solution of 50 mg (0.08 mmol) of **1** and ca. 100 mg (0.7 mmol) of PMe_2Ph in 5 mL of THF was stirred for 1 h at room temperature. The yellow precipitate **14** that formed was collected by filtration, washed with Et_2O, and vacuum dried: ^1H NMR (CD_2Cl_2) δ 7.7–6.6 (m, 25 H), 6.28 (s, 10 H), 3.49 (m, 4 H), 1.81 (m, 4 H), 1.52 (d, J = 7.6 Hz, 6 H), 0.52 (s, 3 H); ^{31}P $\{^1H\}$ NMR (CD_2Cl_2) δ −9.3 (s).

$[Cp_2Zr(H)(PMe_2Ph)_2][BPh_4]$ (15). NMR scale: a solution of **1** and 17 equiv of PMe_2Ph in THF-d_8 was charged with 1 atm of H_2 and monitored by ^1H NMR. **1** disappeared and **15** formed (NMR yield ca. 80%) with a $t_{1/2}$ of 8 min. Prep scale: A slurry of 0.40 g (0.64 mmol) of **1** and 0.48 g (3.5 mmol) of PMe_2Ph in 25 mL of THF was charged with 1 atm of H_2 and stirred at room temperature. After 5 min the solid had dissolved to give a pale yellow solution. After 1 h the solvent was removed under vacuum and the residue washed several times with Et_2O (to remove excess PMe_2Ph) and vacuum dried to yield **14** as a pale yellow solid (ca. 80% pure, containing Et_2O and unidentified Cp_2Zr products; δ 6.33 and 5.98 (d, J = 1.7 Hz; possibly the mono(dimethylphenylphosphine) complex)). Attempts to recrystallize this compound by concentrating and cooling THF solutions or by addition of Et_2O or hexane to CH_2Cl_2 or THF solutions gave oils: ^1H NMR (CD_2Cl_2) δ 7.8–6.6 (m, BPh_4^- and PMe_2Ph), 5.56 (t, J_{P-H} = 2.0 Hz, 10 H), 2.14 (t, J_{P-H} = 102 Hz, 1 H), 1.74 (pseudotriplet, $|J_{H-P} - J_{H-P'}|$ = 7.3 Hz, 12 H); ^{31}P NMR (CD_2Cl_2) δ 16.5 (d, J_{H-P} = 102 Hz).

$[Cp_2Zr(H)(PMePh_2)_2][BPh_4]$ (16). In an NMR tube experiment a THF-d_8 solution of **1** and 17 equiv of $PMePh_2$ was charged with 1 atm of H_2 at 23 °C and the reaction monitored by ^1H NMR. **1** disappeared and **16** formed (NMR yield >90%) with a $t_{1/2}$ of ca. 5 h. Prep scale: a slurry of 0.385 g (0.61 mmol) of **1** and 1.0 mL (5.3 mmol) of $PMePh_2$ in 25 mL of THF was charged with 1 atm of H_2 and stirred at room temperature for 45 h to yield a yellow solution. **16** was obtained as pale yellow solid (ca. 75% purity) as described above for **15**; recrystallization attempts failed as for **15**. NMR spectra indicated ca. 20% $PMePh_2$ dissociation in CD_2Cl_2: ^1H NMR (CD_2Cl_2) δ 7.9–6.6 (m, BPh_4^- and $PMePh_2$), 5.54 (t, $J_{^{31}P-^1H}$ = 2.0 Hz, 10 H), 2.62 (t, $J_{^{31}P-^1H}$ = 99 Hz, 1 H), 2.06 (t, $J_{apparent}$ = 3.8 Hz, 6 H). ^{31}P NMR (CD_2Cl_2) δ 33.1 (d, $J_{^1H-^{31}P}$ = 99 Hz).

$[Cp_2Zr(CH_3)(PMe_2CH_2CH_2PMe_2)][BPh_4]$ (11). THF (20 mL) was added by vacuum transfer to a mixture of 0.80 g (1.3 mmol) **1** and 0.27 g (1.8 mmol) of 1,2-bis(dimethylphosphino)-

ethane. The reaction mixture was warmed to room temperature and stirred for 30 min, and a white precipitate formed. The product was collected by filtration, washed with two 5-mL portions of cold THF, and dried under vacuum. The product was recrystallized from hot THF or CH_2Cl_2/Et_2O: yield 0.81 g (84%); ^1H NMR (CD_2Cl_2) δ 7.5–6.7 (m, 20 H, BPh_4^-), 5.68 (t, J = 1.2 Hz, 10 H, Cp), 1.66 (m, CH_2), 1.30 (pseudoquartet, $|J_{P-Me}-J_{P'-Me}|$ = 7.1 Hz, 12 H, $P-CH_3$), –0.12 (pseudoquartet, $|J_{P-Me}-J_{P'-Me}|$ = 19.5 Hz, 3 H, $Zr-CH_3$) CH_3) $^{31}P\{^1H\}$ NMR (THF-d_8) AB pattern δ 7.8, 4.9 (J_{P-P} = 52.8 Hz); ^{13}C NMR (CD_2Cl_2) δ 164 (q, J_{B-C} = 49.5 Hz), 136, 126, 122, 107 (Cp), 26.8 (m, dmpe), 24.9 (m, dmpe), 14.8 (m, $Zr-CH_3$), 14.6 (m, $P-CH_3$), 13.3 (m, $P-CH_3$). Anal. Calcd: C, 69.77; H, 7.00; P, 8.78; Zr, 12.92. Found: C, 68.00; H, 6.82; P, 8.89; Zr, 12.82.

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Supplementary Material Available: Tables of bond lengths and angles, anisotropic thermal parameters, and hydrogen atom coordinates for **13** (5 pages); a listing of observed and calculated structure factors (20 pages). Ordering information is given on any current masthead page.

Chemistry of $[CpCr(CO)_3]_2$. Synthesis of $Cp_2Cr_2(CO)_4S$, $Cp_2Cr_2(CO)_4S_2$, and $Cp_2Cr_2(CO)_5S_2$. Crystal Structure and Reactivity of $Cp_2Cr_2(CO)_4S_2$ and $Cp_2Cr_2(CO)_5S_2$

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The instantaneous reaction of $[CpCr(CO)_3]_2$ (Cp = η^5-C_5H_5) in tetrahydrofuran or toluene with stoichiometric amounts of elemental sulfur produced $Cp_2Cr_2(CO)_4S$ (**1**) and $Cp_2Cr_2(CO)_5S_2$ (**2**) in near quantitative yields. A solution of **2** on standing 1 h at ambient temperature gave a mixture of $Cp_2Cr_2(CO)_4S_2$ (**3**) (76%) and **1**. The transformation of the very labile complex **2** to **3** with the cleavage of a CO ligand thence to the linear multiple bonded Cr–S–Cr complex **1** with extrusion of a S atom and finally to $Cp_4Cr_4S_4$ was demonstrated by a time-dependent NMR study at 30 °C. When **2** was treated with $CF_3SO_3CH_3$, one of the S atoms was immediately methylated, giving $[Cp_2Cr_2(CO)_5S_2(CH_3)](SO_3CF_3)$ (**4**) as a fine black unstable solid, which decomposed in solution to give **1** and $[Cp_4Cr_4S_4(CH_3)](SO_3CF_3)$ (**5**). Complexes **1**–**3** have been characterized by elemental, spectral, and crystal structure analyses. The structure of **1** has been reported previously. Crystals of **2** are monoclinic, $P2_1/n$, with a = 11.638 (4) Å, b = 15.508 (5) Å, c = 9.825 (3) Å, β = 111.56 (2)°, and Z = 4. Crystals of **3** are monoclinic, $P2_1/c$, with a = 8.214 (1) Å, b = 11.464 (2) Å, c = 16.182 (3) Å, β = 92.44 (1)°, and Z = 4. The disulfur ligand bridges the two chromium centers asymmetrically μ-η^1,η^2 in **2** and symmetrically μ-η^2 in **3**. S–S distances [2.010 (4) Å, **2**; 1.990 (1) Å, **3**] are similar to those found in other transition-metal μ-S_2 complexes. Metal atoms in both complexes exhibit 4:3, 7-coordination.

Introduction

In the last few years there has been a rapidly increasing interest in the syntheses and structural determinations of sulfur-rich transition-metal complexes. In particular, the disulfur ligand has attracted considerable attention,[1] primarily on account of its versatility in bonding and coordination modes[2] and hence its high potential in the generation of new metal-cluster complexes. Disulfur complexes are also of interest because, like their dioxygen and dinitrogen analogues, they have biological[3] and catalytic[4] implications. They are known to occur with a number of transition metals but are still relatively uncommon, and very little is known of the reactions of the S_2 ligands. Our preliminary communication[5] has described the syntheses and structures of $Cp_2Cr_2(CO)_4S$ (**1**) and $Cp_2Cr_2(CO)_5S_2$ (**2**). Earlier, Legzdins[6] and co-workers had reported the preparation of **1** from the reaction of Na[$CpCr(CO)_3$] with $S_3N_3Cl_3$ together with its structure. Very recently, Herrmann[7] et al. have also synthesized the analogous compounds $(C_5Me_5)_2Cr_2(CO)_4S$ and $(C_5Me_5)_2Cr_2(CO)_5S_2$ by a similar reaction. We report herein the relevant details for the preparation of **1**, **2**, and $Cp_2Cr_2(CO)_4S_2$ (**3**) from the reaction of $[CpCr(CO)_3]_2$ with

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