complex was the only species remaining after ca. 9 h. This reaction could also be monitored by NMR; these data are given in Table IV. After 2–3 h reaction time, a precipitate formed. The reaction was allowed to proceed overnight, and the product was isolated by filtration. After being washed with $CH_2Cl_2$, it was dried under vacuum. Analysis ($^1H$, $^{31}P$, NMR; IR) showed it to be pure **1b**. Yield: 1.80 g, 74%.

**(b) Diphosphine = $Ph_2P(CH_2)_3PPh_2$.** A similar reaction was carried out by using 0.87 g (1.3 mmol) of $Rh[Ph_2P(CH_2)_3PPh_2](CO)I$, 15 mL of $CH_2Cl_2$, and 0.25 mL (4 mmol) of $CH_3I$. The reaction was allowed to proceed for 3 days due to the sparing solubility of $Rh[Ph_2P(CH_2)_3PPh_2](CO)I$. After this time infrared analysis of the solution showed complete loss of the carbonyl band at 1992 $cm^{-1}$ and formation of **1a** at 1701 $cm^{-1}$. The product was isolated by filtration, washed with $CH_2Cl_2$, and dried under vacuum. Yield: 0.96 g, 91%.

**Kinetic Measurements—General Procedure.** For these experiments, the catalyst charge consisted of the appropriate amounts of **1a**, $[Me_4N][Ru(CO)_3I_3]$, and $CH_3I$. The rhodium and ruthenium complexes were combined in 40 mL of methanol in a 100-mL stirred Parr minireactor. The reactor was purged of air by pressure/venting several times with 2:1 $H_2/CO$. The $CH_3I$ was then added via syringe, and the reactor was sealed. A hydrogen/carbon monoxide (2:1 ratio) gas mixture was used to pressure the reactor to 400 psi; if no leaks were noted, the reactor was heated to an internal temperature of 140 °C. $H_2/CO$ was again added to bring the pressure to 970 psi. Gas uptake was monitored by the pressure drop in the reactor with an ElectroSyn 8600 digital pressure meter. When the pressure dropped to 920 psi, it was manually repressured to 970 psi. These measurements were generally halted after 1-h reaction time, and the products were analyzed in the usual manner. Plots of total gas uptake vs time were generally linear for at least the first 45 min; significant deviation from linearity occurred at reaction times much longer than 60 min.

**Solubility Measurements.** In a glovebox a 0.038 M solution of **1a** in methanol (0.61 g, 0.75 mmol, in 20 mL) was charged to a 3-oz Fisher Porter glass reaction vessel. A magnetic stir bar was used for thorough mixing. A thermocouple was inserted through the top of the reactor and immersed in the solution. The vessel was attached to a high-pressure gas manifold, and 40 psig of carbon monoxide was added. The tube was immersed in a hot oil bath such that the oil and liquid levels were coincident. Upon reaching 139 °C not all of complex dissolved. The reactor was cooled, and an additional 20 mL of methanol was added to give a 0.019 M solution. Upon heating to 139 °C most of the complex dissolved, and only a few small crystals remained at the gas/liquid interface. This procedure was repeated once more, using 10 mL of methanol to give a 0.015 M solution. This resulted in complete solution of **1a** at 139 °C.

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**Registry No.** **1a**, 122924-33-8; **1b**, 67913-10-4; **1c**, 122924-34-9; **1d**, 122924-35-0; **1e**, 122924-36-1; **1f**, 122924-37-2; $Ph_2P(CH_2)_3PPh_2$, 6737-42-4; $Ph_2P(CH_2)_2PPh_2$, 1663-45-2; $Ph_2PCH_2C(CH_3)_2CH_2PPh_2$, 80326-98-3; $Ph_2P(CH_2)_2CH(CH_3)PPh_2$, 94631-05-7; $(p\text{-tol})_2P(CH_2)_3P(p\text{-tol})_2$, 115583-11-4; $(p\text{-ClC}_6H_4)_2P(CH_2)_3P(p\text{-ClC}_6H_4)_2$, 114076-81-2; $(C_6H_{11})_2P(CH_2)_2P(C_6H_{11})_2$, 23743-26-2; $Ph_2P(CH_2)_4PPh_2$, 7688-25-7; $(p\text{-tol})_2P(CH_2)_2P(p\text{-tol})_2$, 70320-30-8; $Rh[Ph_2P(CH_2)_3PPh_2]_2Cl$, 71264-67-0; $CH_3CHO$, 75-07-0; $CH_3CH_2OH$, 64-17-5; $Rh(CO)_2(acac)$, 83642-66-4; $CH_3{}^{13}CO_2H$, 1563-79-7; $^{13}CH_3{}^{13}CHO$, 1632-98-0; $^{13}CH_3I$, 4227-95-6; $Rh[Ph_2P(CH_2)_3PPh_2](H)I_2$, 122924-38-3; $[(CH_3)_4N][Ru(CO_3)I_3]$, 122924-39-4; $[Rh(CO)_2Cl]_2$, 14523-22-9; $Rh(CO)_2(Cl)(I)^-$, 122924-40-7; $Rh[Ph_2P(CH_2)_3PPh_2](CO)I$, 122924-41-8; $Rh[Ph_2P(CH_2)_2PPh_2](CO)(CH_3)I_2$ (isomer A), 122924-42-9; $Rh[Ph_2P(CH_2)_2PPh_2](CO)I$, 122924-43-0; $Rh[Ph_2P(CH_2)_2PPh_2](CO)(CH_3)I_2$ (isomer B), 123000-57-7.

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# Synthesis and Chemistry of Cationic Alkyl, Alkenyl, and Allyl Complexes Derived from the Soluble, Cationic Hydride $(C_5H_4Me)_2Zr(H)(THF)^+$

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Reaction of $Cp'_2Zr(CH_2Ph)_2$ ($Cp' = C_5H_4Me$) with $[Cp'_2Fe][BPh_4]$ in THF produces the cationic benzyl complex $[Cp'_2Zr(CH_2Ph)(THF)][BPh_4]$ (**4**) which contains a normal $\eta^1$-benzyl ligand. Hydrogenolysis of **4** in THF solution (1 atm of $H_2$, 23 °C) produces the soluble cationic hydride complex $[Cp'_2Zr(H)(THF)][BPh_4]$ (**5**). Hydride **5** reacts with olefins $H_2C{=}CH_2R$ to yield cationic alkyl complexes $[Cp'_2Zr(CH_2CH_2R)(THF)][BPh_4]$ (**8a**, R = H; **8b**, R = Me; **8c**, R = Et), with 2-butyne to give the cationic 2-butenyl complex $[Cp'_2Zr\{(E)\text{-}C(Me){=}C(H)(Me)\}(THF)][BPh_4]$ (**9**), and with allene to give the allyl complex $[Cp'_2Zr(\eta^3\text{-}C_3H_5)(THF)][BPh_4]$ (**13**). Solutions of **4**, **5**, or **13** in $CH_2Cl_2$ catalyze the polymerization of ethylene to polyethylene. Solutions of **5** and of **8a**,**c** in THF catalyze the oligomerization of ethylene to butene, hexene, and octene. Alkyl complexes **8a–c** also insert 2-butyne to give cationic alkenyl complexes $[Cp'_2Zr\{(Z)\text{-}C(Me){=}C(Me)(R)\}(THF)][BPh_4]$ (**10a**, R = Et; **10b**, R = $^n$Pr; **10c**, R = $^n$Bu). No evidence for multiple 2-butyne insertion or for competing $\beta$-H elimination reactions is observed. The structure of the cationic alkenyl complex $[Cp'_2Zr\{(Z)\text{-}C(Me){=}C(Me)(^nPr)\}(THF)][BPh_4]$ (**10b**) has been determined by X-ray diffraction. Complex **10b** crystallizes in space group $P2_1/n$ with $a = 12.084$ (4) Å, $b = 20.469$ (9) Å, $c = 16.436$ (2) Å, $\beta = 100.26$ (2)°, $V = 4000$ (2) Å$^3$, and $Z = 4$. The alkenyl ligand lies in the plane between the two Cp′ ligands in the exo conformation, and the THF ligand is rotated 50° from the optimum conformation for Zr–O $\pi$ bonding.

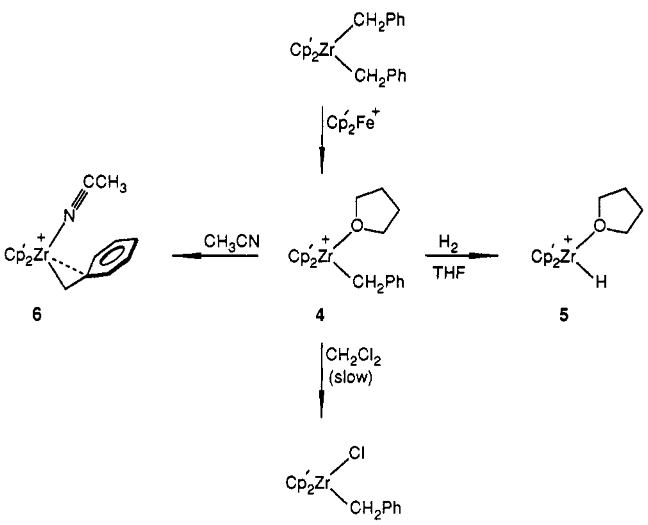
Cationic, $d^0$ metal–alkyl complexes $Cp_2M(R)^+$ (M = Ti, Zr; Cp = $\eta^5\text{-}C_5H_5$) have been implicated as active species in classical soluble $Cp_2MX_2/AlR_nX_{3-n}$ Ziegler–Natta olefin polymerization catalyst systems as well as in the recently developed $Cp_2MX_2$/alumoxane systems.[1,2] Similar actinide species $(C_5Me_5)_2Th(CH_3)^+$ play an important role in the chemistry of supported $(C_5Me_5)_2Th(CH_3)_2$ catalysts.[3] We recently reported that $Cp_2Zr(R)(THF)^+$ complexes are formed by one-electron oxidation of neutral $Cp_2ZrR_2$ precursors, can be isolated and studied as the $BPh_4^-$ salts (eq 1), and do indeed polymerize ethylene under mild

$$Cp_2ZrR_2 + [Cp'_2Fe][BPh_4] \xrightarrow{THF} [Cp_2Zr(R)(THF)][BPh_4] + \tfrac{1}{2}R\text{-}R + Cp'_2Fe \quad (1)$$

conditions in the absence of Al cocatalysts or supports.[4,5] These observations support the proposed role of cationic species in the transition-metal/Al systems.[6] Furthermore, the $Cp_2Zr(R)(THF)^+$ series offers a simple model system for fundamental studies of problems in polymerization catalysis.

A major objective of our current work in this area is to develop a general synthesis of $Cp_2Zr(R)(L)^+$ complexes for use in mechanistic studies of insertion and β-H elimination reactions and for comparison with neutral $Cp_2M^{III}(R)$ compounds.[7,8] With this aim in mind we have investigated the synthesis of cationic hydride complexes $Cp_2Zr(H)(L)_n^+$ which should provide general entry to cationic alkyl and alkenyl systems via reaction with olefins and acetylenes, respectively. We recently reported the synthesis of $Cp_2Zr(H)(THF)^+$ (**1**) and the related $PMe_3$ complex $Cp_2Zr(H)(PMe_3)_2^+$ (**2**) via reaction of $Cp_2Zr(CH_3)(THF)^+$ (**3**) with $H_2$ in the absence and presence of $PMe_3$.[9] However, **1** does not react with olefins efficiently because it is insoluble, and **2** reacts with olefins only slowly at elevated temperatures because the $PMe_3$ ligands are not labile. We now report that reaction of $[(C_5H_4Me)_2Zr(CH_2Ph)(THF)][BPh_4]$ (**4**) with $H_2$ provides the soluble, cationic hydride $[(C_5H_4Me)_2Zr(H)(THF)][BPh_4]$ (**5**) which readily reacts with olefins to give cationic alkyl complexes $[(C_5H_4Me)_2Zr(R)(THF)][BPh_4]$, and with allene to give $[(C_5H_4Me)_2Zr(\eta^3\text{-}C_3H_5)(THF)][BPh_4]$. The reactions of the cationic hydride and alkyl complexes with 2-butyne and with ethylene are discussed and compared with those of related neutral $Cp_2M^{III}(R)$ and $Cp_2M^{IV}(R)(X)$ compounds.

**Scheme I**



## Results

**Synthesis of $(C_5H_4Me)_2Zr(CH_2Ph)(L)^+$ Complexes.** The reaction of $Cp'_2Zr(CH_2Ph)_2$ ($Cp' = \eta^5\text{-}C_5H_4Me$) with $[Cp'_2Fe][BPh_4]$ proceeds rapidly when a THF slurry of the reactants is warmed from −78 to 23 °C to yield $[Cp'_2Zr(CH_2Ph)(THF)][BPh_4]$ (**4**, 100% NMR) which can be isolated as an orange crystalline solid (Scheme I). The unsubstituted ferrocinium salt $[Cp_2Fe][BPh_4]$ may be used in this reaction but is less thermally stable than $[Cp'_2Fe][BPh_4]$. The $^1H$ NMR spectrum (Table I) of a $CD_2Cl_2$ solution of **4** exhibits resonances for a coordinated THF ligand (δ 3.25 (α-$CH_2$), 1.70 (β-$CH_2$) vs δ 3.67, 1.77 for free THF) as well as resonances for the Cp′ and $CH_2Ph$ ligands and the $BPh_4^-$ counterion. The $^1H$ NMR signals for the ortho hydrogens of the Zr–$CH_2Ph$ ligand of **4** are not shifted upfield from the normal Ph region, indicating that this complex contains a normal $\eta^1$-benzyl ligand.[10] Complex **4** is slowly ($t_{1/2}$ = ca. 15 h, 23 °C) converted to $Cp'_2Zr(CH_2Ph)Cl$ in $CH_2Cl_2$ solution but is stable in THF solution.

Dissolution of **4** in $CH_3CN$ produces $[Cp'_2Zr(\eta^2\text{-}CH_2Ph)(CH_3CN)][BPh_4]$ (**6**) which can be isolated as an orange solid ($\nu_{CN}$ = 2304, 2273 $cm^{-1}$). The $\eta^2$ structure of the benzyl ligand of **6** is established by the observation of high-field $^1H$ NMR signals for the ortho hydrogens and high-field $^{13}C$ signals for the methylene and ipso carbons of this ligand.[10] An analogous structure has been established by X-ray crystallography for the $C_5H_5$ analogue $[Cp_2Zr(\eta^2\text{-}CH_2Ph)(CH_3CN)][BPh_4]$.[4a]

**Synthesis of $[Cp'_2Zr(H)(THF)][BPh_4]$ (5).** The reaction of benzyl complex **4** with $H_2$ (1 atm, 23 °C, 72 h) in THF produces the soluble hydride complex $[Cp'_2Zr(H)(THF)][BPh_4]$ (**5**) in high yield (100% NMR scale, 72% isolated) and 1 equiv of toluene (Scheme I). Complex **5** has been characterized by NMR and IR spectroscopy,

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**Table I. NMR Data**[a]

| compd (solv) | $^1$H NMR | assign | $\{^1\mathrm{H}\}^{13}\mathrm{C}$ NMR[b] | assign |
|---|---|---|---|---|
| $\mathrm{Cp'_2Zr(CH_2Ph)_2}$ ($\mathrm{C_6D_6}$) | 7.35–7.15 (m, 4 H) | $\mathrm{Ar}\mathit{H}$ | 152.54 | Ar ipso |
|  | 7.00–6.89 (m, 6 H) | $\mathrm{Ar}\mathit{H}$ | 128.38 | Ar |
|  | 5.56–5.41 (m, 8 H) | $\mathrm{C_5}\mathit{H}_4\mathrm{CH_3}$ | 126.16 | Ar |
|  | 1.84 (s, 4 H) | $\mathrm{ZrC}\mathit{H}_2\mathrm{Ph}$ | 123.02 | $\mathrm{(CH)_4}\mathit{C}\mathrm{CH_3}$ |
|  | 1.67 (s, 6 H) | $\mathrm{C_5H_4C}\mathit{H}_3$ | 121.17 | Ar |
|  |  |  | 114.13 | $\mathrm{(}\mathit{C}\mathrm{H)_4CCH_3}$ |
|  |  |  | 111.32 | $\mathrm{(}\mathit{C}\mathrm{H)_4CCH_3}$ |
|  |  |  | 61.10 | $\mathrm{Zr}\mathit{C}\mathrm{H_2Ph}$ |
|  |  |  | 14.56 | $\mathrm{(CH)_4C}\mathit{C}\mathrm{H_3}$ |
| $\mathrm{BPh_4^-}$ ($\mathrm{CD_3CN}$) | 7.43–7.35 (m, 8 H) | ortho | 164.86 (q, $J_{BC}$ = 49) | ipso |
|  | 7.06 (b t, $J$ = 7.0, 8 H) | meta | 136.81 | meta |
|  | 6.91 (b t, $J$ = 7.1, 4 H) | para | 126.57 (q, $J_{BC}$ = 3) | ortho |
|  |  |  | 122.77 | para |
| $\mathrm{BPh_4^-}$ (THF-$d_8$) | 7.38–7.26 (m, 8 H) | ortho | 165.0 (q, $J_{BC}$ = 50) | ipso |
|  | 6.90 (b t, $J$ = 7.1, 8 H) | meta | 136.9 | meta |
|  | 6.75 (b t, $J$ = 7.0, 4 H) | para | 125.7 (q, $J_{BC}$ = 3) | ortho |
|  |  |  | 121.9 | para |
| $\mathrm{BPh_4^-}$ ($\mathrm{CD_2Cl_2}$) | 7.35 (m, 8 H) | ortho | 163.5 (q, $J_{BC}$ = 49 Hz) | ipso |
|  | 7.05 (b t, $J$ = 7.4 Hz, 8 H) | meta | 135.4 | meta |
|  | 6.90 (b t, $J$ = 7.2 Hz, 4 H) | para | 125.7 | ortho |
|  |  |  | 121.7 | para |
| $\mathrm{Cp'_2Zr(CH_2Ph)(THF)^+}$ (**4**) (THF-$d_8$) | 7.24–7.17 (m, 2 H) | ortho |  |  |
|  | 6.98–6.91 (m, 3 H) | m + p |  |  |
|  | 6.35–6.05 (b m, 8 H) | $\mathrm{C_5}\mathit{H}_4\mathrm{Me}$ |  |  |
|  | 2.58 (s, 2 H) | $\mathrm{ZrC}\mathit{H}_2\mathrm{Ph}$ |  |  |
|  | 2.05 (s, 6 H) | $\mathrm{C_5H_4C}\mathit{H}_3$ |  |  |
| $\mathrm{Cp'_2Zr(CH_2Ph)(THF)^+}$ (**4**) ($\mathrm{CD_2Cl_2}$) | obscured | Ph |  |  |
|  | 6.2–6.0 (m, 8 H) | $\mathrm{C_5}\mathit{H}_4\mathrm{Me}$ |  |  |
|  | 3.25 (m, 4 H) | $\mathrm{O(C}\mathit{H}_2\mathrm{CH_2)_2}$ |  |  |
|  | 2.66 (s, 2 H) | $\mathrm{ZrC}\mathit{H}_2\mathrm{Ph}$ |  |  |
|  | 2.11 (s, 6 H) | $\mathrm{C_5H_4C}\mathit{H}_3$ |  |  |
|  | 1.70 (m, 4 H) | $\mathrm{O(CH_2C}\mathit{H}_2\mathrm{)_2}$ |  |  |
| $\mathrm{Cp'_2ZrH(THF)^+}$ (**5**) (THF-$d_8$) | 6.1–5.6 (vb m, 8 H) | $\mathrm{C_5}\mathit{H}_4\mathrm{Me}$ | not observed | $\mathrm{(CH_4)}\mathit{C}\mathrm{CH_3}$ |
|  | 5.88 (b s, 1 H) | $\mathrm{Zr}\mathit{H}$ | 109.41 (vb) | $\mathrm{(}\mathit{C}\mathrm{H)_4CCH_3}$ |
|  | 2.22 (s, 6 H) | $\mathrm{C_5H_4C}\mathit{H}_3$ | 15.85 | $\mathrm{(CH)_4C}\mathit{C}\mathrm{H_3}$ |
| $\mathrm{Cp'_2Zr(CH_2Ph)(CH_3CN)^+}$ (**6**) ($\mathrm{CD_3CN}$) | 7.28–7.21 (m, 3 H) | m, p | 133.59 | m or o |
|  | 6.81–6.76 (m, 2 H) | ortho | 130.71 | o or m |
|  | 5.90–5.28 (m, 8 H) | $\mathrm{C_5}\mathit{H}_4\mathrm{Me}$ | 129.64 | para |
|  | 2.64 (s, 2 H) | $\mathrm{ZrC}\mathit{H}_2\mathrm{Ph}$ | 126.81 | ipso |
|  | 1.96 (s, 6 H) | $\mathrm{C_5H_4C}\mathit{H}_3$ | 123.48 | $\mathrm{(CH)_4}\mathit{C}\mathrm{CH_3}$ |
|  |  |  | 112.30 | $\mathrm{(}\mathit{C}\mathrm{H)_4CCH_3}$ |
|  |  |  | 109.63 | $\mathrm{(}\mathit{C}\mathrm{H)_4CCH_3}$ |
|  |  |  | 46.24 | $\mathrm{Zr}\mathit{C}\mathrm{H_2Ph}$ |
|  |  |  | 15.19 | $\mathrm{(CH)_4C}\mathit{C}\mathrm{H_3}$ |
| $\mathrm{Cp'_2Zr\{NC(CH_3)H\}(CH_3CN)^+}$ (**7**) ($\mathrm{CD_3CN}$) | 8.60 (q, $J$ = 5, 1 H) | $\mathrm{{=}C(CH_3)}\mathit{H}$ | 171.89 | $\mathrm{N{=}}\mathit{C}\mathrm{(H)CH_3}$ |
|  | 6.15–6.00 (m, 8 H) | $\mathrm{C_5}\mathit{H}_4\mathrm{Me}$ | 127.15 | $\mathrm{(CH)_4}\mathit{C}\mathrm{CH_3}$ |
|  | 2.06 (s, 6 H) | $\mathrm{C_5H_4C}\mathit{H}_3$ | 112.69 | $\mathrm{(}\mathit{C}\mathrm{H)_4CCH_3}$ |
|  | 1.89 (d, $J$ = 5, 3 H) | $\mathrm{{=}C(C}\mathit{H}_3\mathrm{)H}$ | 109.74 | $\mathrm{(}\mathit{C}\mathrm{H)_4CCH_3}$ |
|  |  |  | 27.61 | $\mathrm{N{=}C(H)}\mathit{C}\mathrm{H_3}$ |
|  |  |  | 15.12 | $\mathrm{(CH)_4C}\mathit{C}\mathrm{H_3}$ |
| $\mathrm{Cp'_2ZrEt(THF)^+}$ (**8a**) (THF-$d_8$) | 6.24–6.12 (m, 8 H) | $\mathrm{C_5}\mathit{H}_4\mathrm{Me}$ | 128.90 | $\mathrm{(CH)_4}\mathit{C}\mathrm{CH_3}$ |
|  | 2.09 (s, 6 H) | $\mathrm{C_5H_4C}\mathit{H}_3$ | 116.27 | $\mathrm{(}\mathit{C}\mathrm{H)_4CCH_3}$ |
|  | 1.41 (m, $J$ = 6.7, 3 H) | $\mathrm{CH_2C}\mathit{H}_3$ | 113.94 | $\mathrm{(}\mathit{C}\mathrm{H)_4CCH_3}$ |
|  | 1.17 (m, $J$ = 6.7, 2 H) | $\mathrm{C}\mathit{H}_2\mathrm{CH_3}$ | 60.61 | $\mathrm{Zr}\mathit{C}\mathrm{H_2CH_3}$ |
|  |  |  | 17.52 | $\mathrm{ZrCH_2}\mathit{C}\mathrm{H_3}$ |
|  |  |  | 14.48 | $\mathrm{(CH)_4C}\mathit{C}\mathrm{H_3}$ |
| $\mathrm{Cp'_2Zr(Et)(THF)^+}$ (**8a**) ($\mathrm{CD_2Cl_2}$, –50 °C) | 6.14–5.90 (m, 8 H) | $\mathrm{C_5}\mathit{H}_4\mathrm{Me}$ | 127.9 (s) | $\mathrm{(CH)_4}\mathit{C}\mathrm{CH_3}$ |
|  | 3.09 (m, 4 H) | $\mathrm{O(C}\mathit{H}_2\mathrm{CH_2)_2}$ | 115.1 (d, $J$ = 173) | $\mathrm{(}\mathit{C}\mathrm{H)_4CCH_3}$ |
|  | 2.05 (s, 6 H) | $\mathrm{C_5H_4C}\mathit{H}_3$ | 114.1 (d, $J$ = 173) | $\mathrm{(}\mathit{C}\mathrm{H)_4CCH_3}$ |
|  | 1.68 (m, 4 H) | $\mathrm{O(CH_2C}\mathit{H}_2\mathrm{)_2}$ | 113.2 (d, $J$ = 179) | $\mathrm{(}\mathit{C}\mathrm{H)_4CCH_3}$ |
|  | 1.31 (b t, $J$ = 7, 3 H) | $\mathrm{ZrCH_2C}\mathit{H}_3$ | 112.1 (d, $J$ = 175) | $\mathrm{(}\mathit{C}\mathrm{H)_4CCH_3}$ |
|  | 1.08 (b q, $J$ = 7, 2 H) | $\mathrm{ZrC}\mathit{H}_2\mathrm{CH_3}$ | 76.7 (t, $J$ = 153) | $\mathrm{O(}\mathit{C}\mathrm{H_2CH_2)_2}$ |
|  |  |  | 60.6 (t, $J$ = 116) | $\mathrm{Zr}\mathit{C}\mathrm{H_2CH_3}$ |
|  |  |  | 25.3 (t, $J$ = 137) | $\mathrm{O(CH_2}\mathit{C}\mathrm{H_2)_2}$ |
|  |  |  | 17.9 (q, $J$ = 125) | $\mathrm{ZrCH_2}\mathit{C}\mathrm{H_3}$ |
|  |  |  | 14.5 (q, $J$ = 128) | $\mathrm{(CH)_4C}\mathit{C}\mathrm{H_3}$ |
| $\mathrm{Cp'_2Zr(^nPr)(THF)^+}$ (**8b**) (THF-$d_8$) | 6.22–6.11 (m, 8 H) | $\mathrm{C_5}\mathit{H}_4\mathrm{Me}$ | 129.10 | $\mathrm{(CH)_4}\mathit{C}\mathrm{CH_3}$ |
|  | 2.08 (s, 6 H) | $\mathrm{C_5H_4C}\mathit{H}_3$ | 116.48 | $\mathrm{(}\mathit{C}\mathrm{H)_4CCH_3}$ |
|  | 1.63 (m, 2 H) | $\mathrm{C}\mathit{H}_2$ | 114.10 | $\mathrm{(}\mathit{C}\mathrm{H)_4CCH_3}$ |
|  | 1.19 (m, 2 H) | $\mathrm{C}\mathit{H}_2$ | 72.76 | $\mathrm{Zr}\mathit{C}\mathrm{H_2CH_2CH_3}$ |
|  | 0.95 (t, $J$ = 7.1, 3 H) | $\mathrm{CH_2C}\mathit{H}_3$ | 27.37 | $\mathrm{ZrCH_2}\mathit{C}\mathrm{H_2CH_3}$ |
|  |  |  | 20.76 | $\mathrm{ZrCH_2CH_2}\mathit{C}\mathrm{H_3}$ |
|  |  |  | 14.58 | $\mathrm{(CH)_4C}\mathit{C}\mathrm{H_3}$ |
| $\mathrm{Cp'_2Zr(^nBu)(THF)^+}$ (**8c**) (THF-$d_8$) | 6.18–6.11 (m, 8 H) | $\mathrm{C_5}\mathit{H}_4\mathrm{Me}$ | 129.10 (s) | $\mathrm{(CH)_4}\mathit{C}\mathrm{CH_3}$ |
|  | 2.07 (s, 6 H) | $\mathrm{C_5H_4C}\mathit{H}_3$ | 116.54 (d, $J$ = 175) | $\mathrm{(}\mathit{C}\mathrm{H)_4CCH_3}$ |
|  | 1.57 (m, 2 H) | $\mathrm{C}\mathit{H}_2$ | 114.15 (d, $J$ ca. 175) | $\mathrm{(}\mathit{C}\mathrm{H)_4CCH_3}$ |
|  | 1.26 (sx, $J$ = 7.4, 2 H) | $\mathrm{C}\mathit{H}_2\mathrm{CH_3}$ | 69.62 (t, $J$ = 116) | $\mathrm{Zr}\mathit{C}\mathrm{H_2CH_2}$ |
|  | 1.19 (m, 2 H) | $\mathrm{C}\mathit{H}_2$ | 36.20 (t, $J$ = 122) | $\mathrm{ZrCH_2}\mathit{C}\mathrm{H_2}$ |
|  | 0.89 (t, $J$ = 7.3, 3 H) | $\mathrm{CH_2C}\mathit{H}_3$ | 29.43 (t, $J$ = 123) | $\mathit{C}\mathrm{H_2CH_3}$ |
|  |  |  | 14.63 (q, $J$ = 128) | $\mathrm{(CH)_4C}\mathit{C}\mathrm{H_3}$ |
|  |  |  | 13.66 (q, $J$ = 124) | $\mathrm{CH_2}\mathit{C}\mathrm{H_3}$ |

**Table I** (Continued)

| compd (solv) | $^1$H NMR | assign | $\{^1\mathrm{H}\}^{13}$C NMR$^b$ | assign |
|---|---|---|---|---|
| $\mathrm{Cp'_2Zr[(Me)C{=}C(H)(Me)](THF)^+}$ (**9**) (THF-$d_8$) | 5.98–5.75 (m, 8 H) | $\mathrm{C_5}\mathit{H}_4\mathrm{Me}$ | 208.64 (s) | $\mathrm{Zr}\mathit{C}\mathrm{(Me)}{=}$ |
| | 4.74 (qq, $J$ = 5.6, 1.5, 1 H) | $=\mathrm{C}\mathit{H}\mathrm{Me}$ | 129.61 (s) | $\mathrm{(CH)_4}\mathit{C}\mathrm{CH_3}$ |
| | 2.30 (dq, $J$ = 1.5, 0.9, 3 H) | $\mathrm{ZrC(C}\mathit{H}_3\mathrm{)}{=}$ | 117.30 (d, $J$ = 171) | $\mathrm{(}\mathit{C}\mathrm{H)_4CCH_3}$ |
| | 1.82 (s, 6 H) | $\mathrm{C_5H_4C}\mathit{H}_3$ | 112.67 (d, $J$ = 166) | $\mathrm{(}\mathit{C}\mathrm{H)_4CCH_3}$ |
| | 1.66 (dq, $J$ = 5.6, 0.9, 3 H) | $=\mathrm{CHC}\mathit{H}_3$ | 111.05 (d, $J$ = 171) | $\mathrm{(}\mathit{C}\mathrm{H)_4CCH_3}$ |
| | | | 107.97 (d, $J$ = 176) | $\mathrm{(}\mathit{C}\mathrm{H)_4CCH_3}$ |
| | | | 95.55 (dsp, 150, 6) | $=\mathit{C}\mathrm{(H)(CH_3)}$ |
| | | | 71.26 | $\mathrm{O(}\mathit{C}\mathrm{H_2CH_2)_2}$ |
| | | | 27.58 | $\mathrm{O(CH_2}\mathit{C}\mathrm{H_2)_2}$ |
| | | | 21.62 (qd, 126, 11) | $=\mathrm{CH}\mathit{C}\mathrm{H_3}$ |
| | | | 14.88 (q, $J$ = 127) | $\mathrm{(CH)_4C}\mathit{C}\mathrm{H_3}$ |
| | | | 11.12 (q, $J$ = 128) | $\mathrm{Zr(}\mathit{C}\mathrm{H_3)C}{=}$ |
| $\mathrm{Cp'_2Zr[(Me)C{=}C(Et)(Me)](THF)^+}$ (**10a**) (THF-$d_8$) | 6.12–6.09 (m, 2 H) | $\mathrm{C_5}\mathit{H}_4\mathrm{Me}$ | 174.26 (s) | $\mathrm{Zr}\mathit{C}\mathrm{(Me)}{=}$ |
| | 5.92–5.89 (m, 2 H) | $\mathrm{C_5}\mathit{H}_4\mathrm{Me}$ | 144.18 (s) | $=\mathit{C}\mathrm{EtMe}$ |
| | 5.85–5.82 (m, 4 H) | $\mathrm{C_5}\mathit{H}_4\mathrm{Me}$ | 129.50 (s) | $\mathrm{(CH)_4}\mathit{C}\mathrm{CH_3}$ |
| | 1.98 (s, 6 H) | $\mathrm{C_5H_4C}\mathit{H}_3$ | 115.69 (d, $J$ = 175) | $\mathrm{(}\mathit{C}\mathrm{H)_4CCH_3}$ |
| | 1.82 (q, $J$ = 8, 2 H) | $\mathrm{C}\mathit{H}_2\mathrm{CH_3}$ | 113.79 (d, $J$ = 172) | $\mathrm{(}\mathit{C}\mathrm{H)_4CCH_3}$ |
| | 1.70 (b s, 3 H) | $=\mathrm{C(C}\mathit{H}_3\mathrm{)Et}$ | 110.30 (d, $J$ = 172) | $\mathrm{(}\mathit{C}\mathrm{H)_4CCH_3}$ |
| | 1.10 (t, $J$ = 8, 3 H) | $\mathrm{CH_2C}\mathit{H}_3$ | 108.14 (d, $J$ = 174) | $\mathrm{(}\mathit{C}\mathrm{H)_4CCH_3}$ |
| | 0.68 (bs, 3 H) | $\mathrm{ZrC(C}\mathit{H}_3\mathrm{)}{=}$ | 71.22 | $\mathrm{O(}\mathit{C}\mathrm{H_2CH_2)_2}$ |
| | | | 34.60 (t, $J$ = 124) | $\mathit{C}\mathrm{H_2CH_3}$ |
| | | | 27.62 | $\mathrm{O(CH_2}\mathit{C}\mathrm{H_2)_2}$ |
| | | | 20.71 (q, $J$ = 125) | $\mathit{C}\mathrm{H_3}$ |
| | | | 14.67 (q, $J$ = 128) | $\mathrm{(CH)_4C}\mathit{C}\mathrm{H_3}$ |
| | | | 12.77 (q, $J$ = 126) | $\mathit{C}\mathrm{H_3}$ |
| | | | 2.58 (q, $J$ = 124) | $\mathit{C}\mathrm{H_3}$ |
| $\mathrm{Cp'_2Zr[(Me)C{=}C(Me)(^nPr)](THF)^+}$ (**10b**) (THF-$d_8$) | 6.16–5.85 (m, 8 H) | $\mathrm{C_5}\mathit{H}_4\mathrm{Me}$ | 174.87 (s) | $\mathrm{Zr(Me)}\mathit{C}{=}$ |
| | 3.96–3.53 (m, 6 H) | $\mathrm{O(C}\mathit{H}_2\mathrm{CH_2)_2}$<br>$\mathrm{O(CD}\mathit{H}\mathrm{CD_2)_2}$ | 143.75 (s) | $=\mathit{C}\mathrm{(Me)(^nPr)}$ |
| | 1.99 (s, 6 H) | $\mathrm{C_5H_4C}\mathit{H}_3$ | 127.21 (s) | $\mathrm{(CH)_4}\mathit{C}\mathrm{Me}$ |
| | 1.84–1.30 (m, ∼15 H) | $=\mathrm{C(C}\mathit{H}_3\mathrm{)(C}\mathit{H}_2\mathrm{C}\mathit{H}_2\mathrm{CH_3)}$<br>$\mathrm{O(CH_2C}\mathit{H}_2\mathrm{)_2}$<br>$\mathrm{O(CD_2CD}\mathit{H}\mathrm{)_2}$ | 115.67 (d, $J$ = 171) | $\mathrm{(}\mathit{C}\mathrm{H)_4CMe}$ |
| | 1.01 (t, $J$ = 5, 3 H) | $\mathrm{CH_2C}\mathit{H}_3$ | 113.79 (d, $J$ = 174) | $\mathrm{(}\mathit{C}\mathrm{H)_4CMe}$ |
| | 0.69 (b s, 3 H) | $\mathrm{ZrC(C}\mathit{H}_3\mathrm{)}{=}$ | 110.62 (d, $J$ = 175) | $\mathrm{(}\mathit{C}\mathrm{H)_4CMe}$ |
| | | | 108.30 (d, $J$ = 175) | $\mathrm{(}\mathit{C}\mathrm{H)_4CMe}$ |
| | | | 44.19 (t, $J$ = 125) | $=\mathrm{C(Me)(}\mathit{C}\mathrm{H_2Et)}$ |
| | | | 21.93 (t, $J$ = 121) | $\mathrm{CH_2CH_2Me}$ |
| | | | 21.20 (q, $J$ = 123) | $=\mathrm{C(}\mathit{C}\mathrm{H_3)(^nPr)}$ |
| | | | 14.86 (q, $J$ = 124) | $\mathrm{CH_2CH_2}\mathit{C}\mathrm{H_3}$ |
| | | | 14.62 (q, $J$ = 127) | $\mathrm{(CH)_4C}\mathit{C}\mathrm{H_3}$ |
| | | | 2.69 (q, $J$ = 123) | $\mathrm{ZrC(}\mathit{C}\mathrm{H_3)}{=}$ |
| $\mathrm{Cp'_2Zr[(Me)C{=}C(Me)(^nBu)](THF)^+}$ (**10c**) (THF-$d_8$) | 6.16–5.85 (m, 8 H) | $\mathrm{C_5}\mathit{H}_4\mathrm{Me}$ | 174.72 (s) | $\mathrm{Zr(Me)}\mathit{C}{=}$ |
| | 3.69–3.53 (m, 6 H) | $\mathrm{O(C}\mathit{H}_2\mathrm{CH_2)_2}$<br>$\mathrm{O(CD}\mathit{H}\mathrm{CD_2)_2}$ | 143.90 (s) | $=\mathit{C}\mathrm{(Me)(^nBu)}$ |
| | 1.99 (s, 6 H) | $\mathrm{C_5H_4C}\mathit{H}_3$ | 127.34 (s) | $\mathrm{(CH)_4}\mathit{C}\mathrm{CH_3}$ |
| | 1.84–1.20 (m, ∼16 H) | $=\mathrm{C(C}\mathit{H}_3\mathrm{)(C}\mathit{H}_2\mathrm{C}\mathit{H}_2\mathrm{C}\mathit{H}_2\mathrm{Me)}$<br>$\mathrm{O(CH_2C}\mathit{H}_2\mathrm{)_2}$<br>$\mathrm{O(CD_2CD}\mathit{H}\mathrm{)_2}$ | 115.82 (d, $J$ = 172) | $\mathrm{(}\mathit{C}\mathrm{H)_4CMe}$ |
| | 0.98 (t, $J$ = 5, 3 H) | $\mathrm{CH_2C}\mathit{H}_3$ | 113.99 (d, $J$ = 172) | $\mathrm{(}\mathit{C}\mathrm{H)_4CMe}$ |
| | 0.67 (b s, 3 H) | $\mathrm{Zr(C}\mathit{H}_3\mathrm{)C}{=}$ | 110.63 (dm, $J$ = 170, 7) | $\mathrm{(}\mathit{C}\mathrm{H)_4CMe}$ |
| | | | 108.44 (dm, $J$ = 174, 7) | $\mathrm{(}\mathit{C}\mathrm{H)_4CMe}$ |
| | | | 41.96 (t, $J$ = 123) | $=\mathrm{C(Me)(}\mathit{C}\mathrm{H_2{}^nPr)}$ |
| | | | 31.10 (t, $J$ = 123) | $\mathrm{CH_2CH_2Et}$ |
| | | | 24.20 (t, $J$ = 125) | $\mathrm{CH_2CH_2Me}$ |
| | | | 21.28 (q, $J$ = 125) | $=\mathrm{C(}\mathit{C}\mathrm{H_3)(^n(Bu)}$ |
| | | | 14.62 (q, $J$ = 125) | $\mathrm{(CH)_4C}\mathit{C}\mathrm{H_3}$ |
| | | | 14.43 (q, $J$ = 125) | $\mathrm{CH_2CH_2}\mathit{C}\mathrm{H_3}$ |
| | | | 2.70 (q, $J$ = 123) | $\mathrm{ZrC(}\mathit{C}\mathrm{H_3)}{=}$ |
| $\mathrm{Cp'_2Zr(\eta^3\text{-}C_3H_5)(THF)^+}$ (**13**) ($\mathrm{CD_2Cl_2}$) | 6.27 (p, $J$ = 12.1, 1 H) | $\eta^3\text{-}\mathrm{CH_2C}\mathit{H}\mathrm{CH_2}$ | | |
| | 5.78 (m, 8 H) | $\mathrm{C_5}\mathit{H}_4\mathrm{CH_3}$ | | |
| | 3.54 (m, 4 H) | $\mathrm{O(C}\mathit{H}_2\mathrm{CH_2)_2}$ | | |
| | 3.21 (d, $J$ = 12.1, 4 H) | $\eta^3\text{-}\mathrm{C}\mathit{H}_2\mathrm{CHC}\mathit{H}_2$ | | |
| | 2.06 (s, 6 H) | $\mathrm{C_5H_4C}\mathit{H}_3$ | | |
| | 1.83 (m, 4 H) | $\mathrm{O(CH_2C}\mathit{H}_2\mathrm{)_2}$ | | |
| $\mathrm{Cp'_2Zr(\eta^3\text{-}C_3H_5)(THF)^+}$ (**13**) (THF-$\mathrm{d_8}$) | 6.29 (p, $J$ = 12.1, 1 H) | $\eta^3\text{-}\mathrm{CH_2C}\mathit{H}\mathrm{CH_2}$ | 136.7 | $\eta^3\text{-}\mathrm{CH_2}\mathit{C}\mathrm{HCH_2}$ |
| | 5.85 (br s, 8 H) | $\mathrm{C_5}\mathit{H}_4\mathrm{CH_3}$ | 123.7 | $\mathrm{(CH)_4}\mathit{C}\mathrm{CH_3}$ |
| | 3.22 (d, $J$ = 12.1, 4 H) | $\eta^3\text{-}\mathrm{C}\mathit{H}_2\mathrm{CHC}\mathit{H}_2$ | 114.3 | $\mathrm{(}\mathit{C}\mathrm{H)_4CCH_3}$ |
| | 2.00 (s, 6 H) | $\mathrm{C_5H_4C}\mathit{H}_3$ | 109.1 | $\mathrm{(}\mathit{C}\mathrm{H)_4CCH_3}$ |
| | | | 73.4 | $\eta^3\text{-}\mathit{C}\mathrm{H_2CH}\mathit{C}\mathrm{H_2}$ |
| | | | 15.0 | $\mathrm{(CH)_4}\mathit{C}\mathrm{H_3}$ |

[a] 23 °C unless indicated. Chemical shifts in ppm; $J$ values in Hz. [b] $J_{\mathrm{CH}}$ from gated decoupled spectra.

elemental analysis, and chemical derivatization. These data suggest that **5** has a monomeric, terminal M–H structure in solution as shown in Scheme I; however, the solid-state structure is uncertain.

The $^1$H NMR spectrum (Table I) of a THF-$d_8$ solution of **5** contains a broad singlet at $\delta$ 5.88 (1 H) which is absent from the spectrum of the corresponding deuteride complex $\mathrm{[Cp'_2Zr(D)(THF)][BPh_4]}$ (**5**-$d_1$, prepared from **4** and $\mathrm{D_2}$; coproduct toluene-$d_1$) and is assigned to the M–H ligand. This resonance is within the range normally observed for terminal hydrides in neutral $\mathrm{Cp_2Zr^{IV}}$ compounds and is far downfield of the range observed for bridging hydrides: e.g.

$[Cp'_2Zr(H)(\mu\text{-}H)]_2$ ($\delta$ 3.75 ($H_{term}$), −2.98 ($H_{br}$);[11] [(tetrahydroindenyl)$_2$Zr(H)($\mu$-H)]$_2$ ($\delta$ 4.59 ($H_{term}$), −1.56 ($H_{br}$));[12] $(C_5Me_5)_2ZrH_2$ ($\delta$ 7.46); $(C_5Me_5)_2Zr(H)(OCH_3)$ ($\delta$ 5.70);[13] $[Cp_2Zr(R)(\mu\text{-}H)]_2$ ($\mu$-H ca. $\delta$ −2).[14] Closely related, isoelectronic (neglecting f electrons) neutral group III and lanthanide hydride complexes $Cp_2M(H)(THF)$ exhibit resonances for *both* bridging and terminal M–H ligands in this range: e.g. $[(C_5H_4Me)_2Y(\mu\text{-}H)(THF)]_2$ ($\delta$ 2.31); $[(C_5H_4Me)_2Lu(\mu\text{-}H)(THF)]_2$ ($\delta$ 4.99);[15] $(C_5Me_5)_2Sc(H)(THF)$ ($\delta$ ($H_{term}$) 4.8).[8b] However, metal substitution undoubtedly has a major influence on $\delta$ (M–H) in these systems.

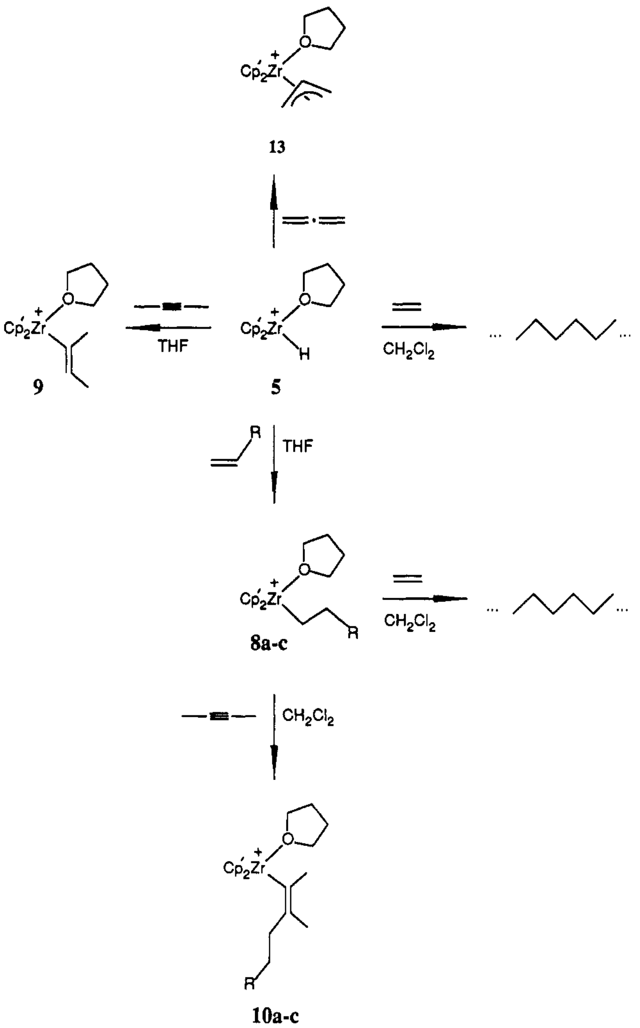
Attempted crystallization of **5** by slow cooling of, or addition of toluene to, THF solutions gives a beige solid hydride product which is only sparingly soluble in THF. The IR spectrum of this material contains an M–H stretch absorption at 1390 cm$^{-1}$ ($\nu_{M\text{-}D}$ 990 cm$^{-1}$). This band is closer to the range normally exhibited by bridging (1300–1380 cm$^{-1}$) rather than terminal (1500–1560 cm$^{-1}$) hydrides in neutral $Cp_2Zr^{IV}$ systems but is not unambiguously diagnostic for either structure.[16] For comparison, isoelectronic $Cp_2M^{III}(H)(THF)$ complexes with both terminal and bridging structures exhibit $\nu_{M\text{-}H}$ similar to that for **5**: e.g. $[(C_5H_4Me)_2Lu(\mu\text{-}H)(THF)]_2$ (1340 cm$^{-1}$); $(C_5Me_5)_2Sc(H)(THF)$ (1390 cm$^{-1}$). The M–H stretch for the $C_5H_5$ analogue of **5**, $Cp_2Zr(H)(THF)^+$ (**1**), appears at 1450 cm$^{-1}$.[9]

The presence of hydride and THF ligands in **5** is clearly established by derivatization reactions with unsaturated substrates. For example, **5** reacts upon dissolution with $CH_3CN$ to produce insertion product **7** with liberation of THF (eq 2). The neutral hydride $Cp_2Zr(H)(Cl)$ undergoes similar insertion reactions.[17]

$$\underset{\mathbf{5}}{Cp'_2Zr(H)(THF)^+} + CH_3CN \rightarrow \underset{\mathbf{7}}{Cp'_2Zr[N{=}C(CH_3)(H)](CH_3CN)^+} + THF \quad (2)$$

**Reaction of 5 with Olefins. Synthesis of Cationic Alkyl Complexes.** Cationic hydride complex **5**, generated in situ in THF solution from **4**, reacts rapidly with olefins $H_2C{=}CHR$ (R = H, Me, Et) at room temperature to give yellow, cationic alkyl complexes $[Cp'_2Zr(CH_2CH_2R)(THF)][BPh_4]$ (**8a**, R = H; **8b**, R = Me; **8c**, R = Et; Scheme II) which can be isolated in 80–90% yield by precipitation with toluene. These reactions are directly analogous to olefin hydrozirconation by $Cp_2Zr(H)(Cl)$.[18] Note that cationic alkyl complexes **8** are not accessible by oxidation reactions analogous to eq 1 since the requisite dialkyls $Cp'_2Zr(CH_2CH_2R)_2$ are not stable. Key spectroscopic features for **8a–c** (Table I) include characteristic patterns for the alkyl ligands in the $^1H$ NMR spectra and $^{13}C$ resonances at $\delta$ 60–70 for the $ZrCH_2CH_2R$ carbons. A sharp singlet for the $C_5H_4CH_3$ hydrogens is observed in each case and provides a convenient means of assessing purity. There is no evidence for agostic interaction in these complexes even though $\beta$-hydrogens are present.[19] For example, the C–H coupling constants for the ethyl group of **8a** are normal, and no low-energy C–H stretching vibrations are observed in the IR spectrum of this complex.

Scheme II



Cationic alkyl complexes **8a–c** are soluble and thermally stable in THF but slowly decompose in $CH_2Cl_2$ (e.g. $t_{1/2}$ for **8a** = ca. 28 h, 23 °C). These reactions were not studied in detail but likely involve Cl$^-$ abstraction from solvent as observed for **4**. A low *T* (−78 °C) $^1H$ NMR spectrum of a $CD_2Cl_2$ solution of ethyl derivative **8a** exhibits resonances for coordinated THF at $\delta$ 3.10 ($\alpha$-$CH_2$) and 1.68 ($\beta$-$CH_2$). No evidence for THF dissociation is observed under these conditions. A spectrum of the above solution under the same conditions but with 2.6 equiv of excess THF added exhibits separate resonances for coordinated (1 equiv) and free THF. This establishes that exchange of coordinated and added free THF is slow on the NMR time scale under these conditions and that **8a** (like **3**) does not coordinate a second equivalent of THF. Exchange of coordinated and free THF is rapid on the NMR time scale at room temperature in $CD_2Cl_2$ and THF-$d_8$ solvents.

**Reactions of 5 and 8 with 2-Butyne. Synthesis and Solution Structures of Cationic Alkenyl Complexes.**

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Cationic hydride complex **5**, generated in situ, reacts readily with 2-butyne in THF at room temperature to give $[Cp'_2Zr\{(E)\text{-}C(CH_3){=}C(H)(CH_3)\}(THF)][BPh_4]$ (**9**, Scheme II) which can be isolated as a beige solid by precipitation with toluene (98%). Complex **9** has been characterized by $^1H$ and $^{13}C$ NMR spectroscopy (Table I). The IR spectrum of **9** exhibits a weak, broad band centered at 1630 $cm^{-1}$ which is assigned to the C=C stretch. The geometry of the alkenyl ligand is established by hydrolysis which gives *cis*-2-butene as the sole organic product. Similarly, cationic alkyls **8a–c** react with 2-butyne in $CH_2Cl_2$ solvent under mild conditions to produce the insertion products $[Cp_2Zr\{(Z)\text{-}C(CH_3){=}C(CH_3)(R)\}(THF)][BPh_4]$ (**10a–c**, Scheme II). There is no evidence for multiple 2-butyne insertions or for competing $\beta$-H eliminations[7b] in any of these reactions.

The solution behavior and structures of cationic alkenyl complexes **9** and **10a–c** have been probed by $^1H$ and $^{13}C$ NMR spectroscopy (Table I). The ambient-temperature $^1H$ NMR spectrum of a $CD_2Cl_2$ solution of **10b** containing 2 equiv of added excess THF exhibits separate signals for coordinated (1 equiv) and free THF. Similar results are obtained with **10a**. The ambient-temperature $^{13}C$ spectra of concentrated THF-$d_8$ solutions of **9** and **10a** exhibit resonances for coordinated and free THF as well as coordinated and free THF-$d_8$.[20] These observations establish that for these cationic alkenyl complexes THF exchange is fast on the chemical time scale but, in contrast to the case for **8a–c**, slow on the NMR time scale at ambient temperature. Consistent with this conclusion, the sides of the Cp′ rings are inequivalent and ABCD patterns are observed for the unsubstituted ring carbons in the $^{13}C$ spectra. The $^1H$ NMR results also indicate that **10a** and **10b** do not coordinate a second equivalent of THF.

For both **9** and **10**, only a single Cp′ ring methyl resonance, and only a single set of alkenyl resonances are observed in both the $^1H$ and $^{13}C$ spectra of THF-$d_8$ solutions at ambient temperature. These results are consistent either with the existence of a single isomer in which the alkenyl ligand lies in the plane between the two Cp′ ligands or with rapid rotation about the Zr–C bond. Two isomers are possible for a $Cp_2M(alkenyl)(X)$ complex in which the alkenyl ligand lies in the plane between the Cp ligands: an endo isomer in which the alkenyl double bond is directed toward X and an exo isomer in which it is directed away from X. Slow (NMR time scale) interconversion of endo/exo isomers is observed for the $d^0$ butenyl complex $(C_5Me_5)_2Hf(H)[(E)\text{-}C(CH_3){=}CH(CH_3)]$ (**11**) and the $d^2$ complex $(C_5Me_5)_2Nb(CO)[(E)\text{-}C(CH_3){=}CH(CH_3)]$ (**12**).[21] In both cases, substantial differences in the butenyl $\beta$-H and $\alpha$-$CH_3$ $^1H$ chemical shifts (ca. $\Delta\delta = 0.2–1.4$), and the alkenyl $^{13}C$ chemical shifts (ca. $\Delta\delta = 1–33$) of the two isomers are observed. Low-temperature $^1H$ NMR spectra (−70 °C, 500 MHz) of THF-$d_8$ solutions of **9** and of **10a** exhibit no broadening or splitting of the Cp′ methyl or alkenyl resonances. Similarly, the −70 °C $^{13}C$ spectrum (50.3 MHz) of **9** is unchanged from the ambient-temperature spectrum. Given the large $^1H$ and $^{13}C$ NMR spectral differences observed for the exo and endo isomers of **11** and **12** noted above, these observations strongly suggest that cationic Zr alkenyl complexes **9** and **10a** exist in solution as single exo or endo isomers (with the alkenyl ligand in the plane between the Cp′ ligands) and not as rapidly interconverting pairs.

**Table II. Positional Parameters for $[Cp'_2Zr\{(Z)\text{-}C(Me){=}C(Me)(^nPr)\}(THF)][BPh_4]$ (10b)**

| atom | *x* | *y* | *z* | *B*,[a] Å² |
|---|---|---|---|---|
| Zr | −0.18790 (8) | 0.57047 (5) | 0.78418 (6) | 4.08 (2) |
| O1 | −0.1773 (5) | 0.6025 (4) | 0.6524 (4) | 5.0 (2) |
| C1 | −0.2439 (9) | 0.4564 (6) | 0.7028 (7) | 5.3 (2)* |
| C2 | −0.2528 (8) | 0.4689 (5) | 0.7890 (6) | 4.5 (2)* |
| C3 | −0.285 (1) | 0.4227 (6) | 0.8371 (8) | 6.3 (3)* |
| C4 | −0.317 (1) | 0.3545 (7) | 0.8033 (9) | 7.9 (3)* |
| C5 | −0.276 (1) | 0.4295 (9) | 0.930 (1) | 10.8 (5)* |
| C6 | −0.381 (2) | 0.412 (1) | 0.962 (2) | 15.6 (7)* |
| C7 | −0.344 (2) | 0.421 (1) | 1.061 (2) | 17.0 (8)* |
| C11 | −0.0121 (9) | 0.5017 (5) | 0.8430 (7) | 5.1 (2)* |
| C12 | −0.0448 (9) | 0.5382 (6) | 0.9051 (7) | 5.9 (3)* |
| C13 | −0.027 (1) | 0.6033 (6) | 0.8904 (8) | 6.6 (3)* |
| C14 | 0.012 (1) | 0.6080 (6) | 0.8164 (8) | 6.8 (3)* |
| C15 | 0.0176 (9) | 0.5457 (6) | 0.7869 (8) | 5.8 (3)* |
| C16 | −0.001 (1) | 0.4281 (7) | 0.8405 (8) | 7.3 (3)* |
| C21 | −0.293 (1) | 0.6263 (6) | 0.8842 (8) | 6.9 (3)* |
| C22 | −0.370 (1) | 0.5864 (6) | 0.8349 (8) | 6.2 (3)* |
| C23 | −0.383 (1) | 0.6115 (6) | 0.7543 (8) | 6.3 (3)* |
| C24 | −0.3163 (9) | 0.6665 (6) | 0.7563 (8) | 5.9 (3)* |
| C25 | −0.257 (1) | 0.6755 (6) | 0.8335 (8) | 6.5 (3)* |
| C26 | −0.260 (1) | 0.6233 (8) | 0.980 (1) | 10.0 (4)* |
| C32 | −0.268 (1) | 0.5936 (6) | 0.5790 (8) | 6.8 (3)* |
| C33 | −0.2216 (9) | 0.6208 (6) | 0.5091 (7) | 6.1 (3)* |
| C34 | −0.146 (1) | 0.6740 (6) | 0.5449 (8) | 6.4 (3)* |
| C35 | −0.097 (1) | 0.6496 (6) | 0.6302 (8) | 6.3 (3)* |
| B | −0.7809 (9) | 0.1512 (5) | −0.0770 (7) | 3.5 (2)* |
| C1P | −0.8248 (8) | 0.0788 (5) | −0.1156 (6) | 4.3 (2)* |
| C2P | −0.9052 (8) | 0.0423 (5) | −0.0849 (6) | 4.3 (2)* |
| C3P | −0.9426 (9) | −0.0191 (6) | −0.1159 (7) | 5.5 (3)* |
| C4P | −0.902 (1) | −0.0439 (6) | −0.1787 (8) | 6.3 (3)* |
| C5P | −0.820 (1) | −0.0122 (7) | −0.2104 (8) | 6.9 (3)* |
| C6P | −0.7816 (9) | 0.0485 (6) | −0.1781 (7) | 5.8 (3)* |
| C11P | −0.6760 (8) | 0.1395 (5) | 0.0000 (6) | 4.4 (2)* |
| C12P | −0.6388 (9) | 0.1889 (5) | 0.0559 (7) | 5.1 (2)* |
| C13P | −0.547 (1) | 0.1809 (6) | 0.1206 (8) | 6.2 (3)* |
| C14P | −0.4906 (9) | 0.1231 (6) | 0.1280 (7) | 6.2 (3)* |
| C15P | −0.5224 (9) | 0.0730 (6) | 0.0759 (7) | 6.1 (3)* |
| C16P | −0.6152 (8) | 0.0812 (5) | 0.0116 (7) | 4.9 (2)* |
| C21P | −0.8824 (7) | 0.1880 (5) | −0.0412 (6) | 3.6 (2)* |
| C22P | −0.9566 (8) | 0.2319 (5) | −0.0878 (6) | 4.4 (2)* |
| C23P | -1.0471 (9) | 0.2610 (5) | −0.0554 (7) | 5.1 (2)* |
| C24P | -1.0613 (9) | 0.2479 (5) | 0.0224 (7) | 5.1 (2)* |
| C25P | −0.9919 (9) | 0.2051 (6) | 0.0702 (7) | 5.3 (3)* |
| C26P | −0.9035 (8) | 0.1758 (5) | 0.0377 (6) | 4.7 (2)* |
| C31P | −0.7451 (8) | 0.1963 (5) | −0.1497 (6) | 4.3 (2)* |
| C32P | −0.6566 (9) | 0.2414 (5) | −0.1356 (7) | 5.1 (2)* |
| C33P | −0.635 (1) | 0.2836 (6) | −0.1980 (8) | 6.7 (3)* |
| C34P | −0.697 (1) | 0.2800 (7) | −0.2758 (8) | 7.3 (3)* |
| C35P | −0.7806 (9) | 0.2368 (6) | −0.2934 (7) | 6.3 (3)* |
| C36P | −0.8051 (9) | 0.1954 (6) | −0.2300 (7) | 5.5 (3)* |
| C1X | −0.0107 | 0.5593 | 0.8463 | 0* |
| C2X | −0.3219 | 0.6331 | 0.8126 | 0* |

[a] Parameters with an asterisk were refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as $(^4/_3)[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$.

Published ambient-temperature spectra for neutral $Cp_2Zr(alkenyl)(Cl)$ complexes and $Cp_2Y(alkenyl)(THF)$ complexes all exhibit a single Cp resonance and a single pattern for the alkenyl ligand.[8d,22] Apparently, low-temperature NMR studies have not been performed on these systems. Slow exo/endo interconversion has been observed for the $d^2$ complexes $Cp_2W(H)[(Z)\text{-}C(CO_2Me){=}C(CO_2Me)H]$ and $Cp_2W(H)\{(Z)\text{-}C(CF_3){=}C(CF_3)H\}$.[23]

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(20) $^{13}C\{^1H\}$ NMR (THF-$d_8$): free THF, $\delta$ 68.22, 26.36; free THF-$d_8$, $\delta$ 67.40, 25.30; **9**-coordinated THF, $\delta$ 71.27, 27.60; **9**-coordinated THF-$d_8$, $\delta$ 70.24, 26.36. **10a**-coordinated THF, $\delta$ 71.22, 27.26; **10a**-coordinated THF-$d_8$, $\delta$ 70.28, 26.41.

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**Table III. Selected Bond Distances (Å) and Angles (deg) for $[Cp'_2Zr\{C(Me){=}C(Me)(^nPr)\}(THF)][BPh_4]$**

| | | | |
|---|---|---|---|
| | Bond Distances | | |
| Zr–O1 | 2.289 (6) | Zr–C11 | 2.588 (9) |
| Zr–C2 | 2.227 (9) | Zr–C12 | 2.48 (1) |
| Zr–H1A | 2.32 | Zr–C13 | 2.46 (2) |
| Zr–C1 | 2.72 (1) | Zr–C14 | 2.50 (1) |
| C1–C2 | 1.46 (1) | Zr–C15 | 2.53 (1) |
| C2–C3 | 1.33 (1) | Zr–C21 | 2.52 (1) |
| C3–C4 | 1.53 (2) | Zr–C22 | 2.51 (1) |
| C3–C5 | 1.52 (2) | Zr–C23 | 2.47 (1) |
| C5–C6 | 1.50 (3) | Zr–C24 | 2.50 (1) |
| C6–C7 | 1.62 (3) | Zr–C25 | 2.49 (1) |
| O1–C32 | 1.49 (1) | Zr–C1x | 2.2217 (8) |
| O1–C35 | 1.46 (1) | Zr–C2x | 2.2003 (9) |
| C32–C33 | 1.47 (1) | C11–C16 | 1.51 (1) |
| C33–C34 | 1.47 (1) | C21–C26 | 1.55 (2) |
| C34–C35 | 1.51 (1) | | |
| | Bond Angles | | |
| O1–Zr–C2 | 112.4 (3) | Zr–C2–C3 | 145.2 (8) |
| C1x–Zr–C2x | 130.61 (4) | Zr–C2–C1 | 92.4 (6) |
| O1–Zr–H1A | 61.7 (1) | C2–C3–C5 | 124 (1) |
| O1–Zr–C1x | 105.5 (2) | C2–C3–C4 | 121 (1) |
| O1–Zr–C2x | 101.7 (2) | C1–C2–C3 | 121.9 (9) |
| C2–Zr–H1A | 52.4 (3) | C4–C3–C5 | 115 (1) |
| C2–Zr–C1x | 101.7 (3) | C32–O1–C35 | 107.8 (7) |
| C2–Zr–C2x | 104.8 (2) | | |

[a] C*n*x denotes Cp′ ring centroid.

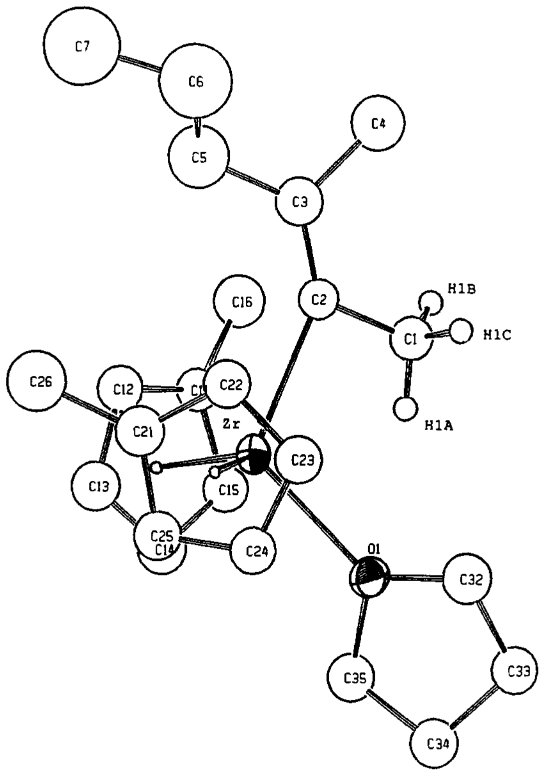

**Figure 1.** Structure of the $Cp'_2Zr\{(Z)\text{-}C(Me){=}C(Me)(^nPr)\}(THF)^+$ cation (**10b+**). Hydrogen atoms except H1a–c are removed for clarity.

**Solid-State Structure of $[Cp'_2Zr\{(Z)\text{-}C(CH_3){=}C(CH_3)(^nPr)\}(THF)][BPh_4]$ (10b).** The solid-state structure of **10b** was determined by single-crystal X-ray diffraction and consists of discrete $Cp'_2Zr\{(Z)\text{-}C(Me){=}C(Me)(^nPr)\}(THF)^+$ and $BPh_4^-$ ions. The structure of the cation is shown in Figure 1, selected bond lengths and angles are listed in Table II, and atomic coordinates are listed in Table III. The cation of **10b** adopts a normal bent metallocene structure with the Cp′–Zr–Cp′ angle and Zr–C and Zr–centroid distances in the range observed for other cationic and neutral zirconocene complexes.[4,5,11,24]

The alkenyl ligand lies in the plane between the two Cp′ ligands in the exo conformation. The *Z* geometry confirms that 2-butyne insertion into Zr–R bonds occurs in a cis fashion. The Zr–C($sp^2$) distance (2.229 (9) Å) is slightly longer than the Zr–C($sp^2$) distance in the neutral, crowded alkenyl complex $Cp_2Zr\{C(Ph){=}CMe_2\}Cl$ (2.296 (3) Å)[25] and is slightly shorter than the Zr–C($sp^3$) distance in **3** (2.256 (10) Å).[5] This distance is nearly identical, after correction for differences in ionic radii,[26] with the Ti–C distance in Eisch's Ti cation $Cp_2TiC(SiMe_3){=}C(Ph)(Me)^+$.[1a] π-Donation from the alkenyl ligand to the LUMO of the 16-electron $Zr^{IV}$ center, which is localized in the plane between the two Cp′ ligands, is precluded by symmetry.[27] The normal Zr—C and C═C distances and the normal structure of the $Cp'_2Zr$ framework of **10b** also establish that π donation to higher energy (perpendicular), empty Zr–Cp′ antibonding orbitals is not significant. Such π interactions have been invoked to explain deviations from normal M–Cp bonding in compounds such as $Cp_2Mo(NO)R$.[28]

The Zr–C2–C3 angle (145.2°) and the O1–Zr–C2 angle (112.1°) associated with the alkenyl ligand are considerably larger than the expected values of 120 and 95–99°, respectively, apparently as a result of steric factors. There are several close H–H contacts between the propyl group and the Cp′ ligands and between the C1 methyl group and the THF ligand. Pivoting of the alkenyl ligand to reduce either of these angles would increase these nonbonded steric interactions. An interesting feature associated with the exo conformation and distorted structure of the alkenyl ligand is the close contact between Zr and the α-$CH_3$ group (Zr–C1 distance (2.725 (10) Å)). The H atoms on C1 were found on electron density maps, but their positions are uncertain due to normal limitations of the X-ray method. Nevertheless, it is clear that H1a is within 2.4 Å of the Zr center and is located in the plane containing the Zr-based LUMO.[27] These Zr–C and Zr–H distances are at the long end of the range observed for agostic C–H interactions in $d^0$ metal systems (after correction for differences in metal radii if necessary) and suggest that a weak agostic interaction is present in this case.[29] No unusual features associated with an agostic interaction are observed in the NMR and IR spectra.

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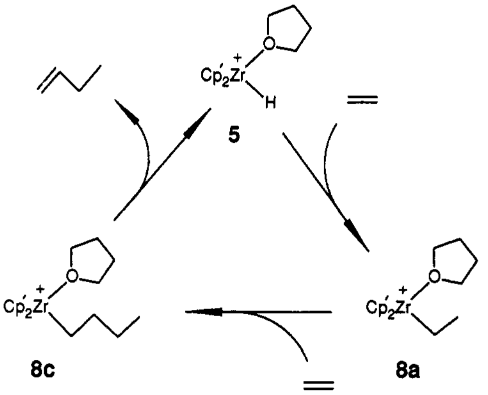
(28) See ref 27 and (a) Cotton, F. A.; Rusholme, G. A. *J. Am. Chem. Soc.* **1972**, *94*, 402. (b) Calderon, J. L.; Cotton, F. A.; Legdzins, P. *J. Am. Chem. Soc.* **1969**, *91*, 2528. (c) Huttner, G.; Brintzinger, H. H.; Bell, L. G.; Friedrich, P.; Bejenke, V.; Neugebauer, D. *J. Organomet. Chem.* **1978**, *145*, 329.

(29) For several cases distances are in the ranges 2.5–2.6 Å (Zr–C) and 2.1–2.5 Å (Zr–H). See ref 1d and: (a) Erker, G.; Fromberg, W.; Angermund, K.; Schlund, R.; Kruger, C. *J. Chem. Soc., Chem. Commun.* **1986**, 372. (b) Cayais, J. Z.; Babaian, E. A.; Hrncir, D. C.; Bott, S. G.; Atwood, J. L. *J. Chem. Soc., Dalton Trans.* **1986**, 2743. For Ti cases see: (c) Dawoodi, Z.; Green, M. L. H.; Mtwetwa, V. S. B.; Prout, K.; Schultz, A. J.; Williams, J. M.; Koetzle, T. F. *J. Chem. Soc., Dalton Trans.* **1986**, 1629. (d) Park, J. W.; Mackenzie, P. B.; Schaefer, W. P.; Grubbs, R. H. *J. Am. Chem. Soc.* **1986**, *108*, 6402.

In a previous study it was found that the THF ligand of cationic methyl complex **3** lies nearly perpendicular to the plane between the two Cp ligands in an orientation which allows for near maximum overlap of the p-type O lone pair and the Zr LUMO.[5a] The short Zr–O distance and chemical reactivity data support the existence of a four-electron ($\sigma,\pi$) donor THF in this complex. The orientation of the THF ligand in **10b** is most clearly shown in Figure 2, which is the view down the Zr–O bond. The Zr–O bond is 12° out of the C35–O–C32 plane of the THF ligand; i.e., the O is nearly planar as for **3** and other THF complexes.[30] However, the dihedral angle between the C35–O–C32 plane of the THF ligand and the O–Zr–C2 plane is 140.26°; i.e., the THF ligand is rotated 50° from the angle of maximum Zr–O $\pi$ overlap. The Zr–O distance (2.288 (6) Å) is significantly longer than that of **3** (2.12 (1) Å). These structural data suggest that the Zr–O $\pi$ interaction in **10b** is diminished relative to that in **3**. The weaker $\pi$ interaction may simply result from the steric crowding described above or may be the result of electronic factors. The increased electron density at Zr in **10b** vs **3**, resulting from the Me substituents on the Cp ligands[31] and possibly the agostic C–H interaction, is expected to reduce the Lewis acidity of the Zr center and may weaken the Zr–O $\pi$ bond. Structural data for additional compounds are needed to resolve this issue.

**Reaction of 5 with Allene. Synthesis of $Cp'_2Zr(allyl)(THF)^+$ (13).** Hydride **5** reacts rapidly with allene in THF solution to yield cationic allyl complex **13** which was isolated by crystallization from $Et_2O$/THF (Scheme II). IR and NMR data for **13** establish the dynamic $\eta^3$-allyl structure in Scheme II. The IR spectrum of **13** exhibits a band at 1543 $cm^{-1}$ which is characteristic of an $\eta^3$-allyl ligand.[32] This band is absent from the IR spectra of **8a** and $[Cp'_2Zr(CH_3)(THF)][BPh_4]$[33] which are otherwise nearly identical with that of **13**. In contrast, $\sigma$-allyl complexes exhibit a C=C stretch at 1580–1620 $cm^{-1}$.[32] The low-temperature (158 K) $^1H$ NMR spectrum of **13** (360 MHz, THF-$d_8$) exhibits two broad singlets for the syn H's, two broad singlets for the anti H's, and a broad singlet for the central H of the allyl ligand, two $C_5H_4CH_3$ resonances and a complex $C_5H_4Me$ pattern consistent with eight inequivalent H's.[34] This spectrum is consistent with the structure shown in Scheme II. At this temperature syn/anti and/or exo/endo exchange is sufficiently rapid to broaden the allyl resonances and mask the H–H couplings but is not fast enough to collapse the resonances of the inequivalent (endo and exo) pairs of syn and anti hydrogens. The 233 K $^1H$ NMR spectrum of **13** exhibits a broad $AX_4$ pattern for the allyl ligand, a singlet for the $C_5H_4CH_3$ groups, and an ABCD pattern for $C_5H_4Me$ ring hydrogens consistent with rapid syn/anti and endo/exo exchange of the allyl ligand and slow exchange of THF.[34] At 297 K, the $C_5H_4Me$ pattern is a broad singlet consistent with fast THF exchange. Rotation about the Zr–$\pi$-allyl bond causes Cp′Me exchange and endo/exo exchange but not syn/anti exchange. The latter process requires $\pi$-$\sigma$ isomerization and rotation about the $ZrCH_2$–$CHCH_2$ bond of the $\sigma$-allyl intermediate. For comparison, IR results suggest that $Cp_2Zr(C_3H_5)Cl$ has a $\sigma$-allyl ligand and that $Cp_2Zr(C_3H_5)_2$ has one $\sigma$- and one $\pi$-allyl ligand, and X-ray results establish that $CpZr(allyl)_3$ has one $\sigma$-, one $\pi$-, and one distorted $\sigma,\pi$-allyl ligand.[35]

**Scheme III**



**Reactions of $[Cp'_2Zr(R)(THF)][BPh_4]$ Complexes with Ethylene. Dimerization vs Polymerization.** As noted above, the reaction of cationic hydride complex **5** with ethylene in THF solution at 23 °C initially produces ethyl complex **8a** which can be isolated in high yield. However, in a slower reaction ethylene is catalytically oligomerized to a mixture of 1-butene, 1-hexene, and 1-octene under these conditions. This reaction likely proceeds by a standard insertion/$\beta$-H elimination mechanism as shown in Scheme III.[36] Consistent with this scheme, THF solutions of ethyl complex **8a** and butyl complex **8c** catalytically oligomerize ethylene with activity similar to that of **5**. The higher olefins arise from further reaction of ethylene with Zr–Bu and Zr–hexyl intermediates. Ethyl complex **8a** does not undergo significant reaction with 1-butene at ambient temperature, suggesting that reaction of 1-butene with $Cp'_2Zr(R)(THF)^+$ intermediates is not an important chain growth step.[37] $^1H$ NMR monitoring of this reaction reveals the presence of $Cp'_2Zr(R)(THF)^+$ complexes (**8a** and **8c** cannot be distinguished after significant formation of $\alpha$-olefins due to overlapping resonances) and the absence of cationic hydride **5**. Thus for this system, the catalyst resting state is one of the alkyl intermediates and not hydride **5**.[38]

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(30) For example see: (a) Evans, W. J.; Dominguez, R.; Hanusa, T. P. *Organometallics* **1986**, *5*, 263. (b) Girolami, G. S.; Milam, S. N.; Suslick, K. S. *Inorg. Chem.* **1987**, *26*, 343. (c) van der Heijden, H., Schaverien, C. J.; Orpen, A. G. *Organometallics* **1989**, *8*, 255. (d) den Haan, K. H.; Luinstra, G. A.; Meetsma, A.; Teuben, J. H. *Organometallics* **1987**, *6*, 1509. (e) Clark, D. L.; Sattelberger, A. P.; Bott, S. G.; Vrtis, R. N. *Inorg. Chem.* **1989**, *28*, 1771.

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(34) $^1H$ NMR spectrum for **13**: (a) 158 K, THF-$d_8$, 360 MHz, $\delta$ 7.5–6.5 (m, 20 H, $BPh_4^-$), 6.44 (br s, 1 H, $\eta^3$-$CH_2CHCH_2$), 6.18 (br s, 1 H), 6.08 (br s, 1 H), 6.04 (br s, 3 H), 5.99 (br s, 1 H), 5.87 (br s, 1 H), 5.82, 5.80 (br d, 2 H) $C_5H_4Me$, 4.01 (br s, 1 H), 3.75 (br s, 1 H) allyl syn, 2.74 (br s, 1 H), 2.44 (br s, 1 H) allyl anti, 2.16 (s, 3 H), 1.97 (s, 3 H) $C_5H_4CH_3$; (b) 233 K, 7.29 (br s, 8 H), 6.90 (t, $J$ = 7.0 Hz, 8 H), 6.77 (t, $J$ = 6.8 Hz, 4 H), 6.35 (p, $J$ = 12.1, 1 H), 5.98 (m, 2 H), 5.91 (m, 1 H), 5.89 (m, 1 H), 5.83 (m, 1 H), 3.22 (br d, $J$ = 12 Hz, 4 H), 2.01 (s, 6 H).

(35) (a) Martin, H. A.; Lemaire, P. J.; Jellinek, F. *J. Organomet. Chem.* **1968**, *14*, 149. (b) Erker, G.; Berg, K.; Angermund, K.; Kruger, C. *Organometallics* **1987**, *6*, 2620.

(36) (a) Review: Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987; p 593. (b) Cramer, R. *Acc. Chem. Res.* **1968**, *1*, 186. (c) Smith, P. D.; Klendworth, D. D.; McDaniel, M. P. *J. Catal.* **1987**, *105*, 187.

(37) A THF-$d_8$ solution of **8a** containing excess 1-butene evolves minor amounts of ethylene after days at ambient temperature, presumably as a result of $\beta$-H elimination followed by trapping of **5** with butene. The other expected product **8c** cannot be distinguished from **8a** under these conditions due to overlapping resonances.

(38) Compare to ESCA results for alumoxane ethylene polymerization catalyst systems in ref 1b.

As reported previously, the cationic Cp complexes $Cp_2Zr(R)(THF)^+$ (R = $CH_3$ (**3**), $CH_2Ph$) catalyze the polymerization of ethylene in $CH_2Cl_2$ solution.[4a,5] Similarly the Cp′ complexes **4**, **5**, and **13** polymerize ethylene (1 atm) in $CH_2Cl_2$ solvent at room temperature.

## Discussion and Comparison with Other Systems

Neutral early metal hydrides undergo alkyne and olefin insertions to yield alkenyl and alkyl complexes, respectively; for $d^0$ systems cis insertions are invariably observed.[39] Similar reactivity is observed for cationic hydride complex **5**. Neutral $Cp_2Zr(R)(Cl)$ complexes do not react with internal alkynes or with olefins.[40] In contrast, cationic alkyl complexes **8a–c** undergo clean single insertion of 2-butyne and multiple insertions of ethylene (i.e. polymerization) under mild conditions. The increased reactivity of the $Cp'_2Zr(R)(THF)^+$ complexes results from the high lability of the THF ligand and the enhanced Lewis acidity of the cationic metal center. This combination promotes coordination and activation of 2-butyne, ethylene, or other substrates and opens up reaction pathways which are unavailable to neutral $Cp_2Zr(R)(Cl)$ and $Cp_2Zr(R)_2$ complexes.[41,42]

The insertion reactivity of $Cp'_2Zr(R)(THF)^+$ complexes is clearly related to the extent and rate of THF dissociation. In the case of ethylene, insertion is much more rapid in $CH_2Cl_2$ than in THF, presumably as a result of the higher steady state concentration of the 14-electron species $Cp'_2Zr(R)^+$ (or its $CH_2Cl_2$ solvate) in the former solvent.[43] This difference is reflected in observed activities and product molecular weights (polymer vs oligomer). In the case of 2-butyne, single insertions are observed with **5** and **8a–c** to give alkenyl complexes **9** and **10a–c** which are unreactive with excess alkyne. The lack of further insertion is attributed to the relative nonlability of the THF ligands in the alkenyl complexes (exchange slow on the NMR time scale).[44] More detailed kinetic studies of ligand exchange and 2-butyne insertion reactions of these systems are in progress.

The highly coordinatively unsaturated neutral complex $(C_5Me_5)_2Sc(CH_3)$ also inserts 2-butyne to produce $(C_5Me_5)_2Sc\{C(CH_3){=}C(CH_3)_2\}$.[8b] However, in contrast to the simple insertions observed for **5** and **8a–c**, the 2-butyne reactions of analogous Sc alkyls containing β-hydrogens proceed by initial rate-limiting β-H elimination and subsequent trapping of $Cp^*_2ScH$ by 2-butyne insertion.[7b] This difference between the $(C_5Me_5)_2Sc$ and $Cp'_2Zr^+$ systems may result from several factors including (i) inhibition of insertion by steric crowding in the $(C_5Me_5)_2ScCH_2CH_2R$ systems and (ii) inhibition of β-H elimination in **8a–c** by π donation from the THF ligand[9] which utilizes the required metal-centered empty orbital. Investigation of the reactions of $Cp'_2Zr(R)(L)^+$ complexes with other substrates may provide a better understanding of these differences.[44]

## Experimental Section

**General Considerations.** All manipulations were performed under an inert atmosphere or under vacuum by using a Vacuum Atmospheres drybox or a high vacuum line. Solvents were purified by initial distillation from an appropriate drying/deoxygenating agent followed by vacuum transfer from same.[45] NMR spectra were obtained on a JEOL FX-90Q, Nicolet 200, or Bruker 300 or 360 instrument. $^1H$ and $^{13}C$ chemical shifts are reported vs $Me_4Si$ and were determined by reference to the residual $^1H$ or $^{13}C$ solvent peaks. IR spectra (KBr) were recorded on Perkin-Elmer 238 or Mattson Cygnus 25 instruments. Elemental analyses were performed by Analytische Laboratorien or Shwarzkopf Microanalytical Laboratory Inc. $ZrCl_4$ was purchased from Cerac and sublimed (250 °C, $10^{-4}$ Torr) before use. Olefins were purchased from Matheson (ethylene, propene, 1-butene) or Aldrich (*cis*- and *trans*-2-butenes) and used as received. 2-Butyne was purchased from Aldrich and vacuum transferred from activated 4A molecular sieves directly into reaction vessels. $Na[BPh_4]$ and $(C_5H_4Me)_2Fe$ were used as received from Aldrich. $K[CH_2Ph]$ was prepared by Schlosser's method.[46]

**$[Cp'_2Fe][BPh_4]$.** An Erlenmeyer flask was charged with 1,1′-dimethylferrocene (5.06 g, 23.6 mmol) and concentrated sulfuric acid (Analytical Reagent grade, 50 mL). This mixture was stirred at 25 °C for 40 min to give a viscous blue-green solution, which was added to 1200 mL of ice water with stirring. Filtration of this solution removed a small amount of gummy orange-brown solid. The resulting clear, deep blue solution was added to a stirred solution of $Na[BPh_4]$ (8.081 g, 23.61 mmol) in 1000 mL of distilled water. The light blue precipitate that formed was collected by filtration, washed with 5 × 500 mL of $H_2O$, and dried by suction (12 h) and under high vacuum (12 h); yield 11.57 g, 91.9%.

**$Cp'_2ZrCl_2$.**[47] Methylcyclopentadiene dimer (60 mL) was cracked under $N_2$ to provide crude Cp′H, which was then distilled through a 20-cm Vigreux column (74–75 °C) and collected in a flask cooled to −78 °C. Cp′H (12.4 mL, 10.0 g, 0.125 mol) and toluene (300 mL) were placed in a 500-mL three-neck flask equipped with a mechanical stirring shaft, reflux condenser, and septum inlet. Rapid stirring was initiated, and a hexane solution of $^n$BuLi (13.4 mL, 9.5 M, 0.13 mol) was added via syringe over a period of 10 min. The resulting warm, viscous slurry of colorless solid was stirred for an additional 10 min, at which time the septum inlet was replaced, under $N_2$ counterflow, with a solid addition side arm containing $ZrCl_4$ (14.7 g, 0.063 mol). Addition of the $ZrCl_4$ to the stirred slurry (over a period of 15 mins) resulted in a noticeable reduction of the reaction mixture's viscosity. This stirred mixture was heated and allowed to reflux for 48 h. The reaction mixture was allowed to cool, and the volatiles were removed in vacuo. The residue was slurried in 400 mL of $CH_2Cl_2$ and extracted with 4 N aqueous HCl (1 × 150 mL and 3 × 50 mL). The green $CH_2Cl_2$ solution was dried over $MgSO_4$ and stripped of volatiles in a rotary evaporator. The residue was crystallized from toluene (80 mL) to afford 15.57 g of large off-white plates. The dark brown residue from the filtrate was sublimed (160 °C, $10^{-4}$ Torr) to give an additional 3.1 g of product, yield 93%.

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[39] (a) $Cp_2Zr(H)Cl$: Hart, D. W.; Blackburn, T. F.; Schwartz, J. *J. Am. Chem. Soc.* **1975**, *97*, 679. (b) $(C_5Me_5)_2Sc(H)$: Thompson, M. E.; Bercaw, J. E. *Pure Appl. Chem.* **1984**, *56*, 1. (c) $(C_5Me_5)_2HfH_2$: Roddick, D. M.; Fryzuk, M. D.; Seidler, P. F.; Hillhouse, G. L.; Bercaw, J. E. *Organometallics* **1985**, *4*, 97.

[40] For example see: Yoshida, T.; Negishi, E. *J. Am. Chem. Soc.* **1981**, *103*, 4985.

[41] Cationic, $d^0$ alkylidene/metallocyclobutane complexes are active species in olefin metathasis catalyst systems for similar reasons. (a) Kress, J.; Osborn, J. A.; Greene, R. M. E.; Ivin, K. J.; Rooney, J. J. *J. Am. Chem. Soc.* **1987**, *109*, 899. (b) Kress, J.; Osborn, J. A. *J. Am. Chem. Soc.* **1983**, *105*, 6346. (c) Wengrovius, J. H.; Schrock, R. R. *Organometallics* **1982**, *1*, 148.

[42] This concept is well developed for late metal systems, e.g.: (a) Flood, T. C.; Statler, J. A. *Organometallics* **1984**, *3*, 1795. (b) Clark, H. C.; Jablonski, C. R. *Inorg. Chem.* **1974**, *13*, 2213. (c) Crabtree, R. H. *Acc. Chem. Res.* **1979**, 12, 331.

[43] The isolation of mono-THF complexes **8**, **9**, and **10** from THF solutions, the similarity of their $^1H$ NMR spectra in $CD_2Cl_2$ and THF-$d_8$, and the observations that **8** and **10** do not coordinate a second equivalent of THF in $CD_2Cl_2$ solution in the presence of excess THF argue against the formation of (unreactive) bis-THF complexes in THF solution.

[44] (a) For comparison, cationic alkenyl complexes $Cp'_2Zr(alkenyl)(CH_3CN)^+$ undergo $CH_3CN$ insertion faster than do cationic alkyl complexes $Cp'_2Zr(R)(CH_3CN)^+$. LaPointe, R. E.; Jordan, R. F., manuscript in preparation. (b) $Cp_2Zr(CH_2CH_2R)(L)^+$ complexes which lack π-donor ligands, e.g. $Cp'_2Zr(CH_2CH_2R)(CH_3CN)^+$ (**8b,c** in $CH_3CN$) and $Cp'_2Zr(CH_2CH_2R)(PMe_3)^+$, undergo β-H elimination. LaPointe, R. E.; Bradley, P. K.; Jordan, R. F., manuscript in preparation.

[45] Perrin, D. D.; Armarego, W. L. F.; Perrin, D. R. *Purification of Laboratory Chemicals*; Pergamon: New York, 1980.

[46] (a) Schlosser, M. *J. Organomet. Chem.* **1967**, *8*, 9. (b) Schlosser, M.; Hartmann, J. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 248. (c) Bulls, A. R.; Schaefer, W. P.; Serfas, M.; Bercaw, J. E. *Organometallics* **1987**, *6*, 1219.

[47] Reynolds, L. T.; Wilkinson, G. *J. Inorg. Nucl. Chem.* **1959**, *9*, 86.

**$Cp'_2Zr(CH_2Ph)_2$.**[48] To a flask charged with $Cp'_2ZrCl_2$ (5.000 g, 15.61 mmol) and $KCH_2Ph$ (4.066 g, 31.22 mmol) was added 150 mL of toluene at −78 °C. This reaction mixture was allowed to warm to 25 °C and stirred for a total of 2 h, giving a slurry of dark solid in a deep yellow-orange solution. The solid was removed by filtration and extracted with 2 × 30 mL of toluene. Solvent was removed from the filtrate under vacuum, giving an orange-red oil. After further evacuation at 50 °C for 1 h, the viscous product was dissolved in 150 mL of refluxing hexanes. Slow cooling of this orange solution to −78 °C, with stirring, gave a thick slurry of fine yellow-orange needles, which were collected by filtration. The crystals were dried in vacuo for 12 h; yield 6.04 g, 89.6%.

**$[Cp'_2Zr(CH_2Ph)(THF)][BPh_4]$ (4).** To a 100-mL flask containing $Cp'_2Zr(CH_2Ph)_2$ (4.000 g, 9.265 mmol) and $[Cp'_2Fe][BPh_4]$ (5.200 g, 9.750 mmol, 5% excess) was added 80 mL of THF at −78 °C. The reaction mixture was then warmed to 25 °C with a water bath. A rapid reaction occurred upon warming, giving a deep orange solution and a small amount of unreacted blue $[Cp'_2Fe][BPh_4]$. After the solution was stirred for 5 h at 25 °C, no trace of blue solid was left. The reaction mixture was stripped of solvent in vacuo to give a red oil. Addition of 40 mL of toluene and stirring converted the oil to a red orange solid and an orange-brown solution. The solid was isolated by filtration, washed with 20 mL of toluene, and dried. The solid was dissolved in 20 mL of THF, the solution cooled to −78 °C, and 30 mL of toluene transferred in under vacuum. Warming this mixture initially produced a red oil. Further stirring at 25 °C caused the product to crystallize. The volume of this mixture was reduced to 40 mL and the solid isolated by filtration, washed with a 10-mL portion of toluene, and dried in vacuo to give 5.36 g of crude product. The crude product was slurried in 40 mL of THF (in which it is only slightly soluble). Filtration of this slurry followed by continuous extraction of the collected solid (25 × 20 mL THF) gave a thick slurry of orange-red crystals. The slurry was cooled to ca. −40 °C by brushing the flask with a dry ice/acetone soaked swab. The crystals were collected by filtration, washed with 5 mL of cold THF, and dried overnight in vacuo, affording 4.19 g of orange-red crystalline product (61.8% overall). Anal. Calcd for $C_{47}H_{49}BOZr$: C, 77.13; H, 6.75; Zr, 12.46. Found: C, 76.85; H, 6.71; Zr, 12.70.

**Reaction of 4 with $CD_2Cl_2$.** A solution of 4 (20 mg, 0.027 mmol) in $CD_2Cl_2$ (0.4 mL) was prepared in an NMR tube under vacuum. Monitoring of the $^1H$ NMR spectrum of this sample showed the gradual disappearance of 4 and formation of $Cp'_2Zr(CH_2Ph)(Cl)$.[48] This reaction was ca. 50% complete after 15 h at 23 °C. After 40 h the reaction was complete, and resonances for free THF and product were observed. The characteristic $BPh_4^-$ resonances were no longer visible and were replaced by a broad multiplet that effectively obscured the entire phenyl region (presumably due to reaction between $BPh_4^-$ and "$CD_2Cl^+$", generated by chloride abstraction from the solvent).

**$[Cp'_2Zr(H)(THF)][BPh_4]$ (5).**[49] A Teflon-valved 60-mL glass bomb was charged with 4 (750 mg, 1.02 mmol), THF (20 mL, transferred at −196 °C), and $H_2$ ( 1 atm, at −196 °C). The bomb was sealed, allowed to warm to 25 °C, and stirred for 3 days. Red-orange solid 4 was gradually consumed, and a pale straw colored solution of 5 formed. This solution was degassed and poured into a 100-mL flask attached to a frit assembly. Filtration of this solution removed a small amount of colorless solid, which could not be redissolved in THF. The volume of the filtrate was reduced to 10 mL in vacuo, and another small portion of colorless solid separated. Cooling this mixture to −78 °C did not cause any more solid to come out of solution. Toluene (10 mL) was added by vacuum transfer to the cold solution, and the mixed solvent system was warmed to 25 °C. Upon reduction of the volume to 10 mL in vacuo a thick slurry of beige solid was obtained. The slurry was thinned by an additional 5 mL of toluene and filtered. The solid product was washed with 2 × 5 mL toluene and dried in vacuo overnight to give 480 mg of beige 5, 72%. IR (KBr): $\nu_{ZrH}$ 1390 $cm^{-1}$. A solution IR was not attempted since absorbances due to THF (the only suitable solvent) obscure the region where Zr–H and Zr–D bands are expected. Anal. Calcd for $C_{40}H_{43}BOZr$: C, 74.86; H, 6.75; Zr, 14.21. Found: C, 74.60; H, 6.72; Zr, 13.95.

**$[Cp'_2Zr(D)(THF)][BPh_4]$ (5-$d_1$).** 5-$d_1$ was prepared in the same manner as 5, but $D_2$ was substituted for $H_2$. IR (KBr): $\nu_{ZrD}$ 990 $cm^{-1}$. $^2H$ NMR (THF): $\delta$ 5.88 (s, Zr-D).

**$[Cp'_2Zr\{N{=}C(H)(CH_3)\}(NCCH_3)][BPh_4]$ (7).** A THF solution of 5 was prepared as described above from 4 (530 mg, 0.724 mmol), degassed, and transferred to a 50-mL flask attached to a frit assembly. The volatiles were removed in vacuo, and 10 mL of $CH_3CN$ was condensed into the flask at −78 °C. The flask was warmed to 25 °C, and the contents were stirred to produce a clear light orange solution. The solution volume was reduced to 0.5 mL, and 20 mL of $Et_2O$ was condensed in. The resulting pale orange solid was isolated by filtration, washed with 3 × 5 mL of $Et_2O$, and dried in vacuo overnight to afford 340 mg of solid, yield 66%. IR (KBr): $\nu_{C\equiv N}$ 2309, 2280 $cm^{-1}$; $\nu_{C=N}$ 1700 $cm^{-1}$. Anal. Calcd for $C_{40}H_{41}BN_2Zr$: C, 73.71; H, 6.34; Zr, 13.99. Found: C, 73.48; H, 6.39; Zr, 13.90.

**$[Cp'_2Zr(Et)(THF)][BPh_4]$ (8a).** A pale yellow THF solution of 5 was prepared as described above from 4 (1.009 g, 1.378 mmol), degassed at −78 °C, and placed under 1 atm of ethylene. The reaction mixture was warmed to 25 °C and stirred, turning bright yellow as soon as a vortex had formed. After being stirred for 5 h, the solution was degassed and poured into a 100-mL flask attached to a frit assembly. The solution was filtered and the volume reduced to 10 mL, causing a yellow solid to separate. This slurry was cooled to −78 °C and the solid isolated by filtration. After overnight vacuum drying, 530 mg of waxy yellow solid was collected. A second crop was obtained when the filtrate residue from the initial isolation was redissolved in 2 mL of THF and 10 mL of toluene was added. Filtration and vacuum drying gave another 324 mg of yellow solid, for a total of 854 mg, 92.5%. Anal. Calcd for $C_{42}H_{47}BOZr$: C, 75.31; H, 7.07; Zr, 13.62. Found: C, 75.35; H, 7.22; Zr, 13.66.

**$[Cp'_2Zr(^nBu)(THF)][BPh_4]$ (8c).** A THF solution of 5 was prepared from 4 (700 mg, 0.956 mmol), degassed, and placed under 1 atm of 1-butene at 25 °C. The resulting bright yellow solution was stirred for 2 h, then degassed, and poured into a 100-mL flask attached to a frit assembly. The solution was then filtered and reduced in volume to 5 mL in vacuo, and 20 mL of toluene was added. The resulting slurry was reduced in volume slightly and the solid collected by filtration. The solid was washed with a 2-mL portion of toluene and dried in vacuo overnight, giving 602 mg of pale yellow product, 90.3%. Anal. Calcd for $C_{44}H_{51}BOZr$: C, 75.72; H, 7.37; Zr, 13.07. Found: C, 75.37; H, 7.21; Zr, 13.45.

**$[Cp'_2Zr\{(E)\text{-}C(Me){=}C(H)(Me)\}(THF)][BPh_4]$ (9).** A THF solution of 5 was prepared from 4 (650 mg, 0.888 mmol). This solution was cooled to −196 °C, degassed and 2-butyne (ca. 10 mmol, excess) was added by vacuum transfer. This mixture was warmed to 25 °C and stirred for 1 day. The resulting very pale yellow solution was transferred to a 100-mL flask attached to a frit assembly, filtered, and reduced in volume to 5 mL in vacuo. Addition of 20 mL of toluene produced a slurry of off-white solid. This solid was collected by filtration, washed with 2 mL of toluene, and vacuum dried overnight; yield 604 mg off white product, 97.7%. IR (KBr): $\nu_{C=C}$ 1630 $cm^{-1}$. Thermal instability precluded elemental analysis.

**Hydrolysis of 9.** A solution of 9 (100 mg) in 0.5 mL of THF-$d_8$ was placed in a 10-mL flask. The solution was frozen at −196 °C and a single drop of oxygen free water (large excess) added under $N_2$ counterflow. The flask was then evacuated, sealed, and warmed to 25 °C. The clear colorless solution was stirred for 30 min, and then freeze–pump–thaw degassed at −196 °C. The reaction mixture was warmed to −78 °C, and the volatiles were vacuum transferred to an NMR sample tube which contained 0.4 mL of $C_6D_6$ at −196 °C. An ambient temperature $^1H$ NMR spectrum of this sample showed the presence of only *cis*-2-butene (by comparison to authentic samples of *cis*- and *trans*-2-butene).

**$[Cp'_2Zr\{(Z)\text{-}C(Me){=}C(Me)(Et)\}(THF)][BPh_4]$ (10a).** A THF solution of 8a was generated, as described above, from 4 (890 mg, 1.216 mmol). The volatiles were removed from the solution in vacuo. The residue was dissolved in 10 mL of $CH_2Cl_2$ and 2-butyne (ca. 10 mmol, excess) added at −78 °C. This mixture

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[48] Brindly, P. B.; Scotton, M. J. *J. Chem. Soc., Perkin Trans. 2* **1981**, 2, 419. The authors report a 44% yield of $Cp'_2Zr(CH_2Ph)_2$ from reaction of the dichloride with $2PhCH_2MgCl$; however, $MgCl_2$ is difficult to remove completely using this procedure.

[49] Solutions of 5 are also obtained from hydrogenolysis of $[Cp'_2Zr(Me)(THF)][BPh_4]$. Bradley, P.; LaPointe, R. E.; Jordan, R. F., unpublished results.

**Table IV. Summary of Crystallographic Data for $[Cp'_2Zr\{C(Me){=}C(Me)(^nPr)\}(THF)][BPh_4]$ (10b)**

| | |
|---|---|
| empirical formula | $C_{47}H_{55}BOZr$ |
| fw | 738.01 |
| cryst size, mm | 0.2 × 0.3 × 0.5 |
| cryst color | amber |
| $T$, K | 295 |
| space group | $P2_1/n$ |
| $a$, Å | 12.084 (4) |
| $b$, Å | 20.469 (2) |
| $c$, Å | 16.436 (2) |
| $\beta$, deg | 100.26 (2) |
| $V$, Å$^3$ | 4000 (2) |
| $Z$ | 4 |
| $\mu$, cm$^{-1}$ | 3.07 |
| $d$(calcd), g/cm$^3$ | 1.225 |
| radiatn | Mo K$\alpha$ ($\lambda$ = 0.71073 Å) |
| scan type | $\theta$–$2\theta$ |
| scan limit, deg | $2 \le 2\theta \le 40$ |
| scan speed, deg/min | variable, 0.6–5 |
| data collected | $\pm h,+k,\pm l$ |
| no. of reflectns collected | 7738 |
| no. of unique intensities | 3880 |
| agreement btwn equiv reflectns | 2% |
| no. of $F > 3\sigma(F)$ | 2120 |
| no. of reflectns in refinement | 2120 |
| no. of least-squares parameters | 211 |
| $R(F)$ | 0.056 |
| $R(\mathrm{w}F)$ | 0.089 |
| goodness of fit | 1.43 |
| max parameter shift/esd | 0.03 |

was allowed to warm to 25 °C and stirred for 15 min before the volatiles were removed in vacuo. The residue was dissolved in 15 mL of THF to give a light yellow solution which was filtered and reduced in volume to 8 mL. The concentrated solution was cooled to −78 °C and 15 mL of toluene added by vacuum transfer. The resulting faintly cloudly solution was warmed to 25 °C and reduced in volume to 20 mL. As the concentration of THF was reduced, the product separated as a light yellow solid. The solid was collected by filtration, washed with 2 mL toluene, and dried in vacuo, yield 830 mg, 94.3%. IR (KBr): $\nu_{C=C}$ 1620 cm$^{-1}$. Anal. Calcd for $C_{46}H_{53}BOZr$: C, 76.32; H, 7.38; Zr, 12.60. Found: C, 76.16; H, 7.21; Zr, 12.80.

**$[Cp'_2Zr\{(Z)\text{-}C(Me){=}C(Me)(^nBu)\}(THF)][BPh_4]$ (10c).** A THF solution of **8c** was prepared as above from 4 (625 mg, 0.854 mmol). The volatiles were removed from the solution in vacuo. The residue was dissolved in 20 mL of $CH_2Cl_2$, and an excess (2 mmol) of 2-butyne was added. The resulting mixture was warmed to 25 °C and stirred for 30 min. The volatiles were then removed under vacuum, and the foamy, slightly greenish yellow solid obtained was triturated with a 10-mL portion of THF and dried overnight. The resulting yellow gum was dissolved in 15 mL of THF. Addition of 15 mL of $Et_2O$ caused precipitation of a light yellow solid, which was isolated by filtration, washed with one 4-mL portion of $Et_2O$, and dried overnight. This partially purified solid was only slightly soluble in THF. Recrystallization from THF afforded 190 mg of pale yellow 12, 29.6%. IR (KBr): $\nu_{C=C}$ 1590 cm$^{-1}$. Anal. Calcd for $C_{48}H_{57}BOZr$: C, 76.49; H, 7.51; Zr, 12.36. Found: C, 76.54; H, 7.53; Zr, 12.10.

**$[Cp'_2Zr(\eta^3\text{-}C_3H_5)(THF)][BPh_4]$ (13).** A THF solution of 5 was prepared as described above from 4 (0.620 g, 0.833 mmol), degassed at −78 °C, warmed to 23 °C, and charged with 400 Torr of allene. The solution was stirred for 20 min at 23 °C during which time it turned yellow. The solution was degassed, poured into a flask attached to a frit assembly, and filtered. The filtrate was concentrated to 5 mL, and 5 mL of $Et_2O$ was condensed in. The resulting thick slurry was thinned with 10 mL of THF and filtered. The yellow solid was washed with $Et_2O$ and dried under vacuum; yield 0.196 g, 34.5%. Anal. Calcd for $C_{43}H_{47}BOZr$: C, 75.74; H, 6.95; Zr, 13.38. Found: C, 75.48; H, 6.78; Zr, 13.45.

**X-ray Crystal Structural Determination of $[Cp'_2Zr\{(Z)\text{-}C(Me){=}C(Me)(^nPr)\}(THF)][BPh_4]$ (10b).** Crystallographic data for **10b** is summarized in Table IV. An irregular crystal fragment, grown by slow cooling of a THF solution, was sealed in a glass capillary under $N_2$. The capillary was mounted with the [140] direction roughly parallel to the $\varphi$ axis on an Enraf-Nonius CAD-4 diffractometer equipped with a graphite monochromater. Mo K$\alpha$ radiation was used. Intensities were measured by the $\theta$–$2\theta$ scan method ($\theta$ scan range = 0.6 + 0.35 tan $\theta$; background measured 25% below and 25% above scan range; (peak counting time)/(background counting time) = 2/1; horizontal aperture 2.5–3.0 mm depending on angle). Lorentz and polarization corrections were made. Adsorption corrections were made empirically and ranged from 0.91 to 0.99. The three standard reflections used to monitor decay indicated a decay of less than 1.8% so correction for decay was not made. Cell dimensions were obtained from 25 reflections between 10 and 26° ($2\theta$), with 17 of these >20° ($2\theta$).

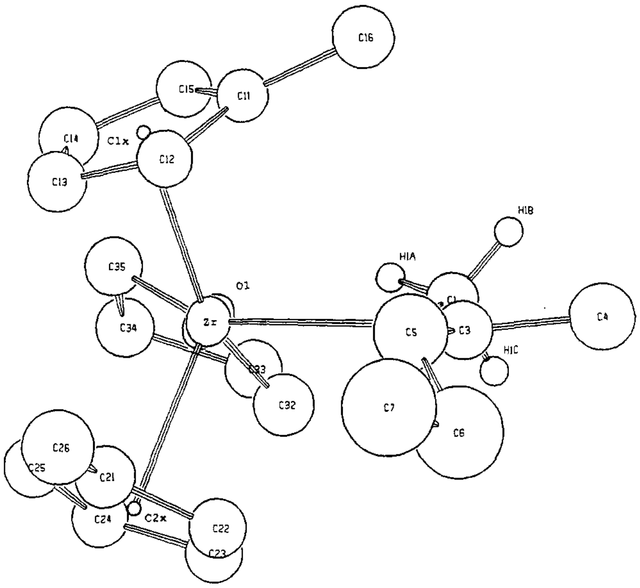

**Figure 2.** Structure of the $Cp'_2Zr\{(Z)\text{-}C(Me){=}C(Me)(^nPr)\}(THF)^+$ cation; view down the Zr–O1 bond.

The Zr atom position was found from the Patterson function,[50] and a single pass with DIRDIF[51] gave all the remaining non-H atom positions. The structure was refined by full-matrix least-squares methods. With the Zr and O atom anisotropic and no H atoms included, $R$ = 0.074. In successive electron density maps, all H atoms were found except those on C6 and C7 and one on C4. All H atoms were put in idealized positions and kept fixed during refinement. With 211 parameters and 2120 observations, $R$ = 0.056 and $R_w$ = 0.089, goodness of fit = 1.43, and maximum parameter shift/esd = 0.03. Weights[52] used have the form $w = 1/s^2$, where $s$ = estimated $s(F) + PF^2$, where $P$ = 0.05 and the estimated $s$ is the larger of the estimates propagated from counting statistics or estimated from agreement among equivalent reflections. The maximum residual electron density in the final difference map = 0.058 e/Å$^3$. Thermal ellipsoids/spheres in Figures 1 and 2 are drawn at the 25% probability level.

Since H1a is close to Zr, the H1a–c atoms were removed and the refinement carried out for several cycles. The $R$ value increased to 0.058, and the difference map showed the H1a–c atoms at essentially the same positions as when first found (Zr–H1a = 2.296 Å, C1–H1a = 1.14 Å). The distances and angles were regularized and kept fixed for the final refinement cycles ($R$ = 0.056, Zr–H1a = 2.32 Å, C1–H1a = 0.96 Å).

**Ethylene Oligomerization. (a) With 5a.** A 5-mm NMR tube was charged with solid $[Cp'_2Zr(H)(THF)][BPh_4]$ (**5a**) (20 mg, 0.031 mmol), THF-$d_8$ (0.3 mL), and ethylene (0.31 mmol, 10 equiv) and sealed with a torch. After 3 h of mixing at ambient temperature, all (insoluble) hydride was consumed, to give a clear yellow solution. A $^1$H NMR spectrum showed only $[Cp'_2ZrEt(THF)][BPh_4]$ (**8a**) and excess ethylene. Continued monitoring of the sample showed the gradual disappearance of the ethylene resonance, along

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(50) Crystallographic programs used are those of the Enraf-Nonius SDP package.

(51) DIRDIF, direct methods for diffraction structure, as implemented in the Enraf-Nonius software.

(52) Killean, R. C. G.; Lawrence, J. L. *Acta. Crystallogr. B* **1969**, *B25*, 1750.

with growth of signals in the alkyl and vinyl regions. After 12 days at ambient temperature most ethylene was consumed and the volatiles were vacuum transferred to another NMR tube. Comparison of the proton NMR spectrum of this sample to that of an authentic sample suggested the presence of 1-butene along with other hydrocarbon species. GCMS analysis of the volatiles confirmed the presence of 1-butene, 1-hexene, and 1-octene.

**(b) With 8a or 8c.** Two sealed tube NMR samples were prepared, each containing $[Cp'_2Zr(Et)(THF)][BPh_4]$ (**8a**) or $[Cp'_2Zr(^nBu)(THF)][BPh_4]$ (**8c**) (10 mg, 0.015 mmol), ethylene (0.30 mmol, 20 equiv) and THF-$d_8$ (~0.4 mL). The samples were placed in a 50 °C bath for 3.5 h, and then monitored by $^1H$ NMR. The spectra of both samples were virtually identical and contained resonances corresponding to **8a**, ethylene, and $\alpha$-olefins. Integration of the *Me*Cp resonance of **8a** vs the overlapping $\mathit{Me}CH_2(CH_2CH_2)_n\mathit{C}(H){=}CH_2$ ($n$ = 0–2) resonance of the $\alpha$-olefins, indicated yields of 1 equiv of $\alpha$-olefins from **8a** and 1.3 equiv from **8c**. (Similar experiments with greater amounts of ethylene show higher initial rates of $\alpha$-olefin production.) During the course of an additional 7 days at 50 °C the ethylene resonances in the two samples continued to decline as $\alpha$-olefin resonances grew in, along with a peak at $\delta$ 0.85 ppm (ethane, from the thermal decomposition of **8a**). At the end of this period the spectra ($^1H$ NMR and GCMS) of both samples were indistinguishable.

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**Registry No.** **4**, 123264-22-2; **5**, 123264-24-4; **5**-$d_1$, 123264-26-6; **7**, 123264-28-8; **8a**, 123264-30-2; **8b**, 123264-43-7; **8c**, 123264-36-8; **9**, 123264-32-4; **10a**, 123264-34-6; **10b**, 123288-95-9; **10c**, 123264-38-0; **13**, 123264-40-4; $[Cp'_2Fe][BPh_4]$, 123264-20-0; $Cp'_2ZrCl_2$, 12109-71-6; $Cp'_2Zr(CH_2Ph)_2$, 78179-71-2; $Cp'_2Fe$, 1291-47-0; Cp′H, 26519-91-5; $ZrCl_4$, 10026-11-6; $KCH_2Ph$, 2785-29-7; $Cp'_2Zr(CH_2Ph)(Cl)$, 123264-41-5; $CD_2Cl_2$, 1665-00-5; ethylene, 74-85-1; 1-butene, 106-98-9; 2-butyne, 503-17-3; allene, 463-49-0; 1-hexene, 592-41-6; 1-octene, 111-66-0.

**Supplementary Material Available:** Tables of bond distances, bond angles, H atom positional parameters, and anisotropic thermal parameters (8 pages); a listing of $h$, $k$, $l$, $F_o$, and $F_c$ values (8 pages). Ordering information is given on any current masthead page.

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# Reductive Elimination of Hydrogen from $H_3Ru_3(\mu_3\text{-}COMe)(CO)_9$ and Ligand Substitution on $HRu_3(\mu\text{-}COMe)(CO)_{10}$. Mechanistic Information from High-Pressure Kinetics

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The carbonylation of $H_3Ru_3(\mu_3\text{-}COMe)(CO)_9$ and hydrogenation of $HRu_3(\mu\text{-}COMe)(CO)_{10}$ were studied as a function of pressure up to 200 MPa. Carbonylation of the former cluster, forming the latter, is characterized by a volume of activation of +20 ± 2 cm$^3$ mol$^{-1}$, whereas the reverse reaction exhibits an activation volume of +9.6 ± 0.6 cm$^3$ mol$^{-1}$. These results are combined with predicted partial molar volumes to construct a volume profile for the overall process, from which it follows that both reaction steps follow a dissociative mechanism.

## Introduction

Reductive elimination of molecular hydrogen is one of the elementary reactions of hydrogen bonded to metals, occurring for monometallic complexes, metal surfaces, and metal clusters. Unlike hydrogen ligands on monometallic complexes, reductive elimination from clusters typically involves hydrides that bridge two or more metals in the ground-state structure. The mechanism of this reaction is of fundamental interest both with respect to the unique chemistry of molecular metal clusters and with respect to the cluster–surface analogy. The kinetics of reductive elimination have been determined previously for three trimetallic cluster systems—$(\mu\text{-}H)_3M_3(\mu_3\text{-}CX)(CO)_9$ (M = Ru[1] or Os[2] (X = OMe)), for which each of the three hydride ligands is bridging two metal atoms in the ground state, and $H(\mu\text{-}H)Os_3(CO)_{11}$,[3] for which one hydride is bridging and one is terminally coordinated. Both studies found first-order kinetics for reactions with CO, with entropies of activation of +8 (±2) ($(\mu\text{-}H)_3Ru_3(\mu_3\text{-}COMe)(CO)_9$) and −6.9 eu ($H(\mu\text{-}H)Os_3(CO)_{11}$). The mechanism in each case conforms to eq 1 and 2, with $M_3$ = $HRu_3(COMe)(CO)_9$ or

$$H_2M_3 \underset{k_2}{\overset{k_1}{\rightleftharpoons}} M_3 + H_2 \tag{1}$$

$$M_3 + CO \underset{k_4}{\overset{k_3}{\rightleftharpoons}} M_3(CO) \tag{2}$$

$Os_3(CO)_{11}$. The rate-determining step for elimination of hydrogen under a carbon monoxide atmosphere is indicated by rate constant $k_1$. The deuterium kinetic isotope effect of 1.4 (±0.1) ($(\mu\text{-}H)_3Ru_3(\mu_3\text{-}COMe)(CO)_9$) could be interpreted in terms of either rate-determining reductive elimination or rate-determining hydride migration. Relative rates for reductive elimination from mixed-metal clusters have suggested that only one metal atom is involved in the transition state.[4] To distinguish between

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