Table V. Comparative Rates and Activation Parameters for Carbon Monoxide Displacement in $Co_4(CO)_{12}$ Derivatives[a]

complex	10^4k, s^{-1}	ΔH^*,[b] kcal mol^{-1}	ΔS^*,[b] eu
$Co_4(CO)_{12}$	3.27	24.9 ± 1.9	2.9 ± 5.9
$Co_4(CO)_{11}P(OMe)_3$	2.03	26.8 ± 1.0	8.2 ± 3.5
$Co_4(CO)_{11}P(OEt)_3$	3.37	27.5 ± 3.3	11.0 ± 10.2
$Co_4(CO)_{10}[P(OMe)_3]_2$	4.77	27.1 ± 1.1	10.7 ± 3.7
$Co_4(CO)_9$(tripod)	1.71	24.2 ± 3.3	−0.52 ± 10.2
$Co_4(CO)_7$(dppm)(tripod)	0.355	24.7 ± 1.0	−0.83 ± 3.0

[a] For the reaction $Co_4(CO)_{12-n}L_n + (excess)^{13}CO \rightarrow Co_4(^{13}CO)_{12-n}L_n + {}^{12}CO$ at 40 °C; values taken from ref 5 and 6. [b] Error limits represent 90% confidence limits.

lustrated by the representative plots of the data employed in computing rate constants and activation parameters for dissociative CO loss in this cobalt cluster species (Figures 5 and 6). Comparative rate constants and activation parameters for the system investigated herein, as well as those previously reported, are collected in Table V.

As is indicated in Table V, the rates of CO ligand dissociation from the apical cobalt sites of $Co_4(CO)_9$(tripod) and $Co_4(CO)_7$(dppm)(tripod) are quite similar, with the latter species being some 5 times slower. The activation parameters for the two processes are the same within experimental error. Hence, substitution of the CO ligands at a cobalt center in the tetranuclear cluster by a phosphine ligand only slightly retards the rate for dissociation of the remaining carbon monoxide groups from that cobalt center. This result serves to underscore our contention that the rate acceleration for CO dissociation displayed by some metal carbonyl clusters upon phosphorus donor ligand substitution[13] is due, to a large part, to steric induction by virtue of the cluster's framework dictating spatial confrontations between ligands.[14]

Acknowledgment. The financial support of the Robert A. Welch Foundation is greatly appreciated.

Registry No. 1, 75801-99-9; **2a**, 82264-81-1; **2b**, 93254-00-3; **2c**, 93254-01-4; **3a**, 93254-02-5; **3b**, 93254-03-6; **4**, 93279-94-8; **5**, 93279-95-9; **6**, 93254-04-7.

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Halide, Hydride, Alkyl, and Dinitrogen Complexes of Bis(pentamethylcyclopentadienyl)hafnium[†,‡]

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Bis(pentamethylcyclopentadienyl)hafnium dichloride ($Cp^*{}_2HfCl_2$, $Cp^* = \eta^5\text{-}C_5Me_5$) is obtained by treatment of $HfCl_4$ with lithium pentamethylcyclopentadienide in refluxing xylenes. The dioodide derivative is obtained from $Cp^*{}_2HfCl_2$ with BI_3. The dihydrido derivative is obtained via treatment of $Cp^*{}_2HfCl_2$ with *n*-butyllithium under an atmosphere of H_2. Treatment of $Cp^*{}_2HfH_2$ with alkyl halides (RX) affords either $Cp^*{}_2HfX_2$ or $Cp^*{}_2HfHX$ and alkane depending on the nature of RX. The reaction of phenyllithium and $Cp^*{}_2HfH_2$ provides a novel route to the phenyl hydride derivative $Cp^*{}_2HfH(Ph)$. The variance of the chemical shift of the hydride with X for complexes of the type $Cp^*{}_2HfH(X)$ (X = hydride, alkyl, alkenyl, aryl, halide, alkoxide, amide) is discussed in terms of paramagnetic shielding. The dinitrogen complex $\{Cp^*{}_2HfN_2\}_2N_2$ is obtained in modest yield by Na/K reduction of $Cp^*{}_2HfI_2$ and is isostructural with the zirconium analogue. $Cp^*{}_2HfH_2$ forms an adduct with CO. Under high pressures of CO, reductive elimination of H_2 and generation of $Cp^*{}_2Hf(CO)_2$ is observed. Treatment of $Cp^*{}_2Hf(CO)_2$ with H_2 (3 atm) at 125 °C cleanly affords $Cp^*{}_2HfH(OCH_3)$ and 1 equiv of CO; $Cp^*{}_2Hf(CO)_2$ with $Cp^*{}_2MH_2$ (M = Zr, Hf) under H_2 yields *cis*-$(Cp^*{}_2HfH)(Cp^*{}_2MH)(\mu\text{-}OCH{=}CHO)$. Warming of $Cp^*{}_2HfH_2(CO)$ under H_2 yields $Cp^*{}_2HfH(OCH_3)$, *cis*-$(Cp^*{}_2HfH)_2(\mu\text{-}OCH{=}CHO)$, *trans*-$(Cp^*{}_2HfH)_2(\mu\text{-}OCH{=}CHO)$, and $(Cp^*{}_2HfH)_2(\mu\text{-}OCH_2CH_2O)$. The relative yields of the individual products depend critically on reaction conditions, and the complexity of these reactions has thwarted all attempts to elucidate their mechanisms. Treatment of $Cp^*{}_2HfH_2$ with olefins of the formula $CH_2{=}CRR'$ or *tert*-butylacetylene gives alkyl hydrides $Cp^*HfH(CH_2CHRR')$ or the alkenyl hydride $Cp^*{}_2HfH(CH{=}CHCMe_3)$, which are very resistant to reductive elimination. Ethylene induces loss of alkane (CH_3CHRR') or $CH_2{=}CHCMe_3$; however, with formation of the hafnacyclopentane derivative $Cp^*{}_2\overline{Hf(CH_2CH_2CH_2CH_2})$. Hydrogenation of the alkyl hydride complexes or $Cp^*{}_2HfH(CH_2{=}CHCMe_3)$ affords $Cp^*{}_2HfH_2$ and CH_3CHRR' or $CH_3CH_2CMe_3$.

Introduction

The chemistry of organometallic derivatives of titanium and zirconium bearing two pentamethylcyclopentadienyl groups as ancillary ligands has proven to be rich and varied. Permethyltitanocene and permethylzirconocene derivatives are often more stable than the ($\eta^5\text{-}C_5H_5$) analogues and offer the practical advantages of higher solubility and crystallinity. Moreover, the steric bulk of the pentamethylcyclopentadienyl group discourages oligomerization through single atom bridges (e.g., H, O, N), thus rendering permethylmetallocene derivatives monomeric. In view of the greater stability of the organometallic de-

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[†] Dedicated to Earl L. Muetterties, respected scientist and friend.

[‡] Contribution No. 7048.

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rivatives generally observed for the third-row (5d) transition metal relative to the first- (3d) or second-row (4d) congeners, we anticipated that some key species that mediate the reaction chemistry of permethyltitanocene and permethylzirconocene derivatives would be isolable for the hafnium analogues.

We report herein the synthesis of halide, hydride, alkyl, and dinitrogen complexes of permethylhafnocene together with some aspects of their chemistry.

Results and Discussion

Hafnium tetrachloride undergoes metathesis with pentamethylcyclopentadienyllithium to give, sequentially, $(Cp^*HfCl_3)_x$ (1) ($Cp^* \equiv \eta^5\text{-}C_5Me_5$) and then $Cp^*_2HfCl_2$ (2) according to eq 1 and 2. Formation of 2 is best effected

$$\mathrm{HfCl_4 + LiCp^* \xrightarrow{120\ ^\circ C} \underset{\mathbf{1}}{(Cp^*HfCl_3)_x} + LiCl} \tag{1}$$

$$\mathrm{\underset{\mathbf{1}}{(Cp^*HfCl_3)_x} + LiCp^* \xrightarrow{\geq 140\ ^\circ C} \underset{\mathbf{2}}{Cp^*_2HfCl_2} + LiCl} \tag{2}$$

in high boiling hydrocarbon solvents such as xylenes or mesitylene (≥140 °C at reflux); attempts to prepare 2 by using lower boiling solvents such as toluene or THF result in the isolation of 1 in nearly quantitative yields even in the presence of excess LiCp*. Colorless 2 can be converted to the bright yellow diiodo complex $Cp^*_2HfI_2$ (3) by its stoichiometric reaction with BI_3 in aromatic hydrocarbon solvents (eq 3). While 2 is an air-stable compound, 3 slowly hydrolyzes upon exposure to atmospheric moisture.

$$\mathrm{\underset{\mathbf{2}}{Cp^*_2HfCl_2} + {}^2/_3BI_3 \rightarrow \underset{\mathbf{3}}{Cp^*_2HfI_2} + {}^2/_3BCl_3} \tag{3}$$

Treatment of toluene solutions of 2 with 2 equiv of *n*-butyllithium under an atmosphere of dihydrogen provides a convenient, one-step synthesis of the dihydrido complex $Cp^*_2HfH_2$ (4) as shown in eq 4. Crystallization

$$\mathrm{\underset{\mathbf{2}}{Cp^*_2HfCl_2} + 2BuLi \xrightarrow[1\ atm]{H_2} \underset{\mathbf{4}}{Cp^*_2HfH_2} + 2LiCl + 2C_4H_{10}} \tag{4}$$

from cold petroleum ether affords good yields (60–80%) of 4 as colorless, air-sensitive crystals. Proton NMR spectroscopy (see Table I), infrared spectroscopy (ν(HfH) 1590 cm^{-1}, ν(HfD) 1135 cm^{-1}), and elemental analysis support the formulation of 4. The extremely low-field resonance (δ 15.57, C_6D_6 solvent) of the hydride ligands of 4 is in striking contrast to the characteristic high-field resonances of most group 5–8 transition-metal hydrido complexes[1] but is consistent with the trend established by the Ti and Zr analogues of 4: $Cp^*_2TiH_2$ (δ 0.28)[2] and $Cp^*_2ZrH_2$ (δ 7.47).[3] The hydride ligands of 4 undergo statistical exchange with hydrogen gas; thus, stirring solutions of 4 under a deuterium atmosphere at ambient temperatures results in formation of $Cp^*_2HfD_2$ (4-d_2). This is in contrast to the zirconium system for which $Cp^*_2ZrD_2$ is stable only at low temperatures, with deuterium exchange into the Cp* rings occurring slowly even at 25 °C.[4]

While 4 is moderately stable for extended periods in saturated or aromatic hydrocarbon solvents, it reacts with most halogenated hydrocarbons to form hafnium–halide bonds. Thus, 4 reacts cleanly at −78 °C with 2 equiv of MeI to form 3 and methane quantitatively (eq 5). This reaction appears to be a radical process.[5] Less reactive alkyl halides (i.e., poorer X· sources than CH_3I) interact with 4 to give isolable monohalogenated products. For example, CH_3Cl and CH_3Br react with 4 in stoichiometric fashion to afford Cp^*_2HfHX (5, X = Cl; 6, X = Br) (eq 6). The monochloro derivative 5 can be isolated as an analytically pure colorless powder, but the bromo analogue 6 is typically contaminated with ~5% of $Cp^*_2HfBr_2$.

$$\mathrm{\underset{\mathbf{4}}{Cp^*_2HfH_2} + 2CH_3I \xrightarrow{-78\ ^\circ C} \underset{\mathbf{3}}{Cp^*_2HfI_2} + 2CH_4} \tag{5}$$

$$\mathrm{\underset{\mathbf{4}}{Cp^*_2HfH_2} + CH_3X \xrightarrow{25\ ^\circ C} \underset{\substack{\mathbf{5},\ X\,=\,Cl\\ \mathbf{6},\ X\,=\,Br}}{Cp^*_2HfHX} + CH_4} \tag{6}$$

4 serves as a source for a number of other monohydrido derivatives, such as hydroxides ($Cp^*_2HfH(OH)$),[6] alkoxides ($Cp^*_2HfH(OR)$),[7] and amides ($Cp^*_2HfH(NR_2)$).[6,8] Additionally, treatment of benzene solutions of 4 with 1 equiv of PhLi provides a novel route to the hydrido aryl complex $Cp^*_2HfH(Ph)$ (7) as shown in eq 7. It is noteworthy that related reactions, involving less hydridic transition-metal hydrides, give instead anionic species derived from simple deprotonation.[9] All of these hafnium monohydrides are characterized by low-field resonances (15.6 > δ (Hf*H*) > 7.0) for the hydride ligands in their ^1H NMR spectra. Table II summarizes the hydride chemical shifts for several $Cp^*_2HfH(X)$ complexes. As can be seen, the closed-shell, 18-electron complexes $Cp^*_2HfH(\eta^3\text{-}C_3H_5)$ and $Cp^*_2HfH_2(CO)$ exhibit chemical shifts significantly upfield of the formally open-shell, 16-electron derivatives. For X groups not capable of π-donation (H, alkyl, alkenyl, aryl) the hydride resonates at δ >12. Moreover, for the remaining compounds with X = heteroatom, a correlation appears to exist for the hydride chemical shift and the extent of π-donation from X into the empty $1a_1$-type orbital on the $[Cp^*_2HfH]$ fragment. Hence, the chemical shifts decrease in the order Br > Cl > F and OH ≈ OR > NH_2, precisely the order of increasing π-donating ability. Although the amide hydride compounds with alkyl or aryl substituents on nitrogen appear to be exceptions to these generalizations, we have shown that unfavorable steric interactions between the amide substituents and Cp* groups twist the Hf–NRR′ (but *not* the Hf–NH_2) moiety from the orientation for donation of the nitrogen lone pair into the empty metal $1a_1$ orbital.[6]

$$\mathrm{Cp^*_2HfH_2 + PhLi \rightarrow \underset{\mathbf{7}}{Cp^*_2HfH(Ph)} + LiH} \tag{7}$$

Whereas the factors responsible for this trend are not fully understood, the hydride chemical shift does seem to correlate with the energy of this $1a_1$ orbital (nonbonding, π-antibonding, or σ,π-antibonding). In view of the low-field position of these hydride resonances, it is clear that paramagnetic shielding (σ_p)[1] must be at least as important as diamagnetic shielding (σ_d), since one would conclude on the basis of the latter alone that the proton is extremely deshielded (i.e., ~ H^+) in direct contradiction to the hy-

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[1] Buckingham, A. D.; Stevens, P. J. *J. Chem. Soc.* **1964**, 2747.

[2] The value is obtained under an H_2 atmosphere; thus it may be slightly shifted from the value in the absence of H_2. In any event, the trend of δ(Hf) → δ(Ti) is not affected. Bercaw, J. E.; Marvich, R. H.; Bell, L. G.; Brintzinger, H. H. *J. Am. Chem. Soc.* **1972**, *94*, 1219.

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[4] The rate of D incorporation into the methyl positions of $Cp^*_2ZrH_2$ at 84 °C follows the rate law: rate = $(5 \times 10^{-4}\ s^{-1})[Cp^*_2ZrH_2]$ (excess D_2). Bercaw, J. E. *Adv. Chem. Ser.* **1978**, *No. 167*, 135.

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dridic (i.e., $\sim$ H$^-$) chemical reactivity of these hydrides. The extent of paramagnetic shielding should reflect the temperature independent paramagnetism (TIP) of the compound, the magnitude of which normally varies inversely with the HOMO – LUMO energy difference (ΔE). Consistent with these suggestions, the lowest field hydride shifts are found with X = H or R, for which the 1a$_1$ orbital is nonbonding (ΔE small, TIP large), intermediate shifts for X = π-donors for which the 1a$_1$ orbital is π-antibonding (ΔE intermediate, TIP intermediate), and the smallest downfield shifts for closed-shell, 18-electron compounds for which the 1a$_1$ orbital is σ- and π-antibonding (ΔE large, TIP small). Irregardless of the validity of these qualitative arguments, the empirical trends noted here should prove (and have[6] proven) useful in predicting the structure of compounds of the types Cp*$_2$HfH(X), especially when X has the potential to contribute either one or three electrons to the valence shell of hafnium.

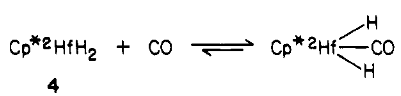
Permethylhafnocene diiodide (3) reacts with dinitrogen under reducing conditions to produce the hafnium(II) dinitrogen complex {Cp*$_2$Hf(N$_2$)}$_2$(μ-N$_2$) (8) in moderate yield (20–35%) as metallic green crystals (magenta in solution). The best route to 8 entails reduction of 3 with Na/K alloy (1:5 Na/K) in cold (–41 °C) 1,2-dimethoxyethane (DME) under 1 atm of dinitrogen (eq 8). Choice

$$\underset{3}{2\mathrm{Cp^*_2HfI_2}} \xrightarrow[\text{DME } (-41\ ^\circ\mathrm{C})]{\text{Na/K, N}_2} \underset{8}{\{\mathrm{Cp^*_2Hf(N_2)}\}_2(\mu\text{-N}_2)} \qquad (8)$$

of reducing agent and careful control of reaction conditions (solvent, temperature, reaction time) is critical for formation and successful isolation of 8.[11] Crystals of 8 are stable for extended periods when stored under a dinitrogen atmosphere at –20 °C, but in solution (C$_6$D$_6$) 8 decomposes over the course of several days with precipitation of an insoluble white product, even under 1 atm of N$_2$. 8 is probably isostructural with its zirconium analogue {Cp*$_2$Zr(N$_2$)}$_2$(μ-N$_2$) (9).[12] The infrared spectrum of 8 exhibits three prominent bands corresponding to ν(NN) at 2000 (s), 1962 (vs), and 1538 (s) cm^{-1} (cf. ν(NN) = 2041 (s), 2006 (vs), and 1556 (s) cm^{-1} for 9).[12] The ^{1}H NMR spectrum of 8 at 25 °C consists of two singlets ($\Delta\nu$ = 1.8 Hz at 90 MHz), assignable to two pairs of inequivalent C$_5$Me$_5$ ligands, which coalesce at +46 °C to give a single, averaged C$_5$Me$_5$ resonance. For comparison, the ring protons of 9 coalesce at +11 °C at 220 MHz.[13]

Reactions of Cp*$_2$HfH$_2$ with Carbon Monoxide. Carbon monoxide has been observed to react with the 16-electron complex Cp*$_2$ZrH$_2$ to form a carbonyl adduct, Cp*$_2$ZrH$_2$(CO), which is spectroscopically observable but which reacts above –50 °C to yield zirconium products containing reduced CO ligands, the exact nature of which depends on reaction conditions. Slow warming of solutions of Cp*$_2$ZrH$_2$(CO) in the absence of residual CO or H$_2$ cleanly produces the dimeric enediolate complex *trans*-(Cp*$_2$ZrH$_2$)$_2$(μ-OCH=CHO) in >95% yield. In the presence of excess Cp*$_2$ZrH$_2$ and H$_2$, monomeric Cp*$_2$ZrH(OCH$_3$) is formed.[14]

Similar reactivity is observed between Cp*$_2$HfH$_2$ and CO. 4 readily adds carbon monoxide at –41 °C (0.87 equiv of CO/Hf) to generate the electron precise carbonyl dihydride Cp*$_2$HfH$_2$(CO) (10) (eq 9). Although 10 is



$$\underset{4}{\mathrm{Cp^*_2HfH_2}} + \mathrm{CO} \rightleftharpoons \underset{10}{\mathrm{Cp^*_2Hf(H)_2(CO)}} \qquad (9)$$

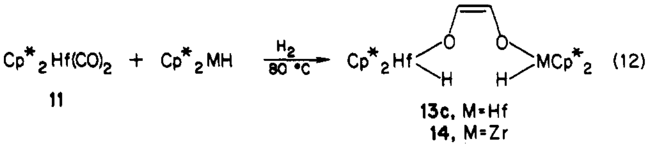
thermally unstable and has therefore evaded isolation, solution infrared (ν(CO) = 2036 cm^{-1}),[15] ^{1}H NMR (δ-(HfH_2(CO)) 2.67 $^2J_{^{13}\mathrm{CH}}$ = 21.5 Hz) and ^{13}C NMR (δ(CO) 224.4 (t)) spectroscopic data suggest a symmetrical coordination about Hf with the CO ligand in the central equatorial position mutually cis to the hydride ligands. Warming of 10 in the presence of CO favors reductive elimination of H$_2$ and formation of Cp*$_2$Hf(CO)$_2$ (11).[16] Indeed, a toluene solution of 4 subjected to 1500 psi of CO at 20 °C yields exclusively 11, which can be isolated as purple crystals in ~75% yield (eq 10). Treatment of 11

$$\underset{4}{\mathrm{Cp^*_2HfH_2}} \xrightarrow[20\ ^\circ\mathrm{C}]{\text{1500 psi of CO}} \underset{11}{\mathrm{Cp^*_2Hf(CO)_2}} + \mathrm{H_2} \qquad (10)$$

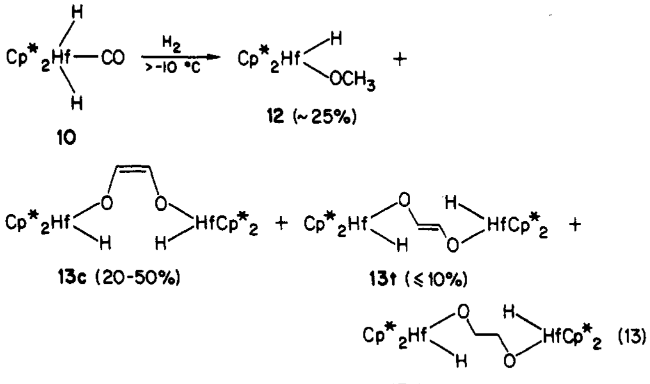
with H$_2$ (3 atm, 125 °C) results in the clean reduction of one carbonyl ligand to afford Cp*$_2$HfH(OCH$_3$) (12) and carbon monoxide (eq 11). Reaction of equimolar amounts

$$\underset{11}{\mathrm{Cp^*_2Hf(CO)_2}} + 2\mathrm{H_2} \xrightarrow[125\ ^\circ\mathrm{C}]{3\text{ atm}} \underset{12}{\mathrm{Cp^*_2HfH(OCH_3)}} + \mathrm{CO} \qquad (11)$$

of 11 and 4 or Cp*$_2$ZrH$_2$ under H$_2$ cleanly produces *cis*-(Cp*$_2$HfH)$_2$(μ-OCH=CHO) (13c) or *cis*-(Cp*$_2$HfH)(Cp*$_2$ZrH)(μ-OCH=CHO) (14) (eq 12). While each of



these latter three reactions have precedent in the analogous Zr system,[14] it is noteworthy that warming of 10 above –10 °C under H$_2$ initiates a complex series of reactions, leading to the formation of several products whose relative abundances vary widely with reaction conditions. The complexity of these reactions is in contrast with the zirconium system that is more selective with regard to product distribution. Four major hafnium-containing species are produced, as judged by ^{1}H NMR, ^{13}C NMR, and infrared spectroscopic data (eq 13): 12 (~25% yield), 13c (20–50%



yield), *trans*-(Cp*$_2$HfH)$_2$(μ-OCH=CHO) (13t) ($\leq$10% yield), and (Cp*$_2$HfH)$_2$(μ-OCH$_2$CH$_2$O) (15) (15–25% yield).

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(11) Efforts to prepare 8 using other reducing agents, solvents, and hafnium sources often resulted in a change in color of the reaction medium to the appropriate red-purple, but isolation of 8 in any appreciable quantity from the reactions was uniformly unsuccessful.

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Table I. NMR and IR Data[a]

compd	IR, cm^{-1}	NMR assign	NMR type	NMR chem shift	NMR coupling const, Hz
Cp^*HfCl_3 (**1**)		$C_5(CH_3)_5$	^1H	1.93 s	
$Cp^*_2HfCl_2$ (**2**)		$C_5(CH_3)_5$	^1H	1.88 s	
$Cp^*_2HfI_2$ (**3**)		$C_5(CH_3)_5$	^1H	2.00 s	
$Cp^*_2HfH_2$ (**4**)	$\nu(HfH)$ 1590	$C_5(CH_3)_5$	^1H	2.04 s	
	$\nu(HfD)$ 1135	HfH		15.57 s	
Cp^*_2HfHCl (**5**)		$C_5(CH_3)_5$	^1H	1.98 s	
		HfH		12.68 s	
Cp^*_2HfHBr (**6**)		$C_5(CH_3)_5$	^1H	1.99 s	
		HfH		13.75 s	
$Cp^*_2HfH(Ph)$ (**7**)	$\nu(HfH)$ 1630	$C_5(CH_3)_5$	^1H	1.78 s	
		HfH		13.14 s	
		C_6H_5		6.67 m	
		C_6H_5		6.98 m	
$(Cp^*_2HfN_2)_2N_2$ (**8**)	$\nu(N_2)$ 2000, 1962, 1538	$C_5(CH_3)_5$	^1H	1.92 s	
		$C_5(CH_3)_5$		1.90 s	
$Cp^*_2HfH_2(CO)$ (**10**)[b]	$\nu(CO)$ 2036[15]	$C_5(CH_3)_5$	^1H	1.92 s	
		HfH		2.67 s	$^2J_{CH} = 21.5$
		$Hf(CO)$	^{13}C	224.4 t	$^2J_{CH} = 21.5$
$Cp^*_2Hf(CO)_2$ (**11**)	$\nu(CO)$ 1940, 1845 $\nu(^{13}CO)$ 1890, 1800	$C_5(CH_3)_5$	^1H	1.77 s	
$Cp^*_2HfH(OCH_3)$ (**12**)	$\nu(HfH)$ 1650	$C_5(CH_3)_5$	^1H	1.98 s	
	$\nu(CO)$ 1160	HfH		9.92 s	
		$Hf(OCH_3)$		3.83 s	
		$Hf(OCH_3)$	^{13}C	57.2 q	$^1J_{HC} = 138$
cis-$(Cp^*_2HfH)_2(\mu\text{-}OCH{=}CHO)$ (**13c**)	$\nu(HfH)$ 1655	$C_5(CH_3)_5$	^1H	2.04 s	
	$\nu(C{=}C)$ 1633	HfH		10.53 s	
	$\nu(CO)$ 1170	$(OCH{=}CHO)$		5.27 s	
		$(O^{13}CH{=}^{13}CHO)$	^{13}C	127.7 AA'XX'	$^1J_{HC} = 175.9$ $^2J_{HC} = 20.9$ $^1J_{CC} = 90$ $^3J_{HH} = 4.5$
trans-$(Cp^*_2HfH)_2(\mu\text{-}OCH{=}CHO)$ (**13t**)	$\nu(HfH)$ 1650	$C_5(CH_3)_5$	^1H	2.04 s	
	$\nu(C{=}C)$ 1580	HfH		10.21 s	
	$\nu(CO)$ 1224	$OCH{=}CHO$		6.47 s	
		$O^{13}CH{=}^{13}CHO$	^{13}C	135.5 AA'XX'	$^1J_{HC} = 174.1$ $^2J_{HC} = 6.7$ $^1J_{CC} = 98.7$ $^3J_{HH} = 9.8$
$(Cp^*_2HfH)(Cp^*_2ZrH)(\mu\text{-}OCH{=}CHO)$ (**14**)	$\nu(HfH)$ 1655	$[C_5(CH_3)_5]_2Hf$	^1H	2.04 s	
	$\nu(ZrH)$ 1595	$[C_5(CH_3)_5]_2Zr$		2.02 s	
	$\nu(C{=}C)$ 1630	HfH		10.60 s	
		ZrH		6.12 s	
		$HfOCH{=}CHOZr$		5.13 AB	$^3J_{HH} = 4$
$(Cp^*_2HfH)_2(\mu\text{-}OCH_2CH_2O)$ (**15**)	$\nu(CO)$ 1150	$C_5(CH_3)_5$	^1H	1.98 s	
		HfH		9.92 s	
		OCH_2CH_2O		4.13 s	
		$O^{13}CH_2{}^{13}CH_2O$	^{13}C	77.0 t	$^1J_{HC} = 137$
$Cp^*_2HfH(CH_2CH_3)$ (**16**)	$\nu(HfH)$ 1630	$C_5(CH_3)_5$	^1H	1.90 s	
		$HfCH_2CH_3$		0.03 g	$^3J_{HH} = 8$
		$HfCH_2CH_3$		0.68 t	$^3J_{HH} = 8$
		HfH		12.41 s, br	

$Cp^*_2HfH(CH_2CHMe_2)$ (**17**)	ν(HfH) 1636	$C_5(CH_3)_5$	^1H	1.96 s	
		Hf*H*		13.64 s	
		$HfCH_2CH(CH_3)_2$ (*CH*₂)		−0.21 d	$^3J_{HH} = 6$
		$HfCH_2CH(CH_3)_2$ (*CH*₃)		1.02 d	$^3J_{HH} = 6$
$Cp^*_2HfH(CH_2CH_2Ph)$ (**18**)	ν(HfH) 1620	$C_5(CH_3)_5$	^1H	1.93 s	
		Hf*H*		13.71 s	
		$HfCH_2CH_2Ph$ (Hf*CH*₂)		0.30 m	
		$HfCH_2CH_2Ph$ (*Ph*)		7.30 m	
$Cp^*_2\overline{Hf(CH_2CH_2CH_2CH_2)}$ (**19**)		$C_5(CH_3)_5$		1.84 s	
		$HfCH_2CH_2CH_2CH_2$ (Hf*CH*₂, *CH*₂)		0.44 m	
		$HfCH_2CH_2CH_2CH_2$ (*CH*₂*CH*₂)		2.10 m	
$Cp^*_2HfH(CH{=}CHCMe_3)$ (**20**)	ν(HfH) 1625 ν(HfD) 1155 ν(C=C) 1560	$C_5(CH_3)_5$	^1H	1.91 s	
		Hf*H*		12.83 s	
		CH=CHC*Me*₃		1.09 s	
		CH=CHCMe₃		5.80 d	$^3J_{HH} = 21$
		CH=*CH*CMe₃		4.81 d	$^3J_{HH} = 21$
$Cp^*_2Hf(CH_2CH_3)(CH{=}CHCMe_3)$ (**21**)	ν(C=C) 1558	$C_5(CH_3)_5$	^1H	1.78 s	
		Hf*CH*₂CH₃		−0.08 q	$J_{HH} = 7.5$
		HfCH₂*CH*₃		1.29 t	$J_{HH} = 7.5$
		CH=CHC*Me*₃		1.07 s	
		CH=CHCMe₃		5.23 d	$^3J_{HH} = 19$
		CH=*CH*CMe₃		4.87 d	$^3J_{HH} = 19$

[a] ^1H (90-MHz) and ^{13}C (22.5-MHz) NMR spectra measured in benzene-d_6 at ambient temperature unless otherwise specified. IR spectra measured as Nujol mulls. [b] NMR spectra measured in toluene-d_6.

Table II. ^1H NMR Chemical Shifts for the Hydride Resonance for Compounds of the Formula $Cp^*_2HfH(X)$

X	δ	ref
H	15.6	this work
$CH_2CH(CH_3)_2$	13.6	this work
Br	13.5	5
C_6H_5	13.1	this work
CH_3	13.0	10
$CH{=}CHCMe_3$	12.8	this work
Cl	12.7	5
CH_2CH_3	12.2	this work
NHC_6H_5	11.6	6, 8
$N(CH_3)_2$	11.5	6, 8
$NH(p\text{-}C_6H_4CH_3)$	11.4	6, 8
F	11.1	5
OH	10.2	6
OCH_3	9.9	this work
$OCH_2CH_2CH(CH_3)_2$	9.9	7
NH_2	9.1	6
$(\eta^3\text{-}C_3H_5)$	3.6	7
H(CO)	2.7	14

A mixture of **13t** and **15** may be extracted away from **12** and **13c** with petroleum ether. There is little doubt concerning the identity of **13t**, as ^1H NMR, ^{13}C NMR (see Table I), and IR data are strictly analogous to values reported for the zirconium analogue. The structure of **15** is suggested by spectral data, which closely compares to spectral values of the related monomer **12**. Furthermore, while the trans enediolate dimer is the sole product in the thermal reactions of $Cp^*_2ZrH_2(CO)$ (see above), **13c** is consistently the major product in the thermal reactions of **10**. It is not clear what factors are responsible for these differences in reactivity between the Zr and Hf systems. The complexity and sensitivity of product distribution in this system have thwarted all attempts toward elucidation of the underlying mechanistic features.

Reactions of $Cp^*_2HfH_2$ with Unsaturated Hydrocarbons. Solutions of **4** react smoothly with ethylene, styrene, or isobutylene to afford the corresponding alkyl hydride complexes (quantitatively as judged by ^1H NMR spectroscopy), as shown in eq 14. This formal insertion

$$Cp^*_2HfH_2 + CH_2{=}CRR' \rightarrow Cp^*_2HfH(CH_2CHRR') \qquad (14)$$

16, R = R′ = H
17, R = R′ = Me
18, R = H, R′ = Ph

reaction of an olefin into a Hf–H bond is facile for ethylene and styrene, proceeding to completion in minutes at 20 °C. In contrast, the reaction of **4** with isobutylene requires higher temperatures (80 °C), longer reaction times (hours), and excess olefin to effect the insertion, probably due to increased steric interactions between the disubstituted olefin and the C_5Me_5 rings of **4**. The alkyl hydrides **16**, **17**, and **18** exhibit remarkable thermal stability, undergoing negligible decomposition after hours at 80 °C. Such stability is in contrast to most cis alkyl hydride complexes that have a proclivity toward reductive elimination of alkane, typically at or below ambient temperature,[17] but consistent with the observed thermal stability of related Zr alkyl hydrides.[18] The large activation energy expected for the transformation from a 16-electron Hf(IV) species (e.g., **16**, **17**, **18**) to a 14-electron Hf(II) species ("Cp^*_2Hf") upon reductive elimination of alkane might well be responsible for the thermal stability of these cis alkyl hydride complexes.

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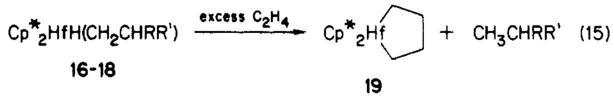
[17] (a) Norton, J. R. *Acc. Chem. Res.* **1979**, *12*, 139. (b) Halpern, J. *Ibid.* **1982**, *15*, 332 and references therein.

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

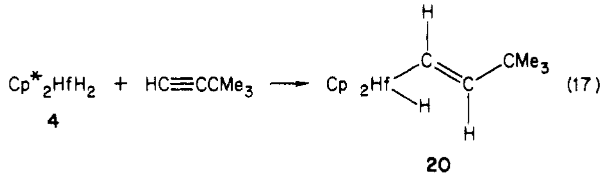
Excess ethylene does, however, induce elimination of alkane from **16**, **17**, or **18** with formation of the metallacyclopentane complex $Cp^*_2\overline{Hf(CH_2CH_2CH_2CH_2})$ (**19**) (eq 15). Additionally, these alkyl hydride complexes are subject to hydrogenolysis under mild (1 atm H_2, 20 °C, <1 h) conditions to afford the parent dihydride **4** and the appropriate alkane (eq 16). Reactions 14 and 15 have been examined in detail for the related $Cp^*_2ZrH(CH_2CHMe_2)$ system,[18] and mechanistic aspects of these reactions have been previously discussed.



(15)

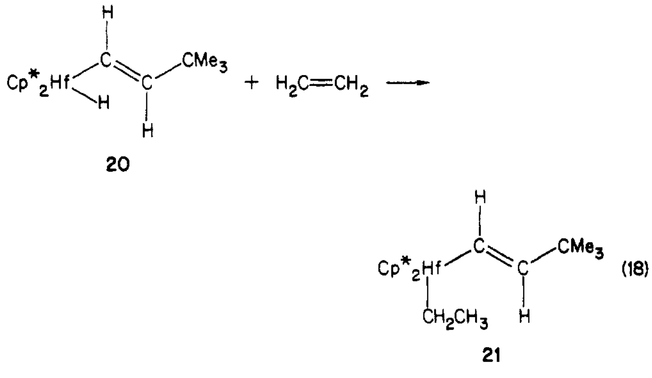
$$\underset{\textbf{16-18}}{Cp^*_2HfH(CH_2CHRR')} \xrightarrow{H_2} \underset{\textbf{4}}{Cp^*_2HfH_2} + CH_3CHRR' \qquad (16)$$

In a reaction akin to the regioselective insertions of unactivated olefins into Hf–H bonds of **4** discussed above, toluene solutions of **4** react smoothly with 1 equiv of *tert*-butylacetylene at ambient temperature to yield $Cp^*_2HfH(CH{=}CHCMe_3)$ (**20**) (>95% yield by ^1H NMR) (eq 17) as a colorless, crystalline solid.[19,20] Infrared (ν(HfH) 1625 cm^{-1}, ν(HfD) 1155 cm^{-1}, ν(C=C) 1560 cm^{-1}) and ^1H NMR ($^3J_{HH}$ = 21 Hz, C*H*=C*H*CMe$_3$) spectroscopic data support the formulation of **20** as a trans alkenyl hydride complex. Like **16**, **17**, and **18**, the alkenyl hydride **20** is quite thermally stable, with benzene solutions of **19** under 1 atm of N_2 showing no noticeable decomposition (^1H NMR) after days at 125 °C.



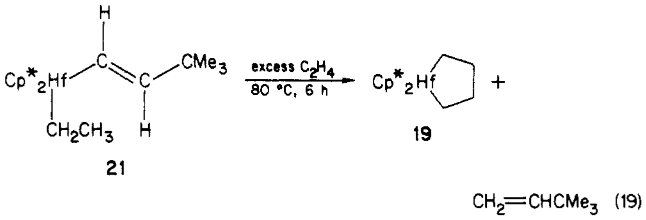
(17)

Solutions of **20** react cleanly with ethylene at 20 °C to yield $Cp^*_2Hf(CH_2CH_3)(CH{=}CHCMe_3)$ (**21**) as a colorless oil, as shown in eq 18. Solution infrared (ν(C=C) 1560 cm^{-1}) and ^1H NMR ($^3J_{HH}$ = 19 Hz, C*H*=C*H*CMe$_3$) spectroscopic data (Table I) identify **21** as product of ethylene insertion into the HfH bond of **20**. This insertion reaction contrasts with that of $Cp^*_2ZrH(CH_2CHMe_2)$, where ethylene insertion into the Zr–H bond is known to be thermodynamically unfavorable.[18]

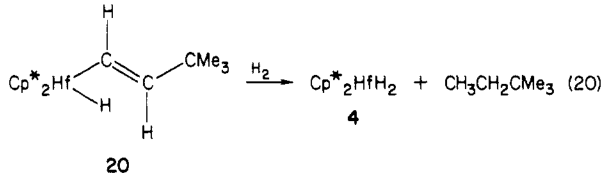


(18)

Thermolysis of **21** in the presence of excess ethylene results in quantitative generation of **19** and neohexene (80 °C, 6 h), according to eq 19. Analogously to reaction 16, **20** reacts with H_2 in stepwise fashion to yield the dihydride **4** and neohexane (80% conversion after 72 h at 20 °C), shown in eq 20. Attempts to prepare other σ-alkenyl hydrides using less bulky terminal acetylenes resulted in the isolation of double inserted, bis(alkenyl) products reported elsewhere.[20]



$CH_2{=}CHCMe_3$ (19)



(20)

Conclusions

A series of bis(pentamethylcyclopentadienyl)hafnium(II) and -hafnium(IV) complexes have been prepared, which complements an existing set of analogous zirconium derivatives, $Cp^*_2ZrL_x$. The zirconium complexes are generally prepared from the versatile Zr(II) dinitrogen complex $\{Cp^*_2Zr(N_2)\}_2(\mu\text{-}N_2)$ that can be prepared in high yield by a straightforward reduction of $Cp^*_2ZrCl_2$ under N_2. Although the Hf analogue of this Zr dinitrogen dimer exists, its synthesis is a rather cumbersome process and yields of $\{Cp^*_2Hf(N_2)\}_2(\mu\text{-}N_2)$ are mediocre. Thus, its usefulness as a synthetic starting material is limited. For the $Cp^*_2HfL_x$ system, the dihydride complex $Cp^*_2HfH_2$ has been found to be convenient entry into a number of hydrido Hf(IV) systems, $Cp^*_2HfH(X)$ (X = a uninegative ligand).

The reactivity of carbon monoxide toward $Cp^*_2HfH_2$ has been investigated and found to be similar to that observed for CO with $Cp^*_2ZrH_2$. It was hoped that mechanistic details and perhaps the nature of key intermediates involved in the $Cp^*_2ZrH_2$/CO system could be elucidated in the hafnium system, since reactions of third transition series metals are known to be, as a rule, kinetically slower than analogous reactions involving their first- or second-row counterparts. Unfortunately, poor product selectivity was observed for the reduction of CO by $Cp^*_2HfH_2$, precluding any meaningful mechanistic evaluation of reaction pathways.

$Cp^*_2HfH_2$ undergoes insertion reactions with terminal olefins and the sterically encumbered terminal acetylene $HC{\equiv}CCMe_3$ to afford hafnium alkyl hydride and alkenyl hydride complexes, respectively. These complexes are surprisingly thermally stable with respect to reductive elimination reactions but readily decompose in the presence of ethylene to yield the metallacyclopentane complex $Cp^*_2\overline{Hf(CH_2CH_2CH_2CH_2})$.

While the reactions reported herein generally parallel those of the related $ZrCp^*_2$ system, some differences in reactivity are evidenced. Various reasons for these differences may be advanced; one of the most important is that the Zr(IV) → Zr(II) couple is energetically more accessible than the Hf(IV) → Hf(II) couple; thus mechanisms involving such couples are undoubtedly more facile for Zr

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[19] For related reactions see: (a) Nakamura, A.; Otsuka, S. *J. Am. Chem. Soc.* **1972**, *94*, 1886. (b) Longato, B.; Bresadola, S. *Inorg. Chem.* **1982**, *21*, 168. (c) Schwartz, J.; Labinger, J. A. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 333. (d) Hart, D. W.; Blackburn, T. F.; Schwartz, J. *J. Am. Chem. Soc.* **1975**, *97*, 679. (e) Labinger, J. A.; Hart, D. W.; Seibert, W. E.; Schwartz, J. *J. Am. Chem. Soc.* **1975**, *97*, 3851.

[20] McDade, C.; Bercaw, J. E., *J. Organomet. Chem.*, in press.

than for Hf. Conversely, reactions involving M(II) → M(IV) oxidations are probably more favored for M = Hf than for M = Zr.

Experimental Section

General Considerations. All manipulations were carried out by using either high vacuum line or glovebox techniques. Solvents were purified by vacuum transfer first from $LiAlH_4$ or benzophenone ketyl and then from titanocene prepared as described earlier.[21] Hydrogen, deuterium (Matheson), and nitrogen were purified by passage over MnO on vermiculite[22] and activated 4-Å molecular sieves. Carbon monoxide, ethylene, and isobutylene (Matheson) were used directly from the cylinder. All other reagents were degassed and transferred from 4-Å molecular sieves or used as received.

^1H NMR spectra were recorded with Varian EM 390 or JEOL FX90Q spectrometer. Infrared spectra were measured on a Beckman 4240 spectrometer as Nujol mulls and are reported in inverse centimeters. Many reactions were carried out in sealed NMR tubes and monitored by NMR spectroscopy. A typical example is the reaction of $Cp^*_2HfH(CH_2CHMe_2)$ (17) with H_2: 30 mg (0.06 mmol) of 17 was placed in an NMR tube sealed to a 14/20 ground glass joint and fitted with a Teflon needle adapter. Benzene-d_6 was vacuum transferred into the tube at −78 °C, 1 atm H_2 admitted, and the tube cooled to −196 °C and sealed with a torch.

Procedures. Cp^*HfCl_3 (1). A 250-mL flask fitted with reflux condensor and needle valve was charged with 5.0 g (15.6 mmol) of $HfCl_4$, 2.4 g (16.9 mmol) of $LiC_5(CH_3)_5$, and 100 mL of toluene and refluxed under 1 atm argon for for 2 days. Solvent was removed in vacuo, and the solid residue was transferred to a sublimator. Sublimation (105 °C, 10^{-4} torr) yielded 5.7 g (87%) of white crystalline Cp^*HfCl_3:[23] IR 1070, 1026, 880, 807, 720, 595, 422 cm^{-1}. Anal. Calcd for $C_{10}H_{15}Cl_3Hf$: C, 28.59; H, 3.60; Cl, 25.32. Found: C, 28.53; H, 3.54; Cl, 25.18.

$Cp^*_2HfCl_2$ (2). Xylene (400 mL) was distilled into a 1-L three-necked flask equipped with gas inlet tube, vigreaux column, and solid addition ampule. A 24.7-g (0.181-mmol) sample of C_5Me_5H was syringed into solution under argon counterflow, solution was cooled to −10 °C, and 115 mL of 1.6 M *n*-BuLi (0.184 mmol) was syringed in. Solution turned yellow immediately and after several hours at 25 °C appeared orange and gelatinous. After 24 h, 23.1 g (0.072 mmol) of $HfCl_4$ was added by addition ampule, solvent removed under vacuum, and residue suspended in 200 mL of CH_2Cl_2 and 200 mL of 4 M HCl. Mixture was filtered, organic layer separated, and aqueous layer extracted three times with 50 mL of CH_2Cl_2. The methylene chloride fractions were combined, dried over Na_2SO_4, and filtered, and solvent was removed under vacuum. Crystalline solid was transferred to a thimble and Soxhlet extracted with CCl_4. The receiving flask was cooled, and crystalline, off-white (2) (26.4 g, 70.5%) was collected and dried. Anal. Calcd for $C_{20}H_{30}Cl_2Hf$: C, 46.21; H, 5.82; Cl, 13.64; Hf, 34.33. Found: C, 46.26; H, 5.72; Cl, 13.48; Hf, 33.98.

$Cp^*_2HfI_2$ (3). An 8.0-g sample of $Cp^*_2HfCl_2$ (15.4 mmol) and 4.0 g of BI_3 were dissolved in 100 mL of toluene, and the solution was stirred for 6 h at ambient temperature. The solvent was removed under vacuum, and the resulting yellow solid was washed with petroleum ether and then dried under vacuum for 12 h to yield 9.25 g (86%). Anal. Calcd for $C_{20}H_{30}HfI_2$: C, 34.18; H, 4.30. Found: C, 35.10, 34.99; H, 4.30, 4.30. Alternatively, the complex could be prepared in quantitative yield by treatment of $Cp^*_2HfH_2$ with excess (∼4 equiv) CH_3I in toluene. Removal of solvent yielded the pure diiodo compound.

$Cp^*_2HfH_2$ (4). A 10-g (19.2-mmol) sample of $Cp^*_2HfCl_2$ was slurried in ca. 100 mL of toluene at −78 °C. A 1.6 M hexane solution of *n*-BuLi (27 mL, 42.2 mmol) was added via syringe under argon counterflow; argon was removed quickly in vacuo, 1 atm of H_2 was admitted, and the reaction was allowed to warm. Uptake of H_2 commensed at room temperature, proceeding smoothly over the course of several hours. After gas uptake ceased, the reaction mixture was stirred an additional 12 h. Solvents were removed in vacuo, and the residue was taken up in 60 mL of petroleum ether, filtered, and washed thoroughly. The filtrate was concentrated and cooled to −78 °C, precipitating white crystalline 4. Filtering, washing with cold petroleum ether, and drying in vacuo yielded 6.0 g (70%): IR 1600, 1490, 1450, 1065, 1025, 804, 768, 694, 570 cm^{-1}. Anal. Calcd for $C_{20}H_{32}Hf$: C, 53.27; H, 7.15; Hf, 39.58. Found: C, 53.23; H, 6.98; Hf, 39.78.

Cp^*_2HfHCl (5). In a thick-walled glass reaction vessel was placed 1.59 g (3.5 mmol) of $Cp^*_2HfH_2$ dissolved in 10 mL of benzene, followed by 1.0 equiv of CH_3Cl. The flask was immersed in an oil bath, and the contents were stirred at 80 °C for 12 h and then transferred into a filter–frit assembly. The benzene was removed under vacuum, and the residue was washed with cold petroleum ether to yield 1.37 g (80%) of a colorless powder. Anal. Calcd for $C_{20}H_{31}ClHf$: C, 49.49; H, 6.44; Cl, 7.30. Found: C, 49.72; H, 5.49; Cl, 7.29.

Cp^*_2HfHBr (6) was prepared analogously from $Cp^*_2HfH_2$ and CH_3Br except that the solution was stirred at ambient temperature for 12 h. A ^1H NMR spectrum of the resulting colorless powder showed ∼5% of an impurity, presumed to be $Cp^*_2HfBr_2$. Anal. Calcd for $C_{20}H_{31}BrHf$: C, 45.34; H, 5.90; Br, 15.08. Found: C, 44.02; H, 5.61; Br, 16.59.

$Cp^*_2HfH(Ph)$ (7). A 3.02-g (6.7-mmol) sample of $Cp^*_2HfH_2$ was dissolved in 60 mL of petroleum ether, the solution was cooled to −78 °C, 3.3 mL (7.3 mmol) in 2.2 M (70:30 cyclohexane/diethyl ether) phenyllithium solution was added via syringe, and the reaction mixture was allowed to warm to room temperature. After 18 h at 25 °C the reaction mixture was filtered, and the filtrate was concentrated and cooled to −78 °C. The resultant white precipitate was filtered off and dried in vacuo, giving 1.82 g (52%) of 7: IR 3045, 1650, 1568, 1487, 1414, 1238, 1059, 1050, 1023, 804, 785, 726, 716 cm^{-1}. Anal. Calcd for $C_{26}H_{36}Hf$: C, 59.25; H, 6.88. Found: C, 58.93; H, 6.89.

$\{Cp^*_2Hf(N_2)\}_2(\mu\text{-}N_2)$ (8). In a 500-mL round bottomed flask were placed 9.25 g (13.2 mmol) of $Cp^*_2HfI_2$ and 1.5 g of NaK alloy (1:5 Na/K). A 100-mL sample of 1,2-dimethoxyethane was distilled into the flask, and the contents were vigorously stirred at −41 °C (acetonitrile/LN_2 slush) under 1 atm of N_2. The solution immediately turned brown and then slowly burgundy. After about 4 h, a green metallic mirror formed on the bottom of the flask. At this time, stirring was ceased and the solution was allowed to sit at −78 °C for about 30 min. A large amount of dark green material had precipitated that was isolated by filtration. The filtrate was taken to dryness and the residue added to the green solid. The combined solids were dissolved in benzene (∼75 mL) and filtered quickly to yield a magenta solution. The benzene was removed under vacuum and petroleum ether (150 mL) added to the red residue. The resulting mixture was stirred for 6 h under N_2 at ambient temperature and then filtered to yield 1.26 g (20%) of sparkling metallic green crystals: IR (Nujol mull) ν(NN) 2000 (s), 1962 (vs), 1538 (s) cm^{-1}. Anal. Calcd for $C_{20}H_{30}HfN_3$: C, 48.93; H, 6.16; N, 8.56. Found: C, 49.44; H, 6.09; N, 7.89.

$Cp^*_2HfH_2(CO)$ (10). Onto 185 mg (0.410 mmol) of $Cp^*_2HfH_2$ was condensed 10 mL of toluene at −78 °C. CO (2.773 mmol) was admitted, and the solution was stirred for 90 min. The solution was frozen at liquid N_2 temperature. Residue gas was passed through a series of liquid N_2-cooled traps via a Toepler pump; CO collected amounted to 2.421 mmol, giving CO uptake as 0.352 mmol (0.86 mol/mol).

$Cp^*_2Hf(CO)_2$ (11). A high-pressure reactor, charged with 4.0 g (8.87 mmol) of $Cp^*_2HfH_2$ and 60 mL of toluene, was pressured to 1500 psi of CO and stirred at room temperature 1 h. The resultant dark maroon solution was transferred to a frit assembly, the volume was reduced, and the solution was cooled to −78 °C. A total of 3.30 g (74%) of 11 was collected: IR 1940, 1845, 1485, 1433, 1163, 1030, 800 cm^{-1}. Anal. Calcd for $C_{22}H_{30}O_2Hf$: C, 52.33; H, 5.99; Hf, 35.35. Found: C, 52.34; H, 5.87; Hf, 35.19.

$Cp^*_2HfH(OCH_3)$ (12). A thick-walled glass reaction vessel with Teflon needle valve was charged with 230 mg (0.455 mmol) of $Cp^*_2Hf(CO)_2$, 10 mL of toluene, and 5 mmol (2 atm) of H_2 and heated to 150 °C for 24 h. The pale yellow solution was transferred to a sublimator, the solvent was removed in vacuo, and pale yellow 12 was collected by sublimation (100 °C, 10^{-4} torr): IR 1650, 1160,

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[21] Marvich, R. H.; Brintzinger, H. H. *J. Am. Chem. Soc.* **1971**, *93*, 2046.

[22] Brown, T. L.; Dickerhoof, D. W.; Bafus, D. A.; Morgan, G. L. *Rev. Sci. Instrum.* **1962**, *33*, 491.

[23] Blenkers, J.; DeLiefde Meijer, H. J.; Teuben, J. H. *J. Organomet. Chem.* **1981**, *218*, 383.

1026, 805, 614, 458 cm^{-1}. Anal. Calcd for $C_{21}H_{34}OHf$: C, 52.43; H, 7.13; Hf, 37.11. Found: C, 52.31; H, 6.95; Hf, 36.99.

***cis*-{$Cp^*_2HfH\}_2(\mu$-OHC═CHO) (13c).** A thick-walled glass reaction vessel with a Teflon needle valve was charged with 0.30 g (0.59 mmol) of $Cp^*_2Hf(CO)_2$, 0.27 g (0.59 mmol) of $Cp^*_2HfH_2$, 10 mL of toluene, and 5 mmol (2 atm) of H_2 and stirred at 80 °C for 2 weeks. The resultant yellow solution was transferred to a frit assembly; workup with petroleum ether afforded 0.140 g (25%) of white, microcrystalline **13c**: IR 1655, 1633, 1325, 1170, 1077, 1027, 840 cm^{-1}. Anal. Calcd for $C_{21}H_{32}OHf$: C, 52.66; H, 6.73; Hf, 37.26. Found: C, 52.71; H, 6.62; Hf, 37.12.

***cis*-$(Cp^*_2HfH)(Cp^*_2ZrH)(\mu$-OCH═CHO) (14).** In a manner analogous to **13c**, 260 mg (0.51 mmol) of **11**, 190 mg (0.51 mmol) of $Cp^*_2ZrH_2$, 10 mL of toluene, and 5 mmol (2 atm) of H_2 were stirred at 80 °C for 24 h. Workup yielded 245 mg (56.5%) of light yellow microcrystalline **14**: IR 1655, 1630, 1595, 1320, 1165, 1075, 1027, 840 cm^{-1}. Anal. Calcd for $C_{42}H_{64}O_2HfZr$: C, 57.94; H, 7.41; Hf, 20.50; Zr, 10.48. Found: C, 57.83; H, 7.31; Hf, 20.32; Zr, 10.41.

$Cp^*_2HfH(CH_2CH_3)$ (16). A solution of 0.60 g (1.25 mmol) of $Cp^*_2HfH_2$ in 15 mL of petroleum ether was stirred at room temperature under 200 torr of ethylene for 1 h. Excess ethylene was removed and the solution concentrated and cooled to −78 °C to yield 0.39 g (61%) (**16**): IR 1630, 1488, 1022, 919, 802, 778 cm^{-1}. Anal. Calcd for $C_{22}H_{36}Hf$: C, 55.15; H, 7.57; Hf, 37.76. Found: C, 55.63; H, 7.42; Hf, 37.10.

$Cp^*_2HfH(CH_2CHMe_2)$ (17). A thick-walled glass reaction vessel with a Teflon needle valve was charged with 1.0 g (2.0 mmol) of $Cp^*_2HfH_2$, 5 mL of toluene, and 8 mmol of isobutylene, and stirred at 80 °C for 2 days. Volatiles were removed in vacuo; workup with petroleum ether afforded 0.795 g (71%) of **17**: IR 1636, 1302, 1155, 1028, 805, 770 cm^{-1}. Anal. Calcd for $C_{24}H_{40}Hf$: C, 56.85; H, 7.95; Hf, 35.20. Found: C, 56.68; H, 8.12; Hf, 34.94.

$Cp^*_2HfH(CH_2CH_2Ph)$ (18). To a stirred solution of 0.41 g (0.91 mmol) of $Cp^*_2HfH_2$ in 15 mL of toluene at −78 °C was added 110 mL (0.96 mmol) of styrene via syringe under argon counterflow. The solution was warmed to room temperature and stirred an additional 30 min, toluene was removed in vacuo, and the solid residue was worked up with petroleum ether to afford 0.36 g (71%) of white crystalline **18**: IR 3060, 16.20, 1492, 1053, 1030, 975, 806, 776 cm^{-1}.

$Cp^*_2\overline{Hf(CH_2CH_2CH_2CH_2})$ (19). A thick-walled glass reaction vessel with a Teflon needle valve was charged with 1.0 g (2.22 mmol) of $Cp^*_2HfH_2$, 10 mL of toluene, and 72.6 mmol of ethylene and stirred at 80 °C for 24 h. Solvent and excess ethylene were removed, and 0.80 g (61%) of off-white **19** was crystallized from petroleum ether: IR 1490, 1022, 993 cm^{-1}. Anal. Calcd for $C_{24}H_{38}Hf$: C, 57.08; H, 7.58; Hf, 35.34. Found: C, 57.06; H, 7.59; Hf, 35.43.

$Cp^*_2HfH(CH═CHCMe_3)$ (20). A 2.50-mmol sample of *tert*-butylacetylene was condensed at −195 °C onto a solution of 1 g (2.22 mmol) of $Cp^*_2HfH_2$ in 15 mL of petroleum ether, stirred for 30 min at −78 °C, and allowed to warm to room temperature. The solution was concentrated to ca. 5 mL and cooled to 78 °C to yield 0.56 g (47%) of white, crystalline **20**: IR 1624, 1560, 1490, 1360, 1232, 1218, 1204, 1064, 1026, 1005, 805 cm^{-1}. Anal. Calcd for $C_{26}H_{42}Hf$: C, 58.58; H, 7.94; Hf, 33.48. Found: C, 58.32; H, 7.89; Hf, 33.26.

$Cp^*_2Hf(CH_2CH_3)(CH═CHCMe_3)$ (21). A 3.0-mmol sample of ethylene was condensed at −195 °C onto a solution of 0.66 g (1.24 mmol) of **20** in 10 mL of toluene, warmed to room temperature, and stirred for 2 days. Volatiles were removed in vacuo to leave a colorless oil. Analysis of this residue by ^1H NMR indicated 95% **21**: IR 1558, 1490, 1357, 1250, 1215, 1206, 1060, 1021, 1000, 801 cm^{-1}.

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Registry No. 1, 75181-08-7; **2**, 85959-83-7; **3**, 92786-75-9; **4**, 81956-87-8; **5**, 91295-01-1; **6**, 92786-76-0; **7**, 92786-77-1; **8**, 92786-78-2; **10**, 75687-92-2; 11, 76830-38-1; **12**, 92786-79-3; **13c**, 92935-38-1; **13t**, 92786-80-6; **14**, 92786-81-7; **15**, 92786-82-8; **16**, 92786-83-9; **17**, 92786-84-0; 18, 92786-85-1; **19**, 92786-86-2; **20**, 92786-87-3; **21**, 92786-88-4; $HfCl_4$, 13499-05-3; $LiC_5(CH_3)_5$, 51905-34-1; BI_3, 13517-10-7; CH_3I, 74-88-4; CH_3Cl, 74-87-3; CH_3Br, 74-83-9; phenyllithium, 591-51-5; ethylene, 74-85-1; isobutylene, 115-11-7; styrene, 100-42-5; *tert*-butylacetylene, 917-92-0.

Polyoxoanion-Supported Organoactinides: The $[(C_5H_5)_3U(MW_5O_{19})_2]^{5-}$ Anions (M = Nb, Ta) and Their Thorium Analogues $[(C_5H_5)_3Th(MW_5O_{19})_2]^{5-}$†

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The $MW_5O_{19}{}^{3-}$ anions, M = Nb and Ta, react with $(C_5H_5)_3AcCl$, Ac = Th and U, to form the $[(C_5H_5)_3Ac(MW_5O_{19})_2]^{5-}$ anions. According to a single crystal X-ray diffraction study of $(C_5H_5)_3U(NbW_5O_{19})_2[(\eta\text{-}C_4H_9)_4N]_5$ [a = 13.668 (4) Å, b = 24.172 (6) Å, c = 21.190 (6) Å, α = 98.58 (3)°, β = 98.15 (3)°, γ = 104.64 (3)°; triclinic; $P_{\bar{1}}—C_i^1$; Z = 2], IR spectroscopy, and ^{17}O NMR spectroscopy, all four complexes contain trigonal-bipyramidal actinide centers having three equatorial η^5-C_5H_5 ligands and two axial κ^1O-MW_5O_{19} ligands where the terminal OM oxygens in the MW_5O_{19} ligands coordinate to the actinide centers. The actinide–oxygen bonds in these complexes are quite labile: $[(C_5H_5)_3Th(NbW_5O_{19})_2]^{5-}$ and $[(C_5H_5)_3Th(TaW_5O_{19})_2]^{5-}$ equilibrate in CH_3NO_2 within 15 min at 25 °C to form $[(C_5H_5)_3Th(NbW_5O_{19})(TaW_5O_{19})]^{5-}$ in approximately statistical amounts.

Introduction

Since the actinide elements are known to form stable organic[2] and polyoxoanion[3] complexes, the synthesis of polyoxoanion-supported organoactinide complexes is a reasonable objective. Polyoxoanion-supported organoactinides offer the possibility of combining several features of known organometallic complexes in a unique fashion. Large, planar ligands such as C_5H_5, C_8H_8, and $(CH_3)_5C_5$ are known to be effective as auxiliary ligands due to their

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† Dedicated to the memory of Earl Muetterties and the standards he upheld.

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