shielding for the adjacent carbon of the phenyl substituent in the ^{13}C NMR spectra of 2 are recorded compared to the corresponding values of the acyl carbonyl of the bridging benzoyl complexes 1.

Conclusion. The reaction conditions described provide heterobimetallic complexes of chromium and manganese with σ,π-bridging benzene and benzoyl ligands in reasonable yields. The advantage of using lithiated arenes above those where anionic transition-metal precursors were employed is found in the stronger nucleophilicity of these reagents. The negative charge is highly localized on the arene ring and on the metalated carbon, instead of being delocalized over the whole complex, resulting in a very reactive reagent and a more general method for the preparation of bridged benzene or benzoyl dimers of chromium.

Whereas the formation of bridged benzoyl dimers is promoted by the smaller, stronger π-acceptor ligands (CO, P(OMe)$_3$), bridged benzene dimers are found with the larger and more basic PPh$_3$ ligand on the manganese. Furthermore, phenyl migration for the reaction with dppe is promoted during the chelation step of the bidentate

ligand. Close correlation with these results were obtained by Herberhold,[51] who showed that PPh$_3$ inhibits cyclopentadienyl migration in Fe(η^5-C$_5$H$_5$){η^5-C$_5$H$_4$Mn(CO)$_4$-(PPh$_3$)} and promotes it in Fe(η^5-C$_5$H$_5$){η^5-C$_5$H$_4$C(O)}Mn-(CO)$_3$(dppe).

Registry No. 1a, 138090-85-4; 1b, 138128-53-7; 1c, 138090-86-5; 1d, 138090-87-6; 2, 57347-34-9; 3a, 138090-88-7; 3b, 138128-54-8; 3c, 138090-89-8; 3d, 138090-90-1; 4a, 138090-91-2; 4b, 138090-92-3; (η^6-C$_6$H$_6$)Cr(CO)$_3$, 12082-08-5; (η^6-C$_6$H$_5$F)Cr(CO)$_3$, 12082-05-2; [Mn(CO)$_5$Br], 14516-54-2; Mn(CO)$_3$(PPh$_3$)$_2$Br, 14244-44-1; (η^6-(1,4-C$_6$H$_4$Br$_2$))Cr(CO)$_3$, 117939-67-0.

Supplementary Material Available: For 1a and 3c, tables of bond distances, bond angles, anisotropic temperature factors, and hydrogen atom coordinates (11 pages); tables of observed and calculated structure factors (30 pages). Ordering information is given on any current masthead page.

(51) Herberhold, M.; Kniesel, H. *J. Organomet. Chem.* **1987**, *334*, 347.

Alkanediyl and Related Derivatives of Permethylhafnocene

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The reactions of Cp*$_2$HfH$_2$ (Cp* = (η^5-C$_5$Me$_5$)) with α,ω-dienes (1,3-butadiene, 1,4-pentadiene, 1,5-hexadiene and 1,6-heptadiene) in a 2:1 molar ratio yield the new binuclear alkanediyl derivatives Cp*$_2$-(H)Hf(CH$_2$)$_n$Hf(H)Cp*$_2$ (n = 4–7). The reactions of Cp*$_2$HfH$_2$ with the same dienes in a 1:1 molar ratio lead to the mononuclear compounds Cp*$_2$(H)Hf(η^3-CH$_2$CHCHCH$_3$), Cp*$_2$HfCH$_2$(CH$_2$)$_2$CH(CH$_3$), Cp*$_2$-HfCH$_2$(CH$_2$)$_3$CH(CH$_3$), and the α-hafna-ω-alkene Cp*$_2$(H)HfCH$_2$(CH$_2$)$_4$CH=CH$_2$, respectively. Allene reacts with Cp*$_2$HfH$_2$ (1:1) to cleanly afford the allyl hydride derivative, Cp*$_2$(H)Hf(η^3-CH$_2$CHCH$_2$); reaction with a 1:2 ratio yields a mixture of products, one of which appears to be Cp*$_2$(H)Hf(CH$_2$)$_3$Hf(H)Cp*$_2$. Reaction of Cp*$_2$HfH$_2$ with acetylene yields Cp*$_2$(H)HfCH=CH$_2$, which does not react with excess Cp*$_2$HfH$_2$ to yield the ethanediyl derivative. 1,3-Pentadiene and Cp*$_2$HfH$_2$ cleanly yield Cp*$_2$(H)Hf(η^3-CH$_2$CHCHCH$_2$CH$_3$). The thermal stabilities and reactions of some of these derivatives with excess diene, ethylene, CO, H$_2$, and H$_2$O have been investigated. The possibility of extending this chemistry to the permethyltitanocene and permethylzirconocene systems has also been explored.

Introduction

Binuclear alkanediyl complexes may be useful models for hydrocarbons bound to metal catalyst surfaces in important reactions such as olefin polymerization and the Fischer–Tropsch reaction. They may also serve as precursors for the synthesis of bifunctional organic compounds. In recent years, the number of known transition-metal alkanediyl compounds has increased dramatically.[2,3] Apart from the ethanediyl complexes of zirconium, [Cp$_2$ZrCl]$_2$(μ-CH$_2$CH$_2$) and [Cp$_2$ZrCl(AlEt$_3$)]$_2$(μ-CH$_2$CH$_2$),[4a,b] and the novel complexes M$_2$X$_6$(PEt$_3$)$_4$-

(CH$_2$CH$_2$) (M = Zr, Hf; X = Cl, Br) prepared by Cotton and Kibala,[4c] there are few such complexes known for the early transition metals. It was the object of this study to investigate the synthesis of alkanediyl complexes of some of the early transition metals and to compare their chemistry with that of the known mononuclear alkyl complexes.

Results and Discussion

Alkyl hydride complexes of hafnium have been previously prepared in our laboratories using the following route:[5]

$$\text{Cp*}_2\text{HfH}_2 + \text{CH}_2=\text{CHR} \rightarrow \text{Cp*}_2\text{Hf(H)(CH}_2\text{CH}_2\text{R)} \quad (1)$$
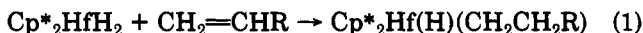
This reaction, formally 1,2 insertion of an olefin into a Hf–H bond, proceeds quantitatively and cleanly to yield the thermally stable mononuclear alkyl hydride complexes.

(1) Present address: Department of Chemistry, University of Cape Town, Private Bag, Rondesbosch 7700, South Africa
(2) Moss, J. R.; Scott, L. G. *Coord. Chem. Rev.* **1984**, *60*, 171.
(3) Casey, C. P.; Audett, J. L. *Chem. Rev.* **1986**, *86*, 329.
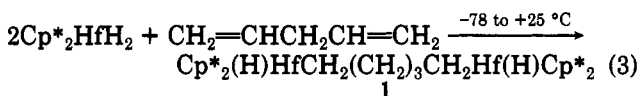(4) (a) Kaminsky, W.; Sinn, H. *Liebigs Ann. Chem.* **1975**, 424 and 438. (b) Kaminsky, W.; Kopf, J.; Sinn, H.; Vollmer, H. J. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 629. (c) Cotton, F. A.; Kibala, P. A. *Inorg. Chem.* **1990**, *29*, 3192.

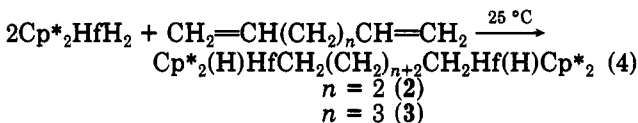(5) Roddick, D. M.; Fryzuk, M. D.; Seidler, P. F.; Hillhouse, G. L.; Bercaw, J. E. *Organometallics* **1985**, *4*, 97.

An adaptation of this route using 2 mol of Cp*$_2$HfH$_2$ with an appropriate α,ω-diene may be expected to result in two insertions to yield the binuclear alkanediyl hydride complexes (eq 2).
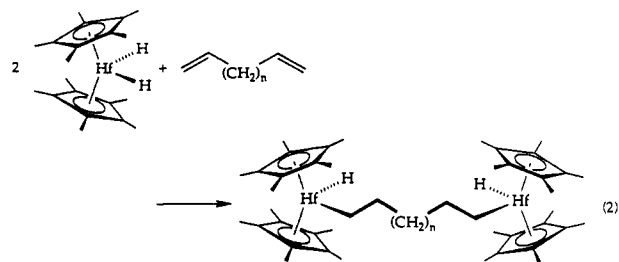
Indeed, this synthetic strategy works well for $n = 1–3$. Reaction of Cp*$_2$HfH$_2$ with 1,4-pentadiene in a 2:1 molar ratio affords the 1,7-dihafnaheptane, Cp*$_2$(H)-HfCH$_2$CH$_2$CH$_2$CH$_2$CH$_2$Hf(H)Cp*$_2$ (1), in good yields (ca. 80% by ^{1}H NMR spectroscopy; 61% isolated) (eq 3).

$$2Cp*_2HfH_2 + CH_2{=}CHCH_2CH{=}CH_2 \xrightarrow{-78 \text{ to } +25 \text{ °C}}$$
$$Cp*_2(H)HfCH_2(CH_2)_3CH_2Hf(H)Cp*_2 \quad (3)$$
$$1$$

Similarly, reaction of a 2:1 molar ratio of Cp*$_2$HfH$_2$ and 1,5-hexadiene yields the 1,8-dihafnaoctane, Cp*$_2$(H)-HfCH$_2$(CH$_2$)$_4$CH$_2$Hf(H)Cp*$_2$ (2), in 89% isolated yield, whereas reaction with 1,6-heptadiene appears to cleanly produce 1,9-dihafnanonane, Cp*$_2$(H)HfCH$_2$-(CH$_2$)$_5$CH$_2$Hf(H)Cp*$_2$ (3) (eq 4).

$$2Cp*_2HfH_2 + CH_2{=}CH(CH_2)_nCH{=}CH_2 \xrightarrow{25 \text{ °C}}$$
$$Cp*_2(H)HfCH_2(CH_2)_{n+2}CH_2Hf(H)Cp*_2 \quad (4)$$
$$n = 2 \ (2)$$
$$n = 3 \ (3)$$

With smaller dienes the reaction with Cp*$_2$HfH$_2$ is less selective, and products other than the desired α,ω-di-hafnaalkanes are generated. Thus, a mixture of unreacted Cp*$_2$HfH$_2$, Cp*$_2$(H)HfCH$_2$CH$_2$CH$_2$CH$_2$Hf(H)Cp*$_2$ (4), and the crotyl hydride derivative Cp*$_2$(H)Hf(η^3-CH$_2$CHCH-(CH$_3$)) (vide infra) were prepared from a 2:1 mixture of Cp*$_2$HfH$_2$ and butadiene. Due to its lower solubility, 4 may be isolated from this product mixture, albeit in only 14% yield. Similarly, reaction of a 2:1 mixture of Cp*$_2$HfH$_2$ and allene affords unreacted Cp*$_2$HfH$_2$ and the allyl hydride derivative, Cp*$_2$(H)Hf(η^3-CH$_2$CHCH$_2$) in addition to the desired 1,5-hafnapentane, Cp*$_2$(H)-HfCH$_2$CH$_2$CH$_2$Hf(H)Cp*$_2$ (5). Unfortunately, 5 proved too unstable for isolation of an analytically pure sample.

Reaction of Cp*$_2$HfH$_2$ with 0.5 equiv of acetylene affords 0.5 equiv of unreacted dihydride along with 0.5 equiv of the new compound Cp*$_2$(H)HfCH=CH$_2$ (6) (eq 5). Even
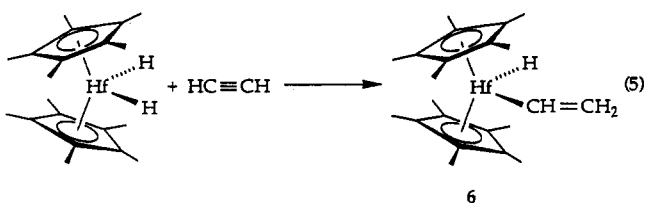
after extended reaction times there is no evidence for further reaction to yield the desired 1,4-dihafnabutane derivative, presumably due to unfavorable steric crowding of the bulky permethylhafnocene moieties. The vinyl hydride derivative 6 is obtained quantitatively (^{1}H NMR spectroscopy) by reaction of Cp*$_2$HfH$_2$ and acetylene (1:1) and may be isolated as a white microcrystalline solid (33%).[6] 6 shows no tendency to reductive eliminate
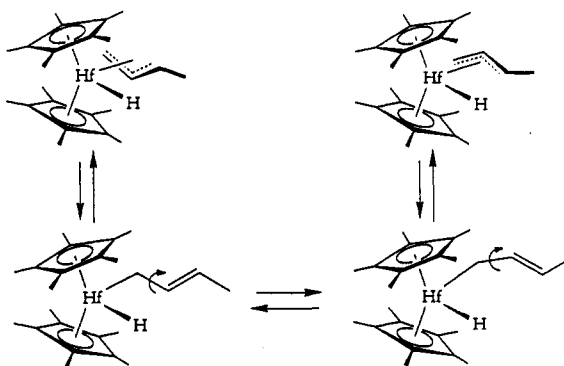
ethylene even on heating at 80 °C for 5 days.

As a part of this study, we have also investigated the reactions of these dienes with a full 1 equiv of Cp*$_2$HfH$_2$. Reaction of allene (1:1) quantitatively affords the known allyl hydride derivative Cp*$_2$(H)Hf(η^3-CH$_2$CHCH$_2$) (7)[7] (eq 6). An X-ray crystal structure determination by Roddick
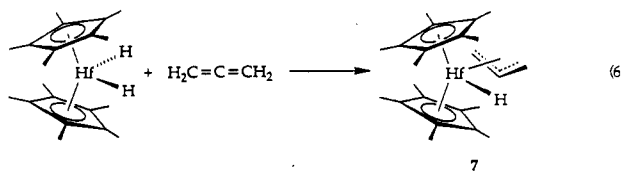
clearly established the η^3 coordination geometry for the allyl ligand. Similarly, reaction of butadiene and Cp*$_2$HfH$_2$ (1:1) quantitatively (^{1}H NMR spectroscopy) yields the crotyl hydride derivative 8 (eq 7). Room-temperature ^{1}H
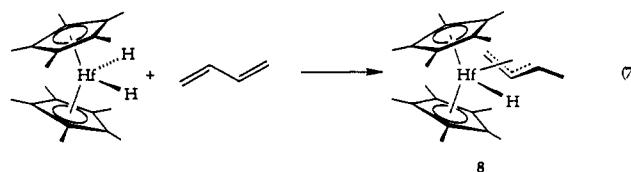
NMR data, specifically, the single resonance for both [η^5-C$_5$(CH$_3$)$_5$] ligands, the doublet for the methylene hydrogens, the doublet of triplets ($^3J_{HH}$ = 17, $^3J_{HH}$ = 10 Hz) for the 2-hydrogen [CH$_2$CHCH(CH$_3$)], and the doublet of quartets ($^3J_{HH}$ = 17, $^3J_{HH}$ = 6 Hz) for the 3-methine hydrogen [CH$_2$CHCH(CH$_3$)], are indicative of a fluxional [syn-η^3-CH$_2$CHCH(CH$_3$)] arrangement (Scheme I). As shown, the sterically preferred rearrangement from [Hf-(η^3-CH$_2$CHCH(CH$_3$)] to [HfCH$_2$CH=CH(CH$_3$)] is sufficient to equate the methylene and pentamethylcyclopentadienyl hydrogens; however, rearrangement to the secondary η^1-allyl intermediate [HfCH(CH$_3$)CH=CH$_2$] may also be occurring. Of course, the latter must be generated as the precursor to the crotyl hydride derivative in the reaction with butadiene, even though rapid (and reversible) addition to form the primary product [Cp*$_2$-(H)HfCH$_2$CH$_2$CH=CH$_2$] almost certainly precedes eventual buildup of the thermodynamically stable tautomer 8. As noted above, when present in excess, Cp*$_2$HfH$_2$ appears to trap [Cp*$_2$(H)HfCH$_2$CH$_2$CH=CH$_2$] as Cp*$_2$(H)-HfCH$_2$CH$_2$CH$_2$CH$_2$Hf(H)Cp*$_2$ (4) competitively with its rearrangement to 8.

Whereas the reaction of Cp*$_2$HfH$_2$ with 1,4-pentadiene (2:1) does afford 1,7-dihafnaheptane (1) in good yield, a

(6) The low isolated yield is due to the very high solubility of Cp*$_2$-(H)HfCH=CH$_2$, even in petroleum ether.
(7) Roddick, D. M. Ph.D. Thesis, California Institute of Technology, 1984.

1:1 mixture yields a quite different final product, the hafnamethylcyclopentane $Cp*_2HfCH_2CH_2CH_2CH(CH_3)$ (9) (ca. 70%), together with 1 (ca. 25%) (eq 8). The ^1H

$$Cp*_2HfH_2 + \diagup\!\!\!\diagdown\!\!\!\diagup\!\!\!\diagdown \longrightarrow \qquad + \qquad (8)$$

9 (ca. 70%)

1 (ca. 25%)
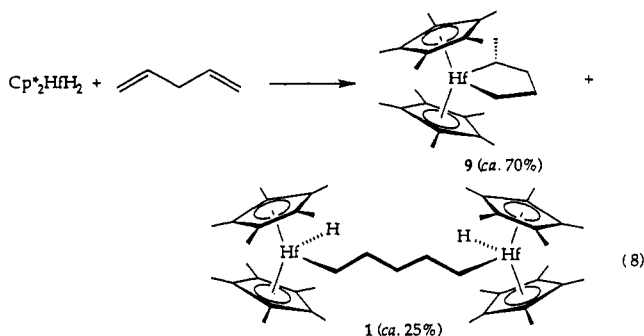
NMR data (Table I) for 9 are not readily interpreted, even from selective decoupling experiments;[8] however, the ^{13}C NMR data (Table I) are quite distinctive. When a toluene-d_8 solution of $Cp*_2HfH_2$ and 1,4-pentadiene (1:1) is monitored by ^1H NMR spectroscopy, by beginning at –80 °C and then warming slowly to room temperature, two products are observed initially: a new compound exhibiting a η^5-C_5Me_5 resonance at δ 1.92, assigned as $Cp*_2(H)HfCH_2CH_2CH_2CH=CH_2$ (ca. 70%), and 1 (ca. 30%). At –40 °C the metallacycle 9 begins to appear as the 1-hafna-5-hexene steadily decreases in concentration. At +20 °C the distribution of products is $Cp*_2(H)HfCH_2CH_2CH_2CH=CH_2$ (ca. 6%), 9 (ca. 68%), and 1 (ca. 26%). These results suggest that the rates for formation of $Cp*_2(H)HfCH_2CH_2CH_2CH=CH_2$ from $Cp*_2HfH_2$ and 1,4-pentadiene and for formation of $Cp*_2(H)$-$HfCH_2CH_2CH_2CH_2CH_2Hf(H)Cp*_2$ from $Cp*_2HfH_2$ and $Cp*_2(H)HfCH_2CH_2CH_2CH=CH_2$ are comparable at low temperature, and that intramolecular olefin insertion for $Cp*_2(H)HfCH_2CH_2CH_2CH=CH_2$ to yield the hafnamethylcyclopentane 9 occurs only above –40 °C (eq 9).

$$Cp*_2HfH_2 + \diagup\!\!\!\diagdown\!\!\!\diagup\!\!\!\diagdown \xrightarrow{-80°C} \left[\quad \right] \xrightarrow{-40°C} \qquad (9)$$

9
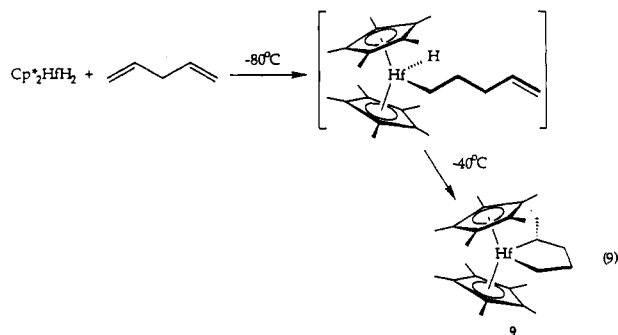
Reaction of 1,3-pentadiene and $Cp*_2HfH_2$ (1:1) yields what appears from ^1H NMR data (Table I) to be the ethylallyl hydride derivative $Cp*_2(H)Hf(\eta^3$-CH_2CHCH-$(CH_2CH_3))$. Thus, this substrate behaves like a substituted butadiene (vide supra), with no indication of products that would arise from the reaction of $Cp*_2HfH_2$ with 1,4-pentadiene.

The reaction of $Cp*_2HfH_2$ with 1,5-hexadiene (1:1) proceeds similarly: initially a mixture of $Cp*_2(H)$-$HfCH_2CH_2CH_2CH_2CH=CH_2$ and $Cp*_2(H)$-$HfCH_2CH_2CH_2CH_2CH_2CH_2Hf(H)Cp*_2$ is generated, which on standing at room temperature for 4 days yields what appears from ^1H and ^{13}C NMR data (Table I) to be haf-
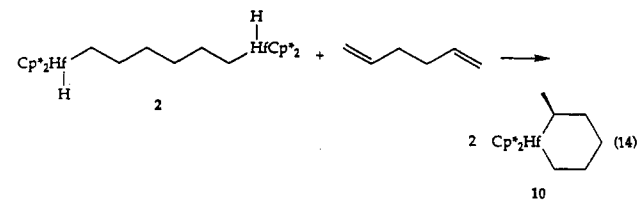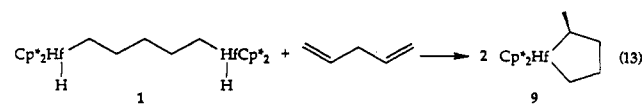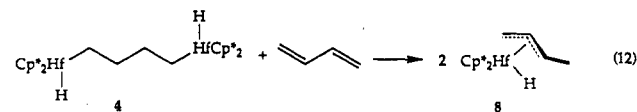
namethylcyclohexane 10 (eq 10).

$$Cp*_2HfH_2 + \diagup\!\!\!\diagdown\!\!\!\diagup\!\!\!\diagdown\!\!\!\diagup \longrightarrow \left[\quad \right] \longrightarrow \qquad (10)$$

10
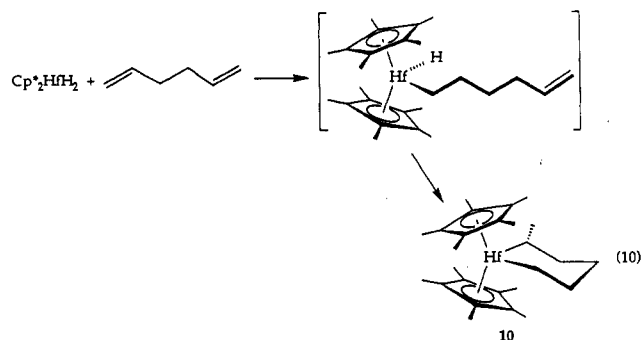
The reaction of $Cp*_2HfH_2$ with 1,6-heptadiene (1:1) proceeds somewhat differently. As with 1,4-pentadiene and 1,5-hexadiene, the α-hafna-ω-alkene is observed along with the α,ω-dihafnaalkane impurity, but for the longer chain, cyclization to the seven-membered hafnacycle does not ensue. Moreover, experiments carried out with different ratios of $Cp*_2HfH_2$:1,6-heptadiene are indicative of a slow equilibrium between $Cp*_2(H)$-$HfCH_2CH_2CH_2CH_2CH_2CH=CH_2$ (11) and $Cp*_2(H)$-$HfCH_2CH_2CH_2CH_2CH_2CH_2CH_2Hf(H)Cp*_2$ (3) (eq 11).

$$2 \qquad \rightleftharpoons \qquad$$

11

$$\diagup\!\!\!\diagdown\!\!\!\diagup\!\!\!\diagdown\!\!\!\diagup + \qquad \qquad (11)$$

3
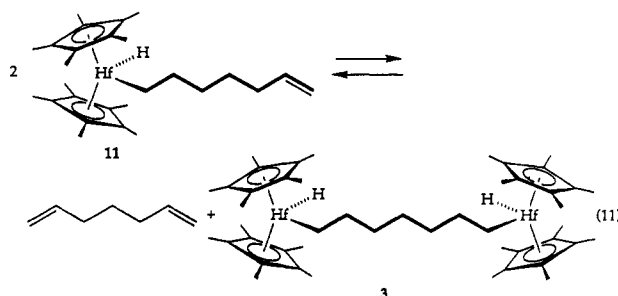
Pure 11 is obtained only in the presence of excess 1,6-heptadiene, whereas isolated samples of 11 slowly convert in solution to mixtures containing 3 and 1,6-heptadiene over several hours at room temperature.

The smaller carbon number members of the series of dihafnaalkanes also react slowly with excess α,ω-diene at room temperature over a period of 1–4 days to afford the same products observed by using a full equivalent of diene with $Cp*_2HfH_2$ (eqs 12–14).

$$Cp*_2Hf\diagup\!\!\!\diagdown\!\!\!\diagup HfCp*_2 + \diagup\!\!\!\diagdown\!\!\!\diagup\!\!\!\diagdown \longrightarrow 2\; Cp*_2Hf\diagup \qquad (12)$$

4   8

$$Cp*_2Hf\diagup\!\!\!\diagdown\!\!\!\diagup\!\!\!\diagdown HfCp*_2 + \diagup\!\!\!\diagdown\!\!\!\diagup\!\!\!\diagdown\!\!\!\diagup \longrightarrow 2\; Cp*_2Hf\bigcirc \qquad (13)$$

1   9

$$Cp*_2Hf\diagup\!\!\!\diagdown\!\!\!\diagup\!\!\!\diagdown\!\!\!\diagup HfCp*_2 + \diagup\!\!\!\diagdown\!\!\!\diagup\!\!\!\diagdown\!\!\!\diagup \longrightarrow$$

2

$$2\; Cp*_2Hf\bigcirc \qquad (14)$$

10

The thermal stabilities of these α,ω-dihafnaalkanes $Cp*_2(H)HfCH_2(CH_2)_{n+2}CH_2Hf(H)Cp*_2$ (n = 0 (4), 1 (1), 2 (2)) are relatively high, considering that alkyl hydride derivatives generally undergo rapid reductive elimination of alkane.[9] When heated in benzene-d_6 at 80 °C, di-

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(8) The assignments for 9 given in Table I are consistent with the results of selective ^1H-decoupling experiments, except for the unusually large $^5J_{HH}$ observed between the α methylene and methine hydrogens (i.e. [HfCH_2CH_2CH_2CH(CH_3)]).

(9) Parkin, G.; Bercaw, J. E. *Organometallics* 1989, 8, 1172.

Table I. ¹H and ¹³C NMR Data[a]
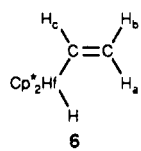
assgnt	δ, ppm	J, Hz	assgnt	δ, ppm	J, Hz
		$[Cp*_2HfH]_2(\mu\text{-}(CH_2)_5)$ (1)			
$C_5(CH_3)_5$	2.01 (s)		$C_5(CH_3)_5$	117.3	
HfH	12.71 (s)		$C_5(CH_3)_5$	11.9	
HfCH_2	0.18 (m)[b]		HfCH_2	63.3 (t)	$^1J_{CH} = 111$
HfCH$_2CH_2$	1.02 (br quin)[b]		HfCH$_2CH_2$	23.5 (t)	$^1J_{CH} = 120$
HfCH$_2$CH$_2CH_2$	1.57 (quin)[b]	$^3J_{HH} = 7$	HfCH$_2$CH$_2CH_2$	46.2 (t)	$^1J_{CH} = 126$
		$[Cp*_2HfH]_2(\mu\text{-}(CH_2)_6)$ (2)			
$C_5(CH_3)_5$	2.01 (s)		$C_5(CH_3)_5$	116.6	
HfH	12.77 (s)		$C_5(CH_3)_5$	11.7	
HfCH_2	0.10 (m)		HfCH_2	63.5	$^1J_{CH} = 114$
HfCH$_2CH_2$	1.07 (br)		HfCH$_2CH_2$	24.5	$^1J_{CH} = 116$
HfCH$_2$CH$_2CH_2$	1.62 (br quin)		HfCH$_2$CH$_2CH_2$	38.7	$^1J_{CH} = 123$
		$[Cp*_2HfH]_2(\mu\text{-}(CH_2)_7)$ (3)			
$C_5(CH_3)_5$	1.96		$C_5(CH_3)_5$	116.6	
HfH	12.84		$C_5(CH_3)_5$	12.3	
HfCH_2	0.05 (t)		HfCH_2	63.4	
HfCH$_2CH_2$	1.06 (br q)		HfCH$_2CH_2$	24.9	
HfCH$_2$CH$_2CH_2$,	1.62 (br)		HfCH$_2$CH$_2CH_2$	39.2	
HfCH$_2$CH$_2$CH$_2CH_2$			HfCH$_2$CH$_2$CH$_2CH_2$	30.7	
		$[Cp*_2HfH]_2(\mu\text{-}(CH_2)_4)$ (4)			
$C_5(CH_3)_5$	2.00 (s)		$C_5(CH_3)_5$	116.6	
HfH	12.70 (s)		$C_5(CH_3)_5$	12.3	
HfCH_2	0.12 (br)		HfCH_2	64.9 (t)	$^1J_{CH} = 112$
HfCH$_2CH_2$	0.91 (br)		HfCH$_2CH_2$	32.4 (t)	$^1J_{CH} = 118$
		$[Cp*_2HfH]_2(\mu\text{-}(CH_2)_3)$ (5)[c]			
$C_5(CH_3)_5$	1.94 (s)		HfCH_2	0.02 (m)	
HfH	1.84 (s)		HfCH$_2CH_2$	1.05 (m)	

6

assgnt	δ, ppm	J, Hz	assgnt	δ, ppm	J, Hz
$C_5(CH_3)_5$	1.95 (s)		Hb	6.03 (dd)	$^2J_{HH} = 18$
HfH	12.99 (s)				$^3J_{HH}(cis) = 4$
Ha	6.60 (dd)	$^2J_{HH} = 17$	Hc	4.80 (dd)	$^3J_{HH}(cis) = 4$
		$^3J_{HH}(trans) = 22$			$^2J_{HH}(trans) = 22$
		Cp*$_2$(H)Hf(crotyl) (8)			
$C_5(CH_3)_5$	1.82 (s)		CH_3CHCH	2.72 (dq)	$^3J_{HH} = 6, 17$
HfH	4.22 (s)		$CHCHCH_2$	3.75 (dt)	$^3J_{HH} = 10, 17$
CH_3CH	2.35 (d)	$^3J_{HH} = 6$	$CHCH_2$	1.05 (d)	$^3J_{HH} = 10$
		Cp*$_2\overline{HfCH_2CH_2CH_2C}H(CH_3)$ (9)			
$C_5(CH_3)_5$	1.89 (s)		$C_5(CH_3)_5$	12.5, 12.3	
HfCH_2	0.42 (m)		HfCH_2	45.9 (t)	$^1J_{CH} = 118$
HfCH$_2$CH$_2CH_2$	1.74 (br m), 2.22 (br m)		HfCH$_2$CH$_2CH_2$	34.2 (t), 29.9 (t)	$^1J_{CH} = 120, 123$
HfCH	2.92 (tq)	$J = 2, 10$	HfCH	60.9 (d)	$^1J_{CH} = 116$
CHCH_3	1.31 (d)		HfCH_3	20.3 (q)	$^1J_{CH} = 125$
$C_5(CH_3)_5$	118.2, 117.7				
		Cp*$_2$(H)Hf (ethylallyl)			
$C_5(CH_3)_5$	1.81 (s)		CH_3CH_2CH	2.65 (m)	
HfH	4.16 (s)		CH_3CH_2CHCH	3.73 (dt)	$^3J_{HH} = 11, 10$
CH_3CH_2	1.27 (t)	$^3J_{HH} = 7$	$CH_3CH_2CHCHCH_2$	1.03 (d)	$^3J_{HH} = 11$
CH_3CH_2	2.59 (q)	$^3J_{HH} = 7$			
		Cp*$_2$HfH(CH$_2$)$_4$CH=CH$_2$			
$C_5(CH_3)_5$	1.93 (s)		$C_5(CH_3)_5$	12.5	
HfH	12.79 (s)		HfCH_2	62.3	
HfCH_2	−0.04		HfCH$_2CH_2$	24.2	
HfCH$_2$CH$_2CH_2$	1.52 (quin)		HfCH$_2$CH$_2CH_2$	37.9	
HfCH$_2$CH$_2$CH$_2CH_2$	3.12 (m)		HfCH$_2$CH$_2$CH$_2CH_2$	34.8	
CH=CH$_2$	5.94 (m)		CH=CH$_2$	138.3	
CH=CH_2	5.1 (m)		CH=CH_2	114.1	
$C_5(CH_3)_5$	117				
		Cp*$_2\overline{HfCH_2CH_2CH_2CH_2C}H(CH_3)$ (10)			
$C_5(CH_3)_5$	1.85 (s), 1.82 (s)		$C_5(CH_3)_5$	12.5	$^2J_{CH} = 125$
HfCH_2	0.78 (m)		$C_5(CH_3)_5$	12.3	$^2J_{CH} = 126$
CHCH_2	1.24 (dt)	$J = 5, 14$	HfCH_2	62.9	$^1J_{CH} = 116$
CHCH$_2CH_2$,	3.13, 2.74		$CHCH_2$	43.3	$^1J_{CH} = 120$
HfCH$_2$CH_2			CHCH$_2CH_2$	35.4	$^1J_{CH} = 118$
HfCH	1.04 (m)		HfCH$_2CH_2$	33.6	$^1J_{CH} = 121$
CHCH_3	1.01 (s)		HfCH	64.8	$^1J_{CH} = 108$
$C_5(CH_3)_5$	118.1, 117.7		$CHCH_3$	20.0	$^1J_{CH} = 124$

Table I (Continued)

assgnt	δ, ppm	J, Hz	assgnt	δ, ppm	J, Hz
		Cp*$_2$(H)Hf(CH$_2$)$_5$CH=CH$_2$ (11)			
C$_5$(CH$_3$)	1.94 (s)		C$_5$(CH$_3$)$_5$	12.3	
HfH	12.81 (s)		HfCH$_2$	62.6	
HfCH$_2$	-0.02 (m)		HfCH$_2$CH$_2$	24.0	
HfCH$_2$CH$_2$	0.97 (quin)	$^3J_{HH}$ = 8	HfCH$_2$CH$_2$CH$_2$	38.5	
HfCH$_2$CH$_2$CH$_2$	1.45 (quin)	$^3J_{HH}$ = 8	HfCH$_2$CH$_2$CH$_2$CH$_2$	30.0	
HfCH$_2$CH$_2$CH$_2$CH$_2$	1.51 (quin)	$^3J_{HH}$ = 8	HfCH$_2$CH$_2$CH$_2$CH$_2$CH$_2$	35.0	
CH=CH$_2$	5.87 (m)		CH=CH$_2$	140.0	
CH=CH$_2$	5.05 (m)		CH=CH$_2$	114.5	
C$_5$(CH$_3$)$_5$	116.7				
		Cp*$_2$(H)Hf(CH$_2$)$_4$CH$_3$			
C$_5$(CH$_3$)$_5$	1.95		C$_5$(CH$_3$)$_5$	116.7	
HfH	12.82 (s)		C$_5$(CH$_3$)$_5$	12.3	
HfCH$_2$	0.00 (t)		HfCH$_2$	62.8	
HfCH$_2$CH$_2$	0.96 (m)		HfCH$_2$CH$_2$	23.6	
HfCH$_2$CH$_2$CH$_2$, HfCH$_2$CH$_2$CH$_2$CH$_2$	1.45 (m)		HfCH$_2$CH$_2$CH$_2$	41.0	
CH$_3$	1.02 (t)		HfCH$_2$CH$_2$CH$_2$CH$_2$	24.3	
			CH$_3$	15.2	
		Cp*$_2$ZrCH$_2$CH$_2$CH$_2$CH(CH$_3$)			
C$_5$(CH$_3$)$_5$	1.83 (s)		C$_5$(CH$_3$)$_5$	118.8, 118.3	
ZrCH$_2$	0.56 (m)		C$_5$(CH$_3$)$_5$	12.4, 12.2	
ZrCH$_2$CH$_2$, ZrCH$_2$CH$_2$CH$_2$	1.54 (dt), 1.45 (m), 0.87 (m)		ZrCH$_2$	44.2	
CH	2.45 (m)		ZrCH$_2$CH$_2$CH$_2$	36.4, 32.2	
CH$_3$	1.08 (d)		ZrCH	57.8	
			CHCH$_3$	20.9	
		Cp*$_2$ZrCH$_2$CH$_2$CH$_2$CH$_2$CH(CH$_3$)			
C$_5$(CH$_3$)$_5$	1.81, 1.79		C$_5$(CH$_3$)$_5$	12.4, 12.2	
CHCH$_2$	1.36 (dt)	J = 6, 13	ZrCH$_2$	56.9	
ZrCH$_2$CH$_2$CH$_2$	2.65 (m)		CHCH$_2$	42.6	
CH	1.12 (m)		CH$_2$CH$_2$, CH$_2$CH$_2$CH$_2$	35.4, 33.5	
ZrCH$_2$, CHCH$_3$	0.84 (d)	J = 8	ZrCH	57.3	
C$_5$(CH$_3$)$_5$	118.6, 118.3		CHCH$_3$	19.5	
		[Cp*$_2$HfI]$_2$(μ-(CH$_2$)$_5$)			
C$_5$(CH$_3$)$_5$	1.98 (s)		HfCH$_2$CH$_2$	1.61 (br quin)	
HfCH$_2$	0.25 (m)		HfCH$_2$CH$_2$CH$_2$	1.54 (br quin)	

^{a} Measured in C$_6$D$_6$ unless otherwise stated; s = singlet, m = multiplet, quin = quintet, br = broad, t = triplet, d = doublet, q = quartet. ^{b} Assignments were confirmed by selective proton-decoupling experiments. ^{c} Sample is component of mixture and only identified by NMR spectroscopy.

hafnahexane 4 affords in less than 1 h a mixture of products consisting largely of Cp*$_2$HfH$_2$ with other unidentified compounds. Dihafnaheptane 1 and dihafnaoctane 2 are considerably more stable; after ca. 20 h at 80 °C samples remain largely unchanged, with only traces of Cp*$_2$HfH$_2$ being formed under these conditions. Their stabilities appear to be comparable to the pentyl hydride compound, Cp*$_2$(H)HfCH$_2$CH$_2$CH$_2$CH$_2$CH$_3$, obtained quantitatively (^{1}H NMR spectroscopy) from reaction of Cp*$_2$HfH$_2$ with 1-pentene.

The reactivities of these new compounds are quite reminiscent to those for the mononuclear alkyl hydride derivatives of permethylhafnocene.[5,10] Thus, treatment of Cp*$_2$(H)HfCH$_2$CH$_2$CH$_2$CH$_2$CH$_2$Hf(H)Cp*$_2$ (1) with H$_2$ (4 atm) in benzene-d_6 yields Cp*$_2$HfH$_2$ and pentane after 1 h at room temperature. Reaction with water again yields pentane, together with a mixture of Cp*$_2$Hf(OH)$_2$ and Cp*$_2$Hf(H)(OH).[11] Ethylene (1:1 or 2:1, 25 °C) reacts with 1 over several days to produce several products, including Cp*$_2$(H)HfCH$_2$CH$_3$. No ethylene polymerization occurs under these conditions. With CO (2 atm) 1 and 2 undergo rather complex reactions affording a multitude of products (^{1}H NMR spectroscopy).

The reactivities of Cp*$_2$MH$_2$ (M = Ti, Zr) with 1,4-pentadiene and 1,5-hexadiene have also been investigated

briefly. Both substrates react rapidly with Cp*$_2$TiH$_2$[12] (2:1) in toluene-d_8 to yield (likely paramagnetic) species exhibiting one or more broad resonances attributable to pentamethylcyclopentadienyl ligands. Thus, if dititanaalkanes are generated, they are unstable at room temperature.

Moderately stable products are obtained in reactions with permethylzirconocene dihydride. ^{1}H NMR spectra for reaction mixtures obtained by mixing Cp*$_2$ZrH$_2$ with 1,4-pentadiene (2:1) in benzene-d_6, thawing and warming to room temperature, revealed a mixture of Cp*$_2$ZrCH$_2$CH$_2$CH$_2$CH(CH$_3$) and another compound (^{1}H NMR: δ 1.94 (Cp*) and 5.26 (ZrH)) which we believe to be the alkanediyl compound Cp*$_2$(H)-ZrCH$_2$CH$_2$CH$_2$CH$_2$CH$_2$Zr(H)Cp*$_2$. The latter is rather labile, however, and decomposes after 30 min at room temperature. The former may be obtained in nearly quantitative yield (^{1}H NMR spectroscopy) from a mixture of Cp*$_2$ZrH$_2$ and 1,4-pentadiene (1:1) (see Table I). Cp*$_2$ZrCH$_2$CH$_2$CH$_2$CH(CH$_3$), too, is less stable than the hafnium analogue, decomposing completely after 1 day in solution to a multitude of products. The reaction sequence involving Cp*$_2$ZrH$_2$ and 1,5-hexadiene also appears similar to that for the hafnium system, and moderately stable

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species tentatively identified as Cp*$_2$ <u>ZrCH$_2$CH$_2$CH$_2$CH$_2$CH(CH$_3$)</u> (see Table I) and Cp*$_2$(H)-ZrCH$_2$CH$_2$CH$_2$CH$_2$CH$_2$CH$_2$Zr(H)Cp*$_2$ (^{1}H NMR: δ 1.93 (Cp*) and 5.36 (ZrH)) have been produced.[13]

Conclusions

The relatively robust nature of alkyl hydride derivatives of permethylhafnocene and their ready synthesis from alkenes and Cp*$_2$HfH$_2$ have permitted the synthesis of the first series of alkanediyl complexes of this metal and the only series of hydrido alkanediyl complexes, L$_n$(H)M-(CH$_2$)$_m$M(H)L$_n$, so far as we are aware. The synthetic strategy of using α,ω-dienes and Cp*$_2$HfH$_2$ works well for 1,4-pentadiene, 1,5-hexadiene, and 1,6-heptadiene, but only if care is taken to assure that 2 equiv of Cp*$_2$HfH$_2$ are added. With smaller dienes the reactions are less selective, affording the allyl hydride or crotyl hydride in addition to the desired 1,5-dihafnapentane and 1,6-dihafnahexane, respectively. The vinyl hydride derivative, obtained from Cp*$_2$HfH$_2$ and acetylene, does not react further with Cp*$_2$HfH$_2$ to yield the desired 1,4-dihafnabutane. When a larger ratio of diene:Cp*$_2$HfH$_2$ is employed, mononuclear products, the allyl hydride, hafnamethylcycloalkane, or α-hafna-ω-alkene derivatives, are obtained. Treatment of the alkanediyl derivatives with additional diene affords these same mononuclear products, indicating that for Cp*$_2$(H)HfCH$_2$(CH$_2$)$_n$CH$_2$Hf(H)Cp*$_2$ β H elimination to release Cp*$_2$HfH$_2$ is facile. The thermal stabilities of the α,ω-dihafnaalkanes are comparable to the mononuclear alkyl hydride derivatives of permethylhafnocene, and their reactivities with H$_2$, H$_2$O, and ethylene are also similar. Thus, our results reveal no special influence of the ω-hafnium substituent on the reactivity of these alkyl hydride derivatives of permethylhafnocene. The reactivity of permethylzirconocene dihydride with 1,4-pentadiene and 1,5-hexadiene is very similar, although the products Cp*$_2$(H)ZrCH$_2$(CH$_2$)$_n$CH$_2$Zr(H)Cp*$_2$ (n = 3, 4) and <u>Cp*$_2$ZrCH$_2$(CH$_2$)$_n$CH(CH$_3$)</u> (n = 2, 3) are less stable. No stable titanium analogues could be obtained in the reactions of the dienes with Cp*$_2$TiH$_2$, almost certainly due to the reduced stability of alkyl hydride derivatives of the 3d metal, Ti.

Experimental Section

General Considerations. All manipulations were carried out using high-vacuum lines and glovebox techniques. Solvents and reagents were dried, degassed, and purified as described previously.[5]

NMR spectra were recorded using a Varian EM 390 (90 MHz) or a JEOL GX400Q (^{1}H, 399.78 MHz; ^{13}C, 100.38 MHz) spectrometer. Low-temperature NMR experiments were carried out using a JEOL FX90Q (^{1}H, 89.56 MHz) spectrometer. Infrared spectra were measured as Nujol mulls using KBr plates on a Beckman IR 4240 spectrophotometer.

Molecular weights were determined using the vapor-phase osmometry techniques developed by Singer and described by Clark.[14]

Mass spectra were recorded using a Du Pont 492B spectrometer at 70-eV ionizing voltage. Microanalyses were performed by the Caltech Microanalytical Laboratory.

The compounds Cp*$_2$HfH$_2$,[5] Cp*$_2$ZrH$_2$,[15] and Cp*$_2$TiH$_2$[12] were prepared as previously reported. Ethylene, butadiene, and allene were purchased from Matheson, subjected to two freeze–pump–thaw cycles at –196 °C, and then vacuum-transferred at 25 °C.

1,4-Pentadiene, 1,5-hexadiene, and 1,6-heptadiene were purchased from Aldrich, dried over activated 4-Å molecular sieves, and then vacuum-transferred before use. Argon, nitrogen, and hydrogen were purified over MnO on vermiculite and activated molecular sieves.

NMR Tube Reactions. All of the reactions described were initially carried out in NMR tubes, and then representative reactions were carried out on a preparative scale.

The reactions in NMR tubes were carried out as follows: Approximately 20 mg of the starting material and 0.5 mL of the solvent, benzene-d_6 or toluene-d_8 was loaded into an NMR tube which was attached to a 14/20 ground glass joint. The tube was loaded in the glovebox and then sealed with a needle valve or calibrated glass bulb. Accurately known amounts of the volatile dienes or other reagents were then condensed into the evacuated tube at –196 °C. The tube was sealed and allowed to warm to room temperature with shaking. The NMR spectra of the reaction mixtures were then recorded. For reactions monitored at low temperatures, the sealed tubes, prepared as above, were stored at –78 °C and loaded into the NMR probe which had been pre-cooled to the desired temperature with a reference tube.

Cp*$_2$(H)Hf(CH$_2$)$_5$Hf(H)Cp*$_2$ (1). A sample of 1.00 g (2.22 mol) of Cp*$_2$HfH$_2$ was weighed into a 50-mL flask and attached to a swivel-frit assembley in the glovebox. A 10-mL portion of toluene was then condensed onto this solid followed by 1,4-pentadiene (1.11 mmol) from a gas bulb. The reaction mixture was allowed to warm initially to –78 °C, was stirred at this temperature for 5 min, and then was warmed to room temperature and stirred for 1 h. The toluene was removed and 30 mL of petroleum ether condensed onto the pale yellow solid. The mixture was cooled to –78 °C and filtered. The resulting white solid was washed with 5 mL of petroleum ether and dried to give 0.65 g (61%) of 1: mp 165–169 °C; IR ν(Hf–H) 1604 cm^{-1}. Anal. Calcd for C$_{45}$H$_{72}$Hf$_2$: C, 55.72; H, 7.48; M, 970. Found: C, 56.01; H, 7.43; M, 976.

Cp*$_2$(H)Hf(CH$_2$)$_6$Hf(H)Cp*$_2$ (2). A 50-mL flask was loaded with 0.495 g (1.10 mmol) of Cp*$_2$HfH$_2$ and the flask attached to a swivel-frit assembley. A 25-mL volume of petroleum ether was then condensed into the flask. The solution was cooled to –196 °C, and 1,5-hexadiene (0.55 mmol) was condensed into the flask. The flask was warmed to –78 °C, stirred at this temperature for 5 min, and then warmed to room temperature. The reaction mixture was stirred at room temperature for 1 h and then filtered. The solid product was washed with two portions each of 5 mL of petroleum ether and dried to give 0.48 g (89%) of the white microcrystalline solid 2: mp 195–200 °C. The product was re-crystallized from toluene at –78 °C. IR: ν(Hf–H) 1612 (w), 1550 (sh) cm^{-1}. Anal. Calcd for C$_{46}$H$_{74}$Hf$_2$: C, 56.14; H, 7.58. Found: C, 56.49; H, 7.48.

Cp*$_2$(H)Hf(CH$_2$)$_4$Hf(H)Cp*$_2$ (4). Cp*$_2$HfH$_2$ (0.43 g, 0.96 mmol) was weighed into a 25-mL flask of a swivel-frit assembley and 8 mL of petroleum ether condensed in at –78 °C. The solution was allowed to warm to room temperature and filtered to remove slight cloudiness. Butadiene (0.48 mmol) was condensed into the flask at –196 °C from a gas bulb, and the mixture was allowed to warm to –78 °C and was stirred at this temperature for 5 min. The reaction mixture was then allowed to warm to room temperature and was stirred for a further 30 min. The reaction flask containing a white suspension and pale yellow solution was then cooled to 0 °C for 30 min, and the white microcrystalline solid 4 was filtered off and dried to give 0.065 g (14%): mp 179–183 °C; IR ν(Hf-H) = 1620 cm^{-1}. Anal. Calcd for C$_{44}$H$_{70}$Hf$_2$: C, 55.28; H, 7.38. Found: C, 54.96; H, 7.33.

Cp*$_2$HfH(CH=CH$_2$) (6). The dihydride Cp*$_2$HfH$_2$ (0.50 g, 1.12 mmol) was weighed into a 25-mL flask and connected to a swivel-frit assembley in the glovebox. A 10-mL volume of petroleum ether was condensed into the flask at –78 °C, and the flask was then cooled to –196 °C. Acetylene (1.13 mmol) was condensed into the flask, which was allowed to warm to –78 °C with stirring at this temperature for 3 min. The reaction mixture was then allowed to warm to room temperature and was stirred for 30 min. The slightly cloudy solution was filtered and the solvent reduced from the filtrate to ca. 3 mL. This solution was cooled to –78 °C, and the resulting solid was filtered and dried to give 6 as white crystals: 0.18 g, (33%); mp 214–216 °C. Anal. Calcd for C$_{22}$H$_{34}$Hf: C, 55.40; H, 7.18. Found: C, 55.30; H, 7.05. On standing in the glovebox for 4 months, the ^{1}H NMR spectrum

(13) The 7-zircona-1-heptene hydride, Cp*$_2$(H)-ZrCH$_2$CH$_2$CH$_2$CH$_2$CH=CH$_2$, does not appear to build up in these reaction mixtures, however.

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of 1 now showed that a new vinyl species had formed which may be Cp*$_2$Hf(OH)CH=CH$_2$: δ (C$_6$D$_6$) 1.80 (s) (Cp*), 4.18 (s) (OH) 6.83 (dd, J_{HH} = 20 and 15 Hz) (CH$_2$=), 6.54 (dd, J_{HH} = 16 and 5 Hz) (CH$_2$=), 5.39 (dd, J_{HH} = 20 and 5 Hz) (-CH=) ppm, as well as weak peaks at δ 1.85 (s) (Cp*) and 2.97 (s) (OH) ppm corresponding to Cp*$_2$Hf(OH)$_2$.

Cp*$_2$HfH(crotyl) (8). A sample of 0.485 g (1.08 mmol) of Cp*$_2$HfH$_2$ was weighed into a 25-mL flask of a swivel-frit assembley, and 10 mL of toluene was condensed into the flask. The flask was cooled to -196 °C, and butadiene (1.09 mmol) was condensed in from a gas bulb. The reaction mixture was warmed to -78 °C, stirred for 10 min, and then allowed to warm to room temperature. The almost colorless solution was then stirred for 23 h at room temperature, during which time the solution turned yellow. The solvent was removed under reduced pressure, and 10 mL of petroleum ether was condensed in. The solution was filtered, concentrated, and then cooled to -78 °C when a pale yellow microcrystalline compound formed. This was filtered and dried to give 0.13 g (24%) of 8: mp 136–145 °C, IR ν(Hf–H) 1578 (w), 1624 (sh) cm^{-1}. Anal. Calcd for C$_{24}$H$_{38}$Hf: C, 57.08; H, 7.58. Found: C, 57.51; H, 7.66.

Cp*$_2$HfCH$_2$CH$_2$CH$_2$CH(CH$_3$) (9). A 50-mL flask was loaded with 0.52 g (1.15 mmol) of Cp*$_2$HfH$_2$, and 10 mL of toluene was condensed in at -78 °C. The solution was then cooled to -196 °C, and 1,4-pentadiene (1.15 mmol) was condensed in from a gas bulb. The reaction solution was allowed to warm to room temperature and was stirred at this temperature for 23 h. The solvent was removed to yield a yellow residue, and 15 mL of petroleum

ether was condensed in. The clear yellow solution was concentrated and cooled to -78 °C. The resulting solid was filtered off to give 0.34 g (57%) of lemon yellow crystals of 9: mp 166–171 °C. Anal. Calcd for C$_{20}$H$_{32}$Hf: C, 57.85; H, 7.77; M, 519. Found: C, 57.66; H, 7.51; M, 467. The mass spectrum showed peak envelopes with the most abundant peak of the envelope at 518 (M$^+$): 485, 478 (M − C$_3$H$_6$)$^+$, 466, 450 (M − C$_5$H$_{10}$)$^+$, and 223 (M − C$_5$H$_{10}$)$^{2+}$ (assignments in parentheses).

Shape-Selective and Asymmetric Cyclopropanation of Alkenes Catalyzed by Rhodium Porphyrins

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Rhodium porphyrins catalyze the cyclopropanation of simple alkenes by diazo esters. Functionalized catalysts that mediate selective cyclopropanation reactions might be of use in organic synthesis, particularly since the porphyrin catalysts generally provide syn cyclopropyl esters as the major product. In this report we examine the possibility of engineering shape selectivity and asymmetric induction into this system. We show that the iodorhodium derivative of an optically active macrocycle, the "chiral wall" porphyrin, does mediate the enantioselective cyclopropanation of prochiral olefins. Enantiomeric excesses of 10–60% are observed. In addition, the substrate selectivities of hindered (RhTMPI) and unhindered (RhTTPI) simple porphyrins were assessed. In both cases, mono-, di-, and trisubstituted aliphatic olefins undergo reaction at nearly equivalent rates but tetrasubstituted alkenes are cyclopropanated poorly, especially when the crowded catalyst is employed. In the case of bulkier aromatic alkenes, extremely high cis/trans substrate selectivity is observed. These observations have led to a model for the geometry of interaction between the putative metallocarbene and the alkene that rationalizes the relative reactivity of the many substrates investigated. The relevance of these results to the rational design of more selective asymmetric catalysts is also discussed.

Metalloporphyrins mediate a number of interesting stoichiometric and catalytic reactions, including olefin epoxidation[1-5] and cyclopropanation[6], alkane hydroxylation,[7,8] Diels–Alder cycloadditions,[9] cleavage of amides,[10] and a number of other processes. Recently, several laboratories have made progress toward engineering novel selectivities into these reactions for the purposes of mimicking the properties of certain heme-containing enzymes or creating novel reagents for organic synthesis.

Much of this activity has focused on alkene epoxidation and alkane hydroxylation systems which mimic the cyto-

chrome P-450 family of monooxygenases, and a number of reports of interesting asymmetric and shape-selective

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