

# Reactions of Alkyl and Hydride Derivatives of Permethylzirconocene and Permethylhafnocene with Carbon Monoxide. Synthesis and Reactivity Studies of Aldehyde Complexes of Zirconium and Hafnium

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The alkyl hydride derivatives  $\text{Cp}^*\text{M}(\text{H})(\text{CH}_2\text{CHMe}_2)$  ( $\text{Cp}^* = \eta^5\text{-C}_5\text{Me}_5$ ;  $\text{M} = \text{Zr, Hf}$ ) react with carbon monoxide at low temperature to yield the  $\eta^2$ -acyl hydride complexes  $\text{Cp}^*\text{M}(\text{H})(\eta^2\text{-CO-CH}_2\text{CHMe}_2)$  (**1a, b**), which on warming to room temperature under CO afford the carbonyl/isovaleraldehyde adducts  $\text{Cp}^*\text{M}(\text{CO})(\eta^2\text{-O=CHCH}_2\text{CHMe}_2)$  (**4a, b**). The zirconium derivative **4a** slowly loses its coordinated CO and rearranges to the enolate hydride  $\text{Cp}^*\text{Zr}(\text{H})(\text{OCH=CHCHMe}_2)$  (**3**). By contrast  $\text{Cp}^*\text{Hf}(\text{CO})(\eta^2\text{-O=CHCH}_2\text{CHMe}_2)$  (**4b**) rearranges without loss of CO to the cyclic enediolate tautomer  $\text{Cp}^*\text{Hf}(\text{OCH=C}(\text{CH}_2\text{CHMe}_2)\text{O})$  (**5**), most likely by a 1,2H shift from the cyclic acyl derivative  $\text{Cp}^*\text{Hf}(\eta^2\text{-COCH}(\text{CH}_2\text{CHMe}_2)\text{O})$ . The coordinatively unsaturated  $\eta^2$ -isovaleraldehyde adduct of permethylzirconocene [ $\text{Cp}^*\text{Zr}(\eta^2\text{-O=CHCH}_2\text{CHMe}_2)$ ] is implicated in reactions of the acyl hydride  $\text{Cp}^*\text{Zr}(\text{H})(\eta^2\text{-COCH}_2\text{CHMe}_2)$  (**1a**) with the trapping substrates ethylene, 2-butyne, dihydrogen, and *tert*-butylacetylene to yield  $\text{Cp}^*\text{Zr}[\text{OCH}(\text{CH}_2\text{CHMe}_2)\text{CH}_2\text{CH}_2]$  (**12**),  $\text{Cp}^*\text{Zr}[\text{OCH}(\text{CH}_2\text{CHMe}_2)\text{C}(\text{CH}_3)=\text{C}(\text{CH}_3)]$  (**13**),  $\text{Cp}^*\text{Zr}(\text{H})(\text{OCH}_2\text{CH}_2\text{CHMe}_2)$  (**14**), and  $\text{Cp}^*\text{Zr}(\text{C}\equiv\text{CCMe}_3)(\text{OCH}_2\text{CH}_2\text{CHMe}_2)$  (**15**). Carbonylations of the hafnacyclopentane  $\text{Cp}^*\text{Hf}(\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2)$  (**9**) and the alkenyl hydride  $\text{Cp}^*\text{Hf}(\text{H})(\text{trans-CH=CHCMe}_3)$  do not show direct evidence for  $\eta^2$ -cyclopentanone or  $\eta^2$ -aldehyde intermediates. The former does, however, proceed directly to the bicyclic enediolate complex **11** most likely by the subsequent carbonylation of the cyclopentanone adduct. The latter undergoes carbonylation first to the hafna-oxacyclopentene  $\text{Cp}^*\text{Hf}[\text{CH}(\text{CMe}_3)\text{CH=CHO}]$ , which reacts further with CO to yield hafna-dioxo-cycloheptadiene  $\text{Cp}^*\text{Hf}[\text{OCH=C}(\text{CMe}_3)\text{CH=CHO}]$  (**19**). Possible mechanisms for these processes are discussed. The general features of this chemistry complement theoretical and experiment results from the Hofmann group presented in the preceding article<sup>17)</sup>.

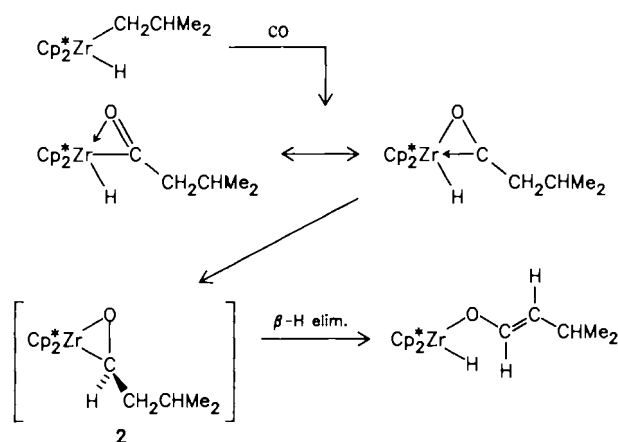
Transition metal mediated carbon-carbon bond-forming reactions, particularly those involving carbon monoxide, alkenes, and alkynes, are of continuing interest in organometallic chemistry<sup>2)</sup>. The ability of early transition metal compounds to effect a variety of stoichiometric C-C bond forming transformations has received much attention<sup>3)</sup>. Work in our laboratories has established a number of carbon-carbon coupling reactions for group 4 permethyl-

**Reaktionen von Alkyl- und Hydrid-Derivaten von Permethylzirconocen und Permethylhafnocen mit Kohlenmonoxid. Synthese und Reaktivitätsstudien von Zirconium- und Hafnium-Komplexen**

Die Alkyl-hydrid-Derivate  $\text{Cp}^*\text{M}(\text{H})(\text{CH}_2\text{CHMe}_2)$  ( $\text{Cp}^* = \eta^5\text{-C}_5\text{Me}_5$ ;  $\text{M} = \text{Zr, Hf}$ ) reagieren mit Kohlenmonoxid bei niedriger Temperatur zu den  $\eta^2$ -Acyl-hydrid-Komplexen  $\text{Cp}^*\text{M}(\text{H})(\eta^2\text{-CO-CH}_2\text{CHMe}_2)$  (**1a, b**), die beim Erwärmen auf Raumtemperatur unter CO die Carbonyl/Isovaleraldehyd-Addukte  $\text{Cp}^*\text{M}(\text{CO})(\eta^2\text{-O=CHCH}_2\text{CHMe}_2)$  (**4a, b**) liefern. Das Zirconiumderivat **4a** verliert langsam das koordinierte CO und lagert zu dem Enolat-hydrid  $\text{Cp}^*\text{Zr}(\text{H})(\text{OCH=CHCHMe}_2)$  (**3**) um. Im Gegensatz dazu lagert sich  $\text{Cp}^*\text{Hf}(\text{CO})(\eta^2\text{-O=CHCH}_2\text{CHMe}_2)$  (**4b**) ohne CO-Verlust zu dem cyclischen Endiolat-Tautomeren  $\text{Cp}^*\text{Hf}(\text{OCH=C}(\text{CH}_2\text{CHMe}_2)\text{O})$  (**5**) um, sehr wahrscheinlich durch 1,2-H-Verschiebung im cyclischen Acylderivat  $\text{Cp}^*\text{Hf}(\eta^2\text{-COCH}(\text{CH}_2\text{CHMe}_2)\text{O})$ . Für das Auftreten des koordinativ ungesättigten  $\eta^2$ -Isovaleraldehyd-Addukts von Permethylzirconocen [ $\text{Cp}^*\text{Zr}(\eta^2\text{-O=CHCH}_2\text{CHMe}_2)$ ] spricht, daß das Acyl-hydrid  $\text{Cp}^*\text{Zr}(\text{H})(\eta^2\text{-COCH}_2\text{CHMe}_2)$  (**1a**) mit Ethylen, 2-Butin,  $\text{H}_2$  und *tert*-Butylacetylen zu  $\text{Cp}^*\text{Zr}[\text{OCH}(\text{CH}_2\text{CHMe}_2)\text{CH}_2\text{CH}_2]$  (**12**),  $\text{Cp}^*\text{Zr}[\text{OCH}(\text{CH}_2\text{CHMe}_2)\text{C}(\text{CH}_3)=\text{C}(\text{CH}_3)]$  (**13**),  $\text{Cp}^*\text{Zr}(\text{H})(\text{OCH}_2\text{CH}_2\text{CHMe}_2)$  (**14**) bzw.  $\text{Cp}^*\text{Zr}(\text{C}\equiv\text{CCMe}_3)(\text{OCH}_2\text{CH}_2\text{CHMe}_2)$  (**15**) reagiert. Die Carbonylierung des Hafnacyclopentans  $\text{Cp}^*\text{Hf}(\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2)$  (**9**) und des Alkenyl-hydrids  $\text{Cp}^*\text{Hf}(\text{H})(\text{trans-CH=CHCMe}_3)$  ergibt keinen direkten Hinweis auf  $\eta^2$ -Cyclopentan- oder  $\eta^2$ -Aldehyd-Zwischenstufen. **9** geht dabei jedoch direkt in den bicyclischen Endiolat-Komplex **11** über, sehr wahrscheinlich durch Carbonylierung des Cyclopentanon-Addukts. Das Alkenyl-hydrid andererseits geht Carbonylierung zum Hafna-oxacyclopenten  $\text{Cp}^*\text{Hf}[\text{CH}(\text{CMe}_3)\text{CH=CHO}]$  ein, das mit CO zum Hafna-dioxo-cycloheptadien  $\text{Cp}^*\text{Hf}[\text{OCH=C}(\text{CMe}_3)\text{CH=CHO}]$  (**19**) weiterreagiert. Mögliche Mechanismen für diese Prozesse werden diskutiert. Unsere Befunde ergänzen theoretische und experimentelle Ergebnisse des Arbeitskreises Hofmann in der vorstehenden Mitteilung<sup>17)</sup>.

talocene derivatives utilizing carbon monoxide as a substrate<sup>4)</sup>. The reaction of the isobutyl hydride derivative  $\text{Cp}^*\text{Zr}(\text{H})(\text{CH}_2\text{CHMe}_2)$  ( $\text{Cp}^* = \eta^5\text{-C}_5\text{Me}_5$ ) with CO is representative of this class of reactions. Labeling studies of the overall reaction (Scheme 1) implicated an aldehyde adduct (**2**) as an intermediate. Complex **2** could not, however, be directly observed, since facile  $\beta\text{H}$  elimination readily afforded the final enolate hydride product<sup>4a)</sup>.

Scheme 1



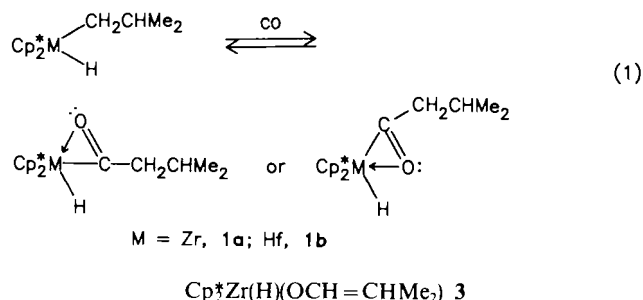
Recently, Erker has reported a number of carbonylation reactions for zirconocene alkyl and hydride complexes, and in several cases coordinated aldehyde or ketone complexes were identified and characterized<sup>5</sup>. In each case binuclear complexes with bridging aldehyde or ketone ligands were obtained. Moreover, Grubbs and Waymouth have reported aluminium-complexed aldehyde and ketone adducts of zirconocene,  $\text{Cp}_2\text{Zr}(\mu, \eta^2\text{-O}=\text{CRR}')(\mu\text{-Cl})\text{AlR}_2$ , obtained by Lewis acid-induced coupling of zirconium alkyl and acyl ligands<sup>6</sup>. As part of our continuing investigations of alkyl and hydride derivatives of permethylzirconocene and permethylhafnocene,  $\text{Cp}_2^*\text{MRR}'$  (M = Zr, Hf; R, R' = alkyl, hydride, etc.), we report herein our studies of the carbonylation of compounds of this type. The steric control provided by two pentamethylcyclopentadienyl ligands precludes bimolecular pathways, and in some cases isolation of stable, monomeric intermediates as well as final products proved possible. For example, treatment of the isobutyl hydride derivatives with excess CO at low temperatures yields moderately stable carbonyl/isovaleraldehyde adducts  $\text{Cp}_2^*\text{M}(\text{CO})(\eta^2\text{-O}=\text{CHCH}_2\text{CHMe}_2)$  (M = Zr, Hf), supporting the intermediacy of **2** in Scheme 1. Facile migration of hydride, and in some cases alkyl groups, to dihapto-acyl ligands affording coordinatively unsaturated and highly reactive aldehyde or ketone adducts,  $[\text{Cp}_2^*\text{M}(\eta^2\text{-O}=\text{CRR}')]_2$ , appear to be a general feature of these reactions.

## Results

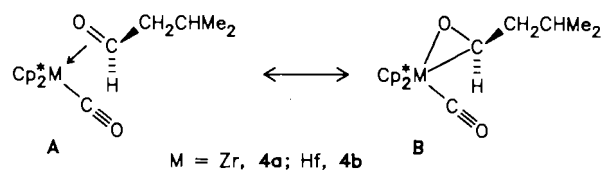
### 1. Synthesis and Reactivity of $\text{Cp}_2^*\text{M}(\text{CO})(\eta^2\text{-O}=\text{CHR})$ (M = Zr, Hf; R = $\text{CH}_2\text{CHMe}_2$ , $\text{C}_5\text{H}_6$ )

Toluene solutions of  $\text{Cp}_2^*\text{M}(\text{H})(\text{CH}_2\text{CHMe}_2)$  (M = Zr, Hf) react quantitatively with CO (1 atm) at  $-50^\circ\text{C}$  to yield the corresponding dihapto-acyl hydrides  $\text{Cp}_2^*\text{M}(\text{H})(\eta^2\text{-OC-CH}_2\text{CHMe}_2)$  (M = Zr, **1a**; M = Hf, **1b**). Characteristic  $^1\text{H-NMR}$  and  $^{13}\text{C}\{^1\text{H}\}\text{-NMR}$  spectra (Table 1) for **1b** (e.g.  $\text{Me}_2\text{CHCH}_2\text{CO}$ :  $\delta = 335.9$ ) are indicative of a single isomeric species at this temperature<sup>7</sup>.

As previously reported, the reaction of  $\text{Cp}_2^*\text{Zr}(\text{H})(\text{CH}_2\text{-CHMe}_2)$  with carbon monoxide at  $25^\circ\text{C}$  gives the enolate hydride **3** together with a small amount ( $\approx 5\%$ ) of  $\text{Cp}_2^*\text{Zr}$ -



(CO)<sub>2</sub><sup>4a</sup>. However, when solutions of **1a** or **1b** are stirred vigorously in toluene under 1 atm of CO at  $-78^\circ\text{C}$  and allowed to warm to room temperature over the course of several hours, the carbonyl/isovaleraldehyde adducts  $\text{Cp}_2^*\text{M}(\text{CO})(\eta^2\text{-O}=\text{CHCH}_2\text{CHMe}_2)$  (M = Zr, **4a**; Hf, **4b**) are obtained in  $\approx 80\%$  yield ( $^1\text{H NMR}$ )<sup>8</sup>. The new compounds may be isolated from hexamethyldisiloxane solution as highly soluble orange powders.  $^1\text{H}$ - and  $^{13}\text{C}$ -NMR and infrared data are in accord with their formulations. For example, the  $^1\text{H-NMR}$  spectrum for **4b** shows two singlets for the inequivalent  $\eta^5\text{-C}_5\text{Me}_5$  ligands, a broad singlet for the aldehyde proton, and a pair of doublets for the diastereotopic isobutyl methyl groups. Moreover, the gated  $^{13}\text{C-NMR}$  spectrum for labeled **4b**, prepared from  $\text{Cp}_2^*\text{Hf}(\text{H})(\text{CH}_2\text{CHMe}_2)$  and  $^{13}\text{CO}$ , exhibits a small coupling ( $^2J_{\text{CC}} = 9.8$  Hz) between the terminal carbonyl ( $\delta = 252.5$ ) and isovaleraldehyde carbonyl ( $\delta = 84.2$ ;  $^1J_{\text{CH}} = 156$  Hz) carbons. Although the aldehyde proton and carbon signals are upfield from free aldehydes<sup>9</sup> (Table 1), they compare favorably with those reported for the structurally characterized  $\mu, \eta^2$ -aldehyde complex  $\text{Cp}_2\text{Zr}(\mu\text{-H})(\mu, \eta^2\text{-O}=\text{CCHCH}_3)\text{Zr}(\text{H})\text{-Cp}_2$ <sup>10</sup>. Strong carbonyl absorptions at 1940 and 1930  $\text{cm}^{-1}$  for **4a** and **4b** are at significantly lower frequencies than for the formally tetravalent metal carbonyl adducts  $\text{Cp}_2^*\text{M}(\text{H})_2(\text{CO})$  (2044  $\text{cm}^{-1}$ , M = Zr; 2036  $\text{cm}^{-1}$  for M = Hf)<sup>11</sup>, more like the symmetric modes for the divalent dicarbonyls  $\text{Cp}_2^*\text{M}(\text{CO})_2$  (1942  $\text{cm}^{-1}$ , M = Zr; 1940  $\text{cm}^{-1}$ , M = Hf)<sup>4a,4b</sup>. The absence of any additional bands above 1200  $\text{cm}^{-1}$ , assignable to the aldehyde carbonyl stretching mode, is also noteworthy<sup>12</sup>. Thus, substantial contributions from both canonical forms **A** and **B** are indicated from these infrared data.



Both **4a** and **4b** are only moderately stable, decomposing slowly at  $25^\circ\text{C}$ . The carbonyl ligand is quite labile, scrambling with  $^{13}\text{CO}$  (2 atm) within several minutes at  $0^\circ\text{C}$  (eq. 2).

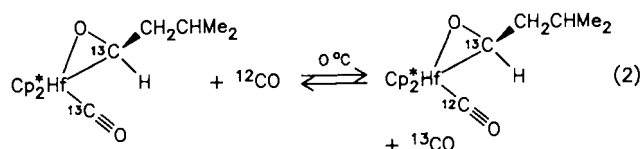


Table 1. NMR<sup>a)</sup> data

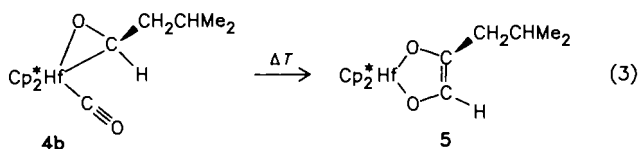
Compound	Assignment	Chemical shift	Coupling [Hz]
1a <sup>b)</sup>	C <sub>5</sub> (CH <sub>3</sub> ) <sub>5</sub>	1.70 s	
	C(O)CH <sub>2</sub> CHMe <sub>2</sub>	1.05 d	5.4
	C(O)CH <sub>2</sub> CHMe <sub>2</sub>	2.37 d, br	
	ZrH	3.53 s, br	
1b <sup>c)</sup>	C <sub>5</sub> (CH <sub>3</sub> ) <sub>5</sub>	1.78 s	6.0
	C(O)CH <sub>2</sub> CHMe <sub>2</sub>	1.12 d	
	C(O)CH <sub>2</sub> CHMe <sub>2</sub>	2.50 d, br	
	HfH	7.03 s	
4a	C <sub>5</sub> (CH <sub>3</sub> ) <sub>5</sub>	1.70, 1.75 s	
	O = CHCH <sub>2</sub> CHMe <sub>2</sub>	1.23, 1.27 d	6.0
4b	O = CHCH <sub>2</sub> CHMe <sub>2</sub>	2.47 t, br	9.5
	C <sub>5</sub> (CH <sub>3</sub> ) <sub>5</sub>	1.67, 1.71 s	
4b	O = CHCH <sub>2</sub> CHMe <sub>2</sub>	1.18, 1.20 d	6.0
	O = CHCH <sub>2</sub> CHMe <sub>2</sub>	2.21 d, br	10.1
	O = <sup>13</sup> CHCH <sub>2</sub> CHMe <sub>2</sub>	84.22 ddd	<sup>1</sup> J <sub>CH</sub> = 156.2, <sup>2</sup> J <sub>CC</sub> = 9.8, <sup>2</sup> J <sub>CH</sub> = 8.0, <sup>2</sup> J <sub>CC</sub> = 9.8
5	Hf( <sup>13</sup> CO)	252.49 d	
	C <sub>5</sub> (CH <sub>3</sub> ) <sub>5</sub>	1.89 s	
	CH <sub>2</sub> CHMe <sub>2</sub>	1.09 d	6.0
	OC(CH <sub>2</sub> CHMe <sub>2</sub> ) = CHO	6.30 s	
6 <sup>d)</sup>	O <sup>13</sup> C(CH <sub>2</sub> CHMe <sub>2</sub> ) = <sup>13</sup> CHO	6.30 dd	<sup>1</sup> J <sub>CH</sub> = 177, <sup>2</sup> J <sub>CH</sub> = 21.5
	O <sup>13</sup> C(CH <sub>2</sub> CHMe <sub>2</sub> ) = <sup>13</sup> CHO	146.8 dd, br	<sup>1</sup> J <sub>CC</sub> = 82.5, <sup>2</sup> J <sub>CH</sub> = 21.5
	O <sup>13</sup> C(CH <sub>2</sub> CHMe <sub>2</sub> ) = <sup>13</sup> CHO	131.6 dd	<sup>1</sup> J <sub>CC</sub> = 82.5, <sup>1</sup> J <sub>CH</sub> = 177
6 <sup>d)</sup>	C <sub>5</sub> (CH <sub>3</sub> ) <sub>5</sub>	1.64, 1.68 s	
	CH <sub>2</sub> CHMe <sub>2</sub>	0.87, 0.93 d	49, 4.9
	<sup>13</sup> CHO	4.88 dd	10.1, 2.7
	<sup>13</sup> CHO	94.4 dddd	J <sub>CC</sub> = 13.6, 37.1, <sup>1</sup> J <sub>CH</sub> = 136.7, <sup>1</sup> J <sub>CH</sub> = 5.9, J <sub>CC</sub> = 37.1, J <sub>CC</sub> = 13.6
7	<sup>13</sup> C = O	213.6 d	
	<sup>13</sup> C = O	310.6 d	
	C <sub>5</sub> (CH <sub>3</sub> ) <sub>5</sub>	1.57, 1.72 s	
8	OCHPh	7.02 m, 7.33 m, 7.62 m	
	OCHPh	3.36 s	
	C <sub>5</sub> (CH <sub>3</sub> ) <sub>5</sub>	1.87 s	
8	OC(Ph) = CHO	6.7 – 7.77 m	
	OC(Ph) = CHO	7.34 s	
	O <sup>13</sup> C(Ph) = <sup>13</sup> CHO	7.34 dd	<sup>1</sup> J <sub>CH</sub> = 176.3, <sup>2</sup> J <sub>CH</sub> = 22.4
	O <sup>13</sup> C(Ph) = <sup>13</sup> CHO	146.42 dd	<sup>1</sup> J <sub>CC</sub> = 83.5, <sup>2</sup> J <sub>CH</sub> = 22.4
10 <sup>h)</sup>	O <sup>13</sup> C(Ph) = <sup>13</sup> CHO	134.73 dd	<sup>1</sup> J <sub>CC</sub> = 83.5, <sup>1</sup> J <sub>CH</sub> = 176.3
	C <sub>5</sub> (CH <sub>3</sub> ) <sub>5</sub>	1.71 s	
	O = CCH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub>	0.23 m	
	O = CCH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub>	1.93 m	
11	O = CCH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub>	2.55 m	
	O = CCH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub>	344.0 s	
	C <sub>5</sub> (CH <sub>3</sub> ) <sub>5</sub>	1.91 s	
	OCCH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CO	1.66 m	
	OCC <sub>2</sub> H <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CO	2.29 m	
	OCCH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CO	139.82 s	
	OCCH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CO	31.85 t	<sup>1</sup> J <sub>CH</sub> = 125
OCCH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CO	24.32 t	<sup>1</sup> J <sub>CH</sub> = 125	
12 <sup>i)</sup>	C <sub>5</sub> (CH <sub>3</sub> ) <sub>5</sub>	1.85, 1.90 s	
	OCH(CH <sub>2</sub> CHMe <sub>2</sub> )CHH'CHH'	4.51 ddt	<sup>1</sup> J <sub>CH</sub> = 10.9, 9.3, 3.3
	OCH(CH <sub>2</sub> CHMe <sub>2</sub> )CHH'CHH'	1.004, 1.006 d	<sup>1</sup> J <sub>CH</sub> = 6.7
	OCH(CH <sub>2</sub> CHMe <sub>2</sub> )CHH'CHH'	2.65 dddd	<sup>1</sup> J <sub>CH</sub> = 12.5, 7.4, 3.3, 1.8
	OCH(CH <sub>2</sub> CHMe <sub>2</sub> )CHH'CHH'	2.52 dddd	<sup>1</sup> J <sub>CH</sub> = 12.5, 12.5, 10.9, 6.4
	OCH(CH <sub>2</sub> CHMe <sub>2</sub> )CHH'CHH'	1.51 ddd	<sup>1</sup> J <sub>CH</sub> = 12.5, 12.5, 7.4
	OCH(CH <sub>2</sub> CHMe <sub>2</sub> )CHH'CHH'	0.12 ddd	<sup>1</sup> J <sub>CH</sub> = 12.5, 6.4, 1.8
	OCH(CH <sub>2</sub> CHMe <sub>2</sub> )CHH'CHH'	78.20 d	<sup>1</sup> J <sub>CH</sub> = 139.1
	OCH(CH <sub>2</sub> CHMe <sub>2</sub> )CHH'CHH'	42.37, 49.98, 50.24	
	OCH(CH <sub>2</sub> CHMe <sub>2</sub> )CHH'CHH'	22.88, 24.11, 25.80	
	13	C <sub>5</sub> (CH <sub>3</sub> ) <sub>5</sub>	1.85, 1.87 s
OCH(CH <sub>2</sub> CHMe <sub>2</sub> )C(CH <sub>3</sub> ) = C(CH <sub>3</sub> )		4.77 t, br	11.2
OCH(CH <sub>2</sub> CHMe <sub>2</sub> )C(CH <sub>3</sub> ) = C(CH <sub>3</sub> )		1.04, 1.08 d	6.6
OCH(CH <sub>2</sub> CHMe <sub>2</sub> )C(CH <sub>3</sub> ) = C(CH <sub>3</sub> )		1.69 s, br	
OCH(CH <sub>2</sub> CHMe <sub>2</sub> )C(CH <sub>3</sub> ) = C(CH <sub>3</sub> )		1.59 s	
OCH(CH <sub>2</sub> CHMe <sub>2</sub> )C(CH <sub>3</sub> ) = C(CH <sub>3</sub> )		82.3 d	J <sub>CH</sub> = 133
OCH(CH <sub>2</sub> CHMe <sub>2</sub> )C(CH <sub>3</sub> ) = C(CH <sub>3</sub> )		46.6 t	J <sub>CH</sub> = 125
OCH(CH <sub>2</sub> CHMe <sub>2</sub> )C(CH <sub>3</sub> ) = C(CH <sub>3</sub> )		152.1, 184.5 s	
OCH(CH <sub>2</sub> CHMe <sub>2</sub> )C(CH <sub>3</sub> ) = C(CH <sub>3</sub> )		24.1, 21.2, 19.9, 15.5	
C <sub>5</sub> (CH <sub>3</sub> ) <sub>5</sub>		1.95 s	
14	OCH <sub>2</sub> CH <sub>2</sub> CHMe <sub>2</sub>	4.13 t	J = 8.0
	OCH <sub>2</sub> CH <sub>2</sub> CHMe <sub>2</sub>	0.90 d	J = 6.0
	ZrH	5.69 s	
15	C <sub>5</sub> (CH <sub>3</sub> ) <sub>5</sub>	2.00 s	
	C ≡ CCMe <sub>3</sub>	1.38 s	
	OCH <sub>2</sub> CH <sub>2</sub> CHMe <sub>2</sub>	4.17 t	7.0
	OCH <sub>2</sub> CH <sub>2</sub> CHMe <sub>2</sub>	0.98 d	6.0
16 <sup>c)</sup>	C <sub>5</sub> (CH <sub>3</sub> ) <sub>5</sub>	1.90 s	
	C(O)CH = CHCMe <sub>3</sub>	7.68 d	15.1
	C(O)CH = CHCMe <sub>3</sub>	6.59 d	15.1
	C(O)CH = CHCMe <sub>3</sub>	0.95 s	
	HfH	7.13 s, br	
	C(O)CH = CHCMe <sub>3</sub>	320.34 s	

Table 1 (Continued)

Compound	Assignment	Chemical shift	Coupling [Hz]
17	$C_5(CH_3)_5$	1.86, 1.89 s	
	$OCH=CHCHMe_3$	6.46 dd	5.3, 3.0
	$OCH=CHCHMe_3$	5.20 dd	5.3, 6.0
	$OCH=CHCHMe_3$	0.45 dd	6.0, 3.0
	$OCH=CHCHMe_3$	1.30 s	
	$OCH=CHCHMe_3$	137.32 d	$J_{CH} = 175.2$
	$OCH=CHCHMe_3$	111.27 d	$J_{CH} = 159.3$
	$OCH=CHCHMe_3$	72.86 d	$J_{CH} = 124.5$
18	$C_5(CH_3)_5$	1.81, 1.87 s	
	$OCH=CHCH(CMe_3)CO$	7.10 dd	6.0, 3.0
	$OCH=CHCH(CMe_3)CO$	4.29 dd	6.0, 3.0
	$OCH=CHCH(CMe_3)CO$	2.90 dd	3.0, 3.0
	$OCH=CHCH(CMe_3)CO$	1.30 s	
	$OCH=CHCH(CMe_3)CO$	148.5 d	$J_{CH} = 177$
	$OCH=CHCH(CMe_3)CO$	103.6 d	$J_{CH} = 161$
	$OCH=CHCH(CMe_3)CO$	72.9 d	$J_{CH} = 115$
	$OCH=CHCH(CMe_3)CO$	307.3	
19	$C_5(CH_3)_5$	1.91 s	
	$OCH=CHC(CMe_3)=CHO$	7.01 dd	$J = 7.2, 0.8$
	$OCH=CHC(CMe_3)=CHO$	4.33 dd	$J = 7.2, 0.9$
	$OCH=CHC(CMe_3)=CHO$	7.05 s, br	
	$OCH=CHC(CMe_3)=CHO$	1.23 s	

<sup>a</sup>) <sup>1</sup>H- (90 MHz) and <sup>13</sup>C- (22.5 MHz) NMR spectra taken in [D<sub>6</sub>]benzene at ambient temperature, unless otherwise indicated. Chemical shifts in δ relative to internal TMS or residual protons or carbons in solvents. Long range <sup>13</sup>C-<sup>1</sup>H coupling is reported only when a coupling constant could be determined. — <sup>b</sup>) <sup>1</sup>H NMR recorded at -70°C ([D<sub>8</sub>]toluene). — <sup>c</sup>) <sup>1</sup>H NMR recorded at -70°C ([D<sub>8</sub>]toluene). — <sup>d</sup>) Cp\*<sub>2</sub>Hf(<sup>13</sup>CO)(η<sup>2</sup>-O<sup>13</sup>CHCH<sub>2</sub>CHMe<sub>3</sub>). — <sup>e</sup>) Cp\*<sub>2</sub>Hf(O<sup>13</sup>C(CH<sub>2</sub>CHMe<sub>3</sub>)=<sup>13</sup>CHO). — <sup>f</sup>) <sup>1</sup>H NMR recorded at -14°C; <sup>13</sup>C NMR at -30°C ([D<sub>8</sub>]toluene). — <sup>g</sup>) Cp\*<sub>2</sub>Hf(O<sup>13</sup>C(Ph)=<sup>13</sup>CHO). — <sup>h</sup>) <sup>1</sup>H NMR recorded at -50°C ([D<sub>8</sub>]toluene). — <sup>i</sup>) Cp\*<sub>2</sub>Zr-OCH(CH<sub>2</sub>CHMe<sub>3</sub>)CHH'CHH' (12), H' *cis* to methine H. <sup>1</sup>H NMR recorded on Bruker 500 ([D<sub>6</sub>]benzene) at ambient temperature. — <sup>j</sup>) <sup>13</sup>C NMR recorded at -10°C ([D<sub>8</sub>]toluene).

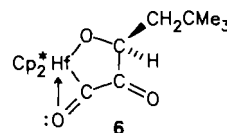
When heated at 80°C for 1 hour, **4a** cleanly loses an equivalent of CO and affords the enolate hydride **3**. Curiously, under these same conditions **4b** undergoes a clean rearrangement to the cyclic enediolate **5**, without loss of CO (eq. 3).



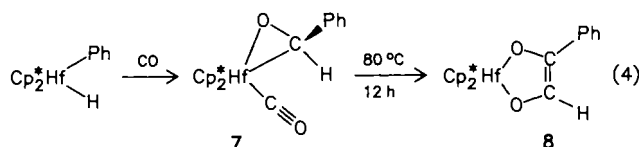
When toluene solution of **4b** are cooled below 0°C under carbon monoxide, a dramatic, reversible color change from orange to lime green is observed. <sup>1</sup>H-NMR spectra of the lime green solutions indicate an essentially complete conversion of **4b** to a new species **6**. Compound **6** is not observed at low temperature if toluene solutions of **4b** are cooled under N<sub>2</sub>, nor is there any evidence for the zirconium analog of **6** when solutions of **4a** are cooled under CO.

A tentative structural assignment for **6** may be made on the basis of the following: (1) the <sup>1</sup>H-NMR spectrum differs only slightly from that for **4b** (Table 1), the major difference being that the resonance previously attributed to the aldehyde proton of **4b** is shifted downfield to δ = 4.88 (dd, <sup>3</sup>J<sub>HH</sub> = 10.1, 2.7 Hz). (2) The <sup>13</sup>C-NMR spectrum for **6**-<sup>13</sup>C<sub>3</sub>, obtained by treating **4b**-<sup>13</sup>C<sub>2</sub> (prepared from **1b** and <sup>13</sup>CO) with additional <sup>13</sup>CO, shows three enhanced signals at δ = 94.4 (dddd, J<sub>CC</sub> = 13.6, 37.1; <sup>1</sup>J<sub>CH</sub> = 136.7; <sup>3</sup>J<sub>CH</sub> = 5.9 Hz), at δ = 213.6 (d, J<sub>CC</sub> = 37.1 Hz), and at δ = 310.6 Hz (d, J<sub>CC</sub> = 13.6 Hz). (3) Treatment of **4b**-<sup>13</sup>C<sub>2</sub> with <sup>13</sup>CO yields a product with only the δ = 94.4 and 213.6 resonances

enhanced, indicating that the carbon responsible for the δ = 310.6 resonance is derived from ambient CO. (4) the infrared spectrum of **6** (toluene solution, -50°C) shows two strong acyl bands at 1724 and 1640 cm<sup>-1</sup>, but no bands in the 1800–2100 cm<sup>-1</sup> region. The structure shown below is consistent with these data; however, alternative structures may also be envisioned.



Isolation of analytical samples of the carbonyl/aldehyde adducts **4a** and **4b** is plagued by the rather low yields of these reactions and persistent impurities. Since the reactions of other alkyl hydride derivatives with carbon monoxide yield (with similar low selectivity) products analogous to **4** with similar instabilities, it appears that the β hydrogens of the alkyl group are problematic. The reaction of the phenyl hydride derivative Cp\*<sub>2</sub>Hf(H)(C<sub>6</sub>H<sub>5</sub>) with carbon monoxide was therefore examined. Indeed, although the reaction with CO (3 atm) is rather slow, proceeding over the course of several hours at 25°C, the carbonyl/benzaldehyde adduct Cp\*<sub>2</sub>Hf(CO)(η<sup>2</sup>-O=CHPh) (**7**) is cleanly obtained (>95%, <sup>1</sup>H NMR) (eq. 4).

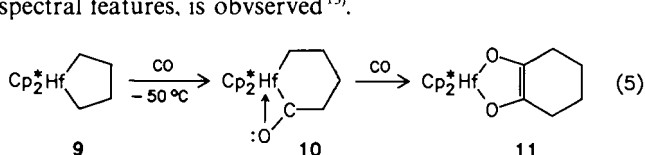


Orange crystalline **7** may be isolated (66% yield) as an analytically pure, thermally rather stable material. The monomeric formulation for **7** was confirmed by its solution molecular weight.  $^1\text{H-NMR}$  monitoring of reaction (4) indicated no buildup of an intermediate carbonyl adduct of the phenyl hydride or a benzoyl hydride species.

When heated at  $80^\circ\text{C}$  for 12 hours, **7** cleanly rearranges to an enediolate complex  $\text{Cp}_2^*\text{Hf}(\overline{\text{OC}(\text{C}_6\text{H}_5)=\text{CHO}})$  (**8**) analogous to **5** (eq. 4). In contrast to **4b**, no spectral changes are observed when solutions of **7** are cooled under an atmosphere of carbon monoxide.

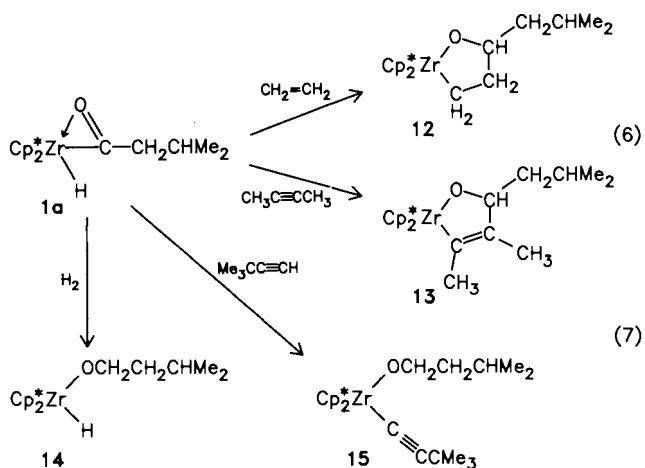
## 2. Reaction of $\text{Cp}_2^*\text{Hf}(\overline{\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2})$ (**9**) with Carbon Monoxide

The similarity of the reaction of  $\text{Cp}_2^*\text{Zr}(\text{H})(\overline{\text{CH}_2\text{CHMe}_2})$  with CO to the reaction of  $\text{Cp}_2^*\text{Zr}(\overline{\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2})$  with  $\text{CO}^{4a)}$  prompted us to investigate the reaction of **9**<sup>4b)</sup> with CO in hopes of observing a cyclopentanone adduct of permethylhafnocene. Monitoring the reaction at  $-50^\circ\text{C}$  by  $^1\text{H}$ - and  $^{13}\text{C-NMR}$  spectroscopy reveals that **9** is slowly converted to hafnacyclohexanone  $\text{Cp}_2^*\text{Hf}(\eta^2\text{-COCH}_2\text{CH}_2\text{-CH}_2\text{CH}_2)$  (**10**) with a  $^{13}\text{C-NMR}$  resonance at  $\delta = 344$ , characteristic of a dihapto-carbonyl carbon (eq. 5). Slowly warming **10** under CO failed to yield a carbonyl/cyclohexanone adduct; rather, direct appearance of the bicyclic enediolate complex **11** (eq. 5), with characteristic NMR (Table 1) and infrared [ $\nu(\text{C}=\text{C})$  at  $1640\text{ cm}^{-1}$ ;  $\nu(\text{C}-\text{O})$  at  $1210\text{ cm}^{-1}$ ] spectral features, is observed<sup>13)</sup>.



## 3. Reaction of $\text{Cp}_2^*\text{Zr}(\text{H})(\eta^2\text{-O}=\text{CCH}_2\text{CHMe}_2)$ (**1a**) with Ethylene, 2-Butyne, Dihydrogen, and *tert*-Butylacetylene

The facility with which the carbonyl and  $\eta^2$ -aldehyde ligands of **4b** and **7** couple (vide supra) suggested the possibility that similar reactivity might be observed if the CO ligand were replaced by other substrates. Attempts to trap the presumed coordinatively unsaturated  $\eta^2$ -isovaleraldehyde intermediate [ $\text{Cp}_2^*\text{Zr}(\eta^2\text{-O}=\text{CHCH}_2\text{CHMe}_2)$ ] by slow



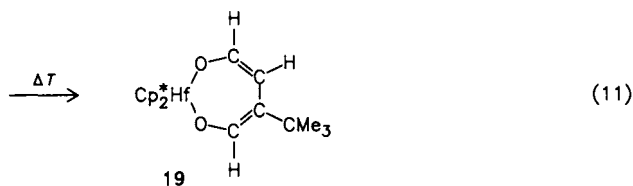
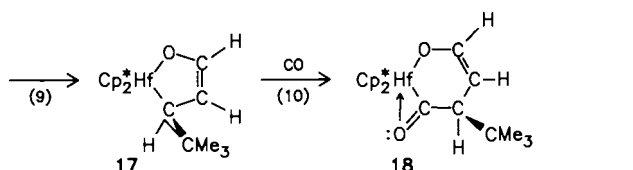
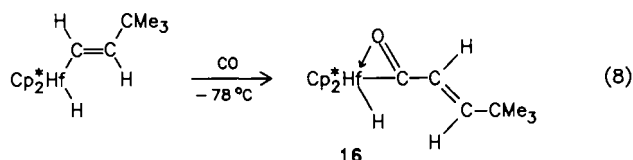
warming of solutions of **1a** with donors such as pyridine or methyl isonitrile yielded no tractable products. However, treatment of cold toluene solutions of **1a** with excess ethylene or excess 2-butyne quantitatively ( $^1\text{H NMR}$ ) yields the white, microcrystalline zircona-oxa-metallacycles **12** and **13** as shown in equation (6).

Monitoring these reactions by  $^1\text{H NMR}$  reveals that the disappearance of resonances due to **1a** and the simultaneous appearance of signals due to **12** or **13** occurs at approximately  $-30^\circ\text{C}$ , independent of the  $[\text{C}_2\text{H}_4]$  or  $[\text{CH}_3\text{-C}\equiv\text{CCH}_3]$ . Characteristic  $^1\text{H}$ - and  $^{13}\text{C-NMR}$  data, particularly the close similarity of those for **12** to those for  $\text{Cp}_2^*\text{Ti}(\overline{\text{OCH}(\text{CH}_3)\text{CH}_2\text{CH}_2})^{14)}$  are quite diagnostic of the structures indicated.

The isovaleraldehyde intermediate may also be trapped by addition of  $\text{H}_2$  or the acetylenic C-H bond of *tert*-butylacetylene (eq. 7). The products **14** and **15** are isolated in good yields.

## 4. Reactions of $\text{Cp}_2^*\text{Hf}(\text{H})(\text{trans-CH}=\text{CHCMe}_3)$ with Carbon Monoxide

Like the alkyl hydride derivatives reported thus far, the alkenyl hydride complex  $\text{Cp}_2^*\text{Hf}(\text{H})(\text{trans-CH}=\text{CHCMe}_3)^{15)}$  reacts readily with carbon monoxide (1 atm) at  $-78^\circ\text{C}$  via CO insertion into the metal-carbon bond, affording  $\text{Cp}_2^*\text{Hf}(\text{H})(\eta^2\text{-COCH}=\text{CHCMe}_3)$  (**16**) (eq. 8).



The characteristic low field acyl carbon resonance at  $\delta = 320.5$  and the large vinylic  $^3J_{\text{HH}}$  proton coupling constant of 15.1 Hz suggests a dihapto-acyl structure analogous to **1b** with the *trans* stereochemistry about the carbon carbon double bond preserved.

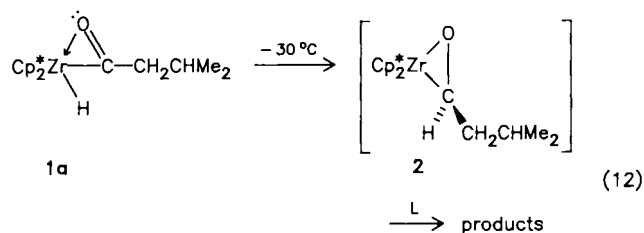
On warming to  $\approx -10^\circ\text{C}$  in vacuo **16** rearranges to the hafna-oxo-metallacyclopentene **17**, isolable as a thermally unstable orange oil. The structure indicated is clearly established by its spectroscopic data (Table 1) and by its chemical reactivity. Specifically, further treatment of **17** with excess carbon monoxide at  $25^\circ\text{C}$  quantitatively ( $^1\text{H NMR}$ ) yields the insertion product **18** (eq. 10). Compound **18** may be

isolated from petroleum ether as an orange crystalline solid. Its  $^1\text{H-NMR}$  spectrum closely resembles that for **17**, the most notable difference being a substantial downfield shift of the resonance assigned to the  $\text{HfCH}(\text{CMe}_3)$  proton. Assignment of the highly coupled vinylic carbon and proton resonances was facilitated by examining the spectra for  $\text{Cp}_2^*\text{Hf}(\eta^2\text{-COCD}(\text{CMe}_3)\text{CH}=\text{CD}_2)$  (**18-d**), prepared from  $\text{Cp}_2^*\text{Hf}(\text{D})(\text{trans-CH}=\text{CDCMe}_3)$ , which was in turn prepared from  $\text{Cp}_2^*\text{HfD}_2$  and  $\text{HC}\equiv\text{CCMe}_3$ . Characteristic infrared [ $\nu(\text{CO})$  at  $1610\text{ cm}^{-1}$ ] and  $^{13}\text{C}$  NMR data ( $\text{HfCO}$   $\delta = 307.3$ ) further support the  $\eta^2$ -acyl formulation for **18**.

This cyclic acyl derivative rearranges at  $80^\circ\text{C}$  by a formal 1,2-hydrogen shift to the final product, the hafna-dioxo-cycloheptadiene derivative **19** (eq. 11). The thermal rearrangement of **18** to **19** obeys first order kinetic for  $>3$  half lives with  $k = 1.5 \times 10^{-4}\text{ s}^{-1}$  at  $80^\circ\text{C}$ . A moderate kinetic deuterium isotope effect ( $k_{\text{H}}/k_{\text{D}} = 3.6$ ) is observed for rearrangement of **18-d**.

## Discussion

The reactivity of the acyl hydride derivatives **1a** and **1b** differs markedly from that of late transition metal acyl hydrides, which typically either undergo rapid reductive elimination of aldehyde or decarbonylate and subsequently reductively eliminate alkane from the resulting metal carbonyl derivative<sup>16</sup>. This difference may be readily ascribed to the highly oxophilic nature of coordinatively unsaturated group 4 metallocenes, which encourages  $\eta^2$ -coordination of the acyl group and thus directs the reaction toward products which ultimately contain  $\text{Zr-O}$  or  $\text{Hf-O}$  bonds.

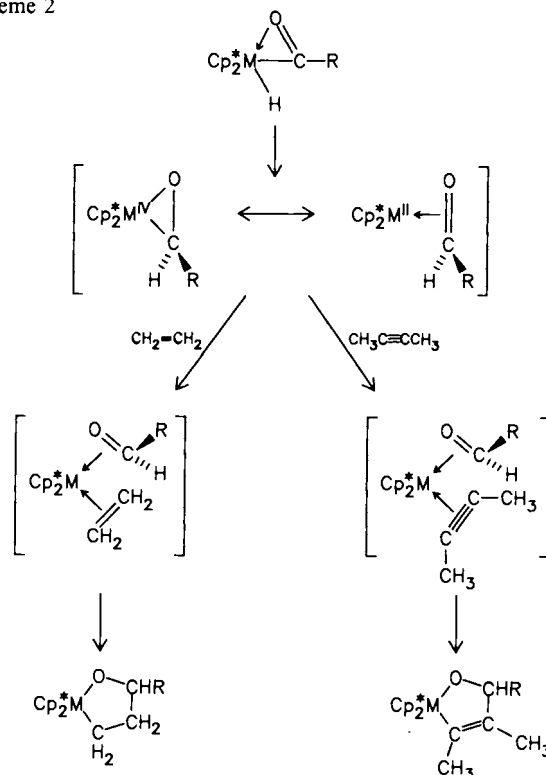


The facile migration of hydride to the acyl carbon for **1a** to form a reactive  $\eta^2$ -isovaleraldehyde adduct, as implicated from earlier labeling studies, is supported by the observed carbonyl/isovaleraldehyde adduct **4a**. Calculations by Hofmann, Stauffert, Frede, and Tatsumi<sup>17</sup> on the related  $\text{Cp}_2^*\text{Zr}(\eta^2\text{-COCH}_3)(\text{CH}_3)/\text{CO}$  system reveal a clear preference for acyl-alkyl (and, by extension, acyl-hydride) coupling in the reaction with CO leading to the final enediolate product. Further considerations implicate the incoming carbonyl ligand as an essential participant in the acetyl-methyl coupling step<sup>17</sup>. Moreover, Grubbs and Waymouth have established that Lewis acids (e.g.  $\text{AlClR}_2$ ) facilitate alkyl-acyl coupling in affording ketone complexes of zirconocene<sup>6</sup>. On the other hand, we observe that the rates of reaction of the acyl hydride **1a** with CO and other trapping ligands ( $\text{C}_2\text{H}_4$ ,  $\text{CH}_3\text{C}\equiv\text{CCH}_3$ ,  $\text{H}_2$ , or  $\text{HC}\equiv\text{CCMe}_3$ ) qualitatively are independent of both the nature of the trapping ligand and its concentration. Thus, for **1a** unassisted (by incoming trap-

ping ligand or external Lewis acid) hydride migration to the acyl carbon of **1a** to yield the reactive  $\eta^2$ -isovaleraldehyde adduct **2** appears to be indicated (eq. 12). The more rapid migration and coupling reactions for hydride as compared with alkyl generally observed for organotransition metal compounds<sup>18</sup> may account for the fact that hydride migration proceeds unassisted.

The relatively electron rich zirconium center in **2** is suggested by the IR data for the carbonyl adduct **4a** and is reflected in reactions of the coordinatively unsaturated intermediate adduct [ $\text{Cp}_2^*\text{Zr}(\eta^2\text{-O}=\text{CHCH}_2\text{CHMe}_2)$ ] such as oxidative coupling of the isovaleraldehyde ligand with ethylene and 2-butyne to afford metallacycles **12** and **13** (eq. 6) as well as the addition of  $\text{H}_2$  and the C-H bond of *tert*-butylacetylene to yield enolates **14** and **15** (eq. 7). These reactions (Schemes 2 and 3) are reminiscent of the reactivity exhibited by other  $\eta^2$ -carbonyl and related adducts such as [ $\text{Cp}_2\text{Ti}(\eta^2\text{-O}=\text{C}=\text{CH}_2)_2$ ]<sup>13a</sup> and  $\text{Cp}_2^*\text{Zr}(\text{C}_5\text{H}_5\text{N})(\eta^2\text{-O}=\text{C}=\text{CH}_2)$ <sup>19</sup>, [ $\text{Cp}_2\text{M}(\eta^2\text{-O}=\text{C}=\text{CPh}_2)_2$ ] ( $\text{M} = \text{Ti}, \text{Zr}$ )<sup>20</sup>, [ $\text{Cp}_2\text{Zr}(\text{benzynes})$ ]<sup>3d,e</sup>, and a butadiene complex of zirconocene<sup>21</sup>, and complement the reactions of  $\text{Cp}_2^*\text{Ti}(\eta^2\text{-C}_2\text{H}_4)$  with unsaturated substrates<sup>14</sup>.

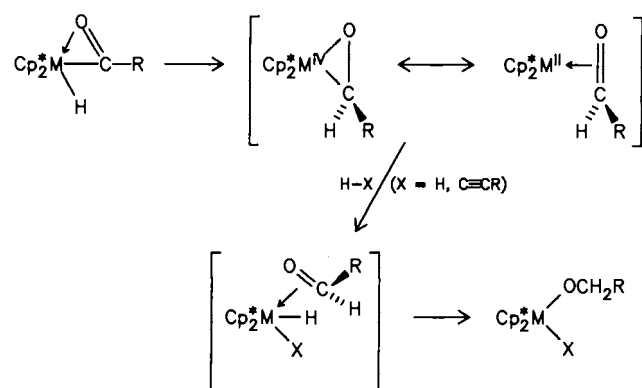
Scheme 2



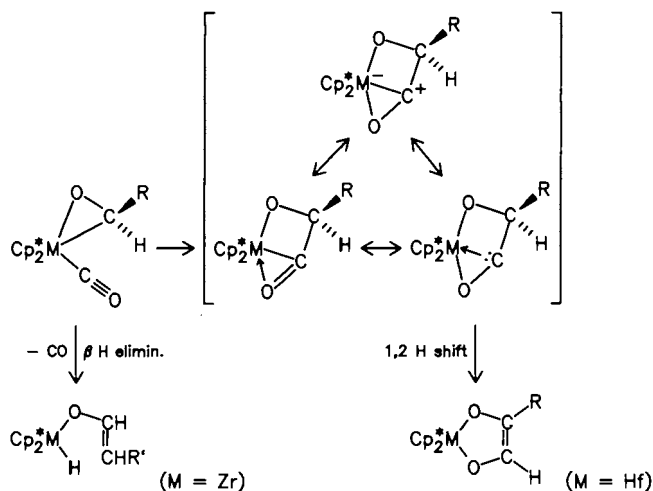
The coupling of carbonyl and aldehyde ligands for **4b** and **7** to yield the enediolates **5** and **8** (eqs. 3 and 4) has precedent in early transition metal chemistry. Erker and co-workers have reported reversible insertion of CO into the  $\text{Zr-C}$  bond of a binuclear formaldehyde adduct of zirconocene to form a spectroscopically characterized acyl complex  $\text{Cp}_2\text{Zr}(\mu\text{-OCHCH}_2\text{Ph})(\mu\text{-OCCH}_2\text{O})\text{ZrCp}_2$ , which undergoes thermolysis to yield an enediolate complex as final product<sup>10</sup>. Whereas conversion to the enediolate in the Erker system

is proposed to occur via a ketene intermediate, we favor a 1,2 hydrogen shift process for enediolate formation (Scheme 4).

Scheme 3



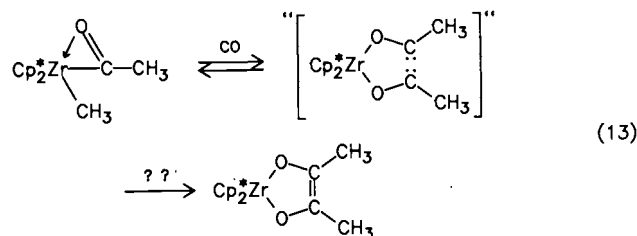
Scheme 4



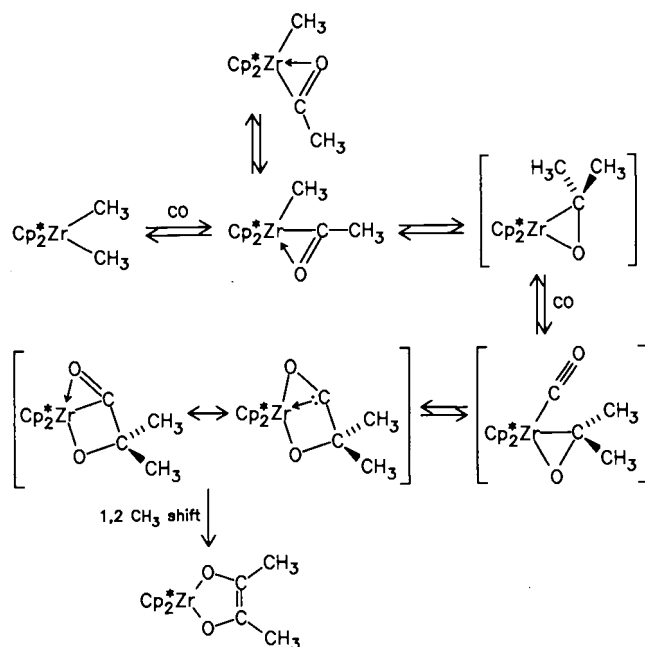
A closely related 1,2 shift has been proposed for a related thorium acyl derivative<sup>22</sup>. Interestingly, the thermal rearrangement of **18** to **19** (eq. 11) proceeds qualitatively at the same rate as the thermolysis of **4b**, suggesting that both proceed by the same rate determining (1,2 H shift) step.

The convenient in situ generation of reactive  $\eta^2$ -aldehyde adducts of zirconocene and hafnocene (Schemes 1 and 2) suggested extensions to the analogous ketone derivatives. The failure to observe a cyclopentanone adduct of permethylhafnocene, although disappointing, is not surprising in view of severe steric interactions between the 2 and 5 methylene groups of  $\eta^2$ -O=CCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub> with the  $\eta^5$ -C<sub>5</sub>Me<sub>5</sub> ligands. The reactivity of **9** with carbon monoxide does, however, proceed by analogy to that observed for metallacyclobutane derivatives and Cp<sup>\*</sup><sub>2</sub>Zr(CH<sub>3</sub>)<sub>2</sub>. Although the reaction of Cp<sup>\*</sup><sub>2</sub>Zr(CH<sub>3</sub>)<sub>2</sub> with CO had previously been rationalized in terms of intramolecular carbene-carbene coupling for an incipient bis(oxycarbene) species (eq. 13), the present results as well as those reported in the preceding article<sup>17</sup> implicate the alternative shown in Scheme 5. The keysteps are methyl migration to the carbonyl carbon of the

$\eta^2$ -acetyl ligand (which may proceed by CO addition to Zr), CO insertion into the Zr—C bond of the  $\eta$ -acetone adduct, and a 1,2 methyl shift to the  $\eta^2$ -acyl carbon atom.



Scheme 5



Finally, although the reaction of the vinyl hydride derivative Cp<sup>\*</sup><sub>2</sub>Hf(H)(*trans*-CH=CHCMe<sub>3</sub>) with CO also failed to provide direct evidence for an  $\eta^2$ -aldehyde adduct, the final metallacyclic product **17** (eq. 9) may be rationalized by invoking intramolecular olefin trapping of such an intermediate (viz. [Cp<sup>\*</sup><sub>2</sub>Hf( $\eta^2$ , $\eta^2$ -O=CHCH=CHCMe<sub>3</sub>)], closely analogous to the bimolecular trapping of the isovaleraldehyde complex with ethylene yielding **12** (eq. 6).

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## Experimental

All manipulations were performed using either glove box or high vacuum line techniques described earlier<sup>23</sup>. Hexamethyldisiloxane, 2-butyne, and *tert*-butylacetylene were stored under vacuum over 4-Å molecular sieves. Ethylene and carbon monoxide were used directly as received. — Elemental analyses: Alfred Bernhardt and Dornis and Kolbe Analytical Laboratories. — <sup>1</sup>H NMR: EM-390, JEOL FX 90 Q, and Bruker 500 MHz spectrometers. — <sup>13</sup>C NMR: JEOL FX 90 Q spectrometer. — Infrared spectra: Beckman 4240 spectrometer, nujol mulls, unless otherwise noted. — Low temperature infrared spectra: IR cell designed by Hinsberg<sup>24</sup>.

Cp<sup>\*</sup><sub>2</sub>Zr(CO)( $\eta^2$ -O=CHCH<sub>2</sub>CHMe<sub>2</sub>) (**4a**): A solution of Cp<sup>\*</sup><sub>2</sub>Zr(H)(CH<sub>2</sub>CHMe<sub>2</sub>)<sup>14a</sup> (0.55 g) in 10 ml of toluene was cooled to

–78°C, 1 atm carbon monoxide admitted, and with vigorous stirring the solution was allowed to warm slowly to room temp. over the course of several hours. Volatiles were removed in vacuo, and the resultant orange oily solid was taken up in approximately 5 ml of hexamethyldisiloxane. 80 mg of solid **4a** (85% pure, <sup>1</sup>H NMR) was collected by slow cooling to –78°C and filtering cold. The oily filtrate consisted largely (≈70%) of **4a**. – IR: 1940 cm<sup>-1</sup> s, 1160, 1027, 920, 845. – Due to slow decomposition, even at 25°C, reliable elemental analyses could not be obtained.

$Cp_2^*Hf(CO)(\eta^2-O=CHCH_2CHMe_2)$  (**4b**): Moderately pure (≈85%, <sup>1</sup>H NMR) samples of **4b** may be obtained using the same procedure described for **4a**. Again, its instability at 25°C precluded obtaining elemental analyses. – IR:  $\tilde{\nu} = 1930\text{ cm}^{-1}$  s, 1150, 1030, 927, 842. – Heating crude **4b** in benzene at 80°C for 1 h yielded **5**, which is isolable only as a rather impure (≈80%, <sup>1</sup>H NMR) orange oil.

$Cp_2^*Hf(CO)(\eta^2-O=CHC_6H_5)$  (**7**): A thick-walled glass reaction vessel with a teflon needle valve was charged with 0.50 g (0.95 mmol) of  $Cp_2^*Hf(H)(C_6H_5)^{40}$ , 10 ml of toluene, and ca. 3.5 atm carbon monoxide and stirred for 24 h at room temperature. Solvent and residual CO were removed in vacuo, and the orange solid residue was taken up in petroleum ether to give 0.36 g (66%) of light orange **7**. – IR:  $\tilde{\nu} = 1956\text{ cm}^{-1}$  s, 1600, 1492, 1230, 1120, 1069, 1027, 750, 700.

$C_{28}H_{36}HfO_2$  (583.2) Calcd. C 57.68 H 6.22 Hf 30.61  
Found C 57.76 H 6.30 Hf 30.68  
Mol. mass 592 (ebullimetric in benzene)<sup>22,25</sup>

$Cp_2^*Hf(\overline{OC(C_6H_5)=CHO})$  (**8**): The procedure described for **7** was used except that 0.33 g of  $Cp_2^*Hf(H)(C_6H_5)$ , 10 ml of toluene, and 3.5 atm CO were stirred for 3 d at 80°C. Similar workup of the highly soluble orange residue yielded 67 mg of orange **8**. – IR:  $\tilde{\nu} = 1600\text{ cm}^{-1}$ , 1580, 1563, 1480, 1320, 1295, 1120, 1070, 1046, 1025, 870, 757, 692, 680, 583, 475.

$C_{28}H_{36}HfO_2$  (583.2) Calcd. C 57.68 H 6.22 Hf 30.61  
Found C 57.64 H 6.16 Hf 30.70

**Bicyclic Enediolate Complex 11**: A solution of 0.20 g of  $Cp_2^*Hf(CH_2CH_2CH_2CH_2)$  (**9**)<sup>40</sup> in 10 ml of toluene was cooled to –78°C and stirred under 1 atm CO for 2 h, generating an orange solution of the acyl metallacycle **10**. The solution was allowed to warm slowly to room temp., and the volatiles were removed in vacuo. 5 ml of petroleum ether was distilled onto the residue, and the solution was cooled to –78°C, precipitating orange crystalline **11** (0.11 g, 40%). – IR:  $\tilde{\nu} = 1640\text{ cm}^{-1}$ , 1353, 1210, 1157, 1100, 1025, 900, 720.

$C_{26}H_{38}HfO_2$  (561.2) Calcd. C 55.66 H 6.83 Hf 31.81  
Found C 55.38 H 6.85 Hf 31.69

$Cp_2^*Zr[\overline{OCH(CH_2CHMe_2)CH_2CH_2}]$  (**12**): A solution of 0.34 g (0.71 mmol) of  $Cp_2^*Zr(H)(CH_2CHMe_2)$  in 10 ml of toluene under 1 atm CO was cooled to –78°C and stirred for 0.5 h to quantitatively form the acyl hydride derivative **1a**. Excess CO was removed in vacuo, and ethylene (2.3 mmol) was admitted. The reaction mixture was warmed slowly to room temp., volatiles were removed and ca. 7 ml of petroleum ether was condensed into the flask to dissolve the brown residue. Cooling the resulting solution to –78°C, filtering, and washing the precipitate once with cold petroleum ether afforded 0.165 g (46%) of white **12**. – IR:  $\tilde{\nu} = 1363\text{ cm}^{-1}$ , 1090, 1078, 1010, 952, 846, 580.

$C_{27}H_{44}OZr$  (475.8) Calcd. C 68.15 H 9.32 Zr 19.17  
Found C 68.11 H 9.19 Zr 19.36

$Cp^*Zr[\overline{OCH(CH_2CHMe_2)C(CH_3)C=C(CH_3)}]$  (**13**): A solution of **1a** at –78°C derived from 0.30 g (0.60 mmol) of  $Cp_2^*Zr(H)$

( $CH_2CHMe_2$ ) was prepared following the procedure described for **12**. Removal of excess CO and slow warming in the presence of 2-butyne (7.1 mmol) yielded, upon recrystallization from cold petroleum ether, 0.20 g (57%) of **13**. – IR:  $\tilde{\nu} = 1563\text{ cm}^{-1}$  [ $\nu(Zr-H)$ ], 1486, 1365, 1167, 1120, 1090, 1058, 1040, 990, 950, 840, 802.

$C_{29}H_{46}OZr$  (501.9) Calcd. C 69.40 H 9.24 Zr 18.17  
Found C 69.16 H 9.07 Zr 18.45

$Cp_2^*Zr(H)(OCH_2CH_2CHMe_2)$  (**14**): A solution of **1a** derived from 0.350 g (0.78 mmol)  $Cp_2^*Zr(H)(CH_2CHMe_2)$  was treated with 1 atm of  $H_2$  at –42°C and warmed slowly to room temp. with vigorous stirring. Removal of solvents and sublimation of **14** from the oily residue (100°C, 10<sup>-4</sup> Torr) afforded 0.235 g (63%) of **14**. – IR:  $\tilde{\nu} = 1565\text{ cm}^{-1}$  [ $\nu(Zr-H)$ ], 1510, 1230, 1140, 1105, 1026, 986, 857, 765.

$C_{25}H_{42}OZr$  (449.8) Calcd. C 66.75 H 9.41  
Found C 66.83 H 9.73

$Cp_2^*Zr(C\equiv CMe_3)(OCH_2CH_2CHMe_2)$  (**15**): A solution of **1a** derived from 0.30 g (0.57 mmol) of  $Cp_2^*Zr(H)(CH_2CHMe_2)$  was treated with 7.1 mmol of *tert*-butylacetylene at –42°C and warmed slowly to room temp. with vigorous stirring. Removal of volatiles yielded a colorless oil, identified by IR and <sup>1</sup>H-NMR spectroscopy as >90% **15**. – IR:  $\tilde{\nu} = 2090\text{ cm}^{-1}$  [ $\nu(C\equiv C)$ ], 1378, 1246, 1205, 1138, 1105, 1025, 984, 730.

$Cp_2^*Hf[\overline{CH(CMe_3)CH=CHO}]$  (**17**): A solution of 0.10 g (0.19 mmol) of  $Cp_2^*Hf(H)(trans-CH=CHCMe_3)^{15}$  in 10 ml of toluene was stirred at –78°C for 1 h under 1 atm of CO to generate the acyl hydride derivative **16**. Excess CO was removed in vacuo, and the bright yellow solution was allowed to warm slowly to room temperature. The solvent was removed, leaving a thermally unstable orange oil identified by <sup>1</sup>H-NMR spectroscopy as >90% **17**. – IR:  $\tilde{\nu} = 1545\text{ cm}^{-1}$  [ $\nu(C=C)$ ], 1358, 1236, 1159, 1098, 1041, 1023, 870, 800.

$Cp_2^*Hf[\overline{\eta^2-COCH(CMe_3)CH=CHO}]$  (**18**): A solution of 0.21 g (0.40 mmol) of  $Cp_2^*Hf(H)[trans-CH=CH(CMe_3)]$  in 5 ml of petroleum ether was stirred for 1 h under 1 atm CO at –78°C, then allowed to warm to room temperature. The solution slowly turned deep orange upon warming, precipitating bright orange crystal overnight. Cooling to –78°C and filtering yielded 0.095 g (40%) of **18**. – IR:  $\tilde{\nu} = 1610\text{ cm}^{-1}$  [ $\nu(C-O)$ ], 1590 [ $\nu(C=C)$ ], 1358, 1286, 1260, 1110, 1040, 1024, 968, 838, 752.

$C_{28}H_{42}HfO_2$  (589.2) Calcd. C 57.09 H 7.19 Hf 30.30  
Found C 57.13 H 7.16 Hf 30.11

$Cp_2^*Hf[\overline{OCH=C(CMe_3)CH=CHO}]$  (**19**): A thick-walled glass reaction vessel with teflon needle valve was charged with 0.50 g (0.85 mmol) of **18**, 10 ml of toluene and 700 Torr CO and heated at 80°C for 6 h. Removal of volatiles in vacuo and recrystallization from petroleum ether afforded 0.30 g (60%) of off-white **19**. – IR ([D<sub>6</sub>]benzene):  $\tilde{\nu} = 1590\text{ cm}^{-1}$  [ $\nu(C=C)$ ], 1460, 1423, 1378, 1358, 1311, 1240 s, 1188 s, 1084, 1045, 1022, 883, 763, 587.

$C_{28}H_{42}HfO_2$  (589.2) Calcd. C 57.09 H 7.19 Hf 30.30  
Found C 57.17 H 7.30 Hf 30.17

**Kinetic Measurements**: The kinetics of the thermal rearrangement of **18** to **19** were followed by <sup>1</sup>H-NMR spectroscopy, monitoring the ratio of the *tert*-butyl resonances of reactant and product. All of the kinetic runs obeyed first order kinetics for >2.5 half lives. Sealed NMR tubes were maintained at 80° (±1)°C in a constant temperature bath, and spectra were measured every 15 min. Two runs on **18-d<sub>0</sub>** ([**18-d<sub>0</sub>**] = 0.18, 0.36 M in [D<sub>6</sub>]benzene) yielded rate constants of 1.51 × 10<sup>-4</sup> s<sup>-1</sup> and 1.50 × 10<sup>-4</sup> s<sup>-1</sup>, and one run on **18-d<sub>2</sub>** gave a rate constant of 0.41 × 10<sup>-4</sup> s<sup>-1</sup> ( $k_H/k_D = 3.6$ ).



## CAS Registry Numbers

**1a**: 120333-04-2 / **1b**: 120333-05-3 / **4a**: 120332-89-0 / **4b**: 120332-90-3 / **5**: 120332-91-4 / **6**: 120333-06-4 / **7**: 120332-92-5 / **8**: 120332-93-6 / **9**: 92786-86-2 / **10**: 120332-94-7 / **11**: 120332-95-8 / **12**: 120332-96-9 / **13**: 120332-97-0 / **14**: 120332-98-1 / **15**: 120332-99-2 / **16**: 120333-00-8 / **17**: 120333-01-9 / **18**: 120333-02-0 / **19**: 120333-03-1 / Cp\*Zr(H)(CH<sub>2</sub>CHMe<sub>2</sub>): 67108-86-5 / Cp\*Hf(H)(CH<sub>2</sub>-CHMe<sub>2</sub>): 92786-84-0 / Cp\*Hf(H)(C<sub>6</sub>H<sub>5</sub>): 92786-77-1 / Cp\*Hf(H)-(trans-CH=CHCMe<sub>3</sub>): 92786-87-3 / CH<sub>2</sub>=CH<sub>2</sub>: 74-85-1 / CH<sub>3</sub>-C≡CCH<sub>3</sub>: 503-17-3 / Me<sub>3</sub>CC≡CH: 917-92-0 / D<sub>2</sub>: 7782-39-0

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reactivity patterns observed; however, we cannot rule out a facile equilibrium with a (more stable) O-central isomer.

<sup>8)</sup> The product mixture also contains roughly equal amounts of Cp\*Zr(H)(OCH=CHMe<sub>2</sub>) and Cp\*Zr(H)(CO)<sub>2</sub> (ca. 20%).

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