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Reduction of Carbon Monoxide Promoted by Alkyl and Hydride Derivatives of Permethylzirconocene

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Abstract: Bis(pentamethylcyclopentadienyl)dihydrozirconium(IV), ($\eta^5\text{-C}_5\text{Me}_5$)₂ZrH₂ (**2**) is prepared by the reaction of H₂ with {($\eta^5\text{-C}_5\text{Me}_5$)₂ZrN₂}₂N₂ (**1**). **2** forms unstable adducts with PF₃ and CO at –80 °C. The carbonyl adduct ($\eta^5\text{-C}_5\text{Me}_5$)₂ZrH₂(CO) yields {($\eta^5\text{-C}_5\text{Me}_5$)₂ZrH₂}₂(OCH=CHO) and/or ($\eta^5\text{-C}_5\text{Me}_5$)₂ZrH(OCH₃), depending on reaction conditions. Carbonylation of ($\eta^5\text{-C}_5\text{Me}_5$)₂Zr(CH₃)₂ obtained from ($\eta^5\text{-C}_5\text{Me}_5$)₂ZrCl₂ and methyllithium, yields successively ($\eta^5\text{-C}_5\text{Me}_5$)₂Zr(CH₃)(CH₃CO) and ($\eta^5\text{-C}_5\text{Me}_5$)₂Zr(O(CH₃)C=C(CH₃)O). The zirconacyclopentane complex ($\eta^5\text{-C}_5\text{Me}_5$)₂Zr(CH₂(CH₂)₂CH₂) (**10**) is prepared from **1** and ethylene. Carbonylation of **10** affords ($\eta^5\text{-C}_5\text{Me}_5$)₂Zr(H)-(OC=CH(CH₂)₂CH₂). Treatment of **2** with isobutylene yields ($\eta^5\text{-C}_5\text{Me}_5$)₂Zr(H)(CH₂CHMe₂) (**13**), which undergoes a reaction with CO to form ($\eta^5\text{-C}_5\text{Me}_5$)₂Zr(H)(OCH=CHCHMe₂) (**15**). The results of ¹³C and deuterium labeling studies indicate that the conversion of **13** to **15** is mediated by ($\eta^5\text{-C}_5\text{Me}_5$)₂Zr(H)(Me₂CHCH₂CO). The observed patterns for these reactions of alkyl and hydride derivatives of zirconium with CO are attributed to carbenoid character of the carbonyl carbon resulting from an unusual "side-on" coordination of acyl and formyl groups.

Introduction

The development of homogeneous catalysts for selective conversion of CO and H₂ to alkanes or alcohols is a problem of growing interest. Homogeneous systems thus far reported to catalyze the reduction of CO by H₂ include the Rh-based ethylene glycol synthesis,² methanation promoted by Os₃(CO)₁₂ or Ir₄(CO)₁₂,³ and most recently the catalytic

production of methane, ethane, propane, and isobutane by Ir₄(CO)₁₂ in molten NaCl·2AlCl₃.⁴

We recently reported that H₂ stoichiometrically reduces ligated CO in certain carbonyl compounds of zirconium:⁵

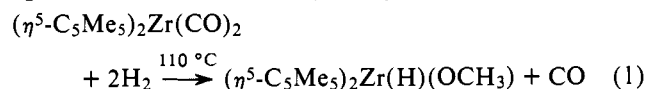
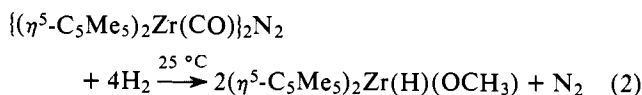


Table I. Proton Nuclear Magnetic Resonance Data

Compd	Solvent			NMR, δ
$(\eta^5\text{-C}_5\text{Me}_5)_2\text{ZrH}_2$ (2)	Benzene- d_6	$[\text{C}_5(\text{CH}_3)_5]$	s	2.02
		ZrH ₂	s	7.46
$(\eta^5\text{-C}_5\text{Me}_5)_2\text{ZrH}_2(\text{PF}_3)$ (3)	Toluene- d_8 -50 °C	$[\text{C}_5(\text{CH}_3)_5]$	s	1.77
		ZrH ₂ (PF ₃)	dq	0.55 (² $J_{\text{H}^{31}\text{P}} = 108$ Hz, ³ $J_{\text{H}^{19}\text{F}} = 21.5$ Hz)
$(\eta^5\text{-C}_5\text{Me}_5)_2\text{ZrH}_2(\text{CO})$ (4)	Toluene- d_8 -64 °C	$[\text{C}_5(\text{CH}_3)_5]$	s	1.84
		ZrH ₂ (CO)	s	1.07
		ZrH ₂ (¹³ CO)	d	1.07 (² $J_{\text{H}^{13}\text{C}} = 25.1$ Hz)
$\{(\eta^5\text{-C}_5\text{Me}_5)_2\text{ZrH}\}_2(\text{OCHCHO})$ (5)	Toluene- d_8	$[\text{C}_5(\text{CH}_3)_5]$	s	1.94
		OCH=CHO	s	6.55
		ZrH	s	5.73
		O ¹³ CH= ¹³ CHO		10-line AA'XX' pattern (¹ $J_{\text{H}^{13}\text{C}} = 177$, ¹ $J_{^{13}\text{C}^{13}\text{C}} = 99$, ² $J_{\text{H}^{13}\text{C}} = 7.5$, ³ $J_{\text{HH}} = 9$ Hz)
$\{(\eta^5\text{-C}_5\text{Me}_5)_2\text{ZrI}\}_2(\text{OCHCHO})$ (6)	Benzene- d_6	$[\text{C}_5(\text{CH}_3)_5]$	s	1.94
		OCH=CHO	s	6.83
		O ¹³ CH= ¹³ CHO		10-line AA'XX' pattern (¹ $J_{\text{H}^{13}\text{C}} = 180.3$, ¹ $J_{^{13}\text{C}^{13}\text{C}} = 100$, ² $J_{\text{H}^{13}\text{C}} = 7$, ³ $J_{\text{HH}} = 10$ Hz) ^a
$(\eta^5\text{-C}_5\text{Me}_5)_2\text{Zr}(\text{CH}_3)_2$ (7)	Benzene- d_6	$[\text{C}_5(\text{CH}_3)_5]$	s	1.78
		Zr(CH ₃) ₂	s	-0.62
$(\eta^5\text{-C}_5\text{Me}_5)_2\text{Zr}(\text{CH}_3)(\text{CH}_3\text{CO})$ (8)	Benzene- d_6	$[\text{C}_5(\text{CH}_3)_5]$	s	1.65
		Zr(CH ₃)	s	-0.05
		Zr(CH ₃ CO)	s	2.32
$(\eta^5\text{-C}_5\text{Me}_5)_2\text{Zr}(\text{O}(\text{CH}_3)\text{C}=\text{C}(\text{CH}_3)\text{O})$ (9)	Benzene- d_6	$[\text{C}_5(\text{CH}_3)_5]$	s	1.86
		O(CH ₃)C=C(CH ₃)O	s	1.91
$(\eta^5\text{-C}_5\text{Me}_5)_2\text{Zr}(\text{CH}_2(\text{CH}_2)_2\text{CH}_2)$ (10)	Benzene- d_6	$[\text{C}_5(\text{CH}_3)_5]$	s	1.82
		CH ₂ (CH ₂) ₂ CH ₂	m	0.50
		CH ₂ (CH ₂) ₂ CH ₂	m	1.95
$(\eta^5\text{-C}_5\text{Me}_5)_2\text{Zr}(\text{H})(\text{OC}=\text{CHCH}_2\text{CH}_2\text{CH}_2)$ (11)	Benzene- d_6	$[\text{C}_5(\text{CH}_3)_5]$	s	1.97
		ZrH	s	6.07
		OC=CHCH ₂ CH ₂ CH ₂	m	4.42
		OC=CHCH ₂ CH ₂ CH ₂	m	2.0-2.5
$(\eta^5\text{-C}_5\text{Me}_5)_2\text{Zr}(\text{I})(\text{OC}=\text{CHCH}_2\text{CH}_2\text{CH}_2)$ (12)	Benzene- d_6	$[\text{C}_5(\text{CH}_3)_5]$	s	1.94
		OC=CHCH ₂ CH ₂ CH ₂	m	4.55
		OC=CHCH ₂ CH ₂ CH ₂	m	2.0-2.5
$(\eta^5\text{-C}_5\text{Me}_5)_2\text{Zr}(\text{H})(\text{CH}_2\text{CHMe}_2)$ (13a)	Benzene- d_6	$[\text{C}_5(\text{CH}_3)_5]$	s	1.93
		ZrH	s	6.43
		ZrCH ₂ CH(CH ₃) ₂	d	-0.04 (³ $J_{\text{H-H}} = 7$ Hz)
		ZrCH ₂ CH(CH ₃) ₂	d	1.00 (³ $J_{\text{H-H}} = 6.5$ Hz)
$(\eta^5\text{-C}_5\text{Me}_5)_2\text{Zr}(\text{D})(\text{CH}_2\text{CDMe}_2)$ (13b)	Benzene- d_6	ZrCH ₂ CD(CH ₃) ₂	s	-0.04
		ZrCH ₂ CD(CH ₃) ₂	s	1.00
$(\eta^5\text{-C}_5\text{Me}_5)_2\text{Zr}(\text{H})(\text{Me}_2\text{CHCH}_2\text{CO})$ (14a)	Toluene- d_6 -50 °C	$[\text{C}_5(\text{CH}_3)_5]$	s	1.82
		ZrH	s	3.66
		(CH ₃) ₂ CHCH ₂ CO	d	1.20 (³ $J_{\text{H-H}} = 7$ Hz)
$(\eta^5\text{-C}_5\text{Me}_5)_2\text{Zr}(\text{D})(\text{Me}_2\text{CDCH}_2\text{CO})$ (14b)	Toluene- d_6 -40 °C	(CH ₃) ₂ CHCH ₂ CO	d	2.54 (³ $J_{\text{H-H}} = 7$ Hz)
		(CH ₃) ₃ CDCH ₂ CO	s	1.20
		(CH ₃) ₂ CDCH ₂ CO	s	2.54
$(\eta^5\text{-C}_5\text{Me}_5)_2\text{Zr}(\text{H})(\text{Me}_2\text{CHCH}_2^{13}\text{CO})$ (14c)	Toluene- d_6 -40 °C	ZrH	d	3.61 (² $J_{^{13}\text{C-H}} = 9$ Hz)
		(CH ₃) ₂ CHCH ₂ CO	d	1.20 (³ $J_{\text{H-H}} = 7$ Hz)
		(CH ₃) ₂ CHCH ₂ CO	dd	1.18 (² $J_{^{13}\text{C-H}} = 5$ Hz, ³ $J_{\text{H-H}} = 7$ Hz)
$(\eta^5\text{-C}_5\text{Me}_5)_2\text{Zr}(\text{H})(\text{OCH}=\text{CHCHMe}_2)$ (15a)	Benzene- d_6	$[\text{C}_5(\text{CH}_3)_5]$	s	1.94
		ZrH	s	6.04
		OCH=CHCH(CH ₃) ₂	d	6.63 (³ $J_{\text{H-H}} = 12$ Hz) ^a
		OCH=CHCH(CH ₃) ₂	dd	4.61 (³ $J_{\text{H-H}} = 12$ Hz ^a ³ $J_{\text{H-H}} = 8$ Hz)
$(\eta^5\text{-C}_5\text{Me}_5)_2\text{Zr}(\text{H})(\text{OCD}=\text{CHCDMe}_2)$ (15b)	Benzene- d_6	(CH=CHCH(CH ₃) ₂	d	1.07 (³ $J_{\text{H-H}} = 6.5$ Hz)
		OCD=CHCD(CH ₃) ₂	s	4.58
		(CD-CHCD(CH ₃) ₂	s	1.10
$(\eta^5\text{-C}_5\text{Me}_5)_2\text{Zr}(\text{H})(\text{O}^{13}\text{CH}=\text{CHMe}_2)$ (15c)	Toluene- d_6	$[\text{C}_5(\text{CH}_3)_5]$	s	1.90
		ZrH	s	5.91
		OCH=CHCH(CH ₃) ₂	dd	6.53 (³ $J_{\text{HH}} = 12$, ¹ $J_{^{13}\text{C-H}} = 173$ Hz)
		OCH=CHCH(CH ₃) ₂	m	4.51
		OCH=CHCH(CH ₃) ₂	d	1.07 (³ $J_{\text{H-H}} = 7$ Hz)

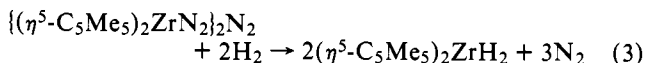
^a See note 34.



While not (yet) catalytic, this system provides an opportunity to examine certain features of the reduction mechanism, in particular the presumed migratory insertion of CO into a transition metal hydride bond. We have therefore extended our investigations of these reactions and have examined the reactivity of hydride and alkyl derivatives of the types $(\eta^5\text{-C}_5\text{Me}_5)_2\text{ZrH}_2$, $(\eta^5\text{-C}_5\text{Me}_5)_2\text{Zr}(\text{H})(\text{R})$, and $(\eta^5\text{-C}_5\text{Me}_5)_2\text{ZrR}_2$ toward CO. Herein we report the results of those studies.

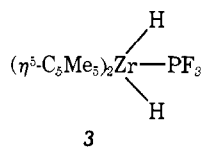
Results

1. Reactions of $(\eta^5\text{-C}_5\text{Me}_5)_2\text{ZrH}_2$ with CO. By virtue of the lability of its ligated N_2 $\{(\eta^5\text{-C}_5\text{Me}_5)_2\text{ZrN}_2\}_2\text{N}_2$ (**1**) serves as a convenient starting material for a variety of derivatives of bis(pentamethylcyclopentadienyl)zirconium. Treatment of **1** with H_2 at 0°C in toluene or hexane affords $(\eta^5\text{-C}_5\text{Me}_5)_2\text{ZrH}_2$ (**2**) in quantitative yield:



Unlike polymeric $\{(\eta^5\text{-C}_5\text{H}_5)_2\text{ZrH}_2\}_x$,^{8,9} pale yellow **2** is very soluble in hydrocarbons. Its molecular weight, analytical data (see Experimental Section), NMR spectrum (Table I), and IR spectrum ($\nu(\text{Zr-H})$ 1555 cm^{-1} ; $\nu(\text{Zr-D})$ 1100 cm^{-1}) are entirely in accord with a monomeric, pseudotetrahedral structure analogous to $(\eta^5\text{-C}_5\text{Me}_5)_2\text{ZrCl}_2$. The low-field chemical shift observed for the hydride hydrogen atoms of **2** (δ 7.46) is in direct contrast to the characteristic high-field resonances for group 5-8 transition metal hydrides, but intermediate to the hydride resonances for $(\eta^5\text{-C}_5\text{Me}_5)_2\text{TiH}_2$ (δ 0.28) and $(\eta^5\text{-C}_5\text{Me}_5)_2\text{HfH}_2$ (δ 15.6).

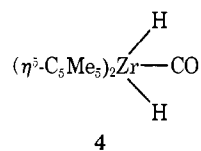
$(\eta^5\text{-C}_5\text{Me}_5)_2\text{ZrH}_2$ (**2**) is formally a 16-electron complex and thus adds certain donor molecules. Thus **2** absorbs PF_3 at -80°C in toluene to yield the unstable, 18-electron complex $(\eta^5\text{-C}_5\text{Me}_5)_2\text{ZrH}_2(\text{PF}_3)$ (**3**). On the basis of its ^1H NMR spectrum at -50°C (Table I), the structure of **3** appears to be analogous to $(\eta^5\text{-C}_5\text{H}_5)_2\text{TaH}_3$ ¹⁰ with PF_3 occupying the central equatorial position mutually cis to both hydride ligands:



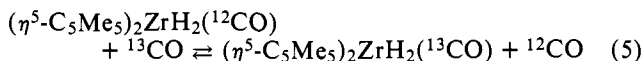
Interestingly $\text{P}(\text{OCH}_3)_3$, $\text{P}(\text{C}_6\text{H}_5)_3$, and $\text{P}(\text{CH}_3)_3$ do not appear to form adducts analogous to **3**; the ^1H NMR spectra of solutions of **2** containing 2-10 molar equiv of these ligands give no indication of additional species at 25°C . **2** does, however, absorb CO (0.97 mol/mol **2**) in toluene at -78°C to generate the carbonyl hydride $(\eta^5\text{-C}_5\text{Me}_5)_2\text{ZrH}_2(\text{CO})$ (**4**). Although **4** is not sufficiently stable for its isolation (see below), it has been characterized in solution at low temperatures. Thus **4** reacts with excess HCl at -78°C to yield $(\eta^5\text{-C}_5\text{Me}_5)_2\text{ZrCl}_2$, H_2 , and CO in accord with the equation



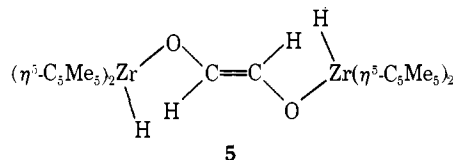
The ^1H NMR spectrum for **4** (Table I) is consistent with a structure analogous to **3**, and the doublet with $^2J_{^{13}\text{C-H}} = 25\text{ Hz}$ observed for the hydride resonance for **4**- ^{13}CO is only consistent with a two-bond coupling, thus indicating a carbon-bonded carbonyl, i.e.,



Whereas residual CO may be removed at -78°C without significant decomposition of **4**, the CO ligand is somewhat labile. ^{13}CO labeling studies indicate 0.21 mol of ^{13}CO exchanged per mol of **4** after 30 min at -78°C ($\bar{p}(\text{CO}) = 0.5\text{ atm}$):



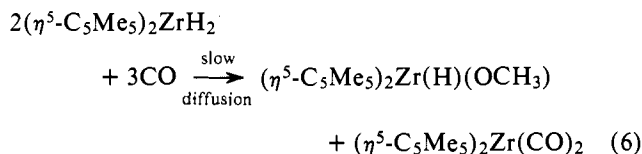
When solutions of **4** are allowed to warm above -50°C , $\{(\eta^5\text{-C}_5\text{Me}_5)_2\text{ZrH}\}_2(\text{OCH}=\text{CHO})$ (**5**) is obtained in nearly quantitative yield. The structure of this rather unexpected



compound is supported by analytical data (see Experimental Section), by its infrared spectrum ($\nu(\text{Zr-H})$ 1580 cm^{-1} , $\nu(\text{Zr-D})$ 1130 cm^{-1} ; $\nu(\text{C-O})$ 1205 cm^{-1} , $\nu(^{13}\text{C-O})$ 1180 cm^{-1}), and most characteristically by ^1H and ^{13}C NMR data for $\{(\eta^5\text{-C}_5\text{Me}_5)_2\text{ZrH}\}_2(\text{O}^{13}\text{CH}=\text{CHO})$, prepared from **2** and ^{13}CO : an AA'XX' pattern¹¹ for the H and ^{13}C atoms of the $(-\text{O}^{13}\text{CH}=\text{CHO}-)$ bridge (Table I).

Furthermore, **5** reacts smoothly with methyl iodide to afford methane and $\{(\eta^5\text{-C}_5\text{Me}_5)_2\text{ZrI}\}_2(\text{OCH}=\text{CHO})$ (**6**). The IR spectrum ($\nu(\text{C-O})$ 1195 cm^{-1} , $\nu(^{13}\text{C-O})$ 1175 cm^{-1}) and ^1H and ^{13}C NMR data for **6** (Table I) indicate a structure analogous to that for **5**. The preliminary results of an x-ray structure determination for **6** are fully in accord with that suggested above, although some difficulties in final refinement have been encountered.¹²

$\{(\eta^5\text{-C}_5\text{Me}_5)_2\text{ZrH}\}_2(\text{OCH}=\text{CHO})$ (**5**) is also obtained when $(\eta^5\text{-C}_5\text{Me}_5)_2\text{ZrH}_2(\text{CO})$ (**4**) is warmed under an atmosphere of H_2 . When **4** is allowed to warm in the presence of both H_2 and $(\eta^5\text{-C}_5\text{Me}_5)_2\text{ZrH}_2$ (**2**), however, both $(\eta^5\text{-C}_5\text{Me}_5)_2\text{Zr}(\text{H})(\text{OCH}_3)$ (**16**) and **5** are formed; **2** is quantitatively recovered.⁵ The relative yields of **5** and **16** depend on the amount of **2** which is added. Thus with a 1.29 molar ratio of **2**:**4**, **16** and **5** are obtained in a 12:1 molar ratio; whereas with **2**:**4** = 0.22, **16** and **5** are formed in a 0.74:1 molar ratio. In addition we find that slow diffusion of CO into an N_2 -blanketed solution of $(\eta^5\text{-C}_5\text{Me}_5)_2\text{ZrH}_2$ (**2**) at 25°C (conditions for which there is continuously a high ratio of **2**:**4**) affords only $(\eta^5\text{-C}_5\text{Me}_5)_2\text{Zr}(\text{H})(\text{OCH}_3)$ (no detectable **5**) and a transient dark red color characteristic of $\{(\eta^5\text{-C}_5\text{Me}_5)_2\text{ZrN}_2\}_2\text{N}_2$ and/or $\{(\eta^5\text{-C}_5\text{Me}_5)_2\text{Zr}(\text{CO})\}_2\text{N}_2$.^{6,7} After several hours at 25°C the final solution contains a 1:1 mixture of $(\eta^5\text{-C}_5\text{Me}_5)_2\text{Zr}(\text{H})(\text{OCH}_3)$ and $(\eta^5\text{-C}_5\text{Me}_5)_2\text{Zr}(\text{CO})_2$:



2. Reactions of $(\eta^5\text{-C}_5\text{Me}_5)_2\text{Zr}(\text{CH}_3)_2$ and $(\eta^5\text{-C}_5\text{Me}_5)_2\text{Zr}(\text{CH}_2(\text{CH}_2)_2\text{CH}_2)$ with CO. In order to provide a basis for understanding the apparent migratory insertion of CO into a Zr-H bond for $(\eta^5\text{-C}_5\text{Me}_5)_2\text{ZrH}_2(\text{CO})$, we have investigated the reactivity of zirconium alkyls toward CO. The preparation of $(\eta^5\text{-C}_5\text{Me}_5)_2\text{Zr}(\text{CH}_3)_2$ (**7**) follows that previously described for the parent compound $(\eta^5\text{-C}_5\text{H}_5)_2\text{Zr}(\text{CH}_3)_2$:¹³

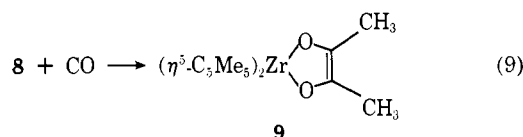


The latter has been reported to add CO reversibly affording $(\eta^5\text{-C}_5\text{H}_5)_2\text{Zr}(\text{CH}_3)(\text{CH}_3\text{CO})$, which was structurally characterized by x-ray diffraction methods.¹⁴ Similarly **7** reacts with CO (1 atm) in benzene solution according to the equation

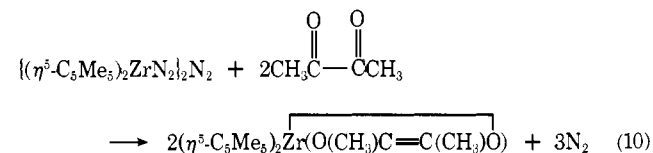


Isolation of $(\eta^5\text{-C}_5\text{Me}_5)_2\text{Zr}(\text{CH}_3)(\text{CH}_3\text{CO})$ (**8**) has not been possible owing to its lability and high solubility; however, the similarity of its ¹H NMR spectrum (Table I) and infrared spectrum ($\nu(\text{C-O})$ 1537 cm^{-1} (THF solution)) to those for $(\eta^5\text{-C}_5\text{H}_5)_2\text{Zr}(\text{CH}_3)(\text{CH}_3\text{CO})$ ($[\eta^5\text{-C}_5\text{H}_5]$ singlet, δ 5.35 (10 H), CH_3CO singlet δ 2.41 (3 H), ZrCH_3 singlet, δ 0.45 (3 H); $\nu(\text{C-O})$ 1545 cm^{-1} (Nujol mull)) leaves little doubt that the two acyl methyl compounds are isostructural.

8 reacts further with CO at 70 °C in benzene over a period of several hours to afford only $(\eta^5\text{-C}_5\text{Me}_5)_2\text{Zr}(\text{O}(\text{CH}_3)\text{C}=\text{C}(\text{CH}_3)\text{O})$ (**9**). This structure is supported by ¹H NMR

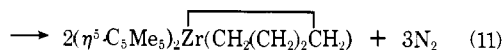


(Table I), analytical, mass spectral, and infrared data (see Experimental Section), and by the fact that **9** may be prepared independently by reaction of $\{(\eta^5\text{-C}_5\text{Me}_5)_2\text{ZrN}_2\}_2\text{N}_2$ with biacetyl (eq 10). In contrast to the quantitative conversion of

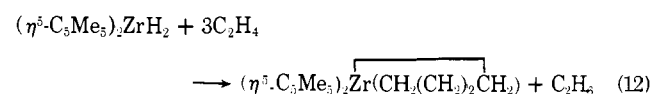


8 to **9**, $(\eta^5\text{-C}_5\text{H}_5)_2\text{Zr}(\text{CH}_3)(\text{CH}_3\text{CO})$ undergoes a complicated series of reactions with CO at 70 °C (benzene) leading to several products.

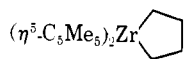
$\{(\eta^5\text{-C}_5\text{Me}_5)_2\text{ZrN}_2\}_2\text{N}_2$ absorbs ethylene (4.2 mol/mol **1**) at 25 °C in toluene solution with evolution of N₂ to afford $(\eta^5\text{-C}_5\text{Me}_5)_2\text{Zr}(\text{CH}_2(\text{CH}_2)_2\text{CH}_2)$ (**10**) in nearly quantitative yield (eq 11). **10** is also obtained from $(\eta^5\text{-C}_5\text{Me}_5)_2\text{ZrH}_2$ and $\{(\eta^5\text{-C}_5\text{Me}_5)_2\text{ZrN}_2\}_2\text{N}_2 + 4\text{C}_2\text{H}_4$



ethylene at 25 °C according to the equation

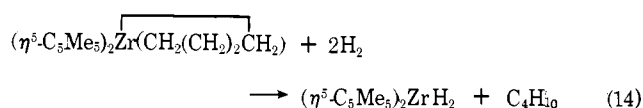
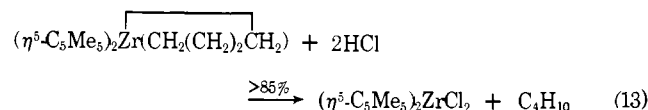


¹H NMR (Table I) and infrared data (see Experimental Section) are most consistent with a structure containing the zirconacyclopentane moiety. Furthermore, **10** reacts with 2

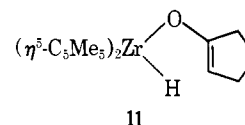


10

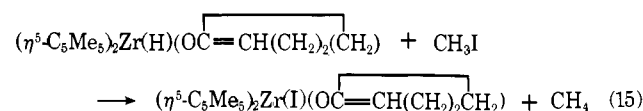
equiv of HCl according to eq 13 and with excess H₂ (eq 14) to yield predominantly butane.



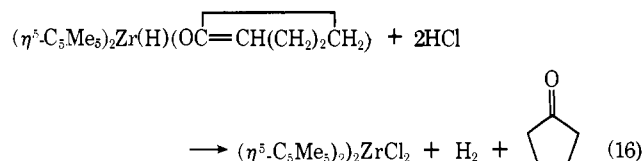
$(\eta^5\text{-C}_5\text{Me}_5)_2\text{Zr}(\text{CH}_2(\text{CH}_2)_2\text{CH}_2)$ absorbs CO (1.0 mol/mol **10**) rapidly at 25 °C to yield a white crystalline product (**11**) together with a small amount (~5%) of $(\eta^5\text{-C}_5\text{Me}_5)_2\text{Zr}(\text{CO})_2$. **11** may also be obtained by prolonged photolysis ($\lambda > 480$ nm) of toluene solutions of $(\eta^5\text{-C}_5\text{Me}_5)_2\text{Zr}(\text{CO})_2$ under ethylene. On the basis of its physical properties and its chemical reactivity, **11** appears to have the structure shown. Thus the



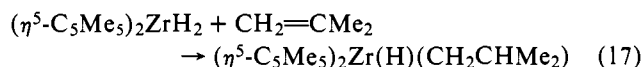
¹H NMR spectrum of **11** (benzene-*d*₆) exhibits a singlet at δ 1.97 (30 H) attributable to the methyl groups of the $[\eta^5\text{-C}_5(\text{CH}_3)_5]$ rings, a singlet at δ 6.07 (1 H) due to the Zr-H moiety, a multiplet at δ 4.42 (1 H) due to the vinylic hydrogen, and a broad multiplet in the region δ 2.0–2.5 (6 H) attributable to the methylene hydrogens of the cyclopentene ring. The ¹H NMR spectrum of **11** prepared from **10** and ¹³CO shows no large splitting of any of these resonances, indicating that no hydrogen atoms are bonded directly to the ¹³C atom in **11**. Its infrared spectrum exhibits characteristic bands at 1628 ($\nu(\text{C}=\text{C})$), 1275 ($\nu(\text{C}-\text{O})$), and 1538 cm^{-1} ($\nu(\text{Zr}-\text{H})$), the first two bands shifting to 1595 and 1250 cm^{-1} for **11** prepared from **10** and ¹³CO. Furthermore, **11** reacts smoothly with methyl iodide to yield $(\eta^5\text{-C}_5\text{Me}_5)_2\text{Zr}(\text{I})(\text{OC}=\text{CH}(\text{CH}_2)_2\text{CH}_2)$ (**12**) with the evolution of CH₄ (0.94 mol/mol **11**) according to eq 15. As expected, infrared and ¹H NMR spectra



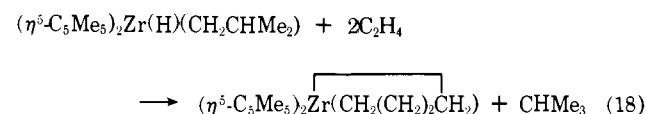
(Table I) for **12** are nearly identical with those for **11** with the notable absence of the IR band at 1538 cm^{-1} and the NMR resonance at δ 6.07 attributed to the Zr-H moiety of **11**. Treatment of **11** with HCl in diethyl ether affords cyclopentanone in moderate yields (55% GLC).



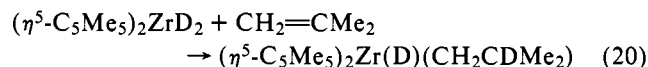
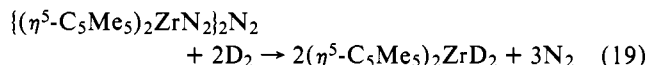
3. Reaction of $(\eta^5\text{-C}_5\text{Me}_5)_2\text{Zr}(\text{H})(\text{CH}_2\text{CHMe}_2)$ with CO. Benzene solutions of $(\eta^5\text{-C}_5\text{Me}_5)_2\text{ZrH}_2$ (**2**) react with excess isobutylene over a period of several minutes at room temperature to afford $(\eta^5\text{-C}_5\text{Me}_5)_2\text{Zr}(\text{H})(\text{CH}_2\text{CHMe}_2)$ (**13a**) in nearly quantitative yield (NMR).



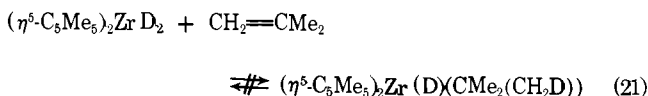
The contrast between the reactivity of $(\eta^5\text{-C}_5\text{Me}_5)_2\text{ZrH}_2$ with isobutylene and that with ethylene (eq 12) may be attributed to steric factors. The stability of **13** is indeed remarkable: benzene solutions are stable for hours at 50 °C, even in the presence of excess isobutylene.¹⁵ When treated with ethylene at 25 °C, however, **13** is smoothly converted to **10** with release of isobutane (eq 18).



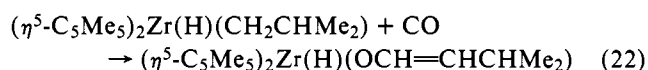
$(\eta^5\text{-C}_5\text{Me}_5)_2\text{Zr}(\text{D})(\text{CH}_2\text{CDMe}_2)$ (**13b**) may be prepared according to the equations



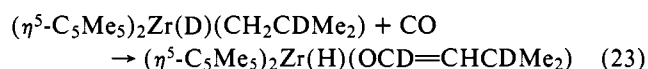
This sequence must be carried out below 5 °C to avoid deuterium exchange with methyl hydrogens of the pentamethylcyclopentadienyl groups for $(\eta^5\text{-C}_5\text{Me}_5)_2\text{ZrD}_2$.¹⁶ The addition of isobutylene appears to be entirely regiospecific, since ¹H NMR spectra for **13b** (Table I) indicate no scrambling (<5%) of deuterium with the isobutyl methyl hydrogens, as would be expected if $(\eta^5\text{-C}_5\text{Me}_5)_2\text{Zr}(\text{D})(\text{CMe}_2(\text{CH}_2\text{D}))$ were reversibly formed (eq 21).



$(\eta^5\text{-C}_5\text{Me}_5)_2\text{Zr}(\text{H})(\text{CH}_2\text{CHMe}_2)$ (**13a**) reacts with CO rapidly in toluene at 25° to afford $(\eta^5\text{-C}_5\text{Me}_5)_2\text{Zr}(\text{H})(\text{OCH}=\text{CHCHMe}_2)$ (**15a**) (eq 22) together with a small amount (ca. 5%) of $(\eta^5\text{-C}_5\text{Me}_5)_2\text{Zr}(\text{CO})_2$. This reaction was monitored at low temperature by ¹H NMR spectrometry (toluene-*d*₈). At -50 °C under 1 atm CO, **13a** is slowly converted to a new species which is assigned the structure $(\eta^5\text{-C}_5\text{Me}_5)_2\text{Zr}(\text{H})(\text{Me}_2\text{CHCH}_2\text{CO})$ (**14a**) on the basis of its ¹H NMR spectrum (Table I) and by analogy with $(\eta^5\text{-C}_5\text{Me}_5)_2\text{Zr}(\text{CH}_3)(\text{CH}_3\text{CO})$ (see Scheme II). That this transient intermediate is the acyl, not formyl, derivative is further supported by the ¹H NMR data for **14c** obtained from **13a** and ¹³C. Thus the magnitude of the ¹³C coupling to the hydride and methylene hydrogen atoms (9 and 5 Hz, respectively) for $(\eta^5\text{-C}_5\text{Me}_5)_2\text{Zr}(\text{H})(\text{Me}_2\text{CHCH}_2^{13}\text{CO})$ (**14c**) rules out such a possibility (cf. ¹J_{13C-H} = 173 Hz for **15c**, Table I). Further warming of these solutions to -20 °C leads to rearrangement of **14** to the final product $(\eta^5\text{-C}_5\text{Me}_5)_2\text{Zr}(\text{H})(\text{OCH}=\text{CHCHMe}_2)$ (**15**).



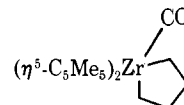
Significantly, $(\eta^5\text{-C}_5\text{Me}_5)_2\text{Zr}(\text{D})(\text{CH}_2\text{CDMe}_2)$ (**13b**) affords $(\eta^5\text{-C}_5\text{Me}_5)_2\text{Zr}(\text{H})(\text{OCD}=\text{CHCDMe}_2)$ (**15b**) when treated with CO (eq 23), thus indicating that both the isobutyl and hydride moieties are transferred to the carbonyl carbon atom and that hydrogen which ultimately resides at zirconium originates at the methylene carbon of the isobutyl group.



The mechanistic implications of these results are discussed in the following section.

Discussion

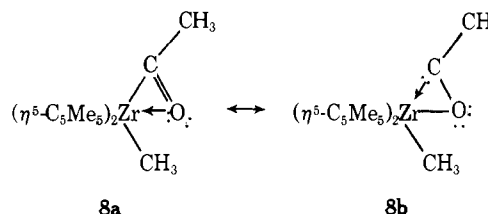
These alkyl and hydride derivatives of bis(pentamethylcyclopentadienyl)zirconium undergo facile reactions with carbon monoxide to yield final products in which the carbonyl oxygen is bonded to zirconium. In the case of $(\eta^5\text{-C}_5\text{Me}_5)_2\text{ZrH}_2$ the initial carbonyl adduct, $(\eta^5\text{-C}_5\text{Me}_5)_2\text{ZrH}_2(\text{CO})$, has been identified and shown to have a structure with CO carbon bonded to zirconium in the central equatorial position (Scheme I). Similar structures may be reasonably assumed for the initial carbonyl adducts of $(\eta^5\text{-C}_5\text{Me}_5)_2\text{Zr}(\text{CH}_3)_2$ and $(\eta^5\text{-C}_5\text{Me}_5)_2\text{Zr}(\text{H})(\text{CH}_2\text{CHMe}_2)$. However, for $(\eta^5\text{-C}_5\text{Me}_5)_2\text{Zr}(\text{CH}_2(\text{CH}_2)_2\text{CH}_2)$, it appears more reasonable that the adduct has the structure shown below, since the alternative



with CO positioned within the five-membered ring must be highly unfavorable.

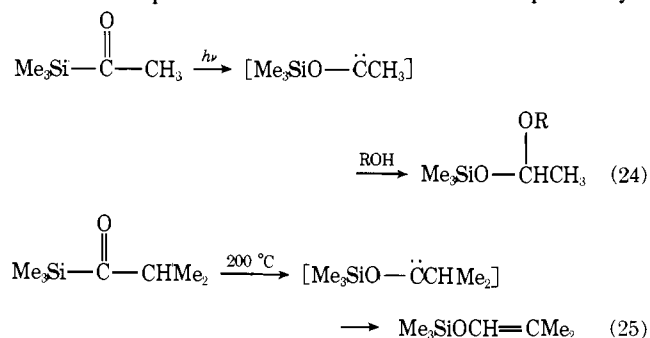
Subsequent migratory insertion of CO into Zr-alkyl or Zr-H bonds occurs with remarkable facility in all cases. The results of the study of the reaction of $(\eta^5\text{-C}_5\text{Me}_5)_2\text{Zr}(\text{H})(\text{CH}_2\text{CHMe}_2)$ with ¹³CO establish that alkyl migration is favored over hydride migration for this system. Indeed, initial quantitative conversion of $(\eta^5\text{-C}_5\text{Me}_5)_2\text{ZrH}_2$ to $(\eta^5\text{-C}_5\text{Me}_5)_2\text{ZrH}_2(\text{CO})$ vis-à-vis formation of acyls from CO and $(\eta^5\text{-C}_5\text{Me}_5)_2\text{Zr}(\text{CH}_3)_2$ and $(\eta^5\text{-C}_5\text{Me}_5)_2\text{Zr}(\text{H})(\text{CH}_2\text{CHMe}_2)$ without buildup of detectable concentrations of their carbonyl adducts bespeaks the relative ease of alkyl as compared to hydride migration.

The facility of these migratory insertions and the subsequent reactivity of these acyl and formyl complexes may be ascribed to the unusual bonding mode of these groups to zirconium. A "side-on" coordination of the acyl group has recently been established by Floriani and co-workers for $(\eta^5\text{-C}_5\text{H}_5)_2\text{Zr}(\text{CH}_3)(\text{CH}_3\text{CO})$ ¹⁴ and $(\eta^5\text{-C}_5\text{H}_5)_2\text{TiCl}(\text{CH}_3\text{CO})$.¹⁷ Analogous "side-on" bonding of acyl and formyl groups is strongly inferred in these bis(pentamethylcyclopentadienyl)zirconium systems in light of the structure features shared by all of these compounds. Indeed, the similarity of infrared and ¹H NMR data for $(\eta^5\text{-C}_5\text{Me}_5)_2\text{Zr}(\text{CH}_3)(\text{CH}_3\text{CO})$ to those for $(\eta^5\text{-C}_5\text{H}_5)_2\text{Zr}(\text{CH}_3)(\text{CH}_3\text{CO})$ dictates nearly identical structures. Interaction of an acyl oxygen lone pair of electrons with the empty, low-lying orbital located in the equatorial plane of the $(\eta^5\text{-C}_5\text{Me}_5)_2\text{Zr}$ moiety enables the zirconium atom to achieve a full 18-electron valence shell (**8a**). An additional resonance structure (**8b**) can also contribute to the bonding,



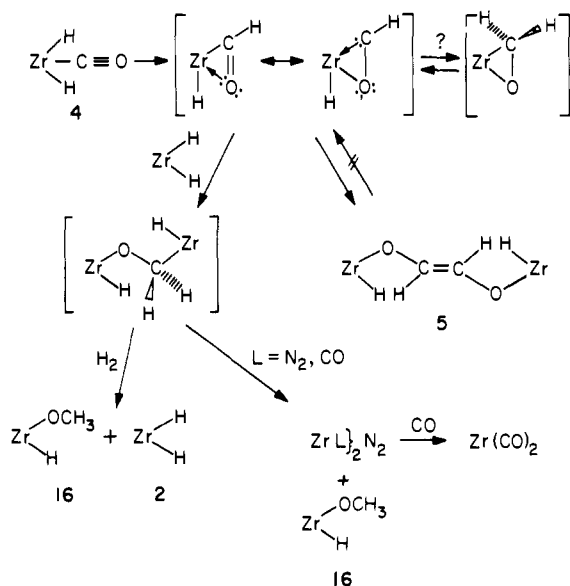
however. In this representation the acyl group is bonded to zirconium both by a full covalent zirconium-oxygen bond and a dative interaction of the oxycarbene lone pair completing the valence shell at zirconium. The resultant carbenoid character of the acyl center allows rationalization of many of the reaction patterns observed in these systems.

The products obtained from pyrolysis or photolysis of acylsilanes have been shown to arise via siloxycarbene intermediates.^{18,19} Subsequent reactions of these oxycarbene intermediates include dimerization, insertion into O-H bonds of solvent alcohol, and intramolecular insertion into α C-H bonds.²⁰ The products obtained from reactions of permethyl-

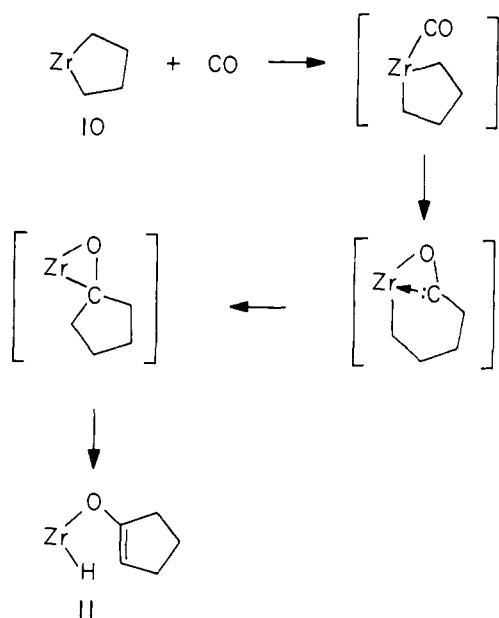


zirconocene acyl and formyl intermediates appear to derive from similar processes.

Scheme I



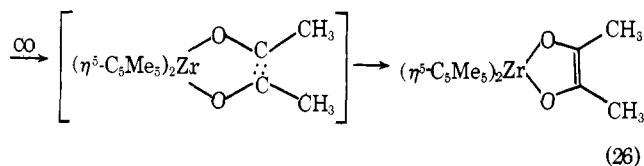
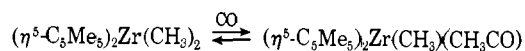
Scheme II



Although we have not yet directly detected the presumed formyl hydride intermediate proposed in Scheme I, dimerization of an incipient oxymethylene species, $(\eta^5\text{-C}_5\text{Me}_5)_2\text{Zr}(\text{H})(\text{OCH})$, would provide a reasonable pathway to the product, $\{(\eta^5\text{-C}_5\text{Me}_5)_2\text{ZrH}\}_2(\mu\text{-OCH}=\text{CHO})$. A trans stereochemistry about the enediolate bridge is imposed by the steric bulk of the $[(\eta^5\text{-C}_5\text{Me}_5)_2\text{ZrH}]$ units. In the presence of $(\eta^5\text{-C}_5\text{Me}_5)_2\text{ZrH}_2$, insertion of the oxymethylene into one of the zirconium hydride bonds would be expected to compete with dimerization. Subsequent reductive elimination of $(\eta^5\text{-C}_5\text{Me}_5)_2\text{ZrH}(\text{OCH}_3)$, induced by H₂ or by good π -acid ligands such as CO and N₂,¹⁵ thus yields concurrently $(\eta^5\text{-C}_5\text{Me}_5)_2\text{ZrH}_2$ or $\{(\eta^5\text{-C}_5\text{Me}_5)_2\text{ZrL}\}_2\text{N}_2$ (L = CO, N₂),^{6,7} respectively (Scheme I). A reversible and competing intramolecular insertion of the oxymethylene into the remaining zirconium hydride bond of $(\eta^5\text{-C}_5\text{Me}_5)_2\text{ZrH}(\text{OCH})$ to afford a formaldehyde adduct may occur; however, such a pathway appears nonproductive in this system.²¹

The reactivity of $(\eta^5\text{-C}_5\text{Me}_5)_2\text{Zr}(\text{CH}_3)(\text{CH}_3\text{CO})$ with additional carbon monoxide may be similarly rationalized. Thus insertion of CO into the remaining Zr-CH₃ bond pro-

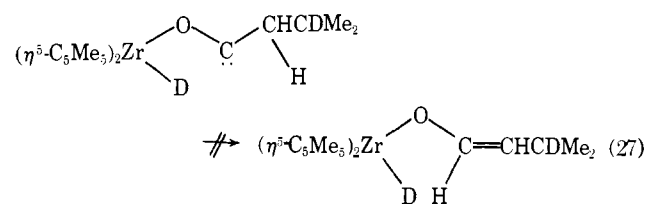
vides a bis(acetyl) and, hence, functionally a bis(oxycarbene) complex which undergoes subsequent intramolecular dimerization to $(\eta^5\text{-C}_5\text{Me}_5)_2\text{Zr}(\text{O}(\text{CH}_3)\text{C}=\text{C}(\text{CH}_3)\text{O})$.



The reaction of the zirconacyclopentane complex $(\eta^5\text{-C}_5\text{Me}_5)_2\text{Zr}(\text{CH}_2(\text{CH}_2)_2\text{CH}_2)$ (10) with carbon monoxide appears to take a somewhat different course, however. Unlike $(\eta^5\text{-C}_5\text{Me}_5)_2\text{Zr}(\text{CH}_3)_2$ (7), 10 reacts instantaneously with CO at 25 °C to yield an enolate hydride. Although we have little information available concerning the mechanism of this reaction, the formation of the final product 11 may be rationalized by assuming that the reaction of 10 with CO proceeds as outlined in Scheme II. Thus insertion of CO into the zirconacyclopentane ring would generate an acyl which is forced by ring strain to have its acyl carbon cis to the remaining zirconium-carbon bond of the metallocycle. This proximity and the incipency of a five-membered ring may encourage a second insertion, this time of the oxycarbene into the second Zr-C bond, thus affording a cyclopentanone adduct of permethylzirconocene. The final step would then involve simple β-hydride abstraction to yield the observed enolate hydride derivative.

Whitesides, McDermott, and Wilson have investigated the reaction of the related, but much less stable, titanacyclopentane derivative, $(\eta^5\text{-C}_5\text{H}_5)_2\text{Ti}(\text{CH}_2(\text{CH}_2)_2\text{CH}_2)$, with CO and have observed formation of free cyclopentanone, presumably by reductive elimination from a cyclic acyl intermediate.²² Conversely, we observe no free cyclopentanone²¹ in our system, although this ketone may be obtained in good yield by treatment of $(\eta^5\text{-C}_5\text{Me}_5)_2\text{Zr}(\text{H})(\text{OC}=\text{CHCH}_2\text{CH}_2\text{CH}_2)$ with HCl.

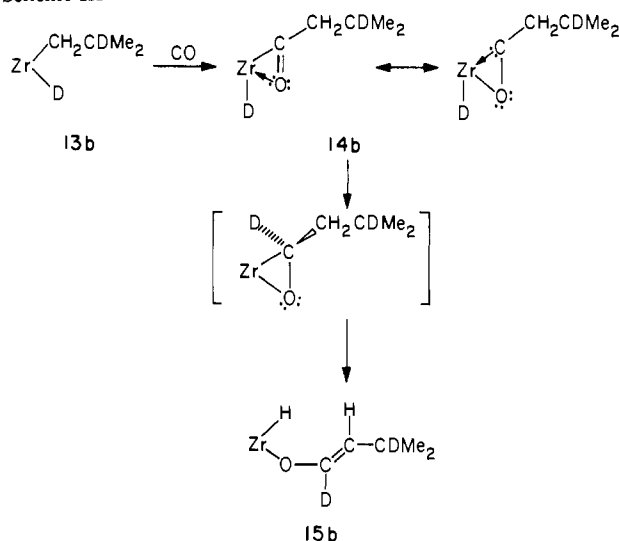
The reaction of the isobutyl hydride derivative, $(\eta^5\text{-C}_5\text{Me}_5)_2\text{Zr}(\text{H})(\text{CH}_2\text{CHMe}_2)$ (13), with carbon monoxide proved to be mechanistically the most transparent of the systems we have investigated thus far. Rearrangement of the initial product, $(\eta^5\text{-C}_5\text{Me}_5)_2\text{Zr}(\text{H})(\text{Me}_2\text{CHCH}_2\text{CO})$ (14), to the enolate hydride, $(\eta^5\text{-C}_5\text{Me}_5)_2\text{Zr}(\text{H})(\text{OCH}=\text{CHCHMe}_2)$ (15), could be taken as an indication that this oxycarbenoid undergoes insertion into adjacent carbon-hydrogen bonds (eq 27), as is observed for free oxycarbenes. The



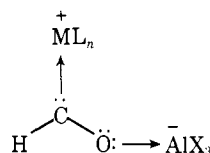
results of the deuterium labeling studies (eq 23) clearly rule out this simple mechanism, however, and suggest that outlined in Scheme III. Thus the final location of the deuterium which originally resides at zirconium indicates that the oxycarbenoid prefers to insert into the Zr-H bond, reminiscent of the proposed reaction of the oxymethylene species $(\eta^5\text{-C}_5\text{Me}_5)_2\text{Zr}(\text{H})(\text{OCH})$ with $(\eta^5\text{-C}_5\text{Me}_5)_2\text{ZrH}_2$. Such insertion provides the aldehyde adduct, which can undergo subsequent β-hydride abstraction thus affording the enolate hydride 15.

Carbonylation of hydride and alkyl derivatives of permethylzirconocene leads in some instances to products similar to those which might have been expected with more familiar (e.g., group 8) organometallic compounds; albeit enolate hy-

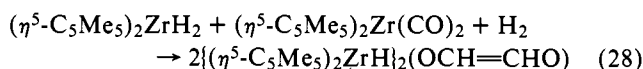
Scheme III



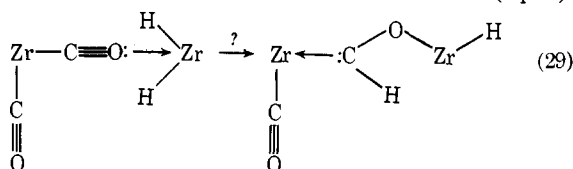
drides, rather than aldehydes or ketones, are produced. In other cases products are derived from coupling of carbonyl carbon atoms (**5** and **9**). These reaction patterns may be rationalized most simply on the basis of an "oxycarbenoid" reactivity imparted to carbon by the unusual coordination of the acyl (or formyl) group to the permethylzirconocene moiety. The reductive coupling of CO is reminiscent of the Fischer-Tropsch synthesis of linear alkanes from carbon monoxide and hydrogen,^{23,24} and may implicate "side-on" formyl and acyl intermediates in this process. In this context it is interesting to note that homogeneous reduction of CO to produce alcohols or hydrocarbons of carbon number greater than one has been possible thus far only in systems containing either alkyl aluminum hydrides²⁵ or aluminum chloride,⁴ respectively. Both of these reagents (or their degradation products) may function as powerful Lewis acids, suggesting that oxycarbene structures such as that shown below might mediate these reactions.



Facile migratory insertion of CO into zirconium hydride bonds is clearly implied in the reaction of $(\eta^5\text{-C}_5\text{Me}_5)_2\text{ZrH}_2$ with carbon monoxide. It is important to note, however, that our results do not require an intramolecular rearrangement of $(\eta^5\text{-C}_5\text{Me}_5)_2\text{ZrH}_2(\text{CO})$ to $(\eta^5\text{-C}_5\text{Me}_5)_2\text{Zr}(\text{H})(\text{OCH})$. The hydridic character of the hydrogen ligands in these compounds suggests that formyl intermediates may be generated by an alternative mechanism analogous to the reduction of coordinate CO by boron hydrides.²⁶⁻²⁸ The observation that $(\eta^5\text{-C}_5\text{Me}_5)_2\text{ZrH}_2$ (**2**) reduces $(\eta^5\text{-C}_5\text{Me}_5)_2\text{Zr}(\text{CO})_2$ to $\{(\eta^5\text{-C}_5\text{Me}_5)_2\text{ZrH}_2(\mu\text{-OCH=CHO})\}$ in quantitative yield over several hours at 25 °C



does indeed suggest that **2** could serve to transfer hydride to CO which is coordinated to another zirconium center (eq 29).



Nonetheless, we see no compelling reason to discard intramolecular hydride transfer for the rearrangement of $(\eta^5\text{-C}_5\text{Me}_5)_2\text{ZrH}_2(\text{CO})$ to $(\eta^5\text{-C}_5\text{Me}_5)_2\text{Zr}(\text{H})(\text{OCH})$, especially considering the much faster rate for the conversion of $(\eta^5\text{-C}_5\text{Me}_5)_2\text{ZrH}_2(\text{CO})$ to $\{(\eta^5\text{-C}_5\text{Me}_5)_2\text{ZrH}_2(\text{OCH=CHO})\}$ relative to that for eq 28. Hopefully, the results of kinetic studies and our attempts to model some of these steps with isocyanides will shed more light on these crucial points.

Experimental Section

General Considerations. All of the manipulations were carried out using either high vacuum line or glove box techniques. Solvents were purified by vacuum transfer first from LiAlH_4 , then from "titanocene", prepared as described earlier.²⁹ NMR solvents, benzene- d_6 and toluene- d_8 (Stohler, Inc.), were vacuum transferred from "titanocene". Hydrogen and deuterium (MCB) were purified by passage over activated 4 Å molecular sieves and MnO on vermiculite.³⁰ Carbon monoxide (MCB) was used directly from the cylinder. Isobutylene (MCB) and ethylene (Union Carbide) were transferred through a trap at -78 °C.

¹H NMR spectra were recorded using Varian A-60A, EM-390, or HR-220 spectrometers. ¹³C NMR spectra were obtained using a T-60 (FT) spectrometer. Infrared spectra were measured on Perkin-Elmer 180 and 457 and Beckman IR-12 spectrophotometers.

Several reactions were carried out in sealed NMR tubes and monitored by NMR spectrometry. A typical example is the reaction of $(\eta^5\text{-C}_5\text{Me}_5)_2\text{ZrH}_2$ (**2**) with CO: ca. 20 mg (0.05 mmol) of **2** was transferred to an NMR tube sealed to a ground glass joint and fitted with a Teflon needle valve adapter. Toluene- d_8 (0.3 mL) was distilled into the tube at -78 °C, 1 atm of carbon monoxide was introduced, and the tube was sealed with a torch.

Procedures. $(\eta^5\text{-C}_5\text{Me}_5)_2\text{ZrH}_2$. To **1** (206 mg, 0.255 mmol) was condensed 10 mL of toluene at -78 °C, H_2 (4.156 mmol) was introduced, and the reaction mixture was allowed to warm to 25 °C. After stirring for 2 h at 25 °C the color changed from dark red to pale blue.³¹ The residual N_2/H_2 mixture was passed through a series of liquid N_2 cooled traps and collected via a Toepler pump. $\text{N}_2 + \text{H}_2$ amounted to 4.371 mmol. This mixture was cycled over CuO at 320 °C to convert H_2 to H_2O , which was removed in a liquid N_2 cooled trap. N_2 (0.732 mmol, 2.87 mmol/mmol **1**) remained. Thus residual H_2 was 3.639 mmol, and H_2 consumed was 0.517 mmol (1.01 mmol/mmol Zr). The residue obtained after removal of toluene in vacuo was taken up in 10 mL of petroleum ether and filtered. The filtrate was cooled to -78 °C and crystalline **2** precipitated. The crystalline slurry was filtered off and the filtrate and crystalline mass were dried in vacuo, isolated yield 133 mg (72%). Anal. Calcd for $\text{C}_{20}\text{H}_{32}\text{Zr}$: C, 66.10; H, 8.80. Found: C, 66.29; H, 8.54. Molecular weight determined cryoscopically for 85.7 mg of **2** per g of C_6H_6 : 402 ± 30 (calculated 394).

$(\eta^5\text{-C}_5\text{Me}_5)_2\text{ZrH}_2(\text{PF}_3)$. To 68.1 mg (0.187 mmol) of **2** was condensed 8 mL of toluene at -78 °C, PF_3 (0.395 mmol) was introduced, and the reaction mixture was stirred for 30 min at this temperature. The color of the solution changed from yellow to red-brown. Residual gases were passed into a liquid N_2 cooled trap. Toepler pump analysis indicated no H_2 evolution. After the trap containing PF_3 was warmed to -78 °C, residual PF_3 was collected. PF_3 remaining amounted to 0.229 mmol; thus PF_3 consumed was 0.166 mmol (0.888 mmol/mmol **2**). **3** decomposed upon warming above ca. -20 °C as determined by NMR (Table I).

$(\eta^5\text{-C}_5\text{Me}_5)_2\text{ZrH}_2(\text{CO})$. To 157 mg (0.431 mmol) of **2** was condensed 8 mL of toluene at -80 °C. CO (2.102 mmol) was introduced and the mixture was stirred for 30 min at this temperature. Residual gas was passed through a series of liquid N_2 cooled traps via a Toepler pump, and CO collected was 1.667 mmol; thus CO absorbed amounted to 0.435 mmol (1.01 mmol/mol **2**). Treatment of the residual solution with 3 equiv of anhydrous HCl yielded a gas mixture consisting of 0.846 mmol CO/mol **2** and 1.77 mmol H_2 /mmol **2**, as determined by procedures similar to those described above. The residue after removal of toluene consisted of pure (NMR) $(\eta^5\text{-C}_5\text{Me}_5)_2\text{ZrCl}_2$.

In a separate experiment 0.215 mmol of $(\eta^5\text{-C}_5\text{Me}_5)_2\text{ZrH}_2(^{12}\text{CO})$ was prepared at -78 °C as described above; 1.224 mmol of ^{13}CO (Stohler, ^{12}CO 9.9%, ^{13}CO 90.1%) was admitted (ca. 0.5 atm). After 30 min of rapid stirring of the mixture at -78 °C, residual CO was collected. Mass spectrometry indicated that the composition was ^{12}CO 13.6%, ^{13}CO 86.4%. Thus 0.045 mmol of ^{12}CO appeared in the gas

phase as a result of exchange of 4-(^{12}CO) with the gas phase, corresponding to approximately 0.21 turnover according to eq 5.

$\{(\eta^5\text{-C}_5\text{Me}_5)_2\text{ZrH}\}(\mu\text{-OCH=CHO})$. Toluene solutions of **4**, prepared as described above, were allowed to warm slowly to 25 °C. The color of the solution deepened between -40 and -20 °C. No CO or H₂ evolution accompanied the reaction. Concentration of the toluene solution to 2 mL and addition of 10 mL of petroleum ether afforded yellow, microcrystalline **5** in ca. 70% yield. Anal. Calcd for C₂₁H₃₂OZr: C, 64.39; H, 8.24; Zr 23.29. Found: C, 64.09; H, 8.40; Zr, 23.30.

$\{(\eta^5\text{-C}_5\text{Me}_5)_2\text{Zr}\}_2(\mu\text{-OCH=CHO})$. **2** (758 mg, 2.085 mmol) was converted to **5** as described above. The resulting solution (20 mL of toluene) was cooled to -78 °C, 6 mmol of CH₃I was introduced, and the mixture was stirred while warming slowly to 25 °C. A gradual color change from yellow to orange occurred at 25 °C. The evolved CH₄ was collected by a Toepler pump as described above, and its identity as CH₄ was confirmed by quantitative recovery after cycling at 320 °C through CuO and by its IR spectrum. Methane amounted to 1.717 mmol (0.824 mmol/mmol Zr). Toluene and residual CH₃I were removed in vacuo. The residue was recrystallized from toluene/petroleum ether to afford 620 mg (57%) of **6**. Large, well-formed crystals were obtained by slow removal of solvent from a 1:1 benzene/toluene solution of **6** at 0 °C. Anal. Calcd for C₂₁H₃₁OIZr: C, 48.73; H, 6.04; I, 24.52; Zr, 17.62. Found: C, 49.03; H, 6.09; I, 24.20; Zr, 17.61.

Structure Determination for $\{(\eta^5\text{-C}_5\text{Me}_5)_2\text{Zr}\}_2(\mu\text{-OCH=CHO})$. A series of Weissenberg and precession photographs (Cu K α and Mo K α radiation) indicated a monoclinic unit cell with the systematic absences $h0l$, $h + l$ odd. A crystal of dimensions 0.5 × 0.25 × 0.15 mm was mounted in a glass capillary under N₂ with its long axis slightly skew to the ϕ axis of a G.E. XRD-5 quarter-circle diffractometer automated by Datex. Unit cell dimensions were obtained by a least-squares fit of the $\sin^2 \theta/\lambda^2$ values of 43 reflections measured on the diffractometer. Using Mo K α radiation monochromated with a graphite crystal, one hemisphere of data was measured between 1.5 and 43° in 2θ , using a θ - 2θ scan technique at a scan rate of 1°/min; 30-s background counts were taken before and after each scan. The scan width varied linearly from 2.3° at $2\theta = 5^\circ$ to 2.8° at $2\theta = 30^\circ$. Intensities of three check reflections measured every 100 reflections showed no crystal decomposition during data collection. Every reflection was collected in two equivalent octants and the data were averaged to form a unique monoclinic data set containing 5026 reflections. A variance $\sigma^2(F_o^2)$ was calculated for each reflection based on counting statistics plus a term $(0.02S)^2$ where S is the scan count. Intensities and their weights were corrected for Lorentz and polarization effects but not for absorption ($\mu = 19.4 \text{ cm}^{-1}$). The data were then placed on an absolute scale by means of a Wilson plot, with scattering factors for all atoms calculated by the method of Cromer and Mann.³² The zirconium and iodine atoms were treated as anomalous scatterers using values of $\Delta f'$ and $\Delta f''$ given by Cromer and Lieberman.³³ Reflections having $F_o^2 < 1.5 \sigma(F_o^2)$ were deleted, leaving 4344 reflections for the working data set.

$(\eta^5\text{-C}_5\text{Me}_5)_2\text{Zr}(\text{CH}_3)_2$. $(\eta^5\text{-C}_5\text{Me}_5)_2\text{ZrCl}_2$ (1 g, 2.3 mmol) was slurried in 30 mL of diethyl ether at -78 °C. A 2.3 M diethyl ether solution of methylolithium (2.5 mL, 5.75 mmol) was added via syringe, and the mixture was allowed to warm with stirring to room temperature. After 3 h at 25 °C the mixture was cooled to -78 °C, and 1 mL of methanol added to destroy excess methylolithium. Solvents were removed in vacuo, the residue was taken up in 60 mL of petroleum ether, the solution was filtered, and the filtrate was slowly cooled to -78 °C. White crystals of **7** precipitated. The crystalline mass was filtered off and dried under reduced pressure. Anal. Calcd for C₂₂H₃₆Zr: C, 67.50; H, 9.20; Zr, 23.30. Found: C, 67.33; H, 9.08; Zr, 23.52.

$(\eta^5\text{-C}_5\text{Me}_5)_2\text{Zr}(\text{OC}(\text{CH}_3)=\text{C}(\text{CH}_3)\text{O})$. A thick-walled glass reaction vessel with Teflon needle valve was charged with 0.30 g (0.75 mmol) of **7**, 10 mL of toluene, and 5 mmol (1 atm) of CO and heated at 75 °C for 24 h. The resulting solution was transferred to a sublimator in a glove box, solvent was removed in vacuo, and purple, microcrystalline **9** was collected by sublimation (100 °C, 10⁻⁴ Torr). Anal. Calcd for C₂₄H₃₆O₂Zr: C, 64.38; H, 8.10; Zr, 20.37. Found: C, 64.13; H, 7.92; Zr, 20.11. Mass spectrum m/e (rel intensity) M⁺ (for ⁹⁰Zr, ¹²C, ¹H, ¹⁶O): 446 (5), 451 (8), 450 (32), 449 (10), 448 (38), 447 (45), 446 (100), 403 (9), 311 (20), 241 (8), 223 (9), 152 (10), 137 (10), 119 (10), 43 (5).

$(\eta^5\text{-C}_5\text{Me}_5)_2\text{Zr}(\text{CH}_2(\text{CH}_2)_2\text{CH}_2)$. To 380 mg (0.471 mmol) of **1** in

15 mL of toluene was added 3.80 mmol of ethylene at -78 °C. The mixture was stirred as it was allowed to warm slowly to 25 °C. After 2 h at 25 °C residual gases were removed and passed through a series of liquid N₂ cooled traps. N₂ (1.35 mmol) (2.86 mmol/mmol **1**) was collected, then discarded. After all traps were warmed to -78 °C, 1.85 mmol of ethylene was collected; thus 1.95 mmol of C₂H₄ (2.07 mmol/mmol Zr) was consumed. Toluene was removed, and the bright yellow product was recrystallized from petroleum ether. Anal. Calcd for C₂₄H₃₈Zr: C, 69.00; H, 9.17; Zr, 21.84. Found: C, 68.76; H, 8.92; Zr, 21.57.

To a frozen solution of 200 mg (0.478 mmol) of **10** in 10 mL of toluene was added 0.96 mmol of anhydrous HCl at -196 °C, and the mixture was warmed to 25 °C. After 2 h the gases were separated and collected by a series of traps and a Toepler pump. Butane (0.405 mmol) (0.85 mmol/mmol **10**) was collected and identified by its infrared spectrum.

10 (30 mg) was dissolved in 0.5 mL of benzene-*d*₆ and sealed under 1 atm H₂ in a NMR tube. After several hours at 25 °C, the NMR spectrum indicated that **10** was converted to **2** and a 2:1 molar ratio of butane and ethane, respectively.

Reaction of Ethylene with $(\eta^5\text{-C}_5\text{Me}_5)_2\text{ZrH}_2$. To 253 mg (0.696 mmol) of **2** in 15 mL of toluene at -78 °C was added 4.19 mmol of ethylene. The mixture was stirred as it warmed slowly to 25 °C. After 2 h at 25 °C the residual gases (2.56 mmol) were collected by a Toepler pump and identified as a mixture of ethane and ethylene by IR. The residue was identified as **10** by ¹H NMR spectrometry.

$(\eta^5\text{-C}_5\text{Me}_5)_2\text{Zr}(\text{H})(\text{OC}=\text{CH}(\text{CH}_2)_2\text{CH}_2)$. To a stirred solution of 400 mg (0.958 mmol) of **10** in 15 mL of toluene at -78 °C was added 3.78 mmol of carbon monoxide. The mixture was stirred as it warmed slowly to 25 °C. After 2 h at 25 °C residual gases were collected by a Toepler pump; 2.60 mmol of carbon monoxide was collected; thus 1.08 mmol (1.13 mmol/mmol **10**) was absorbed. NMR analysis of the light tan powder indicated 95 mol % **11** and 5 mol % $(\eta^5\text{-C}_5\text{Me}_5)_2\text{-Zr}(\text{CO})_2$. Recrystallization from petroleum ether afforded white, crystalline **11**. Anal. Calcd for C₂₅H₃₈OZr: C, 67.35; H, 8.59; Zr, 20.46. Found: C, 67.56; H, 8.50; Zr, 21.03.

11 may also be obtained via photolysis of $(\eta^5\text{-C}_5\text{Me}_5)_2\text{Zr}(\text{CO})_2$ in the presence of ethylene: 40 mg of $(\eta^5\text{-C}_5\text{Me}_5)_2\text{Zr}(\text{CO})_2$, 0.5 mL of toluene-*d*₃, and 0.35 mmol of ethylene were sealed off in a NMR tube. Photolysis at 25 °C was carried out using a Hanovia medium-pressure Hg lamp filtered through a no. 3-71 Corning yellow sharp-cut filter with cutoff at 490 nm. The progress of the reaction was monitored by ¹H NMR spectrometry and was complete to **11** after 72 h. An identical sample stored in the dark for 72 h showed no reaction.

$(\eta^5\text{-C}_5\text{Me}_5)_2\text{Zr}(\text{I})(\text{OC}=\text{CH}(\text{CH}_2)_2\text{CH}_2)$. To 131 mg (0.294 mmol) of **11** in 10 mL of toluene was added 1.04 mmol of CH₃I at -78 °C. The solution was warmed slowly to 25 °C with stirring. After 2 h at 25 °C CH₄ (0.276 mmol, 0.94 mmol/mmol **11**) was collected by a Toepler pump and identified by its IR spectrum. The residue was identified as pure **12** by ¹H NMR spectrometry (Table I).

Reaction of $(\eta^5\text{-C}_5\text{Me}_5)_2\text{Zr}(\text{H})(\text{OC}=\text{CH}(\text{CH}_2)_2\text{CH}_2)$ with HCl. To a frozen solution of 173 mg (0.39 mmol) of **11** in 10 mL of diethyl ether at -196 °C was added 0.80 mmol of anhydrous HCl. The mixture was warmed slowly to 25 °C with stirring, volatiles were transferred to a flask in vacuo, and the solution was concentrated to 1 mL by removing diethyl ether at -80 °C. The remaining solution, analyzed by GLC using an OV-101 column and decane as internal standard, contained 0.21 mmol of cyclopentanone (55% yield).

$(\eta^5\text{-C}_5\text{Me}_5)_2\text{Zr}(\text{H})(\text{CH}_2\text{CHMe}_2)$. **2** (30 mg), 0.4 mmol of isobutylene, and 0.3 mL of benzene-*d*₆ were sealed in an NMR tube. Conversion of **2** to **13** was monitored by ¹H NMR spectrometry and found to be quantitative after several minutes at 34 °C. **13** was isolated as follows. To a solution of 580 mg (1.6 mmol) of **2** in 30 mL of petroleum ether (bp 30-60 °C) was admitted 5 mmol of isobutylene. After 1 h at 25 °C solvent and excess isobutylene were removed in vacuo, leaving 5 mL of solution. Slow cooling to -78 °C provided 390 mg (58%) of yellow, microcrystalline **13**, which was filtered off, washed with petroleum ether at -78 °C, and dried in vacuo. Anal. Calcd for C₂₄H₄₀Zr: C, 68.66; H, 9.61; Zr, 21.73. Found: C, 68.50; H, 9.38; Zr, 21.42.

$(\eta^5\text{-C}_5\text{Me}_5)_2\text{Zr}(\text{D})(\text{CH}_2\text{CDMe}_2)$ was prepared from $(\eta^5\text{-C}_5\text{Me}_5)_2\text{ZrD}_2$, obtained via treatment of a pentane slurry of **1** with 1 atm of D₂ at 0 °C for 1 h, by treatment with excess isobutylene for 4 h at 0 °C. **13b** was isolated as described above.

$(\eta^5\text{-C}_5\text{Me}_5)_2\text{Zr}(\text{H})(\text{OCH}=\text{CHCHMe}_2)$. A solution of 210 mg (0.5 mmol) of **13** in pentane was cooled to -78 °C, 1 atm of CO was ad-

mitted, and the solution was allowed to warm slowly to room temperature with stirring. Solvent was removed in vacuo to leave an orange oil. Analysis of this residue by ^1H NMR indicated 95 mol % **15** with 5 mol % $(\eta^5\text{-C}_5\text{Me}_5)_2\text{Zr}(\text{CO})_2$. A diethyl ether solution (15 mL) of 140 mg of **15** was treated with 0.4 mL of 12 M HCl at -80°C , and the mixture was stirred as it warmed slowly to room temperature. After 1 h the volatiles were removed in vacuo at -78°C , the solution was warmed and filtered, and the filtrate was dried over 4 \AA molecular sieves. The remaining organic layer was transferred in vacuo and the volatile fraction analyzed by GLC (SE-30 column). Isovaleraldehyde, identified by comparison to an authentic sample, was the only detectable compound other than solvent.

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- (12) $(\eta^5\text{-C}_5\text{Me}_5)_2\text{Zr}(\mu\text{-OCH=CHO})_2$ crystallizes in the monoclinic space group Pn with $a = 17.137\text{ \AA}$, $b = 16.308\text{ \AA}$, $c = 17.179\text{ \AA}$, $\beta = 114.65^\circ$, $Z = 4$, $\rho_{\text{calcd}} = 1.58\text{ g cm}^{-3}$, and $\mu = 19.4\text{ cm}^{-1}$ with Mo $K\alpha$. Details of the data collection are described in the Experimental Section. A Patterson map showed the positions of all zirconium and iodine atoms, and several structure factor calculations interspersed by Fourier maps revealed the approximate locations of all remaining atoms. Unfortunately, disorder in the bridging $-\text{OCH=CHO}-$ moieties and a general inability to refine light atom positions made least-squares refinement difficult. It should be noted that the ratio $\sum Z_{\text{heavy}}^2 / \sum Z_{\text{light}}^2$ is 5.18 in this structure, a value far above the optimal ratio of 1.0 for the heavy atom method. Although exact positional parameters could not be defined, the gross features of the structure are in agreement with those indicated by the NMR results. The R factor $(\sum |F_o| - |F_c|) / \sum |F_o|$ is presently 0.09, based on 4344 reflections.
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