also thank the Eastman Kodak Co. for a fellowship (to M.E.T.). The use of the facilities at the University of South Carolina Regional NMR Center, funded by the National Science Foundation (Grant CHE82-07445), is acknowledged.

Registry No. $\{[HB(3,5\text{-}Me_2PZ)_3]Zr(O\text{-}t\text{-}Bu)_2Cl\}$, 87307-02-6; $\{[HB(3,5\text{-}Me_2PZ)_3]Zr(O\text{-}t\text{-}Bu)Me_2\}$, 87307-03-7; $\{[HB(3,5\text{-}Me_2PZ)_3]Zr(O\text{-}t\text{-}Bu)_2Me\}$, 87307-04-8; $\{[HB(3,5\text{-}Me_2PZ)_3]Zr(O\text{-}t\text{-}Bu)(\eta^2\text{-}C(Me)NCMe_3)Me\}$, 87307-05-9; $\{[HB(3,5\text{-}Me_2PZ)_3]Zr(O\text{-}t\text{-}Bu)(C{\equiv}CMe)_2\}$, 87307-06-0; $\{[HB(3,5\text{-}Me_2PZ)_3]ZR(O\text{-}t\text{-}Bu)_2(C{\equiv}CMe)\}$, 87318-58-9; $\{[HB(3,5\text{-}Me_2PZ)_3]Zr(O\text{-}t\text{-}Bu)_2(CY_2Ph)_2\}$, 87307-07-1; $\{[HB(3,5\text{-}Me_2PZ)_3]Zr(O\text{-}t\text{-}Bu)(\eta^2\text{-}C(CH_2Ph)NCMe_3)CH_2Ph\}$, 87307-08-2; $[HB(3,5\text{-}Me_2PZ)_3]ZrCl_3$, 80041-67-4; $[HB(3,5\text{-}Me_2PZ)_3]Zr(O\text{-}t\text{-}Bu)Cl_2$, 84695-13-6; KO-$t$-Bu, 865-47-4; MeBr, 74-83-9; t-BuOH, 75-65-0; t-BuNC, 7188-38-7; $MeC{\equiv}CLi$, 4529-04-8; $PhCH_2Cl$, 100-44-7; $PhCD_2OH$, 21175-64-4; $PhCD_2Cl$, 33712-34-4; methyl benzoate, 93-58-3.

Supplementary Material Available: Tables of fractional coordinates of H atoms and anisotropic thermal motion parameters and listings of structural factor amplitudes for $[HB(3,5\text{-}Me_2pz)_3]Zr(O\text{-}t\text{-}Bu)(\eta^2\text{-}C(Me)NCMe_3)Me$ (12 pages). Ordering information is given on any current masthead page.

Phosphinomethyl Complexes of Zirconium: Preparation, Complexation Capabilities, and Structural and Chemical Characteristics

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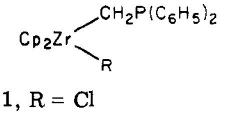
Received July 19, 1983

Syntheses of $Cp_2Zr(Cl)CH_2PPh_2$ (1) and $Cp_2Zr(CH_2PPh_2)_2$ (4) are described as is the X-ray crystal structure determination of the latter: monoclinic, space group $P2_1/a$, $a = 17.377$ (1) Å, $b = 12.844$ (1) Å, $c = 13.250$ (1) Å, $\beta = 96.084$ (6); $V = 2940.6$ (3) Å^3, $Z = 4$. As was found earlier for 1, the geometry about Zr is normal, and no Zr–P interaction is evident. Reduction of 1 with Na/Hg produces a fairly stable paramagnetic Zr(III) species formulated as $Cp_2ZrCH_2PPh_2$. The latter is monomeric and, similar to a simple Zr(III) alkyl model compound, decomposes in solution mostly via intermolecular H transfer from a Cp ring to Zr-bound carbon. Mechanisms for the chemistry of these Zr(III) species are suggested on the basis of an isotopic labeling study. Reaction of 1 with $Cr(CO)_5THF$ produces crystalline $Cp_2Zr(Cl)CH_2PPh_2Cr(CO)_5$: monoclinic, space group $P2_1/n$, $a = 11.346$ (9) Å, $b = 13.696$ (7) Å, $c = 17.609$ (13) Å, $\beta = 99.88$ (6)°, $V = 2696$ (3) Å^3, $Z = 4$. Reaction of 4 with (norbornadiene)$Cr(CO)_4$ produces $Cp_2Zr(\mu\text{-}CH_2PPh_2)_2Cr(CO)_4$, containing a severely hindered six-membered ring in a twist-boat conformation: monoclinic, space group $P2_1/n$, $a = 12.932$ (5) Å, $b = 16.966$ (3) Å, $c = 19.160$ (5) Å, $\beta = 97.88$ (3) Å, $V = 4164$ Å^3, $Z = 4$. Both Cr complexes display relatively normal Zr and Cr geometric environments with no unexpected interactions evident.

Introduction

As one part of an ongoing study of compounds containing both "early" and "late" transition metals, we recently reported the synthesis and some chemistry of zirconocene derivatives containing the (diphenylphosphino)methyl ligand.[2] These compounds are the first examples of such complexes containing either a group 4 or 5 metal and are unique in displaying exclusively η^1 bonding between ligand and metal (compounds 1–4). By way of comparison, Schmidbaur and others have reported the preparation of a number of phosphinomethyl complexes of group 8 metals, all of which display exclusively η^2 bonding in a three-membered M–C–P ring.[3] Related structures containing sulfur or nitrogen in place of phosphorus have also been reported;[4] only in the case of a single nitrogen system has evidence been obtained for an η^1-bonded species as well (compound 5).[4c] A theoretical



1, R = Cl
2, R = $n\text{-}C_8H_{17}$
3, R = $(CH_2)_4CH{=}CH_2$
4, R = $CH_2P(C_6H_5)_2$

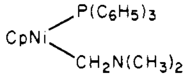


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Table I. Crystal Data

	$Cp_2Zr(Cl)CH_2PPh_2$ (1)	$Cp_2Zr(Cl)CH_2PPh_2Cr(CO)_5$ (12)	$Cp_2Zr(CH_2PPh_2)_2$ (4)	$Cp_2Zr(CH_2PPh_2)_2Cr(CO)_4$ (17)
mol wt, amu	456.1	648.1	619.8	783.9
d(calcd) (140 K), g cm^{-3}	1.56	1.60	1.40	1.34[a]
max cryst dim, mm	0.4 × 0.4 × 0.1	0.06 × 0.04 × 0.04	0.05 × 0.03 × 0.01	0.51 × 0.20 × 0.09
space group	$Pna2_1$	$P2_1/n$	$P2_1/a$	$P2_1/n$
molecules/unit cell	4	4	4	4[a]
cell constants[b]				
a, Å	7.92 (1)	11.346 (9)	17.377 (1)	12.932 (5)
b, Å	11.93 (5)	13.696 (7)	12.844 (1)	16.966 (3)
c, Å	20.59 (6)	17.609 (13)	13.250 (1)	19.160 (5)
β, deg		99.88 (6)	96.084 (6)	97.88 (3)
cell vol, Å^3	1946 (10)	2696 (3)	2940.6 (3)	4164 (2)
abs coeff *μ*, cm^{-1}	7.7	9.6	4.9	6.2

[a] Includes molecule of diglyme ($CH_3OCH_2CH_2OCH_2CH_2OCH_3$, mol wt 134.18) at 43% occupancy; measured density at 25 °C = 1.35 g cm^{-3}. [b] Mo Kα radiation, λ = 0.710 69 Å, graphite monochromator.

discussion of some of the reasons behind these complexation preferences has been presented elsewhere.[5] We present here a full report on the preparation, properties, and structural characteristics of zirconocenes 1 and 4. These include comparisons with related zirconocene alkyls and results of experiments designed to probe the complexation ability of the tertiary phosphine with the central zirconium itself, as well as with a separate transition-metal fragment. Full crystallographic characterizations of several compounds will be described.

Results and Discussion

Chloro[(diphenylphosphino)methyl]zirconocene (1). Preparation of 1 in reasonable yield requires very slow addition of the tetramethylethylenediamine (TMEDA) complex of [(diphenylphosphino)methyl]lithium[6] to zirconocene dichloride in tetrahydrofuran (THF) at low temperature (−78 °C). Attempts to utilize uncomplexed [(diphenylphosphino)methyl]lithium, or the complexed reagent at temperatures above −78 °C, led to mixtures of 1 and the disubstitution product 4 containing a preponderance of 4 even at early stages of the reaction, i.e., in the presence of a large excess of Cp_2ZrCl_2. This observation is consistent with the general behavior of all but the most sterically hindered alkyllithiums in reaction with metallocene dihalides. The technique described gives rise to a deep purple crude product (the color is due to some reduction of Cp_2ZrCl_2 under the reaction conditions) from which isolated yields of better than 50% of 1 may be obtained (eq 1). The somewhat unexpectedly low solubility of 1 in diethyl ether, relative to 4, Cp_2ZrCl_2, or its reduction products, allows convenient purification by ether extraction of the crude product followed by low-temperature recrystallization.

$$\mathrm{Cp_2ZrCl_2} \xrightarrow[\mathrm{THF},-78\ ^\circ\mathrm{C}]{\mathrm{Ph_2PCH_2Li\cdot TMEDA}} \underset{1}{\mathrm{Cp_2Zr(Cl)CH_2PPh_2}} \qquad (1)$$

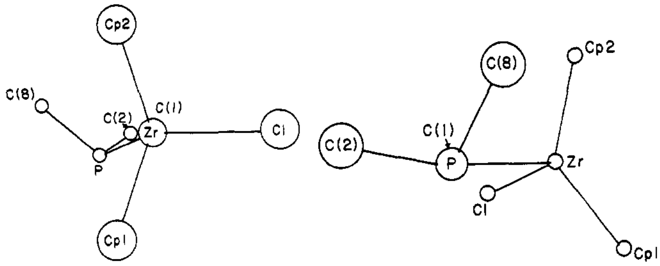

Figure 1. Newman projections sighting down Zr–C(1) (left) and P–C(1) bonds of $Cp_2Zr(Cl)CH_2PPh_2$ (1).

Pure 1 is a pale yellow crystalline solid showing the air and moisture sensitivity expected of typical zirconocene chloroalkyls. The far-IR spectrum of 1 in the solid state is dominated by a band at 347 cm^{-1}, indicative of the remaining covalent Zr–Cl bond. The determination of the structure of this compound by X-ray crystallography has already been reported.[2] In spite of the presence of a low-lying vacant orbital on Zr, no evidence for any direct Zr–P interaction in the solid state is found in the structural data. The intramolecular Zr–P distance is 3.75 Å, the Zr–C–P angle is 130.1°, and, on the basis of the presumed location of the phosphorus lone pair, neither distance nor orientation considerations favor interaction with the Zr center. This is most clearly illustrated by means of Newman projections sighting down the Zr–C(1) and P–C(1) bonds (Figure 1). In the former, the Cl–Zr–C(1)–P system is seen to be in an extended, almost anti conformation (dihedral angle = 162.5°). The latter projection shows the dihedral angle between the C(1)–Zr bond and the inferred P lone-pair orbital axis to be 71°. Summary of the crystal data for this and three other compounds considered in this paper are presented in Tables I and II. A fragment MO calculation approach[5] reproduces the experimental structure rather nicely as a local minimum for the hypothetical $Cp_2Zr(Cl)CH_2PH_2$ (e.g., ∠Zr–C–P = 140°). However, it predicts a second, more stable form with a Zr–C–P angle of 80° *and a fully developed Zr–P bond* (6). It is therefore likely that the observed solid-state structure of 1 is a result of steric interactions of the phenyl group that disfavor the cyclic alternative. NMR measurements that might have been expected to reveal the presence of a small amount of cyclic isomer in equilibrium with 1 are in fact inconclusive. The methylene proton resonance occurs at relatively low field (δ 1.68) but is well within normal limits for compounds of the general formula $Cp_2Zr(Cl)CH_2MR_n$ where MR_n is a bulky, heteroatom-containing group.[7] The P–C–H splitting of 2.9 Hz is normal for an uncomplexed tertiary phosphine. More intriguing is the long range coupling of 0.26 Hz between phosphorus and the Cp ring

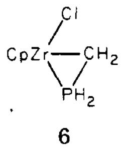

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Table II. Selected Bond Lengths (Å) and Angles (deg)

	$Cp_2Zr(Cl)CH_2PPh_2$[a] (1)	$Cp_2Zr(Cl)CH_2PPh_2Cr(CO)_5$ (12)	$Cp_2Zr(CH_2PPh_2)_2$ (4)	$Cp_2Zr(CH_2PPh_2)_2Cr(CO)_4$ (17)
d_{Zr-Cl}	2.453	2.439 (1)		
d_{Zr-CH_2}	2.281	2.328 (6)	2.284 (8), 2.340 (9)	2.292 (9), 2.329 (9)
∠CH_2-Zr-Cl/CH_2	92.3	97.2 (1)	100.2 (3)	93.5 (3)
$d_{Zr-C(Cp)}$(range)	2.475-2.534	2.482-2.535 (6)	2.460-2.560 (14)	2.504-2.570 (10)
d_{P-CH_2}	1.834	1.813 (6)	1.808 (9), 1.813 (9)	1.816 (9), 1.817 (9)
$d_{P-C(Ph)}$(range)	1.809, 1.829	1.834 (6), 1.853 (6)	1.848-1.868 (10)	1.838-1.862 (10)
∠Zr-CH_2-P	131.1	134.2 (3)	122.2 (5), 129.0 (5)	122.4 (4), 128.1 (5)
d_{P-Cr}		2.412(2)		2.404 (3), 2.412 (3)
∠CH_2-P-Cr		116.4 (2)		117.8 (3), 120.5 (3)
∠C(Ph)-P-Cr(range)		109.0 (2), 118.0 (2)		108.2-120.0 (3)
$d_{Cr-C(\text{trans to P})}$		1.840 (7)		1.848 (10), 1.854 (9)
$d_{Cr-C(\text{cis to P})}$(range)		1.869-1.878 (6)		1.873 (11), 1.883 (11)
d_{C-O}(range)		1.150-1.165 (8)		1.146-1.160 (14)
∠P-Cr-C(trans)		175.9 (2)		172.1 (3), 176.7 (3)
∠P-Cr-C(cis)(range)		86.3-97.3 (2)		85.1-98.7 (3)
∠P-Cr-P				92.4 (1)

[a] Reference 2.

Table III. Proton NMR Data

		δ (m, *J* (Hz))		
compound	solv	C_5H_5	$ZrCH_2P$	PPh_2
$Cp_2Zr(Cl)CH_2PPh_2$ (1)	THF-d_8	6.21 (d, 0.26)[a]	1.68 (d, 3)	7.1-7.7 (m)
	C_6D_6	5.81 (s)	1.84 (d, 3)	6.9-7.7 (m)
$Cp_2Zr(CH_2PPh_2)_2$ (4)	THF-d_8	6.04 (t, 0.15)[a]	0.93 (d, 3)	7.1-7.5 (m)
	C_6D_6	5.76 (s)	0.97 (d, 3)	7.0-7.7 (m)
$Cp_2Zr(Cl)CH_2PPh_2Cr(CO)_5$ (12)	THF-d_8	6.20 (s)	*b*	7.1-7.8 (m)
	C_6D_6	5.72 (s)	1.82 (d, 11)	7.0-7.9 (m)
$Cp_2Zr[CH_2PPh_2Cr(CO)_5]_2$ (15)	THF-d_8	5.92 (s)	1.23 (d, 12)	7.2-7.9 (m)
	C_6D_6	5.59 (s)	1.06 (d, 12)	6.9-8.0 (m)
$Cp_2Zr(CH_2PPh_2)_2Cr(CO)_4$ (17)	THF-d_8	5.85 (s)	1.57 (d, 7)	7.3-7.7 (m)
	C_6D_6	5.30 (s)	1.50 (d, 6)	7.0-7.9 (m)
Cp_2ZrCl_2	THF-d_8	6.49 (s)		
	C_6D_6	5.92 (s)		
$(Cp_2ZrCl)_2O$	THF-d_8	6.32 (s)		
	C_6D_6	6.02 (s)		
CH_3PPh_2	THF		1.57 (d, 4)	7.1-7.5 (m)
	C_6D_6		1.45 (d, 4)	7.0-7.7 (m)

[a] Confirmed by measurement at both 90 and 360 MHz. [b] Obscured by solvent absorption at δ 1.75.

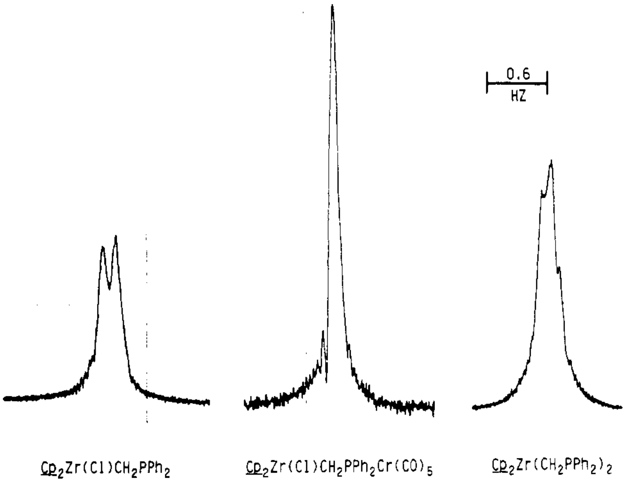

Figure 2. ^1H NMR C_5H_5 resonances for **1** (left), **12** (center), and **4** (right).

protons (Figure 2). However, if one counts the Cp–Zr as containing partial C–Zr "bonds", this coupling becomes analogous to four-bond interactions seen in a number of systems, e.g., $(CH_3)_2Si(Cl)CH_2PR_2$, where $J_{PCSiCH} = 0.5–1.0$ Hz.[8] The phosphorus-31 NMR displays a single peak at

Table IV. Proton-Decoupled ^{31}P NMR Data[a]

compound	δ(^{31}P)	Δδ(coord)	ref
CH_3PPh_2	−26.9		*b*
$CH_3PPh_2Cr(CO)_5$	+35.0	+61.9	*b*
$Cp_2Zr(Cl)CH_2PPh_2$ (1)	−1.8		*b*
$Cp_2Zr(Cl)CH_2PPh_2Cr(CO)_5$ (12)	+56.6	+58.4	*b*
$Cp_2Zr(CH_2PPh_2)_2$ (4)	−4.6		*b*
$Cp_2Zr[CH_2PPh_2Cr(CO)_5]_2$ (15)	+51.9	+56.5	*b*
$CH_2(CH_2PPh_2)_2$	−17.3		*c*
$CH_2(CH_2PPh_2)_2Cr(CO)_4$	+41.4	+58.7	*c*
$Cp_2Zr(CH_2PPh_2)_2Cr(CO)_4$ (17)	+60.8	+65.4	*b*

[a] All spectra were recorded at 81 MHz in CD_2Cl_2 at 20 °C. Chemical shifts are reported in δ; values downfield from external H_3PO_4 are positive in sign. Δδ(coord) signifies downfield shift of signal upon coordination. [b] This work. [c] Reference 31.

−1.8 ppm (upfield from external H_3PO_4), also fairly normal for a simple tertiary phosphine. Tables III and IV contain NMR data for this and the other compounds prepared in this study. In any event, it seems unlikely that direct Zr–P interaction is present to any significant extent in solutions of **1**. Molecular weight determinations (isopiestic vapor pressure technique, dimethyl ether) indicate **1** to be strictly monomeric.

Bis[(diphenylphosphino)methyl]zirconocene (4). Reaction of Cp_2ZrCl_2 with 2 equiv of [(diphenyl-

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Table V. Experiments with Zirconocene Alkyl Halides

expt	system	product (% yield[a])	% deuterated alkane
1	0.11 M 7 + H_2O	octane (100, GC)	0
2	0.11 M 7 + D_2O	octane	82 ± 11
3	0.10 M 8 + H_2O	decane (100, GC)	0
4	0.10 M 8 + D_2O	decane	84 ± 11
5	0.11 M 7 + excess Na/Hg	octane (100, GC)	0
6	0.10 M 8 + excess Na/Hg	decane	58 ± 4[b]
7	0.05 M each 7 and 8 + excess Na/Hg	octane	22 ± 4
		decane	48 ± 4[c]
8	0.005 M each 7 and 8 + excess Na/Hg	octane	0
		decane	18 ± 4
9	0.81 M 7 + excess Na/Hg	octane (≥70, GC)	0
10	0.81 M 7 in THF-d_8 + excess Na/Hg	octane	0
11	0.02 M 7 in THF-d_8 + excess Na/Hg	octane	40 ± 3
12	0.11 M 7 + excess CH_3PPh_2 + excess Na/Hg	octane (100, GC)	
13	0.11 M 7 + 0.15 M CH_3PPh_2 + excess Na/Hg	9 (55, NMR)	
14	0.11 M 7 + 0.17 M CH_3PPh_2 + excess Na/Hg	9 (63, NMR)	
15	0.57 M 7 + 0.85 M CH_3PPh_2 + 1 equiv of Na/Hg	9 (75, NMR)	
16	0.066 M 7 + 0.12 M CH_3PPh_2 + 0.5 equiv of Na/Hg	9 (60, NMR)	

[a] If, and how measured. [b] 40% d_1 and 18% d_2. [c] 35% d_1 and 13% d_2.

phosphino)methyl]lithium, either free or as the TMEDA complex, readily results in conversion to the light brown bis(phosphine) complex 4 in essentially quantitative yield (NMR) (eq 2). The TMEDA complex is the reagent of

$$Cp_2ZrCl_2 \xrightarrow[\text{THF, 25 °C}]{2Ph_2PCH_2Li} \underset{\mathbf{4}}{Cp_2Zr(CH_2PPh_2)_2} \qquad (2)$$

choice because it is more readily prepared, and in higher yield, than is the uncomplexed (phosphinomethyl)lithium itself. Recrystallization from ether–hydrocarbon mixtures separates the product from an oily mixture of TMEDA and small amounts of reduced species. Pure crystalline 4 is relatively resistant to decomposition by oxygen or moisture and may be handled for short periods outside of an inert atmosphere.

The spectroscopic properties of 4 are predictable on the basis of the observations made on mono(phosphine) 1. Proton NMR shows a methylene doublet at δ 0.92 while the Cp ring protons appear as a triplet ($J_{PCZrCpH} \approx 0.15$ Hz) at δ 6.05 (Figure 2). The phosphorus-31 resonance appears at −4.6 ppm. An intense Zr–C stretch at 464 cm^{-1} is the most prominent feature in the far-IR. The X-ray structure determined for 4 shows the conformations of the two phosphinomethyl ligands to be different (Figure 3); the two Zr–P distances in the molecule are 3.64 and 3.70 Å, again, well outside the range required for direct interaction to be inferred. Newman projections down the two Zr–C bonds (Figure 4) show one C–Zr–C–P system to be anti and the other to be gauche in conformation (dihedral angles 163.2° and 68.6°, respectively). As we have no evidence that the two ligands are distinguishable from each other in solution, we assume that this result is an artifact due to crystal packing.

Reduction Chemistry of Zirconocene Alkyl Halides in General. In our preliminary study[2] we reported the observation of an unusually persistent, apparently monomeric Zr(III) species upon one-electron reduction of 1 (eq 3). Although derivatives of zirconocene in the +2 and

$$\underset{\mathbf{1}}{Cp_2Zr(Cl)CH_2PPh_2} \xrightarrow[\text{THF}]{\text{Na/Hg}} \text{Zr(III) species} \qquad (3)$$

+4 oxidation states have proved to be sources of remarkably varied and useful reactivity, the +3 oxidation state, of considerable importance in the chemistry of Ti, is much less accessible in the case of Zr. Only a very few examples of stable zirconocene derivatives containing Zr(III) are known, most of them being diamagnetic dimers,[9] and virtually nothing is known about the reaction chemistry of this sort of species.

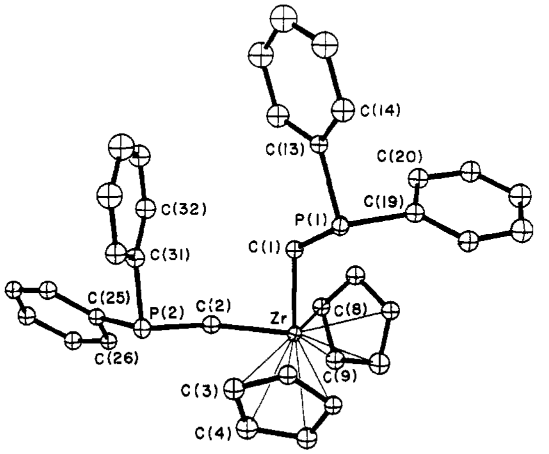

Figure 3. Representation of $Cp_2Zr(CH_2PPh_2)_2$ (4) with 50% thermal ellipsoids.

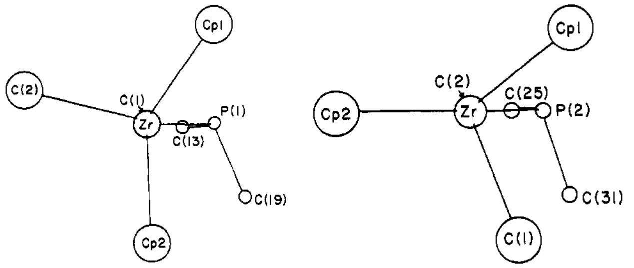

Figure 4. Newman projections sighting down Zr–C bonds of $Cp_2Zr(CH_2PPh_2)_2$ (4).

For preliminary study reductions of THF solutions of zirconocene *n*-octyl chloride[10] (7) by 0.8% Na/Hg were followed by NMR and ESR, and volatile products were identified by GC and mass spectrometry. The reaction requires 1 equiv of Na, is complete in 1 h at room temperature, and the major organic product, formed in high

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(9) Dimers: (a) Gell, K. I.; Harris, T. V.; Schwartz, J. *Inorg. Chem.* **1981**, *20*, 481. (b) Pez, G. P.; Putnik, C. F.; Suib, S. L.; Stucky, G. D. *J. Am. Chem. Soc.* **1979**, *101*, 6933. (c) Issleib, K.; Häckert, H. *Z. Naturforsch., B: Anorg. Chem., Org. Chem., Biochem., Biophys., Biol.* **1966**, *21B*, 519. Monomers: (d) Gynane, M. J. S.; Jeffery, J.; Lappert, M. F. *J. Chem. Soc., Chem. Commun.* **1978**, 34. (e) Lappert, M. F.; Raston, C. L. *Ibid.* **1980**, 1284.

(10) Schwartz, J. In "New Applications of Organometallic Reagents in Organic Synthesis"; Seyferth, D., Ed.; Elsevier: Amsterdam, 1976.

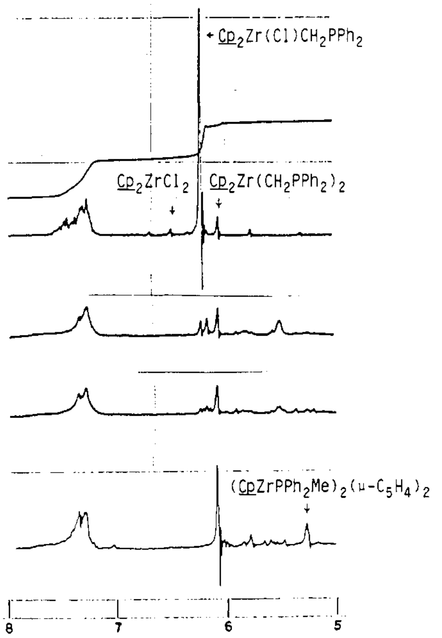


Figure 5. Reduction of 1 by Na/Hg in THF: top scan, ^{1}H NMR before reduction; second scan, after several hours; third scan, after several days; bottom scan, after 3 weeks.

(70–100%) yield, is *n-octane*. Only traces of 1-octene are detected. The source of the hydrogen atom in the alkane has been determined by a series of isotopic labeling and crossover experiments, the results of which are presented in Table V. For these experiments the substrate $(C_5D_5)_2Zr(Cl)(n\text{-}C_{10}H_{21})$ (8) was prepared containing ca. 90% deuterium in the rings. The results indicate that (1) the hydrogen is derived chiefly from the cyclopentadienyl rings (experiment 6), (2) there is a significant intermolecular component involved at some point in the reaction (experiment 7), and (3) at lower substrate concentrations the solvent can effectively compete as a hydrogen source (cf. experiments 10 and 11).

Solutions of 7 upon reduction show several weak ESR signals with *g* values ranging from 1.97 to 2.00. One signal is observed at ca. $g = 1.99$ flanked by very weak satellite peaks whose positions are consistent with the sextet expected from splitting by one ^{91}Zr(III) nucleus (abundance = 11.23%, $I = {}^5/_2$, $a = 18.0$ G). At least one simple, monomeric Zr(III) species is therefore present although its structure is not evident from the ESR data alone. In the presence of excess methyldiphenylphosphine reduction of 7 gives rise to high yields of both octane and the dimeric Zr(III) phosphine complex 9[9a] (eq 4) (Table V, experiments 12–16). The Zr(II) phosphine 10 is present in these reductions, but its concentration never builds up beyond trace amounts.

$$Cp_2Zr(Cl)(n\text{-}C_8H_{17}) \xrightarrow[\text{MePPh}_2\text{, THF}]{\text{Na/Hg}} \underset{\text{ca. }85\%}{\text{octane}} + \underset{\text{ca. }1\%}{\text{1-octene}} + \underset{\mathbf{9},\ 75\%}{[CpZr(MePPh_2)]_2[\mu\text{-}(\eta^1{:}\eta^5\text{-}C_5H_4)]_2} \underset{\mathbf{10}}{Cp_2Zr(MePPh_2)_2} \quad (4)$$

Reduction Chemistry of 1. The Na/Hg reduction of 1 is faster than that of 7, but the buildup of diamagnetic products is considerably slower. The disappearance of starting material is closely paralleled by the appearance of a persistent, very intense Zr(III) ESR signal.[2] At the stage of reaction when all of the 1 has been consumed (NMR) and the ESR signal has reached maximum intensity, 93% of the Cl is liberated as a precipitate (presumably NaCl) but only traces of dimer 9 are present. If the reaction mixture is quenched with D_2O at this stage, $(C_6H_5)_2PCH_2D$ is isolated; thus the σ Zr–C bond of 1 has *not* been cleaved during the one-electron reduction process itself. The paramagnetic reduction product is remarkably stable in solution. Only after several weeks at 27 °C does the unquenched reaction mixture finally become ESR silent; dimer 9 is again the major organometallic product, along with smaller amounts of bis(phosphine) 4 (Figure 5). Addition of D_2O at this point, followed by benzene extraction, affords mostly undeuterated $(C_6H_5)_2PCH_3$ (Figure 6).

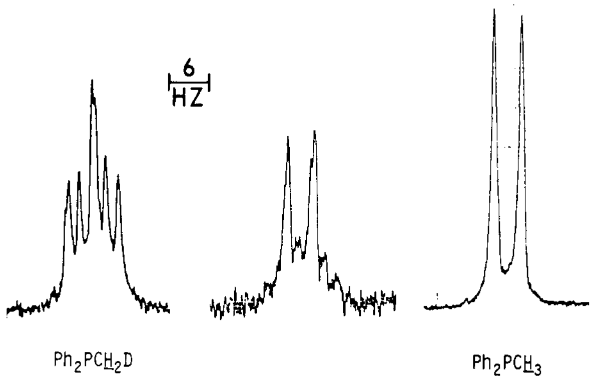
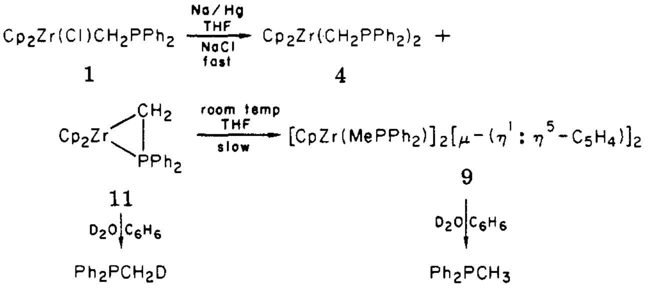


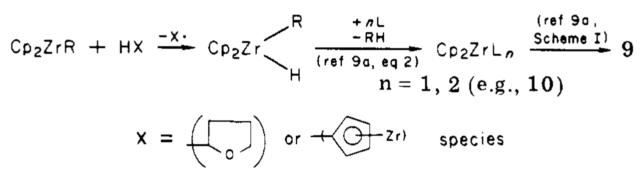
Figure 6. ^{1}H NMR methyl resonance of CH_3PPh_2 derived from (left) D_2O quench of freshly reduced solution of 1, (center) D_2O quench of solution of 1 1 week after reduction, and (right) commercial sample.

Scheme I. Na/Hg Reduction of $Cp_2Zr(Cl)CH_2PPh_2$ (1)

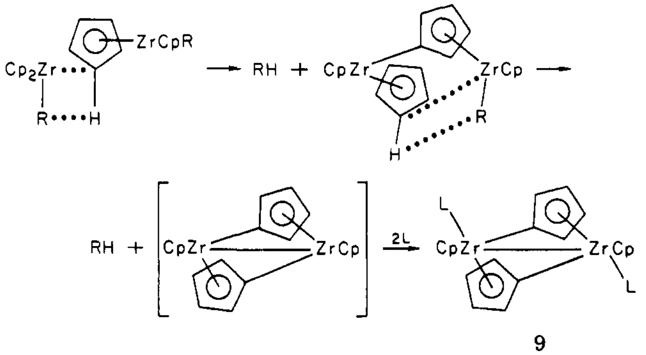


Assuming that the generation of octane from 7 and methyldiphenylphosphine (complexed as 9) from 1 follow similar pathways, it appears that loss of Cl^- to generate $Cp_2Zr^{III}R$ is the major primary process in both cases. In the case of $R = CH_2PPh_2$ we formulate this species as 11 on the basis of the spectroscopic and chemical evidence and suggest that its remarkable stability derives from intramolecular complexation of phosphine, as predicted by theory[5] (Scheme I). In support of this proposal, we find that removal of solvent from freshly reduced THF solutions of 1 and a careful sequence of solvent extractions allow the isolation of a paramagnetic pink powder that displays the characteristic, intense ESR (doublet superimposed on doublet of sextets) upon redissolution in THF. In the ^{1}H NMR a characteristically broad ($w_{1/2} \approx 10$ Hz) signal at ca. δ 5.5 is observed together with broadened phenyl absorption. No other major NMR resonances have been located. Most important, the material is found to be unquestionably monomeric in dimethyl ether. With use of 4-bromobiphenyl as a standard (mol wt 233), solution volume equilibrium is reached within hours in the isopiestic apparatus, resulting in a molecular weight of 395 ± 40 for the zirconium species (calculated mol wt for $Cp_2ZrCH_2PPh_2 = 420$). The value remains constant for several days in solution at 25 °C. The magnetic susceptibility at 30 °C, measured via the Evans NMR method in benzene, is 1.90 ± 0.10. Thus the formulation of this species as 11 appears quite well supported and, in par-

Scheme II. Radical Pathway for a 11 → 9 Type Transformation



Scheme III. Four-Center Mechanism

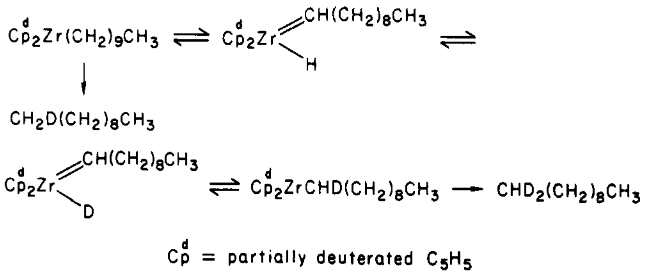


ticular, is consistent with structures assigned by Schwartz to the paramagnetic, Zr(III)-containing, transient products of oxidative addition of alkyl halides to phosphine complexes of dicyclopentadienylzirconium(II).[11] The major difference between **11** and these latter systems (or the reduction product of **7**, for that matter) is the remarkable stability of the intramolecularly coordinated Zr(III) species. This has allowed us to begin investigating the properties and chemistry of this unusual metallocene derivative.

Mechanistic Considerations. The general question of mechanism in these transformations is still unresolved. The formation of bis(phosphine) **4** as a side product may simply involve loss of $^-CH_2PPh_2$ instead of Cl^- from the radical anion of **1**, followed by reaction of this carbanion with a molecule of unreacted **1**. Zirconium–carbon bond cleavage upon one-electron reduction is calculated to be feasible,[5] although no quantitative estimate of its likelihood relative to the more obvious Zr–Cl cleavage can be made at this time.

The formation of Zr(III) dimers such as **9** in these systems poses a more intriguing mechanistic problem. To date only odd-electron chemistry, in the form of either atom abstraction or radical coupling, has been demonstrated for monomeric zirconocene(III) species.[11,12] These reactions, however, take place under oxidizing conditions. An application of a radical mechanism to our reduced system is shown in Scheme II. Two points make this path unlikely. First, the strong preference for removal of hydrogen from a Cp ring (sp^2 bound) as opposed to the THF solvent (sp^3 bound) except at very low substrate concentration (Table V, lines 6 and 7) argues against a radical abstraction.[13] Second, such an abstraction would take the system into the Zr(II)/Zr(IV) regime studied by Schwartz and co-workers.[9a] Although in our reductions we can see the presence of small amounts of **10**, which is known to slowly convert to **9** at room temperature, the *prompt* appearance of **9** in our experiments (Table V, lines 13–16) rules out such a Zr(II) species as a stoichiometric precursor.

Scheme IV. Ring/Alkyl Hydrogen Exchange Pathway via α-Elimination



We feel, therefore, that the formation of **9** from Zr(III) monomers most likely involves some sort of even-electron mechanism, perhaps involving "four-center" bond shifts of the sort attributed to reactions of several Zr(IV),[14] U(IV), and Th(IV)[15] systems (Scheme III). The successful isolation of **11** suggests that substituted derivatives will also be accessible. Hopefully, comparative studies of these compounds will provide more direct evidence concerning the mechanism of this process. We note that the observation of both odd- and even-electron processes in Zr(III) chemistry has precedent in the reactions of U(III),[16,17] and several similarities have already been noted in the chemistries of group 4 metallocene derivatives and the corresponding complexes of actinide elements.[18]

One other oddity remains: in several Na/Hg reduction experiments involving ring-deuterated *n*-decylzirconocene chloride (**8**), mass spectra of the decane produced display M + 2 ion peak intensities 4–5 times larger than expected, based on the intensities of the M and M + 1 ion peaks. This translates into a significant amount (ca. 15%) of *decane-*d_2 being present in the product (Table V, lines 6 and 7). The octane obtained in the crossover experiment exhibits only slightly more than the expected M + 2 intensity; thus the process leading to introduction of the second deuterium is predominantly, if not exclusively, intramolecular. This result requires an exchange process between ring and alkyl hydrogens and is most reasonably rationalized as proceeding via a metal hydride. The latter could be formed via either α- or β-elimination; the low intensity of the M − 15 ions in the mass spectra of alkanes makes it impossible for us to distinguish between the two possibilities. Exchange of hydrogen between Cp ligands and metal sites has been reported to proceed readily in the zirconocene borohydrides[19] as well as upon thermolysis of dimethyltitanocene.[20] The latter study, and others,[21] clearly indicate the involvement of metal carbenes[22] resulting from α-elimination. A route to alkane-d_2 that

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[11] (a) Williams, G. M.; Schwartz, J. *J. Am. Chem. Soc.* **1982**, *104*, 1122. (b) Williams, G. M.; Gell, K. I.; Schwartz, J. *Ibid.* **1980**, *102*, 3660.

[12] Van Leeuwen, P. W. N. M.; Van der Heijden, H.; Roobeek, C. F.; Frijus, J. H. G. *J. Organomet. Chem.* **1981**, *209*, 169.

[13] No reaction involving cyclopentadienyl C–H bond cleavage was noted in a study of the reactions of several $Cp_2Zr(R)X$ and Cp_2ZrR_2 with either nitroxyl or thiyl radicals: Brindley, P. R.; Scotton, M. J. *J. Organomet. Chem.* **1981**, *222*, 89.

[14] Gell, K. I.; Posin, B.; Schwartz, J.; Williams, G. M. *J. Am. Chem. Soc.* **1982**, *104*, 1846.

[15] Fagan, P. J.; Manriquez, J. M.; Maatta, E. A.; Seyam, A. M.; Marks, T. J. *J. Am. Chem. Soc.* **1981**, *103*, 6650.

[16] Finke, R. G.; Schiraldi, D. A.; Hirose, Y. *J. Am. Chem. Soc.* **1981**, *103*, 1875.

[17] Fagan, P. J.; Manriquez, J. M.; Marks, T. J.; Vollmer, S. H.; Day, V. W. *Organometallics* **1982**, *1*, 170.

[18] E.g., compare: Manriquez, J. M.; McAlister, D. R.; Sanner, R. D.; Bercaw, J. E. *J. Am. Chem. Soc.* **1978**, *100*, 2716. Katahira, D. A.; Moloy, K. G.; Marks, T. J. *Organometallics* **1982**, *1*, 1723. A general, critical discussion of the similarities and differences between these systems has been presented.[15]

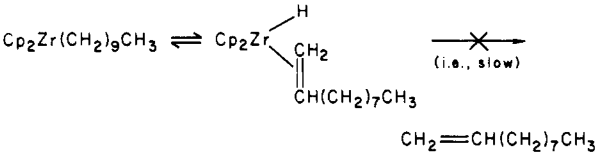
[19] Marks, T. J.; Kolb, J. R. *J. Am. Chem. Soc.* **1975**, *97*, 3397.

[20] See: Erskine, G. J.; Hartgerink, J.; Weinberg, E. L.; McCowan, J. D. *J. Organomet. Chem.* **1979**, *170*, 51 and references therein.

[21] E.g.: Chang, B.-H.; Tung, H.-S.; Brubaker, C. H., Jr. *Inorg. Chim. Acta* **1981**, *51*, 143.

[22] See also: Schwartz, J.; Gell, K. I. *J. Organomet. Chem.* **1980**, *184*, Cl; Wengrovius, J. H.; Schrock, R. R. *Ibid.* **1981**, *205*, 319. Hartner, F. W., Jr.; Schwartz, J.; Clift, S. M. *J. Am. Chem. Soc.* **1983**, *105*, 640.

follows this pathway is shown (Scheme IV). The β-elimination alternative can only operate if the alkene in the intermediate alkene hydride complex is tightly bound, as we only see traces of alkene among the reduction products (eq 5). Experiments designed to distinguish between these



(5)

possibilities are underway. Nevertheless, these studies clearly indicate the operation of at least some parallel mechanistic processes in Zr(III) and Zr(IV) metallocenes, in addition to the C–H activation capabilities of the former species.

Intermolecular Complexation Chemistry of 1 and 4. The phosphine ligands of 1 and 4 appear to possess reactivity typical of tertiary phosphines in general. Reaction of solutions of either zirconocene derivative with preformed solutions of $Cr(CO)_5THF$ results at room temperature in relatively rapid decolorization of the latter and formation at high yield of the corresponding (phosphine)$Cr(CO)_5$ complexes. The reaction (eq 6) between

$$\underset{\mathbf{1}}{Cp_2Zr(Cl)CH_2PPh_2} \xrightarrow[\text{THF}]{Cr(CO)_5THF} \underset{\mathbf{12}}{Cp_2Zr(Cl)CH_2PPh_2Cr(CO)_5} \quad (6)$$

mono(phosphine) 1 and $Cr(CO)_5THF$ may be followed in the form of a rather striking NMR titration. At 90 MHz with extreme spectral expansion, the narrow doublet corresponding to the cyclopentadienyl protons of 1 is gradually replaced by the signal due to 12. This signal, which appears less than 0.01 ppm upfield from that of 1, is a *sharp singlet* with a $w_{1/2} < 0.2$ Hz (Figure 7). A similar phenomenon occurs upon reaction of $Cr(CO)_5THF$ with silylmethylphosphine (13), whereupon a long-range coupling of ca. 0.9 Hz between phosphorus and the silylmethyl protons in the uncomplexed phosphine disappears and only a broadened singlet can be seen in the spectrum of the chromium complex (eq 7). We take these observations to indicate that the mechanisms of long-range NMR coupling in both 1 and 13 are similar and probably operate in a through-space manner between the phosphorus lone pair and the protons in question.

$$\underset{\mathbf{13}}{ClSi(CH_3)_2CH_2PPh_2} \xrightarrow{Cr(CO)_5THF} \underset{\mathbf{14}}{ClSi(CH_3)_2CH_2PPh_2Cr(CO)_5} \quad (7)$$

The X-ray structure of mono(phosphine) complex 12 has been determined. Although generally similar in geometry around the Zr atom to 1, 12 displays a significantly longer Zr–C σ bond (2.33 vs. 2.28 Å) and a larger Cl–Zr–C angle (97.4 vs. 90.4°). The Zr–C–P angle is opened even further to 133.7°, and the nonbonding Zr–P distance is 3.82 Å. All these observations are reasonably attributable to steric effects. Similarly, the pentacarbonylchromium phosphine moiety possesses an unexceptional structure. Concerning the potential for metal–metal, metal–ligand, or ligand–ligand interactions between groups otherwise not directly bonded to one another, the molecule shows a 5.30-Å distance between Zr and Cr. The closest approach between Zr and a Cr-bound ligand involves a distance of 4.15 Å to one carbonyl oxygen; 5.38 Å separates Cr from the Cl atom in a molecule in an adjacent unit cell (the *intramolecular* separation is >6 Å). A view of the molecule is shown in Figure 8. Except for small perturbations of a steric nature, therefore, the molecule appears to consist of totally normal and essentially noninteracting $Cp_2Zr(R)Cl$ and $Cr(CO)_5L$ units. Small differences are evident in the IR and NMR relative to simpler model systems, e.g., 12 shows J_{PCH} = 11 Hz and CO stretching frequencies of 1930 and 2050 cm^{-1}, to be compared with J_{PCH} = 7 Hz and ν_{CO} = 1937 and 2070 cm^{-1} for $CH_3PPh_2Cr(CO)_5$. The presence of modest

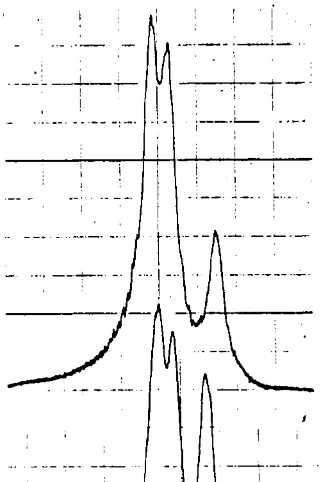


Figure 7. ^1H NMR of C_5H_5 resonances during reaction of 1 with $Cr(CO)_5THF$. Top to bottom: 10%, 30%, 60%, and 90% complete reaction.

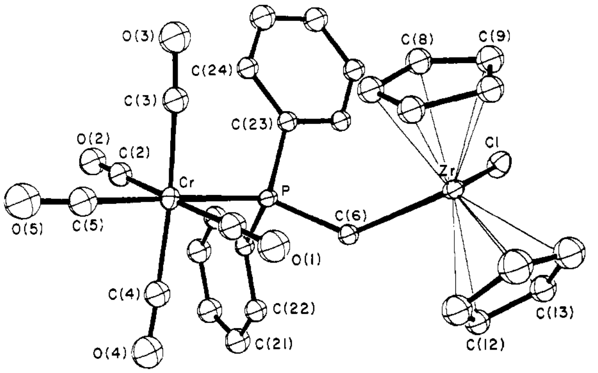


Figure 8. Representation of $Cp_2Zr(Cl)CH_2PPh_2Cr(CO)_5$ (12).

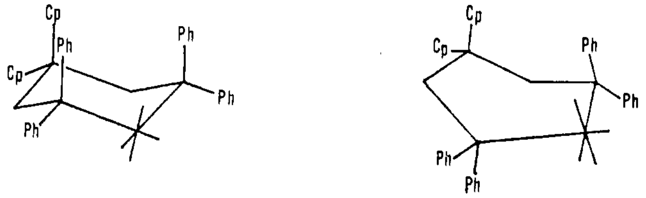


Figure 9. Sketches of chair (left) and twist-boat (right) conformations of $Cp_2Zr(\mu\text{-}CH_2PPh_2)_2ML_4$ (**17**).

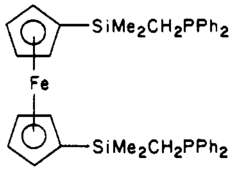
inductive interactions in the system are sufficient to account for these differences, however. The phosphorus-31 NMR signal of **12** appears at +56.6 ppm. The shift upon complexation is 58.4 ppm downfield, to be compared with a 61.9 ppm shift upon complexation of methyldiphenylphosphine to $Cr(CO)_5$. The molecule is in fact a model system of sorts, potentially set up to display distinctive chemistry upon appropriate refunctionalization of one of its metal centers, but otherwise showing no unusual characteristics in the absence of such an outside influence.

The corresponding reaction of bis(phosphine) **4** with $Cr(CO)_5THF$ proceeds in an analogous fashion (eq 8). The

$$\underset{\mathbf{4}}{Cp_2Zr(CH_2PPh_2)_2} \xrightarrow[\text{THF}]{2Cr(CO)_5THF} \underset{\mathbf{15}}{Cp_2Zr[CH_2PPh_2Cr(CO)_5]_2} \quad (8)$$

product **15** likewise displays no exceptional spectroscopic properties relative to simple Cp_2ZrR_2Cl or $Cr(CO)_5L$ systems. It is, however, extraordinarily air and moisture sensitive, much more so than any compound discussed herein with the exception of Zr(III) monomer **11**.

Bis(phosphine) **4** is in addition a potential chelating ligand, however, and we wished to test the possibility that it might be able to function in this manner toward an octahedral metal fragment. We had earlier found that the ferrocene-derived bis(phosphine) **16**, although capable of



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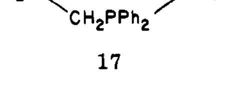
chelation of unhindered square-planar or tetrahedral fragments such as NiX_2, was sterically prevented from forming similar monomeric complexes with octahedral centers; instead, macrocyclic higher oligomers were isolated.[8b] With use of Dreiding models, we could predict with confidence in the case of **4** that extreme steric hindrance would surely prevent formation of a complex such as **17** in any conformation approaching a cyclohexane-like



17

chair structure. The problem lay not so much in interference involving the four ligands on M (as was the case with complexes of **16**) but rather with conventional, severe 1,3-diaxial interactions of cyclopentadienyl and phenyl rings of the zirconocene bis(phosphine) itself (Figure 9). Conventional cyclohexane chemistry predicts that such systems may still exist by adopting twist-boat conformations, however, and examples in the complexation chemistry of several metals are known.[23] Indeed, the models clearly showed the removal of the offending steric interactions in **17** upon flipping the ring into a boat and relaxing to the symmetrical (C_2) twist-boat form (Figure 9). Several attempts were made to prepare such a complex. Direct thermal reaction of **4** with $Cr(CO)_6$ in refluxing benzene for 10 h causes extensive decomposition of the zirconocene. At 40 °C, the reaction is very slow an the only major new IR absorption evident after 24 h is at 1880 cm^{-1}, indicative of a *trans*-$Cr(CO)_4L_2$ structure. It is unlikely that the phosphines of one molecule of **4** are capable of spanning the trans positions of an octahedral metal; therefore, we assume that oligomeric products were being formed in this reaction although we made no attempt to separate or purify them.

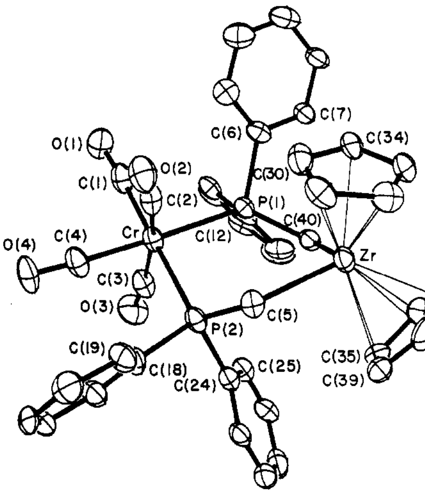


Figure 10. Representation of $Cp_2Zr(\mu\text{-}CH_2PPh_2)_2Cr(CO)_4$ (**17**, $ML_4 = Cr(CO)_4$).

We then turned to the (norbornadiene)$Cr(CO)_4$ complex as a source of $Cr(CO)_4$. Slow addition of a THF solution of the chromium complex to an equimolar quantity of **4** at room temperature resulted in a deep orange solution from which an 86% yield of yellow powder was isolated upon removal of solvent. Numerous attempts at purification of this material were made. Due to its solubility in aromatic and ethereal solvents, crystallization was attempted by slow diffusion of petroleum ether into solutions of the crude product in benzene, 1:1 ether–THF, THF, and diglyme. In the first two cases only microcrystalline material could be obtained, at best. Well-defined crystals formed in the THF–petroleum ether system after an extended period of time, but these disappointingly collapsed to a fine powder upon attempted removal of solvent. We were more fortunate with the crystals obtained by using diglyme–petroleum ether and therefore were able to undertake a full structural determination of this substance. The yellow needlelike crystals, which were found to have an anomalously low density of 1.35, were monoclinic with the cell dimensions listed in Table I. Systematic extinctions indicated space group $P2_1/n$ with $Z = 4$, and the structure was solved by heavy-atom techniques. Refinement to $R = 0.084$ was achieved after identification of the presence of a nonstoichiometric quantity of diglyme in the structure. The latter refined to 43% occupancy, resulting in excellent ultimate agreement with the experimentally measured density.

The product is indeed the simple, monomeric structure we had sought, i.e., **17** with $ML_4 = Cr(CO)_4$. The major features are as expected (Figure 10). The geometries

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[23] See, e.g.: Guimerans, R. R.; Olmstead, M. M.; Balch, A. L. *J. Am. Chem. Soc.* **1983**, *105*, 1677; *Inorg. Chem.* **1983**, *22*, 2223.

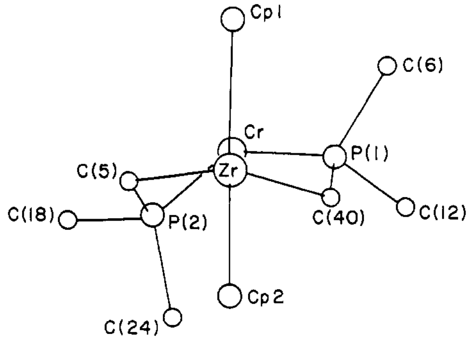

Figure 11. View of 17 (ML_4 = $Cr(CO)_4$) looking approximately down Zr–Cr axis.

about Zr, Cr, and the two phosphorus atoms are somewhat distorted to relieve steric crowding; for example, the carbonyl ligands on Cr are significantly bent out of linearity, away from the center of the ring. The twist-boat itself is also somewhat distorted, presumably as a result of packing constraints (Figure 11). Nonetheless, the preparation of **17** demonstrates in principle the ability of **4** to act as a chelating ligand in spite of its steric bulk. As we plan in future studies to utilize compounds such as **12** in experiments aimed at inducing interactions either between pairs of metals linked by a phosphinomethyl bridge or between ligands on these metals, the successful synthesis of **17** provides a model of sorts for possible cyclic intermediates or transition states that may be involved in such reactions.

Conclusions. The successful syntheses of zirconocene derivatives containing the (diphenylphosphino)methyl ligand has allowed the preparation of several novel types of heterobimetallic systems. These include simple acyclic bridged species as well as a remarkably hindered cyclic bimetallic complex. Aside from the expected steric effects, significant metal–metal interaction is conspicuously lacking in these molecules, effectively making them stable models for proposed studies in which such interaction will be deliberately sought by refunctionalization at one or both metal centers. Synthesis of these complexes has also opened the way for a systematic study of the heretofore relatively inaccessible zirconocene(III) system via the unusually stable $Cp_2ZrCH_2PPh_2$ derivative. Although detailed study of this latter compound is just getting underway, it is clear from the results obtained so far that zirconocene(III) systems are capable of displaying a variety of mechanistically quite distinct chemical processes. In addition to the previously observed radical chemistry, a facile sp^2 C–H bond activation process has been identified, and a possible α-elimination pathway inferred as well. Appropriate structural modifications in those substrates are currently underway to further test the mechanistic ideas presented herein and perhaps further extend the range of chemistry available from these systems.

Experimental Section

General Procedures. All preparations were carried out under an atmosphere of prepurified N_2 by using either Schlenck techniques or a Vacuum Atmosphere Drilab. Solvents were rendered water and oxygen free by room temperature distillation at high vacuum from sodium benzophenone ketyl or dianion (admixed with tetraglyme in the case of saturated hydrocarbons). $Ph_2PCH_2Li \cdot TMEDA$,[8b] Ph_2PCH_2Li,[24] and $Cr(CO)_4$ (norbornadiene)[25] were prepared by literature methods. All other organic reagents were redistilled under N_2 and degassed before drybox use. $Cr(CO)_6$ (Pressure) was resublimed before use; Cp_2ZrCl_2 (Aldrich) was used as received. Spectroscopic measurements utilized the following instrumentation: IR/far-IR, Beckman IR-8, Perkin-Elmer 180; ^1H NMR, Varian A60-A, Varian EM-390, Nicolet NT-360; ^{31}P NMR, Nicolet NT-200 at 81 MHz. Molecular weight determinations were carried out by using the "isopiestic" vapor pressure equilibrium method with Me_2O as the solvent and 4-bromobiphenyl (mol wt 233, Eastman) as the standard.[26] The bulbs of the vapor pressure apparatus (modified by the attachment of two joints fitted with Teflon stopcocks and suitable for connection to a vacuum line) were charged in the drybox with weighed quantities of sample and standard, respectively. Dimethyl ether was rendered water and oxygen free by condensation onto a sodium–benzophenone mixture, followed by distillation onto a mixture of 1 and sodium amalgam. The latter step was found to be necessary in order to provide solvent pure enough for use in molecular weight determination of Zr(III) species **11**. The purified ether was then condensed at −196 °C into each bulb of the molecular weight apparatus (ca. 1-mL each), the apparatus was evacuated, and the stopcocks were closed. When the solvent had melted and dissolved the solids in each bulb, volumes of each solution were carefully measured at frequent intervals. Equilibration (presumably to equal concentration) was achieved in generally less than 24 h at room temperature (internal pressure ca. 5 atm). Molecular weights of the samples were calculated in the usual way. Elemental analyses were carried out by the Galbraith, the Dornis und Kolbe, or the U.C. Berkeley Microanalytical Laboratory. These gave generally unsatisfactory results for alkylzirconocenes.[27] Mass spectrometry experiments were carried out by Mr. Paul Bruins at the U.C. Davis Chemistry Department and Mr. Kei Miyano at the U.C. Davis Facility for Advanced Instrumentation. Magnetic susceptibilities were determined by using the Evans method.[28]

Chlorobis(η^5-cyclopentadienyl)[(diphenylphosphino)methyl]zirconium (1). A solution of 3.64 g (11.3 mmol) of [(diphenylphosphino)methyl]lithium–*N,N,N′,N′*-tetramethyl-1,2-diaminoethane complex in 250 mL of THF was added dropwise over a 12-h period to a rapidly stirred solution of 3.00 g (10.3 mmol) of dichlorobis(η^5-cyclopentadienyl)zirconium in 250 mL of THF at −78 °C under N_2. A bright red color developed during the course of the addition. The mixture was allowed to come to room temperature, volatiles were removed at high vacuum, and the dark purple residue was extracted with 10 × 200 mL of ether (several hours of stirring per extraction). Cooling of the extracts to −40 °C caused precipitation of impure **1**. Removal of solvent from the filtrate, reextraction with 200 mL of ether, and cooling afforded some additional material for a total yield of 3.61 g of nearly white solid. NMR analysis shows this to consist of 87% **1**, 6% **4**, and 6% Cp_2ZrCl_2 by weight; the actual yield of **1** is therefore 3.14 g or 67% based upon Cp_2ZrCl_2. The last ether supernatant contains mostly unreacted Cp_2ZrCl_2 and **4**, both of which are more soluble than **1**. Further purification was effected by dissolution of the crude product in a minimum quantity of THF and layering the solution with three volumes of petroleum ether. Upon diffusional mixing of the solvents needlelike crystals of **1** suitable for crystallography were isolated: mp 151–154 °C dec; NMR (THF-d_8) δ 1.68 (d, J = 3 Hz), 6.21 (d, J = 0.25 Hz), 7.1–7.7 (m); NMR (benzene-d_6) δ 1.84 (d, J = 3 Hz), 5.81 (s), 6.9–7.7 (m); Far-IR (Nujol) 347 (s, br), 504 (s) cm^{-1}. Anal. Calcd for $C_{23}H_{22}ClPZr$: C, 60.57; H, 4,86; P, 6.79; Zr, 20.00; mol wt, 456. Found: C, 60.76; H, 5.03; P, 6.20; Zr, 18.49; mol wt (isopiestic, dimethyl ether), 452, 469 (±45).

Bis(η^5-cyclopentadienyl)bis[(diphenylphosphino)methyl]zirconium (4). To a solution of 1.80 g (6.2 mmol) of dichlorobis(η^5-cyclopentadienyl)zirconium in 200 mL of THF was added dropwise, with stirring, a solution of 4.00 g (12.4 mmol) of [(diphenylphosphino)methyl]lithium–tetramethylethylenediamine complex in 200 mL of THF at 25 °C under N_2. Removal of solvent under high vacuum left a light brown, oily residue which was stirred with four 200-mL portions of diethyl ether. The ether solutions were filtered to remove LiCl and cooled to −40 °C,

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[25] Bennett, M. A.; Pratt, L.; Wilkinson, G. *J. Chem. Soc.* **1961**, 2037. Eisch, J. J.; King, R. B. "Organometallic Syntheses"; Academic Press: New York, 1965; Vol. 1, p 122.

[26] See: Clark, E. P. *Ind. Eng. Chem., Anal. Ed.* **1941**, *13*, 820.

[27] Cf.: Planalp, R. P.; Andersen, R. A.; Zalkin, A. *Organometallics* **1983**, *2*, 16.

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precipitating a light brown solid. The supernatants were combined and evaporated, and the residue was extracted with one 200-mL ether portion which was also chilled. Combined precipitates weighed 3.43 g (90% crude yield). This material may be recrystallized from either ether alone or an ether–THF–petroleum ether mixture. The latter is more convenient, yielding 2.94 g light brown, crystalline 4 (77% yield): mp 166–168 °C dec; NMR (THF-d_8) δ 0.93 (d, J = 3 Hz), 6.04 (t, $J \approx 0.15$ Hz), 7.1–7.5 (m); NMR (benzene-d_6) δ 0.97 (d, J = 3 Hz), 5.76 (s), 7.0–7.7 (m); Far-IR (Nujol) 399 (w), 464 (s), 511 (s) cm^{-1}. Anal. Calcd for $C_{36}H_{34}P_2Zr$: C, 69.76; H, 5.53. Found: C, 67.80; H, 5.80.

Chlorobis(η^5-cyclopentadienyl)[μ-[(diphenylphosphino)methyl-*C*,*P*]](pentacarbonylchromium)zirconium (12). A solution of $Cr(CO)_5THF$ was prepared as follows: an irradiation vessel was constructed by attachment of a Pyrex tube to a Pyrex 250-mL 14/20 standard taper round-bottom flask. The test tube portion of the assembly was charged with ca. 1.0 g of hexacarbonylchromium and 25 mL of THF under N_2. This mixture was degassed via two freeze–pump–thaw cycles. The stirred mixture was then irradiated at 0 °C by using a medium-pressure Hanovia lamp for 24 h. Every 4–6 h irradiation was interrupted and evolved CO removed by freezing the slurry with liquid N_2 and evacuation of the irradiation vessel. The orange-red solution was then cooled to −40 °C, allowing unreacted $Cr(CO)_6$ to be removed as a precipitate.

A solution of 85 mg (0.19 mmol) of 1 in 1 mL of THF was treated with small portions of the $Cr(CO)_5THF$ solution until the color of the latter persisted after several minutes. After removal of solvent, the residue was dissolved in 2 mL of benzene and the product isolated by layering the solution with petroleum ether and allowing the solvents to mix by diffusion. The pale yellow prismatic crystalline product (100 mg, 80% yield) appeared to be ≥95% pure (major contaminant is unreacted $Cr(CO)_6$ by IR): mp 186–194 °C dec (darkens above ca. 155 °C); NMR (benzene-d_6) δ 1.82 (d, J = 11 Hz), 5.72 (s), 7.0–7.9 (m); IR (THF) 1930 (vs), 2050 (m) cm^{-1}. Anal. Calcd for $C_{28}H_{22}ClCrO_5PZr$: C, 51.88; H, 3.42; Cl, 5.47. Found: C, 46.50, 46.29; H, 4.11, 3.34; Cl, 6.61, 4.28.

Bis(η^5-cyclopentadienyl)bis[μ-[(diphenylphosphino)methyl-*C*,*P*]]bis(pentacarbonylchromium)zirconium (15). A solution of 0.397 g (0.640 mmol) of 4 in 150 mL of THF was rapidly stirred while 9.3 mL of an 0.138 M solution of $Cr(CO)_5THF$ (1.280 mmol) was added dropwise. The reaction was monitored by NMR and addition stopped when the Cp signal of the starting material at δ 6.04 was no longer visible. The mixture was stirred for 1 h and stripped in vacuo leaving a dark red oil. Trituration with 2 × 30 mL of petroleum ether left 0.482 g (75% yield) of an extremely air- and moisture-sensitive light red powder: NMR (benzene-d_6) δ 1.06 (d, J = 12 Hz), 5.59 (s), 6.9–8.0 (m); IR (THF) 1930 (vs), 2050 (m) cm^{-1}. Anal. Calcd for $C_{46}H_{34}Cr_2O_{10}P_2Zr$: C, 55.03; H, 3.41; P, 6.17. Found: C, 53.97; H, 3.98; P, 6.07.

Bis(η^5-cyclopentadienyl)bis[μ-[(diphenylphosphino)methyl-*C*,*P*]](*cis*-tetracarbonylchromium)zirconium (17). A solution of 0.30 g (1.2 mmol) of (norbornadiene)tetracarbonylchromium in 75 mL of THF was added dropwise over a period of 1 h to a rapidly stirred solution of 0.75 g (1.2 mmol) of 4 in 75 mL of THF under N_2 at 25 °C. A color change in the latter from light brown to light yellow and finally to red-orange was noted. The mixture was stirred for 18 h and volatile material removed under high vacuum. The light yellow powdery residue was washed with several portions of petroleum ether leaving 0.81 g (86% yield) of 17, spectroscopically ≥98% pure, and solvent free: NMR (benzene-d_6) δ 1.50 (d, J = 6 Hz), 5.30 (s), 7.0–7.9 (m); NMR (THF-d_8) δ 1.57 (d, J = 7 Hz), 5.85 (s), 7.3–7.7 (m); IR (CCl_4) 1880, 1916, 1994, 2000 cm^{-1}. Anal. Calcd for $C_{40}H_{34}ZrP_2CrO_4$: C, 61.28; H, 4.38. Found: C, 59.83, 63.43; H, 4.42, 4.91.

For the purpose of carrying out an X-ray crystal structure determination on 17, recrystallization was attempted via diffusional mixing of several combinations of solvents: benzene–petroleum ether (the compound is in fact not very benzene soluble; unsuitable microcrystalline product obtained); ether–THF–petroleum ether (crystals obtained, but too small to be suitable); THF–petroleum ether (apparently suitable crystals obtained which, however, collapsed to powder upon removal from solvent); diglyme–petroleum ether (suitable needlelike crystals obtained).

X-ray Crystal Structure Determinations. General Data. Crystals were grown for compounds 4, 12, and 17 as described above. Due to the moisture and air sensitivity of these materials, crystals were coated with epoxy resin before removal from the drybox and mounting. Details of procedure followed for each system are described separately. Computer programs used included a package developed by Prof. H. Hope for structure solution and full-matrix least-squares refinement on compounds 4 and 12. The rapid data collection technique used for 4 and 12 has been described elsewhere.[29] Programs used for blocked-cascade refinements on 4 and 12, and for all work involving 17, were those of the SHELXTL, Version 3, July 1981 package. Calculations were performed on a DGC Eclipse S/230 computer. Scattering factors were from common sources.[30] Absorption corrections were not applied.

X-ray Crystal Structure Determination for Bis[(diphenylphosphino)methyl]zirconocene (4). A prismatic crystal of 4 was coated with liquid epoxy, mounted, and cooled to 140 K in a stream of N_2. Final lattice parameters as determined from a least-squares refinement of the angular settings for 22 reflections accurately centered on the Syntex $P2_1$ diffractometer are given in Table I. Systematic extinctions in $0k0$ for $k = 2n + 1$ and in $h0l$ for $h = 2n + 1$ uniquely determined the space group to be $P2_1/a$. Data for 3853 reflections using an ω scan technique at a speed of 58.6 deg min^{-1} in the range $2\theta < 45°$ were obtained. The intensities of two check reflections were monitored throughout the data collection and showed no significant changes.

The position of the zirconium atom was determined via Patterson synthesis, and a subsequent Fourier map revealed the positions of the two phosphorus atoms. A second Fourier permitted the location of all 36 carbon atoms. With use of 2316 reflections for which $I > 3\sigma(I)$, full-matrix least-squares refinement of the 39 isotropic atoms gave an R factor of 0.078. The zirconium and phosphorus atoms were made anisotropic, and hydrogen atom positions were calculated. Allowing the hydrogens to ride on bonded carbon atoms, blocked-cascade least-squares refinement of 172 parameters led to final $R = 0.060$ and $R_w = 0.058$. A final difference Fourier map showed no feature greater than 1.0 e Å^{-3}. Final values of positional and thermal parameters are given in Tables VI, IX, and X.

X-ray Crystal Structure Determination for [(Diphenylphosphino)methyl]zirconocene Chloride–Chromium Pentacarbonyl Complex (12). Following the general procedure outlined for 4, lattice parameters were determined (Table I), and the space group was found to be $P2_1/n$ on the basis of systematic extinctions in $0k0$ for $k = 2n + 1$ and in $h0l$ for $h + l = 2n + 1$. Data for 3724 reflections were recorded; two check reflections showed no loss in intensity.

The zirconium atom was located on a Patterson map, and a single Fourier map revealed the positions of chlorine, chromium, and phosphorus. All non-hydrogen atoms were located on a second Fourier. Full-matrix least-squares refinement using 3036 reflections for which $I > 3\sigma(I)$ gave $R = 0.072$. With Zr, Cr, Cl, and P anisotropic and hydrogen atoms riding on bonded carbon atoms, blocked-cascade refinement gave final $R = 0.048$ and $R_w = 0.052$. The most prominent feature on a final difference Fourier map was 1.32 e Å^{-3}, apparently a spurious image of the Zr atom. Final values of positional and thermal parameters are given in Tables XII, XV, and XVI.

X-ray Crystal Structure Determination for Bis[(diphenylphosphino)methyl]zirconium–Chromium Tetracarbonyl Complex (17). Following the general procedure outlined for 4, lattice parameters were determined (Table I), and the space group was found to be $P2_1/n$. Data for 7996 reflections using an ω scan technique at a speed of 8 deg min^{-1} in the range $2\theta < 50°$ was obtained. Two check reflections showed no loss in intensity.

The structure was again phased by using a Patterson synthesis. All the atoms in the title compound were identified as were six additional carbon and three oxygen atoms at less than unit occupancy, corresponding to a molecule of diglyme.

Blocked-cascade least-squares refinement was carried out by

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using 4612 reflections with $I > 2\sigma(I)$, all non-hydrogen atoms except those in the diglyme anisotropic, and hydrogen atoms riding on carbons in the title complex molecule only. The occupancy of the diglyme molecule converged to 0.43, and final $R = 0.084$ and $R_w = 0.091$ were obtained. No feature larger than a hydrogen atom remained on a difference Fourier map. Final values of positional and thermal parameters are given in Tables XVIII, XX, and XXI.

Reduction Experiments Using Zirconocene Alkyl Halides. Preparation. Zirconocene *n*-octyl chloride (7) was prepared by a literature procedure. Zirconocene *n*-decyl chloride, ca. 90% ring-deuterated (8), was prepared as follows. Cyclopentadiene dimer (25 g, 0.19 mol) was cracked by distillation (hood, positive pressure of N_2) from a 180 °C pot through a short Vigreux column directly into an ice-cooled flask containing 40 mL of D_2O into which 0.1 g of sodium methoxide and 3 drops of benzyltrimethylammonium hydroxide solution had been introduced. After 1 day of rapid stirring the phases were separated and the cyclopentadiene was redistilled onto fresh D_2O–NaOMe–$BzMe_3N^+OH^-$. After an additional day of stirring this procedure was repeated once more. This time the cyclopentadiene was separated, dried over $MgSO_4$, degassed, and transferred into the drybox. A portion of this liquid (ca. 2 mL) was taken up in 25 mL of ether, cooled to −40 °C, and treated with excess *n*-butyllithium in hexane (2.4 M, 25 mL, 0.06 mol) dropwise. The precipitated solid was collected by filtration, washed with 2 × 5 mL of ether, and allowed to dry. No weight was taken as solid lithium cyclopentadienide occludes diethyl ether.

Ring-deuterated zirconocene dichloride was then prepared by treating a suspension of 2.22 g (9.5 mmol) of $ZrCl_4$ in 10 mL of THF with a solution of 1.34 g (ca. 17–18 mmol) of Li(Cp-d_n) in 10 mL of THF. After stirring at 27 °C for 1 h and removal of solvent, the residual solids were exhaustively extracted with ether. The combined extracts upon evaporation yielded 1.58 g (ca. 57%) of crude $(Cp\text{-}d_n)_2ZrCl_2$, of uncertain deuterium content. The latter was determined by using the straightforward analysis described below and ordinary 70-eV mass spectrometric data.

With the assumption of statistical distribution of D and H, the Bernoulli process of binomial expansion was used to calculate relative amounts of d_n, d_{n-1}, etc. species that would be present in a molecular fragment containing n hydrogens, for several different D/H ratios. These values were then fitted to the peak intensities in the isotope envelopes of several fragments in the $(Cp\text{-}d_n)_2ZrCl_2$ mass spectrum, using the known isotope ratios for C, Zr, and Cl in the calculation. A sample calculation for the Cp_2ZrCl^+ fragment is presented in the supplementary material to illustrate the procedure. The result of the calculation on several fragments was an overall deuteration of 89 ± 3%, with the best statistical agreement being 92% from the Cp_2ZrCl^+ ion. This corresponds to a $(Cp\text{-}d_n)_2ZrCl_2$ composition of 45% d_{10}, 37% d_9, 14% d_8, 3% d_7, and 1% d_6 or less. For convenience we have identified this mixture as $(C_5D_5)_2ZrCl_2$ throughout the paper.

This material (0.27 g, 0.9 mmol) was reduced to the monohydride via the usual procedure utilizing LiAlH(O-*t*-Bu)$_3$ (0.23 g, 0.9 mmol) in THF (1 mL). The hydride was collected by filtration, washed with THF, and treated directly with excess 1-decene. After the hydride had reacted, giving a homogeneous solution, all volatiles were removed at high vacuum, and the resulting viscous oil was triturated with petroleum ether. Decantation from a small amount of precipitated solid and removal of solvent left the ring-deuterated zirconocene *n*-decyl chloride (8) as a viscous oil which was used without further purification.

Hydrolysis of both the *n*-octyl- and ring-deuterated *n*-decylzirconocene chlorides gave the corresponding alkanes in quantitative yield (GC). Analysis of the decane from 8 showed a mass spectrum identical with that of commercial, undeuterated material.

Reduction. THF solutions of both 7 (0.11 M) and 8 (0.10 M) were prepared. After dilution to the required concentration, these were reduced with a large excess of 0.53% sodium amalgam. Reduction was complete in less than 1 h at room temperature, and the results were analyzed by GC and MS for yield and deuterium content of the alkane produced. Several additional experiments were carried out (a) at higher concentrations of 7, (b) with 7 in THF-d_8, (c) with utilization of an equivalent or a deficiency of Na/Hg, and (d) in the presence of CH_3PPh_2. In the case of experiments "d", several of which were carried out in NMR tubes, the formation of the dimeric zirconocene(III) phosphine 9 was revealed by the appearance of a pattern of signals in the δ 5–6 region of the proton NMR characteristic of the bridging $\eta^1{:}\eta^5$-C_5H_4 groups. Table V presents the results of all of these experiments in detail.

Reduction Experiments Using Chloro[(diphenylphosphino)methyl]zirconocene (1). Three solutions of 1 in THF were prepared for parallel, timed reduction experiments, as follows.

Analysis for Cleavage of Zr–C Bond. A solution of 0.119 g (0.26 mmol) of 1 in 8 mL of THF was treated with 0.776 g (0.27 mmol) of 0.8% Na/Hg. The mixture was stirred, and 0.5-mL aliquots were taken at various times after the start of the reaction. Each aliquot was treated with several drops of D_2O and stripped of THF in vacuo and the residue dissolved in ca. 50 μL of C_6D_6. Each solution was analyzed by NMR at 90 MHz using a microcell/thick-walled NMR tube. At times ≤4 h the signal corresponding to the methyl protons of methyldiphenylphosphine was found to be a clean doublet of 1:1:1 triplets at δ 1.43 with $J_{PCH} = 4$ Hz and $J_{DCH} = 2$ Hz. Addition of D_2O to an unreduced solution of 1 afforded a material with the same NMR; this was therefore assumed to be CH_2DPPh_2. At times ≥12 h a simple doublet, $J_{PCH} = 4$ Hz, began to appear at δ 1.45. Over a period of 2 weeks this doublet, superimposable with the NMR signal from CH_3PPh_2, gradually became the major feature in this region of the spectrum, with the aforementioned multiplet nearly disappearing.

ESR Analysis. Analysis for Cleavage of Zr–Cl Bond. A solution of 0.093 g (0.20 mmol) of 1 in 8 mL of THF was treated with 0.686 g (0.24 mmol) of 0.8% Na/Hg as described above. Small aliquots (ca. 0.3-mL each) were removed for ESR analysis at various times after the start of the reaction. The characteristic pattern for 11 (d superimposed on d of sextets, $g = 1.98$, $a_{Zr} = 13.5$ G, $a_P = 19.5$ G) was seen immediately, reaching maximum intensity in under 12 h. THF-insoluble material formed at this stage was collected, treated with 2 mL of water, filtered, acidified with nitric acid, and treated with 3 mL of 0.1 M aqueous $AgNO_3$. After the mixture was warmed briefly, allowed to cool, and filtered, 0.025 g (0.17 mmol) of AgCl was collected (85% yield). This analysis was repeated in a preparative experiment (vide infra).

The ESR-active THF solution was monitored over a period of 2 weeks, after which ESR signal intensity was found to have diminished to about 20% of its maximum value.

NMR Analysis. A solution of 0.094 g (0.20 mmol) of 1 in 0.6 mL of THF was treated with 0.792 g (0.28 mmol) of 0.8% Na/Hg in an NMR tube. The tube was shaken for 1–2 min, and a spectrum was recorded. This procedure was repeated several times over a period of an hour. The Cp signal for 1 gradually diminished to ca. 9% of its initial intensity. A signal for $Cp_2Zr(CH_2PPh_2)_2$ (4), initially present as only a very minor contaminant (ca. 2%), grew in intensity, and an unidentified, broad singlet at δ 5.5 appeared. After the mixture was left standing for 24 h, the signal for 1 was nearly gone (2% initial intensity), more bis(phosphine) 4 was present, and signals for Zr(III) dimer 9 were just visible. An intense ESR signal for 11 was visible. After 2 weeks, 1 was no longer present, the signal at δ 5.5 had disappeared, and 4 was present in 16% yield and 9 in 26% yield (calculated by using integration of phenyl region and solvent peaks as standards).

Preparation and Isolation of Reduction Product of 1: Bis(η^5-cyclopentadienyl)[η^2-(diphenylphosphino)methyl]zirconium (11). To a rapidly stirred solution of 0.298 g (0.65 mmol) of 1 in 50 mL of THF was added ca. 2 mL of 0.66% Na/Hg (ca. 0.8 mmol) dropwise, whereupon the initially pale yellow solution took on a crimson color. NMR analysis at this stage showed 1 to have been completely consumed. The reaction mixture was decanted and then filtered through a frit, and the residual Hg pool was stirred with several small (ca. 2-mL) THF portions which were likewise filtered. The combined gray THF-insoluble solids were treated in the manner described previously, resulting in the isolation of 0.088 g (0.61 mmol) of solid AgCl (94% yield).

The red THF filtrate was reduced to a dark red oil in vacuo and triturated with 20 mL of petroleum ether. Filtration gave a pale reddish powder which was stirred with two more 20-mL portions of petroleum ether, followed again by filtration. The powder was then washed with several additional small (ca. 2-mL) portions of solvent. Total weight of solid material isolated in this manner was 0.145 g (53% yield): ESR (THF) $g = 1.98$, $a(^{31}P) = 19.5$ G (doublet), $a(^{91}Zr) = 13.5$ G (sextet). Anal. Calcd for $C_{23}H_{22}ZrP$: C, 65.68; H, 5.27; Zr, 21.69; P, 7.36; Cl, 0.00. Found: C, 60.30, 67.72; H, 4.91, 4.94; Zr, 20.30; P, 6.67; Cl, 1.95.

The magnetic susceptibility was estimated by preparing a 1% solution in benzene, which gave rise to an 8.5-Hz shift of the solvent resonance at 90 MHz. This gives rise to $\chi_g = (3.60 \pm 0.36) \times 10^{-6}$, $\chi_M = (1.51 \pm 0.15) \times 10^{-3}$, and $\mu_{eff} = 1.90 \pm 0.10$.

Acknowledgment. We wish to thank Professors R. G. Bergman, N. J. Cooper, and T. J. Marks for helpful discussions. We thank the Committee on Research of the University of California and the University of California at Davis NMR Facility for financial support. Purchase of the NT-200 and NT-360 instruments was made possible by an instrumentation grant from the National Science Foundation (Grant CHE-79-04832). Grateful acknowledgment is also made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for the support of this research.

Registry No. 1, 74380-49-7; 4, 74395-16-7; 7, 54634-14-9; 8, 87184-11-0; 11, 87184-10-9; 12, 74379-16-1; 15, 87184-09-6; 17, 87184-08-5.

Supplementary Material Available: Listings of atomic coordinates (Tables VI, XII, and XVIII), bond lengths (Tables VII, XIII, and XIX), bond angles (Tables VIII, XIV, and XX), temperature factors (Tables IX, XV, and XXI), derived hydrogen coordinates (Tables X, XVI, and XXII), and structure factors (Tables XI, XVII, and XXIII) for **4**, **12**, and **17** and a description of the determination of D/H distribution in "$(C_5D_5)_2ZrCl$" (79 pages). Ordering information is given on any current masthead page.

Structural Consequences of Oxidation of Ferrocene Derivatives. 1. [0.0]Ferrocenophanium Picrate Hemihydroquinone

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Received August 1, 1983

The crystal and molecular structures of the title compound I, $C_{20}H_{16}Fe_2^{+}\cdot C_6H_2N_3O_7^{-}\cdot{}^1/_2(C_6H_6O_2)$, were determined. The plane of the picrate lies essentially parallel to the planes of the cyclopentadienyl rings of the ferrocenophane with indication of some degree of charge transfer. The hydroquinone is hydrogen bonded to the O(1) oxygen atoms of two picrates and lies essentially normal to the picrate and to the ferrocenophane separating two-dimensional layers of picrate–ferrocenophane stacks. The iron–iron distance is 363.6 (1) pm, 34 (2) pm shorter than in the neutral ferrocenophane, supporting a theory that the average valency of this ferrocenophane monocation is due at least partially to an iron–iron interaction and not exclusively to an interaction through the cyclopentadienyl rings.

Introduction

The preparation[1-5] of [0.0]ferrocenophane (II) and the subsequent preparation of its mono-[2-5] and dications[5,6] have led to an extensive investigation of the physical properties of these compounds, both experimentally[1-13] and theoretically.[14] Of principal concern were questions on the interaction between the iron atoms and on the average or mixed valency of the monocation. The results[15] of the crystal and molecular structure of II excluded the likelihood of an iron–iron interaction in that compound. The observed iron–iron distance in II of 398 (2) pm is 6 pm longer than that expected from perfectly aligned cyclopentadienyl rings with the iron atoms on the axes normal to the centroids of those rings. A very small repulsion is all that can be discerned. On the other hand, the observation that the monocation is average valent, by virtue of the identical irons observed in both Mössbauer[3,5,8,10] and ESCA[3,5,13] measurements, requires a strong iron–iron interaction. The interaction may be directly between the irons[8,9,11,12] or through the cyclopentadienyl rings[5-7,10,14] or by both paths. These unreconciled theories prompted the present work: the determination of the crystal structure of the monocation, as exemplified by the title compound, I.

Table I. Crystal Data

mol formula	$C_{20}H_{16}Fe_2\cdot C_6H_2N_3O_7\cdot{}^1/_2(C_6H_6O_2)$
mol wt	651.14
space group	$P\bar{1}$
a, pm	1039.9 (1)
b, pm	1374.8 (4)
c, pm	1022.5 (1)
α, deg	91.01 (2)
β, deg	118.99 (1)
γ, deg	78.23 (1)
V, nm^3	1.2462
Z	2
ρ_{calcd} g/cm^3	1.770
abs coeff, cm^{-1}	11.89
2θ range, deg	2–60
reflctns used ($F > 3\sigma$)	8025
parameters refined	5245
scan width	463
$R(F) = \Sigma\lvert F_o - F_c\rvert/\Sigma\lvert F_o\rvert$	$0.75 + 0.35 \tan\theta$
$R_w(F) = \Sigma\lvert F_o - F_c\rvert w^{1/2}/$	0.039
$\Sigma\lvert F_o\rvert w^{1/2}$ ($w = 1/(\sigma^2(F) +$	0.038
$0.0005F^2$))	0.07
max shift/error (non-H)	0.12
max shift/error (H)	510
residual electron density, e nm^{-3}	

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