$(PhCN)_2PtBr_2$, 15130-13-9; ferrocene, 102-54-5; methyl disulfide, 624-92-0; 1,1′-dilithioferrocene, 33272-09-2; isopropyl disulfide, 4253-89-8; isobutyl disulfide, 1518-72-5; phenyl disulfide, 882-33-7; benzyl disulfide, 150-60-7.

Supplementary Material Available: A table of electronic absorption spectra of the ferrocenyl sulfides, tables of anisotropic thermal parameters, isotropic thermal parameters, and least-squares planes, a table of torsion angles, and a table of observed structure factors, standard deviations, and differences for $Fe(C_5H_4S\text{-}i\text{-}Bu)_2PdCl_2$ (29 pages). Ordering information is given on any masthead page.

Synthesis, Structure Determinations, and Reduction of $(C_5H_5)_2Zr(Cl)CH_2PMe_2$ and $(C_5Me_5)_2Zr(Cl)CH_2PPh_2$

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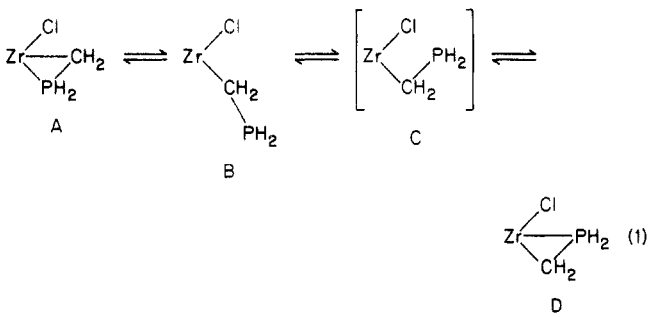
The syntheses and X-ray crystallographic analyses of $Cp_2Zr(Cl)CH_2PMe_2$ (2) and $(C_5Me_5)_2Zr(Cl)CH_2PPh_2$ (3) are reported. The former is monoclinic of space group $P2_1/n$ with a = 8.077 (3) Å, b = 14.896 (6) Å, c = 11.704 (3) Å, β = 99.27 (3)°, V = 1389.8 (8) Å^3, and Z = 4. This compound is structurally very similar to $Cp_2Zr(Cl)CH_2PPh_2$ in possessing an extended, almost anti conformation for the Cl–Zr–C–P fragment about the Zr–C bond and a nonbonded Zr···P distance of 3.72 Å. The permethylcyclopentadienyl complex is monoclinic of space group $P2_1/n$ with a = 10.285 (3) Å, b = 20.739 (5) Å, c = 14.078 (8) Å, β = 96.79 (4)°, V = 2982 (2) Å^3, and Z = 4. In spite of the much bulkier ligands, this compound contains a gauche-like Cl–Zr–C–P system with a 31° dihedral angle and a relatively short 3.56-Å Zr···P distance. One electron reduction of 2 produces a persistent P-bound Zr(III) species. In contrast, reduction of 3 gives a Zr(III) species lacking appreciable Zr–P interaction. The possible consequences of electronic and steric factors on these structures are discussed.

Introduction

Ever since the synthesis of $Cp_2Zr(Cl)CH_2PPh_2$ (1) in 1980[1] we have been intrigued by the unusual structural characteristics of this molecule. In spite of the presence of a lone pair on phosphorus and coordinative unsaturation at the metal, no bonding interaction between them exists. Indeed, a calculation on the model system $Cp_2Zr(Cl)$-CH_2PH_2 gives rise to three structural minima (eq 1,



(1)

structures A, B, and D). The large P···Zr nonbonding distance (3.75 Å) and the 130° Zr–C–P angle in 1 are reproduced well in structure B and are explained by a strong P–Zr repulsive electronic interaction that exists in this geometry. Two different geometries (A and D) with full Zr–P bonds are actually calculated to be more stable than the open form, although neither is observed. An electronic barrier separates B from A, while conversion to D requires rotation to C, which is not a local energy minimum, and should collapse directly to the Zr–P bonded structure. Assuming the validity of the calculations, the lack of Zr–P bonding in 1 is due both to these barriers to structural interconversion and to steric destabilization of the Zr–P bonded forms due to the substituents on phosphorus. The electronic barrier is found to vanish upon reduction of the metal and loss of chloride ion. Thus phosphine complexation to both zirconocene[1,3] and titanocene[4,5] derivatives is observed with the metal in the +3 oxidation state. Preliminary results from a study of niobocene +4 and +3 derivatives show that similar effects are operative in the group 5 metals as well.[6]

Table I. Crystal Data

	$(C_5H_5)_2ZrCl$-(CH_2PMe_2)	$(C_5Me_5)_2ZrCl$-(CH_2PPh_2)
mol wt, amu	331.95	596.35
d(calcd) (140 K), g cm^{-3}	1.59	1.33
max cryst dim, mm	0.075 × 0.25 × 0.50	0.08 × 0.25 × 0.30
space group	$P2_1/n$	$P2_1/n$
molecules/unit cell	4	4
cell constants[a]		
a, Å	8.077 (3)	10.285 (3)
b, Å	14.896 (6)	20.739 (5)
c, Å	11.704 (3)	14.078 (8)
β, deg	99.27 (3)	96.79 (4)
cell vol, Å^3	1389.8 (8)	2982 (2)
abs coeff μ, cm^{-1}	10.5	5.2

[a] T = 140 K; Mo Kα radiation, λ = 0.71069 Å, graphite monochromator.

(1) Schore, N. E.; Hope, H. *J. Am. Chem. Soc.* **1980**, *102*, 4251.
(2) Hofmann, P.; Stauffert, P.; Schore, N. E. *Chem. Ber.* **1982**, *115*, 2153.
(3) Schore, N. E.; Young, S. J.; Olmstead, M. M.; Hofmann, P. *Organometallics* **1983**, *2*, 1769.
(4) Etienne, M.; Choukroun, R.; Basso-Bert, M.; Dahan, F.; Gervais, D. *Nouv. J. Chem.* **1984**, *8*, 531. Etienne, M.; Choukroun, R.; Gervais, D. *J. Chem. Soc., Dalton Trans.* **1984**, 915.
(5) LeBlanc, J. E.; Moise, C.; Maisonnat, A.; Poilblanc, R.; Charrier, C.; Mathey, F. *J. Organomet. Chem.* **1982**, *231*, C43.
(6) Schore, N. E. and Tueting, D. R., unpublished results.

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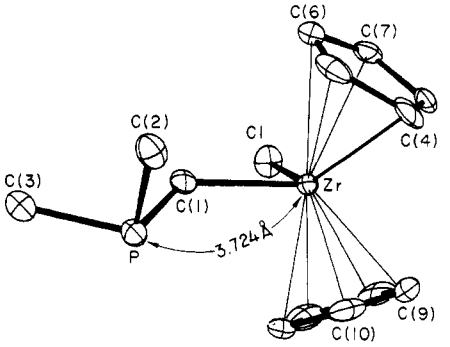


Figure 1. Computer-drawn representation of **2**.

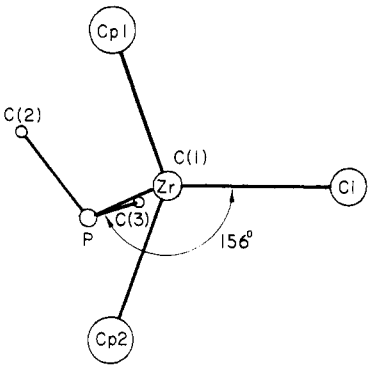


Figure 2. Newman projection of **2** sighting down Zr–C(1) bond.

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

	$(C_5H_5)_2Zr(Cl)CH_2PPh_2$[a]	$(C_5H_5)_2Zr(Cl)CH_2PMe_2$	$(C_5Me_5)_2Zr(Cl)CH_2PPh_2$
d_{Zr-Cl}	2.453	2.457 (2)	2.428 (1)
d_{Zr-CH_2}	2.281	2.272 (6)	2.317 (5)
d_{CH_2-P}	1.834	1.833 (7)	1.829 (5)
$d_{P-C(Me\ or\ Ph)}$	1.809, 1.829	1.845 (7), 1.843 (7)	1.836 (5), 1.847 (5)
$d_{Zr-C(Cp)}$ (range)	2.475–2.534	2.481 (7)–2.545 (7)	2.540 (5)–2.585 (5)
$CH_2-Zr-Cl$	92.3	95.4 (2)	97.1 (1)
$Zr-CH_2-P$	131.1	129.9 (3)	117.9 (2)
$Cp-Zr-Cp$[b]	130.7	129.4	136.4

[a] Reference 1. [b] Refers to ring centroids.

In order to approach situations in which phosphine bonding to Zr(IV) might be observable, we have prepared and structurally characterized $Cp_2Zr(Cl)CH_2PMe_2$, where steric hindrance at phosphorus is reduced, and $(C_5Me_5)_2Zr(Cl)CH_2PPh_2$, whose permethylated Cp ligands introduce additional electron density at the metal comparable to that associated with one-electron reduction.[7] The results of these studies are reported herein.

Results and Discussion

The synthesis of $Cp_2Zr(Cl)CH_2PMe_2$ (**2**) was carried out via reaction of Me_2PCH_2Li and Cp_2ZrCl_2 in THF at −78 °C, essentially the method of Karsch et al.,[8] and the product was crystallized from ether solution at −20 °C. The structure of **2** is closely analogous to that of **1**, showing in particular an extended, nearly anti conformation for the Cl–Zr–C–P fragment (dihedral angle = 156°), an unusually open Zr–C–P bond angle of 130°, and a nonbonded Zr–P distance of 3.724 Å (Figure 1 and 2 and Tables I, II, IV, and V). Thus, in spite of the reduced steric hindrance and increased basicity at phosphorus, no evidence for

Table III. ^{31}P NMR Data[a]

compd	δ	compd	δ
CH_3PPh_2	−26.2	$(CH_3)_3P$	−61.8
$(C_5H_5)_2Zr(Cl)CH_2PPh_2$	−1.8[b]	$(C_5H_5)_2Zr(Cl)CH_2PMe_2$	−34.8
$(C_5Me_5)Zr(Cl)CH_2PPh_2$	−12.5		

[a] Proton-decoupled spectra were recorded at 81 MHz in C_6D_6 at 20 °C. Chemical shifts are reported in δ; values downfield from external H_3PO_4 are positive in sign. [b] Reference 3 (spectrum recorded in CD_2Cl_2 solvent).

Table IV. Atom Coordinates (×10⁴) and Temperature Factors (Å² × 10³) for 2

atom	x	y	z	U[a]
Zr	3604 (1)	3047 (1)	4702 (1)	15 (1)
Cl	5410 (2)	3772 (1)	6331 (2)	30 (1)
P	1797 (2)	846 (1)	5373 (2)	20 (1)
C(1)	3422 (8)	1715 (4)	5619 (5)	20 (2)
C(2)	2417 (9)	177 (5)	4184 (6)	25 (2)
C(3)	2511 (9)	53 (5)	6560 (6)	26 (2)
C(4)	3883 (9)	2785 (5)	2641 (6)	28 (3)
C(5)	4662 (9)	2046 (5)	3229 (6)	30 (3)
C(6)	6098 (10)	2335 (5)	3968 (6)	32 (3)
C(7)	6231 (8)	3260 (5)	3802 (6)	28 (2)
C(8)	4854 (8)	3552 (5)	3010 (6)	24 (2)
C(9)	1149 (9)	3856 (5)	3598 (7)	34 (3)
C(10)	550 (8)	3040 (6)	3925 (6)	31 (2)
C(11)	640 (8)	3039 (5)	5124 (6)	26 (2)
C(12)	1334 (9)	3846 (5)	5551 (7)	35 (3)
C(13)	1664 (9)	4348 (5)	4604 (8)	38 (3)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table V. Atom Coordinates (×10⁴) and Temperature Factors (Å² × 10³) for 3

atom	x	y	z	U[a]
Zr	6378 (1)	2453 (1)	3553 (1)	14 (1)
Cl	5053 (1)	2078 (1)	2118 (1)	20 (1)
P	8257 (1)	1224 (1)	2594 (1)	19 (1)
C(1)	7847 (5)	1602 (2)	3694 (3)	18 (2)
C(2)	9748 (5)	748 (2)	2967 (3)	17 (2)
C(3)	10438 (5)	491 (2)	2260 (3)	22 (2)
C(4)	11595 (5)	164 (2)	2459 (4)	28 (2)
C(5)	12118 (5)	70 (2)	3395 (4)	31 (2)
C(6)	11465 (5)	309 (2)	4118 (4)	28 (2)
C(7)	10293 (5)	646 (2)	3915 (3)	25 (2)
C(8)	7051 (5)	570 (2)	2415 (3)	18 (2)
C(9)	6118 (5)	578 (2)	1613 (3)	25 (2)
C(10)	5185 (5)	97 (2)	1461 (4)	33 (2)
C(11)	5164 (6)	−406 (2)	2102 (4)	34 (2)
C(12)	6091 (5)	−428 (2)	2889 (3)	28 (2)
C(13)	7019 (5)	53 (2)	3048 (3)	24 (2)
C(14)	8497 (5)	2957 (2)	3059 (3)	19 (2)
C(15)	8143 (5)	3322 (2)	3844 (3)	17 (2)
C(16)	6964 (5)	3655 (2)	3531 (3)	14 (2)
C(17)	6559 (5)	3472 (2)	2577 (3)	17 (2)
C(18)	7512 (5)	3057 (2)	2287 (3)	19 (2)
C(19)	9816 (5)	2652 (2)	3025 (4)	29 (2)
C(20)	9044 (5)	3424 (3)	4760 (3)	31 (2)
C(21)	6439 (5)	4234 (2)	3998 (3)	24 (2)
C(22)	5415 (5)	3753 (2)	1949 (3)	28 (2)
C(23)	7568 (6)	2811 (3)	1275 (3)	28 (2)
C(24)	4218 (5)	2128 (2)	4175 (3)	18 (2)
C(25)	5167 (5)	1690 (2)	4601 (3)	16 (2)
C(26)	6094 (5)	2040 (2)	5238 (3)	15 (2)
C(27)	5696 (5)	2701 (2)	5201 (3)	17 (2)
C(28)	4551 (5)	2757 (2)	4534 (3)	17 (2)
C(29)	2971 (5)	1951 (3)	3577 (3)	30 (2)
C(30)	5088 (5)	973 (2)	4474 (3)	22 (2)
C(31)	7175 (5)	1758 (2)	5920 (3)	26 (2)
C(32)	6261 (6)	3203 (2)	5912 (3)	26 (2)
C(33)	3661 (5)	3332 (2)	4380 (4)	32 (2)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

(7) Gassman, P. G.; Macomber, D. W.; Hershberger, J. W. *Organometallics* **1983**, *2*, 1470.
(8) Karsch, H. H.; Müller, G.; Krüger, C. *J. Organomet. Chem.* **1984**, *273*, 195. See also: Engelhardt, L. M.; Jacobsen, B. E.; Raston, C. L.; White, A. H. *J. Chem. Soc., Chem. Commun.* **1984**, 220.

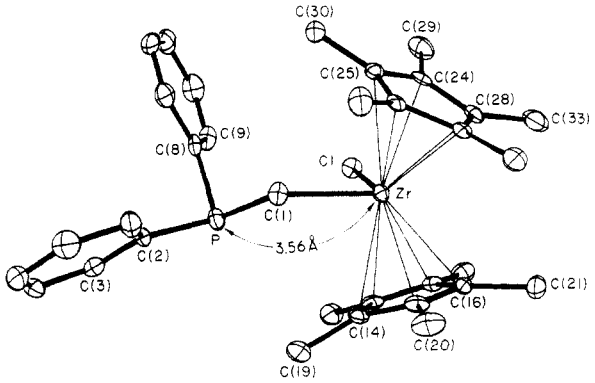


Figure 3. Computer-drawn representation of **3**.

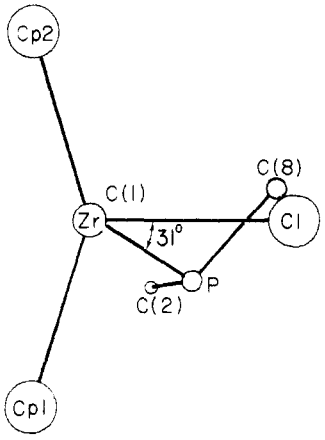


Figure 4. Newman projection of **3** sighting down Zr–C(1) bond.

conversion to a Zr–P bonded species is obtained. Variable-temperature ^{1}H NMR measurements over the range −75 to +60 °C show only very minor chemical shift changes, nothing of the magnitude that might be expected if equilibration with another major structural isomer were taking place.

Replacement of C_5H_5 ligands by C_5Me_5 increases both steric hindrance and electron density at the metal. The latter presumably "softens" the metal as an electrophile as well, however,[9] thus perhaps promoting better orbital overlap in a possible Zr–P bonded geometry. In order to ascertain the balance between these diverse factors experimentally, attempts were made to synthesize two compounds $(C_5Me_5)_2Zr(Cl)CH_2PPh_2$ (**3**) and $(C_5Me_5)_2Zr(Cl)$-CH_2PMe_2. Only the former could be readily obtained in pure form; suitable crystals for X-ray analysis were obtained by THF recrystallization. The structure (Figure 3) shows significant differences compared with the unsubstituted Cp systems. Most obvious is a completely different, nearly gauche conformation for the Cl–Zr–C–P fragment (dihedral angle = 31°), apparently putting the tertiary phosphine in position for possible partial overlap with the central lobe of the LUMO at the metal (Figure 4). In the plane of the LUMO, the steric hindrance of the C_5Me_5 rings is least severe in the direction of this central lobe, and this, presumably, is the primary factor in inducing the change in solid-state conformational preference. Interestingly, however, the observed Zr–P nonbonding distance in **3** is 3.56 Å, 0.1–0.2 Å *shorter* than that observed in any other compound of this general type. Likewise, the Zr–C–P angle is 118°, also the smallest yet to be observed. For comparison, a similar structural element is found in $Cp_2Zr(CH_2PPh_2)_2$, in which one of the two phosphino-

(9) Parr, R. G.; Pearson, R. G. *J. Am. Chem. Soc.* **1983**, *105*, 7512.

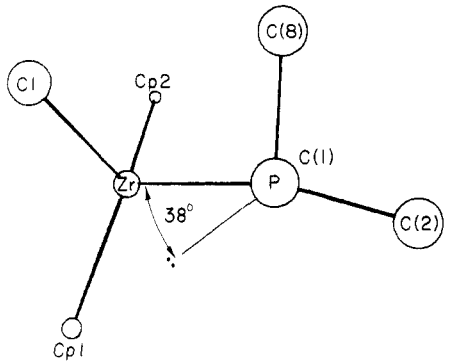
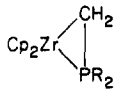


Figure 5. Newman projection of **3** sighting down P–C(1) bond.

methyl ligands displays a true gauche conformation (C–Zr–C–P dihedral angle = 69°) in the solid state with d_{Zr-P} = 3.64 Å and ∠Zr–C–P = 122°.[3] How can **3**, with much more steric hindrance at the metal due to the permethylated rings, exhibit such a significantly shortened Zr–P nonbonding distance?

It is tempting to invoke an attractive electronic interaction between Zr and P and to describe **3** as exhibiting geometry C in eq 1; that is, it *should* collapse without resistance to D *but is sterically prevented from doing so.* However, the observed Zr–P distance is really quite large: ca. 0.8 Å longer than typical Zr–P bond lengths.[8,10] In addition, the lone pair on phosphorus is not well aligned for overlap with the metal LUMO in the "equatorial" plane of the molecule: the conformation about the CH_2–P bond (Figure 5) implies a dihedral angle of 38° between the Zr–C bond and the P lone pair. Phosphorus-31 NMR measurements, in accord with these structural observations, show little indication of the characteristic downfield shifts that would be expected to accompany significant P–metal interaction (Table III). Thus the presence of Zr–P attraction is called into question. We clearly do not know enough about the characteristics of these systems as a whole to determine all the reasons behind these structural differences or, for that matter, whether or not they are electronically significant.

It is possible, however, to determine whether Zr-P bonding is ultimately sterically permitted in either of these systems, simply by effecting one-electron reduction of the metal.[1-3] We earlier showed[1,3] that reduction of **1** by dilute sodium amalgam results in quantitative release of chloride (determined gravimetrically) and forms a long-lived paramagnetic species formulated as **4a** on the basis of ESR



4a, R = Ph
b, R = Me

($a(^{31}P)$ = 19.5 G and $a(^{91}Zr)$ = 13.5 G), molecular weight determination (*isopiestic*), and D_2O treatment (forms DCH_2PPh_2 by Zr–C bond cleavage). Reduction of **2** with 1.2% Na/Hg proceeds very much like that of **1**, producing a long-lived paramagnetic species showing significant hyperfine coupling of the unpaired electron with both P and Zr nuclei ($a(^{31}P)$ = 20.2 G and $a(^{91}Zr)$ = 13.2 G). Due to the similarities in the ESR spectra of the reduced species, we presume that $2^{-}\cdot$ also loses chloride, forming **4b**. In

(10) Fischer, M. B.; James, E. J.; McNeese, T. J.; Nybing, S. C.; Posin, B.; Wong-Ng, W.; Wreford, S. S. *J. Am. Chem. Soc.* **1980**, *102*, 4941. Fryzuk, M. D.; Williams, H. D.; Rettig, S. J. *Inorg. Chem.* **1983**, *22*, 863. Choukroun, R.; Dahan, F.; Gervais, D. *J. Organomet. Chem.* **1984**, *266*, C33. Young, S. J.; Hope, H.; Schore, N. E. *Organometallics* **1984**, *3*, 1585.

contrast, reduction of **3** is more difficult (requiring at least 1.6% Na/Hg) and clearly produces a strikingly different ESR-active species, displaying $a(^{91}Zr)$ = 104.3 G and *no observable hyperfine interaction with phosphorus* whatsoever. Control experiments (i.e., Na/Hg reductions of $(C_5Me_5)_2ZrCl_2$, $(C_5Me_5)_2ZrCl_2$ + $MePPh_2$, or $(C_5Me_5)_2Zr(CH_2PPh_2)_2$) do not result in significant generation of any persistent ESR-active species. As in the case of **1**, the insoluble residue remaining after reduction of **3** is found to contain chloride ion, and D_2O treatment of the supernatant leads exclusively to DCH_2PPh_2. We therefore propose that the reduction of **3** leads to a paramagnetic Zr(III) species best represented by **5**, containing no Zr–P bonding. The implication is that permethyl substitution

$$(C_5Me_5)_2ZrCH_2PPh_2$$
5

on the Cp rings sterically prohibits Zr–P bonding, even when it might be strongly favored electronically. It would thus appear that observation of the predicted Zr–P bonding in structures such as these will be an elusive goal.[11]

Experimental Section

General Data. All preparations were carried out under an atmosphere of prepurified N_2 or Ar 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. Ph_2PCH_2Li,[12] Me_2PCH_2Li,[13] and $(C_5Me_5)_2ZrCl_2$[14] were prepared by literature methods. Cp_2ZrCl_2 (Aldrich) was used as received. Spectroscopic data were collected on Varian EM-390, Nicolet NT-200, and Nicolet NT-360 NMR spectrometers. Elemental analyses were carried out by Dornis und Kolbe and Galbreath Microanalytical Laboratories.

Chlorobis(η^5-cyclopentadienyl)[(dimethylphosphino)methyl]zirconium (2). A solution of 0.15 g (1.83 mmol) of [(dimethylphosphino)methyl]lithium in 100 mL of THF was added dropwise over an 8-h period to a rapidly stirred solution of 0.55 g (1.88 mmol) of dichlorobis(η^5-cyclopentadienyl)zirconium in 250 mL of THF at −78 °C under Ar. The mixture was allowed to come to room temperature and was stirred for an additional 3 h. The volatiles were removed at high vacuum, and the brown residue was extracted with 2 × 300 mL of ether (several hours of stirring per extraction). Cooling of the extracts to −20 °C caused precipitation of **2** (0.50 g). Reduction of the filtrate solvent volume to ca. 150 mL and cooling afforded 10% additional product. The combined solids were then washed with 3 × 10 mL of *n*-hexane for a total yield of 0.55 g (91%) of **2**, pure by 360-MHz NMR. Small crystals suitable for crystallography were isolated from a saturated solution of **2** in ether which was cooled to −20 °C: NMR (benzene-d_6) δ 0.98 (d, J = 4.78 Hz, 6 H), 1.06 (d, J = 3.25 Hz, 2 H), 5.91 (d, J = 0.23 Hz, 10 H). Anal. Calcd for $C_{13}H_{18}ClPZr$: C, 47.04; H, 5.47; Cl, 10.68. Found: C, 46.90; H, 5.42; Cl, 10.66.

Chlorobis(η^5-pentamethylcyclopentadienyl)[(diphenylphosphino)methyl]zirconium (3). A solution of 0.055 g (0.27 mmol) of [(diphenylphosphino)methyl]lithium in 50 mL of THF was added dropwise over a 3-h period to a rapidly stirred solution of 0.11 g (0.25 mmol) of dichlorobis(η^5-pentamethylcyclopentadienyl)zirconium in 100 mL of THF at −78 °C under N_2. The mixture was allowed to come to room temperature and stirred for an additional 2 h. The volatiles were removed at high vacuum, and the yellow residue was extracted with 2 × 100 mL of ether. The extracts were combined, and the volume was reduced to ca. 25 mL as the product precipitated. The mixture was filtered affording 0.11 g (75%) of **3**, pure by 360-MHz NMR. Crystals suitable for crystallography were isolated from a saturated solution of **3** in THF which was cooled to −20 °C: NMR (benzene-d_6) δ 1.03 (d, J = 3.85 Hz, 2 H), 1.78 (s, 30 H), 7.00–7.40 (m, 10 H). Anal. Calcd for $C_{33}H_{42}ClPZr$: C, 66.46; H, 7.10; Cl, 5.95. Found: C, 65.92; H, 6.50; Cl, 6.14.

Reduction of 3. A sample of **3** weighing 17.0 ± 0.5 mg (0.029 mmol) was dissolved in 5 mL of benzene and stirred over 10 g of 1.7% Na/Hg. After 4 h the ESR signal attributed to **5** was readily observable. Stirring was continued for 2 days to complete the reduction. Suspended solids were collected by filtration; the amalgam was further washed with 3 × 5 mL of benzene to ensure transfer of any precipitate. The filtrate was treated with D_2O, leading to the appearance of the characteristic proton NMR signals of DCH_2PPh_2[3] (note: no NMR signals due to $Ph_2PCH_2^-$ were present prior to this step). The gray precipitate collected above was treated with several 2-mL portions of 0.3% aqueous HNO_3 and filtered. This filtrate, upon treatment with ca. 0.5 mL of 0.1 M aqueous $AgNO_3$, yielded 2.6 ± 0.2 mg of AgCl, corresponding to 64 ± 7% of the Cl originally present as **3**. On this scale manipulative losses are unavoidable, although their magnitude is difficult to estimate.

X-ray Crystal Structure Determinations

General Data. Crystals were grown for compounds **2** and **3** described above. Due to the moisture and air sensitivity of these materials, crystals were coated with epoxy resin before removal from the drybox. Data were collected on a Syntex $P2_1$ diffractometer equipped with a low-temperature apparatus. No loss in intensity of two standard reflections was observed in either case. Computer programs used were those of SHELXTL, Version 4.[15] Scattering factors were from common sources.[16] Absorption corrections were not applied. Crystal data are collected in Table I.

X-ray Crystal Structure Determination for 3. Intensity data were collected to $2\theta_{max}$ of 45° in the quadrant $h,k,\pm l$ using an ω scan of 1° width at 15° min^{-1} and a 1° offset for background counts. The space group was determined by a series of axial photographs and preliminary fast scans showing the conditions $0k0$, $k = 2n$, and $h0l$, $h + l = 2n$. A total of 4326 reflections were collected, of which 3890 were unique; R(merge) = 0.020. Of these, 723 were suppressed as unobserved ($F < 2.5\sigma(F)$), leaving 3167 for solution and refinement of the structure. The structure was solved by direct methods. No difficulty was encountered in the location of all the atoms, including hydrogen atoms. In the final cycles of refinement, non-hydrogen atoms were assigned anisotropic thermal parameters, while hydrogen atoms were included at calculated positions using a riding model and U_{iso} = $1.2U_{iso}$ (bonded carbon atom). The largest feature in the final difference map was 0.46 e Å^{-3} and of no possible chemical significance. A weighting scheme of $w = 1/\sigma^2(F)$ was used. Final agreement factors were R = 0.049 and R_w = 0.039 (355 parameters).

X-ray Crystal Structure Determination for 2. Data collection and space group determination followed the above procedure. Due to the slightly poorer crystal quality, ω scans of 1.6° width, a 1.2° offset for background, and a speed of 10° min^{-1} were used. A total of 2079 reflections were measured; 1785 were unique, R(merge) = 0.027; 1509 were retained for solution and refinement ($F > 2.5\sigma(F)$). Refinement was carried out as for **3** except that the two sets of methyl hydrogen atoms had common isotropic thermal parameters that were allowed to refine. These converged at U = 0.034 Å^2 for H(2A), H(2B), and H(2C) and 0.029 Å^2 for H(3A), H(3B), and H(3C). No feature larger than 0.50 e Å^{-3} remained on a final difference map. Final agreement factors were R = 0.041 and R_w = 0.030 (153 parameters).

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Registry No. 2, 90967-69-4; 3, 96898-11-2; 4b, 96898-12-3; 5, 96898-13-4; Cp_2ZrCl_2, 1291-32-3; $(C_5Me_5)_2ZrCl_2$, 54039-38-2; Me_2PCH_2Li, 64065-06-1.

Supplementary Material Available: Listings of bond lengths (Tables X and XI), bond angles (Tables VI and XII), temperature factors (Tables VII and XIII), derived hydrogen coordinates (Tables VIII and XIV), and structure factors (Tables IX and XV) (36 pages). Ordering information is given on any current masthead page.

Alkylidyne–Alkylidyne Coupling Induced by Carbon Monoxide Addition to the Bis(alkylidyne) Cluster $Fe_3(CO)_9(\mu_3\text{-}CCH_3)(\mu_3\text{-}COC_2H_5)$: An Unexpected Reversible Reaction. X-ray Structure of $Fe_3(CO)_9[P(C_6H_5)_3](\mu_3\text{-}\eta^2\text{-}CH_3C{\equiv}COC_2H_5)$

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The bis(alkylidyne) cluster $Fe_3(CO)_9(\mu_3\text{-}CCH_3)(\mu_3\text{-}COC_2H_5)$ reacts with carbon monoxide, at room temperature and under 20 atm, leading quantitatively to $Fe_3(CO)_{10}(\mu_3\text{-}\eta^2\text{-}CH_3C{\equiv}COC_2H_5)$ (1). Coupling of the two alkylidynes is established from ^{13}C NMR data. Unexpectedly, this reaction is easily reversible and 1 reverts back to the bis(alkylidyne) starting material in solution at room temperature or, more slowly, in the solid state at room temperature. Coupling of the two alkylidyne ligands is confirmed by an X-ray diffraction study of the more stable complex $Fe_3(CO)_9[P(C_6H_5)_3](\mu_3\text{-}\eta^2\text{-}CH_3C{\equiv}COC_2H_5)$ (2). 2 crystallizes in the triclinic space group C_i^1—$P\bar{1}$, with cell dimensions a = 9.667 (1) Å, b = 18.335 (3) Å, c = 9.329 (1) Å, α = 98.02 (1)°, β = 100.62 (1)°, γ = 78.74 (1)°, and Z = 2. The structure was solved and refined to R and R_w values of 0.035 and 0.036, respectively, using 4273 reflections. Coupling of the two alkylidynes into the $CH_3C{\equiv}COC_2H_5$ alkyne $\mu_3\text{-}\eta^2$-bonded to an iron triangle is confirmed. The overall geometry of the molecule gives evidence of extensive electron delocalization which is discussed. Possible reasons for the easy cleavage of the carbon–carbon triple bond also are discussed.

Introduction

Carbon–carbon bond formation between alkylidene ligands bonded to polynuclear complexes and unsaturated organic molecules has received much study,[1] but similar reactions of alkylidyne ligands bonded to polynuclear clusters have attracted much less attention.[2]

Continuing our investigation into the possibility of carbon–carbon bond formation starting with alkylidyne ligands bonded to trinuclear iron clusters,[3] we were interested in the study of possible coupling of these ligands with carbon monoxide. We report here the study of the reaction of carbon monoxide with the $Fe_3(CO)_9(\mu_3\text{-}CCH_3)(\mu_3\text{-}COC_2H_5)$ cluster.[3c]

Experimental Section

All reactions were performed under a nitrogen atmosphere. Infrared spectra were recorded with a Perkin-Elmer 225 spectrometer. ^1H NMR spectra were obtained with a Bruker WH90 spectrometer and ^{13}C NMR spectra with a Bruker WM250 instrument. $Fe_3(CO)_9(\mu_3\text{-}CCH_3)(\mu_3\text{-}COC_2H_5)$ was prepared by the action of $[(C_2H_5)_3O]BF_4$ on $[Fe_3(CO)_9(\mu_3\text{-}CCH_3)(\mu_3\text{-}CO)][P(C_6H_5)_4]$.[4]

Preparation of $Fe_3(CO)_{10}(\mu_3\text{-}\eta^2\text{-}CH_3C{\equiv}COC_2H_5)$ (1). $Fe_3(CO)_9(\mu_3\text{-}CCH_3)(\mu_3\text{-}COC_2H_5)$ (0.5 g), dissolved in 20 mL of pentane, was introduced into a 100-mL stainless-steel autoclave and pressurized under 20 atm of carbon monoxide. The solution was stirred for 48 h. After depressurization, the solution was cooled to −78 °C, yielding 0.5 g of a green powder (1). Low stability prevented good chemical analysis of this product, but a parent ion was detected in the mass spectrum (m/z 532) with fragment ions corresponding to successive loss of 10 CO ligands: IR ν(CO) (hexadecane) 2088 (m), 2045 (s), 2028 (s), 2003 (m), 1989 (m), 1979 (m), 1977 (m), 1962 (m), 1925 (w, br) cm^{-1}; ^1H NMR (C_6D_6) 3.94 (q, J = 7.3 Hz, OCH_2), 2.32 (CH_3), 1.10 ppm (t, J = 7.3 Hz, OCH_2CH_3); ^{13}C NMR (CD_2Cl_2, −20 °C) 224.8 ($FeCOC_2H_5$), 208.7 (CO), 155.6 ($FeCCH_3$), 69.4 (OCH_2CH_3), 32.2 (CCH_3), 14.2 ppm (OCH_2CH_3).

Preparation of $Fe_3(CO)_9[P(C_6H_5)_3](\mu_3\text{-}\eta^2\text{-}CH_3C{\equiv}COC_2H_5)$ (2). $Fe_3(CO)_9(\mu_3\text{-}CCH_3)(\mu_3\text{-}COC_2H_5)$ (0.5 g) was treated as for 1. To the solution of 1 then was added $P(C_6H_5)_3$ (0.3 g) dissolved in a small amount of pentane, and the solution was allowed to

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