

rapidly upon exposure to air.

Compound **8** has been observed to display some chemical properties which are characteristic of other transition-metal carbonyl hydrides.¹⁸ It is deprotonated by strong bases to give **9**. It reacts rapidly at 25 °C with CCl₄ or HCCl₃ to produce **3c** but does not react with CH₂Cl₂. At 25 °C in THF, the arene is rapidly displaced by P-(C₆H₅)₃ or P(C₄H₉)₃. In THF, hexane, or acetone solution, carbon monoxide reacts with **8** in a rather unusual reaction to produce *endo*-(η^5 -C₆HMe₆)Mn(CO)₃. This reaction will be the topic of a subsequent publication.

The conjugate base of **8**, (η^6 -C₆Me₆)Mn(CO)₂⁻ (**9**), was synthesized by deprotonation of **8** with MeLi and by the reduction of **3a** with sodium naphthalide in THF. The IR spectrum, in THF solution in each case, displays one broad intense band, at 1840 cm⁻¹ for the lithium salt and 1860 cm⁻¹ for the sodium salt. The anion, formed by either method, was further characterized by its reaction with MeI to form **6a**. The nucleophilicity of **9**, demonstrated in this reaction, suggests that this anion would be an effective intermediate in the synthesis of a large number of derivatives of the (η^6 -arene)manganese dicarbonyl fragment. Studies of the nucleophilicity of **9** toward organic and metal-containing substrates are in progress.

In summary, the syntheses of compounds **3a-f** and **5** introduce a new class of compounds which is isoelectronic with the extensively studied species (η^5 -C₅H₅)Fe(CO)₂X. It has been shown that the Me₃NO method of preparing compounds **3** and **4** is superior to the photolysis method,

giving larger yields and requiring much shorter reaction times. It has also been shown that (arene)manganese carbonyl halides and the anion **8** can be synthesized and used in the preparation of derivatives that contain the (η^6 -C₆H_nMe_{6-n})Mn(CO)₂ unit. The synthetic utility of compounds **3b** and **3f** is demonstrated in this study by their use in the synthesis of the species **6a,b**, **7a,b**, **8**, and **9**.

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Registry No. **1a**, 46930-53-4; **2**, 100858-08-0; **3a**, 91230-49-8; **3b**, 91230-50-1; **3c**, 91230-51-2; **3d**, 100858-01-3; **3e**, 91230-52-3; **3f**, 100858-02-4; **4a**, 100858-04-6; **4b**, 100898-52-0; **4c**, 100858-06-8; **5**, 100858-07-9; **6a**, 65643-58-5; **6b**, 65643-62-1; **7a**, 41638-97-5; **7b**, 34852-71-6; **8**, 91230-53-4; (η^6 -C₆Me₆)Mn(CO)₂[PF₆], 38958-98-4; (η^6 -C₆HMe₆)Mn(CO)₃[PF₆], 65643-64-3; (η^6 -C₆H₃Me₃)Mn(CO)₃[PF₆], 35399-67-8; (η^6 -C₆H₅)Mn(CO)₃[PF₆], 38834-51-4.

Supplementary Material Available: ORTEP drawings and stereoviews of compound **3c** and tables of fractional coordinates and isotropic thermal parameters, observed and calculated structure factors, anisotropic thermal parameters, bond lengths and bond angles, bond distances and angles involving the centroid of C₃-C₈, and least-squares plane analysis of the arene ring atoms for compound **3c** (27 pages). Ordering information is given on any current masthead page. Crystallographic data are also available, in microfiche form only, from the Chemistry Library, Indiana University, Bloomington, IN 47405. Request IUMSC Report 84902 when ordering.

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Functionalized Group 4 Metallocene Complexes as Binucleating Ligands: Synthesis and Structural Characterization of Tetracarbonyl[[*P,P'*-bis((diphenylphosphino)cyclopentadienyl)]dichlorozirconium(IV)]molybdenum(0)

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The metathesis of lithium (diphenylphosphino)cyclopentadienide with bis(tetrahydrofuran)tetrachlorozirconium in benzene leads to the formation of [(C₆H₅)₂P(C₅H₄)₂]ZrCl₂ (**1**) in 70% yield. This functionalized canted zirconocene species readily displaces the norbornadiene from (norbornadiene)-tetracarbonylmolybdenum to give [(C₆H₅)₂P(C₅H₄)₂]ZrCl₂Mo(CO)₄ (**2**) in 88% yield. The CO stretches observed in the infrared spectrum of **2** are consistent with *cis*-disubstituted molybdenum tetracarbonyl complexes L₂Mo(CO)₄, where L₂ = 2PPh₃ or (CH₂PPh₂)₂. This heterobinuclear complex forms triclinic crystals of *P*1 symmetry from chloroform/hexanes. The refined lattice parameters are *a* = 9.866 (2) Å, *b* = 11.218 (3) Å, *c* = 17.900 (4) Å, α = 85.32 (2)°, β = 83.88 (2)°, γ = 66.81 (2)°, *V* = 1808.8 (7) Å³, and ρ_{calcd} = 1.597 g cm⁻³. Full-matrix least-squares refinement (based on *F*_o²) converged with final discrepancy indices of *R*(*F*_o) = 0.0288 and *R*(*F*_o²) = 0.0399. The zirconium-molybdenum separation in **2** of 4.8524 (3) Å rules out any direct metal-metal interaction. The structure of **2** is remarkable in that, despite the chelation of the molybdenum atom by **1**, the coordination spheres of both metals show very little difference from the individual mononuclear components, zirconocene dichloride and (bis(diphenylphosphino)methane)-tetracarbonylmolybdenum. The chloride atoms in **2** can be substituted by methyl groups via reaction with methylmagnesium bromide to give [(C₆H₅)₂P(C₅H₄)₂]Zr(CH₃)₂Mo(CO)₄ (**3**) in 75% yield.

Bimetallic complexes in which two different metals with widely differing reactivity are in close proximity have re-

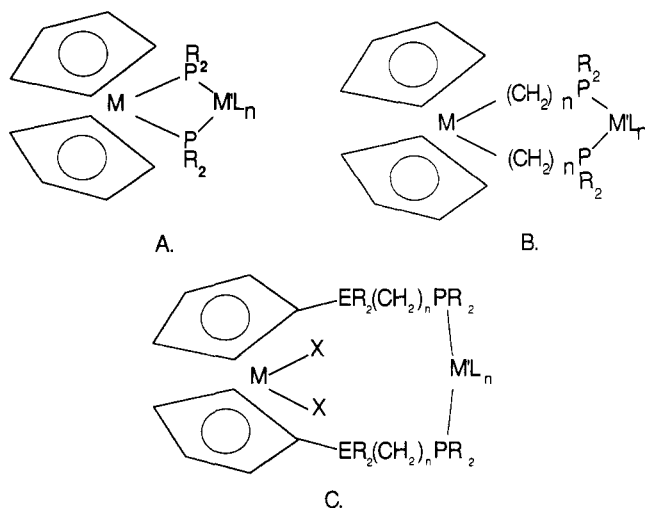
ceived considerable attention.¹ This molecular arrangement provides the opportunity of introducing new patterns of reactivity arising from the interactions of the metals either with each other or with ligands on the adjacent metal. These interactions are important in understanding

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the enhanced reactivity of some polymetallic complexes,² modeling bimetallic catalysts, and developing complexes which activate important feedstock molecules like carbon monoxide under mild conditions. Complexes in which the later (group 6–10) transition metals are joined to the oxophilic group 4 transition metals are of particular interest since it is known that Lewis acids promote CO insertion into metal–alkyl bonds to give metal acyls.³ Also, intermolecular reactions between group 6 carbonyls and group 4 metallocene complexes have resulted in the coupling of a carbonyl ligand and the group 4 metal center via the CO's oxygen⁴ (for example, $(\text{Cp})_2\text{Zr}(\mu\text{-OC}(\text{C}_4\text{H}_9))\text{Cr}(\text{CO})_5$,^{4a} $(\text{C}_5(\text{CH}_3)_5)_2\text{Zr}(\mu\text{-CO})_2\text{MoCp}(\text{CO})_2$ ^{4b}). In addition, methyl group transfer from zirconium to the carbonyl carbon from molybdenum has been observed which results in the binuclear complex $\text{Cp}_2\text{Zr}(\mu\text{-OC}(\text{CH}_3))(\mu\text{-OC})\text{MoCp}(\text{CO})$.⁵

Several group 4–late-transition-metal binuclear complexes in which the metals are linked by bridging ligands have been recently reported. The link between the two metals in such systems can be a pair of μ -phosphido ligands (A),⁶ dangling phosphines (B),⁷ a cyclopentadienyl ring linked to a phosphine by a molecular chain (C),⁸ or the (diphenylphosphino)cyclopentadienyl anion.^{8a,9} The latter ligand system has been of considerable utility in forming heterobimetallic complexes where a derivatized metal complex or metallo ligand may act as a monodentate ligand^{8a,9,10} or a chelating bidentate ligand.¹¹



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Herein is described the synthesis and characterization of a bidentate metallo ligand, bis((diphenylphosphino)cyclopentadienyl)dichlorozirconium(IV) (1). Treatment of (norbornadiene)tetracarbonylmolybdenum(0) with 1 has led to the isolation of a new heterobimetallic complex, tetracarbonyl[[P,P'-bis((diphenylphosphino)cyclopentadienyl)]dichlorozirconium(IV)]molybdenum(0) (2), which has been characterized by chemical analysis, multinuclear NMR measurements (¹H, ¹³C, ³¹P), and an X-ray structure determination. Reaction of 2 with methylmagnesium bromide results in the formation of the dimethyl analogue of 2, [(C₆H₅)₂P(C₅H₄)]₂Zr(CH₃)₂Mo(CO)₄ (3) which has been characterized by chemical analysis and ¹H NMR and infrared spectroscopy.

Experimental Section

All manipulations were carried out by using standard Schlenk techniques under an atmosphere of prepurified nitrogen or in a Labconco glovebox fitted with a drying train filled with prepurified nitrogen. Solvents were reagent grade or better and were further purified prior to their use. Tetrahydrofuran (THF) was distilled from potassium benzophenone ketyl. Hexanes and benzene were distilled from sodium–potassium amalgam. Dichloromethane was dried over Linde 4A molecular sieves and freeze–thaw degassed three times before use. Li[(C₆H₅)₂P(C₅H₄)] was prepared by modifying Casey's preparation^{8a} for use with Schlenk techniques. Bis(tetrahydrofuran)tetrachlorozirconium(IV)¹² and (norbornadiene)tetracarbonylmolybdenum(0)¹³ were prepared by literature methods.

¹H NMR spectra were obtained on an IBM WSP-200 NMR spectrometer operating at 200.132 MHz and were referenced by either the residual proton resonance or internal Me₄Si. ¹³C{¹H} and ³¹P{¹H} NMR spectra were obtained with the same instrument by using the broad-band probe operating at 50.323 and 81.015 MHz, respectively. The phosphorus-31 spectra were referenced to 85% H₃PO₄ in a coaxial capillary tube. Infrared spectra were recorded on a Perkin-Elmer Model 283 spectrometer and calibrated with a polystyrene standard. Microanalyses were performed by Schwarzkopf Microanalytical Laboratories of Woodside, NY.

Bis((diphenylphosphino)cyclopentadienyl)dichlorozirconium (1). Lithium (diphenylphosphino)cyclopentadienide (0.91 g, 3.5 mmol) is loaded into a 50-mL Schlenk flask containing a magnetic stirring bar. Half that molar amount of bis(tetrahydrofuran)tetrachlorozirconium (0.66 g) was added directly to the same flask. Freshly distilled benzene (25 mL) was added. Upon stirring at room temperature, the suspension darkens and then fades over the next 2 h. Then the reaction mixture was gently refluxed for 2 h. The suspension was then filtered through a 3-cm bed of Celite on a glass frit, and the pale orange filtrate was collected in a 50-mL Schlenk flask. The filter cake was washed two times with 5-mL portions of benzene; the second washing was colorless. The solvent was removed in vacuo, and a dry yellow product was obtained. After being washed with four 10-mL portions of hexanes, the light tan product was dried in vacuo overnight. The yield was 0.81 g or 70% based on Li[(C₆H₅)₂P(C₅H₄)]. ¹H NMR: phenyl, two multiplets at δ 7.35, 7.1 (20 H); Cp ring, α , δ 6.21 ($J_{\text{H-H}} = 2.44$ Hz, $J_{\text{P-H}} = 0.98$ Hz, 4 H); Cp ring, β , δ 6.09 ($J_{\text{H-H}} = 2.44$ Hz, $J_{\text{P-H}} = 0.50$ Hz, 4 H). ¹³C{¹H} NMR (chloroform-*d*₁): phenyl rings, ipso, δ 136.83 ($J_{\text{P-C}} = 11.0$ Hz), ortho, 133.91 ($J_{\text{P-C}} = 20.75$ Hz), meta, 128.55 ($J_{\text{P-C}} = 7.32$ Hz),

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para, α , 129.29; Cp ring, δ 125.14 ($J_{P-C} = 18.3$ Hz); 122.17 ($J_{P-C} = 11.0$ Hz); 118.24. $^{31}\text{P}\{^1\text{H}\}$ NMR (vs. 85% H_3PO_4): δ -18.2. Carbon-Hydrogen Anal. Calcd for $\text{C}_{34}\text{H}_{28}\text{Cl}_2\text{P}_2\text{Zr}$ (found): C, 61.81 (62.81); H, 4.27 (4.51).

Tetracarbonyl[[P,P'-bis((diphenylphosphino)cyclopentadienyl)]dichlorozirconium(IV)]molybdenum(0) (2). Bis(diphenylphosphino)cyclopentadienyl)dichlorozirconium (0.27 g, 0.41 mmol) was loaded into a 50-mL Schlenk flask containing a magnetic stirring bar. A nearly equimolar amount of (norbornadiene)tetracarbonylmolybdenum(0) (0.114 g, 0.381 mmol) was added to an addition funnel which was evacuated and N_2 filled three times. Both solids were dissolved separately in ca. 8 mL of dichloromethane, and the (norbornadiene)tetracarbonylmolybdenum(0) solution was added dropwise to yield a slightly turbid yellow solution. After filtration through a fine porosity Schlenk frit, 30 mL of hexanes were slowly added and the layered system was left overnight to allow slow mixing.

The volume of the supernatant liquid above the crystalline precipitate when then reduced in vacuo to ca. 10 mL. The solid was collected on a fine porosity frit, washed twice with 2-mL portions of benzene, and dried in vacuo for 6 h. The yield was 0.290 g (88%). This material was analytically pure. Crystals suitable for the X-ray structure determination were grown from a chloroform solution of **2** layered with hexanes. Solid **2** is relatively air-stable but should be stored under nitrogen for extended periods. Solutions are moderately air sensitive, turning brown and depositing a brown solid within hours. Infrared spectrum: carbonyl region (CH_2Cl_2 solution) 2022 (m), 1930 (sh), 1910 (s) cm^{-1} ; (KBr pellet) 2020 (m), ca. 1920 (br s) cm^{-1} . Carbon-hydrogen and chlorine analyses performed on the crystalline product support the given formulation. Calcd for $\text{C}_{38}\text{H}_{28}\text{O}_4\text{P}_2\text{Cl}_2\text{MoZr}$ (Found): C, 52.54 (51.89); H, 3.25 (3.16); Cl, 8.16 (8.06). ^1H NMR (C_6D_6): phenyl, δ 7.52 (m), 6.99 (m, 20 H); Cp, 6.53 (m, 4 H), 6.17 (m, 4 H). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): phenyl ring, δ 137.1 (m), 133.3 (s), 131.2 (s), 128.4 (s); Cp, δ 122.7 (s), 122.2 (s), 120.1 (m); CO, δ 210, apparent singlet, and δ 213.4 apparent doublet, $J_{P-C} = 16$ Hz, $^{31}\text{P}\{^1\text{H}\}$ NMR: singlet, δ 30.89.

Tetracarbonyl[[P,P'-bis((diphenylphosphino)cyclopentadienyl)]dimethylzirconium(IV)]molybdenum(0). A Schlenk flask fitted with a magnetic stirring bar was loaded with 0.28 g of **2** (0.32 mmol) and then evacuated/nitrogen filled three times. About 20 mL of freshly distilled benzene was added, and a yellow suspension was obtained. This was placed in an ice bath, 0.30 mL of methylmagnesium bromide in diethyl ether (2.7 M, 0.81 mmol) was added, and the ice bath was removed. The reaction mixture grows paler immediately, and a nearly colorless suspension was obtained in 1 h. The solvents are removed in vacuo, and the residue was then washed with two 5-mL portions of hexanes, then dried, and extracted with 5 mL of benzene. This suspension was then filtered through a fine porosity glass frit to yield a light tan solution and the filter cake washed twice with 0.5-mL portions of benzene. The washings are combined with the filtrate, hexanes are added (10 mL), and the vessel is closed and stored in the freezer overnight. A white crystalline precipitate was obtained from which the supernatant was removed by cannula and the solid washed twice with hexanes and dried in vacuo 2 h. The yield was 0.20 g or 75% based on **2**. Carbon-hydrogen analysis performed on the crystalline product support formulation as $[(\text{C}_6\text{H}_5)_2\text{P}(\text{C}_5\text{H}_4)]_2\text{Zr}(\text{CH}_3)_2\text{Mo}(\text{CO})_4 \cdot 0.5\text{C}_6\text{H}_6$. Calcd for $\text{C}_{43}\text{H}_{37}\text{O}_4\text{P}_2\text{MoZr}$ (Found): C, 59.56 (59.60); H, 4.30 (4.37). Infrared spectrum: carbonyl region (CH_2Cl_2 solution) 2025 (s), 1928 (sh), 1908 (s), 1895 (sh) cm^{-1} . ^1H NMR (C_6D_6): δ 7.62 (m, 8 H), 7.00 (m, 12 H), 6.19 (m, 4 H), 6.14 (m, 4 H), -0.185 (s, 6 H).

X-ray Data Collection and Structural Analysis of 2. A yellow parallelepiped shaped crystal was wedged into a glass capillary tube, sealed under a prepurified nitrogen atmosphere, and optically aligned on a Picker goniostat that is computer controlled by a Krisel Control diffractometer automation system. Analogous procedures to those described previously¹⁴ were used to determine the lattice parameters of the triclinic unit cell and the orientation matrix and to collect the intensity data at 298 K. The raw intensity data for the 5887 independent reflections with $F_o^2 > \sigma(F_o^2)$ were corrected for absorption¹⁵ and Lorentz-polarization

Table I. Data for X-ray Diffraction Analysis of $[\text{C}_5\text{H}_4\text{P}(\text{C}_6\text{H}_5)_2]_2\text{ZrCl}_2\text{Mo}(\text{CO})_4$

A. Crystal Data	
crystal system	triclinic
space group	$P\bar{1}$ (C_i , no. 2)
<i>a</i> , Å	9.866 (2)
<i>b</i> , Å	11.218 (3)
<i>c</i> , Å	17.900 (4)
α , deg	85.32 (2)
β , deg	83.88 (2)
γ , deg	66.81 (2)
<i>V</i> , Å ³	1808.8 (7)
fw, amu	868.06
<i>d</i> (calcd), g/cm ³	1.597
<i>Z</i>	2
μ , cm ⁻¹	9.00
B. Data Collection and Analysis Summary	
cryst dimens, mm	0.425 × 0.325 × 0.55
reflectns sampled	$\pm h, \pm k, l$ ($5 \leq 2\theta \leq 50^\circ$)
2θ range for centered reflectns	$35^\circ < 2\theta < 39^\circ$
scan rate	$2^\circ/\text{min}$
scan width, deg	$1.1 + 0.8 \tan \theta$
no. of std reflectns	3
% cryst decay	none
total no. of measd reflectns	6622
no. of unique data used	5887 ($F_o^2 > \sigma(F_o^2)$)
agreement between equivalent data	
$R_{av}(F_o)$	0.018
$R_{av}(F_o^2)$	0.033
transmissn coeff	0.705–0.770
<i>P</i>	0.030
discrepancy indices	
$R(F_o)$	0.0288
$R(F_o^2)$	0.0399
$R_w(F_o^2)$	0.0608
σ_1	1.40
no. of variables	545
data to parameter ratio	10.8:1

effects. Specific details regarding the refined lattice parameters and the data collection procedures are summarized in Table I.

Initial coordinates for the molybdenum and zirconium atoms were interpolated from an *E* map calculated on the basis of phases determined by MULTAN78.¹⁶ The positions of the remaining non-hydrogen atoms were located from subsequent Fourier summations. All of the hydrogen atoms were located in the first difference Fourier synthesis calculated with only low-angle data ($(\sin \theta)/\lambda < 0.40 \text{ \AA}^{-1}$). Full-matrix least-squares refinement^{17–21} (based on F_o^2) with anisotropic temperature factors for the 48 non-hydrogen atoms and isotropic temperature factors for the 28 hydrogen atoms converged with final discrepancy indices of $R(F_o) = 0.0288$, $R(F_o^2) = 0.0399$, and $R_w(F_o^2) = 0.0608$ with $\sigma_1 = 1.40$. The maximum parameter shift to error ratio did not exceed

(15) The absorption correction was performed with the use of the general polyhedral shape routine of the program DTALIB. The distance from the crystal center to each face and the corresponding orientation angles (ϕ and χ) needed to place each fact in diffracting position were provided to define the crystal's shape, size, and orientation with respect to the diffractometer's coordinate system.

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(17) The least-squares refinement¹⁸ of the X-ray diffraction data was based upon the minimization of $\sum w_i |F_o^2 - S^2 F_c^2|$, where w_i is the individual weighting factor and *S* is the scale factor. The discrepancy indices were calculated from the expressions $R(F_o) = \sum |F_o| - |F_c| / \sum |F_o|$, $R(F_o^2) = \sum |F_o^2 - F_c^2| / \sum |F_o^2|$, and $R_w(F_o^2) = [\sum w_i |F_o^2 - F_c^2|^2 / \sum w_i F_o^4]^{1/2}$. The standard deviation of an observation of unit weight, σ_1 , equals $[\sum w_i |F_o^2 - F_c^2|^2 / (n - p)]^{1/2}$, where *n* is the number of observations and *p* is the number of parameters varied in the last refinement cycle.

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Table II. Positional Parameters for $[\text{C}_5\text{H}_4\text{P}(\text{C}_6\text{H}_5)_2]_2\text{ZrCl}_2\text{Mo}(\text{CO})_4$

atom	x	y	z	atom	x	y	z
Mo	0.76957 (2)	0.62411 (2)	0.28705 (1)	C34	1.1029 (4)	0.2957 (3)	0.3789 (2)
Zr	1.11360 (2)	0.71025 (2)	0.09761 (1)	C35	1.1403 (4)	0.1664 (3)	0.3993 (2)
Cl1	0.90654 (8)	0.72578 (7)	0.03107 (4)	C36	1.1814 (4)	0.0760 (3)	0.3460 (2)
Cl2	1.26516 (9)	0.74937 (7)	-0.00964 (4)	C37	1.1851 (5)	0.1145 (3)	0.2727 (2)
P1	0.77271 (6)	0.84460 (6)	0.24266 (3)	C38	1.1474 (4)	0.2444 (3)	0.2507 (2)
P2	1.04940 (6)	0.51174 (6)	0.28092 (3)	H1	1.110 (2)	0.771 (2)	0.260 (1)
O1	0.4239 (2)	0.7470 (2)	0.2922 (1)	H2	1.272 (3)	0.846 (3)	0.171 (2)
O2	0.7439 (3)	0.5243 (3)	0.1309 (1)	H3	1.108 (3)	0.988 (2)	0.072 (1)
O3	0.7245 (3)	0.6941 (3)	0.4586 (1)	H4	0.866 (3)	0.986 (3)	0.098 (2)
O4	0.7475 (3)	0.3622 (2)	0.3465 (2)	H5	1.054 (3)	0.464 (2)	0.115 (1)
C1	0.5512 (3)	0.7036 (3)	0.2908 (2)	H6	1.246 (3)	0.460 (3)	0.016 (2)
C2	0.7620 (3)	0.5641 (3)	0.1843 (2)	H7	1.436 (3)	0.518 (3)	0.079 (2)
C3	0.7476 (3)	0.6705 (3)	0.3964 (2)	H8	1.336 (3)	0.556 (2)	0.210 (1)
C4	0.7581 (3)	0.4570 (3)	0.3250 (2)	H9	0.527 (3)	0.970 (3)	0.341 (2)
C5	0.9350 (2)	0.8642 (2)	0.1931 (1)	H10	0.458 (4)	1.092 (3)	0.444 (2)
C6	1.0794 (3)	0.8174 (2)	0.2180 (1)	H11	0.627 (4)	1.161 (3)	0.484 (2)
C7	1.1678 (3)	0.8648 (2)	0.1681 (1)	H12	0.856 (4)	1.086 (3)	0.422 (2)
C8	1.0780 (3)	0.9445 (2)	0.1125 (2)	H13	0.924 (3)	0.971 (3)	0.325 (2)
C9	0.9376 (3)	0.9442 (2)	0.1272 (1)	H14	0.595 (3)	0.804 (2)	0.138 (1)
C10	1.1550 (3)	0.5163 (2)	0.1908 (1)	H15	0.419 (3)	0.926 (3)	0.062 (2)
C11	1.1278 (3)	0.4812 (2)	0.1214 (1)	H16	0.337 (4)	1.156 (3)	0.062 (2)
C12	1.2440 (3)	0.4764 (2)	0.0674 (1)	H17	0.463 (3)	1.244 (3)	0.129 (2)
C13	1.3452 (3)	0.5081 (3)	0.1022 (1)	H18	0.625 (3)	1.120 (3)	0.207 (2)
C14	1.2917 (3)	0.5331 (2)	0.1773 (1)	H19	1.345 (3)	0.395 (2)	0.329 (1)
C15	0.7329 (3)	0.9517 (2)	0.3217 (1)	H20	1.483 (4)	0.433 (3)	0.412 (2)
C16	0.5913 (3)	0.9927 (3)	0.3584 (2)	H21	1.376 (3)	0.614 (3)	0.483 (2)
C17	0.5527 (4)	1.0710 (3)	0.4189 (2)	H22	1.130 (3)	0.744 (3)	0.472 (2)
C18	0.6550 (4)	1.1080 (3)	0.4454 (2)	H23	0.996 (3)	0.711 (2)	0.386 (1)
C19	0.7952 (4)	1.0677 (3)	0.4102 (2)	H24	1.069 (4)	0.357 (3)	0.414 (2)
C20	0.8338 (3)	0.9918 (3)	0.3480 (2)	H25	1.143 (4)	0.146 (4)	0.447 (2)
C21	0.6279 (3)	0.9464 (2)	0.1821 (1)	H26	1.204 (3)	-0.004 (3)	0.361 (2)
C22	0.5625 (3)	0.8920 (3)	0.1383 (1)	H27	1.212 (4)	0.056 (4)	0.236 (2)
C23	0.4539 (3)	0.9703 (4)	0.0920 (2)	H28	1.147 (4)	0.270 (3)	0.200 (2)
C24	0.4116 (4)	1.1021 (4)	0.0905 (2)				
C25	0.4765 (4)	1.1569 (3)	0.1332 (2)				
C26	0.5835 (3)	1.0803 (3)	0.1790 (2)				
C27	1.1559 (3)	0.5486 (2)	0.3475 (1)				
C28	1.3028 (3)	0.4668 (3)	0.3554 (1)				
C29	1.3820 (4)	0.4918 (3)	0.4061 (2)				
C30	1.3168 (4)	0.5987 (4)	0.4496 (2)				
C31	1.1715 (4)	0.6800 (4)	0.4427 (2)				
C32	1.0912 (3)	0.6547 (3)	0.3920 (1)				
C33	1.1068 (2)	0.3363 (2)	0.3036 (1)				

^a The estimated standard deviation in parentheses for this and all subsequent tables refer to the least significant figures.

0.1 during the last cycle. A final difference Fourier summation was virtually featureless with the largest residual peak being 0.51 e/Å³.

The values for the refined positional parameters are provided in Table II for all of the atoms. The interatomic distances and bond angles and their esd's are given in Table III. Tables of the refined thermal parameters, the carbon-hydrogen distances and angles, the pertinent least-squares planes, and the calculated and observed structure factors for 2 are available as supplementary material.²²

Results and Discussion.

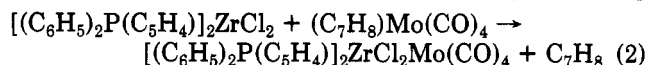
Preparation of 1 and 2. The functionalized metallocene, bis((diphenylphosphino)cyclopentadienyl)dichlorozirconium(IV) (1) is readily prepared by the metathesis of lithium (diphenylphosphino)cyclopentadienide with bis(tetrahydrofuran)tetrachlorozirconium in benzene (eq 1) as a pale tan powder in 70% yield. The proton

$$2\text{Li}[(\text{C}_6\text{H}_5)_2\text{P}(\text{C}_5\text{H}_4)] + \text{ZrCl}_4 \cdot 2\text{THF} \rightarrow [(\text{C}_6\text{H}_5)_2\text{P}(\text{C}_5\text{H}_4)]_2\text{ZrCl}_2 + 2\text{LiCl} \quad (1)$$

NMR spectrum of 1 is consistent with a metallocene dihalide complex in which one of the protons on each cyclopentadienyl ring has been replaced with a diphenyl-

phosphino group. The P-H coupling constants are similar to those reported by Casey et al. for $\text{Li}[(\text{C}_6\text{H}_5)_2\text{P}(\text{C}_5\text{H}_4)]^{10a}$ and $\text{Cp}[(\text{C}_6\text{H}_5)_2\text{P}(\text{C}_5\text{H}_4)]\text{ZrCl}_2$.^{9b} The ³¹P NMR spectrum shows a singlet at δ -18.2, showing that the two phosphorus atoms are equivalent on the NMR time scale. The position of the resonance is very similar to that of free $\text{Li}[(\text{C}_6\text{H}_5)_2\text{P}(\text{C}_5\text{H}_4)]$, $\text{Cp}[(\text{C}_6\text{H}_5)_2\text{P}(\text{C}_5\text{H}_4)]\text{ZrCl}_2$, $[(\text{C}_6\text{H}_5)_2\text{P}(\text{C}_5\text{H}_4)]_2\text{TiCl}_2$,^{8a} and $(\text{C}_5\text{H}_4)(\text{CH}_2)_2\text{P}(\text{C}_6\text{H}_5)_2\text{ZrCl}_2$.^{8a}

Addition of a CH_2Cl_2 solution of $(\text{C}_7\text{H}_8)\text{Mo}(\text{CO})_4$ to a stirred solution of 1 in CH_2Cl_2 produces a darker yellow solution from which 2 may be precipitated by the addition of hexanes in 88% yield (see (2)). The carbonyl stretching



region of the infrared spectrum of 2 in dichloromethane is consistent with a cis-disubstituted $\text{Mo}(\text{CO})_4\text{L}_2$ complex. Comparison of the CO stretching frequencies of 2 with some other bis(phosphine) complexes of tetracarbonylmolybdenum which contain a chelating diphosphine such as bis(diphenylphosphino)methane²³ and bis(diphenylphosphino)ethane²⁴ or even two triphenylphosphine ligands²⁴ shows that there is little effect upon these absorptions when the phosphine is appended to the cyclo-

(22) The computer programs that were employed during the X-ray structural analysis are described in: Nicholson, G. A.; Petersen, J. L.; McCormick, B. J. *Inorg. Chem.* 1980, 19, 195.

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Table III. Interatomic Distances (Å) and Bond Angles (deg) for Non-Hydrogen Atoms of $[\text{C}_5\text{H}_4\text{P}(\text{C}_6\text{H}_5)_2]_2\text{ZrCl}_2\text{Mo}(\text{CO})_4^{a,b}$

A. Interatomic Distances							
Mo-P1	2.547 (1)	Mo-P2	2.538 (1)	C7-C8	1.412 (4)	C12-C13	1.399 (5)
Mo-C1	1.977 (3)	Mo-C4	1.982 (3)	C8-C9	1.384 (4)	C13-C14	1.399 (4)
Mo-C2	2.028 (3)	Mo-C3	2.034 (3)	C9-C5	1.427 (4)	C14-C10	1.426 (4)
Zr-Cl1	2.414 (1)	Zr-Cl2	2.425 (1)	C15-C16	1.394 (4)	C27-C28	1.392 (3)
Zr-Cp(1)	2.220 (3)	Zr-Cp(2)	2.220 (3)	C16-C17	1.367 (5)	C28-C29	1.369 (5)
Zr-C5	2.540 (2)	Zr-Cl0	2.556 (2)	C17-C18	1.371 (6)	C29-C30	1.378 (5)
Zr-C6	2.481 (3)	Zr-Cl1	2.520 (3)	C18-C19	1.372 (5)	C30-C31	1.375 (5)
Zr-C7	2.474 (3)	Zr-Cl2	2.501 (2)	C19-C20	1.384 (5)	C31-C32	1.379 (5)
Zr-C8	2.544 (3)	Zr-Cl3	2.510 (2)	C20-C15	1.379 (5)	C32-C27	1.381 (3)
Zr-C9	2.573 (2)	Zr-Cl4	2.528 (2)	C21-C22	1.378 (5)	C33-C34	1.389 (4)
P1-C5	1.828 (3)	P2-C10	1.834 (4)	C22-C23	1.390 (4)	C34-C35	1.377 (4)
P1-C15	1.840 (3)	P2-C27	1.840 (3)	C23-C24	1.367 (6)	C35-C36	1.363 (5)
P1-C21	1.834 (2)	P2-C33	1.844 (2)	C24-C25	1.365 (6)	C36-C37	1.348 (6)
C1-O1	1.153 (3)	C4-O4	1.142 (4)	C25-C26	1.371 (4)	C37-C38	1.389 (5)
C2-O2	1.146 (4)	C3-O3	1.143 (4)	C26-C21	1.388 (4)	C38-C33	1.369 (4)
C5-C6	1.419 (3)	C10-C11	1.416 (4)	Mo...Zr	4.8524 (3)		
C6-C7	1.401 (4)	C11-C12	1.405 (4)				
B. Bond Angles							
P1-Mo-P2	93.96 (2)	P2-Mo-C1	177.2 (1)	C5-C6-C7	109.0 (2)	C10-C11-C12	109.2 (3)
P1-Mo-C1	88.5 (1)	P2-Mo-C2	92.2 (1)	C6-C7-C8	107.6 (2)	C11-C12-C13	108.0 (2)
P1-Mo-C2	96.8 (1)	P2-Mo-C3	94.7 (1)	C7-C8-C9	108.4 (2)	C12-C13-C14	108.0 (3)
P1-Mo-C3	91.0 (1)	P2-Mo-C4	88.4 (1)	C8-C9-C5	109.0 (2)	C13-C14-C10	109.1 (3)
P1-Mo-C4	177.1 (1)	C4-Mo-C2	84.8 (1)	P1-C15-C16	117.4 (2)	P2-C27-C28	120.1 (2)
C1-Mo-C2	86.2 (1)	C4-Mo-C3	87.1 (1)	P1-C15-C20	124.7 (2)	P2-C27-C32	121.1 (2)
C1-Mo-C3	86.6 (1)	C2-Mo-C3	169.2 (1)	C20-C15-C16	117.9 (3)	C32-C27-C28	118.8 (3)
C1-Mo-C4	89.2 (1)	Cp(1)-Zr-Cp(2)	130.2 (1)	C15-C16-C17	121.3 (3)	C27-C28-C29	120.6 (3)
Cl1-Zr-Cl2	96.69 (3)	Mo-P2-C10	118.3 (1)	C16-C17-C18	120.1 (3)	C28-C29-C30	120.1 (3)
Mo-P1-C5	122.9 (1)	Mo-P2-C27	120.8 (1)	C17-C18-C19	119.3 (3)	C29-C30-C31	119.9 (4)
Mo-P1-C15	111.4 (1)	Mo-P2-C33	110.9 (1)	C18-C19-C20	120.9 (4)	C30-C31-C32	120.0 (3)
Mo-P1-C21	116.5 (1)	C10-P2-C27	102.2 (1)	C19-C20-C15	120.4 (3)	C31-C32-C27	120.5 (3)
C5-P1-C15	101.7 (1)	C10-P2-C33	102.9 (1)	P1-C21-C22	121.1 (2)	P2-C33-C34	117.9 (2)
C5-P1-C21	100.8 (1)	C27-P2-C33	98.8 (1)	P1-C21-C26	120.2 (2)	P2-C33-C38	124.0 (2)
C15-P1-C21	100.2 (1)	Mo-C4-O4	178.1 (3)	C26-C21-C22	118.8 (2)	C38-C33-C34	118.1 (2)
Mo-C1-O1	178.2 (3)	Mo-C3-O3	174.0 (3)	C21-C22-C23	120.4 (3)	C33-C34-C35	120.6 (3)
Mo-C2-O2	170.8 (3)	P2-C10-C11	125.1 (2)	C22-C23-C24	119.6 (4)	C34-C35-C36	120.5 (3)
P1-C5-C6	126.7 (2)	P2-C10-C14	128.4 (2)	C23-C24-C25	120.5 (3)	C35-C36-C37	119.3 (3)
P1-C5-C9	126.8 (2)	C14-C10-C11	105.7 (2)	C24-C25-C26	120.3 (3)	C36-C37-C38	121.2 (3)
C9-C5-C6	106.0 (2)			C25-C26-C21	120.5 (3)	C37-C38-C33	120.2 (3)

^a The esd's given in parentheses for the interatomic distances and bond angles were calculated from the standard errors in the fractional coordinates of the corresponding atomic positions. ^b Cp(*n*) denotes the centroid of the cyclopentadienyl ring.

pentadienyl ring. However, the CO stretching frequencies show a significant shift to lower energy in analogous μ -diphenylphosphides metallogligands. As expected, the stretching frequencies observed are higher than those reported for the more basic bis(dimethylphosphino)methane ligand²⁵ or for the μ -phosphido complexes of the group 4 metals with group 6 tetracarbonyls.⁶ This comparison might lead one to predict that metal complexes of 1 might exhibit the chemistry of the simpler diphosphine complexes.

The proton NMR spectrum of 2 shows slight downfield shifts of the cyclopentadienyl ring proton resonances compared to 1. The proton-decoupled ³¹P NMR spectrum shows a singlet at δ 30.9 (compared to δ -18.2 for 1) which indicates that the two phosphorus atoms are equivalent on the NMR time scale. The downfield shifts are indicative of coordination of the phosphorus atom of the phosphine. The most informative region of the carbon-13 NMR spectrum is the carbonyl region where two ill-resolved resonances are seen; a broad singlet at δ 210 and a broad doublet ($J_{\text{C-P}}$ = 16 Hz) at δ 213.4. These chemical shifts are similar to those observed for *cis*-Mo(CO)₄-(PPh₂(CH₂)₂PPh₂).²⁶ The poor resolution of the spectrum prevented the determination of all the ³¹P-Mo-¹³C coupling constants, but the observation of these two signals shows that the carbonyl ligands are not fluxional at room

temperature as has been observed by other workers.²⁷

X-ray Structure of 2. The results of the single-crystal X-ray structure determination confirm that the metallo ligand 1 has replaced the norbornadiene ligand on the tetracarbonylmolybdenum(0) moiety to give 2 (see Figure 1 for a perspective view and atom numbering scheme). The unit cell of 2 contains two discrete molecules with no close intermolecular contacts. Figure 2 shows that the molybdenum atom does not lie in the open portion of the pocket formed by the canted cyclopentadienyl rings but is located to the side of this pocket. The Zr-Mo separation of 4.8524 (3) Å rules out any direct bonding interaction. The functionalized cyclopentadienyl rings are slightly staggered; the angle subtended by the two C(Cp)-P vectors is 32.5°. This arrangement appears to be responsible for the 0.15-Å displacement of the Mo atom from the plane defined by Zr, Cl1, and Cl2. A dihedral angle of 67.2° between the planes defined by P1, P2, Mo and Cl1, Cl2, Zr is observed.

The pseudotetrahedral coordination about the zirconium atom in 2 is comparable to that found for metallocene dihalides. Despite the presence of bulky diphenylphosphino groups which are further bound to the molybdenum, the ring centroid-Zr-ring centroid angle (130.2°), Zr-Cl bond length (2.42 Å (average)), Zr-C bond length (2.52 ± 0.03 Å), and Cl-Zr-Cl angle (96.69°) are surprisingly similar to that of zirconocene dichloride.²⁸ Although

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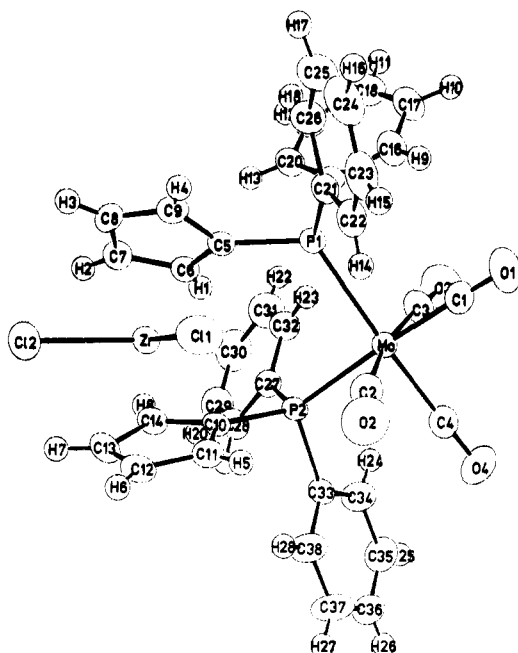


Figure 1. Perspective view of the molecular structure of $[(C_6H_5)_2P(C_5H_4)]_2ZrCl_2Mo(CO)_4$ with the atom labeling scheme. The thermal ellipsoids are scaled to enclose 50% probability. The radii of the spheres for the hydrogen atoms have been reduced arbitrarily for purposes of clarity. Atoms C15, C19, and H19 are hidden behind atoms C21, C26 and C11, respectively.

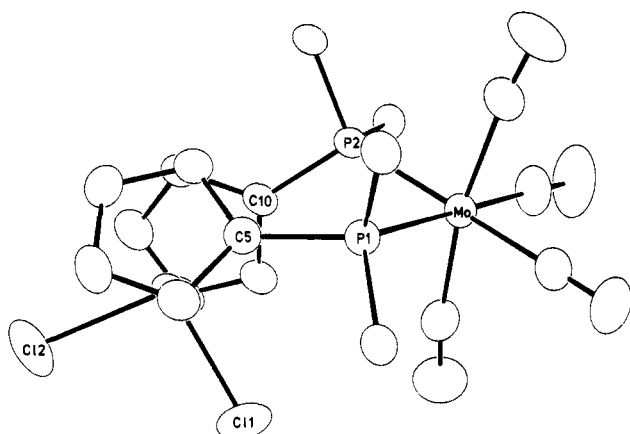


Figure 2. A view of $[(C_6H_5)_2P(C_5H_4)]_2ZrCl_2Mo(CO)_4$ from a point perpendicular to the C11-Zr-Cl2 plane. The phenyl rings and hydrogen atoms have been omitted for purposes of clarity.

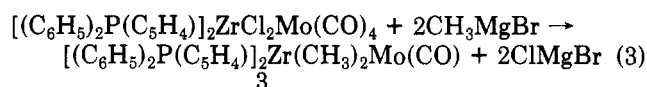
the cyclopentadienyl rings are planar (± 0.001 Å from the corresponding least-squares plane), the bond distances and angles show some distortion by the phosphine substituent: C-C bond lengths and angles average 1.422 Å and 106° , respectively, at the P-substituted carbon and 1.400 Å and 109° respectively, at the unsubstituted carbons. This degree of distortion is analogous to that observed in [1]-ferrocenophanes²⁹ and bis((diphenylphosphino)cyclopentadienyl)iron binuclear complexes.¹¹

The slightly distorted octahedral coordination about the molybdenum atom is derived from bending back of the "axial" carbonyl ligands, CO(2) and CO(3), as indicated by the C2-Mo-C3 angle of 169° . The corresponding angle in (dpm)Mo(CO)₄ is 168° ,³⁰ this similarity suggests that

the swept-back orientation of these CO ligands may arise from steric interactions with the phenyl rings. Within the "equatorial" plane of ligands P1, P2, C1, and C4 the P-Mo-P angle of 93.96° shows the greatest deviation from the ideal 90° but is only slightly smaller than the 95.3° observed in tetracarbonyl $[[P,P'\text{-bis}((\text{diphenylphosphino})\text{cyclopentadienyl})]\text{iron}]\text{molybdenum}(0)$ ¹¹ and much smaller than the $98\text{--}103^\circ$ observed in the μ -phosphido complexes.⁶ This result suggests that 1 can undergo rotation of the two canted cyclopentadienyl rings to find the least sterically hindered conformation whereas in the ferrocenyl complexes, the two rings which are parallel before complexation, must assume a canted, more strained configuration. Both the μ -phosphido and (diphenylphosphido)cyclopentadienyl complexes have large bites compared to dpm. For example, in (dpm)Mo(CO)₄ the P-Mo-P angle is 67° . The remainder of the bond angles in the equatorial plane are very near 90° . The Mo-P bond lengths (2.54 Å (average), trans Mo-C bonds (1.98 Å), and the cis Mo-C bonds (2.03 Å (average) are very similar to those found by Butler et al. in tetracarbonyl $[[P,P'\text{-bis}((\text{diphenylphosphino})\text{cyclopentadienyl})]\text{iron}]\text{molybdenum}(0)$ ^{11a} and in the bis(μ -phosphido) complexes of tetracarbonylmolybdenum.⁶

The geometry about the phosphorus atoms in 2 more strongly resembles that in $CpTiCl_2[\mu-(C_5H_4)P(C_6H_5)_2]_2Mn(Cp)(CO)_2$ ^{9a} rather than $(CO)_3Mo[\mu-(C_5H_4)P(C_6H_5)_2]_2Mn(Cp)(CO)_2$.^{10a} The major difference is the cyclopentadienyl carbon-phosphorus-metal (C-P-M) angle which is $120 \pm 3^\circ$ (average) in 2. The corresponding angles in $CpTiCl_2[\mu-(C_5H_4)P(C_6H_5)_2]_2Mn(Cp)(CO)_2$ and $(CO)_3Mo[\mu-(C_5H_4)P(C_6H_5)_2]_2Mn(Cp)(CO)_2$ are $116.3(5)^\circ$ and $103.6(2)^\circ$, respectively. The other angles and the P-C bond lengths in these three complexes are very similar (M-P-C(Ph) = $115 \pm 5^\circ$, C(Ph)-P-C(Ph) = $100 \pm 5^\circ$) to each other and (dpm)Mo(CO)₄. The difference lies in the metal-metal separation. The molybdenum-manganese complex has a metal-metal bond of 3.054 Å, whereas the titanium-manganese complex has a large nonbonded metal-metal separation of 5.49 Å. The metal-metal bond in $(CO)_3Mo[\mu-(C_5H_4)P(C_6H_5)_2]_2Mn(Cp)(CO)_2$ distorts the geometry about the phosphorus by compressing the Cp-P-M angle. In 2, the zirconium-molybdenum separation is 4.8524(3) Å which allows for a more relaxed geometry about the phosphorus compared to a metal-metal bonded system, but the constraint of two ligating functions on 2 results in a shorter metal-metal separation than in $CpTiCl_2[\mu-(C_5H_4)P(C_6H_5)_2]_2Mn(Cp)(CO)_2$.

Methylation of 2. Treatment of a yellow benzene suspension of 2 with CH_3MgBr gives a nearly colorless suspension from which the dimethyl analogue of 2, $[(C_6H_5)_2P(C_5H_4)]_2Zr(CH_3)_2Mo(CO)_4$, (3) may be isolated (eq 3).



The infrared spectrum of this compound is nearly identical with that of 2 strongly implying that this product also bears a cis-disubstituted Mo(CO)₄ fragment. The proton NMR spectrum of the aromatic region is similar to that observed for 1 and 2. In addition to these signals, however, a singlet at $\delta -0.19$ is observed. This chemical shift is close to that observed for the methyl protons in $Cp_2Zr(CH_3)_2$ ³¹ which also suggests simple substitution of methyl groups for the chloride ligands. Preliminary NMR

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studies show that colorless benzene- d_6 solutions of **3** under vacuum in sealed tubes are stable at room temperature but heating them above 40 °C results in red-brown solutions whose NMR spectra bear only the signals of the starting material. Further studies are in progress to investigate the thermal decomposition and other reactions of **3**.

Summary

The metathesis of $\text{Li}[(\text{C}_6\text{H}_5)_2\text{P}(\text{C}_5\text{H}_4)]$ with $\text{ZrCl}_4 \cdot 2\text{THF}$ in benzene offers a convenient, high yield synthesis of the metallo ligand **1**. This complex readily reacts with $(\text{C}_7\text{H}_5)\text{Mo}(\text{CO})_4$ to give **2**. NMR spectroscopy shows no strong interactions of the two metals other than some small but significant shifts in proton and phosphorus resonances (downfield). Infrared data suggest that **1** and similar complexes where the diphenylphosphine moiety is attached to the Cp ring will behave (at least spectroscopically) as triphenylphosphines or chelating bis(diphenylphosphino)alkanes. The crystal structure of **2** shows very little distortion about the coordination spheres of the two metals which is consistent with a lack of strong interactions between the metals. However, the chelating metallo ligand **1** binds the molybdenum atom nearly 0.6 Å closer than the nonbonded single phosphine bridged Ti-Mn system. The chlorides bonded to the zirconium atom in **2** are readily

exchanged for methyl groups using methylmagnesium bromide. These spectroscopic and structural data suggest that this functionalized sandwich juxtaposes the two metals without significantly altering their physical and chemical properties. Studies are in progress to investigate the spectroscopic, electrochemical, and chemical properties of **3** and similar heterobinuclear complexes derived from **1** and **2**.

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Registry No. **1**, 100898-54-2; **2**, 100898-55-3; $[(\text{C}_6\text{H}_5)_2\text{P}(\text{C}_5\text{H}_4)]_2\text{Zr}(\text{CH}_3)_2\text{Mo}(\text{CO})_4$, 100898-56-4; $\text{Li}[(\text{C}_6\text{H}_5)_2\text{P}(\text{C}_5\text{H}_4)]$, 83272-80-4; $\text{ZrCl}_4 \cdot 2\text{THF}$, 21959-01-3; (norbornadiene)tetracarbonylmolybdenum(0), 12146-37-1.

Supplementary Material Available: Tables of refined thermal parameters, the carbon-hydrogen distances and angles, the pertinent least-squares planes, and calculated and observed structure factor amplitudes (27 pages). Ordering information is given on any current masthead page.

Reaction of $(\eta^5\text{-CH}_3\text{C}_5\text{H}_4)\text{Mn}(\text{CO})_2(\text{THF})$ with PhCH_2N_3 To Yield Binuclear $(\eta^5\text{-CH}_3\text{C}_5\text{H}_4)_2\text{Mn}_2(\text{CO})_3[\mu\text{-C}(\text{O})\text{N}(\text{CH}_2\text{Ph})\text{N}_2]$, an Intermediate in the Formation of Benzyl Isocyanate

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The reaction of benzyl azide with $(\eta^5\text{-CH}_3\text{C}_5\text{H}_4)\text{Mn}(\text{CO})_2(\text{THF})$ results in the formation of $(\eta^5\text{-CH}_3\text{C}_5\text{H}_4)_2\text{Mn}_2(\text{CO})_3[\mu\text{-C}(\text{O})\text{N}(\text{CH}_2\text{Ph})\text{N}_2]$ (**1**). The structure of **1** has been established by an X-ray diffraction study. It crystallizes in the space group $P2_1/n$ with $a = 7.2175$ (8) Å, $b = 14.3614$ (17) Å, $c = 21.2811$ (20) Å, $\beta = 99.531$ (9)°, $V = 2175.4$ (3) Å³, and $Z = 4$. The structure refined to $R_F = 0.0449$ and $R_{wF} = 0.0476$ for the 2826 reflections with $F_o \geq 3\sigma(F_o)$. Each Mn is coordinated by a $\eta^5\text{-CH}_3\text{C}_5\text{H}_4$ ligand and by a CO. The Mn-Mn bond (2.777 (1) Å) is bridged by the $\mu\text{-C}(\text{O})\text{N}(\text{CH}_2\text{Ph})\text{N}_2$ ligand and by a weakly semibridging CO (Mn(1)-C(3) = 2.608 (5) Å). Complex **1** is photoactive, producing $(\eta^5\text{-CH}_3\text{C}_5\text{H}_4)\text{Mn}(\text{CO})_2(\text{THF})$ and PhCH_2NCO when irradiated in THF solution. Irradiation of methanol solutions of **1** produces methyl *N*-benzylcarbamate. The entire reaction sequence represents the stepwise carbonylation of benzyl azide to benzyl isocyanate proceeding through a stable binuclear intermediate.

Recent studies have indicated that triply bridging nitrene ligands in metal clusters have an interesting derivative chemistry. The coupling of $\mu_3\text{-NR}$ ligands with carbenes,^{1a} acyls,^{1b} and hydrides² is now documented. These $\mu_3\text{-NAr}$ ligands have also been proposed as key intermediates in the homogeneous catalyzed reduction of nitroaromatics by $\text{Fe}_3(\text{CO})_{12}$ and $\text{Ru}_3(\text{CO})_{12}$ to yield car-

bamates and other organics.³ Nitrene-containing metal clusters are clearly in need of further study, but one problem that may limit the development of their chemistry is the scarcity of compounds which contain $\mu_3\text{-NR}$ ligands and the lack of general, high-yield synthetic routes to them.⁴

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