

250-MHz ^1H NMR spectra and Dr. A. Pagelot for recording the 400-MHz ^1H NMR spectra.

Registry No. 1a, 95045-81-1; 1b, 95045-82-2; $[\text{Ag}(\mathbf{1a})_2](\text{O}_3\text{SCF}_3)$, 95045-84-4; $[\text{Ag}(\mathbf{1b})_2](\text{O}_3\text{SCF}_3)$, 95045-86-6; $[\text{Cu}(\mathbf{1b})_2](\text{O}_3\text{SCF}_3)$, 95045-88-8; ^{15}N , 14390-96-6; ^{109}Ag , 14378-38-2; 5-R-thiophene-2-carbaldehyde (R = H), 98-03-3; 5-R-thiophene-2-carbaldehyde (R = Me),

13679-70-4; (R,S)-1,2-diaminocyclohexane, 1436-59-5.

Supplementary Material Available: Tables of positional and thermal parameters for all atoms (Table SII) and of observed and calculated structure factors, a complete list of bond lengths and bond angles (Table SIII) of $[\text{Ag}(\mathbf{1b})_2](\text{O}_3\text{SCF}_3)$, and an ORTEP drawing containing the complete numbering scheme (41 pages). Ordering information is given on any current masthead page.

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Binuclear Phosphido-Bridged Complexes That Link Titanium and Zirconium to Tungsten and Iron. Crystal and Molecular Structure of $\text{ZrW}(\mu\text{-PPh}_2)_2\text{Cp}_2(\text{CO})_4$

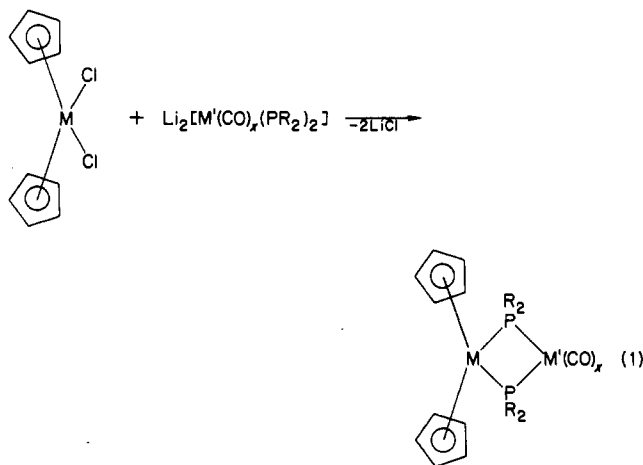
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The new complexes $\text{ZrW}(\mu\text{-PPh}_2)_2\text{Cp}_2(\text{CO})_4$, $\text{ZrFe}(\mu\text{-PR}_2)_2\text{Cp}_2(\text{CO})_3$ (R = Ph, cyclohexyl), $\text{TiW}(\mu\text{-PPh}_2)_2\text{Cp}'_2(\text{CO})_4$ ($\text{Cp}' = \text{C}_5\text{H}_4\text{CH}_3$), and $\text{TiFe}(\mu\text{-PPh}_2)_2\text{Cp}'_2(\text{CO})_3$ have been prepared by the reaction of $\text{Li}_2[\text{W}(\text{CO})_4(\text{PPh}_2)_2]$ and $\text{Li}_2[\text{Fe}(\text{CO})_3(\text{PR}_2)_2]$ with Cp_2ZrCl_2 and $\text{Cp}'_2\text{TiCl}_2$. They have been spectroscopically characterized, and $\text{ZrW}(\mu\text{-PPh}_2)_2\text{Cp}_2(\text{CO})_4$ has been further defined by an X-ray diffraction study. It crystallizes in the space group $P2_1/c$ with $a = 14.644(4) \text{ \AA}$, $b = 16.932(4) \text{ \AA}$, $c = 17.003(3) \text{ \AA}$, $\beta = 100.13(2)^\circ$, $V = 4150(3) \text{ \AA}^3$, and $Z = 4$. The structure refined to $R = 0.047$ and $R_w = 0.067$ for the 3340 reflections with $I > 2\sigma(I)$. The W and Zr atoms are bridged by two $\mu\text{-PPh}_2$ ligands with the Zr further coordinated by two $\eta^5\text{-C}_5\text{H}_5$ ligands and the W by four CO's. The Zr center has a pseudotetrahedral coordination geometry, and W has a nearly perfect octahedral ligand arrangement. The W-Zr distance is 3.289(1) \AA , implying a weak metal-metal interaction at best.

Heterobimetallic complexes are of current interest because of the possibility of obtaining unique chemistry and of stabilizing ligands in unusual coordination modes as a consequence of combining metals with widely different sets of chemical properties.¹ Particularly interesting are combinations of oxophilic group 4¹⁷ transition metals with metals from groups 6-10¹⁷ as these may alter the stability and/or reactivity of formyl, acyl, carbene, and other ligands involved in carbon monoxide reduction chemistry.² Complexes with bridging ligands are desirable since the latter should effectively hold the metals in close proximity and prevent metal separation during reaction.

Using the general synthetic reaction of eq 1, we have been able to prepare a series of bis(phosphido)-bridged TiW, TiFe, ZrW, and ZrFe complexes. The syntheses of these complexes, some



- (1) (a) Roberts, D. A.; Geoffroy, G. L. In "Comprehensive Organometallic Chemistry"; Wilkinson, G., Stone, F. G. A., Abel, E., Eds.; Pergamon Press: Oxford, England, 1982; Chapter 40. (b) Foley, H. C.; Finch, W. C.; Pierpont, C. G.; Geoffroy, G. L. *Organometallics* **1982**, *1*, 1379. (c) LaCroce, S. J.; Cutler, A. R. *J. Am. Chem. Soc.* **1982**, *104*, 2312. (d) Casey, C. P.; Jordan, R. F.; Rheingold, A. L. *Organometallics* **1984**, *3*, 504. (e) Barger, P. T.; Bercaw, J. E. *Organometallics* **1984**, *3*, 279. (f) Ho, S. C. H.; Straus, D. A.; Armantrout, V.; Schaefer, W. P.; Grubbs, R. H. *J. Am. Chem. Soc.* **1984**, *106*, 2210. (2) (a) Caulton, K. G. *J. Mol. Catal.* **1981**, *13*, 71. (b) Wolczanski, P. T.; Threlkel, R. S.; Bercaw, J. E. *J. Am. Chem. Soc.* **1979**, *101*, 218. (c) Marcella, J. A.; Huffman, J. C.; Caulton, K. G.; Longato, B.; Norton, J. R. *J. Am. Chem. Soc.* **1982**, *104*, 6360.

of their general reactivity characteristics, and the X-ray structural characterization of the ZrW derivative are described herein. Similar $\text{TiMo}(\mu\text{-PPhH})_2\text{Cp}_2(\text{CO})_4$ and $\text{ZrMo}(\mu\text{-PPhH})_2\text{Cp}_2(\text{CO})_4$ complexes were earlier prepared by Johannsen and Stelzer,³ but structural details were not given. Baker⁴ has also mentioned the preparation and structure determination of a similar $\text{HfMo}(\mu\text{-PEt}_2)_2\text{Cp}_2(\text{CO})_4$ complex.

Experimental Section

All manipulations were carried out in standard Schlenk glassware under N_2 that had been purified by passage over BASF catalysts and Linde 5- \AA molecular sieves. Solvents were reagent grade or better and were dried by stirring over Na/benzophenone followed by distillation under N_2 . Methylolithium, PhLi , $n\text{-BuLi}$, $\text{Li}[\text{BHET}_3]$, Cp_2ZrCl_2 ($\text{Cp} = \eta^5\text{-C}_5\text{H}_5$) (Aldrich Chemical Co.), $\text{W}(\text{CO})_6$, PCy_2H ($\text{Cy} = \text{cyclohexyl}$), PPh_2H , PPh_2Me (Strem Chemical Co.), $\text{Fe}(\text{CO})_5$ (Alfa Chemical Co.), and $\text{Cp}'_2\text{TiCl}_2$ ($\text{Cp}' = \eta^5\text{-C}_5\text{H}_4\text{CH}_3$) (Pressure Chemical Co.) were purchased from commercial sources. Spectroscopic instruments used in this work have been previously described.^{1b}

Preparation of $\text{Fe}(\text{CO})_3\text{L}_2$ ($\text{L} = \text{PPh}_2\text{H}$, PCy_2H). To a hexane solution of $\text{Fe}(\text{CO})_5$ (2.5 g, 12.8 mmol) in a 500 mL Schlenk flask was added PPh_2H (4.4 mL, 25.1 mmol). This solution was irradiated with a Pyrex-filtered Hanovia 450-W medium-pressure Hg-discharge lamp for 22 h while being stirred. The formation of a yellow precipitate of $\text{Fe}(\text{CO})_3(\text{PPh}_2\text{H})_2$ was observed as the reaction progressed. The solution was filtered, and $\text{Fe}(\text{CO})_3(\text{PPh}_2\text{H})_2$ was collected as a yellow powder in 40% yield (2.22 g, 4.3 mmol). This known⁵ compound was spectroscopically characterized. ^1H NMR (benzene- d_6): δ 7.9 (PPh_2H , d, $J_{\text{PH}} = 363 \text{ Hz}$). The corresponding $\text{Fe}(\text{CO})_3(\text{PCy}_2\text{H})_2$ complex was similarly prepared from $\text{Fe}(\text{CO})_5$ and PCy_2H . ^1H NMR (benzene- d_6): δ 4.82 (PCy_2H , d, $J_{\text{PH}} = 334 \text{ Hz}$). MS: m/e 536 (M^+).

Preparation of $\text{ZrW}(\mu\text{-PPh}_2)_2\text{Cp}_2(\text{CO})_4$ (1). Methylolithium (1.3 M, 2.56 mL, 3.48 mmol) was added via syringe to a THF (20 mL) solution of $\text{cis-W}(\text{CO})_4(\text{PPh}_2\text{H})_2$ (1.62 g, 1.74 mmol) at 22 $^\circ\text{C}$. The resultant orange solution was stirred for 15 min and added via transfer needle to a 20-mL THF solution of Cp_2ZrCl_2 (0.500 g, 1.71 mmol). This solution was allowed to stir for 3 h at 22 $^\circ\text{C}$, the solvent was removed in vacuo, and the residue was extracted with benzene until the washings were colorless. Removal of the benzene in vacuo left yellow 1 in 92% yield (1.36 g, 1.54 mmol). Recrystallization from toluene at 0 $^\circ\text{C}$ gave ana-

- (3) Johannsen, G.; Stelzer, O. *Chem. Ber.* **1977**, *110*, 3438. (4) Baker, R. T. (Du Pont CRD), private communication. Baker, R. T.; Tulip, T. H.; Wreford, S. S. *Inorg. Chem.*, following paper in this issue. (5) Smith, J. G.; Thompson, D. T. *J. Chem. Soc. A* **1967**, 1694. (6) Keiter, R. L.; Sun, Y. Y.; Brodack, J. W.; Cary, L. W. Cary, L. W. *J. Am. Chem. Soc.* **1979**, *101*, 2638.

lytically pure material. Anal. Calcd for $C_{38}H_{30}O_4P_2ZrW$: C, 51.40; H, 3.41. Found: C, 51.45; H, 3.38. 1H NMR (22 °C, benzene- d_6): δ 8.2–7.0 (m, Ph), 5.07 (s, C_5H_5). MS: m/e 888 (M^+), 860 ($M^+ - CO$), 832 ($M^+ - 2CO$), 804 ($M^+ - 3CO$), 776 ($M^+ - 4CO$).

Preparation of $ZrFe(\mu-PCy_2)_2Cp_2(CO)_4$ (2a). *n*-Butyllithium (1.6 M, 1.1 mL, 1.70 mmol) was added via syringe to a 25-mL solution of $Fe(CO)_3(PCy_2H)_2$ (0.455 g, 0.85 mmol) at 0 °C. The resultant solution was allowed to stir for 0.5 h at 22 °C and then added dropwise via transfer needle to a 15-mL THF solution of Cp_2ZrCl_2 (0.250 g, 0.85 mmol). This solution was allowed to stir overnight at 22 °C, and the solvent was removed in vacuo. The oily brown residue was extracted with benzene until the washings were colorless. Concentration of the benzene extracts led to the deposition of yellow microcrystalline **2a**. Following recrystallization from toluene, analytically pure material was obtained in 36% yield (0.23 g). Anal. Calcd for $C_{38}H_{34}O_3P_2ZrFe$: C, 58.80; H, 7.15. Found: C, 58.61; H, 7.34. 1H NMR (22 °C benzene- d_6): δ 5.21 (s, Cp), 2.66–1.00 (m, C_6H_{11}). MS: m/e 754 (M^+), 726 ($M^+ - CO$), 698 ($M^+ - 2CO$), 670 ($M^+ - 3CO$).

Preparation of $ZrFe(\mu-PPh_2)_2Cp_2(CO)_3$ (2b). *n*-Butyllithium (1.6 M, 2.3 mL, 3.7 mmol) was added via syringe to a 20-mL THF solution of $Fe(CO)_3(PPh_2H)_2$ (0.850 g, 1.7 mmol) at 22 °C. The resultant dark solution was allowed to stir for 15 min and then added dropwise via transfer needle to a 20-mL THF solution of Cp_2ZrCl_2 (0.484 g, 1.7 mmol). This solution was allowed to stir for 2 h at 22 °C, and the solvent was removed in vacuo. The oily residue was washed with hexane until the washings were colorless. Removal of the remaining hexane in vacuo left **2b** as an impure yellow powder in low yield (16%, 0.2 g, 0.27 mmol). The best analysis obtained for $C_{37}H_{30}O_3P_2ZrFe$ was as follows. Anal. Found: C, 52.90; H, 3.98 (calcd: C, 60.72; H, 4.14). 1H NMR (22 °C, benzene- d_6): δ 8.06–6.9 (m, Ph), 5.06 (s, C_5H_5). MS: m/e 730 (M^+), 702 ($M^+ - CO$), 674 ($M^+ - 2CO$), 646 ($M^+ - 3CO$).

Preparation of $TiW(\mu-PPh_2)_2Cp_2(CO)_3$ (3). *n*-Butyllithium (1.6 M, 1.88 mL, 3.0 mmol) was added via syringe to 20 mL of a THF solution of *cis*- $W(CO)_4(PPh_2H)_2$ (1.00 g, 1.5 mmol). This solution was allowed to stir at 22 °C for 15 min and then added dropwise via transfer needle to 20 mL of a THF suspension of Cp_2TiCl_2 (0.415 g, 1.5 mmol). This red solution was allowed to stir for 2 h at 22 °C, and the solvent was removed in vacuo. Attempts to isolate **3** as a pure powder by recrystallization from CH_2Cl_2 /hexane and chromatography on alumina were unsuccessful as samples of **3** were persistently contaminated with 5–10% Cp'_2TiCl_2 . 1H NMR (22 °C, benzene- d_6): δ 7.9–6.9 (m, Ph), 4.98 (s, C_5H_5), 4.92 (s, C_5H_4), 2.06 (s, CH_3). MS: m/e 874 (M^+), 846 ($M^+ - CO$), 818 ($M^+ - 2CO$), 790 ($M^+ - 3CO$), 762 ($M^+ - 4CO$).

Preparation of $TiFe(\mu-PPh_2)_2Cp_2(CO)_3$ (4). *n*-Butyllithium (1.6 M, 0.61 mL, 0.96 mmol) was added via syringe to a 20-mL THF solution of $Fe(CO)_3(PPh_2H)_2$ (0.250 g, 4.88 mmol) at 22 °C. This solution was allowed to stir for 15 min and then added dropwise to a 20-mL THF solution of Cp_2TiCl_2 (0.135 g, 4.88 mmol). The resultant red solution was stirred overnight at 22 °C, and the solvent was removed in vacuo. The residue was washed with benzene until the washings were colorless. Removal of the residual benzene in vacuo gave a mixture of starting materials and **4**. Attempts to isolate pure **4** from reaction mixtures by solvent extraction and chromatography were unsuccessful.

Reactions of Complexes 1 and 2 with Alkylolithium and Borohydride Reagents. In all cases, ≥ 1 -equiv amounts of an alkylolithium reagent (methylolithium, *n*-butyllithium, phenyllithium) or borohydride ($LiBH_4$) were added dropwise by syringe to 20-mL THF solutions of **1** and **2** (0.10 mmol) at –78 °C and the mixtures then warmed first to 0 °C and then to 22 °C. The reactions were monitored by IR and ^{31}P NMR spectroscopy, but in no case were clean conversions observed.

X-ray Diffraction Study of 1. Yellow crystals of **1** were grown by slow evaporation of a saturated THF/ Et_2O /2-methoxyethyl ether solution of the complex. A suitable crystal was mounted in an arbitrary orientation on a glass fiber on a eucentric goniometer. The Enraf-Nonius programs SEARCH and INDEX were employed to obtain an orientation matrix for data collection and to provide cell dimensions.^{7a} Details of the data collection and reduction procedures have been previously described.^{7b} All data were converted to $|F_o|$ values following correction for absorption (empirical ψ -scan technique, 96.3–99.9% transmission coefficients) and for Lp effects. Pertinent crystal and intensity data are listed in Table I.

The W, Zr, and P atoms were located by Patterson heavy-atom techniques. The coordinates of the remaining non-hydrogen atoms were determined by successive least-squares refinements and difference Fourier maps. Four molecules of recrystallization solvent 2-methoxyethyl ether,

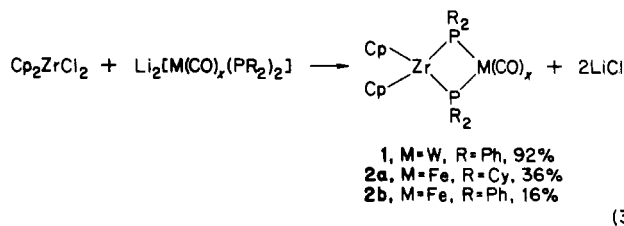
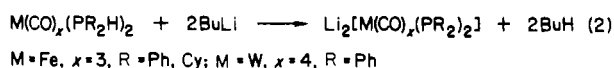
Table I. Crystal and Intensity Data for $ZrW(\mu-PPh_2)_2Cp_2(CO)_4 \cdot C_6H_{14}O_3$ (1)

mol formula	$C_{44}H_{44}O_3P_2WZr$
cryst dimens, mm	$0.15 \times 0.15 \times 0.22$
cryst symm	monoclinic
space group	$P2_1/c$
<i>a</i> , Å	14.644 (4)
<i>b</i> , Å	16.932 (4)
<i>c</i> , Å	17.003 (3)
β , deg	100.13 (2)
<i>V</i> , Å ³	4150 (3)
<i>Z</i>	4
ρ (calcd), g cm ⁻³	1.635
abs coeff, cm ⁻¹	31.997
<i>T</i> , °C	22
diffractometer	Enraf-Nonius CAD4
radiation	Mo K α ($\lambda = 0.71073$ Å)
monochromator	graphite cryst
scan type	$\theta-2\theta$
scan speed, deg min ⁻¹	1.0–5.0
takeoff angle, deg	2.8
scan width, deg	$0.8 + 0.347 \tan \theta$
std refens	3 every 1 h (no decay)
2θ scan range, deg	$3.2 < 2\theta < 42.1$
data collcd	<i>h</i> , <i>k</i> , $\pm l$
no. of unique data	4474
no. of unique data with $I > 2\sigma(I)$	3340
<i>R</i>	0.047
<i>R</i> _w	0.067
esd	1.628
max shift/error	0.01

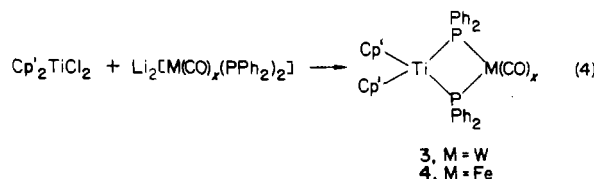
$CH_3OCH_2CH_2OCH_2CH_2OCH_3$, were also found in the unit cell with a slight positional disorder as evidenced by the magnitude of the thermal parameters for the refined molecule. In the final cycle, least-squares convergence was achieved upon refinement of the positional and anisotropic thermal parameters of all non-hydrogen atoms. The structure converged to $R = 0.047$ and $R_w = 0.067$, where $R = \sum ||F_o| - |F_c|| / \sum |F_o|$, $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum wF_o^2]^{1/2}$, $w = 1/(\sigma(F_o))^2$, $\sigma(F_o) = \sigma(F_o^2)/2F_o$, and $\sigma(F_o^2) = [(\sigma(I_{RAW}))^2 + (0.06F_o^2)^2]^{1/2}$. A final difference Fourier map showed no unusual peaks; the highest peak of $1.0 e \text{ \AA}^{-3}$ was located in the vicinity of the slightly disordered 2-methoxyethyl ether solvent of crystallization. Final positional parameters are listed in Table II, and relevant bond distances and angles are summarized in Table III. Tables of thermal parameters, complete bond lengths and angles, and structure factors are available as supplementary material.

Results and Discussion

Synthesis and Spectroscopic Characterization. The new ZrFe and ZrW complexes discussed herein were prepared by the sequence of reactions 2 and 3. The corresponding TiFe and TiW



complexes were prepared by a similar procedure using Cp'_2TiCl_2 ($Cp' = C_5H_4CH_3$), eq 4. These reactions apparently proceed by



(7) (a) All programs used in this study are part of the Enraf-Nonius Structure Determination Package, Enraf-Nonius, Delft, Holland, 1975, revised 1982. (b) Horrocks, W. D.; Ishley, J. N.; Whittle, R. R. *Inorg. Chem.* **1982**, *21*, 3265.

nucleophilic substitution of the halides on the group 4 metals by the phosphide ligands, a reaction that also brings the metals

Table II. Atomic Positional Parameters of $ZrW(\mu\text{-PPh}_2)_2\text{Cp}_2(\text{CO})_4$

atom	x	y	z	$B, \text{\AA}^2$
W	0.15568 (4)	0.12930 (3)	0.06586 (3)	2.23 (1)
Zr	0.25071 (8)	0.14346 (7)	0.25555 (7)	2.28 (3)
P1	0.1051 (2)	0.2138 (2)	0.1737 (2)	2.64 (8)
P2	0.2991 (2)	0.0603 (2)	0.1387 (2)	2.45 (8)
O1	0.0373 (7)	-0.0161 (6)	0.1074 (6)	4.7 (3)
O2	0.1925 (8)	0.0430 (7)	-0.0899 (6)	5.5 (3)
O3	0.2811 (7)	0.2717 (6)	0.0310 (6)	5.0 (3)
O4	-0.0158 (8)	0.1986 (7)	-0.0473 (7)	6.0 (3)
O61	0.269 (1)	0.6361 (8)	0.9672 (8)	8.0 (4)*
O64	0.4405 (9)	0.6049 (8)	0.9122 (8)	7.2 (3)*
O67	0.568 (1)	0.4979 (9)	0.8454 (9)	9.2 (4)*
C1	0.0792 (9)	0.0381 (8)	0.0945 (7)	2.9 (3)
C2	0.179 (1)	0.0729 (9)	-0.0315 (9)	3.9 (4)
C3	0.2337 (9)	0.2204 (8)	0.0432 (7)	2.8 (3)
C4	0.047 (1)	0.1752 (9)	-0.0038 (9)	4.1 (4)
C10	-0.012 (1)	0.1979 (8)	0.1946 (8)	3.3 (3)*
C11	-0.0775 (9)	0.1529 (8)	0.1442 (8)	3.2 (3)*
C12	-0.168 (1)	0.1421 (8)	0.1643 (9)	3.7 (3)*
C13	-0.191 (1)	0.175 (1)	0.233 (1)	4.7 (4)*
C14	-0.127 (1)	0.221 (1)	0.284 (1)	5.4 (4)*
C15	-0.035 (1)	0.2306 (9)	0.2630 (9)	4.4 (3)*
C20	0.1006 (8)	0.3205 (7)	0.1571 (7)	2.3 (3)*
C21	0.089 (1)	0.3516 (9)	0.0812 (9)	3.8 (3)*
C22	0.084 (1)	0.435 (1)	0.070 (1)	4.9 (4)*
C23	0.090 (1)	0.485 (1)	0.134 (1)	4.8 (4)*
C24	0.101 (1)	0.453 (1)	0.211 (1)	5.1 (4)*
C25	0.106 (1)	0.3714 (9)	0.2206 (9)	4.0 (3)
C30	0.3009 (9)	-0.0496 (8)	0.1369 (8)	2.8 (3)*
C31	0.243 (1)	-0.0920 (9)	0.0803 (8)	3.4 (3)*
C32	0.254 (1)	-0.1759 (9)	0.0760 (9)	4.1 (3)*
C33	0.320 (1)	-0.213 (1)	0.129 (1)	4.8 (4)*
C34	0.375 (1)	-0.172 (1)	0.188 (1)	5.3 (4)*
C35	0.367 (1)	-0.087 (1)	0.1935 (9)	4.5 (3)*
C40	0.4082 (9)	0.0775 (8)	0.0992 (8)	3.0 (3)*
C41	0.404 (1)	0.1069 (9)	0.0273 (9)	4.1 (3)*
C42	0.492 (1)	0.1158 (9)	-0.004 (1)	4.8 (4)*
C43	0.572 (1)	0.098 (1)	0.0443 (9)	4.6 (4)*
C44	0.575 (1)	0.070 (1)	0.121 (1)	6.1 (4)*
C45	0.491 (1)	0.060 (1)	0.149 (1)	5.0 (4)*
C50	0.316 (1)	0.2787 (8)	0.236 (1)	4.4 (4)
C51	0.3848 (9)	0.2230 (8)	0.2199 (9)	3.7 (4)
C52	0.4160 (9)	0.1831 (9)	0.2935 (9)	3.9 (4)
C53	0.373 (1)	0.2162 (9)	0.3532 (9)	4.5 (4)
C54	0.308 (1)	0.2734 (9)	0.3172 (9)	4.6 (4)
C55	0.149 (1)	0.1112 (9)	0.3569 (9)	4.6 (4)
C56	0.245 (1)	0.087 (1)	0.3884 (8)	4.9 (4)
C57	0.267 (1)	0.0249 (8)	0.3436 (9)	3.9 (4)
C58	0.1913 (9)	0.0071 (8)	0.2819 (8)	3.4 (3)
C59	0.1212 (9)	0.0595 (9)	0.2908 (8)	3.5 (3)
C60	0.166 (2)	0.628 (1)	0.953 (2)	10.1 (7)*
C62	0.306 (2)	0.680 (1)	0.910 (1)	8.3 (6)*
C63	0.408 (2)	0.678 (1)	0.929 (1)	8.8 (6)*
C65	0.547 (2)	0.592 (2)	0.933 (2)	16 (1)*
C66	0.560 (3)	0.506 (2)	0.924 (2)	17 (1)*
C68	0.656 (3)	0.479 (3)	0.837 (3)	21 (2)*

^a Starred atoms were refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $\frac{1}{3}[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos \gamma)B(1,2) + ac(\cos \beta)B(1,3) + bc(\cos \alpha)B(2,3)]$. ^b Refined isotropically.

together to yield the binuclear products. This "bridge-assisted"^{1a} synthetic reaction has proven to be extremely versatile and generally gives high yields of the desired products.^{1a,8} Although the yield of the ZrW complex **1** (eq 3) was high, the remainder of the products were isolated in rather low yields, which we attribute largely to their general instability (see below). Also, the TiFe

Table III. Relevant Bond Distances (Å) and Angles (deg) in $ZrW(\mu\text{-PPh}_2)_2\text{Cp}_2(\text{CO})_4$

Bond Distances			
W-Zr	3.289 (1)	Zr-C50	2.524 (12)
W-P1	2.537 (3)	Zr-C51	2.541 (11)
W-P2	2.529 (3)	Zr-C52	2.486 (11)
Zr-P1	2.619 (3)	Zr-C53	2.532 (11)
Zr-P2	2.631 (3)	Zr-C54	2.518 (12)
W-C1	2.016 (13)	Zr-C55	2.525 (12)
W-C2	1.994 (14)	Zr-C56	2.469 (11)
W-C3	1.996 (12)	Zr-C57	2.491 (11)
W-C4	1.972 (12)	Zr-C58	2.536 (11)
C50-C51	1.44 (2)	Zr-C59	2.525 (11)
C50-C54	1.40 (2)	C55-C56	1.47 (2)
C51-C52	1.43 (2)	C55-C59	1.43 (2)
C52-C53	1.41 (2)	C56-C57	1.37 (2)
C53-C54	1.41 (2)	C57-C58	1.42 (2)
		C58-C59	1.39 (2)

Bond Angles			
W-P1-Zr	79.25 (8)	P2-W-C2	86.3 (3)
W-P2-Zr	79.16 (8)	P2-W-C3	89.8 (3)
P1-Zr-P2	98.30 (9)	P2-W-C4	172.3 (4)
P1-W-P2	103.27 (9)	C1-W-C2	91.1 (4)
P1-W-C1	90.7 (3)	C1-W-C3	177.2 (4)
P1-W-C2	170.4 (3)	C1-W-C4	91.2 (5)
P1-W-C3	87.3 (3)	C2-W-C3	91.2 (5)
P1-W-C4	84.4 (4)	C2-W-C4	86.0 (5)
P2-W-C1	88.7 (3)	C3-W-C4	90.6 (5)

Table IV. Spectroscopic Data

complex	IR ^a ν_{CO} , cm ⁻¹	³¹ P NMR ^b	
		δ	$J_{\text{P-}^{183}\text{W}}$, Hz
1 (ZrW)	2012 m, 1926 sh, 1908 s	156.7	149
2a (ZrFe)	1971 m, 1898 s	153.7	
2b (ZrFe)	1995 m, 1932 s	145.2	
3 (TiW)	2010 m, 1930 sh, 1905 s	196.4	152
4 (TiFe)	1996 m, 1933 s	170.7	
Fe(CO) ₃ (PPh ₂ H) ₂	1977 w, 1967 w, 1892 s	53 ^c	
Fe(CO) ₃ (PCy ₂ H) ₂	1964 w, 1844 sh, 1873 s	67.6 ^d	
cis-W(CO) ₄ (PPh ₂ H) ₂	2022 m, 1928 s, sh, 1905 vs, 1890 s, sh	-3.7 ^e	112

^a THF solution. ^b C₆D₆ solution, 25 °C. ^c $J_{\text{P-H}} = 363$ Hz. ^d $J_{\text{P-H}} = 334$ Hz. ^e $J_{\text{P-H}} = 336$ Hz.

and TiW complexes were not obtained pure as they were persistently contaminated with Cp₂TiCl₂ and rapidly decomposed during recrystallization. Likewise, the ZrFe complex **2b** was persistently contaminated with Fe(CO)₃(PPh₂H)₂.

The ZrW complex **1** has been completely characterized by an X-ray diffraction study (Figure 1) which shows the structure indicated in eq 3. Spectroscopic data (Table IV) imply that the ZrFe, TiW, and TiFe complexes have similar structures. All show ³¹P NMR resonances for the $\mu\text{-PPh}_2$ ligands in the same δ 145→197 spectral region. The IR spectra of the W-containing complexes **1** and **3** (Table IV) show two principal bands that are similar in position to the corresponding ν_{CO} bands of cis-W(CO)₄(PPh₂H)₂, implying a similar amount of electron density at W in the three complexes. The Fe-containing complexes **2** and **4** show ν_{CO} bands similar to each other, but these are blue shifted by about 20–40 cm⁻¹ from those of the corresponding Fe(CO)₃(PR₂H)₂ precursor complexes.

Crystal and Molecular Structure of ZrW($\mu\text{-PPh}_2$)₂Cp₂(CO)₄ (1**).** An ORTEP drawing of ZrW($\mu\text{-PPh}_2$)₂Cp₂(CO)₄ is shown in Figure 1. The Zr and W atoms are bridged by the two $\mu\text{-PPh}_2$ ligands with W further coordinated by four CO's and Zr by the two Cp ligands. The coordination geometry about W is clearly octahedral whereas the Zr center shows the usual distorted tet-

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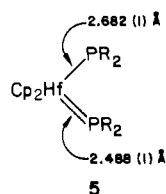
Table V. Structural Parameters and ^{31}P NMR Data for a Series of $(\text{CO})_4\text{W}(\mu\text{-PPh}_2)_2\text{ML}_x$ and Related Complexes

compd	M-M, Å	M-P-M, deg	δ	ref
$(\text{CO})_4\text{W}(\mu\text{-PPh}_2)_2\text{Pt}(\text{PPh}_3)$	2.764 (1)	70.8 (1) 70.6 (1)	173.8	10
$(\text{CO})_4\text{W}(\mu\text{-PPh}_2)_2\text{PtL}$ (L = $\text{CH}_3\text{O}_2\text{CC}\equiv\text{CCO}_2\text{CH}_3$)	2.795 (1)	72.4 (1) 72.5 (1)	187.1	10
$(\text{CO})_4\text{W}(\mu\text{-PPh}_2)_2\text{IrH}(\text{COD})$	2.893 (1)	74.2 (2) 73.6 (2)	157.6	15
$(\text{CO})_4\text{W}(\mu\text{-PPh}_2)_2\text{IrH}(\text{CO})(\text{PPh}_3)$	2.8764 (6)	72.7 (1) 72.9 (1)	132.8	11
$(\text{CO})_3[\text{C}(\text{OMe})\text{Ph}]\text{W}(\mu\text{-PPh}_2)_2\text{IrH}(\text{CO})(\text{PPh}_3)$	2.858 (1)	73.0 (1) 72.6 (1)	119.3 97.7	11
$(\text{CO})_4\text{W}(\mu\text{-PPh}_2)_2\text{ZrCp}_2$	3.289 (1)	79.25 (8) 79.16 (8)	156.7	<i>a</i>
$(\text{CO})_4\text{W}(\mu\text{-PPh}_2)_2\text{Re}(\text{CO})_3\text{CH}_3$	3.014 (1)	76.1 (1) 76.2 (1)	177.8	16

^a This work.

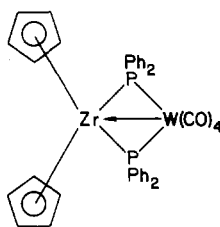
rahedral geometry characteristic of MCp_2X_2 complexes.

The Zr-P distances in **1** are slightly shorter than the Hf-P single-bond distances found in $\text{Cp}_2\text{Hf}(\text{PR}_2)_2$ ⁹ (**5**) but are consistent



with a single bond between these atoms. The W-P distances of 2.529 (3) and 2.537 (3) Å compare well to those found in other $(\text{CO})_4\text{W}(\mu\text{-PPh}_2)_2\text{M}$ structures. For example, in $(\text{CO})_4\text{W}(\mu\text{-PPh}_2)_2\text{Pt}(\text{PPh}_3)$ ¹⁰ and $(\text{CO})_4\text{W}(\mu\text{-PPh}_2)_2\text{IrH}(\text{CO})(\text{PPh}_3)$ ¹¹ the corresponding distances are 2.509 (4), 2.507 (3) Å and 2.528 (2), 2.534 (2) Å, respectively. The $\text{W}(\mu\text{-P})_2\text{Zr}$ core of complex **1** is essentially planar with a dihedral angle of 1.6° between the P1-Zr-P2 and P1-W-P2 planes.

An important issue concerns the degree of direct metal-metal interaction in **1**. One possible formulation of the complex is with a donor-acceptor bond from $\text{W}(0)$ to the electron-deficient $\text{Zr}(\text{IV})$ center:



The W-Zr separation of 3.289 (1) Å is clearly long, but it could indicate some degree of metal-metal interaction. There are no reported structures with Zr-W bonds with which to compare this distance, but it is similar to the 3.297 (1) Å Zr-Mo distance found in $\text{Cp}_2\text{Zr}(\mu\text{-OCCH}_3)\text{Mo}(\text{CO})_2\text{Cp}$, which has been described as having a metal-metal bond.¹² However, if a metal-metal bond is present in **1**, it must be relatively weak since the small blue shift in the ν_{CO} bands of the $\text{W}(\text{CO})_4$ portion of **1** compared to that of $\text{W}(\text{CO})_4(\text{PPh}_2\text{H})_2$ indicates little change in electron density

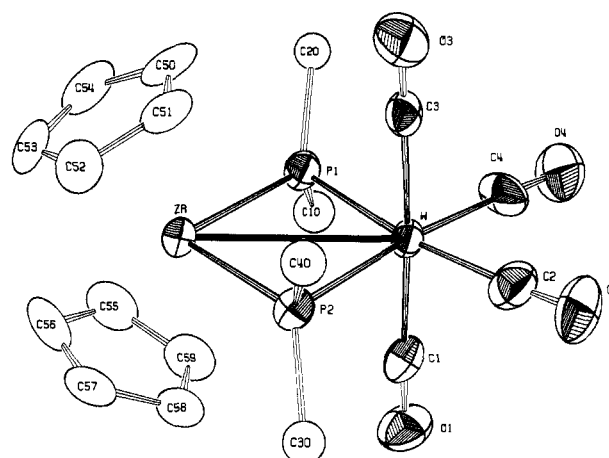


Figure 1. ORTEP drawing of $\text{ZrW}(\mu\text{-PPh}_2)_2\text{Cp}_2(\text{CO})_4$ (**1**). Thermal ellipsoids are drawn at the 50% probability level, and only the phenyl carbons attached to phosphorus in the $\mu\text{-PPh}_2$ ligands are drawn for clarity.

on W in constructing the complex. This is in contrast to the situation found for the related complexes $(\text{CO})_4\text{W}(\mu\text{-PPh}_2)_2\text{IrH}(\text{CO})(\text{PPh}_3)$ ¹¹ ($\Delta\nu_{\text{CO}} \approx 20 \text{ cm}^{-1}$) and $(\text{CO})_4\text{W}(\mu\text{-PPh}_2)_2\text{Pt}(\text{PPh}_3)_2$ ($\Delta\nu_{\text{CO}} \approx 20 \text{ cm}^{-1}$)¹⁰ where metal-metal bonds are clearly present. The more pronounced blue shift ($20\text{--}40 \text{ cm}^{-1}$) of the IR bands in the ZrFe and TiFe complexes **2** and **4** as compared to that of the $\text{Fe}(\text{CO})_3(\text{PR}_2\text{H})_2$ precursor complexes would seem to imply a more pronounced metal-metal interaction in these complexes than in **1**.

One interesting spectroscopic problem that arises in connection with the question of metal-metal bonding in **1** and the related complexes discussed herein concerns the ^{31}P NMR chemical shifts for the $\mu\text{-PR}_2$ ligands (Table IV). Literature data indicate that $\mu\text{-PR}_2$ ligands in compounds with metal-metal bonds generally exhibit downfield ($\delta 300\text{--}50$) ^{31}P NMR resonances whereas upfield ($\delta 50\text{--}200$) resonances are observed for compounds in which the $\mu\text{-PR}_2$ ligands bridge two metals not joined by a metal-metal bond.^{13,14} Thus, ^{31}P NMR data for complexes **1-4** would imply metal-metal bonds in these complexes, contrary to the more definitive crystallographic results for **1**. Carty^{13c} has established a correlation between M-P-M angles and ^{31}P NMR chemical shifts for a series of related $\text{Fe}_2(\mu\text{-PPh}_2)(\mu\text{-X})(\text{CO})_6$

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complexes and has pointed out that the latter is a very sensitive function of bond angle. In the above-mentioned Fe_2 compounds, a variation of bond angle of only $\sim 6^\circ$ gave a chemical shift variation of 80 ppm.^{13c} We have structurally characterized several $(\text{CO})_4\text{W}(\mu\text{-PPh}_2)_2\text{ML}_n$ complexes^{10,11,15,16} and have tried to correlate structural results to ^{31}P NMR chemical shift data for these compounds. However, no obvious correlation exists among the metal-metal distances, M-P-M angles, and ^{31}P NMR data, as illustrated in Table V. This result is perhaps not too surprising since the metal-ligand combinations employed in the metal fragment linked to the $(\text{CO})_4\text{W}(\mu\text{-PPh}_2)_2$ unit vary considerably. However, these data do point out serious problems in employing the $\mu\text{-PR}_2$ chemical shift/metal-metal bond correlation.¹⁴ The correlation appears to be best used for closely related series of compounds in which one or more members have been structurally characterized.

Stability and Reactivity of Complexes 1-4. Complexes 1-3 are stable in air for ~ 1 week in the solid state before showing signs of decomposition. However, solutions of the complexes decompose

within minutes following air exposure. Complex 4, although never obtained pure, is more air sensitive than 1-3. The reactivities of complexes 1 and 2 were briefly explored with $\text{Li}[\text{BHEt}_3]$, CH_3Li , BuLi , and PhLi in attempts to form formyl and acyl derivatives in which these ligands could perhaps be stabilized by bridging between the metals, presumably with oxygen bound to the oxophilic Zr center. However, in no case were stable products isolated. Infrared monitoring showed that no reaction occurred when 1 and 2 were allowed to react with $\text{Li}[\text{BHEt}_3]$ and CH_3Li . Reaction of these complexes with PhLi at -78°C did yield new ν_{CO} bands at lower energy (e.g., $1 + \text{PhLi} \rightarrow$ bands at 1925, 1850, 1840 cm^{-1}) but all workup attempts led to decomposition of the product(s) formed. Also, infrared monitoring revealed that no reaction occurred when complexes 1 and 2 were heated (70°C) or irradiated ($>300\text{ nm}$) in the presence of $\text{PhC}\equiv\text{CPh}$, PMePh_2 , and CS_2 .

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Registry No. 1, 95465-26-2; $1\text{-C}_6\text{H}_{14}\text{O}_3$, 95465-28-4; 2a, 95465-29-5; 2b, 95465-30-8; 3, 95465-31-9; 4, 95465-32-0; $\text{Fe}(\text{CO})_3(\text{PPh}_2\text{H})_2$, 18399-67-2; $\text{Fe}(\text{CO})_3(\text{PCy}_2\text{H})_2$, 95483-60-6; *cis*- $\text{W}(\text{CO})_4(\text{PPh}_2\text{H})_2$, 70505-43-0; Cp_2ZrCl_2 , 1291-32-3; Cp_2TiCl_2 , 1282-40-2; $\text{Li}_2[\text{Fe}(\text{CO})_3(\text{PPh}_2)_2]$, 95465-33-1; $\text{Li}_2[\text{Fe}(\text{CO})_3(\text{PCy}_2)_2]$, 95465-34-2; $\text{Li}_2[\text{W}(\text{CO})_4(\text{PPh}_2)_2]$, 88930-39-6; $\text{Fe}(\text{CO})_5$, 13463-40-6; PPh_2H , 829-85-6; PCy_2H , 829-84-5.

Supplementary Material Available: Table of anisotropic thermal parameters, structure factors, and bond lengths and angles for 1 (22 pages). Ordering information is given on any current masthead page.

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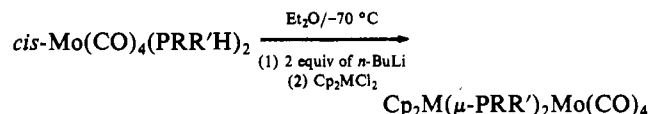
Synthesis and Molecular Structures of Diorganophosphido-Bridged Heterobimetallic Complexes

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The "metal-containing bis(phosphine)" $\text{Cp}_2\text{Hf}(\text{PEt}_2)_2$ reacts with $\text{Ni}(\text{CO})_4$, $\text{Fe}_2(\text{CO})_9$, and $(\text{NBD})\text{Mo}(\text{CO})_4$ to form the diethylphosphido-bridged heterobimetallic complexes $\text{Cp}_2\text{Hf}(\mu\text{-PEt}_2)_2\text{M}(\text{CO})_m$, where $\text{Cp} = \eta^5\text{-C}_5\text{H}_5$, NBD = norbornadiene, and $\text{M} = \text{Ni}$, Fe , Mo with $n = 2, 3, 4$, respectively. The singly bridged intermediate $\text{Cp}_2\text{Hf}(\text{PEt}_2)(\mu\text{-PEt}_2)\text{Fe}(\text{CO})_4$ was also prepared. The molecular structure of $\text{Cp}_2\text{Hf}(\mu\text{-PEt}_2)_2\text{Mo}(\text{CO})_4$, determined by X-ray diffraction, consists of edge-shared pseudotetrahedral 16e Hf(IV) and pseudooctahedral 18e Mo(0) centers with a planar HfP_2Mo bridging unit and a $\text{Hf}\cdots\text{Mo}$ separation of 3.400 (1) Å. The complex crystallizes in space group $C_{2h}^2-P2_1/n$ (No. 14)—with four molecules in a cell of dimensions $a = 13.315$ (3) Å, $b = 18.294$ (6) Å, $c = 10.103$ (2) Å, and $\beta = 91.21$ (2)°.

The most widely used synthetic route¹ to diorganophosphido-bridged, early-late heterobimetallic complexes involves the deprotonation of metal-coordinated secondary phosphines and reaction of the resulting anions with a transition-metal halide. An example² relevant to this work is shown as follows.



$\text{R} = \text{R}' = \text{Me}; \text{R} = \text{Ph}, \text{R}' = \text{H}, \text{SiMe}_3$

$\text{M} = \text{Ti}, \text{Zr}$

$\text{Cp} = \eta^5\text{-C}_5\text{H}_5$

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We recently reported³ the synthesis and molecular structure of the neutral "metal-containing bis(phosphine)" $\text{Cp}_2\text{Hf}(\text{PEt}_2)_2$, which contains both single and double Hf-P bonds. We have used this and analogous complexes⁴ to bind $\text{Ni}(1,5\text{-COD})$, $\text{M}(\text{PR}_3)$ (M

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