

Monophosphido-Bridged Early/Late Heterobimetallic Complexes: Cooperative Activation of CO

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The reactions of the metal-metal bonded complexes $[\text{CpM}(\text{CO})_3]_2$ ($\text{M} = \text{Mo}, \text{W}$) with $\text{Cp}_2\text{Zr}(\text{PR}_2)_2$ ($\text{R} = \text{Ph}, \text{Cy}$) result in reduction of the M-M bond and oxidation of one of the phosphido ligands, yielding the monophosphido-bridged heterobimetallic species $\text{Cp}_2\text{Zr}(\mu\text{-PR}_2)(\eta^1\text{-}\eta^2\text{-OC})\text{M}(\text{CO})\text{Cp}$ ($\text{M} = \text{Mo}, \text{R} = \text{Ph}, 1; \text{M} = \text{Mo}, \text{R} = \text{Cy}, 2; \text{M} = \text{W}, \text{R} = \text{Ph}, 3$) and P_2R_4 . Alternatively, the heterobimetallic complex 1 and the byproduct PPh_2H are formed by reaction of $\text{CpMo}(\text{CO})_3\text{H}$ with $\text{Cp}_2\text{Zr}(\text{PPh}_2)_2$. Complex 1 crystallizes in the space group $P2_1/n$ with $a = 11.537$ (3) Å, $b = 19.567$ (6) Å, $c = 10.892$ (4) Å, $\beta = 95.52$ (2)°, $Z = 4$, and $V = 2447$ (1) Å³. The presence of a single phosphido bridge between the Zr and Mo was confirmed by the X-ray study. Heterobimetallic cooperative activation of CO is evidenced by the bridging carbonyl moiety which is η^1 to Mo and η^2 to Zr. Complex 1 undergoes no reaction with a number of nucleophilic and electrophilic reagents under a variety of conditions. The lack of reactivity at the $\eta^1\text{-}\eta^2$ bound carbonyl is attributed to the oxophilicity of Zr and the inhibition of reaction brought about by the steric demands of the cyclopentadienyl rings and bridging phosphido group.

Introduction

Heterogeneous complexes containing both early, oxophilic, and late, electron-rich metal centers have been the subject of numerous recent studies.¹ One of the reasons for interest in such species is the potential for applications in carbon oxide reduction chemistry. Such early/late heterobimetallic complexes combine the Lewis acidity of the early metals with known abilities of the late metals for activation of hydrogen. Numerous synthetic routes to compounds containing such metal combinations have been developed. In order to ensure the bimetallic nature of such heterobimetallic complexes, bridging ligands, including thiolates²⁻¹⁹ and a variety of pendent chelates,²⁰⁻⁴⁸ have

been employed. Of these early/late heterobimetallic complexes, few provide the metal atom proximity or nec-

(1) Some recent examples of early/late heterobimetallic systems include: (a) Gambarotta, S.; Stella, S.; Floriani, C.; Chiesi-Villa, A.; Gucustini, C. *Angew. Chem., Int. Ed., Engl.* 1986, 25, 254. (b) Hamilton, D. M.; Willis, W. M.; Stucky, G. D. *J. Am. Chem. Soc.* 1981, 103, 4255. (c) Merola, J. S.; Gentile, R. A.; Ansell, G. B.; Modrick, M. A.; Zentz, S. *Organometallics* 1982, 1, 1731. (d) Merola, J. S.; Campo, K. S.; Gentile, R. A.; Modrick, M. A.; Zentz, S. *Organometallics* 1984, 3, 334. (e) De Boer, E. J. M.; De With, J.; Orpen, A. G. *J. Chem. Soc., Chem. Commun.* 1985, 1666. (f) Sartain, W. J.; Selegue, J. P. *Organometallics* 1984, 3, 1922. (g) Longato, B.; Norton, J. R.; Huffman, J. C.; Marsella, J. A.; Caulton, K. G. *J. Am. Chem. Soc.* 1981, 103, 209. (h) Martin, B. D.; Matchett, S. A.; Norton, J. R.; Anderson, O. P. *J. Am. Chem. Soc.* 1985, 105, 7952. (i) Longato, B.; Martin, B. D.; Norton, J. R.; Anderson, O. P. *Inorg. Chem.* 1985, 24, 1389. (j) Marsella, J. A.; Huffman, J. C.; Caulton, K. C.; Logato, B.; Norton, J. R. *J. Am. Chem. Soc.* 1982, 104, 6360. (k) Barger, P. T.; Bercaw, J. E. *J. Organomet. Chem.* 1980, 201, C39. (l) Barger, P. T.; Bercaw, J. E. *Organometallics* 1984, 3, 278. (m) Erker, G.; Dorf, U.; Benn, R.; Rhiendart, R. D.; Peterson, J. L. *J. Am. Chem. Soc.* 1984, 106, 7649. (n) Erker, G.; Dorf, U.; Mynott, R.; Tsay, Y. H.; Kruger, C. *Angew. Chem., Int. Ed. Engl.* 1985, 24, 584. (o) Erker, G.; Dorf, U.; Kruger, C.; Tsay, Y. H. *Organometallics* 1987, 6, 680. (p) Mashima, K.; Jyodoi, K.; Ohyoshi, A.; Takaya, H. *J. Chem. Soc., Chem. Commun.* 1986, 1145. (q) Awang, M. R.; Barr, R. D.; Green, M.; Howard, J. A. K.; Marder, T. B.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* 1985, 2009. (r) Behrens, U.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.*, 1984, 1605. (s) Barr, R. D.; Green, M.; Howard, J. A. K.; Marder, T. B.; Moore, I.; Stone, F. G. A. *J. Chem. Soc., Chem. Commun.* 1983, 746. (t) Weinstock, I.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *J. Am. Chem. Soc.* 1986, 108, 8298. (u) Mackenzie, P. B.; Ott, K. C.; Grubbs, R. H. *Pure Appl. Chem.* 1984, 56, 59. (v) Park, J. W.; Mackenzie, P. B.; Schaefer, W. P.; Grubbs, R. H. *J. Am. Chem. Soc.* 1986, 108, 6402. (w) Dawkins, G. M.; Green, M.; Mead, K. A.; Salaun, J. Y.; Stone, F. G. A.; Woodward, P. *J. Chem. Soc., Dalton Trans.* 1983, 527. (x) Sartain, W. J.; Selegue, J. P. *J. Am. Chem. Soc.* 1985, 107, 5818.

(2) Kopf, H.; Rathlein, K. H. *Angew. Chem., Int. Ed. Engl.* 1969, 8, 980.

(3) Braterman, P. S.; Wilson, V. A.; Joshi, K. K. *J. Chem. Soc. A* 1971, 191.

(4) Ruffing, C. J.; Rauchfuss, T. B. *Organometallics* 1985, 4, 524. (5) Cameron, T. S.; Prout, K. C.; Rees, G. V.; Green, M. L. H.; Joshi, K. K.; Davies, G. R.; Kilbourn, B. T. *J. Chem. Soc., Chem. Commun.* 1971, 14.

(6) Braterman, P. S.; Wilson, V. A.; Joshi, K. K. *J. Organomet. Chem.* 1971, 31, 123.

(7) Davies, G. R.; Kilbourn, B. T. *J. Chem. Soc. A* 1971, 87.

(8) Kotz, J. C.; Vining, W.; Coco, W.; Rosen, R.; Dias, A. R.; Garcia, M. H. *Organometallics* 1983, 2, 68.

(9) Douglas, W. E.; Green, M. L. H. *J. Chem. Soc., Dalton Trans.* 1972, 1796.

(10) Werner, H.; Ulrich, B.; Schubert, U.; Hofmann, P.; Zimmer-gasser, B. *J. Organomet. Chem.* 1985, 297, 27.

(11) Braterman, P. S.; Wilson, V. A. *J. Organomet. Chem.* 1971, 31, 131.

(12) White, G. S.; Stephan, D. W. *Inorg. Chem.* 1985, 24, 1499.

(13) Wark, T. A.; Stephan, D. W. *Inorg. Chem.* 1987, 26, 363.

(14) White, G. S.; Stephan, D. W. *Organometallics* 1987, 6, 2169.

(15) Douglas, W. E.; Green, M. L. H.; Prout, K. C.; Rees, G. V. *J. Chem. Soc., Chem. Commun.* 1971, 896.

(16) White, G. S.; Stephan, D. W. *Organometallics* 1988, 7, 903.

(17) Prout, K.; Critchley, S. R.; Rees, G. V. *Acta Crystallogr., Sect. B* 1974, 30, 2305.

(18) Joshi, K. K.; Wardle, R.; Wilson, V. A. *Inorg. Nucl. Chem. Lett.* 1970, 6, 49.

(19) Daran, J. C.; Meunier, B.; Prout, K. *Acta Crystallogr., Sect. B* 1979, 35, 1709.

(20) Burger, V. H.; Kluess, C. *J. Organomet. Chem.* 1973, 56, 269.

(21) Osborne, A. G.; Whiteley, R. H. *J. Organomet. Chem.* 1979, 181, 425.

(22) Pasynskii, A. A.; Skripkin, Y. V.; Kalinnikov, V. T.; Porai-Koshits, M. A.; Antsyshkina, A. S.; Sadikov, G. G.; Ostrikova, V. N. *J. Organomet. Chem.* 1979, 165, 49.

(23) Etienne, M.; Choukroun, R.; Gervais, D. *J. Chem. Soc., Dalton Trans.* 1984, 915.

(24) Burger, H.; Kluess, C. *Z. Anorg. Allg. Chem.* 1976, 423, 112.

(25) Razuvaev, G. A.; Domrachev, G. A.; Sharutin, V. V.; Suvorova, O. N. *J. Organomet. Chem.* 1977, 141, 313.

(26) Shore, N. E. *J. Am. Chem. Soc.* 1979, 101, 7410.

(27) Tueting, D. R.; Iyer, S. R.; Shore, N. E. *J. Organomet. Chem.* 1987, 320, 349.

(28) Leblanc, J. C.; Moise, C.; Maisonnat, A.; Poilblanc, R.; Charrier, C.; Mathy, F. *J. Organomet. Chem.* 1982, 231, C43.

(29) Rausch, M. D.; Edwards, B. H.; Rogers, R. D.; Atwood, J. L. *J. Am. Chem. Soc.* 1983, 105, 3882.

(30) Casey, C. P.; Nief, F. *Organometallics* 1985, 4, 1218.

(31) Tikkanen, W.; Fujita, Y.; Petersen, J. L. *Organometallics* 1986, 5, 888.

(32) Demerseman, B.; Dixneuf, P. H.; Douglade, J.; Mercier, R. *Inorg. Chem.* 1982, 21, 3942.

(33) Shore, N. E.; Young, S. J.; Olmstead, M. M.; Hofmann, P. *Organometallics* 1983, 2, 1769.

(34) Choukroun, R.; Gervais, D. *J. Organomet. Chem.* 1984, 266, C37.

(35) Senocq, F.; Basso-Bert, M.; Choukroun, R.; Gervais, D. *J. Organomet. Chem.* 1985, 297, 155.

(36) Etienne, M.; Choukroun, R.; Basso-Bert, M.; Dahan, F.; Gervais, D. *Nouv. J. Chem.* 1984, 8, 531.

essary geometry for the activation of a carbonyl moiety bound to the late metal center by a Lewis acidic, early metal. Phosphide-bridged early/late heterobimetallic complexes offer an appropriate geometry to achieve such cooperative, bimetallic activation of carbon monoxide. Furthermore, phosphide bridges are attractive as they resemble PR_3 ligands found in many mononuclear catalyst systems and are generally chemically robust. We⁴⁹⁻⁵² and others⁵³⁻⁶¹ have previously described phosphido-bridged complexes in which two phosphido groups link early and late metal centers. Here, we describe the first early/late heterobimetallic complexes in which single phosphido groups link the constituent metals affording early metal activation of a late metal-bound carbonyl moiety.

Experimental Section

General Data. All preparations were done under an atmosphere of dry, O_2 -free N_2 . Solvents were reagent grade and were distilled from the appropriate drying agents under N_2 and degassed by the freeze-thaw method at least three times prior to use. 1H and $^{13}C\{^1H\}$ NMR spectra were recorded on a Bruker AC-300 spectrometer operating at 300 and 75 MHz, respectively. Trace amounts of protonated solvents were used as reference, and chemical shifts are reported relative to $SiMe_4$. $^{31}P\{^1H\}$ NMR spectra were recorded by using a Bruker AC-200 NMR spectrometer operating at 81 MHz and are reported relative to 85% H_3PO_4 as an external reference. Infrared absorption data were recorded on a Nicolet 5DX Fourier transform IR spectrometer. Cyclic voltammetric experiments were performed by using a BAS CV-27 potentiostat, a platinum disk electrode, and a Ag/AgCl electrode as the reference. $Na[BPh_4]$ was used as the supporting electrolyte. Combustion analyses were performed by Galbraith Laboratories Inc., Knoxville, TN. PMe_3 , PCy_3 , MeLi, BuLi, $LiEt_3H$, Cp_2ZrCl_2 , $[CpMo(CO)_3]_2$, and $[CpW(CO)_3]_2$ were purchased from the Aldrich Chemical Co. $Cp_2Zr(PPh_2)_2$, $CpMo(CO)_3H$, and $Cp_2Zr(PCy_2)_2$ were prepared by literature methods.^{51,62}

- (37) Karsch, H. H.; Muller, G.; Kruger, C. *J. Organomet. Chem.* **1984**, *273*, 195.
 (38) Choukroun, R.; Iraqi, A.; Gervais, D. *J. Organomet. Chem.* **1986**, *311*, C60.
 (39) Choukroun, R.; Iraqi, A.; Gervais, D.; Daran, J. C.; Jeannin, Y. *Organometallics* **1987**, *6*, 1197.
 (40) Senocq, F.; Randrianlimanana, C.; Thorez, A.; Kalck, P.; Choukroun, R.; Gervais, D. *J. Chem. Soc., Chem. Commun.* **1984**, 1376.
 (41) Choukroun, R.; Gervais, D.; Jaud, J.; Kalck, P.; Senocq, F. *Organometallics* **1986**, *5*, 67.
 (42) Senocq, F.; Randrianlimanana, C.; Thorez, A.; Kalck, P. *J. Mol. Catal.* **1986**, *35*, 213.
 (43) Ferguson, G. S.; Wolczanski, P. T. *Organometallics* **1985**, *4*, 1601.
 (44) Ferguson, G. S.; Wolczanski, P. T. *J. Am. Chem. Soc.* **1986**, *108*, 8293.
 (45) Thewalt, U.; Schomberg, D. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1975**, *30*, 636.
 (46) Shore, N. E.; Hope, H. *J. Am. Chem. Soc.* **1980**, *102*, 4251.
 (47) Choukroun, R.; Gervais, D. *J. Chem. Soc., Chem. Commun.* **1982**, 1300.
 (48) Doroda, R. J.; Wilkinson, G.; Hursthouse, M. H.; Malik, K. M. A.; Thornton-Pett, M. *J. Chem. Soc., Dalton Trans.* **1980**, 2315.
 (49) Gelmini, L.; Matassa, L. C.; Stephan, D. W. *Inorg. Chem.* **1985**, *24*, 2585.
 (50) Gelmini, L.; Stephan, D. W. *Inorg. Chim. Acta* **1986**, *111*, L17.
 (51) Gelmini, L.; Stephan, D. W. *Inorg. Chem.* **1986**, *25*, 1222.
 (52) Gelmini, L.; Stephan, D. W. *Organometallics* **1988**, *7*, 849.
 (53) Johannsen, G.; Stelzer, O. *Chem. Ber.* **1977**, *110*, 3448.
 (54) Stelzer, O.; Unger, E.; Wray, V. *Chem. Ber.* **1977**, *110*, 3430.
 (55) Targos, T. S.; Rosen, R. P.; Whittle, R. R.; Geoffroy, G. L. *Inorg. Chem.* **1985**, *24*, 1375.
 (56) Baker, R. T.; Tulip, T. H.; Wreford, S. S. *Inorg. Chem.* **1985**, *24*, 1379.
 (57) Drew, M. G. B.; Wade, S. R.; Wailbridge, M. G. H.; Willey, G. R. *J. Chem. Soc., Dalton Trans.* **1986**, 714.
 (58) Baker, R. T.; Tulip, T. H. *Organometallics* **1986**, *5*, 839.
 (59) Ritchey, J. M.; Zozulin, A. J.; Wroblewski, D. A.; Ryan, R. R.; Wasserman, H. J.; Moody, D. C.; Paine, R. T. *J. Am. Chem. Soc.* **1985**, *107*, 501.
 (60) Ortiz, J. N. *J. Am. Chem. Soc.* **1986**, *108*, 550.
 (61) Hay, P. J.; Ryan, R. R.; Salazar, K. V.; Wroblewski, D. A.; Sattelberger, A. P. *J. Am. Chem. Soc.* **1986**, *108*, 313.
 (62) King, R. B.; Stone, F. G. A. *Inorg. Synth.* **1963**, *7*, 99.

Table I. Crystallographic Parameters

formula	$C_{29}H_{25}MoO_2PZr$
cryst color, form	orange-yellow blocks
a , Å	11.537 (3)
b , Å	19.567 (6)
c , Å	10.892 (4)
β , deg	95.52 (2)
cryst syst	monoclinic
space group	$P2_1/n$
V , Å ³	2447 (1)
D (calcd), g cm ⁻³	1.69
Z	4
cryst dimens, mm	$0.31 \times 0.35 \times 0.25$
abs coeff, μ , cm ⁻¹	9.14
radiatn (λ , Å)	Mo $K\alpha$ (0.71069)
temp, °C	24
scan speed, deg/min	2.0–5.0 ($\theta/2\theta$ scan)
scan range, deg	1.0 below $K\alpha_1$ 1.0 above $K\alpha_2$
bkgd/scan time ratio	0.5
data collected	3542
no. of unique data ($F_o^2 > 3\sigma(F_o^2)$)	2503
no. of variables	307
R , %	2.44
R_w , %	2.56
largest Δ/σ in the final least-squares cycle	0.011
max residual electron density (e/Å ³)	0.36
atom associated	Zr

Synthesis of $Cp_2Zr(\mu-PPh_2)(\eta^1-\eta^2-OC)Mo(CO)Cp$ (1). (i) From $[CpMo(CO)_3]_2$. To a solution of $[CpMo(CO)_3]_2$ (0.450 g, 0.92 mmol) in 35 mL of THF was added a solution of $Cp_2Zr(PPh_2)_2$ (1.080 g, 1.84 mmol) in 10 mL of THF. The mixture was stirred for 5 h. The solvent volume was reduced to about 10 mL under vacuum. Slow addition of n -hexane (50 mL) caused the precipitation of a yellow solid. The solid was isolated by filtration and the solid washed with an additional 50 mL of n -hexane (yield 0.851 g, 71%). Crystals of 1 were obtained by slow diffusion of pentane into a THF solution of 1.

(ii) From $CpMo(CO)_3H$. To a solution of $CpMo(CO)_3H$ (0.100 g, 0.46 mmol) in 15 mL of THF was added $Cp_2Zr(PPh_2)_2$ (0.240 g, 0.40 mmol). The reaction was stirred for 8 h. The reaction was monitored by $^{31}P\{^1H\}$ NMR spectroscopy (yield 80% determined by NMR). Anal. Calcd for $C_{29}H_{25}MoO_2PZr$: C, 55.85; H, 4.04. Found: C, 55.40; H, 4.26. 1H NMR (C_6D_6 , δ , ppm): 5.38 (s, Cp), 5.29 (s, Cp), 5.05 (s, Cp), 6.90–7.40 (m, Ph). $^{31}P\{^1H\}$ NMR (THF, δ , ppm): 161.5 (s). $^{13}C\{^1H\}$ NMR (THF, δ , ppm): 109.8 (Cp), 107.0 (Cp), 89.3 (Cp), 125.9 (Ph), 126.9 (Ph), 131.4 (Ph), 136.8 (Ph), 234.9 (CO), 224.0 (CO). IR (KBr, cm^{-1}): 1842, 1575.

Synthesis of $Cp_2Zr(\mu-PCy_2)(\mu-OC)Mo(CO)Cp$ (2). This compound was prepared via reaction of $[CpMo(CO)_3]_2$ (0.310 g, 0.63 mmol) and $Cp_2Zr(PCy_2)_2$ (0.779 g, 1.26 mmol) by using a procedure similar to that described for 1 (yield 0.630 g, 75%). Anal. Calcd for $C_{29}H_{37}MoO_2PZr$: C, 54.79; H, 5.87. Found: C, 54.21; H, 5.90. 1H NMR (C_6D_6 , δ , ppm): 5.72 (s, Cp), 5.63 (s, Cp), 5.08 (s, Cp), 0.90–2.50 (m, Cy). $^{31}P\{^1H\}$ NMR (THF, δ , ppm): 188.6 (s). IR (KBr, cm^{-1}): 1827, 1574.

Synthesis of $Cp_2Zr(\mu-PPh_2)(\mu-OC)W(CO)Cp$ (3). To a solution of $Cp_2Zr(PPh_2)_2$ (0.150 g, 0.253 mmol) in 35 mL of THF was added a solution of $[CpW(CO)_3]_2$ (0.084 g, 0.126 mmol) in 10 mL of THF. The mixture was stirred at 25 °C for 12 h and then at 70 °C for 3 h. The solvent volume was reduced to about 10 mL under vacuum. Slow addition of n -hexane (50 mL) caused the precipitation of a yellow solid. The solid was isolated by filtration and the solid washed with an additional 50 mL of n -hexane (yield 0.150 g, 83%). 1H NMR (C_6D_6 , δ , ppm): 5.40 (s, Cp), 5.31 (s, Cp), 4.97 (s, Cp), 7.4–6.9 (m, Ph). $^{31}P\{^1H\}$ NMR (THF, δ , ppm): 130.4 ($[J(W-P)] = 171$ Hz). $^{13}C\{^1H\}$ NMR (THF, δ , ppm): 109.6 (Cp), 107.2 (Cp), 87.1 (Cp), 125.6 (Ph), 127.3 (Ph), 131.6 (Ph), 136.8 (Ph). IR (KBr, cm^{-1}): 1821, 1579.

Attempted Reactions of 1. Reactions of 1 with a variety of reagents were attempted under similar conditions. 1 (0.050–0.100 g) was combined with one or, in some cases, excess equivalents of each of the following reactants: PMe_3 , PCy_3 , MeCN, MeLi, n -BuLi, t -BuLi, PhLi, $Me_3O^+BF_4^-$, and $LiEt_3H$. THF or acetone

Table II. Positional Parameters^a

atom	x	y	y	atom	x	y	z
Mo	978 (1)	2520 (1)	-1659 (1)	Zr	2497 (1)	3922 (1)	-1522 (1)
P	708 (1)	3463 (1)	-3091 (1)	O1	3051 (2)	3139 (1)	-4 (3)
O2	-733 (3)	3152 (2)	56 (3)	C1	2230 (3)	2856 (2)	-605 (4)
C2	-81 (3)	2937 (2)	-605 (4)	C11	-676 (3)	3934 (2)	-3270 (3)
C12	-732 (3)	4622 (2)	-3574 (4)	C13	-1794 (4)	4965 (2)	-3711 (4)
C14	-2795 (4)	4622 (3)	-3544 (4)	C15	-2759 (4)	3941 (3)	-3268 (4)
C16	-1707 (3)	3601 (2)	-3133 (4)	C21	853 (3)	3270 (2)	-4736 (3)
C22	1752 (3)	2853 (2)	-5041 (4)	C23	1880 (4)	2695 (2)	-6256 (4)
C24	1116 (4)	2929 (2)	-7200 (4)	C25	219 (4)	3338 (2)	-6908 (4)
C26	77 (4)	3504 (2)	-5695 (4)	C31	815 (4)	4560 (2)	-752 (4)
C32	1498 (4)	5044 (2)	-1322 (5)	C33	2556 (4)	5106 (2)	-603 (5)
C34	2559 (4)	4645 (2)	381 (4)	C35	1476 (4)	4326 (2)	289 (4)
C41	3454 (4)	3971 (2)	-3504 (4)	C42	3826 (4)	4545 (3)	-2822 (5)
C43	4528 (4)	4320 (3)	-1763 (5)	C44	4573 (4)	3615 (3)	-1808 (5)
C45	3917 (3)	3392 (2)	-2879 (4)	C51	502 (4)	1699 (2)	-3247 (5)
C52	-224 (4)	1582 (2)	-2313 (4)	C53	490 (4)	1394 (2)	-1244 (5)
C54	1644 (4)	1392 (2)	-1525 (5)	C55	1642 (2)	1581 (2)	-2774 (5)

^a Multiplied by 10⁴.

Table III. Selected Bond Distances and Angles

Distances (Å)			
Zr-Mo	3.250 (1)	Mo-P	2.417 (1)
Mo-C2	1.936 (5)	Mo-C51	2.386 (4)
Mo-C53	2.330 (4)	Mo-C54	2.337 (4)
Zr-P	2.704 (1)	Zr-C1	2.344 (4)
Zr-C31	2.519 (4)	Zr-C32	2.500 (4)
Zr-C34	2.504 (4)	Zr-C35	2.520 (4)
Zr-C42	2.502 (4)	Zr-C43	2.506 (4)
Zr-C45	2.532 (4)	P-C11	1.837 (4)
O1-C1	1.230 (5)	O2-C2	1.168 (5)
Mo-C1	1.876 (4)	Mo-C52	2.369 (4)
Mo-C55	2.370 (4)	Zr-O1	2.298 (3)
Zr-C33	2.523 (4)	Zr-C41	2.519 (4)
Zr-C44	2.517 (4)	P-C21	1.855 (4)
Angles (deg)			
P-Mo-Zr	54.6 (1)	C21-P-Zr	123.0 (1)
C1-Mo-P	99.8 (1)	Zr-C1-Mo	100.2 (2)
C2-Mo-P	90.6 (1)	O1-C1-Zr	72.6 (2)
P-Zr-Mo	46.8 (1)	O2-O2-Mo	176.2 (4)
C1-Zr-P	81.4 (1)	C1-Mo-Zr	45.2 (1)
O1-Zr-P	112.1 (1)	C2-Mo-Zr	89.2 (1)
Zr-P-Mo	78.6 (1)	C2-Mo-C1	89.0 (2)
C11-P-Zr	120.3 (1)	C1-Zr-Mo	34.6 (1)
		O1-Zr-Mo	65.3 (1)
		O1-Zr-C1	30.7 (1)
		C11-P-Mo	120.5 (1)
		C21-P-Mo	116.7 (1)
		C21-P-C11	99.1 (2)
		O1-C1-Mo	172.7 (3)
		C1-O1-Zr	76.7 (2)

were used as solvents for these reactions. The reactions were allowed to stand for between 8 and 12 h, and some of the reactions were heated to 70 °C for 4–8 h or photolyzed for 8 h in a quartz reaction vessel. The progress of each reaction was monitored by ³¹P{¹H} NMR spectroscopy. In all cases, no reaction occurred as evidenced by the observation of signals arising from the reactants.

X-ray Data Collection and Reduction. Diffraction experiments were performed on a four-circle Syntex P2₁ diffractometer with graphite-monochromatized Mo K α radiation. The initial orientation matrix was obtained from 15 machine-centered reflections selected from a rotation photograph. These data were used to determine the crystal system. Partial rotation photographs around each axis were consistent with a monoclinic crystal system. Ultimately, 32 reflections ($20^\circ < 2\theta < 25^\circ$) were used to obtain the final lattice parameters and the orientation matrix. Machine parameters, crystal data, and data collection parameters are summarized in Table I. The observed extinctions were consistent with the space group P2₁/n. The $\pm h, +k, +l$ data were collected in one shell ($4.5^\circ < 2\theta < 45.0^\circ$), and three standard reflections were recorded every 197 reflections. Their intensities showed no statistically significant change over the duration of the data collection. The data were processed by using the SHELX-76 program package on the computing facilities at the University of Windsor. A total of 2503 reflections with $F_o^2 > 3\sigma(F_o^2)$ were used in the refinement.

Structure Solution and Refinement. Non-hydrogen atomic scattering factors were taken from the literature tabulations.^{63–65}

The Zr and Mo atom positions were determined by using direct methods. The remaining non-hydrogen atoms were located from successive difference Fourier map calculations. The refinements were carried out by using full-matrix least-squares techniques on F , minimizing the function $w(|F_o| - |F_c|)^2$ where the weight, w , is defined as $4F_o^2/2\sigma(F_o^2)$ and F_o and F_c are the observed and calculated structure factor amplitudes, respectively. In the final cycles of refinement all the non-hydrogen atoms were assigned anisotropic temperature factors. Hydrogen atom positions were calculated and allowed to ride on the carbon to which they are bonded assuming a C–H bond length of 0.95 Å. Hydrogen atom temperature factors were fixed at 1.10 times the isotropic temperature factor of the carbon atom to which they are bonded. In all cases the hydrogen atom contributions were calculated but not refined. The final values of R and R_w are given in Table I. The maximum Δ/σ on any of the parameters in the final cycles of the refinement and the location of the largest peaks in the final difference Fourier map calculation are also given in Table I. The residual electron densities were of no chemical significance. The following data are tabulated: positional parameters (Table II) and selected bond distances and angles (Table III). Thermal parameters (Table S1), hydrogen atom parameters (Table S2), and values of $10F_o$ and $10F_c$ (Table S3) have been deposited as supplementary material.

Results and Discussion

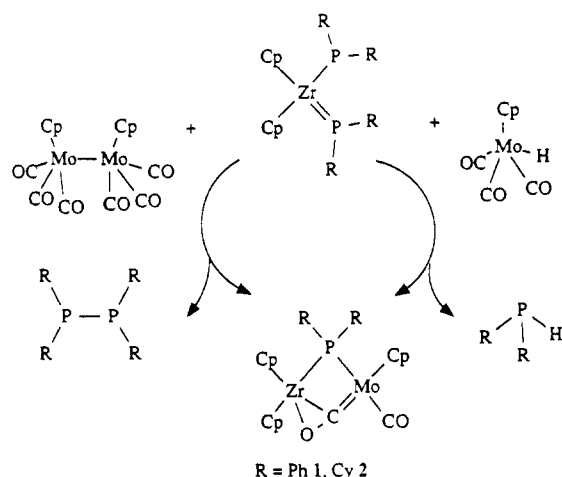
The reaction of 2 equiv of Cp₂Zr(PPh₂)₂ with [CpMo(CO)₃]₂ in THF results in a gradual color change from red-black to yellow over a 12-h period. Monitoring of the

(63) Cromer, D. T.; Mann, J. B. *Acta Crystallogr., Sect. A: Cryst. Phys., Diffraction, Theor. Gen. Crystallogr.* 1968, A24, 324.

(64) Cromer, D. T.; Mann, J. B. *Acta Crystallogr., Sect. A: Cryst. Phys., Diffraction, Theor. Gen. Crystallogr.* 1968, A24, 390.

(65) Cromer, D. T.; Waber, J. T. *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974.

Scheme I. Synthetic Route to Monophosphido-Bridged Heterobimetallics



reaction by $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy showed loss of the resonance arising from $\text{Cp}_2\text{Zr}(\text{PPh}_2)_2$ and the growth of two equally intense resonances attributable to P_2Ph_4 and to the new species 1, respectively (Scheme I). Isolation of 1 is achieved by precipitation with hexane and recrystallization. The ^{31}P chemical shift of the phosphido group in 1 is similar to that seen for $\text{Cp}_2\text{Zr}(\mu\text{-PPh}_2)_2\text{Mo}(\text{CO})_4$,⁴⁹ suggesting the presence of a phosphido bridge. ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR data for 1 show resonances attributable to phenyl groups. In addition, ^1H resonances at 5.38, 5.29, and 5.05 ppm as well as $^{13}\text{C}\{^1\text{H}\}$ resonances at 109.8, 107.0, and 89.3 ppm are attributable to three inequivalent cyclopentadienyl groups. The upfield resonances are assigned to the Mo-bound cyclopentadienyl ring, while the two downfield resonances arise from the inequivalent cyclopentadienyl rings on Zr. A similar situation has been observed for $\text{Cp}_2\text{Zr}(\mu\text{-OCMe})(\eta^1\text{-}\eta^2\text{-OC})\text{Mo}(\text{CO})\text{Cp}$.^{18j} The upfield resonances for the cyclopentadienyl groups in 1 are consistent with the presence of an electron-donating phosphido group. Resonances are also observed in the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum at 234.9 and 224.0 ppm, suggesting inequivalent carbonyl moieties. IR absorptions observed at 1842 and 1575 cm^{-1} are attributable to terminal and bridging carbonyl moieties, respectively. These spectroscopic data as well as combustion analyses were consistent with the formulation of 1 as $\text{Cp}_2\text{Zr}(\mu\text{-PPh}_2)(\eta^1\text{-}\eta^2\text{-OC})\text{Mo}(\text{CO})\text{Cp}$.

Norton et al.^{18g-j} have shown that in related heterobimetallic complexes, the nature of bridging carbonyl groups remains ambiguous despite ample spectroscopic data. In the case of 1, a similar situation arises. The IR stretching frequency of the bridging carbonyl in 1 is similar to that seen in the isocarbonyl-bridged heterobimetallic $\text{Cp}_2\text{ZrMe}(\mu\text{-OC})\text{Mo}(\text{CO})_2\text{Cp}^{18h,i}$ and to that observed for the $\eta^1\text{-}\eta^2$ carbonyl-bridged complexes (Table IV). The ^{13}C NMR resonance of the bridging carbonyl carbon in 1 is about 10 ppm downfield of the resonance assigned to the terminal carbonyl, as is the case in $\text{Cp}_2\text{ZrMe}(\mu\text{-OC})\text{Mo}(\text{CO})_2\text{Cp}$. However, this resonance is also within 5 ppm of the resonances assigned to the terminal carbonyls of $\text{Cp}_2\text{Zr}(\mu\text{-OCMe})(\eta^1\text{-}\eta^2\text{-OC})\text{Mo}(\text{CO})\text{Cp}$,^{18g,j} $\text{Cp}_2\text{ZrMe}(\mu\text{-OC})\text{Mo}(\text{CO})_2\text{Cp}$,^{18h,i} and $\text{Cp}_2\text{Zn}(\eta^2\text{-OCMe})(\mu\text{-OC})\text{Mo}(\text{CO})_2\text{Cp}$.¹⁸ⁱ It is clear that the ranges of IR and NMR spectral parameters for the various bridging carbonyl bonding modes overlap. Thus, structural data are required to unambiguously determine the nature of the bridging carbonyl moiety.

An X-ray crystallographic study of 1 revealed that crystals of 1 are made up of unit cells each containing four

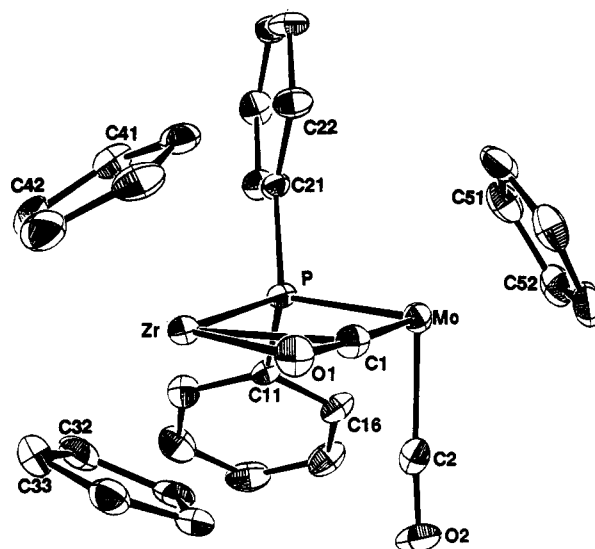


Figure 1. ORTEP drawing of molecule 1; 20% thermal ellipsoids are shown. Hydrogen atom are omitted for clarity.

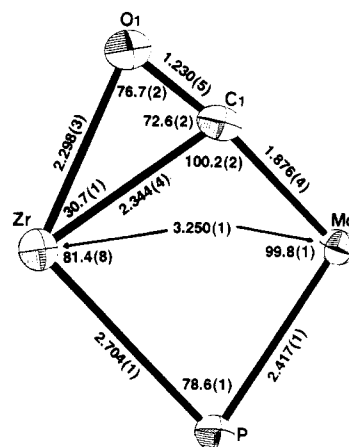
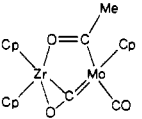
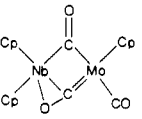
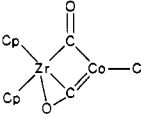
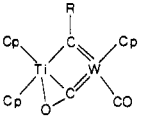
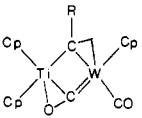
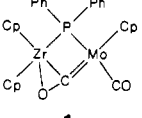


Figure 2. Structural details of the core of 1.

discrete molecules. The closest nonbonding distance between molecules in the unit cell is 2.220 Å (H16-H23). Selected interatomic distances and angles are given in Table III. An ORTEP drawing of the molecule is shown in Figure 1. The study confirmed the general formulation of 1 given above. The coordination sphere of Zr and Mo are best described as pseudotetrahedral. Two cyclopentadienyl rings are π -bonded to Zr. A single diphenylphosphido group and a carbonyl moiety complete the Zr coordination sphere and bridge to the Mo. A cyclopentadienyl group and a terminal carbonyl complete the Mo coordination shell. The M-C bond distances in the Cp_2Zr and CpMo fragments average 2.514 and 2.358 Å, respectively, and are typical. The C-O bond distance in the terminal carbonyl bound to Mo is typical, as are the bond distances and angles within the PPh_2 fragment, and thus requires no further comment.

The structural details of the central core of 1 are shown in Figure 2. The Zr-P distance of 2.704 (1) Å is significantly longer and the Mo-P distance of 2.417 (1) Å is shorter than the corresponding distances found in $\text{Cp}_2\text{Zr}(\mu\text{-PPh}_2)_2\text{Mo}(\text{CO})_4$ ⁴⁹ (Zr-P = 2.631 (1) Å; Mo-P = 2.545 (1) Å). These differences may arise from steric interactions in 1 between the phenyl rings of the phosphido group and the cyclopentadienyl rings on Zr. The closest approach between phenyl ring C21-C26 and cyclopentadienyl ring C41-C45 is substantially shorter (H22-H45 = 2.182 Å) than that seen for the rings (H35-H24 =

Table IV. Spectral and Structural Parameters for η^1 - η^2 Carbonyl-Bridged Early/Late Heterobimetallics^a

compd	$\nu(\text{CO})$	C-O	M-C	M-O	M'-C	M-M'	ref
	1534	1.241 (1)	2.343 (3)	2.271 (2)	1.875 (3)	3.297 (1)	1g,j
	1560	1.22 (1)	2.22 (1)	2.26 (1)	1.95 (1)	3.073 (1)	22
	1683	1.200 (9)	2.272 (8)	2.431 (5)	1.689 (8)	2.926 (1)	1k
	1578	1.21 (4)	2.20 (3)	2.27 (2)	1.90 (3)	2.977 (4)	1s,w
	1649	1.213 (5)	2.222 (4)	2.285 (3)	1.906 (5)	3.082 (2)	1q
	1580	1.230 (5)	2.344 (4)	2.298 (3)	1.876 (4)	3.250 (1)	herein

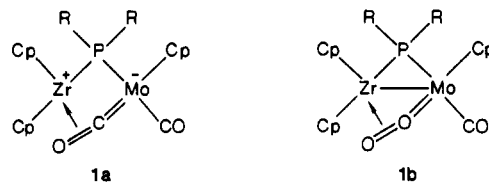
^aStretching frequencies are given in cm^{-1} ; bond distances are given in Å.

2.621 Å and H22-H55 = 2.431 Å). This interaction may result in the relative lengthening of the Zr-P bond, affording better donation of the phosphorus lone pair to Zr.

A carbonyl group also bridges the two metals. The Mo-C1 bond distance of 1.876 (4) Å is similar to that found in the η^1 - η^2 carbonyl-bridged complex $\text{Cp}_2\text{Zr}(\mu\text{-OCMe})(\eta^1\text{-}\eta^2\text{-OC})\text{Mo}(\text{CO})\text{Cp}$ and the isocarbonyl-bridged complexes $\text{Cp}_2\text{Zr}(\eta^2\text{-OCMe})(\mu\text{-OC})\text{Mo}(\text{CO})_2\text{Cp}^{11}$ (1.879 (4) Å) and $\text{Cp}_2\text{Ti}(\text{THF})(\mu\text{-OC})\text{Mo}(\text{CO})_2\text{Cp}^{1c}$ (1.874 (7) Å). It is much shorter than Mo-C distances found in molybdenum carbene complexes and approaches that found in molybdenum-carbyne species.^{1j} The Mo-C1 bond length is considerably shorter than the Mo-C2 bond. This suggests that donation of electron density from the π system of the bridging CO to Zr enhances back-bonding from Mo to C(1).^{1j} The Zr-C1 and Zr-O1 distances of 2.344 (4) and 2.298 (3) Å, respectively, are indicative of η^2 bonding to Zr. The Zr-C distance in 1 is identical with that found in $\text{Cp}_2\text{Zr}(\mu\text{-OCMe})(\eta^1\text{-}\eta^2\text{-OC})\text{Mo}(\text{CO})\text{Cp}^{1s,j}$ while the Zr-O distance is ca. 0.03 Å longer in 1 than in $\text{Cp}_2\text{Zr}(\mu\text{-OCMe})(\eta^1\text{-}\eta^2\text{-OC})\text{Mo}(\text{CO})\text{Cp}^{1s,j}$ (2.271 (2) Å). The longer Zr-O bond length is consistent with the poorer Lewis acidity of the $\text{Cp}_2\text{ZrPPh}_2$ fragment compared to that of the Cp_2ZrOCMe moiety. The Zr-O1 distance is slightly shorter than the Zr-C1 distance, consistent with the electronegativity of oxygen and the oxophilicity of Zr. C-O bond order reduction is evidenced by the long C1-O1 distance (1.230 (5) Å) and is consistent with the IR stretching frequency. It is noteworthy that the η^1 - η^2 mode of binding is more effective at lengthening the C-O bond than is isocarbonyl bonding such as that seen in $\text{Cp}_2\text{Zr}(\eta^2\text{-OCMe})(\mu\text{-OC})\text{Mo}(\text{CO})_2\text{Cp}^{11}$ (1.207 (5) Å). Of the known complexes containing similar η^1 - η^2 bound CO moieties (Table IV) only $\text{Cp}_2\text{Zr}(\mu\text{-OCMe})(\eta^1\text{-}\eta^2\text{-OC})\text{Mo}(\text{CO})\text{Cp}^{1s,j}$ was found to contain a slightly longer C-O bond. This is again consistent with relative Lewis acidity of the Zr atoms

in these compounds. Nonetheless, the C-O bond distance found in 1 is indicative of significant bond order reduction to something less than 2.

The Zr-Mo distance in 1 (3.250 (1) Å) is significantly longer than the metal-metal separations found in related heterobimetallics (Table IV). In addition it is also substantially longer than the metal-metal bonds seen in the complexes $(\text{Me}_2\text{N})_3\text{TiM}(\text{CO})_2\text{Cp}$ (M = Ru, 2.663 (1) Å; M = Fe, 2.567 (1) Å).^{1f,x} The Zr-Mo distance in 1 is similar to that seen in $\text{Cp}_2\text{Zr}(\mu\text{-PPh}_2)_2\text{Mo}(\text{CO})_4^{49}$ (3.299 (1) Å), suggesting that direct Zr-Mo bonding in 1 is weak. Invoking a metal-metal bond (1b) allows the formal satisfaction of the 18-electron rule, while its absence implies a zwitterionic formulation (1a). Further insight into the

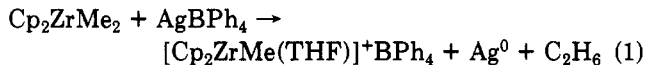


degree of metal-metal interaction is indicated by the Zr-P-Mo angle. Typically, angles of less than 80° at bridging atoms have been cited as evidence for metal-metal bonding. The Zr-P-Mo angle of 78.6 (1)° in 1 is slightly smaller than the analogous angle of 79.3 (1)° found in $\text{Cp}_2\text{Zr}(\mu\text{-PPh}_2)_2\text{Mo}(\text{CO})_4^{49}$. This again seems to imply that Zr-Mo bonding is weak. Steric interactions (vide supra) may inhibit a closer approach of the two metal atoms. Thus, we favor the zwitterionic formulation of 1.

In a manner similar to that used to prepare 1, $\text{Cp}_2\text{Zr}(\text{PCy}_2)_2$ and $[\text{CpMo}(\text{CO})_3]_2$ react to yield $\text{Cp}_2\text{Zr}(\mu\text{-PCy}_2)(\eta^1\text{-}\eta^2\text{-OC})\text{Mo}(\text{CO})\text{Cp}$ (2) and P_2Cy_4 (Scheme I). Similarly, reaction of $\text{Cp}_2\text{Zr}(\text{PPh}_2)_2$ with $[\text{CpW}(\text{CO})_3]_2$ yields the tungsten analogue of 1, i.e., $\text{Cp}_2\text{Zr}(\mu\text{-}$

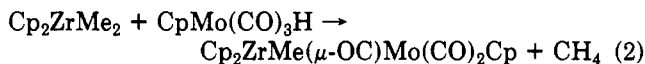
$\text{PPh}_2)(\eta^1\text{-}\eta^2\text{-OC})\text{W}(\text{CO})\text{Cp}$ (**3**) and the byproduct P_2Ph_4 . The IR spectra of **2** and **3** show bridging CO stretching frequencies at 1574 and 1579 cm^{-1} , suggesting the presence of $\eta^1\text{-}\eta^2$ carbonyl moieties.

Reactions in which alkyl ligands bound to Zr are oxidized, affording mononuclear solvated Zr cations, have been studied by Jordan et al.⁶⁶ (eq 1). The present reaction



actions are similar in that oxidation of a phosphido ligand, bound to Zr, by the M–M bonded species affords what can be considered a Zr cation whose coordination shell is completed by interaction with the late metal carbonyl fragment. The mechanism of this redox coupling reaction in the formation of these monophosphido-bridged heterobimetallics is not known. However, a heterotrimetallic species may be an intermediate in the electron-transfer process resulting in the reduction of the M–M bond and oxidation of the phosphide ligand. A mechanistic study of these reactions is currently underway.

Compound **1** was also prepared via reaction of $\text{CpMo}(\text{CO})_3\text{H}$ and $\text{Cp}_2\text{Zr}(\text{PPh}_2)_2$ with the concomitant formation of PPh_2H . The acidity of the Mo hydride results in the facile protonation of the Zr-bound phosphide and the subsequent cleavage of the Zr–P bond (Scheme I). The complex $\text{Cp}_2\text{ZrMe}(\mu\text{-OC})\text{Mo}(\text{CO})_2\text{Cp}$ is formed in a similar reaction between Cp_2ZrMe_2 and $\text{CpMo}(\text{CO})_3\text{H}$, in which methane is eliminated¹¹ (eq 2). In reactions of $\text{Cp}_2\text{Zr-}$



$(\text{PPh}_2)_2$ with less acidic late metal hydrides, diposphido-bridged heterobimetallics are formed. For example, we have previously described the formation of $\text{Cp}_2\text{M}'(\mu\text{-PR}_2)_2\text{M}(\text{CO})\text{H}(\text{PPh}_3)$ ($\text{M}' = \text{Zr, Hf}$; $\text{M} = \text{Rh, Ir}$; $\text{R} = \text{Ph, Cy}$) via reactions of $\text{Cp}_2\text{M}(\text{PR}_2)_2$ with $(\text{Ph}_3\text{P})_3\text{M}(\text{CO})\text{H}$.⁵² Similarly, reaction of $\text{Cp}_2\text{Zr}(\text{PPh}_2)_2$ with $\text{HRe}(\text{CO})_5$ or $\text{CpRu}(\text{CO})_2\text{H}$ affords the diposphido-bridged hydrido complexes $\text{Cp}_2\text{Zr}(\mu\text{-PPh}_2)_2\text{ReH}(\text{CO})_3$ and $\text{Cp}_2\text{Zr}(\mu\text{-PPh}_2)_2\text{RuHCp}$, respectively.⁶⁷

The lability of the CO moieties in **1** was investigated. Variable-temperature NMR experiments showed no evidence of any exchange processes. Attempts to effect substitution reactions in which ligands replace the carbonyl bonded to Zr failed. PMe_3 , PCy_3 , or MeCN did not react even under reflux or UV photolysis. In contrast, termi-

nal/bridging carbonyl exchange has been shown to occur in the isocarbonyl-bridged complex $\text{Cp}_2\text{ZrMe}(\mu\text{-OC})\text{Mo}(\text{CO})_2\text{Cp}^{11}$ and the $\eta^1\text{-}\eta^2$ carbonyl-bridged complex $\text{Cp}_2\text{Zr}(\mu\text{-CO})(\eta^1\text{-}\eta^2\text{-OC})\text{RhCp}$,^{1k,l} each with activation energies of less than 8 kcal/mol. In addition, donor ligands replaced the carbonyl from the Zr coordination sphere in $\text{Cp}_2\text{ZrMe}(\mu\text{-OC})\text{Mo}(\text{CO})_2\text{Cp}$ yielding a Zr cation and a Mo anion. The presence of the phosphido bridge in **1** appears to enhance the stability of the bound carbonyl moiety by providing a chelate effect as well as steric inhibition to substitution reactions.

Attempts to effect reactions on the $\eta^1\text{-}\eta^2$ carbonyl moiety also met with failure. In the presence of excess MeLi , $n\text{-BuLi}$, $t\text{-BuLi}$, PhLi , LiEt_3H , or $\text{Me}_3\text{O}^+\text{BF}_4^-$ and under prolonged or forcing (reflux) conditions, **1** does not undergo reaction. In addition, cyclic voltammetry of **1** showed no redox activity in the range +1.0 to –1.5 V vs Ag/AgCl . Similar lack of reactivity observed for the related complexes $\text{Cp}_2\text{Zr}(\eta^2\text{-OCMe})(\eta^1\text{-}\eta^2\text{-OC})\text{Mo}(\text{CO})\text{Cp}$,^{1,8,j} $\text{Cp}_2\text{Nb}(\mu\text{-CO})(\eta^1\text{-}\eta^2\text{-OC})\text{Mo}(\text{CO})\text{Cp}$,²² and $\text{Cp}_2\text{Ti}(\mu\text{-CR})(\eta^1\text{-}\eta^2\text{-OC})\text{W}(\text{CO})\text{Cp}^{1,s,w}$ was attributed to the steric demands of the cyclopentadienyl rings on the two constituent metal atoms. In the case of **1**, the steric demands are enhanced by the presence of the diphenylphosphido moiety.

In summary, the reaction of zirconocene diphosphides with the M–M bonded species $[\text{CpM}(\text{CO})_3]_2$ or the related hydrides provides synthetic routes to monophosphido-bridged early/late heterobimetallics, a class of compounds which is heretofore unknown. These compounds are among the few in which cooperative activation of a CO moiety by coordination to both a late and an early metal is center observed. Steric demands of ancillary ligands in such heterobimetallics may control the reactivity of the activated carbonyl moiety. The generality of this redox coupling reaction in the formation of new heterobimetallics and the chemistry of related complexes in which ancillary ligand bulk is reduced are the subjects of current research efforts.

Acknowledgment. Financial support from NSERC of Canada is gratefully acknowledged.

Registry No. **1**, 120416-89-9; **2**, 120416-90-2; **3**, 120416-91-3; $[\text{CpMo}(\text{CO})_3]_2$, 12091-64-4; $\text{Cp}_2\text{Zr}(\text{PPh}_2)_2$, 86013-25-4; $\text{CpMo}(\text{CO})_3\text{H}$, 12176-06-6; $\text{Cp}_2\text{Zr}(\text{PCy}_2)_2$, 86013-24-3; $[\text{CpW}(\text{CO})_3]_2$, 12091-65-5; PMe_3 , 594-09-2; PCy_3 , 2622-14-2; MeCN , 75-05-8; MeLi , 917-54-4; $n\text{-BuLi}$, 109-72-8; $t\text{-BuLi}$, 594-19-4; PhLi , 591-51-5; $\text{Me}_3\text{O}^+\text{BF}_4^-$, 420-37-1; LiEt_3H , 22560-16-3.

Supplementary Material Available: Tables of thermal and hydrogen atom parameters and bond distances and angles (5 pages); a listing of values of $10F_o$ and $10F_c$ (9 pages). Ordering information is given on any current masthead page.

(66) Jordan, R. F.; LaPointe, R. E.; Bajgur, C. S.; Echols, S. F.; Willett, R. *J. Am. Chem. Soc.* **1987**, *109*, 4111.

(67) Stephan, D. W.; Zheng, P. Y.; Nadasdi, T. T., unpublished results.