Synthesis, Structure, Fluxional Behavior, and Addition Reaction of the Metal–Metal-Bonded Heterobimetallic Phosphido-Bridged Complex $CpW(CO)_2(\mu\text{-}PPh_2)Mo(CO)_5$

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The heterobimetallic phosphido-bridged complex $CpW(CO)_2(\mu\text{-}PPh_2)Mo(CO)_5$ **(1)** was prepared by the reaction of $CpW(CO)_3PPh_2$ with $Mo(CO)_4(C_7H_8)$. Treatment of 1 with CO produced $CpW(CO)_3(\mu\text{-}PPh_2)Mo(CO)_5$ **(2)**. The structures of 1 and 2 were determined by single-crystal X-ray diffraction. Crystal data for 1: $C_{24}H_{15}MoO_7PW$, space group $P2_1/n$, $a = 14.464(7)$ Å, $b = 11.6743(12)$ Å, $c = 14.7639(14)$ Å, $\beta = 97.916(12)°$, $V = 2469.3(6)$ Å^3, $Z = 4$. The structure was refined to $R = 0.054$ and $R_w = 0.055$. Crystal data for **2**: $C_{25}H_{15}MoO_8PW$, space group $P2_1/n$, $a = 9.6322(16)$ Å, $b = 12.4673(21)$ Å, $c = 20.813(3)$ Å, $\beta = 94.476(12)°$, $V = 2472.7(7)$ Å^3, $Z = 4$. The structure was refined to $R = 0.035$ and $R_w = 0.044$. The W–Mo distance was 3.2056(16) Å in 1, indicative of a W–Mo bond. The long distance between W and Mo (4.5192(14) Å) in 2 indicates that no metal–metal bond exists in the complex. Fluxional behavior involving the exchange of four Mo CO ligands cis to the phosphido bridge in 1 was studied by variable-temperature ^{13}C NMR spectroscopy. Addition reactions between 1 and Lewis bases L (L = PPh_2H, PMe_3, $P(OMe)_3$) produced $CpW(CO)_3(\mu\text{-}PPh_2)Mo(CO)_4(L)$ **(3)** with L regiospecifically and stereospecifically coordinating to the Mo cis to the phosphido bridge. The structure of $CpW(CO)_3(\mu\text{-}PPh_2)Mo(CO)_4(PMe_3)$ **(3a)** was determined by single-crystal X-ray diffraction. Crystal data for **3a**: $C_{27}H_{24}MoO_7P_2W$, space group $P2_1/n$, $a = 11.756(4)$ Å, $b = 16.423(6)$ Å, $c = 14.968(3)$ Å, $\beta = 98.397(20)°$, $V = 2858.8(14)$ Å^3, $Z = 4$. The structure was refined to $R = 0.026$ and $R_w = 0.031$. Reaction of 1 with PPh_3 produced $CpW(CO)_2(\mu\text{-}PPh_2)Mo(CO)_4(PPh_3)$ with a metal–metal bond and with PPh_3 occupying the position trans to the phosphido bridge. Complexes with similar structures were synthesized by removal of one CO from 3 to regenerate the metal–metal bond to produce $CpW(CO)_2(\mu\text{-}PPh_2)Mo(CO)_4L$ (**4**; L = PPh_2H, PMe_3, $P(OMe)_3$), in which L regiospecifically and stereospecifically coordinates to the Mo and is trans to the phosphido bridge.

Introduction

One special feature of binuclear metal–metal-bonded phosphido-bridged complexes is the influence of the metal–metal bond on the reactions.[1] The metal–metal bond functions as a switch to control the reaction according to the properties of the ligand on the complex.[1a,b] This behavior provides not only an empty site for further ligand coordination to the binuclear complex when the metal–metal bond opens[1b] but also a driving force for further reaction (e.g. migration of the ligand) when the metal–metal bond re-forms.[1a] This property can also be considered as a cooperative effect of the two adjacent metals in the binuclear complex.

For heterobimetallic phosphido-bridged complexes, the metal–metal bond can be considered as a donor–acceptor bond.[1d,2] When the metal–metal bond opens, an empty site is contributed to the metal where the dative metal–metal bond was originally coordinated. Thus, the dative metal–metal bond acts as a directional switch. Such directional opening of the dative metal–metal bond was demonstrated by the addition of a Lewis base to heterobimetallic phosphido-bridged[1b,2b,3] and arsino-bridged complexes.[4]

The reactivity site of binuclear complexes can be controlled by careful selection of the metals and their ligands to construct binuclear complexes with the desired direction of the metal–metal dative bond. We have thus set out to prepare and study a series of such compounds.[5]

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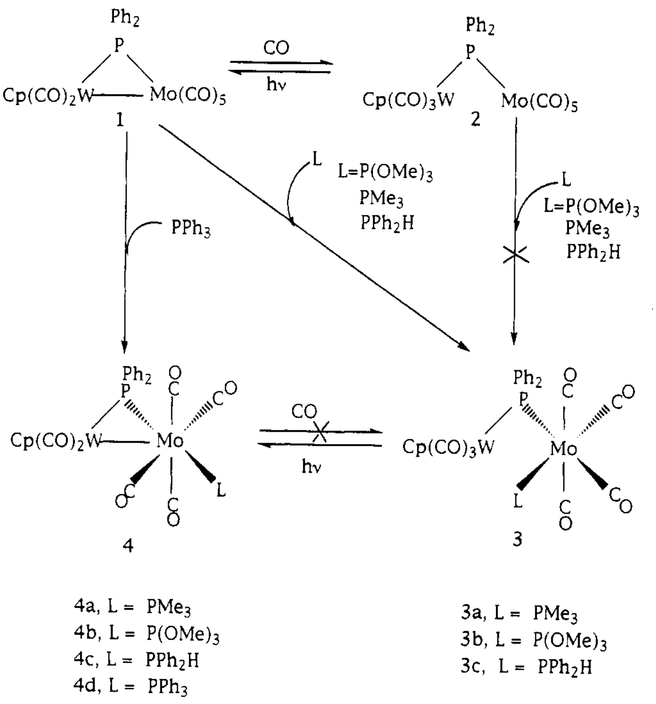
Scheme 1



The bimetallic complex $CpW(CO)_2(\mu\text{-}PPh_2)Mo(CO)_5$ (**1**) with a dative Mo–W bond was synthesized, and the addition reaction of the complex toward different Lewis bases was studied. We found that the addition of the Lewis base opened the metal–metal bond. Nevertheless, the addition did not occur at the W atom, as expected, but proceeded stereospecifically and regiospecifically at the Mo atom with the base occupying the position cis to the phosphido bridge. Reported herein are the synthesis, structure, fluxional behavior, and reactivity studies of $CpW(CO)_2(\mu\text{-}PPh_2)Mo(CO)_5$. Scheme 1 shows reactions that comprise the main focus of our work. The products of the addition reaction have been characterized spectroscopically, and the structure of $CpW(CO)_3(\mu\text{-}PPh_2)\text{-}Mo(CO)_4(PMe_3)$ (**3a**) was also determined by a complete single-crystal X-ray diffraction study.

Experimental Section

Unless otherwise stated, all reactions and manipulations of air-sensitive compounds were carried out at ambient temperatures under an atmosphere of purified N_2 with standard procedures. A 450-W Hanovia medium-pressure quartz mercury-vapor lamp (Ace Glass) and a Pyrex Schlenk tube as a reaction vessel were used in the photoreactions. Infrared (IR) spectra were recorded on a Perkin-Elmer 882 infrared spectrophotometer. ^1H, ^{13}C, and ^{31}P NMR spectra were measured by using Bruker AMX-500, MSL-200, AC-200, and AC-300 spectrometers. ^{31}P NMR shifts are referenced to 85% H_3PO_4. Except as noted, NMR spectra were collected at room temperature. Electron impact (EI) and fast-atom bombardment (FAB) mass spectra were recorded on a VG 70-250S or a JEOL JMS-HX 110 mass spectrometer. Microanalyses were performed by the Microanalytic Laboratory at National Cheng Kung University, Tainan, Taiwan.

Materials. THF was distilled from potassium and benzophenone under an atmosphere of N_2 immediately before use. Other solvents were purified according to established procedures.[6] The metal carbonyls $M(CO)_6$ (M = Mo, W), PPh_2Cl, PMe_3, PPh_2H, and PPh_3 were obtained from Strem; $P(OMe)_3$ was purchased from Merck, and ^{13}CO (99 atom % ^{13}C) was obtained from Isotec. Other reagents and solvents were obtained from various commercial sources and used as received. $Mo(CO)_4(C_7H_8)$,[7] $Na[CpW(CO)_3]\cdot 2DME$,[8] and $WCp(CO)_3PPh_2$[9] were prepared by literature procedures.

Synthesis of $CpW(CO)_2(\mu\text{-}PPh_2)Mo(CO)_5$ (1). A yellow suspension of $Na[CpW(CO)_3]\cdot 2DME$ (0.36 g, 0.68 mmol) in 50 mL of toluene was cooled to 0 °C. A solution of 0.12 mL (0.65 mmol) of PPh_2Cl in 25 mL of toluene was then added slowly to the above solution. After 1 h, the solution turned orange-red. $Mo(CO)_4(C_7H_8)$ (0.18 g, 0.60 mmol) was then added to the above solution. The solution turned red immediately. After the solution was stirred overnight, solvent was removed and the residue was chromatographed on silica gel. Elution with CH_2Cl_2/hexane (1:4) afforded two fractions. The solvent was removed. A trace amount of yellow solid was obtained from the first band and was not identified. The purple solid **1** was obtained from the second band. Yield: 0.14 g (32%). Anal. Calcd for $C_{24}H_{15}O_7PMoW$: C, 39.67; H, 2.07. Found: C, 39.83; H, 1.67. IR spectrum (THF, ν(CO)): 2071 m, 1957 s, 1930 m, 1861 w cm^{-1}. IR spectrum (hexane, ν(CO)): 2073 m, 2004 vw, 1984 m, 1957 s, 1937 m, 1876 w cm^{-1}. ^1H NMR spectrum ($CDCl_3$): δ 7.77 (m, 2H), 7.42 (m, 3H), 7.20 (m, 3H), 6.98 (m, 2H), 5.17 (s, 5H). $^{31}P\{^1H\}$ NMR spectrum (THF): δ 170.46 (J_{P-W} = 342.6 Hz). $^{13}C\{^1H\}$ NMR spectrum ($CDCl_3$): δ 226.73 (d, $^2J_{P-C}$ = 7.51 Hz, CO), 221.80 (s, CO), 208.28 (d, $^2J_{P-C}$ = 12.08 Hz, CO), 206.43 (br, CO), 143.15 (d, J_{P-C} = 11.07 Hz, *ipso*-C PPh_2), 142.31 (d, J_{P-C} = 12.83 Hz, *ipso*-C′, PPh_2), 133.94 (d, $^2J_{P-C}$ = 8.45 Hz, *o*-C, PPh_2), 131.68 (d, $^2J_{P-C}$ = 11.2 Hz, *o*-C′, PPh_2), 129.81 (s, *p*-C, PPh_2), 129.03 (s, *p*-C′, PPh_2), 128.31 (m, *m*-C, *m*-C′, PPh_2), 91.75 (s, C_5H_5). MS (FAB): M^+ *m/z* 726.

Synthesis of $CpW(CO)_3(\mu\text{-}PPh_2)Mo(CO)_5$ (2). A solution of **1** (0.27 g, 0.30 mmol) in 15 mL of THF was stirred under 1 atm of CO overnight. The solution changed from purple to yellowish brown. The solvent was then removed, and the residue was chromatographed on silica gel. Elution with CH_2Cl_2/hexane (1:4) afforded two fractions. The first band, which was purple, was unreacted **1**. The second band was yellow. After the solvent was removed, **2** was obtained as a yellow solid. Yield: 0.10 g (44%). Anal. Calcd for $C_{25}H_{15}O_8PMoW$: C, 39.82; H, 1.99. Found: C, 39.56; H, 2.26. IR spectrum (THF, ν(CO)): 2067 m, 2025 m, 1948 s, 1938 sh, 1914 m cm^{-1}. ^1H NMR spectrum ($CDCl_3$): δ 7.60 (br, 4H), 7.34 (m, 6H), 5.32 (br, 5H). $^{31}P\{^1H\}$ NMR spectrum (THF): δ −41.66 (s). MS (FAB): M^+ *m/z* 754.

Thermolysis of 2. A solution of 1.80 g of **2** in 100 mL of THF was heated at reflux temperature for 6 h under N_2. The solution changed from yellow to purple. The solvent was then removed, and the residue was chromatographed on silica gel and eluted with CH_2Cl_2 to afford a purple band. After the solvent was removed, **1** was obtained as a purple solid. Yield: 1.10 g (64%).

Synthesis of $CpW(CO)_3(\mu\text{-}PPh_2)Mo(CO)_4(PMe_3)$ (3a). Complex **1** (0.40 g, 0.55 mmol) was dissolved in 25 mL of THF under N_2 at room temperature. To this solution was added 70 μL of PMe_3 (0.69 mmol). After 1 h, the solution changed from purple to reddish brown. After 90 min, the solvent was removed and the residue was chromatographed on grade III Al_2O_3 and eluted with CH_2Cl_2/hexane (1:4) to afford two fractions. The first band was unreacted **1**. The second band was yellow. After the solvent was removed, **3a** was obtained as a yellow solid. Yield: 0.25 g (57%). Anal. Calcd for $C_{27}H_{24}O_7P_2MoW$: C, 40.43; H, 2.99. Found: C, 39.97; H, 2.91. IR spectrum (THF, ν(CO)): 2026 w, 2007 s, 1951 s, 1901 s, 1888 sh, 1853 m cm^{-1}. ^1H NMR spectrum ($CDCl_3$): δ 7.60 (m, 4H), 7.28 (m, 6H), 5.49 (s, 5H), 0.86

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(d, $^2J_{P-H}$ = 6.7 Hz, 9H). $^{31}P\{^1H\}$ NMR spectrum (THF): δ −36.20 (d), −22.27 (d, $^2J_{P-P}$ = 26.0 Hz). MS(FAB): (M − CO)$^+$ *m/z* 776.

Synthesis of CpW(CO)$_3$(μ-PPh$_2$)Mo(CO)$_4$(P(OMe)$_3$) (3b). To a purple solution of 1 (0.60 g, 0.83 mmol) in 30 mL of THF was added 153 μL of P(OMe)$_3$ (1.30 mmol) under N_2 at room temperature. After 2 h, the solution changed to brown. The solvent was then removed, and the residue was chromatographed on grade III Al_2O_3 and eluted with CH_2Cl_2/hexane (1:4) to afford four fractions. The first band was unreacted **1**, the second band was yellow, and the third band was purple-red. Only trace amounts of products were obtained from the second and third bands, and the products were not identified. The fourth band was yellow. After the solvent was removed, **3b** was obtained as a greenish yellow solid. Yield: 0.44 g (65%). Anal. Calcd for $C_{27}H_{24}O_{10}P_2MoW$: C, 38.12; H, 2.82. Found: C, 37.82; H, 2.71. IR spectrum (THF, ν(CO)): 2030 s, 2013 m, 1931 s, 1900 m, 1871 cm^{-1}. ^{1}H NMR spectrum (CDCl$_3$): δ 7.66 (m, 4H), 7.30 (m, 6H), 5.37 (br, 5H), 3.36 (d, $^3J_{P-H}$ = 11.0 Hz, 9H). $^{31}P\{^1H\}$ NMR spectrum (THF): δ 157.73 (d), −38.11 (d, $^2J_{P-P}$ = 26.0 Hz, J_{P-W} = 82 Hz). MS(FAB): (M − CO)$^+$ *m/z* 822.

Synthesis of CpW(CO)$_3$(μ-PPh$_2$)Mo(CO)$_4$(PPh$_2$H) (3c). To a purple solution of 1 (0.30 g, 0.41 mmol) in 30 mL of THF was added 87 μL of PPh$_2$H (0.50 mmol) under N_2 at room temperature. After 90 min, the solution changed to reddish brown. The solvent was then removed, and the residue was chromatographed on grade III Al_2O_3 and eluted with CH_2Cl_2/hexane (1:4) to afford three fractions. The first band was unreacted 1, and the second band was yellow. Only a trace amount of product was obtained from the second band, and it was not identified. The third band was greenish yellow. After the solvent was removed, **3c** was obtained as a greenish yellow solid. Yield: 0.24 g (63%). Anal. Calcd for $C_{36}H_{26}O_7P_2MoW$: C, 47.37; H, 2.85. Found: C, 47.26; H, 2.89. IR spectrum (THF, ν(CO)): 2028 m, 2012 m, 1932 s, 1908 s, 1896 sh, 1863 m cm^{-1}. ^{1}H NMR spectrum (CDCl$_3$): δ 7.63 (br), 7.30 (br), 5.45 (br, 5H). 4.74 (dd, J_{P-H} = 326 Hz, $^3J_{P-H}$ = 6.9 Hz, 1H). $^{31}P\{^1H\}$ NMR spectrum (CDCl$_3$): δ 20.98 (s, br), −36.29 (d, $^2J_{P-P}$ = 21.4 Hz). MS(FAB): (M − CO)$^+$ *m/z* 885.

Synthesis of CpW(CO)$_2$(μ-PPh$_2$)Mo(CO)$_4$(PPh$_3$) (4d). To a purple solution of 1 (0.30 g, 0.41 mmol) in 20 mL of THF was added PPh$_3$ (0.11 g, 0.42 mmol) under N_2 at room temperature. The mixture was stirred overnight. A cloudy brownish purple mixture was obtained. The solvent was then removed, and the residue was chromatographed on grade III Al_2O_3 and eluted with CH_2Cl_2/hexane (1:4) to afford three fractions. The first band was unreacted 1, and the second band was yellow. After the solvent was removed, a gray solid was obtained. The compound was identified as Mo(CO)$_5$PPh$_3$[10] (yield 0.11 g, 54%) according to its spectroscopic data. The third band was red. After the solvent was removed, **4d** was obtained as a deep red solid. The yield was 0.12 g (30%). Anal. Calcd for $C_{41}H_{30}O_6P_2MoW$: C, 51.29; H, 3.12. Found: C, 50.97; H, 3.20. IR spectrum (THF, ν(CO)): 2029 w, 1968 vw, 1928 s, 1916 s, 1844 m cm^{-1}. ^{1}H NMR spectrum (CDCl$_3$): δ 7.41 (m, 25H), 5.06 (s, 5H). $^{31}P\{^1H\}$ NMR spectrum (THF): δ 43.27 (d), 168.26 (d, $^2J_{P-P}$ = 27.1 Hz, J_{P-W} = 325.5 Hz). $^{13}C\{^1H\}$ NMR spectrum (CDCl$_3$): δ 230.95 (d, $^2J_{P-C}$ = 15.87 Hz, CO), 223.54 (s, CO), 211.50 (vbr, CO), 91.24 (s, C_5H_5). MS (FAB): M$^+$ *m/z* 960.

Synthesis of CpW(CO)$_2$(μ-PPh$_2$)Mo(CO)$_4$(PMe$_3$) (4a). A solution of **3a** (0.10 g) in THF (35 mL) was irradiated with UV for 15 min at 10 °C. The solution changed from yellow to red. The solvent was then removed, and the residue was chromatographed on silica gel. Elution with CH_2Cl_2/hexane (1:4) afforded three fractions. After the solvent was removed, trace amounts of products were obtained from the first and the third bands, which were purple and yellow, respectively. They were not identified. The second band was red. After the solvent was removed, **4a** was obtained as a red solid. Yield: 35 mg (36%). Anal. Calcd for $C_{26}H_{24}O_6P_2MoW$: C, 40.34; H, 3.13. Found: C, 40.41; H, 2.74. IR spectrum (THF, ν(CO)): 2025 m, 1959 w, 1923 s, 1905 s, 1840 m cm^{-1}. ^{1}H NMR spectrum (CDCl$_3$): δ 7.80 (m, 2H), 7.35 (m, 3H), 7.22 (m, 3H), 7.00 (m, 2H), 5.02 (s, 5H), 1.70 (d, $^2J_{P-H}$ = 8.3 Hz). $^{31}P\{^1H\}$ NMR spectrum (THF): δ −7.21 (d), 171.79 (d, $^2J_{P-P}$ = 24.4 Hz, J_{P-W} = 322.0 Hz). MS (FAB): M$^+$ *m/z* 776.

Synthesis of CpW(CO)$_2$(μ-PPh$_2$)Mo(CO)$_4$(P(OMe)$_3$) (4b). A solution of **3b** (0.10 g) in THF (35 mL) was irradiated with UV for 15 min at 10 °C. The solution changed from yellow to red. The solvent was then removed, and the residue was chromatographed on silica gel with CH_2Cl_2/hexane (1:4) as the eluent to afford two fractions. The solvent was removed from the second major band. A red solid was obtained. Yield: 51 mg (54%). Anal. Calcd for $C_{26}H_{24}O_9P_2MoW$: C, 37.98; H, 2.95. Found: C, 38.10; H, 2.99. IR spectrum (THF, ν(CO)): 2036 m, 1969 vw, 1925 vs, 1846 m cm^{-1}. ^{1}H NMR spectrum (CDCl$_3$): δ 7.85 (m, 2H), 7.39 (m, 3H), 7.21 (m, 2H), 7.02 (m, 3H), 5.07 (d, $^3J_{P-H}$ = 11.7 Hz, 5H), 3.72 (dd, $^3J_{P-H}$ = 11.7 Hz, $^5J_{P-H}$ = 1.2 Hz). $^{31}P\{^1H\}$ NMR spectrum (THF): δ 169.70 (d), 162.36 (d, $^2J_{P-P}$ = 49.5 Hz, J_{P-W} = 329.6 Hz). MS (FAB): M$^+$ *m/z* 822.

Synthesis of CpW(CO)$_2$(μ-PPh$_2$)Mo(CO)$_4$(PPh$_2$H) (4c). A solution of **3c** (0.10 g) in THF (35 mL) was irradiated with UV for 15 min at 10 °C. The solution changed from yellow to red. The solvent was then removed, and the residue was chromatographed on silica gel with CH_2Cl_2/hexane (1:4) as eluent to afford two fractions. The solvent was removed from the second band. A red solid was obtained. Yield: 51 mg (54%). Anal. Calcd for $C_{35}H_{26}O_6P_2MoW$: C, 47.54; H, 2.94. Found: C, 47.12; H, 2.72. IR spectrum (THF, ν(CO)): 2034 m, 1930 s, 1920 sh, 1846 m cm^{-1}. $^{31}P\{^1H\}$ NMR spectrum (THF): δ 16.18 (d), 166.94 (d, $^2J_{P-P}$ = 26.2 Hz, J_{P-W} = 326.7 Hz). MS (FAB): M$^+$ *m/z* 886.

Preparation of ^{13}CO-Enriched 2. A solution of 1 (3.0 g, 4.1 mmol) in THF (100 mL) in a 250-mL Schlenk flask was stirred under 1 atm of ^{13}CO for 4 days. The solution changed from purple to yellowish brown. After chromatography on silica gel, 2.80 g (93% yield) of ^{13}CO-enriched 2 was obtained. IR spectrum (THF, ν(CO)): 2059 m, 2024 m, 1935 s, 1912 sh cm^{-1}. $^{31}P\{^1H\}$ NMR spectrum (THF): δ −141.17. MS (FAB): M$^+$ *m/z* 758. Over 11 atom % enrichment was obtained, according to the parent peak pattern of the mass spectrum of the enriched **2**.

Preparation of ^{13}CO-Enriched 1. A solution of 115 mg of ^{13}CO-enriched 2 in 10 mL of THF was irradiated with UV for 20 min between freeze–thaw cycles. The solution changed from yellow to purple. ^{13}CO-enriched 1 was separated after chromatography on silica gel. Yield: 18 mg (16%). IR spectrum (THF, ν(CO)): 2070 m, 1951 s, vbr, 1860 m cm^{-1}. $^{31}P\{^1H\}$ NMR spectrum (THF): δ 170.50 (J_{P-W} = 347.2 Hz). MS (FAB): M$^+$ *m/z* 730. About 9 atom % enrichment was obtained according to the parent peak pattern of the mass spectrum of the enriched **1**.

Reaction of 2 with PR$_3$ (R = Ph, Me, OMe) and PPh$_2$H. To a yellow solution containing 200 mg (0.27 mmol) of **2** in 20 mL of THF was added 34 μL (36 mg, 0.15 mmol) of P(OMe)$_3$. The solution was stirred in the dark at room temperature overnight. No color change was observed. Results of a ^{31}P NMR study of the reaction mixture indicated the existence of the unreacted **2** and P(OMe)$_3$ and small amounts of unidentified impurities.

Similar reaction conditions were applied to the reaction between **1** and PPh$_3$, PPh$_2$H, and PMe$_3$. No complex **3** was observed in the reaction product, according to ^{31}P NMR spectra of the reaction mixtures.

Reaction between 4 and CO. A solution of **4b** (60 mg) in THF was stirred under 1 atm of CO overnight at room temperature. A ^{31}P NMR study of the solution indicated that no reaction took place between **4b** and CO. Similar conditions were applied to complexes **4a,c,d**. No reaction was observed, as indicated by a ^{31}P NMR study of the reaction mixture.

Structure Determination of 1, 2, and 3a. Crystals of complexes **1**, **2**, and **3a** were grown by slow diffusion of hexanes into the saturated solutions of the relevant complexes (**1** in CH$_2$-

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Table 1. Crystal and Intensity Collection Data for 1, 2, and 3a

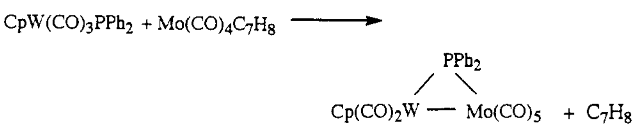
	1	2	3a
mol formula	$C_{24}H_{15}MoWO_7P$	$C_{25}H_{15}MoO_8PW$	$C_{27}H_{24}MoO_7P_2W$
mol wt	726.02	754.15	802.22
space group	$P2_1/n$	$P2_1/n$	$P2_1/n$
a (Å)	14.464(7)	9.6322(16)	11.756(4)
b (Å)	11.6743(12)	12.4673(21)	16.423(6)
c (Å)	14.7639(14)	20.814(3)	14.968(3)
β (deg)	97.916(12)	94.476(12)	98.397(20)
V (Å^3)	2469.3(6)	2472.7(7)	2858.8(14)
ρ(calcd) (Mg m^{-3})	1.913	2.026	1.864
Z	4	4	4
cryst dimens (mm)	0.10 × 0.20 × 0.38	0.25 × 0.16 × 0.315	0.39 × 0.41 × 0.35
abs coeff μ(Mo Kα) (mm^{-1})	5.35	5.36	4.69
temp	room temp	room temp	room temp
radiation	Mo Kα (λ = 0.709 30 Å)	Mo Kα (λ = 0.709 30 Å)	Mo Kα (λ = 0.709 30 Å)
2θ range (deg)	45	45	45
scan type	2θ–ω	2θ–ω	2θ–ω
no. of reflns	3220	3220	3723
no. of obsd rflns	2546 (>2.5σ (I))	2337 (>2.0σ (I))	3022 (>2.5σ (I))
variables	320	325	343
R	0.054	0.035	0.026
R_w	0.055	0.044	0.031
S	3.39	1.93	1.49
ΔF (e/Å^3)	<1.370	<0.810	<0.830
$(\Delta/\sigma)_{max}$	0.043	0.039	0.006

Cl_2; **2** and **3a** in THF) at −15 °C. Cell dimensions and space group data were obtained by standard methods on an Enraf-Nonius CAD4 diffractometer. Details of data collection and refinement are given in Table 1.

The coordinates of heavy atoms were obtained from Patterson syntheses. The positions of the remaining non-hydrogen atoms were obtained from Fourier syntheses. For complex **1**, inspection of a difference Fourier revealed severe disorders (Figure 1). There were dominant and minor fractions; the ratio was determined to be 0.85:0.15. Except for W (anisotropic) and P (isotropic), the minor portion was fixed in the final refinement. The final model of the major fraction was obtained with all non-hydrogen atoms refined anisotropically and the H atom at idealized positions with R = 5.4% and R_w = 5.0%. The final positional parameters are listed in Tables 2 (**1**), 3 (**2**), and 4 (**3a**). Selected interatomic distances and bond angles are given in Tables 5 (**1** and **2**) and 6 (**3a**). The thermal parameters for these complexes are provided in the supplementary material.

Results and Discussion

Syntheses, Spectroscopic Characterization, and Molecular Structures of 1 and 2. The new W–Mo complex **1** was synthesized by the reaction of $CpW(CO)_3PPh_2$ with $Mo(CO)_4(C_7H_8)$. The metallophosphine $CpW(CO)_3PPh_2$ acted as a ligand to replace the C_7H_8 to form the complex:



1

When **1** was stirred under 1 atm of CO, complex **2**, which lacks a metal–metal bond, was obtained. The addition of CO to complex **1** was reversible. When **2** was heated in THF at reflux temperature under N_2 or irradiated with UV light, CO was removed from **2** to regenerate **1**. Both complexes were stable at room temperature in air in the solid state.

The $^{31}P\{^1H\}$ NMR spectrum of **1** in THF at room temperature shows a resonance at 170.4 ppm with J_{P-W} = 342 Hz. This relatively downfield resonance reveals the existence of a metal–metal bond in the complex.[11] In contrast, the relatively upfield resonance at −41.7 ppm in the $^{31}P\{^1H\}$ NMR of **2** indicates the opening of the W–P–Mo triangle in the complex.[11] Nevertheless, the J_{P-W} value cannot be observed because of the broad signal.

The W–Mo complexes **1** and **2** were further characterized by single-crystal X-ray diffraction methods. Structures of them are shown in Figures 2 and 3.

In **2**, a W–Mo distance of 4.5192(14) Å indicates that there is no metal–metal bond. One can consider the metallophosphine $CpW(CO)_3PPh_2$ to be a ligand similar to PR_3. Thus, five CO's and $CpW(CO)_3PPh_2$ coordinate to the Mo^0 atom to form a distorted octahedron. Similar examples of the metallophosphine ligand $CpFe(CO)_2PPh_2$ coordinated to $M(CO)_5$ (M = Cr, Mo, W) to form $CpFe(CO)_2(\mu\text{-}PPh_2)M(CO)_5$ with structures similar to that of **2** has been reported.[5a]

In complex **1**, the Mo–C(4)–O(4) angle 169.3(13)° indicates a semibridging carbonyl. The observed IR at 1876 cm^{-1} at room temperature and $^{13}C\{^1H\}$ NMR at 218.69 ppm (see below) at 210 K indicate a real interaction between the W atom and the CO(4) ligand. The W–Mo distance (3.2054(16) Å) in **1** falls between the W–Mo distances reported for the complexes $CpMo(CO)_2(\mu\text{-}SMe)W(CO)_5$ (3.131(1) Å)[12a] and $[HB(pz)_3](CO)_2W(\mu\text{-}CS)Mo(CO)_2(Ind)$ (3.3102(4) Å; Ind = η-C_9H_7, indenyl; $HB(pz)_3$ = hydrotris(1-pyrazolyl)borate).[12b] It is, however, significantly longer than the W–Mo distance in $MoW_2(\mu\text{-}CC_6H_4Me\text{-}4)_2(\mu\text{-}CO)_2(CO)_4(\eta\text{-}C_5H_5)_2$ (2.938(1) Å)[12c] and is similar to that in $(\eta\text{-}C_5H_5)(CO)_3MoW(CO)_2\{C\text{–}O\text{–}(CH_2)_2\text{-}CH_2\}(\eta\text{-}C_5H_5)\}$ (3.239(4) Å),[12d] which has no bridging ligand.

(11) (a) Carty, A. J.; Maclaughlin, S. A.; Nucciarone, D. In *Phosphorus-31 NMR Spectroscopy in Stereochemical Analysis: Organic Compounds and Metal Complexes*; Verkade, J. G., Quin, L. P., Eds.; VCH: New York, 1987; Chapter 16, and references cited therein. (b) Carty, A. J. *Adv. Chem. Ser.* **1982**, *No. 196*, 163. (c) Garrou, P. E. *Chem. Rev.* **1981**, *81*, 229.

(12) (a) Guerchais, J. E.; LeQuere, J. L.; Petillon, F. Y.; Manojlovic-Muir, L.; Muir, K. W.; Sharp, D. W. A. *J. Chem. Soc., Dalton Trans.* **1982**, 283. (b) Doyle, R. A.; Daniels, L. M.; Angelici, R. J. *J. Am. Chem. Soc.* **1989**, *111*, 4995. (c) Garriedo, G. A.; Howard, J. A. K.; Marsden, K.; Stone, F. G. A.; Woodward, P. *J. Chem. Soc., Dalton Trans.* **1984**, 1589. (d) Adams, H.; Bailey, N. A.; Winter, M. J. *J. Chem. Soc., Dalton Trans.* **1984**, 273.

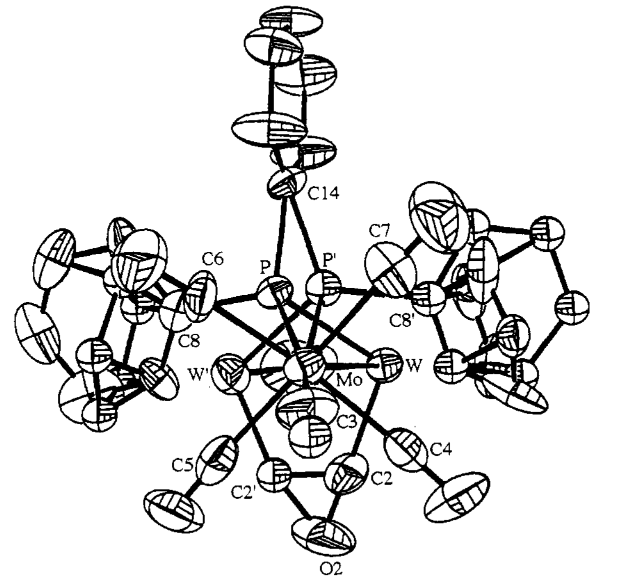
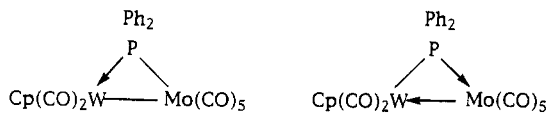


Figure 1. ORTEP drawing of the disordered molecular structure of 1.

Table 2. Atomic Coordinates and Isotropic Thermal Parameters (Å²) for 1

atom	*x*	*y*	*z*	B_{eq}
W	0.30641(5)	0.13387(7)	0.03996(5)	3.06(3)
Mo	0.19111(9)	0.24447(12)	−0.13982(9)	3.12(6)
P	0.1976(3)	0.2872(4)	0.0298(3)	2.70(20)
C1	0.3640(12)	0.2393(15)	0.1401(12)	6.0(10)
C2	0.4144(12)	0.1963(16)	−0.0142(13)	4.3(10)
C3	0.1539(12)	0.2398(17)	−0.2786(11)	5.3(10)
C4	0.2843(11)	0.1146(13)	−0.1636(10)	4.1(8)
C5	0.2917(12)	0.3699(14)	−0.1543(10)	4.3(8)
C6	0.0977(11)	0.3750(12)	−0.1465(10)	4.1(8)
C7	0.0881(12)	0.1248(15)	−0.1286(10)	4.8(9)
C8	0.2336(12)	0.4318(14)	0.0614(10)	2.9(8)
C9	0.3139(13)	0.4666(15)	0.0470(12)	3.8(9)
C10	0.3454(15)	0.5728(21)	0.0679(13)	6.9(14)
C11	0.2805(15)	0.6493(17)	0.1057(12)	5.5(11)
C12	0.1930(15)	0.6145(17)	0.1214(12)	5.3(11)
C13	0.1669(14)	0.5050(15)	0.0982(12)	4.5(10)
C14	0.0894(10)	0.2614(13)	0.0798(10)	3.5(7)
C15	0.0014(11)	0.2789(18)	0.0333(10)	5.7(11)
C16	−0.0727(11)	0.2686(16)	0.0804(10)	4.7(9)
C17	−0.0639(11)	0.2449(18)	0.1708(11)	5.5(10)
C18	0.0219(12)	0.2306(19)	0.2174(10)	6.1(11)
C19	0.0997(11)	0.2377(18)	0.1749(10)	5.8(10)
C20	0.3592(16)	−0.0354(18)	0.1120(15)	6.5(12)
C21	0.3400(14)	−0.0548(20)	0.0208(15)	6.8(13)
C22	0.2484(13)	−0.0493(14)	−0.0045(12)	3.8(9)
C23	0.2064(18)	−0.0157(17)	0.0717(16)	7.3(15)
C24	0.2766(16)	−0.0010(16)	0.1461(13)	5.5(12)
O1	0.4005(9)	0.2799(13)	0.2003(8)	7.9(8)
O2	0.4763(8)	0.2342(12)	−0.0454(9)	7.4(8)
O3	0.1341(11)	0.2354(14)	−0.3538(7)	9.7(10)
O4	0.3285(9)	0.0486(11)	−0.1897(8)	6.9(7)
O5	0.3437(8)	0.4318(11)	−0.1673(8)	6.6(7)
O6	0.0483(9)	0.4476(11)	−0.1570(10)	8.1(8)
O7	0.0333(9)	0.0592(11)	−0.1254(10)	8.5(9)

The metal–metal bond in 1 can be considered as a covalent bond between Mo^{I} and W^{I} (structure a) or a donor–acceptor bond from Mo^{0} to W^{II} (structure b). We



a b

prefer the latter assignment, which is similar to descriptions given earlier for $(PPh_3)(CO)_3Fe(\mu\text{-}PPh_2)Ir(CO)_2(PPh_3)$[3a] and $(CO)_5W(\mu\text{-}PPh_2)Re(CO)_4$.[1b] The Mo–W bond in 1 can be considered as the donation of an electron pair from one of the filled t_{2g} orbitals of Mo to the adjacent W such that the Mo–W dative bond acts as the fifth ligand, donating two electrons to W, in addition to the two CO's, the μ-PPh_2, and the Cp ligands coordinated to W. Consistent with this view is the observation that the Mo–W vector bisects an edge of the distorted molybdenum octahedron and the Mo atom lies on the least-squares plane consisting of P, C(3), C(4), and C(6). The Mo–W vector was only 1.34° off the plane.[13]

Table 3. Atomic Coordinates and Isotropic Thermal Parameters (Å²) for 2

atom	*x*	*y*	*z*	B_{eq}
W	0.50793(6)	0.75999(4)	0.15894(3)	2.40(2)
Mo	0.79180(12)	0.78949(9)	0.00525(6)	2.64(5)
P	0.74705(34)	0.71501(25)	0.11909(16)	2.33(14)
O1	0.2663(10)	0.6059(8)	0.1857(6)	5.3(6)
O2	0.4328(11)	0.6367(8)	0.0271(5)	4.5(5)
O3	0.6604(11)	0.6235(8)	0.2743(4)	3.9(5)
O4	0.8461(13)	1.0346(8)	0.0398(6)	6.3(7)
O5	0.8717(12)	0.8551(10)	−0.1306(6)	6.0(7)
O6	1.1186(11)	0.7494(10)	0.0492(6)	6.0(6)
O7	0.7245(14)	0.5554(9)	−0.0534(6)	7.0(7)
O8	0.4759(11)	0.8513(9)	−0.0453(6)	5.8(6)
C1	0.3546(15)	0.6611(11)	0.1756(7)	3.2(7)
C2	0.4608(14)	0.6801(11)	0.0753(6)	2.9(6)
C3	0.6067(14)	0.6705(10)	0.2302(8)	3.4(7)
C4	0.8282(15)	0.9448(12)	0.0312(7)	3.6(7)
C5	0.8393(15)	0.8308(12)	−0.0819(8)	3.9(8)
C6	1.0027(16)	0.7594(12)	0.0348(6)	3.8(7)
C7	0.7475(15)	0.6333(13)	−0.0293(7)	3.7(8)
C8	0.5887(16)	0.8268(11)	−0.0253(7)	4.0(7)
C9	0.3492(15)	0.8999(11)	0.1594(10)	4.8(9)
C10	0.4323(19)	0.9254(11)	0.1136(8)	4.3(9)
C11	0.5758(17)	0.9402(10)	0.1461(10)	4.9(10)
C12	0.5745(16)	0.9196(11)	0.2116(9)	4.1(8)
C13	0.4347(17)	0.8976(11)	0.2207(8)	4.1(8)
C21	0.7771(13)	0.5672(9)	0.1204(6)	2.3(6)
C22	0.6767(14)	0.4913(9)	0.1287(6)	2.8(6)
C23	0.7045(16)	0.3830(10)	0.1257(6)	3.4(7)
C24	0.8327(18)	0.3491(11)	0.1137(8)	4.7(9)
C25	0.9363(17)	0.4231(12)	0.1058(7)	4.3(8)
C26	0.9082(15)	0.5307(11)	0.1092(7)	3.5(7)
C31	0.8879(12)	0.7578(10)	0.1855(6)	2.7(6)
C32	0.9459(14)	0.6898(11)	0.2343(7)	3.4(6)
C33	1.0489(15)	0.7240(13)	0.2818(7)	4.3(8)
C34	1.0974(15)	0.8291(14)	0.2843(7)	3.8(8)
C35	1.0393(15)	0.8978(11)	0.2352(7)	3.8(7)
C36	0.9340(14)	0.8645(10)	0.1872(7)	3.5(7)

Variable-Temperature ^{13}C NMR and Fluxional Behavior of $CpW(CO)_2(\mu\text{-}PPh_2)Mo(CO)_5$. The broad hump at 206.43 ppm observed in the $^{13}C\{^{1}H\}$ NMR of complex 1 at room temperature indicates a possible exchange of metal carbonyl ligands. In order to understand this fluxional behavior, variable-temperature ^{13}C NMR of enriched 1 was undertaken (Figure 4).

At 210 K, the two CO signals, C1 (δ 228.11, $^{2}J_{C-P}$ = 15.0 Hz, J_{C-W} = 120.9 Hz) and C2 (δ 223.11, J_{C-W} = 133.9 Hz), are assigned to CO ligands coordinated to the W on the basis of observations of their tungsten satellites. The signal C4 (218.69 ppm) belongs to the semibridging carbonyl because bridging carbonyl has a relatively downfield

(13) Equation of the plane: $[10.65(6)]x + [7.86(5)]y - [2.46(5)]z = 4.292(5)$. Distances (Å) to the plane from the atoms in the plane: P, −0.003(7); C(3), −0.081(24); C(4), 0.039(22); C(6), 0.057(21). χ^2 for this plane is 22.399. Distances (Å) to the plane from the atoms out of the plane: W, −0.075(14); Mo, 0.010(8).

(14) Smith, J. G.; Thompson, T. D. *J. Chem. Soc. A* **1967**, 1694.

Table 4. Atomic Coordinates and Isotropic Thermal Parameters (Å²) for 3a

atom	*x*	*y*	*z*	B_{eq}
W	0.74191(2)	0.63069(2)	0.38926(2)	2.79(1)
Mo	0.75461(5)	0.38405(3)	0.25710(4)	2.51(2)
P1	0.67827(14)	0.53626(9)	0.24870(11)	2.37(7)
P2	0.91553(15)	0.40525(11)	0.16171(12)	3.08(8)
O1	0.5788(5)	0.3340(4)	0.0834(4)	6.6(3)
O2	0.8365(5)	0.2035(3)	0.2566(4)	5.1(3)
O3	0.9344(5)	0.3996(4)	0.4351(4)	6.1(3)
O4	0.5901(5)	0.3102(3)	0.3828(4)	5.2(3)
O5	0.5968(5)	0.7527(3)	0.2579(4)	5.8(3)
O6	0.9780(4)	0.5774(4)	0.3330(4)	5.3(3)
O7	0.8823(6)	0.7929(4)	0.4037(4)	8.5(4)
C1	0.6397(6)	0.3557(4)	0.1442(5)	3.5(3)
C2	0.8069(6)	0.2702(4)	0.2565(5)	3.4(3)
C3	0.8711(6)	0.3993(4)	0.3705(5)	3.6(3)
C4	0.6463(6)	0.3420(4)	0.3365(5)	3.5(3)
C5	0.6497(7)	0.7062(4)	0.3019(5)	3.9(4)
C6	0.8899(7)	0.5975(4)	0.3488(5)	3.8(3)
C7	0.8311(8)	0.7347(5)	0.3983(5)	5.5(4)
C8	0.7786(6)	0.5495(5)	0.5204(4)	3.8(3)
C9	0.7660(7)	0.6307(5)	0.5456(5)	4.7(4)
C10	0.6534(7)	0.6555(4)	0.5158(5)	4.2(4)
C11	0.5944(6)	0.5895(5)	0.4677(5)	3.9(3)
C12	0.6715(7)	0.5257(4)	0.4716(5)	3.9(4)
C13	1.0517(7)	0.3667(5)	0.2212(6)	5.8(5)
C14	0.9664(6)	0.5009(4)	0.1208(5)	4.3(4)
C15	0.8976(8)	0.3474(5)	0.0580(6)	6.2(5)
C21	0.7086(5)	0.5844(4)	0.1427(4)	2.6(3)
C22	0.7811(6)	0.6515(4)	0.1392(4)	3.4(3)
C23	0.8031(7)	0.6804(4)	0.0559(5)	4.5(4)
C24	0.7516(8)	0.6446(5)	−0.0238(5)	4.6(4)
C25	0.6802(7)	0.5793(5)	−0.0196(5)	4.5(4)
C26	0.6594(6)	0.5481(4)	0.0622(4)	3.3(3)
C31	0.5187(5)	0.5442(3)	0.2321(4)	2.4(3)
C32	0.4593(6)	0.6038(4)	0.1778(5)	3.2(3)
C33	0.3408(6)	0.6116(4)	0.1745(5)	4.3(4)
C34	0.2812(6)	0.5613(5)	0.2225(5)	4.2(4)
C35	0.3371(6)	0.5007(4)	0.2730(5)	3.7(3)
C36	0.4559(5)	0.4924(4)	0.2775(4)	3.0(3)

position in comparison with the corresponding terminal carbonyls. The doublet C3 (208.58 ppm, $^2J_{C-P}$ = 11.09 Hz) is assigned to the molybdenum CO trans to the phosphido bridge on the basis of its relatively downfield position in comparison with the resonance positions of the other terminal CO's of Mo.[15] The remaining signals (C5, C6, C7) are assigned to the other CO ligands on Mo cis to the phosphido-bridge ligand. The observed similarity of the $^2J_{P-C}$ value (11.09 Hz) of the cis CO signal C5 to the $^2J_{P-C}$ value (11.09 Hz) of the trans CO signal C3 for Mo is not common. However, a similar observation of a $^2J_{P-C}$ value of cis CO larger than the $^2J_{P-C}$ value of trans CO for Mo has been reported for $(CO)_5MoP(O\text{-}i\text{-}Pr)_3$.[16]

We interpret the ^{13}C NMR observations as follows. At 210 K, all carbonyls were rigid and no intramolecular exchange occurred among carbonyl ligands. At 223 K, exchange took place among the three cis molybdenum carbonyl ligands and the semibridging CO, as indicated by the broadening of their NMR signals (C4, C5, C6, C7).

At 320 K, the signal for C1 broadened. This indicates an additional exchange process of the CO ligands. Two kinds of exchange are possible. One is the exchange between this tungsten CO and the other cis CO ligands on Mo. At higher temperature (330 K), however, the compound decomposed and the coalescence point could not be obtained. The other possibility is the dissociation and reassociation of this tungsten CO in solution at high temperature. The ligand exchange experiment was unsuccessful for this purpose because the reaction between 1 and ^{13}CO resulted in the formation of the non-metal–metal-bonded complex 2.

The exchange of the semibridging carbonyl ligand with the other three cis CO ligands may proceed through the rotation of the Mo–P bond (Scheme 2). The rotation of the Mo–P bond requires the cleavage and the re-formation of the metal–metal dative bond. The cleavage of the

Table 5. Selected Bond Lengths (Å) and Bond Angles (deg) in Complexes 1 and 2

complex 1		complex 2	
Bond Lengths			
W–Mo	3.2054(16)	W···Mo	4.5192(14)
Mo–P	2.542(5)	Mo–P	2.639(4)
Mo–C3	2.046(16)	Mo–C4	2.027(15)
Mo–C4	2.090(16)	Mo–C5	2.003(16)
Mo–C5	2.095(17)	Mo–C6	2.068(16)
Mo–C6	2.029(15)	Mo–C7	2.098(16)
Mo–C7	2.066(16)	Mo–C8	2.020(16)
W–P	2.374(5)	W–P	2.621(3)
W–C1	2.014(16)	W–C1	1.994(16)
W–C2	1.989(19)	W–C2	1.999(14)
C1–O1	1.079(20)	W–C3	1.984(15)
C2–O2	1.149(22)	C1–O1	1.137(18)
C3–O3	1.110(19)	C2–O2	1.137(17)
C4–O4	1.104(20)	C3–O3	1.146(18)
C5–O5	1.080(20)	C4–O4	1.142(19)
C6–O6	1.106(19)	C5–O5	1.145(20)
C7–O7	1.108(21)	C6–O6	1.119(18)
		C7–O7	1.100(19)
		C8–O8	1.145(19)
Bond Angles			
W–P–Mo	81.31(14)	W–P–Mo	118.44(12)
P–Mo–C3	163.8(5)	P–Mo–C4	98.1(4)
P–Mo–C4	111.7(4)	P–Mo–C5	173.3(4)
P–Mo–C5	91.8(4)	P–Mo–C6	87.3(4)
P–Mo–C6	80.5(4)	P–Mo–C7	85.9(4)
P–Mo–C7	89.0(5)	P–Mo–C8	94.9(4)
P–W–C1	77.8(5)	P–W–C1	129.1(4)
P–W–C2	104.4(5)	P–W–C2	73.5(4)
Mo–C3–O3	178.8(18)	P–W–C3	76.7(4)
Mo–C4–O4	169.3(13)	Mo–C4–O4	173.6(12)
Mo–C5–O5	175.3(13)	Mo–C5–O5	177.3(12)
Mo–C6–O6	174.4(14)	Mo–C6–O6	175.5(12)
Mo–C7–O7	177.6(15)	Mo–C7–O7	172.9(13)
W–C1–O1	168.3(18)	Mo–C8–O8	176.2(12)
W–C2–O2	178.8(16)	W–C1–O1	178.8(12)
		W–C2–O2	178.4(11)
		W–C3–O3	175.3(12)

Table 6. Selected Bond Lengths (Å) and Bond Angles (deg) in Complex 3a

Bond Lengths			
W···Mo	4.5198(17)	W–C6	2.000(8)
Mo–P1	2.6527(18)	W–C7	1.998(9)
Mo–P2	2.5549(19)	O1–C1	1.129(9)
Mo–C1	2.057(8)	O2–C2	1.149(9)
Mo–C2	1.969(7)	O3–C3	1.131(10)
Mo–C3	2.035(8)	O4–C4	1.151(9)
Mo–C4	1.988(7)	O5–C5	1.133(10)
W–P1	2.6327(17)	O6–C6	1.144(10)
W–C5	2.002(8)	O7–C7	1.127(11)
Bond Angles			
W–P1–Mo	117.55(6)	P1–W–C7	129.99(23)
P1–Mo–P2	96.78(6)	Mo–C1–O1	174.8(6)
P1–Mo–C1	89.87(18)	Mo–C2–O2	179.3(6)
P1–Mo–C2	176.83(20)	Mo–C3–O3	173.0(6)
P1–Mo–C3	96.03(19)	W–C4–O4	172.8(6)
P1–Mo–C4	96.56(19)	W–C5–O5	174.8(6)
P1–W–C5	77.25(20)	W–C6–O6	174.3(6)
P1–W–C6	75.86(20)	W–C7–O7	179.3(8)

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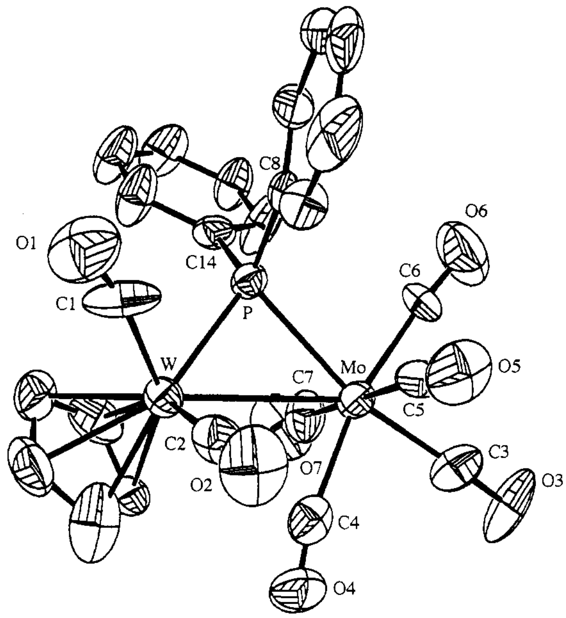

Figure 2. ORTEP drawing of 1. Hydrogen atoms are omitted.

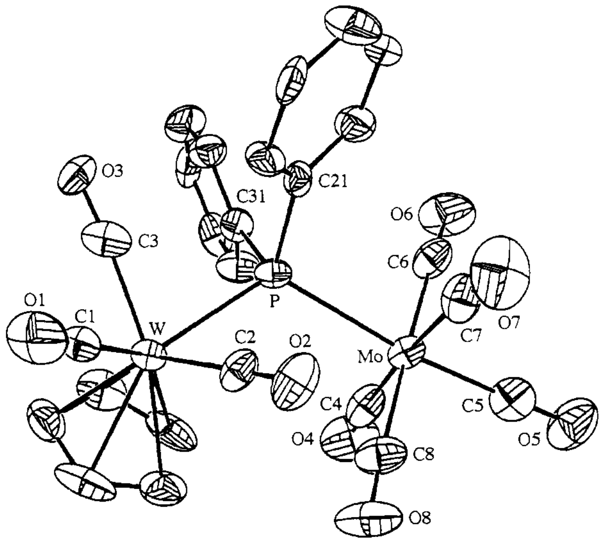

Figure 3. ORTEP drawing of 2. Hydrogen atoms are omitted.

metal–metal bond in phosphido-bridged complexes is usually accompanied by an upfield shift of the ^{31}P NMR signal. Variable-temperature ^{31}P NMR of 1 did not show any change of resonance position of the phosphido phosphorus. This indicates that the cleavage and the re-formation of the Mo–W bond are so rapid that the exchange time scale is beyond the NMR detection limit.

This type of fluxional behavior seems general for mono(phosphido)-bridged carbonyl complexes.[5,17] Note that the mechanism involving cleavage of the metal–phosphido bridge bond and the rotation of the metal–metal bond has been proposed to explain the fluxional behavior which involves the exchanges of terminal CO on one of the metal moieties in the bis(phosphido)-bridged complex.[18]

Addition of Phosphine (PMe_3, PPh_2H, $P(OMe)_3$) and CO to 1. Reaction of 1 with phosphine L (L = PMe_3, PPh_2H, $P(OMe)_3$) at room temperature yielded $CpW(CO)_3(\mu\text{-}PPh_2)Mo(CO)_4L$ (**3**) with L regiospecific and stereospecific on the Mo site cis to the phosphido-bridge ligand (Scheme 1). The regiospecific assignment is revealed by the absence of J_{P-W} for the signal of L in the ^{31}P NMR of **3**. A downfield shift of the phosphido-bridge phosphorus signal in the ^{31}P NMR indicates the cleavage of the metal–metal bond. The structure of $CpW(CO)_3(\mu\text{-}PPh_2)Mo(CO)_4(PMe_3)$ was further characterized by a single-crystal X-ray diffraction study (Figure 5).

The long distance between W and Mo (4.5198(14) Å) indicates that no metal–metal bond exists between the two metals. The PMe_3 ligand is coordinated to the Mo and is cis to the phosphido bridge. The replacement of CO in **2** with PMe_3 does not increase the repulsion between the W and the Mo moieties in **3a**. This is shown by the observation that the distance between W and Mo and the W–P–Mo angle in **3a** are almost the same as the distance between W and Mo and the W–P–Mo angle in **2**.

The regiospecific and stereospecific addition of phosphines to 1 is of interest because the addition of a Lewis base to heterobimetallic phosphido-bridged complexes with a metal–metal dative bond usually produces complexes with the base coordinated to the metal at the place where the metal–metal dative bond originally coordinated (if the metal–metal bond cleaved).[1b,2b,3,4] In this case, the phosphine should coordinate to the W atom. However, the phosphine may initially coordinate to W to form the kinetic product and further migration of the phosphine to the adjacent Mo may occur as in the case of $(CO)_4Fe(\mu\text{-}AsMe_2)Co(CO)_2L_2$ (L = PMe_3, $P(OMe)_3$).[4a] The regiospecific addition on Mo may also be due to the steric effect because of the bulky Cp and μ-PPh_2 ligands and the incoming phosphine. In order to evaluate these factors, we used ^{13}CO in the addition reaction.

The $^{13}C\{^1H\}$ NMR spectrum of ^{13}CO-enriched **2** shows only one doublet at 206.8 ppm with $^2J_{P-C}$ = 6.3 Hz. No other signals in the terminal carbonyl region were observed. Although the $^{13}C\{^1H\}$ NMR of nonenriched **2** cannot be obtained because of the low solubility and slow decomposition of the complex in solution in long-term NMR measurements, the doublet is assigned to the cis-CO of Mo. The assignment is based on the absence of J_{C-W} satellites and the favorable comparison with the reported resonance at δ 206.5 (J_{P-C} = 7.7 Hz) of for the cis CO signal in $Cp(CO)_2Fe(\mu\text{-}PPh_2)Mo(CO)_5$.[5] This indicates that CO addition to 1 was regiospecific and stereospecific on the Mo site and that the addition was cis to the phosphido-bridged ligands. This result excludes both intramolecular ligand migration from W to Mo and the steric influence of Cp and μ-PPh_2 ligands, because no tungsten terminal CO signal was observed. Formation of **3** from **1** requires the loss of one CO from Mo and the addition of one CO to W. There are two possible sources for this added W CO ligand. One possibility is that carbon monoxide on Mo may first be substituted by the phosphine ligand to form the metal–metal-bonded complex **5** (Scheme 3). Free CO from the environment may react with **5** to form **2**. The other possibility is the intramolecular migration of the semibridging CO on Mo to the adjacent W during the reaction. A reaction between **1** and $P(OMe)_3$ under ^{13}CO was carried out to produce **3b**. Both the mass spectrum and ^{13}C NMR of the product indicate no ^{13}CO was introduced into the product. In addition, the complex **4** (trans isomer of **5**) prepared from the irradiation of the corresponding **3** did not react with CO to regenerate **3**.

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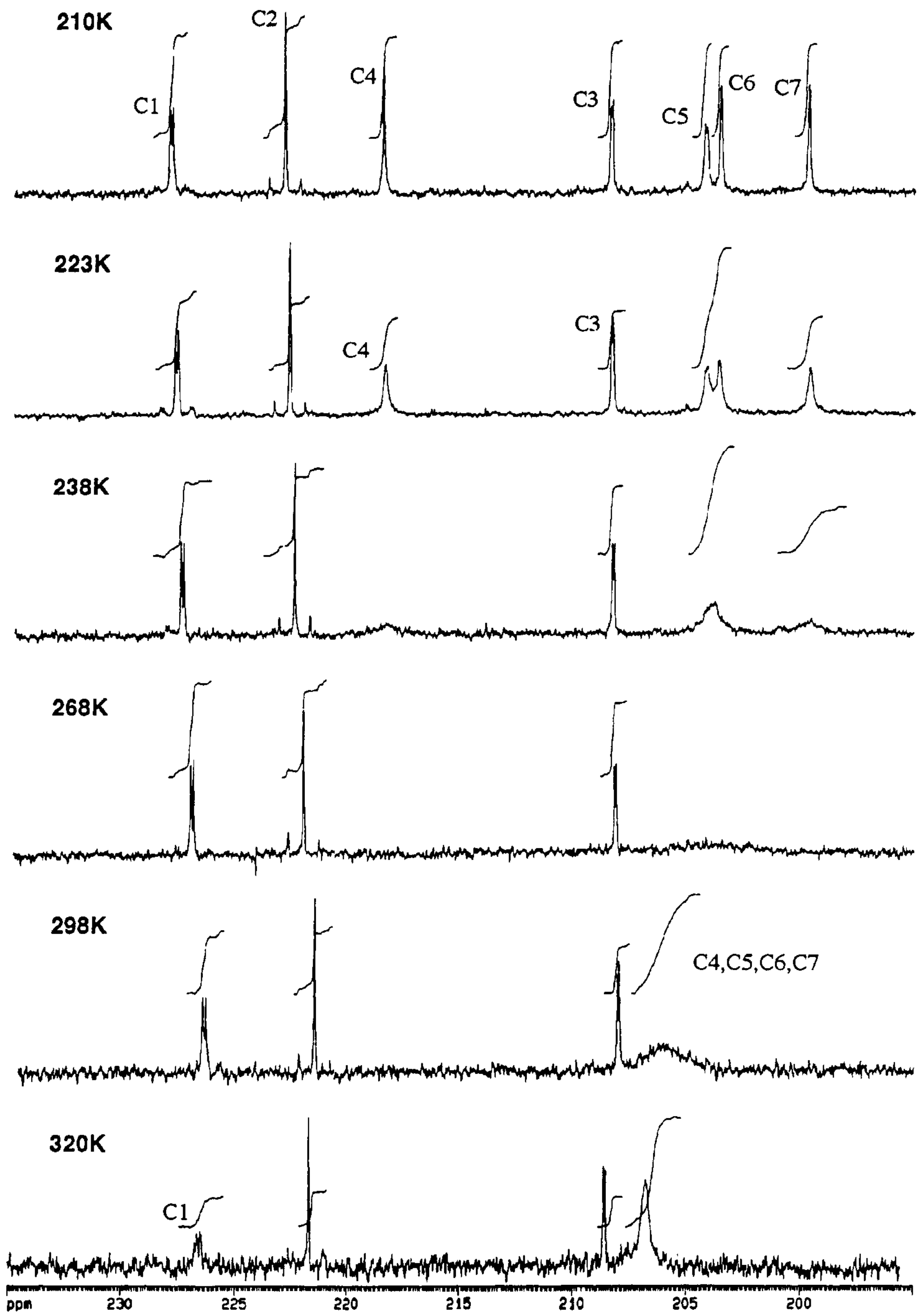
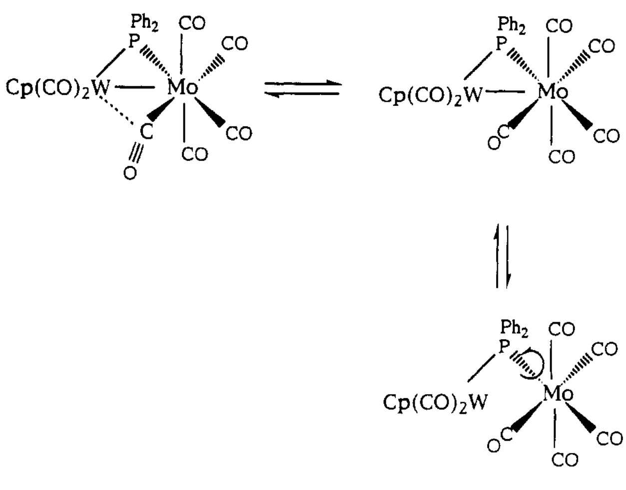


Figure 4. Variable-temperature $^{13}C\{^1H\}$ NMR spectra of 1 in CD_2Cl_2. Only the carbonyl region is shown.

These observations exclude the intermolecular CO addition to the W atom in the reaction.

Role of the Metal–Metal Dative Bond in the Addition Reaction. If we consider $Cp(CO)_3WPPh_2$ in complexes 2 and 3 as a ligand, complex 3 can be considered as a disubstituted $Mo(CO)_4LL'$ complex with L′ = $Cp(CO)_3WPPh_2$ and L = PPh_2H, $P(OMe)_3$, PMe_3. The substitution of group VI metal carbonyl complexes usually requires high temperature.[19] The metallophosphine ligand $Cp(CO)_3WPPh_2$ did not activate the $Mo(CO)_5$ moiety for further substitution, since no complex 3 was observed when complex 2 was allowed to react with $P(OMe)_3$ in THF overnight. However, addition reactions between 1 and phosphine ligands to form 3 proceeded at room temperature within several hours.

Scheme 2



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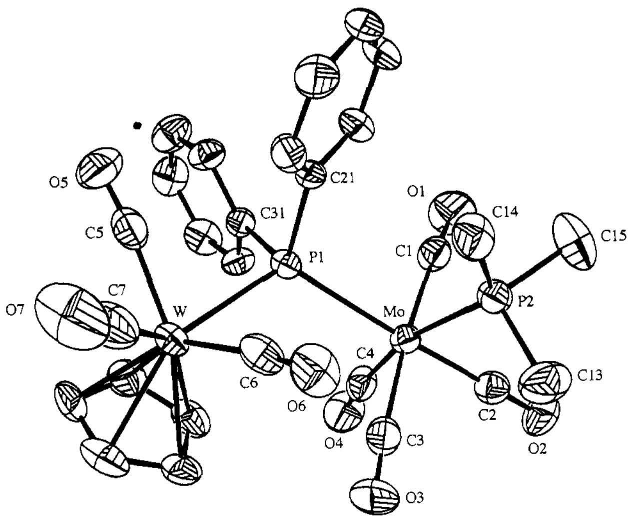
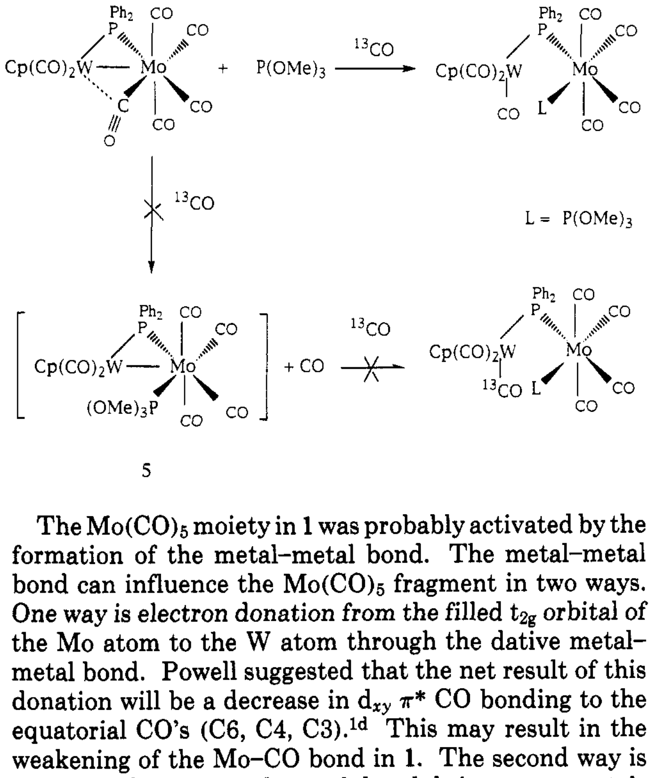


Figure 5. ORTEP drawing of **3a**. Hydrogen atoms are omitted.

Scheme 3



The $Mo(CO)_5$ moiety in **1** was probably activated by the formation of the metal–metal bond. The metal–metal bond can influence the $Mo(CO)_5$ fragment in two ways. One way is electron donation from the filled t_{2g} orbital of the Mo atom to the W atom through the dative metal–metal bond. Powell suggested that the net result of this donation will be a decrease in d_{xy} π^* CO bonding to the equatorial CO's (C6, C4, C3).[1d] This may result in the weakening of the Mo–CO bond in **1**. The second way is that the dative metal–metal bond brings two metals together such that the adjacent tungsten is able to activate one of the Mo carbonyl ligands through the donation of the electron from the electron-rich tungsten atom to the π^* orbital of the adjacent molybdenum CO to form a semibridging CO ligand.[20]

Formation of the metal–metal dative bond in **1** thus can be considered as a switch, which triggers the substitution of the Mo carbonyl by the activation of one of the Mo carbonyls through the adjacent W atom. The labilization of the metal–CO group by the metal–metal-bonded adjacent metal in phosphido-bridged complexes has been suggested in the $(CO)_4Ru(\mu\text{-}PPh_2)Co(CO)_3$ system.[21] This phenomenon of activation of one of the metal fragments by the adjacent metal through metal–metal dative bond formation can also be considered as a cooperativity effect of the adjacent metal in heterobimetallic complexes.

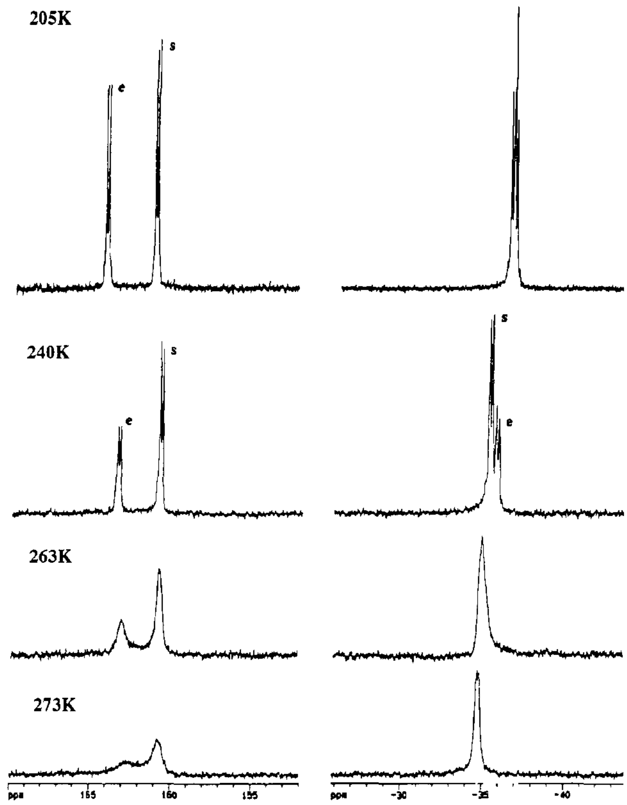


Figure 6. Variable-temperature $^{31}P\{^1H\}$ NMR spectra of **3b** in CD_2Cl_2.

Conformational Isomers of 3. Both variable-temperature $^{31}P\{^1H\}$ NMR (Figure 6) and variable-temperature ^1H NMR (Figure 7) of **3** indicate that two isomers exist in equilibrium in solution. The upfield phosphido-bridge signal in the $^{31}P\{^1H\}$ NMR indicates that a metal–metal bond does not exist in either isomer. Low-temperature $^{13}C\{^1H\}$ NMR of the ^{13}CO-enriched **3b** indicates that there were two conformational isomers with one having the phosphine on the Mo eclipsed with the W moiety (isomer **e**) and the other having all ligands on the Mo staggered with respect to the W moiety (isomer **s**, Figure 8) in the solution.

Figure 9 shows the $^{13}C\{^1H\}$ NMR spectrum of **3b** in the metal carbonyl region at 205 and 240 K. Signals C_g and $C_{g'}$ are assigned to CO_g in isomer **e** and CO_g in isomer **s**, respectively, due to the observed J_{C-W} satellite. The signal $C_{a,b}$ is assigned to the two equivalent CO_a and CO_b ligands in isomer **e**. Signals $C_{a'}$ and $C_{b'}$ are assigned to the CO_a and CO_b ligands in isomer **s**, respectively. On the basis of the integration of signals, the ratio of isomer **e** to isomer **s** was 8:10 at 205 K. When the temperature was raised to 240 K, the ratio of isomer **e** to isomer **s** in solution changed to 6:10. This observation further supports the assignment, since the eclipsed form should have higher energy due to the steric hindrance of the ligands in the complex.

The $^{13}C\{^1H\}$ resonance positions in **3b** corresponding to the *ipso*-C carbons of the phenyl group (Ph_a and Ph_b) in the diphenylphosphido-bridged ligand further support that the isomers represent eclipsed and staggered conformational isomers. In isomer **e**, the signals of *ipso*-C_a and *ipso*-C_b should be equivalent. In isomer **s**, they should

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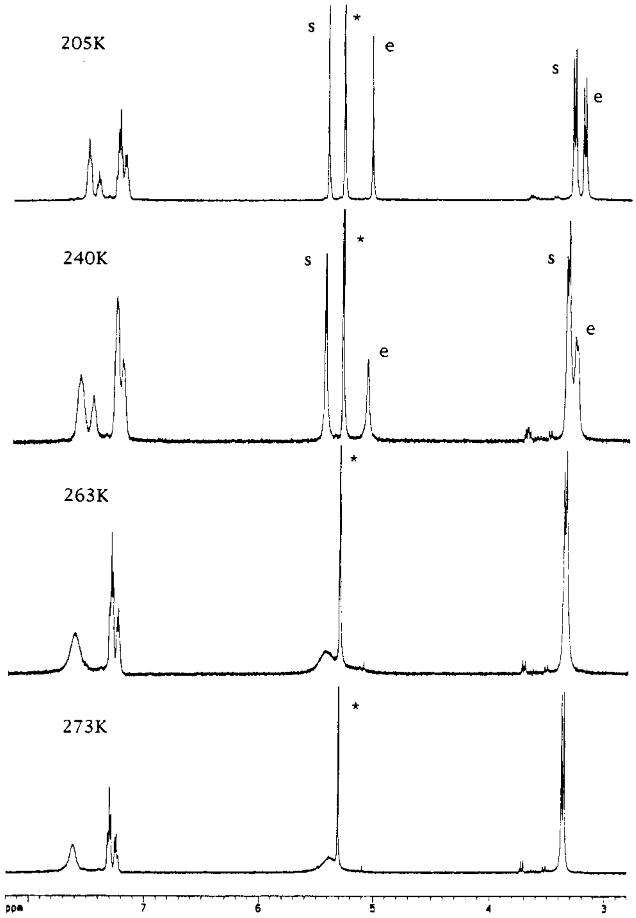

Figure 7. Variable-temperature ^1H NMR spectra of **3b** in CD_2Cl_2. Solvent signals are indicated with asterisks.

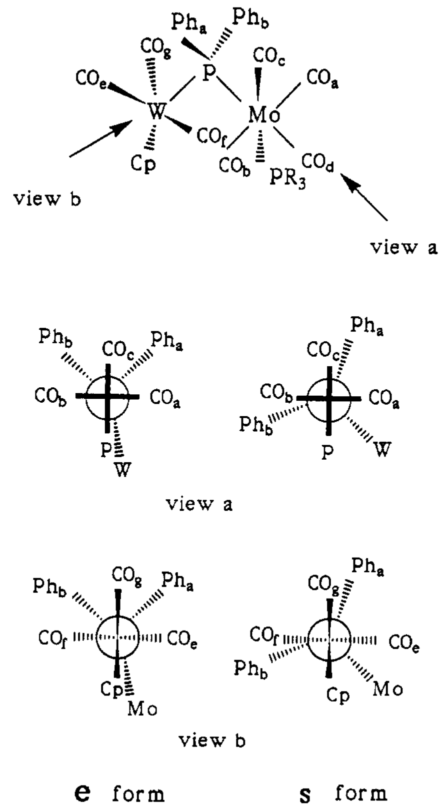

Figure 8. Conformation isomers of **3**.

not be equivalent. In the solution mixture of isomer **e** and isomer **s**, three *ipso*-C signals should be observed with one *ipso*-$C_{a,b}$ signal corresponding to the equivalent *ipso*-C_a and *ipso*-C_b in the **e** isomer and two signals corresponding to *ipso*-$C_{a'}$ and *ipso*-$C_{b'}$ in the **s** isomer. Similarly, signals corresponding to *o*-C, *m*-C, and *p*-C should follow the same argument. In all, there should be 12 sets of phenyl signals, with 8 sets corresponding to the staggered isomer and 4 sets corresponding to the eclipsed isomer. Indeed, 6 sets of signals corresponding to *ipso*-$C_{a,b}$ (d, 140.27 ppm, J_{P-C} = 9.05 Hz), *ipso*-$C_{a'}$ (s, 145.0 ppm), *ipso*-$C_{b'}$ (d, 141.18 ppm, J_{P-C} = 3.40 Hz), *o*-$C_{a'}$ (d, 134.71 ppm, J_{P-C} = 3.40 Hz), *o*-$C_{b'}$ (d, 131.76 ppm, J_{P-C} = 7.55 Hz), and *o*-$C_{a,b}$ (d, 132.16 ppm, J_{P-C} = 6.04 Hz) are clearly observed. For *m*-C and *p*-C, the signals cannot be clearly assigned due to overlap but are clear enough to support the above argument (Figure 10).

The interconversion between isomers **e** and **s** probably occurs through the rotation of the M–P(phosphido) bond (M = Mo, W). From the variable-temperature NMR data, the isomer **s** is more stable at higher temperatures. The equilibrium also depends on the phosphine ligands. On the basis of ^{13}C NMR, the ratios of **e** isomer to **s** isomer were 1:5 for **3a** (L = PMe_3, 205 K, CD_2Cl_2), 3:5 for **3b** (L = $P(OMe)_3$, 205 K, CD_2Cl_2), and 1:6 for **3c** (L = PPh_2H, 210 K, $CDCl_3$).

Syntheses and Spectroscopic Characterization of $CpW(CO)_2(\mu\text{-}PPh_2)Mo(CO)_4(L)$ (4; L = PPh_3, PPh_2H, PMe_3, $P(OMe)_3$). Reaction of **1** with PPh_3 produces **4d** (Scheme 1). The downfield resonance in the ^{31}P NMR of the phosphido phosphorus at 168.26 ppm ($^2J_{P-P}$ = 27.1 Hz, J_{P-W} = 325.5 Hz) indicates the presence of the metal–metal bond. The PPh_3 is coordinated to the Mo, because no coupling between W and P is observed. Although we did not obtain a single-crystal X-ray structure determination of **4d**, the PPh_3 is believed to occupy the position trans to the phosphido bridge. This assignment is based on ^{13}C NMR of the complex. One doublet at 230.95 ppm ($^2J_{P-C}$ = 15.87 Hz) and one singlet at 223.54 ppm are observed in the terminal carbonyl region. These two signals are assigned to two terminal CO's on tungsten, since they compared favorably with 226.73 ppm ($^2J_{P-C}$ = 17.6 Hz) and 221.80 ppm for the tungsten terminal CO resonances of **1**. No Mo terminal CO signal was observed. Because the exchange of cis CO's on Mo in **1** results in the flattening of their CO signals in the NMR and trans CO is not involved in the fluxional behavior, the absence of observable Mo terminal CO groups indicates the absence of a trans CO and the presence of four cis CO ligands. Thus, the phosphine occupies the trans position.

One of the carbonyl ligands in **3** can be removed by photolysis to generate **4**. The downfield resonance position of the phosphido phosphorus indicates the presence of the metal–metal bond. On the basis of the similarity of the IR to that of **4d**, the phosphine ligands in **4** occupy the position trans to the phosphido bridge.

The reaction between **1** and PPh_3 to produce **4d** instead of opening the metal–metal bond to form $CpW(CO)_3(\mu\text{-}PPh_2)Mo(CO)_4(PPh_3)$ (as in the case of the other phosphine ligands PMe_3, $P(OMe)_3$, and PPh_2H) can be explained by the steric hindrance of the bulky PPh_3 group. Therefore, PPh_3 may initially react with **1** to form **3d**. Because of the steric hindrance of the bulky PPh_3, re-formation of the metal–metal bond following loss of one CO from **3d** produces **4d** as the thermodynamic product. The direct substitution of the Mo carbonyl ligand in **1** by PPh_3 is unlikely, because no complex **4** is observed in the

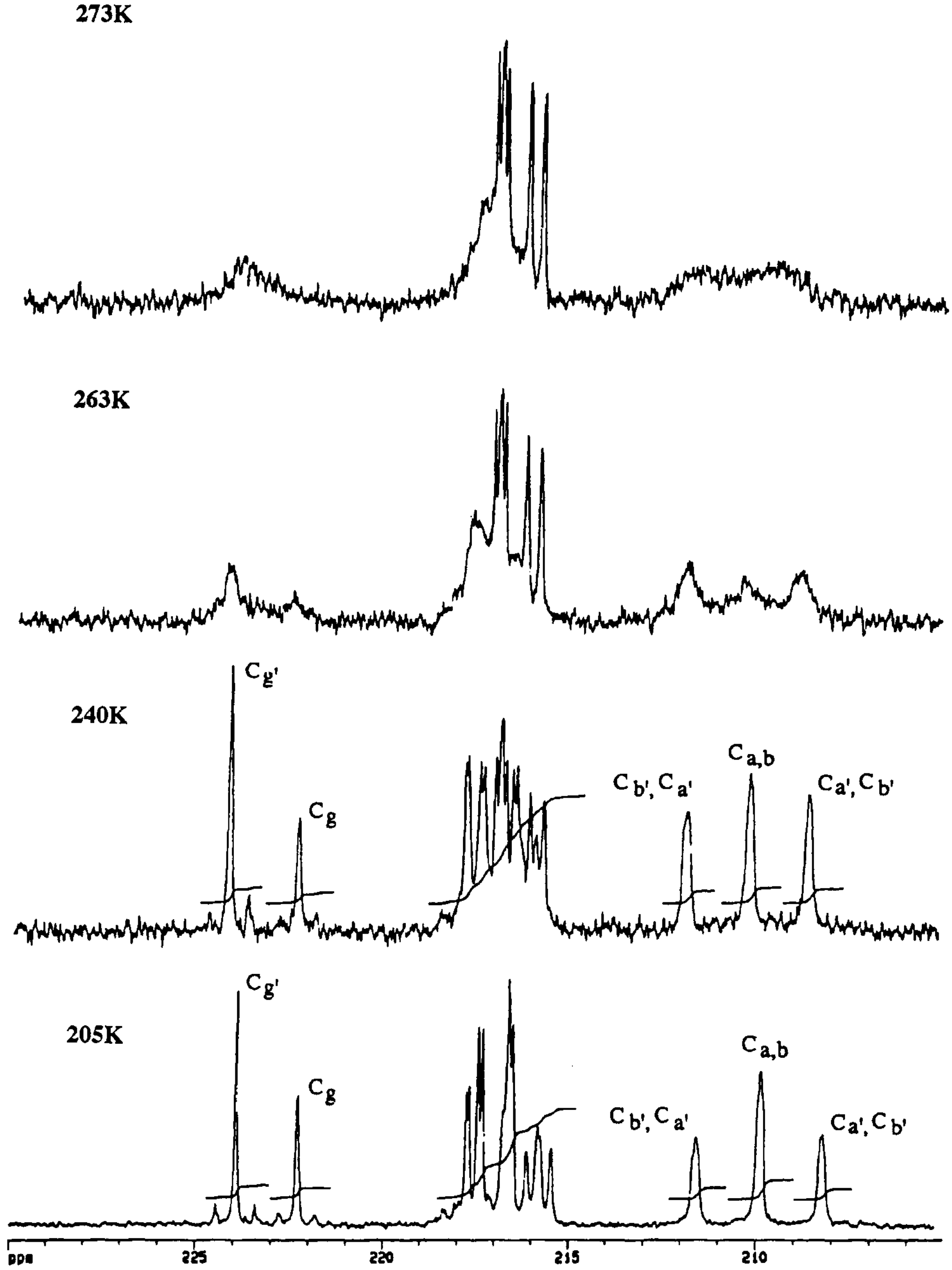

Figure 9. Variable-temperature $^{13}C\{^1H\}$ NMR spectra of **3b**. Only the carbonyl region is shown.

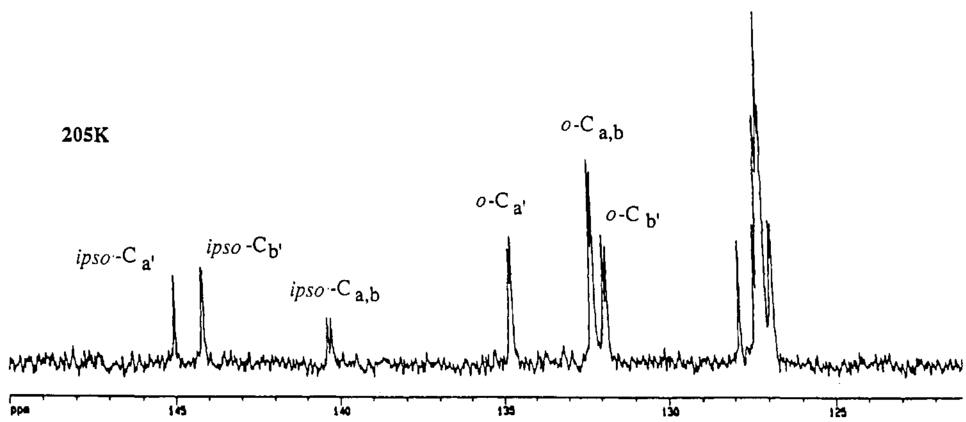

Figure 10. Phenyl region of the $^{13}C\{^1H\}$ NMR spectrum of **3b** at 205 K.

reaction between the other phosphine ligand and **1** when the reaction is followed by ^{31}P NMR spectroscopy.

The strain from the repulsion between the cis phosphine ligand and ligands on the adjacent tungsten can also be released by the formation of the trans isomer **3-trans** since trans isomers were the thermodynamic products of bis(phosphine)molybdenum carbonyls.[22] However, pyrolysis of **3b** results in the formation of **4b**. These results indicate that the reaction path to CO removal to form the metal–metal bonded complex is favored at elevated temperatures. The steric hindrance in the proposed complex **3d** may also be released by the fragmentation of the product, as indicated by the isolation of a large amount of $Mo(CO)_5PPh_3$ as the side product. Reaction between 1 and the bulky PEt_3 at room temperature overnight resulted in fragmentation of the complex, further supporting the above statement.

Conclusions

Heterobimetallic phosphido-bridged complexes with metal–metal dative bond, $CpW(CO)_2(\mu\text{-}PPh_2)Mo(CO)_5$, and without a metal–metal bond, $CpW(CO)_3(\mu\text{-}PPh_2)Mo(CO)_5$, were synthesized and their structures were determined by single-crystal X-ray diffraction methods. Fluxional behavior involving the exchange of four Mo carbonyl ligands cis to the phosphido bridge through the rotation of the M–P bond in 1 was observed by ^{13}C NMR spectrometry.

Addition of CO and a Lewis base to **2** was regiospecific and stereospecific on the Mo and was cis to the phosphido bridge. The structure of **3a** was determined by single-crystal X-ray methods. Results from the addition reaction under ^{13}CO demonstrated that the transfer of CO from Mo to W was intramolecular. The adjacent metal was believed to assist the addition reaction through the formation of a metal–metal dative bond.

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Supplementary Material Available: Listings of crystal data and refinement details, calculated atomic coordinates, anisotropic thermal parameters, and bond distances and angles and figures giving additional views of compounds **1**, **2**, and **3a** (34 pages). Ordering information is given on any current masthead page.

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