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Substitution Reactions of $CpW_2(CO)_7(\mu\text{-}PPh_2)$ with Diphosphine Ligands

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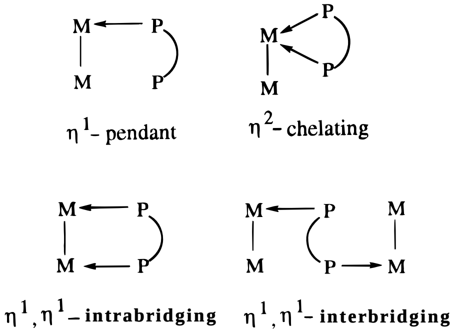
The known complex $CpW_2(CO)_7(\mu\text{-}PPh_2)$ (**1**) has been prepared in good yield from the reaction of $CpW(CO)_3(PPh_2)$ and $W(CO)_4(NCMe)_2$. Compound **1** reacts with the diphosphines PPh_2XPPh_2 (**2**−**5** for X = CH_2, C_2H_4, C_3H_7, and $(C_5H_4)_2Fe$, respectively) to produce $CpW_2(CO)_6(\mu\text{-}PPh_2)(\eta^1\text{-}(PPh_2)_2X)$ (**2a**, **3a**, **4a**, and **5a**), $CpW_2(CO)_5(\mu\text{-}PPh_2)(\eta^2\text{-}(PPh_2)_2X)$ (**2b**, **3b**, and **4b**), and $[CpW_2(CO)_6(\mu\text{-}PPh_2)]_2(\eta^1,\eta^1\text{-}(PPh_2)_2X)$ (**3c**, **4c**, and **5c**). Treating compound **1** with Me_3NO in acetonitrile solution gives $CpW_2(CO)_6(\mu\text{-}PPh_2)(NCMe)$ (**6**). Further treatment of compound **6** with Me_3NO in acetonitrile solution affords $CpW_2(CO)_5(\mu\text{-}PPh_2)(NCMe)_2$ (**7**). Reaction of compound **7** and $CpW(CO)_3(PPh_2)$ leads to $[CpW(CO)_2(\mu\text{-}PPh_2)]_2W(CO)_4$ (**8**). All of the new complexes have been characterized by IR and ^1H and ^{31}P NMR spectroscopies, mass spectrometry, and elemental analyses. **6** was also characterized by X-ray crystallography.

Introduction

The bidentate diphosphine ligands $R_2P(CH_2)_nPR_2$ are interesting to chemists due to their various modes of coordination toward metal atoms[1] and possible catalytic activities of many of their complexes.[2] Recently the organometallic diphosphine ligands, particularly the ferrocenyl derivatives $(R_2PC_5H_4)_2Fe$, have attracted considerable research attention since they also provide a convenient route to the syntheses of bimetallic or polymetallic cluster complexes.[3] Four binding modes have been observed for diphosphines coordinated to bimetallic complexes: η^1-pendant, η^2-chelating, η^1,η^1-intrabridging, and η^1,η^1-interbridging (Chart 1). It has been illustrated that preference for a particular coordination mode depends on the substituents of the phosphine ligands and the ancillary ligands on the metal atoms, as well as the length of linking chains between the two phosphine moieties.[4] For example, the steric bulk of phenyl groups, combined with only one methylene unit separating the two phosphine groups, makes $Ph_2PCH_2PPh_2$ (dppm) difficult to bind bulky metal complexes in an η^1,η^1-intrabridging or an η^1,η^1-interbriding mode.[5]

Chart 1



One of the general reaction patterns for metallophosphines of the type $[M]PPh_2$ ([M] = $CpW(CO)_3$,[6] $CpMo(CO)_3$,[6] $CpRu(CO)_2$,[7] $CpFe(CO)_2$,[7,8] $Co(CO)_4$[9]) is to prepare bimetallic phosphido-bridged complexes.[10] We have improved the synthesis of ditungsten phosphido complex $CpW_2(CO)_7(\mu\text{-}PPh_2)$[11] (**1**) by treating $W(CO)_4(NCMe)_2$ with $CpW(CO)_3(PPh_2)$. As part of our general interest in the systematic chemistry of diphosphine ligands with homonuclear and heteronuclear metal clusters,[12] the present work explores the reactions of

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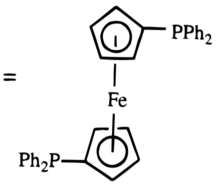
compound **1** with dppm, dppe, dppp, and dppf, which lead to formation and characterization of several new cluster complexes containing W_2, W_2Fe, W_3, W_4, and W_4Fe metal cores.

dppf =



Experimental Section

General Procedures. $CpW(CO)_3(PPh_2)$[13] and $W(CO)_4(NCMe)_2$[14] were prepared according to the literature method. Bis(diphenylphosphino)methane (dppm), bis(diphenylphosphino)ethane (dppe), bis(diphenylphosphino)propane (dppp), and 1,1′-bis(diphenylphosphino)ferrocene (dppf) from Aldrich were used as received. Tetrahydrofuran (THF) was distilled from sodium benzophenone ketyl immediately before use. Dichloromethane and acetonitrile were distilled from calcium hydride before use. Preparative thin-layer chromatographic (TLC) plates were prepared from silica gel (Merck, GF 254). ^1H and ^{31}P NMR spectra were obtained on a Varian VXR-300 spectrometer at 300 and 121.4 MHz, respectively. IR spectra were taken on a Hitachi-2001 spectrometer. Fast-atom bombardment (FAB) mass spectra were obtained on a VG-5022 mass spectrometer. Elemental analyses were performed at the National Science Council Regional Instrumentation Center at National Chen-Kung University, Tainan, Taiwan.

Improved Synthesis of $CpW_2(CO)_7(\mu\text{-}PPh_2)$ (1). An oven-dried, 100 mL Schlenk flask was equipped with a magnetic stir bar and a rubber serum stopper. The stopper was briefly removed, and $CpW(CO)_3(PPh_2)$ (2.30 g, 2.84 mmol) was added against a nitrogen flow. Freshly distilled dichloromethane (10 mL) and THF (10 mL) were added with a gastight syringe to dissolve $Cp(CO)_3W(PPh_2)$. A THF (20 mL) solution of $W(CO)_4(NCMe)_2$ (1.07 g, 2.84 mmol) was then introduced slowly by means of a cannula through the serum stopper. The flask was placed in a water bath at 40 °C for 8 h, forming a dark purple solution. The volatile materials were removed under vacuum, and the residue was subjected to TLC, eluting with dichloromethane/hexane (1:1, v/v). Isolation of material from the purple band gave the known complex $CpW_2(CO)_7(\mu\text{-}PPh_2)$[11] (**1**) (1.40 g, 1.72 mmol) in 61% yield. Mass spectroscopy (FAB): m/z 814 (M^+, ^{184}W), $814 - 28n$ ($n = 1-7$, $M^+ - nCO$). IR (CH_3CN, ν_{CO}): 2076 (m), 1963 (s, br), 1930 (m), 1857 (w) cm^{-1}. ^1H NMR (CD_2Cl_2, 20 °C): δ 5.20 (s, 5H, Cp), 7.65−6.90 (m, 10H, Ph). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 20 °C): δ 149.14 (s; with ^{183}W satellites, $^1J_{W-P} = 132$ and 324 Hz). Anal. Calcd for $C_{24}H_{15}O_7PW_2$: C, 35.41; H, 1.86. Found: C, 35.45; H, 2.01.

Reaction of $CpW_2(CO)_7(\mu\text{-}PPh_2)$ (1) and dppm. Compound **1** (210 mg, 0.26 mmol), dppm (107 mg, 0.28 mmol), and THF (50 mL) were placed in a 100 mL round-bottomed flask, equipped with a reflux condenser and a magnetic stir bar. The solution was refluxed under nitrogen for 20 h. The solvent was removed under vacuum, and the residue was subjected to TLC, eluting with dichloromethane/hexane (1:2, v/v). Isolation of material forming the first brownish-red band gave $CpW_2(CO)_6(\mu\text{-}PPh_2)(\eta^1\text{-dppm})$ (**2a**) (240 mg, 0.21 mmol, 80%). Isolation of material from the second brownish-red band gave $CpW_2(CO)_5(\mu\text{-}PPh_2)(\eta^2\text{-dppm})$ (**2b**) (20 mg, 0.017 mmol, 7%).

Characterization of 2a. Mass spectroscopy (FAB): m/z 1170 (M^+, ^{184}W), $1170 - 28n$ ($n = 1-6$, $M^+ - nCO$). IR (THF, ν_{CO}): 2024 (w), 1964 (w), 1932 (s), 1914 (s, br), 1850 (m) cm^{-1}. ^1H NMR ($CDCl_3$, 20 °C): δ 3.55 (m, 2H, CH_2), 5.07 (s, 5H, Cp), 7.82−6.90 (m, 30H, Ph). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 20 °C): δ −24.79 (d, $^2J_{P-P} = 78$ Hz), 8.99 (dd, $^2J_{P-P} = 78$ and 29 Hz; with ^{183}W satellites, $^1J_{W-P} = 261$ Hz), 143.89 (d, $^2J_{P-P} = 29$ Hz; with ^{183}W satellites, $^1J_{W-P} = 157$ and 305 Hz). Anal. Calcd for $C_{48}H_{37}O_6P_3W_2$: C, 49.26; H, 3.19. Found: C, 49.81; H, 3.47.

Characterization of 2b. Mass spectroscopy (FAB): m/z 1142 (M^+, ^{184}W), $1142-28n$ ($n = 1-5$, $M^+ - nCO$). IR (THF, ν_{CO}): 1988 (w), 1916 (s), 1890 (s), 1862 (s), 1834 (w) cm^{-1}. ^1H NMR (CD_2Cl_2, 20 °C): δ 4.90 (m, 1H, CH_2), 4.97 (s, 5H, Cp), 5.25 (m, 1H, CH_2), 7.81−6.71 (m, 30H, Ph). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 20 °C): δ −41.43 (dd, $^2J_{P-P} = 7$ and 33 Hz; with ^{183}W satellites, $^1J_{W-P} = 187$ Hz), −22.12 (dd, $^2J_{P-P} = 7$ and 57 Hz; with ^{183}W satellites, $^1J_{W-P} = 220$ Hz), 115.78 (dd, $^2J_{P-P} = 33$ and 57 Hz; with ^{183}W satellites, $^1J_{W-P} = 209$ and 248 Hz). Anal. Calcd for $C_{47}H_{37}O_5P_3W_2$: C, 49.41; H, 3.26. Found: C, 49.69; H, 3.45.

Reaction of $CpW_2(CO)_7(\mu\text{-}PPh_2)$ (1) and dppe. Compound **1** (70 mg, 0.086 mmol) and dppe (37 mg, 0.092 mmol) in THF (15 mL) solution was refluxed under nitrogen for 20 h and worked up in a fashion identical with that above. Isolation of the material from the first brownish-red band on TLC gave $CpW_2(CO)_6(\mu\text{-}PPh_2)(\eta^1\text{-dppe})$ (**3a**) (45 mg, 0.038 mmol, 44%), from the second brownish-red band gave $[CpW_2(CO)_6(\mu\text{-}PPh_2)]_2(\eta^1,\eta^1\text{-dppe})$ (**3c**) (31 mg, 0.016 mmol, 37%), and from the third brownish-red band gave $CpW_2(CO)_5(\mu\text{-}PPh_2)(\eta^2\text{-dppe})$ (**3b**) (7 mg, 0.006 mmol, 7%).

Characterization of 3a. Mass spectroscopy (FAB): m/z 1184 (M^+, ^{184}W), $1184 - 28n$ ($n = 1-6$, $M^+ - nCO$). IR (THF, ν_{CO}): 2024 (w), 1966 (w), 1932 (s), 1904 (s), 1850 (m) cm^{-1}. ^1H NMR (CD_2Cl_2, 20 °C): δ 1.95 (m, 2H, CH_2), 2.75 (m, 2H, CH_2), 5.08 (s, 5H, Cp), 7.80−6.92 (m, 30H, Ph). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 20 °C): δ −12.62 (d, $^3J_{P-P} = 38$ Hz), 11.60 (dd, $^2J_{P-P} = 28$, $^3J_{P-P} = 38$ Hz; with ^{183}W satellites, $^1J_{W-P} = 255$ Hz), 143.29 (d, $^2J_{P-P} = 28$ Hz; with ^{183}W satellites, $^1J_{W-P} = 158$ and 310 Hz). Anal. Calcd for $C_{49}H_{39}O_6P_3W_2$: C, 49.69; H, 3.32. Found: C, 50.07; H, 3.51.

Characterization of 3b. Mass spectroscopy (FAB): m/z 1156 (M^+, ^{184}W), $1156 - 28n$ ($n = 1-5$, $M^+ - nCO$). IR (THF, ν_{CO}): 1982 (w), 1916 (s), 1880 (s), 1854 (s) cm^{-1}. ^1H NMR (CD_2Cl_2, 20 °C): δ 2.03, 2.47 (m, 1H, CH_2), 3.07 (m, 2H, CH_2), 4.85 (s, 5H, Cp), 7.76−6.78 (m, 30H, Ph). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 20 °C): δ 26.62 (dd, $J_{P-P} = 7$ and 28 Hz; with ^{183}W satellites, $^1J_{W-P} = 215$ Hz), 45.38 (dd, $J_{P-P} = 7$ and 59 Hz; with ^{183}W satellites, $^1J_{W-P} = 220$ Hz), 106.59 (dd, $J_{P-P} = 28$ and 59 Hz; with ^{183}W satellites, $^1J_{W-P} = 222$ and 234 Hz). Anal. Calcd for $C_{48}H_{39}O_5P_3W_2$: C, 49.85; H, 3.40. Found: C, 50.31; H, 3.52.

Characterization of 3c. Mass spectroscopy (FAB): m/z 1970 (M^+, ^{184}W), 1184 ($M^+ - [CpW_2(CO)_6(PPh_2)]$), $1184-28n$ ($n = 1-6$). IR (THF, ν_{CO}): 2024 (w), 1968 (w), 1932 (s), 1904 (s, br), 1850 (m) cm^{-1}. ^1H NMR (CD_2Cl_2, 20 °C): δ 2.57 (br, 4H, CH_2), 5.07 (s, 10H, Cp), 7.76−6.86 (m, 40H, Ph). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 20 °C): δ 11.15 (d, $J_{P-P} = 27$ Hz; with ^{183}W satellites, $^1J_{W-P} = 261$ Hz), 143.58 (d, $J_{P-P} = 27$ Hz; with ^{183}W satellites, $^1J_{W-P} = 156$ and 305 Hz). Anal. Calcd for $C_{72}H_{54}O_{12}P_4W_4$: C, 43.89; H, 2.76. Found: C, 43.88; H, 3.10.

Reaction of $CpW_2(CO)_7(\mu\text{-}PPh_2)$ and dppp. Compound **1** (81 mg, 0.1 mmol) and dppp (60 mg, 0.14 mmol) in THF (10 mL) solution was refluxed under nitrogen for 15 h and worked up in a fashion identical with that above. Isolation of the material from the first brownish-red band on TLC gave $CpW_2(CO)_6(\mu\text{-}PPh_2)(\eta^1\text{-dppp})$ (**4a**) (59 mg, 0.049 mmol, 49%), from the second brownish-red band gave $CpW_2(CO)_5(\mu\text{-}PPh_2)(\eta^2\text{-dppp})$ (**4b**) (15 mg, 0.013 mmol, 13%), and from the third brownish-red band gave $[CpW_2(CO)_6(\mu\text{-}PPh_2)]_2(\eta^1,\eta^1\text{-dppp})$ (**4c**) (28 mg, 0.014 mmol, 28%).

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Characterization of 4a. Mass spectroscopy (FAB): *m/z* 1198 (M^+, ^{184}W), 1198 − 28*n* ($n = 1-6$, $M^+ - n$CO). IR (THF, ν_{CO}): 2024 (w), 1967 (w), 1931 (s), 1909 (s, br), 1848 (m) cm^{-1}. ^{1}H NMR (CD_2Cl_2, 20 °C): δ 1.48 (m, 2H, CH_2), 2.11 (m, 2H, CH_2), 2.89 (m, 2H, CH_2), 5.03 (s, 5H, Cp), 7.76−6.92 (m, 30H, Ph). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 20 °C): δ −17.82 (s), 7.20 (d, $^2J_{P-P} = 27$ Hz; with ^{183}W satellites, $^1J_{W-P} = 255$ Hz), 143.30 (d, $^2J_{P-P} = 27$ Hz; with ^{183}W satellites, $^1J_{W-P} = 158$ and 307 Hz). Anal. Calcd for $C_{50}H_{41}O_6P_3W_2$: C, 50.11; H, 3.45. Found: C, 49.62; H, 3.66.

Characterization of 4b. Mass spectroscopy (FAB): *m/z* 1170 (M^+, ^{184}W), 1170 − 28*n* ($n = 1-5$, $M^+ - n$CO). IR (THF, ν_{CO}): 1974 (w), 1914 (s), 1869 (s), 1851 (s) cm^{-1}. ^{1}H NMR (CD_2Cl_2, 20 °C): δ 1.98 (m, 2H, CH_2), 2.40, 2.51 (m, 1H, CH_2), 2.76 (m, 3H, CH_2), 4.83 (s, 5H, Cp), 7.58−6.81 (m, 30H, Ph). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 20 °C): δ −16.45 (t, $^2J_{P-P} = 29$ Hz; with ^{183}W satellites, $^1J_{W-P} = 205$ Hz), −2.64 (dd, $^2J_{P-P} = 29$ and 56 Hz; with ^{183}W satellites, $^1J_{W-P} = 208$ Hz), 107.61 (dd, $^2J_{P-P} = 29$ and 56 Hz; with ^{183}W satellites, $^1J_{W-P} = 226$ Hz). Anal. Calcd for $C_{49}H_{41}O_5P_3W_2$: C, 50.27; H, 3.53. Found: C, 49.62; H, 3.66.

Characterization of 4c. Mass spectroscopy (FAB): *m/z* 1984 (M^+, ^{184}W). IR (THF, ν_{CO}): 2024 (w), 1964 (w), 1931 (s), 1908 (s, br), 1849 (m) cm^{-1}. ^{1}H NMR (CD_2Cl_2, 20 °C): δ 2.72 (br, 2H, CH_2), 2.84 (br, 4H, CH_2), 5.32 (s, 10H, Cp), 7.74−6.88 (m, 40H, Ph). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 20 °C): δ 6.72 (d, $^2J_{P-P} = 28$ Hz; with ^{183}W satellites, $^1J_{W-P} = 255$ Hz), 143.10 (d, $^2J_{P-P} = 27$ Hz; with ^{183}W satellites, $^1J_{W-P} = 159$ and 305 Hz). Anal. Calcd for $C_{73}H_{56}O_{12}P_4W_4$: C, 44.18; H, 3.45. Found: C, 44.41; H, 3.27.

Reaction of $CpW_2(CO)_7(\mu\text{-}PPh_2)$ (1) and dppf. A solution of compound **1** (91 mg, 0.11 mmol) and dppf (73 mg, 0.132 mmol) in THF (15 mL) was refluxed under nitrogen for 20 h. The products were worked up in a fashion identical with that above. Isolation of the material from the third, brown-red band on TLC gave $CpW_2(CO)_6(\mu\text{-}PPh_2)(\eta^1\text{-dppf})$ (**5a**) (96 mg, 0.072 mmol, 65%) and from the fourth brown-red band gave $[CpW_2(CO)_6(\mu\text{-}PPh_2)]_2(\eta^1,\eta^1\text{-dppf})$ (**5c**) (28 mg, 0.014 mmol, 14%).

Characterization of 5a. Mass spectroscopy (FAB): *m/z* 1341 (M^+, ^{184}W), 1341 − 28*n* ($n = 1-6$, $M^+ - n$CO), 554 (dppf). IR (THF, ν_{CO}): 2024 (w), 1964 (w), 1932 (s), 1911 (s, br), 1849 (m) cm^{-1}. ^{1}H NMR (CD_2Cl_2, 20 °C): δ 3.81, 4.04, 4.16, 4.40 (s, 2H, C_5H_4), 5.08 (s, 5H, Cp), 7.77−6.95 (m, 30H, Ph). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 20 °C): δ −17.75 (s), 9.93 (d, $^2J_{P-P} = 28$ Hz; with ^{183}W satellites, $^1J_{W-P} = 262$ Hz), 143.80 (d, $^2J_{P-P} = 28$ Hz; with ^{183}W satellites, $^1J_{W-P} = 181$ and 307 Hz). Anal. Calcd for $C_{57}H_{43}O_6P_3FeW_2$: C, 51.08; H, 3.23. Found: C, 51.23; H, 3.36.

Characterization of 5c. Mass spectroscopy (FAB): *m/z* 2127 (M^+, ^{184}W), 1342 ($M^+ - CpW_2(CO)_6(PPh_2)$). IR (THF, ν_{CO}): 2024 (w), 1964 (w), 1932 (s), 1906 (s, br), 1850 (m) cm^{-1}. ^{1}H NMR (CD_2Cl_2, 20 °C): δ 3.85−4.24 (m, C_5H_4), 5.06 (s, 10H, Cp), 7.40 (m, 40H, Ph). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 20 °C): δ 10.72 (d, $^2J_{P-P} = 28$ Hz; with ^{183}W satellites, $^1J_{W-P} = 264$ Hz), 143.73 (d, $^2J_{P-P} = 28$ Hz; with ^{183}W satellites, $^1J_{W-P} = 153$ and 307 Hz). Anal. Calcd for $C_{80}H_{58}O_{12}P_4FeW_4$: C, 45.19; H, 2.75. Found: C, 45.06; H, 2.94.

Preparation of $CpW_2(CO)_6(\mu\text{-}PPh_2)(NCMe)$ (6). $CpW_2(CO)_7(\mu\text{-}PPh_2)$ (**1**) (1 g, 1.2 mmol) and acetonitrile (20 mL) were placed in an oven-dried 100 mL Schlenk flask, equipped with a magnetic stir bar and a rubber serum stopper, under nitrogen atmosphere. A solution of Me_3NO (110 mg, 1.45 mmol) in acetonitrile (10 mL) was slowly introduced into the flask *via* a syringe over a period of 30 min. The mixture was stirred at room temperature for 1 h, at which point the IR spectrum showed no absorptions due to compound **1**. During reaction, the color changed from purple to dark red. The solution was concentrated to ca. 15 mL, and methanol (15 mL) was slowly introduced into the flask. The flask was placed in a freezer at −20 °C overnight to form dark red crystals, characterized as $CpW_2(CO)_6(\mu\text{-}PPh_2)(NCMe)$ (**6**) (856 mg, 1.04 mmol, 87%). Mass spectroscopy (FAB): *m/z* 827 (M^+, ^{184}W), 786 (M^+ − NCMe), 786−28*n* ($n = 1-6$). IR (CH_3CN, ν_{CO}): 2018 (m), 1931 (s, br), 1881 (m), 1848 (w) cm^{-1}. ^{1}H NMR (CD_2Cl_2, 20 °C): δ 1.93 (s, 3H, Me), 5.19 (s, 5H, Cp), 7.84−7.02 (m, 10H, Ph). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, −50 °C): δ 164.10 (s; with ^{183}W satellites, $^1J_{W-P} = 138$ and 332 Hz). Anal. Calcd for $C_{25}H_{18}NO_6PW_2$: C, 36.31; H, 2.19; N, 1.69. Found: C, 35.57; H, 2.22; N, 1.76.

Preparation of $CpW_2(CO)_5(\mu\text{-}PPh_2)(NCMe)_2$ (7). $CpW_2(CO)_6(\mu\text{-}PPh_2)(NCMe)$ (**6**) (500 mg, 0.6 mmol) and acetonitrile (15 mL) were placed in an oven-dried 100 mL Schlenk flask, equipped with a magnetic stir bar and a rubber serum stopper, under nitrogen atmosphere. A solution of Me_3NO (54 mg, 0.72 mmol) in acetonitrile (10 mL) was slowly introduced into the flask over a period of 30 min. The mixture was stirred at room temperature for 30 min, at which point the IR spectrum showed no absorptions due to compound **6**. The solution was concentrated to ca. 10 mL, and methanol (10 mL) was added. The flask was placed in a freezer at −20 °C for 5 days to give dark red crystals, characterized as $CpW_2(CO)_5(\mu\text{-}PPh_2)(NCMe)_2$ (**7**) (380 mg, 0.45 mmol, 75%). Mass spectroscopy (FAB): *m/z* 840 (M^+, ^{184}W), 758 (M^+ − 2 NCMe), 758 − 28*n* ($n = 1-5$). IR (CH_3CN, ν_{CO}): 1958 (m), 1912 (s), 1865 (sh), 1842 (s) cm^{-1}. ^{1}H NMR (CD_2Cl_2, 20 °C): δ 1.92 (s, br, 6H, Me), 5.14 (s, 5H, Cp), 7.78−6.94 (m, 10H, Ph). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, −50 °C): δ 138.96 (s; with ^{183}W satellites, $^1J_{W-P} = 161$ and 303 Hz). Anal. Calcd for $C_{26}H_{21}N_2O_5PW_2$: C, 37.17; H, 2.52; N, 3.33. Found: C, 36.16; H, 2.50; N, 2.96.

Structure Determination for $CpW_2(CO)_6(\mu\text{-}PPh_2)(NCMe)$ (6). A suitable crystal of compound **6** with approximate dimensions of 0.25 × 0.33 × 0.33 mm was mounted on a glass fiber and aligned on a Rigaku AFC7S diffractometer. Diffraction data were collected with graphite-monochromated Mo Kα radiation using the $\omega-2\theta$ scan technique. Lattice parameters were determined from 20 carefully centered reflections in the range $6.9 < 2\theta < 12.4°$. The systematic absences of $h0l$ ($h + l \neq 2n$) and $0k0$ ($k \neq 2n$) uniquely determine the space group to be $P2_1/n$ (No. 14, nonstandard setting). The data were collected at 24 °C with a maximum 2θ value of 47.0°. Scans with width of $(0.94 + 0.30 \tan \theta)°$ were made at a speed of 16.0°/min (in ω). Of the 4144 reflections which were collected, 3973 were unique ($R_{int} = 0.079$). The intensities of three representative reflections were measured after every 150 reflections; no decay was observed. An empirical absorption correction based on azimuthal scans of several reflections was applied which resulted in transmission factors ranging from 0.70 to 1.00. The data were corrected for Lorentz and polarization effects. The structure was solved by direct methods[15] and expanded using Fourier techniques.[16] The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. The final cycle of full-matrix least-squares refinement was based on 3219 observed reflections ($I > 3.00\sigma(I)$) and 311 variable parameters. All calculations were carried out with the TEXSAN crystallographic software package of the Molecular Structure Corp.[17] A summary of relevant crystallographic data is provided in Table 1.

Reactions of $CpW_2(CO)_6(\mu\text{-}PPh_2)(NCMe)$ (6) with dppm, dppe, dppp, and dppf. A typical reaction, $CpW_2(CO)_6(\mu\text{-}PPh_2)(NCMe)$ (**6**) (246 mg, 0.3 mmol) and dppm (120 mg, 0.33 mmol) were placed in a 50 mL Schlenk flask under N_2, and 10 mL of THF was introduced. The solution was stirred at room temperature for 10 min, at which point the IR spectrum showed no absorptions due to compound **6**. The solvent was removed under vacuum and the residue separated by TLC. $CpW_2(CO)_6(\mu\text{-}PPh_2)(\eta^1\text{-dppm})$ (**2a**) was isolated in 88% yield.

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(15) SIR92: Altomare, A.; Cascarano, M.; Giacovazzo, C.; Guagliardi, A. *J. Appl. Crystallogr.* **1993**, *26*, 343.

(16) DIRDIF94: Beurskens, P. T.; Admiraal, G.; Beurskens, G.; Bosman, W. P.; de Gelder, R.; Israel, R.; Smits, J. M. M. Technical Report of the Crystallography Laboratory, University of Nijmegen, The Netherlands, 1994.

(17) TEXSAN: Crystal Structure Analysis Package, Molecular Structure Corp., 1985, 1992.

Table 1. Experimental Data for the X-ray Diffraction Study of Compound 6

chem formula: $C_{25}H_{18}O_6NPW_2$	fw: 827.09
$a = 14.656(4)$ Å	space group: $P2_1/n$ (No. 14)
$b = 11.524(2)$ Å	$T = 24$ °C
$c = 15.082(5)$ Å	$\lambda = 0.710\ 69$ Å
$\beta = 92.86(3)°$	$D_{calcd} = 2.159$ g/cm^3
$V = 2543(1)$ Å^3	$\mu = 91.50$ cm^{-1}
$Z = 4$	$R^a = 0.056$
$2\theta_{\max} = 47.0°$	$R_w{}^b = 0.057$
goodness of fit: 3.35	

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum wF_o{}^2]^{1/2}$.

The reaction of compound **6** and dppe afforded $CpW_2(CO)_6(\mu\text{-}PPh_2)(\eta^1\text{-dppe})$ (**3a**) (43%) and $[CpW_2(CO)_6(\mu\text{-}PPh_2)]_2(\eta^1,\eta^1\text{-dppe})$ (**3c**) (9%).

The reaction of compound **6** and dppp afforded $CpW_2(CO)_6(\mu\text{-}PPh_2)(\eta^1\text{-dppp})$ (**4a**) (48%) and $[CpW_2(CO)_6(\mu\text{-}PPh_2)]_2(\eta^1,\eta^1\text{-dppp})$ (**4c**) (7%).

The reaction of compound **6** and dppf afforded $CpW_2(CO)_6(\mu\text{-}PPh_2)(\eta^1\text{-dppf})$ (**5a**) (46%) and $[CpW_2(CO)_6(\mu\text{-}PPh_2)]_2(\eta^1,\eta^1\text{-dppf})$ (**5c**) (11%).

Reactions of $CpW_2(CO)_5(\mu\text{-}PPh_2)(NCMe)_2$ (7) with dppm, dppe, dppp, and dppf. Typically, $CpW_2(CO)_5(\mu\text{-}PPh_2)(NCMe)_2$ (**7**) (240 mg, 0.3 mmol) and dppm (120 mg, 0.33 mmol) were placed in a 50 mL Schlenk flask under N_2 and 10 mL of THF was introduced. The solution was stirred at room temperature for 30 min, at which point the IR spectrum showed no absorptions due to compound **7**. The solvent was removed under vacuum and the residue separated by TLC. $CpW_2(CO)_6(\mu\text{-}PPh_2)(\eta^1\text{-dppm})$ (**2a**) (6%) and $CpW_2(CO)_5(\mu\text{-}PPh_2)(\eta^2\text{-dppm})$ (**2b**) (73%) were isolated.

The reaction of compound **7** and dppe afforded $CpW_2(CO)_6(\mu\text{-}PPh_2)(\eta^1\text{-dppe})$ (**3a**) (10%), $CpW_2(CO)_5(\mu\text{-}PPh_2)(\eta^2\text{-dppe})$ (**3b**) (41%), and $[CpW_2(CO)_6(\mu\text{-}PPh_2)]_2(\eta^1,\eta^1\text{-dppe})$ (**3c**) (4%).

The reaction of compound **7** and dppp afforded $CpW_2(CO)_6(\mu\text{-}PPh_2)(\eta^1\text{-dppp})$ (**4a**) (14%), $CpW_2(CO)_5(\mu\text{-}PPh_2)(\eta^2\text{-dppp})$ (**4b**) (37%), and $[CpW_2(CO)_6(\mu\text{-}PPh_2)]_2(\eta^1,\eta^1\text{-dppp})$ (**4c**) (11%).

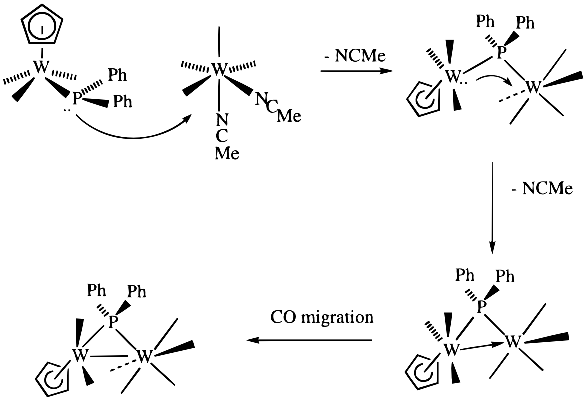
The reaction of compound **7** and dppf afforded $CpW_2(CO)_6(\mu\text{-}PPh_2)(\eta^1\text{-dppf})$ (**5a**) (21%) and $[CpW_2(CO)_6(\mu\text{-}PPh_2)]_2(\eta^1,\eta^1\text{-dppf})$ (**5c**) (5%).

Synthesis of $[CpW(CO)_2(\mu\text{-}PPh_2)]_2W(CO)_4$ (8). $CpW_2(CO)_5(\mu\text{-}PPh_2)(NCMe)_2$ (**7**) (350 mg, 0.42 mmol) and THF (15 mL) were placed in an oven-dried 100 mL Schlenk flask, equipped with a magnetic stir bar and a rubber serum stopper. A solution of $CpW(CO)_3(PPh_2)$ (260 mg, 0.5 mmol) in THF (15 mL) was slowly added into the flask. The mixture was stirred under N_2 at ambient temperature for 8 h. The solvent was removed under vacuum, and the residue was dissolved in dichloromethane and subjected to TLC, eluting with dichloromethane/ hexane (1:2, v/v). A small amount of compound **1** (7 mg, <2%) was obtained from the first, purple band. The material from the second, orange-red band afforded $[CpW(CO)_2(\mu\text{-}PPh_2)]_2W(CO)_4$ (**8**) (320 mg, 0.25 mmol, 60%). Mass spectroscopy (FAB): m/z 1276 (M^+, ^{184}W), $1276 - 28n$ ($n = 1-8$). IR (THF, ν_{CO}): 2032 (w), 1984 (w), 1943 (s), 1930 (sh), 1915 (s), 1860 (m) cm^{-1}. ^1H NMR (CD_2Cl_2, 20 °C): δ 4.93 (s, 5 H, Cp), 5.10 (s, 10H, Cp), 5.13 (s, 5H, Cp), 7.92−6.88 (m, 40H, Ph). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 20 °C): δ 132.93 (d, $^2J_{P-P} = 12$ Hz; with ^{183}W satellites, $^1J_{W-P} = 119$ and 306 Hz), 128.59 (s; with ^{183}W satellites, $^1J_{W-P} = 127$ and 293 Hz), 124.30 (d, $^2J_{P-P} = 12$ Hz; with ^{183}W satellites, $^1J_{W-P} = 127$ and 303 Hz). Anal. Calcd for $C_{42}H_{30}O_8P_2W_3$: C, 39.53; H, 2.37. Found: C, 39.32; H, 2.56.

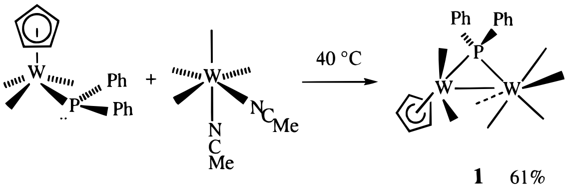
Results and Discussion

Synthesis of $CpW_2(CO)_7(\mu\text{-}PPh_2)$ (1). Treatment of $CpW(CO)_3(PPh_2)$ with $W(CO)_4(NCMe)_2$ at 40 °C for 8 h affords the known complex $CpW_2(CO)_7(\mu\text{-}PPh_2)$[11] (**1**) as the only metal-containing product (eq 1). Shyu and co-workers have previously reported similar reaction of $Cp(CO)_3W(PPh_2)$ and $W(CO)_5(THF)$ at room temperature, but producing compound **1** and $CpW_2(CO)_8(\mu\text{-}PPh_2)$ (**9**) in moderate yields (eq 2). Furthermore, irradiating **9** led to **1**, while no reaction was observed upon thermolysis of **9**.[11]

Scheme 1

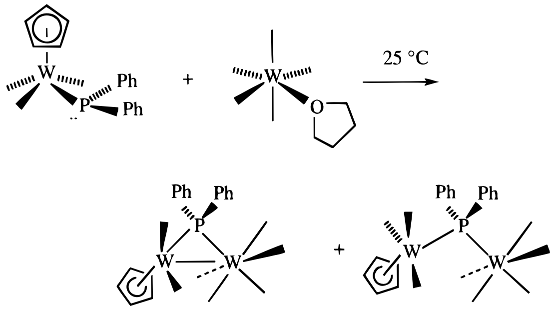


1



(1)

1 61%



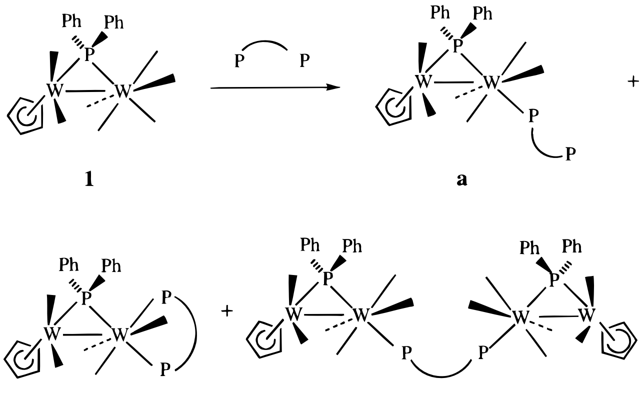
(2)

1 21% **9** 17%

Obviously, forming the W−W bond from **9** to **1** requires activation of a strongly-bonded carbonyl ligand through photolysis. In the present work two carbonyls of $W(CO)_6$ have been replaced by the more labile acetonitrile ligands. Thus, the metallic phosphido species could first attack $W(CO)_4(NCMe)_2$ to generate $CpW(CO)_3(\mu\text{-}PPh_2)W(CO)_4(NCMe)$, followed by W−W bond formation with elimination of the remaining acetonitrile ligand and CO migration to give compound **1** (Scheme 1).

Compound **1** forms air-stable, purple crystals. The structure of **1** consists of a bimetallic $Cp(CO)_2WW(CO)_5$ group bridged by a diphenylphosphido ligand, where the W−W vector about bisects an edge of the $W(CO)_5(P)$ octahedron.[11]

Reactions of $CpW_2(CO)_7(\mu\text{-}PPh_2)$ and Diphosphines. Treating $CpW_2(CO)_7(\mu\text{-}PPh_2)$ (**1**) with Ph_2PXPPh_2 (X = CH_2, C_2H_4, C_3H_6, and $(C_5H_4)_2Fe$) in refluxing THF for 15−20 h generates a series of products containing η^1-pendant (**a**), η^2-chelating (**b**), and η^1,η^1-interbridging (**c**) diphosphine ligands (eq 3). There is no indication for forming the complexes with the diphosphine ligands in an η^1,η^1-intrabridging mode, presumably due to steric bulk of the cyclopentadienyl



P⌒P =		
dppm	**2a** (80%) + **2b** (7%)	
dppe	**3a** (44%) + **3b** (7%)	+ **3c** (44%)
dppp	**4a** (49%) + **4b** (13%)	+ **4c** (28%)
dppf	**5a** (65%)	+ **5c** (14%)

(3)

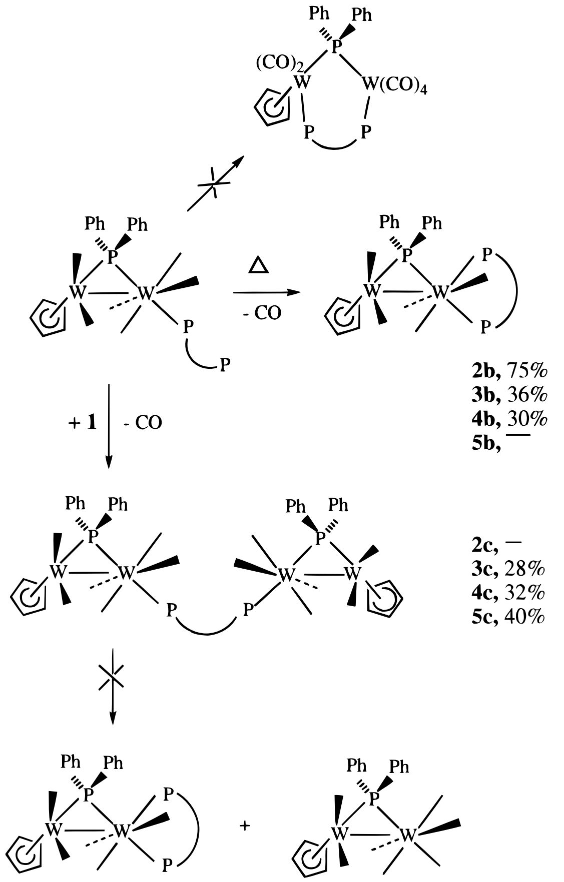
and phenyl groups making the CpW(CO)(PPh_2) moiety too crowded to coordinate another phosphine group. By contrast, thermal reactions between the heterobimetallic analogue (CpW)Mo$(CO)_7$(μ-PPh_2) and diphosphines (dppm and dppe) afforded (CpW)Mo$(CO)_5$(μ-PPh_2)(η^2-dppm) and (CpW)Mo$(CO)_5$(μ-PPh_2)(η^2-dppe) with dppm and dppe ligands chelating the molybdenum atom as the only isolated products.[18] It is apparent that the weaker Mo−CO bond strength[19] relative to W−CO accelerates substitution of two adjacent carbonyl ligands by diphosphine at elevated temperature.

Thermolysis of **a** complexes results in decarbonylation and chelation of the dangling phosphine to give **b** complexes (except **5a**). However, **c** complexes are obtained as major products (except **2a**) if compound **1** is present. Interestingly, heating **c** complexes does not lead to CO transfer to regenerate **1** and **b** complexes. The results are summarized in Scheme 2.

The ratio of **b** and **c** complexes is different, depending on the type of linking chains between the two PPh_2 moieties. It is obvious that the small bite angle of dppm (ca. 65°)[20] favors the chelated product **2b**, while only a methylene unit separating two bulky PPh_2 groups makes **2c** too unstable to be isolated. On the other hand, the two PPh_2 groups in dppf are separated by a large ferrocenyl moiety and are free to form bidentate complex **5c**, but its large bite angle (ca. 98°)[12a,21] hinders **5b** from being generated. Since the dppe and dppp ligands are able to form stable five- and six-membered chelating rings and would not impose strong steric interactions between the two PPh_2 groups, both the **b**- and **c**-types of products result.

Characterization of 2a, 3a, 4a, and 5a. These compounds show very similar ^{31}P NMR spectra and almost identical IR absorption patterns in the carbonyl region, suggesting great resemblance of their structures. It is likely that the η^1-diphosphine ligand replaces a carbonyl trans to the phosphido ligand to minimize repulsions with the Cp and the μ-PPh_2 groups. In the analogous complexes $CpW_2(CO)_6(\mu\text{-}PPh_2)(PX_3)$ (X = OMe, Et, and Ph) the monodentate phosphine ligands were found trans to the bridging diphenylphosphido group.[11]

Scheme 2



The IR spectra in the CO region of **a** complexes are shifted to lower energy compared with that of **1**, consistent with the stronger σ-donor and weaker π-acceptor ability of phosphine ligand relative to CO.[1c,22] The $^{31}P\{^1H\}$ NMR spectrum for **4a**, presented in Figure 1a, is assigned on the basis of chemical shifts and coupling patterns of the signals. It is apparent that W−W bond is retained in **a** complexes since their phosphido resonances are comparable with the parent complex **1** (δ 149.14), whereas a significant upfield ^{31}P resonance for PPh_2 bridging two metal atoms without a metal−metal bond has been observed for $Cp(CO)_3W(\mu\text{-}PPh_2)W(CO)_5$ (δ −62.72),[11] $Cp(CO)_3W(\mu\text{-}PPh_2)Mo(CO)_5$ (δ −41.66),[18] and $Cp(CO)_3W(\mu\text{-}PPh_2)Fe(CO)_3$ (δ −10.41).[10d]

Characterization of 2b, 3b, and 4b. The ^{31}P NMR spectra of these complexes are alike and their IR absorption patterns in the carbonyl region are almost identical, again suggesting similar structures for them. The $^{31}P\{^1H\}$ spectrum of **4b**, shown in Figure 1b, consists of three sets of resonance signals accompanied by ^{183}W satellites. This indicates that all the phosphorus atoms are coordinated to the tungsten atoms. It is probable the dangling phosphine in **a** complexes replaces a carbonyl cis to the phosphido group to form **b** complexes. We note that the resonance at δ −16.46 shows equal coupling to the other two cis phosphorus atoms ($^2J_{P-P}$ = 29 Hz), thus appearing as a pseudo-

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[18] Wu, W.-J.; Hsu, J.-Y.; Wen, Y.-S.; Shyu, S.-G. *J. Chin. Chem. Soc.* **1995**, *42*, 533.

[19] Marks, T. J., Ed. *Bonding Energetics in Organometallic Compounds*; ACS Symposium Series 428; American Chemical Society: Washington, DC, 1990.

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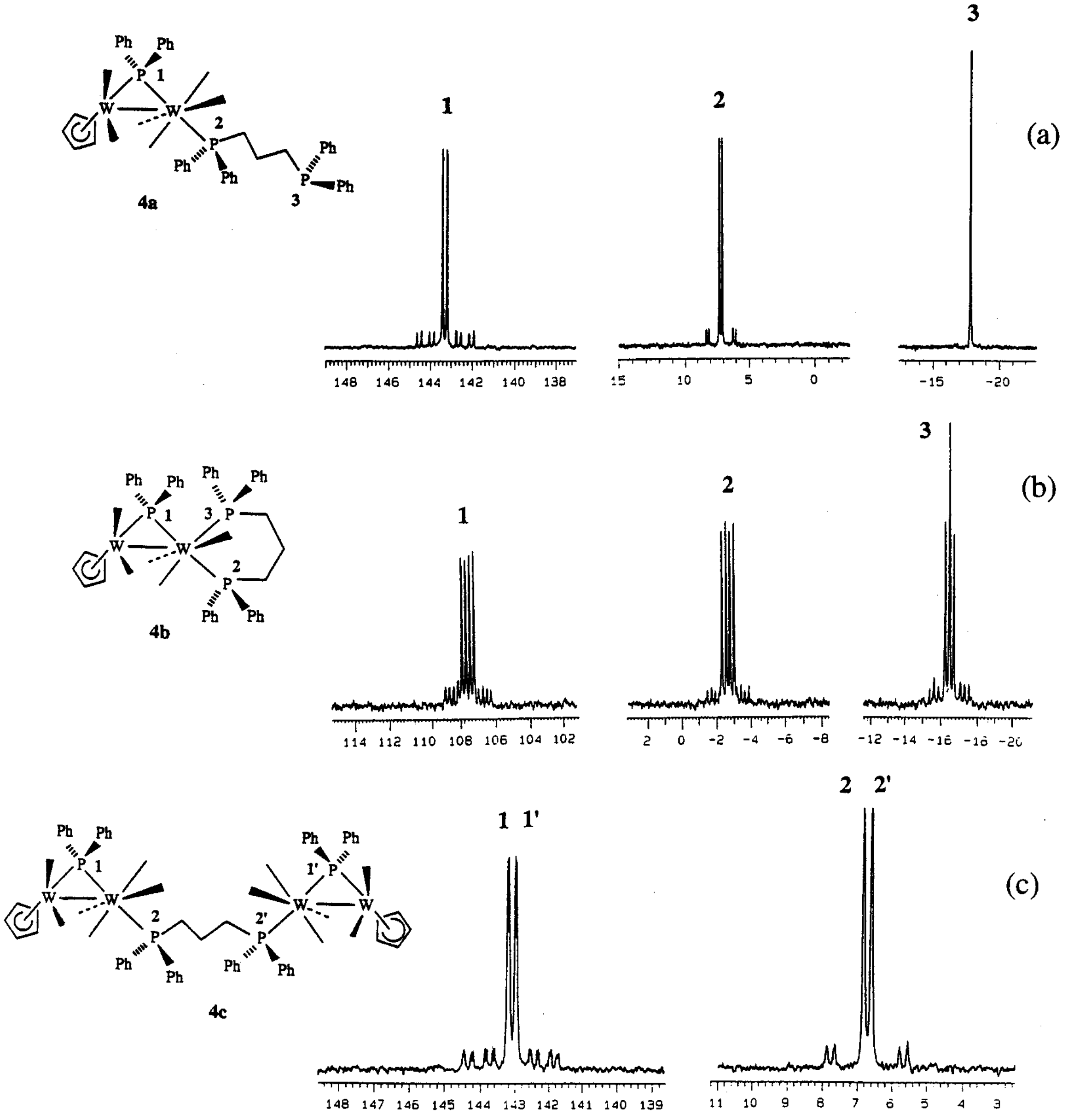

Figure 1. $^{31}P\{^1H\}$ NMR spectra of (a) $CpW_2(CO)_6(\mu\text{-}PPh_2)(\eta^1\text{-dppp})$ (**4a**), (b) $CpW_2(CO)_5(\mu\text{-}PPh_2)(\eta^2\text{-dppp})$ (**4b**), and (c) $[CpW_2(CO)_6(\mu\text{-}PPh_2)]_2(\eta^1,\eta^1\text{-dppp})$ (**4c**) in CD_2Cl_2 at 20 °C.

triplet. The IR absorptions in the CO region of **b** complexes are in lower energy region than those of **a** complexes, in agreement with chelation of the good electron-donating phosphine ligands.

Characterization of 3c, 4c, and 5c. The IR spectra of **3c**, **4c**, and **5c** in the carbonyl stretching region are essentially identical and closely matching those of **a** complexes, indicating that the $CpW_2(CO)_6(\mu\text{-}PPh_2)$ moieties in the **a**- and **c**-types of complexes are structurally similar. Apparently, **c** complexes consist of two identical $[CpW_2(CO)_6(\mu\text{-}PPh_2)]$ units bound to a diphosphine ligand in a fashion similar to that for **a** complexes. Thus, the $^{31}P\{^1H\}$ NMR spectrum of **4c**, illustrated in Figure 1c, shows two doublet signals with each accompanied by two pairs of ^{183}W satellites. The ^1H NMR spectrum of **4c** includes a multiplet at δ 7.30 for the phenyl protons, a singlet at δ 5.32 for the Cp protons, and two broad signals δ at 2.72 and 2.84 in an 1:2 ratio for the propylene protons. An inversion center or a plane of symmetry is apparently passing through the **c** complexes to result in equivalent phosphido, phosphine, and Cp groups.

Syntheses and Characterization of $CpW_2(CO)_6(\mu\text{-}PPh_2)(NCMe)$ (6) and $CpW_2(CO)_5(\mu\text{-}PPh_2)(NCMe)_2$ (7). Since reactions of **1** and diphosphines require elevated temperature and lead to several products, we decided to prepare more reactive substrates by replacing carbonyls with labile ligands. Thus, treating $CpW_2(CO)_7(\mu\text{-}PPh_2)$ with 1 equiv of Me_3NO in CH_3CN solution effects displacement of a CO ligand by solvent molecule to generate $CpW_2(CO)_6(\mu\text{-}PPh_2)(NCMe)$ (**6**) in 87% yield. Further reaction of **6** and Me_3NO in CH_3CN affords $CpW_2(CO)_5(\mu\text{-}PPh_2)(NCMe)_2$ (**7**) in 75% yield.

Both compounds **6** and **7** form dark red, air-stable crystalline solids. The IR spectrum of **6** shows four CO absorption peaks ranging from 2018 to 1848 cm^{-1}, which are apparently between those measured for **1** and **a** complexes. This is consistent with the electron-donating ability of the ligands in the order $PR_3 > NCMe > CO$.[23] The variable-temperature $^{31}P\{^1H\}$ NMR spectra exhibit a broad resonance at 25 °C, while a sharp singlet at δ

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(23) Morris, M. J. In *Comprehensive Organometallic Chemistry II*; Abel, E. W., Stone, F. G. A., Wilkinson, G., Eds.; Pergamon: Oxford, U.K., 1995; Vol. 5.

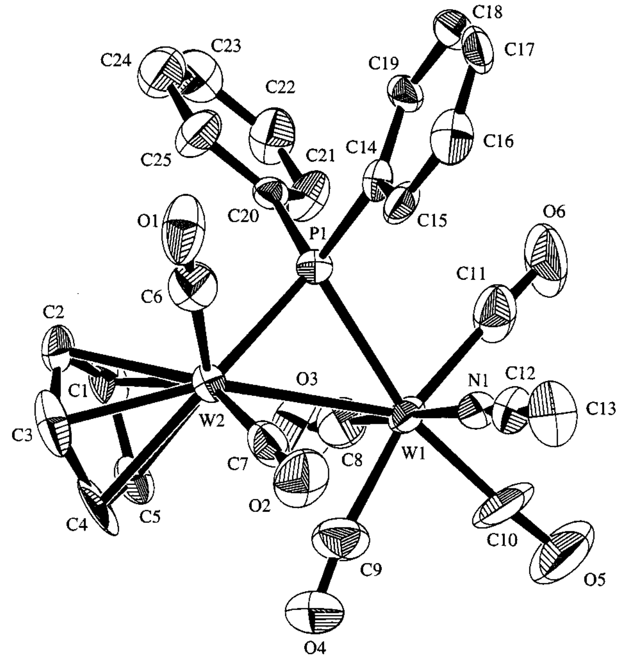


Figure 2. ORTEP diagram of $CpW_2(CO)_6(\mu\text{-}PPh_2)(NCMe)$ (**6**), showing the atomic labeling used in the text.

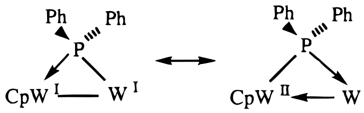
164.10 with two pairs of ^{183}W satellites is observed at −40 °C. The results suggest that compound **6** is fluxional in solution, presumably through rotation of a tungsten−phosphido bond within rapid cleavage and re-formation of the W−W bond.[24] A plausible alternative pathway is via 3-fold rotation[25] of the carbonyl and acetonitrile ligands in the $W(CO)_4(NCMe)$ unit without breaking the W−W bond.

The FAB mass spectrum of **7** presents the molecular ion peak at $m/z = 840$ for ^{184}W and ions corresponding to loss of two acetonitriles and five carbonyls. The $^{31}P\{^1H\}$ NMR spectrum at 25 °C shows a broad resonance at δ 138.94, which becomes a sharp singlet accompanied by two pairs of ^{183}W satellites at −50 °C. The ^1H NMR spectrum shows a multiplet in the range δ 7.78−6.94 for the phenyl protons, a singlet at δ 5.14 for the Cp protons, and a broad singlet at δ 1.92 for the acetonitrile protons. Equivalence of the two acetonitrile ligands is presumably through a dynamic process similar to that proposed for **6**.

Table 2. Selected Bond Lengths (Å) and Bond Angles (deg) of Compound 6

	Bond Lengths		
W1−W2	3.171(1)	W1−P1	2.513(4)
W1−N1	2.21(1)	W1−C8	1.94(2)
W1−C9	2.08(2)	W1−C10	1.98(2)
W1−C11	2.03(2)	W2−P1	2.364(4)
W2−C1	2.36(2)	W2−C2	2.30(1)
W2−C3	2.27(2)	W2−C4	2.36(2)
W2−C5	2.38(2)	W2−C6	1.93(2)
W2−C7	1.92(2)	P1−C14	1.81(1)
P1−C20	1.81(1)	O1−C6	1.16(2)
O2−C7	1.18(2)	O3−C8	1.19(2)
O4−C9	1.12(2)	O5−C10	1.16(2)
O6−C11	1.14(2)	N1−C12	1.14(2)
C1−C2	1.41(2)	C1−C5	1.42(2)
C2−C3	1.40(3)	C3−C4	1.41(3)
C4−C5	1.35(2)	C12−C13	1.47(2)
	Bond Angles		
W2−W1−P1	47.42(9)	W2−W1−N1	90.3(3)
W2−W1−C8	88.3(5)	W2−W1−C9	65.7(5)
W2−W1−C10	147.9(6)	W2−W1−C11	127.2(5)
P1−W1−N1	90.5(3)	P1−W1−C8	90.1(5)
P1−W1−C9	113.0(5)	P1−W1−C10	164.6(6)
P1−W1−C11	79.8(5)	N1−W1−C8	177.5(6)
N1−W1−C9	87.4(6)	N1−W1−C10	88.6(7)
N1−W1−C11	90.7(6)	C8−W1−C9	90.1(7)
C8−W1−C10	91.5(8)	C8−W1−C11	91.8(7)
C9−W1−C10	82.3(8)	C9−W1−C11	167.1(7)
C10−W1−C11	84.9(8)	W1−W2−P1	51.54(9)
W1−W2−C1	99.9(4)	W1−W2−C2	134.1(5)
W1−W2−C3	147.3(5)	W1−W2−C4	113.3(6)
W1−W2−C5	90.5(4)	W1−W2−C6	120.9(4)
W1−W2−C7	84.1(5)	P1−W2−C1	95.5(4)
P1−W2−C2	109.7(5)	P1−W2−C3	145.0(6)
P1−W2−C4	148.5(6)	P1−W2−C5	115.5(5)
P1−W2−C6	80.7(4)	P1−W2−C7	107.8(5)
C6−W2−C7	79.5(7)	W1−P1−W2	81.0(1)
W1−P1−C14	114.8(4)	W1−P1−C20	119.3(5)
W2−P1−C14	124.7(4)	W2−P1−C20	115.8(5)
C14−P1−C20	101.7(6)	W1−N1−C12	177(1)
W2−C6−O1	178(1)	W2−C7−O2	176(1)
W1−C8−O3	178(1)	W1−C9−O4	165(1)
W1−C10−O5	173(2)	W1−C11−O6	176(1)
N1−C12−C13	176(1)		

Crystal Structure of $CpW_2(CO)_6(\mu\text{-}PPh_2)(NCMe)$ (6). Crystals suitable for X-ray diffraction were grown from acetonitrile/methanol at −20 °C. An ORTEP drawing of **6** is shown in Figure 2. Selected bond distances and bond angles are given in Table 2. The molecule consists of $Cp(CO)_2W$ and $W(CO)_4(NCMe)$ units connected by a tungsten−tungsten bond and a bridging diphenylphosphido group. The W1−W2 length of 3.171(1) Å is between those measured for $CpW_2(CO)_7(\mu\text{-}PPh_2)$ (**1**) (3.194(1) Å) and $CpW_2(CO)_6(\mu\text{-}PPh_2)(P(OMe)_3)$ (3.151(1) Å),[11] consistent with strengthening of W−W bond by stronger electron-donating ligands. The phosphido group bridges the two tungsten atoms unequally, such that the W2−P1 bond length (2.364(4) Å) is significantly shorter than that of W1−P1 (2.513(4) Å). It is apparent that the resonance structure shown on the right side of the pair is dominated for **6**, leading to stronger binding between the P1 and W2 atoms.



W1 and W2 atoms are each linked to four and two terminal carbonyls, respectively. The W−CO lengths associated with the W2 atom are equal, being 1.93(2) Å, while those associated with the W1 atom are scattered from 1.94(2) to 2.08(2) Å. The W−CO angles are in the range of 165(2) to 178(1)°. Although the angle W1−C9−O4 = 165(1)° might indicate a semibridging structure,[4, 24] which plausibly accounts for the IR absorption at 1848 cm^{-1}, the W2···C9 distance of 2.99(2) Å is too long to support this suggestion.

The cyclopentadienyl ring is bonded to the W2 atom asymmetrically, with C2−W2 (2.30(1) Å) and C3−W2 (2.27(2) Å) distances being shorter than the C1−W2 (2.36(2) Å), C4−W2 (2.36(2) Å), and C5−W2 (2.38(2) Å) distances, presumably due to steric influence from the adjacent C8−O3 and phenyl (C20−C25) groups. Nevertheless, the observed variation of these bond lengths is within the range typically found for metal−carbon distances in $\eta^5\text{-}C_5H_5$ metal complexes.

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(24) Shyu, S.-G.; Hsu, J.-Y.; Lin, P.-J.; Wu, W.-J.; Peng, S.-M.; Lee, G.-H.; Wen, Y.-S. *Organometallics* **1994**, *13*, 1699.

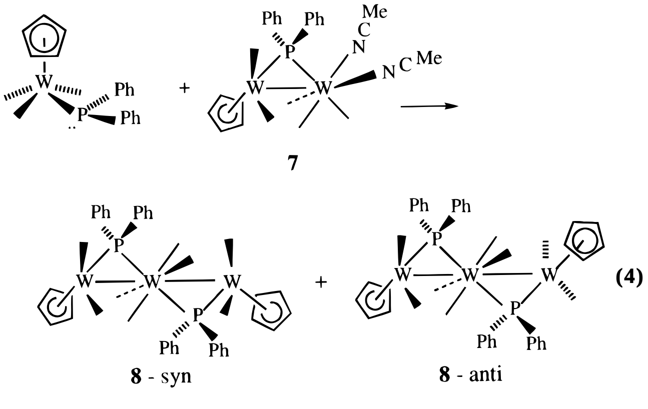
(25) Gavens, P. D.; Mays, M. J. *J. Organomet. Chem.* **1978**, *162*, 389.

The C9, W1, W2, and P1 atoms are essentially coplanar, so the geometry about the W1 atom can be viewed as an edge-capped octahedron with acetonitrile ligand occupying an axial position cis to the phosphido group. In contrast, the P(OMe)$_3$ ligand in CpW$_2$(CO)$_6$(μ-PPh$_2$)(P(OMe)$_3$) was found at an equatorial position trans to the μ-PPh$_2$ group.[11] Since both MeCN and P(OMe)$_3$ ligands are better σ-donor and poorer π-acceptors than CO, the cis position is expected to be more favored by these ligands to achieve stronger W to CO back-bonding, in agreement with what is observed for **6**. However, the fact that P(OMe)$_3$ assumes a less crowded trans position indicates that steric effects, when present, are the governing factors in determining ligand configuration.

Reactions of Compound 6 and 7 with Diphosphines. CpW$_2$(CO)$_6$(μ-PPh$_2$)(NCMe) (**6**) undergoes facile ligand substitution reaction with dppm at room temperature to give **2a** exclusively in 88% yield. Similar reactions with dppe, dppp, and dppf produce **3a**, **4a**, and **5a**, respectively, in ca. 50% yield, together with the dimeric products, **3c**, **4c**, and **5c** in low yields (ca. 10%). Interestingly, running the reaction of **6** with 0.5 equiv of dppm at 60 °C for 1 min in an NMR tube shows the ^{31}P resonances for **2a** and two small multiplets at δ 142.58 and 16.86 matching the data expected for [CpW$_2$(CO)$_6$(μ-PPh$_2$)]$_2$(η^1,η^1-dppm) (**2c**), but attempts to isolate this new product have been unsuccessful. Apparently, the short methylene chain in **2c** induces strong intramolecular steric repulsions between the two bimetallic units and leads to ready decomposition.

Treatment of CpW$_2$(CO)$_5$(μ-PPh$_2$)(NCMe)$_2$ (**7**) with dppm, dppe, dppp, and dppf at room temperature affords the products same as from thermal reactions shown in eq 3. There is no indication of formation of CpW$_2$(CO)$_5$(μ-PPh$_2$)(η^2-dppf) (**5b**), though it is expected to be a kinetic product. It is probable the large dppf bite angle makes **5b** too crowded to be obtained.

Synthesis and Characterization of [CpW$_2$(CO)$_6$(μ-PPh$_2$)]$_2$W(CO)$_4$ (8). Since treating CpW(CO)$_3$(PPh$_2$) with W(CO)$_4$(NCMe)$_2$ yielded CpW$_2$(CO)$_7$(μ-PPh$_2$) (**1**), we investigated if CpW(CO)$_3$(PPh$_2$) could replace the acetonitrile ligands in CpW$_2$(CO)$_5$(μ-PPh$_2$)(NCMe)$_2$ (**7**) to generate a tritungsten cluster complex. Indeed, [CpW(CO)$_2$(μ-PPh$_2$)]$_2$W(CO)$_4$ (**8**) is afforded in 60% by conducting the reaction at room temperature for 8 h (eq 4). Haines has previously shown[8b] the reaction of CpFe(CO)$_2$(PPh$_2$) and RhCl$_3$ to give {[CpFe(CO)$_2$(μ-PPh$_2$)]$_2$Rh}$^+$.



Compound **8** forms slightly air- and thermal-sensitive, orange-red crystals. The FAB mass spectrum presents the molecular ion peak at m/z = 1276 (^{184}W) and ion multiplets due to loss of eight carbonyls. The ^{1}H NMR spectrum shows a complex multiplet in the range δ 7.92−6.88 for the phenyl protons, and three singlets at δ 5.13, 5.10, and 4.93 in an 1:2:1 ratio for the Cp protons. Moreover, the ^{31}P{^{1}H} NMR spectrum, shown in Figure 3, includes two doublets at δ 132.93 and 124.30 ($^2J_{P-P}$ = 12 Hz) and a singlet at δ 128.59 in a 1:1:2 ratio, indicating the presence of two isomers in equal quantity for **8**. Since all the ^{31}P signals are accompanied by two pairs of ^{183}W satellites and their chemical shifts are compatible with that recorded for **1**, the two CpW(CO)$_2$(PPh$_2$) units in **8** appear to bind W(CO)$_4$ in a fashion similar to compound **1**. It is likely that the two phosphido groups are trans to each other and the two external tungsten atoms cap opposite edges of W(CO)$_4$(P)$_2$ octahedron to minimize steric interactions. Thus two isomers, **8**-*syn* and **8**-*anti*, can be obtained when CpW(CO)$_3$(PPh$_2$) approaches **7** with their Cp groups on the same side (*syn*) or opposite sides (*anti*) of the W$_3$P$_2$ plane. Since the geometry of **8**-*syn* reveals no symmetry, the two Cp units and phosphido atoms are not equivalent and lead to separate ^{1}H and ^{31}P resonances, whereas an inversion center is apparently imposed at the central tungsten atom of **8**-*anti* to result in equivalent phosphido and Cp groups. We have tried to grow crystals suitable for X-ray diffraction study but failed, presumably due to disorder from mixing of the two isomers.

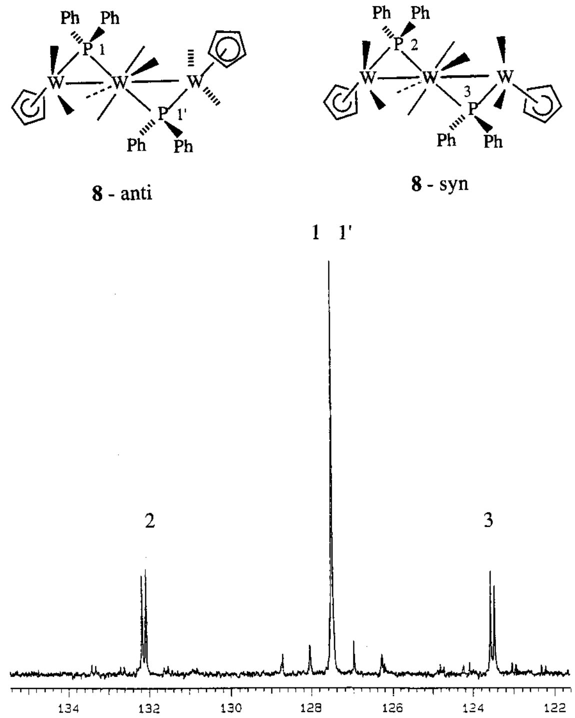


Figure 3. ^{31}P{^{1}H} NMR spectrum of [CpW(CO)$_2$(μ-PPh$_2$)]$_2$W(CO)$_4$ (**8**) in CD$_2$Cl$_2$ at 20 °C, showing the presence of two isomers in a 1:1 ratio.

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Supporting Information Available: Text describing X-ray procedures and complete tables of crystallographic data, positional and B_{eq} parameters, anisotropic displacement parameters, bond lengths, and bond angles (17 pages). Ordering information is given on any current masthead page.

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