ELSEVIER

Journal of Organometallic Chemistry 489 (1995) 113–122

Journal of Organometallic Chemistry

Synthesis, structure and substitution reactions of the binuclear phosphido-bridged complex $Cp(CO)_2\overline{W(\mu\text{-}PPh_2)W}(CO)_5$

Shin-Guang Shyu [a,*], Wen-Jin Wu [a], Yuh-Shang Wen [a], Shie-Ming Peng [b], Gene-Hsiang Lee [b]

[a] *Institute of Chemistry, Academia Sinica, Taipei, Taiwan 11529, Taiwan*
[b] *Department of Chemistry, National Taiwan University, Taipei, Taiwan, Taiwan*

Received 15 June 1994; in revised form 10 August 1994

Abstract

Bimetallic phosphido-bridged complexes $CpW(CO)_3(\mu\text{-}PPh_2)W(CO)_5$ (**1**) and $Cp\overline{W(CO)_2(\mu\text{-}PPh_2)W}(CO)_5$ (**2**) were prepared by the reaction of $CpW(CO)_3PPh_2$ with $W(CO)_5THF$. The structures of **1** and **2** were determined by single X-ray diffraction. Crystal data for **1**: $C_{25}H_{15}O_8PW_2$, space group, $P2_1/n$ with $a = 9.6234$ (18) Å, $b = 12.4514$ (20) Å, $c = 20.750$ (4) Å, $\beta = 98.445$ (14)°, $V = 2459.4$ (7) Å^3, $Z = 4$. The structure was refined to $R = 0.031$ and $R_w = 0.035$. Crystal data for **2**: $C_{24}H_{15}O_7PW_2$, space group, $P2_1/n$ with $a = 14.4801$ (11) Å, $b = 11.6628$ (12) Å, $c = 14.732$ (3) Å, $\beta = 97.893$ (11)°, $V = 2464.3$ (6) Å^3, $Z = 4$. The structure was refined to $R = 0.054$ and $R_w = 0.050$. The long distance between W and W (4.5096 (11) Å) in **1** indicates that no metal–metal bond exists in the complex. The W–W distance was 3.1942 (12) Å in **2**, indicative of a W–W bond. Substitution reactions between **2** and Lewis bases L (L = PPh_3, PEt_3, $P(OMe)_3$) produced $Cp\overline{W(CO)_2(\mu\text{-}PPh_2)W}(CO)_4(L)$ (**3**) with L regiospecifically and stereospecifically coordinating to the $W(CO)_4$ moiety *trans* to the phosphido bridge. The structure of $Cp\overline{W(CO)_2(\mu\text{-}PPh_2)W}(CO)_4\{P(OMe)_3\}$ (**3a**) was determined by single-crystal X-ray diffraction. Crystal data for **3a**: $C_{26}H_{24}O_9P_2W_2$, space group, $P2_1$ with $a = 9.2231$ (16) Å, $b = 15.868$ (3) Å, $c = 10.745$ (3) Å, $\beta = 110.282$ (18)°, $V = 1475.1$ (5) Å^3, $Z = 2$. The structure was refined to $R = 0.037$ and $R_w = 0.039$. Under similar reaction conditions, complex **1** did not react with L.

Keywords: Tungsten; Group 6; Carbonyl; π-bonding; Cyclopentadienyl; Bridging ligand

---

1. Introduction

One special feature of binuclear metal–metal bonded phosphido-bridged complexes is the influence of the metal–metal bond in the reactions [1]. First, 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 reforms [1a]. Second, one metal may exert an activating influence on the adjacent metal through the metal–metal bond [1d]. We have reported that the carbonyl ligand on Mo in $Cp(CO)_2\overline{W(\mu\text{-}PPh_2)Mo}(CO)_5$ (**5**) can be substituted by a Lewis base L (L = PPh_2H, PMe_3, $P(OMe)_3$) with the opening of the metal–metal bond to produce $Cp(CO)_3W(\mu\text{-}PPh_2)Mo(CO)_4L$ (**6**) under very mild conditions [2]. The origin of this cooperativity effect was proposed as the influence of the $CpW(CO)_2$ moiety on the $Mo(CO)_5$ through the metal–metal bond in the complex. Carbonyl ligands on the tungsten is less facile towards substitution than carbonyl ligands on the molybdenum. We thus synthesized $Cp(CO)_3W(\mu\text{-}PPh_2)W(CO)_5$ (**1**) and $Cp(CO)_2\overline{W(\mu\text{-}PPh_2)W}(CO)_5$ (**2**), and studied their substitution reaction towards Lewis bases L (L = PPh_3, PEt_3, $P(OMe)_3$) in order to evaluate the cooperativity effect between the metals in the complexes. We found that the carbonyl ligand in **2** was substituted with a Lewis base L with the metal–metal bond remaining intact to produce $Cp(CO)_2\overline{W(\mu\text{-}PPh_2)W}(CO)_4L$ (**3**) with L regiospecifically and stereospecifically coordinating to the $W(CO)_4$ fragment *trans* to the phosphido bridge. However, complex **1** was

---

[*] Corresponding author.

SSDI 0022-328X(94)05152-6

intact under similar reaction conditions. Reported herein are the synthesis, structure, and reactivity studies of **2**. Scheme 1 shows the reactions that comprise the main focus of our work. The structures of complexes **1** and $\mathrm{Cp(CO)_2\overline{W(\mu\text{-}PPh_2)W}(CO)_4\{P(OMe)_3\}}$ (**3a**) were also determined by a complete single-crystal X-ray diffraction study.

2. Experimental section

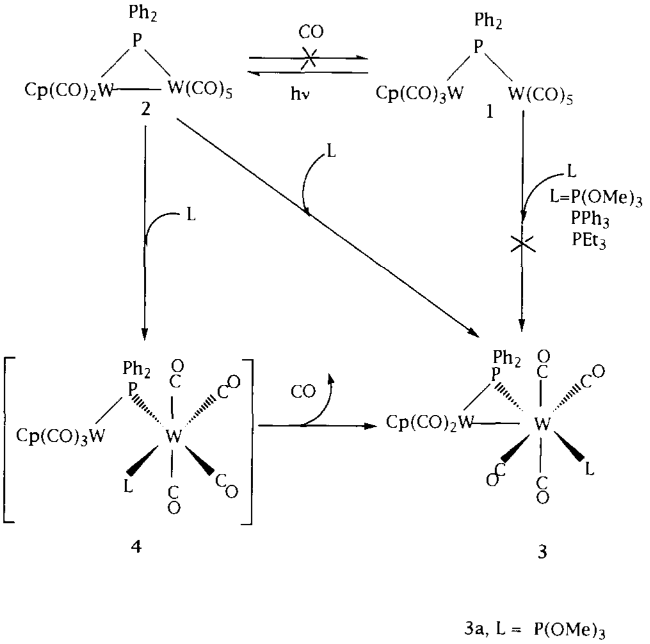
Unless otherwise stated, all reactions and manipulations of air-sensitive compounds were carried out at ambient temperatures under an atmosphere of purified N_2 with standard procedures. A 450 W Hanovia medium-pressure quartz mercury-vapor lamp (Ace Glass) and a Pyrex Schlenk tube as a reaction vessel were used in the photoreactions. Infrared (IR) spectra were recorded on a Perkin-Elmer 882 infrared spectrophotometer. ^{1}H, ^{13}C and ^{31}p NMR spectra were measured 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 in the Microanalytic Laboratory at National Cheng Kung University, Tainan, Taiwan.

2.1. 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 [3]. Tungsten hexacarbonyl, PPh_2Cl, PEt_3 and PPh_3 were obtained from Strem; $P(OMe)_3$ was purchased from Merck. Other reagents and solvents were obtained from various commercial sources and used as received. $\mathrm{Na[CpW(CO)_3]\cdot 2DME}$ [4] and $\mathrm{WCp(CO)_3PPh_2}$ [5] were prepared by literature procedures.

2.2. Synthesis of $\mathrm{CpW(CO)_3(\mu\text{-}PPh_2)W(CO)_5}$ (1) and $\mathrm{Cp\overline{W(CO)_2(\mu\text{-}PPh_2)W}(CO)_5}$ (2)

A yellow solution of $\mathrm{Na[CpW(CO)_3]\cdot 2DME}$ (5.33 g, 9.94 mmol) in 100 ml of THF was cooled to 0°C. A solution of 1.84 ml (9.97 mmol) of PPh_2Cl in 50 ml of THF was then added slowly to the above solution. After 1 h, the color of the solution turned to orange red. Meanwhile, $\mathrm{W(CO)_5\cdot THF}$ was prepared in situ by UV photolysis of $W(CO)_6$ (5.0 g, 14.2 mmol) in THF. The orange red solution of $\mathrm{CpW(CO)_3PPh_2}$ was then added slowly to the above solution at 0°C. The solution turned to dark red immediately. After stirring overnight at room temperature, the solvent was removed and the residue was chromatoghraphed on silica gel. Elution with CH_2Cl_2/hexane (1:4) afforded two fractions. A purple solid **2** was obtained from the first band. Yield: 1.66 g (21%). (Found: C, 35.14; H, 2.03. Calc. for $C_{24}H_{15}O_7PW_2$: C, 35.41; H, 1.86). IR spectrum (THF, ν(CO)): 2073m, 1954s, 1930s, 1861w cm^{-1}. ^{1}H NMR spectrum ($CDCl_3$): δ 7.75 (m, 2H), 7.43 (m, 3H), 7.28 (m, 3H), 7.00 (m, 2H), 5.17 (s, 5H, C_5H_5). ^{13}C{^{1}H} NMR spectrum ($CDCl_3$): 226.56 (d, J(C–P) = 17.9 Hz, CpW–CO), 221.74 (s, CpW–CO), 197.71 (d, J(C–P) = 12.7 Hz, W–CO), 196.0 (br, W–CO), 142.36 (d, J(P–C) = 15.30 Hz, *ipso*-C, PPh_2), 141.46 (d, J(P–C) = 16.35 Hz, *ipso*-C′, PPh_2), 134.37 (d, J(P–C) = 9.21 Hz, *o*-C, PPh_2), 131.80 (d, J(P–C) = 11.47 Hz, *o*-C′, PPh_2), 129.97 (s, *p*-C, PPh_2), 129.27 (s, *p*-C′, PPh_2), 128.64 (d, J(P–C) = 9.81 Hz, *m*-C, PPh_2), 128.15 (d, J(P–C) = 11.87 Hz, *m*-C′, PPh_2), 91.87 (s, C_5H_5). ^{31}P{^{1}H} NMR spectrum (THF): δ 145.9 (J(P–W) = 325.3 Hz, J(P–W) = 131.1 Hz). MS(FAB), M^{+1} m/z 814. The second band was yellow in color. After removing the solvent, **1** was obtained as a yellow solid. Yield: 1.42 g (17%). (Found: C, 35.63; H, 1.45. Calc. for $C_{25}H_{15}O_8PW_2$: C, 35.66; H, 1.80). IR spectrum (THF, ν(CO)): 2065m, 2026m, 1941s, 1927s, 1910sh cm^{-1}. ^{1}H NMR spectrum ($CDCl_3$): δ 7.38 (br, 12H), 5.36 (s, 5H, C_5H_5). ^{31}P{^{1}H} NMR spectrum (THF): δ −62.72 (s, J(P–W) = 214.8 Hz, J(P–W) = 92.7 Hz). M^{+1} m/z 842.



3a, L = $P(OMe)_3$
3b, L = PPh_3
3c, L = PEt_3

Scheme 1.

2.3. Synthesis of $Cp\overline{W(CO)_2(\mu\text{-}PPh_2)W}(CO)_4(P(OMe)_3)$ (3a)

To a purple solution of **2** (0.20 g, 0.25 mmol) in 15 ml of THF was added 30 μl of $P(OMe)_3$ (0.25 mmol) under N_2 at room temperature. The solution changed to dark red after the solution was heated under reflux overnight. 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 in color, was unreacted **2**. The second band was reddish brown. After the solvent was removed, a red solid **3a** was obtained. Yield: 0.20 g (88%). (Found: C, 34.36; H, 2.67. Calc. for $C_{26}H_{24}O_9P_2W_2$: C, 34.31 H, 2.66). IR spectrum (THF, ν(CO)): 2034w, 1966vw, 1931s, 1917s, 1846m cm^{-1}. ^1H NMR spectrum ($CDCl_3$): δ 7.78 (m, 2H), 7.37 (m, 3H), 7.22 (m, 3H), 6.99 (m, 3H), 5.07 (s, 5H, C_5H_5), 3.70 (d, 9H, $^2J(P\text{–}H) = 11.7$ Hz, $POCH_3$). $^{31}P\{^1H\}$ NMR spectrum (THF): δ 142.6 (d, $^2J(P\text{–}P) = 50.9$ Hz, $J(P\text{–}W) = 314.8$ Hz, $J(P\text{–}W) = 155.0$ Hz, μ-PPh_2), 134.5 (d, $^2J(P\text{–}P) = 50.9$ Hz, $J(P\text{–}W) = 421.0$ Hz, $P(OMe)_3$). MS(FAB), M^{+1} m/z 910.

2.4. Synthesis of $Cp\overline{W(CO)_2(\mu\text{-}PPh_2)W}(CO)_4(PPh_3)$ (3b)

To a purple solution of **2** (0.20 g, 0.25 mmol) in 30 ml of THF was added PPh_3 (0.064 g, 0.25 mmol) under N_2 at room temperature. The solution changed to dark red after the mixture was heated at reflux temperature overnight. 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 in color was unreacted **2**. The second bad was red. After the solvent was removed, red solid **3b** was obtained. Yield: 0.18 g (71%). (Found: C, 46.72; H, 2.74. Calc. for $C_{41}H_{30}O_6P_2W_2$: C, 46.97; H, 2.88). IR spectrum (THF, ν(CO)): 2027w, 1960vw, 1928s, 1908s, 1843m cm^{-1}. ^1H NMR spectrum ($CDCl_3$): δ 7.41 (m, 25H), 5.06 (s, 5H, C_5H_5). $^{31}P\{^1H\}$ NMR spectrum (THF): δ 143.0 (d, $^2J(P\text{–}P) = 28.5$ Hz, μ-PPh_2), 21.05 (d, $^2J(P\text{–}P) = 28.5$ Hz, PPh_3). $^{13}C\{^1H\}$ NMR spectrum ($CDCl_3$): 230.91 (d, $J(C\text{–}P) = 17.0$ Hz, CpW–CO), 223.68 (s, CpW–CO), 198 (br, W–CO), MS(FAB), M^{+1} m/z 1048.

2.5. Synthesis of $Cp\overline{W(CO)_2(\mu\text{-}PPh_2)W}(CO)_4(PEt_3)$ (3c)

To a purple solution of **2** (0.20 g, 0.25 mmol) in 30 ml of THF was added 50 μl PEt_3 (0.34 mmol) under N_2 at room temperature. The solution changed to dark red after the mixture was heated under reflux overnight. 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 in color, was unreacted **2**. The second band was red. After the solvent was removed, a red solid **3c** was obtained. Yield: 0.13 g (45%). (Found: C, 38.89; H, 2.99. Calc. for $C_{29}H_{30}O_6P_2W_2$: C, 38.53; H, 3.34). IR spectrum (THF, ν(CO)): 2021m, 1951w, 1924s, 1901s, 1840m cm^{-1}. ^1H NMR spectrum ($CDCl_3$): δ 7.77 (m, 2H), 7.38 (m, 3H), 7.22 (m, 3H), 6.99 (m, 2H), 5.04 (s, 5H, C_5H_5), 2.07 (dq, 6H, $^2J(H\text{–}H) = 7.63$ Hz, $^2J(P\text{–}H) = 7.63$ Hz, PCH_2), 1.13 (dt, 9H, $^2J(H\text{–}H) = 7.48$ Hz, $^2J(P\text{–}H) = 16.02$ Hz, PCH_2CH_3). $^{31}P\{^1H\}$ NMR spectrum (THF): δ 140.1 (d, $^2J(P\text{–}P) = 24.4$ Hz; $J(P\text{–}W) = 309.2$ Hz, $J(P\text{–}W) = 158.4$ Hz, μ-PPh_2), -2.9 (d, $^2J(P\text{–}P) = 24.4$ Hz; $J(P\text{–}W) = 214.8$ Hz, PEt_3). MS (FAB), M^{+1} m/z 904.

2.6. Reaction of 1 with PR_3 (R = Ph, Et, OMe)

To a yellow solution containing 100 mg (0.125 mmol) of **1** in 20 ml of THF was added 30 μl (0.25 mmol) of $P(OMe)_3$. The solution was heated under reflux overnight and no color change was observed. Results of a ^{31}P NMR study of the reaction mixture indicated the existence of unreacted **1** and $P(OMe)_3$ and small amount of unidentified impurities. Similar reaction conditions were applied to the reaction between **1** and PR_3 (R = Ph, Et). Unreacted **1**, PR_3 (R = Ph, Et) and a small amount of unidentified impurities were observed in the reaction product according to the ^{31}P NMR spectra of the reaction mixture.

2.7. Reaction between 2 and CO

A solution of **2** in THF was stirred overnight under 1 atom of CO. No color change was observed. Only **2** was observed in the ^{31}P NMR spectrum of the solution.

2.8. Thermolysis of 1

A solution of **1** in THF was heated under reflux under N_2 overnight in the dark. No color change was observed. Only **1** was observed in the ^{31}P NMR spectrum of the solution.

2.9. Photolysis of 1

Compound **1** (1.77 g) was dissolved in 70 ml of THF under N_2. The solution was irradiated with UV for 2 h. The color of the solution changed from yellow to reddish brown. The ^{31}P NMR of the mixture indicated that all of **1** was used in the reaction. The solvent was then removed and the residue was chromatographed on grade III Al_2O_3. Elution with hexane afforded two fractions. Only a trace amount of product was obtained from the first band which was pink in color, and was not identified. The second band was purple in color.

After the solvent was removed, **2** was obtained as a purple solid. Yield: 0.203 g (12%).

2.10. Structure determination of *1, 2, 3a*

Crystals of complexes **1**, **2** and **3a** were grown by slow diffusion of hexanes to the saturated solutions of the relevant complexes in CH_2Cl_2 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 the heavy atoms were obtained from Patterson syntheses. The positions of the remaining non-hydrogen atoms were obtained from Fourier synthesis. For complex **2**, inspection of a difference Fourier revealed severe disorders (Fig. 1). There were dominant and minor fractions; the ratio was determined to be 0.8 : 0.2. 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 H atoms at idealized positions with $R = 5.4\%$ and $R_w = 5.0\%$. The final positional parameters of the complexes are listed in Tables 2 (**1**), 3 (**2**), and 4 (**3a**). Selected interatomic distances and bond angles are given in Table 5 (**1** and **2**) and 6 (**3a**).

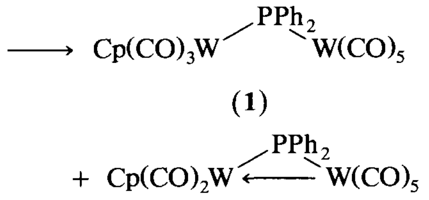
Additional material available from the Cambridge Crystallographic Data Center comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

3. Results and discussion

3.1. Synthesis, spectroscopic characterization and molecular structures of *1* and *2*

The new W–W complexes **1** and **2** were synthesized by the reaction of $CpW(CO)_3PPh_2$ with $W(CO)_5(THF)$. The metallophosphine $CpW(CO)_3PPh_2$ acted as a ligand to replace the THF ligand on $W(CO)_5(THF)$ to form the complexes according to Eq. (1) [6].

$CpW(CO)_3PPh_2 + W(CO)_5(THF)$



$$\longrightarrow \mathrm{Cp(CO)_3W}\overset{\mathrm{PPh_2}}{\diagup\;\diagdown}\mathrm{W(CO)_5}$$

(1)

$$+\ \mathrm{Cp(CO)_2W}\overset{\mathrm{PPh_2}}{\overset{\diagup\;\diagdown}{\longleftarrow}}\mathrm{W(CO)_5} \qquad (1)$$

(2)

Replacement of the THF ligand on $W(CO)_5(THF)$ with $CpW(CO)_3PPh_2$ should form **1**. The formation of **2** in the reaction could be due to the elimination of one CO from **1** under the synthetic conditions. Thermolysis of **1** in THF under N_2 for 12 h did not produce **2**. UV irradiation of **1** in THF produced **2** in 12% yield, which might provide a reasonable explanation for the formation of **2**. However, no **2** was observed after the THF solution of **1** was stirred under household fluorescence light at room temperature for 12 h. Therefore, the formation of **2** in the reaction could go through a different, unknown reaction path.

The $^{31}P\{^1H\}$ NMR spectrum of **2** in THF at room temperature shows resonance at 145.9 ppm with two sets of J(P–W) satellites. This relatively downfield resonance reveals the existence of a metal–metal bond [7]. In contrast, the relatively upfield resonance at −62.7 ppm with two sets of J(P–W) satellites in the $^{31}P\{^1H\}$ NMR of **1** indicates the opening of the W–P–W triangle [7]. The W–W complexes **1** and **2** were further characterized by single X-ray diffraction studies. Structures are shown in Figs. 2 and 3.

Table 1
Crystal and intensity collection data for **1**, **2** and **3a**

	1	2	3a
Molecular formula	$C_{25}H_{15}O_8PW_2$	$C_{24}H_{15}O_7PW_2$	$C_{26}H_{24}O_9P_2W_2$
Mol. wt.	842.06	814.03	910.12
Space group	$P2_1/n$	$P2_1/n$	$P2_1$
a (Å)	9.6234 (18)	14.4801 (11)	9.2231 (16)
b (Å)	12.4514 (20)	11.6628 (12)	15.868 (3)
c (Å)	20.750 (4)	14.732 (3)	10.745 (3)
α (°)	–	–	–
β (°)	98.445 (14)	97.893 (11)	110.282 (18)
γ (°)	–	–	–
V (Å^3)	2459.4 (7)	2464.3 (6)	1475.1 (5)
ρ (calc.) (mg m^{-3})	2.274	2.189	2.049
Z	4	4	2
Crystal dimensions (mm)	0.31 × 0.31 × 0.34	0.10 × 0.20 × 0.50	0.50 × 0.44 × 0.25
Absolute coefficient μ (Mo Kα) (mm^{-1})	9.66	9.63	8.11
Temperature	Room temperature	Room temperature	Room temperature
Radiation (Mo K$\alpha\lambda$, Å)	0.71073	0.71073	0.71073
2θ range (°)	45	45	50
Scan type	$2\theta-\omega$	$2\theta-\omega$	$2\theta-\omega$
No. of reflections	3207	4329	2684
No. of observed	2626		
($> 2.0\sigma(I)$)	2890		
($> 2.0\sigma(I)$)	2248		
($> 2.5\sigma(I)$) reflections			
Variables	325	325	353
R	0.031	0.054	0.037
R_w	0.035	0.050	0.039
S	2.48	3.41	1.70
ΔF (e Å^{-3})	0.780	1.440	1.450
$(\Delta/\sigma)_{max}$	< 0.011	< 0.056	< 0.072

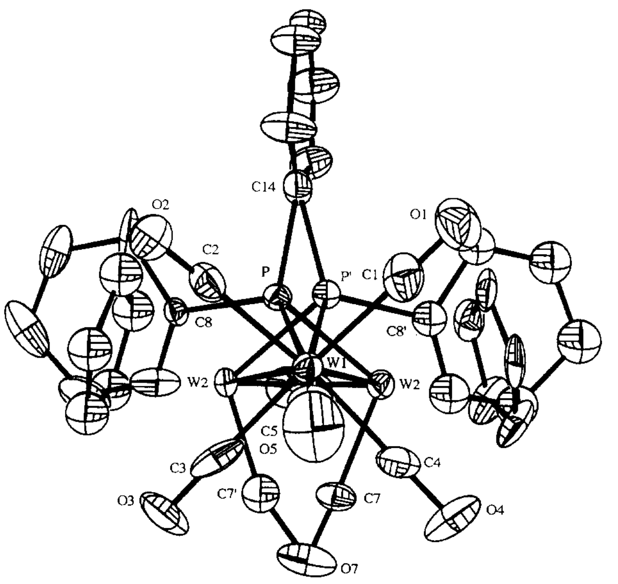


Fig. 1. ORTEP drawing of disordered molecular structure of **2**.

In **1**, a W–W distance of 4.5096(11) Å indicates that there is no metal–metal bond. The metallophosphine $CpW(CO)_3PPh_2$ can be considered to be a ligand similar to PR_3. Thus, five COs and $CpW(CO)_3PPh_2$ coordinate to the W(1) atom to form a distorted octahedron.

The W–W distance (3.1943(12) Å) in **2** falls within the range of W–W distances reported for other mono-bridging complexes [8]. It is slightly shorter than the unsupported W–W single bond (3.222(1) Å) in $Cp_2W_2(CO)_6$ [9] and longer than the W–W distance (3.0256(4) Å) in bis (μ-diphenylphosphido) complex $W_2(CO)_8(\mu\text{-}PPh_2)_2$ [10].

We prefer to formulate the metal–metal bonding in **2** as a donor–acceptor bond from a $W(1)^0$ center to $W(2)^{II}$, similar to descriptions given earlier for $Cp(CO)_2W(\mu\text{-}PPh_2)Mo(CO)_5$ [2], $(PPh_3)(CO)_3Fe(\mu\text{-}PPh_2)Ir(CO)_2(PPh_3)$ [11], and $(CO)_5W(\mu\text{-}PPh_2)Re(CO)_4$ [1b]. The W(1)–W(2) bond in **2** can be consid-

Table 2
Atomic coordinates for **1**

Atom	x	y	z	B_{iso}
W1	0.29194(6)	0.78964(5)	0.00456(3)	2.66(3)
W2	0.00829(5)	0.76079(5)	0.15845(3)	2.46(2)
P	0.24765(34)	0.71520(29)	0.11820(16)	2.39(15)
O1	0.3424(13)	1.0354(9)	0.0393(6)	6.2(7)
O2	−0.0245(10)	0.8517(9)	−0.0473(5)	5.3(6)
O3	0.2219(13)	0.5571(9)	−0.0541(5)	6.1(7)
O4	0.3717(11)	0.8533(10)	−0.1297(5)	5.9(7)
O5	0.6191(10)	0.7482(11)	0.0490(5)	6.1(7)
O6	0.1606(10)	0.6231(9)	0.2749(4)	4.3(6)
O7	−0.2325(10)	0.6059(9)	0.1875(5)	5.1(6)
O8	−0.0693(11)	0.6367(8)	0.0255(5)	4.6(5)
C1	0.3256(15)	0.9441(14)	0.0294(8)	4.3(8)
C2	0.0874(17)	0.8290(12)	−0.0278(7)	4.1(8)
C3	0.2451(15)	0.6382(15)	−0.0335(7)	4.5(9)
C4	0.3397(16)	0.8316(13)	−0.0816(7)	4.2(8)
C5	0.5039(17)	0.7607(14)	0.0344(7)	4.7(9)
C6	0.1070(13)	0.6706(11)	0.2327(7)	2.9(7)
C7	−0.1448(14)	0.6594(12)	0.1784(7)	3.3(7)
C8	−0.0410(13)	0.6780(12)	0.0733(7)	3.2(7)
C9	0.0696(16)	0.9405(11)	0.1410(9)	4.2(9)
C10	−0.0640(18)	0.9293(12)	0.1097(8)	4.5(9)
C11	−0.1475(15)	0.9043(11)	0.1575(9)	4.4(9)
C12	−0.0620(16)	0.9010(12)	0.2197(7)	4.1(8)
C13	0.0733(15)	0.9217(11)	0.2103(8)	4.1(8)
C21	0.2759(14)	0.5676(10)	0.1186(6)	2.5(6)
C22	0.1776(14)	0.4905(12)	0.1274(6)	3.1(7)
C23	0.1986(15)	0.3827(11)	0.1237(6)	3.4(7)
C24	0.3307(19)	0.3474(11)	0.1125(7)	4.4(9)
C25	0.4366(16)	0.4218(12)	0.1046(7)	4.1(8)
C26	0.4106(15)	0.5287(12)	0.1089(6)	3.5(7)
C31	0.3890(13)	0.7595(12)	0.1853(6)	3.1(7)
C32	0.4376(14)	0.8664(11)	0.1887(7)	3.5(7)
C33	0.5407(15)	0.8978(13)	0.2367(7)	3.8(8)
C34	0.5973(15)	0.8312(14)	0.2829(7)	4.1(8)
C35	0.5481(14)	0.7255(13)	0.2820(6)	3.8(8)
C36	0.4466(14)	0.6894(12)	0.2348(7)	3.7(7)

ered as the donation of an electron pair from one of the filled t_{2g} orbitals of W(1) to the adjacent W(2) such that the W(1)–W(2) dative bond acts as the fifth ligand, donating two electrons to W(2), in addition to the two COs, the μ-PPh_2, and the Cp ligands coordinated to W(2). Consistent with this view is the observation that the W(1)–W(2) vector bisects an edge of the distorted W(1) octahedron and the W(1) atom lies on the least squares plane consisting of P, C(5), C(4), C(2). The W(1)–W(2) vector was only 1.13° off the plane [12].

In complex **2**, the W(1)–C(4)–O(4) angle 174.1 (15)° could indicate a semibridging carbonyl. The observed IR at 1861 cm^{-1} at room temperature and the W(2)–C(4) distance (2.982(18) Å) which is shorter than the sum of the atomic radius of W (1.30 Å) [13] and the van der Waals radius of C (1.85 Å) [13], further supports this assignment [14]. This semibridging carbonyl and the other three W(1) COs which are *cis* to the phosphido bridge are fluxional in solution at room temperature as indicated by the observed broad hump at 196.0 ppm in its ^{13}C NMR spectrum. The exchange of the four *cis* W(1) COs probably proceed through the rotation of the W(1)–P bond. This type of fluxional behavior has been reported for several mono (μ-phosphido) carbonyl complexes [2,6a,15].

3.2. *Substitution reaction between 2 and phosphine ($P(OMe)_3$, PPh_3, PEt_3)*

Reaction of **2** with phosphine L (L = $P(OMe)_3$, PPh_3, PEt_3) in THF at reflux temperature yielded **3** with L regiospecifically and stereospecifically coordinating to the W(1) *trans* to the phosphido bridge. A downfield shift of the phosphido-bridge phosphorus signal in the ^{31}P NMR (140.1–143.0 ppm) indicates that the metal–metal bond exists. The regiospecific and stereospecific assignment is revealed by the ^{13}C NMR spectrum of **3b**. The observed signals at δ 230.91 (d, $^2J(P–C) = 17.11$ Hz) and 223.68(s) are assigned to the W(2) COs based on a favorable comparison with the reported resonances at δ 230.95 (d, $^2J(P–C) = 15.87$ Hz) and 223.54(s) for the W CO signals in the ^{13}C NMR spectrum of $Cp(CO)_2\overline{W(\mu\text{-}PPh_2)Mo}(CO)_4(PPh_3)$

Table 3
Atomic coordinates for **2**

Atom	x	y	z	B_{iso}
W1	0.19136(5)	0.24519(8)	−0.14029(4)	3.08(3)
W2	0.30635(7)	0.13445(9)	0.03891(6)	3.36(4)
P	0.1964(4)	0.2866(5)	0.0294(4)	3.0(3)
C1	0.0919(14)	0.1234(19)	−0.1344(13)	5.9(12)
C2	0.0966(12)	0.3764(18)	−0.1465(12)	4.4(10)
C3	0.2883(14)	0.3630(21)	−0.1563(12)	6.3(12)
C4	0.2822(12)	0.1223(20)	−0.1651(12)	5.1(11)
C5	0.1561(12)	0.2426(22)	−0.2761(11)	5.0(10)
C6	0.3669(11)	0.2359(23)	0.1459(11)	5.7(12)
C7	0.4166(14)	0.1967(22)	−0.0164(13)	4.2(12)
C8	0.2337(13)	0.4337(18)	0.0620(12)	2.7(9)
C9	0.3147(15)	0.464(3)	0.0476(14)	5.5(15)
C10	0.3444(18)	0.569(3)	0.0673(16)	7.2(18)
C11	0.2827(20)	0.658(3)	0.1066(16)	8.0(18)
C12	0.1928(19)	0.6145(23)	0.1224(15)	6.1(15)
C13	0.1621(22)	0.5041(20)	0.0969(14)	6.1(16)
C14	0.0905(12)	0.2599(18)	0.0813(10)	4.2(9)
C15	0.0041(11)	0.2739(23)	0.0352(10)	5.6(13)
C16	−0.0752(11)	0.2647(22)	0.0795(10)	4.7(10)
C17	−0.0632(11)	0.2469(21)	0.1729(11)	4.9(10)
C18	0.0234(13)	0.237(3)	0.2164(11)	6.6(14)
C19	0.0994(12)	0.2399(22)	0.1744(11)	5.3(11)
C20	0.3622(18)	−0.036(3)	0.1108(17)	6.8(16)
C21	0.3411(19)	−0.0619(24)	0.0212(18)	6.8(16)
C22	0.2510(19)	−0.0509(19)	−0.0025(15)	5.6(15)
C23	0.2027(17)	−0.0160(20)	0.0722(16)	5.0(13)
C24	0.2763(19)	−0.0037(22)	0.1437(15)	5.6(15)
O1	0.0361(10)	0.0557(14)	−0.1296(11)	8.4(10)
O2	0.0454(10)	0.4472(14)	−0.1576(11)	7.7(10)
O3	0.3457(10)	0.4321(14)	−0.1697(10)	7.9(10)
O4	0.3319(11)	0.0496(15)	−0.1877(9)	8.2(10)
O5	0.1362(11)	0.2405(17)	−0.3540(8)	8.8(11)
O6	0.4033(9)	0.2705(15)	0.2052(7)	6.7(8)
O7	0.4783(8)	0.2379(19)	−0.0458(9)	8.5(11)

[2]. The observed broad hump at 199 ppm, which is assigned to the four fluxional W(1) COs *cis* to the phosphido bridge, and the absence of the corresponding *trans* CO signal indicates that the phosphine ligand occupies the position *trans* to the phosphido bridge (Fig. 5). No reaction was observed when the mixture of **2** and phosphines was stirred overnight at room temperature.

The structure of **3a** was determined by single-crystal X-ray diffraction study. The W(1)–W(2) distance was 3.1510(12) Å which indicates that a metal–metal bond exists in the complex. It is 0.04 Å shorter than the W(1)–W(2) distance in **2**. The replacement of the CO ligand from **2** with a better electron donor ligand $P(OMe)_3$ to form **3a** could enhance the basicity of the W(1) moiety which resulted in the strengthening of the dative bonding. The $P(OMe)_3$ ligand is coordinated to the W(1) atom and is *trans* to the phosphido bridge. The W(1)–P(1) distance (2.479(5) Å) in **3a** is shorter than the corresponding W(1)–P distance (2.538(5) Å) in **2**. This can be explained by the replacement of the CO ligand with a poor π-acceptor ligand phosphine [16].

Unlike complex **5**, reaction of **2** with phosphine resulted in the substitution of one W(1) CO with phosphine instead of opening the metal–metal bonding to produce an addition product $Cp(CO)_3W(\mu\text{-}PPh_2)W(CO)_4L$(**4**) (Scheme 1) [2]. One possibility is that the W–W bonding in **2** is stronger than the W–Mo bonding in **5** such that direct substitution of one CO on the W(1) dominated in **2**. The stronger metal–metal bond in **2** may be indicated by the inertness of the complex towards CO since complex **5** reacts with CO under very mild conditions (room temperature, 1 atm of CO) to produce the addition product $Cp(CO)_3W(\mu\text{-}PPh_2)Mo(CO)_5$ [2]. The other possibility is that the

Table 4
Atomic coordinates for **3a**

Atom	*x*	*y*	*z*	B_{iso}
W1	0.34473(8)	0.23580	0.22531(7)	2.72(3)
W2	0.43505(8)	0.29276(5)	−0.01921(7)	2.70(3)
P1	0.4765(5)	0.3636(3)	0.1849(4)	2.5(2)
P2	0.2187(6)	0.1358(3)	0.3233(5)	3.9(2)
O1	0.3955(21)	0.3355(10)	0.4920(15)	7.0(10)
O2	0.6685(16)	0.1424(9)	0.3430(15)	5.8(8)
O3	0.2307(17)	0.1012(8)	−0.0076(14)	5.1(8)
O4	0.0230(16)	0.3257(9)	0.0944(16)	6.2(9)
O5	0.3964(17)	0.4722(8)	−0.1349(17)	6.2(9)
O6	0.0907(16)	0.2915(12)	−0.1846(15)	6.6(8)
O12	0.2995(17)	0.0485(9)	0.3835(15)	5.7(8)
O13	0.0549(16)	0.1090(9)	0.2238(14)	5.4(8)
O14	0.1869(25)	0.1709(13)	0.4496(17)	10.5(14)
C1	0.3821(23)	0.2987(13)	0.3940(21)	4.9(11)
C2	0.5493(21)	0.1806(14)	0.2997(19)	4.5(11)
C3	0.2802(19)	0.1566(12)	0.0773(17)	3.6(9)
C4	0.1396(19)	0.2879(13)	0.1404(19)	4.3(10)
C5	0.4133(23)	0.4059(11)	−0.0918(23)	5.1(12)
C6	0.2217(20)	0.2913(12)	−0.1100(22)	4.6(11)
C7	0.6658(21)	0.2884(10)	−0.549(17)	3.9(9)
C8	0.6868(20)	0.2397(14)	0.0388(20)	4.8(10)
C9	0.5785(22)	0.1655(11)	0.0026(22)	4.6(11)
C10	0.4895(22)	0.1753(13)	−0.1355(21)	4.6(11)
C11	0.5517(26)	0.2588(12)	−0.1620(23)	5.9(13)
C12	0.3438(33)	−0.0085(12)	0.3062(33)	8.4(20)
C13	−0.0344(26)	0.0447(14)	0.2496(25)	6.0(13)
C14	0.1348(46)	0.1431(34)	0.5250(32)	15.8(36)
C21	0.3842(19)	0.4623(10)	0.2010(18)	2.9(8)
C22	0.2453(20)	0.4866(10)	0.1071(17)	3.3(9)
C23	0.1661(23)	0.5580(13)	0.1285(21)	4.6(11)
C24	0.2185(25)	0.6008(12)	0.2372(21)	4.7(11)
C25	0.3586(27)	0.5788(12)	0.3354(20)	5.0(12)
C26	0.4343(23)	0.5089(11)	0.3202(17)	3.7(9)
C31	0.6801(19)	0.3847(11)	0.2896(18)	3.3(8)
C32	0.7619(26)	0.4389(13)	0.2340(22)	5.5(12)
C33	0.9117(24)	0.4536(17)	0.2985(26)	6.7(14)
C34	0.9874(22)	0.4184(17)	0.4243(26)	7.4(14)
C35	0.9057(26)	0.3676(15)	0.4835(27)	7.6(14)
C36	0.7509(22)	0.3513(13)	0.4107(21)	4.6(10)

Table 5
Selected bond lengths (Å) and bond angles (°) in complex **1** and **2**

Complex **1**		Complex **2**	
Selected bond lengths (Å)			
W(1)–W(2)	4.5096(11)	W(1)–W(2)	3.1942(12)
W(1)–P	2.626(3)	W(1)–P	2.538(5)
W(1)–C(1)	2.005(18)	W(1)–C(1)	2.033(22)
W(1)–C(2)	2.044(16)	W(1)–C(2)	2.049(20)
W(1)–C(3)	2.069(18)	W(1)–C(3)	2.001(25)
W(1)–C(4)	1.981(15)	W(1)–C(4)	2.013(21)
W(1)–C(5)	2.074(17)	W(1)–C(5)	1.996(16)
W(2)–P	2.625(3)	W(2)–P	2.376(3)
W(2)–C(6)	2.026(15)	W(2)–C(6)	2.067(18)
W(2)–C(7)	2.029(15)	W(2)–C(7)	2.024(21)
W(2)–C(8)	2.040(15)	C(1)–O(1)	1.14(3)
C(1)–O(1)	1.163(21)	C(2)–O(2)	1.108(24)
C(2)–O(2)	1.129(19)	C(3)–O(3)	1.19(3)
C(3)–O(3)	1.106(21)	C(4)–O(4)	1.19(3)
C(4)–O(4)	1.119(18)	C(5)–O(5)	1.145(19)
C(5)–O(5)	1.117(19)	C(6)–O(6)	1.037(20)
C(6)–O(6)	1.118(17)	C(7)–O(7)	1.15(3)
C(7)–O(7)	1.113(18)		
C(8)–O(8)	1.116(17)		
Selected bond angels (°)			
W(1)–P–W(2)	118.36(13)	W(1)–P–W(2)	81.02(18)
P–W(1)–C(1)	98.6(4)	P–W(1)–C(1)	90.9(6)
P–W(1)–C(2)	96.0(4)	P–W(1)–C(2)	80.2(5)
P–W(1)–C(3)	88.1(4)	P–W(1)–C(3)	93.4(5)
P–W(1)–C(4)	173.5(5)	P–W(1)–C(4)	112.6(5)
P–W(1)–C(5)	87.3(4)	P–W(1)–C(5)	163.6(6)
P–W(2)–C(6)	77.7(4)	P–W(2)–C(6)	80.1(6)
P–W(2)–C(7)	128.9(4)	P–W(2)–C(7)	105.5(7)
P–W(2)–C(8)	178.8(18)		
W(1)–C(1)–O(1)	175.3(13)	W(1)–C(1)–O(1)	178.8(18)
W(1)–C(2)–O(2)	178.0(12)	W(1)–C(2)–O(2)	174.1(16)
W(1)–C(3)–O(3)	179.0(13)	W(1)–C(3)–O(3)	177.2(15)
W(1)–C(4)–O(4)	177.2(13)	W(1)–C(4)–O(4)	174.1(15)
W(1)–C(5)–O(5)	177.4(14)	W(1)–C(5)–O(5)	179.6(19)
W(2)–C(6)–O(6)	177.9(12)	W(1)–C(6)–O(6)	167.9(23)
W(2)–C(7)–O(7)	177.2(12)	W(1)–C(7)–O(7)	176.3(22)
W(2)–C(8)–O(8)	177.1(12)		

Table 6
Selected bond lengths (Å) and bond angles (°) in complex **3a**

Bond length		Bond angle	
W(1)–W(2)	3.1513(12)	W(1)–P(1)–W(2)	80.96(13)
W(1)–P(1)	2.478(4)	P(1)–W(1)–P(2)	162.50(16)
W(1)–P(2)	2.414(5)	P(1)–W(1)–C(1)	79.0(5)
W(1)–C(1)	1.992(22)	P(1)–W(1)–C(2)	88.6(6)
W(1)–C(2)	1.980(19)	P(1)–W(1)–C(3)	114.4(5)
W(1)–C(3)	1.951(20)	P(1)–W(1)–C(4)	91.5(6)
W(1)–C(4)	1.975(19)	P(1)–W(2)–C(5)	83.9(7)
W(2)–P(1)	2.375(5)	P(1)–W(2)–C(6)	106.9(7)
W(2)–C(5)	1.941(18)	W(1)–C(1)–O(1)	176.3(17)
W(2)–C(6)	1.869(18)	W(1)–C(2)–O(2)	175.9(18)
O(1)–C(1)	1.17(3)	W(1)–C(3)–O(3)	172.3(13)
O(2)–C(2)	1.199(23)	W(1)–C(4)–O(4)	174.0(17)
O(3)–C(3)	1.235(23)	W(2)–C(5)–O(5)	178.2(18)
O(4)–C(4)	1.179(24)	W(2)–C(6)–O(6)	170.4(18)
O(5)–C(5)	1.138(21)		
O(6)–C(6)	1.196(23)		

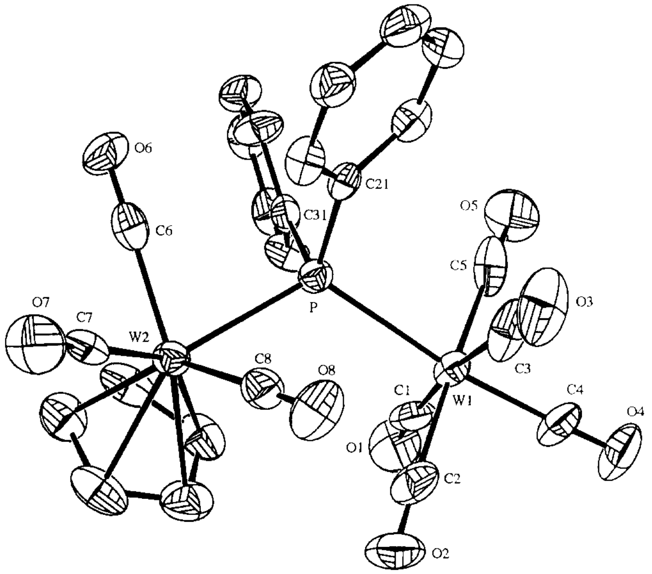


Fig. 2. ORTEP drawing of **1**. Hydrogen atoms are omitted.

addition product **4** was formed as an intermediate and lost a CO to produce **3** under the reaction conditions. Substitution of CO from W carbonyl usually requires a higher temperature than substitution of CO from Mo carbonyl. If the influence of the $CpW(CO)_2$ moiety on the adjacent metals in both complexes **2** and **5** is similar, substitution of CO from W(1) in **2** should require a higher temperature than substitution of CO from Mo in **5**. Indeed, higher temperature and longer reaction time (refluxing temperature in THF for overnight) were required in the reaction between **2** and

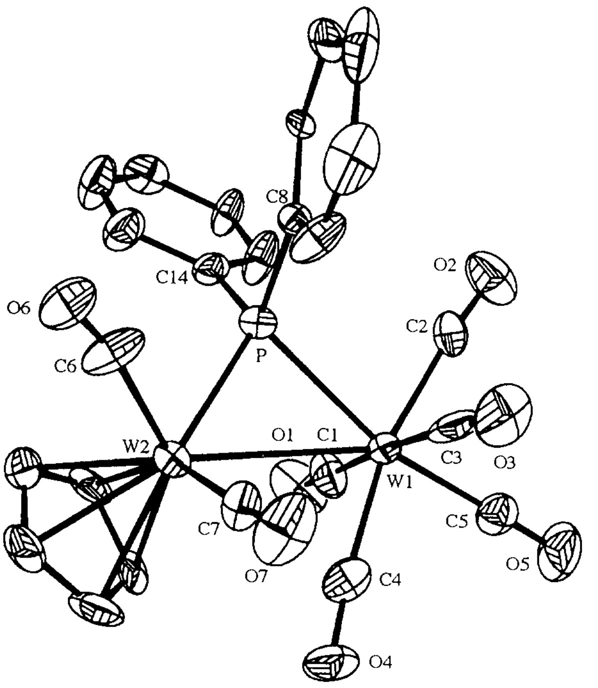


Fig. 3. ORTEP drawing of **2**. Hydrogen atoms are omitted.

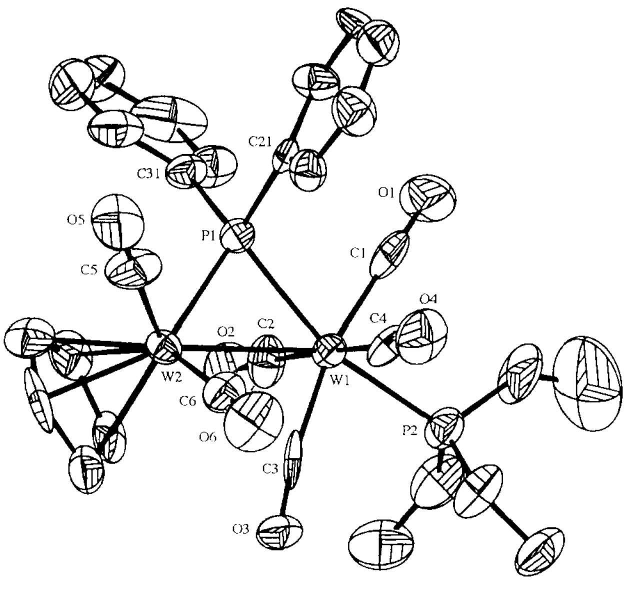


Fig. 4. ORTEP drawing of **3a**. Hydrogen atoms are omitted.

Lewis bases than in the corresponding reaction between complex **5** and Lewis bases (room temperature in THF for several hours). However, at higher temperature, complex **4** may lose one CO to produce **3** since $\mathrm{Cp(CO)_3}\overline{\mathrm{W}(\mu\text{-}\mathrm{PPh_2})\mathrm{Mo}}\mathrm{(CO)_4\{P(OMe)_3\}}$ produces $\mathrm{Cp(CO)_2}\overline{\mathrm{W}(\mu\text{-}\mathrm{PPh_2})\mathrm{Mo}}\mathrm{(CO)_4\{P(OMe)_3\}}$ under thermal conditions [2]. However, following the reaction by ^{31}P NMR spectroscopy, no intermediate was observed; the life time of the intermediate could be very short, resulting in the isolation of **3** as the only product.

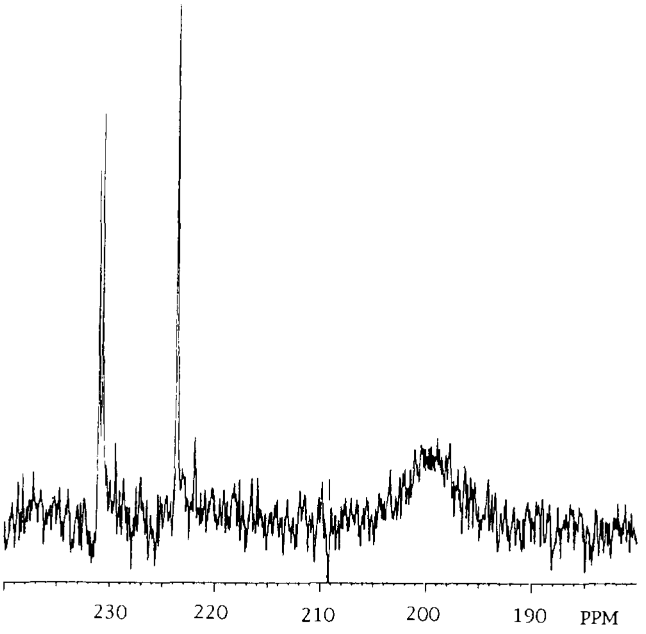


Fig. 5. Carbonyl region of the ^{13}C{^{1}H} NMR spectrum of **3b** at 300 K.

3.3. Role of the metal–metal dative bond in the substitution reaction

In the $\mathrm{(CO)_4}\overline{\mathrm{Ru}(\mu\text{-}\mathrm{PPh_2})\mathrm{Co}}\mathrm{(CO)_3}$ system, reaction between $\mathrm{(CO)_4}\overline{\mathrm{Ru}(\mu\text{-}\mathrm{PPh_2})\mathrm{Co}}\mathrm{(CO)_3}$ and phosphines L (L = $\mathrm{PPh_2Me}$, $\mathrm{PMe_2Ph}$, $\mathrm{PPh_2H}$) produced $\mathrm{(CO)_2L_2}\overline{\mathrm{Ru}(\mu\text{-}\mathrm{PPh_2})\mathrm{Co}}\mathrm{(CO)_3}$ instead of $\mathrm{(CO)_3L}\overline{\mathrm{Ru}(\mu\text{-}\mathrm{PPh_2})\mathrm{Co}}\mathrm{(CO)_2L}$. [17] Since $\mathrm{(CO)_3(PPh_3)}\overline{\mathrm{Ru}(\mu\text{-}\mathrm{PPh_2})\mathrm{Co}}\mathrm{(CO)_2(PPh_3)}$ can be prepared by other synthetic routes, labilization of CO groups on Ru by the metal–metal bond in the complex was proposed to be one of the possible reasons [17].

One way to evaluate the influence of the metal–metal bond in the substitution reaction is to construct two types of complexes having a similar framework with and without a metal–metal bond, and to compare their substitution reactions under similar conditions. Complexes **1** and **2** are suitable for this purpose. First, both complexes have a similar framework, **2** with metal–metal bonding and **1** without. Second, complex **1** was inert when its THF solution was heated under reflux overnight. This thermal stability makes the comparison feasible because many non-metal–metal bonded phosphido-bridged complexes convert to the metal–metal bonded complexes under relatively mild conditions [1b,2,11].

Carbonyl ligands on W in **1** were inert towards phosphine when a THF solution of **1** and phosphine was heated under reflux overnight. On the other hand, when **2** was reacted with phosphines under similar conditions, the substituted complex **3** was obtained. These observations clearly indicate that CO ligands on W in **2** were labilized by the metal–metal bond.

The $\mathrm{W(CO)_5}$ moiety in **2** was probably activated by the electron donation from the filled t_{2g} orbital of the W(1) atom to the W(2) atom through the dative metal–metal bond. The net result of this donation will be a decrease in $d_{xy} \rightarrow \pi^*$ to the equatorial CO/s [1d,2], which induces weakening of the W–CO bond in **2**. The adjacent metal W(2) may also labilize the W(1)–CO group through the donation of the electron from the electron rich W(2) to the π^* orbital of the adjacent W(1)–CO bond to form the semibridging carbonyl ligand similar to complex **5** [2].

4. Conclusions

Binuclear phosphido-bridged complexes without a metal–metal bond, **1**, and with a metal–metal bond **2**, were synthesized in order to study the influence of the metal–metal bond in the substitution reaction. Structures of both complexes were determined by single-crystal X-ray diffraction methods.

Substitution of CO in **2** by phosphines was regiospecific and stereospecific on the W(1) and *trans* to the phosphido bridge. The structure of **3a** was determined by single crystal X-ray methods. Under similar conditions, the W(1) CO in **1** was inert towards phosphines. The metal–metal bond in **2** was believed to labilize the carbonyl ligand on W(1).

Acknowledgment

We wish to thank the National Science Council, Republic of China, and Academia Sinica for financial support of this work.

References

[1] (a) S.-G. Shyu and A. Wojcicki, *Organometallics, 4* (1985) 1457; (b) W.C. Mercer, R.R. Whittle, E.W. Burkhardt and G.L. Geoffroy, *Organometallics, 4* (1985) 68; (c) J. Powell, J.F. Sawyer and M.V.R. Stainer, *Inorg. Chem., 28* (1989) 4461; (d) J. Powell, C. Coutoure and M.R. Gregg, *J. Chem. Soc., Chem. Commun.*, (1988) 1208.

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

[3] D.D. Perrin, W.L.F. Armarego and D.R. Perrin, *Purification of Laboratory Chemicals*, Pergamon, Oxford, 1966.

[4] R. Bender, P. Braunstein, J.-M. Jud and Y. Dusausoy, *Inorg. Chem., 22* (1983) 3394.

[5] (a) H. Adams, N.A. Bailey, A.N. Day, M.J. Morris and M.M. Harrison, *J. Organomet. Chem., 407* (1991) 247; (b) W. Malisch, R. Maisch, I.J. Colquhoun and W. McFarlane, *J. Organomet. Chem., 220* (1981) C1.

[6] (a) S.G. Shyu, J.Y. Hsu and Y.-S. Wen, *J. Organomet. Chem., 453* (1993) 97; (b) D.A. Roberts and G.L. Geoffroy, in G. Wilkinson, F.G.A. Stone and E. Abel (eds.), *Comprehensive Organometallic Chemistry*, Vol. 6. Pergamon Press, London, 1982, pp. 780–783; (c) J.C.T.R. Burckett-St. Launent, R.J. Haines, C.R. Nolte and N.D.C.T. Steen, *Inorg. Chem., 19* (1980) 577; (d) R.J. Haines, R. Mason, J.A. Zubieta and R.C. Nolte, *J. Chem. Soc., Chem. Commum.*, (1972) 990; (e) R.G. Hayter, *Inorg. Chem., 2* (1963) 1031; (f) P. Braunstein and E. de Jesus, *J. Organomet. Chem., 365* (1989) C19.

[7] (a) A.J. Carty, S.A. Maclaughlin and D. Nucciarone, in J.G. Verkade and L.P. Quin (eds.) *Phosphorus-31 NMR Spectroscopy in Stereochemical Analysis. Organic Compounds and Metal Complexes*, VCH, New York, 1987, Ch. 16 and refs. therein. (b) P.E. Garrou, *Chem. Rev., 81* (1981) 229.

[8] (a) J. Levisalles, H. Rudler, F. Dahan and Y. Jeannin, *J. Organomet. Chem., 188* (1980) 193; (b) J. Levisalles, F. Rose-Munch, H. Rudler, J.C. Daran, Y. Dromzee and Y. Jeannin, *J. Chem. Soc., Chem. Commun.*, (1980) 685; (c) H. Berke, P. Harter, G. Hutter and L. Zsolnai, *Chem. Ber.*, 115 (1982) 695; (d) H. Fischer, S. Zeuner and K. Ackermann, *J. Chem. Soc., Chem. Commun.*, (1984) 684.

[9] R.D. Adams, D.M. Collins and F.A. Cotton, *Inorg. Chem., 13* (1974) 1086.

[10] S.-G. Shyu, M. Calligaris, G. Nardin and A. Wojcicki. *J. Am. Chem. Soc., 109* (1987) 3617.

[11] D.A. Roberts, G.R. Steinmetz, M.J. Breen, P.M. Shulman, E.D. Morrison, M.R. Duttera, C.W. DeBrosse, R.R. Whittle and G.L. Geoffroy, *Organometallics, 2* (1983) 846.

[12] Equation of the plane: 10.60 (8) $X + 7.92$ (7)$Y - 2.28(6)Z =$ 4.287(7). Distances (Å) to the plane from the atoms in the plane. P − 0.003(9), C(2) 0.05(3), C(4) 0.05(3), C(5) −0.08(3). Chi squared for this plane 13.247. Distances (Å) to the plane from the atoms out of the plane. W(1) 0.003(10), W(2) −0.063(20).

[13] J. Emsley, *The Elements*, Oxford University Press, New York, 1989.

[14] D.S. Ginley, R. Bock, M.S. Wrighton, B. Fishcher, D.L. Tipton and R. Bau, *J. Organomet. Chem., 407* (1978) 247.

[15] S.G. Shyu, P.-J. Lin, T.-Y. Dong and Y.-S. Wen, *J. Organomet. Chem., 460* (1993) 229.

[16] S.W. Kirtley, in G. Wilkinson, F.G.A. Stone and E. Abel (eds.), Comprehension Organometallic Chemistry, Vol. 3, Pergamon, London, 1982, pp. 842–844.

[17] R. Regragui, P.H. Dixneuf, N.J. Taylor and A.J. Carty, *Organometallics, 25* (1986) 1.