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Synthesis, structure and fluxional behavior of phosphido-bridged complex $\mathrm{Cp\overline{W(CO)_2(\mu\text{-}PPh_2)Cr}(CO)_5}$

Shin-Guang Shyu, Jiun-Yi Hsu and Yuh-Shang Wen

Institute of Chemistry, Academia Sinica, Taipei (Taiwan, ROC)

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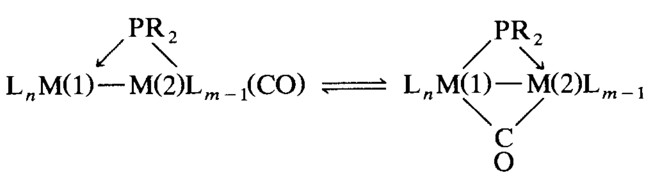
Abstract

The metal–metal bonded phosphido-bridged complex $\mathrm{Cp\overline{W(CO)_2(\mu\text{-}PPh_2)Cr}(CO)_5}$ has been synthesized by the reaction of $\mathrm{CpW(CO)_3PPh_2}$ with $\mathrm{Cr(CO)_5THF}$. The solid state structure of the complex was determined by single-crystal X-ray diffraction. A semibridging carbonyl and a dative Cr–W bond of length 3.09 Å were observed. Results from variable temperature ^{13}C NMR spectroscopy indicates four CO ligands, coordinated to Cr and *cis* to the phosphido bridge, which exchange with one another at room temperature.

1. Introduction

Since the discovery [1] of mono phosphido-bridged heterobimetallic carbonyl complexes with metal–metal bond, many complexes of this type have been prepared and their structures determined by X-ray diffraction [2,3]. There are two possible structures for this kind of complex, one with bridging carbonyl or semibridging carbonyl [3] and the other without [2]. Electron counting of both structures is in accordance with the 18 electron rule. One can consider the phosphido bridge as a three electron donor. For structure **A**, the phosphido ligand donates two electrons to M(1) and is covalently bonded to M(2). For structure **B**, the coordination bonding and covalent bonding are reversed. Both types of structure have been observed and determined by X-ray diffraction [2,3c].



(A) **(B)**

Complexes with both types of structures in solution have been proposed [4]. The equilibrium between these two isomers may involve the opening and closing of the bridging carbonyl–metal–metal triangle [4]. In order to investigate the fluxional behavior of the metal–metal bonded phosphido-bridged complex, we synthesized a new complex of this kind with a weak semibridging carbonyl $\mathrm{Cp\overline{W(CO)_2(\mu\text{-}PPh_2)Cr}(CO)_5}$. Here, we report its solid state structure and its variable temperature ^{13}C NMR spectra. Novel fluxional behavior was observed involving exchange of four *cis* CO ligands on the seven coordinated Cr.

2. Experimental section

Unless otherwise stated, all reactions and manipulations of air-sensitive compounds were carried out with standard procedures at ambient temperature under purified N_2. Infrared (IR) spectra were recorded on a Perkin-Elmer 882 infrared spectrophotometer. ^{1}H NMR spectra were obtained on a Bruker AC-200 spectrometer. ^{13}C NMR spectra were recorded on a Bruker MSL-200 at 50.32 MHz or on a Bruker ASM-500 spectrometer at 125.76 MHz. Both ^{1}H and ^{13}C chemical shifts are given in ppm downfield from the internal standard $\mathrm{Me_4Si}$. ^{31}P NMR spectra were obtained on the Bruker MSL-200 at 81.00 MHz or on a Bruker ASM-500 spectrometer at 202.5 MHz. Chemical shifts are reported with reference to 85% H_3PO_4. Except as noted, these NMR spectra were collected at room

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Correspondence to: Dr. S.-G. Shyu.

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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. Elemental analyses were performed by use of a Perkin-Elmer 2400 CHN elemental analyzer.

2.1. Materials

THF was distilled from K and benzophenone under an atmosphere of N_2 immediately before use. Other solvents were purified according to established procedures [5]. Metal carbonyls $M(CO)_6$ (M = Cr, W), PPh_2Cl were obtained from Strem. ^{13}CO (99 atom% ^{13}C) was purchased from Isotec. Other reagents and solvents were obtained from various commercial sources and used as received. The complex $Cr(CO)_5THF$ was prepared *in situ* by photolysis of $Cr(CO)_6$ in THF [6]. $Cr(CO)_4(C_7H_8)$ [7], $Na[CpW(CO)_3]\cdot 2DME$ [8] and $WCp(CO)_2PPh_2$ [9] were prepared by literature procedures.

2.2. Preparation of $Cp(CO)_3W(\mu\text{-}PPh_2)Cr(CO)_5$ (1) and $Cp(CO)_2\overline{W(\mu\text{-}PPh_2)Cr}(CO)_5$ (2)

2.2.1. Method a: Reaction between $CpW(CO)_3PPh_2$ and $Cr(CO)_5THF$

A solution of $Na[CpW(CO)_3]\cdot 2DME$ (1.14 g, 2.13 mmol) in 75 ml toluene was cooled to 0°C. Solution of 0.4 ml (2.1 mmol) of PPh_2Cl in 50 ml of toluene was then slowly added into the above solution. After 1 h, the color of the solution turned to orange red. Solvent was removed and an orange red solid was obtained. At the same time, $Cr(CO)_5THF$ was generated *in situ* by photolysis of $Cr(CO)_6$ (1.00 g, 4.54 mmol) in 80 ml THF with a 450 Watt Hanovia medium-pressure quartz mercury-vapor lamp (Ace Glass) for 4 h. This solution was then mixed with the orange red solid generated as previously stated. The mixture was allowed to stir for one day. Solvent was then removed and the residue chromatographed on silica gel. Elution with CH_2-Cl_2 : hexane(1 : 4) afforded two fractions. After the solvent was removed, a red solid, **2**, was obtained from the first fraction. Yield 0.11 g (7.25%). Anal. Calcd. for $C_{24}H_{15}O_7PCrW$: C, 42.25; H, 2.22. Found: C, 42.09; H, 2.28%. IR spectrum (THF, ν(CO)): 2057m, 1959s, 1941s, 1906m, 1869w cm^{-1}. ^1H NMR spectrum ($CDCl_3$): δ 7.80 (m, 2H), 7.43 (m, 3H), 7.27 (m, 3H), 7.01 (m, 2H), 5.2 (s, 5H). $^{31}P\{^1H\}$ NMR spectrum (THF): δ 178.8 (J(P–W) = 326.2 Hz). MS(EI), M^{+1} m/z 682.

A yellow solid, **1**, was obtained after solvent was removed from the second fraction. Yield, 0.31 g (20.0%). Anal. Calcd. for $C_{25}H_{15}O_8PCrW$: C, 42.28; H, 2.13. Found: C, 41.87; H, 2.56%. IR spectrum (THF, ν(CO)): 2056w, 2024w, 1946s, 1929s, 1915m, cm^{-1}. ^1H NMR spectrum ($CDCl_3$): δ 7.5 (m, 10H), 5.33 (s, 5H). $^{31}P\{^1H\}$ NMR spectrum (THF): δ −24.2 (J(P–W) = 89.1 Hz). MS(FAB), M^{+1} m/z 710.

2.2.2. Method b: Reaction between $CpW(CO)_3PPh_2$ and $Cr(CO)_4(C_7H_8)$

A yellow suspension of $Na[CpW(CO)_3]\cdot 2DME$ (6.00 g, 11.19 mmol) in 100 ml THF was cooled to 0°C. Solution of 2.1 ml (11.3 mmol) of PPh_2Cl in 25 ml of THF was then slowly added into the above solution. After 30 min, the solution turned orange red. A yellow solution of 3.0 g $Cr(CO)_4(C_7H_8)$ in 50 ml THF was then added. The mixture turned red immediately. After stirring overnight, solvent was removed and the residue was chromatographed on grade III Al_2O_3. Elution with CH_2Cl_2 : hexane(1 : 4) afforded two fractions. The first (yellow) band was intact $Cr(CO)_4(C_7H_8)$. The second band was deep red. After the solvent was removed, a red solid was obtained. It was characterized by various spectra and identified as $Cp(CO)_2\overline{W(\mu\text{-}PPh_2)Cr}(CO)_5$. Yield, 2.4 g (31.3%).

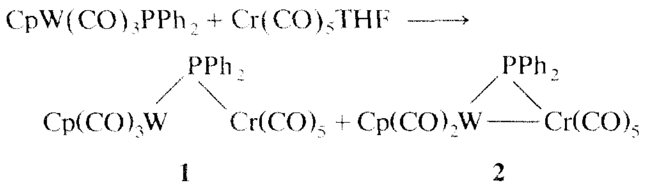
2.3. Crystallographic analyses of $Cp\overline{W(CO)_2(\mu\text{-}PPh_2)\text{-}Cr}(CO)_5$

A suitable crystal of **2** was obtained by slow diffusion of hexane into a saturated solution of **2** in CH_2Cl_2 under air at 0°C. Diffraction measurements were carried out on an Enraf-Nonius CAD-4 diffractometer. Space group and crystal collection data for **2** are given in Table 1.

3. Results and discussion

3.1. Preparation of $Cp\overline{W(CO)_2(\mu\text{-}PPh_2)Cr}(CO)_5$ (2)

We prepared the new complex **2** by adding the THF solution of $Cr(CO)_5THF$ to the solution of metallophosphine $CpW(CO)_3PPh_2$ in toluene under N_2 atmosphere at 0°C. The metallophosphine ligand replaced the THF ligand on $Cr(CO)_5THF$ and bridged the metals to form the non metal–metal bonded complex $CpW(CO)_3(\mu\text{-}PPh_2)Cr(CO)_5$ (major) and metal–metal bonded complex $Cp\overline{W(CO)_2(\mu\text{-}PPh_2)Cr}(CO)_5$ (minor) (eqn. (1)) [10].



$CpW(CO)_3PPh_2 + Cr(CO)_5THF \longrightarrow$

1 **2**

(1)

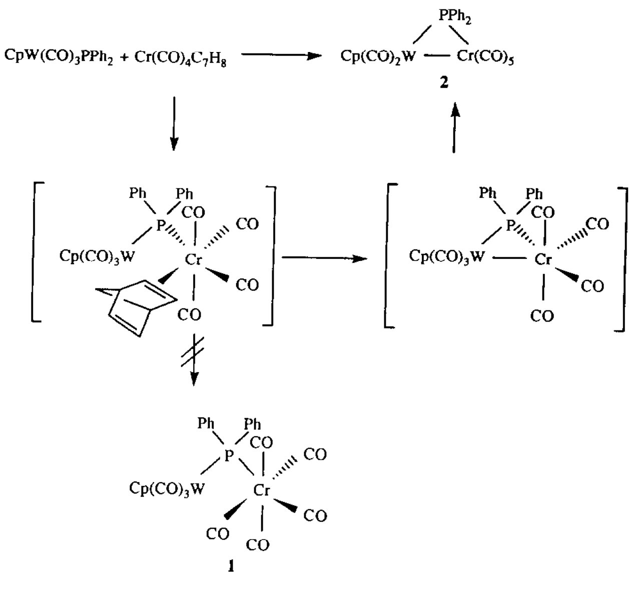
Structural analysis of **1** has not yet been made. However, the mass spectrum of **1** shows parent peak with m/z at 710 which is consistent with the empirical

TABLE 1. Crystal and intensity collection data for complex **2**

Molecular formula	$C_{24}H_{15}CrO_7PW$
Mol. wt.	667.07
Crystal system	Monoclinic
Space group	$P2_1/c$
a (Å)	10.916(3)
b (Å)	11.7895(16)
c (Å)	19.006(3)
α (deg)	-
β (deg)	101.900(16)
γ (deg)	-
V (Å^3)	2393.3(8)
ρ (calc.) (Mg m^{-3})	1.851
Z	4
Crystal dimensions (mm)	0.38×0.38×0.47
Absolute coefficient μ (Mo Kα) (mm^{-1})	5.46
Temperature	Room temperature
Radiation	Mo Kα λ = 0.70930 Å
2θ range	45°
Scan type	$2\theta-\omega$
No. of reflections	3421
No. of observed reflections	2620(> 2.0σ)
Variables	307
R	0.026
R_w	0.033
S	1.85
ΔF (e/Å^3)	< 0.350
$(\Delta/\sigma)_{max}$	0.003

formula of $CpW(CO)_3(\mu\text{-}PPh_2)Cr(CO)_5$. The ratio of the intensity of its ^{31}P signal to the intensity of the $J(^{31}P\text{-}W)$ satellite is 11:1. This indicates that the phosphorus is coordinated to only one tungsten [11*]. Its ^{31}P NMR signal at upfield position indicates that there is no metal–metal bond between the metals [12]. In addition, the spectroscopic data (IR, ^1H NMR and ^{31}P NMR) of **1** are similar to $CpW(CO)_3(\mu\text{-}PPh_2)Mo(CO)_5$ whose structure has been determined by X-ray diffraction [13*].

The complex **2** can also be prepared by the reaction of $CpW(CO)_3PPh_2$ with $Cr(CO)_4(C_7H_8)$. The metallophosphine ligand is considered properly to replace one olefin–Cr bonding at the first step. Concurrent formation of the metal–metal bond and breakage of the second olefin–Cr bond occur followed by the rearrangement of CO ligands in the complex produced (**2**) (Scheme 1). The mechanism for transposition of one CO from W to Cr is not clear. The replacement of the second olefin–Cr bond by free CO from the environment is excluded because no complex **1** was obtained from the reaction.



Scheme 1.

3.2. Molecular structure of $CpW(CO)_2(\mu\text{-}PPh_2)Cr(CO)_5$

Red crystals of **2** were obtained by slow diffusion of hexane into the saturated solution of **2** in dichloromethane at 0°C. Single X-ray diffraction study of the complex was carried out. Its atomic positional parameters and selected bond lengths and bond angles are listed in Tables 2 and 3. The ORTEP drawing is shown in Fig. 1.

A Cr–W distance of 3.09 Å indicates the existence of a Cr–W single bond on the basis of the other crystallographically characterized compound $[(\eta\text{-}Me_6\text{-}C_6)(OC)_2Cr(\mu\text{-}CC_6H_4Me\text{-}4)W(CO)_2(\eta\text{-}C_5H_5)]\cdot$ [14]. We consider this bonding as a donor-acceptor bond [15] from the Cr^0 center to W^{II}. The Cr–W dative bond can be considered 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 fact that the Cr–W vector bisects an edge of the distorted chromium octahedron. The Cr atom lies on the least-squares plane consisting of P, C(4), C(5) and C(2) atoms. The Cr–W vector is 2.5° off the plane [16*]. The Cr–W bond can be considered as a donation of an electron pair from one of the filled t_{2g} orbitals of Cr to the adjacent W [17].

For the satisfaction of the 18 electron counting rule, the three electron donating phosphido bridge ligand should donate two electrons to the Cr and one electron to the W atom. The Cr–P distance 2.391 Å is shorter than the Cr–P distance 2.422 Å in the corresponding $(CO)_5Cr(PPh_3)$ [18]. This suggests a stronger Cr–P bond with more partial double bond character between metal and phosphorus in the complex than the corre-

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* Reference number with an asterisk indicates a note in the list of references.

sponding Cr–P bond in $(CO)_5Cr(PPh_3)$. This is consistent with the observations that the Cr–C(4) distance of the CO *trans* to the phosphido-bridged ligand in the complex is greater than the corresponding M–C distance of *trans* CO (1.844(4) Å) in $Cr(CO)_5(PPh_3)$ [18b].

The Cr–C(2)–O(2) angle 163.0° indicates a semibridging carbonyl [19]. The W–C(2) distance 2.78 Å is relatively long. However, it is smaller than the sum of the atomic radius of W (1.30 Å) [20] and the van der Waals radius of C (1.85 Å) [20]. This indicates that the bonding between the semibridging CO and the W atom is relatively weak.

Distortion of linear CO to slightly bent CO due to steric factors in the phosphido-bridged complex have been reported [17]. Nevertheless, the long distance between the bending CO and the other ligands of the adjacent W in **2** indicates that this possibility is unlikely to exist here (Fig. 1). In addition, the dative Cr–W bond results in the oxidation state of W being +1 and of Cr +1 [19]. Together with the electron donating ligand Cp, W has relatively larger electron density than the adjacent Cr. Thus, the W atom releases electrons to stabilize the molecule by donating electrons to the π^* orbital of the CO ligand on the adjacent Cr to form the semibridging CO [19].

3.3. Spectroscopic data of 2

The ^{31}P NMR of **2** in THF at room temperature shows resonance at 178.8 ppm with J(P–W) 326.2 Hz. This relatively downfield resonance is consistent with the presence of metal–metal bond in the complex [12]. The intensity ratio of the phosphorus signal to the J(P–W) satellites is 11 : 1, indicating that phosphorus is coordinated to only one tungsten [11]. The mass spectrum of the complex shows a parent peak with m/z at 682, which is inconsistent with the empirical formula of $\overline{CpW(CO)_2(\mu\text{-}PPh_2)Cr}(CO)_5$. IR of **2** in THF shows absorption of the terminal CO units at around 2000 cm^{-1}. We assign low frequency absorption at 1867 cm^{-1} to the semibridging carbonyl because its value is lower than the absorption frequencies of terminal carbonyls of $CpW(CO)_3PPh_2$ [9b] and $Cr(CO)_5PPh_2H$ [21].

3.4. Variable temperature ^{13}C NMR and fluxional behavior of 2

Bridging CO has a relatively downfield resonance compared with that of terminal CO [22]. Thus, if fluxional behavior involves the opening and closing of semibridging CO, ^{13}C NMR would be the best method for studying this behavior. In order to investigate the possible fluxional behavior, we enriched the complex **2** with ^{13}CO and variable temperature ^{13}C NMR spectra were taken (Fig. 2).

At 323 K, a broad hump, a; two singlets, b and c; and another broad peak, d were observed at 228, 222.2, 220.8, and 217 ppm, respectively. At 300 K, signal a (228 ppm) was sharpened to a broad doublet and signal d (217 ppm) was flattened. In addition, J(P–C) was observed for signal c (222.2 ppm, (J(P–C) = 3.75 Hz). At 280 K, signal a (228.5 ppm, J(P–C) = 17.5 Hz) was

TABLE 2. Atomic coordinates and isotropic thermal parameters ($Å^2$) for **2**

Atom	x	y	z	B_{iso}
W	0.24133(3)	0.23090(2)	0.23075(1)	3.32(1)
Cr	0.40341(10)	0.17564(9)	0.38012(5)	3.14(5)
P	0.21762(16)	0.28728(14)	0.34687(9)	2.97(8)
O1	0.5711(5)	0.3809(5)	0.3744(3)	6.5(3)
O2	0.5263(5)	0.0926(5)	0.2604(3)	5.9(3)
O3	0.2462(6)	−0.0381(5)	0.3792(3)	6.7(4)
O4	0.6149(5)	0.0293(5)	0.4572(3)	6.7(3)
O5	0.3838(7)	0.2569(5)	0.5283(3)	7.2(4)
O6	0.4721(6)	0.3508(5)	0.1898(3)	6.2(3)
O7	0.1212(7)	0.4669(6)	0.1914(3)	8.5(4)
C1	0.5068(7)	0.3064(7)	0.3761(4)	4.2(4)
C2	0.4644(7)	0.1271(6)	0.2970(4)	4.0(3)
C3	0.3016(7)	0.0432(7)	0.3793(4)	4.3(4)
C4	0.5356(7)	0.0865(7)	0.4284(4)	4.7(4)
C5	0.3879(7)	0.2238(7)	0.4723(4)	4.5(4)
C6	0.3871(8)	0.3099(6)	0.2071(4)	4.2(4)
C7	0.1687(8)	0.3815(7)	0.2076(4)	5.3(4)
C9	0.2193(9)	0.0333(7)	0.2049(5)	5.3(4)
C10	0.1072(10)	0.0731(8)	0.2221(5)	6.4(5)
C11	0.0557(8)	0.1549(10)	0.1696(6)	7.2(6)
C12	0.1405(10)	0.1635(8)	0.1208(4)	6.5(5)
C13	0.2392(8)	0.0900(7)	0.1426(4)	5.1(4)
C21	0.2300(6)	0.4328(5)	0.3813(3)	3.1(3)
C22	0.3000(7)	0.5123(6)	0.3522(4)	4.1(3)
C23	0.3162(8)	0.6198(7)	0.3797(5)	5.2(4)
C24	0.2650(8)	0.6511(6)	0.4367(4)	5.0(4)
C25	0.1980(8)	0.5737(7)	0.4666(4)	4.6(4)
C26	0.1795(6)	0.4653(6)	0.4389(4)	3.7(3)
C31	0.0765(7)	0.2379(6)	0.3754(4)	4.0(4)
C32	0.0781(8)	0.1760(7)	0.4379(5)	5.4(4)
C33	−0.0346(12)	0.1477(9)	0.4571(6)	8.1(7)
C34	−0.1451(12)	0.1797(10)	0.4152(9)	9.6(9)
C35	−0.1474(9)	0.2400(9)	0.3539(9)	8.9(8)
C36	−0.0379(8)	0.2699(7)	0.3333(6)	6.1(5)
H9	0.269	−0.033	0.228	6.2
H10	0.059	0.049	0.261	6.9
H11	−0.028	0.190	0.159	7.5
H12	0.135	0.224	0.083	7.0
H13	0.313	0.088	0.119	5.9
H22	0.338	0.490	0.311	5.0
H23	0.366	0.677	0.358	6.0
H24	0.274	0.729	0.456	5.7
H25	0.161	0.594	0.509	5.2
H26	0.127	0.410	0.460	4.6
H32	0.162	0.153	0.469	6.9
H33	−0.030	0.100	0.504	9.9
H34	−0.220	0.156	0.433	10.8
H35	−0.232	0.261	0.325	10.2
H36	−0.041	0.318	0.288	7.3

TABLE 3. Selected bond lengths (Å) and angles (°) in complex **2**

Length		Angle	
W–Cr	3.0891(12)	W–P–Cr	80.92(6)
W–P	2.3696(17)	Cr–W–P	49.84(5)
W–C(2)	2.783(7)	Cr–W–C(2)	37.79(16)
W–C(6)	1.974(8)	P–W–C(6)	109.12(21)
W–C(7)	1.957(9)	P–W–C(7)	80.65(23)
Cr–P	2.3908(21)	W–C(2)–O(2)	117.0(5)
Cr–C(1)	1.921(9)	Cr–C(1)–O(1)	177.7(6)
Cr–C(2)	1.924(8)	Cr–C(2)–O(2)	163.0(7)
Cr–C(3)	1.915(8)	Cr–C(3)–O(3)	176.9(7)
Cr–C(4)	1.866(8)	Cr–C(4)–O(4)	178.2(7)
Cr–C(5)	1.882(8)	Cr–C(5)–O(5)	176.3(7)
P–C(21)	1.831(7)	W–C(6)–O(6)	175.5(6)
P–C(31)	1.830(7)	W–C(7)–O(7)	176.3(8)
O(1)–C(1)	1.129(10)	W–Cr–P	49.24(5)
O(2)–C(2)	1.141(10)	P–Cr–C(1)	91.21(21)
O(3)–C(3)	1.132(10)	P–Cr–C(2)	111.41(22)
O(4)–C(4)	1.144(10)	P–Cr–C(3)	89.28(23)
O(5)–C(5)	1.143(10)	P–Cr–C(4)	165.42(25)
O(6)–C(6)	1.152(10)	P–Cr–C(5)	81.14(24)
O(7)–C(7)	1.146(11)		

further sharpened. At 250 K coupling between C and W were clearly observed for signals a (222.2 ppm) and b (220.8 ppm) with J(P–W) of 162.0 Hz and 174.9 Hz, respectively. Four broad peaks (d1, d2, d3 and d4) appeared at 228.5, 216.1, 214.2, and 209.9 ppm, respectively, and their intensity ratio was 1 : 1 : 1 : 1. At 210 K, all peaks were sharpened and J(P–C) was clearly observed for signal d2 (216.1 ppm). The intensity ratio of all seven signals was 1 : 1 : 1 : 1 : 1 : 1 : 1 corresponding to the seven CO ligands in the complex.

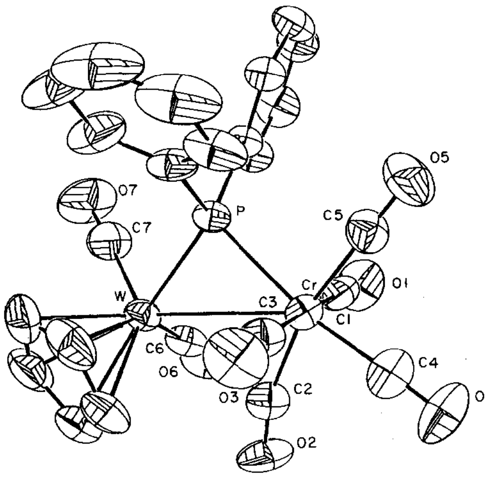


Fig. 1. ORTEP drawing of **2**. Hydrogen atoms are omitted. Non bonding distances (Å): C(2) ··· C(9) 3.085(11), C(2) ··· C(6) 2.771(10), C(2) ··· W 2.783(7).

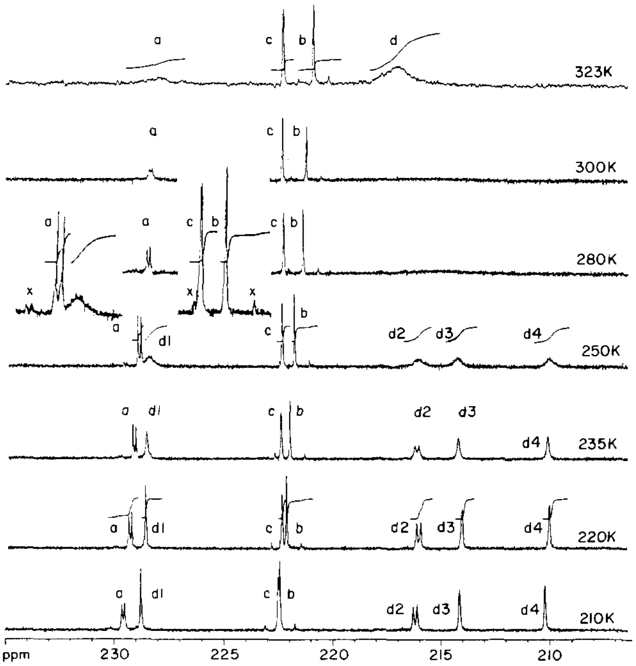
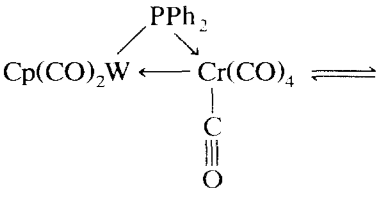


Fig. 2. Variable temperature $^{13}C\{^1H\}$ NMR spectrum of **2**. Only carbonyl region is shown. J(P–W) satellites are marked x.

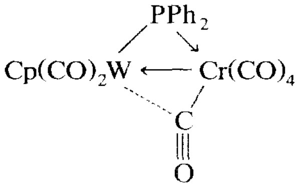
We assign the two CO signals, a and b, to CO ligands coordinated to the W, based on observations of their tungsten satellites. The signal d1 belongs to the semibridging carbonyl because bridging carbonyl has a relatively downfield position compared with the corresponding terminal carbonyls [22]. The doublet c is assigned to the chromium CO *trans* to the phosphido bridge on the basis of its position relatively downfield compared with the resonance positions of the other terminal CO's of Cr [20c,21]. The remaining CO signals (d2, d3 and d4) are assigned to the other *cis* CO's. The large J(P–C) value of the *cis* CO resonance of signal d2 compared with the small J(P–C) value of the *trans* CO resonance c is not unexpected because the *cis* CO J(P–C) values are usually larger than the *trans* CO J(P–C) values in the $Cr(CO)_5PR_3$ system [23].

We interpret the ^{13}C NMR observations as follows. Below 235 K, all carbonyls are rigid and no intramolecular exchange occurs among carbonyl ligands. Above 235 K, exchange takes place among the three *cis* chromium carbonyl ligands and the semibridging CO (with signal at 228.7 ppm) as indicated by the broadening of their NMR signals (d2, d3, d4 and d1). Signals of the *trans* CO ligand, c, and two tungsten terminal carbonyl ligands, a and b, remain unchanged up to 280 K, indicating that these three ligands do not involve themselves in the exchanging process. However, above 300 K, the broadening of the tungsten CO signal a at 228.2 ppm is observed to indicate the additional exchange process of the CO ligands. There are two possible kinds of exchange. One is the exchange between this CO and the other *cis* CO ligands because the other tungsten CO signal and the *trans* chromium CO ligands signals remain unchanged through the whole process. However, at higher temperature (343 K), decomposition of the compound occurs and a coalescence point cannot be obtained. The other possibility is the dissociation and reassociation of this tungsten CO in the solution. The ligand exchange experiment is unsuccessful for this purpose because the reaction between **2** and ^{13}CO results in the formation of the non-metal–metal bonded complex **1**.

The exchange of the semibridging carbonyl ligand and the other three *cis* CO ligands may go through the rotation of the Cr–P bond. The rotation of the Cr–P NMR requires the breakage and reformation of the metal–metal dative bond. The breakage of the metal–metal bond in phosphido-bridged complexes is usually accompanied by an upfield shift of the ^{31}P resonance. Variable temperature ^{31}P NMR of **2** did not show any change of the resonance position. This indicates that the breakage and reformation of the Cr–W bond are so rapid that the exchange time scale is beyond the NMR detection limit.



A′



B′

The rotation of the Cr–P bond may be preceded by the opening of the semibridging CO to form a complex with structure **A′** [24]. We did not find any signal corresponding to the terminal CO's in **A′**. However, we cannot rule out the possibility of the formation of **A′**. The reason we did not observed **A′** in the spectra might be due to the rapid rotation of the Cr–P bond right after the cleavage of the W-semibridging CO bonding.

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References and notes

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13 S.G. Shyu, unpublished result. Spectroscopic data of $CpW(CO)_3(\mu\text{-}PPh_2)Mo(CO)_5$: IR spectrum (THF, ν(CO)): 2067w, 2025w, 1948s, 1938sh, 1914m cm^{-1}. ^1H NMR spectrum ($CDCl_3$): δ 7.5 (m, 10H), 5.3 (s, 5H). $^{31}P\{^1H\}$ NMR spectrum (THF): δ −41.7.

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