STUDIES ON BINUCLEAR COMPLEXES.

THE SYNTHESIS AND MOLECULAR STRUCTURE OF PdMo(μ-Ph$_2$Ppy)$_2$(μ-CO)(CO)$_2$ · 0.5CH$_2$Cl$_2$

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Summary

Reaction of Mo(CO)$_4$(Ph$_2$Ppy)$_2$(Ph$_2$Ppy = 2-(diphenylphosphino)pyridine) with (1,5-cyclooctadiene)PdCl$_2$ gave PdMo(μ-Ph$_2$Ppy)$_2$(μ-CO)(CO)$_2$ · 0.5CH$_2$Cl$_2$. The molecular structure was determined by X-ray diffraction. The complex crystallized in the monoclinic space group $P2_1/c$ with a 14.615(2), b 15.358(3), c 17.721(2) Å, β = 97.18(1)°, Z = 4. The final R = 0.055 and R_w = 0.065 values were for independent reflections. The structure of the binuclear complex indicates that it possesses a Pd–Mo bond which has a bond length of 2.817(1) Å. The palladium atom is five-coordinated and the molybdenum atom is seven-coordinated. Both metal atoms possess the formal oxidation state +1. The molecule is chiral and belongs to the C_1 point group. Different types of spectra are also discussed.

Introduction

The heterobinuclear complexes form an important topic in organometallic chemistry [1, 2]. These complexes usually possess a particular bonding pattern and may activate a series of small molecules, such as CO, SO$_2$, acetylene, etc. In order to compare the structure and reactivity with different heterobinuclear complexes we synthesized a new Pd–Mo binuclear complex with (diphenylphosphino)pyridine ligands. The molecular structure of the complex was determined and different types of spectra are also discussed.

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Results and discussion

Synthesis and spectra
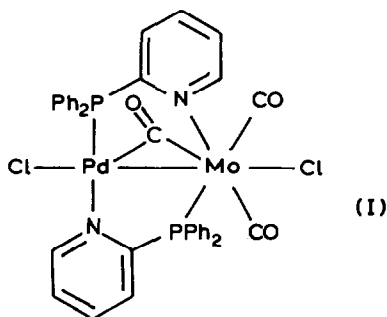
Complex PdMo(μ-Ph$_2$Ppy)$_2$(μ-CO)(CO)$_2$Cl$_2$ (I) was obtained in high yield by the reaction of Mo(CO)$_4$(Ph$_2$Ppy)$_2$ with (1,5-COD)PdCl$_2$. The process includes an oxidation-elimination reaction by the Pd^{2+} compound toward the Mo^0 compound to form a Mo$^+$ fragment possessing seven-coordination and simultaneously a metal–metal bond. This type of reaction is known [3]. In this synthesis, rearrangement of the bridging Ph$_2$Ppy ligand also occurs. The mechanism of the rearrangement is still not clear. The five-coordinate palladium with formal oxidation state +1 is less known. One of the rare representatives is the following complex [4]:
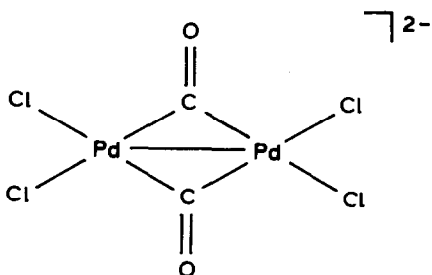
Complex(I) is stable in air and water, and is soluble in dichloromethane and chloroform.

The IR spectrum of this complex indicates a low frequency absorption (1740 cm^{-1}) for carbonyl, which is characteristic of a bridging carbonyl. In the Raman spectrum of the 100–250 cm^{-1} region an intense band at 180 cm^{-1} is observed. This band can be assigned to the vibration of the Pd–Mo bond, because the ν(M–M') bands are usually observed as the most intense bands [5]. In the far-IR spectrum, vibration of the Pd–Mo bond was not observed.

In the ^{31}P {^{1}H} NMR spectrum a doublet (21.67 and 31.09 ppm) of doublets was observed (Fig. 1). This indicates that the phosphorus atoms are in different chemical environments and a P–Pd–Mo–P three-bond coupling with a coupling of 9.7 Hz. exists. This has been proved by X-ray diffraction analysis of the complex.

The electronic absorption spectrum of this complex gives two bands in the low frequency region (Fig. 2). They are assigned to $\sigma \rightarrow \sigma^*$ (29890 cm^{-1}) and $d_\pi \rightarrow \sigma^*$ (24120 cm^{-1}) transitions, respectively. The $\sigma \rightarrow \sigma^*$ type transition is characteristic of a singly bonded metal–metal complex and the energy of the transition generally falls within 20000–30000 cm^{-1} [6].
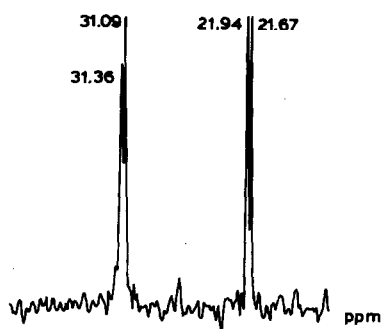
Fig. 1. $^{31}P\{^1H\}NMR$ spectrum of $PdMo(\mu\text{-}Ph_2Ppy)_2(\mu\text{-}CO)(CO)_2Cl_2$.
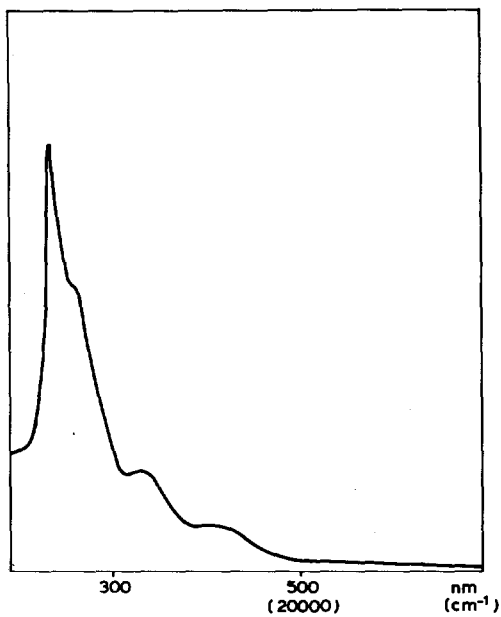

Fig. 2. Electronic absorption spectrum of $PdMo(\mu\text{-}Ph_2Ppy)_2(\mu\text{-}CO)(CO)_2Cl_2$.

Fig. 3. FD-mass spectrum of $PdMo(\mu\text{-}Ph_2Ppy)_2(\mu\text{-}CO)(CO)_2Cl_2$.

Two groups of isotope peaks were observed in field desorption mass spectrometry (FD-MS) (Fig. 3). One of the low mass numbers is assigned to $[PdMo(Ph_2Ppy)_2Cl]^+$ which is formed by losing one chlorine and three carbonyl ligands from around the Mo atom in an electric field.

$$PdMo(\mu\text{-}Ph_2Ppy)_2(\mu\text{-}CO)(CO)_2Cl_2 \rightarrow \left[PdMo(\mu\text{-}Ph_2Ppy)_2Cl\right]^+$$
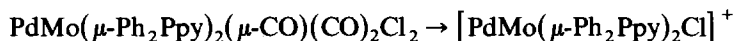
The other group of isotope peaks is assigned to $[Pd(\mu\text{-}Ph_2Ppy)_2Cl^+$, which is formed by breaking of the Pd–Mo bond.

$$\left[PdMo(\mu\text{-}Ph_2Ppy)_2Cl\right]^+ \rightarrow \left[Pd(\mu\text{-}Ph_2Ppy)_2Cl\right]^+$$
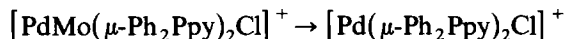
Description of molecular structure

The molecular structure of the complex is shown in Fig. 4. There are two disordered molecules of dichloromethane in the unit cell and they have no obvious intermolecular contacts with the complex molecule. The molecule belongs to the C_1 point group and is chiral. The N(2), C(2), Cl' and Pd atoms lie in one plane (Plane 2), with the molybdenum atom located in the center, 0.247 Å from Plane 2, towards the bridging carbonyl group. The P, N(1), Cl, and Mo atoms lie in another plane (Plane 1), with the palladium atom located in the center, 0.077 Å from Plane 1, towards the bridging carbonyl group. The dihedral angle is 33.6° between the two planes. There is a bridging carbonyl between the palladium and molybdenum atoms. Plane 4, which is determined by Pd, Mo and C(1) atoms, forms a dihedral angel of 83.4° with Plane 1. The molybdenum is seven-, and the palladium is five-coordinated.

The two bridging Ph_2Ppy ligands are arranged head-to-tail.

The Pd–Mo distance (2.817(1) Å) is shorter than the few, known, Pd–Mo bond lengths (for example; the average Pd–Mo bond length is 2.846 Å in the complex $Mo_2Pd_2(CO)_6(PEt_3)_2(\eta\text{-}C_5H_5)_2)$ [7].

The P–Pd–N(1) and Mo–Pd–Cl angles are 173.4(1) and 176.78(6)°, respectively, thus P and N(1) are *trans* with respect to Pd. The Pd–Cl bond distance (2.391(2) Å) is close to the larger value of known Pd–Cl distances (2.24–2.45 Å), the reason for this may be the strong *trans* effect of the M–M bond [8].

The C(3)–Mo–P' bond angle is almost a straight line (175.6°) with C(3) and P' at axial positions. The N(2)–Mo–P' angle, with N(2) at the equatorial position, is 95.5°. N(2) and P' are *cis* with respect to Mo, the terminal carbonyl groups are also *cis*.

The situation of the bridging carbonyl is of much interest because this carbonyl could either be bridging or semibridging [9, 2a]. As illustrated in Fig. 6, the Pd-carbonyl bond distance is within the known range for Pd-bridging carbonyls [10]. According to the general principle, the bridging carbonyl gives each metal one electron and both metals then have 17-electron configurations. Because the carbonyl interacts with these two metal atoms through σ–σ overlap, the two electrons of the
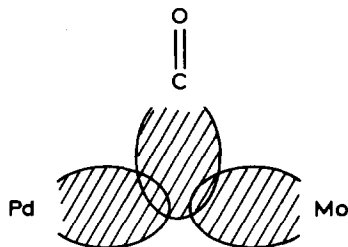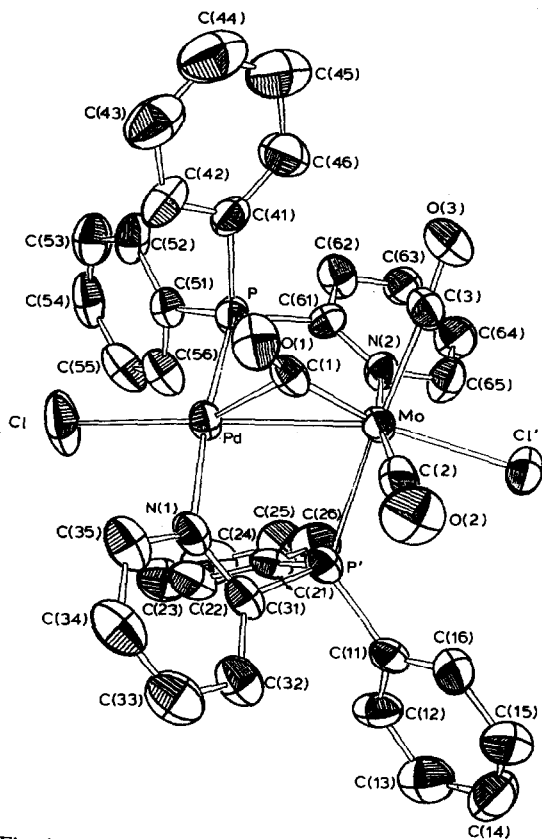
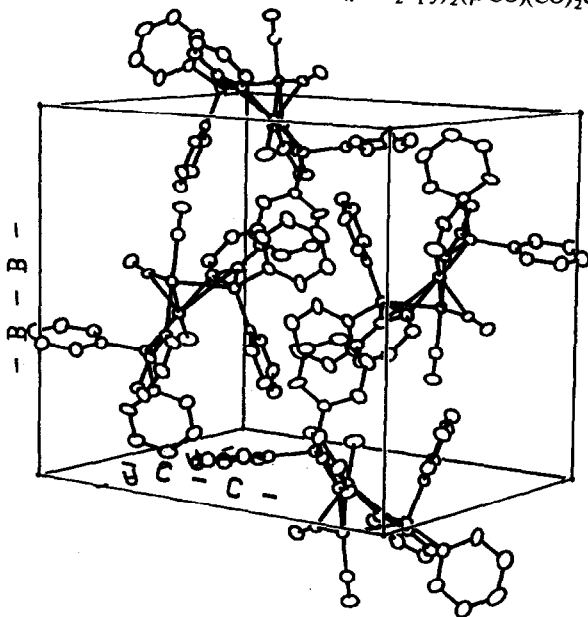Fig. 4. Molecular structure of PdMo(μ-Ph$_2$Ppy)$_2$(μ-CO)(CO)$_2$Cl$_2$.

Fig. 5. Packing of molecules in a unit cell.
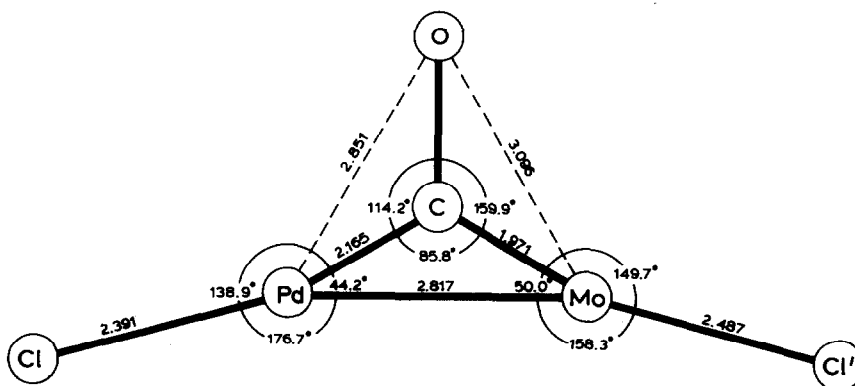
Fig. 6. The planar portion of the bridging carbonyl in PdMo(μ-Ph$_2$Ppy)$_2$(μ-CO)(CO)$_2$Cl$_2$.

carbonyl are delocalized; formally the palladium and molybdenum are still looked at as having the stable 16- and 18-electron configurations.

Experimental

Synthesis

All reactions were carried out under nitrogen. cis-Mo(CO)$_4$(mor)$_2$ (mor = morpholine) was prepared as described in Ref. 11.

Different types of spectra were recorded using the following instruments: NMR: FX-90Q; IR: WFD-14; Raman: SPEX-1403; far-IR: 170-sx; UV: Shimazu UV-240; FD-MS: Hitachi M-80.

Preparation of cis-Mo(CO)$_4$(Ph$_2$Ppy)$_2$. A solution of 1.9 g (5 mmol) of Mo(CO)$_4$(mor)$_2$ and 2.6 g (10 mmol) of Ph$_2$Ppy in 60 ml of dichloromethane was refluxed for 40 min. After cooling, 20 ml of absolute methanol was added to the

TABLE 1

DATA OF X-RAY STRUCTURE ANALYSIS OF PdMo(μ-Ph$_2$Ppy)$_2$(μ-CO)(CO)$_2$Cl$_2$

Formula	C$_{37}$H$_{28}$Cl$_2$MoN$_2$O$_3$P$_2$Pd
MW	883.79
a (Å)	14.615(2)
b (Å)	15.358(3)
c (Å)	17.721(2)
β (degree)	97.18(1)
V (Å^3)	3946.5
Z	4
d_{calcd} (g cm^{-3})	1.44
Space group	Monoclinic; $P2_1/c$
Scan mode	$\omega/2\theta$
Radiation	Mo–K_α
$2\theta_{max}$ (degree)	25
No. of unique reflections	3381
R	0.055
R_w	0.065

TABLE 2

FRACTIONAL ATOMIC COORDINATES AND ANISOTROPIC THERMAL PARAMETERS FOR NON-HYDROGEN ATOMS FOR $PdMo(\mu\text{-}Ph_2Ppy)_2(\mu\text{-}CO)(CO)_2Cl_2$

Atom	x	y	z	$B(\text{Å}^2)$
Pd	0.27298(8)	0.05304(9)	0.74823(8)	2.85(2)
Mo	0.14044(9)	−0.0474(1)	0.81158(8)	2.64(3)
P	0.1600(3)	0.3509(3)	0.2216(3)	3.0(1)
P'	0.2860(3)	0.5281(3)	0.4065(3)	2.9(1)
Cl'	0.0564(3)	0.6123(4)	0.4115(3)	4.8(1)
Cl	0.3886(3)	0.3588(4)	0.2017(4)	6.5(1)
C(1)	0.184(1)	0.555(1)	0.211(1)	2.8(3)
C(2)	0.182(1)	0.669(1)	0.302(1)	4.1(4)
C(3)	0.022(1)	0.555(1)	0.242(1)	3.4(4)
N(1)	0.3741(8)	0.541(1)	0.2854(8)	3.3(3)
N(2)	0.075(1)	0.4150(9)	0.3381(8)	3.0(3)
C(31)	0.380(1)	0.569(1)	0.357(1)	3.2(4)
C(21)	0.321(1)	0.417(1)	0.433(1)	3.1(4)
C(11)	0.303(1)	0.588(1)	0.497(1)	3.5(4)
C(51)	0.197(1)	0.237(1)	0.223(1)	3.1(4)
C(61)	0.076(1)	0.348(1)	0.291(1)	3.1(4)
C(41)	0.093(1)	0.369(1)	0.129(1)	3.5(4)
C(12)	0.350(1)	0.550(2)	0.562(1)	4.4(4)
C(13)	0.365(1)	0.600(2)	0.630(1)	5.9(5)
C(14)	0.326(2)	0.688(2)	0.630(1)	6.5(6)
C(15)	0.280(1)	0.723(2)	0.565(1)	5.6(6)
C(16)	0.268(1)	0.673(1)	0.499(1)	4.7(5)
C(22)	0.401(1)	0.379(1)	0.415(1)	4.3(5)
C(23)	0.425(1)	0.294(1)	0.439(1)	5.1(5)
C(24)	0.366(2)	0.252(1)	0.982(1)	5.7(6)
C(25)	0.286(2)	0.285(1)	0.499(1)	5.3(5)
C(26)	0.263(1)	0.370(1)	0.475(1)	4.9(5)
C(32)	0.477(1)	0.628(1)	0.389(1)	4.2(5)
C(33)	0.492(1)	0.338(1)	0.659(1)	5.1(5)
C(34)	0.500(1)	0.365(1)	0.734(1)	5.0(5)
C(35)	0.433(1)	0.573(1)	0.237(1)	4.5(5)
C(42)	0.144(1)	0.390(1)	0.070(1)	4.6(5)
C(43)	0.099(2)	0.401(2)	0.003(1)	6.4(6)
C(44)	−0.004(2)	0.607(2)	0.016(1)	7.6(7)
C(45)	0.049(2)	0.629(2)	0.958(1)	6.7(6)
C(46)	0.002(2)	0.643(1)	0.883(1)	5.3(5)
C(52)	0.169(1)	0.319(1)	0.663(1)	4.3(4)
C(53)	0.196(2)	0.407(1)	0.672(1)	5.0(5)
C(54)	0.246(1)	0.435(1)	0.736(1)	5.1(5)
C(55)	0.273(1)	0.379(2)	0.798(1)	5.4(6)
C(56)	0.249(1)	0.291(1)	0.790(1)	4.7(5)
C(62)	0.018(1)	0.275(1)	0.293(1)	4.0(5)
C(63)	0.040(1)	0.772(1)	0.151(1)	4.2(5)
C(64)	0.038(1)	0.661(2)	0.600(1)	4.6(5)
C(65)	0.981(1)	0.591(1)	0.605(1)	4.3(4)
O(1)	0.1939(9)	0.5821(9)	0.1507(7)	4.5(3)
O(2)	0.206(1)	0.7613(9)	0.798(1)	6.2(4)
O(3)	0.0412(9)	0.441(1)	0.8007(8)	5.5(4)

reaction mixture. The dichloromethane was evaporated and the pale-yellow precipitate was filtered off, washed with methanol and dried. Yield: 2.8 g (76%) M.p. 164–166°C (dec.).

Elemental analysis: Found: C, 62.39; H, 4.31; N, 4.17. $C_{38}H_{28}MoN_2O_4P_2$ calcd.: C, 62.13; H, 3.82; N, 3.82%.

^{31}P {^1H}NMR(CDCl$_3$): δ 40.65 ppm.

IR (ν(CO), KBr disc): 2000, 1940, 1885, 1840 cm^{-1}.

Preparation of PdMo(μ-Ph$_2$Ppy)$_2$(μ-CO)(CO)$_2$Cl$_2$ · 0.5CH$_2$Cl$_2$. A solution of 1.47 g (2 mmol) of *cis*-Mo(CO)$_4$(Ph$_2$Ppy)$_2$ and 0.57 g (2 mmol) of (1,5-C$_8$H$_{12}$)PdCl$_2$ in 50ml of dichloromethane was refluxed for 12 h. After the solution was cooled, 20ml of absolute methanol was added. The dichloromethane was evaporated and the dark-brown crystals which precipitated, were collected by filtration, and washed with ethyl ether. The product was recrystallized from CH$_2$Cl$_2$/CH$_3$OH. Yield: 1.5 g (81%) M.p. 214–216°C.

Elemental analysis: Found: C, 47.72; H, 3.12; N, 2.82. $C_{37}H_{28}Cl_2MoN_2O_3P_2Pd$ · 0.5CH$_2$Cl$_2$ calcd.: C, 47.95; H, 3.23; N, 3.23%.

^{31}P{^1H}NMR(CDCl$_3$): δ 21.67, 31.09 ppm; $^3J_{pp}$ 9.7 Hz.

IR(ν(CO), KBr disc): 1990, 1900, 1765 cm^{-1}.

Raman (ν(Pd–Mo), KBr disc): 180 cm^{-1}.

UV(CH$_2$Cl$_2$): 29890 ($\sigma \rightarrow \sigma^\star$), 24120($d_\pi \rightarrow \sigma^\star$) cm^{-1}.

FD-MS *m/z*: 664, 666, 667, 668, 669, 671, 672, 673, 674, 767, 770, 771, 772.

TABLE 3

BOND DISTANCES(Å) FOR PdMo(μ-Ph$_2$Ppy)$_2$(μ-CO)(CO)$_2$Cl$_2$

Pd–Mo	2.817(1)	C(11)–C(16)	1.408(9)
Pd–P	2.221(2)	C(51)–C(56)	1.398(9)
Pd–Cl	2.391(2)	C(51)–C(52)	1.393(9)
Pd–Cl	2.165(6)	C(61)–C(62)	1.405(8)
Pd–N1	2.113(5)	C(41)–C(42)	1.398(9)
Mo–P′	2.559(2)	C(41)–C(46)	1.388(9)
Mo–Cl′	2.487(2)	C(12)–C(13)	1.414(10)
Mo–C(1)	1.971(6)	C(13)–C(14)	1.468(12)
Mo–C(2)	1.976(7)	C(14)–C(15)	1.364(12)
Mo–C(3)	2.006(6)	C(15)–C(16)	1.397(10)
Mo–N(2)	2.320(5)	C(22)–C(23)	1.401(9)
P–C(51)	1.829(6)	C(23)–C(24)	1.410(10)
P–C(61)	1.844(6)	C(24)–C(25)	1.359(11)
P–C(41)	1.825(6)	C(25)–C(26)	1.416(9)
P′–C(31)	1.827(6)	C(32)–C(33)	1.405(9)
P′–C(21)	1.828(6)	C(33)–C(34)	1.387(10)
P′–C(11)	1.834(7)	C(34)–C(35)	1.415(9)
C(1)–O(1)	1.170(6)	C(42)–C(43)	1.379(10)
C(2)–O(2)	1.130(8)	C(43)–C(44)	1.391(13)
C(3)–O(3)	1.113(6)	C(44)–C(45)	1.410(12)
N(1)–C(31)	1.337(7)	C(45)–C(46)	1.417(10)
N(1)–C(35)	1.381(8)	C(52)–C(53)	1.412(9)
N(2)–C(61)	1.329(7)	C(53)–C(54)	1.341(10)
N(2)–C(65)	1.377(7)	C(54)–C(55)	1.429(11)
C(31)–C(32)	1.398(8)	C(55)–C(56)	1.397(10)
C(21)–C(22)	1.387(8)	C(62)–C(63)	1.388(9)
C(21)–C(26)	1.393(8)	C(63)–C(64)	1.371(9)
C(11)–C(12)	1.388(9)	C(64)–C(65)	1.375(9)

X-ray diffraction analysis

A solution of this complex in dichloromethane was cooled slowly and allowed to stand for several days. A columnar dark-brown crystal was obtained. A crystal of approximate dimensions $0.2 \times 0.3 \times 0.3$ mm, was mounted on a glass fiber in an arbitrary orientation. Preliminary examination and data collection were performed with Mo-K_α radiation ($\lambda = 0.71073$ Å) on an Enraf–Nonius CAD-4 computer-controlled kappa-axis diffractometer equipped with a graphite monochromator.

TABLE 4

BOND ANGLES (DEGREE) FOR PdMo(η-Ph$_2$Ppy)$_2$(μ-CO)(CO)$_2$Cl$_2$

Mo–Pd–P	85.30(4)	C(21)–P′–C(11)	103.5(3)
Mo–Pd–Cl	176.68(6)	Mo–C(1)–O(1)	159.9(5)
Mo–Pd–C(1)	44.2(2)	Mo–C(2)–O(2)	178.8(7)
Mo–Pd–N(1)	89.4(1)	C(31)–N(1)–C(35)	120.4(5)
P–Pd–Cl	95.14(7)	C(61)–N(2)–C(65)	117.3(5)
P–Pd–C(1)	92.6(2)	P′–C(31)–N(1)	112.4(4)
P–Pd–N(1)	173.4(1)	P′–C(31)–C(32)	124.2(5)
Cl–Pd–C(1)	138.9(2)	N1–C(31)C(32)	123.3(6)
Cl–Pd–N(1)	89.9(1)	P′–C(21)–C(22)	123.7(5)
C(1)–Pd–N(1)	86.5(2)	P′–C(21)–C(26)	116.3(5)
Pd–Mo–P′	69.00(4)	C22–C(21)–C(26)	120.0(6)
Pd–Mo–Cl′	158.26(5)	P′–C(11)–C(12)	121.4(5)
Pd–Mo–C(1)	50.0(2)	P′–C(11)–C(16)	118.3(6)
Pd–Mo–C(2)	104.5(2)	C(12)–C(11)–C(16)	120.3(7)
Pd–Mo–C(3)	111.8(2)	P–C(51)–C(52)	121.2(5)
Pd–Mo–N(2)	85.5(1)	P–C(51)–C(56)	115.7(5)
P′–Mo–Cl′	91.31(6)	C(52)–C(51)–C(56)	122.9(6)
P′–Mo–C(1)	105.4(2)	P–C(61)–N(2)	117.2(4)
P′–Mo–C(2)	85.7(2)	P–C(61)–C(62)	119.5(5)
P′–Mo–C(3)	175.6(2)	N(2)–C(61)–C(62)	123.3(6)
P′–Mo–N(2)	95.5(1)	P–C(41)–C(42)	115.5(5)
Cl′–Mo–C(1)	149.7(2)	P–C(41)–C(46)	122.6(6)
Cl′–Mo–C(2)	82.2(2)	C(42)–C(41)–C(46)	121.8(6)
Cl′–Mo–C(3)	87.2(2)	C(11)–C(12)–C(13)	119.6(8)
Cl′–Mo–N(2)	87.4(1)	C(12)–C(13)–C(14)	118.3(8)
C(1)–Mo–C(2)	74.3(3)	C(13)–C(14)–C(15)	121.1(8)
C(1)–Mo–C(3)	77.8(2)	C(14)–C(15)–C(16)	118.8(8)
C(1)–Mo–N(2)	115.2(2)	C(11)–C(16)–C(15)	121.9(7)
C(2)–Mo–C(3)	98.2(3)	C(21)–C(22)–C(23)	120.4(7)
C(2)–Mo–N(2)	169.6(2)	C(22)–C(23)–C(24)	119.0(7)
C(3)–Mo–N(2)	80.3(2)	C(23)–C(24)–C(25)	120.9(8)
C(51)–P–C(61)	100.8(3)	C(24)–C(25)–C(26)	120.1(7)
C(51)–P–C(41)	106.4(3)	C(21)–C(26)–C(25)	119.6(7)
C(61)–P–C(41)	105.9(3)	C(31)–C(32)–C(33)	117.4(7)
C(31)–P′–C(21)	104.2(3)	C(32)–C(33)–C(34)	119.5(7)
C(31)–P′–C(11)	102.4(3)	C(33)–C(34)–C(35)	120.8(7)
N(1)–C(35)–C(34)	118.4(7)	C(53)–C(54)–C(55)	122.1(7)
C(41)–C(42)–C(43)	119.5(7)	C(54)–C(55)–C(56)	117.6(7)
C(42)–C(43)–C(44)	120.0(8)	C(51)–C(56)–C(55)	119.2(7)
C(43)–C(44)–C(45)	121.1(8)	C(61)–C(62)–C(63)	118.3(6)
C(44)–C(45)–C(46)	118.7(8)	C(62)–C(63)–C(64)	118.7(6)
C(41)–C(46)–C(45)	118.9(8)	C(63)–C(64)–C(65)	120.4(6)
C(51)–C(52)–C(53)	116.8(7)	N(2)–C(65)–C(64)	121.9(6)
C(52)–C(53)–C(54)	121.4(7)		

TABLE 5

THE IMPORTANT LEAST-SQUARE PLANES AND DIHEDRAL ANGLES (DEGREE) BETWEEN THE PLANES FOR $PdMo(\mu\text{-}Ph_2Ppy)_2(\mu\text{-}CO)(CO)_2Cl_2$

No. of Plane	Atoms in the Plane					Dihedral Angle	2	3	4
1	Mo	Cl	P	N(1)	Pd	1	33.6	50.6	83.4
2	Pd	Cl'	C(2)	N(2)	Mo	2		81.7	51.9
3	Pd	C(3)	Cl'	P'	Mo	3			133.5
4	Pd	Mo	C(1)						

Cell constants and an orientation matrix for data collection were obtained from least-squares refinement of 25 reflections from the setting angles measured by the computer controlled diagonal slit method of centering. The data were collected at room temperature by $\omega/2\theta$ scan technique. A total of 7463 reflections in the range of $2° \leqslant \theta \leqslant 25°$ were collected. After the Lorentz and polarization corrections were applied, the correction for the absorption was achieved by empirical formula [12]. The cell parameters and the conditions in data collections are listed in Table 1.

The structure was solved by direct method. The positions of Pd and Mo were found from the E-map. The coordinates of non-hydrogen atoms were obtained through several difference-Fourier syntheses. Only the 3381 reflections having intensities greater than 3.0 (times their standard deviation) were used in the refinement. The final unweighted and weighted agreement factors were $R = 0.055$ and $R_w = 0.065$. The highest peak in the final difference-Fourier map was of 1.32 $e/Å^3$.

All calculations were performed on a PDP-11 computer with SDP-PLUS [13].

Fractional atomic coordinates and anisotropic thermal parameters for the non-hydrogen atoms are given in Table 2. The bond distances and bond angles are given in Tables 3 and 4, respectively. The important least-squares planes and dihedral angles between the planes are given in Table 5.

Acknowledgements

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