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CHELATING AND MONODENTATE COORDINATION MODES OF THE TETRAPHENYLDIPHOSPHOXANE (Ph_2POPPh_2) LIGAND

EDWARD H. WONG *, LATA PRASAD *, ERIC J. GABE * and FONTAINE C. BRADLEY
Department of Chemistry, University of New Hampshire, Durham, New Hampshire 03824 (U.S.A.) and Chemistry Division, National Research Council of Canada, Ottawa, K1A 0R9 (Canada)

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Summary

The crystal and molecular structures of the Cr and Mo complexes *cis*-$(CO)_4$-$\overline{\mathrm{M(PPh_2OP}}\mathrm{Ph_2)}$ have been determined.

Mo complex: $C_{28}H_{20}O_5P_2Mo$, triclinic, $P\bar{1}$, a 10.016(2), b 11.419(3), c 13.237(3) Å, α 106.18(2), β 95.78(2), γ 112.78(2)°, $Z = 2$, $D_{calc} = 1.515$ Mg m^{-3}. The final residual is $R_F = 0.027$ for 3718 observed reflections at 23°C.

Cr complex: $C_{28}H_{20}O_5P_2Cr$, triclinic, $P\bar{1}$, a 9.887(1), b 11.435(2), c 13.020(2) Å, α 106.43(1), β 95.05(1), γ 112.59(1)°, $Z = 2$, D_{calc} 1.438 Mg m^{-3}. The final residual is $R_F = 0.043$ for 2817 observed reflections at 23°C.

The two structures are isomorphous with approximate octahedral coordination geometry around each metal and feature the tetraphenyldiphosphoxane Ph_2POPPh_2 ligand in a chelating mode.

Hydrolysis of the Cr, Mo, and W chelate complexes under basic conditions yielded the *cis*-$(CO)_4M(PPh_2O)_2H^-$ species which can be reconverted to the parent *cis*-$(CO)_4\overline{\mathrm{M(PPh_2OP}}\mathrm{Ph_2)}$ by acidification and dehydration using trifluoroacetic acid in trifluoroacetic anhydride.

A monodentate coordination mode of the Ph_2POPPh_2 ligand was identified in the complex $(CO)_5MoPPh_2OPPh_2$ prepared from the reaction of $ClPPh_2$ with $(CO)_5MoPPh_2O^-$. This monodentate ligand becomes chelating upon warming of the complex in solution.

Although diphosphines of the type R_2PXPR_2 where X is a methylene or alkylamino- bridging unit have long been known to form four-membered chelate rings in their complexes with transition metals, no structural characterization of a chelating diphosphoxane (R_2POPR_2) ligand has appeared [1,2]. The

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$(EtO)_2POP(OEt)_2$, $(CF_3)_2POP(CF_3)_2$, and Ph_2POPPh_2 ligands coordinate predominantly in a bridging mode between two metal atoms in a variety of bimetallic complexes of Fe [3,4], Mo [5], W [6], Ni [7], Pd and Pt [8]. Haines, Pidcock et al. have rationalized the lack of chelating P—O—P complexes as a result of the unfavorably large P—O—P angles (120—160°) that would have to be accommodated in a four-membered chelate ring structure [4,8].

Recently, Choi and Muetterties reported the isolation of $(MeO)_2POP(OMe)_2$ complexes of Mo, W, and Re which may contain the tetramethyl diphosphite ligand as a chelator [9]. Gray and Kraihanzel were the first to prepare a *cis*-$(CO)_4Mo(PPh_2OPPh_2)$ complex from the reaction of *cis*-$(CO)_4Mo(PPh_2O)_2H^-$ with acyl chlorides or chlorophosphines [10]. Spectral evidence suggested the possibility of a chelating diphosphoxane ligand. We have recently prepared similar *cis*-$(CO)_4M(PPh_2OPPh_2)$ complexes (M = Cr, Mo, W) from the direct reaction of diphosphine monoxide $PPh_2PPh_2(O)$ and the metal hexacarbonyl in refluxing diglyme [11]. In all three products, the $\nu_{asym}(POP)$ bands were found to be in the 750—790 cm^{-1} region of the IR, strongly suggesting reduction of the normal P—O—P angles to lower values. We present here X-ray structural studies of the Cr- and Mo-complexes that establish the existence of the P—O—P chelate and also spectral evidence for a monodentate tetraphenyldiphosphoxane complex.

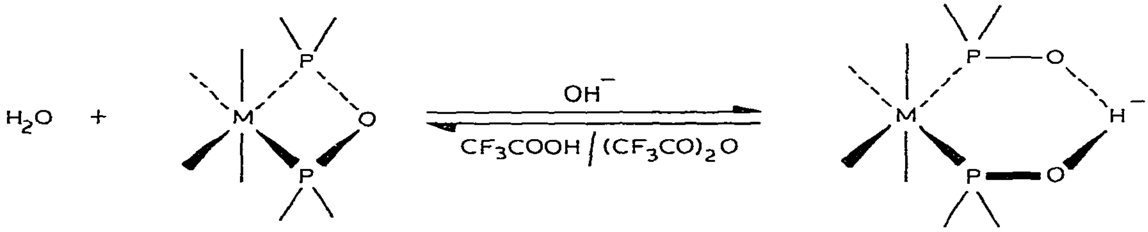
Results and discussion

The two compounds *cis*-$(CO)_4\overline{Mo(PPh_2OP}Ph_2)$ and *cis*-$(CO)_4\overline{Cr(PPh_2OP}Ph_2)$ form isomorphous crystals and their molecular structures are shown in Fig. 1. Both contain planar four-membered chelate rings featuring the Ph_2POPPh_2 ligand. Maximum deviation from planarity is 0.007 Å for the oxygen atom in the Cr complex and 0.0007 Å in the Mo complex. This ligand, together with the two axial and two equatorial carbonyls form a distorted octahedral coordination geometry around each metal atom. The chelate rings are shown in Fig. 2. Important observations include the P—O—P angle of only 103.3(1)° in the Mo complex and 100.2(1)° in the Cr analog. This can be compared to the P—O—P angle of the bridging $(EtO)_2POP(OEt)_2$ ligand in $[(EtO)_2POP(OEt)_2]_2$-$Fe_2(CO)_5$ of 119.3(5)° [4]. Typical P—O—P angles in cyclic triphosphates and pyrophosphates range from 120 to 160° [12].

The P—Mo—P angle of 63.82(3) and P—Cr—P angle of 66.76(4)° represent some of the smallest values reported. Noteworthy also are the long P—O distances of between 1.66—1.67 Å in both chelate rings. These match the calculated covalent single bond distance (1.66 Å) for a P—O bond and may suggest insignificant *dπ—pπ* interaction.

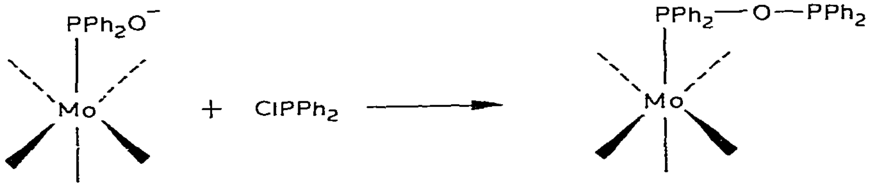
A useful comparison can be made for the series of three *cis*-$(CO)_4\overline{Mo(PPh_2\text{-}XP}Ph_2)$ chelate structures where X = CH_2, NEt, and O (Table 1). With the increasingly electronegative bridging atoms, we observe an opening up of the P—X—P angle, a decrease of the P—Mo—P angle and a shortening of the Mo—P bond distance. This last trend may suggest increasing *dπ—dπ* interaction between the Mo and phosphorus atoms and is consistent with the lengthening of the Mo—carbonyl bonds *trans* to the phosphorus donors.

The four-membered chelate rings in these complexes are rapidly hydrolyzed in aqueous THF under basic conditions:



The *cis*-(CO)$_4$Mo(PPh$_2$O)$_2$H$^-$ anion was first reported by Gray and Kraihanzel [13]. Interestingly, the ring opening can be reversed by treatment with trifluoroacetic acid in trifluoroacetic anhydride. Gray has reported the use of acyl chlorides and chlorophosphines in causing the same transformation in the Mo complex [10]. It is possible that traces of HCl together with the water-scavenging chlororeagents are responsible for that ring closure.

In order to examine the possible formation of a monodentate PPh$_2$OPPh$_2$ ligand, (CO)$_5$MoPPh$_2$O$^-$Na$^+$ was allowed to react with ClPPh$_2$ in THF and a white, crystalline compound that analyzed as (CO)$_5$MoPPh$_2$OPPh$_2$ was isolated:



The IR spectrum of this compound contained a ν_{asym}(POP) band at 860 cm^{-1}. Its ^{31}P {^{1}H} NMR spectrum is an AX pattern (Fig. 3) as expected for a mono-

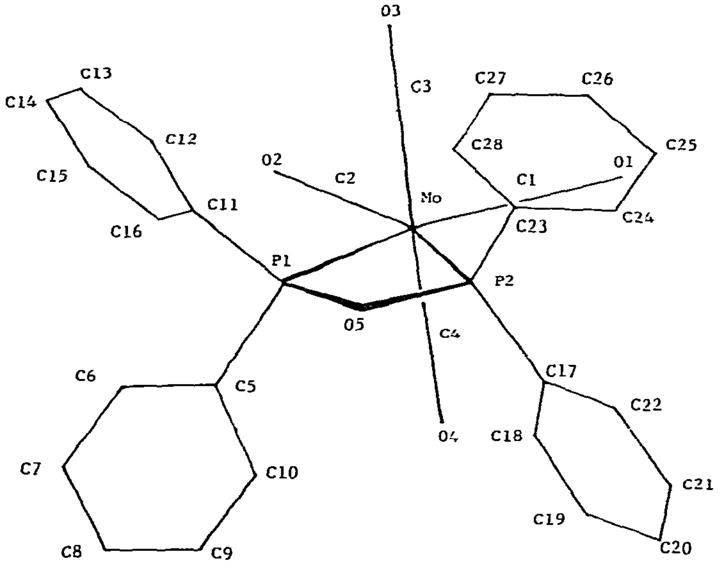


Fig. 1(a). Molecular structure of *cis*-(CO)$_4$Mo(PPh$_2$OPPh$_2$).

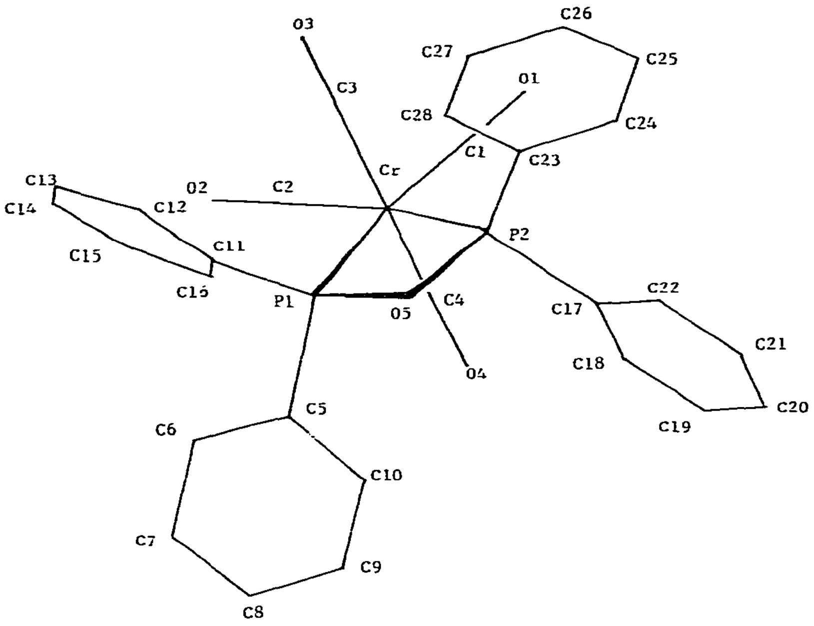


Fig. 1(b). Molecular structure of *cis*-(CO)$_4$Cr(PPh$_2$OPPh$_2$).

dentate diphosphoxane ligand. By comparison with the chemical shift of the chelating ligand in *cis*-(CO)$_4$Mo(PPh$_2$OPPh$_2$) at 134.8 ppm, a value of −14 ppm can be estimated for the chemical shift contribution of the four-membered ring (Δ_R) [11,14]. This compares reasonably well with the reported value of −19.3 ppm for the Δ_R of the chelate ring in *cis*-(CO)$_4$Mo(PPh$_2$CH$_2$PPh$_2$) [14].

Upon warming in solution to 60°C, (CO)$_5$MoPPh$_2$OPPh$_2$ loses CO and forms the *cis*-(CO)$_4$Mo(PPh$_2$OPPh$_2$) complex. We have recently reported the thermal conversion of diphosphine monoxide complexes (CO)$_5$MPPh$_2$P(O)Ph$_2$ (M = Cr, Mo, W) to the corresponding *cis*-(CO)$_4$M(PPh$_2$OPPh$_2$) complexes [11]. The isolation of this monodentate diphosphoxane complex suggests a plausible path-

TABLE 1

COMPARISON OF CHELATE GEOMETRIES IN *cis*-(CO)$_4$Mo(PPh$_2$XPPh$_2$) COMPLEXES

X	Angles (°)		Distances (Å)		Ref.
	P—X—P	P—Mo—P	Mo—P	Mo—C [c]	
CH$_2$	95.6(4)	67.3(1)	2.501(2) 2.535(2)	1.92(1) 1.94(1)	[1]
NEt	104(1)	64.8(2)	2.505(5) [a]	1.99(1) [b]	[2]
O	103.3(1)	63.82(3)	2.458(1) 2.476(1)	1.985(3) 1.981(3)	This work

[a] Average of two values. [b] Average of all Mo—C distances. [c] Mo—carbonyls *trans* to phosphorus. All esd's refer to last digit given.

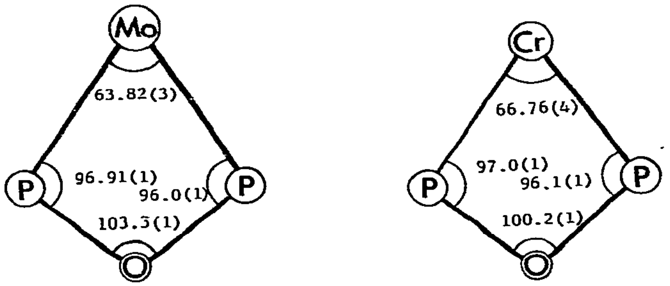
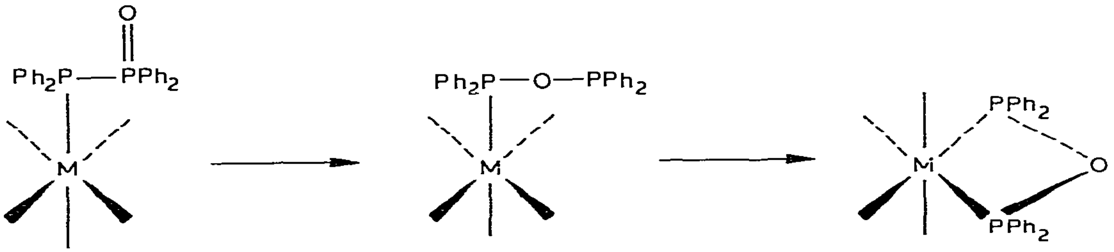


Fig. 2. Angles of the chelate rings.

way for the conversions:



The complex $(CO)_5MoPPh_2OPPh_2$ represents the fourth established coordination mode of tetraphenyldiphosphine oxide ($PPh_2P(O)Ph_2$) and its tautomer tetraphenyldiphosphoxane (PPh_2OPPh_2) (Fig. 4). Further interesting coordination chemistry of these versatile ligands can be anticipated.

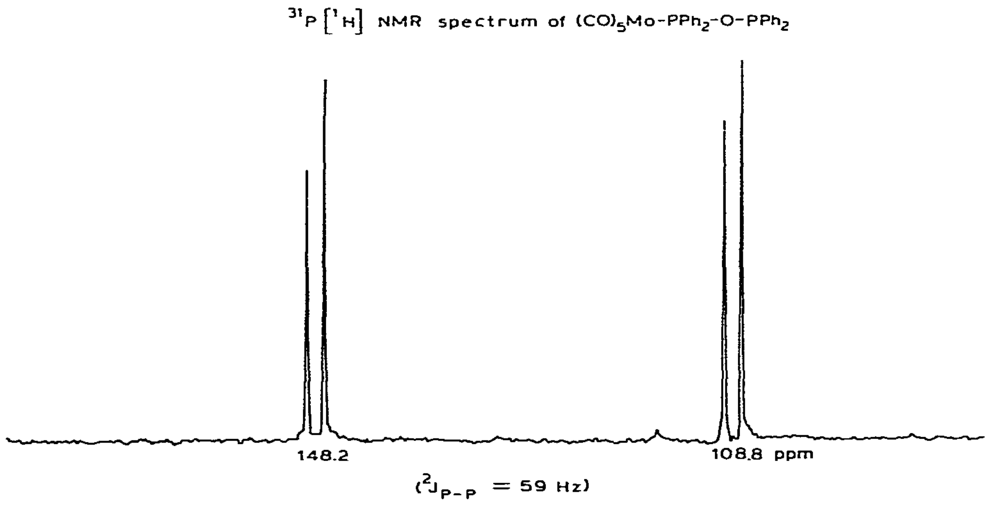


Fig. 3. $^{31}P\{^1H\}$ NMR spectrum of $(CO)_5MoPPh_2OPPh_2$

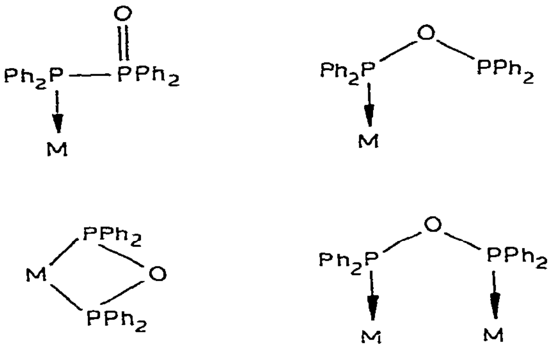


Fig. 4. Known coordination modes of $Ph_2\overset{O}{\overset{\|}{P}}PPh_2$ and its tautomer Ph_2POPPh_2.

Experimental

All reactions and purifications were performed under dry, deoxygenated nitrogen in Schlenk glassware.

Methylene chloride and hexane were distilled from CaH_2 and THF from Na-benzophenone ketyl. The Cr- and Mo-complexes *cis*-$(CO)_4\overline{M(PPh_2OP}Ph_2)$ were prepared as described in literature [11]. The *cis*-$(CO)_4Mo(PPh_2O)_2H^-$ complex as its triethylammonium salt and the $(CO)_5MoPPh_2O^-$ NEt_3H^+ compound were prepared according to Kraihanzel's methods [5,13]. Chlorodiphenylphosphine was purchased from Organometallics, Inc., E. Hempstead, N.H. and vacuum-distilled before use.

Infrared spectra were recorded using a Perkin—Elmer 283 spectrometer. $^{31}P\{^1H\}$ NMR spectra were run on a JEOL-FX 90Q FT-NMR spectrometer with D-lock and shifts were referenced to external 85% H_3PO_4. Elemental analyses were performed at the University of New Hampshire by the Instrumentation Center.

X-ray structural determinations

Both the Cr- and Mo-complexes *cis*-$(CO)_4\overline{M(PPh_2OP}Ph_2)$ were recrystallized from CH_2Cl_2/ethanol by layering. Details of data collection are similar and are given below for the Mo complex (Cr complex in parentheses where different).

Data were collected with the $\theta/2\theta$ scan with profile analysis to a 2θ max = 50° using Mo-K_α radiation [15]. The crystal used was 0.3 × 0.25 × 0.2 mm (0.25 × 0.25 × 0.2 mm) and 4703 (5419) reflections were measured of which 4603 (4491) were unique and 3718 (2817) gave $I_{net} > 3\sigma(I_{net})$. The absorption factor is 0.646 (0.598) mm^{-1} and corrections were therefore not made, though intensities were corrected for direct beam polarization [16]. The cell parameters were obtained by least squares from the setting angles of 40 reflections with $2\theta > 30°$.

The heavy atoms were located in a Patterson map and all the other non-hydrogen atoms were located in a heavy-atom phased Fourier map. The structures were first refined by block-diagonal least squares, which lowered the residual to $R_F = 0.059$ for the Mo complex and 0.063 for the Cr complex. The

H atoms were then included at their calculated positions and refined isotropically. An extinction correction was included [17].

The scattering curves for neutral atoms were taken from the International Tables for X-ray Crystallography [18]. The final residuals are: $R_F = 0.027$ and $R_{WF} = 0.021$ for the Mo complex using 3718 observed reflections, $R_F = 0.043$ and $R_{WF} = 0.021$ for all 4603 reflections; the Cr complex has $R_F = 0.043$ and $R_{WF} = 0.027$ for 2817 observed reflections ($R_F = 0.084$ and $R_{WF} = 0.028$ for all 4491 reflections). The atomic positional and equivalent isotropic temperature factors are given in Table 2. The anisotropic temperature factors are given in the supplementary data.

Important bond distances and angles are given in Table 3.

All calculations were performed using the NRC PDP8-E system of programs [19].

Hydrolysis of cis-$(CO)_4\overline{M(PPh_2OPPh_2})$*; M = Cr, Mo, W*

The procedure for the Mo complex is typical: An amount of 100 mg (0.17 mmol) of the complex and one pellet of NaOH were stirred in 0.5 ml H_2O and 5 ml THF. After 0.5 h, the reaction mixture was evaporated to dryness and washed with 2 ml of cold water. The chilled suspension was filtered to give 50 mg of white solid. Metathesis with NEt_3HCl in water gave NEt_3H^+ $(CO)_4Mo(PPh_2O)_2H^-$ identical to an authentic sample. Use of triethylamine in place of NaOH yielded this product directly using the same workup procedure. The complex can be recrystallized from CH_2Cl_2/CH_3OH.

The Cr- and W-analogs can be similarly prepared. All products gave satisfactory CHN elemental analyses.

The $^{31}P\ \{^1H\}$ NMR data are listed in Table 4.

Reaction of cis-$(CO)_4M(PPh_2O)_2H^-$ *with* $TFA/(CF_3CO)_2O$

The procedure for the Mo complex is typical:

An amount of 100 mg (0.14 mmol) of the complex as its NEt_3H^+ salt was dissolved in 4 ml CH_2Cl_2. One ml of wet trifluoroacetic anhydride was added to give a light yellow solution. After 0.5 h, TLC and ^{31}P NMR indicated formation of the *cis*-$(CO)_4\overline{Mo(PPh_2OPPh_2})$ complex. Evaporation yielded a light yellow powder which was washed with water and dried to give 60 mg (75%) of the chelate complex. This can be recrystallized from CH_2Cl_2/CH_3OH by slow evaporation.

The Cr- and W-analogs were similarly prepared and identified.

Synthesis of $(CO)_5MoPPh_2OPPh_2$

An amount of 1.00 g (1.85 mmol) of $NEt_3H^+(CO)_5MoPPh_2O^-$ was added to 500 mg of a 50% NaH dispersion in oil. After addition of 15 ml of THF, the effervescence subsided within 0.5 h. The suspension was filtered to give a light yellow solution. This was evaporated to dryness to remove the NEt_3 completely. A solution of 1.30 (5.8 mmol) of $ClPPh_2$ in 10 ml of THF was prepared. An amount of 3.2 ml was withdrawn via syringe and added dropwise to the above residue. The suspension was made up to 10 ml with THF and stirred for 0.5 h. After evaporation to dryness, the residue was extracted with 20 ml of n-hexane. Filtration through Celite gave a very light yellow solution. This was slowly con-

(Continued on p. 331).

TABLE 2A

ATOMIC POSITIONAL PARAMETERS AND EQUIVALENT ISOTROPIC THERMAL FACTORS FOR THE *cis*-$(CO)_4\overline{\mathrm{Mo(PPh_2OP}}\mathrm{Ph_2})$ STRUCTURE (esd's refer to the last digit given)

	x	*y*	*z*	B_{eq} [a]
Mo	0.15280(3)	0.47822(3)	0.294770(21)	1.943(6)
P(1)	0.30119(8)	0.39611(7)	0.18260(6)	2.094(20)
P(2)	0.36831(8)	0.65315(7)	0.26140(6)	2.173(20)
O(1)	0.0105(3)	0.65013(25)	0.43011(21)	6.11(10)
O(2)	−0.06713(24)	0.20120(20)	0.30620(18)	4.46(8)
O(3)	0.3462(3)	0.50428(24)	0.51029(17)	4.91(8)
O(4)	−0.0707(3)	0.44705(23)	0.09189(18)	4.88(8)
O(5)	0.42255(19)	0.54615(17)	0.18566(14)	2.26(5)
C(1)	0.0641(3)	0.5872(3)	0.38230(25)	3.41(10)
C(2)	0.0102(3)	0.3038(3)	0.30087(23)	2.76(9)
C(3)	0.2812(3)	0.4976(3)	0.43278(23)	2.90(9)
C(4)	0.0127(3)	0.4580(3)	0.16250(23)	2.92(9)
C(5)	0.2415(3)	0.3010(3)	0.03848(21)	2.27(8)
C(6)	0.1913(3)	0.1622(3)	0.00219(23)	3.23(9)
C(7)	0.1446(4)	0.0870(3)	−0.1071(3)	4.11(11)
C(8)	0.1490(4)	0.1514(3)	−0.18110(24)	3.91(10)
C(9)	0.1956(4)	0.2873(3)	−0.14731(24)	3.90(11)
C(10)	0.2419(3)	0.3640(3)	−0.03717(23)	3.19(9)
C(11)	0.4180(3)	0.3256(3)	0.22875(20)	2.14(8)
C(12)	0.3678(3)	0.2402(3)	0.28736(24)	2.91(9)
C(13)	0.4537(4)	0.1810(3)	0.3192(3)	3.55(10)
C(14)	0.5898(4)	0.2079(3)	0.2955(3)	3.59(10)
C(15)	0.6417(3)	0.2940(3)	0.2389(3)	3.87(11)
C(16)	0.5567(3)	0.3522(3)	0.20479(24)	3.07(9)
C(17)	0.3421(3)	0.7452(3)	0.17563(21)	2.29(8)
C(18)	0.4397(3)	0.7807(3)	0.11039(24)	3.16(10)
C(19)	0.4189(4)	0.8502(3)	0.0444(3)	3.73(11)
C(20)	0.3016(4)	0.8836(3)	0.0436(3)	3.96(11)
C(21)	0.2054(4)	0.8497(3)	0.1074(3)	4.04(11)
C(22)	0.2249(3)	0.7801(3)	0.17473(24)	2.98(9)
C(23)	0.5403(3)	0.7751(3)	0.35828(21)	2.19(8)
C(24)	0.5743(3)	0.9112(3)	0.39490(24)	3.41(10)
C(25)	0.7057(4)	1.0039(3)	0.4711(3)	4.28(11)
C(26)	0.8036(3)	0.9599(3)	0.5082(3)	3.86(10)
C(27)	0.7718(3)	0.8263(3)	0.47329(24)	3.55(10)
C(28)	0.6389(3)	0.7319(3)	0.39814(23)	2.87(9)
H(6)	0.187(3)	0.117(3)	0.0567(20)	5.4(7)
H(7)	0.108(3)	−0.008(3)	−0.1314(22)	6.9(8)
H(8)	0.126(3)	0.094(3)	−0.2612(22)	7.2(9)
H(9)	0.196(3)	0.336(3)	−0.1965(22)	7.3(9)
H(10)	0.280(3)	0.4614(24)	−0.0096(19)	4.8(7)
H(12)	0.268(3)	0.223(3)	0.3050(20)	5.2(7)
H(13)	0.414(3)	0.116(3)	0.3529(21)	6.8(8)
H(14)	0.642(3)	0.161(3)	0.3170(22)	6.5(8)
H(15)	0.738(3)	0.325(3)	0.2284(23)	7.2(9)
H(16)	0.591(3)	0.412(3)	0.1639(19)	5.4(7)
H(18)	0.520(3)	0.757(3)	0.1089(21)	6.1(8)
H(19)	0.490(3)	0.874(3)	0.0024(22)	6.4(8)
H(20)	0.286(3)	0.931(3)	−0.0050(22)	6.8(8)
H(21)	0.137(3)	0.877(3)	0.1120(23)	7.8(9)
H(22)	0.159(3)	0.7603(25)	0.2251(19)	4.8(7)
H(24)	0.498(3)	0.940(3)	0.3639(20)	5.7(7)
H(25)	0.728(3)	1.098(3)	0.4987(24)	8.3(9)
H(26)	0.895(3)	1.031(3)	0.5612(20)	6.1(8)
H(27)	0.835(3)	0.790(3)	0.4957(22)	7.0(8)
H(28)	0.618(3)	0.638(3)	0.3709(19)	5.0(7)

[a] B_{eq} is the arithmetic mean of the principal axes of the thermal ellipsoid.

TABLE 2B

ATOMIC POSITIONAL PARAMETERS AND EQUIVALENT ISOTROPIC THERMAL FACTORS FOR THE *cis*-$(\mathrm{CO})_4\overline{\mathrm{Cr}(\mathrm{PPh_2O}\mathrm{P}}\mathrm{Ph_2})$ STRUCTURE (esd's refer to the last digit given)

	x	y	z	B_{eq} [a]
Cr	0.16598(7)	0.48161(7)	0.29179(5)	2.115(17)
P(1)	0.30447(12)	0.39875(10)	0.18317(9)	2.09(3)
P(2)	0.36572(12)	0.64935(10)	0.26057(9)	2.15(3)
O(1)	0.0278(4)	0.6477(3)	0.4268(3)	6.23(14)
O(2)	−0.0471(3)	0.2170(3)	0.30273(25)	4.35(11)
O(3)	0.3484(3)	0.5057(3)	0.50162(22)	4.61(11)
O(4)	−0.0524(3)	0.4489(3)	0.09617(23)	4.47(11)
O(5)	0.4273(3)	0.54571(23)	0.18226(19)	2.16(8)
C(1)	0.0822(5)	0.5849(4)	0.3771(3)	3.48(15)
C(2)	0.0328(4)	0.3196(4)	0.2971(3)	2.45(12)
C(3)	0.2839(4)	0.4989(4)	0.4214(3)	2.70(13)
C(4)	0.0334(4)	0.4607(4)	0.1676(3)	2.66(13)
C(5)	0.2410(4)	0.3007(4)	0.0363(3)	2.17(12)
C(6)	0.1939(4)	0.1609(4)	0.0029(3)	3.11(14)
C(7)	0.1465(5)	0.0864(4)	−0.1094(3)	3.90(15)
C(8)	0.1481(5)	0.1499(4)	−0.1843(3)	3.74(15)
C(9)	0.1915(5)	0.2867(4)	−0.1514(3)	3.66(15)
C(10)	0.2368(5)	0.3626(4)	−0.0400(3)	3.01(14)
C(11)	0.4230(4)	0.3273(4)	0.2294(3)	2.16(12)
C(12)	0.3696(4)	0.2384(4)	0.2854(3)	2.93(14)
C(13)	0.4579(5)	0.1800(4)	0.3183(3)	3.53(16)
C(14)	0.5987(5)	0.2123(4)	0.2975(4)	3.56(15)
C(15)	0.6527(5)	0.3032(5)	0.2446(4)	3.74(16)
C(16)	0.5653(5)	0.3608(4)	0.2089(3)	3.13(14)
C(17)	0.3407(4)	0.7422(4)	0.1751(3)	2.34(12)
C(18)	0.4386(4)	0.7767(4)	0.1069(3)	3.01(14)
C(19)	0.4179(5)	0.8450(4)	0.0405(3)	3.68(16)
C(20)	0.3015(5)	0.8822(4)	0.0417(4)	3.85(16)
C(21)	0.2043(5)	0.8486(4)	0.1089(4)	3.88(16)
C(22)	0.2228(4)	0.7792(4)	0.1769(3)	2.92(14)
C(23)	0.5407(4)	0.7717(4)	0.3592(3)	2.19(12)
C(24)	0.5730(5)	0.9078(4)	0.3932(3)	3.45(14)
C(25)	0.7083(5)	1.0006(4)	0.4697(4)	4.08(16)
C(26)	0.8027(5)	0.9561(4)	0.5093(3)	3.97(15)
C(27)	0.7722(5)	0.8209(4)	0.4759(3)	3.37(15)
C(28)	0.6378(4)	0.7290(4)	0.4023(3)	2.87(13)
H(6)	0.199(4)	0.115(3)	0.067(3)	5.8(10)
H(7)	0.111(4)	−0.013(4)	−0.132(3)	7.6(12)
H(8)	0.130(4)	0.100(4)	−0.259(3)	7.5(12)
H(9)	0.195(4)	0.339(3)	−0.209(3)	5.8(11)
H(10)	0.259(4)	0.466(3)	−0.018(3)	6.3(11)
H(12)	0.271(4)	0.219(4)	0.308(3)	8.6(13)
H(13)	0.417(4)	0.114(3)	0.365(3)	6.6(11)
H(14)	0.665(4)	0.160(4)	0.326(3)	9.6(14)
H(15)	0.747(5)	0.325(4)	0.224(3)	11.5(15)
H(16)	0.601(4)	0.430(3)	0.163(3)	6.4(11)
H(18)	0.521(4)	0.745(4)	0.108(3)	7.7(12)
H(19)	0.486(4)	0.869(4)	−0.013(3)	9.7(14)
H(20)	0.290(4)	0.934(4)	−0.012(3)	8.4(13)
H(21)	0.130(4)	0.881(4)	0.111(3)	8.7(13)
H(22)	0.161(4)	0.758(3)	0.231(3)	6.9(11)
H(24)	0.500(4)	0.938(4)	0.355(3)	7.2(12)
H(25)	0.734(4)	1.105(4)	0.494(3)	8.4(13)
H(26)	0.898(4)	1.025(3)	0.557(3)	6.7(11)
H(27)	0.843(4)	0.788(4)	0.509(3)	7.6(12)
H(28)	0.620(4)	0.636(3)	0.387(3)	6.5(11)

[a] B_{eq} is the arithmetic mean of the principal axes of the thermal ellipsoid.

TABLE 3A

IMPORTANT BOND DISTANCES AND ANGLES FOR THE *cis*-$(\mathrm{CO})_4\overline{\mathrm{Mo(PPh_2OP}}\mathrm{Ph_2})$ STRUCTURE
(esd's refer to the last digit given)

Bond distances (Å)

Mo—P(1)	2.458(1)	P(1)—C(5)	1.814(3)
Mo—P(2)	2.476(1)	P(1)—C(11)	1.803(3)
Mo—C(1)	1.985(3)	P(2)—C(17)	1.805(3)
Mo—C(2)	1.981(3)	P(2)—C(23)	1.816(3)
Mo—C(3)	2.030(3)	C(1)—O(1)	1.149(4)
Mo—C(4)	2.029(3)	C(2)—O(2)	1.154(4)
P(1)—O(5)	1.659(2)	C(3)—O(3)	1.125(4)
P(2)—O(5)	1.667(2)	C(4)—O(4)	1.133(4)

Bond angles (°)

P(1)—Mo—P(2)	63.82(3)	Mo—P(1)—O(5)	96.9(1)
P(1)—Mo—C(2)	99.2(1)	C(5)—P(1)—C(11)	101.7(2)
P(1)—Mo—C(3)	92.1(1)	C(5)—P(1)—O(5)	101.5(2)
P(1)—Mo—C(4)	91.7(1)	Mo—P(2)—C(17)	122.4(1)
P(2)—Mo—C(1)	102.3(1)	Mo—P(2)—C(23)	126.9(1)
P(2)—Mo—C(3)	91.4(1)	Mo—P(2)—O(5)	96.0(1)
P(2)—Mo—C(4)	91.7(1)	C(17)—P(2)—C(23)	102.3(2)
C(1)—Mo—C(2)	94.7(1)	O(5)—P(2)—C(17)	103.0(2)
C(1)—Mo—C(3)	89.8(1)	O(5)—P(2)—C(23)	100.6(2)
C(1)—Mo—C(4)	86.9(1)	P(1)—O(5)—P(2)	103.3(1)
C(2)—Mo—C(3)	86.5(1)	Mo—C(1)—O(1)	177.9(3)
C(2)—Mo—C(4)	91.3(1)	Mo—C(2)—O(2)	176.7(3)
C(3)—Mo—C(4)	175.9(1)	Mo—C(3)—O(3)	176.6(3)
Mo—P(1)—C(5)	126.0(1)	Mo—C(4)—O(4)	176.4(3)
Mo—P(1)—C(11)	122.6(1)		

TABLE 3B

IMPORTANT BOND DISTANCES AND ANGLES FOR THE *cis*-$(\mathrm{CO})_4\overline{\mathrm{Cr(PPh_2OP}}\mathrm{Ph_2})$ STRUCTURE
(esd's refer to the last digit given)

Bond distances (Å)

Cr—P(1)	2.314(1)	P(1)—C(5)	1.829(4)
Cr—P(2)	2.227(1)	P(1)—C(11)	1.815(4)
Cr—C(1)	1.867(4)	P(2)—C(17)	1.802(4)
Cr—C(2)	1.839(4)	P(2)—C(23)	1.825(4)
Cr—C(3)	1.879(4)	C(1)—O(1)	1.148(5)
Cr—C(4)	1.886(4)	C(2)—O(2)	1.163(5)
P(1)—O(5)	1.657(3)	C(3)—O(3)	1.142(5)
P(2)—O(5)	1.672(3)	C(4)—O(4)	1.142(5)

Bond angles (°)

P(1)—Cr—P(2)	66.76(4)	Cr—P(1)—O(5)	97.0(1)
P(1)—Cr—C(2)	97.4(1)	C(5)—P(1)—C(11)	101.9(1)
P(1)—Cr—C(3)	92.4(1)	C(5)—P(1)—O(5)	101.2(1)
P(1)—Cr—C(4)	91.7(1)	Cr—P(2)—C(17)	123.0(1)
P(2)—Cr—C(1)	100.6(1)	Cr—P(2)—C(23)	126.8(1)
P(2)—Cr—C(3)	92.1(1)	Cr—P(2)—O(5)	96.1(1)
P(2)—Cr—C(4)	92.1(1)	C(17)—P(2)—C(23)	102.1(2)
C(1)—Cr—C(2)	95.3(1)	O(5)—P(2)—C(17)	102.8(3)
C(1)—Cr—C(3)	90.3(1)	O(5)—P(2)—C(23)	100.1(3)
C(1)—Cr—C(4)	87.6(1)	P(1)—O(5)—P(2)	100.2(1)
C(2)—Cr—C(3)	89.0(1)	Cr—C(1)—O(1)	177.9(4)
C(2)—Cr—C(4)	90.3(1)	Cr—C(2)—O(2)	177.5(4)
C(3)—Cr—C(4)	175.1(1)	Cr—C(3)—O(3)	176.3(4)
Cr—P(1)—C(5)	101.2(1)	Cr—C(4)—O(4)	176.1(4)
Cr—P(1)—C(11)	123.1(1)		

TABLE 4

$^{31}P\{^1H\}$ NMR DATA (Referenced to external 85% H_3PO_4)

Compound	Chemical shift (ppm) [a]
$NEt_3H^+(CO)_4Cr(PPh_2O)_2H^-$	135.6
$NEt_3H^+(CO)_4Mo(PPh_2O)_2H^-$	113.9
$NEt_3H^+(CO)_4W(PPh_2O)_2H^-$	93.8 (^1J(W—P) 260 Hz)
$(CO)_5MoPPh_2OPPh_2$	108.8 and 148.2 (^2J(P—P) 59 Hz)

[a] Spectra run in $CDCl_3$ solution.

centrated in vacuo to about 5 ml. A microcrystalline white solid was isolated by filtration. A second extraction with n-hexane and concentration gave a combined yield of 700 mg (60%) of the compound. Satisfactory CHN analyses were obtained. Its IR spectrum in Nujol mull included carbonyl bands at 2060m, 1994m, and 1930s, bd; and the POP(asym)band at 860 cm^{-1} (s, bd).

Thermal rearrangement of $(CO)_5MoPPh_2OPPh_2$

A sample of the complex was dissolved in C_6D_6 and loaded into an NMR tube. $^{31}P\{^1H\}$ NMR spectra were recorded with the probe at 60° C. After complete disappearance of the starting complex, a single signal at 134.8 ppm was observed. The identity of this product was confirmed by TLC and IR to be *cis*-$(CO)_4\overline{Mo(PPh_2O}PPh_2)$.

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