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COORDINATED TAUTOMERS OF A BIS-(PHOSPHORYL)-PHOSPHINE: ASSEMBLAGE OF GROUP VIB METAL COMPLEXES CONTAINING DIPHOSPHOXANE (P–O–P) LINKAGES

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Summary

Reactions of the hydrogen-bridged chelates *cis*-$(CO)_4M(PPh_2O-)_2H^-$ (M = Cr, Mo, W) with Cl_2PPh yield complexes of the type *cis*-$(CO)_4M(-PPh_2-P(O)Ph-O-PPh_2)$ containing five-membered chelate rings. X-ray structural determination of the Mo complex confirmed the formation of the heterocycle.

Crystal data: space group $C2/c$; a 16.477(3), b 19.845(3), c 20.512(4) Å; β 106.61(2)°; $Z = 8$, D_{calc} 1.421 Mg m^{-3}. The final residual is 0.027 for 4737 observed reflections. The five-membered chelate ring is nonplanar with the phosphoryl P 0.888(2) Å out of an approximate plane containing the other four atoms. For the tungsten analogue, ^{31}P NMR data are consistent with the initial formation of a six-membered heterocyclic intermediate: *cis*-$(CO)_4W(PPh_2-O)_2PPh$, which tautomerizes readily to give the final product. Six-membered chelate rings containing the $(PPh_2O)_2PPh$ ligand can be assembled by the reaction of *cis*-$(CO)_4Mo(PPh_2Cl)_2$ with $(CO)_5M-PPhO_2H^-$ (M = Cr, Mo). Complexes of the type *cis*-$(CO)_4Mo(PPh_2O-)_2PPh-M(CO)_5$ (M = Cr, Mo) were isolated. Reaction of Cl_2PPh with two equivalents of $(CO)_5Mo-PPh_2O^-$ yields $PhP(-OPPh_2-Mo(CO)_5)_2$. The above complexes represent coordination-stabilized $PhP(-OPPh_2)_2$ and $(Ph_2P-)\text{-}\overset{O}{\overset{\|}{P}}Ph(OPPh_2)$ tautomers of the unknown bis-(phosphoryl)-phosphine $\overset{O}{\overset{\|}{P}}hP-PPh_2)_2$.

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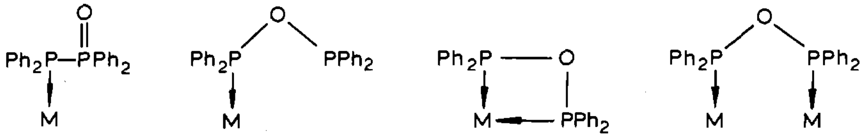
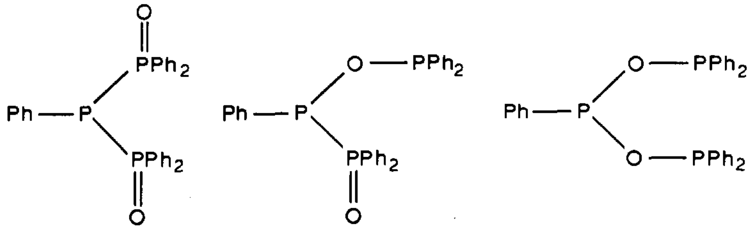
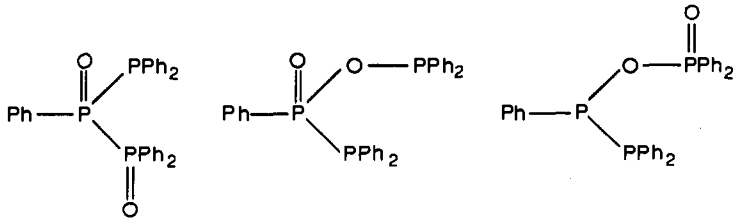
Introduction

Phosphoryl-phosphines containing $\text{P}-\overset{\text{O}}{\overset{\|}{\text{P}}}$ units and their diphosphoxane (P–O–P) tautomers are potentially useful ligands. We have recently investigated the coordination chemistry of $\text{Ph}_2\text{P}-\overset{\text{O}}{\overset{\|}{\text{P}}}\,\text{Ph}_2$ and its tautomer $\text{Ph}_2\text{P–O–PPh}_2$, and have found at least four distinct coordination modes [1,2]:

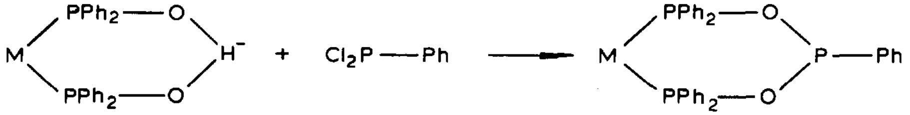


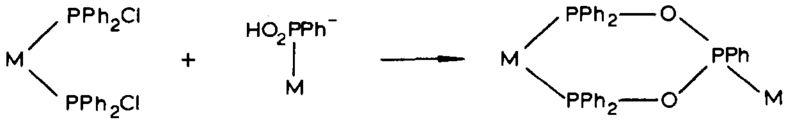
Although bis-(phosphoryl)-phosphines like $((\text{RO})_2\overset{\text{O}}{\overset{\|}{\text{P}}}-)_2\text{PPh}$ and $((\text{RO})\text{Ph}\overset{\text{O}}{\overset{\|}{\text{P}}}-)_2\text{PPh}$ are known [3,4], neither $(\text{Ph}_2\overset{\text{O}}{\overset{\|}{\text{P}}}-)_2\text{PPh}$ nor its tautomers have been reported. These compounds would potentially be versatile donors:



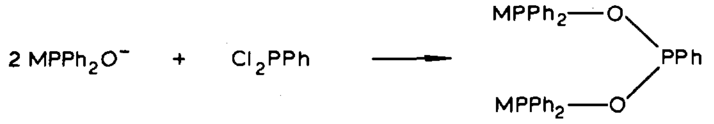


A plausible approach to prepare complexes of these unknown species is by assemblage of metal phosphine moieties using P–O–P linkages. We report here our attempts to construct the coordinated $(\text{Ph}_2\text{PO}-)_2\text{PPh}$ tautomer using the following three routes:


(1)



(2)



(3)

Results and discussion

When the hydrogen-bridged complex NEt_3H^+ *cis*-$(CO)_4Mo(PPh_2O-)_2H^-$ was reacted with Cl_2PPh in CH_2Cl_2 according to reaction 1, a white, crystalline solid that analyzed as $(CO)_4Mo(PPh_2O-)_2PPh$ (I) was isolated. Its proton-decoupled ^{31}P NMR spectrum (Fig. 1, Table 1), however, exhibited a twelve-line AMX pattern which is inconsistent with the symmetrical six-membered chelate structure of the desired product.

A single-crystal X-ray diffraction study of I revealed an approximately octahedral coordination geometry around the Mo atom. In addition to the four carbonyls, a five-membered chelate ring was found (Fig. 2). This ring consists of Mo, P(1) with two phenyl groups, P(2) with one phenyl and one terminal oxygen O(31), oxygen O(23), and P(3) with two phenyl groups (Fig. 3). Four of the ring atoms (Mo, P(1), O(23), P(3)) are reasonably planar (maximum deviation 0.081 Å), but P(2) is 0.888(2) Å out of this plane. Two distinct Mo–P distances are found: Mo–P(1) at 2.522(1) and Mo–P(3) at 2.460(1) Å. The two ring O–P distances are also different; O(23)–P(2) is 1.610(2) Å while O(23)–P(3) is 1.674(2) Å. The dihedral angle between rings 1A and 1B is 72.4(1)° and that between rings 3A and 3B is 83.9(1)°. Other selected bond distances and angles are listed in Table 2.

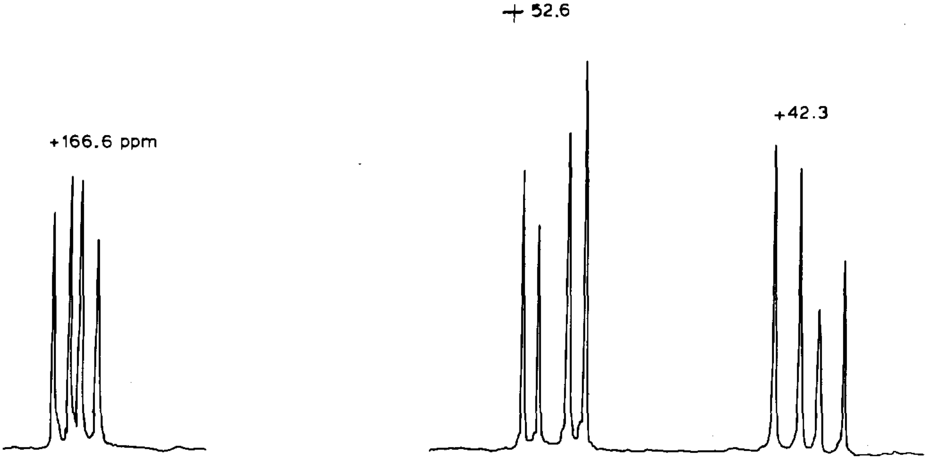


Fig. 1 $^{31}P\{^1H\}$ NMR spectrum of *cis*-$(CO)_4Mo-(PPh_2-P(O)Ph-O-PPh_2)$.

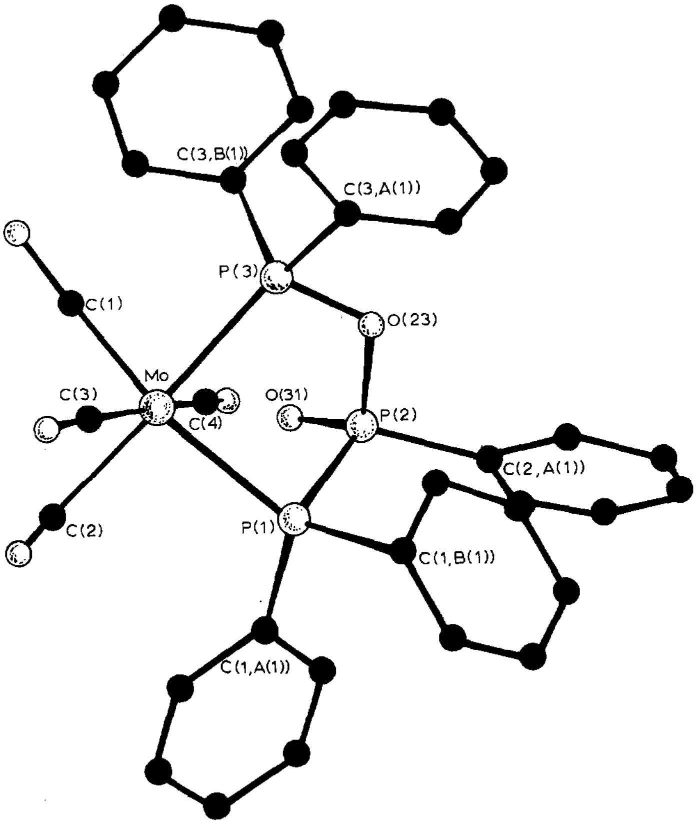


Fig. 2. Molecular structure of *cis*-$(CO)_4\overline{Mo\text{–}(PPh_2\text{–}P(O)Ph\text{–}O\text{–}P}Ph_2)$.

TABLE 1

$^{31}P\{^1H\}$ NMR DATA OF THE COMPLEXES. (δ in ppm, J in Hz; Spectra were run in $CDCl_3$ and referenced to external 85% H_3PO_4. See ref. 10)

Complexes	δ(A)	δ(M)	δ(X)	J(AX)	J(AM)	J(MX)
cis-$(CO)_4\overline{\underset{M}{M}(-PPh_2-\underset{X}{P}(O)Ph-O-\underset{A}{P}}Ph_2)$						
M = Cr (II)	192.5	73.6	44.2	49	39	63
M = Mo (I)	166.6	52.6	42.3	39	23	63
M = W (IV)	141.7	34.8	42.4	29	20	49
				(J(WA) 273, J(WM) 225)		
cis-$(CO)_4W(-\underset{X}{PPh_2}-O-)_2\underset{A}{PPh}$, (III)	168.9		114.5	78		
				(J(WX) 269)		
cis-$(CO)_4Mo(-\underset{X}{PPh_2}-O-)_2\underset{A}{PPh}-M(CO)_5$						
M = Cr (Vb)	213.0		141.1	29		
M = Mo (Va)	192.0		141.1	29		
$\underset{A}{PhP}(-O-\underset{X}{PPh_2}-Mo(CO)_5)_2$ (VI)	165.0		143.4	44		

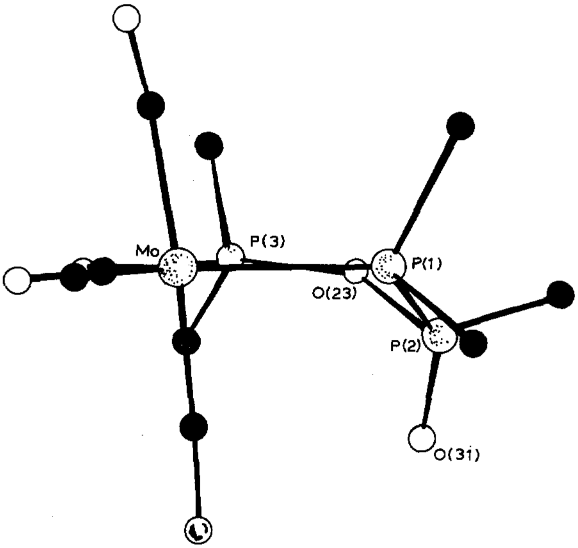


Fig. 3. Side-view of the chelate ring.

The complex is therefore the coordinated $(Ph_2P{-})\overset{\overset{O}{\|}}{P}Ph(-OPPh_2)$ tautomer of $PhP(-\overset{\overset{O}{\|}}{P}Ph_2)_2$. Neither tautomer is known in the uncomplexed state.

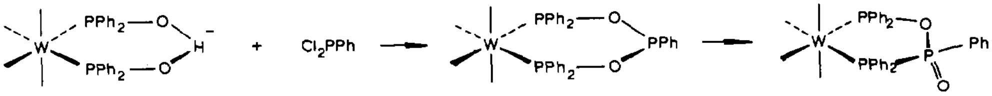
The reaction of NEt_3H^+ *cis*-$(CO)_4Cr(PPh_2O-)_2H^-$ with Cl_2PPh proceeds similarly to give *cis*-$(CO)_4\overline{Cr(-PPh_2-P(O)Ph-O-P}Ph_2)$ (II) as a white solid. Reaction of NEt_3H^+ *cis*-$(CO)_4W(PPh_2O-)_2H^-$ with Cl_2PPh, however, gives a transient species, III, with an AX_2 pattern in its ^{31}P spectrum (Table 1). This rapidly disappears to yield the AMX pattern of the isolated product, *cis*-$(CO)_4\overline{W(PPh_2-P(O)Ph-O-P}Ph_2)$ (IV). The spectral data are consistent with the formation of an intermediate

TABLE 2

SELECTED BOND DISTANCES (Å) AND ANGLES (°) FOR THE *cis*-$(CO)_4\overline{Mo(PPh_2P(O)PhOP}Ph_2)$ STRUCTURE (e.s.d.'s refer to the last digit given)

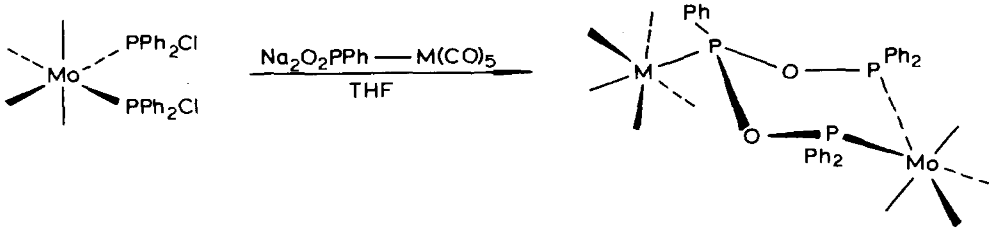
Mo–P(1)	2.522(1)	P(1)–P(2)	2.228(2)
Mo–P(3)	2.460(1)	P(2)–O(31)	1.466(2)
Mo–C(1)	1.975(3)	P(2)–O(23)	1.610(2)
Mo–C(2)	2.007(3)	O(23)–P(3)	1.674(2)
Mo–C(3)	2.010(3)		
Mo–C(4)	2.053(3)		
P(1)–Mo–P(3)	82.3(1)	P(1)–P(2)–C2A(1)	115.0(2)
P(1)–Mo–C(3)	96.7(1)	O(31)–P(2)–O(23)	115.6(2)
P(1)–Mo–C(4)	87.0(1)	O(31)–P(2)–C2A(1)	114.1(2)
Mo–P(1)–P(2)	100.7(1)	P(2)–O(23)–P(3)	120.6(2)
C1A(1)–P(1)–C1B(1)	104.6(2)	O(23)–P(3)–Mo	113.0(2)
P(1)–P(2)–O(23)	99.3(1)	C3A(1)–P(3)–C3B(1)	100.9(2)
P(1)–P(2)–O(31)	110.3(2)		

cis-$(CO)_4W(-PPh_2O-)_2PPh$ with a symmetrical six-membered ring. This complex then tautomerizes to give the final product:



The driving force for this tautomerization may be the formation of a P=O bond and(or) the favored closing up of a six-membered ring into a five-membered ring structure. The Cr and Mo reactions may follow the same reaction path. A summary of the ^{31}P spectral data is presented in Table 1.

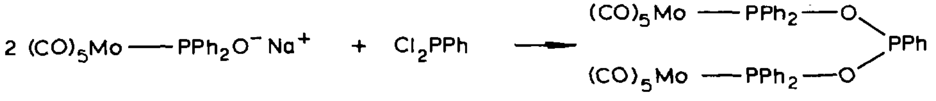
Using reaction 2, we were able to prepare the symmetrical six-membered chelate ring based on $(PPh_2O-)_2PPh$. The complex *cis*-$(CO)_4Mo(PPh_2Cl)_2$ reacts slowly with the sodium salt of $(CO)_5Mo-PPhO_2H^-$ in THF to give a white solid (Va). The sodium salt of $(CO)_5Cr-PPhO_2H^-$ can also be used to give a heterobimetallic product (Vb):



(M = Cr, Mo)

Both complexes exhibit the expected AX_2 pattern in their ^{31}P spectra (Table 1). Coordination of the $M(CO)_5$ moiety to the P(2) lone pair may stabilize it from tautomerization into the $(Ph_2P)\overset{O}{\overset{\|}{P}}Ph(-OPPh_2)$ structure. Kraihanzel and Gray have prepared *cis*-$(CO)_4Mo(PPh_2O-)_2\overset{O}{\overset{\|}{P}}-CH_2Cl$ which also appeared to have a six-membered chelate structure featuring the $(Ph_2PO-)_2P$ ligand [5]. In this case, the P(2) lone pair has been tied up with a terminal oxygen atom.

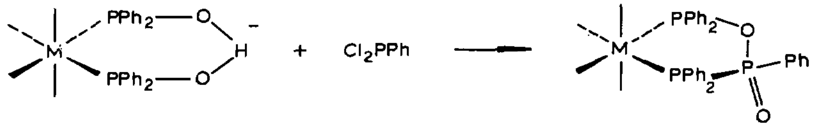
When two equivalents of $Na^+(CO)_5Mo-PPh_2O^-$ were allowed to react with Cl_2PPh in accord with reaction 3, we were able to isolate the expected $((CO)_5Mo-PPh_2O-)_2PPh$ complex (VI) in good yield.



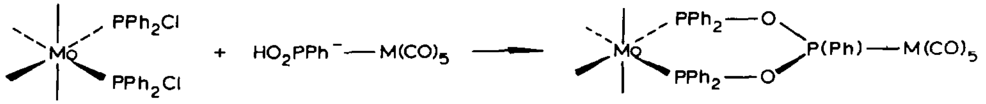
The fact that VI instead of the $(CO)_5Mo-(PPh_2-)\overset{O}{\overset{\|}{P}}Ph(-OPPh_2)-Mo(CO)_5$ tautomer was isolated is of interest. It suggests that the driving force behind the tautomerization of *cis*-$(CO)_4M(PPh_2O-)_2PPh$ intermediates to *cis*-$(CO)_4$-$M(-PPh_2-P(O)Ph-O-PPh_2)$ may be the preferred formation of a five-membered chelate ring over a six-membered one.

Conclusions

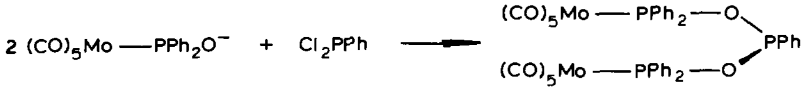
By assemblage of metal phosphine compounds using P–O–P linkages, three types of complexes have been prepared:



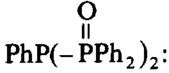
(M = Cr, Mo, W)



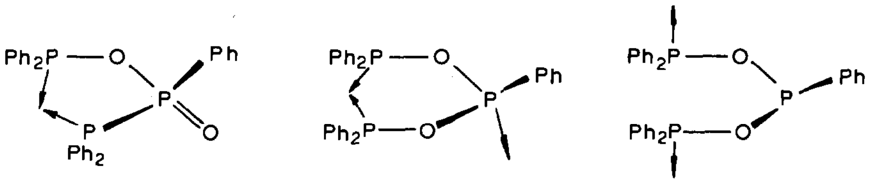
(M = Cr, Mo)



These complexes represent three of the many potential coordination modes of the tautomers of



$\mathrm{PhP(-\overset{\overset{O}{\|}}{P}Ph_2)_2}$:



These results suggest that the coordination chemistry of bis-(phosphoryl)-phosphines and their tautomers may indeed be worthy of attention. Even when these ligands are unstable or unknown in their free states, assemblage of reactive metal phosphine units via P–O–P linkages provides a versatile synthetic alternative.

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 sodium benzophenone ketyl. Dichlorophenylphosphine was purchased from Organometallics Inc., E. Hempstead, N.H. and was vacuum-distilled before use. The hydrogen-bridged chelates *cis*-$NEt_3H^+(CO)_4M(PPh_2O-)_2H^-$ were prepared by literature procedures [2,6]. $NEt_3H^+(CO)_5Mo{-}PPhO_2H^-$ was prepared according to Kraihanzel's method [6]. $NEt_3H^+(CO)_5Cr{-}PPhO_2H^-$ was prepared from the hydrolysis of $(CO)_5Cr-$

$PPhCl_2$ under basic conditions. NaH as a 50% oil dispersion was purchased from Ventron.

Infrared spectra were recorded using a Perkin–Elmer 283 spectrometer. ^{31}P NMR spectra were run on a JEOL-FX 90Q FT-NMR spectrometer with D-lock and chemical shifts are reported as referenced to external 85% H_3PO_4. All new complexes gave satisfactory (within 0.4%) elemental (C, H) analyses which were performed by the UNH Instrumentation Center.

Preparation of cis-$(CO)_4M(-PPh_2-P(O)Ph-O-PPh_2)$*; M = Cr, Mo, W (I, II, IV)*

The following procedure for the Mo complex is typical:

An amount of 230 mg (0.32 mmol) of NEt_3H^+ *cis*-$(CO)_4Mo(PPh_2O-)_2H^-$ was dissolved in 5 ml of CH_2Cl_2. A quantity of 440 mg (2.45 mmol) of Cl_2PPh was dissolved and made up to 10.0 ml volume in CH_2Cl_2. 1.3 ml of this solution was removed by syringe and slowly added to the Mo complex solution. The yellow-brown solution turned greenish within minutes. After one hour, the light yellow reaction mixture was concentrated in vacuo to about 2 ml in volume. About 10 ml of methanol was added with stirring. Slow evaporation of this solution using a N_2-stream yielded a white, microcrystalline solid. This was filtered and vacuum-dried to give a 60–70% yield of the *cis*-$(CO)_4Mo(-PPh_2-P(O)Ph-O-PPh_2)$ complex.

Synthesis of $(CO)_5M-PPh(-O-PPh_2)_2Mo(CO)_4$*; M = Cr, Mo (Vb, Va)*

An amount of 250 mg (0.58 mmol) of $NEt_3H^+(CO)_5Cr-PPhO_2H^-$ and 100 mg of NaH (50% oil dispersion) were stirred in 20 ml of THF until the effervescence had ceased. This was filtered through a fine-frit to give a light yellow solution. The solution was evaporated to dryness in vacuum and evacuated for about 3 h. A quantity of 370 mg, 0.57 mmol, of *cis*-$Mo(CO)_4(PPh_2Cl)_2$ was added; followed by 10 ml of THF. The yellow solution developed turbidity within minutes. After overnight stirring at room temperature, TLC indicated incomplete reaction. After 2 additional days at room temperature, the cloudy solution was filtered through Celite and the

TABLE 3

INFRARED DATA IN THE CARBONYL REGION OF THE COMPLEXES (Spectra were run as Nujol mulls)

Complex	Absorptions (cm^{-1})
cis-$(CO)_4M(-PPh_2-P(O)Ph-O-PPh_2)$	
M = Cr	2010w, 1946m, 1919s, bd, 1892s, 1876s
M = Mo	2020w, 1952sh, 1936s, bd, 1985s, 1882s
M = W	2016w, 1943sh, 1919s, bd, 1891s, 1875s
cis-$(CO)_4Mo(-PPh_2O-)_2PPh-M(CO)_5$	
M = Cr	2060w, 2029w, 1985m, 1965sh, 1947s, 1929s, 1911s, 1904s
M = Mo	2070w, 2029w, 1992w, 1970sh, 1952s, 1934s, 1912s, 1905s
$PhP(-OPPh_2-Mo(CO)_5)_2$	2062w, 1956m, sh, 1940s, 1921s

TABLE 4

ATOMIC POSITIONAL PARAMETERS AND EQUIVALENT ISOTROPIC THERMAL FACTORS FOR THE STRUCTURE (with e.s.d.'s in parentheses)

	x	y	z	B_{eq} ^{a}
Mo	0.127748(14)	0.372508(11)	0.184917(11)	3.048(10)
P(1)	0.18589(4)	0.46112(3)	0.12238(3)	3.07(3)
P(2)	0.30494(4)	0.48884(3)	0.20149(3)	3.14(3)
O(23)	0.34105(9)	0.41452(7)	0.22452(8)	3.30(8)
P(3)	0.27889(4)	0.35564(3)	0.24376(3)	3.14(3)
O(31)	0.28575(10)	0.52998(8)	0.25459(8)	3.84(9)
C(1)	0.10277(16)	0.30214(12)	0.24451(14)	4.25(14)
O(1)	0.09342(13)	0.25968(9)	0.27987(10)	6.67(13)
C(2)	0.00462(15)	0.38265(13)	0.13446(12)	3.89(13)
O(2)	−0.06621(11)	0.38607(10)	0.10605(9)	5.87(12)
C(3)	0.12485(16)	0.29696(13)	0.11899(13)	4.40(14)
O(3)	0.11498(14)	0.25238(10)	0.08209(10)	7.18(13)
C(4)	0.11394(15)	0.44792(11)	0.24945(13)	3.59(13)
O(4)	0.10167(12)	0.48925(19)	0.28371(19)	5.53(11)
C1A(1)	0.13341(15)	0.54230(12)	0.09938(11)	3.18(11)
C1A(2)	0.04619(16)	0.54418(13)	0.07991(14)	4.43(14)
C1A(3)	0.00349(17)	0.60390(14)	0.05815(15)	5.24(16)
C1A(4)	0.04726(17)	0.66165(13)	0.05602(13)	4.66(15)
C1A(5)	0.13384(18)	0.66114(13)	0.07638(14)	4.82(15)
C1A(6)	0.17664(16)	0.60125(13)	0.09730(13)	4.39(14)
C1B(1)	0.22253(14)	0.43788(12)	0.04894(11)	3.27(12)
C1B(2)	0.21971(17)	0.48113(13)	−0.00427(13)	4.71(15)
C1B(3)	0.24966(20)	0.46021(16)	−0.05775(14)	6.03(18)
C1B(4)	0.28133(19)	0.39720(16)	−0.05857(14)	6.00(17)
C1B(5)	0.28449(19)	0.35373(14)	−0.00608(15)	5.88(17)
C1B(6)	0.25478(17)	0.37371(13)	0.04749(13)	4.54(14)
C2A(1)	0.38694(14)	0.52285(11)	0.16924(12)	3.29(12)
C2A(2)	0.40680(15)	0.59037(12)	0.18192(12)	3.71(13)
C2A(3)	0.47020(17)	0.61923(13)	0.15975(13)	4.59(14)
C2A(4)	0.51458(17)	0.58130(14)	0.12626(15)	5.18(15)
C2A(5)	0.49507(18)	0.51458(14)	0.11294(16)	5.93(19)
C2A(6)	0.43111(17)	0.48521(13)	0.13425(15)	4.96(16)
C3A(1)	0.32949(14)	0.28107(11)	0.22239(11)	3.06(12)
C3A(2)	0.39121(17)	0.28304(12)	0.18896(14)	4.66(15)
C3A(3)	0.42546(19)	0.22383(14)	0.17282(15)	5.82(18)
C3A(4)	0.39837(18)	0.16296(13)	0.18986(14)	5.06(16)
C3A(5)	0.33758(17)	0.15997(12)	0.22348(13)	4.58(16)
C3A(6)	0.30317(17)	0.21901(12)	0.23908(12)	4.21(14)
C3B(1)	0.31836(16)	0.35452(11)	0.33611(12)	3.43(13)
C3B(2)	0.40399(18)	0.34932(13)	0.36809(13)	4.88(14)
C3B(3)	0.43394(20)	0.34576(15)	0.43830(15)	6.54(18)
C3B(4)	0.37729(23)	0.34583(15)	0.47648(14)	7.02(21)
C3B(5)	0.29278(22)	0.35023(16)	0.44521(14)	6.69(20)
C3B(6)	0.26248(18)	0.35554(13)	0.37505(13)	4.89(15)
H1A(2)	0.0164(13)	0.5033(10)	0.0817(10)	5.2(6)
H1A(3)	−0.0551(14)	0.6027(11)	0.0443(10)	5.8(6)
H1A(4)	0.0183(13)	0.7015(10)	0.0390(9)	4.8(6)
H1A(5)	0.1661(14)	0.7021(11)	0.0759(10)	5.3(6)
H1A(6)	0.2360(13)	0.6000(10)	0.1102(10)	4.5(6)
H1B(2)	0.1951(13)	0.5242(10)	−0.0055(10)	5.0(6)
H1B(3)	0.2442(15)	0.4905(12)	−0.0932(11)	7.4(7)

TABLE 4 (continued)

	x	y	z	B_{eq} [a]
H1B(4)	0.2986(15)	0.3838(11)	−0.0945(11)	6.9(7)
H1B(5)	0.3064(15)	0.3089(11)	−0.0042(11)	6.7(7)
H1B(6)	0.2598(14)	0.3427(10)	0.0852(10)	5.2(6)
H2A(2)	0.3779(13)	0.6147(10)	0.2069(9)	4.9(6)
H2A(3)	0.4841(14)	0.6654(10)	0.1693(10)	5.4(6)
H2A(4)	0.5572(14)	0.6024(11)	0.1132(10)	5.8(6)
H2A(5)	0.5205(15)	0.4888(11)	0.0867(11)	6.7(7)
H2A(6)	0.4175(13)	0.4392(10)	0.1240(10)	5.1(6)
H3A(2)	0.4072(13)	0.3247(10)	0.1765(10)	4.8(6)
H3A(3)	0.4661(14)	0.2262(11)	0.1507(10)	6.2(7)
H3A(4)	0.4222(13)	0.1230(10)	0.1785(10)	5.2(6)
H3A(5)	0.3180(13)	0.1167(10)	0.2376(10)	5.2(6)
H3A(6)	0.2627(14)	0.2167(10)	0.2629(10)	5.2(6)
H3B(2)	0.4397(13)	0.3462(10)	0.3412(10)	4.9(6)
H3B(3)	0.4920(15)	0.3415(12)	0.4612(11)	7.2(7)
H3B(4)	0.3974(16)	0.3455(12)	0.5274(11)	7.7(7)
H3B(5)	0.2525(16)	0.3511(12)	0.4721(12)	8.6(8)
H3B(6)	0.2015(14)	0.3603(10)	0.3539(10)	5.8(6)

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

filtrate evaporated to dryness. Extraction with 2 × 20 ml of n-hexane and slow concentration of the extract in vacuo yielded about 100 mg of white solid. This can be recrystallized from CH_2Cl_2/hexane. The Mo analogue was similarly prepared. Infrared data are collected in Table 3.

Preparation of $PhP(-OPPh_2-Mo(CO)_5)_2$ (VI)

An amount of 1.05 g (1.95 mmol) of $NEt_3H^+(CO)_5MoPPh_2O^-$ and 250 mg of NaH (50% in oil, prewashed with hexane to remove the oil) were stirred in 20 ml of THF until effervescence had subsided. The suspension was filtered through a fine frit to give a very light yellow solution. This was thoroughly evacuated to dryness. About 10 ml of THF was added to the solid residue to give a clear solution. A quantity of 680 mg (3.8 mmol) of Cl_2PPh was dissolved in 10.0 ml of THF. An amount of 2.6 ml of this was added to the Mo solution. A turbid solution resulted. After 20 min, the suspension was filtered through Celite to give a clear solution. This was evaporated down to an oily residue and extracted with 15 ml of hexane. Filtration through Celite and evaporation of the filtrate yielded a white semi-solid. This was recrystallized at −20°C from n-hexane to give about 450 mg of white, microcrystalline solid product.

X-ray structural determination

Crystals of *cis*-$(CO)_4Mo(-PPh_2-P(O)Ph-O-PPh_2)$ were grown from CH_2Cl_2 by slow evaporation. Intensity data were collected from a 0.4 × 0.4 × 0.3 mm crystal using Mo-K_α radiation with $\theta/2\theta$ scan technique and profile analysis [7]. A total of 5701 reflections were measured of which 4738 gave $I_{net} > 2.5\sigma(I_{net})$. The intensities were processed but no absorption corrections were made since $\mu = 5.36$ cm^{-1}. The cell parameters were derived from the setting angles of 50 reflections with $2\theta > 45°$.

The structure was solved by a routine application of MULTAN [8], which yielded the Mo and P atomic positions. A difference map revealed the remaining nonhydrogen atoms. Refinement by block-diagonal least squares proceeded smoothly and hydrogen atoms were included in the later stages at their calculated positions and refined isotropically. The final agreement indices were $R_F = 0.027$ and $R_W = 0.022$ for all the observed data and $R_F = 0.037$ and $R_W = 0.022$ for all the data. Scattering curves for neutral atoms were from the International Tables for X-ray Crystallography (1974). All calculations were performed using the NRC PDP-8E system of programs [9]. The atomic positional and equivalent isotropic temperature factors are given in Table 4. Anisotropic temperature factors and structure factor tables are available as supplementary material from the authors.

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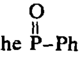
10 Assignments for X and M in I, II and IV are made assuming the chemical environment of the  $\overset{O}{\overset{\|}{P}}\text{–Ph}$ group phosphorus (X) to be essentially unchanged for all three complexes (i.e. 44.2, 42.3, 42.4 ppm respectively for Cr, Mo, and W). The M values for I, II, and IV then follow expected trends for Cr, Mo, and W phosphine shifts.[11]
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