Journal of Organometallic Chemistry, 233 (1982) 321—331
Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

DIPHOSPHINE MONOXIDE LIGANDS: COMPLEXES OF TETRAPHENYLDIPHOSPHINE OXIDE WITH GROUP VIB METAL CARBONYLS

EDWARD H. WONG * and RICHARD M. RAVENELLE

Department of Chemistry, University of New Hampshire, Durham, New Hampshire 03824 (U.S.A.)

ERIC J. GABE *, FLORENCE L. LEE and LATA PRASAD

Chemistry Division, National Research Council of Canada, Ottawa, K1A OR9 (Canada)

(Received December 16th, 1981; in revised form February 16th, 1982)

Summary

Tetraphenyldiphosphine monoxide forms complexes of the type $(CO)_5M$-$[PPh_2P(O)Ph_2]$ with Group VIB metals (M = Cr, Mo, W). The crystal and molecular structure of the Mo-complex has been determined: $MoP_2O_6C_{29}H_{20}$, Monoclinic Space Group $P2_1/n$, a 13.776(1), b 16.811(2), c 12.162(1) Å, β 90.36(1)°; $Z = 4$ and D_c 1.47 Mg m^{-3}. R_F is 0.038 for 5006 observed reflections. The Mo atom is found to be coordinated to the originally trivalent phosphorus atom while the ligand P—P bond remains intact and the oxygen atom is uncomplexed. The overall conformation around the P—P bond is staggered.

Heating of these complexes in diglyme resulted in loss of CO and tautomerization of the diphosphine oxide ligand into the chelating diphosphoxane in products identified as *cis*-$(CO)_4\overline{\mathrm{M(PPh_2OP}}\mathrm{Ph_2})$.

Reaction of excess OP_2Ph_4 with *cis*-$(CO)_4M(NHC_5H_{10})_2$ yielded H-bonded heterocycles of the type *cis*-$(CO)_4\overline{\mathrm{M[PPh_2P(Ph_2)O \cdots HN}}\mathrm{C_5H_{10}]}$ which are inert towards displacement of the remaining piperidine ligand.

Introduction

Diphosphine monoxides $(OPR_2PR'_2)$ can exist in several tautomeric forms: $R_2P(O)PR'_2$, $R_2POPR'_2$, or $R_2PP(O)R'_2$ [1]. For tetraphenyldiphosphine oxide (R = R′ = phenyl), the thermodynamically favored form is $Ph_2PP(O)Ph_2$. The free ligand thus contains both hard (O=P) and soft (P) donor sites. Potentially, OP_2Ph_4 and its diphosphoxane (Ph_2POPPh_2) tautomer can function in monodentate (Fig. 1: a, b, c), chelating (d, e), or bridging modes (f, g).

---

* Issued as NRCC publication no. 20206.

0022-328X/82/0000—0000/$02.75

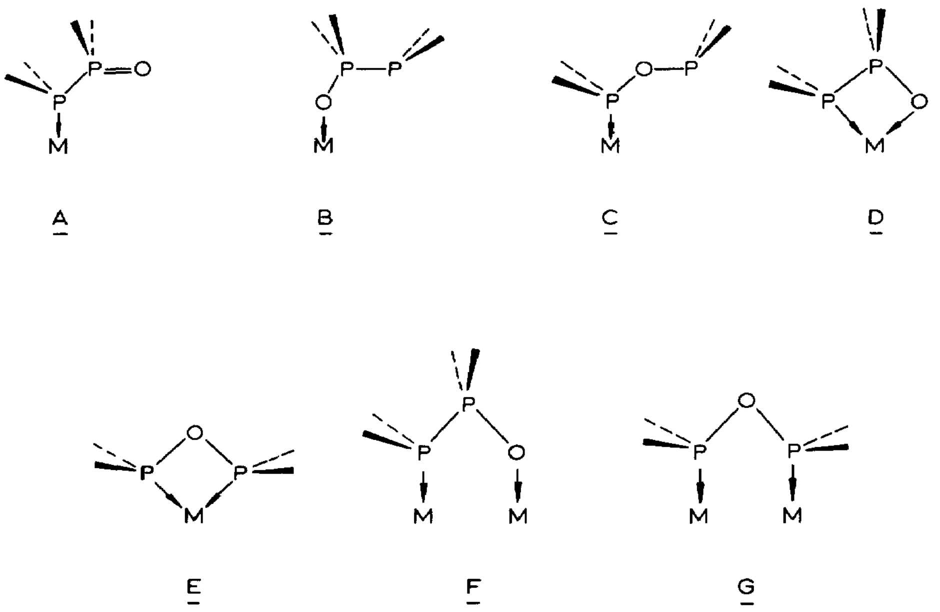


Fig. 1.

Of these possibilities, only g has been reported in the complex $(CO)_5MoPPh_2$-$OPh_2PMo(CO)_5$ prepared indirectly from coordinated chlorophosphines [2]. We have examined the direct substitution reaction of OP_2Ph_4 with Group VIB metal carbonyls and we report here our findings.

Results and discussion

Direct reaction of OP_2Ph_4 with $Mo(CO)_6$ proceeded smoothly in refluxing ethanol to give $(CO)_5Mo(OP_2Ph_4)$. The structure of this product has been established by spectral and X-ray techniques.

The important distances, angles as well as the atomic numbering scheme are shown in Fig. 2. A stereoview of the molecule is presented in Fig. 3. The crystal structure contains a Mo atom coordinated to five carbonyl groups and the formerly trivalent P(1) atom of the diphosphine oxide ligand. The P(1)—P(2) bond remains intact at 2.238(1) Å and the oxygen atom on P(2) is uncoordinated. The overall configuration around the P(1)—P(2) bond is staggered with the Mo—P(1) and P(2)—O torsional angle at 61.0(1)°. The Mo—P(1) distance at 2.534(1), $Mo—CO_{ax}$ at 1.969(3), $C—O_{ax}$ at 1.158(3), and average $C—O_{eq}$ at 1.144(3) Å are all similar to reported values for the $(CO)_5MoPPh_3$ complex [3a].

It is interesting that the four phenyl rings adopt a *gauche*-conformation (see Fig. 3) about the P—P bond, whereas in $(CO)_3Ni(Ph_2PPPh_2)Ni(CO)_3$ the *anti*-conformation was found instead [3b]. Also worthy of note is the distortion of three of the phenyl rings (1, 2 and 3). These contain average C(1)—C(2) and C(1)—C(6) distances of 1.38, C(2)—C(3) and C(5)—C(6) of 1.40, and C(3)—C(4) and C(4)—C(5) distances of only 1.35 Å. In addition, the average C(3)—C(4)—C(5) angle for these rings is 121.4°.

Analogous reactions of OP_2Ph_4 failed with $Cr(CO)_6$ and $W(CO)_6$ in ethanol.

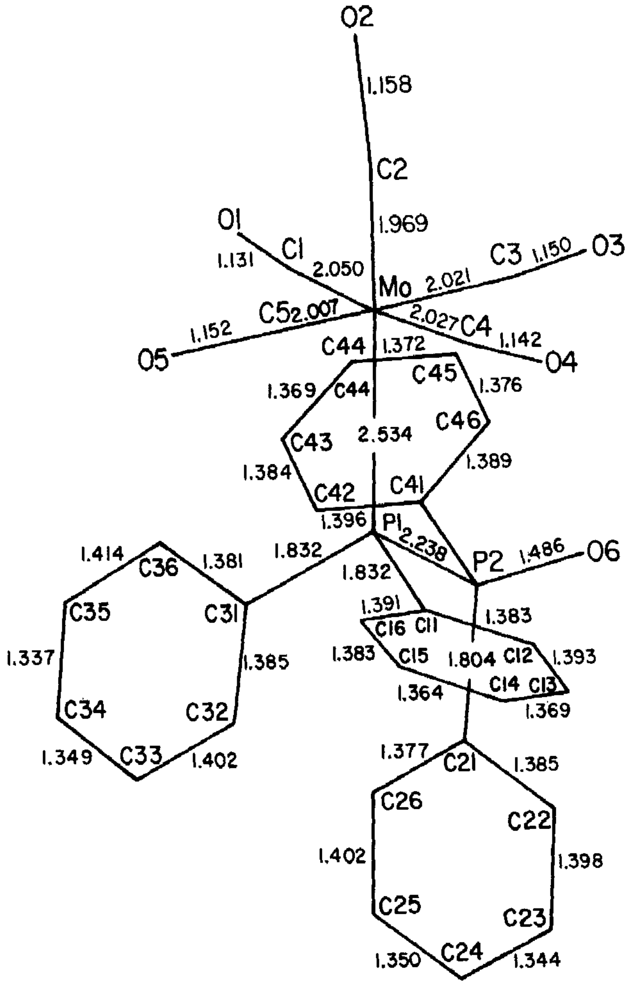


Fig. 2(a). Bond distances in $(CO)_5Mo(OP_2Ph_4)$.

P1 -	Mo -	C1		95.3
P1 -	Mo -	C2		173.2
P1 -	Mo -	C3		96.4
C1 -	Mo -	C3		88.3
C1 -	Mo -	C4		174.9
C2 -	Mo -	C4		89.7
C2 -	Mo -	C5		88.3
C3 -	Mo -	C5		176.8
C4 -	Mo -	C5		90.2
Mo -	P1 -	C11		110.4
P2 -	P1 -	C31		104.9
P1 -	P2 -	O6		108.6
C21 -	P2 -	C41		109.1
P1 -	P2 -	C21		111.8
P1 -	P2 -	C41		103.4
P2 -	C41 -	C42		125.5

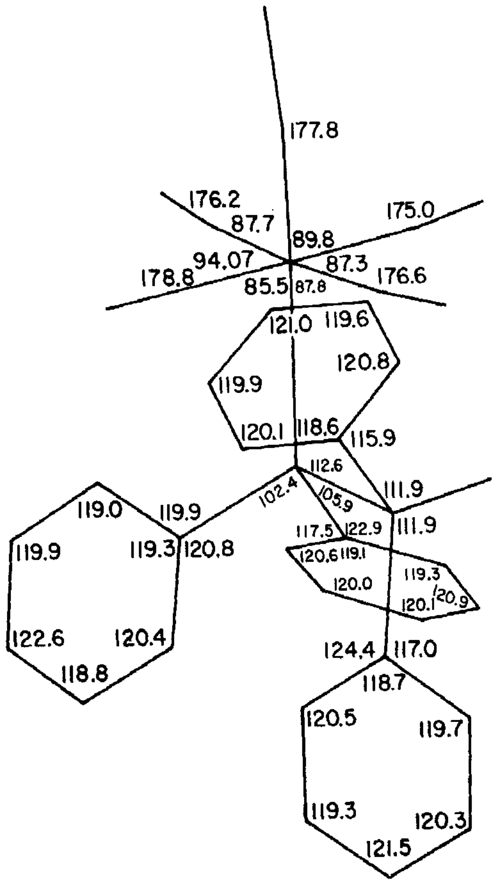


Fig. 2(b). Bond angles in the structure.

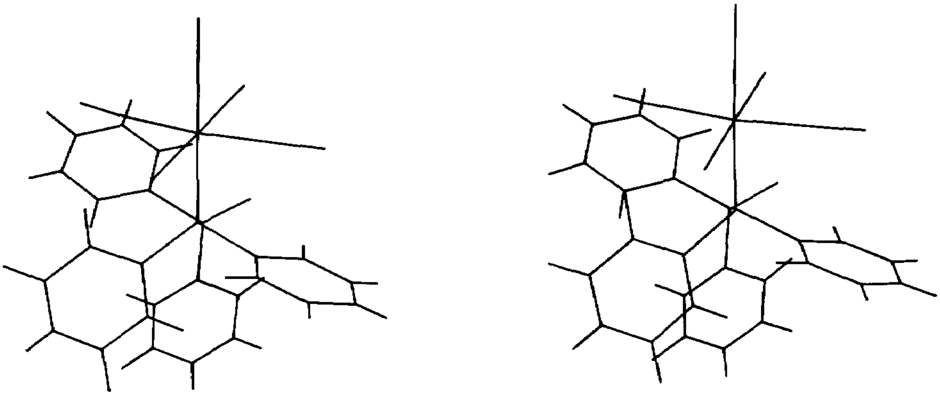


Fig. 3. Stereoview of the $(CO)_5Mo(OP_2Ph_4)$ structure.

These hexacarbonyls reacted instead with OP_2Ph_4 at 120° in diglyme solvent to give yellow products that were characterized as *cis*-$(CO)_4M(OP_2Ph_4)$ by IR and elemental analysis. A similar Mo-complex was obtained by prolonged heating of $(CO)_5Mo(OP_2Ph_4)$ in ethanol or diglyme. Gray has previously reported formation of the same *cis*-$(CO)_4Mo(PPh_2OPPh_2)$ complex from the reaction of *cis*-$(CO)_4Mo(PPh_2O)_2H^-$ with chlorophosphines and acyl chlorides [20].

The infrared spectra of all three products showed the absence of terminal P=O bands in the 1100—1200 cm^{-1} region. They all have strong new bands near 750—785 cm^{-1} (Table 1) which may be assigned to the P—O—P group [2,4]. Furthermore, a single type of phosphorus was found in each complex according to the ^{31}P NMR spectra (Table 2). There are at least two reasonable structures for these compounds (Fig. 4):

Structure **A** would contain the ligand functioning as a diphosphoxane chelate (mode e) while **B** would have the bridging diphosphoxane ligand (mode g). Previously reported diphosphoxane bridges in $(CO)_5MoR_2POPR'_2Mo(CO)_5$ have their asymmetric P—O—P bands in the infrared at 860—895 cm^{-1} [2].

Since ν_{asym} has been predicted to decrease with the P—O—P angle, the much lower values of 750—785 cm^{-1} in these complexes may suggest a significantly

TABLE 1

INFRARED DATA

Compound	ν(P—O—P) [a] (cm^{-1})	ν(N—H) [b] (cm^{-1})	ν(N—D) [b] (cm^{-1})
cis-$(CO)_4M(Ph_2POPPh_2)$			
M = Cr	760, 784	—	—
M = Mo	758, 773	—	—
M = W	760, 777	—	—
cis-$(CO)_4M(OP_2Ph_4)(NHC_5H_{10})$			
M = Cr	—	3170	—
M = Mo	—	3240	2392
M = W	—	3238	2390

[a] Spectra taken as Nujol Mulls. [b] Spectra taken in C_2Cl_4 solutions.

TABLE 2

^{31}P NMR DATA OF THE COMPLEXES

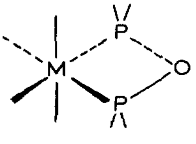
Compound	Chemical shift [a]					J(W—P) (Hz)
	δ(PO)	Δ(PO)	δ(P)	Δ(P)	J(P—P) (Hz)	
$Ph_2P—P(O)Ph_2$ (L)	35.2		—23.2			
$(CO)_5M—L$						
M = Cr	34.1	—1.1	50.1	+73.3	106	
Mo	33.9 [b]	—1.3	31.7 [b]	+54.9	107	
W	34.6	—0.6	14.4	+37.6	90	238
cis-$(CO)_4M—L(NHC_5H_{10})$						
M = Cr	39.9	+4.7	46.8	+70.0	159	
Mo	37.9	+2.7	30.0	+53.2	144	
W	38.8	+3.6	16.5	+39.7	127	227
cis-$(CO)_4M(Ph_2POPPh_2)$						
M = Cr			163.2			
Mo			134.8			
W			106.2			215

[a] Chemical shifts are in ppm from 85% H_3PO_4. Spectra taken in $CDCl_3$. [b] Since chemical shift difference is small, these assignments may be reversed.

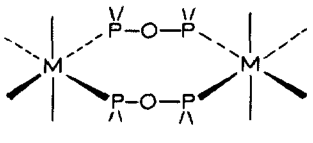
smaller P—O—P angle as required by a chelating structure [4]. Structural data on the related bridging $(EtO)_2POP(OEt)_2$ ligand in $(EtO)_2POP(OEt)_2Fe_2(CO)_5$ revealed a P—O—P angle of 119.3°. [5] A chelating P—O—P group would necessarily have a smaller angle and has not been previously observed. A molecular weight determination on the *cis*-$(CO)_4Mo(OP_2Ph_4)$ complex supports a monomeric formulation. The chelating P—O—P ligand structure A is favored for these products at this time. An X-ray structural study is in progress on the Mo-compound.

Monosubstituted $(CO)_5M[PPh_2P(O)Ph_2]$ complexes of Cr and W were prepared from the appropriate $(CO)_5MCH_3CN$ derivatives [7]. Structures similar to that of the Mo-complex are suggested by their IR and ^{31}P NMR data (Tables 2 and 3). Both Cr and W complexes thermally rearrange with CO loss to the respective *cis*-$(CO)_4M(PPh_2OPPh_2)$ complexes upon heating in diglyme.

In attempting to prepare disubstituted products of the type $(CO)_4M(OP_2Ph_4)_2$, *cis*-$(CO)_4M(NHC_5H_{10})_2$ compounds (M = Cr, Mo, W), first reported by Darensbourg [8], were reacted with excess OP_2Ph_4 in methylene chloride. In all three cases, only a single piperidine was displaced and yellow complexes of



A



B

Fig. 4.

TABLE 3

INFRARED DATA OF THE COMPLEXES IN THE CARBONYL REGION (in cm^{-1})

(All spectra were taken in cyclohexane solution)

Compound	
$(CO)_5M$—L (L = OP_2Ph_4)	
M = Cr	2058(w), 1956(s), 1946(s)
M = Mo	2062(w), 1963(s), 1931(s)
M = W	2068(w), 1954(s), 1944(s)
$(CO)_4M$—L	
M = Cr	2012(m), 1942(s), 1922(s), 1918(s)
M = Mo	2024(m), 1946(s), 1933(s), 1923(s)
M = W	2020(m), 1939(s), 1925(s), 1916(s)
$(CO)_4M$—L(NHC_5H_{10})	
M = Cr	2004(w), 1900(s), 1880(s), 1833(s)
M = Mo	2010(w), 1920(s), 1905(s), 1872(s)
M = W	2005(w), 1912(s), 1894(s), 1869(s)

the type *cis*-$(CO)_4M(OP_2Ph_4)$ (NHC_5H_{10}) were isolated. Inspection of their IR spectra revealed shifts of the N—H stretching frequencies to lower energies compared to the parent bis-piperidine compounds (Table 1). The Cr-complex, for example, exhibited a shift of almost 100 cm^{-1}. Furthermore, its P—O band is decreased by 17 cm^{-1} from the value in $(CO)_5Cr[PPh_2P(O)Ph_2]$. Upon deuteration, the N—H stretch of *cis*-$(CO)_4Mo(OP_2Ph_4)$ (NHC_5H_{10}) at 3240 cm^{-1} is shifted to a value of 2392 cm^{-1} in the NDC_5H_{10} analog. The ^{31}P NMR spectra of all three complexes showed the expected AB pattern and $^1J(PP)$ values indicative of P—P bonding (Table 2). Additionally, all three $\delta(PO)$ values exhibit coordination shifts of a few ppm downfield. These spectral results suggest that intramolecular H-bond exists between the diphosphine oxygen and the amino-H (Fig. 5).

Darensbourg and coworkers have already noted the effect of intramolecular H-bonding in the phosphite displacement of piperidine from *cis*-$(CO)_4Mo$-(piperidine)$_2$ [9]. A weak O—H interaction was in fact discovered in the structure of an isolated intermediate, *cis*-$(CO)_4Mo(NHC_5H_{10})(P(OMe)_3)$ [10]. In our complexes, intramolecular H-bonding seems especially effective since further piperidine displacement using OP_2Ph_4 did not occur even in solvents like THF.

Our results are summarized in Scheme 1.

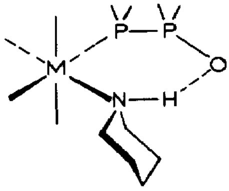
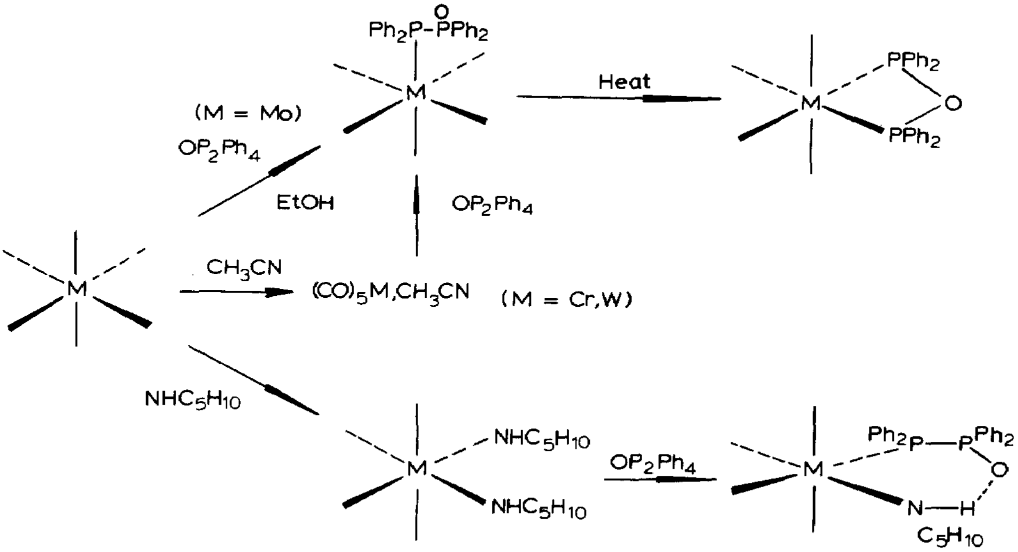


Fig. 5.

The ^{31}P NMR spectra

The ^1H-decoupled ^{31}P NMR data is presented in Tab. 2. For complexes of the type $(CO)_5M(OP_2Ph_4)$ assignments can be made if the chemical shift of the oxygen bearing phosphorus changes minimally upon coordination of the tertiary phosphorus atom to the metal. Based on this assumption, the upfield part of the AB pattern is assigned to the metal-coordinated P-atom. Further support for this comes from the observation of ^{183}W—^{31}P satellites around the upfield signals for the W-complex. The decrease in coordination shifts (ΔP) from Cr to Mo to W (73.3 to 54.9 to 37.6 ppm) is typical of phosphine complexes of this family of metal carbonyls [11,12].

SCHEME 1



Similar assignments can be made for the *cis*-$(CO)_4M(OP_2Ph_4)(NHC_5H_{10})$ complexes.

If the free ligand chemical shifts of Ph_2POPPh_2 were available, it would be most instructive to discuss the *cis*-$(CO)_4M(PPh_2OPPh_2)$ complexes in terms of their chelate ring effects [13]. Unfortunately such data is not yet available; it will be useful to prepare non-chelate complexes of the type $MPPh_2OPPh_2$ (c) for such comparisons.

Experimental section

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

Metal hexacarbonyls were purchased from Ventron Chem. Co. Tetraphenyldiphosphine oxide was prepared according to literature method [1(a)].

Diglyme was predried with CaH_2 and vacuum-distilled from Na-benzophenone ketyl. Methylene chloride and hexane were distilled from CaH_2. *cis*-$(CO)_4M(NHC_5H_{10})_2$ were prepared by literature methods [10].

Infrared spectra were recorded using a Perkin—Elmer 283 spectrophotometer.

TABLE 4

ANALYTICAL DATA OF THE COMPLEXES

Compound	Found (calcd.) (%)		
	C	H	N
$(CO)_5M$—(OP_2Ph_4)			
M = Cr	59.87 (60.17)	3.53 (3.46)	
M = Mo	56.08 (55.96)	3.25 (3.22)	
M = W	48.84 (49.04)	2.88 (2.82)	
$(CO)_4M(Ph_2POPPh_2)$			
M = Cr	60.92 (61.05)	3.75 (3.63)	
M = Mo	56.37 (56.58)	3.33 (3.39)	
M = W	49.40 (49.25)	2.95 (2.93)	
$(CO)_4M(OP_2Ph_4)(NHC_5H_{10})$			
M = Cr	62.01 (62.36)	4.66 (4.88)	2.16 (2.20)
M = Mo	58.38 (58.37)	4.69 (4.57)	2.03 (2.06)
M = W	51.69 (51.62)	4.07 (4.04)	1.80 (1.82)

^{31}P NMR spectra were run on a JEOL-FX 90Q FT-NMR spectrometer with D-lock and all chemical shifts were referenced to external 85% H_3PO_4. Elemental analyses were performed by the Instrumentation Center at UNH (Tab. 4). Osmometry molecular-weight determination was done by Schwartzkopf Analytical Company, Woodside, New York.

Preparation of $(CO)_5Mo(OP_2Ph_4)$

An amount of 600 mg (1.5 mmol) of OP_2Ph_4 and 400 mg (1.5 mmol) of $Mo(CO)_6$ were refluxed in absolute ethanol (20 ml) for 2 h. The resulting light yellow solution was slowly cooled to 0° C whereupon pale yellow crystals formed and were collected, washed with ether, and dried to give 500 mg (0.8 mmol, 53%) of the product.

Preparation of $(CO)_5M(OP_2Ph_4)$*; M = Cr, W*

Equivalent quantities of $(CO)_5M(CH_3CN)$ prepared by literature methods [7], and OP_2Ph_4 were dissolved in sufficient CH_2Cl_2 to give a clear solution. After stirring for 1 h, the solution was concentrated to half the volume and an equal amount of ethanol added. Upon slow evaporation of the solution, the product crystallized as a microcrystalline yellow solid in 50—60% yield.

Preparation of $(CO)_4M(PPh_2OPPh_2)$*; M = Cr, Mo, W*

A mixture of 1.5 mmol of $M(CO)_6$ and 1.5 mmol of OP_2Ph_4 was heated in 20 ml of diglyme at 120° C. After approximately two equivalents of CO had

TABLE 5

ATOMIC PARAMETERS *x*, *y*, *z* AND B_{iso}. E.s.d.'s refer to the last digit printed

	x	*y*	*z*	B_{iso}
Mo	0.475598(19)	0.314882(14)	0.036518(20)	3.506(10)
P(1)	0.52670(5)	0.27460(4)	0.22914(5)	2.99(3)
P(2)	0.54435(5)	0.14288(4)	0.24729(6)	3.24(3)
O(1)	0.26146(15)	0.24484(12)	0.04742(18)	6.43(13)
O(2)	0.41397(17)	0.38701(12)	−0.19034(15)	7.01(14)
O(3)	0.53744(15)	0.15721(12)	−0.08728(16)	6.31(13)
O(4)	0.69131(16)	0.37286(13)	−0.00354(17)	7.31(14)
O(5)	0.42154(16)	0.48028(11)	0.14308(17)	6.74(14)
O(6)	0.62129(13)	0.11585(9)	0.17072(14)	4.00(10)
C(1)	0.33777(21)	0.26969(15)	0.04753(23)	4.43(15)
C(2)	0.43807(23)	0.35926(17)	−0.10741(22)	5.15(17)
C(3)	0.51583(20)	0.21264(16)	−0.03780(22)	4.50(15)
C(4)	0.61320(22)	0.35387(17)	0.01324(21)	5.03(16)
C(5)	0.44019(21)	0.41969(16)	0.10438(23)	4.61(16)
C(11)	0.64503(18)	0.31794(14)	0.26388(18)	3.04(11)
C(12)	0.73148(19)	0.27738(14)	0.25063(22)	3.77(14)
C(13)	0.81889(20)	0.31761(17)	0.26606(23)	4.86(15)
C(14)	0.82012(21)	0.39660(17)	0.29353(23)	4.95(16)
C(15)	0.73511(22)	0.43701(16)	0.30634(23)	4.90(16)
C(16)	0.64750(21)	0.39823(15)	0.29157(22)	4.24(15)
C(21)	0.57076(20)	0.11509(14)	0.38759(20)	3.67(14)
C(22)	0.66129(22)	0.08242(16)	0.40865(23)	4.89(17)
C(23)	0.68559(24)	0.05850(18)	0.5154(3)	6.23(19)
C(24)	0.6221(3)	0.06822(18)	0.59777(25)	6.78(21)
C(25)	0.5331(3)	0.09945(19)	0.57985(24)	7.10(21)
C(26)	0.50636(24)	0.12245(17)	0.47311(24)	5.82(19)
C(31)	0.45202(19)	0.30459(14)	0.34618(20)	3.76(13)
C(32)	0.49244(24)	0.31292(18)	0.45011(21)	5.91(18)
C(33)	0.4345(3)	0.33536(20)	0.5392(3)	8.43(25)
C(34)	0.3386(3)	0.34670(18)	0.5223(3)	8.21(24)
C(35)	0.29689(24)	0.33869(17)	0.4234(3)	7.30(21)
C(36)	0.35397(21)	0.31815(16)	0.33138(24)	5.18(16)
C(41)	0.42639(19)	0.10444(14)	0.20888(20)	3.27(13)
C(42)	0.33913(20)	0.12248(14)	0.26110(21)	4.06(15)
C(43)	0.25277(21)	0.09088(16)	0.2205(24)	4.99(17)
C(44)	0.25308(22)	0.04169(17)	0.13237(23)	5.30(17)
C(45)	0.33815(23)	0.02238(16)	0.08080(22)	5.01(17)
C(46)	0.42425(21)	0.05426(15)	0.11812(21)	4.22(15)
H(12)	0.7312(15)	0.2195(11)	0.2282(16)	3.9(5)
H(13)	0.8746(17)	0.2877(12)	0.2566(17)	5.6(6)
H(14)	0.8780(16)	0.4250(13)	0.3015(17)	5.6(6)
H(15)	0.7348(17)	0.4958(12)	0.3240(17)	5.5(6)
H(16)	0.5896(15)	0.4244(12)	0.3024(15)	3.9(5)
H(22)	0.7019(16)	0.0734(12)	0.3494(17)	5.3(6)
H(23)	0.7557(19)	0.0321(13)	0.5318(19)	7.9(8)
H(24)	0.6430(20)	0.0532(15)	0.6702(20)	8.8(8)
H(25)	0.4830(20)	0.1067(15)	0.6417(20)	8.7(8)
H(26)	0.4451(18)	0.1428(13)	0.4586(19)	7.5(7)
H(32)	0.5597(19)	0.3052(15)	0.4619(20)	9.3(8)
H(33)	0.4661(22)	0.3434(16)	0.6200(23)	11.1(10)
H(34)	0.3021(23)	0.3601(16)	0.5789(22)	11.0(10)
H(35)	0.2197(21)	0.3479(15)	0.4137(21)	9.5(9)
H(36)	0.3236(16)	0.3158(12)	0.2581(16)	4.9(6)
H(42)	0.3408(16)	0.1591(12)	0.3209(17)	5.3(6)
H(43)	0.1953(16)	0.1071(12)	0.2571(17)	5.4(6)
H(44)	0.1854(18)	0.0177(13)	0.1018(18)	7.1(7)
H(45)	0.3388(17)	−0.0137(12)	0.0175(17)	5.9(7)
H(46)	0.4831(16)	0.0405(12)	0.0839(16)	4.9(6)

evolved, the dirty yellow solution was stripped of the diglyme and $M(CO)_6$ by shortpath distillation. The resulting residue was extracted with 10 ml of CH_2Cl_2, filtered through Celite and the filtrate diluted with ethanol. Slow evaporation of the solution gave the products as yellow solids. Yields were in the 40—60% range. A molecular weight determination of the Mo-complex in THF by osmometry gave a value of 560 ± 50 (calcd. for $Mo(CO)_4(OP_2Ph_4)$: 594).

Preparation of $(CO)_4M(OP_2Ph_4)(NHC_5H_{10})$; M = Cr, Mo, W

The synthesis of the Mo-complex is typical: An amount of 207 mg (0.55 mmol) of *cis*-$(CO)_4Mo(NHC_5H_{10})_2$ and 422 mg (1.1 mmol) of OP_2Ph_4 were dissolved in 20 ml of CH_2Cl_2 to give a clear yellow solution. After 1 h of stirring at room temperature, the solution was concentrated in vacuo to 5 ml and methanol added dropwise until turbidity persisted. Further slow evaporation precipitated a bright yellow, light-sensitive solid product in 60—70% yield. The *N*-deuterated complexes were prepared from NDC_5H_{10}.

X-ray Structure determination of $(CO)_5Mo(OP_2Ph_4)$

The diffraction intensities of an approximately 0.4 × 0.4 × 0.3 mm crystal were collected using graphite-monochromatized Mo-K_α radiation. The $\theta/2\theta$ scan technique was used and the data were subjected to profile analysis [14]. The data was collected to $2\theta = 60°$ giving a total of 9443 measurements of which there were 8257 independent reflections and 5006 were judged to be observed at the $2.5\sigma(I)$ level. Lorentz and polarization factors, [15] were applied but no absorption correction was performed (μ 6.04 cm^{-1}). The cell parameters were obtained by least-squares refinement of the setting angles of 60 reflections with 2θ larger than 50 degrees (Mo-$K_{\alpha(1)} = 0.70932$).

The Mo atom was found by application of MULTAN [16], and then a heavy atom-phased Fourier map revealed the two phosphorus atoms and 31 non-hydrogen atoms. The initial R-value was 19% and a subsequent Fourier map revealed all 38 non-hydrogen atoms. Successive isotropic refinement cycles lowered the residual to $R_F = 0.079$. The hydrogen atomic positions were calculated and their positional parameters were refined anisotropically by the block diagonal least squares method. The final agreement factors are $R_F = 0.038$ and $R_W = 0.023$ with counting statistics weights. Final positional parameters and equivalent isotropic temperature factors are listed in Table 5, further supplementary data can be obtained [17]. All calculations were carried out using the NRC system of programs for the PDP-8 [18] and scattering factors were taken from International Tables for X-ray Crystallography [19].

Acknowledgement

We thank Mr. J. Baldvins for help in parts of the synthesis. We also thank the National Science Foundation for an instrument grant towards the purchase of the FT-NMR spectrometer.

References

1 (a) J. McKechnie, D.S. Payne, and W. Sim, J. Chem. Soc., (1965) 3500; (b) I.F. Lutsenko and V.L. Foss, Pure and Appl. Chem., 52 (1980) 917.
2 C.S. Kraihanzel and C.M. Bartish, J. Amer. Chem. Soc., 94 (1972) 3572.
3 (a) F.A. Cotton, D.J. Darensbourg and W.H. Isley, Inorg. Chem., 20 (1981) 578; (b) R.H.B. Mais, P.G. Owston, D.T. Thompson, A.M. Wood, J. Chem. Soc., A, (1967) 1744.
4 D.E.C. Corbridge, Top. in Phos. Chem., 6 (1969) 282.
5 F.A. Cotton, R.J. Haines, B.E. Hanson and J.C. Sekutowski, Inorg. Chem., 17 (1978) 2010.
6 A.L. du Preez, I.L. Marais, R.J. Haines, A. Pickcock and M. Safari, J. Chem. Soc. Dalton, (1981) 1918.
7 D.P. Tate, Inorg. Chem., 1 (1962) 433.
8 D.J. Darensbourg and R.L. Kump, Inorg. Chem., 17 (1978) 2680.
9 J. Ewen and D.J. Darensbourg, J. Amer. Chem. Soc., 97 (1975) 6874.
10 J.L. Atwood and D.J. Darensbourg, Inorg. Chem., 16 (1977) 2314.
11 S.O. Grim, D.A. Wheatland, W.J. McFarlane, J. Amer. Chem. Soc., 89 (1967) 5573.
12 P.E. Pregosin and R.W. Kunz, ^{31}P and ^{13}C NMR of Transition Metal Phosphine Complexes, Springer-Verlag, Berlin, 1979.
13 P.E. Garrou, Chem. Rev., 81 (1981) 229.
14 D.F. Grant and E.J. Gabe, J. Appl. Cryst., 11 (1978) 114.
15 Y. LePage, E.J. Gabe and L.D. Calvert, J. Appl. Cryst., 12 (1979) 25.
16 G. Germain, P. Main and M.M. Woolfson, Acta Cryst., A27 (1971) 368.
17 Lists of structure factors and anisotropic thermal parameters have been deposited as supplementary material can be obtained from the authors.
18 A.C. Larson and E.J. Gabe, in H. Shenk, R. Olthof—Hazekamp, M. Van Koningsvel and G.C. Bassi (Eds.), Computing in Crystallography, p. 81. Delft University Press 1978.
19 International Tables for X-ray Crystallography, Vol. IV, Table 22B, p. 99. Birmingham; Kynoch; Kynoch Press 1974.
20 G.M. Gray, Ph.D. Thesis, Lehigh University, 1978.