Journal of Organometallic Chemistry, 277 (1984) 403–415
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

TRIMETHYLPHOSPHINE COMPLEXES OF MOLYBDENUM AND TUNGSTEN. THE SYNTHESIS AND CHEMICAL PROPERTIES OF $MoCl_4(PMe_3)_3$ AND THE CRYSTAL AND MOLECULAR STRUCTURES OF $WCl_4(PMe_3)_3$ AND $MoO(acac)_2PMe_3$

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(Received May 30th, 1984)

Summary

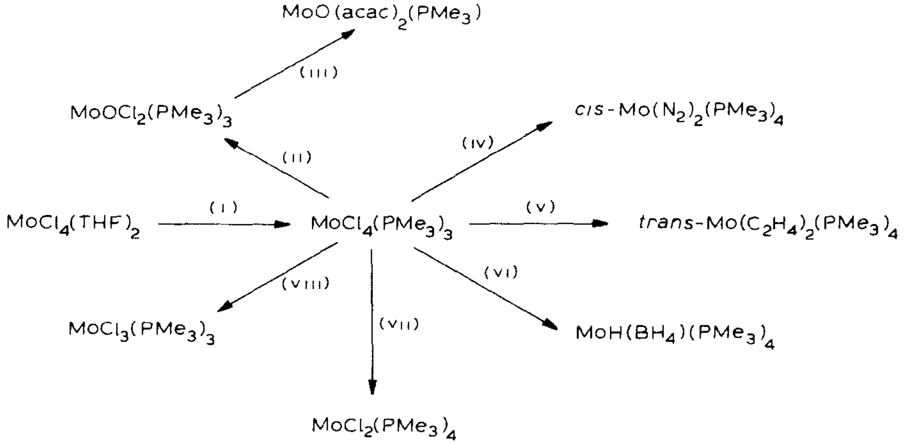
The seven-coordinate compound $MoCl_4(PMe_3)_3$ has been prepared by the room temperature reaction of $MoCl_4(THF)_2$ and PMe_3. This complex is a useful starting material for the synthesis of other trimethylphosphine derivatives of molybdenum. Reduction, under different experimental conditions, affords the known complexes $MoCl_3(PMe_3)_3$, $MoCl_2(PMe_3)_4$, *cis*-$Mo(N_2)_2(PMe_3)_4$ and *trans*-$Mo(C_2H_4)_2(PMe_3)_4$. Interaction with H_2O, in the presence of an excess of PMe_3 produces $MoOCl_2(PMe_3)_3$ which gives $MoO(acac)_2PMe_3$ by reaction with Tl(acac). The oxoacetylacetonate complex crystallizes in the monoclinic space group $P2_1/c$ with a 14.155(6), b 9.984(4), c 12.629(1) Å, β 98.80(5)° and D_{calc} 1.44 g cm^{-3} for $Z = 4$. A final R value of 0.026 based on 1332 observed reflections was obtained. The molybdenum coordination is pseudo-octahedral with the oxo and phosphine ligands in a *cis* configuration. The Mo–O(oxo) separation is 1.676(5) Å.

The crystal structure of the tungsten analogue of $MoCl_4(PMe_3)_3$ has also been determined. $WCl_4(PMe_3)_3$ crystallizes in the monoclinic space group $P2_1/c$ with unit cell constants a 14.835(4), b 11.422(2), c 11.568(3) Å, β 91.92(2)° and D_{calc} 1.88 g cm^{-3} for $Z = 4$. The final R value based on 1613 independent observed reflections is 0.040. The tungsten atom is seven-coordinate, the ligands describing an approximate capped octahedron with a chlorine atom capping the face defined by the three phosphorous atoms. The unique W–Cl distance is 2.417(5) Å, while the remaining W–Cl and W–P bond lengths average 2.45(3) and 2.551(3) Å respectively.

0022-328X/84/$03.00

Introduction

A large number of compounds of composition $MoCl_4L_n$ ($n = 2, 3$) are known for a variety of donor ligands, and some of them are important starting materials for the preparation of a variety of molybdenum complexes in different oxidation states [1]. We wish to report the synthesis of the trimethylphosphine derivative $MoCl_4(PMe_3)_3$, from the room temperature reaction of $MoCl_4(THF)_2$ and PMe_3, and some further reactions of this versatile starting material, which provide convenient routes to other trimethylphosphine derivatives of molybdenum in several oxidation states (see Scheme 1). The crystal and molecular structures of the oxomolybdenum(IV) species, $MoO(acac)_2PMe_3$, and of the seven-coordinate tungsten complex, $WCl_4(PMe_3)_3$, are also reported.



SCHEME 1. i. PMe_3, (THF); ii. H_2O, PMe_3, (THF); iii. Tlacac, (THF); iv. Na(disp.) PMe_3, N_2, (THF); v. Na(Hg), PMe_3, C_2H_4, (THF); vi. $NaBH_4$, PMe_3, (EtOH); vii. Na(Hg), PMe_3, (THF); viii. Na(Hg), (THF).

Results and discussion

Synthesis of $MoCl_4(PMe_3)_3$ and X-ray structure of $WCl_4(PMe_3)_3$

The complex $WCl_4(PMe_3)_3$ was first prepared by Sharp and Schrock [2] from WCl_4 and PMe_3. This compound, and the bis(phosphine) species, $WCl_4(PMe_3)_2$, can also be obtained by reduction [3] of WCl_6 with PMe_3 in toluene at 120 °C. We have now obtained the molybdenum analogue, $MoCl_4(PMe_3)_3$, from the reaction of $MoCl_4(THF)_2$ and PMe_3 (eq. 1). $MoCl_4(PMe_3)_3$ is a red-purple crystalline solid,

$$MoCl_4(THF)_2 + 3PMe_3 \xrightarrow[20\,^\circ C]{THF} MoCl_4(PMe_3)_3 \qquad (1)$$

moderately stable to air in the solid state, but very sensitive in solution. As expected, it is paramagnetic, and the ^1H NMR consists of a fairly broad resonance centered at ca. δ −17 ppm. Its low solubility has precluded cryoscopic molecular weight and solution magnetic moment determinations.

Seven-coordination in MX_4L_3 complexes (M = Mo, W), has only been established in a small number of cases [4]. It was therefore of interest to carry out a structural determination on one of the trimethylphosphine derivatives, $MCl_4(PMe_3)_3$. Since no structural information is available [4c] for seven-coordinate W^{IV} and, single crystals of the tungsten species are easier to obtain than those of the molybdenum analogue, $WCl_4(PMe_3)_3$ was the obvious choice.

The molecular structure and atom labeling scheme for $WCl_4(PMe_3)_3$ are presented in Fig. 1. The tungsten atom is seven-coordinate with the structure best described as a capped octahedron approaching the ideal C_{3v} symmetry. Chlorine atoms Cl(1), Cl(2) and Cl(4) occupy the uncapped face with Cl(3) capping the face formed by the three phosphorus atoms. This is the same type of structure found for $[MoCl_4(PMe_2Ph)_3]\cdot EtOH$ [5] and $MoBr_4(PMe_2Ph)_3$ [6].

The choice of a capped octahedron to describe the polyhedron formed by the seven unidentate ligands is supported in two ways. First, the average angles (Table 1) about the tungsten atom [Cl(3)–W–Cl(uncapped face) 127(5)°; Cl(3)–W–P(capped face) 74.6(5)°; Cl–W–Cl(uncapped face) 87(3)°; P–W–P(capped face) 113(3)°; Cl–W–P(*trans*) 158(5)°; Cl–W–P(*cis*) 77(1)°] agree with those found for $[MoCl_4(PMe_2Ph)_3]\cdot EtOH$ [5] and other seven coordinate molecules of C_{3v} symmetry [4a]. Secondly, the three shape determining dihedral angles, δ', [7] defined by the planes Cl(3), P(2), P(3)–Cl(1), P(2), P(3); Cl(3), P(1), P(3)–Cl(2), P(1), P(3); and Cl(3), P(1), P(2)–Cl(4), P(1), P(2) are 13.8, 10.8, and 25.5° respectively. These values are near the idealized values of 16.2° found for a C_{3v} capped octahedron [7]. Similar calculations using C_{2v} monocapped trigonal prism and D_{5h} pentagonal bipyramid models indicated that these latter polyhedra did not adequately describe the structure of $WCl_4(PMe_3)_3$. The W–Cl(3) bond distance (the capping chlorine atom) is

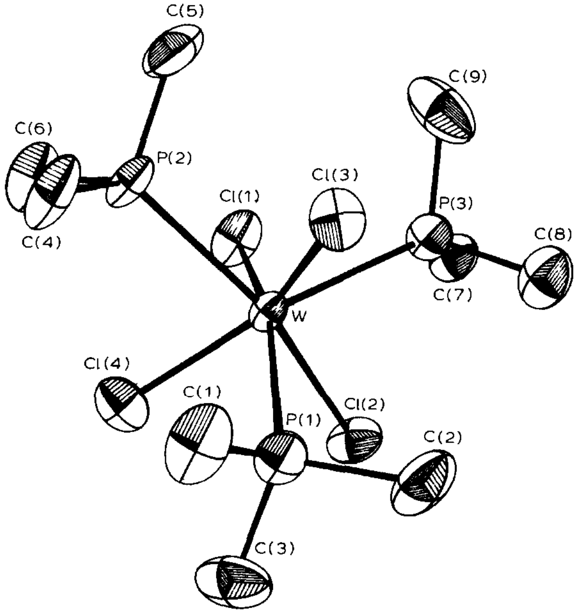


Fig. 1. Molecular structure and atom labeling scheme for $WCl_4(PMe_3)_3$. The atoms are represented by their 50% probability ellipsoids for thermal motion.

0.03 Å longer at 2.417(5) Å than the average of the other three W–Cl separations (2.45(3) Å). This was observed in both $[MoCl_4(PMe_2Ph)_3]\cdot EtOH$ [5] and $MoBr_4(PMe_2Ph)_3$ [6].

It is interesting to note a distortion in the C_{3v} symmetry involving a chlorine in the uncapped face (Cl(4)) not observed in the two similar structures previously determined. The W–Cl(4) distance, 2.416(5) Å is shorter than observed for the other two chlorines in the uncapped face (average 2.46(1) Å). The corresponding Cl(4)–W–P(3) angle, 153.0(2)°, and W–P(3) bond distance, 2.548(5) Å, are significantly different than the averages for the other Cl(uncapped face)–W–P(*trans*) angles (161(1)°) and W–P distances (2.552(1) Å). In one of the alternative C_{2v} models, Cl(4) would be the capping atom in a trigonal prismatic polyhedron. Perhaps these differences are the result of a slight distortion of the C_{3v} model toward the C_{2v} model.

Reduction of $MoCl_4(PMe_3)_3$

The complex $MoCl_4(PMe_3)_3$ is a useful starting material for the synthesis of a number of trimethylphosphine derivatives of molybdenum in oxidation states four

TABLE 1

BOND DISTANCES (Å) AND ANGLES (°) FOR $WCl_4(PMe_3)_3$

Atoms	Distance	Atoms	Distance
W–Cl(1)	2.450(5)	W–Cl(2)	2.470(5)
W–Cl(3)	2.417(5)	W–Cl(4)	2.416(5)
W–P(1)	2.552(5)	W–P(2)	2.553(5)
W–P(3)	2.548(5)	P(1)–C(1)	1.83(2)
P(1)–C(2)	1.81(2)	P(1)–C(3)	1.80(2)
P(2)–C(4)	1.82(2)	P(2)–C(5)	1.80(2)
P(2)–C(6)	1.79(2)	P(3)–C(7)	1.84(2)
P(3)–C(8)	1.83(2)	P(3)–C(9)	1.76(3)
Atoms	Angle	Atoms	Angle
Cl(1)–W–Cl(2)	91.1(2)	Cl(1)–W–Cl(3)	125.0(2)
Cl(2)–W–Cl(3)	123.4(2)	Cl(1)–W–Cl(4)	85.1(2)
Cl(2)–W–Cl(4)	85.9(2)	Cl(3)–W–Cl(4)	133.0(2)
Cl(1)–W–P(1)	160.0(2)	Cl(2)–W–P(1)	76.5(2)
Cl(3)–W–P(1)	75.0(2)	Cl(4)–W–P(1)	78.4(2)
Cl(1)–W–P(2)	77.7(2)	Cl(2)–W–P(2)	161.9(2)
Cl(3)–W–P(2)	74.6(2)	Cl(4)–W–P(2)	79.0(2)
P(1)–W–P(2)	109.8(2)	Cl(1)–W–P(3)	75.6(2)
Cl(2)–W–P(3)	75.8(2)	Cl(3)–W–P(3)	74.1(2)
Cl(4)–W–P(3)	153.0(2)	P(1)–W–P(3)	115.4(2)
P(2)–W–P(3)	114.2(2)	W–P(1)–C(1)	116.4(7)
W–P(1)–C(2)	112.1(7)	C(1)–P(1)–C(2)	104(1)
W–P(1)–C(3)	115.6(8)	C(1)–P(1)–C(3)	102(1)
C(2)–P(1)–C(3)	106(1)	W–P(2)–C(4)	115.4(7)
W–P(2)–C(5)	114.6(7)	C(4)–P(2)–C(5)	105(1)
W–P(2)–C(6)	118.0(8)	C(4)–P(2)–C(6)	102(1)
C(5)–P(2)–C(6)	100(1)	W–P(3)–C(7)	117.3(7)
W–P(3)–C(8)	114.2(7)	C(7)–P(3)–C(8)	103.5(9)
W–P(3)–C(9)	116.8(8)	C(7)–P(3)–C(9)	101(1)
C(8)–P(3)–C(9)	101(1)		

and lower (Scheme 1). Reduction with 1 equivalent of sodium amalgam in THF, at 20 °C, yields $MoCl_3(PMe_3)_3$, [8], while in the presence of 2 equivalents of Na/Hg, *trans*-$MoCl_2(PMe_3)_4$ is obtained [9]. This behavior is similar to that displayed by $WCl_4(PMe_3)_3$ [2]. In an attempt to carry out the synthesis of hydride complexes of molybdenum containing trimethylphosphine as coligand [10], we reacted a suspension of $MoCl_4(PMe_3)_3$ in ethanol with an excess of $NaBH_4$. Instead of the expected polyhydride, we obtained a blue, crystalline complex, identified as $MoH(BH_4)(PMe_3)_4$, by comparison of its IR and NMR spectra with those of an authentic sample [8].

Of more interest are the reductions of $MoCl_4(PMe_3)_3$ to Mo^0 species. We have recently prepared the dinitrogen complex *cis*-$Mo(N_2)_2(PMe_3)_4$, by reduction of $MoCl_3(PMe_3)_3$ with dispersed sodium under dinitrogen [11]. The reduction of $MoCl_4(PMe_3)_3$ to the dinitrogen complex takes place under similar conditions (eq. 2) and with comparable or somewhat better yield than the original procedure,

$$MoCl_4(PMe_3)_3 \xrightarrow[\text{PMe}_3\text{, THF}]{\text{Na dispers., N}_2} cis\text{-}Mo(N_2)_2(PMe_3)_4 \qquad (2)$$

although it suffers from the disadvantage that, owing to the low solubility of both $MoCl_4(PMe_3)_3$ and sodium metal in THF, larger volumes of solvent and longer reaction periods are required (see Experimental).

The bis(ethylene) complex, *trans*-$Mo(C_2H_4)_2(PMe_3)_4$, originally prepared [11] by ethylene displacement of the coordinated dinitrogen molecules in *cis*-$Mo(N_2)_2(PMe_3)_4$, can be conveniently obtained from $MoCl_4(PMe_3)_3$. Treatment of a suspension of the latter complex in THF with an excess of sodium amalgam, under ethylene, produces reduction to $MoCl_3(PMe_3)_3$ and subsequent formation of a grey-greenish solution. Addition at this stage of ca. 0.8 equivalent of PMe_3 and further stirring at room temperature for a period of 3–4 h provides, after work-up, white crystals of *trans*-$Mo(C_2H_4)_2(PMe_3)_4$ in good yields (eq. 3).

$$MoCl_4(PMe_3)_3 + Na/Hg \xrightarrow[\text{THF}]{C_2H_4\text{,}PMe_3} trans\text{-}Mo(C_2H_4)_2(PMe_3)_4 \qquad (3)$$

This one-pot synthesis is obviously more straightforward and convenient than the one previously described [11], since it avoids prior formation of the dinitrogen complex.

The facility with which the above reactions take place, prompted us to attempt the preparation of the recently described CO_2 complex, *trans*-$Mo(CO_2)_2(PMe_3)_4$ [12] by the direct reduction of $MoCl_4(PMe_3)_3$ under an atmosphere of carbon dioxide. Unfortunately, the reaction of $MoCl_4(PMe_3)_3$ and Na/Hg, under CO_2, is complex and affords only very small yields of $Mo(CO_2)_2(PMe_3)_4$ (ca. 3%). *trans*-$MoCl_2(PMe_3)_4$ and *cis*-$Mo(CO)_2(PMe_3)_4$ are also formed in this reaction.

Synthesis and X-ray structure of $MoO(acac)_2PMe_3$

Oxomolybdenum(IV) complexes can be obtained by different synthetic methods which include oxygen abstraction by phosphine from dioxomolybdenum(VI) complexes [13], reaction of a high oxidation state molybdenum halide with alcohol in the presence of the appropriate ligand [13,14], and ligand addition or displacement reaction of oxomolybdenum(IV) complexes [13–16]. As an extension of our earlier work on oxotungsten(IV) and oxomolybdenum(IV) complexes [3,17], we have now prepared the acetylacetonate complex, $MoO(acac)_2PMe_3$, by the two step sequence of eq. 4. The new compound can be isolated as black, well formed crystals, very soluble in hydrocarbon and ether solvents. The IR spectrum of this complex shows broad bands at 1580 and 1500 cm^{-1} due to vibrations derived from the acac ligands, and a strong absorption at 940 cm^{-1} corresponding to coordinated PMe_3, with a shoulder at ca. 960 cm^{-1} possibly due to ν(Mo=O). The ^1H NMR (C_6D_6, 35 °C) shows only three resonances for the acac methyl protons (δ 2.6, 2.2, 1.9 ppm) due to accidental degeneracy of two CH_3 groups, but in $(CD_3)_2CO$ the four resonances are clearly observed at 2.5, 2.0, 1.9 and 1.8 ppm.

$$MoCl_4(PMe_3)_3 \xrightarrow[PMe_3]{H_2O} MoOCl_2(PMe_3)_3 \xrightarrow{Tl(acac)} MoO(acac)_2PMe_3 \qquad (4)$$

The molecular structure and atom labeling scheme for $MoO(acac)_2PMe_3$ are presented in Fig. 2. The molybdenum resides in a distorted-octahedral environment with the oxo and phosphine ligands *cis* to each other and *trans* to one oxygen each of an acac moiety.

The bonding in this compound appears normal. The Mo–O(5) oxo bond distance 1.676(5) Å, (Table 2) is very near the 1.70 Å found for monooxo Mo^{IV} complexes [4b]. Most Mo–P bond lengths range from 2.3–2.6 Å but cluster around 2.47 Å [18] and the Mo–P distance of 2.468(2) Å found in the title compound is in good agreement with this.

As expected the Mo–O(2) distance *trans* to the oxo ligand (2.168(5) Å) is longer than the average of the other three Mo–O separations (2.10(4) Å). In the Mo^{VI} compound, $MoO_2(acac)_2$ [19], the Mo–O distances *trans* to the oxo groups averaged 2.20(1) Å while the other Mo–O bond lengths averaged 1.98(1) Å. Mo–O separations of 2.071 Å were found in the Mo^{III} complex, $Mo(acac)_3$ [20].

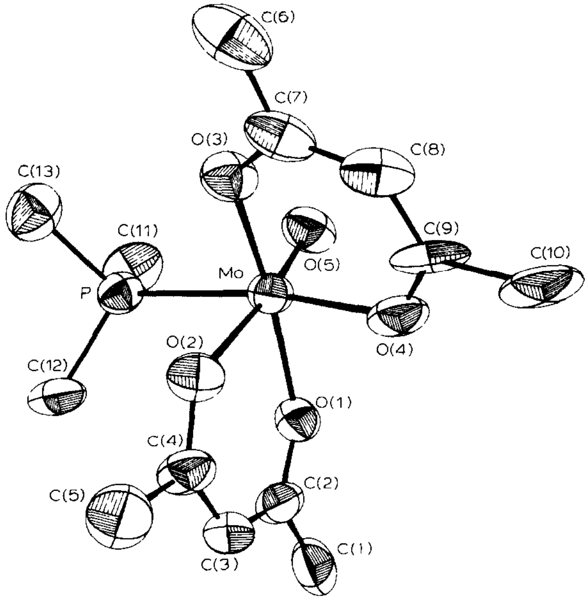


Fig. 2. Molecular structure of $MoO(acac)_2PMe_3$.

The rest of the bonding in the acac ligands also appears normal. The C–O, C–CH and C–CH_3 distances average 1.285(7), 1.38(1), and 1.50(1) Å, respectively.

Experimental

Microanalysis were by Pascher Microanalytical Laboratory, Bonn. The IR spectra were recorded on a Perkin–Elmer model 577, in Nujol mulls. ^1H NMR spectra were taken at 60 MHz on a Perkin–Elmer R-12B. All preparations and other operations were carried out under oxygen-free nitrogen following conventional Schlenk techniques. Solvents were dried and degassed before use. The compound $MoCl_4(THF)_2$ was prepared as described in the literature [21] and the ligand PMe_3 was obtained by the method of Wolfsberger and Schmidbaur [22].

Preparation of $MoCl_4(PMe_3)_3$

To a magnetically stirred suspension of $MoCl_4(THF)_2$ (3 g, ca. 8 mmol) in THF

TABLE 2

BOND DISTANCES (Å) AND ANGLES (°) FOR $MoO(acac)_2PMe_3$

Atoms	Distance	Atoms	Distance
Mo–O(1)	2.053(4)	Mo–O(2)	2.168(5)
Mo–O(3)	2.109(5)	Mo–O(4)	2.132(5)
Mo–O(5)	1.676(5)	Mo–P	2.468(2)
O(1)–C(2)	1.285(8)	O(2)–C(4)	1.290(8)
O(3)–C(7)	1.276(8)	O(4)–C(9)	1.29(1)
C(1)–C(2)	1.51(1)	C(2)–C(3)	1.39(1)
C(3)–C(4)	1.37(1)	C(4)–C(5)	1.479(9)
C(6)–C(7)	1.51(1)	C(7)–C(8)	1.38(1)
C(8)–C(9)	1.38(1)	C(9)–C(10)	1.52(1)
C(11)–P	1.799(7)	C(12)–P	1.819(8)
C(13)–P	1.803(7)		
Atoms	**Angle**	**Atoms**	**Angle**
O(1)–Mo–O(2)	81.9(2)	O(1)–Mo–O(3)	161.9(2)
O(2)–Mo–O(3)	80.6(2)	O(1)–Mo–O(4)	84.7(2)
O(2)–Mo–O(4)	83.3(2)	O(3)–Mo–O(4)	88.6(2)
O(1)–Mo–O(5)	101.8(2)	O(2)–Mo–O(5)	173.0(2)
O(3)–Mo–O(5)	96.0(2)	O(4)–Mo–O(5)	102.9(2)
O(1)–Mo–P	91.7(1)	O(2)–Mo–P	83.9(1)
O(3)–Mo–P	91.2(1)	O(4)–Mo–P	167.0(1)
O(5)–Mo–P	90.0(2)	Mo–O(1)–C(2)	133.4(5)
Mo–O(2)–C(4)	130.8(5)	Mo–O(3)–C(7)	125.9(5)
Mo–O(4)–C(9)	123.8(5)	O(1)–C(2)–C(1)	113.2(7)
O(1)–C(2)–C(3)	124.6(7)	C(1)–C(2)–C(3)	122.2(7)
C(2)–C(3)–C(4)	125.6(7)	O(2)–C(4)–C(3)	123.7(6)
O(2)–C(4)–C(5)	116.1(7)	C(3)–C(4)–C(5)	120.2(7)
O(3)–C(7)–C(6)	114.4(8)	O(3)–C(7)–C(8)	126.1(8)
C(6)–C(7)–C(8)	119.6(8)	C(7)–C(8)–C(9)	128.4(8)
O(4)–C(9)–C(8)	127.1(7)	O(4)–C(9)–C(10)	113.2(9)
C(8)–C(9)–C(10)	119.7(9)	Mo–P–C(11)	113.2(3)
Mo–P–C(12)	115.7(2)	C(11)–P–C(12)	105.0(4)
Mo–P–C(13)	116.5(3)	C(11)–P–C(13)	102.7(4)
C(12)–P–C(13)	102.1(4)		

(100 ml), PMe_3 (2.4 ml, ca. 24 mmol) was slowly added, and the mixture stirred for 2–3 h at room temperature. The resulting dark red solution was filtered and the solid $MoCl_4(PMe_3)_3$ extracted with 40 ml of THF and 2 × 20 ml of CH_2Cl_2. The combined filtrates were partially evaporated in vacuo and then cooled at −25 °C for 24 h to afford the title complex as dark red-purple microcrystals (2 g, 55%). The reaction can also be carried out in dry CH_2Cl_2 with similar yield. $MoCl_4(PMe_3)_3$ is soluble in CH_2Cl_2 and sparingly soluble in THF. Anal. Found: C, 23.0; H, 5.8. $MoC_9H_{27}Cl_4P_3$ calcd.: C, 23.1; H, 5.8%. IR (Nujol) 1415m, 1290m, 1270s, 945s, 845m, 730s, 665m, cm^{-1}. ^1H NMR (CH_2Cl_2) δ (ppm) −17 brs.

Reduction of $MoCl_4(PMe_3)_3$

(a) With sodium amalgam. A stirred suspension of $MoCl_4(PMe_3)_3$ (0.94 g, 2 mmol) in THF (45 ml) was reacted with sodium amalgam (1%, 11 g, 4 mmol Na) and PMe_3 (0.2 ml, 2 mmol) under argon. After 2 h of stirring, the solution was decanted and centrifuged and the solvent removed in vacuo until crystallization began. Cooling at −20 °C overnight afforded yellow crystals of *trans*-$MoCl_2(PMe_3)_4$. Further crystallization of the mother liquor afforded two more crops of crystals (total yield 0.64 g, 65%). If the reduction is carried out using 1 equivalent of sodium, $MoCl_3(PMe_3)_3$ is obtained.

(b) With $NaBH_4$. $MoCl_4(PMe_3)_3$ (1.4 g, 3 mmol), PMe_3 (0.3 ml, 3 mmol) and an excess of $NaBH_4$ (1 g) were stirred in 50 ml of ethanol, at room temperature for 2 h. The mixture was then taken to dryness and the resulting violet residue extracted with 100 ml of diethyl ether. Centrifugation, partial removal of the solvent until incipient crystallization and cooling at −20 °C overnight afforded blue-violet crystals of $MoH(BH_4)(PMe_3)_4$ in ca. 45% yield.

(c) Dispersed Na under N_2. $MoCl_4(PMe_3)_3$ (2.8 g, 6 mmol) was added to a vigorously stirred suspension of dispersed sodium (ca. 1.15 g, 50 mmol, prepared from commercial 40% dispersion in mineral oil) in THF (200 ml) under N_2. After stirring for 2–3 h all the $MoCl_4(PMe_3)_3$ had been taken into solution and the color became first brown and then very dark red. This suspension was stirred for another 30–40 min, during which time a green color, that quickly faded, developed. 0.4 ml of PMe_3 (4 mmol) was then added and the mixture stirred overnight under dinitrogen. The resulting solution was centrifuged, the solvent removed in vacuo, and the residue extracted with petroleum ether (60 ml). Centrifugation, partial removal of the solvent in vacuo, and cooling at −30 °C overnight afforded yellow crystals of *cis*-$Mo(N_2)_2(PMe_3)_4$. The total yield from this and subsequent crystallizations of the mother liquor was 1.4 g, ca. 60% (referred to PMe_3). The reduction can be carried out directly from $MoCl_4(THF)_2$ as follows: $MoCl_4(THF)_2$ (3.85 g, 10 mmol) and PMe_3 (3 ml, 30 mmol) were stirred at room temperature in 100 ml of THF for ca. 2 h. The solid $MoCl_4(PMe_3)_3$ was filtered off, washed with 2 × 30 ml of THF, and then suspended into 200 ml of THF. The reaction was continued as above to finally yield ca. 1.45 g of the dinitrogen complex (35% yield referred to PMe_3).

(d) Sodium amalgam under C_2H_4. Synthesis of trans-$Mo(C_2H_4)_2(PMe_3)_4$. To a suspension of 0.9 g of amalgamated (1%) sodium in ethylene saturated THF (90 ml) was added 2.8 g of $MoCl_4(PMe_3)_3$ (6 mmol). The mixture was stirred at room temperature under an atmosphere of ethylene until all the $MoCl_4(PMe_3)_3$ had been taken into solution and the color changed to grey-greenish. Approximately 25 min after the appearance of the green color 0.4 ml (4 mmol) of PMe_3 were added and the

mixture further stirred at room temperature for 4–5 h. The suspension was then centrifuged and the solution evaporated to dryness. White crystals of the ethylene complex were obtained (1.55 g, 60% yield) after extraction with 35–40 ml of petroleum ether, centrifugation, partial removal of the solvent and cooling at −30 °C overnight. This complex can also be obtained in a one-pot synthesis from $MoCl_4(THF)_2$ (3.82 g, 10 mmol), as described above for the dinitrogen compound. The resulting $MoCl_4(PMe_3)_3$ was suspended in 80 ml of THF and the suspension transfered into a flask containing sodium amalgam (1%, 0.9 g of sodium, ca. 40 mmol) and 20 ml of THF (yield 2.2 g, 55%).

Preparation of $MoO(acac)_2(PMe_3)$

PMe_3 (0.2 ml, 2 mmol) and H_2O (ca. 1 mmol) were added to a suspension of $MoCl_4(PMe_3)_3$ (0.48 g, 1 mmol) in 50 ml of THF. The mixture was stirred at 50–60 °C overnight and the resulting suspension evaporated to dryness. The green residue was crystallized from ethanol, to yield 0.33 g of $MoOCl_2(PMe_3)_3$ (80%). $MoOCl_2(PMe_3)_3$ was characterized by comparison of its properties (color, solubility, and particulary IR and ^1H NMR) with those of an authentic sample [17]. 0.33 g of $MoOCl_2(PMe_3)_3$ (ca. 0.8 mmol) and Tl(acac) (0.7 g excess) were stirred at room temperature in 40 ml of THF for ca. 12–14 h. The solvent was then removed under vacuo and the residue extracted with 30 ml of Et_2O. After centrifugation, the solvent was again evaporated under vacuum and the residue disolved in 30 ml of a 2/1 mixture of petroleum/diethyl ether. Centrifugation, concentration to ca. 15 ml and cooling at −25 °C for 7–10 days afforded black crystals of the title compound in low yields (20–25%). Crystallization of this complex is difficult and in several more attempted reactions only one further crop of crystals could be obtained. In those cases in which crystallization proved difficult, removal of the solvent in vacuo produced a black residue displaying IR bands identical to those of the pure crystals. Anal. Found: C, 40.4; H, 6.0. $MoC_{13}H_{23}PO_5$ calcd.: C, 40.4; H, 6.0%. IR (Nujol) 3040w, 1560s, 1500s, 960sh, 940s, cm^{-1}. ^1H NMR (CD_3COCD_3): δ (ppm) 5.6 and 5.4 (s, 1, acac-CH), 2.5, 2.0, 1.9 and 1.8 (s, 3, acac-CH_3) and 1.17 (d, 9, PMe_3, J(PH) 8 Hz).

X-ray data collection, structure determination, and refinement for $WCl_4(PMe_3)_3$

Single crystals of the air-sensitive compound were sealed under N_2 in thin-walled glass capillaries. Final lattice parameters as determined from a least-squares refinement of $((\sin\theta)/\lambda)^2$ values for 15 reflections ($\theta > 20°$) accurately centered on the diffractometer are given in Table 3. The space group was uniquely determined as $P2_1/c$ from the systematic absences in $0k0$ for $k = 2n + 1$ and in $h0l$ for $l = 2n + 1$.

Data were collected on an Enraf-Nonius CAD-4 diffractometer by the θ–2θ scan technique. The method has been previously described [23]. A summary of data collection parameters is given in Table 3. The intensities were corrected for Lorentz and polarization effects, and for absorption.

Calculations were carried out with the SHELX system of computer programs [24]. Neutral atom scattering factors for W, Cl, P and C were taken from Cromer and Waber [25], and the scattering for tungsten was corrected for the real and imaginary components of anomalous dispersion using the table of Cromer and Liberman [26]. Scattering factors for H were from ref. 27.

The position of the tungsten atom was revealed by the inspection of a Patterson map. A difference Fourier map phased on the tungsten atom readily revealed the positions of the nonhydrogen atoms. Least-squares refinement with isotropic thermal parameters led to $R = \Sigma||F_0| - F_c||/\Sigma|F_0| = 0.071$. The methyl hydrogen atoms were located with the aid of a difference Fourier map and their parameters were not refined. Refinement of the nonhydrogen atoms with anisotropic temperature factors led to final values of $R = 0.040$ and $R_w = 0.041$. A final difference Fourier showed no feature greater than 0.3 e^- $Å^{-3}$. The weighting scheme was based on unit weights; no systematic variation of $w(|F_0| - |F_c|)$ vs. $|F_0|$ or $(\sin\theta)/\lambda$ was noted. The final values of the positional parameters are given in Table 4 [28].

X-ray data collection, structure determination, and refinement for MoO(acac)$_2$PMe$_3$

Single crystals of the compound, were sealed in thin-walled glass capillaries prior to X-ray examination. Final lattice parameters as determined from a least-squares refinement of the angular settings of 25 reflections ($\theta > 20°$) accurately centered on the diffractometer are given in Table 3.

Data were collected as described for the previous compound. The intensities were corrected for Lorentz and polarization effects, but not for absorption. Neutral-atom scattering factors were obtained as noted above, and that of molybdenum was corrected for the real and imaginary components of anomalous dispersion.

The position of the molybdenum atom was revealed by inspection of a Patterson map, and the subsequent calculation of a difference Fourier map allowed the

TABLE 3

CRYSTAL DATA AND SUMMARY OF INTENSITY DATA COLLECTION AND STRUCTURE REFINEMENT

Compound	$WCl_4(PMe_3)_3$	MoO(acac)$_2$PMe$_3$
Mol wt.	553.9	382.2
Space group	$P2_1/c$	$P2_1/c$
Cell constants		
a (Å)	14.835(4)	14.155(6)
b (Å)	11.422(2)	9.984(4)
c (Å)	11.568(3)	12.629(11)
β (deg)	91.92(2)	98.80(5)
V (Å^3)	1959.0	1763.7
Molecules/unit cell	4	4
ρ(calc) (g cm^{-3})	1.88	1.44
μ(calc) (cm^{-1})	70.08	8.39
Radiation	Mo-K_α	Mo-K_α
Max crystal dimensions (mm)	0.55 × 0.58 × 0.58	0.20 × 0.36 × 0.57
Scan width	$0.80 + 0.20 \tan\theta$	$0.80 + 0.20 \tan\theta$
Standard reflections	(10,0,0) (0,0,4) (0,8,0)	(0, −2,0) (0,0,8) (4,0,0)
Decay of standards	±2%	±1%
Reflections measured	2495	2308
2θ range	≤ 42°	≤ 44°
Reflections collected	1613	1332
No. of parameters varied	154	181
GOF	5.30	1.64
R	0.040	0.026
R_w	0.051	0.033

location of the remaining nonhydrogen atoms. Refinement with isotropic thermal parameters led to a reliability index of $R = 0.091$. The hydrogen atoms were located with the aid of a difference Fourier map and were not refined. Refinement of the nonhydrogen atoms with anisotropic temperature factors led to final values of $R = 0.026$ and $R_w = 0.033$. A final difference Fourier showed no feature greater than 0.3 $e^- \text{Å}^{-3}$. The weighting scheme was based on unit weights; no systematic

TABLE 4

FINAL FRACTIONAL COORDINATES FOR $WCl_4(PMe_3)_3$

Atom	x/a	y/b	z/c
W	0.25706(5)	0.48108(5)	0.28069(7)
Cl(1)	0.3765(3)	0.6260(4)	0.3171(5)
Cl(2)	0.1420(3)	0.6184(4)	0.3497(5)
Cl(3)	0.2378(4)	0.3664(4)	0.1060(5)
Cl(4)	0.2818(4)	0.4292(5)	0.4817(4)
P(1)	0.1216(4)	0.3495(4)	0.3153(5)
P(2)	0.3997(3)	0.3571(4)	0.2704(5)
P(3)	0.2364(4)	0.6281(4)	0.1163(5)
C(1)	0.140(1)	0.192(2)	0.303(2)
C(2)	0.029(1)	0.377(2)	0.213(2)
C(3)	0.074(2)	0.361(2)	0.456(2)
C(4)	0.383(1)	0.199(2)	0.278(2)
C(5)	0.463(1)	0.379(2)	0.142(2)
C(6)	0.487(2)	0.379(2)	0.379(2)
C(7)	0.241(1)	0.784(2)	0.154(2)
C(8)	0.129(1)	0.614(2)	0.035(2)
C(9)	0.314(2)	0.621(2)	0.005(2)
H(1)[C(1)]	0.0900	0.1420	0.3152
H(2)[C(1)]	0.2048	0.1741	0.3399
H(3)[C(1)]	0.1482	0.1653	0.2189
H(4)[C(2)]	0.0516	0.3621	0.1223
H(5)[C(2)]	0.0014	0.4506	0.2025
H(6)[C(2)]	−0.0364	0.3534	0.2341
H(7)[C(3)]	0.0600	0.4411	0.4648
H(8)[C(3)]	0.1237	0.2953	0.5080
H(9)[C(3)]	0.0164	0.3312	0.4893
H(10)[C(4)]	0.4454	0.1590	0.2722
H(11)[C(4)]	0.3375	0.1672	0.3516
H(12)[C(4)]	0.3189	0.1727	0.2257
H(13)[C(5)]	0.4787	0.4755	0.1249
H(14)[C(5)]	0.5214	0.3302	0.1497
H(15)[C(5)]	0.4237	0.3511	0.0705
H(16)[C(6)]	0.4576	0.3625	0.4527
H(17)[C(6)]	0.5287	0.3167	0.3938
H(18)[C(6)]	0.5257	0.4501	0.3700
H(19)[C(7)]	0.2884	0.7799	0.2183
H(20)[C(7)]	0.2319	0.8137	0.0606
H(21)[C(7)]	0.2068	0.8476	0.1943
H(22)[C(8)]	0.1342	0.5402	−0.0155
H(23)[C(8)]	0.0792	0.6224	0.0809
H(24)[C(8)]	0.1172	0.6820	−0.0223
H(25)[C(9)]	0.3183	0.5593	−0.0318
H(26)[C(9)]	0.3047	0.7015	−0.0428
H(27)[C(9)]	0.3802	0.6195	0.0404

variation of $w(|F_0|-|F_c|)$ vs. $|F_0|$ or $(\sin\theta)/\lambda$ was noted. The final values of the positional parameters are given in Table 4 [28].

Acknowledgement

We gratefully acknowledge concession of a research grant (A.G.) from the Spanish Ministerio de Educacion y Ciencia, generous financial support (to E.C.) by

TABLE 5

FINAL FRACTIONAL COORDINATES FOR MoO(acac)$_2$PMe$_3$

Atom	x/a	y/b	z/c
Mo	0.20222(4)	0.38982(6)	0.01888(5)
P	0.0920(1)	0.2628(2)	0.1148(1)
O(1)	0.2440(3)	0.2187(5)	−0.0512(3)
O(2)	0.3098(3)	0.3237(5)	0.1494(3)
O(3)	0.1998(3)	0.5541(5)	0.1235(4)
O(4)	0.3217(3)	0.4793(6)	−0.0380(4)
O(5)	0.1097(3)	0.4404(5)	−0.0712(4)
C(1)	0.3109(6)	0.0197(8)	−0.1032(6)
C(2)	0.3071(6)	0.1286(7)	−0.0208(6)
C(3)	0.3664(5)	0.1278(8)	0.0777(6)
C(4)	0.3656(5)	0.2210(8)	0.1575(6)
C(5)	0.4300(5)	0.2055(9)	0.2607(6)
C(6)	0.2323(7)	0.7623(8)	0.2063(6)
C(7)	0.2532(6)	0.6575(8)	0.1274(6)
C(8)	0.3249(6)	0.6794(8)	0.0667(7)
C(9)	0.3549(5)	0.597(1)	−0.0089(7)
C(10)	0.4358(6)	0.6416(9)	−0.0677(7)
C(11)	−0.0201(5)	0.2247(9)	0.0326(6)
C(12)	0.1365(6)	0.1027(8)	0.1702(6)
C(13)	0.0552(6)	0.3436(8)	0.2295(6)
H(1)	0.3052	0.0366	−0.1766
H(2)	0.2508	−0.0431	−0.0966
H(3)	0.3809	−0.0274	−0.0850
H(4)	0.4196	0.0456	0.0960
H(5)	0.3917	0.1979	0.3100
H(6)	0.4765	0.2866	0.2733
H(7)	0.4761	0.1238	0.2617
H(8)	0.2691	0.8541	0.2021
H(9)	0.2590	0.7223	0.2703
H(10)	0.1532	0.7774	0.2002
H(11)	0.3676	0.7730	0.0820
H(12)	0.4516	0.5789	−0.1208
H(13)	0.5047	0.6561	−0.0237
H(14)	0.4104	0.7284	−0.0983
H(15)	−0.0507	0.3020	−0.0072
H(16)	−0.0770	0.1893	0.0680
H(17)	0.0004	0.1539	−0.0111
H(18)	0.1400	0.0646	0.1042
H(19)	0.0826	0.0581	0.2046
H(20)	0.2072	0.1064	0.2130
H(21)	0.1075	0.3622	0.2866
H(22)	0.0003	0.2833	0.2511
H(23)	0.0215	0.4317	0.2092

the Comision Asesora de Investigacion Cientifica y Tecnica, CAICYT, and support (to J.L.A.) from the U.S. National Science Foundation.

Supplementary material available: Tables of thermal parameters and observed and calculated structure factors for both compounds (21 pages) are available from NAPS % Microfiche Publications, P.O. Box 3513, Grand Central Station, New York, NY 10163, NAPS document no. 04237.

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28 See paragraph at the end of paper regarding supplementary material.