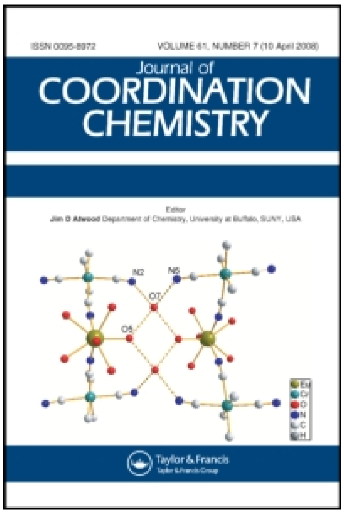

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OXOHALIDE COMPLEXES OF MOLYBDENUM AND TUNGSTEN WITH OXYGEN DONOR LIGANDS

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Molybdenum(V) and (VI) and tungsten (VI) complexes of formulae $MoOX_3$.RPPh, MO_2X_2.RPPh and MoO_2X_2.RPOEt, where RPPh = bis[(diphenylphosphinyl)methyl]phenylphosphine oxide and RPOEt = bis[(diphenylphosphinyl)methyl]ethyl phosphinate, M = Mo or W and X = Cl, Br or I, have been isolated. Molar conductance, magnetic susceptibility, IR, electronic, ^{1}H and ^{31}P NMR measurements are discussed. All the complexes isolated have octahedral geometry in which the potentially terdentate ligands are coordinated to the metal through two P=O groups.

Keywords: Molybdenum, tungsten, oxohalides, phosphine oxides

INTRODUCTION

The coordination chemistry of the group VI elements is dominated by the formation and stability of oxo-species in the +5 and +6 oxidation states. Current interest in these complexes derives mainly from their involvement in a variety of industrial and biological oxidation processes.[1,2] There is a remarkable number of reports on molybdenum and tungsten oxohalide complexes including different types of ligands, particularly those with nitrogen and oxygen donor atoms.[3-12] Regarding phosphine oxide ligands, however, investigations are mostly confined to thoroughly explored triphenylphosphine oxide (TPPO) compounds.[3,13-19] There have been only rare oxohalide complexes reported containing other phosphoryl oxygen ligands, such as $P[N(CH_3)_2]_3O$,[20] $(i\text{-}C_3H_7O)_2P(O)CH_2C(O)N(C_2H_5)_2$ {DiPDECMP},[21] $(C_6H_5)_2P(O)CH_2CH_2P(O)(C_6H_5)_2$ {EDPO}[13] or $(C_2H_5)_2PCH_2CH_2P(O)(C_2H_5)_2$,[22] where the two latter ligands were formed by an adventitious reaction with oxygen.

As a part of an integrated study of complexing properties of organophosphorus ligands,[23] a series of Mo(V), Mo(VI) and W(VI) oxohalide complexes with some potentially terdentate phosphine oxide ligands has been prepared.

Most of the known oxohalo compounds of molybdenum and tungsten have been prepared from the corresponding metal oxohalide and the ligand. A number of Mo(V) oxohalide complexes, $MoOCl_3$.2L, were formed by reaction of $MoCl_5$ with oxygen donor ligands,[3,9] where, it is thought, $MoCl_5$ abstracts oxygen from the ligand to form $MoOCl_3$, which then reacts with the remaining ligand. In some cases M(V) oxohalide complexes (M = Mo or W) resulted from the reduction of M(VI) species and abstraction of a chlorine atom from $MOCl_4$.[7]

However, following the use of di- and trisubstituted carbonyl complexes of molybdenum and tungsten in the preparation of the 7-coordinate dihalides,

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$M(CO)_3LX_2$,[23] we considered it appropriate to study the halogen oxidation of these zero-valent carbonyls under more extreme conditions, as a direct route to oxo-complexes of high oxidation number. There are only a few reports on oxohalo complexes prepared similarly.[4,13] In this way we also obtained oxoiodide complexes.

EXPERIMENTAL

Materials

The ligands RPPh and RPOEt and their tri- and tetracarbonyl complexes, as starting materials for oxohalo species, were prepared as outlined previously.[23] Molybdenum and tungsten hexacarbonyls, as well as MoO_2Cl_2 and MoO_2Br_2 were used as purchased (JM Alfa Products). Solvents were purified in the usual manner.

Physical measurements

IR spectra were run in KBr pellets or in nujol mulls supported between CsI plates in the region 4000–200 cm^{-1} using a Perkin-Elmer 580B spectrophotometer. Electronic spectra were measured on a Cary 219 spectrophotometer in CH_3CN and CH_2Cl_2 using 1 cm silica cells. ^1H NMR spectra were recorded on a Varian Gemini-300 spectrometer in $CDCl_3$, using TMS as internal standard. ^{31}P NMR, operating at 202 MHz, were measured on a Varian VXR-500S instrument in $CDCl_3$ using 0.1 M H_3PO_4 as an external reference. The measurements were performed with 10 mg of substance dissolved in 0.7 cm^3 of solvent in 5 mm tubes, at ambient temperature. Some ^{31}P NMR spectra were recorded at −40°C.

Conductivity measurements were performed at room temperature on 10^{-3} M nitrobenzene and nitromethane solutions, using a Tacussel conductivity bridge, type Cd 7. Magnetic measurements were carried out at 22°C using the Gouy method with $CuSO_4.5H_2O$ as calibrant.

Preparation of complexes

The complexes were prepared in two different ways. When metal oxohalides (MoO_2Cl_2 and MoO_2Br_2) were used, equimolar amounts of the ligand in CH_2Cl_2 and the appropriate oxohalide dissolved in CH_2Cl_2, to which about 10% of absolute ethanol was added, were mixed together. The reaction mixture was refluxed for several hours under argon, and *n*-heptane used to precipitate the corresponding $MO_2X_2.L$ complex in high yield. When starting from metal(0) carbonyl complexes, these were dissolved or dispersed in a suitable solvent and treated with a certain excess of halogen, under or without a stream of argon. In most cases, oxidation was completed by air-reflux of the reaction mixture. In some cases *n*-heptane was used for precipitation of complexes.

$MoO_2Cl_2.RPPh$

Some 0.060 g of MoO_2Cl_2 (0.30 mmol) dissolved in 4.5 cm^3 of CH_2Cl_2 and 0.5 cm^3 of absolute ethanol was added to the ligand RPPh (0.166 g, 0.30 mmol) dissolved in 3 cm^3 of CH_2Cl_2. The reaction mixture was refluxed under argon for several hours and then allowed to stand overnight. Then *n*-heptane was added in excess and the white precipitate of MoO_2Cl_2.RPPh filtered off, washed with *n*-heptane and dried over P_2O_5 *in vacuo*. The yield was 90% (0.203 g).

MoO_2Br_2.RPPh

Some 0.147 g (0.20 mmol) of $Mo(CO)_3$(RPPh) was dissolved in 15 cm^3 of CH_2Cl_2 and 0.056 g of bromine (0.35 mmol) in 20 cm^3 of the same solvent was added dropwise. After the reaction mixture was stirred in the cold (~5°C) for several hours, it was warmed to room temperature and *n*-heptane added. The resulting suspension was refluxed in air for one hour and the yellow crystals which separated were filtered off, washed and dried. The yield was 80% (0.135 g). The same complex was also prepared directly from MoO_2Br_2 and RPPh, in a manner analogous to that for MoO_2Br_2.RPOEt, described below.

MoO_2I_2.RPPh

To a solution of 0.147 g of $Mo(CO)_3$(RPPh) (0.20 mmol) in 15 cm^3 of CH_2Cl_2 was added iodine (0.102 g, 0.40 mmol) in CH_2Cl_2 (40 cm^3) with stirring at 0 to 5°C during three hours. After the reaction mixture was stirred for an additional two hours, it was left overnight. The resulting solution was refluxed for a short time, then *n*-heptane was added and the cream coloured precipitate, formed with a yield of 70% (0.140 g), isolated as usual.

$MoOBr_3$.RPPh

To a suspension of 0.147 g (0.20 mmol) of $Mo(CO)_3$(RPPh) in 10 cm^3 of CCl_4, 0.080 g (0.50 mmol) of bromine in 20 cm^3 of the same solvent was added dropwise and the reaction mixture stirred and cooled at 0 to 5°C under argon for several hours. The yellow precipitate was filtered off, washed with a small amount of dry CCl_4 and dried under P_2O_5 *in vacuo*. The yield was 85% (0.154 g).

$MoOI_3$.RPPh

A suspension of the complex $Mo(CO)_3$(RPPh) (0.147 g, 0.20 mmol) in CCl_4 (15 cm^3) was treated with iodine (0.127 g, 0.50 mmol) dissolved in 50 cm^3 of the same solvent, in the course of three hours, under argon. The mixture was cooled to −5°C, stirred for several hours and then left to stand overnight. The orange-yellow precipitate was filtered off, washed with CCl_4 and dried over P_2O_5 *in vacuo*. The yield was 71% (0.150 g).

WO_2Br_2.RPPh

The complex $W(CO)_3$(RPPh) (0.164 g, 0.20 mmol) was suspended in CCl_4 (10 cm^3) and then treated with bromine (0.064 g, 0.40 mmol) dissolved in CCl_4 (10 cm^3), over one hour with stirring and cooling to 10°C. The reaction mixture was allowed to stand overnight. The mixture was then refluxed in air for two hours, the cream coloured precipitate filtered off, washed and dried. The yield was 83% (0.154 g).

WO_2I_2.RPPh

To a solution of $W(CO)_3$(RPPh) (0.164 g, 0.20 mmol) in CH_2Cl_2 (20 cm^3) an excess of iodine (0.102 g, 0.40 mmol) in the same solvent (40 cm^3) was added in the course of three hours. The solution was then air-refluxed for several hours and afterwards the volume reduced by evaporation. After a day, *n*-heptane was added, resulting in the formation of an orange-yellow precipitate with a yield of 0.153 g (75%).

MoO_2Cl_2.RPOEt

A solution of 0.060 g of MoO_2Cl_2 (0.30 mmol) in 4.5 cm^3 of CH_2Cl_2 and 0.5 cm^3 of absolute ethanol was added to the RPOEt ligand (0.157 g, 0.30 mmol) dissolved in 3 cm^3 of CH_2Cl_2 under a stream of dry argon. The reaction mixture was refluxed for two hours, then cooled and allowed to stand overnight. A threefold excess of *n*-heptane was used to precipitate the white solid MoO_2Cl_2.RPOEt. After filtration, this was washed with *n*-heptane and dried over P_2O_5 *in vacuo*. The yield was 0.195 g (90%).

MoO_2Br_2.RPOEt

Some 0.072 g of MoO_2Br_2 (0.25 mmol) was dissolved in a mixture of 10 cm^3 of CH_2Cl_2 and 1 cm^3 of absolute ethanol with heating under argon. The RPOEt ligand (0.130 g, 0.25 mmol) dissolved in 5 cm^3 of CH_2Cl_2 was added, and the reaction mixture refluxed for 4 hours, then allowed to stand overnight. The solution was partially evaporated and an excess of *n*-heptane added. After stirring for one hour, a light-yellow precipitate of MoO_2Br_2.RPOEt was formed with a yield of 88% (0.178 g).

The same complex was also obtained by bromine oxidation of $Mo(CO)_4$(RPOEt). The tetracarbonyl (0.146 g, 0.20 mmol) was dispersed in 10 cm^3 of CCl_4 and an excess of bromine (0.064 g, 0.40 mmol) dissolved in 10 cm^3 of the same solvent added. The reaction mixture was cooled to −10°C and stirred under argon. Next day, the reaction mixture was refluxed for one hour, and the precipitate filtered off, washed with CCl_4 and dried over P_2O_5 *in vacuo*. The yield was 71% (0.115 g).

MoO_2I_2.RPOEt

$Mo(CO)_4$(RPOEt) (0.146 g, 0.20 mmol) was dispersed in *n*-heptane, and iodine (0.089 g, 0.35 mmol) in CCl_4 (35 cm^3) added during two hours. The reaction mixture was refluxed with stirring for several hours, and left overnight. The yellow precipitate of MoO_2I_2.RPOEt was isolated by filtration, washed with *n*-heptane and dried. The yield was 72% (0.130 g).

RESULTS AND DISCUSSION

Preparation and properties

Molybdenum(V) and (VI) and tungsten(VI) complexes of the formulae $MoOX_3$.RPPh, MO_2X_2.RPPh and MoO_2X_2.RPOEt, where RPPh = bis[(diphenylphosphinyl)methyl]phenylphosphine oxide and RPOEt = bis[(diphenylphosphinyl)methyl]ethyl phosphinate, M = Mo or W and X = Cl, Br or I, were isolated. The oxobromide and oxoiodide species were obtained by halogen oxidation of the corresponding tri- and tetracarbonyl complexes.[23] An excess of bromine or iodine was used, followed in most cases by air-reflux of the reaction mixture. The course of the reaction appeared to depend on the solvent, as different products were obtained with RPPh when dichloromethane or CCl_4 were used. Namely, the carbonyl complexes are soluble in CH_2Cl_2 and carbon monoxide is lost spontaneously. After treating with halogen, air-reflux completes the oxidation, yielding in all cases MO_2X_2.L (L = RPPh, RPOEt) species. Mo(V) complexes, however, were isolated only from CCl_4 solutions; the starting carbonyls were dispersed in this solvent and CO molecules are not necessarily removed instantaneously. Because of the large excess of halogen used, it is possible that the ligand itself decomposes to some degree, liberating oxygen. Processes similar to those where an oxygen donor ligand is treated with $MoCl_5$ might have taken place.[3] Otherwise, carbon tetrachloride could contain traces of oxygen to such a degree as favoured the formation of Mo(V) species, and at the same time preventing their hydrolysis.

Dioxodibromo complexes were also prepared by the direct method using MoO_2Br_2 and the corresponding ligand. Detailed analyses showed no differences in the properties of the substances prepared by the two different methods. The oxochloride compounds were prepared by direct reaction of MoO_2Cl_2 and ligands.

Tungsten(V) complexes appeared to be unstable relative to tungsten(VI) species and all attempts to prepare WOX_3.L species by the described methods resulted in the isolation of tungsten(VI) compounds, or a mixture of W(V) and W(VI) species. During the iodine oxidation of $W(CO)_3$(RPPh), on removal of the main product, a small amount of a dark solid remained on the sides of the flask. Its IR spectrum corresponded to that expected for WOI_3.RPPh, but the small amount of material obtained prevented us from analysing it thoroughly.

In the course of the preparation of tungsten oxohalide complexes with RPOEt, removal of the ethyl group from the ligand takes place, as preliminary analyses suggest. In that way, complexes analogous to those obtained with [bis(diphenylphosphinyl)methyl]phosphinic acid (RPOH) resulted. The Mo(V) complexes tend to oxidize, forming a mixture of +5 and +6 oxidation states, if kept in air. The M(VI) species are moderately stable in air, but are better kept under argon.

TABLE I
Analytical data for the complexes.

Complex	Colour	M(%)		P(%)		Cl/Br/I(%)	
		Calc.	Found	Calc.	Found	Calc.	Found
MoO_2Cl_2.RPPh	White	12.7	12.4	12.3	12.4	9.4	9.3
MoO_2Br_2.RPPh	Yellow	11.4	11.2	11.0	10.9	19.0	18.7
MoO_2I_2.RPPh	Cream	10.3	10.2	9.9	10.0	27.1	26.9
$MoOBr_3$.RPPh	Yellow	10.6	10.3	10.3	10.2	26.5	26.6
$MoOI_3$.RPPh	Orange-yellow	9.2	9.0	8.9	8.7	36.4	36.4
WO_2Br_2.RPPh	Cream	19.8	19.4	10.0	9.8	17.2	17.0
WO_2I_2.RPPh	Orange-yellow	18.0	17.7	9.1	8.9	24.8	25.0
MoO_2Cl_2.RPOEt	White	13.3	13.3	12.9	12.7	9.9	9.8
MoO_2Br_2.RPOEt	Light yellow	11.9	11.6	11.5	11.6	19.7	19.5
MoO_2I_2.RPOEt	Yellow	10.6	10.3	10.3	10.1	28.1	27.8

All the new complexes are listed in Table I. Their susceptibilities, conductances and significant electronic, NMR and infrared spectral data are summarized in Tables

II, III and IV. The isolated complexes have low conductivities in nitromethane and nitrobenzene. Those of the bromides and chlorides are insignificant, but the values obtained for the iodide complexes suggest that a small amount of ionization might take a place (Table IV).

Magnetic moments and electronic spectra

The magnetic moments for $MoOBr_3.RPPh$ and $MoOI_3.RPPh$ are close to the spin-only value for the molybdenum ion considered (Table II). As expected, all M(VI) complexes were found to be diamagnetic.

TABLE II

Electronic spectral data[a] and magnetic susceptibilies for Mo(V) complexes.

Complex	λ_{max} (nm)	ε ($M^{-1}cm^{-1}$)	μ_{eff}. (B.M.)
$MoOBr_3.RPPh$	715 439	25 1300	1.68
$MoOI_3.RPPh$	720 435	20 1050	1.74

[a] CH_3CN solution.

The electronic absorption spectra of the two Mo(V) complexes are in quite good agreement with a monomeric octahedral configuration. Visible spectra in CH_2Cl_2 and CH_3CN agree with those reported for other oxohalo Mo(V) complexes,[5,24-26] and consist of two distinct bands at ~440 nm and ~715 nm (Table II). The weak, lower energy band is assigned to the transition b_2^* ($4d_{xy}$, Mo–X Π^*) $\rightarrow e^*(4d_{xz,\,yz}$, MO–O $\Pi^*)$, according to most earlier interpretations. The nature of the electronic transition responsible for the higher energy band is not so straightforward. Most authors ascribe this band to the $b_2^*(4d_{xy}$, Mo–X $\Pi^*) \rightarrow b_1^*(4d_{x^2-y^2}$, Mo–X $\delta^*)$ transition, although other assignments have been proposed.[18,20] In the present case, in regard to its intensity, this transition could also be of the charge transfer type, involving transfer of an electron from a bonding Π orbital associated with the oxygen to either non-bonding or anti-bonding orbitals. Besides strong charge transfer bands, the UV spectra of all the complexes display invariably three or four sharp bands in the narrow region 260–275 nm, due to the presence of phenyl rings.[6,8]

NMR spectra

In the ^1H NMR spectrum of the RPOEt ligand the methyl protons of the OCH_2CH_3 group resonate as a triplet at 0.82 ppm, while the methylene protons adjacent to the electronegative oxygen atom resonate as a quintet at 3.76 ppm. The two pairs of bridging CH_2 protons give a complex multiplet centred at 3.39 ppm. The complexity is due to the non-equivalence of the CH_2 protons as well as coupling with phosphorus atoms. In the spectrum of the RPOEt complex two pairs of CH_2 signals are observed, one shifted downfield and the other upfield from the corresponding multiplet in the spectrum of the ligand. The resonance due to the protons of the ethoxy group shows only minor shift. It is obvious that the bridging CH_2 protons are significantly non-equivalent thus indicating changes of electronic structure and geometry upon coordination.

The methylene protons of the RPPh ligand show a signal of *quasi* triplet appearance centred at 3.80 ppm, with intensities 2:3:2. However, in the spectrum of the MoO_2Cl_2.RPPh complex, this triplet is transformed into two rather broad and well separated signals of approximate intensity ratio 1:1; one is downfield at 4.32 ppm, while the other is upfield at 3.53 ppm. As in the previous case this clearly indicates that coordination of the ligand molecule has occurred. Phenyl proton resonances are not very informative since they give a complex and practically unchanged multiplet between 7 and 8 ppm.[23]

^{31}P NMR spectroscopy gives more direct information concerning the structure and formation of the complexes since phosphorus atoms are incorporated in the ligand backbone. ^{31}P NMR data for ligands and oxochloro complexes are presented in Table III.

TABLE III

^{31}P NMR chemical shifts (δ/ppm),[a] coordination induced shifts (Δ/ppm)[b] and two-bond phosphorus–phosphorus coupling constants [$^2J(P,P)$/Hz].[c]

Compound		P atoms		
		P_A'	P_B	P_A''
RPOEt	δ	25.06	38.55	P_A'
	^2J	10.38(d)	10.38(t)	
MoO_2Cl_2.RPOEt[d]	δ	37.71	47.45	22.92
	Δ	12.65	8.90	−2.14
	^2J	10.99(d)	10.68(t)	10.99(d)
RPPh	δ	26.49	27.84	P_A'
	^2J	12.10(d)	12.50(t)	
MoO_2Cl_2.RPPh[e]	δ	39.12	44.02	23.66
	Δ	12.63	16.18	−2.83
	^2J	15.26(d)	15.26(d)	3.05(d)

[a] In $CDCl_3$ solution. Shifts are referenced to 0.1 M H_3PO_4 as external standard; resolution ±0.6 Hz or ±3 ppb. [b] Difference of ^{31}P shifts between the complex and the ligand. [c] Constants are given as mean values; (d) = doublet, (t) = triplet. [d] Since in the ligands P_A'=O and P_A''=O groups cannot be distinguished we deliberately assign P_A'=O to be the coordinated one. [e] Measured at −40°C.

The ^{31}P proton broadband decoupled spectrum of the RPOEt ligand, $^{31}P\{^1H\}$, shows two signals, a triplet and a doublet of intensity ratio 1:2, centred at 38.55 ppm and 25.06 ppm, respectively (Fig. 1.). The triplet is assigned to the central phosphorus atom of the ligand, P_B, symmetrically linked to two chemically equivalent phosphorus atoms, P_A' and P_A'', two bonds away. Corresponding two-bond P–P coupling amounts to 10.38 Hz. Downfield positioning of the triplet mainly originates from the electronegative oxygen atom directly bound to P_B, which causes deshielding.[27] The upfield doublet, assigned to the equivalent P_A' and P_A'' nuclei coupled with the P_B nucleus, is thus shifted due to ring current effects involving phenyl groups linked to these nuclei.

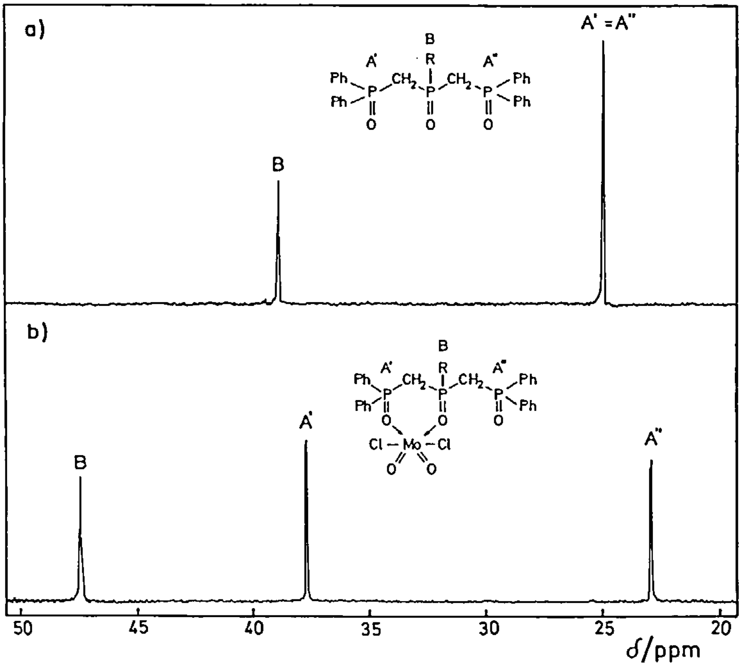

FIGURE 1 $^{31}P\{^1H\}$ NMR spectra of a) RPOEt and b) MoO_2Cl_2.RPOEt.

In the $^{31}P\{^1H\}$ spectra of the MoO_2Cl_2.RPOEt complex, a triplet and two doublets with intensity ratio 1:1:1 is seen (Fig. 1). The coordination of the ligand through two P=O groups removes the chemical equivalence of P_A' and P_A'' giving two well separated doublets instead of the one observed in the ligand itself. ^{31}P chemical shift differences between the complex and the ligand molecule, *i.e.*, coordination induced shifts (Δ/ppm), substantiate coordination through P_B=O and P_A'=O or P_A''=O (see comments in Table III). Accordingly, P_B and P_A' are significantly shifted downfield, 8.90 ppm and 12.65 ppm, respectively. On the contrary, the phosphorus of the uncoordinated P=O group, P_A'', is shifted upfield about 2.0 ppm. The similar values of $^2J(P,P)$ and the same signal multiplicity found for both the RPOEt ligand and its complex indicate rather weak binding between the metal and the ligand at room temperature.

$^{31}P\{^1H\}$ spectra of the RPPh ligand show a triplet and a doublet with intensity ratio 1:2, just like the spectrum of RPOEt. The triplet is centred at 27.84 ppm, the doublet at 26.49 ppm. In comparison with the RPOEt ligand, the P_B triplet of the RPPh ligand is shifted upfield by 10.71 ppm. This is due to ring current effects introduced by substitution of the phenyl group at P_B. The P_A' and P_A'' nuclei show slight deshielding of 1.43 ppm compared to RPOEt, most probably due to small steric rearrangements caused by the presence of the phenyl ring on P_B. A similar argument may be used to explain higher values of $^2J(P,P)$ in RPPh (12.50 Hz) than in RPOEt (10.38 Hz).

The $^{31}P\{^1H\}$ spectrum of the MoO_2Cl_2.RPPh complex shows three rather broad lines at room temperature, indicating some exchange process. At −40°C the spectra consist of three doublets.Two of them, centred at 44.02 ppm and at 39.12 ppm, are well defined, showing splitting of ~15.0 Hz. The third signal, positioned at 23.66 ppm, has splitting of just ~3.0 Hz. The signal intensities relate as 1:1:1. The well defined doublets are assigned to P_A' and P_B of the coordinated phosphoryl groups, assuming that the upfield signal belongs to P_A'. This assumption is based on similar coordination induced shifts for P_A' in both the RPOEt and the RPPh complexes ($\Delta = 12.65$ ppm and 12.63 ppm, respectively), but which here are significantly different for P_B ($\Delta = 8.90$ ppm and 16.18 ppm, respectively). It follows that deshielding of P_B in the RPPh complex is 7.28 ppm greater than in the RPOEt complex, obviously due to different substitution at this atom. Similar shielding for P_A'' (uncoordinated P=O group) in both complexes, *i.e.*, −2.14 ppm in MoO_2Cl_2.RPOEt and −2.83 ppm in MoO_2Cl_2.RPPh, corroborates the assignment as well. The significant changes in signal multiplicities and in magnitudes of $^2J(P,P)$ for the RPPh complex at −40°C is probably the consequence of geometric and electronic changes due to stronger metal–ligand binding at lower temperatures.

Infrared spectra

Details of the infrared spectra of the isolated species are presented in Table IV. Besides the vibrational spectrum of the coordinated ligand with notable lowering of the phosphorus–oxygen stretching frequencies, the most prominent features of the spectra are very strong bands in the region 900–1000 cm^{-1}, ascribed to the multiple metal–oxygen bonds. There is no indication of the existence of any M–O–M linkage, as this would cause absorption at lower energy. The Mo(V) complexes $MoOBr_3$.RPPh and $MoOI_3$.RPPh, possessing a single molybdenyl oxygen, display a strong absorption band at ~980 cm^{-1}, as expected for a compound containing an Mo(V)=O group. The Mo(VI) complexes, containing the MoO_2^{2+} group, absorb at lower frequencies, 910–960 cm^{-1}, since the extent of Π-bonding between molybdenum and any one oxygen is less than in the former case. Two $Mo–O_t$ (t = terminal) bands in virtually all M(VI) compounds (Table IV) is strongly indicative of a *cis*-dioxo structure. Splitting between the two modes ranges from ~40 cm^{-1} in molybdenum complexes to ~55 cm^{-1} in tungsten cases, the symmetric mode being of higher frequency.

TABLE IV
IR spectral[a] and molar conductivity[b] data for the isolated oxohalide complexes.

Complex	ν(P=O) (cm^{-1})	ν($M–O_t$) (cm^{-1})	ν(M–X) (cm^{-1})	Λ_M ($cm^2\,\Omega^{-1}\,mol^{-1}$)
MoO_2Cl_2.RPPh	1166 vs, 1200 sh	952, 911 s	324 m	1.2
MoO_2Br_2.RPPh	1161 vs	950, 909 s	250 m	3.2
MoO_2I_2.RPPh	1161 vs	953, 912 s		9.6
$MoOBr_3$.RPPh	1154 s, 1200 sh	982 vs	255 m	5.0
$MoOI_3$.RPPh	1151 vs	981 vs		9.2
WO_2Br_2.RPPh	1158 vs, 1200 sh	966, 916 s		3.3
WO_2I_2.RPPh	1165 vs	969, 914 s		10.1
MoO_2Cl_2.RPOEt	1176 vs, 1194 sh	952, 911 s	326 m	0.3
MoO_2Br_2.RPOEt	1172 vs, 1192 sh	951, 910 s	251 m	2.9
MoO_2I_2.RPOEt	1164 vs	956, 912 s		8.6

[a] KBr pellets. [b] Nitrobenzene, 10^{-3} M.

It has been noted[28,29] that v(Mo–O$_t$) depends on ligand donor properties for a number of N and O donor ligands. Observed decrease in Mo–O$_t$ stretching frequencies with increasing ligand donicity is interpreted in terms of a progressive reduction in the transfer of Π-bonding charge from O$_t$ to molybdenum with increasing ligand-to-metal charge transfer. The v(Mo–O$_t$) values obtained for the present species are very close to those obtained for other phosphine oxide (DiPDECMP, EDPO and TPPO) complexes (Table V), and in view of increasing donicity the order CH_3CN < THF < phosphine oxides < DMF < DMSO is indicated.

TABLE V

Ligand donicity and v(Mo–O$_t$) values for some $MoO_2X_2.L_2$ and $MoO_2X_2.L'$ complexes.[a]

Ligand	Donicity[b]	v(Mo-O$_t$) (cm^{-1}) Chlorides	Bromides	References
CH_3CN	14.1	960, 920		28
THF	20.1	958, 920	958, 917	28
DMF	26.6	942, 907		28
		939, 905		5
DMSO	29.8	921, 892	922, 890	28
RPPh		952, 911	950, 909	this work
RPOEt		952, 911	951, 910	this work
DiPDECMP		950, 909		21
EDPO		945, 903	940, 897	13
TPPO		947, 905	946, 903	13
		950, 908	949, 906	this work

[a] L = monodentate ligand, L′ = bidentate ligand. [b] From reference 27.

An IR band of medium intensity for MoO_2Cl_2.RPPh and MoO_2Cl_2.RPOEt at 324 and 326 cm^{-1}, respectively, is attributed to the asymmetric stretching of the Mo–Cl bond. The corresponding band in oxobromide complexes appears around 250 cm^{-1} in molybdenum species. For the tungsten complex it could not be precisely assigned as it either matches with an M–O$_t$ out-of-plane rocking vibration[29] or is situated at lower wavenumbers, as indicated elsewhere.[8,30]

As already noted, phosphorus–oxygen stretching frequencies are considerably lowered on coordination. Both free ligands show three absorption bands in the v(P=O) region at 1215, 1192 and 1163 cm^{-1} for RPPh and at 1245, 1220 and 1190 cm^{-1} for RPOEt. Bands due to the central phosphoryl group of the ligands (1215 and 1245 cm^{-1}) disappear in the spectra of their complexes indicating coordination of the group in both cases. Peak maxima of the only band present in the spectra of the complexes appear at 1150–1165 cm^{-1} (for RPPh complexes) and at 1160–1175 cm^{-1} (for RPOEt complexes). A shoulder on the higher energy side of the v(P=O) band, at ~1200 cm^{-1}, can account for the uncoordinated terminal P=O group. The decrease in v(P=O) reflects the weakening of this bond on coordination to the metal. The more electronegative chloride ion causes v(P=O) frequencies to be higher for oxochloride than for oxobromide and oxoiodide complexes.

From the available evidence the new complexes appear to be reasonably straightforward compounds containing six-coordinate metal atoms. The inner coordination sphere in the MO_2X_2.L complexes should consist of two terminal oxygen atoms, two terminal halogens and two phosphoryl oxygen atoms of an apparently bidentate ligand, while in the $MoOX_3$.RPPh complexes the metal is surrounded by one terminal oxygen atom, three halogens and two ligand oxygen atoms. As already mentioned, the ^{31}P NMR spectra provide strong evidence that coordination of the ligands occurs through the central P=O and one of the terminal P=O groups.

Literature data[17,18,20–22] establishes a general principle that in mixed-ligand complexes the weaker Π-bonding donors are found to be *trans* to the terminal oxygen atoms, where they are not directly competing for available empty metal 4d orbitals. It might be supposed that in MO_2X_2.RPPh and MoO_2X_2.RPOEt (M = Mo, W; X = Cl, Br or I) the neutral phosphoryl oxygen-donor atoms are *trans* to the O_t atoms, while the X^- donors should be *cis* to O_t and mutually *trans* (Fig. 2). Accordingly, in the $MoOX_3$.RPPh complexes, the only oxo-ligand should be *trans* to one phosphoryl oxygen, and hence the three halogen atoms must be in a meridional arrangement (Fig. 3). These presumably octahedral species must be subjected to strong tetragonal distortion due to the molybdenyl oxygen.

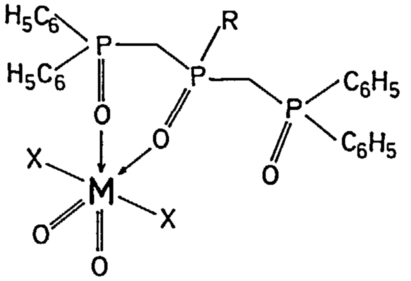

FIGURE 2 The proposed structure for MO_2X_2.L complexes, M = Mo or W; X = Cl, Br or I; L = RPPh or RPOEt.

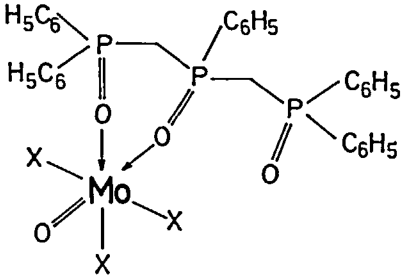

FIGURE 3 The proposed structure for $MoOX_3$.RPPh complexes, X = Br, I.

The bonds *trans* to O_t are long and usually weakened since the atoms in these *trans* positions suffer greater repulsion from the Π-bonding charge flowing from O_t into the d orbitals of the metal. In a view of the proposed structure for the present species the total *trans* influence should be higher in MoO_2X_2.RPPh than in $MoOX_3$.RPPh complexes, and consequently the Mo–O–(P) bond should be weaker in the former cases. This agrees with the fact that ν(P=O) values are found to be higher in Mo(VI) as compared to Mo(V) complexes (Table IV).

Changing the halide groups in $MoO_2X_2.L$ complexes from the more electronegative chlorine atom to bromine and iodine has a very small effect on the ν(Mo–O_t) values (Table IV) and hence, probably, on structure. This illustrates how insensitive these complexes are to the nature of the group *cis* to the terminal oxygen atoms.

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