The Co-ordination Chemistry of Molybdenum and Tungsten. Part 9.[1-3] Oxomolybdenum-(IV) and -(V) Complexes of Methyl-substituted Bidentate Group 5B Ligands

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The preparation of oxomolybdenum(V) complexes $[MoOCl_3(L-L)]$ with the bidentate ligands (L–L) 1,3-bis(dimethylphosphino)propane, 1,3-bis(dimethylarsino)propane, (3-dimethylphosphinopropyl)dimethylarsine, *o*-phenylenebis(dimethylarsine), and (2-dimethylarsinophenyl)dimethylstibine are described. On the basis of their e.s.r. spectra the first three complexes have *fac* structures. Oxomolybdenum(IV) cations $[MoO(Cl)(L-L)_2]^+$ have been prepared from $[MoOCl_2(PMe_2Ph)_3]$ and L–L, and are shown by ^{1}H n.m.r. to have *trans*-pseudo-octahedral structures.

WE recently reported[4] the synthesis of a range of oxomolybdenum(V) complexes of phenyl-substituted phosphorus and arsenic bidentate ligands, $[MoOCl_3(L-L)]$, and their reduction under appropriate conditions to oxomolybdenum(IV) cations, $[MoO(Cl)(L-L)_2]^+$. The properties of the complexes and the conditions under which reduction occurred were markedly affected by the nature of L–L. In view of this we have extended our studies to some methyl-substituted analogues of L–L in order to examine the effect of increased donor power.

RESULTS AND DISCUSSION

Oxomolybdenum(V) *Complexes*.—The reaction of $[MoOCl_3(thf)_2]$ (thf = tetrahydrofuran) with *o*-phenylenebis(dimethylarsine) (pdma),† (2-dimethylarsinophenyl)dimethylstibine (dmads), 1,3-bis(dimethylphosphino)propane (dmpp), 1,3-bis(dimethylarsino)propane (dmap), and (3-dimethylphosphinopropyl)dimethylarsine (dmpda) in benzene produced the red or brown crystalline $[MoOCl_3(L-L)]$ (Table 1). The complexes are air- and moisture-sensitive solids which are poorly soluble in organic solvents. They have magnetic moments of

TABLE 1

		Analysis (%) [a]			μ	I.r. bands (cm^{-1})		Electronic spectra ($10^{-3}\bar{\nu}$/cm^{-1}) [c]		^{1}H N.m.r. (Me region only) [f]
Complex	Colour	C	H	X [b]	B.M.	M=O	M–X	d	e	
$[MoOCl_3(dmpp)]$	Red	22.1 (21.9)	4.8 (4.7)	27.7 (27.8)	1.75	940	325s, 310s, 260s		21.7, 15.1	
$[MoOCl_3(dmpda)]$	Red	19.0 (19.7)	4.1 (4.2)	25.3 (24.9)	1.71	940	320 (sh), 300s, 260s		20.3, 14.9	
$[MoOCl_3(dmap)]$	Red	18.2 (17.9)	3.9 (3.8)	22.6 (22.6)	1.75	951	335s, 325s, 270s		19.8, 15.0	
$[MoOCl_3(pdma)]$	Brown	24.0 (23.8)	3.6 (3.2)	20.7 (21.1)	1.70	952	335s, 325s, 275 (sh)		19.6, 14.8	
$[MoOCl_3(dmads)]$	Red	22.8 (21.8)	3.4 (2.9)	18.5 (19.3)	1.69	948	335s, 315s, 273s		19.5, 14.8	
$[MoO(Cl)(dmpp)_2][BPh_4]$	Pink	55.9 (57.4)	6.6 (7.0)	5.5 (4.5)	*g*	950	272	19.22 (101)	19.2	8.50 (t), 8.58 (t) (1 : 1)
$[MoO(Cl)(dmpda)_2][BPh_4]$	Pink	52.3 (51.6)	6.4 (6.3)	4.5 (4.1)	*g*	949	250	18.65 (75)	18.5	8.50 (s), 8.52 (s), 8.58 (t), 8.62 (t) (1 : 1 : 1 : 1)
$[MoO(Cl)(dmap)_2][BPh_4]$	Pink	45.4 (47.0)	5.8 (5.8)	3.5 (3.7)	*g*	945	270	18.01 (89)	17.9	8.70 (s), 8.77 (s) (1 : 1)
$[MoO(Cl)(pdma)_2][BPh_4]$	Pink	51.0 (50.8)	5.3 (5.0)	3.5 (3.5)	*g*	949	265	19.30 (96)	19.3	8.16 (s), 8.18 (s) (1 : 1)
$[MoO(NCS)(pdma)_2][BPh_4]$	Purple–pink	51.5 (50.9)	5.6 (4.9)	1.7 (1.3)	*g*	949	2 020 ν(CN)	19.73 (105)	19.4	8.10 (s), 8.20 (s) (1 : 1)
$[MoO(Cl)(dmads)_2][BPh_4]$	Pink	48.3 (46.6)	5.2 (4.6)	2.9 (3.2)	*g*	951	265	18.63 (78)	18.5	8.16, 8.18, 8.19, 8.21 (1 : 1 : 1 : 1)
$[MoO(NCS)(dmads)_2][BPh_4]$	Pink	46.9 (46.8)	5.1 (4.5)	1.3 (1.2)	*g*	949	2 030 ν(CN)	19.27 (84)	18.7	

[a] Calculated values are given in parentheses. [b] Cl or N. [c] Absorption coefficients (ε/dm^3 mol^{-1} cm^{-1}) are given in parentheses. [d] In CH_2Cl_2 solution. [e] Solid reflectance. [f] In $CDCl_3$; relative to internal $SiMe_4$. [g] Diamagnetic.

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† The complex $[MoOCl_3(pdma)]$, with μ = 1.49 B.M. and two ν(Mo=O) frequencies at 965 and 932 cm^{-1}, was reported by D. G. Blight, D. L. Kepert, R. Mandyczewsky, and K. R. Trigwell, *J.C.S. Dalton*, 1972, 313, from $MoCl_5$ or $MoCl_3O$ in methanol or acetone and pdma. It was suggested that the complex was seven-co-ordinate.

[1] Part 8, C. A. McAuliffe and B. J. Sayle, *Bioinorg. Chem.*, submitted for publication.

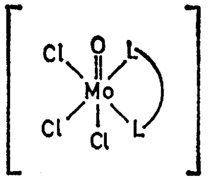
[2] Part 7, C. A. McAuliffe, F. P. McCullough, M. J. Parrott, C. A. Rice, B. J. Sayle, and W. Levason, *J.C.S. Dalton*, 1977, 1762.

[3] Part 6, J. Dilworth, C. A. McAuliffe, and B. J. Sayle, *J.C.S. Dalton*, 1977, 849.

[4] W. Levason, C. A. McAuliffe, and B. J. Sayle, *J.C.S. Dalton*, 1976, 1177.

ca. 1.7 B.M.,* consistent with d^1 Mo^V, and exhibit a strong ν(Mo=O) band in the range 940—960 cm^{-1} and three ν(Mo–Cl) bands at *ca.* 335, *ca.* 320, and *ca.* 270 cm^{-1}, *similar* to the analogous complexes of the phenyl-substituted ligands.[4] Insufficient solubility prevented the solution electronic spectra being obtained, but the solid reflectance spectra exhibit the two characteristic absorptions[5] at *ca.* 20 000 ($^2B_1 \leftarrow {}^2B_2$) and *ca.* 15 000 cm^{-1} ($^2E \leftarrow {}^2B_2$).

The e.s.r. spectrum of $[MoOCl_3(dmpp)]$ in dichloromethane at room temperature consists of a main absorption (due to ^{96}Mo with $I = 0$) split into a triplet ($g_{av.}$ 1.972). The triplet splitting indicates that the two phosphorus atoms (^{31}P, $I = \frac{1}{2}$) are in equivalent environments and hence that the complex has a *fac* structure, (1). Weak satellites due to ^{95}Mo and ^{97}Mo ($I = \frac{5}{2}$, 25%) are also evident. The complex $[MoOCl_3(dmap)]$ exhibits an e.s.r. spectrum consisting of a main line split into a septuplet (Figure) of relative intensity 1 : 2 : 3 : 4 : 3 : 2 : 1, consistent with two equivalent arsenics (^{75}As, $I = \frac{3}{2}$), and hence the *fac* structure, (1), also. The observed e.s.r. spectrum of $[MoOCl_3(dmpda)]$ shows an apparent quintuplet splitting of the main line, again interpretable in terms of coupling to ^{31}P and ^{75}As nuclei in the same environment. The e.s.r. spectra of $[MoOCl_3(L–L)]$ (L–L = pdma or dmads) were poorly resolved and not interpretable in terms of a definite stereochemistry. In contrast to the e.s.r. spectra of the complexes of the phenyl-substituted ligands,[4] those of the present complexes show no resolvable chlorine hyperfine splitting $\langle a \rangle$ (^{35}Cl, ^{37}Cl) less than 1.5 G. This may suggest that the increased σ-donor power of the methyl-substituted ligands results in greater polarity of the Mo–Cl bonds, and this decreased covalency decreases the extent to which the odd electron is delocalised on to the chlorines, hence the loss of the chlorine hyperfine splitting.



(1)

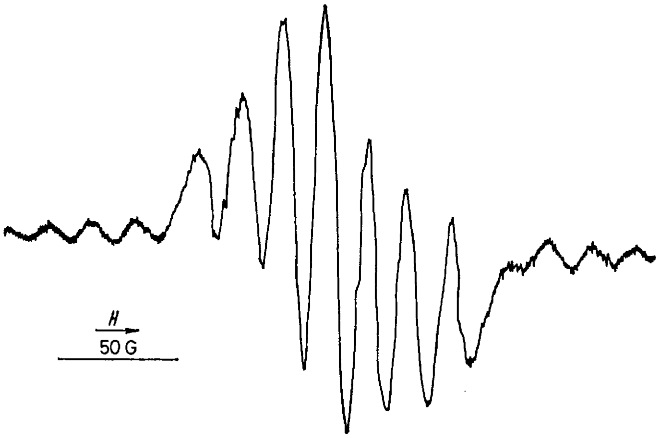


FIGURE E.s.r. spectrum of $[MoOCl_3(dmap)]$ in CH_2Cl_2

TABLE 2

E.s.r. data for solutions (*ca.* 10^{-3} mol dm^{-3}) in CH_2Cl_2 at room temperature

Complex	$g_{av.}$	$10^{-4}A_{iso.}/cm^{-1}$	
		Mo	L
$[MoOCl_3(dmpp)]$	1.972		2.2 (^{31}P)
$[MoOCl_3(dmpda)]$	1.970		2.1 (^{31}P, ^{75}As)
$[MoOCl_3(dmap)]$	1.972		1.8 (^{75}As)
$[MoOCl_3(pdma)]$	1.965	4.25	
$[MoOCl_3(dmads)]$	1.969	4.60	

The reaction of $[MoOCl_3(thf)_2]$ with $Me_2SbCH_2CH_2CH_2SbMe_2$ (dmsp) produced a tarry product and no complex could be isolated. This decomposition is probably due to reduction of the Mo^V by dmsp; the latter often behaves differently from the stibine–arsine ligand dmads.† The complex $[MoOCl_3(dmads)]$ is a very rare example of co-ordination of a stibine donor to a transition metal in a high oxidation state.

Oxomolybdenum(IV) *Complexes*.—Although the phenyl-substituted ligands cleanly reduced $[MoOCl_3(L–L)]$ to $[MoO(Cl)(L–L)_2]^+$, attempted similar reactions with the methyl-substituted ligands afforded black tars. The required $[MoO(Cl)(L–L)_2]^+$ were cleanly produced by treatment of $[MoOCl_2(PMe_2Ph)_3]$[7] with L–L (L–L = pdma, dmads, dmpp, dmap, or dmpda) in ethanol, followed by precipitation as the tetraphenylborates. All the complexes are pink crystalline solids which are indefinitely stable in dry air, are 1 : 1 electrolytes (Λ 60—68 S cm^2 mol^{-1} in 10^{-3} mol dm^{-3} nitromethane), and are diamagnetic. The i.r. spectra exhibit one strong ν(Mo=O) band at *ca.* 950 cm^{-1} and one ν(Mo–Cl) at *ca.* 270 cm^{-1}, both essentially insensitive to changes in L–L suggesting that O is *trans* to Cl [structure (2)]. Only one single band was observed in the electronic spectra either in solution or in the solid state; the low absorption coefficients and the fact that shifts in $E_{max.}$ exhibit a reasonable spectrochemical series with changes in L–L (allowing for the effects of different ring sizes) (Table 1) suggest that the absorption is predominantly *d–d* in character.

The structure of the cations was confirmed as (2) by a study of their ^1H n.m.r. spectra. The cations [MoO(Cl)-

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* Throughout this paper: 1 B.M. ≈ 9.27×10^{-24} A m^2; 1 G = 10^{-4} T.

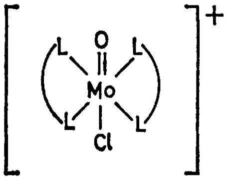
† For example, with $FeCl_3$, dmads gives $[FeCl_2(dmads)_2][FeCl_4]$, but dmsp is chlorinated to give $Me_2Sb(Cl_2)CH_2CH_2CH_2Sb(Cl_2)Me_2$.[6]

[5] A. B. P. Lever, 'Inorganic Electronic Spectroscopy,' Elsevier, Amsterdam, 1968.

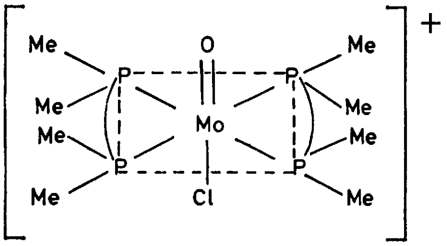
[6] W. Levason, C. A. McAuliffe, and S. M. Nelson, unpublished work.

[7] A. V. Butcher and J. Chatt, *J. Chem. Soc.* (*A*), 1970, 2652.

$(L{-}L)_2]^+$ (L–L = pdma or dmap) exhibit two clearly spaced methyl resonances of intensity 1 : 1 which are due to the inequivalence of the methyl groups above and below the As_4 plane (*i.e.* those neighbouring to the O and those neighbouring to Cl). The other possible isomer would give a much more complex n.m.r. spectrum. The ^1H n.m.r. spectrum of $[MoO(Cl)(dmads)_2]^+$ is similar except that the presence of two different donor atoms (As and Sb) results in four methyl resonances (1 : 1 : 1 : 1). The spectrum of $[MoO(Cl)(dmpp)_2][BPh_4]$ is more complex, consisting of a multiplet at τ 2.6—3.4 ($[BPh_4]^-$), a multiplet at τ 8.06 ($[CH_2]_3$), and two signals at τ 8.50 and 8.58. Under high resolution the latter two signals resemble incompletely resolved triplets, but there are further weak absorptions between the 'triplets.' The spectrum is interpretable in terms of a *trans* cation, (3), the two signals resulting from the methyl groups above and below the P_4 plane with the 'triplets' due to the virtually coupled *trans*-phosphorus atoms. Similarly, the methyl region of the ^1H n.m.r. spectrum of $[MoO(Cl)(dmpda)_2][BPh_4]$ exhibits two incompletely resolved Me–As resonances and two apparent triplets due to Me–P groups, once again consistent with a *trans* structure (2), and shows that the phosphines in the plane are in mutually *trans* positions. The fact that the observed n.m.r. spectra show extra weak absorptions and the intensities of the 'triplets' differ from the 1 : 2 : 1 expected is due to deviation from first-order behaviour due to the small chemical-shift differences.[8]



(2)



(3)

Metathesis of $[MoO(Cl)(L{-}L)_2][BPh_4]$ (L–L = pdma or dmads) with K[NCS] in boiling ethanol yielded the corresponding $[MoO(NCS)(L{-}L)_2][BPh_4]$, which have similar structures to the chloro-complexes on the basis of their ^1H n.m.r. spectra (Table 1), whilst the i.r. spectra confirm that isothiocyanato-co-ordination is present.[9] Attempted metathesis with LiX (X = Br or I) did not go to completion, the products obtained appearing to be mixtures of the required $[MoO(X)(L{-}L)_2][BPh_4]$ and unchanged chloro-complex.

EXPERIMENTAL

All the reactions were carried out under a dinitrogen atmosphere using standard dry-box and Schlenk-tube techniques. Trichloro-oxobis(tetrahydrofuran)molybdenum(V)[10] and trichlorotris(dimethylphenylphosphine)-oxomolybdenum(IV),[7] and the ligands pdma,[11] dmads,[12] dmpp,[13] dmpda,[13] dmap,[14] and dmsp[15] were prepared by literature methods. The $[MoOCl_3(L{-}L)]$ complexes were prepared by the general method described previously.[4]

$[MoO(Cl)(L{-}L)_2][BPh_4]$ (*General Method*).—A boiling ethanol (25 cm^3) solution of $[MoOCl_2(PMe_2Ph)_3]$ (1.2 g, 2 mmol) was treated with excess of L–L (5 mmol) and the mixture was stirred under reflux for 15 min. Addition of an ethanolic solution of sodium tetraphenylborate (2.1 mmol) caused precipitation of a pink solid. The solid was filtered from the cold solution, rinsed with ethanol (5 × 10 cm^3), and dried, yields *ca.* 75%.

The complexes $[MoO(NCS)(L{-}L)_2][BPh_4]$ (L–L = pdma or dmads) were prepared by metathesis of $[MoO(Cl)(L{-}L)_2]$-$[BPh_4]$ with K[NCS] in boiling ethanol, yields *ca.* 60%.

Physical measurements were made as previously described.[4]

[7/487 *Received*, 21*st March*, 1977]

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[8] See, for example, R. M. Lynden-Bell, G. G. Mather, and A. Pidcock, *J.C.S. Dalton*, 1973, 715.

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[10] K. Feenan and G. W. A. Fowles, *Inorg. Chem.*, 1965, **4**, 310.

[11] R. D. Feltham, R. S. Nyholm, and A. Kasenally, *J. Organometallic Chem.*, 1965, **7**, 285.

[12] B. R. Cook, C. A. McAuliffe, and D. W. Meek, *Inorg. Chem.*, 1971, **10**, 2676.

[13] G. Kordoscky, B. R. Cook, J. C. Cloyd, and D. W. Meek, *Inorg. Synth.*, 1973, **14**, 14.

[14] D. J. Thornhill and A. R. Manning, *J.C.S. Dalton*, 1973, 2086.

[15] R. J. Dickinson, W. Levason, C. A. McAuliffe, and R. V. Parish, *J.C.S. Chem. Comm.*, 1975, 272.