Co-ordination Chemistry of Molybdenum. Part II.[1] Oxomolybdenum-(IV) and -(V) Complexes of Diphosphine, Diarsine, and Arsine-phosphine Ligands

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Reaction of [$MoCl_3O(thf)_2$] (thf = tetrahydrofuran) with bidentate ligands [L–L = $Ph_2PCH_2CH_2PPh_2$ (dppe); $Ph_2AsCH_2CH_2AsPh_2$ (dpae); *cis*-$Ph_2PCH{=}CHPPh_2$ (dppen); *cis*-$Ph_2AsCH{=}CHAsPh_2$ (dpaen); $Ph_2AsCH_2CH_2PPh_2$ (dadpn); *cis*-$Ph_2AsCH{=}CHPPh_2$ (dadpen); $C_6H_4(PPh_2$-*o*$)_2$ (pdpp); and $C_6H_4(AsPh_2$-*o*$)(PPh_2$-*o*$)$ (pdadp)] has led to the isolation of [$MoCl_3O$(L–L)] complexes. Refluxing these complexes in methanol leads to partial reduction to form [$Mo^{IV}ClO$(L–L$)_2$][$Mo^{V}Cl_4O$], but reflux in methanol in the presence of L–L and Na[BPh_4] results in complete reduction to [MoClO(L–L$)_2$][BPh_4]. These complexes have been characterised by the use of i.r., electronic-absorption, and e.p.r. spectroscopy. E.p.r. spectra suggest that the [$MoCl_3O$(L–L)] (L–L = dppe or dppen) species have a *fac* structure in dichloromethane. Considerable hyperfine structure, and *g* values *ca.* 1.97, have been observed for the e.p.r.-active species.

A LARGE number of complexes of trichloro-oxomolybdenum(V) of types [$MoCl_3OL_2$] and [$MoCl_3O$(L–L)] have been prepared with neutral unidentate (L) and bidentate (L–L) ligands.[2] The majority of these contain 'hard' oxygen- or nitrogen-donor atoms, as expected in view of the high oxidation state of the metal. Only rarely have the heavier Group 5B donor ligands been complexed to Mo^{V}, *viz.* [$MoCl_3O(PPh_3)_2$],[3] [$MoCl_3O$(dppe)] [4,*] (dppe = $Ph_2PCH_2CH_2PPh_2$), and [Mo(pdma)Cl_3O] [5] [pdma = $C_6H_4(AsMe_2$-*o*$)_2$]. Here we report the synthesis and spectroscopic properties of a number of molybdenum(V) complexes of phosphorus- and arsenic-donor bidentate ligands, and the formation of chloro-oxomolybdenum(IV) species, [MoClO(L–L$)_2$]$^+$, by reduction of the complexes of Mo^{V}. This is the first report of e.p.r. spectra of molybdenum(V) complexes containing phosphorus and arsenic donors.

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[*] This complex has previously been prepared from [$MoCl_3O(thf)_2$] (thf = tetrahydrofuran).[6]

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EXPERIMENTAL

All reactions and manipulations were carried out under a nitrogen atmosphere. Solvents were dried and freshly distilled under nitrogen before use. Commercial molybdenum pentachloride was purified by sublimation and converted into trichloro-oxobis(tetrahydrofuran)molybdenum(v) by the literature method.[7] The ligands were prepared by literature methods: Ph$_2$PCH$_2$PPh$_2$ (dppm);[8] dppe;[7] Ph$_2$AsCH$_2$CH$_2$AsPh$_2$ (dpae);[9] Ph$_2$PCH$_2$CH$_2$AsPh$_2$ (dadpe);[10] *cis*-Ph$_2$PCH=CHPPh$_2$ (dppen);[11] *cis*-Ph$_2$AsCH=CHAsPh$_2$ (dpaen);[12] *cis*-Ph$_2$PCH=CHAsPh$_2$ (dadpen);[10] C$_6$H$_4$(PPh$_2$-*o*)$_2$ (pdpp);[13] C$_6$H$_4$(AsPh$_2$-*o*)$_2$ (pdpa);[14] C$_6$H$_4$-(AsPh$_2$-*o*)(PPh$_2$-*o*) (pdadp);[15] C$_6$H$_4$(PPh$_2$-*o*)(SbPh$_2$-*o*) (pdpds);[16] and C$_6$H$_4$(AsPh$_2$-*o*)(SbPh$_2$-*o*) (pdads).[16]

The complexes were prepared by the following general routes.

[MoCl$_3$O(L–L)].—A solution of the appropriate ligand (0.003 mol) in dichloromethane (15 cm^3) was added to a suspension of [MoCl$_3$O(thf)$_2$] (1.0 g, 0.0028 mol) in benzene (15 cm^3). The deep red solution was stirred at room temperature for 15 min and then concentrated by removing the solvent *in vacuo* to give crystals of the product. The product was filtered, rinsed with benzene (5 cm^3) and hexane (5 cm^3), and dried *in vacuo.*

[MoCl$_{2.5}$O(L–L)] (L–L = dppen *or* dadpen).—The appropriate [MoCl$_3$O(L–L] (0.001 mol) was heated under reflux in methanol (20 cm^3) for *ca.* 20 min during which time a deep purple solution formed. Diethyl ether (10 cm^3) was added and the mixture allowed to cool and stand overnight to yield purple crystals. These were filtered off, rinsed with methanol (5 cm^3) and diethyl ether (5 cm^3), and dried *in vacuo.*

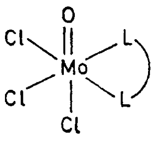
[MoClO(L–L)$_2$][BPh$_4$].—The complex [MoCl$_3$O(L–L)] (0.001 mol) was heated under reflux in methanol with excess of L–L (2 : 1 ratio of L–L : complex) to form a deep purple solution. Sodium tetraphenylborate (0.001 mol) in methanol (10 cm^3) was added resulting in immediate precipitation of pink or purple solids. These were washed with hot methanol (2 × 5 cm^3), benzene (5 cm^3), and diethyl ether (5 cm^3) and dried *in vacuo.*

Physical measurements were made as previously described,[17] and e.p.r. spectra were obtained in dichloromethane solution (*ca.* 10^{-3} mol dm^{-3}) at room temperature using a Varian E9 e.p.r. spectrometer.

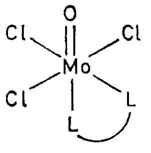
RESULTS AND DISCUSSION

[MoCl$_3$O(L–L)] *Complexes.*—The reaction of trichloro-oxobis(tetrahydrofuran)molybdenum(v) in benzene–dichloromethane with the ditertiary phosphines dppe, dppen, and pdpp, the ditertiary arsines dpae and dpaen, and the arsinephosphines dadpe, pdadp, and dadpen produced crystalline [MoCl$_3$O(L–L)]. The analogous reactions with the diarsine pdpa and the antimony-containing ligands pdpds and pdads yielded only intractable black oils. The dppm ligand also failed to yield a crystalline product, possibly due to the decreased tendency to chelate to molybdenum because of the shorter ligand backbone.[18]

The [MoCl$_3$O(L–L)] complexes (Table 1) are unstable in moist air and slightly soluble in benzene or dichloromethane in which they behave as non-electrolytes. The mull i.r. spectra exhibited one single strong absorption at 930—950 cm^{-1}, assignable to ν(Mo=O) of the terminal molybdenum–oxygen moiety; there is no evidence for the presence of an oxo-bridge (Mo–O–Mo).[19] The far-i.r. spectra were complicated by the presence of strong ligand absorptions, but in general they exhibited three strong bands assignable to terminal ν(Mo–Cl) vibrations (Table 1). There have been very few assignments of Mo–Cl vibrations [20–22] and thus it was not possible to differentiate between the two possible structures (I) and (II) by vibrational spectroscopy.



(I)



(II)

The electronic spectra of the complexes in the solid state and in dichloromethane solution (Table 1) were similar in profile, though in some cases not identical in band position. The spectra consisted of an intense absorption at 19 000—20 500 cm^{-1} and a weak absorption at 14 000—16 000 cm^{-1}, which may be tentatively assigned to the ${}^2B_1 \leftarrow {}^2B_2$ and ${}^2E \leftarrow {}^2B_2$ transitions,[23] respectively. The large molar absorption coefficients of the high-energy band indicate considerable borrowing of charge-transfer intensity.

Butcher and Chatt [4] prepared a red [MoCl$_3$O(dppe)] species by reaction of molybdenum(v) chloride in methanol–ethanol with the diphosphine, and their product appears to be identical with the one we have isolated using [MoCl$_3$O(thf)$_2$] as starting material. When brown [MoCl$_3$O(dppen)] was boiled in methanol it was converted into a red isomer; presumably these are structures (I) and (II). The differences in i.r. and electronic spectra between the two forms are quite small (Table 1).

In order to examine the possibility of isolating other isomers, the reaction of all the ligands with molyb-

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denum(V) chloride in methanol–ethanol[4] was studied.* The dppe ligand yielded only red [$MoCl_3O$(dppe)], but dppen and pdpp produced [$MoCl_3O$(L–L)] (the brown isomer in the case of dppen) and a second product, [$MoCl_{2.5}O$(L–L)], could be isolated from the mother liquor on standing in the presence of diethyl ether (see below). The arsinephosphine ligands dadpen and pdadp failed to yield any [$MoCl_3O$(L–L)] complex by this route but, again, [$MoCl_{2.5}O$(L–L)] could be isolated on standing. No reaction was apparent between the diarsine ligands or dadpe and 'alcoholic $MoCl_5$'. These last ligands also will not react with [$MoCl_3O(thf)_2$] in thf, but only do so in benzene, suggesting that our inability to isolate products from methanol is due to the decreased ability of these ligands to co-ordinate to the 'hard' Mo^V in the presence of the competing alcohol oxygen donors.

TABLE 1

Analytical, physical, and spectroscopic data for the molybdenum complexes

Complex	Colour	M.p. (θ_c/°C)	$\mu_{eff.}$ B.M.	Analysis (%) [a]			I.r. (cm^{-1})		Electronic (10^3 cm^{-1})	
				C	H	Cl	ν(Mo=O)	ν(M–Cl)	b	c
[$MoCl_3O$(dppe)]	Red	223	1.71	50.5 (50.5)	4.1 (3.9)	16.7 (17.2)	941	330, 310, 280	19.60 (2 400)	19.6, 15.2
[$MoCl_3O$(dppen)]	Brown	241	1.71	50.8 (50.7)	3.5 (3.6)	17.1 (17.3)	941	338, 312, 272	20.31 (2 600), 15.05 (200)	20.1, 15.7
	Red	235	1.70	50.6 (50.7)	3.7 (3.6)	17.5 (17.3)	940	310, 269	21.10 (1 600), 15.06 (230)	20.0, 15.4
[$MoCl_3O$(dadpe)]	Red	218	1.70	46.8 (47.2)	3.8 (3.6)	15.7 (16.2)	945	330, 308, 270		
[$MoCl_3O$(dadpen)]	Red	221	1.71	47.1 (47.4)	3.0 (3.3)	15.9 (16.2)	932	335, 309, 268	20.05 (1 400), 13.91 (115)	19.8, 15.4
[Mo(dpae)Cl_3O]	Red	207	1.69	44.0 (44.3)	3.9 (3.4)	14.8 (15.1)	939	345, 315, 269	20.20 (750), 14.25 (180)	20.0, 14.3
[Mo(dpaen)Cl_3O]	Red	210	1.70	44.0 (44.4)	3.4 (3.1)	15.6 (15.2)	935	340, 316, 265	20.10 (940), 14.60 (195)	19.8, 15.1
[$MoCl_3O$(pdpp)]	Mauve	246	1.71	54.3 (54.2)	3.9 (3.6)	16.0 (15.7)	952	335, 322, 261	19.75 (1 600), 13.63 (410)	19.6, 14.1
[$MoCl_3O$(pdadp)]	Mauve	252	1.70	51.3 (50.8)	3.2 (3.4)	15.1 (15.0)	950	340, 335, 260	20.05 (2 955), 14.85 (185)	19.8, 14.8
[$MoClO(dppe)_2$][BPh_4] [d]	Pale blue	216	e	72.6 (72.6)	5.5 (5.4)	2.9 (2.8)	940	289	17.73 (59)	17.8
[$MoClO(dppen)_2$][BPh_4]	Pink	222	e	72.8 (72.4)	5.2 (5.1)	2.6 (2.8)	938	289	18.71 (80)	18.8
[$MoClO(dadpe)_2$][BPh_4]	Yellow-pink	219	e	67.8 (67.6)	5.0 (5.0)	2.7 (2.7)	926	285	21.49 (70)	21.5
[$MoClO(dadpen)_2$][BPh_4]	Pink	221	e	68.2 (67.8)	5.3 (4.8)	2.4 (2.6)	940	286	18.82 (47)	18.8
[$MoClO(pdpp)_2$][BPh_4]	Pink	226	e	74.7 (74.2)	5.2 (5.0)	2.3 (2.6)	939	280	18.38 (56)	18.4
[$MoClO(pdadp)_2$][BPh_4]	Pink	223	e	70.1 (69.7)	4.9 (4.7)	2.5 (2.5)	940	285	22.10 (59)	
[$MoClO(dppen)_2$][$MoCl_4O$] [d]	Mauve	245	1.88 [f]	52.0 (52.3)	3.6 (3.7)	14.5 (14.9)	980, 938	325, 285	19.9 (960), 14.82 (130)	18.8, 15.0
[$MoClO(dadpen)_2$][$MoCl_4O$]	Mauve	238	1.82 [f]	47.1 (47.4)	3.0 (3.3)	15.9 (16.2)	978, 940	325, 275, 265		18.8, 14.8
[$MoClO(pdpp)_2$][$MoCl_4O$]	Mauve	247	1.79 [f]	55.9 (55.7)	3.9 (3.7)	13.9 (13.7)	982, 941	331, 281		
[$MoClO(pdadp)_2$][$MoCl_4O$]	Mauve	235	1.79 [f]	51.9 (52.1)	3.4 (3.5)	12.4 (12.8)	982, 940	329, 283		

[a] Calculated values are given in parentheses. [b] In dichloromethane; absorption coefficients ($\varepsilon/dm^3\ mol^{-1}\ cm^{-1}$) are given in parentheses. [c] Solid reflectance. [d] The conductivity values for the $[BPh_4]^-$ and $[MoCl_4O]^-$ salts in 10^{-3} mol dm^{-3} nitromethane fall in the range 63—70 S cm^2 mol^{-1}. [e] Diamagnetic. [f] Moment of the molybdenum(V) species.

[$MoCl_{2.5}O$(L–L)] *Complexes*.—These pink air-stable crystalline complexes are 1 : 1 electrolytes in nitromethane and are thus formulated as [$Mo^{IV}ClO(L–L)_2$]-[Mo^VCl_4O]. This formulation is also suggested from the way in which these complexes react with methanolic Na[BPh_4] to produce [$MoClO(L–L)_2$][BPh_4]. The [$MoClO(L–L)_2$][$MoCl_4O$] complexes are paramagnetic and e.p.r. data (see below) suggest that the 'active' molybdenum species is $[MoCl_4O]^-$. The i.r. spectra showed ν(Mo=O) at 980 and *ca.* 940 cm^{-1}, assignable to anion and cation, respectively, and ν(Mo–Cl) at *ca.* 325 (anion) and 270—290 cm^{-1} (cation).

It is thus apparent that for the four ligands dppen, pdpp, dadpen, and pdadp, reaction with $MoCl_5$ in methanol results in partial reduction to Mo^{IV}. The preformed complexes [$MoCl_3O$(L–L)] (L–L = dppen, pdpp, dadpen, and pdadp), synthesised from [$MoCl_3(thf)_2$], undergo this partial reduction in boiling methanol, suggesting that [MoClO(L–L)][$MoCl_4O$] are produced by reduction of the corresponding [$MoCl_3O$(L–L)] and do not result from the presence of Mo^{IV} in 'alcoholic $MoCl_5$' before the addition of ligand. In the presence of excess of the appropriate ligand the [$MoCl_3O$(L–L)] complexes are completely reduced to Mo^{IV} and, after addition of Na[BPh_4], almost quantitative yields of [$MoClO(L–L)_2$]-[BPh_4] were obtained.

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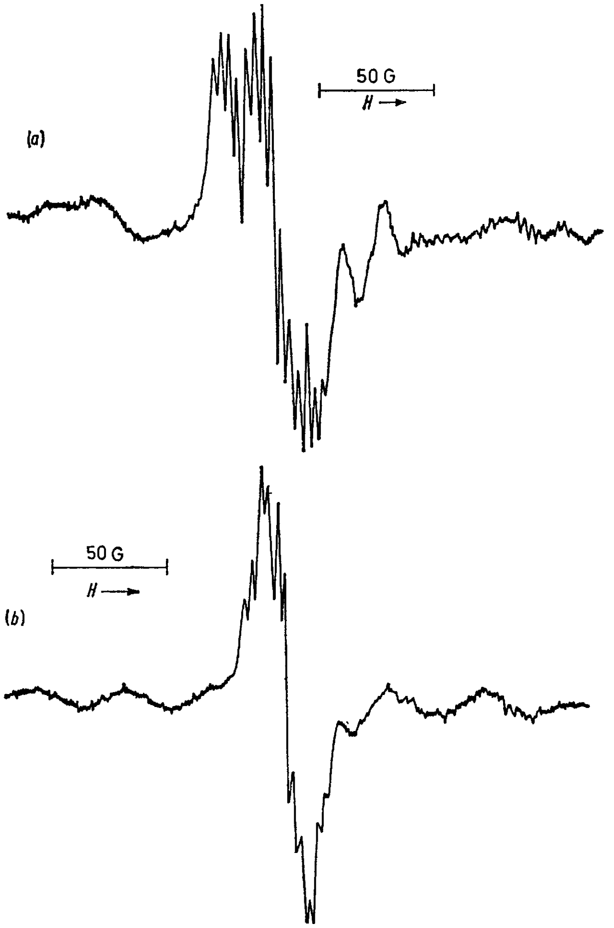
* Butcher and Chatt[4] obtained a second isomer of [$MoCl_3O$(dppe)] from boiling isopropyl alcohol.

$[MoClO(L\text{-}L)_2][BPh_4]$.—These complexes are diamagnetic, stable to dry air, and 1 : 1 electrolytes in nitromethane. The complexes $[MoClO(L\text{-}L)_2][BPh_4]$ (L–L = dppe and dppen) are identical to products of this formula which were previously isolated.[4] An *X*-ray structure determination[6] of $[MoClO(dppe)_2][ZnCl_3{\cdot}OCMe_2]$ revealed the presence of a six-co-ordinate cation with O *trans* to Cl. The mull i.r. spectra of all the molybdenum(IV) complexes reported here exhibited one ν(Mo=O) at slightly lower frequencies (Table 1) than those of the complexes of Mo^V, and there was a single ν(Mo–Cl) at 280—290 cm^{-1}. The electronic spectra exhibited only one weak absorption (Table 1) below the high-energy charge-transfer bands, but absorption varied in energy with changes in the ligand in an unexpected manner.



E.p.r. spectra of (*a*) $[MoCl_3O(dppe)]$ and (*b*) $[MoCl_3O(pdpp)]$

E.P.R. Spectra.—The isotropic e.p.r. spectra of the molybdenum(V) complexes were obtained in solutions of dichloromethane or benzene. The results are shown in Table 2, and the Figure contains typical spectra. All the complexes exhibited molybdenum hyperfine splitting which is typical of molybdenum(V) species, and consisted of a central line due to the molybdenum with no nuclear spin (75% abundance) flanked by six weaker satellites due to the isotopes ^{95}Mo and ^{96}Mo ($I = \frac{5}{2}$, 25%).

The e.p.r. spectra of all the complexes showed considerable hyperfine structure due to interaction of the unpaired electron with the nuclear spin of the ligand atoms ($I = \frac{1}{2}$, ^{31}P; $\frac{3}{2}$, ^{75}As; $\frac{5}{2}$, ^{35}Cl and ^{37}Cl). The spectrum of $[MoCl_3O(dppe)]$ is shown in the Figure, and is interpretable as indicating that this complex has the *fac* structure (I). The central band, of width 66×10^{-4} cm^{-1}, was split into a multiplet of 14 lines. This can be explained in the following way. Splitting of the main line due to two equivalent phosphorus atoms would be expected to give three lines, and if this splitting is less than the linewidth of the main line this results in a central line flanked by two shoulders. Interaction with two equivalent chlorine atoms splits each of these lines into a septuplet, thus resulting in a spectrum consisting of 14 lines. The chlorine *trans* to the oxo-group does not appear to have any superhyperfine coupling with the molybdenum electron.

Since both the red and brown isomeric forms of $[MoCl_3O(dppen)]$ give rise to almost identical e.p.r. spectra in dichloromethane (Table 2), and since the pattern is similar to that for $[MoCl_3O(dppe)]$ (although the ^{31}P splitting is not as pronounced as for the dppe complex), we suggest that only one species exists in solution and that it has structure (I). Moreover, the electronic spectra of both solutions are almost identical (Table 1).

The $[MoCl_3O(pdpp)]$ complex exhibited an e.p.r. spectrum consisting of a central line flanked by six satellites, although two of the satellites were partly obscured by the main line. The main line was split into a multiplet of 11 lines, and the satellites on the high-field side were resolved into 11 lines. The 11 lines probably result from superimposition and overlap of lines, thus making it exceedingly difficult to analyse the spectrum. The coupling between the smaller peaks is 3.5×10^{-4} cm^{-1} and this is thus probably the chlorine superhyperfine coupling.

The remainder of the complexes gave e.p.r. spectra with very complex fine structure (Table 2) and in some cases there are two species present in solution. However, the multiplicity of lines does allow us to conclude that there is superhyperfine interaction between the molybdenum electron and the chlorine, phosphorus, and arsenic ligands.

The magnitudes of the isotropic $g_{av.}$ values are interesting. In the co-ordination compounds of Mo^V studied so far, those with N and/or O donors[24,25] give $g_{av.}$ values of 1.95 and lower. Higher *g* values have only been reported for sulphur donors,[1,24] and this has been interpreted in terms of delocalisation of the metal electron into the sulphur ligand orbitals, thus reducing the hyperfine splitting and increasing the *g* value towards that of the free electron. Where hyperfine or superhyperfine splittings have been observed, low values of metal hyperfine splitting and high values of superhyperfine splitting are consistent with much electron delocalis-

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[25] C. A. McAuliffe and B. J. Sayle, unpublished work.

ation over the ligands. In this study, the first e.p.r. study of Mo^V bound to P or As donors, the values of the $g_{av.}$ are similar to those obtained for S donors and no doubt the same mechanism applies in both cases. Since no chlorine-hyperfine coupling has been previously reported for ligand adducts of $MoCl_3O$,* it seems reasonable to suggest that the presence of P and As donors in these complexes has allowed the Mo–Cl bonds to become sufficiently covalent in character to allow chlorine-hyperfine coupling to occur.

TABLE 2

Electron paramagnetic resonance spectra of the molybdenum(V) complexes [a]

Complex	$g_{av.}$	10^4 Linewidth/ cm^{-1} Full signal	10^4 Linewidth/ cm^{-1} Central line	$10^4 A_{iso}$ (Mo)/cm^{-1}	A_{iso}(L–L)/cm^{-1}	Fine structure
$[MoCl_3O(dppe)]$	1.967	370	66	46	3.5 (Cl) 15 (P)	Central line split into 14 lines; six satellites due to Mo h.f.s.
$[MoCl_3O(dppen)]$ (*b*)	1.970	288	56	46	3.5 (Cl) 14 (P)	Central line split into 14 lines; six satellites due to Mo h.f.s.
(*c*)	1.965	296	65	44	3.5 (Cl) 13 (P)	
$[MoCl_3O(pdpp)]$	1.970	244	50	42	3.5 (Cl)	Central line split into 11 lines; six satellites, high-field set resolved into 11 lines
$[MoCl_3O(dadpe)]$	1.965 1.955	340		42 46	3.5 (Cl)	Very asymmetric and poorly resolved; two different species present giving two superimposed sets of central line, plus six satellites. Central line further split by s.h.f. coupling (Cl)
$[MoCl_3O(dadpen)]$	1.969 1.956	320		40 46	3.5 (Cl)	Two superimposed sets of main line + six satellites, due to two different species; 16 lines observed in central region
$[MoCl_3O(pdadp)]$	1.967			40	3.5 (Cl)	Central line split into asymmetric pattern of 16 lines; six satellites due to Mo h.f.s.
$[MoClO(dppen)_2][MoCl_4O]$	1.949	276		53		Central line and six satellites; no h.f. structure
$[MoClO(dadpen)_2][MoCl_4O]$	1.951	268		55		Central line and six satellites; no h.f. structure

[a] In dichloromethane (10^{-3} mol dm^{-3}) at room temperature; h.f.s. = hyperfine splitting, s.h.f. = superhyperfine. [b] Brown isomer. [c] Red isomer. We recommend a discussion of 'distortional isomerism' by Chatt *et al.* (*Chem. Comm.*, 1970, 1399) for another example of isomerism in complexes of Mo.

The $[MoClO(L–L)_2][MoCl_4O]$ complexes exhibited e.p.r. spectra in dichloromethane which show the presence of paramagnetic molybdenum(V) species. They showed the expected main-line and six-line hyperfine structure. However, no superhyperfine structure was observed and this confirms that the e.p.r.-active species does not have co-ordinated L–L. Also, the isotopic g values are lower and $A_{iso.}$(Mo) is larger than in the $[MoCl_3O(L–L)]$ complexes (Table 2). In fact these values are very close to those obtained elsewhere for the $[MoCl_4O]^-$ anion,[26] thus supporting the formulation of these complexes as $[MoClO(L–L)_2][MoCl_4O]$ species.

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* However, a referee has asked us to point out that chlorine-superhyperfine coupling has been observed for $[NH_4]_2[MoCl_5O]$ (P. T. Manohara and M. T. Rogers, *J. Chem. Phys.*, 1968, **49**, 5510).

[26] I. N. Marov, Y. N. Dubrov, V. K. Belyaeva, and A. N. Ermakov, *Doklady Akad. Nauk S.S.S.R.*, 1966, **171**, 385.