Displacement of Tetrahydrofuran Ligands by Tripodal Phosphines. Crystal Structure of $[MoCl_3\{N(CH_2CH_2PPh_2)_3\}]\cdot C_4H_8O$ *

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The complexes $[MoCl_3\{P(CH_2CH_2PPh_2)_3\}]\cdot thf$ and $[MoCl_3\{N(CH_2CH_2PPh_2)_3\}]\cdot thf$ (thf = tetrahydrofuran) have been prepared from $[MoCl_3(thf)_3]$ by ligand replacement reaction of thf. An X-ray crystal structure investigation of $[MoCl_3\{N(CH_2CH_2PPh_2)_3\}]\cdot thf$ shows a distorted-octahedral structure with a meridional arrangement of the three chlorine ligands. The amine acts as tridentate ligand with a pendant PPh_2 group.

The chemistry of molybdenum in low oxidation states, especially those aspects with relevance to nitrogen fixation, has been extensively studied in recent years. Molybdenum dinitrogen complexes are frequently prepared by reduction of a suitable precursor complex under a nitrogen atmosphere. In this sense, $[MoCl_3L_3]$ compounds (L = phosphine) have been used by several authors as precursors, but their low solubility and paramagnetic behaviour usually makes their characterisation difficult. Moreover, the possibilities of *fac* and *mer* isomers and the formation of dimers add complications to a rationalisation of the reduction chemistry of these complexes. The reaction of $[MoCl_3(thf)_3]$ (thf = tetrahydrofuran) with an excess of PMe_3 yields *mer*-$[MoCl_3(PMe_3)_3]$,[1] but the analogous reaction with PMe_2Ph yields a mixture of *fac*- and *mer*-$[MoCl_3(PMe_2Ph)_3]$.[2] With toluene under reflux, *mer*-$[MoCl_3(PMe_3)_3]$ gives a diamagnetic red solid with stoichiometry $[\{MoCl_3(PMe_3)_2\}_n]$. However, $[MoCl_3(thf)_3]$ with PEt_3 under reflux gives $[MoCl_3(PEt_3)_3]$ which has not been fully characterised, and with PEt_2Ph gives $[Mo_2Cl_6(PEt_2Ph)_3]$.[3]

The reaction of bis(diphenylphosphino)methane (dppm) with $[MoCl_3(thf)_3]$ yields a solid of composition $[MoCl_3(dppm)]$, but magnetic studies suggest the existence of dilute molybdenum(III) centres and weak Mo–Mo bonds.[4] Reduction of $[MoCl_4(thf)_2]$ with amalgamated granular tin[5,6] in the presence of PPh_3 and triphos, *viz.* $PPh(CH_2CH_2PPh_2)_2$, in thf as solvent, produces $[MoCl_3(triphos)]$.

Most compounds $[MoCl_3L_3]$ are not yet well characterised because it is seldom possible to prepare single crystals for study by X-ray diffraction. In this paper we report the synthesis of new complexes with formula $[MoCl_3L]$ where L is $N(CH_2CH_2PPh_2)_3$ or $P(CH_2CH_2PPh_2)_3$, tripodal tertiary amine or phosphine compounds able to act as tetradentate donor ligands. The crystal structure of $[MoCl_3\{N(CH_2CH_2PPh_2)_3\}]\cdot thf$ reveals that the ligand is actually tridentate with a pendant PPh_2 group.

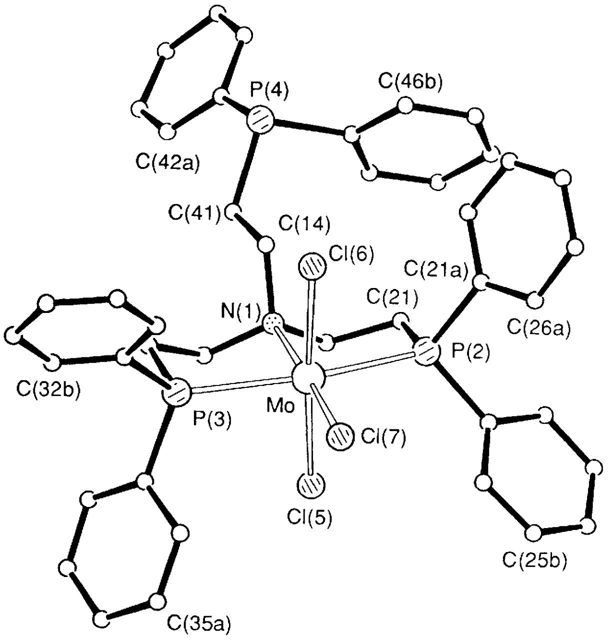

Fig. 1 View of the complex molecule in $[MoCl_3\{N(CH_2CH_2PPh_2)_3\}]\cdot thf$, indicating the atom numbering scheme

Results and Discussion

The reaction of $[MoCl_3(thf)_3]$ with $L = E(CH_2CH_2PPh_2)_3$ (E = N or P) in thf leads to the formation of $[MoCl_3L]\cdot thf$. The substitution is slow and reactions at room temperature often lead to impure samples. Heating the reaction mixture at 50 °C overnight significantly increases the yield and pure compounds are then obtained.

For $[MoCl_3\{N(CH_2CH_2PPh_2)_3\}]\cdot thf$, recrystallisation from thf solution yielded yellow crystals suitable for X-ray analysis. The crystal structure has been determined and final atomic coordinates for all non-hydrogen atoms are listed in Table 1. Fig. 1 shows a view of the complex molecule which has a distorted-octahedral arrangement around the Mo atom of three

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* Trichloro[tris(2-diphenylphosphinoethyl)amine-κ^3N,P,P']molybdenum–tetrahydrofuran(1/1).

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1991, Issue 1, pp. xviii–xxii.

Table 1 Final atomic coordinates (fractional × 10^4) for $[MoCl_3\{N(CH_2CH_2PPh_2)_3\}]\cdot$thf with estimated standard deviations (e.s.d.s) in parentheses

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Mo	3 860.3(2)	3 487.0(2)	3 318.6(2)	C(35a)	799(3)	3 493(2)	4 179(4)
N(1)	5 156(2)	3 557(1)	4 692(2)	C(36a)	1 563(3)	3 278(2)	3 969(3)
C(12)	5 478(3)	4 241(2)	4 783(3)	C(31b)	3 042(3)	1 885(2)	4 063(3)
C(13)	4 802(3)	3 401(2)	5 480(3)	C(32b)	2 813(4)	1 492(3)	4 680(4)
C(14)	5 974(3)	3 129(2)	4 757(3)	C(33b)	2 613(5)	853(3)	4 467(5)
P(2)	4 803.1(8)	4 323.3(5)	2 832.4(7)	C(34b)	2 624(4)	615(3)	3 648(6)
C(21)	5 742(3)	4 480(2)	3 959(3)	C(35b)	2 821(4)	999(3)	3 017(5)
C(21a)	5 403(3)	4 123(2)	2 015(3)	C(36b)	3 030(3)	1 639(2)	3 228(4)
C(22a)	6 210(4)	3 769(3)	2 260(3)	P(4)	7 882.1(9)	2 879.2(6)	5 590.3(9)
C(23a)	6 635(4)	3 608(3)	1 615(4)	C(41)	6 746(3)	3 110(2)	5 707(3)
C(24a)	6 246(4)	3 785(3)	716(4)	C(41a)	8 691(3)	2 968(2)	6 795(3)
C(25a)	5 413(5)	4 116(3)	441(4)	C(42a)	8 432(4)	2 993(3)	7 572(4)
C(26a)	4 982(4)	4 291(3)	1 086(3)	C(43a)	9 099(4)	3 052(3)	8 464(4)
C(21b)	4 254(3)	5 083(2)	2 394(3)	C(44a)	10 014(5)	3 092(3)	8 568(5)
C(22b)	4 793(4)	5 603(2)	2 353(3)	C(45a)	10 299(5)	3 054(4)	7 832(5)
C(23b)	4 373(6)	6 173(3)	1 963(4)	C(46a)	9 638(4)	2 986(4)	6 945(5)
C(24b)	3 428(6)	6 216(3)	1 617(4)	C(41b)	8 144(3)	3 625(2)	5 090(3)
C(25b)	2 896(5)	5 711(3)	1 642(4)	C(42b)	8 211(3)	4 215(3)	5 517(4)
C(26b)	3 295(4)	5 137(2)	2 022(3)	C(43b)	8 402(4)	4 761(3)	5 116(5)
P(3)	3 308.0(7)	2 727.3(5)	4 323.8(7)	C(44b)	8 543(4)	4 732(4)	4 277(5)
C(31)	4 356(3)	2 745(2)	5 376(3)	C(45b)	8 476(4)	4 165(4)	3 835(4)
C(31a)	2 339(3)	3 016(2)	4 663(3)	C(46b)	8 281(3)	3 603(3)	4 229(3)
C(32a)	2 318(3)	2 980(2)	5 551(3)	Cl(5)	3 181.3(7)	4 355.5(5)	3 917.8(7)
C(33a)	1 546(4)	3 201(3)	5 751(4)	Cl(6)	4 628.9(8)	2 683.2(5)	2 721.9(7)
C(34a)	792(4)	3 460(3)	5 068(4)	Cl(7)	2 492.4(8)	3 422.5(6)	1 963.0(7)
The thf molecule							
O(8)	−720(5)	4 384(4)	1 987(5)	C(83)	−12(11)	4 220(7)	937(9)
C(81)	−54(10)	4 898(6)	2 234(8)	C(84)	−683(10)	3 923(7)	1 258(10)
C(82)	434(9)	4 747(7)	1 569(9)				

Table 2 Selected bond dimensions (lengths in Å, angles in °) in $[MoCl_3\{N(CH_2CH_2PPh_2)_3\}]\cdot$thf with e.s.d.s in parentheses

(*a*) About the Mo atom			
Mo–N(1)	2.332(3)	Mo–Cl(5)	2.417(1)
Mo–P(2)	2.524(1)	Mo–Cl(6)	2.395(1)
Mo–P(3)	2.541(1)	Mo–Cl(7)	2.376(1)
N(1)–Mo–P(2)	80.5(1)	P(3)–Mo–Cl(6)	95.2 *
N(1)–Mo–P(3)	81.1(1)	Cl(5)–Mo–Cl(6)	175.5 *
P(2)–Mo–P(3)	161.2 *	N(1)–Mo–Cl(7)	177.2(1)
N(1)–Mo–Cl(5)	87.0(1)	P(2)–Mo–Cl(7)	101.2 *
P(2)–Mo–Cl(5)	86.8 *	P(3)–Mo–Cl(7)	97.0 *
P(3)–Mo–Cl(5)	88.5 *	Cl(5)–Mo–Cl(7)	91.0 *
N(1)–Mo–Cl(6)	91.1(1)	Cl(6)–Mo–Cl(7)	91.1 *
P(2)–Mo–Cl(6)	88.9 *		
(*b*) In the amine ligand			
N(1)–C(12)	1.503(5)	P(3)–C(31)	1.830(3)
N(1)–C(13)	1.511(6)	P(3)–C(31a)	1.816(5)
N(1)–C(14)	1.502(5)	P(3)–C(31b)	1.823(4)
P(2)–C(21)	1.846(4)	P(4)–C(41)	1.850(4)
P(2)–C(21a)	1.823(5)	P(4)–C(41a)	1.836(5)
P(2)–C(21b)	1.814(4)	P(4)–C(41b)	1.841(5)

* E.s.d. less than 0.05°.

chloride ligands in *mer* co-ordination, one nitrogen and two phosphorus atoms. The ligand is thus tridentate using the nitrogen and two phosphorus atoms as donors. The alkyl chain binding nitrogen to the other phosphorus atom, P(4), remains as a free arm of the ligand. The molecular structure is analogous to that of $[CrCl_3\{P(CH_2CH_2PPh_2)_3\}]$ established as *mer*,[7] and it is reasonable to suppose that $[MoCl_3\{P(CH_2CH_2PPh_2)_3\}]\cdot$thf also exists as the *mer* isomer.

Selected bond lengths and angles are listed in Table 2. The Mo–P and Mo–Cl distances are very similar to those found in other octahedral compounds of Mo^{III}.[8,9] The shortest Mo–Cl distance is observed for the chlorine atom opposite to nitrogen in approximate *trans* position. This fact can be interpreted in terms of the relative softness of the Lewis acidity of Mo^{III}, which leads to tighter binding of the softer Lewis base, Cl, instead of the relatively harder N. The co-ordination of N and two P atoms, instead of three P atoms, must increase the stability of $[MoCl_3\{N(CH_2CH_2PPh_2)_3\}]$ because of a higher chelate effect, which compensates the stability loss caused by a weaker nitrogen binding in relation to phosphorus.

The choice of a meridional geometry seems to be principally electronic in origin and can be explained simply in terms of decreasing electrostatic repulsions between X^- (X = Cl, Br or I).[10] The adoption of a facial geometry is more common in related compounds with X^- replaced by neutral ligands such as carbonyls.

The angles in the molybdenum co-ordination sphere also show deviations from the idealised octahedral values, mainly in the chelating N–Mo–P angles which are close to 81°. Almost identical values have been observed for the analogous angles in $[CrCl_3\{P(CH_2CH_2PPh_2)_3\}]$,[7] in contrast with reported values for angles P–Mo–P of 92.3(2) and 96.9(3)° for *mer*-$[MoI_3(PMe_3)_3]$,[10] where no chelate rings are possible.

The thf solvent molecule appears fairly well ordered. Intermolecular contacts, between discrete molecules, are at normal van der Waals distances.

Experimental

Microanalyses were by Butterworth Microanalytical Laboratories, Middlesex.

IR absorption spectra were recorded as Nujol mulls, or KBr pellets on a Pye-Unicam SP3-300 spectrophotometer.

All preparations and manipulations were carried out under oxygen-free nitrogen, following conventional Schlenk techniques.[11] Solvents were dried and degassed before use. All chemicals used were of reagent grade or comparable purity. The ligand tris(2-diphenylphosphinoethyl)amine was prepared from $KPPh_2 \cdot 2(1,4\text{-dioxane})$[12] and $N(CH_2CH_2Cl)_3$[13] as previously described;[14] tris(2-diphenylphosphinoethyl)phosphine was obtained from Aldrich-Chemie.

The complexes $[MoCl_4(thf)_2]$ and $[MoCl_3(thf)_3]$ were prepared by published procedures.[4]

Trichloro[*tris*(2-*diphenylphosphinoethyl*)*amine*]*molybdenum*(III)-*Tetrahydrofuran*(1/1), $[MoCl_3\{N(CH_2CH_2PPh_2)_3\}] \cdot thf$.—A solution of tris(2-diphenylphosphinoethyl)amine (1.62 g, 2.48 mmol) in thf (40 cm^3) was added to a suspension of $[MoCl_3(thf)_3]$ (1.04 g, 2.48 mmol) in thf (25 cm^3) and the mixture stirred at 50 °C overnight. The resulting yellow-green suspension was filtered and the microcrystalline yellow product washed with thf and light petroleum (b.p. 50–70 °C) and dried in vacuum. Recrystallisation from thf gave yellow crystals of the pure product. Yield 1.52 g, 68% (Found: C, 59.50; H, 5.40; N, 1.50. $C_{46}H_{50}Cl_3MoNOP_3$ requires C, 59.55; H, 5.45; N, 1.50%). IR (KBr pellet): ν_{max}/cm^{-1} 3010w, 2960w, 2800w, 1630m, 1470m, 1420s, 1110m, 750s, 740s, 690s, 500m and 320s.

Trichloro[*tris*(2-*diphenylphosphinoethyl*)*phosphine*]*molybdenum*(III)-*Tetrahydrofuran*(1/1), $[MoCl_3\{P(CH_2CH_2PPh_2)_3\}] \cdot thf$.—*Method* 1. This compound was prepared by a method analogous to that described above for the amine complex. Reaction times of 24 h at room temperature or 8 h at 50 °C led to yields close to 70% (Found: C, 58.20; H, 5.40; Cl, 11.70; P, 12.70. $C_{46}H_{50}Cl_3MoOP_4$ requires C, 58.45; H, 5.35; Cl, 11.25; P, 13.10%). IR (KBr pellet): ν_{max}/cm^{-1} 3040w, 2920w, 2890w, 1470s, 1420s, 1390s, 1125s, 1095s, 740s, 680s, 520m and 310m.

Method 2. The compound $[MoCl_4(thf)_2]$ (0.60 g, 1.5 mmol) and amalgamated granular tin (0.18 g, 1.5 mmol) were added to a thf (40 cm^3) solution of PPh_3 (0.75 g, 2.90 mmol) and the phosphine ligand (1.0 g, 1.49 mmol). Within seconds the entire reaction mixture became a dark brown suspension. Stirring was continued for 20 h at room temperature and the tin was then decanted and removed. A bright yellow solid was obtained after filtering and washing with thf. Yield very low (< 10%).

X-Ray Structure Determination of $[MoCl_3\{N(CH_2CH_2PPh_2)_3\}] \cdot thf$.—Air-stable yellow crystals were grown from a thf solution, under dinitrogen, over several weeks.

Crystal data. $C_{42}H_{42}Cl_3MoNP_3 \cdot C_4H_8O$, $M = 928.1$, monoclinic, space group $P2_1/n$ (equivalent to no. 14), $a = 15.111(1)$, $b = 20.949(2)$, $c = 15.259(1)$ Å, $\beta = 110.002(6)°$, $U = 4539.0$ Å^3, $Z = 4$, $D_c = 1.358$ g cm^{-3}, $F(000) = 1916$, μ(Mo-Kα) = 6.0 cm^{-1}, λ(Mo-K$\bar{\alpha}$) = 0.710 69 Å.

An irregularly shaped crystal, *ca.* 0.35 × 0.35 × 0.45 mm, was mounted, in air, on a glass fibre. After preliminary photographic examination it was transferred to an Enraf-Nonius CAD4 diffractometer (with monochromated radiation), where accurate cell dimensions were refined from the goniometer settings of 25 reflections (θ *ca.* 12.5°), each centred in four orientations, and intensity data were measured for reflections having $1.5 < \theta < 20°$.

During processing, corrections were applied for Lorentz and polarisation effects, for deterioration (by *ca.* 40% over the whole data collection), absorption (a minimal correction, from semiempirical, ψ-scan methods), and to eliminate negative net intensities (by Bayesian statistical methods). 7980 Unique reflections (5382 of which were considered 'observed' having $I > 2\sigma_I$) were entered into the SHELX system[15] for structure determination (by conventional Patterson methods) and refinement (by large-block-matrix least-squares methods). Anisotropic thermal parameters were allowed for all non-hydrogen atoms in the complex. The atoms in the thf molecules and the hydrogen atoms (included in idealised positions in the ligand) were refined isotropically.

At convergence, $R = 0.058$ and $R_g = 0.061$[15] for 6846 reflections (those having $I > \sigma_I$), weighted $w = (\sigma_F^2 + 0.000\,64F^2)^{-1}$, and 513 parameters refined in two blocks. The only peaks of significance (maximum *ca.* 0.6 e Å^{-3}) in a final difference map were in the region of the thf molecule.

Scattering factor curves were taken from ref. 16. Computer programs have been noted above and in Table 4 of ref. 17, and were run on a MicroVAX II machine in the Nitrogen Fixation Laboratory.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

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References

1 J. L. Atwood, W. E. Hunter, E. Carmona and G. Wilkinson, *J. Chem. Soc., Dalton Trans.*, 1980, 467.
2 M. W. Anker, J. Chatt, G. J. Leigh and A. G. Wedd, *J. Chem. Soc., Dalton Trans.*, 1975, 2639.
3 E. Carmona, A. Galindo and L. Sánchez, *Polyhedron*, 1984, **3**, 347.
4 J. R. Dilworth and R. L. Richards, *Inorg. Synth.*, 1980, **20**, 119.
5 J. A. Baumann, G. E. Bossard, T. A. George, D. B. Howell, L. M. Koczon, R. K. Lester and C. M. Noddings, *Inorg. Chem.*, 1985, **24**, 3568.
6 T. A. George and R. C. Tisdale, *J. Am. Chem. Soc.*, 1985, **107**, 5157.
7 L. R. Gray, A. L. Hale, W. Levason, F. P. McCullough and M. Webster, *J. Chem. Soc., Dalton Trans.*, 1984, 47.
8 L. K. Fong, J. R. Fox, B. M. Foxman and N. J. Cooper, *Inorg. Chem.*, 1986, **25**, 1880.
9 B. Pietsch and L. Dahlenburg, *Inorg. Chim. Acta*, 1988, **145**, 195.
10 B. E. Owens, R. Poli and A. Rheingold, *Inorg. Chem.*, 1989, **28**, 1456.
11 D. F. Shriver, *Manipulation of Air Sensitive Compounds*, McGraw Hill, New York, 1969.
12 K. Issleib and A. Tzschach, *Chem. Ber.*, 1959, **92**, 1118.
13 J. P. Mason and D. J. Gasch, *J. Am. Chem. Soc.*, 1938, **60**, 2816.
14 R. Morasi and L. Sacconi, *Inorg. Synth.*, 1976, **16**, 174.
15 G. M. Sheldrick, SHELX 76, Program for crystal structure determination, University of Cambridge, 1976.
16 *International Tables for X-Ray Crystallography*, Kynoch Press, Birmingham, 1974, vol. 4, pp. 99 and 149.
17 S. N. Anderson, R. L. Richards and D. L. Hughes, *J. Chem. Soc., Dalton Trans.*, 1986, 245.

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