The Reactions of Dinitrogen Complexes of Molybdenum with Thiols and Sulphenyl Halides

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The dinitrogen complex *trans*-$[Mo(N_2)_2(dpe)_2]$ (dpe = $Ph_2PCH_2CH_2PPh_2$) reacts with thiols RSH (R = Et, Pr^n, Bu^n, or Ph) in tetrahydrofuran (thf) to give the diamagnetic complexes $[Mo(SR)_2(dpe)_2]$, together with dihydrogen and two mole equivalents of dinitrogen. *trans*-$[Mo(N_2)_2(depe)_2]$ (depe = $Et_2PCH_2CH_2PEt_2$) gives $[Mo(SPh)_2(depe)_2]$ with thiophenol. With PhSCl, *trans*-$[Mo(N_2)_2(dpe)_2]$ gives $[MoCl(SPh)(dpe)_2]$ and $2N_2$, but with an excess of PhSBr, $[MoBr_2(dpe)_2]Br_3$ results. The dithio-complexes act as bidentate sulphur-donor ligands and the paramagnetic thio-bridged binuclear complexes $[(dpe)_2Mo(SR)_2MoCl_4]$ and $[(dpe)_2Mo(SBu^n)_2MoCl_3(thf)]Cl$ (R = Ph, Et, Pr^n, and Bu^n) have been prepared, whose magnetic moments indicate bond formation between molybdenum atoms. The diamagnetic adduct $[(dpe)_2Mo(SBu^n)_2Mo(CO)_4]$ has also been obtained.

MOLYBDENUM is an essential requirement of nitrogenase and might bind dinitrogen as a first step in its reduction to ammonia.[1] We have therefore attempted to protonate dinitrogen when it is bound to molybdenum and have already described the reaction of hydrogen halides with *trans*-$[Mo(N_2)_2(dpe)_2]$ (dpe = $Ph_2PCH_2CH_2PPh_2$) which yields complexes of the N_2H_2 ligand.[2] In view of this reaction and the occurrence of thiol groupings in nitrogenase we have investigated the reactions of *trans*-$[Mo(N_2)_2(dpe)_2]$ with thiols. Protonation of dinitrogen did not occur, however, but a new series of dithio-derivatives of molybdenum were obtained which are described below.

Reactions with Thiols.—On treatment of *trans*-$[Mo(N_2)_2(dpe)_2]$ with thiols in thf solution, reaction of the dinitrogen ligand did not occur, but, as is often found for dinitrogen complexes,[3] there was an oxidative addition to the metal with quantitative evolution of dinitrogen together with dihydrogen [equation (1)]. The dithio-

$$\textit{trans}\text{-}[Mo(N_2)_2(dpe)_2] + 2RSH \xrightarrow{thf} \underset{(A)}{[Mo(SR)_2(dpe)_2]} + H_2 + 2N_2 \quad (1)$$

compounds (A) are non-conducting in nitromethane or dichloromethane solutions, diamagnetic, poorly soluble yellow solids except for R = Ph, when the compound is red. Only the SPr^n and SBu^n derivatives were sufficiently soluble for molecular-weight determination, which showed them to be monomeric in dichloroethane solution.

Reaction (1) proceeded smoothly at room temperature *via* an initially formed green solution, but no intermediate in the reaction could be isolated. $[Mo(SPh)_2(dpe)_2]$ Was also prepared from $[MoH_n(dpe)_2]$[4] (n = 2 or 4) and PhSH or as in equation (1), but using PhSSPh instead of PhSH. The related dinitrogen complex $[Mo(N_2)_2(depe)_2]$(depe = $Et_2PCH_2CH_2PEt_2$) also gave an analogous bis(phenylthio)-derivative with PhSH but the reaction was much slower than in (1).

A number of dithio-derivatives of molybdenum are known which also have cyclopentadienyl groups as ligands and a feature of their chemistry is that they form dinuclear complexes in which the ligating thio-groups bridge to a second metal atom.[5] Similarly, $[Mo(SBu^n)_2(dpe)_2]$ reacts to give the binuclear compound (B) [equation (2)]. Compound (B) is diamagnetic, non-

$$[Mo(SBu^n)_2(dpe)_2] + [Mo(CO)_4C_7H_8] = \underset{(B)}{[(dpe)_2Mo(SBu^n)_2Mo(CO)_4]} + C_7H_8 \quad (2)$$

$$(C_7H_8 = \text{norbornadiene})$$

conducting, and has bands in the CO stretching region (2 025, 1 923, 1 904, and 1 884 cm^{-1}) which are very close to those of $[Mo(CO)_4(MeSCH_2CH_2SMe)]$ (2 030, 1 919, 1 905, and 1 868 cm^{-1})[6] which contains a chelate disulphide ligand. In solution, (B) is rather sensitive to air and thus gives a somewhat low molecular-weight value, but it is clearly binuclear and its similarity to the disulphide derivative indicates that its SBu^n groups bridge the two molybdenum atoms.

A related series of binuclear compounds may also be obtained [equation (3)]. These binuclear compounds are

$$[Mo(SR)_2(dpe)_2] + [MoCl_4(R'CN)_2] \xrightarrow{thf} [(dpe)_2Mo(SR)_2MoCl_4] + 2R'CN \quad (3)$$

$$(R = Ph, Et, Pr^n, \text{ or } Bu^n;\ R' = Me \text{ or } Et)$$

yellow-brown crystalline solids. They conduct in nitromethane or dichloromethane solutions owing to the presence of a labile chloride which is easily displaced by thf if they are recrystallised from solutions containing it [*e.g.* equation (4)]. (Because of this behaviour and their

$$[(dpe)_2Mo(SBu^n)_2MoCl_4] \xrightarrow[CH_2Cl_2]{thf} \underset{(C)}{[(dpe)_2Mo(SBu^n)_2MoCl_3(thf)]Cl} \quad (4)$$

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[1] J. Chatt in 'Proceedings of the First International Conference on the Chemistry and Uses of Molybdenum,' ed. P. C. H. Mitchell, Climax Molybdenum Company Limited, London, 1973, p. 224.

[2] J. Chatt, G. A. Heath, and R. L. Richards, *J.C.S. Chem. Comm.*, 1972, 1010.

[3] J. Chatt and R. L. Richards in 'The Chemistry and Biochemistry of Nitrogen Fixation,' ed. J. R. Postgate, Plenum Press, London, 1971, p. 57.

[4] See A. Frigo, G. Pussi, and A. Turco, *Gazzetta*, 1971, **101**, 637, for a discussion on the formulation of this compound.

[5] A. R. Dias and M. L. H. Green, *J. Chem. Soc.* (*A*), 1971, 1951; W. E. Douglas and M. L. H. Green, *J.C.S. Dalton*, 1972, 1796, and references therein.

[6] H. C. E. Manners-Koutz and G. Wilkinson, *J. Chem. Soc.*, 1962, 4454.

rather low solubility molecular-weight data are unreliable.)

Compound (C) may also be synthesised from [$MoCl_4$-($thf)_2$] and the dithio-compound. It is disrupted by an excess of EtCN regenerating the dithio-starting material which indicates that (C) and its analogues are μ-dithio-complexes. Complex (C) and its analogues are dark brown, crystalline, 1 : 1 electrolytes in solution and tend to retain solvent of crystallisation (Table).

Compound	Appearance	M.p.[a] (θ/°C)	M [b]	Λ_M/Ω^{-1} cm^2 mol^{-1}	μ_{eff}/B.M. (295 °C)	Analyses (%) [d]			
						C	H	Cl	S
[$Mo(SPh)_2(dpe)_2$]	Red prisms	210—230				69.5 (69.3)	5.7 (5.2)		5.9 (5.8)
[$Mo(SEt)_2(dpe)_2$]	Yellow prisms	238—240				66.3 (66.3)	6.1 (5.7)		6.3 (6.3)
[$Mo(SPr^n)_2(dpe)_2$]	Yellow crystals	220—222	957 (1 042)			66.6 (66.9)	6.1 (6.0)		
[$Mo(SBu^n)_2(dpe)_2$]	Yellow crystals	216—218	1 020 (1 070)			67.4 (67.4)	6.4 (6.2)		6.2 (6.0)
[$(dpe)_2Mo(SPh)_2MoCl_4$]	Purplish solid	200—230				56.2 (57.0)	4.7 (4.3)	10.7 (10.5)	4.9 (4.8)
[$(dpe)_2Mo(SEt)_2MoCl_4$]	Yellow-brown solid	201—207		46 [e]		53.6 (53.7)	5.2 (4.6)	11.3 (11.3)	
[$(dpe)_2Mo(SPr^n)_2MoCl_4$]	Yellow-brown solid	200—210		49 [c]	3.4	54.2 (54.4)	5.2 (4.8)	11.7 (11.1)	
[$(dpe)_2Mo(SBu^n)_2MoCl_4$]	Light brown crystals	218—222		47 [e]	3.2	55.1 (55.1)	4.9 (5.0)	11.2 (10.8)	
[$(dpe)_2Mo(SEt)_2MoCl_3(thf)]Cl\cdot\frac{1}{2}CH_2Cl_2$	Light brown crystals	225—229		86 [c]	3.6	53.5 (53.2)	5.1 (4.9)	12.9 (13.0)	
[$(dpe)_2Mo(SPr^n)_2MoCl_3(thf)]Cl\cdot\frac{1}{2}CH_2Cl_2$	Brown crystals	211—218		68 [c]	3.8	53.7 (53.8)	5.5 (5.1)	12.7 (12.7)	
[$(dpe)_2Mo(SBu^n)_2MoCl_3(thf)]Cl\cdot\frac{1}{2}CH_2Cl_2$	Brown crystals	215—223		73 [c]	3.6	54.1 (54.4)	5.4 (5.3)	12.5 (12.5)	
[$(dpe)_2Mo(SBu^n)_2MoCl_3(thf)]Cl$	Dark brown crystals	211—223		59 [c]	3.7	55.7 (55.7)	5.6 (5.4)	9.8 (10.3)	
[$Mo(SPh)Cl(dpe)_2$]	Red crystals	216—218				66.9 (67.1)	5.5 (5.2)	3.1 (3.4)	
[$(dpe)_2Mo(SBu^n)_2Mo(CO)_4$]	Orange-brown crystals	Decomp. >180	1 150 (1 278)			60.5 (60.1)	5.0 (5.2)		
[$Mo(SPh)_2(depe)_2$]	Orange-brown crystals	180—195				53.2 (52.9)	8.1 (8.1)		

[a] In sealed evacuated tubes with decomposition. In $C_2H_4Cl_2$ solution. [c] In $MeNO_2$ solution. [d] Calculated values in parentheses. [e] In CH_2Cl_2 solution.

dpe = 1,2-bis(diphenylphosphino)ethane [$Ph_2PCH_2CH_2PPh_2$], depe = 1,2-bis(diethylphosphino)ethane [$Et_2PCH_2CH_2PEt_2$].

Magnetic Properties.—These binuclear complexes are paramagnetic with moments at 295 °C which are too high [3.2—3.8 B.M. (Table)] for them to be regarded simply as adducts of the Mo^{IV} (d^2) ion formed by donation of lone pairs of electrons from the sulphur atoms of the diamagnetic Mo^{II} (d^4) species. There must therefore be, in addition to the μ-dithio-linkage, a molybdenum–molybdenum interaction. This would produce a low-lying bonding orbital into which two electrons could be placed. The remaining four metal electrons would then be placed singly into the remaining non-bonding *d*-orbitals so that the system could be formally regarded as a molybdenum(III) (d^3) ion joined to a molybdenum(V) (d^1) ion *via* a metal–metal bond and the μ-dithio-groups. The observed magnetic moment is less than the spin-only value because of spin–orbit coupling but an antiferromagnetic interaction also seems very likely. Although the plot of $1/\chi_m$ *versus* temperature for [$(dpe)_2Mo(SPr^n)_2$-$MoCl_4$] is fairly linear from 249 to 87 K, there is a distinct curvature to lower temperatures (Figure) suggesting that the system could have a Neél point below 87 K. This magnetic behaviour, together with the i.r. spectrum of compound (B) and the disruption of compound (C), leaving the [$Mo(SBu^n)_2(dpe)_2$] unit intact, confirms that these compounds are μ-dithio-complexes.

Spectroscopic data for these compounds are not detailed in this paper since they are not generally diagnostic of structure, but two points are worth noting. The i.r. spectra of the μ-dithio-complexes containing thf, while difficult to assign in the 500—1 500 cm^{-1} regions because of the large number of ligand bands, nevertheless show bands at about 1 025 and 870 cm^{-1} which are assigned to this ligand. The compounds [$(dpe)_2Mo(SR)_2$-$MoCl_4$] show strong broad i.r. bands assigned to Mo–Cl stretching [R = Et, 335, 305; R = Pr^n, 332, 309; R = Bu^n, 333, 305 cm^{-1}] in a similar pattern to those of *cis*-[$MoCl_4$dpe],[7] consistent with the expected *cis*-configuration of the $MoCl_4(SR)_2$ grouping in these molecules. In view of the ready reactions of [$Mo(SR)_2$-$(dpe)_2$] (R = alkyl) in solution, a *cis*-configuration seems most likely for these yellow complexes whereas the red -SPh- analogue, which reacts much more slowly, may have the *trans*-configuration.

Attempts were made to reduce the $MoCl_4$ moiety in its binuclear complexes with zinc and also with magnesium in the presence of dpe, hoping to incorporate dinitrogen into the complexes. No nitrogen-containing products were isolated from these reactions, however.

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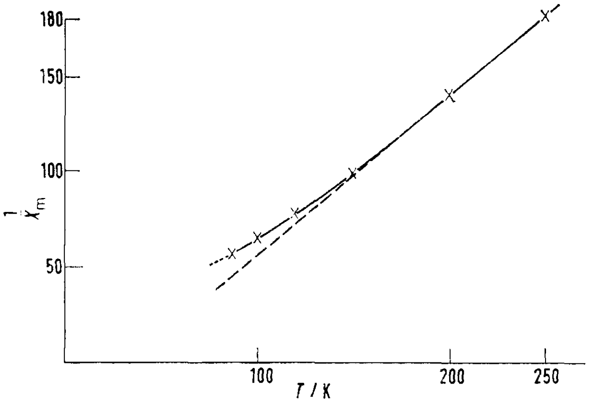
[7] A. V. Butcher and J. Chatt, *J. Chem. Soc.* (*A*), 1970, 2652.

Reactions with Sulphenyl Halides.—Although organic acid chlorides react with the ligating dinitrogen of molybdenum and tungsten bis-dinitrogen complexes [8] and the PhS^+ ion was reported to react with dinitrogen, [9] no such interaction occurred when *trans*-$[Mo(N_2)_2(dpe)_2]$ was treated with PhSX (X = Cl or Br).

Quantitative evolution of dinitrogen occurred with PhSCl, with formation of a diamagnetic, non-conducting, monothio-derivative [equation (5)].

$$trans\text{-}[Mo(N_2)_2(dpe)_2] + PhSCl \xrightarrow{thf} [MoCl(SPh)(dpe)_2] + 2N_2 \quad (5)$$

Benzenesulphenyl bromide did not react analogously, but gave at −25 °C in thf solution with one mole equivalent of the dinitrogen complex, a thermally unstable pink complex. This complex had a strong band at 2 030 cm^{-1} (Nujol mull), contained nitrogen, and is probably the molybdenum(I) species *trans*-$[Mo(N_2)_2(dpe)_2]^+$ previously obtained [10] by iodine oxidation of *trans*-$[Mo(N_2)_2(dpe)_2]$. A large excess of PhSBr oxidised the dinitrogen complex further, with loss of dinitrogen to give $[MoBr_2(dpe)_2]Br_3$, which was also obtained if an excess of dibromine was used as reagent. The fate of the sulphur-containing products was not investigated.



Plot of $1/\chi_m$ *vs.* T for $[(dpe)_2Mo(SPr^n)_2MoCl_4]$

These reactions are further illustrations of the synthetic potential of dinitrogen complexes [3] which may be regarded as a source of a very reactive low-valent metal centre by ready loss of dinitrogen.

EXPERIMENTAL

The molybdenum complexes $[MoCl_4(EtCN)_2]$,[11] $[MoCl_4(thf)_2]$,[11] $[MoH_n(diphos)_2]$,[12] $[Mo(CO)_4C_7H_8]$,[13] and *trans*-$[Mo(N_2)_2(diphos)_2]$[14] (diphos = dpe or depe) were prepared and purified by established methods. Benzenesulphenyl halides were prepared by the action of the halogen on diphenyl disulphide; PhSCl was purified by vacuum distillation before use, but PhSBr was used as formed. The thiols used were reagent grade and were distilled before use. I.r. spectra were determined using Perkin-Elmer 337 or Grubb–Parsons DM4 instruments. N.m.r. spectra were measured on Varian HA100 or T60 instruments and mass spectra were obtained with an AEI MS10 instrument. Melting points were determined *in vacuo* on an Electrothermal melting-point apparatus. Conductivities were measured using a Portland Electronics Conductivity Bridge. Magnetic susceptibilities were measured using a Faraday balance and molecular weights were determined with a Hitachi–Perkin-Elmer model 115 osmometer. Analyses were by Mr. A. G. Olney of these laboratories or Dr. A. Bernhardt, West Germany. Solvents were purified and dried by standard methods and distilled in an atmosphere of dinitrogen before use. All reactions were carried out under dinitrogen or *in vacuo* using standard techniques as appropriate. Analytical data *etc.* for compounds prepared are shown in the Table. Typical preparations of these compounds are given below.

Bis[bis(diphenylphosphino)ethane]bis(ethylthio)molybdenum, $[Mo(SEt)_2(dpe)_2]$.—Ethanethiol (0.09 cm^3, 1.2 mmol) was condensed onto a solution of *trans*-$[Mo(N_2)_2(dpe)_2]$ (0.23 g, 0.24 mmol) in thf (30 cm^3) at −196 °C. After the mixture had warmed to 20 °C and been set aside for a further 5 h a yellow solid precipitated. Dinitrogen (10.1 cm^3, 0.45 mmol) and dihydrogen (5.0 cm^3, 0.22 mmol) were evolved. The relative amounts of dihydrogen and dinitrogen were determined by measuring the total volume of gas before and after removal of dihydrogen from the mixture, by oxidising it with CuO at 450 °C and freezing out (at −196 °C) the water produced. The gases were identified in this and in other experiments by mass spectrometry.

The solid was filtered, washed with hexane (2 × 10 cm^3), and dried *in vacuo* to give the *complex* as bright yellow crystals (0.17 g, 0.17 mmol, 71%). The Pr^n and Bu^n derivatives were prepared similarly.

Bis[bis(diphenylphosphino)ethane]bis(phenylthio)molybdenum, $[Mo(SPh)_2(dpe)_2]$ (D).—(a) *By reaction of* trans-$[Mo(N_2)_2(dpe)_2]$ *with* PhSH. Thiophenol (0.15 cm^3, 1.4 mmol) was added to a stirred solution of the dinitrogen complex (0.25 g, 0.26 mmol) in thf (30 cm^3) *in vacuo*. The initial orange solution gradually became, during 4 h, green, then brown, finally precipitating a red solid after 12 h. Dinitrogen (11.4 cm^3, 0.51 mmol) and dihydrogen (5.6 cm^3, 0.25 mmol) were evolved. The solid was filtered, washed with hexane (2 × 10 cm^3), and dried *in vacuo* giving the complex as deep red *prisms* (0.2 g, 0.13 mmol, 69%).

(b) *By reaction of* trans-$[Mo(N_2)_2(dpe)_2]$ *with* PhSSPh. Diphenyl disulphide (0.1 g, 0.45 mmol) and the dinitrogen complex (0.18 g, 0.19 mmol) were dissolved in thf (40 cm^3) and the solution was stirred for 48 h. The solvent was reduced in volume (20 cm^3) and hexane (20 cm^3) was added, to precipitate a red powder. This was filtered off, washed with hexane (2 × 10 cm^3), and dried *in vacuo* affording complex (D) with identical i.r. spectrum and m.p. to an authentic sample.

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[9] D. C. Owsley and G. K. Helenkamp, *J. Amer. Chem. Soc.*, 1967, **89**, 4558.

[10] T. A. George and C. D. Siebold, *Inorg. Chem.*, 1973, **12**, 2548.

[11] E. A. Allen, B. J. Brisdon, and G. W. A. Fowles, *J. Chem. Soc.*, 1964, 4531.

[12] F. Pennella, *Chem. Comm.*, 1971, 158.

[13] M. A. Bennett, L. Pratt, and G. Wilkinson, *J. Chem. Soc.*, 1961, 2037.

[14] J. Chatt and A. G. Wedd, *J. Organometallic Chem.*, 1971, **27**, C15; J. Chatt, G. A. Heath, and R. L. Richards, *J.C.S. Dalton*, 1974, 2074.

(c) *By reaction of* [MoH$_n$(dpe)$_2$] *with* PhSH. Thiophenol (0.3 g) was added to [MoH$_n$(dpe)$_2$] (0.56 g, 0.58 mmol) in thf (35 cm^3) and the mixture was stirred under dinitrogen for 78 h, when a bright red precipitate of (D) separated (0.4 g, 0.36 mmol, 65%) which was filtered off, washed with hexane, dried, and identified (i.r. and m.p.).

Bis[bis(diethylphosphino)ethane]bis(phenylthio)molybdenum, [Mo(SPh)$_2$(depe)$_2$].—Thiophenol (0.08 cm^3, 0.86 mmol) was added to a stirred solution of *trans*-[Mo(N$_2$)$_2$(depe)$_2$] complex (0.045 g, 0.077 mmol) in thf (25 cm^3). The solution was heated at reflux for 48 h, when the orange colour gradually changed to a dark brown. The solvent was then removed *in vacuo* leaving a brown powder which gave orange-brown *crystals* from thf–hexane (0.037 g, 0.048 mmol, 62%).

Di-μ-alkylthio-bis[bis(diphenylphosphino)ethane](tetrachloromolybdenum)molybdenum, [(dpe)$_2$Mo(SR)$_2$MoCl$_4$].—The dithio-complex (0.15 mmol) and the complex [MoCl$_4$(R′CN)$_2$] (R′ = Me or Et) (0.15 mmol) were stirred in thf (30 ml) for *ca.* 3 h. The resulting brown precipitate was filtered off, recrystallised from CH$_2$Cl$_2$–thf (3 : 1 v/v) to give brown crystals of the required *complex* [(dpe)$_2$Mo(SR)$_2$MoCl$_4$] (R = Et, Pr^n, and Bu^n). The analogue with R = Ph was similarly prepared; yields were close to 60%. If these complexes were recrystallised from CH$_2$Cl$_2$–thf (1 : 3 v/v), then dark brown *crystals* of the complexes [(dpe)$_2$Mo(SR)$_2$MoCl$_3$(thf)]Cl containing $\frac{1}{2}$CH$_2$Cl$_2$ of crystallisation were obtained in 75—85% yield.

Bis[bis(diphenylphosphino)ethane]-di-μ-n-butylthio-trichloro-(tetrahydrofuranmolybdenum)molybdenum Chloride, [(dpe)$_2$Mo(SBu^n)$_2$MoCl$_3$(thf)]Cl.—Tetrahydrofuran (35 cm^3) was added to the dithio-complex (0.32 g, 0.3 mmol) and [MoCl$_4$(thf)$_2$] (0.114 g, 0.3 mmol) and an immediate brown-black precipitate was formed. The mixture was stirred for 2 h, filtered, and the dark solid crystallised from CH$_2$Cl$_2$–thf, to give brown-black *crystals* of [(dpe)$_2$Mo(SBu^n)$_2$MoCl$_3$(thf)]Cl (0.21 g, 0.15 mmol, 50%). If the reaction was allowed to proceed for 24 h without isolation of the above intermediate, a dark brown solid was obtained which was filtered off as above and recrystallised from CH$_2$Cl$_2$–thf to give dark brown crystals of [(dpe)$_2$Mo(SBu^n)$_2$MoCl$_4$] (0.2 g, 55%).

Reaction of [(dpe)$_2$Mo(SBu^n)$_2$MoCl$_4$(thf)] *with* EtCN.—The binuclear complex (0.06 g, 0.05 mmol) was dissolved in EtCN (30 cm^3). The solution was stirred for 2 h when a yellow-orange precipitate formed which was filtered off, washed with hexane (2 × 5 cm^3), and dried *in vacuo*. It was shown by its i.r. spectrum and m.p. to be [Mo(SBu^n)$_2$(dpe)$_2$] (yield 80%).

Bis[bis(diphenylphosphino)ethane]di-μ-n-butylthio-(tetracarbonylmolybdenum)molybdenum, [(dpe)$_2$Mo(SBu^n)$_2$Mo(CO)$_4$].—[Mo(SBu^n)$_2$(dpe)$_2$] (0.25 g, 0.23 mmol) and [Mo(CO)$_4$(C$_7$H$_8$)] (0.8 g, 0.26 mmol) were heated in thf (40 cm^3) under reflux for 10 h to give a dark brown solution. The solvent was removed *in vacuo* to leave a dark brown oily residue which was dissolved in benzene (3 cm^3) and chromatographed. (Alumina, grade 3, 15 × 2 cm column.) Benzene–hexane (2 : 1 v/v) eluted a red-brown band, which gave the *complex* as a brown solid on removal of the solvent. The product was further purified by recrystallisation from benzene–hexane as brown *crystals* (0.09 g, 0.73 mmol, 52%).

[Bis(bisdiphenylphosphino)ethane]chloro(phenylthio)molybdenum, [MoCl(SPh)(dpe)$_2$].—Benzenesulphenyl chloride (0.07 g, 0.5 mmol) was added to a stirred solution of the dinitrogen complex (0.47 g, 0.5 mmol) in thf (50 cm^3). The orange solution gradually darkened during a period of 18 h to give a deep brown solution from which the solvent and any unchanged PhSCl were removed *in vacuo*. The residue was redissolved in thf, filtered, and reduced in volume (10 cm^3) *in vacuo*. On addition of hexane (20 cm^3) a red solid precipitated from the solution which was filtered and purified by reprecipitation from thf–hexane to give a red crystalline *solid* of [MoCl(SPh)(dpe)$_2$] (0.26 g, 0.25 mmol, 50%).

Reaction of trans-[Mo(N$_2$)$_2$(dpe)$_2$] *with Benzenesulphenyl Bromide.*—(a) Benzenesulphenyl bromide (0.54 mmol) was added to a solution of the dinitrogen complex (0.26 g, 0.27 mmol) in thf (40 cm^3) at −25 °C and the mixture was stirred in the dark for 3 h. The resulting pink solution was poured into hexane (150 cm^3) at −25 °C and the pink precipitate which formed was rapidly filtered and dried *in vacuo*. The i.r. spectrum of the pink solid in Nujol showed a strong band at 2 030 cm^{-1} which diminished in intensity during a period of a few minutes. At temperatures over −10 °C the pink solid changed to a pale yellow compound in which the band at 2 030 cm^{-1} was absent. Nitrogen analysis of the pink complex showed the presence of nitrogen (N = 1.2%) but this value diminished rapidly because of thermal decomposition.

(b) Benzenesulphenyl bromide (3.2 mmol) was added at −25 °C to a solution of the dinitrogen complex (0.40 g, 0.42 mmol) in thf (60 cm^3) and the mixture was stirred for 4 h. A red solution formed which deposited *dibromobis(diphenylphosphinoethane)molybdenum tribromide,* [MoBr$_2$(dpe)$_2$]Br$_3$, as lustrous purple crystals [0.3 g, 61%, m.p. 168—170 °C; μ_{eff} = 3.7 B.M.; Λ_{m} = 67 Ω cm^{-2} mol^{-1} in 10^{-3}M-CH$_2$Cl$_2$ [60 Ω cm^{-2} mol^{-1} expected for a 1 : 1 electrolyte [15]] (Found C, 48.6; H, 3.9; Br, 31.2. C$_{52}$H$_{48}$Br$_5$Mo requires C, 48.3; H, 3.7; Br, 30.9%).

Reaction with Dibromine.—The above experiments were repeated, but using the same molecular quantities of dibromine rather than PhSBr. The same products were obtained in similar yields.

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