The Preparation, Structure, and Reactions of the Mononuclear Thiolate–Hydride Complexes $[MoH(SR)(dppe)_2]$ (R = Bulky Alkyl or Aryl Group, dppe = $Ph_2PCH_2CH_2PPh_2$); *X*-Ray Structure Determination of *cis*-$[MoH(SC_6H_2Pr^i{}_3$-2,4,6)$(dppe)_2]$†

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Reaction of *trans*-$[Mo(N_2)_2(dppe)_2]$ (dppe = $Ph_2PCH_2CH_2PPh_2$) with the bulky thiols RSH (R = Pr^i, Bu^t, $C_6H_2Me_3$-2,4,6, $C_6H_2Pr^i{}_3$-2,4,6, or $C_6H_2BrPr^i{}_2$-4,2,6) at reflux in tetrahydrofuran (thf) gives the green hydride complexes $[MoH(SR)(dppe)_2]$. The complex *cis*-$[MoH(SC_6H_2Pr^i{}_3$-2,4,6)-$(dppe)_2]\cdot 0.5C_6H_5Me$ has a distorted octahedral structure, with distances: Mo–S 2.402(2), Mo–H 1.61(9), Mo–P 2.380(2)—2.465(2) Å. The ^1H hydride resonances of these compounds occur in the range −3.98 to −4.98 p.p.m. (relative to $SiMe_4$) and show fluxionality at room temperature with respect to the phosphorus atoms except for R = $C_6H_2BrPr^i{}_2$-4,2,6. Other spectroscopic properties of the compounds are used as a basis to discuss the mechanism of their formation. The complex $[MoH(SC_6H_2Pr^i{}_3$-2,4,6)$(dppe)_2]$ reacts at 20 °C with CO or Bu^tNC to give the known compounds $[Mo(CO)_2(dppe)_2]$ and $[Mo(Bu^tNC)_2(dppe)_2]$, and with PhSH to give *trans*-$[Mo(SPh)_2(dppe)_2]$.

Studies of the structure and mode of action of nitrogenase suggest that the reduction of dinitrogen by this enzyme occurs at a single molybdenum centre with a sulphur environment and that this centre may carry hydride ligands which are displaced upon dinitrogen uptake.[1,2]

We have therefore sought to synthesise mononuclear hydride complexes of molybdenum with sulphur-containing co-ligands, initially turning our attention to thiolate as a co-ligand. Previous to this work, only one mononuclear thiolate–hydride complex of molybdenum had been reported,[3] $[MoH(C_6H_4S_2\text{-}1,2)_3]^{3-}$. Indeed, there are few examples of this class of complex for any metal. They are restricted to the series $[IrH(X)(SR)(CO)(PPh_3)_2]$ (X = halide, R = alkyl or aryl),[4] $[IrH(Ph_2PCH_2CH_2SH)(CO)]^+$,[5] $[RhH(Cl)(SC_6H_4Me)(PPh_3)_2]$,[6] and $[RuH(SR)(PPh_3)_2]$,[7] which are generally unstable with respect to elimination of the thiol.

During the course of our earlier studies[8] on the reactions of thiols (RSH, R = alkyl or aryl) with *trans*-$[Mo(N_2)_2(dppe)_2]$ (dppe = $Ph_2PCH_2CH_2PPh_2$) to give the series *trans*-$[Mo(SR)_2(dppe)_2]$, we noticed that the reactions proceeded through a green intermediate stage. We reasoned that use of bulky RSH reagents [R = Pr^i, Bu^t, $C_6H_2Me_3$-2,4,6 (Htmbt), $C_6H_2Pr^i{}_3$-2,4,6 (Htpbt), or $C_6H_2BrPr^i{}_2$-4,2,6 (Hbdpbt)] might stabilise intermediates in the reaction and the use of these thiols has led to the isolation of the first series of mononuclear hydride–thiolate complexes of molybdenum, $[MoH(SR)(dppe)_2]$. Their preparation has been briefly described[9] and here we give full details of their properties including possible mechanisms of their formation, their reactions with CO and Bu^tNC, and the *X*-ray structure determination of a representative complex, *cis*-$[MoH(tpbt)(dppe)_2]$.

Results and Discussion

The reaction of *trans*-$[Mo(N_2)_2(dppe)_2]$ in tetrahydrofuran (thf) with sterically demanding thiols, RSH, gives the bright green, thiolate–hydride complexes $[MoH(SR)(dppe)_2]$ (**A**) as shown in equation (1) (SR = SPr^i, SBu^t, tmbt, tpbt, or bdpbt).

$$trans\text{-}[Mo(N_2)_2(dppe)_2] + RSH \xrightarrow[1\ h]{thf,\ 60\ °C} [MoH(SR)(dppe)_2]\ (\mathbf{A}) + 2N_2 \quad (1)$$

Complexes (**A**) are stable in air for short periods and in solution in thf and CH_2Cl_2 under N_2, but decompose rapidly in methanol. They react rapidly in thf with carbon monoxide, generating the known species *trans*-$[Mo(CO)_2(dppe)_2]$ (which isomerises to the *cis* compound),[10] with elimination of RSH. A similar reaction occurs, albeit more slowly, with Bu^tNC, giving *trans*-$[Mo(Bu^tNC)_2(dppe)_2]$.[11] Compounds (**A**) may be converted to *trans*-$[Mo(SR')_2(dppe)_2]$[8] by reaction with less bulky thiols R′SH (R′ = Pr^n or Ph) at room temperature (see later).

Table 1 lists the microanalytical and spectroscopic properties of complexes (**A**). The ν(MoH) values observed in the i.r. spectra span the range 1 660—1 735 cm^{-1}, which is low in comparison to those of other thiolate–monohydride complexes such as $[RuH(SR)(PPh_3)_2]$ [R = Me, CH_2Ph, or Ph; ν(RuH) at 1 985—1 995 cm^{-1}][7] and $[IrH(SMe)(dppe)_2]^+$ [ν(IrH) at 2 132 cm^{-1}],[4] although in the range usually observed for polyhydrides of molybdenum.[12] The electronic spectra show a peak in the range 595—641 nm (Table 1) and intense charge-transfer bands are seen below 500 nm.

The $^{31}P\text{-}\{^1H\}$ n.m.r. spectra in thf or CH_2Cl_2 show a broad signal in the region −57.0 to −69.5 p.p.m. [relative to $P(OMe)_3$, Table 1] which is downfield of the parent complex *trans*-$[Mo(N_2)_2(dppe)_2]$ (−75.3 p.p.m.). The broadness of the signal suggested that complexes (**A**) are fluxional and therefore variable-temperature n.m.r. spectra were obtained. The ^{31}P n.m.r. spectrum of $[MoH(tpbt)(dppe)_2]$ was examined in some detail. At −60 °C it resolves into an ABCD multiplet pattern as shown in Figure 1(*a*) (derived coupling constants and shifts for the low-temperature form are in Table 1). This pattern is consistent with the solid-state structure of the complex (see below).

The ^1H n.m.r. spectra of compounds (**A**) showed in general a quintet resonance for the hydride ligand in the range −3.98 to −4.98 p.p.m. (relative to $SiMe_4$, Table 1) as expected for coupling of the fluxional hydride to the four phosphorus atoms. The values of $|^2J(PH)|$ (45—47 Hz) are not unexpected for

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† *cis*-Bis[1,2-bis(diphenylphosphino)ethane]hydrido(2,4,6-triisopropylbenzene-1-thiolato)molybdenum(II).

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1987, Issue 1, pp. xvii—xx.

Table 1. Microanalytical and spectroscopic properties of $[MoH(SR)(dppe)_2]$

Compound	Colour	Analysis[a] (%)		$\nu(MoH)$[b]/ cm^{-1}	Electronic spectrum[c] $\lambda_{max.}$/nm ($\varepsilon/dm^3\ mol^{-1}\ cm^{-1}$)	$\delta(^{31}P)$[d]/ p.p.m.	$\delta(Mo-^1H)$[e]/ p.p.m.	$^2J(PH)$/Hz
		C	H					
$[MoH(SPr^i)(dppe)_2]$	Olive green	68.5 (68.3)	5.9 (5.7)	1 690	595 (1 768) 599[f]	−58.0	−4.85	45.40 ± 0.01
$[MoH(SBu^t)(dppe)_2]$	Olive green	68.8 (68.5)	5.7 (5.8)	1 700	604 (1 360)	−57.0	−3.98	45.04 ± 0.01
$[MoH(tmbt)(dppe)_2]$	Bright green	70.4 (70.1)	6.1 (5.8)	1 710	625 (893)	−61.1	−4.98	46.40 ± 0.07
$[MoH(bdpbt)(dppe)_2]$	Bright green	65.1 (65.1)	6.0 (5.4)	1 660	641 (1 025)	−62.0	−4.78	46.0 ± 3.0
$[MoH(tpbt)(dppe)_2]$	Bright green	71.5 (71.3)	6.6 (6.4)	1 735	637 (1 235) 638[f]	−69.5[g]	−4.75	47.0 ± 2.0

[a] Calculated values in parentheses. [b] Nujol mulls. [c] *ca.* 3×10^4 mol dm^{-3} thf solutions except where indicated. [d] Broad resonance in thf solution relative to $P(OMe)_3$. [e] In CD_2Cl_2 solution relative to $SiMe_3$, centre of quintet. [f] *ca.* 3×10^{-4} mol dm^{-3} CH_2Cl_2 solutions. [g] At −60 °C resolves into ABCD spectrum, parameters derived by simulation: δ_A −37.01, δ_B −57.57, δ_C −65.60, δ_D −85.06 p.p.m.; J_{AB} 32.00, J_{AC} 11.00, J_{AD} 11.00, J_{BC} 19.00, J_{BD} 8.00, J_{CD} 144.79 Hz.

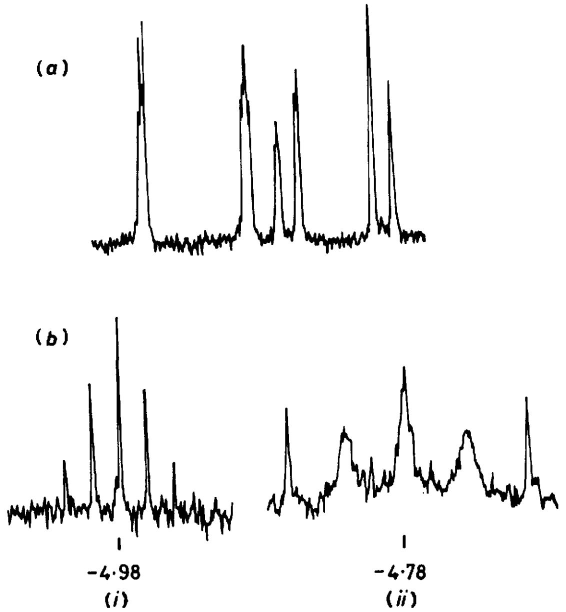


Figure 1. (*a*) Low-temperature ^{31}P n.m.r. spectrum of $[MoH(tpbt)(dppe)_2]$ (see Table 1 for details) and (*b*) ^1H n.m.r. spectra of $[MoH(SR)(dppe)_2]$ [SR = tmbt (*i*) or bdpbt (*ii*)]

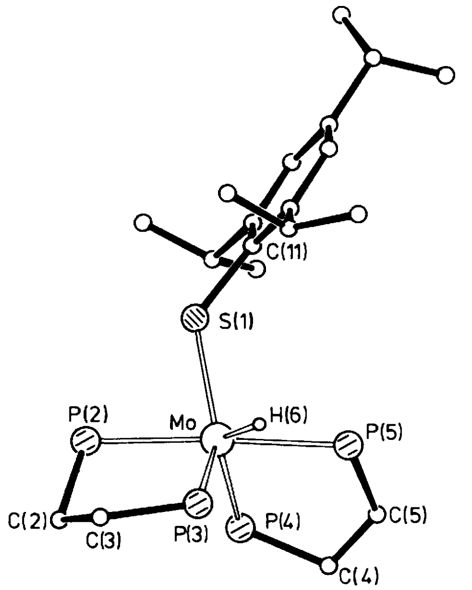


Figure 2. View of the core of the Mo complex molecule and the tpbt ligand

hydrides which contain both *cis*- and *trans*-phosphorus co-ligands.[12]

The resonance pattern of $[MoH(bdpbt)(dppe)_2]$ is exceptional in that the hydride resonance is not the simple quintet usually observed for molybdenum–hydride compounds of this type, which are generally fluxional at ambient temperature [Figure 1(*b*)(*i*)]. Instead a 'semi-rigid' multiplet is observed [Figure 1(*b*)(*ii*)].[13] It appears that the electron-withdrawing nature of the bdpbt ligand favours one particular isomer even at room temperature; possibly this is the *cis*-octahedral configuration (see below). Its poor solubility precluded low-temperature studies; the spectrum simplified, as expected, at higher temperatures, but some decomposition occurred.

Crystal Structure of cis-$[MoH(tpbt)(dppe)_2]$.—A single crystal of $[MoH(tpbt)(dppe)_2]$, grown from toluene, was structurally characterised by *X*-ray crystallography and found to have the structure shown in Figures 2 and 3. The complex crystallises with half a molecule of toluene, disordered about a centre of symmetry. Table 2 contains the atomic parameters; selected bond distances and angles are given in Table 3.

The structure of *cis*-$[MoH(tpbt)(dppe)_2]$ shows the molybdenum atom to be surrounded by six ligands in a very distorted *cis*-octahedral array. The dppe ligands each straddle an axial and an equatorial position, with the hydride and thiolate co-ordinating in the remaining *cis*-equatorial sites.

The structure usually observed for complexes $[MoL_2(dppe)_2]$ (L = neutral or ionic ligand) is a *trans*-octahedral arrrangement of ligands as seen in *trans*-$[Mo(SBu^n)_2(dppe)_2]$[8] and *trans*-$[Mo(NH)Br(dppe)_2]Br{\cdot}MeOH$.[14]

A *cis* conformation is reported for the crystal structure of '*cis*-$[MoCl_2(dppe)_2]$'[15] and we have examined it in some detail to compare its dimensions with *cis*-$[MoH(tpbt)(dppe)_2]$. However, close inspection of the dichloride structure and its method of preparation strongly suggest the presence of two hydride ligands. The yellow crystal used for that structural study was obtained by the reaction of $SnPh_2Cl_2$ and *trans*-

Table 2. Final atomic co-ordinates (fractional × 10^4) for [MoH(tpbt)(dppe)$_2$]·0.5C_6H_5Me, with e.s.d.s in parentheses

Atom	*x*	*y*	*z*
Mo	4 850.6(4)	2 041.4(2)	7 901.7(2)
H(6)	5 299(81)	2 106(45)	8 541(38)
S(1)	2 943(1)	2 270.1(7)	8 069.1(6)
C(11)	2 329(5)	2 923(3)	8 408(2)
C(12)	2 436(5)	2 951(3)	8 973(2)
C(13)	1 841(5)	3 428(3)	9 209(3)
C(14)	1 146(5)	3 865(3)	8 913(3)
C(15)	1 054(5)	3 818(3)	8 356(3)
C(16)	1 633(5)	3 358(3)	8 097(2)
C(121)	3 118(5)	2 474(3)	9 332(2)
C(122)	2 396(6)	1 908(3)	9 440(3)
C(123)	3 711(6)	2 744(4)	9 870(3)
C(141)	533(6)	4 378(3)	9 204(3)
C(142)	−587(7)	4 555(5)	8 932(4)
C(143)	1 250(8)	4 928(4)	9 338(4)
C(161)	1 460(5)	3 351(3)	7 476(3)
C(162)	359(6)	3 028(4)	7 264(3)
C(163)	1 540(7)	4 014(3)	7 226(3)
P(2)	3 870(1)	1 126.9(7)	7 423.6(6)
C(21a)	2 995(5)	1 190(3)	6 763(2)
C(22a)	1 975(5)	1 531(3)	6 748(3)
C(23a)	1 282(6)	1 592(3)	6 257(3)
C(24a)	1 567(6)	1 328(4)	5 794(3)
C(25a)	2 560(6)	998(4)	5 804(3)
C(26a)	3 265(6)	926(3)	6 290(3)
C(21b)	2 947(5)	587(3)	7 765(2)
C(22b)	2 893(5)	633(3)	8 319(2)
C(23b)	2 287(6)	186(3)	8 576(3)
C(24b)	1 738(6)	−300(3)	8 292(3)
C(25b)	1 771(6)	−343(3)	7 745(3)
C(26b)	2 374(5)	91(3)	7 483(3)
C(2)	4 963(5)	533(3)	7 326(2)
C(3)	5 635(5)	431(3)	7 876(2)
P(3)	6 137(1)	1 190.7(8)	8 217.1(7)
C(31a)	6 219(4)	937(3)	8 933(2)
C(32a)	5 373(5)	1 114(3)	9 232(3)
C(33a)	5 363(6)	924(4)	9 766(3)
C(34a)	6 200(6)	546(4)	10 004(3)
C(35a)	7 062(6)	360(3)	9 724(3)
C(36a)	7 057(5)	536(3)	9 187(3)
C(31b)	7 633(5)	1 186(3)	8 117(2)
C(32b)	8 442(5)	1 477(3)	8 474(3)
C(33b)	9 583(6)	1 511(4)	8 386(3)
C(34b)	9 906(6)	1 239(4)	7 936(3)
C(35b)	9 144(6)	942(4)	7 578(4)
C(36b)	7 997(6)	917(4)	7 661(3)
P(4)	5 652(2)	2 546(1)	7 179.0(8)
C(41a)	4 708(6)	3 084(3)	6 740(3)
C(42a)	3 611(6)	2 892(3)	6 582(3)
C(43a)	2 902(7)	3 244(4)	6 204(3)
C(44a)	3 275(8)	3 798(4)	5 987(3)
C(45a)	4 366(8)	3 997(4)	6 145(3)
C(46a)	5 084(7)	3 650(3)	6 516(3)
C(41b)	6 270(6)	2 106(3)	6 641(3)
C(42b)	5 601(7)	1 885(4)	6 196(3)
C(43b)	6 029(7)	1 551(4)	5 789(3)
C(44b)	7 143(8)	1 427(5)	5 822(4)
C(45b)	7 812(8)	1 622(6)	6 246(4)
C(46b)	7 398(8)	1 968(5)	6 664(4)
C(4)	6 812(8)	3 063(5)	7 445(3)
C(5)	6 708(8)	3 339(5)	7 896(3)
P(5)	5 953(2)	2 901.6(9)	8 390.0(8)
C(51a)	5 308(6)	3 614(3)	8 668(3)
C(52a)	4 363(5)	3 873(3)	8 372(3)
C(53a)	3 871(6)	4 434(3)	8 547(3)
C(54a)	4 338(7)	4 723(4)	9 012(3)
C(55a)	5 269(8)	4 475(4)	9 312(3)
C(56a)	5 766(7)	3 920(3)	9 142(3)
C(51b)	7 028(6)	2 739(3)	8 969(3)
C(52b)	8 189(8)	2 880(4)	8 981(5)
C(53b)	8 946(9)	2 739(5)	9 445(6)
C(54b)	8 556(9)	2 463(5)	9 882(5)
C(55b)	7 420(9)	2 319(4)	9 886(4)
C(56b)	6 682(7)	2 460(3)	9 423(3)
Toluene solvent (site occupancy factors 0.5)			
C(71)	−36(13)	−388(7)	−203(6)
C(72)	−42(12)	−543(7)	340(5)
C(73)	69(12)	55(7)	673(6)
C(74)	145(14)	643(8)	507(6)
C(75)	114(16)	813(9)	−72(7)
C(76)	−21(10)	201(6)	−420(5)
C(77)	−92(17)	−1 053(10)	−519(8)

Table 3. Selected bond lengths (Å) and angles (°) for [MoH(tpbt)(dppe)$_2$]. E.s.d.s are in parentheses; those of angles subtended at the Mo atom are less than 0.05°

Mo–S(1)	2.402(2)	Mo–P(4)	2.380(2)
Mo–P(2)	2.465(2)	Mo–P(5)	2.454(2)
Mo–P(3)	2.411(2)	Mo–H(6)	1.61(9)
S(1)–C(11)	1.807(6)		
S(1)–Mo–P(2)	80.8	P(3)–Mo–P(5)	96.1
S(1)–Mo–P(3)	131.6	P(4)–Mo–P(5)	78.8
S(1)–Mo–P(4)	121.2		
S(1)–Mo–P(5)	102.9	H(6)–Mo–S(1)	90.8(34)
P(2)–Mo–P(3)	79.8	H(6)–Mo–P(2)	127.9(34)
P(2)–Mo–P(4)	101.2	H(6)–Mo–P(3)	68.1(34)
P(2)–Mo–P(5)	175.7	H(6)–Mo–P(4)	126.1(34)
P(3)–Mo–P(4)	105.9	H(6)–Mo–P(5)	50.5(34)
Mo–S(1)–C(11)	132.6(2)		
Torsion angles in the dppe ligands			
P(2)–C(2)–C(3)–P(3)	−51(1)	P(4)–C(4)–C(5)–P(5)	33(1)

[Mo(N$_2$)$_2$(dppe)$_2$] in MeOH over several weeks.[15] This solution would be likely to generate HCl, which is known to react with *trans*-[Mo(N$_2$)$_2$(dppe)$_2$] to give the yellow, eight-co-ordinate complex [MoH$_2$Cl$_2$(dppe)$_2$].[16] If the compound reported as '*cis*-[MoCl$_2$(dppe)$_2$]' is actually [MoH$_2$Cl$_2$(dppe)$_2$], some of the unusual features of that structure may be explained as discussed below.

The inter-phosphine angle (P$_{eq.}$–Mo–P$_{eq.}$) of '*cis*-[MoCl$_2$(dppe)$_2$]' is 125.7(5)°, which is very large considering the presence of two chlorides in this plane. For comparison, in [MoH(tpbt)(dppe)$_2$] this angle is only 105.9°. This suggests the presence of two hydride ligands between the phosphorus atoms in '*cis*-[MoCl$_2$(dppe)$_2$]', pushing them apart. The Cl(1)–Mo–Cl(2) bond angle in '*cis*-[MoCl$_2$(dppe)$_2$]' is 79.7(4)° which is small in comparison to other *cis*-dichlorides.[15] If the Cl–Mo–Cl and P$_{eq.}$–Mo–P$_{eq.}$ bond angles are compared with those of the known hydride complexes [MH$_2$Cl$_2$L$_2$] (M = Ta or W, L = diphosphine or 2 × monophosphine), a similarity is observed: *e.g.*, [TaH$_2$Cl$_2$(dmpe)$_2$][17] (dmpe = Me$_2$PCH$_2$CH$_2$PMe$_2$; P$_{eq.}$–M–P$_{eq.}$ 121.1, Cl–M–Cl 85.0°), [WH$_2$Cl$_2$(PMe$_2$Ph)$_4$],[18] (120.8, 79.9°), and [WH$_2$Cl$_2$(PMe$_3$)$_4$]BF$_4$[19] (116.8, 84.4°). The apparent large steric strain in the structure of

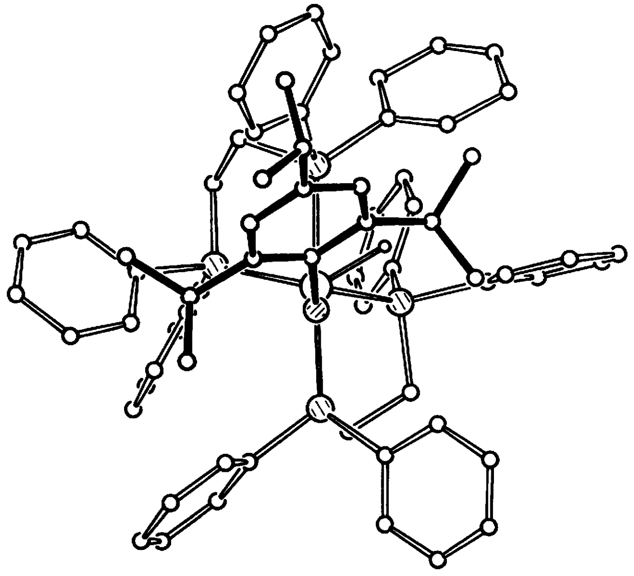


Figure 3. View of a molecule of *cis*-[MoH(tpbt)(dppe)$_2$]. The tpbt ligand has the solid bonds in the foreground

'*cis*-[MoCl$_2$(dppe)$_2$]' and the long Mo–Cl bond distances (noted in the original paper[15]), together with the method of preparation of the crystal, therefore strongly suggest that the true formulation of this complex is [MoH$_2$Cl$_2$(dppe)$_2$].

The Mo–P$_{ax.}$ distances in *cis*-[MoH(tpbt)(dppe)$_2$] are 2.465(2) and 2.454(2) Å which are, as expected, longer than the Mo–P$_{eq.}$ distances of 2.411(2) and 2.380(2) Å, where the P atoms are approximately *trans* to S(1) and H(6) respectively.

The Mo–S(1) bond distance is 2.402(2) Å which is longer than in other Mo^{II} complexes such as *trans*-[Mo(SBu^n)$_2$-(dppe)$_2$].[8] The Mo–S(1)–C(11) bond angle of 132.6(2)° is also large compared with those in other thiolate complexes, where it is equal to or less than the ideal sp^2 angle of 120°; *e.g.* in *trans*-[Mo(SBu^n)$_2$(dppe)$_2$] it is 120.07(4)°, in [Mo(CO)(η^5-C$_5$H$_5$)-(CF$_3$C$_2$CF$_3$)(SC$_6$F$_5$)][20] 105.7(1)°, in [Mo(SBu^t)$_4$] 118.8(6)°,[21] and in [MoO(SPh)$_4$] 108.8°.[22] The large angle in *cis*-[MoH-(tpbt)(dppe)$_2$] may be a reflection of the large steric congestion in this molecule; the close interactions between the thiolate ligand and the phenyl groups of the dppe ligands appear to be minimised by increasing the Mo–S–C angle.

The hydride ligand was located in a Fourier difference map and its parameters were refined satisfactorily. We also noted that the area of the face of the co-ordination polyhedron defined by P(3), P(5), and S(1) was significantly larger than that of any other P$_2$S face, thus confirming the location of the hydride. The hydride is on the same side of the sulphur as the C$_6$H$_2$Pr$^i_3$-2,4,6 group and hence does not interact with the sulphur lone-pair electrons.

Mechanism of Formation of trans-[Mo(SR)$_2$(dppe)$_2$] (R = Pr^n *or* Ph).—The reaction between *trans*-[Mo(N$_2$)$_2$(dppe)$_2$] and sterically undemanding thiols (RSH; R = Pr^n or Ph) in thf yields *trans*-[Mo(SR)$_2$(dppe)$_2$] according to the stoicheiometry defined by equation (2). The products, *trans*-[Mo(SR)$_2$(dppe)$_2$], have been isolated and fully characterised,[8] and the evolved dinitrogen and dihydrogen identified by mass spectrometry.

$$\begin{aligned} trans\text{-}[\mathrm{Mo(N_2)_2(dppe)_2}] + 2\mathrm{RSH} \longrightarrow \\ trans\text{-}[\mathrm{Mo(SR)_2(dppe)_2}] + 2\mathrm{N_2} + \mathrm{H_2} \quad (2) \end{aligned}$$

The isolation of *cis*-[MoH(tpbt)(dppe)$_2$], which almost certainly represents a model for an intermediate in reaction (2) led us to investigate the kinetics and mechanism of this reaction. Specifically, the reactions with PhSH and Pr^{n}SH have been studied, and because of the intense colours of the products, *trans*-[Mo(SR)$_2$(dppe)$_2$], it was most convenient to monitor the reactions using u.v.–visible spectrophotometry.

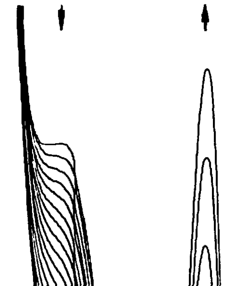


Figure 4. The spectrophotometric time course of the reaction between *trans*-[Mo(N$_2$)$_2$(dppe)$_2$] and PhSH, in the range λ = 330—810 nm. (The apparent small peak at λ = 650 nm is an artefact of the spectrophotometer)

Reaction between trans-[Mo(N$_2$)$_2$(dppe)$_2$] *and* RSH (R = Pr^n *or* Ph).—The reactions between *trans*-[Mo(N$_2$)$_2$(dppe)$_2$] and Pr^{n}SH or PhSH are very similar. In neither case could any intermediate be detected in the wavelength range λ = 310—810 nm under the conditions used ([Mo] = 0.05 mmol dm^{-3}, [RSH] = 25.0—300.0 mmol dm^{-3}). Furthermore, a well defined isosbestic point is maintained at λ = 475 nm (R = Ph, Figure 4). In the reaction with Pr^{n}SH, minor deviations from the isosbestic point (λ = 435 nm) are observed after two half-lives.

The kinetics of the reactions between *trans*-[Mo(N$_2$)$_2$(dppe)$_2$] and thiol were all studied under pseudo-first-order conditions, [RSH]/[Mo] > 20, at 25.0 °C in thf. Under these conditions, the reaction with both PhSH and Pr^{n}SH exhibited a first-order dependence on the concentration of *trans*-[Mo(N$_2$)$_2$(dppe)$_2$], but the dependence on the concentration and nature of the thiol was complicated.

Under all conditions studied, the rate of the reaction between *trans*-[Mo(N$_2$)$_2$(dppe)$_2$] and Pr^{n}SH is independent of the concentration of thiol, with $k_{obs.} = (1.9 \pm 0.2) \times 10^{-4}$ s^{-1}. In contrast, the reaction with PhSH exhibits a complicated

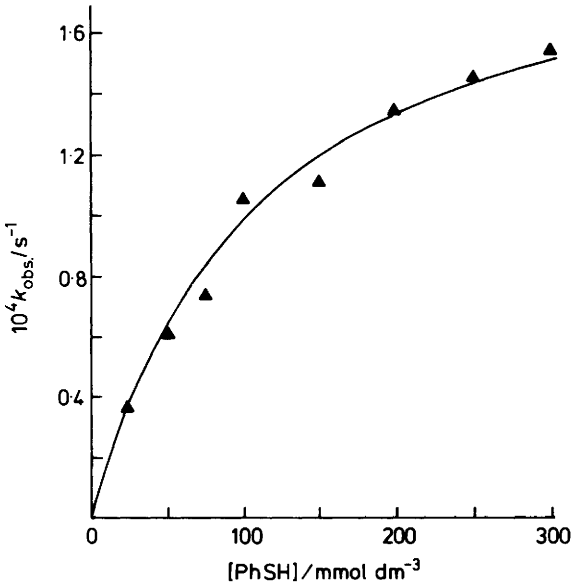
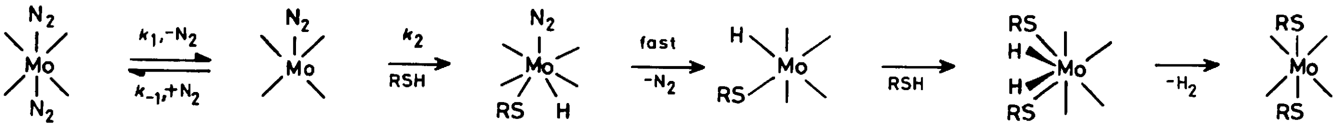


Figure 5. The non-linear dependence of $k_{obs.}$ on the concentration of PhSH in the reaction between *trans*-[Mo(N$_2$)$_2$(dppe)$_2$] and PhSH in thf. The curve is that described by equation (3)

Table 4. Kinetic data for the reaction between *trans*-[Mo(N$_2$)$_2$(dppe)$_2$] and RSH (R = Pr^n or Ph) in thf at 25.0 °C

R	[Mo(N$_2$)$_2$(dppe)$_2$]/ mmol dm^{-3}	[RSH]/ mmol dm^{-3}	$10^4k_{obs.}$/ s^{-1}
Pr^n	0.05	50.0	1.9
		100.0	2.0
		200.0	2.1
		400.0	2.0
		800.0	1.8
	0.10	200.0	1.7
		800.0	2.3
Ph	0.05	25.0	0.36
		50.0	0.60
		75.0	0.73
		100.0	1.06
		150.0	1.11
		200.0	1.34
		250.0	1.45
		300.0	1.54
	0.10	50.0	0.63
		100.0	1.10
		200.0	1.30
	0.025	200.0	1.25



Scheme 1. Mechanism for the reaction between *trans*-[Mo(N$_2$)$_2$(dppe)$_2$] and RSH (R = Pr^n or Ph) (phosphine ligands omitted for clarity)

dependence on the concentration of thiol. At low concentrations of PhSH, the reaction exhibits a first-order dependence on the concentration of thiol, whereas at higher concentrations the reaction rate becomes independent of the concentration of PhSH, as shown in Figure 5 and described in equation (3).

$$k_{obs.} = \frac{(1.8 \pm 0.2) \times 10^{-3}[\text{PhSH}]}{1 + (10.2 \pm 0.2)[\text{PhSH}]} \qquad (3)$$

The kinetic data for the reactions of *trans*-[Mo(N$_2$)$_2$(dppe)$_2$] with both thiols are shown in Table 4.

These kinetic results are consistent with the mechanism shown in Scheme 1. The initial, rate-limiting step involves the loss of dinitrogen from *trans*-[Mo(N$_2$)$_2$(dppe)$_2$] to yield the reactive, five-co-ordinate, 16-electron species [Mo(N$_2$)(dppe)$_2$]. Subsequent oxidative-addition of the thiol to this intermediate withdraws electron density from the metal centre, thus labilising the remaining dinitrogen ligand to generate the 16-electron species [MoH(SR)(dppe)$_2$]. Rapid attack by a further molecule of thiol on [MoH(SR)(dppe)$_2$] gives [MoH$_2$(SR)$_2$(dppe)$_2$], which subsequently eliminates dihydrogen to yield the product, *trans*-[Mo(SR)$_2$(dppe)$_2$].

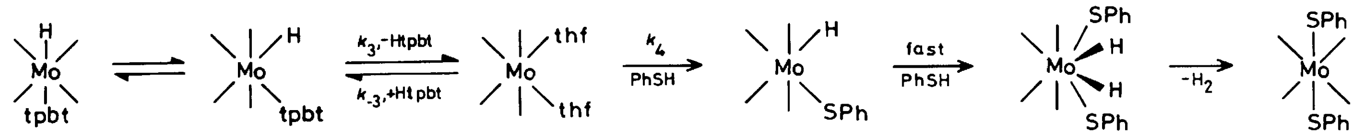
Assuming that loss of dinitrogen from *trans*-[Mo(N$_2$)$_2$(dppe)$_2$] is rate limiting, and treating [Mo(N$_2$)(dppe)$_2$] as a steady-state intermediate, the derived rate law is that shown in equation (4), where $k'_{-1} = k_{-1}[\text{N}_2]$, since the reactions were all studied in thf saturated with dinitrogen.

$$k_{obs.} = \frac{k_1k_2[\text{RSH}]}{k'_{-1} + k_2[\text{RSH}]} \qquad (4)$$

This equation is consistent with the rate law observed for the reaction with PhSH shown in equation (3), where $k_1 = (1.8 \pm 0.3) \times 10^{-4}$ s^{-1} and $(k_2/k'_{-1})^{\text{PhSH}} = 10.2 \pm 0.2$. The rate law shown in equation (4) is also consistent with the studies using Pr^{n}SH, since if $(k_2/k'_{-1})^{\text{Pr}^n\text{SH}} > 1$, then equation (4) simplifies to $k_{obs.} = k_1$, in excellent agreement with the value observed using this thiol. The conclusion that k_1 corresponds to the loss of dinitrogen from *trans*-[Mo(N$_2$)$_2$(dppe)$_2$] is corroborated by comparison with the values determined previously for this process, in the reactions of *trans*-[Mo(N$_2$)$_2$(dppe)$_2$] with alkyl halides [$k_1 = (1.3 \pm 0.2) \times 10^{-4}$ s^{-1}][23] and PhCN [$k_1 = 2.8 \times 10^{-4}$ s^{-1}, T = 27.0 °C].[24]

Clearly the kinetics of reaction (2), as described above, give no information about the intimate mechanism of this reaction after the oxidative-addition of the thiol to [Mo(N$_2$)(dppe)$_2$]. However, there are two species which are of fundamental importance in this mechanism, [MoH(SR)(dppe)$_2$] and [MoH$_2$(SR)$_2$(dppe)$_2$], and it is important to explain on what precedent such species have been invoked in this pathway.

As we have discussed, the species [MoH(SR)(dppe)$_2$] is isolable when a sterically demanding thiolato-group is present, and certainly *cis*-[MoH(tpbt)(dppe)$_2$] represents a structural model for this intermediate. The variable-temperature ^{31}P n.m.r. spectra of [MoH(tpbt)(dppe)$_2$] suggest that in solution at ambient temperature a rapid interconversion of the *cis* and *trans* isomers can occur (see above). If, as seems likely, such a process operates with analogues containing less sterically demanding thiols, then reaction of either isomer of [MoH(SR)(dppe)$_2$] with a further molecule of thiol generates [MoH$_2$(SR)$_2$(dppe)$_2$]. Several isomers of this latter species are possible, but it seems most likely that only that containing *cis*-hydride



Scheme 2. Mechanism for the reaction between [MoH(tpbt)(dppe)$_2$] and PhSH (phosphine ligands omitted for clarity)

ligands (to allow facile reductive-elimination of dihydrogen) is on the product-forming pathway. Analogues of [MoH$_2$(SR)$_2$(dppe)$_2$], such as [MH$_2$Cl$_2$(dppe)$_2$][16,18] (M = Mo or W), are known to lose dihydrogen for M = Mo but are stable for M = W.[16] The greater steric congestion in the thiolato-complexes is an additional driving force for the reductive-elimination.

Attempts were made to detect intermediates in the reactions between *trans*-[Mo(N$_2$)$_2$(dppe)$_2$] and RSH (R = Ph or Pr^n) using ^{31}P n.m.r. spectroscopy, under limiting concentrations of thiol, [RSH]/[Mo] = 2.1. No intermediates were detected in the reaction with Pr^{n}SH, but in the reaction with PhSH, besides the resonances attributable to *trans*-[Mo(N$_2$)$_2$(dppe)$_2$] and *trans*-[Mo(SPh)$_2$(dppe)$_2$], a further transient signal at −58 p.p.m. [relative to P(OMe)$_3$] is observed. We tentatively assign this resonance to the green intermediate stage reported earlier,[8] [MoH(SPh)(dppe)$_2$].

Reaction between [MoH(tpbt)(dppe)$_2$] *and* PhSH.—The reaction between [MoH(tpbt)(dppe)$_2$] and an excess of PhSH in thf to yield *trans*-[Mo(SPh)$_2$(dppe)$_2$] occurs with the stoicheiometry described by equation (5).

$$[\mathrm{MoH(tpbt)(dppe)_2}] + 2\mathrm{PhSH} \longrightarrow \textit{trans}\text{-}[\mathrm{Mo(SPh)_2(dppe)_2}] + \mathrm{Htpbt} + \mathrm{H_2} \quad (5)$$

The kinetics of the reaction were studied using an excess of PhSH, under pseudo-first-order conditions. No intermediate was detected under these conditions, and well defined isosbestic points were maintained at λ = 425 and 590 nm throughout the reaction. The kinetics of the reaction exhibited a first-order dependence on the concentrations of both [MoH(tpbt)(dppe)$_2$] and PhSH as described in equation (6). The kinetic data for this reaction are shown in Table 5.

$$-\mathrm{d}[\mathrm{MoH(tpbt)(dppe)_2}]/\mathrm{d}t = (4.7 \pm 0.2) \times 10^{-4}[\mathrm{MoH(tpbt)(dppe)_2}][\mathrm{PhSH}] \quad (6)$$

The simple rate law shown in equation (6), together with the quantitative formation of *trans*-[Mo(SPh)$_2$(dppe)$_2$] can be rationalised by the mechanism shown in Scheme 2. Reductive-elimination of Htpbt from *cis*-[MoH(tpbt)(dppe)$_2$] generates the highly reactive solvated species [Mo(thf)$_2$(dppe)$_2$]. Subsequent attack by two further molecules of PhSH generates [MoH(SPh)(dppe)$_2$] and [MoH$_2$(SPh)$_2$(dppe)$_2$] successively. Reductive-elimination of dihydrogen from the latter species yields the product, *trans*-[Mo(SPh)$_2$(dppe)$_2$]. If reductive-elimination of Htpbt from *cis*-[MoH(tpbt)(dppe)$_2$] is rate limiting, and [Mo(thf)$_2$(dppe)$_2$] is a steady-state intermediate, then the derived rate law is that shown in equation (7).

$$k_{\mathrm{obs.}} = \frac{k_3k_4[\mathrm{PhSH}]}{k_{-3}[\mathrm{Htpbt}] + k_4[\mathrm{PhSH}]} \quad (7)$$

Under the experimental conditions k_{-3}[Htpbt] > k_4[PhSH]; consequently equation (7) reduces to the simpler form $k_{\mathrm{obs.}} = k_3k_4/k'_{-3}$[PhSH], where $k'_{-3} = k_{-3}$[Htpbt] (since the experiments were, in effect, performed at a constant concentration of Htpbt). Consistent with this rate law, the addition of [Htpbt] = 1.0 mmol dm^{-3} is sufficient to suppress any detectable reaction for 1 h when [PhSH] = 100.0 mmol dm^{-3}.

Table 5. Kinetic data for the reaction between [MoH(tpbt)(dppe)$_2$] and PhSH in thf at 25.0 °C[a]

[PhSH]/mmol dm^{-3}	$10^4k_{\mathrm{obs.}}$/s^{-1}
25.0	0.15
50.0	0.28
50.0[b]	0.24
100.0[b]	0.60
200.0	0.93
200.0[b]	1.1
200.0[c]	1.1
400.0	2.0
400.0[b]	1.8
800.0	3.8

[a] Concentration of [MoH(tpbt)(dppe)$_2$] = 0.5 × 10^{-4} mol dm^{-3} unless otherwise stated. [b] Concentration of [MoH(tpbt)(dppe)$_2$] = 1.0 × 10^{-4} mol dm^{-3}. [c] Concentration of [MoH(tpbt)(dppe)$_2$] = 2.0 × 10^{-4} mol dm^{-3}.

Although the reaction between *cis*-[MoH(tpbt)(dppe)$_2$] and PhSH to form *trans*-[Mo(SPh)$_2$(dppe)$_2$] involves the initial elimination of Htpbt, such a pathway is clearly nonsensical for the intermediate, [MoH(SPh)(dppe)$_2$], involved in the reaction of *trans*-[Mo(N$_2$)$_2$(dppe)$_2$] with thiophenol. Thus although *cis*-[MoH(tpbt)(dppe)$_2$] represents a structural model for the intermediates, [MoH(SR)(dppe)$_2$], the bulky thiolato-group so dominates the reactivity of the former complex that its reaction mechanisms cannot be considered as typical of those of the intermediates.

Experimental

All materials were handled using standard Schlenk techniques under pure dinitrogen. All solvents were rigorously dried and distilled under dry dinitrogen prior to use.

I.r. spectra were determined by Pye-Unicam SP2000 or Perkin-Elmer SP3-200 instruments. N.m.r. spectra were measured on a JEOL FX90Q spectrometer with a JEOL NM-PVT variable-temperature controller by Mr. C. Macdonald (A.F.R.C., Unit of Nitrogen Fixation).

Electronic spectra were recorded on Perkin-Elmer Lambda 5 or Pye-Unicam SP1800 spectrophotometers. Microanalyses were performed by Mrs. A. G. Olney (University of Sussex) and Mr. C. Macdonald (A.F.R.C., Unit of Nitrogen Fixation).

Thiols (RSH; R = Pr^i, Bu^t, or Ph) were used as purchased from Aldrich Chemicals Ltd. The thiols 2,4,6-trimethylbenzenethiol, 2,4,6-tri-isopropylbenzenethiol, and 4-bromo-2,6-di-isopropylbenzenethiol were kindly provided by Dr. P. J. Blower and Ms. A. May. The complex *trans*-[Mo(N$_2$)$_2$(dppe)$_2$] was prepared by literature methods.[16] A typical preparation of a [MoH(SR)(dppe)$_2$] complex is shown below.

Bis[1,2-*bis*(*diphenylphosphino*)*ethane*]*hydrido*(*propane*-2-*thiolato*)*molybdenum*(II), [MoH(SPr^i)(dppe)$_2$].—*trans*-[Mo(N$_2$)$_2$(dppe)$_2$] (0.3 g, 0.32 mmol) and Pr^{i}SH (0.06 g, 0.8 mmol) in thf (25 cm^3) were heated to 60 °C for 1 h under dinitrogen, to give a dark green solution. The solution was filtered and the volume reduced to *ca.* 15 cm^3 *in vacuo.* Pentane (25 cm^3) was added and the solution left at -4 °C for *ca.* 6 h to give a dark green microcrystalline product. The solid was filtered off, washed with pentane (3×10 cm^3), and dried *in vacuo*. The product was analytically pure $[MoH(SPr^i)(dppe)_2]$ (0.21 g, 0.22 mmol, 69%).

Kinetic Studies.—All kinetic studies were performed on a Pye-Unicam SP1800 spectrophotometer, equipped with a thermostatted cell holder. The temperature in the cell holder was maintained at 25.0 °C by recirculating water from a Grant SE10 thermostatted tank.

All reactions were monitored by scanning the range λ = 310—810 nm at various times to produce the reaction time-course diagram, as exemplified by Figure 4. The rate constant was then calculated at a convenient wavelength of maximum absorbance change (*i.e.*, λ = 530 nm for reactions with PhSH; λ = 460 nm for reactions with Pr^nSH), by the normal semi-logarithmic plots.[25] Such plots were linear for at least two half-lives.

X-*Ray Analysis of cis*-$[MoH(tpbt)(dppe)_2]\cdot 0.5C_6H_5Me$.—*Crystal data.* $C_{67}H_{72}MoP_4S\cdot 0.5C_7H_8$, M = 1 175.3, monoclinic, space group $P2_1/c$ (no. 14), a = 11.875(1), b = 20.946(3), c = 24.780(6) Å, β = 97.34(1)°, U = 6 112.7 $Å^3$, Z = 4, D_c = 1.277 g cm^{-3}, $F(000)$ = 2 468, $\lambda(Mo\text{-}K_{\bar{\alpha}})$ = 0.710 69 Å, $\mu(Mo\text{-}K_\alpha)$ = 3.8 cm^{-1}.

A small, deep green rectangular plate crystal ($0.20 \times 0.33 \times 0.39$ mm) was sealed under dinitrogen in a capillary tube. After photographic examination, the crystal was mounted on an Enraf–Nonius CAD4 diffractometer. Using monochromated Mo-K_α radiation, accurate cell dimensions were calculated from the centring of 25 reflections with θ = 10—11°, and intensity data were measured for θ in the range 1.5—20°. During processing of these data, corrections were made for Lorentz polarisation effects, slight deterioration, absorption (by semi-empirical methods), and negative intensities. 5 683 Unique planes (of which 4 183 were 'observed', having $I > 2\sigma_I$) were input to the SHELX program system,[26] and the structure was solved from Patterson and electron-density maps.

The hydride ligand was located in a difference Fourier map and refined satisfactorily. All other H atoms were placed in idealised positions (the methyl H atoms in staggered arrangements) and allowed to ride on the C atoms to which they were bonded. A toluene solvent molecule was found to occupy one of the pair of sites about a centre of symmetry.

All non-H atoms of the complex were refined anisotropically by block-diagonal least-squares methods,[27] and at convergence, R = 0.068 and R' = 0.064 for all 5 683 reflections weighted: $w = (\sigma_F^2 + 0.000\,91F^2)^{-1}$.

Most of the computer programs used in this analysis have been described in the legend to Table 4 of ref. 28.

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