DALTON

Disproportionation and reduction of hydrazine at a molybdenum–thiolate centre: crystal structures of [MoH($SC_6H_2Pr^i{}_3$-2,4,6)$_3$(NH_3)($PMePh_2$)] and [MoH($SC_6H_2Pr^i{}_3$-2,4,6)$_3$(NH_2NHPh)($PMePh_2$)]

Peter B. Hitchcock,[a] **David L. Hughes,**[b] **Michael J. Maguire,**[a] **Katayoun Marjani**[a] **and Raymond L. Richards** *,[b]

[a] *School of Chemistry, Physics and Environmental Sciences, University of Sussex, Brighton, UK BN1 9RQ*
[b] *John Innes Centre, Nitrogen Fixation Laboratory, Norwich Research Park, Norwich, UK NR4 7UH*

In the presence of [MoH($SC_6H_2Pr^i{}_3$-2,4,6)$_3$($PMePh_2$)] in tetrahydrofuran (thf), anhydrous N_2H_4 disproportionates to N_2 and NH_3 or is reduced to NH_3 by Zn–$HOC_6H_3Pr^i{}_2$-2,6 (69–81% conversion over 16 h). Reaction of [MoH($SC_6H_2Pr^i{}_3$-2,4,6)$_3$($PMePh_2$)] with anhydrous N_2H_4 in thf–MeOH at low temperature gave the complex [MoH($SC_6H_2Pr^i{}_3$-2,4,6)$_3$(NH_3)($PMePh_2$)] which was shown by a crystal-structure determination to have a trigonal girdle of thiolate ligands with essentially apical NH_3 and $PMePh_2$ ligands [*d*(Mo–N), 2.298(15); *d*(Mo–S) (mean), 2.339(5) Å]. A similar reaction using NH_2NHPh instead of N_2H_4 gave [MoH($SC_6H_2Pr^i{}_3$-2,4,6)$_3$(NH_2NHPh)($PMePh_2$)], which has an analogous crystal structure to [MoH($SC_6H_2Pr^i{}_3$-2,4,6)$_3$(NH_3)($PMePh_2$)] [*d*(Mo–N), 2.278(5); *d*(Mo–S) (mean), 2.332(2); *d*(N–N) 1.451(7) Å]. Spectroscopic data for these compounds are discussed in terms of their structures. The unstable adduct [MoH($SC_6H_2Pr^i{}_3$-2,4,6)$_3$(NH_2NMe_2)($PMePh_2$)] has been characterised spectroscopically in solution.

The reduction of N_2H_4 to NH_3 and its disproportionation to NH_3 and N_2 are catalysed by a limited number of metal complexes, *e.g.* the mononuclear compound [W(C_5Me_5)Me_3(η^2-N_2H_4)][1] and cluster anions such as [$MoFe_3S_4Cl_3$($C_6Cl_4O_2$)(MeCN)]$^{2-}$ catalyse[2] the disproportionaton and reduction of hydrazine. The site of binding of N_2H_4 in the last case appears to be the molybdenum, since $PhNHNH_2$ has been shown to bind at Mo in the above cluster.[3] These observations have relevance to the possible function of nitrogenase in that bound hydrazine, and derivatives of it such as N_2H_2, $NNH_2{}^{2-}$ or $NNH_3{}^-$, are likely intermediates in the reduction of N_2, whether at a mononuclear or a multinuclear site.[4]

Molybdenum–thiolate complexes have also been used to model aspects of nitrogenase chemistry, in particular the reduction of hydrazine and also the binding of hydrogen to sulfur-ligated metal centres. In one such demonstration of the catalytic disproportionation and reduction of hydrazine, the catalyst precursor is the binuclear complex [Mo_2Cl_4{2-SC_5H_3N-($SiMe_3$)-3}$_2$(μ-S_2){μ-2-SC_5H_3NH($SiMe_3$)-3}] and the catalyst itself may be binuclear also, but this has not been established.[5] The binuclear complex [Mo_2(η-C_5H_5)$_2$(μ-Cl)(μ-SMe)$_3$] has been shown to catalyse the disproportionation of hydrazine and a binuclear amido complex [Mo_2(η-C_5H_5)$_2$(μ-NH_2)(μ-SMe)$_3$] has been isolated, although it is unclear whether the last complex is an intermediate on the reaction pathway.[6]

The present study involves the use of the unsaturated thiolate–hydride complex [MoH($SC_6H_2Pr^i{}_3$-2,4,6)$_3$($PMePh_2$)] **1**.[7] This compound was prepared to examine the behaviour of hydride ligands at a metal which also carries sulfur-donor groups; its electronically unsaturated nature generates a variety of reactions including S–C bond cleavage of thiolate ligands[8] and formation of adducts such as [MoH($SC_6H_2Pr^i{}_3$-2,4,6)$_3$(C_5H_5N)($PMePh_2$)].[9] When **1** was treated with N_2H_4, the complex [MoH($SC_6H_2Pr^i{}_3$-2,4,6)$_3$(NH_3)($PMePh_2$)] **2** was obtained as described in detail below. This observation prompted an investigation to see if disproportionation and reduction of hydrazine are catalysed by **1**.

Results and Discussion

Disproportionation and reduction of hydrazine

The results of this study are presented in Table 1. As can be seen from these data, when hydrazine was treated with **1** in tetrahydrofuran (thf) alone there was a moderate and rather slow conversion to N_2 and NH_3 by disproportionation [reaction (1)].

$$3N_2H_4 \longrightarrow N_2 + 4NH_3 \qquad (1)$$

In the presence of methanol as proton source but with no added reductant, disproportionation was still the predominant reaction, but clearly ammonia was produced by reduction [reaction (2)] in addition to that produced by disproportionation, especially at higher hydrazine ratios.

$$N_2H_4 + 2H^+ + 2e^- \longrightarrow 2NH_3 \qquad (2)$$

The extent of disproportionation was monitored for the methanol system by measurement of the amount of N_2 evolved in the reaction, then the yield of NH_3 produced by disproportionation was calculated from this value assuming that reaction (1) occurs. Ammonia produced in excess of this value was assumed to arise from a competing reduction reaction.

In the presence of **1**, with zinc as reductant and $HOC_6H_3Pr^i{}_2$-2,6 as proton source, high (69–81%) conversion of hydrazine to ammonia occurred over a period of around 16 h in thf solution. The highest levels of disproportionation and reduction were at relatively low ratios of hydrazine to Mo, as has been observed in other systems and attributed to precipitation of product or of starting material, as their ammonium salts, at higher ratios of hydrazine.[2,10]

As described below, the adducts [MoH($SC_6H_2Pr^i{}_3$-2,4,6)$_3$(NH_2NHPh_2)($PMePh_2$)] **3** (from reaction of $PhNHNH_2$) and [MoH($SC_6H_2Pr^i{}_3$-2,4,6)$_3$(NH_3)($PMePh_2$)] **2** (from reaction of NH_2NH_2) have been structurally characterised and the adduct [MoH($SC_6H_2Pr^i{}_3$-2,4,6)$_3$(NMe_2NH_2)($PMePh_2$)] **4** has been characterised in solution. These results indicate that at least in

Table 1 Catalytic disproportionation and reduction of hydrazine by complex **1**

Mo[a]	N_2H_4 : Mo	N_2[b]	NH_3[b,c]	NH_3[d]	Conversion[e] (%)
1.4[f]	1.1 : 1	0.2 (0.4)	0.8 (1.5, **0.8**)	0	55.2, 0
0.7	1.1 : 1	0.3 (0.4)	1.4 (1.5, **1.1**)	0.3	78.4, 12.7
0.5	15.6 : 1	1.8 (5.2)	10.4 (20.8, **7.2**)	3.2	34.6, 10.2
0.3	26.0 : 1	1.8 (8.7)	25.3 (34.7, **7.2**)	18.1	20.8, 34.8
1.0	64.0 : 1	6.1 (21.3)	59 (85.3, **24.4**)	25.6	26.5, 28.3
0.3[g]	6.3 : 1	—	10.2 (12.6)	10.2	—, 80.9
0.45[g]	5.7 : 1	—	8.0 (11.4)	8.0	—, 70.1
0.3[g]	12.7 : 1	—	19.7 (25.4)	19.7	—, 77.5
0.3[e]	21.1 : 1	—	29.2 (42.2)	29.2	—, 69.2

[a] Concentration of Mo, mol × 10^{-4}; solvent thf–MeOH 3 : 1 unless otherwise stated; reaction time 16–18 h; all reactions repeated three times. [b] Yield; maximum possible in parentheses, in equivalents relative to Mo, according to $3\ N_2H_4 \longrightarrow N_2 + 4NH_3$ or $N_2H_4 \longrightarrow 2NH_3$ as appropriate. [c] In bold, yield of NH_3 calculated from disproportionation, based on N_2 evolved. [d] Yield of NH_3 produced by reduction. [e] Conversion of N_2H_4 to product (by disproportionation, by reduction). [f] thf Solution. [g] 16 Equivalents Zn and 12 equivalents of $HOC_6H_3Pr^i_2$-2,6 (per N_2H_4) added, reliable N_2 evolution data could not be monitored in system used (see Experimental section).

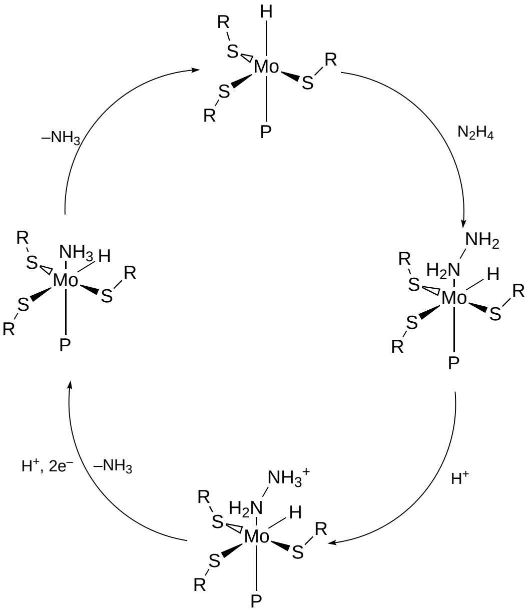

Fig. 1 Scheme of catalytic reduction of hydrazine at a single molybdenum site

Table 2 Selected intramolecular distances (Å) and angles (°) for $[MoH(SC_6H_2Pr^i_3\text{-}2,4,6)_3(NH_3)(PMePh_2)]$ **2**, with estimated standard deviations (e.s.d.s) in parentheses

Mo(1)–S(1)	2.331(5)	Mo(1)–S(2)	2.354(4)
Mo(1)–S(3)	2.332(5)	Mo(1)–P(1)	2.365(5)
Mo(1)–N(1)	2.298(15)	S(1)–C(14)	1.81(2)
S(2)–C(29)	1.81(2)	S(3)–C(44)	1.81(2)
Mo(2)–S(4)	2.343(5)	Mo(2)–S(5)	2.358(5)
Mo(2)–S(6)	2.335(5)	Mo(2)–P(2)	2.365(5)
Mo(2)–N(2)	2.298(14)	S(4)–C(72)	1.78(2)
S(5)–C(87)	1.77(2)	S(6)–C(102)	1.77(2)
S(1)–Mo(1)–S(2)	110.0(2)	S(1)–Mo(1)–S(3)	131.7(2)
S(1)–Mo(1)–P(1)	81.0(2)	S(1)–Mo(1)–N(1)	88.6(4)
S(2)–Mo(1)–S(3)	117.4(2)	S(2)–Mo(1)–P(1)	119.2(2)
S(2)–Mo(1)–N(1)	82.7(4)	S(3)–Mo(1)–P(1)	84.1(2)
S(3)–Mo(1)–N(1)	88.6(4)	P(1)–Mo(1)–N(1)	157.8(4)
S(4)–Mo(2)–S(5)	111.3(2)	S(4)–Mo(2)–S(6)	131.1(2)
S(4)–Mo(2)–P(2)	81.8(2)	S(4)–Mo(2)–N(2)	89.0(4)
S(5)–Mo(2)–S(6)	116.8(2)	S(5)–Mo(2)–P(2)	118.3(2)
S(5)–Mo(2)–N(2)	82.6(4)	S(6)–Mo(2)–P(2)	83.4(2)
S(6)–Mo(2)–N(2)	88.7(3)	P(2)–Mo(2)–N(2)	159.0(4)

outline, the disproportionation and reduction reactions occur *via* initial adduct formation at a single Mo site. The further mechanism of the disproportionation reaction is unclear, since although it undoubtedly occurs at molybdenum, it presumably involves a multiple sequence of steps or polynuclear species at some stage [see equation (1)]. The further mechanism of reduction of hydrazine might only require a single Mo site; an outline scheme for reduction is shown in Fig. 1. This scheme is similar to that proposed by Coucouvanis and co-workers[2] for reduction of hydrazine at the single Mo site in cluster anions such as $[MoFe_3S_4Cl_3(C_6Cl_4O_2)(MeCN)]^{2-}$.

Clearly this type of activation of hydrazine has relevance to the reduction of N_2 by nitrogenase, particularly since hydrazine can be obtained from the enzyme by quenching[10] and bound hydrazine may therefore lie on the N_2 reduction path, assuming that the process involves activation of N_2 at a sulfur-ligated Mo or other metal site. Although binding of N_2 at a thiolate-ligated molybdenum site has not yet been demonstrated, isolation of such a compound may only be a matter of time, since a thiolate–dinitrogen complex of the related metal rhenium, $[Re(SC_6H_2Pr^i_3\text{-}2,4,6)_3(N_2)(PPh_3)]$, is known.[11]

Preparation and structure of $[MoH(SC_6H_2Pr^i_3\text{-}2,4,6)_3(NH_3)(PMePh_2)]$ 2

The reaction of complex **1** with anhydrous hydrazine in thf–MeOH at 0 °C produced a green-brown solution after 30 min. Slow crystallisation of the reaction solution at −20 °C following addition of ice-cold MeOH gave, after about 2 weeks, grass green crystals of complex **2** which were suitable for X-ray analysis. Complex **2** as produced above is very air- and temperature-sensitive, but when carefully purified it is moderately stable at room temperature in the absence of air. Analytical data for **2**, its spectroscopic properties (see Experimental section) and analogy with complexes such as $[MoH(SC_6H_2Pr^i_3\text{-}2,4,6)_3(C_5H_5N)(PMePh_2)]$[9] are consistent with the formulation $[MoH(SC_6H_2Pr^i_3\text{-}2,4,6)_3(NH_3)(PMePh_2)]$. Thus **2** shows a broad N–H stretching absorption at 3200–3400 cm^{-1} and a weak Mo–H stretching absorption at 1890 cm^{-1}; its proton-coupled ^{31}P resonance is a doublet centred at δ −86.8 [^2J(PMoH) = 86.7 Hz], a pattern typical of such molybdenum hydrides with the hydride *cis* to the phosphine.[8,9] It shows a broad singlet ^{14}N NMR resonance at δ −72.1 (relative to liquid $MeNO_2$). The molecular structure of **2** is shown in Fig. 2 and selected bond lengths and angles are in Table 2. The structure shows two very similar, independent molecules, each with the Mo on a local, pseudo-mirror plane of symmetry; the ligand atoms S(2), N(1) and P(1) lie in this plane through Mo(1), and S(5), N(2) and P(2) are in a similar plane through Mo(2). Each complex has an equatorial trigonal array of thiolate ligands with the typical 'two-up-one-down' arrangement found in this class of thiolate complex,[8,9] together with apical $PMePh_2$ and NH_3 ligands. Although the hydrogen atoms could not be located, the infrared data discussed above and each Mo–N distance of 2.298(15) Å are consistent with an NH_3 rather than

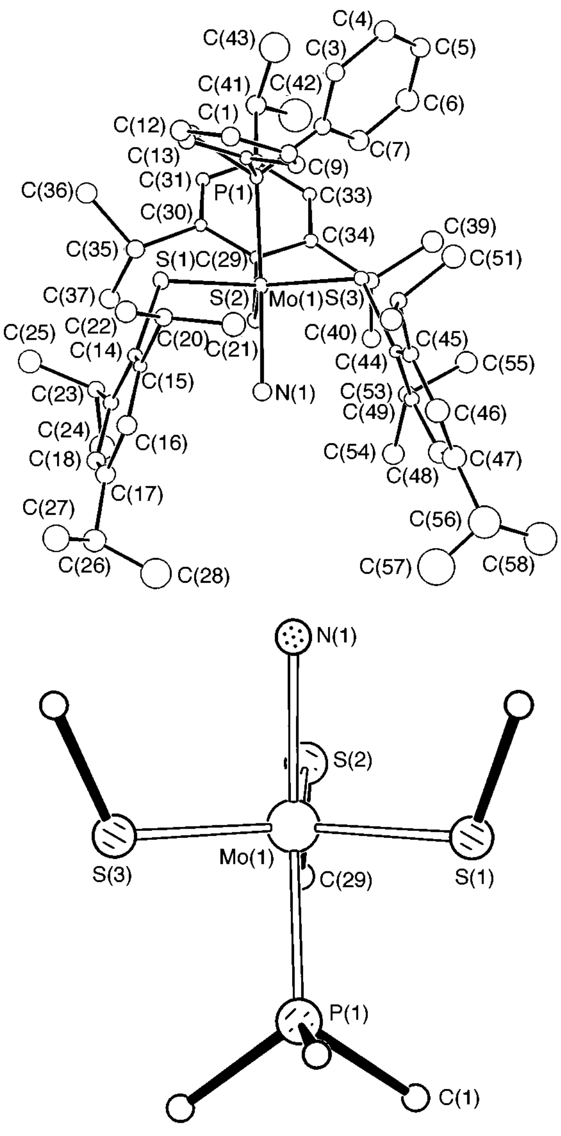

Fig. 2 Crystal structure of one of the two very similar molecules of $[MoH(SC_6H_2Pr^i_3\text{-}2,4,6)_3(NH_3)(PMePh_2)]$ **2** and the core of that molecule; in this and later figures, the orientation of the core diagram is the same. The two S atoms subtending the largest angle at the Mo atom are horizontal and the P and N atoms are in a plane parallel to that of the paper

an NH_2 or an NH group. None of the hydrogen atoms of either NH_3 ligand appears to be involved in any hydrogen bonds; these ligands are effectively screened from intermolecular interactions by the bulky thiolate ligands.

The hydride ligand could not be located but is clearly present as noted above. In this respect the structure of **2** is in fact very similar to the distorted trigonal pyramidal structure of $[MoH(SC_6H_2Pr^i_3\text{-}2,4,6)_3(C_5H_5N)(PMePh_2)]$,[7] which is reproduced in Fig. 3 for ease of reference. In this structure the hydride ligand is considered to occupy a position roughly in the equatorial plane between the S(2) and S(2′) atoms (see Fig. 3) since the angle subtended at Mo by these atoms is considerably larger than the other S–Mo–S angles and is sufficiently large to accommodate the hydride, which will also probably lie off the trigonal plane towards the phosphorus.[7,9,12] The corresponding angles in the structure of **2** are S(1)–Mo–S(3) [131.7(2)°] and S(4)–Mo(2)–S(6) [131.1(2)°], and we therefore suggest that the hydrides in **2** are located on the pseudo-mirror planes and somewhere in the faces defined by P(1)S(1)S(3) and P(2)S(4)S(6). This is the hydride position found in the low-temperature crystal structure of the analogue $[WH(SeC_6H_2Pr^i_2\text{-}2,4,6)_3(PMe_2Ph)_2]$.[13] The Mo–S distances and Mo–S–C angles are in the ranges usually observed for thiolate complexes of this type.[7]

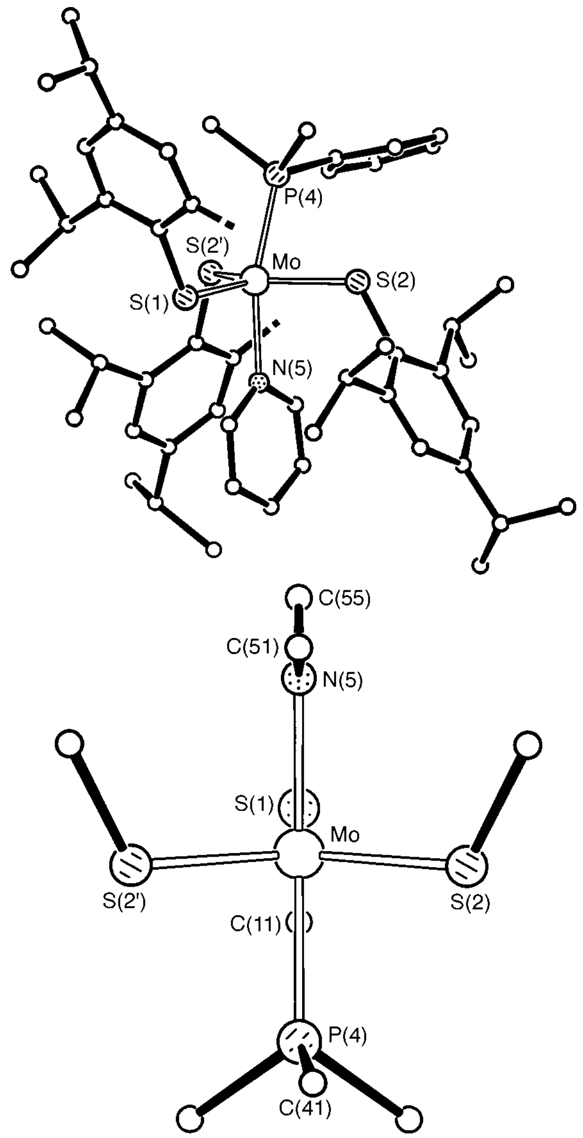

Fig. 3 Crystal structure of $[MoH(SC_6H_2Pr^i_3\text{-}2,4,6)_3(C_5H_5N)(PMePh_2)]$ and its core, taken from ref. 7

We were unable to isolate any other molybdenum complex from these reactions, even when all manipulations were carried out at 0 °C.

Preparation and structure of $[MoH(SC_6H_2Pr^i_3\text{-}2,4,6)_3(NH_2NHPh)(PMePh_2)]$ 3

Compound **1** reacts with NH_2NHPh in thf–MeOH at room temperature to produce grass green crystals of $[MoH(SC_6H_2Pr^i_3\text{-}2,4,6)_3(NH_2NHPh)(PMePh_2)]$ **3** which are diamagnetic and stable at room temperature for many weeks in the absence of air. The NH_2NHPh ligand gives rise to NH stretching absorptions at 3200–3400 cm^{-1} and NH_2 bending absorptions at 1560–1640 cm^{-1}. The weak Mo–H absorption is at 1900 cm^{-1} and the hydride resonance is a doublet at δ 2.6 with the same coupling as is observed in the proton-coupled ^{31}P doublet resonance at δ −86.5 [^2J(PMoH) = 84.7 Hz].

The molecular structure of **3** is shown in Fig. 4 and selected bond dimensions are in Table 3. As for complex **2**, complex **3** has the three sulfur atoms of the thiolate ligands in the ‘two-up-one-down’ configuration in the equatorial plane with the NH_2NHPh and $PMePh_2$ ligands in the apical sites. The hydride ligand was not conclusively located, but using the arguments developed for complex **2**, since the S(1)–Mo–S(2) angle (129.3°) is the largest in the equatorial plane, one would expect to find the hydride on the plane which bisects the S(1)–S(2) vector and

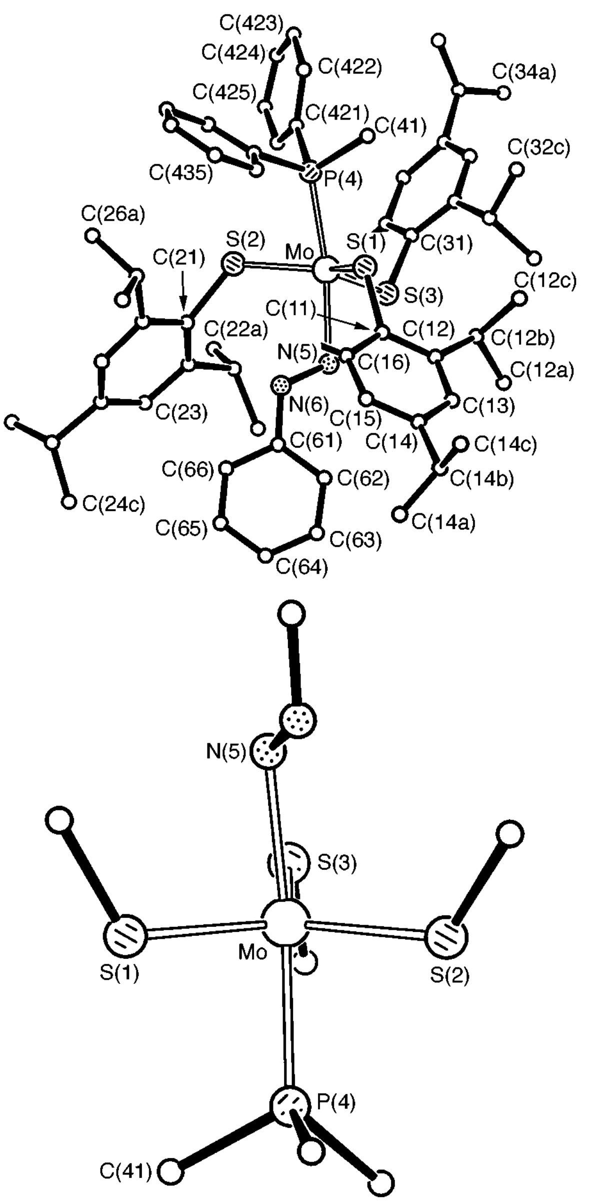

Fig. 4 Crystal structure of [MoH(SC$_6$H$_2$Pr$^i_3$-2,4,6)$_3$(NH$_2$NHPh)(PMePh$_2$)] **3** and its core; two of the isopropyl groups have been omitted for clarity

Table 3 Selected molecular dimensions in [MoH(SC$_6$H$_2$Pr$^i_3$-2,4,6)$_3$(NH$_2$NHPh)(PMePh$_2$)] **3**. Bond lengths in Å, angles in °, e.s.d.s in parentheses

(a) About the Mo atom			
Mo–S(1)	2.314(1)	Mo–P(4)	2.426(2)
Mo–S(2)	2.327(2)	Mo–N(5)	2.278(5)
Mo–S(3)	2.356(1)		
S(1)–Mo–S(2)	129.3*	S(1)–Mo–P(4)	83.3*
S(1)–Mo–S(3)	116.1(1)	S(2)–Mo–P(4)	80.9(1)
S(2)–Mo–S(3)	114.0(1)	S(3)–Mo–P(4)	117.3*
S(1)–Mo–N(5)	85.6(1)	S(2)–Mo–N(5)	96.1(1)
S(3)–Mo–N(5)	79.6(1)	P(4)–Mo–N(5)	162.8(1)
(b) In the thiolate ligands			
S(1)–C(11)	1.801(5)	S(3)–C(31)	1.795(4)
S(2)–C(21)	1.805(4)		
Mo–S(1)–C(11)	118.2(2)	Mo–S(3)–C(31)	114.4(2)
Mo–S(2)–C(21)	123.6(2)		
(c) In the phosphine ligand			
P(4)–C(41)	1.820(5)	P(4)–C(431)	1.839(6)
P(4)–C(421)	1.810(5)		
Mo–P(4)–C(41)	114.7(3)	C(41)–P(4)–C(421)	101.7(3)
Mo–P(4)–C(421)	119.4(2)	C(41)–P(4)–C(431)	99.5(3)
Mo–P(4)–C(431)	116.8(2)	C(421)–P(4)–C(431)	101.8(3)
(d) In the phenylhydrazine ligand			
N(5)–N(6)	1.451(7)	N(6)–C(61)	1.425(7)
Mo–N(5)–N(6)	112.8(4)	N(5)–N(6)–C(61)	117.4(5)

* E.s.d. is less than 0.05°.

on the S(1)P(4)S(2) face. Thus the six-fold co-ordination might be described as either octahedral or capped trigonal bipyramidal, much distorted in either case.

The hydrazine ligand adopts a *trans* conformation in the Mo–N–N–C group [torsion angle 179.0(4)°]. The three hydrogen atoms on the hydrazine N atoms were all located in difference maps and refined satisfactorily. These atoms appear to be screened from any intermolecular interactions by the large neighbouring thiolate ligands: there are short intramolecular N · · · S contacts, but not in the right direction for the formation of good hydrogen bonds. The N(5)–N(6) bond distance [1.451(7) Å] is consistent with an N–N single bond (1.424 Å).[14] The Mo–N(5) bond distance [2.278(5) Å] lies between the Mo–N distances in **2** [each 2.298(15) Å] and that in [MoH(SC$_6$H$_2$Pr$^i_3$-2,4,6)$_3$(C$_5$H$_5$N)(PMePh$_2$)] [2.244(9) Å].[7] The Mo–S distances and Mo–S–C angles are unexceptional.

During this work we found that if in the preparation of **3** 2 equivalents of NH$_2$NHPh were used and the reaction mixture was layered with MeOH after 5 h, followed by standing the solution at −20 °C, green crystals of complex **2** were obtained in low yield (see Experimental section). Although we were unable to detect NH$_2$Ph from this reaction by GC/MS in repeated attempts, probably because the yield was very low, nevertheless this result indicates that after first binding NH$_2$NHPh to Mo as in **3** the N–N bond has been cleaved. A similar result has been observed in more extensive work by Coucouvanis *et al.*[3] who demonstrated the stoichiometric and catalytic reduction of NH$_2$NHPh to NH$_3$ and NH$_2$Ph in the presence of [MoFe$_3$S$_4$Cl$_3$(NH$_2$NHPh)]$^{2-}$.

Reaction of [MoH(SC$_6$H$_2$Pr$^i_3$-2,4,6)$_3$(PMePh$_2$)] 1 with NMe$_2$NH$_2$

Treatment of compound **1** under the same conditions as for its reaction with NH$_2$NHPh gave a grass green oily compound **4** which was air- and temperature-sensitive and could not be obtained as a pure solid. In solution it showed N–H absorptions at 3310–3240 cm^{-1} and an Mo–H absorption at 1900 cm^{-1}. Its proton-coupled ^{31}P NMR spectrum showed a doublet δ −86.7 with a coupling constant of 85.2 Hz. Since these properties are so similar to those of **3**, we formulate **4** as [MoH(SC$_6$H$_2$Pr$^i_3$-2,4,6)$_3$(NH$_2$NMe$_2$)(PMePh$_2$)].

Conclusion

We have shown that catalysis of disproportionation or reduction of anhydrous hydrazine occurs in the presence of the electronically and co-ordinatively unsaturated complex [MoH(SC$_6$H$_2$Pr$^i_3$-2,4,6)$_3$(PMePh$_2$)] **1**. Although precise knowledge of the mechanism of these reactions requires detailed study, isolation of the adducts [MoH(SC$_6$H$_2$Pr$^i_3$-2,4,6)$_3$(NH$_3$)(PMePh$_2$)] and [MoH(SC$_6$H$_2$Pr$^i_3$-2,4,6)$_3$(NH$_2$NR$_2$)(PMePh$_2$)] (NR$_2$ = NHPh or NMe$_2$) indicates that the reduction process is likely to occur at the single Mo centre of the starting complex **1**. This observation lends support to the suggested mechanism of reduction of hydrazine[3] at the Mo in heteroclusters such as [MoFe$_3$S$_4$Cl$_3$(C$_6$Cl$_4$O$_2$)(MeCN)]$^{2-}$, and also to the possibility of such a reduction at the sulfur-ligated Mo site of nitrogenase.[4]

Experimental

2,4,6-Triisopropylbenzenethiol[15] and $[MoH(SC_6H_2Pr^i_3\text{-}2,4,6)_3(PMePh_2)]$[8] were prepared by published methods. Other reagent chemicals were used as purchased from Aldrich Chemical Co.

All manipulations were carried out under a dinitrogen atmosphere using conventional Schlenk tube and syringe or glove-box techniques unless otherwise stated. Reaction solvents were dried and freshly distilled under dinitrogen. The NMR spectra were measured using a JEOL GSX270 spectrometer and infrared spectra with a Perkin-Elmer 883 spectrometer. Elemental analyses were carried out by Microanalytical Services, University of Surrey, or by Butterworth Analytical Laboratories, Ltd.

Disproportionation and reduction studies

The method given is general. Full details of individual experiments are given in Table 1, where all data are the average of three separate determinations.

In experiments without Zn added, degassed anhydrous hydrazine was added to $[MoH(SC_6H_2Pr^i_3\text{-}2,4,6)_3(PMePh_2)]$ in suspension in degassed thf or thf–MeOH (3 : 1) in a sealed vessel under a vacuum. After a suitable reaction time the vessel was opened to the vacuum line and the evolved gas quantified with a Töpler pump and shown to be pure N_2 by mass spectrometry. About one third of the volume of the solution was then distilled under vacuum into 0.05 M H_2SO_4 (15 cm^3), to which was added, under pure argon, aqueous NaOH (15 cm^3, 10% w/v) and the NH_3 thus released was distilled into 0.05 M H_2SO_4 (15 cm^3). The remaining solvent was removed in a vacuum and the resulting brown, oily solid was treated with aqueous NaOH (15 cm^3, 10% w/v) and the NH_3 released distilled into 0.05 M H_2SO_4 (15 cm^3). The ammonium content of the H_2SO_4 solutions was then determined by the indophenol test[16] and the residual hydrazine monitored by the aminobenzaldehyde test.[17] Nitrogen balance was >90% in all cases. Blank experiments with hydrazine alone gave only very low levels of ammonia.

In experiments with added zinc and $HOC_6H_3Pr^i_2\text{-}2,6$, the protocol of Schrock *et al.*[1] was used: $[MoH(SC_6H_2Pr^i_3\text{-}2,4,6)_3(PMePh_2)]$, amalgamated zinc, $HOC_6H_3Pr^i_2\text{-}2,6$, and thf were added to a flask sealed under argon with a rubber septum. After addition of the appropriate ratio of hydrazine *via* the septum, the mixture was stirred for 16–18 h, then 0.05 M H_2SO_4 (15 cm^3) was injected into the flask and the mixture stirred for 20 min. The solvent was then removed in a vacuum and the residual oily solid was treated with aqueous NaOH (15 cm^3, 10% w/v) and the NH_3 released distilled into 0.05 M H_2SO_4 (15 cm^3) followed by analysis as above.

Preparations

$[MoH(SC_6H_2Pr^i_3\text{-}2,4,6)_3(NH_3)(PMePh_2)]$ 2. Anhydrous hydrazine (0.06 g, 1.9 mmol) was added *via* a syringe to an ice-cold, filtered solution of freshly prepared $[MoH(SC_6H_2Pr^i_3\text{-}2,4,6)_3(PMePh_2)]$ (1.16 g, 1.12 mmol) in thf–MeOH (20 cm^3 of 1 : 1 solution). The resulting green-brown solution was stirred for 30 min at 0 °C, filtered from a small amount of yellowish green powder, then layered with MeOH and left at −20 °C to produce *light green crystals* which were suitable for X-ray crystallographic study (0.4 g, 34%) (Found: C, 68.2; H, 8.7; N, 1.4. $C_{58}H_{86}MoNPS_3$ requires: C, 68.3; H, 8.5; N, 1.4%). IR (Nujol): ν(N–H) 3200–3400 (br); ν(Mo–H) 1890w cm^{-1}. NMR (CD_2Cl_2): ^1H δ 2.6 and 3.8 (spt, C*H*Me_2), 0.99 [d, PCH_3Ph, ^2J(PH) 57.7 Hz], 7.0–7.2 (m, aromatic); ^{31}P [proton-coupled, relative to $P(OMe)_3$] δ −86.8 [d, ^2J(PMoH) 86.7 Hz]; ^{14}N (relative to liquid $MeNO_2$) δ −72.1 (br s).

$[MoH(SC_6H_2Pr^i_3\text{-}2,4,6)_3(NH_2NHPh)(PMePh_2)]$ 3. Phenylhydrazine (0.05 g, 0.5 mmol) was added by syringe to a filtered solution of freshly prepared $[MoH(SC_6H_2Pr^i_3\text{-}2,4,6)_3(PMePh_2)]$ (0.26 g, 0.27 mmol) in thf–MeOH (20 cm^3 of 1 : 1 solution). The resulting dark green solution was stirred at 0 °C for 3 h then at 20 °C for 18 h. The grass green solid product was precipitated by reduction of the volume of solution under vacuum to ≈5 cm^3 followed by addition of cold MeOH (15 cm^3). Crystallisation of the product by slow diffusion of hexane into a thf solution at −20 °C produced *dark green single crystals* which were suitable for X-ray crystallography (0.09 g, 31%) (Found: C, 69.0; H, 8.0; N, 2.8. $C_{64}H_{91}MoN_2PS_3$ requires: C, 69.2; H, 8.2; N, 2.5%). IR (Nujol): ν(N–H) 3200–3400 (br), 1560–1640 (br); ν(Mo–H) 1900w cm^{-1}. NMR (CD_2Cl_2): ^1H δ 2.6 [d, Mo–H, ^2J(HMoP) 84.7], 2.8–2.9 and 3.4–3.5 (spt, C*H*Me_2), 1.6 [d, PCH_3Ph, ^2J(PH) 57.7 Hz], 7.0–7.2 (m, aromatic); ^{31}P [proton-coupled, relative to $P(OMe)_3$] δ −86.5 [d, ^2J(PMoH) 84.7 Hz].

$[MoH(SC_6H_2Pr^i_3\text{-}2,4,6)_3(NH_2NMe_2)(PMePh_2)]$ 4. Reaction of NH_2NMe_2 with $[MoH(SC_6H_2Pr^i_3\text{-}2,4,6)_3(PMePh_2)]$ under the same conditions as used for NH_2NHPh gave a very air- and temperature-sensitive oily compound which could not be purified but whose analysis showed the presence of nitrogen in roughly the correct value for the proposed formulation. IR (Nujol): ν(N–H) 3240–3310 (br); ν(Mo–H) 1900w (br) cm^{-1}. NMR (CD_2Cl_2): ^{31}P [proton-coupled, relative to $P(OMe)_3$] δ −86.7 [d, ^2J(PMoH) 85.2 Hz].

Crystallography

Crystal data for complex 2. $C_{58}H_{86}MoNPS_3$, $M = 1020.4$, triclinic, space group $P\bar{1}$ (no. 2), $a = 12.789(3)$, $b = 12.830(4)$, $c = 36.807(11)$ Å, $\alpha = 87.80(2)$, $\beta = 81.04(2)$, $\gamma = 88.17(2)$°, $U = 5959$ Å^3, $Z = 4$, $D_c = 1.14$ g cm^{-3}, $F(000) = 2184$, μ(Mo-Kα) = 3.7 cm^{-1}, $T = 173$ K.

A bright green crystal, size 0.2 × 0.2 × 0.1 mm, was mounted on a glass fibre and coated with paraffin. The crystal was transferred to an Enraf-Nonius CAD4 diffractometer (with monochromated Mo radiation). Accurate cell dimensions were determined using 25 reflections with θ between 7 and 10°, each reflection centred in four different orientations of the reflection plane. For the structure analysis intensities of 8166 unique reflections, of which 5136 had $F^2 > 2\sigma_{F^2}$, were measured to $\theta_{max} = 18°$. Measurement was curtailed at this point which was the time limit beyond which the low-temperature system could not maintain temperature. The crystal system and space group were determined from the intensity measurements and the structure was solved using the heavy atom method in the SHELXS 86 program.[18] Lorentz-polarisation and empirical absorption corrections were applied but a decay correction was unnecessary. A check was made for any higher symmetry space group but none was found. The structure contains two very similar, independent molecules which have some differences between them, notably in the orientation of the C(41), C(42) and C(43) isopropyl group and the C(8) to C(13) phenyl group. Thus they are not related by symmetry.

The refinement was carried out using full-matrix least-squares methods in the MOLEN program.[19] The Mo, S and P atoms were refined anisotropically, C and N atoms isotropically. The hydrogen atoms on the C atoms were placed in idealised positions and their thermal parameters, U_{iso}, allowed to ride with the parent atom ($U_{iso} = 1.3\ U_{eq}$ of C atoms); the hydride H and H's on N were not located and so were omitted. The final refinement resulted in an R factor of 0.081 and R' of 0.088[19] for the 5136 'observed' reflections weighted $w = \sigma_F^{-2}$. There were peaks to 0.8 e Å^{-3} in the final difference map. The final drawing was done using ORTEP.[20]

Crystal data for complex 3. $C_{64}H_{91}MoN_2PS_3$, $M = 1111.5$, triclinic, space group $P\bar{1}$ (no. 2), $a = 13.239(2)$, $b = 13.344(1)$, $c = 18.989(2)$ Å, $\alpha = 80.691(8)$, β 70.305(9), $\gamma = 86.112(10)$°, $U = 3116.4(6)$ Å^3, $Z = 2$, $D_c = 1.184$ g cm^{-3}, $F(000) = 1188$, μ(Mo-Kα) = 3.6 cm^{-1}, λ(Mo-Kα) = 0.710 69 Å.

Crystals were dark green, approximately cubic blocks. One, ≈$0.33 \times 0.33 \times 0.36$ mm, was mounted on a glass fibre and after photographic examination transferred to an Enraf-Nonius CAD4 diffractometer (with monochromated Mo radiation). Accurate cell dimensions were determined using 25 reflections, $\theta \approx 10.5°$, each reflection centred in four different orientations of the reflection plane. Diffraction intensities were measured by the ω–θ scan method to $\theta_{max} = 22°$.

During processing, corrections were applied for Lorentz-polarisation effects and crystal deterioration (three reflections monitored throughout the data collection showed intensities which fell steadily and uniformly to ≈56.6% of their starting values). The intensities were corrected for absorption (by semiempirical ψ-scan techniques) and to eliminate negative net intensities (by Bayesian statistical methods). 7608 Unique reflections, of which 5103 were 'observed' having $I > 2\sigma_I$, were then entered into the SHELX[21] program system and the structure was solved using the heavy-atom method and refined using full-matrix least-squares methods. The hydrogen atoms on the C atoms were placed in idealised positions and their thermal parameters allowed to ride on those of the parent C atoms.

The hydrogen atoms on N were located in a difference map and were refined with geometric constraints; the isotropic thermal parameters of all the hydrogen atoms were refined freely. The hydride ligand was not conclusively located and was not included in the refinement process. All non-hydrogen atoms were allowed anisotropic thermal parameters. The final refinement resulted in an R factor of 0.082 and R_g of 0.060[21] for all reflections weighted $w = (\sigma_F^2 + 0.000\,38F^2)^{-1}$; for the 5103 unobserved data only, R and R_g were 0.049 and 0.050 respectively. There were only two significant peaks in the final difference map at ≈0.72 (close to the Mo atom) and ≈0.59 e Å^{-3} (close to the phenyl ring).

Scattering factor curves for neutral atoms were from ref. 14. Computer programs used in this analysis have been noted above and in Table 4 of ref. 22 and were run on the MicroVAX 3600 instrument in the NFL.

CCDC reference number 186/777.

Acknowledgements

We thank the Ministry of Culture and Higher Education of the Islamic Republic of Iran for a maintenance grant to K. M. and the BBSRC for support of this work.

References

1 R. R. Schrock, T. E. Glassman, M. G. Vale and M. Kol, *J. Am. Chem. Soc.*, 1993, **115**, 725.

2 K. D. Demadis, S. M. Malinak and D. Coucouvanis, *Inorg. Chem.*, 1996, **35**, 4038 and refs. therein.

3 D. Coucouvanis, P. E. Mosier. K. D. Demadis, S. Patton, S. M. Malinak, C. G. Kim and M. A. Tyson, *J. Am. Chem. Soc.*, 1993, **115**, 12 193.

4 R. L. Richards, *Coord. Chem. Rev.*, 1996, **154**, 83 and refs. therein.

5 E. Block, G. Ofori-Okai, H. Kang and J. Zubieta, *J. Am. Chem. Soc.*, 1992, **114**, 758.

6 P. Schollhammer, F. Y. Petillon, S. Poder-Guillou, J. Y. Saillard, J. Talarmin and K. W. Muir, *Chem. Commun.*, 1996, 2633.

7 D. L. Hughes, N. J. Lazarowych, M. J. Maguire, R. H. Morris and R. L. Richards, *J. Chem. Soc.*, *Dalton Trans.*, 1995, 5.

8 T. E. Burrow, D. L. Hughes, A. J. Lough, M. J. Maguire, R. H. Morris and R. L. Richards, *J. Chem. Soc.*, *Dalton Trans.*, 1995, 1315.

9 T. E. Burrow, A. Hills, D. L. Hughes, J. D. Lane, N. J. Lazarowych, M. J. Maguire, R. H. Morris and R. L. Richards, *J. Chem. Soc.*, *Dalton Trans.*, 1991, 2519.

10 R. N. F. Thorneley, R. R. Eady and D. J. Lowe, *Nature* (*London*), 1978, **272**, 557.

11 J. R. Dilworth, J. Hu, R. Thompson and D. L. Hughes, *J. Chem. Soc.*, *Chem. Commun.*, 1992, 551.

12 T. E. Burrow, A. J. Lough, R. H. Morris and R. L. Richards, *Can. J. Chem.*, 1995, **73**, 1092.

13 T. E. Burrow, A. J. Lough, R. H. Morris and R. L. Richards, *Inorg. Chim. Acta*, 1997, **259**, 125.

14 *International Tables for X-Ray Crystallography*, Kynoch Press, Birmingham, 1974, vol. IV, pp. 99 and 149.

15 P. J. Blower, J. R. Dilworth, J. P. Hutchinson and J. A. Zubieta, *J. Chem. Soc.*, *Dalton Trans.*, 1985, 1533.

16 A. L. Chaney and E. P. Marbach, *Clin. Chem.*, 1962, **8**, 130.

17 G. W. Watt and J. D. Chrisp, *Anal. Chem.*, 1952, **24**, 2006.

18 G. M. Sheldrick, *Acta Crystallogr.*, *Sect. A*, 1990, **46**, 467.

19 C. K. Fair, MOLEN, Structure Determination System, Enraf-Nonius, Delft, 1990.

20 C. K. Johnson, ORTEP II, Report ORNL-5138, Oak Ridge National Laboratory, Oak Ridge, TN, 1976.

21 G. M. Sheldrick, SHELX, Program for crystal structure determination, University of Cambridge, 1976; also SHELXN, an extended version, 1977.

22 S. N. Anderson, R. L. Richards and D. L. Hughes, *J. Chem. Soc.*, *Dalton Trans.*, 1986, 245.

Received 12*th August* 1997; *Paper* 7/05886A