Molybdenum Complexes Containing Hydride and Sulphur Donor Ligands. Synthesis and Properties of $Mo(H)_2(S_2C_6H_3R)(PMePh_2)_3$, R = H, Me

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Reaction of 1,2,4-$(HS)_2RC_6H_3$ (1 equiv.) with $[Mo(N_2)_2(PMePh_2)_4]$ or $[MoH_4(PMePh_2)_4]$ gives $[Mo(H)_2(S_2C_6H_3R)(PMePh_2)_3]$, R = H, Me, the first dihydride complexes of Mo with sulphur co-ligands.

A variety of compounds of molybdenum co-ordinated predominantly by sulphur ligands catalyse the transfer of hydrogen to or from substrates. These include homogeneous hydrogenation catalysts,[1] the enzyme nitrogenase,[2—6] and heterogeneous hydrodesulphurization catalysts.[7,8] Intermediates with Mo–H bonds have not been observed in these reactions, but have sometimes been proposed.[4—6] Only a few complexes of Mo with some sulphur and hydride ligands have been reported and all are monohydrides.[9—11] We have discovered routes to the first dihydrides of this type.

The reaction of $[Mo(N_2)_2(PMePh_2)_4]$[12,13] with one equivalent of 1,2,4-$(HS)_2RC_6H_3$, [R = H (benzene-1,2-dithiol)[14]

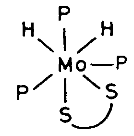

Figure 1

or R = Me (toluene-3,4-dithiol)][14] in benzene yields the green dihydride complexes (**1a**) and (**1b**)† [reaction (1)]. A

$$[Mo(H)_2(L)(PMePh_2)_3]$$

(**1**)

a; $L = S_2C_6H_4\text{-}1,2$
b; $L = S_2C_6H_3Me\text{-}1,2,4$
c; $L = S_2C_2H_4$

similar route was employed by Richards and co-workers to prepare complexes $[Mo(H)(SR)(dppe)_2]$[10,11] (dppe = $Ph_2PCH_2CH_2PPh_2$) and $[Mo(SR)_2(dppe)_2]$[15,16] by the reaction of $[Mo(N_2)_2(dppe)_2]$ with one and two equivalents, respectively, of certain thiols HSR. The complexes can also be prepared from $[MoH_4(PMePh_2)_4]$ [reaction (2)].[17] If these reactions are carried out with two equivalents of sulphur ligand, then the new complexes $[Mo(S_2C_6H_3R)_2(PMePh_2)_2]$‡ are produced in high yield.

$$[Mo(N_2)_2(PMePh_2)_4] + 1,2,4\text{-}(HS)_2RC_6H_3 \rightarrow (\mathbf{1}) + PMePh_2 + 2\,N_2 \quad (1)$$

$$[MoH_4(PMePh_2)_4] + 1,2,4\text{-}(HS)_2RC_6H_3 \rightarrow (\mathbf{1}) + PMePh_2 + 2\,H_2 \quad (2)$$

Complexes (**1a**) and (**1b**) are green, oxygen-sensitive solids. Spectral data† indicate that they have fluxional, seven-co-ordinate geometries. The local environment about Mo is as shown in Figure 1.

The ^{31}P n.m.r. spectrum of (**1a**) gives one singlet at 295 K but three broad peaks at 200 K (400 MHz). The proton coupled spectrum at 295 K is a triplet with J_{PH} 54 Hz. The hydride resonance is a 2-proton quartet. The T_1 value of 278 ms (200 MHz, 200 K) for the hydrides of (**1b**) suggests that there is no H–H interaction of the type proven for $[Mo(\eta^2\text{-}H_2)(CO)_3(PPr^i_3)_2]$.[19] Related dihydrides of Mo^{IV} with oxygen or nitrogen donors are $Mo(H)_2(PMePh_2)_3(O_2CCF_3)_2$[20] and $[Mo(H)_2(PMePh_2)_3(CH_3CN)_3]^{2+}$.[21]

Reactions similar to (1) or (2) involving ethane-1,2-dithiol as the sulphur ligand yield the complex $[Mo(H)_2(S_2C_2H_4)(PMePh_2)_3]$ (**1c**)† which has only been observed in solution because it readily decomposes with evolution of ethylene to give a black precipitate.

Dideuteride complexes (**1a**) and (**1b**) have the intriguing property of exchanging D with ^1H from HS groups on added dithiol ligands. ^1H, D, and ^{31}P n.m.r. spectra were obtained to characterize the reaction of excess of sulphur ligand with a mixture of Mo(H)(D) and $Mo(D)_2$ isotopomers of (**1**) prepared from $[MoD_4(PMePh_2)_4]$ as in reaction (2). A typical product distribution is as in reaction (3).

$$\begin{aligned}&2[Mo(D)_2(S_2C_6H_4)(PMePh_2)_3] + 2\,C_6H_4(SH)_2 \rightarrow \\ &\quad [Mo(H\text{ or }D)_2(S_2C_6H_4)(PMePh_2)_3] + [Mo(S_2C_6H_4)_2\text{-}\\ &\quad (PMePh_2)_2] + C_6H_4(SD\text{ or }SH)_2 + PMePh_2 \\ &\qquad\qquad + 2H_2/HD/D_2 \quad (3)\end{aligned}$$

The mechanism of these exchange reactions is under investigation; it is likely that isotopes of hydrogen are migrating from the metal to co-ordinated thiolate ligands and back again. This contrasts with the chemistry of some sulphido bridged complexes of molybdenum where all reactions of hydrogen atoms appear to take place at sulphur and not at the metal.[1] To date none of the complexes has yielded crystals suitable for crystallography.

We acknowledge an operating grant from the Natural Sciences and Engineering Research Council of Canada to R. H. M. Dr. R. L. Richards is thanked for preprints of his work. We thank the Mass Spectrometry Centre, Medical Genetics, University of Toronto for the FAB MS spectra.

Received, 17th June 1987; Com. 847

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† (**1a**), 40% yield *via* reaction (2), ^{31}P n.m.r. (p.p.m. relative to H_3PO_4): δ (C_6H_6, 295 K, 80.1 MHz) +50.08 (s), δ ($PhMe/C_6D_6$, 203 K, 160.2 MHz) +61.6, +52.0, and +49.0 (all br.); ^1H n.m.r.: δ (C_6D_6, 200 MHz) −2.27 (q, MoH, J_{PH} 55 Hz), 1.72 (m, MeP), 6.9 (m, PhP *m*-, *p*-H), 7.3 (m, PhP *o*-H), 7.14 and 8.48 (AA′XX′) J_{AX} 7.9, $J_{AA'}$ 6.7, $J_{AX'}$ 1.3, $J_{XX'}$ 0 Hz; A = 4-, 5-H; X = 3-, 6-H of $S_2C_6H_4$); ν(MoH) (Nujol) 1824 cm^{-1}; $\lambda_{max.}$ (C_6H_6) 635 and 388 nm. Satisfactory elemental analyses were obtained.

(**1b**), 54% yield *via* reaction (2): sample is always contaminated with a little $Mo(S_2C_6H_3Me)_2(PMePh_2)_2$; ^{31}P n.m.r. δ (C_6H_6, 295 K) +50.23 (s) p.p.m.; ^1H n.m.r. δ (C_6D_6) −2.27 (q, MoH, J_{PH} 54 Hz), 1.72 (m, MeP), 2.27 (s, $\mathit{Me}C_6H_3$), 6.9—7.4 (m, PhP), 7.0 (X of ABX), and 8.2—8.4 (AB of ABX, $MeC_6\mathit{H}_3$).

(**1c**), ^{31}P n.m.r.: δ (PhMe, 295 K) 48.49 (s) p.p.m.; ^1H n.m.r.: δ (C_6D_6) −2.11 (q, MoH, J_{PH} 55 Hz), 1.70 (m, MeP), 2.18 and 2.25 (m, C_2H_4), and 7.0—7.5 (m, PhP).

‡ Complexes $Mo(S_2C_6H_3R)_2(PMePh_2)_2$ were characterised by fast-atom bombardment mass spectrometry and ^1H and ^{31}P n.m.r. spectroscopy. $Mo(S_2C_6H_4)_2(PMe_3)_2$ was reported in ref. 18.