Journal of Organometallic Chemistry, 286 (1985) C3—C4
Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

Preliminary communication

THIOLATE-HYDRIDE COMPLEXES OF MOLYBDENUM(II)

CAROLINE SHORTMAN and RAYMOND L. RICHARDS*
AFRC Unit of Nitrogen Fixation, University of Sussex, Brighton BN1 9QJ (Great Britain)

(Received January 21st, 1985)

Summary

The stable thiolate hydrides *trans*-$[MoH(SR)(dppe)_2]$ (dppe = $Ph_2PCH_2CH_2PPh_2$; R = Pr^i, Bu^t, $C_6H_2(C_3H_7)_3$-2,4,6; $C_6H_2(CH_3)_3$-2,4,6 or C_6H_2Br-4, $(C_3H_7)_2$-2,6) have been prepared by treatment of *trans*-$[Mo(N_2)_2(dppe)_2]$ with RSH.

Although mononuclear hydride complexes of molybdenum with thiolate co-ligands have relevance to current theories of the function of the active site of nitrogenase [1], their preparation has hitherto proved elusive. Indeed, only a few metal complexes of this type have been isolated [2,3,4,5], although they have been observed as reaction intermediates [3,4]. This appears to be a result of the tendency for reductive elimination of the parent thiol, e.g. $[IrH(SPh)Cl(CO)(PPh_3)_2]$ loses PhSH rather easily [5].

However, during the course of our studies of the reactions of dinitrogen complexes with thiols [6], we have been able to isolate the first examples of stable mononuclear hydride-thiolate complexes of molybdenum as green crystals (A, eq. 1).

$$trans\text{-}[Mo(N_2)_2(dppe)_2] + RSH \xrightarrow[60^\circ C]{THF} \underset{(A)}{trans\text{-}[MoH(SR)(dppe)_2]} + 2N_2 \qquad (1)$$

(R = Pr^i, Bu^t, $C_6H_2(C_3H_7)_3$-2,4,6; $C_6H_2(CH_3)_3$-2,4,6 or C_6H_2Br-4$(C_3H_7)_2$-2,6)

The use of bulky R groups is essential for the stability and isolation of compounds A. If smaller substituent groups (R′) are employed, bis(thiolate) complexes B are obtained (eq. 2) [4].

$$trans\text{-}[Mo(N_2)_2(dppe)_2] + 2R'SH \rightarrow \underset{(B)}{trans\text{-}[Mo(SR')_2(dppe)_2]} + H_2 + 2N_2 \qquad (2)$$

(R′ = C_6H_4X-4 (X = H, F, Cl, CH_3,
OCH_3, NH_2); Et, Pr^n or Bu^n)

0022-328X/85/$03.30

Reactions 2 proceed via green intermediates [4] which are probably thiolate hydrides, but they could not be isolated.

Compounds A are assigned the *trans*-configuration on the basis of their singlet ^{31}P NMR spectra (Table 1). Their ^1H NMR spectra (Table 1) show the hydride resonance as a quintet in the range −3.98 to −4.98 ppm. The analogue *trans*-$[IrH(SMe)(dppe)_2]PF_4$ shows a quintet ^1H resonance at −14.8 ppm [7].

TABLE 1

THIOLATO HYDRIDE COMPLEXES OF MOLYBDENUM(II) $[MoH(SR)(dppe)_2]$

R	ν(MoH) (cm^{-1}) [a]	$\delta(^1H)$ (ppm) [b]	^2J(PH) (Hz)	$\delta(^{31}P)$ ppm [c]
Bu^t	1700	−3.98	45.04±0.01	−57.0
Pr^i	1690	−4.85	45.5 ±0.01	−58.0
$C_6H_2(C_3H_7)_3$-2,4,6	1735	−4.75	47 ±2.0	−69.5
$C_6H_2(CH_3)_3$-2,4,6	1710	−4.98	46.4 ±0.7	−61.1
C_6H_2Br-4$(C_3H_7)_2$-2,4	1660	−4.78	46 ±3.0	−62.0

[a] Nujol mulls. [b] In CD_2Cl_2 solution, rel. $SiMe_4$, centre of quintet. [c] Broad resonance in THF solution, rel. $P(OMe)_3$.

It is likely that the steric bulk of the R group in reaction 1 prevents further attack by thiol at the molybdenum. If compounds A are treated with an excess of the smaller thiol, R'SH, then they are smoothly converted into *trans*-$[Mo(SR')_2(dppe)_2]$.

Reductive elimination of the bulky thiols is induced by treatment with neutral donors such as CO or PhNC, and gives the known compounds $[Mo(XY)_2(dppe)_2]$ (XY = CO or PhNC) [7] with no sign of insertion into the Mo—H or Mo—S bonds.

References

1 C. Veeger and W.E. Newton (Eds.), Advances in Nitrogen Fixation Research, M. Nijhoff and W. Junk, The Hague, 1984; J. Chatt, L.M.C. Pina and R.L. Richards New Trends in the Chemistry of Nitrogen Fixation, (Eds.), Academic Press, London, 1980.

2 T.B. Rauchfuss and D.M. Roundhill, J. Am. Chem. Soc., 97 (1975) 3386.

3 K. Osakada, T. Yamamoto and A. Yamamoto, Inorg. Chim. Acta, 90 (1984) L5.

4 J. Chatt, J.P. Lloyd and R.L. Richards, J. Chem. Soc. Dalton Trans., (1976), 56; C. Shortman and R.L. Richards, unpublished results.

5 T. Gains and D.M. Roundhill, Inorg. Chem., 13 (1974) 2521.

6 D. Povey and R.L. Richards, J. Chem. Soc. Dalton, Trans., (1984) 2585 and ref. therein.

7 J. Chatt, C.M. Elson, A.J.L. Pombeiro, R.L. Richards and G.H.D. Royston, J. Chem. Soc. Dalton Trans., (1978) 165 and ref. therein.