

**Preliminary communication**

**THIOLATE-HYDRIDE COMPLEXES OF MOLYBDENUM(II)**

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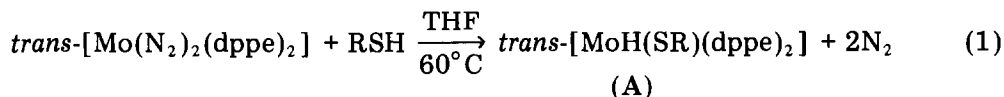
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**Summary**

The stable thiolate hydrides *trans*-[MoH(SR)(dppe)<sub>2</sub>] (dppe = Ph<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>PPh<sub>2</sub>; R = Pr<sup>i</sup>, Bu<sup>t</sup>, C<sub>6</sub>H<sub>2</sub>(C<sub>3</sub>H<sub>7</sub>)<sub>3</sub>-2,4,6; C<sub>6</sub>H<sub>2</sub>(CH<sub>3</sub>)<sub>3</sub>-2,4,6 or C<sub>6</sub>H<sub>2</sub>Br-4, (C<sub>3</sub>H<sub>7</sub>)<sub>2</sub>-2,6) have been prepared by treatment of *trans*-[Mo(N<sub>2</sub>)<sub>2</sub>(dppe)<sub>2</sub>] with RSH.

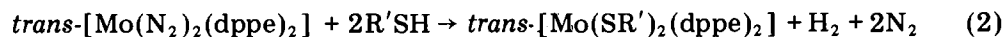
Although mononuclear hydride complexes of molybdenum with thiolate co-ligands have relevance to current theories of the function of the active site of nitrogenase {1}, their preparation has hitherto proved elusive. Indeed, only a few metal complexes of this type have been isolated [2,3,4,5], although 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<sub>3</sub>)<sub>2</sub>] 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).



(R = Pr<sup>i</sup>, Bu<sup>t</sup>, C<sub>6</sub>H<sub>2</sub>(C<sub>3</sub>H<sub>7</sub>)<sub>3</sub>-2,4,6; C<sub>6</sub>H<sub>2</sub>(CH<sub>3</sub>)<sub>3</sub>-2,4,6 or C<sub>6</sub>H<sub>2</sub>Br-4(C<sub>3</sub>H<sub>7</sub>)<sub>2</sub>-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].



(R' = C<sub>6</sub>H<sub>4</sub>X-4 (X = H, F, Cl, CH<sub>3</sub>, OCH<sub>3</sub>, NH<sub>2</sub>); Et, Pr<sup>n</sup> or Bu<sup>n</sup>) (B)

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  $^{31}\text{P}$  NMR spectra (Table 1). Their  $^1\text{H}$  NMR spectra (Table 1) show the hydride resonance as a quintet in the range  $-3.98$  to  $-4.98$  ppm. The analogue *trans*- $[\text{IrH}(\text{SMe})(\text{dppe})_2]\text{PF}_4$  shows a quintet  $^1\text{H}$  resonance at  $-14.8$  ppm [7].

TABLE 1

THIOLATO HYDRIDE COMPLEXES OF MOLYBDENUM(II)  $[\text{MoH}(\text{SR})(\text{dppe})_2]$ 

| R  | $\nu(\text{MoH})$ ( $\text{cm}^{-1}$ ) <sup>a</sup> | $\delta(^1\text{H})$ (ppm) <sup>b</sup> | $^2J(\text{PH})$ (Hz) | $\delta(^{31}\text{P})$ ppm <sup>c</sup> |
|--|---|---|-----------------------|--|
| Bu <sup>t</sup>  | 1700  | -3.98                                   | 45.04±0.01            | -57.0                                    |
| Pr <sup>i</sup>  | 1690  | -4.85                                   | 45.5 ±0.01            | -58.0                                    |
| $\text{C}_6\text{H}_2(\text{C}_3\text{H}_7)_3$ -2,4,6          | 1735  | -4.75                                   | 47 ±2.0               | -69.5                                    |
| $\text{C}_6\text{H}_2(\text{CH}_3)_3$ -2,4,6                   | 1710  | -4.98                                   | 46.4 ±0.7             | -61.1                                    |
| $\text{C}_6\text{H}_2\text{Br-4}(\text{C}_3\text{H}_7)_2$ -2,4 | 1660  | -4.78                                   | 46 ±3.0               | -62.0                                    |

<sup>a</sup> Nujol mulls. <sup>b</sup> In  $\text{CD}_2\text{Cl}_2$  solution, rel.  $\text{SiMe}_4$ , centre of quintet. <sup>c</sup> Broad resonance in THF solution, rel.  $\text{P}(\text{OMe})_3$ .

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,  $\text{R}'\text{SH}$ , then they are smoothly converted into *trans*- $[\text{Mo}(\text{SR}')_2(\text{dppe})_2]$ .

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

## References

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