The Reaction of *trans*-Bis(dinitrogen)bis(bisdiphenylphosphinoethane)molybdenum with Tetrakis(ethylthio-μ_3-sulphido-ferrate)(2-)

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Summary We find that no ammonia is formed in the reaction between *trans*-$[Mo(N_2)_2(dpe)_2]$ (dpe = $Ph_2PCH_2CH_2PPh_2$), $[Fe_4S_4(SEt)_4]^{2-}$ and hydrogen chloride, the main products being $[MoCl_2(dpe)_2]^+$, H_2S, EtSH, H_2, iron chlorides and, quantitatively, N_2.

It has recently been reported that low yields of ammonia are produced by the interaction of *trans*-$[Mo(N_2)_2(dpe)_2]$ and salts of the ion $[Fe_4S_4(SEt)_4]^{2-}$ (A^{2-}) followed by acidification.[1] Few details have been published but the reaction appeared important. Here we report our attempts to repeat it.

Equimolar quantities of the molybdenum and iron complexes (the latter as $[AsPh_4]^+$ or as $[NBu^n{}_4]^+$ salts) in tetrahydrofuran–methanol solution were stirred together for 20 h under vacuum. About 90% of the ligating dinitrogen was evolved as gas during this period. The addition of an excess of hydrogen chloride (anhydrous or aqueous) caused evolution of the remaining 10% of dinitrogen as gas. If shorter interaction periods were used, correspondingly less dinitrogen was evolved before the hydrogen chloride addition and more afterwards, the total evolution being quantitative to within experimental error.

The above experiments were repeated under dinitrogen. After the addition of hydrochloric acid the solvent was removed by distillation and the residue extracted with water. The aqueous extract was made alkaline with potassium hydroxide and distilled into acid. No ammonia was found in the distillate by the indophenol test although some nitrogeneous material (perhaps tributylamine) was present when the $[NBu^n_4]^+$ salt was used. It was demonstrated that this did not arise from the molybdenum complex by using *trans*-$[Mo(^{15}N_2)_2(dpe)_2]$ under $^{15}N_2$, when no ^{15}N nitrogenous material ($^{15}NH_3$ or other) was detected by isotopic analysis of the nitrogen.

With an excess of hydrogen chloride the reaction is as in the Scheme.

$$\textit{trans}\text{-}[Mo(N_2)_2(dpe)_2] + [NBu^n_4]_2[Fe_4S_4(SEt)_4] \xrightarrow[\text{THF/MeOH}]{\text{excess HCl}}$$
$$[MoCl_2(dpe)_2][FeCl_4] + FeCl_2 + 2[NBu^n_4][FeCl_4]$$
$$+ H_2S + 4EtSH + 2N_2 + H_2.$$

SCHEME

The products were determined qualitatively and N_2 also determined quantitatively. Analogously, (I), dinitrogen, and iron(II) chloride are obtained when iron(III) chloride is used in place of A^{2-}.

Cyclic voltammetric investigation of the interaction of $[NBu^n_4]_2A$ with *trans*-$[Mo(N_2)_2(dpe)_2]$ in tetrahydrofuran–methanol solution (containing LiCl) showed initially only the redox waves characteristic of the two starting materials ($E_{p_a} = -0{\cdot}19$ V and $+0{\cdot}03$ V, first reversible oxidation waves). After about 2 h the waves associated with the Mo-N_2 complexes began to decay and a new oxidation wave appeared ($E_{p_a} = -0{\cdot}65$ V). This wave was observed to the same extent in a solution of the Mo–N_2 complex alone after 5 h. Thus the only observed reaction is an accelerated decomposition of the dinitrogen complex. The waves of A^{2-} are not affected by the above decomposition.

We would not expect the Mo–N_2 complex to be reduced by A^{2-} because it is very difficult to reduce ($E_{p_c} > -2{\cdot}0$ V) and A^{2-} is a weak reducing agent ($E_{p_a} = +0{\cdot}03$ V). We conclude that under the above conditions there is no reduction of *trans*-$[Mo(N_2)_2(dpe)_2]$ by the iron-sulphur cluster (A^{2-}) and that the addition of hydrogen chloride to the mixture of those compounds causes cleavage of the iron–sulphur cluster and loss of N_2 from the dinitrogen complex.

In recent correspondence, since the submission of this manuscript, van Tamelen and Gladysz agree with our finding that dinitrogen in the molybdenum complex is not reduced by the sulphur–iron cluster anion. Nevertheless in their experiments they find ammonia which they believe is derived by reduction of some nitrogenous impurity in their $[Mo(N_2)_2(dpe)_2]$, prepared by the method of George and Seibold;[3] ours was obtained by another method.[4]

We gratefully acknowledge the gift of a sample of $[NBu^n_4]_2A$ from Professor G. N. Schrauzer.

(*Received*, 28*th December* 1973; *Com.* 1743.)

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[1] E. E. van Tamelen, verbally at the 24th Congress of the International Union of Pure and Applied Chemistry, Hamburg, 1973, p. 152.

[2] *Chem. Eng. News*, Sept. 24th, 1973, p. 15.

[3] T. A. George and C. D. Seibold, *J. Organometallic Chem.*, 1971, **30**, C13.

[4] J. Chatt and A. G. Wedd, *J. Organometallic Chem.*, 1971, **27**, C15.