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Preliminary communication

MECHANISM OF DISPLACEMENT OF DINITROGEN FROM *cis*-$[Mo(N_2)_2(PMe_2Ph)_4]$ AND *trans*-$[Mo(N_2)_2(Ph_2PCH_2CH_2PPh_2)_2]$ BY ISOCYANIDES. EVIDENCE FOR THE FIRST MIXED COMPLEX OF DINITROGEN AND ISOCYANIDE

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Summary

Sequential displacement of both N_2 ligands from *cis*-$[Mo(N_2)_2(PMe_2Ph)_4]$ by CNMe occurs by a dissociative (I_d) mechanism (k_2/k_1 ~5, k_1 = 0.020 min^{-1} at 273 K) via the intermediate *cis*-$[Mo(N_2)(CNMe)(PMe_2Ph)_4]$. For t-BuNC substitution, the only detected intermediate appears to be $[Mo(CNBu\text{-}t)(PMe_2Ph)_4]$ and no intermediate was detected in reactions of *trans*-$[Mo(N_2)_2(Ph_2PCH_2CH_2PPh_2)_2]$ with CNMe. N_2 appears to be labilised by *cis*-ligands in the order t-BuNC > CNMe > N_2 > NCR.

We have previously reported the formation of the complexes *trans*-$[Mo(CNR)_2(dppe)_2]$ (R = Me, t-Bu or 4-MeC_6H_4, dppe = $Ph_2PCH_2CH_2PPh_2$) and *cis*-$[Mo(CNR)_2(PMe_2Ph)_4]$ by treatment of the corresponding dinitrogen complexes with RNC in solution under irradiation or at reflux [1,2]. We are now studying the mechanism of these substitution reactions under milder conditions (273 K in the dark) and report here the detection of intermediates by ^{31}P NMR and electrochemical techniques.

In the reaction of *cis*-$[Mo(N_2)_2(PMe_2Ph)_4]$ (I) with CNMe (50 molar excess) in THF an unstable intermediate (II) was observed by cyclic voltammetry (Pt electrode, 0.2 *M* $[NBu_4]BF_4$ supporting electrolyte). II has an irreversible oxidation wave whose potential (E_p^{ox} −0.45 V vs. SCE) lies between those of I (−0.23 V) and *cis*-$[Mo(CNMe)_2(PMe_2Ph)_4]$ (−0.62 V) and its ^{31}P NMR spectrum shows two quintets (both intensity 1) and a triplet (intensity 2). These observations suggest the formulation *cis*-$[Mo(N_2)(CNMe)(PMe_2Ph)_4]$ for

II. Oxidation of II is thus easier than of *cis*-$[Mo(CNMe)_2(PMe_2Ph)_4]$ because of the replacement of one N_2 by the better net donor [3] MeNC.

Under pseudo first-order conditions, the step controlling the rate of formation of II is first order in I concentration and zero order in RNC concentration. The value of the rate constant k_1 ($0.020\ \text{min}^{-1}$ at 273 K) is independent of RNC and close to the value obtained for N_2-substitution in I by RCN [4], consistent with N_2 loss being the rate determining step as shown in reactions 1 and 2.

$$\underset{\text{(I)}}{\textit{cis}\text{-}[Mo(N_2)_2(PMe_2Ph)_4]} \xrightarrow{k_1} [Mo(N_2)(PMe_2Ph)_4] + N_2 \tag{1}$$

$$[Mo(N_2)(PMe_2Ph)_4] + CNMe \xrightarrow{\text{fast}} \underset{\text{(II)}}{\textit{cis}\text{-}[Mo(N_2)(CNMe)(PMe_2Ph)_4]} \tag{2}$$

$$\textit{cis}\text{-}[Mo(N_2)(CNMe)(PMe_2Ph)_4] \xrightarrow{k_2} \underset{\text{(III)}}{[Mo(CNMe)(PMe_2Ph)_4]} \tag{3}$$

$$[Mo(CNMe)(PMe_2Ph)_4] + CNMe \xrightarrow{\text{fast}} \textit{cis}\text{-}[Mo(CNMe)_2(PMe_2Ph)_4] \tag{4}$$

The reaction of *trans*-$[Mo(N_2)_2(dppe)_2]$ with RNC also occurs through a similar dissociative mechanism, as does reaction of RCN [4] ($k_1 = 1.0 \times 10^{-4}\ \text{min}^{-1}$ at 273 K), but no intermediate monoisocyanide complex could be detected.

The displacement of dinitrogen from II was also studied and the data are consistent with the second dinitrogen dissociation as the rate limiting step (reactions 3 and 4) with $k_2 \sim 0.09\ \text{min}^{-1}$ at 273 K. The reaction profile is thus the same as that proposed for RCN substitution [4].

The ratio $k_2/k_1 \sim 5$ indicates a greater *cis*-N_2-labilising effect of MeNC (in II) compared to N_2 (in I). In analogous displacement of N_2 from I by RCN [4], the ratio $k_2/k_1 = 0.03$, thus yielding a *cis*-N_2-labilising order MeNC $>$ N_2 $>$ RCN, which is the order of π-accepting properties of these ligands [3,5]. A strong *trans*-labilising effect of MeNC is also apparent, since no intermediate could be detected during its reaction with *trans*-$[Mo(N_2)(dppe)_2]$ i.e. k_2/k_1 is at least 17.

Although MeNC has a greater net ($\sigma + \pi$) donor effect than N_2 at most metal sites [6] and might be expected, relative to N_2, to stabilise binding of an N_2 co-ligand, the fact that MeNC is the strongest labilising ligand implies that it is the π-interaction which determines labilisation of N_2.

Evidence for a five-coordinate intermediate of the type (III) (reaction 3) has been obtained from reaction of t-BuNC with I. This intermediate appears to have trigonal pyramidal geometry (doublet plus quartet, 3/1 intensity in the ^{31}P NMR spectrum) and decays with a rate constant of $0.05\ \text{min}^{-1}$ at 273 K. Its rate of formation is the same as that observed for loss of the first N_2 ligand (k_1 above), thus the rate of N_2 loss from the hypothetical $[Mo(N_2)(\text{t-BuNC})(PMe_2Ph)_4]$ must be much greater than k_1 and therefore greater than k_2 for the MeNC reaction i.e. t-BuNC has a greater *cis*-labilising effect than MeNC.

The varying stabilities, depending upon R, of the intermediates II and III reflect the relative electronic and steric properties of RNC and we are extending the range of R groups to give further information on the factors influencing the course of these displacement reactions.

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References

1 J. Chatt, A.J.L. Pombeiro and R.L. Richards, J. Organometal. Chem., 190 (1980) 297.
2 J. Chatt, C.M. Elson, A.J.L. Pombeiro, R.L. Richards and G.H.D. Royston, J. Chem. Soc. Dalton, (1978) 165.
3 J. Chatt, J.R. Dilworth and R.L. Richards, Chem. Rev., 78 (1978) 608.
4 B.J. Carter, J.E. Bercaw and H.B. Gray, J. Organometal. Chem., 181 (1979) 105; J. Chatt, R.A. Head, G.J. Leigh and C.J. Pickett, J. Chem. Soc. Dalton, (1979) 1638.
5 B.M. Bancroft, P.F. Jarrod, A.G. Maddock, M.J. Mays and B.E. Pinter, J. Amer. Chem. Soc., 94 (1972) 647.
6 J. Chatt, G.J. Leigh, C.T. Kan, C.J. Pickett and D.R. Stanley, J. Chem. Soc. Dalton, in press.