

Preliminary communication

MECHANISM OF DISPLACEMENT OF DINITROGEN FROM *cis*-[Mo(N₂)₂(PMe₂Ph)₄] AND *trans*-[Mo(N₂)₂(Ph₂PCH₂CH₂PPh₂)₂] BY ISOCYANIDES. EVIDENCE FOR THE FIRST MIXED COMPLEX OF DINITROGEN AND ISOCYANIDE

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Summary

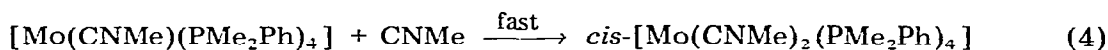
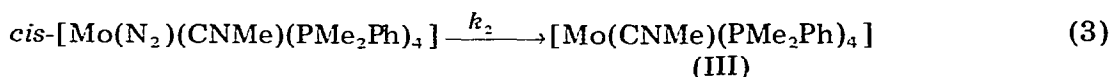
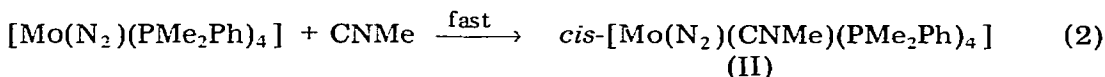
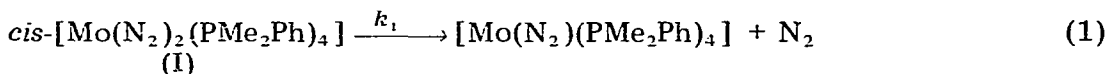
Sequential displacement of both N₂ ligands from *cis*-[Mo(N₂)₂(PMe₂Ph)₄] by CNMe occurs by a dissociative (*I_d*) mechanism ($k_2/k_1 \sim 5$, $k_1 = 0.020 \text{ min}^{-1}$ at 273 K) via the intermediate *cis*-[Mo(N₂)(CNMe)(PMe₂Ph)₄]. For *t*-BuNC substitution, the only detected intermediate appears to be [Mo(CN*t*-Bu)(PMe₂Ph)₄] and no intermediate was detected in reactions of *trans*-[Mo(N₂)₂(Ph₂PCH₂CH₂PPh₂)₂] with CNMe. N₂ appears to be labilised by *cis*-ligands in the order *t*-BuNC > CNMe > N₂ > NCR.

We have previously reported the formation of the complexes *trans*-[Mo(CNR)₂(dppe)₂] (R = Me, *t*-Bu or 4-MeC₆H₄, dppe = Ph₂PCH₂CH₂-PPh₂) and *cis*-[Mo(CNR)₂(PMe₂Ph)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 ³¹P NMR and electrochemical techniques.

In the reaction of *cis*-[Mo(N₂)₂(PMe₂Ph)₄] (I) with CNMe (50 molar excess) in THF an unstable intermediate (II) was observed by cyclic voltammetry (Pt electrode, 0.2 M [NBu₄]BF₄ supporting electrolyte). II has an irreversible oxidation wave whose potential ($E_p^{\text{ox}} -0.45 \text{ V vs. SCE}$) lies between those of I (-0.23 V) and *cis*-[Mo(CNMe)₂(PMe₂Ph)₄] (-0.62 V) and its ³¹P NMR spectrum shows two quintets (both intensity 1) and a triplet (intensity 2). These observations suggest the formulation *cis*-[Mo(N₂)(CNMe)(PMe₂Ph)₄] for

II. Oxidation of II is thus easier than of I but harder than of *cis*-[Mo(CNMe)₂(PMe₂Ph)₄] because of the replacement of one N₂ 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 min⁻¹ at 273 K) is independent of RNC and close to the value obtained for N₂-substitution in I by RCN [4], consistent with N₂ loss being the rate determining step as shown in reactions 1 and 2.



The reaction of *trans*-[Mo(N₂)₂(dppe)₂] with RNC also occurs through a similar dissociative mechanism, as does reaction of RCN [4] ($k_1 = 1.0 \times 10^{-4}$ 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 $k_2 \sim 0.09$ 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*-N₂-labilising effect of MeNC (in II) compared to N₂ (in I). In analogous displacement of N₂ from I by RCN [4], the ratio $k_2/k_1 = 0.03$, thus yielding a *cis*-N₂-labilising order MeNC > N₂ > 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(N₂)(dppe)₂] i.e. k_2/k_1 is at least 17.

Although MeNC has a greater net ($\sigma + \pi$) donor effect than N₂ at most metal sites [6] and might be expected, relative to N₂, to stabilise binding of an N₂ co-ligand, the fact that MeNC is the strongest labilising ligand implies that it is the π -interaction which determines labilisation of N₂.

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 ³¹P NMR spectrum) and decays with a rate constant of 0.05 min⁻¹ at 273 K. Its rate of formation is the same as that observed for loss of the first N₂ ligand (k_1 above), thus the rate of N₂ loss from the hypothetical [Mo(N₂)(*t*-BuNC)(PMe₂Ph)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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