Mechanism of Alkylation of Dinitrogen Co-ordinated to Molybdenum(0) and Tungsten(0)

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Summary The alkylation reactions of co-ordinated N_2 in $[M(N_2)_2(dppe)_2]$ (M = Mo or W; dppe = $Ph_2PCH_2CH_2PPh_2$) proceed *via* a rate-controlling loss of one dinitrogen ligand, co-ordination of alkyl halide, homolytic splitting of the carbon–halogen bond, and attack of the carbon-centred free radical upon the remaining dinitrogen ligand.

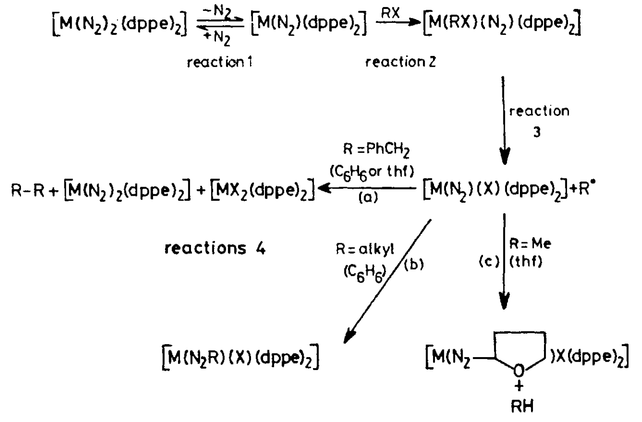
The reactions of $[M(N_2)_2(dppe)_2]$ [M = Mo or W; dppe = 1,2-bis(diphenylphosphino)ethane] with alkyl halides can give rise to alkyldiazenido-complexes,[1] diazoalkane-N^2 complexes,[2] or diazobutanol-N^2 complexes,[3] depending upon the alkyl halide and solvent. We propose that the reactions proceed as in the Scheme.

There is a predissociation of N_2 from the bis(dinitrogen) complex, (reaction 1, Scheme). The intermediate $[M(N_2)$-

$[M(N_2)(dppe)_2]$ then reacts with an alkyl halide (reaction 2).[4] The evidence for this is as follows. The reactions when $M = Mo$, $X = I$ or Br proceed in the dark, whereas when $M = W$ irradiation by visible light is necessary. The redox potentials *vs.* S.C.E. of the complexes $[M(N_2)_2(dppe)_2]$ are essentially the same,[4,5] and so are the charge-transfer spectra,[5] implying that electron transfer to the alkyl halide is not involved. The reactions with a 100-fold excess of alkyl halide in tetrahydrofuran (thf) are pseudo-first-order in $[M(N_2)_2(dppe)]$ and are essentially free of side-reactions; $k = ca.\ 10^{-4}\ s^{-1}$ for $M = Mo$ in the dark. 1 mol of dinitrogen is evolved whether the reactions take place under N_2 or Ar. The rates are independent of R for R = Me, Et, or Bu^n. As supporting evidence, we note that reaction (5) needs activation by light when $M = W$, but when $M = Mo$ light is not necessary. The $^{14}N_2$–$^{15}N_2$

$$[M(N_2)_2(dppe)_2] + 2CO \rightarrow [M(CO)_2(dppe)_2] + 2N_2 \qquad (5)$$

exchange proceeds rapidly in diffuse daylight with $[M(N_2)_2(dppe)_2]$ ($M = Mo$), but does not occur under similar conditions when $M = W$. Reaction (6) has kinetics consistent with an analogous dissociative mechanism, $k\ ca.\ 1{\cdot}5 \times 10^{-4}\ s^{-1}$.[6]



SCHEME.

$$[Mo(N_2)_2(dppe)_2] + PhCN \longrightarrow [Mo(N_2)(PhCN)(dppe)_2] + N_2 \qquad (6)$$

The intermediate M^0 species $[M(RX)(N_2)(dppe)_2]$ (which we can isolate if $X = CN$) homolyses to form R• radicals and the M^I species $[M(N_2)X(dppe)_2]$ (reaction 3). The evidence for this is that when the reaction of MeI with $[W(N_2)_2(dppe)_2]$ is carried out in thf in the presence of a ten-fold excess of $[NBu^n_4]Br$, ultimately only $[WI\{N_2CH(CH_2)_3OH\}(dppe)_2]^+$ is formed, and none of the corresponding bromide. This indicates that RX is attached to M *via* X, and that the M–X bond remains intact subsequently. Reaction mixtures of RX and $[M(N_2)_2(dppe)_2]$ in benzene generate R• radicals (irradiation required when $M = W$) and R• can be trapped on nitrosodurene and identified by the e.s.r. spectrum. We see no e.s.r. signals assignable to an M^I species. In thf solution, we observe signals assignable to $\overline{O[CH_2]_3CH}\cdot$, and the evolution of CH_4 when R = Me. Evidently $[M(N_2)X(dppe)_2]$ as produced in the reaction is very short lived. Stable $[Mo(N_2)X(dppe)_2]$ ($X = Cl$ or Br) complexes have been claimed by other workers,[7,8] but our attempts to repeat this preparation have yielded only a mixture of $[Mo(N_2)_2(dppe)_2]$ and $[MoX_2(dppe)_2]$. The occurrence of free radicals is confirmed by the reaction of $[W(N_2)_2(dppe)_2]$ with $CH_2{=}CH[CH_2]_4Br$ which produces $[WBrN_2CH_2{\cdot}\overline{CH[CH_2]_3CH_2}(dppe)_2]$ in high yield, and not the hex-5-enyldiazenido-N^2-complex.[9] The hex-5-enyl radical rearranges to give the cyclopentylmethyl radical in a first order reaction with a rate constant of *ca.* $10^5\ s^{-1}$.[10]

The next stage, when the reaction is conducted in benzene solution, is the attack of R• on co-ordinated dinitrogen (reaction 4b). However in thf solution when R• is a highly reactive radical such as Me•, it attacks thf to generate a tetrahydrofuranyl radical and RH (equation 4c). The tetrahydrofuranyl radical then attacks the co-ordinated N_2 in the same manner as R•. More stable radicals, whether produced in benzene or thf, dimerise; *e.g.* benzyl bromide yields $[MBr_2(dppe)_2]$ and bibenzyl (reaction 4a). Radicals of intermediate stability give a mixture of the above types of products.

The reactions involving *gem*-dibromides, $R^1R^2CBr_2$,[2] appear to proceed analogously *via* radicals $\cdot CR^1R^2Br$. We have detected $\cdot CH_2Br$ in the reaction of $[Mo(N_2)_2(dppe)_2]$ and CH_2Br_2 in benzene. Apparently complexes $[MBr(N_2CR^1R^2Br)(dppe)_2]$ are formed first and the carbon-bound bromine then ionises from the complex. However these reactions are complex and products other than the diazoalkane complex are often isolated.

The results are summarised in the Scheme.

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