The Mechanism of the Secondary Alkylation of Dinitrogen and the Relationship between Structure and Reactivity in the Alkylation of Co-ordinated Dinitrogen

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Summary Dinitrogen loss from a range of bis(N_2)-complexes of Mo and W is the common rate-determining step in the primary alkylation of the remaining co-ordinated N_2, whereas the second alkylation of co-ordinated N_2 is a typical S_N2 reaction, the rates of these reactions are sensitive to both the metal and the co-ligands and those factors which encourage the first alkylation are those which inhibit the second

WE have recently shown[1,2] that the monoalkylation of coordinated dinitrogen in the complexes *trans*-$[\mathrm{M(N_2)_2(Ph_2PCH_2CH_2PPh_2)_2}]$ (M = Mo or W) by alkyl halides, RX, occurs according to reaction sequence (i). The rate-determining step is the loss of dinitrogen.

$$\begin{array}{ll}
[\mathrm{M(N_2)_2(Ph_2PCH_2CH_2PPh_2)_2}] & \\
\quad \rightleftharpoons k_1 & \\
[\mathrm{M(N_2)(Ph_2PCH_2CH_2PPh_2)_2}] + \mathrm{N_2} & \\
\quad \downarrow \mathrm{RX} & \\
[\mathrm{M(N_2)(XR)(Ph_2PCH_2CH_2PPh_2)_2}] & \\
\quad \downarrow & \\
[\mathrm{M(N_2)(X)(Ph_2PCH_2CH_2PPh_2)_2}] + \mathrm{R}\cdot & \\
\quad \downarrow & \\
[\mathrm{M(N_2R)(X)(Ph_2PCH_2CH_2PPh_2)_2}] & \mathrm{(i)}
\end{array}$$

We have now determined the mechanism of the secondary alkylation whereby diazenido-complexes are converted into hydrazido(2−) complexes, reaction (ii). We have also determined those factors which control the course and rate of reaction between alkyl halides and a number of dinitrogen complexes *trans*-$[\mathrm{M(N_2)_2(diphos)_2}]$ (diphos = $\mathrm{Et_2PCH_2CH_2PEt_2}$ or $\mathrm{Ar_2PCH_2CH_2PAr_2}$; Ar = p-$\mathrm{MeOC_6H_4}$, p-$\mathrm{MeC_6H_4}$, Ph, p-$\mathrm{ClC_6H_4}$, or p-$\mathrm{CF_3C_6H_4}$) and *cis*-$[\mathrm{M(N_2)_2(PMe_2Ph)_4}]$.

$$\begin{array}{ll}
[\mathrm{M(N_2R)(X)(Ph_2PCH_2CH_2PPh_2)_2}] + \mathrm{RX} & \\
\quad \downarrow k_2 & \\
[\mathrm{M(N_2R_2)(X)(Ph_2PCH_2CH_2PPh_2)_2}]\mathrm{X} & \mathrm{(ii)}
\end{array}$$

The reaction of $[\mathrm{MBr(N_2Me)(Ph_2PCH_2CH_2PPh_2)_2}]$ with MeI in tetrahydrofuran (thf) at room temperature is first order in complex and in alkyl halide. For M=W, the reaction with MeI is 38 times faster than the reaction with EtI, which is typical of S_N2 reactions, and some 6 times faster than for M=Mo and MeI. We conclude that the secondary alkylation is a typical bimolecular nucleophilic substitution, and that the $\mathrm{N_2Me}$ group is much more nucleophilic when attached to W than to Mo (see Table).

TABLE

Complex	$E_{\frac{1}{2}}^{\mathrm{ox}}$/V [a]	$\nu(\mathrm{N_2})/\mathrm{cm^{-1}}$	k_1(rel.) [b]
trans-$[\mathrm{Mo(N_2)_2\{(}p\text{-}\mathrm{CF_3C_6H_4)_2PCH_2CH_2P(}p\text{-}\mathrm{CF_3C_6H_4)_2\}_2}]$	+0·22	1990 (KBr)	112
trans-$[\mathrm{Mo(N_2)_2\{(}p\text{-}\mathrm{ClC_6H_4)_2PCH_2CH_2P(}p\text{-}\mathrm{ClC_6H_4)_2\}_2}]$	+0·05	1975 (KBr)	73
trans-$[\mathrm{Mo(N_2)_2(Ph_2PCH_2CH_2PPh_2)_2}]$	−0·16	1975 (KBr)	46
trans-$[\mathrm{Mo(N_2)_2\{(}p\text{-}\mathrm{MeC_6H_4)_2PCH_2CH_2P(}p\text{-}\mathrm{MeC_6H_4)_2\}_2}]$	−0·25	1970 (KBr)	38
trans-$[\mathrm{Mo(N_2)_2\{(}p\text{-}\mathrm{MeOC_6H_4)_2PCH_2CH_2P(}p\text{-}\mathrm{MeOC_6H_4)_2\}_2}]$	−0·30	1960 (KBr)	26
trans-$[\mathrm{Mo(N_2)_2(Et_2PCH_2CH_2PEt_2)_2}]$	−0·43	1925 (KBr)	1
cis-$[\mathrm{Mo(N_2)_2(PMe_2Ph)_4}]$	−0·23 [c]	1931,1998 (benzene)	5700
cis-$[\mathrm{W(N_2)_2(PMe_2Ph)_4}]$	−0·07 [c]	1940,2025 (benzene)	12
Reaction		$10^5 k_2/\mathrm{l\ mol^{-1}s^{-1}}$ [d]	
trans-$[\mathrm{MoBr(N_2CH_3)(Ph_2PCH_2CH_2PPh_2)_2}]$ + MeI		48	
trans-$[\mathrm{WBr(N_2CH_3)(Ph_2PCH_2CH_2PPh_2)_2}]$ + MeI		260	
trans-$[\mathrm{WBr(N_2CH_3)(Ph_2PCH_2CH_2PPh_2)_2}]$ + EtI		7	

[a] Measured at Pt electrode in 0·2M $[\mathrm{NBu_4}][\mathrm{BF_4}]$–thf at 20 °C. [b] Relative rate constants at 298 K. k_1 absolute at 298 K for *trans*-$[\mathrm{Mo(N_2)_2(Et_2PPh_2CH_2PEt_2)_2}]$ in thf = $3{\cdot}7 \times 10^{-6}\mathrm{s^{-1}}$. [c] Irreversible; quoted potential = $E\mathrm{p^{ox}}$. [d] Measured in thf: 0·2M $[\mathrm{NBu_4}][\mathrm{BF_4}]$ at 20·6 °C for four concentrations of RX in the range 0·2–0·8M, and concentration of complex *ca.* 5mM.

The rates of the reactions of $[\mathrm{M(N_2)_2(Et_2PCH_2CH_2PEt_2)_2}]$ complexes differ from those of the $\mathrm{Ph_2PCH_2CH_2PPh_2}$ analogues. For M = Mo, the only nitrogen-containing product isolable after reaction with EtBr or MeBr in benzene is $[\mathrm{MoBr(N_2R_2)(Et_2PCH_2CH_2PEt_2)_2}]^+$. No such product could be isolated for M = W, even with a large excess of MeBr in benzene at room temperature during 24 h, with tungsten-filament lamp irradiation, and $[\mathrm{W(N_2)_2(Et_2PCH_2CH_2PEt_2)_2}]$ was recovered virtually quantitatively. Qualitatively, this reactivity parallels the observed labilities of $\mathrm{N_2}$ in all the parent complexes, but, in addition, whereas for $[\mathrm{M(N_2)_2(Ph_2PCH_2CH_2PPh_2)_2}]$ $k_1 > k_2[\mathrm{RBr}]$, for $[\mathrm{M(N_2)_2(Et_2PCH_2CH_2PEt_2)_2}]$ $k_1 < k_2[\mathrm{RBr}]$. The parallel with $\mathrm{N_2}$ lability extends even to *cis*-$[\mathrm{M(N_2)_2(PMe_2Ph)_4}]$ where no nitrogen-containing products have been observed. The relative values for k_1, under the same conditions in the dark, are Mo:W = 475:1 (see Table) as determined from initial rates of reaction with MeI, comparable with the rates of $\mathrm{N_2}$ loss.

The rates of the first alkylation reactions parallel the lability of $\mathrm{N_2}$ in cases where inner-sphere electron transfer to RX is involved. The more electron-rich the complex [reflected in a lower value of $\nu(\mathrm{N_2})$ and a more negative value of $E_{\frac{1}{2}}^{\mathrm{ox}}$], the less labile the $\mathrm{N_2}$, and the slower the rate of the reaction with RX (see Table). On the other hand, increased electron-richness in a system will promote the nucleophilicity of a bound $\mathrm{N_2R}$ group, and hence accelerate the second alkylation step. For dinitrogen complexes which are alkylated by mechanisms (i) and (ii), those factors which assist the first alkylation are precisely those which hinder the second. However, systems such as $[\mathrm{M(N_2)(SCN)(Ph_2PCH_2CH_2PPh_2)_2}]^-$, which are very electron-rich, are alkylated *via* an outer-sphere electron transfer process (iii) rather than by sequence (i).[3] In such systems, lability of $\mathrm{N_2}$ is no longer critical and sequences (ii) and (iii) are favoured by the same factors.

$$\begin{array}{ll}
[\mathrm{M(N_2)(SCN)(Ph_2PCH_2CH_2PPh_2)_2}]^- + \mathrm{RX} & \\
\quad \downarrow & \\
[\mathrm{M(N_2)(SCN)(Ph_2PCH_2CH_2PPh_2)_2}] + \mathrm{R}\cdot\ (+\ \mathrm{X^-}) & \\
\quad \downarrow & \\
[\mathrm{M(N_2R)(SCN)(Ph_2PCH_2CH_2PPh_2)_2}] & \mathrm{(iii)}
\end{array}$$

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