The Formation of a Nitrogen to Carbon Bond in a Reaction of a Dinitrogen Complex

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Summary Organic acid chlorides, RCOCl, react with *trans*-$[W(N_2)_2(dpe)_2]$ (dpe = $Ph_2PCH_2CH_2PPh_2$) to produce complexes $[(dpe)_2Cl_2W(N_2HCOR)]$ from which HCl can be removed to form chelated aroyl- and acyl-azo-*N*,*O*-complexes, $[(dpe)_2ClW(\text{–}N{=}N\text{–}COR)]$.

DINITROGEN in its stable complexes is usually no more reactive than free dinitrogen. The only well-defined reaction involves formation of bridging-dinitrogen complexes from the mono-*hapto*-complexes.[1] Reactions of the dinitrogen ligand which lead to the formation of organo-nitrogen complexes are particularly significant in the designing of a catalyst for the direct conversion of molecular nitrogen to organo-nitrogen compounds. We now report a reaction which results in the formation of a N–C bond.

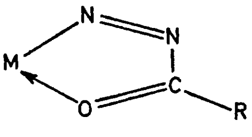
Previously amines have been obtained in low yields during nitriding reactions involving dinitrogen and Grignard reagents in the presence of titanium compounds and the like,[2] or by the addition of ketones to soluble nitride complexes obtained by the strong reduction of titanium complexes in the presence of dinitrogen,[3] in both cases followed by hydrolysis. Unstable dinitrogen complexes are probably intermediates in the formation of the nitride solutions in both of the above reactions, as they are in Shilov's reduction of dinitrogen to hydrazine.[4,5] This is the first reported reaction of a stable dinitrogen complex leading to an organo-nitrogen compound.

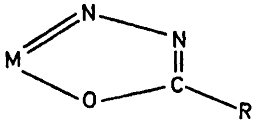
We find that acid chlorides, RCOCl (R = Me, Et, Ph, or *p*-$MeOC_6H_4$) react with *trans*-$[W(N_2)_2(dpe)_2]$[6] with quantitative evolution of 1 mol of dinitrogen. Pink diamagnetic complexes are isolated which we formulate as $[WCl_2(dpe)_2(N_2HCOR)]$ (I) on the basis of elemental analyses and physical data. Perhaps traces of moisture provide the hydrogen chloride required by the stoicheiometry.

Preliminary mass spectral studies of the complexes (I) provide some evidence of parent ions but the most abundant tungsten-containing ions are $[WCl(dpe)_2\{RCON_2(H)\}]^+$ which lose the fragment $RCON_2$ (or $RCON_2H$) to form $[WCl(dpe)_2]^+$, confirmed by the appearance of the appropriate metastable peaks. There are also strong peaks corresponding to RCN^+, in accord with the presence of a N–C bond in these complexes.

The complexes have no N≡N stretching band in their i.r. spectra, but all have a band at about **1700** cm^{-1}, assigned to ν (CO) of the acyl group. This band is not shifted upon ^{15}N substitution of (I; R = Me), but bands at 1510 and 1365 cm^{-1} shift to 1500 and 1325 cm^{-1}, respectively.

The presence of the hydrogen atom in the nitrogen-containing ligand of the complexes (I) (suggested by their diamagnetism) is supported by observation of a broad band centred at 2750 cm^{-1}, characteristic of protonic N–H and shifted to 2150 cm^{-1} upon deuteriation. Furthermore, the ^1H n.m.r. spectrum of (I; R = CH_3) exhibits a broad resonance, integrating for one proton, at $\tau = -3{\cdot}8$, which becomes a doublet $\{|J(^{15}N\text{–}H)| = 95\ \text{Hz}\}$ upon ^{15}N substitution. It has not been determined which nitrogen atom is protonated, and in this respect the formulation in equation (1) is arbitrary.


(a)


(b)

The proton is removed by triethylamine, giving triethylamine hydrochloride and a new series of yellow diamagnetic complexes [WCl(dpe)$_2$(N$_2$COR)] (II) in which ν (CO) is lowered to 1550—1575 cm^{-1}, indicating that the azo-ligand is probably chelating through the carbonyl oxygen. The reaction is reversed by hydrochloric acid, equation (1), and the opening of the ring closely parallels that of the benzoylhydrazido(3-)rhenium(v) chelate ring, equation (2).[7]

$$[Cl(dpe)_2W(N_2COR)] \xrightarrow{HCl} [Cl_2(dpe)_2W{=}N\text{–}NH\text{–}COR] \qquad (1)$$

$$[Cl_2(PPh_3)_2Re(N_2COR)] \xrightarrow{L} [Cl_2(dpe)_2LRe\text{–}N{=}N\text{–}COR] \qquad (2)$$

Upon ^{15}N substitution of (II; R = Me), the ν (CO) band at 1575 cm^{-1} does not shift but a band at 1338 cm^{-1} [ν (N_2)] shifts to 1298 cm^{-1}. Apparently the acyl- or aroylazo(1$^-$)-structure (a) is a closer approximation to the structure of the tungsten complexes (II) than is (b) which was held to be important for the rhenium chelate complexes, the ν (CO) bands of which are so low as to be masked by ligand absorptions.[7]

Initial investigations show that *trans*-[Mo(N$_2$)$_2$(dpe)$_2$] reacts analogously with organic acid chlorides.

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