The Reduction of Ligating Dinitrogen to yield a Ligating N_2H_2 Moiety

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Summary Reaction of *trans*-$[M(N_2)_2(dppe)_2]$ ($M = Mo$ or W, dppe = $Ph_2PCH_2CH_2PPh_2$) with hydrogen halides (HY) yields $[MY_2(N_2H_2)(dppe)_2]$ which, when $M = W$ and $Y = Cl$, gives salts $[WCl(N_2H_2)(dppe)_2]Z$ ($Z = BPh_4^-$ or ClO_4^-) with sodium tetraphenylborate or lithium perchlorate; $[WH(N_2)_2(dppe)_2][HCl_2]$ may also be obtained by reaction of *trans*-$[W(N_2)_2(dppe)_2]$ with hydrogen chloride.

ATTEMPTS to protonate and reduce mono-*hapto*-dinitrogen complexes usually lead to the protonation and oxidation of the metal with liberation of dinitrogen, sometimes together with dihydrogen,[1] but hydrazine and ammonia have been obtained, apparently by the reduction of some unstable binuclear μ-dinitrogen complexes.[2] These observations, together with theoretical considerations which indicate that mono-*hapto*-dinitrogen will be more difficult to reduce than molecular nitrogen, have led to the continued speculation that bridging dinitrogen complexes must be involved in the reduction of dinitrogen on nitrogenase.[3] However, spurred by the discovery that dinitrogen is protonated in bis-dinitrogen-molybdenum(0) and -tungsten(0) complexes during their reaction with some acid chlorides containing traces of hydrogen chloride, [4] *e.g.*

$$[W(N_2)_2(dppe)_2] + MeCOCl + HCl \rightarrow [WCl_2(N_2HCOMe)(dppe)_2] + N_2$$

we have investigated their direct protonation by acid. We find that when these bis-dinitrogen complexes are treated with hydrogen chloride or bromide, only one molecule of ligating dinitrogen is lost; the second is diprotonated and reduced to yield an N_2H_2 complex. Although this complex has not yet been reduced to ammonia, its formation is probably important in understanding the nitrogenase action, especially as it is now considered that only one molybdenum atom occurs in two of the most thoroughly investigated nitrogenases[5] (from *Klebsiella pneumoniae* and *Clostridium pasteurianum*).

TABLE

Compound	ν (N–X)[a] cm^{-1}	n.m.r. (p.p.m.)	
$[WCl_2(N_2H_2)(dppe)_2]$	3270m, 2920m	3·05[b]	P–CH_2
		6·5,[b] 5·8[c]	N_2H_2
$[WCl_2(N_2D_2)(dppe)_2]$	2430m, 2120m	3·05	P–CH_2
$[WCl_2(^{15}N_2H_2)(dppe)_2]$	3270m, 2920m	3·05[b]	P–CH_2
		5·8[c]	N_2H_2
$[WBr_2(N_2H_2)(dppe)_2]$	3270m, 2930m	3·05[b]	P–CH_2
		6·3[b]	N_2H_2
$[WBr_2(N_2D_2)(dppe)_2]$	2470m, 2190m	3·05[b]	P–CH_2
$[MoBr_2(N_2H_2)(dppe)_2]$	3300m, 2720ms,br	too insoluble	
$[MoBr_2(N_2D_2)(dppe)_2]$	2470m, 2065—2190ms,br		
$[WCl(N_2H_2)(dppe)_2]BPh_4$	3340w, 3230m	2·60[c]	P–CH_2
		3·0[c]	N_2H_2
$[WCl(N_2D_2)(dppe)_2]BPh_4$	2515w, 2380m	2·60[c]	P–CH_2
$[WCl(N_2H_2)(dppe)_2]ClO_4$	3330m, 3230m, 3130w	2·66[c]	P–CH_2
		2·8[c]	N_2H_2
$[WCl(N_2D_2)(dppe)_2]ClO_4$	2490m, 2370m, 2255w		
$[MoBr_2(N_2H_2)(depe)_2]$	3174m, 3078w, 2978.	0·4—2[c]	PC_2H_5 and PCH_2
		3·3[c]	possibly N_2H_2
$[MoBr_2(N_2D_2)(depe)_2]$	2405m, 2312m, 2190m		
$[WH(N_2)_2(dppe)_2][HCl_2]$	1995s[d]	$-3·50$	W–H
$[WH(^{15}N_2)(dppe)_2][HCl_2]$	1935s[e]	$-3·50$	W–H

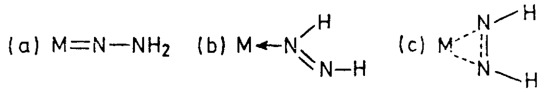
[a] Nujol or hexachlorobutadiene mulls. [b] In $CDCl_3$ solution at 100 MHz, relative to tetramethylsilane internal standard. [c] In CD_2Cl_2 solution. [d] $\nu(N_2)$. [e] $\nu(^{15}N_2)$. dppe = $Ph_2PCH_2CH_2PPh_2$. depe = $Et_2PCH_2CH_2PEt_2$.

When the complexes *trans*-$[M(N_2)_2(dppe)_2]$ ($M = W$ or Mo) or *trans*-$[Mo(N_2)_2(depe)_2]$ (depe = $Et_2PCH_2CH_2PEt_2$) are treated with six or more moles of XY (X = H or D; M = W and Y = Cl or Br; or M = Mo and Y = Br) in tetrahydrofuran at 0° they protonate to give high yields of $[MY_2(N_2X_2)(dppe)_2]$ or $[MoBr_2(N_2X_2)(depe)_2]$ with quantitative evolution of one mole of dinitrogen and no X_2. However, *trans*-$[Mo(N_2)_2(dppe)_2]$ evolves both molecules of dinitrogen on treatment with hydrogen chloride to form a molybdenum hydrido-species, and with only two moles of hydrogen chloride *trans*-$[W(N_2)_2(dppe)_2]$ protonates at the metal to give $[WH(N_2)_2(dppe)_2][HCl_2]$.

The compounds $[MY_2(N_2X_2)(dppe)_2]$ contain one labile halogen, Y. They conduct only slightly in dichloroethane but are 1 : 1 electrolytes in nitrobenzene and on treatment with sodium tetraphenylborate or lithium perchlorate the tungsten compounds give the salts $[WY(N_2X_2)(dppe)_2]Z$ ($Z = BPh_4^-$ or ClO_4^-). The molybdenum compounds have not yet been investigated. The complex $[WCl_2(N_2H_2)(dppe)_2]$ is converted by acetyl chloride or acetic anhydride into the known $[WCl_2(N_2HCOMe)(dppe)_2]$.[4]

Spectroscopic and other data for these protonated species are shown in the Table, which also includes $^{15}N_2$ derivatives. All the compounds examined show a broad resonance, integrating for two protons, which is assigned to the N_2H_2 group. This resonance from the compound $[WCl_2(^{15}N_2H_2)(dppe)_2]$ remains a singlet at temperatures down to −70° when it splits to an asymmetric multiplet. This suggests that rapid proton exchange is occurring even under the very dry conditions we employed. The observed proton shift is very sensitive to protic impurities in the n.m.r. solvent.

The N_2H_2 group may be bound as a 1-η-hydrazido(2−)† group as in (a), a 1-η-di-imine as (b) or even a 1-2-η-di-imine as (c) (M = Mo or W).



The wide ν(NH) splitting (about 350 cm^{-1} compared to about 100 cm^{-1} for a primary amine)[6] and the asymmetric n.m.r. pattern of the $^{15}N_2H_2$ complex at −70° favour structure (b) in [$WCl_2(N_2H_2)(dppe)_2$] but preliminary data from some related N_2H_2 complexes *e.g.* [$WCl(N_2H_2)(dppe)_2$]-BPh_4 (see Table) suggest that the N_2H_2 ligand may adopt the forms (a) or (c). The form of the ligating N_2H_2 is doubtless determined by the electronic and steric requirements of the metal, dependent on the other ligands in the complex.

It has been proposed that nitrogenase might function by first binding dinitrogen to a metal as a mono-*hapto* ligand, which is then protonated.[7] The above compounds may therefore be regarded as models for part of this sequence which finally leads to ammonia. We are now investigating the further reduction of the N_2H_2 complexes.

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† η is the IUPAC recommended symbol for '*hapto*'.

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