Polynuclear Dinitrogen Complexes

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Summary The complex *trans*-[ReCl(N_2)(PMe_2Ph)$_4$] reacts with a great variety of electron-acceptor molecules to form polynuclear dinitrogen complexes, apparently by addition of the acceptor atom to the terminal nitrogen atom of the dinitrogen ligand.

THE REACTIONS of the pale yellow complex, *trans*-[ReCl(N_2)(PMe_2Ph)$_4$] (I), with acceptor molecules are of two types. One type yields products having $\nu(N_2)$ increased by about 80 cm^{-1}, which corresponds to oxidation to the cation [ReCl(N_2)(PMe_2Ph)$_4$]$^+$, such as has been observed in the reaction of [ReCl(N_2)($Ph_2PCH_2CH_2PPh_2$)$_2$] with silver and copper(II) salts.[1] The second type gives products with decreased $\nu(N_2)$. These appear to be adducts having dinitrogen bridging between the rhenium and the acceptor atom. Only a few of the latter are known,[2] and all contain early transition metals as acceptors.

We now find that adduct-type products are formed with molecules containing all kinds of acceptor atoms. However, some strong electron acceptors (*e.g.* BCl_3 and $AlCl_3$) do not form them but cause dinitrogen evolution, and some give longer-lived products, presumably adducts, which readily lose dinitrogen or undergo other change. Most of the isolated products are 1 : 1 adducts formed by the addition of the complex (I) to the acceptor molecule, or to a simple derivative of it. All are solid except that from triethylaluminium, which is an oil.

In their effects on $\nu(N_2)$ the acceptor systems which form adducts fall into two classes.

(1) When the acceptor atom has vacant *d*-orbitals which can accept bonding π-electrons from the dinitrogen molecule the lowering of $\nu(N_2)$ is very great, as in the early transition metal and phosphorus pentafluoride adducts.

(2) Where the non-bonding *d*-orbitals are singly or doubly occupied (*e.g.* Cr^{III} or Pt^{II} respectively), or vacant but not energetically accessible (*e.g.* Al^{III}) the lowering of $\nu(N_2)$ is rather small. These observations support our suggestion that an electron "push-pull" mechanism is responsible for weakening of the dinitrogen triple bond in the complexes with the early transition metals.[2] Although the N≡N triple bond in the Re–N≡N–(acceptor-atom) system appears to be much weakened, it will not tend towards a double bond as in azobenzene, and the system will remain essentially linear.

The acceptor molecules tried and products obtained, together with pertinent properties, are listed in the Table. The terminal nitrogen atom in (I) appears to have complexing properties somewhat similar to those of the nitrogen atom in methyl cyanide. Dinitrogen has the characteristics of a very soft base. However, in complex (I) where $\nu(N_2)$ is exceptionally low (1922 cm^{-1}), the terminal nitrogen atom takes on more of the character of a hard base.

In the presence of an excess of some early transition metal halide complexes, particularly those of molybdenum and titanium, there is a tendency for more atoms of the early transition metal to become associated with complex (I), so producing a further lowering of $\nu(N_2)$.

About half the products listed in the Table have been obtained in reasonably pure condition. Meticulous work is needed before they can be formulated exactly owing to their very high molecular weights and the great reactivity of the early transition metal halides. This survey, however, is backed by $^{15}N{\equiv}^{15}N$ identification of $\nu(N_2)$ in typical examples, and thorough investigation of the molybdenum and tungsten products. We find that the reaction of (I) with [$MoCl_4L_2$] [L = Et_2O, tetrahydrofuran (THF), or $PEtPh_2$], in anhydrous conditions under dinitrogen, gives green adducts as previously reported.[2] These contain additional oxygen which we have been unable to exclude, and we now formulate them [(PMe_2Ph)$_4$ClRe(N_2)$MoOCl_3$L]. The blue products obtained with an excess of [$MoCl_4L_2$] are [(PMe_2Ph)$_4$ClRe(N_2)Mo_2OCl_5L].

It is highly probable that these and other products from acceptor molecules listed in the Table are dinitrogen-bridged, because *trans*-[ReCl(CO)(PMe_2Ph)$_4$] does not give analogous products with those reagents tried, except triethylaluminium. Its reaction with triethylaluminium would be expected in view of the addition of triethylalumin-

Colours and $\nu(N_2)$ *(cm^{-1}) of products from* $[ReCl(N_2)(PMe_2Ph)_4]$ *with electron acceptor molecules*

Acceptor Class (1)	Colour	$\nu(^{14}N_2)$[a]	$\nu(^{15}N_2)$[a]	Ratio[b]
$[TiCl_3(THF)_3]$ $TiCl_3$ $[TiCl_3(MeCN)_3]$	blue	1805	1750	1:1
$TiCl_3$ $[TiCl_3(MeCN)_3]$ [c]	red	n.a.[d]	—	[e]
$ZrCl_4$	yellow–brown	1790	1747	1:1
$HfCl_4$	yellow–orange	1824	1762	[e]
$[VCl_3(MeCN)_3]$	purple	1800	—	1:1
$NbCl_5$	green	1630	—	[e]
$TaCl_5$	brown	1695	1635	[e]
TaF_5	yellow	n.a.	—	[e]
$[MoCl_4(Et_2O)_2]$	emerald green	1795	1745	1:1
$[MoCl_4(THF)_2]$	emerald green	1795	—	1:1
$[MoCl_4(PMePh_2)_2]$	emerald green	1810	—	1:1
$[MoCl_4(PEtPh_2)_2]$	emerald green	1810	—	1:1
$[MoCl_4(PPh_3)_2]$	emerald green	1805	—	1:1
$[MoCl_4(Et_2O)_2]$[c]	bright blue	1680	1625	1:2
$[MoCl_4(THF)_2]$[c]	bright blue	1680	—	1:2
$[MoCl_4(PMePh_2)_2]$[c]	purple	n.a.	—	1:2
$[WCl_4(PMe_2Ph)_2]$	brown	1730	—	1:1
$[ReOCl_3(PPh_3)_2]$	green	1842	—	[e]
PF_5	pale pink	1640	1592	[f]
Class (2)				
$ScCl_3$	brown	1870	—	[f]
$[CrCl_3(THF)_3]$	violet–purple	1890	—	1:1
$[MoCl_3(THF)_3]$	green–brown	1850	—	[e]
$FeCl_2(THF)_{1\cdot5}$	red	1860	1795	[f]
$CoCl_2(THF)_{1\cdot5}$	blue	1855	1795	[f]
$[Pt_2Cl_4(PEt_3)_2]$	yellow[g]	1890	1825	[e]
$ZnCl_2(THF)_2$	cream	1880	1820	[f]
$AlEt_3$	pale yellow	1890	1845	[e]

$TiCl_4$ and TiF_4 oxidise the complex (I) to a product which is probably a salt of $[ReCl(N_2)(PMe_2Ph)_4]^+$, because $\nu(N_2) = 2010\ cm^{-1}$. The pink PF_5 product changed on storage into a similar green product. $LaCl_3$, $[CdCl_2(PEt_2Ph)_2]$, BCl_3, $AlCl_3$, $GaCl_3$, and WCl_6 gave colours and N_2 evolution.

[a] Nujol mulls.
[b] Ratio of Re to acceptor atoms in the product.
[c] An excess of acceptor.
[d] n.a. = not assignable.
[e] Ratio not determined.
[f] Thermally unstable but isolable products.
[g] Dissociates, and reverts to its components on attempted isolation.

ium to other carbonyl complexes of low $\nu(C\equiv O)$.[3] Carbonyl and dinitrogen complexes are so similar that any other type of reaction, such as the removal of chloride ion by the acceptor molecule, would occur equally easily in both.

Where two acceptor atoms are attached to the rhenium dinitrogen complex, it seems the more probable that only one acceptor atom in a dinuclear entity is attached to the terminal nitrogen atom, but both acceptor atoms could be attached. It seems unlikely on steric grounds that the nitrogen atom adjacent to the rhenium could be a point of attachment.

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