A Series of Nitrogen Complexes of Rhenium(I)

By J. CHATT,* J. R. DILWORTH, and G. J. LEIGH

(*A.R.C. Unit of Nitrogen Fixation, University of Sussex, Brighton* BN1 9QJ)

Summary The degradation of a benzoylazo-complex of rhenium(III) in the presence of various tertiary phosphines leads to a series of nitrogen complexes of rhenium(I) having low $\nu(N\equiv N)$.

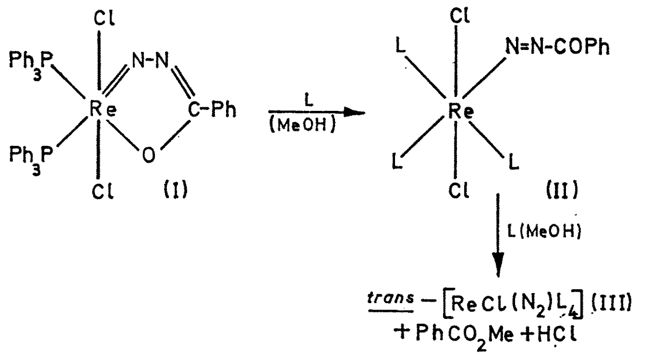
SEVERAL individual nitrogen complexes derived from metals of Group VIII have been discovered at intervals over the past three years, but many are ill-characterised and unstable.[1] We now report the first series of nitrogen complexes containing a non-Group VIII metal, only the second reasonably extensive series of crystalline and well defined nitrogen complexes,[2] and the first paramagnetic nitrogen complex (see Table).

Nitrogen complexes of rhenium-(I) *and* -(II), *and some carbonyl analogues*

Compound	m.p.[a]	$\nu(N\equiv N)$ (cm.$^{-1}$)	
		Chloroform	Nujol mull
$[ReCl(N_2)(Ph_2PCH_2{\cdot}CH_2{\cdot}PPh_2)_2]$	295—297°	1980s	1935m, 1940m, 1979s
$[ReCl(N_2)(PMe_2Ph)_4]$	165—169°	1925s	1920s
$[ReCl(N_2)(Ph_2PCH_2{\cdot}PPh_2)_2]$	243—246°	1980s	1990s, 1970m
$[ReCl(N_2)(Ph_2PCH{=}CHPPh_2)_2]$	310—312°	1979s	1982s, 2000m
$[ReBr(N_2)(Ph_2PCH_2{\cdot}CH_2{\cdot}PPh_2)_2]$[b]		1980s	1990s, 1960w
$[ReCl(N_2)(PMePh_2)_4]$[b]		1922s	1919s, 1939s
$[ReCl(N_2)(PPh_3)_2(CH_3C[OCH_2]_3P)_2]$	285—289°	insol.	2035s
$[ReCl(N_2)(Ph_2PCH_2{\cdot}CH_2{\cdot}PPh_2)_2]Cl$[b]		2060s	2035s
		$\nu(C\equiv O)$ cm.$^{-1}$	
$[ReCl(CO)(Ph_2PCH_2{\cdot}CH_2{\cdot}PPh_2)_2]$	> 345°	1810s	1820sh, 1795s
$[ReCl(CO)(PMe_2Ph)_4]$[c]	120—125°[d]		1790s

[a] With decomposition in sealed evacuated tube, on Kofler block *ca.* 40° lower.
[b] Not yet obtained analytically pure.
[c] Prepared by H. P. Gunz in this laboratory.
[d] With decomposition on Kofler block.
s—strong m—medium w—weak

The rhenium(I) nitrogen complexes are pale yellow compounds of type $[ReCl(N_2)(PR_3)_4]$ (PR_3 = mono- or equivalent di-tertiary phosphines) obtained by the degradation of (I)[3] according to the Scheme, and are thermally quite stable. Only the less sterically hindered phosphines take the reaction to completion, and the rate depends on the phosphine; thus dimethylphenylphosphine takes 2 hr., and methyldiphenylphosphine 24 hr., whereas diethylphenyl- and ethyldiphenyl-phosphines carry the reaction only to the benzoylazo-compound, type (II), as does dimethylphenylarsine. The complex (III; $L_2 = Ph_2PCH_2{\cdot}CH_2{\cdot}PPh_2$) may be obtained directly from (I) by the Scheme, or by treating (III; L = PMe_2Ph) with the diphosphine in boiling toluene for 14 hr., which illustrates how strongly the nitrogen is held by rhenium(I).



SCHEME. L = *mono- or half di- tertiary phosphine.* (*See Table.*)

In the ^1H n.m.r. spectra the methyl protons of $[ReCl(N_2)(PMe_2Ph)_4]$ and the methylene protons of $[ReCl(N_2)(Ph_2PCH_2{\cdot}CH_2{\cdot}PPh_2)_2]$ give rise to broad singlets, as they do in the corresponding carbonyl complexes. There is no ^{31}P–^1H coupling, and temperature-variation experiments suggest that this is not an exchange phenomenon. Thus it seems likely that the chlorine and nitrogen are in mutually *trans*-positions.

The nitrogen stretching frequencies are the lowest recorded, and those of the carbonyl analogues are correspondingly low. The parallel between the carbonyl and the nitrogen stretching frequencies (see Table) suggests that a neutral complex containing a terminal carbonyl group with low $\nu(C\equiv O)$ will generally have a nitrogen analogue.

In chloroform the nitrogen complexes are oxidised by chlorine to rhenium(III) or rhenium(IV) complexes depending on the phosphine, with quantitative evolution of nitrogen. However the compound $[ReCl(N_2)(Ph_2PCH_2{\cdot}CH_2{\cdot}PPh_2)_2]$, chlorinated in carbon tetrachloride, precipitates a purple, paramagnetic, unstable salt, presumably $[ReCl(N_2)(Ph_2PCH_2{\cdot}CH_2{\cdot}PPh_2)_2]Cl$, although its C, H, and N analyses are rather low. It has Λ *ca.* 18·8 mhos (nitrobenzene), μ_{eff} = 1·9 B.M., and a strong i.r. band at 2035 cm.$^{-1}$, presumably $\nu(N\equiv N)$. It is reduced to the original nitrogen complex by amalgamated zinc, in tetrahydrofuran under argon.

The rhenium(I) nitrogen complexes are generally very stable, but the purely aliphatic $[ReCl(N_2)(Me_2PCH_2{\cdot}CH_2{\cdot}PMe_2)_2]$ is much less stable than its aromatic analogue.

Despite their low N≡N stretching frequencies these complexes have not yet been reduced to yield ammonia. Although the terminal nitrogen atom is shielded by the phosphine ligands, it is reasonably open to attack, and these nitrogen complexes react readily with titanous chloride, cupric chloride, silver nitrate, and similar salts to give products not yet characterized, but with a shifted ν(N≡N).

Added in proof: $[ReCl(N_2)(PMe_2Ph)_4]$ has been obtained directly from molecular nitrogen by the method of ref. 2.

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[1] For references see A. D. Allen and F. Bottomley, *Accounts Chem. Res.*, 1968, **1**, 360; R. Murray and D. C. Smith, *Co-ordination Chem. Rev.*, 1968, **3**, 429.

[2] J. Chatt, G. J. Leigh, and R. L. Richards, *Chem. Comm.*, 1969, 515.

[3] J. Chatt, J. R. Dilworth, G. J. Leigh, and R. J. Paske in "Progress in Co-ordination Chemistry," ed. M. Cais, Elsevier, Amsterdam, 1968, p. 246.