Dinitrogen Complexes of Rhenium(I) and Rhenium(II)

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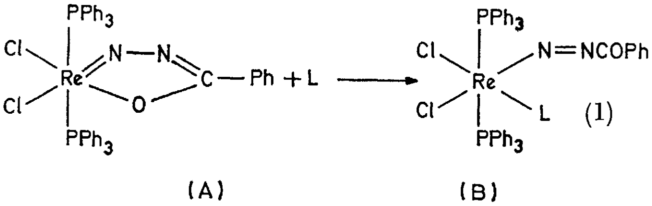
Dinitrogen complexes of rhenium(I) are prepared by the reaction of benzoylazo-complexes, $[Re(N{=}NCOPh)Cl_2(PPh_3)_xL_y]$ (L = monodentate ligand or $\frac{1}{2}$ bidentate ligand; $x = 0$ or 2, $x + y = 3$), with certain ligands in boiling methanol. The dinitrogen complexes are of the type *trans*-$[ReCl(N_2)L_xL'_y]$ (L = a variety of organophosphines; L′ = L or some other organophosphine, CO or PF_3; $x + y = 4$). For L = L′ = PMe_2Ph the dinitrogen complex has an exceptionally low $\nu(N_2)$ (1925 cm^{-1}). Despite its low $\nu(N_2)$, it is not easily reduced and strong Brønsted acids protonate the metal rather than the bound dinitrogen. On oxidation, the dinitrogen complexes form moderately stable paramagnetic cations, *e.g.*, *trans*-$[ReCl(N_2)(Ph_2PCH_2CH_2PPh_2)_2]^+$.

We have described briefly the preparation of a series of six-co-ordinate diamagnetic rhenium(I) dinitrogen complexes of the general formula *trans*-$[ReCl(N_2)L_xL'_y]$ (L = one of a variety of mono- or bi-dentate organophosphines; L′ = L or some other organophosphine, CO, or PF_3).[1] Here we describe the series in full, and the oxidation of the more stable members to paramagnetic cationic dinitrogen complexes of rhenium(II).

Synthesis of the Dinitrogen Complexes of Rhenium(I).—These are obtained from the green chelate complex (A) which reacts with a great variety of ligands to form benzoylazo-rhenium compounds (B) (Reaction 1).[2]



(1)

(A) (B)

However, a few ligands in boiling methanol carry the reaction further (Reaction 2) to give the neutral dinitrogen complexes listed in Table 1. Since methyl benzoate is also a product, the reaction is probably initiated by the nucleophilic attack of methanol or methoxide ion on the carbonyl carbon. Ethanol in place of methanol gave an impure product, difficult to separate from paramagnetic impurities, and the strong nucleophile methyl-lithium gave a very impure product having ' dinitrogen bands ' in its i.r. spectrum.

$$(B) + MeOH + L \longrightarrow \begin{matrix}[ReCl(N_2)(PPh_3)_2L_2]\\ \text{or}\\ [ReCl(N_2)L_4]\end{matrix} + PhCOOMe + HCl\ (+\ 2PPh_3) \quad (2)$$

The ligands which carry the reaction through to the dintrogen complex (see Table 1) usually contain phosphorus as a donor atom or atoms, the only exceptions being carbon monoxide and *o*-phenylenebis(dimethylarsine). Some ligands, *e.g.*, PMe_2Ph, replace all of the triphenylphosphine from the co-ordination sphere in forming the dinitrogen complex; others, *e.g.*, PF_3, do not. It is not clear what determines the capacity of ligands to produce the dinitrogen complexes but steric crowding is undoubtedly important in these octahedral systems.[3,4] Thus dimethylphenylphosphine forms a dinitrogen complex much more rapidly than does methyldiphenylphosphine. The reaction stops at the azo-stage with triethylphosphine, diethylphenylphosphine, ethyldiphenylphosphine, dimethylphenylarsine, 1,2-bis(diphenylarsino)ethane, and pyridine. Triphenylphosphine in ethanol cannot convert (A) even to the azo-stage. Relatively small ligands with a tendency to stabilise a low oxidation state seem best able to produce the dinitrogen complexes. The dinitrogen complexes produced are listed in Table 1, which includes $^{15}N{\equiv}^{15}N$ analogues.

The mechanism of formation by nucleophilic attack at the carbonyl carbon is supported by preliminary experiments which indicate that the addition of alkali to the reaction medium increases the reaction rate, as does a nitro-group in the *para*-position of the phenyl group of the benzoylhydrazido(3−) moiety in (A), whereas a *p*-methoxy-group decreases it.[2]

The cinnamoylhydrazido(3−) analogue of (A) also reacts to form dinitrogen complexes and much faster than (A) itself, but it was not possible to obtain a dinitrogen complex from it which could not also be obtained from (A).

Properties of the Rhenium(I) *Complexes*.—The dinitrogen complexes are all stable in air at room temperature for considerable periods. Not all have been obtained analytically pure and often difficulty was experienced in purification, the principal contaminant being the intermediate benzoylazo-complex. Prolonged reaction times lead to loss of dinitrogen and the formation of very soluble yellow materials. The complex $[ReCl(N_2)(PMe_2Ph)_4]$ was also obtained by the reduction of $[ReCl_3(PMe_2Ph)_3]$ in tetrahydrofuran by sodium amalgam in the presence of dinitrogen. I.r. and ^1H n.m.r. spectral evidence indicate that the dinitrogen complexes have the chlorine *trans* to the dinitrogen. This was confirmed for $[ReCl(N_2)(PMe_2Ph)_4]$ by an *X*-ray analysis, which shows that the four phosphorus atoms are at the corners of a puckered square, with the N_2 and Cl occupying the two remaining vertices of the octahedron.[3]

The ^1H n.m.r. spectra of (I), (III), (VIII), and (XII) (Table 1) were measured in deuteriochloroform solution.

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[1] J. Chatt, J. R. Dilworth, and G. J. Leigh, *Chem. Comm.*, 1969, 687.

[2] J. Chatt, J. R. Dilworth, G. J. Leigh, and, in part, V. D. Gupta, *J. Chem. Soc.*, (*A*) 1971, 2631.

[3] D. A. Bright and J. A. Ibers, *Inorg. Chem.*, 1969, **8**, 703.

[4] B. R. Davis and J. A. Ibers, *Inorg. Chem.*, 1971, **10**, 578.

The spectrum of complex (I) shows three peaks only; a multiplet with a maximum at τ *ca.* 7·5 (*ortho*-protons), another with a maximum at *ca.* 7·2 (*meta*- and *para*-protons) and a singlet at 1·55 (methyl protons). There is no P–H coupling, a phenomenon noticed by us in the spectrum of $[ReCl(CO)(PMe_2Ph)_4]$ [5] and other complexes where four phosphorus atoms are co-ordinated in a plane about a metal ion. This has been found by others.[6] The spectrum of (III) likewise shows a singlet (τ 2·9) for the *N*-methyl protons and no indication of P–H coupling; the methylene groups of (XII) also give rise to a singlet (τ 2·5). These spectra are all consistent with *trans*-configurations.

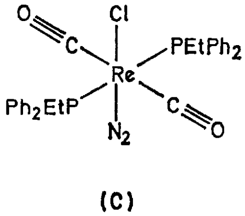
TABLE 1

Dinitrogen complexes of rhenium(I)

	Complex	M.p.[a]	Crystalline form	Analysis Calculated % C	 H	 N	 Found % C	 H	 N	$\nu(N\equiv N)$	*M* [c] (calculated value in parenthesis)
(I)	$[ReCl(N_2)(PMe_2Ph)_4$	165—169	Chunky yellow prisms	48·0	5·5	3·5	48·0	5·7	3·7	1925	730 (797)
(II)	$[ReCl(N_2)(PMePh_2)_4]$	162—166	Pale yellow needles	59·7	5·0	2·7	60·0	4·9	2·5	1925	
(III)	$[ReCl(N_2)(Me_2NPF_2)_4]$	164—167	Pale yellow solid	13·6	3·4	12·0	14·3	3·6	11·5	2075	
(IV)	$[ReCl(N_2)(PF_3)_2(PPh_3)_2]$		Orange-yellow solid							2090	
(V)	$[ReCl(N_2)(PHPh_2)_4]$	205—208	Yellow solid	58·0	4·4	2·8	58·4	4·9	2·2	2010	
(VI)	$[ReCl(N_2)(PH_2Ph)_2(PPh_3)_2]$ [d]	225—229	Brown solid	58·0	4·4	2·8	56·7	4·5	2·2	2000	
(VII)	$[ReCl(N_2)(CO)_2(PPh_3)_2]$	263—267	Yellow needles	55·0	3·5	3·4	55·1	3·8	2·9	2105, 2020, 1935 [f]	802 (830)
(VIII)	$[ReCl(N_2)(CO_2)(PEtPh_2)_2]$	148—153	Yellow needles	49·0	4·1	3·8	49·3	4·2	3·7	2100, 2055, 1920 [f]	
(IX)	$[ReCl(N_2)(CO)_2(PPh_2Pr^n)_2]$	163—166	Yellow needles	50·4	4·5	3·7	51·0	4·7	2·9	2080, 2005, 1920 [f]	741 (762)
(X)	$[ReCl(N_2)\{P(OCH_2)_3CCH_3\}_2(PPh_3)_2]$	285—289	Pale yellow insoluble solid	51·4	4·5	2·6	50·8	4·6	2·7	2035 [e]	Too insol.
(XI)	$[ReCl(N_2)(Ph_2PCH_2PPh_2)_2]$	243—246	Pale yellow needles	59·3	4·4	2·8	59·1	4·5	2·6	1980	813 (956)
(XII)	$[ReCl(N_2)(Ph_2PCH_2CH_2PPh_2)_2]$	295—297	Yellow plates	59·7	4·6	2·7	59·7	4·7	2·7	1980	1170 (1045)
(XIII)	$[ReCl(N_2)(Ph_2P(CH_2)_3PPh_2)_2]$	266—271	Yellow plates	60·2	4·8	2·6	60·0	4·8	2·5	1950	1120 (1042)
(XIV)	$[ReCl(N_2)(Ph_2PCH{=}CHPPh_2)_2]$ [d]	310—312	Yellow plates	59·9	4·3	2·6	61·2	4·8	2·6	1980	
(XV)	$[ReCl(N_2)(o\text{-}Me_2AsC_6H_4AsMe_2)_2]$ [d]		Yellow oil							1960 [e]	
(XVI)	$[ReBr(N_2)(Ph_2PCH_2CH_2PPh_2)_2]$ [d]		Yellow plates							1980	
(XVII)	$[ReCl(^{15}N_2)(PMe_2Ph)_4]$		Chunky yellow prisms							1860	
(XVIII)	$[ReCl(^{15}N_2)(Ph_2PCH_2CH_2PPh_2)_2]$		Yellow plates							1915	
(XIX)	$[ReCl(^{15}N_2)(CO)_2(PPh_3)_2]$		Yellow needles							2060, 1995, 1935 [f]	

[a] In sealed evacuated tubes. [b] In cm^{-1}, in chloroform solution. [c] Determined osmometrically in 1,2-dichloroethane. [d] Not obtained analytically pure. [e] Recorded in Nujol mulls. [f] Coupling between N_2 and CO vibrations prevents assignment of a band to pure $\nu(N\equiv N)$.

The ^1H n.m.r. spectrum of (VIII) shows P–H coupling, presumably because the complex is of lower symmetry than (I), (III), and (XII). The methyl groups of the phosphine ligands give rise to a 1 : 4 : 6 : 4 : 1 quintet, the separation between the outer components $|^5J(HCCPReP) + {}^3J(HCCH)|$ being 17 Hz. This is consistent with strong P–P coupling of *trans*-phosphorus atoms, indicating (C) as the most probable structure.



(C)

The ^{19}F n.m.r. spectrum of (III) consists of a doublet at 40·7 p.p.m. downfield of CCl_3F with a splitting $|^1J(PF)|$ of 1064 Hz. This is also consistent with equivalent fluorine and hence phosphorus atoms, and thus a *trans*-configuration.

An aqueous solution of a dinitrogen complex, which we expect to be $[ReCl(N_2)\{P(CH_2OH)_3\}_4]$, was obtained directly from (A) and $P(CH_2OH)_3$ in ethanol. After removal of solvent, a yellow syrup which would not crystallise was formed. It had a band in its i.r. spectrum at 2000 cm^{-1}, in the region expected for $\nu(N_2)$. Treatment with ferric chloride or silver nitrate produced gaseous dinitrogen, and its solutions in water appear to be stable indefinitely.

Rhenium(I) dinitrogen complexes are amongst the most stable dinitrogen complexes known. Thus (I) (Table 1) is converted to (XII) by heating it with 1,2-bis(diphenylphosphino)ethane in toluene under reflux for 4 h. The chloride ligand is inert and cannot be replaced by azide, nor does (I) react with phenyl-lithium in tetrahydrofuran or phenylmagnesium bromide in ether. Certain dinitrogen complexes undergo exchange reactions with dihydrogen,[7] *e.g.*, reaction (3), but neither (I) nor (XII) reacts with dihydrogen (1 atm., benzene solution at reflux), nor does (I) react with carbon monoxide under these conditions. However, in toluene at reflux, $[ReCl(CO)_2(PMe_2Ph)_3]$ is formed.

$$[CoH(N_2)(PPh_3)_3] + H_2 \rightleftharpoons [CoH_3(PPh_3)_3] + N_2 \qquad (3)$$

Generally the more basic the co-ligands with dinitrogen in analogous complexes, the lower $\nu(N_2)$.[8] Our rhenium complexes follow this pattern; thus of compounds in Table 1, PMe_2Ph produces the lowest $\nu(N_2)$ [1925 cm^{-1} in (I)] and PF_3 produces the highest

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[5] J. Chatt, J. R. Dilworth, H. P. Gunz, and G. J. Leigh, unpublished observations.

[6] B. L. Shaw and R. M. Slade, *J. Chem. Soc.* (*A*), 1971, 1184.

[7] A. Sacco and M. Rossi, *Inorg. Chim. Acta*, 1968, **2**, 127.

[8] J. Chatt, D. P. Melville, and R. L. Richards, *J. Chem. Soc.* (*A*), 1969, 2841.

[2090 cm^{-1} in (IV)]. The frequencies in the bis(carbonyl)dinitrogen complexes (VII)—(IX) are not *directly* comparable with those of the other dinitrogen complexes, because the carbonyl and dinitrogen vibrations are coupled. Each complex shows three bands in the $\nu(N_2)$ or $\nu(CO)$ region of the i.r. spectrum. Comparison of the spectra of (VII) and (XIX) shows a 45 cm^{-1} shift of the highest frequency band and a 25 cm^{-1} shift of the medium frequency band whereas the lowest frequency band is unchanged. A pure $^{15}N\equiv^{15}N$ vibration in this region of the spectrum would be expected to show a shift of *ca.* 60 cm^{-1} compared to a pure $^{14}N\equiv^{14}N$ vibration.

The very high frequencies of N–N vibrations in the spectra of complexes originally formulated $[Re(NH_2)(CO)_2(N_2)(PMe_2Ph)_2]$ *etc.* were wrongly assigned; the complexes are isocyanates and not dinitrogen complexes.[9]

None of the rhenium(I) dinitrogen complexes shows any bands assignable to ν(Re–Cl) in their far-i.r. spectra.

Reactions of the Dinitrogen Complexes as Lewis Bases.—Assuming that the lower $\nu(N_2)$ of the rhenium(I) dinitrogen complexes might be associated with a greater negative charge on the terminal nitrogen atom than in the dinitrogen complexes of higher $\nu(N_2)$, we investigated the ability of $[ReCl(N_2)(PMe_2Ph)_4]$ (I) to act as an electron donor and found that it forms numerous adducts of extremely low $\nu(N_2)$ (1880—1680 cm^{-1}) with Lewis acids. These have been described briefly,[10] and that with chromium(III) chloride in detail.[11] Those with aluminium alkyls, rhenium, molybdenum, and tungsten compounds, and with titanium chlorides are under detailed investigation. The complex $[ReCl(N_2)(Ph_2PCH_2CH_2PPh_2)_2]$ (XII) of higher $\nu(N_2)$ forms adducts only with very strong Lewis acids, *e.g.*, tantalum(V) chloride.[12]

Oxidation of the Rhenium(I) *to Rhenium*(II) *Complexes.*—Rhenium(I) dinitrogen complexes generally react with oxidising transition metal salts such as silver nitrate, iron(III) chloride, and copper(II) chloride in ethanol at room temperature to yield rhenium(II) dinitrogen complexes in good yield (70—85%). The principal salts thus prepared are detailed in Table 2. The rhenium(II) salts may also be prepared by careful oxidation with the equivalent amounts of halogen, yields being somewhat lower than with oxidising metal salts. The salts are all paramagnetic, and those tested are 1 : 1 electrolytes in nitrobenzene solution. As expected, $\nu(N_2)$ of the cations is some 80 cm^{-1} higher than in the parent rhenium(I) complexes. In solution, $\nu(N_2)$ is virtually independent of anion (see Table 2), in contrast to the salts of $[Ru(NH_3)_5(N_2)]^{2+}$ for which a strong counter-anion dependence has been found. This dependence has been attributed mainly to an anion–cation interaction through the ammonia hydrogens,[13] and analogous interactions cannot occur in the rhenium(II) salts.*

That the rhenium(II) tetrachloroferrate(III) contains the tetrachloroferrate anion was proved by the similarity of the ^{57}Fe Mössbauer spectrum with that of $[NEt_4][FeCl_4]$. The cation probably has C_{4v} symmetry [*i.e.*, the same as the rhenium(I) complexes] because the e.s.r. spectrum of $[ReCl(N_2)(Ph_2PCH_2CH_2PPh_2)_2][ClO_4]$ in a chloroform glass at 80 K shows only two signals, with *g*-values of 1·64 and 2·00. The salts with the smaller anions lose their dinitrogen rather more readily than do those with the larger.

The solid rhenium(II) dinitrogen complexes are obtained in green or purple forms, depending upon the solvent used for recrystallisation. Both forms generally give purple solutions, but $[ReCl(N_2)(PMe_2Ph)_4]^+$ salts can also persist as the green form in solution. The purple forms appear metastable in the solid state, and change to the green forms on standing *in vacuo* or under dinitrogen. It is not clear where the difference between the two solid forms lies. Their e.s.r. spectra are very similar, so that the gross stereochemistry is probably the same. The diffuse reflectance u.v. spectra show characteristic bands at 620 nm (green) and 590 nm (purple). The i.r. spectra (4000—800 cm^{-1}) are very similar except for $\nu(N_2)$ which differ by *ca.* 10 cm^{-1}. There are, however, distinct differences between 600 and 800 cm^{-1}, in a region generally assigned to phenyl vibrations. The difference does not lie in the dinitrogen because the isosteric $[OsCl_2(Ph_2PCH_2CH_2PPh_2)_2]$ can be oxidised to $[OsCl_2(Ph_2PCH_2CH_2PPh_2)_2]^+$, salts of which also exist in two forms, and which also show differences in the 600—800 cm^{-1} region of their i.r. spectra. These may be further examples of distortional isomerism as suggested for the blue and green forms of *cis-mer*-$[MoOCl_2(PMe_2Ph)_3]$.[14]

The analogous rhenium(I) carbonyl, $[ReCl(CO)(Ph_2PCH_2CH_2PPh_2)_2]$, is oxidised by iron(III) chloride to a rhenium(II) carbonyl cation, but not by silver nitrate or copper(II) chloride. Only green forms of these salts are known.[5] The dicarbonyls $[ReCl(CO)_2(N_2)(PR_3)_2]$ {(VII)—(IX)} are not oxidised by metallic salts, even in ethanol at reflux. This greater resistance to oxidation is presumably a reflection of the greater *d*-electron withdrawal by carbon monoxide as compared both with dinitrogen and with tertiary phosphines. The rhenium(II) carbonyls are more readily reduced than the rhenium(II) dinitrogen complexes. Both regenerate the parent rhenium(I) complexes with amalgamated zinc in tetrahydrofuran, and on refluxing in ethanol, but cold ethanolic sodium tetraphenylborate

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* *Note added in proof.* This explanation has since been challenged; see J. E. Ferguson, J. L. Love, and W. T. Robinson, *Inorg. Chem.*, 1972, **11**, 1662.

[9] J. T. Moelwyn-Hughes, A. W. B. Garner, and A. S. Howard, *J. Chem. Soc.* (*A*), 1971, 2361.

[10] J. Chatt, J. R. Dilworth, G. J. Leigh, and R. L. Richards, *Chem. Comm.*, 1970, 955.

[11] J. Chatt, R. C. Fay, and R. L. Richards, *J. Chem. Soc.* (*A*), 1971, 702.

[12] J. Chatt, M. B. Hounslea, and G. J. Leigh, unpublished results.

[13] J. Chatt, G. J. Leigh, and N. Thankarajan, *J. Chem. Soc.* (*A*), 1971, 3168.

[14] J. Chatt, Lj. Manojlovic-Muir, and K. W. Muir, *Chem. Comm.*, 1971, 655.

reduces only the carbonyl salts. This parallels the relatively easier oxidation of the rhenium(I) dinitrogen complexes.

Further Oxidation of the Complexes.—Oxidation of the rhenium(II) dinitrogen complexes causes complete loss of dinitrogen. Thus (XII) reacts with silver nitrate in ethanol at reflux to give a precipitate of metallic silver and a red-brown solution, from which ammonium hexafluorophosphate precipitates $[ReCl(Ph_2PCH_2CH_2PPh_2)_2][PF_6]_2$. Silver perchlorate produces the perchlorate analogue, which is diamagnetic and is a 1 : 2 electrolyte in nitrobenzene solution. Both (I) and (XII) react with an excess of chlorine in chloroform, the former yielding $[ReCl_4(PMe_2Ph)_2]$ and the latter $[ReCl_2(Ph_2PCH_2CH_2PPh_2)_2]Cl$. The carbonyl analogue of (I) produces $[ReCl_3(CO)(PMe_2Ph)_2]$ under the same conditions, and the carbonyl analogue of (XII) reacts in two stages, producing $[ReCl(CO)(Ph_2PCH_2CH_2PPh_2)_2]Cl$ and then $[ReCl_4(Ph_2PCH_2CH_2PPh_2)]$.[5] Complex (VII) loses all its carbon monoxide and dinitrogen on treatment with dichlorine, but the rhenium-containing product has not been identified; 1,2-bis(diphenylphosphino)ethane yields $[ReCl(CO)(Ph_2PCH_2CH_2PPh_2)_2]$, and $CH_3C(CH_2PPh_2)_3$ produces $[ReCl(CO_2\{CH_3C(CH_2PPh_2)_3\}]$, confirming that carbon monoxide is more strongly bound than dinitrogen to rhenium(I).

Attempted Reactions of Co-ordinated Dinitrogen.—We have tried by a variety of methods to reduce the dinitrogen in $[ReCl(N_2)(PMe_2Ph)_4]$ to ammonia. Unless otherwise indicated, the reactions were carried out under argon at room temperature. After the reaction, the reaction mixture was made strongly alkaline and the volatiles steam-distilled into standard sulphuric acid. The absorption of ammonia by the acid solution was checked quantitatively by evaporation to dryness and oxidation of the residue in a vacuum system by sodium hypobromite to dinitrogen. The following reagents and solvents were investigated: sodium borohydride–ethanol (at room temperature and at reflux); hydrogen sulphide–benzene; zinc–glacial acetic acid; lithium naphthalide–thf; lithium naphthalide–titanium(III) chloride–thf; lithium naphthalide–vanadium(III) chloride–thf. Only the last mixture produced ammonia from $[ReCl(N_2)(PMe_2Ph)_4]$ and then in *ca.* 25% yield. However, because lithium naphthalide–vanadium(III) chloride reacts with gaseous N_2 to form a nitride, this does not prove that co-ordinated dinitrogen has been reduced.[15,16] Aqueous solutions containing $[ReCl(N_2)\{P(CH_2OH)_3\}_4]$ produced no ammonia either with acid titanium(III) chloride solution, or with the hydrogenase from *Desulfovibrio desulfuricans*.

In contrast to the above, nitrido-complexes, such as $[ReCl_2N(PMe_2Ph)_3]$, give quantitative yields of ammonia with sodium borohydride in refluxing ethanol.

We also attempted to convert the co-ordinated dinitrogen to an azo-ligand (N=N–R, R = organic radical) by reaction with a variety of organic electrophilic reagents. $[Et_3O][BF_4]$ reacts with the rhenium(I) complexes at room temperature in thf to give intractable nitrogen-free products. The Wittig reagents, $Ph_3P{=}CHPh$, $Ph_3P{=}CHCO_2CH_3$, and $Ph_3P{=}NCOPh$, do not react, even in benzene at reflux. $[Ph_3C][BF_4]$ in thf oxidises the rhenium(I) complexes to the rhenium(II). Both phenylmagnesium bromide and trityl-lithium are without action on the rhenium(I) complexes in thf solution although trityl-lithium reduces the rhenium(II) to the rhenium(I) dinitrogen complex. However, benzoylchloride gives a product which contains a benzoylazo-group (*cf.* ref. 17) and the reaction is still under investigation.[18]

The treatment of a benzene solution of $[ReCl(N_2)(Ph_2PCH_2CH_2PPh_2)_2]$ with nitrogen oxide in the presence of dioxygen at room temperature produces $[ReCl(N_2)(Ph_2PCH_2CH_2PPh_2)_2](NO_2)$. This compound is a 1 : 1 electrolyte in nitrobenzene and its i.r. spectrum has $\nu(N_2)$ at 2000 cm^{-1} and bands in the 1200 and 1400 cm^{-1} region assignable to the nitrite anion.

The ^1H n.m.r. spectrum of a solution of $[ReCl(N_2)(PMe_2Ph)_4]$ in trifluoroacetic acid showed a broad hydridic resonance around τ 17·5. No gas is liberated during this reaction and the product can be precipitated as an unstable tetraphenylborate salt with $\nu(N_2)$ at 2000 cm^{-1}, suggesting that it is $[ReHCl(N_2)(PMe_2Ph)_4][BPh_4]$.

It is clear that the dinitrogen in these rhenium complexes is not easily reduced, despite the low $\nu(N_2)$. Although the bound dinitrogen is sufficiently negative to display definitie Lewis base activity,[19] the metal is evidently more basic and is preferentially attacked by the proton. However more bulky, non-oxidising Lewis acids are unable to attack the metal, and so become attached to the dinitrogen ligand.

EXPERIMENTAL

All reactions involving free tertiary phosphines were carried out under pure, dry nitrogen. Reagent grade solvents were used unless otherwise indicated.

I.r. spectra were recorded on Unicam SP 1200 (Nujol mulls 400—4000 cm^{-1}), Grubb-Parsons DM 4 (Nujol mulls 200—500 cm^{-1}), and R.I.I.C. FS 620 (polythene discs and Nujol mulls 40—400 cm^{-1}) spectrometers. ^1H and ^{19}F n.m.r. spectra were recorded with Varian A60 and HA100 instruments for solutions in deuteriochloroform with tetramethylsilane as an internal standard for protons. Magnetic moments were measured with a Faraday balance calibrated against cobalt mercury thiocyanate, and m.p.s were recorded in sealed, evacuated tubes on an Electrothermal melting point apparatus.

Chlorotetrakis(dimethylphenylphosphine)dinitrogenrhenium(I).—(a) [*N*-Benzoylhydrazido(3—)*N′*,*O*]dichlorobis(triphenylphosphine)rhenium(V) [Compound (A)] (3·0 g, 1·0 mol) and dimethylphenylphosphine (3·0 g, 6·6 mol) in 1 : 1

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[15] T. P. M. Beelen and W. Van Erk, *Rec. Trav. chim.*, 1971, **90**, 1197.

[16] M. E. Volpin, V. S. Lenenko, and V. B. Shur, *Izvest. Akad. Nauk S.S.S.R.*, 1971, 463.

[17] J. Chatt, G. A. Heath, and G. J. Leigh, *Chem. Comm.*, 1972, 444.

[18] J. Chatt, G. A. Heath, N. E. Hooper, and G. J. Leigh, unpublished observations.

[19] J. Chatt, R. H. Crabtree, and R. L. Richards, *Chem. Comm.*, **1972**, **534**.

benzene–methanol (60 ml) were heated under reflux for 2 h. Further refluxing of the reaction mixture yields products containing no nitrogen and should be avoided. The resulting orange-yellow solution was evaporated at 15 mmHg to an orange oil and methanol (100 ml) added. After several hours at 0°, the *complex* separated as a pale yellow solid (1·6 g, 61%), and was recrystallised as chunky yellow plates from benzene–methanol or ethanol.

(b) *From dinitrogen gas.* Trichlorotris(dimethylphenylphosphine)rhenium(III) (0·30 g) and 2% sodium amalgam (10 g) in anhydrous THF were shaken under a dinitrogen pressure of 90 atm. for 110 h at room temperature. The solvent was evaporated at 10^{-2} mmHg and the *complex* precipitated as a pale yellow solid by the addition of methanol (25 ml). Recrystallisation from benzene–methanol gave pale yellow plates with identical m.p. and i.r. spectrum to $[ReCl(N_2)(PMe_2Ph)_4]$ prepared as in (a).

The ^{15}N *analogue* (XVII) was prepared by method (a) from ^{15}N-labelled compound (A).

Chloro(dinitrogen)tetrakis(methyldiphenylphosphine)-rhenium(I) (II).—Compound (A) (1·0 g, 1·0 mol) and methyldiphenylphosphine (2·1 g, 9·6 mol) in methanol (40 ml) were heated under reflux for 22 h. The *complex* precipitated from solution as a pale yellow solid (0·47 g, 81%) and was recrystallised as pale yellow needles from benzene–methanol.

Chlorotetrakis(dimethylaminodifluorophosphine)(dinitrogen)rhenium(I) (III).—Compound (A) (0·50 g, 1·0 mol) and dimethylaminodifluorophosphine (0·80 g, 13·1 mol) in dry, freshly distilled benzene (40 ml) were heated under reflux for 15 min. The resulting orange-yellow solution was evaporated at 10^{-2} mmHg to an orange-yellow oil, and the *complex* precipitated as an orange-yellow solid (0·23 g, 61%) by the addition of dry pentane (40 ml) and recrystallised as pale yellow prisms from benzene–pentane.

Chloro(dinitrogen)bis(trifluorophosphine)bis(triphenylphosphine)rhenium(I) (IV).—Compound (A) (0·50 g) in dry methanol (40 ml) was stirred in a sealed vessel under a pressure of *ca.* 2 atm. of trifluorophosphine for 24 h. The *complex* precipitated from solution as an orange-yellow solid, but it was not, however, obtained analytically pure.

Chloro(dinitrogen)tetrakis(diphenylphosphine)rhenium(I) (V).— [*N*-Cinnamoylhydrazido(3—)*N′*,*O*]dichlorobis(triphenylphosphine)rhenium(V) [2] (1·0 g) and diphenylphosphine (2·0 g, 10·1 mol) were stirred at room temperature in 1 : 1 benzene–ethanol (30 ml) for 1 h. The resulting reddish solution was evaporated to a reddish oil at 10^{-2} mmHg, and the *complex* precipitated as a yellowish solid (0·61 g, 54%) by the addition of diethyl ether (30 ml). The complex was purified by repeated washings with diethyl ether.

Chloro(dinitrogen)bis(phenylphosphine)bis(triphenylphosphine)rhenium(I) (VI).—[*N*-Cinnamoylhydrazido(3—)*N′*,*O*]-dichlorobis(triphenylphosphine)rhenium(V) [2] (1·0 g) and phenylphosphine (1·0 g, 8·6 mol) were stirred at room temperature in 1 : 1 benzene–ethanol (30 ml) for 1 h. The resulting pale yellow solid (0·75 g, 72%) was filtered off, washed thoroughly with benzene and ethanol and recrystallised from benzene–hexane.

Dicarbonylchloro(dinitrogen)bis(triphenylphosphine)-rhenium(I) (VII).—Compound (A) (2·0 g) in 1 : 1 benzene–methanol (70 ml) was heated under reflux for 2 h while passing a stream of dry carbon monoxide through the solution. The *complex* precipitated from solution as a pale yellow solid (1·6 g, 87%), which was recrystallised as fine yellow needles from benzene–methanol.

The ^{15}N *analogue* (XIX) was prepared similarly from ^{15}N-labelled compound (A).

Dicarbonylchloro(dinitrogen)bis(diphenylethylphosphine)-rhenium(I) (VIII).—Benzoylazodichlorotris(diphenylethylphosphine)rhenium(III) [2] (1·0 g) in 1 : 1 benzene–methanol was heated under reflux for 3 h, while bubbling a stream of dry carbon monoxide through the solution. The pale yellow solution was evaporated at 20 mmHg to 15 ml and the *complex* precipitated as a pale yellow solid by the addition of methanol (50 ml) (0·65 g, 81%). The complex was recrystallised as bright yellow needles from benzene–methanol. *Chlorodicarbonyl(dinitrogen)bis(diphenyl-n-propylphosphine)rhenium*(I) (IX) was obtained analogously in 60% yield.

Chloro(dinitrogen)bis(4-methyl-2,6,7-trioxa-1-phospha-[2,2,2]tricyclo-octane)bis(triphenylphosphine)rhenium(I) (X).—Compound (A) (1·0 g), and 4-methyl-2,6,7-trioxa-1-phospha[2,2,2]tricyclo-octane (2·1 g, 7·2 mol) in methanol (40 ml) were heated under reflux for 2 h. The *complex* precipitated from solution as a pale yellow solid (0·9 g, 77%) which was too insoluble in common organic solvents for recrystallisation, and was purified by several washings with benzene.

Bis[bis(diphenylphosphino)methane]chloro(dinitrogen)-rhenium(I) (XI).—Compound (A) (1·0 g) and bis(diphenylphosphino)methane (2·4 g, 5·7 mol) were heated under reflux in methanol (50 ml) for 14 h. The *complex* precipitated from solution as an orange-yellow solid (0·86 g, 77%), and was recrystallised as pale yellow needles from chloroform–methanol.

Bis[1,2-bis(diphenylphosphino)ethane]chloro(dinitrogen)-rhenium(I) (XII).—Compound (A) (1·0 g) and 1,2-bis(diphenylphosphino)ethane (2·5 g, 5·6 mol) were heated under reflux in methanol (50 ml) for 12 h. The complex precipitated from solution as a pale yellow solid (0·94 g, 80%) and was recrystallised from chloroform–methanol as pale yellow plates. The ^{15}N-labelled *analogue* (XVIII) was prepared similarly from ^{15}N-labelled compound (A).

Bis[1,3-bis(diphenylphosphino)propane]chloro(dinitrogen)-rhenium(I) (XIII).—Compound (A) (1·0 g) and 1,3-bis-(diphenylphosphino)propane (2·4 g, 5·7 mol) in methanol (50 ml) were heated under reflux for 14 h. The *complex* precipitated from solution as an orange-yellow solid (0·86 g, 75%) and was recrystallised from chloroform–methanol as pale yellow needles.

Bis[1,2-bis(diphenylphosphino)ethylene]chloro(dinitrogen)-rhenium(I) (XIV).—Compound (A) (0·5 g) and 1,2-bis-(diphenyl)phosphine)ethylene (1·5 g, 6·9 mol) in methanol (50 ml) were heated under reflux for 2 h. The *complex* precipitated from solution as an orange-yellow solid (0·71 g, 62%), which was recrystallised as small yellow plates from chloroform–methanol.

Chloro(dinitrogen)bis[o-phenylenebis(dimethylarsine)]-rhenium(I) (XV).—Compound (A) (0·80 g) and *o*-phenylenebis(dimethylarsine) (2·9 g, 11·5 mol) in methanol (40 ml) were heated under reflux for 12 h. The resulting pale orange-red solution was evaporated to near dryness at 10^{-2} mmHg and the complex precipitated as an orange-yellow oil by the addition of hexane (40 ml). Prepared in this manner the dinitrogen complex was always contaminated with a benzoylazo-complex and attempts at separation and recrystallisation were not successful.

Bis[1,2-bis(diphenylphosphino)ethane]bromo(dinitrogen)-rhenium(I) (XVI).—Prepared similarly to complex (XII) using the bromo-analogue of complex (A), as a microcrystalline yellow powder.

Rhenium(II) *Dinitrogen Complexes*.—Three general methods were employed for the preparation of the rhenium(II) dinitrogen complexes and these are indicated below. Anion exchange reactions were used where necessary to prepare the range of complexes detailed in Table 2.

Method A. A solution of the Re^{I} dinitrogen complex in chloroform was treated with the stoicheiometric quantity of halogen (0·5 mol dichlorine or 1·5 mol dibromine or di-iodine) at 0°, and the mixture stirred for 15 min. Addition of diethyl ether precipitated the complex as a purple solid which was recrystallised from chloroform–diethyl ether.

Method B. A suspension of the Re^{I} dinitrogen complex (0·5 g) in ethanol (40 ml) was stirred for 30 min at 0° with silver nitrate (0·3 g). The resulting suspension was filtered to remove metallic silver. Addition of an excess of an alcoholic solution of the sodium salt of an appropriate anion precipitated the Re^{II} dinitrogen complex, which was recrystallised from chloroform–diethyl ether.

TABLE 2

Rhenium(II) dinitrogen complexes of the type $[ReCl(N_2)L_4]^+X^-$

		Analysis								
		Calculated %			Found %					
L_4	X	C	H	N	C	H	N	Crystalline form	ν(N≡N) [a]	Method of preparation [b]
$(Ph_2PCH_2CH_2PPh_2)_2$	Cl	57·6	4·4	2·5	57·0	5·0	2·2	Purple or green needles	2055	A
$(Ph_2PCH_2CH_2PPh_2)_2$	Br_3	48·5	3·7	2·2	48·2	3·7	2·0	Purple or green needles	2060	A
$(Ph_2PCH_2CH_2PPh_2)_2$	I_3	43·7	3·4	2·0	45·3	3·7	2·0	Purple or green needles	2055	A
$(Ph_2PCH_2CH_2PPh_2)_2$	ClO_4	54·2	4·2	2·4	53·5	4·3	2·2 [c]	Purple plates	2055	A, B
$(Ph_2PCH_2CH_2PPh_2)_2$	BF_4	55·1	4·3	2·5	54·9	4·6	2·3	Purple or green needles	2060	A, B
$(Ph_2PCH_2CH_2PPh_2)_2$	PF_6	52·3	4·0	2·3	52·0	4·2	2·4	Purple needles or green prisms	2060	A, B
$(Ph_2PCH_2CH_2PPh_2)_2$	$FeCl_4$	49·8	3·7	2·2	49·4	3·7	2·2 [d]	Purple needles	2060	A, C
$(Ph_2PCH_2CH_2PPh_2)_2$	$CuCl_2$	52·8	4·1	2·2	52·4	4·3	2·2	Purple needles	2055	C
$(Ph_2PCH{=}CHPPh_2)_2$	$FeCl_4$	50·3	3·5	2·3	50·9	3·7	2·1	Green needles	2065	C
$(PMe_2Ph)_4$	$FeCl_4$	38·4	4·4	2·8	37·6	4·6	2·8	Pink needles	2010, 2040, 2055 [e]	A, C

[a] In cm^{-1}, in chloroform solution. [b] For details see Experimental section. [c] Cl Found 6·2, calc. 6·0%. [d] Cl Found 15·6, calc. 14·8%. [e] Recorded as Nujol mull.

Method C. A suspension of the Re^{I} dinitrogen complex (0·5 g) in ethanol (40 ml) was stirred at room temperature with the copper(II) chloride or iron(III) chloride (0·5 g). The Re^{II} dinitrogen complex precipitated from solution as a purple solid and was recrystallised from chloroform–diethyl ether. In this method the metal salt disproportionates to provide the anion, and other anions may be introduced by ion-exchange.

Bis[1,2-*bis*(*diphenylphosphino*)*ethane*]*chlororhenium*(III) *Perchlorate*.—(i) Complex (XII) (0·50 g) and silver nitrate (0·50 g) were heated under reflux in ethanol (40 ml) for 0·5 h. The resulting suspension was cooled and filtered. Addition of a saturated solution of lithium perchlorate in ethanol (30 ml) caused the *complex* to crystallise from solution as brown prisms (Found: C, 50·9; H, 4·1; Cl, 7·1. $C_{52}H_{48}Cl_3O_8P_4Re$ requires C, 51·5; H, 4·0; Cl, 8·8%). The molar conductivity in nitrobenzene (8·6 × 10^{-4}M) is 44·1 Ω^{-1} cm^2 mol^{-1}, corresponding to a 2 : 1 electrolyte. The complex deflagrates mildly on heating. (ii) An identical sample was prepared by treating complex (XII) with silver perchlorate under similar conditions.

Bis[1,2-*bis*(*diphenylphosphino*)*ethane*]*chlororhenium*(III) *Tetrafluoroborate*.—Prepared similarly to the perchlorate in (i) above, using ammonium tetrafluoroborate. The *complex* crystallised from solution as orange-brown prisms (Found: C, 52·2; H, 4·3. $C_{52}H_{48}B_2ClF_8P_4Re$ requires C, 52·4; H, 4·0%).

Bis[1,2-*bis*(*diphenylphosphino*)*ethane*]*chlororhenium*(III) *Hexafluorophosphate*.—Prepared similarly to the perchlorate salt (i) using ammonium hexafluorophosphate. The complex crystallised from the ethanolic solution as orange-brown prisms (Found: C, 47·9; H, 3·9. $C_{52}H_{48}ClF_{12}P_6Re$ requires C, 47·6; H, 3·7%).

Reactions of Dicarbonylchloro(*dinitrogen*)*bis*(*triphenylphosphine*)*rhenium*(I).—(a) *Dichlorine*. In a typical experiment, 76·4 mg of complex (VII) in chloroform (10 ml) were placed in a reaction vessel equipped with a break seal and degassed. A saturated solution of dichlorine in carbon tetrachloride (3 ml) was distilled *in vacuo* into the reaction vessel, which was then sealed off. The vessel was then heated to 120° for 1 h, cooled, and the gases transferred *via* a cold trap to a constant volume gas manometer using a Toepler pump. The total volume of gases liberated ($2CO + N_2$) was then measured (5·98 ml, 97%).

This gas mixture was then cycled through a silica U-tube containing copper oxide, electrically heated to 400°. The resulting gas mixture ($CO_2 + N_2$) was then returned to the gas manometer to check that no leakage had occurred. Finally, the gas mixture ($CO_2 + N_2$) was cycled through a cold-trap at −196° condensing out the CO_2. The U-tube was then warmed and the volume of CO_2 measured in the gas manometer (3·93 ml, 95%).

(b) 1,2-*Bis*(*diphenylphosphino*)*ethane*. Complex (VII) and 1,2-bis(diphenylphosphino)ethane (200 mg) in benzene (15 ml) were heated in a sealed evacuated tube equipped with a break seal at 120° for 1·5 h. The volume of gas ($CO + N_2$) was measured as above (2·56 ml, 84%). The solvent was removed *in vacuo* and the yellow residue recrystallised as pale yellow plates from chloroform–methanol, and shown to be identical with an authentic sample of $[ReCl(CO)(Ph_2PCH_2CH_2PPh_2)_2]$.[5]

(c) 1-*Diphenylphosphino*-2,2-*bis*(*diphenylphosphinomethyl*)*ethane* (*triphos*). Complex (VII) (91 mg) and triphos (200 mg) in benzene (15 ml) were heated at 100° for 2 h in a sealed evacuated vessel equipped with a break seal. Pure dinitrogen was liberated (2·9 ml, 89%). The solvent was removed *in vacuo* and the product recrystallised as yellow prisms from benzene–methanol. It was shown to have the same m.p. and i.r. spectrum as an alternatively prepared sample of $[ReCl(CO)_2(triphos)]$.[5]

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