The Basic Strengths of some Dinitrogen Complexes of Molybdenum(0), Tungsten(0), Rhenium(I), and Osmium(II)

By **Joseph Chatt,* Robert H. Crabtree, Edward A. Jeffery,** and **Raymond L. Richards,** A.R.C. Unit of Nitrogen Fixation, University of Sussex, Brighton BN1 9QJ

The formation of adducts containing the grouping M–XY–AlR_3 by the reaction, in benzene solution, of the Lewis acids AlR_3 (R = Me, Ph, or Cl) with the XY (XY = CO or N_2) ligand in a variety of molybdenum(0), tungsten(0), rhenium(I), and osmium(II) complexes, has been examined by i.r. and ^1H n.m.r. spectroscopy, and in some cases by the isolation of crystalline 1 : 1 adducts. The order of relative basic strengths thf > *trans*-$[ReCl(N_2)(PMe_2Ph)_4]$ > *trans*-$[Mo(N_2)_2(dpe)_2]$ > *trans*-$[W(N_2)_2(dpe)_2]$ > *trans*-$[ReCl(N_2)(PMe_2Ph)_2\{P(OMe)_3\}_2]$ > *trans*-$[ReCl(CO)(PMe_2Ph)_4]$ > Et_2O > *mer*-$[OsCl_2(N_2)(PEt_2Ph)_3]$ (thf = tetrahydrofuran, dpe = $Ph_2PCH_2CH_2PPh_2$) towards trimethylaluminium in benzene has been deduced from ^1H n.m.r. studies of the equilibrium between trimethylaluminium, the above compounds and diethyl ether. Comparison of the dipole moments of the pair of compounds *trans*-$[ReCl(XY)(PMe_2Ph)_4]$ (XY = N_2 or CO) shows that the dinitrogen ligand is only slightly more negatively charged than carbonyl.

PREVIOUS papers from this laboratory have briefly described the formation of adducts between a wide range of electron-acceptor molecules and the dinitrogen complex *trans*-$[ReCl(N_2)(PMe_2Ph)_4]$.[1-3] In this paper we describe in detail our studies[4] of the interaction between the Lewis acids AlR_3 (R = Me, Ph, or Cl), present as Al_2R_6 or $AlMe_3,Et_2O$ and some dinitrogen complexes of molybdenum(0), tungsten(0), rhenium(I), osmium(II), and iridium(I) and some of their carbonyl analogues. The compounds investigated were chosen so as to give as wide a range of metal sites having ligating dinitrogen as possible, to see how the basic character of ligating dinitrogen depended upon its environment.

Adducts formed by carbonyl complexes of several transition metals with various Al^{III} Lewis acid species are known and appear to contain aluminium bound to the terminal oxygen of ligating carbon monoxide, confirmed in several cases by *X*-ray data.[5,6]

I.r. and ^1H N.m.r.—The dinitrogen complexes of Table 1, which we shall call the parent dinitrogen complexes, react in benzene solution at room temperature with the trimethylaluminium moiety to form diamagnetic 1 : 1 adducts, in which the strong sharp i.r. absorption assigned to the dinitrogen stretching mode at $\nu(N_2)$ cm^{-1} is replaced by a similar absorption at a lower frequency $\nu^1(N_2)$ cm^{-1}. The shifts $\Delta\nu(N_2) = \nu(N_2) - \nu^1(N_2)$ are tabulated in Table 1. The adducts are broken up by the addition of an excess of tetrahydrofuran, whereupon the band at $\nu(N_2)$ cm^{-1} of the parent complex reappears. Cautious ethanolysis of the adducts yields methane and the unchanged parent complex quantitatively. Adducts of the same type were also formed between triphenylaluminium and dinitrogen complexes of molybdenum(0), tungsten(0), and rhenium(I), but not those of osmium(II). Aluminium chloride gave adducts with some of the rhenium(I) complexes of Table 1, but destroyed many with loss of dinitrogen. In the case of *cis*-$[W(N_2)_2(PMe_2Ph)_4]$ with trimethylaluminium at −78° an adduct appeared to be formed, which decomposed with loss of dinitrogen on warming, whereas the adduct with triphenylaluminium was stable at ambient temperatures.

The rhenium(I) dinitrogen complexes[7] shown in Table 1 were investigated because they provide a unique range of ligand environments where dinitrogen may be in the same co-ordination sphere as ligands whose donor atoms can be phosphorus, nitrogen, or sulphur. The differing electronic situations in these compounds result in a range of $\nu(N_2)$ values and a plot of $\Delta\nu(N_2)$ against $\nu(N_2)$ for their trimethylaluminium and triphenylaluminium adducts shows a maximum of $\Delta\nu(N_2)$ near $\nu(N_2) = 1970$ cm^{-1} (Figure 1). The compound *mer*-$[Re(Me_2NCS_2)(N_2)(PMe_2Ph)_3]$ is exceptional since its $\Delta\nu(N_2)$ value lies off the curve of Figure 1, perhaps owing to interaction of further trimethyl-

---

[1] J. Chatt, J. R. Dilworth, R. L. Richards, and J. R. Sanders, *Nature*, 1969, **224**, 1201.

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

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

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

[5] D. F. Shriver and A. Alich, *Co-ordination Chem. Rev.*, 1972, **8**, 15 and references therein.

[6] G. J. Gainsford, R. R. Schrieke, and J. D. Smith, *Chem. Comm.*, 1972, 650.

[7] J. Chatt, J. R. Dilworth, and G. J. Leigh, (*a*) *Chem. Comm.*, 1969, 687; (*b*) *J.C.S. Dalton*, 1973, 612.

TABLE 1

ν(XY) and $\Delta\nu$(XY) for parent compounds and adducts in benzene solution

	Parent compound *	Parent ν(XY)	AlMe$_3$ adduct ν^1(XY)	AlMe$_3$ adduct $\Delta\nu$(XY)	AlPh$_3$ adduct ν^1(XY)	AlPh$_3$ adduct $\Delta\nu$(XY)	AlCl$_3$ adduct ν^1(XY)	AlCl$_3$ adduct $\Delta\nu$(XY) †
(1)	*mer*-[ReCl(N_2)(PMe$_2$Ph)$_3$(C_5H_5N)]	1914	1905	9	*a*		*b*	
(2)	*trans*-[ReCl(N_2)(PMePh$_2$)$_4$]	1919	1906	13	1859	60	1856	63
(3)	*trans*-[ReCl(N_2)(PMe$_2$Ph)$_4$]	1923	1894	29	1877	46	1857	66
(4)	*mer*-[Re(Me$_2$NCS$_2$)(N_2)(PMe$_2$Ph)$_3$]	1945	1906[c]	39	*a*		*a*	
(5)	*trans*-[ReCl(N_2)(dpp)$_2$]	1949[d]	1862	87	1875	74	1902	47
(6)	*trans*-[ReCl(N_2)(dpe)$_2$]	1967[d]	1858	109	1874	93	*b*	
(7)	*trans*-[ReBr(N_2)(dpe)$_2$]	1980[d]	1878	102	*a*		*a*	
(8)	*trans*-[ReCl(N_2)(dpm)$_2$]	1981[d]	1888	93	*a*		*b*	
(9)	*trans*-[ReCl(N_2)(PMe$_2$Ph)$_2${P(OMe)$_3$}$_2$]	2000	1946	54	1927	73	*b*	
	trans-[ReCl($^{15}N_2$)(PMe$_2$Ph)$_4$]	1860[e]	1833[e]	27[e]	*a*		*a*	
	trans-[ReCl(CO)(PMe$_2$Ph)$_4$]	1782	1722[c]	60	1682	100	1634[c]	148
	trans-[ReCl(CO)(dpe)$_2$]	1803[d]	1677[c]	126	1653	150	1630[c]	173
	trans-[ReCl(CO)$_3$(PEtPh$_2$)$_2$]	1905 1960 2060w	1738 1780 1838w 1899w 1891		*a*		*a*	
	trans-[ReCl(CO)$_3$(PPh$_3$)$_2$]	1915 1949 2049w	1728 1780 1860w 1978		*a*		*a*	
	trans-[Mo(N_2)$_2$(dpe)$_2$]	1979 2020w	1883 2098mw	94 −78	1847 2115m	132 −95	*b*	
	trans-[Mo($^{15}N_2$)$_2$(dpe)$_2$]	1912[e]	1838[e]	74	*a*		*a*	
	cis-[W(N_2)$_2$(PMe$_2$Ph)$_4$]	1933 2003	*b*		1846 2025	87 −22	*b*	
	trans-[W(N_2)$_2$(dpe)$_2$]	1948 2015w	1869 2059mw	79 −44	1846 2076mw	102 −61	*b*	
	cis-[W(CO)$_2$(dpe)$_2$][f]	1852 1788	1762 1682	90 106	*a*		*a*	
	mer-[OsCl$_2$(N_2)(PEt$_2$Ph)$_3$]	2063	1982	81	*g*		*b*	
	mer-[OsCl$_2$(N_2)(PMe$_2$Ph)$_3$]	2079	1979	100	*g*		*b*	
	mer-[OsCl$_2$(N_2)(PEtPh$_2$)$_2$]	2090	1968	122	*g*		*b*	

* dpp = $Ph_2PCH_2CH_2CH_2PPh_2$, dpe = $Ph_2PCH_2CH_2PPh_2$, dpm = $Ph_2PCH_2PPh_2$. † In cm^{-1}, m = medium, w = weak, all bands are strong unless marked otherwise.

[a] Not measured. [b] Adduct decomposed. [c] Broad band. [d] Chloroform solution (see text). [e] $^{15}N_2$ Absorption. [f] Two AlMe$_3$ units attached (see text). [g] No reaction.

aluminium moieties with the dithiocarbamate ligands. Complexes with $\nu(N_2) > 2000$ cm^{-1} do not form adducts under our conditions. The intensity of i.r. absorption owing to N_2 stretching is not greatly affected by adduct formation. In the one case measured, the molar extinction coefficient (at 1894 cm^{-1}) of the adduct AlMe$_3$,[ReCl(N_2)(PMe$_2$Ph)$_4$] is greater by 14% than that of the parent complex (at 1923 cm^{-1}).

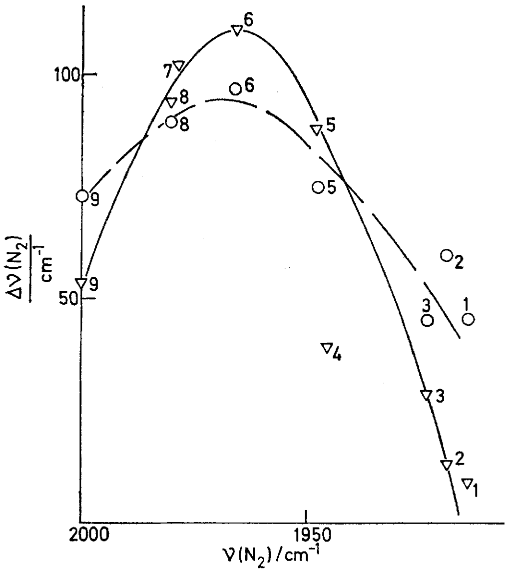

FIGURE 1 Plots of $\nu(N_2)$ against $\Delta\nu(N_2)$ for rhenium(I) dinitrogen complexes; values and identifying numbers from Table 1; ▽, AlMe$_3$; ○, AlPh$_3$

The bis-dinitrogen complexes trans-[M(N_2)$_2$(dpe)$_2$] (M = Mo or W) form only 1 : 1 adducts in which the very weak i.r. absorption due to the A_{1g} mode of the parent complex gains considerable intensity and moves to higher wave number ($\Delta\nu = -44$ to -95 cm^{-1}) whereas the intense absorption (A_{2u}) moves to lower wave number ($\Delta\nu = 79$ to 132 cm^{-1}). This increased splitting is doubtless the effect of the reduced symmetry of the adducts. No bands which could be assigned to a 2 : 1 adduct were observed even in the presence of a 30 fold molar excess of trimethylaluminium. Figure 2a illustrates the effect of triphenylaluminium on the solution spectrum of *trans*-[Mo(N_2)$_2$(dpe)$_2$] and Figure 2b that of trimethlyaluminium on the spectrum of *trans*-[ReCl(N_2)(dpe)$_2$]. I.r. data for some $^{15}N_2$ derivatives are also included in Table 1. Both CO bands of *cis*-[W(CO)$_2$(dpe)$_2$] decrease in frequency on adduct formation, probably because each carbonyl group binds to aluminium, as Shriver has observed for *cis*-[Mo(CO)$_2$(phen)(PPh$_3$)$_2$] [5] (phen = 1,10-phenanthroline).

The marked lowering of $\nu(N_2)$ or ν(CO) in these adducts strongly suggests that the point of attachment of the trimethylaluminium moiety is the terminal N or O atom, the ligating atom being sterically inaccessible.

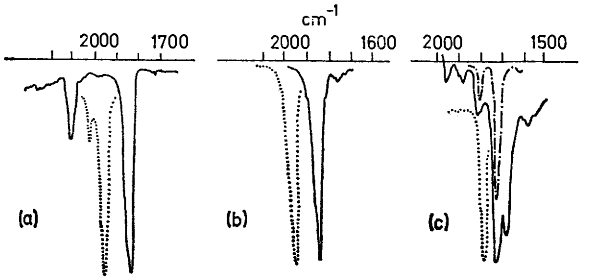

FIGURE 2 I.r. spectra (cm^{-1}) of adducts in benzene; (a), · · · · *trans*-$[Mo(N_2)_2(dpe)_2]$; —— $[Mo(N_2)(N_2AlPh_3)(dpe)_2]$; (b), · · · · *trans*-$[ReCl(N_2)(dpe)_2]$; —— $[ReCl(N_2AlMe_3)(dpe)_2]$; (c), · · · · *trans*-$[ReCl(CO)(PMe_2Ph)_4]$; —— $[ReCl(CO)(PMe_2Ph)_4] + AlMe_3$; —·—·— $[ReCl(CO)(PMe_2Ph)_4] + AlMe_3,Et_2O$ (*ca.* 10M in excess)

These frequencies would be raised by electron withdrawal if the attachment were to the metal or halide ligand. This attachment is in accord with the known structures[5,6] of similar bridged carbonyl complexes and the tendency of dinitrogen to form M–N–N–M bridges (M = metal).[8]

TABLE 2

^{1}H N.m.r. and equilibrium data [a]

Compound	AlMe$_3$ Chemical shift of adduct	Chemical shift of phosphine ligands			K
		Parent	Adduct	Assignment	
Tetrahydrofuran					70
trans-$[ReCl(N_2)(PMe_2Ph)_4]$	10·03	8·4	8·43	P–CH_3	20·6
trans-$[Mo(N_2)_2(dpe)_2]$	10·37	7·65	7·71	P–CH_2	33 (16·5) [b]
trans-$[W(N_2)_2(dpe)_2]$ [c]	10·20	7·64	7·68	P–CH_2	15 (7·5) [b]
trans-$[ReCl(N_2)(PMe_2Ph)_2\{P(OMe)_3\}_2]$	10·03	7·85 6·61	8·07 6·87	P–CH_3 P–OCH_3	5·5
trans-$[ReCl(CO)(PMe_2Ph)_4]$	10·01	8·37	8·41	P-CH_3	3·3
Et_2O					1
mer-$[OsCl_2(N_2)(PEt_2Ph)_3]$ [c]	9·93	8·03 9·24	8·13 9·26	P–CH_2 P–CH$_2$–CH_3	0·3
Al_2Me_6	10·33				

[a] Chemical shifts measured at 34 °C in benzene solution expressed relative to Me_4Si, $\tau \pm 0{\cdot}01$. [b] Halved for comparative purposes to account for the presence of two basic sites in the molecule. The formation of only 1 : 1 adducts was assumed (see p. 1168). [c] Adduct slowly decomposes.

The ^{1}H n.m.r. spectra of the trimethylaluminium adducts in benzene solution show that the resonances of the protons on the phosphine ligands are only slightly affected by adduct formation, thus these ligands are not abstracted on reaction. The trimethylaluminium protons show one sharp resonance which is shifted, in all but one complex adduct, to slightly lower field relative to hexamethyldialuminium, in contrast to the trimethylaluminium adducts with organic bases where the resonance occurs slightly up-field.[9] The trimethylaluminium protons in the adducts of compounds of osmium(II) and rhenium(I) (Table 2) resonate at a uniquely low field.

Solutions containing mixtures of trimethylaluminium adduct and parent transition-metal complex or hexamethyldialuminium show a single methyl resonance indicating rapid exchange of $AlMe_3$ units. The chemical shift (τ_{Me}) depends upon r, the ratio of the molar equivalent concentration of parent complex to that of aluminium compound, *e.g.* *trans*-$[ReCl(N_2)(PMe_2Ph)_4]$ to $\frac{1}{2}[Al_2Me_6]$ or $AlMe_3,Et_2O$. A plot of τ_{Me} *versus* r is shown in Figure 3 for *trans*-$[ReCl(N_2)(PMe_2Ph)_4]$ and $AlMe_3$. Its shape is characteristic of the formation of a 1 : 1 complex with little or no tendency to dissociate or co-ordinate another molecule of Lewis acid or base.[10] Addition of a little diethyl ether to a solution for which $r > 1$ sets up the equilibrium (1),

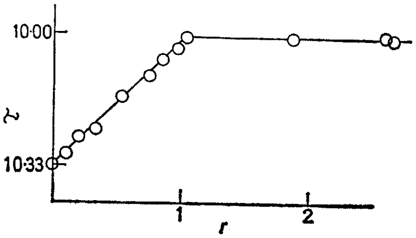

FIGURE 3 Plot of chemical shift of $AlMe_3$ protons against mixing ratio r with *trans*-$[ReCl(N_2)(PMe_2Ph)_4]$

$$AlMe_3,Et_2O + [ReCl(XY)(PMe_2Ph)_4] \underset{30^\circ}{\overset{\text{benzene}}{\rightleftharpoons}} Et_2O + [ReCl(XYAlMe_3)(PMe_2Ph)_4] \quad (1)$$

for which

$$K = \frac{\{[ReCl(XYAlMe_3)(PMe_2Ph)_4]\}\{Et_2O\}}{\{[ReCl(XY)(PMe_2Ph)_4]\}\{AlMe_3,Et_2O\}} \quad (2)$$

({ } is used to designate molar concentrations because [ ] is used to enclose complex entities).

Attainment of the equilibrium (1) (XY = N_2) leads to ^{1}H n.m.r. spectra of which Figure 4 is typical. The methylaluminium resonance, b, is intermediate between that for the transition metal adduct, a, and that for

---

[8] See J. Chatt and G. J. Leigh, *Chem. Soc. Rev.*, 1972, **1**, 121.

[9] N. R. Fetter and D. W. Moore, *Canad. J. Chem.*, 1964, **42**, 885; J. L. Atwood and G. D. Stucky, *J. Amer. Chem. Soc.*, 1967, **89**, 5362.

[10] R. A. Craig and R. E. Richards, *Trans. Faraday Soc.*, 1963, **59**, 1962.

$AlMe_3,Et_2O$, c, (determined in separate experiments) and its position gives the proportion of Lewis acid bound to the transition metal complex, since $\tau_b = \tau_a n_a + \tau_c n_c$ (n_a = mole fraction adduct; n_c = mole fraction $AlMe_3,Et_2O$). By integration of the characteristic peaks of the species in solution their total concentrations may be found and a value for K calculated. K was shown to have a constant value for solutions of different composition confirming the validity of equations (1) and (2).

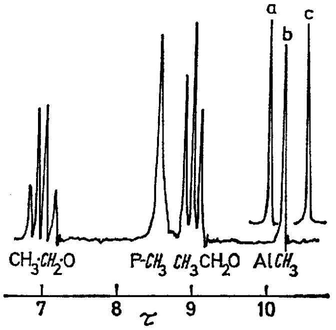

FIGURE 4 ^1H N.m.r. spectrum of a mixture of *trans*-$[ReCl(N_2)(PMe_2Ph)_4]$, $AlMe_3$, and Et_2O; a, adduct; b, equilibrium mixture; c, $AlMe_3,Et_2O$

Table 2 lists the values of τ_{Me} and K for six complexes whose purity and stability allowed accurate measurements to be made. Taking K as a measure of the relative basic character of the Y atom of the co-ordinated XY ligand towards trimethylaluminium in benzene solution, it can be seem that co-ordinated dinitrogen is more basic than co-ordinated carbon monoxide in the pair of compounds *trans*-$[ReCl(XY)(PMe_2Ph)_4]$ and generally more basic than diethyl ether. The majority of Lewis acids which form adducts with *trans*-$[ReCl(N_2)(PMe_2Ph)_4]$, such as $[VCl_3(MeCN)_3]$ or $[MoCl_4(thf)_2]$,[1,2] oxidise the molybdenum(0) and tungsten(0) complexes and fail to react with carbonyl complexes. Trimethylaluminium on the other hand, as a non-oxidising addend, is particularly well suited to distribution equilibrium studies of the above type.

Careful addition of pentane or hexane to benzene or toluene solutions of some of the adducts containing an excess of trimethylaluminium, led to their separation as crystals whose solid state i.r. spectra showed the characteristic frequencies near $\nu^1(XY)$ cm^{-1}. Their solution ^1H n.m.r. spectra showed the presence of trimethylaluminium and transition metal complex in 1 : 1 ratio together with, in certain cases, solvent of crystallisation. Microanalytical data confirmed the formulations shown in Table 3.

The presence of an excess of trimethylaluminium in the above solutions served to protect the crystals from traces of air or protic substances and allowed slow crystallisation, to give in several cases single crystals; unfortunately they were unsuitable for X-ray structure determinations. They decomposed in most cases on standing, even *in vacuo* at —10°, in a matter of days and were instantly destroyed on contact with air or with water vapour. This extreme sensitivity made molecular weight determinations of these compounds (cryoscopy in dry benzene) very difficult and at best low values were obtained (Table 3 gives an example).

Monocarbonyl complexes of rhenium(I) each gave a single i.r. absorption $[\nu^1(CO)]$ with triphenylaluminium. Trimethylaluminium or aluminium trichloride, however, gave broad irregular absorptions of half peak width 50—100 cm^{-1} indicating a number of species were present in solution. Nevertheless, only 1 : 1 adducts could be crystallised from the solutions and 90% recovery of the pure parent monocarbonyl complexes was obtained from the solutions by cautious addition of ethanol. In the presence of a small quantity of diethyl ether these broad absorptions were replaced by a single strong absorption at $\nu^1(CO)$ corresponding to the adduct and a weak absorption at $\nu(CO)$ due to the presence of a small quantity of parent complex (Figure 2c). The value of K for *trans*-$[ReCl(CO)(PMe_2Ph)_4]$ rises slightly with diethyl ether concentration, possibly because of the suppression of further co-ordination of trimethylaluminium to other weakly basic sites in the complex by competition with ether.

TABLE 3

Analytical data for trimethylaluminium adducts

Compound	Appearance	Yield/%	Analyses [a] C	H	N	Al	Cl
trans-$[ReCl(N_2AlMe_3)(PMe_2Ph)_4]$ [b]	Yellow octahedra	80	48·1 (48·1)	6·2 (6·1)	3·3 (3·2)	3·2 (3·1)	4·0 (4·1)
trans-$[ReCl(N_2AlMe_3)(dpe)_2]$	Yellow needles	60	59·2 (59·1)	5·2 (5·1)	2·6 (2·5)	2·3 (2·4)	3·0 (3·2)
mer-$[ReCl(N_2AlMe_3)(PMe_2Ph)_3(C_5H_5N)]$	Red prisms	65	46·9 (47·1)	6·0 (5·8)	5·0 (5·1)	3·3 (3·3)	
trans-$[ReCl(COAlMe_3)(dpe)_2]$	Colourless needles	80	59·9 (60·1)	5·4 (5·1)		2·6 (2·4)	3·2 (3·2)
$[ReCl(CO)_2(COAlMe_3)(PPh_3)_2]$ [c]	Pink prisms	70	56·2 (55·9)	4·5 (4·4)		3·4 (3·0)	3·8 (3·9)
trans-$[Mo(N_2)(N_2AlMe_3)(dpe)_2],\frac{1}{2}C_6H_{14},\frac{1}{2}C_7H_8$	Dark red prisms	55	66·5 (66·5)	6·6 (6·2)	5·2 (5·1)	2·6 (2·4)	
trans-$[W(N_2)(N_2AlMe_3)(dpe)_2],\frac{1}{2}C_6H_{14},\frac{1}{2}C_7H_8$	Black prisms	60	62·2 (61·7)	6·1 (5·7)	4·3 (4·7)	2·3 (2·3)	

[a] Calculated values in parentheses. [b] Additional analytical data, P, 14·0 (14·2); Re, 21·2 (21·3); M (in 0·45% benzene solution) 620 (870). [c] Configuration uncertain.

Such further co-ordination would account for the broad absorptions observed and the near quantitative recovery of the parent complex on ethanolysis.

Boron compounds such as BR_3 (R = Ph, F, H, Cl, or Br) failed to give adducts with even the most basic dinitrogen or carbonyl complexes. Mostly decomposition occurred but in some cases (R = F, Cl, or Br) oily products which had ν(CO) raised by *ca.* 100 cm^{-1} were obtained.

The compounds *trans*-$[IrCl(CO)(PPh_3)_2]$, *trans*-$[IrCl(CO)(O_2)(PPh_3)_2]$ and *trans*-$[IrCl(N_2)(PPh_3)_2]$ all showed a small Δν of about -12 cm^{-1} in benzene solution with trimethylaluminium but nevertheless crystallised unchanged from the solutions. Boron trifluoride is known to form a 1 : 1 adduct with a raised ν(CO) (Δν(CO) = -111 cm^{-1}) with *trans*-$[IrCl(CO)(PPh_3)_2]$ in which a metal–boron bond is thought to be present.[11] Possibly these observations indicate an interaction of trimethylaluminium with the iridium atoms of the above compounds. The compounds $[ReCl(CO)_2(N_2)(PR_3)_2]$ (PR_3 = PPh_3 or $PEtPh_2$) are unaffected by trimethylaluminium, but the corresponding tricarbonyl[12] species do interact, and where PR_3 = PPh_3 a 1 : 1 adduct has been crystallised (Table 3). However, the solution spectra of these adducts show 5 bands (Table 1) suggesting a more complicated reaction. Owing to this and to the coupling of the carbonyl vibrations, Δν(CO) has not been assigned a value.

None of the dinitrogen complexes studied reacted with trimethylaluminium to methylate the dinitrogen ligand. Similarly there was no methylation of co-ordinated carbon monoxide, but a trimethylaluminium-induced reaction was discovered (reaction 3). The addition of dimethylphenylphosphine did not increase the yield. The presence of trimethylaluminium is essential for the reaction to occur, since in its absence the dicarbonyl complex is not substituted by an excess of the neat phosphine at 150° (sealed tube).

$$[ReCl(CO)_2(PMe_2Ph)_3] + AlMe_3 \xrightarrow[\text{reflux, 1h}]{\text{benzene}} [ReCl(CO)(PMe_2Ph)_4] + \text{rhenium compounds} + \text{aluminium compounds} \quad (3)$$

Dipole Moment Measurements.—As a complementary study of the electronic behaviour of co-ordinated dinitrogen and carbonyl ligands we have attempted to measure the difference in dipole moment between pairs of analogous dinitrogen and carbonyl complexes. We find that in benzene solution at 25·0° only the pair *trans*-$[ReCl(XY)(PMe_2Ph)_4]$ (XY = CO or N_2) of all those available to us has sufficient thermal stability together with purity and solubility for accurate measurements. The measured moments were 1·25 D (XY = N_2) and 2·0 D (XY = CO) respectively. As expected the moments are closely similar. If we make the reasonable assumption that the chlorine lies at the negative end of the dipole and that the bond moments of all bonds common to the two molecules are the same in both, then the dinitrogen is only slightly more negative than the carbon monoxide in the above pair of compounds.

Conclusion.—In its complexes of low ν(N_2), terminal dinitrogen has, towards trimethylaluminium, a basic strength comparable with, and generally rather greater than, diethyl ether. The basic nature of the N_2 ligand depends upon the other ligands in the complex. In particular *trans*-$[ReCl(N_2)(PMe_2Ph)_4]$, which has the lowest ν(N_2) of the complexes studied, is the most basic. When two PMe_2Ph ligands of this complex are substituted by less basic $P(OMe)_3$ ligands, then ν(N_2) rises and the basic strength of the dinitrogen ligand falls. The implication of this is that the more electron density the ligating dinitrogen takes into its π^*-orbitals from the metal *d*-orbitals, the more basic is the terminal N atom.

EXPERIMENTAL

Manipulations and preparations of the complexes listed in Table 1 were carried out under dinitrogen or *in vacuo* according to references 7 and 13—16, except for the new complexes *trans*-$[ReCl(N_2)(PMe_2Ph)_2\{P(OMe)_3\}_2]$ and *mer*-$[Re(Me_2NCS_2)(N_2)(PMe_2Ph)_3]$ whose preparations are described below. I.r. spectra were determined on a Unicam SP 1200 instrument. Analyses were by Mr. A. G. Olney of Sussex University and by the Alfred Bernhardt Microanalytical Laboratories. Benzene, toluene, and paraffin hydrocarbon solvents were shaken with concentrated sulphuric acid, washed and distilled from calcium hydride under dry dinitrogen. Diethyl ether and tetrahydrofuran were distilled from sodium diphenylketyl. Trimethylaluminium was used as supplied by Ethyl Corporation. Triphenylaluminium was prepared by the method of Mole.[17] Organoaluminium compounds were stored under dinitrogen in glass phials which were transferred to a dinitrogen-filled glove box for use.

I.r. Studies.—Typically the parent complex (about 30 mg) was dissolved in benzene (1 cm^3) and trimethylaluminium (0·05 cm^3) was added in the glove box. This solution was drawn into a syringe and loaded into an i.r. solution cell (0·2 mm KBr plates) which was tightly stoppered. The cell could then be removed from the glove box and the spectrum was run in the region 1600—2200 cm^{-1} on slow scan with a suitably adjusted benzene-filled variable pathlength cell in the reference beam. For the measurements of intensities a sample was weighed and a benzene solution made up to known volume with trimethylaluminium. The area under the peak was determined by Simpson's rule. The validity of this technique was confirmed by trials on peaks from various solutions of known concentration. Nujol mulls were made up in dry, degassed Nujol in the glove box. The Ir^I complexes did not give crystalline adducts but with trimethylaluminium

---

[11] R. N. Scott, D. F. Shriver, and L. Vaska, *J. Amer. Chem. Soc.*, 1968, **90**, 1079.

[12] J. R. Dilworth, D.Phil. Thesis, University of Sussex, 1969.

[13] J. Chatt and A. G. Wedd, *J. Organometallic Chem.*, 1971, **27**, C15.

[14] J. Chatt, G. J. Leigh, and R. L. Richards, *J. Chem. Soc.* (*A*), 1970, 2243, and references therein.

[15] B. Bell, J. Chatt, and G. J. Leigh, *Chem. Comm.*, 1970, 842.

[16] F. Canzini and F. Zingales, *Gazzetta*, 1962, **92**, 343.

[17] T. Mole, *Austral. J. Chem.*, 1963, **16**, 794.

showed i.r. bands as follows: *trans*-[IrCl(CO)($PPh_3)_2$], 1972, (1964); [IrCl(CO)(O_2)($PPh_3)_2$], 2008, (2000); *trans*-[IrCl(N_2)($PPh_3)_2$], 2119, (2105). (Values in cm^{-1} and ν(XY) of the parent complexes in parentheses).

^1H N.m.r. Spectroscopy.—Solutions for study were made up in n.m.r. tubes in the dinitrogen-filled glove box using Hamilton syringes (0·5 cm^3). Diethyl ether was injected through No. 13 Subaseals capping the tubes for the distribution studies. No decomposition of a sample of trimethylaluminium kept in an n.m.r. tube capped with a Subaseal in the glove box was observed after 3 months. Integration of the peaks gave the mole fractions of the species present in the adduct solutions and in the ether distribution experiments. The concentration ranges employed were: transition metal complex, 1—8 × 10^{-2} M; Et_2O, 1—80 × 10^{-2} M; $AlMe_3$ 0·5—12 × 10^{-2} M; the spectra were measured at 34 ± 2°.

Crystallisation.—In initial experiments solutions of adducts were made up by distillation of dry solvents and neat trimethylaluminium *in vacuo*, but glove box techniques were found to give better results and large crystals of the adducts could be grown by addition of the paraffin hydrocarbon at room temperature and allowing the solution to stand at −10° for up to two days. Typically [ReCl(N_2)($PMe_2Ph)_4$] (1 g) was dissolved in benzene (5 cm^3) and trimethylaluminium (0·5 cm^3) added. Petroleum ether (60—80°, 10 cm^3) gave octahedral *crystals* of the adduct over 1—2 days at −10°.

Treatment of Adduct Solutions with Alcohol.—To solutions containing trimethylaluminium adducts under dinitrogen was added an excess of tetrahydrofuran and then, dropwise and with ice cooling, ethanol. After a few minutes, a gelatinous precipitate appeared. The solution was warmed to 40° and allowed to stand for 30 min. After removing the solvent *in vacuo* at 40° the precipitated solid was extracted with chloroform or benzene three times. The resulting solution was reduced to about a quarter volume *in vacuo* and the product isolated by addition of methanol or hexane.

trans-*Chloro(dinitrogen)bis(dimethylphenylphosphine)bis(trimethyl phosphite)rhenium*(I).—Freshly prepared, crude [Re(N_2COPh)Cl_2($PMe_2Ph)_3$] [7] (1 g) was suspended in dry methanol (60 cm^3) and toluene (20 cm^3) and P(OMe)$_3$ (2 cm^3) and NEt_3 (5 ml) were added (NEt_3 catalyses the reaction). The solution was yellow after 90 min reflux and gave a yellow oil on removal of the solvent. Treatment of the yellow oil with methanol (6 ml) gave, after slow crystallisation, the *complex* as light yellow prisms (0·3 g, 30%). ν(N_2) (benzene) = 2000 cm^{-1} (Found: C, 34·5; H, 5·5; N, 3·6. $C_{22}H_{40}ClN_2O_6P_4Re$ requires C, 34·2; H, 5·2; N, 3·6%). ^1H N.m.r.; chemical shifts τ, multiplicity, integral found, (calculated), assignment, J_{PH}; *ca.* 2·8, multiplet 10·1 (10·0), *Ph*; 6·60, triplet, 18, (18·0), *P(OMe)*$_3$, 3·92 Hz; 7·84, triplet, 12·3 (12·0), *P-Me*$_2$, 2·5 Hz.

mer-*Dimethyldithiocarbamato(dinitrogen)tris(dimethylphenylphosphine)rhenium*(I)*.—[ReCl(N_2)($PMe_2Ph)_4$] (2 g) and Na[Me_2NCS],$2H_2O$ (2 g) were heated under reflux in acetone (60 cm^3) for 30 min. After removal of solvent *in vacuo*, the resulting solid was extracted with ether (60 cm^3) and petroleum ether (b.p. 100—120°, 10 cm^3) was added to the solution. After concentrating the solution at 60° to 15 cm^3 and cooling it to 20°, the *product* separated as orange plates (0·82 g, 40%) ν(N_2) = 1945 cm^{-1} (benzene) (Found: C, 43·2; H, 5·3; N, 5·4. $C_{27}H_{39}N_3P_3S_2Re$ requires C, 43·3; H, 5·2; N, 5·6%). ^1H N.m.r.; 2·6, complex multiplet, 15·5 (15), *Ph*; 6·62, singlet, 5·8 (6), *Me*N; 8·0, quartet, 12·1 (12), P*Me* 2·6 Hz; 8·4, doublet, 6·0 (6) P*Me*, 4·8 Hz.

trans-*Chloro(carbonyl)tetrakis(dimethylphenylphosphine)rhenium*(I).—[ReCl(CO)$_2$($PMe_2Ph)_3$] (2 g) was dissolved in benzene (20 cm^3) and trimethylaluminium (0·4 ml) added. After heating the solution at reflux for 1 h and cooling to 20° ethanol was added as above, the *product* was extracted with chloroform, recrystallised from chloroform–methanol and identified by its i.r. spectrum (0·8 g, 35%) (Found: C, 50·0; H, 5·7. $C_{33}H_{44}ClOP_4Re$ requires C, 50·2; H, 5·6%).

Attempted Reaction of Chloro(dicarbonyl)tris(dimethylphenylphosphine)rhenium(I) *with Dimethylphenylphosphine*.—[ReCl(CO)$_2$($PMe_2Ph)_3$] (0·1 g) was heated with PMe_2Ph (0·8 g) in a sealed, evacuated tube for 5 h at 150°. The solution i.r. spectrum of the product showed bands due to the starting material at 1932 and 1842 cm^{-1} and no bands due to the monocarbonyl complex {ν(CO) = 1782 cm^{-1}}.

Dipole Moments.—Dipole moments were determined in purified dry benzene at 25·0 ± 0·1° under dry dinitrogen with a DM 01 dipole meter. The complexes *trans*-[ReCl(XY)($PMe_2Ph)_4$] were recrystallised from benzene–hexane until they were analytically pure. The dipole moment determination was made difficult by the low solubility and small moment of the compounds. $_EP$ was estimated by comparison with similar compounds and the measured value (XY = N_2) agreed to within 0·1 cm^3. 100 Determinations of the dielectric constants of each of two samples of the dinitrogen and of the carbonyl complex in solution showed a high internal consistency and invariance with time. The results are reported in the Table below where the symbols have their usual meanings.[18] The calculations were performed according to Sutton.[19]

Compound	$10^3\omega$	$\Delta\varepsilon/\omega$	$10^2\Delta n$ *$/\omega$	$-\Delta v/\omega$	$_TP$	$_EP$	$_OP$	μ(D)
trans-[ReCl(N_2)($PMe_2Ph)_4$]	4·585	0·7866			275·3		28·8	1·25
	5·638	0·8175			279·9		33·5	
	25·516		1·303			214·2		
	6·807			0·49				
trans-[ReCl(CO)($PMe_2Ph)_4$]	1·707	1·134		(0·49)	328	(214)	81	2·0
	5·423	1·1117			324		78	

* At 589 nm.

[2/2563 *Received*, 13*th November*, 1972]

---

[18] J. Chatt and B. L. Shaw, *J. Chem. Soc.*, 1959, 705.

[19] K. B. Everard, R. A. W. Hill, and L. E. Sutton, *Trans. Faraday Soc.*, 1950, **46**, 417.

* We are indebted to J. R. Dilworth for this preparation.