Redox-potential–Structure Relationships in Metal Complexes. Part 4.† Electron-poor Dinitrogen Complexes of Rhenium(I)

By **G. Jeffery Leigh,* Robert H. Morris, Christopher J. Pickett,*** and **David R. Stanley,** A.R.C. Unit of Nitrogen Fixation, University of Sussex, Brighton BN1 9RQ
Joseph Chatt, School of Molecular Sciences, University of Sussex, Brighton BN1 9QJ

The systematic syntheses of some new electron-poor $Re^{I}(N_2)$ complexes are described. The oxidation potentials of these complexes vary essentially linearly with $\nu(N_2)$ whilst only those with $E_{\frac{1}{2}}^{ox} >$ *ca.* +0.8 V *versus* the saturated calomel electrode react with LiMe. In general, the nature of the product(s) of reaction of these complexes with LiR (R = alkyl or aryl) depend upon R. For example, $[ReCl(CO)_2(N_2)(PPh_3)_2]$ reacts with LiMe–H$^+$ to give $[ReCl\{C(OH)Me\}(CO)(N_2)(PPh_3)_2]$, but with LiPh–H$^+$ gives the five-co-ordinate $[ReCl(CO)_2(PPh_3)_2]$. We have not observed attack by LiR upon N_2 in any of the complexes. The apparent selectivity of the site of attack by LiR is discussed.

THE factors which determine the activation of N_2 bound to a transition-metal site, M_s, in the complexes $[M_s(N_2)]$, where M_s = transition metal + ligands, are of fundamental interest. The particular transition metal, its oxidation state, and the other ligands around the metal will necessarily determine the electronic condition of the co-ordinated N_2 in $[M_s(N_2)]$ and hence its reactivity towards nucleophiles, electrophiles, or radicals. A simple concept, which we have shown to be useful in rationalising certain gross properties of closed-shell octahedral species, is that of the *electron-richness* or *-poorness* of the binding site M_s. By electron-richness or -poorness we mean the tendency of the site to release or accept electron density onto a given ligand, including N_2. As an indication of such electron-richness or -poorness we have suggested that the reversible one-electron oxidation potential of $[M_2(L)]$, where L = N_2, CO, or other two-electron donor ligand, is a convenient probe since this generally reflects the energy with which the electrons in the highest occupied molecular orbital (h.o.m.o.) of each complex are held, and hence the effective nuclear charge on the metal.[1,2] As a guide, those complexes which oxidise at potentials >0.00 V *versus* the standard hydrogen electrode (s.h.e.) we define as electron-poor whilst those which oxidise at potentials <0.00 V we define as electron-rich. Complexes $[M_s(L)]$ which are electron-rich might be expected to show a tendency towards attack by electrophiles, whilst those which are electron-poor a tendency towards attack by nucleophiles.[2]

In order to explore such relationships further we have now systematically synthesised a range of electron-poor $Re^{I}(N_2)$ complexes, whose redox potentials lie within a range of *ca.* 1 V, and have surveyed their reactions, under standard conditions, with nucleophilic organolithium reagents.

RESULTS AND DISCUSSION

Synthesis of the Complexes.—The reaction of the complex $[\overline{ReCl_2(N_2CO}Ph)(PPh_3)_2]$, (A), with tertiary phosphines, PR_3, has been shown to yield a range of dinitrogen complexes of the type *trans*-$[ReCl(N_2)(PR_3)_4]$ according to reaction (1), whilst reaction of (A) with carbon monoxide has been shown to give *trans*-$[ReCl(CO)_2(N_2)(PPh_3)_2]$ according to reaction (2).[3] We have

$$[\overline{ReCl_2(N_2CO}Ph)(PPh_3)_2] + 4PR_3 \xrightarrow{MeOH} [ReCl(N_2)(PR_3)_4] + 2PPh_3 + PhCOCl \quad (1)$$

$$[\overline{ReCl_2(N_2CO}Ph)(PPh_3)_2] + CO \xrightarrow{MeOH} [ReCl(CO)_2(N_2)(PPh_3)_2] + PhCOCl \quad (2)$$

now found that by allowing (A) to react with carbon monoxide or with organophosphites in a two-stage reaction, a further range of $Re^{I}(N_2)$ complexes which are relatively electron-poor and which have up to five different ligands surrounding the Re atom can be synthesised according to the Scheme. The initial stage involves the synthesis of new benzoyldiazenido-complexes (B), (C), and (D), the preparation and characterisation of which are given, together with those of the new dinitrogen complexes (1)—(8), in the Experimental section. We have also synthesised two new cationic $Re^{I}(N_2)$ complexes *via* chloride abstraction from $[ReCl(N_2)(dppe)_2]$ [dppe = 1,2-bis(diphenylphosphino)ethane] by $Tl[BF_4]$ in the presence of CH_3CN or PhCN, reaction (3).

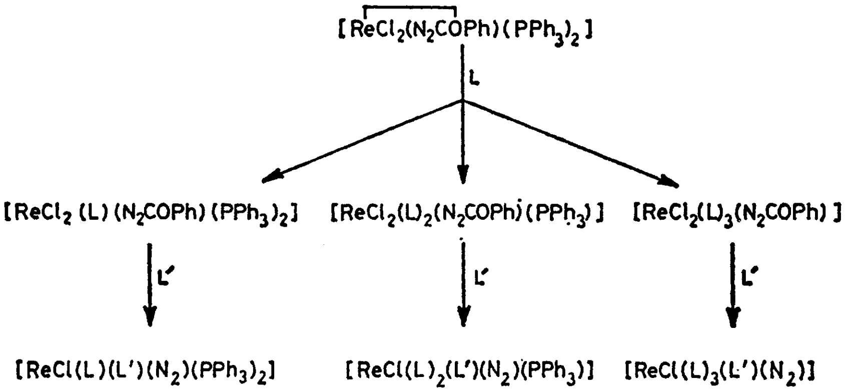
$$[ReCl(N_2)(dppe)_2] + Tl[BF_4] \xrightarrow{RCN} [Re(N_2)(NCR)(dppe)_2][BF_4] + TlCl \quad (3)$$

Oxidation Potentials, Infrared Spectral Data $[\nu(N_2)]$, *and Electron-poorness*.—Cyclic voltammetry of the rhenium(I) complexes at a Pt electrode in tetrahydrofuran (thf)–0.2 mol dm^{-3} $[NBu_4][BF_4]$ reveals that each complex undergoes a diffusion-controlled, reversible, one-electron oxidation. Over the range of scan rates 0.01—0.3 V s^{-1}, i_p^{ox} is proportional to $\nu^{\frac{1}{2}}$, i_p^{red}/i_p^{ox} is close to unity, and $|E_p^{ox} - E_p^{red}|$ is *ca.* 60—80 mV, for each complex. The Table lists the E_p^{ox} and $\nu(N_2)$ data for the complexes investigated.

The Figure shows a plot of $\nu(N_2)$ *versus* $E_{\frac{1}{2}}^{ox}$ for the series in which the Cl–Re–N_2 axis is constant and the ligands *cis* to N_2 change, and also for the more limited bis(diphosphine) series in which the ligand *trans* to N_2 is changed. The data for the former series show that

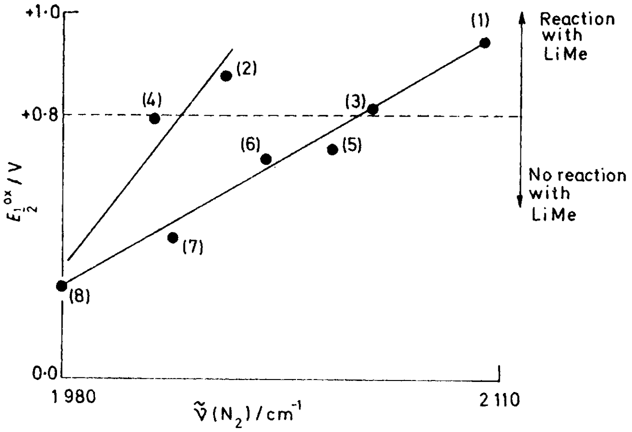
---

† Part 3, B. A. L. Crichton, J. R. Dilworth, C. J. Pickett, and J. Chatt, *J. Chem. Soc., Dalton Trans.*, 1981, 419.



Scheme

ν(N_2) responds essentially monotonically to a change in $E_{\frac{1}{2}}^{ox}$ and that the slope is *ca.* 150 cm^{-1} V^{-1}. Previously we showed[1] that there is a linear correlation between ν(N_2) and $E_{\frac{1}{2}}^{ox}$ for a range of complexes *trans*-[Mo(N_2)(L)(dppe)$_2$], except where L = CO, and that Δν(N_2)/Δ$E_{\frac{1}{2}}^{ox}$ was *ca.* 110 cm^{-1} V^{-1}. For the isoelectronic rhenium series the slope is somewhat smaller, *ca.* 70 cm^{-1} V^{-1}, but the data relating to this *trans* influence must be viewed with caution since L is limited to the ligands Cl^-, MeCN, and PhCN and the scatter is considerable.



Correlation of ν(N_2), $E_{\frac{1}{2}}^{ox}$, and reactivity towards LiMe

Nevertheless, a smaller response of ν(N_2) for a given change in $E_{\frac{1}{2}}^{ox}$ for the rhenium as compared to the molybdenum series is intuitively reasonable for the following reasons. The effective positive nuclear charge on Re must be greater than on Mo (as the rhenium complexes oxidise at potentials >1.2 V more positive than their molybdenum analogues). This being so, the rhenium centre will tend to retain and/or demand more electron density from L than will Mo. Thus, on changing L from a less to a more electron-donating ligand, the effective nuclear charge on Re should change more than on Mo undergoing a similar perturbation: this will be reflected in Δ$E_{\frac{1}{2}}^{ox}$. Similarly, for a given ligand change, Mo will allow more negative charge to drift onto N_2 than will Re, thus Δν(N_2) will be greater for the former metal than for the latter. Both these factors will work to decrease Δν_{N_2}/Δ$E_{\frac{1}{2}}^{ox}$ for Re compared to Mo.

Reactivity of Rhenium(I) *Complexes towards Organolithium Reagents*.—We have previously shown[4] that the most electron-poor of our complexes [ReCl(CO)$_2$(N_2)(PPh$_3$)$_2$], (1), reacts with LiMe–H^+ according to reaction (4) to give a hydroxycarbene complex, (E), in high yield. We find that (1) also reacts with other LiR species but that the products are sensitive to the nature of R. Thus LiPh–H^+ gives the five-co-ordinate species, [Re(CO)$_2$Cl(PPh$_3$)$_2$], (F),[5] and N_2, according to reaction (5). Similarly (1) reacts with LiBu^t to give [ReCl(CO)$_2$(PPh$_3$)$_2$], (F), but with LiBu^s a mixture of two products is formed, (F), and the s-butylhydroxycarbene analogue of (E); whilst with LiBu^n, (1) appears to give essentially only the n-butylhydroxycarbene analogue of (E). These results suggest that steric factors may be important in determining the reaction pathway of (1) with LiR. In no case have we observed attack of LiR upon the N_2 ligand.

Redox potentials and i.r. frequencies for the complexes (1)—(8)

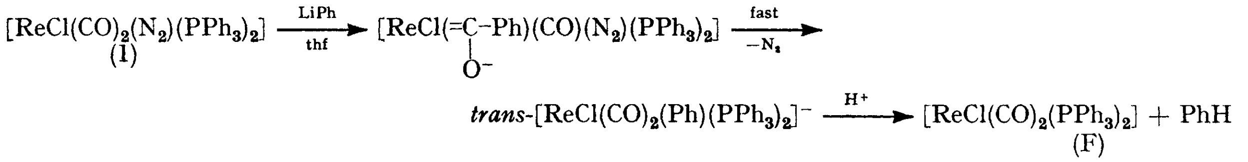
	Complex[a]	$E_{\frac{1}{2}}^{ox}$/V[b]	ν(N_2)/ cm^{-1}[c]
(1)	[ReCl(CO)$_2$(N_2)(PPh$_3$)$_2$]	1.01	2 115
(2)	[Re(N_2)(NCPh)(dppe)$_2$]$^+$	0.91	2 028
(3)	[ReCl(CO)(N_2){P(OMe)$_3$}$_3$]	0.81	2 072
(4)	[Re(N_2)(NCMe)(dppe)$_2$]$^+$	0.79	2 008
(5)	[ReCl(CO)(N_2){P(OMe)$_3$}(PPh$_3$)$_2$]	0.69	2 060
(6)	[ReCl(N_2)(dmope)$_2$]	0.66	2 040
(7)	[ReCl(N_2){P(OMe)$_3$}$_4$]	0.42	2 013
(8)	[ReCl(N_2)(dppe)$_2$]	0.28	1 980

[a] dppe = Ph$_2$PCH$_2$CH$_2$PPh$_2$; dmope = (MeO)$_2$PCH$_2$CH$_2$P(OMe)$_2$. [b] Measured in thf–0.2 mol dm^{-3} [NBu$_4$][BF$_4$], scan rate 0.3 V s^{-1}, Pt electrode, concentration of complex *ca.* 5 × 10^{-3} mol dm^{-3}. $E_{\frac{1}{2}}^{ox}$ quoted *versus* the saturated calomel electrode (s.c.e.). Estimated error ±0.02 V. [c] Solution spectra, CH$_2$Cl$_2$. Estimated error ±2 cm^{-1}.

$$(1) \xrightarrow[\text{(ii) HBF}_4]{\text{(i) LiMe}} \underset{\text{(E)}}{[\text{ReCl}\{\text{C(OH)Me}\}(\text{CO})(\text{N}_2)(\text{PPh}_3)_2]} \quad (4)$$

$$(1) \xrightarrow[\text{(ii) HBF}_4]{\text{(i) LiPh}} \underset{\text{(F)}}{[\text{ReCl}(\text{CO})_2(\text{PPh}_3)_2]} + \text{N}_2 \quad (5)$$

The formation of (F) in the reaction of (1) with LiPh and LiBu^t–H^+ is intriguing. Solution i.r. studies have shown that (1) reacts rapidly with LiPh to give an intermediate which shows a single ν(CO) band at 1 870 cm^{-1} but no band attributable to $\nu(N_2)$. The product (F) is formed immediately upon quenching this intermediate with HBF_4 as shown by the appearance of new ν(CO) bands at 1 935 and 1 850 cm^{-1} and the discharge of the band at 1 870 cm^{-1}. Clearly, this reaction suggests conversion from a more to a less symmetric arrangement of the CO ligands. An adequate rationalisation of these observations is that LiPh attacks at the metal, perhaps *via* an initial attack upon CO followed by migration according to reaction (6).



$$\underset{(1)}{[ReCl(CO)_2(N_2)(PPh_3)_2]} \xrightarrow[\text{thf}]{\text{LiPh}} [ReCl(=\underset{O^-}{\underset{|}{C}}-Ph)(CO)(N_2)(PPh_3)_2] \xrightarrow[-N_2]{\text{fast}}$$

$$trans\text{-}[ReCl(CO)_2(Ph)(PPh_3)_2]^- \xrightarrow{H^+} \underset{(F)}{[ReCl(CO)_2(PPh_3)_2]} + PhH \quad (6)$$

An alternative explanation would be that nucleophilic attack upon the CO is competitive with an electron transfer [reaction (7)].

$$\begin{tikzcd} (1) \arrow[r, "LiR", "e"'] & {[ReCl(CO)_2(PPh_3)_2]^- + N_2 + R\cdot} \arrow[d, "{H^+, -e}"] \\ & \underset{(F)}{[ReCl(CO)_2(PPh_3)_2]} \end{tikzcd} \quad (7)$$

Certainly, the product (F) undergoes two successive one-electron reductions at quite negative potentials in thf–0.2 mol dm^{-3} $[NBu_4][BF_4]$ which we interpret according to reaction (8) and the starting material, (1), can be reduced irreversibly at *ca.* −2.2 V *versus* a standard calomel electrode (s.c.e.).

$$\underset{\substack{\text{trigonal}\\\text{bipyramidal}}}{(F)} \xrightarrow{\substack{\text{irrev.}\\ e}} \underset{\substack{\text{square}\\\text{pyramidal}}}{[ReCl(CO)_2(PPh_3)_2]^-} \underset{-e}{\overset{e}{\rightleftharpoons}} [ReCl(CO)_2(PPh_3)_2]^{2-} \quad (8)$$

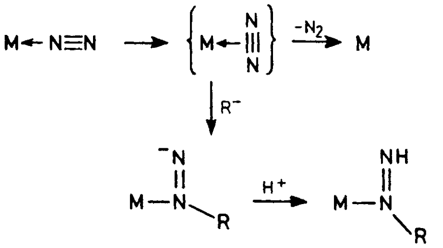
We have not distinguished between these two possible reaction pathways although the former appears more feasible from a consideration of the reactivity of $[ReCl(CO)_3(PPh_3)_2]$, (G), the tricarbonyl analogue of (1). This reacts with LiR (R = Me or Ph) to give metathesis products, (H), according to reaction (9). If we postulate

$$\underset{(G)}{[ReCl(CO)_3(PPh_3)_2]} \xrightarrow[-LiCl]{LiR} \underset{(H)}{[Re(CO)_3(PPh_3)_2R]} \quad (9)$$

initial attack upon the metal, or upon CO followed by rearrangement and loss of Cl^- [rather than N_2 as in reaction (6)], a parallel with the reaction of (1) with LiR is evident. The complex $[ReCl(CO)_5]$ which is considerably electron-poorer than any of our complexes[4] reacts with LiR to give an hydroxycarbene complex[6] rather than a metathesis product, but presumably in this complex there is less steric pressure favouring ligand expulsion and the greater charge on the Re should enhance the Re–Cl bond energy thus disfavouring alkyl migration and consequent halide loss. We find that of the complexes (2)—(8) which are progressively *less* electron-poor (see Table), only (2) and (3) react with LiMe under our conditions. The complex *trans*-$[Re(N_2)(NCPh)(dppe)_2]^+$, (2), gives a red ether-soluble oil which we have not further characterised, whilst $[ReCl(CO)(N_2)\{P(OMe)_3\}_3]$, (3), appears to be attacked at the CO ligand. From this latter reaction we have obtained an oil which shows $\nu(N_2)$ at 2 000 cm^{-1}; the shift in $\nu(N_2)$ of around 70 cm^{-1} from that of the starting material is similar to that observed in the reaction of (1) with LiMe–H^+. It is therefore probably an hydroxycarbene complex.

Evidently, reaction with LiMe, irrespective of the site of attack or of the final product, is markedly influenced by the 'electron-poorness' of the Re atom since only those complexes which oxidise at potentials >*ca.* +0.8 V *vs.* s.c.e. are reactive under our conditions. The Figure illustrates the apparent dependence of reactivity upon $E_{\frac{1}{2}}^{ox}$ for the complexes and clearly $\nu(N_2)$ is not an adequate indicator of potential reactivity for such complexes.

It remains to consider why LiR reagents attack N_2 in $[Mn(C_5H_5)(CO)_2(N_2)]$ and $[Re(C_5H_5)(CO)_2(N_2)]$ but not in the rhenium(I) complexes we have described.[7] In the complex $[Mn(C_5H_5)(CO)_2(N_2)]$, $\nu(N_2)$ is some 45 cm^{-1} higher in energy than in our most electron-poor complex, (1), although we would not expect the former to oxidise at a potential significantly more positive than that of the latter.[4] The N_2 in the cyclopentadienyl complexes is particularly labile and is readily displaced by other two-electron donor ligands; N_2 in (1) is not labile and not replaced under mild conditions even by CO. This may be the key to the reactivity pattern. It is possible that R^- attack upon co-ordinated N_2 requires that the N_2 adopt a product-like transition state, and, where N_2 is labile, this transition state might be energetically more accessible. Thus one explanation of the preferential attack by LiR upon N_2 in the cyclopentadienyl complexes *vis a vis* the complex (1) is that attack takes place upon 'sideways' bound N_2 [equation (10)]. We have as yet no evidence to confirm this



(10)

hypothesis but we believe it attractive enough to merit further investigation.[8]

EXPERIMENTAL

Preparation of Complexes.—All reactions were carried out in air unless otherwise stated. Infrared data were obtained on a Unicam SP200 spectrometer, and ^{1}H and ^{31}P n.m.r. data were obtained using a JEOL FX-90C spectrometer and δ values for the latter are quoted upfield from $P(OMe)_3$. Complexes $[ReCl(N_2)(dppe)_2]$, $[ReCl(CO)_2(N_2)(PPh_3)_2]$ and $[ReCl_2(N_2COPh)(PPh_3)_2]$ (' green chelate ') were prepared by literature techniques.[3,5]

All compounds decomposed on melting in air. The dppe complexes turned brown at *ca.* 200 °C before melting.

Benzoyldiazenidocarbonyldichlorobis(triphenylphosphine)-rhenium, (B). Carbon monoxide was bubbled through a suspension of ' green chelate ' (0.50 g, 0.55 mmol) in benzene (100 cm^3) at 20 °C for 1.3 h. Upon addition of methanol (30 cm^3) the complex formed green *crystals* which were collected, washed with MeOH, and dried *in vacuo*. Yield 0.31 g, 60%; m.p. 170—175 °C (decomp.) (Found: C, 56.4; H, 4.0; N, 3.0. $C_{44}H_{35}Cl_2N_2O_2P_2Re$ requires C, 56.1; H, 3.75; N, 2.95%). I.r. (Nujol): ν(CO) 2 010s, ν(NN) 1 555m, ν(C=O) 1 675m cm^{-1}.

Benzoyldiazenidodichlorobis(trimethyl phosphite)(triphenylphosphine)rhenium, (C). Trimethyl phosphite (0.17 cm^3, 1.4 mmol) and ' green chelate ' (0.50 g, 0.55 mmol) were stirred in benzene (20 cm^3) under dinitrogen for 0.25 h at 50 °C, and 0.50 h at reflux. The brown solution was reduced to 2 cm^3 at 10^{-2} mmHg * and methanol (30 cm^3) added. A small amount of ' green chelate ' was filtered off and the orange filtrate concentrated until orange crystals of the *complex* separated. These were washed with cold methanol and dried *in vacuo*. Yield 0.15 g, 30%; m.p. 163—170 °C (decomp.) (Found: C, 41.5; H, 4.5; N, 3.20. $C_{31}H_{38}Cl_2N_2O_7P_3Re$ requires C, 41.4; H, 4.20; N, 3.10%). I.r. (Nujol): ν(CO) 1 653m, ν(NN) 1 507s, 1 237s cm^{-1}. Ligand bands at 1 047vs, 1 033vs {$P(OMe)_3$}, 745s, 698s, 522s (PPh_3) cm^{-1}. N.m.r.: ^{1}H [$CDCl_3$, room temperature (r.t.)] δ 3.59 [d, 9 H, CH_3 *cis* to PPh_3, $|J(PH)|$ 9 Hz], 3.93 [d, 9 H, CH_3 *trans* to PPh_3, $|J(PH)|$ 10 Hz], 7.18—7.93 (m, 2 OH, C_6H_5]; ^{31}P (CH_2Cl_2, r.t.) 39.13 [dd, 1 P, $P_A(OMe)_3$ *trans* to P_CPh_3, $|J(P_AP_C)|$ 412.6 Hz], 43.4 [dd, 1 P, $P_B(OMe)_3$ *trans* to Cl, $|J(P_AP_B)|$ 37 Hz], 136.40 [dd, 1 P, P_CPh_3 *cis* to $P_B(OMe)_3$, $|J(P_BP_C)|$ 33 Hz].

Benzoyldiazenidodichlorotris(trimethyl phosphite)rhenium, (D). The mother-liquor from the preparation of (C) above contains a mixture of complexes which were converted to (D) by adding an excess of $P(OMe)_3$ and proceeding as for (C) above. Yield *ca.* 0.10 g, *ca.* 20% (Found: C, 25.4; H, 4.50; N, 3.75. $C_{16}H_{32}Cl_2N_2O_{10}P_3Re$ requires C, 25.2; H, 4.25; N, 3.65). N.m.r.: ^{1}H ($CDCl_3$, r.t.) δ 3.81—3.92 [4 s, 27 H, CH_3, $|J(PH)|$ 27 Hz], 7.2—7.96 (m, 5 H, C_6H_5); ^{31}P ($CDCl_3$, r.t.) 37.56 (s).

Benzonitrilebis[1,2-bis(diphenylphosphino)ethane](dinitrogen)rhenium tetrafluoroborate, (2). Thallium tetrafluoroborate (0.30 g, 1.03 mmol) and $[ReCl(N_2)(dppe)_2]$ (0.50 g, 0.48 mmol) were heated in benzonitrile (1.0 cm^3) and dichloromethane (2.0 cm^3) at reflux under dinitrogen for 10 h. The mixture was then cooled to room temperature, filtered, and the filtrate reduced to 1 cm^3 at 10^{-2} mmHg. Diethyl ether was then added dropwise until the solution became cloudy, and it was then allowed to stand, depositing clumps of *orange needles*, yield 0.20 g, 30%; m.p. 241—249 °C (decomp.), as well as large triangular orange plates (0.10 g). The needles and plates were separated manually, and the needles recrystallised from dichloromethane–diethyl ether (Found: C, 58.8; H, 4.45; N, 3.1. $C_{59}H_{53}BF_4N_3P_4Re$ requires C, 59.0; H, 4.45; N, 3.40%). I.r. (Nujol): ν(NN) = 2 028 cm^{-1}.

Carbonylchloro(dinitrogen)tris(trimethyl phosphite)rhenium, (3). Sodium methoxide (0.07 g, 1.3 mmol) was added to a stirred solution, saturated with carbon monoxide, of (D) (0.60 g, 0.79 mmol) in dry thf (30 cm^3) and methanol (0.075 cm^3, 2.3 mmol). The solution was stored in the dark under carbon monoxide at 20 °C until it had turned pale yellow (*ca.* 0.75 h). It was then filtered and reduced at 10^{-2} mmHg and 30 °C to a yellow oil, and extracted with boiling light petroleum (b.p. 40—60 °C in all cases, 20 cm^3). The extract was filtered and concentrated while hot until it turned cloudy. Pale yellow *crystals* were deposited at room temperature. These were washed at −40 °C with light petroleum, dried *in vacuo* for several hours, and recrystallised from hot light petroleum. Yield 0.20 g, 40%; m.p. 133—135 °C (decomp.) (Found: C, 18.6; H, 4.55; N, 4.35. $C_{10}H_{27}ClN_2O_{10}P_3Re$ requires C, 17.5; H, 4.20; N, 4.30%). N.m.r.: ^{1}H ($CDCl_3$ r.t.) δ 3.80—3.93 (m, CH_3); ^{31}P (CH_2Cl_2, r.t.) 21.74 [d, $|J(PP)| < 23.8$ Hz], 21.78 (t).

Bis[1,2-bis(diphenylphosphino)ethane](dinitrogen)(methyl cyanide)rhenium tetrafluoroborate, (4). This complex was prepared in an analogous fashion to (2) (Found: C, 56.7; H, 4.50; N, 3.20. $C_{55}H_{51}BF_4N_3P_4Re$ requires C, 56.9; H, 4.50; N, 3.70%). N.m.r.: ^{1}H ($CDCl_3$, r.t.) δ 6.6—7.25 (m, 20 H, C_6H_5), 2.2—2.9 (m, 8 H, PCH_2), 1.70 (s, 3 H, CH_3CN); ^{31}P (CH_2Cl_2, r.t.) 111.46 (s).

Carbonylchloro(dinitrogen)(trimethyl phosphite)bis(triphenylphosphine)rhenium, (5). Carbon monoxide was bubbled through a suspension of ' green chelate ' (0.50 g, 0.55 mmol) in benzene (12 cm^3) at 20 °C during 2 h. The green-brown solution was purged with dinitrogen, treated with trimethyl phosphite (0.25 cm^3, 2.0 mmol) and methanol (12 cm^3), and heated under reflux for 1 h. Upon cooling, the complex separated as white crystals (0.10 g). Addition of methanol (20 cm^3) to the mother-liquor yielded a further 0.20 g of crystals. Total yield, 60%; m.p. 149—154 °C (decomp.) (Found: C, 52.0; H, 4.45; N, 3.00. $C_{40}H_{39}ClN_2O_4P_3Re$ requires C, 51.9; H, 4.25; N, 3.00%). N.m.r.: ^{1}H ($CDCl_3$, r.t.) δ 3.25 [d, 9 H, CH_3 $|J(PH)|$ 10 Hz], 7.42—7.92 (m, 30 H, C_6H_4); ^{31}P (CH_2Cl_2, r.t.), 34.22 [t, $P(OMe)_3$, $|J(PP)|$ 32.5 Hz], 57.89 (d, PPh_3).

Chloro(dinitrogen)tetrakis(trimethyl phosphite)rhenium, (7). To a solution of (C) (0.40 g, 0.52 mmol) and trimethyl phosphite (0.20 cm^3, 1.6 mmol) in dry methanol (50 cm^3) under dinitrogen was added sodium methoxide (0.030 g, 0.55 mmol) and the solution heated under reflux until it became colourless (*ca.* 0.3 h). It was reduced to a thick oil at 10^{-2} mmHg and extracted with boiling light petroleum (2 × 15 cm^3), and the extract reduced to 5 cm^3 by evaporation in air to yield white crystals of the *complex* which were dried *in vacuo* for 5 h at 60 °C and then recrystallised from hot light petroleum. Yield 0.15 g, 40%; m.p. 168—170 °C (decomp.) (Found: C, 19.4; H, 4.85; N, 3.75. $C_{12}H_{36}ClN_2O_{12}P_4Re$ requires C, 19.3; H, 4.85; N, 3.75%).

Alternatively, methyl-lithium may be used in place of sodium methoxide. Methyl-lithium (0.81 cm^3 of a solution in diethyl ether, 0.84 mol dm^{-3}, 0.68 mmol) was added to a

---

* Throughout this paper: 1 mmHg ≈ 13.6 × 9.8 Pa.

solution of (2) (0.52, 0.68 mmol) and trimethyl phosphite (0.084 cm^3, 0.64 mmol) in dry toluene (30 cm^3). The colour changed from orange to deep red and the solution was stirred for 10 min, filtered through Celite, treated with methanol (1 cm^3), and then concentrated until purple crystals were deposited. These were recrystallised from light petroleum and shown to be (7) by i.r. and ^1H n.m.r. spectroscopy. Yield 0.24 g, 50%. N.m.r.: ^1H (C_6D_6, r.t.) δ 3.70 (m, CH_3); ^{31}P (CH_2Cl_2, r.t.) 21.44 (s, P).

Carbonylchloro(dinitrogen)[hydroxy(methyl)carbene]bis(triphenylphosphine)rhenium, (E). Methyl-lithium (2 cm^3 of 0.84 mol dm^{-3} solution in diethyl ether) was added under an atmosphere of dry dinitrogen to a suspension of (1) (0.16 g, 0.19 mmol) in thf (25 cm^3). The yellow solid rapidly dissolved and the solution acquired an orange-red colour. After 3—4 min stirring at room temperature HBF_4 (0.5 cm^3, 40% aqueous) was added whereupon the solution colour changed immediately to orange-brown. This solution was concentrated *in vacuo* to *ca.* 15 cm^3 and methanol (50 cm^3) was then added; the *product* was deposited as bright orange microcrystals after standing this solution overnight at 0 °C under N_2. Yield 0.092 g, 57%; m.p. 204—210 °C (decomp.) (Found: C, 55.4; H, 4.2; Cl, 4.15; F, 0.0; N, 3.35. $C_{39}H_{34}ClN_2O_2P_2Re$ requires C, 55.35; H, 4.00; Cl, 4.20; F, 0.0; N, 3.30%). I.r. (Nujol): $\nu(N{\equiv}N)$ 2 040s, $\nu(CO)$ 1 895s, $\nu(C{-}O)$ 1 280s, cm^{-1}. N.m.r.: ^1H and ^{31}P data have been reported previously;[4] ^{15}N (thf, r.t., reference CD_3NO_2 upfield negative) -109.3 [d, 1 N, ReNN, $|J(^{15}N^{15}N)|$ 4 Hz]. The second nitrogen was not observed. ^{15}N-labelled (E) was prepared from ^{15}N-labelled (1), as above.

Reactions of complexes (2)—(8) with LiMe or other LiR were carried out as described for (1) above.

Chloropentakis(triphenyl phosphite)rhenium. Attempts at preparing triphenyl phosphite benzoyldiazenido- or dinitrogen complexes *via* the reaction of $P(OPh)_3$ with 'green chelate' gave only $[ReCl\{P(OPh)_3\}_5]$. Triphenyl phosphite (3.5 cm^3, 13 mmol) and 'green chelate' (0.50 g, 0.55 mmol) were heated in benzene (30 cm^3) under N_2 under reflux for 0.7 h. The orange solution was reduced to 4 cm^3 at 100 °C (10^{-2} mmHg) and then treated with pentane dropwise until white crystals formed. These were filtered off, washed with diethyl ether (2 × 25 cm^3), recrystallised from chloroform–diethyl ether, and dried *in vacuo*. Yield 0.7 g, 70%; m.p. 127—134 °C (decomp.) (Found: C, 60.7; H, 4.35; N, 0.0. $C_{90}H_{75}ClO_{15}P_5Re$ requires C, 61.0; H, 4.25; N, 0.0%).

Bis(benzonitrile)bis[1,2-bis(diphenylphosphino)ethane]rhenium tetrafluoroborate. The orange *plates* obtained during the preparation of (2) above were analytically pure. Yield 0.10 g, 16%; m.p. 276—280 °C (decomp.) (Found: C, 62.2; H, 5.20; N, 1.95. $C_{66}H_{58}BF_4N_2P_4Re$ requires C, 61.2; H, 5.45; N, 2.20%). I.r.: $\nu(CN)$ 2 200m, 2 176s cm^{-1} (Nujol).

Redox-potential Measurements.—The preparation of supporting electrolyte, the purification of solvents, and the measurement techniques have been described previously.[9] Cyclic voltammograms were recorded on a Philips X-Y recorder type PM8041 using a type DT2101 Hi-Tek potentiostat and a type 01 Chemical Electronics waveform generator. The potentials quoted were internally referenced to the $[Mo(N_2)_2(dppe)_2]^0$–$[Mo(N_2)_2(dppe)_2]^+$ couple which has $E_{\frac{1}{2}}^{ox} = -0.16$ V *versus* s.c.e. in thf–0.2 mol dm^{-3} $[NBu_4][BF_4]$.*

We thank Mrs. J. E. Tolhurst (née Kendrick) and Mr. F. B. Normanton for valuable experimental assistance and the Canadian Government for a N.R.C. Scholarship (to R. H. M.). Compound (4) was first prepared by Drs. W. Hussain and D. A. Rankin, whose work we have quoted.

[0/1299 *Received*, 18*th August*, 1980]

---

* In addition to the primary reversible oxidation process, each rhenium(I) complex underwent a secondary *irreversible* one-electron oxidation at potentials *ca.* 0.9 V more positive than their $^1E_{\frac{1}{2}}^{ox}$.

REFERENCES

[1] Part 2, J. Chatt, G. J. Leigh, H. Neukomm, C. J. Pickett, and D. R. Stanley, *J. Chem. Soc., Dalton Trans.*, 1980, 121.

[2] J. Chatt, C. T. Kan, G. J. Leigh, C. J. Pickett, and D. R. Stanley, *J. Chem. Soc., Dalton Trans.*, 1980, 2032.

[3] J. Chatt, J. R. Dilworth, and G. J. Leigh, *J. Chem. Soc., Dalton Trans.*, 1973, 612.

[4] J. Chatt, G. J. Leigh, C. J. Pickett, and D. R. Stanley, *J. Organomet. Chem.*, 1980, **184**, C64—C66.

[5] J. Chatt, J. R. Dilworth, H. P. Gunz, and G. J. Leigh, *J. Organomet. Chem.*, 1974, **64**, 245.

[6] K. P. Darst and C. M. Lukehart, *J. Organomet. Chem.*, 1979, **171**, 65.

[7] D. Sellman and W. Weiss, *Angew. Chem. Internat. Ed. Engl.*, 1977, **16**, 880.

[8] T. Yamabe, K. Hori, T. Minato, and K. Fukui, *Inorg. Chem.*, 1980, **19**, 2154.

[9] C. J. Pickett and D. Pletcher, *J. Chem. Soc., Dalton Trans.*, 1976, 749.