

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

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The systematic syntheses of some new electron-poor $\text{Re}^{\text{I}}(\text{N}_2)$ complexes are described. The oxidation potentials of these complexes vary essentially linearly with $\nu(\text{N}_2)$ whilst only those with $E_{\text{p}}^{\text{ox}} > \text{ca. } +0.8 \text{ V}$ 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, $[\text{ReCl}(\text{CO})_2(\text{N}_2)(\text{PPh}_3)_2]$ reacts with LiMe–H⁺ to give $[\text{ReCl}(\text{C}(\text{OH})\text{Me})(\text{CO})(\text{N}_2)(\text{PPh}_3)_2]$, but with LiPh–H⁺ gives the five-co-ordinate $[\text{ReCl}(\text{CO})_2(\text{PPh}_3)_2]$. 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.

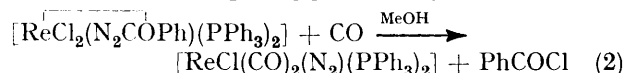
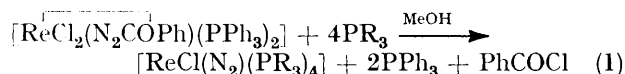
THE factors which determine the activation of N_2 bound to a transition-metal site, M_s , in the complexes $[\text{M}_s(\text{N}_2)]$, where M_s = transition metal + ligands, are of fundamental interest. The particular transition metal, its oxidation state, and the other ligands around the metal will necessarily determine the electronic condition of the co-ordinated N_2 in $[\text{M}_s(\text{N}_2)]$ 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 $[\text{M}_2(\text{L})]$, 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 $>0.00 \text{ V}$ versus the standard hydrogen electrode (s.h.e.) we define as *electron-poor* whilst those which oxidise at potentials $<0.00 \text{ V}$ we define as *electron-rich*. Complexes $[\text{M}_s(\text{L})]$ 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* $\text{Re}^{\text{I}}(\text{N}_2)$ complexes, whose redox potentials lie within a range of *ca.* 1 V, and have surveyed their reactions, under standard conditions, with nucleophilic organolithium reagents.

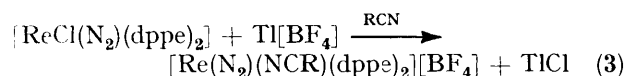
RESULTS AND DISCUSSION

Synthesis of the Complexes.—The reaction of the complex $[\text{ReCl}_2(\text{N}_2\text{COPh})(\text{PPh}_3)_2]$, (A), with tertiary phos-

phines, PR_3 , has been shown to yield a range of dinitrogen complexes of the type *trans*- $[\text{ReCl}(\text{N}_2)(\text{PR}_3)_4]$ according to reaction (1), whilst reaction of (A) with carbon monoxide has been shown to give *trans*- $[\text{ReCl}(\text{CO})_2(\text{N}_2)(\text{PPh}_3)_2]$ according to reaction (2).³ We have



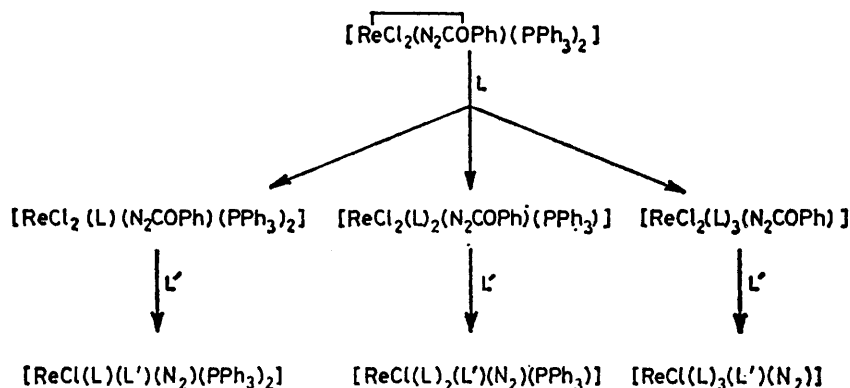
now found that by allowing (A) to react with carbon monoxide or with organophosphites in a two-stage reaction, a further range of $\text{Re}^{\text{I}}(\text{N}_2)$ complexes which are relatively *electron-poor* and which have up to five different ligands surrounding the Re atom can be synthesised according to the Scheme. The initial stage involves the synthesis of new benzyldiazenido-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 $\text{Re}^{\text{I}}(\text{N}_2)$ complexes *via* chloride abstraction from $[\text{ReCl}(\text{N}_2)(\text{dppe})_2]$ [dppe = 1,2-bis(diphenylphosphino)ethane] by $\text{Ti}[\text{BF}_4]$ in the presence of CH_3CN or PhCN, reaction (3).



Oxidation Potentials, Infrared Spectral Data $[\nu(\text{N}_2)]$, and *Electron-poorness.*—Cyclic voltammetry of the rhenium(I) complexes at a Pt electrode in tetrahydrofuran (thf)–0.2 mol dm⁻³ $[\text{NBu}_4][\text{BF}_4]$ 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 $\nu^{\frac{1}{2}}$, $i_{\text{p}}^{\text{red}}/i_{\text{p}}^{\text{ox}}$ is close to unity, and $|E_{\text{p}}^{\text{ox}} - E_{\text{p}}^{\text{red}}|$ is *ca.* 60–80 mV, for each complex. The Table lists the E_{p}^{ox} and $\nu(\text{N}_2)$ data for the complexes investigated.

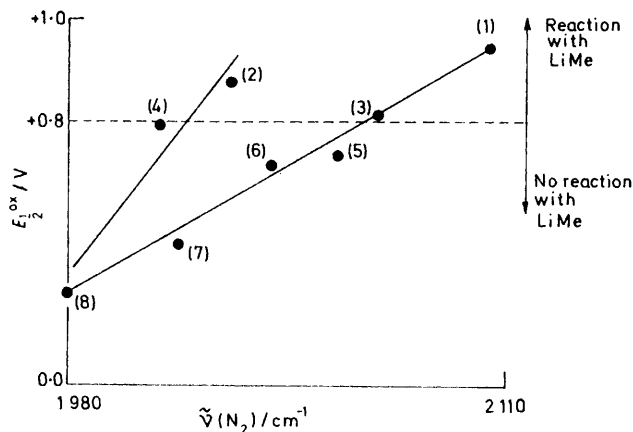
The Figure shows a plot of $\nu(\text{N}_2)$ versus E_{p}^{ox} for the series in which the Cl–Re– N_2 axis is constant and the ligands *cis* to N_2 change, and also for the more limited bis(diphosphine) series in which the ligand *trans* to N_2 is changed. The data for the former series show that

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



SCHEME

$\nu(\text{N}_2)$ responds essentially monotonically to a change in E_1^{ox} and that the slope is *ca.* $150 \text{ cm}^{-1} \text{ V}^{-1}$. Previously we showed¹ that there is a linear correlation between $\nu(\text{N}_2)$ and E_1^{ox} for a range of complexes *trans*-[Mo(N₂)(L)(dppe)₂], except where L = CO, and that $\Delta\nu(\text{N}_2)/\Delta E_1^{\text{ox}}$ was *ca.* $110 \text{ cm}^{-1} \text{ V}^{-1}$. For the isoelectronic rhenium series the slope is somewhat smaller, *ca.* $70 \text{ cm}^{-1} \text{ V}^{-1}$, 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 $\nu(\text{N}_2)$, E_1^{ox} , and reactivity towards LiMe

Nevertheless, a smaller response of $\nu(\text{N}_2)$ for a given change in E_1^{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 $>1.2 \text{ V}$ 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 ΔE_1^{ox} . Similarly, for a given ligand change, Mo will allow more negative charge to drift onto N₂ than will Re, thus $\Delta\nu(\text{N}_2)$ will be greater for the former metal

than for the latter. Both these factors will work to decrease $\Delta\nu_{\text{N}_2}/\Delta E_1^{\text{ox}}$ for Re compared to Mo.

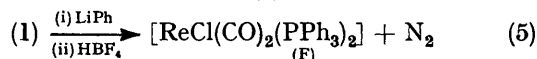
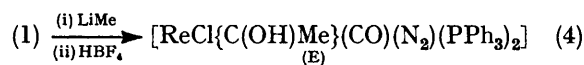
Reactivity of Rhenium(I) Complexes towards Organolithium Reagents.—We have previously shown⁴ that the most

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

Complex ^a	$E_1^{\text{ox}}/\text{V}^b$	$\nu(\text{N}_2)/\text{cm}^{-1}^c$
(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) ₂]	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) ₂]	0.42	2 013
(8) [ReCl(N ₂)(dppe) ₂]	0.28	1 980

^a dppe = Ph₂PCH₂CH₂PPh₂; dmope = (MeO)₃PCH₂CH₂P(OMe)₂. ^b Measured in thf-0.2 mol dm⁻³ [NBu₄][BF₄], scan rate 0.3 V s⁻¹, Pt electrode, concentration of complex *ca.* $5 \times 10^{-3} \text{ mol dm}^{-3}$. E_1^{ox} quoted *versus* the saturated calomel electrode (s.c.e.). Estimated error $\pm 0.02 \text{ V}$. ^c Solution spectra, CH₂Cl₂. Estimated error $\pm 2 \text{ cm}^{-1}$.

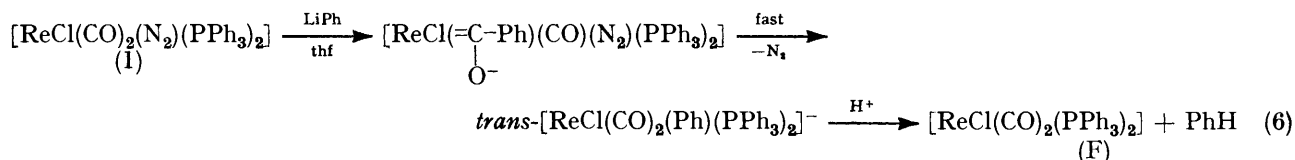
electron-poor of our complexes [ReCl(CO)₂(N₂)(PPh₃)₂], (1), reacts with LiMe-H⁺ according to reaction (4) to give a hydroxycarbene complex, (E), in high yield. We find that (1) also reacts with other LiR species but that the products are sensitive to the nature of R. Thus LiPh-H⁺ gives the five-co-ordinate species, [Re(CO)₂Cl(PPh₃)₂], (F),⁵ and N₂, according to reaction (5). Similarly (1)



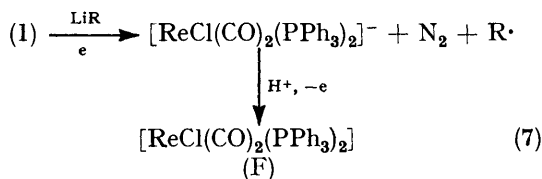
reacts with LiBu^t to give [ReCl(CO)₂(PPh₃)₂], (F), but with LiBu^s a mixture of two products is formed, (F), and the *s*-butylhydroxycarbene analogue of (E); whilst with LiBuⁿ, (1) appears to give essentially only the *n*-butylhydroxycarbene analogue of (E). These results suggest that steric factors may be important in determining the reaction pathway of (1) with LiR. In no case have we observed attack of LiR upon the N₂ ligand.

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

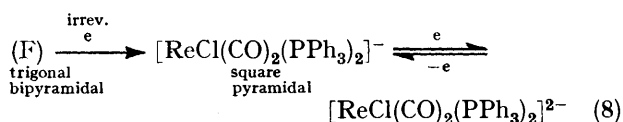
intermediate which shows a single $\nu(\text{CO})$ band at $1\ 870\ \text{cm}^{-1}$ but no band attributable to $\nu(\text{N}_2)$. The product (F) is formed immediately upon quenching this intermediate with HBF_4 as shown by the appearance of new $\nu(\text{CO})$ bands at $1\ 935$ and $1\ 850\ \text{cm}^{-1}$ and the discharge of the band at $1\ 870\ \text{cm}^{-1}$. 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).



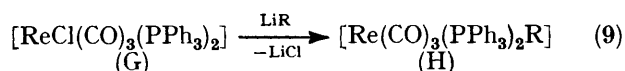
An alternative explanation would be that nucleophilic attack upon the CO is competitive with an electron transfer [reaction (7)].



Certainly, the product (F) undergoes two successive one-electron reductions at quite negative potentials in thf - $0.2\ \text{mol dm}^{-3}$ $[\text{NBu}_4][\text{BF}_4]$ which we interpret according to reaction (8) and the starting material, (1), can be reduced irreversibly at *ca.* $-2.2\ \text{V}$ *versus* a standard calomel electrode (s.c.e.).



We have not distinguished between these two possible reaction pathways although the former appears more feasible from a consideration of the reactivity of $[\text{ReCl}(\text{CO})_3(\text{PPh}_3)_2]$, (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



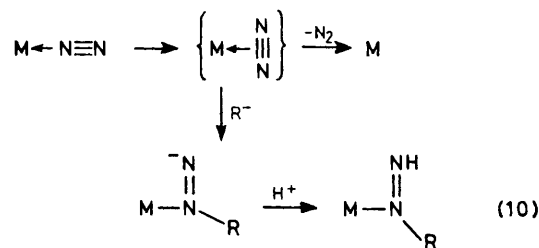
initial attack upon the metal, or upon CO followed by rearrangement and loss of Cl^- [rather than N_2 as in reaction (6)], a parallel with the reaction of (1) with LiR is evident. The complex $[\text{ReCl}(\text{CO})_5]$ which is considerably electron-poorer than any of our complexes⁴ reacts with LiR to give a hydroxycarbene complex⁶ 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*- $[\text{Re}(\text{N}_2)(\text{NCPH})(\text{dppe})_2]^+$, (2), gives a red ether-soluble oil which we have not further characterised, whilst $[\text{ReCl}(\text{CO})(\text{N}_2)\{\text{P}(\text{OMe})_3\}_3]$, (3), appears to be attacked at the CO ligand. From this latter reaction we have obtained an oil which shows $\nu(\text{N}_2)$ at $2\ 000\ \text{cm}^{-1}$; the shift in $\nu(\text{N}_2)$ of around $70\ \text{cm}^{-1}$ 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 $>ca.$ $+0.8\ \text{V}$ *vs.* s.c.e. are reactive under our conditions. The Figure illustrates the apparent dependence of reactivity upon $E_{1/2}^{\text{ox}}$ for the complexes and clearly $\nu(\text{N}_2)$ is not an adequate indicator of potential reactivity for such complexes.

It remains to consider why LiR reagents attack N_2 in $[\text{Mn}(\text{C}_5\text{H}_5)(\text{CO})_2(\text{N}_2)]$ and $[\text{Re}(\text{C}_5\text{H}_5)(\text{CO})_2(\text{N}_2)]$ but not in the rhenium(I) complexes we have described.⁷ In the complex $[\text{Mn}(\text{C}_5\text{H}_5)(\text{CO})_2(\text{N}_2)]$, $\nu(\text{N}_2)$ is some $45\ \text{cm}^{-1}$ 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

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 ¹H and ³¹P 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(N₂)(dppe)₂], [ReCl(CO)₂(N₂)(PPh₃)₂] and [ReCl₂(N₂COPh)(PPh₃)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 cm³) at 20 °C for 1.3 h. Upon addition of methanol (30 cm³) 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. C₄₄H₃₅Cl₂N₂O₂P₂Re 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 cm³, 1.4 mmol) and 'green chelate' (0.50 g, 0.55 mmol) were stirred in benzene (20 cm³) under dinitrogen for 0.25 h at 50 °C, and 0.50 h at reflux. The brown solution was reduced to 2 cm³ at 10⁻² mmHg* and methanol (30 cm³) 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. C₃₁H₃₈Cl₂N₂O₂P₃Re 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 (PPh₃) cm⁻¹. N.m.r.: ¹H [CDCl₃, room temperature (r.t.)] δ 3.59 [d, 9 H, CH₃ *cis* to PPh₃, |J(PH)| 9 Hz], 3.93 [d, 9 H, CH₃ *trans* to PPh₃, |J(PH)| 10 Hz], 7.18–7.93 (m, 2 OH, C₆H₅); ³¹P (CH₂Cl₂, r.t.) 39.13 [dd, 1 P, P_A(OMe)₃ *trans* to P_CPh₃, |J(P_AP_C)| 41.2 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_CPh₃ *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. C₁₆H₃₂Cl₂N₂O₁₀P₃Re requires C, 25.2; H, 4.25; N, 3.65). N.m.r.: ¹H (CDCl₃, r.t.) δ 3.81–3.92 [4 s, 27 H, CH₃, |J(PH)| 27 Hz], 7.2–7.96 (m, 5 H, C₆H₅); ³¹P (CDCl₃, 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(N₂)(dppe)₂] (0.50 g, 0.48 mmol) were heated in benzonitrile (1.0 cm³) and dichloromethane (2.0 cm³) at reflux under dinitrogen for 10 h. The mixture was then cooled to room temperature, filtered, and the filtrate reduced to 1 cm³ 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. C₅₉H₅₃BF₄N₃P₄Re 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 cm³) and methanol (0.075 cm³, 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 cm³). 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. C₁₀H₂₇ClN₂O₁₀P₃Re requires C, 17.5; H, 4.20; N, 4.30%). N.m.r.: ¹H (CDCl₃, r.t.) δ 3.80–3.93 (m, CH₃); ³¹P (CH₂Cl₂, 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. C₅₅H₅₁BF₄N₃P₄Re requires C, 56.9; H, 4.50; N, 3.70%). N.m.r.: ¹H (CDCl₃, r.t.) δ 6.6–7.25 (m, 20 H, C₆H₅), 2.2–2.9 (m, 8 H, PCH₂), 1.70 (s, 3 H, CH₃CN); ³¹P (CH₂Cl₂, 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 cm³) at 20 °C during 2 h. The green-brown solution was purged with dinitrogen, treated with trimethyl phosphite (0.25 cm³, 2.0 mmol) and methanol (12 cm³), and heated under reflux for 1 h. Upon cooling, the complex separated as white crystals (0.10 g). Addition of methanol (20 cm³) 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. C₄₀H₃₉ClN₂O₄P₃Re requires C, 51.9; H, 4.25; N, 3.00%). N.m.r.: ¹H (CDCl₃, r.t.) δ 3.25 [d, 9 H, CH₃, |J(PH)| 10 Hz], 7.42–7.92 (m, 30 H, C₆H₅); ³¹P (CH₂Cl₂, r.t.) 34.22 [t, P(OMe)₃, |J(PP)| 32.5 Hz], 57.89 (d, PPh₃).

Chloro(dinitrogen)tetrakis(trimethyl phosphite)rhenium, (7). To a solution of (C) (0.40 g, 0.52 mmol) and trimethyl phosphite (0.20 cm³, 1.6 mmol) in dry methanol (50 cm³) 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 cm³), and the extract reduced to 5 cm³ 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. C₁₂H₃₆ClN₂O₁₂P₄Re 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 cm³ of a solution in diethyl ether, 0.84 mol dm⁻³, 0.68 mmol) was added to a

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

solution of (2) (0.52, 0.68 mmol) and trimethyl phosphite (0.084 cm³, 0.64 mmol) in dry toluene (30 cm³). The colour changed from orange to deep red and the solution was stirred for 10 min, filtered through Celite, treated with methanol (1 cm³), 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 (C₆D₆, r.t.) δ 3.70 (m, CH₃); ³¹P (CH₂Cl₂, r.t.) 21.44 (s, P).

Carbonylchloro(dinitrogen)[hydroxy(methyl)carbene]bis(triphenylphosphine)rhenium, (E). Methyl-lithium (2 cm³ 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 cm³). The yellow solid rapidly dissolved and the solution acquired an orange-red colour. After 3—4 min stirring at room temperature HBF₄ (0.5 cm³, 40% aqueous) was added whereupon the solution colour changed immediately to orange-brown. This solution was concentrated *in vacuo* to ca. 15 cm³ and methanol (50 cm³) was then added; the product was deposited as bright orange microcrystals after standing this solution overnight at 0 °C under N₂. 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. C₃₉H₃₄ClN₂O₂P₂Re requires C, 55.35; H, 4.00; Cl, 4.20; F, 0.0; N, 3.30%. I.r. (Nujol): ν(N≡N) 2 040s, ν(CO) 1 895s, ν(C—O) 1 280s, cm⁻¹. N.m.r.: ¹H and ³¹P data have been reported previously;⁴ ¹⁵N (thf, r.t., reference CD₃NO₂ upfield negative) -109.3 [d, 1 N, ReNN, |J(¹⁵N¹⁵N)| 4 Hz]. The second nitrogen was not observed. ¹⁵N-labelled (E) was prepared from ¹⁵N-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 benzyldiazenido- or dinitrogen complexes *via* the reaction of P(OPh)₃ with 'green chelate' gave only [ReCl{P(OPh)₃}]₅. Triphenyl phosphite (3.5 cm³, 13 mmol) and 'green chelate' (0.50 g, 0.55 mmol) were heated in benzene (30 cm³) under N₂ under reflux for 0.7 h. The orange solution was reduced to 4 cm³ 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 cm³), 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. C₉₀H₇₅ClO₁₅P₅Re 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. C₆₆H₅₈BF₄N₂P₄Re requires C, 61.2; H, 5.45; N, 2.20%). I.r.: ν(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(N₂)₂(dppe)₂]⁰—[Mo(N₂)₂(dppe)₂]⁺ couple which has E₁^{ox} = -0.16 V versus s.c.e. in thf-0.2 mol dm⁻³ [NBu₄][BF₄].*

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* 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 E₁^{ox}.

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