The Preparation and Properties of Some Diphosphines R₂PCH₂CH₂PR₂ (R = Alkyl or Aryl) and of their Rhenium(ı) Dinitrogen Derivatives†

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The synthesis of a range of diphosphines $R_2PCH_2CH_2PR_2$ from $Cl_2PCH_2CH_2PCl_2$ is described. The properties of a series of complexes $[ReCl(N_2)(R_2PCH_2CH_2PR_2)_2]$ derived from them are discussed. The relationship between the values of $E_{\frac{1}{2}}^{ox}$ and $v(N_2)$ for the complexes suggests that electron-withdrawing substituents on the diphosphine upset the usual balance of σ and π effects in rhenium–dinitrogen bonding.

We have recently described [1,2] the synthesis of the diphosphine $Cl_2PCH_2CH_2PCl_2$ which is the precursor of a range of tetra-alkyl- and tetra-aryl-diphosphines. These diphosphines enabled us to prepare a range of bis(dinitrogen) complexes of molybdenum and tungsten,[3] and we were able to show that $E_{\frac{1}{2}}^{ox}$ for these complexes is affected by phosphine substituents principally inductively, whereas $v(N_2)$ shows the N_2 to be conjugated with the phosphine substituents. We also showed how metal–dinitrogen bond-breaking was facilitated by electron-withdrawing diphosphines. In this paper we describe the extension of this work to rhenium complexes of general formula $[ReCl(N_2)(diphosphine)_2]$, as well as the detailed preparation of the diphosphines themselves.

Results and Discussion

Preparation of the Diphosphines.—We have developed a synthesis of $Cl_2PCH_2CH_2PCl_2$,[1] based on a method originally described in a patent.[4] The variant described here is an improvement on that described [1,2] by us elsewhere.

This route (1) avoids biologically active phosphorus–sulphur

$$PCl_3 + P + C_2H_4 \longrightarrow Cl_2PCH_2CH_2PCl_2 \quad (1)$$
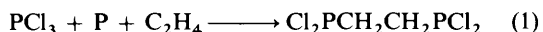
derivatives, but has the drawback that it is apparently iron-catalysed, and does not proceed in a glass-lined autoclave unless considerable areas of metal are exposed to the reaction mixture. The autoclave is then attacked, yielding iron phosphide. The autoclave begins to deteriorate after several runs, showing surface cracks. This requires careful checking to ensure that the autoclave is always able to withstand the reaction pressure (*ca.* 140 atm at maximum). We have not investigated in detail alternative possibilities, such as catalysis by iron powder in a glass-lined autoclave.

The 1,2-bis(dichlorophosphino)ethane was treated with a variety of alkyl-lithium and Grignard reagents to yield the following diphosphines, as detailed in the Experimental section: $R_2PCH_2CH_2PR_2$ (R = Me, Et, cyclo-C_6H_{11}, C_6H_4OMe-*p*, C_6H_4Me-*p*, C_6H_4Me-*o*, $C_6H_2Me_3$-2,4,6, $C_6H_4NMe_2$-*p*, C_6H_4Cl-*p*, $C_6H_4CF_3$-*p*, C_6F_5 or Ph); in addition, reaction with the appropriate hydroxy compound yielded $(RO)_2PCH_2CH_2$-$P(OR)_2$ (R = Me or Ph). The properties of the diphosphines are summarised in Table 1.

The data are unexceptional. Note that there is no simple correlation between ^{31}P-$\{^1H\}$ n.m.r. chemical shifts and any Hammett substituent constants.

Dinitrogen Complexes of Rhenium.—These complexes were generally prepared by the reaction of [*N*-benzoylhydrazido-(3 −)-*N′*,*O*]dichlorobis(triphenylphosphine)rhenium(v)(1)(the 'green chelate')[5] with the diphosphine. The compounds of the type $[ReCl(N_2)(R_2PCH_2CH_2PR_2)_2]$ are all air-stable, pale yellow compounds with a strong band assignable to $v(N_2)$ in their i.r. spectra (Table 2). The materials have the same structure as do all the compounds of this type so far prepared (Cl *trans* to N_2) since the ^{31}P-$\{^1H\}$ n.m.r. spectra all consist of a simple singlet resonance.

Particular problems were experienced in preparing derivatives of $R_2PCH_2CH_2PR_2$ where R = Me, Et, or $C_6H_4CF_3$-*p*. The product from the reaction of the green chelate (1) and $Me_2PCH_2CH_2PMe_2$ is green, air-sensitive crystals. It has an i.r. band assignable to $v(N_2)$ at 1 935vs br, cm⁻¹ but we were unable to rationalise its analytical data (Found: C, 37.9; H, 7.25; N, 2.00%).

Reaction of the green chelate (1) with $Et_2PCH_2CH_2PEt_2$ invariably gave a product which analysed for $[ReCl(N_2)$-$(Et_2PCH_2CH_2PEt_2)_2]\cdot2PPh_3$. The ^{31}P n.m.r. spectrum suggests that the PPh_3, at least in solution, is not co-ordinated. The desired material free of PPh_3 was finally obtained by a modified work-up (see Experimental section).

Reaction of the green chelate (1) with $(p\text{-}CF_3C_6H_4)_2$-$PCH_2CH_2P(C_6H_4CF_3$-*p*$)_2$ always gave a product with a nitrogen content lower than that required by the expected dinitrogen complex. The same was true of the product obtained by reaction of the diphosphine with $[ReCl(N_2)(PMe_2Ph)_4]$. Assuming that the product is a mixture of the required dinitrogen complex with some other species, $[ReCl(N_2)\{(p\text{-}CF_3C_6H_4)_2PCH_2CH_2P(C_6H_4CF_3$-*p*$)_2\}_2]$ could not be obtained with a purity greater than *ca.* 60%. An alternative explanation is that the product contains a single N_2 bridging two rheniums, but we think this unlikely on the following grounds. The i.r. spectrum has a strong band assignable to $v(N_2)$ and uncharacteristic of a bridging species. The ^{31}P-$\{^1H\}$ n.m.r. spectrum suggests the presence of at least two species, one giving rise to a singlet and the other a typical AB pattern. Finally, there are two electroactive species present, both of which undergo reversible oxidation. We conclude that the product is a mixture of the desired dinitrogen complex together with a decomposition product.

The lability of N_2 in a complex with electron-withdrawing phosphines is to be expected on the grounds of reduced back-bonding into the dinitrogen antibonding orbitals, and has been demonstrated in molybdenum and tungsten chemistry. That being so, the second species in the mixture should be $[ReCl\{p\text{-}CF_3C_6H_4)_2PCH_2CH_2P(C_6H_4CF_3$-*p*$)_2\}_2]$.

An analogue, $[ReCl(Ph_2PCH_2CH_2PPh_2)_2]$, has been char-

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† *Non-S.I. units employed:* atm = 101 325 Pa, mmHg = 133 Pa.

Table 1. Physical data for diphosphines $R_2PCH_2CH_2PR_2$

| Diphosphine R | Yield (%) | M.p. (°C) | Analysis^a (%) | | ^{31}P N.m.r.^{b} (δ/p.p.m.) | ^1H N.m.r.^{c} (δ/p.p.m.) |
			C	H		
C_6H_4OMe-p	70	98	69.2 (69.5)	6.35 (6.30)	−157.2 (s) [C_6H_6]	1.93 (t, 1, CH_2, J_{HH} = 4.0), 3.76 (s, 3, OCH_3); 6.68 (s), 6.84 (s), 7.18 (m) (total 4, C_6H_4) [$CDCl_3$]
C_6H_4Me-p	38	144	79.3 (79.1)	7.10 (7.05)	−155.5 (s) [C_6H_6]	2.00 (s, 3, CH_3), 3.28 (t, 1, CH_2); 6.78 (s), 6.86 (s), 7.26 (m) (total 4, C_6H_4) [C_6D_6]
C_6H_4Me-o	8	—	78.0 (79.1)	7.35 (7.05)	−174.7 (s) [thf]	2.05 (t, 1, CH_2, J_{HH} = 4.5), 2.84 (s, 3, CH_3), 6.93—7.30 (m, br, C_6H_4) [$CDCl_3$]
$C_6H_2Me_3$-2,4,6	19	313	78.4 (80.5)	8.70 (8.55)	−159.0 (s) [C_6H_6]	2.09 (s, 6, o-CH_3), 2.19 (s, 3, p-CH_3), 2.1—2.3 (m, CH_2), 6.69 (s, br, 2, C_6H_2) [CD_2Cl_2]
$C_6H_4NMe_2$-p^d	27	—	72.2 (72.6)	8.10 (7.75)	−157.8 (s) [thf]	1.99 (t, 1, CH_2, J_{HH} = 3.0), 2.89 (s, 6, CH_3); 6.61 (s), 6.71 (s), 7.27 (s) (total 4, C_6H_4) [$CDCl_3$]
C_6H_4Cl-p	34	155	58.0 (58.2)	3.85 (3.75)	−155.1 (s) [thf]	1.98 (t, 1, CH_2, J_{HH} = 4.0), 7.25 (m, 4, C_6H_4) [$CDCl_3$]
$C_6H_4CF_3$-p	46	198	53.4 (53.8)	3.40 (3.00)	−152.9 (s) [thf]	2.12 (t, 1, CH_2, J_{HH} = 4.5), 7.29—7.88 (m, br, 4, C_6H_4) [$CDCl_3$]
C_6F_5	21	289	41.5 (41.2)	1.10 (0.55)	−184.3 (s) [thf]	2.56 (t, CH_2, J_{HH} = 7.1) [$CDCl_3$]^e
OPh	72	85	67.7 (67.5)	5.55 (5.25)	−138.2 (s) [C_6H_6]	2.24 (t, 1, CH_2, J_{HH} = 8.0), 6.70—7.43 (m, br, 5, C_6H_5) [C_6D_6]

^{a} Required values in parentheses. ^{b} Data in parentheses indicate singlets, solvent in square brackets. ^{c} Data in parentheses indicate multiplicity, **relative intensity**, assignment, and coupling constant (Hz); m = multiplet, br = broad, s = singlet, t = triplet; solvent in square brackets. ^{d} N, 9.70 (9.80%). ^{e} ^{19}F N.m.r. spectrum in $CDCl_3$ shows multiplets at *ca.* −130.5, −149, and −159 p.p.m. (ref. $CFCl_3$) arising from C_6F_5.
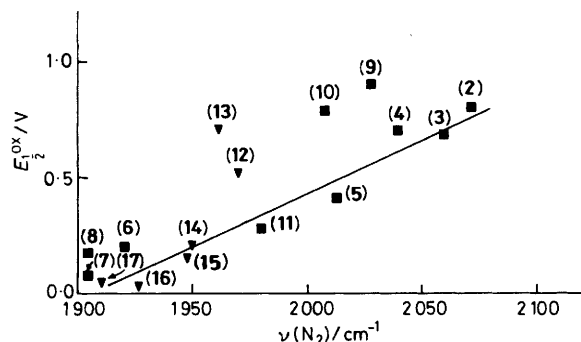
Figure. Plot of $v(N_2)$ *versus* $E_{\frac{1}{2}}^{ox}$ for a range of rhenium complexes [(▼) new complexes, (■) from previous work] having N_2 *trans* to Cl: [$ReCl(N_2)(CO)\{P(OMe_3)\}_3$] (2),^{9} [$ReCl(N_2)(PPh_3)_2\{P(OMe)_3\}_2$] (3),^{9} [$ReCl(N_2)\{(MeO)_2PCH_2CH_2P(OMe)_2\}_2$] (4),^{9} [$ReCl(N_2)\{P-(OMe)_3\}_4$](5),^{9}[$ReCl(N_2)(PMe_2Ph)_4$](6),^{5}[$ReCl(N_2)(py)(PMe_2Ph)_3$] (7) (py = pyridine), [$ReCl(N_2)(py)(PMePh_2)_3$] (8) [both (7) and (8), J. Chatt, C. M. Elson, N. E. Hooper, and G. J. Leigh, *J. Chem. Soc., Dalton Trans.*, 1975, 2392], [$Re(N_2)(PhCN)(Ph_2PCH_2CH_2PPh_2)_2$]$^+$ (9),^{9} [$Re(N_2)(MeCN)(Ph_2PCH_2CH_2PPh_2)_2$]$^+$ (10),^{9}[$ReCl(N_2)(Ph_2PCH_2-CH_2PPh_2)_2$] (11),^{5} [$ReCl(N_2)\{(p$-$ClC_6H_4)_2PCH_2CH_2P(C_6H_4Cl$-$p)_2-\}_2$] (12), [$ReCl(N_2)\{(p$-$CF_3C_6H_4)_2PCH_2CH_2P(C_6H_4CF_3$-$p)_2\}_2$] (13), [$ReCl(N_2)\{(p$-$MeC_6H_4)_2PCH_2CH_2P(C_6H_4Me$-$p)_2\}_2$] (14), [$ReCl-(N_2)\{(p$-$MeOC_6H_4)_2PCH_2CH_2P(C_6H_4OMe$-$p)_2\}_2$] (15), [$ReCl(N_2)-(Et_2PCH_2CH_2PEt_2)_2$] (16), [$ReCl(N_2)\{(C_6H_{11})_2PCH_2CH_2P(C_6-H_{11})_2\}_2$] (17)

acterised by *X*-ray crystallography, and has been shown not to react with N_2, though it does react with CO and MeNC. It has a five-co-ordinate trigonal-bipyramidal structure.^{6} We have isolated [$ReCl\{(p$-$CF_3C_6H_4)_2PCH_2CH_2P(C_6H_4CF_3$-$p)_2\}_2$] from the reaction of the diphosphine with [$ReCl(N_2)(PMe_2Ph)_4$], characterised it by analysis and by i.r. and n.m.r. spectroscopy, and shown that it is indeed responsible for the AB pattern of phosphorus resonances and that it is one of the electroactive species produced upon attempted preparation of the dinitrogen complex. Hence, it must also have a five-co-ordinate trigonal-bipyramidal structure. It does not react with N_2, but does react with CO and MeNC (see below).

The Figure shows a plot of $E_{\frac{1}{2}}^{ox}$ for all the rhenium(I) dinitrogen complexes with dinitrogen *trans* to chlorine which we have reported, including those described here, against $v(N_2)$. The new compounds with the modified diphosphines are (12)—(17); compounds described elsewhere are (2)—(11). We have omitted [$ReCl(N_2)(CO)_2(PPh_3)_2$] which apparently oxidises irreversibly and for which no clear assignment to $v(N_2)$ can be made.^{7} For the majority of compounds there is a reasonably linear relationship between $E_{\frac{1}{2}}^{ox}$ and $v(N_2)$. This is to be expected if the energy of the highest occupied molecular orbital (h.o.m.o.) rises or falls as the amount of charge passed onto the dinitrogen, principally *via* the p_π-d_π system, decreases or increases.^{3} The interaction of the substituents with the dinitrogen is probably inductive (see below). There are four compounds which appear to be anomalous: (9) and (10), (12) and (13).

Compounds (9) and (10) are charged species, and consequently might not be expected to conform to the pattern exhibited by closed-shell neutral species. Compounds (12) and (13), with electron-withdrawing substituents in the phosphine aryl ring, exhibit an anomalous behaviour which parallels that of their molybdenum and tungsten analogues^3 but is even more extreme. For molybdenum and tungsten, we attributed this to the change in the relative importance of phosphine σ-donation and π-acceptance, which seems to be invariant with all the other complexes. Presumably the anomaly arises in the same way here, with the π-acceptance of the phosphine being predominant and the σ-donation relatively weaker. Omitting the four anomalous compounds, we obtained the least-squares best fit straight line shown in the Figure, correlation coefficient 0.985, with equation $v(N_2)$ = 1 908 + 212$E_{\frac{1}{2}}^{ox}$.

We also investigated the correlations of $E_{\frac{1}{2}}^{ox}$ and $v(N_2)$ individually with each of the Hammett functions σ and σ$^+$ for the various tetra-aryldiphosphines. The best linear correlation has a correlation coefficient of 0.994 for $E_{\frac{1}{2}}^{ox}$ and σ. The correlations of $v(N_2)$ were exceedingly poor. This suggests that the metal-based h.o.m.o. is affected inductively by the phosphine substituents, as was found for molybdenum and tungsten compounds, but that through conjugation from P to N_2 may not be significant.

In the past, $v(N_2)$ has been taken to be a measure of d_π-p_π

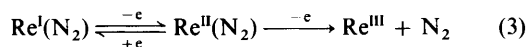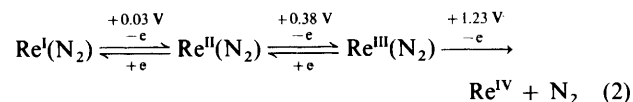**Table 2.** Physical data for new rhenium diphosphine complexes

Compound	Form	M.p.ᵃ (°C)	v(N₂)ᵇ/cm⁻¹ I.r.	v(N₂)ᵇ/cm⁻¹ Raman	Analysisᶜ (%) C	H	N	$E_{\frac{1}{2}}^{ox\,d}$	³¹P N.m.r.ᵉ (δ/p.p.m.)	¹H N.m.r.ᶠ (δ/p.p.m.)
$[ReCl(N_2)\{(C_6H_{11})_2PCH_2CH_2P(C_6H_{11})_2\}_2]$	White crystals	240	1911	1912	57.1 (57.0)	8.85 (8.60)	2.55 (2.50)	0.04	−95.3	2.0—2.8 (s, br, **8**, PCH₂), 0.8—2.0 (m, br, **88**, CH₂ + CH) [C₆D₆]
$[ReCl(N_2)\{Et_2PCH_2CH_2PEt_2\}_2]\cdot 2PPh_3$	Pale yellow prisms	210	1927	1927	56.7 (56.2)	6.65 (6.80)	2.40 (2.30)	0.03	−113.3, −145.9	1.13, 1.62, 2.08 (m, br, **24**, CH₃ + CH₂); 7.28, 7.32 (m, **15**, C₆H₅) [CD₂Cl₂]
$[ReCl(N_2)\{Et_2PCH_2CH_2PEt_2\}_2]$	Pale yellow crystals	—	1925	—	36.2 (36.3)	7.30 (7.35)	3.95 (4.25)	0.03	−113.5	1.28—1.34 (m, **24**, CH₃), 1.80—1.98 (m, br, **8**, PCH₂CH₂), 2.09—2.56 (m, **16**, CH₂) [C₆D₆]
$[ReCl(N_2)\{(p\text{-}MeOC_6H_4)_2PCH_2CH_2P(C_6H_4OMe\text{-}p)\}_2]$	Light yellow crystals	287	1948	1948	56.0 (55.8)	5.00 (5.25)	2.15 (1.90)	0.15	−116.4	1.36 (s, br, **8**, CH₂), 3.75 (s, **12**, CH₃); 6.50 (s), 6.58 (s), 6.74 (s), 6.82 (m), 7.30 (m) (total **32**, C₆H₄) [CDCl₃]
$[ReCl(N_2)\{(p\text{-}MeC_6H_4)_2PCH_2CH_2P(C_6H_4Me\text{-}p)\}_2]$	Light yellow crystals	292 (d)	1950	—	59.4 (62.1)	5.60 (5.55)	2.25 (2.40)	0.21	−115.5	1.28 (s, br, **8**, CH₂), 2.26 (s, br, **12**, CH₃); 6.86 (m), 6.35 (m) (total **32**, C₆H₄) [CDCl₃]
$[ReCl(N_2)\{Ph_2PCH_2CH_2PPh_2\}_2]$	Light yellow plates	281ᵍ, 300	1980	—	59.7 (59.7)	4.70 (4.60)	2.70 (2.70)	0.29	−112.8	2.2—3.4 (m, br, **8**, CH₂), 6.6—7.9 (m, br, **40**, C₆H₅) [CDCl₃]
$[ReCl(N_2)\{(p\text{-}ClC_6H_4)_2PCH_2CH_2P(C_6H_4Cl\text{-}p)\}_2]$	Light yellow crystals	285 (d)	1970	—	47.2 (48.1)	3.05 (3.75)	2.10 (1.90)	0.52	−114.7	2.0—2.8 (s, br, **8**, CH₂), 6.6—7.8 (m, br, **32**, C₆H₄) [CDCl₃]
$[ReCl(N_2)\{(p\text{-}CF_3C_6H_4)_2PCH_2CH_2P(C_6H_4CF_3\text{-}p)\}_2]$	Light yellow crystals	195 (d)	1962	—	45.4 (45.3)	2.75 (2.55)	1.75 (1.75)	0.71	−115.2ʰ	1.6—2.5 (d, br, **8**, CH₂), 6.9—8.1 (m, br, **32**, C₆H₄) [CD₂Cl₂]
$[ReCl\{(p\text{-}CF_3C_6H_4)_2PCH_2CH_2P(C_6H_4CF_3\text{-}p)\}_2]$	Orange crystals	185	—	—	46.1 (46.2)	2.70 (2.60)	0.0 (0.0)	0.24	−112.68ⁱ, −114.01, −152.32, −153.65	1.5—2.4 (m, br, **8**, CH₂), 6.4—8.4 (m, br, **32**, C₆H₄) [C₆D₆]
$cis\text{-}[ReCl(CNMe)\{(p\text{-}CF_3C_6H_4)_2PCH_2CH_2P(C_6H_4CF_3\text{-}p)\}_2]$	Yellow-orange crystals	249ᵍ	2 080ʲ	—	47.7 (46.4)	3.25 (3.70)	0.85 (0.85)	0.34	−115.2	0.5—1.0 (s, **3**, CH₃), 1.5—2.8 (m, br, **8**, CH₂), 5.8—8.0 (m, br, **32**, C₆H₄) [CDCl₃]
$[ReCl(CO)\{(p\text{-}CF_3C_6H_4)_2PCH_2CH_2P(C_6H_4CF_3\text{-}p)\}_2]$	Orange crystals	262	1 820ʲ	—	48.0 (48.0)	3.00 (3.25)	0.0 (0.0)	0.35	−110.2	1.1—1.6 (m, br, **8**, CH₂), 6.5—7.2 (m, br, **32**, C₆H₄) [C₆D₆]
$trans\text{-}[ReCl(CNMe)\{(p\text{-}CF_3C_6H_4)_2PCH_2CH_2P(C_6H_4CF_3\text{-}p)\}_2]$	Yellow crystals	—	1 830ʲ	—	47.9 (46.4)	3.35 (2.70)	0.90 (0.85)	0.19	−153.6	2.17 (s, **3**, CH₃), 2.2—2.5 (m, br, **8**, CH₂), 7.3—7.9 (m, br, **32**, C₆H₄) [CDCl₃]

ᵃ (d) = With decomposition. ᵇ KBr discs. ᶜ Calculated values in parentheses. ᵈ Volts versus a saturated calomel electrode. ᵉ In benzene, with trimethyl phosphite as external standard. ᶠ Data in parentheses indicate multiplicity, relative intensity, assignment, coupling constant (Hz), solvent in square brackets. ᵍ Changes before melting. ʰ −111.4 p.p.m. in CH₂Cl₂. ⁱ $J_{PP} = 48.3$ Hz. ʲ v(NC) or v(CO).

bonding and hence of metal–dinitrogen bond strength.[8] In the rhenium series, there is no smooth curve for $E_{\frac{1}{2}}^{ox}$ against $v(N_2)$ such as was observed[3] in molybdenum and tungsten. The values of $v(N_2)$ in the CF_3 and Cl cases would, on the basis of the observed values of $E_{\frac{1}{2}}^{ox}$, be expected to be ca. 2 050 and 2 020 cm^{-1}, respectively, instead of ca. 1 965 cm^{-1} as actually observed. The range of $v(N_2)$ is very narrow, and the compound with R = $C_6H_4CF_3$-p loses N_2 much more easily than e.g. the complex with R = Ph. Clearly $v(N_2)$ is not a measure of metal–dinitrogen bond strength interaction in these complexes, and $v(N_2)$ is probably not determined primarily by back-bonding from the metal into the dinitrogen. The strong π-acceptor ability of the diphosphines should decrease the significance of π-bonding involving N_2 and increase the relative significance of the metal–dinitrogen σ bond. Since the lone-pair electrons of N_2 are in an orbital which is weakly N–N bonding in the free molecule, the use of these electrons in metal–dinitrogen bonding should also lead to some N–N bond weakening.

A plot of $E_{\frac{1}{2}}^{ox}$ for the new rhenium compounds against $E_{\frac{1}{2}}^{ox}$ for the tungsten compounds[3] discussed earlier is linear, with a coefficient of correlation of 0.99. Evidently the factors which affect $E_{\frac{1}{2}}^{ox}$ are the same in both series, and since the slope is unity, the parallel is complete, with effects of the same kind and magnitude. The correlation for $v(N_2)$ is much less good (correlation coefficient 0.92) and is certainly less significant than the $E_{\frac{1}{2}}^{ox}$ correlation. The range of $v(N_2)$ is marginally greater for tungsten than for rhenium.

All the complexes undergo one-electron reversible oxidations, but subsequent oxidations are also observable. It was shown a considerable time ago that $[ReCl(N_2)(Ph_2PCH_2-CH_2PPh_2)_2]$ can be oxidised to give reasonably stable monocationic salts containing Re^{II}.[9] No dinitrogen complexes of rhenium in a higher oxidation state were observed. Nevertheless, the oxidation of the dinitrogen complex with the most basic diphosphine, $(C_6H_{11})_2PCH_2CH_2P(C_6H_{11})_2$, shows a Re^{III} dinitrogen complex stable on the cyclic voltammetry time-scale. The relative oxidation patterns are shown in reaction sequences (2) (R = $cyclo$-C_6H_{11}) and (3) (all others). We have yet to obtain the Re^{III} dinitrogen complex in a pure state.

$$Re^I(N_2) \underset{+e}{\overset{-e}{\rightleftharpoons}} Re^{II}(N_2) \underset{+e}{\overset{-e}{\rightleftharpoons}} Re^{III}(N_2) \xrightarrow{-e}$$

$$\overset{+0.03\ V}{} \qquad \overset{+0.38\ V}{} \qquad \overset{+1.23\ V}{}$$

$$Re^{IV} + N_2 \quad (2)$$

$$Re^I(N_2) \underset{+e}{\overset{-e}{\rightleftharpoons}} Re^{II}(N_2) \xrightarrow{-e} Re^{III} + N_2 \quad (3)$$

The reaction of $[ReCl\{(p$-$CF_3C_6H_4)_2PCH_2CH_2P(C_6H_4CF_3$-$p)_2\}_2]$ with MeNC occurs in two stages. An immediate reaction yields what is apparently cis-$[ReCl(CNMe)\{(p$-$CF_3C_6H_4)_2$-$PCH_2CH_2P(C_6H_4CF_3$-$p)_2\}_2]$. After heating in tetrahydrofuran (thf) under reflux for 50 h, this is completely isomerised to the $trans$ isomer. Both isomers have been adequately characterised. In contrast, the reaction with CO is relatively slow, and we have isolated a single product, $trans$-$[ReCl(CO)\{(p$-$CF_3C_6H_4)_2$-$PCH_2CH_2P(C_6H_4CF_3$-$p)_2\}_2]$. The comparable i.r. and redox data of the derivatives of $(p$-$CF_3C_6H_4)_2PCH_2CH_2P(C_6H_4CF_3$-$p)_2$ and of $Ph_2PCH_2CH_2PPh_2$ are collected in Table 3.

From Table 3, it appears that the values of $v(XY)$ for all trifluoromethyl-substituted diphosphine derivatives are anomalously low. Simple arguments about inductive effects would lead to the expectation of considerably higher values of $v(XY)$. Whatever the reason, the effect appears real. Concerning the electrochemical data, a priori it might be expected that the stronger donating diphosphine would give more easily oxidisable products, and CO (being more electron-withdrawing than N_2), to produce carbonyls less easily oxidised than the corresponding dinitrogen complex. This pattern seems to be

Table 3. I.r. and redox data for some complexes $[ReCl(L)-(R_2PCH_2CH_2PR_2)_2]$ (R = Ph or $C_6H_4CF_3$-p; L = CO, N_2, or MeNC)

	R = Ph		R = $C_6H_4CF_3$-p	
	$E_{\frac{1}{2}}^{ox}$/V	$v(XY)^*$/cm^{-1}	$E_{\frac{1}{2}}^{ox}$/V	$v(XY)^*$/cm^{-1}
N_2	+0.29	1 980	+0.71	1 962
MeNC	+0.08	1 810	+0.18	1 830
CO	+0.68	1 815	+0.35	1 820

* $v(N_2)$, $v(CN)$, or $v(CO)$.

fulfilled, with the exception of $[ReCl(CO)\{(p$-$CF_3C_6H_4)_2$-$PCH_2CH_2P(C_6H_4CF_3$-$p)_2\}_2]$. If the $E_{\frac{1}{2}}^{ox}$ value can be confirmed, then there is no obvious explanation.

The data show that the generalisations we made earlier[3] on the basis of molybdenum and tungsten chemistry also hold true broadly for rhenium. However, detailed extrapolation of those findings to rhenium is clearly not always possible.

Experimental

All reactions and compound manipulations were carried out in Schlenk apparatus under nitrogen or argon, as appropriate. All solvents were dried and distilled under dinitrogen before use. I.r. spectra were recorded in KBr discs (unless otherwise stated) on a Perkin-Elmer 527 spectrometer. Calibration with respect to indene for the N_2 stretching region is consistent with an accuracy of ± 2 cm^{-1}. Raman spectra were obtained in sealed glass ampoules using a krypton laser (red line at 647.1 nm, power 25—85 mW) on a modified Cary 82 spectrometer, by courtesy of Professor I. R. Beattie and Dr. S. J. Ogden, University of Southampton; the data are accurate to ± 1 cm^{-1}.

Hydrogen-1 n.m.r. data were obtained in deuteriated solvents with tetramethylsilane as internal standard using Varian EM-360 and JEOL PTF100 spectrometers; ^{31}P n.m.r. spectra were obtained using a JEOL-FX90Q spectrometer with trimethyl phosphite as external standard. Melting points were obtained under dinitrogen using an Electrothermal melting point apparatus, and are uncorrected. Oxidation potentials are quoted versus the standard calomel electrode and were obtained in a two-compartment three-electrode cell with platinum electrodes and a silver wire pseudo-reference electrode. The electrolyte was 0.2 mol dm^{-3} $[NBu^n_4][BF_4]$ in thf. Analyses were by Mr. A. G. Olney, University of Sussex.

1,2-*Bis(dichlorophosphino)ethane*.—This was prepared by a modification of our published route.[1] Phosphorus trichloride (380 cm^3, 4.3 mol) and yellow phosphorus (33.6 g, 1.08 mol) in small pieces (ca. 1 cm^3) were placed in a lined stainless steel rocking autoclave, capacity 1 litre, and the assembly flushed with dinitrogen twice and then with ethylene. It was then charged with ethylene to a pressure of 50 atm, and heated at 200 °C for 19 h, with oscillations at ca. 20 per min. The autoclave was then cooled to 20 °C, vented, flushed with dinitrogen, opened, and the liquid poured into a Schlenk flask (volume 500 cm^3) under dinitrogen, most of the yellow solid residue being retained in the autoclave (CAUTION: the residue is spontaneously inflammable if allowed to become dry). The residue was cautiously quenched with ice-water, which produced copious fumes and some flames (CAUTION: this residue is very pyrophoric, and a very efficient fume-cupboard should be used for its disposal). The liquid was distilled at atmospheric pressure to remove any excess of PCl_3 and other volatiles, and the product distilled at 66 °C (0.5 mmHg). Yield ca. 140 g, 40% based on phosphorus. This procedure gives about

twice the yield of our earlier published route.[1] A comparable yield cannot be achieved by the older method, even with doubled quantities.

The diphosphines $R_2PCH_2CH_2PR_2$ with R = Me, Et, and cyclo-C_6H_{11} were prepared as described earlier.[1] Those having R = C_6H_4OMe-p, C_6H_4Me-p, and $C_6H_2Me_3-2,4,6$ were prepared by the method of Burt et al.,[1] by the reaction of an excess of the Grignard reagents p-$MeOC_6H_4MgBr$, p-MeC_6H_4MgBr, or $2,4,6$-$Me_3C_6H_2MgBr$, respectively, with $Cl_2PCH_2CH_2PCl_2$ in diethyl ether. The products were isolated by quenching the reaction mixtures with saturated aqueous ammonium chloride solution, separating the ethereal layer, and drying it with anhydrous sodium sulphate. This solution was then reduced in volume to ca. 50 cm^3, the compounds precipitated with methanol, and then finally recrystallised by dissolving in thf and adding methanol (see Table 1 for details).

All the diphosphines described here are white solids, except $(MeO)_2PCH_2CH_2P(OMe)_2$,[11] which is a colourless liquid.

1,2-Bis[bis(p-chlorophenyl)phosphino]ethane.—Diethyl ether (570 cm^3) and p-ClC_6H_4Br (59.5 g, 0.31 mmol) were added to a 2-l three-necked flask fitted with a mechanical stirrer, pressure-equalised dropping funnel, and reflux condenser. A solution of n-butyl-lithium (190 cm^3, 1.64 mol dm^{-3}, 0.311 mol) in hexane was added dropwise over 2 h with vigorous stirring at room temperature. The yellow solution was then cooled to -40 °C, and a solution of $Cl_2PCH_2CH_2PCl_2$ (10.5 cm^3, 0.065 mol) in diethyl ether (100 cm^3) added dropwise with vigorous stirring during 20 min. The contents of the flask were allowed to warm to 20 °C, and stirred at 20 °C for 1 h. During this time a white precipitate formed. The reaction mixture was quenched with water (400 cm^3) and the ethereal layer dried with anhydrous sodium sulphate. The ether was removed at 10^{-3} mmHg, thf (40 cm^3) was added to dissolve the oily residue, and then methanol (80 cm^3) was added. The solution was reduced at 10^{-3} mmHg until a white solid appeared. The solution was then cooled at 0 °C for 2 h, filtered, the precipitate washed with methanol (3 × 20 cm^3) and dried at 10^{-3} mmHg.

A similar method was used for the diphosphines below.

1,2-Bis[bis(pentafluorophenyl)phosphino]ethane.—A solution of n-butyl-lithium (73.8 cm^3, 1.5 mol dm^{-3}, 0.111 mol) in hexane was added dropwise over 20 min to a stirred solution of C_6F_5Br (27.4 g, 0.111 mol) in diethyl ether (150 cm^3) at -30 °C. The dark brown solution was stirred for 10 min, and cooled to -75 °C and then $Cl_2PCH_2CH_2PCl_2$ (4.0 cm^3, 0.025 mol) in diethyl ether was added dropwise to the solution. Once addition was complete, the mixture was allowed to warm to 20 °C, the pink-brown precipitate changing to white. After stirring for 2 h, the mixture was quenched with hydrochloric acid (2 mol dm^{-3}, 200 cm^3). The crude white solid was filtered off and recrystallised from methanol-thf.

1,2-Bis[bis(p-dimethylaminophenyl)phosphino]ethane.—A solution of n-butyl-lithium (115 cm^3, 1.18 mol dm^{-3}, 0.136 mol) in hexane was added dropwise over 90 min to a stirred solution of p-$Me_2NC_6H_4Br$ (27.1 g, 0.136 mol) in diethyl ether (400 cm^3) at room temperature. The mixture was stirred for a further 15 min and cooled to -70 °C, and then $Cl_2PCH_2CH_2PCl_2$ (5.0 cm^3, 0.031 mol) in diethyl ether (200 cm^3) added dropwise over 90 min, during which time the mixture was always cooler than -30 °C. The mixture was allowed to warm to room temperature, and stored for 12 h. The reaction mixture, containing a white precipitate, was quenched with water (40 cm^3) and a yellow solid filtered off from both liquid phases. This was dissolved in thf (400 cm^3) and combined with a solution obtained by dissolving the remaining solid in the reaction vessel with thf. The combined thf solutions were dried over anhydrous

sodium sulphate, reduced to 50 cm^3 at 10^{-3} mmHg and the crude product precipitated with methanol (80 cm^3). Additional product was obtained by reducing the diethyl ether phase obtained earlier to 20 cm^3 at 10^{-3} mmHg, and adding methanol. The combined products were washed with methanol (3 × 45 cm^3), dried, and recrystallised from methanol-thf.

1,2-Bis[bis(p-trifluoromethylphenyl)phosphino]ethane.—A solution of n-butyl-lithium (92 cm^3, 1.18 mol dm^{-3}, 0.109 mol) in hexane was added dropwise over 60 min to a stirred solution of p-$CF_3C_6H_4Br$ (24.7 g, 0.109 mol) in diethyl ether (400 cm^3) at 20 °C, producing a red colour. The mixture was cooled to -70 °C, stirred, and a solution of $Cl_2PCH_2CH_2PCl_2$ (4.0 cm^3, 0.025 mol) in diethyl ether (120 cm^3) added dropwise during 1 h. The reactants were allowed to warm to 20 °C, and stored for 12 h. A white precipitate formed. The reaction mixture was quenched with water (400 cm^3), and the ethereal layer was separated and dried over anhydrous sodium sulphate. The volume was reduced to ca. 40 cm^3 at 10^{-3} mmHg, and methanol (80 cm^3) added. The white precipitate was filtered off, washed with methanol (2 × 40 cm^3), and dried.

1,2-Bis(di-o-tolylphosphino)ethane.—A solution of n-butyl-lithium (71.3 cm^3, 1.64 mol dm^{-3}, 0.117 mol) in hexane was added dropwise during 30 min at 20 °C to a stirred solution of o-MeC_6H_4Br (20.0 g, 0.117 mol) in diethyl ether (100 cm^3). The reactants were stirred for a further 10 min, cooled to -50 °C, and $Cl_2PCH_2CH_2PCl_2$ (4.0 cm^3, 0.025 mol) in diethyl ether (50 cm^3) added dropwise during 15 min. The mixture was allowed to warm to 20 °C, stirred for a further 60 min, and quenched with water (200 cm^3). The crude product was filtered off and recrystallised from methanol-thf.

1,2-Bis(diphenoxyphosphino)ethane.—Phenol (9.28 g, 0.099 mol), triethylamine (freshly distilled from $Li[AlH_4]$, 13.8 cm^3, 0.099 mol) and diethyl ether (100 cm^3) were cooled to -75 °C, and $Cl_2PCH_2CH_2PCl_2$ (4.0 cm^3, 0.025 mol) added dropwise with vigorous stirring during 20 min. The mixture was then allowed to warm to 20 °C, diethyl ether (100 cm^3) added, and the mixture stirred for a further 2 h, during which time a white precipitate of triethylamine hydrochloride formed. This was filtered off and rejected, the filtrate reduced to 5 cm^3 at 10^{-3} mmHg and the white solid produced was filtered off, washed with pentane, and dried.

1,2-Bis(dimethoxyphosphino)ethane was prepared by the literature method[10] from methanol, trimethylamine, and $Cl_2PCH_2CH_2PCl_2$ in ca. 30% yield. In solution in C_6D_6, proton resonances are observed at τ 8.37 (t, 4 H, CH_2, J_{HH} = 7.2 Hz), 6.60 (d, 12 H, CH_3O, broad); there is a single ^{31}P resonance at δ 44.3 p.p.m. in C_6H_6. This material is air sensitive.

All the rhenium complexes were prepared by fundamentally the same method from the green chelate (1). The preparations are essentially similar, but differ in detail.

Bis[1,2-bis(diethylphosphino)ethane]chloro(dinitrogen)-rhenium(I)-Triphenylphosphine (1/2).—To a slurry of [N-benzoylhydrazido(3—)-N',O]dichlorobis(triphenylphosphine)-rhenium(v) (1) (1.47 g, 1.61 mmol) in benzene (110 cm^3) was added 1,2-bis(diethylphosphino)ethane (3.0 cm^3, 12.9 mmol) and the mixture heated under reflux. After 30 min the intense green colour of the initial rhenium complex had disappeared and the solution was light brown. After 90 min, the solution was cooled to 0 °C and kept for 48 h. Large pale yellow prisms were filtered off from the solution, washed with methanol (2 × 2 cm^3), and dried in vacuo.

This material could not be freed of triphenylphosphine by recrystallisation. The required product was obtained from a reaction not in benzene but in methanol plus sodium methoxide

(2.2 mmol). After 2 h at reflux, the mixture was reduced to small volume (*ca.* 10 cm³), benzene (50 cm³) added and heated to reflux for a further hour. It was then taken to dryness, and the residue extracted with ether (2 × 15 cm³). Upon reducing the extract to half-volume and cooling, pale yellow crystals of *bis*-[1,2-*bis*(*diethylphosphino*)*ethane*]*chloro*(*dinitrogen*)*rhenium*(I) separated in *ca.* 20% yield.

Bis[1,2-*bis*(*dicyclohexylphosphino*)*ethane*]*chloro*(*dinitrogen*)-*rhenium*(I).—A mixture of (**1**) (0.46 g, 0.50 mmol) and the diphosphine (0.51 g, 1.2 mmol) in methanol (70 cm³) was heated under reflux for 5 h. The orange-red solution was taken to dryness and the oily residue stirred in ether (50 cm³) for 2 h. The cream solid was filtered off, washed with ether (3 × 10 cm³), and dried *in vacuo*. Yield 36%.

Bis[1,2-*bis*(*di*-p-*methoxyphenylphosphino*)*ethane*]*chloro*-(*dinitrogen*)*rhenium*(I).—A mixture of (**1**) (0.63 g, 0.69 mmol) and the diphosphine (0.91 g, 2.0 mmol) was heated under reflux in benzene (70 cm³) for 0.5 h. The orange-red solution was reduced to *ca.* 25 cm³ and addition of ether (20 cm³) gave a light brown solid, which was washed with ether and dried. This solid was stirred in thf (20 cm³), filtered, and methanol added to the filtrate to give the microcrystalline *product* which was filtered off, washed with methanol and ether and dried *in vacuo*. Yield 17%.

Bis[1,2-*bis*(*di*-p-*tolylphosphino*)*ethane*]*chloro*(*dinitrogen*)-*rhenium*(I).—The diphosphine (1.39 g, 1.5 mmol) was added to [ReCl(N₂)(PMe₂Ph)₄] (0.56 g, 0.70 mmol) in toluene (40 cm³). The mixture was heated to reflux for 4 h. The light brown solution was reduced to *ca.* 5 cm³ at 10^{-3} mmHg and hexane added to precipitate the pale yellow *solid*, which was dried *in vacuo*. Yield 15%.

Bis[1,2-*bis*(*diphenylphosphino*)*ethane*]*chloro*(*dinitrogen*)-*rhenium*(I).—The diphosphine (0.87 g, 2.2 mmol) and NaOMe (0.064 g, 1.12 mmol) were added to compound (**1**) (0.91 g, 0.99 mmol) in methanol (50 cm³) and the mixture was heated to reflux for 2.5 h. A pale yellow solid precipitated, and was washed with ether. More solid could be obtained from the mother-liquor by evaporating to dryness, extracting with benzene (80 cm³), and heating to reflux for 1 h together with NaOMe (0.064 g, 1.2 mmol). The pale yellow solid was filtered off and recrystallised from dichloromethane–hexane. Yield 60%. This procedure is to be preferred to that already published.[5]

Bis[1,2-*bis*(*di*-p-*chlorophenylphosphino*)*ethane*]*chloro*-(*dinitrogen*)*rhenium*(I).—A suspension of (**1**) (1.0 g, 1.1 mmol) and the diphosphine (1.29 g, 2.40 mmol) in methanol (50 cm³) was heated to reflux for 4 h, forming a light brown solution. Unreacted compound (**1**) was filtered off, and the filtrate taken to dryness, leaving an oil. On addition of ether, a yellow solid formed which, by i.r. [v(CO) = 1 650 cm⁻¹, no v(N₂)] is a diazenido-complex. The yellow solid in benzene (50 cm³) was heated under reflux for 1 h. The yellow solution was reduced to small volume and ether added yielding a pale yellow *solid*. Yield 45%.

Bis{1,2-*bis*[*di*(p-*trifluoromethylphenyl*)*phosphino*]*ethane*}-*chloro*(*dinitrogen*)*rhenium*(I).—A mixture of (**1**) (1.0 g, 1.1 mmol) and the diphosphine (1.61 g, 2.4 mmol) in methanol (50 cm³) was treated with NaOMe (0.074 g, 1.32 mmol). An immediate reaction gave a yellow *precipitate*, which was filtered off, washed with methanol and recrystallised as a pale yellow solid from ether. Yield 57%.

We were not able to obtain pure dinitrogen complexes from other diphosphines, though the complexes undoubtedly exist. For example, the dinitrogen complex associated with (*p*-

Me₂NC₆H₄)₂PCH₂CH₂P(C₆H₄NMe₂-*p*)₂ has v(N₂) = 1 930 cm⁻¹ though we could not characterise it.

Bis{1,2-*bis*[*di*(p-*trifluoromethylphenyl*)*phosphino*]*ethane*}-*chlororhenium*(I).—To a solution of [ReCl(N₂)(PMe₂Ph)₄] (0.25 g, 0.03 mmol) in toluene (70 cm³) was added the diphosphine (0.46 g, 0.069 mmol) and the mixture heated under reflux for 12 h. The orange solution was taken to dryness yielding an oil. This was dissolved in ether (3 cm³) and hexane (10 cm³), and a white solid (diphosphine) removed after 16 h at −10 °C. The filtrate was reduced to 2 cm³, and hexane (10 cm³) added to precipitate an orange *solid*. Yield 48%.

cis-*Bis*{1,2-*bis*[*di*(p-*trifluoromethylphenyl*)*phosphino*]*ethane*}-*chloro*(*methyl isocyanide*)*rhenium*(I).—Methyl isocyanide (0.011 g, 0.27 mmol) was added to a solution of [ReCl{(*p*-CF₃C₆H₄)₂-PCH₂CH₂P(C₆H₄CF₃-*p*)₂}₂] (0.20 g, 0.13 mmol) in thf (20 cm³). The colour changed immediately to yellow-orange, and after stirring for 0.5 h, the solution was reduced to *ca.* 1 cm³ at 10^{-3} mmHg, and hexane (20 cm³) was added. Hexane was evaporated slowly until solid began to appear. The solution was then left at −10 °C for 16 h, and the orange solid was filtered off and dried *in vacuo*. Yield 50%.

trans-*Bis*{1,2-*bis*[*di*(p-*trifluoromethylphenyl*)*phosphino*]-*ethane*}*chloro*(*methyl isocyanide*)*rhenium*(I).—A mixture of [ReCl{(*p*-CF₃C₆H₄)₂PCH₂CH₂P(C₆H₄CF₃)₂-*p*}₂] (0.21 g, 0.13 mmol) and methyl isocyanide (0.010 cm³, 0.26 mmol) in thf (20 cm³) was heated under reflux for 50 h. The resultant yellow solution was reduced to *ca.* 5 cm³ *in vacuo*, and hexane (25 cm³) added. This precipitated a yellow *solid*, which was filtered off and dried *in vacuo*. Yield 60%.

Bis{1,2-*bis*[*di*(p-*trifluoromethylphenyl*)*phosphino*]*ethane*}-*carbonylchlororhenium*(I).—Carbon monoxide was bubbled slowly into a solution of [ReCl{(*p*-CF₃C₆H₄)₂PCH₂CH₂-P(C₆H₄CF₃)₂-*p*}₂] (0.34 g, 0.22 mmol) in thf (80 cm³) heated to reflux during 12 h. The solvent was then removed almost to dryness at 10^{-3} mmHg and hexane added to yield a yellow-orange *solid*, which was filtered off and dried *in vacuo*. Yield 40%.

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