# Syntheses and Redox Properties of Mixed Isocyanide, Carbonyl, or Nitrile Complexes of Rhenium(I) *trans*-[Re(CNMe)L($Ph_2PCH_2CH_2PPh_2$)$_2$]X [L = CNR (R = Alkyl or Aryl), CO, or NCMe; X = Cl, $BF_4$, or $PF_6$]

**M. Fernanda N. N. Carvalho and Armando J. L. Pombeiro** *
*Centro de Química Estrutural, Complexo I, Instituto Superior Técnico, Av. Rovisco Pais, 1096 Lisbon Codex, Portugal*

Complexes *trans*-[Re(CNMe)L(dppe)$_2$]X [**1**; L = CNR (R = Me, Bu$^t$, Ph, $C_6H_4Me$-4, $C_6H_4Cl$-4, or $C_6H_2Pr^i_3$-2,4,6), CO, or NCMe; dppe = $Ph_2PCH_2CH_2PPh_2$; X = Cl, $BF_4$, or $PF_6$] were prepared from the reaction of *trans*-[ReCl(CNMe)(dppe)$_2$] with the appropriate substrate (L), either in the presence of TlX (**1**; X = $BF_4$ or $PF_6$), in tetrahydrofuran (thf) or $CH_2Cl_2$, or in the absence of the thallium salt (**1**; X = Cl) in refluxing $CH_2Cl_2$; the latter route was also applied to the syntheses of *trans*-[Re(CNR)$_2$(dppe)$_2$]Cl [R = Me or $C_6H_2Pr^i_3$-2,4,6 (**2**)] directly from the dinitrogen complex *trans*-[ReCl($N_2$)(dppe)$_2$]. At a platinum electrode, in thf or NCMe–0.2 mol dm$^{-3}$ [$Bu_4N$][$BF_4$], complexes (**1**) undergo at least one reversible single-electron oxidation by cyclic voltammetry. The observed values of the half-wave oxidation potential are in agreement with those predicted from the application of equations relating the electrochemical ligand parameter $P_L$, electron richness $E_s$, and polarisability β of the binding metal centre; these parameters were also estimated for the {Re(CNR)(dppe)$_2$}$^+$ sites. An expression is also proposed to estimate the redox potential of mixed-ligand complexes of the type [$M'_sL(L')$] ($M'_s$ = 14-electron metal site), as the average of the redox potential of [$M'_sL_2$] and [$M'_sL'_2$]; the conditions for its application are discussed and it was shown to be valid for complexes (**1**).

The electronic properties and chemical behaviour of ligating isocyanides are determined, apart from intrinsic factors, by the properties of the co-ordination site namely its π-electron releasing ability.[1,2]

As part of our electrochemical study on the activation of isocyanides by transition-metal centres, we have previously described the preparation and the redox properties of the complexes *trans*-[M(CNR)$_2$(dppe)$_2$] (M = Mo or W, dppe = $Ph_2PCH_2CH_2PPh_2$),[3,4] *trans*-[ReCl(CNR)(dppe)$_2$],[4,5] *trans*-[ReL$_2$(dppe)$_2$][$BF_4$] (L = CO or CNR),[6] and *trans*-[FeH(CNR)(dppe)$_2$][$BF_4$].[7] By cyclic voltammetry at a platinum electrode, in tetrahydrofuran (thf) or NCMe–0.2 mol dm$^{-3}$ [$NBu_4$][$BF_4$], they commonly show at least one reversible (or quasi-reversible) single-electron oxidation (two successive reversible one-electron oxidations are observed for the rhenium chloro complexes).

For a common isocyanide ligand, the half-wave oxidation potential ($E_{\frac{1}{2}}^{ox}$) of these complexes spans a wide range (*e.g. ca.* 1.4 V for the CNMe compounds),[3–7] in agreement with a large variation of the electronic properties of the metal sites which were also shown[5,6] to influence the net electron-acceptor ability (see below) of the isocyanide.

Moreover, for several series of closed-shell octahedral-type complexes, [$M_sL$], with 16-electron square-pyramidal metal sites {$M_s$}, the relationship between the redox potential and the electronic properties of the ligands and metal centres has been described by expression (1),[8] which relates the redox potential

$$E_{\frac{1}{2}}^{ox}[M_sL] = E_s + \beta P_L \qquad (1)$$

with a ligand constant, the $P_L$ ligand parameter, the electron richness ($E_s$), and the polarisability (β) of the binding metal centre. The parameter $P_L$ is defined by equation (2) and is a measure of the net electron donor/acceptor character of the ligand (the stronger the net donor character of L, the more negative is $P_L$). The parameter $E_s$ is defined as $E_{\frac{1}{2}}^{ox}$ of the carbonyl complex [equation (3)] (the lower this parameter, the higher is the electron richness of the metal centre).[8]

$$P_L = E_{\frac{1}{2}}^{ox}[Cr(CO)_5L] - E_{\frac{1}{2}}^{ox}[Cr(CO)_6] \qquad (2)$$

$$E_s = E_{\frac{1}{2}}^{ox}[M_s(CO)] \qquad (3)$$

These equations were tentatively extended[9] to other octahedral 18-electron complexes of the types [$M_sL_n$] with 14-electron ($n$ = 2) or 12-electron ($n$ = 3) metal sites and an expression was proposed[6] to estimate $E_{\frac{1}{2}}^{ox}$ of octahedral closed-shell complexes of the type [$M'_sL_2$], with 14-electron square-planar metal centres {$M'_s$}, such as *trans*-[Re(CNR)$_2$(dppe)$_2$][$BF_4$].

Moreover, the additivity of $P_L$ was recognised[9,10] in some cases, whereas the possibility of its dependence on the metal site was demonstrated[5,6] at least for isocyanides, whose geometry (linear or bent) is dependent on the co-ordination centre. Hence, at the neutral {ReCl(dppe)$_2$} centre, with a much higher electron richness than the cationic {ReL(dppe)$_2$}$^+$ (L = CO or CNR) or the pentacarbonyl {Cr(CO)$_5$}, the isocyanides behave as much stronger net electron acceptors than at the latter sites; accordingly, they exhibit $P_L$ values at {ReCl(dppe)$_2$} which are 0.26 V higher than at {ReL(dppe)$_2$}$^+$ where $P_L$ is assumed to be identical to that known for isocyanides at the low electron-rich {Cr(CO)$_5$} site (herein denoted by $P_L^l$ where the superscript stands for 'low value' or 'linear geometry' which is the expected one for isocyanides at metal centres with a low electron richness) [equation (4)].[6] In the related manganese

$$P_L(CNR)\{ReCl(dppe)_2\} = 0.26 + P_L^l(CNR) \qquad (4)$$

complex *trans*-[Mn(CNMe)(CO)($Ph_2PCH_2PPh_2$)$_2$]$^+$ the isocyanide is also considered[11] to display the $P_L^l$ value.

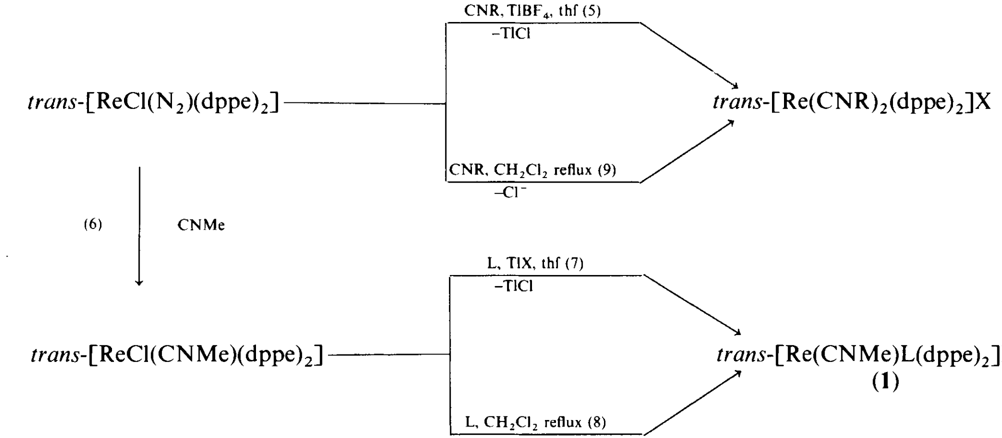
Such behaviour is again taken into account in the present study where the validity of expressions (1) and (4) is tested for *trans*-[Re(CNMe)L(dppe)$_2$]$^+$ (L = CO, CNR, NCMe, or Cl) whose redox potential spans a wide range of *ca.* 1.1 V.

## Results and Discussion

*Syntheses and Characterisation of Complexes* trans-[Re(CNMe)L(dppe)$_2$]X [**1**; L = CNR (R = Me, Bu$^t$, $C_6H_4Me$-4, Ph, $C_6H_4Cl$-4, *or* $C_6H_2Pr^i_3$-2,4,6), CO, *or* NCMe; X = Cl, BF$_4$, *or* PF$_6$] *and trans*-[Re(CNC$_6$H$_2$Pr$^i_3$-2,4,6)$_2$(dppe)$_2$]Cl (**2**).—Dinitrogen is commonly a labile ligand and its complexes are convenient sources for the syntheses of compounds with isoelectronic species such as isocyanides,[2-6] nitriles,[12] alkyne,[13] or alkyne-derived [13,14] ligands.

Hence, *e.g.*, the bis(isocyanide) complexes *trans*-[M(CNR)$_2$(dppe)$_2$] (M = Mo or W, R = alkyl or aryl) [3] have been prepared from the reaction of *trans*-[M(N$_2$)$_2$(dppe)$_2$] with the appropriate isocyanide, whereas the homologous rhenium(I) compounds *trans*-[Re(CNR)$_2$(dppe)$_2$][BF$_4$] are obtained upon treatment of *trans*-[ReCl(N$_2$)(dppe)$_2$] with isocyanide in tetrahydrofuran (thf), in the presence of a halide abstractor (TlBF$_4$) [equation (5), X = BF$_4$].

We now report the syntheses of the related mixed isocyanide compounds *trans*-[Re(CNMe)L(dppe)$_2$]X [**1**; L = CNR (R = Bu$^t$, $C_6H_4Me$-4, Ph, $C_6H_4Cl$-4, or $C_6H_2Pr^i_3$-2,4,6), CO, or NCMe; X = BF$_4$, PF$_6$, or Cl] either through a similar route [equation (7); L = CNR (R = Bu$^t$, $C_6H_4Me$-4, or $C_6H_4Cl$-4); X = BF$_4$ or PF$_6$], but starting from *trans*-[ReCl(CNMe)(dppe)$_2$] [which is obtained from the parent N$_2$ complex, equation (6)], or following a more convenient procedure by refluxing (for *ca.* 20—24 h) a dichloromethane solution of the methyl isocyanide complex in the presence of the appropriate substrate [equation (8); L = CNR (R = Me, Bu$^t$, $C_6H_4Me$-4, Ph, $C_6H_4Cl$-4, or $C_6H_2Pr^i_3$-2,4,6) or NCMe; X = Cl].



The latter procedure does not involve addition of the thallium salt and leads to analytically pure complexes in a cleaner way and in higher yields than those obtained through the former route which requires separation of the rhenium products from the thallium salts. Moreover, it may also be applied to the preparation of the di-isocyanide compounds *trans*-[Re(CNR)$_2$(dppe)$_2$]$^+$ from the dinitrogen precursor and, *e.g.*, *trans*-[Re(CNMe)$_2$(dppe)$_2$]Cl and *trans*-[Re(CNC$_6$H$_2$Pr$^i_3$-2,4,6)$_2$(dppe)$_2$]Cl (**2**) have been prepared in this way [equation (9)]. Tetrahydrofuran may replace dichloromethane in reaction (9), but the corresponding monoisocyanide complexes *trans*-[ReCl(CNR)(dppe)$_2$] appear to be the main products, whereas the di-isocyanide compounds are obtained in lower yields even upon extended refluxing and under tungsten light irradiation (*e.g.* for R = $C_6H_4OMe$-4). In route (7), CH$_2$Cl$_2$ was used instead of thf, for the synthesis of *trans*-[Re(CNMe)(CO)(dppe)$_2$][BF$_4$].

Complexes (**1**) and (**2**) are yellow and were characterised by their i.r., $^1$H and $^{31}$P n.m.r. spectroscopic properties, elemental analysis, and molar conductivity (Tables 1 and 2). Their i.r. spectra show bands in the range 2 150—1 960 cm$^{-1}$ *assigned to* C–N stretching of the isocyanide ligands and, as expected, the aryl isocyanides exhibit ν(CN) at lower values than those for the alkyl isocyanides which are known to be weaker π acceptors.

A singlet is observed in their $^{31}$P-{$^1$H} n.m.r. spectra, in agreement with the *trans* geometry which is also suggested by the unique main i.r. ν(CN) band for the complexes with two identical isocyanide ligands and by the absence, in the $^1$H n.m.r. spectra, of the phenyl triplets, slightly upfield from the bulk of the complex phenyl resonance, which are diagnostic [2b,15] of a *cis* geometry. For the aromatic isocyanide complexes, the resonance of the *ortho* protons is observed as the expected [6,16] doublet [$^3J$(HH) *ca.* 6—9 Hz] at δ 6.3—7.0, *i.e.* slightly upfield from the dppe phenyl complex resonance; however for the phenyl isocyanide complex, the two *ortho* protons are not equivalent and their resonances occur as two overlapping doublets. Such doublets are obviously absent for complexes (**1**; L = CNC$_6$H$_2$Pr$^i_3$-2,4,6) and (**2**) whose isopropyl C*H*Me$_2$ resonances occur as higher-field multiplets, *e.g.* a septet [$^3J$(HH) = 7.5 Hz, at δ 2.01] for the four *ortho* isopropyl substituents of complex (**2**).

The i.r. and n.m.r. data of complex (**1**; L = CNMe, X = Cl) agree with those reported[6] for the analogous complex with tetrafluoroborate as counter ion.

Complexes (**1**) and (**2**) behave as 1:1 electrolytes in nitromethane solutions in agreement with their ionic formulation.

*Redox Properties of Complexes trans*-[Re(CNMe)L(dppe)$_2$]X (**1**; L = CNR, CO, *or* NCMe).—*General.* By cyclic voltammetry, each of the complexes (**1**) shows a one-electron diffusion-controlled (obeying the criterion $i_p^{ox}/v^{\frac{1}{2}}$ = constant) reversible (or quasi-reversible) oxidation (for scan rates, *v*, in the range 0.05—0.5 V s$^{-1}$), at a platinum-wire electrode, in thf (or NCMe)–0.2 mol dm$^{-3}$ [NBu$_4$][BF$_4$]. The corresponding values of the half-wave oxidation potential ($E_{\frac{1}{2}}^{ox}$) for these complexes (except for L = CNC$_6$H$_2$Pr$^i_3$-2,4,6 where no reliable data were collected, due to decomposition) are listed in Table 3; they are in volts relative to the saturated calomel electrode (s.c.e.) and have been measured by using as internal reference the couples *trans*-[Mo(N$_2$)$_2$(dppe)$_2$]$^{0/+}$, *trans*-[ReCl(N$_2$)(dppe)$_2$]$^{0/+}$, or [Fe-

**Table 1.** Analytical and physical data for complexes *trans*-[Re(CNMe)L(dppe)$_2$]X (**1**) and *trans*-[Re(CNC$_6$H$_2$Pr$^i_3$-2,4,6)$_2$(dppe)$_2$]Cl (**2**)

| Complex, L | X | Colour | Yield (%) | I.r. (cm$^{-1}$)$^a$ ν(CN) or ν(CO) | Analysis$^b$ (%) C | H | N |
|---|---|---|---|---|---|---|---|
| (**1**), CO$^c$ | BF$_4$ | Yellow | 30 | 2 170m<br>1 890s | 56.3<br>(56.4) | 4.5<br>(4.4) | 1.4<br>(1.2) |
| (**1**), CNC$_6$H$_4$Cl-4$^d$ | Cl | Yellow | 80 | 2 140m<br>2 015s<br>1 990vs | 59.0<br>(59.4) | 4.9<br>(4.6) | 2.5<br>(2.3) |
| (**1**), CNPh$^{c,e}$ | Cl | Yellow | 70 | 2 135m<br>2 015s<br>1 970vs | 61.3<br>(61.3) | 5.1<br>(4.7) | 2.4<br>(2.3) |
| (**1**), CNC$_6$H$_4$Me-4$^f$ | Cl | Pale yellow | 70 | 2 127m<br>2 034 (sh)<br>2 000vs | 58.9<br>(58.5) | 4.9<br>(4.7) | 2.6<br>(2.2) |
| (**1**), CNMe | Cl$^{c,g}$ | Pale yellow | 70 | 2 082s | 59.4<br>(59.4) | 5.4<br>(4.8) | 2.4<br>(2.5) |
|  | PF$_6$$^h$ | Pale yellow | 40 | 2 070s | 56.2<br>(56.2) | 5.1<br>(4.8) | 2.1<br>(2.2) |
| (**1**), CNBu$^t$ | Cl$^i$ | Yellow | 75 | 2 114w<br>2 060 (sh)<br>2 030s<br>1 999 (sh) | 59.1<br>(59.5) | 5.1<br>(5.1) | 2.1<br>(2.3) |
|  | BF$_4$$^j$ | Pale yellow | 40 | 2 115s<br>2 050 (sh)<br>2 020s | 53.6<br>(53.7) | 5.5<br>(4.7) | 2.3<br>(2.1) |
| (**1**), CNC$_6$H$_2$Pr$^i_3$-2,4,6 | Cl | Pale yellow | 60 | 2 150m<br>2 120m<br>1 980s | 59.1<br>(59.3) | 5.6<br>(5.4) | 1.9<br>(1.9) |
| (**1**), NCMe$^c$ | Cl | Pale yellow | 55 | 2 140w<br>2 065s | 59.0<br>(59.4) | 2.5<br>(2.5) | 5.2<br>(4.8) |
| (**2**)$^{c,k}$ | Cl | Yellow | 30 | 2 098w<br>2 027w<br>1 960s | 70.5<br>(69.4) | 6.7<br>(6.6) | 2.2<br>(2.2) |

[a] In KBr pellet. [b] Required values in parentheses. [c] With 0.5CH$_2$Cl$_2$ of crystallisation. [d] With 0.25CH$_2$Cl$_2$ of crystallisation; similar i.r. data for the PF$_6^-$ analogue [2 140m, 2 030 (sh), and 1 995s cm$^{-1}$]. [e] $\Lambda_M$ (nitromethane) = 85 $\Omega^{-1}$ cm$^2$ mol$^{-1}$. [f] With 1.5CH$_2$Cl$_2$ of crystallisation; similar i.r. data for the BF$_4^-$ analogue [2 120m, 2 040 (sh), and 2 000vs cm$^{-1}$]. [g] $\Lambda_M$ (nitromethane) = 73 $\Omega^{-1}$ cm$^2$ mol$^{-1}$. [h] With thf of crystallisation. [i] With 0.75CH$_2$Cl$_2$ of crystallisation. [j] With 2CH$_2$Cl$_2$ of crystallisation. [k] $\Lambda_M$ (nitromethane) = 56 $\Omega^{-1}$ cm$^2$ mol$^{-1}$.

($\eta^5$-C$_5$H$_5$)$_2$]$^{\circ/+}$ $\{E^{ox}_{\frac{1}{2}}$ = −0.16, +0.28, or +0.54(5) V *vs.* s.c.e., respectively, in 0.2 mol dm$^{-3}$ [NBu$_4$][BF$_4$]–thf$\}$.

Although for this anodic wave the peak current ratio $i^{ox}_p/i^{red}_p$ is close to 1.0, the peak current separation, $\Delta E_p = E^{ox}_p - E^{red}_p$, in thf is usually considerably higher [*e.g.* $\Delta E_p$ *ca.* 0.10 V for (**1**; L = CNPh)] than the expected value (59 mV) for a single-electron reversible process; however, such behaviour is commonly observed[4,5,7] for reversible redox processes of related systems in the high-resistance thf medium.

Nevertheless, the values of $E^{ox}_{\frac{1}{2}}$ (*vs.* s.c.e.) in thf do not differ appreciably from those obtained in NCMe where the $\Delta E_p$ reversibility criterion is obeyed.

The number of electrons involved in this wave was estimated by comparing the current functions $i_p v^{-\frac{1}{2}} C^{-1}$ ($C$ = concentration) of complexes (**1**) with that of *trans*-[ReCl(N$_2$)(dppe)$_2$] or *trans*-[Mo(N$_2$)$_2$(dppe)$_2$], and the value obtained (one electron) was confirmed by controlled-potential electrolysis.

As reported[6] for *trans*-[Re(CNR)$_2$(dppe)$_2$][BF$_4$], a second anodic wave could be observed in NCMe [*e.g.* complex (**1**; L = NCMe) exhibits a second reversible oxidation at $^{II}E^{ox}_{\frac{1}{2}}$ = 1.11 V], whereas for complex (**1**; L = CNC$_6$H$_4$Cl-4) which is harder to oxidise than the other mixed isocyanide compounds an irreversible cathodic wave was also detected; however, these redox processes were not investigated further.

The values (Table 3) of the half-wave oxidation potential for the first wave, $E^{ox}_{\frac{1}{2}}$, of complexes (**1**; L = CO or CNR) are about 0.5—0.7 V more anodic than those observed[5] for the neutral homologous *trans*-[ReCl(L)(dppe)$_2$] and fall in the

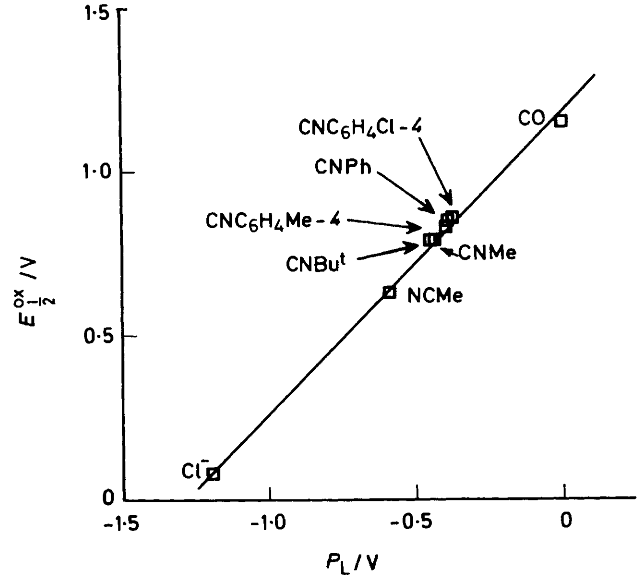


**Figure.** Linear least-squares fit of $E^{ox}_{\frac{1}{2}}$ for *trans*-[Re(CNMe)L(dppe)]$^+$ (**1**; L = CO, CNR, NCMe, or Cl$^-$) *vs.* $P_L$

range known[6] for comparable cationic compounds *trans*-[ReL$_2$(dppe)$_2$][BF$_4$] (L = CNR or CO). These observations are in agreement with the expected lower electron richness of the

**Table 2.** Proton and $^{31}P$ n.m.r. data for complexes *trans*-[Re(CNMe)L(dppe)$_2$]X (**1**) and *trans*-[Re(CNC$_6$H$_2$Pr$^i_3$-2,4,6)$_2$(dppe)$_2$]Cl (**2**)

| | $^1H$ N.m.r.[a] | | | | |
|---|---|---|---|---|---|
| Complex, L | X | δ | Integration | Assignment | $^{31}P$-{$^1H$} N.m.r.[b] |
| (**1**), CO[c] | Cl | 7.6—7.5(m) | 40 | Ph(dppe) | |
| | | 2.6—2.3(m) | 8 | CH$_2$(dppe) | |
| | | 0.01(s) | 3 | CNMe | |
| (**1**), CNC$_6$H$_4$Cl-4[c] | Cl[d] | 7.3—6.9(m) | 42 | Ph(dppe) + CNC$_6$H$_4$Cl, *meta* to N | |
| | | 6.16(d)[e] | 2 | CNC$_6$H$_4$Cl, *ortho* to N | |
| | | 2.82(s) | 3 | CNMe | |
| | | 2.6—2.3(m) | 8 | CH$_2$(dppe) | |
| (**1**), CNPh[c] | Cl | 7.3—6.9(m) | 43 | Ph(dppe) + CNC$_6$H$_5$, *meta* and *para* to N | |
| | | 6.31(d)[f] | 1 | CNC$_6$H$_5$, *ortho* to N | |
| | | 6.30(d)[f] | 1 | | |
| | | 2.77(s) | 3 | CNMe | |
| | | 2.6—2.3(m) | 8 | CH$_2$(dppe) | |
| (**1**), CNC$_6$H$_4$Me-4 | Cl[c] | 7.3—6.9(m) | 42 | Ph(dppe) + CNC$_6$H$_4$Me, *meta* to N | −108.8 |
| | | 6.21(d)[g] | 2 | CNC$_6$H$_4$Me, *ortho* to N | |
| | | 2.75(s) | 3 | CNMe | |
| | | 2.6—2.3(m) | 8 | CH$_2$(dppe) | |
| | | 2.29(s) | 3 | CNC$_6$H$_4$Me | |
| | BF$_4$[h] | 7.5—7.2(m) | 42 | Ph(dppe) + CNC$_6$H$_4$Me, *meta* to N | −109.1 |
| | | 7.01(d)[f] | 2 | CNC$_6$H$_4$Me, *ortho* to N | |
| | | 2.82(s) | 3 | CNMe | |
| | | 2.6—2.3(m) | 8 | CH$_2$(dppe) | |
| | | 2.29(s) | 3 | CNC$_6$H$_4$Me | |
| (**1**), CNMe[i] | Cl | 7.2—6.9(m) | 40 | Ph(dppe) | −105.3[i] |
| | | 3.00(s) | 6 | CNMe | |
| | | 2.57(t, br)[j] | 8 | CH$_2$(dppe) | |
| (**1**), CNBu$^t$ | Cl[i] | 7.6—6.8(m) | 40 | Ph(dppe) | |
| | | 2.77(s) | 3 | CNMe | |
| | | 2.8—2.6(m) | 8 | CH$_2$(dppe) | |
| | | 1.13(s) | 9 | CNBu$^t$ | |
| | BF$_4$[h] | 7.6—6.5(m) | 40 | Ph(dppe) | |
| | | 2.53(s) | 3 | CNMe | |
| | | 2.5—2.0(m) | 8 | CH$_2$(dppe) | |
| | | 1.06(s) | 9 | CNBu$^t$ | |
| (**1**), CNC$_6$H$_2$Pr$^i_3$-2,4,6[i] | Cl | 7.5—6.6(m) | 42 | Ph(dppe) + CNC$_6$H$_2$Pr$^i_3$ | −110.2 |
| | | 3.4—3.3(m) | 1 | CH(Pr$^i$) | |
| | | 2.9—2.4(m) | 10 | CH$_2$(dppe) + CH(Pr$^i$) | |
| | | 2.28(s) | 3 | CNMe | |
| | | 1.21(t)[k] | 12 | CH$_3$(Pr$^i$) | |
| | | 0.69(d)[f] | 6 | CH$_3$(Pr$^i$) | |
| (**1**), NCMe[c] | Cl | 7.3—6.7(m) | 40 | Ph(dppe) | −104.9 |
| | | 2.5—2.3(m) | 8 | CH$_2$(dppe) | |
| | | 1.73(s) | 3 | CNMe + NCMe | |
| | | 1.50(s) | 3 | | |
| (**2**) | Cl | 7.2—6.9(m) | 40 | Ph(dppe) | |
| | | 6.57(s) | 4 | CNC$_6$H$_2$Pr$^i_3$ | |
| | | 2.9—2.6(m) | 10 | CH$_2$(dppe) + CH(*para*-Pr$^i$) | |
| | | 2.01(spt)[g] | 4 | CH(*ortho*-Pr$^i$) | |
| | | 1.08(d)[g] | 12 | CH$_3$(*para*-Pr$^i$) | |
| | | 0.30(d)[g] | 24 | CH$_3$(*ortho*-Pr$^i$) | |

[a] δ Values relative to internal SiMe$_4$; s = singlet, d = doublet, t = triplet, spt = septet, m = complex multiplet, and br = broad. [b] δ Values in p.p.m. upfield from external P(OMe)$_3$. [c] In CD$_2$Cl$_2$. [d] Analogous spectrum for the PF$_6$ analogue. [e] $^3J$(HH) = 9 Hz. [f] $^3J$(HH) = 6 Hz. [g] $^3J$(HH) = 7.5 Hz. [h] In CDCl$_3$. [i] In (CD$_3$)$_2$CO. [j] Triplet due to coupling to phosphorus nuclei, $J$(PH) = 7 Hz. [k] Resulting from two overlapping doublets, $^3J$(HH) = 7 Hz.

cationic rhenium centres relative to the neutral {ReCl(dppe)$_2$} site.

The oxidation potential of the complexes in the series *trans*-[Re(CNMe)L(dppe)$_2$]$^+$ extended to the known[5] compound *trans*-[ReCl(CNMe)(dppe)$_2$] (*i.e.* L = CO, CNR, NCR, or Cl$^-$ ) increases in the order L = Cl$^-$ < NCMe < CNBu$^t$ ≈ CNMe < CNC$_6$H$_4$Me-4 < CNPh < CNC$_6$H$_4$Cl-4 < CO, reflecting the increase in the net electron-acceptor character (as measured by $P_L$) of the ligand L. A plot of $E^{ox}_{\frac{1}{2}}$ for complexes (**1**; L = CO, CNR, NCR, or Cl$^-$) *vs.* $P_L$ is shown in the Figure and an excellent linear correlation [expressed by equation (10) obtained by the least squares method; $R$ = 0.998] appears to be followed over the very wide range of $P_L$ values (*ca.* 1.2 V)[8] spanning that of a strong net electron acceptor such as CO ($P_L$ = 0) and that of an effective net electron donor such as Cl$^-$ ($P_L$ = −1.19 V).

$$E^{ox}_{\frac{1}{2}}[\mathrm{Re(CNMe)L(dppe)_2}]^+ = 1.18 + 0.916\,P_L(\mathrm{L}) \quad (10)$$

*Estimate of $E^{ox}_{\frac{1}{2}}$ for trans*-[Re(CNMe)L(dppe)$_2$]$^+$ (L = CO, *CNR, NCMe, or* $Cl^-$*) from* $E_s$ *and* $\beta$ *of the Metal Centre.*—Since the electrochemical parameters $E_s$ and $\beta$ may be estimated (or are known) for a variety of $\{ReL(dppe)_2\}^+$ sites (Table 4), it is possible to predict the redox potential of complexes $[Re(CNMe)L(dppe)_2]^+$ by equations (11) or (12) derived through the application of equation (1) either to the $\{Re(CNMe)(dppe)_2\}^+$ or to the $\{ReL(dppe)_2\}^+$ centre, respectively.

$$E_{\frac{1}{2}}^{ox}\,[Re(CNMe)L(dppe)_2]^+ = E_s\,\{Re(CNMe)(dppe)_2\}^+ + \beta\{Re(CNMe)(dppe)_2\}^+ \,.\, P_L(L) \quad (11)$$

$$E_{\frac{1}{2}}^{ox}\,[Re(CNMe)L(dppe)_2]^+ = E_s\,\{ReL(dppe)_2\}^+ + \beta\{ReL(dppe)_2\}^+ \,.\, P_L(CNMe) \quad (12)$$

By taking into consideration the dependence of the isocyanide $P_L$ on the metal site [equation (4)], expression (12) assumes the form (12a) or (12b), corresponding to $P_L$(CNMe) values of −0.43 or −0.17 V,[6] for L different or equal to $Cl^-$, respectively.

$$E_{\frac{1}{2}}^{ox}\,[Re(CNMe)L(dppe)_2]^+ = E_s\,\{ReL(dppe)_2\}^+ - 0.43\,\beta\{ReL(dppe)_2\}^+ \quad (12a)$$

$$E_{\frac{1}{2}}^{ox}\,[ReCl(CNMe)(dppe)_2] = E_s\,\{ReCl(dppe)_2\} - 0.17\,\beta\{ReCl(dppe)_2\} \quad (12b)$$

**Table 3.** Experimental and estimated half-wave oxidation potentials ($E_{\frac{1}{2}}^{ox}$) for the one-electron reversible oxidation of *trans*-$[Re(CNMe)L(dppe)_2]^+$

| L | Exptl.[a] $E_{\frac{1}{2}}^{ox}$/V | Estimated $E_{\frac{1}{2}}^{ox}$/V Equation (13) | (12)[b] | (14) |
|---|---|---|---|---|
| CO | 1.15 | 1.15 | 1.15 | 1.11 |
| $CNC_6H_4Cl$-4 | 0.86[c] | 0.82 | 0.87 | 0.89 |
| CNPh | 0.85 | 0.81 | 0.85 | — |
| $CNC_6H_4Me$-4 | 0.83 | 0.80 | 0.84 | 0.86 |
| CNMe | 0.79 | 0.76 | 0.76 | 0.79 |
| $CNBu^t$ | 0.79 | 0.76 | 0.75 | 0.80 |
| NCMe | 0.63[d] | 0.63 | — | — |
| $Cl^-$ | 0.08[e] | 0.08 | 0.10 | (−0.25) |

[a] Experiments carried out in 0.2 mol $dm^{-3}$ $[NBu_4][BF_4]$–thf at a platinum-wire electrode, by cyclic voltammetry. $E_{\frac{1}{2}}^{ox}$ values in V (±0.01) relative to s.c.e., see Experimental section. [b] The derived equation (12a) was considered for all cases except for L = $Cl^-$ when equation (12b) was selected. [c] Irreversible cathodic wave observed at $E_p^{red} = -2.18$ V. [d] In NCMe, a second anodic reversible and a third anodic irreversible wave are also observed (at $^{II}E_{\frac{1}{2}}^{ox} = 1.11$ and at $^{III}E_p^{ox} = 1.49$ V, respectively). [e] Ref. 5.

For the $\{ReCl(dppe)_2\}$ and $\{Re(CO)(dppe)_2\}^+$ sites (L = $Cl^-$ or CO, respectively), the $E_s$ and $\beta$ values (Table 4) were taken from the literature,[5,6] whereas for the isocyanide centres $\{Re(CNR)(dppe)_2\}^+$ (L = CNR) they have been estimated as shown in Appendix 1, from knowledge of the auxiliary $\{Re(CO)(dppe)_2\}^+$ centre[6] and of the redox potential for the members of the related series *trans*-$[ReCl(CNR)(dppe)_2]$.[5] The values of $E_s$ and $\beta$ obtained for those centres are given in Table 4.

By taking the $E_s$ and $\beta$ values estimated for the $\{Re(CNMe)(dppe)_2\}^+$ site (1.15 and 0.90 V, respectively, Table 4), equation (11) assumes form (13) which is comparable with the experimentally observed linear correlation [Figure and equation (10)] between $E_{\frac{1}{2}}^{ox}$ for complexes (**1**) and $P_L$. The values $E_{\frac{1}{2}}^{ox}$ for these complexes estimated from the application of equations (13) and (12a) or (12b) (the latter for L = $Cl^-$) are

$$E_{\frac{1}{2}}^{ox}\,[Re(CNMe)L(dppe)_2]^+ = 1.15 + 0.90\,P_L(L) \quad (13)$$

given in Table 4 and close agreement (within 40 mV) with the experimental values is observed.

$E_{\frac{1}{2}}^{ox}$ *for trans-*$[Re(CNMe)L(dppe)_2]^+$*(L = CNR or CO) as the Average of* $E_{\frac{1}{2}}^{ox}$ *for trans-*$[Re(CNMe)_2(dppe)_2]^+$ *and trans-*$[ReL_2(dppe)_2]^+$.—Except for the chloro complex (**1**; L = $Cl^-$), the redox potential of the mixed-ligand complexes *trans*-$[Re(CNMe)L(dppe)_2]^+$ is close to the average of those presented by the related *trans*-$[Re(CNMe)_2(dppe)_2]^+$ and *trans*-$[ReL_2(dppe)_2]^+$ (L = CNR or CO)[6] [equation (14) and

$$E_{\frac{1}{2}}^{ox}\,[Re(CNMe)L(dppe)_2] = \tfrac{1}{2}\{E_{\frac{1}{2}}^{ox}\,[Re(CNMe)_2(dppe)_2]^+ + E_{\frac{1}{2}}^{ox}\,[ReL_2(dppe)_2]^+ \quad (14)$$

Table 3]. Such a correlation would be expected as a particular case of the general equation (15), where $\{M_s'\}$ stands for a square-planar 14-electron metal site, which is now proposed and is valid (see Appendix 2) if the two metal sites $\{M_s'L\}$ and $\{M_s'L'\}$ have similar polarisabilities [condition (16)], assuming also that equation (1) is applicable to any of these centres and that the parameter $P_L$ does not vary with the metal site.

$$E_{\frac{1}{2}}^{ox}[M_s'LL'] = \tfrac{1}{2}\{E_{\frac{1}{2}}^{ox}[M_s'L_2] + E_{\frac{1}{2}}^{ox}[M_s'L_2']\} \quad (15)$$

$$\beta\{M_s'L\} = \beta\{M_s'L'\} \quad (16)$$

**Table 4.** Electrochemical data and estimated parameters $E_s$ and $\beta$ used for the application of equations (12)—(14) to estimate the redox potential for *trans*-$[Re(CNMe)L(dppe)_2]^{+\,a}$

| | $[ReCl(L)(dppe)_2]$ | | $[ReL_2(dppe)_2]^+$ | | $\{ReL(dppe)_2\}^+$ | |
|---|---|---|---|---|---|---|
| L | $P_L$[b] | $E_{\frac{1}{2}}^{ox}$[c] | $P_L$[c,d] | $E_{\frac{1}{2}}^{ox}$[e] | $E_s$[f] | $\beta$[f] |
| CO | 0[g] | 0.68 | 0[g] | 1.42 | 1.42[h] | 0.62[h] |
| $CNC_6H_4Cl$-4 | −0.11 | 0.30 | −0.37 | 0.98 | 1.19 | 0.75 |
| CNPh | −0.12 | 0.27 | −0.38[g] | — | 1.18 | 0.76 |
| $CNC_6H_4Me$-4 | −0.13 | 0.24 | −0.39 | 0.93 | 1.18 | 0.79 |
| $CNC_6H_4OMe$-4 | −0.14 | 0.19 | −0.40 | 0.88 | 1.17 | 0.82 |
| CNMe | −0.17 | 0.08 | −0.43[g] | 0.79 | 1.15 | 0.90 |
| $CNBu^t$ | −0.18 | 0.06 | −0.44 | 0.80 | 1.15 | 0.92 |
| $Cl^-$ | −1.19[g] | −1.29[i] | −1.19[g] | −1.29[i] | 0.68[j] | 3.4[j] |

[a] $P_L$, $E_{\frac{1}{2}}^{ox}$, and $E_s$ values in V *vs.* s.c.e. [b] Values taken from ref. 6 or estimated by using equation (4), except when stated otherwise. [c] Values taken from ref. 5, except for L = CNPh (which was measured in this study) and for L = $Cl^-$ (see footnote *i*). [d] For the isocyanide ligands (L = CNR), the low $P_L$ values, $P_L^l$, were considered. [e] Values taken from ref. 6, unless stated otherwise. [f] Values estimated in the present study (see Appendix 1), unless stated otherwise. [g] Ref. 8. [h] Ref. 6. [i] Ref. 17. [j] Ref. 5.

A similar polarisability of the two metal sites implies an analogous sensitivity of the redox potential of their complexes to a change of the variable ligand. Moreover, since the polarisability of a metal site is strongly affected by the axial ligand (*e.g.* a low $P_L$ value of the latter, *i.e.* a strong net electron-donor character tends to favour a high polarisability of the site),[6,8] condition (16) and, hence, equation (15) are expected to be valid in cases where the ligands L and L′ have comparable electron donor/acceptor properties.

Accordingly, equation (15) appears to be valid within the cationic centres $\{ReL(dppe)_2\}^+$, with related isocyanide or carbonyl ligands (L = CNR or CO), and whose polarisabilities lie within a restricted range (*ca.* 0.6—0.9). However, the neutral site $\{ReCl(dppe)_2\}$ exhibits a much higher polarisability ($\beta = 3.4$);[5] it has a chloride ligand which is a much stronger electron donor than the isocyanides or the carbonyl and presents a much lower ability to buffer changes in electron density at the metal.

Therefore, it would not be surprising if equation (15) is invalid for any pair of metal centres of the type $\{ReCl(dppe)_2\}$–$\{ReL(dppe)_2\}^+$ (L = CNR or CO).

The complex *trans*-$[ReCl(CNMe)(dppe)_2]$ or *trans*-$[ReCl(CO)(dppe)_2]$ has a value of $E_{\frac{1}{2}}^{ox}$ (0.08 or 0.68 V, respectively)[5] which is more anodic than the average (−0.25 or −0.025 V, respectively) of those for *trans*-$[ReCl_2(dppe)_2]^-$ (−1.29 V)[17] and *trans*-$[Re(CNMe)_2(dppe)_2]^+$ (0.79 V) or *trans*-$[Re(CO)_2(dppe)_2]^+$ (1.24 V), respectively.[6] In *trans*-$[ReCl(L)(dppe)_2]$ (L = CNR or CO) the electronic charge donated to the metal by the strong electron-donor $Cl^-$ ligand is partially removed by the effective $\pi$-acceptor isocyanide or carbonyl ligand, whereas in the dichloro complex such charge removal is not possible; as a result, the former are harder to oxidise than would be expected on the basis of equation (14).

Moreover, in the case of the pairs of sites $\{ReCl(dppe)_2\}$–$\{Re(CNR)(dppe)_2\}^+$ an additional reason for the failure of equation (14) (see Appendix 2) results from the fact that the $P_L$ of the isocyanide ligand differs at these metal centres.

Other data, in the literature, may also be correlated according to equation (15). They concern complexes such as *trans*-$[MoL(L')(dppe)_2]$[8] and, commonly, the *cis* isomers of $[M(CO)_4L(L')]$ [M = Cr or W; L,L′ = CO, CNBu$^t$, NCMe, pyridine (py), or $PPh_3$][18] and $[Ru(bipy)_2L(L')]^{2+}$ (bipy = 2,2′-bipyridine; L,L′ = $PPh_3$, py, or $Cl^-$).[19]

## Conclusions

A convenient synthetic route for complexes of the type *trans*-$[Re(CNMe)L(dppe)_2]^+$, also for the related *trans*-$[ReL_2(dppe)_2]^+$, based on chloride replacement by L in $CH_2Cl_2$, was developed for a variety of ligands L (carbonyl, isocyanides, or nitriles) and their effect on the redox potential was studied. The half-wave oxidation potential was shown to vary linearly with the electrochemical ligand parameter $P_L$ (a measure of the net electron donor/acceptor character of the ligand), in agreement with expressions derived from an equation proposed by other authors,[8] known to be applicable to different metal centres, and whose validity was demonstrated in the present study for $\{Re(CNMe)(dppe)_2\}^+$ even when binding ligands presenting a net electron-acceptor character spread over a very wide range of $P_L$ values; the dependence of $P_L$ on the electron richness of the ligating metal site[5,6] was confirmed for isocyanide ligands and the electron richness ($E_s$) and polarisability ($\beta$) were estimated for metal centres with isocyanides, of the type $\{ReL(dppe)_2\}^+$.

The redox potential of mixed-ligand complexes of the type $[M_s'L(L')]$ (where $M_s'$ denotes a 14-electron metal site), such as *trans*-$[ReL(L')(dppe)_2]^+$ (L,L′ = CNR or CO), was shown to be given by the average of those for $[M_s'L_2]$ and $[M_s'L'_2]$, provided that the sites $\{M_s'L\}$ and $\{M_s'L'\}$ have similar polarisability, *i.e.* the redox potential of their complexes would present a similar sensitivity to a change of the variable ligand.

## Experimental

All the manipulations and reactions were carried out in the absence of air using standard inert-gas flow and vacuum techniques. Solvents were purified by standard procedures. The complexes *trans*-$[ReCl(N_2)(dppe)_2]$[20] and *trans*-$[ReCl(CNMe)(dppe)_2]$,[2c] CNMe and the other isocyanides[21] were prepared by published methods; 2,4,6-tri-isopropylphenyl isocyanide was kindly provided by Dr. R. Herrmann of the University of Munich.

Infrared measurements were carried out on a Perkin-Elmer 683 or 457 spectrometer, $^1H$ and $^{31}P$ n.m.r. spectra on a Bruker CXP 300, JEOL JNM-PS-100, or JEOL PFT 100 Fourier-transform spectrometer. The electrochemical experiments were carried out on an EG&G PAR 173 potentiostat/galvanostat and an EG&G PARC 175 universal programmer. The redox potentials of the complexes were measured by cyclic voltammetry in 0.2 mol dm$^{-3}$ $[NBu_4][BF_4]$–thf or NCMe, at a platinum electrode. The $E_{\frac{1}{2}}^{ox}$ values are quoted relative to the s.c.e. by using as internal reference the couples *trans*-$[Mo(N_2)_2(dppe)_2]^{0/+}$, *trans*-$[ReCl(N_2)(dppe)_2]^{0/+}$, or $[Fe(\eta^5\text{-}C_5H_5)_2]^{0/+}$ {$E_{\frac{1}{2}}^{ox}$ at −0.16, +0.28, or +0.54(5) V *vs.* s.c.e., respectively, in 0.2 mol dm$^{-3}$ $[NBu_4][BF_4]$–thf}.

*Syntheses of Complexes trans*-$[Re(CNMe)L(dppe)_2]X$ [**1**; L = CNR (R = Me, Bu$^t$, $C_6H_4Me$-4, Ph, $C_6H_4Cl$-4, *or* $C_6H_2Pr^i_3$-2,4,6), CO, *or* NCMe; X = $BF_4$, $PF_6$, *or* Cl].—X = $BF_4$ *or* $PF_6$. The isocyanide complexes [**1**; L = CNR (R = Me, Bu$^t$, $C_6H_4Me$-4, or $C_6H_4Cl$-4); X = $BF_4$ or $PF_6$] were prepared following the procedure[6] used for the synthesis of *trans*-$[Re(CNR)_2(dppe)_2][BF_4]$. As a typical example, *trans*-$[Re(CNMe)(CNC_6H_4Cl\text{-}4)(dppe)_2][PF_6]$ was prepared from *trans*-$[ReCl(CNMe)(dppe)_2]$ in the following way. Tetrahydrofuran (thf) (50 cm$^3$) was added to a mixture of *trans*-$[ReCl(CNMe)(dppe)_2]$ (0.20 g, 0.19 mmol) with $TlPF_6$ (0.10 g, 0.29 mmol) and $CNC_6H_4Cl$-4 (0.042 g, 0.31 mmol), and the system was stirred at ambient temperature for 10 h. The undissolved thallium salts were then filtered off; concentration *in vacuo* of the filtered solution followed by addition of diethyl ether led to the precipitation of *trans*-$[Re(CNMe)(CNC_6H_4Cl\text{-}4)(dppe)_2][PF_6]$ as a yellow solid which was filtered off, washed with diethyl ether, dried *in vacuo*, and recrystallised from dichloromethane–diethyl ether (0.075 g, *ca.* 30% yield).

The carbonyl complex (**1**; L = CO; X = $BF_4$) was prepared in a related way, using $CH_2Cl_2$ as solvent. Accordingly, CO gas was bubbled for 10 min through a solution of *trans*-$[ReCl(CNMe)(dppe)_2]$ (0.210 g, 0.198 mmol) in $CH_2Cl_2$ (20 cm$^3$), in the presence of $TlBF_4$ (70 mg, 0.24 mmol), and the system was stirred for 3 h. The solution was then filtered, concentrated *in vacuo* to about 10 cm$^3$, filtered and concentrated again; the carbonyl complex was then precipitated by addition of diethyl ether as a yellow solid (contaminated with the parent complex and other products) which was recrystallised from $CH_2Cl_2$–$Et_2O$ (*ca.* 0.065 g, 30% yield).

X = Cl. The complexes with $Cl^-$ as the counter ion [**1**; L = CNR (R = Me, Bu$^t$, $C_6H_4Me$-4, Ph, $C_6H_4Cl$-4, or $C_6H_2Pr^i_3$-2,4,6) or NCMe] were prepared simply by refluxing a $CH_2Cl_2$ solution of the parent *trans*-$[ReCl(CNMe)(dppe)_2]$ complex in the presence of an excess of the appropriate isocyanide or of acetonitrile. In a typical experiment, a dichloromethane (30 cm$^3$) solution of *trans*-$[ReCl(CNMe)(dppe)_2]$ (0.20 g, 0.19 mmol) and $CNC_6H_4Me$-4 (0.025 g, 0.21 mmol) was refluxed for 2 d. Slight concentration *in vacuo* of the final solution followed by the addition of diethyl ether gave a yellow precipitate of *trans*-$[Re(CNMe)(CNC_6H_4Me\text{-}4)$-

$(dppe)_2]Cl$ which was filtered off, washed with diethyl ether, and dried *in vacuo* (*ca.* 0.15 g, 70% yield).

The acetonitrile complex (**1**; L = NCMe; X = Cl) was prepared in a similar way, by refluxing for 20 h a solution of *trans*-$[ReCl(CNMe)(dppe)_2]$ (0.230 g, 0.217 mmol) in $CH_2Cl_2$ (20 $cm^3$)–NCMe (20 $cm^3$); the solution was then filtered, slightly concentrated *in vacuo*, and the product was precipitated as a crystalline yellow solid (*ca.* 0.13 g, 55% yield) upon addition of diethyl ether.

*Syntheses of Complexes trans*-$[Re(CNR)_2(dppe)_2]Cl$ [R = Me, $C_6H_2Pr^i_3$-2,4,6 (**2**), *or* $C_6H_4OMe$-4] *from trans*-$[ReCl(N_2)(dppe)_2]$.—The di-isocyanide complexes were conveniently prepared by refluxing a dichloromethane solution of *trans*-$[ReCl(N_2)(dppe)_2]$ with an excess of the appropriate isocyanide. Less conveniently, they were also formed in refluxing thf solution, although the corresponding monoisocyanide complexes were the main products, even under more drastic conditions (extended refluxing periods and under irradiation). Typical examples are as follows.

*trans*-$[Re(CNMe)_2(dppe)_2]Cl$. A dichloromethane (50 $cm^3$) solution of *trans*-$[ReCl(N_2)(dppe)_2]$ (0.50 g, 0.48 mmol) with CNMe (0.20 $cm^3$, 4.24 mmol) was refluxed for 24 h and then concentrated *in vacuo*; addition of diethyl ether led to the precipitation of *trans*-$[Re(CNMe)_2(dppe)_2]Cl$ as a yellow solid which was filtered off, washed with diethyl ether, and dried *in vacuo* (*ca.* 0.40 g, 70% yield).

*trans*-$[Re(CNC_6H_4OMe\text{-}4)_2(dppe)_2]Cl$. The isocyanide $CNC_6H_4OMe$-4 (0.185 g, 1.39 mmol) was added to a suspension of *trans*-$[ReCl(N_2)(dppe)_2]$ (0.254 g, 0.242 mmol) in thf (35 $cm^3$) and the mixture was refluxed under argon for 18 d (irradiation by a 150-W tungsten-filament bulb was maintained for 8 d). The resulting yellow solid of *trans*-$[Re(CNC_6H_4OMe\text{-}4)_2(dppe)_2]Cl$ was filtered off, washed with thf–pentane, and dried *in vacuo*; a further crop could be obtained from the filtered solution by addition of pentane followed by cooling (total yield *ca.* 0.030 g, *ca.* 10%). Concentration of the mother-liquor and cooling led to precipitation of the monoisocyanide complex *trans*-$[ReCl(CNC_6H_4OMe\text{-}4)(dppe)_2]$[5] which was the main product (*ca.* 0.070 g, 25% yield).

## Appendix 1

*Estimate of* $E_s$ *and* β *for* $\{Re(CNR)(dppe)_2\}^+$.—By definition of $E_s$ [equation (3)] for $\{Re(CNR)(dppe)_2\}^+$ [equation (A1)] followed by the application of expression (1), one obtains equation (A2) or, by considering the known[6] values of $E_s$ and β for $\{Re(CO)(dppe)_2\}^+$, the derived form (A3) which allows one to estimate the electron richness for that site (the values are given in Table 4).

$$E_s\{\mathrm{Re(CNR)(dppe)_2}\}^+ = E_{\frac{1}{2}}^{\mathrm{ox}}[\mathrm{Re(CNR)(CO)(dppe)_2}]^+ \quad \text{(A1)}$$

$$E_s\{\mathrm{Re(CNR)(dppe)_2}\}^+ = E_s\{\mathrm{Re(CO)(dppe)_2}\}^+ + \beta\{\mathrm{Re(CO)(dppe)_2}\}^+ \,.\, P_L{}^1(\mathrm{CNR}) \quad \text{(A2)}$$

$$E_s\{\mathrm{Re(CNR)(dppe)_2}\}^+ = 1.42 + 0.62\, P_L{}^1(\mathrm{CNR}) \quad \text{(A3)}$$

Moreover, the polarisability of the site, $\beta\{Re(CNR)(dppe)_2\}^+$, may be estimated from equation (A4) derived from the application of expression (1) to the $[ReCl(CNR)(dppe)_2]$ complexes, with known[5] redox potentials, and the values obtained are also presented in Table 4.

$$\beta\{\mathrm{Re(CNR)(dppe)_2}\}^+ = \frac{E_{\frac{1}{2}}^{\mathrm{ox}}[\mathrm{ReCl(CNR)(dppe)_2}] - E_s\{\mathrm{Re(CNR)(dppe)_2}\}^+}{P_L(\mathrm{Cl^-})} \quad \text{(A4)}$$

Hence, the parameters $E_s$ and β for the isocyanide centres $\{Re(CNR)(dppe)_2\}^+$ have been estimated by considering the knowledge of those parameters for an auxiliary site, $\{Re(CO)(dppe)_2\}^+$,[6] and of the redox potentials of a series of complexes[5] with the former site and an auxiliary ligand ($Cl^-$), *i.e.* *trans*-$[ReCl(CNR)(dppe)_2]$.

## Appendix 2

*Deduction of Expression* (15).—Assuming that $P_L$ is independent of the metal site, from the application of equation (1) to each of the $[M'_sL(L')]$, $[M'_sL_2]$, or $[M'_sL'_2]$ complexes (where $\{M'_s\}$ stands for a 14-electron square-planar metal site), one obtains expressions (A5)—(A8).

$$E_{\frac{1}{2}}^{\mathrm{ox}}[M'_sL(L')] = E_s\{M'_sL\} + \beta\{M'_sL\}\,.\,P_L(L') \quad \text{(A5)}$$

$$E_{\frac{1}{2}}^{\mathrm{ox}}[M'_sL(L')] = E_s\{M'_sL'\} + \beta\{M'_sL'\}\,.\,P_L(L) \quad \text{(A6)}$$

$$E_{\frac{1}{2}}^{\mathrm{ox}}[M'_sL_2] = E_s\{M'_sL\} + \beta\{M'_sL\}\,.\,P_L(L) \quad \text{(A7)}$$

$$E_{\frac{1}{2}}^{\mathrm{ox}}[M'_sL'_2] = E_s\{M'_sL'\} + \beta\{M'_sL'\}\,.\,P_L(L') \quad \text{(A8)}$$

By comparing the expressions resulting from the combinations (A5) + (A6) and (A7) + (A8), equation (15) is obtained provided the metal sites $\{M'_sL\}$ and $\{M'_sL'\}$ have identical β values [equation (16)], *i.e.* the redox potential of their complexes is similarly affected by a change of the variable axial ligand.

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