Reactions of the Multiply Bonded Dirhenium Complexes $[Re_2X_4(L{-}L)_2]^{n+}$ (X = Cl or Br, L–L = $Ph_2PCH_2CH_2PPh_2$ or $Ph_2PCH_2CH_2AsPh_2$; *n* = 0 or 1) with Isocyanides and Nitriles. Reaction without Metal–Metal Bond Disruption†

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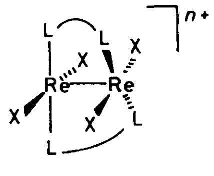
The reaction of paramagnetic $[Re_2X_4(L{-}L)_2]PF_6$ with RNC (X = Cl or Br, L–L = $Ph_2PCH_2CH_2PPh_2$ or $Ph_2PCH_2CH_2AsPh_2$, R = Pr^i or Bu^t) proceeds with reduction of the dirhenium core to yield the diamagnetic complexes $[Re_2X_3(L{-}L)_2(CNR)]PF_6$. These isocyanide-containing compounds can be oxidized to the paramagnetic dications using $NOPF_6$ as the oxidant. The reactions of complexes $[Re_2X_4(L{-}L)_2]PF_6$ with nitriles RCN (R = Me or Et) in the presence of $TlPF_6$ yield the paramagnetic complexes $[Re_2X_3(L{-}L)_2(NCR)][PF_6]_2$, which can be reduced to the corresponding monocations using $LiBEt_3H$ or cobaltocene as the reductants. The staggered rotational geometry of the parent complexes $[Re_2X_4(L{-}L)_2]^{n+}$ (*n* = 0 or 1) is believed to be retained in $[Re_2X_3(L{-}L)_2(CNR)]^{n+}$ and $[Re_2X_3(L{-}L)_2(NCR)]^{n+}$ (*n* = 1 or 2).

Most multiply bonded dimetal complexes are readily cleaved by π-acceptor ligands such as CO, NO, RNC (R = alkyl), and R′NC (R′ = aryl).[1,2] We have made use of this reactivity to develop procedures for the synthesis of homoleptic mononuclear isocyanide complexes of molybdenum,[3–6] tungsten,[4–6] rhenium,[7–9] ruthenium,[10] and osmium,[10] and of some related carbonyl[11] and nitrosyl[12] derivatives. Quite recently, we have discovered that the triply bonded phosphine-bridged complex $[Re_2Cl_4(dppm)_2]$ (dppm = $Ph_2PCH_2PPh_2$),[13,14] reacts with CO,[15] RNC,[16] and RCN[17] ligands (R = alkyl) to afford dirhenium complexes in which a metal–metal bond is preserved. The interesting results which have emerged from these studies[15–17] prompt us to report the nature of the products that are formed upon reacting the triply bonded dirhenium(II) complexes $[Re_2X_4(dppe)_2]$ and $[Re_2X_4(dpadppe)_2]$ (X = Cl or Br; dppe = $Ph_2PCH_2CH_2PPh_2$, dpadppe = $Ph_2PCH_2CH_2AsPh_2$) with isocyanide (RNC) and nitrile (RCN) ligands. Some of these results have been the subject of a preliminary communication.[16]

Results and Discussion

The dirhenium(II) complexes $[Re_2X_4(L{-}L)_2]$ (X = Cl or Br, L–L = dppe or dpadppe) possess a Re–Re triple bond ($\sigma^2\pi^4\delta^2\delta^{*2}$ electronic configuration) and a staggered rotational geometry as depicted in (I) (*n* = 0 or 1).[1,18,19] We had



(I)

reasoned that because of the stability of the six-membered $\overline{Re{-}Re{-}PCH_2CH_2P}$ and $\overline{Re{-}Re{-}PCH_2CH_2As}$ rings, these complexes might resist Re≡Re bond cleavage upon reaction with CO and RNC ligands, in contrast to the situation with the analogous, kinetically labile, dirhenium(II) species $[Re_2X_4L_4]$ (L = unidentate phosphine).[2,7,11] This has proven to be the case. Essentially no reaction occurs between $[Re_2X_4(L{-}L)_2]$ and CO or RNC (or even RCN) over periods of 2—24 h. However, since this lack of reactivity may reflect in part the poor solubility properties of the starting complexes, we explored the reactions of their more soluble one-electron oxidized congeners $[Re_2X_4(L{-}L)_2]PF_6$ ($\sigma^2\pi^4\delta^2\delta^{*1}$ electronic configuration).[20] These species react smoothly with isocyanides RNC (R = Pr^i or Bu^t) and with nitriles RCN (R = Me or Et) to give products in which a Re–Re multiple bond is preserved. No reaction with CO was observed, even in the presence of $TlPF_6$ (added in an attempt to labilize a Re–X bond).

(*a*) *Isocyanide Complexes*.—The green-brown air-stable complexes $[Re_2X_3(L{-}L)_2(CNR)]PF_6$ (X = Cl or Br, L–L = dppe or dpadppe, R = Pr^i or Bu^t) were isolated in quite high yield upon reacting (I) (*n* = 1) with 2—4 mol equiv. of RNC (see Experimental section) in CH_2Cl_2. These complexes resist further reaction with excess RNC or with nitriles RCN (under reflux). Accordingly, they represent a rare instance of a group of stable multiply bonded dimetal species that contain co-ordinated isocyanide ligands.

Solutions of these complexes behave as 1:1 electrolytes in acetone (Λ_m = 90—120 Ω^{-1} cm^2 mol^{-1} for $c_m = 1 \times 10^{-3}$ mol dm^{-3}) and their i.r. spectra (Nujol mull and CH_2Cl_2 solution) show a single, sharp ν(C≡N) mode (2 140–2 160 cm^{-1}). The integrated intensities for the dppe (or dpadppe) and RNC resonances in the ^1H n.m.r. spectra of these complexes (measured in CD_2Cl_2 or $CDCl_3$) are in accord with the proposed stoicheiometry. These data, along with electrochemical properties, are summarized in Table 1.

Cyclic voltammetric measurements on solutions of these complexes in 0.2 mol dm^{-3} tetra-n-butylammonium hexafluorophosphate–dichloromethane show the presence of a couple at $E_{\frac{1}{2}} \simeq +0.65$ V *vs.* Ag/AgCl, which corresponds to a one-electron oxidation, together with an irreversible reduction at $E_{p,c} \simeq -1.5$ V *vs.* Ag/AgCl (see Table 1 and Figure 1). The one-electron oxidation can be accomplished chemically by treating dichloromethane solutions of $[Re_2X_3(L{-}L)_2(CNR)]PF_6$ with one mol equiv. of $NOPF_6$. This procedure was used to prepare samples of the dppe complexes $[Re_2X_3(dppe)_2(CNR)][PF_6]_2$ (X = Cl or Br, R = Pr^i or Bu^t). Solutions of the resulting dark brown salts in 0.2 mol dm^{-3} $[NBu^n{}_4]PF_6$–CH_2Cl_2 display the expected cyclic voltammograms; the reversible process at +0.65 V now corresponds to a one-electron reduction (Figure 1). Dichloromethane solutions of $[Re_2X_3(dppe)_2(CNR)][PF_6]_2$

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† *Non-S.I. units employed:* G = 10^{-4} T, B.M. = 9.274×10^{-24} J T^{-1}.

Table 1. Spectroscopic and electrochemical properties of $[Re_2X_3(L\text{–}L)_2(CNR)]^{n+}$ (X = Cl or Br, L–L = dppe or dpadppe, R = Pr^i or Bu^t, n = 1 or 2)

Complex	I.r.,[a] $\nu(C{\equiv}N)/cm^{-1}$	^1H N.m.r.,[b] $\delta(CNR)$/p.p.m.	Half-wave potentials[c] (1) $E_{\frac{1}{2}}$	(2) $E_{p,c}$
$[Re_2Cl_3(dppe)_2(CNBu^t)]PF_6$	2 157s 2 147s[d]	0.80 (s)[e]	+0.62 (ox)	−1.4
$[Re_2Br_3(dppe)_2(CNBu^t)]PF_6$	2 155s 2 145s[d]	0.91 (s)	+0.67 (ox)	−1.4
$[Re_2Cl_3(dpadppe)_2(CNBu^t)]PF_6$	2 145s 2 149s[d]	0.69 (s)	+0.59 (ox)	−1.5
$[Re_2Br_3(dpadppe)_2(CNBu^t)]PF_6$	2 141s 2 145s[d]	0.80 (s)	+0.66 (ox)	−1.5
$[Re_2Cl_3(dppe)_2(CNPr^i)]PF_6$	2 155s 2 155s[d]	0.66 (d), 3.60 (m)[e]	+0.62 (ox)	−1.5
$[Re_2Br_3(dppe)_2(CNPr^i)]PF_6$	2 155s 2 155s[d]	0.83 (d), 3.45 (m)	+0.68 (ox)	−1.45
$[Re_2Cl_3(dppe)_2(CNBu^t)][PF_6]_2$	2 166s	[f]	+0.62 (red)	−1.4
$[Re_2Br_3(dppe)_2(CNBu^t)][PF_6]_2$	2 161s	[f]	+0.68 (red)	−1.4
$[Re_2Cl_3(dppe)_2(CNPr^i)][PF_6]_2$	2 178s	[f]	+0.60 (red)	−1.5
$[Re_2Br_3(dppe)_2(CNPr^i)][PF_6]_2$	2 172s	[f]	+0.68 (red)	−1.45

[a] Nujol mull unless stated otherwise. [b] Spectra recorded in CD_2Cl_2 unless stated otherwise, with the resonances of the isocyanide ligand referenced internally to the residual protons of the solvent (δ 5.35 p.p.m.). [c] Measured on 0.2 mol dm^{-3} $[NBu^n_4]PF_6$–CH_2Cl_2 solutions by the cyclic voltammetric technique (V *vs.* Ag/AgCl). Scan rate ν = 200 mV s^{-1}. [d] CH_2Cl_2 solution. [e] Spectra recorded in $CDCl_3$ (referenced to residual protons of solvent, δ 7.32 p.p.m.). [f] Paramagnetic complex.

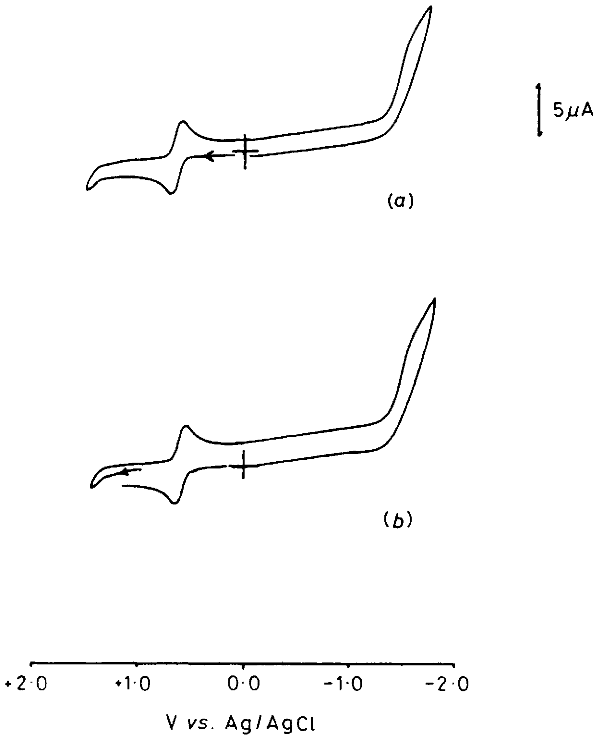

Figure 1. Cyclic voltammograms (scan rate 200 mV s^{-1} at a platinum-bead electrode) in 0.2 mol dm^{-3} $[NBu^n_4]PF_6$–CH_2Cl_2 of (*a*) $[Re_2Cl_3(dppe)_2(CNBu^t)]PF_6$ and (*b*) $[Re_2Cl_3(dppe)_2(CNBu^t)][PF_6]_2$

have magnetic moments of *ca.* 1.4 B.M. as measured by the Evans method.[21] *X*-Band e.s.r. spectral measurements (CH_2Cl_2 glass at −160 °C) show that all four complexes possess very similar spectral properties, with a complex broad signal between 1 250 and 5 000 G which reflects the low symmetry of these molecules and hyperfine coupling to the phosphorus and rhenium nuclei.[20]

Oxidation of the Re_2^{4+} core to Re_2^{5+} results in a shift of the $\nu(C{\equiv}N)$ mode to higher energy by up to 20 cm^{-1} (Table 1). The sense of this shift accords with the expected decrease in π back-bonding (from Re_2^{n+} to RNC) as the metal oxidation state increases. Another spectral change is seen in the electronic absorption spectra (Figure 2). Dichloromethane solutions of $[Re_2X_3(L\text{–}L)_2(CNR)]PF_6$ have two characteristic absorption maxima ($\lambda_{max.}$) at 700—630 nm (ε *ca.* 150) and 475—460 nm (ε *ca.* 10^3). Their oxidized congeners possess bands at $\lambda_{max.} \simeq 900$ nm (ε *ca.* 400) and $\lambda_{max.} \simeq 540$ nm (ε *ca.* 10^3). The band at 900 nm is assigned to the δ→δ* transition of the Re_2^{5+} core; this is expected to be observed at quite low energy.[1,22–24]

(*b*) *Nitrile Complexes.*—The nitrile-substituted derivative of (**I**) cannot be prepared *via* direct reaction with hot acetonitrile or propionitrile. However, in the presence of $TlPF_6$ the purple mononitrile species $[Re_2X_3(L\text{–}L)_2(NCR)][PF_6]_2$ (X = Cl or Br, L–L = dppe or dpadppe, R = Me or Et) were formed in good yield. The TlX which precipitates can be removed by filtration and the product isolated through slow addition of diethyl ether to the filtrate. This is a non-reductive process since both the starting material and the product are derivatives of the Re_2^{5+} core. Thus the difference in reaction between RNC and RCN towards (**I**) (n = 1) presumably reflects the greater reducing power of the isocyanide ligands.

As far as we can tell, these complexes must be close structural analogues of the isocyanide-containing species $[Re_2X_3(L\text{–}L)_2(CNR)][PF_6]_2$. Their *X*-band e.s.r. spectra (CH_2Cl_2 glass at −160 °C) are very similar to those of the corresponding isocyanide complexes.* Their electronic absorption spectra (in CH_2Cl_2) show a band at $\lambda_{max.} \simeq 1\,200$ nm (ε *ca.* 200—300) due to the δ→δ* transition, as well as other transitions at $\lambda_{max.}$ = 700—650 (ε *ca.* 200) and $\lambda_{max.}$ = 570—525 (ε *ca.* 800). The i.r.-active $\nu(C{\equiv}N)$ mode of these nitrile complexes was too weak to be observed, with the exception of the i.r. spectrum of $[Re_2Cl_3(dppe)_2(NCEt)][PF_6]_2$ [$\nu(C{\equiv}N)$ at 2 250 cm^{-1}]. This result is

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* The poor solubility properties of $[Re_2X_3(L\text{–}L)_2(NCR)][PF_6]_2$ in suitable solvents precluded the determination of accurate magnetic moments by the Evans method.

Table 2. ^{1}H N.m.r. spectroscopic and electrochemical properties of $[Re_2X_3(L\text{-}L)_2(NCR)]^{n+}$ (X = Cl or Br, L-L = dppe or dpadppe, R = Me or Et, *n* = 1 or 2)

Complex	^{1}H N.m.r.,[a] δ(RCN)/p.p.m.	Half-wave potentials[b] (1) $E_{\frac{1}{2}}$	(2) $E_{p,c}$
$[Re_2Cl_3(dppe)_2(NCMe)]PF_6$	1.70 (s)[c]	+0.53 (ox)	−1.5
$[Re_2Br_3(dppe)_2(NCMe)]PF_6$	1.85 (s)	+0.58 (ox)	−1.5
$[Re_2Cl_3(dppe)_2(NCEt)]PF_6$	0.44 (t), 1.65 (q)	+0.51 (ox)	−1.5
$[Re_2Br_3(dpadppe)_2(NCMe)]PF_6$	2.32 (s)	+0.59 (ox)	−1.45
$[Re_2Cl_3(dppe)_2(NCMe)][PF_6]_2$	*d*	+0.53 (red)	−1.5
$[Re_2Br_3(dppe)_2(NCMe)][PF_6]_2$	*d*	+0.60 (red)	−1.5
$[Re_2Cl_3(dppe)_2(NCEt)][PF_6]_2$	*d*	+0.50 (red)	−1.5
$[Re_2Br_3(dpadppe)_2(NCMe)][PF_6]_2$	*d*	+0.60 (red)	−1.45

[a] Spectra recorded in CD_2Cl_2 unless stated otherwise, with the resonances of the nitrile ligand referenced internally to the residual protons of the solvent (δ 5.35 p.p.m.). [b] Measured on 0.2 mol dm^{-3} $[NBu^n{}_4]PF_6$–CH_2Cl_2 solutions by the cyclic voltammetric technique (V *vs.* Ag/AgCl). Scan rate v = 200 mV s^{-1}. [c] Spectra recorded in $CDCl_3$ (referenced to residual protons of solvent, δ 7.32 p.p.m.). [d] Paramagnetic complex.

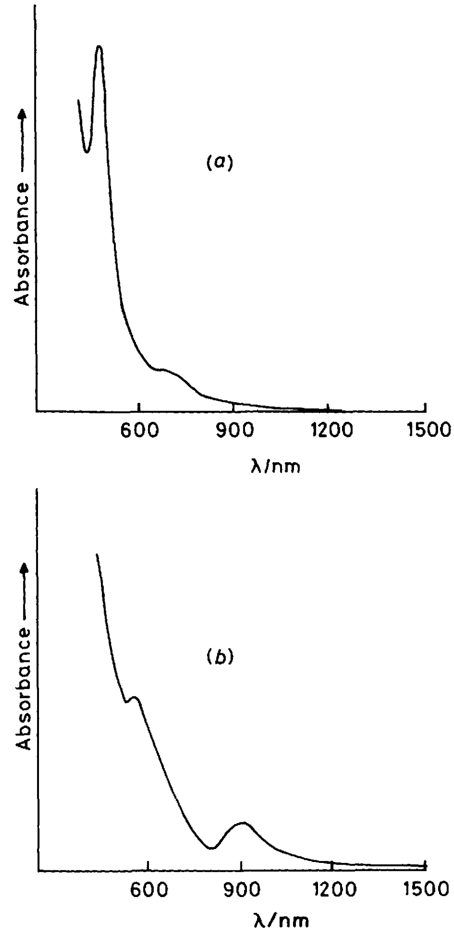


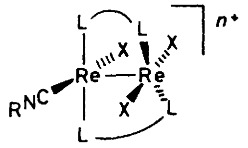
Figure 2. Electronic absorption spectra (1 × 10^{-3} mol dm^{-3} dichloromethane solution) of (*a*) $[Re_2Cl_3(dppe)_2(CNBu^t)]PF_6$ and (*b*) $[Re_2Cl_3(dppe)_2(CNBu^t)][PF_6]_2$

not surprising since we have also failed to observe ν(C≡N) in the i.r. spectra of $[Re_2Cl_3(dppm)_2(NCR)_2]PF_6$ (dppm = $Ph_2PCH_2PPh_2$).[17]

Acetone solutions (*ca.* 1 × 10^{-3} mol dm^{-3}) of these complexes have conductivities typical of those expected for a 1:2 electrolyte (Λ_m = 170—200 Ω^{-1} cm^2 mol^{-1}). In 0.2 mol dm^{-3} $[NBu^n{}_4]PF_6$–CH_2Cl_2, cyclic voltammetry revealed a reversible one-electron reduction ($E_{\frac{1}{2}} \simeq +0.55$ V *vs.* Ag/AgCl) together with a second, irreversible, process at $E_{p,c} \simeq -1.5$ V *vs.* Ag/AgCl (Table 2). The shift of the first couple to more negative potentials, relative to $[Re_2X_3(L\text{-}L)_2(CNR)]^{2+/1+}$, is a further reflection of the superior electron-withdrawing capability of RNC over RCN as far as the metal centre(s) is concerned. The chemical reduction of the dicationic nitrile complexes to $[Re_2X_3(L\text{-}L)_2(NCR)]^+$ can be achieved using $LiBEt_3H$ (or cobaltocene) as the reducing agent. The green monocationic salts now exhibit a reversible one-electron oxidation and an irreversible reduction in their cyclic voltammograms (Table 2), and they behave as 1:1 electrolytes in acetone (Λ_m = 115—140 Ω^{-1} cm^2 mol^{-1} for c_m *ca.* 1 × 10^{-3} mol dm^{-3}). These complexes are diamagnetic and have consistent ^{1}H n.m.r. spectra (Table 2) whose integrated intensity ratios (RCN to dppe or dpadppe) are in excellent accord with the stoicheiometry $[Re_2X_3(L\text{-}L)_2(NCR)]PF_6$. Their electronic absorption spectra resemble quite closely the related spectra of their monoisocyanide analogues [in CH_2Cl_2, $\lambda_{max.}$ = 680—650 nm (ε *ca.* 120) and 545—510 nm (ε *ca.* 220)].

In other studies of the reactivity of the dications, we found that while 4-methylpyridine brought about reduction to the monocation no reaction was observed with $TlPF_6$/RCN, excess RNC, or CO, at least in so far as we could judge using ^{1}H n.m.r. and i.r. spectroscopies.

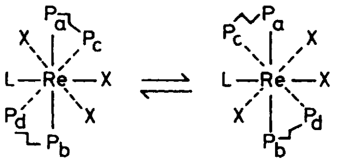
Structural Considerations.—The striking similarity between the spectroscopic and electrochemical properties of the monoisocyanide and mononitrile complexes implies a close similarity in structure. Since the properties of these complexes are in turn similar to those of the parent compounds $[Re_2X_4(L\text{-}L)_2]$ (**I**), we believe that they maintain the original staggered $Re_2X_4L_4$ skeleton, with one of the halide ligands replaced by an isocyanide or a nitrile, (**II**). Whereas (**I**) (*n* = 0) possesses two reversible one-electron oxidations ($E_{\frac{1}{2}}$ *ca.* +0.25 V and *ca.* +1.0 V *vs.* a saturated calomel electrode as measured by cyclic voltammetry),[20] we find that (**II**) (*n* = 1) exhibits a one-electron oxidation ($E_{\frac{1}{2}}$ *ca.* +0.65 V *vs.* Ag/AgCl) and an irreversible reduction at *ca.* −1.5 V (a one-electron process



(**II**)

based upon a consideration of current). Therefore, in the case of (**II**) the redox processes are shifted to more positive potentials compared to the isoelectronic parent complex (**I**). This leads to the disappearance of the second oxidation [it presumably shifts to a potential just above that accessed by our measurements (*ca.* +1.7 V)] and the detection of a reduction within the solvent limits. This behaviour is analogous to that seen in the conversion of $[Re_2Cl_4(dppm)_2]$ (two, one-electron oxidations) to the bis-nitrile derivatives $[Re_2Cl_3(dppm)_2(NCR)_2]^+$ (one oxidation and one reduction).[17] Indeed, the electrochemical properties of (**II**) resemble closely those reported for $[Re_2Cl_3(dppm)_2(NCR)_2]^+$.

In spite of the basic structural similarity within the series of complexes $[Re_2X_3(L\text{–}L)_2(CNR)]^+$ and $[Re_2X_3(L\text{–}L)_2(NCR)]^+$, we do observe some differences in solution dynamics. The $^{31}P\text{-}\{^1H\}$ spectra of $[Re_2X_3(dppe)_2(CNBu^t)]PF_6$ (X = Cl or Br) consist of two broad singlets in a 1:1 intensity ratio due to the bridging dppe ligands (Table 3). This result is consistent with our structural assignment (**II**) provided there is a fluxional process which renders the two sides of the molecule equivalent. Tentatively, we propose that this process involves a twisting motion about the Re–Re bond as depicted below. If this interconversion is rapid on the n.m.r. time-scale, then the molecule will possess an apparent plane of symmetry containing L, the halide *trans* to L, and the two rhenium atoms. Two sets of equivalent phosphorus nuclei will result: (P_a,P_b) and (P_c,P_d). The $^{31}P\text{-}\{^1H\}$ n.m.r spectrum will be that of an AA′BB′ type if large coupling (with respect to chemical shift difference) between (P_a,P_b) and (P_c,P_d) is present. If such coupling is small, then an AA′XX′ pattern will result. Since there is no observable coupling between A and X, then two singlets corresponding to $\nu_A(P_a,P_b)$ and $\nu_X(P_c,P_d)$ will be seen.



The same mirror plane which leads to the equivalence of the phosphorus nuclei will also be reflected by a simplification in the ^1H n.m.r. spectrum of the methylene groups of the dppe ligands. This will lead to two types of methylene protons in the ^1H n.m.r. as is observed (Table 3). The signals are very broad due to coupling with the phosphorus nuclei and the interconversion of the 'axial' and 'equatorial' protons present on each methylene group.

As exchange is slowed, the mirror plane present in the fast-exchange limit is no longer present and all phosphorus nuclei are chemically inequivalent. This will manifest itself in a second-order $^{31}P\text{-}\{^1H\}$ spectrum, because of the large P–P coupling present $[^2J_{P\text{–}P}\ (trans)]$. Such spectra could appear as triplets as is observed for the other dppe complexes for which $^{31}P\text{-}\{^1H\}$ n.m.r. spectra have been recorded (Table 3). The ^1H n.m.r. spectra in the $\text{–}CH_2CH_2\text{–}$ region will be complex as all eight CH_2 protons are now inequivalent. If the assumption is made that the chemical shifts of the protons for each methylene group are similar, then four broad resonances will be seen, as we have observed (Table 3).

Conclusions

Complex cations of the types $[Re_2X_3(L\text{–}L)_2(CNR)]^{n+}$ and $[Re_2X_3(L\text{–}L)_2(NCR)]^{n+}$ (X = Cl or Br, L–L = dppe or dpadppe, R = Pr^i or Bu^t for RNC and R = Me or Et for RCN, *n* = 1 or 2) represent a new group of species that expand considerably the known substitution chemistry of the multiply bonded Re_2^{4+} and Re_2^{5+} cores. The isolation of the stable isocyanide complexes provides an insight into the intermediates that may be formed in the cleavage of many multiply bonded dimetal complexes by isocyanides and other π-acceptor ligands.[1,2]

Experimental

Starting Materials.—The complexes $[Re_2X_4(L\text{–}L)_2]PF_6$ (X = Cl or Br, L–L = dppe or dpadppe) were prepared according to the literature method which involves oxidation of $[Re_2X_4(L\text{–}L)_2]$ by NO^+.[20] The neutral $[Re_2X_4(L\text{–}L)_2]$ complexes are most conveniently synthesized by displacement of PPr^n_3 from $[Re_2X_4(PPr^n_3)_4]$ using dppe or dpadppe.[18] The Pr^iNC and Bu^tNC ligands were prepared using the standard literature method.[25] The nitriles, along with solvents used in the preparation of the complexes, were of commercial grade and were thoroughly deoxygenated and/or distilled prior to use. The dppe and dpadppe ligands were purchased from Strem Chemicals and used without further purification.

Reaction Procedures.—All reactions were performed under a nitrogen atmosphere using standard vacuum-line techniques.

A. Monoisocyanide Complexes.—(*i*) $[Re_2Cl_3(dppe)_2(CNBu^t)]PF_6$. In a typical reaction, $[Re_2Cl_4(dppe)_2]PF_6$ (0.10 g, 0.07 mmol) was dissolved in dichloromethane (5 cm^3). The purple solution immediately turned green-brown upon the addition of 4 mol equiv. of Bu^tNC (29 μl, 0.28 mmol). The resulting solution was stirred at room temperature for 1 h. The crude product was precipitated from the reaction solution by the addition of diethyl ether (20 cm^3). The green-brown product was purified by dissolving it in an acetone solution (5 cm^3) containing KPF_6 (0.050 g). The acetone was removed by

Table 3. $^{31}P\text{-}\{^1H\}$ and ^1H n.m.r. spectra of $[Re_2X_3(dppe)_2(CNR)]^+$ and $[Re_2X_3(dppe)_2(NCR)]^+$ (X = Cl or Br, R = Pr^i or Bu^t for RNC and R = Me for RCN)

Complex	$^{31}P\text{-}\{^1H\}$,[a] δ/p.p.m.	^1H,[b] δ/p.p.m.
$[Re_2Cl_3(dppe)_2(CNBu^t)]PF_6$	−1.05 (s), −15.42 (s)	3.93, 3.06[c]
$[Re_2Br_3(dppe)_2(CNBu^t)]PF_6$	−8.15 (s), −11.55 (s)	3.84, 2.99[d]
$[Re_2Cl_3(dppe)_2(CNPr^i)]PF_6$	−2.19 (t), −3.05 (t)	~4.3, ~4.1, ~3.9, ~3.2
$[Re_2Cl_3(dppe)_2(NCMe)]PF_6$	+0.04 (t), −0.84 (t)	4.60, ~3.7, ~3.1, ~2.75
$[Re_2Br_3(dppe)_2(NCMe)]PF_6$	+1.51 (t), −5.10 (t)[e]	4.55, 3.85, 3.05, 2.85[d]

[a] Recorded in $[^2H_6]$acetone with aqueous 85% H_3PO_4 as an external standard; under these conditions PF_6^- was used as an internal reference (δ −144.76 p.p.m.). [b] Recorded in $CDCl_3$ unless stated otherwise. Data are for the $\text{–}CH_2CH_2\text{–}$ resonances; the ^1H n.m.r. spectral data for the co-ordinated RNC and RCN ligands are given in Tables 1 and 2. [c] Essentially the same spectrum was observed in CD_2Cl_2. In this latter solvent no temperature dependence of the spectrum was observed down to *ca.* −80 °C. [d] Recorded in CD_2Cl_2. [e] An additional resonance at δ −0.26 p.p.m. is attributed to an impurity.

evaporation and the residue extracted with dichloromethane. The extract was filtered to remove any excess of KPF_6 and diethyl ether was slowly added to the filtrate to precipitate the desired product. It was filtered off, washed with diethyl ether and dried *in vacuo*; yield 0.077 g, 75% (Found: C, 45.1; H, 4.1; Cl, 6.8. $C_{57}H_{57}Cl_3F_6NP_5Re_2$ requires C, 45.5; H, 3.8; Cl, 6.7%).

The following three Bu^{t}NC complexes were prepared by using a similar procedure to that described above.

(*ii*) $[Re_2Br_3(dppe)_2(CNBu^t)]PF_6$. Yield 72% (Found: C, 42.2; H, 4.3. $C_{57}H_{57}Br_3F_6NP_5Re_2$ requires C, 41.8; H, 3.5%).

(*iii*) $[Re_2Cl_3(dpadppe)_2(CNBu^t)]PF_6$. Yield 71% (Found: C, 43.2; H, 4.0; Cl, 7.3. $C_{57}H_{57}As_2Cl_3F_6NP_3Re_2$ requires C, 43.0; H, 3.6; Cl, 6.7%).

(*iv*) $[Re_2Br_3(dpadppe)_2(CNBu^t)]PF_6$. Yield 68% (Found: C, 40.1; H, 3.75. $C_{57}H_{57}As_2Br_3F_6NP_3Re_2$ requires C, 39.65; H, 3.3%).

(*v*) $[Re_2Cl_3(dppe)_2(CNPr^i)]PF_6$. Synthesis of this complex involved the addition of 2.5 mol equiv. of Pr^{i}NC (15.6 μl, 0.17 mmol) to a dichloromethane solution (5 cm^3) of $[Re_2Cl_4(dppe)_2]PF_6$ (0.10 g, 0.07 mmol). Work-up of the resulting green solution was similar to the procedure described in *A*(*i*); yield 0.056 g, 55% (Found: C, 44.9; H, 4.3. $C_{56}H_{55}Cl_3F_6NP_5Re_2$ requires C, 45.1; H, 3.7%).

(*vi*) $[Re_2Br_3(dppe)_2(CNPr^i)]PF_6$. This complex was prepared using a procedure similar to that in *A*(*v*). Yield 53% (Found: C, 41.7; H, 4.3. $C_{56}H_{55}Cl_3F_6NP_5Re_2$ requires C, 41.3; H, 3.4%).

(*vii*) $[Re_2Cl_3(dppe)_2(CNBu^t)][PF_6]_2$. A quantity of $[Re_2Cl_3(dppe)_2(CNBu^t)]PF_6$ (0.10 g, 0.066 mmol) was dissolved in dichloromethane (5 cm^3) at 0 °C. To this chilled solution was added 1.5 mol equiv. of $NOPF_6$ (0.018 g, 0.10 mmol). Evolution of NO(g), accompanied by a change in colour from green-brown to dark brown, occurred immediately. The solution was warmed to room temperature and stirred for 0.5 h. The brown product was precipitated from solution by the addition of diethyl ether (20 cm^3). It was collected, washed with diethyl ether and dried *in vacuo*; yield 0.069 g, 63% (Found: C, 41.5; H, 3.5. $C_{57}H_{57}Cl_3F_{12}NP_6Re_2$ requires C, 41.3; H, 3.7%).

The following three complexes were prepared by using a similar procedure to that described in *A*(*vii*).

(*viii*) $[Re_2Br_3(dppe)_2(CNBu^t)][PF_6]_2$. Yield 65% (Found: C, 38.3; H, 3.7. $C_{57}H_{57}Br_3F_{12}NP_6Re_2$ requires C, 38.4; H, 3.2%).

(*ix*) $[Re_2Cl_3(dppe)_2(CNPr^i)][PF_6]_2$. Yield 42%. The identity of this product was based upon its spectroscopic and electrochemical properties.

(*x*) $[Re_2Br_3(dppe)_2(CNPr^i)][PF_6]_2$. Yield 42%. The identity of this product was based upon its spectroscopic and electrochemical properties.

B. Mononitrile Complexes.—(*i*) $[Re_2Cl_3(dppe)_2(NCMe)][PF_6]_2$. In a typical reaction, $[Re_2Cl_4(dppe)_2]PF_6$ (0.10 g, 0.07 mmol) and $TlPF_6$ (0.024 g, 0.07 mmol) were dissolved in 5 cm^3 of acetonitrile. The purple solution was stirred at room temperature for 12 h. The TlCl which had precipitated was removed by filtration. Slow addition of diethyl ether (50 cm^3) yielded the purple product in crystalline form. It was collected, washed with diethyl ether and dried *in vacuo*; yield 0.066 g, 60% (Found: C, 40.7; H, 3.6; Cl, 6.5. $C_{54}H_{51}Cl_3F_{12}NP_6Re_2$ requires: C, 40.35; H, 3.2; Cl, 6.6%).

The following three complexes were prepared using a similar procedure to that described in *B*(*i*).

(*ii*) $[Re_2Br_3(dppe)_2(NCMe)][PF_6]_2$. Yield 55% (Found: C, 37.5; H, 3.7. $C_{54}H_{51}Br_3F_{12}NP_6Re_2$ requires C, 37.3; H, 3.0%).

(*iii*) $[Re_2Cl_3(dppe)_2(NCEt)][PF_6]_2$. Yield 45% (Found: C, 40.9; H, 3.7; Cl, 6.1. $C_{55}H_{53}Cl_3F_{12}NP_6Re_2$ requires C, 40.75; H, 3.3; Cl, 6.6%).

(*iv*) $[Re_2Br_3(dpadppe)_2(NCMe)][PF_6]_2$. Yield 71% (Found: C, 36.0; H, 3.0. $C_{54}H_{51}As_2Br_3F_{12}NP_4Re_2$ requires C, 35.5; H, 2.8%).

(*v*) $[Re_2Cl_3(dppe)_2(NCMe)]PF_6$. A solution of $[Re_2Cl_3(dppe)_2(NCMe)][PF_6]_2$ (0.1 g, 0.062 mmol) in 5 cm^3 of tetrahydrofuran (thf) was treated with one mol equiv. of $LiBEt_3H$ in thf. The purple solution turned green-brown within minutes of stirring at room temperature. The reaction solution was stirred for 0.5 h. The green-brown product was precipitated by the addition of diethyl ether (20 cm^3). The crude solid was recrystallized from dichloromethane–diethyl ether. It was collected, washed with diethyl ether and dried *in vacuo*; yield 0.065 g, 72% (Found: C, 44.3; H, 4.1. $C_{54}H_{51}Cl_3F_6NP_5Re_2$ requires C, 44.4; H, 3.5%). In this synthetic procedure, an acetone solution of cobaltocene could be used in place of $LiBEt_3H$.

The following three complexes were prepared using a procedure similar to that described in *B*(*v*).

(*vi*) $[Re_2Br_3(dppe)_2(NCMe)]PF_6$. Yield 77% (Found: C, 40.1; H, 3.5. $C_{54}H_{51}Br_3F_6NP_5Re_2$ requires C, 40.65; H, 3.2%).

(*vii*) $[Re_2Cl_3(dppe)_2(NCEt)]PF_6$. Yield 75% (Found: C, 44.2; H, 3.9. $C_{55}H_{53}Cl_3F_6NP_5Re_2$ requires C, 44.75; H, 3.6%).

(*viii*) $[Re_2Br_3(dpadppe)_2(NCMe)]PF_6$. Yield 70% (Found: C, 38.2; H, 3.7. $C_{54}H_{51}As_2Br_3F_6NP_3Re_2$ requires C, 38.5; H, 3.1%).

Physical Measurements.—Infrared spectra were recorded as Nujol mulls or CH_2Cl_2 solutions using an IBM Instruments IR/32 Fourier transform (4 000—400 cm^{-1}) spectrometer. Electronic absorption spectra were recorded on IBM Instruments 9 420 u.v.–visible (900—200 nm) and Cary 17 (2 000—900 nm) spectrophotometers. Electrochemical experiments were carried out by using a Bioanalytical Systems Inc. model CV-1A instrument on dichloromethane solutions containing 0.2 mol dm^{-3} $[NBu^n{}_4]PF_6$ as supporting electrolyte; $E_{\frac{1}{2}}$ values $[(E_{p,a} + E_{p,c})/2]$ were referenced to the Ag/AgCl electrode at room temperature and are uncorrected for junction potentials. $^{31}P-\{^1H\}$ N.m.r. spectra were recorded on a Varian XL-200 spectrometer operated at 80.98 MHz with an internal deuterium lock using aqueous 85% H_3PO_4 as an external standard. Positive chemical shifts were measured downfield from H_3PO_4. ^1H N.m.r. spectra were also recorded on a Varian XL-200 spectrometer. Resonances were referenced internally to the residual protons in the incompletely deuteriated solvent. Conductivities were measured on an Industrial Instruments Inc. model RC 16B2 conductivity bridge. *X*-Band e.s.r. spectra of dichloromethane solutions were recorded at *ca.* −160 °C with the use of a Varian E-109 spectrometer. Magnetic susceptibility measurements were done by the Evans method on dichloromethane solutions of the complexes using a 90 MHz Perkin-Elmer R32 spectrometer.

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