

Reactions of the Dirhenium(II) Complexes $[\text{Re}_2\text{X}_4(\text{dppm})_2]$ ($\text{X} = \text{Cl}$ or Br , $\text{dppm} = \text{Ph}_2\text{PCH}_2\text{PPh}_2$) with Isocyanides. Part 2.[†] The A-Frame-like Monoisocyanide Species $[\text{Re}_2(\mu\text{-X})(\mu\text{-dppm})_2\text{X}_3(\text{CNR})]^{n+}$ ($\text{R} = \text{Me}$, Bu^t , or $\text{C}_6\text{H}_3\text{Me}_2\text{-2,6}$; $n = 0$ or 1)[†]

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The triply bonded complexes $[\text{Re}_2\text{X}_4(\text{dppm})_2]$ ($\text{X} = \text{Cl}$ or Br , $\text{dppm} = \text{Ph}_2\text{PCH}_2\text{PPh}_2$) react with RNC ($\text{R} = \text{Me}$, Bu^t , or $\text{C}_6\text{H}_3\text{Me}_2\text{-2,6}$) to yield the monoisocyanide adducts $[\text{Re}_2\text{X}_4(\text{dppm})_2(\text{CNR})]$. The spectroscopic properties of these species are in accord with the presence of isomers in solution. Chemical oxidation of the neutral complexes to their corresponding paramagnetic monocations produces a single isomer in each instance. The solid-state structure of $[\text{Re}_2\text{Cl}_4(\text{dppm})_2(\text{CNBu}^t)]$ has been shown to be that of the A-frame-like molecule $[\text{Cl}_2\text{Re}(\mu\text{-Cl})(\mu\text{-dppm})_2\text{ReCl}(\text{CNBu}^t)]$. The retention of a Re-Re multiple bond is supported by both structural work ($\text{Re-Re} = 2.30 \text{ \AA}$) and a qualitative treatment of the bonding which is consistent with the presence of a slightly weakened triple bond.

The reactions of multiply bonded dimetal complexes with π -acceptor ligands, *e.g.* CO , NO , RNC ($\text{R} = \text{alkyl}$), or $\text{R}'\text{NC}$ ($\text{R}' = \text{aryl}$) invariably result in the cleavage of the metal-metal bond.^{2,3} These cleavage reactions have been observed to lead to products in which the resulting mononuclear fragments have subsequently undergone non-reductive substitution,^{4,5} reductive substitution,⁴⁻⁶ or simple 'adduct' formation^{7,8} by the π -acceptor ligand. In examining the related reactivity of the dirhenium(II) complex $[\text{Re}_2\text{Cl}_4(\text{dppm})_2]$ ($\text{dppm} = \text{Ph}_2\text{PCH}_2\text{PPh}_2$),^{9,10} we have discovered that the bridging dppm ligands confer a remarkable stability upon the dimetal unit and prevent its disruption in the presence of an excess of a π -acceptor ligand even under quite forcing reaction conditions. In the case of CO , both monocarbonyl and dicarbonyl complexes can be isolated^{11,12} but an even richer chemistry ensues in the case of reactions with isocyanide ligands. In this report we describe the nature of the 1:1 adducts that are formed between $[\text{Re}_2\text{X}_4(\text{dppm})_2]$ ($\text{X} = \text{Cl}$ or Br) and RNC or $\text{R}'\text{NC}$. Some of these results have been the subject of a preliminary communication.¹³

Results and Discussion

(a) *Synthesis, Spectroscopic Properties, and Redox Behaviour.*—The triply bonded dirhenium(II) complex $[\text{Re}_2\text{Cl}_4(\text{dppm})_2]$ possesses a staggered rotational geometry.¹⁰ The reactions of this complex and its bromide analogue¹⁴ with one equivalent of RNC ($\text{R} = \text{Me}$, Bu^t , or $\text{C}_6\text{H}_3\text{Me}_2\text{-2,6}$) in acetone or toluene for *ca.* 30 min produce the red-brown, air-stable 1:1 adducts $[\text{Re}_2\text{X}_4(\text{dppm})_2(\text{CNR})]$ in high yield ($\geq 60\%$). These reactions, which contrast with the facile cleavage of the triple bond of $[\text{Re}_2\text{X}_4(\text{PR}_3)_4]$ ($\text{X} = \text{Cl}$ or Br , $\text{PR}_3 = \text{monodentate tertiary phosphine}$),⁴ presumably reflect the stability of the five-membered $\text{Re-Re-PCH}_2\text{P}$ rings. This behaviour resembles that seen in the reaction of $[\text{Re}_2\text{Cl}_4(\text{dppm})_2]$ with CO ; in this instance, the formation of the

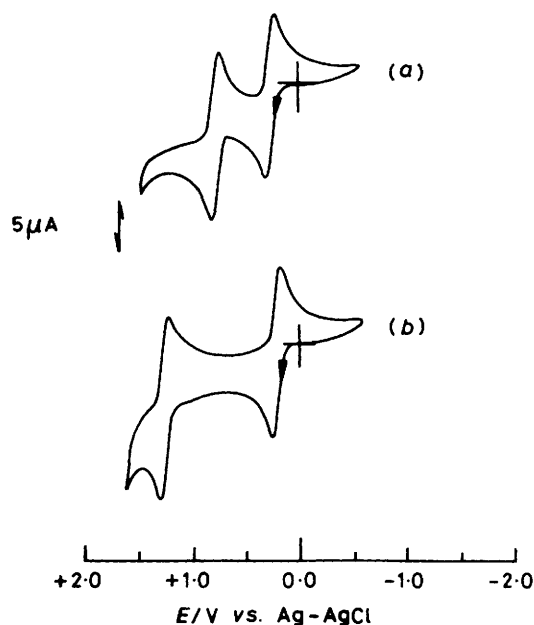


Figure 1. Cyclic voltammograms (scan rate 200 mV s^{-1} at a Pt-bead electrode) in $0.1 \text{ mol dm}^{-3} \text{ NBu}^t_4\text{PF}_6\text{-CH}_2\text{Cl}_2$ of (a) $[\text{Re}_2\text{Cl}_4(\text{dppm})_2]$ and (b) $[\text{Re}_2\text{Cl}_4(\text{dppm})_2(\text{CNBu}^t)]$.

1:1 adduct $[\text{Re}_2(\mu\text{-Cl})(\mu\text{-dppm})_2\text{Cl}_3(\text{CO})]$ precedes that of $[\text{Re}_2(\mu\text{-Cl})(\mu\text{-CO})(\mu\text{-dppm})_2\text{Cl}_3(\text{CO})]$.^{11,15}

Cyclic voltammetric measurements on solutions of these complexes in $0.1 \text{ mol dm}^{-3} \text{ NBu}^t_4\text{PF}_6\text{-CH}_2\text{Cl}_2$ show the presence of two reversible one-electron processes, both of which correspond to oxidations (Table 1 and Figure 1). An irreversible reduction occurs close to the solvent limit for complexes derived from the bromide $[\text{Re}_2\text{Br}_4(\text{dppm})_2]$. For the chloro-species, both processes at positive potentials are characterized by $i_{p,c}/i_{p,a}$ ratios of unity (or close to it) and constant $i_p/v^{1/2}$ ratios for sweep rates (v) between 50 and 400 mV s^{-1} in accord with diffusion

[†] Non-S.I. units employed: $G = 10^{-4} \text{ T}$, $B. M. = 0.927 \times 10^{-23} \text{ A m}^2$.

Table 1. Electrochemical and spectroscopic properties of $[\text{Re}_2\text{X}_4(\text{dppm})_2(\text{CNR})]^{n+}$ ($n = 0$ or 1)

Complex	Half-wave potentials ^a			$\lambda^b/\text{nm}(\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1})$	¹ H N.m.r.; $\delta(\text{p.p.m.})^c$		³¹ P- $\{^1\text{H}\}$ n.m.r., $\delta(\text{p.p.m.})^e$
	E_1/V		$E_{\text{p,c}}/\text{V}$		$-\text{CH}_2-$ ^d	CH_3-	
[Re ₂ Cl ₄ (dppm) ₂ -(CNMe)]	+1.31(ox)	+0.32(ox)		666 (80), 537 (175)	+5.65 ^f	+2.79	−6.51, −7.44 ^{g,h}
[Re ₂ Cl ₄ (dppm) ₂ -(CNBu ⁱ)]	+1.31(ox)	+0.20(ox)		670 (150), 481 (630)	+5.78, +5.60	+0.97	−6.39, −11.23 ⁱ
[Re ₂ Cl ₄ (dppm) ₂ -(CNC ₆ H ₃ Me ₂ -2,6)]	+1.27(ox)	+0.31(ox)		695 (125), 480(sh)	+5.61 ^f	+1.98	−1.04, −7.89 ^h
[Re ₂ Br ₄ (dppm) ₂ -(CNBu ⁱ)]	+1.43 ^j	+0.35(ox)	−1.63	780 (100), 500 (1 650)	+5.99, +5.66	+1.19	−4.76, −24.87 ^k
[Re ₂ Br ₄ (dppm) ₂ -(CNC ₆ H ₃ Me ₂ -2,6)]	+1.32 ^j	+0.49(ox)	−1.43	780 (200), 500 (2 050)	+5.80 ^f	+1.44	−0.08, −28.83 ^k
[Re ₂ Cl ₄ (dppm) ₂ -(CNMe)]PF ₆	+1.30(ox)	+0.31(red)		1 225 (450), 795 (125), 514 (900)	/		
[Re ₂ Cl ₄ (dppm) ₂ -(CNBu ⁱ)]PF ₆	+1.32(ox)	+0.21(red)		1 175 (900), 770 (130), 494 (1 100)	/		
[Re ₂ Br ₄ (dppm) ₂ -(CNBu ⁱ)]PF ₆	+1.43 ^j	+0.35(red)	−1.63	1 235 (1 300), 800 (125), 505 (2 100)	/		
[Re ₂ Cl ₄ (dppm) ₂ -(CNC ₆ H ₃ Me ₂ -2,6)]PF ₆	+1.30(ox)	+0.34(red)		1 260 (750), 750 (250), 511 (1 250)	/		

^a Measured on $0.1 \text{ mol dm}^{-3} \text{ NBu}^n_4\text{PF}_6-\text{CH}_2\text{Cl}_2$ solutions by the cyclic voltammetric technique (V vs. Ag–AgCl). Scan rate $\nu = 200 \text{ mV s}^{-1}$.

^b Spectra recorded in CH_2Cl_2 . ^c Spectra recorded in CD_2Cl_2 and referenced internally to the residual protons of the incompletely deuteriated solvent (δ 5.35 p.p.m.). ^d AB pattern with superimposed P–H coupling. ^e Spectra recorded in a 1:1 mixture of $\text{CH}_2\text{Cl}_2-\text{CD}_2\text{Cl}_2$, unless otherwise stated, with aqueous 85% H_3PO_4 as an external standard. ^f Overlapping AB pattern. ^g Recorded in 1:1 $\text{CH}_2\text{Cl}_2-\text{CDCl}_3$ solution. ^h AA'BB' pattern; chemical shifts are of the most intense inner components of the pattern. ⁱ AA'BB' pattern; chemical shifts based upon simulated spectrum (see Figure 2). ^j $E_{p,a}$ values. ^k AA'XX' pattern; chemical shifts are those of the central component of each set of peaks. ^l Paramagnetic complex.

Table 2. Infrared spectra of $[\text{Re}_2\text{X}_4(\text{dppm})_2(\text{CNR})]^{n+}$ ($n = 0$ or 1)

Complex	$\nu(\text{C}\equiv\text{N})/\text{cm}^{-1}$ ^a		
	Nujol mull	CH_2Cl_2	C_6H_6
$[\text{Re}_2\text{Cl}_4(\text{dppm})_2(\text{CNMe})]$	2 193(sh) 2 160s	2 199(sh) 2 166s	<i>b</i>
$[\text{Re}_2\text{Cl}_4(\text{dppm})_2(\text{CNBu}^i)]$	2 103(sh) 2 060s	2 133s 2 110(sh) 2 060m	<i>b</i>
$[\text{Re}_2\text{Cl}_4(\text{dppm})_2(\text{CNC}_6\text{H}_3\text{Me}_2-2,6)]$	2 060m 1 979s	2 075s 2 040(sh) 2 006m	<i>b</i>
$[\text{Re}_2\text{Br}_4(\text{dppm})_2(\text{CNBu}^i)]$	2 097s 2 067s	2 133m 2 101s 2 066m	2 126(sh) 2 097m 2 060m
$[\text{Re}_2\text{Br}_4(\text{dppm})_2(\text{CNC}_6\text{H}_3\text{Me}_2-2,6)]$	2 027m 1 995s	2 041s 2 006m	2 031s 1 998m
$[\text{Re}_2\text{Cl}_4(\text{dppm})_2(\text{CNMe})]\text{PF}_6$	2 195s	2 195s	<i>b</i>
$[\text{Re}_2\text{Cl}_4(\text{dppm})_2(\text{CNBu}^i)]\text{PF}_6$	2 149s	2 151s	<i>b</i>
$[\text{Re}_2\text{Cl}_4(\text{dppm})_2(\text{CNC}_6\text{H}_3\text{Me}_2-2,6)]\text{PF}_6$	2 106s	2 108s	<i>b</i>
$[\text{Re}_2\text{Br}_4(\text{dppm})_2(\text{CNBu}^i)]\text{PF}_6$	2 141s	2 145s	<i>b</i>

^a Abbreviations: m = medium; s = strong; sh = shoulder. ^b Limited solubility, or insolubility, in this solvent precluded recording the i.r. spectrum.

control. Values of ΔE_p for the coupled anodic and cathodic peaks were *ca.* 100 mV at $\nu = 200 \text{ mV s}^{-1}$ and they increased with increasing sweep rate. These properties are consistent with the electron-transfer processes being electrochemically quasi-reversible. Chemical reversibility has been demonstrated and will be discussed later. Conductivity measurements performed on acetone solutions of these complexes (*ca.* $1 \times 10^{-3} \text{ mol dm}^{-3}$) are in accord with their formulation as neutral species ($\Lambda_M \approx 5 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$). Their electronic absorption spectral data, which are summarized in Table 1, reveal similarities to other Re_2^{4+} core complexes.¹⁶

The ¹H n.m.r. spectra (measured in CD_2Cl_2) integrate in

accord with the 1:1 stoichiometry of the complexes. The resonances due to the methyl protons of the co-ordinated MeNC, BuⁿNC, and 2,6-Me₂C₆H₃NC ligands appear as singlets at room temperature, while the methylene protons of the dppm ligands exhibit a basic AB pattern with superimposed P–H coupling ($J_{\text{H-H}}$ 12.7–14.3, $J_{\text{P-H}}$ 4.5–5.1 Hz). Data obtained from the ³¹P- $\{^1\text{H}\}$ n.m.r. spectral measurements indicate that the *trans*-bridging disposition of the dppm ligands has been preserved. Also, the presence of AA'BB' and AA'XX' patterns for the chloride and bromide complexes, respectively, is indicative of different environments about each of the two metal centres. The ¹H and ³¹P- $\{^1\text{H}\}$ n.m.r. spectral data are given in

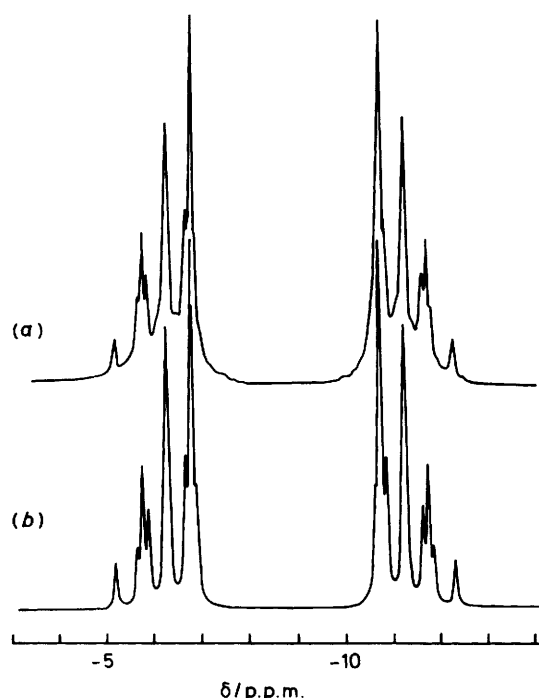
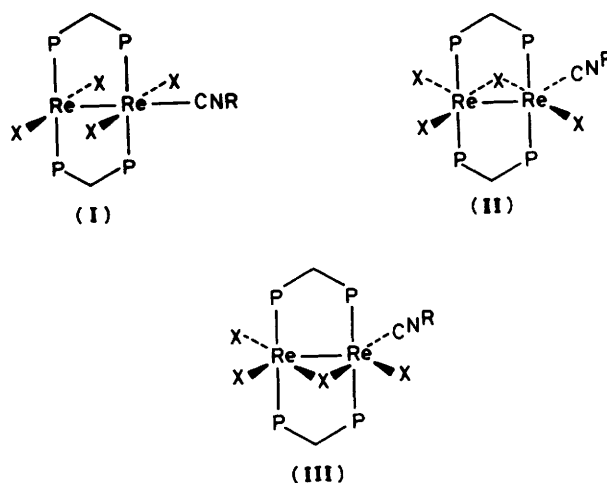


Figure 2. $^{31}\text{P}\{-^1\text{H}\}$ N.m.r. spectrum of $[\text{Re}_2\text{Cl}_4(\text{dppm})_2(\text{CNBu}')]$ recorded in $\text{CH}_2\text{Cl}_2\text{-CD}_2\text{Cl}_2$: (a) observed and (b) calculated. The simulation of this AA'BB' spectrum gave the following parameters: $\delta_{\text{A}} = -6.39$, $\delta_{\text{B}} = -11.23$ p.p.m., $J_{\text{AA}'} = 232.3$, $J_{\text{BB}'} = 212.1$, $J_{\text{AB}} = 79.7$, and $J_{\text{AB}'} = 1.2$ Hz

Table 1, and the $^{31}\text{P}\{-^1\text{H}\}$ spectrum of $[\text{Re}_2\text{Cl}_4(\text{dppm})_2(\text{CNBu}')] (observed and simulated) is shown in Figure 2.$

The Nujol mull i.r. spectra of the monoisocyanide complexes display two $\nu(\text{C}\equiv\text{N})$ modes at frequencies characteristic of a terminally co-ordinated RNC ligand (Table 2). While the presence of two such modes could arise from solid-state effects, the spectra of CH_2Cl_2 or benzene solutions of the complexes also show more than one peak (Table 2). The more soluble bromo-derivatives exhibit a change in the relative intensities of the $\nu(\text{C}\equiv\text{N})$ peaks with change in solvent. A similar solvent dependence has been observed for the $\nu(\text{C}\equiv\text{O})$ modes of the structurally analogous monocarbonyl species $[\text{Re}_2\text{Cl}_4(\text{dppm})_2(\text{CO})]$.¹¹ These findings indicate that, in solution at least, the complexes $[\text{Re}_2\text{X}_4(\text{dppm})_2(\text{CNR})]$ exist as a mixture of isomers. These isomers can be detected on the relatively fast i.r. time-scale, while within the slower time frame of the n.m.r. technique only an averaged signal is observed. In an attempt to slow the isomerization process, a variable-temperature ^1H n.m.r. spectral study was carried out on a sample of $[\text{Re}_2\text{Cl}_4(\text{dppm})_2(\text{CNBu}')] in CD_2Cl_2 solution. As the temperature was lowered, the resonance due to the $\text{Bu}'\text{NC}$ ligand broadened slightly, but it never collapsed prior to reaching the lower temperature limit of -85°C .$

Based upon the preceding information we suggest that the isomers present are those represented by (I), (II), and/or (III) shown below. Isomer (I) is the species most likely to be formed first upon interacting $[\text{Re}_2\text{X}_4(\text{dppm})_2]$ with an isocyanide ligand but can easily rearrange to (II) and (III) (presumably through very low-energy pathways) by two sequential anticlockwise (or clockwise) motions about the plane containing the halide and RNC ligands. In this, a single halide bridge is formed [to give (II)]; this subsequently breaks and a new bridge forms [to give (III)]. Note that in this simple mechanism the RNC remains bound to a single Re atom. This

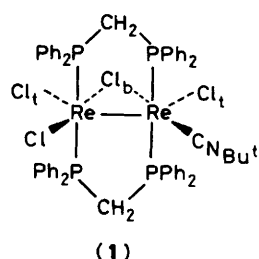


observation is a reasonable one since detailed n.m.r. spectral measurements on the analogous fluxional carbonyl complex $[\text{Re}_2\text{Cl}_4(\text{dppm})_2(^{13}\text{CO})]$ revealed¹¹ that the CO ligand is bound to only one of the Re atoms at all times and does not become involved in the formation of a $\mu\text{-CO}$ bridge.

Oxidation of the monoisocyanide complexes using one equivalent of NOPF_6 or $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)_2]\text{PF}_6$ results in formation of the rose-coloured monocations $[\text{Re}_2\text{X}_4(\text{dppm})_2(\text{CNR})]^+\text{PF}_6^-$ ($\text{X} = \text{Cl}$ or Br , $\text{R} = \text{Me}$, Bu' , or $\text{C}_6\text{H}_3\text{Me}_2\text{-2,6}$). The electrochemistry of these oxidized species shows a process at E_1 ca. $+0.3$ V vs. Ag-AgCl (corresponding to a reduction), as well as the other redox processes which characterize the neutral Re_2^{4+} core complexes (see Table 1). Their formulation as monocations has been confirmed by conductivity measurements performed on 1×10^{-3} mol dm^{-3} acetone solutions of the complexes; $\Lambda_{\text{M}} = 100\text{--}120 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$. Their electronic absorption spectral properties are given in Table 1; an intense low-energy feature at λ_{max} ca. 1200 nm is often typical of complexes which contain the paramagnetic Re_2^{5+} core.¹⁶⁻¹⁸ The X-band e.s.r. spectra of $[\text{Re}_2\text{Cl}_4(\text{dppm})_2(\text{CNR})]\text{PF}_6$, measured as dichloromethane glasses, exhibit a broad complex signal between 500 and 4000 G which is centred at $g = 2.85$. The observed magnetic moments, determined by the Evans method,¹⁹ are consistent with the complexes possessing one unpaired electron, $\mu_{\text{obs.}} \approx 1.6$ B.M.

Oxidation of the monoisocyanide complexes by one electron appears to generate a single isomer. The i.r. spectra, recorded as Nujol mulls or dichloromethane solutions, display a single sharp band assigned to a terminally co-ordinated isocyanide ligand (Table 2). The frequency is shifted to higher wavenumbers relative to $\nu(\text{C}\equiv\text{N})$ of the neutral complex, as expected with the decrease in π -backbonding from Re_2^{5+} to RNC. Reduction back to the neutral species (using an acetone solution of cobaltocene) regenerates the same mixture of isomers that was present originally (as monitored by i.r. spectroscopy).

(b) *Structural Considerations.*—While single crystals of $[\text{Re}_2\text{Cl}_4(\text{dppm})_2(\text{CNBu}')] of sufficient quality to justify an X-ray crystal-structure analysis could be grown from dichloromethane solution, subsequent structure refinement was frustrated by a disorder problem. Nonetheless, the structure was established to be that of the A-frame-like molecule (I), which is isomer (III) discussed in the preceding section. The disorder involves the Cl and $\text{Bu}'\text{NC}$ ligands trans to the bridging Cl ligand (the basic structural details are presented in the Experimental section). The structure closely resembles that of the monocarbonyl derivative $[\text{Re}_2\text{Cl}_4(\text{dppm})_2(\text{CO})]$,¹⁵ where a$

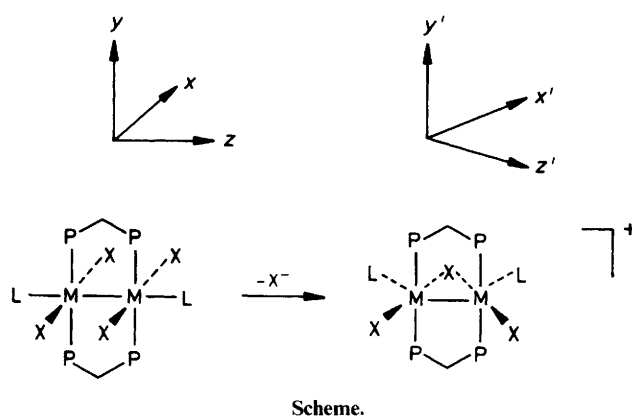


similar disorder is present but the structure solution has proven tractable. A Re-Re distance of 2.30(1) Å is clearly indicative of the retention of a multiple bond, a point which is discussed further in section (c). The comparable bond distance in triply bonded $[\text{Re}_2\text{Cl}_4(\text{dppm})_2]$ is 2.234(3) Å.¹⁰ Other distances of note in (1) are Re-P 2.47(1), Re-Cl_t 2.56(2), and Re-Cl_b 2.52(2) Å. The angle at the bridging Cl ligand is *ca.* 54° which compares with that (55°) in the structure of $[\text{Re}_2\text{Cl}_4(\text{dppm})_2(\text{CO})]$.¹⁵ As far as we can ascertain, the crystal(s) selected for the structure solution were representative of the bulk. This signifies that at least in the solid-state $[\text{Re}_2\text{Cl}_4(\text{dppm})_2(\text{CNBu}^t)]$ (and probably the MeNC and 2,6-Me₂C₆H₃NC analogues) exists primarily as the A-frame-like isomer (III).

(c) *A Consideration of the Metal-Metal Bonding in $[\text{Re}_2\text{Cl}_4(\text{dppm})_2\text{L}]$ (L = CNR or CO).*—The extent of metal-metal bonding in A-frame molecules containing only weakly bonding or non-bonding interactions between the metal centres has been addressed by Hoffman and Hoffmann.²⁰ The Re-Re bonds in $[\text{Re}_2(\mu\text{-Cl})(\mu\text{-dppm})_2\text{Cl}_3(\text{CNR})]$ and $[\text{Re}_2(\mu\text{-Cl})(\mu\text{-dppm})_2\text{Cl}_3(\text{CO})]$ ¹⁵ are substantially shorter than the M-M bonds in other chloro-bridged A-frame structures. For example, the Rh atoms in $[\text{Rh}_2(\mu\text{-Cl})(\mu\text{-dppm})_2(\text{CO})_2]^+$ are at a non-bonding distance of 3.152 Å.²¹ The M-μ-Cl-M angles in these complexes (54–55° in the Re systems; 82° in the Rh system) indicate that the bridging atom confers a negligible effect on the M-M bond length. It is thus apparent that much of the Re-Re multiple bond character of $[\text{Re}_2\text{Cl}_4(\text{dppm})_2]$ is preserved upon the addition of CNR or CO. In an effort to explain the multiple metal-metal bonding within this unusual structural unit, we offer the following qualitative scheme.

We start with $[\text{Re}_2\text{X}_4(\text{dppm})_2]$ as a prototypical d^5 - d^5 dimer containing a $\sigma^2\pi^4\delta^2\delta^{*2}$ Re-Re triple bond.² We assume, for convenience, that the molecule is in an eclipsed conformation, an assumption that does not affect the Re-Re bonding. We now allow two weak σ donors L to ligate in the axial positions of the molecule. The effect of this ligation will be a slight weakening of the Re-Re bond due to the donation of a small amount of electron density into the σ^* orbital. We will neglect this effect and assume that $[\text{Re}_2\text{X}_4(\text{dppm})_2\text{L}_2]$ possesses a $\sigma^2\pi^4\delta^2\delta^{*2}$ triple bond. An A-frame structure can be formed from this molecule by rotation of the two $\text{ReX}_2\text{P}_2\text{L}$ fragments about the P-Re-P axis in a disrotatory fashion and elimination of one of the X groups, thereby yielding $[\text{Re}_2(\mu\text{-X})(\mu\text{-dppm})_2\text{X}_2\text{L}_2]^+$ (Scheme). The bridging X[−] ligand acts as a four-electron donor whereas all the others are two-electron donors. If the metal orbitals are allowed to rotate along with the Re atoms, then we preserve the same orbitals for Re-Re bonding, though referenced to a new co-ordinate system (Scheme). We will assume a rotation of 30° which generates an A-frame with a Re-μ-X-Re angle of 60°, close to that observed crystallographically.

In order to describe the metal-metal interactions in the A-frame (denoted σ' , π' , δ' , and δ'^*) in terms of diatomic σ , π , δ , and δ^* interactions, the rotated d orbitals must be referenced to the unrotated co-ordinate system. The transformation between



the two systems, for a rotation of 30°, is given by $x' = \frac{\sqrt{3}}{2}x + \frac{1}{2}z$, $y' = y$, and $z' = -\frac{1}{2}x + \frac{\sqrt{3}}{2}z$. Using this transformation the rotated d orbitals can be expressed in terms of the unrotated orbitals as shown below and thus the Re-Re interactions in

$$\begin{aligned}d_{z^2}' &= \frac{5}{8}d_{z^2} - \frac{3}{4}d_{xz} + \frac{\sqrt{3}}{8}d_{x^2-y^2} \\d_{xz}' &= \frac{3}{4}d_{z^2} + \frac{1}{2}d_{xz} - \frac{\sqrt{3}}{4}d_{x^2-y^2} \\d_{yz}' &= \frac{\sqrt{3}}{2}d_{yz} - \frac{1}{2}d_{xy} \\d_{xy}' &= \frac{1}{2}d_{yz} + \frac{\sqrt{3}}{2}d_{xy}\end{aligned}$$

the A-frame, referred to standard diatomic interactions, are given below.

$$\begin{aligned}d_{z^2}' - d_{z^2} &= \frac{25}{64}\sigma + \frac{9}{16}\pi + \frac{3}{64}\delta \\d_{xz}' - d_{xz} &= \frac{9}{16}\sigma + \frac{1}{4}\pi + \frac{3}{16}\delta \\d_{yz}' - d_{yz} &= \frac{3}{4}\pi + \frac{1}{4}\delta \\d_{xy}' - d_{xy} &= \frac{1}{4}\pi + \frac{3}{4}\delta\end{aligned}$$

Within this model, the Re-Re triple bond is preserved upon formation of the A-frame, although we may envisage it as a 'bent' triple bond. In terms of diatomic interactions the $\sigma'^2\pi'^4\delta'^2\delta'^{*2}$ triple bond becomes a $\sigma^{\frac{3}{2}}\pi^{\frac{5}{2}}\delta^{\frac{3}{2}}\delta'^{*2}\pi^{\frac{1}{2}}$ triple bond. The effects on the metal-metal bond upon rotation of $[\text{Re}_2\text{X}_4(\text{dppm})_2\text{L}_2]$ into the A-frame $[\text{Re}_2(\mu\text{-X})(\mu\text{-dppm})_2\text{X}_2\text{L}_2]^+$ are therefore the transfer of nominally $\frac{1}{2}$ e from π bonding to δ bonding orbitals and $\frac{1}{2}$ e from δ antibonding to π antibonding orbitals. Both of these will tend to weaken the Re-Re triple bond somewhat.

Although some very broad assumptions have been made, *e.g.* the π -backbonding abilities of RNC and CO have been neglected, this model is in accord with the experimental observations. The Re-Re bond length of 2.30–2.35 Å in the A-frame systems is only slightly longer than those in other complexes containing 'standard diatomic' Re-Re triple bonds.^{2,10,22} Also, the ready accessibility of two one-electron oxidations in the A-frame, as measured by cyclic voltammetry, is consistent with the highest energy electrons residing in Re-Re antibonding orbitals. Quantitative molecular-orbital calculations aimed at substantiating the qualitative model presented here will be performed in the near future.

(d) *Concluding Remarks.*—The neutral multiple bonded complexes $[\text{Re}_2\text{X}_4(\text{dppm})_2(\text{CNR})]$ (X = Cl or Br; R = Me, Bu^t, or 2,6-Me₂C₆H₃), appear to exist as isomers in solution although in the solid state we have definitive evidence only for the A-frame-like isomer (III). A single isomer is obtained upon oxidizing these complexes to their monocations (isolated as their PF₆[−] salts). The isolation of $[\text{Re}_2\text{X}_4(\text{dppm})_2(\text{CNR})]$ provides evidence in support of our earlier suggestion that the reaction of $[\text{Re}_2\text{Cl}_4(\text{dppm})_2]$ with nitriles R'CN to give

$[\text{Re}_2\text{Cl}_3(\text{dppm})_2(\text{NCR}')_2]^+$ proceeds *via* the A-frame-like species $[\text{Re}_2\text{Cl}_4(\text{dppm})_2(\text{NCR}')_2]$.²³ These monoisocyanide adducts provide only the second series of multiply bonded dimetal complexes that contain isocyanide ligands and which have been stabilized towards metal-metal bond cleavage. The previous examples are the complexes $[\text{Re}_2\text{X}_3(\text{L-L})_2(\text{CNR})]\text{PF}_6$ ($\text{X} = \text{Cl}$ or Br ; $\text{L-L} = \text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$ or $\text{Ph}_2\text{AsCH}_2\text{-CH}_2\text{PPh}_2$; $\text{R} = \text{Pr}^i$ or Bu^i).^{1,16} The reactivity of the new complexes towards nitrile ligands and carbon monoxide is currently under investigation and will be reported in due course.

Experimental

Starting Materials.—The dirhenium(II) complex $[\text{Re}_2\text{Cl}_4(\text{dppm})_2]$ was prepared, according to the reported method, from $[\text{Re}_2\text{Cl}_6(\text{P}(\text{Bu}^n)_3)_2]$ and dppm ,⁹ while the bromo-derivative $[\text{Re}_2\text{Br}_4(\text{dppm})_2]$ was synthesized from the reaction between $[\text{Re}_2\text{Br}_4(\text{PPR}^n)_4]$ and dppm in refluxing benzene, as described in the literature.¹⁴ The bromide complex was recrystallized from $\text{CH}_2\text{Cl}_2\text{-Et}_2\text{O}$ prior to use. Pertinent n.m.r. spectral data for this complex are as follows: ^1H n.m.r. ($[\text{C}_6\text{H}_6]$ /acetone) δ 5.65 p.p.m. (quintet, $-\text{CH}_2-$ of dppm), $^{31}\text{P}\{-^1\text{H}\}$ n.m.r. ($\text{CH}_2\text{Cl}_2\text{-CD}_2\text{Cl}_2$) δ +5.60 p.p.m. (singlet). The MeNC and Bu^iNC ligands were prepared using standard literature procedures,^{23,24} while 2,6- $\text{Me}_2\text{C}_6\text{H}_3\text{NC}$ was purchased from Fluka Chemicals and used without further purification. The oxidant $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)_2]\text{PF}_6$ was prepared using the reported method with minor modifications.²⁵ The solvents used in the preparation of the complexes were of commercial grade and were thoroughly deoxygenated prior to use. All reactions were performed under a nitrogen atmosphere using standard vacuum-line techniques.

Monoisocyanide Complexes.—(i) $[\text{Re}_2\text{Cl}_4(\text{dppm})_2(\text{CNBu}^i)]\cdot 0.5\text{CH}_2\text{Cl}_2$. In a typical reaction, $[\text{Re}_2\text{Cl}_4(\text{dppm})_2]$ (0.20 g, 0.16 mmol) was dissolved in acetone (5 cm^3). The purple solution immediately turned red-brown upon addition of 1 mol equiv. of Bu^iNC (0.0165 cm^3 , 0.16 mmol). The reaction mixture was stirred at room temperature for 30 min until a red-brown solid precipitated. The solid was recrystallized by dissolving it in dichloromethane (5 cm^3) and slowly adding diethyl ether (30 cm^3). The desired product, which precipitated upon standing, was collected, washed with diethyl ether, and dried *in vacuo*; yield 0.20 g, 94% (Found: C, 46.6; H, 3.9; Cl, 12.8. $\text{C}_{55.5}\text{H}_{54}\text{Cl}_5\text{NP}_4\text{Re}_2$ requires C, 47.3; H, 3.9; Cl, 12.6%). The presence of half a molecule of CH_2Cl_2 was verified by measuring the ^1H n.m.r. spectrum in CDCl_3 .

The following complexes were prepared by using a similar procedure: $[\text{Re}_2\text{Br}_4(\text{dppm})_2(\text{CNBu}^i)]$, yield 60% (Found: C, 42.1; H, 4.2; Br, 20.9. $\text{C}_{55}\text{H}_{53}\text{Br}_4\text{NP}_4\text{Re}_2$ requires C, 42.8; H, 3.5; Br, 20.7%); $[\text{Re}_2\text{Cl}_4(\text{dppm})_2(\text{CNMe})]$, yield 80% (Found: C, 46.95; H, 3.9. $\text{C}_{52}\text{H}_{47}\text{Cl}_4\text{NP}_4\text{Re}_2$ requires C, 47.1; H, 3.95%); and $[\text{Re}_2\text{Cl}_4(\text{dppm})_2(\text{CNC}_6\text{H}_3\text{Me}_2\cdot 2,6)]\cdot 0.5\text{CH}_2\text{Cl}_2$, yield 91% (Found: C, 48.5; H, 3.9; Cl, 11.9. $\text{C}_{59.5}\text{H}_{54}\text{Cl}_5\text{NP}_4\text{Re}_2$ requires C, 49.0; H, 3.75; Cl, 12.2%).

(ii) $[\text{Re}_2\text{Br}_4(\text{dppm})_2(\text{CNC}_6\text{H}_3\text{Me}_2\cdot 2,6)]$. The synthesis of this complex involved the dropwise addition of a toluene solution (3 cm^3) of 2,6- $\text{Me}_2\text{C}_6\text{H}_3\text{NC}$ (0.0074 g, 0.056 mmol) to a toluene solution (5 cm^3) of $[\text{Re}_2\text{Br}_4(\text{dppm})_2]$ (0.083 g, 0.055 mmol). The resulting red solution was stirred for 5 min and the volume of solution then reduced to *ca.* 4 cm^3 under a stream of gaseous nitrogen. Diethyl ether was added to precipitate the desired product. It was filtered off, washed with diethyl ether, and dried *in vacuo*; yield 0.064 g, 71% (Found: C, 45.4; H, 3.7. $\text{C}_{59}\text{H}_{53}\text{Br}_4\text{NP}_4\text{Re}_2$ requires C, 44.5; H, 3.4%).

Oxidation of Monoisocyanide Complexes.— $[\text{Re}_2\text{Cl}_4(\text{dppm})_2(\text{CNBu}^i)]\text{PF}_6$. A quantity of $[\text{Re}_2\text{Cl}_4(\text{dppm})_2(\text{CNBu}^i)]$ (0.10 g, 0.073 mmol) was dissolved in dichloromethane (5 cm^3). To this

solution was added 1.1 mol equiv. of NOPF_6 (0.014 g, 0.08 mmol). Evolution of NO gas, accompanied by a change in colour from red-brown to red, occurred within 15 min of stirring the solution at room temperature. The stirring was continued for an additional 15 min, then the reaction mixture was filtered to remove any unreacted NOPF_6 . The rose-coloured product was precipitated from the filtrate by the addition of diethyl ether (25 cm^3). It was collected, washed with diethyl ether, and dried *in vacuo*; yield 0.083 g, 75% (Found: C, 43.7; H, 3.9; Cl, 9.2. $\text{C}_{55}\text{H}_{53}\text{Cl}_4\text{F}_6\text{NP}_5\text{Re}_2$ requires C, 43.7; H, 3.5; Cl, 9.4%). This oxidation can also be achieved using $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)_2]\text{PF}_6$ as the oxidant in dichloromethane solution.

The following complexes were prepared in an analogous manner: $[\text{Re}_2\text{Br}_4(\text{dppm})_2(\text{CNBu}^i)]\text{PF}_6$, yield 78% (Found: C, 38.8; H, 3.6. $\text{C}_{55}\text{H}_{53}\text{Br}_4\text{F}_6\text{NP}_5\text{Re}_2$ requires C, 39.1; H, 3.2%); $[\text{Re}_2\text{Cl}_4(\text{dppm})_2(\text{CNC}_6\text{H}_3\text{Me}_2\cdot 2,6)]\text{PF}_6$, yield 70% (Found: C, 44.7; H, 3.6; Cl, 9.0. $\text{C}_{59}\text{H}_{53}\text{Cl}_4\text{F}_6\text{NP}_5\text{Re}_2$ requires C, 45.4; H, 3.4; Cl, 9.1%); and $[\text{Re}_2\text{Cl}_4(\text{dppm})_2(\text{CNMe})]\text{PF}_6$, yield 70% (Found: C, 42.1; H, 3.8. $\text{C}_{52}\text{H}_{47}\text{Cl}_4\text{F}_6\text{NP}_5\text{Re}_2$ requires C, 42.5; H, 3.2%).

Reduction of $[\text{Re}_2\text{Cl}_4(\text{dppm})_2(\text{CNBu}^i)]\text{PF}_6$. A quantity of $[\text{Re}_2\text{Cl}_4(\text{dppm})_2(\text{CNBu}^i)]\text{PF}_6$ (0.10 g, 0.066 mmol) was dissolved in acetone (5 cm^3) and treated with 1 mol equiv. of cobaltocene (0.012 g, 0.066 mmol). The reaction mixture was stirred at room temperature for 20 min. After this time, the neutral dirhenium species had precipitated from the solution. It was collected and recrystallized by dissolving in dichloromethane and slowly adding diethyl ether. It was filtered off, washed with diethyl ether, and dried *in vacuo*; yield 0.065 g, 72%. The identity of the reduced complex was confirmed through a comparison of its electrochemical and spectroscopic properties with those of an authentic sample.

Physical Measurements.—I.r. spectra were recorded as Nujol mulls or solutions in CH_2Cl_2 or benzene using an IBM Instruments IR/32 Fourier-transform ($4\,800\text{--}400\text{ cm}^{-1}$) spectrometer. Electronic absorption spectra were recorded on IBM Instruments 9 420 u.v.-visible ($900\text{--}200\text{ nm}$) and Cary 17 ($2\,000\text{--}900\text{ nm}$) spectrophotometers. Electrochemical experiments were carried out by using a Bioanalytical Systems Inc. model CV-1A instrument on dichloromethane solutions containing $0.1\text{ mol dm}^{-3}\text{ NBu}^n_4\text{PF}_6$ as supporting electrolyte. E_3 values $[(E_{p,a} + E_{p,c})/2]$ were referenced to the Ag-AgCl electrode and are uncorrected for junction potentials. Under the same experimental conditions the ferrocenium-ferrocene couple has $E_3 = +0.47\text{ V vs. Ag-AgCl}$. $^{31}\text{P}\{-^1\text{H}\}$ n.m.r. spectra were recorded on a Varian XL-200 spectrometer operated at 80.98 MHz, with an internal deuterium lock and 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 deuterated 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 method¹⁹ on dichloromethane solutions of the complexes using a Varian XL-200 spectrometer.

Microanalyses were performed by Dr. H. D. Lee of the Purdue University microanalytical laboratory.

Preparation of Single Crystals of $[\text{Re}_2\text{Cl}_4(\text{dppm})_2(\text{CNBu}^i)]$.—Dark red crystals of $[\text{Re}_2\text{Cl}_4(\text{dppm})_2(\text{CNBu}^i)]$ were obtained by dissolving a 0.1 g sample of the complex in dichloromethane (2 cm^3) in a 5-mm n.m.r. tube and layering with diethyl ether (1.5 cm^3). Crystals deposited on the side of the tube within 5 d. Because of a disorder problem, the structure solution did not

proceed to a stage sufficient to warrant publication of the full structural details. However, the basic crystallographic details (at 25 °C) are as follows: monoclinic, space group $P2_1$, $a = 15.007(7)$, $b = 15.091(7)$, $c = 26.282(14)$ Å, $\beta = 90.22(2)^\circ$, $U = 5980(9)$ Å³, $Z = 4$, $D_c = 1.524$ g cm⁻³, $\mu(\text{Mo-K}\alpha) = 45.1$ cm⁻¹. Conventional heavy-atom methods were used in the structure solution which was terminated at the stage $R(F) = 0.13$ and $R'(F) = 0.15$ for 6720 observed reflections having $F_o^2 > 3\sigma(F_o^2)$. A total of 7435 unique reflections were collected ($2 < 2\theta < 50^\circ$) on an Enraf-Nonius CAD-4 diffractometer using graphite-monochromated Mo-K α radiation. Further details of the data set, and the structure solution and refinement may be obtained from Dr. P. E. Fanwick of this Department.

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