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Note

Dirhenium(II) complexes containing monodentate and polydentate nitrile ligands

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Abstract

The complex $Re_2Cl_4(\mu\text{-dppa})_2$ (dppa = $Ph_2PNHPPh_2$) has been reacted with EtCN and PhCN to afford the complexes $[Re_2Cl_3(\mu\text{-dppa})_2(NCR)_2]PF_6$ (R = Et or Ph), $[Re_2Cl_3(\mu\text{-}HN_2C_2Et_2)(\mu\text{-dppa})_2(NCEt)]Cl$ and $[Re_2Cl_3(\mu\text{-}HN_2C_2Et_2)(\mu\text{-dppa})_2(NCEt)](PF_6)_2$ which are derivatives of the $[Re_2]^{4+}$, $[Re_2]^{5+}$ and $[Re_2]^{6+}$ cores, respectively. This behaviour is similar to the reactions of $Re_2Cl_4(\mu\text{-dppm})_2$ (dppm = $Ph_2PCH_2PPh_2$) with monodentate nitriles. The reactions of $Re_2Cl_4(\mu\text{-dppm})_2$ with the polydentate nitrile ligands 1,4-dicyanobenzene (1,4-DCB), 1,4-dicyanobut-2-ene (1,4-DCBE) and tris(2-cyanoethyl)phosphine (CEP) also give complexes of this same type in which the nitrile ligand utilizes only one of its CN groups. This is confirmed by an X-ray crystal structure determination of $[Re_2Cl_3(\mu\text{-dppm})_2(1,4\text{-DCB})_2]PF_6$, in which the $Re{\equiv}Re$ bond is retained (Re–Re distance 2.2637(12) Å) and the 1,4-DCB ligands are monodentate. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Crystal structures; Rhenium complexes; Nitrile complexes; Dinuclear complexes

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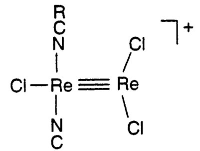
1. Introduction

The dirhenium(II) complex $Re_2Cl_4(\mu\text{-dppm})_2$, where dppm = $Ph_2PCH_2PPh_2$, has been shown to react with organic nitrile ligands to afford complexes of the type $[Re_2Cl_3(\mu\text{-dppm})_2(NCR)_2]^+$ which have the structure represented in **I** (dppm ligands omitted) [1].



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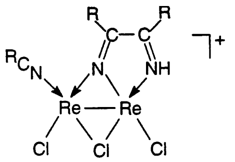

II

In addition, several complexes that are derived from $Re_2Cl_4(\mu\text{-dppm})_2$, and which retain the $[Re_2(\mu\text{-dppm})_2]$ unit, have also been found to form these bis-nitrile complexes [2,3]. The X-ray crystal structures of salts of these cations where RCN = EtCN, PhCN or 1,2-dicyanobenzene (1,2-DCB) have been determined [1–3]. These complexes are implicated as intermediates in the reductive coupling of nitriles by $Re_2Cl_4(\mu\text{-dppm})_2$ [4], which is a consequence of the reducing ability of the electron-rich dirhenium(II) core [5,6]. The products of these reductive coupling reactions are the paramagnetic species $[Re_2Cl_3(\mu\text{-}HN_2C_2R_2)(\mu\text{-dppm})_2(NCR)]^+$ (structure **II**, with dppm ligands omitted), which are in turn easily oxidized to their diamagnetic dirhenium(III) congeners $[Re_2Cl_3(\mu\text{-}HN_2C_2R_2)(\mu\text{-dppm})_2(NCR)]^{2+}$ [4].

In the present report, we have extended these nitrile reactivity studies in order to establish whether other dirhenium(II) starting materials behave in a like manner. For this purpose, we have chosen the complex $Re_2Cl_4(\mu\text{-dppa})_2$, where dppa = $Ph_2PNHPPh_2$ [6–8], whose reactivity has not previously been studied. In addition, we have examined the reactivity of $Re_2Cl_4(\mu\text{-dppm})_2$ towards polydentate nitriles with the objective of generating polymeric $\{[Re{\equiv}Re]^{4+}\}_\infty$ compounds whose redox chemistry would be of interest in view of the possibility of forming paramagnetic chains.

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2. Experimental

2.1. Starting materials and reaction procedures

The standard literature procedure was used to prepare $Re_2Cl_4(\mu\text{-dppm})_2$ (**1**) [9] and $Re_2Cl_4(P\text{-n-}Pr_3)_4$ [10]. A new higher yield synthesis of $Re_2Cl_4(\mu\text{-dppa})_2$ (**2**) [6,7] was developed. A mixture of $Re_2Cl_4(P\text{-n-}Pr_3)_4$ [10] (0.200 g, 0.173 mmol) and dppa (0.200 g, 0.519 mmol) in 6 ml of toluene was heated at reflux for 16 h in a flask that contained a pine boiling stick. The resulting purple crystals were filtered off, washed with toluene, and dried under a vacuum; yield 0.198 g (89%). The product was identified as **2** on the basis of a comparison of its electrochemical and spectroscopic properties with the literature data for this compound [6,7].

Tris(2-cyanoethyl)phosphine (CEP) and $NOPF_6$ were purchased from Strem Chemicals Inc., while 1,4-dicyanobenzene (1,4-DCB) and 1,4-dicyanobut-2-ene (1,4-DCBE) were obtained from the Aldrich Chemical Co. These reagents were used without further purification. Solvents were obtained from commercial sources and thoroughly deoxygenated prior to use. Reactions were carried out under an atmosphere of N_2. IR spectra, NMR spectra and single scan cyclic voltammetric (CV) measurements (recorded in 0.1 M $n\text{-}Bu_4NPF_6$–CH_2Cl_2 with a scan rate of 200 mV s^{-1} at a Pt-bead electrode) were determined as described previously [11]. Elemental microanalyses were performed by Dr. H.D. Lee of the Purdue University Microanalytical Laboratory.

*2.2. Reactions of $Re_2Cl_4(\mu\text{-dppa})_2$ (**2**) with propionitrile*

*2.2.1. Synthesis of $[Re_2Cl_3(\mu\text{-dppa})_2(NCEt)_2]PF_6$ (**3a**)*

A sample of **2** (0.100 g, 0.078 mmol) was mixed with KPF_6 (0.20 g, 1.08 mmol) in 10 ml of acetone and 0.5 ml of propionitrile. The reaction mixture was stirred at room temperature (r.t.) for 30 min, then reduced to about one-half volume by vacuum evaporation, the mixture filtered, and the filtrate added to ca. 40 ml of diethyl ether and stirred for 30 min. The resulting beige coloured solid was filtered off, extracted into approximately 10 ml of dichloromethane and the extract again reduced in volume (approximately 5 ml). An excess of diethyl ether was added to re-precipitate the title compound **3a**; yield 0.097 g (83%). *Anal.* Calc. for $C_{54}H_{52}Cl_3F_6N_4P_5Re_2$: C, 43.11; H, 3.48. Found: C, 42.91; H, 3.56%. IR (Nujol mull): $\nu(CN) = 2273(vw)$ cm^{-1}, $\nu(P\text{–}F)$ of $[PF_6]^- = 840(vs)$ cm^{-1}. ^1H NMR (recorded in CD_2Cl_2): δ +7.9 to +7.2 (m, 40H, C_6H_5), δ +1.58 (q, 4H, CH_2), δ +0.48 (t, 6H, CH_3). $^{31}P\{^1H\}$ NMR (recorded in CD_2Cl_2): AA′BB′ pattern with multiplets at δ +53.2 and δ +44.2, δ ca. −144 (heptet, $[PF_6]^-$). CV: $E_{1/2}(ox) = +0.56$ V ($\Delta E_p = 70$ mV), $E_{1/2}(red) = -1.28$ V ($\Delta E_p = 90$ mV) versus Ag/AgCl. Conductivity (1.0×10^{-3} M solution in acetone): 97 Ω^{-1} cm^2 mol^{-1}.

*2.2.2. Synthesis of $[Re_2Cl_3(\mu\text{-dppa})_2(NCPh)_2]PF_6$ (**3b**)*

A procedure similar to that described in Section 2.2.1 afforded **3b**, which was identified on the basis of its spectroscopic properties; yield 74%. IR (Nujol mull): $\nu(CN) = 2253(vw)$ cm^{-1}, $\nu(P\text{–}F)$ of $[PF_6]^- = 842(vs)$ cm^{-1}. ^1H NMR (recorded in $CDCl_3$): δ +7.9 to +6.9 (m, 50H, C_6H_5). $^{31}P\{^1H\}$ NMR (recorded in $CDCl_3$): AA′BB′ pattern with multiplets at δ +51.8 and δ +43.2, δ ca. −144 (heptet, $[PF_6]^-$).

*2.2.3. Synthesis of $[Re_2Cl_3(\mu\text{-}HN_2C_2Et_2)(\mu\text{-dppa})_2(NCEt)]Cl$ (**4**)*

A sample of **2** (0.070 g, 0.054 mmol) in propionitrile (5 ml) was heated at reflux for 4 h. The resulting green reaction solution was filtered and the filtrate treated with 50 ml of diethyl ether. The precipitate of **4** was filtered off, washed with diethyl ether and dried under a vacuum; yield 0.067 g (85%). *Anal.* Calc. for $C_{66}H_{52}Cl_3F_6N_4P_5Re_2$: C, 47.18; H, 4.03; N, 4.83. Found: C, 47.12; H, 3.81; N, 4.51%. IR (Nujol mull): $\nu(NH)$ of $HN_2C_2Et_2 = 3358(w)$ cm^{-1}, $\nu(CN)$ of $EtCN = 2273(vw)$ cm^{-1}. CV: $E_{1/2}(ox) = +0.28$V ($\Delta E_p = 70$ mV), $E_{1/2}(red) = -0.66$ V ($\Delta E_p = 60$ mV) versus Ag/AgCl.

*2.2.4. Synthesis of $[Re_2Cl_3(\mu\text{-}HN_2C_2Et_2)(\mu\text{-dppa})_2(NCEt)](PF_6)_2$ (**5**)*

A mixture of **4** (0.04 g, 0.028 mmol) and $NOPF_6$ (0.015 g, 0.087 mmol) in 5 ml of dichloromethane was stirred for 1 h at r.t. The title compound was isolated as a red solid by use of a work-up procedure similar to that described in Section 2.2.1; yield 0.039 g (81%). *Anal.* Calc. for $C_{57.5}H_{59}Cl_4F_{12}N_5P_6Re_2$ (i.e. **5** · $0.5CH_2Cl_2$): C, 39.50; H, 3.40; N, 4.00. Found: C, 39.45; H, 3.69; N, 3.60%. The presence of a small amount of lattice CH_2Cl_2 was confirmed by a ^1H NMR spectrum recorded in $CDCl_3$. IR (Nujol mull): $\nu(NH)$ of $HN_2C_2Et_2 = 3338(w)$ cm^{-1}, $\nu(CN)$ of $EtCN = 2287(vw)$ cm^{-1}, $\nu(P\text{–}F)$ of $[PF_6]^- = 845(vs)$ cm^{-1}. ^1H NMR (recorded in CD_2Cl_2): δ +7.8 to +7.1 (m, 40H, Ph), δ +4.73(q, 2H, CH_2''), δ +4.15(q, 2H, CH_2'), δ +2.25(q, 2H, CH_2), δ +1.55 (t, 3H, CH_3''), δ +0.58 (t, 3H, CH_3), δ −0.05 (t, 3H, CH_3'). $^{31}P\{^1H\}$ NMR (recorded in CD_2Cl_2): AA′BB′ pattern with multiplets at δ +34.6 and δ +28.0, δ ca. −144 (heptet, $[PF_6]^-$). CV: $E_{1/2}(red) = +0.26$ V ($\Delta E_p = 60$ mV), $E_{1/2}(red) = -0.68$ V ($\Delta E_p = 60$ mV) versus Ag/AgCl. Conductivity (1.0×10^{-3} M solution in acetone): 175 Ω^{-1} cm^2 mol^{-1}.

2.3. Reactions of $Re_2Cl_4(\mu\text{-dppm})_2$ (**1**) with polydentate nitrile ligands

2.3.1. Synthesis of $[Re_2Cl_3(\mu\text{-dppm})_2(1,4\text{-DCB})_2]PF_6$ (**6**)

A mixture of **1** (0.200 g, 0.156 mmol), KPF_6 (0.40 g, 2.17 mmol) and 1,4-dicyanobenzene (0.50 g, 3.90 mmol) in 20 ml of acetone was stirred at r.t. for 2 h. A work-up procedure similar to that described in Section 2.2.1 afforded the orange–brown title complex **6**; yield 0.208 g (81%). *Anal.* Calc. for $C_{66}H_{52}Cl_3F_6N_4P_5Re_2$: C, 48.07; H, 3.18; Cl, 6.45. Found: C, 48.03; H, 3.25; Cl, 6.58%.

2.3.2. Synthesis of $[Re_2Cl_3(\mu\text{-dppm})_2(1,4\text{-DCBE})_2]PF_6$ (**7**)

A mixture of **1** (0.100 g, 0.078 mmol), KPF_6 (0.20 g, 1.14 mmol) and 1,4-dicyanobut-2-ene (0.5 ml, 3.8 mmol) in 10 ml of acetone was reacted and worked-up following the procedure described in Section 2.3.1; yield 0.114 g (91%). *Anal.* Calc. for $C_{62}H_{56}Cl_3F_6N_4P_5Re_2$: C, 46.40; H, 3.52. Found: C, 46.04; H, 3.52%.

2.3.3. Synthesis of $[Re_2Cl_3(\mu\text{-dppm})_2(CEP)_2]PF_6$ (**8**)

The reaction of **1** (0.100 g, 0.078 mmol), KPF_6 (0.20 g, 1.14 mmol), CEP (0.50 g, 2.59 mmol) in 10 ml of acetone afforded **8** when the procedure described in Section 2.3.1 was used; yield 0.110 g (79%). *Anal.* Calc. for $C_{68}H_{68}Cl_3F_6N_6P_7Re_2$: C, 45.91; H, 3.85; Cl, 5.98. Found: C, 45.83; H, 3.92; Cl, 6.04%.

2.3.4. Synthesis of $[Re_2Cl_3(\mu\text{-dppm})_2(CEP)_2](PF_6)_2$ (**9**)

The oxidation of a sample of **8** (0.060 g, 0.034 mmol) by $NOPF_6$ (0.007 g, 0.040 mmol) in 5 ml of dichloromethane was carried out at r.t. for 30 min, the reaction mixture filtered, and the filtrate reduced in volume to approximately 2 ml. The addition of an excess of diethyl ether afforded **9** as a purple powder; yield 0.052 g (80%). Its identity was based primarily on its electrochemical and conductivity properties (see Section 3).

Table 1
Crystallographic data for $[Re_2Cl_3(\mu\text{-dppm})_2(1,4\text{-DCB})_2]PF_6$ (**6**)

Chemical formula	$Re_2Cl_3P_5F_6N_4C_{66}H_{52}$
Formula weight	1648.80
Space group	*Pbca* (no. 61)
a (Å)	15.930(7)
b (Å)	25.758(8)
c (Å)	34.848(15)
V (Å^3)	14 298(17)
Z	8
ρ_{calc} (g cm^{-3})	1.528
μ(Mo Kα)(mm^{-1})	3.697
Transmission factors: min./max.	0.18/0.74
$R(F_o)$ [a]	0.052
$R_w(F_o^2)$ [b]	0.181
GoF	0.999

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ for $F_o^2 > 2\sigma(F_o^2)$.

[b] $R_w = [\Sigma w(|F_o^2| - |F_c^2|)^2/\Sigma w|F_o^2|^2]^{1/2}$.

2.4. X-ray crystallography

Suitable single crystals of $[Re_2Cl_3(\mu\text{-dppm})_2(1,4\text{-DCB})_2]PF_6$ (**6**) were obtained as orange plates by layering a solution of this complex in dichloromethane with n-pentane, followed sequentially by layers of n-hexane and n-heptane. The data collection was carried out at 296(±1) K on an Enraf–Nonius CAD 4 diffractometer equipped with a graphite monochromator. Lorentz and polarization corrections were applied to the data set. The crystallographic data for **6** are given in Table 1.

The structure was solved by use of the structure solution program PATTY in DIRDIF92 [12]. The remaining atoms were located in succeeding difference Fourier syntheses. Hydrogen atoms were placed in calculated positions according to idealized geometries with C–H = 0.95 Å and $U(H) = 1.3U_{eq}(C)$. They were included in the refinement but constrained to ride on the atom to which they are bonded. An empirical absorption correction [13] was applied. The final refinements were performed by the use of the program SHELXL-97 [14]. The structure was refined in full-matrix least-squares where the function minimized was $\Sigma w(|F_o|^2 - |F_c|^2)^2$, where w is the weighting factor defined as $w = 1/[\sigma^2(F_o)^2 + (0.0814P)^2 + 26.7660P]$ where $P = (F_o^2 + 2F_c^2)/3$. The highest peak in the final difference Fourier had a height of 0.93 e Å^{-3}.

3. Results and discussion

The reactions of $Re_2Cl_4(\mu\text{-dppa})_2$ (**2**) with EtCN and PhCN in the presence of KPF_6 proceed as described previously for the complex $Re_2Cl_4(\mu\text{-dppm})_2$ (**1**) [1], namely, the formation of the unsymmetrical bis-nitrile complexes $[(RCN)_2ClRe(\mu\text{-dppa})_2ReCl_2]PF_6$ (R = Et (**3a**) or Ph (**3b**)) with a structure as shown in **I**. The spectroscopic and electrochemical properties of **3a** and **3b** are given in Section 2 and are very similar to those of their dppm analogues [1]. Furthermore, the use of more forcing reaction conditions in the case of the EtCN reaction (4 h reflux in neat proprionitrile in the absence of KPF_6) converted **2** to the paramagnetic $[Re_2]^{5+}$ complex $[Re_2Cl_3(\mu\text{-}HN_2C_2Et_2)(\mu\text{-dppa})_2(NCEt)]Cl$ (**4**) in which the $\mu\text{-}HN_2C_2Et_2$ ligand has resulted from the reductive coupling of two EtCN molecules. This same reaction course occurs when **1** is reacted with nitriles under similar conditions [4]. When **4** is reacted with $NOPF_6$ in dichloromethane it is oxidized to the diamagnetic $[Re_2]^{6+}$ congener of **4**, i.e. $[Re_2Cl_3(\mu\text{-}HN_2C_2Et_2)(\mu\text{-dppa})_2(NCEt)](PF_6)_2$ (**5**). The properties of **4** and **5** (see Section 2) resemble closely

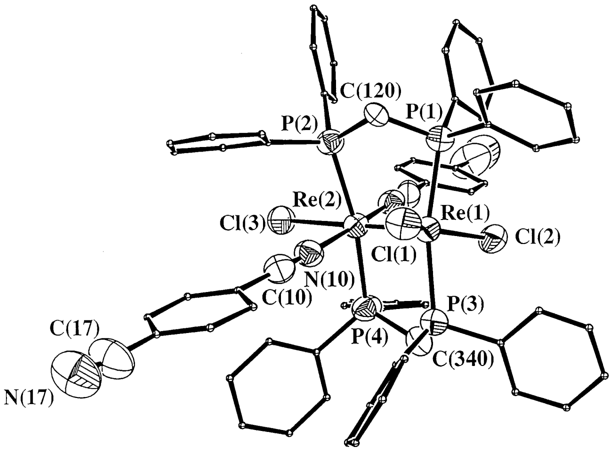
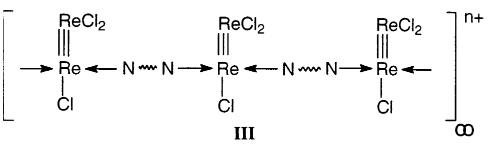


Fig. 1. ORTEP [15] representation of the structure of the dirhenium unit present in the structure of $[Re_2Cl_3(\mu\text{-dppm})_2(1,4\text{-DCB})_2]PF_6$ (**6**). The thermal ellipsoids are drawn at the 50% probability level except for the phenyl group carbon atoms which are circles of arbitrary radius. The unlabeled C and N atoms of the second 1,4-DCB ligand are N(20), C(20), C(27) and N(27), with atom N(20) being coordinated to Re(2).

those of their dppm analogues [4] so that they must be close structural analogues. These results clearly establish the close relationship between **1** and **2** in their reactivity towards nitrile ligands.

The second part of this study involved the reactivity of **1** towards polydentate nitrile ligands. We had previously shown that 1,2-dicyanobenzene (1,2-DCB) reacts with **1** in the presence of KPF_6 to afford $[Re_2Cl_3(\mu\text{-dppm})_2(1,2\text{-DCB})_2]PF_6$, possessing structure **I**, in which each 1,2-DCB ligand possesses one coordinated and one uncoordinated CN group. With the use of 1,4-dicyanobenzene (1,4-DCB) or 1,4-dicyanobut-2-ene (1,4-DCBE) in place of 1,2-DCB, similar bis-nitrile complexes were obtained. The important spectroscopic and electrochemical properties of **6** and **7** are summarized in Table 3. Note in particular the close similarity between the CVs of **6** and **7** and those of other complexes of these types [1,3]. A single crystal X-ray structure determination of the 1,4-DCB complex **6** confirmed the close relationship of these complexes to others with this stoichiometry [1–3]. An ORTEP [15] representation of the structure of the dirhenium cation present in the structure of **6** is shown in Fig. 1 and important bond distances and angles are listed in Table 2. The Re–Re distance of 2.2637(12) Å is similar to that in $[Re_2Cl_3(\mu\text{-dppm})_2(1,2\text{-DCB})_2]PF_6$ (2.265(1) Å) [3]; all other bond distances and angles are normal [1–3]. The torsional angles Cl(1)–Re(1)–Re(2)–N(10), Cl(2)–Re(1)–Re(2)–N(20), P(1)–Re(1)–Re(2)–P(2) and P(3)–Re(1)–Re(2)–P(4) are 25.8°, 24.7°, 25.8° and 24.8°, respectively, which shows the presence of a partially staggered rotational conformation in this Re–Re triply bonded complex.

It had been our hope that complexes **6** and **7** could be used as precursors to polymeric dirhenium(II) complexes of the type represented in structure **III** (dppm ligands omitted).



III

However, it appears that either the weak σ-donor ability of the unbound CN group in **6** and **7** or the presence of unfavourable steric interactions between the phenyl groups of neighbouring dppm ligands in adjacent dirhenium units prevented the formation of such species. Note that 1,4-DCB has been used to link $Rh_2(\mu\text{-}O_2CCH_3)_4$ units in polymeric chains through *axial* Rh–N coordination [16]. Our unsuccessful synthetic strategies included, (i) the reaction of **1** with one or fewer equivalents of 1,4-DCB or 1,4-DCBE, (ii) the reaction of **1** with an equivalent of **6** or **7** under a variety of reaction conditions. Future studies will involve the reactions of **6** and **7** with other substitutionally labile dirhenium species, which are less sterically crowded.

Table 2
Important bond distances (Å) and angles (°) for the complex $[Re_2Cl_3(\mu\text{-dppm})_2(1,4\text{-DCB})_2]PF_6$ (**6**) [a]

Distances			
Re(1)–Re(2)	2.2637(12)	Re(2)–Cl(3)	2.536(4)
Re(1)–Cl(2)	2.364(5)	N(10)–C(10)	1.13(2)
Re(1)–Cl(1)	2.364(5)	N(17)–C(17)	1.16(3)
Re(1)–P(1)	2.434(4)	N(20)–C(20)	1.13(2)
Re(1)–P(3)	2.438(5)	N(27)–C(27)	1.13(2)
Re(2)–N(20)	2.015(5)	C(10)–C(11)	1.48(3)
Re(2)–N(10)	2.029(16)	C(14)–C(17)	1.39(3)
Re(2)–P(4)	2.478(5)	C(20)–C(21)	1.47(3)
Re(2)–P(2)	2.481(4)	C(24)–C(27)	1.44(3)
Angles			
Re(2)–Re(1)–Cl(2)	106.18(13)	N(20)–Re(2)–P(2)	96.0(4)
Re(2)–Re(1)–Cl(1)	107.46(13)	N(10)–Re(2)–P(2)	85.8(4)
Cl(2)–Re(1)–Cl(1)	146.34(18)	Re(1)–Re(2)–P(2)	94.64(11)
Re(2)–Re(1)–P(1)	96.05(11)	P(4)–Re(2)–P(2)	170.42(17)
Cl(2)–Re(1)–P(1)	93.28(16)	N(20)–Re(2)–Cl(3)	84.1(4)
Cl(1)–Re(1)–P(1)	84.55(15)	N(10)–Re(2)–Cl(3)	87.5(4)
Re(2)–Re(1)–P(3)	98.78(12)	Re(1)–Re(2)–Cl(3)	178.20(11)
Cl(2)–Re(1)–P(3)	83.85(16)	P(4)–Re(2)–Cl(3)	85.68(16)
Cl(1)–Re(1)–P(3)	89.76(16)	P(2)–Re(2)–Cl(3)	85.11(15)
P(1)–Re(1)–P(3)	165.12(16)	C(10)–N(10)–Re(2)	176.1(16)
N(20)–Re(2)–N(10)	171.2(6)	C(20)–N(20)–Re(2)	172.1(16)
N(20)–Re(2)–Re(1)	94.2(4)	N(10)–C(10)–C(11)	178(2)
N(10)–Re(2)–Re(1)	94.3(4)	N(17)–C(17)–C(14)	168(3)
N(20)–Re(2)–P(4)	85.7(4)	N(20)–C(20)–C(21)	174.9(19)
N(10)–Re(2)–P(4)	91.2(4)	N(27)–C(27)–C(24)	176(3)
Re(1)–Re(2)–P(4)	94.65(12)		

[a] Numbers in parentheses are e.s.d. values in the least significant digits.

As an alternative strategy to obtaining polymeric dirhenium complexes we looked at the potential for 2-cyanoethylphosphine (CEP) to act as a multidentate donor. The complex $[Re_2Cl_3(\mu\text{-dppm})_2(CEP)_2]PF_6$ (**8**) was isolated and characterized by IR and NMR spectroscopy and cyclic voltammetry (Table 3). The CV of **8** is very similar to that of other nitrile bound complexes of this type. Interestingly, this complex can be oxidized to the paramagnetic complex $[Re_2Cl_3(\mu\text{-dppm})_2(CEP)_2](PF_6)_2$ (**9**) through the use of $NOPF_6$; complex **9** has the same CV as that of **8** (Table 3) and behaves as a 1:2 electrolyte in acetone ($\Lambda_m = 164\ \Omega^{-1}\ cm^2\ mol^{-1}$ for a 1×10^{-3} M solution). The $^{31}P\{^1H\}$ NMR spectrum of **8** shows an AA′BB′ pattern with the most intense peaks of the component multiplets at δ −5.5 and δ −6.0. An additional singlet at δ −21.5 is due to the unbound phosphorus atoms of the two CEP ligands; the $^{31}P\{^1H\}$ NMR spectrum of free CEP shows a singlet at δ −20.8. The ^1H NMR spectrum of free CEP shows resonances for the methylene protons at δ +2.62 (m, 6H) and δ +1.93 (m, 6H). The resonance at δ +2.62 represents the CH_2 protons bound to the P atom of CEP, while the other set of CH_2 protons are for those bound to CN. In spite of the inequivalence of the $-CH_2CH_2CN$ units once one of them is bound to Re in complex **8**, the resonance at $\delta \sim +1.7$ is not resolved into two sets of multiplets (ratio 1:2) but appears as an unresolved single broad resonance.

We note that although **8** contains uncoordinated P and CN groups, it did not react with $Re_2Cl_4(\mu\text{-dppm})_2$ (**1**). This may simply reflect unfavourable steric effects and the conformational requirements of the dangling CEP ligands.

Table 3
Spectroscopic and cyclic voltammetric data for dirhenium(II)-nitrile complexes of the type $[Re_2Cl_3(\mu\text{-dppm})_2(LL)_2]PF_6$ (LL = 1,4-DCB, 1,4-DCBE or CEP)

Complex	IR spectra (cm^{-1}) [a]		^1H NMR spectra (δ) [b]	$^{31}P\{^1H\}$ NMR spectra (δ) [b,c]	CV half-wave potentials [d]			Λ_m [e]
	ν(CN)	ν(P–F)			$E_{1/2}$(ox)	$E_{1/2}$(red)	$E_{p,c}$	
$[Re_2Cl_3(\mu\text{-dppm})_2(1,4\text{-DCB})_2]PF_6$ (**6**)	2235(m)	840vs	8.0–7.0(m, 48H, Ph), 5.80(m, 4H, CH_2 of dppm)	−4.0(m), −4.9(m)	+0.75(60)	−1.16(70)	−1.52	92
$[Re_2Cl_3(\mu\text{-dppm})_2(1,4\text{-DCBE})_2]PF_6$ (**7**)	2278(vw), 2253(w)	841s	7.9–7.0(m, 40H, Ph), 5.80(m, 4H, CH_2 of dppm), 5.20(m, 2H, CH) [f], 5.02(m, 2H, CH) [f], 3.05(m, 4H, CH_2) [f], 2.60(m, 4H, CH_2) [f]	−5.9(s, br)	+0.68(70)	−1.29(80)		95
$[Re_2Cl_3(\mu\text{-dppm})_2(CEP)_2]PF_6$ (**8**)	2249(w, br)	839s	7.9–7.1(m, 40H, Ph), 5.80(m, 4H, CH_2 of dppm), 2.48(m, 12H, CH_2) [f], ~1.7(m, 12H, CH_2) [f,g]	−5.5(m), −6.0(m), −21.5(s) [g]	+0.66(60)	−1.28(80)		

[a] Recorded as Nujol mulls. Abbreviation: s, strong; m, medium; w, weak; br, broad.

[b] Spectra recorded in $CDCl_3$ unless otherwise stated.

[c] These spectra contain AA′BB′ patterns for the P atoms of the μ-dppm ligands; in the case of **7** this pattern is unresolved. Septet at δ −144 due to $[PF_6]^-$ is also observed in all spectra.

[d] Measurements carried out on solutions in 0.1 M n-Bu_4NPF_6–CH_2Cl_2 and referenced to the Ag/AgCl electrode with a scan rate of 200 mV s^{-1} at a Pt-bead electrode. Under these experimental conditions $E_{1/2} = +0.47$ V for the ferrocenium/ferrocene couple. $E_p (= E_{p,a} - E_{p,c})$ values given in parentheses.

[e] Molar conductivity ($\Omega^{-1}\ cm^2\ mol^{-1}$) recorded on 1.0×10^{-3} M solutions in acetone.

[f] Resonance for the coordinated ligand 1,2-DCBE or CEP.

[g] Spectrum recorded in CD_2Cl_2.

4. Supplementary material

Tables giving full details for the crystal data and data collection parameters, atomic positional parameters, anisotropic thermal parameters, bond distances and bond angles for **6** are available on request from author R.A.W.

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