

Coupling of Edge-Sharing Bioctahedral Dirhenium(II) Units through the Agency of  $[\text{N}(\text{CN})_2]^-$ ,  $[\text{C}(\text{CN})_3]^-$ , and  $[\text{Ni}(\text{CN})_4]^{2-}$  Linkages

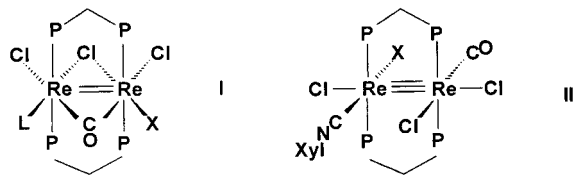
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## Introduction

We have recently described the synthesis and characterization of a variety of diphosphine-bridged bioctahedral dirhenium(II) complexes, including those of types I and II, in which ligand X has the capability of bridging to other metal species to afford homo- and heterometallic complexes that contain redox-active dirhenium units and might display interesting solid-state properties.<sup>1</sup> To date, we have focused



our attention on cases where X is thiocyanate or a cyanide-containing bridging unit, and we have been successful in isolating several mixed-metal  $\text{Re}_4\text{Pd}_2$ ,  $\text{Re}_2\text{Ag}$ ,  $\text{Re}_2\text{W}$ ,  $\text{Re}_2\text{Pt}$ , and  $\text{Re}_2\text{Rh}$  assemblies,<sup>1</sup> with the use of complexes of type I as precursors when  $\text{L} = \text{CO}$  and  $\text{PP} = \text{Ph}_2\text{PCH}_2\text{PPh}_2$  (dppm) or  $\text{Ph}_2\text{PC}(\text{=CH}_2)\text{PPh}_2$  (dppE). We now report the first instances in which pairs of edge-sharing bioctahedral dirhenium(II) complexes are linked via  $[\text{N}(\text{CN})_2]^-$ ,  $[\text{C}(\text{CN})_3]^-$ , and  $[\text{Ni}(\text{CN})_4]^{2-}$  units to give products in which there is significant electronic communication between the pairs of dirhenium centers. These compounds are of the type  $[\text{Re}_2\text{Cl}_3(\mu\text{-PP})_2(\text{CO})_2]_2(\mu\text{-X})$ , where  $\text{PP} = \text{dppm}$  or  $\text{dppE}$  and  $\text{X} = \text{N}(\text{CN})_2$ ,  $\text{C}(\text{CN})_3$ , or  $\text{Ni}(\text{CN})_4$ , and they have been characterized on the basis of their electrochemical and spectroscopic properties and by X-ray crystallography. This study is part of a more general investigation into the incorporation of multiply bonded dirhenium complexes into supramolecular assemblies.<sup>1–3</sup>

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- (1) (a) Kuang, S.-M.; Fanwick, P. E.; Walton, R. A. *Inorg. Chem.* **2000**, *39*, 2968. (b) Kuang, S.-M.; Fanwick, P. E.; Walton, R. A. *Inorg. Chem.* **2001**, *40*, 5682.  
 (2) Bera, J. K.; Angaridis, P.; Cotton, F. A.; Petrukhina, M. A.; Fanwick, P. E.; Walton, R. A. *J. Am. Chem. Soc.* **2001**, *123*, 1515.  
 (3) (a) Kuang, S.-M.; Fanwick, P. E.; Walton, R. A. *Inorg. Chem. Commun.*, accepted for publication. (b) Kuang, S.-M.; Fanwick, P. E.; Walton, R. A. *Inorg. Chem.*, accepted for publication.

## Experimental Section

**A. Starting Materials.** The dirhenium complexes  $\text{Re}_2\text{Cl}_4(\mu\text{-dppm})_2(\text{CO})_2$  (**1**),<sup>4</sup>  $[\text{Re}_2\text{Cl}_3(\mu\text{-dppE})_2(\text{CO})_2(\text{NCMe})]\text{PF}_6$  (**2**),<sup>1,5</sup>  $[\text{Re}_2\text{Cl}_3(\mu\text{-dppm})_2(\text{CO})_2(\text{NCMe})]\text{PF}_6$  (**3**),<sup>6</sup> and  $[\text{Re}_2\text{Cl}_3(\mu\text{-dppm})_2(\text{CO})_2(\text{CNXyl})(\text{NCMe})]\text{PF}_6$  (**4**),<sup>7</sup> all of which have edge-sharing bioctahedral structures of type I, were prepared by the literature methods. The compound  $(n\text{-Bu}_4\text{N})_2\text{Ni}(\text{CN})_4$  was prepared by the literature method;<sup>8</sup> its IR spectrum (KBr pellet) showed  $\nu(\text{CN}) = 2110(\text{s}) \text{ cm}^{-1}$ . The reagents  $\text{Na}[\text{N}(\text{CN})_2]$  and  $\text{K}[\text{C}(\text{CN})_3]$  were purchased from commercial sources (Aldrich Chemical Co. or Strem Chemicals) and used as received. Samples of the new complexes  $\text{Re}_2\text{Cl}_3\text{-}[\text{N}(\text{CN})_2](\mu\text{-dppm})_2(\text{CO})_2$  (**5**) and  $\text{Re}_2\text{Cl}_3[\text{C}(\text{CN})_3](\mu\text{-dppm})_2(\text{CO})_2$  (**6**) were obtained from the reactions between  $\text{Re}_2\text{Cl}_4(\mu\text{-dppm})_2(\text{CO})_2$  and  $\text{Na}[\text{N}(\text{CN})_2]$  and  $\text{K}[\text{C}(\text{CN})_3]$  with the use of the exact same procedures that were used previously to prepare the analogous dppE complexes.<sup>1b</sup> For **5**, yield 73%. IR spectrum ( $\text{cm}^{-1}$ ):  $\nu(\text{CN})$  2299(mw), 2238(m), and 2172(vs);  $\nu(\text{CO})_t$  1976(s);  $\nu(\text{CO})_b$  1718(m).  $^3\text{P}\{^1\text{H}\}$  NMR spectrum ( $\text{CDCl}_3$ ):  $\delta$  -12.5(m) and -19.2(m) (centers of a symmetrical AA'BB' pattern). For **6**, yield 78%. IR spectrum ( $\text{cm}^{-1}$ ):  $\nu(\text{CN})$  2229(w) and 2174(vs);  $\nu(\text{CO})_t$  1984(vs);  $\nu(\text{CO})_b$  1716(m).  $^3\text{P}\{^1\text{H}\}$  NMR spectrum ( $\text{CDCl}_3$ ):  $\delta$  -12.9(m) and -20.3(m) (centers of a symmetrical AA'BB' pattern). The properties of **5** and **6** resemble very closely those reported for their dppE analogues.<sup>1b</sup> Solvents were obtained from commercial sources and were deoxygenated by purging with dinitrogen prior to use.

**CAUTION:** Special precautions should be taken in handling thallium(I) compounds which are toxic.

**B. Synthesis of Dirhenium Coupled Products. (i) Synthesis of  $[\text{Re}_2\text{Cl}_3(\mu\text{-dppm})_2(\text{CO})_2]_2[\mu\text{-N}(\text{CN})_2]\text{Cl}$  (**7**).** A mixture of  $\text{Re}_2\text{Cl}_4(\mu\text{-dppm})_2(\text{CO})_2$  (**1**) (67 mg, 0.05 mmol),  $\text{Re}_2\text{Cl}_3[\text{N}(\text{CN})_2](\mu\text{-dppm})_2(\text{CO})_2$  (**5**) (69 mg, 0.05 mmol), and  $\text{TIPF}_6$  (17.5 mg, 0.05 mmol) was stirred in 20 mL of dichloromethane for 7 days under an atmosphere of dinitrogen, then filtered to remove any insoluble materials, and the filtrate evaporated to afford a yellow-brown solid residue. This solid was washed with diethyl ether ( $2 \times 5 \text{ mL}$ ) and recrystallized from 1,2- $\text{C}_2\text{H}_4\text{Cl}_2$ /benzene to yield yellow-brown crystals; yield 95 mg (70%). This product did not give a satisfactory

- (4) Cotton, F. A.; Daniels, L. M.; Dunbar, K. R.; Falvello, L. R.; Tetrick, S. M.; Walton, R. A. *J. Am. Chem. Soc.* **1985**, *107*, 3524.  
 (5) Kuang, S.-M.; Fanwick, P. E.; Walton, R. A. *Inorg. Chim. Acta* **2000**, *300–302*, 434.  
 (6) Cotton, F. A.; Dunbar, K. R.; Falvello, L. R.; Walton, R. A. *Inorg. Chem.* **1985**, *24*, 4180.  
 (7) Fanwick, P. E.; Price, A. C.; Walton, R. A. *Inorg. Chem.* **1988**, *27*, 2601.  
 (8) Mason, W. R.; Gray, H. B. *J. Am. Chem. Soc.* **1968**, *90*, 5721.

## NOTE

C and H microanalysis, but its properties showed it was pure, and a single-crystal X-ray structure analysis supported the composition. IR spectrum (KBr pellet,  $\text{cm}^{-1}$ ):  $\nu(\text{CN})$  2215(vs) and  $\sim 2180(\text{sh})$ ;  $\nu(\text{CO})_t$  1978(vs);  $\nu(\text{CO})_b$  1713(m).  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum ( $\text{CDCl}_3$ ):  $\delta -11.4(\text{m})$  and  $-18.6(\text{m})$  (AA'BB' pattern).  $^1\text{H}$  NMR spectrum ( $\text{CDCl}_3$ ):  $\delta +7.9$  to  $+6.9$  (80H, Ph of dppm),  $\delta +4.35$ -(m) and  $+4.15(\text{m})$  (8H, ABX<sub>4</sub> pattern,  $-\text{CH}_2-$  of dppm). Conductivity ( $1.0 \times 10^{-3}$  M solutions,  $\Omega^{-1} \text{cm}^2 \text{mol}^{-1}$ ): 120 (acetonitrile), 93 (acetone).

### (ii) Synthesis of $[\text{Re}_2\text{Cl}_3(\mu\text{-dppm})_2(\text{CO})_2]_2[\mu\text{-C}(\text{CN})_3]\text{Cl}$ (**8**).

The reaction between **1**,  $\text{Re}_2\text{Cl}_3[\text{C}(\text{CN})_3](\mu\text{-dppm})_2(\text{CO})_2$  (**6**), and TlPF<sub>6</sub> in dichloromethane was carried out with use of the procedure described for the synthesis of **7** (see subsection B(i)); yield 61%. Anal. Calcd for  $\text{C}_{112}\text{H}_{96}\text{Cl}_{11}\text{N}_3\text{O}_4\text{P}_8\text{Re}_4$  (i.e.,  $8 \cdot 2\text{C}_2\text{H}_4\text{Cl}_2$ ): C, 45.90; H, 3.30. Found: C, 45.20; H, 3.38. IR spectrum (KBr pellet,  $\text{cm}^{-1}$ ):  $\nu(\text{CN})$  2236(w) and 2181(vs);  $\nu(\text{CO})_t$  1985(vs);  $\nu(\text{CO})_b$  1710(m).  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum ( $\text{CDCl}_3$ ):  $\delta -10.8(\text{m})$  and  $-19.6(\text{m})$  (AA'BB' pattern).  $^1\text{H}$  NMR spectrum ( $\text{CDCl}_3$ ):  $\delta +7.9$  to  $+6.9$  (80H, Ph of dppm),  $\delta +4.35(\text{m})$  and  $+4.15(\text{m})$  (8H, ABX<sub>4</sub> pattern,  $-\text{CH}_2-$  of dppm). Conductivity ( $1 \times 10^{-3}$  M solution,  $\Omega^{-1} \text{cm}^2 \text{mol}^{-1}$ ): 106 (acetonitrile), 95 (acetone).

### (iii) Synthesis of $[\text{Re}_2\text{Cl}_3(\mu\text{-dppE})_2(\text{CO})_2]_2[\mu\text{-Ni}(\text{CN})_4]$ (**9**).

A solution of (*n*-Bu<sub>4</sub>N)<sub>2</sub>[Ni(CN)<sub>4</sub>] (16.0 mg, 0.025 mmol) in dichloromethane (5 mL) was added to a solution of  $[\text{Re}_2\text{Cl}_3(\mu\text{-dppE})_2(\text{CO})_2(\text{NCMe})]\text{PF}_6$  (**2**) (74 mg, 0.05 mmol) in 30 mL of dichloromethane and the clear solution left undisturbed under a dinitrogen atmosphere for 24 h to facilitate crystal growth. The red crystals that resulted were filtered off and washed with diethyl ether ( $2 \times 10$  mL); yield 67 mg (73%). Anal. Calcd for  $\text{C}_{115}\text{H}_{94}\text{Cl}_{12}\text{N}_4\text{NiO}_4\text{P}_8\text{Re}_4$  (i.e.,  $9 \cdot 3\text{CH}_2\text{Cl}_2$ ): C, 44.95; H, 3.08. Found: C, 44.13; H, 3.18. IR spectrum (KBr pellet,  $\text{cm}^{-1}$ ):  $\nu(\text{CN})$  2129(m);  $\nu(\text{CO})_t$  1972-(vs);  $\nu(\text{CO})_b$  1737(m).

### (iv) Synthesis of $[\text{Re}_2\text{Cl}_3(\mu\text{-dppm})_2(\text{CO})_2]_2[\mu\text{-Ni}(\text{CN})_4]$ (**10**).

A procedure similar to that described in subsection B(iii) was used but with  $[\text{Re}_2\text{Cl}_3(\mu\text{-dppm})_2(\text{CO})_2(\text{NCMe})]\text{PF}_6$  (**3**) (73 mg, 0.05 mmol) in place of **2**; yield 45%. Anal. Calcd for  $\text{C}_{111}\text{H}_{94}\text{Cl}_{12}\text{N}_4\text{NiO}_4\text{P}_8\text{Re}_4$  (i.e.,  $10 \cdot 3\text{CH}_2\text{Cl}_2$ ): C, 44.94; H, 3.15. Found: C, 44.49; H, 3.54. IR spectrum (KBr pellet,  $\text{cm}^{-1}$ ):  $\nu(\text{CN})$  2145 (split peak, mw);  $\nu(\text{CO})_t$  1974(vs);  $\nu(\text{CO})_b$  1729(m).

### (v) Synthesis of $[\text{Re}_2\text{Cl}_3(\mu\text{-dppm})_2(\text{CO})(\text{CNXyl})]_2[\mu\text{-Ni}(\text{CN})_4]$ (**11**).

A solution of (*n*-Bu<sub>4</sub>N)<sub>2</sub>[Ni(CN)<sub>4</sub>] (6.5 mg, 0.01 mmol) in 5 mL of acetone was added to a solution of  $[\text{Re}_2\text{Cl}_3(\mu\text{-dppm})_2(\text{CO})(\text{CNXyl})(\text{NCMe})]\text{PF}_6$  (**4**) (34 mg, 0.02 mmol) in 20 mL of this same solvent. The clear solution was left undisturbed for 72 h and filtered, and the brown microcrystals were washed with acetone ( $2 \times 10$  mL) and diethyl ether ( $2 \times 10$  mL); yield 16 mg (55%). Anal. Calcd for  $\text{C}_{124}\text{H}_{106}\text{Cl}_6\text{N}_6\text{NiO}_2\text{P}_8\text{Re}_4$ : C, 50.04; H, 3.59. Found: C, 49.67; H, 3.60. IR spectrum (KBr pellet,  $\text{cm}^{-1}$ ):  $\nu(\text{CN})$  (XylNC and  $\mu\text{-Ni}(\text{CN})_4$ ) 2106(s);  $\nu(\text{CO})_b$  1703(m).

**C. X-ray Crystal Structure Determinations.** Single crystals of composition  $[\text{Re}_2\text{Cl}_3(\mu\text{-dppE})_2(\text{CO})_2]_2[\mu\text{-Ni}(\text{CN})_4] \cdot 6\text{CH}_2\text{Cl}_2$  (**9**·6CH<sub>2</sub>Cl<sub>2</sub>) were obtained directly from the reaction mixture (see subsection B(iii)). The data collection was carried out on a Nonius Kappa CCD diffractometer. Lorentz and polarization corrections were applied to the data set. The key crystallographic data are given in Table 1.

The structure was solved using the structure solution program PATTY in DIRDIF-99.<sup>9</sup> The remaining non-hydrogen atoms were located in succeeding difference Fourier syntheses. Hydrogen atoms

**Table 1.** Crystallographic Data for the Dirhenium Complex of Composition  $[\text{Re}_2\text{Cl}_3(\mu\text{-dppE})_2(\text{CO})_2]_2[\mu\text{-Ni}(\text{CN})_4] \cdot 6\text{CH}_2\text{Cl}_2$  (**9**·6CH<sub>2</sub>Cl<sub>2</sub>)

empirical formula	C <sub>118</sub> H <sub>100</sub> Cl <sub>18</sub> N <sub>4</sub> NiO <sub>4</sub> P <sub>8</sub> Re <sub>4</sub>
fw	3327.59
space group	<i>P</i> 2 <sub>1</sub> / <i>n</i> (No. 14)
<i>a</i> , Å	16.2380(5)
<i>b</i> , Å	18.4616(5)
<i>c</i> , Å	20.4851(6)
$\alpha$ , deg	90
$\beta$ , deg	99.0071(14)
$\gamma$ , deg	90
<i>V</i> , Å <sup>3</sup>	6065.3(6)
<i>Z</i>	2
$\rho_{\text{calcd}}$ , g/cm <sup>3</sup>	1.822
$\mu$ , mm <sup>-1</sup>	4.742
radiation ( $\lambda$ , Å)	Mo K $\alpha$ (0.710 73)
temp, K	150
<i>R</i> ( <i>F</i> <sub>o</sub> ) <sup>a</sup>	0.055
<i>R</i> <sub>w</sub> ( <i>F</i> <sub>o</sub> <sup>2</sup> ) <sup>b</sup>	0.126
GO <sub>F</sub>	1.068

$$^a R = \frac{|F_o| - |F_c|}{|F_o|} \text{ with } F_o^2 > 2\sigma(F_o^2). \quad ^b R_w = \frac{[\sum w(|F_o^2| - |F_c^2|)^2]}{\sum w|F_o^2|^{1/2}}.$$

bound to carbon were placed in calculated positions according to idealized geometries with C–H = 0.95 Å and *U*(H) = 1.3*U*<sub>eq</sub>(C). They were included in the refinement but constrained to ride on the atom to which they are bonded. An empirical absorption correction using SCALEPACK<sup>10</sup> was applied. The final refinements were performed by the use of the program SHELXL-97.<sup>11</sup>

The structure solution and refinement of the crystal of **9**·6CH<sub>2</sub>Cl<sub>2</sub> proceeded routinely, and all non-hydrogen atoms were refined with anisotropic thermal parameters. The Ni atom of the  $[\mu\text{-Ni}(\text{CN})_4]$  unit is located at a crystallographic inversion center. The three CH<sub>2</sub>Cl<sub>2</sub> molecules in the asymmetric unit were well behaved. The largest peak in the final difference Fourier was 1.09 e<sup>−</sup>Å<sup>−3</sup>.

Single crystals of compound **7**, that were of composition **7**·5C<sub>2</sub>H<sub>4</sub>Cl<sub>2</sub>, were obtained from 1,2-C<sub>2</sub>H<sub>4</sub>Cl<sub>2</sub>/benzene in the monoclinic space group *C*2/*c* with cell parameters *a* = 34.0460(7) Å, *b* = 20.0419(5) Å, *c* = 20.5738(5) Å,  $\beta$  = 96.113(2)°, *V* = 13 958.6(6) Å<sup>3</sup>, *Z* = 4. The refinement converged to *R*(*F*<sub>o</sub>) = 0.079 and *R*<sub>w</sub>(*F*<sub>o</sub><sup>2</sup>) = 0.202 for 15 468 reflections with *I* > 2σ(*I*). No major problems were encountered in the refinement of the monocation present in **7**, other than a disordering of the amido nitrogen atom N(3) of the  $[(\mu\text{-NC})\text{N}(\text{CN})]^-$  ligand over two positions, each with 50% occupancy. However, the poor quality of the data set (collected at 150 (±1) K) resulted in large thermal parameters for the C and Cl atoms of the 1,2-C<sub>2</sub>H<sub>4</sub>Cl<sub>2</sub> solvent molecules, for several of the phenyl ring C atoms of the dppm ligands, and for the chloride anion. Because the full structure did not refine satisfactorily, full details are not reported.

**D. Physical Measurements.** Infrared spectra were recorded as KBr pellets on a Perkin-Elmer 2000 FT-IR spectrometer.  $^1\text{H}$  and  $^{31}\text{P}\{^1\text{H}\}$  NMR spectra were obtained with the use of a Varian INOVA 300 spectrometer. Proton resonances were referenced internally to the residual protons in the incompletely deuterated solvent. The  $^{31}\text{P}\{^1\text{H}\}$  spectra were recorded at 121.6 MHz, with 85% H<sub>3</sub>PO<sub>4</sub> as an external standard. Electrochemical measurements were carried out with the use of a BAS Inc. model CV-27 instrument in conjunction with a BAS Model RXY recorder and were recorded on dichloromethane solutions that contained 0.1 M tetra-*n*-butylammonium hexafluorophosphate (TBAH) as supporting electrolyte. *E*<sub>1/2</sub> values, determined as (*E*<sub>p,a</sub> + *E*<sub>p,c</sub>)/2, were referenced to the silver/silver chloride (Ag/AgCl) electrode at 25

(9) Beurskens, P. T.; Beurskens, G.; deGelder, R.; Garcia-Granda, S.; Gould, R. O.; Israel, R.; Smits, J. M. M. *The DIRDIF-99 Program System*; Crystallography Laboratory, University of Nijmegen: Netherlands, 1998.

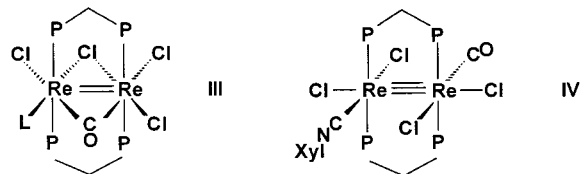
(10) Otwinowski, Z.; Minor, W. *Methods Enzymol.* **1996**, 276, 307.

(11) Sheldrick, G. M. *SHELXL-97. A Program for Crystal Structure Refinement*; University of Gottingen: Gottingen, Germany, 1997.

°C and were uncorrected for junction potentials. Under our experimental conditions,  $E_{1/2} = +0.47$  V versus Ag/AgCl for the ferrocenium/ferrocene couple. Conductivity measurements were obtained by the use of a YSI model 35 conductance meter. Elemental microanalyses were performed by Dr. H. D. Lee of the Purdue University Microanalytical Laboratory.

## Results and Discussion

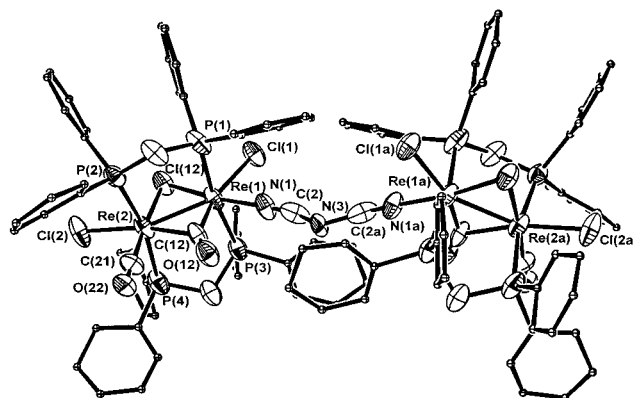
In our previous study,<sup>1b</sup> we had incorporated  $[\text{N}(\text{CN})_2]^-$  and  $[\text{C}(\text{CN})_3]^-$  into bioctahedral dirhenium complexes of types I and II (see Introduction) through exchange with a terminal chloride ligand of the precursors III (L = CO or XylNC) and IV. In the case of I and II, we chose not to



isolate all possible compounds of these types but instead prepared representative examples only. In the present study, we have expanded the number of edge-sharing bioctahedral compounds of type I that are available by isolating the complexes  $\text{Re}_2\text{Cl}_3[\text{N}(\text{CN})_2](\mu\text{-dppm})_2(\text{CO})_2$  (**5**) and  $\text{Re}_2\text{Cl}_3[\text{C}(\text{CN})_3](\mu\text{-dppm})_2(\text{CO})_2$  (**6**). Their properties (see Experimental Section) show them to be very similar structurally to their dppE analogues, the tricyanomethanide derivative of which had previously been the subject of an X-ray crystal structure determination.<sup>1b</sup> In accord with our earlier expectation that compounds of types I and II could be used to obtain higher nuclearity assemblies through the complexation of other dirhenium units by the uncoordinated cyano groups that are present, we have used complexes **5** and **6** to prepare examples of “dimers-of-dimers”, involving pairs of coupled dirhenium units, that are of a new type, being derived from *edge-sharing* bioctahedra.

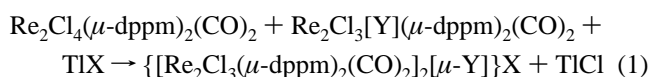
The dirhenium(II) complexes  $\text{Re}_2\text{Cl}_3[\text{N}(\text{CN})_2](\mu\text{-dppm})_2(\text{CO})_2$  (**5**) and  $\text{Re}_2\text{Cl}_3[\text{C}(\text{CN})_3](\mu\text{-dppm})_2(\text{CO})_2$  (**6**) react with an equivalent amount of  $\text{Re}_2\text{Cl}_4(\mu\text{-dppm})_2(\text{CO})_2$  (**1**) in the presence of a thallium(I) salt (TIPF<sub>6</sub> or TlO<sub>3</sub>SCF<sub>3</sub>) to afford in good yield the new tetra-rhenium complexes  $\{[\text{Re}_2\text{Cl}_3(\mu\text{-dppm})_2(\text{CO})_2]_2[\mu\text{-Y}]\}^+\text{Cl}^-$ , where Y = N(CN)<sub>2</sub> (**7**) or C(CN)<sub>3</sub> (**8**). The presence of Tl(I) is essential for the reaction to proceed (it is presumably needed to labilize the Cl bound cis to the  $\mu\text{-CO}$  ligand in **5**), but surprisingly, neither  $[\text{PF}_6]^-$  nor  $[\text{O}_3\text{SCF}_3]^-$  are incorporated into the final product, on the basis of the characterization of these products by IR and <sup>31</sup>P NMR spectroscopies and the X-ray structure determination of a crystal of **7**. The behavior of **7** and **8** as 1:1 electrolytes is confirmed by conductivity measurements of their solutions in acetonitrile and acetone ( $\sim 1.0 \times 10^{-3}$  M). The <sup>31</sup>P{<sup>1</sup>H} NMR spectra of **7** and **8** show the expected AA'BB' splitting patterns, and their IR spectra confirm the presence of terminal and bridging CO ligands ( $\nu(\text{CO})_t$  at  $\sim 1980$  cm<sup>-1</sup> and  $\nu(\text{CO})_b$  at  $\sim 1710$  cm<sup>-1</sup>) (see Experimental Section).

X-ray data sets were collected (at 150 (±1) K) on crystals that were grown from three separate preparative samples of



**Figure 1.** ORTEP<sup>12</sup> representation of the structure of the  $\{[\text{Re}_2\text{Cl}_3(\mu\text{-dppm})_2(\text{CO})_2]_2[\mu\text{-N}(\text{CN})_2]\}^+$  cation present in  $7 \cdot 5\text{C}_2\text{H}_4\text{Cl}_2$ . Thermal ellipsoids are drawn at the 50% probability level except for the phenyl group carbon atoms of the dppm ligands which are circles of arbitrary radius. Selected bond distances (Å) are as follows: Re(1)–Re(2) 2.5839(7), Re(1)–N(1) 2.065(13), Re(1)–Cl(1) 2.422(3), Re(1)–Cl(12) 2.442(3), Re(1)–C(12) 1.95(2), Re(2)–Cl(2) 2.435(4), Re(2)–Cl(12) 2.477(3), Re(2)–C(12) 2.169(13), Re(2)–C(21) 1.91(2).

**7.** Although all sets of data were of marginal quality, in all instances the structure of the tetra-rhenium cation was identical, and its parameters were firmly established (Figure 1). While the anion was satisfactorily modeled as  $[\text{Cl}]^-$ , we are uncertain as to its origin. The reaction times necessary to maximize the yields of **7** and **8** were long (about one week), so solvent participation ( $\text{CH}_2\text{Cl}_2$ ) or decomposition of a portion of the dirhenium precursor complex(es) could be the explanation. Nonetheless, it is unclear why exchange of  $[\text{PF}_6]^-$  or  $[\text{O}_3\text{SCF}_3]^-$  for  $[\text{Cl}]^-$  does not occur, and what we had assumed would be a simple reaction (i.e., eq 1; X = PF<sub>6</sub> or O<sub>3</sub>SCF<sub>3</sub>; Y = N(CN)<sub>2</sub> or C(CN)<sub>3</sub>) is apparently not the case.



During the structure refinement of **7**, attempts were made to model the anion as  $[\text{F}]^-$  or  $[\text{H}_2\text{PO}_4]^-$ , both of which could have formed by decomposition of the  $[\text{PF}_6]^-$  anion (from TIPF<sub>6</sub>) during the course of the long reactions, but this gave unsatisfactory solutions. Furthermore, IR spectroscopy excluded the presence of phosphate anion. Anion exchange reactions carried out on **7** and **8**, after the isolation of these products, did not lead to the stoichiometric incorporation of other anions. Also, our attempts to grow X-ray quality crystals of **7** from other solvent systems and to obtain suitable crystals of **8** were not successful.

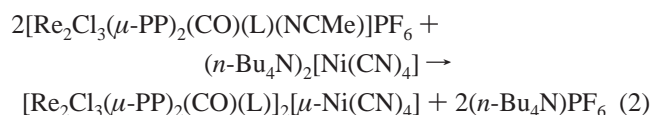
The structure determination of the tetra-rhenium cation, which is depicted in the ORTEP<sup>12</sup> representation shown in Figure 1, reveals that the Re–Re distance of 2.5839(7) Å is very similar to those found for the dirhenium units present in  $\text{Re}_2\text{Cl}_4(\mu\text{-dppm})_2(\text{CO})_2$  (2.584(1) Å)<sup>4</sup> and  $\text{Re}_2\text{Cl}_3[\text{C}(\text{CN})_3](\text{CO})_2(\mu\text{-dppE})_2$  (2.5823(6) Å).<sup>1b</sup> The Re–N distance involving the  $\mu\text{-N}(\text{CN})_2$  linker is 2.065(13) Å and, therefore, comparable to the Re–N distances present in the complex

(12) Johnson, C. K. *ORTEP II*; Report ORNL-5138; Oak Ridge National Laboratory: Oak Ridge, TN, 1976.

## NOTE

$\text{Re}_2[\text{N}(\text{CN})_2]_4(\mu\text{-dppm})_2(\text{DMF})_2$  (range 2.039(8)–2.052(9) Å)<sup>1b</sup>; in the latter compound, all  $[\text{N}(\text{CN})_2]^-$  ligands are bound in a monodentate fashion. Unfortunately, the relatively poor quality of the data for **7** and the disorder involving the  $\mu\text{-}[\text{N}(\text{CN})]$  unit preclude us from drawing further comparisons between the structural parameters for the dicyanoamido ligands in these two complexes. We assume that the structure of the related tricyanomethanide complex **8** involves the bridging of two dirhenium units by two of the cyano groups of a single  $[\text{C}(\text{CN})_3]^-$  bridge. This type of bridge is encountered in the polymeric diruthenium(III,II) complexes  $[\text{Ru}_2(\mu\text{-O}_2\text{CCH}_3)_4(\mu\text{-L})]_\infty$  (L =  $[\text{N}(\text{CN})_2]^-$  or  $[\text{C}(\text{CN})_3]^-$ ), which are the only previous examples of assemblies of multiply bonded dimetal complexes that utilize these polycyano linker ligands.<sup>13</sup>

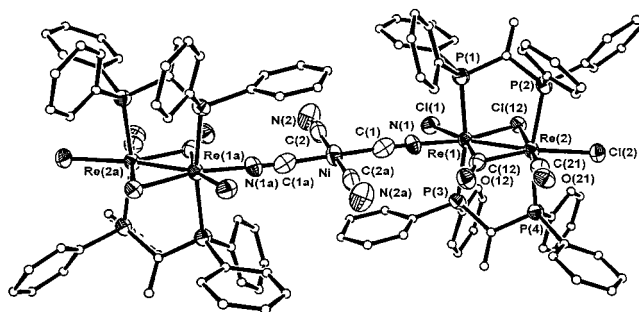
To eliminate the presence of “free” anions in the structures of these coupled dirhenium species, we reacted mixtures of the nitrile-containing precursors **2–4** with  $(n\text{-Bu}_4\text{N})_2\text{Ni}(\text{CN})_4$  in the hope that  $[\text{Ni}(\text{CN})_4]^{2-}$  would substitute the acetonitrile ligand in each of two  $[\text{Re}_2\text{Cl}_3(\mu\text{-PP})_2(\text{CO})(\text{L})(\text{NCMe})]_2^+$  cations and form neutral, coupled products of the type  $[\text{Re}_2\text{Cl}_3(\mu\text{-PP})_2(\text{CO})(\text{L})]_2[\mu\text{-Ni}(\text{CN})_4]$  (eq 2, where PP = dppE when L = CO and PP = dppm when L = CO or XylNC).



This strategy was successful in all three reactions attempted and afforded complexes **9–11**. Their IR spectra are similar and show that the terminal CO or XylNC ligands and bridging CO ligand are retained in all cases; in the case of **11**, the  $\nu(\text{CN})$  modes of XylNC and  $\mu\text{-}[\text{Ni}(\text{CN})_4]$  overlap, and only a single intense band is observed. While complexes **9** and **10** are insoluble in polar and nonpolar solvents, complex **11** was slightly soluble in dichloromethane, and we were able to record a cyclic voltammogram (vide infra), although satisfactory NMR spectra could not be obtained in this or any other solvent.

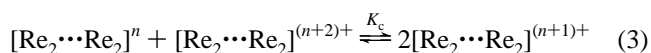
The identity of **9** was established by X-ray crystallography, and an ORTEP<sup>12</sup> representation of the structure is shown in Figure 2. Important bond lengths and bond angles are listed in the caption to Figure 2. The Ni atom is located at a crystallographic inversion center. The individual dirhenium units, which are structurally very similar to those present in the structure of **7**, have a Re–Re distance of 2.5768(5) Å. The Re–N distance of 2.062(9) Å is essentially the same as that involving the  $[\text{N}(\text{CN})_2]^-$  linker in **7**. Within the bridging  $[\mu\text{-Ni}(\text{CN})_4]$  unit, the Ni–C distance for the trans CN groups bound to Re is shorter (by  $\sim 0.02$  Å) than the Ni–C distance for the pair of unbound cyanides. The Re–N $\equiv$ C, Ni–C $\equiv$ N and *trans*-C–Ni–C angles are in the range 176–180°. This structure is the first for a multiply bonded dimetal complex that contains a  $[\text{Ni}(\text{CN})_4]^{2-}$  linker ligand.

Complexes **7**, **8**, and **11** are sufficiently soluble in 0.1 M TBAH–CH<sub>2</sub>Cl<sub>2</sub> to obtain cyclic voltammetric data, which



**Figure 2.** ORTEP<sup>12</sup> representation of the structure of the molecule  $[\text{Re}_2\text{Cl}_3(\mu\text{-dppE})_2(\text{CO})_2]_2[\mu\text{-Ni}(\text{CN})_4]$  present in  $\mathbf{9} \cdot 6\text{CH}_2\text{Cl}_2$ . Thermal ellipsoids are drawn at the 50% probability level except for the phenyl group carbon atoms of the dppm ligands which are circles of arbitrary radius. Selected bond distances (Å) and bond angles (deg) are as follows: Re(1)–Re(2) 2.5768(5), Re(1)–N(1) 2.062(9), Re(1)–Cl(1) 2.418(2), Re(1)–Cl(12) 2.462(2), Re(1)–C(12) 1.961(10), Re(2)–Cl(2) 2.428(2), Re(2)–Cl(12) 2.479(2), Re(2)–C(12) 2.189(10), Re(2)–C(21) 1.880(11), N(1)–C(1) 1.123(14), N(2)–C(2) 1.128(15), Ni–C(1) 1.878(14), Ni–C(2) 1.908(14); Re(1)–Cl(12)–Re(2) 62.87(6), Re(1)–C(12)–Re(2) 76.6(4), Re(1)–C(12)–O(12) 146.8(8), Re(2)–Cl(12)–O(12) 136.0(8), Re(1)–N(1)–C(2) 176.5(8), Ni–C(1)–N(1) 177.0(10), Ni–C(2)–N(2) 176.2(12).

show clear evidence for electronic coupling between the dirhenium units in these complexes. The CV data are summarized in Table 2, and the single-scan CVs of **7** and **8** are shown in Figure 3. The data in Table 2 include those for the dirhenium complexes **1**, **3–6**, and  $\text{Re}_2\text{Cl}_4(\mu\text{-dppm})_2(\text{CO})(\text{CNXyl})$ .<sup>4,6,7,14</sup> The shifts in potentials between  $\text{Re}_2\text{Cl}_4(\mu\text{-dppm})_2(\text{CO})_2$  (**1**) and  $\text{Re}_2\text{Cl}_4(\mu\text{-dppm})_2(\text{CO})(\text{CNXyl})$ , and those that occur upon substituting a Re–Cl bond by  $[\text{N}(\text{CN})_2]^-$ ,  $[\text{C}(\text{CN})_3]^-$ , and MeCN, are consistent with the potentials we observe for **7**, **8**, and **11**. In addition, all three of these complexes show the presence of pairs of sequential one-electron redox processes for  $E_{1/2}(\text{ox})$  and  $E_{1/2}(\text{red})(1)$ , although, in the case of **11**, the pair of processes labeled as  $E_{1/2}(\text{red})(1)$  are not resolved. The values for the comproportionation constants  $K_c$  for the equilibria represented by eq 3 can be calculated from the relationship shown in eq 4, where  $\Delta E_{1/2}$  represents the separation between the  $E_{1/2}$  values of the coupled processes.<sup>15–18</sup>



$$K_c = \exp(\Delta E_{1/2}/25.69) \quad (4)$$

For **7**, the values of  $\Delta E_{1/2}(\text{ox})$  and  $\Delta E_{1/2}(\text{red})$  are 180 and 120 mV, respectively, and therefore,  $K_c = 1.10 \times 10^3$  and 115, respectively. In the case of **8**, in which  $[\text{N}(\text{CN})_2]^-$  has been replaced by  $[\text{C}(\text{CN})_3]^-$ , the values of  $K_c$  are  $2.49 \times 10^4$  and  $1.10 \times 10^3$ . These electrochemical data indicate that the electronic communication between the dirhenium units in **8** is greater than in **7**. The corresponding data for **11** show that  $\Delta E_{1/2} = 160$  mV, and therefore,  $K_c = 506$  for the sequential one-electron oxidations associated with the pair

(14) Cotton, F. A.; Dunbar, K. R.; Price, A. C.; Schwotzer, W.; Walton, R. A. *J. Am. Chem. Soc.* **1986**, *108*, 4843.

(15) Cayton, R. H.; Chisholm, M. H.; Huffman, J. C.; Lobkovsky, E. B. *J. Am. Chem. Soc.* **1991**, *113*, 8709.

(16) Cotton, F. A.; Lin, C.; Murillo, C. A. *Inorg. Chem.* **2001**, *40*, 478.

(17) Ren, T.; Zou, G.; Alvarez, J. C. *Chem. Commun.* **2000**, 1197.

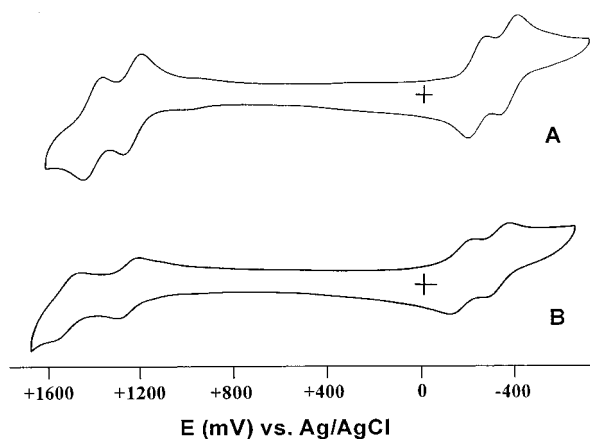
(18) Richardson, D. E.; Taube, H. *Inorg. Chem.* **1981**, *20*, 1278.

(13) Miyasaka, H.; Clérac, R.; Campos-Fernández, C. S.; Dunbar, K. R. *Inorg. Chem.* **2001**, *40*, 1663.

**Table 2.** Cyclic Voltammetric Half-Wave Potentials for Several Dirhenium Complexes Including **7**, **8**, and **11**<sup>a</sup>

complex	$E_{1/2}(\text{ox})$	$E_{1/2}(\text{red})(1)$	$E_{1/2}(\text{red})(2)$	ref
$\text{Re}_2\text{Cl}_4(\mu\text{-dppm})_2(\text{CO})_2$ ( <b>1</b> )	+0.91	-0.57	-1.6 <sup>b</sup>	4
$\text{Re}_2\text{Cl}_3[\text{N}(\text{CN})_2](\mu\text{-dppm})_2(\text{CO})_2$ ( <b>5</b> )	+1.12	-0.37	-1.27	<i>c</i>
$\text{Re}_2\text{Cl}_3[\text{C}(\text{CN})_3](\mu\text{-dppm})_2(\text{CO})_2$ ( <b>6</b> )	+1.14	-0.28	-1.18	<i>c</i>
$[\text{Re}_2\text{Cl}_3(\mu\text{-dppm})_2(\text{CO})_2(\text{NCMe})]\text{PF}_6$ ( <b>3</b> )	+1.46	-0.14	-1.12	6
$\text{Re}_2\text{Cl}_4(\mu\text{-dppm})_2(\text{CO})(\text{CNXyl})$	+0.60	-0.81	<i>d</i>	14
$[\text{Re}_2\text{Cl}_3(\mu\text{-dppm})_2(\text{CO})(\text{CNXyl})(\text{NCMe})]\text{PF}_6$ ( <b>4</b> )	+1.18	-0.35	-1.30	7
<b>7</b>	+1.36/+1.18 <sup>e</sup>	-0.27/-0.39 <sup>e</sup>	-1.28 <sup>e</sup>	<i>c</i>
<b>8</b>	+1.50/+1.24	-0.16/-0.34	-1.20	<i>c</i>
<b>11</b>	+0.89/+0.73	-0.67 <sup>f</sup>	<i>d</i>	<i>c</i>

<sup>a</sup> Data from single scan CVs are in volts vs Ag/AgCl. Experimental conditions are given in the Experimental Section. <sup>b</sup>  $E_{p,c}$  value. <sup>c</sup> This work. <sup>d</sup> Outside the range of our measurements. <sup>e</sup> Identical values obtained by the use of DPV. <sup>f</sup> Process broadened but sequential one-electron reductions are not resolved.



**Figure 3.** Single scan cyclic voltammograms of solutions of **7** (A) and **8** (B) in 0.1 M TBAH- $\text{CH}_2\text{Cl}_2$  showing the sequential one-electron oxidations and one-electron reductions associated with the electronically coupled pairs of dirhenium units.

of coupled dirhenium units. All three complexes have  $K_c$  values for  $E_{1/2}(\text{ox})$  that are greater than the value of 100 (or less) that typically characterizes weakly coupled valence-

trapped systems (Robin-Day class I behavior).<sup>15</sup> For complex **8**, the value of  $K_c$  ( $\sim 3 \times 10^4$ ) places it in the intermediate regime between being a valence-trapped system and exhibiting extensive delocalization between two redox centers ( $K_c > 10^6$ , Robin-Day class III behavior).

Further studies are underway involving the use of  $[\text{N}(\text{CN})_2]^-$ ,  $[\text{C}(\text{CN})_3]^-$ , and  $[\text{Ni}(\text{CN})_4]^{2-}$  to couple multiply bonded dirhenium units that possess Re-Re bond orders and stereochemistries different from those reported here.

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**Supporting Information Available:** X-ray crystallographic files in CIF format. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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