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Mixed-Metal Assemblies Containing Multiply Bonded Dirhenium Species Linked through Thiocyanate- and Cyanide-Containing Bridging Units

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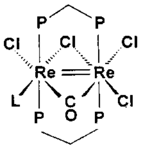
The lability of the terminal Re−Cl bond that is cis to the bridging CO ligand in the edge-sharing bioctahedral complexes $Re_2(\mu\text{-}Cl)(\mu\text{-}CO)(\mu\text{-}PP)_2Cl_3(L)$, where PP = $Ph_2PC({=}CH_2)PPh_2$ (dppE) when L = CO (**1**) and PP = $Ph_2PCH_2PPh_2$ (dppm) when L = CO (**2**) or XylNC (**3**), has been exploited in the preparation of mixed-metal Re_4Pd_2, Re_2Ag, Re_2W, Re_2Pt, and Re_2Rh assemblies, in which the dirhenium units are bound to the other metals through NCS or CN bridges. These complexes, which retain the Re═Re bonds of the parent dirhenium complexes, comprise the novel centrosymmetric complex $[Re_2Cl_3(\mu\text{-}dppE)_2(CO)_2(\mu\text{-}NCS)]_2Pd_2(\mu\text{-}SCN)(\mu\text{-}NCS)Cl_2$ (**9**), and the trimetallic complexes $Re_2Cl_3(\mu\text{-}dppE)_2(CO)_2[(\mu\text{-}NC)Ag(CN)]$ (**10**), $Re_2Cl_3(\mu\text{-}dppE)_2(CO)_2[(\mu\text{-}NC)W(CO)_5]$ (**11**), $[Re_2Cl_3(\mu\text{-}dppE)_2(CO)_2\{(\mu\text{-}NC)Pt(CN)(CN\text{-}t\text{-}Bu)_2\}]PF_6$ (**12**), $[Re_2Cl_3(\mu\text{-}dppE)_2(CO)_2\{(\mu\text{-}N(CN)_2)Rh(CO)(PPh_3)_2\}]O_3SCF_3$ (**13**), and $Re_2Cl_3(\mu\text{-}dppm)_2(CO)_2[(\mu\text{-}NC)W(CO)_5]$ (**16**). The identities of **9** and **16** have been established by X-ray crystallography, and all complexes characterized by IR and NMR spectroscopy and cyclic voltammetry. The reactions of the dicarbonyl complex **1**, and the isomeric pair of complexes $Re_2Cl_4(\mu\text{-}dppm)_2(CO)(CNXyl)$, which have edge-sharing bioctahedral (ESBO) (**3**) and open bioctahedral (OBO) (**4**) geometries, with $Na[N(CN)_2]$ and $K[C(CN)_3]$ have been used to prepare complexes in which the uncoordinated CN groups have the potential to coordinate other mono- or dimetal units to form extended arrays. The complexes which have been prepared and characterized are the monosubstituted species $Re_2Cl_3(X)(\mu\text{-}dppE)_2(CO)_2$ (X = $N(CN)_2$ (**14**) or $C(CN)_3$ (**15**)) and $Re_2Cl_3(X)(\mu\text{-}dppm)_2(CO)(CNXyl)$ (X = $N(CN)_2$ (**17**) or $C(CN)_3$ (**18**) with ESBO structures; X = $N(CN)_2$ (**19**) or $C(CN)_3$ (**20**) with OBO structures), of which **15**, **18**, and **20** have been characterized by single-crystal X-ray structure determinations. The substitutional labilities of the Re−Cl bonds in the complexes $Re_2Cl_4(\mu\text{-}dppm)_2(CO)$ (**5**), $Re_2Cl_4(\mu\text{-}dppm)_2(CNXyl)$ (**6**), and $Re_2Cl_4(\mu\text{-}dppm)_2$ (**7**) toward $Na[N(CN)_2]$ and $K[C(CN)_3]$ have also been explored and the complexes $Re_2Cl_3(X)(\mu\text{-}dppm)_2(CO)$ (X = $N(CN)_2$ (**21**) or $C(CN)_3$ (**22**)), $Re_2Cl_3(X)(\mu\text{-}dppm)_2(CNXyl)$ (X = $N(CN)_2$ (**23**) or $C(CN)_3$ (**24**)), $Re_2Cl_2(X)_2(\mu\text{-}dppm)_2(CNXyl)$ (X = $N(CN)_2$ (**25**) or $C(CN)_3$ (**26**)), $Re_2[N(CN)_2]_4(\mu\text{-}dppm)_2$ (**27**), and $Re_2[C(CN)_3]_4(\mu\text{-}dppm)_2$ (**28**) isolated in good yield. Single-crystal X-ray structure determinations of **24**, **26**, and **27** have shown that the Re−Re triple bonds present in the starting materials **5**−**7** are retained in these products.

Introduction

We have demonstrated previously that the Cl ligand which is cis to the CO ligand in edge-sharing bioctahedral (ESBO) complexes of type **I** (L = CO or XylNC; PP = $Ph_2PCH_2PPh_2$ (dppm) or $Ph_2PC({=}CH_2)PPh_2$ (dppE)) and that which is trans to the XylNC ligand in complexes of type **II** (PP = dppm) are labile to substitution by neutral ligands such as CO, RNC, and RCN.[1−10] In all cases, these substitutions proceed with retention of stereochemistry. The substitution of the most kinetically labile Cl ligand in complexes of types **I** and **II** by *monoanionic* ligands has not previously been studied. In the present paper we describe such a study in which we have used anionic ligands that have the capability of bridging to other metal centers and thereby enable, in principle, the assembly of mixed-metal complexes. For this purpose we have used thiocyanate- and cyanide-containing functionalities and the dirhenium starting materials $Re_2Cl_4(\mu\text{-}dppE)_2(CO)_2$ (**1**), $Re_2Cl_4(\mu\text{-}dppm)_2(CO)_2$ (**2**), and $Re_2Cl_4(\mu\text{-}dppm)_2(CO)(CNXyl)$ (**3**), which are all of structure type **I**, as well as the open bioctahedral (OBO) isomer of type **II**, $Re_2Cl_4(\mu\text{-}dppm)_2(CO)(CNXyl)$ (**4**). In addition, we have examined the substitutional lability of the Cl ligands in the complexes $Re_2Cl_4(\mu\text{-}dppm)_2(CO)$ (**5**), $Re_2Cl_4(\mu\text{-}dppm)_2(CNXyl)$ (**6**), and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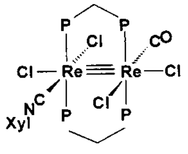
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$Re_2Cl_4(\mu\text{-dppm})_2$ (**7**) toward the dicyanamide ($[N(CN)_2]^-$) and tricyanomethanide ($[C(CN)_3]^-$) ligands. A preliminary report has previously been communicated.[11]

Experimental Section

The dirhenium complexes $Re_2Cl_4(\mu\text{-dppm})_2$,[12] $Re_2Cl_4(\mu\text{-dppm})_2(CO)$,[13] $Re_2Cl_4(\mu\text{-dppm})_2(CNXyl)$,[14] $Re_2Cl_4(\mu\text{-dppE})_2(CO)_2$,[10] $Re_2Cl_4(\mu\text{-dppm})_2(CO)_2$,[13] $Re_2Cl_4(\mu\text{-dppm})_2(CO)(CNXyl)$ (ESBO isomer, **I**),[15] and $Re_2Cl_4(\mu\text{-dppm})_2(CO)(CNXyl)$ (OBO isomer, **II**)[6] were prepared by standard literature procedures. Samples of $Et_4N[W(CO)_5(CN)]$[16] and *trans*-$Pt(CN)_2(CN\text{-}t\text{-}Bu)_2$[17,18] were obtained by the use of literature methods, while *trans*-$Rh[N(CN)_2](CO)(PPh_3)_2$ was prepared by the reaction of *trans*-$RhCl(CO)(PPh_3)_2$ (69 mg) with $Na[N(CN)_2]$ (9 mg) in a mixed methanol (10 mL)/dichloromethane (30 mL) solution. The mixture was refluxed for 18 h, and the solvents were evaporated to low volume to afford a yellow powder that was washed with diethyl ether. The purity of the product was established by $^{31}P\{^1H\}$ NMR spectroscopy (in $CDCl_3$): doublet at $\delta = +31.1$ and $+29.6$ ($J(Rh-P) = 122.4$ Hz). The reagents $TlPF_6$, NaSCN, AgCN, $K[Ag(CN)_2]$, $Na[N(CN)_2]$, and $K[C(CN)_3]$ were purchased from commercial sources (Aldrich Chemical Co., Strem Chemicals, or J. T. Baker Chemical Co.) and used as received. The compound TlO_3SCF_3 was prepared by the literature method.[19] Solvents were obtained from commercial sources and were deoxygenated by purging with dinitrogen prior to use. All reactions were performed under an atmosphere of dinitrogen.

Routine IR spectra, NMR spectra, and cyclic voltammetric measurements were determined as described previously.[20] Elemental microanalyses were performed by Dr. H. D. Lee of the Purdue University Microanalytical Laboratory.

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

A. Reactions of $Re_2Cl_4(\mu\text{-dppE})_2(CO)_2$ (1). 1. Synthesis of $Re_2Cl_3(NCS)(\mu\text{-dppE})_2(CO)_2$ (8). A solution of NaSCN (8.1 mg, 0.10 mmol) in methanol (5 mL) was added to a solution of **1** (136 mg, 0.10 mmol) in 30 mL of dichloromethane. The mixture was stirred at room temperature for 4 h, during which time the reaction color changed from yellow to green to red-brown. The resulting mixture was filtered to remove insoluble materials, and the filtrate was removed under reduced pressure to give a red-brown solid that was washed with methanol (2 × 3 mL) and diethyl ether (2 × 5 mL). Recrystallization from CH_2Cl_2/Et_2O gave **8** as red-brown microcrystals. Yield: 106 mg (77%). Anal. Calcd for $C_{56}H_{46}Cl_5NO_2P_4Re_2S$ (i.e., **8**$\cdot CH_2Cl_2$): C, 45.74; H, 3.15. Found: C, 46.22; H, 3.17. When an excess of NaSCN (5 equiv) was used in this reaction, the same product was obtained.

2. Synthesis of $[Re_2Cl_3(\mu\text{-dppE})_2(CO)_2(\mu\text{-NCS})]_2Pd_2(\mu\text{-SCN})(\mu\text{-NCS})Cl_2$ (9). A solution of NaSCN (4.0 mg, 0.05 mmol) in methanol (5 mL) was added to a mixture of **8** (69 mg, 0.05 mmol) and $Pd(1,5\text{-COD})Cl_2$ (14 mg, 0.05 mmol) in 30 mL of dichloromethane. The mixture was stirred at room temperature for 24 h and filtered and the volume of the filtrate reduced to ca. 3 mL. The addition of diethyl ether (20 mL) afforded a yellow-brown precipitate of **9** that was filtered off, washed with diethyl ether (20 mL), and dried. Recrystallization from CH_2Cl_2/C_6H_6 gave brown crystals. Yield: 66 mg (84%). Anal. Calcd for $C_{124}H_{100}Cl_8N_4O_4P_8Pd_2Re_4S_4$ (i.e., **9**$\cdot 2C_6H_6$): C, 44.76; H, 3.03. Found: C, 44.92; H, 2.97.

3. Synthesis of $Re_2Cl_3(\mu\text{-dppE})_2(CO)_2[Ag(CN)_2]$ (10). A solution of $K[Ag(CN)_2]$ (20.0 mg, 0.1 mmol) in methanol (5 mL) was added to a solution of **1** (136 mg, 0.10 mmol) in 40 mL of CH_2Cl_2. The mixture was refluxed for 48 h and then filtered to remove insoluble products, and the volume of the filtrate was reduced to ca. 3 mL before treatment with an excess of diethyl ether (20 mL) to precipitate the title complex. Yield: 96 mg (65%). Anal. Calcd for $C_{56}H_{44}AgCl_3N_2O_2P_4Re_2$: C, 45.22; H, 2.98. Found: C, 44.26; H, 3.11.

When **1** was reacted with an excess of AgCN (10 equiv) with the use of the same reaction conditions and workup procedure, the identical product **10** was isolated on the basis of microanalytical data and its spectroscopic and electrochemical properties. Yield: 61%. Anal. Found: C, 45.54; H, 3.13.

4. Synthesis of $Re_2Cl_3(\mu\text{-dppE})_2(CO)_2[(\mu\text{-NC})W(CO)_5]$ (11). i. Procedure A. A quantity of solid $Et_4N[W(CO)_5(CN)]$ (48 mg, 0.10 mmol) and a quantity of TlO_3SCF_3 (35 mg, 0.10 mmol) were added to a solution of **1** (136 mg, 0.10 mmol) in 40 mL of CH_2Cl_2. The mixture was stirred at room temperature for 48 h and then filtered and the filtrate evaporated to afford a brown-green solid that was recrystallized from CH_2Cl_2/Et_2O to give small green-brown crystals. Yield: 65 mg (39%). Anal. Calcd for $C_{60}H_{44}Cl_3NO_7P_4Re_2W$: C, 42.96; H, 2.64. Found: C, 42.76; H, 3.01.

ii. Procedure B. A stoichiometric quantity of TlO_3SCF_3 (35 mg, 0.10 mmol) was added to a solution of **1** (136 mg, 0.10 mmol) in 40 mL of CH_3CN. The mixture was stirred at room temperature for 72 h and filtered and the filtrate evaporated to give the yellow complex $[Re_2Cl_3(\mu\text{-dppE})_2(CO)_2(NCMe)]O_3SCF_3$ (90 mg). This product was dissolved in 30 mL of dichloromethane and the solution treated with $Et_4N[W(CO)_5(CN)]$ (29 mg, 0.06 mmol). The mixture was stirred at room temperature for 24 h, and a workup similar to that described for procedure A produced the title complex. Yield: 72 mg (43% based on **1**).

5. Synthesis of $[Re_2Cl_3(\mu\text{-dppE})_2(CO)_2\{(\mu\text{-NC})Pt(CN)(CN\text{-}t\text{-}Bu)_2\}]PF_6$ (12). Following the addition of $TlPF_6$ (35 mg, 0.10 mmol) to a solution of **1** (136 mg, 0.10 mmol) and *trans*-$Pt(CN)_2(CN\text{-}t\text{-}Bu)_2$ (41 mg, 0.10 mmol) in 80 mL of CH_2Cl_2, the mixture was stirred at room temperature for 7 days and then filtered. The volume of the yellow filtrate was reduced to ca. 3 mL, and then diethyl ether (20 mL) was added to give a yellow powder that was washed with diethyl ether (3 × 5 mL). Yield: 73 mg (38%). Anal. Calcd for $C_{66}H_{62}Cl_3F_6N_4O_2P_5PtRe_2$: C, 42.58; H, 3.31. Found: C, 43.43; H, 3.66.

6. Synthesis of $[Re_2Cl_3(\mu\text{-dppE})_2(CO)_2\{(\mu\text{-}N(CN)_2)Rh(CO)(PPh_3)_2\}]O_3SCF_3$ (13). A mixture of **1** (136 mg, 0.10 mmol), *trans*-$Rh[N(CN)_2](CO)(PPh_3)_2$ (72 mg, 0.10 mmol), and TlO_3SCF_3 (35 mg, 0.10 mmol) in 80 mL of dichloromethane was stirred at room temperature for 18 h and filtered and the yellow filtrate reduced in volume to ca. 5 mL. The addition of 30 mL of diethyl ether produced a brown precipitate that was filtered off, washed with diethyl ether (3 × 5 mL), and dried. Yield: 153 mg (70%). Anal. Calcd for $C_{96}H_{78}Cl_7F_3N_3O_6P_6Re_2RhS$ (i.e., **13**$\cdot 2CH_2Cl_2$): C, 48.69; H, 3.32. Found: C, 47.79; H, 3.45.

7. Synthesis of $Re_2Cl_3[N(CN)_2](\mu\text{-dppE})_2(CO)_2$ (14). A solution of $Na[N(CN)_2]$ (9.0 mg, 0.10 mmol) in methanol (5 mL) was added to a solution of **1** (136 mg, 0.10 mmol) in 40 mL of dichloromethane. The mixture was refluxed for 24 h and then filtered. The volume of the filtrate was reduced to ca. 3 mL, followed by treatment with diethyl ether (20 mL) to precipitate a brown powder that was filtered off and washed with methanol (2 × 5 mL) and diethyl ether (3 × 5 mL). Yield: 92 mg (66%). Anal. Calcd for $C_{56}H_{44}Cl_3N_3O_2P_4Re_2$: C, 48.26; H, 3.18. Found: C, 48.06; H, 3.42.

8. Synthesis of $Re_2Cl_3[C(CN)_3](\mu\text{-dppE})_2(CO)_2$ (15). The reaction between a solution of $K[C(CN)_3]$ (13.0 mg, 0.10 mmol) in methanol (5 mL) and a solution of **1** (136 mg, 0.10 mmol) in dichloromethane (40 mL) was carried out for 18 h and then worked-up as described in section A.7 to afford the title compound as a red powder. Yield: 118 mg (83%). Anal. Calcd for $C_{58}H_{44}Cl_3N_3O_2P_4Re_2$: C, 49.14; H, 3.13. Found: C, 48.34; H, 3.45.

B. Reaction of $Re_2Cl_4(\mu\text{-dppm})_2(CO)_2$ (2). Synthesis of $Re_2Cl_3(\mu\text{-dppm})_2(CO)_2[(\mu\text{-NC})W(CO)_5]$ (16). A procedure very similar to

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that described for dppE analogue **11** (procedure A in section A.4) afforded this green-colored complex from the reaction among **2** (134 mg, 0.10 mmol), $Et_4N[W(CO)_5(CN)]$ (35 mg, 0.10 mmol), and $TlPF_6$ (35 mg, 0.10 mmol). The crude product was recrystallized by the vapor diffusion between diisopropyl ether and a mixed 1,2-dichloroethane/benzene solution of the complex. Yield: 56 mg (34%). Anal. Calcd for $C_{66}H_{54}Cl_5NO_7P_4Re_2W$ (i.e., **16**$\cdot C_6H_6\cdot C_2H_4Cl_2$): C, 43.30; H, 2.97. Found: C, 43.07; H, 2.97.

C. Reactions of $Re_2Cl_4(\mu$-dppm$)_2$(CO)(CNXyl) (ESBO Isomer, I) (3). 1. Synthesis of $Re_2Cl_3[N(CN)_2](\mu$-dppm$)_2$(CO)(CNXyl) (17). A procedure similar to that described in section A.7 was used in the reaction between $Na[N(CN)_2]$ (9.0 mg, 0.10 mmol) and **3** (144 mg, 0.10 mmol). Yield: 92 mg (62%). Anal. Calcd for $C_{62}H_{53}Cl_3N_4OP_4Re_2$: C, 50.56; H, 3.63. Found: C, 50.00; H, 3.64.

2. Synthesis of $Re_2Cl_3[C(CN)_3](\mu$-dppm$)_2$(CO)(CNXyl) (18). The reaction of $Na[C(CN)_3]$ with **3** was carried out with the use of a procedure similar to that described in section A.8. This compound was obtained as brown crystals by the vapor diffusion of diisopropyl ether into a mixed 1,2-dichloroethane/benzene solution of the crude product. Yield: 75%. Anal. Calcd for $C_{64}H_{53}Cl_3N_4OP_4Re_2$: C, 51.36; H, 3.57. Found: C, 52.13; H, 4.06.

D. Reactions of $Re_2Cl_4(\mu$-dppm$)_2$(CO)(CNXyl) (OBO Isomer, II) (4). 1. Synthesis of $Re_2Cl_3[N(CN)_2](\mu$-dppm$)_2$(CO)(CNXyl) (19). A solution of $Na[N(CN)_2]$ (9.0 mg, 0.10 mmol) in methanol (5 mL) was added to a stoichiometric quantity of **4** (144 mg, 0.10 mmol) in 40 mL of dichloromethane. The mixture was stirred at room temperature for 24 h and filtered and the red filtrate evaporated to afford a red powder. This solid was washed with methanol (2 × 5 mL) and diethyl ether (3 × 5 mL) and then dried. Yield: 96 mg (65%). Anal. Calcd for $C_{62}H_{53}Cl_3N_4OP_4Re_2$: C, 50.56; H, 3.63. Found: C, 50.42; H, 3.67.

2. Synthesis of $Re_2Cl_3[C(CN)_3](\mu$-dppm$)_2$(CO)(CNXyl) (20). A procedure similar to that described in section D.1, but with the use of $K[C(CN)_3]$ (13.0 mg, 0.10 mmol) in place of $Na[N(CN)_2]$, afforded the title complex. It was obtained in pure crystalline form by the vapor diffusion of diisopropyl ether into a 1,2-dichloroethane solution of the crude product. Yield: 118 mg (79%). Anal. Calcd for $C_{64}H_{53}Cl_3N_4OP_4Re_2$: C, 51.36; H, 3.57. Found: C, 51.70; H, 3.85.

E. Reactions of $Re_2Cl_4(\mu$-dppm$)_2$(CO) (5). 1. Synthesis of $Re_2Cl_3[N(CN)_2](\mu$-dppm$)_2$(CO) (21). The reaction between **5** (131 mg, 0.10 mmol) and $Na[N(CN)_2]$ (9.0 mg, 0.10 mmol) was carried out with the use of a procedure similar to that described in section D.1. Yield: 90 mg (67%). Anal. Calcd for $C_{54.5}H_{47}Cl_6N_3OP_4Re_2$ (i.e., **21**$\cdot 1.5CH_2Cl_2$): C, 44.33; H, 3.24. Found: C, 44.32; H, 3.15.

2. Synthesis of $Re_2Cl_3[C(CN)_3](\mu$-dppm$)_2$(CO) (22). The title complex was obtained by the use of a procedure very similar to that described in section E.1, but with $K[C(CN)_3]$ (13.0 mg, 0.10 mmol) in place of $Na[N(CN)_2]$. Yield: 96 mg (70%). Anal. Calcd for $C_{55}H_{44}Cl_3N_3OP_4Re_2$: C, 48.37; H, 3.25. Found: C, 47.68; H, 3.53.

F. Reactions of $Re_2Cl_4(\mu$-dppm$)_2$(CNXyl) (6). The reactions of **6** with $Na[N(CN)_2]$ and $K[C(CN)_3]$ were carried out with the use of procedures essentially identical to those described in section D.1 except that both 1:1 and 1:2 substituted complexes were obtained by adjusting the appropriate stoichiometries of the reagents.

1. Synthesis of $Re_2Cl_3[N(CN)_2](\mu$-dppm$)_2$(CNXyl) (23). Yield: 73%. Anal. Calcd for $C_{62}H_{55}Cl_5N_4P_4Re_2$ (i.e., **23**$\cdot CH_2Cl_2$): C, 48.68; H, 3.62. Found: C, 49.22; H, 3.64.

2. Synthesis of $Re_2Cl_3[C(CN)_3](\mu$-dppm$)_2$(CNXyl) (24). This compound was recrystallized by the vapor diffusion of diisopropyl ether into a 1,2-dichloroethene solution of the crude product. Yield: 75%. Anal. Calcd for $C_{65}H_{57}Cl_5N_4P_4Re_2$ (i.e., **24**$\cdot C_2H_4Cl_2$): C, 49.85; H, 3.64. Found: C, 49.82; H, 3.61.

3. Synthesis of $Re_2Cl_2[N(CN)_2]_2(\mu$-dppm$)_2$(CNXyl) (25). Yield: 76%. Anal. Calcd for $C_{63}H_{53}Cl_2N_7P_4Re_2$: C, 51.29; H, 3.62. Found: C, 50.45; H, 4.23.

4. Synthesis of $Re_2Cl_2[C(CN)_3]_2(\mu$-dppm$)_2$(CNXyl) (26). This compound was recrystallized by the vapor diffusion of diisopropyl ether into a mixed chloroform/benzene solution of the crude product. Yield: 65%. Anal. Calcd for $C_{69}H_{55}Cl_8N_7P_4Re_2$ (i.e., **26**$\cdot 2CHCl_3$): C, 47.03; H, 3.15. Found: C, 47.74; H, 3.19. When a larger excess of $K[C(CN)_3]$ (4.5 equiv) was used to perform this reaction, the same product was obtained.

G. Reactions of $Re_2Cl_4(\mu$-dppm$)_2$ (7). 1. Synthesis of $Re_2[N(CN)_2]_4(\mu$-dppm$)_2$ (27). A quantity of **7** (128 mg, 0.10 mmol) was added to a solution of $Na[N(CN)_2]$ (36 mg, 0.40 mmol) in methanol (50 mL) and the reaction mixture stirred at room temperature for 48 h. A green solid was obtained by filtration and washed with methanol (2 × 5 mL) and diethyl ether (2 × 5 mL). Yield: 103 mg (76%), assuming the composition $Re_2[N(CN)_2]_4(\mu$-dppm$)_2(MeOH)_2$ as supported by ^1H NMR spectroscopy. This complex was recrystallized from $Et_2O/HCONMe_2$ to afford crystals of composition $Re_2[N(CN)_2]_4(\mu$-dppm$)_2(DMF)_2\cdot 3DMF$ as shown by single-crystal X-ray crystallography. Neither of these products gave satisfactory C and H microanalyses, although both were pure as established by IR and NMR spectroscopies.

2. Synthesis of $Re_2[C(CN)_3]_4(\mu$-dppm$)_2$ (28). The reaction between **7** (20 mg, 0.015 mmol) and $K[C(CN)_3]$ (8.7 mg, 0.068 mmol) in methanol (10 mL) for 24 h at room temperature gave a brown-colored mixture that was filtered, and the filtrate was evaporated to dryness. The brown solid was washed with methanol (2 × 5 mL) and then diethyl ether. Yield: 18.5 mg (82%). Like its dicyanamide analogue **27**, complex **28** did not give a satisfactory C and H microanalysis but was judged pure on the basis of its spectroscopic properties.

H. Single-Crystal X-ray Crystallography. Single crystals of $[Re_2Cl_3(\mu$-dppE$)_2(CO)_2(\mu$-NCS$)]_2Pd_2(\mu$-SCN$)(\mu$-NCS$)Cl_2$ (**9**) were grown at room temperature by the slow evaporation of a solution in dichloromethane/benzene (1:1). In the case of $Re_2Cl_3[C(CN)_3](\mu$-dppE$)_2(CO)_2$ (**15**), $Re_2Cl_3(\mu$-dppm$)_2(CO)_2[(\mu$-NC$)W(CO)_5]$ (**16**), and $Re_2Cl_3[C(CN)_3](\mu$-dppm$)_2$(CO)(CNXyl) (OBO isomer) (**20**), crystals were obtained by the slow diffusion of diisopropyl ether vapor into mixed 1,2-dichloroethane/benzene solutions of the complexes, while for $Re_2Cl_3[C(CN)_3](\mu$-dppm$)_2$(CO)(CNXyl) (ESBO isomer) (**18**), $Re_2Cl_3[C(CN)_3](\mu$-dppm$)_2$(CNXyl) (**24**), and $Re_2Cl_2[C(CN)_3]_2(\mu$-dppm$)_2$(CNXyl) (**26**), diisopropyl ether diffusion into solutions of these complexes in mixed 1,2-dichloroethane/1,2-dichlorobenzene, 1,2-dichloroethane, and mixed chloroform/benzene, respectively, was used. Suitable single crystals of the complex $Re_2[N(CN)_2]_4(\mu$-dppm$)_2$ (**27**) were obtained by the vapor diffusion of diethyl ether into a solution of the complex in $HCONMe_2$(DMF) at room temperature. Subsequent structure analysis showed that the single crystals chosen for the structure analyses were of compositions **9**$\cdot 10C_6H_6$, **15**$\cdot C_2H_4Cl_2$, **16**$\cdot C_6H_6\cdot C_2H_4Cl_2$, **18**$\cdot 0.436C_2H_4Cl_2$, **20**$\cdot C_2H_4Cl_2$, **24**$\cdot H_2O$, **26**$\cdot 2CHCl_3$, and **27**$(DMF)_2\cdot 3DMF$.

The crystals were mounted onto glass fibers in random orientations. The data collections for all crystals, except those of compound **24**, were performed on a Nonius KappaCCD diffractometer. In the case of **24**, intensity data were collected on a Bruker Smart 1000 CCD at the Department of Chemistry of the Chinese University of Hong Kong. The crystallographic data for all eight compounds are given in Table 1.

The structures of **9**, **15**, **16**, **18**, **20**, **26**, and **27** were solved using the structure solution program PATTY in DIRDIF92,[21] while direct methods were used to reveal the positions of the Re atoms in the structure of **24**. The remaining non-hydrogen atoms were located in succeeding difference Fourier syntheses. The hydrogen atoms were placed in calculated positions according to idealized geometries with $C-H = 0.95$ Å, and $U(H) = 1.3U_{eq}(C)$ for **9**, **15**, **16**, **18**, **20**, **26**, and **27** and $U(H) = 1.2U_{eq}(C)$ for **24**. They were included in the refinement but constrained to ride on the atom to which they were bonded. Empirical absorption corrections were applied; SCALEPACK[22] was used in all cases except **24**, for which the method of Kopfmann and Huber[23] was used. The structures were refined in full-matrix least-squares, where the function minimized was $\sum w(|F_o|^2 - |F_c|^2)^2$ and the weighting factor w was of the form $w = 1/[\sigma^2(F_o^2) + (AP)^2 + BP]$, where $P = (F_o^2 + 2F_c^2)/3$. The final refinements were performed by the use of the program SHELXL-97.[24] Carbon atoms C(4), C(113),

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[22] Otwinowski, Z.; Minor, W. *Methods Enzymol.* **1996**, *276*, 307.

[23] Kopfmann, G.; Huber, R. *Acta Crystallogr.* **1968**, *A24*, 348.

[24] Sheldrick, G. M. *SHELXL97. A Program for Crystal Structure Refinement*; University of Gottingen: Gottingen, Germany, 1997.

Table 1. Crystallographic Data for the Dirhenium Complexes of Composition $[Re_2Cl_3(\mu\text{-dppE})_2(CO)_2(\mu\text{-NCS})]_2Pd_2(\mu\text{-SCN})(\mu\text{-NCS})Cl_2\cdot 10C_6H_6$ (**9**), $Re_2Cl_3[C(CN)_3](\mu\text{-dppE})_2(CO)_2\cdot C_2H_4Cl_2$ (**15**), $Re_2Cl_3(\mu\text{-dppm})_2(CO)_2[(\mu\text{-NC})W(CO)_5]\cdot C_6H_6\cdot C_2H_4Cl_2$ (**16**), $Re_2Cl_3[C(CN)_3](\mu\text{-dppm})_2(CO)(CNXyl)\cdot 0.436C_2H_4Cl_2$ (**18**), $Re_2Cl_3[C(CN)_3](\mu\text{-dppm})_2(CO)(CNXyl)\cdot C_2H_4Cl_2$ (**20**), $Re_2Cl_3[C(CN)_3](\mu\text{-dppm})_2(CNXyl)\cdot H_2O$ (**24**), $Re_2Cl_2[C(CN)_3]_2(\mu\text{-dppm})_2(CNXyl)\cdot 2CHCl_3$ (**26**), and $Re_2[N(CN)_2]_4(\mu\text{-dppm})_2(DMF)_2\cdot 3DMF$ (**27**)

	9	**15**	**16**	**18**	**20**	**24**	**26**	**27**
empirical formula	$C_{172}H_{148}Cl_8N_4O_4P_8Pd_2Re_4S_4$	$C_{60}H_{48}Cl_5N_3O_2P_4Re_2$	$C_{66}H_{54}Cl_5NO_7P_4Re_2W$	$C_{64.87}H_{54.74}Cl_{3.87}N_4OP_4Re_2$	$C_{66}H_{57}Cl_5N_4OP_4Re_2$	$C_{63}H_{55}Cl_3N_4OP_4Re_2$	$C_{69}H_{55}Cl_8N_7P_4Re_2$	$C_{73}H_{79}N_{17}O_5P_4Re_2$
fw	3952.39	1516.63	1830.58	1539.96	1595.78	1486.82	1762.17	1770.85
space group	$P2_1/c$ (no. 14)	$P\bar{1}$ (no. 2)	$P2_1/n$ (no. 14)	$C2/c$ (no. 15)	$P2_12_12_1$ (no. 19)	$Pna2_1$ (no. 33)	$P2_1/n$ (no. 14)	$P\bar{1}$ (no. 2)
a, Å	18.6374(5)	12.4307(14)	15.0095(3)	40.3280(8)	12.88650(10)	22.795(5)	14.3659(3)	12.7110(5)
b, Å	21.8098(5)	15.6295(14)	19.3976(5)	13.5887(3)	19.4144(4)	15.442(3)	28.2054(10)	17.1115(8)
c, Å	20.1559(6)	18.061(2)	22.8577(6)	27.7616(4)	24.9646(4)	18.095(4)	17.5348(6)	20.5011(10)
α, deg	90	100.162(7)	90	90	90	90	90	94.886(3)
β, deg	104.9915(13)	90.857(5)	95.5766(17)	106.8915(12)	90	90	100.5410(19)	104.735(4)
γ, deg	90	109.607(7)	90	90	90	90	90	91.920(3)
V, Å^3	7914.1(7)	3243.3(13)	6623.5(5)	14557.1(9)	6245.7(3)	6369.4(23)	6985.1(7)	4289.7(7)
Z	2	2	4	8	4	4	4	2
ρ_{calcd}, g/cm^3	1.658	1.553	1.836	1.405	1.697	1.565	1.676	1.371
μ, mm^{-1}	3.630	4.125	5.817	3.636	4.288	4.068	3.955	2.983
temp, K	193	173	295	150	173	293	173	173
$R(F_o)^a$	0.064	0.056	0.054	0.043	0.038	0.060	0.058	0.059
$R_w(F_o^2)^b$	0.116	0.132	0.133	0.105	0.084	0.136	0.130	0.151
GOF	1.092	0.971	1.020	0.977	1.037	1.007	1.035	1.048

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

C(114), C(115), C(223), and C(415) of **24** were refined isotropically because of the relatively poor quality of the data collected. During the course of the structure refinements of **9**, **15**, **16**, **18**, **20**, **24**, **26**, and **27**, molecules from the recrystallization solvents were found to be cocrystallized with the complexes in the asymmetric units. These were included in the analyses and refined satisfactory. In the cases of **15**, **18**, and **27**, another unidentified and badly disordered solvent molecule was removed by the squeeze option in PLATON.[25] For **20** and **24** the absolute structures were determined by refinement. The enantiomers chosen had absolute structure parameters of −0.005(6) and 0.02(2), respectively. Non-hydrogen atoms were refined with anisotropic thermal parameters.

The largest remaining peaks in the final difference maps of **9**, **15**, **16**, **18**, **20**, **24**, **26**, and **27** were 1.36, 1.42, 2.04, 1.30, 1.22, 2.89, 2.17, and 2.07 e/Å^3, respectively.

Full structural data for the complexes are available as Supporting Information. The key bond distances and angles are given in Figures 1−8.

Results and Discussion

The present study focused primarily on two aspects of the reactivity of bioctahedral dirhenium(II) complexes of types **I** and **II** discussed in the Introduction. First, the substitutional lability of the chloro ligands of **I** and **II** toward monoanionic ligands that are capable of bridging different metal centers was investigated. Second, we explored the use of the resulting substituted complexes to generate mixed-metal assemblies that retain the multiply bonded dirhenium cores. The specific dirhenium starting materials used were the ESBO complexes (type **I**) $Re_2Cl_4(\mu\text{-dppE})_2(CO)_2$ (**1**),[10] $Re_2Cl_4(\mu\text{-dppm})_2(CO)_2$ (**2**),[13] and $Re_2Cl_4(\mu\text{-dppm})_2(CO)(CNXyl)$ (**3**),[15] and the OBO complex (type **II**) $Re_2Cl_4(\mu\text{-dppm})_2(CO)(CNXyl)$ (**4**).[6] Compound **4** is the only one of this type with the OBO structure that is known. The compounds that are formed upon reacting the bioctahedral complexes **1−4** with the thiocyanate- and cyanide-containing reagents NaSCN, AgCN, $K[Ag(CN)_2]$, $Et_4N[W(CO)_5(CN)]$, *trans*-$Pt(CN)_2(CN\text{-}t\text{-}Bu)_2$, *trans*-$Rh[N(CN)_2](CO)(PPh_3)_2$, $Na[N(CN)_2]$, and $K[C(CN)_3]$ are listed in Table 2 (they are denoted as **8−20**), along with their important IR and $^{31}P\{^1H\}$ NMR spectral properties and cyclic voltammetric half-wave potentials. The reactions that lead to **8−20** are shown in Schemes 1 and 2.

A further aspect of the present study involved an examination of the reactions of the complexes $Re_2Cl_4(\mu\text{-dppm})_2(L)$ (L = CO (**5**) or XylNC (**6**)), and of $Re_2Cl_4(\mu\text{-dppm})_2$ (**7**), toward $Na[N(CN)_2]$ and $K[C(CN)_3]$. These results are summarized in Scheme 3, and the reaction products are listed in Table 2 (as complexes **21−28**), along with their important properties. The significance of these reactions is that complexes **5−7** are themselves the starting materials (or intermediates) in the preparation of the bioctahedral complexes **2−4**,[6,13,15] so that this seemed an opportune time to contrast the Re−Cl bond lability in the entire set of dirhenium(II) dppm complexes **2−7**.

Note that while compounds **8−15** all contain the dppE ligand, compounds **16−28** contain dppm. This difference is one of convenience in the availability of starting materials. Since prior studies had established that there is no significant difference in the chemistry of analogous dirhenium(II) complexes that contain the dppE and dppm ligands,[10,13,15] we believe that the types of complexes obtained in the present study are *independent* of whether dppE or dppm is used as the ancillary phosphine ligand.

(a) Reactions with the Bioctahedral Dirhenium Complexes 1−4. The lability of one chloro ligand in **1−4** in the presence of stoichiometric quantities of anionic or neutral thiocyanate- and cyanide-containing reagents produces complexes that retain the same basic structures as that of their precursors (Scheme 1). Certain of these reactions, namely, those producing **11−13** and **16**, require the addition of 1 equiv of a thallium(I) reagent (TlO_3SCF_3 or $TlPF_6$) to enhance the labilization of this Cl ligand. In all instances, the specific Cl ligand that is displaced is the same one that is substituted by neutral CO, RNC, or RCN ligands.[1−10] An alternative means of preparing **11** utilizes the acetonitrile-containing intermediate $[Re_2Cl_3(\mu\text{-dppE})_2(CO)_2(NCMe)]O_3SCF_3$, from which the labile nitrile ligand is readily displaced by $[W(CO)_5CN]^-$.

The unsymmetrical nature of complexes **8−20** is confirmed by the presence of AA′BB′ patterns in their $^{31}P\{^1H\}$ NMR spectra (Table 2), and the IR spectra of these complexes show that the bridging and/or terminal bonding modes of the CO and XylNC ligands as present in **1−4** are very similar to those in the products **8−20** (Table 2). The cyclic voltammetric (CV) properties of the ESBO complexes **8−18**, which differ from those of the two OBO complexes **19** and **20**, are similar to one another (Table 2) and show the same pattern of redox processes

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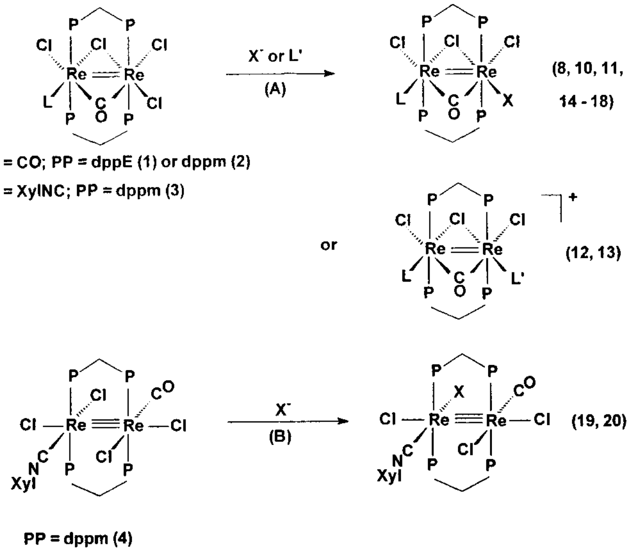
(25) Sluis, P. V. D.; Spek, A. L. *Acta Crystallogr.* **1990**, *A46*, 194.

Table 2. Selected Spectroscopic and Electrochemical Data for Dirhenium(II) Complexes Containing Bridging Phosphines

complex	compd no.	IR, ν(CN) and ν(CO), cm^{-1} [a]	$^{31}P\{^1H\}$ NMR, chem shift, δ [b]	CV half-wave potentials, V[c]	$E_{1/2}$ (red)(1)	$E_{1/2}$ (red)(2)
				$E_{1/2}$(ox)		
$Re_2Cl_3(NCS)(\mu\text{-dppE})_2(CO)_2$	**8**	2081 (s), *1961 (s), 1729 (s)*	+12.7 (m), +1.1 (m)	+0.96(70)	−0.45(60)	−1.33(80)
$[Re_2Cl_3(\mu\text{-dppE})_2(CO)_2(\mu\text{-NCS})]_2\text{-}Pd_2(\mu\text{-SCN})(\mu\text{-NCS})Cl_2$	**9**	2082 (s), *1964 (s), 1726 (m)*	+12.5 (m), +0.9 (m)	+0.93(60)	−0.46(60)	−1.34(80)
$Re_2Cl_3(\mu\text{-dppE})_2(CO)_2[Ag(CN)_2]$	**10**	2170 (w), 2125 (w), *1976 (s), 1735 (m)*	+13.9 (m), +1.9 (m)	+1.34(100)	−0.34(100)	−1.32(160)
$Re_2Cl_3(\mu\text{-dppE})_2(CO)_2[(\mu\text{-NC})W(CO)_5]$	**11**	2118 (w), 2055 (m), 1970 (m), 1924 (vs), *1735 (m)*[d]	+17.1 (m),+4. 8 (m)	+0.98[f]	−0.41(60)	−1.31(80)
$[Re_2Cl_3(\mu\text{-dppE})_2(CO)_2\{(\mu\text{-NC})Pt(CN)\text{-}(CN\text{-}t\text{-}Bu)_2\}]PF_6$	**12**	2237 (m), 2177 (m), 2155 (m), *1980 (vs), 1735 (m)*	+13.3 (m), +0.7 (m)	∼+1.4[g]	−0.25(70)	−1.18(70)
$[Re_2Cl_3(\mu\text{-dppE})_2(CO)_2\{(\mu\text{-}N(CN)_2)Rh\text{-}(CO)(PPh_3)_2\}]O_3SCF_3$	**13**	2209 (vs), 2170 (m), 1992 (vs), *1719 (m)*[d]	+28.7 (d),[e] +13.0 (m), −0.5(m)	∼+1.3[f]	−0.30(70)	−1.27(100)
$Re_2Cl_3[N(CN)_2](\mu\text{-dppE})_2(CO)_2$	**14**	2296 (w), 2236 (m), 2173 (vs), *1974 (s), 1720 (m)*	+12.1 (m), −0.1 (m)	+1.09(60)	−0.39(60)	−1.30(70)
$Re_2Cl_3[C(CN)_3](\mu\text{-dppE})_2(CO)_2$	**15**	2228 (w), 2176 (m), *1982 (s), 1719 (m)*	+12.8 (m), −0.4 (m)	+1.13(70)	−0.30(60)	−1.21(70)
$Re_2Cl_3(\mu\text{-dppm})_2(CO)_2[(\mu\text{-NC})W(CO)_5]$	**16**	2118 (w), 2053 (m), 1982 (m), 1920 (vs), 1901 (m), *1735 (m)*[d]	−6.0 (m), −19.3(m)	+0.93(75)	−0.36(70)	−1.26(130)
$Re_2Cl_3[N(CN)_2](\mu\text{-dppm})_2(CO)(CNXyl)$	**17**	2280 (m), 2221 (m), *2177 (s), 1670 (m)*	−15.0 (m), −21.5 (m)	+0.89(60)	−0.50(60)	−1.37(70)
$Re_2Cl_3[C(CN)_3](\mu\text{-dppm})_2(CO)(CNXyl)$	**18**	2229 (w), 2176 (s), *2118 (m), 1650 (m)*	−14.6 (m), −21.2 (m)	+0.90(60)	−0.48(70)	−1.36(110)
$Re_2Cl_3[N(CN)_2](\mu\text{-dppm})_2(CO)(CNXyl)$	**19**	2294 (w), 2230 (m), 2172 (vs), *2082 (s), 1962 (s)*	−5.8 (m), −11.2 (m)	+1.21(60)	−0.92[h]	
$Re_2Cl_3[C(CN)_3](\mu\text{-dppm})_2(CO)(CNXyl)$	**20**	2185 (s), 2153 (vs), *2096 (s), 1961 (s)*	−5.8 (m), −10.8 (m)	+1.33[f]	−0.85[h]	
$Re_2Cl_3[N(CN)_2](\mu\text{-dppm})_2(CO)$	**21**	2300 (w), 2229 (m), 2173 (vs), *1984 (s)*	−3.0 (m), −12.0 (m)	+0.68(70)	−1.25[h]	
$Re_2Cl_3[C(CN)_3](\mu\text{-dppm})_2(CO)$	**22**	2171 (s), 2075 (m), *1991 (m−s)*	−2.6 (m), −12.6 (m)	+0.78(60)	−1.14[h]	
$Re_2Cl_3[N(CN)_2](\mu\text{-dppm})_2(CNXyl)$	**23**	2295 (w), 2229 (m), 2172 (vs), *2088 (s)*	−6.4 (s)	+0.45(70)[i]	−1.56[h]	
$Re_2Cl_3[C(CN)_3](\mu\text{-dppm})_2(CNXyl)$	**24**	2229 (w), 2178 (vs), *2099 (s)*	−5.9 (s)	+0.48(60)[i]	−1.46[h]	
$Re_2Cl_2[N(CN)_2]_2(\mu\text{-dppm})_2(CNXyl)$	**25**	2294 (w), 2233 (m), 2174 (vs), *2097 (s)*	−1.6 (m), −7.7 (m)	+0.69(70)	−1.39[h]	
$Re_2Cl_2[C(CN)_3]_2(\mu\text{-dppm})_2(CNXyl)$	**26**	2217 (w), 2176 (s), 2114 (m), *2065 (vs)*	+0.1 (m), −8.5 (m)	+1.01(60)	−1.15(80)	
$Re_2[N(CN)_2]_4(\mu\text{-dppm})_2$	**27**	2290 (m), 2229 (m), 2168 (vs)	−5.7 (s)	*j*		
$Re_2[C(CN)_3]_4(\mu\text{-dppm})_2$	**28**	2221 (w), 2177 (s), 2161 (vs)	−8.1 (s)	*j*		

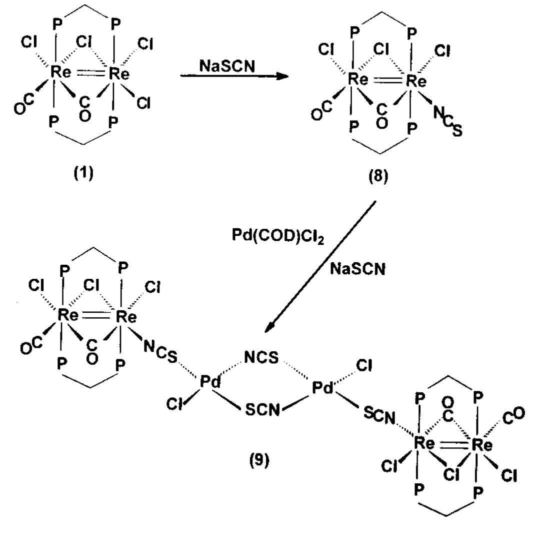
[a] IR spectra recorded as KBr pellets. Abbreviations: vs = very strong, s = strong, m = medium, w = weak. Bands assigned to ν(CO) and ν(CN) of the CO and XylNC ligands that were originally present in the starting materials **1**−**6** are shown in italics. Other bands are assigned to ν(CO) or ν(CN) that originate from the thiocyanate- or cyanide-containing reagents that were reacted with **1**−**6**. [b] NMR spectra recorded in $CDCl_3$ solutions, except for **8**, **9**, **11**, **12** and **21** (recorded in CD_2Cl_2), and **27** and **28** (recorded in $(CD_3)_2SO$). Abbreviations: s = singlet, d = doublet, m = multiplet. For AA′BB′ patterns, the centers of the two multiplets are given. [c] Data are given for dirhenium-centered processes and are based upon single-scan cyclic voltammograms (scan rate (ν) 200 mV/s) measured in 0.1 M TBAH/CH_2Cl_2 solutions at a Pt-bead electrode and referenced to the Ag/AgCl electrode. Under our experimental conditions $E_{1/2} = +0.47$ V for the ferrocenium/ferrocene couple. $E_{1/2}$ values are for one-electron processes with $i_{p,a} = i_{p,c}$, and numbers in parentheses are the approximate values of ΔE_p ($= E_{p,a} - E_{p,c}$) for the processes. [d] The $\nu(CO)_t$ mode of CO that is bound directly to the dirhenium core is overlapped by the ν(CO) modes of the other metal-containing fragment. [e] Doublet assigned to the two PPh_3 ligands bound to Rh ($J_{Rh-P} = 121.6$ Hz). [f] $E_{p,a}$ value. [g] Poorly defined $E_{1/2}$ value close to the solvent limit. [h] $E_{p,c}$ value. [i] This compound has a second reversible one-electron oxidation at $E_{1/2} = +1.48$ V (ΔE_p = 80 mV). [j] The cyclic voltammogram shows only broad poorly defined processes.

Scheme 1. Products from the Reactions of Complexes **1**−**4** with Monoanionic and Neutral Thiocyanate- and Cyanide-Containing Ligands[a]



[a] Reactions A: PP = dppE; L = CO; X = NCS (**8**), $Ag(CN)_2$ (**10**), $(NC)W(CO)_5$ (**11**), $N(CN)_2$ (**14**), or $C(CN)_3$ (**15**). PP = dppm; L = CO; X = $(NC)W(CO)_5$ (**16**); L = XylNC; X = $N(CN)_2$ (**17**) or $C(CN)_3$ (**18**). PP = dppE; L = CO; L′ = $(NC)Pt(CN)(CN\text{-}t\text{-}Bu)_2$ (**12**) or $[N(CN)_2]Rh(CO)(PPh_3)_2$ (**13**). Reactions B: PP = dppm; X = $N(CN)_2$ (**19**) or $C(CN)_3$ (**20**).

Scheme 2. Reaction of **1** with NaSCN and $Pd(COD)Cl_2$ To Form Complexes **8** and **9**



as are observed in the CVs of the parent bioctahedral complexes **1**−**3**.[10,13,15] The conclusion that the reactions of **1**−**4** proceed with retention of stereochemistry is born out by representative single-crystal X-ray structure determinations on complexes **9**, **15**, **16**, **18**, and **20**. The ORTEP[26] representations of these structures are shown in Figures 1−5, along with the important bond distances and angles. We shall next consider the individual reactions in more detail.

The reaction of NaSCN (1−5 equiv) with the dppE complex **1** in methanol affords red-brown crystals of the N-bound

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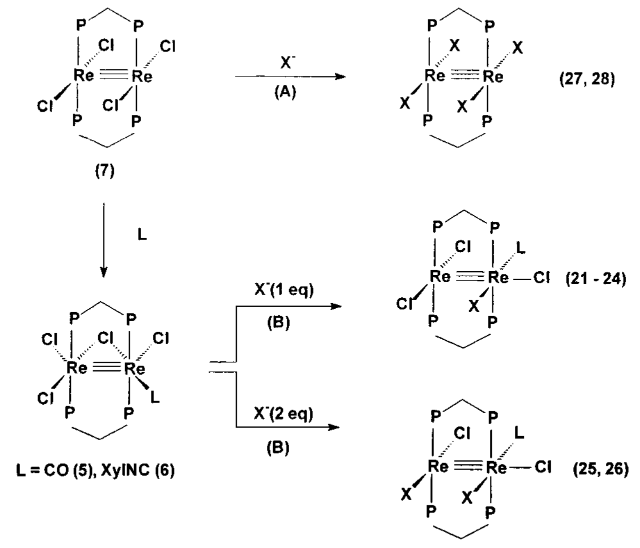
(26) Johnson, C. K. ORTEP Report ORNL-5138; Oak Ridge National Laboratory: Oak Ridge, TN, 1976.

Scheme 3. Products from the Reactions of Complexes **5**−**7** with the Monoanionic $[N(CN)_2]^-$ and $[C(CN)_3]^-$ Ligands[a]



[a] In all instances PP = dppm. Several of the complexes depicted in this scheme have staggered or partially staggered rotational geometries (see the text). This deviation from an eclipsed geometry is not shown here. Reactions A: X = $N(CN)_2$ (**27**) or $C(CN)_3$ (**28**). Reactions B: L = CO; X = $N(CN)_2$ (**21**) or $C(CN)_3$ (**22**). L = XylNC; X = $N(CN)_2$ (**23**) or $C(CN)_3$ (**24**). L = XylNC; X = $N(CN)_2$ (**25**) or $C(CN)_3$ (**26**).

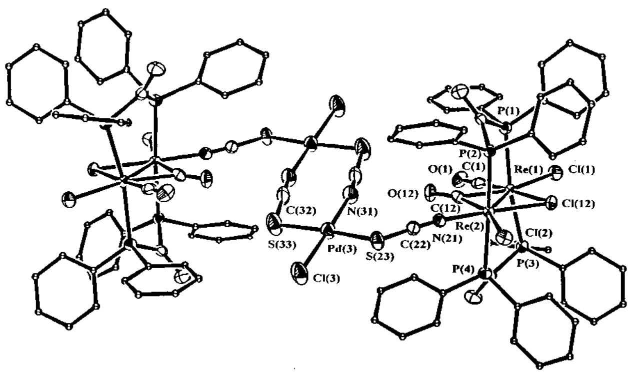


Figure 1. ORTEP[26] representation of the structure of the Re_4Pd_2 cluster **9**. Thermal ellipsoids are drawn at the 50% probability level except for the phenyl group atoms of the dppE ligands, which are circles of arbitrary radius. The molecule contains an inversion center which is coincident with the center of the $[Pd(\mu\text{-SCN})(\mu\text{-NCS})Pd]$ ring. Selected bond distances (Å) and bond angles (deg) are as follows: Re(1)−Re(2) 2.5775(4), Re(1)−C(1) 1.915(10), Re(1)−C(12) 2.192(8), Re(1)−Cl(1) 2.427(2), Re(1)−Cl(12) 2.4739(19), Re(2)−C(12) 1.973(9), Re(2)−N(21) 2.064(7), Re(2)−Cl(2) 2.419(2), Re(2)−Cl(12) 2.4456(19), Pd(3)−N(31) 2.002(8), Pd(3)−Cl(3) 2.287(3), Pd(3)−S(33) 2.326(3), Pd(3)−S(23) 2.333(3), S(23)−C(22) 1.647(9), S(33)−C(32) 1.670(12), N(21)−C(22) 1.148(11), C(32)−N(31) 1.130(12); Re(1)−C(12)−Re(2) 76.2(3), Re(1)−Cl(12)−Re(2) 63.19(5), O(1)−C(1)−Re(1) 178.3(8), O(12)−C(12)−Re(1) 136.6(6), O(12)−C(12)−Re(2) 147.2(7), C(22)−N(21)−Re(2) 171.1(7), C(22)−S(23)−Pd(3) 107.7(3), C(32)−S(33)−Pd(3) 104.0(4), N(21)−C(22)−S(23) 175.2(8), N(31)−C(32)−S(33) 179.2(10).

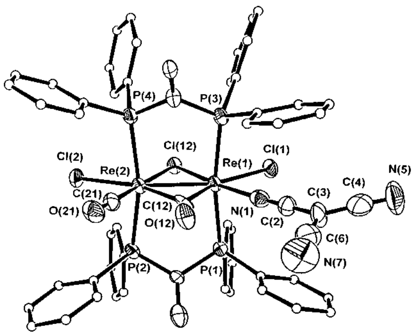


Figure 2. ORTEP[26] representation of the structure of the dirhenium complex $Re_2Cl_3[C(CN)_3](\mu\text{-dppE})_2(CO)_2$ (**15**). The thermal ellipsoids are drawn at the 50% probability level, except for the phenyl group atoms of the dppE ligands, which are circles of arbitrary radius. Selected bond distances (Å) and bond angles (deg) are as follows: Re(1)−Re(2) 2.5823(6), Re(1)−C(12) 1.957(11), Re(1)−N(1) 2.036(11), Re(1)−Cl(1) 2.423(3), Re(1)−Cl(12) 2.454(3), Re(2)−C(21) 1.882(13), Re(2)−C(12) 2.149(11), Re(2)−Cl(2) 2.420(3), Re(2)−Cl(12) 2.461(3), N(1)−C(2) 1.156(13), C(2)−C(3) 1.373(17); Re(1)−C(12)−Re(2) 77.8(4), Re(1)−Cl(12)−Re(2) 63.38(6), O(21)−C(21)−Re(2) 178.5(11), O(12)−C(12)−Re(1) 145.4(9), O(12)−C(12)−Re(2) 136.8(9), C(2)−N(1)−Re(1) 177.4(10), N(1)−C(2)−C(3) 176.8(14).

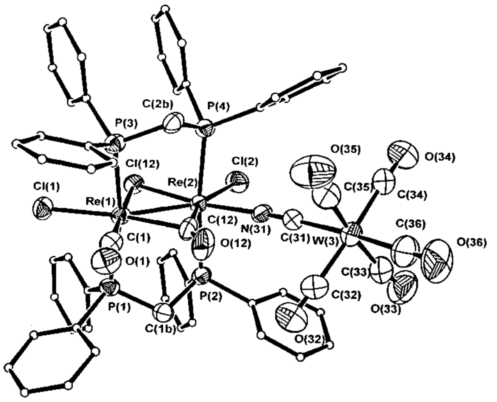


Figure 3. ORTEP[26] representation of the structure of the dirhenium complex $Re_2Cl_3(\mu\text{-dppm})_2(CO)_2[(\mu\text{-NC})W(CO)_5]$ (**16**). The thermal ellipsoids are drawn at the 50% probability level except for the phenyl group atoms of the dppm ligands, which are circles of arbitrary radius. Selected bond distances (Å) and bond angles (deg) are as follows: Re(1)−Re(2) 2.5898(4), Re(1)−C(1) 1.896(9), Re(1)−C(12) 2.205(8), Re(1)−Cl(1) 2.410(2), Re(1)−Cl(12) 2.4638(19), Re(2)−C(12) 1.975(9), Re(2)−N(31) 2.095(7), Re(2)−Cl(2) 2.428(2), Re(2)−Cl(12) 2.4564(19), W(3)−C(31) 2.181(9), W(3)−C(36) 1.998(12), W(3)−C(32) 2.001(13), N(31)−C(31) 1.123(11); Re(1)−C(12)−Re(2) 76.3(3), Re(1)−Cl(12)−Re(2) 63.52(5), O(1)−C(1)−Re(1) 178.3(8), O(12)−C(12)−Re(1) 135.7(7), O(12)−C(12)−Re(2) 148.0(7), C(31)−N(31)−Re(2) 167.1(8), N(31)−C(31)−W(3) 174.4(9).

thiocyanate complex $Re_2Cl_3(NCS)(\mu\text{-dppE})_2(CO)_2$ (**8**) in high yield. The structure of **8** was confirmed by X-ray crystallography (Re−Re distance 2.58 Å), but poor crystal quality resulted in an unsatisfactory structure refinement, with several of the carbon atoms of the phenyl rings being nonpositive definite. However, when this reaction is carried out in the presence of Pd(1,5-COD)Cl_2 and an excess of NaSCN, the Re_4Pd_2 cluster **9** is formed in ca. 85% yield. In the structure of **9** (Figure 1) the uncoordinated sulfur of the N-bound thiocyanato ligand present in **8** is used to complex a Pd atom in the assembly of this cluster, the formation of which is represented in Scheme 2. The asymmetric unit, which comprises half of the molecule with an inversion center being coincident with the center of the $[Pd_2(\mu\text{-SCN})_2]$ core, also contains five benzene molecules, the carbon atoms of which were refined anisotropically. A full representation of the Re_4Pd_2 unit is shown in Figure 1. The Re−Re double bond that is present in **1** (Re−Re = 2.5748(5) Å)[10] is retained in **9**, which has a Re−Re distance of 2.5775(4) Å. Overall the structural parameters for the individual dirhenium units present in **1** and **9** are very similar. In **9** there are two types of bridging thiocyanato ligands present, and this leads to two different Pd−S bonds; however, these distances are very similar (2.333(3) and 2.326(3) Å).

The mixed-metal complexes **10**−**13**, all of which are believed to be structurally similar to **8**, were obtained upon the reaction

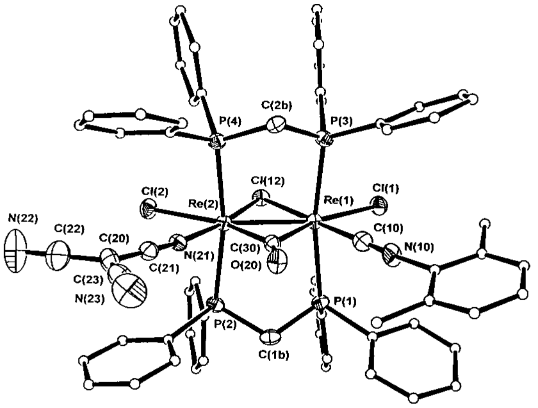


Figure 4. ORTEP[26] representation of the structure of the ESBO isomeric form of the dirhenium complex $Re_2Cl_3[C(CN)_3](\mu$-dppm$)_2$(CO)(CNXyl) (**18**). The thermal ellipsoids are drawn at the 50% probability level except for the phenyl group atoms of the dppm ligands and the xylyl group atoms of the XylNC ligand, which are circles of arbitrary radius. Selected bond distances (Å) and bond angles (deg) are as follows: Re(1)−Re(2) 2.5672(3), Re(1)−C(10) 1.975(6), Re(1)−C(30) 2.103(5), Re(1)−Cl(1) 2.4281(12), Re(1)−Cl(12) 2.4629(12), Re(2)−C(30) 1.990(5), Re(2)−N(21) 2.051(4), Re(2)−Cl(2) 2.4236(12), Re(2)−Cl(12) 2.4385(12), N(10)−C(10) 1.152(7), N(21)−C(21) 1.141(7), C(20)−C(21) 1.399(8); Re(1)−C(30)−Re(2) 77.64(18), Re(1)−Cl(12)−Re(2) 63.17(3), O(20)−C(30)−Re(1) 139.3(4), O(20)−C(30)−Re(2) 143.0(4), N(10)−C(10)−Re(1) 177.9(5), C(21)−N(21)−Re(2) 174.2(4), N(21)−C(21)−C(20) 177.5(6).

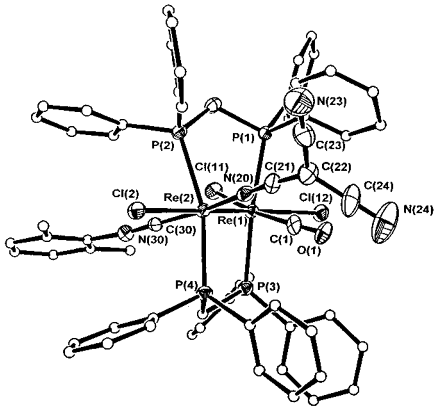


Figure 5. ORTEP[26] representation of the structure of the open OBO isomeric form of the dirhenium complex $Re_2Cl_3[C(CN)_3](\mu$-dppm$)_2$(CO)(CNXyl) (**20**). The thermal ellipsoids are drawn at the 50% probability level except for the phenyl group atoms of the dppm ligands and the xylyl group atoms of the XylNC ligand, which are circles of arbitrary radius. Selected bond distances (Å) and bond angles (deg) are as follows: Re(1)−Re(2) 2.3776(3), Re(1)−C(1) 1.907(7), Re(1)−Cl(11) 2.4147(16), Re(1)−Cl(12) 2.5583(15), Re(2)−C(30) 1.999(6), Re(2)−N(20) 2.094(5), Re(2)−Cl(2) 2.4735(15), N(20)−C(21) 1.166(8), N(30)−C(30) 1.177(8), C(21)−C(22) 1.365(10); Re(2)−Re(1)−Cl(12) 158.69(4), Re(1)−Re(2)−Cl(2) 168.38(4), N(30)−C(30)−Re(2) 173.3(6), C(21)−N(20)−Re(2) 175.3(5), C(22)−C(21)−N(20) 174.9(8).

of the dppE complex **1** with the salts $K[Ag(CN)_2]$ and $[(Et_4N)W(CO)_5(CN)]$,[16] and with the neutral ligands *trans*-$Pt(CN)_2(CN$-*t*-$Bu)_2$[17,18] and *trans*-$Rh[N(CN)_2](CO)(PPh_3)_2$, the latter compound being a new reagent.

The silver(I) cyanide complex **10** is also formed by the reaction of **1** with an excess of AgCN. This reaction presumably proceeds by the following stoichiometry:

$$Re_2Cl_4(\mu\text{-dppE})_2(CO)_2 + 2AgCN \rightarrow Re_2Cl_3(\mu\text{-dppE})_2(CO)_2[Ag(CN)_2] + AgCl$$

We were unable to obtain the monocyanide complex $Re_2Cl_3(\mu$-dppE$)_2(CO)_2(CN)$, analogous to the thiocyanate complex **8**, by the reaction of either **1** or $[Re_2Cl_3(\mu$-dppE$)_2(CO)_2(NCMe)]O_3SCF_3$ with NaCN or KCN.

While the structures of complexes **10**−**13** were not determined by X-ray crystallography, the structure of **11** must closely resemble that of its dppm analogue **16**, which was prepared by a similar procedure (Scheme 1). The structure of **16** (Figure 3) is discussed later. Note that the coordination of the $[W(CO)_5(CN)]^-$ anion has been reported previously in the case of the quadruply bonded complexes $Re_2(\mu\text{-}O_2CCMe_3)_4[NCW(CO)_5]_2$[27] and *trans*-$[Mo_2(\mu\text{-}O_2CMe)_2(\mu\text{-}Ph_2PN(Me)PPh_2)_2[NCW(CO)_5]_2$,[28] but in these compounds the $[W(CO)_5(CN)]^-$ ligands are proposed to be collinear with the $M\overset{4}{-}M$ bonds. The spectroscopic and electrochemical properties of **11** and **16** are strikingly similar (Table 2). In addition to the dirhenium-based redox processes listed in Table 2, both complexes show processes in their CVs that are characteristic of the CN-coordinated $[W(CO)_5(CN)]^-$ ligand.[27] For **11**, a broad irreversible process at $E_{p,a} = +0.98$ V (with $E_{p,c} \simeq +0.9$ V) is followed by a reversible one-electron oxidation at $E_{1/2} = +1.43$ V ($\Delta E_p = 100$ mV) close to the limit of our measurements (+1.60 V). In the case of the CV of **16**, an irreversible oxidation at $E_{p,a} = +0.85$ V that is again assigned to the CN-bound $[W(CO)(CN)]^-$ ligand[27] is clearly resolved from a reversible dirhenium core oxidation at $E_{1/2} = +0.93$ V. These processes are followed by a less well-defined oxidation at $E_{1/2} \simeq +1.4$ V. On the basis of the CV data for **16**, we attribute the irreversible appearance of processes at ca. +0.95 V in the CV of **11** to the overlap of reversible and irreversible oxidations that are associated with the dirhenium and tungsten cores, respectively. Note that complexes **12** and **13** show strong bands at 842 and 1271 cm^{-1}, respectively, in their IR spectra that confirm the presence of the $[PF_6]^-$ and $[O_3SCF_3]^-$ anions.

The reactions of **1** with sodium dicyanamide ($Na[N(CN)_2]$) and potassium tricyanomethanide ($K[C(CN)_3]$) gave complexes **14** and **15** with ESBO structures, while the reaction of the dppm analogue of **1** (i.e., **2**) with $Et_4N[W(CO)_5(CN)]$[16] produced complex **16**, which, as mentioned previously, is a close analogue of **11** (vide supra). In all instances, the isolated complexes **10**−**16** contain Lewis base donors that are believed to bind to the dirhenium core through an essentially linear bridging cyanide group. The crystal structures of complexes **15** and **16**, both of which confirm the presence of CN bridges, are shown in Figures 2 and 3.

Both **15** and **16** contain dirhenium units that resemble those present in **9** with Re−Re double bond distances of 2.5823(6) and 2.5898(4) Å, respectively. Also, like **9**, the μ-CO bridge in these two complexes is unsymmetrical with Re−C distances that differ by ca. 0.19−0.23 Å, the shorter distance involving the Re atom that is bound to the cyanide-containing ligand. These exact same structural features are found in the structures of **9** (Figure 1) and the previously characterized propionitrile complex $[Re_2Cl_3(\mu$-dppm$)_2(CO)_2(NCEt)]PF_6$.[1] In the latter complex,[1] the Re−N distance is 2.03(2) Å, whereas the Re−N distances in **15** and **16** are 2.036(11) and 2.095(7) Å, respectively; the angles Re(1) −N(1)−C(2) for **15** and Re(2)−N(31)−C(31) for **16** are 177.4(10)° and 167.1(8)°, respectively.

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(27) Kuhn, F. E.; Goncalves, I. S.; Lopes, A. D.; Lopes, J. P.; Romao, C. C.; Wachter, W.; Mink, J.; Hajba, L.; Parola, A. J.; Pina, F.; Sotomayor, J. *Eur. J. Inorg. Chem.* **1999**, 295.

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Preliminary studies of the reactions of complex **14**, whose structure is believed to be similar to that of **15** and can therefore be expected to contain an uncoordinated CN group, show that it reacts with **1** in the presence of an equivalent of TlO_3SCF_3 to afford the tetrarhenium complex $\{[Re_2Cl_3(\mu\text{-dppE})_2(CO)_2]_2[\mu\text{-(NC)N(CN)}]\}O_3SCF_3$ in which the dicyanamide ligand bridges two identical dirhenium units. A preliminary X-ray crystal structure determination has confirmed the structure of the tetrarhenium unit. More detailed studies are now underway to examine the ability of complexes **14** and **15**, and others of this type (vide infra), to serve as synthons in the assembly of mixed-metal clusters, and the results of this study will be reported in due course upon completion of the necessary structural characterizations.

The substitution of the terminal Cl ligand of $Re_2Cl_4(\mu\text{-dppE})_2(CO)_2$ (**1**) by $[N(CN)_2]^-$ and $[C(CN)_3]^-$ prompted us to examine the reactions of salts of these anions with the mixed CO/XylNC complexes **3** and **4**, which constitute an isomeric pair. Complex **3** has an ESBO structure similar to those of **1** and **2**, while **4** has an OBO structure. These four reactions produced complexes **17**−**20**, in which the Cl ligand that is substituted is the same one previous studies[1−10] had shown is the most labile (see Scheme 1). The important spectroscopic and electrochemical properties of these complexes, which are given in Table 2, show similarities within the pairs **17**/**18** and **19**/**20**. The single-crystal X-ray structural characterizations of the pair of isomers **18** and **20** demonstrate conclusively that the stereochemistries of the precursors **3** and **4** are retained (see Figures 4 and 5). The Re−Re bond distances of **18** and **20** are 2.5672(2) and 2.3776(3) Å, respectively; these values are in accord with the presence of a Re−Re double bond in **18** and a Re−Re triple bond in **20**, and can be contrasted with Re−Re bond distances of 2.581(2) Å in **1**[15] and 2.378(3) Å in $[Re_2Cl_3(\mu\text{-dppm})_2(CO)(CNXyl)(NCCH_3)]O_3SCF_3$, respectively, the latter complex being a structural analogue of **4** in which the same Cl ligand that is displaced by $[C(CN)_3]^-$ in forming **20** is substituted by acetonitrile. The OBO complex **20** possesses a partially staggered rotational geometry characterized by torsional angles P(1)−Re(1)−Re(2)−P(2), P(3)−Re(1)−Re(2)−P(4), Cl(11)−Re(1)−Re(2)−C(30), and C(1)−Re(1)−Re(2)−N(20) of 25.7°, 16.8°, 29.3°, and 26.4°, respectively. Just as we find that isomers **3** and **4** do not interconvert, neither do the isomeric tricyanomethanide complexes **18** and **20**, or their dicyanamide analogues **17** and **19**.

(b) Reactions with the Coordinatively Unsaturated Dirhenium Complexes $Re_2Cl_4(\mu\text{-dppm})_2(L)$ (L = CO (5) or XylNC (6)) and $Re_2Cl_4(\mu\text{-dppm})_2$ (7). Complexes **5** and **6**, which are formed from **7**,[13,14] are known to be quite reactive toward additional equivalents of organic π-acceptor ligands.[2,5,6,13,14,20,29−31] In the present paper, we examine for the first time the substitutional lability of **5** and **6** toward monoanionic ligands, specifically through their reactions with the salts $Na[N(CN)_2]$ and $K[C(CN)_3]$. One or two Re−Cl bonds of **5** and **6** can be substituted to afford complexes **21**−**26** as represented by reactions B in Scheme 3. Each pair of complexes **21**/**22**, **23**/**24**, and **25**/**26** shows very similar spectroscopic and electrochemical properties (Table 2), implying that the structures of each pair are similar. Note that the reactions of **5** with 2 equiv of $Na[N(CN)_2]$ and $K[C(CN)_3]$ failed to give the pure carbonyl analogues of the isocyanide-containing complexes **25** and **26**. Single-crystal X-ray structure determinations were carried out on the representative complexes $Re_2Cl_3[C(CN)_3](\mu\text{-dppm})_2(CNXyl)$ (**24**) and $Re_2Cl_2[C(CN)_3]_2(\mu\text{-dppm})_2(CNXyl)$ (**26**). Relevant structural information is provided in Figures 6 and 7.

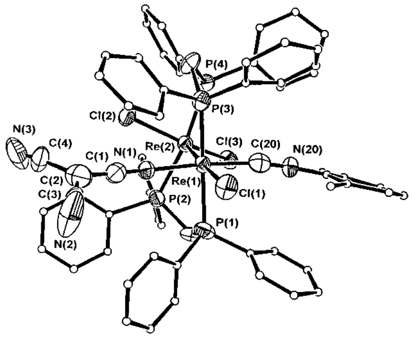

Figure 6. ORTEP[26] representation of the structure of the dirhenium complex $Re_2Cl_3[C(CN)_3](\mu\text{-dppm})_2(CNXyl)$ (**24**). The thermal ellipsoids are drawn at the 50% probability level except for the phenyl group atoms of the dppm ligands and the xylyl group atoms of the XylNC ligands, which are circles of arbitrary radius. Selected bond distances (Å) and bond angles (deg) are as follows: Re(1)−Re(2) 2.2766(10), Re(1)−C(20) 2.02(2), Re(1)−N(1) 2.102(12), Re(1)−Cl(1) 2.541(5), Re(2)−Cl(2) 2.355(5), Re(2)−Cl(3) 2.367(4), N(1)−C(1) 1.14(2), N(20)−C(20) 1.18(2), C(1)−C(2) 1.39(3); Re(2)−Re(1)−Cl(1) 178.10(13), N(20)−C(20)−Re(1) 169(2), C(1)−N(1)−Re(1) 174(2), N(1)−C(1)−C(2) 177(2).

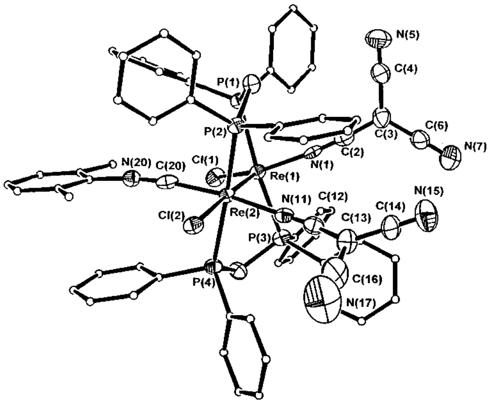

Figure 7. ORTEP[26] representation of the structure of the dirhenium complex $Re_2Cl_2[C(CN)_3]_2(\mu\text{-dppm})_2(CNXyl)$ (**26**). The thermal ellipsoids are drawn at the 50% probability level except for the phenyl group atoms of the dppm ligands and the xylyl group atoms of the XylNC ligands, which are circles of arbitrary radius. Selected bond distances (Å) and bond angles (deg) are as follows: Re(1)−Re(2) 2.2856(5), Re(1)−N(1) 1.988(7), Re(1)−Cl(1) 2.357(2), Re(2)−C(20) 2.023(9), Re(2)−N(11) 2.105(8), Re(2)−Cl(2) 2.501(2), N(1)−C(2) 1.148(11), N(11)−C(12) 1.155(10), N(20)−C(20) 1.168(10), C(2)−C(3) 1.386(13), C(12)−C(13) 1.375(13); Re(1)−Re(2)−Cl(2) 177.31(5), N(20)−C(20)−Re(2) 172.5(7), C(2)−N(1)−Re(1) 173.9(7), C(12)−N(11)−Re(2) 169.3(7), N(1)−C(2)−C(3) 176.5(10), N(11)−C(12)−C(13) 173.8(10).

The structures **24** and **26** are closely related with Re−Re triple bond distances of 2.2766(10) and 2.2856(5) Å, respectively, and similar partially staggered rotational geometries which are characterized by values for the torsional angles P(1)−Re(1)−Re(2)−P(2) and P(3)−Re(1)−Re(2)−P(4) of 24.6° and 25.0°, respectively, in the case of **24**, and 29.7° and 27.7°, respectively, for **26**. The two $C(CN)_3$ ligands are bound to different Re atoms in the structure **26** and have a syn disposition to one another.

The final pair of reactions we studied was that of $Re_2Cl_4(\mu\text{-dppm})_2$ (**7**) with $Na[N(CN)_2]$ and $K[C(CN)_3]$ (see reactions A in Scheme 3). Both products (**27** and **28**) possess similar

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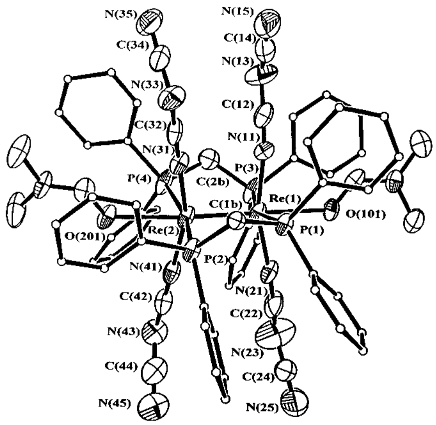

Figure 8. ORTEP[26] representation of the structure of the dirhenium complex $Re_2[N(CN)_2]_4(\mu\text{-dppm})_2(DMF)_2$ (**27**). The thermal ellipsoids are drawn at the 50% probability level except for the phenyl group atoms of the dppm ligands, which are circles of arbitrary radius. Selected bond distances (Å) and bond angles (deg) are as follows: Re(1)−Re(2) 2.2960(5), Re(1)−N(11) 2.042(8), Re(1)−N(21) 2.046(8), Re(1)−O(101) 2.376(6), Re(2)−N(31) 2.039(8), Re(2)−N(41) 2.052(9), Re(2)−O(201) 2.501(6), N(11)−C(12) 1.139(12), N(21)−C(22) 1.143(13), N(31)−C(32) 1.159(12), N(41)−C(42) 1.138(12); N(11)−Re(1)−N(21) 162.7(3), N(31)−Re(2)−N(41) 160.1(3), C(12)−N(11)−Re(1) 173.0(8), C(22)−N(21)−Re(1) 175.7(9), C(32)−N(31)−Re(2) 178.6(7), C(42)−N(41)−Re(2) 179.3(8).

spectroscopic properties that accord with a single pure product being formed in each case, but neither complex gave satisfactory elemental microanalyses, presumably because of incomplete combustion. However, the structure of **27** was established by X-ray crystallography on a sample that was recrystallized from DMF/diethyl ether. The crystals were of composition $Re_2[N(CN)_2]_4(\mu\text{-dppm})_2(DMF)_2 \cdot 3DMF$, and the structure of this dirhenium complex, which contains two axially bound DMF ligands, was found to resemble that of the previously characterized complex $Re_2(NCBH_3)_4(\mu\text{-dppm})_2(H_2O)_2$.[32] The structure of **27** is shown in Figure 8. The Re−Re distance of 2.2960(5) Å is almost the same as that found for its cyanotrihydroborato analogue (2.2874(5) Å),[32] which contains two axially bound water molecules. Also, like the latter complex, **27** assumes a rotational geometry intermediate between those of fully eclipsed and fully staggered conformations. This is shown by the torsional angles P(1)−Re(1)−Re(2)−P(2), P(3)−Re(1)−Re(2)−P(4), N(11)−Re(1)−Re(2)−N(31), and N(21)−Re(1)−Re(2)−N(41), which are 15.2°, 11.7°, 20.0°, and 14.3°, respectively. The axial DMF ligands, which are characterized by a ν(CO) band at 1650 cm^{-1} in the IR spectrum of **27**, do not undergo exchange when this compound is reacted with ligands as different as 4-methylpyridine and carbon monoxide.

(c) Concluding Remarks. The present study represents the first in which ESBO and OBO multiply bonded dirhenium complexes that contain a $[Re_2(\mu\text{-PP})_2]^{4+}$ core (PP = $Ph_2PC(=CH_2)PPh_2$ (dppE) or $Ph_2PCH_2PPh_2$ (dppm)) have been incorporated into mixed-metal assemblies of the types Re_2M_2 and Re_2M' (M = Pd; M′ = Ag, W, Pt, or Rh) in which M and M′ are bound to the Re_2 cores through NCS- or CN-containing linkages. The isolation of the complexes $Re_2Cl_3(X)(\mu\text{-dppm})_2(L)$ and $Re_2Cl_2(X)_2(\mu\text{-dppm})_2(L)$, where X = $N(CN)_2$ or $C(CN)_3$ and L = CO or XylNC, as well as $Re_2[N(CN)_2]_4(\mu\text{-dppm})_2$ and $Re_2[C(CN)_3]_4(\mu\text{-dppm})_2$ provides a range of starting materials that can be used to access multidimensional arrays that contain redox-active dirhenium units and may have interesting solid-state properties. Such studies are currently underway in our laboratory. In this context, we note that the first report has recently appeared describing the use of $[N(CN)_2]^-$ and $[C(CN)_3]^-$ as anionic linkers for constructing assemblies containing diruthenium(II,III) units.[33] However, in these instances, diruthenium acetate $[Ru_2(\mu\text{-}O_2CCH_3)_4]^+$ is linked into polymeric chains through its *axial* coordination sites.

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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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