Reactions of the Dirhenium(II) Complexes $Re_2X_4(\mu\text{-dppm})_2$ (X = Cl, Br; dppm = $Ph_2PCH_2PPh_2$) with Isocyanides. 11.[1] A Triply Bonded Dirhenium Complex Containing a Labile Acetonitrile Ligand. Synthesis, Structural Characterization, and Reactivity of $[(XylNC)(CH_3CN)ClRe(\mu\text{-dppm})_2ReCl_2(CO)]O_3SCF_3$

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The reaction of the open bioctahedral form of $Re_2Cl_4(\mu\text{-dppm})_2(CO)(CNXyl)$ (**1**), where XylNC = 2,6-dimethylphenyl isocyanide, with TlO_3SCF_3 in the presence of acetonitrile proceeds with retention of stereochemistry at the dirhenium unit to afford the complex $[Re_2Cl_3(\mu\text{-dppm})_2(CO)(CNXyl)(NCCH_3)]O_3SCF_3$ (**3**). The single-crystal X-ray structure determination of **3** shows that a Re≡Re bond is retained (the Re−Re distance is 2.378(3) Å) and that it is the chloride ligand trans to the XylNC ligand of **1** which is labilized. Complex **1** reacts with TlO_3SCF_3 in a noncoordinating solvent to produce the unsymmetrical complex $[Re_2Cl_3(\mu\text{-dppm})_2(CO)(CNXyl)]O_3SCF_3$ (**2**), through loss of this same chloride ligand of **1** and CO transfer from the adjacent Re center. The acetonitrile ligand of **3** is very labile and is readily displaced by XylNC and *t*-BuNC, with retention of stereochemistry, to produce complexes of stoichiometry $[Re_2Cl_3(\mu\text{-dppm})_2(CO)(CNXyl)(CNR)]O_3SCF_3$ (R = Xyl, **4a**; R = *t*-Bu, **4b**). In a noncoordinating solvent, the nitrile ligand of **3** is lost and **2** is formed following CO transfer; this conversion is reversed upon the reaction of **2** with acetonitrile. When **3** is treated with CO, the acetonitrile ligand is again displaced, but in this instance the reaction is accompanied by a structure change to produce an edge-sharing bioctahedral complex of the type $[Re_2(\mu\text{-CO})(\mu\text{-Cl})(\mu\text{-dppm})_2Cl_2(CO)(CNXyl)]O_3SCF_3$ (**5**).

Introduction

Our recent investigations into the chemistry of multiply bonded dirhenium(II) complexes containing π-acceptor ligands have revealed that differences in halide and isocyanide ligands, and/or the nature of the reaction solvent, can affect the formation of different isomeric forms of the products.[2,3] A prime example is the reaction between $Re_2Cl_4(dppm)_2(CO)$ and XylNC, where XylNC = xylyl isocyanide. When acetone is used as the solvent, this reaction yields an edge-sharing bioctahedral complex $(XylNC)ClRe(\mu\text{-Cl})(\mu\text{-CO})(\mu\text{-dppm})_2ReCl_2$,[4] whereas in acetonitrile an open bioctahedral isomeric form of this complex, $(XylNC)Cl_2Re(\mu\text{-dppm})_2ReCl_2(CO)$, **1**, is formed.[3]

We have previously reported that complex **1** reacts with TlO_3SCF_3 in the presence of a further equivalent of XylNC to afford the complex $[(XylNC)_2ClRe(\mu\text{-dppm})_2ReCl_2(CO)]O_3SCF_3$,[3] which is another example of a molecule with an open bioctahedral structure. In examining further the reactions of **1**, we have found that it reacts with TlO_3SCF_3, in a noncoordinating solvent such as dichloromethane, to give the unsymmetrical, coordinatively unsaturated complex $[(XylNC)(CO)ClRe(\mu\text{-dppm})_2ReCl_2]O_3SCF_3$, **2**, while in acetonitrile the complex $[(XylNC)(MeCN)ClRe(\mu\text{-dppm})_2ReCl_2(CO)]O_3SCF_3$, **3**, which contains a mixed CO/isocyanide/nitrile ligand set, is produced. The synthesis, characterization, and reactivity of **2** and **3** are described, including details of the interconversion of **2** and **3**.

Experimental Section

Starting Materials and General Procedures. The compounds $Re_2Cl_4(dppm)_2(CO)(CNXyl)$, **1**,[3] and TlO_3SCF_3[5] were prepared according to the literature procedures. However, **1** was recrystallized from CH_2Cl_2/Et_2O to remove trace amounts of the CH_3CN solvent prior to use. 2,6-Dimethylphenyl isocyanide, XylNC, was purchased from Fluka Chemical Corp., CO gas was obtained from Matheson Gas Products Co., and $TlPF_6$ was purchased from Strem Chemicals. These reagents were used as received. Solvents were obtained from commercial sources and were deoxygenated by purging with dinitrogen gas prior to use. All reactions were performed under an atmosphere of dry dinitrogen. Infrared, ^1H and $^{31}P\{^1H\}$ NMR, and cyclic voltammetric measurements were carried out as described previously.[2] Elemental microanalyses were performed by Dr. H. D. Lee of the Purdue University Microanalytical Laboratory.

A. Synthesis of $[Re_2Cl_3(dppm)_2(CO)(CNXyl)]O_3SCF_3$, 2. A quantity of **1** (50.0 mg, 0.0347 mmol) was allowed to react with 13.5 mg of TlO_3SCF_3 (0.0382 mmol) in 15 mL of dichloromethane solvent. Within a period of 2 h, the starting red-purple suspension changed color to pale green. The reaction was stopped after 16 h, a white solid (TlCl) was filtered off, and the pale green filtrate was reduced in volume to ca. 1 mL. A small volume of $i\text{-}Pr_2O$ (0.5 mL) was added to this concentrated filtrate, and the solvents were allowed to slowly evaporate at 25 °C. The title complex, $[Re_2Cl_3(dppm)_2(CO)(CNXyl)]O_3SCF_3$, **2**, was collected as a crop of tiny green crystals after 4 h; yield 53.0 mg (>95%). Anal. Calcd for $C_{61}H_{53}Cl_3F_3NO_4P_4Re_2S$: C, 47.09; H, 3.43; N, 0.90. Found: C, 46.12; H, 3.35; N, 0.99. When 1,2-dichloroethane was used as the reaction solvent, a similar result was obtained.

B. Synthesis of $[Re_2Cl_3(dppm)_2(CO)(CNXyl)(NCCH_3)]O_3SCF_3$, 3. (i) From $Re_2Cl_4(dppm)_2(CO)(CNXyl)$, 1. A mixture of **1** (50.0 mg, 0.0347 mmol) and TlO_3SCF_3 (13.5 mg, 0.0382 mmol) was treated with 15 mL of dichloromethane and 25 μL of acetonitrile. The resulting

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mixture was stirred at 25 °C for 3 h. The reaction was stopped after 20 h, and the white precipitate of TlCl was filtered off. The volume of the red filtrate was reduced to ca. 1 mL, and 20 mL of Et_2O was added to induce precipitation of **3** as a red powder. The product was filtered off and washed with Et_2O; yield 53.0 mg (96%). Anal. Calcd for $C_{63}H_{56}Cl_3F_3N_2O_4P_4Re_2S$: C, 47.38; H, 3.53; N, 1.75. Found: C, 46.27; H, 3.44; N, 1.61.

Two modifications of this procedure were used, but neither resulted in any significant differences in the product purity or yield. First, a mixture of **1** (50.0 mg, 0.0347 mmol) and TlO_3SCF_3 (13.5 mg, 0.0382 mmol) was treated with 15 mL of dichloromethane until the reaction suspension changed color to pale green; only at this point was the 25 μL of acetonitrile then added to the reaction mixture. The resulting mixture was stirred at 25 °C for 24 h. During this period, the reaction mixture changed color from green to yellow and finally to orange-red; yield 52.0 mg (94%). Second, acetonitrile (15 mL) was used as the reaction solvent and the reaction carried out at 25 °C for 19 h; yield 85%.

(ii) **From $Re_2Cl_4(dppm)_2(CO)$.** A mixture of the monocarbonyl complex $Re_2Cl_4(dppm)_2(CO)$ (50.0 mg, 0.0381 mmol), 1 equiv of XylNC (5.0 mg, 0.0381 mmol), and TlO_3SCF_3 (15.0 mg, 0.0424 mmol) was treated with 10 mL of acetonitrile. A green suspension formed first and then changed color to red. The reaction was stopped after 7 h, the white precipitate of TlCl was filtered off, and the red filtrate was concentrated to ca. 3 mL. Complex **3** was collected as red crystals after slow evaporation of the remaining solvent at 25 °C; yield 53.2 mg (87%).

C. Interconversion of 2 and 3. (i) Reaction of 2 with Acetonitrile. A quantity of **2** (20.0 mg, 0.0129 mmol) was dissolved in 8 mL of acetonitrile and the resulting solution then stirred at 25 °C for 18 h. The reaction mixture changed color from green to brown within ca. 10 min and then slowly converted to an orange solution during the course of the reaction. The red compound **3** was isolated when the solvent was evaporated and the residue washed with Et_2O; yield 20.0 mg (97%).

(ii) Thermolysis of 3 to 2. A solution of **3** (80.0 mg, 0.0501 mmol) in 25 mL of dichloromethane was heated to reflux for 18 h. A green solution formed during this period. The volume of this solution was reduced to ca. 1 mL, and 20 mL of Et_2O was added to induce precipitation. A pale tan solid was collected by filtration. The IR and solution ^1H and $^{31}P\{^1H\}$ NMR spectra of this product showed it to be a mixture of **2** and **3** in an approximate 50/50 ratio; yield 72.5 mg. Longer reaction times afforded similar results. However, when this product mixture was redissolved in *fresh* dichloromethane and the procedure of heating and product isolation repeated several times, a much higher conversion of **3** to **2** (>80%) was achieved.

D. Reactions of $[Re_2Cl_3(dppm)_2(CO)(CNXyl)(NCCH_3)]O_3SCF_3$, 3, with Isocyanides RNC. (i) R = Xylyl. A quantity of **3** (40.0 mg, 0.0250 mmol) was mixed with XylNC (3.5 mg, 0.0267 mmol) and 15 mL of dichloromethane, and the mixture was stirred at 25 °C for 20 h. A red suspension formed initially but redissolved completely in about 2 h. The volume of the solution was reduced to ca. 1 mL, and 20 mL of Et_2O was then added to induce precipitation of the red complex $[Re_2Cl_3(dppm)_2(CO)(CNXyl)_2]O_3SCF_3$, **4a**, which was filtered off and washed with Et_2O; yield 31.5 mg (75%). The identity of this product was based on a comparison of its spectroscopic and electrochemical properties with those of a sample prepared by the previously reported method.[3]

(ii) R = *tert*-Butyl. The reaction of **3** (60.0 mg, 0.0376 mmol) with *t*-BuNC (5 μL, 0.0442 mmol) in 15 mL of dichloromethane for 16 h at 25 °C afforded a red solution. A workup procedure similar to that described in section D(i) gave the red complex $[Re_2Cl_3(dppm)_2(CO)(CNXyl)(CN\text{-}t\text{-}Bu)]O_3SCF_3$, **4b**; yield 54.2 mg (88%). Anal. Calcd for $C_{66}H_{62}Cl_3F_3N_2O_4P_4Re_2S$: C, 48.37; H, 3.81; N, 1.71. Found: C, 48.06; H, 3.75; N, 1.72.

E. Reaction of $[Re_2Cl_3(dppm)_2(CO)(CNXyl)(NCCH_3)]O_3SCF_3$, 3, with CO. A suspension of **3** (45.0 mg, 0.0281 mmol) in 15 mL of dichloromethane was slowly purged with CO gas for 5 min and the resulting mixture then stirred at 25 °C for 19 h. A green solution formed during this period. The solvent was removed, and the residue was redissolved in a minimum amount of dichloromethane (ca. 0.5 mL). An excess of Et_2O (ca. 2.0 mL) was added to induce precipitation of the carbonyl complex $[(XylNC)ClRe(\mu\text{-}Cl)(\mu\text{-}CO)(\mu\text{-dppm})_2ReCl(CO)]O_3SCF_3$, **5**. The green product was filtered off and dried; yield 38.5 mg (86%). Anal. Calcd for $C_{62}H_{53}Cl_3F_3NO_5P_4Re_2S$: C, 47.02; H, 3.37; N, 0.88. Found: C, 47.41; H, 3.57; N, 0.98. The identity of this complex was also based on a comparison of its spectroscopic and electrochemical data with those of the known compound $[(XylNC)ClRe(\mu\text{-}Cl)(\mu\text{-}CO)(\mu\text{-dppm})_2ReCl(CO)]PF_6$.[6]

Table 1. Crystallographic Data for $[Re_2Cl_3(\mu\text{-dppm})_2(CO)(CNXyl)(NCCH_3)]O_3SCF_3\cdot CH_3CN$ (**3**)

empirical formula	$Re_2Cl_3SP_4F_3O_4N_3C_{65}H_{59}$	Z	4
fw	1637.93	ρ_{calcd}, g/cm^3	1.616
space group	$P2_1/n$ (No. 14)	μ, cm^{-1} (Mo, K$_\alpha$)	40.67
a, Å	17.556(3)	transm factors min/max	0.56/0.87
b, Å	14.988(3)	data with $I > 3.0\sigma(I)$	5276
c, Å	25.699(7)		
β, deg	93.98(7)	$R^a/R_w{}^b$	0.041/0.049
V, Å^3	6745(5)	largest shift/error	0.08
		GOF^c	0.341

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w = \{\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2\}^{1/2}$; $w = 1/\sigma^2(|F_o|)$. [c] Goodness-of-fit $= [\sum w(|F_o| - |F_c|)^2/(N_{observns} - N_{params})]^{1/2}$.

X-ray Crystallography. Single crystals of the complex $[Re_2Cl_3(\mu\text{-dppm})_2(CO)(CNXyl)(NCCH_3)]O_3SCF_3$, **3**, which were suitable for X-ray diffraction analysis were grown from an acetonitrile solution by slow evaporation of the solvent at 25 °C. A red plate of **3**, having approximate dimensions of 0.40 × 0.40 × 0.23 mm, was mounted on a glass fiber in a random orientation. The data collection was performed on an Enraf-Nonius CAD4 computer-controlled diffractometer with graphite-monochromatized Mo Kα radiation at 293 K. The cell constants for data collection were based on 25 reflections obtained in the range $16 < \theta < 18°$, measured by the computer-controlled diagonal-slit method of centering. Three standard reflections were measured after every 5000 s of beam time during data collection to monitor the crystal stability. Lorentz and polarization corrections were applied to the data set. An empirical absorption correction[7] was also applied, but no correction for extinction was made. Calculations were performed on an AlphaServer 2100 computer by the use of the MolEN[8] structure determination package.

Compound **3** crystallized in the monoclinic crystal system. The systematic absences observed for the data set were consistent with space group $P2_1/n$. The structure was solved by a combination of direct methods (SIR92)[9] and difference Fourier syntheses. All non-hydrogen atoms except C(21) in this structure were refined anisotropically. Atom C(21) was refined with isotropic thermal parameters. The hydrogen atoms were calculated by the use of idealized geometries with C−H = 0.95 Å and $U(H) = 1.3U_{eq}(C)$. Their contributions were added to the structure factor calculations, but their positions were not refined. During the course of the structure refinement, a CH_3CN molecule from the crystallization solvent was found cocrystallized with the complex in the asymmetric unit. Atoms of this solvent molecule were located and refined satisfactorily. The structure was refined in full-matrix least squares where the function minimized was $\sum w(|F_o| - |F_c|)^2$, where w is the weighting factor defined as $w = 1/\sigma^2(F_o)$. Corrections for anomalous scattering were applied to the anisotropically refined atoms.[10] The final residuals for **3** were $R = 0.041$ and $R_w = 0.049$ with GOF = 0.341. The highest peak in the final difference Fourier was 0.94 e/Å^3.

The crystallographic data for compound **3** are given in Table 1, while important intramolecular bond lengths and angles are given in Table 2.

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Table 2. Selected Bond Distances (Å) and Bond Angles (deg) for $[Re_2Cl_3(\mu\text{-dppm})_2(CO)(CNXyl)(NCCH_3)]O_3SCF_3\cdot CH_3CN$ (**3**)[a]

Distances

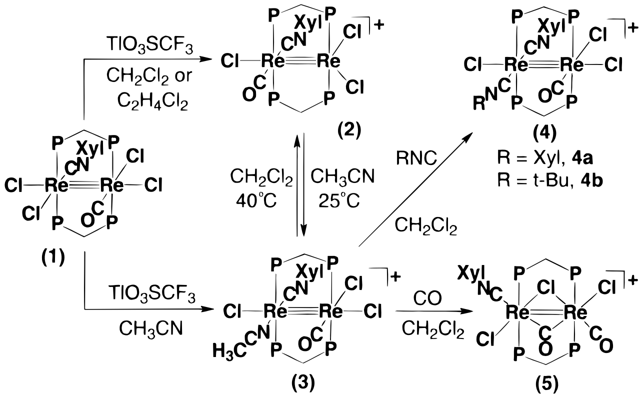
Re(1)−Re(2)	2.378(3)	Re(2)−P(3)	2.489(11)
Re(1)−Cl(11)	2.412(11)	Re(2)−N(30)	2.12(4)
Re(1)−Cl(12)	2.550(11)	Re(2)−C(20)	2.03(5)
Re(1)−P(1)	2.502(11)	C(10)−O(10)	1.15(5)
Re(1)−P(4)	2.469(12)	C(20)−N(20)	1.17(5)
Re(1)−C(10)	1.92(5)	N(20)−C(21)	1.41(5)
Re(2)−Cl(21)	2.467(11)	N(30)−C(30)	1.07(6)
Re(2)−P(2)	2.476(12)	C(30)−C(31)	1.49(8)

Angles

Re(2)−Re(1)−Cl(11)	107.5(3)	Re(1)−Re(2)−N(30)	102.2(10)
Re(2)−Re(1)−Cl(12)	161.6(3)	Re(1)−Re(2)−C(20)	87.7(11)
Re(2)−Re(1)−P(1)	98.6(3)	Cl(21)−Re(2)−N(30)	88.4(10)
Re(2)−Re(1)−P(4)	91.8(3)	Cl(21)−Re(2)−C(20)	81.7(11)
Re(2)−Re(1)−C(10)	81.9(13)	Cl(21)−Re(2)−P(3)	80.5(4)
Cl(11)−Re(1)−Cl(12)	90.0(4)	Cl(21)−Re(2)−P(2)	86.0(4)
Cl(11)−Re(1)−P(1)	93.3(4)	P(2)−Re(2)−P(3)	166.4(4)
Cl(11)−Re(1)−P(4)	84.0(4)	P(2)−Re(2)−N(30)	93.7(11)
Cl(11)−Re(1)−C(10)	169.9(13)	P(2)−Re(2)−C(20)	87.5(11)
Cl(12)−Re(1)−P(1)	85.7(4)	P(3)−Re(2)−N(30)	87.6(11)
Cl(12)−Re(1)−P(4)	84.3(4)	P(3)−Re(2)−C(20)	89.0(11)
Cl(12)−Re(1)−C(10)	80.3(13)	N(30)−Re(2)−C(20)	169.9(15)
P(1)−Re(1)−P(4)	169.6(4)	Re(1)−C(10)−O(10)	176(4)
P(1)−Re(1)−C(10)	88.7(13)	Re(2)−C(20)−N(20)	172(3)
P(4)−Re(1)−C(10)	92.3(13)	C(20)−N(20)−C(21)	169(4)
Re(1)−Re(2)−Cl(21)	169.4(3)	Re(2)−N(30)−C(30)	176(4)
Re(1)−Re(2)−P(2)	94.4(3)	N(30)−C(30)−C(31)	177(6)
Re(1)−Re(2)−P(3)	98.5(3)		

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

Scheme 1. Reactions of the Bioctahedral Complex $Re_2Cl_4(\mu\text{-dppm})_2(CO)(CNXyl)$, **1**



Results and Discussion

The reactions of the bioctahedral dirhenium(II) complex $Re_2Cl_4(\mu\text{-dppm})_2(CO)(CNXyl)$, **1**, which we have examined in the present investigation, are summarized in Scheme 1. Important spectroscopic data for the reaction products **2**−**5** are summarized in Table 3.

The conversion of **1** to the coordinatively unsaturated complex **2**, upon reaction of the former with TlO_3SCF_3, occurs through labilization of the Re−Cl bond which is trans to the XylNC ligand and CO transfer from the adjacent Re center. This reaction course therefore resembles that reported previously for the reactions of TlO_3SCF_3 with the analogous bromo analogue of **1** (i.e., $Re_2Br_4(\mu\text{-dppm})_2(CO)(CNXyl)$) and with the *t*-BuNC-containing derivative $Re_2Br_4(\mu\text{-dppm})_2(CO)(CN\text{-}t\text{-}Bu)$.[2] The IR and ^1H NMR spectroscopic properties and electrochemical properties of **2** closely resemble those of these bromo analogues.[2] The only significant spectroscopic difference is seen in the $^{31}P\{^1H\}$ spectra; for **2**, a fairly broad singlet (fwhm = 0.28 ppm) is observed which is probably an unresolved AA′BB′ pattern, whereas the analogous bromo complex[2] shows a distinct, well-resolved AA′BB′ pattern with multiplets centered at δ −9.0 and −14.5. The cyclic voltammetric properties of **2** in 0.1 M TBAH−CH_2Cl_2 (scan rate 200 mV s^{-1}, potentials vs Ag/AgCl) show a reversible couple, corresponding to a one-electron oxidation of the bulk complex, with an $E_{1/2}$ value of +0.96 V, and an irreversible reduction at $E_{p,c} = -0.89$ V (there is a coupled process at $E_{p,a} = -0.28$ V with $i_{p,a} \ll i_{p,c}$). This behavior is very similar to that reported for $[Re_2Br_3(\mu\text{-dppm})_2(CO)(CNXyl)]O_3SCF_3$ which has $E_{1/2}(\text{ox}) = +0.99$ V and $E_{p,c} = -0.77$ V.[2]

If the reaction between **1** and TlO_3SCF_3 is carried out in the presence of acetonitrile, the coordinatively saturated species **3**, which contains a mixed CO/XylNC/CH_3CN ligand set, is formed. An alternative approach to the synthesis of **3** utilizes the reaction of the monocarbonyl complex $Re_2Cl_4(\mu\text{-dppm})_2(CO)$[11] with 1 equiv each of XylNC and TlO_3SCF_3 in acetonitrile. This reaction proceeds through the intermediacy of **1**, which is known to be formed by the reaction of $Re_2Cl_4(\mu\text{-dppm})_2(CO)$ with XylNC in acetonitrile.[3]

We had shown previously[3] that the reaction of **1** with TlO_3SCF_3 in the presence of XylNC affords the bis(xylyl isocyanide) complex $[Re_2Cl_3(\mu\text{-dppm})_2(CO)(CNXyl)_2]O_3SCF_3$ (**4a**), which has been structurally characterized. Note also that the *tert*-butyl isocyanide complex $Re_2Cl_4(\mu\text{-dppm})_2(CO)(CN\text{-}t\text{-}Bu)$, which is essentially isostructural with **1**, reacts in a similar such fashion with $TlPF_6$ and an additional equivalent of *t*-BuNC to form $[Re_2Cl_3(\mu\text{-dppm})_2(CO)(CN\text{-}t\text{-}Bu)_2]PF_6$.[12,13] The reaction of the acetonitrile-containing complex **3** with the isocyanide ligands XylNC and *t*-BuNC affords the complexes **4a** and **4b**, respectively, through displacement of the labile CH_3CN ligand. The properties of the different samples of **4a**, as obtained by these two different routes, are identical. These conversions support a close structural relationship among **3**, **4a**, and **4b**, which has been confirmed by a single-crystal X-ray structure determination of **3**. An ORTEP[14] drawing of the dirhenium cation of **3** is shown in Figure 1. The structure of **3** very closely resembles that of **4a**,[3] with Re−Re bond distances in accord with the retention of a $Re\equiv Re$ bond (2.378(3) Å for **3** and 2.3833(8) Å for **4a**[3]). The comparable Re−C, Re−Cl, and Re−P distances in the two structures are similar. The Re−N distance of 2.12(4) Å is normal for a nitrile ligand bound to a dirhenium(II) center.[15] As expected, the absence of an electronic barrier to rotation about the $Re\equiv Re$ bond in **3**, results in a partially staggered rotational geometry. The torsional angles P(1)−Re(1)−Re(2)−P(2), P(4)−Re(1)−Re(2)−P(3), Cl(11)−Re(1)−Re(2)−C(20), and C(10)−Re(1)−Re(2)−N(30) have values of 22.55(13), 27.68(13), 27.36(34), and 25.70(50)°, respectively, somewhat larger on average than the comparable angles in the structure of **4a** (20.2, 10.6, 24.3, and 17.8°, respectively).[3] These differences reflect compromises between steric effects and the conformational requirements of the μ-dppm ligands within these compact dinuclear complexes.

The conversions of **3** into **4a** and **4b** occur with retention of stereochemistry as shown by the structural characterizations of

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Table 3. Spectroscopic Data for Dirhenium Complexes Derived from the Reactions of $Re_2Cl_4(\mu\text{-dppm})_2(CO)(CNXyl)$ (**1**)

compd no.[a]	IR, cm^{-1} [b]		^{1}H NMR, δ[c,d]		
	ν(CN)	ν(CO)	$-CH_2-$ of dppm	CH_3 of XylNC	$^{31}P\{^1H\}$ NMR, δ[c,e]
2	2154 (ms)	2030 (vs)	6.12 (m, 2H), 5.77 (m, 2H)	2.03 (s, 6H)	−9.1 (s)
3	2288 (vw),[f] 2094 (vs)	1958 (vs)	5.74 (m, 2H), 5.57 (m, 2H)	2.60 (s, vbr, 6H)[g]	−7.1, −7.4
4a[h]	2144 (m), 2116 (vs)	1944 (s)	6.20 (m, 2H),5.88 (m, 2H)	1.84 (s, 6H),1.65 (s, 6H)	−8.5,[i] −8.8[i]
4b	2172 (m), 2112 (vs)	1962 (vs)	6.15 (m, 2H),5.80 (m, 2H)	1.62 (s, 6H)[j]	−7.1, −11.1
5	2188 (m)	1966 (vs), 1768 (s)	4.72 (m, 2H),4.56 (m, 2H)	2.17 (s, 6H)	−6.0, −8.9

[a] Compound numbering as shown in Scheme 1. [b] IR spectra recorded as Nujol mulls. Abbreviations: ms = medium strong, vw = very weak, vs = very strong, m = medium. [c] NMR spectra recorded on $CDCl_3$ solutions of the complexes. Abbreviations: m = multiplet, vbr = very broad, s = singlet. [d] Resonances for the phenyl ring protons occur in the range $\delta = 6.8-8.0$. [e] With the exception of compound **2**, resonances appear as AA′BB′ multiplets. Unless otherwise indicated, the centers of the two multiplets are quoted. [f] The ν(CN) mode of the coordinated MeCN. [g] The methyl resonance of the coordinated CH_3CN is at $\delta = 2.25$ (s, 3H). [h] Data for this complex taken from ref 3. [i] Most intense component. [j] The resonance for the *t*-BuNC ligand is at $\delta = 1.35$ (s, 9H).

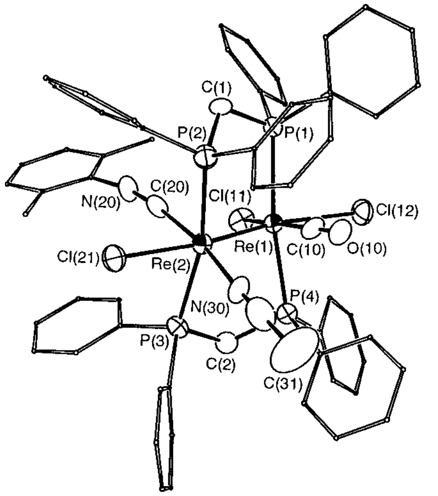
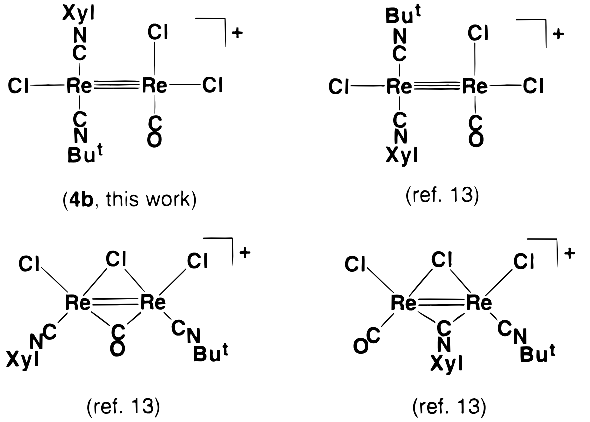


Figure 1. ORTEP[14] representation of the dirhenium cation $[Re_2Cl_3(\mu\text{-dppm})_2(CO)(CNXyl)(NCCH_3)]^+$ as present in **3**. The thermal ellipsoids are drawn at the 50% probability level except for those of the phenyl group atoms of the dppm ligands and the xylyl group atoms of the XylNC ligand, which are circles of arbitrary radius.

Chart 1. Structural Isomers of the Dirhenium Cation $[Re_2Cl_3(\mu\text{-dppm})_2(CO)(CNXyl)(CN\text{-}t\text{-}Bu)]^+$ with the μ-dppm Ligands Omitted for Clarity



(**4b**, this work)

(ref. 13)

(ref. 13)

(ref. 13)

3 (Figure 1) and **4a** (R = Xyl).[3] This observation also accords with the structural identity of the complex cation $[Re_2Cl_3(\mu\text{-dppm})_2(CO)(CN\text{-}t\text{-}Bu)_2]^+$ which can be prepared through the reaction of $[Re_2Cl_3(\mu\text{-dppm})_2(CO)(CN\text{-}t\text{-}Bu)(NCR)]PF_6$, a close structural analogue of **3**, with *t*-BuNC.[12,13] Furthermore, complexes of the type $[Re_2Cl_3(\mu\text{-dppm})_2(CO)(CN\text{-}t\text{-}Bu)(NCR)]PF_6$, where R = CH_3 or C_2H_5, which are obtained by the reaction of $Re_2Cl_4(\mu\text{-dppm})_2(CO)(CN\text{-}t\text{-}Bu)$ with $TlPF_6$ in the presence of an excess of the nitrile RCN,[13] almost certainly have a structure closely akin to that of **3**, with *t*-BuNC in place of XylNC. Interestingly, the product which is produced when $[Re_2Cl_3(\mu\text{-dppm})_2(CO)(CN\text{-}t\text{-}Bu)(NCCH_3)]PF_6$ is reacted with XylNC is an isomer of **4b**.[13] The spectroscopic properties of this product[13] differ from those of **4b** (Table 3), but reveal that, like those in **4b**, the CO, *t*-BuNC, and XylNC ligands are all terminally bound. Since the conversions of **3** to **4a** and **4b** proceed with retention of stereochemistry (Scheme 1), the isomer which is formed from the treatment of $[Re_2Cl_3(\mu\text{-dppm})_2(CO)(CN\text{-}t\text{-}Bu)(NCCH_3)]PF_6$ with XylNC[13] must possess a structure very similar to that shown in Scheme 1 for **4b**, *but with the t-BuNC and XylNC ligands switched*, i.e. with the XylNC ligand syn to the CO (Chart 1). Of further note is our earlier finding[13] that $[Re_2Cl_3(\mu\text{-dppm})_2(CO)(CNXyl)(CN\text{-}t\text{-}Bu)]PF_6$ exists in two other structural forms, both of which are based upon the edge-sharing bioctahedral geometry (Chart 1). These other isomers are of the types $[Re_2(\mu\text{-Cl})(\mu\text{-CO})(\mu\text{-dppm})_2Cl_2(CNXyl)(CN\text{-}t\text{-}Bu)]PF_6$ and $[Re_2(\mu\text{-Cl})(\mu\text{-CNXyl})(\mu\text{-dppm})_2Cl_2(CO)(CN\text{-}t\text{-}Bu)]PF_6$, in which the three π-acceptor ligands have an all-cis arrangement relative to one another.[13] Accordingly, the $[Re_2Cl_3(\mu\text{-dppm})_2(CO)(CNXyl)(CN\text{-}t\text{-}Bu)]^+$ cation has now been identified in four quite distinct stereochemistries (see Chart 1).

Another noteworthy feature of the reaction chemistry summarized in Scheme 1 is the reversibility of interconversion of **2** and **3**. While the presence of only trace amounts of acetonitrile cause the conversion of **2** to **3**, this reaction can be reversed upon heating solutions of the nitrile complex **3**, provided the acetonitrile can be removed from the system by distillation. In the case of salts of the bis(isocyanide) complex cations of the type $[Re_2X_3(\mu\text{-dppm})_2(CO)(CNR)_2]^+$ which possess the open bioctahedral structure $[(RNC)_2XRe(\mu\text{-dppm})_2ReX_2(CO)]^+$ (this work and refs 12 and 13), we observed no corresponding loss of RNC ligands under these same conditions. Presumably, other nitrile-containing complexes which are similar to **3**[2,13] will very likely exhibit nitrile ligand loss upon mild thermolysis.

The final reaction shown in Scheme 1 is the carbonylation of **3** under mild conditions to form the bis(carbonyl) complex **5**. This reaction product is analogous to that obtained from the reaction of the *t*-BuNC analogue of **3** (i.e., $[Re_2Cl_3(\mu\text{-dppm})_2(CO)(CN\text{-}t\text{-}Bu)(NCCH_3)]PF_6$) and CO, which affords the edge-sharing bioctahedral complex $[Re_2(\mu\text{-Cl})(\mu\text{-CO})(\mu\text{-dppm})_2Cl_2(CO)(CN\text{-}t\text{-}Bu)]PF_6$.[13] The latter complex, which has been structurally characterized by X-ray crystallography,[6] and its xylNC analogue have spectroscopic and electrochemical properties very similar to those recorded for the triflate salt **5** (see Table 3), thereby supporting the structural formulation given in Scheme 1 for complex **5**. Furthermore, when a solution of **5** in 1,2-dichloroethane is refluxed for 4 h, it converts to the all-cis edge-sharing bioctahedral form of this complex. The latter species has been shown[6] to be the thermodynamically favored form of these two isomers, and this transformation is diagnostic of the structure shown for **5** in Scheme 1.

Concluding Remarks

The reaction chemistry which is summarized in Scheme 1 confirms that, for dirhenium(II) halide complexes of the type $Re_2X_4(\mu\text{-dppm})_2(CO)(CNR)$ which possess the same type of *open bioctahedral* structure as represented by **1**, the most labile Re−X bond is the one which is trans to the RNC ligand. This behavior is independent of the nature of the halide (X can be Cl or Br) and the isocyanide ligand (R can be *t*-Bu or Xyl).[1−3,13] The sequence of substitution reactions shown in the conversion of complex **1** to **3**, and then to **4a** and **4b**, occurs with retention of stereochemistry when the added ligand is a nitrile or isocyanide. This same situation seems to hold in the case of the reactions of bromo analogues of **1** (i.e., $Re_2Br_4(\mu\text{-dppm})_2(CO)(CNR)$, where R = *t*-Bu or Xyl) with nitriles.[2,16] However, this is not so when XylNC is reacted with the tetrabromo complex $Re_2Br_4(\mu\text{-dppm})_2(CO)(CNXyl)$; in this system, the reaction chemistry is quite complicated, and edge-sharing bis(μ-bromo)-bridged species are the major products.[1]

The carbonylation of **3** to afford the bis(carbonyl) complex **5**, which has an edge-sharing bioctahedral structure with one of the CO ligands in a bridging mode, is typical of all those reactions we have studied[1,6,13,17] in which a species of stoichiometry $[Re_2X_3(\mu\text{-dppm})_2(CO)_2(CNR)]^{n+}$ is formed (n = 0 or 1). This ligand set, in which two CO ligands and one RNC ligand are present, always gives this type of edge-sharing bioctahedral geometry in one of two isomeric forms, viz., that shown for **5** in Scheme 1, or one in which the three π-acceptor ligands are in an all-cis disposition relative to one another on one side of the molecule.

From the present study and one earlier investigation,[13] we have established that the dirhenium cation $[Re_2Cl_3(\mu\text{-dppm})_2(CO)(CNXyl)(CN\text{-}t\text{-}Bu)]^+$ can exist in one of four distinct isomeric forms (see Chart 1). We also note that the bioctahedral complex $[Re_2Cl_3(\mu\text{-dppm})_2(CO)(CNXyl)(NCCH_3)]O_3SCF_3$ (**3**), in which the Re−Re bond is formally of order 3.0, is the second isomeric form of this cation to be isolated and characterized. The other isomer is the edge-sharing bioctahedral species $[Re_2(\mu\text{-}CO)(\mu\text{-}Cl)(\mu\text{-dppm})_2Cl_2(CNXyl)(NCCH_3)]PF_6$,[13] which has an all-cis arrangement of CO, CNXyl, and $NCCH_3$ ligands. The latter complex is prepared[13] from the reaction of the other isomer of **1**, i.e., the edge-sharing bioctahedral form $Re_2(\mu\text{-}CO)(\mu\text{-}Cl)(\mu\text{-dppm})_2Cl_3(CNXyl)$,[4] with $TlPF_6$ in the presence of acetonitrile.[13] This reaction, like the conversion of **1** to **3**, proceeds with retention of stereochemistry.

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Supporting Information Available: Tables giving full details of the crystal data and data collection parameters (Table S1), atomic positional parameters (Tables S2 and S3), anisotropic thermal parameters (Table S4), bond distances (Table S5), and bond angles (Table S6) for **3** (9 pages). An X-ray crystallographic file, in CIF format, is available on the Internet. Ordering and access information is given on any current masthead page.

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