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Reactions of the Dirhenium(II) Complexes $Re_2X_4(\mu\text{-dppm})_2$ (X = Cl, Br; dppm = $Ph_2PCH_2PPh_2$) with Isocyanides. 19.[1] Studies of the Reactions of Five Structural Isomers of $Re_2Cl_2(\mu\text{-dppm})_2(CO)(CNXyl)_3$ That Lead to the Dirhenium(I) Complexes $[Re_2(\mu\text{-Cl})(\mu\text{-CO})(\mu\text{-dppm})_2(CNXyl)_4]O_3SCF_3$ and $[Re_2Cl(\mu\text{-dppm})_2(CO)(CNXyl)_3(NCCH_3)]O_3SCF_3$

Yan Ding, Phillip E. Fanwick, and Richard A. Walton*

Department of Chemistry, Purdue University, 1393 Brown Building,
West Lafayette, Indiana 47907-1393

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Three of the five known isomers of $Re_2Cl_2(\mu\text{-dppm})_2(CO)(CNXyl)_3$ (labeled **4″−8″** in accord with earlier work) react with 1 equiv each of XylNC and TlO_3SCF_3 in benzene to produce the symmetrical dirhenium(I) complex $[Re_2(\mu\text{-Cl})(\mu\text{-CO})(\mu\text{-dppm})_2(CNXyl)_4]O_3SCF_3$ (**I**) in good yield. Isomers **4″**, **6″**, and **8″** are converted to **I**, while **5″** gives an unidentified mixture and isomer **7″** is unreactive. When the reactions of **4″**, **5″**, **6″**, and **8″** with TlO_3SCF_3 are carried out in acetonitrile *in the absence of XylNC*, the compound $[Re_2Cl(\mu\text{-dppm})_2(CO)(CNXyl)_3(NCCH_3)]O_3SCF_3$ can be isolated in three stable isomeric forms (**A**−**C**). Isomer **B** is unreactive, while **A** and **C** react with XylNC in benzene to afford **I**. Single-crystal X-ray structure determinations have been carried out on compounds **I** and **B**.

Introduction

The incorporation of up to four π-acceptor ligands about the coordination sphere of the $[Re_2(\mu\text{-dppm})_2]^{4+}$ unit (dppm = $Ph_2PCH_2PPh_2$) has been accomplished[1−11] in the following reaction sequence which utilizes the triply bonded dirhenium(II) complex $Re_2Cl_4(\mu\text{-dppm})_2$ as the starting material:

$$Re_2Cl_4(\mu\text{-dppm})_2 \xrightarrow{+CO} Re_2Cl_4(\mu\text{-dppm})_2(CO) \qquad (1)^{2,3}$$

$$Re_2Cl_4(\mu\text{-dppm})_2(CO) \xrightarrow{+XylNC} Re_2Cl_4(\mu\text{-dppm})_2(CO)(CNXyl) \qquad (2)^{3,4}$$

$$Re_2Cl_4(\mu\text{-dppm})_2(CO)(CNXyl) \xrightarrow[-Cl^-]{+XylNC/Tl^+} [Re_2Cl_3(\mu\text{-dppm})_2(CO)(CNXyl)_2]^+ \qquad (3)^{4-10}$$

$$[Re_2Cl_3(\mu\text{-dppm})_2(CO)(CNXyl)_2]^+ \xrightarrow[-Cl^-]{+XylNC/Tl^+} [Re_2Cl_3(\mu\text{-dppm})_2(CO)(CNXyl)_3]^{2+} \qquad (4)^{1,11}$$

Several of the analogous bromo complexes have also been isolated and characterized.[3,8,12−15]

These systems are noteworthy for the remarkably large number of stable structural isomers that can be isolated, the dependence of the Re−Re bond order on the structure of the isomer, and the rich reversible redox chemistry that many of these complexes possess.[1−15] For example, our most recent study[1,15] has led to the isolation of four structurally distinct, noninterconvertible isomers of the $[Re_2Cl_2(\mu\text{-dppm})_2(CO)(CNXyl)_3]^{2+}$ cation, each of which exhibits reversible redox chemistry that leads in two instances to coupled redox/isomerization processes. In all, the $[Re_2Cl_2(\mu\text{-dppm})_2(CO)(CNXyl)_3]^{n+}$ species (n = 2, 1, or 0) exist in seven structural variants, which possess Re−Re bond orders of 3, 2, 1.5, 1 or 0.

In the present report, we describe the results of our investigation into the possibility of adding a fifth π-acceptor ligand in place of a chloride ligand. This has been accomplished by starting from three of the five known isomers of the neutral dirhenium(I) complex $Re_2Cl_2(\mu\text{-dppm})_2(CO)(CNXyl)_3$.[1] A single isomeric form of $[Re_2Cl(\mu\text{-dppm})_2(CO)(CNXyl)_4]O_3SCF_3$ is isolated and has been structurally characterized. Evidence is also presented for the existence of three stable isomers of the mixed $CO/XylNC/CH_3CN$ dirhenium(I) species $[Re_2Cl(\mu\text{-dppm})_2(CO)(CNXyl)_3(NCCH_3)]^+$.

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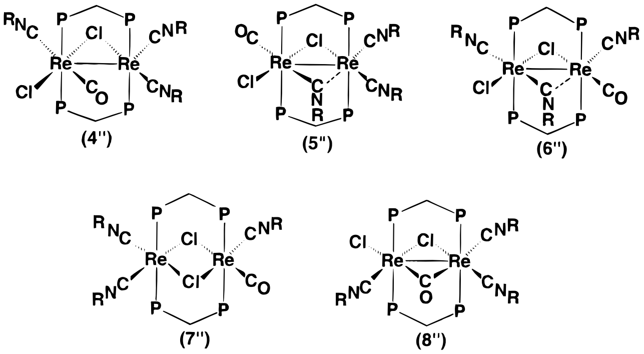
Chart 1. Isomers **4″**−**8″** of the Dirhenium(I) Complex $Re_2Cl_2(\mu\text{-dppm})_2(CO)(CNXyl)_3$ (R = Xyl)



Experimental Section

Starting Materials and General Procedures. The five isomers of the dirhenium(I) complex $Re_2Cl_2(\mu\text{-dppm})_2(CO)(CNXyl)_3$ that were used in the present study were prepared as described previously.[1] To permit easy comparison with our earlier report,[1] we will designate the isomers as **4″**, **5″**, **6″**, **7″**, and **8″** in accord with our previous compound labeling scheme;[1] their structures are represented in the Results and Discussion section (see Chart 1). Thallium(I) triflate, TlO_3SCF_3, was obtained by the literature procedure.[16] Samples of 2,6-dimethylphenyl isocyanide (XylNC) were purchased from Fluka Chemical Corp., and $(\eta^5\text{-}C_5H_5)_2Co$ was from Strem Chemicals Inc. 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.

Caution! *Special precautions should be taken in handling thallium(I) compounds, which are toxic.*

A. Synthesis of $[Re_2Cl(\mu\text{-dppm})_2(CO)(CNXyl)_4]O_3SCF_3$. A mixture comprising $Re_2Cl_2(\mu\text{-dppm})_2(CO)(CNXyl)_3$ (isomer **4″**) (71.4 mg, 0.044 mmol), TlO_3SCF_3 (15.5 mg, 0.044 mmol), and XylNC (5.8 mg, 0.044 mmol) in 10 mL of benzene was heated at reflux for 2 days. The reaction mixture was cooled, the volatiles was removed with use of a rotatory evaporator, the residue was extracted with 10 mL of dichloromethane, and the extract was filtered. The filtrate was evaporated to dryness to yield an orange solid, which was washed with benzene (5 mL) and dried under a vacuum; yield 50.5 mg (62%). Anal. Calcd for $C_{88}H_{80}ClF_3N_4O_4P_4Re_2S$: C, 56.27; H, 4.29. Found: C, 55.91; H, 4.18. Conductivity measurement (in acetone): $\Lambda_m = 119\ \Omega^{-1}\ cm^2\ mol^{-1}$.

This same product was obtained when isomer **6″** or **8″** of $Re_2Cl_2(\mu\text{-dppm})_2(CO)(CNXyl)_3$ (Chart 1) was used in place of **4″**. For example, a quantity of **8″** (53.1 mg, 0.033 mmol) was reacted with a mixture of TlO_3SCF_3 (11.5 mg, 0.033 mmol) and XylNC (5.0 mg, 0.038 mmol) in 10 mL of benzene following the procedure described above for isomer **4″**. Following completion of the reaction, the mixture was stripped to dryness, the residue extracted with CH_2Cl_2 (10 mL), the extract filtered, and the filtrate concentrated to ca. 1 mL. A quantity of diethyl ether (15 mL) was added to precipitate a brown solid, which was filtered off, washed with diethyl ether (2 × 5 mL), and dried under a vacuum; yield 31.7 mg (52%). The spectroscopic and electrochemical properties of these samples were identical with those exhibited by the product obtained from **4″**. The same results were obtained when 1,2-dichloroethane or ethanol was used as the reaction solvent in place of benzene.

When isomer **5″** of $Re_2Cl_2(\mu\text{-dppm})_2(CO)(CNXyl)_3$ was reacted with stoichiometric quantities of TlO_3SCF_3 and XylNC in benzene (or 1,2-dichloroethane), a mixture of unidentified products was obtained. There was no evidence for the presence of $[Re_2Cl(\mu\text{-dppm})_2(CO)(CNXyl)_4]O_3SCF_3$. A similar reaction involving isomer **7″** in refluxing benzene for 2 days led to the quantitative recovery of the starting material.

B. Synthesis of $[Re_2Cl(\mu\text{-dppm})_2(CO)(CNXyl)_3(NCCH_3)]O_3SCF_3$. (i) Isomer A. Quantities of $Re_2Cl_2(\mu\text{-dppm})_2(CO)(CNXyl)_3$ (isomer **4″**) (56.8 mg, 0.0348 mmol) and TlO_3SCF_3 (15.0 mg, 0.0424 mmol) were mixed together and then treated with a mixture of acetonitrile (5 mL) and benzene (10 mL), the latter solvent being present to solubilize the **4″**. The mixture was heated at reflux for ca. 8 h, the off-white solid removed by filtration, and the filtrate evaporated to dryness. The residue was extracted with a small volume of dichloromethane (ca. 1 mL), the extract filtered, and diethyl ether (15 mL) added to precipitate a green solid. This product was collected by filtration, washed with diethyl ether (2 × 5 mL), and dried under a vacuum; yield 57.7 mg (93%). Anal. Calcd. for $C_{81}H_{74}ClF_3N_4O_4P_4Re_2S$: C, 54.40; H, 4.17. Found: C, 54.29; H, 4.09. Conductivity measurement (in acetone): $\Lambda_m = 121\ \Omega^{-1}\ cm^2\ mol^{-1}$.

When a similar reaction was carried out between isomer **8″** of $Re_2Cl_2(\mu\text{-dppm})_2(CO)(CNXyl)_3$ (12.3 mg, 0.0075 mmol) and TlO_3SCF_3 (3.0 mg, 0.0085 mmol) in 5 mL of acetonitrile, workup gave a brown solid; yield 11.9 mg (89%). The spectroscopic and electrochemical properties of this product were essentially identical with those of isomer **A** of $[Re_2Cl(\mu\text{-dppm})_2(CO)(CNXyl)_3(NCCH_3)]O_3SCF_3$ as prepared from **4″**.

(ii) Isomer B. The reaction between $Re_2Cl_2(\mu\text{-dppm})_2(CO)(CNXyl)_3$ (isomer **5″**) (71.8 mg, 0.0440 mmol) and TlO_3SCF_3 (15.6 mg, 0.0441 mmol) in 10 mL of acetonitrile was carried out under reflux conditions for ca. 8 h. Workup as described in section B(i) afforded a brown solid; yield 65.6 mg (83%). Anal. Calcd. for $C_{81.5}H_{75}Cl_2F_3N_4O_4P_4Re_2S$ (i.e. $[Re_2Cl(dppm)_2(CO)(CNXyl)_3(NCCH_3)]O_3SCF_3\cdot 0.5CH_2Cl_2$): C, 53.46; H, 4.13. Found: C, 53.73; H, 4.13. Conductivity measurement (in acetone): $\Lambda_m = 133\ \Omega^{-1}\ cm^2\ mol^{-1}$.

(iii) Isomer C. The reaction of $Re_2Cl_2(\mu\text{-dppm})_2(CO)(CNXyl)_3$ (isomer **6″**) (51.6 mg, 0.0314 mmol) with TlO_3SCF_3 (12.0 mg, 0.0339 mmol) in 10 mL of acetonitrile was carried out as described in section B(ii). Workup gave a brown solid (yield 37.2 mg; 66%) whose spectroscopic and electrochemical properties indicated was a mixture of isomer **A** and a third isomer (**C**) in ca. 1:1 proportions.

C. Synthesis of $[Re_2Cl(\mu\text{-dppm})_2(CO)(CNXyl)_3(NCC_2H_5)]O_3SCF_3$. The propionitrile analogue of isomer **B** of $[Re_2Cl(\mu\text{-dppm})_2(CO)(CNXyl)_3(NCCH_3)]O_3SCF_3$ was prepared by the reaction of **5″** (39.4 mg, 0.024 mmol) with TlO_3SCF_3 (9.0 mg, 0.026 mmol) in 5 mL of refluxing propionitrile through the use of a procedure similar to that described in section B(i); yield 23.7 mg (54%). Anal. Calcd. for $C_{82}H_{76}ClF_3N_4O_4P_4Re_2S$: C, 54.65; H, 4.25. Found: C, 54.26; H, 4.19.

D. Redox Chemistry of $[Re_2Cl(\mu\text{-dppm})_2(CO)(CNXyl)_4]O_3SCF_3$. A mixture of the title complex (51.1 mg, 0.027 mmol) and $[(\eta^5\text{-}C_5H_5)_2Fe]O_3SCF_3$ (9.6 mg, 0.027 mmol) was added to 5 mL of dichloromethane, the mixture stirred for 3 h, and then 15 mL of diethyl ether added. The green solid was filtered off, washed with diethyl ether (2 × 5 mL), and dried under vacuum; yield 49.0 mg (85%). Anal. Calcd for $C_{89}H_{80}ClF_6N_4O_7P_4Re_2S$ (i.e. $[Re_2Cl(dppm)_2(CO)(CNXyl)_4](O_3SCF_3)_2$): C, 52.72; H, 3.98. Found: C, 52.46; H, 3.94.

When a sample of $[Re_2Cl(\mu\text{-dppm})_2(CO)(CNXyl)_4](O_3SCF_3)_2$ (10.6 mg, 0.0052 mmol) was reacted with $(\eta^5\text{-}C_5H_5)_2Co$ (1.0 mg, 0.0053 mmol) in 5 mL of dichloromethane for 2 h, it reconverted to orange $[Re_2Cl(\mu\text{-dppm})_2(CO)(CNXyl)_4]O_3SCF_3$; yield 9.1 mg (92%).

E. Redox Chemistry of Isomer B of $[Re_2Cl(\mu\text{-dppm})_2(CO)(CNXyl)_3(NCCH_3)]O_3SCF_3$. A mixture of the title compound (34.8 mg, 0.020 mmol) and $[(\eta^5\text{-}C_5H_5)_2Fe]O_3SCF_3$ (6.6 mg, 0.020 mmol) was reacted in 5 mL of dichloromethane for 3 h. The reaction mixture was filtered, the filtrate concentrated to ca. 1 mL, and 15 mL of diethyl ether added. The brown microcrystalline product was collected by filtration, washed with diethyl ether (2 × 15 mL), and dried under a vacuum; yield 29.1 mg (76%). Anal. Calcd for $C_{82}H_{74}ClF_6N_4O_7P_4Re_2S_2$ (i.e. $[Re_2Cl(dppm)_2(CO)(CNXyl)_3(NCCH_3)](O_3SCF_3)_2$): C, 50.84; H, 3.85. Found: C, 50.75; H, 3.96. Conductivity measurement (in acetone): $\Lambda_m = 189\ \Omega^{-1}\ cm^2\ mol^{-1}$.

The product $[Re_2Cl(\mu\text{-dppm})_2(CO)(CNXyl)_3(NCCH_3)](O_3SCF_3)_2$ is reduced to $[Re_2Cl(\mu\text{-dppm})_2(CO)(CNXyl)_3(NCCH_3)]O_3SCF_3$ when treated with a stoichiometric quantity of $(\eta^5\text{-}C_5H_5)_2Co$ in dichloromethane; yield 89%.

F. Reactions of $Re_2Cl_2(\mu\text{-dppm})_2(CO)(CNXyl)_3$ with XylNC and TlO_3SCF_3 in Acetonitrile. (i) Isomer 4″. A mixture of $Re_2Cl_2(\mu\text{-dppm})_2(CO)(CNXyl)_3$ (isomer **4″**) (50.9 mg, 0.0312 mmol), TlO_3SCF_3 (11.0 mg, 0.0311 mmol), and XylNC (4.1 mg, 0.0313 mmol) were

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combined with 10 mL of acetonitrile. The mixture was heated at reflux for 2 days and then filtered. The filtrate was taken to dryness with the use of a rotary evaporator. The residue was extracted with dichloromethane (3 mL) and the extract filtered. Diethyl ether (15 mL) was added to precipitate a yellow-orange solid, which was collected by filtration, washed by diethyl ether, and dried under a vacuum; yield 32.2 mg (55%). The spectroscopic and electrochemical properties of the product showed it was $[Re_2Cl(dppm)_2(CO)(CNXyl)_4]O_3SCF_3$. The low yield is due to the poor solubility of the starting material **4″**, much of which remains after 2 days reaction.

(ii) Isomer 5″. The reaction between $Re_2Cl_2(dppm)_2(CO)(CNXyl)_3$ (isomer **5″**) (45.5 mg, 0.0279 mmol), TlO_3SCF_3 (10.0 mg, 0.0283 mmol), and XylNC (4.0 mg, 0.0305 mmol) in CH_3CN (10 mL) was carried out for 40 h. The workup procedure was similar to that of section F(i); yield 39.9 mg (80%). The spectroscopic and electrochemical properties of the product indicated that it was $[Re_2Cl(dppm)_2(CO)(CNXyl)_3(NCCH_3)]O_3SCF_3$ (isomer **B**).

(iii) Isomer 6″. A mixture of $Re_2Cl_2(\mu\text{-dppm})_2(CO)(CNXyl)_3$ (isomer **6″**) (51.3 mg, 0.0316 mmol), XylNC (6.0 mg, 0.046 mmol), TlO_3SCF_3 (15.0 mg, 0.0424 mmol), and 10 mL of acetonitrile was heated at reflux for ca. 8 h. The reaction mixture was allowed to cool to room temperature, the off-white precipitate of TlCl filtered off, and the filtrate allowed to evaporate to dryness. The residue was dissolved in 3 mL of dichloromethane and filtered, and 20 mL of diethyl ether was added to the filtrate to precipitate a brown solid. This product was filtered off, washed with diethyl ether (2 × 10 mL), and dried under a vacuum; yield 30.2 mg. A combination of $^{31}P\{^1H\}$ NMR spectroscopy and cyclic voltammetry showed the product to be a mixture of $[Re_2Cl(\mu\text{-dppm})_2(CO)(CNXyl)_4]O_3SCF_3$ and isomer **C** of $[Re_2Cl(\mu\text{-dppm})_2(CO)(CNXyl)_3(NCCH_3)]O_3SCF_3$ in ca. 1:4 proportions.

G. Reaction of $[Re_2Cl(\mu\text{-dppm})_2(CO)(CNXyl)_3(NCCH_3)]O_3SCF_3$ with XylNC in Benzene. (i) Isomer A. A sample of isomer **A** (51.3 mg, 0.0287 mmol) was mixed with XylNC (4.5 mg, 0.034 mmol) and 10 mL of benzene. This mixture was heated at reflux for ca. 8 h, the solvent removed by use of a rotatory evaporator, and the residue dissolved in 2 mL of dichloromethane. The extract was filtered and diethyl ether (2 × 5 mL) added to precipitate an orange brown solid, which was collected by filtration; yield 34.5 mg (64%). IR spectroscopy and cyclic voltammetry showed this product to be $[Re_2Cl(\mu\text{-dppm})_2(CO)(CNXyl)_4]O_3SCF_3$.

(ii) Isomer B. A similar procedure to that described in section G(i) led to the quantitative recovery of isomer **B**.

(iii) Isomer C. A sample of $[Re_2Cl(\mu\text{-dppm})_2(CO)(CNXyl)_3(NCCH_3)]O_3SCF_3$, comprising a mixture of the isomers **A** and **C** (see section B(iii)) was converted to $[Re_2Cl(\mu\text{-dppm})_2(CO)(CNXyl)_4]O_3SCF_3$ when a procedure similar to that described in section G(i) was used; yield 54%.

H. X-ray Crystallography. Single crystals of $[Re_2Cl(dppm)_2(CO)(CNXyl)_4]O_3SCF_3$ and isomer **B** of $[Re_2Cl(dppm)_2(CO)(CNXyl)_3(NCCH_3)]O_3SCF_3$ were grown by slow diffusion of diethyl ether into dichloromethane solutions of the complexes at room temperature. The crystals were mounted on glass fibers in a random orientation. The data collections were performed on a Nonius KappaCCD diffractometer. The crystallographic data for the compounds are given in Table 1.

The structures were solved by the use of the Patterson heavy-atom method to reveal the positions of the Re atoms. The remaining non-hydrogen atoms were located in succeeding difference Fourier syntheses. The hydrogen atoms were placed in the calculated positions according to idealized geometries with C−H = 0.95 Å and $U(H) = 1.3U_{eq}(C)$. They were included in the refinement but restrained to ride on the atom to which they are bonded. An empirical absorption correction[17] was applied. All calculations were carried out with an AlphaServer 2000 computer. The final refinements were performed by the use of the program SHELXL-97.[18]

During the course of the structure analysis of $[Re_2Cl(dppm)_2(CO)(CNXyl)_4]O_3SCF_3$, the dirhenium unit was found to be located about an inversion center so that bridging CO ligand was disordered with the bridging chloride ligand. A 50:50 disorder model for CO:Cl was refined satisfactorily. The $[CF_3SO_3]^-$ anion was disordered so badly that the squeeze option in PLATON[19] was used to remove the anion. All non-hydrogen atoms were refined with anisotropic thermal parameters.

Table 1. Crystallographic Data for the Dirhenium Complexes $[Re_2(\mu\text{-Cl})(\mu\text{-CO})(\mu\text{-dppm})_2(CNXyl)_4]O_3SCF_3$ (**I**) and $[Re_2Cl(\mu\text{-dppm})_2(CO)(CNXyl)_3(NCCH_3)]O_3SCF_3$ (Isomer **B**) (**II**)

	I	II
empirical formula	$C_{88}H_{80}ClF_3N_4O_4P_4Re_2S$	$C_{81}H_{74}ClF_3N_4O_4P_4Re_2S$
fw	1878.45	1788.33
space group	$C2/m$ (No. 12)	$P\bar{1}$ (No. 2)
a, Å	15.5808(11)	14.7789(9)
b, Å	21.7521(18)	15.9222(8)
c, Å	13.5611(11)	20.4073(12)
α, deg		101.155(3)
β, deg	113.336(6)	99.379(3)
γ, deg		105.285(4)
V, Å^3	4220.1(12)	4427.0(10)
Z	2	2
ρ_{calcd}, g/cm^3	1.478	1.341
μ, mm^{-1}	3.019	2.942
radiation (λ, Å)	Mo Kα (0.710 73)	Mo Kα (0.710 73)
trans-factors, min/max	0.42, 0.63	0.21, 0.58
temp, K	295	203
$R(F_o)^a$	0.062	0.062
$R_w(F_o^2)^b$	0.154	0.169
GOF	1.054	1.061

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

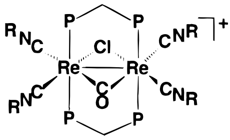
Disorder problems were also encountered in the refinement of the structure of $[Re_2Cl(dppm)_2(CO)(CNXyl)_3(NCCH_3)]O_3SCF_3$ (isomer **B**). These involved a disordered solvent molecule and a badly disordered $[CF_3SO_3]^-$ anion; both were removed by use of the squeeze option in PLATON.[19] All non-hydrogen atoms of the cation were refined with anisotropic thermal parameters.

I. Physical Measurements. Routine IR spectra, ^1H and $^{31}P\{^1H\}$ NMR spectra, and cyclic voltammetric (CV) measurements were determined as described previously.[12] Elemental microanalyses were carried out by Dr. H. D. Lee of the Purdue University Microanalytical Laboratory.

Results and Discussion

In an earlier study,[1] we were able to isolate and characterize, through a combination of spectroscopic measurements and single-crystal X-ray crystal structure determinations, five structural isomers of the neutral dirhenium(I) complex $Re_2Cl_2(\mu\text{-dppm})_2(CO)(CNXyl)_3$ (Chart 1). We will keep the same isomer labeling scheme (**4″**−**8″**) as used previously.[1] The reactions of isomers **4″**−**8″** with a further 1 equiv of XylNC will be described in the present report.

A. Synthesis and Characterization of $[Re_2(\mu\text{-Cl})(\mu\text{-CO})(\mu\text{-dppm})_2(CNXyl)_4]O_3SCF_3$ (I). The reactions of isomers **4″**, **6″**, and **8″** (Chart 1) with 1 equiv each of XylNC and TlO_3SCF_3 in refluxing benzene afford the title complex **I** (R = Xyl) in good yield. On the other hand, isomer **5″** produced a mixture of unidentified products, none of which proved to be $[Re_2(\mu\text{-Cl})(\mu\text{-CO})(\mu\text{-dppm})_2(CNXyl)_4]O_3SCF_3$. Isomer **7″** (Chart 1) showed no reactivity under these conditions, in accord with our



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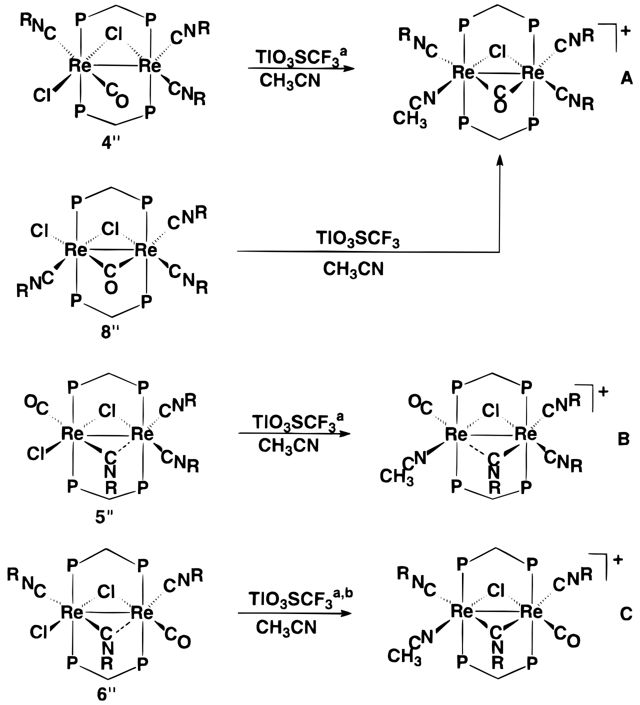
Scheme 1. Products from the Reactions of **4″**, **5″**, **6″**, and **8″** with TlO_3SCF_3 in Acetonitrile (R = Xyl)



[a] This reaction is assumed to proceed with retention of stereochemistry; the structure of **B** has been confirmed by X-ray crystallography. [b] This reaction produces a mixture of isomers **A** and **C** (see Results and Discussion).

previous findings regarding the stability of the $[Re_2(\mu\text{-Cl})_2(\mu\text{-dppm})_2]^{n+}$ unit when complexed by CO and XylNC ligands.[1,8]

Since the same isomer of the complex $[Re_2Cl(\mu\text{-dppm})_2(CO)(CNXyl)_4]O_3SCF_3$ (compound **I**) is formed from different isomers of $Re_2Cl_2(\mu\text{-dppm})_2(CO)(CNXyl)_3$ (**4″**, **6″**, and **8″**), it is presumably the most thermodynamically stable form. The structure of $[Re_2(\mu\text{-Cl})(\mu\text{-CO})(\mu\text{-dppm})_2(CNXyl)_4]O_3SCF_3$ was established by X-ray crystallography, and an ORTEP[20] representation of the dirhenium cation is shown in Figure 1. Important structural parameters are listed in Table 2. The dirhenium cation is located about an inversion center so that the bridging Cl and CO ligands are disordered, and the four XylNC ligands are rendered identical by symmetry. The 50:50 disorder model for μ-CO and μ-Cl was refined satisfactorily, and half of this disorder is represented in Figure 1. In addition to this disorder problem, the quality of the structure determination of **I** was negatively impacted by a badly disordered triflate anion. Accordingly, while the edge-sharing bioctahedral geometry of the dirhenium(I) cation is clearly established, we hesitate to discuss further most of the structural parameters which, nonetheless, appear to be normal for complexes of this type which are based upon the $[Re_2(\mu\text{-dppm})_2]^{2+}$ unit. We note that the Re–Re distance for **I** of 2.9420(6) Å is consistent with the presence of a Re–Re bond that is necessary to ensure an 18e/18e configuration and is a little shorter than the Re–Re single bond lengths of 3.0442(7) and 3.0434(9) Å that have been determined[1] for the dirhenium(I) complexes **4″** and **6″**, respectively (Chart 1).

The labilization of the terminal Re–Cl bonds of **4″** and **8″** (Chart 1) and coordination of an additional XylNC ligand would produce directly the symmetrical structure $[Re_2(\mu\text{-Cl})(\mu\text{-CO})(\mu\text{-dppm})_2(CNXyl)_4]^+$ (**I**). However, such a reaction course in the case of **5″** and **6″** should first lead to different isomeric forms with structures of the type $[Re_2(\mu\text{-Cl})(\mu\text{-CNXyl})(\mu\text{-dppm})_2(CO)(CNXyl)_3]^+$. While the isomer that is initially formed from **6″** must rearrange to the more thermodynamically stable **I**, the isomer of $[Re_2Cl(\mu\text{-dppm})_2(CO)(CNXyl)_4]O_3SCF_3$ that is formed from **5″**, and which would have an all-cis arrangement of the XylNC ligands, presumably decomposes during the course of the reaction and **I** is not produced. An alternative mechanism in the case of **6″** involves its isomerization to **8″** *prior to* the substitution of the terminal Cl ligand by XylNC. This isomerization is known to occur in benzene.[1]

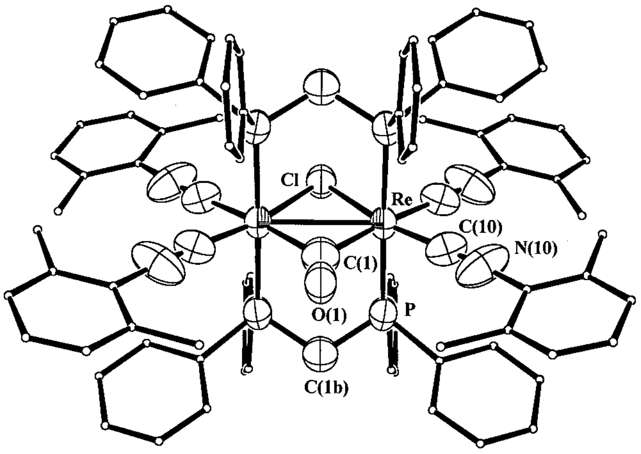


Figure 1. ORTEP[20] representation of the structure of the dirhenium cation present in $[Re_2(\mu\text{-Cl})(\mu\text{-CO})(\mu\text{-dppm})_2(CNXyl)_4]O_3SCF_3$ (**I**). This representation shows half of the disorder involving the bridging CO and Cl ligands. The thermal ellipsoids are drawn at the 50% 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.

Table 2. Important Bond Distances (Å) and Bond Angles (deg) for the Complex $[Re_2(\mu\text{-Cl})(\mu\text{-CO})(\mu\text{-dppm})_2(CNXyl)_4]O_3SCF_3$ (**I**)[a]

	Distances		
Re–Re	2.9420(6)	Re(1)–P	2.4089(18)
Re(1)–Cl	2.611(10)	C(1)–O(1)	1.07(5)
Re(1)–C(1)	2.13(3)	C(10)–N(10)	1.152(11)
Re(1)–C(10)	1.962(8)		
	Angles		
C(1)–Re–C(10)	89.6(8)	Re–Cl–Re	68.6(3)
C(10)–Re–C(10)	88.3(5)	Re–C(1)–Re	87.2(16)
Cl–Re–C(1)	102.0(9)	Re–C(1)–O(1)	136.3(9)
Cl–Re–C(10)	80.2(3)	Re–C(10)–N(10)	175.9(8)
P–Re–P	178.41(7)		

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

The spectroscopic properties of **I** are straightforward, and the IR spectra and $^{31}P\{^1H\}$NMR spectra are listed in Table 3. The ^1H NMR spectral data are available as Supporting Information. The bridging ν(CO) mode is observed in the Nujol mull IR spectrum at 1784 cm^{-1}. A singlet in the $^{31}P\{^1H\}$ NMR spectrum is consistent with the symmetrical structure for the dirhenium cation. The cyclic voltammetric properties for 0.1 M $n\text{-}Bu_4NPF_6/CH_2Cl_2$ solutions of **I** show the expected[1] two one-electron oxidations to the analogous $[Re_2]^{3+}$ and $[Re_2]^{4+}$ species. The oxidation to $[Re_2(\mu\text{-Cl})(\mu\text{-CO})(\mu\text{-dppm})_2(CNXyl)_4](O_3SCF_3)_2$ can be accomplished chemically through the use of $[(\eta^5\text{-}C_5H_5)_2Fe]O_3SCF_3$ as the oxidant. The properties of this green product are given in Table 3. Interestingly, the oxidation is accompanied by a small *decrease* in the IR-active ν(CO) mode. The oxidized

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(20) (a) Johnson, C. K. *ORTEP II*; Report ORNL-5138; Oak Ridge National Laboratory: Oak Ridge, TN, 1976. (b) Farrugia, L. J. *J. Appl. Crystallogr.* **1997**, 565.

Table 3. Selected Spectroscopic and Cyclic Voltammetric Data for Dirhenium Species of the Types $[Re_2(\mu\text{-Cl})(\mu\text{-CO})(\mu\text{-dppm})_2(CNXyl)_4]^{n+}$ (n = 1 or 2) and $[Re_2Cl(\mu\text{-dppm})_2(CO)(CNXyl)_3(NCR)]^{n+}$ (n = 1 or 2; R = CH_3 or C_2H_5)

	IR, cm^{-1} [a]	chem shift, δ[b]	CV half-wave potentials, V[c]		
complex	ν(CN) and ν(CO)	$^{31}P\{^1H\}$ NMR	$E_{p,a}$	$E_{p,c}$	$E_{1/2}$
$[Re_2(\mu\text{-Cl})(\mu\text{-CO})(\mu\text{-dppm})_2(CNXyl)_4]O_3SCF_3$ (**I**)	~2110 (sh), ~1960 (br, sh), 2057 (vs), 2018 (s, br), ~1890 (w, sh), *1784 (m)*	+3.2 (s)			+0.98 (65),[i] +0.41(60)[i]
$[Re_2(\mu\text{-Cl})(\mu\text{-CO})(\mu\text{-dppm})_2(CNXyl)_4](O_3SCF_3)_2$	2123 (vs), 2102 (sh), 2089 (vs), *1769(m−s)*	*g*			+0.97 (60),[i] +0.41 (70)[j]
$[Re_2Cl(\mu\text{-dppm})_2(CO)(CNXyl)_3(NCCH_3)]O_3SCF_3$ (isomer **A**)	2287 (vw)?,[f] 2087 (vs), 2051 (vs), 2015 (vs), 1959 (s, vbr), 1890 (br, sh), *1800m*	+10.0 (m),[h] +4.9 (m)[h]			+0.81 (70),[i] +0.32 (80)[i]
$[Re_2Cl(\mu\text{-dppm})_2(CO)(CNXyl)_3(NCCH_3)]O_3SCF_3$ (isomer **B**)	2251 (w),[f] 2090 (s), 2045 (vs), 2016 (w), 1914 (s), 1814 (vs)	+10.4 (m),[h] −1.6 (m)[h]	+1.25	+0.57	+0.38 (60)[i]
$[Re_2Cl(\mu\text{-dppm})_2(CO)(CNXyl)_3(NCCH_3)](O_3SCF_3)_2$[d]	2101 (s), 2061 (s), 1950 (m−s), 1900(s)	*g*	+1.24	+0.57	+0.38 (65)[j]
$[Re_2Cl(\mu\text{-dppm})_2(CO)(CNXyl)_3(NCCH_3)]O_3SCF_3$ (isomer **C**)	2257 (w),[f] 2042 (vs), 2005 (vs), 1917 (vs, br), 1800 (m−s)	+7.3 (m),[h] +0.3 (m)[h]	+1.00		+0.42 (70)[i]
$[Re_2Cl(\mu\text{-dppm})_2(CO)(CNXyl)_3(NCC_2H_5)]O_3SCF_3$[e]	2234 w,[f] 2076 (sh), 2031 (vs), 2001 (s), 1940 (s), 1829 (m−s)	+9.7 (m),[h] −1.9 (m)[h]	+1.28	+0.58	+0.38 (60)[i]

[a] IR spectra recorded as Nujol mulls. Bands assigned with confidence to ν(CO) modes are given in italics. All compounds have a strong band at ~1270 cm^{-1} assigned to the triflate anion. Abbreviations: s = strong, m = medium, w = weak, br = broad, sh = shoulder. [b] NMR spectra recorded on CD_2Cl_2 solutions. Abbreviations: s = singlet, m = multiplet. [c] Data are based upon single scan cyclic voltammograms measured on 0.1 M TBAH/CH_2Cl_2 solutions and referenced to the Ag/AgCl electrode with a scan rate (ν) of 200 mV/s at a Pt-bead 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 $i_{p,a} = i_{p,c}$. Numbers in parentheses are the values of $E_{p,a} - E_{p,c}$ (in mV) for the process. [d] Oxidized congener of isomer **B**. [e] This compound has a structure similar to that of isomer **B** of the analogous acetonitrile complex. [f] ν(CN) of the nitrile ligand. [g] Paramagnetic. [h] Center of a multiplet which is part of an AA′BB′ pattern. [i] Oxidation for the bulk complex. [j] Reduction for the bulk complex.

complex is readily reduced back to **I** upon its treatment with $(\eta^5\text{-}C_5H_5)_2Co$.

b. Synthesis and Characterization of Isomers of the Acetonitrile Complex $[Re_2Cl(\mu\text{-dppm})_2(CO)(CNXyl)_3(NCCH_3)]O_3SCF_3$. The conversion of **4″**, **6″** and **8″** (Chart 1) to $[Re_2(\mu\text{-Cl})(\mu\text{-CO})(\mu\text{-dppm})_2(CNXyl)_4]O_3SCF_3$ required the use of the noncoordinating solvent benzene. When the reactions between **4″**, **5″**, or **6″** and XylNC/TlO_3SCF_3 mixtures were carried out in the presence of the coordinating solvent acetonitrile, isomers of the complex $[Re_2Cl(\mu\text{-dppm})_2(CO)(CNXyl)_3(NCCH_3)]O_3SCF_3$ were also produced thereby complicating this chemistry. To clarify the nature of these products, complexes **4″**, **5″**, **6″**, and **8″** were reacted with TlO_3SCF_3 in acetonitrile *in the absence of added XylNC.* On the basis of the spectroscopic and electrochemical properties of the products (Table 3), three distinct isomeric forms of $[Re_2Cl(\mu\text{-dppm})_2(CO)(CNXyl)_3(NCCH_3)]O_3SCF_3$ were isolated (Scheme 1). These will be designated as isomers **A**−**C**. These reactions of **4″**−**6″**, in which the terminal Re−Cl bond is replaced by acetonitrile, are assumed to proceed with retention of stereochemistry; in this event, the analogous reaction of **8″** must involve a rearrangement step during the breaking of the Re−Cl bond since this isomer gives the same product as that formed from **4″**. The structure of **B** has been confirmed by X-ray crystallography (vide infra). Note that the conversion of **6″** to isomer **C** of $[Re_2Cl(\mu\text{-dppm})_2(CO)(CNXyl)_3(NCCH_3)]O_3SCF_3$ is accompanied by the formation of significant quantities of isomer **A** and, consequently, we have not been able to obtain pure samples of **C**. Since **A** and **C** do not interconvert, they must be formed by separate pathways during the substitution of the Re−Cl bond. We have shown previously[1] that while **4″**−**6″** do not interconvert, isomer **6″** can isomerize to **8″**. Since **8″** converts to isomer **A** (see Scheme 1), it is likely that the partial isomerization of **6″** to **8″** during the reaction of **6″** with TlO_3SCF_3/CH_3CN mixtures gives rise to the contamination of **C** by **A**.

The structural identity of isomer **B** was established by X-ray crystallography. While single crystals of **A** were obtained, the dirhenium cation was disordered and we were unable to establish the location of the acetonitrile ligand in the equatorial plane. Unfortunately, suitable single crystals of **C** could not be obtained. Accordingly, the structures of **A** and **C** remain to be confirmed. An ORTEP[20] representation of the structure of the dirhenium cation present in **B** is shown in Figure 2, and the most important bond distances and angles are listed in Table 4. The Re− Re distance of 3.0873(6) Å accords with a rather long Re−Re bond and, therefore, an 18e/18e configuration for the two metal atoms of the cation. The structure resembles closely that of the precursor complex **5″** from which it is derived. The structural parameters for isomer **B** can be most usefully compared with those of **6″**, which has also been structurally characterized. Both contain a fairly symmetrical chloro-bridge and a very unsymmetrical XylNC bridging ligand (almost

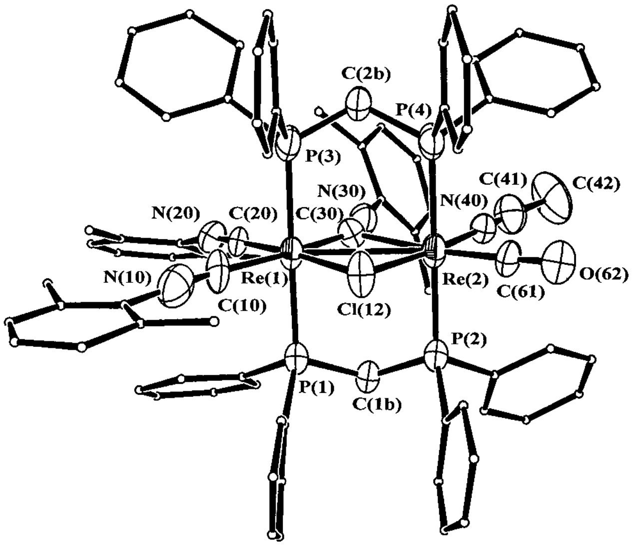

Figure 2. ORTEP[20] representation of the structure of the dirhenium cation $[Re_2(\mu\text{-Cl})(\mu\text{-CNXyl})(\mu\text{-dppm})_2(CO)(CNXyl)_2(NCCH_3)]^+$ as present in isomer **B** of $[Re_2Cl(\mu\text{-dppm})_2(CO)(CNXyl)_3(NCCH_3)]O_3SCF_3$ (**II**). The thermal ellipsoids are drawn at the 50% 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.

Table 4. Important Bond Distances (Å) and Bond Angles (deg) for Isomer **B** of [$Re_2Cl(\mu$-dppm$)_2(CO)(CNXyl)_3(NCCH_3)]O_3SCF_3$ (**II**)[a]

Distances			
Re(1)−Re(2)	3.0873(6)	Re(2)−P(4)	2.391(4)
Re(1)−C(10)	1.948(14)	Re(2)−P(2)	2.400(3)
Re(1)−C(20)	1.962(14)	Re(2)−Cl(12)	2.443(3)
Re(1)−C(30)	2.058(14)	Re(2)−C(30)	2.477(13)
Re(1)−P(1)	2.416(3)	C(10)−N(10)	1.223(17)
Re(1)−P(3)	2.434(3)	C(20)−N(20)	1.149(15)
Re(1)−Cl(12)	2.505(3)	C(30)−N(30)	1.200(16)
Re(2)−C(61)	1.830(12)	N(40)−C(41)	1.104(16)
Re(2)−N(40)	2.022(11)	O(62)−C(61)	1.216(14)
Angles			
C(10)−Re(1)−C(20)	89.8(5)	C(61)−Re(2)−Cl(12)	97.9(4)
C(10)−Re(1)−C(30)	168.3(6)	N(40)−Re(2)−Cl(12)	174.8(3)
C(20)−Re(1)−C(30)	78.5(5)	P(4)−Re(2)−Cl(12)	91.23(12)
C(10)−Re(1)−P(1)	89.2(4)	P(2)−Re(2)−Cl(12)	90.55(12)
C(20)−Re(1)−P(1)	87.2(3)	C(61)−Re(2)−C(30)	168.1(5)
C(30)−Re(1)−P(1)	89.8(3)	N(40)−Re(2)−C(30)	81.2(4)
C(10)−Re(1)−P(3)	91.7(4)	P(4)−Re(2)−C(30)	88.3(3)
C(20)−Re(1)−P(3)	93.2(3)	P(2)−Re(2)−C(30)	89.7(3)
C(30)−Re(1)−P(3)	89.4(3)	Cl(12)−Re(2)−C(30)	93.9(3)
P(1)−Re(1)−P(3)	178.99(11)	Re(2)−Cl(12)−Re(1)	77.19(10)
C(10)−Re(1)−Cl(12)	88.1(4)	Re(1)−C(30)−Re(2)	85.3(5)
C(20)−Re(1)−Cl(12)	176.8(3)	N(10)−C(10)−Re(1)	170.3(12)
C(30)−Re(1)−Cl(12)	103.6(4)	N(20)−C(20)−Re(1)	174.4(11)
P(1)−Re(1)−Cl(12)	90.39(12)	N(30)−C(30)−Re(1)	152.9(10)
P(3)−Re(1)−Cl(12)	89.29(12)	N(30)−C(30)−Re(2)	121.8(9)
C(61)−Re(2)−N(40)	86.9(5)	C(41)−N(40)−Re(2)	175.6(11)
C(61)−Re(2)−P(4)	90.1(4)	O(62)−C(61)−Re(2)	176.1(12)
N(40)−Re(2)−P(4)	86.9(3)	C(10)−N(10)−C(11)	178.3(15)
C(61)−Re(2)−P(2)	91.4(4)	C(20)−N(20)−C(21)	168.5(12)
N(40)−Re(2)−P(2)	91.2(3)	C(30)−N(30)−C(31)	170.2(12)
P(4)−Re(2)−P(2)	177.45(13)	N(40)−C(41)−C(42)	173.7(17)

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

terminally bound in **6″**). In the case of **B**, the bridging Re−C distances Re(1)−C(30) and Re(2)−C(30) are 2.058(14) and 2.477(13) Å, respectively, while the Re−C distances Re(1)−C(10) and Re(1)−C(20) are 1.948(14) and 1.962(4) Å, respectively. The latter values are typical for terminally bound XylNC ligands in this type of dirhenium complex.[1]

When the acetonitrile containing isomers **A**−**C** are reacted with 1 equiv of XylNC in benzene, **A** and **C** convert to [$Re_2(\mu$-Cl$)(\mu$-CO$)(\mu$-dppm$)_2(CNXyl)_4]O_3SCF_3$ while isomer **B** does not react. The conversion of **C** to [$Re_2(\mu$-Cl$)(\mu$-CO$)(\mu$-dppm$)_2(CNXyl)_4]O_3SCF_3$ must involve an isomerization step prior to or after the replacement of CH_3CN by XylNC. The stability of isomer **B** to substitution of the acetonitrile ligand is supported by the observation that it does not exchange with propionitrile even under reflux conditions. Note that the propionitrile complex [$Re_2(\mu$-Cl$)(\mu$-dppm$)_2(CO)(CNXyl)_3(NCC_2H_5)]O_3SCF_3$ can be prepared by the reaction of **5″** with TlO_3SCF_3 in propionitrile; its properties (Table 3) are in accord with it possessing the same structure as its acetonitrile analogue **B**.

The aforementioned reactions explain the behavior which is observed when **4″**−**6″** are reacted with 1 equiv each of XylNC and TlO_3SCF_3 *in acetonitrile*. Compound **4″** converts to [$Re_2(\mu$-Cl$)(\mu$-CO$)(\mu$-dppm$)_2(CNXyl)_4]O_3SCF_3$ via the intermediacy of isomer **A** of the acetonitrile complex. However, **5″** is converted to the substitutionally inert isomer **B** of [$Re_2(\mu$-Cl$)(\mu$-dppm$)_2(CO)(CNXyl)_3(NCCH_3)]O_3SCF_3$, and therefore, the tetrakis(xylyl isocyanide) complex **I** is not formed. In the case of **6″**, a mixture of **I** and isomer **C** of [$Re_2(\mu$-Cl$)(\mu$-dppm$)_2(CO)(CNXyl)_3(NCCH_3)]O_3SCF_3$ is produced. As mentioned previously, **6″** first converts to a mixture of isomers **A** and **C** in acetonitrile. In the presence of XylNC, **A** then converts to **I** while **C** is unreactive toward XylNC in the presence of an excess of the acetonitrile solvent.

Concluding Remarks

The present study has provided the first example of the incorporation of five π-acceptor ligands into the coordination sphere of the [$Re_2(\mu$-dppm$)_2]^{n+}$ species through a series of ligand substitutions and redox reactions which originated with the electron-rich triply bonded complex $Re_2Cl_4(\mu$-dppm$)_2$. The substitution of the terminal chloro ligand in isomers **4″**, **6″**, and **8″** of $Re_2Cl_2(\mu$-dppm$)_2(CO)(CNXyl)_3$ by XylNC in the presence of TlO_3SCF_3 occurs to give the symmetrical isomer [$Re_2(\mu$-Cl$)(\mu$-CO$)(\mu$-dppm$)_2(CNXyl)_4]O_3SCF_3$ (**I**) when the reactions are carried out in benzene. The reactions between the four isomers **4″**, **5″**, **6″**, and **8″** of $Re_2Cl_2(\mu$-dppm$)_2(CO)(CNXyl)_3$ and acetonitrile give three isomers of [$Re_2Cl(\mu$-dppm$)_2(CO)(CNXyl)_3(NCCH_3)]O_3SCF_3$ (**A**−**C**), each of which is believed to possess an edge-sharing bioctahedral geometry. The latter results show that the isomer chemistry of complexes which are derivable from $Re_2Cl_4(\mu$-dppm$)_2$ can be extended to include those with mixed CO/isocyanide/nitrile ligand sets.

Supporting Information Available: A table giving ^{1}H NMR spectral data for dirhenium(I) complexes and X-ray crystallographic files in CIF format for complexes [$Re_2(\mu$-Cl$)(\mu$-CO$)(\mu$-dppm$)_2(CNXyl)_4]O_3SCF_3$ (**I**) and isomer **B** of [$Re_2Cl(\mu$-dppm$)_2(CO)(CNXyl)_3(NCCH_3)]O_3SCF_3$ (**II**). This material is available free of charge via the Internet at http://pubs.acs.org.

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