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Reactions of the Dirhenium(II) Complexes $Re_2X_4(\mu$-dppm$)_2$ (X = Cl, Br; dppm = $Ph_2PCH_2PPh_2$) with Isocyanides. 21.[1] A Comparison with the Complexes $Re_2Cl_4(\mu$-dppE$)_2$ and $Re_2Cl_4(\mu$-dcpm$)_2$ (dppE = $Ph_2PC(=CH_2)PPh_2$; dcpm = $Cy_2PCH_2PCy_2$) and the Structural Characterization of Complexes of the Types $Re_2Cl_4(\mu$-LL$)_2$(CNR), $Re_2Cl_4(\mu$-LL$)_2$(CNR$)_2$, and $[Re_2Cl_3(\mu$-LL$)_2$(CNR$)_3]^+$ (LL = dppm, dppE, dcpm; R = *t*-Bu, Xyl)

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A study of the reactions between the triply bonded dirhenium(II) complexes $Re_2Cl_4(\mu$-LL$)_2$, where LL = $Ph_2PCH_2PPh_2$ (dppm), $Ph_2PC(=CH_2)PPh_2$ (dppE), or $Cy_2PCH_2PCy_2$ (dcpm), with the isocyanides *t*-BuNC and XylNC (Xyl = 2,6-dimethylphenyl) show that complexes of the type $Re_2Cl_4(\mu$-LL$)_2$(CNR), $Re_2Cl_4(\mu$-LL$)_2$(CNR$)_2$, and $[Re_2Cl_3(\mu$-LL$)_2$(CNR$)_3]^+$ are formed sequentially. Several of these have been structurally characterized by X-ray crystallography: $Re_2Cl_4(\mu$-dppm$)_2$(CNXyl) (**2**), $Re_2Cl_4(\mu$-dcpm$)_2$(CNXyl) (**11**), $Re_2Cl_4(\mu$-dppE$)_2$(CN-*t*-Bu$)_2$ (**6**), $Re_2Cl_4(\mu$-dcpm$)_2$(CN-*t*-Bu$)_2$ (**12**), and $[Re_2Cl_3(\mu$-dppE$)_2$(CN-*t*-Bu$)_3]$Cl (**7**). Complex **2** has an A-frame-like structure with a single μ-Cl bridging ligand, whereas for **11** the structure is like that of **2** but without this bridge, viz., $Cl_2Re(\mu$-dppm$)_2ReCl_2$(CNXyl) with a Re−Cl bond approximately collinear with Re≡Re. The symmetrical complexes **6** and **12** are essentially isostructural and have an anti-arrangement of the two *t*-BuNC ligands. Complex **7** has the open bioctahedral structure $[(t\text{-BuNC})_2ClRe(\mu\text{-dppE})_2ReCl_2(\text{CN-}t\text{-Bu})]^+$, which is quite different from that of the edge-sharing bioctahedron found in salts of the $[Re_2Cl_3(\mu$-dppm$)_2$(CNXyl$)_3]^+$ cation and its neutral congener $Re_2Cl_3(\mu$-dppm$)_2$(CNXyl$)_3$; preliminary crystallographic data for the latter compound show the structure to be (XylNC)ClRe(μ-Cl)(μ-CNXyl)(μ-dppm$)_2$ReCl(CNXyl) with an all-*cis* arrangement of XylNC ligands. The Re−Re bond distances of **2**, **6**, **7**, **11**, and **12** occur in the range 2.289−2.380 Å and are consistent in all instances with the retention of a Re≡Re bond, albeit weakened by some degree of Re→CNR(π*) back-bonding.

Introduction

The reactions of $Re_2Cl_4(\mu$-dppm$)_2$ (dppm = $Ph_2PCH_2PPh_2$) with CO lead to the incorporation of up to three of these ligands into the dimetal coordination sphere to afford the complexes $Re_2Cl_4(\mu$-dppm$)_2$(CO),[2,3] $Re_2Cl_4(\mu$-dppm$)_2$(CO$)_2$,[2] and $[Re_2Cl_3(\mu$-dppm$)_2$(CO$)_3]^+$.[4] In addition, several extensive series of dirhenium(II) complexes have been isolated and structurally characterized which contain a combination of CO along with up to three xylyl isocyanide ligands, viz., $Re_2Cl_4(\mu$-dppm$)_2$(CO)(CNXyl),[3,5] $[Re_2Cl_3(\mu$-dppm$)_2$(CO)(CNXyl$)_2]^+$,[5−11] and $[Re_2Cl_2(\mu$-dppm$)_2$(CO)(CNXyl$)_3]^{2+}$.[12,13] Several of the analogous bromo complexes are also known.[3,4,9] These compounds exist in a variety of stable isomeric forms that are notable for the dependence of the Re−Re bond order on the structure of the isomer, and the rich metal-based redox chemistry that they exhibit.[3,5−17]

Although earlier work had also led to the isolation of several dirhenium(II) isocyanide complexes of the types $Re_2Cl_4(\mu$-dppm$)_2$(CNR),[18] $[Re_2Cl_3(\mu$-dppm$)_2$(CNR$)_2]PF_6$,[19,20] and $[Re_2Cl_3(\mu$-dppm$)_2$(CNR$)_3]PF_6$,[20] these compounds have remained inadequately characterized and their chemistry little explored. To establish the structural identity of these types of complexes, we have performed a comparative study of the reaction chem-

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istry of the triply bonded dirhenium(II) complexes $Re_2Cl_4(\mu\text{-dppm})_2$,[21,22] $Re_2Cl_4(\mu\text{-dppE})_2$ (dppE = $Ph_2PC({=}CH_2)PPh_2$),[23] and $Re_2Cl_4(\mu\text{-dcpm})_2$ (dcpm = $Cy_2PCH_2PCy_2$)[24] with *tert*-butyl isocyanide (*t*-BuNC) and 2,6-dimethylphenyl isocyanide (XylNC) and, in so doing, have been able to clarify the structures of several of these isocyanide complexes.

Experimental Section

A. Starting Materials and General Procedures. The complexes $Re_2Cl_4(\mu\text{-dppm})_2$ (**1**),[25] $Re_2Cl_4(\mu\text{-dppE})_2$ (**4**),[23] and $Re_2Cl_4(\mu\text{-dcpm})_2$ (**10**)[24] were prepared by the standard reported procedures, as was the complex $Re_2Cl_4(\mu\text{-dppm})_2(CNXyl)$ (**2**),[18] and the reagent TlO_3SCF_3.[26] The neutral dirhenium(II,I) complex $Re_2Cl_3(\mu\text{-dppm})_2(CNXyl)_3$ (**3**) was prepared from $[Re_2Cl_3(\mu\text{-dppm})_2(CNXyl)_3]O_3SCF_3$ by use of cobaltocene as the reducing agent and a procedure similar to that described previously starting with the analogous $[PF_6]^-$ salt.[20] Samples of 2,6-dimethylphenyl isocyanide (XylNC) were purchased from Fluka Chemical Corp., whereas $TlPF_6$, *t*-BuNC, and $(\eta^5\text{-}C_5H_5)_2Co$ were obtained from Strem Chemicals. These commercial reagents were used as received. Solvents were obtained from commercial sources and were deoxygenated by purging with dinitrogen before use. All reactions were performed under an atmosphere of dinitrogen.

Routine IR spectra, NMR spectra, and cyclic voltammetric measurements were determined as described previously.[14] 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.

B. Reactions of $Re_2Cl_4(\mu\text{-dppE})_2$ (4) with Isocyanides. 1. Synthesis of $Re_2Cl_4(\mu\text{-dppE})_2(CNXyl)$ (5). A quantity of **4** (65 mg, 0.05 mmol) was dissolved in 30 mL of dichloromethane, and a solution of XylNC (5.2 mg, 0.04 mmol) in dichloromethane (5 mL) was added dropwise with stirring while maintaining a temperature of −10 °C. The reaction mixture was stirred for a further 30 min and then allowed to warm to room temperature, and the solvent was removed under reduced pressure. The residue was washed with diethyl ether and dried. The $^{31}P\{^1H\}$ NMR spectrum of the product (recorded in $CDCl_3$) showed that it consists of the desired complex **5** (see Results and Discussion), unreacted starting material **4**,[23] and a small amount of an unidentified impurity. The amount of the latter species increased when the reaction was performed at room temperature and with an increase in the mole proportions of XylNC used. This impurity exhibits an AA′BB′ pattern in its $^{31}P\{^1H\}$ NMR spectrum with $\delta = +26.8$ and $+8.8$ for the centers of the two multiplets.

2. Synthesis of $Re_2Cl_4(\mu\text{-dppE})_2(CN\text{-}t\text{-}Bu)_2$ (6). A quantity of *t*-BuNC (22.5 μL, 0.20 mmol) was added to a solution of **4** (131 mg, 0.10 mmol) in 30 mL of dichloromethane. The resulting mixture was stirred for 24 h at room temperature and then filtered. The volume of the brown solution was then reduced to about 3 mL, and an excess of diethyl ether (20 mL) was added to give a brown precipitate of **6**, which was filtered off, washed with 20 mL of diethyl ether, and dried under reduced pressure; yield, 108 mg (73%). This complex was recrystallized from 1,2-$C_2H_4Cl_2$/diethyl ether to afford brown crystals. Anal. Calcd for $C_{65}H_{68}Cl_7N_2P_4Re_2$ (i.e., $\mathbf{6}\cdot 1.5C_2H_4Cl_2$): C, 48.14; H, 4.22; N, 1.73. Found: C, 48.04; H, 4.21; N, 1.69. The presence of lattice 1,2-$C_2H_4Cl_2$ was confirmed by ^1H NMR spectroscopy.

3. Synthesis of $[Re_2Cl_3(\mu\text{-dppE})_2(CN\text{-}t\text{-}Bu)_3]Cl$ (7). The reaction between **4** (200 mg, 0.15 mmol) and *t*-BuNC (68 μL, 0.60 mmol) was performed in 40 mL of dichloromethane at room temperature for 48 h. The mixture was filtered, and the green filtrate was reduced in volume to ca. 5 mL. An excess of diethyl ether was added to afford a green precipitate of **7**, which was filtered off, washed with 20 mL of diethyl ether, and dried under reduced pressure; yield, 143 mg (60%). Anal. Calcd for $C_{67}H_{71}Cl_4N_3P_4Re_2$: C, 51.70; H, 4.60. Found: C, 51.00; H, 4.91.

4. Synthesis of $[Re_2Cl_3(\mu\text{-dppE})_2(CN\text{-}t\text{-}Bu)_3]PF_6$ (8). The reaction between **4** (131 mg, 0.10 mmol) and *t*-BuNC (45 μL, 0.40 mmol) was performed as described in section B.3 in the presence of an equivalent of $TlPF_6$ (35 mg, 0.10 mmol). After 24 h, the green reaction mixture was filtered and the green filtrate worked up in the usual way to afford green microcrystals of **8**; yield, 92 mg (55%). Anal. Calcd for $C_{68}H_{73}Cl_5F_6N_3P_5Re_2$ (i.e., $\mathbf{8}\cdot CH_2Cl_2$): C, 46.65; H, 4.20; N, 2.40. Found: C, 46.12; H, 4.22; N, 2.85. The presence of lattice CH_2Cl_2 was confirmed by ^1H NMR spectroscopy.

5. Synthesis of $[Re_2Cl_3(\mu\text{-dppE})_2(CN\text{-}t\text{-}Bu)_2]O_3SCF_3$ (9). A mixture of the bis(*t*-butyl isocyanide) complex **6** (100 mg, 0.07 mmol) and TlO_3SCF_3 (24 mg, 0.07 mmol) in 30 mL of dichloromethane was stirred at room temperature for 48 h. The resulting pale-green solution was filtered to remove insoluble impurities, the volume of the filtrate was reduced to about 3 mL, and diethyl ether (15 mL) was added to afford a pale-yellow-green precipitate of **9**, which was filtered off, washed with 20 mL of diethyl ether, and dried under reduced pressure; yield, 72 mg (65%). Anal. Calcd for: $C_{63}H_{62}Cl_3F_3N_2O_3P_4Re_2S$: C, 47.68; H, 3.94. Found: C, 47.45; H, 3.57.

The analogous green hexafluorophosphate salt $[Re_2Cl_3(\mu\text{-dppE})_2(CN\text{-}t\text{-}Bu)_2]PF_6$ was produced when $TlPF_6$ was used in place of TlO_3SCF_3. Its spectroscopic and electrochemical properties are essentially identical to those of **6** with the exception of the presence of a band at 841(vs) cm^{-1} in its IR spectrum, due to the $[PF_6]^-$ anion, in place of a triflate band at 1267(vs) cm^{-1}.

C. Reactions of $Re_2Cl_4(\mu\text{-dcpm})_2$ (10) with Isocyanides. 1. Synthesis of $Re_2Cl_4(\mu\text{-dcpm})_2(CNXyl)$ (11). A mixture of **10** (100 mg, 0.075 mmol) and XylNC (10 mg, 0.075 mmol) was stirred in acetone (10 mL) for 1 day. The orange microcrystalline sample of **11** was collected by vacuum filtration, washed with acetone, and dried under reduced pressure; yield, 0.076 g (69%). Anal. Calcd for $C_{59}H_{101}Cl_4NP_4Re_2$: C, 48.45; H, 6.96; Cl, 9.70. Found: C, 48.07; H, 7.28; Cl, 9.81.

The reaction of **11** with a further quantity of XylNC (1.5 equiv) in acetone at room temperature for 5 days led to the formation of a purple powder, which cyclic voltammetric measurements showed was a mixture of products. We were unable to obtain the bis(xylyl isocyanide) complex $Re_2Cl_4(\mu\text{-dcpm})_2(CNXyl)_2$.

2. Synthesis of $Re_2Cl_4(\mu\text{-dcpm})_2(CN\text{-}t\text{-}Bu)_2$ (12). A mixture of **10** (100 mg, 0.075 mmol) and *t*-BuNC (17 μL, 0.165 mmol) was stirred in acetone (10 mL) for 1 day, and the green insoluble product, **12**, was collected by vacuum filtration, washed with acetone, and dried under reduced pressure; yield, 0.089 g (79%). Anal. Calcd for $C_{60}H_{110}Cl_4N_2P_4Re_2$: C, 48.12; H, 7.40; Cl, 9.47. Found: C, 48.81; H, 7.71; Cl, 9.68.

D. Reactions of $Re_2Cl_4(\mu\text{-dppm})_2$ (1) with *t*-BuNC. 1. Excess *t*-BuNC. A mixture of **1** (128 mg, 0.10 mmol) and 4 equiv of *t*-BuNC (45 μL, 0.40 mmol) in 30 mL of dichloromethane was stirred for 48 h at room temperature. The reaction mixture was filtered, the volume of the green filtrate was reduced to ca. 5 mL, and diethyl ether (40 mL) was added to precipitate a green solid which was filtered off, washed with 20 mL of diethyl ether, and dried under reduced pressure; yield, 98 mg (64%). The spectroscopic and electrochemical properties of this product showed that it was the chloride salt $[Re_2Cl_3(\mu\text{-dppm})_2(CN\text{-}t\text{-}Bu)_3]Cl$ (**13**), by comparison with the properties of the previously characterized $[PF_6]^-$ salt.[20] This compound resembled closely the analogous dppE complex **7** (see section B.3).

2. Two Equivalents of *t*-BuNC. A stoichiometric quantity of *t*-BuNC (22.5 μL, 0.20 mmol) was added to a solution of **1** (128 mg, 0.10 mmol) in 30 mL of dichloromethane. The mixture was stirred at room temperature and worked up after set periods of time (5 min, 30 min, or 2 days) by evaporating the reaction mixture to dryness under reduced pressure. In addition, the reaction was performed for 1 min, and the product was precipitated by the addition of a large excess of diethyl ether. The products from these four reactions were characterized by

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Table 1. Crystallographic Data for the Dirhenium Isocyanide Complexes $Re_2Cl_4(\mu\text{-dppm})_2(CNXyl)$(**2**), $Re_2Cl_4(\mu\text{-dppE})_2(CN\text{-}t\text{-}Bu)_2\cdot 3C_2H_4Cl_2$ (**6**), $[Re_2Cl_3(\mu\text{-dppE})_2(CN\text{-}t\text{-}Bu)_3]Cl$ (**7**), $Re_2Cl_4(\mu\text{-dcpm})_2(CNXyl)\cdot(CH_3)_2CO$ (**11**), and $Re_2Cl_4(\mu\text{-dcpm})_2(CN\text{-}t\text{-}Bu)_2\cdot CH_2Cl_2$ (**12**)

	2	**6**	**7**	**11**	**12**
empirical formula	$C_{59}H_{53}Cl_4NP_4Re_2$	$C_{68}H_{76}Cl_{10}N_2P_4Re_2$	$C_{67}H_{71}Cl_4N_3P_4Re_2$	$C_{62}H_{107}Cl_4NOP_4Re_2$	$C_{61}H_{112}Cl_6N_2P_4Re_2$
fw	1414.10	1772.20	1556.44	1520.66	1582.60
space group	$P4_32_12$ (No. 96)	$P2_1/n$ (No. 14)	$P\bar{1}$ (No. 2)	$P\bar{2}_1/c$ (No. 14)	$P\bar{1}$ (No. 2)
a, Å	15.0903(4)	14.4494(2)	12.679(4)	23.2164(5)	13.9247(2)
b, Å	15.0903(4)	34.0915(5)	14.422(3)	12.4916(3)	15.0320(3)
c, Å	26.1521(7)	15.5458(2)	19.997(4)	25.3930(5)	16.9804(3)
α, deg	90	90	97.13	90	87.0330(12)
β, deg	90	92.3135(7)	108.39(3)	106.0421(11)	77.0095(10)
γ, deg	90	90	90.07(3)	90	79.2906(10)
V, Å^3	5955.3(5)	7651.6(3)	3439.8(13)	7077.5(5)	3402.80(15)
Z	4	4	2	4	2
ρ_{calcd}, g/cm^3	1.577	1.538	1.608	1.422	1.544
μ, mm^{-1}	4.385	3.677	3.806	3.741	3.970
radiation (λ,Å)	Mo Kα (0.71073)	Mo Kα (0.71073)	Mo Kα (0.71073)	Mo Kα (0.71073)	Mo Kα (0.71073)
temp, K	203	193	293	293	295
$R(F_o)^a$	0.071	0.049	0.036	0.052	0.026
$R_w(F_o^2)^b$	0.178	0.145	0.090	0.117	0.060
GOF	1.161	1.050	1.026	1.007	1.044

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

$^{31}P\{^1H\}$ NMR spectroscopy on CD_2Cl_2 solutions. Further details are presented under Results and Discussion.

E. X-ray Crystallography. Single crystals of $Re_2Cl_4(\mu\text{-dppm})_2(CNXyl)$ (**2**) were grown by the slow diffusion of diethyl ether into a dichloromethane solution of the complex whereas single crystals of $Re_2Cl_4(\mu\text{-dppE})_2(CN\text{-}t\text{-}Bu)_2$ (**6**) and $[Re_2Cl_3(\mu\text{-dppE})_2(CN\text{-}t\text{-}Bu)_3]Cl$ (**7**) were obtained by the slow diffusion of di-isopropyl ether vapor into 1,2-dichloroethane solutions of the complexes. With $Re_2Cl_4(\mu\text{-dcpm})_2(CNXyl)$ (**11**) and $Re_2Cl_4(\mu\text{-dcpm})_2(CN\text{-}t\text{-}Bu)_2$ (**12**), crystals were grown by layering acetone on top of dichloromethane solutions of the complexes at room temperature. The crystals were mounted on glass fibers in random orientations. The data collections for **2**, **6**, **11**, and **12** were performed on a Nonius KappaCCD diffractometer. For **7**, intensity data were collected on a four-circle Rigaku AFC7R diffractometer in the variable ω-scan mode at the Department of Chemistry of the Chinese University of Hong Kong. In all instances, Mo Kα radiation (λ = 0.71073 Å) was used. The crystallographic data for all five compounds are given in Table 1.

The structures of **6**, **11**, and **12** were solved by the use of the Patterson heavy-atom method, whereas direct methods were used for **2** and **7** to reveal the positions of the Re atoms. The remaining nonhydrogen 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) = 1.3 U_{eq}(C) for **6**, **11**, and **12** and U(H) = 1.2 U_{eq}(C) for **2** and **7**. They were included in the refinement but constrained to ride on the atom to which they were bonded. Empirical absorption corrections were applied; SCALEPACK[27] was used in **2**, **6**, **11**, and **12**, whereas the method of Kopfmann and Huber[28] was used for **7**. All 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 has the form $w = 1/[\sigma^2(F_o^2) + (AP)^2 + BP]$, where $P = (F_o^2 + 2F_c^2)/3$. The calculations were performed on an AlphaServer 2000 for **6**, **11**, and **12** and a PC[29] for **2** and **7**. The final refinements were performed by the use of the program SHELXL-97.[30]

A disorder problem was encountered during the refinement of the structure of $Re_2Cl_4(dppm)_2(CNXyl)$ (**2**). There was only half an independent molecule in the asymmetric unit. The XylNC ligand was disordered with the terminal chlorine atom Cl(2). This disorder is generated by a 2-fold axis through the bridging chlorine atom Cl(12) and the midpoint of the Re−Re bond. Both Cl(2) and the XylNC ligand were set at 50% occupancy. The xylyl group was refined with isotropic thermal parameters. All the other nonhydrogen atoms were refined anisotropically. The absolute structure was determined by refinement. The enantiomer chosen has the absolute structure parameter of 0.020-(15).

For the complex $Re_2Cl_4(\mu\text{-dppE})_2(CN\text{-}t\text{-}Bu)_2$ (**6**), three 1,2-dichloroethane molecules from the crystallization solvents were found cocrystallized with **6** in the asymmetric unit. They were included in the analysis and refined satisfactorily. All non-hydrogen atoms were refined anisotropically.

No solvent of crystallization or disorder problems were encountered in the structure solution of $[Re_2Cl_3(\mu\text{-dppE})_3(CN\text{-}t\text{-}Bu)_3]Cl$ (**7**), and all non-hydrogen atoms were refined anisotropically.

During the structure analysis of $Re_2Cl_4(dcpm)_2(CNXyl)$ (**11**), a solvent molecule, acetone, was found to be cocrystallized with the complex in the asymmetric unit. It was included in the analysis and was refined satisfactorily. Another solvent molecule, which was badly disordered, was removed by the use of the squeeze option in PLATON.[31] All nonhydrogen atoms were refined with anisotropic thermal parameters.

There are two-half independent molecules of $Re_2Cl_4(\mu\text{-dcpm})_2(CN\text{-}t\text{-}Bu)_2$ (**12**) in the asymmetric unit as well as a molecule of dichloromethane, one of the solvents used in recrystallization. All nonhydrogen atoms were refined anisotropically.

The largest remaining peak in the final difference maps of **2**, **6**, **7**, **11**, and **12** were 1.51, 1.52, 0.49, 1.14, and 1.10 e/Å^3, respectively.

Results and Discussion

The clarification of the nature of the products that are formed upon the reactions of $Re_2Cl_4(\mu\text{-dppm})_2$, $Re_2Cl_4(\mu\text{-dppE})_2$, and $Re_2Cl_4(\mu\text{-dcpm})_2$ with t-BuNC and XylNC focuses first on establishing unambiguously the structure of the previously isolated 1:1 complex $Re_2Cl_4(\mu\text{-dppm})_2(CNXyl)$ and, by implication, that of its t-BuNC analogue.[18] The second part of this presentation deals with the nature of 1:1, 1:2, and 1:3 isocyanide complexes that are formed on reacting $Re_2Cl_4(\mu\text{-dppE})_2$ and $Re_2Cl_4(\mu\text{-dcpm})_2$ with t-BuNC and XylNC, and their comparison with the related complexes of $Re_2Cl_4(\mu\text{-dppm})_2$. The key aspects of the reactions leading to the 1:2 and 1:3 complexes are shown in Scheme 1.

A. The Structural Identity of $Re_2Cl_4(\mu\text{-dppm})_2(CNXyl)$ (2). The spectroscopic and electrochemical properties of complexes of the type $Re_2Cl_4(\mu\text{-dppm})_2(CNR)$ (R = Me, t-Bu, or Xyl) are very similar to one another and signal a close structural relationship between all three complexes.[18] IR spectroscopy indicated the presence of isomers in the solid state *and* in

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(28) Kopfmann, G.; Huber, R. *Acta Crystallogr.* **1968**, *A24*, 348.
(29) Farrugia, L. J. *WinGX-A Windows Program for Crystal Structure Analysis*; University of Glasgow: Glasgow, U.K., 1998.
(30) Sheldrick, G. M. *SHELXL97. A Program for Crystal Structure Refinement*; University of Gottingen: Gottingen, Germany, 1997.
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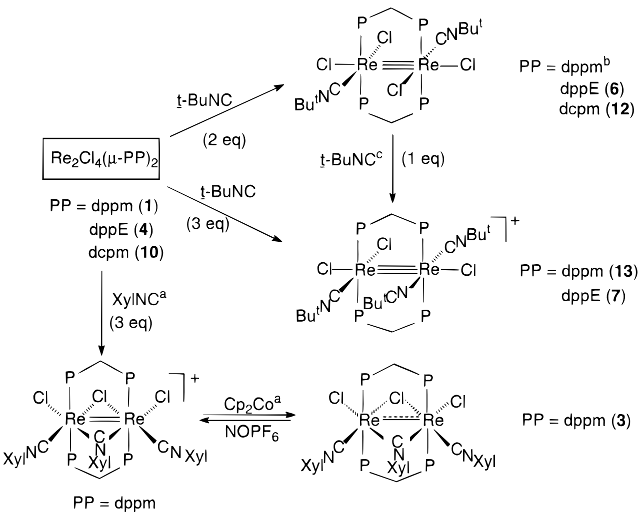
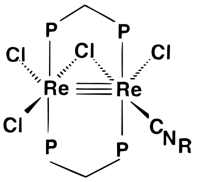
Scheme 1. 1:2 and 1:3 Isocyanide Complexes Derived from Re$_2$Cl$_4$(μ-LL)$_2$ (LL = dppm, dppE, or dcpm)[a]

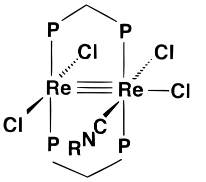


[a] (a) See also data reported in ref 20. (b) This compound was identified in solution only. (c) Reaction performed for PP = dppm or dppE only.

solutions of these complexes in organic solvents; these isomers contain terminally bound RNC ligands. A partial crystal structure determination on Re$_2$Cl$_4$(μ-dppm)$_2$(CN-*t*-Bu) showed it to have the A-frame-like structure Cl$_2$Re(μ-Cl)(μ-dppm)$_2$ReCl(CN-*t*-Bu) with a Re−Re distance of ca. 2.30 Å.[18] This structure is represented in **I**. A disorder involving the terminal *t*-BuNC and Cl ligands *trans* to the Cl-bridge frustrated our attempts to adequately solve the structure.[18] This same type of disorder has been found in the fully refined structures of the analogous carbonyl complexes Re$_2$X$_4$(μ-dppm)$_2$(CO) (X = Cl[3] or Br[14]), and in the structure determination of Re$_2$Cl$_4$(μ-dppm)$_2$(CNXyl) (**2**) as described herein. An ORTEP[32] representation of the structure of **2** is shown in Figure 1. Important structural parameters are given in Table 2. The disorder is generated by a 2-fold axis that passes through the bridging Cl atom Cl(12) and bisects the Re−Re bond. The Re−Re distance for **2** of 2.3195(9) Å is similar to the analogous triply bonded Re−Re distances for Re$_2$Cl$_4$(μ-dppm)$_2$(CO)[3] and Re$_2$Br$_4$(μ-dppm)$_2$(CO),[14] which are 2.338(1) Å and 2.336(1) Å, respectively. The slightly shorter bond for **2** accords with the weaker π-accepting ability of XylNC compared with CO and, therefore, a diminished weakening of the Re−Re π and/or δ bonding components through Re→RNC (π^*) back-bonding (relative to Re→CO(π^*)).



I



II

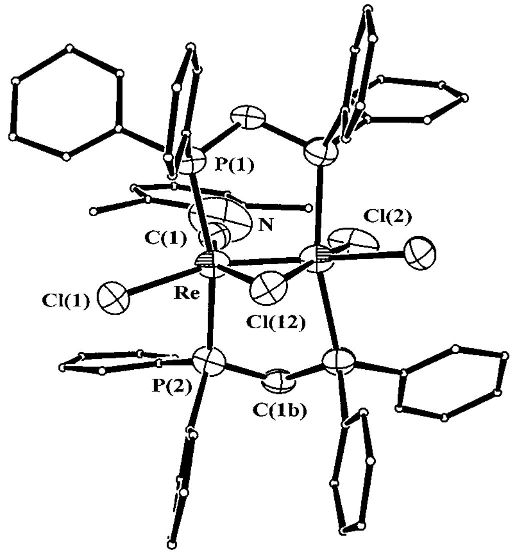


Figure 1. ORTEP[32] representation of the structure of the dirhenium complex Re$_2$Cl$_4$(μ-dppm)$_2$(CNXyl) (**2**). This representation shows one-half of the disorder involving the terminal XylNC and Cl ligands which are *trans* to the bridging Cl ligand. The thermal ellipsoids are drawn at the 50% 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$_2$Cl$_4$(μ-dppm)$_2$(CNXyl) (**2**)[a]

Distances			
Re−Re′	2.3195(9)	Re′−Cl(2)	2.342(7)
Re−C(1)	1.90(3)	Re−P(1)	2.461(3)
Re−Cl(1)	2.533(3)	Re−P(2)	2.431(3)
Re−Cl(12)	2.539(3)		
Angles			
Re′−Re−C(1)	87.9(8)	Re′−Re−Cl(12)	62.82(4)
Re−Re′−Cl(2)	114.2(3)	Cl(2)−Re′−Cl(12)	173.65(19)
P(1)−Re−P(2)	163.78(10)	Cl(1)−Re−Cl(12)	88.11(8)
C(1)−Re−Cl(1)	121.5(8)	Re−Cl(12)−Re′	54.36(8)
Re′−Re−Cl(1)	150.00(7)	N−C(1)−Re	175(3)
C(1)−Re−Cl(12)	150.3(8)		

[a] Numbers in parentheses are estimated standard deviations in the least significant digits. The unlabeled Re atom in Figure 1 is denoted Re′ in this table.

B. The Reactions of Re$_2$Cl$_4$(μ-dppE)$_2$ (4) and Re$_2$Cl$_4$(μ-dcpm)$_2$ (10) with Isocyanides. This study was prompted by our interest in comparing the reactivity and redox properties of the previously described complex Re$_2$Cl$_4$(μ-dppm)$_2$ (**1**)[25,33] with those of the more recently synthesized complex Re$_2$Cl$_4$(μ-dcpm)$_2$ (**10**).[24] We had anticipated some differences in reactivity because of the greater basicity of the dcpm ligand compared with dppm. In contrast, a close similarity between the reactivity of **1** and its dppE analogue Re$_2$Cl$_4$(μ-dppE)$_2$ (**4**) was to be expected.[23]

Preliminary experiments demonstrated that the spectroscopic and electrochemical properties of 1:1 complex Re$_2$Cl$_4$(μ-dppE)$_2$(CNXyl) (**5**) resembled those of Re$_2$Cl$_4$(μ-dppm)$_2$(CNXyl) (**2**). The important spectroscopic data for **5** are presented in Table 3. A cyclic voltammogram (CV), recorded on a solution of **5** in 0.1 M *n*-Bu$_4$NPF$_6$−CH$_2$Cl$_2$, shows a reversible oxidation at $E_{1/2}$ = +0.33 V and an irreversible oxidation at $E_{p,a}$ = +1.40 V vs Ag/AgCl. The corresponding CV of **2** shows processes at +0.31 V and +1.27 V vs Ag/AgCl.[18] This similarity implies that these complexes possess, not unexpectedly, a close structural relationship. Both display AA′BB′ patterns in their ^{31}P{^{1}H} NMR spectra. Note that the presence of two terminal ν(CN) modes in the IR spectrum of **5** (Table 3), just as observed previously for **2**,[18] signifies the presence of two isomers in the solid state, one of which possesses structure **I**.

Although the μ-dcpm complex **10** reacts with 1 equiv of XylNC in acetone to afford the 1:1 complex Re$_2$Cl$_4$(μ-dcpm)$_2$-

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(32) (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.

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Table 3. Selected Spectroscopic Data for Isocyanide Complexes of Dirhenium(II)

complex	no.	IR, cm^{-1} [a] ν(CN) and ν(CO)	chem shift, δ[b] ^{31}P{^{1}H} NMR
Re$_2$Cl$_4$(μ-dppE)$_2$(CNXyl)	**5**	2070(s), ~2000(sh)	+16.8(m), +9.8(m)[c]
Re$_2$Cl$_4$(μ-dppE)$_2$(CN-*t*-Bu)$_2$	**6**	2103(vs)	+10.8(s)
[Re$_2$Cl$_3$(μ-dppE)$_2$(CN-*t*-Bu)$_3$]Cl	**7**	2170(m-w), 2141(vs), 2106(s)	+10.2(m), +4.3(m)
[Re$_2$Cl$_3$(μ-dppE)$_2$(CN-*t*-Bu)$_3$]PF$_6$	**8**	2176(m−w), 2142(vs), 2110(s)	+10.2(m), +4.3(m)
[Re$_2$Cl$_3$(μ-dppE)$_2$(CN-*t*-Bu)$_2$]O$_3$SCF$_3$	**9**	2163(s), 2105(sh)	+7.3(m), +1.5(m)
Re$_2$Cl$_4$(μ-dcpm)$_2$(CNXyl)	**11**	2036(s), 2004(m)	−15.0(m)
Re$_2$Cl$_4$(μ-dcpm)$_2$(CN-*t*-Bu)$_2$	**12**	2096(s), 2065(vs)	−10.0(s,br)
[Re$_2$Cl$_3$(μ-dppm)$_2$(CN-*t*-Bu)$_3$]Cl	**13**	2142(vs), 2111(s)	−5.6(m), −12.3(m)

[a] IR spectra recorded as Nujol mulls or KBr pellets. All compounds that contain the triflate anion have a strong band at ~1270 cm^{-1}. Abbreviations: s = strong, m = medium, w = weak, br = broad, sh = shoulder. [b] NMR spectra recorded on CD$_2$Cl$_2$ solutions unless otherwise indicated. Abbreviations: s = singlet, m = multiplet. For AA′BB′ patterns, the centers of the two multiplets are given. [c] Spectrum recorded in CDCl$_3$.

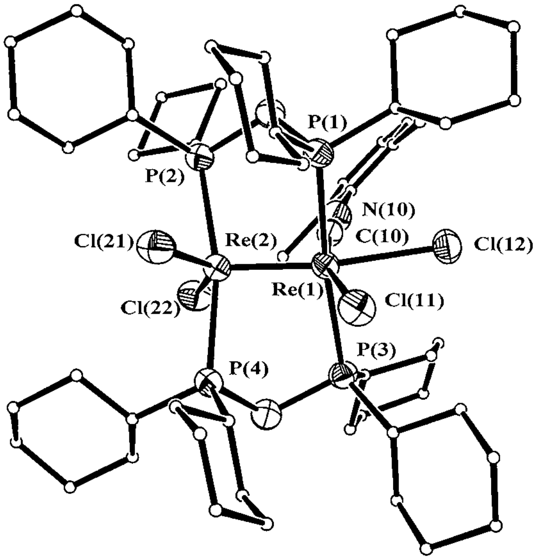

Figure 2. ORTEP[32] representation of the structure of the dirhenium complex Re$_2$Cl$_4$(μ-dcpm)$_2$(CNXyl) (**11**). The thermal ellipsoids are drawn at the 50% probability level except for the cyclohexyl group atoms of the dcpm ligands and the xylyl group atoms of the XylNC ligands which are circles of arbitrary radius.

Table 4. Important Bond Distances (Å) and Bond Angles (deg) for the Complex Re$_2$Cl$_4$(μ-dcpm)$_2$(CNXyl)·(CH$_3$)$_2$CO (**11**)[a]

Distances			
Re(1)−Re(2)	2.2887(3)	Re(2)−Cl(21)	2.3652(15)
Re(1)−C(10)	1.952(6)	Re(2)−Cl(22)	2.3750(14)
Re(1)−Cl(11)	2.4331(14)	Re(2)−P(4)	2.4414(14)
Re(1)−P(1)	2.4923(14)	Re(2)−P(2)	2.4704(14)
Re(1)−P(3)	2.5142(14)	N(10)−C(10)	1.190(7)
Re(1)−Cl(12)	2.6165(15)	N(10)−C(11)	1.416(7)

Angles			
C(10)−Re(1)−Re(2)	89.14(15)	P(3)−Re(1)−Cl(12)	87.20(5)
C(10)−Re(1)−Cl(11)	162.00(16)	Re(1)−Re(2)−Cl(21)	113.81(4)
Re(2)−Re(1)−Cl(11)	108.82(4)	Re(1)−Re(2)−Cl(22)	109.33(4)
C(10)−Re(1)−P(1)	91.05(16)	Cl(21)−Re(2)−Cl(22)	136.71(6)
Re(2)−Re(1)−P(1)	89.72(4)	Re(1)−Re(2)−P(4)	93.90(4)
Cl(11)−Re(1)−P(1)	90.21(5)	Cl(21)−Re(2)−P(4)	88.64(5)
C(10)−Re(1)−P(3)	90.44(16)	Cl(22)−Re(2)−P(4)	84.96(5)
Re(2)−Re(1)−P(3)	95.79(4)	Re(1)−Re(2)−P(2)	99.10(4)
Cl(11)−Re(1)−P(3)	86.69(5)	Cl(21)−Re(2)−P(2)	88.12(5)
P(1)−Re(1)−P(3)	174.31(5)	Cl(22)−Re(2)−P(2)	88.64(5)
C(10)−Re(1)−Cl(12)	77.62(16)	P(4)−Re(2)−P(2)	166.81(5)
Re(2)−Re(1)−Cl(12)	166.47(4)	N(10)−C(10)−Re(1)	175.5(5)
Cl(11)−Re(1)−Cl(12)	84.49(5)	C(10)−N(10)−C(11)	169.2(6)
P(1)−Re(1)−Cl(12)	87.76(5)		

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

(CNXyl) (**11**), the solid-state structure of this compound is different from that of **2** and, by implication, from its aforementioned dppE analogue **5**. The ORTEP[32] representation of the structure of **11** is shown in Figure 2, and important bond distances and angles are given in Table 4. This structure is related to that of **2** (see Figure 1 and structure **I**) by the breaking of the μ-Cl bridge of **2** and the simple rotation of the [ReCl$_2$(CNR)] unit so that it assumes the relationship to the adjacent [ReCl$_2$] unit that is shown in structure **II**. This is presumably a relatively low-energy process and could account for the presence of two isomers. It is tempting to propose that the same pair of isomers are present in samples of **2**, **5**, and **11** (i.e., structures **I** and **II**), but that the structure of isomer **I** has been determined in **2**, whereas isomer **II** is the one characterized from the crystals of **11**. Supporting this possibility is our earlier discovery that the monocarbonyl complexes Re$_2$X$_4$(μ-dppm)$_2$(CO) (X = Cl, Br)[3,14] have two structural isomers, one of which has the same structure as that of **I**, whereas the other has an open structure like that of **II**, with terminal halide and CO ligands; because of a disorder problem the exact location of the CO ligand could not be determined.[14]

The Re−Re distance of 2.2887(3) Å for the unbridged isomeric form **11** is similar to that of **2**, supporting the presence of a Re−Re multiple bond in both instances. The Re−Cl distances at the higher coordination number Re center Re(1) are, as expected, longer than the distances Re(2)−Cl(21) and Re(2)−Cl(22). The distance of 2.4331(14) Å for Re(1)−Cl(11) is ca. 0.05 Å longer than both of the Re(2)−Cl distances, partly because of the *trans* effect of the XylNC ligand. The distance Re(1)−Cl(12) of 2.6161(15) Å is the longest for all the Re−Cl bonds, and is typical of axial Re−Cl coordination in dirhenium(II) complexes.[5,14,34] This relatively weak bond is characterized by a significant deviation from linearity with the Re≡Re bond; the angle Re(2)−Re(1)−Cl(12) is 166.47(4)°. This compound possesses a partially staggered structure in the solid state as reflected by the torsional angles P(1)−Re(1)−Re(2)−P(2), P(3)−Re(1)−Re(2)−P(4), C(11)−Re(1)−Re(2)−Cl(21), and C(10)−Re(1)−Re(2)−Cl(22) which are 35.9°, 32.3°, 34.1°, and 36.6°, respectively.

Like the other 1:1 complexes with XylNC, complex **11** shows two terminal ν(CN) modes in its IR spectrum and an AA′BB′ pattern in its ^{31}P{^{1}H} NMR spectrum, although a clear resolution into two multiplets does not occur, and a single broad multiplet is observed instead (see Table 3). The CV of **11** (recorded in 0.1 M *n*-Bu$_4$NPF$_6$−CH$_2$Cl$_2$) resembles those for **2**[18] and **5** (Table 3) in showing two one-electron oxidations, with $E_{1/2}$ values of +1.29 V and +0.11 V vs Ag/AgCl; the ΔE_p ($=E_{p,a} - E_{p,c}$) values are 75 and 70 mV, respectively.

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(34) Wu, W.; Subramony, J. A.; Fanwick, P. E.; Walton, R. A. *Inorg. Chem.* **1996**, *35*, 6784.

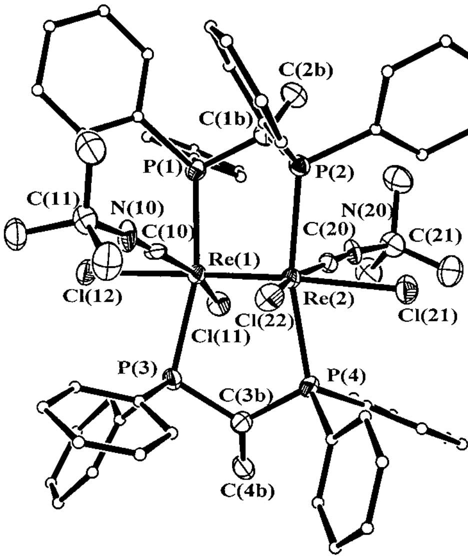

Figure 3. ORTEP[32] representation of the structure of the dirhenium complex $Re_2Cl_4(\mu\text{-dppE})_2(CN\text{-}t\text{-}Bu)_2$ (**6**). The thermal ellipsoids are drawn at the 50% probability level except for the phenyl group atoms of the dppE ligands which are circles of arbitrary radius.

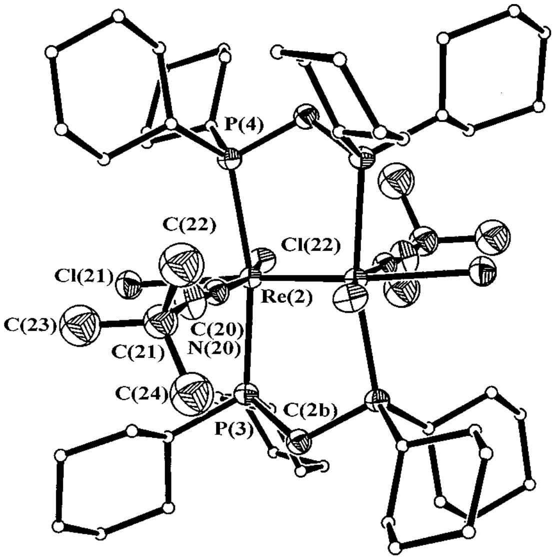

Figure 4. ORTEP[32] representation of the structure of one of the independent molecules of the dirhenium complex $Re_2Cl_4(\mu\text{-dcpm})_2(CN\text{-}t\text{-}Bu)_2$ (**12**). The unlabeled Re atom is Re(2)′. The thermal ellipsoids are drawn at the 50% probability level except for the cyclohexyl group atoms of the dcpm ligands which are circles of arbitrary radius.

Several attempts to isolate a pure sample of the 1:2 complex $Re_2Cl_4(\mu\text{-dcpm})_2(CNXyl)_2$ were unsuccessful.[35] Similarly, we had not obtained the analogous 1:2 complexes $Re_2Cl_4(\mu\text{-dppm})_2(CNR)_2$ (R = Xyl or *t*-Bu) in an earlier study,[20] although the 1:3 species $[Re_2Cl_3(\mu\text{-dppm})_2(CNR)_3]^+$ were isolated; the latter will be discussed in more detail later in this section. However, with the use of *t*-butyl isocyanide we were able to obtain the bis-isocyanide complexes $Re_2Cl_4(\mu\text{-dppE})_2(CN\text{-}t\text{-}Bu)_2$ (**6**) and $Re_2Cl_4(\mu\text{-dcpm})_2(CN\text{-}t\text{-}Bu)_2$ (**12**) in ca. 75% yield. The spectroscopic properties of **6** and **12** established the presence of terminal *t*-BuNC ligands and a symmetric structure as demonstrated by a singlet in the $^{31}P\{^1H\}$ NMR spectra (Table 3). These conclusions were confirmed by single-crystal X-ray structure demonstrations of both complexes. The ORTEP[32] representations of the structures are shown in Figures 3 and 4, and important bond distances and angles are given in Tables 5 and 6. Both complexes possess the same open bioctahedral structure with axial Re−Cl bonds and an anti-arrangement of *t*-BuNC ligands. These two structures resemble those of the triply bonded dirhenium(II) bioctahedral complexes of the type $Re_2X_4(\mu\text{-dppm})_2(CO)(CN\text{-}t\text{-}Bu)$ (X = Cl, Br)[3,14] which have this same type of bioctahedral structure.

Table 5. Important Bond Distances (Å) and Bond Angles (deg) for the Complex $Re_2Cl_4(\mu\text{-dppE})_2(CN\text{-}t\text{-}Bu)_2{\cdot}3C_2H_4Cl_2$ (**6**)[a]

Distances

Re(1)−Re(2)	2.3497(4)	Re(2)−Cl(22)	2.4330(17)
Re(1)−C(10)	2.016(8)	Re(2)−P(4)	2.4696(19)
Re(1)−Cl(11)	2.4512(17)	Re(2)−P(2)	2.4797(19)
Re(1)−P(1)	2.4520(19)	Re(2)−Cl(21)	2.5793(19)
Re(1)−P(3)	2.4605(19)	C(10)−N(10)	1.154(9)
Re(1)−Cl(12)	2.5779(18)	C(20)−N(20)	1.154(9)
Re(2)−C(20)	2.016(7)		

Angles

C(10)−Re(1)−Re(2)	88.3(2)	Re(1)−Re(2)−Cl(22)	106.20(5)
C(10)−Re(1)−Cl(11)	166.4(2)	C(20)−Re(2)−P(4)	90.1(2)
Re(2)−Re(1)−Cl(11)	104.84(5)	Re(1)−Re(2)−P(4)	97.51(5)
C(10)−Re(1)−P(1)	89.55(19)	Cl(22)−Re(2)−P(4)	88.54(6)
Re(2)−Re(1)−P(1)	99.90(5)	C(20)−Re(2)−P(2)	85.0(2)
Cl(11)−Re(1)−P(1)	91.69(6)	Re(1)−Re(2)−P(2)	94.91(5)
C(10)−Re(1)−P(3)	90.1(2)	Cl(22)−Re(2)−P(2)	93.11(6)
Re(2)−Re(1)−P(3)	94.61(5)	P(4)−Re(2)−P(2)	166.48(6)
Cl(11)−Re(1)−P(3)	85.32(6)	C(20)−Re(2)−Cl(21)	78.2(2)
P(1)−Re(1)−P(3)	165.47(7)	Re(1)−Re(2)−Cl(21)	165.06(5)
C(10)−Re(1)−Cl(12)	80.0(2)	Cl(22)−Re(2)−Cl(21)	87.59(6)
Re(2)−Re(1)−Cl(12)	167.57(5)	P(4)−Re(2)−Cl(21)	76.73(6)
Cl(11)−Re(1)−Cl(12)	86.64(6)	P(2)−Re(2)−Cl(21)	89.93(6)
P(1)−Re(1)−Cl(12)	84.24(6)	N(10)−C(10)−Re(1)	175.0(7)
P(3)−Re(1)−Cl(12)	81.39(6)	N(20)−C(20)−Re(2)	173.2(6)
C(20)−Re(2)−Re(1)	88.1(2)	C(10)−N(10)−C(11)	174.7(8)
C(20)−Re(2)−Cl(22)	165.7(2)	C(20)−N(20)−C(21)	167.4(7)

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

Table 6. Important Bond Distances (Å) and Bond Angles (deg) for the Complex $Re_2Cl_4(\mu\text{-dcpm})_2(CN\text{-}t\text{-}Bu)_2{\cdot}CH_2Cl_2$ (**12**)[a]

Distances

Re(1)−Re(1)′	2.3797(3)	Re(2)−Re(2)′	2.3804(3)
Re(1)−C(10)	1.989(4)	Re(2)−C(20)	1.979(4)
Re(1)−Cl(12)	2.4451(10)	Re(2)−Cl(22)	2.4555(9)
Re(1)−P(2)	2.4912(10)	Re(2)−P(3)	2.4988(10)
Re(1)−P(1)	2.5096(10)	Re(2)−P(4)	2.5076(9)
Re(1)−Cl(11)	2.6113(10)	Re(2)−Cl(21)	2.5945(11)
C(10)−N(10)	1.156(5)	C(20)−N(20)	1.160(5)

Angles

C(10)−Re(1)−Re(1)′	86.57(11)	C(20)−Re(2)−Re(2)′	84.38(11)
C(10)−Re(1)−Cl(12)	164.53(11)	C(20)−Re(2)−Cl(22)	164.50(12)
Re(1)′−Re(1)−Cl(12)	108.60(3)	Re(2)′−Re(2)−Cl(22)	111.12(3)
C(10)−Re(1)−P(2)	93.12(11)	C(20)−Re(2)−P(3)	92.51(11)
Re(1)′−Re(1)−P(2)	95.65(2)	Re(2)′−Re(2)−P(3)	97.00(2)
Cl(12)−Re(1)−P(2)	88.49(3)	Cl(22)−Re(2)−P(3)	86.12(3)
C(10)−Re(1)−P(1)	90.28(11)	C(20)−Re(2)−P(4)	92.70(11)
Re(1)′−Re(1)−P(1)	101.02(2)	Re(2)′−Re(2)−P(4)	98.58(2)
Cl(12)−Re(1)−P(1)	83.97(3)	Cl(22)−Re(2)−P(4)	84.82(3)
P(2)−Re(1)−P(1)	163.15(3)	P(3)−Re(2)−P(4)	163.98(3)
C(10)−Re(1)−Cl(11)	80.70(11)	C(20)−Re(2)−Cl(21)	80.34(12)
Re(1)′−Re(1)−Cl(11)	166.36(3)	Re(2)′−Re(2)−Cl(21)	164.60(3)
Cl(12)−Re(1)−Cl(11)	84.41(4)	Cl(22)−Re(2)−Cl(21)	84.19(4)
P(2)−Re(1)−Cl(11)	80.26(3)	P(3)−Re(2)−Cl(21)	81.89(3)
P(1)−Re(1)−Cl(11)	84.02(3)	P(4)−Re(2)−Cl(21)	84.08(3)
N(10)−C(10)−Re(1)	174.1(4)	N(20)−C(20)−Re(2)	176.0(4)
C(10)−N(10)−C(11)	169.8(4)	C(20)−N(20)−C(21)	172.2(4)

[a] Data for the two independent molecules in the unit cell are compared. Numbers in parentheses are estimated standard deviations in the least significant digits.

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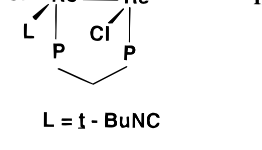
(35) Siwajek, M. J., Ph.D. Thesis, Purdue University, 1999.

The Re−Re distances for **6** and **12** are 2.3497(4) Å and 2.3797(3) Å, respectively, and closely resemble the distance of 2.3805(14) Å found in the structure of $Re_2Br_4(\mu\text{-dppm})_2(CO)(CN\text{-}t\text{-Bu})$.[14] As expected, the axial Re−X bonds (those collinear with Re≡Re) are longer than the corresponding equatorial Re−X bonds by 0.13−0.17 Å. The Re−Re−Cl_{ax} bond angles, which are in the range 164.6−167.6° (Tables 5 and 6) for these two complexes, are similar to the angle of 166.5° found in the structure of compound **11** (Table 4). Because the two crystallographically independent dirhenium molecules in the crystal of **12** are located about inversion centers, they are each required to possess rigorously eclipsed rotational geometries. No such requirement exists in the crystal of **6**, and the molecule in the asymmetric unit has a partially staggered rotational geometry with values for the 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(20), and Cl(10)−Re(1)−Re(2)−Cl(22) of 18.2°, 24.3°, 27.8°, and 23.6°, respectively.

Despite the close structural relationship established between **6** and **12**, these complexes display some differences in their CV properties (recorded on solutions in 0.1 M $n\text{-}Bu_4NPF_6$−CH_2Cl_2). The single scan CV of **6** showed broad waves at $E_{p,a} = +0.72$ V and $E_{p,c} = -1.24$ V vs Ag/AgCl, whereas the CV of **12** showed major processes at $E_{1/2}(ox) = +1.30$ V ($\Delta E_p = 60$ mV) and $E_{p,c} = -1.19$ V vs Ag/AgCl, along with coupled processes at $E_{p,a} = +0.96$ V and $E_{p,c} = +0.41$ V vs Ag/AgCl.

As mentioned previously, we had not isolated the analogous bis-isocyanide complex $Re_2Cl_4(\mu\text{-dppm})_2(CN\text{-}t\text{-Bu})_2$ in our earlier study of the reactions between this dirhenium(II) complex and *t*-BuNC,[20] because of the reaction conditions we used, in which KPF_6 or $TlPF_6$ were added to the reaction mixtures. In the presence of these reagents, the 1:2 complex $Re_2Cl_4(\mu\text{-dppm})_2(CN\text{-}t\text{-Bu})_2$ would have converted to $[Re_2Cl_3(\mu\text{-dppm})_2(CN\text{-}t\text{-Bu})_2]PF_6$ because of the labilization of one of the Re−Cl bonds.[20] This was confirmed in the present study by the reactions of $Re_2Cl_4(\mu\text{-dppE})_2(CN\text{-}t\text{-Bu})_2$ (**6**), a close analogue of the unknown complex $Re_2Cl_4(\mu\text{-dppm})_2(CN\text{-}t\text{-Bu})_2$, with TlO_3SCF_3 and $TlPF_6$, which produce a complex of stoichiometry $[Re_2Cl_3(\mu\text{-dppE})_2(CN\text{-}t\text{-Bu})_2]Y$ (Y = O_3SCF_3 or PF_6). The spectroscopic properties of the triflate salt **9** (given in Table 3) closely resemble those of the green isomeric form of $[Re_2Cl_3(\mu\text{-dppm})_2(CN\text{-}t\text{-Bu})_2]PF_6$ [20] which shows ν(CN) modes in its IR spectrum at 2160(s) and 2127(m) cm^{-1}, and an AA′BB′ pattern in its $^{31}P\{^1H\}$ NMR spectrum. The CV of a 0.1 M $n\text{-}Bu_4NPF_6$−CH_2Cl_2 solution of **9** displays a one-electron oxidation at $E_{1/2}(ox) = +0.64$ V and an irreversible reduction process at $E_{p,c} = -1.31$ V vs Ag/AgCl. These processes can be contrasted with those at $E_{1/2} = +0.65$ V and $E_{p,c} = -1.64$ V vs Ag/AgCl in the CV of $[Re_2Cl_3(\mu\text{-dppm})_2(CN\text{-}t\text{-Bu})_2]PF_6$. Conductivity measurements on a 1.0×10^{-3} M solution of **9** in acetonitrile confirmed that it behaved as a 1:1 electrolyte ($\Lambda_m = 136\ \Omega^{-1}\ cm^2\ mol^{-1}$). Based on the aforementioned properties, we propose that **9** has a structure similar to that of its dppm analogue, structure **III**.



III

L = t - BuNC

In view of the preceding observations, it seemed very likely that $Re_2Cl_4(\mu\text{-dppm})_2(CN\text{-}t\text{-Bu})_2$ could in fact be isolated. To this end, we reinvestigated the reaction between $Re_2Cl_4(\mu\text{-dppm})_2$ (**1**) and *t*-BuNC in dichloromethane *in the absence of TlO_3SCF_3 or $TlPF_6$*. Under these conditions, and with the presence of an *excess* of *t*-BuNC (four or more equivalents), the chloride salt $[Re_2Cl_3(\mu\text{-dppm})_2(CN\text{-}t\text{-Bu})_3]Cl$ (**13**) was formed; its spectroscopic properties, which are given in Table 3, are essentially identical with those of the previously isolated $[PF_6]^-$ salt.[20] Compound **13** will be considered in more detail later in this section. We next studied the reactions between **1** and 2 equiv of *t*-BuNC in dichloromethane as a function of time; see Experimental section D.2 for details of the procedures that were followed. In all instances, the nature of the product(s) was monitored by $^{31}P\{^1H\}$ NMR spectroscopy on CD_2Cl_2 solutions. When $t \simeq 1$ min, the NMR spectrum showed the presence of only one product that exhibited a symmetrical AA′BB′ pattern with multiplets centered at $\delta = -5.9$ and $\delta = -10.0$. This is the same 1:1 complex $Re_2Cl_4(\mu\text{-dppm})_2(CN\text{-}t\text{-Bu})$ we had isolated in an earlier study.[18] With an increase in time (t ≃ 5 min), the spectrum consisted of an AA′BB′ pattern caused by an unknown species (multiplets centered at $\delta = -9.7$ and $\delta = -13.8$) along with a singlet ($\delta = -9.72$), which overlapped the downfield of these two multiplets; this resonance is assigned to the symmetrical 1:2 complex $Re_2Cl_4(\mu\text{-dppm})_2(CN\text{-}t\text{-Bu})_2$. With a further increase in time ($t = 30$ min) the resonance caused by $Re_2Cl_4(\mu\text{-dppm})_2(CN\text{-}t\text{-Bu})_2$ remained unchanged, whereas the AA′BB′ pattern caused by the unknown species decreased in intensity as a new AA′BB′ pattern ($\delta = -5.7$ and $\delta = -12.4$) emerged as a result of the formation of the tris-isocyanide complex cation $[Re_2Cl_3(\mu\text{-dppm})_2(CN\text{-}t\text{-Bu})_3]^+$.[20] At $t = 2$ days, the spectrum showed the presence of $Re_2Cl_4(\mu\text{-dppm})_2(CN\text{-}t\text{-Bu})_2$ along with some $[Re_2Cl_3(\mu\text{-dppm})_2(CN\text{-}t\text{-Bu})_3]^+$. These experiments provide good evidence for the formation of $Re_2Cl_4(\mu\text{-dppm})_2(CN\text{-}t\text{-Bu})_2$ and also demonstrate the ease with which the tris-isocyanide cation is generated.

As we have established previously,[20] and confirmed in this study (see above), the reaction of an excess of *t*-BuNC with $Re_2Cl_4(\mu\text{-dppm})_2$ affords the complex $[Re_2Cl_3(\mu\text{-dppm})_2(CN\text{-}t\text{-Bu})_3]Cl$. Salts of the analogous XylNC-containing complex $[Re_2Cl_3(\mu\text{-dppm})_2(CNXyl)_3]^+$ have also been isolated,[20] and it is clear from differences between the spectroscopic and electrochemical properties of the *t*-BuNC and XylNC species that they possess different structures.[20] Previous attempts to obtain X-ray quality crystals of these complexes were unsuccessful.[20]

In the present study we find that the complex $Re_2Cl_4(\mu\text{-dppE})_2$ (**4**) reacts with *t*-BuNC to afford the tris-isocyanide complexes $[Re_2Cl_3(\mu\text{-dppE})_2(CN\text{-}t\text{-Bu})_3]Y$, where Y = Cl (**7**) or PF_6 (**8**), thereby establishing the similarity of this system to $Re_2Cl_4(\mu\text{-dppm})_2$. These two complexes possess spectroscopic properties very similar to one another (Table 3) and to $[Re_2Cl_3(\mu\text{-dppm})_2(CN\text{-}t\text{-Bu})_3]PF_6$[20] and $[Re_2Cl_3(\mu\text{-dppm})_2(CN\text{-}t\text{-Bu})_3]Cl$ (**13**) (Table 3). Therefore, we are confident in assigning them similar structures. The IR spectra of these pairs of dppm and dppE complexes show ν(CN) modes which are characteristic of terminally bound *t*-BuNC ligands, an interpretation that is confirmed by a single-crystal X-ray structure determination of $[Re_2Cl_3(\mu\text{-dppE})_2(CN\text{-}t\text{-Bu})_3]Cl$ (**7**). This complex possesses an open bioctahedral structure which is related to that of the bis-isocyanide complex $Re_2Cl_4(\mu\text{-dppE})_2(CN\text{-}t\text{-Bu})_2$ (**6**) by the replacement of a Cl ligand *trans* to one of the *t*-BuNC ligands by another *t*-BuNC ligand, thereby generating a dirhenium(II) cationic species. An ORTEP[32] representation of this structure is shown in Figure 5 and important bond distances and angles are given in Table 7.

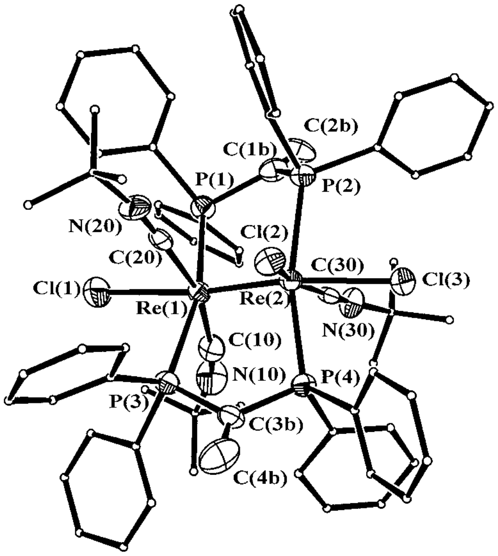


Figure 5. ORTEP[32] representation of the structure of the dirhenium cation in the complex $[Re_2Cl_3(\mu\text{-dppE})_2(CN\text{-}t\text{-}Bu)_3]Cl$ (**7**). The thermal ellipsoids are drawn at the 50% probability level except for the phenyl group atoms of the dppE ligands and the *tert*-butyl group atoms of the *t*-BuNC ligands which are circles of arbitrary radius.

Table 7. Important Bond Distances (Å) and Bond Angles (deg) for the Complex $[Re_2Cl_3(\mu\text{-dppE})_2(CN\text{-}t\text{-}Bu)_3]Cl$ (**7**)[a]

	Distances		
Re(1)−Re(2)	2.3451(10)	Re(2)−Cl(2)	2.427(3)
Re(1)−C(20)	2.054(12)	Re(2)−P(4)	2.448(4)
Re(1)−C(10)	2.099(14)	Re(2)−P(2)	2.477(4)
Re(1)−P(1)	2.468(4)	Re(2)−Cl(3)	2.566(3)
Re(1)−P(3)	2.498(4)	C(10)−N(10)	1.16(2)
Re(1)−Cl(1)	2.571(4)	C(20)−N(20)	1.15(2)
Re(2)−C(30)	2.05(2)	C(30)−N(30)	1.13(2)
	Angles		
C(20)−Re(1)−C(10)	163.6(7)	Re(1)−Re(2)−P(2)	97.51(8)
C(20)−Re(1)−Re(2)	89.5(4)	Cl(2)−Re(2)−P(2)	93.48(12)
C(10)−Re(1)−Re(2)	106.7(4)	P(4)−Re(2)−P(2)	166.30(12)
C(20)−Re(1)−P(1)	86.5(4)	C(30)−Re(2)−Cl(3)	75.4(4)
C(10)−Re(1)−P(1)	94.0(5)	Re(1)−Re(2)−Cl(3)	164.83(7)
Re(2)−Re(1)−P(1)	97.13(9)	Cl(2)−Re(2)−Cl(3)	89.62(11)
C(20)−Re(1)−P(3)	89.7(5)	P(4)−Re(2)−Cl(3)	79.68(13)
C(10)−Re(1)−P(3)	85.8(5)	P(2)−Re(2)−Cl(3)	86.74(13)
Re(2)−Re(1)−P(3)	97.05(8)	C(30)−Re(2)−P(4)	91.7(4)
P(1)−Re(1)−P(3)	165.26(12)	Re(1)−Re(2)−P(4)	96.09(9)
C(20)−Re(1)−Cl(1)	82.8(4)	Cl(2)−Re(2)−P(4)	84.65(11)
C(10)−Re(1)−Cl(1)	81.2(4)	C(30)−Re(2)−P(2)	86.6(5)
Re(2)−Re(1)−Cl(1)	171.74(10)	N(10)−C(10)−Re(1)	172.0(14)
P(1)−Re(1)−Cl(1)	79.5(2)	N(20)−C(20)−Re(1)	174.9(10)
P(3)−Re(1)−Cl(1)	85.9(2)	N(30)−C(30)−Re(2)	175.1(12)
C(30)−Re(2)−Re(1)	90.3(4)	C(10)−N(10)−C(11)	163(2)
C(30)−Re(2)−Cl(2)	165.0(3)	C(20)−N(20)−C(21)	172(2)
Re(1)−Re(2)−Cl(2)	104.58(9)	C(30)−N(30)−C(31)	167.8(12)

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

The Re−Re distance for **7** is 2.3451(10) Å, a value which is almost identical to its bis-isocyanide precursor complex **6** [2.3497(4) Å]. This distance is also similar to that of the Re≡Re bond in the triflate salt of the isomeric form of the cation $[Re_2Cl_3(\mu\text{-dppm})_2(CO)(CNXyl)_2]^+$ [2.3833(8) Å][5] in which there are two XylNC ligands *trans* to one another and the CO is bound to the adjacent Re atom. As is typical for this type of dirhenium complex, the axial Re−Cl bonds of **7** [Re(1)−Cl(1) and Re(2)−Cl(3)] are longer than the equatorial bond Re(2)−Cl(2) by ca. 0.14 Å. The angles Re(1)−Re(2)−Cl(3) = 164.83(7)° and Re(2)−Re(1)−Cl(1) = 171.74(10)° show some deviation from linearity, whereas the three Re−C−N angles are within the narrow range 172−175°, signifying the absence of a significant degree of Re→CNR(π^*) back-bonding. As is the case with the bis-isocyanide complex **6**, the tris-isocyanide **7** has a partially staggered rotational geometry with torsional angles P(1)−Re(1)−Re(2)−P(2), P(3)−Re(1)−Re(2)−P(4), C(20)−Re(1)−Re(2)−Cl(2), and C(10)−Re(1)−Re(2)−C(30) of 18.8°, 24.5°, 28.1°, and 28.6°, respectively.

With the structures of the $[Re_2Cl_3(\mu\text{-dppE})_2(CN\text{-}t\text{-}Bu)_3]^+$ and $[Re_2Cl_3(\mu\text{-dppm})_2(CN\text{-}t\text{-}Bu)_3]^+$ firmly established, it is now appropriate to consider the structure of the previously reported XylNC complex $[Re_2Cl_3(\mu\text{-dppm})_2(CNXyl)_3]^+$.[20] Although attempts to structurally characterize the Cl^-, $[PF_6]^-$, and $[O_3SCF_3]^-$ salts of this cation have so far been unsuccessful, we were able to obtain X-ray quality single crystals of the neutral paramagnetic congener $Re_2Cl_3(\mu\text{-dppm})_2(CNXyl)_3$ (**3**). This compound was obtained by the one-electron reduction of the triflate salt through the use of cobaltocene in acetone. Crystals were grown by the slow diffusion of diethyl ether into a dichloromethane solution of the complex. Although the structure was that of the edge-sharing bioctahedron $(XylNC)ClRe(\mu\text{-}Cl)(\mu\text{-}CNXyl)(\mu\text{-dppm})_2ReCl(CNXyl)$, with an all-*cis* arrangement of XylNC ligands and a Re−Re distance of 2.73 Å, the poor quality of the data set prevented us from obtaining a fully refined, publishable structure. However, the present study has enabled us to clarify the nature of the structural difference that exists between the pair $[Re_2Cl_3(\mu\text{-dppm})_2(CN\text{-}t\text{-}Bu)_3]^+$ and $[Re_2Cl_3(\mu\text{-dppm})_2(CNXyl)_3]^+$.[20]

Concluding Remarks

The synthesis and unambiguous structural characterization of a series of organic isocyanide complexes of the types $Re_2Cl_4(\mu\text{-LL})_2(CNR)$, $Re_2Cl_4(\mu\text{-LL})_2(CNR)_2$, and $[Re_2Cl_3(\mu\text{-LL})_2(CNR)_3]Cl$, where LL = dppm, dppE, or dcpm and R = *t*-Bu or Xyl, has for the first time allowed for an understanding of the isomer chemistry that is possible with this class of compounds. The present study provides the clarification of the structural chemistry that is a necessary prelude to exploring the reaction chemistry of these compounds toward other π-acceptor ligands. These studies are currently underway.

Supporting Information Available: Five 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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