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Reactions of the Dirhenium(II) Complexes $Re_2X_4(dppm)_2$ (X = Cl, Br; dppm = $Ph_2PCH_2PPh_2$) with Isocyanides. 5.[1] Mixed Carbonyl–Isocyanide and Carbonyl–Isocyanide–Nitrile Complexes of Stoichiometry $[Re_2Cl_3(dppm)_2(CO)(CNR)(L)]PF_6$ (R = *t*-Bu, xyl (Xylyl); L = *t*-BuNC, xylNC, MeCN, EtCN). Structural Characterization of the Cation $[Cl_2(CO)Re(\mu\text{-dppm})_2ReCl(CN\text{-}t\text{-}Bu)_2]^+$

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Several dirhenium(II) species that contain mixed sets of carbonyl, isocyanide, and/or nitrile ligands have been prepared from the reactions between $Re_2Cl_4(dppm)_2(CO)(CNR)$ (dppm = $Ph_2PCH_2PPh_2$; R = *t*-Bu, xyl (xylyl)) and the appropriate ligands, in the presence of $TlPF_6$. Thus, the reaction of $Re_2Cl_4(dppm)_2(CO)(CN\text{-}t\text{-}Bu)$ with *t*-BuNC and $TlPF_6$ in acetone gives the complex $[Re_2Cl_3(dppm)_2(CO)(CN\text{-}t\text{-}Bu)_2]PF_6$ (**1**). Crystals of this complex grown from CH_2Cl_2–methanol proved to be those of the salt $[Re_2Cl_3(dppm)_2(CO)(CN\text{-}t\text{-}Bu)_2](PF_6)_{0.5}(OMe)_{0.5}$, which crystallizes in the triclinic space group $P\bar{1}$ with the following unit cell dimensions: $a = 12.125$ (2) Å, $b = 23.877$ (4) Å, $c = 11.694$ (2) Å, $\alpha = 100.74$ (1)°, $\beta = 90.38$ (1)°, $\gamma = 76.34$ (1)°, $V = 3230$ (2) Å^3, $Z = 2$. The structure was refined to $R = 0.038$ ($R_w = 0.063$) for 6512 data with $F^2 > 3.0\sigma(F^2)$. The dirhenium(II) cation, which can be represented as $[Cl_2(CO)Re(\mu\text{-dppm})_2Re(CN\text{-}t\text{-}Bu)_2Cl]^+$ is the first structurally characterized dirhenium complex of this kind in which the CO ligand is not bridging the two metal centers. The Re–Re distance of 2.379 (1) Å is consistent with a $Re\equiv Re$ bond. Other complexes of this same kind, viz., $[Cl_2(CO)Re(\mu\text{-dppm})_2Re(CN\text{-}t\text{-}Bu)(L)Cl]PF_6$, have been prepared by a similar method in the case of L = xylNC (**2a**), MeCN (**4a**), and EtCN (**4b**). This behavior contrasts with the reactions of $Re_2Cl_4(dppm)_2(CO)(CNxyl)$, a complex that has a structure different from that of its *t*-BuNC analogue, namely, $Cl_2Re(\mu\text{-}Cl)(\mu\text{-}CO)(\mu\text{-dppm})_2ReCl(CNxyl)$. It reacts with *t*-BuNC to give complexes which have the same stoichiometry as **2a** but which are clearly different isomeric forms (**2b** and **2c**). Reaction at room temperature gives **2b**, a species in which the xylNC ligand is believed to bridge the Re–Re bond. When 1,2-dichloroethane solutions of **2b** are refluxed for 12 h, isomerization to **2c** occurs. In this complex the xylNC ligand is now terminally bound while the carbonyl group is bridging. The mixed carbonyl–isocyanide–nitrile salts $[Re_2Cl_3(dppm)_2(CO)(CNxyl)(NCR')]PF_6$ (**5a**, R′ = Me; **5b**, R′ = Et) also possess this edge-sharing bioctahedral structure with a μ-CO group. The nitrile ligands in complexes of the types **4** and **5** are labile and may be displaced by the π-acceptors CO and RNC; i.e., $[Re_2Cl_3(dppm)_2(CO)(CNR)(NCR')]PF_6$ complexes react with CO and RNC to give complexes of the types $[Re_2Cl_3(dppm)_2(CO)_2(CNR)]PF_6$ and $[Re_2Cl_3(dppm)_2(CO)(CNR)_2]PF_6$, respectively.

Introduction

The reactivity of the triply bonded dirhenium(II) complexes $Re_2X_4(\mu\text{-dppm})_2$ (X = Cl, Br; dppm = bis(diphenylphosphino)methane) toward carbon monoxide, isocyanides, and nitriles has been investigated in detail.[1-10] In all those products which have at least one carbonyl group and which possess the M_2L_{10} edge-sharing bioctahedral structure, a CO ligand bridges the Re–Re bond. We now describe the synthesis and characterization of the complexes $[Re_2Cl_3(dppm)_2(CO)(CN\text{-}t\text{-}Bu)_2]PF_6$[11] and $[Re_2Cl_3(dppm)_2(CO)(CN\text{-}t\text{-}Bu)(CNxyl)]PF_6$, which have structures different from that encountered previously; i.e., the CO ligand is terminally bound. Complexes in which there are mixed sets of carbonyl, isocyanide, and nitrile ligands, viz. $[Re_2Cl_3(dppm)_2(CO)(CNR)(NCR')]PF_6$, are also reported. The nitrile ligands in these complexes are labile and have been found to undergo substitution by CO and RNC.

Experimental Section

Starting Materials. The monocarbonyl complex $Re_2Cl_4(dppm)_2(CO)$, the dicarbonyl complex $Re_2Cl_4(dppm)_2(CO)_2$, the mixed carbonyl–isocyanide complexes $Re_2Cl_4(dppm)_2(CO)(CNR)$, where R = *t*-Bu or xylyl, and $[Re_2Cl_3(dppm)_2(CO)(CN\text{-}t\text{-}Bu)_2]PF_6$ (**1**), and the mixed carbonyl–nitrile complex $[Re_2Cl_3(dppm)_2(CO)(NCMe)_2]PF_6$ were prepared from the reactions between $Re_2Cl_4(dppm)_2$ and the appropriate ligands according to the reported methods.[1,3,4] The isocyanide ligand *t*-BuNC was prepared by a standard procedure,[12] while xylyl isocyanide (xylNC) was obtained from Fluka Chemicals. Carbon monoxide (99.9%) was purchased from Matheson Gas Products, while cobaltocene and thallium(I) hexafluorophosphate were obtained from Strem Chemicals. These reagents were used without further purification. Solvents used in the preparation of the complexes were of commercial grade and were thoroughly deoxygenated prior to use.

Reaction Procedures. All reactions were performed under an atmosphere of dry dinitrogen or under 1 atm of carbon monoxide.

A. Reactions of $Re_2Cl_4(dppm)_2(CO)(CNR)$ with Isocyanides. (i) $[Re_2Cl_3(dppm)_2(CO)(CN\text{-}t\text{-}Bu)(CNxyl)]PF_6$ (2a). A mixture of $Re_2Cl_4(dppm)_2(CO)(CN\text{-}t\text{-}Bu)$ (0.20 g, 0.14 mmol), $TlPF_6$ (0.055 g, 0.16 mmol), and 1 equiv of xylNC (0.019 g, 0.14 mmol) in acetone (10 mL) was stirred for 24 h. The resulting brown reaction mixture was filtered to remove the precipitated TlCl and the filtrate evaporated to dryness. The residue was redissolved in a small volume of dichloromethane, the mixture was filtered, and to the filtrate was added an excess of diethyl ether to yield a brown precipitate. This was filtered off and dried under vacuum. The complex was recrystallized from dichloromethane–diethyl ether at 0 °C to afford a brown powder; yield 0.17 g (75%). Anal. Calcd for $C_{65}H_{62}Cl_3F_6N_2OP_5Re_2$: C, 47.75; H, 3.82. Found: C, 48.50; H, 3.74.

(ii) $[Re_2Cl_3(dppm)_2(CO)(CNxyl)(CN\text{-}t\text{-}Bu)]PF_6$ (2b and 2c). (a) Room-Temperature Conditions. Isomer **2b** was prepared by stirring a mixture of $Re_2Cl_4(dppm)_2(CO)(CNxyl)$ (0.20 g, 0.14 mmol), $TlPF_6$ (0.055 g, 0.16 mmol), and 1 equiv of *t*-BuNC (15 μL, 0.14 mmol) in dichloromethane (10 mL) at room temperature for 24 h. The resulting

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brown reaction mixture was filtered to remove the TlCl, and the filtrate was worked up in the same manner as that described in section A(i), to yield the complex as a brown crystalline solid. It was recrystallized from dichloromethane–diethyl ether at 0 °C; yield 0.16 g (70%). Anal. Calcd for $C_{65}H_{62}Cl_3F_6N_2OP_5Re_2$: C, 47.75; H, 3.82. Found: C, 47.86; H, 3.86.

(b) Reflux Conditions. Isomer **2c** was prepared by the use of the same starting material and reagents as described in section A(ii)(a), except that the reaction was carried out in refluxing 1,2-dichloroethane for 12 h. The resulting green-brown solution was worked up in the same manner as that described in section A(i), to yield the complex as a green crystalline solid; yield 80%. Anal. Calcd for $C_{65}H_{62}Cl_3F_6N_2OP_5Re_2$: C, 47.75; H, 3.82. Found: C, 46.75; H, 3.80.

B. Isomerization of [$Re_2Cl_3(dppm)_2(CO)(CNxyl)(CN$-*t*-Bu)]$PF_6$ (2b). This brown isomer (0.10 g, 0.061 mmol) was refluxed in 10 mL of 1,2-dichloroethane for 20 h. The solution was cooled, and hexane ($\simeq$50 mL) was added to precipitate a green solid, which was filtered off, washed with diethyl ether, and then recrystallized from dichloromethane–hexane at 0 °C; yield 85%. The cyclic voltammogram and IR spectrum of this product were found to be exactly the same as those for isomer **2c**.

C. Reduction of [$Re_2Cl_3(dppm)_2(CO)(CNxyl)(CN$-*t*-Bu)]$PF_6$ (2b). The reduction of this complex was achieved chemically by dissolving a quantity of it (0.10 g, 0.061 mmol) in acetone (5 mL) and then adding an acetone solution (2 mL) containing 1 equiv of cobaltocene (0.012 g, 0.063 mmol). When the solution was stirred at room temperature for 30 min, a green solid precipitated from the reaction mixture. This product, i.e. $Re_2Cl_3(dppm)_2(CO)(CNxyl)(CN$-*t*-Bu) (**3**), was filtered off, washed with acetone to remove any unreacted cobaltocene as well as the $[(\eta^5\text{-}C_5H_5)_2Co]PF_6$ reaction byproduct, then washed with diethyl ether, and finally recrystallized from dichloromethane–hexane at 0 °C; yield 0.073 g (80%). Anal. Calcd for $C_{65}H_{62}Cl_3N_2OP_4Re_2$: C, 52.40; H, 4.19. Found: C, 51.21; H, 4.51.

D. Reactions of $Re_2Cl_4(dppm)_2(CO)(CNR)$ with Nitriles. (i) [$Re_2Cl_3(dppm)_2(CO)(CN$-*t*-Bu)(NCMe)]PF_6 (4a). A mixture of $Re_2Cl_4(dppm)_2(CO)(CN$-*t*-Bu) (0.20 g, 0.14 mmol) and $TlPF_6$ (0.055 g, 0.16 mmol) was stirred in 10 mL of dichloromethane–acetonitrile (1:1) for 5 h. The reaction mixture was filtered to remove the white precipitate of TlCl. The dark red filtrate was evaporated to dryness under a stream of dinitrogen, and the residue was then extracted into 10 mL of dichloromethane. An excess of diethyl ether was added to produce a pink precipitate. This was filtered off and dried under vacuum; yield 0.18 g (80%). Anal. Calcd for $C_{58}H_{56}Cl_3F_6N_2OP_5Re_2$: C, 45.10; H, 3.65. Found: C, 44.33; H, 3.66.

(ii) [$Re_2Cl_3(dppm)_2(CO)(CN$-*t*-Bu)(NCEt)]PF_6 (4b). The preparation of this complex is analogous to that described in section D(i); yield 80%. Anal. Calcd for $C_{59}H_{58}Cl_3F_6N_2OP_5Re_2$: C, 45.46; H, 3.75. Found: C, 44.73; H, 3.78.

(iii) [$Re_2Cl_3(dppm)_2(CO)(CNxyl)(NCMe)]PF_6$ (5a). A mixture of $Re_2Cl_4(dppm)_2(CO)(CNxyl)$ (0.20 g, 0.14 mmol) and $TlPF_6$ (0.050 g, 0.14 mmol) was stirred in 15 mL of dichloromethane–acetonitrile (1:1) for 18 h. The resulting green solution (and white precipitate of TlCl) was worked up in exactly the same fashion as that described in section D(i). The green crystalline solid was recrystallized from dichloromethane–diethyl ether at 0 °C; yield 0.19 g (85%). Anal. Calcd for $C_{62}H_{52}Cl_3F_6N_2OP_5Re_2$: C, 46.75; H, 3.29; Cl, 6.68. Found: C, 46.81; H, 3.43; Cl, 7.18.

(iv) [$Re_2Cl_3(dppm)_2(CO)(CNxyl)(NCEt)]PF_6$ (5b). The preparation of this complex is analogous to that described in section D(iii); yield 0.12 g (55%). Anal. Calcd for $C_{63}H_{58}Cl_3F_6N_2OP_5Re_2$: C, 47.09; H, 3.64. Found: C, 47.17; H, 3.66.

E. Reactions of [$Re_2Cl_3(dppm)_2(CO)(CNR)(NCMe)]PF_6$ with Carbon Monoxide and Isocyanides. The IR spectra and electrochemical properties of the complexes described in this section were found to be identical with those of complexes of the same stoichiometries that were prepared by alternative routes as described in ref 1 or 9 or in sections A(i) and A(ii) of the present paper. Accordingly, microanalytical data were not obtained for any of these products.

(i) [$Re_2Cl_3(dppm)_2(CO)_2(CN$-*t*-Bu)]$PF_6$. A quantity of [$Re_2Cl_3(dppm)_2(CO)(CN$-*t*-Bu)(NCMe)]$PF_6$ (0.060 g, 0.039 mmol) was dissolved in dichloromethane (15 mL). Carbon monoxide was gently bubbled into the solution for 6 h. The resulting green solution was treated with an excess of hexane to yield a green precipitate. This was filtered off, washed with diethyl ether, and dried under vacuum; yield 0.049 g (80%).

(ii) [$Re_2Cl_3(dppm)_2(CO)(CN$-*t*-Bu$)_2$]PF_6 (1). A mixture comprising [$Re_2Cl_3(dppm)_2(CO)(CN$-*t*-Bu)(NCMe)]PF_6 (0.030 g, 0.019 mmol), 1 equiv of *t*-BuNC (2.1 μL, 0.020 mmol), and dichloromethane (5 mL) was stirred for 24 h. An excess of diethyl ether was added to the solution to produce a brown precipitate of **1**. This was filtered off, washed with diethyl ether, and then dried under vacuum; yield 0.021 g (70%).

(iii) [$Re_2Cl_3(dppm)_2(CO)(CN$-*t*-Bu)(CNxyl)]PF_6 (2a). A mixture comprising [$Re_2Cl_3(dppm)_2(CO)(CN$-*t*-Bu)(NCMe)]PF_6 (0.030 g, 0.019 mmol), 1 equiv of xylNC (0.0025 g, 0.019 mmol), and dichloromethane (5 mL) was stirred for 24 h. Workup of the resulting brown solution was carried out in exactly the same manner as that described in section E(ii) to give **2a**; yield 0.025 g (80%).

(iv) [$Re_2Cl_3(dppm)_2(CO)_2(CNxyl)]PF_6$. A quantity of [$Re_2Cl_3(dppm)_2(CO)(CNxyl)(NCMe)]PF_6$ (0.030 g, 0.019 mmol) was dissolved in dichloromethane (10 mL). Carbon monoxide was gently bubbled into the solution for 18 h. The brown-yellow solution was treated with an excess of hexane to yield a yellow precipitate, which was washed with diethyl ether and dried under vacuum; yield 0.025 g (80%).

(v) [$Re_2Cl_3(dppm)_2(CO)(CNxyl)(CN$-*t*-Bu)]$PF_6$ (2b). A mixture of [$Re_2Cl_3(dppm)_2(CO)(CNxyl)(NCMe)]PF_6$ (0.10 g, 0.063 mmol), 1 equiv of *t*-BuNC (7.0 μL, 0.066 mmol), and dichloromethane (10 mL) was allowed to react for 14 h. The solution, which gradually turned from green to brown, was treated with an excess of diethyl ether to yield a brown precipitate. This was filtered off and dried under vacuum; yield 0.075 g (75%).

(vi) [$Re_2Cl_3(dppm)_2(CO)(CNxyl)_2]PF_6$. A mixture of [$Re_2Cl_3(dppm)_2(CO)(CNxyl)(NCMe)]PF_6$ (0.033 g, 0.019 mmol), 1 equiv of xylNC (0.0025 g, 0.019 mmol), and dichloromethane (5 mL) was stirred for 18 h. The resulting brown solution was treated with an excess of hexane to yield a yellow-brown precipitate. This was filtered off, washed with diethyl ether, and dried under vacuum; yield 0.022 g (70%). The IR spectrum and electrochemical properties of this material confirmed the presence of two isomers[1] in roughly equal amounts. No attempt was made to separate them, as this reaction was performed on a very small scale.

F. Reaction of [$Re_2Cl_3(dppm)_2(CO)(NCMe)_2]PF_6$ with Carbon Monoxide. [$Re_2Cl_3(dppm)_2(CO)_2(NCMe)]PF_6$. A quantity of [$Re_2Cl_3(dppm)_2(CO)(NCMe)_2]PF_6$ (0.10 g, 0.067 mmol) was dissolved in dichloromethane (20 mL) and stirred under an atmosphere of CO ($\simeq$1.1 atm) for 24 h. The green solution was treated with an excess of hexane to yield a yellow-green precipitate, which was filtered off, washed with diethyl ether, and dried under vacuum; yield 0.092 g (90%). The IR spectrum and electrochemical properties of this material were identical with those of the complex of this same stoichiometry that was prepared by an alternative route.[9]

G. Reaction of [$Re_2Cl_3(dppm)_2(CO)_2(NCMe)]PF_6$ with Xylyl Isocyanide. [$Re_2Cl_3(dppm)_2(CO)_2(CNxyl)]PF_6$. A mixture of [$Re_2Cl_3(dppm)_2(CO)_2(NCMe)]PF_6$ (0.035 g, 0.023 mmol), 1 equiv of xylNC (0.0031 g, 0.024 mmol), and acetone (5 mL) was stirred for 24 h. The resulting brown solution was evaporated to dryness under a stream of dinitrogen and the residue extracted with a small volume of dichloromethane. This filtrate was then treated with an excess of hexane to yield a brown precipitate, which was filtered off, washed with diethyl ether, and dried under vacuum; yield 0.028 g (75%). The IR spectrum and electrochemical properties of this material were identical with those of the complex of this same stoichiometry that was prepared by alternative route.[1]

Preparation of Single Crystals of [$Re_2Cl_3(dppm)_2(CO)(CN$-*t*-Bu$)_2$]PF_6 (1). A batch of red-brown crystals were grown by dissolving approximately 0.05 g of this compound in $\simeq$3 mL of dichloromethane contained in a small vial. Approximately 2 mL of methanol was carefully layered on top of this solution, and the vial was then capped. Very slow evaporation was allowed to take place, through a small hole in the cap, for a period of 1 week until red-brown crystals formed on the side and at the bottom of the vial.

X-ray Crystallographic Procedures. The structure of the complex was determined by application of general procedures that are described more fully elsewhere.[13] A single crystal of dimensions 0.17 × 0.14 × 0.05 mm was mounted on a glass fiber with epoxy resin. The crystal was indexed, and data were collected on a Enraf-Nonius CAD-4 diffractometer equipped with a graphite monochromator and a standard-focus molybdenum X-ray tube. The crystal was found to belong to the triclinic space group $P\bar{1}$. Crystal data and information relating to data collection and structure refinement are listed in Table I. The cell parameters are based on 25 reflections with $15.9 < \theta < 21.6°$. Three standard reflections were measured every 5000 s of beam exposure during data collection and displayed no systematic variation in intensity.

Calculations were performed on a PDP11/34 computer using the Enraf-Nonius structure determination package. The atoms were located and refined for an initial Patterson map. During the course of the structure analysis, it became apparent that there was only one PF_6^- anion for the two dirhenium cations in the unit cell. This did not satisfy the

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Table I. Crystallographic Data and Data Collection Parameters for $[Re_2Cl_3(dppm)_2(CO)(CN\text{-}t\text{-}Bu)_2](PF_6)_{0.5}(OMe)_{0.5}$[a]

formula	$Re_2Cl_3P_{4.5}F_3O_{1.5}N_2C_{61.5}H_{63.5}$
fw	1530.82
space gp	$P\bar{1}$
a, Å	12.125 (2)
b, Å	23.877 (1)
c, Å	11.694 (2)
α, deg	100.74 (1)
β, deg	90.38 (1)
γ, deg	76.34 (1)
V, Å^3	3230 (2)
Z	2
d_{calcd}, g cm^{-3}	1.574
cryst dimens, mm	0.17 × 0.14 × 0.05
temp, °C	22.0
radiation (wavelength, Å)	Mo$K\alpha$ (0.71073)
monochromator	graphite
linear abs coeff, cm^{-1}	40.90
abs cor applied	empirical[b]
diffractometer	Enraf-Nonius CAD4
scan method	θ–2θ
h,k,l limits	−12 to +12, 0 to +25, −12 to +12
2θ range, deg	4.00–45.00
scan width, deg	0.85 + 0.35 tan θ
takeoff angle, deg	4.80
programs used	Enraf-Nonius SDP
F_{000}	1508.0
p factor used in weighting	0.070
no. of data collected	8394
no. of data with $I > 3.0\sigma(I)$	6512
no. of variables	19
largest shift/esd in final cycle	0.77
R[c]	0.038
R_w[d]	0.063
goodness of fit[e]	1.304

[a] Numbers in parentheses following certain data are estimated standard deviations occurring in the least significant digit. [b] Walker, N.; Stuart, D. *Acta Crystallogr., Sect. A*: *Found. Crystallogr.* **1983**, *A39*, 158. [c] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [d] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$; $w = 1/\sigma^2(F_o)$. [e] Goodness of fit $= [\sum w(|F_o| - |F_c|)^2/(N_{observns} - N_{params})]^{1/2}$.

charge requirements for this complex. The largest peak in the difference Fourier map at this stage was less than 2.5 e Å^{-3}. Subsequent refinement of this residual electron density suggested the presence of a small molecule that we concluded could be a methoxide anion. This lies on a general position and is disordered within the unit cell. Refinement was carried out on this assumption. Accordingly, there is a total of two anions per unit cell, each occupying sites of half-occupancy, so that the stoichiometry of the crystals is $[Re_2Cl_3(dppm)_2(CO)(CN\text{-}t\text{-}Bu)_2](PF_6)_{0.5}(OCH_3)_{0.5}$.

An empirical absorption correction was applied.[14] The linear absorption coefficient was 40.90 cm^{-1}. No correction was made for extinction. The least-squares program minimized the function $\sum w(|F_o| - |F_c|)^2$, where w is a weighting factor defined as $w = 1/\sigma^2(F_o)$. All atoms except the C and O atoms of the methoxide anion were refined anisotropically, and corrections for anomalous scattering were applied.[15] Hydrogens were not included in the least-squares refinement. The final residuals were $R = 0.038$, $R_w = 0.063$, for 6512 data with $I > 3\sigma(I)$.

Further details concerning the data set, the structure solution, and the structure refinement may be obtained from P.E.F. Figure 1 shows the structure of the cation with the methyl groups and phenyl rings omitted for clarity. Table II lists the atomic positional parameters and their errors for non-phenyl atoms, while Table III lists important intramolecular bond distances and angles. Tables listing positional parameters and their errors for phenyl ring atoms (Table S1), thermal parameters (Table S2), and complete bond distances and bond angles (Table S3 and S4, respectively) are available as supplementary material, as well as a figure (Figure S1) showing the full atomic numbering scheme.

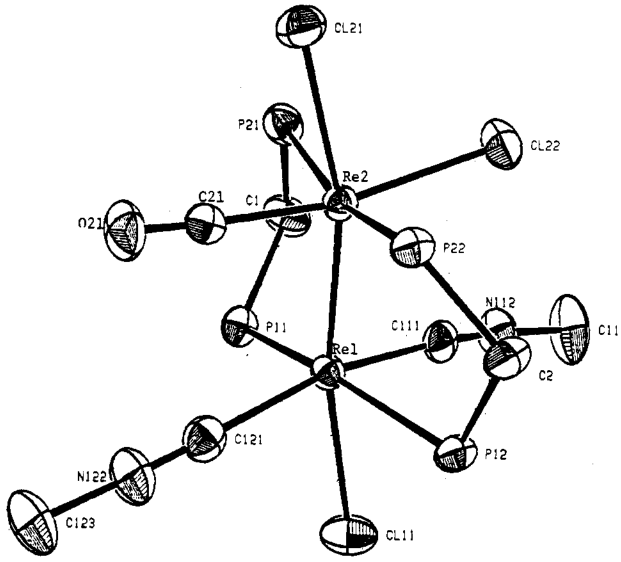

Figure 1. ORTEP view of the structure of the $[Re_2Cl_3(dppm)_2(CO)(CN\text{-}t\text{-}Bu)_2]^+$ cation with the methyl groups and phenyl rings omitted. The thermal ellipsoids are drawn at the 50% probability level.

Table II. Positional Parameters and Equivalent Isotropic Displacement Parameters (Å^2) for Non-Phenyl Atoms and Their Estimated Standard Deviations

atom	x	y	z	B[a]
Re(1)	0.15427 (3)	0.28101 (2)	0.33063 (3)	1.752 (8)
Re(2)	0.23795 (3)	0.21366 (2)	0.15997 (3)	1.801 (8)
Cl(11)	0.1021 (3)	0.3423 (1)	0.5288 (2)	3.38 (6)
Cl(21)	0.2735 (2)	0.1602 (1)	−0.0502 (2)	3.12 (6)
Cl(22)	0.4241 (2)	0.1630 (1)	0.2058 (2)	3.07 (6)
P(1)	$^1/_2$	$^1/_2$	0	5.2 (1)
P(11)	0.0327 (2)	0.2182 (1)	0.3819 (2)	2.24 (6)
P(12)	0.2875 (2)	0.3468 (1)	0.3424 (2)	2.24 (6)
P(21)	0.1698 (2)	0.1269 (1)	0.1924 (2)	2.56 (6)
P(22)	0.3300 (2)	0.2833 (1)	0.0893 (2)	2.19 (5)
F(13)	0.497 (1)	0.4612 (6)	0.095 (1)	14.2 (5)
F(11)	0.417 (1)	0.5545 (6)	0.077 (1)	14.1 (4)
F(12)	0.602 (1)	0.5187 (6)	0.061 (1)	15.0 (5)
O(21)	0.0220 (6)	0.2632 (4)	0.0405 (6)	3.7 (2)
N(112)	0.3288 (7)	0.2088 (4)	0.4857 (7)	2.8 (2)
N(122)	−0.0623 (8)	0.3704 (4)	0.2520 (8)	3.8 (2)
C(1)	0.117 (1)	0.1425 (5)	0.345 (1)	3.1 (3)
C(2)	0.3875 (8)	0.3243 (4)	0.2159 (8)	2.5 (2)
C(21)	0.0999 (8)	0.2458 (4)	0.0890 (8)	2.1 (2)
C(111)	0.2707 (8)	0.2330 (4)	0.4251 (9)	2.3 (2)
C(113)	0.405 (1)	0.1825 (6)	0.570 (1)	4.7 (3)
C(114)	0.359 (2)	0.1344 (8)	0.608 (2)	10.8 (5)
C(115)	0.519 (1)	0.166 (1)	0.525 (2)	10.8 (6)
C(116)	0.386 (2)	0.227 (1)	0.683 (2)	12.4 (8)
C(121)	0.0168 (9)	0.3400 (5)	0.2771 (9)	2.7 (2)
C(123)	−0.167 (1)	0.4080 (6)	0.216 (1)	5.5 (4)
C(124)	−0.150 (2)	0.4684 (7)	0.239 (2)	12.4 (7)
C(125)	−0.265 (1)	0.405 (1)	0.300 (2)	11.8 (7)
C(126)	−0.179 (2)	0.3839 (9)	0.085 (2)	10.9 (6)
C(1002)	0.241 (4)	−0.005 (2)	0.508 (4)	10 (1)*
O(1001)	0.109 (3)	−0.010 (1)	0.511 (3)	12.0 (9)*

[a] Anisotropically refined atoms are given in the form of isotropic equivalent thermal parameter defined as $^4/_3[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$. Values marked with an asterisk are for isotropically refined atoms.

Physical Measurements. Infrared spectra were recorded as Nujol mulls between KBr plates with an IBM Instruments IR 32 or Perkin-Elmer 1800 Fourier transform (4000–400 cm^{-1}) spectrometers. Electronic absorption spectra were recorded on IBM Instruments 9420, Hewlett-Packard HP8451A (900–300 nm), and Cary 17 (1800–900 nm) UV–visible spectrophotometers. Electrochemical measurements were carried out on dichloromethane solutions that contained 0.1 M tetra-*n*-butylammonium hexafluorophosphate (TBAH) as supporting electrolyte. $E_{1/2}$ values, determined as $(E_{p,a} + E_{p,c})/2$, were referenced to the silver/silver chloride (Ag/AgCl) electrode at room temperature and are uncorrected for junction potentials. Under our experimental conditions $E_{1/2} = +0.47$ V vs Ag/AgCl for the Cp_2Fe^+/Cp_2Fe couple. Voltammetric experiments were performed with a Bioanalytical Systems Inc.

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(14) Walker, N.; Stuart, D. *Acta Crystallogr., Sect. A*: *Found. Crystallogr.* **1983**, *A39*, 158.

(15) (a) Cromer, D. T. *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV, Table 2.3.1. (b) For the scattering factors used in the structure solution see: Cromer, D. T.; Waber, J. T. *Ibid.*, Table 2.2B.

Table III. Selected Bond Distances (Å) and Angles (deg) for $[Re_2Cl_3(dppm)_2(CO)(CN\text{-}t\text{-}Bu)_2]^{+\,a}$

Distances

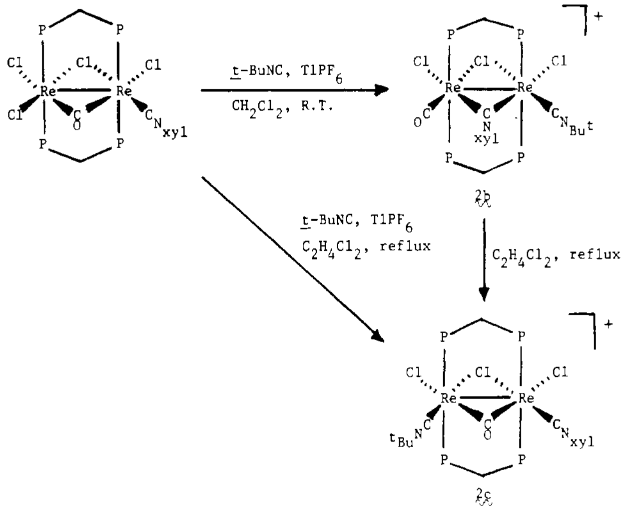
Re(1)–Re(2)	2.3787 (5)	Re(2)–C(21)	1.922 (9)
Re(1)–Cl(11)	2.496 (2)	P(11)–C(1)	1.83 (1)
Re(1)–P(11)	2.485 (3)	P(12)–C(2)	1.83 (1)
Re(1)–P(12)	2.493 (3)	P(21)–C(1)	1.84 (1)
Re(1)–C(111)	2.05 (1)	P(22)–C(2)	1.85 (1)
Re(1)–C(121)	2.09 (1)	O(21)–C(21)	1.13 (1)
Re(2)–Cl(21)	2.538 (2)	N(112)–C(111)	1.13 (1)
Re(2)–Cl(22)	2.404 (3)	N(112)–C(113)	1.47 (1)
Re(2)–P(21)	2.494 (3)	N(122)–C(121)	1.13 (1)
Re(2)–P(22)	2.468 (3)	N(122)–C(123)	1.48 (2)

Angles

Re(2)–Re(1)–Cl(11)	168.33 (7)	Re(1)–Re(2)–P(22)	94.63 (6)
Re(2)–Re(1)–P(11)	94.67 (6)	Re(1)–Re(2)–C(21)	84.5 (3)
Re(2)–Re(1)–P(12)	97.29 (6)	Cl(21)–Re(2)–Cl(22)	89.93 (8)
Re(2)–Re(1)–C(111)	87.9 (2)	Cl(21)–Re(2)–P(21)	85.3 (1)
Re(2)–Re(1)–C(121)	106.6 (3)	Cl(21)–Re(2)–P(22)	82.59 (9)
Cl(11)–Re(1)–P(11)	86.77 (9)	Cl(21)–Re(2)–C(21)	77.6 (3)
Cl(11)–Re(1)–P(12)	79.1 (1)	Cl(22)–Re(2)–P(21)	87.5 (1)
Cl(11)–Re(1)–C(111)	80.7 (3)	Cl(22)–Re(2)–P(22)	87.2 (1)
Cl(11)–Re(1)–C(121)	84.9 (3)	Cl(22)–Re(2)–C(21)	167.4 (3)
P(11)–Re(1)–P(12)	162.84 (9)	P(21)–Re(2)–P(22)	166.74 (8)
P(11)–Re(1)–C(111)	82.8 (3)	P(21)–Re(2)–C(21)	92.7 (3)
P(11)–Re(1)–C(121)	92.9 (3)	P(22)–Re(2)–C(21)	89.8 (3)
P(12)–Re(1)–C(111)	85.4 (3)	C(111)–N(112)–C(113)	175 (1)
P(12)–Re(1)–C(121)	95.4 (3)	C(121)–N(122)–C(123)	178 (1)
C(111)–Re(1)–C(121)	165.2 (4)	Re(2)–C(21)–O(21)	175.6 (8)
Re(1)–Re(2)–Cl(21)	161.86 (6)	Re(1)–C(111)–N(112)	173.9 (8)
Re(1)–Re(2)–Cl(22)	107.89 (6)	Re(1)–C(121)–N(122)	175 (1)
Re(1)–Re(2)–P(21)	98.56 (6)		

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

Scheme I. Reactions of $Re_2Cl_4(dppm)_2(CO)(CNxyl)$ To Give **2b** and **2c**



Model CV-1A instrument in conjunction with a Hewlett-Packard Model 7035 B X-Y recorder. X-Band ESR spectra of frozen dichloromethane solutions were recorded at −160 °C with the use of a Varian E-109 spectrometer. Conductivity measurements were performed on 1×10^{-3} M acetone solutions with an Industrial Instruments Inc. Model RC-16B2 conductivity bridge. $^{31}P\{^1H\}$ NMR spectra were recorded on a Varian XL-200 spectrometer operated at 80.98 MHz and using an internal deuterium lock and 85% H_3PO_4 as an external standard. ^1H NMR spectra were obtained on a Varian XL-200 spectrometer. Resonances were referenced internally to the protio component in the incompletely deuteriated solvent.

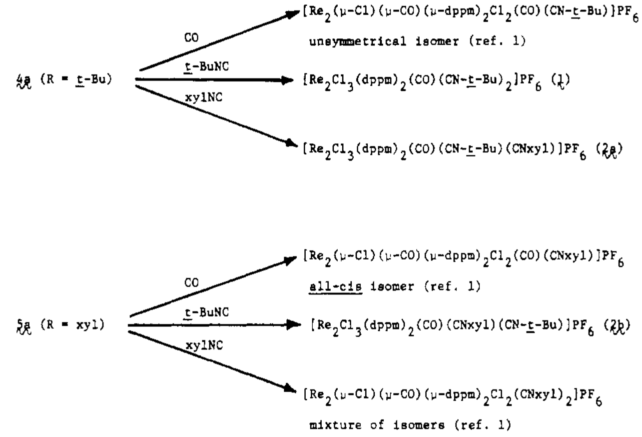
Analytical Procedures. Elemental microanalyses were performed by Dr. H. D. Lee of the Purdue University Microanalytical Laboratory.

Results

Some of the more important transformations observed in this work are summarized in Schemes I and II.

A. Reactions of $Re_2Cl_4(dppm)_2(CO)(CNR)$ (R = *t*-Bu, xyl) with Isocyanides. The monocarbonyl complex $Re_2Cl_4(dppm)_2(CO)$[3,4] is known to react with 1 equiv of isocyanide to yield complexes of stoichiometry $Re_2Cl_4(dppm)_2(CO)(CNR)$ (R = *t*-Bu, xyl), which differ structurally.[4] The xylyl isocyanide derivative has been shown by X-ray crystallography to possess an edge-shared bioctahedral structure in which the CO ligand is bridging, viz. $Cl_2Re(\mu\text{-}Cl)(\mu\text{-}CO)(\mu\text{-}dppm)_2ReCl(CNxyl)$.[4] This complex reacts with additional xylNC, in the presence of $TlPF_6$, to form $[Re_2Cl_3(dppm)_2(CO)(CNxyl)_2]PF_6$, which exists in two isomeric forms, both of which contain a bridging carbonyl ligand.[1]

Scheme II. Reactions of $[Re_2Cl_3(dppm)_2(CO)(CNR)(NCMe)]PF_6$ (**4a**, R = *t*-Bu; **5a**, R = xyl) with CO and Isocyanides[a]



[a] All reactions were carried out with CH_2Cl_2 as the reaction solvent.

The *tert*-butyl isocyanide complex $Re_2Cl_4(dppm)_2(CO)(CN\text{-}t\text{-}Bu)$ contains no bridging CO or isocyanide ligand and most likely has a structure that can be represented as $Cl_2(CO)Re(\mu\text{-}dppm)_2ReCl_2(CN\text{-}t\text{-}Bu)$.[4] It reacts with a further 1 equiv of *t*-BuNC, in the presence of $TlPF_6$, to give the complex $[Re_2Cl_3(dppm)_2(CO)(CN\text{-}t\text{-}Bu)_2]PF_6$ (**1**). The possibility that **1** and, by implication, $Re_2Cl_4(dppm)_2(CO)(CN\text{-}t\text{-}Bu)$[4] do not possess an edge-shared bioctahedral geometry has been examined. A batch of red-brown crystals of **1** was grown from a dichloromethane–methanol solvent mixture, and a suitable single crystal was selected and subjected to an X-ray structure analysis. Subsequent analysis of the data indicated that the crystal was that of the salt $[Re_2Cl_3(dppm)_2(CO)(CN\text{-}t\text{-}Bu)_2](PF_6)_{0.5}(OMe)_{0.5}$ (see Experimental Section). The infrared spectrum (Nujol mull) and CV (cyclic voltammogram) of the crystals were found to be the same as those of the bulk synthetic batches of the complex. This sample was ESR silent (1:1 CH_2Cl_2–toluene at −150 °C), in accord with the expected diamagnetism of the cation. The ^1H NMR spectrum of these crystals (recorded in $(CD_3)_2CO$) showed a resonance at $\delta = +3.33$ that may be attributed to methanol (CH_3); this could form through the reaction of methoxide anion with trace amounts of water present in the solvent. We note that the identification of methoxide ion in the structure of transition-metal complexes is not without precedent.[16]

The structure of the cation (Figure 1) resembles that of a molecule of the M_2L_8 type,[17] with two additional chloride ligands in axial positions. Some important bond distances and angles for $[Re_2Cl_3(dppm)_2(CO)(CN\text{-}t\text{-}Bu)_2]^+$ are listed in Table III.

The complex $Re_2Cl_4(dppm)_2(CO)(CN\text{-}t\text{-}Bu)$ reacts with 1 equiv of xylyl isocyanide, in the presence of $TlPF_6$, to yield the mixed-isocyanide species $[Re_2Cl_3(dppm)_2(CO)(CN\text{-}t\text{-}Bu)(CNxyl)]PF_6$ (**2a**). The IR spectrum and electrochemical properties of **2a**, which are summarized in Table IV, resemble closely those of **1**. All three π-acceptor ligands are terminally bound. The CV of **2a** in 0.1 M TBAH–CH_2Cl_2 displays an oxidation at $E_{1/2} = +1.55$ V and two irreversible reductions at $E_{p,c} = -0.55$ and −0.76 V (vs Ag/AgCl) together with several product waves. In the ^1H NMR spectrum of the complex there are two resonances for the methyl groups of the isocyanides: $\delta = +1.60$ for the *t*-Bu

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(16) See, for example: Bino, A. *J. Am. Chem. Soc.* **1987**, *109*, 275.

(17) (a) Cotton, F. A.; Walton, R. A. *Multiple Bonds Between Metal Atoms*; Wiley: New York, 1982. (b) Cotton, F. A.; Walton, R. A. *Struct. Bonding (Berlin)* **1985**, *62*, 1.

Table IV. Spectroscopic and Electrochemical Data for **2a–c** and **3**

complex	no.	IR spectra, cm^{-1} [a] ν(CN)	ν(CO)	CV half-wave potentials, V[b] $E_{1/2}(1)$	$E_{1/2}(2)$	$E_{1/2}(3)$	electronic abs spectra, λ, nm (ε)[c]	^1H NMR, δ[d] RNC	$-CH_2-$[e]	$^{31}P\{^1H\}$ NMR, δ[f]
$[Re_2Cl_3(dppm)_2(CO)(CN\text{-}t\text{-}Bu)(CNxyl)]PF_6$	**2a**	2161 s 2134 vs	1927 s	see text			520 sh	+1.60[g] +1.86[i]	+5.66[h]	−5.1 −8.6
$[Re_2Cl_3(dppm)_2(CO)(CNxyl)(CN\text{-}t\text{-}Bu)]PF_6$	**2b**	2174 s 1823 m, br	1980 s	+0.90 (ox)	−0.11 (red)	−1.05 (red)	970 (60), 444 (7500)	+0.30[g] +3.75[i]	+4.65[j] +4.75[j]	−19.7 −33.2
$[Re_2Cl_3(dppm)_2(CO)(CNxyl)(CN\text{-}t\text{-}Bu)]PF_6$	**2c**	2171 s 2140 s	1690 m	+1.34 (ox)	−0.29 (red)	−1.24 (red)	1180 (180), 800 (400), 400 (7300)	+0.83[g] +3.78[i]	+4.11[j] +4.50[j]	−15.7 −22.6
$Re_2Cl_3(dppm)_2(CO)(CNxyl)(CN\text{-}t\text{-}Bu)$	**3**	2132 s 1680 m, br	1932 s	+0.90 (ox)	−0.10 (ox)	−1.04 (red)	~725 br sh, 624 (1650), 446 (4100)	k		k

[a] Recorded as Nujol mulls. [b] Measured on 0.1 M TBAH–CH_2Cl_2 solutions and referenced to the Ag/AgCl electrode. Scan rate v = 200 mV/s at a Pt-bead electrode. [c] Dichloromethane solutions. [d] Spectra recorded in CD_2Cl_2. [e] The $-CH_2-$ resonances of the dppm ligands. [f] These spectra were recorded in CH_2Cl_2 with aqueous H_3PO_4 as an external standard. The spectra appear as AA′BB′ patterns; chemical shifts are of the most intense components of the pattern. [g] Methyl resonances of the *t*-Bu group. [h] Complex multiplet. [i] Methyl resonances of the xylyl group. [j] These $-CH_2-$ resonances appear as an AB pattern with superimposed P–H coupling. [k] Paramagnetic complex.

group and $\delta = +1.86$ for the xylyl group, which integrate well against the phenyl resonances. A complex AA′BB′ pattern is observed in the $^{31}P\{^1H\}$ NMR spectrum with $\delta = -5.1$ and -8.6 for the most intense inner components of the pattern.

Two other complexes that have the same stoichiometry as **2a**, but that clearly possess a different structural geometry, are prepared from the mixed carbonyl–xylyl isocyanide complex $Re_2Cl_4(dppm)_2(CO)(CNxyl)$ upon its reaction with 1 equiv of *t*-BuNC, in the presence of $TlPF_6$ (Scheme I). Reaction at room temperature gives isomer **2b**, while under reflux conditions isomer **2c** is formed. Note that **2b** and **2c** are formulated slighty differently from **2a** as $[Re_2Cl_3(dppm)_2(CO)(CNxyl)(CN\text{-}t\text{-}Bu)]PF$ i.e., the ordering of the isocyanide ligands in this formulation has been reversed, since while **2a** is derived from $Re_2Cl_4(dppm)_2(CO)(CN\text{-}t\text{-}Bu)$, **2b** and **2c** are formed from $Re_2Cl_4(dppm)_2(CO)(CNxyl)$.

The electrochemical properties of **2b** and **2c** (Table IV) are very similar to one another and also resemble those of most other complexes that contain mixtures of CO and RNC ligands (vide supra), namely one reversible oxidation and two reversible reductions. Hence, it is likely that **2b** and **2c** possess the edge-shared bioctahedral geometry. The IR spectrum of **2b** shows two sharp intense bands at 2174 and 1980 cm^{-1} along with a broad band of medium intensity at 1823 cm^{-1}. Originally, we suspected that this latter absorption was due to a semibridging carbonyl since $\nu(CO)_{terminal}$ modes usually fall between 2100 and 1950 cm^{-1}, while $\nu(CO)_{bridging}$ modes occur between 1770 and 1680 cm^{-1}. The band at 1823 cm^{-1} in **2b** falls between these two ranges. However, the carbon-13 derivative of **2b** was synthesized, i.e. $[Re_2Cl_3(dppm)_2(^{13}CO)(CNxyl)(CN\text{-}t\text{-}Bu)]PF_6$, and its IR spectrum was found to be the same as that for the carbon-12 analogue except that the band at 1980 cm^{-1} had shifted to 1930 cm^{-1}. This is clear-cut evidence that **2b** contains a terminal CO ligand. In all the mixed carbonyl–isocyanide complexes derived from $Re_2X_4(dppm)_2$ that we have reported to date, the ν(CN) modes of the *t*-BuNC ligands are always greater than $\simeq$2160 cm^{-1}, while the ν(CN) modes for the xylNC ligands appear at frequencies of $\simeq$2150 cm^{-1} or below. This suggests that the band at 2174 cm^{-1} in **2b** is most likely due to the *t*-BuNC ligand, thus leaving the band at 1823 cm^{-1} to be accounted for. This could correspond to the ν(CN) mode of a bridging or, possibly, a semibridging xylNC ligand. Unfortunately, we have not yet been successful in growing single crystals of **2b** that are suitable for an X-ray structure determination.

The IR spectrum of isomer **2c** is different from that of **2b** (Table IV). There are two intense bands at 2171 and 2140 cm^{-1} and a sharp band at 1690 cm^{-1} of medium intensity. Carbon-13-labeling studies have established that the band at 1690 cm^{-1} is due to a bridging CO ligand; the ^{13}CO derivative of **2c**, i.e. $[Re_2Cl_3(dppm)_2(^{13}CO)(CNxyl)(CN\text{-}t\text{-}Bu)]PF_6$, has a band for the $\nu(^{13}CO)$ mode at 1640 cm^{-1}. Isomer **2b** is converted into **2c** upon heating in 1,2-dichloroethane (Scheme I). The mechanism is likely to be very similar to that found in the case of the isomerization reactions of $[Re_2Cl_3(dppm)_2(CO)_2(CNR)]PF_6$ and $[Re_2Cl_3(dppm)_2(CO)(CNxyl)_2]PF_6$ that were reported previously.[1]

Isomer **2b** can be reduced by cobaltocene to the green neutral species $Re_2Cl_3(dppm)_2(CO)(CNxyl)(CN\text{-}t\text{-}Bu)$ (**3**). This is analogous to the previously reported chemical reductions of $[Re_2Cl_3(dppm)_2(CO)_2(CN\text{-}t\text{-}Bu)]PF_6$ to give $Re_2Cl_3(dppm)_2(CO)_2(CN\text{-}t\text{-}Bu)$.[1,9] The CV of **3** possesses two couples that correspond to oxidations of the bulk complex and one that is due to a reduction (Table IV). As expected, a shift in the IR-active ν(CN) and ν(CO) modes to lower frequencies is observed on going from the Re_2^{4+} precursor complex to the reduced neutral complex. Note that the broad band at 1823 cm^{-1} in the spectrum of **2b** shifts to 1680 cm^{-1} in **3**. The neutral complex **3** is paramagnetic, as evidenced by its X-band ESR spectrum at −160 °C in dichloromethane–toluene; a broad complex signal is centered at $g \simeq 2.14$. The magnetic moment of a dichloromethane solution of **3** was determined to be 1.72 μ_B by Evans' method.[18]

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(18) Evans, D. F. *J. Chem. Soc.* **1959**, 2003.

Table V. Spectroscopic and Electrochemical Data for **4a**, **4b**, **5a**, and **5b**

		IR spectra, cm^{-1} [a]			CV half-wave potentials, V [b]			
complex	no.	ν(NC)	ν(CN)	ν(CO)	$E_{1/2}(1)$	$E_{1/2}(2)$	$E_{1/2}(3)$	electronic abs spectra, λ, nm (ϵ) [c]
$[\mathrm{Re_2Cl_3(dppm)_2(CO)(CN}\text{-}t\text{-}\mathrm{Bu)(NCMe)]PF_6}$	**4a**	2284 vw	2155 vs	1948 vs		see text		~500 sh
$[\mathrm{Re_2Cl_3(dppm)_2(CO)(CN}\text{-}t\text{-}\mathrm{Bu)(NCEt)]PF_6}$	**4b**	2275 vw	2153 vs	1947 vs		see text		~480 sh
$[\mathrm{Re_2Cl_3(dppm)_2(CO)(CNxyl)(NCMe)]PF_6}$	**5a**	2292 vw	2126 vs	1701 m	+1.18 (ox)	−0.35 (red)	−1.30 (red)	1310 (130), 790 (330), 434 (6600)
$[\mathrm{Re_2Cl_3(dppm)_2(CO)(CNxyl)(NCEt)]PF_6}$	**5b**	2286 vw	2141 vs	1692 m	+1.17 (ox)	−0.32 (red)	−1.26 (red)	1310 (130), 790 (380), 436 (7100)

[a] Recorded as Nujol mulls. [b] Measured on 0.1 M TBAH–$\mathrm{CH_2Cl_2}$ solutions and referenced to the Ag/AgCl electrode. Scan rate v = 200 mV/s at a Pt-bead electrode. [c] Dichloromethane solutions.

B. Synthesis and Characterization of $[\mathrm{Re_2Cl_3(dppm)_2(CO)(CNR)(NCR')]PF_6}$ (4 and 5) (R = *t*-Bu, xyl; R′ = Me, Et). When $\mathrm{Re_2Cl_4(dppm)_2(CO)(CN}\text{-}t\text{-}\mathrm{Bu)}$ is dissolved in a 1:1 mixture of dichloromethane and nitrile, in the presence of $\mathrm{TlPF_6}$, a dark red solution forms along with a white precipitate of TlCl. Workup of these solutions yields pink products of stoichiometry $[\mathrm{Re_2Cl_3(dppm)_2(CO)(CN}\text{-}t\text{-}\mathrm{Bu)(NCR')]PF_6}$ (**4a**, R′ = Me; **4b**, R′ = Et). Conductivity measurements on solutions of **4a** and **4b** in acetone ($\simeq 1 \times 10^{-3}$ M) confirm them to be 1:1 electrolyes ($\Lambda_m \simeq 135\ \Omega^{-1}\ \mathrm{cm^2\ mol^{-1}}$), while IR spectral results, summarized in Table V, show the presence of terminal carbonyl, terminal isocyanide, and terminal nitrile ligands.

The electrochemical properties of these salts are similar to those of **1** and **2a**, i.e. $[\mathrm{Re_2Cl_3(dppm)_2(CO)(CN}\text{-}t\text{-}\mathrm{Bu)L]PF_6}$, where L = *t*-BuNC or xylNC. Complexes **4a** and **4b** possess an irreversible oxidation at $E_{p,a} \simeq +1.6$ V and an irreversible reduction at $E_{p,c} \simeq -0.75$ V (vs. Ag/AgCl). In the case of **4a**, the oxidation at $E_{p,a} = +1.55$ V has a coupled reduction wave at $E_{p,c} \simeq +1.35$ V, while the reduction at −0.74 V has a coupled oxidation wave at $E_{p,a} \simeq -0.54$ V; for neither of these couples is the current ratio $i_{p,a}/i_{p,c}$ equal to unity. The $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR spectrum of the propionitrile derivative **4b** (recorded in $\mathrm{CH_2Cl_2}$) is a complex AA′BB′ pattern with $\delta = -6.8$ and -9.8 for the most intense inner components of the pattern.

Green products result from the reactions of $\mathrm{Re_2Cl_4(dppm)_2(CO)(CNxyl)}$ with an excess of nitrile, in the presence of $\mathrm{TlPF_6}$. These are formulated as $[\mathrm{Re_2Cl_3(dppm)_2(CO)(CNxyl)(NCR')]PF_6}$ (**5a**, R′ = Me; **5b**, R′ = Et) and they have spectroscopic and electrochemical properties different from those of their *t*-BuNC analogues **4a** and **4b** (Table V). IR spectral measurements show terminal nitrile and terminal isocyanide ligands but also a bridging CO ligand (νCO) $\simeq$ 1700 $\mathrm{cm^{-1}}$). This result is not surprising since the starting compound $\mathrm{Re_2Cl_4(dppm)_2(CO)(CNxyl)}$ also contains a bridging CO ligand.[4] The $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR spectrum of **5a** (recorded in $\mathrm{CH_2Cl_2}$) is a complex AA′BB′ pattern with $\delta = -14.1$ and -17.5 for the most intense inner components of the pattern.

A reversible one-electron oxidation at $E_{1/2} \simeq +1.2$ V and two reversible one-electron reductions at $E_{1/2} \simeq -0.35$ V and $E_{1/2} \simeq -1.3$ V (vs Ag/AgCl) are seen in their cyclic voltammograms. Similar electrochemical properties, i.e. one oxidation and two reductions, are observed for the all-cis isomer of $[\mathrm{Re_2Cl_3(dppm)_2(CO)(CNxyl)_2]PF_6}$[1] and complex **2c** (Table IV), which, like **5a** and **5b**, are prepared from $\mathrm{Re_2Cl_4(dppm)_2(CO)(CNxyl)}$. There is also a close resemblance between the electronic absorption spectra of these four complexes.

C. Substitution Reactions of the Nitrile-Containing Complexes 4a and 5a. The lability of the nitrile ligands R′CN in the complexes of types **4** and **5** has been demonstrated by the ready displacement of the acetonitrile ligand in **4a** and **5a** by CO, *t*-BuNC, and xylNC. These reactions, which are summarized in Scheme II, give rise to products that have been described previously in section A or in ref 1.

Discussion

A. Structural Conclusions. The earlier suspicion[4] that the complex $\mathrm{Re_2Cl_4(dppm)_2(CO)(CN}\text{-}t\text{-}\mathrm{Bu)}$ possesses a structure that is quite different from that of its xylyl isocyanide analogue (i.e. $\mathrm{Cl_2Re(\mu\text{-}Cl)(\mu\text{-}CO)(\mu\text{-}dppm)_2ReCl(CNxyl)}$) has been confirmed through the preparation and structural characterization of its derivative with *tert*-butyl isocyanide, viz. $[\mathrm{Re_2Cl_3(dppm)_2(CO)(CN}\text{-}t\text{-}\mathrm{Bu)_2]PF_6}$ (**1**). The structure of the cation (Figure 1) is based upon a metal–metal-bonded $\mathrm{L_5MML_5}$ type of geometry with two trans bridging dppm ligands. The *t*-BuNC ligands are coordinated to the same rhenium atom and are trans to one another, while on the other rhenium atom the carbonyl is trans to a chloride ligand. This result confirms that **1** and its precursor $\mathrm{Re_2Cl_4(dppm)_2(CO)(CN}\text{-}t\text{-}\mathrm{Bu)}$ do indeed possess structures that are different from the more commonly encountered edge-shared bioctahedral species.[1,2,5]

The Re–Re distance of 2.379 (1) Å is in accord with the presence of a $\mathrm{Re}\equiv\mathrm{Re}$ bond, but it is longer and weaker than usual (cf. the Re–Re distance in $[\mathrm{(PhCN)_2ClRe(\mu\text{-}dppm)_2ReCl_2]PF_6}$ of 2.270 (1) Å),[10] because of back-bonding involving the π-components of the $\sigma^2\pi^4\delta^2\delta^{*2}$ metal–metal bond and the π^* orbitals on the terminal CO and *t*-BuNC ligands. However, the Re–Re distance in the structure of the $[\mathrm{Re_2Cl_3(dppm)_2(CO)(CN}\text{-}t\text{-}\mathrm{Bu)_2]^+}$ cation contrasts with the much longer distances (2.58–2.61 Å) found for the complexes that are edge-sharing bioctahedra and contain the $[\mathrm{Re_2(\mu\text{-}Cl)(\mu\text{-}CO)(\mu\text{-}dppm)_2}]$ unit, i.e. $\mathrm{Re_2(\mu\text{-}Cl)(\mu\text{-}CO)(\mu\text{-}dppm)_2Cl_3(CO)}$,[3] $\mathrm{Re_2(\mu\text{-}Cl)(\mu\text{-}CO)(\mu\text{-}dppm)_2Cl_3(CNxyl)}$,[4] $[\mathrm{Re_2(\mu\text{-}Cl)(\mu\text{-}CO)(\mu\text{-}dppm)_2Cl_2(CO)(NCEt)]PF_6}$,[9] $[\mathrm{Re_2(\mu\text{-}Cl)(\mu\text{-}CO)(\mu\text{-}dppm)_2Cl_2(CO)(CN}\text{-}t\text{-}\mathrm{Bu)]PF_6}$,[1] and $[\mathrm{Re_2(\mu\text{-}Cl)(\mu\text{-}CO)(\mu\text{-}dppm)_2Cl_2(CO)_2]PF_6}$.[5] These longer distances are comparable to the Re–Re distance in the doubly bonded dirhenium(III) complex $\mathrm{Re_2(\mu\text{-}Cl)_2(\mu\text{-}dppm)_2Cl_4}$.[19] Thus, the formation of a μ-CO unit in these dirhenium complexes gives the same effect as a net two-electron oxidation from $\mathrm{Re_2}^{4+}$ to $\mathrm{Re_2}^{6+}$, as in the change from $\mathrm{Re_2(\mu\text{-}dppm)_2Cl_4}$ to $\mathrm{Re_2(\mu\text{-}Cl)_2(\mu\text{-}dppm)_2Cl_4}$, where the Re–Re distance increases from 2.234 (3)[20] to 2.616 (1) Å.[19] As mentioned elsewhere,[4,11] such an increase in Re–Re distance in the case of the carbonyl-containing complexes is tantamount to treating the μ-CO ligand as forming a divalent bridge.

The remaining structural features for this complex are normal, as for related complexes that contain the $\mathrm{Re(\mu\text{-}dppm)_2Re}$ unit, e.g. $\mathrm{Re_2(\mu\text{-}dppm)_2Cl_4}$[20] and $[\mathrm{Re_2(\mu\text{-}dppm)_2Cl_3(NCPh)_2]PF_6}$.[10] However, two additional points are worthy of note. First, the nonlinearity of the Re–Re–Cl units (162–168°), which involve the long axial bonds Re(1)–Cl(11) and Re(2)–Cl(21) (2.496 (2) and 2.538 (2) Å, respectively), presumably reflects the minimization of steric repulsions in these relatively crowded axial sites. Second, while the *average* torsional angle (χ) for this complex is 16.8°, the two contributing P–Re–Re–P angles are appreciably different from one another; i.e., P(11)–Re(1)–Re(2)–P(21) and P(12)–Re(1)–Re(2)–P(22) are 11.5 and 22.5°, respectively. These values can be compared with $\chi = 47°$ (average) and $\chi = 22.2°$ for the pairs of P–Re–Re–P torsional angles of $\mathrm{Re_2(\mu\text{-}dppm)_2Cl_4}$[20] and $[\mathrm{Re_2(\mu\text{-}dppm)_2Cl_3(NCPh)_2]PF_6}$,[10] respectively, compounds that, like **1**, possess no bridging groups except the two trans dppm ligands. There is of course no electronic barrier to rotation about the $\mathrm{Re}\equiv\mathrm{Re}$ bond in these complexes,[17] so the value of χ reflects a compromise between steric effects and the conformational demands of the fused $\overline{\mathrm{Re{-}Re{-}PCH_2P}}$ rings.

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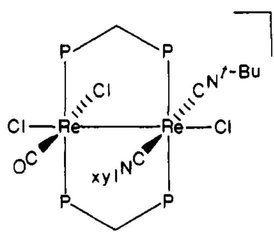
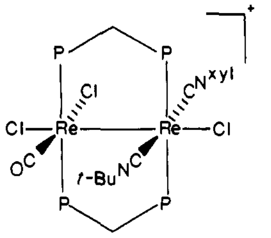
(19) Barder, T. J.; Cotton, F. A.; Lewis, D.; Schwotzer, W.; Tetrick, S. M.; Walton, R. A. *J. Am. Chem. Soc.* **1984**, *106*, 2882.

(20) Barder, T. J.; Cotton, F. A.; Dunbar, K. R.; Powell, G. L.; Schwotzer, W.; Tetrick, S. M.; Walton, R. A. *Inorg. Chem.* **1985**, *24*, 2550.

Since the IR spectrum and electrochemical properties of the complex $[Re_2Cl_3(dppm)_2(CO)(CN\text{-}t\text{-}Bu)(CNxyl)]PF_6$ (**2a**) are very similar to those of **1**, it is likely that **2a** has one of the two structures

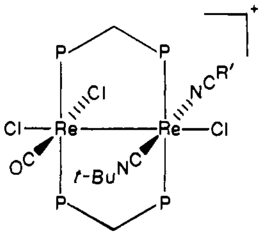


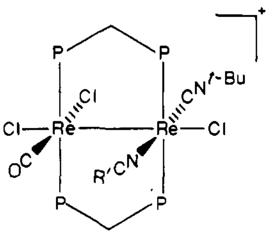


This is of course anticipated because of the similarity in the synthetic procedures for **1** and **2a**, both of which are prepared directly from $Re_2Cl_4(dppm)_2(CO)(CN\text{-}t\text{-}Bu)$.

Complexes **2b** and **2c** are clearly structural isomers of **2a**. Both complexes are prepared from $Re_2Cl_4(dppm)_2(CO)(CNxyl)$, which itself possesses an edge-shared bioctahedral structure.[4] The probable structures of **2b** and **2c** are represented in Scheme I and are based primarily upon their IR spectral properties. These sorts of all-cis arrangements of carbonyl and isocyanide ligands are commonly encountered for other complexes of this type when derived from $Re_2(\mu\text{-}dppm)_2Cl_4$.[2,5]

The preceding observations that concern differences in the structures of the products obtained by reacting $Re_2Cl_4(dppm)_2(CO)(CN\text{-}t\text{-}Bu)$ and $Re_2Cl_4(dppm)_2(CO)(CNxyl)$ with isocyanides are similar to the conclusions that can be reached when nitriles are used in place of the isocyanide ligands. Thus, for the nitrile complexes $[Re_2Cl_3(dppm)_2(CO)(CN\text{-}t\text{-}Bu)(NCR')]PF_6$ (**4a**, R′ = Me; **4b**, R′ = Et), which have properties very similar to those of **1** and **2a**, it must be concluded that **4a** and **4b** possess a structure similar to that of **1**; i.e., the isocyanide and nitrile ligands are coordinated to the same rhenium atom in a trans disposition to one another, while the terminal CO ligand is bonded to the other rhenium atom. Two possible structures are





In a similar vein, the preparation of $[Re_2Cl_3(dppm)_2(CO)(CNxyl)(NCR')]PF_6$ (**5a**, R′ = Me; **5b**, R′ = Et) from $Re_2Cl_4(dppm)_2(CO)(CNxyl)$ gives rise to products whose IR spectra and electrochemical properties are similar to those of the all-cis isomers of $[Re_2Cl_3(dppm)_2(CO)(CNxyl)_2]PF_6$ (see ref 1) and **2c** (Scheme I). Accordingly, structures similar to that of **2c** can be predicted in which the μ-CO, RNC, and R′CN ligands reside on the same side of the molecule in an all-cis arrangement.

The lability of the nitrile ligands in **4a** and **5a** is illustrated in Scheme II. The usefulness of such nitrile displacement reactions is further shown by the conversion of $[Re_2Cl_3(dppm)_2(CO)(NCMe)_2]PF_6$, a complex that possesses an all-cis arrangement of terminal MeCN and μ-CO ligands, into $[Re_2Cl_3(dppm)_2(CO)_2(NCMe)]PF_6$ and $[Re_2Cl_3(dppm)_2(CO)_2(CNxyl)]PF_6$ by its reactions with CO and xylNC in acetone (see Experimental Section). These two latter complexes have been prepared previously by the alternative means of reacting $Re_2Cl_4(dppm)_2(CO)_2$ with MeCN or xylNC, in the presence of $TlPF_6$.[9] These reactions join others that have found a similar utility, namely, the reactions of $[Re_2Cl_3(dppm)_2(CN\text{-}t\text{-}Bu)(NCEt)]PF_6$ with an excess of t-BuNC to yield $[Re_2Cl_3(dppm)_2(CN\text{-}t\text{-}Bu)_3]PF_6$[8] and of $[Re_2Cl_3(dppm)_2(CO)_2(NCEt)]PF_6$ with t-BuNC to give $[Re_2Cl_3(dppm)_2(CO)_2(CN\text{-}t\text{-}Bu)]PF_6$.[9]

B. Concluding Remarks. The work described in the present report establishes that, in addition to the possibility of isomerism occurring with the various edge-shared bioctahedral species that are formed upon reacting $Re_2X_4(dppm)_2$ with CO, isocyanide, and nitrile ligands,[1] there also exist structural isomers that are based upon a L_5MML_5 geometry in which there are no μ-Cl or μ-CO ligands present, viz., in $Re_2Cl_4(dppm)_2(CO)(CN\text{-}t\text{-}Bu)$, $[Re_2Cl_3(dppm)_2(CO)(CN\text{-}t\text{-}Bu)_2]PF_6$ (**1**), $[Re_2Cl_3(dppm)_2(CO)(CN\text{-}t\text{-}Bu)(CNxyl)]PF_6$ (**2a**), and $[Re_2Cl_3(dppm)_2(CO)(CN\text{-}t\text{-}Bu)(NCR')]PF_6$ (**4a**, R′ = Me; **4b**, R′ = Et). The type of structure assumed appears to be strongly influenced by the choice of isocyanide (alkyl or aryl) and, also, the sequence in which the π-acceptors are coordinated to the dirhenium center.

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Supplementary Material Available: A listing of positional parameters and their errors for phenyl ring atoms (Table S1), a listing of thermal parameters (Table S2), complete listings of bond distances (Table S3) and bond angles (Table S4), and a figure showing the full atomic numbering scheme (Figure S1) (14 pages); a table of observed and calculated structure factors (28 pages). Ordering information is given on any current masthead page.