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Reactions of the Dirhenium(II) Complexes $Re_2X_4(dppm)_2$ (X = Cl or Br; dppm = $Ph_2PCH_2PPh_2$) with Isocyanides. 4.[1] Isomerism in Mixed Carbonyl–Isocyanide Complexes of Stoichiometry $[Re_2Cl_3(dppm)_2(CO)_2(CNR)]^{n+}$ (*n* = 0 or 1) and $[Re_2Cl_3(dppm)_2(CO)(CNR)_2]^+$ (R = *t*-Bu or Xylyl), Which Possess Edge-Shared Bioctahedral Structures

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The multiply bonded dirhenium isocyanide complexes $Re_2Cl_4(dppm)_2(CNR)$ (R = *t*-Bu or xylyl) react with gaseous CO at room temperature and 1 atm pressure, in the presence of $TlPF_6$, to yield the mixed isocyanide–carbonyl species $[Re_2Cl_3(dppm)_2(CO)_2(CNR)]PF_6$ (**1a**, R = *t*-Bu; **1b**, R = xylyl). The reaction of $Re_2Cl_4(dppm)_2(CO)(CN\text{-}t\text{-}Bu)$ with CO in the presence of $TlPF_6$ also provides a high yield route to **1a**. In the case of both **1a** and **1b**, thermal isomerization to the isomers (**2a** and **2b**), which contain an all-cis arrangement of CO and CNR ligands, occurs. Complexes **2a** and **2b** and others of this kind can be prepared directly by the reaction of $Re_2Cl_4(dppm)_2(CO)_2$ with RNC in the presence of $TlPF_6$; the xylylNC derivative has also been prepared from the reaction of $Re_2Cl_4(dppm)_2(CO)(CNxylyl)$ with CO and $TlPF_6$. The spectroscopic (IR, NMR, and electronic absorption) and electrochemical properties of **1** and **2**, while generally similar to one another, nonetheless show some important differences. Complexes **1** and **2** can be reduced (by one electron) to their neutral, structurally related analogues **3** and **4**, respectively, by using acetone solutions of cobaltocene. Representative X-ray crystal structures of **1a** and **4** (R = *i*-Pr) have helped aid in the characterization of these systems. Compound **1a**, $[Re_2Cl_3(dppm)_2(CO)_2(CN\text{-}t\text{-}Bu)]PF_6$, crystallizes along with two formula units of dichloromethane in the triclinic system, space group $P1$, with a = 10.950 (4) Å, b = 12.353 (4) Å, c = 13.358 (5) Å, α = 108.55 (3)°, β = 96.56 (3)°, γ = 104.77 (3)°, V = 1618 (1) $Å^3$, and Z = 1. Difference-structure direct methods was found to be the only available technique leading to successful development of the structure. Least-squares refinement of 745 variables to 5478 data gave final residuals of R = 0.025 and R_w = 0.035 and quality of fit 0.896. This compound has an edge-sharing bioctahedral structure and a Re–Re bond distance of 2.605 (1) Å. The equatorial plane, which comprises the $[Re_2Cl_3(CO)_2(CN\text{-}t\text{-}Bu)]$ unit, has a cis arrangement of two CO ligands on one side, while the other side has the *t*-BuNC ligand, viz. Cl(CO)Re(μ-Cl)(μ-CO)ReCl(CN-*t*-Bu). The molecule Cl(CO)Re(μ-Cl)(μ-CO)(μ-$dppm)_2$ReCl(CN-*i*-Pr) (**4**) crystallizes in the tetragonal system, space group $P4_32_12$, with a = 15.033 (7) Å, c = 26.366 (14) Å, V = 5959 (7) $Å^3$, and Z = 4. The structure was refined to residuals of R = 0.054 and R_w = 0.074 and quality of fit 1.558. The Re–Re bond distance is 2.718 (1) Å. The terminal sites occupied by the carbonyl and isocyanide ligands are disordered due to the presence of a crystallographic twofold axis. An infrared spectrum of the crystalline sample used in this study is in accord with the structure found in the solid state. The molecule possesses one bridging and one terminal carbonyl ligand as well as a terminal CN-*i*-Pr ligand. Structural isomerism has also been encountered in the case of the mixed carbonyl–isocyanide complexes of stoichiometry $[Re_2Cl_3(dppm)_2(CO)(CNR)_2]PF_6$ (**5**, R = *t*-Bu; **6** and **7**, R = xylyl). These complexes can be prepared from the monocarbonyl $Re_2Cl_4(dppm)_2(CO)$ or from $Re_2Cl_4(dppm)_2(CO)(CNR)$ by using 2 or 1 equiv of the RNC ligand, respectively, in the presence of $TlPF_6$. Whereas **5** is believed to contain dppm bridges and terminally bound CO and *t*-BuNC ligands, the isomers **6** and **7** of the xylyl isocyanide derivative most likely possess structures that are closely akin to those of **1** and **2**, respectively. Thermal isomerization of **6** to the all-cis isomer **7** occurs in 1,2-dichloroethane.

Introduction

We have discovered that the triply bonded dirhenium(II) species $Re_2(\mu\text{-dppm})_2X_4$ (X = Cl or Br; dppm = bis(diphenylphosphino)methane) react with carbon monoxide and alkyl isocyanide ligands to form complexes such as $Re_2(\mu\text{-}X)(\mu\text{-dppm})_2X_3L$ (L = CO or RNC),[3–6] $Re_2(\mu\text{-Cl})(\mu\text{-CO})(\mu\text{-dppm})_2Cl_3(CO)$,[4] $Re_2Cl_4(dppm)_2(CO)(CNR)$,[6] and $[Re_2Cl_3(dppm)_2(CNR)_2]PF_6$,[1,5] in which a Re–Re multiple bond is preserved. In all such compounds, a pair of bridging dppm ligands is retained. In subsequent studies of the chemistries of these complexes, we have uncovered some interesting cases of structural isomerism and describe in the present report the details of this discovery.

Experimental Section

Starting Materials. The mono(isocyanide) adducts $Re_2Cl_4(dppm)_2(CNR)$, where R = *t*-Bu or xylyl, the monocarbonyl complex $Re_2Cl_4(dppm)_2(CO)$, the dicarbonyl complex $Re_2Cl_4(dppm)_2(CO)_2$, and the mixed carbonyl–isocyanide complexes $Re_2Cl_4(dppm)_2(CO)(CNR)$, where R = *t*-Bu or xylyl, were prepared from the reactions between $Re_2Cl_4(dppm)_2$ and the appropriate ligands according to the reported methods.[3,4,6] The isocyanide ligands *i*-PrNC and *t*-BuNC were prepared by a standard procedure,[7] 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 nitrogen or under 1 atm of carbon monoxide.

A. Reactions of $Re_2Cl_4(dppm)_2(CNR)$ with Carbon Monoxide. (i) $[Re_2Cl_3(dppm)_2(CO)_2(CN\text{-}t\text{-}Bu)]PF_6$ (1a). A mixture of $Re_2Cl_4(dppm)_2(CN\text{-}t\text{-}Bu)$ (0.15 g, 0.11 mmol) and $TlPF_6$ (0.038 g, 0.11 mmol) was suspended in 10 mL of acetone. Carbon monoxide was bubbled through the suspension for 45 min to yield a yellow-green solution and a white precipitate of TlCl. The solution was filtered to remove the TlCl, and KPF_6 (0.05 g) was added to the filtrate. The acetone solution was evaporated to dryness, and the residue was extracted with 10 mL of dichloromethane. The extract was filtered, and diethyl ether was added to the resulting filtrate. A yellow-green product precipitated upon allowing this solution to stand at 0 °C. It was collected, washed with hexane, and dried in vacuo; yield 0.142 g, 85%. Anal. Calcd for $C_{57}H_{53}Cl_3F_6NO_2P_5Re_2$: C, 44.61; H, 3.50. Found: C, 44.56; H, 3.81.

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Table I. Crystal Data for $[Re_2Cl_3(dppm)_2(CO)_2(CN\text{-}t\text{-}Bu)]PF_6{\cdot}2CH_2Cl_2$ (**1a**·$2CH_2Cl_2$) and $Re_2Cl_3(dppm)_2(CO)_2(CN\text{-}i\text{-}Pr)$ (**4**)

	1a	**4**
formula	$Re_2Cl_7P_5F_6O_2NC_{59}H_{57}$	$Re_2Cl_3P_4O_2N_2C_{56}H_{51}$
fw	1701.6	1372.69
space group	$P1$	$P4_32_12$
systematic absences	none	$00l$, $l \neq 4n$; $0k0$, $k \neq 2n$
a, Å	10.950 (4)	15.033 (7)
b, Å	12.353 (4)	15.033 (7)
c, Å	13.358 (5)	26.366 (14)
α, deg	108.55 (3)	90
β, deg	96.56 (3)	90
γ, deg	104.77 (3)	90
V, Å^3	1618 (1)	5959 (7)
Z	1	4
d_{calcd}, g/cm^3	1.75	1.473
cryst size, mm	0.51 × 0.34 × 0.32	0.30 × 0.30 × 0.25
μ(Mo Kα), cm^{-1}	44.3	43.9
data collecn instrument	Syntex P$\bar{1}$	Syntex P$\bar{1}$
radiation (monochromated in incident beam); λ_α, Å	Mo Kα; 0.71073	Mo Kα; 0.71073
orientation reflns: no., range (2θ), deg	15; $24 < 2\theta < 34$	13; $20 < 2\theta < 30$
temp, °C	3.5 ± 2	25 ± 1
scan method	ω–2θ	ω–2θ
data collecn range, 2θ, deg	4.0–55.0	4.0–47.0
no. of unique data, total with $F_o^2 > 3\sigma(F_o^2)$	5866, 5478	2027, 1690
no. of params refined	745	279
trans. factors: max, min	obsd 1.00, 0.88	obsd 1.00, 0.81
R^a	0.0252	0.0544
$R_w{}^b$	0.0352	0.0736
quality of fit indicator^c	0.896	1.558
largest shift/esd, final cycle	0.08	0.34
largest peak, e/Å^3	0.99	1.62

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

(ii) $[Re_2Cl_3(dppm)_2(CO)_2(CNxyl)]PF_6$ (1b). The preparation of this complex is analogous to that described in section A, part i; yield 83%. Anal. Calcd for $C_{61}H_{53}Cl_3F_6NO_2P_5Re_2$: C, 46.35; H, 3.39; Cl, 6.73. Found: C, 45.58; H, 3.66; Cl, 7.11.

B. Reaction of $Re_2Cl_4(dppm)_2(CO)_2$ with Xylyl Isocyanide. $[Re_2Cl_3(dppm)_2(CO)_2(CNxyl)]PF_6$ (2b). A mixture of $Re_2Cl_4(dppm)_2(CO)_2$ (0.10 g, 0.075 mmol), $TlPF_6$ (0.027 g, 0.077 mmol), and 1 equiv of xylNC (0.010 g, 0.076 mmol) in dichloromethane (10 mL) was stirred for 12 h at room temperature. The resulting brown solution was filtered to remove the precipitated TlCl and the filtrate treated with an excess of diethyl ether (~30 mL) to yield a golden brown solid. This complex was recrystallized from acetone/hexanes; yield 0.080 g (68%). Its spectroscopic and electrochemical properties were identical with those of the complex of this same stoichiometry that was prepared by an alternative route (see section C, part ii).

C. Reactions of $Re_2Cl_4(dppm)_2(CO)(CNR)$ with Carbon Monoxide. (i) $[Re_2Cl_3(dppm)_2(CO)_2(CN\text{-}t\text{-}Bu)]PF_6$ (1a). This complex, which was found to be the same isomer as that prepared in section A, part i, was obtained from the reaction between $Re_2Cl_4(dppm)_2(CO)(CN\text{-}t\text{-}Bu)$ (0.080 g, 0.057 mmol) and $TlPF_6$ (0.020 g, 0.058 mmol) in 10 mL of dichloromethane when the mixture was stirred under an atmosphere of carbon monoxide at room temperature for 12 h. The resulting yellow-green solution was worked up in exactly the same manner as that described in section A, part i; yield 0.072 g (82%). This reaction proceeded equally well when acetone was used as the reaction solvent.

(ii) $[Re_2Cl_3(dppm)_2(CO)_2(CNxyl)]PF_6$ (2b). A mixture comprising $Re_2Cl_4(dppm)_2(CO)(CNxyl)$ (0.10 g, 0.069 mmol) and $TlPF_6$ (0.024 g, 0.069 mmol) in 10 mL of dichloromethane was stirred at room temperature under an atmosphere of carbon monoxide for 12 h. The resulting brown solution was worked up in the usual fashion to yield the product as golden brown crystals; yield 0.086 g (79%). Anal. Calcd for $C_{61}H_{53}Cl_3F_6NO_2P_5Re_2$: C, 46.35; H, 3.39. Found: C, 45.46; H, 3.64. This product had spectroscopic and electrochemical properties identical with those described in section B.

D. Isomerization of $[Re_2Cl_3(dppm)_2(CO)_2(CNR)]PF_6$ (1). A quantity of the isomer **1a** (R = *t*-Bu; 0.1 g, 0.065 mmol) was refluxed in 10 mL of 1,2-dichloroethane for 12 h. The solution was cooled, and hexane (~30 mL) was added to precipitate a yellow-green solid. The isolated solid was found to be a mixture of a different isomer of $[Re_2Cl_3(dppm)_2(CO)_2(CN\text{-}t\text{-}Bu)]PF_6$ (**2a**) (i.e. that which had been prepared previously by a different route[8]) and some decomposition products; yield 50%. The yield of this isomer was estimated through a comparison of the electronic absorption spectrum of the mixture with that of an authentic sample.

A similar isomerization of **1b** (R = xylyl) to **2b** occurred upon refluxing $[Re_2Cl_3(dppm)_2(CO)_2(CNxyl)]PF_6$ (**1b**) in 1,2-dichloroethane; yield 80%. The identity of the product as the isomer **2b** was confirmed by its infrared spectrum and cyclic voltammetric properties that were the same as those of a sample of this complex prepared as described in section B.

E. Reduction of $[Re_2Cl_3(dppm)_2(CO)_2(CN\text{-}t\text{-}Bu)]PF_6$ (1a). The reduction of **1a** was achieved chemically by dissolving a quantity of this complex (0.10 g, 0.065 mmol) in 5 mL of acetone and then adding an acetone solution (2 mL) containing 1 equiv of cobaltocene (0.012 g, 0.065 mmol). When the solution was stirred at room temperature for 30 min, a red-violet solid precipitated from the reaction mixture. This was filtered off and washed with acetone to remove any unreacted cobaltocene as well as the $[(\eta^5\text{-}C_5H_5)_2Co]PF_6$ reaction byproduct, and the solid (which was the neutral complex $Re_2Cl_3(dppm)_2(CO)_2(CN\text{-}t\text{-}Bu)$ (**3a**)) was finally washed with diethyl ether and dried in vacuo; yield 0.065 g, 72%. Anal. Calcd for $C_{57}H_{53}Cl_3NO_2P_4Re_2$: C, 49.34; H, 3.86. Found: C, 48.36; H, 3.97.

F. Reactions of $Re_2Cl_4(dppm)_2(CO)$ with Isocyanides. (i) $[Re_2Cl_3(dppm)_2(CO)(CN\text{-}t\text{-}Bu)_2]PF_6$ (5). A mixture of $Re_2Cl_4(dppm)_2(CO)$ (0.20 g, 0.15 mmol), $TlPF_6$ (0.060 g, 0.17 mmol), and 2 equiv of *t*-BuNC (32 μL, 0.30 mmol) in 15 mL of acetone was stirred for 4 h at room temperature. The resulting brown solution was worked up in the same manner as that described in section A, part i, to yield brown crystals of **5**; yield 0.072 g (30%). Anal. Calcd for $C_{61}H_{62}Cl_3F_6N_2OP_5Re_2$: C, 46.17; H, 3.94. Found: C, 46.53; H, 4.09.

(ii) $[Re_2Cl_3(dppm)_2(CO)(CNxyl)_2]PF_6$ (6 and 7). This complex was prepared in two isomeric forms by stirring a mixture of $Re_2Cl_4(dppm)_2(CO)$ (0.20 g, 0.15 mmol) with 2 equiv of xylNC (0.041 g, 0.31 mmol) in 15 mL of acetone at room temperature for 24 h. The yellow precipitate that formed was separated from the green solution by filtration. The filtrate was set aside (vide infra). A cyclic voltammogram of this yellow solid showed the presence of chloride ion and impurities (including $Re_2Cl_4(dppm)(CO)(CNxyl)$). Accordingly, this solid was redissolved in a small volume of dichloromethane and chromotographed on silica gel (60–200 mesh). Elution with acetone yielded a small quantity of the green isomer, **7**, together with some $Re_2Cl_4(dppm)_2(CO)(CNxyl)$. A third fraction, $[Re_2Cl_3(dppm)_2(CO)(CNxyl)_2]Cl$, was eluted with methanol. This eluate was treated with an excess of KPF_6 (0.1 g), the mixture stirred for 30 min, and the resulting solution evaporated to dryness and worked up in exactly the same fashion as that described in section A, part i, to yield the isomer **6** as a yellow powder. It was recrystallized from acetone/diethyl ether at 0 °C; yield 0.036 g (14%). Anal. Calcd for $C_{69}H_{62}Cl_3F_6N_2OP_5Re_2$: C, 49.25; H, 3.71. Found: C, 48.46; H, 3.80.

An excess of hexanes was added to the original green reaction filtrate to yield a green precipitate that was filtered off and dried in vacuo. Since a cyclic voltammogram of this crude product indicated the presence of chloride ion and some impurities, the product was redissolved in a small volume of acetone, metathesized with 0.1 g of KPF_6, and worked up as described above. A green crystalline material (**7**) was obtained upon its recrystallization from acetone/diethyl ether at 0 °C; yield 0.11 g (43%). Anal. Calcd for $C_{69}H_{62}Cl_3F_6N_2OP_5Re_2$: C, 49.25; H, 3.71. Found: C, 50.49; H, 4.71. The ^1H NMR spectrum of this sample (recorded in CD_2Cl_2) showed the presence of a small amount of diethyl ether of crystallization, thereby accounting for the somewhat high C and H elemental microanalyses.

G. Reactions of $Re_2Cl_4(dppm)_2(CO)(CNR)$ with Isocyanides. (i) $[Re_2Cl_3(dppm)_2(CO)(CN\text{-}t\text{-}Bu)_2]PF_6$ (5). An alternative method of preparing this isomer involved the addition of 1 equiv of *t*-BuNC (9 μL, 0.085 mmol) to a suspension of $Re_2Cl_4(dppm)_2(CO)(CN\text{-}t\text{-}Bu)$ (0.116 g, 0.083 mmol) and $TlPF_6$ (0.029 g, 0.083 mmol) in 10 mL of acetone

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[8] Cotton, F. A.; Dunbar, K. R.; Falvello, L. R.; Walton, R. A. *Inorg. Chem.* **1985**, *24*, 4180.

Table II. Electrochemical and Spectroscopic Properties of $[Re_2Cl_3(dppm)_2(CO)_2(CNR)]^{n+}$

complex	IR, cm^{-1} [a]		half-wave potentials, V [b]			electronic abs spectrum	^1H NMR, δ [d]		$^{31}P\{^1H\}$
	$\nu(CN)$	$\nu(CO)$	$E_{1/2}(1)$	$E_{1/2}(2)$	$E_{1/2}(3)$	λ, nm (ϵ) [c]	RNC	$-CH_2-$ [e]	NMR, δ [f]
$[Re_2Cl_3(dppm)_2(CO)_2(CN\text{-}t\text{-}Bu)]PF_6$ (**1a**)	2210 ms	1952 vs 1771 ms	+1.42 (ox)	−0.09 (red)	−0.92 (red)	1150 (170) br, 829 (550)	+1.12 s	+4.85 +5.16	−9.27 −9.75
$[Re_2Cl_3(dppm)_2(CO)_2(CNxyl)]PF_6$ (**1b**)	2178 s	1960 vs 1775 s	+1.41 (ox)	−0.06 (red)	−0.85 (red)	1125 (170) br, 818 (470)	+2.24 s	+5.05 +5.18	−8.44 −9.64
$[Re_2Cl_3(dppm)_2(CO)_2(CNxyl)]PF_6$ (**2b**)	2159 s	2004 s 1704 s	+1.74 (ox)	+0.08 (red)	−0.90 (red)	~1000 br, sh, 813 (535)	+2.12 s	+4.76 +5.33	
$Re_2Cl_3(dppm)_2(CO)_2(CN\text{-}t\text{-}Bu)$ (**3a**)	2162 s	1906 vs 1709 s	+1.41 (ox)	−0.10 (ox)	−0.93 (red)	1290 (550), 550 (2100)	*g*		*g*

[a] Recorded as Nujol mulls. Very similar spectra obtained on CH_2Cl_2 solutions with $\nu(CN)$ and $\nu(CO)$ modes located within 14 cm^{-1} of the corresponding bands in the mull spectra. [b] Measured on 0.1 M TBAH–CH_2Cl_2 solutions and referenced to the Ag/AgCl electrode, with scan rate (v) 200 mV/s at a Pt-bead electrode. Under our experimental conditions $E_{1/2}$ = +0.47 V for the ferrocenium/ferrocene couple. [c] Dichloromethane solutions. [d] Spectra recorded in acetone-d_6 and referenced internally to the residual protons of the incompletely deuteriated solvent (δ +2.05). [e] The $-CH_2-$ resonances of the dppm ligands appear as an AB pattern with superimposed P–H coupling. [f] These spectra, which were recorded in a 2:1 mixture of CH_2Cl_2–$CDCl_3$ with aqueous H_3PO_4 as an external standard, appear as AA′BB′ patterns. Chemical shifts are of the most intense inner components of the pattern. [g] Paramagnetic complex.

at room temperature. After a reaction time of 12 h, the resulting brown solution was worked up in exactly the same manner as that described in section A, part i, to yield the product as brown crystals; yield 0.051 g (39%). The infrared spectrum and electrochemical properties of this product were identical with those of the product described in section F, part i.

(ii) $[Re_2Cl_3(dppm)_2(CO)(CNxyl)_2]PF_6$ (6 and 7). These two isomers can also be prepared by the addition of 1 equiv of xylNC (0.010 g, 0.076 mmol) to a suspension of $Re_2Cl_4(dppm)_2(CO)(CNxyl)$ (0.10 g, 0.070 mmol) in 10 mL of acetone. The mixture was stirred at room temperature for 12 h to yield a yellow precipitate in a green solution. Metathesis with KPF_6 and workup of these two products were carried out as described in section F, part ii: yield of the yellow isomer, **6**, 0.033 g (28%); yield of the green isomer, **7**, 0.036 g (31%). The electrochemical properties of these two products were identical with those of the samples described in section F, part ii.

H. Isomerization of $[Re_2Cl_3(dppm)_2(CO)(CNxyl)_2]PF_6$ (6). This yellow isomer (0.10 g, 0.059 mmol) was refluxed in 10 mL of 1,2-dichloroethane for 12 h. The solution was cooled, and hexane (~50 mL) was added to precipitate a green solid, which was washed with diethyl ether and dried in vacuo. A cyclic voltammogram and infrared spectrum of this product showed it to be a mixture of **7** (the green isomer) and some decomposition products.

Preparation of Single Crystals of $[Re_2Cl_3(dppm)_2(CO)_2(CN\text{-}t\text{-}Bu)]PF_6$ (1a) and $Re_2Cl_3(dppm)_2(CO)_2(CN\text{-}i\text{-}Pr)$ (4). Crystals of **1a** were grown in a 5-mm NMR tube by dissolving a sample of the complex in CH_2Cl_2 and carefully layering hexane on top. After a few days the green crystals had deposited on the sides of the tube. Large octahedral-shaped crystals of **4** were grown by slow diffusion of hexanes into a dichloromethane solution of the complex in a Schlenk tube under nitrogen. The blue crystals formed on the bottom and sides of the container after several days.

X-ray Crystal Structure Analyses. Geometric and intensity data for both $[Re_2Cl_3(dppm)_2(CO)_2(CN\text{-}t\text{-}Bu)]PF_6\cdot 2CH_2Cl_2$ (**1a**) and $[Re_2Cl_3(dppm)_2(CO)_2(CN\text{-}i\text{-}Pr)]$ (**4**) were taken from crystals mounted at the ends of glass fibers and covered with epoxy. In each case a sample crystal of appropriate dimensions was cleaved from a larger single crystal. All crystallographic data were taken according to routine procedures described previously,[9] by a Syntex $P\bar{1}$ autodiffractometer. Pertinent crystal data and data-collection parameters are given in Table I. Routine data reduction[10] included, for each data set, an empirical absorption correction[11] based on azimuthal scans of several reflections with diffractometer angle χ near 90°.

For the structures of **1a** and **4**, the positions of the unique Re atoms were derived from Patterson maps.

The structure of **1a** has a single formula unit in the crystallographic unit cell. The cation $[Re_2Cl_3(dppm)_2(CO)_2(CN\text{-}t\text{-}Bu)]^+$ is acentric, there is no disorder, and the space group is $P1$. The positions of the ligated P and Cl atoms in the complex cation were located in a difference Fourier map; however, after that point no further development of the correct structure occurred through the usual procedure of alternating refinements and difference maps. The remainder of the structure was developed in a straightforward manner via the use of the difference-structure direct-methods technique[12] as implemented in the computer program DIRDIF. The use of this method was interleaved with least-squares refinement.

At the end of structure development, full-matrix least-squares refinement was used to fit 745 variable parameters to 5478 data, for a data-to-parameter ratio of 7.35:1. The correct enantiomorph gave unweighted and weighted R factors of 0.0252 and 0.0352, respectively, and the incorrect enantiomorph gave corresponding values of R = 0.0322 and R_w = 0.0464. The least-squares residuals for the correct structure are defined and summarized in Table I. Following the final refinement, listings of R values as functions of $|F_o|$, $(\sin\theta)/\lambda$, and data-collection order showed no observable trends.

The structure of **4** was developed in a series of alternating least-squares refinements and difference Fourier maps. The final full-matrix refinement involved 279 variable parameters and 1690 data, for a data-to-parameter ratio of 6.06. The refinement converged with residuals (Table

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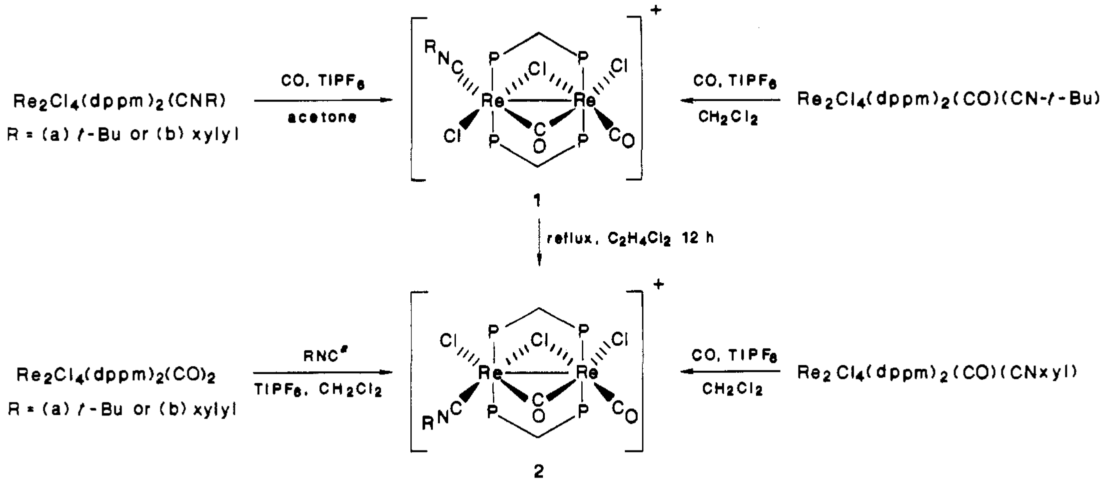
Table III. Atomic Positional Parameters and Equivalent Isotropic Displacement Parameters (Å^2) and Their Estimated Standard Deviations for $[Re_2Cl_3(dppm)_2(CO)_2(CN\text{-}t\text{-}Bu)]PF_6\cdot 2CH_2Cl_2$ (**1a**·$2CH_2Cl_2$)

atom	*x*	*y*	*z*	*B*[a]	atom	*x*	*y*	*z*	*B*[a]
Re(1)	−0.017	0.104	0.027	1.708 (5)	C(31)	−0.255 (1)	−0.4356 (8)	0.1881 (8)	4.7 (2)
Re(2)	0.01638 (2)	−0.10688 (2)	−0.02719 (2)	1.826 (5)	C(32)	−0.196 (1)	−0.3157 (8)	0.1965 (8)	4.6 (2)
Cl(1)	0.1906 (2)	0.0789 (2)	0.0884 (1)	2.57 (4)	C(33)	0.0047 (7)	−0.0088 (6)	−0.2459 (5)	2.0 (1)
Cl(2)	−0.1834 (2)	0.1881 (2)	−0.0067 (2)	2.58 (4)	C(34)	0.2208 (7)	0.2079 (7)	−0.1317 (6)	2.7 (2)
Cl(3)	0.1634 (2)	−0.2226 (2)	−0.0273 (2)	3.20 (4)	C(35)	0.2555 (9)	0.1979 (8)	−0.2324 (7)	3.8 (2)
P(1)	−0.1046 (2)	0.0904 (2)	0.1861 (1)	1.76 (3)	C(36)	0.386 (1)	0.250 (1)	−0.2315 (8)	4.7 (2)
P(2)	−0.0344 (2)	−0.1404 (2)	0.1390 (2)	2.19 (4)	C(37)	0.478 (1)	0.315 (1)	−0.134 (1)	5.6 (3)
P(3)	0.0490 (2)	0.1392 (2)	−0.1357 (1)	2.07 (4)	C(38)	0.436 (1)	0.323 (1)	−0.036 (1)	5.7 (3)
P(4)	0.0729 (2)	−0.1109 (2)	−0.2026 (2)	2.18 (4)	C(39)	0.3080 (9)	0.2695 (9)	−0.0384 (8)	3.9 (2)
C(1)	−0.1566 (7)	−0.0456 (6)	−0.0620 (6)	2.5 (2)	C(40)	−0.0311 (7)	0.2259 (7)	−0.1903 (6)	2.4 (2)
O(1)	−0.2640 (6)	−0.0927 (5)	−0.1102 (5)	3.8 (2)	C(41)	0.0333 (9)	0.3477 (7)	−0.1599 (7)	3.4 (2)
C(2)	−0.1255 (7)	−0.2430 (7)	−0.1101 (6)	2.5 (2)	C(42)	−0.030 (1)	0.4174 (7)	−0.1975 (8)	4.2 (2)
O(2)	−0.2137 (7)	−0.3236 (5)	−0.1599 (5)	4.1 (2)	C(43)	−0.154 (1)	0.3682 (8)	−0.2604 (8)	4.5 (2)
C(3)	0.0845 (8)	0.2923 (7)	0.1167 (7)	2.9 (2)	C(44)	−0.2183 (9)	0.2451 (9)	−0.2887 (8)	4.6 (2)
N(1)	0.1385 (7)	0.3888 (6)	0.1654 (6)	3.4 (2)	C(45)	−0.1571 (8)	0.1731 (8)	−0.2541 (7)	3.4 (2)
C(4)	0.216 (1)	0.5134 (9)	0.2286 (9)	4.9 (3)	C(46)	0.2416 (7)	−0.0761 (6)	−0.2152 (6)	2.4 (2)
C(5)	0.351 (1)	0.500 (1)	0.276 (1)	7.9 (4)	C(47)	0.2697 (8)	−0.1137 (8)	−0.3181 (7)	3.6 (2)
C(6)	0.235 (2)	0.577 (1)	0.144 (1)	8.5 (5)	C(48)	0.400 (1)	−0.085 (1)	−0.3256 (8)	5.2 (3)
C(7)	0.148 (2)	0.566 (1)	0.311 (2)	11.0 (6)	C(49)	0.4995 (9)	−0.032 (1)	−0.2359 (8)	4.9 (2)
C(8)	−0.1561 (7)	−0.0667 (6)	0.1778 (6)	2.2 (1)	C(50)	0.4695 (8)	0.005 (1)	−0.1352 (9)	4.7 (2)
C(9)	−0.0047 (7)	0.1701 (6)	0.3227 (6)	2.4 (2)	C(51)	0.3464 (8)	−0.0159 (8)	−0.1232 (7)	3.3 (2)
C(10)	−0.0632 (9)	0.1703 (7)	0.4093 (6)	3.3 (2)	C(52)	0.0026 (8)	−0.2541 (7)	−0.3117 (6)	3.0 (2)
C(11)	0.010 (1)	0.2247 (9)	0.5160 (7)	4.3 (2)	C(53)	0.056 (1)	−0.3450 (8)	−0.3133 (7)	4.3 (2)
C(12)	0.147 (1)	0.2802 (9)	0.5317 (8)	4.7 (3)	C(54)	0.008 (1)	−0.4550 (9)	−0.3978 (9)	5.6 (3)
C(13)	0.204 (1)	0.2802 (9)	0.4443 (8)	4.3 (2)	C(55)	−0.091 (1)	−0.473 (1)	−0.483 (1)	6.0 (3)
C(14)	0.1266 (8)	0.2257 (7)	0.3404 (6)	2.9 (2)	C(56)	−0.147 (1)	−0.387 (1)	−0.481 (1)	7.4 (4)
C(15)	−0.2515 (7)	0.1317 (6)	0.1984 (6)	2.3 (1)	C(57)	−0.099 (1)	−0.2765 (9)	−0.3940 (8)	5.0 (3)
C(16)	−0.2416 (8)	0.2522 (7)	0.2526 (7)	3.3 (2)	P(5)	−0.3451 (3)	0.8723 (2)	0.4554 (2)	4.28 (6)
C(17)	−0.3506 (9)	0.2862 (9)	0.2660 (9)	4.6 (2)	F(1)	−0.3260 (8)	0.7439 (7)	0.4124 (6)	7.4 (2)
C(18)	−0.4740 (8)	0.2015 (9)	0.2242 (9)	4.9 (2)	F(2)	−0.3621 (8)	1.0000 (6)	0.4994 (8)	8.2 (2)
C(19)	−0.4839 (9)	0.085 (1)	0.1702 (8)	4.6 (2)	F(3)	−0.4955 (7)	0.8132 (7)	0.4328 (6)	6.6 (2)
C(20)	−0.3741 (8)	0.0468 (8)	0.1540 (8)	3.8 (2)	F(4)	−0.3267 (7)	0.8732 (7)	0.5751 (5)	6.3 (2)
C(21)	0.0935 (7)	−0.0888 (6)	0.2595 (6)	2.5 (2)	F(5)	−0.1933 (8)	0.9343 (9)	0.4775 (8)	10.1 (3)
C(22)	0.0643 (9)	−0.0658 (8)	0.3612 (7)	3.7 (2)	F(6)	−0.358 (1)	0.8751 (8)	0.3370 (6)	9.9 (3)
C(23)	0.157 (1)	−0.029 (1)	0.4508 (8)	5.2 (3)	C(58)	−0.552 (2)	−0.302 (2)	−0.105 (2)	8.9 (5)
C(24)	0.285 (1)	−0.016 (1)	0.4428 (9)	5.7 (3)	Cl(4)	−0.6719 (5)	−0.4407 (4)	−0.1708 (5)	10.4 (2)
C(25)	0.320 (1)	−0.042 (1)	0.3417 (9)	5.2 (3)	Cl(5)	−0.4715 (7)	−0.3045 (6)	0.0154 (6)	14.1 (2)
C(26)	0.2205 (9)	−0.0763 (8)	0.2508 (7)	3.4 (2)	Cl(6)	0.5576 (9)	0.352 (1)	0.5402 (9)	11.4 (4)
C(27)	−0.1171 (7)	−0.2968 (6)	0.1244 (6)	2.4 (2)	Cl(7),C[b]	0.561 (1)	0.4720 (9)	0.599 (1)	17.4 (5)
C(28)	−0.0966 (9)	−0.3917 (7)	0.0476 (7)	3.6 (2)	Cl(8),C[b]	0.518 (1)	0.5844 (9)	0.582 (1)	15.3 (4)
C(29)	−0.156 (1)	−0.5080 (8)	0.0430 (8)	4.2 (2)	Cl(9)	0.397 (1)	0.6082 (9)	0.5957 (9)	10.2 (3)
C(30)	−0.231 (1)	−0.5279 (7)	0.1144 (8)	3.9 (2)					

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $^4/_3[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos\gamma)\beta_{12} + ac(\cos\beta)\beta_{13} + bc(\cos\alpha)\beta_{23}]$. [b] Site modeled as $^1/_2$ Cl + $^1/_2$ C.

Scheme I. Synthesis and Isomerization of $[Re_2Cl_3(dppm)_2(CO)_2(CNR)]PF_6$ (R = *t*-Bu or Xylyl)



[a] This reaction was reported previously[8] in the case of R = *t*-Bu.

I) of $R = 0.054$, $R_w = 0.074$, and quality of fit 1.56. The space group of **4** was $P4_32_12$, and so the structure defines the enantiomorph. A refinement of the inverted structure in space group $P4_12_12$ converged with $R = 0.065$, $R_w = 0.086$, and quality of fit 1.82.

The dinuclear complex, with an edge-sharing bioctahedral structure, lies across a crystallographic twofold axis that bisects the Re–Re vector. The terminal carbonyl and isopropyl isocyanide ligands are disordered about the symmetry axis, with a common carbon atom site and a second site that was modeled as $^1/_2$ N (from the isocyanide) plus $^1/_2$ O (from the carbonyl). The isopropyl group, as we shall now describe, was not included in the refinement.

During the development of the structure of **4**, difference maps did not

Table IV. Selected Bond Distances (Å) and Angles (deg) and Their Estimated Standard Deviations for $[Re_2Cl_3(dppm)_2(CO)_2(CN\text{-}t\text{-}Bu)]PF_6\cdot 2CH_2Cl_2$ (**1a**·$2CH_2Cl_2$)[a]

Re(1)–Re(2)	2.605 (1)	Re(2)–P(4)	2.480 (2)	P(3)–C(34)	1.843 (8)
Re(1)–Cl(1)	2.454 (2)	Re(2)–C(1)	2.265 (9)	P(3)–C(40)	1.810 (9)
Re(1)–Cl(2)	2.385 (2)	Re(2)–C(2)	1.886 (6)	P(4)–C(33)	1.824 (9)
Re(1)–P(1)	2.469 (2)	P(1)–C(8)	1.841 (7)	P(4)–C(46)	1.827 (8)
Re(1)–P(3)	2.492 (2)	P(1)–C(9)	1.829 (7)	P(4)–C(52)	1.804 (7)
Re(1)–C(1)	1.978 (6)	P(1)–C(15)	1.817 (8)	C(1)–O(1)	1.173 (8)
Re(1)–C(3)	2.165 (7)	P(2)–C(8)	1.830 (8)	C(2)–O(2)	1.144 (8)
Re(2)–Cl(1)	2.476 (1)	P(2)–C(21)	1.826 (7)	C(3)–N(1)	1.119 (9)
Re(2)–Cl(3)	2.409 (2)	P(2)–C(27)	1.848 (7)	N(1)–C(4)	1.464 (10)
Re(2)–P(2)	2.482 (2)	P(3)–C(33)	1.849 (6)		
Re(2)–Re(1)–Cl(1)	58.53 (4)	Re(1)–Re(2)–C(1)	47.3 (2)	Re(2)–P(2)–C(21)	120.2 (3)
Re(2)–Re(1)–Cl(2)	138.02 (3)	Re(1)–Re(2)–C(2)	118.6 (3)	Re(2)–P(2)–C(27)	116.6 (2)
Re(2)–Re(1)–P(1)	94.52 (5)	Cl(1)–Re(2)–Cl(3)	90.39 (6)	C(8)–P(2)–C(21)	106.9 (3)
Re(2)–Re(1)–P(3)	93.73 (5)	Cl(1)–Re(2)–P(2)	88.69 (6)	C(8)–P(2)–C(27)	102.0 (4)
Re(2)–Re(1)–C(1)	57.3 (3)	Cl(1)–Re(2)–P(4)	97.05 (6)	C(21)–P(2)–C(27)	102.8 (4)
Re(2)–Re(1)–C(3)	141.8 (3)	Cl(1)–Re(2)–C(1)	105.0 (2)	Re(1)–P(3)–C(33)	107.4 (3)
Cl(1)–Re(1)–Cl(2)	163.41 (5)	Cl(1)–Re(2)–C(2)	175.5 (3)	Re(1)–P(3)–C(34)	119.8 (3)
Cl(1)–Re(1)–P(1)	95.33 (6)	Cl(3)–Re(2)–P(2)	87.50 (8)	Re(1)–P(3)–C(40)	116.3 (3)
Cl(1)–Re(1)–P(3)	92.98 (7)	Cl(3)–Re(2)–P(4)	83.44 (8)	C(33)–P(3)–C(34)	103.8 (3)
Cl(1)–Re(1)–C(1)	115.8 (3)	Cl(3)–Re(2)–C(1)	164.4 (2)	C(33)–P(3)–C(40)	104.6 (3)
Cl(1)–Re(1)–C(3)	83.3 (3)	Cl(3)–Re(2)–C(2)	93.5 (3)	C(34)–P(3)–C(40)	103.2 (4)
Cl(2)–Re(1)–P(1)	85.37 (7)	P(2)–Re(2)–P(4)	169.29 (7)	Re(2)–P(4)–C(33)	107.9 (2)
Cl(2)–Re(1)–P(3)	85.35 (7)	P(2)–Re(2)–C(1)	95.4 (2)	Re(2)–P(4)–C(46)	120.4 (3)
Cl(2)–Re(1)–C(1)	80.8 (3)	P(2)–Re(2)–C(2)	89.2 (3)	Re(2)–P(4)–C(52)	114.4 (3)
Cl(2)–Re(1)–C(3)	80.1 (3)	P(4)–Re(2)–C(1)	91.8 (2)	C(33)–P(4)–C(46)	107.4 (4)
P(1)–Re(1)–P(3)	170.50 (7)	P(4)–Re(2)–C(2)	85.7 (3)	C(33)–P(4)–C(52)	104.4 (4)
P(1)–Re(1)–C(1)	88.0 (3)	C(1)–Re(2)–C(2)	71.3 (3)	C(46)–P(4)–C(52)	100.9 (4)
P(1)–Re(1)–C(3)	89.2 (3)	Re(1)–Cl(1)–Re(2)	63.79 (4)	Re(1)–C(1)–Re(2)	75.4 (2)
P(3)–Re(1)–C(1)	92.5 (3)	Re(1)–P(1)–C(8)	110.2 (3)	Re(1)–C(1)–O(1)	149.0 (7)
P(3)–Re(1)–C(3)	87.2 (3)	Re(1)–P(1)–C(9)	120.9 (3)	Re(2)–C(1)–O(1)	135.6 (6)
C(1)–Re(1)–C(3)	160.9 (4)	Re(1)–P(1)–C(15)	115.6 (3)	Re(2)–C(2)–O(2)	178.2 (8)
Re(1)–Re(2)–Cl(1)	57.68 (5)	C(8)–P(1)–C(9)	102.9 (4)	Re(1)–C(3)–N(1)	178.1 (9)
Re(1)–Re(2)–Cl(3)	147.83 (4)	C(8)–P(1)–C(15)	102.3 (4)	C(3)–N(1)–C(4)	177. (1)
Re(1)–Re(2)–P(2)	94.93 (5)	C(9)–P(1)–C(15)	102.6 (3)	P(1)–C(8)–P(2)	111.5 (4)
Re(1)–Re(2)–P(4)	95.78 (5)	Re(2)–P(2)–C(8)	106.6 (3)	P(3)–C(33)–P(4)	110.7 (4)

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

show the three carbon atoms of the isopropyl group of the isopropyl isocyanide ligand. In a full, contoured difference Fourier of this part of the unit cell, we observed evidence of a dynamic disorder that evidently prevented discrete Fourier peaks from being located in the usual peak-search procedure. In particular, one Fourier section, taken perpendicular to the Re(1)–C(2)–(O(2),N(2)) line, 0.90 Å away from the position of (O(2),N(2)), clearly shows a semiannulus of electron density which encompasses positions that could be occupied by the middle carbon atom of an isopropyl group disordered by rotation about the C(2)–N(2) bond. (The isocyanide ligand appears to be bent at the nitrogen atom.)

Although the details of the geometry of this ligand are obscured by the disorder, the contoured difference map shows clear evidence of the isopropyl group of the isocyanide ligand. The refinement of the remainder of the structure did not show any adverse effects from the disorder and the necessary exclusion of the three atoms involved.

Nineteen sections of the final difference map of the disordered region are available as supplementary material.

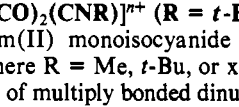
Physical Measurements. Infrared spectra were recorded as Nujol mulls between KBr plates with an IBM Instruments IR 32 Fourier transform (4000–400 cm^{-1}) spectrometer. Electronic absorption spectra were recorded on IBM Instruments 9420 (900–300 nm) and Cary 17 (1800–900 nm) UV-visible spectrophotometers. 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. Voltammetric experiments were performed with a Bioanalytical Systems Inc. Model CV-1A instrument in conjunction with a Hewlett-Packard Model 7035B 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 using an internal deuterium lock and 85% H_3PO_4 as an external standard. ^1H NMR spectra were obtained on a Varian XL-200 or Nicolet NT-200 spectrometer. Resonances were referenced internally to the impurity in the deuteriated solvent.

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

Results and Discussion

(a) Preparation and Spectroscopic and Redox Characteristics of $[Re_2Cl_3(dppm)_2(CO)_2(CNR)]^{n+}$ (R = *t*-Bu or xylyl; *n* = 0 or 1).

The dirhenium(II) monoisocyanide complexes $Re_2Cl_4(dppm)_2(CNR)$, where R = Me, *t*-Bu, or xylyl, represent some of the first examples of multiply bonded dinuclear complexes that contain an isocyanide ligand.[3,5,13,14] The X-ray crystal structure of $Re_2Cl_4(dppm)_2(CN\text{-}t\text{-}Bu)$ has shown[3] that it possesses a terminal *t*-BuNC ligand which is trans to a bridging Cl ligand:



This coordinately unsaturated molecule, which can be considered as derived from an edge-shared bioctahedral M_2L_{10} system, has an open coordination site in a bridging position and can be expected to be quite reactive. We find that the complexes $Re_2Cl_4(dppm)_2(CNR)$, where R = *t*-Bu or xylyl, react with CO(g) at room temperature, in the presence of $TlPF_6$, to produce the dicarbonyl derivatives $[Re_2Cl_3(dppm)_2(CO)_2(CNR)]PF_6$ (**1**) in high yield (Scheme I).

The spectroscopic and electrochemical properties of **1** are summarized in Table II. These complexes are characterized by three redox couples as measured by cyclic voltammetry, $E_{1/2}(ox) \simeq +1.4$ V, $E_{1/2}(red) \simeq -0.1$ V, and $E_{1/2}(red) \simeq -0.9$ V vs. Ag/AgCl; their Nujol mull IR spectra display a single terminal $\nu(CN)$ mode and two $\nu(CO)$ modes, one of which corresponds to a bridging CO ligand, while the other is due to a terminally coordinated CO. Conductivity measurements, performed on 1

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Table V. Atomic Positional Parameters and Equivalent Isotropic Displacement Parameters (Å^2) for [$Re_2Cl_3(dppm)_2(CO)_2(CN$-*i*-Pr)] (**4**)

atom	*x*	*y*	*z*	B^a
Re(1)	0.21474 (7)	0.86432 (7)	0.20950 (4)	2.33 (2)
Cl(1)	0.2730 (4)	0.7269	0.250	2.9 (1)
Cl(2)	0.3458 (4)	0.8677 (5)	0.1539 (2)	3.3 (1)
P(1)	0.1330 (5)	0.7729 (4)	0.1473 (2)	2.7 (1)
P(2)	0.2973 (5)	0.9698 (4)	0.2625 (3)	2.8 (1)
O(1)	0.046 (1)	0.954	0.250	4.9 (7)^b
C(1)	0.101 (2)	0.899	0.250	2.3 (7)^b
C(7)	0.021 (2)	0.750 (2)	0.1714 (9)	2.5 (6)
C(8)	0.170 (2)	0.665 (2)	0.125 (1)	3.9 (6)
C(9)	0.261 (3)	0.647 (2)	0.132 (1)	5.5 (8)
C(10)	0.301 (3)	0.561 (2)	0.114 (1)	6.6 (9)
C(11)	0.240 (3)	0.506 (2)	0.090 (1)	6.0 (9)
C(12)	0.141 (3)	0.527 (3)	0.084 (1)	8 (1)
C(13)	0.116 (2)	0.605 (2)	0.100 (1)	3.5 (7)
C(14)	0.107 (2)	0.825 (2)	0.088 (1)	4.0 (7)
C(15)	0.173 (2)	0.883 (2)	0.065 (1)	4.0 (6)
C(16)	0.160 (3)	0.925 (2)	0.020 (1)	7 (1)
C(17)	0.071 (2)	0.904 (2)	−0.005 (1)	6.5 (9)
C(18)	0.004 (2)	0.850 (2)	0.013 (1)	7.0 (9)
C(19)	0.022 (2)	0.814 (2)	0.064 (1)	4.6 (7)
C(20)	0.289 (2)	1.086 (2)	0.237 (1)	3.1 (6)
C(21)	0.227 (2)	1.146 (2)	0.255 (1)	4.3 (7)
C(22)	0.224 (2)	1.225 (2)	0.231 (1)	6.6 (9)
C(23)	0.264 (3)	1.244 (2)	0.189 (1)	8 (1)
C(24)	0.330 (2)	1.182 (2)	0.172 (1)	5.8 (9)
C(25)	0.341 (2)	1.101 (2)	0.195 (1)	5.7 (8)
C(26)	0.413 (2)	0.961 (2)	0.279 (1)	3.6 (6)
C(27)	0.458 (2)	0.879 (2)	0.2686 (9)	4.4 (7)
C(28)	0.552 (2)	0.874 (3)	0.284 (1)	8 (1)
C(29)	0.600 (2)	0.949 (2)	0.309 (1)	6.2 (9)
C(30)	0.553 (2)	1.025 (2)	0.310 (1)	5.5 (8)
C(31)	0.457 (2)	1.037 (2)	0.297 (1)	4.5 (7)
ON(2)^c	0.131 (1)	1.021 (1)	0.1544 (8)	4.8 (5)^b
C(2)	0.165 (2)	0.962 (2)	0.177 (1)	3.8 (6)^b

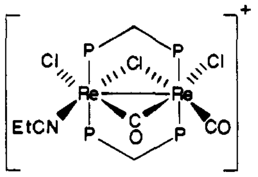
^{a} Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as $^4/_3[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos\gamma)\beta_{12} + ac(\cos\beta)\beta_{13} + bc(\cos\alpha)\beta_{23}]$. ^{b} Atoms were refined isotropically. ^{c} Site modeled as $^1/_2$ O + $^1/_2$ N. See text.

× 10^{-3} M acetone solutions of the complexes, are in accord with their formulation as 1:1 electrolytes (Λ_M = 115–135 Ω^{-1} cm^2 mol^{-1}). The electronic absorption spectra of the two complexes, R = *t*-Bu and xylyl, are quite similar. There is a broad feature at $\lambda_{max} \simeq$ 1150 nm (ϵ = 170) along with a more intense absorption at $\lambda_{max} \simeq$ 820 nm ($\epsilon \simeq$ 500).

The NMR spectral properties of **1** are also listed in Table II. The ^{1}H NMR spectra give correct integrations for the proposed stoichiometry, i.e., two dppm ligands per isocyanide, and the $-CH_2-$ protons of the dppm ligands appear as an AB pattern. An AA′BB′ pattern was observed in the $^{31}P\{^1H\}$ NMR spectra of each of the complexes. These data are in accord with a molecule that possesses low symmetry.

The aforementioned electrochemical and spectroscopic properties of **1** are quite similar (but not identical) to those exhibited by complexes of this same stoichiometry (i.e. [$Re_2Cl_3(dppm)_2(CO)_2L$]PF_6 (**2**), where L = RNC or R′CN) that have been prepared by a different route,[8] namely, the reaction of the dicarbonyl complex $Re_2(\mu$-Cl)(μ-CO)(μ-dppm)$_2Cl_3$(CO) with 1 equiv of L in the presence of $TlPF_6$ (Scheme I). (Note that the xylNC derivative, **2b**, is described herein for the first time (see Experimental Section and Table II).) This is clearly seen in the case of L = *t*-BuNC, for which the two different synthetic methods have clearly given different compounds (**1a** and **2a**), e.g. IR (Nujol mull) ν(CN) 2210 cm^{-1} and ν(CO) 1952 and 1771 cm^{-1} for [$Re_2Cl_3(dppm)_2(CO)_2$(CN-*t*-Bu)]PF_6 (**1a**) and IR (Nujol mull) ν(CN) 2184 cm^{-1} and ν(CO) 2002 and 1705 cm^{-1} for [$Re_2Cl_3(dppm)_2(CO)_2$(CN-*t*-Bu)]PF_6 (**2a**). Other differences are seen in the electronic absorption and NMR spectra and electrochemical properties of these two complexes: [$Re_2Cl_3(dppm)_2(CO)_2$(CN-*t*-Bu)]PF_6 (**1a**), λ_{max} (CH_2Cl_2) 1150 and 829 nm, $^{31}P\{^1H\}$ NMR ($CH_2Cl_2/CDCl_3$) δ −9.27 and −9.75, CV (in TBAH-CH_2Cl_2) $E_{1/2}$(ox) = +1.42 V, $E_{1/2}$(red) = −0.09 V, and $E_{1/2}$(red) = −0.92 V; [$Re_2Cl_3(dppm)_2(CO)_2$(CN-*t*-Bu)]PF_6(**2a**), λ_{max} (acetone) 1070 and 790 nm, $^{31}P\{^1H\}$ NMR (CH_2Cl_2/CD_2Cl_2) δ −11.96 and −23.31, CV (in TBAH-CH_2Cl_2) $E_{1/2}$(ox) = +1.70 V, $E_{1/2}$(red) = −0.04 V, and $E_{1/2}$(red) = −1.03 V.

A comparison of the IR spectral and electrochemical data for the xylNC derivatives **1b** and **2b** is given in Table II. An X-ray crystal structure determination of the propionitrile derivative of type **2** (i.e. [$Re_2Cl_3(dppm)_2(CO)_2$(NCEt)]PF_6) has shown[8] that it possesses an edge-shared bioctahedral structure with an all-cis arrangement of the Cl ligands:



2 (L = EtCN)

This same type of all-cis geometry was also observed for the only other trisubstituted dirhenium complex that has previously been structurally characterized, viz., [$Re_2(\mu$-Cl)(μ-C=NH-*t*-Bu)(μ-dppm)$_2Cl_2$(CN-*t*-Bu)$_2$]PF_6.[1,15]

The preceding observations imply that **1** and **2** are structural isomers. Accordingly, **1** cannot possess this same all-cis arrangement of chloride ligands, and these complexes therefore represent a new structural configuration for an M_2L_{10} system of this type which contain three π-acceptor ligands. The all-cis arrangement appears to be more favored thermodynamically, and in accord with this we find that **1** can be converted into **2** by refluxing 1,2-dichloroethane solutions of these complexes for 12 h (Scheme I). This conversion proceeds in 50% or greater yield and is accompanied by some decomposition to unidentified species. Under similar conditions, **2** does not undergo any changes and can be recovered in virtually quantitative yield. An X-ray crystal structure analysis of **1a** (R = *t*-Bu) confirms that this species does indeed possess a structure different from that of **2a** (vide infra). The thermal conversion of **1** to **2**, therefore, must involve bond-breaking and bond-re-forming processes that can more easily lead to a greater degree of decomposition than if isomerization were simply a consequence of a partial "merry-go-round" process involving the ligands in the $Re_2Cl_3(CO)_2$(CNR) plane.

A further reflection of these isomerization differences is seen in the reactions of $Re_2Cl_4(dppm)_2$(CO)(CNR) (R = *t*-Bu or xylyl) with CO. These two neutral mixed carbonyl–isocyanide complexes have different structures, which may be represented as follows:[6] $Re_2(\mu$-Cl)$_2$(μ-dppm)$_2Cl_2$(CO)(CN-*t*-Bu)[16] and $Re_2(\mu$-Cl)(μ-CO)(μ-dppm)$_2Cl_3$(CNxyl). They in turn react differently with CO in the presence of $TlPF_6$; the *t*-BuNC derivative reacts to give isomer **1a** while the xylNC complex gives exclusively isomer **2b** (see Scheme I). This is reasonable since $Re_2Cl_4(dppm)_2$(CO)(CNxyl) has a structure that is closely akin to that of the dicarbonyl complex $Re_2Cl_4(dppm)_2(CO)_2$[4] and, accordingly, it reacts in an analogous fashion to give the all-cis geometry.

Isomer **1a** (R = *t*-Bu) can be reduced by cobaltocene to the red-violet neutral species $Re_2Cl_3(dppm)_2(CO)_2$(CN-*t*-Bu) (**3a**). This is analogous to the previously reported chemical reduction of **2** to give $Re_2Cl_3(dppm)_2(CO)_2L$ (**4**), where L = CH_3CN, C_2H_5CN, C_6H_5CN, *i*-PrNC, and *t*-BuNC.[8] Attempts to isolate a sample of the related xylNC complex, **3b**, were unsuccessful although solutions could be generated electrochemically in 0.2 M TBAH-CH_2Cl_2. The ESR spectrum of a frozen solution (−160 °C) was essentially the same as that of the *t*-BuNC analogue. In its electrochemistry, **3a** possesses two couples corresponding to oxidations and one due to a reduction (Table II). As expected, a shift in the IR-active ν(CN) and ν(CO) modes to lower fre-

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(15) Barder, T. J.; Powell, D.; Walton, R. A. *J. Chem. Soc., Chem. Commun.* **1985**, 550.

(16) An alternative structural formulation for this complex is based upon a M_2L_{10} geometry without bridging chloride ligands, i.e. Cl_2(CO)Re(μ-dppm)$_2ReCl_2$(CN-*t*-Bu).

Table VI. Selected Bond Distances (Å) and Angles (deg) for $[Re_2Cl_3(dppm)_2(CO)_2(CN\text{-}i\text{-}Pr)]$ (**4**)[a]

Re(1)–Re(1′)	2.718 (1)	Re(1)–C(1)	2.08 (2)	P(2)–C(7′)	1.89 (2)
Re(1)–Cl(1)	2.484 (2)	Re(1)–C(2)	1.86 (3)	P(2)–C(20)	1.88 (3)
Re(1)–Cl(2)	2.457 (1)	P(1)–C(7)	1.83 (3)	P(2)–C(26)	1.80 (2)
Re(1)–P(1)	2.467 (7)	P(1)–C(8)	1.81 (3)	O(1)–C(1)	1.16 (2)
Re(1)–P(2)	2.451 (7)	P(1)–C(14)	1.79 (3)	ON(2)[b]–C(2)	1.18 (4)
Re(1′)–Re(1)–Cl(1)	56.8 (1)	Cl(2)–Re(1)–C(1)	163.6 (2)	C(7)–P(1)–C(14)	100 (1)
Re(1′)–Re(1)–Cl(2)	146.0 (2)	Cl(2)–Re(1)–C(2)	91.9 (9)	C(8)–P(1)–C(14)	100 (1)
Re(1′)–Re(1)–P(1)	93.5 (2)	P(1)–Re(1)–P(2)	172.5 (2)	Re(1)–P(2)–C(7′)	112.4 (8)
Re(1′)–Re(1)–P(2)	93.2 (2)	P(1)–Re(1)–C(1)	94.1 (4)	Re(1)–P(2)–C(20)	111.2 (8)
Re(1′)–Re(1)–C(1)	49.28 (9)	P(1)–Re(1)–C(2)	86.2 (9)	Re(1)–P(2)–C(26)	125 (1)
Re(1′)–Re(1)–C(2)	122.0 (9)	P(2)–Re(1)–C(1)	87.8 (4)	C(7′)–P(2)–C(20)	104 (1)
Cl(1)–Re(1)–Cl(2)	89.5 (2)	P(2)–Re(1)–C(2)	87.4 (9)	C(7′)–P(2)–C(26)	99 (1)
Cl(1)–Re(1)–P(1)	89.9 (2)	C(1)–Re(1)–C(2)	72.9 (9)	C(20)–P(2)–C(26)	102 (1)
Cl(1)–Re(1)–P(2)	96.5 (2)	Re(1)–Cl(1)–Re(1′)	66.3 (1)	Re(1)–C(1)–Re(1′)	81.4 (6)
Cl(1)–Re(1)–C(1)	106.1 (1)	Re(1)–P(1)–C(7)	109.4 (8)	Re(1)–C(1)–O(1)	139.3 (6)
Cl(1)–Re(1)–C(2)	175.9 (8)	Re(1)–P(1)–C(8)	124 (1)	P(1)–C(7)–P(2′)	109 (1)
Cl(2)–Re(1)–P(1)	90.8 (2)	Re(1)–P(1)–C(14)	116 (1)	Re(1)–C(2)–ON(2)[b]	176 (3)
Cl(2)–Re(1)–P(2)	85.5 (2)	C(7)–P(1)–C(8)	103 (1)		

[a] Numbers in parentheses are estimated standard deviations in the least significant digits. [b] Site modeled as $^1/_2$ O + $^1/_2$ N. See text.

quencies is observed on going from the Re_2^{4+} precursor complex to the reduced neutral complex, which formally, at least, contains an Re_2^{3+} core. The electronic absorption spectrum of $Re_2Cl_3(dppm)_2(CO)_2(CN\text{-}t\text{-}Bu)$ (Table II) is quite similar to those of the isomeric species $Re_2Cl_3(dppm)_2(CO)_2L$, where L = RNC or R′CN.[8] The neutral complex **3a** is paramagnetic, as evidenced by its X-band ESR spectrum at −160 °C in dichloromethane; a broad signal is centered at $g \simeq 2.1$. The magnetic moment of a CH_2Cl_2 solution of **3a** was determined to be 1.7 μ_B by the Evans method.[17]

(b) X-ray Crystal Structures of $[Re_2Cl_3(dppm)_2(CO)_2(CN\text{-}t\text{-}Bu)]PF_6$ (1a) and $Re_2Cl_3(dppm)_2(CO)_2(CN\text{-}i\text{-}Pr)$ (4). To aid in the characterization of these systems, we succeeded in growing crystals of complex **1a** and a representative of type **4** (L = *i*-PrNC), the latter being derived from **2** (i.e. $[Re_2Cl_3(dppm)_2(CO)_2(CN\text{-}i\text{-}Pr)]PF_6$) by a one-electron reduction.[8] Unfortunately we have not yet been able to obtain suitable single crystals of **3a**, which is an isomer of **4** (vide supra).

Atomic coordinates and selected molecular geometrical parametes for the structure of **1a** are given in Tables III and IV, respectively; the corresponding results from the structure of compound **4** are given in Tables V and VI. Plots of the molecular structures and atom-labeling schemes of **1a** and **4** are given in Figures 1 and 2, respectively.

The structures of the dinuclear complexes **1a** and **4** are both representative of the M_2L_{10} edge-sharing bioctahedral structural type. The Re–Re distance in **1a**, 2.605 (1) Å, is comparable to that found[8] in the structure of $[Re_2Cl_3(dppm)_2(CO)_2(NCEt)]PF_6$ (**2**) (2.586 (1) Å), which also has a formal Re_2^{4+} core. The propionitrile derivative **2**, unlike **1a**, has an all-cis arrangement of π-bonding ligands in the equatorial plane. In the structure of the highly reduced species **4**, which has a formal Re_2^{3+} core, the Re–Re distance is 2.718 (1) Å. This is comparable to the average distance of 2.704 (1) Å found[1] for $[Re_2(\mu\text{-}Cl)(\mu\text{-}C{=}NH\text{-}t\text{-}Bu)(\mu\text{-}dppm)_2Cl_2(CN\text{-}t\text{-}Bu)_2]^+$, which like **4** possesses an all-cis arrangement of ligands in the equatorial plane. By way of establishing a point of reference for the Re–Re distances, we note that the Re–Re double bond in $Re_2Cl_6(dppm)_2$—which has a Re_2^{6+} core—is 2.616 Å.[18] It is clear that reduction by two electrons, from Re_2^{6+} to Re_2^{4+}, in such edge-sharing bioctahedral species does not result in a lengthening of the metal-to-metal distance, while a further reduction to a formal Re_2^{3+} core is accompanied by an increase of about 0.1 Å in the metal–metal separation.

The folding of the bridging dppm ligands in both **1a** and **4** is similar to that found previously[1,8] in dirhenium compounds containing bridging dppm entities and carbonyl and isocyanide or nitrile ligands. That is, both bridgehead methylene carbon atoms are folded to the side of the molecule containing the π-bonding ligands. In the case of **1a**, in which one side of the equatorial plane has two carbonyl ligands and the other side has the *tert*-butyl isocyanide ligand, the bridgehead carbon atoms envelop the side containing the two carbonyl groups.

While complex **4** could in principle have mirror symmetry in the equatorial plane, it crystallizes in a pattern disordered about a twofold symmetry axis that passes through the bridging ligands. The disordered portion of the structure comprises only the terminal carbonyl and isopropyl isocyanide ligands. In contrast, compound **1a** crystallizes without disorder and without crystallographic symmetry, in space group *P*1, with one formula unit per unit cell. For the sake of completion, we examined possible disordered models available with space group $P\bar{1}$ and found the disorder too severe to be consistent with the excellent X-ray scattering properties of crystals of **1a**. In any event, it is pointless to impose disorder when reduction of the symmetry of the model reveals a fully ordered structure.

(c) Isomerization in the Case of $[Re_2Cl_3(dppm)_2(CO)(CNR)_2]PF_6$ (R = *t*-Bu or Xylyl). In our search for further examples of isomerism in edge-shared bioctahedral complexes derived from $Re_2Cl_4(dppm)_2$, we have discovered that a change from the two carbonyl and one isocyanide ligand combination, seen in complexes **1–4**, to one carbonyl and two isocyanides gives systems that also display structural isomerism, as we shall now describe.

We have previously shown[6] that the monocarbonyl complex $Re_2Cl_4(dppm)_2(CO)$, which bears a very close structural relationship to its mono(isocyanide) analogue, reacts with 1 equiv of an isocyanide to generate complexes of stoichiometry $Re_2Cl_4(dppm)_2(CO)(CNR)$ (where R = *i*-Pr, *t*-Bu, xylyl, or mesityl). We now find that the reactions of the monocarbonyl with 2 equiv of *t*-BuNC or xylNC (or of the corresponding monocarbonyl–mono(isocyanide) complexes with 1 equiv of isocyanide) in the presence of $TlPF_6$ or KPF_6 yield salts of stoichiometry $[Re_2Cl_3(dppm)_2(CO)(CNR)_2]PF_6$. Spectroscopic and electrochemical data for the three complexes isolated (**5–7**) are listed in Table VII. Acetone solutions of **5–7** ($\sim 10^{-3}$ M) possess conductivities that are characteristic of 1:1 electrolytes (132, 117, and 114 Ω^{-1} cm^2 mol^{-1}, respectively).

In the case of the *t*-BuNC derivative **5**, the carbonyl ligand is clearly terminal (based upon IR spectral data), in contrast to the case for the xylyl isocyanide derivatives **6** and **7** (vide infra) and the other complexes described in this report (complexes **1–4**), in which one carbonyl bridges the Re–Re bond. As it turns out, this result is not especially surprising since $Re_2Cl_4(dppm)_2(CO)(CN\text{-}t\text{-}Bu)$ (one of the starting materials for this complex) also contains terminally bound carbonyl and isocyanide ligands.[6] In this regard, complex **5** may resemble structurally the tris(isocyanide) complex $[Re_2Cl_3(dppm)_2(CN\text{-}t\text{-}Bu)_3]PF_6$, in which all three *t*-BuNC ligands are terminally bound.[1] Its electrochemical properties, as measured by the CV technique, are similar to those of $[Re_2Cl_3(dppm)_2(CN\text{-}t\text{-}Bu)_3]PF_6$,[1] and no reversible processes are observed.

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

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

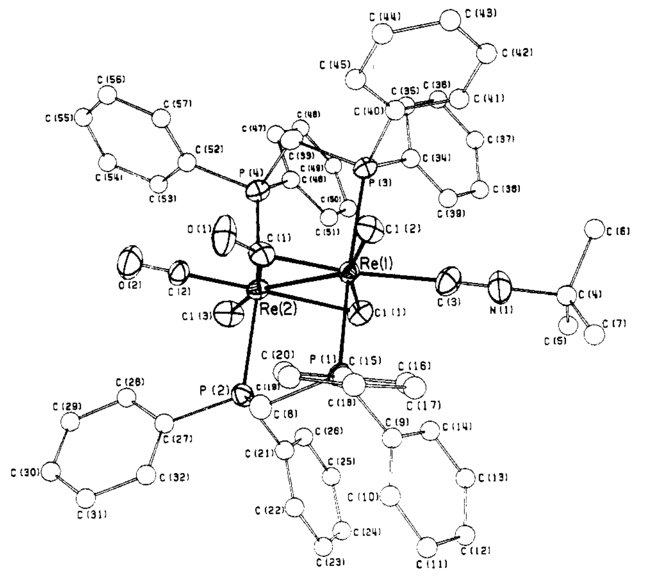

Figure 1. ORTEP drawing of the complex cation $[Re_2Cl_3(dppm)_2(CO)_2(CN\text{-}t\text{-}Bu)]^+$, showing the atom-labeling scheme. Carbon atoms of the phenyl and *tert*-butyl groups are shown as small circles; all other atoms are shown as their 50% probability ellipsoids.

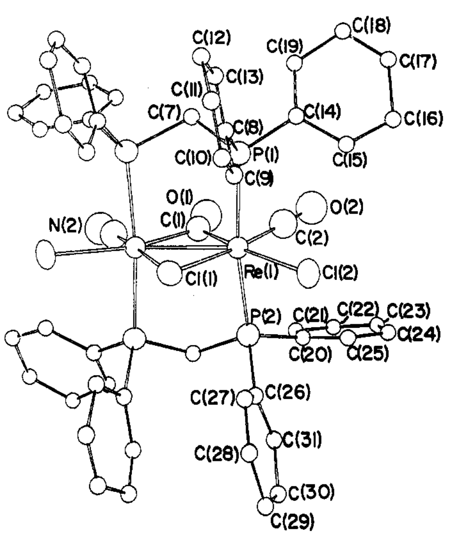

Figure 2. ORTEP drawing of the molecule $[Re_2Cl_3(dppm)_2(CO)_2(CN\text{-}i\text{-}Pr)]$, showing the atom-labeling scheme.

Solutions in 0.1 M TBAH–CH_2Cl_2 display an irreversible oxidation at $E_{p,a}$ = +1.63 V and an irreversible reduction at $E_{p,c}$ = –0.8 V (both vs. Ag/AgCl) together with several product waves. In the ^1H NMR spectrum of this complex there are two resonances for the *t*-Bu groups, at δ +1.02 and +1.20, which integrate well against the phenyl resonances. A recent X-ray crystal structure determination on the salt $[Re_2Cl_3(dppm)_2(CO)(CN\text{-}t\text{-}Bu)_2](PF_6)_{0.5}(OMe)_{0.5}$ has confirmed that the CO and *t*-BuNC ligands are terminally bound and that there are no chloride bridges present.[19]

The IR spectroscopic properties of the xylyl isocyanide complexes **6** and **7** clearly show the presence of a bridging carbonyl ligand and terminal isocyanide ligands (Table VII). Their electrochemical properties resemble those of **1** and **2** (see Table II) insofar as their cyclic voltammograms on 0.1 M TBAH–CH_2Cl_2 solutions display one reversible oxidation and two reversible reductions. The ^1H NMR spectrum of **7** shows a single sharp resonance at δ +2.08 for the methyl groups on the xylNC ligands, implying the equivalence of these two ligands, whereas the related spectrum for **6** shows resonances at δ +1.60 and +1.64 (both singlets), most likely signifying the presence of inequivalent xylNC ligands. The $^{31}P\{^1H\}$ NMR spectrum of **7** shows a singlet

Table VII. Electrochemical and Spectroscopic Properties of $[Re_2Cl_3(dppm)_2(CO)(CNR)_2]PF_6$

complex	IR, cm^{-1} [a]		half-wave potentials, V [b]			electronic abs spectrum	^1H NMR, δ [d]		$^{31}P\{^1H\}$ NMR, δ [f]
	ν(CN)	ν(CO)	$E_{1/2}(1)$	$E_{1/2}(2)$	$E_{1/2}(3)$	λ, nm (ϵ) [c]	RNC	$-CH_2-$ [e]	
$[Re_2Cl_3(dppm)_2(CO)(CN\text{-}t\text{-}Bu)_2]PF_6$ (**5**)	2178 m 2155 s	1960 s	see text			500 (sh), 314 (12000)	+1.02 s +1.20 s	+6.12[h] +6.33[h]	–6.29 –11.50
$[Re_2Cl_3(dppm)_2(CO)(CNxyl)_2]PF_6$ (**6**)	2137 s 2000 s	1701 m, br	+0.98 (ox)	–0.05 (red)	–0.98 (red)	700 (210), 448 (6300)	+1.60 s[g] +1.64 s[g]	+4.74[h] +4.85[h]	–20.75 –23.21
$[Re_2Cl_3(dppm)_2(CO)(CNxyl)_2]PF_6$ (**7**)	2149 s 2140 s	1688 s	+1.39 (ox)	–0.22 (red)	–1.14 (red)	1180 (240), 816 (480), 447 (6400)	+2.08 s[g]	+4.28[i]	–14.33

[a] Recorded as Nujol mulls. Very similar spectra were obtained on CH_2Cl_2 solutions with ν(CN) and ν(CO) modes located within 10 cm^{-1} of the corresponding bands in the mull spectra. [b] Measured on 0.1 M TBAH–CH_2Cl_2 solutions and referenced to the Ag/AgCl electrodes, with scan rate (v) 200 mV/s at a Pt-bead electrode. Under our experimental conditions $E_{1/2}$ = +0.47 V for the ferrocenium/ferrocene couple. [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 CD_2Cl_2 with aqueous H_3PO_4, as an external standard. The spectra of **5** and **6** appear as AA'BB' patterns; chemical shifts are of the most intense inner components of the pattern. The spectrum of **7** is a singlet. [g] CH_3- resonances of the xylyl group. [h] These $-CH_2-$ resonances appear as an AB pattern with superimposed P–H coupling. [i] Complex multiplet.

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(19) Fanwick, P. E.; Price, A. C.; Walton, R. A., unpublished results.

at δ −14.33 whereas that of **6** displays a complex AA′BB′ pattern with superimposed P–H coupling (Table VII). Accordingly, the spectroscopic evidence supports the green isomer **7** as most likely possessing an all-cis disposition of the three π-acceptor ligands (as is also the case for complexes **2a** and **2b**) while **6** may well have a structure closely akin to that of **1a** and **1b**. If this is the case, we would expect **6** to be converted to **7** upon heating, in a fashion similar to the conversion of **1** to **2** (vide supra). This has been confirmed upon heating yellow **6** in 1,2-dichloroethane for 12 h (see Experimental Section). The solution slowly changed from yellow to green, and upon workup the green isomer **7** was identified on the basis of its electrochemical and infrared spectral properties.

(d) Concluding Remarks. The present work clearly establishes that isomerism can occur in edge-shared bioctahedral complexes that contain π-acceptor RNC and CO ligands and that are derived from multiply bonded dimetal precursor complexes. In the case of complexes that contain three such ligands, an all-cis configuration appears to be the thermodynamically favored one. Apparently, the considerable kinetic stability of the isomers $[Re_2Cl_3(dppm)_2(CO)_2(CNR)]PF_6$ (**1**, R = *t*-Bu or xylyl) and $[Re_2Cl_3(dppm)_2(CO)(CNR)_2]PF_6$ (**6**, R = xylyl) may reflect the high activation energy barriers associated with the bond-breaking–bond-making processes that must accompany their conversion to $[Re_2Cl_3(dppm)_2(CO)_2(CNR)]PF_6$ (**2**, R = *t*-Bu or xylyl) and $[Re_2Cl_3(dppm)_2(CO)(CNR)_2]PF_6$ (**7**, R = xylyl), respectively. The crystal structure of the reduced complex $Re_2Cl_3(dppm)_2(CO)_2(CN\text{-}i\text{-}Pr)$, which is derived from the all-cis isomer $[Re_2Cl_3(dppm)_2(CO)_2(CN\text{-}i\text{-}Pr)]PF_6$, shows that it retains the basic structure of its parent, a conclusion that had previously been inferred from IR spectroscopic and electrochemical measurements.[8]

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Supplementary Material Available: For the crystal structures of **1a** and **4**, full tables of bond distances and bond angles and tables of anisotropic displacement parameters and, for **4**, figures showing 19 contoured sections of the final difference Fourier map (33 pages); for both crystal structures, listings of observed and calculated structure factors (37 pages). Ordering information is given on any current masthead page.

Notes

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Electrochemistry of (μ-Porphinato)bis[dicarbonylrhodium(I)] Complexes. Oxidative Conversion of $(P)[Rh(CO)_2]_2$ to $[(P)Rh]^+$, Where P = Octaethyl- or Tetraphenylporphyrin

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Rhodium(I) porphyrins of the form $(TPP)[Rh(CO)_2]_2$ and $(OEP)[Rh(CO)_2]_2$, where TPP and OEP are the dianions of tetraphenylporphyrin and octaethylporphyrin, respectively, have two rhodium atoms bonded to two of the four nitrogen atoms on the porphyrin ring.[1-5] Two carbonyl ligands complete the approximate square-planar arrangement around each rhodium atom. The Rh(I) ions are on opposite sides of the porphyrin plane, and a metal–metal separation of 3.09 Å is reported for $(OEP)[Rh(CO)_2]_2$.[6,7] This distance is too long to suggest a direct rhodium–rhodium bond.

The photochemistry[8,9] and chemical reactivity[1-5,10] of bimetallic Rh(I) porphyrins have been reported, but their electrochemical properties have never been investigated. The combination of the two rhodium atoms with the porphyrin ring presents an interesting system. An electrochemical oxidation of these species may lead to formation of reactive intermediates such as are observed in the chemistry of monomeric or dimeric rhodium porphyrins.[11-17]

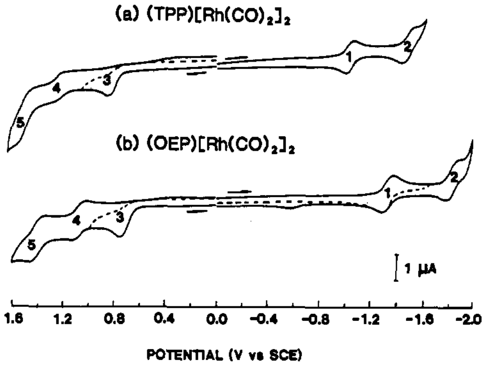

Figure 1. Cyclic voltammograms of (a) 8.1×10^{-4} M $(TPP)[Rh(CO)_2]_2$ and (b) 5.9×10^{-4} M $(OEP)[Rh(CO)_2]_2$ in PhCN containing 0.1 M TBAP. Scan rate = 100 mV/s.

This work presents the electrochemistry of $(TPP)[Rh(CO)_2]_2$ and $(OEP)[Rh(CO)_2]_2$ in benzonitrile (PhCN) and methylene chloride (CH_2Cl_2). Either one or two reversible one-electron reductions and up to three one-electron oxidations are observed depending upon the solvent media. The first oxidation involves a $Rh(I) \rightleftharpoons Rh(II)$ transition for one of the two rhodium atoms and is followed by a chemical reaction resulting in $[(P)Rh]^+$ formation. This is the first example of direct metal insertion in porphyrin chemistry that is triggered by an electrochemical oxidation. The electrochemistry was monitored by electronic absorption spectroscopy and FTIR, and on the basis of these data an overall reaction mechanism is formulated.

Experimental Section

(μ-Tetraphenylporphinato)bis[dicarbonylrhodium(I)], $(TPP)[Rh(CO)_2]_2$, and (μ-octaethylporphinato)bis[dicarbonylrhodium(I)], (OEP)-

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