

This would mean that the formation of molybdenum(0) carbonyl complexes would be accompanied by the production of compounds with the metal in a higher oxidation state.

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Supplementary Material Available: Full tables of bond lengths and angles and tables of anisotropic displacement parameters for compounds **2** and **3** and a stereoscopic ORTEP view of the unit cell for compound **3** (8 pages); listings of observed and calculated structure factors for **2** and **3** (26 pages). Ordering information is given on any current masthead page.

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Reactions of the Dirhenium(II) Complexes $\text{Re}_2\text{X}_4(\text{dppm})_2$ ($\text{X} = \text{Cl}$ or Br ; $\text{dppm} = \text{Ph}_2\text{PCH}_2\text{PPh}_2$) with Isocyanides. 3.¹ Dinuclear Species Containing Two or Three Isocyanide Ligands

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The triply bonded dirhenium(II) compound $\text{Re}_2\text{Cl}_4(\text{dppm})_2$ ($\text{dppm} = \text{Ph}_2\text{PCH}_2\text{PPh}_2$) reacts with 2 equiv of *t*-BuNC to yield the bis(isocyanide) species $[\text{Re}_2\text{Cl}_3(\text{dppm})_2(\text{CN-}t\text{-Bu})_2]^+$ (isolated as its PF_6^- salt) in two isomeric forms (green and yellow). The reaction between the monoisocyanide complexes $\text{Re}_2\text{Cl}_4(\text{dppm})_2(\text{CNR})$ ($\text{R} = t\text{-Bu}$ or *xylyl*) and an excess of a nitrile $\text{R}'\text{CN}$ ($\text{R}' = \text{Me}$, *Et*, or *Ph*) in the presence of KPF_6 produces the mixed isocyanide-nitrile complexes $[\text{Re}_2\text{Cl}_3(\text{dppm})_2(\text{CNR})(\text{NCR}')]\text{PF}_6$. The probable structures of these new products are discussed in light of structural data for the previously characterized bis(nitrile) derivatives. Complexes containing three RNC ligands $[\text{Re}_2\text{Cl}_3(\text{dppm})_2(\text{CNR})_3]^+$ ($\text{R} = t\text{-Bu}$ or *xylyl*) have been isolated by the reaction of $[\text{Re}_2\text{Cl}_3(\text{dppm})_2(\text{CN-}t\text{-Bu})(\text{NCEt})]\text{PF}_6$ or $\text{Re}_2\text{Cl}_4(\text{dppm})_2$ with ca. 4 equiv of *t*-BuNC and of $[\text{Re}_2\text{Cl}_3(\text{dppm})_2(\text{CN}xylyl)(\text{NCPH})]\text{PF}_6$ with 2.5-equiv of *xylyl*NC. These products provide further examples of structural isomerism in compounds with edge-shared bioctahedral geometries. A novel complex that contains a μ -iminyl ligand, $[\text{Re}_2(\mu\text{-Cl})(\mu\text{-C}=\text{NH-}t\text{-Bu})(\mu\text{-dppm})_2\text{Cl}_2(\text{CN-}t\text{-Bu})_2]\text{PF}_6$, has been isolated as a byproduct in the synthesis of the green isomer of stoichiometry $[\text{Re}_2\text{Cl}_3(\text{dppm})_2(\text{CN-}t\text{-Bu})_2]\text{PF}_6$. This complex, which has been characterized by X-ray crystallography, forms monoclinic crystals in space group $P2_1/a$, with the following unit cell dimensions: $a = 22.841$ (4) Å, $b = 25.949$ (5) Å, $c = 24.076$ (4) Å; $\beta = 93.34$ (1)°. With $Z = 8$, the asymmetric unit is defined by two independent molecules of the complex cation **5** and two hexafluorophosphate anions, all of which reside on general positions. The dirhenium molecules **5a** and **5b** are structurally identical, and their corresponding bond distances and angles are very similar. Some average values: $\text{Re-Re} = 2.704$ [1] Å, $\text{Re-Cl}(\text{terminal}) = 2.437$ [4] Å, $\text{Re-Cl}(\text{bridge}) = 2.434$ [1] Å, $\text{Re-C}(\text{terminal}) = 1.98$ [1] Å, $\text{Re-C}(\text{bridge}) = 1.98$ [2] Å, $\text{Re-P} = 2.455$ [3] Å, $\text{Re-Cl-Re} = 67.45$ [5]°, $\text{Re-C-Re} = 85.9$ [5]°, $\text{C}(\text{bridge})\text{-N-CMe}_3 = 131$ [1]°. All new products have been fully characterized by electrochemical and spectroscopic measurements. In addition, the redox chemistry of some of the complexes has been explored. Of special note is the chemical oxidation and reduction of $[\text{Re}_2\text{Cl}_3(\text{dppm})_2(\text{CN}xylyl)_3]\text{PF}_6$ to give paramagnetic $[\text{Re}_2\text{Cl}_3(\text{dppm})_2(\text{CN}xylyl)_3](\text{PF}_6)_2$ and $\text{Re}_2\text{Cl}_3(\text{dppm})_2(\text{CN}xylyl)_3$, respectively.

Introduction

In contrast to the facile cleavage of the Re-Re triple bond of $\text{Re}_2\text{X}_4(\text{PR}_3)_4$ ($\text{X} = \text{Cl}$ or Br ; PR_3 representing a monodentate phosphine ligand) by CO and RNC ligands,^{3,4} the analogous phosphine-bridged species $\text{Re}_2(\mu\text{-dppm})_2\text{X}_4$ ($\text{dppm} = \text{Ph}_2\text{PCH}_2\text{PPh}_2$) react to give products in which a Re-Re bond is preserved.^{1,5-8} In previous studies, we have examined the chemistry of the novel 1:1 isocyanide complexes $\text{Re}_2(\mu\text{-X})(\mu\text{-dppm})_2\text{X}_3(\text{CNR})$, which possess an A-frame-like structure.^{1,7} The present report describes the nature of the species that are found in the reactions between $\text{Re}_2\text{Cl}_4(\text{dppm})_2$ and an excess of RNC, including the isolation and structural characterization of the μ -iminyl complex $[\text{Re}_2(\mu\text{-Cl})(\mu\text{-C}=\text{NH-}t\text{-Bu})(\mu\text{-dppm})_2\text{Cl}_2(\text{CN-}$

$t\text{-Bu})_2]\text{PF}_6$. Some of this chemistry has been the subject of two preliminary communications.^{7,9}

Experimental Section

Starting Materials. The dirhenium complexes $\text{Re}_2\text{Cl}_4(\text{dppm})_2$ and $\text{Re}_2\text{Cl}_4(\text{dppm})_2(\text{CNR})$, where $\text{R} = t\text{-Bu}$ or *xylyl* (*xylyl*), were prepared according to the literature methods.^{1,7,10} The *t*-BuNC ligand was prepared by using the reported procedure,¹¹ while the *xylyl*NC ligand was purchased from Fluka Chemicals and used without further purification. The nitriles, along with other solvents, were thoroughly deoxygenated prior to use. The NOPF_6 was purchased from Alfa Products, cobaltocene was obtained from Strem Chemicals, and HBF_4 was obtained from Aldrich Chemical Co. as a 1.5 M solution in water.

Reaction Procedures. All reactions were performed in a nitrogen atmosphere using standard vacuum line techniques.

A. Bis(isocyanide) Complexes. (i) $[\text{Re}_2\text{Cl}_3(\text{dppm})_2(\text{CN-}t\text{-Bu})_2]\text{PF}_6$ (1, Green Isomer). A solution of $\text{Re}_2\text{Cl}_4(\text{dppm})_2$ (0.20 g, 0.16 mmol) and *t*-BuNC (16.5 μL , 0.16 mmol) in 5 mL of dichloromethane was stirred for 2 min. An additional 16.5 μL of *t*-BuNC was then added, and the green-brown solution was stirred for 30 min. Addition of diethyl ether (30 mL) precipitated the crude product. The resulting green solid was collected and then redissolved in 15 mL of an acetone solution saturated with KPF_6 . Diethyl ether (~100 mL) was added and the mixture al-

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lowed to stand for 20 min. The solid was filtered off and washed with diethyl ether. (The emerald green filtrate and diethyl ether washings were set aside for further workup, see section D.) The solid was dissolved in dichloromethane (20 mL), an equal volume of diethyl ether was added, and the mixture then filtered to remove excess KPF_6 and a small amount of a yellow solid (see section A part ii). An excess of hexanes was added to the green filtrate to precipitate the green product, which was filtered off, washed with hexane, and dried in vacuo; yield 0.15 g, 62%. Anal. Calcd for $\text{C}_{60}\text{H}_{62}\text{Cl}_3\text{F}_6\text{N}_2\text{P}_3\text{Re}_2$: C, 46.23; H, 4.01; Cl, 6.82. Found: C, 45.78; H, 3.94; Cl, 6.99. This same product may be prepared by treating $\text{Re}_2\text{Cl}_4(\text{dppm})_2(\text{CN-}t\text{-Bu})$ with 1 equiv of $t\text{-BuNC}$ in dichloromethane solution.

(ii) $[\text{Re}_2\text{Cl}_3(\text{dppm})_2(\text{CN-}t\text{-Bu})_2]\text{PF}_6$ (2, Yellow Isomer). A solution of $\text{Re}_2\text{Cl}_4(\text{dppm})_2$ (0.10 g, 0.08 mmol) and $t\text{-BuNC}$ (8.3 μL , 0.08 mmol) in 5 mL of acetone was stirred for 2 min. An acetone solution (5 mL) containing TiPF_6 (27 mg, 0.08 mmol) and $t\text{-BuNC}$ (8.3 μL , 0.08 mmol) was then added dropwise with stirring. Following this addition, the yellow-brown mixture was stirred for 30 min and then filtered to remove the TiCl that had formed. Slow addition of 50 mL of diethyl ether precipitated the yellow crystalline product. It was collected, washed with diethyl ether, and dried in vacuo; yield 0.080 g, 66%. Anal. Calcd for $\text{C}_{60}\text{H}_{62}\text{Cl}_3\text{F}_6\text{N}_2\text{P}_3\text{Re}_2$: C, 46.23; H, 4.01; Cl, 6.82. Found: C, 45.49; H, 3.83; Cl, 6.51.

B. Mixed Isocyanide-Nitrile Complexes. (i) $[\text{Re}_2\text{Cl}_3(\text{dppm})_2(\text{CN-}t\text{-Bu})(\text{NCMe})]\text{PF}_6$. In a typical reaction, $\text{Re}_2\text{Cl}_4(\text{dppm})_2(\text{CN-}t\text{-Bu})$ (0.1 g, 0.073 mmol) and KPF_6 (0.0135 g, 0.073 mmol) were suspended in 4 mL of acetone and acetonitrile (2 mL) was added. The red-brown suspension yielded a golden brown solution after it was stirred vigorously for 2 h. The solution was filtered to remove the KCl that had formed. Diethyl ether (~50 mL) was then added to the golden brown filtrate and the desired product precipitated. It was collected by filtration, washed with diethyl ether, and dried in vacuo; yield 0.090 g, 81%. Anal. Calcd for $\text{C}_{67}\text{H}_{76}\text{Cl}_3\text{F}_6\text{N}_3\text{P}_3\text{Re}_2$: C, 45.11; H, 3.73. Found: C, 44.57; H, 3.69.

The following three mixed isocyanide-nitrile complexes were prepared by using a procedure similar to that described in section B part i.

(ii) $[\text{Re}_2\text{Cl}_3(\text{dppm})_2(\text{CN-}t\text{-Bu})(\text{NCEt})]\text{PF}_6$. Yield: 80%. Anal. Calcd for $\text{C}_{68}\text{H}_{78}\text{Cl}_3\text{F}_6\text{N}_3\text{P}_3\text{Re}_2$: C, 45.48; H, 3.83; Cl, 6.95. Found: C, 44.81; H, 3.65; Cl, 7.58.

(iii) $[\text{Re}_2\text{Cl}_3(\text{dppm})_2(\text{CNxyl})(\text{NCMe})]\text{PF}_6$. Yield: 76%. Anal. Calcd for $\text{C}_{61}\text{H}_{56}\text{Cl}_3\text{F}_6\text{N}_2\text{P}_3\text{Re}_2$: C, 46.80; H, 3.62. Found: C, 46.52; H, 3.67.

(iv) $[\text{Re}_2\text{Cl}_3(\text{dppm})_2(\text{CNxyl})(\text{NCPH})]\text{PF}_6$. Yield: 85%. Anal. Calcd for $\text{C}_{66}\text{H}_{58}\text{Cl}_3\text{F}_6\text{N}_2\text{P}_3\text{Re}_2$: C, 48.70; H, 3.60; Cl, 6.54. Found: C, 48.32; H, 3.78; Cl, 7.46.

C. Oxidation of the Mixed Isocyanide-Nitrile Complexes. (i) $[\text{Re}_2\text{Cl}_3(\text{dppm})_2(\text{CN-}t\text{-Bu})(\text{NCMe})](\text{PF}_6)_2$. The complexes described in section B may be oxidized chemically with 1 equiv of NOPF_6 in dichloromethane solution. For example, a quantity of $[\text{Re}_2\text{Cl}_3(\text{dppm})_2(\text{CN-}t\text{-Bu})(\text{NCMe})]\text{PF}_6$ (0.1 g, 0.066 mmol) was dissolved in 5 mL of dichloromethane to yield a golden solution. One equivalent (11.5 mg, 0.066 mmol) of NOPF_6 was added, thereby generating a red-violet solution and evolving $\text{NO}(\text{g})$. The resulting solution was stirred at room temperature for 20 min and then filtered to remove any unreacted NOPF_6 . Diethyl ether (~30 mL) was added to the filtrate to precipitate, upon standing, a rose-colored solid. It was collected, washed with diethyl ether, and dried in vacuo; yield 0.075 g, 69%. The identity of this product was based upon its spectroscopic and electrochemical properties.

(ii) $[\text{Re}_2\text{Cl}_3(\text{dppm})_2(\text{CN-}t\text{-Bu})(\text{NCEt})](\text{PF}_6)_2$. Yield: 70%. Anal. Calcd for $\text{C}_{68}\text{H}_{78}\text{Cl}_3\text{F}_{12}\text{N}_2\text{P}_6\text{Re}_2$: C, 41.54; H, 3.50. Found: C, 41.26; H, 3.57.

(iii) $[\text{Re}_2\text{Cl}_3(\text{dppm})_2(\text{CNxyl})(\text{NCMe})](\text{PF}_6)_2$. Yield: 83%. This species was identified by using electrochemical and spectroscopic techniques.

(iv) $[\text{Re}_2\text{Cl}_3(\text{dppm})_2(\text{CNxyl})(\text{NCPH})](\text{PF}_6)_2$. Yield: 75%. Anal. Calcd for $\text{C}_{66}\text{H}_{58}\text{Cl}_3\text{F}_{12}\text{N}_2\text{P}_6\text{Re}_2$: C, 44.71; H, 3.31. Found: C, 44.61; H, 3.43.

D. Isolation of $[\text{Re}_2(\mu\text{-Cl})(\mu\text{-C}=\text{NH-}t\text{-Bu})(\mu\text{-dppm})_2\text{Cl}_2(\text{CN-}t\text{-Bu})_2]\text{PF}_6 \cdot 0.5\text{CH}_2\text{Cl}_2$ (5). The emerald green filtrate from section A part i was evaporated to dryness, and the resulting blue-green solid was washed with methanol and then with diethyl ether. The product was recrystallized from dichloromethane-diethyl ether and dried in vacuo; yield 0.030 g, 13%. Anal. Calcd for $\text{C}_{65.5}\text{H}_{73}\text{Cl}_4\text{F}_6\text{N}_3\text{P}_3\text{Re}_2$: C, 46.67; H, 4.37. Found: C, 46.70; H, 4.34. The identity of this particular product was based upon a single-crystal X-ray structure analysis, preliminary details of which are reported in ref 9.

E. Tris(isocyanide) Complexes. (i) $[\text{Re}_2\text{Cl}_3(\text{dppm})_2(\text{CN-}t\text{-Bu})_3]\text{PF}_6$ (3). A solution of $[\text{Re}_2\text{Cl}_3(\text{dppm})_2(\text{CN-}t\text{-Bu})(\text{NCEt})]\text{PF}_6$ (0.10 g, 0.065 mmol) in dichloromethane (5 mL) was treated with 4 equiv of $t\text{-BuNC}$ (28 μL , 0.26 mmol) and then stirred at room temperature for 4 h. The light green solid that precipitated was filtered off, washed with diethyl ether, and dried in vacuo; yield 0.072 g, 67%. Anal. Calcd for

$\text{C}_{65}\text{H}_{71}\text{Cl}_3\text{F}_6\text{N}_3\text{P}_3\text{Re}_2$: C, 47.52; H, 4.37. Found: C, 46.64; H, 4.63.

The corresponding chloride salt of this complex could be prepared from the reaction between $\text{Re}_2\text{Cl}_4(\text{dppm})_2$ and 3 equiv of $t\text{-BuNC}$ in acetone. It was identified on the basis of its electrochemical and spectroscopic properties. Some preliminary details of its spectroscopic properties are described in ref 9.

(ii) $[\text{Re}_2\text{Cl}_3(\text{dppm})_2(\text{CNxyl})_3]\text{PF}_6$ (4). A quantity of $[\text{Re}_2\text{Cl}_3(\text{dppm})_2(\text{CNxyl})(\text{NCPH})]\text{PF}_6$ (0.1 g, 0.061 mmol) was dissolved in 5 mL of dichloromethane to yield a golden brown solution. This was treated with a dichloromethane solution (2 mL) containing 2.5 equiv of xylNC (0.020 g, 0.15 mmol) whereupon the reaction mixture turned dark red within 30 min. It was stirred at room temperature for 4 h and then treated with an excess of diethyl ether (~25 mL). The brick red product that had precipitated from the reaction solution was collected, washed with diethyl ether, and dried in vacuo; yield 0.096 g, 87%. Anal. Calcd for $\text{C}_{77}\text{H}_{71}\text{Cl}_3\text{F}_6\text{N}_3\text{P}_3\text{Re}_2$: C, 51.75; H, 4.02. Found: C, 51.04; H, 4.28.

F. Redox Behavior of $[\text{Re}_2\text{Cl}_3(\text{dppm})_2(\text{CNxyl})_3]\text{PF}_6$. (i) $[\text{Re}_2\text{Cl}_3(\text{dppm})_2(\text{CNxyl})_3](\text{PF}_6)_2$. The oxidation can be achieved chemically by adding a slight excess of NOPF_6 (0.008 g, 0.046 mmol) to 5 mL of a dichloromethane solution containing $[\text{Re}_2\text{Cl}_3(\text{dppm})_2(\text{CNxyl})_3]\text{PF}_6$ (0.075 g, 0.042 mmol). The solution was stirred at room temperature for 30 min whereupon the color changed from dark red to orange-brown. The reaction mixture was filtered to remove any unreacted NOPF_6 , and an equal volume of diethyl ether was added to the filtrate to yield an orange-brown solid. This was filtered off and then washed with diethyl ether and dried in vacuo; yield 0.065 g, 80%. Anal. Calcd for $\text{C}_{77}\text{H}_{71}\text{Cl}_3\text{F}_{12}\text{N}_3\text{P}_6\text{Re}_2$: C, 47.86; H, 3.71. Found: C, 46.88; H, 4.16.

(ii) $\text{Re}_2\text{Cl}_3(\text{dppm})_2(\text{CNxyl})_3$. The treatment of $[\text{Re}_2\text{Cl}_3(\text{dppm})_2(\text{CNxyl})_3]\text{PF}_6$ (0.075 g, 0.042 mmol) with cobaltocene (0.009 g, 0.048 mmol) in 5 mL of acetone yielded a bright green solution. This was stirred for 30 min at room temperature during which time a green solid precipitated from the reaction solution. It was filtered off, washed with acetone, to remove excess cobaltocene, and then with hexanes, and dried in vacuo; yield 0.050 g, 72%. Anal. Calcd for $\text{C}_{77}\text{H}_{71}\text{Cl}_3\text{N}_3\text{P}_4\text{Re}_2$: C, 56.33; H, 4.37. Found: C, 54.79; H, 4.62.

Preparation of Single Crystals of $[\text{Re}_2(\mu\text{-Cl})(\mu\text{-C}=\text{NH-}t\text{-Bu})(\mu\text{-dppm})_2\text{Cl}_2(\text{CN-}t\text{-Bu})_2]\text{PF}_6$. Crystals of this complex were prepared in one of two ways. Crystals of a sample prepared as described in section D were grown from a dichloromethane-diethyl ether mixture. Alternatively, a sample of the green isomer of $[\text{Re}_2\text{Cl}_3(\text{dppm})_2(\text{CN-}t\text{-Bu})_2]\text{PF}_6$ (1) (section A part i) was dissolved in dichloromethane and an equal volume of diethyl ether carefully layered over it in a 5-mm quartz NMR tube. The crystal selected for an X-ray structure analysis proved to be that of the μ -iminyl derivative, which is present as an impurity in the sample of 1. The structures of both sets of crystals were found to be identical, preliminary details of the structure of a sample from the first batch having been reported in ref 9. We have not yet found a crystal of 1 that is suitable for an X-ray structure analysis.

X-ray Crystallography. A small crystal of $[\text{Re}_2\text{Cl}_3(\text{dppm})_2(\text{CNMe})_2(\text{CNHCMe}_3)]\text{PF}_6$ (5) of approximate dimensions $0.20 \times 0.15 \times 0.12$ mm was mounted at the end of a glass fiber and covered with epoxy cement. Geometric and intensity data were taken by an Enraf-Nonius CAD-4 automated diffractometer using procedures described previously.¹² Pertinent crystallographic data and unit cell parameters for 5 are given in Table I. The crystal was indexed on 25 intense reflections in the range $20^\circ < 2\theta < 30^\circ$ that were located by an automatic search routine. The crystal system was found to be monoclinic, and the symmetry and lattice dimensions were verified by axial photography. Least-squares analysis was used to refine the cell dimensions and the orientation matrix.

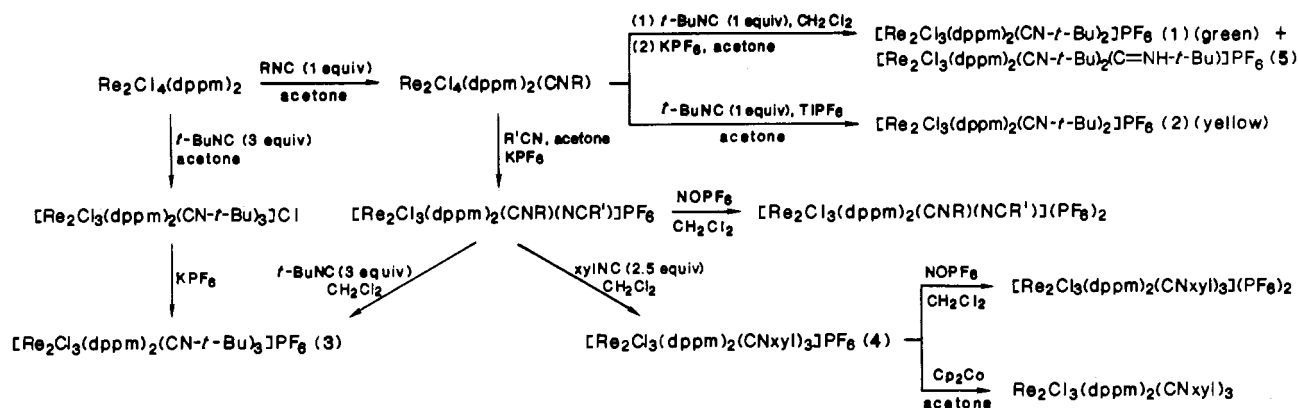
The intensity data, gathered by the ω - 2θ scan technique, were reduced by routine procedures.¹³ Absorption corrections were applied, based on azimuthal scans of several reflections with diffractometer angle χ near 90° .¹⁴ After equivalent data had been averaged, there remained 6657 data with $F_o^2 \geq 3\sigma(F_o^2)$ that were used in the development and refinement of the structure.

The four unique rhenium atoms in the structure were located from a Patterson map. The subsequent development of the coordination spheres of the two separate dirhenium molecules was routine. All non-hydrogen atoms were located with an alternating sequence of least-squares refinements and difference Fourier maps. The refinement was completed in two blocks, with each block comprising one of the crystallographically independent molecules plus the overall scale factor. In the final least-

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(13) Crystallographic computing was done on a PDP-11/60 (RSX-11 MV4.1) with PDP-11 simulated VAXSDP and on a VAX-11/780 (VMS V4.1).

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Scheme I. Reactions of $\text{Re}_2\text{Cl}_4(\text{dppm})_2$ with Isocyanides

squares refinement, 164 atoms were refined, 105 of them isotropically, due in part to insufficient data for complete anisotropic refinement and also to the extremely long computing times required. In a final cycle, 477 parameters were refined, giving a data:parameter ratio of 13.95 and residuals of $R = 0.053$ and $R_w = 0.057$. The quality-of-fit indicator was 1.317 after refinement, and in a final difference Fourier map, there was one peak above $1 \text{ e}/\text{\AA}^3$, which was a ghost of a heavy atom.

Physical Measurements. Infrared spectra were recorded as Nujol mulls or CH_2Cl_2 solutions using an IBM Instruments IR/32 Fourier transform ($4000\text{--}400 \text{ cm}^{-1}$) spectrometer. Electronic absorption spectra were recorded on IBM Instruments 9420 UV-visible ($900\text{--}200 \text{ nm}$) and Cary 17 ($2000\text{--}900 \text{ nm}$) spectrophotometers. Electrochemical experiments were carried out by using a Bioanalytical Systems, Inc., Model CV-1A instrument on dichloromethane solutions containing 0.1 M tetra-*n*-butylammonium hexafluorophosphate (TBAH) as supporting electrolyte. $E_{1/2}$ values $\{[E_{pa} + E_{pc}]/2\}$ were referenced to the Ag/AgCl electrode at room temperature and are uncorrected for junction potentials. $^{31}\text{P}\{^1\text{H}\}$ NMR spectra were recorded on a Varian XL-200 spectrometer operated at 80.98 MHz with an internal deuterium lock using aqueous $85\% \text{ H}_3\text{PO}_4$ as an external standard. Positive chemical shifts were measured downfield from H_3PO_4 . ^1H NMR spectra were also recorded on a Varian XL-200 spectrometer. Resonances were referenced internally to the residual protons in the incompletely deuterated solvent. Conductivities were measured on an Industrial Instruments, Inc., Model RC 16B2 conductivity bridge. X-Band ESR spectra of dichloromethane solutions were recorded at ca. $-160 \text{ }^\circ\text{C}$ with the use of a Varian E-109 spectrometer. Magnetic susceptibility measurements were done by the Evans method on dichloromethane solutions of the complexes using a Varian XL-200 spectrometer.

Microanalyses were performed by Dr. H. D. Lee of the Purdue University microanalytical laboratory.

Results and Discussion

Complexes of the type $[\text{Re}_2\text{X}_4(\text{LL})_2]\text{PF}_6$, where $\text{X} = \text{Cl}$ or Br and $\text{LL} = \text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$ or $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{AsPh}_2$, have been shown to undergo reaction with RNC , where $\text{R} = i\text{-Pr}$ or $t\text{-Bu}$, to yield the monosubstituted products $[\text{Re}_2\text{Cl}_3(\text{LL})_2(\text{CNR})]\text{PF}_6$.^{7,15} These air-stable complexes have proven resistant toward reaction with additional equivalents of isocyanide, thereby hindering our efforts to establish a possible stepwise process that might eventually lead to the cleavage of these multiple bonds by π -acceptor RNC ligands. However, the related triply bonded diphosphine-bridged complex $\text{Re}_2\text{Cl}_4(\text{dppm})_2$ reacts with up to 3 equiv of isocyanide to give several very stable well-defined species that provide insights into the nature of the dirhenium species which can form prior to metal-metal bond cleavage.

(a) Synthesis and Characterization of the Disubstituted Complexes $[\text{Re}_2\text{Cl}_3(\text{dppm})_2(\text{L})(\text{L}')]\text{PF}_6$ ($\text{L} = \text{L}' = t\text{-BuNC}$ When $n = 1$; $\text{L} = \text{RNC}$, $\text{L}' = \text{R}'\text{CN}$ When $n = 1$ or 2). The reaction between $\text{Re}_2\text{Cl}_4(\text{dppm})_2$ and 2 equiv of $t\text{-BuNC}$ yields two complexes of stoichiometry $[\text{Re}_2\text{Cl}_3(\text{dppm})_2(\text{CN-}t\text{-Bu})_2]\text{PF}_6$, one green (1) and the other yellow (2). These complexes may also be prepared by treating preformed $\text{Re}_2\text{Cl}_4(\text{dppm})_2(\text{CN-}t\text{-Bu})$ with 1 equiv of $t\text{-BuNC}$. Formation of 2 is favored in the presence of TIPF_6 , which

Table I. Crystal Data for $[\text{Re}_2\text{Cl}_3(\text{dppm})_2(\text{CNCMe}_3)_2(\text{CNH}_3\text{CMe}_3)]\text{PF}_6$

formula	$\text{Re}_2\text{Cl}_3\text{F}_6\text{P}_5\text{N}_3\text{C}_{65}\text{H}_{72}$
fw	1642.94
space group	$P2_1/a$
syst absences	$(0k0), k \neq 2n; (h0l), h \neq 2n$
$a, \text{\AA}$	22.841 (4)
$b, \text{\AA}$	25.949 (5)
$c, \text{\AA}$	24.076 (4)
α, deg	90
β, deg	93.34 (1)
γ, deg	90
$V, \text{\AA}^3$	14246 (5)
Z	8
$d_{\text{calcd}}, \text{g}/\text{cm}^3$	1.532
cryst size, mm	$0.20 \times 0.15 \times 0.12$
$\mu(\text{Mo K}\alpha), \text{cm}^{-1}$	37.193
data colln instrum	Enraf-Nonius CAD4
radiation monochromated in incident beam ($\lambda, \text{\AA}$)	$\text{Mo K}\alpha (0.71073)$
orientation reflens: no. range (2θ), deg	25, $20 \leq 2\theta \leq 30$
temp, $^\circ\text{C}$	25 ± 1
scan method	ω -scan
data colln range (2θ), deg	$4 \leq 2\theta \leq 45$
no. of unique data with $F_o^2 > 3\sigma(F_o^2)$	6657
no. of params refined	477
transmissn factors, %: max, min	99.1, 78.3
R^a	0.053
R_w^b	0.057
quality-of-fit indicator ^c	1.317
largest shift/esd, final cycle	0.06
largest peak, $\text{e}/\text{\AA}^3$	1.0

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

apparently labilizes a Re-Cl bond (precipitating TiCl) prior to attack by the *second* equivalent of $t\text{-BuNC}$. In the absence of such a halide-labilizing agent, green isomer 1 can be isolated in ca. 60% yield. By reacting $\text{Re}_2\text{Cl}_4(\text{dppm})_2(\text{CNR})$, where $\text{R} = t\text{-Bu}$ or *xylyl*, with an excess of nitrile $\text{R}'\text{CN}$ ($\text{R}' = \text{Me}$, Et , or Ph) in acetone (instead of with RNC) in the presence of KPF_6 , we were able to prepare the analogous mixed isocyanide-nitrile complexes $[\text{Re}_2\text{Cl}_3(\text{dppm})_2(\text{CNR})(\text{NCR}')]\text{PF}_6$. These results are summarized in Scheme I.

Both 1 and 2 behave as 1:1 electrolytes in acetone solution ($\Lambda_M = 100\text{--}120 \text{ } \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$), but they exhibit distinctly different spectroscopic properties (see Table II). Each complex displays only terminal $\nu(\text{C}\equiv\text{N})$ modes in their IR spectra. The same is true of the mixed isocyanide-nitrile complexes, whose spectroscopic properties resemble overall those of 1 and 2 and clearly imply the presence of terminal RNC ligands only.

The bis(isocyanide) complex 1 and the mixed species $[\text{Re}_2\text{Cl}_3(\text{dppm})_2(\text{CNR})(\text{NCR}')]\text{PF}_6$ possess spectroscopic and electrochemical properties (Table II) that are similar to those of

(15) Anderson, L. B.; Tetrick, S. M.; Walton, R. A. *J. Chem. Soc., Dalton Trans.* 1986, 55.

Table II. Electrochemical, Infrared, and Electronic Absorption Spectroscopic Properties of the Disubstituted Complexes $[\text{Re}_2\text{Cl}_3(\text{dppm})_2(\text{L})(\text{L}')]^n$ ($n = 1$ or 2)

complex	IR spectra $\nu(\text{CN}),^a \text{ cm}^{-1}$		CV half-wave potentials, ^c V		electronic abs spectra ^d $\lambda_{\text{max}}, \text{ nm } (\epsilon)$
	R'CN	RNC	(1) $E_{1/2}$	(2) $E_{p,c}$	
$[\text{Re}_2\text{Cl}_3(\text{dppm})_2(\text{CN}-t\text{-Bu})_2]\text{PF}_6$ (1)		2127 m 2160 s 2184 sh	+0.65 (ox)	-1.64	600 (250), 440 sh
$[\text{Re}_2\text{Cl}_3(\text{dppm})_2(\text{CN}-t\text{-Bu})_2]\text{PF}_6$ (2)		2126 vs 2164 m	+1.04 (ox)	-1.07	700 (100), 420 (750)
$[\text{Re}_2\text{Cl}_3(\text{dppm})_2(\text{CN}-t\text{-Bu})(\text{NCMe})]\text{PF}_6$	<i>b</i>	2157 s	+0.66 (ox)	-1.40	688 (100), 490 sh
$[\text{Re}_2\text{Cl}_3(\text{dppm})_2(\text{CN}-t\text{-Bu})(\text{NCEt})]\text{PF}_6$	<i>b</i>	2157 s	+0.65 (ox)	-1.40	678 (130), 450 sh
$[\text{Re}_2\text{Cl}_3(\text{dppm})_2(\text{CN}_{\text{xy}})(\text{NCMe})]\text{PF}_6$	<i>b</i>	2110 s	+0.70 (ox)	-1.40	694 (200), 490 sh
$[\text{Re}_2\text{Cl}_3(\text{dppm})_2(\text{CN}_{\text{xy}})(\text{NCPH})]\text{PF}_6$		2253 w	+0.72 (ox)	-1.35	693 (160), 510 sh
$[\text{Re}_2\text{Cl}_3(\text{dppm})_2(\text{CN}-t\text{-Bu})(\text{NCMe})](\text{PF}_6)_2$		2288 w	+0.63 (red)	-1.40	950 (400), 665 (200), 552 (900)
$[\text{Re}_2\text{Cl}_3(\text{dppm})_2(\text{CN}-t\text{-Bu})(\text{NCEt})](\text{PF}_6)_2$		2280 w	+0.63 (red)	-1.40	955 (475), 670 (125), 552 (1000)
$[\text{Re}_2\text{Cl}_3(\text{dppm})_2(\text{CN}_{\text{xy}})(\text{NCMe})](\text{PF}_6)_2$		2290 w	+0.69 (red)	-1.40	975 (450), 680 (200), 564 (1000)
$[\text{Re}_2\text{Cl}_3(\text{dppm})_2(\text{CN}_{\text{xy}})(\text{NCPH})](\text{PF}_6)_2$		2280 m	+0.72 (red)	-1.35	1020 (400), 680 (200), 567 (900)

^aSpectra were recorded as Nujol mulls. Abbreviations are as follows: s = strong, m = medium, w = weak, sh = shoulder. ^bToo weak to be observed. ^cMeasured on 0.1 M TBAH- CH_2Cl_2 solutions by the cyclic voltammetric technique with a scan rate of $v = 200 \text{ mV/s}$ and referenced to Ag/AgCl. ^dRecorded on CH_2Cl_2 solutions; sh = shoulder.

Table III. NMR Spectral Data for Mixed Isocyanide-Nitrile Complexes of the Type $[\text{Re}_2\text{Cl}_3(\text{dppm})_2(\text{L})(\text{L}')]\text{PF}_6$

complex	¹ H NMR, ^a δ			
	RNC	R'CN	$-\text{CH}_2$ ^b	³¹ P{ ¹ H} NMR, ^c δ
$[\text{Re}_2\text{Cl}_3(\text{dppm})_2(\text{CN}-t\text{-Bu})_2]\text{PF}_6$ (1)	+0.68 s		+6.00 ^e	-10.71, -15.15 ^{f,g}
$[\text{Re}_2\text{Cl}_3(\text{dppm})_2(\text{CN}-t\text{-Bu})_2]\text{PF}_6$ (2)	+2.03 s, +1.24 s		+6.00, +5.42	+5.08, -13.35 ^{f,h}
$[\text{Re}_2\text{Cl}_3(\text{dppm})_2(\text{CN}-t\text{-Bu})(\text{NCMe})]\text{PF}_6$	+0.62 s	+1.38 s	+5.85	-8.56 ⁱ
$[\text{Re}_2\text{Cl}_3(\text{dppm})_2(\text{CN}-t\text{-Bu})(\text{NCEt})]\text{PF}_6$	+0.59 s	+0.53 t, +1.56 q	+5.86, +5.28	-8.59 ⁱ
$[\text{Re}_2\text{Cl}_3(\text{dppm})_2(\text{CN}_{\text{xy}})(\text{NCMe})]\text{PF}_6$	+1.98 s	+1.31 s	+5.90, +5.58	-6.05 ⁱ
$[\text{Re}_2\text{Cl}_3(\text{dppm})_2(\text{CN}_{\text{xy}})(\text{NCPH})]\text{PF}_6$	+2.04 s	<i>d</i>	+5.95, +5.67	-5.34, -6.83 ^j

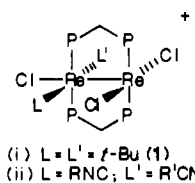
^aMeasured on CD_2Cl_2 solutions and referenced to the residual protons in the solvent ($\delta = +5.35$). Abbreviations are as follows: s = singlet, t = triplet, q = quartet. ^bThe $-\text{CH}_2-$ protons of the dppm ligands appear (unless otherwise stated) as an AB pattern with superimposed P-H coupling. ^cSpectra recorded in $\text{CDCl}_3/\text{CH}_2\text{Cl}_2$ (1:1), unless stated otherwise, with 85% aqueous H_3PO_4 as an external standard. ^dThese appear with the phenyl protons of the dppm ligands. ^eAn apparent pentet ($J(\text{P}-\text{H}) \approx 5.3 \text{ Hz}$). ^fSpectra recorded in a 3:1 mixture of $\text{CH}_2\text{Cl}_2/\text{acetone}-d_6$. ^gAA'BB' pattern. ^hAA'XX' pattern. ⁱBroad singlet. ^jChemical shifts are of the most intense inner components of the AA'BB' pattern.

the related triply bonded, structurally characterized, bis(nitrile) complexes.¹⁶ Each complex possesses a couple at $E_{1/2} \approx +0.65 \text{ V}$, corresponding to an oxidation, as well as an irreversible reduction at $E_{p,c} \approx -1.5 \text{ V}$, as measured by cyclic voltammetry in 0.1 M TBAH- CH_2Cl_2 solution and referenced to the Ag/AgCl electrode.

The ¹H NMR spectrum of **1**, recorded in CD_2Cl_2 , exhibits a single resonance due to the *t*-BuNC ligands and a multiplet (an apparent pentet) for the $-\text{CH}_2-$ protons of the dppm ligands (see Table III). Its ³¹P{¹H} NMR spectrum, measured in a 3:1 mixture of $\text{CH}_2\text{Cl}_2/\text{acetone}-d_6$, displays an AA'BB' pattern.¹⁷ The ¹H NMR spectra of the mixed isocyanide-nitrile complexes $[\text{Re}_2\text{Cl}_3(\text{dppm})_2(\text{CNR})(\text{NCR}')]\text{PF}_6$ (Table III), recorded in CD_2Cl_2 , possess resonances due to the RNC and R'CN (R' = alkyl) ligands and an AB pattern with superimposed P-H coupling for the methylene protons of the dppm ligands. Their ³¹P{¹H} NMR spectra (Table III), in a 1:1 mixture of $\text{CH}_2\text{Cl}_2/\text{CDCl}_3$, exhibit an apparent singlet, except for $[\text{Re}_2\text{Cl}_3(\text{dppm})_2(\text{CN}_{\text{xy}})(\text{NCPH})]\text{PF}_6$, which displays a clearly resolved AA'BB' pattern.¹⁸

On the basis of the similarities between the electrochemical redox properties, electronic absorption spectra, and NMR spectral properties of **1**, $[\text{Re}_2\text{Cl}_3(\text{dppm})_2(\text{CNR})(\text{NCR}')]\text{PF}_6$, and the

structurally characterized bis(nitrile) complexes,¹⁶ we propose that these new products possess the analogous structure



Whereas the bis(nitrile) complex cation (R' = Ph) has been shown to be twisted about the Re-Re bond (the P-Re-Re-P torsion angle being 22°),¹⁶ we cannot (of course) infer anything concerning the details of the rotational geometry in the case of $[\text{Re}_2\text{Cl}_3(\text{dppm})_2(\text{CN}-t\text{-Bu})_2]\text{PF}_6$ (**1**) and $[\text{Re}_2\text{Cl}_3(\text{dppm})_2(\text{CNR})(\text{NCR}')]\text{PF}_6$ from these electrochemical and spectroscopic measurements.

Like the previously characterized bis(nitrile) complexes,^{16,19} the mixed isocyanide-nitrile species can be oxidized chemically to the paramagnetic dication $[\text{Re}_2\text{Cl}_3(\text{dppm})_2(\text{CNR})(\text{NCR}')](\text{PF}_6)_2$ with 1 equiv of NOPF_6 in dichloromethane solution (Scheme I). These red-violet products are 2:1 electrolytes in acetone ($C_m \sim 1 \times 10^{-3} \text{ M}$) with $\Lambda_m = 180\text{--}200 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$. Their X-band ESR spectral properties, measured at -160°C in a dichloromethane glass, are similar to other halo-phosphine complexes that contain the Re_2^{3+} core.^{1,15} Their magnetic moments are $\sim 1.5 (\pm 0.1) \mu_B$, as measured by the Evans method in dichloromethane solution. The electrochemical, IR, and electronic absorption spectroscopic properties of these compounds are summarized in Table II and show a very close resemblance to the corresponding data for $[\text{Re}_2\text{Cl}_3(\text{dppm})_2(\text{NCR}')_2](\text{PF}_6)_2$.¹⁹

Electrochemical measurements on the yellow isomer of stoichiometry $[\text{Re}_2\text{Cl}_3(\text{dppm})_2(\text{CN}-t\text{-Bu})_2]\text{PF}_6$ (**2**) show that it is

(16) Barder, T. J.; Cotton, F. A.; Falvello, L. R.; Walton, R. A. *Inorg. Chem.* **1985**, *24*, 1258.

(17) Simulation of the ³¹P{¹H} NMR spectrum of **1** gave the following parameters: $\delta_A = -10.71$, $\delta_B = -15.15$, $J_{AA'} = 198.8 \text{ Hz}$, $J_{BB'} = 178.5 \text{ Hz}$, $J_{AB} = 78.5 \text{ Hz}$, $J_{AB'} = 2.6 \text{ Hz}$.

(18) These ³¹P{¹H} NMR spectra display a remarkable similarity to those of the structurally characterized bis(nitrile) complexes $[\text{Re}_2\text{Cl}_3(\text{dppm})_2(\text{NCR}')_2]\text{PF}_6$.¹⁶ In the case of the alkyl nitrile complexes an apparent singlet is observed, and it is only when the phenyl groups are present on the nitrile ligands that the chemical shift differences between the two sets of inequivalent phosphorus atoms become large enough to see the appearance of a resolved AA'BB' pattern.

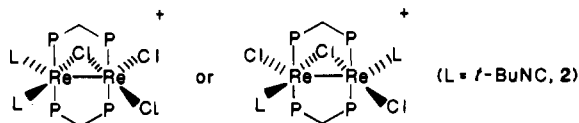
(19) Dunbar, K. R.; Powell, D.; Walton, R. A. *Inorg. Chem.* **1985**, *24*, 2842.

Table IV. Electrochemical and Spectroscopic Properties of $[\text{Re}_2\text{Cl}_3(\text{dppm})_2(\text{CNR})_3]^{n+}$ ($n = 0, 1, \text{ or } 2$)

complex	IR spectra $\nu(\text{CN})^a, \text{cm}^{-1}$	CV half-wave potentials, ^b V				electronic abs spectra ^c $\lambda_{\text{max}}, \text{nm} (\epsilon)$	³¹ P{ ¹ H} NMR, δ
		(1) $E_{1/2}$	(2) $E_{1/2}$	(3) $E_{1/2}$	(4) $E_{1/2}$		
$[\text{Re}_2\text{Cl}_3(\text{dppm})_2(\text{CN-}t\text{-Bu})_3]\text{PF}_6$	2170 m, 2143 vs, 2106 s	+1.18 ^e	+1.01 ^e	-1.08 ^f		~700 sh, 600 (150), ~400 sh ^g	-6.83, -12.73 ^h
$[\text{Re}_2\text{Cl}_3(\text{dppm})_2(\text{CNxyl})_3]\text{PF}_6$	2132 m, 2078 vs, 2051 vs, 1994 sh ^d	+1.21 (ox)	+0.38 (ox)	-0.22 (red)	-1.03 (red)	1245 (300), 454 (20 000)	-23.3 ⁱ
$[\text{Re}_2\text{Cl}_3(\text{dppm})_2(\text{CNxyl})_3](\text{PF}_6)_2$	2174 m, 2137 s, 2114 sh	+1.20 (ox)	+0.38 (red)	-0.22 (red)	-1.03 (red)		
$\text{Re}_2\text{Cl}_3(\text{dppm})_2(\text{CNxyl})_3$	2052 w, 1991 s, 1865 vs	+1.21 (ox)	+0.38 (ox)	-0.22 (ox)	-1.03 (red)		

^a Measured as Nujol mulls. Abbreviations are as follows: s = strong, m = medium, w = weak, sh = shoulder. ^b Measured on 0.1 M TBAH- CH_2Cl_2 solutions by the cyclic voltammetric technique with a scan rate $\nu = 200 \text{ mV/s}$ and referenced to Ag/AgCl. ^c Recorded on CH_2Cl_2 solutions unless otherwise stated. ^d In CH_2Cl_2 solution $\nu(\text{CN})$ modes are observed at 2137 s, 2078 vs, and 1997 sh cm^{-1} . ^e E_{pa} value. ^f E_{pc} value. ^g Recorded on an acetone solution. ^h AA'BB' pattern. Spectrum recorded in $\text{CH}_2\text{Cl}_2/\text{acetone-}d_6$ (3:1) with 85% aqueous H_3PO_4 as an external standard. ⁱ An apparent singlet. Spectrum recorded in $\text{CD}_2\text{Cl}_2/\text{CH}_2\text{Cl}_2$ (1:1).

electronically quite different from **1**, with a reversible oxidation at $E_{1/2} = +1.40 \text{ V}$ and a reduction at $E_{1/2} = -1.07 \text{ V}$ vs. Ag/AgCl (Table II). Its ³¹P{¹H} NMR spectrum, measured in a 3:1 mixture of $\text{CH}_2\text{Cl}_2/\text{acetone-}d_6$, exhibits an AA'XX' pattern.²⁰ The ¹H NMR spectrum of **2**, recorded in CD_2Cl_2 , displays two resonances due to the coordinated *t*-BuNC ligands and an AB pattern for the methylene protons of the dppm ligands. These features imply a rather unsymmetrical structure (certainly one of lower symmetry than **1**) with inequivalent isocyanide ligands. An A-frame-like structure such as either



is a strong possibility. In any event, we see here clear evidence for structural isomers, as is also the case for the neutral "ligand-deficient" complexes $\text{Re}_2\text{X}_4(\text{dppm})_2(\text{L})$ ($\text{L} = \text{CO}$ or RNC).^{1,5-7}

(b) Complexes Containing Three Isocyanide Ligands. The reaction between $\text{Re}_2\text{Cl}_4(\text{dppm})_2$ and 3 equiv of *t*-BuNC in acetone affords a green complex of stoichiometry $\text{Re}_2\text{Cl}_4(\text{dppm})_2(\text{CN-}t\text{-Bu})_3$, which behaves as a 1:1 electrolyte in acetone ($\Lambda_m = 100 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$ for $C_m = 1.08 \times 10^{-3} \text{ M}$) and can be converted into the salt $[\text{Re}_2\text{Cl}_3(\text{dppm})_2(\text{CN-}t\text{-Bu})_3]\text{PF}_6$ (**3**) by reaction with KPF_6 (Scheme 1). An alternative synthesis of **3** was provided through the reaction between $[\text{Re}_2\text{Cl}_3(\text{dppm})_2(\text{CN-}t\text{-Bu})(\text{NCEt})]\text{PF}_6$ and *t*-BuNC in dichloromethane solution. We found no evidence (as monitored by IR spectroscopy and electrochemical measurements) for the intermediate formation of $[\text{Re}_2\text{Cl}_3(\text{dppm})_2(\text{CN-}t\text{-Bu})_2]\text{PF}_6$, which might have been expected to occur if simple displacement of EtCN by *t*-BuNC was the first step in the reaction. In a related reaction, we found that when the complex $[\text{Re}_2\text{Cl}_3(\text{dppm})_2(\text{CNxyl})(\text{NCPH})]\text{PF}_6$ was treated with 2.5 equiv of xylNC in dichloromethane, a very different product results. The brick red complex $[\text{Re}_2\text{Cl}_3(\text{dppm})_2(\text{CNxyl})_3]\text{PF}_6$ was isolated from the dark red reaction solution upon the addition of diethyl ether (Scheme 1). While the stoichiometry of this compound (**4**) is identical with that of its *t*-BuNC analogue, *i.e.* three RNC ligands bound to the dirhenium center, it clearly possesses a different structure based upon electrochemical and spectroscopic measurements. Some representative properties are shown in Table IV.

The electrochemical properties of green **3** show that it possesses only irreversible redox processes (Figure 1), and its IR spectrum displays bands indicative of terminally coordinated isocyanide ligands (see Table IV). Complex **4** resembles **3** in displaying only terminal $\nu(\text{CN})$ modes in its IR spectrum (Table IV), and it is a 1:1 electrolyte in acetone ($\Lambda_m = 125 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$ for $C_m = 1.0 \times 10^{-3} \text{ M}$). It differs most notably in exhibiting a rich, reversible electrochemistry with four one-electron couples in the potential range +1.3 to -1.1 V vs. Ag/AgCl (Table IV and Figure

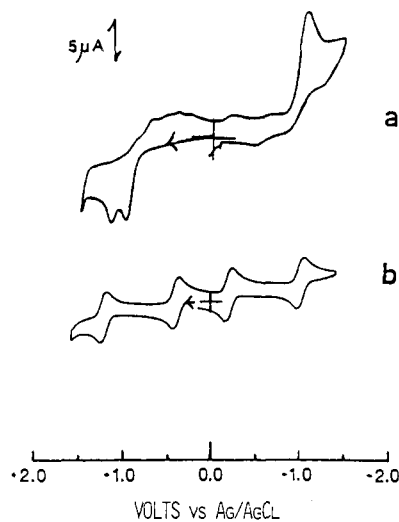


Figure 1. Cyclic voltammograms (scan rate 200 mV/sec at a Pt-bead electrode) of $[\text{Re}_2\text{Cl}_3(\text{dppm})_2(\text{CNR})_3]\text{PF}_6$ in 0.1 M TBAH- CH_2Cl_2 solution: (a) R = *tert*-butyl; (b) R = xyl.

1). The oxidation at $E_{1/2} = +0.38 \text{ V}$ and the reduction at $E_{1/2} = -0.22 \text{ V}$ are accessible chemically (Scheme 1). The oxidation can be achieved through the use of 1 equiv of NOPF_6 in dichloromethane solution. The resulting paramagnetic dication exhibits a broad anisotropic ESR signal (recorded at -160°C in a dichloromethane glass) between 1.0 and 4.0 kG that is centered at $g \sim 2.70$. A magnetic moment determination by the Evans method (recorded in dichloromethane) gave a value of $\mu_{\text{eff}} = 1.7 (\pm 0.1) \mu_B$. A conductivity measurement in a $1 \times 10^{-3} \text{ M}$ acetone solution is consistent with the formulation of this species as a dication ($\Lambda_m = 175 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$).

An acetone solution of **4** can be reduced to the bright green, neutral complex $\text{Re}_2\text{Cl}_3(\text{dppm})_2(\text{CNxyl})_3$ by cobaltocene. Although we were unable to obtain an analytically pure sample of this complex (see Experimental Section), nonetheless, its properties are in accord with this formulation. It displays a broad signal at $g \sim 2.3$ in its ESR spectrum (-160°C in a dichloromethane glass) and a reduction process and three oxidation processes in its cyclic voltammogram (Table IV). However, most diagnostic of these redox changes is the very pronounced shift of $\nu(\text{CN})$ to lower frequencies as the core charge on $[\text{Re}_2\text{Cl}_3(\text{dppm})_2(\text{CNxyl})_3]^{n+}$ ($n = 2, 1, \text{ or } 0$) decreases. This reflects the increase in metal-to-isocyanide π -back-bonding as the charge at the dirhenium center decreases, *i.e.* as the metal center becomes more electron rich.

While we suspect that complexes **3** and **4** represent examples of two of the structural isomers that are possible for species of the type $[\text{Re}_2\text{Cl}_3(\mu\text{-dppm})_2(\text{CNR})_3]^{n+}$, we have not yet been able to grow crystals of either complex of a quality sufficient to determine their X-ray crystal structures and thereby confirm this point. However, it is clear that both complexes differ from a third complex we have isolated that contains three isocyanide or isocyanide-derived ligands, *viz.*, the μ -iminy species $[\text{Re}_2(\mu\text{-Cl})(\mu\text{-$

(20) Simulation of the ³¹P{¹H} NMR spectrum of **2** gave the following parameters: $\delta_A = +5.08$, $\delta_X = -13.35$, $J_{AA'} = 162.2 \text{ Hz}$, $J_{XX'} = 130.4 \text{ Hz}$, $J_{AX} = 61.7 \text{ Hz}$, $J_{AX'} = 7.7 \text{ Hz}$.

Table V. Atomic Positional Parameters and Equivalent Isotropic Displacement Parameters (\AA^2) and Their Estimated Standard Deviations for $[\text{Re}_2\text{Cl}_3(\text{dppm})_2(\text{CNCMe}_3)_2(\text{CNHCMe}_3)]\text{PF}_6^a$

atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> , \AA^2	atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> , \AA^2
Re(1)	0.17563 (4)	0.04160 (4)	0.03061 (4)	2.39 (2)	C(65)	0.321 (1)	-0.094 (1)	-0.019 (1)	4.7 (7)*
Re(2)	0.29495 (4)	0.04471 (4)	0.04294 (4)	2.51 (2)	P(9)	0.2294 (4)	0.2684 (3)	0.2526 (3)	4.9 (2)
Cl(1)	0.0862 (3)	-0.0069 (3)	0.0406 (3)	3.7 (2)	F(1)	0.2359 (9)	0.2626 (7)	0.1870 (6)	9.5 (6)
Cl(2)	0.2359 (3)	-0.0300 (2)	0.0660 (2)	2.9 (1)	F(2)	0.2971 (8)	0.2634 (8)	0.2647 (8)	10.0 (7)
Cl(3)	0.3821 (3)	-0.0045 (3)	0.0703 (3)	4.2 (2)	F(3)	0.2245 (9)	0.2093 (7)	0.2578 (7)	8.7 (6)
P(1)	0.1623 (3)	0.0759 (3)	0.1245 (3)	3.2 (2)	F(4)	0.2257 (8)	0.2749 (7)	0.3170 (6)	8.6 (6)
P(2)	0.1734 (3)	0.0067 (3)	-0.0641 (2)	2.8 (2)	F(5)	0.1645 (9)	0.275 (1)	0.2418 (8)	12.0 (8)
P(3)	0.2938 (3)	0.0733 (3)	0.1404 (3)	3.1 (2)	F(6)	0.239 (1)	0.3280 (7)	0.2469 (9)	12.0 (8)
P(4)	0.3060 (3)	0.0104 (3)	-0.0505 (3)	3.0 (2)	Re(3)	0.82137 (5)	0.51425 (4)	0.53720 (4)	2.56 (2)
N(1)	0.0888 (8)	0.1255 (7)	-0.0178 (8)	3.7 (5)	Re(4)	0.70391 (5)	0.52487 (4)	0.52079 (4)	2.83 (2)
N(2)	0.4012 (8)	0.1189 (8)	0.0269 (8)	3.9 (5)	Cl(4)	0.9147 (3)	0.5078 (3)	0.4931 (2)	4.1 (2)
N(3)	0.2250 (8)	0.1432 (7)	-0.0040 (8)	3.0 (5)	Cl(5)	0.7700 (3)	0.5175 (3)	0.4456 (2)	3.3 (1)
C(1)	0.121 (1)	0.0961 (9)	0.0010 (9)	3.4 (6)	Cl(6)	0.6185 (3)	0.5270 (3)	0.4547 (3)	4.3 (2)
C(2)	0.041 (1)	0.161 (1)	-0.040 (1)	5.3 (7)*	P(5)	0.8397 (3)	0.6079 (3)	0.5346 (3)	2.9 (2)
C(3)	0.060 (1)	0.177 (1)	-0.100 (1)	8 (1)*	P(6)	0.8154 (3)	0.4204 (3)	0.5319 (3)	3.3 (2)
C(4)	-0.018 (1)	0.135 (1)	-0.033 (1)	7.7 (9)*	P(7)	0.7085 (3)	0.6191 (3)	0.5122 (3)	3.5 (2)
C(5)	0.046 (1)	0.209 (1)	-0.004 (1)	9 (1)*	P(8)	0.6841 (3)	0.4324 (3)	0.5261 (3)	3.0 (2)
C(6)	0.356 (1)	0.095 (1)	0.030 (1)	3.8 (6)*	N(4)	0.9189 (8)	0.5030 (8)	0.6326 (7)	3.6 (5)
C(7)	0.458 (1)	0.142 (1)	0.024 (1)	4.8 (7)*	N(5)	0.6112 (9)	0.5437 (9)	0.6092 (8)	5.0 (6)
C(8)	0.460 (1)	0.191 (1)	0.061 (1)	5.6 (8)*	N(6)	0.7417 (9)	0.5215 (8)	0.6441 (8)	4.2 (5)*
C(9)	0.498 (1)	-0.101 (1)	-0.041 (1)	6.5 (8)*	C(66)	0.8779 (9)	0.5078 (9)	0.6007 (8)	2.5 (5)*
C(10)	0.465 (1)	0.161 (1)	-0.037 (1)	5.3 (7)*	C(67)	0.976 (1)	0.494 (1)	0.668 (1)	3.9 (6)*
C(11)	0.237 (1)	0.0950 (8)	0.0157 (8)	3.0 (6)	C(68)	0.981 (1)	0.534 (1)	0.712 (1)	6.3 (8)*
C(12)	0.263 (1)	0.190 (1)	-0.011 (1)	5.2 (7)*	C(69)	0.973 (1)	0.438 (1)	0.691 (1)	5.7 (8)*
C(13)	0.221 (1)	0.233 (1)	-0.036 (1)	6.1 (8)*	C(70)	1.027 (1)	0.495 (1)	0.630 (1)	6.6 (8)*
C(14)	0.307 (1)	0.179 (1)	-0.062 (1)	5.9 (8)*	C(71)	0.642 (1)	0.536 (1)	0.577 (1)	4.0 (7)
C(15)	0.300 (1)	0.206 (1)	0.041 (1)	5.0 (7)*	C(72)	0.560 (1)	0.552 (1)	0.644 (1)	7.2 (9)*
C(16)	0.229 (1)	0.112 (1)	0.1499 (9)	3.4 (6)	C(73)	0.509 (2)	0.565 (1)	0.606 (1)	9 (1)*
C(17)	0.2415 (9)	0.0247 (8)	-0.0962 (9)	2.4 (5)	C(74)	0.552 (1)	0.504 (1)	0.673 (1)	8 (1)*
C(18)	0.102 (1)	0.123 (1)	0.129 (1)	3.6 (6)	C(75)	0.575 (2)	0.594 (1)	0.684 (1)	9 (1)*
C(19)	0.047 (1)	0.107 (1)	0.119 (1)	3.7 (6)*	C(76)	0.7594 (9)	0.5211 (8)	0.5895 (8)	2.3 (5)*
C(20)	-0.001 (1)	0.139 (1)	0.130 (1)	5.5 (7)*	C(77)	0.778 (1)	0.516 (1)	0.698 (1)	4.1 (6)*
C(21)	0.009 (1)	0.189 (1)	0.148 (1)	7.8 (9)*	C(78)	0.808 (1)	0.463 (1)	0.705 (1)	4.6 (6)*
C(22)	0.067 (1)	0.207 (1)	0.158 (1)	5.9 (8)*	C(79)	0.730 (1)	0.521 (1)	0.743 (1)	6.8 (8)*
C(23)	0.114 (1)	0.172 (1)	0.150 (1)	5.8 (8)*	C(80)	0.821 (1)	0.561 (1)	0.705 (1)	5.1 (7)*
C(24)	0.146 (1)	0.035 (1)	0.1809 (9)	3.6 (6)	C(81)	0.774 (1)	0.644 (1)	0.5541 (8)	3.7 (7)
C(25)	0.127 (1)	0.059 (1)	0.232 (1)	4.5 (7)*	C(82)	0.7468 (9)	0.400 (1)	0.5610 (9)	3.1 (6)
C(26)	0.113 (1)	0.025 (1)	0.277 (1)	5.2 (7)*	C(83)	0.897 (1)	0.6308 (9)	0.5826 (9)	3.0 (6)
C(27)	0.118 (1)	-0.029 (1)	0.273 (1)	4.2 (6)*	C(84)	0.886 (1)	0.660 (1)	0.629 (1)	5.0 (7)*
C(28)	0.136 (1)	-0.052 (1)	0.224 (1)	4.7 (7)*	C(85)	0.937 (1)	0.682 (1)	0.661 (1)	5.6 (7)*
C(29)	0.148 (1)	-0.018 (1)	0.176 (1)	4.3 (6)*	C(86)	0.995 (1)	0.676 (1)	0.647 (1)	5.0 (7)*
C(30)	0.1165 (9)	0.0309 (9)	-0.1154 (8)	2.8 (6)	C(87)	1.004 (1)	0.645 (1)	0.601 (1)	4.9 (7)*
C(31)	0.060 (1)	0.0156 (9)	-0.1086 (8)	2.7 (5)*	C(88)	0.955 (1)	0.625 (1)	0.570 (1)	4.2 (6)*
C(32)	0.013 (1)	0.0294 (9)	-0.1492 (9)	3.7 (6)*	C(89)	0.860 (1)	0.643 (1)	0.4720 (9)	3.3 (6)
C(33)	0.029 (1)	0.059 (1)	-0.194 (1)	4.5 (7)*	C(90)	0.869 (1)	0.696 (1)	0.475 (1)	5.8 (8)*
C(34)	0.088 (1)	0.076 (1)	-0.201 (1)	5.4 (7)*	C(91)	0.881 (1)	0.724 (1)	0.429 (1)	5.9 (8)*
C(35)	0.131 (1)	0.058 (1)	-0.159 (1)	4.4 (7)*	C(92)	0.882 (1)	0.701 (1)	0.377 (1)	6.2 (8)*
C(36)	0.1698 (9)	-0.064 (1)	-0.0762 (9)	3.1 (6)	C(93)	0.878 (1)	0.645 (1)	0.373 (1)	4.6 (7)*
C(37)	0.158 (1)	-0.0974 (8)	-0.0352 (9)	2.3 (5)*	C(94)	0.864 (1)	0.617 (1)	0.422 (1)	3.8 (6)*
C(38)	0.155 (1)	-0.150 (1)	-0.050 (1)	4.6 (7)*	C(95)	0.816 (1)	0.386 (1)	0.464 (1)	4.5 (7)
C(39)	0.162 (1)	-0.166 (1)	-0.105 (1)	5.4 (7)*	C(96)	0.797 (1)	0.335 (1)	0.461 (1)	4.8 (7)*
C(40)	0.166 (1)	-0.131 (1)	-0.147 (1)	4.6 (7)*	C(97)	0.799 (1)	0.311 (1)	0.407 (1)	5.9 (8)*
C(41)	0.169 (1)	-0.080 (1)	-0.135 (1)	3.5 (6)*	C(98)	0.824 (1)	0.337 (1)	0.362 (1)	6.3 (8)*
C(42)	0.352 (1)	0.1163 (9)	0.1673 (9)	3.1 (6)	C(99)	0.846 (1)	0.388 (1)	0.368 (1)	4.9 (7)*
C(43)	0.343 (1)	0.168 (1)	0.180 (1)	4.8 (7)*	C(100)	0.842 (1)	0.413 (1)	0.419 (1)	4.0 (6)*
C(44)	0.391 (1)	0.195 (1)	0.206 (1)	4.7 (7)*	C(101)	0.873 (1)	0.3784 (9)	0.5703 (9)	2.7 (5)*
C(45)	0.446 (1)	0.175 (1)	0.211 (1)	5.5 (7)*	C(102)	0.927 (1)	0.376 (1)	0.547 (1)	4.2 (6)*
C(46)	0.458 (1)	0.125 (1)	0.198 (1)	6.6 (8)*	C(103)	0.965 (1)	0.340 (1)	0.569 (1)	7.1 (9)*
C(47)	0.412 (1)	0.093 (1)	0.173 (1)	4.9 (7)*	C(104)	0.955 (1)	0.311 (1)	0.618 (1)	7.1 (9)*
C(48)	0.293 (1)	0.0272 (8)	0.1972 (9)	3.3 (6)	C(105)	0.901 (1)	0.318 (1)	0.642 (1)	5.2 (7)*
C(49)	0.308 (1)	-0.0259 (9)	0.1912 (9)	3.4 (6)*	C(106)	0.857 (1)	0.355 (1)	0.617 (1)	5.5 (7)*
C(50)	0.312 (1)	-0.061 (1)	0.239 (1)	5.9 (8)*	C(107)	0.712 (1)	0.6503 (9)	0.4456 (9)	3.0 (6)
C(51)	0.293 (1)	-0.037 (1)	0.290 (1)	5.6 (7)*	C(108)	0.701 (1)	0.623 (1)	0.396 (1)	4.1 (6)*
C(52)	0.280 (1)	0.014 (1)	0.295 (1)	5.1 (7)*	C(109)	0.702 (1)	0.647 (1)	0.344 (1)	5.3 (7)*
C(53)	0.281 (1)	0.048 (1)	0.2507 (9)	3.8 (6)*	C(110)	0.714 (1)	0.700 (1)	0.341 (1)	5.7 (8)*
C(54)	0.366 (1)	0.0354 (9)	-0.0906 (8)	3.2 (6)	C(111)	0.725 (1)	0.726 (1)	0.391 (1)	6.6 (8)*
C(55)	0.422 (1)	0.017 (1)	-0.076 (1)	4.4 (6)*	C(112)	0.722 (1)	0.702 (1)	0.446 (1)	5.6 (8)*
C(56)	0.470 (1)	0.031 (1)	-0.108 (1)	5.7 (7)*	C(113)	0.648 (1)	0.658 (1)	0.540 (1)	5.9 (9)
C(57)	0.457 (1)	0.068 (1)	-0.155 (1)	5.4 (7)*	C(114)	0.655 (1)	0.678 (1)	0.591 (1)	6.9 (9)*
C(58)	0.399 (1)	0.089 (1)	-0.167 (1)	5.1 (7)*	C(115)	0.605 (2)	0.711 (1)	0.611 (1)	9 (1)*
C(59)	0.355 (1)	0.072 (1)	-0.134 (1)	4.2 (6)*	C(116)	0.559 (2)	0.717 (1)	0.572 (1)	9 (1)*
C(60)	0.3171 (9)	-0.0594 (9)	-0.0620 (9)	2.8 (6)	C(117)	0.554 (1)	0.692 (1)	0.517 (1)	8 (1)*
C(61)	0.324 (1)	-0.075 (1)	-0.118 (1)	4.8 (7)*	C(118)	0.603 (1)	0.662 (1)	0.503 (1)	7.7 (9)*
C(62)	0.338 (1)	-0.128 (1)	-0.129 (1)	5.5 (7)*	C(119)	0.625 (1)	0.4118 (8)	0.5674 (9)	2.7 (6)
C(63)	0.339 (1)	-0.163 (1)	-0.087 (1)	5.2 (7)*	C(120)	0.633 (1)	0.382 (1)	0.614 (1)	4.7 (7)*
C(64)	0.329 (1)	-0.147 (1)	-0.035 (1)	7.2 (9)*	C(121)	0.579 (1)	0.363 (1)	0.640 (1)	4.5 (7)*

Table V (Continued)

atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> , Å ²	atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> , Å ²
C(122)	0.523 (1)	0.371 (1)	0.619 (1)	6.9 (9)*	C(130)	0.641 (1)	0.344 (1)	0.469 (1)	5.7 (8)*
C(123)	0.517 (1)	0.405 (1)	0.574 (1)	6.8 (9)*	P(10)	0.7733 (4)	0.8215 (3)	0.2376 (3)	5.4 (2)
C(124)	0.565 (1)	0.424 (1)	0.547 (1)	5.1 (7)*	F(7)	0.699 (1)	0.3738 (9)	0.7424 (9)	13.0 (8)
C(125)	0.665 (1)	0.3938 (9)	0.4623 (9)	3.0 (6)	F(8)	0.774 (1)	0.343 (1)	0.785 (1)	25 (1)
C(126)	0.680 (1)	0.4103 (9)	0.4117 (9)	3.4 (6)*	F(9)	0.749 (1)	0.322 (1)	0.705 (1)	17.3 (9)
C(127)	0.670 (1)	0.380 (1)	0.364 (1)	5.7 (8)*	F(10)	0.749 (1)	0.2698 (9)	0.780 (1)	19 (1)
C(128)	0.646 (1)	0.331 (1)	0.366 (1)	5.5 (7)*	F(11)	0.674 (1)	0.800 (1)	0.742 (1)	25 (1)
C(129)	0.629 (1)	0.313 (1)	0.421 (1)	7.1 (9)*	F(12)	0.800 (1)	0.821 (1)	0.1809 (9)	21 (1)

* Values marked with an asterisk indicate that the atoms were refined isotropically. Anisotropically refined atoms are given in the form of the equivalent isotropic displacement parameter defined as $\frac{1}{3}[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos \gamma)\beta_{12} + ac(\cos \beta)\beta_{13} + bc(\cos \alpha)\beta_{23}]$.

$\text{C}=\text{NH}-t\text{-Bu}(\mu\text{-dppm})_2\text{Cl}_2(\text{CN}-t\text{-Bu})\text{PF}_6$ (**5**). The blue-green paramagnetic complex **5** was obtained in low yield (ca. 13%) from the filtrate of the reaction that affords the green bis(isocyanide) complex **1**. A crystal obtained in this fashion was subjected to an X-ray crystal structure analysis and was shown to be that of the solvate $[\text{Re}_2(\mu\text{-Cl})(\mu\text{-C}=\text{NH}-t\text{-Bu})(\mu\text{-dppm})_2\text{Cl}_2(\text{CN}-t\text{-Bu})_2]\text{PF}_6 \cdot \text{H}_2\text{O} \cdot 0.5\text{CH}_2\text{Cl}_2$; preliminary details of this structure determination have already been reported.⁹ Later, in a continuing effort to solve the structure of **1** we obtained a batch of crystals from which we selected one that, to our surprise and consternation, proved (once again) to be a crystal of **5**. It is the full details of this structure solution that are discussed in the following section (c). A few crystals of **5** were apparently present as an impurity in **1** as we were able to demonstrate by using cyclic voltammetry measurements.

The dirhenium(II,III) complex **5** behaves as a 1:1 electrolyte in acetone ($\Lambda_m = 125 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$ for $C_m = 0.97 \times 10^{-3} \text{M}$) and shows terminal $\nu(\text{CN})$ modes in its Nujol mull IR spectrum (2145 s, 2112 s, $\sim 2025 \text{sh cm}^{-1}$). While we do not observe a $\nu(\text{C}=\text{N})$ mode that could be attributed to the bridging μ -iminyl ligand, a sharp, weak feature at 3350cm^{-1} is assignable to $\nu(\text{N}-\text{H})$. These results are in accord with other literature data for complexes that contain the $\mu\text{-C}=\text{NH}-t\text{-Bu}$ moiety.²¹ The paramagnetism of **5** is reflected by its well-resolved X-band ESR spectrum (dichloromethane-toluene glass (40:100) at -160°C), in which a complex, anisotropic pattern that displays Re and P hyperfine structure is located between 1.6 and 4.4 kG.²² The complex possesses a well-defined redox chemistry (as measured by cyclic voltammetry) with a reversible one-electron oxidation at +0.22 V and a reversible one-electron reduction at -0.73V in 0.1 M TBAH- CH_2Cl_2 .

The formation of **5** must involve a redox-protonation reaction of some precursor complex. Attempts to protonate $[\text{Re}_2\text{Cl}_3(\text{dppm})_2(\text{CN}-t\text{-Bu})_3]^+$ and a 1:1 mixture of **1** and $t\text{-BuNC}$ using $\text{HBF}_4(\text{aq})/\text{acetone}$ failed to give **5**. Accordingly, the mechanism of its formation remains unclear.

(c) **X-ray Crystal Structure of $[\text{Re}_2(\mu\text{-Cl})(\mu\text{-C}=\text{NH}-t\text{-Bu})(\mu\text{-dppm})_2\text{Cl}_2(\text{CN}-t\text{-Bu})_2]\text{PF}_6$.** Crystal structure solutions were carried out independently (at Purdue and Texas A&M Universities) on two separate samples of this complex. Only details of the latter of the two studies will be described here. Compound **5** crystallizes with a large unit cell consisting of two molecular formulas per asymmetric unit. The two independent dimeric cations **5a** and **5b** are structurally identical. The atomic positional parameters for the two molecules of $[\text{Re}_2\text{Cl}_3(\text{dppm})_2(\text{CNMe}_3)_2(\text{CNHCMe}_3)]\text{PF}_6$ are listed in Table V. Complete tables of anisotropic thermal parameters, bond distances, bond angles, and structure factor data are available as supplementary material. Figures 2 and 3 show the structures and atom-labeling schemes for **5a** and **5b**, respectively. The geometry of the complex is that of an edge-shared bioctahedron with trans bridging dppm ligands spanning the dimetal unit. The disposition of the six ligands in the equatorial plane of the two Re atoms is such that the two terminal CNMe_3 ligands and the bridging $\text{C}=\text{NHCMe}_3$ group are on the same side of the molecule. The other three

Table VI. Selected Bond Distances in Angstroms and Their Estimated Standard Deviations for $[\text{Re}_2\text{Cl}_3(\text{dppm})_2(\text{CNMe}_3)_2(\text{CNHCMe}_3)]\text{PF}_6$ (**5a,b**)

Re(1)-Re(2)	2.705 (1)	N(1)-C(2)	1.51 (3)
Re(1)-Cl(1)	2.424 (6)	N(2)-C(6)	1.21 (3)
Re(1)-Cl(2)	2.436 (5)	N(2)-C(7)	1.44 (3)
Re(1)-P(1)	2.465 (6)	N(3)-C(11)	1.36 (3)
Re(1)-P(2)	2.452 (6)	N(3)-C(12)	1.50 (3)
Re(1)-C(1)	1.99 (2)	C(2)-C(4)	1.52 (4)
Re(1)-C(11)	2.03 (2)	C(7)-C(8)	1.56 (3)
Re(2)-Cl(2)	2.432 (5)	C(12)-C(13)	1.57 (3)
Re(2)-Cl(3)	2.440 (6)	C(18)-C(19)	1.35 (3)
Re(2)-P(3)	2.460 (6)	Re(3)-Re(4)	2.703 (1)
Re(2)-P(4)	2.450 (6)	Re(3)-Cl(4)	2.442 (5)
Re(2)-C(6)	1.97 (3)	Re(3)-Cl(5)	2.438 (5)
Re(2)-C(11)	1.92 (3)	Re(3)-P(5)	2.469 (7)
P(1)-C(16)	1.87 (2)	Re(3)-P(6)	2.443 (7)
P(1)-C(18)	1.86 (3)	Re(3)-C(66)	1.95 (2)
P(2)-C(17)	1.84 (2)	Re(3)-C(76)	1.96 (2)
P(2)-C(30)	1.85 (2)	Re(4)-Cl(5)	2.430 (5)
P(3)-C(16)	1.82 (2)	Re(4)-Cl(6)	2.445 (6)
P(3)-C(42)	1.82 (2)	Re(4)-P(7)	2.457 (7)
P(4)-C(17)	1.82 (2)	Re(4)-P(8)	2.446 (7)
P(4)-C(54)	1.84 (2)	Re(4)-C(71)	2.03 (3)
N(1)-C(1)	1.14 (2)	Re(4)-C(76)	2.03 (2)

positions are occupied by chlorine ligands. Selected bond distances for the two independent dimeric cations **5a** and **5b** are listed in Table VI. The important angles for the molecules are given in Table VII. Average values for some of these distances and angles are listed in Table VIII.

The average Re-Re distance is $2.704 [1] \text{Å}$, which is somewhat longer than the double bond of $\text{Re}_2(\mu\text{-Cl})_2(\mu\text{-dppm})_2\text{Cl}_4$ ($2.616 (1) \text{Å}$)²³ and nearly the same as the value found for $\text{Re}_2\text{Cl}_3(\text{dppm})_2(\text{CO})_2(\text{CNC}_3\text{H}_7)$ ($2.718 (2) \text{Å}$),⁸ a highly reduced complex with a formal Re_2^{3+} core. Other distances to note are $\text{Re}-\text{C}_t = 1.98 [1] \text{Å}$, $\text{Re}-\text{C}_b = 1.98 [2] \text{Å}$, $\text{C}_t-\text{N}_t = 1.15 [2] \text{Å}$, and $\text{C}_b-\text{N}_b = 1.38 [2] \text{Å}$. These are all within expected ranges for terminal isocyanides and bridging iminyl type groups. Important angles are $\text{Re}-\text{Cl}_b-\text{Re} = 67.45 [5]^\circ$, $\text{Re}-\text{C}_b-\text{Re} = 85.9 [5]^\circ$, $\text{C}_t-\text{N}_t-\text{CMe}_3 = 172 [1]^\circ$, and $\text{C}_b-\text{N}_b-\text{CMe}_3 = 131 [1]^\circ$. The angle of 131° for $\mu\text{-C}-\text{NH}-\text{CMe}_3$ and the $\text{C}=\text{N}$ distance of 1.38Å are consistent with the idea that protonation has occurred at the nitrogen atom of the bridging isocyanide.^{21,24,25}

(d) **Concluding Remarks.** In contrast with the ease with which the dimolybdenum(II) complexes $\text{Mo}_2\text{X}_4(\text{dppm})_2$ ($\text{X} = \text{Cl}, \text{Br}, \text{or I}$) react with an excess of alkyl isocyanide (>2 equiv) to yield the mononuclear complex species $[\text{MoX}(\text{CNR})_4(\text{dppm})]^+$, $[\text{Mo}(\text{CNR})_5(\text{dppm})]^{2+}$, and $[\text{Mo}(\text{CNR})_6]^{2+}$ (the product depending on the stoichiometry of the reaction),²⁶ the dirhenium(II) complexes $\text{Re}_2\text{X}_4(\text{dppm})_2$ ($\text{X} = \text{Cl}$ or Br) show a marked kinetic stability to metal-metal bond cleavage. Our previous isolation of the 1:1 complexes $\text{Re}_2\text{X}_4(\text{dppm})_2(\text{CNR})$,^{1,2} together with that of $[\text{Re}_2\text{Cl}_3(\text{dppm})_2(\text{CNR})_2]\text{PF}_6$, $[\text{Re}_2\text{Cl}_3(\text{dppm})_2(\text{CNR})_3](\text{PF}_6)_2$, and $[\text{Re}_2\text{Cl}_3(\text{dppm})_2(\text{CNR})(\text{NCR}')]\text{PF}_6$ in the present work,

(21) Adams, R. D.; Golembeski, N. M. *J. Am. Chem. Soc.* **1979**, *101*, 2579.

(22) For a trace of this ESR spectrum see: Barder, T. J. Ph.D. Thesis, Purdue University, 1984; Figure 6.6.

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

(24) Adams, R. D.; Golembeski, N. M. *Inorg. Chem.* **1979**, *18*, 2255.

(25) Willis, S.; Manning, A. R.; Stephens, F. S. *J. Chem. Soc., Dalton Trans.* **1981**, 332.

(26) Harwood, W. S.; Qi, J.-S.; Walton, R. A. *Polyhedron* **1986**, *5*, 15.

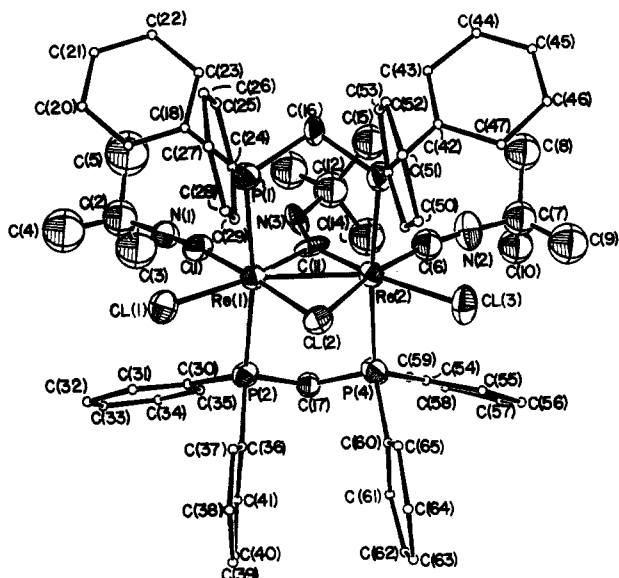


Figure 2. Molecular structure of **5a** with the atom-labeling scheme. With the exception of the carbons of the phenyl rings, the atoms are represented by their 50% probability ellipsoids.

Table VII. Important Bond Angles in Degrees and Their Estimated Standard Deviations for $[\text{Re}_2\text{Cl}_3(\text{dppm})_2(\text{CNCMe}_3)_2(\text{CNHCMes}_3)]\text{PF}_6$ (**5a**)

Re(2)–Re(1)–Cl(1)	148.0 (2)	Re(4)–Re(3)–Cl(4)	145.9 (1)
Re(2)–Re(1)–Cl(2)	56.2 (1)	Re(4)–Re(3)–Cl(5)	56.1 (1)
Re(2)–Re(1)–P(1)	93.7 (2)	Re(4)–Re(3)–P(5)	93.7 (2)
Re(2)–Re(1)–P(2)	94.6 (2)	Re(4)–Re(3)–P(6)	92.4 (2)
Re(2)–Re(1)–C(1)	128.2 (7)	Re(4)–Re(3)–C(66)	136.9 (6)
Re(2)–Re(1)–C(11)	45.2 (7)	Re(4)–Re(3)–C(76)	48.4 (6)
Cl(1)–Re(1)–Cl(2)	91.8 (2)	Cl(4)–Re(3)–Cl(5)	89.8 (2)
Cl(2)–Re(1)–C(1)	175.5 (7)	Cl(4)–Re(3)–C(66)	77.3 (6)
Cl(2)–Re(1)–C(11)	101.4 (7)	Cl(4)–Re(3)–C(76)	165.6 (6)
Cl(1)–Re(1)–C(1)	83.8 (8)	Cl(5)–Re(3)–C(66)	166.9 (6)
Cl(1)–Re(1)–C(11)	166.8 (7)	Cl(5)–Re(3)–C(76)	104.5 (6)
P(1)–Re(1)–P(2)	171.7 (2)	P(5)–Re(3)–P(6)	171.9 (2)
C(1)–Re(1)–C(11)	83 (1)	C(66)–Re(3)–C(76)	88.5 (8)
Re(1)–Re(2)–Cl(2)	56.3 (1)	C(66)–Re(3)–Cl(5)	56.4 (1)
Re(1)–Re(2)–Cl(3)	144.8 (2)	Re(3)–Re(4)–Cl(6)	147.6 (1)
Re(1)–Re(2)–P(3)	93.2 (2)	Re(3)–Re(4)–P(7)	93.8 (2)
Re(1)–Re(2)–P(4)	93.0 (2)	Re(3)–Re(4)–P(8)	94.5 (2)
Re(1)–Re(2)–C(6)	136.5 (7)	Re(3)–Re(4)–C(71)	130.0 (7)
Re(1)–Re(2)–C(11)	48.4 (6)	Re(3)–Re(4)–C(76)	46.2 (6)
Cl(2)–Re(2)–Cl(3)	88.5 (2)	Cl(5)–Re(4)–Cl(6)	91.3 (2)
Cl(2)–Re(2)–C(6)	167.2 (7)	Cl(5)–Re(4)–C(71)	172.8 (7)
Cl(2)–Re(2)–C(11)	104.7 (7)	Cl(5)–Re(4)–C(76)	102.6 (6)
Cl(3)–Re(2)–C(6)	70.7 (7)	Cl(6)–Re(4)–C(71)	82.4 (7)
Cl(3)–Re(2)–C(11)	166.7 (7)	Cl(6)–Re(4)–C(76)	165.8 (6)
P(3)–Re(2)–P(4)	172.6 (2)	P(7)–Re(4)–P(8)	171.7 (2)
C(6)–Re(2)–C(11)	88 (1)	C(71)–Re(4)–C(76)	83.9 (9)
Re(1)–Cl(2)–Re(2)	67.5 (1)	Re(3)–Cl(5)–Re(4)	67.4 (1)
Re(1)–P(1)–C(16)	109.9 (7)	Re(3)–P(5)–C(81)	110.3 (8)
Re(1)–P(1)–C(18)	115.3 (8)	Re(3)–P(5)–C(83)	115.3 (8)
Re(1)–P(2)–C(17)	108.9 (8)	Re(3)–P(6)–C(82)	107.9 (8)
Re(2)–P(3)–C(16)	109.6 (7)	Re(4)–P(7)–C(81)	109.5 (8)
Re(2)–P(3)–C(48)	121.4 (7)	Re(4)–P(7)–C(107)	121.8 (8)
Re(2)–P(4)–C(17)	110.5 (7)	Re(4)–P(8)–C(82)	109.2 (8)
Re(1)–C(1)–N(1)	176 (2)	C(66)–N(4)–C(67)	173 (2)
C(1)–N(1)–C(2)	174 (3)	C(71)–N(5)–C(72)	168 (3)
C(6)–N(2)–C(7)	174 (3)	C(76)–N(6)–C(77)	130 (2)
C(11)–N(3)–C(12)	132 (2)	Re(3)–C(66)–N(4)	169 (2)
Re(2)–C(6)–N(2)	167 (2)	Re(4)–C(71)–N(5)	175 (2)
Re(1)–C(11)–Re(2)	86.4 (9)	Re(3)–C(76)–Re(4)	85.4 (8)
Re(1)–C(11)–N(3)	124 (2)	Re(3)–C(76)–N(6)	150 (2)
Re(2)–C(11)–N(3)	150 (2)	Re(4)–C(76)–N(6)	124 (2)

demonstrates the stabilizing influence of the bridging dppm ligands. When the corresponding monodentate phosphine complexes $\text{Re}_2\text{X}_4(\text{PR}_3)_4$ are reacted with an excess of RNC, mononuclear

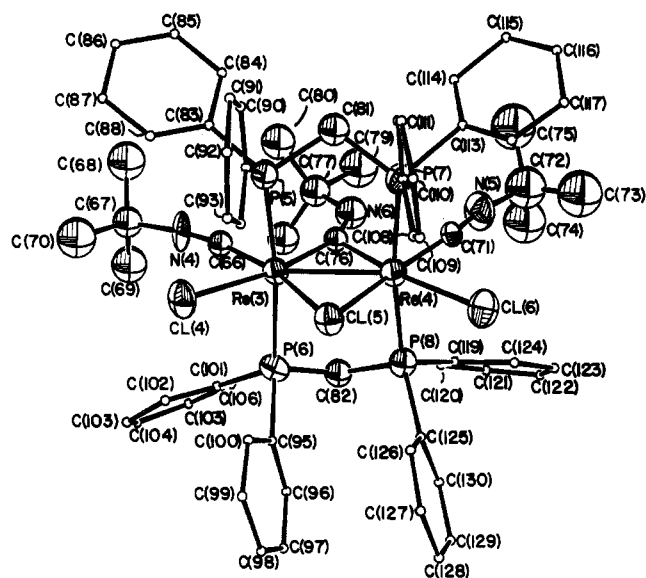


Figure 3. Structure and atom-labeling scheme for the complex cation **5b**.

Table VIII. Average Bond Distances in Angstroms and Bond Angles in Degrees for $[\text{Re}_2\text{Cl}_3(\text{dppm})_2(\text{CNCMe}_3)_2(\text{CNHCMes}_3)]\text{PF}_6^{a,b}$

Re–Re	2.704 [1]	C _t –N _i	1.15 [2]
Re–Cl _t	2.437 [4]	N _i –CMe ₃	1.49 [1]
Re–Cl _b	2.434 [1]	C _b –N _b	1.38 [2]
Re–C _t	1.98 [1]	N _b –CMe ₃	1.505 [5]
Re–C _b	1.98 [2]	P–CH ₂	1.84 [7]
Re–P	2.455 [3]	P–C(ring)	1.839 [7]
Re–Cl _b –Re	67.45 [5]	Re–C _t –N _i	171 [2]
Re–C _b –Re	85.9 [5]	C _b –N _b –CMe ₃	131 [1]
Re–Re–Cl _t	146.5 [7]	C _t –N _i –CMe ₃	172 [1]
Re–Re–P	93.6 [4]	P–CH ₂ –P	110 [1]

^a t = terminal; b = bridging. ^b Numbers in brackets are deviations obtained from the expression $[\sum \Delta_i^2 / (n - 1)]^{1/2}$, where Δ_i is the deviation of the *i*th value from the arithmetic mean and *n* is the total number of values averaged.

rhenium(I) complexes are formed very easily and in high yield.⁴ The isocyanide complexes prepared from the reactions of $\text{Re}_2\text{Cl}_4(\text{dppm})_2$ may provide insights into the sort of intermediates which can be expected to form (but which have never been isolated or even detected) prior to metal–metal bond disruption in the case of $\text{Re}_2\text{X}_4(\text{PR}_3)_4$. Note that when $\text{Re}_2\text{Cl}_4(\text{dppm})_2$ is refluxed with a large excess of RNC for periods of 24 h or so, considerable degradation to mononuclear rhenium(I) species is evidenced⁴ by the appearance of $\nu(\text{CN})$ bands at ~ 2080 and ~ 2050 cm^{-1} in the IR spectrum of the resulting complex reaction mixtures.

Our isolation and characterization of the novel μ -imino complex $[\text{Re}_2(\mu\text{-Cl})(\mu\text{-C}=\text{NH-}i\text{-Bu})(\mu\text{-dppm})_2\text{Cl}_2(\text{CN-}i\text{-Bu})_2]\text{PF}_6$ provides an interesting development in the chemistry of these complexes, for it is the first time that we have encountered evidence for ligand-based reactivity in the case of RNC bound to a dimetal unit. Further studies along these lines are currently in progress.

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Supplementary Material Available: Full listings of bond distances, bond angles, and anisotropic displacement parameters from the crystal structure of $[\text{Re}_2\text{Cl}_3(\text{dppm})_2(\text{CNCMe}_3)_2(\text{CNHCMes}_3)]\text{PF}_6$ (11 pages); a listing of observed and calculated structure factors from the crystal structure of $[\text{Re}_2\text{Cl}_3(\text{dppm})_2(\text{CNCMe}_3)_2(\text{CNHCMes}_3)]\text{PF}_6$ (34 pages). Ordering information is given on any current masthead page.