# Reactions of the dirhenium(II) complexes $Re_2X_4(\mu\text{-dppm})_2$ (X = Cl, Br; dppm $= Ph_2PCH_2PPh_2$) with isocyanides

# Part XX [1]. Oxidation of the complexes $Re_2X_4(\mu\text{-dppm})_2(L)$ (X = Cl or Br; dppm $= Ph_2PCH_2PPh_2$; L = $t$-BuNC, XylNC or CO) to the edge-sharing bioctahedral dirhenium(III) cations $[Re_2(\mu\text{-X})_2(\mu\text{-dppm})_2X_3(L)]^+$

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Dedicated to Professor F. Albert Cotton on the occasion of his 70th Birthday in recognition of his outstanding contributions as a mentor and to the evolution of modern inorganic chemistry.

## Abstract

The reactions of the halogens $X_2$ (X = Cl or Br) with the diamagnetic dirhenium(II) complexes $Re_2X_4(\mu\text{-dppm})_2(L)$, where dppm $= Ph_2PCH_2PPh_2$, X = Cl or Br, and L = XylNC (xylyl isocyanide), $t$-BuNC or CO, and with salts of the edge-sharing bioctahedral species $[Re_2X_3(\mu\text{-dppm})_2(CO)(NCMe)_2]^+$, provide convenient routes to the dirhenium(III) species $[Re_2X_5(\mu\text{-dppm})_2(L)]^+$. These cations, where L = XylNC, $t$-BuNC or CO, have been isolated as their halide (Cl$^-$ or Br$_3^-$), $[PF_6]^-$ and $[O_3SCF_3]^-$ salts. IR spectroscopy shows that terminal RNC and CO ligands are present, and a crystal structure determination of the complex $[Re_2Cl_5(\mu\text{-dppm})_2(CO)]PF_6$ confirms that the cation has the edge-sharing bioctahedral structure $[Re_2(\mu\text{-Cl})_2(\mu\text{-dppm})_2Cl_3(CO)]^+$ with a formal Re=Re bond (Re–Re distance = 2.6607(4) Å). $^{31}$P-NMR spectroscopy indicates that these salts are weakly paramagnetic, with their P resonances exhibiting unusually large upfield shifts. © 2000 Elsevier Science S.A. All rights reserved.

*Keywords:* Carbonyl complexes; Crystal structure; Dirhenium(II) complexes; Dirhenium(III) complexes; Isocyanide complexes

## 1. Introduction

Previous studies on the monocarbonyl and monoisocyanide complexes $Re_2X_4(\mu\text{-dppm})_2(L)$, where X = Cl or Br, dppm $= Ph_2PCH_2PPh_2$ and L = CO, $t$-BuNC or xylylNC (XylNC), have shown that the predominant structural form in the solid state is that of the A-frame isomer **I** (i.e. $Re_2(\mu\text{-X})X_3(\mu\text{-dppm})_2(L)$)[2–5].
A second isomeric form with an open structure, without the bridging μ-X ligand, has also been established [5].

**I**
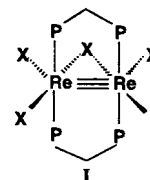
These 1:1 adducts of $Re_2X_4(\mu\text{-dppm})_2$ with RNC and CO are remarkably stable towards loss of the π-acceptor ligands. Furthermore, they show interesting reactivity when treated with further equivalents of RNC and CO ligands [3,5–7] and with alkynes [8,9].

The triply bonded dirhenium(II) synthons $Re_2X_4(\mu\text{-dppm})_2$ [10–12], which are the precursors to $Re_2X_4(\mu\text{-dppm})_2(L)$, are readily oxidized to the edge-sharing bioctahedral dirhenium(III) complexes $Re_2(\mu\text{-X})_2X_4(\mu\text{-}$

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[1] For Part XIX see Ref. [1].

dppm)$_2$ [13,14], in which there is a Re=Re bond ($\sigma^2\pi^2\delta^2\delta^{*2}$ configuration). In the present report, we describe the nature of the products that are formed upon the halogenation of the complexes Re$_2$X$_4$($\mu$-dppm)$_2$(L), where X = Cl or Br when L = CO and X = Cl when L = t-BuNC or XylNC.

## 2. Experimental

### 2.1. Starting materials and reaction procedures

The complexes Re$_2$X$_4$($\mu$-dppm)$_2$ (X = Cl or Br) [15], Re$_2$X$_4$($\mu$-dppa)$_2$ (dppa = Ph$_2$PNHPPh$_2$; X = Cl or Br) [13,16], Re$_2$X$_4$($\mu$-dppm)$_2$(CO) (X = Cl or Br) [2,3], Re$_2$Cl$_4$($\mu$-dppm)$_2$(CNR) (R = t-Bu or Xyl) [4], Re$_2$Br$_4$($\mu$-dppm)$_2$(CNXyl) [4] and [Re$_2$Cl$_3$($\mu$-dppm)$_2$(CO)(NCMe)$_2$]PF$_6$ [3] were prepared according to literature procedures. Samples of [Re$_2$Br$_3$($\mu$-dppm)$_2$(CO)(NCMe)$_2$]PF$_6$ were obtained by the use of a procedure similar to that described for its chloro analog [3], as were the triflate salts [Re$_2$X$_3$($\mu$-dppm)$_2$(CO)(NCMe)$_2$]O$_3$SCF$_3$ [17]. The compounds Re$_2$Cl$_6$($\mu$-dppm)$_2$ and Re$_2$Cl$_6$($\mu$-dppa)$_2$ (dppa = Ph$_2$PNHPPh$_2$) were prepared by the previously reported procedures [13,14]. Samples of Re$_2$Cl$_6$($\mu$-dppa)$_2$ were also obtained by the following alternative procedure. A sample of Re$_2$Cl$_4$($\mu$-dppa)$_2$ [13,16] (0.100 g, 0.078 mmol) was heated in 15 ml of 1,2-dichloroethane and the resulting solution treated with 5 ml of dichloromethane which had been saturated with Cl$_2$ gas. The mixture was stirred for ca. 5 min, the reaction volume was then reduced to ca. 3 ml, and an excess of diethyl ether added to precipitate the purple product. Yield 0.92 g (87%). The cyclic voltammetric properties of this sample were identical to the literature data [13]. The bromo complex Re$_2$Br$_6$($\mu$-dppm)$_2$ was prepared from the reaction between Re$_2$Br$_4$($\mu$-dppm)$_2$ (0.200 g, 0.134 mmol) in 10 ml of dichloromethane and 4 ml of a solution of Br$_2$ in 1,2-dichloroethane. The dark-purple solution was stirred for ca. 10 min, reduced in volume to ca. 5 ml, and treated with an excess of diethyl ether to produce the desired complex. Yield 0.190 g (86%). Anal. Calc. for C$_{51}$H$_{46}$Br$_6$Cl$_2$P$_4$Re$_2$ (i.e. Re$_2$Br$_6$($\mu$-dppm)$_2$·CH$_2$Cl$_2$): C, 35.92; H, 2.71. Found: C, 36.16; H, 2.67%. The presence of a molecule of lattice solvent CH$_2$Cl$_2$ was confirmed by $^1$H-NMR spectroscopy. The cyclic voltammetry (CV) of this product (recorded in 0.1 M n-Bu$_4$NPF$_6$–CH$_2$Cl$_2$ with a Pt-bead electrode) was very similar to that of Re$_2$Cl$_6$($\mu$-dppm)$_2$ [13], with processes at $E_{1/2}$(ox) = + 1.53 and + 0.85 V; $E_{1/2}$(red) = − 0.40 and − 1.23 V vs. Ag | AgCl. A procedure similar to that described for Re$_2$Br$_6$($\mu$-dppm)$_2$ was used to convert Re$_2$Br$_4$($\mu$-dppa)$_2$ [16] to the green complex Re$_2$Br$_6$($\mu$-dppa)$_2$. Yield 77%. This product was identified on the basis of its CV (recorded in 0.1 M n-Bu$_4$NPF$_6$-CH$_2$Cl$_2$

with a Pt-bead electrode): $E_{1/2}$(ox) = + 1.52 and + 0.85 V; $E_{1/2}$(red) = − 0.32 and − 1.11 V vs. Ag | AgCl. These properties are very similar to those of other complexes of this type (see above).

All other reagents and solvents were obtained from commercial sources and used as received. Syntheses were performed under an atmosphere of dry nitrogen. Routine IR spectra, $^1$H-, $^{31}$P-, $^{31}$P{$^1$H}-NMR spectra and cyclic voltammetric measurements were recorded as previously described [5]. Temperature range $^{31}$P-NMR spectra were recorded with the use of a Varian XL-200A spectrometer and referenced to 85% H$_3$PO$_4$ as an external standard. Elemental microanalyses were performed by Dr H.D. Lee of the Purdue University Microanalytical Laboratory.

### 2.2. Synthesis of complexes of the type [Re$_2$X$_5$($\mu$-dppm)$_2$(L)]Y

#### 2.2.1. [Re$_2$Cl$_5$($\mu$-dppm)$_2$(CO)]Cl (1)

A solution of Re$_2$Cl$_4$($\mu$-dppm)$_2$(CO) (0.200 g, 0.153 mmol) in dichloromethane (10 ml) was mixed with 5 ml of a saturated solution of Cl$_2$ in 1,2-dichloroethane and then stirred for 2 min. The resulting purple solution was reduced in volume to ca. 5 ml. An excess of diethyl ether was added to precipitate a purple solid, which was filtered off, washed with 3 × 15 ml of diethyl ether, and dried under a vacuum. Yield 0.185 g (86%). A satisfactory C and H microanalysis could not be obtained, but the spectroscopic and cyclic voltammetric properties of this product (see Section 3) agreed closely with those for the analogous structurally characterized [PF$_6$]$^-$ salt (see Section 2.2.2). Attempts to convert [Re$_2$Cl$_5$($\mu$-dppm)$_2$(CO)]Cl to [Re$_2$Cl$_5$($\mu$-dppm)$_2$(CO)]PF$_6$ by reaction with TlPF$_6$ were unsuccessful due to the decomposition of the chloride salt in solution.

#### 2.2.2. [Re$_2$Cl$_5$($\mu$-dppm)$_2$(CO)]PF$_6$ (2)

The mixed CO−acetonitrile complex [Re$_2$Cl$_3$($\mu$-dppm)$_2$(CO)(NCMe)$_2$]PF$_6$ (0.200 g, 0.133 mmol) was stirred in dichloromethane (10 ml) for 5 min and ca. 5 ml of a saturated solution of Cl$_2$ gas in 1,2-dichloroethane was added. The mixture was stirred for 2 min, filtered, and the filtrate reduced in volume to ca. 5 ml. The addition of an excess of diethyl ether afforded a purple solid, which was filtered off and dried under vacuum. Yield 0.165 g (83%). Anal. Calc. for C$_{51}$H$_{44}$Cl$_5$F$_6$OP$_5$Re$_2$: C, 41.07; H, 2.97. Found: C, 40.10; H, 2.86%. The identity of this product was confirmed by X-ray crystallography.

#### 2.2.3. [Re$_2$Cl$_5$($\mu$-dppm)$_2$(CO)]O$_3$SCF$_3$ (3)

The complex [Re$_2$Cl$_3$($\mu$-dppm)$_2$(CO)(NCMe)$_2$]O$_3$SCF$_3$ was converted to the title complex by the use of a procedure similar to that described in Section 2.2.2 but with a reaction time of 2 h. Yield 85%. Anal. Calc. for C$_{52}$H$_{44}$Cl$_3$F$_3$O$_4$P$_4$Re$_2$S: C, 41.76; H, 2.97. Found: C,

42.16; H, 3.01%. The identity of this product was also based upon the close similarity of its properties to those of the analogous [PF$_6$]$^-$ salt.

### 2.2.4. [Re$_2$Br$_5$(μ-dppm)$_2$(CO)]Br$_3$ (**4**)

A solution of Re$_2$Br$_4$(μ-dppm)$_2$(CO) (0.352 g, 0.236 mmol) in 20 ml of dichloromethane was stirred for 5 min. and then treated with ca. 0.1 ml of liquid Br$_2$ (0.31 g, 1.94 mmol). The brown solution, which darkened immediately upon the addition of Br$_2$, was allowed to stand for 8 h during which time black crystals deposited. The reaction mixture was then filtered and the crystals washed with 2 × 15 ml portions of diethyl ether and dried under a vacuum. Yield 0.398 g (92%). Anal. Calc. for C$_{51}$H$_{44}$Br$_8$OP$_4$Re$_2$: C, 33.87; H, 2.45. Found: C, 33.88; H, 2.41%. The presence of the tribromide ion was confirmed by X-ray crystallography, which also revealed an edge-sharing bioctahedral geometry for the dirhenium cation (Re–Re distance 2.76 Å). Unfortunately, a disorder problem precluded the location and refinement of the CO ligand. Consequently, the structure refinement was abandoned, but there is no doubt that this compound has a structure closely similar to that of the chloro complex [Re$_2$Cl$_5$(μ-dppm)$_2$(CO)]PF$_6$ (see Section 3).

### 2.2.5. [Re$_2$Br$_5$(μ-dppm)$_2$(CO)]PF$_6$ (**5**)

This dark-green complex was prepared from [Re$_2$Br$_3$(μ-dppm)$_2$(CO)(NCMe)$_2$]PF$_6$ (0.200 g, 0.122 mmol) by the use of a procedure similar to that described in Section 2.2.2 for the chloro analog. Yield 0.170 g (81%). Anal. Calc. for C$_{51}$H$_{44}$Br$_5$F$_6$OP$_5$Re$_2$; C, 35.75; H, 2.59. Found: C, 33.95; H, 2.70%.

### 2.2.6. [Re$_2$Br$_5$(μ-dppm)$_2$(CO)]O$_3$SCF$_3$ (**6**)

This complex was prepared upon mixing a dichloromethane solution of [Re$_2$Br$_3$(μ-dppm)$_2$(CO)(NCMe)$_2$]O$_3$SCF$_3$ with a 1,2-dichloroethane solution of Br$_2$ with use of a procedure similar to that described in Section 2.2.2. Yield 90%. Anal. Calc. for C$_{52}$H$_{44}$Br$_5$F$_3$O$_4$P$_4$Re$_2$S: C, 36.36; H, 2.58. Found: C, 35.70; H, 2.44%.

### 2.2.7. [Re$_2$Cl$_5$(μ-dppm)$_2$(CNXyl)]Cl (**7**)

In a typical reaction, Re$_2$Cl$_4$(μ-dppm)$_2$(CNXyl) (0.100 g, 0.071 mmol) was added to 5 ml of dichloromethane, the solution stirred for 10 min, and 2 ml of 1,2-dichloroethane, which had been saturated with Cl$_2$ gas, was then added. The mixture was stirred (2 min) and the volume of the reaction solution reduced to ca. 2 ml. The addition of an excess of diethyl ether afforded a purple solid which was filtered off, washed with diethyl ether and dried under vacuum. Yield 0.087 g (83%). Anal. Calc. for C$_{60}$H$_{55}$Cl$_8$NP$_4$Re$_2$ (i.e. [Re$_2$Cl$_5$(dppm)$_2$(CNXyl)]Cl·CH$_2$Cl$_2$): C, 45.90; H, 3.53. Found: C, 46.15; H, 3.64%.

### 2.2.8. [Re$_2$Cl$_5$(μ-dppm)$_2$(CN-t-Bu)]Cl (**8**)

A procedure similar to that described in Section 2.2.7 was used to convert Re$_2$Cl$_4$(μ-dppm)$_2$(CN-t-Bu) to [Re$_2$Cl$_5$(μ-dppm)$_2$(CN-t-Bu)]Cl, but this product was contaminated with Re$_2$Cl$_6$(μ-dppm)$_2$ as a result of partial decomposition of the starting material during the chlorination process. However, this product can be 'purified' by anion exchange (see below).

### 2.2.9. [Re$_2$Cl$_5$(μ-dppm)$_2$(CNXyl)]O$_3$SCF$_3$ (**9**)

A mixture of [Re$_2$Cl$_5$(μ-dppm)$_2$(CNXyl)]Cl (0.160 g, 0.107 mmol) and TlO$_3$SCF$_3$ (0.039 g, 0.110 mmol) in dichloromethane (15 ml) was stirred at room temperature for 24 h. The white precipitate of TlCl was filtered off, and the purple filtrate reduced in volume to ca. 5 ml. This solution was layered with diethyl ether (40 ml) to induce precipitation of a product, which was filtered off, washed with diethyl ether (2 × 10 ml) and dried under a vacuum. Yield 0.149 g (87%). Anal. Calc. for C$_{60}$H$_{53}$Cl$_5$F$_3$NO$_3$P$_4$Re$_2$S: C, 45.07; H, 3.34; Cl, 11.09. Found: C, 45.05; H, 3.53; Cl, 11.29%.

### 2.2.10. [Re$_2$Cl$_5$(μ-dppm)$_2$(CN-t-Bu)]O$_3$SCF$_3$ (**10**)

A procedure similar to that described in Section 2.2.9 was used to convert impure [Re$_2$Cl$_5$(μ-dppm)$_2$(CN-t-Bu)]Cl to the title complex. Yield 88%. Anal. Calc. for C$_{56}$H$_{53}$Cl$_5$F$_3$NO$_3$P$_4$Re$_2$S: C, 43.38; H, 3.45; Cl, 11.47. Found: C, 43.48; H, 3.58; Cl, 11.30%.

### 2.2.11. [Re$_2$Cl$_5$(μ-dppm)$_2$(CNXyl)]PF$_6$ (**11**)

The reaction between [Re$_2$Cl$_5$(μ-dppm)$_2$(CNXyl)]Cl (0.100 g, 0.07 mmol) and TlPF$_6$ (0.024 g, 0.07 mmol) in dichloromethane (15 ml) was carried out as described in Section 2.2.9. Yield 0.085 g (78%).

### 2.2.12. [Re$_2$Cl$_5$(μ-dppm)$_2$(CN-t-Bu)]PF$_6$ (**12**)

A procedure similar to that described in Section 2.2.9 was used to convert [Re$_2$Cl$_5$(μ-dppm)$_2$(CN-t-Bu)]Cl to the title complex. Yield 76%.

### 2.2.13. [Re$_2$Br$_5$(μ-dppm)$_2$(CNXyl)]Br$_3$ (**13**)

A quantity of Re$_2$Br$_4$(μ-dppm)$_2$(CNXyl) (0.100 g, 0.063 mmol) in 5 ml of dichloromethane was treated with a 2 ml solution of liquid Br$_2$ in 1,2-dichloroethane and then stirred for ca. 10 min. The dark-green solution was reduced in volume to ca. 2 ml and an excess of diethyl ether added. A green solid precipitated upon cooling this mixture to 0°C. Yield 0.091 g (73%). Anal. Calc. for C$_{59}$H$_{53}$Br$_8$NP$_4$Re$_2$: C, 37.07; H, 2.79. Found: C, 38.09; H, 2.96%.

## 2.3. Redox chemistry of the complexes [Re$_2$Cl$_5$(μ-dppm)$_2$(L)]Y

### 2.3.1. Synthesis of Re$_2$Cl$_5$(μ-dppm)$_2$(CNXyl)

A mixture of [Re$_2$Cl$_5$(μ-dppm)$_2$(CNXyl)]Cl (**7**) (0.100 g, 0.07 mmol) and (η$^5$-C$_5$H$_5$)$_2$Co (0.017 g, 0.09 mmol)

in 6 ml of acetone was stirred at room temperature for 2 h, and the insoluble green product filtered off, washed with acetone (2 × 10 ml) and diethyl ether (2 × 10 ml), and dried under a vacuum. Yield 0.065 g (67%). The product was recrystallized from a 1:1 mixture of dichloromethane and di-isopropyl ether. Anal. Calc. for $C_{60}H_{55}Cl_7NP_4Re_2$ (i.e. $Re_2Cl_5(dppm)_2(CNXyl)\cdot CH_2Cl_2$: C, 46.96; H, 3.61. Found: C, 47.29; H, 3.63%. The use of $^1H$-NMR spectroscopy confirmed the presence of lattice solvent $CH_2Cl_2$. This same complex can be produced through the use of the triflate salt **9** in place of **7**.

### 2.3.2. Synthesis of $Re_2Cl_5(\mu\text{-}dppm)_2(CN\text{-}t\text{-}Bu)$

The reaction between $[Re_2Cl_5(\mu\text{-}dppm)_2(CN\text{-}t\text{-}Bu)]Cl$ (**8**) (0.100 g, 0.06 mmol) and $(\eta^5\text{-}C_5H_5)_2Co$ (0.017 g, 0.09 mmol) in acetone, followed by work-up as described in Section 2.3.1, afforded the title complex. Yield 0.059 g(60%). The use of the triflate salt **10** in place of **8** afforded the same product, which was identified on the basis of its electrochemical and spectroscopic properties.

### 2.3.3. Attempted synthesis of $Re_2Cl_5(\mu\text{-}dppm)_2(CO)$

Various attempts were made to reduce $[Re_2Cl_5(\mu\text{-}dppm)_2(CO)]PF_6$ (**2**) to the one-electron reduction product $Re_2Cl_5(\mu\text{-}dppm)_2(CO)$. Reactions between **2** and different stoichiometric quantities of $(\eta^5\text{-}C_5H_5)_2Co$ or $(\eta^5\text{-}C_5Me_5)_2Fe$ in dichloromethane at room temperature or $-78°C$ were carried out for periods of up to 30 min. In all instances, a dark-green product was isolated, which proved to be $Re_2Cl_4(\mu\text{-}dppm)_2(CO)$, based upon its CV properties and IR spectrum [2], along with evidence for a small amount of another product (possibly $Re_2Cl_5(\mu\text{-}dppm)_2(CO)$), which was identified by a $\nu(CO)$ band at 2000 cm$^{-1}$.

### 2.4. X-ray crystallography

Suitable single crystals of $[Re_2Cl_5(\mu\text{-}dppm)_2(CO)]PF_6$ (**2**) were obtained by the slow diffusion of di-isopropyl ether into a solution of the complex in 1,2-dichloroethane.

The data collection was performed at $293 \pm 1$ K on a Nonius Kappa CCD diffractometer. Lorentz and polarization corrections were applied to the data. The crystallographic data are presented in Table 1.

The structure was solved using the structure solution program PATTY in DIRDIF92 [18]. The remaining atoms were located in succeeding difference Fourier syntheses. Hydrogen atoms were placed in calculated positions according to idealized geometries with C–H = 0.95 Å and $U(H) = 1.3\ U_{eq}(C)$. They were included in the refinement but constrained to ride on the atom to which they are bonded. An empirical absorption correction using SCALEPACK [19] was applied. The final refinements were performed by the use of the program SHELXL-97 [20].

During the course of the structural analysis of $[Re_2Cl_5(\mu\text{-}dppm)_2(CO)]PF_6$ the dirhenium unit was found to be located about an inversion center so that each of the four terminal sites in the equatorial plane was $(CO)_{0.25}/Cl_{0.75}$. However, these CO and Cl ligands were resolved in the disorder. The structure was satisfactorily modeled in this way. The structure of **1** was refined in full-matrix least squares where the function minimized was $\Sigma w(|F_o|^2 - |F_c|^2)^2$, where $w = 1/[\sigma^2(F_o)^2 + (0.0392P)^2 + 10.1274P]$ and $P = (F_o^2 + 2F_c^2)/3$. The highest peak/hole in the final difference Fourier had heights of $1.27/-2.43$ e Å$^{-3}$.

The important intramolecular bond distances and angles for the structure of **1** are given in Table 2.

## 3. Results and discussion

### 3.1. Synthetic procedures and preliminary characterization

The 1:1 adducts of the triply bonded dirhenium(II) complexes $Re_2X_4(\mu\text{-}dppm)_2$ (X = Cl or Br) with CO, $t\text{-}BuNC$ and XylNC react with the appropriate halogen $X_2$ to afford the dirhenium(III) complexes $[Re_2X_5(\mu\text{-}dppm)_2(L)]X$ (Eq. (1)).

$$Re_2X_4(\mu\text{-}dppm)_2(L) + X_2 \rightarrow [Re_2X_5(\mu\text{-}dppm)_2(L)]X \quad (1)$$
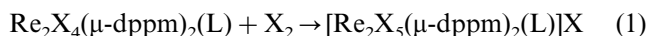
In the case of X = Br and L = CO, the isolated complex contains the $[Br_3]^-$ anion rather than Br$^-$. The course of these reactions resembles the oxidations of $Re_2X_4(\mu\text{-}dppm)_2$ to $Re_2X_6(\mu\text{-}dppm)_2$ (X = Cl or Br) and of $Re_2X_4(\mu\text{-}dppa)_2$ to $Re_2X_6(\mu\text{-}dppa)_2$ (X = Cl or Br) (see Refs. [13,14] and Section 2.1).

Table 1
Crystallographic data for the complex $[Re_2Cl_5(\mu\text{-}dppm)_2(CO)]PF_6$ (**2**)

| | |
|---|---|
| Chemical formula | $C_{51}H_{44}Cl_5F_6OP_5Re_2$ |
| Formula weight | 1491.44 |
| Space group | $P\bar{1}$ (No. 2) |
| $a$ (Å) | 11.2645(3) |
| $b$ (Å) | 12.6994(3) |
| $c$ (Å) | 13.5212(4) |
| $\alpha$ (°) | 88.4142(16) |
| $\beta$ (°) | 66.2077(14) |
| $\gamma$ (°) | 64.1305(16) |
| $V$ (Å³) | 1566.44(9) |
| $Z$ | 1 |
| $D_{calc.}$ (g cm$^{-3}$) | 1.581 |
| $\mu$ (Mo–K$_\alpha$) (mm$^{-1}$) | 4.304 |
| Transmission factors (min/max) | 0.33/0.47 |
| $R$ [a]/$R_w$ [b] | 0.035/0.102 |
| Largest shift/estimated S.D. in final cycle | 0.00 |
| GOF | 1.110 |

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

Table 2
Important bond distances (Å) and angles (°) for the complex [Re$_2$Cl$_5$(μ-dppm)$_2$(CO)]PF$_6$ (**2**) [a]

*Bond lengths*

| | | | |
|---|---|---|---|
| Re–Re′ | 2.6607(4) | Re′–Cl | 2.3934(14) |
| Re–C(1) | 1.93(5) | Re–P(2) | 2.4906(15) |
| Re–C(2) | 2.10(3) | Re–P(1) | 2.4908(15) |
| Re–Cl(1) | 2.356(3) | O(1)–C(1) | 1.18(5) |
| Re–Cl(2) | 2.357(3) | O(2)–C(2) | 0.97(4) |
| Re–Cl | 2.3904(13) | | |

*Bond angles* [b]

| | | | |
|---|---|---|---|
| Cl(1)–Re–Cl(2) | 77.87(11) | Cl(2)–Re–P(2) | 84.90(8) |
| C(1)–Re–Cl | 74.5(13) | Cl–Re–P(2) | 88.17(5) |
| C(2)–Re–Cl | 173.4(8) | C(1)–Re–P(1) | 90.0(12) |
| Cl(1)–Re–Cl | 85.36(8) | C(2)–Re–P(1) | 84.8(7) |
| Cl(2)–Re–Cl | 161.93(9) | Cl(1)–Re–P(1) | 84.47(7) |
| Cl–Re–Cl | 112.41(4) | Cl(2)–Re–P(1) | 89.76(7) |
| C(1)–Re–P(2) | 84.3(12) | Cl–Re–P(1) | 95.30(5) |
| C(2)–Re–P(2) | 90.9(7) | P(2)–Re–P(1) | 172.27(5) |
| Cl(1)–Re–P(2) | 88.94(7) | Re–Cl–Re′ | 67.59(4) |

[a] Numbers in parentheses are estimated S.D. in the least significant digits.

[b] The label Re′ is used for the unlabeled Re atom in Fig. 1; this atom and all other unlabeled non-phenyl group atoms in this Figure are related to the labeled atoms by a crystallographic inversion center. The atoms labeled as C(1), O(1) and Cl(2) that are not shown in Fig. 1, are the other CO and Cl ligand atoms that arise from the other half of the disorder in the asymmetric unit involving the terminal CO and Cl ligands.

Anion exchange of $X^-$ by $[PF_6]^-$ and $[O_3SCF_3]^-$ can be accomplished through the use of the TlPF$_6$ and TlO$_3$SCF$_3$ reagents in the case of the *t*-BuNC and XylNC complexes, but with the monocarbonyls [Re$_2$X$_5$(μ-dppm)$_2$(CO)]Y (Y = PF$_6$ or O$_3$SCF$_3$) a preferred strategy involved the reactions of X$_2$ with the all-*cis* dirhenium(II) complexes [Re$_2$X$_3$(μ-dppm)$_2$(CO)-(NCMe)$_2$]Y(**II**) [3,17] according to Eq. (2).



**II**

$$[Re_2X_3(\mu\text{-dppm})_2(CO)(NCMe)_2]Y + X_2$$
$$\rightarrow [Re_2X_5(\mu\text{-dppm})_2(CO)]Y + 2MeCN$$
$$(Y = [PF_6]^- \text{ or } [O_3SCF_3]^-) \tag{2}$$
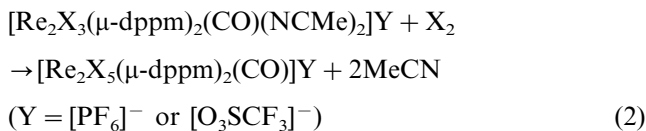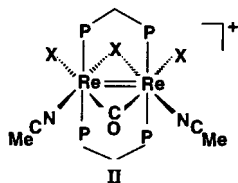
The chloride salts [Re$_2$Cl$_5$(μ-dppm)$_2$(CO)]Cl and [Re$_2$Cl$_5$(μ-dppm)$_2$(CN-*t*-Bu)]Cl were not particularly stable in solution, whereas the analogous [PF$_6$]$^-$ and [O$_3$SCF$_3$]$^-$ salts were much more stable. Solutions of [Re$_2$Cl$_5$(μ-dppm)$_2$(CO)]Cl decompose to give mixtures in which the majority species is the monocarbonyl precursor Re$_2$Cl$_4$(μ-dppm)$_2$(CO).

The complexes that were prepared in the present study, along with the compound numbering scheme and their IR spectra and CV properties are given in Table 3. Conductivity measurements on acetone solutions of several of the complexes confirmed their behavior as 1:1 electrolytes. Each compound displays an intense $v(CN)_t$ or $v(CO)_t$ mode in its Nujol mull IR spectrum, although in a few instances this band is split. The similarity of the CV properties of all the complexes implies a close structural similarity; each exhibits a reversible one-electron oxidation and two reversible one-electron reductions which are shifted by ca. 0.2 V to more negative potentials in the case of compounds **7**–**13**, in accordance with the greater σ-donor ability of the RNC ligands compared to CO. In all cases, these three processes for the chloro complexes are shifted by at least 0.40 V to more positive potentials compared to the corresponding oxidation and two reductions seen in the CV of Re$_2$Cl$_6$(μ-dppm)$_2$ [13].

Successful attempts were made to access the one-electron reduction at $E_{1/2}$ ca. + 0.05 V in the case of the isocyanide complexes **7**–**10**, through the use of the one-electron reductant cobaltocene. The dark-green paramagnetic products Re$_2$Cl$_5$(μ-dppm)$_2$(CNXyl) (**14**) and Re$_2$Cl$_5$(μ-dppm)$_2$(CN-*t*-Bu) (**15**) were isolated in yields of 60% or greater. The two products dissolved in acetone to produce solutions which were essentially non-conducting ($Λ_m$ values < 10 Ω$^{-1}$ cm$^2$ mol$^{-1}$). The Nujol mull IR spectra of **14** and **15** show sharp, intense $v(CN)$ bands at 2130 and 2144 cm$^{-1}$, respectively; these frequencies are shifted by ca. − 50 cm$^{-1}$ compared to the salts of the parent cations, in accord with the lower oxidation state of the dimetal core in **14** and **15** and an increase in Re→CNR(π*) back bonding. The CV properties of **14** and **15** are essentially identical to those of the complexes **7**–**12** (Table 3) with the exception that the processes labeled as $E_{1/2}$(red)(1) correspond to oxidations of the bulk complexes in the case of **14** and **15**. These two compounds possess broad, poorly-defined signals in their $^1$H-NMR spectra and no resonances are observed in the $^{31}$P{$^1$H}-NMR spectra. The X-band ESR spectrum of **14**, recorded as a 1:1 CH$_2$Cl$_2$–toluene glass at 110 K, exhibits two broad signals with $g_\perp$ and $g_\parallel$ values of ca. 2.6 and 2.2, respectively. Similar attempts were made to reduce the monocarbonyl complex **2** to its neutral Re$_2$Cl$_5$(μ-dppm)$_2$(CO) form by the use of cobaltocene and (η$^5$-C$_5$Me$_5$)$_2$Fe as one-electron reductants to access the process at $E_{1/2}$(red) = + 0.35 V. Under our experimental conditions, this neutral dirhenium(III,II) carbonyl complex was found to be unstable and the dirhenium(II) complex Re$_2$Cl$_4$(μ-dppm)$_2$(CO) was identified as the predominant product (by the use of CV and IR spectroscopy), although a $v(CO)$ band of medium intensity at 2000 cm$^{-1}$ in the IR spectrum of the resulting reaction mixture could be due to small quantities of Re$_2$Cl$_5$-

Table 3
IR spectra and cyclic voltammetric properties of $[Re_2X_5(\mu\text{-dppm})_2(L)]Y$ ($X = Cl$ or $Br$; $L = CO$, $t\text{-Bu}$ or $Xyl$; $Y = Cl$, $Br_3$, $PF_6$ or $O_3SCF_3$)

| Complex | Compound no. | IR spectra ($cm^{-1}$) [a] | | | CV half-wave potentials (V) [b] | | | Conductivity ($\Lambda_m$) [c] |
|---|---|---|---|---|---|---|---|---|
| | | $v$(CO) or $v$(CN) | $v$(SO) | $v$(PF$_6$) | $E_{1/2}$(ox) | $E_{1/2}$(red)(1) | $E_{1/2}$(red)(2) | |
| $[Re_2Cl_5(\mu\text{-dppm})_2(CO)]Cl$ | **1** | 2048(s) | | | +1.43(70) | +0.35(60) | −0.57(70) | 89 |
| $[Re_2Cl_5(\mu\text{-dppm})_2(CO)]PF_6$ | **2** | 2061(s), 2047(s) | | 839(vs) | +1.43(60) | +0.35(60) | −0.56(70) | |
| $[Re_2Cl_5(\mu\text{-dppm})_2(CO)]O_3SCF_3$ | **3** | 2067(s) | 1258(vs) | | +1.43(70) | +0.35(60) | −0.55(70) | |
| $[Re_2Br_5(\mu\text{-dppm})_2(CO)]Br_3$ | **4** | 2032(s) | | | +1.35(70) [d] | +0.36(60) | −0.59(70) | 83 |
| $[Re_2Br_5(\mu\text{-dppm})_2(CO)]PF_6$ | **5** | 2028(s) | | 840(vs) | +1.35(80) | +0.37(70) | −0.49(60) | |
| $[Re_2Br_5(\mu\text{-dppm})_2(CO)]O_3SCF_3$ | **6** | 2037(s), 2030(s) | 1262(vs) | | | | | |
| $[Re_2Cl_5(\mu\text{-dppm})_2(CNXyl)]Cl$ | **7** | 2180(s) | | | +1.26(70) | +0.07(60) | −0.83(60) | 102 |
| $[Re_2Cl_5(\mu\text{-dppm})_2(CN\text{-}t\text{-Bu})]Cl$ | **8** | 2192(s), 2161(sh) | | | +1.21(90) | +0.03(70) | −0.89(80) | 95 |
| $[Re_2Cl_5(\mu\text{-dppm})_2(CNXyl)]O_3SCF_3$ | **9** | 2188(s) | 1264(vs) | | +1.24(70) | +0.07(60) | −0.84(60) | 91 |
| $[Re_2Cl_5(\mu\text{-dppm})_2(CN\text{-}t\text{-Bu})]O_3SCF_3$ | **10** | 2196(s) | 1264(vs) | | +1.20(70) | +0.03(60) | −0.89(60) | 96 |
| $[Re_2Cl_5(\mu\text{-dppm})_2(CNXyl)]PF_6$ | **11** | 2180(s) | | 840(vs) | +1.25(70) | +0.08(60) | −0.80(60) | 89 |
| $[Re_2Cl_5(\mu\text{-dppm})_2(CN\text{-}t\text{-Bu})]PF_6$ | **12** | 2190(s) | | 838(vs) | +1.19(70) | +0.03(60) | −0.90(70) | 95 |
| $[Re_2Br_5(\mu\text{-dppm})_2(CNXyl)]Br_3$ | **13** | 2169(s) | | | +1.22(60) [d] | +0.15(70) | −0.69(60) | |

[a] Recorded as Nujol mulls.

[b] Measurements carried out on 0.1 M $n\text{-Bu}_4NPF_6$–$CH_2Cl_2$ solutions and referenced to the Ag | AgCl electrode with a scan rate of 200 mV s$^{-1}$ at a Pt-bead electrode. Under these experimental conditions, $E_{1/2} = +0.47$ V vs. Ag | AgCl for the ferrocenium/ferrocene couple. $\Delta E_p(E_{p,a}-E_{p,c})$ values are given in parentheses.

[c] Molar conductivity, $\Omega^{-1}$ cm$^2$ mol$^{-1}$. Recorded on $1 \times 10^{-3}$ M solutions of the compounds in acetone.

[d] This compound also displays irreversible processes at $E_{p,a}$ ca. +1.0 and +0.8 V vs. Ag | AgCl in its CV due to the [Br$_3$]$^-$ anion.
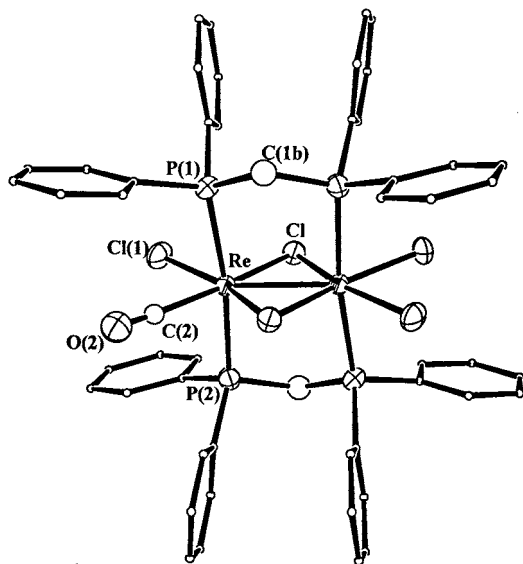
Fig. 1. ORTEP representation [21] of the structure of the [Re₂(μ-Cl)₂(μ-dppm)₂Cl₃(CO)]⁺ cation as present in **2**. This representation shows one-quarter of the disorder involving the terminal CO and Cl ligands. Each terminal site in the equatorial plane is $(CO)_{0.25}/Cl_{0.75}$.

(μdppm)₂(CO). The frequency for this $v(CO)$ mode is shifted by about $-60$ cm⁻¹ relative to the spectrum of [Re₂Cl₅(μ-dppm)₂(CO)]PF₆; this shift is comparable to that for the IR-active $v(CN)$ mode of [Re₂Cl₅(μ-dppm)₂(CNXyl)]PF₆ when this compound is reduced to Re₂Cl₅(μ-dppm)₂(CNXyl).

### 3.2. Crystal structure of [Re₂Cl₅(μ-dppm)₂(CO)]PF₆ and other structural considerations

The structures of the dirhenium compounds of the type [Re₂X₅(μ-dppm)₂(L)]Y were confirmed as being di-μ-halo bridged bioctahedral species (see **III**) by a single-crystal X-ray structural analysis of the complex [Re₂Cl₅(μ-dppm)₂(CO)]PF₆ (**2**). An ORTEP representation [21] of the structure is given in Fig. 1 and key structural parameters are listed in Table 2.



**III**
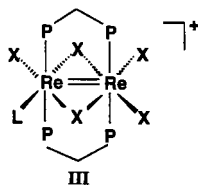
Formally, this structure is derived from that of Re₂Cl₆(μ-dppm)₂ [13] by the replacement of a terminal chloride ligand by CO or RNC and the generation of a monocation[2]. This substitution process need not result in a change in the Re–Re bond order, which is two in the case of Re₂Cl₆(μ-dppm)₂ (i.e. a $\sigma^2\pi^2\delta^2\delta^{*2}$ configuration) [13]. Indeed, the Re–Re bond length is 2.6607(4) Å in

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[2] Note that the reactions of Re₂Cl₆(μ-dppm)₂ with CO or XylNC in the presence of Tl⁺ failed to produce [Re₂Cl₅(μ-dppm)₂(L)]⁺.
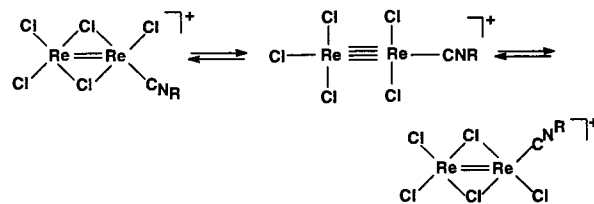


Scheme 1. Possible fluxional process for compounds of the type [Re₂Cl₅(μ-dppm)₂(CNR)]Cl (R = XylNC (**7**) or *t*-BuNC (**8**)).

[Re₂Cl₅(μ-dppm)₂(CO)]PF₆ and, therefore, only 0.045 Å longer than the Re–Re distance in Re₂Cl₆(μ-dppm)₂ [13]. Accordingly, it is reasonable to conclude that a Re=Re bond is present in **2**, and in other compounds of this type, albeit one that is weakened (relative to Re₂Cl₆(μ-dppm)₂) through some degree of Re→CO (or RNC) $\pi^*$ back bonding. The Re–Cl_b bonds are longer than the terminal bonds Re–Cl_t in **2** by ca. 0.03 Å, although this comparison is complicated by the disorder between the terminal CO and Cl ligands as described in more detail in Section 2.4. The Re–Cl_b and Re–Cl_t bonds in Re₂Cl₆(μ-dppm)₂ [13] are essentially identical, in accord with a shorter Re–Re bond distance and more tightly bound bridging chlorides. The Re–P distances for **2** are identical (2.491 Å) and slightly longer than those present in the symmetrical complex Re₂Cl₆(μ-dppm)₂ (2.478 and 2.471 Å) [13] and, like the latter compound, complex **2** possesses a chair conformation for the [Re₂P₄C₂] ring. The [PF₆]⁻ anion refined satisfactorily and showed no evidence of disorder.

Another property of complexes **1–13** which shows a close comparison to the behavior of Re₂Cl₆(μ-dppm)₂, is the unusual upfield shifts of the ³¹P-NMR resonances. As was discussed previously [13], a consequence of the weak paramagnetism of Re₂Cl₆(μ-dppm)₂ is a broad resonance at $\delta$ $-140.6$ in its room temperature ³¹P-NMR spectrum (recorded in 1:1 CH₂Cl₂–CDCl₃); this resonance is shifted ca. 118 ppm upfield of the free ligand resonance. In the present study, we have remeasured this spectrum over the temperature range 20–50°C (in CDCl₃) and find that the resonance shifts upfield from $\delta$ $-138$ to $\delta$ $-147$. These same measurements on the isostructural complex Re₂Cl₆(μ-dppa)₂ (dppa = Ph₂PNHPPh₂) show very similar behavior to that of Re₂Cl₆(μ-dppm)₂, with the resonance shifting from $\delta$ $-155$ at $+20$°C to $\delta$ $-170$ at $+50$°C. The bromo analog Re₂Br₆(μ-dppm)₂ was not soluble enough for us to obtain satisfactory NMR spectral data, but the isostructural compound Re₂Br₆(μ-dppa)₂ was sparingly soluble and its ³¹P-NMR spectrum recorded in CDCl₃ at room temperature exhibited a broad resonance at $\delta$ $-316$.

The CO-containing chloro compounds **1**, **2** and **3** each show a single resonance at $\delta$ ca. $-97$ (spectra recorded in CDCl₃ or CD₂Cl₂). These upfield shifts are again consistent with weak paramagnetic behavior. The

^{31}P-NMR spectrum of $[Re_2Cl_5(\mu\text{-dppm})_2(CO)]Cl$ (**1**) was recorded over the temperature range $+76°C$ to $-80°C$, using $CD_2Cl_2$ as the solvent below $+20°C$ and $1,2\text{-}C_2H_4Cl_2$ above this temperature. A single resonance is observed at $\delta -115$ at the high-temperature limit and this shifts progressively downfield as the temperature is lowered to $-40°C$ ($\Delta\delta/\Delta T$ ca. 0.28 ppm/$°C$). Coalescence is observed at ca. $-50°C$ and by $-80°C$ the spectrum has the appearance of a broad closely spaced AA′BB′ pattern (resonances at $\delta -81.5$ and $-82.5$). We attribute this behavior to a fluxional species which is weakly paramagnetic through thermal population of triplet states (such as $\sigma^2\pi^2\delta^2\delta^{*1}\pi^{*1}$) at higher temperatures. This fluxionality may involve a 'merry-go-round' process of the type we have discussed previously for closely related edge-sharing bioctahedral species [22]. The corresponding CO-containing bromo complex **5** exhibits a broad resonance at $\delta -207$ in its ^{31}P-NMR spectrum (recorded at 20°C in $1,2\text{-}C_2H_4Cl_2$). This upfield shift is far greater than that observed for the chloro analogs **1**–**3** but resembles the very large upfield shift exhibited by the complex $Re_2Br_6(\mu\text{-dppa})_2$ compared to its chloro analog.

In contrast to the behavior of the monocarbonyl complexes, the isocyanide analogues $[Re_2Cl_5(\mu\text{-dppm})_2(CNXyl)]Cl$ (**7**) and $[Re_2Cl_5(\mu\text{-dppm})_2(CN\text{-}t\text{-Bu})]Cl$ (**8**) show an AA′BB′ pattern in their ^{31}P-NMR spectra (recorded in $CD_2Cl_2$), with the multiplets being centered at $\delta -90$ and $-261$, and $\delta -84$ and $-251$, respectively. A temperature range study of the spectrum of **7** was carried out from $+20$ to $-70°C$. The pattern does not change over this range although these two multiplets shift progressively downfield; at the low temperature limit they are observed at $\delta -73$ and $-211$, respectively. These data indicate that **7** and **8** do not exhibit the same type of fluxional process as their carbonyl analogues **1**–**3**; the AA′BB′ pattern signifies the preservation of an unsymmetrical structure over this temperature range. However, a more limited type of fluxionality is not precluded, namely, that illustrated in Scheme 1 in which the isocyanide ligand remains bound to one Re atom. In support of this possibility we note that the solution IR spectra of **7** and **8** (recorded in $CH_2Cl_2$) display two $\nu(CN)$ modes (2183 and 2150 $cm^{-1}$ for **7**, 2192 and 2164 $cm^{-1}$ for **8**), which could correspond to the two structures shown in Scheme 1.

## 4. Conclusions

Although the edge-sharing bioctahedral complex $Re_2Cl_6(\mu\text{-dppm})_2$ fails to react with the organic isocyanide ligands XylNC and $t$-BuNC and with carbon monoxide to produce species of the type $[Re_2Cl_5(\mu\text{-dppm})_2(L)]^+$, salts of these cations and their bromo analogues can be generated by reactions of the dirheni-

um(II) complexes $Re_2X_4(\mu\text{-dppm})_2(L)$ (X = Cl or Br; L = XylNC, $t$-BuNC or CO) and $[Re_2X_3(\mu\text{-dppm})_2(CO)(NCMe)_2]^+$ (X = Cl or Br) with the appropriate halogen ($X_2$). The complexes of the type $[Re_2X_5(\mu\text{-dppm})_2(L)]Y$ constitute the first multiply bonded $[Re_2]^{6+}$ compounds that contain these $\pi$-acceptor ligands, which have been structurally characterized in the solid state. Their stability is sufficient to enable their complete characterization. This paucity of higher oxidation state multiply bonded dirhenium complexes that contain $\pi$-acceptor ligands contrasts with the plethora of dirhenium(II) complexes which have RNC or CO ligands bound to the $[Re_2(\mu\text{-dppm})_2]$ unit, in combination with chloride or bromide ligands [2–7,22].

## 5. Supplementary material

Full details for the crystal data and data collection parameters, atomic positional parameters, anisotropic thermal parameters, bond distances and bond angles for **2** have been deposited with the Cambridge Crystallographic Data Center (deposit number 134045). Copies of this information may be obtained free of charge from: The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: $+44\text{-}1223\text{-}336033$; email: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

## References

[1] Y. Ding, P.E. Fanwick, R.A. Walton, Inorg. Chem. 38 (1999) 5165.

[2] F.A. Cotton, L.M. Daniels, K.R. Dunbar, L.R. Falvello, S.M. Tetrick, R.A. Walton, J. Am. Chem. Soc. 107 (1985) 3524.

[3] F.A. Cotton, K.R. Dunbar, A.C. Price, W. Schwotzer, R.A. Walton, J. Am. Chem. Soc. 108 (1986) 4843.

[4] L.B. Anderson, T.J. Barder, D. Esjornson, R.A. Walton, B.E. Bursten, J. Chem. Soc. Dalton Trans. 34 (1986) 2607.

[5] W. Wu, P.E. Fanwick, R.A. Walton, Inorg. Chem. 34 (1995) 5810.

[6] W. Wu, P.E. Fanwick, R.A. Walton, Inorg. Chim. Acta 242 (1996) 81.

[7] Y. Ding, W. Wu, P.E. Fanwick, R.A. Walton, Inorg. Chem. 38 (1999) 1918.

[8] K.-Y. Shih, P.E. Fanwick, R.A. Walton, Organometallics 12 (1993) 347.

[9] D.A. Kort, W. Wu, P.E. Fanwick, R.A. Walton, Trans. Met. Chem. 20 (1995) 625.

[10] A.C. Price, R.A. Walton, Polyhedron 6 (1987) 729.

[11] R.A. Walton, Polyhedron 8 (1989) 1689.

[12] F.A. Cotton, R.A. Walton, Multiple Bonds Between Metal Atoms, second ed., Oxford University Press, Oxford, UK, 1993.

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

[14] S.M.V. Esjornson, Ph.D. Thesis, Purdue University, 1989.

[15] A.R. Cutler, D.R. Derringer, P.E. Fanwick, R.A. Walton, J. Am. Chem. Soc. 110 (1988) 5024.

[16] D.R. Derringer, P.E. Fanwick, J. Moran, R.A. Walton, Inorg. Chem. 28 (1989) 1384.

[17] J. Chantler, R.A. Walton, unpublished results.

[18] P.T. Beurskens, G. Admirall, G. Beurskens, W.P. Bosman, S. Garcia-Granda, R.O. Gould, J.M.M. Smits, C. Smykalla, The DIRDIF92 Program System, Technical Report, Crystallography Laboratory, University of Nijmegen, Netherlands, 1992.

[19] Z. Otwinowski, W. Minor, Methods Enzymol. 276 (1996) 307.

[20] G.M. Sheldrick, SHELXL-97. A Program for Crystal Structure Refinement. University of Göttingen, Germany, 1997.

[21] C.K. Johnson, ORTEP II, Rep. ORNL-5138, Oak Ridge National Laboratory, TN, 1976.

[22] Y. Ding, D.A. Kort, W. Wu, P.E. Fanwick, R.A. Walton, J. Organomet. Chem. 573 (1999) 87.