Structural Characterization of Dirhenium(II) Complexes of the Type $Re_2Cl_4(\mu\text{-PP})(PR_3)_2$, Where PP Represents a Bridging Phosphine of the Type $R_2PCH_2PR_2$ or R_2PNHPR_2

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Received August 22, 1997

Introduction

The triply-bonded dirhenium(II) complex $Re_2Cl_4(\mu\text{-dppm})_2$ (dppm = $Ph_2PCH_2PPh_2$), which was first reported in 1976,[1] has proved to be a very useful synthon to access extensive series of complexes in which the stable, metal−metal-bonded $Re_2(\mu\text{-dppm})_2$ unit is retained.[2] In spite of the extensive chemistry which has now been developed for complexes which contain the electron-rich triple-bond ($\sigma^2\pi^4\delta^2\delta^{*2}$ configuration),[2] there exist few examples of mixed-phosphine complexes in which the $(Re{\equiv}Re)^{4+}$ core is present. To date, the chemistry of the electron-rich triple bond has been dominated by the aforementioned $Re_2Cl_4(\mu\text{-dppm})_2$, and its bromo analogue, and by the monodentate phosphine analogues $Re_2X_4(PR_3)_4$ (X = Cl, Br).[2]

On a few occasions over the last 20 years, we have succeeded in obtaining examples of complexes of the type $Re_2Cl_4(\mu\text{-PP})(PR_3)_2$, where PP represents a bidentate phosphine ligand with a single bridgehead group, which are hybrids of $Re_2Cl_4(\mu\text{-dppm})_2$, and its like, and $Re_2Cl_4(PR_3)_4$. The complexes we have isolated and characterized are $Re_2Cl_4(\mu\text{-dppm})(PR_3)_2$ (PR_3 = PMe_3, PEt_3)[1,3,4] and $Re_2Cl_4(\mu\text{-dppa})(PR_3)_2$ (dppa = $Ph_2PNHPPh_2$; PR_3 = PMe_3, PMe_2Ph),[3−5] but we were not able to obtain X-ray-quality crystals to confirm the structure of this class of compound.

In recent work, which was aimed at synthesizing the dirhenium(II) complex $Re_2Cl_4(\mu\text{-dcpm})_2$ (dcpm = $Cy_2PCH_2PCy_2$; Cy = cyclohexyl) and exploring its chemical reactivity, we isolated the compound $Re_2Cl_4(\mu\text{-dcpm})(PMe_3)_2$ and returned to the question of its structure and that of other complexes of this type. The results of this study are reported herein, along with the successful completion of the crystal structure of the prototypical $Re_2Cl_4(\mu\text{-dppm})(PMe_3)_2$.

Experimental Section

Starting Materials and General Procedures. The complexes $(n\text{-}Bu_4N)_2Re_2Cl_8$, *cis*-$Re_2(O_2CCH_3)_2Cl_4L_2$ (L = H_2O, py), and $Re_2Cl_4(PMe_3)_4$ were prepared according to standard literature procedures.[3,6,7] Trimethylphosphine and dppm were obtained from commercial sources and used without further purification. A sample of bis(dicyclohexylphosphino)methane (dcpm) was provided by Professor I. P. Rothwell. Solvents were dried and deoxygenated prior to use. All reactions were carried out under a dry dinitrogen atmosphere. Spectroscopic and cyclic voltammetric measurements were performed as described previously.[8] Elemental microanalyses were carried out by Dr. H. D. Lee of the Purdue University Microanalytical Laboratory.

A. Preparation of $Re_2Cl_4(\mu\text{-dcpm})_2$, 1. (i) A mixture of *cis*-$Re_2(O_2CCH_3)_2Cl_4(H_2O)_2$ (0.125 g, 0.187 mmol) and dcpm (0.192 g, 0.472 mmol) was suspended in ethanol (20 mL) in the presence of a pine boiling stick. The reaction mixture was refluxed for 1 day. The resulting purple crystals were harvested from the reaction vessel and from the boiling stick, washed with ethanol and diethyl ether, and dried in vacuo; yield 0.105 g (42%).

The reaction between *cis*-$Re_2(O_2CCH_3)_2Cl_4(py)_2$ and dcpm afforded $Re_2Cl_4(\mu\text{-dcpm})_2$ by the use of a procedure similar to that described above; yield 60%.

(ii) A mixture of $(n\text{-}Bu_4N)_2Re_2Cl_8$ (0.200 g, 0.175 mmol) and dcpm (0.159 g, 0.390 mmol) was suspended in ethanol (20 mL) in the presence of a pine boiling stick. The reaction mixture was refluxed for 3 days. The resulting purple crystals were washed with ethanol and diethyl ether and dried in vacuo; yield 0.160 g (69%). Anal. Calcd for $C_{50}H_{92}Cl_4P_4Re_2$: C, 45.11; H, 6.96. Found: C, 45.44; H, 6.91.

B. Preparation of $Re_2Cl_4(\mu\text{-dcpm})(PMe_3)_2$, 2. (i) An excess of trimethylphosphine (1.0 mL) was added to a mixture of $(n\text{-}Bu_4N)_2Re_2Cl_8$ (0.200 g, 0.175 mmol) and dcpm (0.157 g, 0.385 mmol) in 1-propanol (20 mL). The reaction mixture was refluxed for 3 days. The resulting dark green powder was washed with 1-propanol and diethyl ether and dried in vacuo; yield 0.111 g (59%). Anal. Calcd for $C_{31}H_{64}Cl_4P_4Re_2$: C, 34.64; H, 6.00; Cl, 13.19. Found: C, 34.92; H, 6.12; Cl, 12.96.

(ii) This complex was also prepared by use of a procedure analogous to the standard literature preparation of $Re_2Cl_4(\mu\text{-dppm})(PMe_3)_2$.[3] A mixture of $Re_2Cl_4(PMe_3)_4$ (0.100 g, 0.122 mmol) and dcpm (0.050 g, 0.122 mmol) was suspended in 1-propanol (10 mL) in the presence of a pine boiling stick. The reaction mixture was refluxed for 2 days. The resulting green-gray crystals were filtered off, washed with ethanol and diethyl ether, and dried in vacuo; yield 0.032 g (25%).

Other procedures for the synthesis of this complex were unsuccessful. These attempts included the direct reaction of $Re_2Cl_4(\mu\text{-dcpm})_2$ with an excess of PMe_3 and of $Re_2Cl_4(\mu\text{-dcpm})_2$ with $Re_2Cl_4(PMe_3)_4$.

X-ray Crystallography. A batch of $Re_2Cl_4(\mu\text{-dppm})(PMe_3)_2$ was prepared by use of a literature procedure in which $Re_2Cl_4(PMe_3)_4$ is reacted with an excess of dppm.[3] Crystals of $Re_2Cl_4(\mu\text{-dppm})(PMe_3)_2{\cdot}0.75C_6H_5CH_3$ were obtained by the following method. A solution of the compound in CH_2Cl_2 was prepared and toluene added dropwise to this solution until a slight turbidity was observed. The resulting solution was then sealed in a Schlenk tube and placed in a Dewar vessel filled with dry ice for a period of 1 week, replenishing the dry ice as necessary. Within the week small, plate-shaped crystals appeared which were suitable for single-crystal X-ray analysis, although of marginal quality.

The crystals did not appear to decompose appreciably under air for short periods of time. A small plate, of dimensions 0.3 × 0.2 × 0.05 mm, was attached to the tip of a quartz fiber using a dab of hydrocarbon stopcock grease and immediately placed in a stream of cold N_2 (ca. −60 °C). Several hundred reflections were centered and used for determination and refinement of the cell parameters. Axial images did not reveal any symmetry higher than triclinic. After data collection,

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S0020-1669(97)01078-1 CCC: $15.00

Table 1. Crystallographic Data for the Dirhenium Complex $Re_2Cl_4(\mu\text{-dppm})(PMe_3)_2 \cdot 0.75C_6H_5CH_3$

empirical formula	$C_{36.25}H_{46}Cl_4P_4Re_2$
fw	1119.88
space group	$P\bar{1}$ (No. 2)
a, Å	12.1830(6)
b, Å	18.693(2)
c, Å	19.886(2)
α, deg	64.78(2)
β, deg	81.410(6)
γ, deg	89.777(8)
V, Å^3	4042.0(6)
Z	4
ρ_{calcd}, g/cm^3	1.840
μ, mm^{-1}	6.432
radiation (λ, Å)	Mo Kα (0.710 73)
transm factors, min/max	0.16/0.75
temp, K	213(2)
R1,[a] wR2[b] $[I > 2\sigma(I)]$	0.057, 0.148
R1,[a] wR2[b] (all data)	0.068, 0.158

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$.

the reflections were corrected for absorption anisotropy effects and merged using a local adaptation of the program SORTAV.[9]

The initial solution for this structure was obtained by direct methods, in which the positions of the metal atoms and the first coordination sphere were determined. The remaining carbon atoms and solvent of crystallization were found by successive cycles of least-squares refinement followed by electron density maps. Before the final least-squares cycle, hydrogen atoms were placed in idealized positions. Details of the crystallography and crystal parameters are given in Table 1.

Results and Discussion

Our interest in obtaining samples of $Re_2Cl_4(\mu\text{-dcpm})_2$ (**1**) stemmed from the anticipation that **1** might serve as a more potent reductant than $Re_2Cl_4(\mu\text{-dppm})_2$ in the reductive coupling of small organic molecules at the dirhenium(II) core, such as the reductive coupling of organic nitriles[10] and of CO with terminal alkynes,[11] because of the greater basicity of dcpm compared to dppm. While dcpm reacts with *cis*-$Re_2(O_2CCH_3)_2Cl_4L_2$ (L = H_2O, py) in ethanol to afford dark purple crystalline $Re_2Cl_4(\mu\text{-dcpm})_2$ in respectable yield (40−60%), a preferable procedure is to reflux ethanol solutions containing (n-$Bu_4N)_2Re_2Cl_8$ and dcpm for a period of 3 days since this affords **1** in consistently higher yield (ca. 70%).

The cyclic voltammograms (CV's) of solutions of **1** in 0.1 M n-Bu_4NPF_6−CH_2Cl_2 exhibit two reversible one-electron oxidations at $E_{1/2} = -0.05$ and +0.93 V vs Ag/AgCl; these reversible couples possess ΔE_p values (i.e., $E_{p,a} - E_{p,c}$) of 100 mV at a sweep rate of 200 mV/s. The first of these processes is shifted by ca. 35 mV to more negative potentials compared to data reported for $Re_2Cl_4(\mu\text{-dppm})_2$ ($E_{1/2}(\text{ox}) = +0.29$ and +0.87 V vs Ag/AgCl),[12] in accord with a more electron-rich metal core being present in **1**. The ^1H NMR spectrum of a solution of **1** in CD_2Cl_2 at 25 °C consists of several broad, unstructured resonances between δ +4.0 and +1.0, including a broad peak at δ +3.90 due to the bridgehead $-CH_2-$ resonance of dcpm; these features provide little in the way of definitive structural information other than confirming the presence of the dcpm ligand. The $^{31}P\{^1H\}$ NMR spectrum shows a sharp singlet at δ −5.8; this can be contrasted with δ −10.0 for the free ligand in CD_2Cl_2. We have not yet obtained single crystals of **1** which are of a quality sufficient to determine its X-ray crystal structure, although this complex can be safely assumed to be essentially isostructural with both $Re_2Cl_4(\mu\text{-dppa})_2$[12] and $Re_2Cl_4(\mu\text{-dppm})_2$.[13]

Surprisingly, we have found **1** to be much less reactive toward ligand molecules such as CO, RNC, RCN, and PMe_3 than is $Re_2Cl_4(\mu\text{-dppm})_2$,[2] an observation we attribute to the more sterically crowded nature of $Re_2Cl_4(\mu\text{-dcpm})_2$, **1**, rather than to electronic factors, since the Re_2^{4+} core in **1** is more electron-rich than that in $Re_2Cl_4(\mu\text{-dppm})_2$, as judged by cyclic voltammetric measurements (vide supra). The failure of $Re_2Cl_4(\mu\text{-dcpm})_2$, **1**, to react with PMe_3 to afford $Re_2Cl_4(\mu\text{-dcpm})(PMe_3)_2$ was surprising, given the ease of converting $Re_2Cl_4(\mu\text{-dppm})_2$ to $Re_2Cl_4(\mu\text{-dppm})(PMe_3)_2$ upon its reaction with PMe_3.[4] We also reported previously that $Re_2Cl_4(PMe_3)_4$ and $Re_2Cl_4(PEt_3)_4$ react with an excess of dppm to yield $Re_2Cl_4(\mu\text{-dppm})(PMe_3)_2$[3] and $Re_2Cl_4(\mu\text{-dppm})(PEt_3)_2$,[1] respectively, while $Re_2Cl_4(PMe_3)_4$ and $Re_2Cl_4(PMe_2Ph)_4$ convert to $Re_2Cl_4(\mu\text{-dppa})(PMe_3)_2$[3] and $Re_2Cl_4(\mu\text{-dppa})(PMe_2Ph)_2$,[5] respectively, when reacted with an excess of the dppa ligand, so there is ample precedent for the stability of complexes of the type $Re_2Cl_4(\mu\text{-PP})(PR_3)_2$. However, we were successful in obtaining $Re_2Cl_4(\mu\text{-dcpm})(PMe_3)_2$, **2**, by two other procedures, namely, the reactions among (n-$Bu_4N)_2Re_2Cl_8$, dcpm, and PMe_3, and between $Re_2Cl_4(PMe_3)_4$ and dcpm, both in refluxing 1-propanol.

The properties of **2** closely mirror those of $Re_2Cl_4(\mu\text{-dppm})(PMe_3)_2$, and other complexes of this type, which we described and contrasted previously.[3] The CV of a solution of **2** in 0.1 M n-Bu_4NPF_6−CH_2Cl_2 shows a reversible one-electron oxidation at $E_{1/2} = +0.49$ V ($\Delta E_p = 80$ mV) and an irreversible oxidation at $E_{p,a} = +1.40$ V with an associated product wave at $E_{p,c} = -0.55$ V vs Ag/AgCl. The two oxidations (+0.49 and +1.40 V) are similar to processes at $E_{1/2} = +0.58$ V and $E_{p,a} = +1.28$ V vs Ag/AgCl in the CV of $Re_2Cl_4(\mu\text{-dppm})(PMe_3)_2$.[3] The ^1H NMR spectrum of **2** in CD_2Cl_2 consists of a triplet at δ +4.45 ($^2J_{P-H} = 9.7$ Hz) for the bridgehead $-CH_2-$ resonance of the μ-dcpm ligand and broad cyclohexyl resonances at δ +3.60, +2.89, +2.27, and +0.41, as well as a complex series of overlapping multiplets from δ +2.1 to +0.9 due to the remaining cyclohexyl proton resonances and those of the methyl groups of the PMe_3 ligands. The observation of a binomial triplet for the bridgehead $-CH_2-$ resonance of μ-dcpm supports a cis disposition of this ligand with respect to the two PMe_3 ligands since the P−P coupling should be small. Furthermore, the ^{31}P NMR spectrum shows a broad singlet at δ +8.83 for the P atoms of the μ-dcpm ligand and a binomial 10-line pattern at δ −24.8 for the pair of chemically and magnetically equivalent PMe_3 ligands ($^2J_{P-H} \simeq 9.5$ Hz). The corresponding $^{31}P\{^1H\}$ NMR spectrum of **2** consists of two slightly broadened singlets. These spectral features mirror exactly those reported for $Re_2Cl_4(\mu\text{-dppm})(PMe_3)_2$ and other complexes of this type[3] and accord with the structure (**I**) that has been confirmed by X-ray crystallography for the complex $Re_2Cl_4(\mu\text{-dppm})(PMe_3)_2$.

The crystals of the compound $Re_2Cl_4(\mu\text{-dppm})(PMe_3)_2$ contain the molecules shown in Figure 1. These enantiomers occur in two crystallographically distinct pairs, each pair having a different crystallographic inversion center relating its members. The chirality of each molecule is based on the internal twist,

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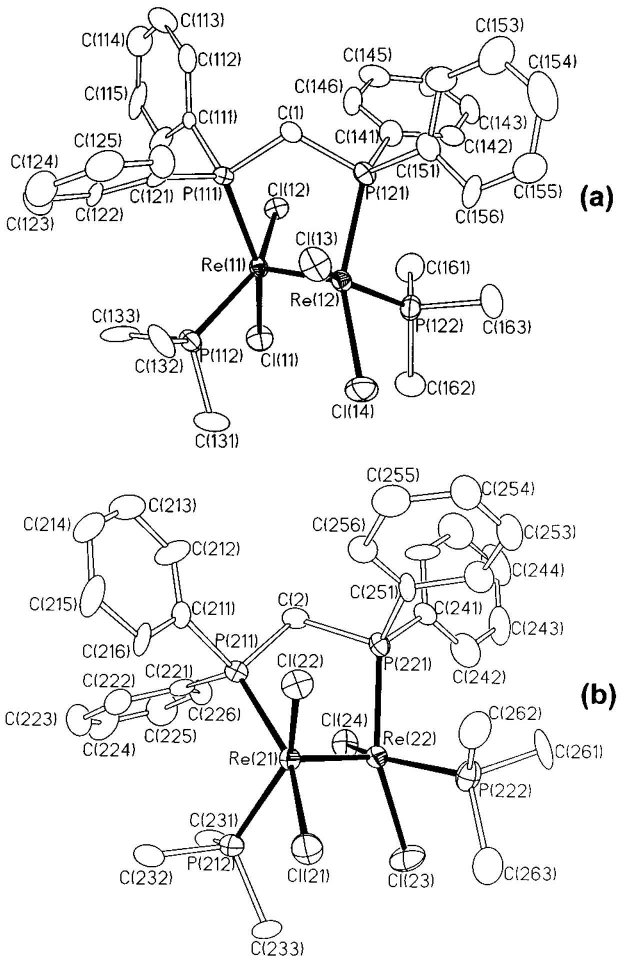
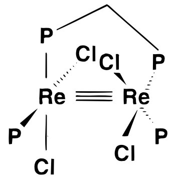


Figure 1. Perspective drawings of the $Re_2Cl_4(\mu\text{-dppm})(PMe_3)_2$ molecule in its crystallographically independent forms: (a) molecule 1; (b) molecule 2. Atoms are represented by thermal ellipsoids at the 40% probability level.



I

(P = PMe_3, PEt_3 or PMe_2Ph;
$\widehat{P\ P}$ = dppm, dppa or dcpm)

which is in the opposite sense for the members of each pair. Figure 2 shows the torsional conformation for one of the molecules. The crystallographically distinct molecules are nearly identical. Selected dimensions are given in Table 2. The two independent Re−Re distances are 2.238(1) and 2.242(1) Å so that the difference, 0.004 Å, is barely at the 3σ level, 0.0042. This is in accord with the established insensitivity of multiple bonds between transition metal atoms to deformation when subjected to different packing environments.[14]

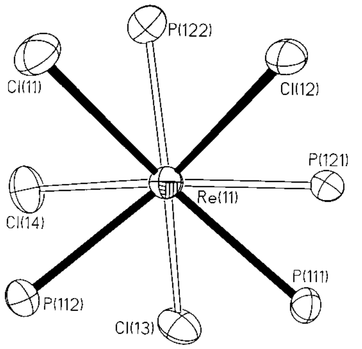


Figure 2. Axial view of molecule 1. That for molecule 2 is virtually identical. The torsion angles (each with an esd of about 0.1°) are as follows. (a) About Re(11)−Re(12): Cl(11), P(122) 37.7; Cl(12), P(121) 47.6; P(111), Cl(13) 43.3; P(112), Cl(14) 36.1°. (b) About Re(21)−Re(22): Cl(21), P(222) 37.3; Cl(22), P(221) 47.2; P(211), Cl(24) 43.0; P(212), Cl(23) 35.8°.

Table 2. Selected Bond Distances (Å) and Bond Angles (deg) for the Complex $Re_2Cl_4(\mu\text{-dppm})(PMe_3)_2{\cdot}0.75C_6H_5CH_3$[a]

Distances

molecule 1		molecule 2	
Re(11)−Re(12)	2.2381(7)	Re(21)−Re(22)	2.2419(7)
Re(11)−Cl(12)	2.385(3)	Re(21)−Cl(22)	2.380(3)
Re(11)−P(112)	2.390(4)	Re(21)−P(212)	2.388(4)
Re(11)−P(111)	2.417(4)	Re(21)−P(211)	2.405(3)
Re(11)−Cl(11)	2.419(3)	Re(21)−Cl(21)	2.429(3)
Re(12)−P(121)	2.358(4)	Re(22)−P(221)	2.367(4)
Re(12)−P(122)	2.380(4)	Re(22)−P(222)	2.388(4)
Re(12)−Cl(13)	2.413(4)	Re(22)−Cl(24)	2.402(3)
Re(12)−Cl(14)	2.415(4)	Re(22)−Cl(23)	2.405(4)

Angles

molecule 1		molecule 2	
Re(12)−Re(11)−Cl(12)	115.94(8)	Re(22)−Re(21)−Cl(22)	115.98(8)
Re(12)−Re(11)−P(112)	95.82(9)	Re(22)−Re(21)−P(212)	97.39(9)
Cl(12)−Re(11)−P(112)	147.57(12)	Cl(22)−Re(21)−P(212)	146.06(12)
Re(12)−Re(11)−P(111)	93.28(8)	Re(22)−Re(21)−P(211)	93.45(8)
Cl(12)−Re(11)−P(111)	86.77(12)	Cl(22)−Re(21)−P(211)	86.64(12)
P(112)−Re(11)−P(111)	98.37(12)	P(212)−Re(21)−P(211)	97.89(12)
Re(12)−Re(11)−Cl(11)	110.86(9)	Re(22)−Re(21)−Cl(21)	110.45(9)
Cl(12)−Re(11)−Cl(11)	80.06(12)	Cl(22)−Re(21)−Cl(21)	80.24(12)
P(112)−Re(11)−Cl(11)	82.70(12)	P(212)−Re(21)−Cl(21)	82.52(13)
P(111)−Re(11)−Cl(11)	155.67(12)	P(211)−Re(21)−Cl(21)	155.90(12)
Re(11)−Re(12)−P(121)	92.65(8)	Re(21)−Re(22)−P(221)	92.54(8)
Re(11)−Re(12)−P(122)	96.76(9)	Re(21)−Re(22)−P(222)	97.14(9)
P(121)−Re(12)−P(122)	98.31(13)	P(221)−Re(22)−P(222)	98.34(13)
Re(11)−Re(12)−Cl(13)	111.91(9)	Re(21)−Re(22)−Cl(24)	114.27(9)
P(121)−Re(12)−Cl(13)	83.16(12)	P(221)−Re(22)−Cl(24)	83.26(12)
P(122)−Re(12)−Cl(13)	151.23(13)	P(222)−Re(22)−Cl(24)	148.50(12)
Re(11)−Re(12)−Cl(14)	116.11(9)	Re(21)−Re(22)−Cl(23)	114.17(10)
P(121)−Re(12)−Cl(14)	150.88(12)	P(221)−Re(22)−Cl(23)	152.85(12)
P(122)−Re(12)−Cl(14)	83.45(14)	P(222)−Re(22)−Cl(23)	83.65(14)
Cl(13)−Re(12)−Cl(14)	81.90(14)	Cl(24)−Re(22)−Cl(23)	81.37(13)

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

Concluding Remarks. The full structural characterization of a molecule of the type $Re_2Cl_4(\mu\text{-PP})(PR_3)_2$ opens the way for further studies of the reactivity of these compounds. To date, there is a paucity of such work; the only previous literature report involves the ligand substitution reactions of $Re_2Cl_4(\mu\text{-dppm})(PMe_3)_2$ and $Re_2Cl_4(\mu\text{-dppa})(PMe_3)_2$ with $Ph_2PCH_2CH_2PPh_2$ (dppe) and $Ph_2PCH_2CH_2AsPh_2$ (arphos) to afford the complexes $Re_2Cl_4(\mu\text{-dppm})(\mu\text{-dppe})$, $Re_2Cl_4(\mu\text{-dppm})(\mu\text{-arphos})$, and $Re_2Cl_4(\mu\text{-dppa})(\mu\text{-dppe})$.[4] A noteworthy feature of the structure of $Re_2Cl_4(\mu\text{-dppm})(PMe_3)_2$ and other complexes of this type is the existence of a *cis*-$ReCl_2PP'$ geometry at each rhenium center.

Acknowledgment. We thank the National Science Foundation, through Grant No. CHE94-09932 to R.A.W. and Grant No. CHE93-13797 to F.A.C., for support of this work. We thank Dr. Lee M. Daniels for preparing the crystallographic work for publication.

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Supporting Information Available: Tables giving crystal data and full details for the structure refinement, atomic positional parameters, anisotropic displacement parameters, and bond distances and angles for $Re_2Cl_4(\mu\text{-dppm})(PMe_3)_2 \cdot 0.75C_6H_5CH_3$ (13 pages). Ordering information is given on any current masthead page.

IC971078S