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Reaction of $Re_2(\mu\text{-}O_2CCH_3)_4Cl_2$ with Bis(dicyclohexylphosphino)methane (dcpm): Isolation of the Mixed-Valent Complex $O_3ReReCl(\eta^2\text{-dcpm})_2$ Containing an Unsupported Re−Re Bond

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Introduction

The dirhenium(III) acetate complex $Re_2(\mu\text{-}O_2CCH_3)_4Cl_2$ reacts with bidentate phosphine ligands of the type $Ph_2P{-}A{-}PPh_2$ ($A = CH_2$, NH, $C{=}CH_2$, $C(CH_2)_2$) to afford the dirhenium(III,II) and dirhenium(II,II) complexes *cis*- or *trans*-$[Re_2(\mu\text{-}O_2CCH_3)_2Cl_2(\mu\text{-}PP)_2]^+$ and *cis*- or *trans*-$Re_2(\mu\text{-}O_2CCH_3)_2Cl_2(\mu\text{-}PP)_2$.[1−4] The products in these reactions are determined by the choice of reaction conditions and the ligand PP.[1−4]

When $Re_2(\mu\text{-}O_2CCH_3)_4Cl_2$ is reacted with the more basic alkyl phosphine $Me_2PCH_2PMe_2$ (dmpm), the dirhenium(II,II) complex $[Re_2(\mu\text{-}O_2CCH_3)Cl_2(\mu\text{-dmpm})_3]^+$ is formed via the intermediacy of the paramagnetic dirhenium(III,II) species *trans*-$[Re_2(\mu\text{-}O_2CCH_3)_2Cl_2(\mu\text{-dmpm})_2]^+$.[5] This difference in behavior of dmpm, when compared to that of its phenyl analogue $Ph_2PCH_2PPh_2$ (dppm), had been noted previously and is shown most strikingly in the formation of the tris complex $Re_2Cl_4(\mu\text{-dmpm})_3$,[6,7] while dppm forms only $Re_2Cl_4(\mu\text{-dppm})_2$.[8] To understand the effects of the smaller size of dmpm and its greater basicity compared to $Ph_2PCH_2PPh_2$ and related aryl phosphines, we have been studying the dirhenium complexes of $Cy_2PCH_2PCy_2$ (dcpm),[9−11] a phosphine that has a basicity comparable to that of dmpm but exhibits a size more like that of dppm. In this paper, we describe the reaction of dcpm with $Re_2(\mu\text{-}O_2CCH_3)_4Cl_2$ that leads to an unusual mixed-valent dirhenium complex $O_3ReReCl(\eta^2\text{-dcpm})_2$ which contains formally Re(VI) and Re(I) centers and has an unsupported Re−Re bond.

Experimental Section

Starting Materials and General Procedures. The complex $Re_2(\mu\text{-}O_2CCH_3)_4Cl_2$ was prepared by the literature method,[12] while samples of $Cy_2PCH_2PCy_2$ (dcpm) were provided by Professor I. P. Rothwell. Solvents used in the preparation and workup of the complexes were of commercial grade and were used as received. All reactions were carried out under a dry nitrogen atmosphere. ^1H and $^{31}P\{^1H\}$ NMR spectra, infrared spectra, and cyclic voltammetric measurements were carried out as described previously.[13] Elemental microanalyses were carried out by Dr. H. D. Lee of the Purdue University Microanalytical Laboratory. The electrospray ionization (ESI) mass analyses were recorded by Dr. Karl V. Wood with use of a FinniganMAT LCQ (Thermoquest Corp. San Jose, CA) mass spectrometer system. Measurements on compounds **1**−**3** were carried out on CH_2Cl_2/CH_3CN solutions.

Synthesis of $ReOCl(\eta^2\text{-dcpm})_2$ (1) and *trans*-$Re_2(\mu\text{-}O_2CCH_3)_2Cl_2(\mu\text{-dcpm})_2$ (2). A suspension of $Re_2(\mu\text{-}O_2CCH_3)_4Cl_2$ (0.133 g, 0.20 mmol) in 30 mL of ethanol was refluxed for 36 h with an excess of dcpm (0.307 g, 0.75 mmol). The red crystals of **1** were filtered off and washed with fresh ethanol (3 × 5 mL) and diethyl ether (3 × 5 mL) and dried in a vacuum. Yield: 0.139 g (34%). Anal. Calcd for $C_{50}H_{92}ClOP_4Re$: C, 56.93; H, 8.79; Cl, 3.36. Found: C, 56.16; H, 8.38; Cl, 3.43. IR spectrum (KBr pellet): $\nu(Re{=}O)$ 971(s) cm^{-1}. ^1H NMR spectrum (CD_2Cl_2): $\delta = +1.0$ to $+3.0$ (m, 44H, C_6H_{11} of dcpm), $\delta = +4.21$ and $+4.53$ (m, 2H, $-CH_2-$ of dcpm). $^{31}P\{^1H\}$ NMR spectrum (CD_2Cl_2): $\delta = -30.5$. MS(ESI) $m/z = 1054$ for $[M]^+$ (where [M] represents the parent molecule).

The original green reaction filtrate was evaporated to dryness. Addition of diethyl ether gave the insoluble green product *trans*-$Re_2(\mu\text{-}O_2CCH_3)_2Cl_2(\mu\text{-dcpm})_2$ (**2**). Yield: 0.160 g (59%). ^1H NMR spectrum (CD_2Cl_2): $\delta = +1.0$ to $+3.0$ (m, br, overlap of the cyclohexyl ring protons of dcpm and the methyl protons of acetate), $\delta = +4.15$ (m, $-CH_2-$ of dcpm). $^{31}P\{^1H\}$ NMR spectrum (CD_2Cl_2): $\delta = -35.3$.

All attempts to recrystallize compound **2** led to its oxidation to paramagnetic $\mathbf{2}^+$. Thus, recrystallization from CH_2Cl_2/diethyl ether afforded dark green crystals of composition approximating *trans*-$[Re_2(\mu\text{-}O_2CCH_3)_2Cl_2(\mu\text{-dcpm})_2]Cl_{0.8}(ReO_4)_{0.2}$. Anal. Calcd for $C_{54}H_{98}Cl_{2.8}O_{4.8}P_4Re_{2.2}$: C, 44.47; H, 6.73; Cl, 6.82. Found: C, 44.55; H, 6.94; Cl, 7.10. IR spectrum (KBr pellet): $\nu(ReO_4)$ 906(m) cm^{-1}. MS(ESI): $m/z = 1378$ for $[M]^+$, 970 for $[M - \text{dcpm}]^+$ (where [M] represents the parent ion).

Conversion of 1 to $O_3ReReCl(\eta^2\text{-dcpm})_2$ (3). A solution of **1** (60 mg, 0.06 mmol) in dichloromethane (10 mL) in a 25 mL conical flask was placed inside a 200 mL beaker that contained 25 mL of diethyl ether. The beaker was covered with a watch glass. After 1 week, an analytically pure sample of red crystalline **3** was obtained. Yield: ca. 50 mg. Anal. Calcd for $C_{50}H_{92}ClO_3P_4Re_2$: C, 47.17; H, 7.28; Cl, 2.78. Found: C, 47.43; H, 7.35; Cl, 3.12. IR spectrum (KBr pellet): $\nu(ReO_3)$ 941(s), 924(s), 896(s) cm^{-1}. MS(ESI) $m/z = 1273$ for $[M]^+$ (where [M] represents the parent molecule).

X-ray Crystal Structure Determination. Single crystals of **3** were obtained as described above during the slow decomposition of **1** in dichloromethane in the presence of O_2. The data collection was performed at 150 ± 1 K with graphite-monochromated Mo Kα radiation ($\lambda = 0.710\,73$ Å) on a Nonius KappaCCD diffractometer. Lorentz and polarization corrections were applied to the data sets. The important crystallographic details are given in Table 1. The structure was solved using the structure solution program PATTY in DIRDIF92.[14] The remaining atoms were located in succeeding difference Fourier syn-

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Table 1. Crystallographic Data for $Re_2O_3Cl(\mu\text{-dcpm})_2 \cdot CH_2Cl_2$ ($\mathbf{3} \cdot CH_2Cl_2$)

empirical formula	$C_{51}H_{94}Cl_3O_3P_4Re_2$
fw	1357.97
space group	*Pnma* (No. 62)
a, Å	18.0179(4)
b, Å	22.8589(5)
c, Å	13.5102(7)
V, Å^3	5564.4(5)
Z	4
ρ_{calcd}, g/cm^3	1.621
μ(Mo Kα)(mm^{-1})	4.703
R (F_o)[a]	0.048
R_w (F_o^2)[b]	0.106
GOF	1.063

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

theses. Hydrogen atoms were placed in calculated positions according to idealized geometries with $U(H) = 1.3U_{eq}(C)$. They were included in the refinement but constrained to ride on the atom to which they are bonded. An empirical absorption correction using SCALEPACK[15] was applied. The final refinements were performed by the use of the program SHELXL-97.[16]

An orange needle-shaped crystal of $\mathbf{3} \cdot CH_2Cl_2$ having approximate dimensions 0.38 × 0.22 × 0.20 mm was selected for the data collection. A total of 34 524 reflections were collected in the range $5.0° < \theta < 27.5°$, of which 12 622 were unique. A total of 6464 reflections were used in the refinement. However, only reflections with $F_o^2 > 2\sigma|F_o^2|$ were used in calculating R. The final cycle of refinement included 313 variable parameters and converged with unweighted agreement factor $R = 0.048$.

A data set was also collected on a single crystal of the oxidized complex $\mathbf{2}^+$ of composition $[Re_2(\mu\text{-}O_2CCH_3)_2Cl_2(\mu\text{-dcpm})_2]Cl_{0.8}(ReO_4)_{0.2}$. Because of a severe disordering involving some of the carbon atoms of the dcpm ligands, a full structural refinement was not completed. However, the following conclusions were possible. (1) The trans structure of the cation was confirmed. (2) The Re−Re distance is 2.271(2) Å. (3) The anion consists of a mixture of Cl^- and $[ReO_4]^-$ occupying the same general position with approximate occupancies of 0.8 and 0.2, respectively; this conclusion is supported by the elemental microanalyses and the IR spectrum of the crystals which showed the presence of $[ReO_4]^-$. The preliminary crystal data for $[\mathbf{2}]Cl_{0.8}(ReO_4)_{0.2}$ are as follows: space group $P\bar{1}$ (No. 2) with $a = 12.966(2)$, $b = 13.493(2)$, $c = 18.115(2)$ Å, $\alpha = 80.519(9)$, $\beta = 90.410(8)$, $\gamma = 77.322(7)°$, $V = 3046(7)$ Å^3, $Z = 2$.

Results and Discussion

We had anticipated that the reaction of $Re_2(\mu\text{-}O_2CCH_3)_4Cl_2$ with $Cy_2PCH_2PCy_2$ (dcpm) would resemble those of other diphosphines of this type in affording dirhenium(III,II) and/or dirhenium(II,II) complexes *cis*- or *trans*-$[Re_2(\mu\text{-}O_2CCH_3)_2Cl_2(\mu\text{-PP})_2]^{n+}$ ($n = 1$ or 0). We find that dark green *trans*-$Re_2(\mu\text{-}O_2CCH_3)_2Cl_2(\mu\text{-dcpm})_2$ (**2**) is one of two major products. This complex displays a cyclic voltammogram (CV) in 0.1 M $n\text{-}Bu_4NPF_6\text{–}CH_2Cl_2$ (Pt-bead electrode) which consists of reversible processes at $E_{1/2} = +0.78$ V ($\Delta E_p = 60$ mV) and $E_{1/2} = -0.51$ V ($\Delta E_p = 70$ mV) vs Ag/AgCl, each of which corresponds to a one-electron oxidation of the bulk complex. This CV is very similar to those of the analogous complexes with $Ph_2PCH_2PPh_2$ (dppm),[1] $Ph_2PNHPPh_2$ (dppa),[2] $Ph_2PC(=CH_2)PPh_2$ (dppe),[3] and $Ph_2PC(CH_2)_2CPh_2$ (dcpp).[4] While freshly prepared solutions of **2** display ^1H and $^{31}P\{^1H\}$ NMR spectra typical of diamagnetic complexes (see Experimental Section), these solutions convert slowly to paramagnetic *trans*-$[Re_2(\mu\text{-}O_2CCH_3)_2Cl_2(\mu\text{-dcpm})_2]^+$ a reflection of the accessibility of the one-electron oxidation at $E_{1/2} = -0.51$ V. Our attempts to purify **2** by recrystallization led to its oxidation to $\mathbf{2}^+$. These crystals appear to be of composition *trans*-$[Re_2(\mu\text{-}O_2CCH_3)_2Cl_2(\mu\text{-dcpm})_2]Cl_{0.8}(ReO_4)_{0.2}$; the mixed Cl^- and $[ReO_4]^-$ anions which stabilize $\mathbf{2}^+$ presumably arise through the decomposition of a portion of **2** during the recrystallization process, although the recrystallization solvents (CH_2Cl_2 and Et_2O) might also be implicated. The identity of $\mathbf{2}^+$ is supported by a conductivity measurement ($\Lambda_m = 118\ \Omega^{-1}\ cm^2\ mol^{-1}$ for a 1.0×10^{-3} M solution in acetone), an ESI−MS spectrum ($m/z = 1378$ for $[M]^+$), its IR spectrum which shows the ν(Re−O) mode of $[ReO_4]^-$ at 906 cm^{-1}, and an X-ray crystal structure (see Experimental Section) in which refinement of the anion position was consistent with it consisting of a mixture of Cl^- (∼80%) and $[ReO_4]^-$ (∼20%). Unfortunately, a disorder involving some of the cyclohexyl ring carbon atoms prevented us from obtaining a publishable structure. However, we note that this structure is essentially the same that we have recently found for a complex of composition *trans*-$[Re_2(\mu\text{-}O_2CCH_3)_2Cl_2(\mu\text{-dipm})_2]Cl_{0.74}(ReO_4)_{0.26}$ (dipm = $Pr_2{}^iPCH_2PPr_2{}^i$), details of which will be reported in due course.[17]

The other major product in the reaction of $Re_2(\mu\text{-}O_2CCH_3)_4Cl_2$ with dcpm, which accounts for much of the remaining rhenium, is a red complex of composition $ReOCl(dcpm)_2$ (**1**). The source of the oxygen that is incorporated into **1** is unknown; it could originate from trace amounts of water, the ethanol solvent, or the displaced acetate ligands. The stoichiometry of this reaction is obviously complicated, since in addition to the cleavage of the $Re\overset{4}{-}Re$ bond of $Re_2(\mu\text{-}O_2CCH_3)_4Cl_2$ to give the mononuclear Re(III) species **1**, a two-electron reduction has occurred in the conversion of a portion of the starting material to the $[Re_2]^{4+}$ complex **2**.

The formulation of **1** as *trans*-$ReOCl(\eta^2\text{-dcpm})_2$ is supported by its electrospray ionization mass spectrum (Figure 1) that reveals the expected cluster of peaks at $m/z = 1054$ for the parent ion showing the correct isotope distribution pattern. Complex **1** forms essentially nonconducting solutions in acetone and is therefore a nonelectrolyte. Also, the IR spectrum of **1** shows a characteristic terminal ν(Re=O) mode at 971(s) cm^{-1},[18] and a singlet at $\delta = -30.5$ in its $^{31}P\{^1H\}$ NMR spectrum supports the assignment of a symmetrical trans structure. These spectroscopic and conductivity data support this structural formulation of **1** over its alternative formulation as the ionic Re(V) complex $[ReO_2(dcpm)_2]Cl$. A single scan cyclic voltammogram of a solution of **1** in 0.1 M $n\text{-}Bu_4NPF_6\text{–}CH_2Cl_2$ (scan rate 200 mV s^{-1} at a Pt-bead electrode) shows irreversible oxidations at $E_{p,a} = +0.75$ V and +1.06 V vs Ag/AgCl. The process at +1.06 V has a considerably higher current than that at +0.75 V, suggesting that it is probably associated with a multielectron process. While we are unaware of the previous isolation of an oxorhenium(III) complex of this type, the isoelectronic Os(IV) species $[OsOCl(\eta^2\text{-dcpe})_2]^+$ is known (dcpe = $Cy_2PCH_2CH_2PCy_2$),[19] although unlike **1** the latter complex is paramagnetic. However, both **1** and this Os(IV) complex are quite stable and easy to handle.

We have not yet been successful in obtaining single crystals of **1** suitable for an X-ray crystal structure determination. However, when solutions of **1** in dichloromethane were exposed

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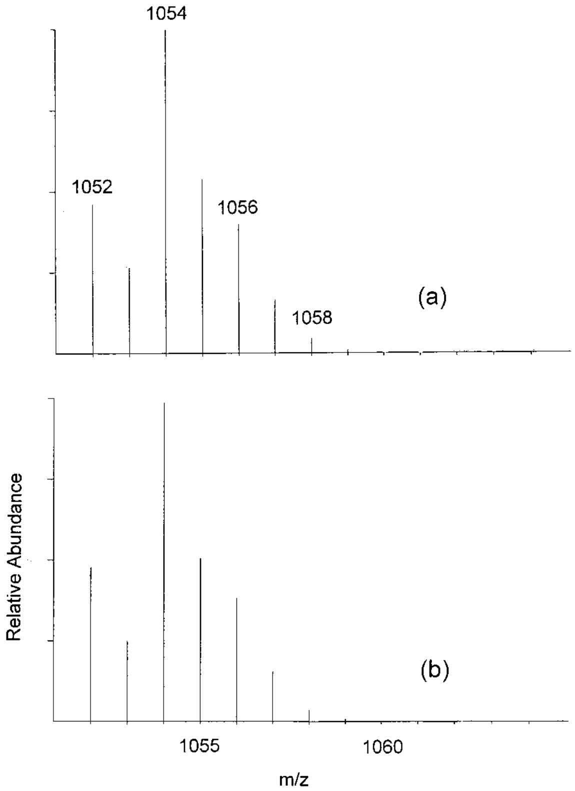
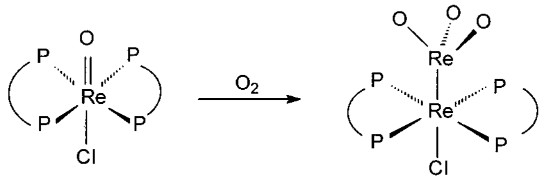


Figure 1. Electrospray ionization mass spectrum of ReOCl(η^2-dcpm)$_2$ (**1**) showing the calculated (a) and experimental (b) isotopic distribution patterns.

to air, we did obtain single crystals of a complex of composition Re$_2$O$_3$Cl(dcpm)$_2$ (**3**). Like **1**, complex **3** is red in color and it proved to be the paramagnetic mixed-valent complex O$_3$ReReCl(η^2-dcpm)$_2$. The conversion of **1** to **3** can be followed by NMR spectroscopy; over a period of 2−3 days the ^{1}H and ^{31}P resonances of diamagnetic **1** collapse as the paramagnetic complex **3** forms. This change is also accompanied by the change of the IR active ν(Re=O) mode of **1** at 971 cm^{-1} to a set of three peaks at 941, 924, and 896 cm^{-1} that presumably include the ν(Re−O) modes of ReO$_3$. On the face of it, **3** bears a fairly close relationship to **1** in that the oxo ligand has been replaced by ReO$_3$. The structure of **3** is shown in Figure 2, and its important structural parameters are listed in Table 2. The crystal contains a molecule of the crystallization solvent CH$_2$Cl$_2$.



1 **3**

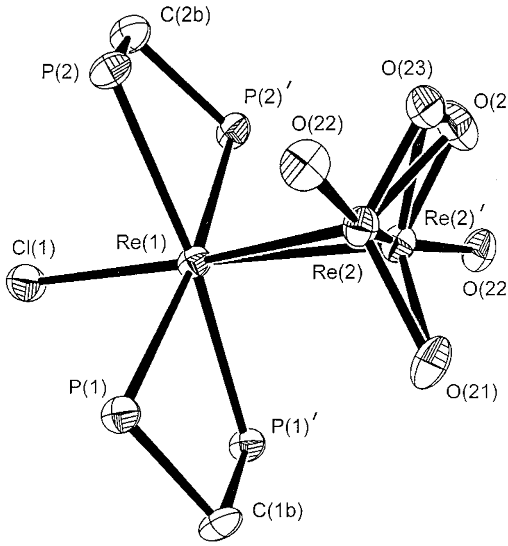


Figure 2. ORTEP representation of the structure of the molecule O$_3$ReReCl(η^2-dcpm)$_2$ (**3**) showing the disorder involving the ReO$_3$ group. Primes denote symmetry generated atoms. Thermal ellipsoids are drawn at the 40% probability level, and the cyclohexyl groups have been omitted for clarity.

Table 2. Important Bond Distances (Å) and Bond Angles (deg) for the Complex Re$_2$O$_3$Cl(μ-dcpm)$_2$·CH$_2$Cl$_2$ (**3**·CH$_2$Cl$_2$)[a]

Distances

Re(1)−Re(2)	2.5398(6)	Re(2)−O(22)	1.731(8)
Re(1)−Cl(1)	2.493(2)	Re(2)−O(21)	1.732(6)
Re(1)−P(1)	2.4710(15)	Re(2)−O(23)′	1.728(8)
Re(1)−P(2)	2.4872(15)		

Angles

Re(2)−Re(1)−Cl(1)	169.338(12)	O(21)−Re(2)−O(23)′	110.7(3)
P(1)−Re(1)−P(2)	111.59(5)	O(22)−Re(2)−O(21)	110.0(5)
P(1)−Re(1)−P(2)′	171.10(5)	O(22)−Re(2)−O(23)′	109.1(4)
P(1)−Re(1)−P(1)′	67.58(7)	Re(1)−Re(2)−O(21)	107.5(2)
P(2)−Re(1)−P(2)′	67.76(7)	Re(1)−Re(2)−O(22)	108.5(3)
P(1)−Re(1)−Cl(1)	89.27(6)	Re(1)−Re(2)−O(23)′	111.1(3)
P(2)−Re(1)−Cl(1)	81.85(6)		

[a] Numbers in parentheses are estimated standard deviations in the least significant digits. Primes denote symmetry generated atoms. The parameters for atoms Re(2)′, O(21), O(22)′, and O(23) that are associated with the other disordered ReO$_3$ group are identical to those for Re(2), O(21), O(22), and O(23)′ that are given above.

The dirhenium complex **3** contains two distinct Re environments, one being pseudotetrahedral (formally Re(VI)) and the other pseudooctahedral (formally Re(I)). The Re−Re bond distance of 2.5398(6) Å in this complex is longer than that present in the related mixed-valent complex O$_3$ReReCl$_2$(η^2-dmpm)$_2$ (dmpm = Me$_2$PCH$_2$PMe$_2$) that was characterized by us previously.[20] The latter complex has a Re−Re distance of 2.4705(5) Å and contains formally Re(VI) and Re(II) centers which possess pseudotetrahedral and pentagonal bipyramidal geometries, respectively.[20] Complex **3** has a crystallographically imposed plane of symmetry that contains Re(1), C(1b), C(2b), Cl(1), and one oxygen atom (O(21)) of the ReO$_3$ group. This results in the remaining atoms of the ReO$_3$ unit, i.e., Re(2), O(22), and O(23), being disordered over two positions with half occupancies (Figure 2). The atoms associated with the two chemically equivalent disordered ReO$_3$ groups are Re(2), O(21), O(22), O(23)′ and Re(2)′, O(21), O(22)′, O(23).

One important difference between **3** and the complex O$_3$ReRe(η^2-dmpm)$_2$Cl$_2$ that we reported earlier[20] is that there is one additional chlorine atom in the latter complex making one of the Re atoms pentagonal bipyramidal. Such an arrangement in **3** may be disfavored due to the presence of the bulky cyclohexyl groups of the dcpm ligands. Nonetheless, the P−Re−P angles for the chelate rings in these two complexes are similar, averaging 67.7° in the case of **3** and 65.9° in the dmpm complex.

A detailed ab initio electronic structure calculation has been carried out on the model complex O$_3$ReRe(H$_2$PCH$_2$PH$_2$)$_2$Cl$_2$.[21]

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It was found out that the electronic constraints associated with the pentagonal pyramid geometry of the $ReCl_2(H_2PCH_2PH_2)_2$ unit induce a significant charge transfer that lead to a d^2-d^4 distribution of metal electrons which corresponds to a Re(V)−Re(III) mixed-valent system. A similar bonding description is not necessarily true in the case of complex **3** as there are adequate valence d-orbitals available on the Re atom of the $ReCl(dcpm)_2$ unit to accommodate six electrons. A formal description of complex **3** as a Re(VI)−Re(I) system is reasonable, but this conclusion requires further investigation.

Since complex **3** arises from the reaction of $ReOCl(\eta^2\text{-dcpm})_2$ with oxygen, it is possible that the previously reported $O_3ReReCl_2(\eta^2\text{-dmpm})_2$[20] is formed by a related, although not identical, reaction. It was isolated as a minor product, along with $Re_2(\mu\text{-}O_2CCH_3)Cl_4(\mu\text{-dmpm})_2$ and $Re_2Cl_4(\mu\text{-dmpm})_3$, in the reaction of *cis*-$Re_2(\mu\text{-}O_2CCH_3)_2Cl_4(H_2O)_2$ with dmpm. This very complicated redox reaction[20] may afford an unsuspected and unidentified intermediate (perhaps $ReOCl_2(\eta^2\text{-dmpm})_2$) that converts to $O_3ReReCl_2(\eta^2\text{-dmpm})_2$ in the presence of O_2 during the separation and purification process that was used in the workup of these reaction products.

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Supporting Information Available: X-ray crystallographic files in CIF format for $\mathbf{3}\cdot CH_2Cl_2$. This material is available free of charge via the Internet at http://pubs.acs.org.

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