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Reaction of Octachlorodirhenate with a Redox-Active Tetrathiafulvalene Phosphine Ligand: Spectroscopic, Magnetic, and Structural Characterization of the Unusual Paramagnetic Salt $[ReCl_2(o\text{-}P2)_2][Re_2Cl_6(o\text{-}P2)]$ (o-P2 = o-$\{P(C_6H_5)_2\}_2(CH_3)_2$TTF)

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Reaction of $[(n\text{-Bu})_4N]_2[Re_2Cl_8]$ with the tetrathiafulvalene phosphine ligand o-$\{P(C_6H_5)_2\}_2(CH_3)_2$TTF ($o$-P2) in refluxing ethanol produces the mixed-nuclearity salt $[ReCl_2(o\text{-}P2)_2][Re_2Cl_6(o\text{-}P2)]$ (**1·2**), composed of the mononuclear Re^{III} complex (**1**) and the mixed-valence $Re^{II}-Re^{III}$ dinuclear anion (**2**). The complex crystallizes as a CH_2Cl_2 solvate in the triclinic space group $P\bar{1}$, $a = 13.4559(1)$ Å, $b = 20.4015(3)$ Å, $c = 21.5538(1)$ Å, $\alpha = 88.261(1)°$, $\beta = 72.987(1)°$, $\gamma = 84.933(1)°$, and $Z = 2$. The molecular cation consists of two trans o-P2 ligands in the equatorial plane and axial chloride ligands. The dinuclear anion adopts an eclipsed geometry with an unsymmetrical coordination environment for the two metal atoms; one Re^{II} center is coordinated to a chelating o-P2 ligand and two chlorides while the other Re atom is coordinated to four chloride ligands. The dinuclear portion of the salt is a monoanion which leads to a formal bond order assignment of 3.5, based on the fact that the molecule possesses an Re_2^{5+} core. The salt was further characterized by infrared and electronic spectroscopies, electrochemistry, and variable temperature magnetic susceptibility; the presence of the individual ions in bulk samples was verified by positive and negative FAB mass spectrometry. Isolation of the two separate ions was achieved by treatment of the salt with $Co(C_5H_5)_2$, which reduces the Re^{III} cation to the Re^{II} complex $ReCl_2(o\text{-}P2)_2$ (**3**). This neutral compound was separated from the byproduct salt $[Co(C_5H_5)_2][Re_2Cl_6(o\text{-}P2)]$ and reoxidized with CCl_4/CH_2Cl_2 or $NOBF_4$ to produce $[ReCl_2(o\text{-}P2)_2][Cl]$ (**1**·[Cl]) and $[ReCl_2(o\text{-}P2)_2][BF_4]$ (**1**·[BF$_4$]), respectively. Compounds **3**, **1**·[Cl], and **1**·[BF$_4$] were identified by a combination of infrared spectroscopy, mass spectrometry, and cyclic voltammetric measurements. Variable temperature dc susceptibility studies of $[ReCl_2(o\text{-}P2)_2][Re_2Cl_6(o\text{-}P2)]$ (**1·2**) revealed classical Curie paramagnetic behavior (with a Curie constant equal to 0.395) and a large temperature independent paramagnetic contribution ($\chi_{TIP} = 9.64 \times 10^{-3}$ emu/mol). The EPR spectrum of **1·2** consists of a broad, complex signal due to hyperfine interactions to both isotopes ^{185,187}Re ($I = {}^5/_2$) and ^{31}P ($I = {}^1/_2$) which is typical for paramagnetic metal−metal bonded dirhenium phosphine compounds.

Introduction

Chelating diphosphines such as bis(diphenylphosphino)methane (dppm), bis(diphenylphosphino)ethane (dppe), and related molecules are known for their ability to stabilize metal complexes through the formation of chelating and bridging interactions.[1−6] Among the commonly encountered diphosphine ligands in dinuclear chemistry are those with an ethane or ethene backbone such as dppe, bis(diphenylphosphino)ethene (dppee), and bis(diphenylphosphino)benzene (dppbe) (Scheme 1), which coordinate to transition metals in a variety of oxidation states.[4,5] The existence of both α (chelating) and β (bridging) isomers of $M_2X_4(LL)_2$ compounds (Scheme 2) (X = halide, LL = dppe and related diphosphines) underscores the flexibility of these ligands and indicates that both kinetic and thermodynamic products can be isolated.[6,7]

In considering molecules that are similar to dppee, we recently turned our interest to tertiary phosphines with tetrathiafulvalene substituents; two examples are depicted in Scheme 3. These molecules resemble dppee and dppbe structurally, in that the two phosphorus donors are connected via a double bond.[8,9]

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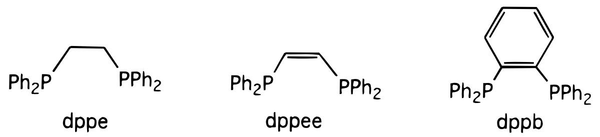
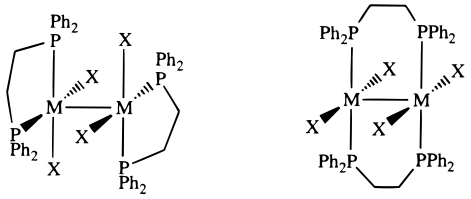
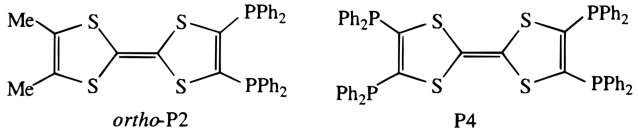
Scheme 1. Schematic Drawings of Various Diphosphine Ligands



Scheme 2. Scheme Depicting α- and *β*-Coordinated Diphosphine Complexes



Scheme 3. Schematic Drawings of New Tetrathiafulvalene-Based Tertiary Phosphine Ligands



The phosphine that was selected for the present study is *o*-{P(C$_6$H$_5$)$_2$}$_2$(CH$_3$)$_2$TTF (*o*-P2), which, in addition to the phosphorus donors, has an electron-rich TTF substituent that can act as an electron donor to metals. The ability of *o*-P2 to chelate to a single metal center was recently documented in our laboratories by the isolation and X-ray characterization of the homoleptic cations [Ni(*o*-P2)$_2$]$^{2+}$, [Pt(*o*-P2)$_2$]$^{2+}$, and [Rh(*o*-P2)$_2$]$^+$ as their [BF$_4$]$^-$ salts.[9] In these cases we did not expect to encounter a bridging mode for the ligand because Ni^{II}, Pt^{II}, and Rh^I complexes do not engage in strong metal−metal bonding. To test whether *o*-P2 could be a bridging ligand we turned to reactions with low-valent metals that form multiple M−M interactions, including those containing Mo$_2^{4+}$ and Re$_2^{6+}$ cores that exhibit interesting photophysical and redox properties.[10,11] Herein we report the reaction of *o*-{P(C$_6$H$_5$)$_2$}$_2$(CH$_3$)$_2$TTF with [*n*-Bu$_4$N]$_2$[Re$_2$Cl$_8$] to yield [Re^{III}Cl$_2$(*o*-P2)$_2$][Re$_2^{II,III}$Cl$_6$(*o*-P2)]. In addition to providing more data on the binding preferences of the *o*-P2 ligand, this salt lends new insight into the reaction pathway(s) of [Re$_2$Cl$_8$]$^{2-}$ with diphosphine ligands. The compound contains two species that are at different points along the reaction pathway, namely, a cation [Re^{III}Cl$_2$(*o*-P2)$_2$]$^+$ that results from nonredox cleavage of the metal−metal bond and [Re$_2^{II,III}$Cl$_6$(*o*-P2)]$^-$, a mixed-valence anion that represents the first step in the reduction of the Re$_2^{III,III}$ core to Re$_2^{II,II}$. The species [Re$_2^{II,III}$Cl$_6$(*o*-P2)]$^-$ constitutes the first example of a dinuclear compound that contains a single chelating diphosphine ligand.

Experimental Section

Physical Measurements. Infrared spectra were recorded on a Nicolet 740 FT-IR spectrophotometer. Spectra in the far-IR range (50−400 cm^{-1}) were recorded on a computer-controlled Nicolet 750 FT-IR spectrophotometer equipped with a TGS/PE detector and a silicon beam splitter set at 2.0 or 4.0 cm^{-1} resolution. ^{1}H NMR spectra were measured on a Varian 300 MHz spectrometer; chemical shifts were referenced relative to the residual proton impurities of CD$_2$Cl$_2$ or chloroform-*d*$_1$. ^{31}P{^{1}H} NMR spectra were obtained on a Varian 300 MHz spectrometer operating at 121.4 MHz and were referenced relative to an external standard of 85% phosphoric acid. Elemental analyses were performed at Desert Analytics, Tucson, AZ. Electrochemical measurements were carried out by using an EG&G Applied Research model 362 scanning potentiostat in conjunction with a BAS model RXY recorder. Cyclic voltammetric experiments were carried out at 22 ± 2 °C on 0.2 M [*n*-Bu$_4$N][BF$_4$]/CH$_2$Cl$_2$ solutions in a cell equipped with a Pt working electrode, a Ag/AgCl reference electrode, and a Pt wire. EPR spectra were measured on a Bruker ESP-300-E spectrometer equipped with an Oxford Instruments ESR-900 continuous flow cryostat. Variable temperature magnetic susceptibility measurements were carried out on a Quantum Design MPMS susceptometer housed in the Physics and Astronomy Department at Michigan State University and funded by the Center for Fundamental Materials Research. Data points were collected over the range 5−340 K at 20 deg intervals in a field of 1000 G. Fast atom bombardment (FAB) mass spectrometry studies were performed on a JEOL HX double-focusing mass spectrometer housed in the National Institutes of Health/Michigan State University Mass Spectrometry Facility.

Starting Materials. *o*-{P(C$_6$H$_5$)$_2$}$_2$(CH$_3$)$_2$TTF (*o*-P2)[8] and [(*n*-Bu)$_4$N]$_2$[Re$_2$Cl$_8$][12] were prepared according to published methods. NOBF$_4$ was purchased from Aldrich Chemical Co. and used as received. Acetonitrile and methylene chloride were distilled over 3 Å molecular sieves. Ethanol was distilled over Mg(OMe)$_2$, and diethyl ether was distilled over sodium−potassium/benzophenone. Unless otherwise specified, all reactions were carried out under an argon atmosphere by using standard Schlenk-line techniques.

[ReCl$_2$(*o*-P2)$_2$][Re$_2$Cl$_6$(*o*-P2)] (1·2). A flask charged with a mixture of [*n*-Bu$_4$N]$_2$[Re$_2$Cl$_8$] (0.104 g, 0.091 mmol) and *o*-P2 (0.131 g, 0.219 mmol) was treated with 10 mL of ethanol and refluxed for 1 h, during which time the solution became yellow-orange with the deposition of a red solid. The mixture was filtered in air, and the solid was washed with copious amounts of EtOH and CH$_3$CN to remove unreacted starting materials followed by ~50 mL of Et$_2$O to dry the solid. Single crystals of the dicholoromethane tetrasolvate were obtained by slow diffusion of CH$_3$CN into a dichloromethane solution of the compound; yield, 0.115 g (72%). Anal. Calcd for **1·2**·CH$_2$Cl$_2$, Re$_3$Cl$_{10}$S$_{12}$P$_6$C$_{97}$H$_{80}$: C, 42.70; H, 2.95. Found: C, 42.74; H, 2.72. Elemental analysis reflects the loss of three of the four interstitial dichloromethane molecules, which is not surprising, given that crystals removed from the mother liquid are observed to rapidly lose their crystallinity. IR (Nujol, cm^{-1}): 329 ($\nu_{\text{Re-Cl}}$), 333 sh($\nu_{\text{Re-Cl}}$), 352 ($\nu_{\text{Re-Cl}}$), 517 ($\nu_{=\text{C-H}}$), 691 ($\nu_{\text{C=C}}$). UV−vis (CH$_2$Cl$_2$): $\lambda_{\max}$ (nm) (ϵ, M^{-1} cm^{-1}) 976 (4.80 × 10^1), 448 (5.0 × 10^3), 322 (6.4 × 10^4), 276 (7.5 × 10^4). CV (0.1 M TBABF$_4$, CH$_2$Cl$_2$, Pt disk electrode vs Ag/AgCl): $E_{1/2}(\text{red})_1 = +0.03$ V, $E(\text{p,c})_2 = -0.79$ V, $E(\text{p,c})_3 = -1.12$ V, $E_{1/2}(\text{ox})_1 = +0.31$ V, $E_{1/2}(\text{ox})_2 = +0.50$ V, $E_{1/2}(\text{ox})_3 = +0.67$ V, $E(\text{p,a})_4 = +1.05$. FAB-MS (*m*/*z*): 1457 ([ReCl$_2$(*o*-P2)$_2$]$^+$), −1186 ([Re$_2$Cl$_6$(*o*-P2)]$^-$). Magnetic moment (μ_B): $\mu_{\text{eff}} = 5.2$ at 340 K (1T), $\mu_{\text{eff}} = 1.9$ at 5 K (1T). EPR (1:1 CH$_2$Cl$_2$/toluene, 4 K): $g = 2.40$.

Reduction of [ReCl$_2$(*o*-P2)$_2$][Re$_2$Cl$_6$(*o*-P2)] (1·2) To Yield ReCl$_2$(*o*-P2)$_2$ (3). A solution of Co(C$_5$H$_5$)$_2$ (0.01 g, 0.053 mmol) in 2 mL of CH$_2$Cl$_2$ was added to [ReCl$_2$(*o*-P2)$_2$][Re$_2$Cl$_6$(*o*-P2)] (**1·2**) (0.100 g, 0.038 mmol) in 5 mL of CH$_2$Cl$_2$, during which time an immediate color change to brown-green ensued. The reaction mixture was stirred for

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Table 1. Summary of Crystallographic Data for $[\text{ReCl}_2(o\text{-P2})_2][\text{Re}_2\text{Cl}_6(o\text{-P2})]\cdot4\text{CH}_2\text{Cl}_2$ ($\mathbf{1\cdot2\cdot}4\text{CH}_2\text{Cl}_2$)

	$\mathbf{1\cdot2\cdot}4\text{CH}_2\text{Cl}_2$
formula	$\text{C}_{100}\text{H}_{86}\text{Cl}_{16}\text{P}_6\text{Re}_3\text{S}_{12}$
fw	2984.03
space group	$P\bar{1}$ (No. 2)
a, Å	13.4559(1)
b, Å	20.4015(3)
c, Å	21.5538(1)
α, deg	88.261(1)
β, deg	72.987(1)
γ, deg	84.933(1)
V, Å^3	5635.85(10)
Z	2
λ(M*o* Kα) wavelength	0.710 73 Å
ρ_{calcd}, Mg/cm^3	1.76
μ, mm^{-1}	3.95
T, °C	-100
R1[a]	0.0751
wR2[b]	0.1594

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

12 h to give a yellow precipitate, which was isolated by filtration, washed three times with 5 mL of CH_2Cl_2, and dried *in vacuo*; yield, 0.031 g (56%). IR (Nujol, cm^{-1}): 330 ($\nu_{\text{Re-Cl}}$), 513 ($\nu_{\overset{\cdot\cdot}{-}\text{C-H}}$), 702 ($\nu_{\text{C}\overset{\cdot\cdot}{-}\text{C}}$). FAB-MS ($m/z$) = +1457 ($[\text{ReCl}_2(\text{P2})_2]^+$), −1457 (<5% of base, $[\text{ReCl}_2(\text{P2})_2]^-$). Magnetic moment ($\mu_B$): $\mu_{\text{eff}} = 5.0$ at 300 K (1T), $\mu_{\text{eff}} = 1.8$ at 2 K (1T).

Oxidation of $\text{ReCl}_2(o\text{-P2})_2$ (3). (i) Preparation of $[\text{ReCl}_2(o\text{-P2})_2][\text{Cl}]$ (1·[Cl]). A small quantity of $\text{ReCl}_2(o\text{-P2})_2$ (**3**) (0.020 g, 0.014 mmol) was stirred in a mixture of 5 mL of CH_2Cl_2 and 10 mL of CCl_4 under refluxing conditions for 3 days. The yellow-orange solution was reduced in volume, and 30 mL of Et_2O was added to precipitate a yellow-orange solid, which was washed with Et_2O and dried *in vacuo*; yield, 0.008 g (38%). IR (Nujol, cm^{-1}): 327 ($\nu_{\text{Re-Cl}}$), 518 ($\nu_{\overset{\cdot\cdot}{-}\text{C-H}}$), 695 ($\nu_{\text{C}\overset{\cdot\cdot}{-}\text{C}}$). FAB-MS ($m/z$): 1457 ($[\text{ReCl}_2(\text{P2})_2]^+$).

(ii) Preparation of $[\text{ReCl}_2(o\text{-P2})_2][\text{BF}_4]$ (1·[BF$_4$]). A 4.2 mL aliquot of a stock solution of NOBF_4 (0.014 g, 0.120 mmol, 10 mL CH_2Cl_2) was slowly added to a mixture of $\text{ReCl}_2(o\text{-P2})_2$ (**3**) (0.054 g, 0.037 mmol) in 5 mL of CH_2Cl_2. The mixture was stirred for 3 days, during which time the solution color gradually became red-brown. The reaction mixture was filtered in air to remove unreacted $\text{ReCl}_2(o\text{-P2})_2$ (**3**) and treated with 30 mL of Et_2O to afford a red-brown precipitate. The resulting solid was isolated by filtration, washed with Et_2O, and dried *in vacuo*; yield 0.035 g (61%). CV (0.2 M TBABF_4, CH_2Cl_2, Pt disk electrode vs Ag/AgCl): $E_{1/2}(\text{ox})_1 = +0.75$ V, $E_{1/2}(\text{ox})_2 = +1.14$ V, $E_{1/2}(\text{red})_1 = +0.07$ V, $E_{1/2}(\text{red})_2 = -0.97$ V. Magnetic moment (μ_B): $\mu_{\text{eff}} = 4.9$ at 300 K (1T), $\mu_{\text{eff}} = 0.7$ at 2 K (1T).

X-ray Crystallographic Studies. Single crystals of $[\text{ReCl}_2(o\text{-P2})_2][\text{Re}_2\text{Cl}_6(o\text{-P2})]\cdot4\text{CH}_2\text{Cl}_2$ ($\mathbf{1\cdot2\cdot}4\text{CH}_2\text{Cl}_2$) were grown by slow diffusion of acetonitrile into a dichloromethane solution of the title compound. A red-orange parallelepiped of approximate dimensions 0.16 × 0.17 × 0.55 mm was secured on the tip of a glass fiber with silicone grease and cooled to −100 ± 1 °C during data collection by using a cold nitrogen stream. The data were collected in a θ range of 0.99−21.72° on a Siemens SMART/CCD area detector diffractometer equipped with monochromated Mo Kα radiation. Successful refinement of the structure was carried out in the triclinic $P\bar{1}$ space group. Of the 21 397 reflections that were collected, 13 226 were determined to be unique ($R(\text{int}) = 0.067$) and 11 595 were observed ($I > 2\sigma(I)$). The data were corrected for absorption with transmission factors ranging from 0.63 to 0.99. The structure was solved by direct methods and refined by full-matrix least squares refinement. Crystallographic computing was performed using SHELXTL, version 5.[13] Crystal parameters and basic information pertaining to data collection and structure refinement are summarized in Table 1, and the positional parameters are given in Table 2.

The asymmetric unit consists of one $[\text{Re}_2\text{Cl}_6(o\text{-P2})]^-$ (**2**) moiety, two half $[\text{ReCl}_2(o\text{-P2})_2]^+$ (**1**) cations residing on centers of inversion, and four solvent molecules. Solvent disorder and poor packing severely affected the scattering ability of the crystal at higher θ angles; data collection was therefore limited to θ less than 21.72°. The poor scattering and the high absorption led to a variety of issues during the refinement of the structure. The solvent disorder was resolved completely for only one of the solvent molecules (C(100), Cl(15), and Cl(16)). Atoms Cl(15), Cl(16), Cl(15B), and Cl(16B) were refined at 50% occupancy in alternate least squares cycles. There is also a possibility that the phenyl groups that involve the atoms C(15)−C(20) and C(21)−C(26) are undergoing a wagging motion. Atoms C(1), C(34), C(41), C(59), C(66), and C(67) were refined isotropically, and hydrogen atoms were placed in calculated positions and allowed to ride on the bonded atom. The methyl hydrogen atoms were included as rigid groups with rotational freedom at the bonded carbon atom. Refinement of all non-hydrogen atoms was carried out with anisotropic temperature factors except as noted above.

Results and Discussion

Preparation of $[\text{ReCl}_2(o\text{-P2})_2][\text{Re}_2\text{Cl}_6(o\text{-P2})]$ (1·2). The unusual salt $[\text{ReCl}_2(o\text{-P2})_2][\text{Re}_2\text{Cl}_6(o\text{-P2})]$ (**1·2**) is prepared in the highest yields from reaction of $[(n\text{-Bu})_4\text{N}]_2[\text{Re}_2\text{Cl}_8]$ with 2.4 equiv of *o*-P2 in refluxing ethanol. The mononuclear cation $[trans\text{-ReCl}_2(o\text{-P2})_2]^+$ (**1**) results from nonredox cleavage of the dimetal unit, which is not particularly surprising given the demonstrated ability of bidentate phosphines to cleave the quadruple bond of $[\text{Re}_2\text{X}_8]^{2-}$ species. Reactions involving other bidentate phosphine ligands with an ethene backbone, such as bis(diphenylphosphino)ethene (dppee)[14] and bis(diphenylphosphino)benzene (dppbe),[15] performed in alcohols produce the analogous complexes $[trans\text{-ReX}_2(\text{LL})_2]\text{X}$ (LL = dppbe, dppee). Similar behavior has also been noted with ligands such as bis(diphenylphosphino)ethane (dppe),[2] bis(diphenylphosphino)amine (dppa),[16b] bis(diethylphosphino)ethane (depe),[16c] and bis(ditolylphosphino)ethane (dtpe).[16d]

The anion in the structure, $[\alpha\text{-Re}_2\text{Cl}_6(o\text{-P2})]^-$ (**2**), results from the substitution of two chlorides on $[\text{Re}_2\text{Cl}_8]^{2-}$ with concomitant reduction of the dirhenium core from Re_2^{6+} to Re_2^{5+}. The reaction conditions are similar to those reported for the synthesis of $\alpha\text{-Re}_2\text{X}_4(\text{dppee})_2$ (X = Cl, Br),[17] but in the present case *only one* chelating diphosphine ligand enters the coordination sphere. It is interesting to note that the dppee reactions proceed with M−M cleavage to yield the mononuclear Re(III) cations $[\text{ReX}_2(\text{dppee})_2]^+$, with no evidence for monosubstituted products of the type encountered in this study. The dinuclear anion **2** appears to be a previously undetected intermediate in the conversion of $[\text{Re}_2\text{X}_8]^{2-}$ compounds to the bis-substituted $\text{Re}_2\text{Cl}_4(\text{P-P})_2$ compounds.

Isolation of $[\text{Re}(o\text{-P2})_2\text{Cl}_2]^+$ from $[\text{ReCl}_2(o\text{-P2})_2][\text{Re}_2\text{Cl}_6(o\text{-P2})]$. Reaction of **1·2** with a slight excess of the reducing agent CoCp_2 affords a yellow solid identified as $\text{ReCl}_2(o\text{-P2})_2$ (**3**) on the basis of infrared, mass spectroscopic, and magnetic susceptibility measurements. This reaction is similar to one reported by Walton *et al*. for the reduction of $[\text{ReCl}_2(\text{dppee})_2]\text{Cl}$ to $\text{ReCl}_2(\text{dppee})_2$.[14] The neutral compound **3** is fairly insoluble, thereby allowing it to be separated from the byproduct salt $[\text{CoCp}_2][\text{Re}_2\text{Cl}_6(o\text{-P2})]$. The FAB mass spectrum of **3** contains a parent ion peak at $m/z = 1457$ for both positive and negative ion spectra, which is consistent with $\text{ReCl}_2(o\text{-P2})_2$.

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Table 2. Positional Parameters (×10^4 for *x*, *y*, *z*; Å^2 × 10^3 for *U*(eq)) for [$ReCl_2$(*o*-P2)$_2$][Re_2Cl_6(*o*-P2)]·4CH_2Cl_2 (**1**·**2**·4CH_2Cl_2)

atom	*x*/*a*	*y*/*b*	*z*/*c*	*U*(eq)[a]	atom	*x*/*a*	*y*/*b*	*z*/*c*	*U*(eq)[a]
Re(1)	−1606(1)	11759(1)	−4022(1)	21(1)	C(37)	−3755(14)	9225(9)	−2177(9)	33(5)
Re(2)	−2198(1)	12723(1)	−3521(1)	23(1)	C(38)	−3149(14)	9294(8)	−1799(9)	30(4)
Re(3)	−5000	5000	0	15(1)	C(39)	−3914(19)	9635(10)	−2724(11)	54(6)
Re(4)	0	10000	−10000	18(1)	C(40)	−2489(18)	9864(10)	−1818(11)	53(7)
Cl(1)	−1863(4)	10927(2)	−3206(2)	34(1)	C(41)	−6369(12)	5863(8)	−1143(8)	20(4)[b]
Cl(2)	175(4)	11495(2)	−4101(2)	37(1)	C(42)	−7069(13)	6299(8)	−716(10)	31(5)
Cl(3)	691(4)	13021(2)	−3333(2)	36(1)	C(43)	−8008(15)	6515(9)	−835(11)	38(5)
Cl(4)	1996(3)	13574(2)	−4278(2)	30(1)	C(44)	−8246(18)	6295(11)	−1355(13)	57(6)
Cl(5)	−3982(3)	12924(2)	−3431(2)	27(1)	C(45)	−7550(18)	5868(11)	−1794(12)	57(7)
Cl(6)	−2699(4)	12412(2)	−2440(2)	38(1)	C(46)	−6615(16)	5646(9)	−1674(11)	42(5)
Cl(7)	−3729(3)	4263(2)	−612(2)	20(1)	C(47)	−4262(14)	5279(7)	−1704(8)	26(4)
Cl(8)	1023(3)	10250(2)	−9357(2)	24(1)	C(48)	−3367(13)	5596(8)	−2057(8)	27(4)
Cl(9)	−2654(9)	6490(6)	−6761(5)	133(4)	C(49)	−2664(14)	5300(9)	−2600(9)	36(5)
Cl(10)	−2428(8)	7589(5)	−6010(5)	123(3)	C(50)	−2868(16)	4704(9)	−2808(10)	41(5)
Cl(11)	111(5)	113697(3)	−1987(3)	71(2)	C(51)	−3724(14)	4393(9)	−2501(9)	36(5)
Cl(12)	−1629(5)	13130(3)	−1071(3)	68(2)	C(52)	−4410(13)	4683(8)	−1947(8)	22(4)
S(1)	−4534(3)	12424(2)	−4968(2)	30(1)	C(53)	−3752(13)	6232(7)	701(8)	22(4)
S(2)	−2707(4)	13059(2)	−5770(2)	34(1)	C(54)	−2989(13)	6060(9)	1009(9)	30(4)
S(3)	−6037(4)	13712(2)	−5153(3)	36(1)	C(55)	−3021(16)	6349(10)	1568(9)	41(5)
S(4)	−4212(4)	114311(2)	−6001(3)	41(1)	C(56)	−3843(17)	6819(10)	1862(11)	48(6)
S(5)	−4978(3)	7095(2)	−1355(2)	25(1)	C(57)	−4591(13)	6969(9)	1561(9)	34(5)
S(6)	−3669(3)	7286(2)	−495(2)	24(1)	C(58)	−4567(14)	6688(8)	988(9)	31(5)
S(7)	−4496(4)	8524(2)	−2001(2)	36(1)	C(59)	−2380(12)	5566(7)	−452(8)	16(4)[b]
S(8)	−3149(4)	8712(2)	−1181(2)	34(1)	C(60)	−1849(13)	5901(8)	−1009(8)	25(4)
S(9)	−1940(4)	11843(2)	−8429(2)	29(1)	C(61)	−821(15)	5672(10)	−1313(10)	40(5)
S(10)	−2475(4)	10594(2)	−7742(2)	28(1)	C(62)	−310(15)	5153(10)	−1067(12)	47(6)
S(11)	−3779(4)	12639(2)	−7342(2)	36(1)	C(63)	−869(15)	4831(9)	−515(11)	40(5)
S(12)	−4351(4)	11422(2)	−6634(2)	41(1)	C(64)	−1891(13)	5045(8)	−233(9)	28(4)
P(1)	−3139(4)	11549(2)	−4262(2)	25(1)	C(65)	−1528(12)	11108(7)	−8893(8)	19(4)
P(2)	−1225(3)	12200(2)	−5086(2)	23(1)	C(66)	−1790(12)	10545(8)	−8559(8)	20(4)[b]
P(3)	−5130(3)	5615(2)	−974(2)	17(1)	C(67)	−2753(12)	11459(8)	−7766(8)	21(4)
P(4)	−3748(3)	5818(2)	−37(2)	16(1)	C(68)	−3512(15)	11789(8)	−7302(9)	33(5)
P(5)	−863(3)	11113(2)	−9742(2)	20(1)	C(69)	−5064(15)	12653(10)	−6804(9)	37(5)
P(6)	−1388(3)	9773(2)	−9002(2)	20(1)	C(70)	−5309(16)	12092(10)	−6478(9)	41(5)
C(1)	−3334(12)	12192(7)	−4829(8)	18(4)[b]	C(71)	−5720(17)	13276(11)	−6798(11)	56(6)
C(2)	−2475(13)	12493(8)	−5199(8)	25(4)	C(72)	−6320(16)	11973(11)	−5980(10)	53(6)
C(3)	−4078(12)	13098(8)	−5440(9)	25(4)	C(73)	−1842(12)	11374(7)	−10148(9)	21(4)
C(4)	−4679(15)	13638(8)	−5541(9)	32(5)	C(74)	−1565(13)	11314(8)	−10814(8)	23(4)
C(5)	−6187(16)	14546(8)	−5354(11)	39(5)	C(75)	−2279(13)	11514(8)	−11150(9)	24(4)
C(6)	−5359(17)	14814(10)	−5725(13)	53(6)	C(76)	−3259(16)	11754(9)	−10822(11)	40(5)
C(7)	−7278(15)	14881(9)	−5034(12)	50(6)	C(77)	−3562(16)	11814(11)	−10154(11)	47(6)
C(8)	−5312(17)	15519(9)	−5977(12)	51(6)	C(78)	−2843(13)	11633(9)	−9806(9)	31(5)
C(9)	−4380(13)	11394(8)	−3663(10)	29(5)	C(79)	−74(11)	11813(7)	−9825(8)	20(4)
C(10)	−4483(15)	11449(8)	−3004(10)	37(5)	C(80)	421(12)	11911(8)	−9351(9)	26(4)
C(11)	−5373(17)	11260(10)	−2556(11)	48(6)	C(81)	1012(14)	12444(9)	−9424(9)	36(5)
C(12)	−6140(17)	11069(11)	−2760(12)	52(6)	C(82)	1137(14)	12866(9)	−9957(10)	36(5)
C(13)	−6067(16)	11007(10)	−3407(15)	63(8)	C(83)	666(14)	12764(8)	−10415(9)	31(4)
C(14)	−5183(16)	11188(8)	−3864(11)	41(5)	C(84)	40(12)	12237(7)	−10351(9)	23(4)
C(15)	−2879(14)	10808(8)	−4741(9)	30(4)	C(85)	−2601(12)	9543(8)	−9113(8)	22(4)
C(16)	−3062(20)	10764(10)	−5327(13)	65(7)	C(86)	−2643(14)	8956(8)	−9393(8)	26(4)
C(17)	−2843(23)	10204(10)	−5685(12)	74(9)	C(87)	−3542(15)	8784(10)	−9495(9)	41(5)
C(18)	−2448(20)	9636(10)	−5454(14)	69(8)	C(88)	−4428(17)	9213(11)	−9354(11)	52(6)
C(19)	−2228(29)	9659(13)	−4908(16)	115(15)	C(89)	−4382(14)	9824(10)	−9110(11)	45(6)
C(20)	−2482(23)	10243(10)	−4525(16)	85(10)	C(90)	−3471(13)	9993(9)	−8999(9)	31(5)
C(21)	−751(14)	11567(9)	−5698(8)	31(4)	C(91)	−1090(12)	9212(8)	−8402(8)	23(4)
C(22)	−107(28)	11054(18)	−5619(14)	139(18)	C(92)	−1367(14)	8572(8)	−8324(9)	32(5)
C(23)	269(32)	10567(20)	−6067(18)	158(21)	C(93)	−1076(17)	8144(10)	−7877(10)	43(5)
C(24)	16(23)	10590(14)	−6623(14)	88(10)	C(94)	−497(17)	8366(8)	−7509(10)	42(6)
C(25)	−661(17)	11069(11)	−6722(12)	56(7)	C(95)	−249(16)	9003(12)	−7559(10)	50(6)
C(26)	−1045(18)	11544(11)	−6260(12)	60(7)	C(96)	−532(13)	9431(7)	−7999(8)	23(4)
C(27)	−292(13)	12817(10)	−5392(8)	31(5)	C(97)	−3159(22)	7233(15)	−6461(15)	87(9)
C(28)	409(15)	12903(10)	−5052(10)	42(5)	C(98)	−1263(18)	13657(12)	−1734(12)	65(7)
C(29)	1155(17)	13344(13)	−5270(12)	66(7)	C(99)	−9454(58)	14460(26)	−3479(31)	307(49)
C(30)	1231(16)	13673(13)	−5845(1)	58(7)	C(100)	1136(37)	12249(19)	−7367(18)	134(15)
C(31)	573(17)	13589(11)	−6205(11)	55(7)	Cl(13)	−8964(13)	15109(7)	−3153(8)	193(6)
C(32)	−184(15)	13150(10)	−5971(9)	38(5)	Cl(14)	−10029(10)	14776(6)	−4095(8)	182(6)
C(33)	−4666(11)	6424(7)	−907(8)	15(4)	Cl(15)[c]	1907(24)	12849(12)	−7640(11)	93(7)
C(34)	−4079(12)	6503(8)	−519(8)	19(4)[b]	Cl(16)[c]	2216(41)	12735(29)	−7517(31)	290(37)
C(35)	−4152(13)	7608(7)	−1124(8)	18(4)	Cl(15B)[c]	−139(37)	12660(19)	−7636(19)	119(10)
C(36)	−3972(12)	8186(7)	−1393(9)	24(4)	Cl(16B)[c]	296(58)	12472(35)	−7668(31)	265(40)

[a] *U*(eq) is defined as one-third of the orthogonalized U_{ij} tensor. [b] Isotropic refinement. [c] 50% occupancy.

These results are in accord with **3** being neutral since both positive and negative ions were detected. The infrared spectrum of **3** exhibits modes due to *o*-P2 at 513 and 702 cm^{-1} and a characteristic ν(Re−Cl) feature at 330 cm^{-1}.

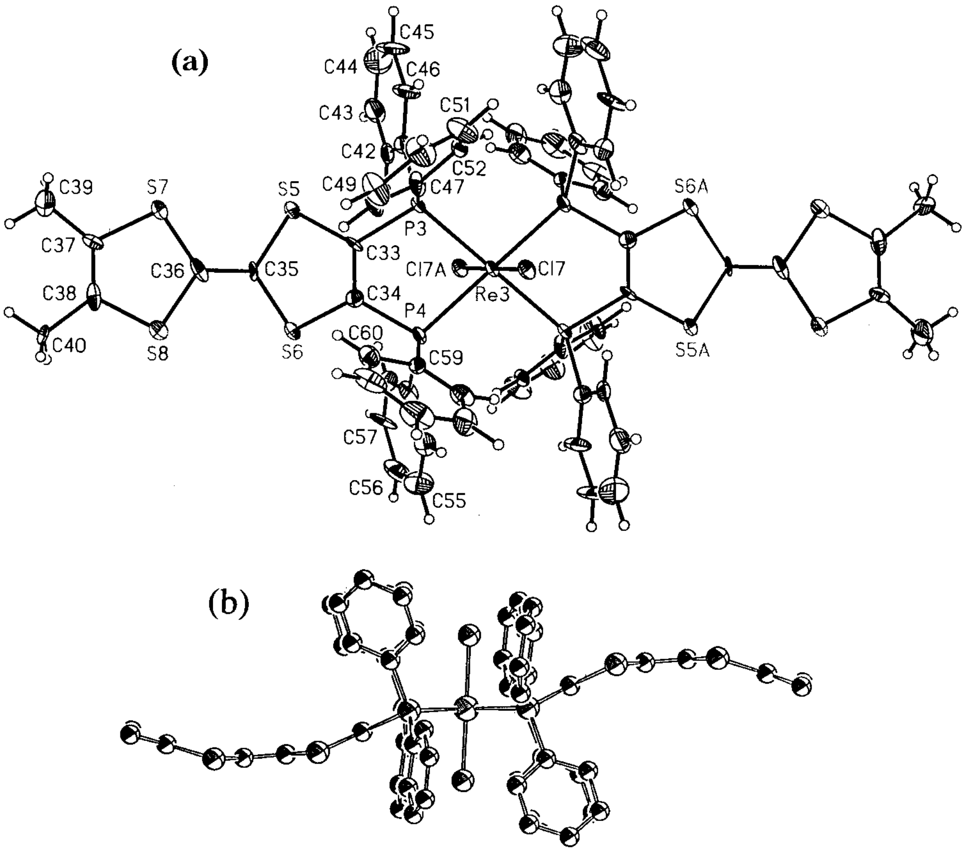

Figure 1. Diagram of the cation $[ReCl_2(o\text{-}P2)_2]^+$ (**1**) with non-hydrogen atoms represented by their 50% probability ellipsoids: viewed from (a) the top and (b) the side.

In order to characterize the cation in the original compound, $ReCl_2(o\text{-}P2)_2$ was reoxidized by gentle refluxing of the compound in CCl_4/CH_2Cl_2. It had been reported earlier that such conditions led to the oxidation of $ReCl_2(dppb)_2$ to $[ReCl_2(dppb)_2][Cl]$.[15] Mass spectroscopic analysis of **1**·[Cl] gives a parent ion peak at $m/z = +1457$, which is in accord with the presence of $[ReCl_2(o\text{-}P2)_2]^+$. On the basis of the chemistry of similar complexes, it is reasonable to assume that **1** retains the trans configuration throughout the redox reactions.[14,15] Alternatively one can treat **3** with $NOBF_4$ to yield $[ReCl_2(o\text{-}P2)_2][BF_4]$ (**1**·$[BF_4]$), but care must be taken not to add excess oxidant, as this will lead to oxidation of the TTF substituents as well. If this occurs, the solution assumes an intense green color which is characteristic of TTF radicals.

Spectroscopic Characterization. The paramagnetic nature of $[ReCl_2(o\text{-}P2)_2][Re_2Cl_6(o\text{-}P2)]$ leads to a broad, featureless ^1H NMR spectrum and the complete absence of $^{31}P\{^1H\}$ NMR signals. The IR spectrum confirms the presence of ν(Re−Cl) stretches at 329, 333, and 352 cm^{-1}. The electronic absorbance spectrum reveals the characteristic phenyl and TTF-based transitions that are attributable to the ligand at 276, 322, and 448 cm^{-1}. The extinction coefficients of the TTF bands are reliable indicators of the number of chromophores in the molecule.[8] Thus on the basis of the fact that free *o*-P2 with four phenyl groups exhibits a band at 276 nm with an ϵ value of 25 000 M^{-1} cm^{-1} and $[ReCl_2(o\text{-}P2)_2][Re_2Cl_6(o\text{-}P2)]$ exhibits a transition at 276 with an ϵ value of 74 600, one can ascertain that the compound contains three TTF phosphines (or 12 phenyl groups). The low-energy transition at 976 nm in the near-IR region signifies a $\delta \rightarrow \delta^*$ transition for a mixed-valence $Re^{II}-Re^{III}$ complex.[2] The FAB mass spectrum of **1·2** displays the highest mass peak at $m/z = +1457$, which is consistent with the presence of the cation $[Re_2Cl_2(o\text{-}P2)_2]^+$. In the negative ion mode, the highest mass peak is at $m/z = -1186$, which is consistent with the anion, $[Re_2Cl_6(o\text{-}P2)]^-$.

Molecular Structure of $[ReCl_2(o\text{-}P2)_2]$ $[Re_2Cl_6(o\text{-}P2)]$ (1·2·4CH$_2$Cl$_2$). Drawings of the ions $[ReCl_2(o\text{-}P2)_2]^+$ (**1**) and $[Re_2Cl_6(o\text{-}P2)]^-$ (**2**) are depicted in Figures 1 and 2. Selected bond distances and angles are provided in Tables 3 and 4, respectively. The asymmetric unit consists of one $[Re_2Cl_6(o\text{-}P2)]^-$ (**1**) moiety, two half $[ReCl_2(o\text{-}P2)_2]^+$ (**2**) units, and four dichloromethane solvent molecules. The cations are six-coordinate molecules with *trans*-chelating diphosphine ligands. The angles ∠P(3)−Re(3)−P(4) and ∠P(4)−Re(3)−Cl(7) are 80.62(13)° and 92.50(13)° for one cation, and ∠P(5)−Re(4)−P(6) = 79.63(14)° and ∠P(6)−Re(4)−Cl(8) = 88.42(14)° for the second, independent cation are comparable to those observed in similar molecules.[14−16] The average Re−Cl and Re−P distances of 2.31(1) and 2.459(3) Å, respectively, are similar to corresponding distances reported for analogous bis-diphosphine complexes, $[ReCl_2(P\text{-}P)_2]^+$ (P-P = dppee, dppbe, dppe, dppa, depe, dtpe). In the *o*-P2 ligand, representative distances, *e.g.*, C(33)−C(34) = 1.33(2) Å and S(5/6)-C(33/34) = 1.74(2) Å, are essentially unchanged relative to the bond lengths in the free phosphine ligand.[19a] These data suggest that there is no pronounced electronic change in the dithiole system due to the electronic donation of the phosphorus to the metal center. The out-of-plane bend of 22° at the S(5) and S(6) positions is similar to those observed for $[Rh(o\text{-}P2)_2][BF_4]$,[9] $[Ni(o\text{-}P2)_2][BF_4]_2$, and $[Pt(o\text{-}P2)_2][BF_4]_2$[19b] and is most likely due to packing influences. The corresponding bend in the

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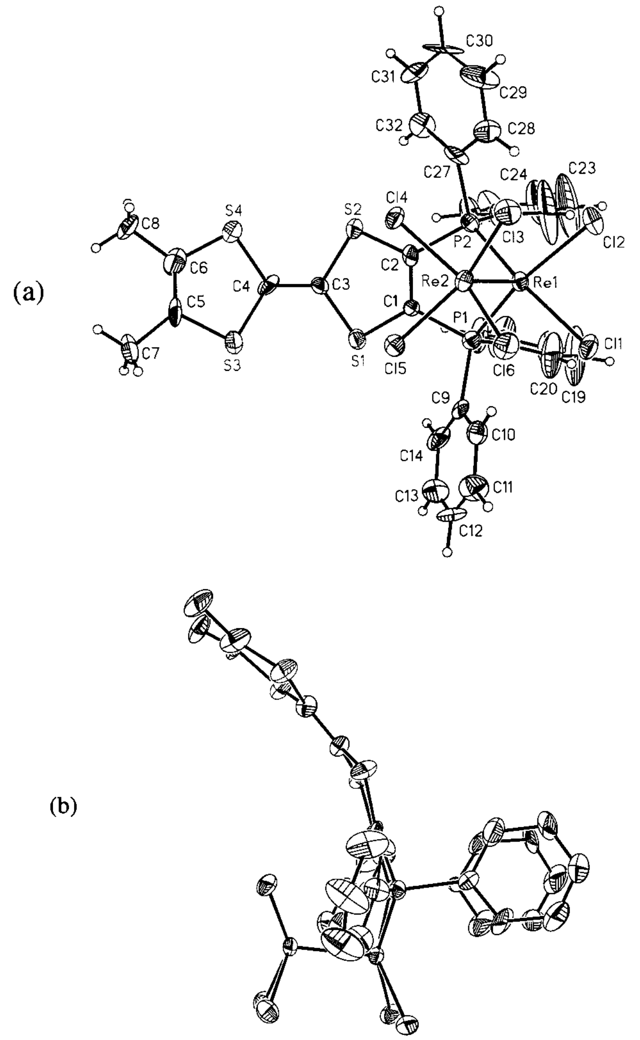

Figure 2. Diagram of the anion [Re_2Cl_6(*o*-P2)]$^-$ (**2**) with non-hydrogen atoms represented by their 50% probability ellipsoids; viewed from (a) the top and (b) the side.

Table 3. Summary of Bond Distances (Å) and Angles (deg) for the Cation [$ReCl_2$(*o*-P2)$_2$]$^+$ (**1**) of [$ReCl_2$(*o*-P2)$_2$][Re_2Cl_6(*o*-P2)]·4CH_2Cl_2 (**1**·**2**·4CH_2Cl_2)

Bond Distances

A	B	A−B (Å)	A	B	A−B (Å)
Re(3)	P(3)	2.456(4)	Re(3)	P(4)	2.457(4)
Re(3)	Cl(7)	2.296(4)	P(3)	C(33)	1.840(14)
P(3)	C(41)	1.83(2)	C(33)	C(34)	1.33(2)
C(33)	S(5)	1.74(2)	S(5)	C(35)	1.77(2)
S(7)	C(37)	1.78(2)	C(37)	C(38)	1.33(3)

Bond Angles

A	B	C	A−B−C (deg)	A	B	C	A−B−C (deg)
P(3)	Re(3)	P(4)	80.62(13)	P(3)	Re(3)	P(4A)	99.38(13)
Cl(7)	Re(3)	P(4)	92.50(13)	Re(3)	P(3)	C(33)	105.5(5)
Re(3)	P(3)	C(41)	123.7(5)	P(3)	C(33)	C(34)	120.3(12)
C(33)	S(5)	C(35)	93.6(7)	S(5)	C(35)	S(6)	114.2(8)

cation containing Re(4) is much smaller, being only 11°. This difference in the out-of-plane bend may account for the slight differences in the magnitude of the bonds and angles within the dithiole rings for the two cations.

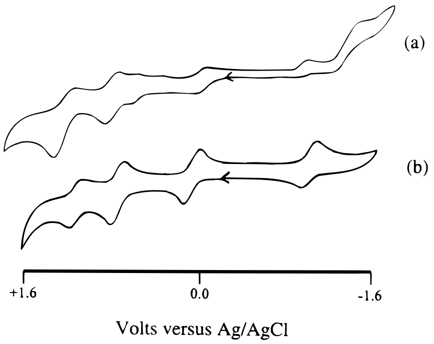

Figure 3. Cyclic voltammograms of (a) [$ReCl_2$(*o*-P2)$_2$][Re_2Cl_6(*o*-P2)] (**1**·**2**) in 0.1 M TBABF$_4$/CH_2Cl_2 and (b) [$ReCl_2$(*o*-P2)$_2$][BF_4] (**1**·[BF_4]) in 0.2 M TBABF$_4$/CH_2Cl_2 at a Pt disk electrode vs Ag/AgCl.

Table 4. Summary of Bond Distances (Å) and Angles (deg) for the Anion [Re_2Cl_6(*o*-P2)]$^-$ (**2**) of [$ReCl_2$(*o*-P2)$_2$][Re_2Cl_6(*o*-P2)]·4CH_2Cl_2 (**1**·**2**·4CH_2Cl_2)

Bond Distances

A	B	A−B (Å)	A	B	A−B (Å)
Re(1)	Re(2)	2.2402(9)	Re(1)	P(1)	2.335(5)
Re(1)	P(2)	2.367(5)	Re(1)	Cl(1)	2.380(4)
Re(1)	Cl(2)	2.367(4)	Re(2)	Cl(3)	2.315(4)
Re(2)	Cl(4)	2.325(4)	Re(2)	Cl(5)	2.351(4)
Re(2)	Cl(6)	2.313(5)	P(1)	C(9)	1.84(2)
P(1)	C(1)	1.82(2)	C(1)	C(2)	1.38(2)
C(1)	S(1)	1.75(2)	C(3)	C(4)	1.36(2)
C(4)	S(4)	1.72(2)	C(5)	C(6)	1.32(3)

Bond Angles

A	B	C	A−B−C (deg)	A	B	C	A−B−C (deg)
Re(1)	Re(2)	Cl(4)	110.04(11)	Re(1)	Re(2)	Cl(3)	100.20(12)
Re(2)	Re(1)	Cl(1)	107.2(12)	Re(2)	Re(1)	Cl(2)	111.32(12)
Re(2)	Re(1)	P(1)	97.23(11)	Cl(2)	Re(1)	Cl(1)	83.1(2)
P(2)	Re(1)	Cl(1)	157.0(2)	Cl(3)	Re(2)	Cl(6)	85.9(2)
Cl(3)	Re(2)	Cl(5)	150.9(2)	Re(1)	P(2)	C(2)	105.8(6)
Cl(2)	Re(1)	P(2)	93.1(2)	P(2)	C(2)	C(1)	116.7(12)
C(1)	C(2)	S(2)	115.6(12)	S(2)	C(3)	S(1)	114.3(9)

The anion, **2**, is an unsymmetrical mixed-valence $Re^{II}-Re^{III}$ molecule with four chloride ions residing on Re(2), and two chloride ions along with one chelating *o*-P2 ligand being coordinated to Re(1) in an eclipsed conformation when viewed down the Re−Re axis. The Re−Re distance is 2.2402(9) Å, which, on the basis of the qualitative overlap scheme for the M_2L_8 geometry, represents a bond order of 3.5 ($\sigma^2\pi^4\delta^2\delta^{*1}$ electronic configuration). This is reasonable given that it is a little longer than the Re−Re quadruple bond in [Bu_4N]$_2$-[Re_2Cl_8], which is 2.222(2) Å,[2] but shorter than the metal−metal distance in the triply bonded compound $Re_2Cl_4(dth)_2$ (2.293(2) Å).[18] It should be noted that this distance is much longer than those in the more symmetrical $Re_2^{II,III}$ phosphine cations [$Re_2Cl_4(PMe_3)_4$]$^+$ (2.205(1) Å) and [$Re_2Cl_4(PMe_2Ph)_4$]$^+$ (2.218(1) Å).[20] This may be due to the fact that the orbitals are more contracted in the cations and therefore the metal ions are required to be closer in order to achieve good overlap. The Re−Cl distances on the "formally" Re(III) center range from 2.313(5) to 2.351(4) Å, as compared to the average distance of ∼2.29(2) Å in [Re_2Cl_8]$^{2-}$.[21] The Re−Cl distances to Re(1) areRe(1)−Cl(1) = 2.380(4) Å and Re(1)−Cl(2) = 2.367(4) Å.

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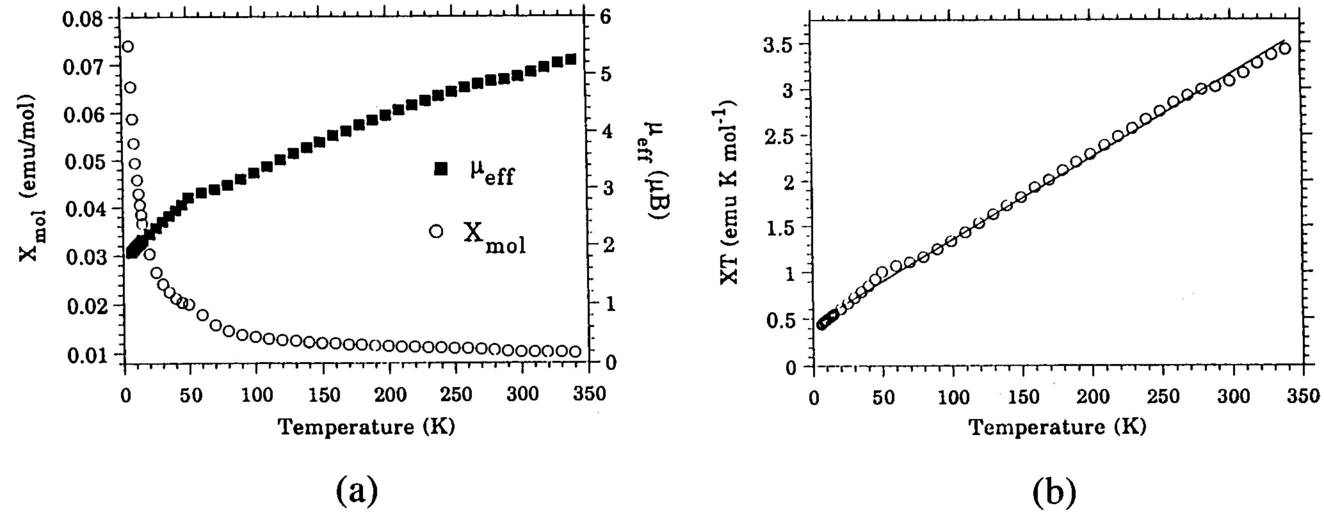

Figure 4. Magnetic data for $[ReCl_2(o\text{-}P2)_2][Re_2Cl_6(o\text{-}P2)]$ (**1·2**): (a) χ_{mol} and μ_{eff} vs T (K) and (b) χT vs T (K) fit to the Curie−Weiss law with a slope of χ_{TIP}.

Table 5. Possible Redox Reactions for the Individual Ions in the Salt $[ReCl_2(o\text{-}P2)_2][Re_2Cl_6(o\text{-}P2)]\cdot 4CH_2Cl_2$ ($\mathbf{1\cdot 2\cdot 4CH_2Cl_2}$)

$[Re^{III}Cl_2(o\text{-}P2)_2]^+$ (**1**)	$[Re_2^{II,III}Cl_6(o\text{-}P2)]^-$ (**2**)
Oxidations (Metal- and Phosphine-Based)	
$Re^{III} \rightarrow Re^{IV}$	$Re_2^{II,III} \rightarrow Re_2^{III,III}$
$Re(o\text{-}P2)_2^0 \rightarrow Re(o\text{-}P2)_2^{2+}$ (2e⁻ total)	$Re_2(o\text{-}P2)^0 \rightarrow Re_2(o\text{-}P2)^+$
$Re(o\text{-}P2)_2^{2+} \rightarrow Re(o\text{-}P2)_2^{4+}$ (2e⁻ total)	$Re_2(o\text{-}P2)^+ \rightarrow Re_2(o\text{-}P2)^{2+}$
Reductions (Metal-Based Only)	
$Re^{III} \rightarrow Re^{II}$	$Re_2^{II,III} \rightarrow Re_2^{II,II}$
$Re^{II} \rightarrow Re^{I}$	

These are longer than corresponding values in $[Re_2Cl_4(PMe_2Ph)_4]^+$ (Re−Cl = 2.33 Å) and $[Re_2Cl_4(PMe_3)_4]^+$ (Re−Cl = 2.34 Å).[20] The only other dinuclear complexes with a single chelating ligand of which we are aware are $[Bu_4N][Re_2Cl_7(dto)]$ (dto = 3,6-dithiaoctane) and $[Bu_4N][Re_2Cl_7(dth)]$;[22] in both of these cases, however, the coordination mode for the bidentate ligand is axial−equatorial rather than equatorial−equatorial.

Cyclic Voltammetric Studies. As Figure 3a shows, the electrochemistry of $[ReCl_2(o\text{-}P2)_2][Re_2Cl_6(o\text{-}P2)]$ in 0.1 M $TBABF_4/CH_2Cl_2$ is quite complicated. This is due to the presence of three redox-active Re ions as well as three TTF phosphine ligands that are each capable of undergoing two one-electron oxidations. The most likely possibilities for redox processes based on the established electrochemistry of the *o*-P2 molecule and similar Re compounds are provided in Table 5. The compound exhibits four TTF phosphine-based oxidation processes and three metal-based reductions, two of which would be expected to be fairly accessible, namely, $Re^{III} \rightarrow Re^{II}$ and $Re_2^{II,III} \rightarrow Re_2^{II,II}$, and one of which would be much less accessible, namely, $Re^{II} \rightarrow Re^{I}$. The two TTF phosphine ligands on the mononuclear cation, **1**, undergo oxidations at the same potential; therefore, the coincidence of these processes leads to a total of 2e⁻ being associated with these couples.

Obviously the only way one can assign the redox processes for the individual ions in **1·2** is to prepare at least one ion separately with an "innocent" counterion. In this vein, we have prepared and measured the electrochemistry for $[Re_2Cl_2(o\text{-}P2)_2][BF_4]$ (Figure 3b). The salt **1**·$[BF_4]$ exhibits couples at $E_{1/2}(ox)_1 = +0.75$ V, $E_{1/2}(ox)_2 = +1.14$ V, and $E_{1/2}(red)_1 = +0.07$ V, with an irreversible reduction process located at $E(p,c)_2 = -1.02$ V. The published data for the related mononuclear Re^{III} salt $[ReCl_2(dppee)_2]Cl$ measured in the same solvent and referenced versus Ag/AgCl include an oxidation from Re^{III} to Re^{IV} at ca. +1.5 V and two reductions corresponding to Re^{III}/Re^{II} and Re^{II}/Re^{I} at −0.2 and ca. −1.4, respectively.[15] On the basis of these results, we conclude that the mononuclear cation **1** is responsible for the oxidations at $E_{1/2}(ox) = +0.67$ V and $E(p,a) = +1.05$, as well as reductions at $E_{1/2}(red) = +0.03$ V and $E(p,c) = -1.12$ V in the CV of **1·2**. These are assigned to the two oxidations of the *o*-P2 ligands and reductions from $Re^{III} \rightarrow Re^{II}$ and $Re^{II} \rightarrow Re^{I}$, respectively. The Re^{III}/Re^{IV} couple for *trans*-$[Re_2Cl_2(dppbe)_2][Cl]$ was reported to occur at +1.51 V,[15] which is beyond the 1.50 V scan range that was used for the current measurements. The remaining features in the cyclic voltammogram of **1·2** are $E_{1/2}(ox)_2 = +0.50$ V, $E_{1/2}(ox)_1 = +0.31$ V, and $E(p,c)_2 = -0.79$ V; these are assigned as two *o*-P2 oxidations and a reduction from $Re_2^{II,III} \rightarrow Re_2^{II,II}$ in the dinuclear anion. The oxidation processes for the coordinated *o*-P2 ligands are shifted to more positive potentials relative to the free ligand ($E_{1/2}(ox)_1 = +0.41$ V, $E_{1/2}(ox)_2 = +0.85$ V), with those associated with the cation occurring at the highest values. This shift to higher potentials is indicative of strong metal−ligand interactions, which leads to an electron-withdrawing effect on the TTF substituents.

Magnetic Properties. (i) $\mathbf{[ReCl_2(o\text{-}P2)_2][Re_2Cl_6(o\text{-}P2)]}$ (1·2). The magnetic susceptibility measurements of **1·2** shown in Figure 4 reveal a Curie paramagnetic behavior for the salt with a Curie constant of $C = 0.395$ and a temperature independent paramagnetism contribution (TIP) ($\chi_{TIP} = 9.64 \times 10^{-3}$ emu/mol).[23] This TIP behavior was previously noted for a similar series of Re^{III} complexes, $ReX_3(PR_2Ph)_2$ (X = Cl, Br; R = Me, Et), although in these cases, χ_{TIP} was somewhat smaller (in the range $1.66-1.36 \times 10^{-3}$ emu/mol).[24] The anion $[Re_2Cl_6(o\text{-}P2)]^-$ is a mixed-valence compound with an overall d^9 configuration and therefore should have an $S = {}^1/_2$ ground state. Given that $C = 0.395$ for $[Re_2Cl_6(o\text{-}P2)]^-$ (**2**) we can estimate μ_{eff} to be ∼1.77 μ_B. This value is in good agreement with moments obtained for similar compounds, such as $[Re_2Cl_4(PMe_2Ph)_4][PF_6]$, which exhibits a moment of ∼1.8 μ_B at

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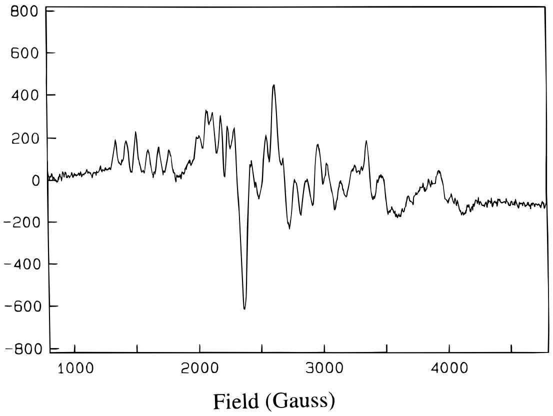

Figure 5. EPR spectrum of $[ReCl_2(o\text{-}P2)_2][Re_2Cl_6(o\text{-}P2)]$ (**1·2**) in a 1:1 toluene/CH_2Cl_2 glass at 4 K.

room temperature,[25] and $[Re_2X_4(dppm)_2][PF_6]$ (X = Cl, Br), which exhibit moments of ~1.5 μ_B.[26]

(ii) $[ReCl_2(o\text{-}P2)_2][BF_4]$ (1·[BF$_4$]). The susceptibility measurements of the separate mononuclear cation, **1**, reveal a TIP ($\chi_{TIP} = 10.7 \times 10^{-3}$ emu/mol) with an extrinsic paramagnetic (Curie) contribution being observed at low temperatures. Assuming that this impurity is an $S = {}^1/_2$ system, it can be estimated that it is 10% of one spin ${}^1/_2$. The value for χ_{TIP} agrees quite well with the previously calculated value for **1·2**.

(iii) $ReCl_2(o\text{-}P2)_2$ (3). The d^5 compound, **3**, contains the same ligand system as **1** and is expected to possess one unpaired electron ($S = {}^1/_2$). The χ versus T data exhibit Curie behavior with a $C = 0.392$ and a $\chi_{TIP} = 9.34 \times 10^{-3}$ emu/mol. This is in agreement with the presence of noninteracting $S = {}^1/_2$ ions ($C = 0.375$ for $S = {}^1/_2$ and $g = 2$). The moment at room temperature is ~4.9 μ_B.

EPR Spectroscopy. The EPR spectrum of $[ReCl_2(o\text{-}P2)_2][Re_2Cl_6(o\text{-}P2)]$ (**1·2**) in a 1:1 CH_2Cl_2/toluene glass at 4 K is shown in Figure 5. A complex pattern is observed that is indicative of hyperfine coupling to the ^{185}Re and ^{187}Re nuclei ($I = {}^5/_2$) and ^{31}P ($I = {}^1/_2$) nuclei. The spectrum is centered at 2833 G ($g = 2.40$). Given the complexity of the spectrum, exact $g_\perp$ and $g_\parallel$ values were not able to be determined. Similar spectra have been reported for 1,3,6-$Re_2Cl_5(PMe_3)_3$ and 1,2,7-$Re_2Cl_5(PMe_3)_3$.[27]

Conclusion

Reaction of the tetrathiafulvalene functionalized tertiary phosphine *o*-P2 with the quadruply bonded dinuclear anion $[Re_2Cl_8]^{2-}$ in alcoholic media results in the isolation of the unusual salt $[ReCl_2(o\text{-}P2)_2][Re_2Cl_6(o\text{-}P2)]$ composed of a mononuclear Re^{III} cation and a mixed-valence $Re_2^{II,III}$ anion. This study was initiated to explore the binding capabilities of *o*-P2, a molecule that structurally resembles ligands such as bis(diphenylphosphino)benzene and bis(diphenylphosphino)ethylene. Accordingly, we anticipated that it would exhibit both α-chelating and β-bridging modes. The latter binding situation has not yet been observed for *o*-P2, however, including in the present study. One could argue that the bridging mode is disfavored due to the rigidity of the ligand,[28] but clearly this is not the case if the bis(diphenylphosphino)benzene (dppbe) ligand can assume both chelating and bridging modes in $Re_2X_4(dppbe)_2$ compounds (X = Cl and Br). The new anion $[\alpha\text{-}Re_2Cl_6(o\text{-}P2)]^-$ (**2**) constitutes the first report of an unbridged M_2L_8 complex containing a single diphosphine ligand and may represent an intermediate in the formation of the, as yet, unknown $\alpha\text{-}Re_2^{II,II}Cl_4(o\text{-}P2)_2$ and $\beta\text{-}Re_2^{II,II}Cl_4(o\text{-}P2)_2$ compounds. Complexes of the type $[\alpha\text{-}Re_2Cl_6(o\text{-}P2)]^-$ with chelating *o*-P2 ligands can be viewed as structural models for extended arrays of metal units bridged by the electronically similar P4 ligand $(Ph_2P)_4TTF$. Further studies of metal−metal-bonded compounds with the *o*-P2 and the P4 ligand are currently underway.

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Supporting Information Available: Tables of crystal data, atomic coordinates, bond lengths and angles, anisotropic displacement parameters, and positional and thermal parameters for **1·2** (18 pages). Ordering information is given on any current masthead page.

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