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An Intramolecular Disproportionation Reaction Leading to the Formation of the Quadruply Bonded Complex $Cl_4ReReCl_2$(dppf) (dppf = 1,1′-Bis(diphenylphosphino)ferrocene). An Example of the Missing 1,3-$Re_2Cl_6(PR_3)_2$ Isomer

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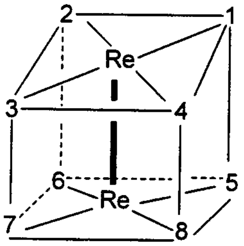
The discovery of the electron-rich Re−Re triple bond as present in complexes of the type $Re_2Cl_4(PR_3)_4$ (where PR_3 represents a *monodentate* tertiary phosphine)[1−3] was followed by studies of their electronic structure[4,5] and the redox chemistry of multiply bonded dirhenium species of the type $Re_2Cl_{6-x}(PR_3)_{2+x}$ ($x = 0$, 1, or 2).[3,5−8] By the mid-1990s the structural chemistry of complexes of these types appeared to be well understood.[3] However, renewed interest in dirhenium compounds that contain various combinations of eight chloride/phosphine ligands, specifically those of the types $Re_2Cl_4(PR_3)_4$, $Re_2Cl_5(PR_3)_3$, and $Re_2Cl_6(PR_3)_2$, which are either monocations, neutral species, or monoanionic species and are derivatives of the $[Re_2]^{6+}$, $[Re_2]^{5+}$, or $[Re_2]^{4+}$ cores, has recently been sparked by some interesting discoveries by Cotton and co-workers,[9−11] who have been able to demonstrate that such compounds can be isolated in different isomeric forms. On the basis of the numbering scheme shown in Chart 1, the following isomers have been isolated and structurally characterized in their cationic, neutral, *and/or* anionic forms: 1,2,7,8- and 1,3,6,8-$[Re_2Cl_4(PR_3)_4]$, 1,2,7- and 1,3,6-$[Re_2Cl_5(PR_3)_3]$, and 1,6- and 1,7-$[Re_2Cl_6(PR_3)_2]$.[2,7,9−11] It was noted that while 1,2- and 1,3- isomers of $Re_2Cl_6(PR_3)_2$ were improbable when PR_3 is a monodentate phosphine, by resorting to *chelating* diphosphines the 1,2-isomer should be isolable.[11] This has been accomplished in the case of salts of the paramagnetic monoanionic species $[Re_2Cl_6(dppp)]^-$ (dppp = $Ph_2P(CH_2)_3PPh_2$)[11] and $[Re_2Cl_6(o\text{-}P2)]^-$ (o-P2 = o-$\{P(C_6H_5)_2\}_2(CH_3)_2$TTF).[12] We now report one of the missing links in this synthetic and structural chemistry, a compound that is of the 1,3-$[Re_2Cl_6(PR_3)_2]$ type, namely, the $[Re_2]^{6+}$ complex Re_2Cl_6(dppf), where dppf = $Fe(C_5H_4PPh_2)_2$.

Chart 1



The reaction of $[n\text{-}Bu_4N]_2Re_2Cl_8$ with $Fe(C_5H_4PPh_2)_2$ in refluxing methanol affords the dark red complex Re_2Cl_6(dppf) (**1**) in essentially quantitative yield.[13] This complex has poor solubility properties in most polar and nonpolar solvents but could be recrystallized from hot 1,2-dichlorobenzene to afford crystals of composition **1**·$4C_6H_4Cl_2$ that were characterized by X-ray crystallography.[14,15] The structure of the dirhenium complex present in **1**·$4C_6H_4Cl_2$ (Figure 1a) shows that the $[Re_2Cl_6P_2]$ unit possesses a 1,3-structure (see Chart 1), the first such example to be isolated. The symmetrical dirhenium unit as originally present in $[Re_2Cl_8]^{2-}$ has undergone an intramolecular disproportionation, such that there are formally Re(IV) and Re(II) centers joined by a Re−Re quadruple bond, in a fashion similar to that by which the dirhenium(III,III) complex *cis*-$Re_2(\mu\text{-}O_2CCH_3)_2Cl_4(H_2O)_2$ reacts with various triarylphosphine ligands to form the Re(IV)−Re(II) alkoxide complexes $(RO)_2Cl_2ReReCl_2(PAr_3)_2$.[16,17] Noteworthy features of this structure are a Re$\overset{4}{-}$Re bond distance of 2.2390(6) Å, which is very similar to such distances in $(RO)_2Cl_2ReReCl_2$-

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(13) Synthesis of **1**: The reaction of $(n\text{-}Bu_4N)_2Re_2Cl_8$ (0.23 g, 0.20 mmol) with $Fe(C_5H_4PPh_2)_2$ (0.12 g, 0.22 mmol) in refluxing methanol for 3 h afforded a dark red solid, which was filtered off while the mixture was hot and washed with 50 mL of hot methanol and then 5 mL of dichloromethane; yield 0.22 g (96%). Anal. Calcd for $C_{34}H_{28}Cl_6FeP_2Re_2$: C, 35.84; H, 2.48. Found: C, 35.16; H, 2.40. The same product was obtained when the reaction was carried out at room temperature and with the use of 1:2 mole proportions of the reagents. IR spectrum (KBr pellet, cm^{-1}): 3058(m), 1585(w), 1572(m-w), 1484(m-s), 1436(s), 1395(m-s), 1317(m), 1190(m), 1170(s), 1164(s), 1094(s), 1062(m-s), 1028(s), 998(m), 892(w), 839(s), 754(s), 700(s), 693(vs). ^1H NMR spectrum (CD_2Cl_2, δ): +8.27 (m, 8H, Ph), +7.52 (m, 12H, Ph), +5.02 (m, 4H, C_5H_4), +3.37(m, 4H, C_5H_4).

(14) The data collection was performed with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) on a Nonius KappaCCD. Lorentz and polarization corrections were applied to the data, and an empirical absorption correction using SCALEPACK was applied. The structure was solved using the structure solution program PATTY in DIRDIF92. The remaining atoms were located in succeeding difference Fourier syntheses. The structure was refined through the use of SHELX-97. Hydrogen atoms were included but constrained to ride on the atom to which they are bonded.

(15) Crystal data for **1**·$4C_6H_4Cl_2$ (223 ± 1 K): space group $C2$ (No. 5) with a = 22.4553(9) Å, b = 11.1536(3) Å, c = 15.8909(6) Å, β = 129.7159(13)°, V = 3061.5(4) Å^3, Z = 2, d_{calcd} = 1.874 g cm^{-3}, μ(Mo Kα) = 4.939 mm^{-1}, 12686 reflections measured (6631 unique). A cutoff $F_o^2 > 2.0\sigma(F_o)^2$ was used for R-factor calculations to give $R(F_o)$ = 0.053, $R_w(F_o^2)$ = 0.134, and GOF = 1.092. The asymmetric unit contains two molecules of 1,2-$C_6H_4Cl_2$, each of which was refined with anisotropic thermal parameters.

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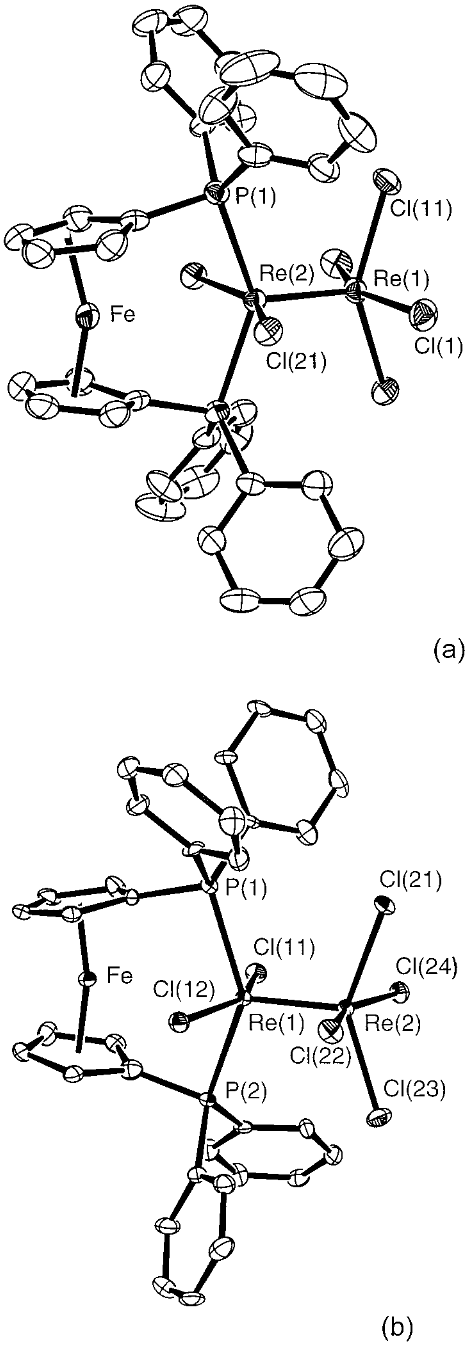

Figure 1. ORTEP representations of the structure of the Re_2Cl_6(dppf) molecule as present in crystals of **1**·$4C_6H_4Cl_2$ (a) and **1** (b). Thermal ellipsoids are drawn at the 50% probability level. The molecule present in crystals of **1**·$4C_6H_4Cl_2$ (a) contains a crystallographic 2-fold rotational axis coincident with the Re−Re···Fe unit. Selected bond distances (Å) and bond angles (deg) are as follows: (a) Re(1)−Re(2) 2.2390(6), Re(1)−Cl(1) 2.322(4), Re(1)−Cl(11) 2.334(4), Re(2)−Cl(21) 2.300(3), Re(2)−P(1) 2.439(3), Cl(1)−Re(1)−Cl(1)′ 154.59(19), Cl(11)−Re(1)−Cl(11)′ 145.4(2), Cl(21)−Re(2)−Cl(21)′ 152.16(18), P(1)−Re(2)−P(1)′ 140.31(18); (b) Re(1)−Re(2) 2.2444(3), Re(2)−Cl(21) 2.295(3), Re(2)−Cl(22) 2.3197(15), Re(2)−Cl(23) 2.324(3), Re(2)−Cl(24) 2.3255(15), Re(1)−Cl(11) 2.3102(15), Re(1)−Cl(12) 2.3148(16), Re(1)−P(1) 2.435(2), Re(1)−P(2) 2.466(2), Cl(22)−Re(2) −Cl(24) 157.92(5), Cl(21)−Re(2)−Cl(23) 141.02(6), Cl(11)−Re(1)−Cl(12) 152.80(6), P(1)−Re(1)−P(2) 141.99(6).

$(PAr_3)_2$ complexes (2.231(1) Å for Ar = Ph[16] and 2.2476(4) for Ar = *p*-MeOPh[17]), an eclipsed rotational geometry about the Re$\overset{4}{-}$Re bond,[18] and the linearity of the Re$\overset{4}{-}$Re···Fe unit, which has a nonbonding Re···Fe distance of 3.585 Å.

The $^{31}P\{^1H\}$ NMR spectrum of **1** (recorded in CD_2Cl_2) consists of a singlet at $\delta = -53.4$, upfield of that for the free phosphine ligand ($\delta = -16.3$ in $CDCl_3$). This upfield shift may reflect a diamagnetic anisotropy effect associated with the Re$\overset{4}{-}$Re bond.[3] The cyclic voltammogram of **1**, recorded in 0.1 M *n*-Bu_4NPF_6−CH_2Cl_2 (Pt-bead electrode, scan rate 200 V s^{-1}, potentials vs Ag/AgCl),[19] shows two reversible processes, one at $E_{1/2} = -0.03$ V, which is associated with the dirhenium core ($[Re_2]^{6+}/[Re_2]^{5+}$), and a phosphinoferrocene-centered process at $E_{1/2} = +1.12$ V, which has been observed in other complexes of this ligand.[20] The free dppf ligand shows this process at $E_{1/2} = +0.69$ V vs Ag/AgCl under our experimental conditions. The dirhenium-based reduction at $E_{1/2} = -0.03$ V can be accessed by the use of $(\eta^5\text{-}C_5H_5)_2Co$ to produce the yellow brown salt $[(\eta^5\text{-}C_5H_5)_2Co][Re_2Cl_6(\text{dppf})]$, which has a CV identical to that of **1**, with the exception of an additional reversible one-electron process at $E_{1/2} = -0.86$ V vs Ag/AgCl due to $[(\eta^5\text{-}C_5H_5)_2Co]^+/(\eta^5\text{-}C_5H_5)_2Co$. The currents associated with the three one-electron processes in the CV of this salt were essentially identical. The reoxidation of the cobaltocenium salt of [**1**]$^-$ to **1** is readily accomplished by the use of $[(\eta^5\text{-}C_5H_5)_2Fe]PF_6$ as the oxidant.[21]

When a suspension of **1** is reacted with PPh_3 in refluxing methanol for 3 days, it converts to a green solid,[22] which, when recrystallized from CH_2Cl_2/diethyl ether, afforded red crystals of solvent-free **1**, which were shown by X-ray crystallography to have a structure (Re−Re and Re···Fe distances of 2.2444(3) and 3.539 Å, respectively) identical to that for the dirhenium unit that is present in crystals of **1**·$4C_6H_4Cl_2$ (Figure 1b).[23] Further characterization of the nature of the unstable green product obtained from the reaction of **1** with PPh_3 is in progress, along with studies of the reactivity of **1** toward reagents such as NaOEt, which are known to substitute Re−Cl bonds in dirhenium(III) complexes,[17] and with CO and RNC which can cleave multiply bonded dirhenium complexes that are not stabilized by *bridging* diphosphine ligands.[3]

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Supporting Information Available: X-ray crystallographic files in CIF format for **1**·$4C_6H_4Cl_2$ and **1**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(18) The torsional angles Cl(1)−Re(1)−Re(2)−Cl(21) and Cl(11)−Re(1)−Re(2)−P(1) are 0.77(17)° and 1.17(17)°, respectively.

(19) Under our experimental conditions $E_{1/2} = +0.47$ V for the $[(C_5H_5)_2Fe]^+/(C_5H_5)_2Fe$ couple.

(20) See, for example: (a) Gimeno, M. C.; Laguna, A.; Sarroca, C. Jones, P. G. *Inorg. Chem.* **1993**, *32*, 5927. (b) Tanase, T.; Matsuo, J.; Onaka, T.; Begum, R. A.; Hamaguchi, M.; Yano, S.; Yamamoto, Y. *J. Organomet. Chem.* **1999**, *592*, 103.

(21) Synthesis of $[(\eta^5\text{-}C_5H_5)_2Co][Re_2Cl_6(\text{dppf})]$ ([**1**]$^-$): A suspension of **1** (0.060 g, 0.05 mmol) in 20 mL of dichloromethane was treated with an excess of cobaltocene (0.040 g, 0.21 mmol) and the mixture stirred at room temperature for 3 h. The solvent was removed under a vacuum and the residue washed with 20 mL of acetone and 10 mL of dichloromethane and then dried; yield 0.065 g (94%). Anal. Calcd for $C_{44}H_{38}Cl_6CoFeP_2Re_2$: C, 39.78; H, 2.88. Found: C, 38.51; H, 2.76. This complex was readily reoxidized to **1** upon its reaction with an excess of $[(\eta^5\text{-}C_5H_5)_2Fe]PF_6$ (1:3 mole proportions) in dichloromethane; yield 93%.

(22) This product, which is insoluble in the reaction solvent, has electrochemical and spectroscopic properties quite different from those of **1**. The ^1H NMR spectrum (recorded in CD_2Cl_2) shows broad resonances, while the $^{31}P\{^1H\}$ spectrum has no resonances attributable to a metal-containing complex. The CV (recorded in 0.1 M *n*-Bu_4NPF_6−CH_2Cl_2) shows couples at $E_{1/2} = +0.68$ and -0.50 V vs Ag/AgCl. This compound, which converts to **1** upon recrystallization from CH_2Cl_2/Et_2O, appears to be an unstable paramagnetic adduct.

(23) Crystal data for **1** (150 ± 1 K): space group $Pna2_1$ (No. 33) with $a = 16.3808(3)$ Å, $b = 15.1447(3)$ Å, $c = 13.9479(3)$ Å, $V = 3460.2(2)$ Å^3, $Z = 4$, $d_{\text{calcd}} = 2.187$ g cm^{-1}, μ(Mo Kα) = 8.076 mm^{-1}, 19831 reflections measured (7811 unique). A cutoff $F_o^2 > 2.0\sigma(F_o)^2$ was used for R-factor calculations to give $R(F_o) = 0.036$, $R_w(F_o^2) = 0.081$, and GOF = 1.037.