The Monocation and Monoanion of $Re_2(\mu\text{-Cl})_2(\mu\text{-dppm})_2Cl_4$ (dppm = $Ph_2PCH_2PPh_2$). An Unusual Pair of Complexes possessing Metal–Metal Bond Orders of 1.5 that differ in Electronic Configuration

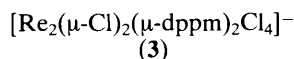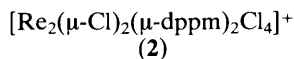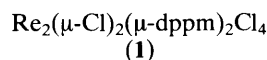## Kim R. Dunbar, Douglas Powell, and Richard A. Walton*

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The one-electron oxidation and one-electron reduction of $Re_2(\mu\text{-Cl})_2(\mu\text{-dppm})_2Cl_4$ (dppm = $Ph_2PCH_2PPh_2$) can be accomplished using $NOPF_6$ and cobaltocene as the oxidant and reductant, respectively, to give paramagnetic ions that possess metal–metal bond orders of 1.5.

Edge-shared bioctahedral structures are commonly encountered in transition metal chemistry,[1] *e.g.* di-μ-halogeno bridged compounds of stoicheiometry $M_2X_6(PR_3)_4$ (X = halide; PR_3 = phosphine donor), some of which possess metal–metal multiple bonds.[2,3] We have recently identified the complex (1) (dppm = $Ph_2PCH_2PPh_2$), and some closely allied derivatives, as being of this structural type and as possessing a new type of Re–Re double bond.[4] A study of the electrochemical properties of (1) has demonstrated the existence of an unexpectedly rich redox chemistry. These findings have led us to isolate the monocation and monoanion of (1), species that possess hitherto unknown types of

metal–metal bonds of order 1.5. Our results hint at the existence of a comparable chemistry for other halide-bridged metal–metal bonded compounds of this type.

$$Re_2(\mu\text{-}Cl)_2(\mu\text{-}dppm)_2Cl_4$$
$$(\mathbf{1})$$

$$[Re_2(\mu\text{-}Cl)_2(\mu\text{-}dppm)_2Cl_4]^+$$
$$(\mathbf{2})$$

$$[Re_2(\mu\text{-}Cl)_2(\mu\text{-}dppm)_2Cl_4]^-$$
$$(\mathbf{3})$$

Cyclic voltammetric measurements on solutions of (**1**) in 0.2 M $Bu^n_4NPF_6$–CH_2Cl_2 show the presence of four (presumably metal-based) couples in the potential range +1.8 to −1.8 V. Those at $E_{1/2}$ +1.63 and +0.81 V vs. Ag/AgCl correspond to one-electron oxidations and those at $E_{1/2}$ −0.54 and −1.41 V vs. Ag/AgCl to one-electron reductions. This behaviour appears to be unprecedented for halide complexes of this structure type which possess multiple metal–metal bonds. Chemical oxidations and reductions have been used to prepare salts of the monocation (**2**) and the monoanion (**3**).

The addition of one equivalent of $NOPF_6$ or $NOBF_4$ to a suspension of the red–purple complex (**1**) in CH_2Cl_2 or MeCN results in the production of a deep blue–purple solution of the cation (**2**) with concomitant loss of NO(g). The product may be precipitated as its PF_6^- or BF_4^- salt in ca. 90% yield by the addition of diethyl ether to the reaction solution. The anionic species (**3**) is readily prepared by the addition of an acetone solution of cobaltocene to an equimolar quantity of (**1**) suspended in this same solvent. The use of cobaltocene as a reducing agent has proved effective in other multiply-bonded dimetal systems.[5,6] The reaction proceeds over a period of 0.5 h, by which time the light green product [(η-$C_5H_5)_2Co][Re_2Cl_6(dppm)_2$] is fully precipitated in essentially quantitative yield.†

The paramagnetic salts of (**2**) and (**3**) possess electrochemical properties which show them to be derivatives of the Re_2^{7+} and Re_2^{5+} cores, respectively, and to have a close structural relationship to the parent complex (**1**).‡ The couples at +0.81 and −0.54 V approached electrochemical reversibility,[7] and the four couples were found to consist of one oxidation and three reductions in the case of (**2**), and three oxidations and one reduction for (**3**).§ An interesting spectroscopic observation concerns the low frequency Nujol mull i.r. spectra of these species. The low frequency spectra (below 400 cm⁻¹) are very similar, with the ν(Re–Cl) modes of (**1**) at 355m, 312s, and 282m cm⁻¹ (ref. 4) all undergoing a small increase in frequency to 360, 318, and 288 cm⁻¹ in the case of (**2**) (PF_6^- salt), and a decrease to 335, 290, and 266 cm⁻¹ in (**3**).

The structural identity of (**2**) has been proven by single crystal X-ray studies. Attempts to grow crystals of [$Re_2Cl_6(dppm)_2$]PF_6 from CH_2Cl_2–ethyl acetate resulted in

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† All reactions were performed under anaerobic conditions and the products, especially (**3**), were stored under an Ar or N_2 atmosphere.

‡ Microanalytical data and conductivity measurements in MeCN (Λ_m ca. 120 ohm⁻¹ cm² mol⁻¹) are fully in accord with these formulations. Salts containing the ions (**2**) and (**3**) are paramagnetic as demonstrated by magnetic susceptibility and low temperature (−170 to −180 °C) e.s.r. spectral measurements, e.g., $\mu_{eff.}$ = 1.82 μ_B for an acetonitrile solution of [$Re_2Cl_6(dppm)_2$]PF_6 as determined by the Evan's method. Full details will be published in due course.

§ In the case of the cobaltocenium salt of (**3**), an additional couple at $E_{1/2}$ −0.86 V vs. Ag/AgCl is due to (η-$C_5H_5)_2Co^+$/(η-$C_5H_5)_2Co$.
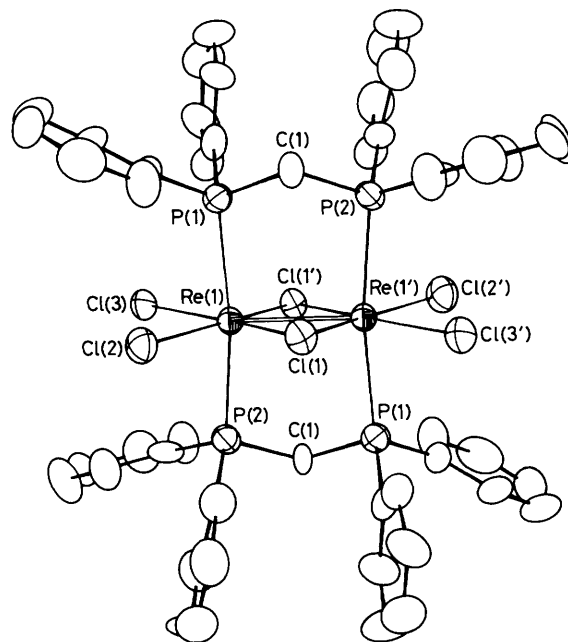

Figure 1. The molecular structure of the cation (**2**). Some important distances (Å) and angles (°) are: Re(1)–Re(1′) 2.6823(6), Re(1)–Cl(1) 2.349(3), Re(1′)–Cl(1) 2.363(3), Re(1)–Cl(2) 2.360(3), Re(1)–Cl(3) 2.353(3), Re(1)–P(1) 2.524(3), Re(1′)–P(2) 2.523(3), P(1)–C(1) 1.84(2), P(2)–C(1) 1.84(1), Re(1′)–Re(1)–Cl(1) 55.52(7), Re(1)–Re(1′)–Cl(1) 55.07(7), Re(1′)–Re(1)–Cl(2) 137.81(8), Re(1′)–Re(1)–Cl(3) 140.04(8), Re(1′)–Re(1)–P(1) 94.13(7), Re(1′)–Re(1)–P(2) 93.68(8), Cl(1)–Re(1)–Cl(1′) 110.6(1), Cl(1)–Re(1)–Cl(2) 82.9(2), Cl(1)–Re(1)–Cl(3) 164.4(2), Cl(2)–Re(1)–Cl(3) 82.1(1), P(1)–Re(1)–P(2) 171.0(1), Re(1)–Cl(1)–Re(1′) 69.40(8).

the very rapid hydrolysis (due to the presence of adventitious water) of the PF_6^- anion to give [$Re_2Cl_6(dppm)_2$]H_2PO_4·H_3PO_4·$4H_2O$ [i.r. (Nujol) ν(P–O) 1055s cm⁻¹]. There is precedent for such a hydrolysis,[8] and for the existence of H_3PO_4 'solvates' of $H_2PO_4^-$ salts.[9,10] Spectroscopic characterizations and electrochemical measurements confirmed that the cation (**2**) had remained unchanged during the hydrolysis. The molecular structure of the cation (**2**) is shown in Figure 1.¶ The phosphato groups in the salt are disordered; accordingly, it has not proved possible to distinguish between what is formally $H_2PO_4^-$ and H_3PO_4, although from the O · · · O distances they are obviously hydrogen-bonded one to the other.

Table 1. Examples of $M_2(\mu\text{-L})_2L_8$ complexes that contain metal–metal bonds of order 1.5.

Complex	Electronic configuration[a]	Metal core
$[Re_2Cl_6(dppm)_2]^+$	$\sigma^2\pi^2\delta^{*2}\delta^1$	Re_2^{7+}
$[Re_2Cl_6(dppm)_2]^-$	$\sigma^2\pi^2\delta^{*2}\delta^2\pi^{*1}$	Re_2^{5+}
$[W_2Cl_4(\mu\text{-OEt})_2(hp)_2]^-$ [b]	$\sigma^2\pi^2\delta^{*1}$	W_2^{7+}
$[W_2Cl_4(\mu\text{-OEt})_2(OEt)_2(py)_2]^+$ [c]	$\sigma^2\pi^1$	W_2^{9+}

[a] Based upon theoretical treatments as described in refs. 12 and 13. [b] hp is the monoanion of 2-hydroxypyridine. [c] py = pyridine.

The most notable structural feature is the Re–Re distance [2.6823(6) Å], which is appreciably longer than that in (**1**) [2.616(1) Å].[4] This is consistent with the reduction in Re–Re bond order from 2 in (**1**) to 1.5 in (**2**), although some of this bond lengthening may well be a consequence of a weakening in the σ and π bonds as a result of the increase in metal charge.[11] This result provides good support for the prediction[12] that the metal–metal bonding in (**1**) and (**2**) can be represented by the $\sigma^2\pi^2\delta^{*2}\delta^2$ and $\sigma^2\pi^2\delta^{*2}\delta^1$ ground state configurations, respectively. On the other hand, a one-electron reduction of (**1**) to paramagnetic (**3**) should lead to a $\sigma^2\pi^2\delta^{*2}\delta^2\pi^{*1}$ ground state configuration, which is also representative of a metal–metal bond order of 1.5. These results, when taken in conjunction with recent data for edge-shared bioctahedral ditungsten complexes that contain the W_2^{9+} and W_2^{7+} cores,[13,14] indicate that for multiply-bonded dimetal complexes of this structure type there exist *four different* electronic configurations that correspond to formal metal–metal bond orders of 1.5 (see Table 1).

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