

Incorporating Multiply Bonded Dirhenium Species [Re₂]ⁿ⁺ (n = 4 or 5) into Assemblies Containing Two or More Such Units

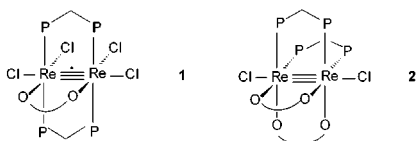
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Received October 5, 2000

The accessibility of paramagnetic dirhenium cores in multiply bonded dirhenium(III,II) complexes, as well as the existence of diamagnetic dirhenium(III,III) and dirhenium(II,II) congeners¹, raises some intriguing possibilities as regards the assembly of mixed oxidation state homometallic extended arrays in rhenium containing systems. We report herein the first designed syntheses of dirhenium complexes that have Re–Re bond orders of 3.5 or 3, contain dicarboxylate bridging linkages, and are examples of “dimers-of-dimers”, hydrogen-bonded chains of “dimers-of-dimers” or cyclic clusters containing three dirhenium pairs. For this purpose, we have used the multiply bonded dirhenium(III, II) and dirhenium(II,II) complexes Re₂(μ-O₂CCH₃)Cl₄(μ-dppm)₂ (1)² and *cis*-Re₂(μ-O₂CCH₃)₂Cl₂(μ-dppm)₂ (2),^{2,3} where dppm =



Ph₂PCH₂PPh₂, which contain substitutionally labile μ-O₂CCH₃ ligands (O–O) in combination with inert, neutral, bridging dppm ligands that stabilize the dirhenium units. This chemistry is the first of its type directed toward incorporating multiply bonded dirhenium complexes into ligand-bridged clusters and polymers and provides some interesting differences from that reported to date on diamagnetic quadruply bonded [Mo₂]⁴⁺ species.^{4–10}

The reaction of **1** with terephthalic acid in refluxing ethanol affords the dark red paramagnetic complex [Re₂Cl₄(μ-dppm)₂]₂(μ-O₂CC₆H₄CO₂) (**3**) in high yield,¹¹ the structure of which is shown in Figure 1.^{12,13} The magnetic properties of **3** and its adipic

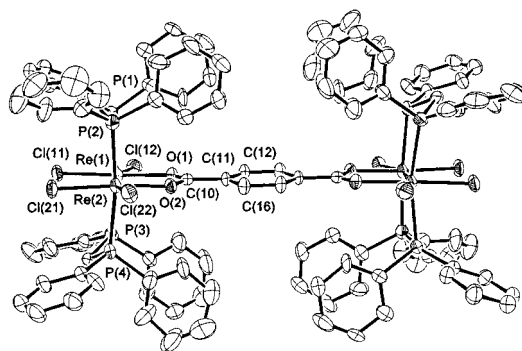


Figure 1. ORTEP representation of the structure of the “dimer of dimers” Re₄ molecule present in **3**·1.5C₂H₄Cl₂. Thermal ellipsoids are drawn at the 40% probability level. Selected bond distances (Å) are: Re(1)–Re(2) 2.2939(6), Re(1)–O(1) 2.085(6), Re(2)–O(2) 2.040(6), Re(1)–Cl(11) 2.362(2), Re(1)–Cl(12) 2.590(3), Re(2)–Cl(21) 2.353(2), Re(2)–Cl(22) 2.595(3), O(1)–C(10) 1.220(12), O(2)–C(10) 1.285(12).

acid analogue [Re₂Cl₄(μ-dppm)₂]₂(μ-O₂C(CH₂)₄CO₂) (**4**), which is obtained from the reaction of **1** with adipic acid using the same procedure as described for **3**, were measured to probe the influence of the organic spacers in transmitting magnetic interactions between the individual paramagnetic [Re₂]⁵⁺ units. The magnetic moments of **3** and **4** at 300 K are 2.45 μ_B and 2.51 μ_B, respectively. While temperature range measurements (down to 2 K) show an antiferromagnetic interaction to be present in **3**, estimated to be –5.8 cm^{–1} (2J) by fitting the experimental data to a dimer model of S = 1/2 (H = –2JS₁S₂), perfect Curie law behavior was observed for **4** down to 2 K.¹⁴

Cyclic voltammetric (CV) and differential pulsed voltammetric (DPV) measurements on solutions of **3** in 0.1 M *n*-Bu₄NPF₆–CH₂Cl₂ reveal clear evidence for electronic coupling between the one-electron oxidation (Re₂⁵⁺ → Re₂⁶⁺) that characterizes each of the component dirhenium units.¹⁵ Two consecutive one-electron

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(11) Synthesis of **3**: A mixture of **1** (104 mg, 0.08 mmol) and terephthalic acid (106 mg, 0.64 mmol) in ethanol was refluxed for 2 days, the red solid filtered off, washed with ethanol (3 × 5 mL) and diethyl ether (3 × 5 mL). The crude product was extracted into 30 mL of 1,2-dichloroethane, the solution evaporated to low volume, and diethyl ether added to precipitate red crystals; yield 86 mg (79%). Anal. Calcd for C₁₁₁H₉₈Cl₁₁O₄P₈Re₄ (i.e., **3**·1.5 C₂H₄Cl₂): C, 46.31; H, 3.43. Found: C, 46.85; H, 3.36. Recrystallization of **3** from a solution in 1,2-dichloroethane/benzene gave X-ray quality crystals.

(12) Crystal data for **3**·1.5C₂H₄Cl₂ (173 ± 1 K): space group P1̄ (No. 2) with a = 13.7382(10) Å, b = 16.3853(14) Å, c = 17.1166(15) Å, α = 103.336(4)°, β = 92.611(6)°, γ = 110.982(6)°, V = 3465.5(11) Å³, Z = 1, d_{calcd} = 1.379 g cm^{–3}, μ(Mo Kα) = 3.874 mm^{–1}, 21 001 reflections measured (11370 unique). A cutoff F_o² > 2σ(F_o²) was used for R-factor calculations to give R(F_o) = 0.057, R_w(F_o²) = 0.149, and GOF = 1.061.

(13) 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 included but constrained to ride on the atom to which they are bonded.

(14) Full details of the magnetic properties of **3** and **4** and related paramagnetic species will be published in due course (Bera, J. K.; Clérac, R.; Walton, R. A. manuscript in preparation).

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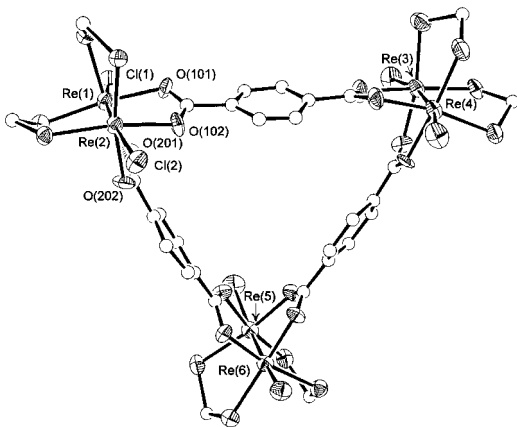


Figure 2. ORTEP representation of the structure of the molecule $\{[\text{Re}_2\text{Cl}_2(\mu\text{-dppm})_2](\mu\text{-O}_2\text{CC}_6\text{H}_4\text{CO}_2)\}_3$ as present in $5 \cdot 2\text{C}_6\text{H}_6 \cdot \text{H}_2\text{O}$ with the phenyl group carbon atoms omitted. Thermal ellipsoids are drawn at the 40% probability level except for the carbon atoms which are circles of arbitrary radius. Selected bond distances (Å) are: Re(1)–Re(2) 2.3192(12), Re(3)–Re(4) 2.3186(13), Re(5)–Re(6) 2.3185(12), Re(1)–Cl(1) 2.514(6), Re(2)–Cl(2) 2.530(5), Re(1)–O(101) 2.114(13), Re(1)–O(201) 2.132(14), Re(2)–O(102) 2.133(13), Re(2)–O(202) 2.159(13).

oxidations are found with $E_{1/2}$ values (vs Ag/AgCl) of $\sim +550$ and $+490$ mV. For the precursor complex **1**, the oxidation is at $+510$ mV (by DPV), while the previously reported CV had given an $E_{1/2}$ value of $+520$ mV.²

The reaction of dicarboxylic acids with **2** has the potential to produce compounds that contain a square arrangement of dirhenium units. However, the X-ray crystal structure of the product that results from the reaction with terephthalic acid, $\{[\text{Re}_2\text{Cl}_2(\mu\text{-dppm})_2](\mu\text{-O}_2\text{CC}_6\text{H}_4\text{CO}_2)\}_3$ (**5**), shows that it contains a triangle of $\{[\text{Re} \equiv \text{Re}]^{4+}\}$ units (Figure 2).^{16,17} The three Re–Re bond distances are essentially identical (2.319 Å) and are similar to the distance of 2.2763(7) Å in the parent complex **2**.³ In accord with this symmetrical structure, the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **5** (in CD_2Cl_2) shows a singlet at $\delta -9.05$ (for **2**, $\delta -10.2$).² While the CV of the dirhenium(II) complex *cis*- $\text{Re}_2(\mu\text{-O}_2\text{CCH}_3)_2\text{Cl}_2(\mu\text{-dppm})_2$ (**2**) shows an accessible one-electron oxidation at $E_{1/2} = +280$ mV versus Ag/AgCl,² that of **5** in 0.1 M *n*-Bu₄NPF₆–CH₂Cl₂ consists of two sequential oxidations with $E_{1/2}$ values (vs Ag/AgCl) of $\sim +400$ mV and $+330$ mV. These are associated with the net overall three-electron oxidation that is possible for the $\{[\text{Re} \equiv \text{Re}]^{4+}\}_3$ core present in **5**. This was confirmed by DPV which gave potentials of $+390$ mV and $+330$ mV for these coupled processes.¹⁵

The use of an excess of *trans*-1,4-cyclohexanedicarboxylic acid in place of terephthalic acid in the reaction with **2** gives $[\text{Re}_2\text{Cl}_2(\mu\text{-dppm})_2](\mu\text{-O}_2\text{CC}_6\text{H}_{10}\text{CO}_2\text{H})_2(\mu\text{-O}_2\text{CC}_6\text{H}_{10}\text{CO}_2)$ (**6**).¹⁸ The crystal structure of **6** (Figure 3)¹⁹ reveals an interesting polymeric structure, in which “dimer-of-dimers” units are linked through intermolecular hydrogen-bonds involving the “free” carboxylic acid groups to generate zigzag chains with the stereochemistry

(15) Cyclic voltammetric measurements were carried out as described previously,² while differential pulsed voltammetry and magnetic data were recorded in the laboratory of Professor Kim R. Dunbar (Texas A & M University).

(16) Synthesis of **5**: The reaction between **2** (104 mg, 0.08 mmol) and terephthalic acid (41 mg, 25 mmol) in refluxing ethanol was carried out as described for **3**¹¹ to afford a red solid that was washed with ethanol and diethyl ether; yield 96 mg (87%). Anal. Calcd for $\text{C}_{174}\text{H}_{144}\text{Cl}_6\text{O}_{12}\text{P}_6\text{Re}_6$: C, 50.62; H, 3.52. Found: C, 49.80; H, 3.81. Recrystallization from 1,2-dichloroethane/benzene gave X-ray quality crystals of composition $5 \cdot 2\text{C}_6\text{H}_6 \cdot \text{H}_2\text{O}$.

(17) Crystal data for $5 \cdot 2\text{C}_6\text{H}_6 \cdot \text{H}_2\text{O}$ (173 ± 1 K): space group $P2_1/c$ (No. 14) with $a = 39.9197(6)$ Å, $b = 22.1491(5)$ Å, $c = 26.6382(8)$ Å, $\beta = 106.6145(8)^\circ$, $V = 22569.8(16)$ Å³, $Z = 4$, $d_{\text{calcd}} = 1.262$ g cm⁻³, $\mu(\text{Mo K}\alpha) = 3.449$ mm⁻¹, 72 223 reflections measured (29 278 unique). A cutoff $F_o^2 > 2\sigma(F_o^2)$ was used for R-factor calculations to give $R(F_o) = 0.091$, $R_w(F_o^2) = 0.243$ and GOF = 0.949.

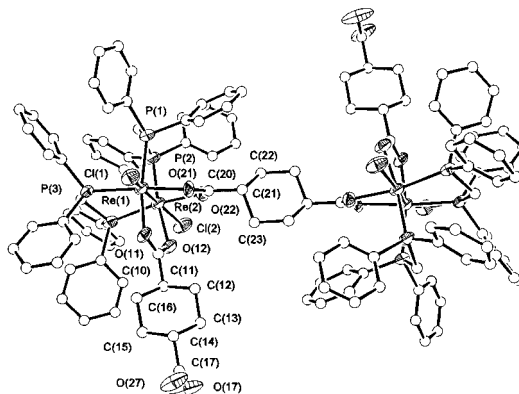


Figure 3. ORTEP representation of the structure of the “dimer of dimers” molecule as present in the crystals of the chain complex $6 \cdot 7\text{C}_2\text{H}_4\text{Cl}_2$. These structural units are linked through hydrogen bonds that are formed between the free carboxylic acid groups (O atoms O(17) and O(27)) of adjacent “dimers of dimers”. Thermal ellipsoids are drawn at the 40% probability level except for the carbon atoms which are circles of arbitrary radius. Selected bond distances (Å) are: Re(1)–Re(2) 2.3172(9), Re(1)–Cl(1) 2.563(4), Re(2)–Cl(2) 2.537(4), Re(1)–O(11) 2.127(10), Re(1)–O(21) 2.126(9).

about each multiply bonded $[\text{Re}_2]$ unit being the same as is present in the structure of **5**.

The potential for the “dimer-of-dimers” unit of **6** to serve as a precursor to mixed metal oxidation state assemblies has been examined. The reaction of the $[n\text{-Bu}_4\text{N}]^+$ salt of **6** with $[\text{Re}_2\text{Cl}_4(\mu\text{-dppm})_2(\text{NCCH}_3)_2]\text{BF}_4$ affords the paramagnetic octanuclear chain complex $[(\mu\text{-dppm})_2\text{Cl}_4\text{Re}_2(\mu\text{-O}_2\text{CC}_6\text{H}_{10}\text{CO}_2)\text{Re}_2\text{Cl}_2(\mu\text{-dppm})_2](\mu\text{-O}_2\text{CC}_6\text{H}_{10}\text{CO}_2)$ (**7**).²⁰ This complex contains a $[\text{Re}_2]^{5+} - [\text{Re}_2]^{4+} - [\text{Re}_2]^{4+} - [\text{Re}_2]^{5+}$ connectivity, the identity of which has been confirmed by a combination of CV and DPV measurements which show behavior characteristic of both $[\text{Re}_2]^{5+}$ and $[\text{Re}_2]^{4+}$ units, present in a 1:1 ratio, with the potentials corresponding closely to these present in complexes **1** and **6**, the latter showing $E_{1/2}(\text{ox})$ values at $+310$ and $+1410$ mV.

The scope and variety of the chemistry that can be developed from the reactions of **1** and **2** with diacids is clearly quite extensive. The ability of these systems to produce mixed oxidation state species that exhibit unusual magnetic properties is of special interest and is under active investigation.

Acknowledgment. One of us (R.A.W.) thanks the John A. Leighty Endowment Fund for support of this work. We are grateful to Dr. Rodolphe Clérac for carrying out the magnetic studies and for helpful discussion.

Supporting Information Available: X-ray crystallographic files in CIF format for $3 \cdot 1.5\text{C}_2\text{H}_4\text{Cl}_2$, $5 \cdot 2\text{C}_6\text{H}_6 \cdot \text{H}_2\text{O}$, and $6 \cdot 7\text{C}_2\text{H}_4\text{Cl}_2$. This material is available free of charge via the Internet at <http://pubs.acs.org>.

JA003589A

(18) Synthesis of **6**: The reaction of **2** (103 mg, 0.08 mmol) with *trans*-1,4-cyclohexanedicarboxylic acid (27 mg, 0.15 mmol) in refluxing ethanol for 2 days produced a red solid that was recrystallized from 1,2-dichloroethane; yield 103 mg (88%). Anal. Calcd for $\text{C}_{132}\text{H}_{136}\text{Cl}_2\text{O}_{12}\text{P}_8\text{Re}_4$ (i.e., $5 \cdot 4\text{C}_2\text{H}_4\text{Cl}_2$): C, 47.57; H, 4.11. Found: C, 47.74; H, 4.12. While the composition of the bulk crystals approached that of $6 \cdot 4\text{C}_2\text{H}_4\text{Cl}_2$, the crystal selected for the X-ray structure determination was found to be of composition $6 \cdot 7\text{C}_2\text{H}_4\text{Cl}_2$.

(19) Crystal data for $6 \cdot 7\text{C}_2\text{H}_4\text{Cl}_2$ (173 ± 1 K): space group $P2_1/n$ (No. 14) with $a = 21.3384(16)$ Å, $b = 16.3098(11)$ Å, $c = 21.3383(11)$ Å, $\beta = 103.585(3)^\circ$, $V = 7218.5(15)$ Å³, $Z = 2$, $d_{\text{calcd}} = 1.669$ g cm⁻³, $\mu(\text{Mo K}\alpha) = 3.868$ mm⁻¹, 23 766 reflections measured (10 183 unique). A cutoff $F_o^2 > 2\sigma(F_o^2) = 0.079$, $R_w(F_o^2) = 0.183$ and GOF = 1.059.

(20) Synthesis of **7**: To a suspension of **6** (0.101 g, 0.03 mmol) in acetonitrile (15 mL) was added *n*-Bu₄NOH (0.1 mL), and the mixture stirred for 30 min. The subsequent addition of an acetonitrile solution of $[\text{Re}_2\text{Cl}_4(\mu\text{-dppm})_2(\text{NCCH}_3)_2]\text{BF}_4$ (0.100 g, 0.07 mmol) resulted in the precipitation of **7**; yield 0.113 g (68%). Anal. Calcd for $\text{C}_{224}\text{H}_{206}\text{Cl}_{12}\text{O}_{12}\text{P}_{16}\text{Re}_8$: C, 48.91; H, 3.71. Found: C, 49.10; H, 3.91. The CV of **7** in 0.1 M *n*-Bu₄NPF₆–CH₂Cl₂ shows the following processes: $E_{1/2}(\text{ox})$ at $+1420$, $+510$ and $+310$ mV, and $E_{p,c}$ at -530 mV (with a product wave at $+100$ mV) vs Ag/AgCl.