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Assemblies of multiply bonded $[Re_2]^{n+}$ cores possessing bond orders of 3 or 3.5 that are linked by dicarboxylate bridges

Jitendra K. Bera,[a] **Rodolphe Clérac,**[b] **Phillip E. Fanwick**[a] **and Richard A. Walton** *[a]

[a] *Department of Chemistry, Purdue University, 1393 Brown Building, West Lafayette, Indiana 47907-1393, USA. E-mail: rawalton@purdue.edu*
[b] *Centre de Recherche Paul Pascal, CNRS UPR 8461, Avenue du Dr. Schweitzer, 33600 Pessac, France*

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An earlier study describing the exchange of the μ-acetato ligands of $Re_2(\mu\text{-}O_2CCH_3)Cl_4(\mu\text{-dppm})_2$ (**1**) and *cis*-$Re_2(\mu\text{-}O_2CCH_3)_2Cl_2(\mu\text{-dppm})_2$ (**2**) by dicarboxylic acids has been expanded to include reactions with the monocarboxylic acid isonicotinic acid, and the dicarboxylic acids adipic acid, 4,4′-biphenyldicarboxylic acid, fumaric acid, *trans*-1,4-cyclohexanedicarboxylic acid and 1,1′-ferrocenedicarboxylic acid. Further examples of complexes that are "dimers-of-dimers" and triangular supramolecular assemblies involving retention of the basic electronic and molecular structures of the dirhenium units present in **1** and **2** have been obtained. In addition, the dirhenium complexes $Re_2(\mu\text{-}O_2CC_6H_4N)Cl_4(\mu\text{-dppm})_2$ (**7**) and *cis*-$Re_2(\mu\text{-}O_2C_6H_{10}CO_2Et)_2Cl_2(\mu\text{-dppm})_2$ (**11**) have been isolated, as well as the trimetallic complex *cis*-$Re_2Cl_2(\mu\text{-dppm})_2[(\mu\text{-}O_2CC_5H_4)_2Fe]$ (**14**) that is formed from the reaction of **2** with $(C_5H_4CO_2H)_2Fe$. The crystal structures of **7**, **11** and **14** are reported.

Introduction

We have shown[1] that the multiply bonded dirhenium(III,II) and dirhenium(II,II) complexes $Re_2(\mu\text{-}O_2CCH_3)Cl_4(\mu\text{-dppm})_2$ (**1**)[2] and *cis*-$Re_2(\mu\text{-}O_2CCH_3)_2Cl_2(\mu\text{-dppm})_2$ (**2**),[2,3] where dppm = $Ph_2PCH_2PPh_2$, which contain labile μ-O_2CCH_3 ligands in combination with substitutionally inert dppm and Cl ligands, react with the dicarboxylic acids terephthalic acid and *trans*-1,4-cyclohexanedicarboxylic acid to afford "dimers-of-dimers", hydrogen-bonded chains of "dimers-of-dimers", and supramolecular triangles that contain three dirhenium pairs. In the present report we examine further the substitutional lability of the acetate groups present in **1** and **2** with the object of expanding the supramolecular chemistry involving the incorporation of dirhenium species into assemblies that contain two or more such units.

Experimental

The dirhenium complexes $Re_2(\mu\text{-}O_2CCH_3)Cl_4(\mu\text{-dppm})_2$ (**1**),[2] *cis*-$Re_2(\mu\text{-}O_2CCH_3)_2Cl_2(\mu\text{-dppm})_2$ (**2**)[2,3] and $Re_2Cl_4(\mu\text{-dppm})_3$ (**3**),[4] and the dicarboxylate-bridged complexes $[Re_2Cl_4(\mu\text{-dppm})_2]_2(\mu\text{-}O_2CC_6H_4CO_2)$ (**4**),[1] [*cis*-$Re_2Cl_2(\mu\text{-dppm})_2(\mu\text{-}O_2CC_6H_4CO_2)]_3$ (**5**)[1] and [*cis*-$Re_2(\mu\text{-}O_2CC_6H_{10}CO_2H)Cl_2(\mu\text{-dppm})_2]_2(\mu\text{-}O_2CC_6H_{10}CO_2)$ (**6**)[1] were prepared by the literature methods. All carboxylic acids and other reagents were obtained from Aldrich Chemical Co., and used as received. Solvents were purchased from commercial sources and were dried and degassed by standard methods and distilled prior to use. All reactions were carried out under an atmosphere of dry dinitrogen.

Routine IR spectra, NMR spectra and cyclic voltammetric measurements were determined as described previously.[5] Differential pulsed voltammetric (DPV) measurements and magnetic data were recorded in the laboratory of Professor Kim R. Dunbar at Texas A & M University. The magnetic susceptibility measurements were obtained with the use of a Quantum Design SQUID magnetometer MPMS-XL and data were collected for complexes **4**, **8**, **9** and **11** at 1000 G on finely divided polycrystalline samples. Data were obtained for **4**, **8** and **9** over the temperature range 1.8 to 300 K and at 300 K for **11**, and were corrected for the sample holder, paramagnetic impurities (S = 1/2, 1% of Curie Law for **4**) and for the experimental diamagnetic contribution calculated from Pascal constants.[6] The electrospray ionization (ESI) mass analyses were recorded by Dr. Karl V. Wood with use of a Finnigan MAT LCQ (Thermoquest Corp. San Jose, CA) mass spectrometer system. Measurements were carried out on CH_2Cl_2/CH_3CN or 1,2-$C_2H_4Cl_2$ solutions. Elemental microanalyses were carried out by Dr. H. D. Lee of the Purdue University Microanalytical Laboratory.

A. Reactions of $Re_2(\mu\text{-}O_2CCH_3)Cl_4(\mu\text{-dppm})_2$ (1)

(i) Synthesis of $Re_2(\mu\text{-}O_2CC_5H_4N)Cl_4(\mu\text{-dppm})_2$ (7). A mixture of **1** (0.111 g, 0.08 mmol) and isonicotinic acid (0.065 g, 0.53 mmol) was refluxed in ethanol for one day. A mixture of $Re_2Cl_4(\mu\text{-dppm})_2$ (**3**) and the carboxylate-exchanged product $Re_2(\mu\text{-}O_2CC_5H_4N)Cl_4(\mu\text{-dppm})_2$ (**7**) was obtained as shown by cyclic voltammetry. The products were separated by hand. Yield of **7**: 0.053 g (47%). Calc. for $C_{56}H_{48}Cl_4NO_2P_4Re_2$: C, 47.87; H, 3.44. Found: C, 47.31; H, 3.47%. MS (ESI): *m/z* 1404 for $[M]^+$ (where [M] represents the parent molecule).

(ii) Synthesis of $[Re_2Cl_4(\mu\text{-dppm})_2]_2(\mu\text{-}O_2C(CH_2)_4CO_2)$ (8). The reaction of **1** (0.107 g, 0.08 mmol) with adipic acid (0.075 g, 0.51 mmol) in refluxing ethanol for 26 h afforded a yellow solid that was filtered off and washed with fresh ethanol (3 × 5 mL) and diethyl ether (3 × 5 mL). The crude product was extracted with hot 1,2-dichloroethane (20 mL), and the extract concentrated and kept at 4 °C to obtain complex **8** as yellow microcrystals; yield 0.077 g (71%). Calc. for $C_{106}H_{96}Cl_8O_4P_8Re_4$: C, 46.97; H, 3.57; Cl, 10.33. Found: C, 45.96; H, 3.56, Cl 10.19%.

(iii) Synthesis of $[Re_2Cl_4(\mu\text{-dppm})_2]_2(\mu\text{-}O_2CC_6H_4C_6H_4CO_2)$ (9). A mixture of **1** (0.103 g, 0.08 mmol) and 4,4′-biphenyldicarboxylic acid (0.151 g, 0.62 mmol) was refluxed in ethanol for 2 days, the insoluble product filtered off and washed with ethanol (2 × 5 mL) and diethyl ether (2 × 5 mL) and then recrystallized from dichloromethane/benzene; yield 0.171 g

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(76%). Calc. for $C_{114}H_{96}Cl_8O_4P_8Re_4$: C, 48.78; H, 3.45; Cl, 10.11. Found: C, 48.01; H, 3.47; Cl, 10.57%.

(iv) Synthesis of $[Re_2Cl_4(\mu\text{-dppm})_2]_2(\mu\text{-}O_2CCH{=}CHCO_2)$ (10). A mixture of **1** (0.111 g, 0.08 mmol) and fumaric acid (0.059 g, 0.51 mmol) was refluxed in ethanol for 8–10 h, the reaction mixture filtered, and the red colored filtrate evaporated to low volume and kept at 4 °C for 12 h. The insoluble product was filtered off and washed with ethanol (2 × 5 mL) and diethyl ether (2 × 5 mL); yield 0.099 g (46%). Cyclic voltammetry showed that **10** was contaminated by small amounts of $Re_2Cl_4(\mu\text{-dppm})_2$ (**3**), the proportion of which increased with increasing reaction time.

(v) Synthesis of *cis*-$Re_2(\mu\text{-}O_2CC_6H_{10}CO_2Et)_2Cl_2(\mu\text{-dppm})_2$ (11). A mixture of **1** (0.119 g, 0.09 mmol) and *trans*-1,4-cyclohexanedicarboxylic acid (0.144 g, 0.84 mmol) was refluxed in ethanol for 3 days. Red crystals of composition **11**·2EtOH were filtered off and washed with fresh ethanol (3 × 5 mL) and diethyl ether (3 × 5 mL); yield: 0.113 g (74%). Calc. for $C_{74}H_{86}Cl_2O_{10}P_4Re_2$ (*i.e.* **11**·2EtOH): C, 52.20; H, 5.09. Found: C, 51.85; H, 5.16%. MS (ESI): *m*/*z* 1575 for $[M - Cl]^+$. ^1H NMR spectrum (δ in CD_2Cl_2): 7.6–6.9 (m, 40H, Ph), 6.40 and 4.95 (m, 4H, CH_2 of dppm), 4.18 (q, 8H, CH_2 of EtOH and $-CO_2Et$), 2.38, 2.10, 1.93 and 1.70–1.43 (m, 20H, C_6H_{10}), 1.34 (t, 12H, CH_3 of EtOH and $-CO_2Et$). $^{31}P\{^1H\}$ NMR spectrum (δ in CD_2Cl_2): −9.32.

B. Reactions of *cis*-$Re_2(\mu\text{-}O_2CCH_3)_2Cl_2(\mu\text{-dppm})_2$ (2)

(i) Synthesis of $[cis\text{-}Re_2Cl_2(\mu\text{-dppm})_2(\mu\text{-}O_2CC_6H_{10}CO_2)]_3$ (12). A mixture of **2** (0.119 g, 0.09 mmol) and *trans*-1,4-cyclohexanedicarboxylic acid (0.016 g, 0.09 mmol) was refluxed in ethanol for 2 days and the yellow product filtered off and washed with ethanol (3 × 5 mL) and diethyl ether (3 × 5 mL); yield 0.113 g (91%). Calc. for $C_{174}H_{162}Cl_6O_{12}P_{12}Re_6$: C, 50.40; H, 3.94. Found: C, 51.06; H, 4.16%. MS (ESI): *m*/*z* 3727 for $[M - Cl - dppm]^+$. ^1H NMR spectrum (δ in CD_2Cl_2): 7.8–6.8 (m, 150H, Ph of dppm), 6.42 and 4.91 (m, 12H, CH_2 of dppm), 2.42–1.43 (m, 30H, C_6H_{10}). $^{31}P\{^1H\}$ NMR spectrum (δ in CD_2Cl_2): −9.87.

(ii) Synthesis of $[cis\text{-}Re_2Cl_2(\mu\text{-dppm})_2(\mu\text{-}O_2C(CH_2)_4CO_2)]_n$ (13). Complex **2** (0.105 g, 0.08 mmol) was reacted with adipic acid (0.015 g, 0.10 mmol) in refluxing ethanol as described in section B(i); yield 0.097 g (90%). Calc. for $C_{56}H_{52}Cl_2O_4P_4Re_2$: C, 49.59; H, 3.86; Cl, 5.23. Found: C, 48.93; H, 3.79; Cl, 5.30%. This product had very poor solubility in common organic solvents.

(iii) Synthesis of *cis*-$Re_2Cl_2(\mu\text{-dppm})_2[(\mu\text{-}O_2CC_5H_4)_2Fe]$ (14). Red crystals of **14** were obtained by the reaction of **2** (0.104 g, 0.08 mmol) with 1,1′-ferrocenedicarboxylic acid (0.033 g, 0.12 mmol) in refluxing ethanol following the procedure described in section B(i); yield 0.112 g (94%). Calc. for $C_{62}H_{52}Cl_2FeO_4P_4Re_2$: C, 50.17; H, 3.53; Cl, 4.78. Found: C, 49.61; H, 3.77; Cl, 4.84%. MS (ESI): *m*/*z* 1484 for $[M]^+$. ^1H NMR spectrum (δ in CD_2Cl_2): 7.8–6.9 (m, 40H, Ph), 6.41 and 5.00 (m, 4H, CH_2 of dppm), 5.41 and 4.59 (m, 8H, C_5H_4). $^{31}P\{^1H\}$ NMR spectrum (δ in CD_2Cl_2): −9.13.

X-Ray crystal structure determinations

Single crystals of composition $Re_2(\mu\text{-}O_2CC_5H_4N)Cl_4(\mu\text{-dppm})_2$ (**7**), *cis*-$Re_2(\mu\text{-}O_2CC_6H_{10}CO_2Et)_2Cl_2(\mu\text{-dppm})_2$·2EtOH (**11**·2EtOH), and *cis*-$Re_2Cl_2(\mu\text{-dppm})_2[(\mu\text{-}O_2CC_5H_4)_2Fe]$·1.43EtOH (**14**·1.43EtOH) were obtained as described in the individual synthetic procedures outlined previously.

The data were collected at 173(±1) K for **7**, **11** and **14**. All measurements were carried out on a Nonius KappaCCD diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). Accurate unit cell parameters and orientation matrices were determined by least-squares refinement of the appropriate number of reflections in the range of $4 < \theta < 27°$. Space groups were determined by use of the program ABSEN.[7] Crystal data and the relevant experimental details on data collections and refinements are given in Table 1. Lorentz and polarization corrections were applied to the data sets.

The structures were solved using the structure solution program PATTY in DIRDIF92.[8] The remaining atoms were located in succeeding difference Fourier syntheses. Hydrogen atoms were placed in calculated positions according to idealized geometries with $U(H) = 1.3\ U_{eq}$ (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[9] was applied in all cases. The final refinements were performed by the use of the program SHELXL-97.[10] All non-hydrogen atoms were refined with anisotropic thermal parameters unless indicated otherwise. Crystallographic drawings were done using the program ORTEP.[11]

The structure solutions and refinements of all three compounds proceeded without significant problem. The crystals of **11** and **14** contained solvent molecules, the non-hydrogen atoms of which were refined with anisotropic thermal parameters in the case of **11** but isotropically for **14**. The two independent molecules of lattice ethanol present in the crystals of **14** refined to occupancies of 0.730 and 0.703.

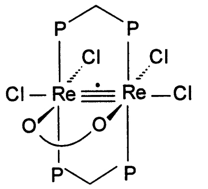
CCDC reference numbers 178305–178307.

See http://www.rsc.org/suppdata/dt/b2/b200561c/ for crystallographic data in CIF or other electronic format.

Results and discussion

(a) Reactions of $Re_2(\mu\text{-}O_2CCH_3)Cl_4(\mu\text{-dppm})_2$ (1) with carboxylic acids

The lability of the acetate ligand of compound **1** is shown by its reaction with isonicotinic acid in refluxing ethanol to afford the dirhenium(III,II) complex $Re_2(\mu\text{-}O_2CC_5H_4N)Cl_4(\mu\text{-dppm})_2$ (**7**). This product was contaminated with a small amount of $Re_2Cl_4(\mu\text{-dppm})_2$ (**3**) which is formed from the competing thermal reduction of **1** in refluxing ethanol.[2]



1

The crystal structure of **7** (Fig. 1) showed it to be similar to that of **1**.[2] The Re–Re bond distance of 2.3055(3)Å in **7** is essentially the same as that of 2.2998(4)Å reported for **1**.[2] The identity of **7** is further supported by its ESI mass spectrum which shows the parent molecule ion at *m*/*z* = 1404 with the correct isotopic splitting pattern. Cyclic voltammetric (CV) measurements on solutions of **7** in 0.1 M n-Bu_4NPF_6(TBAH)–CH_2Cl_2 showed a reversible process at $E_{1/2}$ = +0.57 V *vs.* Ag/AgCl, with ΔE_p = 60 mV, that corresponds to a one-electron oxidation of the bulk complex, and an irreversible reduction at $E_{p,c}$ = −0.53 V *vs.* Ag/AgCl; additional irreversible processes at $E_{p,a}$ = +1.65 V and $E_{p,c}$ = −1.60 V are attributable to the isonicotinate ligand. The CV of **7** resembles that of **1** which has $E_{1/2}$(ox) = +0.52V and $E_{p,c}$ = −0.60 V.[2]

The substitutional lability of the acetate ligand of **1** towards dicarboxylic acids was first established in its reaction with terephthalic acid that produces the centrosymmetric μ-terephthalate complex $[(\mu\text{-dppm})_2Cl_4Re_2](\mu\text{-}O_2CC_6H_4CO_2)[Re_2Cl_4(\mu\text{-dppm})_2]$ (**4**).[1] In the present study we show that adipic acid, 4,4′-biphenyldicarboxylic acid and fumaric acid form the yellow–red colored complexes $[Re_2Cl_4(\mu\text{-dppm})_2]_2(\mu\text{-}O_2C(CH_2)_4CO_2)$ (**8**), $[Re_2Cl_4(\mu\text{-dppm})_2]_2(\mu\text{-}O_2CC_6H_4C_6H_4CO_2)$

Table 1 Crystallographic data for the dirhenium complexes of composition $Re_2(\mu\text{-}O_2CC_5H_4N)Cl_4(\mu\text{-dppm})_2$ (**7**), *cis*-$Re_2(\mu\text{-}O_2CC_6H_{10}CO_2Et)_2Cl_2(\mu\text{-dppm})_2\cdot 2EtOH$ (**11**·2EtOH), and *cis*-$Re_2Cl_2(\mu\text{-dppm})_2[(\mu\text{-}O_2CC_5H_4)_2Fe]\cdot 1.43EtOH$ (**14**·1.43EtOH)

	7	11	14
Formula	$C_{56}H_{48}Cl_4NO_2P_4Re_2$	$C_{74}H_{86}Cl_2O_{10}P_4Re_2$	$C_{64.87}H_{60.60}Cl_2FeO_{5.43}P_4Re_2$
Formula weight	1405.12	1702.71	1550.17
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/n$ (No. 14)	$C2/c$ (No. 15)	$P2_1/c$ (No. 14)
a/Å	17.8053(5)	22.1984(10)	12.4009(2)
b/Å	14.4632(2)	12.4860(4)	17.7630(3)
c/Å	21.1278(5)	25.8565(12)	27.8096(6)
α/°	90	90	90
β/°	105.9273(9)	99.5236(18)	96.7556(12)
γ/°	90	90	90
Z	4	4	4
V/Å^3	5232.0(4)	7067.9(9)	6127.4(3)
D_c/g cm^{-3}	1.784	1.600	1.680
μ(Mo-K$_\alpha$)/mm^{-1}	5.056	3.690	4.468
Reflections			
collected	42362	22575	54835
independent	12282	14030	15590
observed [$I > 2\sigma(I)$]	9566	4885	10599
No. of variables	622	418	705
R_{int}	0.052	0.080	0.066
$R(F_o)^a$	0.036	0.046	0.046
$R_w(F_o^2)^b$	0.080	0.082	0.098
GOF	1.022	0.936	1.021

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

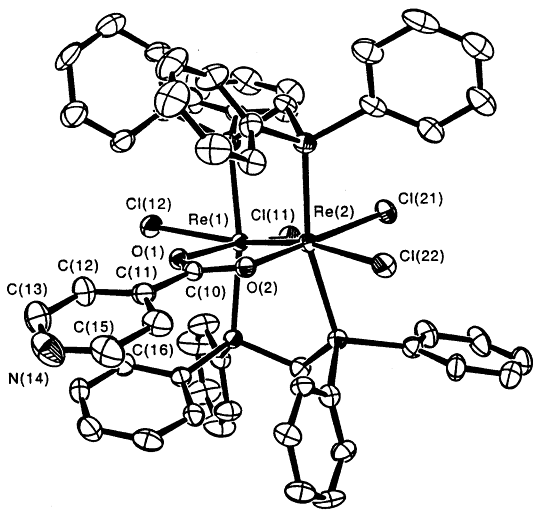


Fig. 1 ORTEP[11] representation of the structure of the dirhenium complex $Re_2(\mu\text{-}O_2CC_5H_4N)Cl_4(\mu\text{-dppm})_2$ (**7**). Thermal ellipsoids are drawn at the 40% probability level. The P atoms are unlabeled; P(1) and P(3) are bound to Re(1), and P(2) and P(4) to Re(2). Selected bond distances (Å) and bond angles (°) are as follows: Re(1)–Re(2) 2.3055(3), Re(1)–O(1) 2.071(3), Re(1)–Cl(11) 2.3511(12), Re(1)–Cl(12) 2.5829(12), Re(2)–O(2) 2.092(3), Re(2)–Cl(21) 2.3653(11), Re(2)–Cl(22) 2.5743(12), O(1)–C(10) 1.268(6), O(2)–C(10) 1.275(5); O(1)–Re(1)–Re(2) 88.55(9), O(1)–Re(1)–Cl(11) 165.81(9), Re(2)–Re(1)–Cl(11) 103.03(3), O(1)–Re(1)–Cl(12) 79.71(9), Re(2)–Re(1)–Cl(12) 163.47(3), Cl(11)–Re(1)–Cl(12) 90.43(4), O(1)–C(10)–O(2) 122.0(4). The torsional angles Cl(11)–Re(1)–Re(2)–Cl(21), P(1)–Re(1)–Re(2)–P(2), P(3)–Re(1)–Re(2)–P(4) and O(1)–Re(1)–Re(2)–O(2) are 16.04(4)°, 11.55(4)°, 13.09(4)° and 4.79(12)°, respectively.

(**9**) and $[Re_2Cl_4(\mu\text{-dppm})_2]_2(\mu\text{-}O_2CCH{=}CHCO_2)$ (**10**) that are probable close structural analogues of **4**.[1]

In order to probe the influence of the organic spacers in transmitting magnetic interactions between the individual paramagnetic dirhenium units in complexes of the type $[(\mu\text{-dppm})_2Cl_4Re_2](\mu\text{-}O_2CRCO_2)[Re_2Cl_4(\mu\text{-dppm})_2]$, we carried out magnetic susceptibility measurements on **4**, **8** and **9** over the temperature range 2 to 300 K. These complexes have magnetic moments at 300 K of 2.45 μ_B, 2.51 μ_B and 2.49 μ_B, respectively, that correspond to g values slightly higher than 2. The effective moment is constant down to 2 K in the case of both **8** and **9**, and perfect Curie Law behavior is observed. This result is in accord with long non-conjugated organic linkers in these two complexes that do not facilitate magnetic interactions between the dirhenium units. In contrast, temperature range measurements (down to 2 K) show an antiferromagnetic interaction to be present in **4**, estimated to be −5.8 cm^{-1} (2J) by fitting the experimental data to a dimer model of $S = 1/2$ ($\mathcal{H} = -2JS_1\cdot S_2$).[1]

The differences in magnetic behavior between **4**, and **8** and **9**, are paralleled by differences in the CV and differential pulsed voltammetric (DPV) properties of solutions of **4** and **9** in 0.1 M TBAH–CH_2Cl_2. CV and DPV measurements on **4** show evidence for electronic coupling between the one-electron oxidation $[Re_2]^{5+} \longrightarrow [Re_2]^{6+}$ that characterizes each of the component dirhenium units. These two reversible one-electron processes have $E_{1/2}$ values of +0.59 V and +0.49 V *vs.* Ag/AgCl, while there are additional coupled reductions at $E_{p,c} \simeq -0.45$ V and −0.53 V *vs.* Ag/AgCl.[1] It is convenient to represent the magnitude of the electronic coupling in a molecule such as **4** in terms of a comproportionation constant K_c for the equilibrium represented in eqn. (1).[12–15]

$$[Re_2\cdots Re_2] + [Re_2\cdots Re_2]^{2+} \overset{K_c}{\rightleftharpoons} 2[Re_2\cdots Re_2]^{+} \qquad (1)$$
$$\text{where } K_c = \exp(\Delta E_{1/2}/25.69)$$

The greater the degree of delocalization in the monocation $[Re_2\text{---}Re_2]^+$, the larger is the value of $\Delta E_{1/2}$ and hence the larger is K_c. In the case of **4**, $\Delta E_{1/2}$ = 100 mV and thus K_c = 49, a value that is characteristic of a weakly coupled valence trapped system, for which a value for K_c of less than 100 is expected. This result accords with the earlier conclusion of Chisholm and co-workers[12] that terephthalate is a poor linker ligand for electronic coupling. While the poor solubility properties of **8** prevented us from obtaining satisfactory electrochemical data for this complex, DPV measurements on its 4,4′-biphenyldicarboxylate bridged analogue (**9**) showed coupled processes $E_{1/2}$(ox) = +0.48 V and +0.44 V *vs.* Ag/AgCl, and $E_{p,c}$ = −0.50 V and −0.55 V *vs.* Ag/AgCl. For the coupled oxidations $\Delta E_{1/2}$ = 40 mV, a value that implies the absence of any significant coupling between the two dirhenium units.

Although **1** reacts with fumaric acid to give what we believe is the expected "dimers-of-dimers" product $[Re_2Cl_4(\mu\text{-dppm})_2]_2(\mu\text{-}O_2CCH{=}CHCO_2)$ (**10**), the analogous reaction with acetylenedicarboxylic acid gave the paramagnetic μ-η^2-acetylene complex Re_2Cl_5(μ-HCCH)(μ-dppm)$_2$, resulting from the decarboxylation of the acetylenedicarboxylic acid. Details of the latter reaction have been communicated previously.[16] The identity of paramagnetic **10** was based primarily upon its CV and DPV properties since it was difficult to isolate it free of small amounts of diamagnetic **3**, which is formed by the competitive reductive decarboxylation of **1**. The electrochemical properties of **10** resemble those of **4** that were discussed previously; there are two coupled one-electron processes at $E_{1/2}$ = +0.56 V and +0.43 V *vs.* Ag/AgCl, as well as irreversible reductions at $E_{p,c}$ = −0.50 V and −0.59 V *vs.* Ag/AgCl. Since the magnitude of $\Delta E_{1/2}$ is greater for **10** than for **4** (130 mV *vs.* 100 mV), the comproportionation constant K_c is larger (158 vs. 49), thereby signifying the presence of a stronger electronic coupling in **10**. The absence of resonances in the ^{31}P NMR spectrum of **10**, and the presence of broad poorly defined resonances in its ^{1}H NMR spectrum, accord with the paramagnetism of this complex.

Attempts to prepare other examples of "dimers-of-dimers" from the reactions of **1** with tetrafluoroterephthalic acid and 1,1′-ferrocenedicarboxylic acid afforded the known dirhenium(II) complex **3**. It is clear that in these instances, reductive decarboxylation of **1** proceeds more rapidly than does carboxylate ligand exchange. The analogous reaction of **1** with *trans*-1,4-cyclohexanedicarboxylic acid unexpectedly gave the dirhenium(II) complex *cis*-$Re_2(\mu\text{-}O_2CC_6H_{10}CO_2Et)_2Cl_2$(μ-dppm)$_2$ (**11**) rather than $[Re_2Cl_4(\mu\text{-dppm})_2]_2(\mu\text{-}O_2CC_6H_{10}CO_2)$. With the use of shorter reaction times we found no evidence for the intermediacy of the latter coupled product. The formation of **11** involves three processes; reduction of the $[Re_2]^{5+}$ core of **1** to $[Re_2]^{4+}$, substitution of the acetate group and two Re–Cl bonds of **1**, and esterification of one of the acid groups of *trans*-1,4-cyclohexanedicarboxylic acid by the ethanol solvent. However, this reaction does not proceed *via* **3**, since the latter complex does not react with *trans*-1,4-cyclohexanedicarboxylic acid in refluxing ethanol.

The structure of **11** was established by X-ray crystallography (Fig. 2) and shown to be closely related to that of *cis*-$Re_2(\mu\text{-}O_2CCH_3)_2Cl_2$(μ-dppm)$_2$.[2] The Re–Re triple bond distance of 2.3120(5) Å is similar to those determined for the analogous acetate complex (2.3151(7) Å)[2] and for *cis*-$Re_2(\mu\text{-}O_2CCH_3)_2Cl_2$(μ-dppa)$_2$, where dppa = $Ph_2PNHPPh_2$ (2.3067(5) Å).[17] The CV of **11** (recorded in 0.1 M TBAH–CH_2Cl_2) shows two reversible one-electron oxidations at $E_{1/2}$ = +0.32 V and +1.39 V *vs.* Ag/AgCl, behavior which resembles that of *cis*-$Re_2(\mu\text{-}O_2CCH_3)_2Cl_2$(μ-dppm)$_2$.[2]

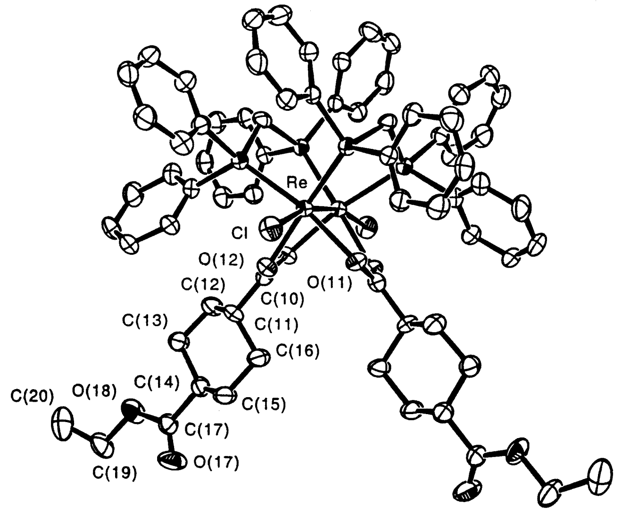
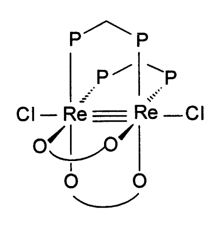


Fig. 2 ORTEP[11] representation of the structure of the dirhenium complex *cis*-$Re_2(\mu\text{-}O_2CC_6H_{10}CO_2Et)_2Cl_2$(μ-dppm)$_2$ (**11**). The thermal ellipsoids are drawn at the 40% probability level. The molecule contains a crystallographic two-fold axis of symmetry. The unlabeled Re atom is Re′ and the unlabeled P atoms are P(1) and P(2). Selected bond distances (Å) and bond angles (°) are as follows: Re–Re′ 2.3120(5), Re–O(11) 2.163(4), Re–O(12) 2.114(4), Re–Cl 2.5362(16), O(11)–C(10) 1.262(7), O(12)–C(10) 1.277(7); O(12)–Re–O(11) 80.44(15), O(12)–Re–Re′ 88.55(11), P(1)–Re–P(2) 93.30(5), Re′–Re–Cl 166.50(4), O(11)–C(10)–O(12) 123.0(5).

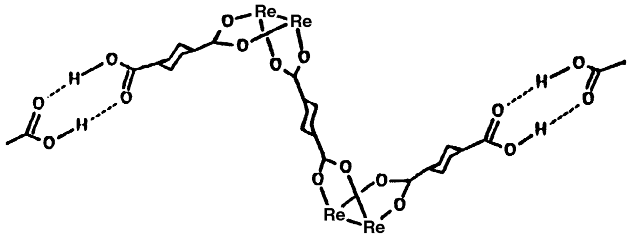
(b) Reactions of *cis*-$Re_2(\mu\text{-}O_2CCH_3)_2Cl_2$(μ-dppm)$_2$ (2) with carboxylic acids

We had anticipated that the reactions of dicarboxylic acids with **2**, a complex that contains a pair of exchangeable *cis* μ-acetato ligands, might afford compounds in which there were a square arrangement of dirhenium(II) units.



2

When **2** was reacted with terephthalic acid, *trans*-1,4-cyclohexanedicarboxylic acid or adipic acid in refluxing ethanol the red insoluble products [*cis*-Re_2Cl_2(μ-dppm)$_2$(μ-dicarboxylate)]$_n$ were obtained. In the cases of the terephthalate (**5**) and *trans*-1,4-cyclohexanedicarboxylate (**12**) complexes, n = 3 as shown previously by an X-ray crystal structure of **5**,[1] and in the present study in the case of **12** by an ESI mass spectrum (see Experimental). Note that a strict adherence to 1 : 1 proportions of reagents is necessary to produce **12**, since if more than 1.5 equivalents of the acid are used the reaction favors the complex [*cis*-$Re_2(\mu\text{-}O_2CC_6H_{10}CO_2H)Cl_2(\mu\text{-dppm})_2]_2(\mu\text{-}O_2CC_6H_{10}CO_2)$ (**6**);[1] the latter complex is an infinite polymer in which "dimers-of-dimers" are linked through intermolecular hydrogen-bonds involving the "free" carboxylic acid groups to generate zig-zag chains (see Scheme 1). The adipate complex **13** was too insoluble in suitable solvents for us to grow X-ray quality crystals or obtain electrochemical data or a satisfactory mass spectrum. However, the value of n is probably 3 since the adipate spacer is capable of spanning distances between the adjacent Re_2 units that are similar to those in the analogous terephthalate and *trans*-1,4-cyclohexanedicarboxylate bridged complexes.



Scheme 1

We attribute the stability of the triangular structures of **5** and **12**, relative to a square assembly, to the unfavorable *intramolecular* phenyl–phenyl interactions between *adjacent* [Re_2Cl_2(μ-dppm)$_2$] units that would arise in the square complex as the angle between *cis* carboxylate ligands opens up upon going from a triangular arrangement to a square. With shorter spacers such as oxalate or acetylenedicarboxylate, we failed to isolate any coupled dirhenium complexes when the appropriate acids were reacted with **2**. In the case of acetylenedicarboxylic acid, this is probably a consequence of decarboxylation of the ligand occurring under the reflux conditions that we used since a similar reaction pathway ensues when **1** is reacted with this acid.[16]

The CV of the dirhenium(II) complex *cis*-$Re_2(\mu\text{-}O_2CCH_3)_2Cl_2$(μ-dppm)$_2$ (**2**) shows one-electron oxidations at $E_{1/2}$ = +0.28 V and +1.34 V *vs.* Ag/AgCl.[2] For the terephthalate-bridged complex **5**, the measurement of its CV and DPV properties reveals the presence of sequential coupled oxidation processes with $E_{1/2}$ values of *ca.* +0.40 V and +0.33 V *vs.* Ag/AgCl, along with an irreversible oxidation at $E_{p,c}$ = +1.47 V.[1] The $\Delta E_{1/2}$ value of 70 mV accords with a very small comproportionation constant ($K_c \sim 15$ from eqn. (1)), and therefore with the presence of at most a very weak electronic coupling between the Re_2 units present in **5**. The CV of **12** shows broad processes at $E_{1/2}$ = +0.35 V and $E_{1/2}$ = +1.40 V *vs.* Ag/AgCl. As might be expected, although **12** is structurally related to **5**, the saturated nature of the organic spacer is not conducive to electronic communication between the dirhenium units.

A final reaction between **2** and a dicarboxylic acid that we investigated involved 1,1′-ferrocenedicarboxylic acid, a reagent that has been used previously to couple $[Mo_2]^{4+}$ units into "dimers-of-dimers"[18] or supramolecular squares.[13b] In these cases, the two carboxylate groups on each $[(O_2CC_5H_4)_2Fe]$ moiety are *anti* to one another and can therefore effect the coupling of dimetal units. To our surprise, the reaction of **2** with this diacid afforded exclusively the trimetallic compound *cis*-$Re_2Cl_2(\mu\text{-dppm})_2[(\mu\text{-}O_2CC_5H_4)_2Fe]$ (**14**) in almost quantitative yield, the structure of which is shown in Fig. 3. This compound, which is an example of the thermodynamically stable *cis*-$Re_2(\mu\text{-}O_2CR)_2Cl_2(\mu\text{-dppm})_2$ type, shows dirhenium-based redox processes (both oxidations) in its CV (recorded in 0.1 M TBAH–CH_2Cl_2) at $E_{1/2}$ = +0.31 V and +1.29 V *vs.* Ag/AgCl. These processes, which are reversible (with $i_{p,a} = i_{p,c}$ and ΔE_p = 60 mV), are accompanied by a reversible process at $E_{1/2}$ = +1.12 V (ΔE_p = 60 mV) *vs.* Ag/AgCl that is associated with oxidation of the ferrocene dicarboxylate moiety.

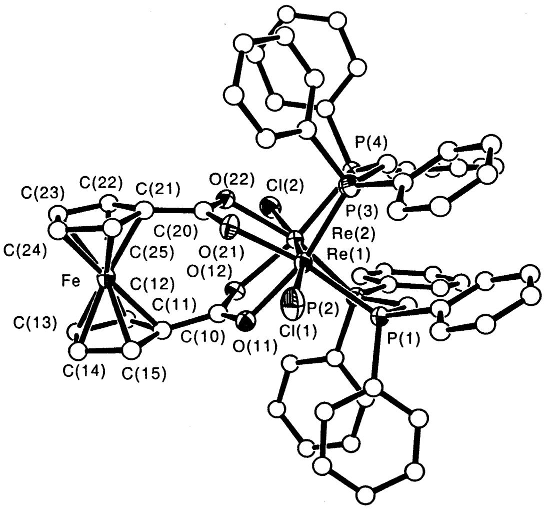


Fig. 3 ORTEP[11] representation of the structure of the complex *cis*-$Re_2Cl_2(\mu\text{-dppm})_2[(\mu\text{-}O_2CC_5H_4)_2Fe]$ (**14**). The thermal ellipsoids are drawn at the 40% probability level except for the carbon atoms which are circles of arbitrary radius. Selected bond distances (Å) and bond angles (°) are as follows: Re(1)–Re(2) 2.3218(3), Re(1)–O(21) 2.102(4), Re(1)–O(11) 2.158(3), Re(2)–O(22) 2.178(3), Re(2)–O(12) 2.115(3), Re(1)–Cl(1) 2.5574(15), Re(2)–Cl(2) 2.5486(14), O(11)–C(10) 1.271(6), O(12)–C(10) 1.264(6), O(21)–C(20) 1.273(6), O(22)–C(20) 1.261(6); O(21)–Re(1)–O(11) 75.72(14), O(12)–Re(2)–O(22) 74.59(13), O(21)–Re(1)–Re(2) 91.30(10), O(11)–Re(1)–Re(2) 86.15(10), O(12)–Re(2)–Re(1) 91.40(10), O(22)–Re(2)–Re(1) 86.20(9), P(3)–Re(1)–P(1) 96.31(5), P(4)–Re(2)–P(2) 94.20(5), Re(2)–Re(1)–Cl(1) 166.27(4), Re(1)–Re(2)–Cl(2) 167.68(3), O(12)–C(10)–O(11) 124.1(5), O(22)–C(20)–O(21) 123.6(5).

Concluding remarks

More often than not, compounds in which pairs of multiply-bonded *dirhenium* units have been incorporated into tetrarhenium clusters, or assemblies of higher nuclearity, have been discovered more by chance than design.[19–22] While there are exceptions, such as the coupling of a pair of $Re_2Cl_4(\mu\text{-dppm})_2$ units through the agency of the bridging 7,7,8,8,-tetracyano-*p*-quinodimethane ligand (TCNQ),[23] designed syntheses of general utility are lacking. We have addressed this deficiency in both our initial report[1] and in the present study, and show that the acetate ligand labilities of $Re_2(\mu\text{-}O_2CCH_3)Cl_4(\mu\text{-dppm})_2$ (**1**) and *cis*-$Re_2(\mu\text{-}O_2CCH_3)_2Cl_2(\mu\text{-dppm})_2$ (**2**) can be used to synthesize dicarboxylate-bridged dirhenium species that include "dimers-of-dimers", triangular assemblies and mixed-metal trimetallic species.

Compound **2** is of special note because it is the thermodynamically stable isomer of a *cis*/*trans* pair.[2,3] With other bridging phosphine ligands, it is the *trans* isomer that is the thermodynamically stable form (*e.g.* *trans*-$Re_2(\mu\text{-}O_2CCH_3)_2Cl_2(\mu\text{-dppE})_2$, where dppE = $Ph_2PC(=CH_2)PPh_2$)[24] and the *trans* isomer can be easily oxidized to its paramagnetic monocationic congener. We are now investigating the acetate ligand lability in compounds of the type $[trans\text{-}Re_2(\mu\text{-}O_2CCH_3)_2Cl_2(\mu\text{-PP})_2]^{0,+}$ with a view to incorporating the $[trans\text{-}Re_2Cl_2(\mu\text{-PP})_2]^{0,+}$ unit into long chain polymers.

Acknowledgements

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