Assemblies of multiply bonded $[\text{Re}_2]^{n+}$ 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 Re₂(μ -O₂CCH₃)Cl₄(μ -dppm)₂ (1) and *cis*-Re₂(μ -O₂CCH₃)₂Cl₂(μ -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 Re₂(μ -O₂CC₆H₄N)Cl₄(μ -dppm)₂ (7) and *cis*-Re₂(μ -O₂CC₆H₁₀CO₂Et)₂Cl₂(μ -dppm)₂ (11) have been isolated, as well as the trimetallic complex *cis*-Re₂Cl₂(μ -dppm)₂[(μ -O₂CC₅H₄)₂Fe] (14) that is formed from the reaction of 2 with (C₅H₄CO₂H)₂Fe. The crystal structures of 7, 11 and 14 are reported.

Introduction

We have shown¹ that the multiply bonded dirhenium(III,II) and dirhenium(II,II) complexes $\text{Re}_2(\mu-O_2\text{CCH}_3)\text{Cl}_4(\mu-\text{dppm})_2$ (1)² and *cis*- $\text{Re}_2(\mu-O_2\text{CCH}_3)_2\text{Cl}_2(\mu-\text{dppm})_2$ (2),^{2,3} where dppm = $\text{Ph}_2\text{PCH}_2\text{PPh}_2$, which contain labile μ -O₂CCH₃ 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 $\text{Re}_2(\mu-O_2\text{CCH}_3)\text{Cl}_4(\mu-\text{dppm})_2$ (1),² *cis*- $\text{Re}_2(\mu-O_2\text{CCH}_3)_2\text{Cl}_2(\mu-\text{dppm})_2$ (2)^{2,3} and $\text{Re}_2\text{Cl}_4(\mu-\text{dppm})_3$ (3),⁴ and the dicarboxylate-bridged complexes $[\text{Re}_2\text{Cl}_4(\mu-\text{dppm})_2]_2(\mu-O_2\text{CC}_6\text{H}_4\text{CO}_2)$ (4),¹ [*cis*- $\text{Re}_2\text{Cl}_2(\mu-\text{dppm})_2$ -($\mu-O_2\text{CC}_6\text{H}_4\text{CO}_2$) (4),¹ [*cis*- $\text{Re}_2\text{Cl}_2(\mu-\text{dppm})_2$ -($\mu-O_2\text{CC}_6\text{H}_4\text{CO}_2$)]₃ (5)¹ and [*cis*- $\text{Re}_2(\mu-O_2\text{CC}_6\text{H}_{10}\text{CO}_2\text{H})\text{Cl}_2$ -($\mu-\text{dppm})_2]_2(\mu-O_2\text{CC}_6\text{H}_{10}\text{CO}_2)$ (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 CH₂Cl₂/CH₃CN or 1,2-C₂H₄Cl₂ solutions. Elemental microanalyses were carried out by Dr. H. D. Lee of the Purdue University Microanalytical Laboratory.

A. Reactions of Re₂(µ-O₂CCH₃)Cl₄(µ-dppm)₂ (1)

(i) Synthesis of $\text{Re}_2(\mu-O_2CC_5H_4N)\text{Cl}_4(\mu-dppm)_2$ (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 $\text{Re}_2\text{Cl}_4(\mu-dppm)_2$ (3) and the carboxylate-exchanged product $\text{Re}_2(\mu-O_2CC_5H_4N)\text{Cl}_4(\mu-dppm)_2$ (7) was obtained as shown by cyclic voltammetry. The products were separated by hand. Yield of 7: 0.053 g (47%). Calc. for $\text{C}_{56}\text{H}_{48}\text{Cl}_4\text{NO}_2\text{P}_4\text{Re}_2$: 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 $[\text{Re}_2\text{Cl}_4(\mu-\text{dppm})_2]_2(\mu-\text{O}_2\text{C}(\text{CH}_2)_4\text{CO}_2)$ (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 C₁₀₆H₉₆Cl₈O₄P₈Re₄: C, 46.97; H, 3.57; Cl, 10.33. Found: C, 45.96; H, 3.56, Cl 10.19%.

(iii) Synthesis of $[\text{Re}_2\text{Cl}_4(\mu-\text{dppm})_2]_2(\mu-O_2\text{CC}_6\text{H}_4\text{C}_6\text{H}_4\text{CO}_2)$ (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 $[\text{Re}_2\text{Cl}_4(\mu\text{-dppm})_2]_2(\mu\text{-O}_2\text{CCH}=\text{CHCO}_2)$ (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 $\text{Re}_2\text{Cl}_4(\mu\text{-dppm})_2$ (3), the proportion of which increased with increasing reaction time.

(v) Synthesis of cis-Re₂(μ -O₂CC₆H₁₀CO₂Et)₂Cl₂(μ -dppm)₂ (11). A mixture of 1 (0.119 g, 0.09 mmol) and *trans*-1,4cyclohexanedicarboxylic 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 C₇₄H₈₆Cl₂O₁₀P₄Re₂ (*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 CD₂Cl₂): 7.6–6.9 (m, 40H, Ph), 6.40 and 4.95 (m, 4H, CH₂ of dppm), 4.18 (q, 8H, CH₂ of EtOH and -CO₂Et), 2.38, 2.10, 1.93 and 1.70–1.43 (m, 20H, C₆H₁₀), 1.34 (t, 12H, CH₃ of EtOH and -CO₂Et). ³¹P{¹H} NMR spectrum (δ in CD₂Cl₂): -9.32.

B. Reactions of cis-Re₂(µ-O₂CCH₃)₂Cl₂(µ-dppm)₂ (2)

(i) Synthesis of $[cis-\text{Re}_2\text{Cl}_2(\mu-\text{dppm})_2(\mu-\text{O}_2\text{CC}_6\text{H}_{10}\text{CO}_2)]_3$ (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 C₁₇₄H₁₆₂Cl₆O₁₂P₁₂Re₆: 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 CD₂Cl₂): 7.8–6.8 (m, 150H, Ph of dppm), 6.42 and 4.91 (m, 12H, CH₂ of dppm), 2.42–1.43 (m, 30H, C₆H₁₀). ³¹P{¹H} NMR spectrum (δ in CD₂Cl₂): -9.87.

(ii) Synthesis of $[cis-Re_2Cl_2(\mu-dppm)_2(\mu-O_2C(CH_2)_4CO_2)]_n$ (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*-Re₂Cl₂(μ -dppm)₂[(μ -O₂CC₅H₄)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 C₆₂H₅₂Cl₂FeO₄P₄Re₂: 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 CD₂Cl₂): 7.8–6.9 (m, 40H, Ph), 6.41 and 5.00 (m, 4H, CH₂ of dppm), 5.41 and 4.59 (m, 8H, C₅H₄). ³¹P{¹H} NMR spectrum (δ in CD₂Cl₂): -9.13.

X-Ray crystal structure determinations

Single crystals of composition $\text{Re}_2(\mu-O_2\text{CC}_5\text{H}_4\text{N})\text{Cl}_4(\mu-dppm)_2$ (7), $cis-\text{Re}_2(\mu-O_2\text{CC}_6\text{H}_{10}\text{CO}_2\text{Et})_2\text{Cl}_2(\mu-dppm)_2\cdot2\text{EtOH}$ (11· 2EtOH), and $cis-\text{Re}_2\text{Cl}_2(\mu-dppm)_2[(\mu-O_2\text{CC}_5\text{H}_4)_2\text{Fe}]\cdot1.43\text{EtOH}$ (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 K α radiation ($\lambda = 0.71073$ Å). Accurate unit cell parameters and orientation

matrices were determined by least-squares refinement of the appropriate number of reflections in the range of $4 < \theta < 27^{\circ}$. 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 SCALEPACK⁹ 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 $Re_2(\mu$ -O_2CCH_3)Cl_4(\mu-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 $\text{Re}_2(\mu\text{-}O_2\text{CC}_5\text{H}_4\text{N})\text{Cl}_4(\mu\text{-}dppm)_2$ (7). This product was contaminated with a small amount of $\text{Re}_2\text{Cl}_4(\mu\text{-}dppm)_2$ (3) which is formed from the competing thermal reduction of 1 in refluxing ethanol.²



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-Bu₄NPF₆(TBAH)– CH₂Cl₂ showed a reversible process at $E_{1/2} = +0.57$ V vs. Ag/AgCl, with $\Delta E_p = 60$ 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 $E_{1/2}(ox) = +0.52$ V 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 [(μ -dppm)₂Cl₄Re₂](μ -O₂CC₆H₄CO₂)-[Re₂Cl₄(μ -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 [Re₂Cl₄(μ -dppm)₂]₂(μ -O₂C(CH₂)₄CO₂) (**8**), [Re₂Cl₄(μ -dppm)₂]₂(μ -O₂CC₆H₄Co₄H₄CO₂)

 $\begin{array}{l} \textbf{Table 1} \quad Crystallographic data for the dirhenium complexes of composition $\operatorname{Re}_2(\mu-O_2CC_5H_4N)Cl_4(\mu-dppm)_2$ (7), $cis-\operatorname{Re}_2(\mu-O_2CC_6H_{10}CO_2Et)_2Cl_2(\mu-dppm)_2$ (7), $cis-\operatorname{Re}_2(\mu-dppm)_2$ (7), $cis-\operatorname{Re}_2(\mu-dpm)_2$ (7), $cis-\operatorname{Re}$

	7	11	14
Formula	C ₅₆ H ₄₈ Cl ₄ NO ₂ P ₄ Re 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)	<i>C</i> 2/ <i>c</i> (No. 15)	$P2_{1}/c$ (No. 14)
aĺÅ	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)
a/°	90	90	90
βl°	105.9273(9)	99.5236(18)	96.7556(12)
yl°	90	90	90
Ż	4	4	4
V/Å ³	5232.0(4)	7067.9(9)	6127.4(3)
$D_c/\mathrm{g~cm}^{-3}$	1.784	1.600	1.680
$\mu(Mo-K_a)/mm^{-1}$	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
$R(F_{a})^{a}$	0.036	0.046	0.046
$R_{\rm w}(F_{\rm c}^2)^b$	0.080	0.082	0.098
GOF	1.022	0.936	1.021
$R = \Sigma F_{o} - F_{c} / \Sigma F_{o} \text{ with } F_{o}^{2} > 2\sigma(F_{o}^{2}).^{b} R$	$R_{\rm w} = [\Sigma w(F_{\rm o}^2 - F_{\rm c}^2)^2 / \Sigma w F_{\rm o} ^2]$	$\binom{2}{2} \binom{2}{2} \binom{1}{2}$	



Fig. 1 ORTEP¹¹ representation of the structure of the dirhenium complex $Re_2(\mu-O_2CC_5H_4N)Cl_4(\mu-dppm)_2$ (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)-Cl(11) 103.03(3), O(1)-CRe(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 P(1)-Re(1)-Re(2)-P(2),Cl(11)-Re(1)-Re(2)-Cl(21),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 $[Re_2Cl_4(\mu-dppm)_2]_2(\mu-O_2CCH=CHCO_2)$ (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 $[(\mu-dppm)_2Cl_4Re_2](\mu-O_2CRCO_2)[Re_2Cl_4(\mu-dppm)_2]$, 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} (2*J*) 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–CH₂Cl₂. CV and DPV measurements on 4 show evidence for electronic coupling between the one-electron oxidation $[\text{Re}_2]^{5+} \rightarrow [\text{Re}_2]^{6+}$ 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

$$[\operatorname{Re}_{2}\cdots\operatorname{Re}_{2}] + [\operatorname{Re}_{2}\cdots\operatorname{Re}_{2}]^{2+} \underbrace{\frac{K_{c}}{\swarrow}}_{2} 2[\operatorname{Re}_{2}\cdots\operatorname{Re}_{2}]^{+}$$
(1)
where $K_{c} = \exp(\Delta E_{1/2}/25.69)$

The greater the degree of delocalization in the monocation $[\text{Re}_2\text{---}\text{Re}_2]^+$, 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-workers¹² 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'-biphenyl-dicarboxylate bridged analogue (9) showed coupled processes $E_{1/2}(\text{ox}) = +0.48$ 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 $[\text{Re}_2\text{Cl}_4(\mu\text{-dppm})_2]_2$ - $(\mu\text{-O}_2\text{CCH}=\text{CHCO}_2)$ (10), the analogous reaction with acetylenedicarboxylic acid gave the paramagnetic μ - η^2 -acetylene complex $\text{Re}_2\text{Cl}_5(\mu$ -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 $E_{\rm p,c} = -0.50$ 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 ³¹P NMR spectrum of 10, and the presence of broad poorly defined resonances in its ¹H 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-Re₂(µ-O₂CC₆H₁₀CO₂Et)₂Cl₂(µdppm)₂ (11) rather than $[Re_2Cl_4(\mu-dppm)_2]_2(\mu-O_2CC_6H_{10}CO_2)$. 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 [Re₂]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*-Re₂- $(\mu$ -O₂CCH₃)₂Cl₂(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*-Re₂(μ -O₂CCH₃)₂-



Fig. 2 ORTEP¹¹ representation of the structure of the dirhenium complex *cis*-Re₂(μ -O₂CC₆H₁₀CO₂Et)₂Cl₂(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).

Cl₂(μ -dppa)₂, where dppa = Ph₂PNHPPh₂ (2.3067(5) Å).¹⁷ The CV of **11** (recorded in 0.1 M TBAH–CH₂Cl₂) 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*-Re₂-(μ -O₂CCH₃)₂Cl₂(μ -dppm)₂.²

(b) Reactions of cis-Re_2(μ -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.



When **2** was reacted with terephthalic acid, *trans*-1,4-cyclohexanedicarboxylic acid or adipic acid in refluxing ethanol the red insoluble products $[cis-\text{Re}_2\text{Cl}_2(\mu-\text{dppm})_2(\mu-\text{dicarboxylate})]_n$ 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 $[cis-\text{Re}_2(\mu-\text{O}_2\text{CC}_6\text{H}_{10}\text{CO}_2\text{H})\text{Cl}_2(\mu-\text{dpm})_2]_2(\mu-\text{O}_2\text{CC}_6\text{H}_{10}\text{CO}_2)$ (**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 insol-



Scheme 1

uble 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 Re₂ units that are similar to those in the analogous terephthalate and *trans*-1,4-cyclohexanedicarboxylate bridged complexes.

We attribute the stability of the triangular structures of **5** and **12**, relative to a square assembly, to the unfavorable *intra-molecular* phenyl–phenyl interactions between *adjacent* $[\text{Re}_2\text{Cl}_2(\mu\text{-dppm})_2]$ 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 acetylenedicarboxylation 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-Re₂(μ -O₂CCH₃)₂-Cl₂(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 Re₂ 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 [Mo₂]⁴⁺ units into "dimers-of-dimers"¹⁸ or supramolecular squares.^{13b} In these cases, the two carboxylate groups on each [(O₂CC₅H₄)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-Re₂Cl₂(µ-dppm)₂[(µ-O₂CC₅H₄)₂Fe] (14) in almost quantitative yield, the structure of which is shown in Fig. 3. This com-

O(22) CI(2)

6 C(20)

C(10) O(11)

0(21)

0(12 C(12)

C(25)

C(15)

C(11

P(3)

P(1)

Re(2)

Re(1)

CI(1)

C(23) C(22) C(21)

C(24

C(13)



pound, which is an example of the thermodynamically stable cis-Re₂(µ-O₂CR)₂Cl₂(µ-dppm)₂ type, shows dirhenium-based redox processes (both oxidations) in its CV (recorded in 0.1 M TBAH–CH₂Cl₂) 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 $\Delta E_p =$ 60 mV), are accompanied by a reversible process at $E_{1/2} = +1.12$ V ($\Delta E_{\rm p} = 60$ mV) vs. Ag/AgCl that is associated with oxidation of the ferrocene dicarboxylate moiety.

Concluding remarks

More often than not, compounds in which pairs of multiplybonded 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 $\text{Re}_2\text{Cl}_4(\mu\text{-dppm})_2$ units through the agency of the bridging 7,7,8,8,-tetracyanop-quinodimethane ligand (TCNQ),23 designed syntheses of general utility are lacking. We have addressed this deficiency in both our initial report¹ and in the present study, and show that the acetate ligand labilities of $Re_2(\mu-O_2CCH_3)Cl_4(\mu-dppm)_2$ (1) and $cis-Re_2(\mu-O_2CCH_3)_2Cl_2(\mu-dppm)_2$ (2) can be used to synthesize dicarboxylate-bridged dirhenium species that include "dimers-of-dimers", triangular assemblies and mixedmetal 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-Re2(µ-O2CCH3)2- $Cl_2(\mu$ -dppE)₂, where dppE = Ph₂PC(=CH₂)PPh₂)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 $[trans-\text{Re}_2(\mu-\text{O}_2\text{CCH}_3)_2\text{Cl}_2(\mu-\text{PP})_2]^{0,+}$ with a view to incorporating the $[trans-\text{Re}_2\text{Cl}_2(\mu-\text{PP})_2]^{0,+}$ unit into long chain polymers.

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