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FULL PAPER

Dirhodium(II) carboxylates as building blocks. Macrocyclic dimers with vertically stacked Rh_2^{4+} units

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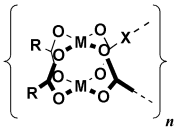
Received 20th September 2000, Accepted 23rd October 2000

Reaction of $Rh_2(OAc)_4$ and H_2L (= 2,7-di-*tert*-butyl-9,9-dimethyl-4,5-xanthenedicarboxylic acid) in *N*,*N*-dimethylaniline gave the singly bridged dimer $(AcO)_3Rh_2LRh_2(OAc)_3$ and three doubly bridged dimers, $(AcO)_2Rh_2L_2Rh_2(OAc)_2$, $(HL)(AcO)Rh_2L_2Rh_2(OAc)_2$, and $(HL)(AcO)Rh_2L_2Rh_2(OAc)(HL)$. Crystal structures of the last two compounds showed a macrocyclic core with a *trans* arrangement of bridging dicarboxylates, with one or two of the four remaining acetate ligands replaced by a bridging ligand bound through one carboxylate only. The rhodium cages are separated by 4.5 Å in the direction of the Rh–Rh axes, and offset horizontally by 2.5 Å so that a rhodium atom of one cage lies over a carboxylate oxygen of the other, with Rh · · · O distances of 2.248–2.286 Å.

Dinuclear tetracarboxylate complexes $M_2(RCO_2)_4$ are a well known class of compounds with four carboxylate ligands arranged at right angles around a central metal axis.[1] The current interest in metal-directed assembly[2] has recently extended to dinuclear complexes, and several cyclic polymers have been prepared by using dicarboxylates as bridges between dimetal units.[3,4] Such metallomacrocycles may have useful physical properties, such as acting as hosts for other molecules. In our approach, macrocycles were constructed using the *cis* connection, **1**, where X is a linking group, with the other pair of *cis* sites blocked by bridging between the R groups.[4] Rhodium was chosen as the metal since $Rh_2(RCO_2)_4$ complexes are diamagnetic and easily handled.[1] The tetracarboxylate framework also contains a *trans* connection, **2**, which could also be used to build macrocycles if X is non-linear. The first examples of this type of macrocycle are reported here. The commercially available U-shaped diacid **3** was chosen as the linking group primarily to reduce the number of possible products; only one ring size, a cyclic 'dimers of dimers', was likely to be formed for geometric reasons. Nevertheless, there was still the question of whether a *trans* orientation across the Rh–O cage would be preferred, and how many bridges could be installed between the Rh_2^{4+} units (up to four in principle). Chisholm and co-workers have previously prepared singly bridged face to face dimers of molybdenum and tungsten tetracarboxylates as models for linear polymers, and demonstrated electronic coupling between the M_2 units.[5] Face to face dirhodium complexes have however not been reported, and multiple bridging is not known for any dinuclear complex.



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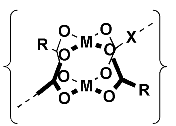

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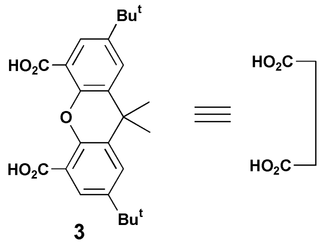

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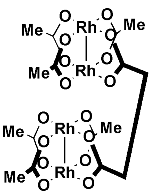

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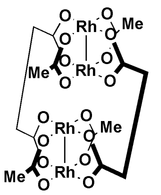

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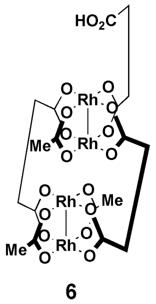

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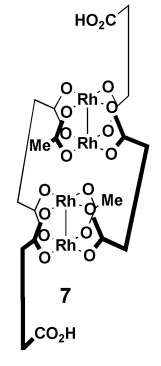

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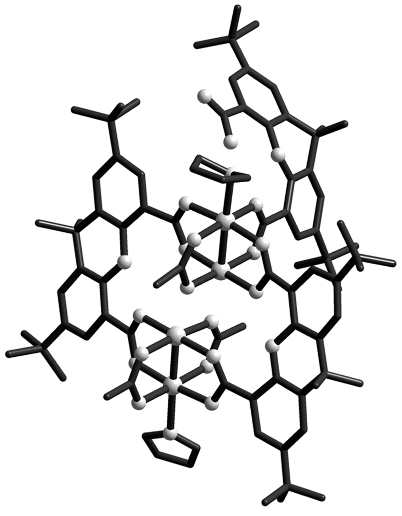
Results

Synthesis

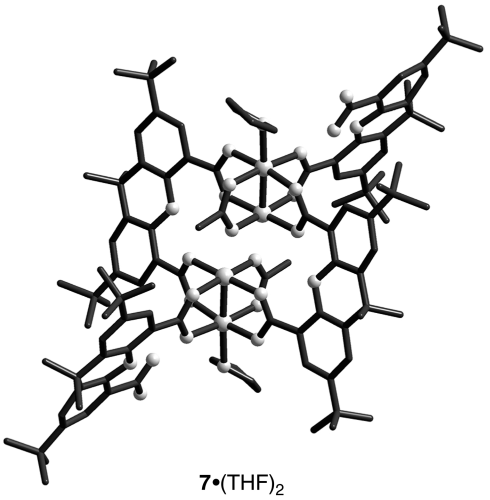
Heating $Rh_2(OAc)_4$ with diacid **3** in *N*,*N*-dimethylaniline at various stoichiometries provided four complexes **4**–**7**, isolated as green solids by chromatography. The reactions were heterogeneous but otherwise quite clean. With a diacid : dirhodium ratio = 1.35 : 1, only doubly bridged complexes **5** (40%), **6** (33%) and **7** (7%) were isolated. With a ratio 0.5 : 1, singly bridged complex **4** (32%) was obtained, along with doubly bridged **5** (24%), **6** (5%) and unchanged $Rh_2(OAc)_4$. Treatment of singly bridged **4** with an excess of **3** rapidly gave a mixture of doubly bridged species **5**–**7**, but **5** reacted with an excess of diacid only slowly, producing **6** and **7** in low yields. Further heating of **6** or **7** under the reaction conditions did not generate triply or quadruply bridged species, but led only to eventual decomposition.

The gross structures of the complexes were deduced from elemental analysis, ^1H NMR and mass spectrometry. The room temperature ^1H NMR spectrum of singly bridged compound **4** has three acetate resonances of equal intensity (δ 2.54, 2.24, and 1.93), implying that the dirhodium cages are offset, making the *trans* related acetates non-equivalent.[6] The doubly bridged

DOI: 10.1039/b007625m



6•(THF)$_2$



7•(THF)$_2$

Fig. 1 Crystal structures of complexes 6·2THF and 7·2TH, with hydrogen atoms and molecules of solvent omitted for clarity.

compound **5** also has non-equivalent acetates (δ 2.46 and 1.88), consistent with an offset geometry. Complex **6** has three acetate resonances (δ 2.60, 2.50 and 1.90) and **7** has one (δ 2.64). There was some ambiguity about the point of attachment of the 'dangling' ligands in **6** and **7**, so their crystal structures were obtained (Fig. 1).

Crystal structures

The Rh–Rh and Rh–O bond lengths for complexes **6** and **7** are similar,[7] and in the normal range for $Rh_2(RCO_2)_4$ compounds,[1] although there are slight helical distortions of the Rh–O cages (average O–Rh–Rh–O torsion of 5° in **6**, 6° in **7**). The cages are separated by 4.5 Å in the direction of the Rh–Rh axis, and offset horizontally by 2.5 Å, so that a rhodium atom of one cage lies over a carboxylate oxygen of the other, with Rh···O distances of 2.248–2.286 Å. The bridging ligands are fairly planar, and tilted at an angle of *ca.* 20° to the Rh–Rh axes, although there is some disorder around the *tert*-butyl substituents due to the flexibility of the central dibenzopyran ring; this flexibility is particularly evident in the dangling ligand on **6**, which although not disordered, is bent by 36°. The C–O bonds of the acid groups point towards the rhodium cages; the carboxylic acid OH hydrogens were not located, but may hydrogen bond to the Rh–O cage and/or dibenzopyran oxygens (O···O distances of 2.6–3.0 Å). This would account for the rather non-polar handling characteristics of these compounds.

Discussion

The two structurally characterised macrocycles have a *trans* arrangement of bridging ligands, and it is likely that **5** also has the same macrocyclic core and that **4** has a similar displacement of rhodium cages.[6] The reason is presumably the stability imparted by Rh···O co-ordination, a type of interaction well documented for monomeric $M_2(RCO_2)_4$ compounds.[8] Perhaps the best comparison is with the dimeric complex THF·$Rh_2(CF_3CO_2)_4$·$Rh_2(CF_3CO_2)_4$·THF in which two THF adducts of $Rh_2(CF_3CO_2)_4$ are held together in a similar offset geometry.[9] Here the Rh···O distance (2.406 Å) is longer than in **6** or **7**, and the Rh–O bond to THF is shorter (2.214 Å). The Rh···O distances in **6** and **7** are also slightly shorter than in crystalline $Rh_2(RCO_2)_4$ complexes (2.337, 2.341 Å),[10] and probably shorter than in liquid crystals (vertical separation of Rh–O cages measured at *ca.* 4.6 Å[8b]). Intramolecular stabilisation may explain why no species with *cis* oriented bridges, or more than two bridges, were isolated, since these compounds could not easily distort to accommodate Rh···O co-ordination. In fact molecular modelling predicts that the *cis* isomer of **5** should be less stable than the *trans* isomer by *ca.* 10 kJ mol^{-1}. The slow reaction of **5** with excess of diacid suggests that it is not the main intermediate *en route* to **6** and **7**, which must arise instead from coupling of *cis*-substituted 'monomeric' dirhodium complexes. The overall picture is of an assembly process which evolves towards the most stable products. Bridging ligand **3** is the right length to promote Rh···O co-ordination; whether there will be a similar preference for *trans* substitution with bridges that do not allow this type of intramolecular interaction remains to be seen.

Experimental

Reactions were performed under argon, and weakly bound solvent ligands removed from the products by heating at 100 °C under vacuum overnight. NMR spectra were recorded at 200 MHz, with TMS as internal reference, FAB mass spectra on a VG7070E instrument using *m*-nitrobenzyl alcohol as matrix. 230–400 mesh silica gel was used for chromatography. Organic extracts were dried over Na_2SO_4.

Preparations

Complexes 5, 6 and 7. 2,7-Di-*tert*-butyl-9,9-dimethyl-4,5-xanthenedicarboxylic acid **3** (0.5 g, 1.22 mmol) and $Rh_2(OAc)_4$ (0.4 g, 0.906 mmol) were stirred in *N*,*N*-dimethylaniline (20.0 ml) at 140 °C for 24 h. The cooled reaction mixture was diluted with dichloromethane, MeCN (2 ml) added, and the purple solution washed three times with aqueous hydrochloric acid (2 M), followed by water. The organic layer was dried and evaporated to a green solid. Chromatography (0 to 6% acetone in dichloromethane) provided first complex **5** (270 mg, 40%), then **7** (70 mg, 7%) and finally **6** (267 mg, 33%) as green solids. Analytical data for **5**: mp >240 °C (Found: C, 47.2; H, 4.7. $C_{29}H_{34}O_9Rh_2$ requires C, 47.56; H, 4.68%); δ_H(200 MHz, 5% v/v d_4-MeOH in $CDCl_3$) 1.31 (36 H, s), 1.58 (12 H, s), 1.88 (6 H, s), 2.46 (6 H, s), 7.47 (4H, d, *J* 2.4) and 7.81 (4H, d, *J* 2.4 Hz); *m*/*z* 1465 (MH$^+$), 1449, 1443 and 1345. Analytical data for **6**: mp >240 °C (Found: C, 53.3; H, 5.3. $C_{81}H_{94}O_{21}Rh_4$ requires C, 53.59; H, 5.22%); δ_H(200 MHz, 5% v/v d_4-MeOH in $CDCl_3$) 1.12 (9H, s), 1.24 (18H, s), 1.31 (18H, s), 1.37 (9H, s), 1.56 (12H, s), 1.57 (6H, s), 1.90 (3H, s), 2.50 (3H, s), 2.60 (3H, s), 2.64 (6H, s), 7.46 (2H, d, *J* 2.4), 7.63 (2H, d, *J* 2.4), 7.74 (1H, d, *J* 2.4), 7.82 (2H, d, *J* 2.4), 7.87 (1H, d, *J* 2.4) and 8.24 (1H, d, *J* 2.4 Hz); *m*/*z* 1815 (MH$^+$), 1799, 1755 and 1739. Analytical data for **7**: mp >240 °C (Found: C, 57.4; H, 5.6. $C_{26}H_{30}O_6Rh$ requires C, 57.68; H, 5.58%); δ_H(200 MHz, 5% v/v d_4-MeOH in $CDCl_3$) 1.14 (18H, s), 1.24 (36H, s), 1.38 (18H, s),1.54 (12H, s),1.58 (12H, s), 2.64 (6H, s), 7.45 (2H, d, *J* 2.4), 7.64 (2H, d, *J* 2.4),

Table 1 Crystal data for complexes **6**·2THF and **7**·2THF

	6·2THF	**7**·2THF
Empirical formula	$C_{81}H_{94}O_{21}Rh_4 \cdot 2C_4H_8O \cdot C_6H_{14}$	$C_{104}H_{120}O_{24}Rh_4 \cdot 2C_4H_8O \cdot 2C_6H_{14}$
Formula weight	2045.83	2482.52
Crystal system	Triclinic	Monoclinic
Space group	*P*1	*P*2$_1$/*n*
a/Å	12.983(3)	14.360(4)
b/Å	14.179(3)	24.341(4)
c/Å	14.632(4)	19.477(5)
α/°	86.10(3)	
β/°	89.93(3)	99.01(3)
γ/°	66.06(3)	
V/Å^3	2455.3(1)	6724(3)
Z	1	2
T/K	213	213
μ(Mo-Kα)/mm^{-1}	0.644	0.478
Data/parameters	13065/1005	9508/626
*R*1 ($I > 2\sigma(I)$)	0.0406	0.0674
*wR*2 (all data)	0.1090	0.2090

7.78 (2H, d, *J* 2.4), 7.90 (4H, d, *J* 2.4) and 8.24 (1H, d, *J* 2.4 Hz); *m*/*z* (FABMS) 2165 (MH$^+$), 2150, 2105, 2061, 2045, 2030, 2014, 1755, 1465 and 1449.

Complex 4. Compound **3** (93 mg, 0.227 mmol) and $Rh_2(OAc)_4$ (0.2 g, 0.452 mmol) were stirred in *N*,*N*-dimethylaniline (10.0 ml) at 140 °C for 24 h. The cooled reaction mixture was diluted with dichloromethane and washed three times with aqueous hydrochloric acid (2 M), followed by water. The organic layer was dried and evaporated to a green solid. Chromatography (0 to 4% methanol in dichloromethane) provided first complex **5** (80 mg, 24%), then **6** (20 mg, 5%) and finally **4** (84 mg, 32%) as green solids. Analytical data for **4**: mp >240 °C (Found: C, 38.1; H, 4.0. $C_{37}H_{40}O_{17}Rh_4$ requires C, 37.84; H, 3.95%); δ_H(200 MHz, $CDCl_3$) 1.28 (18H, s), 1.56 (6H, s), 1.93 (6H, s), 2.24 (6H, s), 2.54 (6H, s), 7.46 (2H, d, *J* 2.4) and 7.68 (2H, d, *J* 2.4 Hz); *m*/*z* (FABMS) 1175 (MH$^+$), 1174(M$^+$), 1159, 1115 and 1071.

Crystallography

Small green prisms of complexes **6** and **7** as the THF adducts were obtained by layering solutions in THF with hexane. Crystallographic data were collected on a STOE-IPDS image plate diffractometer using graphite monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å) at 213 K. Structures were solved by direct methods and refined by full-matrix least squares against F^2 using all data.[11] Non-hydrogen atoms were refined anisotropically with the exception of disordered ones, which were refined isotropically. Hydrogen positions were set geometrically. In both structures there were disordered groups that were split in two positions in the refinement, using distance and anisotropic displacement parameter restraints. For **6**·2THF one *tert*-butyl group on each bridging ligand, both *tert*-butyl groups on the dangling ligand, and both THFs were split. The complex was racemically twinned with a Flack parameter of 20%. In centrosymmetric complex **7**·2THF one *tert*-butyl group, its ring carbon, and the carbons either side of it were split on the bridging ligand; the free carboxyl end of the dangling ligand was split in the same way, but including the carboxyl group and its ring carbon (*i.e.* the four terminal ring carbons plus substituents). Both complexes pack in the crystal with one hexane, but significant voids are still present between the molecules. Some diffuse electron density was detected in these spaces, but it could not unambiguously be assigned. Crystal data are given in Table 1.

CCDC reference number 186/2241.

See http://www.rsc.org/suppdata/dt/b0/b007625m/ for crystallographic files in .cif format.

Modelling

Conformational analysis was performed with CERIUS 2, using the Open Force Field. Harmonic constraints were used to keep the cage Rh–O and Rh–Rh bonds near typical distances (2.0 and 2.4 Å respectively) but similar results were obtained using the default bond lengths. Modelling was found to reproduce the overall geometry of complexes **6** and **7** reasonably well, predicting tilt angles of *ca.* 20° for the bridging ligands.

Acknowledgements

We thank Johnson Matthey PLC for generous loans of rhodium.

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6 Complex **4** exchanges between its two equivalent offset forms on heating; details of this and axial co-ordination to singly and doubly bridged complexes will be reported elsewhere. R. P. Bonar-Law and N. Singh, unpublished results.

7 For complex **6**, Rh(1)–Rh(2) 2.366 Å and Rh(3)–Rh(4) 2.371 Å (where Rh(1) is the upper atom as drawn in Fig. 1), Rh(1)–O(THF) 2.302, Rh(4)–O(THF) 2.315, Rh(2) · · · O 2.248 Å, and Rh(3) · · · O 2.286 Å. Complex **7** is centrosymmetric with Rh(1)–Rh(2) 2.367, Rh–O(THF) 2.284, and Rh(2) · · · O 2.268 Å.

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