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Dirhodium (II) carboxylate complexes as building blocks. *cis*-Chelating dicarboxylic acids designed to bridge the dinuclear core†

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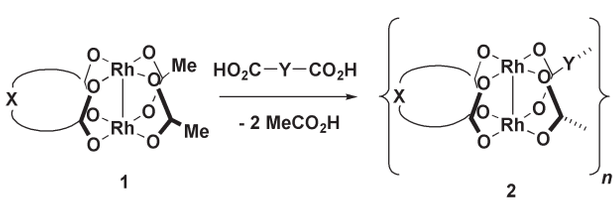
The syntheses and crystal structures of a series of dicarboxylic acids of general structure $HO_2CCR_2OArOCR_2CO_2H$ (LH_2) designed to span a pair of *cis* sites on the dirhodium(II) tetracarboxylate framework are described. Monochelate complexes $LRh_2(OAc)_2$ and bischelate complexes L_2Rh_2 were prepared by heating the diacids with $Rh_2(OAc)_4$ in *N*,*N*-dimethylaniline. Chelates were formed under kinetic control and the best yields were obtained from diacids with methyl groups on the ether side arms and bulky substituents on the aromatic ring next to the ether links. Effective molarities for chelation were measured under thermodynamic control by ^{1}H NMR in tetrachloroethane. The stability of chelates and the conformational properties of diacids were investigated by molecular mechanics and quantum chemical techniques.

Introduction

Metal complexes are versatile building blocks in supramolecular chemistry because metal ligand bonds may be formed reversibly, a selection of well defined geometries is available, and metal centres confer a variety of useful chemical and physical properties on the final assembly.[1] Much use has been made of single metal complexes to organise ligands with one donor atom, such as amines, into a variety of rings, cages and other objects.[1] However mononuclear complexes have limitations when binding ligands which can coordinate in a two point fashion, and here dinuclear complexes offer some advantages, being able to anchor ligands more firmly using two bonds. The robust 'lantern' geometry of dinuclear carboxylates[2] has recently been used to connect molecules bearing carboxylic acid groups at 90 or 180° to give linear or cyclic polymers.[3,4] In our work a dirhodium complex **1** with a pair of *cis* sites blocked off with a chelating dicarboxylate ligand, $^-O_2C–X–CO_2^-$, was condensed with different dicarboxylic acids $HO_2C–Y–CO_2H$ to form macrocycles **2**.[4] This paper reports the design, synthesis and crystal structures of some of the chelating diacid ligands, and studies on the stability of their dirhodium complexes.

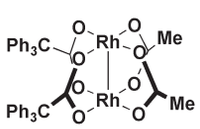


1 **2**

Results

Preliminary studies and chelate design

The current method of macrocycle synthesis requires a complex with a pair of firmly attached *cis*-related carboxylates, otherwise insoluble polymers are formed. Our starting point was the structurally characterised *cis* complex $(Ph_3CCO_2)_2Rh_2(OAc)_2$ **3b**, originally prepared by heating $Rh_2(OAc)_4$ in molten triphenylacetic acid.[5] We found this complex was more conveniently prepared by heating $Rh_2(OAc)_4$ with two equivalents of triphenylacetic acid in *N*,*N*-dimethylaniline, providing **3b** as the major species (57%), along with some of the *trans* isomer **3c** (9%), and the monosubstituted compound $(Ph_3CCO_2)Rh_2(OAc)_3$ **3a** (7%), and trisubstituted species $(Ph_3CCO_2)_3Rh_2(OAc)$ **3d** (11%). It is worth mentioning that *N*,*N*-dimethylaniline (NNDMA) is a particularly effective solvent for carboxylate exchanges of dirhodium complexes since the reactions are complete within a few hours at 130–140 °C (driven by evaporation of acetic acid), reaction mixtures are usually homogeneous, and solvent is easily removed during work-up by an acid wash.



3b

To test the stability of the *cis* arrangement of triphenylacetates in **3b**, the complex was heated with an excess of benzoic acid, looking for selective exchange of the acetate groups by benzoate. However some triphenylacetate exchange occurred, so a kinetically more inert *cis* complex was sought. Reasoning that a bidentate ligand should be displaced less readily due to the chelate effect, aliphatic α,ω-diacids were reacted with $Rh_2(OAc)_4$ to give bridged *cis*-dicarboxylate complexes. The nine carbon diacid was the shortest chain to produce a chelate $(O_2C(CH_2)_7CO_2)Rh_2(OAc)_2$ **4a** (15%), accompanied by some of the bischelate $(O_2C(CH_2)_7CO_2)_2Rh_2$ **4b** (6%) (we use the terms monochelate and bischelate here to refer to dinuclear complexes containing one or two bridges between neighbouring carboxylate ligands). The yield of **4a** was too low to be synthetically useful, so on the basis of modelling studies we next prepared a series of more preorganised diacids **5**–**12**, which turned out to be effective chelates. A related diacid **13**

† Electronic supplementary information (ESI) available: Tables S1 and S2. See http://www.rsc.org/suppdata/nj/b3/b310008a/

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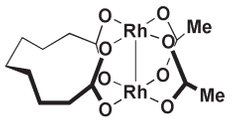
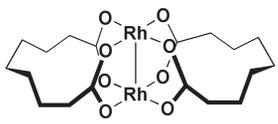
based on the binaphthyl skeleton was also screened, but gave only traces of a monochelate complex.



4a



4b

At this point we became aware of several other *cis*-chelated dirhodium complexes. Taber *et al.* prepared the first such example from diacid acid **14** and $Rh_2(CF_3CO_2)_4$.[6] We have confirmed that **14** is a moderately effective ligand, *vide infra*. Andersen *et al.* have reported polymer-bound chelates prepared by reaction of diacids **16** with $Rh_2(OAc)_4$ (the polymer is attached either *ortho* or *meta* to the phenolic link).[7] We prepared diacid **15** as a chemical model for **16**, but did not isolate a significant amount of chelate on reaction with $Rh_2(OAc)_4$. Gallagher *et al.* have described a dirhodium complex with two *cis*-chelated eleven atom dicarboxylate ligands.[8] More recently several other more sophisticated *cis*-spanning diacids have been used to prepare dirhodium-based catalysts for carbene transfer reactions.[9,10]

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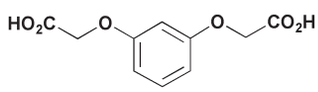

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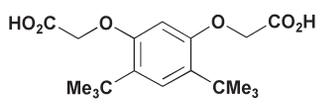

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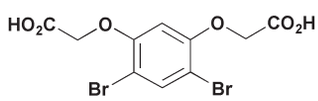

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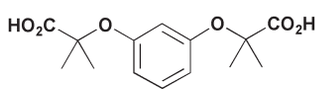

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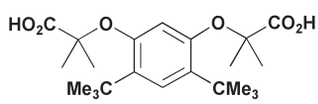

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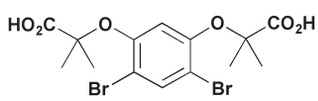

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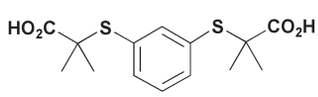

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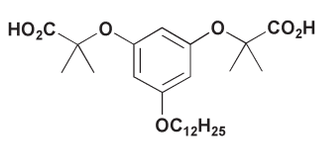

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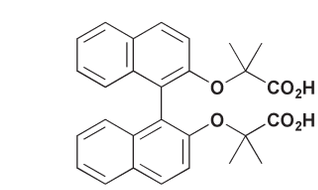

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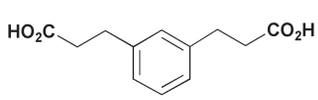

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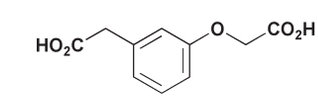

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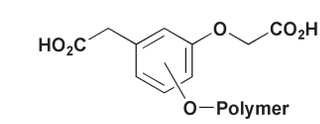
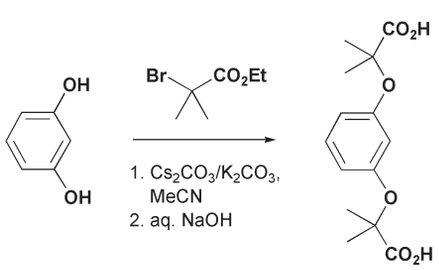


Synthesis of diacids

Diacids **5**, **6**, **8**, **11**, and **12** were prepared in straightforward fashion by O-alkylation of resorcinol or a resorcinol derivative with methyl bromoacetate or ethyl 2-bromo-2-methylpropanoate, followed by ester hydrolysis, illustrated in Scheme 1 for diacid **8**. Benzene-1,3-dithiol was the starting material for the sulfur analogue **11**. The use of Cs_2CO_3 in acetonitrile[11] was found to be efficient for making the more hindered tertiary phenolic ethers. On a large scale most of the Cs_2CO_3 is replaceable by K_2CO_3, and **8** could be prepared this way without the need for chromatography. Attempts to introduce substituents larger than methyl next to the acid group (*e.g.* ethyl, phenyl) by alkylation with the appropriate α-bromoester gave low yields. In the case of bis-*tert*-butyl compound **9**, O-alkylation of 4,6-bis-*tert*-butylresorcinol was slow, and the *tert*-butyl substituents were introduced after ether bond formation by silica gel-catalysed C-alkylation[12] of the diethyl ester of **8**. The bromo substituents in **7** and **10** were also conveniently introduced after O-alkylation by direct bromination.[13]

Synthesis of chelates

Chelates were prepared by heating a 1:1 mixture of diacid and $Rh_2(OAc)_4$ (both 45 mM) in NNDMA at 140 °C. A mixture of unreacted $Rh_2(OAc)_4$, monochelate and bischelate was generally produced and separated by chromatography. The yield of monochelate (Table 1) varies from 14% for complex **5a** without geminal methyl groups or *ortho* substituents to 79% for complex **10a** with both geminal methyls and *ortho* bromines.



Scheme 1 Synthesis of diacid **8**.

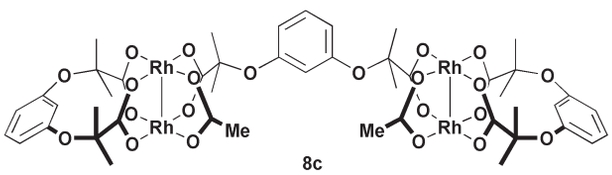
Table 1 Yields and equilibrium constants for chelate formation

Diacid	Monochelate	Yield[a] (%)	Bischelate	Yield (%)	K_1[b]/M
5	**5a**	14	—[c]	—	<10
6	**6a**	47	—	—	560 (±20)
7	**7a**	53	—	—	[d]
8	**8a**	63	**8b**	14	370 (±120)
9	**9a**	69	**9b**	4.5	1890 (±190)
10	**10a**	79	**10b**	6	810 (±50)
11	**11a**	65	—	—	—
12	**12a**	65	**12b**	14	—
14	**14a**	33	**14b**	4	80 (±10)

[a] Diacid (45 mM) and $Rh_2(OAc)_4$ (45 mM) heated at 140 °C for 1–4 h in *N*,*N*-dimethylaniline. [b] Equilibrium constant for formation of monochelate at 100 °C in $C_2D_2Cl_4$. [c] Not isolated. [d] Not measured due to low solubility of **7a**.

The synthesis of **5a** is certainly not clean, with several uncharacterised species formed. By-products from some of the other ligands were characterised, an example being the dimeric compound **8c**, a minor component from the reaction of diacid **8** with $Rh_2(OAc)_4$ at higher concentration (90 mM).

Complexes with geminal methyl groups are more soluble in non-polar solvents than those without. As expected, *tert*-butyl and dodecyloxy substituents on the aromatic ring also increase complex solubility, although *ortho*-bromine substituents decreased it. The sulfur containing complex **11a** was found to be almost insoluble in any solvent, possibly due to intermolecular S–Rh coordination, and had to be isolated as its more readily handled *tert*-butylpyridine adduct.



8c

Reaction of a 1:1 mixture of diacid and $Rh_2(OAc)_4$ should give a statistical 1:2:1 ratio of unreacted $Rh_2(OAc)_4$: monochelate: bischelate, assuming there are no kinetic or thermodynamic features favouring particular species, and that oligomers are not formed. Heating a monochelate or bischelate alone in NNDMA does not result in interconversion, but the reaction can be partly or completely reversed if enough acetic acid is added. Further heating, allowing the excess acetic acid allowed to evaporate, gives the same product distribution as when starting from $Rh_2(OAc)_4$ and diacid. This suggests that monochelates are formed under kinetic control in NNDMA. The greater than statistical ($>50\%$) yields for **7a**–**12a** must then arise because the chelate ligand slows down substitution of the remaining two acetates. Qualitative tlc experiments support this conclusion; when monochelates **8a**, **9a** and **10a** were reacted in parallel with excess benzoic acid, the acetates in **9a** and **10a** were substituted more slowly than those in **8a**.

To compare the relative stabilities of different chelates, conditions were sought under which ring formation was reversible. It was found that chelation under thermodynamic control could be achieved by heating the reactants at relatively high dilution in tetrachloroethane in the presence of acetic acid. Equilibrium constants K_1 (Table 1) were measured by ^{1}H NMR in both the forward direction ($LH_2 + Rh_2(OAc)_4$) and the reverse direction ($LRh_2(OAc)_2 + AcOH$), eqn. 1 (LH_2 = diacid, $LRh_2(OAc)_2$ = monochelate).

$$Rh_2(OAc)_4 + LH_2 \underset{}{\overset{K_1}{\rightleftharpoons}} LRh_2(OAc)_2 + 2\,AcOH \quad (1)$$

Chelate stabilities generally increase in line with isolated yields except for diacids **9** and **10** where the *tert*-butyl-substituted chelate **9a** is more stable than the bromo-substituted chelate **10a**. The equilibrium constant K_2 between monochelate and bischelate, eqn. 2, was measured in once instance, for the **8a**, **8b** pair, giving $K_2 = 63$ (± 14) M. This value is somewhat lower than expected on statistical grounds ($K_1/4 = 93$ M) implying that the first chelate destabilises the second ring slightly.

$$LRh_2(OAc)_2 + LH_2 \underset{}{\overset{K_2}{\rightleftharpoons}} L_2Rh_2 + 2\,AcOH \quad (2)$$

Crystal structures of diacids

In an attempt to correlate structure with stability, X-ray structures of diacid ligands **5**, **6**, **8**, **10** and **11** were obtained, Fig. 1. Suitable crystals of diacids **7** and **9** proved elusive, but the dimethyl ester of **7** was solved, and is included. Compared to the unsubstituted diacid **5**, there is a general trend for the ether arms to be oriented out of the plane of the aromatic ring on introducing *ortho* substituents. Thus the carboxyl groups

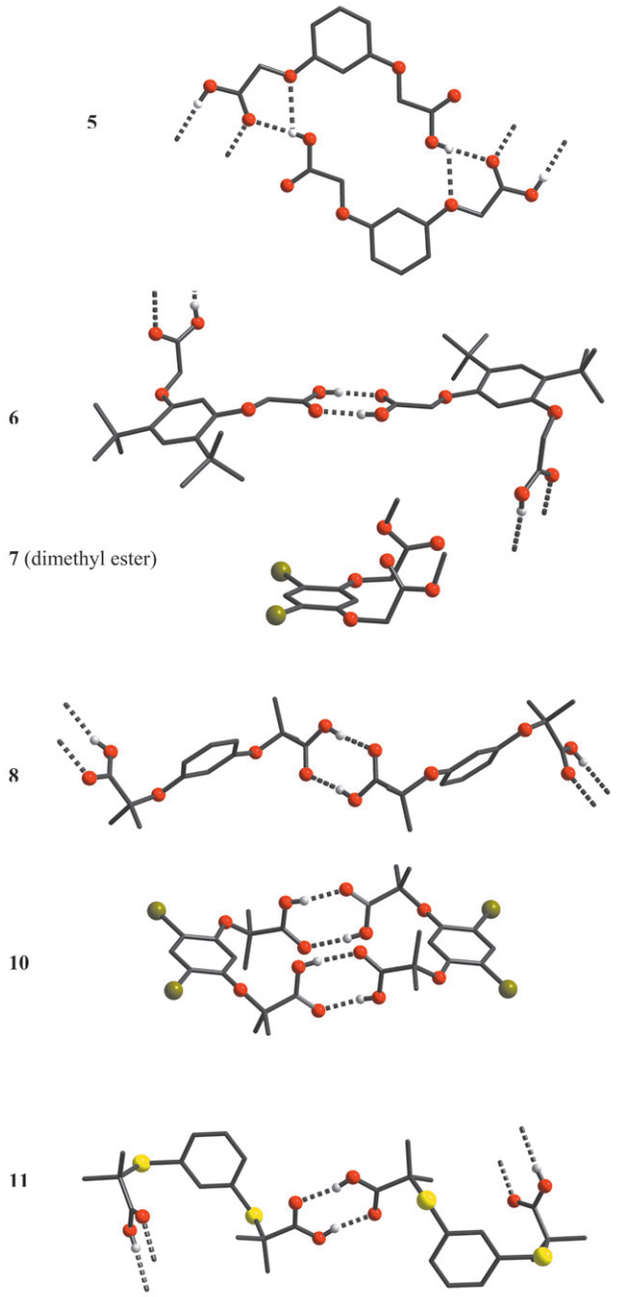


Fig. 1 Crystal structures of diacids (red = oxygen, green = bromine, yellow = sulfur).

adopt a more convergent orientation in the sequence **5**, **6**, **7**, and diacid **10** is also more convergent than diacid **8**. Most of the diacids pack as expected, forming hydrogen bonded chains or dimers.[14] There are numerous C–H···O, C–H···π and in some cases π···π interactions which in combination with the stronger diacid hydrogen bonds presumably determine the structural details.[15] The simplest diacid **5** is the only one for which the carboxylic acids are not all paired. This crystallised as stacks of slightly ruffled 2D sheets with one of the acids linked by a single, unsymmetrically bifurcated hydrogen bond. Closer examination reveals a network of C–H···O interactions both within and between the sheets, with particularly short distances to the singly hydrogen bonded acid.

Modelling studies

The preferred conformations of dimethyl esters of ligands **5**–**15** were explored with molecular mechanics using the MMFF94 force field,[16] Fig. 2. Esters rather than diacids were modelled

since diacids tend to end up intramolecularly hydrogen bonded in gas phase minimisations, whereas in reality any hydrogen bonding is likely to be to the solvent. The pK_a of NNDMA in water[17] (pK_a = 5.15) is higher than typical phenoxyacetic acids (p$K_a \sim 3$) so the acids may in fact be partly dissociated in NNDMA; we have no experimental evidence on this point. Stable conformations are arranged in Fig. 2 according the distance between the carbonyl carbons, with the population of a particular conformation represented by the height of its bar. A pair of *cis* carbonyl carbons is separated by ~3.5 Å in a typical dirhodium chelate complex,[18] so ligands which have most of their low energy conformations approaching this value might be expected to be good ones.

Comparing ligands **5**, **6** and **7**, it is clear that *ortho* substituents are predicted to bring the carbonyls closer together. Thus the major conformation (52% occupied) of the unsubstituted ligand **5** has a CO···CO distance of 8.8 Å whereas the major conformation (59% occupied) of the bisbromo ligand **7** has a CO···CO distance of 4.5 Å. Comparing ligands **5** and **8**, geminal dimethyls are also predicted to preorganise the ligand for chelation. Comparing ligands **8**, **9** and **10**, the main effect of introducing additional aromatic substituents is to reduce the number of extended conformations. Of the ligands **13**, **14** and **15**, only the all-carbon ligand **14** is predicted to have accessible conformations of suitable geometry. Overall, there is a qualitative correlation between the synthetic yields and the degree of preorganisation as estimated from molecular mechanics.

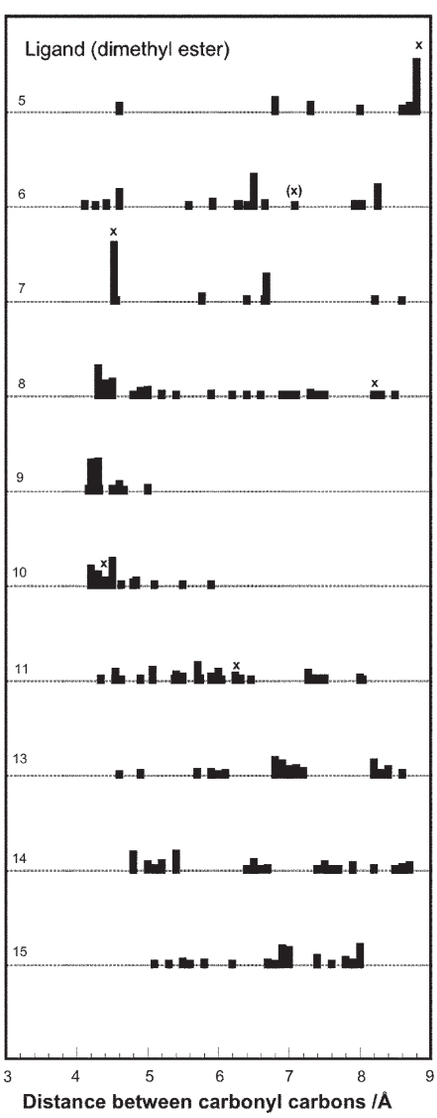


Fig. 2 Calculated conformations of ligand dimethyl esters, plotted as a function of the distance between carbonyl carbons. The population of each conformation is represented by the height of its bar. Conformations marked x are similar to the crystal structure.

For ligands **5** and **7**, the conformations in the crystal (marked with x in Fig. 2) are similar to the expected major solution conformations. However for ligand **8** the solid state conformation is predicted to be one the minor high energy ones in solution (CO···CO = 8.3 Å, 1% occupied), and for **6** none of the calculated conformations are good matches for the solid state structure (the conformation marked (x) is the closest).

To further investigate the thermodynamics of complexation, empirical and quantum mechanical methods were used to model the isodesmic exchange reaction between ligand dimethyl esters (LMe_2) and $Rh_2(OAc)_4$ (eqn. 3).

$$Rh_2(OAc)_4 + LMe_2 \rightleftharpoons LRh_2(OAc)_2 + 2\ AcOMe \quad (3)$$

As a semi-quantitative indication of strain induced on forming the chelate, we subtracted the lowest energy conformation of a ligand diester from the lowest energy conformation of its monochelate, Table 2. For ease of comparison energy differences are quoted relative to the simplest ligand **5**. The overall trend for the resorcinol-based ligands is that chelation becomes more favourable with increasing substitution of ligand **5**, as observed experimentally. According to these calculations ligand **14** forms the least strained complex, although experimentally it is one of the poorer ligands. Significantly, both types of calculation predict that ligands **13** and **15**, which are ineffective chelates, should form much less stable rings.

Discussion

Why is chelate synthesis in NNDMA under kinetic control? The mechanism of carboxylate exchange in dirhodium complexes is not known, but may require prior coordination of the incoming carboxylic acid to the Lewis acidic Rh_2 centre, followed by a thermal rate determining step.[19] A basic solvent like NNDMA would compete with incoming acids for Rh, slowing the kinetics. This assumption is supported by the finding that carboxylate exchange in tetrachloroethane at 100 °C, which is reversible, can be inhibited by donor solvents like 1,4-dioxane and NNDMA. Nevertheless, the acetates of monochelate **8a** are exchangeable in NNDMA under equilibrating conditions[4] suggesting that the thermodynamic stability of the chelates also contributes to the slow kinetics.

A useful measure of the effectiveness of a chelating ligand is its thermodynamic effective molarity (EM),[20] defined for a bidentate ligand as the concentration of a monodentate

Table 2 Calculated energies for chelate formation

Ligand	$\Delta\Delta E$/kJmol^{-1} [a] UFF[b]	$\Delta\Delta E$/kJmol^{-1} DFT[c]
5	0	0
6	−1	−18
7	−6	−11
8	−28	−20
9	−23	−17
10	−18	−22
13	+204	+64
14	−31	−26
15	+69	+19

[a] $\Delta\Delta E = E_{chelate} - E_{ligand(Me)} - (E_{\mathbf{5a}} - E_{\mathbf{5}(Me)})$, where $E_{ligand(Me)}$ is the energy of the ligand dimethyl ester. [b] Universal force field as implemented in Cerius.[2] [c] Density functional method pBP/DN* as implemented in Spartan.

analogue required to give the same degree of reaction. For formation of a monochelate, eqn. 1, the simplest definition is $EM_1 = K_1/K^2$, where K is the equilibrium constant for reaction of one end of the bidentate ligand with $Rh_2(OAc)_4$. Assuming that the acid groups in a diacid are equivalent to acetic acid, then $K \sim 1$, and $EM_1 \sim K_1$ for the diacids (Table 1).[21] There appears to be little thermodynamic data on large ring chelates in the literature with which to compare these numbers, but the polydentate ligands used as siderophores have EMs in the same range.[22] For our purposes the important finding is that the EMs for chelating diacids such as **8** are much higher than the concentrations at which macrocycle self-assembly reactions are run, so corner protection remains effective.

Turning to the conformational properties of the diacids, these ligands incorporate several features familiar from the study of organic reactivity, including steric buttressing by *ortho* substituents, and the 'gem dimethyl effect'.[23] In the present study conformational analysis was found to be a useful and rapid way of rationalising the effectiveness of different ligand designs. The approach is similar to the 'near attack conformation' analysis of rates of intramolecular reactions.[24] Ligands which are not preorganised for chelation such as **5**, **13** and **15** (see Fig. 2) have a greater tendency to react intermolecularly, giving low yields of chelated complexes. The failure to isolate any complex from ligand **15** suggests that the complexes derived from polymer-bound ligand **16** may not in fact be chelated.[7]

There is only limited correlation between the conformation of a ligand in the crystal and the conformation calculated in solution, *e.g.* for diacid **8** the acid groups are pointing in opposite directions in the crystal, Fig. 1, but are calculated to be more convergent in solution, Fig. 2. The large number of intermolecular interactions for **5** is presumably the reason why both ends do not form a hydrogen bonded acid dimer, which is otherwise a fairly persistent supramolecular synthon.[14]

In summary, we have prepared a family of *cis*-spanning ligands for the Rh_2^{4+} core; the ligands are easy to make, and stability and solubility can be adjusted by adding substituents. The picture that emerges from experiment and modelling is that as more substituents are added to the resorcinol *O*,*O*′-diacetic acid skeleton **5**, the energy of the initial state of the chelation process (eqn. 1) is raised more than the final state, increasing the thermodynamic driving force and the rate of the forward reaction. The present work appears to be one of the few instances in which ligands have been designed to chelate dinuclear complexes,[6,9] and polynuclear species in general.[25,26]

Experimental

Diacid ligands and rhodium complexes were prepared under nitrogen. Weakly bound solvent ligands were removed from dirhodium complexes by heating under vacuum overnight. Solvent was the internal reference for NMR spectra in d_6-acetone and d_2-tetrachloroethane, and TMS was the reference in $CDCl_3$ or mixed solvents containing mostly $CDCl_3$. Coupling constants are in Hz. Fast atom bombardment (FAB) mass spectra were obtained on a VG7070E instrument using *m*-nitrobenzyl alcohol as matrix, chemical ionisation (CI) spectra were obtained on a TRIO1000 instrument, and electrospray (ES) spectra were obtained on a Micromass LCT instrument. Masses are quoted for the most intense isotopomer peak in the molecular ion envelope. Silica gel of 230–400 mesh was used for column chromatography. Organic extracts were dried over Na_2SO_4. Solvents dimethylformamide (DMF), dichloromethane (DCM), ethyl acetate (EtOAc), ethanol (EtOH), acetonitrile (MeCN) and methanol (MeOH) were reagent grade, and were dried when necessary using standard procedures. Melting points for metal complexes were $>240\,^{\circ}C$ unless otherwise indicated, and are uncorrected. Diacid **5** was obtained from Lancaster.

(3-Carboxymethoxy-2,5-di-*tert*-butylphenoxy)ethanoic acid (6)

A mixture of 1,3-dihydroxy-2,5-di-*tert*-butylbenzene (0.50 g, 2.25 mmol), methyl bromoacetate (1.5 g, 10 mmol), and K_2CO_3 (1.5 g, 11 mmol) in DMF (2 ml) was stirred at 60 °C for 2 h. The resulting slurry was partitioned between diethyl ether and water. The organic layer was washed several times with water, dried, and evaporated to an oil which solidified on standing under vacuum. The crude dimethyl ester thus obtained was refluxed in a mixture of MeOH (20 ml) and aqueous NaOH (10 M; 1 ml) for 3 h. Most of the MeOH was evaporated under reduced pressure, and the residue acidified with aqueous HCl. The suspension was filtered, washing with water to give **6** as a white solid (0.70 g, 92%), mp 203–205 °C (Found: C, 63.8; H, 7.8. $C_{18}H_{26}O_6$ requires C, 63.89; H, 7.81); δ_H(300 MHz, d_6-acetone) 1.4 (18 H, s), 4.74 (4 H, s), 6.59 (1 H, s), 7.23 (1 H, s); δ_C(75 MHz, d_6-acetone) 29.80, 34.36, 65.11, 99.25, 124.88, 129.70, 155.60, 169.55. *m*/*z* (FAB) 338.2 (M^+).

(3-Carboxymethoxy-2,5-dibromophenoxy)ethanoic acid (7)

A mixture of 1,3-dihydroxybenzene (1.1 g, 10 mmol), methyl bromoacetate (3.4 g, 22 mmol), and K_2CO_3 (3.0 g, 10 mmol) in DMF (3 ml) was stirred at 70 °C for 5 h. The resulting slurry was partitioned between EtOAc–diethyl ether and water. The organic layer was washed several times with water, dried, and evaporated to an oil (2.4 g) which solidified on standing under vacuum. The dimethyl ester of **5** thus produced was pure enough for use in subsequent reactions. δ_H(200 MHz, $CDCl_3$) 3.80 (6 H, s), 4.60 (4 H, s), 6.5 (3 H, m), 7.2 (1 H, m). Bromine (200 μl, 3.90 mmol) was added dropwise to a stirred solution of above dimethyl ester (0.50 g, 1.97 mmol) in DCM (10 ml) at ice-bath temperature. After 30 min the reaction mixture was diluted with DCM, washed with aqueous sodium bisulfite (1 M), and the organic layer dried and evaporated to a white solid. δ_H(200 MHz, $CDCl_3$) 3.80 (6 H, s), 4.66 (4 H, s), 6.44 (1 H, s), 7.72 (1 H, s). The crude dibromo diester thus obtained was heated in a mixture of EtOH (20 ml) and aqueous NaOH (1 M; 8 ml) at 80 °C for 30 min. Most of the EtOH was evaporated under reduced pressure, and the residue acidified with aqueous HCl. The suspension was filtered, washing with a small quantity of cold water to give **7** as a white solid (0.60 g, 79%), mp $>240\,^{\circ}C$ (Found: C, 31.2; H, 2.1. $C_{10}H_8Br_2O_6$ requires C, 31.28; H, 2.10); δ_H(400 MHz, d_6-acetone) 4.86 (4 H, s), 6.90 (1 H, s), 7.73 (1 H, s); *m*/*z* (FAB) 383.2 (M^+); δ_C(100 MHz, d_6-acetone) 66.99, 102.35, 104.46, 137.00, 156.32, 169.69.

2-(3-(1-Carboxy-1-methylethoxy)phenoxy)-2-methylpropanoic acid (8)

K_2CO_3 (27.6 g, 200 mmol) and Cs_2CO_3 (16.3 g, 50 mmol) were added to a stirred solution of 1,3-dihydroxybenzene (5.5 g, 50 mmol) and ethyl 2-bromo-2-methylpropanoate (48.75 g, 250 mmol) in dry MeCN (125 ml). After stirring at 80 °C for 24 h, the reaction mixture was partitioned between ether and water. The yellow organic layer was washed consecutively with hydrochloric acid (2 M), brine, pH 7 buffer solution (1 M), then dried and evaporated to a yellow oil which was left under vacuum (1 mmHg) at 50 °C overnight to remove excess ethyl 2-bromo-2-methylpropanoate. The crude diethyl ester of **8** thus produced (15.9 g, 94%) was pure enough to be used in the next step. δ_H(200 MHz, $CDCl_3$) 1.25 (6 H, t, *J* 7), 1.56 (12 H, s), 4.23 (4 H, q, *J* 7), 6.38 (1 H, t, *J* 2.5), 6.48 (2 H, dd, *J* 8, 2.5), 7.07 (1 H, t, *J* 8); *m*/*z* (FAB) 338 (M^+). Aqueous NaOH

(1 M; 50 ml) was added to a solution of the above diethyl ester (7 g, 20.7 mmol) in EtOH (50 ml) and stirred at 60 °C overnight. The volatiles were removed and the residue was partitioned between EtOAc (50 ml) and aqueous HCl (2 M; 50 ml). The organic layer was dried and evaporated to an oil that crystallised slowly on standing affording **8** (5 g, 86%), mp 94–96 °C (Found: C, 59.72; H, 6.47. $C_{14}H_{18}O_6$ requires C, 59.57; H, 6.43); δ_H(400 MHz, d_6-acetone) 1.57 (12 H, s), 6.52 (1 H, t, *J* 2.3), 6.57 (2 H, dd, *J* 8.2, 2.3), 7.12 (1 H, t, *J* 8.2); δ_C(100 MHz, d_6-acetone) 26.05, 80.09, 111.82, 114.08, 130.32, 157.82, 175.73; *m*/*z* (FAB) 282.2 (M^+), 305.2 ($M + Na^+$).

2-(3-(1-Carboxy-1-methylethoxy)-2,5-di-*tert*-butylphenoxy)-2-methylpropanoic acid (9)

tert-Butyl bromide (7.67 g, 56 mmol) was added to a stirred solution of the diethyl ester of **8** (2.1 g, 6.2 mmol, prepared as described above), Na_2CO_3 (5.95 g, 56 mmol) and silica gel (7 g) in dry tetrachloromethane (50 ml). After stirring at 70 °C for 24 h, the reaction mixture was filtered and the silica washed thoroughly with diethyl ether. The washings were combined with the filtrate and the solvent evaporated to give a pale yellow oil, which was purified by column chromatography (0 to 10% EtOAc in hexane) to give the diethyl ester of **9** as a crystalline solid (1.89 g, 68%) which was used without further purification; (Found: C, 69.4; H, 9.5. $C_{26}H_{42}O_6$ requires C, 69.30; H, 9.39); δ_H(200 MHz, $CDCl_3$) 1.22 (6 H, t, *J* 7), 1.36 (18 H, s), 1.61 (12 H, s), 4.23 (4 H, q, *J* 7), 5.74 (1 H, s), 7.17 (1 H, s); *m*/*z* (FAB) 450.3 (M^+). Aqueous NaOH (1 M; 5 ml) was added to a solution of the above diethyl ester (0.9 g, 2 mmol) in EtOH (15 ml) and stirred at 60 °C overnight. The volatiles were removed and the residue was partitioned between EtOAc and aqueous HCl (2 M). The organic layer was dried and evaporated to give **9** as white crystalline solid (0.72 g, 91%), mp 194–196 °C (Found: C, 67.0; H, 8.7. $C_{22}H_{34}O_6$ requires C, 66.98; H, 8.69); δ_H(400 MHz, d_6-acetone) 1.33 (18 H, s), 1.66 (12 H, s), 6.11 (1 H, s), 7.21 (1 H, s); δ_C(100 MHz, d_6-acetone) 26.42, 30.97, 35.37, 79.09, 106.04, 125.89, 130.82, 153.21, 175.73; *m*/*z* (FAB) 394.3 (M^+), 417.2 ($M + Na^+$).

2-(3-(1-Carboxy-1-methylethoxy)-2,5-dibromophenoxy)-2-methylpropanoic acid (10)

Bromine (77 µl, 1.47 mmol) was added dropwise to a stirred solution of the diethyl ester of **8** (0.25 g, 0.73 mmol, prepared as described above) in DCM (2 ml) at ice-bath temperature. After 10 min the reaction mixture was diluted with DCM, washed with aqueous sodium bisulfite (1 M), and the organic layer dried and evaporated to a light yellow oil (0.358 g) which was pure enough to use in the next step. δ_H(200 MHz, $CDCl_3$) 1.29 (4 H, t, *J* 7), 1.58 (12 H, s), 4.25 (4 H, q, *J* 7), 6.56 (1 H, s), 7.69 (1 H, s). The crude dibromoester thus obtained was heated in a mixture of EtOH (6 ml) and aqueous NaOH (1 M; 3 ml) at 80 °C for 12 h. Most of the EtOH was evaporated under reduced pressure, the residue acidified with aqueous HCl and partitioned between EtOAc and brine. The organic phase was washed with brine, dried, and evaporated to an oil which crystallized on standing to give **10** (0.311 g, 95%), mp 174–176 °C (Found: C, 38.3; H, 3.7. $C_{14}H_{16}Br_2O_6$ requires C, 38.21; H, 3.66); δ_H(300 MHz, d_6-acetone) 1.61 (12 H, s), 6.85 (1 H, s), 7.74 (1 H, s); δ_C(75 MHz, d_6-acetone) 24.81, 81.03, 107.81, 110.77, 135.62, 152.55, 173.89. *m*/*z* (FAB) 439.9 (M^+). Bromoacid **10** was also prepared in 97% yield by direct bromination of diacid **8**, following the same bromination method as above (a beige precipitate formed shortly after addition of bromine).

2-(3-(1-Carboxy-1-methyl(ethylsulfanyl))-phenylsulfanyl)-2-methylpropanoic acid (11)

A mixture of benzene-1,3-dithiol (159 mg, 1.12 mmol), ethyl 2-bromo-2-methylpropanoate (585 mg, 3 mmol), Cs_2CO_3 (1.0 g, 3 mmol) in dry MeCN (5 ml) was stirred at RT for 12 h. After partitioning between diethyl ether and water the yellow organic phase was washed twice with water, dried, and evaporated to an oil. The dimethyl ester of **11** thus produced was pure enough for use in subsequent reactions. δ_H(300 MHz, $CDCl_3$) 1.24 (6 H, t, *J* 7), 1.49 (12 H, s), 4.12 (4 H, q, *J* 7), 7.28 (1 H, m), 7.48 (2 H, dd, *J* 7.5, 1.8), 7.63 (1 H, t, *J* 1.8). The above crude product was refluxed in a mixture of MeOH (12 ml) and aqueous NaOH (1 M; 5 ml) for 5 h. Most of the EtOH was evaporated under reduced pressure, the residue acidified with aqueous HCl and then partitioned between EtOAc and brine. The organic phase was washed with brine, dried, and evaporated to an oil which crystallized on standing to give **11** (0.310 g, 88%), mp 129–131 °C (Found: C, 53.4; H, 5.7. $C_{14}H_{18}O_4S_2$ requires C, 53.48; H, 5.77); δ_H(200 MHz, d_6-acetone) 1.46 (12 H, s), 7.37 (1 H, m), 7.56 (2 H, m), 7.70 (1 H, t, *J* 1.8); *m*/*z* (FAB) 314.1 (M^+); δ_C(75 MHz, d_6-acetone) 25.49, 50.76, 129.11, 132.64, 137.56, 144.51, 174.48.

2-(3-(1-Carboxy-1-methylethoxy)-5-dodecyloxyphenoxy)-2-methylpropanoic acid (12)

A mixture of 1,3,5-trihydroxybenzene (4.0 g, 32 mmol), 1-bromododecane (2.49 g, 10 mmol) and K_2CO_3 (1.5 g, 11 mmol) in DMF (10 ml) was stirred at RT for 8 h, then at 75 °C for 4 h. The resulting reddish slurry was partitioned between diethyl ether and aqueous HCl (1 M). The organic phase was washed twice with water, dried, and evaporated to a yellow solid. Chromatography (30% hexane in EtOAc) provided 1,3-dihydroxy-5-dodecyloxybenzene as beige flakes (0.985 g, 33%) pure enough for use in subsequent reactions. δ_H(200 MHz, d_6-acetone) 0.87 (3 H, br t), 1.1–1.5 (18 H, br m), 1.6–1.8 (2 H, m), 3.86 (2 H, t, *J* 6.6), 5.95 (3 H, m), 8.14 (2 H, s, OH); *m*/*z* (FAB) 295.2 (MH^+). A mixture of 1,3-dihydroxy-5-dodecyloxybenzene (0.35 g, 1.2 mmol), ethyl 2-bromo-2-methylpropanoate (2.0 g, 10 mmol), and Cs_2CO_3 (3.34 g, 10 mmol) in MeCN (3 ml) was stirred at 50 °C for 12 h. The reaction mixture was partitioned between diethyl ether and aqueous HCl (1 M). The organic phase was washed twice with water, dried, and evaporated to a yellow solid. Chromatography (10% EtOAc in hexane) provided the diethyl ester of **12** as a colourless oil (0.410 g, 69%); δ_H(200 MHz, $CDCl_3$) 0.88 (3 H, br t), 1.1–1.5 (24 H, br m), 1.56 (12 H, s), 1.6–1.8 (2 H, m), 3.83 (2 H, t, *J* 6.6), 4.23 (4 H, q, *J* 7), 5.92 (1 H, t, *J* 2), 6.08 (2H, d, *J* 2). The above diethyl ester was then refluxed in a mixture of EtOH (15 ml) and aqueous NaOH (4 ml; 1 M) for 12 h. Most of the EtOH was evaporated under reduced pressure, and the residue partitioned between EtOAc and brine. The organic phase was washed with brine, dried, and evaporated to an oil which crystallized on standing to give **12** (0.363 g, 94% from diester), mp 71–73 °C (Found: C, 66.7; H, 9.1. $C_{26}H_{42}O_7$ requires C, 66.93; H, 9.07); δ_H(300 MHz, d_6-acetone) 0.88 (3 H, br t), 1.1–1.5 (18 H, br m), 1.56 (12 H, s), 1.73 (2 H, m), 3.89 (2 H, t, *J* 6.6), 6.08 (1 H, t, *J* 2), 6.14 (2H, d, *J* 2); *m*/*z* (FAB) 467.3 (MH^+), 489.2 ($M + Na^+$); δ_C(75 MHz, d_6-acetone) 13.56, 22.55, 24.91, 26.09, 31.87, 67.91, 79.02, 99.86, 102.76, 157.32, 159.86, 174.68.

2-(2′-(1-Carboxy-1-methylethoxy)-[1,1′]-binaphthalenyl-2-yloxy)-2-methylpropanoic acid (13)

Caesium carbonate (5.85 g, 18.0 mmol) was added to a stirred solution of (±)-1,1′-binaphthalene-2,2′-diol (1.0 g, 3.5 mmol) and ethyl 2-bromo-2-methylpropanoate (3.5 g, 17.9 mmol) in MeCN (8.0 ml). After heating at 80 °C for 2 hours, the mixture

was partitioned between EtOAc and aqueous HCl. The pale yellow organic layer was washed twice with aqueous HCl, then dried and evaporated to afford an oily yellow solid (0.99 g). Aqueous NaOH (2 M, 5 ml) was added to a solution of the yellow solid in hot EtOH (15 ml) and stirred at 50 °C overnight. The volatiles were removed and the solution was acidified with aqueous HCl causing a white solid to precipitate. This aqueous suspension was heated to near boiling (solid dissolved) and then left to cool. Filtration gave **13** as a white solid (0.57 g, 36%), mp 80–82 °C (Found: C, 73.3; H, 5.7. $C_{28}H_{26}O_6$ requires C, 73.35; H, 5.72); δ_H(400 MHz, d_6-acetone) 1.07 (6 H, s), 1.11 (6 H, s), 6.91 (1 H, d, *J* 8), 7.04 (1 H, t, *J* 8), 7.15 (1 H, t, *J* 8), 7.20 (1 H, d, *J* 9), 7.71 (1 H, d, *J* 8), 7.76 (1 H, d, *J* 9); δ_C(100 MHz, d_6-acetone) 25.2, 26.09, 80.42, 120.36, 124.61, 125.20, 126.91, 127.25, 129.70, 131.02, 135.31, 152.54, 176.43; *m*/*z* (FAB) 458.3 (M^+); *m*/*z* (ES, MeOH) 457.1640 [$(M–H)^-$ requires 457.1651].

3-(3-(2-Carboxyethyl)phenyl)propanoic acid (14)

This diacid was prepared using a minor modification of the literature method.[27] A mixture of malonic acid (8.5 g, 82 mmol) and benzene-1,3-dicarboxaldehyde (3.62 g, 27 mmol) in pyridine (10 ml) was stirred at 50 °C for 2 h and 100 °C for 2.5 h. After cooling the mixture was poured into aqueous sulfuric acid (50 ml, 1 M) and the white precipitate filtered and dried to give 3-(3-(2-carboxyvinyl)phenyl)prop-2-enoic acid as a white powder (5.7 g, 97%). A sample of this crude diacid (436 mg, 2 mmol) was stirred in a mixture of aqueous NaOH (0.5 ml, 6.25 M), water (3 ml) and palladium on carbon (30 mg, 10% w/w) under hydrogen (65 psi) for 24 h. The catalyst was filtered off, and the reaction mixture acidified with conc. aqueous HCl, producing a white precipitate. Acetic acid (0.7 ml) was added and the mixture stirred at 80 °C for 20 min to dissolve the precipitate. On cooling a precipitate was formed again which was filtered off, washing with water, to give diacid **14** as white crystals (130 mg, 29%) mp 134–136 °C (lit 148–150.5 °C) (Found: C, 64.6; H, 6.3. $C_{12}H_{14}O_4$ requires C, 64.85; H, 6.35); δ_H(400 MHz, d_6-acetone) 2.62 (4 H, t, *J* 8), 2.91 (4 H, t, *J* 8), 7.10 (2 H, d, *J* 7), 7.20 (2 H, m); δ_C(100 MHz, d_6-acetone) 31.91, 36.30, 127.28, 129.61, 129.64, 142.46, 174.28; *m*/*z* (CI, NH_3) 240 ($M + NH_4^+$).

(3-Carbomethoxyphenyl)ethanoic acid (15)

Acetyl chloride (0.5 ml) was added to a solution of 3-hydroxyphenylethanoic acid (1.0 g, 6.6 mmol) in dry MeOH (50 ml) and stirred at 50 °C for 1.5 h. Volatiles were evaporated and a solution of the residue in DMF (5 ml) stirred with methyl bromoacetate (1.6 g, 10.5 mmol) and K_2CO_3 (1.6 g, 11.6 mmol) at 80 °C for 3 h. The reaction mixture was diluted with EtOAc, washed three times with water followed by brine, and the organic layer dried and evaporated to a pale yellow oil. Aqueous NaOH (15 ml, 2.5 M) was added to a solution of the preceding oil in MeOH (50 ml) and stirred at 50 °C for 1 h. The volatiles were evaporated and the residue partitioned between EtOAc and aqueous HCl. The organic layer was dried and evaporated to give diacid **15** as a white solid (0.78 g, 57%), mp 130–132 °C (Found: C, 57.2; H, 4.8. $C_{10}H_{10}O_5$ requires C, 57.15; H, 4.80); δ_H(400 MHz, d_6-acetone) 3.62 (2 H, s), 4.72 (2 H, s), 6.86 (1 H, d, *J* 7.5), 6.96 (2 H, m), 7.26 (1 H, t, *J* 7.5); δ_C(100 MHz, d_6-acetone) 41.64, 65.82, 113.94, 117.26, 123.63, 130.55, 137.76, 159.55, 170.64, 173.08; *m*/*z* (CI, NH_3) 228 ($M + NH_4^+$).

Dirhodium complexes. The preparation of dirhodium complexes is illustrated below for **3a–d**. Monochelates and bischelates, green solids unless otherwise indicated, were prepared using the same method but at reactant concentrations 45 mM, following the reactions by tlc (reaction times 0.5 to 4 h, yields in (Table 1). The physical data and crystal structures of dirhodium complexes **8a**, **8b**, **9a**, **9b**, **10a**, **10b** have been described previously.[18]

$(Ph_3CCO_2)_nRh_2(OAc)_{4-n}$ (3a–d)

A solution of triphenylacetic acid (306 mg, 1.06 mmol) and $Rh_2(OAc)_4$ (235 mg, 0.53 mmol) in *N*,*N*-dimethylaniline (8 ml) was stirred at 125 °C for 6.5 h. The cooled reaction mixture was diluted with chloroform (40 ml) and washed with aqueous HCl (2 M) three times. The green solution was dried and evaporated to a green solid. Chromatography (0 to 25% MeCN in DCM) afforded four green compounds **3d** (63 mg, 11%) eluting in neat DCM, **3c** (45 mg, 9%) eluting in 5% MeCN, **3b** (270 mg, 57%) eluting in 10 to 15% MeCN and **3a** (23 mg, 7%) eluting in 20 to 25% MeCN. Analytical data for $(Ph_3CCO_2)_3Rh_2(OAc)$ **3a**: Found: C, 65.70; H, 4.20. $C_{62}H_{48}O_8Rh_2$ requires C, 66.08; H, 4.23; δ_H (200 MHz, $CDCl_3$) 2.16 (3 H, s), 6.80–7.20 (45 H, Ar); *m*/*z* (FAB) 1126.3 (M^+). Analytical data for *cis*-$(Ph_3CCO_2)_2Rh_2(OAc)_2$ **3b**: Found: C, 58.8; H, 4.1. $C_{44}H_{36}O_8Rh_2$ requires C, 58.81; H, 4.04; δ_H(200 MHz, $CDCl_3$) 1.87 (6 H, s), 6.92–6.95 (10 H, Ar), 7.10–7.20 (20 H, Ar); *m*/*z* (FAB) 898.1 (M^+). Analytical data for *trans*-$(Ph_3CCO_2)_2Rh_2(OAc)_2$**3c**: Found: C, 59.0; H, 4.1. $C_{44}H_{36}O_8Rh_2$ requires C, 58.81; H, 4.04; δ_H(200 MHz, $CDCl_3$) 1.60 (6 H, s), 6.80–6.85 (10 H, Ar), 6.90–7.20 (20 H, Ar); *m*/*z* (FAB) 897.9 (M^+). Analytical data for $(Ph_3CCO_2)Rh_2(OAc)_3$ **3d**: Found: C, 46.8; H, 3.6. $C_{26}H_{24}O_8Rh_2$ requires C, 46.59; H, 3.61; δ_H(200 MHz, $CDCl_3$) 1.90 (9 H, s), 6.90–7.20 (15 H, ar); *m*/*z* (FAB) 670.0 (M^+).

$(O_2C(CH_2)_7CO_2)Rh_2(OAc)_2$ (4a) and $(O_2C(CH_2)_7CO_2)_2Rh_2$ (4b)

$Rh_2(OAc)_4$ (200 mg, 0.45 mmol) and nonanedioic (75 mg, 0.40 mmol) in *N*,*N*-dimethylaniline (45 ml) was stirred at 140 °C. After 48 h, the reaction mixture was diluted with chloroform (30 ml) and MeCN (1 ml) and washed with hydrochloric acid (2 M) three times. The solution was dried and evaporated to give a green solid. Chromatography (10 to 35% MeCN in DCM) afforded two green compounds **4b** (15 mg, 6%) eluting at 15 to 20% MeCN and **4a** (35 mg, 15%) eluting at 25 to 35% MeCN. Analytical data for **4a**: δ_H(200 MHz, 5% v/v d_3-MeCN in $CDCl_3$) 0.99 (2 H, m), 1.20 (4 H, m), 1.62 (4 H, m), 1.96 (6 H, s), 2.21 (4 H, m); *m*/*z* (FAB) 509.8 (M^+); *m*/*z* (ES, MeOH) 532.9144 [$(M + MeOH + Na)^+$ requires 532.9166]. **4a**.(4-*tert*-butylpyridine)$_2$: δ_H(200 MHz, $CDCl_3$) 1.12 (2 H, m), 1.25 (4 H, m), 1.40 (18 H, s), 1.60 (4 H, m), 1.90 (6 H, s), 2.12 (4 H, m), 7.65 (4 H, brd), 9.20 (4 H, brs); Analytical data for **4b**: δ_H(200 MHz, 40% v/v d_3-MeCN in $CDCl_3$) 0.95 (4 H, m), 1.25 (8 H, m), 1.60 (8 H, m), 2.10 (8 H, m); *m*/*z* (FAB) 578 (M^+); *m*/*z* (ES, MeOH) 600.9800 [$(M + Na)^+$ requires 600.9729]. **4b**.(4-*tert*-butylpyridine)$_2$: δ_H(200 MHz, $CDCl_3$) 1.15 (4 H, m), 1.29 (8 H, m), 1.40 (18 H, s), 1.61 (8 H, m), 1.90 (6 H, s), 2.15 (8 H, m), 7.65 (4 H, brd), 9.20 (4 H, brs);

Analytical data for **5a**. Found: C, 31.1; H, 2.6. $C_{14}H_{14}O_{10}Rh_2$ requires C, 30.68; H, 2.58; δ_H(200 MHz, d_6-acetone) 1.77 (6 H, s), 4.44 (4 H, s), 5.44 (1 H, t, *J* 2.4), 6.40 (2 H, dd, *J* 8, 2.4), 7.07 (1 H, t, *J* 8); *m*/*z* (FAB) 548.3 (M^+).

Analytical data for **6a**: Found: C, 40.1; H, 4.6. $C_{22}H_{30}O_{10}Rh_2$ requires C, 40.02; H, 4.58; δ_H(200 MHz, 5% v/v d_3-MeCN in $CDCl_3$) 1.31 (18 H, s), 1.94 (6 H, s), 4.44 (4 H, s), 5.47 (1 H, s), 7.12 (1 H, s); *m*/*z* (FAB) 659.9971 [M^+ required 659.9949].

Analytical data for **7a**: Found: C, 23.9; H, 1.7. $C_{18}H_{20}Br_2O_{10}Rh_2$ requires C, 23.82; H, 1.71; δ_H(200 MHz, 5% v/v d_3-MeCN in $CDCl_3$) 1.94 (6 H, s), 4.57 (4 H, s), 5.60 (1 H, s), 7.64 (1 H, s); *m*/*z* (FAB) 705.7 (M^+).

Analytical data for **8c**: Found: C, 39.9; H, 4.1. $C_{45}H_{54}O_{22}Rh_4$ requires C, 40.31; H, 3.97; δ_H(200 MHz, 5% v/v d_4-MeOH in $CDCl_3$) 1.29 (12 H, s),1.36 (12 H, s), 1.39 (12 H, s), 1.91 (6 H, s), 6.05 (5 H, m), 6.50 (4 H, brd), 6.74 (1 H, t, *J* 8), 7.07 (2 H, t, *J* 8); *m*/*z* (FAB) 1369.9 (M^+).

Analytical data for **11a**.(4-*tert*-butylpyridine)$_2$: To keep this complex in solution 4-*tert*-butylpyridine was added during workup and to the chromatography solvent (0 to 2% MeOH in DCM). Red solid, mp 190 °C (dec); δ_H(200 MHz, $CDCl_3$) 1.31 (12 H, s), 1.39 (18 H, s), 1.87 (6 H, s), 7.1–7.4 (4 H, m), 7.56 (4 H, brd), 9.0 (4 H, brd); *m*/*z* (FAB) 770.9928 [M.Bu^{t}Py$^+$ requires 770.9949].

Analytical data for **12a**: Found: C, 45.9; H, 5.9. $C_{30}H_{46}O_{11}Rh_2$ requires C, 45.70; H, 5.88; δ_H(200 MHz, $CDCl_3$) 0.87 (3 H, brt), 1.25 (18 H, brs), 1.42 (12 H, s), 1.70 (2 H, m), 2.01 (6 H, s), 3.81 (2 H, brt), 5.58 (1 H, brt), 6.1 (2H, brd); *m*/*z* (FAB) 789.1 (M^+).

Analytical data for **12b**: Green glass, mp 72–75 °C (Found: C, 55.4; H, 7.1. $C_{52}H_{80}O_{14}Rh_2$ requires C, 55.03; H, 7.10); δ_H(200 MHz, 5% v/v d_4-MeOH in $CDCl_3$) 0.88 (6 H, brt), 1.26 (36 H, s), 1.33 (24 H, br s), 1.72 (4 H, m), 3.83 (4 H, brt), 5.57 (2 H, d, *J* 2), 6.08 (2H, d, *J* 2). *m*/*z* (FAB) 1153.3 (M^+).

Analytical data for **14a**. Found: C, 35.3; H, 3.4. $C_{16}H_{18}O_8Rh_2$ requires C, 35.32; H, 3.33; δ_H(200 MHz, 5% v/v CD_3CN in $CDCl_3$) 1.95 (6H, s), 2.31–2.42 (4H, m), 2.74–2.85 (4H, m), 6.87 (2 H, dd, *J* 7.5, 1.6), 7.00 (1H, brt), 7.11 (1 H, t, *J* 7.5); *m*/*z* (FAB) 543.9 (M^+)

Analytical data for **14b**. Found: C, 44.5; H, 3.9. $C_{24}H_{24}O_8Rh_2$ requires C, 44.61; H, 3.74; δ_H(300 MHz, 1% v/v d_4-MeOH in $CDCl_3$) 2.30–2.41 (8H, m), 2.70–2.81 (8H, m), 6.81–6.92 (6H, m), 7.08–7.17 (2H, m); *m*/*z* (FAB) 646.1 (M^+)

Chelate stability constants. The method is illustrated for reaction of monochelate **8a** with acetic acid. A solution of **8a** (4.8 mg) and d_4-acetic acid (50 μl) in d_2-tetrachloroethane (600 μl) was heated in a septum capped NMR tube at 100 °C until the ^{1}H NMR spectrum no longer changed (~24 h). The geminal methyl resonances for **8a** at 1.33 ppm and free diacid **8** at 1.54 ppm were integrated to give a ratio I_{8a}:I_8 = 1.28. The equilibrium constant was then calculated using $K_1 = I_{8a}(I_{8a} + I_8)[AcOH]^2/(I_8^2[8a]_o) = 392$ M, where $[8a]_o$ is the initial concentration of monochelate. The experiment was repeated using different concentrations of **8a** and acetic acid, adjusting the amounts so that the peaks to be integrated were not too different in intensity. Experiments in the forward direction started from an approximately equimolar mixture of $Rh_2(OAc)_4$ and diacid **8** (*ca* 20 mM each) with various amounts of acetic acid, letting the system come to equilibrium and integrating as above. Because of the difference in magnitude of K_1 and K_2 a negligible amount of bischelate **8b** is present under these conditions. The **8a**, **8b** equilibrium constant K_2 was measured starting from **8b** with the addition of small amounts of acetic acid (5–20 μl).

Modelling. MacSpartan Pro 1.0.3 (Wavefunction Inc.) was used for conformational analysis of diacid ligands, modelled as dimethyl esters (Fig. 2). Rotatable bonds were varied in 30°, 60° or 120° increments using a simulated annealing Monto Carlo-type search and the MMFF94 force field (the default for molecules of this size in MacSpartan), with a further cycle of energy minimisation to ensure convergence. For each ligand several searches starting from different starting geometries were performed until no new conformations less than 10 kJ mol^{-1} above the global minimum were produced. In some cases systematic searches were also run. Conformer populations were calculated using population = *s*.exp($-\Delta E/RT$), where ΔE = (energy of conformation) − (energy of global minimum), and *s* is a number depending on the symmetry of the conformation: for conformations of C_1 symmetry, $s = 4$, for C_2 or C_S, $s = 2$, for C_{2V}, $s = 1$ (Table S1†). Cerius^2 (Accelrys Inc) was used for empirical estimates of the difference in energy between diacid ligands (as dimethyl esters) and monochelate complexes. Low energy conformations were obtained from multiple runs of systematic and Boltzmann jump searches, using the UNIVERSAL 1.02 force field with no charges and no constraints.

PC Spartan Pro 1.0.7 was used for pBP/DN* (dft) calculations (Table S2†). The lowest energy conformation of a ligand (dimethyl ester) according to dft was obtained by reminimising the ten lowest energy conformations previously found by molecular mechanics (MMFF94). The lowest energy conformation of the corresponding dirhodium complex was obtained by first minimising a chelate of arbitrary conformation using dft. The $Rh_2(OAc)_2$ part of the molecule was then fixed, conformations of the chelate ring were generated using MMFF94, and then reminimised using dft with no constraints. Known crystal structures of monochelates have axial ligands (usually pyridines), but these could not be included in dft calculations due to the size of the system. However calculated bond lengths and angles for the dirhodium core were quite close to experimental values,[18] despite the absence of axial ligands. For **8a**, calculated: Rh–Rh = 2.403 Å, and Rh–O (average) = 2.085

Table 3 Crystal data and collection parameters

	5	6	7 dimethyl ester	8	10	11
Empirical formula	$C_{10}H_{10}O_6$	$C_{18}H_{26}O_6$	$C_{12}H_{12}Br_2O_6$	$C_{28}H_{36}O_{12}$	$C_{14}H_{16}Br_2O_6$	$C_{14}H_{18}O_4S_2$
Formula weight	226.18	338.39	412.04	564.57	440.09	314.40
T/K	213(2)	213(2)	213(2)	293(2)	293(2)	213(2)
Crystal system	Triclinic	Monoclinic	Triclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P\bar{1}$	$C2/c$	$P\bar{1}$	$C2/c$	$P2_1n$	$P2_1c$
a/Å	6.7348(2)	19.461(3)	8.694(2)	18.591(2)	11.2340(1)	10.5028(2)
b/Å	7.0518(2)	5.7894(7)	9.240(3)	10.996(2)	7.4699(1)	12.5327(1)
c/Å	11.256(2)	32.412(6)	9.899(3)	21.767(3)	20.1840(2)	12.1758(2)
α	75.30(3)	90	110.10(3)	90	90	90
β	73.98(3)	94.33(2)	98.04(3)	100.15(1)	96.541(1)	92.081(2)
γ	71.04(3)	90	98.76(3)	90	90	90
V/Å^3	477.94(2)	3641.3(1)	722.0(3)	4379.8(1)	1682.8(4)	1601.6(4)
Z	2	8	2	6	4	4
μ(Mo-Kα)/mm^{-1}	0.132	0.092	5.634	0.101	4.841	0.341
Data/parameters	1399/147	2273/219	2155/186	2855/257	2491/205	2453/185
*R*1 ($I > 2\sigma(I)$), *wR*2	0.0311, 0.0763	0.0535, 0.1245	0.0580, 0.1413	0.0697, 0.2529	0.0281, 0.0598	0.0351, 0.0894
*R*1,*R*2 (all data)	0.0390, 0.0790	0.0750, 0.1393	0.0715, 0.1481	0.1291, 0.3050	0.0424, 0.0615	0.0513, 0.0959

(±0.006) Å. From the crystal structure of **8a**.(4-*tert*-butylpyridine)$_2$: Rh–Rh = 2.408 Å, and Rh–O (average) = 2.047 (±0.008) Å.[18]

Crystallography. Suitable crystals of diacids were obtained from the following solvents: **5**, acetone; **6**, diethyl ether; **7** dimethyl ester, MeOH; **8**, acetone, **10**, acetone–hexane; **11**, DCM. None of the crystals contained solvent in the lattice (Table 3). Crystallographic data were collected on a STOE-IPDS image plate diffractometer using graphite monochromated MoK$_\alpha$ radiation (λ = 0.71073 Å).‡ Structure solution by Direct Methods and structure refinement by full-matrix least-squares was based on all data using F^2 (G. M. Scheldrick, SHELX-97, Programs for Crystal Structure Solution and Refinement, University of Göttingen, Germany, 1997). All non-hydrogen atoms were refined anisotropically, with the exception of disordered atoms, which were refined isotropically. Hydrogen positions were placed geometrically. The following were disordered. Diacid **7**: two disordered methyl groups. Disordered atomic positions were split and refined without restraints and one occupancy parameter per disordered group. Diacid **8**: side groups disordered. Disordered atomic positions were split and refined using similar distance and one occupancy parameter per disordered group. Diacid **10**: double bonded oxygen disordered. Disordered atomic position was split and refined without restraints.

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