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Dirhodium(II) carboxylates as building blocks. Synthesis and structures of *cis*-chelate complexes

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Received 13th September 2000, Accepted 6th October 2000
First published as an Advance Article on the web 14th November 2000

Dirhodium tetracarboxylate complexes $(C)Rh_2(OAc)_2$ and $(C)_2Rh_2$, where C is a chelating dicarboxylate of general form *meta*-$C_6H_4(OC(CH_3)_2CO_2^-)_2$, were prepared by heating $Rh_2(OAc)_4$ and diacids in *N*,*N*-dimethylaniline. The structures of six new complexes with one or two chelate rings were obtained, with pyridine ligands (or in one case *N*,*N*-dimethylaniline) co-ordinated to rhodium. The geometries of the molecules are similar, with the aromatic part of the chelate ring tilted out of the plane of the Rh–O cage by 57.5 to 66.6°. The monochelate $Rh_2\{C_6H_4(OC(CH_3)_2CO_2)_2$-*m*$\}(OAc)_2\cdot 2Bu^tPy$ (Bu^tPy = 4-*tert*-butylpyridine) packed in the crystal to generate a hexagonal network of channels of (minimum) diameter 5 Å due to vertical stacking of its axial pyridine ligands. Several other instances of intramolecular CH–π and intermolecular π–π interactions were noted in the packing diagrams. The bischelate $Rh_2\{Ar(OC(CH_3)_2CO_2)_2$-*m*$\}_2\cdot PhNMe_2$, with Ar = 4,6-di-*tert*-butylphenyl, has a polymeric structure displaying a new mode of arene co-ordination. The aromatic ring of the *N*-bound aniline co-ordinates to a neighbouring dirhodium complex *via* the *para* carbon atom with a Rh–C distance of 2.709 Å.

Introduction

Many bidentate ligands can bridge the Rh–Rh bond of the Rh_2^{4+} cation, but dirhodium tetracarboxylates with four carboxylate bridges form perhaps the best known class of compounds.[1] These complexes catalyse a variety of organic reactions, particularly carbene transfer.[2] The characteristic 'paddlewheel' geometry, with ligands arranged at right angles around a central metal axis, has also recently been used to assemble large metallomacrocycles.[3,4] In our work a dirhodium complex **1** with a pair of *cis* sites blocked off with a chelating ligand was condensed with dicarboxylic acids to form macrocycles of various shapes.[4] Its crystal structure showed that the aromatic ring of the chelating dicarboxylate was tilted out of the plane of the Rh–O cage, although the molecule appeared axially symmetrical on the ^1H NMR timescale. In order to examine this asymmetry in more detail, which is also present in macrocycles derived from **1**, we obtained crystal structures of complexes **2** to **7** which are similar to **1**, but have two chelate rings or substituents on the chelate ring(s) (Scheme 1). Numerous symmetrical tetracarboxylate complexes in which all four ligands are the same have been characterised structurally,[1] but there are only a few examples of unsymmetrical species[5] or complexes with bridged ligands.[6]

Results and discussion

Synthesis

cis-Bridged complexes were prepared by heating a 1 : 1 mixture of the appropriate diacid and $Rh_2(OAc)_4$ in *N*,*N*-dimethylaniline at 140 °C with evaporation of acetic acid, affording a mixture of unchanged $Rh_2(OAc)_4$, monochelate and bischelate. Yields of monochelate prepared in this way were generally good, ranging from 63% for **1** to 79% for **4**. Complex **2** was prepared in lower yield (25%) by reaction of dodecanedioic acid with **1**. With the exception of **7**, complexes were crystallised as the pyridine or 4-*tert*-butylpyridine (Bu^tPy) adducts, since these produced robust crystals.

Table 1 Selected bond lengths and angles for complexes **1**–**7**

Complex	Rh–Rh/Å	Rh–N[a]/Å	Bite angle[b]/°	Tilt angle[c]/°
1	2.408	2.226, 2.225	88.8	60
2	2.404	2.251, 2.187	88	59.9
3	2.411	2.237	87.5	61.5
4	2.408	2.228, 2.259	87.8	66.6
5	2.409	2.209	88	59.3
6	2.406	2.239, 2.255	87	63.7
7	2.405	2.315	87.4, 87.5	57.5

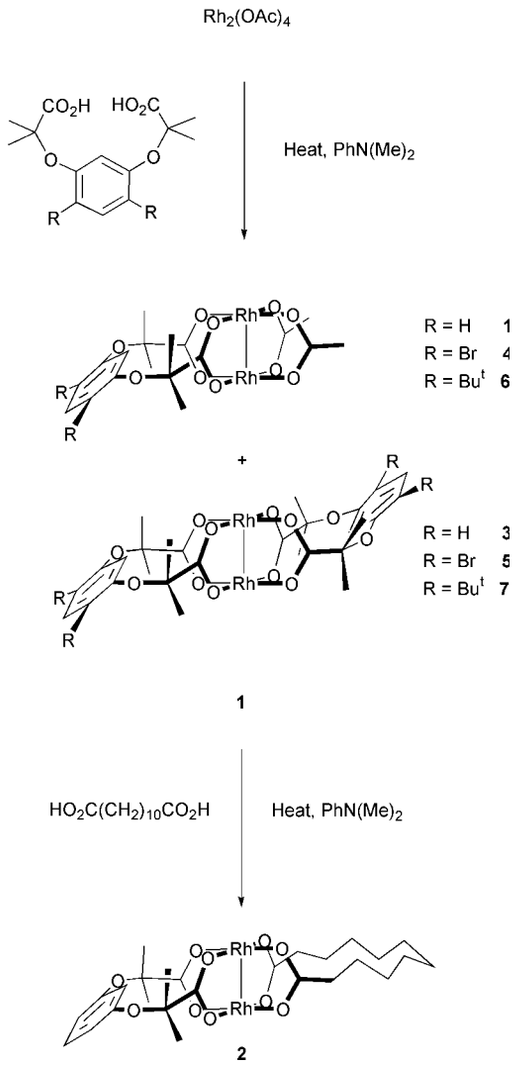
[a] Rh(1)–N(1), Rh(2)–N(2). Rh(1) is the upper atom as drawn in Fig. 1. [b] O–Rh–O angle subtended by the chelate; average of upper and lower planes of carboxylate oxygens. [c] Angle between the plane of carboxylate carbons and that of the aromatic ring in the chelate.

Crystal structures

The structures of complexes **1** to **7**, as the axial adducts, are presented in Fig. 1, with selected bond lengths and angles in Table 1. The most obvious feature is that the aromatic rings of all the chelates are tilted from the plane of the Rh–O cage, as defined by the carboxylate carbons. The tilt angle varies from 57.5 to 66.6°, with the chelate rings being otherwise symmetrical. Like $\mathbf{1}\cdot 2Bu^tPy$, the geminal methyl groups of each of these complexes are in different environments in the crystal, with one C–Me bond aligned parallel to the Rh–Rh axis and the other perpendicular. Single methyl resonances are nevertheless observed for all complexes in solution (with or without axial ligands), so conformational inversion must be fast at room temperature. Indeed molecular modelling suggested that the chelate rings are quite flexible due to rotation around the C–O bonds, allowing the aromatic ring to flip from side to side, exchanging the environment of the methyl groups. Bischelates $\mathbf{3}\cdot 2Bu^tPy$, $\mathbf{5}\cdot 2Bu^tPy$ and $\mathbf{7}\cdot PhNMe_2$ adopt a *trans* geometry in the crystal, perhaps for better packing, since modelling predicts little difference in energy between *cis* and *trans* forms.

The chelate ligands distort the regular square Rh–O cage

DOI: 10.1039/b007428o



Scheme 1 Synthesis of *cis*-chelate complexes.

slightly, pulling the bridged carboxylates inwards so that the O–Rh–O bond angles are a few degrees less than 90° (Table 1). The twelve carbon ring in complex **2**·2Bu^{t}Py has a bite angle of 91°, similar to the angles between the acetate ligands in monochelates (the chain is somewhat disordered in the crystal).

The Rh–Rh bond lengths (2.404–2.411 Å) are in the normal range for amine bisadducts of dirhodium tetracarboxylates,[1] as are the Rh–O bond lengths (1.992–2.061 Å) and Rh–N bond lengths (2.187–2.315 Å). In most cases the pyridine ligands co-ordinate roughly parallel to the Rh–Rh axis, with their planes bisecting O–Rh–O angles, and one of the pyridine *ortho* hydrogens pointing at the aromatic chelate ring, with distances between ring centres, d_R = 5.3–5.5 Å (CH–π distances of 3.1–3.2 Å to the centre of the chelate ring). In complexes **4**·2Py and **6**·2Bu^{t}Py the *ortho* hydrogens are closer with d_R = 4.7–4.9 Å and CH–π distances of 2.7–2.8 Å. The pyridine and chelate rings appear to attract each other in these complexes, which have the largest tilt angles.

Two dirhodium chelates have been reported previously, a bischelate with two eleven atom rings $Rh_2(O_2CC(CH_3)_2CH_2OCH_2C(CH_3)_2CH_2OCH_2C(CH_3)_2CO_2)_2$·2Py[6a] and a monochelate with a nine atom ring, $Rh_2(C_6H_4((CH_2)_2CO_2)_2$-*m*$)(O_2CCF_3)_2$·2Me$_2$CO.[6b] The latter complex is an all carbon version of **1**, but without the geminal methyl groups, and also has a tilted chelate ring in the crystal.

Crystal packing

The supramolecular arrangement of some of the complexes

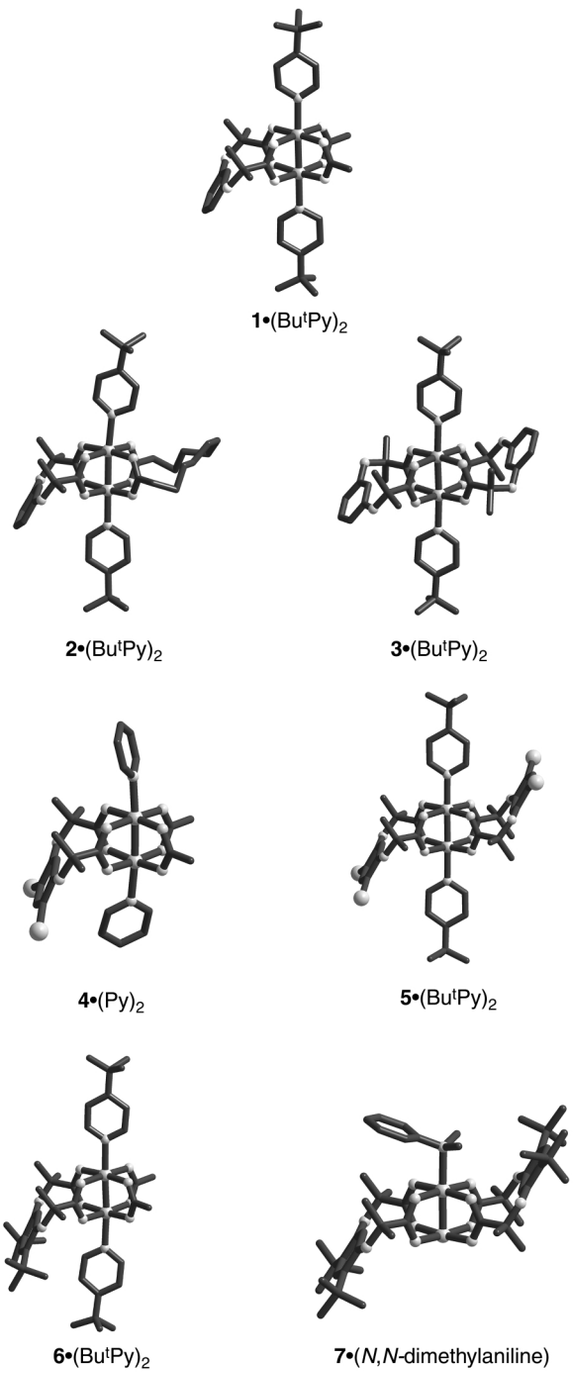


Fig. 1 Crystal structures of complexes **1**–**7** with pyridine, 4-*tert*-butylpyridine or *N*,*N*-dimethylaniline co-ordinated to rhodium (hydrogen atoms and molecules of solvent omitted for clarity).

was unexpected. Complex **1**·2Bu^{t}Py crystallises with a hexagonal array of holes extending along the crystal *c* axis (Fig. 2). These channels, which contain disordered solvent, are spaced 18.7 Å apart and have a minimum diameter of 5 Å (a 5 Å sphere placed in the centre of the channel is in van der Waals contact at the narrowest points). The walls are composed of aromatic chelate rings and methyl groups, and are chiral in individual crystals. Molecules of **1**·2Bu^{t}Py are arranged in a layered hexagonal network in the *xy* plane with corners formed by overlapping 4-*tert*-butylpyridine ligands. These ligands form a stack running along the *c* axis, with d_R = 4.3 Å and successive ligands rotated by 120°. The rings are offset from the central axis by 0.3 Å, inclined to each other at 45°, and in van der Waal contact at their edges, with a shortest distance between neighbouring ring carbons, d_{CC} = 3.2 Å. While the separation between ring centres is larger than the normal parallel π–π stacking

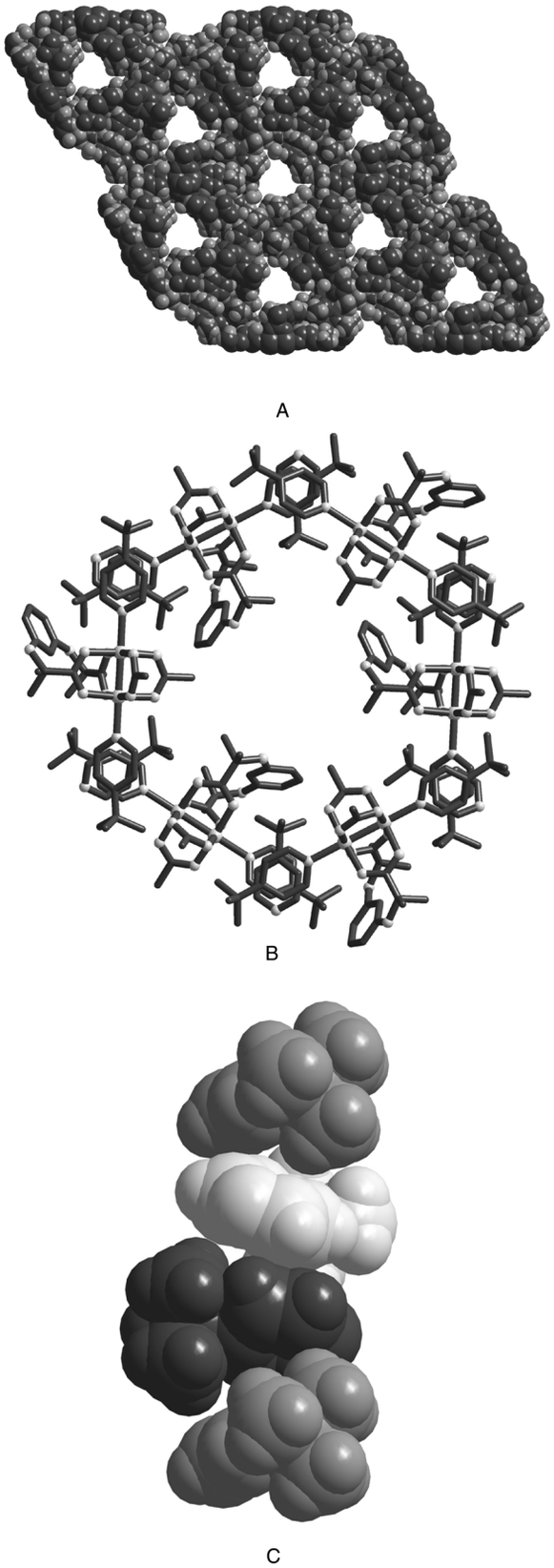


Fig. 2 Views of the packing in the crystal structure of complex **1**·2Bu^{t}Py. A, View down the *c* axis, showing channels of diameter 5 Å. B, Cyclic hexameric motif generating the channels. Two layers of **1**·2Bu^{t}Py and three layers of the axial ligand are shown (hydrogen atoms omitted). C, Space filling view of part of one of the stacks of axial ligands which connect the hexagons.

distance of 3.5 Å[7] due to the *tert*-butyl groups, such stacking may nevertheless contribute to the stability of the crystal.

Perhaps not surprisingly for molecules with several aromatic rings, there are more examples of π–π stacking in the packing diagrams for the other complexes, although no extended arrays. For example, **2**·2Bu^{t}Py stacks so that pairs of axial 4-*tert*-butylpyridine ligands interact in a similar manner to that of **1**·2Bu^{t}Py, but with a larger offset (d_R = 4.2, d_{CC} = 3.4 Å, offset 2.3 Å, tilt 33°), as does **3**·2Bu^{t}Py (d_c = 4.7, d_{CC} = 3.5 Å, offset 2.7 Å, tilt 44°). Molecules of **4**·2Py associate *via* π–π stacking of both the dibromochelate rings (d_R = 3.9 Å, d_{CC} = 3.4 Å, offset 1.2 Å, tilt 0°) and the axial pyridines (d_c = 3.75 Å, d_{CC} = 3.4 Å, offset 1.2 Å, tilt 0°), but **5**·2Bu^{t}Py and **6**·2Bu^{t}Py display no significant π–π or CH–π[8] interactions. The reason that **4**·2Py and **6**·2Bu^{t}Py, which are similar to **1**, do not form lattices with channels may be that there is not enough room for the bulky bromo and *tert*-butyl substituents on the chelate rings which line the channel walls.

The stoichiometry of complex **7**·PhNMe$_2$ appeared unusual at first sight, since structurally characterised dirhodium tetracarboxylate complexes with just one axial ligand are rare. The two known examples, $Rh_2(OAc)_4$·PPh_2(*o*-$MeOC_6H_4$)[9a] and $Rh_2(O_2CCF_3)_4$·THF[9b] are in fact dimers of the form L·$(RCO_2)_4$-Rh_2·$Rh_2(O_2CR)_4$·L, held together by weak intermolecular Rh–O co-ordination. In fact **7**·PhNMe$_2$ is polymeric, with the aromatic ring of the aniline ligand solvating the vacant Lewis acid site on the next molecule (Fig. 3). The centre of the ring is offset by 0.6 Å from the Rh–Rh axis, and tilted at an angle of 20°, with Rh–C distances of 2.709 and 3.077 Å to the *para* and *meta* carbons respectively. Bidentate ligands containing good donor atoms often form 1 : 1 polymers with dirhodium tetracarboxylates,[1] but there appear to be only two examples of arene co-ordination, the polymeric 1 : 1 complexes $Rh_2(O_2CCF_3)_4$·PhCCPh[10a] and $Rh_2(O_2CCF_3)_4$·C_6Me_6,[10b] made by sublimation of $Rh_2(O_2CCF_3)_4$ in the presence of diphenylacetylene or hexamethylbenzene respectively. In both of these complexes dirhodium units co-ordinate almost symmetrically to one double bond of a phenyl ring, with Rh–C distances to the nearest carbons of 2.723 and 2.770 Å. In the present case the complex is much less Lewis acidic than $Rh_2(O_2CCF_3)_4$, and the reason the aromatic ring co-ordinates at all, and then primarily to the *para* carbon, may lie in the electron rich nature of the aniline ligand for which a resonance form with negative charge in the *para* position can be drawn.

Conclusion

The complexes reported here comprise the first set of structurally characterised *cis*-bridged dirhodium tetracarboxylates. The single molecule structures are similar, regardless of the substituents on the aromatic rings, with symmetrical, tilted chelates and little distortion of the Rh–O cages. Several examples of intramolecular CH–π and intermolecular π–π interactions were noted, in particular the stacking of axial 4-*tert*-butylpyridines, leading to an unusual channelled structure[11] for **1**·2Bu^{t}Py. It has yet to be determined if sterically commensurate analogues adopt this arrangement, and if the lattice survives removal or replacement of included solvent, but the passages are large enough to accommodate small molecules such as linear alkanes. The polymeric nature of **7** illustrates a new mode of arene co-ordination to dirhodium complexes, which, if it proves general, could be a useful supramolecular motif.

Experimental

General

Reactions were performed under argon, and weakly bound solvent ligands removed from the products by heating at 100 °C under vacuum overnight. The synthesis of the diacid ligands will be described elsewhere.[12] NMR spectra were recorded at 200 or 300 MHz, with TMS as internal reference. FAB mass spectra were obtained on a VG7070E instrument using *m*-nitrobenzyl alcohol or glycerol as matrix. 230–400 Mesh

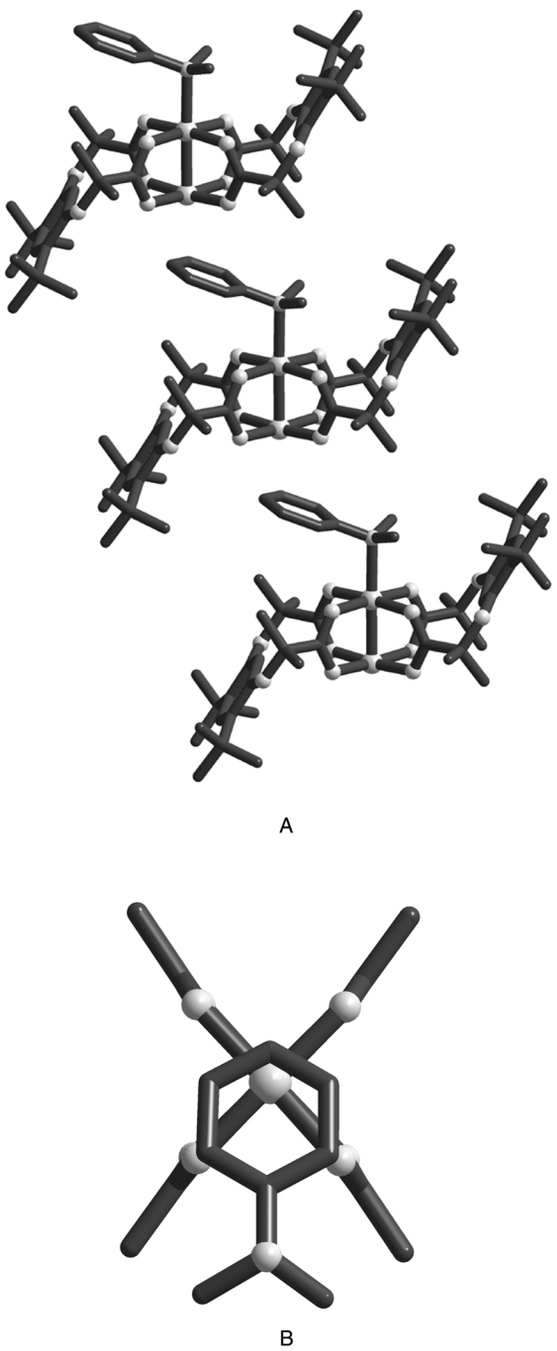


Fig. 3 A, Chains of complex **7**·$PhNMe_2$ in the crystal, showing phenyl–rhodium interaction. B, Detail of the phenyl–rhodium interaction, looking down the Rh–Rh axis (hydrogen atoms omitted).

silica gel was used for column chromatography. Organic extracts were dried over Na_2SO_4. Melting points for complexes were >240 °C. The synthetic method is illustrated below for **1** and **3**. Complexes **4**, **5**, **6**, and **7** were prepared using the same procedure, but at a reactant concentration of 45 mM, following the reactions by TLC (reaction times 0.5 to 4 h).

Preparations

Complexes 1 and 3. 2-[3-(1-Carboxy-1-methylethoxy)-phenoxy]-2-methylpropionic acid (0.315 g, 1.13 mmol) and $Rh_2(OAc)_4$ (0.50 g, 1.13 mmol) were stirred in *N*,*N*-dimethylaniline (50 ml) at 140 °C for 3 h. The cooled reaction mixture was diluted with dichloromethane (DCM) (150 ml), MeCN (10 ml) added, and the purple solution washed three times with aqueous hydrochloric acid (2 M; 100 ml), followed by water. The organic layer was dried and evaporated to a green solid. Chromatography (0 to 15% MeCN in DCM) provided first

Table 2 Crystal and data collection parameters for complexes **1**–**7**

	1	**2**	**3**	**4**	**5**	**6**	**7**
Empirical formula	$C_{36}H_{48}N_2O_{10}Rh_2$	$C_{44}H_{62}N_2O_{10}Rh_2$	$C_{46}H_{58}N_2O_{12}Rh_2$	$C_{28}H_{30}Br_2N_2O_{10}Rh_2$	$Br_4C_{46}H_{54}N_2O_{12}Rh_2$	$C_{44}H_{64}N_2O_{10}Rh_2$	$C_{52}H_{75}NO_{12}Rh_2{\cdot}2Cl_3CH$
Formula weight	874.58	984.90	1036.88	920.24	1352.48	986.92	1350.84
Crystal system	Rhombohedral	Orthorhombic	Triclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	*R*3	*Pbca*	*P*$\bar{1}$	$P2_1/c$	$P2_1/n$	$P2_1/n$	$P2_1/c$
a/Å	31.600(4)	18.088	13.854(2)	11.869(3)	15.1659(19)	9.2589(7)	17.918(3)
b/Å	31.600(4)	26.151	14.0285(19)	13.9267(17)	9.3511(10)	18.9042(16)	9.4795(7)
c/Å	12.700(3)	19.245	14.7149(19)	20.613(4)	19.040(3)	27.476(2)	36.978(4)
α/°			69.171(15)				
β/°			79.073(16)	103.78(2)	98.685	97.132	90.107(16)
γ/°	113.56(1)		63.860(15)				
V/Å^3	10983(3)	9103.1	2397.6(6)	3309.2(10)	2669.2(6)	4772.07(7)	6280.9(12)
Z	9	8	2	4	2	4	4
T/K	293	213	213	293	213	293	213
μ(Mo-Kα)/mm^{-1}	0.720	0.692	0.662	3.314	3.538	0.660	0.751
Data/parameters	6376/421	7178/509	6978/557	5214/397	4202/298	7490/510	9884/652
*R*1 ($I > 2\sigma(I)$)	0.0469	0.0894	0.0382	0.0378	0.0675	0.0466	0.536
*w*R2 (all data)	0.1422	0.2177	0.0672	0.0742	0.1655	0.1191	0.1547

complex **3** as a blue-purple solid (0.120 g, 14%) followed by **1** (0.43 g, 63%) as a green solid. Unchanged $Rh_2(OAc)_4$ was eluted for recycling with 30% MeCN in DCM. Complex **1** (Found: C, 35.7; H, 3.7. $C_9H_{11}O_5Rh$ requires C, 35.78; H, 3.67%): δ_H(200 MHz, 5% v/v d_4-MeOH in $CDCl_3$) 1.38 (12 H, s), 1.91 (6 H, s), 6.07 (1 H, t, *J* 2.2), 6.52 (2 H, dd, *J* 8, 2.2) and 7.09 (1 H, t, *J* 8 Hz); *m*/*z* (FABMS) 603.9 (M^+). Complex **3** (Found: C, 43.6; H, 4.3. $C_{14}H_{16}O_6Rh$ requires C, 43.88; H, 4.21%): δ_H(200 MHz, $CDCl_3$) 1.38 (24 H, s), 6.01 (2 H, br t), 6.52 (4 H, dd, *J* 8, 2.2) and 7.09 (2 H, t, *J* 8 Hz); *m*/*z* (FABMS) 766 (M^+).

Complex 2. Dodecanedioic acid (20 mg, 87 μmol) and complex **1** (50 mg, 83 μmol) were stirred in *N*,*N*-dimethylaniline (5 ml) at 140 °C for 24 h. Work-up and chromatography as described above gave **2** as a green solid (15 mg, 25%) (Found: C, 43.5; H, 5.1. $C_{13}H_{18}O_5Rh$ requires C, 43.71; H, 5.08%); δ_H(200 MHz, $CDCl_3$) 1–1.6 (12 H, br m), 1.40 (12 H, s), 2.25 (4 H, br t), 6.01 (1 H, t, *J* 2.2), 6.45 (2 H, dd, *J* 8, 2.2) and 6.92 (1 H, t, *J* 8 Hz); *m*/*z* (FABMS) 715 (M^+).

Complex 4. Yield 79% (Found: C, 28.6; H, 2.6. $C_9H_{10}BrO_5Rh$ requires C, 28.37; H, 2.65%). δ_H(200 MHz, 5% v/v d_3-MeCN in $CDCl_3$) 1.71 (12 H, s), 2.03 (6 H, s), 6.13 (1 H, s) and 7.57 (1 H, s); *m*/*z* (FABMS) 761.8 (M^+).

Complex 5. Yield 6% (Found: C, 31.1; H, 2.7. $C_{14}H_{14}Br_2O_6Rh$ requires C, 31.08; H, 2.61%). δ_H(bis-*tert*-butylpyridine adduct, 200 MHz, $CDCl_3$) 1.43 (24 H, s), 5.84 (2 H, s), 7.52 (4 H, br s), 7.72 (2 H, s) and 8.60 (4 H, br d); *m*/*z* (FABMS) 1081.6 (M^+).

Complex 6. Yield 69% (Found: C, 43.3; H, 5.4. $C_{13}H_{19}O_5Rh$ requires C, 43.59; H, 5.35%). δ_H(200 MHz, $CDCl_3$) 1.30 (18 H, s), 1.5 (12 H, s), 1.96 (6 H, s), 5.01 (1 H, s) and 7.12 (1 H, s); *m*/*z* (FABMS) 716.1 (M^+).

Complex 7. Yield 4.5%. δ_H(200 MHz, $CDCl_3$) 1.34 (36 H, s), 1.65 (24 H, s), 4.86 (2 H, s) and 7.12 (2 H, s); *m*/*z* (FABMS) 990.2 (M^+).

Crystallography

Amine bisadducts of complexes **2**–**6** were obtained by layering a solution in dichloromethane containing an excess of pyridine or 4-*tert*-butylpyridine with hexane. Crystals of **7** were obtained by allowing a chloroform solution containing *N*,*N*-dimethylaniline to evaporate. Crystallographic data were collected on a STOE-IPDS image plate diffractometer using graphite monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å). Structure solution by Direct Methods and structure refinement by full-matrix least squares was based on all data using F^2.[13] 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 and split on two positions in the refinement using distance and anisotropic displacement parameter restraints: the alkyl chain in **2**, the methyl groups in the *tert*-butylpyridine ligand in **2** (for one pyridine), **3** and **6**, and the chlorine atoms of the two $CHCl_3$ solvent molecules in **7**. The crystal structure **1** is both merohedrally (in higher symmetry 3*m*) and racemically twinned. Crystal and data collection parameters for compounds **1**–**7** are given in Table 2.

CCDC reference number 186/2222.

See http://www.rsc.org/suppdata/dt/b0/b007428o/ for crystallographic files in .cif format.

Modelling

Conformational analysis and molecular dynamics were performed with CERIUS^2, using the Open Force Field.[14] Harmonic constraints were used to keep Rh–O, Rh–N and Rh–Rh bonds near typical distances (2.0, 2.2 and 2.4 Å respectively) but similar results were obtained using the default bond lengths. Modelling was found to reproduce the overall geometry of the chelate rings reasonably well, predicting tilt angles of between 50 and 70°.

Acknowledgements

We thank the EPSRC for financial support, and Johnson Matthey PLC for generous loans of rhodium.

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