Bis[dirhodium(II)] complexes with a $Rh_4(\mu\text{-}Cl)_4$ core: preparation and characterization ‡

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The reaction of $[Rh_2(O_2CPr^n)_4]$ or $[Rh_2(mhp)_4]$ (Hmhp = 2-hydroxy-6-methylpyridine) with a trialkylchlorosilane followed by crystallization from a nitrile unexpectedly gave $[Rh_4(O_2CPr^n)_4Cl_4(CH_3CN)_4]$ **1** or an isomer of $[Rh_4(mhp)_4Cl_4(PhCN)_2]$ both with a 'twisted-cage' $Rh_4(\mu\text{-}Cl)_4$ core, which were studied by X-ray crystallography, cyclic voltammetry and UV/VIS spectroscopy; **1** catalyzed the hydrogenation of acrylic acid in water.

The chloro ligand is interesting because it is substitutionally labile, co-ordinates in both terminal and bridging fashion and has metal–ligand σ- and π-type electronic interactions. When the ligand is bridging it may induce metal–metal indirect electronic interactions through its orbital(s). We have unexpectedly isolated bis[dirhodium(II)] complexes supported by four chloro bridges in low to moderate yields in trials aimed at substituting the bridging ligands of $[Rh_2(O_2CPr^n)_4]$ or $[Rh_2(mhp)_4]$ (Hmhp = 2-hydroxy-6-methylpyridine) with chloro ligands. Stimulated by the work of Cotton and co-workers in preparing $[Rh_2(O_2CCH_3)_2Cl_2(L-L)]$ and $[Rh_2Cl_4(L-L)_2]$ (L–L denotes a diphosphine) by the reaction of $[Rh_2(O_2CCH_3)_4]$ with $(CH_3)_3$-SiCl in the presence of L–L we treated $[Rh_2(O_2CPr^n)_4]$ or $[Rh_2(mhp)_4]$ with trialkylchlorosilane. Since complexes with an $M_4(\mu\text{-}X)_4$ (X = halogen) skeleton similar to that found in $[Rh_4(O_2CPr^n)_4Cl_4(CH_3CN)_4]$ and $[Rh_4(mhp)_4Cl_4(PhCN)_2]$ have been known to us only in the chemistry of Mo^{III} with a limited number of compounds,[2] we report here the preparation, crystal structures and properties of the current $Rh_4(\mu\text{-}Cl)_4$ complexes as a preliminary communication.

Axial-ligand free $[Rh_2(O_2CPr^n)_4]$[3] (2.22 g, 4.0 mmol) was heated with $(C_2H_5)_3SiCl$ (3.0 cm³, 18 mmol) in toluene (70 cm³) at reflux under Ar for 20 h to give a brown precipitate. After collection the precipitate was stirred with 40 mL of CH_3CN to give a yellow-green powder of $[Rh_4(O_2CPr^n)_4Cl_4(CH_3CN)_4]$ **1** in 35% yield. The reaction of *trans*-(hh,tt)-$[Rh_2(mhp)_4]$ (where hh,tt represents head-to-head, tail-to-tail)[4] with $(CH_3)_3SiCl$ in toluene at reflux gave a brown precipitate, which was loaded onto a silica-gel column and eluted with a CH_2Cl_2–CH_3CN mixture (4:1 v/v) to give (hh,hh)-$[Rh_4(mhp)_4Cl_4(CH_3CN)_2]$ [**2**; see Fig. 2 in the following paragraph for the arrangement of the mhp bridging ligands in the '(hh,hh)-isomer'] in 8% yield as the second band (yellow). Although we could obtain only poor-quality single crystals of **2**, layering and solution of **2** in

CH_2Cl_2–PhCN with hexane resulted in axial ligand exchange and gave small brown single crystals of (hh,hh)-$[Rh_4(mhp)_4Cl_4(PhCN)_2]$ **3** which were of moderate quality for X-ray study. When $[Rh_2(O_2CPr^n)_4]$ was refluxed with $(CH_3)_3SiCl$ in CH_3CN until complete consumption of the starting dirhodium complex had occurred (TLC), only a mononuclear rhodium(III) complex, *mer*-$[Rh(CH_3CN)_3Cl_3]$,[5] was isolated.

The crystal structures of **1** § and **3** ¶ are shown in Figs. 1 and 2, respectively. The two Rh^{II}–Rh^{II} units of these $Rh_4(\mu\text{-}Cl)_4$ complexes, each of which contains two bridging carboxylato or mhp ligands spanning a Rh^{II}–Rh^{II} bond, are linked together by four μ-Cl ligands. The two Rh^{II}–Rh^{II} bonds are arranged perpendicularly when viewed along the centers of the Rh–Rh
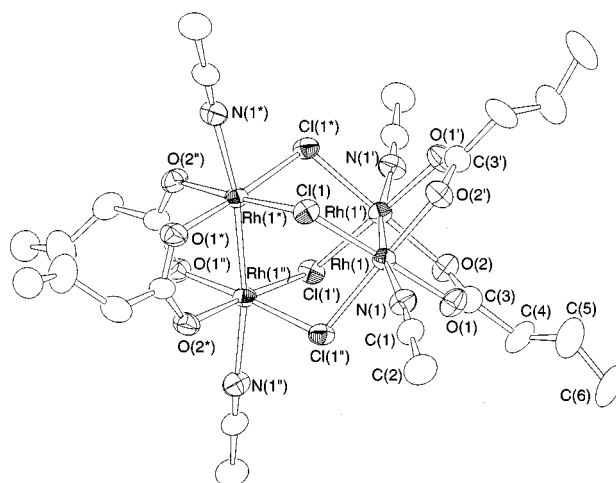
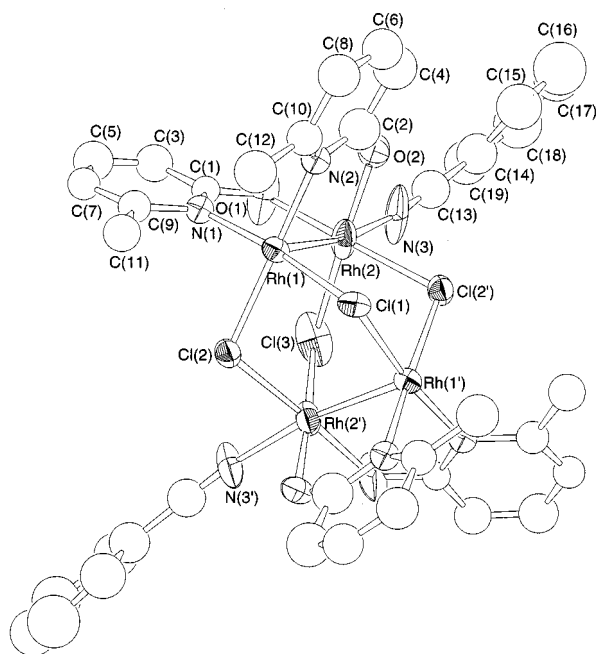**Fig. 1** An ORTEP[7] view of the non-hydrogen atoms of $[Rh_4(O_2CPr^n)_4Cl_4(CH_3CN)_4]$ **1**. Thermal ellipsoids are drawn at the 50% level. The C(6) ellipsoid shows one of the two disordered methyl carbon atoms of the butyrato ligand. The geometry belongs to the S_4 point group. Selected bond lengths (Å) and angles (°): Rh(1)–Rh(1′) 2.5552(9), Rh(1)–Cl(1) 2.330(2), Rh(1)–Cl(1″) 2.317(2), Rh(1)–O(1) 2.029(5), Rh(1)–O(2′) 2.033(5), Rh(1)–N(1) 2.272(6); Rh(1′)–Rh(1)–Cl(1) 99.72(4), Rh(1′)–Rh(1)–Cl(1″) 96.69(4), Rh(1)–Cl(1)–Rh(1*) 107.36(6), Cl(1)–Rh(1)–Cl(1″) 87.81(3)

Fig. 2 An ORTEP view of the non-hydrogen atoms of (hh,hh)-[Rh$_4$(mhp)$_4$Cl$_4$(PhCN)$_2$] **3**. Thermal ellipsoids are drawn at the 50% level. A crystallographic C_2 axis passes through Cl(1) and Cl(3). Selected bond lengths (Å) and angles (°): Rh(1)–Rh(2) 2.537(3), Rh(1)–Cl(1) 2.356(6), Rh(1)–Cl(2) 2.343(7), Rh(1)–N(1) 2.04(2), Rh(1)–N(2) 2.06(2), Rh(2)–Cl(2′) 2.329(7), Rh(2)–Cl(3) 2.328(7), Rh(2)–O(1) 2.02(2), Rh(2)–O(2) 2.02(2), Rh(2)–N(3) 2.13(2); Rh(2)–Rh(1)–Cl(1) 98.9(2), Rh(2)–Rh(1)–Cl(2) 99.2(2), Rh(2)–Rh(1)–N(1) 86.0(6), Rh(2)–Rh(1)–N(2) 86.8(6), Rh(1)–Rh(2)–N(3) 170.8(8), Rh(1)–Cl(1)–Rh(1′) 105.9(3), Rh(1)–Cl(2)–Rh(2′) 107.0(2)

tration was around 10^{-4} mol dm^{-3} (see SUP 57397). The UV/VIS spectrum of the CH$_3$CN solution of **1** showed absorptions at λ_{max} (log ε/mol^{-1} dm^3 cm^{-1}) of 273 (4.36), 308 (4.18), 450 (sh) and 635 nm (2.36), which are similar to the wavelengths of peaks in the diffuse reflectance spectrum of crystalline **1** ground with MgO powder [λ_{max}: 279, 310, 455 (sh) and 638 nm] showing that the solid-state structure of the complex is conserved in solution. Complex **1** is moderately soluble in water (*ca.* 3×10 mg cm^{-3} at room temperature). The comparison of the electronic spectrum of **1** dissolved in water [λ_{max} (log ε/mol^{-1} dm^3 cm^{-1}) of 271 (4.38), 314 (4.25), 460 (sh) and 680 nm (2.34)] with that of its CH$_3$CN solution implies that [Rh$_4$(O$_2$CPr^n)$_4$Cl$_4$(H$_2$O)$_4$] is formed by the substitution of the axial ligands with the conservation of the Rh$_4$(μ-Cl)$_4$ skeletal arrangement.

The cyclic voltammogram‖ of **1** in CH$_3$CN at a Pt button working electrode showed a chemically reversible one-electron oxidation response at 0.84 V *vs.* the ferrocenium–ferrocene couple. Trials to isolate cationic radical salts of **1** have not been successful. In a preliminary trial using **1** as a catalyst precursor in aqueous solution, acrylic acid was hydrogenated in water under 1 atm (101 325 Pa) of hydrogen at room temperature in the presence of **1** in 2 mol% of olefinic acid.

Acknowledgements

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bonds, thus the Rh$_4$(μ-Cl)$_4$ skeleton looks like a twisted cage. The nitrile ligands occupy axial positions both in **1** and **3**. In both of the two Rh$_2^{4+}$ units of **3** the mhp ligands are arranged in a head-to-head manner ['(hh,hh)-isomer'] and the two axial PhCN ligands are bonded at the less hindered axial sites. The Rh^{II}–Rh^{II} bond lengths in **1** and **3** are longer than most Rh–Rh lengths in lantern-type dinuclear Rh^{II} complexes (2.35–2.45 Å),[7] but are still acceptable for a Rh^{II}–Rh^{II} single bond. The distances between the rhodium atoms connected by a μ-Cl bridge are 3.74 and 3.76 Å for **1** and **3**, respectively. These separations are too long for direct Rh–Rh bonding interactions. The bond distances of Rh–N (nitrile) are similar to the corresponding lengths of dinuclear rhodium(II) complexes,[8] while the Rh–(μ-Cl) bond lengths are slightly shorter than the Rh–(μ-Cl) distances in [Rh$_2$(μ-Cl)$_2$(Cl)$_2$(μ-dppm)$_2$] (average 2.460 Å).[1]

The dependence of the UV/VIS spectrum of **1** in CH$_2$Cl$_2$–CH$_3$CN mixed solvents on their mixing ratios and on the concentrations of the complex showed equilibria of the extensive dissociation of the axial ligands when the complex concen-