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

Zhiyong Yang, Hiroki Oki, Masahiro Ebihara and Takashi Kawamura *[†]

Department of Chemistry, Faculty of Engineering, Gifu University, Yanagido, Gifu 501-1193, Japan

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 $[Rh_2(O_2CCH_3)_2Cl_2(L\text{–}L)]$ and $[Rh_2Cl_4(L\text{–}L)_2]$ (L–L denotes a diphosphine) by the reaction of $[Rh_2(O_2CCH_3)_4]$ with $(CH_3)_3SiCl$ 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 $[Rh_4(O_2CPr^n{}_4)Cl_4(CH_3CN)_4]$ 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

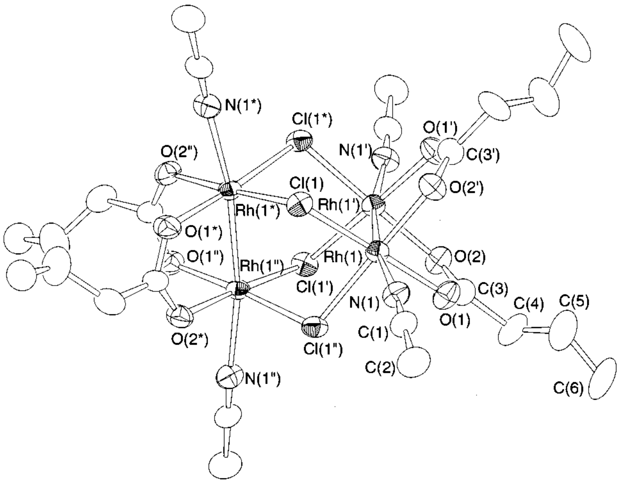

Fig. 1 An ORTEP[7] view of the non-hydrogen atoms of $[Rh_4(O_2CPr^n)_4Cl_4(CH_3CN)_4]$ **1**. Thermal ellipsoids are drawn at the 50% level. The C(6) ellipsoid shows one of the two disordered methyl carbon atoms of the butyrato ligand. The geometry belongs to the S_4 point group. Selected bond lengths (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)

[†] E-Mail: kawamura@apchem.gifu-u.ac.jp

[‡] *Supplementary data available*: UV/VIS absorption spectra of $[Rh_4(O_2CPr^n)_4Cl_4(CH_3CN)_4]$ in CH_3CN, CH_3CN–CH_2Cl_2 and CH_2Cl_2 and electronic spectra of $[Rh_4(O_2CPr^n)_4Cl_4L_4]$ (L = CH_3CN or H_2O). For direct electronic access see http://www.rsc.org/suppdata/dt/1998/2277/, otherwise available from BLDSC (No. SUP 57 397, 3 pp.) or the RSC Library. See Instructions for Authors, 1998, Issue 1 (http://www.rsc.org/dalton).

[§] (Found: C, 26.80; H, 3.63; Cl, 13.29; N, 5.13. $C_{24}H_{40}Cl_4N_4O_8Rh_4$ requires C, 27.04; H, 3.78; Cl, 13.30; N, 5.26%). Crystal data for complex **1**: $M = 1066.04$, tetragonal, space group $I\bar{4}$ (no. 82), $a = 10.512(2)$, $c = 15.660(2)$ Å, $U = 1730.4(6)$ Å³, $Z = 2$, $\mu = 22.27$ cm⁻¹, $T = -80$ °C. Solved by direct methods (SHELXS 86[6]). $R = 0.023$, $R_w = 0.031$ and $S = 1.25$ for 962 unique reflections.

[¶] Crystal data for complex **3**: $C_{38}H_{34}Cl_4N_6O_4Rh_4$, $M = 1192.16$, monoclinic, space group $C2/c$ (no. 15), $a = 12.405(4)$, $b = 24.119(4)$, $c = 14.405(3)$ Å, $\beta = 112.49(2)°$, $U = 3982(1)$ Å³, $Z = 4$, $\mu = 19.42$ cm⁻¹, $T = -80$ °C. Solved by direct methods (SHELXS 86[6]). $R = 0.069$, $R_w = 0.070$ and $S = 1.36$ for 1157 unique reflections. Owing to weak diffraction due to the small size of the crystal, the deduced geometric parameters are not of high quality, but the chemical structure is reliable, CCDC reference number 186/1039. See http://www.rsc.org/suppdata/dt/1998/2277/ for crystallographic files in .cif format.

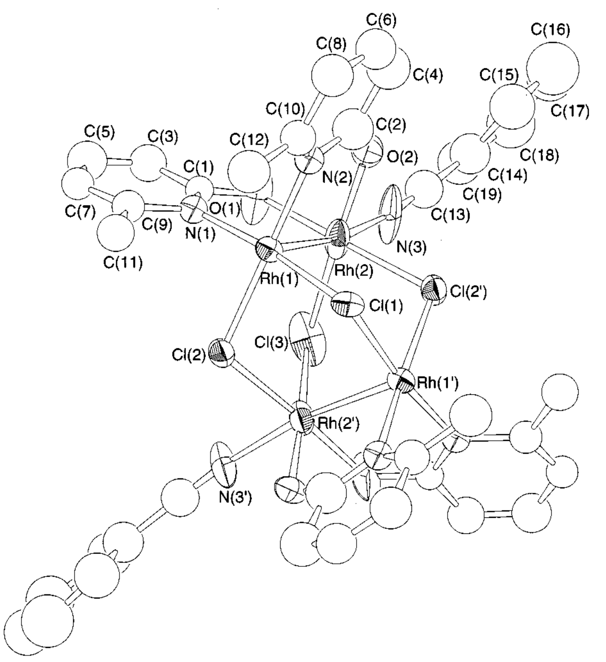

Fig. 2 An ORTEP view of the non-hydrogen atoms of (hh,hh)-$[Rh_4(mhp)_4Cl_4(PhCN)_2]$ **3**. Thermal ellipsoids are drawn at the 50% level. A crystallographic C_2 axis passes through Cl(1) and Cl(3). Selected bond lengths (Å) and angles (°): Rh(1)–Rh(2) 2.537(3), Rh(1)–Cl(1) 2.356(6), Rh(1)–Cl(2) 2.343(7), 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)

bonds, thus the $Rh_4(\mu\text{-}Cl)_4$ 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 $[Rh_2(\mu\text{-}Cl)_2(Cl)_2(\mu\text{-}dppm)_2]$ (average 2.460 Å).[1]

The dependence of the UV/VIS spectrum of **1** in CH_2Cl_2–CH_3CN 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 concentration was around 10^{-4} mol dm^{-3} (see SUP 57397). The UV/VIS spectrum of the CH_3CN 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_3CN solution implies that $[Rh_4(O_2CPr^n)_4Cl_4(H_2O)_4]$ is formed by the substitution of the axial ligands with the conservation of the $Rh_4(\mu\text{-}Cl)_4$ skeletal arrangement.

The cyclic voltammogram‖ of **1** in CH_3CN 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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‖ The supporting electrolyte was 0.1 mol dm^{-3} $Bu^n_4NBF_4$, the counter electrode was Pt wire and the potential was measured relative to a BAS RE-5 Ag^+–Ag–CH_3CN reference electrode and converted to that relative to ferrocenium–ferrocene by measuring the oxidation potential of ferrocene.

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