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Stereochemical Control of Axial Binding for Dirhodium(II) Complexes

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The characterisation of complexes containing metal–metal bonds spanned by ligands such as 6-methyl-2-hydroxypyridine (H{mhp}) and the investigation of their electronic structure is of current interest [1–5]. Recently, we reported the isolation, crystal structure and some photoelectron spectral properties of [$Rh_2(mhp)_4$] [4]; these studies were consistent with the metal–metal bond of length 2.359 (1) Å having the $(\sigma)^2(\pi)^4(\delta)^2(\pi^*)^4(\delta^*)^2$ d-electronic configuration, corresponding to a Rh^{II}–Rh^{II} single bond. This yellow compound was isolated as one product of the reactions between Na(mhp) and [$Rh_2(O_2CMe)_4(MeOH)_2$] or $RhCl_3 \cdot 3H_2O$. We now report that these reactions also yield two green products, X-ray crystallographic studies of which have revealed that they involve a novel arrangement of four mhp ligands about a dimetal centre which leads to axial binding at only one of the rhodium atoms.

The products of the reaction between Na(mhp) and [$Rh_2(O_2CMe)_4(MeOH)_2$] or $RhCl_3 \cdot 3H_2O$ in methanol have been separated chromatographically and the compounds [$Rh_2(mhp)_4${H(mhp)}$_2$] isolated. *Crystal data*: [$Rh_2(mhp)_4${H(mhp)}] $\cdot$0.5 toluene; recrystallised from CH_2Cl_2/toluene. Monoclinic, $P2_1/n$, a = 12.025(2), b = 21.487(4), c = 13.086(3) Å, β = 104.18(1)°, V = 3278 Å^3, Z = 4. 7128 unique reflections with $2\theta \leqslant 60°$ and $I > 2\sigma(I)$ were measured with a Stoe–Siemens 4-circle diffractometer (Mo-K$_\alpha$ radiation, λ = 0.71069 Å), corrected for absorption and used for structure solution. Refinement with all non-hydrogen atoms anisotropic and with constraints on bond lengths, angles and isotropic thermal parameters for hydrogen atoms gives a current R of 5.61% (R_2 = 8.39%). There is evidence of toluene molecules disordered in the structure.

[{$Rh_2(mhp)_4$}$_2$] $\cdot 2CH_2Cl_2$; recrystallised from CH_2Cl_2 and petroleum ether. Tetragonal, $I4_1cd$, a = 21.126(4), c = 24.593(5) Å, V = 10.976 Å^3, Z = 8 for the formula as given. 3487 unique reflections with $2\theta \leqslant 60°$ and $I \geqslant 2\sigma(I)$, measured as indicated above, corrected for absorption, were used for structure solution. With refinement as above, R is currently 3.22% (R_2 = 4.51%). The absolute polarity of the crystal has not yet been determined. The structure consists of $Rh_4(mhp)_8$ units, with crystallographic two-fold rotation symmetry, and CH_2Cl_2 solvent molecules.

All [$M_2(mhp)_4$ (M = Cr, Mo, W, [1] Rh, [4] or Ru [5]) molecules reported so far correspond to approximate D_{2d} symmetry, with each metal being co-ordinated to two nitrogen and two oxygen atoms of the four bridging mhp ligands. Two methyl groups are located at each end of the molecule which appear to restrict the co-ordination of other ligands *trans* to the metal–metal bond.

The molecular frameworks of [$Rh_2(mhp)_4$-{H(mhp)}] and [{$Rh_2(mhp)_4$}$_2$] are illustrated in Figs. 1 and 2, respectively. Both molecules involve the same, hitherto unreported, arrangement of the four mhp ligands spanning the dimetal centre; one oxygen and three nitrogens are co-ordinated to one rhodium and one nitrogen and three oxygens to the other. This arrangement has the interesting consequence that three of the ligands' methyl groups are located at one end of the metal–metal axis and one is located at the other. For the latter location, steric constraints cannot prevent the binding of an additional ligand approximately colinear with the metal–metal axis. The axial ligand of [$Rh_2(mhp)_4$-{H(mhp)}] is co-ordinated *via* its oxygen atom, as

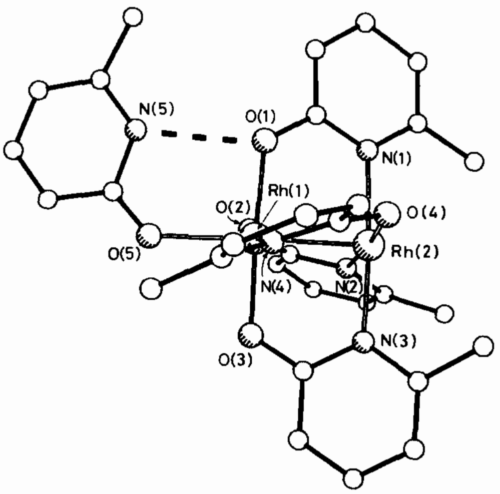

Fig. 1. [$Rh_2(mhp)_4${H(mhp)}] framework.

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TABLE I. Selected Dimensions for Dirhodium(II) Compounds.

Compound	r(Rh–Rh)/Å	r(Rh–O_{eq})/Å	r(Rh–O_{ax})/Å	(Rh–Rh–O_{ax})/degree	Ref.
[$Rh_2(mhp)_4$]	2.359(1)	2.017(4)	–	–	a
[{$Rh_2(mhp)_4$}$_2$]	2.369(1)	2.020(3)†, 2.045(3)*	2.236(3)	164.6(1)	b
[$Rh_2(O_2CCMe_3)_4(H_2O)_2$]	2.371(1)	2.039(2)	2.295(2)	179.8(1)	c
[$Rh_2(mhp)_4${H(mhp)}]	2.383(1)	2.024(4)†	2.195(4)	170.7(1)	b
[$Rh_2(O_2CMe)_4(H_2O)_2$]	2.386(1)	2.039(8)	2.310(3)	176.5(6)	c

^{a}Ref. [4]. ^{b}This work. ^{c}Ref. [7].

† Averaged for oxygens attached to the five co-ordinate Rh but excluding*.

*For the oxygens of the $\overline{RhORhO}$ bridge.

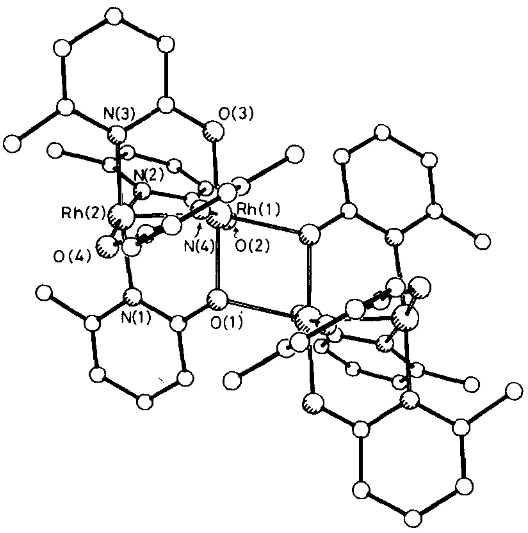

Fig. 2. [{$Rh_2(mhp)_4$}$_2$] framework.

well as being hydrogen bonded† from N(5) to O(1); in [{$Rh_2(mhp)_4$}$_2$], two of the $Rh_2(mhp)_4$ moieties are associated, each binding an oxygen atom of the other to form a central $\overline{RhORhO}$ ring. In both compounds, reduction of non-bonded repulsions at each end of the Rh–Rh bond, *i.e.* between the axial ligand and one methyl group and between the three methyl groups, apparently leads to twisting of the mhp rings, as compared to the more regular arrangements identified previously [1, 4, 5].

As indicated in Table I, the lengths of the Rh–Rh bond in the compounds reported here are only slightly (0.024 and 0.010 Å) longer than that in [$Rh_2(mhp)_4$]. This lengthening is attributed [6] to the axial co-ordination involving overlap of an oxygen lone-pair orbital with a metal orbital having some Rh–Rh σ^* character. However, the effect is small even though, on the basis of the Rh–O_{ax} bond lengths, reasonably strong axial binding is achieved. We note that the length of the Rh–Rh bond in [{$Rh_2(mhp)_4$}$_2$], or [$Rh_2(mhp)_4${H(mhp)}], with one Rh–O_{ax}, does not significantly differ from that in [$Rh_2(O_2CCMe_3)_4(H_2O)_2$] or [$Rh_2(O_2CMe)_4H_2O)_2$], respectively; these latter molecules having two Rh–O_{ax} bonds. A small static trans effect is apparent for the compounds reported here; the Rh–O_{ax} bond(s) are 0.19 ± 0.03 Å longer than the corresponding Rh–O_{eq} bonds.

In solution, [$Rh_2(mhp)_4${(mhp)}] slowly converts to [{$Rh_2(mhp)_4$}$_2$]. This change of axial ligation has prompted investigations of the possibility of achieving single axial co-ordination of other ligands to the $Rh_2(mhp)_4$ moiety. The complexes [$Rh_2(mhp)_4L$] (where L = Ph_3P, Pr^nNH_2, or CO) have been characterised and further studies are in progress.

Acknowledgment

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References

1 F. A. Cotton, P. E. Fanwick, R. H. Niswander and J. C. Sekutowski, *J. Amer. Chem. Soc.*, *100*, 4725 (1978).
2 C. D. Garner, I. H. Hillier, A. A. MacDowell, I. B. Walton and M. F. Guest, *J. Chem. Soc. Faraday II*, *75*, 485 (1979); C. D. Garner, I. H. Hillier, M. J. Knight, A. A. MacDowell, I. B. Walton and M. F. Guest, *J. Chem. Soc. Faraday II*, in press.
3 B. E. Bursten, F. A. Cotton, A. H. Cowley, B. E. Hanson, M. Lattman and G. G. Stanley, *J. Amer. Chem. Soc.*, *101*, 6244 (1979).
4 M. Berry, C. D. Garner, I. H. Hillier, A. A. MacDowell and W. Clegg, *J. Chem. Soc. Chem. Comm.*, 494 (1980).
5 M. Berry, C. D. Garner, I. H. Hillier, A. A. MacDowell and W. Clegg, submitted for publication.
6 G. G. Christoph and Y.-B. Koh, *J. Amer. Chem. Soc.*, *101*, 1422(1979) and references therein.
7 F. A. Cotton and T. R. Felthouse, *Inorg. Chem.*, *19*, 323 (1980) and references therein.

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† This hydrogen atom has not been located; it is assumed to be present because of the chemical formulation based on Rh^{II}, the N(5)– – –O(1) separation of 2.742(12) Å, and the C–O(1) bond length of 1.317(7) Å, which is the longest in the molecule.