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A Structural *Trans*-Influence Controlling the Position of Bridging Hydride Ligands: X-Ray Crystal Structures of $[\{Ru(pz)(pzH)(cod)\}_2(\mu\text{-}H)][PF_6]$ and $[\{Ru_2(pz)_2(Cl)(pzH)(cod)_2\}(\mu\text{-}H)]\cdot C_2H_5OH$ (cod = cycloocta-1,5-diene, pzH = pyrazole)

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We have recently described [1] the X-ray structure of the complex $[\{RuH(pz)(cod)\}_2pzH]$ (1; cod = cycloocta-1,5-diene, pzH = pyrazole) in which a hydride ligand was located in an unsymmetric bridging position. We postulated that the position of the bridging hydride was governed by the relative strengths of the structural *trans*-influence of the ligands coordinated *trans* to the M–H–M bridge. From X-ray crystallographic studies on the compounds (2) and (3), which are structurally very similar to (1), we are now in a position to provide experimental evidence for this proposal.

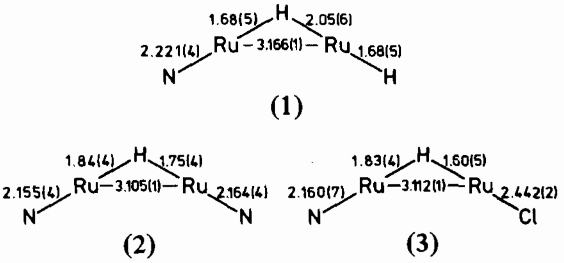
Experimental

$[(cod)(pzH)Ru(\mu\text{-}H)(\mu\text{-}pz)_2RuH(cod)]$ (1), $[(cod)(pzH)Ru(\mu\text{-}H)(\mu\text{-}pz)_2Ru(pzH)(cod)]^+$ (2), $[(cod)(pzH)Ru(\mu\text{-}H)(\mu\text{-}pz)_2RuCl(cod)]$ (3)

Compound (2) was synthesized (60% yield) by the reaction of $[RuH(cod)(NH_2NMe_2)_3][PF_6]$ [2] with pyrazole (2.1 molar equivalents) in acetone under reflux. Compound (3) formed quantitatively on allowing (1) to stand in CH_2Cl_2 over several hours at 20 °C. The NMR spectra of (2) and (3) indicated that the coordination geometry was symmetric in the former and unsymmetric in the latter (Table I). The structures of both compounds were established by three-dimensional X-ray diffraction techniques, see ** right hand column.

Discussion

The core geometries of complexes (1)–(3) are shown in Fig. 1; and the molecular structures of (2) and (3), together with the atom numbering scheme, are depicted in Figs. 2 and 3, respectively. The bridging hydride resides closer to Ru(1) in (1), is symmetrically bridged (within experimental error) in (2), and, resides closer to Ru(2) in (3). Thus, if the X-ray results are reliable, the position of the bridging hydride ligand is clearly influenced by changing a *trans* ligand from H^- to pzH to Cl^-.



(1)

(2)

(3)

Fig. 1. Core geometries of (I), (2) and (3).

Because of the relatively large margin of error associated [3, 4] with locating and refining hydrogen atom positions from data obtained by X-ray diffraction, other structural features which would lend support to the positions determined for the bridging hydrides were sought. It is well known [3] that hydride ligands exert a considerable structural *trans*-influence and it is therefore possible to examine the Ru(1)–N(pyrazole) bond lengths, which are common to all three structures, to deduce indirectly any change in position of the bridging hydride ligand. In compound (1), where the hydride was located closer

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**Crystal data (2): $C_{28}H_{39}F_6N_8PRu_2$, $M = 834.78$, monoclinic, space group $P2_1/n$, $a = 13.961(3)$, $b = 17.950(4)$, $c = 12.398(3)$ Å, $\beta = 91.66(2)°$, $U = 3105.6$ Å^3, $D_c = 1.785$ Mgm^{-3} for $Z = 4$, $F(000) = 1680$, MoKα radiation, $\lambda = 0.71069$ Å, μ(MoKα) = 0.977 mm^{-1}. (3): $C_{27}H_{41}ClN_6\cdot ORu_2$, $M = 703.26$, orthorhombic, space group $P2_12_12_1$, $a = 18.011(4)$, $b = 16.998(3)$, $c = 9.260(2)$ Å, $U = 2835.0$ Å^3, $D_c = 1.6479$ Mgm^{-3} for $Z = 4$, $F(000) = 1432$, μ(MoKα) = 1.070 mm^{-1}. The structures were solved (by Patterson and difference electron density synthesis methods) and were refined using SHELX [8]. Anisotropic temperature factors were used for all non-H atoms; all H atom positions were located and freely refined. The refinements converged with $R = 0.0336$ and $R_w = 0.0322$ for (2) and $R = 0.0310$ and $R_w = 0.0268$ for (3) for 3489 (2), 1940 (3) reflections with $F_o \geqslant 4\sigma(F_o)$ measured in the range $3 \leqslant \theta \leqslant 23°$ at 293 K on a Philips PW1100 4-circle diffractometer (NPRL, CSIR) using crystals of dimensions 0.40 × 0.30 × 0.20 mm grown from acetone–methanol solution (2) and 0.35 × 0.30 × 0.20 mm grown from dichloromethane–ethanol solution (3). The atomic coordinates for these structures are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, U.K. Any request should be accompanied by the full literature citation for this communication.

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TABLE I. NMR Data.[a]

Compound (2)	^1H	δ	11.25 (br, 2H, NH) 8.57 (d, 2H, CH) (pzH) 7.92 (d, 2H, CH) (pzH) 6.75 (t, 2H, CH) (pzH) 6.71 (d, 4H, CH) (pz) 6.06 (t, 2H, CH) (pz) 4.11 (br, 4H), 3.38 (br, 4H), (= CH of cod), 3.20–2.5 (16H, CH_2 of cod), –21.68 (1H, RuH)
	^{13}C		146.5 (1C), 138.8 (2C), 133.8 (1C), 108.7 (1C), 108.4 (1C), (pz and pzH), 89.1, 86.2 (= CH of cod) 33.20, 30.4 (= CH_2 of cod)
Compound (3)	^1H	δ	8.33 (d, 1H, CH), ^3J(HH) 3 Hz) (pzH) 7.71 (d, 2H, CH) (pz) 7.53 (d, 1H, CH) (pzH) 6.60 (t, 1H, CH) (pzH) 6.41 (d, 2H, CH) (pz) 6.01 (t, 2H, CH) (pz) 4.15 (br, 2H), 3.75 (br, 2H) 3.3 (br, 4H) (= CH of cod), 3.1–1.8 (16H, CH_2 of cod), –21.9 (1H, RuH)
	^{13}C		144.5 (1C), 138.4 (2C), 136.2 (2C), 131.8 (1C), 107.7 (1C), 106.6 (2C), (pz and pzH), 91.5, 85.6, 84.3, 82.6 (= CH of cod) 33.0, 32.9, 30.7, 30.0 (= CH_2 of cod)

[a] Abbreviations: d, doublet; t, triplet; ^3J(HH) ≃3 Hz; br, broad.

to Ru(1), the *trans*-Ru(1)–N bond length {2.221(4) Å} is significantly longer {0.061(6) Å} than the analogous bonds in (2) and (3); thus confirming the observed movement* of the hydride towards Ru(2) in (2) and (3) but with equal Ru(1)–H bond lengths in both complexes. The Ru···Ru distance is shorter by *ca.* 0.05 Å in (2) and (3) compared with that in (1) which is also in keeping with the stronger interaction of the hydride with Ru(2).

The differences in the ^1H NMR chemical shift values of the bridging hydride in (1), (2) and (3) provide additional support for the structural observations. Whereas in (1) the value is –7.82 ppm, in (2) and (3) the values are –21.68 and –21.90 ppm, respectively, indicating greater metal–metal interaction.

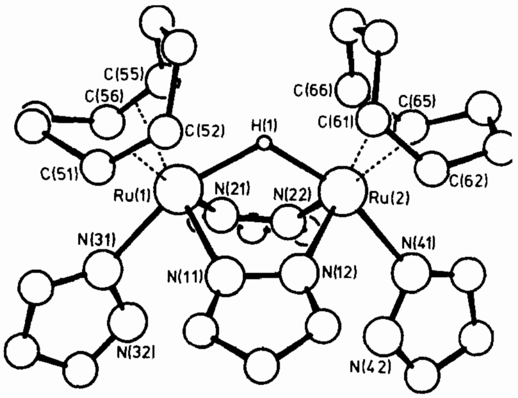

Fig. 2. A perspective view of (2) showing the atom numbering scheme. Selected bond lengths (Å) and angles (°): Ru(1)···Ru(2) 3.105(1), Ru(1)–H(1) 1.84(4), Ru(2)–H(1) 1.75(4), Ru(1)–N(11) 2.069(4), Ru(1)–N(21) 2.082(4), Ru(1)–N(31) 2.155(4), Ru(2)–N(12) 2.080(4), Ru(2)–N(22) 2.077(4), Ru(2)–N(41) 2.164(4), Ru(1)–C(51) 2.212(5), Ru(1)–C(52) 2.203(5), Ru(1)–C(55) 2.209(5), Ru(1)–C(56) 2.205(5), Ru(2)–C(61) 2.210(5), Ru(2)–C(62) 2.208(5), Ru(2)–C(65) 2.211(5), Ru(2)–C(66) 2.209(5), Ru(1)–N(11)–N(12) 115.1(3), Ru(1)–N(21)–N(22) 114.1(3), Ru(2)–N(12)–N(11) 114.2(3), Ru(2)–N(22)–N(21) 115.1(3).

Conclusions

Bridging hydrides have been located [5, 6] previously in unsymmetric positions and there is evidence indicating [5] that if the two metal centres are dissimilar, the hydride will be found closer to the more electron-deficient moiety. The structures of (2) and (3), together with that of (1), represent a unique series in that they provide the first opportunity to determine the location of bridging hydrides

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*Excluding the Ru–H_{br} bond *trans* to pyrazole in (1) as this parameter was not freely refined, an average Ru–H_{br} bond length *trans* to pyrazole of 1.81(5) Å is obtained; thus the differences between this average bond length and the Ru–H_{br} bond length *trans* to H, 0.24(8) Å and the Ru–H_{br} bond length *trans* to Cl, –0.21(7) Å are significant with a probability greater than 0.99.

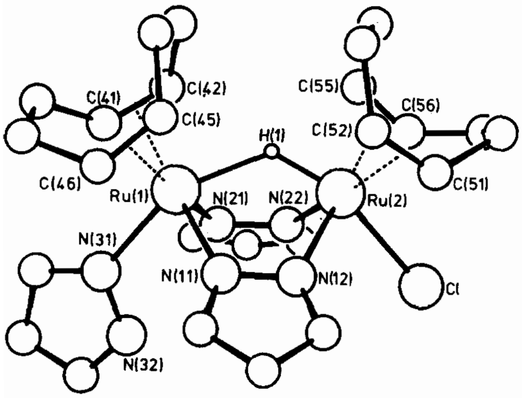

Fig. 3. A perspective view of (3) showing the atom numbering scheme. Selected bond lengths (Å) and angles (°): Ru(1)···Ru(2) 3.112(1), Ru(1)–H(1) 1.83(5), Ru(2)–H(1) 1.60(5), Ru(1)–N(11) 2.084(6), Ru(1)–N(21) 2.091(7), Ru(1)–N(31) 2.160(7), Ru(2)–N(12) 2.080(6), Ru(2)–N(22) 2.074(6), Ru(2)–Cl 2.442(2), Ru(1)–C(41) 2.195(8), Ru(1)–C(42) 2.191(8), Ru(1)–C(45) 2.200(10), Ru(1)–C(46) 2.184(9), Ru(2)–C(51) 2.203(9), Ru(2)–C(52) 2.194(9), Ru(2)–C(55) 2.216(9), Ru(2)–C(56) 2.190(8), Ru(1)–N(11)–N(12) 114.8(5), Ru(1)–N(21)–N(22) 114.2(5), Ru(2)–N(12)–N(11) 115.0(5), Ru(2)–N(22)–N(21) 116.0(5).

in three structurally similar compounds. Preliminary investigations [7] of the reactivity of the compounds have also shown that substitution of the ligands *trans* to the bridging hydride occurs readily, thus allowing the structural *trans*-influence on the bridging hydride to be studied with an extensive range of ligands. These studies will be the subject of future publications.

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