JOURNAL OF THE CHEMICAL SOCIETY

Chemical Communications

Number 20
1984

A Dinuclear Ruthenium Complex with a Semi-bridging Hydride Ligand: *X*-Ray Crystal Structure of [{RuH(pz)(cod)}$_2$pzH] (cod = cyclo-octa-1,5-diene, pzH = pyrazole)

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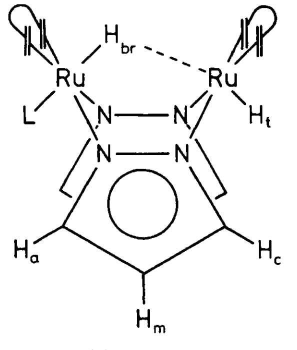
The *X*-ray structure of [{RuH(pz)(cod)}$_2$pzH] (cod = cyclo-octa-1,5-diene, pzH = pyrazole) reveals a semi-bridging hydride ligand [Ru(1)–H(1) 1.68(5) Å, Ru(2)–H(1) 2.05(6) Å, Ru(1)···Ru(2) 3.166(1) Å] in an unsymmetrical dimer with the ruthenium atoms linked by two pyrazolyl ligands; ^{1}H and ^{13}C n.m.r. spectra show that this structure persists in solution.

Transition metal complexes with bridging hydride ligands have been the target of many synthetic endeavours in recent years.[1] In most cases involving homonuclear metal species the bridging hydride was either found or presumed[1,2] to bridge the two metal centres in a symmetric fashion. There have been reports,[3] however, where the non-hydrogen atoms of the central core of a dinuclear species adopt an unsymmetrical geometry, and speculation has arisen[4] as to whether in such complexes the M(μ-H)M bridge is not symmetric. This question has been resolved by an *X*-ray crystal structure determination[5] of [Et$_4$N][Mo$_2$(μ-H)(CO)$_9$PPh$_3$] and a neutron diffraction analysis[6] of [L$_2$Pt(μ-H)$_2$PtHL$_2$] (L$_2$ = Ph$_2$PCH$_2$CH$_2$PPh$_2$), both of which show that the bridging hydride ligands reside in markedly asymmetric positions. In this communication we describe the *X*-ray structure of a diruthenium compound in which the 'bridging' hydride appears to adopt a unique semi-bridging configuration.

Treatment (333 K) of a suspension of [RuH(cod)(NH$_2$NMe$_2$)$_3$][PF$_6$][7] (cod = cyclo-octa-1,5-diene) in ethanol with pyrazole–triethylamine gave an orange precipitate (15 min, 60% yield) of (**1**). The i.r. spectrum showed the presence of a terminal hydride ligand [ν(RuH) 1990 cm^{-1}] whereas the ^{1}H n.m.r. spectrum contained two hydride doublets [*J*(HH) 12 Hz] at high field and resonances for the pyrazole and pyrazolyl hydrogen atoms showing two different ligand environments with the ratio of the ligands being 2 : 1. Since the spectroscopic data† did not allow assignment of the molecular geometry with certainty, an *X*-ray crystallographic study‡ of



(**1**) L = pzH
(**2**) L = PMe$_3$

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† N.m.r. spectroscopic data (CD$_2$Cl$_2$, 273 K) ^{1}H and ^{13}C-{^{1}H} on EM390 and CFT20 instruments respectively; Me$_4$Si internal reference. (**1**): ^{1}H δ 8.48 [d, 1H, CH, ^3J(HH) 3 Hz], 7.54 (d, 1H, CH), 7.27 (d, 2H, H$_c$), 6.59 (t, 1H, CH), 6.28 (d, 2H, H$_a$), 5.86 (t, 2H, H$_m$, pz and pzH), 3.6—3.1 (8H, =CH of cod), 3.0—1.8 (16H, CH$_2$ of cod), −7.82 [H$_{br}$, 1H, ^2J(H$_{br}$H$_t$) 12 Hz], and −10.45 (H$_t$, 1H). ^{13}C δ 143.4 (1C), 140.4(2C), 135.8(2C), 130.3(1C), 107.2(1C), 105.5(2C, pz and pzH), 78.5, 76.5 [=CH of Ru(2)(cod)], 73.0, 68.1 [=CH of Ru(1)(cod)], 33.9, 33.6, 31.7, and 29.5 (CH$_2$ of cod). (**2**): ^{1}H δ 7.31 [d, 2H, H$_c$, ^3J(HH) 3 Hz], 6.87 (d, 2H, H$_a$), 5.93 (t, 2H, H$_b$), 3.4—1.6 (cod, =CH and CH$_2$), 1.38 [d, 9H, CH$_3$, *J*(PH) 8 Hz], −4.5 [d of d, 1H, H$_{br}$, *J*(PH) 75 Hz, *J*(H$_{br}$H$_t$) 12 Hz], and −6.6 [d of d, 1H, H$_t$, *J*(PH) 23 Hz]. ^{13}C δ 140.7(2C), 136.1(2C), 104.8(2C, pz) 78.4, 76.5 [=CH of Ru(2)(cod)], 71.6 [d, *J*(PC) 28 Hz, =CH of Ru(1)(cod)], 66.8 [=CH of Ru(1)(cod)], 34.0, 32.9, 31.8, 30.7 (CH$_2$ of cod), and 16.9 [*C*H$_3$, *J*(PC) 23 Hz].

‡ *Crystal data* for (**1**): $C_{25}H_{36}N_6Ru_2$, M = 622.79, monoclinic, space group $P2_1/c$, a = 15.683(3), b = 10.716(2), c = 14.934(3) Å, β = 94.39(2)°, U = 2502(1) Å^3, Z = 4, D_c = 1.653 Mg m^{-3}, F(000) = 1264, μ(Mo-K_α) = 1.105 mm^{-1}. The structure was solved by Patterson and difference electron density synthesis methods using SHELX[13] and was refined by least-squares procedures. Anisotropic temperature factors were used for all non-H atoms; all the H atom positions were located and refined. The two hydride atoms, when allowed to refine freely, moved unacceptably close to their respective Ru atoms (Ru–H *ca.* 1.2 to 1.4 Å), but whenever the hydride atoms were omitted from the structure, peaks appeared in the electron density difference map in reasonable positions (*ca.* 1.68 Å from the respective Ru atoms). Therefore the two Ru–H bond lengths were constrained in the refinement to each equal 1.68 Å. The refinement converged with R = 0.0330 and R_w = 0.0301 for 2802 unique 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 a crystal of dimensions 0.3 × 0.28 × 0.18 mm grown from dichloromethane–ethanol solution.

The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

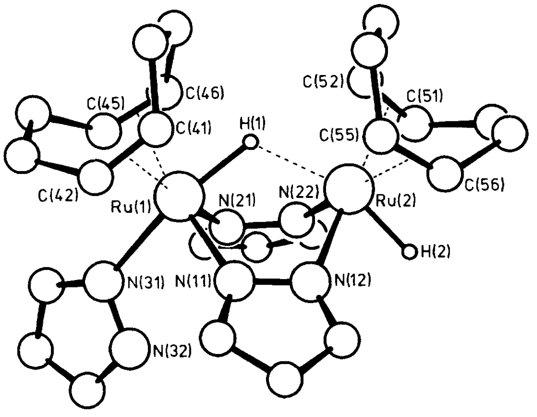
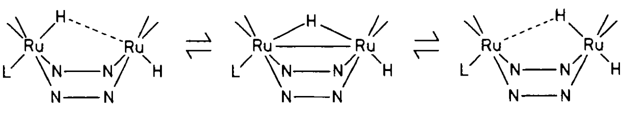


Figure 1. A perspective view of (**1**) showing the atom numbering scheme. The hydrogen atoms, except for H(1) and H(2), have been omitted for clarity. Bond lengths (Å) and angles (°): Ru(1)–Ru(2) 3.166(1), Ru(1)–H(1) 1.68(5), Ru(1)–N(11) 2.094(4), Ru(1)–N(21) 2.111(4), Ru(1)–N(31) 2.221(4), Ru(1)–C(41) 2.185(6), Ru(1)–C(42) 2.180(6), Ru(1)–C(45) 2.189(6), Ru(1)–C(46) 2.190(6), Ru(2)–H(1) 2.05(6), Ru(2)–H(2) 1.68(5), Ru(2)–N(12) 2.083(4), Ru(2)–N(22) 2.083(4), Ru(2)–C(51) 2.169(6), Ru(2)–C(52) 2.161(6), Ru(2)–C(55) 2.152(6), Ru(2)–C(56) 2.160(6), N(11)–N(12) 1.358(6), N(21)–N(22) 1.360(6), N(31)–N(32) 1.351(7); Ru(1)–N(11)–N(12) 116.8(3), Ru(1)–N(21)–N(22) 116.1(3), Ru(2)–N(12)–N(11) 114.3(3), Ru(2)–N(22)–N(21) 114.3(3).

suitable crystals of (**1**), grown from dichloromethane–ethanol, was undertaken.

The molecular structure of (**1**) is depicted in Figure 1, together with the atom numbering scheme. A RuH(cod) unit is linked to a RuH(cod)(pzH) (pzH = pyrazole) unit by two pyrazolyl ligands. The positions of the two hydride atoms were determined from a difference-electron density map; the hydride bonded to Ru(1) forms an unsymmetric bridge to Ru(2) [Ru(1)–H(1) 1.68(5) Å, Ru(2)–H(1) 2.05(6) Å]. Although the hydrogen atom positions must be interpreted with some caution given the relatively large errors associated with their determination by *X*-ray methods and the fact that it was necessary to constrain the Ru–H bond lengths in the refinement,‡ they nevertheless give bond lengths which are in the range found[8] previously for terminal ruthenium–hydride bonds. The solid state structure may be considered as being made up of a core framework of a six-membered ring (the two ruthenium and four pyrazolyl nitrogen atoms) which adopts a boat conformation, thus requiring that the hydride ligand of the 18-valence electron Ru(1) is brought close to the vacant site of the 16-valence electron Ru(2). This interpretation is based on the donor–acceptor model proposed earlier.[5,6] A refinement of the model predicts[5] that the bridging hydride ligand will interact more strongly with the more electron-deficient moiety. We offer a complementary interpretation; in (**1**) the stronger structural *trans* influence of the terminal hydride ligand on Ru(2) *vs.* the pyrazole ligand on Ru(1) forces the bridging hydride ligand to reside closer to Ru(1); thus the *trans* ligands may govern the position of a bridging hydride. That a substantial bonding interaction between H(1) and Ru(2) occurs is evident not only from the close approach [Ru(2)–H(1) 2.05(6) Å] but also from the highly strained boat conformation of the central six membered ring where the Ru–N–N angles are significantly smaller than the normal[9] value of *ca.* 120°. The distance between the two ruthenium atoms [3.166(1) Å] is also very short;[10] it is, however, longer than the range of distances found[11] in compounds with ruthenium–ruthenium bonds which suggests an 'open' M(μ-H)M bond[1] (*i.e.* a two electron three centre bond with little metal–metal interaction).



Scheme 1. L = pzH, PMe_3

The solution structure of (**1**) as deduced from ^1H and ^{13}C n.m.r. studies† is consistent with the solid state structure with the additional observation that site-exchange of the semi-bridging hydride may occur (Scheme 1). The hydride doublet at lower field in the ^1H n.m.r. spectrum of (**1**) is assigned to the bridging hydride in accordance with previous assignments.[12] Treatment of complex (**1**) in dichloromethane with PMe_3 gives an analogous complex (**2**), in which the pyrazole ligand of (**1**) is replaced by PMe_3; in the ^1H n.m.r. spectrum† of (**2**) the resonance at lower field is clearly shown by the magnitude of the *J*(PH) coupling to be due to the bridging hydride ligand.

Previous studies[9,10] have highlighted the bridging potential of the pyrazolyl ligand in the synthesis of dimetal systems. Reactions of the hydrazine hydride precursor to (**1**) with pyrazole under different conditions give other products, *e.g.* the salt $[RuH(cod)(pzH)(NH_2NMe_2)_2][PF_6]$, which is likely to be an ideal precursor to an extensive range of dimetallic complexes, and a cationic salt which is tentatively assigned a dimeric structure with a bridging hydride ligand, $[\{Ru(\mu\text{-}pz)(pzH)(cod)\}_2H][PF_6]$.

Received, 3rd May 1984; Com. 616

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