

HRu₃(CO)₈(PPh₃)B₂H₅: Crystallographic Confirmation of the First M₃B₂-Containing Analogue of Pentaborane(9)

Catherine E. Housecroft,*^a Dorn M. Matthews^a and Arnold L. Rheingold*^b

^a University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, UK

^b Department of Chemistry, University of Delaware, Newark, DE 19716, USA

Photolysis of [HRu₃(CO)₉B₂H₅] with PPh₃ gives the monosubstituted derivative [HRu₃(CO)₈(PPh₃)B₂H₅] in good yield; the molecular structure of this compound is determined and the results confirm that [HRu₃(CO)₈(PPh₃)B₂H₅] is an analogue of [B₅H₉] in which three {BH} units have been replaced by three isolobal {Ru(CO)₂L} (L = CO or PPh₃) fragments, as such, it is the first structurally characterised member of the M₃B₂-class of compound in the series {ML_n}_x{BH}_{5-x}H₄ (M = transition metal; ML_n = two-electron cluster fragment).

Recently we described¹ the synthesis and deprotonation of the triruthenaborane [HRu₃(CO)₉B₂H₅], **1**, a cluster first reported in 1977² but which has eluded crystallographic characterisation. No other cluster with an M₃B₂-core has been reported. We have proposed that **1** is a structural analogue of pentaborane(9) with three {Ru(CO)₃} fragments isolobally replacing three {BH} units (Fig. 1). As such, it belongs to the series of square based pyramidal clusters delineated by Fehlner,^{3,4} monometallic and dimetallic members of which have previously been realised,⁵ the earliest being [(η⁵-C₅H₅)CoB₄H₈]⁶ and [Fe(CO)₃B₄H₈].⁷ Apart from [B₅H₉] itself,⁸ structural characterisation of this group is limited to [(η⁵-C₅H₅)CoB₄H₈]^{9,10} and [Fe₂(CO)₆B₃H₇].¹¹ Here, we report the synthesis, spectroscopic characterisation and crystal structure determination of [HRu₃(CO)₈(PPh₃)B₂H₅], **2**, and confirm the square based pyramidal Ru₃B₂-core proposed for **1**.

Compound **2** was first observed as a product of the reaction of **1** with ≈ 2 equiv. of Ni(CO)₂(PPh₃)₂ in THF (tetrahydrofuran). The solution was photolysed for 2 h. Under these conditions, Ni(CO)₂(PPh₃)₂ functioned simply as a phosphine donor with respect to **1** rather than generating heterometallic metallaborane clusters as had been anticipated. We then prepared **2** directly by photolysing a THF solution of **1** and PPh₃ for 2 h. Separation of the crude mixture by TLC eluting with hexane gave unconverted **1** as the first fraction (about 60% recovery) and bright yellow **2** was collected in ≈ 30% yield as the second fraction.[†]

Crystals of **2** suitable for X-ray diffraction were grown from CH₂Cl₂ layered with hexane.[‡] The molecular structure of **2** along with selected bond distances and angles is shown in Fig. 2. The core structure consists of a distorted square pyramidal arrangement of three ruthenium and two boron atoms, the latter residing in basal sites, which are made inequivalent by the presence of one PPh₃ substituent on one of the basal ruthenium atoms. An alternative description of the structure is to consider **2** as a diboron capped Ru₃-triangle possessing a structure that is analogous to those of the alkyne capped HRu₃(CO)₉{C(CNBU)⁺CPh}¹² and the related

H₃Os₃(CO)₉C(OBC₈H₁₄)BCL.¹³ In this case, the PPh₃ ligand in **2** occupies an equatorial site in the plane containing the three Ru atoms. The carbonyl ligands are all terminal and are unexceptional. The Ru₃-frame is essentially an isosceles triangle with Ru(1)–Ru(3) significantly elongated with respect to Ru(1)–Ru(2) and Ru(2)–Ru(3). This, coupled with the fact that the carbonyl ligands on Ru(1) and Ru(3) bend away from the Ru(1)–Ru(3) vector, is consistent with the placement of a bridging hydride ligand along Ru(1)–Ru(3); this is supported in the ¹H NMR spectrum by a doublet at δ –18.3 and the coupling of 14 Hz is consistent with a *cis* relationship between the hydride and phosphorus atom.

Although no cluster bound H atoms were located by X-ray diffraction, the presence of one terminal hydrogen atom per boron atom, one B–H–B and two inequivalent Ru–H–B bridges is evident from the ¹H NMR spectrum of **2**. By analogy with [B₅H₉], the Ru–H–B bridges should lie along Ru(3)–B(2) and Ru(1)–B(1), respectively. The orientations of the carbonyl ligands on atoms Ru(1) and Ru(3) appear to be

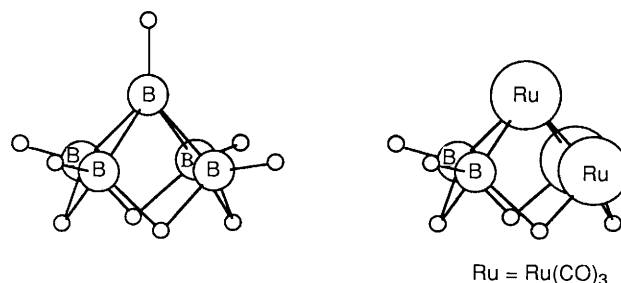


Fig. 1

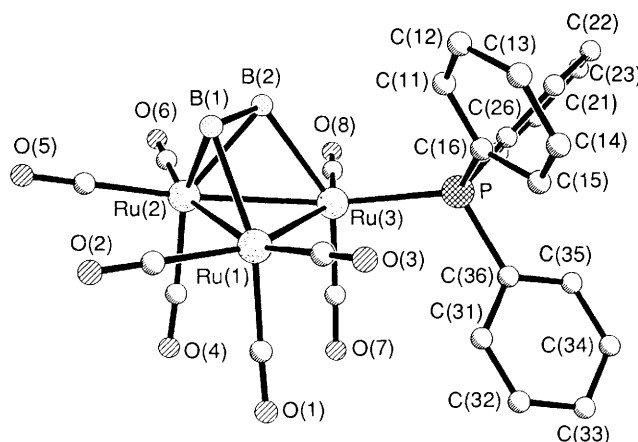


Fig. 2 Molecular structure of **2**: Ru(1)–Ru(3), 3.009(1); Ru(1)–Ru(2), 2.758(1); Ru(2)–Ru(3), 2.767(1); Ru(1)–B(1), 2.27(2); Ru(2)–B(1), 2.24(2); Ru(2)–B(2), 2.23(2); Ru(3)–B(2), 2.30(2); B(1)–B(2), 1.84(2); Ru(3)–P, 2.359(2) Å; Ru(1)–B(1)–B(2), 104.8(10); B(1)–B(2)–Ru(3), 104.8(10); B(2)–Ru(3)–Ru(1), 74.7(5); Ru(3)–Ru(1)–B(1), 75.6(4)°

[†] [HRu₃(CO)₈(PPh₃)B₂H₅], **2**: 400 MHz ¹H NMR (CDCl₃) δ 7.55–7.20 (m, 15 H, Ph), 4.6 (br 1H, BH), 4.1 (br 1H, BH), –1.2 (br 1H, B–H–B), –11.2 (br 1H, Ru–H–B), –12.1 (br 1H, Ru–H–B), –18.3 (d, J_{PH} 14 Hz, Ru–H–Ru); 128 MHz ¹¹B NMR (CDCl₃) δ + 17.6 (unresolved m, 1B), + 14.8 (unresolved m, 1B); 162 MHz ³¹P NMR (CDCl₃) δ + 34; IR (hexane, cm^{–1}) 2089m, 2053vs, 2044m, 2033s, 2021m, 1996m, 1991w; FAB–MS in 3-NBA matrix, *m/z* 818 (P⁺) (calc. for ¹²C₂₆¹H₂₁¹¹B₂¹⁶O₈³¹P¹⁰¹Ru₃ 817).

[‡] Crystal data for **2**: C₂₆H₂₁B₂O₈PRu₃, M_r = 817.2, triclinic, P $\bar{1}$ *a* = 10.947(3), *b* = 12.596(5), *c* = 12.758(4) Å, α = 63.49(3), β = 72.66(2), γ = 86.46(3)°, U = 1497.4(6) Å³, Z = 2, D_c = 1.813 g cm^{–3}, μ(Mo–Kα) = 15.91 cm^{–1}, T = 298 K. Intensity data were collected through the 2θ range of 4–55°. Of 6955 data collected (Siemens P4 diffractometer, SHELXTL PLUS software), 6663 were independent and 4406 with F_o ≥ 4σ(F_o) were observed. R_F = 6.95%, R_{w(F)}} = 8.19%. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

consistent with this proposal; we are currently exploring the bonding in **2**.

The synthetic strategy to obtain **1** and then **2** has been to introduce the borane moiety to a preformed Ru₃-framework, viz. Ru₃(CO)₁₂ or Ru₃(CO)_{12-x}(NCMe)_x (x = 1,2).¹ The molecular structure of **2** leaves a question as to the most relevant description of this compound and of its precursor **1**. As stated above, there is a resemblance between **2** and an M₃-platform capped in the so-called 'parallel' mode¹⁴ by an alkyne. On the other hand, the cluster chemist may convincingly look upon **2** as the first isolobal trimetal analogue of [B₅H₉]. We are currently exploring the reactivity patterns of **1** and **2** in order to establish whether the borane fragment remembers its parentage once it is associated with the trimetal unit, and to establish whether the diborane unit behaves as a ligand or as an integral part of an Ru₃B₂-cluster.

Acknowledgement is made to the Donors of the PRF, administered by the ACS, for support of this research (grant No. 22771-AC3), to the SERC for a studentship (to D. M. M.), to the NSF for a grant towards the purchase of a diffractometer at the University of Delaware, and to Johnson-Matthey for generous loans of RuCl₃.

Received, 25th October 1991; Com. 1/05452J

References

- 1 A. K. Chipperfield, C. E. Housecroft and D. M. Matthews, *J. Organomet. Chem.*, 1990, **384**, C38.
- 2 C. R. Eady, B. F. G. Johnson and J. Lewis, *J. Chem. Soc., Dalton Trans.*, 1977, 477.
- 3 T. P. Fehlner in *Boron Chemistry*, ed. R. W. Parry and G. Kodama, Pergamon, Oxford 1980, p. 95.
- 4 T. P. Fehlner, *Adv. Inorg. Chem.*, 1990, **35**, 199.
- 5 J. D. Kennedy, *Prog. Inorg. Chem.*, 1984, **32**, 519 and references cited therein.
- 6 V. R. Miller and R. N. Grimes, *J. Am. Chem. Soc.*, 1973, **95**, 5078.
- 7 N. N. Greenwood, C. G. Savory, R. N. Grimes, L. G. Sneddon, A. Davison and S. S. Wreford, *J. Chem. Soc., Chem. Commun.*, 1974, 718.
- 8 W. J. Dulmage and W. N. Lipscomb, *J. Am. Chem. Soc.*, 1952, **5**, 260; D. Schwoch, A. B. Burg and R. A. Beaudet, *Inorg. Chem.*, 1977, **16**, 3219; R. Greatrex, N. N. Greenwood, D. W. H. Rankin and H. E. Robertson, *Polyhedron*, 1987, **6**, 1849 and references cited therein.
- 9 L. G. Sneddon and D. Voet, *J. Chem. Soc., Chem. Commun.*, 1976, 118.
- 10 T. L. Venable and R. N. Grimes, *Inorg. Chem.*, 1982, **21**, 887.
- 11 E. L. Andersen, K. J. Haller and T. P. Fehlner, *J. Am. Chem. Soc.*, 1979, **101**, 4390; K. J. Haller, E. L. Andersen and T. P. Fehlner, *Inorg. Chem.*, 1981, **20**, 309.
- 12 S. A. MacLaughlin, J. P. Johnson, N. J. Taylor, A. J. Carty and E. Sappa, *Organometallics*, 1983, **2**, 352.
- 13 D. P. Workman, H.-B. Deng and S. G. Shore, *Angew. Chem., Int. Ed. Engl.*, 1990, **29**, 309; D. P. Workman, D.-Y. Jan and S. G. Shore, *Inorg. Chem.*, 1990, **29**, 3518.
- 14 E. Sappa, A. Tiripicchio and P. Braunstein, *Chem. Rev.*, 1983, **83**, 203.
- 15 P. R. Raithby and M. J. Rosales, *Adv. Inorg. Chem. Radiochem.*, 1985, **29**, 169.