The first rhodaboratrane: $[RhCl(PPh_3)\{B(mt)_3\}](Rh{\rightarrow}B)$ (mt = methimazolyl)†

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The reaction of $[Rh(C_6H_5)Cl_2(PPh_3)_2]$ with $Na[HB(mt)_3]$ (mt = methimazolyl) provides $[RhCl(PPh_3)\{B(mt)_3\}](Rh{\rightarrow}B)$ the first authentic example of a compound with a rhodium–boron dative bond.

Metal–boron dative bonding has long been hypothesised[1] but more recently called into question.[2] It was only with the isolation of the metallaboratranes $[M(CO)(PPh_3)\{B(mt)_3\}](M{\rightarrow}B)$ (Fig. 1, mt = methimazolyl, M = Ru **1**,[3,4] Os **2**[5]) that such interactions were unambiguously authenticated. In these cage structures a transannular bond between the formally zerovalent (d^8) group 8 metal and boron(III) is supported by three methimazolyl buttresses.

Our view of the bonding in such compounds supposes that a d^8-ML_5 fragment constrained to adopt a monovacant octahedral geometry would have a pair of electrons housed in an orbital of σ symmetry with respect to the vacant site. Under normal circumstances a C_{4v} d^8-ML_5 fragment would either relax to a trigonal bipyramidal geometry (*e.g.*, $Fe(CO)_5$) or dissociate a ligand to achieve the electronically favourable d^8-ML_4 square planar geometry (Fig. 2). Neither of these options is available to the geometrically constrained $[M(CO)(PPh_3)\{B(mt)_3\}]$ complexes and accordingly this electron pair is accepted by the trivalent bridgehead boron Lewis acid.

We are therefore currently concerned with exploring the limits of such interactions with respect to two issues: d-occupancy and metal σ-basicity. In the case of d-occupancy, clearly for C_{4v}-ML_5 with less than a d^8 configuration, the σ orbital in question is empty and therefore unable to act in the role of a Lewis base.‡ Indeed, the reactivity of C_{4v}-d^6-ML_5 complexes is dominated by their

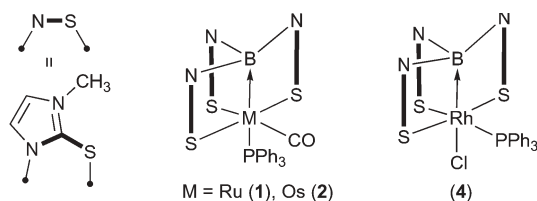σ-Lewis acidity. The question of metal σ-basicity is less straightforward, being a function of metal, oxidation state, charge and co-ligands. Thus the electron rich metal(0) centres in **1** and **2** would seem ideally suited for entering into such interactions. In this paper we wish to report the isolation of the first rhodaboratrane which whilst adopting a geometry and d-occupancy analogous to those of **1** and **2**, has the metal in a positive oxidation state.

The synthesis of the group 8 metallaboratranes discussed above proceeded *via* the reactions of $[M(R)Cl(CO)(PPh_3)_2]$ (R = aryl, vinyl, hydrido) with $Na[HB(mt)_3]$. The σ-organyl (or hydride) ligand in these substrates serves as a hydrogen acceptor and accordingly an isoelectronic rhodium(III) σ-organyl complex was required. The complex $[Rh(C_6H_5)Cl_2(PPh_3)_2]$ **3** has been previously obtained *via* a multi-step procedure, the phenyl ligand arising from fragmentation of an $SbPh_3$ ligand.[6] We find that the same complex may be more conveniently obtained *via* the reaction of Wilkinson's catalyst with phenylmercuric chloride (Scheme 1). In addition to ease, the advantage of this approach is that it is in principle extendable to a range of organomercurial halides although we have not yet explored this avenue.

Treating a dichloromethane–ethanol solution of **3** with $Na[HB(mt)_3]$ does indeed proceed to the formation of the desired rhodaboratrane $[RhCl(PPh_3)\{B(mt)_3\}](Rh{\rightarrow}B)$ **4** in 65% yield.§ When the reaction was carried out in $CDCl_3$ the formation of benzene was confirmed spectroscopically (^1H NMR).

The mechanism of formation is presumably as suggested in Scheme 2 by analogy with that proposed for **1** and **2** *via* (i) bidentate chelation of the $HB(mt)_3$ ligand; (ii) dissociation of a phosphine; (iii) formation of an agostic B–H–Rh interaction; (iv) B–H activation¶ and benzene reductive elimination and finally (v) coordination of the pendant mt group.

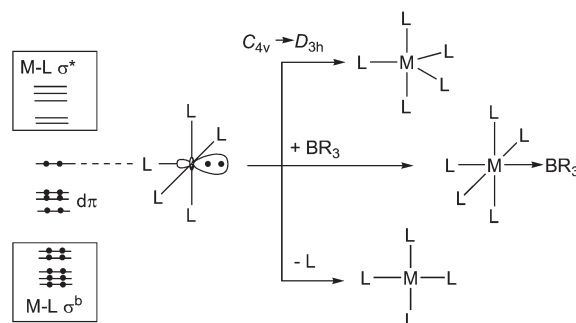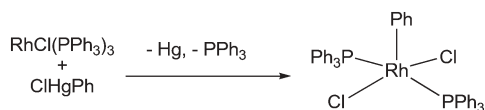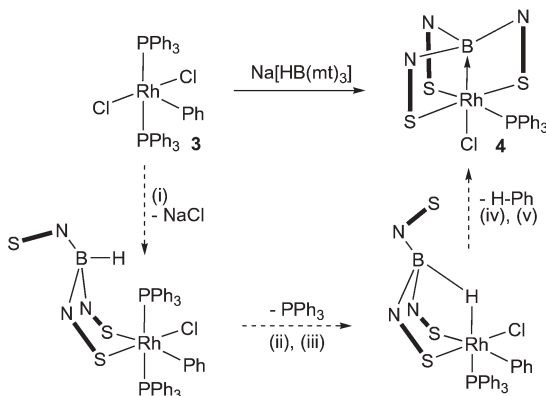The characterisation of **4** included a crystal structure determination,‖ however the formulation also followed from

Fig. 1 Metallaboratranes.

M = Ru (**1**), Os (**2**)

(**4**)

Fig. 2 Various options for an 18-valence electron C_{4v}-d^8 ML_5 complex.

Scheme 1 Synthesis of **3**.

Scheme 2 Suggested mechanism for the formation of **4**.

spectroscopic data. Of particular significance amongst these are (i) the absence of a ν(BH) infrared absorption; (ii) the existence of two methimazolyl environments (^{1}H NMR) and (iii) the appearance of a signal in the ^{31}P{^{1}H} NMR spectrum showing coupling to rhodium (δ 28.8 ppm, $^1J_{RhP}$ = 126 Hz). Notably, this signal shows a slight broadening as a result of interaction with the quadrupolar ^{11}B nucleus (half height width = 8 Hz). Similar broadening was noted in the case of **1** and **2**.

The X-ray analysis of crystals of **4** showed there to be two independent molecules (**A** and **B**) with essentially identical conformations, the rms fit of all the non-hydrogen atoms being *ca.* 0.14 Å (molecule **A** is shown in Fig. 3, molecule **B** in Fig S1 of ESI,† and an overlay of the two molecules in Fig. S2 of ESI†). The
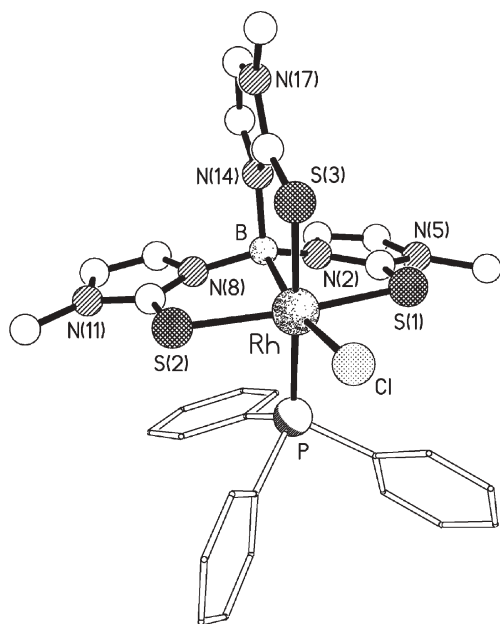

Fig. 3 Molecular geometry of molecule **A** of **4**.

geometry at rhodium is distorted octahedral with *cis* angles in the range **A**: 80.14(5)–101.20(6)° [**B**: 81.01(5)–100.65(5)°]. The Rh–B bond [**A**: 2.132(6), **B**: 2.122(7) Å], which is buttressed by three methimazolyl bridges, is slightly shorter than the corresponding Ru–B distance in **1**, though longer than seen in rhodium boryls[7] (typically in the range 1.96–2.05 Å); however it should be noted that the boron atoms in these latter species are three-coordinate, and the majority also involve five-coordinate rhodium, both factors expected to decrease the Rh–B separations. The geometry at boron is slightly distorted tetrahedral with angles in the range **A**: 106.1(4)–115.4(4)° [**B**: 104.8(5)–114.6(5)°]. As was seen in the structure of ruthenaboratrane **1**, the geometric constraints of accommodating adjacent, and bridged, tetrahedral (boron) and octahedral (rhodium) centres causes distortions in the S(1)- and S(2)-based chelate rings; whereas the fold angle between the {S,C,N,B} and {S,Rh,B} planes of the S(3) five-membered chelate ring is less than 1° for both molecules, the corresponding folds for the S(1) and S(2) chelate rings are *ca.* **A**: 26 and 17° [**B**: 27, 17°], respectively. The mt heterocycle *trans* to the phosphine shows a marginally longer Rh–S separation [Rh–S(3) **A**: 2.3867(15), **B**: 2.3898(15) Å] *cf.* those to S(1) and S(2) [**A**: 2.3704(16), 2.3692(17), **B**: 2.3674(16), 2.3640(16) Å respectively]. In the case of the ruthenaboratrane **1** the phosphine coordinates *trans* to the Ru→B bond whilst in **4** it is the chloride that is *trans* to boron. Since steric factors may be excluded, this preference might be traced to a preference for the weaker π-acid to coordinate *trans* to boron.

The synthesis and structural characterisation of **4** confirms that octahedral d^8-metallaboratrane formation is not limited to the electron rich zerovalent Os and Ru centres in **1** and **2**. Rather, rhodium(I) appears to also be sufficiently basic to enter into dative bonding to boron(III). In this respect it is noteworthy that Rabinovich has very recently obtained a five-coordinate cobaltaboratrane [Co(PPh₃){B(mt)₃}]BPh₄ as a minor side product from the decomposition of [Co(PPh₃){HB(mt)₃}]BPh₄.[8] Since this is a 16-valence electron complex, the bonding does not fit into the simple picture provided by Fig. 1.

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Notes and references

‡ Nevertheless there are examples in the early literature claiming dative interactions between d^6-Cr(CO)$_5$ fragments and boranes[1] which may however be discounted on simple electron counting grounds.
§ Data for **4**. NMR (CDCl₃, 25 °C) ^{1}H (300 MHz): δ_H 3.46 (s, 6H, NMe), 3.67 (s, 3H, NMe), 6.76, 7.65 (br s × 2, 1H × 2, NCH=CH), 6.82, 8.10 (br s × 2, 2H × 2, HCH=CH). ^{31}P{^{1}H} (121.4 MHz): δ_P 28.8 (d, J_{RhP} 125.9 Hz). ^{11}B{^{1}H} (96.2 MHz): δ_B 1.7 (hhw = 50 Hz). Anal. (Calc.) C 48.0 (47.98), H 4.12 (4.03), N 10.99 (11.19%).
¶ The term oxidative addition is in this instance inappropriate since the formal oxidation state of rhodium remains + III.
‖ *Crystal data* for **4**: C₃₀H₃₀BClN₆PRhS₃·3CH₂Cl₂, M = 1005.70, monoclinic, $P2_1/n$ (no. 14), a = 19.1229(9), b = 18.9722(6), c = 25.0598(9) Å, β = 110.156(4)°, V = 8535.0(6) Å³, Z = 8 (two independent molecules), D_c = 1.565 g cm^{-3}, μ(Cu-Kα) = 9.264 mm^{-1}, T = 293 K, yellow prisms; 12 667 independent measured reflections, F^2 refinement, R_1 = 0.045,

$wR_2 = 0.100$, 7916 independent observed absorption-corrected reflections [$|F_o| > 4\sigma(|F_o|)$, $2\theta_{max} = 120°$], 709 parameters. CCDC 248523. See http://www.rsc.org/suppdata/cc/b4/b413305f/ for crystallographic data in .cif or other electronic format.

1 K. B. Gilbert, S. K. Boocock, S. G. Shore, in *Comprehensive Organometallic Chemistry*, ed. E. W. Abel, F. G. A. Stone and G. Wilkinson, 1982, Pergamon, Oxford, **vol. 6**, pp. 880–886.
2 H. Braunschweig, *Angew. Chem., Int. Ed.*, 1998, **37**, 1786.
3 A. F. Hill, G. R. Owen, A. J. P. White and D. J. Williams, *Angew. Chem., Int. Ed.*, 1999, **38**, 2759.
4 M. R. St.-J. Foreman, A. F. Hill, G. R. Owen, A. J. P. White and D. J. Williams, *Organometallics*, 2003, **22**, 4446.
5 M. R. St.-J. Foreman, A. F. Hill, A. J. P. White and D. J. Williams, *Organometallics*, 2004, **23**, 913.
6 R. Cini and A. Cavaglioni, *Inorg. Chem.*, 1999, **38**, 3751.
7 G. J. Irvine, M. J. G. Lesley, T. B. Marder, N. C. Norman, C. R. Rice, E. G. Robins, W. R. Roper, G. R. Whittell and L. J. Wright, *Chem. Rev.*, 1998, **98**, 2685.
8 D. J. Mihalcik, J. L. White, J. M. Tanski, L. N. Zakharov, G. P. A. Yap, C. D. Incarvito, A. L. Rheingold and D. Rabinovich, *Dalton Trans.*, 2004, 1626.