Letters

Three-centre Ru–H–B bonding. A common feature of polyhedral ruthenaborane chemistry

A recent report in metalladicarbaborane chemistry describes a particular B–H–Ru interaction as 'agostic'.[1] Specifically, a *nido*-dicarbaundecaborane-to-ruthenium linkage in the compound $[\mathrm{RuCl\{7,8\text{-}\mu\text{-}S(CH_2CH_2)SC_2B_9H_{10}\}(PPh_3)_2}]$, in which a formal {B–H(*exo*)} unit binds to the metal atom, was cited as novel in this regard. However, it should be pointed out that ruthenium–cluster interactions of this nature have been established for some time in polyhedral boron chemistry. They have been reported to occur not only *via* monodentate {B–H(*exo*)}–Ru interaction, as above and in $[\mathrm{(PPh_3)_2Ru(MeCO_2)_3H_2RuB_{10}H_7(OEt)_2}]$,[2] but also *via* bidendate $\{$B–H(*exo*)$\}_2$–Ru, as in $[\mathrm{(PPh_3)_2ClRuClRu(PPh_3)B_{10}H_8(OEt)_2}]$,[3] and *via* tridentate $\{$B–H(*exo*)$\}_3$–Ru,[4] as in $[\mathrm{(PPh_3)_2ClRuB_{12}H_{11}(NEt_3)}]$.

An agostic interaction in organometallic chemistry is generally interpreted in terms of a two-electron two-centre C–H unit in which the hydrogen atom, or the two electrons in the C–H bond, approach to within bonding distance of the metal atom. In carbon chemistry this occurrence is quite rare in the ground state, and merits comment when encountered. However, in the chemistry of metallaborane and metallaheteroborane clusters, the equivalent interaction, a M–H–B bridge bond, is a very common structural motif.[5]

It is illustrative to consider Ru–H–B linkages more generally in this context, and Table 1 lists data for Ru–H–B bridges from a variety of polyhedral ruthenaborane species. The ruthenium–boron distances range from 215.2 to 248.4 pm, and are thereby generally somewhat towards the higher end of established ranges of ruthenium-to-boron bonding distances in polyhedral metallaboranes and metallaheteroboranes (*ca.* 200–250 pm). Their associated ^{1}H chemical shifts span a large range from $\delta(^1\mathrm{H})$ +1.14 to −17.57. Linkages both of the B–H(*exo*)–M and open-face B–H(*endo*)–M varieties occur throughout both these ranges. There appears to be no particular correlation of $\delta(^1\mathrm{H})$ with ruthenium–boron distances, or with the disposition of the other ligands about ruthenium.

In this context the ruthenium–boron distance of 241 pm[1] for $[\mathrm{RuCl\{7,8\text{-}\mu\text{-}S(CH_2CH_2)SC_2B_9H_{10}\}(PPh_3)_2}]$ is a little longer than the average of reported B–H–Ru distances, but is not exceptionally long. Its associated ^{1}H chemical shift of $\delta(^1\mathrm{H})$

Table 1 Parameters for Ru–H–B linkages in polyhedral ruthenaboranes

Compound	Ru–B	$\delta(^1\mathrm{H})$	*trans* Group	Ref.
$[\mathrm{(PPh_3)_2ClRu(S_2C_2H_4)C_2B_9H_{10}}]$	241	−17.4	Cl	1
$[\mathrm{(PMe_3)(C_5Me_5)RuB_2H_7}]$	230.4(4)	−11.1	$\mathrm{C_5Me_5}$	6
$[\mathrm{(PPh_3)_2(CO)HRuB_3H_8}]$	248.4(6)	−7.23	H	7, 8
	243.9(6)	−9.41	CO	7, 8
$[\mathrm{(C_6Me_6)ClRuB_3H_8}]$	—	−9.50	$\mathrm{C_6Me_6/Cl}$	9
$[\mathrm{\{HB(pz)_3\}(CO)HRuB_3H_8}]^a$	—	−14.34	$\mathrm{HB(pz)_3}$	10
$[\mathrm{(PPh_3)_2(CO)\text{-}2\text{-}RuB_4H_8}]$	—	−9.95	$\mathrm{PPh_3}$	7
	—	−9.31	CO	7
$[\mathrm{(C_5Me_5)(PMe_3)\text{-}3\text{-}RuB_4H_9}]$	220.0(3)	−16.10	$\mathrm{C_5Me_5/PMe_3}$	11
$[\mathrm{(PPh_3)_2(CO)\text{-}2\text{-}RuB_5H_9}]$	—	−8.53	CO	7
	—	−9.79	$\mathrm{PPh_3}$	7
$[\mathrm{(C_6Me_6)\text{-}4\text{-}RuB_5H_9}]$	220.9(7)	−12.39	$\mathrm{C_6Me_6}$	12
	219.7(7)			
$[\mathrm{(PPh_3)_2H\text{-}6\text{-}RuB_9H_{12}(PPh_3)}]$	226.3(11)	−6.26	H	7
	231.1(10)	−8.73	$\mathrm{PPh_3}$	7
$[\mathrm{(PPh_3)_2(CO)\text{-}6\text{-}RuB_9H_{13}}]$	—	−8.56	CO	7
	—	−10.23	$\mathrm{PPh_3}$	7
$[\mathrm{(C_6Me_6)\text{-}6\text{-}RuB_9H_{13}}]$	223.3(8)	−10.05	$\mathrm{C_6Me_6}$	12, 13
$[\mathrm{(C_6Me_6)\text{-}5\text{-}RuB_9H_{13}}]$	—	−15.63	$\mathrm{C_6Me_6}$	14
$[\mathrm{(C_6Me_6)\text{-}5\text{-}RuB_9H_{11}(PPh_3)}]$	—	−17.57	$\mathrm{C_6Me_6}$	13
$[\mathrm{(C_6Me_6)\text{-}5\text{-}RuB_9H_{12}(OMe)}]$	215.2(5)	−16.45	$\mathrm{C_6Me_6}$	15
$[\mathrm{(NMe_2)(PMe_2Ph)(C_6Me_6)\text{-}5\text{-}RuB_9H_{10}}]$	223.3(5)	−13.76	$\mathrm{C_6Me_6}$	16
$[\mathrm{(PPh_3)_2H\text{-}6\text{-}RuB_9H_{12}(PPh_3)}]$	226.3(11)	−6.26	H	7
	231.1(10)	−8.73	$\mathrm{PPh_3}$	7
$[\mathrm{(PMe_2Ph)_3\text{-}6\text{-}RuB_9H_{13}}]$	—	−11.14	$\mathrm{PMe_2Ph}$	17
$[\mathrm{(PPh_3)_2ClRuClRu(PPh_3)B_{10}H_8(OEt)_2}]$	232.5(11)	−1.3	$\mathrm{PPh_3}$	3
	246.0(5)	−13.5	Cl	3
$[\mathrm{(PPh_3)_2ClRuClOs(PPh_3)B_{10}H_8(OEt)_2}]$	—	−0.1	$\mathrm{PPh_3}$	3
	—	−14.2	Cl	3
$[\mathrm{(dppm)ClRuClRu(PPh_3)B_{10}H_8(OEt)_2}]^b$	235.5(16)	−2.5	$\mathrm{PPh_3}$	3
	240.8(19)	−14.8	Cl	3
$[\mathrm{(PPh_3)_2Ru(MeCO_2)_3H_2RuB_{10}H_7(OEt)_2}]$	224.0(6)	+1.14	$\mathrm{PPh_3}$	2
$[\mathrm{(C_6Me_6)RuB_{10}H_{13}}]^-$	232.9(6)	-8.75^c	$\mathrm{C_6Me_6}$	18
	235.6(6)	-8.75^c	$\mathrm{C_6Me_6}$	18
$[\mathrm{(PMe_2Ph)_3RuB_{12}H_{12}}]$	—	−5.41	$\mathrm{PMe_2Ph}$	4
$[\mathrm{(PPh_3)_2ClRuB_{12}H_{11}(NEt_3)}]$	226.9(12)	−0.37	Cl	4
	248.4(12)	−1.16	$\mathrm{PPh_3}$	4
	245.0(11)	−1.16	$\mathrm{PPh_3}$	4

[a] pz = Pyrazol-1-yl. [b] dppm = $\mathrm{Ph_2PCH_2PPh_2}$. [c] Fluxional molecule: $\delta(^1\mathrm{H})$ is the average for two Ru–H–B bridges and one B–H–B bridge.[18]

-17.4, although to relatively high field, is exceeded by that in [7-(PPh_3)-5-(C_6Me_6)-*nido*-5-RuB_9H_{11}], a conventionally *nido*-structured species[13] with a conventional open-face Ru–H(*endo*)–B bridging system. The linkage in question therefore lies towards one end of reported ranges for B–H–Ru interactions, but not uniquely so.

In view of the ubiquity and wide range of boron–hydrogen–metal linkages known, there would therefore seem at present to be no value in singling out such an example of a common established type of B–H–M interaction as having unusual 'agostic' character. This type of B–H(*exo*)–M linkage, out of the context of ruthenium dicarbaundecaborane chemistry, has a long pedigree,[5] going back at least to the structure[19] of [$Cu_2B_{10}H_{10}$] established more than thirty years ago. More unusual M–H–B interactions do however occur; for example, in the macropolyhedral rhodaborane [$(C_5Me_5)_2Rh_2B_{17}H_{19}$][20] a formal BH(*exo*) hydrogen atom appears to be forced into an otherwise ostensibly saturated metal co-ordination sphere, with the metal-to-boron distance being 243(2) pm, associated with a $\delta(^1H)$ value of -5.50.

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