Ruthenatetraboranes: Molecular Structure of $[Ru(B_3H_8)(PPh_3)\{\kappa^3\text{-}HB(pz)_3\}]$ (pz = Pyrazol-1-yl)

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Introduction

A number of "half-sandwich" or "piano-stool" metallatetraboranes have been described, resulting from the metathesis reactions of suitable "half-sandwich" metal halides with salts of the octahydrotriborate anion.[1] Thus the complexes $[MCl(CO)_n(\eta^5\text{-}C_5H_5)]$ ($n = 3$, M = Mo, W; $n = 2$, M = Fe, Ru) and $[Ru_2(\mu\text{-}Cl)_2Cl_2(\eta^6\text{-}C_6Me_6)_2]$ react with either ammonium or thallous salts of the B_3H_8 anion to provide the metallatetraboranes $[M(B_3H_8)(CO)_{n-1}(\eta^5\text{-}C_5H_5)]$[2] and $[Ru(B_3H_8)Cl(\eta^6\text{-}C_6Me_6)]$.[3] Full sandwich metallatetraboranes are also known for titanium[4] and niobium.[5] Bearing in mind the well-established parallels in the coordination chemistry of the cyclopentadienyl and hydrotris(pyrazol-1-yl)borate[6] anions, we have recently described the synthesis of the ruthenatetraborane $[Ru(B_3H_8)(PPh_3)\{\kappa^3\text{-}HB(pz)_3\}]$ (pz = pyrazol-1-yl, Scheme 1)[7] which is notionally related to the previously described complex $[Ru(B_3H_8)(CO)(\eta^5\text{-}C_5H_5)]$[2], for which only limited spectroscopic data are available.

We were eager to place the proposed formulation on a firmer structural footing for two reasons. First, no structural data is available for "half-sandwich" metallatetraboranes, all previous and in general unstable examples having been characterized spectroscopically. Second, the ^{11}B NMR data for $[Ru(B_3H_8)(PPh_3)\{\kappa^3\text{-}HB(pz)_3\}]$ initially appeared unusual in that only two resonances of equal intensity were observed. We have attributed this to the accidental coincidence of signals for the $HB(pz)_3$ and ruthenatetraborane wingtip boron nuclei. We have now obtained single crystals of $[Ru(B_3H_8)(PPh_3)\{\kappa^3\text{-}HB(pz)_3\}]$ suitable for *X* -ray crystallography and report herein the results which confirm our original formulation.

Scheme 1

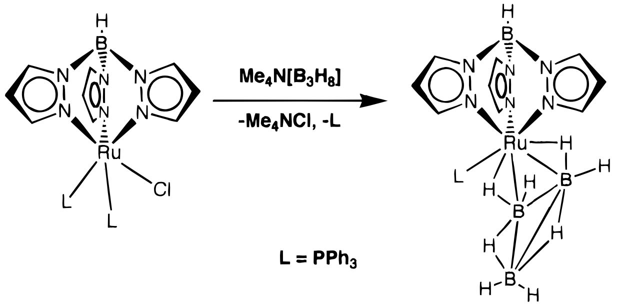

Table 1. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Coefficients ($Å^2 \times 10^3$)

	x	*y*	*z*	*U*(eq)[a]
Ru	6119(1)	3234(1)	2099(1)	25(1)
B(1)	7395(7)	4946(4)	1712(5)	43(3)
B(2)	6468(6)	4150(4)	1069(4)	36(2)
B(3)	6003(6)	4656(4)	1853(4)	40(3)
N(1)	6069(3)	2013(2)	1725(3)	29(1)
N(2)	5150(4)	1530(3)	1762(3)	35(2)
C(3)	5308(6)	782(3)	1501(4)	50(3)
C(4)	6338(6)	777(4)	1279(4)	51(3)
C(5)	6781(5)	1553(3)	1427(3)	36(2)
N(6)	4247(3)	3228(3)	1209(3)	31(1)
N(7)	3559(4)	2574(3)	1278(3)	35(2)
C(8)	2444(5)	2634(4)	641(4)	44(2)
C(9)	2398(5)	3333(4)	159(4)	50(2)
C(10)	3541(5)	3675(4)	537(3)	41(2)
N(11)	5371(3)	2914(3)	3067(3)	29(1)
N(12)	4559(4)	2294(3)	2906(3)	34(2)
C(13)	4209(5)	2192(4)	3613(4)	43(2)
C(14)	4797(5)	2747(4)	4256(4)	42(2)
C(15)	5506(4)	3194(3)	3887(3)	36(2)
B(4)	4093(6)	1901(4)	1961(4)	38(2)
P	8076(1)	3052(1)	3119(1)	26(1)
C(17)	10548(3)	3420(2)	3490(2)	39(2)
C(18)	11583	3552	3271	43(2)
C(19)	11502	3534	2375	53(3)
C(20)	10385	3384	1696	44(2)
C(21)	9350	3252	1914	37(2)
C(16)	9431	3269	2811	29(2)
C(23)	9157(3)	3222(2)	5017(2)	39(2)
C(24)	9500	3661	5817	47(2)
C(25)	9171	4473	5807	47(2)
C(26)	8499	4846	4995	46(2)
C(27)	8156	4407	4195	36(2)
C(22)	8485	3595	4205	30(2)
C(29)	7613(3)	1629(2)	3884(2)	39(2)
C(30)	7764	815	4132	48(2)
C(31)	8672	360	3980	49(3)
C(32)	9429	718	3580	47(2)
C(33)	9278	1531	3332	36(2)
C(28)	8370	1987	3484	29(2)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Results and Discussion

The complex $[Ru(B_3H_8)(PPh_3)\{\kappa^3\text{-}HB(pz)_3\}]$ forms pale yellow crystals suitable for X-ray crystallography by slow diffusion of a dichloromethane solution into ethanol. The results of the structural determination are summarised in Tables 1−3 and Figures 1−3.

The molecular geometry may be described as an *arachno* ruthenatetraborane with an *exo* coordinated $HB(pz)_3$ and an *endo* triphenylphosphine ligand (Figure 1).

In adopting a butterfly-type structure, two sites are available to the PPh_3 and $HB(pz)_3$ ligands for coordination to ruthenium and in principle isomers may arise depending on which of these two sites each ligand occupies (Chart 1). The phosphine ligand is seen to occupy the *endo* position suggesting that it has the more modest steric requirements of the two ligands. However it should be pointed out that by adopting this geometry, one pyrazole ligand fits between the two ruthenium-bound boron

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Table 2. Selected Bond Lengths (Å) and angles (deg) for the complex [Ru(B_3H_8)(PPh_3){HB(pz)$_3$}]

Bond Lengths					
Ru−P	2.317(1)	Ru−B(2)	2.371(7)	Ru-B(3)	2.379(7)
Ru−N(1)	2.099(4)	Ru−N(6)	2.154(3)	Ru−N(11)	2.092(5)
B(1)−B(2)	1.781(9)	B(1)-B(3)	1.792(11)	B(2)-B(3)	1.741(11)

Interbond Angles			
B(2)−Ru−B(3)	43.0(3)	B(2)−Ru−N(1)	114.4(2)
B(3)−Ru−N(1)	155.4(2)	B(2)−Ru−N(6)	86.3(2)
B(3)−Ru−N(6)	84.9(2)	N(1)−Ru−N(6)	83.7(2)
B(2)−Ru−N(11)	152.9(2)	B(3)−Ru−N(11)	110.9(2)
N(1)−Ru−N(11)	89.3(2)	N(6)−Ru−N(11)	83.4(2)
B(2)−Ru−P	101.2(1)	B(3)−Ru−P	103.2(2)
N(1)−Ru−P	89.7(1)	N(6)−Ru−P	171.6(1)
N(11)−Ru−P	91.4(1)	B(2)−B(1)−B(3)	58.3(4)
Ru−B(2)−B(1)	107.2(4)	Ru−B(2)−B(3)	68.8(3)
B(1)−B(2)−B(3)	61.2(4)	Ru−B(3)−B(1)	106.5(4)
Ru−B(3)−B(2)	68.2(3)	B(1)−B(3)−B(2)	60.5(4)

Table 3. Crystallographic Data for [Ru(B_3H_8)(PPh_3){κ^3-HB(pz)$_3$}]

formula: $C_{27}H_{33}B_4N_6PRu$
$a = 11.749(2)$ Å
$b = 16.532(2)$ Å
$c = 15.894(2)$ Å
$\beta = 110.71(2)$ °
$V = 2887.8(6)$ Å^3
$Z = 4$
$\rho_{calc} = 1.419$ g cm^{-3}

fw = 616.9
monoclinic
space group = $P2_1/c$
$\lambda = 0.710\ 73$ Å
μ(Mo Ka) = 0.627 mm^{-1}
$F(000) = 1264$
$T = 293$ K
$R = 0.0426$ ($R_w = 0.0416$)[a]

[a] $R = \sum|F_o - F_c|/\sum|F_o|$; $R_w = \sum[|F_o - F_c|w^{1/2}]/\sum[|F_o|w^{1/2}]$, where $w^{-1} = [\sigma^2(F_o) + g(F_o^2)]$ and $g = 0.0007$.

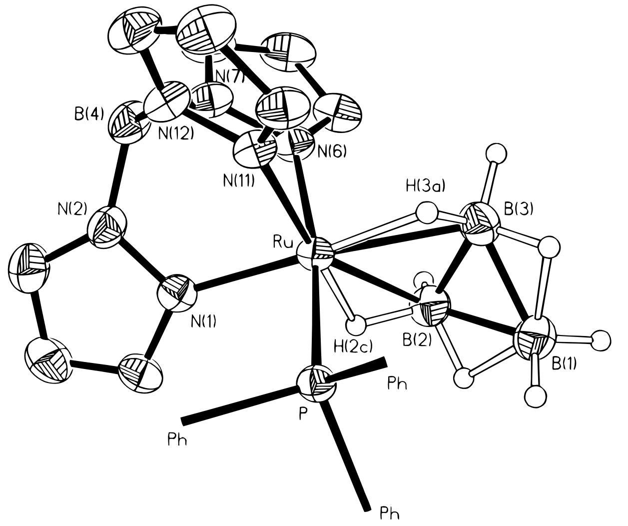


Figure 1. Molecular geometry of [Ru(B_3H_8)(PPh_3){HB(pz)$_3$}]. Pyrazole H-atoms and phenyl groups were omitted for clarity.

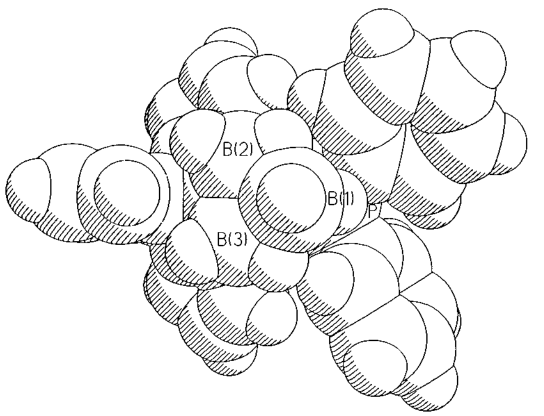
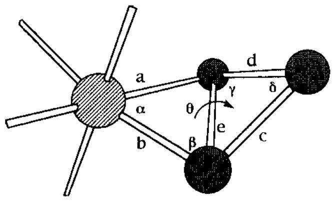


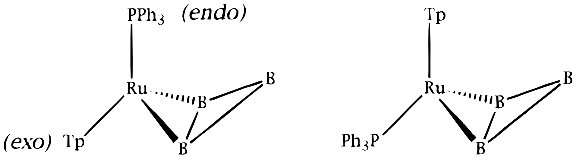
Figure 2. Space-filling representation of [Ru(B_3H_8)(PPh_3){HB(pz)$_3$}] illustrating the efficient accommodation of the triboronate ligand.



Dimension (Å)	(1)	(2)	Dimension (°)	(1)	(2)
a	2.439(6)	2.371(7)	α	41.3(2)	43.0(3)
b	2.484(6)	2.379(7)	β	67.9(3)	68.2(3)
c	1.809(10)	1.792(11)	γ	61.0(4)	61.2(4)
d	1.802(10)	1.781(9)	δ	57.6(3)	58.3(4)
e	1.738(9)	1.741(11)	θ	124.4	125.2

Figure 3. Comparison of geometries for ruthenatetraboranes [RuH(B_3H_8)(CO)(PPh_3)$_2$] (**1**)[8b] and [Ru(B_3H_8)(PPh_3){HB(pz)$_3$}] (**2**).

Chart 1. Possible Conformations for [Ru(B_3H_8)(PPh_3)(Tp)] (Tp = HB(pz)$_3$)



atoms and the wing-tip BH_2 group is in turn able to fit between two phenyl rings. This efficient accommodation of the B_3H_8 ligand between the phosphine and tris(pyrazolyl)borate ligands is evident from the space-filling representation shown in Figure 2.

Alternatively, considering the B−H−Ru bridges as ligands, the ruthenium coordination can be described as octahedral. Most notably, the hydrogen atoms of these bridges are virtually colinear with the bonds between ruthenium and N(1) and N(11) of the trans pyrazole groups (both H−Ru−N angles are 176(2)°). The most notable departure from octahedral geometry is exhibited by the pyrazol trans to the phosphine ligand [P−Ru−N(6) 171.6(1)°] and since this would not be expected on steric grounds, it must be assumed that the clearly stronger *trans* influence of the phosphine [Ru−N(6) 2.154(3) Å] relative to the borane [Ru−N(1) 2.099(4), Ru−N(11) 2.092(5) Å] causes the cage strain within the Ru(pz)$_3$BH moiety to be relaxed primarily through weakening of this pyrazole coordination. In this and our other structural studies of ruthenium complexes of the hydrotris(pyrazolyl)borate ligand we have observed that the three Ru−N vectors are typically contracted from orthogonality, e.g., for [RuCl(PPh_3)$_2${HB(pz)$_3$}] (mean N−Ru−N 85.1°)[7] and [Ru{C(C≡CPh)=CHPh}(CO)(PPh_3){HB(pz)$_3$}] (mean N−Ru−N 85.3°)[12] and in the present example a mean inter pyrazole angle of 85.4° is observed. The RuB_3 butterfly arrangement has an interplanar "hinge" angle of 125° which may be compared with 124° for the ruthenatetraborane [RuH(B_3H_8)(CO)(PPh_3)$_2$],[8] which is itself similarly flattened due presumably to steric effects. The structural parameters for the two ruthenatetraboranes are summarised in Figure 3 for comparison. Within the two RuB_3 units the Ru−B distances are noticeably shorter in [RuH(B_3H_8)(CO)(PPh_3)$_2$] reflecting the different trans ligands; however, in general the dimensions are surprisingly similar, given the different steric properties of the coligands and the recognised low barriers to MB_3H_8 fluxionality. In these two complexes, however, it should be pointed out that the large

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phosphine ligands shield the B_3H_8 ligand from intermolecular packing forces.

To conclude, the pocket offered by two of the phenyl and one of the pyrazolyl groups of the coligands appears ideally suited to favour coordination of the triboronate ligand, and such a cavity does not result from the alternative exo-phosphine coordination.

Experimental Section

The synthesis and spectroscopic characterization of $[Ru(B_3H_8)(PPh_3)\{\kappa^3\text{-}HB(pz)_3\}]$ have been described previously.[7]

Crystal Structure Determination of $[Ru(B_3H_8)(PPh_3)\{\kappa^3\text{-}HB(pz)_3\}]$. Pale yellow prisms were obtained by slow diffusion of ethanol into a solution of the complex in dichloromethane. A crystal of approximate dimensions 0.16 × 0.21 × 0.21 mm was used for the diffraction study. Crystallographic data are summarized in Table 3. Intensity data were collected in the ω scan mode on a Siemens P4/PC diffractometer using Mo Kα radiation to a maximum 2θ value of 50.0°. The structure was solved by direct and difference Fourier methods. Phenyl carbon atoms were refined as idealized rigid bodies, and all remaining non-hydrogen atoms were refined anisotropically. H atoms for the organic ligands were included in calculated positions, assigned isotropic thermal parameter, $U(H) = 1.2U_{eq}(C)$, and allowed to ride on their parent carbons. All the borane-H atoms were located from a difference-Fourier map and refined isotropically (subject to a refined B−H distance constraint for terminal B−H atoms). Computations (Siemens SHELXTL PLUS PC version) were by the full-matrix least-squares method, using absorption corrected data (min. and max. transmission factors of 0.8988 and 0.9197), to R (R_w) = 0.0426 (0.0416) for 3559 independent observed reflections [$F > 4\sigma(F)$]. The final atomic coordinates are given in Table 1, and selected bond lengths and angles, in Table 2.

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Supporting Information Available: Tables giving details of the crystallographic data collection, a full set of bond lengths and angles, anisotropic displacement coefficients, H-atom coordinates, and displacement coefficients for $[Ru(B_3H_8)(PPh_3)\{\kappa^3\text{-}HB(pz)_3\}]$ (7 pages). Ordering information is given on any current masthead page.

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