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Synthesis of the Ruthenaboratranes $[Ru(CS)(PPh_3)\{B(mt)_3\}]$*(Ru→B)*^{8} and $[Ru(CO)(CNR)\{B(mt)_3\}]$*(Ru→B)*^{8} (mt = methimazolyl, R = ^{t}Bu, $C_6H_3Me_2$-2,6, $C_6H_2Me_3$-2,4,6)

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The reaction of $[Ru(CH{=}CH_2)Cl(CS)(PPh_3)_2]$ with $Na[HB(mt)_3]$ (mt = methimazolyl) provides the ruthenaboratrane $[Ru(CS)(PPh_3)\{B(mt)_3\}]$. The reaction of $[Ru(CO)(PPh_3)\{B(mt)_3\}]$ with CO to provide $[Ru(CO)_2\{B(mt)_3\}]$ is reversible, while the phosphine-free ruthenaboratranes $[Ru(CO)(CNR)\{B(mt)_3\}]$ (R = ^{t}Bu, $C_6H_3Me_2$-2,6, $C_6H_2Me_3$-2,4,6) form irreversibly upon addition of isonitriles (CNR) to $[Ru(CO)(PPh_3)\{B(mt)_3\}]$. The crystal structures of the ruthenaboratranes $[Ru(CS)(PPh_3)\{B(mt)_3\}]$, $[Ru(CO)(CN^tBu)(\{B(mt)_3\}]$, and $[Ru(CO)(CNC_6H_2Me_3\text{-}2,4,6)\{B(mt)_3\}]$ are reported.

Introduction

Soon after the first report by Reglinski of the synthesis of sodium hydrotris(methimazolyl)borate[1] differences began to emerge between the coordination chemistry of poly(methimazolyl)borates and Trofimenko's poly(pyrazolyl)borates[2] for which an analogy might otherwise have been entertained. It might have been presumed that the $HB(mt)_3$ (mt = methimazolyl) ligand would simply serve as a hybrid between the facially tridentate $HB(pz)_3$ (pz = pyrazolyl) and 1,4,7-trithiacyclononane ($[9]aneS_3$) ligands, the former providing a "hard" anionic N_3 donor set while the latter provides a "soft" neutral S_3 set. However, this simple analogy failed in our early attempts to prepare organoruthenium derivatives of the $HB(mt)_3$ ligand. In what seemed a trivial extension of the syntheses of $[Ru(CH{=}CH_2)(CO)(PPh_3)([9]aneS_3)]Cl$[3] and $[Ru(CH{=}CH_2)(CO)(PPh_3)\{HB(pz)_3\}]$[4] we found that the product of the reaction of $[Ru(CH{=}CH_2)Cl(CO)(PPh_3)_2]$[5] with $Na[HB(mt)_3]$ was not, as anticipated, the complex $[Ru(R)(CO)(PPh_3)\{HB(mt)_3\}]$ (R = $CH{=}CH_2$). This class of compound remains unknown (other than for R = H)[6] due to the facile formation of a ruthenaboratrane[7,8] $[Ru(CO)(PPh_3)\{B(mt)_3\}]$*(Ru→B)*^{8} (**1**), a complex that provided the first unequivocal proof of the long mooted metal−boron dative bond.[9–11] In the interim we have extended this class of compound to include examples based on osmium, rhodium, iridium, and platinum,[12] while further examples based on iron, cobalt, rhodium, iridium, nickel, and palladium have been provided by the groups of Rabinovich,[13] Tatsumi,[14] Parkin,[15] and Connelly[16] (Chart 1). Although these are all based on methimazole or related hetereocycles, Bourissou has shown that metallaboratranes may also be prepared directly from β-phosphinoboranes.[17] Thus, in a very short time, the viability of metal−boron dative bonding has been demonstrated for all the elements of groups 8–10 and gold. However,

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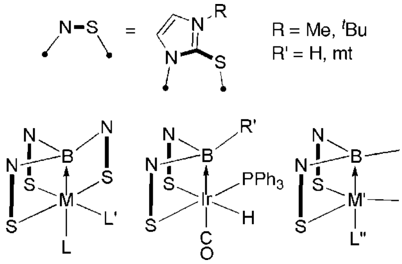
Chart 1. Metallaboratranes^{6-16a}



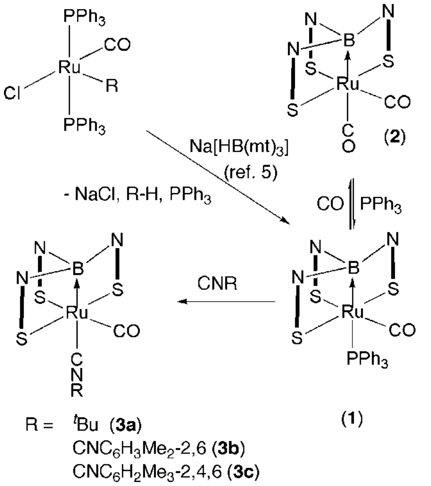
^{a} MLL′ = Ru(CO)(PPh$_3$), Os(CO)(PPh$_3$), Fe(CO)$_2$, RhCl(PPh$_3$), Rh(cod)$^+$, Rh(PMe$_3$)$_2$$^+$, Rh(S$_2$CNEt$_2$), RhH(PPh$_3$), Rh(PPh$_3$)(CNC$_6H_2Me_3$), PtH(PPh$_3$)$^+$, PtI$_2$; M′L″ = Pt(PPh$_3$), NiCl, Pd(PMe$_3$), Co(PPh$_3$)$^+$.

comparatively little is known about the actual nature of this interaction, although the complexes [RhCl(py){(Me$_2$PC$_6$H$_4$)$_2$BPh}],[17] [IrCl(PH$_3$){B(mt^{H})$_3$}],[15a] and [Pd(PMe$_3$){B(mt^{H})$_3$}][15c] have been the subjects of theoretical studies. Herein we report the synthesis of a range of new ruthenaboratranes, in which the π-acidity of the coligands has been varied relative to the archetypal [Ru(CO)(PPh$_3$){B(mt)$_3$}] (**1**), in an attempt to explore the effect of metal basicity on the structural features of the Ru→B bond.

Results and Discussion

Reaction of [Ru(CO)(PPh$_3$){B(mt)$_3$}] (1) with Carbon Monoxide. Parkin has recently described the ferraboratrane [Fe(CO)$_2${B(mim^{tBu})$_3$}] (mim^{tBu} = 2-mercapto-3-*tert*-butylimidazol-1-yl) that arises from the carbonylation of [Fe(CH$_2{}^t$Bu){HB(mim^{tBu})$_3$}][15b] and which is isoelectronic with the original ruthenaboratrane **1**. The dicarbonylruthenaboratrane [Ru(CO)$_2${B(mt)$_3$}] (**2**) therefore seemed a viable compound. We find that passing CO through a solution of **1** in dichloromethane results in the formation of a ca. 2:1 mixture of **1** (ν_{CO} = 1894 cm^{-1}) and a second compound with ν_{CO} = 2011 and 1942 cm^{-1}. On the basis of the relative integrals of the two absorptions, the intercarbonyl angle is close to 90°, suggesting the retention of an octahedral coordination geometry. The reaction does not go to completion, and attempts to obtain a solid by slow concentration under reduced pressure result in complete re-formation of **1**. Addition of CuCl to the mixture does allow the reaction to be driven to completion (IR) by removal of liberated phosphine as (Ph$_3$PCuCl)$_4$. However, we have not yet been successful in obtaining the dicarbonyl species free from the copper-containing side product. The ^{1}H NMR spectrum of the crude product includes a single broad N-CH$_3$ resonance (CDCl$_3$: δ_H = 3.35), suggesting fluxionality. Nevertheless, this behavior is consistent with the reversible formation of the phosphine-free complex [Ru(CO)$_2${B(mt)$_3$}] (**2**) (Scheme 1). Parkin's ferraboratrane has ν_{CO} = 1987, 1964 cm^{-1} (KBr), which might appear to contrast with the values of 2011 and 1942 cm^{-1} for **2**. However, we note that the derived Cotton−Kraihanzel force constants (15.78 and 15.76 N cm^{-1}) are identical within experimental limits; that is, it is presumably a case of the individual CO oscillators being more weakly coupled for iron than for ruthenium, resulting in a smaller difference between the ν_s and ν_{as} frequencies.

Scheme 1. Synthesis and Phosphine Substitution of Ruthenaboratranes



Reactions of [Ru(CO)(PPh$_3$){B(mt)$_3$}] (1) with Isonitriles. Given the reversibility of carbonyl/phosphine substitution, isonitriles that are typically more nucleophilic that CO were investigated on the assumption that dissociation would be less favored. Slow reactions ensue between **1** and isonitriles to provide the phosphine-free ruthenaboratranes [Ru(CO)(CNR){B(mt)$_3$}]*(Ru-B)*[8] (R = ^{t}Bu **3a**, C$_6$H$_3$Me$_2$-2,6 **3b**, C$_6$H$_2$Me$_3$-2,4,6 **3c**) at room temperature. In these cases the reactions proceed to completion on the basis of spectroscopy (IR, ^{1}H NMR); however the actual recovered yields for pure **3a** and **3b** are somewhat compromised by losses associated with the fractional crystallization required for the removal of liberated PPh$_3$. Each ruthenaboratrane was however isolated as a pure compound, allowing complete characterization including the crystallographic analysis of two examples, **3a** and **3c**, the results of which are summarized in Figure 1 and Figure 2 and discussed below.

The complete conversion of **1** to **3** is noteworthy in that the formation of **2** is reversible, with one carbonyl ligand in **2** being readily replaced by the liberated PPh$_3$ while the CO ligand in **3** is not; that is, we see no evidence for the formation of [Ru(CNR)(PPh$_3$){B(mt)$_3$}]. We suspect that in each case it is the ligand trans to the Ru→B bond that is labilized; that is, the ligand most likely to dissociate from **3** would be the isonitrile.

In the strictest sense of the term, the oxidation state of ruthenium in **1**–**3** is zero, given that boron is more electropositive than ruthenium. The ν_{CO} value for **1** (ca. 1890 cm^{-1} depending on solvent) is well within the region typical of mononuclear zerovalent ruthenium complexes with more conventional ligands. In a similar manner, both the ν_{CO} and ν_{CN} values for **3** are comparatively low, the former being virtually unchanged as a result of phosphine/isonitrile substitution. Isonitriles are recognized as being stronger σ-donors and weaker π-acids than CO. By way of contrast with isonitriles, we therefore sought to modify the ruthenaboratrane unit by inclusion of a stronger π-acid. Carbon monosulfide is an exceptionally potent neutral π-acid, with π^*_{CS} orbitals substantially lower in energy than those of CO.[18] This factor contributes to the greater stability

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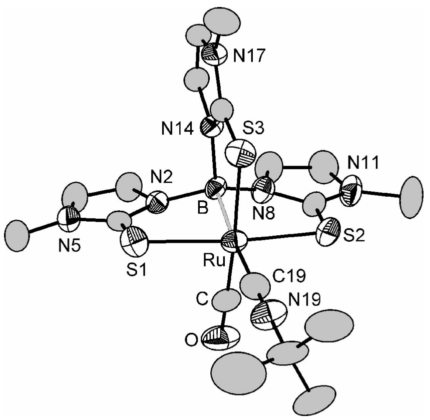

Figure 1. Molecular geometry of [Ru(CO)(CN^{t}Bu){B(mt)$_3$}] (**3a**) in a crystal (40% displacement ellipsoids, octant hatching for heteroatoms, hydrogen atoms omitted). Seleceted distances (Å) and angles (deg): Ru−C 1.816(9), Ru−C19 2.081(8), Ru−B 2.176(7), Ru−S2 2.398(2), Ru−S1 2.411(2), Ru−S3 2.501(2), C19−N19 1.153(10), B−N8 1.558(8), B−N2 1.561(8), B−N14 1.566(9), C−Ru−C19 96.5(3), C−Ru−B 88.3(3), C−Ru−S2 88.4(2), C19−Ru−S2 95.1(2), B−Ru−S2 83.36(18), C−Ru−S1 86.8(2), C19−Ru−S1 99.8(2), B−Ru−S1 82.02(18), C19−Ru−S3 90.1(2), B−Ru−S3 85.1(2), S2−Ru−S3 91.93(7), S1−Ru−S3 91.16(7), N19−C19−Ru 173.4(8), N8−B−N2 113.5(5), N8−B−N14 106.6(5), N2−B−N14 105.7(4), N8−B−Ru 111.2(4), N2−B−Ru 109.9(4), N14−B−Ru 109.6(4).

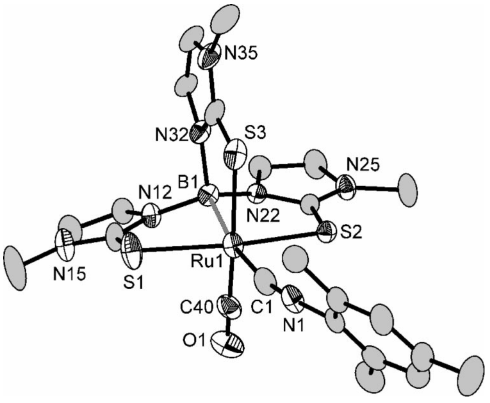

Figure 2. Molecular geometry of [Ru(CO)(CNC$_6$H$_2$Me$_3$-2,4,6){B(mt)$_3$}] (**3c**) in a crystal (40% displacement ellipsoids, octant hatching for heteroatoms, hydrogen atoms omitted). Selected distances (Å) and angles (deg): Ru1−S1 2.4110(11), Ru1−S2 2.3733(9), Ru1−S3 2.4804(12), Ru1−C1 2.023(4), Ru1−C40 1.815(5), Ru1−B1 2.146(4), N1−C1 1.168(5), N12−B1 1.549(5), N22−B1 1.548(5), N32−B1 1.561(5), S1−Ru1−S3 91.26(4), S2−Ru1−S3 91.89(3), C1−Ru1−C40 99.72(17), S1−Ru1−B1 80.65(11), S2−Ru1−B1 85.03(11), S3−Ru1−B1 85.65(11), C40−Ru1−B1 87.79(16), Ru1−C1−N1 168.0(3), N32−B1−N12 106.9(3), N32−B1−N22 104.8(3), N12−B1−N22 113.5(3), N32−B1−Ru1 110.0(2), N12−B1−Ru1 110.9(3), N22−B1−Ru1 110.4(2).

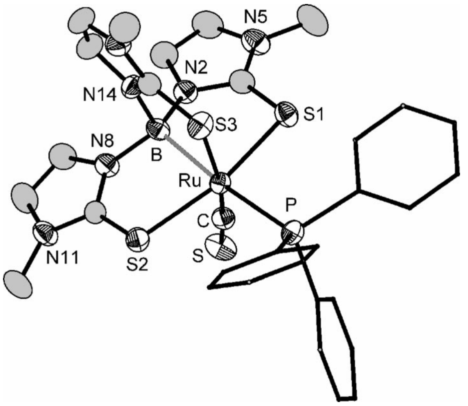

Figure 3. Molecular geometry of [Ru(CS)(PPh$_3$){B(mt)$_3$}] (**4**) in a crystal of **4**·(CHCl$_3$)$_2$ (40% displacement ellipsoids, octant hatching for heteroatoms, hydrogen atoms omitted). Distances (Å) and angles (deg): Ru−C 1.780(5), Ru−B 2.154(5), Ru−S1 2.4079(12), Ru−S2 2.4159(12), Ru−P 2.4569(12), Ru−S3 2.5374(13), C−S 1.569(5), C−Ru−B 85.4(2), C−Ru−S1 88.99(15), B−Ru−S1 83.96(14), C−Ru−S2 87.18(15), B−Ru−S2 82.17(14), C−Ru−P 102.62(15), S1−Ru−P 92.97(4), S2−Ru−P 101.15(4), B−Ru−S3 85.16(15), S1−Ru−S3 92.44(5), S2−Ru−S3 89.14(5), P−Ru−S3 86.89(4), N2−B−N8 113.7(4), N2−B−N14 105.6(4), N8−B−N14 105.6(4), N2−B−Ru 110.9(3), N8−B−Ru 110.4(3), N14−B−Ru 110.4(3).

and also the greater reactivity of thiocarbonyl complexes with respect to nucleophilic attack and migratory insertion processes.[19] Indeed it is this reactivity toward ligand coupling that has recently confounded our attempts to prepare a thiocarbonyl-rhodaboratrane; the reaction of [RhCl(CS)(PPh$_3$)$_2$] with Na[H$_2$B(mt)$_2$] does not provide the simple rhodaboratrane [RhH(CS)(PPh$_3$){BH(mt)$_2$}]*(Rh→B)*[8] (akin to isolable [IrH(CO)(PPh$_3$){BH(mt)$_2$}]*(Ir→B)*[8]),[12e] but rather the product of CS insertion into the Rh→B bond, [RhH(PPh$_3$)-{S=C(PPh$_3$)BH(mt)$_2$}].[12h] In the case of ruthenium however, no such processes were encountered. The reaction of **1** with CS$_2$ has not yet afforded tractable products, and accordingly, an alternative approach was employed, in which the thiocarbonyl ligand was installed at the outset, prior to metallaboratrane assembly. The recently reported vinyl complex [Ru(CH=CH$_2$)Cl(CS)(PPh$_3$)$_2$][20] reacts cleanly with Na[HB(mt)$_3$] to generate ethene, phosphine, and the ruthenboratrane [Ru(CS)(PPh$_3$){B(mt)$_3$}]*(Rh→B)*[8] (**4**), i.e., the thiocarbonyl analogue of **1**. Spectroscopic data for **4** are unremarkable other than to note the characteristically strong infrared absorption associated with the thiocarbonyl ligand (1242 cm^{-1}), which was identified in a region typical of this ligand bound to an electron-rich ruthenium center. The characterization of **4** also included a crystallographic analysis, the results of which are summarized in Figure 3. These are now discussed together with those for the archetype **1**, its osmium carbonyl analogue,[12a] and the two structurally characterized isonitrile derivatives **3a** and **3c**.

The crystal structures of **4**·(CHCl$_3$)$_2$ and **1**·(CHCl$_3$)$_2$ are isomorphous such that the molecular geometry of **4** is thus superficially similar to that of **1** and any secondary variations in the molecular geometry may reasonably be ascribed to the differences in the electronic nature of CO and CS (there are no intermolecular interactions of note). The thiocarbonyl ligand is essentially linear (Ru−C−S 175.1(3)°) with short Ru−C (1.780(5) cf. 1.841 Å for **1**) and C−S bonds (1.569(5) Å). The latter may be compared internally with the thiourea-type C−S multiple bonds of the mt heterocycles (average: 1.712 Å) and might reasonably be described as a triple bond, while the Ru−C bond length also reflects multiple bonding. These two parameters fall within the spread established to date for ruthenium thiocarbonyls,[20,21] though it should be noted that, consistent with the zero oxidation state of ruthenium, the Ru−thiocarbonyl bond is the shortest on record[21a] with the exception of the five-

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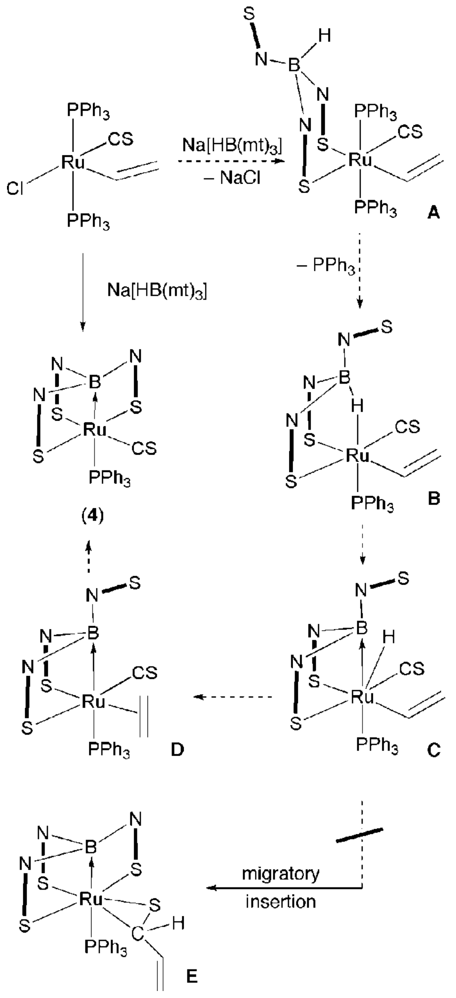
(19) For a review of thiocarbonyl chemistry see: Broadhurst, P. V. *Polyhedron* **1985,** *4*, 1801.

(20) Cowley, A. R.; Hector, A. L.; Hill, A. F.; White, A. J. P.; Williams, D. J.; Wilton-Ely, J. D. E. T. *Organometallics* **2007**, *26*, 6114.

Scheme 2. Mechanism for the Formation of a Thiocarbonyl Metallaboratrane (4)



coordinate ruthenium complex $[\mathrm{RuCl_2(CS)(PCy_3)_2}]$ ($r_{\mathrm{RuC}} = 1.738$ Å), which is readily desulfurised[21j] to the carbido complex $[\mathrm{RuCl_2({\equiv}C)(PCy_3)_2}]$ ($r_{\mathrm{RuC}} = 1.632$ Å).[22]

The synthesis of **4** served a further purpose in that given our currently favored mechanism for metallaboratrane formation, an intermediate with both hydrido and σ-organyl groups is envisaged, with irreversible hydrocarbon elimination contributing to the driving force.

This mechanism is reproduced in Scheme 2 for the proposed intermediates en route from $[\mathrm{Ru(CH{=}CH_2)Cl(CS)(PPh_3)_2}]$ to **4**, the significant species being **C** which follows B−H activation and precedes ethene elimination. The facial coordination of the chelated borane $\mathrm{B(mt)_3}$ requires that hydrido, vinyl, and thiocarbonyl ligands occupy adjacent positions, i.e., well-placed for migratory insertion reactions to occur involving CS and Ru−H, Ru−C, or Ru→B bonds. Notably, the complex $[\mathrm{Ru(CH{=}CH_2)(CS)(PPh_3)([9]aneS_3)}]^+$ is unstable with respect to migratory insertion and formation of the thioacyl isomer $[\mathrm{Ru(\eta^2\text{-}SCCH{=}CH_2)(PPh_3)([9]aneS_3)}]^+$,[23] while the putative rhodaboratrane $[\mathrm{RhH(CS)(PPh_3)\{BH(mt)_2\}}]$ undergoes insertion of CS into the Rh→B rather than Rh−H bond,[12h] despite the previously demonstrated migratory insertion reactions of group 9 hydrido-thiocarbonyls, e.g., in the hydrogenation of $[\mathrm{IrH(CS)(PPh_3)_3}]$ to provide $[\mathrm{IrH_2(SCH_3)(PPh_3)_3}]$ (Scheme 3).[24] Thus the formation of **4** rather than thiopropenoyl, thioformyl, or (**E**) thioaldehyde species would suggest that either such migratory insertion processes do not occur or if they do, that they are reversible. This latter interpretation seems unlikely given that within group 8 the migration of σ-organyls to thiocarbonyl ligands has generally been found to be an irreversible process[25] with the single exception of the thioformyl complex $[\mathrm{Os\{C({=}S)H\}Cl(CO)_2(PPh_3)_2}]$, which is slowly converted *inter alia* to $[\mathrm{OsHCl(CS)(CO)(PPh_3)_2}]$ on prolonged heating.[25d] An alternative mechanism might be considered wherein **B** converts to **D** directly via a B−H/Ru−CH σ-metathesis rather than via d^6-seven-coordinate species **C**. While a seven-coordinate d^6-species such as **C** might seem unusual, it should be noted that since one of the ligands (Ru→B) is a Lewis acid rather than an electron pair donor, the 18-electron rule is not violated. Circumstantial evidence in support of a two-step process (**B** → **C** → **D**) is provided by the conversion of $[\mathrm{Ir(CO)(PPh_3)\{HB(mt)_3\}}]$ to $[\mathrm{IrH(CO)(PPh_3)\{B(mt)_3\}}]$[12e] and of $[\mathrm{Pt(PR_3)_2\{HB(mt)_3\}}]\mathrm{Cl}$ (R = Me, Et) to $[\mathrm{PtH(PR_3)\{B(mt)_3\}}]\mathrm{Cl}$.[12i] In

Scheme 3. Selected Thiocarbonyl Migratory Insertion Reactions ($L = PPh_3$)[2h,23,25]

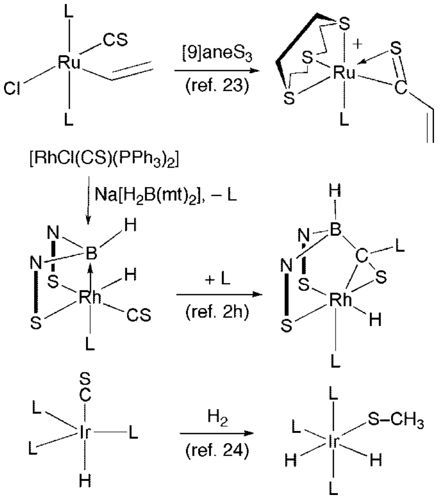


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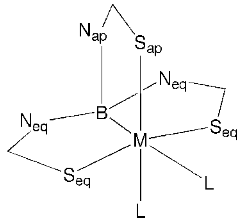
Table 1. Selected Structural Data for Group 8 Metallaboratranes $[\mathrm{ML_2\{B(mt)_3\}}]$*(M→B)*[8]



ML_2	M→B (Å)	$N_{eq}BN_{eq'}$ (deg)	$N_{eq}BN_{ap}$ (deg)	MS_{eq} (Å)	$M-S_{ap}$ (Å)	LML (deg)	M−CO/S (Å)
$Os(CO)(PPh_3)$[12a]	2.171(8)	113.0(7)	104.6(7) 105.6(7)	2.424(2) 2.406(2)	2.493(2)	99.99(7)	1.826(8)
$Ru(CO)(PPh_3)$	2.161(5)	113.9(4)	105.5(4) 105.7(4)	2.4066(14) 2.4112(14)	2.4857(14)	100.89(5)	1.841(5)
$Ru(CS)(PPh_3)$	2.154(5)	113.7(4)	105.6(4) 105.6(4)	2.4079(12) 2.4159(12)	2.5374(13)	102.62(15)	1.780(5)
$Ru(CN^tBu)(CO)$	2.176(7)	113.5(5)	106.6(5) 105.7(4)	2.3984(19) 2.4114(19)	2.501(2)	96.5(3)	1.816(9)
$Ru(CNC_6H_2Me_3)(CO)$	2.146(4)	113.5(3)	106.9(3) 104.8(3)	2.4110(11) 2.3733(9)	2.4804(12)	99.72(17)	1.815(5)
$Fe(CO)_2$[15b][a]	2.111(5)	112.2(4)	107.3(4) 107.6(4)	2.2868(17) 2.2921(17)	2.3273(17)	95.3(2)	1.717(5) 1.803(5)

[a] $[Fe(CO)_2\{B(mim^{tBu})_3\}]$.[15b]

these cases, the absence of a σ-organyl ligand capable of serving as a hydrogen acceptor allows the isolation of hydridometallaboratranes.

Comparison of Metallaboratrane Structures. Table 1 collates selected structural data for group 8 metallaboratranes, and the most immediate point to note is that despite the disparity of ligands in terms of electronic and steric properties, the metal−boron bond spans a remarkably small range (2.146(4)−2.176(7) Å) for the osmium and ruthenium derivatives, while the Fe→B bond is shorter, as expected for a 3d element. Within this narrow spread, it is also noteworthy that the two most similar complexes, **3a** and **3c**, show almost the largest difference. These points taken together suggest that the metal−boron bond length is not especially responsive to the electronic nature of the coligand *in this series*, perhaps reflecting the constraints of inclusion within a cage assembly. A further feature to note is that, again with a wide range of steric profiles for the pairs of coligands, the angles at boron are also insensitive, falling within narrow ranges, close to the ideal tetrahedral value (109°), though in each case these comprise a larger angle between the two equivalent methimazolyl substituents (112.2(4)−113.9(4)°) and a pair of smaller angles that these each make with the unique methimazolyl nitrogen N_{ap} (104.6(7)−107.6(4)°). This deformation is also reflected in the way that boron is consistently close in each case to being coplanar with the unique mt heterocycle but slightly displaced from those of the mutually trans pair. In all cases the trans pair of $M-S_{eq}$ bonds are significantly shorter (ca. 0.1 Å for Ru and Os examples) than the unique apical $M-S_{ap}$ bond. We suspect that these recurrent geometric distortions are more a result of the adjacent accommodation of tetrahedral (B) and octahedral centers (M) within the cage structure than a reflection of any significant base(mt)-stabilized di(methimazolyl)boryl resonance contribution, though this may not be excluded. In all cases the angle between the two nonboratrane coligands is obtuse, which presumably is also a reflection of geometric constraints that make all angles at ruthenium associated with the cage marginally acute.

To conclude, a range of new ruthenaboratranes has been isolated. This includes an example of a thiocarbonyl derivative that is stable, in contrast to the putative rhodaboratrane $[RhH(CS)(PPh_3)\{HB(mt)_2\}]$, which undergoes insertion of the CS ligand into the Rh→B bond. Furthermore, despite the previously demonstrated facility with which the precursor enters into migratory insertion processes,[20] we have not observed any indication of vinyl−thiocarbonyl or hydrido−thiocarbonyl coupling. A notable feature of the archetypal ruthenboratrane **1** is that it has now been demonstrated that the phosphine ligand is labile and readily replaced by CO (reversibly) or isonitriles (irreversibly) under mild conditions, suggesting that **1** may serve as a useful precursor to further metallaboratranes.

Experimental Section

General Considerations. All manipulations were carried out under a dry and oxygen-free nitrogen atmosphere using standard Schlenk, vacuum line, and inert atmosphere drybox techniques, with dried and degassed solvents that were distilled from either calcium hydride (CH_2Cl_2) or sodium−potassium alloy and benzophenone (ethers and paraffins). NMR spectra were obtained at 25 °C on Varian Gemini 300BB (^1H at 300 MHz, ^{13}C at 75.4 MHz) or Jeol FX270 (^1H at 270 MHz, ^{13}C at 67.9 MHz) spectrometers. Chemical shifts (δ) are given relative to internal $SiMe_4$ (^1H, ^{13}C) or external $BF_3\cdot OEt_2$ (^{11}B) and H_3PO_4 (^{31}P), with coupling constants given in Hz. The elemental microanalysis was carried out by the microanalytical service of the Australian National University. The compounds $Na[HB(mt)_3]$,[5] $[Ru(CO)(PPh_3)\{B(mt)_3\}]$ (**1**),[5] and $[Ru(CH{=}CH_2)Cl(CS)(PPh_3)_2]$[20] were prepared according to the indicated published procedures.

Synthesis of $[\mathbf{Ru(CN^tBu)(CO)\{B(mt)_3\}}]$*(Ru→B)*[8] (3a). A solution of $[Ru(CO)(PPh_3)\{B(mt)_3\}]$ (**1**: 0.240 g, 0.32 mmol) in dichloromethane (10 mL) was treated with excess *tert*-butylisonitrile (0.100 g, 1.20 mmol) and the mixture stirred for 18 h. Cyclohexane (20 mL) was added and the total solvent volume reduced *in vacuo* to ca. 6 mL. The mixture was left to stand for 24 h to provide pale yellow crystals, which were isolated by filtration and dried *in vacuo*. Yield: 0.058 g (32%). Crystals suitable for diffractometry were obtained by layering a $CDCl_3$ solution with cyclohexane followed by slow interdiffusion at −20 °C. IR (Nujol): 2103 (ν_{CN}), 2064sh (ν_{CN}) 1896 (ν_{CO}) cm^{-1}. IR (CH_2Cl_2): 2116 (ν_{CN}), 1894 (ν_{CO}) cm^{-1}. FAB-MS *m/z* (%): 563(27) $[M]^+$, 535(51) $[M - CO]^+$, 452(100) $[M - CO - CN^tBu]^+$. NMR ($CDCl_3$, 25 °C) ^1H: δ_H 1.49 (s, 9 H, CCH_3), 3.46, 3.47 (9 H, NCH_3), 6.36 (1H), 6.56(1H), 6.71(2H), 6.93(2H) (s br × 4, $H_2C_3N_2$). $^{13}C\{^1H\}$: δ_C 31.2 ($C\underline{C}H_3$), 33.7(2C), 34.2(1C) (NCH_3), 55.5 ($N\underline{C}Me_3$), 116.5 (BNCH), 122.1(2C), 122.3(1C) (MeNCH), 167.2(1C), 171.1(2C) (CS), 205.9 (CO). $^{11}B\{^1H\}$: δ_B 14.6. Anal. Found: C, 38.83; H, 4.02; N, 17.72; S, 16.62. Calcd for $C_{18}H_{24}BN_7S_3ORu$: C, 38.43; H, 4.30; N, 17.43; S, 17.10. *Crystal data for* **3a**: $C_{18}H_{24}BN_7ORuS_3$, $M = 562.50$, monoclinic, $P2_1/c$ (no. 14), $a = 14.3067(13)$ Å, $b = 13.3228(10)$ Å, $c = 13.0886(11)$ Å, $\beta = 91.665(10)°$, $V = 2493.7(4)$ Å^3, $Z = 4$, $D_c = 1.498$ Mg m^{-3}, μ(Cu Kα) = 7.635 mm^{-1}, $T = 293$ K, yellow blocky plates, Siemens P4 diffractometer; 3679 independent measured reflections, F^2 refinement, $R_1 = 0.057$, $wR_2 = 0.141$, 2723 independent observed absorption-corrected reflections [$F_o > 4\sigma(F_o)$, $2\theta_{max} = 120°$], 310 parameters. CCDC 658585.

Synthesis of [Ru(CNC$_6$H$_3$Me$_2$-2,6)(CO){B(mt)$_3$}]*(Ru→B)*[8] (3b). A solution of [Ru(CO)(PPh$_3$){B(mt$_3$}] (**1**: 0.277 g, 0.37 mmol) in tetrahydrofuran (5 mL) was treated with 2,6-xylylisonitrile (0.054 g, 0.41 mmol) and the mixture stirred for 5 h. Addition of diethyl ether (25 mL) provided a white precipitate, which was isolated by filtration, washed with diethyl ether (5 mL), and dried *in vacuo*. The complex was recrystallized from a mixture of dichloromethane and hexane at −20 °C. Yield: 0.202 g (89%). IR (Nujol): 2065 (ν_{CN}), 1890 (ν_{CO}) cm^{-1}. IR (thf): 2081 (ν_{CN}), 1898 (ν_{CO}) cm^{-1}. IR (CH_2Cl_2): 2080 (ν_{CN}), 1900 (ν_{CO}) cm^{-1}. NMR ($CDCl_3$, 25 °C) ^{1}H: δ_H 2.47 (s, 6 H, CCH_3), 3.43 (6H), 3.49 (3H) (s × 2, NCH_3), 6.41, 6.58 (d x 2, 1 H × 2, $^3J_{HH} \approx 1.8$, $H_2C_3N_2$), 6.96, 7.01 (d × 2, 4 H, $H_2C_3N_2$), 7.10 (m br, 3 H, C_6H_3). ^{13}C{^{1}H}: δ_C 19.2 ($\mathrm{C\underline{C}H_3}$), 33.7 (2C), 34.2 (1C) (NCH_3), 116.5(1C), 116.6 (2C), 122.2(1C), 122.4(2C) ($H_2C_3N_2$), 126.7, 127.3, 134.6 (C_6H_3), 167.2(2C), 170.8(1C) (CS), 206.0 (CO). Anal. Found: C, 43.52; H, 3.68; N, 15.85. Calcd for $C_{22}H_{24}BN_7S_3ORu$: C, 43.28; H, 3.96; N, 16.06.

Synthesis of [Ru(CNC$_6$H$_2$Me$_3$-2,4,6)(CO){B(mt)$_3$}]*(Ru→B)*[8] (3c). A solution of [Ru(CO)(PPh$_3$){B(mt)$_3$}] (**1**: 1.309 g, 1.76 mmol) in dichloromethane (80 mL) was treated with mesitylisonitrile (0.258 g, 1.78 mmol) and the mixture stirred for 2 days. The solvent volume was reduced to ca. 15 mL and then diluted with diethyl ether (30 mL) to provide a colorless precipitate, which was isolated by filtration, washed with diethyl ether (10 mL), and dried *in vacuo*. Yield: 1.06 g (98%). IR (KBr): 2070 (ν_{CN}), 1892 (ν_{CO}) cm^{-1}. IR (CH_2Cl_2): 2082 (ν_{CN}), 1898 (ν_{CO}) cm^{-1}. NMR ($CDCl_3$, 25 °C) ^{1}H: δ_H 2.31 (3H), 2.52 (6H) (s × 2, CCH_3), 3.46 (3H), 3.51 (6H) (s × 2, NCH_3), 6.40, 6.61 (m × 2, 1 H × 2, unique mt), 6.76 (s, 2 H, C_6H_2), 6.87, 7.00 (s × 2, 2 H × 2, equivalent mt). ^{13}C{^{1}H}: δ_C 19.0 (1C), 21.1 (2C) ($\mathrm{C\underline{C}H_3}$), 33.6 (2C), 34.1 (1C) (NCH_3), 116.5, 116.6, 122.2, 122.3 ($H_2C_3N_2$), 128.0 [$C^{3,5}(C_6H_2)$], 134.2 [$C^{2,6}(C_6H_2)$], 136.6 [$C^4(C_6H_2)$], 167.4 (1 CS), 168.3 (2 C=S), 206.1 (CO). Anal. Found: C, 44.38; H, 4.24; N, 15.46; S, 15.06. Calcd for $C_{23}H_{26}BN_7S_3ORu$: C, 44.23; H, 4.20; N,15.70; S, 15.40. *Crystal data for* **3c**: $C_{23}H_{26}BN_7ORuS_3$, $M_w = 624.59$, orthorhombic, *Iba*2, $a = 25.1240(6)$ Å, $b = 13.1240(2)$ Å, $c = 16.4268(3)$ Å, $V = 5416.4(2)$ Å^3, $Z = 8$, $D_c = 1.532$ Mg m^{-3}, μ(Mo Kα) = 0.841 mm^{-1}, $T = 200(2)$ K, Nonius Kappa CCD diffractometer, 6134 independent measured reflections. F^2 refinement, $R_1 = 0.027$, $wR_2 = 0.027$, 4105 independent observed absorption-corrected reflections, [$I > 2\sigma(I)$, $2\theta_{max} = 56°$], 381 parameters, CCDC 658584.

Synthesis of [Ru(CS)(PPh$_3$){B(mt)$_3$}] (4). A solution of [Ru(CH=CH$_2$)Cl(CS)(PPh$_3$)$_2$] (0.200 g, 0.27 mmol) and Na[H-B(mt)$_3$] (0.11 g, 0.29 mmol) in dichloromethane (50 mL) was stirred for 30 min. The resulting yellow-cream solution was filtered through diatomaceous earth and then freed of solvent. The resulting solid was recrystallized from a mixture of dichloromethane and hexane. Yield: 0.08 g (39%). IR (Nujol): 1242 cm^{-1} (ν_{CS}). NMR (C_6D_6, 25 °C) ^{1}H: δ_H 3.31 (3H), 3.52 (6H) (s × 2, NCH_3), 6.38, 6.50 (d × 2, 1 H × 2, $^3J_{HH} = 2.1$, $H_2C_3N_2$), 6.71, 7.00 (d × 2, 2 H × 2, $^3J_{HH} = 2.1$, $H_2C_3N_2$), 7.02–7.15 (m × 2, 15 H, C_6H_5), ^{31}P{^{1}H}: δ_P 24.4 (s br). FAB-MS *m/z* (%): 758(33) [M]$^+$, 496(74) [M − PPh$_3$]$^+$, 452(54)[M − PPh$_3$ − CS]$^+$. Anal. Found: C, 39.85; H, 3.01; N, 8.63; S, 12.32. Calcd for $C_{31}H_{30}BN_6PS_4Ru.2CHCl_3$: C, 39.78; H, 3.24; N, 8.43; S, 12.87. *Crystal data for* **4**: $C_{31}H_{30}BN_6PRuS_4 \cdot 2CHCl_3$, $M_w = 996.44$, triclinic, $P\bar{1}$ (no. 2), $a = 11.9019(9)$ Å, $b = 13.3665(6)$ Å, $c = 14.9119(8)$ Å, $\alpha = 68.943(4)°$, $\beta = 74.221(6)°$, $\gamma = 81.936(4)°$, $V = 2128.1(2)$ Å^3, $Z = 2$, $D_c = 1.555$ Mg m^{-3}, μ(Cu Kα) = 8.906 mm^{-1}, $T = 293$ K, yellow blocky prisms, Siemens P4 diffractometer, 6214 independent measured reflections, F^2 refinement, $R_1 = 0.049$, $wR_2 = 0.127$, 5376 independent observed absorption-corrected reflections [$F_o > 4\sigma(F_o)$, $2\theta_{max} = 120°$], 593 parameters. CCDC 658586.

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Supporting Information Available: Full details of the crystal structure determinations in CIF format, ORTEP representations and tables of selected bond lengths and angles for **3a** (CCDC 658585), **3c** (CCDC 658584), and **4** (CCDC 658585). This material is available free of charge via the Internet at http://pubs.acs.org.

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