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The Sting of the Scorpion: A Metallaboratrane[**]

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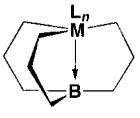
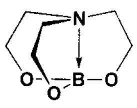
Bis(azolyl)borate chelates are often referred to as "scorpionates" because their coordination geometry can place a hydrogen substituent on boron in close proximity to a metal center constrained within the claws.[1] This arrangement leads in some cases to agostic interactions, however to date none of these situations have involved direct formation of a metal–boron bond (B–H oxidative addition). By extending this conceptual arthropomorphism and in deference to the parable, we confirm that it is indeed "in the nature of the scorpion to sting". Herein we report the first example of a poly(azolyl)borate ligand that undergoes B–H activation (stinging) at one metal center to provide the unprecedented metallaboratrane structural motif (**A**), akin to the more familiar boratrane cages (**B**).[2]

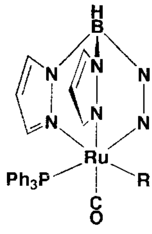


A



B

We have previously described the chemistry of the isoelectronic σ-organyl complexes $[Ru(R)(CO)\{HB(pz)_3\}(PPh_3)]$ (**1**, pz = pyrazol-1-yl; R = vinyl, aryl),[3] and $[Ru(R)(CO)(PPh_3)([9]aneS_3)]^+$ (**2**, $[9]aneS_3$ = 1,4,7-trithiacyclononane),[4] which feature facially tridentate triaza-scorpionate or trithia macrocyclic coligands. The recent report of the new ligand "$HB(mt)_3$" (mt = 2-sulfanyl-1-methylimidazole)[5] suggested to us that the complexes $[Ru(R)(CO)(PPh_3)\{HB(mt)_3\}]$ (**3**) should be readily accessible, and that the $HB(mt)_3$ ligand in such complexes would effectively serve as a hybrid of the $HB(pz)_3$ and $[9]aneS_3$ ligands. In our initial attempts to prepare the complexes **3** we have encountered an unprecedented class of reaction for tris(azolyl)borates, namely the intramolecular activation of the bridgehead B–H bond to provide the first example **4** of a metallaboratrane.



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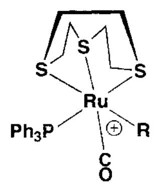
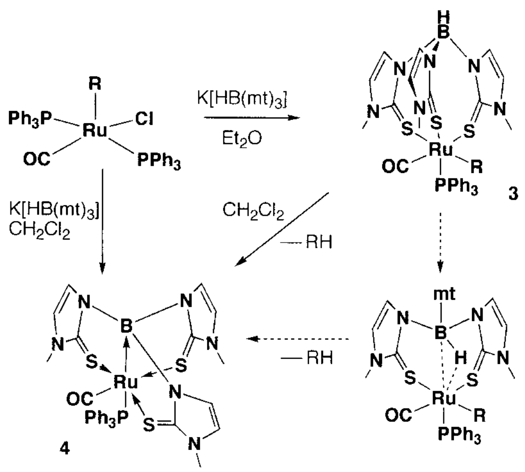


2

The treatment of the complex $[Ru(CH{=}CHCPh_2OH)Cl(CO)(PPh_3)_2]$[6] with $Na[HB(mt)_3]$ (dichloromethane, room temperature) provides high yields of the novel ruthenaboratrane complex $[Ru\{B(mt)_3\}(CO)(PPh_3)]$ (**4**, Scheme 1). The formulation of the yellow complex follows from spectroscopic data and was confirmed by a crystallographic study.[7] The gross composition is reflected in the positive-ion FAB mass spectrum, which includes a molecular ion as the base peak and fragmentations arising from the loss of the carbonyl and phosphane ligands. One singlet resonance (δ = 17.1) is observed for the bridgehead boron atom in the ^{11}B NMR spectrum. The ^1H NMR and $^{13}C\{^1H\}$ NMR spectra are solvent dependent: Thus in $CDCl_3$ a static structure is suggested by the appearance of sharp peaks arising from two mt environments. However, the operation of a fluxional process is apparent in C_6D_6 at room temperature. The infrared spectrum reveals one carbonyl absorption at $\tilde{\nu} = 1888\ cm^{-1}$ (Nujol), a frequency which is suggestive of zero-valent ruthenium (see below).



Scheme 1. Synthesis of **4**. R = $CH{=}CH_2$, $CH{=}CHCPh_2OH$, $CH{=}CH(4\text{-}MeC_6H_4)$, C_6H_5.

The structure of the complex **4**, as revealed from an X-ray diffraction study, is shown in Figure 1.[7] The ruthenium atom adopts a distorted octahedral coordination despite the constraints of bis-chelation, with *cis*-interligand angles in the

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[**] Poly(azolyl)chelate Chemistry, Part 9. A.F.H. gratefully acknowledges the award of a Senior Research fellowship from The Leverhulme Trust and The Royal Society. Ruthenium salts were generously provided by Johnson Matthey Chemicals Ltd. – Part 8: A. F. Hill, A. J. P. White, D. J. Williams, J. D. E. T. Wilton-Ely, *Organometallics* **1998**, *17*, 4249.

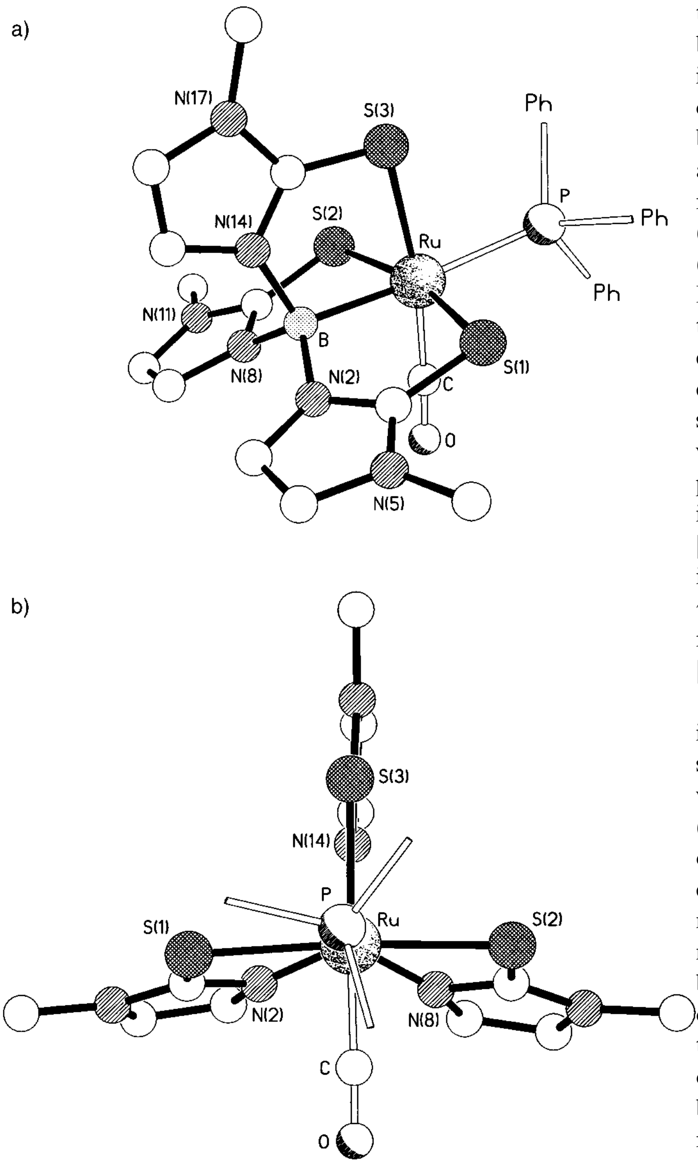

Figure 1. a) Molecular Structure of **4**. Hydrogen atoms and phenyl groups are omitted for clarity. b) Simplified view of **4** normal to the plane defined by N(2), N(8), and N(14).

range 82.7(2)–100.89(5)°. One of the three Ru–S bond lengths, the one that is *trans* to the carbonyl group (that is, adjacent to the bulky phosphane) is, as expected, significantly longer (2.4857(14) Å) than the pair of mutually *trans* Ru–S bonds (Ru–S(1) 2.4066(14), Ru–S(2) 2.4112(14) Å). The coordination at the boron center naturally provides the focus of structural interest: The boron atom is tetrahedrally coordinated with angles in the range 105.5(4)–113.9(4)°, the largest of these (N(8)-B-N(2)) being associated with the *mer*-bis-chelate unit. Distinct foldings of two of the five-membered chelate rings are immediately apparent if the structure is viewed normal to the plane of the three boron-coordinated nitrogen atoms (Figure 1b). Thus, whereas the N(14)-based ring is essentially planar, with a fold of 3° about the S(3)$\cdots$B vector, the S(1)- and S(2)-containing rings are distinctly folded (20 and 27°, respectively). In simplistic terms, this geometry is the most "relaxed" for accommodating linked tetrahedral (B) and octahedral (Ru) centers. The ruthenium–boron bond of 2.161(5) Å is without precedent for comparison, but falls within the range (2.046(7)–2.20(2) Å) found in osmium–σ-boryl complexes,[8, 9] which contain an Os–B π-bonding component, but none of the ring strain that must be accommodated in the tricyclic structure of **4**. Very recently a ruthenium–σ-boryl complex $[Ru\{B(NMe_2)BBr(NMe_2)\}(CO)_2(\eta\text{-}C_5H_5)]$ has also been structurally characterized (Ru–B 2.173(3) Å).[10] Thus it must be concluded that the Ru–B bond in **4** represents a comparatively strong interaction. These results taken together with the observed stereochemistry at the ruthenium atom, which places the boron center in a position *trans* to the stronger donor, lead us to suggest that the canonical representation based on zero-valent ruthenium (Scheme 1) contributes significantly, though probably not exclusively, to the bonding. This type of interaction is clearly novel, but finds loose analogy in the salt $[Et_4N][Fe(BPh_3)(CO)_2(\eta\text{-}C_5H_5)]$, which has been characterized on the basis of spectroscopic data ($\delta(^{11}B) = 28.8$; $\tilde{\nu}(CO) = 1991$, $1920\ cm^{-1}$), and is an intermediate in the reaction of $[Et_4N][Fe(CO)_2(\eta\text{-}C_5H_5)]$ with BPh_3 to provide $[Et_4N][Fe_2(CO)_4(\eta\text{-}C_5H_5)(\eta\text{-}C_5H_4BPh_3)]$.[11]

Although the structure and bonding in complex **4** is novel, in retrospect the likely mechanism by which **4** forms is straightforward. The reaction of $[Ru(R)Cl(CO)(PPh_3)_2]$ (R = vinyl, aryl) with $K[HB(pz)_3]$ is known to provide $[Ru(R)(CO)\{HB(pz)_3\}(PPh_3)]$,[3] which supports the initial formation of $[Ru(CH{=}CHCPh_2OH)(CO)(PPh_3)\{HB(mt)_3\}]$ (**3a**). In contrast to the rigid chelation of the $HB(pz)_3$ ligand, the more expansive chelation of $HB(mt)_3$ might be expected to be more flexible and labile. Dissociation of one mt arm followed by agostic B–H coordination and ultimate oxidative addition of the B–H bond could provide a *cis*-hydrido–vinyl complex that undergoes alkene reductive elimination with formation of **4**. In this context, the elegant synthesis of ruthenium–σ-boryl complexes by Roper and Wright et al. through the reactions of $[Ru(C_6H_5)Cl(CO)(PPh_3)_2]$ with boranes[8, 9] provides compelling support for the proposed mechanism. Given the surprisingly mild conditions under which **4** is formed, this mechanistic conjecture begs the isolation of complexes of the form **3**. The complexes $[Ru(R)Cl(CO)(PPh_3)_2]$ (R = $CH{=}CHCPh_2OH$, $CH{=}CH_2$, $CH{=}CH(4\text{-}MeC_6H_4)$, C_6H_5) were all found to react with $Na[HB(mt)_3]$ in dichloromethane to provide **4**. However, high yields of the complexes $[Ru(R)(CO)(PPh_3)\{HB(mt)_3\}]$ (R = $CH{=}CHCPh_2OH$ (**3a**), $CH{=}CH_2$ (**3b**), $CH{=}CH(4\text{-}MeC_6H_4)$ (**3c**), C_6H_5 (**3d**)) were obtained if the reactions were carried out as a suspension in diethyl ether. Dissolution of the isolated complexes **3** in dichloromethane or chloroform resulted in the smooth and rapid conversion into **4** without liberation of phosphane (^{31}P NMR). This confirms that the complexes bear only one phosphane ligand, in contrast to the recently reported bis(phosphane) complexes $[MR(CO)\{\eta^2\text{-}HB(pz)_3\}(PPh_3)_2]$ (MR = RuH, OsPh), which are isolable intermediates en route to $[MR(CO)\{\eta^3\text{-}HB(pz)_3\}(PPh_3)]$.[12]

Our initial investigations developed from a presumed simple analogy between the coordination chemistry of the $HB(pz)_3$ and $HB(mt)_3$ ligands. The results obtained clearly indicate that both parallels and divergencies may be anticipated in the chemistry of these ligands. The remarkable facility with which the ruthenaboratrane forms may presumably be traced to both the lability of HB(mt)$_3$ chelation and the increased ring size of the chelates, which allows the scorpion's sting to more closely approach the metal center.

Experimental Section

Na[HB(mt)$_3$]: Finely and intimately ground Na[BH$_4$] (2.08 g, 60 mmol) and 1-methylimidazole-2-thiol (Hmt, 25.0 g, 220 mmol) were suspended in xylene (30 mL) and heated under reflux for 2 h. The crude product was filtered off, washed with hot toluene and hexane, and dried in vacuo. Yield 19.17 g (94 %).

4: A mixture of [Ru(CH=CHCPh$_2$OH)Cl(CO)(PPh$_3$)$_2$] (0.36 g, 0.40 mmol) and Na[HB(mt)$_3$] (0.15 g, 0.40 mmol) in dichloromethane (50 mL) was stirred for 30 min and then filtered through diatomaceous earth and freed of volatiles. The residue was crystallized from a mixture of dichloromethane and hexane to provide yellow crystals. Yield 0.24 g (81 %). IR (Nujol): $\tilde{\nu} = 1888$ cm^{-1} (vs; CO); IR (CH$_2$Cl$_2$): $\tilde{\nu} = 1894$ cm^{-1} (vs; CO); ^{1}H NMR (270 MHz, CDCl$_3$, 25 °C)**:** $\delta = 3.43$ (s, 6H; NCH$_3$), 3.60 (s, 3H; NCH$_3$), 6.39, 6.70 (AB, $^3J_{AB} = 2.1$ Hz, 2H; CH=CH), 6.98 and 7.35 ((AB)$_2$, $^3J_{AB} = 2.0$ Hz, 4H; CH=CH), 7.25–7.35 and 7.55–7.61 (m × 2, 15H; C$_6$H$_5$); ^{13}C NMR (68 MHz, CDCl$_3$, 25 °C)**:** $\delta = 206.5$ (RuCO), 170.5, 170.4 (CS), 138.5 (d, $^1J_{PC} = 21.8$ Hz; C1 (C$_6$H$_5$)), 133.6 (d, $^2J_{PC} = 13.4$ Hz; C2, C6 (C$_6$H$_5$)), 128.4 (C4 (C$_6$H$_5$)), 127.8 (d, $^3J_{PC} = 8.9$ Hz; C3, C5 (C$_6$H$_5$)), 122.0 (2C), 119.2 (1C), 116.3 (2C), 113.7 (1C; CH=CH), 34.2 (1C; NCH$_3$), 33.7 (2C; NCH$_3$); ^{11}B NMR (CDCl$_3$, 25 °C, BF$_3$OEt$_2$)**:** $\delta = 17.1$; ^{31}P{^{1}H} NMR (109 MHz, CDCl$_3$, 25 °C, 85 % H$_3$PO$_4$)**:** $\delta = 26.6$ (br s); FAB-MS: *m/z* (%): 743 (4) [M^+], 714 (3) [$M^+ -$ CO], 452 (19) [$M^+ -$ COPPh$_3$]. The complex crystallized from chloroform as a bis-solvate and was also characterized crystallographically.[7]

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Tetrapyrroles as π Donors: A Pd$_2^{2+}$ Unit Sandwiched between Two Helical Bilindione–Palladium Moieties[**]

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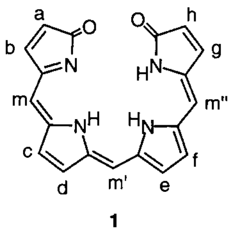
Alan L. Balch[*]

The linear tetrapyrroles of the bilindione family **1**[1] are metabolites of heme degradation which show biological activity (antioxidant[2] and antiviral activity[3]) that is poorly understood at the molecular level. Like porphyrins bilindiones form four-coordinate metal complexes that undergo a variety of changes in redox state, electronic structure, and axial ligation.[4–6] The general mode of coordination of both the bilindiones and porphyrins involves bonding of the four nitrogen atoms to a central metal ion. With the bilindione ligand, the four nitrogen atoms cannot be coplanar when bonded to a relatively small first-row transition metal ion. Consequently, helical complexes result. Here we report on the formation of complexes that involve a larger second-row transition metal ion and in which the metalation of the linear tetrapyrrole results in an unusual sandwich structure.



1

Treatment of octaethylbilindione H$_3$OEB (**1**, a–h = Et) with palladium(II) acetate in chloroform/ethanol followed by chromatography on silica gave dark green crystals of [Pd$_4$(OEB)$_2$] in 66 % yield. The electronic spectrum of the complex which displays bands at 831 nm ($\varepsilon = 2.2 \times 10^4$), 358 nm ($\varepsilon = 4.6 \times 10^4$), and 284 nm ($\varepsilon = 3.7 \times 10^4$), resembles that of [Zn^{II}(OEBOMe)][7] rather those of other complexes in which the tetrapyrrole is coordinated to the metal center simply through four M–N bonds, such as [Co(OEB)][4] and

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