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Analogies between Metallaboratranes, Triboronates, and Boron Pincer Ligand Complexes[†]

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The reaction of $[\mathrm{RuRCl(CO)(PPh_3)_2}]$ (R = C_6H_5, CH=CHPh) with the Yamashita−Nozaki ligand $C_6H_4\{N(CH_2PPh_2)\}_2BH$ (dppBH) results in facile elimination of benzene or styrene and formation of the ruthenium $[\mathrm{PBP}]^-$ pincer complex $[\mathrm{Ru}\{\kappa^3 B,P,P'\text{-dppB}\}\mathrm{Cl(CO)(PPh_3)}]$ via a stepwise sequence that recalls the formation of the ruthenaboratrane $[\mathrm{Ru(CO)(PPh_3)\{B(mt)_3\}}]$ (mt = methimazolyl) from $[\mathrm{RuRCl(CO)(PPh_3)_2}]$ and $\mathrm{Na[HB(mt)_3]}$. This analogy is explored herein, including observations regarding notionally similar processes for triboronate ligands. Thus, while the major product of the reaction of $[\mathrm{Ru(C_6H_5)Cl(CO)(PPh_3)_2}]$ with $[{}^n\mathrm{Bu_4N}][\mathrm{B_3H_8}]$ is the phenylruthenatetraborane $[\mathrm{B_3H_8Ru(C_6H_5)(CO)(PPh_3)_2}]$, the hydrido complex $[\mathrm{B_3H_8RuH(CO)(PPh_3)_2}]$ is also obtained, consistent with alcoholic transfer hydrogenation of the putative complex $[\mathrm{B_3H_7Ru(CO)(PPh_3)_2}]$.

Introduction

Metallaboratranes are compounds in which a metal−boron dative bond is housed within a cage structure, buttressed by two or three methimazolyl groups. In the intervening decade since the first report of such a complex,[1] the field has matured to the point that extensive reviews are now available.[2] With the exception of Bourissou's elegant studies of γ-phosphinoboranes,[3] the vast majority of metallaboratranes arise from the chelate-assisted B−H activation of the B−H bond of a scorpionate ligand bearing two or three heterocycles that each feature a donor group γ to the boron: i.e. bicyclo[0.3.3] and tricyclo[0.3.3.3] geometries (Chart 1).[4] This is at least in part a geometric consequence of the increased chelate size of, for example, poly(methimazolyl)borates relative to the more familiar poly(pyrazolyl)borates,[5] for which metallaboratrane formation has never been observed, presumably due to the geometric strain associated with bicyclo[0.2.2] or tricyclo[0.2.2.2] frameworks (Chart 1).

At the time, this chemistry appeared to us novel; however, on reflection, there have been transformations reported that bear at least a superficial analogy. The reaction of Vaska's complex $[\mathrm{IrCl(CO)(PPh_3)_2}]$ (**1**) with $\mathrm{Na[H_2B(mt)_2]}$ (mt = methimazolyl) afforded the first (albeit *mer*) boron pincer complex, the iridaboratrane $[\mathrm{IrH(CO)(PPh_3)}\{\kappa^3 B,S,S'\text{-HB(mt)_2}\}]$ (**2**) with a

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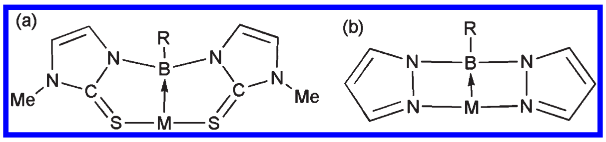
Chart 1. Ring Strain Associated with Bis(azolyl)borane Coordination: (a) Bicyclo[0.3.3] (Observed) and (b) Bicyclo[0.2.2] (Not Observed)

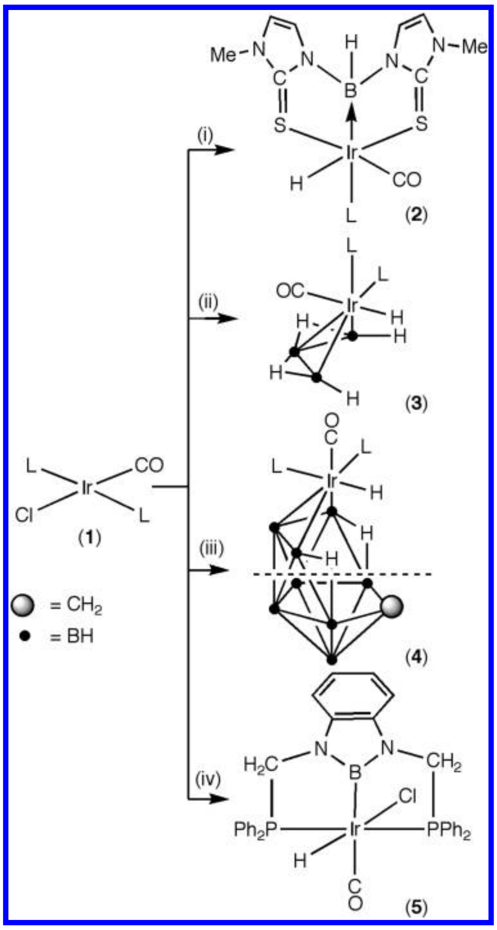


neutral [SBS] pincer.[6] We view this as an octahedral d^8 complex of iridium(I) with a dative Ir→B bond,[7a] though an alternative perspective has been presented.[7b] It had, however, been long since reported that **1** reacts with the octahydrotriboronate anion, $[B_3H_8]^-$, to afford what has been described as a "boraallyl" ($[B_3H_7]^{2-}$) complex of iridium(III), $[B_3H_7IrH(CO)(PPh_3)_2]$ (**3**).[8a] In practice, the reactions of metal halo complexes with all manner of polyboronate and carbapolyboronate anions often result in transfer of a hydrogen atom to the metal center following halide metathesis. This may be illustrated by the reaction of **1** with $[NMe_4][CB_9H_{12}]$, resulting in the formation of the hydrido complex $[CB_8H_{12}IrH(CO)(PPh_3)]$ (**4**), which has an inner coordination sphere geometry akin to **3**.[9] This is but one arbitrary example from a plethora of such reactions.

We had been pondering the parallels in these processes when reports appeared recently of two new classes of boron pincer complexes.[10] The iridium complex $[IrHCl(CO)\{\kappa^3 B,P.P'\text{-dppB}\}]$ (**5**) arises from the reaction of **1** with the bis(β-phosphino)diazaborolidine $o\text{-}C_6H_4(NCH_2PPh_2)_2BH$ (hereafter dppBH),[10a] while the palladium complex $[PdBr\{\kappa^3 B,Se,Se'\text{-}B_{10}C_2H_9(CH_2SePh)_2\}]$ is obtained via cyclometalation of a *m*-dicarbaborane to which are appended selenoether donors.[10c] We therefore feel it instructive to now consider these apparently disparate iridium complexes **2**−**5** together to explore parallels in their formation (Scheme 1). This perspective has led us to prepare the first ruthenium boron pincer complex[11,12] by extending this analogy to the process for ruthenaboratrane formation.

The synthetic routes to each of the complexes **2**−**5** are presumed to each proceed via a common sequence of monodentate and then bidentate coordination of the added ligand followed by the activation of one B−H bond (Scheme 2). This appears especially favorable for iridium(I), but has been shown to occur, albeit less readily, for rhodium(I).[13] This result is perhaps consistent with the more widespread use of iridium vs rhodium complexes in metal-mediated C−B bond-forming proccesses:[14] i.e., it would appear that metal−boron bond strengths increase down a triad.[15]

Scheme 1. Coordinative B−H Activation by Vaska's Complex (1; L = PPh$_3$)[a]



[a] Legend: (i) $K[H_2B(mt)_2]$;[6] (ii) $Tl[B_3H_8]$;[8] (iii) $[Me_4N][C_2B_9H_{12}]$;[9] (iv) $C_6H_4N_2(CH_2PPh_2)_2BH$ (dppBH).[10a]

In each case, the iridium retains a carbonyl ligand; however as noted previously, the ν_{CO} value alone is not a reliable indicator of the electronic environment at iridium, due to the coupling of ν_{CO} and ν_{IrH} modes.[13a,16] These data should certainly be used with caution when making inferences about indicative formal oxidation states, especially when these two ligands assume a mutually trans disposition. It has been suggested[8a] that **3** is an iridium(III) complex of the boraallyl dianion, drawing on the usual isoelectronic bookkeeping relationship: $[C_3H_5]^- = [C_2BH_6]^- = [CB_2H_7]^- = [B_3H_7]^{2-}$. However, this perspective was subsequently revised[8b] when it was suggested that a d^4 iridium(V) complex of the $[B_3H_7]^{4-}$ ligand was more apt, highlighting if nothing else the artifice of oxidation state assignments in covalent compounds. We might just as

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[6] (a) Crossley, I. R.; Hill, A. F.; Willis, A. C. *Organometallics* **2005**, *24*, 1062. (b) Crossley, I. R.; Hill, A. F.; Willis, A. C. *Organometallics* **2009**, *29*, 326.

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[8] (a) Greenwood, N. N.; Kennedy, J. D.; Reed, D. *J. Chem. Soc., Dalton Trans.* **1980**, 196. (b) Bould, J.; Greenwood, N. N.; Kennedy, J. D.; McDonald, W. S. *J. Chem. Soc., Dalton Trans.* **1985**, 1843. (c) Although the value for ν_{CO} was never reported, it may be very crudely estimated from the published spectrum.[8a]

[9] Fontaine, X. L. R.; Kennedy, J. D.; Thornton-Pett, M.; Nestor, K.; Stibr, B.; Jelinik, T.; Base, K. *J. Chem. Soc., Dalton Trans.* **1990**, 2887.

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[11] Depending on what constitutes a "pincer ligand", the ruthenaboratranes $[Ru(CO)(L)\{\kappa^4 B,S,S',S''\text{-}B(mt)_3\}]$ (L = PPh$_3$,[1,4a] CN^{t}Bu, CNC$_6$H$_3$Me$_2$-2,6, CO[12]) might arguably be considered as boron pincers bearing an additional chelate arm.

[12] Crossley, I. R.; Foreman, M. R. St.-J.; Hill, A. F.; Owen, G. R.; White, A. J. P.; Williams, D. J.; Willis, A. C. *Organometallics* **2008**, *27*, 381.

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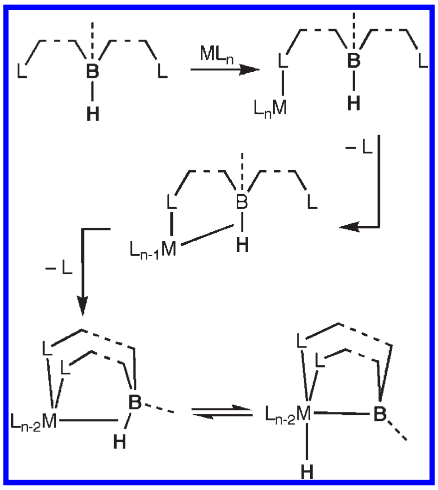
[14] (a) Dang, L.; Lin, Z.; Marder, T. B. *Chem. Commun.* **2009**, 3987. (b) Mkhalid, I. A. I.; Barnard, J. H.; Marder, T. B.; Murphy, J. M.; Hartwig, J. F. *Chem. Rev.* **2010**, *110*, 890.

[15] Rablen, P. R.; Hartwig, J. F.; Nolan, S. P. *J. Am. Chem. Soc.* **1994**, *116*, 4121.

[16] (a) Vaska, L. *J. Am. Chem. Soc.* **1966**, *88*, 4100. (b) Vaska, L. *Chem. Commun.* **1966**, 614. (c) Bath, S. S.; Vaska, L. *J. Am. Chem. Soc.* **1963**, *85*, 3500.

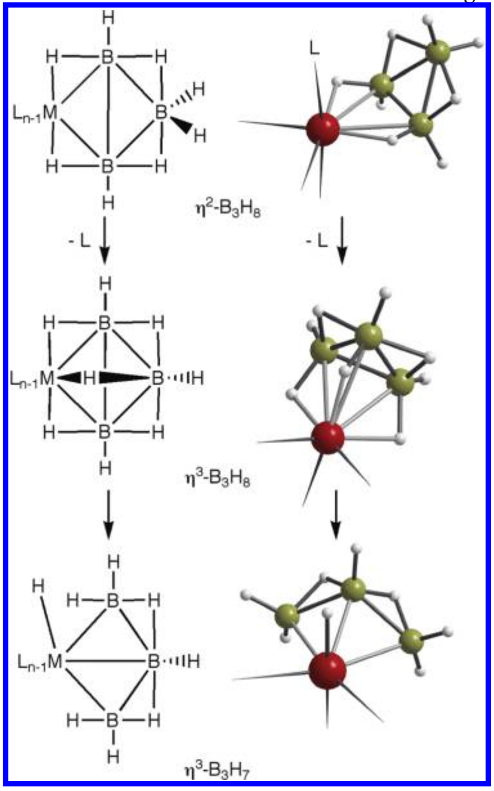
Scheme 2. Chelate-Assisted B−H Activation



easily argue that there is an alternative description of **3** as an iridium(I) complex of the neutral Lewis acid B_3H_7 which is known to form adducts with, for example, PPh_3.[17] On the basis of ν_{CO} (vide supra, KCl: ca. 1990 cm^{-1}),[8c] these higher oxidation state assignments (Ir^{III}, Ir^{V}) would seem of dubious descriptive value and would be contrary to the tenet of electroneutrality. This is perhaps semantics in that oxidation states have little meaning when highly covalent three-dimensional polynuclear clusters are concerned, the bonding of which involves a manifold of valence orbitals.[18] Although no intermediate was reported for the formation of **3**,[8] an indication of how it might form is provided by the complexes $[B_3H_8Mn(CO)_x]$ ($x = 3, 4$), in which the B_3H_8 "ligand" coordinates through either two ($x = 4$) or three ($x = 3$) B−H−Mn interactions.[19,20] Chart 2 relates these three bonding scenarios for the triboronate(8)/triborane(7) continuum.[8,19,21] Notably, "boraallyl" complexes are only known for iridium, platinum, and palladium:[8,22] i.e., metals that readily activate B−H and B−B bonds and thereby find application in hydroboration and borylation catalysis.

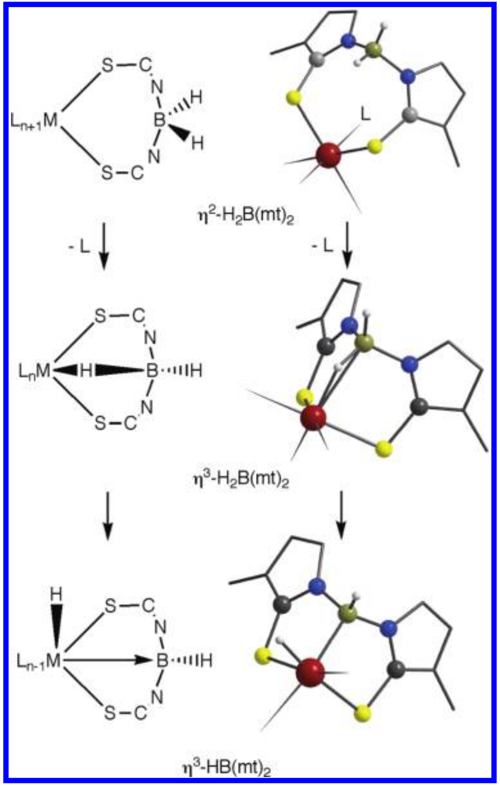
Thus, a 3c−2e B−H−Ir interaction would be plausible en route to the B_3H_7 ligand. In the case of the metallaboratrane **2**, no intermediate is observed; however, the corresponding reaction with $[RhCl(CO)(PPh_3)_2]$ does indeed afford a bis(methimazolyl)borate complexes with an inferred B−H−Rh interaction (Chart 3).[13a] Though this was not confirmed

Chart 2. Bidentate and Tridentate Triboronate Ligands[a]



[a] Coordinates taken from $[B_3H_8Ru(PPh_3)\{HB(pz)_3\}]$,[21] $[B_3H_8Mn(CO)_3]$,[19] and $[B_3H_7IrH(CO)(PPh_3)_2]$.[8]

Chart 3. Bidentate and Tridentate Methimazolylborate and Borane Ligands[a]



[a] Coordinates taken from $[W(CO)\{H_2B(mt)_2\}_2]$,[23a] $[RuH(PPh_3)_2\{H_2B(mt)_2\}]$,[23b] and $[IrH(CO)(PPh_3)\{HB(mt)_2\}]$.[6]

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(18) Wade, K. J. *Adv. Inorg. Chem. Radiochem.* **1976**, *18*, 1.

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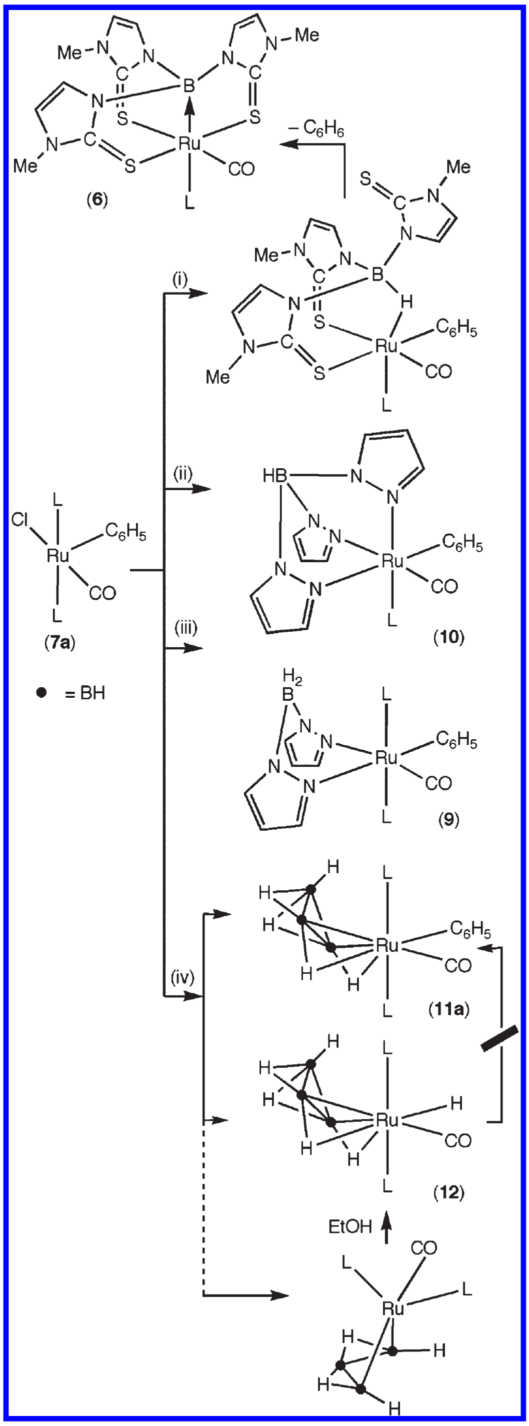
crystallographically, such an interaction was observed for the structurally characterized complex [Rh(COD){κ^3*H,S.S′*-$H_2B(mt)_2$}].[13b] Indeed, we have often encountered this bonding motif in $H_2B(mt)_2$ complexes of metals as diverse as Ti^{IV} and Pt^{IV}.[23]

Drawing upon this topological analogy in the syntheses of **2**−**5**, we presumed that it might serve as a guide in identifying B−H activation processes for other metals. The first metallaboratrane, [Ru(CO)(PPh_3){B(mt)$_3$}] (**6**), arose from the reaction of [Ru(C_6H_5)Cl(CO)(PPh_3)$_2$] (**7a**)[24] with Na[HB(mt)$_3$].[1] It was subsequently possible to isolate the complex [RuH(CO)(PPh_3){κ^3-HB(mt)$_3$}] (**8**) (from Na[HB(mt)$_3$] and [RuHCl(CO)(PPh_3)$_3$]), and while this did upon thermolysis evolve to **6**, the remarkable feature was that the HB(mt)$_3$ ligand was bound to ruthenium via the κ^3*H,S,S′* rather than the expected κ^3*S,S′,S″* mode.[4a,25] We have therefore investigated the reactions of **7a** with [^{n}Bu$_4$N][B_3H_8] and dppBH in search of processes to support this analogy.

Results and Discussion

The reactions of [Ru(C_6H_4Me-4)Cl(CO)(PPh_3)$_2$] (**7b**) with K[$H_2B(pz)_2$] and K[HB(pz)$_3$] (pz = pyrazol-1-yl) have been reported previously and are unremarkable in affording the simple complexes [Ru(C_6H_5Me)(CO)(PPh_3)$_n${$H_nB(pz)_{4-n}$}] (n = 2 (**9b**),[26] 1 (**10b**);[27] Scheme 3).[28] Complexes of the general form [Ru(C_6H_5)(CO)(L)({HB(pz)$_3$}] have in the interim assumed importance in the metal-mediated alkylation of arenes, studied extensively by Gunnoe.[28c,29] Complex **9b** appears stable with respect to phosphine dissociation, and there is no evidence for the $H_2B(pz)_2$ ligand displaying increased hapticity through B−H−Ru interactions,[30] either in solution or in the solid state for the structurally characterized and related complex [Ru(CH=CH_2)(CO)(PPh_3)$_2${κ^2-$H_2B(pz)_2$}].[26]

Scheme 3. Reactions of 7a with Borate Salts (L = PPh$_3$)[a]



[a] Legend: (i) Na[HB(mt)$_3$];[1] (ii) K[HB(pz)$_3$];[27] (iii) K[$H_2B(pz)_2$];[26] (iv) [^{n}Bu$_4$N][B_3H_8].

The reaction of **7b** with [^{n}Bu$_4$N][B_3H_8] has been mentioned briefly[31] and reported to give the organoruthenatetraborane [B_3H_8Ru(C_6H_4Me-4)(CO)(PPh_3)$_2$] (**11b**) on the basis of spectroscopic data, though no structural data were obtained. Indeed, no structural data are available for any examples of

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[25] This coordination mode has also been observed in the complex [RuCl(dmso)$_2${κ^3*H,S,S′*-HB(mt)$_3$}].[23b]

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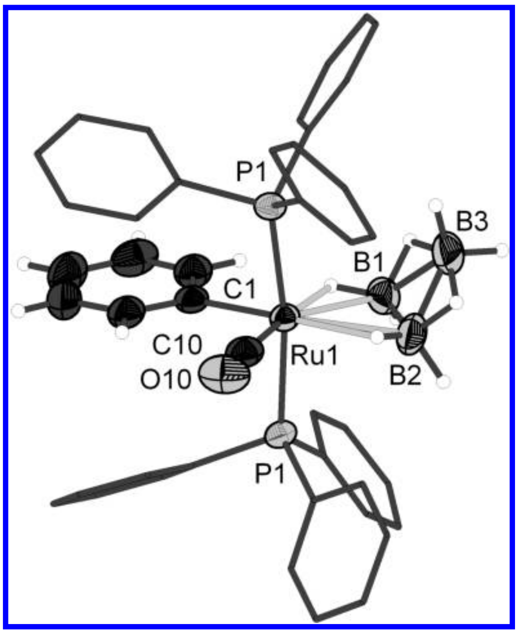

Figure 1. Molecular structure of [$B_3H_8Ru(C_6H_5)(CO)(PPh_3)_2$] (**11a**) in the crystal state (50% displacement ellipsoids, phosphine substituents simplified, one B_3H_8 orientation shown). Selected bond lengths (Å) and angles (deg): Ru1−B2 = 2.470(7), Ru1−B1 = 2.499(7), Ru1−P1 = 2.3848(5), Ru1−C1 = 2.112(4), Ru1−C10 = 1.837(5), B1−B2 = 1.709(12), B1−B3 = 1.768(11), B2−B3 = 1.779(12); P1−Ru1−P1 = 169.54(3), P1−Ru1−C1 = 87.86(2), P1−Ru1−C10 = 85.51(2), P1−Ru1−B1 = 88.47(17), P1−Ru1−B2 = 83.79(17), B1−Ru1−B2 = 40.2(3), Ru1−B1−B2 = 69.0(4), Ru1−B1−B3 = 106.0(5), B2−B1−B3 = 61.5(5).

transition-metal σ-organometallatetraboranes,[20] though an alkylidyne example has been reported.[32] Accordingly, we have explored the similar reaction of **7a** and identified the major product (vide infra) as the ruthenatetraborane complex [$B_3H_8Ru(C_6H_5)(CO)(PPh_3)_2$] (**11a**). The spectroscopic data for **11a** are consistent with the geometry suggested in Scheme 3 and have been confirmed by the crystallographic results summarized in Figure 1. Thus, two signals in a ratio of 2:1 are observed in the $^{11}B\{^1H\}$ NMR spectrum, with the more intense of these, corresponding to the ruthenium-bound boron nuclei, appearing at δ_B −36.8 ppm while the apical boron is observed at δ_B 0.0. Assuming that the RuB_3 unit is static (as suggested by the ^{31}P NMR data, vide infra), it is notable that the chemical shifts of the ruthenium-bound boron nuclei are not especially sensitive to the disparate nature of the phenyl (strong σ-donor) and carbonyl (strong π-acceptor) trans ligands. The $^{31}P\{^1H\}$ NMR spectrum comprises an AB spin system (δ_P 37.13, 35.41), the coupling of which is consistent with the trans arrangement of chemically inequivalent phosphorus nuclei ($^2J_{AB}$ = 258 Hz). The chemical inequivalence of the phosphorus nuclei reflect endo and exo sites on the wingtips of the butterfly RuB_3 arrangement, which does not appear to invert on the ^{31}P NMR time scale at ambient temperatures.

The net donor ability of the triboronate ligand has not been previously assayed, and accordingly Table 1 collates infrared data for a range of complexes of the form [$Ru(C_6H_4\text{-}R\text{-}4)(CO)(L_2)(PPh_3)_2$] (R = H, Me; L_2 = one bidentate or two monodentate ligands). A consideration of these data leads to the conclusion that the triboronate ligand is a comparatively poor donor, consistent with the notion that three-center−two-electron B−H−M interactions constitute weak "ligands".

Table 1. Selected Infrared Data for the Series of Complexes [$Ru(C_6H_4R\text{-}4)(CO)(L_2)(PPh_3)_2$] (R = H, Me)[a]

L_2	R	ν_{CO} (cm^{-1})
$Cl(CO)^{33}$	Me	2055, 1952^{N}
$H_2B(bta)_2{}^{34}$	Me	1955^{N}
$Cl(CNR')^{35}$	Me	1948^{N}
B_3H_8	H	1941^{N}
$H_2B(pz)_2{}^{26}$	H	1937^{D}
$Cl(SNNMe_2)^{39}$	Me	1924^{D}
$Cl(BTD)^{37}$	Me	1921^{N}
pyrCHS^{38a}	H	1919^{D}
mt^{38b}	H	1915^{D}
O_2CH^{36}	Me	1913^{N}
$Cl(BSD)^{37}$	Me	1913^{N}

[a] Abbreviations: *N*, Nujol mull; *D*, CH_2Cl_2 solution; R′, C_6H_4Me-4; pyrCHS, 3,5-dimethyl-4-ethylpyrrole-2-carbothioaldehyde; mt, methimazolyl; BTD, 2,1,3-benzothiadiazole, BSD, 2,1,3-benzoselenadiazole.

The characterization of **11a** included a crystallographic study, the results of which are summarized in Figure 1. The mononuclear ruthenatetraboranes [$B_3H_8RuL_n$] (RuL_n = RuH(CO)-$(PPh_3)_2$,[40] $Ru(PPh_3)\{HB(pz)_3\}$,[21] $RuCl(\eta\text{-}C_6Me_6)$[41,42]) have been structurally characterized previously. The most noteworthy geometric features of **11a** are as follows. (i) There is an almost insignificant (4 esd) elongation of the bond Ru1−B1 (2.499(7) Å), relative to Ru1−B2 (2.470(7) Å), suggesting that the geometric features of the triboronate ligand bonding are not especially responsive to differential trans influences (C_6H_5 cf. CO), as already suggested by ^{11}B NMR data. (ii) The "RuB_3" unit adopts a hinged butterfly geometry[43] with an angle of 123° between the Ru−B1−B2 and B1−B2−B3 planes, consistent with an arachno (divacant octahedron) description.[18] Notably, B3 and the *endo*-H531 are clearly remote from the electron-precise ruthenium center (3.437 and 3.618 Å, respectively) and no direct B−H−Ru interaction needs to be invoked. The phenyl ligand assumes a Ru1−C1 bond length of 2.112(4) Å, which is somewhat longer than that for the five-coordinate complex **7b** (2.056(3) Å),[24a] which presumably arises from a combination of the increased coordination number at ruthenium and perhaps a modest trans influence on the part of the triboronate ligand. The molecule straddles a crystallographic mirror plane that

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(43) Note that the triboronate ligand displays position disorder over two sites that straddle the crystallographically imposed mirror plane normal to the P1−P1* vector.

contains the phenyl and carbonyl groups, but not the B_3H_8 ligand; this is disordered over two sites such that the three boron atoms lie off the plane, as indicated by the $^{31}P\{^1H\}$ NMR data discussed above.

A second product was isolated from the reaction of **7a** with $[Bu_4N][B_3H_8]$, which was identified on the basis of ^1H (δ_H −9.14 t, $^2J_{PH}$ = 20.7 Hz), ^{31}P (δ_P 49.34, 44.03; $^2J_{PP}$ = 249 Hz), and ^{11}B (δ_B 0.21, −36.6, −38.6) NMR spectroscopy as the hydrido complex $[B_3H_8RuH(CO)(PPh_3)_2]$ (**12**).[31,40] We had previously encountered **12** as a minor side product in the reactions of various σ-vinyl complexes, e.g., [Ru(CH=CHPh)Cl(CO)-$(PPh_3)_2$] (**7c**), with $[Me_4N][B_3H_8]$.[31] At the time, we had not considered this unusual in that the precursor vinyl complexes arise from the reversible reaction of $[RuHCl(CO)(PPh_3)_3]$ with alkynes. We therefore presumed that small amounts of the complex "$RuHCl(CO)(PPh_3)_2$" could have been present. However, in the case of **7a** no such β-RuH elimination process is available to afford "$RuHCl(CO)(PPh_3)_2$". We are therefore left to conclude that the triboronate itself plays a role in the cleavage of the phenyl group that competes with the isolation of **11a**. One interpretation that is attractive in the current context is that formation of the triborane(7) complex "$[B_3H_7Ru(CO)(PPh_3)_2]$" is followed rapidly by a transfer hydrogenation reaction with the primary alcohol solvent (Scheme 3).

To explore the parallels suggested above, the reaction of **7a** with dppBH was investigated and found to proceed under remarkably mild conditions (25 °C) to provide the $[PBP]^-$ pincer complex $[RuCl(CO)(PPh_3)\{B(NCH_2PPh_2)_2C_6H_4\}]$ (**13**). Previously, the reactions of **7a** with boranes have been described and shown to require refluxing benzene to ultimately affect benzene elimination and the formation of coordinatively unsaturated σ-boryl complexes **14**.[44] What is especially noteworthy is that the complexes $[RuHCl(CO)(PPh_3)_3]$, **7a**, and **7c** all failed to provide σ-boryl derivatives when treated with o-$C_6H_4(NMe)_2BH$, which may be taken to indicate that one or both phosphino donors play a role in the formation of **13** via chelate-assisted B−H activation (cf. Scheme 2).[44a]

The formulation of **13** as a boron pincer complex of ruthenium(II) follows from spectroscopic data and was confirmed by a crystallographic study (Figure 2). In contrast to Roper and Wright's σ-boryl complexes, which are brightly colored, complex **13** is colorless both in the solid state and in solution. This immediately suggested that the complex was coordinatively saturated, and this was confirmed by the appearance of two resonances in the $^{31}P\{^1H\}$ NMR spectrum. The resonance to lower field (C_6D_6: δ_P 49.59) appeared as a sharp doublet ($^2J_{PP}$ = 13.0 Hz), while the second resonance (δ_P 10.01) was heavily broadened (hhw ca. 60 Hz) such that coupling was not resolved. We have observed a similar degree of broadening in the ^{31}P resonance for the complex **6**, in which one phosphine is trans to the Ru→B dative bond: i.e., quadrupolar broadening only significantly affects the resonance trans to boron, as illustrated for example in the rhodaboratrane complexes $[Rh(PMe_3)_2\{B(mt)_3\}]^+$ and both isomers of $[Rh(CNR)(PPh_3)\{B(mt)_3\}]^+$, wherein ^{31}P NMR signals for phosphorus bound cis to boron were sharp while broadened signals were observed for phosphorus nuclei trans to boron.[4c] Both the $^{11}B\{^1H\}$ and ^{11}B NMR spectra comprised a single broad resonance (CD_2Cl_2: δ_B 52.9 ppm), indicating cleavage of the B−H bond. The ^1H NMR spectrum was informative with respect to the complex stereochemistry, with the diastereotopic phosphinomethylene protons giving rise to two disinct and mutually coupled virtual triplet[45] resonances, confirming both the *trans*-bis(phosphine) arrangement and the low symmetry of the equatorial B, C, P, and Cl donor set. These data indicate the stereochemistry shown in Scheme 4, which was confirmed by the crystallographic results summarized in Figure 2.

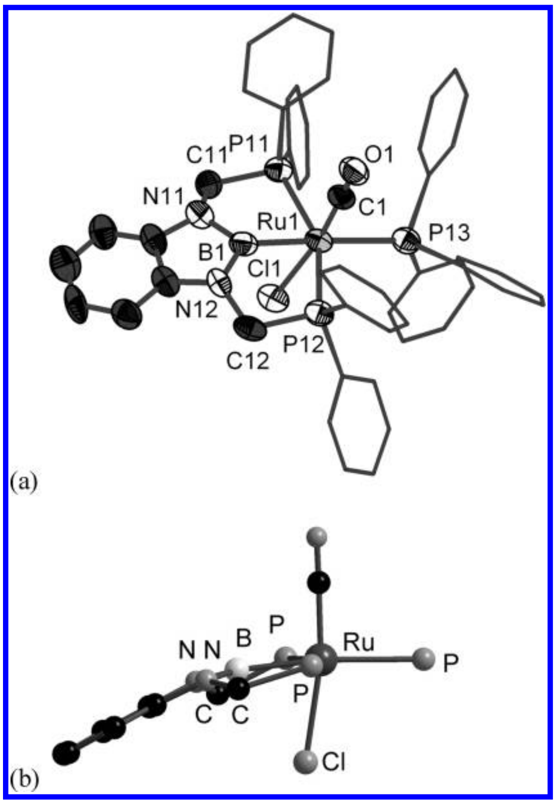

Figure 2. (a) Molecular structure of $[RuCl(CO)(PPh_3)(\kappa^3B,P,P'$-dppB)] (**13**) in the crystal state (50% displacement ellipsoids, hydrogen atoms omitted, phosphine phenyl groups simplified; one of two independent molecules shown). (b) Side view illustrating deformation of the dppB chelate. Selected bond lengths (Å) and angles (deg): Ru1−Cl1 = 2.496(3), Ru1−P11 = 2.369(3), Ru1−P12 = 2.366(3), Ru1−P13 = 2.501(4), Ru1−C1 = 1.860(14), Ru1−B1 = 2.051(15), N11−B1 = 1.459(16), N12−B1 = 1.454(15); Cl1−Ru1−P11 = 87.45(11), Cl1−Ru1−P12 = 86.11(11), P11−Ru1−P12 = 153.48(12), Cl1−Ru1−P13 = 98.59(11), P11−Ru1−P13 = 101.49(11), P12−Ru1−P13 = 104.90(12), Cl1−Ru1−B1 = 74.7(4), P11−Ru1−B1 = 76.4(4), P12−Ru1−B1 = 77.1(4), C1−Ru1−B1 = 95.2(5), N11−B1−N12 = 103.9(11), N11−B1−Ru1 = 126.4(9), N12−B1−Ru1 = 128.3(10).

In addition to confirming the identity of **13**, the crystal structure revealed some features of note. First, the Ru1−B1

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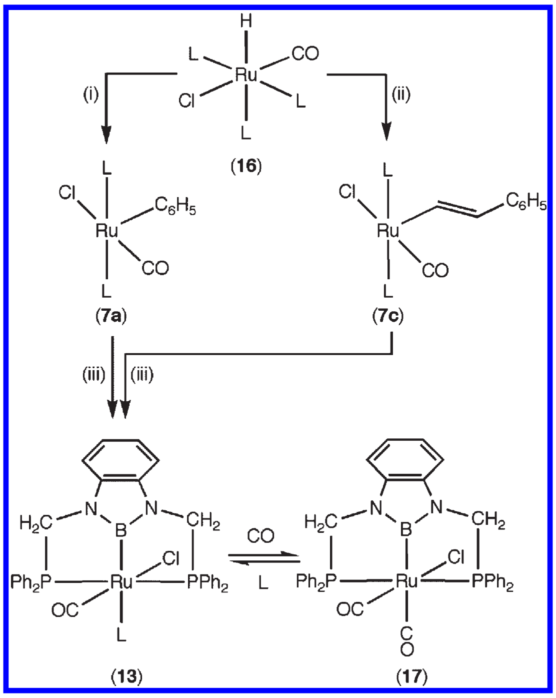
(46) Structural data for octahedral boryl complexes of ruthenium are limited to those for $[Ru(BCat)_2(CO)(L)(PPh_3)_2]$ (Cat = o-$C_6H_4O_2$; L = CO, CNC_6H_4Me-4): (a) Rickard, C. E. F.; Roper, W. R.; Williamson, A.; Wright, L. J. *Organometallics* **2000**, *19*, 4344. Limited data are, however, available for pseudo-octahedral half-sandwich derivatives: (b) Braunschweig, H.; Kollann, C.; Klinkhammer, K. W. *Eur. J. Inorg. Chem.* **1999**, 1523. (c) Braunschweig, H.; Koster, M.; Wang, R. *Inorg. Chem.* **1999**, *38*, 415. (d) Rankin, M. A.; MacLean, D. F.; McDonald, R.; Ferguson, M. J.; Lumsden, M. D.; Stradiotto, M. *Organometallics* **2009**, *28*, 74. Ru−B bond lengths for BCat derivatives span the range 2.047−2.098 Å, while ruthenium aminoboryls have somewhat longer Ru−B bond separations (2.115, 2.173 Å).

Scheme 4. Synthesis of dppB Boron Pincer Complexes of Ruthenium (L = PPh_3)[a]



[a] Legend: (i) $HgPh_2$;[35] (ii) HC≡CPh;[49] (iii) dppBH.

bond length of 2.051(15) Å is somewhat shorter than those found for the octahedral or pseudo-octahedral ruthenium σ-boryl complexes that have been structurally characterized.[46] More data are available for octahedral σ-boryls of osmium (Os−B = 2.085−2.180 Å),[46,47] and given that ruthenium (146 pm) and osmium (144 pm) have comparable covalent radii, this contraction in metal−boron bond length would appear to be noteworthy and is most likely a corollary of the geometric constraints of pincer coordination. Boryl complexes of osmium in which the metal is five-coordinate typically have shorter Os−B separations (2.019−2.082 Å): e.g., the complexes $[Os(BO_2C_2H_4)Cl(CO)_n(PPh_3)_2]$ (Os−B = 2.043 (n = 1) and 2.180 Å (n = 2)).[47a] These constraints are clearly manifested in the contracted P1−Ru1−P2 angle of 153.48(12)° and the acute angles between phosphorus and boron chelate donors (76.4(4), 77.1(4)°). For five- and six-coordinate σ-boryls of ruthenium and osmium ligated by two mutually trans phosphines, the boryl ligand typically lies in the equatorial plane. This not only minimizes steric interactions with the bulky phosphines but also allows the empty p orbital of the trigonal boron center to align with the more π-basic of the two retrodative metal orbitals on offer without competition from the cis carbonyl ligand. However, this is precluded by the pincer geometry. In the event that any (at best modest) degree of π-acidity was possible on the part of the diazaborolinyl ring, this orientation would be the least ideal for retrodonation from ruthenium. The meridional coordination of the dppB ligand introduces some strain, which is also evident in the failure of the ruthenium, phosphorus atoms, and benzodiazoborolinyl ring to achieve coplanarity (Figure 2b).

While the complex **7a** has proven to be a versatile substrate for the formation of bonds between ruthenium and various main-group elements via arene elimination,[1,44,48] it has the drawback that the synthetic route to **7a** (or **7b**) involves the use of organomercurials,[33−35] which are undesirable for large-scale investigations. Alternative precursors to **13** were therefore investigated. The *trans*-β-styryl complex $[Ru(CH{=}CHPh)Cl(CO)(PPh_3)_2]$ (**7c**)[49] was found to react with dppBH in a manner similar to that for **7a**, providing **13** in high yield; however, the synthesis of **7c** is problematic. Depending on the reaction conditions, **7c** is typically contaminated to varying degrees with the isomeric α-styryl complex $[Ru(CPh{=}CH_2)Cl(CO)(PPh_3)_2]$ (**7d**) and also has a tendency to cocrystallize to varying extents with the (pale yellow) tris(phosphine) complex $[Ru(CH{=}CHPh)Cl(CO)(PPh_3)_3]$ (**15**). The optimized synthesis of **13**, therefore, employed the hydrido complex $[RuHCl(CO)(PPh_3)_3]$ (**16**) in the presence of ethynylbenzene to rapidly generate **7c**, in situ and without isolation, for subsequent reaction with dppBH to afford **13** in high yield in a single procedure (Scheme 4).

Just as the phosphine ligand in **6** was found to be labile and to be readily replaced by CO (reversibly) and isonitriles (irreversibly),[12] we find that exposure to carbon monoxide (ca. 1 atm, benzene) immediately converts **13** to the *cis*-dicarbonyl derivative $[RuCl(CO)_2(\kappa^3 B,P,P'\text{-dppB})]$ (**17**) in spectroscopically quantitive yield, indicating that the phosphine dissociates on the chemical time scale but not the $^{31}P\{^1H\}$ NMR time scale (the presence of extraneous PPh_3 does not lead to signal broadening). We have not successfully obtained **17** in analytically pure form, because on the chemical time scale the substitution reaction does appear to be reversible, such that samples of **17** precipitated by addition of hexane are typically contaminated with small amounts of **13**. Attempted removal of solvent under reduced pressure (cf. precipitation) results in complete reversion to **13**. Lin and Marder have computationally investigated the origin of the trans effect of boryl ligands,[50] and the labilization of a σ-donor phosphine ligand in **13** by the strongly trans-directing boryl is now to be expected. The lability of a π-acidic carbonyl ligand in **17** is perhaps more unexpected, though it is also observed in the case of the ruthenaboratrane $[Ru(CO)_2\{B(mt)_3\}]$.[12] Nevertheless, full spectroscopic data may be acquired in solution which are consistent with the *cis*-dicarbonyl geometry. This assignment follows not only from the appearance of two infrared absorbances (CH_2Cl_2: 2035, 1972 cm^{-1}) but also from the ^1H NMR AA′BB′M signature associated with the diastereotopic protons of *trans*-bis(PCH_2) groups lying on either side of a nonsymmetric equatorial plane of donors: i.e., the C_{2v} *trans*-dicarbonyl isomer may be excluded. In contrast to the case for **13**, the $^{31}P\{^1H\}$ NMR spectrum of **17** comprises a single sharp singlet (C_6D_6: δ_P 57.93), while the single resonance observed in the $^{11}B\{^1H\}$ NMR spectrum (δ_B 53.8) is shifted to marginally higher field than that for **13** (δ_B

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52.9). It would thus appear that the chemical shift of the dppB boron nucleus is not especially sensitive to variations in the nature of trans-coordinated ligands.

Concluding Remarks

We began by drawing attention to perceived parallels between the chelate-assisted B−H activation of a number of ligands containing B−H bonds with an iridium substrate and then demonstrated this with reactions of the ruthenium σ-aryl complex **7a**, which has a track record in B−H activation processes.[1,44] However, while the first ruthenium κ^3*B,P,P′*-boron pincer complex[11] has been isolated from dppBH and fully characterized, the "analogous" triboronate ligand failed to proceed to B−H activation (or even adopt κ^3*H,H′,H″* coordination) but rather stopped at an early point along our proposed "general" trajectory (Scheme 2). Iridium appears to show a marked propensity for B−H bond activation that no doubt accounts for its popularity in borylation catalysis. Thus, the utility of iridium complexes presumably relates to special characteristics with respect to the facility of Ir−B bond formation. In the absence of comparative thermochemical data,[15] it would nevertheless seem that M−B bond strengths do increase down group 9. It remains to be seen if this trend is repeated for other triads. One feature to emerge from a comparison of the pincer complex **13** and the metallaboratrane complex **6** is that both appear to demonstrate a pronounced trans effect, even though the two Ru−B bonds have very different character, one being a conventional two-electron covalent bond and the other a two-center−two-electron dative (polar covalent, "coordinate") interaction. It should, however, be noted that steric factors will no doubt play a role in the lability of the unique phosphine in **13**.

Pincer ligands have enjoyed considerable attention of late,[51] though these have generally been based on classical donors (C, N, O, P). The properties that make boron unique among the first-row elements may well translate to useful design features when incorporated as ligating groups within pincer frameworks, whether they involve conventional (Yamashita−Nozaki ligands) or polar covalent (dative) metal−boron interactions (metallaboratranes).

Experimental Section

General Considerations. All manipulations of air-sensitive compounds were carried out under a dry and oxygen-free nitrogen atmosphere using standard Schlenk and vacuum-line techniques, with dry and degassed solvents (Grubbs system). NMR spectra were recorded at 25 °C on a Varian Gemini 300BB (^{1}H at 300.8 MHz, ^{13}C at 75.4 MHz, ^{11}B at 96.23 MHz, and ^{13}P at 121.4 MHz) spectrometer. The chemical shifts (δ) for ^{1}H (ignoring roof effects) and ^{13}C spectra are given in ppm relative to residual signals of the solvent and to external H_3PO_4 or BF_3OEt_2 references for ^{31}P and ^{11}B, respectively; *J* values are given in hertz. "t^v" refers to a virtual triplet resonance with the apparent J_{HP} coupling being quoted. ESI mass spectra were obtained on a ZAB-SEQ4F spectrometer in positive ion mode using a matrix of acetonitrile or dichloromethane and methanol. FAB mass spectra were obtained on an Autospec-Q instument using a nitrobenzyl alcohol matrix. Assignments were verified by simulation of isotopic composition. Elemental microanalysis was performed by the microanalytical service of the Australian National University. Data for X-ray crystallography were collected with a Nonius Kappa CCD diffractometer. The compounds $[Ru(C_6H_5)Cl(CO)(PPh_3)_2]$ (**7a**),[35] $[Ru(CH{=}CHPh)Cl(CO)(PPh_3)_2]$ (**7c**),[49] $[RuHCl(CO)(PPh_3)_3]$ (**16**),[52] $[{}^nBu_4N][B_3H_8]$,[53] and dppBH[10a] were prepared according to published procedures.

Synthesis of $[B_3H_8Ru(C_6H_5)(CO)(PPh_3)_2]$ (11a). A solution of $[RuCl(C_6H_5)(CO)(PPh_3)_2]$ (**7a**; 0.250 g, 0.33 mmol) in dichloromethane (25 mL) was treated with solid $[{}^nBu_4N][B_3H_8]$ (0.100 g, 0.35 mmol), and the mixture was stirred until the red color had discharged (30 min). Addition of EtOH (20 mL) and slow reduction in volume under reduced pressure gave an initial crop of a pale brown solid that was isolated by filtration and identified as the complex $[RuH(B_3H_8)(CO)(PPh_3)_2]$ (**12**; 0.05 g, 21%, 0.07 mmol). Further concentration of the filtrate gave the crude product **11a** as a pale brown solid, which was twice recrystallized from a mixture of CH_2Cl_2 and EtOH to remove residual traces of **12**. Yield of **11a**: 0.18 g (71%, 0.23 mmol). Anal. Found: C, 67.23; H, 5.71. Calcd for $C_{43}H_{43}B_3OP_2Ru$: C, 66.96; H, 5.62. IR (Nujol, cm^{-1}): 2522, 2453 ν_{BH}, 1941 ν_{CO}. NMR ($CDCl_3$, 25 °C). ^{1}H δ_H −8.5, −7.2 (br, RuHB), −1.2 to 0.0 (br, BH), 3.74, 5.91 (br, BH), 6.47 (t, 2 H, $H^{2,6}(RuC_6H_5)$, $J = 7.2$), 7.01−8.03 (m, 33 H, PC_6H_5 and $H^{3-5}(RuC_6H_5)$); $^{13}C\{^1H\}$ δ_C 201.8 (t, RuCO, $^2J_{PC} = 16.6$), 157.4 (t, $^2J_{PC} = 11.2$, $C^1(RuC_6H_5)$), 145.1 ($C^{2,6}(RuC_6H_5)$), 134.5−127.6 (m, PC_6H_5 and $C^{3,5}(RuC_6H_5)$, not resolved), 120.5 ($C^4(RuC_6H_5)$); $^{31}P\{^1H\}$ δ_P 37.13, 35.41 ($^2J_{PP} = 258$); $^{11}B\{^1H\}$ δ_B −36.8 (2 B), 0.0 (1B). FAB−MS (positive ion): *m*/*z* 731 $[M - B_3H_8]^+$, 693 $[M - Ph]^+$, 654 $[M - Ph - B_3H_8]^+$, 625 $[Ru(PPh_3)_2]^+$. Single crystals suitable for diffractometry were grown by slow diffusion of hexane into a saturated solution of **11a** in dichloromethane. Crystal data for **11a**: $C_{43}H_{43}B_3OP_2Ru$, $M_w = 771.26$, orthorhombic, *Pnma*, $a = 10.0015(2)$ Å, $b = 24.0151(5)$ Å, $c = 15.6420(3)$ Å, $V = 3757.0(1)$ Å^3, $Z = 4$, $D_{calcd} = 1.363$ Mg m^{-3}, μ(Mo Kα) = 0.536 mm^{-1}, $T = 200(2)$ K, colorless block, 0.07 × 0.30 × 0.38 mm, 4397 independent reflections. *F* refinement, $R = 0.0291$, $R_w = 0.0294$ for 2297 reflections ($I > 3\sigma(I)$, $2\theta_{max} = 55°$), 258 parameters, 10 restraints, CCDC 776470.

Preparation of $[RuCl(CO)(PPh_3)(dppB)]$ (13). Of the following three procedures, that described in (c) is the most expedient and effective.

(a). A mixture of $[Ru(C_6H_5)Cl(CO)(PPh_3)_2]$ (**7a**; 1.10 g, 1.44 mmol) and dppBH (0.74 g, 1.44 mmol) in benzene (20 mL) was stirred for 2 h and then freed of volatiles. The residue was triturated in an ultrsound bath with a 1:4 mixture of benzene and hexane to afford a pale solid, which was recrystallized from a mixture of dichloromethane and hexane. Yield: 1.152 g (1.22 mmol, 85%).

(b). A mixture of $[Ru(CH{=}CHPh)Cl(CO)(PPh_3)_2]$ (**7c**; 0.050 g, 0.063 mmol) and dppBH (0.032 g, 0.063 mmol) was stirred in dichloromethane (2 mL) for 4 h and then diluted with hexane (2 mL). Concentration under reduced pressure to ca. 2 mL resulted in the formation of a pale cream-colored precipitate, which was isolated by filtration, washed with hexane (2 mL), and dried in vacuo. Yield: 0.050 g (85%, 0.053 mmol).

(c). A suspension of $[RuHCl(CO)(PPh_3)_3]$ (**16**; 0.500 g, 0.53 mmol) in dichloromethane (15 mL) was treated with ethynylbenzene (0.11 mL, 1.16 mmol) and stirred for 15 min to provide a deep red solution (δ_P 32.73). To this was added dppBH (0.27 g, 0.53 mmol), and the mixture was then stirred for 12 h. The mixture was subsequently diluted with hexane (10 mL) and slowly concentrated under reduced pressure to ca. 2 mL and then further diluted with hexane (10 mL). The resulting khaki

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(51) Selected reviews on classes and applications of pincer ligands include: (a) Ballmann, J.; Munha, R. F.; Fryzuk, M. D. *Chem. Commun.* **2010**, 1013. (b) Serrano-Becerra, J. M.; Morales-Morales, D. *Curr. Org. Synth.* **2009**, *6*, 169. (c) Benito-Garagorri, D.; Kirchner, K. *Acc. Chem. Res.* **2008**, *41*, 201. (d) Nishiyama, H. *Chem. Soc. Rev.* **2007**, *36*, 1133. Pugh, D.; Danopoulos, A. A. *Coord. Chem. Rev.* **2007**, *251*, 610. (e) Peris, E.; Crabtree, R. H. *Coord. Chem. Rev.* **2004**, *248*, 2239. (g) Albrecht, M.; van Koten, G. *Angew. Chem., Int. Ed.* **2001**, *40*, 3750.

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solid was isolated by filtration, washed with hexane (10 mL), and then recrystallized from a mixture of benzene and diethyl ether. Yield: 0.302 g (62%, 0.321 mmol). Anal. Found: C, 64.84; H, 4.77; N, 2.72. Calcd for $C_{51}H_{44}BClN_2OP_3Ru$: 65.08; H, 4.71; N, 2.98. IR (CH_2Cl_2, cm^{-1}): 1940 ν_{CO}. NMR (25 °C): ^1H (C_6D_6) δ_H 4.40 (d t^v, 2 H, $PP'CH_B$, $^{2,4}J_{PB} = 2.3$, $^2J_{AB} = 11.7$), 4.49 (d t^v, 2 H, $PP'CH_A$, $^{2,4}J_{PA} = 3.5$, $^2J_{AB} = 11.7$), 6.87−7.30 (m × 4, 35 H, PC_6H_5), 7.66, 773 (m × 2, 4 H, AA′BB′ $N_2C_6H_4$); ^1H (CD_2Cl_2) δ_H 4.32 (d t^v, 2 H, $PP'CH_A$, $^{2,4}J_{PA} = 2.2$, $^2J_{AB} = 11.7$), 4.63 (d t^v, 2 H, $PP'CH_B$, $^{2,4}J_{PB} = 3.6$, $^2J_{AB} = 11.7$), 6.92−7.55 (m × 5, 39 H, $N_2C_6H_4$ and PC_6H_5); $^{13}C\{^1H\}$ (CD_2Cl_2) δ_C 201.4 (m, RuCO), 140.6 (t^v, $C^{1,6}(N_2C_6H_4)$, $^{3,4}J_{PC} = 7$), 137.3 (d, $C^1(PPh_3)$, $^1J_{PC} = 22.7$), 132.5 (t^v, $C^1(PPh_2)$, $^{1,3}J_{PC} = 17.6$), 134.6, 132.3, 128.5, 128.2 (m × 4, $C^{2,3,5,6}(PPh)$), 130.4, 129.9 ($C^4(PPh_2)$), 129.4 ($C^4(PPh_3)$), 118.7, 109.4 ($C^{2-5}(N_2C_6H_4)$), ca. 54.0 (m obscured by CD_2Cl_2 resonance, PCH_2); $^{13}C\{^1H\}$ (C_6D_6) δ_C 201.5 (d t, RuCO, $^2J_{P_2C} \approx {}^2J_{PC} \approx 9$), 141.0 ($t^v$, $C^{1,6}(N_2C_6H_4)$, $^{3,4}J_{PC} = 7.5$), 138.2 (d, $C^1(PPh_3)$, $^1J_{PC} = 22.7$), 137.6 (t^v, $^{2,4}J_{PC} = 16.1$, $C^1(PPh_2)$), 134.8, 134.6, 132.2 (t^v, $C^{2,3,5,6}(PPh)$), 133.0 (t^v, $^{2,4}J_{PC} = 17.5$, $C^1(PPh_2)$), 129.9, 129.4 ($C^4(PPh_2)$), 129.0 ($C^4(PPh_3)$), 119. 0, 109.9 ($C^{2-5}(N_2C_6H_4)$), 53.42 (d t^v, PCH_2, $^{1,3}J_{P2C} = 22.2$, $^{2,3}J_{PC} = 5.7$); $^{31}P\{^1H\}$ (C_6D_6) δ_P 49.59 (d, CH_2P, $^2J_{PP} = 13.0$), 10.01 (s v br, PPh_3); $^{31}P\{^1H\}$ (CD_2Cl_2) δ_P 49.71 (d, CH_2P, $^2J_{PP} = 13.0$), 12.98 (s v br, PPh_3); $^{11}B\{^1H\}$ (CD_2Cl_2) δ_B 52.9. ESI-MS (CH_2Cl_2, positive ion): *m*/*z* 938 $[M]^+$, 906 $[M - Cl]^+$, 877 $[M - Cl - CO]^+$, 644 $[M - PPh_3 - Cl]^+$. Low-quality crystals of **13** suitable for diffractometry were obtained by slow diffusion of hexane into a saturated solution of **13** in dichloromethane. Crystal data for **13**: $C_{51}H_{43}BClN_2OP_3Ru$, $M_w = 940.17$, triclinic, $P\bar{1}$ (No. 2), $a = 13.1923(17)$ Å, $b = 18.0267(17)$ Å, $c = 20.126(3)$ Å, $\alpha = 74.252(8)°$, $\beta = 80.577(4)°$, $\gamma = 87.994(8)°$, $V = 4544.1(10)$ $Å^3$, $Z = 4$, $D_{calcd} = 1.374$ Mg m^{-3}, μ(Mo Kα) = 0.549 mm^{-1}, $T = 200(2)$ K, colorless block, 0.014 × 0.051 × 0.075 mm, 11 968 independent reflections. F^2 refinement, $R = 0.086$, $R_w = 0.1422$ for 6292 reflections ($I > 2\sigma(I)$, $2\theta_{max} = 50°$), 1081 parameters without restraints, CCDC 776471.

Reaction of [RuCl(CO)(PPh$_3$)(dppB)] (13) with CO: Observation of [RuCl(CO)$_2$(dppB)] (17). N.B.: the precursor **13** is significantly less soluble than the dicarbonyl product **17** in a range of solvents and preferentially precipitates from equilibrating mixtures of **13** and **17** during isolation attempts.

(**a**). A suspension of [RuCl(CO)(PPh_3)(dppB)] (**13**; 0.01 g, 0.01 mmol) in C_6D_6 was prepared in an NMR tube that was then connected to a small balloon filled with CO, and the mixture was left to stand for 5 min with occcasional agitation. NMR (C_6D_6, 25 °C): ^1H δ_H 4.27 (d t^v, 2 H, $PP'CH_B$, $^{2,4}J_{PB} = 2.7$, $^2J_{AB} = 12.3$), 4.62 (d t^v, 2 H, $PP'CH_A$, $^{2,4}J_{PA} = 3.8$, $^2J_{AB} = 12.3$), 6.79, 6.88, 7.03, 7.15, 7.39, 7.57, 7.96 (m × 7, 35 H, PPh_2, free PPh_3 and $N_2C_6H_4$); $^{13}C\{^1H\}$ δ_C 197.6 (t, RuCO, $^2J_{PC} \approx 9$), 197.5 (t, RuCO, $^2J_{PC} = 12.4$), 141.1 (t^v, $C^{1,6}(N_2C_6H_4)$, $^{3,4}J_{PC} = 8.6$), 138.7 (t^v, $^{2,4}J_{PC} = 21.1$, $C^1(PC_6H_5)$), 134.8 (t^v, $^{2,4}J_{PC} = 6.2$, $C^{2,6}(PC_6H_5)$), 131.8 (t^v, $^{2,4}J_{PC} = 21.1$, $C^1(PPh_2)$), 131.0 (s, $C^4(PC_6H_5)$), 130.7 (t^v, $^{2,4}J_{PC} = 5.3$, $C^{2,6}(PC_6H_5)$), 129.6 (s, $C^4(PC_6H_5)$), 128.8 (m, $C^{3,5}(PC_6H_5)$), 119.5, 110.5 ($C^{2-5}(N_2C_6H_4)$), 50.91 (d t^v, PCH_2, $^{1,3}J_{P_2C} = 23.0$); $^{31}P\{^1H\}$ δ_P 57.93 (s), −4.65 (free PPh_3); $^{11}B\{^1H\}$(CD_2Cl_2) δ_B 53.8.

(**b**). A Schlenk tube containing a solution of [RuCl(CO)(PPh_3)(dppB)] (**13**; 0.05 g, 0.053 mmol) in CH_2Cl_2 (5 mL) was connected to a small balloon filled with CO, and the mixture was stirred for 2 h. IR (CH_2Cl_2, cm^{-1}): 2035, 1972 ν_{CO}. ESI-MS (CH_2Cl_2, positive ion): *m*/*z* 684 $[M - Cl + MeCN]^+$, 643 $[M - Cl - CO]^+$. Although no molecular ion was observed for $[\mathbf{17}]^+$, the fragmentation pattern and peak intensities were distinct from those for **13**. Concentration of the above solution under reduced pressure followed by dilution with hexane (5 mL) resulted in the formation of a white precipitate that was shown (^{31}P NMR) to be exclusively **13**.

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Supporting Information Available: CIF files giving crystallographic data for **11a** (CCDC 776470) and **13** (CCDC 776471). This material is available free of charge via the Internet at http://pubs.acs.org.