ORGANOMETALLICS

Arrested B–H Activation en Route to Installation of a PBP Pincer Ligand on Ruthenium and Osmium

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Supporting Information

ABSTRACT: The reaction of HB(NCH₂PPh₂)₂C₆H₄-1,2 with [MCl₂(PPh₃)₃] (M = Ru, Os) affords the six-coordinate σ -borane complexes [MCl₂(PPh₃){ σ -BH- κ ²-P,P'-HB-(NCH₂PPh₂)₂-C₆H₄}], in which the B–H bond remains intact while coordinated to the metal center. Replacement of the unique phosphine by π -acceptor ligands, e.g., CO and CNC₆H₂Me₃, induces B–H activation followed by spontaneous dehydrochlorination with the formation of the boryl pincer complexes [RuCl(CA)₂{B(NCH₂PPh₂)₂C₆H₄}] (A = O, NC₆H₂Me₃-2,4,6).

INTRODUCTION

Chelate-assisted activation of B–H bonds has proven to be a versatile route for the construction of polydentate metallaboratrane^{1,2} and boryl pincer assemblies (Scheme 1).² Thus, while nonchelating boranes themselves undergo metal-medi-

Scheme 1. Representative Examples of Metallaboratrane and Boryl Pincer Complexes Arising from Chelate-Assisted B–H Activation: (i) $[IrCl(CO)(PPh_3)_2];^{2a}$ (ii) $[IrCl(CO){P(C_6H_4Me-4)_3}_2];^{2b}$ (c) $[Pd(NCMe)_4](BF_4)_2$, $[Bu_4N]Cl^{2e}$



ated B–H activation in many cases,³ prior coordination of a pendant donor can provide kinetic impetus to assist the progress of the reaction. Pincer ligands based on conventional classical donors (O, N, P, S, C) have enjoyed intense study in recent times,⁴ in particular in the field of catalytic applications.⁵ Those involving more electropositive donors, e.g., silicon⁶ or boron,² have been less studied but might offer specific advantages by virtue of the strong *trans* influence and *trans* effect associated with metal boryl, boratrane, and silyl linkages.⁷

The boranes $HB(NCH_2PR_2)_2C_6H_4$ (R = Ph, Cy, ^tBu) described by Yamashita^{2b,c} are effective pro-ligands for the installation of LXL-PBP⁸ boron pincers onto iridium,^{2b} rhodium,^{2c} ruthenium,^{2i,j} cobalt,^{2k} and platinum^{2f} centers. For the majority of group 9 examples simple insertion of the metal into the B-H bond occurs, increasing the valency⁹ of the metal by two units, and while in the ruthenium and platinum examples this is implicit, subsequent loss of the putative hydride in combination with a co-ligand (chloride for platinum, phenyl for ruthenium) returns the metal to its original valency. The intimate mechanism of chelate-assisted B-H activation evokes the possible intermediacy of σ -borane complexes in which three-center, two-electron (3c-2e) B-H-metal interactions occur. The geometry of the iridium complex [IrHCl{B- $(NCH_2P^tBu_2)_2C_6H_4\}^{2c}$ (B-Ir-H = 63(2)°, B-H = 1.89(6) Å) might at first glance point toward some σ -borane compared with boryl hydride character; however this type of Ybipyramidal geometry is increasingly observed for fivecoordinate d⁶ complexes devoid of π -acidic ligands.¹⁰ Eisenstein has computationally investigated the geometric preferences for d^6 -trans-ML₃(PR₃)₂ complexes,¹¹ concluding that when a single π -donor is present (Cl in this case), the angle between the remaining two pseudoequatorial ligands will contract to afford a

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Y-shaped distorted trigonal bipyramidal geometry. A similar situation has been examined in considerable detail, both experimentally and computationally, for the complex [RhHCl- $(BO_2C_2Me_4)(P^iPr_3)_2$] (B-Rh-H = 70.0(8)°, B…H = 2.02(3) Å).¹²

Herein we wish to report the isolation of examples of sixelectron chelated σ -borane complexes (LLL-P(BH)P pincers), which represent intercepted intermediates in the B–H activation process, including rare structural data for an osmium σ -borane complex.^{13,14} These may be converted via π -acidinduced B–H activation to five-electron LXL-PBP pincer complexes.

RESULTS AND DISCUSSION

We have previously described the facile reaction between $[Ru(C_6H_5)Cl(CO)(PPh_3)_2]$ and $Na[HB(mt)_3]$ (mt = methimazol-1-yl) or $HB(NCH_2PPh_2)_2C_6H_4$ to afford, respectively, the metallaboratrane $[Ru(CO)(PPh_3)\{B(mt)_3\}](Ru \rightarrow B)^{8 \ 1a,15}$ or the σ -boryl pincer complex $[RuCl(CO)(PPh_3)\{\kappa^3-B,P,P'-B(NCH_2PPh_2)_2C_6H_4\}]^{2i}$ A similar strategy employing the silane $HSiPh(NCH_2PPh_2)_2C_6H_4$ affords the σ -sily pincer complex $[RuCl(CO)(PPh_3)\{\kappa^3-P,Si,P'-SiPh-(NCH_2PPh_2)_2C_6H_4\}]$ (Scheme 2).⁶

Scheme 2. Chelate-Assisted B–H and Si–H Bond Activation with $[Ru(C_6H_5)Cl(CO)L_2]$ (i) Na $[HB(mt)_3]$;¹ (ii) HB(NCH₂PPh₂)₂C₆H₄;²ⁱ and (iii) HSiPh(NCH₂PPh₂)₂C₆H₄^{6v}



In each case, the presumed mechanism involves (i) initial coordination of a pendant donor, (ii) formation of a σ -B–H–Ru or σ -Si–H–Ru complex, (iii) B–H or Si–H activation, and (iv) reductive elimination of benzene. This mechanistic proposal is supported by the isolation of the complex [RuH(CO)(PPh₃){ κ^3 -H,S,S'-HB(mt)_3] from the reaction of [RuHCl(CO)(PPh₃)₃] with Na[HB(mt)₃], wherein reductive elimination of dihydrogen (cf. benzene) is less favored, although it may be thermally induced (Scheme 3).¹⁶ In a similar manner, the reaction of [RuHCl(PPh₃)₃] with Na[H₂B(mt)₂] affords a stable complex [RuH(PPh₃)₂{ κ^3 -H,S,S'-H₂B(mt)₂}], in which the 3c-2e B–H–Ru bond remains intact.¹⁷

Scheme 3. Synthesis of Metallaboratranes via B–H Activation: (i) $Na[H_2B(mt)_2];^{2a}$ (ii) $Na[HB(mt)_3]^{16}$



We have therefore considered the reaction of HB- $(NCH_2PPh_2)_2C_6H_4$ with substrates that might be less predisposed to B–H activation and/or subsequent loss of the hydrogen atom once transferred to the metal, so as to intercept a putative σ -borane complex intermediate. The complexes $[MCl_2(PPh_3)_3]$ (M = Ru,¹⁸ Os¹⁹) were found to serve this purpose: A clean reaction ensues between each of these and HB(NCH_2PPh_2)_2C_6H_4 to afford complexes of composition $[MCl_2(PPh_3)\{HB(NCH_2PPh_2)_2C_6H_4\}]$ (M = Ru 1, Os 2, Scheme 4) based on elemental microanalytical and accurate mass spectrometric data.

Scheme 4. Synthesis of σ -Borane Pincer Complexes of Ruthenium and Osmium



The gross geometry follows from the ³¹P{¹H} NMR spectra, which each comprise a doublet and triplet resonance integrating for two and one phosphorus environments, respectively, with ${}^{2}J_{PP}$ of the order typical of a meridional $P_{A}P_{B}P_{A}$ arrangement of the $A_{2}B$ spin system nuclei (1: 23; 2: 12 Hz). The data of particular interest, however, relate to the B–H linkage and whether it remains intact, and it must be said that the ¹H NMR data are equivocal. Had B–H activation occurred to afford a *cis*-hydrido-boryl linkage, a high field double triplet resonance would be expected, with the magnitude of the doublet coupling being indicative of whether the hydride ligand resided cis or pseudo-trans to the unique phosphine. In practice, a broad resonance is observed for both (1: $\delta_{\rm H} = -14.04$; 2: $\delta_{\rm H}$ = -13.72), from which in the case of 2 one might discern dt fine structure clouded by a broadening suggestive of interaction with quadrupolar boron nuclei. Notably, the chemical shift of the resonance for 1 is invariant over the temperature range -70to 60 °C, arguing against this reflecting an equilibrium (¹H NMR time scale) between borane and boryl hydride isomers. Inspection of the infrared spectrum of 1 reveals a weak absorption (KBr: 2259 cm⁻¹) suggestive of a B-H-M interaction rather than discrete terminal B-H or M-H absorptions. The complex [RuH(PPh₃)₂{ κ^3 -H₂S,S'-H₂B(mt)₂}] provides a benchmark with ν_{BH} , ν_{BHRu} , and ν_{RuH} absorptions at 2379, 2120, and 1950 cm⁻¹ respectively,¹⁷ while the free ligand has $\nu_{\rm BH} = 2583 \text{ cm}^{-1}$ (KBr, see Supporting Information). For complex 2 the corresponding infrared absorption appears too weak to be unambiguously identified with confidence.

The identities of 1 and 2 were unequivocally established through X-ray crystallographic studies of both as toluene hemisolvates. While the data for 1 (R = 0.089) afforded a less precise structural model than for 2 (R = 0.022), both were isomorphous, and given the comparable covalent radii for the two metals, it is prudent to discuss the more precise model for 2 as summarized in Figure 1.



Figure 1. (a) Molecular geometry of 2 in a crystal of $2 \cdot (C_6H_5Me)_{0.5}$ (70% displacement ellipsoids, aryl H atoms and solvent omitted). Selected bond lengths (Å) and angles (deg): Os1-Cl1 2.4761(6), Os1-Cl2 2.4644(5), Os1-P1 2.4018(6), Os1-P2 2.3884(6), Os1-P3 2.3460(6), Os1-B1 2.107(2), Os1-H1 1.56(3), N1-B1 1.430(3), N2-B1 1.433(3), B1-H1 1.48(3), P1-Os1-P2 155.19(2), Cl1-Os1-Cl2 82.46(2), P1-Os1-B1 77.77(7), P2-Os1-B1 77.63(7), Os1-H1-B1 87.8(2). (b) Inset shows view along the P1···P2 vector illustrating the impact of secondary interligand interactions upon σborane bonding.

The functionality of interest is the 3c-2e B–H–Os interaction, and while this is clearly established, the poor precision associated with modeling hydrogen atom positions in the vicinity of heavy metals (2: $\mu = 2.93 \text{ mm}^{-1}$), coupled with the constraints imposed by chelation, call for caution in overinterpreting geometrical parameters. Furthermore, incipient dihydrogen bonding between the borane hydrogen (δ^-) and an *ortho*-hydrogen atom (δ^+) of one phenyl group (H1... H721 2.38 Å, $2r_{vdW}(H) = 2.40$ Å) further discombobulates

analysis. Such interactions have been noted for arylphosphines coordinated to conventional ruthenium hydride ligands.^{16,20}

The only structural data available²¹ for another osmium σ borane adduct relate to the metallacyclic complex [OsH{HB-(C₈H₁₄)CH₂PMe₂}(PMe₃)₃] (3, Chart 1) obtained by Baker





and Marder from the reaction of $[OsH(CH_2PMe_2)(PMe_3)_3]$ with 9-borabicyclononane (H-BBN).¹³ Again, as with 2, the B-H–Os interaction is part of a chelate assembly with B-H =1.43(3), Os-H = 1.84(3), and Os-B = 3.005 Å and B-H-Os= $133(2)^{\circ}$, compared with 2, which has B1-H1 = 1.48(3), Os1-H1 = 1.56(3), and Os1-B1 = 2.107 Å and B1-H1-Os1 = $87.8(2)^{\circ}$. Thus, it would appear that the most striking differences between the two complexes are that while 3 involves a five-membered OsHBCP metallacycle compared with the sixmembered rings of the $OsHB(NCP)_2$ metallabicycle in 2, it is the former that displays a much larger Os-H-B angle with little if any direct Os–B interaction. In contrast, the boron in 2 closely approaches the osmium, with the Os1...B1 separation being shorter than observed for the osmaboratrane [Os(CO)- $(PPh_3){B(mt)_3}$ (2.172 Å, four-coordinate boron)¹⁴ and indeed more comparable to Os-B separations between octahedral osmium and three-coordinate boron, which to date²¹ span the range 2.05-2.26 Å.²² Furthermore, the geometry at B1 is marginally pyramidalized with a B(N,N',H)angle sum of 346.2° and B(N,N',Os) angle sum of 357.7° in the opposite sense. Notably, this pyramidalization brings the boron close to Cl1, and while B1, bearing two positively mesomeric amino groups, would not be expected to be especially electrophilic, the B1…Cl1 separation of 2.661 Å is well within the sum of the van der Waals radii $(r_{vdW}(Cl) + r_{vdW}(B) = 3.67)$ Å).^{21,23} Three-center, two-electron B–H–metal interactions are remarkably variable in terms of the B-H-M angle and M… B separation. While few data are available for (noncluster) osmium complexes, many have been recorded for B-H-Ru interactions, 21,24 with B–H–Ru angles spanning the wide range 84-155°, loosely correlating (a geometric corollary) with Ru… B separations in the range 2.12-2.94 Å. Correlation between Ru…B and B-H distances is not convincingly evident, but this is to be expected given the low precision of the H-position modeling. The short Os1…B1 distance coupled with the acute Os-H1-B1 angle therefore places 2 at the extreme "side-on" end of the spectrum of 3c-2e B-H-metal interaction such that little further distortion would be required to sever the B-H bond with formation of discrete boryl and hydrido ligands (vide *infra*). Chart 2 depicts three cases 2^{25-27} along this continuum, with the examples chosen all sharing the common "CpMn- $(CO)_2$ " fragment to emphasize the subtle balance.

Chart 2. Bonding Continuum for B–H–M Interactions with Selected Examples: (a) 3c-2e Pseudoagostic;²⁵ (b) 3c-2e σ -Borane;²⁶ (c) 3c-4e Boryl-Hydrido (i.e., "Oxidative" Addition)²⁷



A further useful comparison between the compounds 2 and 3 relates to the *trans* influence of the borane ligand. It is to be expected that a B–H "ligand" coordinating in a 3c-2e manner would have a lesser *trans* influence than a conventional 2c-2e metal–ligand bond. In the case of 3 (and its ruthenium analogue) it was noted that the PMe₃ ligand *trans* to the borane had an Os–P bond length (2.2657(8) Å) somewhat contracted relative to the two *cis* PMe₃ ligands (2.3375(8), 2.3298(8) Å). Trimethylphosphine is essentially a pure σ -donor ligand, while in the case of 2 chloride is also a potential π -donor capable of supplementing reduced electron density at the metal center, resulting from a weak-field *trans* ligand.

This is indeed what is observed for 2 wherein Os1–Cl2 (2.4644(5) Å) is significantly (23 esd) contracted relative to Os1–Cl1 (2.4761(6) Å) despite being subjected to more steric congestion and a set of three *ortho*-aryl C–H…Cl intermediate²⁸ intraligand hydrogen-bonding interactions (average CH…Cl2: 2.62 Å, r_{vdW} (Cl) + r_{vdW} (H) = 2.95 Å), which would be expected to elongate the Os–Cl2 bond. The steric features of 1 are presented in a space-filling depiction in Figure 2, from which it is also apparent that two π -stacking interactions



Figure 2. Space-filling representation for **1** depicting steric protection afforded to the N₂BHRu linkage (N = dark blue, H = gray, B = pink, π -stacking interactions indicated in yellow and pale blue).

(yellow and pale blue) between phenyl groups of the unique phosphine and those of the pincer ligand contribute to a favorable manifold of intramolecular interactions accounting for the stability of the complex, which might be lost were B–H activation to ensue.

Notably, ¹H NMR data for the complex 3 comprise a single broad resonance at $\delta_{\rm H} = -10.78$ accounting for *both* the terminal Os-H and B-H groups.¹³ This exchange, which is arrested at -80 °C, was interpreted equivocally as involving either dissociation of the borane, leaving behind two terminal Os-H groups, or, alternatively, equilibration via a symmetrical $Os(\mu-H)_2B$ arrangement. Given that this work predated the large number of authenticated examples of metal-boron dative bonding^{15,29} for late transition metals, perhaps one might now also consider a third possibility involving B-H activation to afford the metallaboratranes $[Os(\sigma-H_2)(PMe_3)_3\{\kappa^2-B_{\ell}P-(BBN) CH_2PMe_2)](Os \rightarrow B)^8$ or $[OsH_2(PMe_3)_3\{\kappa^2-B,P-(BBN)-CH_2PMe_2)](Os\rightarrow B)^6$ depending on whether equilibration might be via a dihydrogen or cis-dihydride complex. Such an interpretation would be consistent with the lower activation barrier observed for the osmium complex compared with the ruthenium analogue, given that B-H and C-H activation processes are especially facile for 5d versus 4d metals.

The formation of 1 is complete after 22 h at room temperature. However, ${}^{31}P\{{}^{1}H\}$ and ${}^{1}H$ NMR spectra measured during the course of the reaction indicate the formation and disappearance of an intermediate formulated as shown in Scheme 4. Although this species could not be isolated due to its evolution into 1, the spectroscopic data are consistent with the formation of a positional isomer. Specifically, the highfield ¹H NMR spectrum includes a signal at $\delta_{\rm H} = -7.21$, the broadness of which suggests retention of the B-H connectivity. This peak was sufficiently thermally decoupled from the quadrupolar boron nucleus at -45 °C to observe phosphorusproton coupling, giving a broad doublet with a ${}^{2}J_{PH}$ of approximately 45 Hz, although coupling to the second ³¹P environment was not resolved. The large doublet coupling suggests a *trans* arrangement of the triphenylphosphine and σ borane groups. The ³¹P NMR spectrum further supports this stereochemistry, showing characteristic resonances for an AB₂ spin system $({}^{2}J_{AB} = 25 \text{ Hz})$ with a slightly broadened triplet resonance. Thus, while the " $B(NCH_2PPh_2)_2C_6H_4$ " pincer is well disposed toward meridional coordination by virtue of the trigonal boron donor, the corresponding borane presumably offers more flexibility in the geometry of the B-H-M linkage, possibly allowing the albeit strained occupation of a pseudofacial set of coordination sites.

The formation of 1 and 2 involves liberation of two equivalents of PPh₃, and the ${}^{31}P{}^{1}H$ NMR spectra of both crude reaction mixtures include a peak due to free PPh₃. Given the sharpness of this resonance, we may conclude that phosphine dissociation from 1 and 2 is not apparent on this NMR time scale. Nevertheless, on the chemical time scale it is to be expected that steric pressures may well labilize the phosphine, and this is suggested in the case of 1 by the slow (18 h, 60 °C) reaction with carbon monoxide and the more rapid reaction with CNC₆H₂Me₃-2,4,6 (66 h, 25 °C). The reaction of 1 with CO results in the formation of a compound that is devoid of any resonance in the ¹H NMR attributable to either a B-H or Ru-H group. Infrared and NMR spectroscopic data are consistent with the formation of the boryl pincer complex $[RuCl(CO)_2 \{B(NCH_2PPh_2)_2C_6H_4\}]$ (4), which has been previously observed to arise for the reversible reaction of

[RuCl(CO)(PPh₃){B(NCH₂PPh₂)₂C₆H₄}] with carbon monoxide.²ⁱ We attribute the lack of reversibility in the present case to sequestering of liberated PPh₃ by eliminated HCl. A similar reaction with CNC₆H₂Me₃-2,4,6 is complete within 3 days at room temperature to afford the *cis*-bis(isonitrile) complex [RuCl(CNC₆H₂Me₃-2,4,6)₂{B(NCH₂PPh₂)₂C₆H₄}] (**5**), the ¹H NMR spectrum of which is again devoid of high-field resonances attributable to B–H or Ru–H groups. The appearance of two $\nu_{\rm CN}$ absorbances in the IR spectrum (CH₂Cl₂: 2104, 2061 cm⁻¹) indicates a mutual *cis* disposition of the isonitriles. This inference is supported by two resonances ($\delta_{\rm C} = 168.4, 171.4$) in the ¹³C{¹H} NMR spectrum, which also includes a virtual triple resonance at $\delta_{\rm C} = 51.4$ ($J_{\rm PC} = 23$ Hz) consistent with the *trans* arrangement of the PCH₂ groups.

The ¹¹B{¹H} NMR spectrum of **5** comprises a single resonance at $\delta_{\rm B} = 57.3$ shifted some 8 ppm downfield from that of **1** ($\delta_{\rm B} = 49.2$) and in a region typical of three-coordinate boron in a σ -boryl ligand. It would therefore appear that $\delta_{\rm B}$ is not an entirely definitive parameter for distinguishing σ -borane and σ -boryl coordination modes. The characterization of **5** therefore included a crystallographic study, the results of which are summarized in Figure 3 and confirm the formation of the σ -



Figure 3. Molecular structure of **5** in a crystal (70% displacement ellipsoids, aryl H atoms omitted, aryl groups simplified). Selected bond lengths (Å) and angles (deg): Ru1-Cl1 2.4924(18), Ru1-P1 2.3307(18), Ru1-P2 2.3298(18), Ru1-B1 2.062(8), N1-B1 1.456(8), N2-B1 1.441(9), C60-Ru1 2.048(8), C50-Ru1 1.876(8), C60-Ru1-C50 93.5(3), C60-Ru1-P1 104.9(2), C60-Ru1-P2 101.6(2), P1-Ru1-P2 153.51(7), P1-Ru1-B1 76.2(2), P2-Ru1-B1 77.3(2).

boryl pincer framework including a conventional 2c-2e Ru1– B1 bond length of 2.062(8) Å. The only structural data for a diazaboryl complex of ruthenium are from the related pincer complex [RuCl(CO)(PPh₃){B(NCH₂PPh₂)₂C₆H₄}]²ⁱ and the recently reported hydrido complex [RuH(CO)₂{B-(NCH₂P^tBu₂)₂C₆H₄}].^{2j} The crystal structure of the former comprises two independent molecules with Ru–B bond lengths of 2.051(15) and 2.088(15) Å,²ⁱ while the latter has an intermediate Ru–B bond length of 2.072(8) Å.^{2j} More structural data are available for diazaboryl complexes of osmium,^{22,30} which span the range 2.055–2.082 Å for Os–B separations with the exception of the anomalous complex [Os{B(NHC₆H₄Me-4)₂}(C≡CPh)(CO)₂(PⁱPr₃)₂],^{30a} for which an unusually long Os–B bond (2.256(4) Å) was observed and suggested to arise from the *trans* coordination of a π-acid (CO). The phenomenon of Os–B bond lengthening by *trans* π -acid ligands had been previously demonstrated for dioxaboryl ligands, e.g., $[OsI(BO_2C_6H_4)(CO)_2(PPh_3)_2]$ (*cct* isomer 2.145(5); *ttt* isomer 2.090(3) Å)^{22g} and for $[OsCI-(BO_2C_2H_4)(CO)_n(PPh_3)_2]$ (n = 1, 2.043(4); n = 2, 2.179(7)Å).^{22a} Reflecting perhaps the constraints of chelation, the ruthenium is slightly displaced from the N1–B1–N2–C4–C3 plane, and while the angle sum at B1 is close to ideal (358°), those for N1 and N2 each reveal a slight pyramidalization (352°).

The geometry of 5 affords an opportunity to assess the relative *trans* influences of chloride versus a σ -boryl upon two otherwise identical π -acidic CNC₆H₂Me₃ ligands, and the potency of the σ -boryl ligand in this respect is patently clear with the Ru1-C60 bond length (2.048(8) Å) being some 33 esd longer than that for Ru1-C50 (1.876(8) Å). A similar differential *trans* influence on the part of more conventional σ boryl ligands has been demonstrated in the complexes cis, trans- $[Os(BO_2C_6H_4)(CO)(NCMe)_2(PPh_3)_2]^+$ for σ -donor nitri les_{1}^{22c} [Os(BO₂C₆H₄)(S₂CNEt₂)(CO)(PPh₃)₂] for the sulfur $\sigma + \pi$ donors of a dithiocarbamate chelate,^{22c} and [Os-(BO₂C₆H₄)X(CO)₂(PPh₃)₂] (X = C₆H₄Me-2,^{22e} I^{22g}) for σ donor/ π -acid CO ligands. Against these disparate co-ligand sets, the recurring feature is the demonstration in each case of a potent *trans* influence for σ -boryl ligands. Lin and Marder have computationally investigated the origin of the trans effect of boryl ligands using the Pt-Cl bond length of trans-[PtXCl- $(PMe_3)_2$ as a reporter, leading to the conclusion that this far exceeds that of σ -organyls and hydride ligands and that diazaboryls are among the strongest *trans* influential σ -boryls (exceeded by BH₂ and BMe₂).⁷

The facile conversion of the σ -borane complex 1 into the σ boryl complexes 4 and 5 invites mechanistic conjecture, given that no intermediates were spectroscopically observed.⁷ Spectroscopic data for 1 neither suggest nor exclude the operation of a B-H activation tautomerism to afford sevencoordinated 6 (Scheme 5), from which phosphine might more easily be liberated, given the potent (pseudo)trans effect of the resulting σ -boryl ligand. As noted above, this does not appear to operate on the ${}^{31}P$ NMR time scale. In general, π -acceptor ligands are expected to make C-H or B-H activation processes less favorable, as these ligands are less able to stabilize an increase in metal valency or oxidation state. Coordination of these ligands would, however, be expected to increase the acidity of any resulting metal hydride by stabilizing the conjugate base through retrodonation. Late transition metal hydride ligands are typically protic in nature, while B-H bonds show hydridic character; that is, the proton is most likely lost via the metal, rather than directly from boron. We are therefore inclined to suspect that upon substitution of the unique phosphine by CO, the resulting complex $[RuHCl_2(CO){B (NCH_2PPh_2)_2C_6H_4$] (7a) is prone to spontaneous dehydrochlorination, possibly assisted by the weak base PPh₃. The resulting coordinatively unsaturated complex [RuCl(CO){B- $(NCH_2PPh_2)_2C_6H_4$ (8) would then rapidly capture extraneous CO to afford 4, a reaction implicit in the previously reported conversion of $[RuCl(CO)(PPh_3){B-}$ $(NCH_2PPh_2)_2C_6H_4$] to 4 upon exposure to CO.²ⁱ A similar sequence would be expected to operate in the conversion of 1 to 5, although in that case, while isonitriles are typically more nucleophilic than CO, their reduced π -acidity would make dehydrochlorination of $[RuHCl_2(CNC_6H_2Me_3-2,4,6){B-}$ $(NCH_2PPh_2)_2C_6H_4$] (7b) less facile. We consider B-H/M-

Scheme 5. Mechanistic Conjecture Concerning π -Acid (CA)-Activated σ -Borane/ σ -Boryl Interconversion



Cl σ -metathesis pathways unlikely due to the *anti*-periplanar H–B–M–Cl geometry of **1** and **2**.

CONCLUSIONS

The proposed intermediacy of σ -borane complexes in the installation of Yamashita's boryl pincer ligands "B- $(NCH_2PR_2)_2C_6H_4$ " (R = Ph, Cy, ^tBu) has been substantiated by the isolation of the σ -borane complexes [MCl₂(PPh₃){HB- $(NCH_2PPh_2)_2C_6H_4$] (M = Ru 1, Os 2). Furthermore, the subsequent conversion to boryl pincer ligands via chelateassisted B-H activation could be shown to be induced by varying the nature of the co-ligands, specifically the introduction of π -acceptor ligands. It seems most likely that these processes are induced not by favoring the B-H cleavage reaction itself, but rather by increasing the Brønstead acidity of the resulting metal hydride, favoring subsequent and spontaneous, albeit slow, reductive dehydrohalogenation of the metal center. A recent report by Peters^{2k} documents a twostep process (Scheme 6b) that is effectively the reverse of the borane-boryl interconversion, i.e., addition of dihydrogen across the 2c-2e B-Co bond of a cobalt complex of Yamashita's pincer.

Thus, $[Co(N_2){B(NCH_2P'Bu_2)_2C_6H_4}]$ was shown to react with an amine borane Me₂HNBH₃ to afford a borane pincer complex $[Co(BH_4){\sigma-BH-\kappa^2-P,P'-HB(NCH_2P'Bu_2)_2C_6H_4}]$. The borane pincer is clearly related to that found in 1 and 2 with the exception that one cobalt of the each positionally Scheme 6. Hydrogen Umpolung: Migration of Hydrogen from Metals to Boron across (a) $M \rightarrow BR_{3}$;³¹ (b) $M - BR_{2}$;^{2k} and (c) $M = BR^{33}$ Bonds



disordered Co-H site approaches coplanarity with the benzodiazaborolyl unit compared with 1 and 2, wherein the metal is significantly displaced from the plane.

We have previously shown that a hydride ligand may migrate from a late transition metal to the boron of a metallaboratrane,^{31,32} while Sabo-Etienne has reported the reversible addition of dihydrogen across the Ru=B multiple bond of a ruthenium borylene complex (Scheme 6).³³ In the context of metal-mediated dehydrocoupling catalysis, the ability of a hydrogen atom to change its protic/hydridic nature ("umpolung") by migrating between a metal (BM–H^{δ +}) and boron (M–BH^{δ -}) provides an intriguing and potentially useful dimension to the chemistry of metal–boron linkages.

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. NMR spectra were recorded at 25 °C on a Varian Mercury 300 (¹H at 300.1 MHz, ³¹P at 121.5 MHz) and Varian Inova 300 (¹H at 299.9 MHz, ¹³C at 75.42 MHz, ³¹P at 121.4 MHz, ¹¹B at 96.23 MHz) spectrometers. The chemical shifts (δ) for ¹H and ¹³C spectra are given in ppm relative to residual signals of the solvent, ¹¹B and ³¹P relative to external references (BF₃OEt₂, H₃PO₄). Virtual triplet resonances are indicated by t^v. Low- and high-resolution mass spectra were obtained on a ZAB-SEQ4F spectrometer by positive ion ESI techniques using an acetonitrile matrix by the mass spectrometry service of the Australian National University. Assignments were made relative to M, where M is the molecular cation. Assignments were verified by simulation of isotopic composition for both low- and highresolution levels. 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 $[RuCl_2(PPh_3)_2]$,¹⁸ $[OsCl_2(PPh_3)_3]$,¹⁹ and $HB(NCH_2PPh_2)_2C_6H_4^{2b}$ were prepared according to published procedures. The complex $[Ru\{B(NCH_2PPh_2)_2C_6H_4\}Cl(CO)_2]$ (4) has been reported previously,²ⁱ having been obtained via an alternative route to that described below. Other reagents were used as received from commercial suppliers.

Synthesis of $[Ru{\kappa^3-HB(NCH_2PPh_2)_2C_6H_4]Cl_2(PPh_3)]$ (1). A solution of [RuCl₂(PPh₃)₃]¹⁸ (1.000 g, 1.04 mmol) and HB- $(NCH_2PPh_2)_2C_6H_4$ (0.536 g, 1.04 mmol) in benzene (50 mL) was stirred for 22 h. The solvent was concentrated under reduced pressure to approximately 10 mL, and 15 mL of n-hexane was then added to afford an orange precipitate. The supernatant was removed via cannula filtration, and the precipitate washed with *n*-hexane $(2 \times 15 \text{ mL})$ and dried in vacuo. Yield: 0.887 g (90%). Orange crystals of the toluene hemisolvate $1 \cdot (C_7 H_8)_{0.5}$ suitable for elemental and crystallograhic analysis were obtained by slow diffusion of *n*-hexane into a toluene solution of 1. IR (KBr, cm⁻¹): 3047 ν_{aromCH} ; 2921, 2846 ν_{CH} ; 2259 $\nu_{\rm BHRu}$, 1478, 1435 $\nu_{\rm aromCC}$. NMR (C₆D₆, 298 K) ¹H: $\delta_{\rm H}$ –14.04 (br, 1H, RuHB, hhw = 0.2 ppm), 4.31 (m, 4H, PCH₂), 6.45-8.72 (m, 39 H, N₂C₆H₄ and C₆H₅).¹¹H{¹¹B}: $\delta_{\rm H}$ -14.30 (dt, ²J_{PH} = 19.2 d, 13.2 t). ¹³C{¹H}: 54.9 (t^v, PCH₂, ^{1,3} $J_{PC} = 21$), 111.2, 120.3 [C²⁻⁵(N₂C₆H₄)], 129.3, 131.2 (C_6H_5), 131.6 (t^v , C_6H_5 , $J_{PC} = 5$ Hz), 131.9, 132.2, 132.5, 135.3 (C₆H₅), 135.6 (d, C₆H₅, $J_{PC} = 9$ Hz), 135.9 (C₆H₅), 136.5 (t^v, C₆H₅, $J_{PC} = 6$), 140.0 (t^v, C₆H₅, $^{13}J_{PC} = 17$), 144.7 [t^v, C^{1,6}(C₆H₄N₂), ${}^{3,4}J_{PC} = 7 \text{ Hz}$] (some aryl resonance assignments equivocal or obscured due to C₆D₆ overlap). ¹¹B{¹H}: $\delta_{\rm B}$ 49.2 {¹H}: $\delta_{\rm P}$ 32.1 (d, PPh₂, ²J_{PP} = 22 Hz), 49.2 (t, PPh₃, ${}^{2}J_{PP}$ = 23 Hz). ESI-MS (+ve ion, MeCN): m/z913.6 [M - Cl]⁺. Accurate mass: found 949.1307 [M + H]⁺, calcd for C₅₀H₄₅¹¹B³⁵Cl₂¹⁴N₂³¹P₃¹⁰²Ru 949.1309. Anal. Found: C, 64.37; H, 5.00; N, 3.08. Calcd for C₅₀H₄₄BCl₂N₂RuP₃.0.5(C₇H₈): C, 64.60; H, 4.86; N, 2.82 (the presence of 0.5 equiv of toluene was crystallographically confirmed but due to a high degree of disorder was eliminated employing the PLATON SQUEEZE protocol). Crystal data for $C_{50}H_{44}BCl_2N_2P_3Ru$: $M_r = 948.62$, monoclinic, $P2_1/c$, a =12.4171(8) Å, b = 20.3980(15) Å, c = 18.7584(13) Å, $\beta = 91.922(4)^{\circ}$, V = 4748.5(6) Å³, Z = 4, $D_x = 1.327$ Mg m⁻³, μ (Mo K α) = 0.58 mm⁻¹ T = 200(2) K, orange block, $0.09 \times 0.08 \times 0.06$ mm, 6213 independent reflections. F^2 refinement, R = 0.089, wR = 0.014 for 3786 reflections ($I > 2\sigma(I)$, $2\theta_{max} = 45^{\circ}$), 535 parameters, CCDC 982299.

Intermediate Complex. In the above reaction, consumption of the starting materials occurred within 15 min, with a second complex observed in the reaction mixture that gradually converted to the final product. NMR (C_7D_8 , 298 K) ¹H: δ_H –7.21 (br, 1H, RuH), 4.20 (m, 4H, PCH₂N, assignment equivocal due to overlap with final product, aromatic peaks could not be unambiguously assigned due to impurities). ³¹P{¹H}: δ_P 26.5 (t, PPh₃, ²J_{PP} = 24), 34.5 (d, PPh₂, ²J_{PP} = 25 Hz).

Synthesis of $[Os{\kappa^3-HB(NCH_2PPh_2)_2C_6H_4}CI_2(PPh_3)]$ (2). A solution of $[OsCl_2(PPh_3)_3]^{19}$ (0.100 g, 0.0954 mmol) and HB- $(NCH_2PPh_2)_2C_6H_4$ (0.049 g, 0.0953 mmol) in benzene (5 mL) was stirred for 30 min. The solvent was removed under reduced pressure, and the resulting dark brown-black residue was washed with ethanol (7 mL) and n-hexane (5 mL) and dried in vacuo. Brown crystals of the toluene hemisolvate 2. (C7H8)0.5 suitable for elemental and crystallograhic analysis were obtained by slow diffusion of n-hexane into a toluene solution of 2. Yield: 0.092 g (93%). IR (KBr, $\rm cm^{-1})$: 3051 $\nu_{\rm arom CH}$; 2954, 2924, 2854 $\nu_{\rm CH}$; 1463, 1436 $\nu_{\rm arom CC}.$ NMR (C_6D_6, 298 K) ¹H: $\delta_{\rm H}$ –13.72 (m, 1H, OsH), 4.31 (m, 4H, PCH₂), 6.46–8.68 (m, 39H, N₂C₆H₄ and C₆H₅). ¹³C{¹H}: 55.3 (t^v, PCH₂, ^{1,3} J_{PC} = 24), 111.2, 119.9 $[C^{2-5}(N_2C_6H_4)]$, 130.7, 131.2 (C_6H_5) , 131.3 (d, C_6H_5 , $J_{PC} = 3$ Hz), 132.1 (d, C_6H_5 , $J_{PC} = 9$), 135.0 (d, C_6H_5 , $J_{PC} = 9$), 136.0 (t^v, C_6H_5 , $J_{PC} = 5$), 140.0 [t^v, $C^1(C_6H_5)$, ${}^{1,3}J_{PC} = 21$ Hz], 144.2 $[C^{1,6}(C_6H_4N_2)]$ (some aromatic peaks obscured due to C_6D_6 overlap). ¹¹B{¹H}: δ_B 53.2. ³¹P{¹H}: δ_P 0.3 (d, PPh₂, ²J_{PP} = 12), 7.4 (t, PPh₃, ${}^{2}J_{\text{PP}} = 12$ Hz). ESI-MS (+ve ion, MeCN): m/z 1077.7 [M + K]⁺, 1061.5 $[M + Na]^+$, 1003.6 $[M - Cl]^+$, 967.5 $[M - 2Cl]^+$. Accurate mass: found 1061.1697 $[M + Na]^+$, calcd for $C_{50}H_{44}^{-11}B^{35}Cl_2^{-14}N_2^{-23}Na^{31}P_3^{-192}Os$ 1061.1700. Anal. Found: C, 59.71; H, 4.38; N, 2.20. Calcd for C₅₀H₄₄BCl₂N₂OsP₃·0.5(C₇H₈): C, 59.27;

H, 4.46; N, 2.58 (the presence of 0.5 equiv of toluene was crystallographically confirmed). Crystal data for $C_{50}H_{44}BCl_2N_2OsP_3.0.5(C_7H_8)$: $M_r = 1083.82$, monoclinic, $P2_1/c$, a = 12.4233(1) Å, b = 20.3953(2) Å, c = 18.8159(2) Å, $\beta = 92.0176(6)^\circ$, V = 4764.56(8) Å³, Z = 4, $D_x = 1.511$ Mg m⁻³, μ (Mo K α) = 2.93 mm⁻¹, T = 200(2) K, brown block, 0.31 × 0.18 × 0.17 mm, 10 913 independent reflections. F^2 refinement, R = 0.022, wR = 0.051 for 9626 reflections ($I > 2\sigma(I)$, $2\theta_{max} = 55^\circ$), 598 parameters, CCDC 982298.

Synthesis of $[\operatorname{Ru}\{B(\operatorname{NCH}_2\operatorname{PPh}_2)_2\operatorname{C}_6\operatorname{H}_4\}\operatorname{Cl}(\operatorname{CO}_2)]$ (4). In a J. Young NMR tube, a sample of $[\operatorname{Ru}\{\kappa^3 \operatorname{-HB}(\operatorname{NCH}_2\operatorname{PPh}_2)_2\operatorname{C}_6\operatorname{H}_4\}\operatorname{Cl}_2(\operatorname{PPh}_3)]$ (1) in $\operatorname{C}_6\operatorname{D}_6$ under an atmosphere of argon was frozen using dry ice/ ethanol. The atmosphere in the tube was then evacuated and replaced with carbon monoxide (1 atm, three times), and the solvent was allowed warm to ambient temperature. The mixture was then was heated to 60 °C for 18 h and then analyzed by NMR spectroscopy. The solvent was then removed and the residue dissolved in dichloromethane to obtain IR data. Both NMR and infrared data for the resulting product were consistent with the formation of the previously reported complex $[\operatorname{Ru}\{B(\operatorname{NCH}_2\operatorname{PPh}_2)_2\operatorname{C}_6\operatorname{H}_4\}\operatorname{Cl}(\operatorname{CO}_2)_2]$ (4).² IR: CH₂Cl₂: 2035, 1972 cm⁻¹; KBr: 2027, 1967 cm⁻¹. NMR (C₆D₆, 25 °C) ¹H: $\delta_{\rm H}$ 4.27 (d t^v, 2 H, PP'CH_B, ^{2,4}J_{PB} = 2.7, ²J_{AB} = 12.3), 4.61 (d t^v, 2 H, PP'CH_A, ^{2,4}J_{PA} = 3.8, ²J_{AB} = 12.3), 6.88–7.19, 7.38, 7.96 (m, 24 H, PC₆H₅ and N₂C₆H₄). ³¹P{¹H}: $\delta_{\rm P}$ = 57.91 (s).

Synthesis of [Ru{B(NCH₂PPh₂)₂C₆H₄}Cl(CNC₆H₂Me₃-2,4,6)₂] (5). A solution of $[Ru{\kappa^3-HB(NCH_2PPh_2)_2C_6H_4]Cl_2(PPh_3)]$ (1: 0.100 g, 0.105 mmol) and mesityl isocyanide (0.032 g, 0.22 mmol) in THF (10 mL) was stirred for 66 h. The solvent was removed under reduced pressure. The residue was redissolved in THF (2 mL) and then diluted with n-hexane (5 mL). The supernatant was separated from the precipitate via cannula filtration, and the filtrate was freed of volatiles under reduced pressure. The resulting residue was washed with *n*-hexane (5 + 2 mL) and then diethyl ether (5 + 2 + 2 mL) to give the product as a colorless solid. Despite this extensive washing, ¹H and ${}^{13}C[{}^{1}H]$ (but not ${}^{31}P{}^{1}H$) NMR spectra consistently revealed the presence of trace impurities, which we attribute to isonitrile polymerization (see Supporting Information). Accordingly, satisfactory elemental microanalytical data were not obtained. X-ray quality crystals were obtained by slow evaporation of a DCM/n-hexane solution of the product. Yield: 0.033 g (33%). IR (KBr, cm⁻¹): 3047 ν_{aromCH} ; 2918, 2842 $\nu_{\rm CH}$; 2109, 2073 $\nu_{\rm CN}$; 1475, 1434 $\nu_{\rm aromCC}$. IR (DCM, cm⁻¹): 2104, 2061 $\nu_{\rm CN}$. NMR (CDCl₃, 298 K) ¹H: $\delta_{\rm H}$ 1.47 (s, 6H, CH₃), 2.08 (s, 3H, CH₃), 2.32 (s, 3H, CH₃), 2.42 (s, 6H, CH₃), 4.42 (d.t^v, 2H, PCH_2 , ${}^2J_{HH} = 12$, ${}^{2,4}J_{PH} = 2$), 4.69 (d t^v, 2H, PCH_2 , ${}^2J_{HH} = 12$, ${}^{2,4}J_{PH} = 12$ 4 Hz), 6.39 (s, 2H, C_6H_2), 6.76–8.05 (m, 26H, $N_2C_6H_4$, C_6H_2 and PC_6H_5). ¹³C{¹H}: δ 18.2, 19.4 (*o*-MesCH₃), 21.0, 21.3 (*p*-MesCH₃), 51.4 (t^v, PCH₂, ${}^{1,3}J_{PC} = 23$), 109.0, 117.9 [C²⁻⁵(N₂C₆H₄)], 127.3 (C_6H_5) , 127.8 $(t^v, C_6H_5, J_{PC} = 5)$, 128.2 $(t^v, C_6H_5, J_{PC} = 5)$, 128.3, 128.7, 130.1 (C_6H_5), 130.6 (t^v , C_6H_5 , $J_{PC} = 5$ Hz), 132.9, 134.5, 134.6, 134.7 (C₆H₅), 134.9 (t^v, C₆H₅), $J_{PC} = 6$ Hz), 137.9 (C₆H₅), 139.6 [t^v, C¹(C₆H₅), 134.9 (t^v, C₆H₅), $J_{PC} = 6$ Hz), 137.9 (C₆H₅), 139.6 [t^v, C¹(C₆H₅), ^{1,3} $J_{PC} = 19$ Hz], 141.4 [t^v, C^{1,6}(N₂C₆H₄), ^{3,4} $J_{PC} = 8$], 168.4 (RuC \equiv N), 171.4 (t, RuC \equiv N, ² $J_{PC} = 14$ Hz). ¹¹B^{{1}H}: δ_{B} 57.3. ³¹P{¹H}: $\delta_{\rm P}$ 61.2. ESI-MS (+ve ion, MeCN): m/z 945.4 [M - Cl + $MeCN^{+}$, 905.5 $[M - Cl^{+}$, 760.3 $[M - Cl - CNC_{6}H_{2}Me_{3}]^{+}$. Accurate mass: found 905.2648 [M - Cl]⁺, calcd for C₅₂H₅₀¹¹B¹⁴N₄³¹P₂¹⁰²Ru 905.2647. Crystal data for C₅₂H₅₀BClN₄P₂Ru: $M_{\rm r}$ = 940.28, triclinic, P1 (No. 2), a = 11.2613(4) Å, b = 11.7881(4) Å, $c = 20.5180(8), \ \alpha = 100.1449(16)^{\circ}, \ \beta = 95.749(2)^{\circ}, \ \gamma =$ 118.1335(17)°, V = 2311.12(15) Å³, Z = 2, $D_x = 1.351$ Mg m⁻³, μ (Mo K α) = 0.51 mm⁻¹, T = 200(2) K, colorless prism, 0.18 × 0.07 × 0.04 mm, 8093 independent reflections. F^2 refinement, R = 0.075, wR = 0.010 for 3924 reflections ($I > 2\sigma(I)$, $2\theta_{max} = 50^{\circ}$), 550 parameters, CCDC 982300.

ASSOCIATED CONTENT

S Supporting Information

Crystallographic data for 1 (CCDC 982299), $2 \cdot (C_7 H_8)_{0.5}$ (CCDC 982298), and 5 (CCDC 982300) in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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(10) In contrast to the trigonal bipyramidal geometry, which is preferred for d^8 -ML₅ complexes, the corresponding singlet d^6 -ML₅ system is prone to a Jahn–Teller distortion away from the idealized tbp geometry, for a which an electronic degeneracy (d_{xy} compared with $d_{x_2-y_2}$) would exist. For complexes of the form *trans*-ML₃(PR₃)₂ some relaxation of this requirement might be expected for a heteroleptic ML₃ equaltorial ligand set.

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