Facile Insertion of Rh and Ir into a Boron−Phenyl Bond, Leading to Boryl/Bis(phosphine) PBP Pincer Complexes

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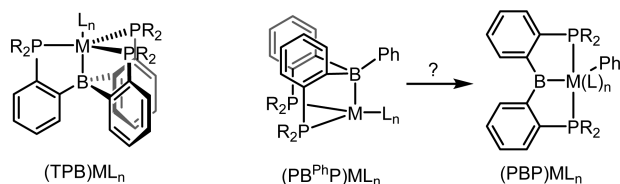[†]Department of Chemistry, Texas A&M University, College Station, Texas 77842, United States
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Ⓢ *Supporting Information*

ABSTRACT: The unexpectedly facile insertion of Rh or Ir into a B−Ph bond (reversible for Rh) converts a borane/bis(phosphine) precursor into a boryl/bis-(phosphine) PBP pincer ligand. Interconversions between the boryl/borane/borate central functionality are demonstrated in reactions with dihydrogen.

Polydentate ligands combining a central boron-based moiety with two or three flanking neutral donors have emerged over the past decade as some of the most versatile frameworks for studies of transition metal reactivity. Much attention has been devoted to complexes with a central borane unit as a Z-type ligand (Figure 1a).[1,2] These molecules raised important

(a) Z-type borane complexes and possible boryl pincer formation

(TPB)MLn (PB^PhP)MLn (PBP)MLn

(b) Known pincer metal complexes with a central boryl X-type donor

M = Ir, Rh, Ru, Pt
(Yamashita and Nozaki)

● = BH, E = S, Se
(Mirkin)

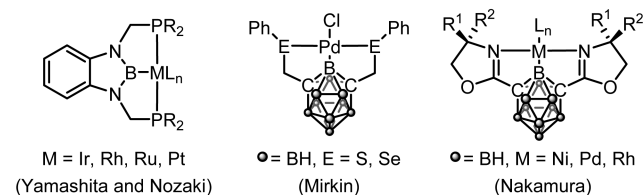● = BH, M = Ni, Pd, Rh
(Nakamura)

Figure 1. Complexes featuring various boron-based ligands.

fundamental questions about the nature and nomenclature of metal−ligand bonding and have already been harnessed in catalysis.[2b,d,e,3] Borane-containing ligands have been treated as robust supporting ligands, but we wondered if they might be vulnerable to insertion of a metal into the boron−aryl bond. In particular, insertion into the B−Ph bond in the PB^PhP ligand[2] (Figure 1a) seemed most plausible, as the B−Ph bond is unbuttressed by a phosphine. Such an insertion would result in a boryl/bis(phosphine) pincer complex. It can be viewed as B−C oxidative addition, which has not been previously observed for classical[4] B−C bonds.

Tridentate pincer-type ligands with a central boryl X-type (Figure 1b) donor were only recently introduced, first by Yamashita and Nozaki.[5] Spokoyny and Mirkin[6] ingeniously constructed a boryl-centered pincer based on the *meta*-dicarborane core, and a similar design was employed by Nakamura.[7] As discussed by Yamashita and Nozaki,[5a] boryl is the strongest *trans*-influence ligand to be incorporated in pincer ligands and thus complements the more common N- and C-based donors. The diarylboryl/bis(phosphine) PBP pincer (Figure 1a) should possess a boryl donor with a more accessible empty orbital compared to the Yamashita/Nozaki ligand (stabilized by π-donation from the amino groups) or the Spokoyny−Mirkin ligand, where the boron orbitals are tied up in the carborane cage. The diarylboryl/bis(phosphine) PBP pincer would have analogous connectivity to the variety of other PXP pincer ligands built on the "bis(*ortho*-phosphinoaryl)X" core, with X = C,[8] N,[9] O,[10] P,[11] Sb,[12] and Si.[13] The analogy with amido-PNP seemed especially intriguing, as the simple "swap" of N with B replaces an electronegative atom carrying a lone pair of electrons with an electropositive atom carrying an empty orbital, while preserving the geometry and charge.

We turned our attention to the report by Bourissou et al. on the isolation of **2-Rh** (Scheme 1) from the reaction of borane/

Scheme 1. Bourissou's Synthesis of Ligand 1 and Its Rh Complex 2-Rh
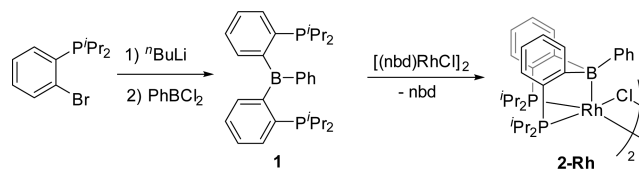
bis(phosphine) ligand **1** with [(nbd)RhCl]₂ as a source of monovalent Rh (nbd = 2,5-norbornadiene).[2a] Keeping in mind the generally greater thermodynamic propensity of 5d versus 4d metals for oxidative addition, we pursued an Ir analogue of the Bourissou synthesis of **2-Rh**. To our delight, thermolysis of **1** with [Ir(COE)₂Cl]₂ at 100 °C for 5 h (COE = cyclooctene) led to the single product (PBP)Ir(Ph) (Cl) (**3-Ir**), a result of the desired insertion of Ir into the B−Ph bond (Scheme 2).

Scheme 2. Synthesis of 3-M via B−C Bond Oxidative Addition[a]
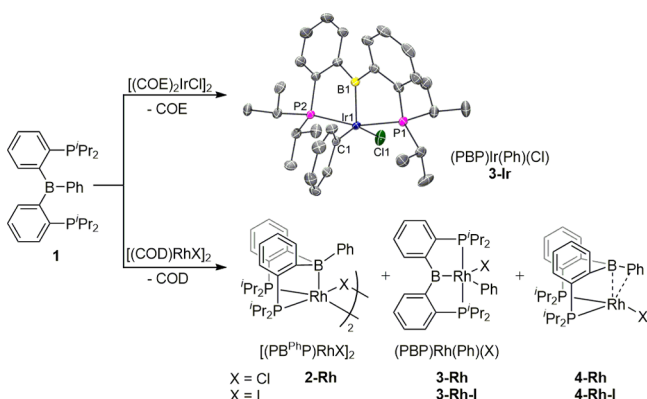
[a]ORTEP drawing (50% probability ellipsoids) of 3-Ir shows selected atom labeling. The molecule of toluene present in the unit cell is not shown. Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg) for 3-Ir: Ir1−B1, 1.988(3); Ir1−Cl1, 2.4096(11); Ir1−C1, 2.029(3); Ir1−P1, 2.3245(9); Ir1−P2, 2.3333(10); P1−Ir1−P2, 162.54(3); B1−Ir1−C1, 98.09(12); B1−Ir1−Cl1, 114.26(10); C1−Ir1−Cl1, 147.49(8).

The downfield ^{11}B NMR chemical shift (δ 75.9 for 3-Ir) appears to be diagnostic for the presence of a diarylboryl ligand.[14] Chemical shifts around ca. 80−90 ppm are common for triorganoboranes with an sp^2-hybridized boron. Diphenylboryl complexes $(C_5Me_5)Ir(PMe_3)(H)$ (BPh$_2$) and CpFe(CO)$_2$BPh$_2$ were reported at 93 and 121 ppm, respectively.[15] Triarylborane adducts with transition metals typically resonate in the 14−30 ppm region[1,2] (δ 20.8 ppm for 2-Rh). 3-Ir displays features in the ^{1}H NMR spectrum associated[16] with the restricted rotation of the phenyl group bound cis to the central pincer donor and sandwiched between the two P^{i}Pr$_2$ flanking donors: C$_6$H$_5$ gives rise to five separate ^{1}H resonances, and one of the four CH$_3$ signals of the P^{i}Pr$_2$ groups is shifted by ~0.5−1.0 ppm upfield from the rest.

An X-ray diffraction study on a single crystal of 3-Ir confirmed the proposed structure. The Ir1−B1 bond length (1.988(3) Å) was comparable to the Ir−B$_{boryl}$ distances (ca. 1.97−1.98 Å) in the Nozaki−Yamashita pincer complexes.[5a,b] The geometry about boron is strictly planar, and the coordination environment of Ir is a distorted square pyramid with boryl trans to the empty site, as would be expected for the strongest trans-influencing ligand.

Bourissou et al. reported three ^{31}P NMR resonances at ambient temperature, resulting from the reaction of 1 with 0.5 equiv of [(nbd)RhCl]$_2$ in CDCl$_3$, and tentatively proposed that they may belong to different conformers of 2-Rh.[17] We observed the same three signals in a reaction of 1 with 0.5 equiv of [Rh(COD)Cl]$_2$ in CDCl$_3$ or C$_6$D$_5$Br (COD = 1,5-cyclo-octadiene); however, we have arrived at a new interpretation of these observations (Scheme 2).

The ratio of the observed three resonances was not affected by thermolysis (in C$_6$D$_5$Br) at 100 °C for 18 h. On the other hand, lowering the total concentration of Rh resulted in a decrease of the relative intensity of the broad ^{31}P NMR resonance assigned to 2-Rh, while the other two resonances remained in the same ratio to each other. This suggested that, in addition to the dimeric 2-Rh, the mixture contained two monomeric isomers. The NMR spectra of this mixture contained features similar to those observed for 3-Ir: an upfield-shifted Me resonance from the P^{i}Pr$_2$ groups in the ^{1}H NMR spectrum and a downfield resonance at 94.3 ppm in the ^{11}B NMR spectrum. These corresponded to the ^{31}P NMR resonance at 50.4 ppm ($J_{Rh−P}$ = 126 Hz).

Utilization of [Rh(COD)I]$_2$ in the reaction with 1 led to a mixture with only two components, with NMR observations closely corresponding to the two monomeric components of the "RhCl" mixture and the ratio unchanged by the variation of total [Rh].

These observations led us to conclude that the RhCl mixture contained 2-Rh, 3-Rh, and a third isomer 4-Rh, while the RhI mixture is composed of 3-Rh-I and 4-Rh-I (Scheme 2). Selected NMR data for all Rh and Ir complexes are collected in Table 1. The exact nature of 4-Rh/4-Rh-I remains undetermined, but the unusually large Rh−P coupling constant (>190 Hz) finds analogy in π-arene complexes of a $(R_3P)_2Rh^I$ fragment, such as $(R_3P)_2Rh(\eta^6$-PhBPh$_3)$. We tentatively propose a structure for 4-Rh/4-Rh-I, where the BPh unit is bound to Rh in a η^x-fashion (x > 1) as a "borabenzyl" π-system. Similar binding modes of B-Ph to transiton metals have been reported.[2f,18] EXSY NMR experiments detected exchange between 2-Rh and 4-Rh.

Next, we explored reactions of the new PBP pincer complexes with dihydrogen. Thermolysis of either 3-Ir or the mixture of 2-Rh, 3-Rh, and 4-Rh under an atmosphere of H$_2$ at 100 °C led to the isolation, upon workup, of the corresponding 5-Ir and 5-Rh with 77 and 89% isolated yields, respectively (Scheme 3). Both 5-

Scheme 3. Synthesis and Reactivity of (PBP)ML$_n$
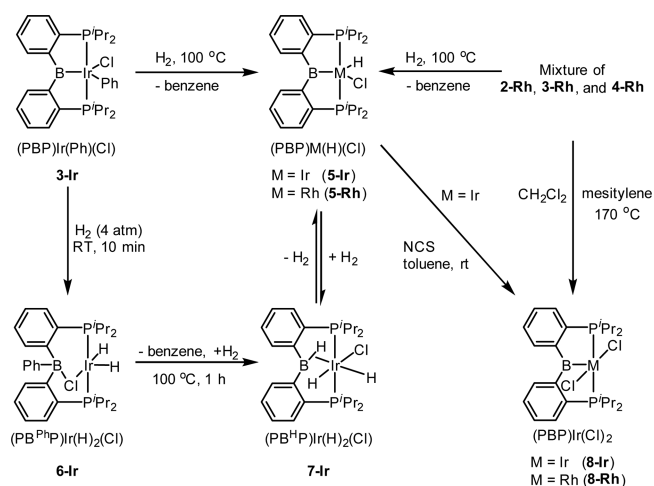
Table 1. ^{11}B NMR and ^{31}P NMR Chemical Shifts of Ir and Rh Complexes (in ppm) and $^2J_{Rh−P}$ Values

compound	3-Ir	5-Ir	6-Ir	7-Ir	8-Ir	2-Rh	3-Rh	4-Rh	3-Rh-I	4-Rh-I	5-Rh	8-Rh
^{11}B NMR	75.9	72.6	11.7	53.7	73.0	20.8	94.3	20.8	95.3	22.5	80.1	91.3
^{31}P NMR	44.9	61.9	37.9	53.5	35.6	65.0−80.0	50.4 (d, $J_{Rh−P}$ = 126 Hz)	88.8 (d, $J_{Rh−P}$ = 194 Hz)	50.4 (d, $J_{Rh−P}$ = 125 Hz)	87.1 (d, $J_{Rh−P}$ = 191 Hz)	63.3 (d, $J_{P−Rh}$ = 126 Hz)	45.6 (d, $J_{Rh−P}$ = 106 Hz)

Ir and **5-Rh** displayed well-resolved multiplets for their hydride resonances (-22.17 ppm (t, J_{H-P} = 11.5 Hz, Ir-*H*) and -18.95 ppm (dt, J_{H-Rh} = 41.0 Hz, J_{H-P} = 9.9 Hz, Rh-*H*)) with no evidence of broadening from coupling to boron. The ^{11}B NMR chemical shifts (**5-Ir**, 72.6 ppm; **5-Rh**, 80.1 ppm) were consistent with a boryl moiety, and the value of $^{1}J_{Rh-P}$ = 126 Hz in **5-Rh** matched that of **3-Rh** and **3-Rh-I**. Thus, the spectroscopic data indicate that **5-M** is a classical boryl/hydride complex of trivalent Rh/Ir.

In the solid-state structures determined by XRD (Figure 2), the strictly planar environment on boron atoms and the short
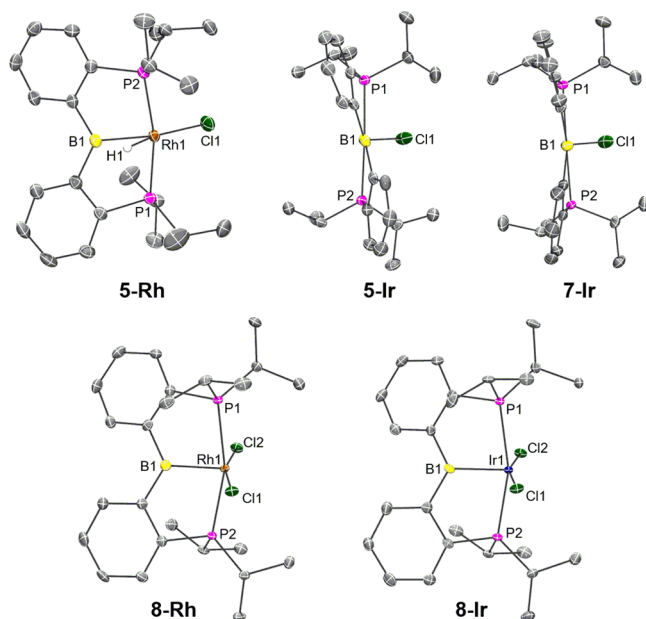

Figure 2. ORTEP drawing (50% probability ellipsoids) of **5-Rh**, **5-Ir**, **7-Ir**, **8-Rh**, and **8-Ir**, showing selected atom labeling. Only one of two independent structures in the unit cell is shown for all structures. Hydrogen atoms (except for the hydrogen on Rh of **5-Rh**) are omitted for clarity.

M−B distances (1.99−2.01 Å)[5a,b] are consistent with the metal−boryl formulation. From the Fourier difference maps, **5-Ir** and **5-Rh** showed the hydrogens on the metal leaning toward the boron atom, similar to the results found by Yamashita[5a,c] and Marder.[19] The XRD-derived and the DFT-calculated[20] values for the B⋯H distance (2.07(4) and 1.82 Å for **5-Ir**; 1.59(3) and 1.48 Å for **5-Rh**) may indicate a residual B−H interaction for Rh, but spectroscopic evidence suggests such interaction to be weak.

Intermediate **6-Ir**, resulting from addition of 1 equiv of H_2, was observed in situ in NMR spectra in the reaction of (PBP)Ir-(Ph)(Cl) (**3-Ir**) with 4 atm of H_2 at room temperature after a few minutes. The loss of boryl metal character is apparent from the upfield ^{11}B NMR resonance at 11.7 ppm, most consistent with a borate. The ^{1}H NMR phenyl group resonances in **6-Ir** were no longer split into five, giving instead the more normal 2:2:1 distribution, suggesting a phenyl shift from Ir to B. The two hydrides gave rise to two doublets of triplets from coupling to each other and two ^{31}P nuclei, definitively placing them on Ir. A single ^{31}P resonance and virtual coupling evident in the ^{1}H NMR spectrum suggest *trans*-disposition of the phosphines. The structure we favor for **6-Ir** (Scheme 3) appears to match the NMR observations best, although we cannot exclude additional

weak interaction with the B−Ph group. **6-Ir** may be viewed as the product of H_2-induced B−C reductive elimination from **3-Ir**.

Thermolysis of **6-Ir** under H_2 atmosphere (100 °C, 1 h) results in a mixture of **7-Ir** and **5-Ir**, in equilibrium with free H_2. The two Ir-bound hydrides in **7-Ir** gave rise to broad resonances in the ^{1}H NMR spectrum at room temperature, but cooling of the solution to -50 °C revealed two sharp signals with clear coupling patterns. The ^{1}H NMR resonance ascribed to BH was not part of the exchange process between the two Ir−H sites.

We were not able to prepare pure bulk samples of **7-Ir** because of facile H_2 loss, but we succeeded in obtaining a single crystal for an X-ray diffraction study. The X-ray structures of **5-Ir** and **7-Ir** contain the same non-hydrogen atoms attached to Ir with similar attendant angles, and the B−H or Ir−H hydrogen atoms of **7-Ir** were not located. However, the Ir−B distance in **7-Ir** (2.137(4) and 2.135(4) Å for two independent molecules) is considerably longer than that in **5-Ir** (2.003(4) and 1.995(4) Å). In addition, the sum of angles from non-hydrogen substituents on boron in **7-Ir** is ca. 357.5 versus 360° for **5-Ir**. These metrics of the structure of **7-Ir** are closely reproduced in the DFT-optimized[20] geometry of this molecule, which also gave a short (1.33 Å) distance for the coordinated B−H. The views of **5-Ir** and **7-Ir** shown in Figure 2 (down the B−Ir view axis) emphasize that the aryl groups on B adopt different conformations in **5-Ir** and **7-Ir**. The structural data and the ^{11}B NMR chemical shift of **7-Ir** (53.7 ppm) are consistent with the proposed σ-borane/dihydride formulation.

5-Ir reacted cleanly with 1 equiv of *N*-chlorosuccinimide in toluene to give (PBP)IrCl$_2$ (**8-Ir**) in 81% yield after workup. The Rh analogue (**8-Rh**) was synthesized via thermolysis of the mixture of **2-Rh**, **3-Rh**, and **4-Rh** in mesitylene in the presence of CH$_2$Cl$_2$ at 170 °C for 18 h.[21] The presence of a boryl ligand was corroborated by ^{11}B NMR spectroscopy (**8-Ir**, 73.0 ppm; **8-Rh**, 91.3 ppm) and by single-crystal X-ray diffraction studies (Figure 2).

In summary, we have shown that boryl/bis(phosphine) PBP pincer complexes can be accessed by facile insertion of Rh and Ir into the B−Ph bond of a borane/bis(phosphine) ligand. This formal B−C oxidative addition can be viewed as an inverse of the B−C reductive elimination postulated in transition-metal-catalyzed C−H borylation catalysis.[22] The PBP ligand displays a diversity of structural forms, with boryl, borane, and borate variants possible.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.5b11706.

> Experimental and spectroscopic details and crystallographic data (PDF)
> X-ray data (CIF)
> DFT coordinate files (ZIP)

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

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