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# Synthesis and Structures of the First Transition-Metal Tris(boryl) Complexes: ($\eta^6$-Arene)Ir($BO_2C_6H_4$)$_3$[†]

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The discovery of transition–metal–catalyzed alkene hydroboration using Wilkinson's catalyst and HBcat (cat = 1,2-$O_2C_6H_4$) by Mãnnig and Nöth[1] led to the development of applications in organic synthesis.[2] The proposed catalytic cycle involved oxidative addition of a B–H bond to the metal center, followed by migratory insertion of alkene into the M–H bond and subsequent reductive elimination of the B–C bond. Recent observations of vinyl boronate esters in several metal–catalyzed alkene hydroborations suggest[3] a competing pathway involving alkene insertion into the M–B bond of a metal–boryl[4,5a,b,e,6,7] (M–$BR_2$) complex. Indeed, we have demonstrated[4] the first stoichiometric example of alkene insertion into an M–B bond in the reaction of the bis(boryl) complex [$(PPh_3)_2RhCl(Bcat)_2$] with 4–vinylanisole. As part of our investigations,[2g,3b,c,4,5] we have examined the reaction of HBcat with several Rh and Ir catalyst precursors and related complexes to obtain a fundamental understanding of B–H activation processes and to isolate any resulting metal–boryl complexes for further reactivity studies. One common feature of many hydroboration catalyst precursors employed[8] is the presence of a coordinated COD ligand (COD = cycloocta-1,5–diene). We have suggested recently[3b,5e] that the COD ligand is not hydroborated efficiently by HBcat and that the nature of the catalytically active species may thus change with time over the course of the reaction. We report herein that the reaction of [($\eta^5$–indenyl)-Ir(COD)] (**1**) with excess HBcat in arene solvents gives excellent isolated yields of the novel tris(boryl)iridium complexes [($\eta^6$–arene)Ir(Bcat)$_3$] [arene = $C_6H_6$ (**2a**), $C_6D_6$(**2b**), $C_6H_5Me$(**2c**), 1,3,5–$C_6H_3Me_3$(**2d**)]. In addition, GC/MS analysis of the filtrates from these reactions allowed us to identify the organic and organoboron reaction byproducts.

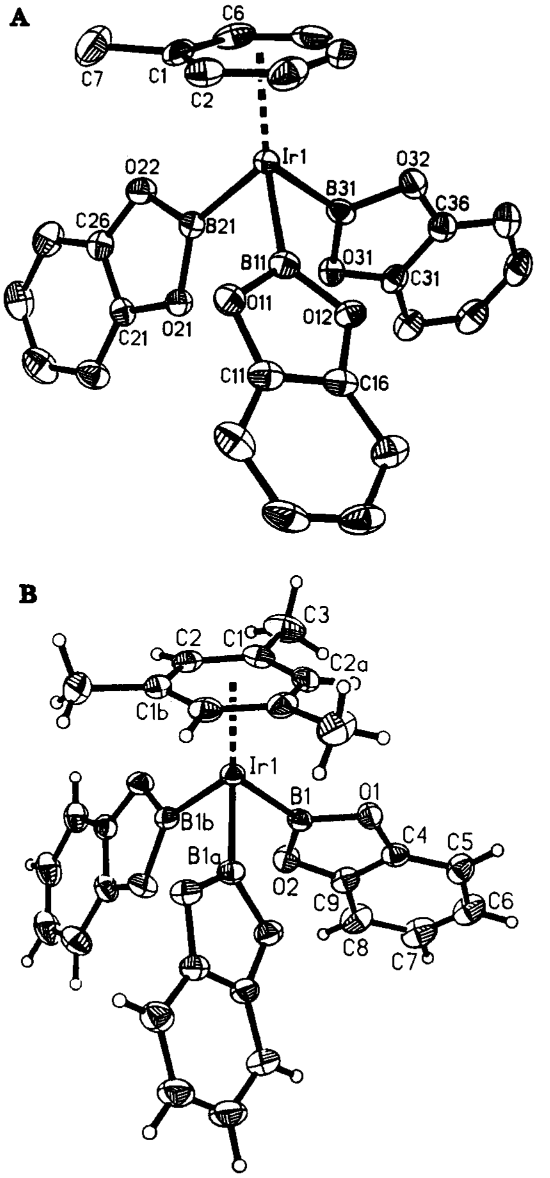

**Figure 1.** (A) Molecular structure of [($\eta^6$–$C_6H_5Me$)Ir(Bcat)$_3$] (**2c**). Selected bond distances (Å) and angles (deg): Ir–B11 = 2.036(4), Ir–B21 = 2.018(5), Ir–B31 = 2.024(5), Ir–C1 = 2.100(5), Ir–C2 = 2.367(5), Ir–C6 = 2.353(4), B11–Ir–B21 = 83.1(2), B11–Ir–B31 = 80.3(2), B21–Ir–B31 = 84.4(2), C1–Ir–B11 = 132.2(2), C1–Ir–B21 = 94.3(2), C1–Ir–B31 = 147.2(2), C2–Ir–B11 = 103.6(2), C2–Ir–B21 = 112.4(2), C2–Ir–B31 = 163.0(2), C6–Ir–B11 = 165.4(2), C6–Ir–B21 = 102.2(2), C6–Ir–B31 = 113.6(2). (B) Molecular structure of [($\eta^6$–$C_6H_3Me_3$)-Ir(Bcat)$_3$] (**2d**). Selected bond distances (Å) and angles (deg): Ir–B1 = 2.016(3), Ir–C1 = 2.366(3), Ir–C2 = 2.335(2), B1–Ir–B1a = 81.6(1), C1–Ir–B1 = 162.3(1), C1–Ir–B1a = 116.1(1), C1–Ir–B1b = 100.3(1), C2–Ir–B1 = 150.5(1), C2–Ir–B1a = 95.9(1), C2–Ir–B1b = 127.3(1), symmetry codes, $a = z, x, y$; $b = y, z, x$.

Reaction of **1** with 5 molar equiv of HBcat in mesitylene solvent at room temperature for 3 h, followed by addition of hexane, resulted in a tan precipitate which was identified as [($\eta^6$–1,3,5-$C_6H_3Me_3$)Ir(Bcat)$_3$] (**2d**)[9] by $^1H$, $^{13}C$, and $^{11}B$ NMR spectroscopy as well as by single–crystal X-ray diffraction. Other arene derivatives (**2a**, **2b**, and **2c**)[9] were prepared and isolated in a similar fashion.

The three–legged piano stool molecular structures of **2c** and

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[†] Dedicated to Professor M. Frederick Hawthorne on the occasion of his 65th birthday.

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(8) In addition to the more common catalyst precursor, [Rh(COD)Cl]$_2$/*n*(phosphine) (phosphine = $PPh_3$, DPPE, DPPB, DIOP), others such as [Rh(COD)($PPh_3$)$_2$]·X (X = $BPh_4$, $PF_6$), [Rh(COD)$_2$]·X (X = $BF_4$, $ClO_4$), and [Ir(COD)($PCy_3$)Py]·$PF_6$ have also been used for metal–catalyzed hydroboration.[2]

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**2d** along with their atom labelings are shown in Figure 1. Compound **2c**[10] crystallizes in the monoclinic space group $P2_1/n$, while **2d**[10] crystallizes in the trigonal space group $R\bar{3}$. The Ir–B bond distance of 2.016(3) Å for **2d** is similar to those of **2c** (2.036(5), 2.024(5), and 2.018(5) Å). These values are also comparable to the Ir–B distances of 2.023(10) Å in *mer*–[IrHCl(Bcat)($PMe_3$)$_3$][7] and 2.045(5) Å in [IrHCl(CO)(Bcat)($PPh_3$)$_2$].[5e] A projection of the Ir atom onto the $C_6$ plane for **2c** shows that the Ir(Bcat)$_3$ unit is slipped away from the centroid of the arene ring by 0.064 Å, with the distance from the Ir atom to the mean arene plane being 1.891 Å. In contrast, the Ir atom in **2d** lies on the crystallographic threefold rotational axis and is situated 1.881(3) Å from the mean plane of the mesitylene ring. The only other structurally characterized $Ir^{III}$ arene complexes are the two solvates [Ir($\eta^5$,$\eta^6$–$C_5Me_4C_3H_6C_6H_2Me_3$)] $(BF_4)_2 \cdot X$ (X = MeOH, $MeNO_2$),[11] for which the Ir–arene plane distances are 1.73(1) Å. The torsion angles between the $BO_2C_2$ plane of the Bcat ligands and the Ir–B–arene centroid are 65.0, 28.3, and 25.9° for **2c** and 41.3° for **2d**.

GC/MS analysis of the filtrate from the reaction of **1** with 5 equiv of HBcat in toluene was quite informative. A representative total ion chromatogram is shown in the supplementary material. The critical observation is that both the COD and the indene ligand are subjected to hydrogenation as well as hydroboration. In addition to cyclooctene, cyclooctane, cyclooctylBcat, and two isomers of cyclooctenylBcat, we observed indene, indan, 1- and 2-indanylBcat, 3-indenylBcat, and 1,3-(Bcat)$_2$indan. The amount of cyclooctane formed was much larger than the amount of cyclooctene, and there was substantially more cyclooctylBcat than the total amount of cyclooctenylBcat. The two isomers of cyclooctenylBcat constitute only trace products. These factors indicate that hydrogenation of COD rather than hydroboration is the major pathway.[5e] Similar organoborane byproducts were obtained for reactions in $C_6H_6$, $C_6D_6$ and mesitylene.

Compound **2d** undergoes complete displacement of the mesitylene ligand when treated with 3 equiv of $PEt_3$ to form the new tris(boryl) complex, *fac*–[($PEt_3$)$_3$Ir(Bcat)$_3$] (**3**).[12] The fact that the arene ring can be displaced readily will allow fine-tuning of electron density at Ir using various phosphines and other ligands. Further investigations of the reactivities of **2d** and **3** with respect to alkene insertion into Ir–B bonds and B–B reductive elimination processes are underway.

We have presented a general, high-yield synthesis of novel [($\eta^6$–arene)Ir(Bcat)$_3$] complexes. Substitution of the $\pi$–bound arene ligand in **2** can result in other *fac*–tris(boryl)iridium derivatives. The fate of the coordinated COD moiety in **1** gives additional insight into the complex transformations of a widely used ligand in hydroboration catalyst precursors.

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**Supplementary Material Available:** Representative total ion chromatogram for the reaction of **1** with 5 equiv of HBcat in toluene, experimental details for the crystal structure determinations, and tables of atomic coordinates, anisotropic thermal parameters, bond distances, and bond angles for **2c** and **2d** (12 pages); observed and calculated structure factors for **2c** and **2d** (26 pages). Ordering information is given on any current masthead page.

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(9) In a typical reaction, a solution of HBcat (594 mg, 4.95 mmol) in toluene (2 mL) was added to a stirred solution of [($\eta^5$-indenyl)Ir(COD)] (396 mg, 0.95 mmol) in toluene (3 mL). After 3 h, 20 mL of hexane was added, and the resulting tan precipitate was collected by filtration, washed with 2 × 5 mL of hexane, and dried *in vacuo* to give **2c** (502 mg, 82%). Anal. Calcd for $C_{25}H_{20}B_3IrO_6$: C, 46.84; H, 3.14. Found: C, 46.70; H, 3.38. $^1H$ NMR (200 MHz, $CD_2Cl_2$): $\delta$ 2.65 (s, 3H, Me), 6.77–7.09 (m (ov), 17H, catecholate + Ph). $^{13}C\{^1H\}$ NMR (50.4 MHz): $\delta$ 20.5 (Me), 100.8 (CH, Ph), 104.3 (CH, Ph), 104.4 (CH, Ph), 111.1 (CH, catecholate), 121.3 (CH, catecholate), 122.5 (C, Ph), 150.3 (C, catecholate). $^{11}B\{^1H\}$ NMR (77 MHz): $\delta$ 37.7 (br). For **2a**: from 448 mg of **1**, 657 mg (97%) of **2a** was obtained. Anal. Calcd for $C_{24}H_{18}B_3IrO_6$: C, 45.97; H, 2.89. Found: C, 47.19; H, 3.14. (This material contained a small amount of benzene of recrystallization, indicated by $^1H$ and $^{13}C$ NMR). $^1H$ NMR: $\delta$ 6.63 (s, 6H, $C_6H_6$), 6.91–6.98 (m, 6H, catecholate), 7.06–7.13 (m, 6H, catecholate). $^{13}C\{^1H\}$ NMR: $\delta$ 104.3 ($C_6H_6$), 111.5 (CH, catecholate), 121.5 (CH, catecholate), 150.5 (C, catecholate). $^{11}B\{^1H\}$ NMR: $\delta$ 37.7 (br). For **2b**: from 212 mg of **1**, 314 mg (97%) of **2b** was obtained. Anal. Calcd for $C_{24}H_{12}B_3D_6IrO_6$: C, 45.53; H/D, 3.82. Found: C, 45.56; H, 3.84. $^1H$ NMR: $\delta$ 6.93–6.99 (m, 6H, catecholate), 7.08–7.15 (m, 6H, catecholate). $^{13}C\{^1H\}$ NMR: $\delta$ 104.5 (t, $C_6D_6$), 111.5 (CH, catecholate), 121.5 (CH, catecholate), 150.5 (C, catecholate). $^{11}B\{^1H\}$ NMR: $\delta$ 37.9 (br). For **2d**: from 164 mg of **1**, 235 mg (89%) of **2d** was obtained. Anal. Calcd for $C_{27}H_{24}B_3IrO_6$: C, 48.47; H, 3.62. Found: C, 48.26; H, 3.87. $^1H$ NMR: $\delta$ 2.65 (s, 9H, Me), 6.51 (s, 3H, Ph), 6.88–6.95 (m, 6H, catecholate), 7.02–7.11 (m, 6H, catecholate). $^{13}C\{^1H\}$ NMR: $\delta$ 20.3 (Me), 102.2 (CH, Ph), 111.1 (CH, catecholate), 121.4 (CH, catecholate), 122.4 (C, Ph), 150.6 (C, catecholate). $^{11}B\{^1H\}$ NMR: $\delta$ 37.8 (br).

(10) Crystal structure data for **2c** (from toluene): formula = $C_{25}H_{20}B_3IrO_6$, FW = 641.08, monoclinic, space group $P2_1/n$ (nonstandard No. 14), $a$ = 10.262(1) Å, $b$ = 13.652(2) Å, $c$ = 16.733(3) Å, $\beta$ = 99.41(1)°, $V$ = 2312.7(5) Å$^3$, $Z$ = 4, $\rho$ = 1.841 g cm$^{-3}$; $T$ = 175 K. Anisotropic refinement of all non–hydrogen atoms (H riding model refined with isotropic thermal parameters; 336 variables) using 3670 unique reflections with $F > 6\sigma(F)$, from 4569 unique data (4819 collected), gave $R$ = 0.0199 and $R_w$ = 0.0222. Crystal structure data for **2d** (from mesitylene): formula = $C_{27}H_{24}B_3IrO_6$, FW = 669.13, trigonal R, space group $R\bar{3}$ (No. 148), $a$ = 10.806(1) Å, $\alpha$ = 90.98(1)°, $V$ = 1261.3(5) Å$^3$, $Z$ = 2, $\rho$ = 1.762 g cm$^{-3}$; $T$ = 200 K. Anisotropic refinement of all non–hydrogen atoms (H riding model refined with isotropic thermal parameters; 120 variables) using 2208 unique reflections with $F >$ $6\sigma(F)$, from 2475 unique data (8335 collected), gave $R$ = 0.0216 and $R_w$ = 0.0248.

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(12) Data for **3** follow. $^1H$ NMR (250 MHz, $CD_2Cl_2$): $\delta$ 1.07 (m, 27H, $CH_3$), 2.08 (m, 18H, $CH_2$), 6.78–6.95 (m, 12H, catecholate). $^{13}C\{^1H\}$ NMR: $\delta$ 9.4 (s, $CH_3$), 23.1 (m, $CH_2$), 110.5 (CH, catecholate), 120.5 (CH, catecholate), 150.9 (C, catecholate). $^{11}B\{^1H\}$ NMR (96 MHz): $\delta$ 44.7 (v br). $^{31}P\{^1H\}$ NMR (81 MHz): $\delta$ –32.1 (br).