Iridium-Promoted B-B Bond Activation: Preparation and X-ray Diffraction Analysis of a *mer*-Tris(boryl) Complex

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ABSTRACT: The tris(boryl) complex $Ir(Bcat)_3\{\kappa^3$-P,O,P-[xant($P^iPr_2)_2$]} (Bcat = catecholboryl; xant($P^iPr_2)_2$ = 9,9-dimethyl-4,5-bis(diisopropylphosphino)xanthene) has been prepared and characterized by X-ray diffraction analysis. The boryl ligands are disposed in a *mer*-arrangement. The Ir-B bonds situated mutually *trans* are about 0.1 Å longer than that disposed *cis* to the other two. An EDA-NOCV analysis has revealed that the π-backdonation from the metal to the p_z atomic orbital of the boron atom decreases about 43% in the longer bonds respect to the shorter one, while the σ-bonding interaction only diminishes about 8%.

Pidcock, Richards and Venanzi defined *trans*-influence, in 1966, as “the tendency of a ligand to weaken the bond *trans* to itself”.[1] It is therefore a thermodynamic concept, which has a noticeable weight on the bond lengths[2] and stability of the coordination compounds.[3] Two ligands with a strong *trans*-influence destabilize the complex, when they are situated mutually *trans*. A strong *trans*-influence is characteristic of strong σ-donating ligands,[4] whereas exists an inverse relation between the *trans*-influence of a ligand and its electronegativity.[5] Pauli repulsion causes the weakening of the bond *trans* to a good σ-donor ligand. Donated electron density is accumulated on the *trans* site of the metal. As a consequence, the ligand at this position undergoes repulsion of the resulting electron cloud. The process can be envisioned as the donation from the *trans* ligand to the σ* orbital of the metal-ligand bond *trans* to it.

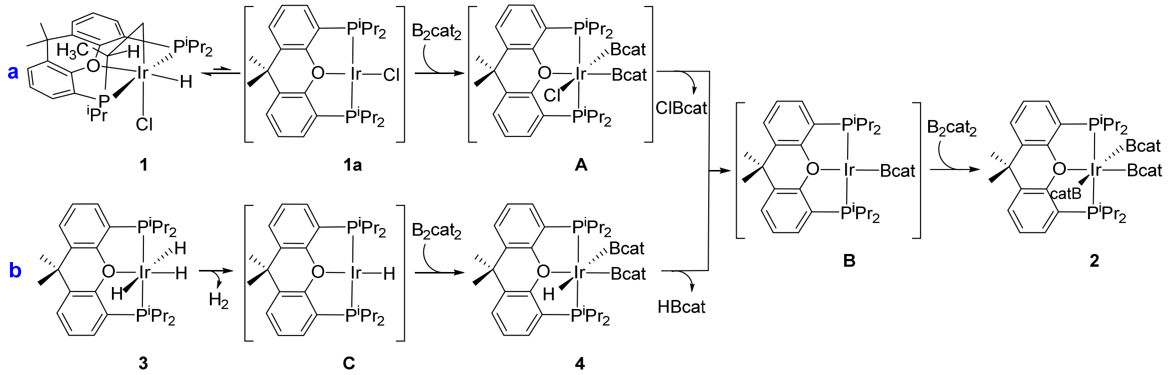
Boryl groups, with a sp^2-hybridized boron atom bearing an “empty” π-orbital, are among the strongest *trans*-influence ligands because of their strong σ-donor character and as a consequence of the electropositive nature of boron.[7] An overwhelming evidence of this is the fact that in all transition-metal complexes characterized by X-ray diffraction analysis, with two [8] or three [9] boryl ligands, they systematically occupy mutually *cis* or *fac* positions, respectively, avoiding the mutually *trans* disposition of two of them. In contrast, a few post-transition-element-bis(boryl) compounds with a linear rearrangement have been reported.[10]

Pincer ligands develop marked abilities to stabilize less common coordination polyhedra due to the disposition of their donor atoms. 9,9-Dimethyl-4,5-bis(diisopropylphosphino)xanthene (xant($P^iPr_2)_2$) is a neutral diphosphine, which has demonstrated to have a higher ability than other ether-diphosphines, such as 9,9-dimethyl-4,5-bis(diphenylphosphino)xanthene (xant($PPh_2)_2$) [11] or bis[(2-diphenylphosphino)phenyl]ether (DPEphos),[12] to act as a pincer ligand,[13] although a few compounds with the diphosphine coordinated as bidentated or *fac* have been also isolated.[14] This communication reveals that the diphosphine xant($P^iPr_2)_2$ has also the capacity of stabilizing transition-metal complexes with two boryl groups disposed mutually *trans*. By using its noticeable ability to coordinate *mer* and its neutral character, we have been able to prepare and to fully characterize an iridium(III) complex bearing three boryl ligands having a *mer* disposition.

The complex was prepared according Scheme 1. Complex IrHCl{κ^4-C,P,O,P-[$CH_2CH(CH_3)P(^iPr)$xant(P^iPr_2)]} (**1** in path *a*)[13b] is a synthetic equivalent of the square-planar species IrCl{κ^3-P,O,P-[xant($P^iPr_2)_2$]} (**1a**), the iridium counterpart of RhCl{κ^3-P,O,P-[xant($P^iPr_2)_2$]}. Like the latter, complex **1a** has a marked ability to activate σ-bonds,[13c] including B-B bonds. Thus, the treatment of toluene solutions of **1** with 3.0 equiv of bis(catecholato)diboron (B_2cat_2), at room temperature, for 15 min gives rise to the quantitative formation of $Ir(Bcat)_3\{\kappa^3$-P,O,P-[xant($P^iPr_2)_2$]} (**2**) and ClBcat, as a result of the B-B bond activation of two molecules of diborane. The process most probably occurs via the intermediates $IrCl(Bcat)_2\{\kappa^3$-P,O,P-[xant($P^iPr_2)_2$]} (**A**) and Ir(Bcat){κ^3-P,O,P-[xant($P^iPr_2)_2$]} (**B**). Attempts to detect them were unsuccessful because of the oxidative addition of the diborane to **1a** and **B** as well as the reductive elimination of ClBcat from **A** appear to be very fast and the formation of **2** is strongly favored; even the addition of 1.0 equiv of diborane to **1** exclusively gives **2** in 50% yield.

The white complex **2** was characterized by X-ray diffraction analysis. The structure (Figure 1) confirmed the *mer*-disposition of the boryl groups. The resulting octahedron displays P(1)-Ir-P(1A), B(1)-Ir-B(1A), and O(1)-Ir-B(2) angles of 160.49(8)º, 175.2(4)º, and 180.000(2)º, respectively. The iridium-boron bond lengths of 2.124(7) Å (Ir-B(1) and Ir-B(1A)) and 2.012(10) Å (Ir-B(2)) are consistent with the strong *trans* influence of the boryl ligands. Thus, the bonds Ir-B(1) and Ir-B(1A), which lie disposed mutually *trans*, are significantly longer (0.1 Å) than Ir-B(2). In agreement with the structure the $^{31}P\{^1H\}$ NMR spectrum shows a singlet for the equivalent P^iPr_2 groups. The $^{11}B\{^1H\}$ NMR spectrum contains a broad signal centered at about 33 ppm due to the three boryl groups.

Scheme 1. Pathways for the Formation of 2



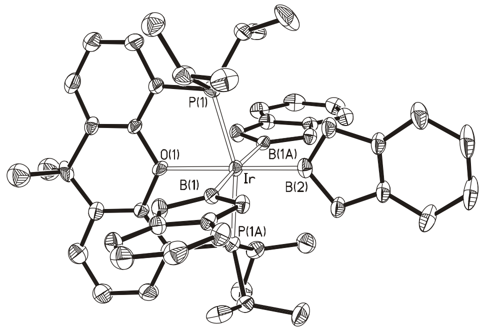


Figure 1. Molecular diagram of complex **2**. Hydrogen atoms are omitted for clarity.

The Ir-B bonds of **2** were analyzed by means of the Energy Decomposition Analysis method coupled to Natural Orbitals of Chemical Valence (EDA-NOCV).[15] To this end, we explored the nature of both Ir-B(2) and Ir-B(1). The fragments were either calculated in their doublet state, that lead to an electron-sharing single bond, or in their electronic singlet state, using charged fragments, which provides a dative Ir←B bond. It has been previously shown that the calculation giving the smallest orbital term ΔE_{orb} indicates the most faithful description of the type of binding,[16] since it also shows the smallest change in the electronic structure of the fragments by the bond formation. According to the data in Table 1, it becomes evident that the chemical bond between the [Ir] and [B] fragments is better described as a covalent (i.e. electron-sharing) σ-single bond. Further inspection of the EDA-NOCV data reveals that the major contribution to the total interaction in both Ir-B bonds comes from the electrostatic term ΔE_{elstat}, which contributes ca. 56-58% to ΔE_{int}. This is not surprising due to the higher electronegativity of the iridium atom which polarizes the Ir-B bond.[17] In agreement with this, the metal center supports a negative charge of -0.40, while the boron atoms have positive charges of +0.80 (B(1)) and +1.06 (B(2)). Interestingly, the partitioning of the ΔE_{orb} by means of the NOCV method suggests that, although the σ-bonding is the main contributor to the Ir-B bond (ca. 76-79%), there is a significant π-backdonation from the transition metal fragment to the p_z atomic orbital of the boron atom (Table 1 and Figure 2). Strikingly, the computed π-backdonation is stronger for Ir-B(2) than for Ir-B(1), which is nicely consistent with the shorter Ir-B distance observed both experimentally and computationally (2.000 Å vs 2.135 Å)

Table 1. EDA-NOCV results (in kcal/mol) computed at the ZORA-BP86-D3/TZ2P+//BP86-D3/def2-TZVPP level

	Ir–B(2)		Ir–B(1)	
	Electron-sharing	**Dative bond**	**Electron-sharing**	**Dative bond**
Fragments	**[Ir]$^{\bullet}$ [B]$^{\bullet}$**	**[Ir]$^{-}$ [B]$^{+}$**	**[Ir]$^{\bullet}$ [B]$^{\bullet}$**	**[Ir]$^{-}$ [B]$^{+}$**
ΔE_{int}	-118.0	-301.2	-100.8	-175.5
ΔE_{Pauli}	217.6	429.2	189.7	370.4
ΔE_{elstat}^{a}	-195.4 (58.2%)	-509.9 (69.8%)	-163.8 (56.4%)	-400.6 (73.4%)
ΔE_{orb}^{a}	-123.2 (36.7%)	-203.5 (27.9%)	-109.0 (37.5%)	-127.6 (23.4%)
ΔE_{disp}^{a}	-17.0 (5.1%)	-17.0 (2.3%)	-17.7 (6.1%)	-17.7 (3.2%)
$\Delta E_{orb}(\sigma)$^{b}	-93.0 (75.5%)	-159.5 (78.4%)	-86.3 (79.2%)	-92.4 (72.4%)
$\Delta E_{orb}(\pi)$^{b}	-15.5 (12.6%)	-10.6 (5.2%)	-8.9 (8.1%)	-7.3 (5.7%)
$\Delta E_{orb}(rest)$^{b}	-14.7 (11.9%)	-33.4 (16.4%)	-13.8 (12.7%)	-27.9 (21.9%)

^{a} The values within parentheses indicate the percentage to the total interaction energy, $\Delta E_{int} = \Delta E_{elstat} + \Delta E_{orb} + \Delta E_{disp.}$ ^{b} The values in parentheses give the percentage contribution to the total orbital interactions ΔE_{orb}.

Complex **2** can be also prepared starting from the trihydride $IrH_3\{\kappa^3$-P,O,P-[xant(P^{i}Pr$_2$)$_2$]} (**3**) and B_2cat_2 (path *b* in Scheme 1) by a similar procedure to that summarized in path a, in agreement with the proved ability of polyhydrides of platinum group metals to activate σ-bonds.[18] The key species for its formation is also **B**. It is now generated via IrH{κ^3-P,O,P-[xant(P^{i}Pr$_2$)$_2$]} (**C**) and IrH(Bcat)$_2${κ^3-P,O,P-[xant(P^{i}Pr$_2$)$_2$]} (**4**), which are the hydride counterparts of the chloride species **1a** and **A**, respectively. However, in this case, intermediate **4** can be detected and even isolated, as a pure white solid in 60% yield, when 1.0 equiv of B_2cat_2 are employed. As expected from the strong *trans*-influence of the boryl ligands, the Bcat groups are disposed mutually *cis*. This is revealed by the diphosphine resonances in the $^{13}C\{^1H\}$ NMR spectrum, which shows two signals at 35.7 and 27.7 ppm for the methyl substituents of the central heterocycle and four signals at 20.3, 19.5, 19.3, and 19.2 ppm for the methyl groups of the isopropyl substituents. The hydride ligand gives rise to a triplet ($^2J_{H-P}$

= 21.6 Hz) at -4.15 ppm, in the ^{1}H NMR spectrum, whereas the ^{31}P{^{1}H} NMR spectrum contains a singlet at 51.2 ppm, due to the equivalent P^{i}Pr$_2$ groups, that is split into a doublet under off-resonance conditions. A broad resonance centered at about 34.0 ppm in the ^{11}B{^{1}H} NMR spectrum for the boryl ligands is another characteristic feature of **4**.

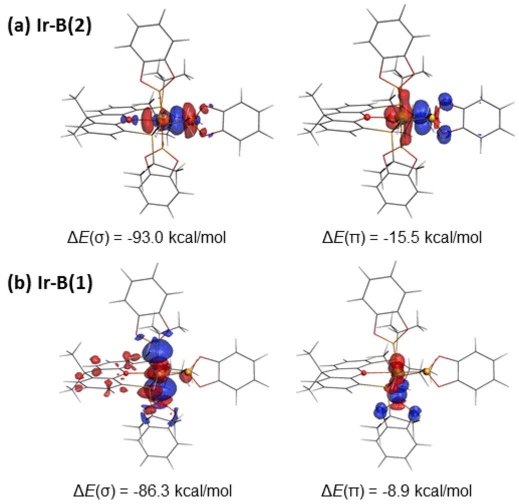
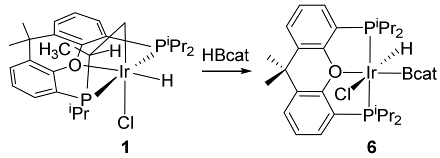


Figure 2. Deformation densities Δρ associated with the strongest pairwise orbital interactions compound **2** for the Ir-B(2) (top) and Ir-B(1) (bottom) bonds. The direction of the charge flow is red →blue.

Complex **4** can be also prepared by reaction of **3** with 2.0 equiv of HBcat. The square-planar boryl species **B** is also the key intermediate of the process (Scheme S1). In this case, it is formed via **C** and the iridium(III)-*trans*-dihydride IrH$_2$(Bcat){κ^3-P,O,P-[xant(P^{i}Pr$_2$)$_2$]} (**5**). The latter was characterized in toluene-d_8 by NMR spectroscopy. Its characteristic features are a triplet ($^2J_{H-P}$ = 17.2 Hz) at -5.57 ppm in the ^{1}H NMR spectrum for the equivalent hydride ligands, and a singlet at 60.6 ppm in the ^{31}P{^{1}H} NMR spectrum, as expected for the equivalent P^{i}Pr$_2$ groups of the *mer*-coordinated ether-diphosphine. This resonance is split into a triplet under off-resonance conditions.

Complex **1a** also activates the H-B bond of HBcat. Thus, the treatment of toluene solutions of its synthetic equivalent **1** with 3.0 equiv of the borane, at room temperature, for 10 min leads to IrHCl(Bcat){κ^3-P,O,P-[xant(P^{i}Pr$_2$)$_2$]} (**6** in Scheme 2), as a result of the oxidative addition of the H-B bond to the iridium(I) center of **1a**. In contrast to **A**, it is stable towards the reductive elimination of ClBcat. As a consequence, complexes **2**-**5** cannot be prepared starting from **1** and HBcat. Complex **6** was isolated as a white solid in 67% yield and was characterized by X-ray diffraction analysis. The structure (Figure S1) shows an octahedral environment around the iridium(III) center with the ether-diphosphine *mer*-coordinated and the boryl group disposed *trans* to the oxygen atom. The Ir-B bond length of 1.947(5) Å is slightly shorter (0.05-0.06 Å) than the Ir-B(2) distance in **2**. In agreement with the *mer* coordination of the diphosphine, the ^{31}P{^{1}H} NMR spectrum displays a singlet at 46.2 ppm due to the equivalent P^{i}Pr$_2$ groups. The hydride resonance appears as a triplet ($^2J_{H-P}$ = 15.4 Hz) at -19.07 ppm, in the ^{1}H NMR spectrum, whereas a broad signal corresponding to the boryl ligand is observed at 36 ppm in the ^{11}B{^{1}H} NMR spectrum.

Scheme 2. Formation of 6



In summary, complexes IrHCl{κ^4-C,P,O,P-[CH$_2$CH(CH$_3$)P(^{i}Pr)xant(P^{i}Pr$_2$)]} and IrH$_3${κ^3-P,O,P-[xant(P^{i}Pr$_2$)$_2$]} promote the activation of the B-B bond of two molecules of B$_2$cat$_2$ to give the tris(boryl) derivative Ir(Bcat)$_3${κ^3-P,O,P-[xant(P^{i}Pr$_2$)$_2$]} via bis(boryl) intermediates IrX(Bcat)$_2${κ^3-P,O,P-[xant(P^{i}Pr$_2$)$_2$]} (X = Cl, H). The tris(boryl) complex displays a *mer*-arrangement of the boryl groups in spite of the very high *trans*-influene of these ligands. The Ir-B bonds disposed mutually *trans* are about 0.1 Å longer than that disposed *cis* to the other two. The EDA-NOCV analysis of these bonds reveals that the main difference between them is observed in the π-back-donation from the metal to the p$_z$ atomic orbital of the boron atom, which decreases about 43% in the longer bonds respect to the shorter one, while the σ-bonding interaction only diminishes about 8%. To sum up, it is certainly possible to isolate transition metal complexes bearing two boryl ligands disposed mutually *trans* and to fully characterize them, even through X-ray diffraction analysis, when their co-ligands are competently selected.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS publications web site.

Experimental section, structural analysis, computational details, and NMR spectra (PDF).

Accession codes

CCDC 1894567 and 1894568 contain the crystallographic data for this paper. These data can be obtained free of charge *via* www.ccdc.cam.ac.uk/data_request/cif, or by e-mailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZm UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interests.

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The tris(boryl) complex Ir(Bcat)$_3${κ^3-P,O,P-[xant(P^{i}Pr$_2$)$_2$]} has been prepared. Its X-ray diffraction analysis structure reveals that the boryl groups are disposed in a *mer* rearrangement despite of the very strong *trans* influence of the boryl ligands. An EDA-NOCV analysis suggests that the π-backdonation from the metal to the p$_z$ atomic orbital of the boron atom decreases about 43% in the Ir-B bonds disposed mutually *trans* with regard to the other one.