

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

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Supporting Information

ABSTRACT: The tris(boryl) complex $\text{Ir}(\text{Bcat})_3\{\kappa^3\text{-P,O,P-}[\text{xant}(\text{P}^i\text{Pr}_2)_2]\}$ [Bcat = catecholboryl; $\text{xant}(\text{P}^i\text{Pr}_2)_2 = 9,9\text{-dimethyl-4,5-bis}(\text{diisopropylphosphino})\text{xanthene}$] 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 ~ 0.1 Å longer than that disposed *cis* to the other two. An energy decomposition analysis method coupled to natural orbitals for chemical valence has revealed that the level of π -back-donation from the metal to the p_z atomic orbital of the boron atom decreases $\sim 43\%$ in the longer bonds with respect to the shorter one, while the level of σ -bonding interaction diminishes by only $\sim 8\%$.

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 effect on the bond lengths² 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 an inverse relation between the *trans* influence of a ligand and its electronegativity exists.⁵ Pauli repulsion causes the weakening of the bond *trans* to a good σ -donor ligand. Donated electron density accumulates 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.⁶

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 Overwhelming evidence of this is the fact that in all transition metal complexes characterized by X-ray diffraction analysis, with two⁸ or three⁹ 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 [$\text{xant}(\text{P}^i\text{Pr}_2)_2$] is a neutral diphosphine, which has been demonstrated to be more able than other ether diphosphines, such as 9,9-dimethyl-4,5-bis(diphenylphosphino)xanthene [$\text{xant}(\text{PPh}_2)_2$]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 bidentate or *fac* have been also isolated.¹⁴ This Communication reveals that the diphosphine $\text{xant}(\text{P}^i\text{Pr}_2)_2$ also has the capacity to stabilize 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 to Scheme 1. Complex $\text{IrHCl}\{\kappa^4\text{-C,P,O,P-}[\text{CH}_2\text{CH}(\text{CH}_3)\text{P}^i\text{Pr}\text{xant}(\text{P}^i\text{Pr}_2)]\}$ (1 in path a)^{13b} is a synthetic equivalent of the square-planar species $\text{IrCl}\{\kappa^3\text{-P,O,P-}[\text{xant}(\text{P}^i\text{Pr}_2)_2]\}$ (1a), the iridium counterpart of $\text{RhCl}\{\kappa^3\text{-P,O,P-}[\text{xant}(\text{P}^i\text{Pr}_2)_2]\}$. 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(catecolato)diboron (B_2cat_2), at room temperature, for 15 min gives rise to the quantitative formation of $\text{Ir}(\text{Bcat})_3\{\kappa^3\text{-P,O,P-}[\text{xant}(\text{P}^i\text{Pr}_2)_2]\}$ (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 $\text{IrCl}(\text{Bcat})_2\{\kappa^3\text{-P,O,P-}[\text{xant}(\text{P}^i\text{Pr}_2)_2]\}$ (A) and $\text{Ir}(\text{Bcat})\{\kappa^3\text{-P,O,P-}[\text{xant}(\text{P}^i\text{Pr}_2)_2]\}$ (B). Attempts to detect them were unsuccessful because the oxidative addition of the diborane to 1a and B and 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–

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Scheme 1. Pathways for the Formation of 2

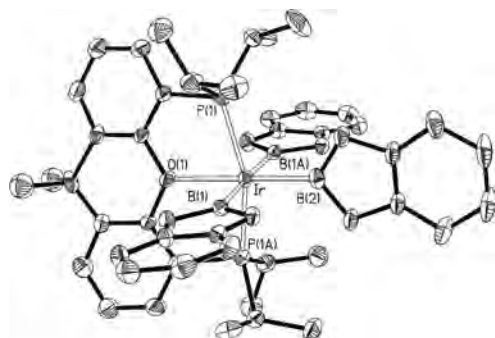
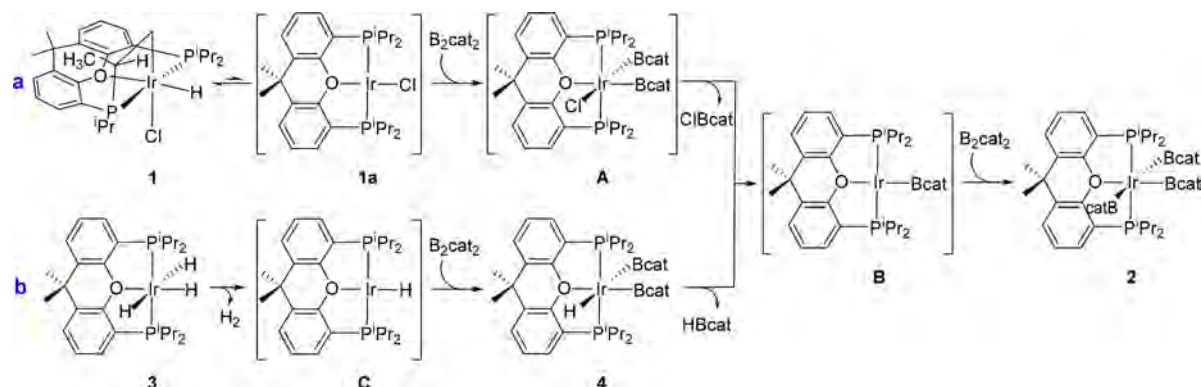


Figure 1. Molecular diagram of complex 2. Hydrogen atoms have been omitted for the sake of clarity.

B(2) angles of 160.49(8)°, 175.2(4)°, and 180.000(2)°, 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 Ir–B(1) and Ir–B(1A) bonds, which lie disposed mutually *trans*, are significantly longer (0.1 Å) than the Ir–B(2) bond. In agreement with the structure, the $^{31}\text{P}\{^1\text{H}\}$ nuclear magnetic resonance (NMR) spectrum shows a singlet for the equivalent P^iPr_2 groups. The $^{11}\text{B}\{^1\text{H}\}$ NMR spectrum contains a broad signal centered at ~ 33 ppm due to the three boryl groups.

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) bonds. The fragments were calculated either in their doublet state, which leads 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 because it also shows the smallest change in the electronic structure of the fragments upon 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 data reveals that the major contribution to the total interaction in both Ir–B bonds comes from the electrostatic term ΔE_{elstat} , which contributes ~ 56 – 58% to ΔE_{int} . This is not surprising due to the higher electronegativity of the iridium atom that polarizes the Ir–B bond.¹⁷ In agreement with this, the metal center supports a negative charge of -0.40 , while the boron

Table 1. EDA-NOCV Results (in kilocalories per mole) 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
	[Ir] [•]	[Ir] [−]	[Ir] [•]	[Ir] [−]
	[B] [•]	[B] ⁺	[B] [•]	[B] ⁺
ΔE_{int}	−118.0	−301.2	−100.8	−175.5
ΔE_{pauli}	217.6	429.2	189.7	370.4
$\Delta E_{\text{elstat}}^a$	−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%)
$\Delta E_{\text{orb}}(\sigma)^b$	−93.0 (75.5%)	−159.5 (78.4%)	−86.3 (79.2%)	−92.4 (72.4%)
$\Delta E_{\text{orb}}(\pi)^b$	−15.5 (12.6%)	−10.6 (5.2%)	−8.9 (8.1%)	−7.3 (5.7%)
$\Delta E_{\text{orb}}(\text{rest})^b$	−14.7 (11.9%)	−33.4 (16.4%)	−13.8 (12.7%)	−27.9 (21.9%)

^aThe values within parentheses indicate the percentage of the total interaction energy ($\Delta E_{\text{int}} = \Delta E_{\text{elstat}} + \Delta E_{\text{orb}} + \Delta E_{\text{disp}}$). ^bThe values in parentheses give the percentage contribution to the total orbital interactions ΔE_{orb} .

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 (~ 76 – 79%), there is a significant π -back-donation from the transition metal fragment to the p_z atomic orbital of the boron atom (Table 1 and Figure 2). Strikingly, the computed π -back-donation is stronger for the Ir–B(2) bond than for the Ir–B(1) bond, which is nicely consistent with the shorter Ir–B distance observed both experimentally and computationally (2.000 Å vs 2.135 Å).

Complex **2** can be also prepared starting from the trihydride $\text{IrH}_3\{\kappa^3\text{-P,O,P-[xant(P}^i\text{Pr}_2)_2]\}$ (**3**) and B_2cat_2 (path b in Scheme 1) by a procedure similar to that summarized in path a, in agreement with the proven 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 $\text{IrH}\{\kappa^3\text{-P,O,P-[xant(P}^i\text{Pr}_2)_2]\}$ (**C**) and $\text{IrH(Bcat)}_2\{\kappa^3\text{-P,O,P-[xant(P}^i\text{Pr}_2)_2]\}$ (**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 is employed.

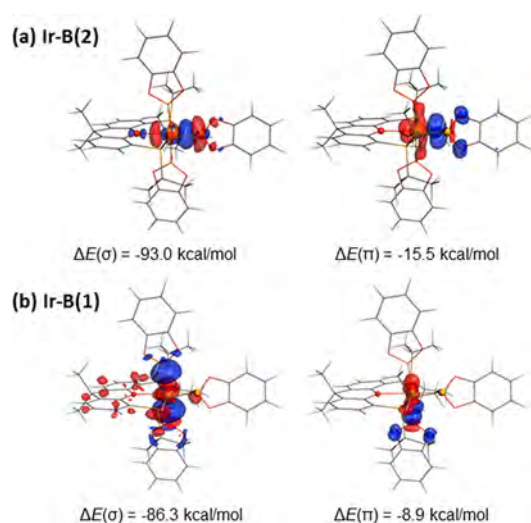


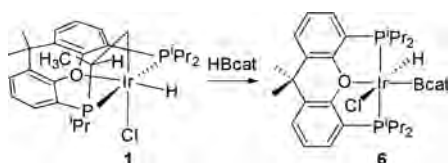
Figure 2. Deformation densities $\Delta\rho$ associated with the strongest pairwise orbital interactions of compound **2** for the Ir–B(2) (top) and Ir–B(1) (bottom) bonds. The direction of the charge flow is from red to blue.

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 $^{13}\text{C}\{^1\text{H}\}$ 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 ($^2J_{\text{H-P}} = 21.6$ Hz) at -4.15 ppm in the ^1H NMR spectrum, whereas the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum contains a singlet at 51.2 ppm, due to the equivalent P^iPr_2 groups, that is split into a doublet under off-resonance conditions. A broad resonance centered at ~ 34.0 ppm in the $^{11}\text{B}\{^1\text{H}\}$ NMR spectrum for the boryl ligands is another characteristic feature of **4**.

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 $\text{IrH}_2(\text{Bcat})\{\kappa^3\text{-P,O,P-}[\text{xant}(\text{P}^i\text{Pr}_2)_2]\}$ (**5**). The latter was characterized in toluene- d_8 by NMR spectroscopy. Its characteristic features are a triplet ($^2J_{\text{H-P}} = 17.2$ Hz) at -5.57 ppm in the ^1H NMR spectrum for the equivalent hydride ligands and a singlet at 60.6 ppm in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum, as expected for the equivalent P^iPr_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 $\text{IrHCl}(\text{Bcat})\{\kappa^3\text{-P,O,P-}[\text{xant}(\text{P}^i\text{Pr}_2)_2]\}$ (**6** in Scheme 2), as a result of the oxidative addition of the H–B bond to the

Scheme 2. Formation of **6**



iridium(I) center of **1a**. In contrast to **A**, it is stable toward 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) bond length in **2**. In agreement with the *mer* coordination of the diphosphine, the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum displays a singlet at 46.2 ppm due to the equivalent P^iPr_2 groups. The hydride resonance appears as a triplet ($^2J_{\text{H-P}} = 15.4$ Hz) at -19.07 ppm in the ^1H NMR spectrum, whereas a broad signal corresponding to the boryl ligand is observed at 36 ppm in the $^{11}\text{B}\{^1\text{H}\}$ NMR spectrum.

In summary, complexes $\text{IrHCl}\{\kappa^4\text{-C,P,O,P-}[\text{CH}_2\text{CH}(\text{CH}_3)\text{-P}(\text{P}^i\text{Pr}_2)\text{xant}(\text{P}^i\text{Pr}_2)]\}$ and $\text{IrH}_3\{\kappa^3\text{-P,O,P-}[\text{xant}(\text{P}^i\text{Pr}_2)_2]\}$ promote the activation of the B–B bond of two molecules of B_2cat_2 to give the tris(boryl) derivative $\text{Ir}(\text{Bcat})_3\{\kappa^3\text{-P,O,P-}[\text{xant}(\text{P}^i\text{Pr}_2)_2]\}$ via bis(boryl) intermediates $\text{IrX}(\text{Bcat})_2\{\kappa^3\text{-P,O,P-}[\text{xant}(\text{P}^i\text{Pr}_2)_2]\}$ ($\text{X} = \text{Cl}$ or H). The tris(boryl) complex displays a *mer* arrangement of the boryl groups in spite of the very strong *trans* influence of these ligands. The Ir–B bonds disposed mutually *trans* are ~ 0.1 Å longer than that disposed *cis* to the other two. 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 by $\sim 43\%$ in the longer bonds with respect to the shorter one, while the level of σ -bonding interaction diminishes only $\sim 8\%$. In summary, 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 website at DOI: 10.1021/acs.inorgchem.9b00339.

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

Accession Codes

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

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Notes

The authors declare no competing financial interest.

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