Bis(borylene) Complexes

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Towards Homoleptic Borylene Complexes: Incorporation of Two Borylene Ligands into a Mononuclear Iridium Species**

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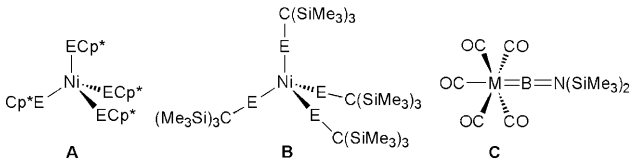
The incorporation of subvalent Group 13 ligands into the coordination sphere of transition metals has always been a challenging task, particularly in the formation of homoleptic complexes. Although metastable or sterically protected subvalent E^I (E = Al, Ga, In) precursors have become accessible during the last few decades,[1] for example, E^I halides,[1,2] $[\{Cp^*E\}_n]$ ($Cp^* = \eta^5$-C_5Me_5),[1,3] and $[\{EC(SiMe_3)_3\}_n]$,[1,4] stable and isolable boron congeners have still not been prepared. For this reason, only homoleptic transition-metal complexes with Al-, Ga-, and In-based ligands have so far been realized, for example, mononuclear $[Ni(ECp^*)_4]$ (**A**; E = Al, Ga)[5,6] and $[Ni\{EC(SiMe_3)_3\}_4]$ (**B**; E = Ga, In),[7,8] as well as numerous heteroleptic examples with two or more E^I ligands.[9]



The corresponding subvalent boron ligands, that is, borylenes, have only been generated directly in the coordination sphere of transition metals[10] to form species such as $[(OC)_5M{=}BN(SiMe_3)_2]$ (**C**; M = Cr, Mo, W).[11] To date, both mononuclear borylene complexes containing more than one borylene substituent as well as homoleptic borylene species have continuously resisted isolation. Nonetheless, borylene complexes have sparked increasing interest in fundamental organometallic research because of their close relationship with important organometallic compounds such as carbene, carbyne, and vinylidene complexes, and the similarity of the bonding properties of borylene and carbonyl ligands. Numerous experimental and computational studies have previously examined these bonding properties in detail.[10] It was thus shown that BR has stronger σ-donor and π-acceptor properties than CO, which makes the M–BR bond even more stable with respect to homolytic dissociation than the M–CO bond, but in turn it is kinetically labile due to the high polarity. Getting back to the series of related ligands mentioned above, the predominance of the CO and carbene ligands in organometallic chemistry is also manifested by the fact that homoleptic complexes have only been accessible with these two ligands. By contrast, the incorporation of two borylene or carbyne ligands into a mononuclear transition-metal complex has always proven problematic. While in the former case a suitable synthetic approach is still lacking,[12] the synthesis of bis(carbyne) species is further hampered by reductive coupling to form acetylenes, particularly with alkyl-substituted carbynes.[13] It has not yet been elucidated whether bis(borylene) complexes are resistant towards reductive coupling. In any case, it would require the availability of experimental data before this question could be clarified. We have been studying borylene complexes for more than a decade now, but all our efforts to synthesize a complex with more than one terminal borylene have so far failed.

Herein, we describe the successful generation and isolation of a long-sought after mononuclear, terminal bis(borylene) complex derived from the [Cp*Ir] half-sandwich fragment, which does not feature additional CO or phosphine ligands in the coordination sphere. We also use both structural data and computational results to address the question of how the borylene ligands affect each other, and eventually provide a preliminary evaluation of this aspect.

The iridium bis(borylene) complex $[(\eta^5$-$C_5Me_5)Ir\{BN(SiMe_3)_2\}_2]$ (**5**) is readily accessible by successive substitution of both CO ligands of $[(\eta^5$-$C_5Me_5)Ir(CO)_2]$ (**1**)[14] by the borylene moieties $\{BN(SiMe_3)_2\}$. Recently, we demonstrated that the corresponding monoborylene complex $[(\eta^5$-$C_5Me_5)(OC)Ir{=}BN(SiMe_3)_2]$ (**3**)[15] can be generated in a straightforward reaction under mild thermal conditions by borylene exchange between $[(OC)_5Mo{=}BN(SiMe_3)_2]$ (**2**)[11b] and **1** (Scheme 1).

Subsequent irradiation of **3** in the presence of a stoichiometric amount of $[(OC)_5Cr{=}BN(SiMe_3)_2]$ (**4**)[11a] in benzene at ambient temperature for 21 h afforded a mixture of the bis(borylene) complex **5**, the heterodinuclear species $[(\eta^5$-$C_5Me_5)(OC)Ir\{\mu$-$BN(SiMe_3)_2\}Cr(CO)_5]$ (**6**),[15b] and **3** in a ratio of approximately 9:6:1, as determined by ^1H NMR spectroscopy. Complex **5** was also obtained directly by photolysis of **1** with two equivalents of **4** in hexane for 20 h

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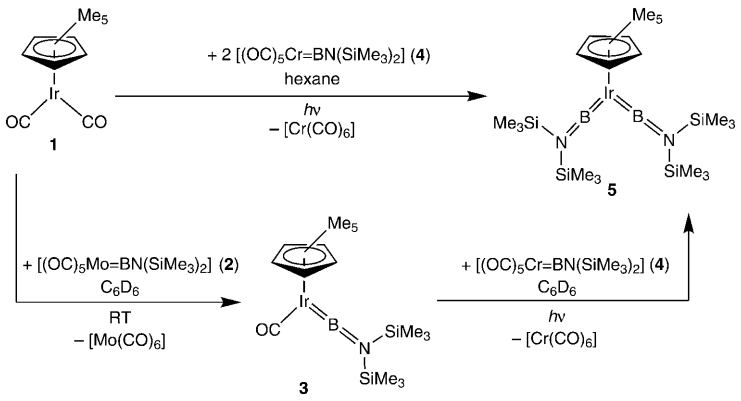
Supporting information for this article (Experimental Section including the synthesis, full characterization, and spectroscopic data of **5**) is available on the WWW under http://dx.doi.org/10.1002/anie.201004103.



Scheme 1. Formation of the terminal bis(borylene) complex **5**.

at ambient temperature, which is a much more convenient and selective route to the bis(borylene) species. The reaction can be easily monitored by $^{11}B\{^1H\}$ and ^1H NMR spectroscopy, which indicates that stepwise CO–borylene exchange occurs in the formation of **5**. Thus, after 4 h, the characteristic signals of precursor **4** ($\delta(^{11}B) = 92$ ppm; $\delta(^1H) = 0.14$ ppm)[11a] decreased in intensity, while those associated with intermediate **3** ($\delta(^{11}B) = 67$ ppm; $\delta(^1H) = 0.26$ ppm) increased concomitantly.[15a] After 11 h of irradiation, the bis(borylene) **5** ($\delta(^{11}B) = 69$ ppm; $\delta(^1H) = 0.37$ ppm) constituted the predominant species in solution. After work-up and crystallization from hexane, **5** was isolated as a colorless, moderately air- and moisture-sensitive crystalline solid in 64% yield. In addition, bis(borylene) **5** did not show any tendency to decompose by reductive elimination, as is observed for related bis(carbyne) species.[13] The NMR spectroscopic data for **5** in solution were consistent with our expectations: the ^{11}B NMR resonance at $\delta = 69$ ppm is found at 33 ppm higher field than that of **4** and falls in the typical range of aminoborylene complexes of late transition metals.[15a,16] Likewise, both the ^1H and ^{13}C NMR spectra feature only one set of signals for the $SiMe_3$ groups, which is in line with earlier results obtained for related half-sandwich aminoborylene species such as $[(\eta^5\text{-}C_5H_5)(OC)_3V{=}BN(SiMe_3)_2]$.[17]

The molecular structure of **5** was ascertained by X-ray diffraction analysis (Figure 1).[18] Complex **5** adopts an overall "two-legged piano stool" geometry in the solid state, which is typical for complexes of the type $[(\eta^5\text{-}C_5R_5)ML_2]$. Although the structure is reminiscent of that of $[(\eta^5\text{-}C_5Me_5)(OC)Ir{=}BN(SiMe_3)_2]$ (**3**), closer inspection reveals some noteworthy differences in regard to the geometry of the {Ir=B=N} moieties in **3** and **5** (Table 1). Thus, the Ir–B bonds in **5** (1.864(3) and 1.863(3) Å) are shortened by 3 pm with respect to that in **3** (1.892(3) Å). By contrast, the B–N bonds of 1.398(3) and 1.393(3) Å in the former are elongated by approximately the same amount compared to the B–N bond in **3** (1.365(4) Å). In line with previous theoretical results by Pandey and Musaev for compounds $[(\eta^5\text{-}C_5H_5)(OC)Ir{=}BN(SiR_3)_2]$ (**3′**: R = H; **3″**: R = Me),[19] **3** and **5** can be considered typical examples of terminal aminoborylene complexes.[11b,15,20] A similar trend can be observed for the C–O bonds in the carbonyl species **1**[14b] and **3** upon CO–borylene exchange (Table 1). The Ir–C bond in **3** (1.824(3) Å) is 2 pm shorter than those in **1** (1.841(5) and 1.847(6) Å), while the respective C–O bond length in **3** (1.170(3) Å) slightly exceeds those in **1** (1.157(7) and 1.147(7) Å). Both trends thus point in the same direction and indicate the presence of stronger Ir–E (E = C, B) and weaker E–X (X = O, N) bond interactions with an increasing number of borylene ligands. However, the differences observed are quite small, and the solid-state data alone appear to be insufficient to unequivocally prove these conclusions.

For this reason we studied the bonding situation in the simplified model complexes **1′**, **3′**, and **5′** (Me groups substituted by H) by quantum chemical calculations.[21] This provided more persuasive evidence for the noticeable electronic influence of the borylene ligand. The optimized structures were in fairly good agreement with experimentally available data, with the calculations overestimating the interatomic distances by only 1–3 pm. As summarized in Table 1, the bond

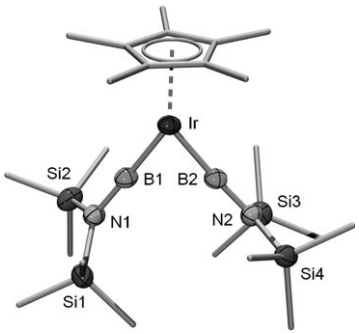


Figure 1. Molecular structure of **5** in the solid state. Thermal ellipsoids are set at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Ir–B1 1.864(3), Ir–B2 1.863(3), B1–N1 1.398(3), B2–N2 1.393(3); Ir-B1-N1 176.5(2), Ir-B2-N2 178.6(2).

Table 1: Selected experimental structural data as well as calculated BDE and WBI values of $[(\eta^5\text{-}C_5R_5)Ir(CO)_2]$ (**1**: R = Me; **1′**: R = H), $[(\eta^5\text{-}C_5R_5)(OC)Ir{=}BN(SiR_3)_2]$ (**3**: R = Me; **3′**: R = H), and $[(\eta^5\text{-}C_5R_5)Ir\{BN(SiR_3)_2\}_2]$ (**5**: R = Me; **5′**: R = H).

		1[14b]	**3**[15a]	**5**
bond lengths [Å]	Ir–C1	1.841(5)	1.824(3)	–
	Ir–C2	1.847(6)	–	–
	C1–O1	1.157(7)	1.170(3)	–
	C2–O2	1.147(7)	–	–
	Ir–B1	–	1.892(3)	1.864(3)
	Ir–B2	–	–	1.863(3)
	B1–N1	–	1.365(4)	1.398(3)
	B2–N2	–	–	1.393(3)
		1′	**3′**	**5′**
BDE [kJ mol^{-1}]	Ir–C	293	316	–
	Ir–B	–	456	470
WBI	Ir–C	1.08	1.12	–
	Ir–B	–	1.25	1.25
	C–O	2.06	2.01	–
	B–N	–	1.05	1.01

dissociation energies (BDE) of the Ir–B bonds in **3′** and **5′** are significantly higher than those of the Ir–CO bonds in **1′** and **3′**, respectively, which accounts for the well-documented strength of the iridium–boron bond. Even more importantly, the calculations support the assumption that borylene ligands strongly affect the coligands in these "piano-stool" complexes as a result of their enhanced σ-donor properties. This is manifested in the strengthening of the Ir–E bonds by 14 and 23 kJ mol^{-1} for carbon and boron, respectively, upon successive replacement of CO by borylene ligands (for example, BDE(Ir–CO): **1′** 293 kJ mol^{-1}, **3′** 316 kJ mol^{-1}; BDE(Ir–B): **3′** 456 kJ mol^{-1}, **5′** 470 kJ mol^{-1}). Stronger Ir–E interactions in combination with weaker E–X bonds in the series **1′**→**3′**→**5′** could also be extracted from the analysis of the corresponding Wiberg bond indices (WBI),[22] thus substantiating the assumptions derived from the solid-state structures. Thus, the experimental and theoretical data both support the presence of an observable electronic influence of the borylene ligand on the other coligands. However, these results should be interpreted carefully, because of the rather small differences observed. Since there is little experimental data available for such systems, we are only able to present our first efforts towards the elucidation of this effect.

In conclusion, we have described the next logical step towards the synthesis of homoleptic transition-metal complexes containing subvalent borylene ligands, that is, the isolation of the mononuclear bis(borylene) species [(η^5-C_5Me_5)Ir{$BN(SiMe_3)_2$}$_2$] (**5**). This complex was prepared under photolytic conditions by borylene transfer from either the monoborylene [(η^5-C_5Me_5)(OC)Ir=$BN(SiMe_3)_2$] (**3**) or preferably from [(η^5-C_5Me_5)Ir(CO)$_2$] (**1**), and is the first example of a complex in which two borylene ligands are bound in a terminal fashion to the same metal center. In contrast to the related bis(carbyne) species, bis(borylene) **5** does not show any tendency to decompose. Analysis of both the structural and theoretical data for **1**, **3**, **5**, and simplified model compounds allowed a preliminary interpretation of the electronic influence of the borylene ligand on the coligands, that is a strengthening of Ir–E interactions (E = B, C) with an increasing number of borylene ligands, and a concomitant weakening of the E–X bonds (X = N, O). Future work in our research group will focus on the preparation of additional bis(borylene) species, which will allow for a more detailed and more reliable investigation of this aspect. Inspired by these results, we also intend to intensify our approach to the ultimate goal of isolating a homoleptic borylene complex.

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