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Resisting B—H oxidative addition: The divergent reactivity of the *o*-carborane and carba-*closo*-dodecaborate ligand substituents

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ABSTRACT

Here, we report a study of two isoelectronic Ir(I) complexes supported by different carboranyl phosphines, bearing either *o*-carborane or carba-*closo*-dodecaborate ligand substituents. The neutral Ir(I) complex containing the *o*-carboranyl phosphine ligand is not isolable and undergoes spontaneous B—H cyclometalation to afford an Ir(III) hydride. In contrast, the anionic Ir(I) complex supported by a phosphine with a carba-*closo*-dodecaborate ligand R-group is stable towards B—H activation. This divergent reactivity has important implications for the design of carborane containing ligands for catalysis. Both compounds are fully characterized by multinuclear NMR spectroscopy, HRMS spectrometry, and single crystal x-ray diffraction studies.

Introduction

The proliferation of contemporary homogenous catalytic methods is largely due to the availability of a diverse array of ligand architectures. Due to their shape and 3-dimensional aromaticity, icosahedral carboranes [1] are an interesting alternative to classical alkyl and aryl ligand substituents. Soon after the discovery of *o*-carborane [2] **1** (Fig 1, left) in 1963 a carboranyl phosphine ligand [3] and complex [4] were reported by Smith. Kumada [5] was the first to implement such ligands in homogenous catalysis, but these and all subsequent systems containing *o*-carborane **1** fragments have not yielded catalysts [6] that surpass the activity of systems supported by ubiquitous trialkyl or triaryl phosphines. Perhaps this non-competitive catalytic behavior is due to the decomposition of the cluster via well-known B-vertex extrusion [1b,7] and B—H cyclometalation reactions. Hawthorne [8] was the first to observe intramolecular B—H oxidative addition of an *o*-carboranyl phosphine, as well as analogous intermolecular reactions with unsubstituted dicarbaborane icosahedra at an Ir(I) center.

In contrast to *o*-carborane **1**, the isoelectronic and weakly coordinating carba-*closo*-dodecaborate anion [1e] **2** (Fig 1, center) is not susceptible to B-vertex extrusion reactions and is renowned for its inert properties, particularly when polyhalogenated [1h,9]. We recently reported the first utilization of the carba-*closo*-dodecaborate as a ligand substituent for a transition metal-based catalyst [10]. Notably, this zwitterionic Au(I) complex, featuring an anionic carboranyl phosphine, is far more active than all known systems for the hydroamination of alkynes. In addition, we reported an unusually stable pseudo-low coordinate zwitterionic Ir(I) compound **3** (Fig 1, right) that does not undergo spontaneous intramolecular B—H oxidative addition [11]. Although not identical, **3** is reminiscent of Hawthorne's unstable Ir(I) complexes [8] and its behavior suggests that ligands bearing a carba-*closo*-dodecaborate substituent [12] are inherently more resistant to B—H activation. Given our interest in catalyst design we are seeking stronger evidence that the carba-*closo*-dodecaborate ligand substituent has enhanced chemical stability towards B—H oxidative addition. Here, we report such a study by the preparation and analysis of two isoelectronic iridium (I) complexes containing phosphines with *o*-carborane and carba-*closo*-dodecaborate moieties, respectively. Where the former *o*-carborane containing complex is not isolable and spontaneously undergoes cyclometalation at one of the B—H vertices, the carba-*closo*-dodecaborate analogue is stable.

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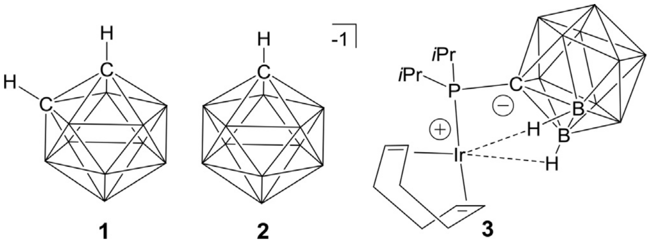

Fig. 1. *o*-Carborane **1**, carba-*closo*-dodecaborate anion **2**, and zwitterionic Ir complex **3**. Unlabeled vertices = B–H.

Results and discussion

Reacting the known [13] *o*-carborane phosphine **4** with ½ an equivalent of (ClIr(COD))$_2$ in hexane solvent results in a color change from light orange to red orange and subsequent formation of a precipitate (Fig 2, next page). Based on Hawthorne's prior observations [8], it was predicted that the ensuing Ir(I) complex **5** would be unstable towards cyclometalation and produce the corresponding Ir(III) complex **6**. Indeed, analysis of the precipitate by ^{1}H NMR spectroscopy shows clean formation of an iridium hydride at −16.42 ppm (d, $^{2}J_{P-H} = 13.1$ Hz), suggesting cyclometalation of the *o*-carborane cluster. The coupling constant is consistent with an iridium (III) hydride disposed *cis* to a phosphine (range $^{2}J_{P-H}$ from 10 to 20 Hz) [8]. In addition to the expected ^{1}H signals for the phosphine *i*Pr-groups and COD protons, two carborane C–H resonances appear in a 4:1 ratio. The presence of two carborane C–H signals suggests the formation of a diastereomeric mixture (**6**′, **6**″), resulting from competitive B–H oxidative addition at the B3 and B6 positions (Fig 2). Such competitive cyclometalations have been observed previously [14] with other metals, and occur preferentially at B3/B6 positions rather than at B4/B5, since the B3/B6 boron atoms are more activated (attached to 2-carbon atoms). All other ligand ^{1}H resonances from the two diastereomers **6**′ and **6**″ are superimposed by coincidence. Analysis of the ^{31}P NMR spectra also shows a 4:1 mixture of compounds and is in agreement with our assignment. The ^{11}B NMR spectrum is uninstructive due to the multitude of broad overlapping resonances, which cannot be resolved. However, the solution and solid-state infrared spectra of complexes **6** show bands typical for B–H stretches of *o*-carborane (2460–2625 cm^{-1}), as well as the presence of an Ir–H absorbance at 2223 cm^{-1} [8].

A single-crystal X-ray diffraction study of one of the diastereomers **6**″ confirms that cyclometalation occurs adjacent to the two carborane carbon atoms (Fig. 2, bottom right). Compound **6**″ adopts a distorted octahedral geometry with the hydride, which was located from the difference electron density map, *cis* to the phosphine ligand. The Ir–P, Ir–B and Ir–Cl bond lengths are 2.320(5), 2.094(2) and 2.498(5) Å, respectively. The cyclooctadiene C–C double bond lengths *trans* to the phosphine (C1–C2 = 1.384(3) Å) and metalated B-vertex (C3–C4 = 1.362(3) Å) are in the typical range (1.35–1.44) for olefins coordinated to Ir [15].

We next turned our attention to preparing a complex bearing a phosphine with a carba-*closo*-dodecaborate substituent, which is isoelectronic with the unstable complex **5**. We predicted that treating the previously reported [11] zwitterion **3** with a nucleophilic chloride source should produce the anionic isoelectronic complex **7** (Fig 3). Thus, treatment of solution of **3** dissolved in C_6H_5F with five equivalents of NMe_4Cl resulted in the formation of an orange precipitate **7**. Analysis of the precipitate by ^{31}P NMR shows the formation of a single new product **7** (s, 32.95 ppm). Importantly, the ^{1}H NMR spectrum of **7** shows no Ir–H resonance, suggesting that the carba-*closo*-dodecaborate substituent is not cyclometalated. Moreover, as indicated by ^{11}B NMR spectroscopy (three resonances 1:5:5 ratio; 5:5 overlapping) the local C_{5v} symmetry of the cluster is retained, confirming that cyclometalation has not occurred. In addition, solution I.R. shows no Ir–H absorbance, ruling out the possibility of a rapid reversible cyclometalation process faster than the NMR time scale.

A single-crystal X-ray diffraction structure confirms the identity of the square planar Ir (I) complex **7** (Fig 3, previous page). While the Ir–P bond length (2.371(7) Å) is similar to complex **6**, the Ir–Cl (2.394(8) Å) and olefin bond lengths (C1–C2 = 1.401(5) Å, C3–C4 = 1.422(5) Å) are comparatively contracted and elongated, respectively. These observations can be explained by the decrease in coordination number and oxidation state, which allows for stronger M-L σ and π interactions. The closest B–H approach to the Ir center is 2.83 (Ir–H1) which is outside the range of typical Ir B–H

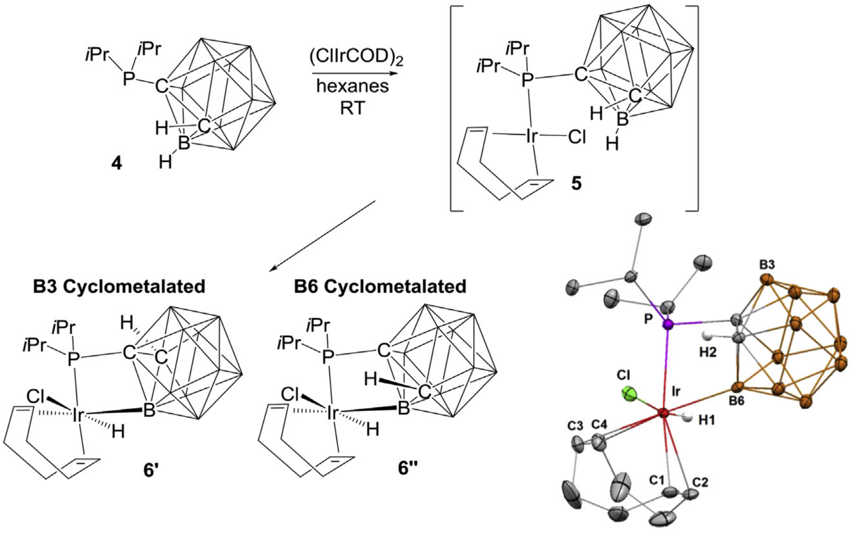

Fig. 2. Synthesis of the cyclometalated Ir complexes **6**. Solid-state structure of diastereomer **6**″. Color code: Gray = C, white = H, violet = P, red = Ir, brown = B, green = chlorine. Unlabeled vertices = B–H. Notable bond lengths (Å): Ir–P = 2.320(5); Ir–B = 2.094(2); Ir–Cl = 2.498(5); C1–C2 = 1.384(3); C3–C4 = 1.362(3). Selected bond angles (°): B–Ir–P = 72.1; P–Ir–Cl = 90.2. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)