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## COMMUNICATION

# Metal-induced B-H bond activation: reactions between half-sandwich Ir and Rh complexes with carboranylthioamide

Bin Xu, Yin-Ping Wang, Zi-Jian Yao, Guo-Xin Jin\*

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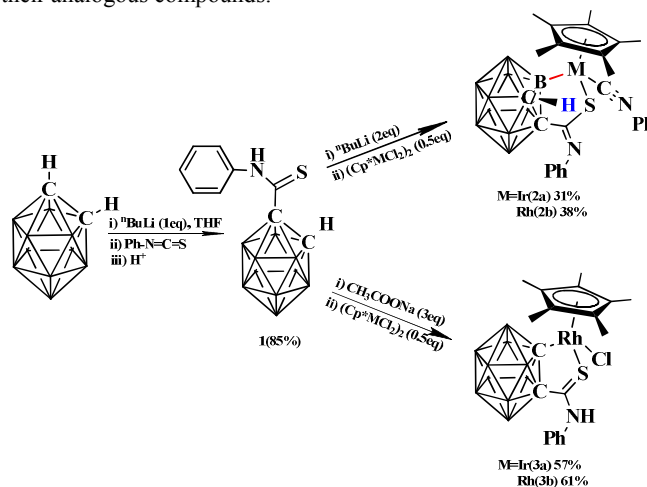
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**Novel half-sandwich metal (Ir, Rh) complexes constructed from carboranylthioamide ligands containing an unexpected metal-boron bond were synthesized and characterized. The strong base *n*-butyllithium is demonstrated of necessity in the reaction process.**

In the past decades derivatives of 1,2-dicarba-*closo*-dodecaborane have raised considerable interest in both their fundamental properties and their wide-ranging potential applications.<sup>1</sup> The rigid backbone, high thermal stability and *pseudo*-aromatic characters of *ortho*-C<sub>2</sub>B<sub>10</sub>H<sub>12</sub> make it an excellent candidate for constructing novel metal complexes. Thus the development of a new type of carborane ligand with functional groups capable of covalent incorporation into a variety of different structures, has become a particularly compelling research challenge.<sup>2</sup> Carboranylthioamide, which arises from a bifunctional donor group isothiocyanate (R-N=C=S) and the rigid carborane unit, is one of the interesting subclasses investigated and is attracting an increasing attention.<sup>3</sup>

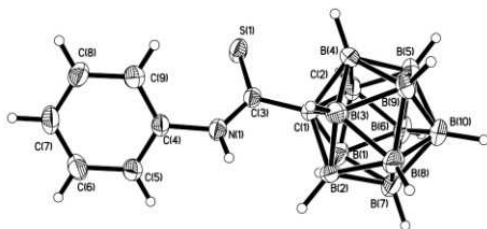
Thioamides are pervasive in organic pharmaceuticals, given the existence of electronegative sulfur and nitrogen atoms, and are usually able to undergo various reactions such as electrophilic additions to give intermediate which have demonstrated vast potential for application in pesticide and pharmaceutical syntheses.<sup>4</sup> However, to date studies of carboranyl-based thioamides and carboranylthioamides are still rare, and even fewer reports on the modification and functionalization exist, although there are a number of papers concerning the same group carboranylamides complexes.<sup>5</sup> Due to our continuing interest in carborane-based ligands and half-sandwich transition metal complexes, in this paper we conducted for the first time investigations into the synthesis, structure and reactivity of a new type of carboranylthioamide ligand, **1** (Scheme 1), from which half-sandwich transition-metal complexes **2a** and **2b**, containing unexpected M-B bonds, were successfully isolated and structurally characterized.

Carboranylthioamide **1** was readily accessible in a straightforward manner by insertion of phenylisothiocyanate into the Li-C bond of 1-Li-1,2-C<sub>2</sub>B<sub>10</sub>H<sub>11</sub>, which can be prepared by *o*-carborane and *n*-BuLi. The compound **1** was obtained as yellow, block-shaped crystals in 85% isolated yield (Scheme 1). The X-ray analysis of **1** suggests that the newly-formed carboranyl ligand contain an amine fragment instead of the original imine group after hydrolysis (Fig. 1). A strong IR band at 3405 cm<sup>-1</sup> is consistent with the presence of a N-H functionality in **1**, the bond lengths of 1.332 Å (C-NH) and 1.637 Å (C=S), in the phenylisothiocyanate functionality are comparable with the corresponding distances in their analogous compounds.<sup>6</sup>



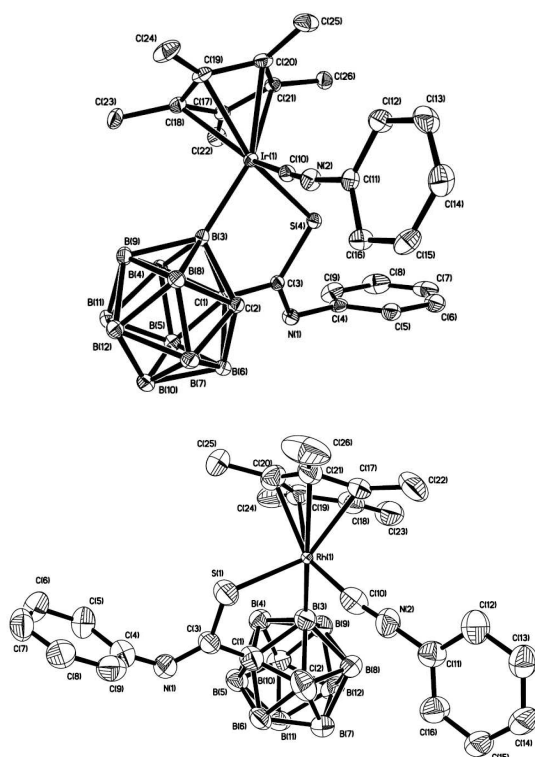
**Scheme 1:** Synthesis of carboranylthioamides and C,S binding mode complexes

To further explore the reactivity of this *N*- and *S*-donors, stable transition metal complexes [Cp\*<sub>2</sub>MCl<sub>2</sub>] (M = Ir, Rh) were treated with **1**. After the addition of 0.5 equiv of dimeric iridium and rhodium compounds to carboranylthioamides in the condition of *n*-



**Fig.1** Molecular structure of ligand **1** with 30% probability ellipsoids.

BuLi (2eq), the reactions proceeded smoothly at room temperature to give the corresponding cyclometalated complexes **2a** and **2b** (Scheme 1). The two products were both purely isolated and their structures were determined by X-ray crystallography (Fig. 2). From the structures demonstrated (Fig. 2), it clearly shows that the complex **2a, b** bears an M-B-C-C-S chelate five-membered ring and a C≡NPh ligand. In comparison with the general carbon-substituted five-membered carboranes,<sup>7</sup> the compounds **2a, b** derive from an unprecedented B-H activation process, thus it is the first time that carboranylthioamide complexes involving B-H activation have been investigated, and we report here the reactions and structural characterization of them and discuss possible mechanisms for the formation of them.



**Fig.2** Molecular structure of **2a** (Ir) and **2b** (Rh) with 30% probability ellipsoids. All hydrogen atoms were omitted for clarity.

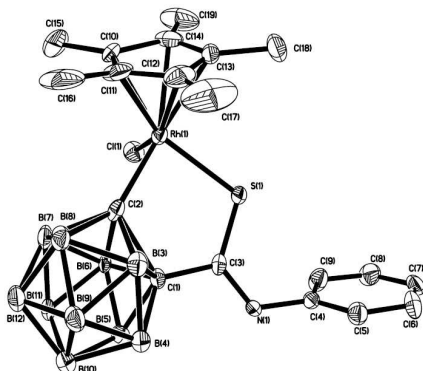
The first indication of the successful cyclometalation in **2a** and **2b** via M-B bond formation is the appearance of singlet resonances in the <sup>11</sup>B NMR spectra at -12.39 ppm and -12.30 ppm, respectively, which are characteristic of metal-bound boron nuclei.<sup>8</sup> In addition, in the relevant <sup>1</sup>H NMR spectrum, two singlets at δ 4.64

and δ 4.63 for **2a** and **2b** can be ascribed to the C<sub>cage</sub> hydrogen signals. The corresponding signal integrals, together with elemental analysis results, suggest the formation of a complex of formula Cp\*M(C≡NPh)(κ<sup>2</sup>(B,S)-1-PhNCS-1,2-C<sub>2</sub>B<sub>10</sub>H<sub>10</sub>). The FT-IR study of the complexes reveals ν(C≡N) bands at 2920 cm<sup>-1</sup> and 2917 cm<sup>-1</sup> for **2a** and **2b** with peak intensities similar to those observed in literature.

Coordination geometry of the Ir (III) center in molecular structure **2a** (Fig. 2) is a distorted pyramidal arrangement. Assuming that Cp\* serves as a three-coordinate ligand, the molecular structure **2a** can be regarded as a six-coordinate with a three-legged piano-stool motif, in which the three legs are one sulfur atom, one boron atom of the metalated *o*-carboranyl unit, and one phenyl isocyanide ligand, respectively. The Ir(1)-C(10)-N(2) angle of 177.2 (3)° and C(10)-N(2)-C(11) angle of 169.1 (3)° within the nitrile groups demonstrate that the metal, carbon, and nitrogen atoms are almost in a linear configuration, and the phenyl nitrile most likely occupies the vacant locations opposite the iridasulfanyl cycle in a cisoid fashion. In addition, the five-membered iridasulfanyl cycle of **2a** shows a folding along the Ir(1)-C(3) vector with a dihedral angle of 19.84° between the Ir(1)-B(3)-C(1)-C(3) and Ir(4)-S(1)-C(3) planes, which is probably due to the great steric crowding around the iridium metal center. The Ir-B(3) distances of 2.090(3) Å (**2a**) and 2.096(14) Å (**2b**) are generally the same as those found in our previous analogous cyclometalated complexes (about 2.120 Å),<sup>9</sup> the slightly shortened bond lengths implying a stronger interaction between the metal and the boron atom.

Metal-induced B-H activation is well-known in carborane chemistry. Hawthorne *et al.* have previously reported a number of metallaborane and metallacarborane complexes involving Rh-*H*-B bonding, among which multiple stable B-M σ bonds can be readily formed between the central metal and terminal boron atoms.<sup>10</sup> In contrast, for many *exo*-metalated or cyclometalated type of complexes containing metal-boron bonds,<sup>8,11</sup> which are generally synthesized as intermediates in catalysis or ligand functionalization, M-*H*-B bonding seemed not to be particularly stable (mainly owing to the poor donating ability of the terminal B-H bond), thus this is the first time that B-H activation carboranylthioamide complexes have been synthesized, the reaction condition, coordination species could all influence the process. Except for the interactions between the metal and boron atom, as mentioned above, during the addition of carboranylthioamide fragment to the metal centre, another molecule of phenyl isocyanide is produced in situ and takes up the one remaining corner of the three-legged geometry (Fig. 2). As for the formation of phenyl isocyanides in **2a** and **2b**, although there is no definite mechanism documented for the transformation of thioamides and isocyanides, it is reported that thioamide derivatives can be converted to isothiocyanate (R-C=N=S) in the presence of *n*-BuLi.<sup>12</sup> Combining with the reactions conducted, thus we propose that the formation of isocyanides may be associated not only with conversion into isothiocyanate but also metal-mediated desulfurization of isothiocyanate, and the latter result in the C=S cleavage reaction of S-containing heterocumulenes.<sup>13</sup> To further support our suspicion and examine the stabilizing influence of *n*-BuLi on the reaction, we performed the parallel reaction (Scheme 1) by adding solid sodium acetate into dry CH<sub>2</sub>Cl<sub>2</sub>. These reactions

were found to proceed only in the presence of strong base (*n*-BuLi), whereas under the condition of the weak base sodium acetate, the reaction gave the *C,S*-coordination mode complex **3** through C-H bond activation rather than complex **2**.



**Fig. 3** Molecular structure of complex **3b** (Rh) with 30% probability ellipsoids. All hydrogen atoms were omitted for clarity.

The *C,S*-coordinated complexes **3a, b** are conveniently prepared by reacting the  $[\text{Cp}^*\text{MCl}_2]_2$  ( $\text{M} = \text{Ir}, \text{Rh}$ ) with carboranylthioamide **1** in  $\text{CH}_2\text{Cl}_2$ , followed by addition of three equivalents of sodium acetate at  $25^\circ\text{C}$  (10h) (Scheme 1). Chromatographic separation of the crude product and subsequent diffusion recrystallization afforded orange, sheet-like crystals, which are highly soluble in polar solvents and stable to air. The  $^1\text{H}$  NMR spectrum of complex **3a, b** exhibits signals confirming the presence of  $\eta^5\text{-C}_5\text{Me}_5$ , amino, and B-H groups. The corresponding signal integrals, together with elemental analysis results, suggest the formation of a complex of formula  $\text{Cp}^*\text{MCl}(\text{1-PhNHCS-1,2-C}_2\text{B}_{10}\text{H}_{10})$  ( $\text{M} = \text{Ir}, \text{Rh}$ ). The IR study of complex **3a, b** reveals peaks at  $3362\text{ cm}^{-1}$  and  $3321\text{ cm}^{-1}$  for N-H stretching vibrations respectively, similar to that of the parent ligand **1**. The crystal of **3a** were not obtained, but an X-ray structure of **3b** (Fig. 3) revealed the expected three-legged piano stool geometry, in which the phenyl isocyanide group is replaced by one chloride. The metal-carbon and metal-sulfur bond lengths are similar to the values reported for the classical  $\text{MC}_2\text{X}_2$  five-membered ring.<sup>14</sup> All those results confirmed *n*-butyllithium to be highly influential in the process of producing the phenyl isocyanide ligand. Moreover, in comparison with complex **2a**, the distortion angle between the  $\text{Ir}(1)\text{-C}(1)\text{-C}(3)\text{-S}(1)$  and  $\text{Rh}(1)\text{-C}(1)\text{-C}(2)$  planes in complex **3b** decrease to  $9.09^\circ$ , thus complex **3b** is less sterically congested since their five-membered rings take up smaller area. It is postulated that for complexes **2a, b** the nitrile fragments and sulfur atoms might both make the iridasulfanylacycle more flexible so that the metals are able to get close to the carborane cage to activate B-H bonds.

## Conclusions

In summary, we have explored the syntheses, structures and reactivity of a novel *mono*-carboranylthioamide ligand. A series of B-H activation carboranylthioamide metal complexes were synthesized and characterized. This is the first time that B-H activation carboranylthioamide compounds are investigated. The addition of strong base (*n*-BuLi) is noteworthy, since it clearly

indicates that its presence is necessary to initiate B-H activation in *o*-carboranes. The reaction conditions and coordination species all play important roles. Exploration of the scopes and implications of this desulfurization process are underway, and it encourages us to study further on the mechanisms for different types of metal-induced B-H activations.

## Notes and references

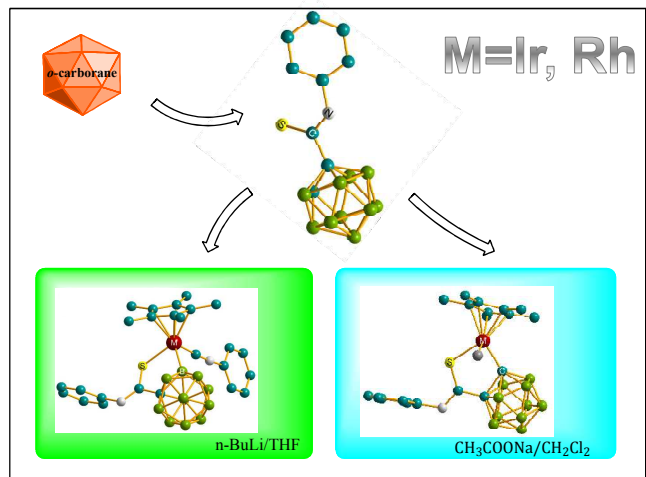
Shanghai Key Laboratory for Molecular Catalysis and Innovative Materials, Department of Chemistry, Fudan University, Shanghai 200433, P. R. China; Fax: +86-21-65641740; Tel: +86-21-65643776; E-mail: gxjin@fudan.edu.cn

† Electronic Supplementary Information (ESI) available: Experimental procedures, characterization and crystallographic data. CCDC 1031988 (**1**), 1031989(**2a**), 1031990(**2b**) and 1031991(**3b**). For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b000000x/.

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## Toc Graphic:



## Text:

A series of half-sandwich iridium and rhodium complexes were prepared from carboranylthioamides, in which metal-induced B-H activation processes occur in the presence of strong base *n*-butyllithium.