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# Nucleophilic addition of carborane anion to Ir, Rh-coordinated Cp* ring: C–C bond formation accompanied by reduction of metal center†

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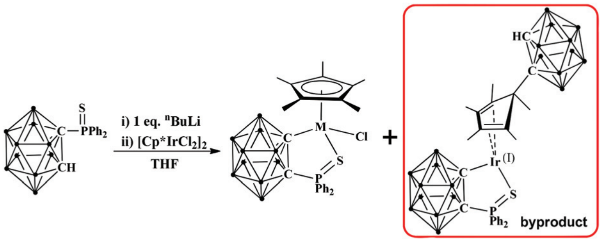
**Reaction of carboranyl anion or its thiolate derivative with a fully-substituted Cp*-based group 9 (Ir, Rh) metal complex affords respectively a C–C bond formation complex and a salt metathesis product. This example represents the first nucleophilic addition attempt in the area of M-Cp* chemistry.**

Nucleophilic ($Nu^-$) addition of carbanions to the arenes in 18-electron transition-metal complexes (such as ($\eta^6$-arene)$Co(CO)_3$ and ($\eta^6$-arene)$Fe^+Cp$) has been used successfully as a specific synthetic application because electron withdrawal by the transition-metal unit of these complexes renders the arene ligand susceptible to nucleophilic attack.[1] In some $Co^2$ and $Fe^3$ dicationic series, the successive addition of two distinct dianionic carbanions should provide heterobifunctional cyclohexadienyl complexes. These types of reactions are easily influenced and restricted by the nature of the nucleophile, arene and solvent. Carbon-based and other strong nucleophiles such as $H^-$ and $CN^-$ have attracted the most intensive study and addition reactions of $Nu^-$ often proceed in the unsubstituted arene site.[4]

The research on half-sandwich transition metal complexes based on various substituted-carboranyl ligands is of great interest because of the excellent electronic and steric effects of the bulky cage.[5] We previously reported the reactivity of monophosphine *o*-carborane sulfide towards half-sandwich iridium and rhodium complexes. During that study a small amount of byproduct **1** was obtained occasionally in the isolation of the C,S-coordination mode iridium complex **A** (Scheme 1).[6] The obtained complex **1** is unexpected: in fact, it is known that the cyclopentadienyl group not only is strongly coordinated to the metal, but it is generally also rather inert. The novel structure of this byproduct has attracted our attention. We speculated that this complex was generated by the direct nucleophilic addition of carboranyl anion to complex **A**. The analogous reaction was reported by Basato *et al.*[4j] In that example, the Cp ring in $[RuCl(Cp)(PPh_3)_2]$ underwent an apparent nucleophilic attack by the carbanion $carb^-$ (Hcarb = 2-Me-1,2-dicarba-*closo*-dodecaborane), to give an $H^-/carb^-$ exchange process, which is favored by coordination of the hydride to the ruthenium center. Although reactions of electron-rich metal centers in cyclopentadienyl ruthenium complexes with nucleophilic reagent carboranyl anions have been reported,[4k,l] no examples have shown the addition reactions of group 9 metal complexes with carboranyl anions. Moreover, activation of a fully-substituted aromatic Cp* fragment has been scarcely reported, because of its high electron density and crowded steric effects. Therefore we believe that this paper represents a successful addition attempt in the area of M-Cp* (M = Ir, Rh) chemistry.



**Scheme 1** Synthesis of C,S-chelated complex A.

As mentioned above, the unexpected complex **1** was isolated as the byproduct during the synthesis of complex **A**. In order to confirm our speculation of the nucleophilic addition reaction, we have investigated reactions of the C,S-coordination mode complex **A** or the analogous rhodium complex **B** with nucleophilic reagent carboranyl lithium. As shown in Scheme 2, carboranyl lithium was added slowly to the solution of **A** or **B** at low temperature, the corresponding addition products **1** and **2** were generated *via* an intramolecular redox in moderate yields after purification by silica chromatography. They are soluble in organic solvents, such as toluene, $CH_2Cl_2$,

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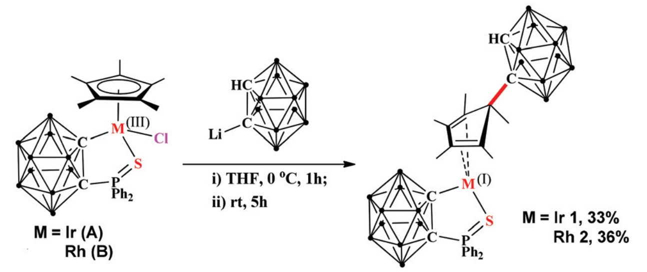


Scheme 2 Nucleophilic reactions of carboranyl lithium with C, S-chelated half-sandwich complexes.

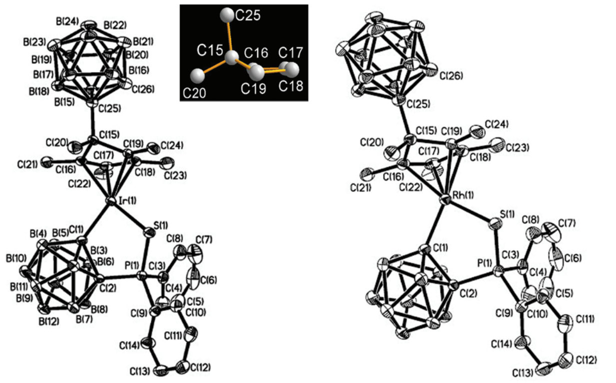
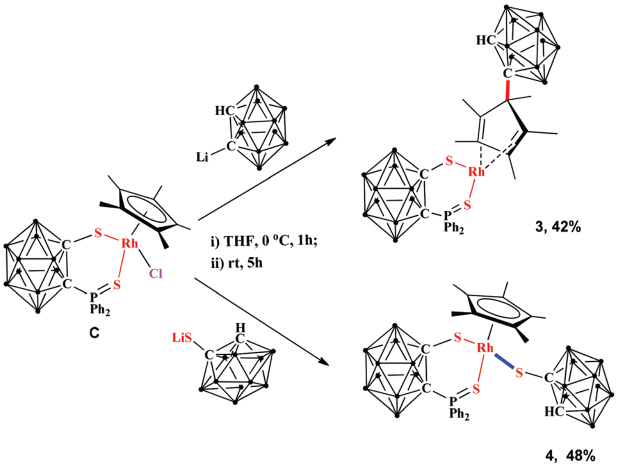


**Fig. 1** Molecular structures of **1** (left) and **2** (right) with 30% probability ellipsoids. (H atoms were omitted.)

and CHCl$_3$, and mostly insoluble in *n*-hexane or diethyl ether. The two complexes are very stable in their solid state, but showed slow decomposition in solution. Because of the formation of the C–C bond, the $^1$H NMR spectrum of complex **1** showed that the resonances of the methyl groups of Cp* was split into three single peaks at $\delta$ 1.53, 1.81, 2.00 ppm. One resonance at about $\delta$ 59.7 ppm was observed in the $^{31}$P NMR spectrum of **1**, which is very similar to that of the starting material **A**. The IR spectrum displays a typical strong and broad characteristic B–H absorption at approximately 2565 cm$^{-1}$, and the absorption at 625 cm$^{-1}$ is ascribed to P═S bond vibrations. The NMR and IR data of **2** is similar to that of **1**.

X-ray structure analysis for **1** and **2** confirmed that they are isomorphous. For complex **1**, the lengths of Ir(1)–C(1) (2.087(5) Å) and S(1)–Ir(1) (2.334(15) Å) bonds are slightly shorter than the corresponding lengths of **A**, and the C(1)–Ir(1)–S(1) angle increased accordingly (from 89.0° to 91.2°). The P–S bond length (2.007(19) Å) is almost identical to that of **A**. The conjugated system of the Cp* ring was destroyed to generate the six-substituted cyclopentadienyl group due to the new C–C bond formation. The longer bond length of C(15)–C(16) (1.555(7) Å) than that of C(16)–C(17) (1.421(8) Å) also indicates the five carbon atoms of this ring are not equivalent. Correspondingly, the absolutely planar five-membered ring was folded with the dihedral angle of 31.3° between the planes of C(15)–C(16)–C(19) and C(16)–C(17)–C(18)–C(19), and the C(25)–C(15)–C(20) angle of 110.4° agrees well with the tetrahedral geometry of the sp$^3$ hybrid C(15) atom (Fig. 1, inset). A similar structural feature was also observed in complex **2**. Interestingly, we found that the Ir(III) center of **A** was reduced to Ir(I) in complex **1** *via* an intramolecular redox, which is scarcely observed in previous studies. According to the reaction mechanism,[4l] the last step of a H-shift does not occur because there is no H atom in the Cp* fragment, and this may be the reason for the metal reduction. The distorted octahedral geometry of the iridium center was transformed to a tetrahedral geometry because of the removal of the chloride ion. To our knowledge, nucleophilic additions generally occurred on the unsubstituted site of the aromatic group, and this is the first example of a fully-substituted Cp* complex employed in this type of reaction. This result may be ascribed to the unique carboranyl anion: its strong basicity[7] lets it serve as a carbanion-bearing electron-withdrawing group like in nitriles; on the other hand, the high steric hindrance may force the attack on the Cp* ring, instead of the metal center. Moreover, another two carbanions LiPh or $^n$BuLi were also used as nucleophiles; unfortunately, only some unidentified products were obtained, which indicates the stabilization effect of the bulky carborane cage.

Besides the C,S-mode complexes **A** and **B**, the addition reaction of the S,S-mode rhodium complex **C** with carboranyl lithium also occurred smoothly (Scheme 3). Similar to **1** and **2**, the $^1$H NMR spectrum of **3** showed that the resonances of the methyl groups of Cp* were split. The structure of complex **3** is shown in Fig. 2. The three-legged piano stool geometry of rhodium no longer exists because of the removal of the chloride ion. The metal center was also reduced by the carboranyl anion *via* an intramolecular redox reaction, and the six-coordinate Rh(III) complex was transformed to the four-coordinate Rh(I) complex. The two Rh–S bond lengths are almost the same as each other. We explored the reactivity of the B,S,S-coordinated Ir complex in this reaction,[6] however no positive result was obtained, which may indicate the removed group plays an important role in this reaction.



Scheme 3 Reactivity of rhodium complex **C** with different nucleophiles.

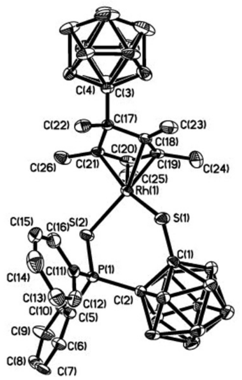


**Fig. 2** Molecular structure of **3** with 30% probability ellipsoids. (H atoms were omitted.)

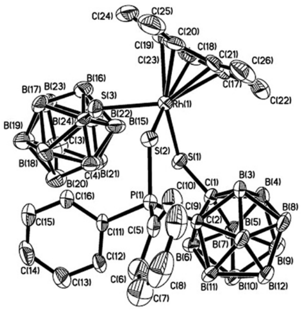


**Fig. 3** Molecular structure of **4** with 30% probability ellipsoids. (H atoms were omitted.)

With complexes **1–3** in hand, we extended our study to other nucleophiles in the reaction. We wondered if the C–X bond could be obtained when other nucleophiles were used in this reaction. Hence, the reaction of carboranyl mono-thiolate derivative $[1\text{-S-}o\text{-C}_2\text{B}_{10}\text{H}_{11}]^-$ with rhodium complex **C** was performed. Unfortunately, this reaction gave the simple $\text{Cl}^-/\text{Nu}^-$ exchange product **4** (Scheme 3), which is a similar result to that observed in our previous study.[8] This appears logical on considering that nucleophilic attack on a coordinated Cp* ring is disfavored, because of its high electron density. The insertion of the sulfur bridge greatly alleviates the crowded steric effects of the metal center so that the metathesis reaction can occur.[4j] On the other hand, according to the hard and soft acid and base theory, this type of reaction is preferred because Rh(III) is a soft acid and the thiolate anion is a softer base compared with carboranyl anion. The structure of **4** is shown in Fig. 3. Density functional theory calculations (DFT) were used to further confirm the experimental results (see ESI†).

In summary, we have shown nucleophilic attacks on a fully-substituted Cp* ring coordinated to fairly electron-rich M(III) complexes *via* an intramolecular redox reaction. The basicity and steric effects of the nucleophilic reagent are crucial to the formation of the corresponding complex. With strong basicity and bulky carboranyl anion, the product with a C–C bond was formed accompanied by the reduction of the metal center; whereas the metathesis product was given when the lower-basicity carboranyl thiolate was employed in such a reaction. A reactivity study of other Ir and Rh complexes is currently underway in our laboratory.

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