

## Cationic metallocarborane species [(Carb)M]<sup>+</sup>: generation and synthetic application

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Our recent studies on the synthesis of metallocarboranes based on the cationic species [(Carb)M]<sup>+</sup> are summarized. The labile complexes [Carb'M(Solv)<sub>3</sub>]<sup>2+</sup> (Carb' = 9-SMe<sub>2</sub>-7,8-C<sub>2</sub>B<sub>9</sub>H<sub>10</sub>; M = Rh or Ir) and [Carb'Fe(C<sub>6</sub>H<sub>6</sub>)]<sup>+</sup> were suggested to use as synthons. The new method was employed to synthesize a great variety of sandwich, half-sandwich, and triple-decker complexes.

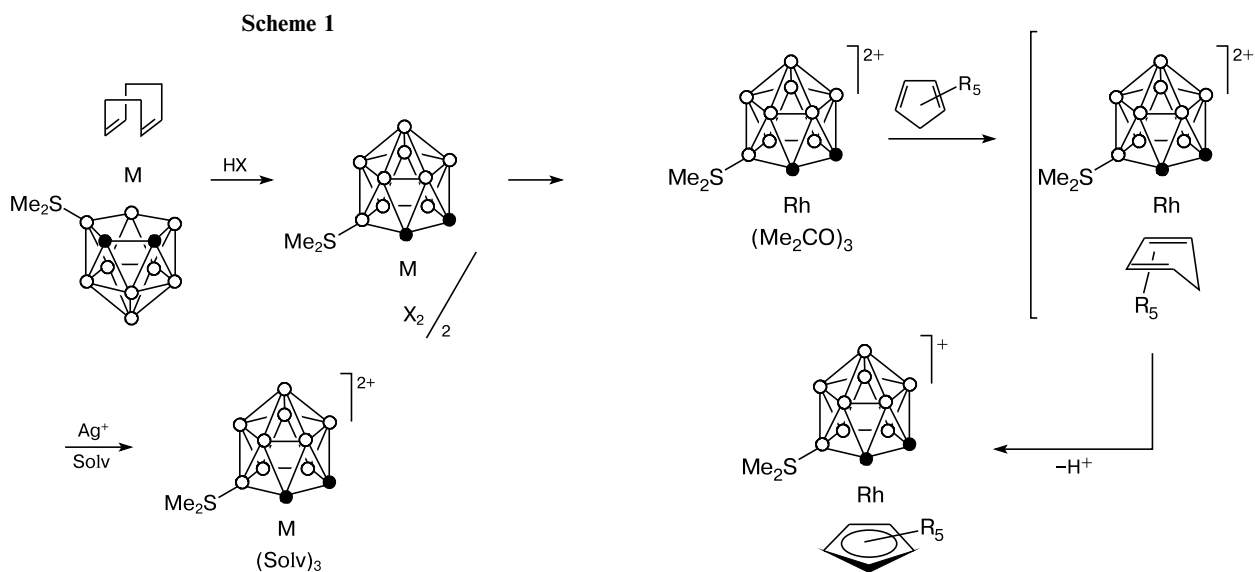
**Key words:** iron, iridium, metallocarboranes, rhodium, sandwich compounds.

The species [CpM]<sup>+</sup> are widely used in organometallic synthesis. In particular, these species react with Cp<sup>-</sup> and C<sub>6</sub>H<sub>6</sub> to form metallocenes MCp<sub>2</sub> and arene complexes [CpM(C<sub>6</sub>H<sub>6</sub>)]<sup>+</sup>, respectively.<sup>1,2</sup> The analogous reactions with MCp<sub>2</sub> produce triple-decker complexes.<sup>3–5</sup> The cationic species [CpM]<sup>+</sup> also proved to be useful in the chemistry of metallocarboranes. For example, these species were used for the synthesis of complexes with the tricarbollide [C<sub>3</sub>B<sub>8</sub>H<sub>11</sub>]<sup>-</sup> (see Ref. 6), phosphadecarbollide [PC<sub>2</sub>B<sub>8</sub>H<sub>10</sub>]<sup>-</sup>,<sup>7</sup> and dicarbollide [9-SMe<sub>2</sub>-7,8-C<sub>2</sub>B<sub>9</sub>H<sub>10</sub>]<sup>-</sup> (see Ref. 8) anions. Due to the single negative charge, these anions are close analogs of Cp<sup>-</sup> in the ability to be

coordinated to transition metals. This suggests the similarity of the cationic species [CarbM]<sup>+</sup> and [CpM]<sup>+</sup>. The present review summarizes our recent results on the generation of the metallocarborane species [Carb'M]<sup>2+</sup> (Carb' = 9-SMe<sub>2</sub>-7,8-C<sub>2</sub>B<sub>9</sub>H<sub>10</sub>; M = Rh or Ir) and [Carb'Fe]<sup>+</sup> and their use in organometallic synthesis.

**Rhodium and iridium complexes.** The rhodium and iridium cyclopentadienyl chloride complexes [Cp\*MCl<sub>2</sub>]<sub>2</sub> are widely used as synthons of the cationic species [Cp\*M]<sup>2+</sup> for the synthesis of arene,<sup>9–11</sup> triple-decker,<sup>5,12–14</sup>

Scheme 2



M = Rh, Ir; X = Cl, Br, I; Solv = Me<sub>2</sub>CO, MeNO<sub>2</sub>

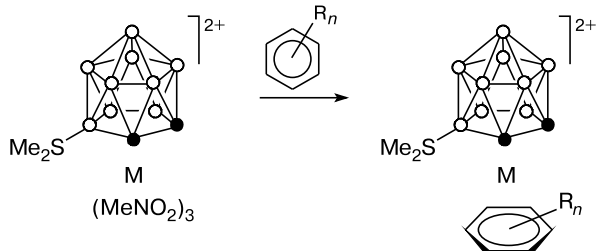
R = H, Me

and metallacarborane<sup>15,16</sup> complexes. We used the related compounds  $[\text{Carb}'\text{MX}_2]_2$  ( $M = \text{Rh}$  or  $\text{Ir}$ ;  $X = \text{Cl}$ ,  $\text{Br}$ , or  $\text{I}$ ) for the generation of rhoda- and iridacarborane species  $[\text{Carb}'\text{M}]^{2+}$ . The starting halide complexes  $[\text{Carb}'\text{MX}_2]_2$  were synthesized by the reaction of the cyclooctadiene derivatives  $\text{Carb}'\text{M}(\text{cod})$  with acids  $\text{HX}$  (Scheme 1).<sup>17,18</sup> The subsequent elimination of the halide ions with  $\text{Ag}^+$  in acetone or nitromethane affords the labile solvate complexes  $[\text{Carb}'\text{M}(\text{Solv})_3]^{2+}$ .

The rhodium acetone solvate reacts with cyclopentadienes to give the cyclopentadienyl complexes  $[\text{Carb}'\text{Rh}(\text{C}_5\text{R}_5)]^+$  through the intermediate formation of diene derivatives (Scheme 2).<sup>19</sup> This reaction is analogous to the synthesis of the decamethylrhodocenium cation by the reaction of  $[\text{Cp}^*\text{Rh}(\text{Me}_2\text{CO})_3]^{2+}$  with  $\text{C}_5\text{Me}_5\text{H}$ .<sup>20</sup>

The reactions of  $[\text{Carb}'\text{M}(\text{MeNO}_2)_3]^{2+}$  with arenes produce the dicationic complexes  $[\text{Carb}'\text{M}(\text{arene})]^{2+}$  ( $M = \text{Rh}$  or  $\text{Ir}$ ) (Scheme 3).<sup>21</sup> It should be noted that the nitromethane solvates are unstable at room temperature. Hence, these compounds should be generated *in situ*. The acetone solvates are stable but, unfortunately, they do not react with arenes.

Scheme 3



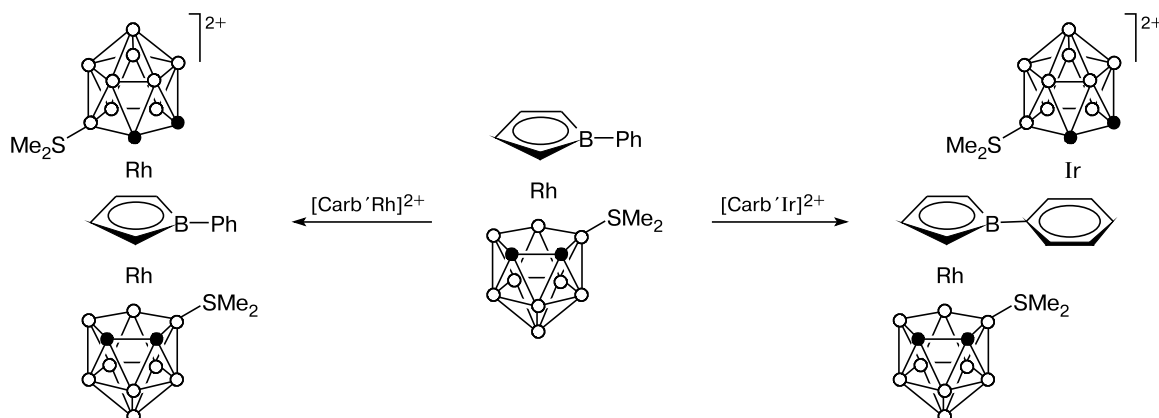
$M = \text{Rh}, \text{Ir}$ ;  $R_n = \text{H}, 1,3\text{-Me}_2, 1,3,5\text{-Me}_3, 1,2,4,5\text{-Me}_4, \text{Me}_6, \text{OMe}$

We found that the rhodacarborane benzene complex  $[\text{Carb}'\text{Rh}(\text{C}_6\text{H}_6)]^{2+}$  is involved in the arene exchange reactions, like the cyclopentadienyl analog  $[\text{Cp}^*\text{Rh}(\text{C}_6\text{H}_6)]^{2+}$ .<sup>22,23</sup> For example, the refluxing of this complex in nitromethane in the presence of anisole for 2 h affords the complex  $[\text{Carb}'\text{Rh}(\text{C}_6\text{H}_5\text{OMe})]^{2+}$ .<sup>21</sup> It should be noted that the arene exchange occurs even at room temperature but at a substantially lower rate. This reaction provides evidence that the complex  $[\text{Carb}'\text{Rh}(\text{C}_6\text{H}_6)]^{2+}$ , along with the solvates  $[\text{Carb}'\text{Rh}(\text{Solv})_3]^{2+}$ , can be used as an equivalent of the species  $[\text{Carb}'\text{Rh}]^{2+}$ .

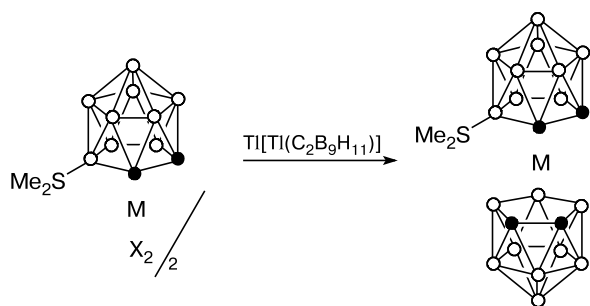
With the aim of synthesizing triple-decker complexes, we studied the reactions of the nitromethane solvates  $[\text{Carb}'\text{M}(\text{MeNO}_2)_3]^{2+}$  with (borole)rhodacarborane  $\text{Carb}'\text{Rh}(\eta^5\text{-C}_4\text{H}_4\text{BPh})$  (Scheme 4).<sup>24,25</sup> The reaction of the rhodium-containing solvate produces the triple-decker complex  $[\text{Carb}'\text{Rh}(\mu\text{-}\eta^5\text{:}\eta^5\text{-C}_4\text{H}_4\text{BPh})\text{RhCarb}']^{2+}$ , whereas the iridium analog gives only the arene-type complex  $[\text{Carb}'\text{Rh}(\mu\text{-}\eta^5\text{:}\eta^6\text{-C}_4\text{H}_4\text{BPh})\text{IrCarb}']^{2+}$ . The formation of the latter complex is apparently associated with low stability of the corresponding triple-decker RhIr structure due to its low symmetry. The lower stability of unsymmetrical triple-decker complexes compared to symmetrical related compounds is a general tendency<sup>26</sup> and is attributed to the asymmetric electron density distribution in the fragment  $\text{M}(\mu\text{-ring})\text{M}'$ , resulting in the loosening of one of the  $\text{M}\text{-}\mu\text{-ring}$  bonds. It should be noted that the analogous reactions of  $\text{Carb}'\text{Rh}(\eta^5\text{-C}_4\text{H}_4\text{BPh})$  with the species  $[\text{Cp}^*\text{M}]^{2+}$  give the opposite result. Thus, these reactions produce the arene-type complex with rhodium and the triple-decker cation with iridium.<sup>24</sup>

In the case of highly reactive anionic ligands, the halide derivatives  $[\text{Carb}'\text{MX}_2]_2$  can be directly used as equivalents of the species  $[\text{Carb}'\text{M}]^{2+}$  (without the preliminary generation of solvates). For example, these derivatives react with thallium dicarbollide to give the unsymmetrical complexes  $\text{Carb}'\text{M}(\eta\text{-}7,8\text{-C}_2\text{B}_9\text{H}_{11})$  ( $M = \text{Rh}$  or  $\text{Ir}$ ) (Scheme 5).<sup>19,27</sup>

Scheme 4



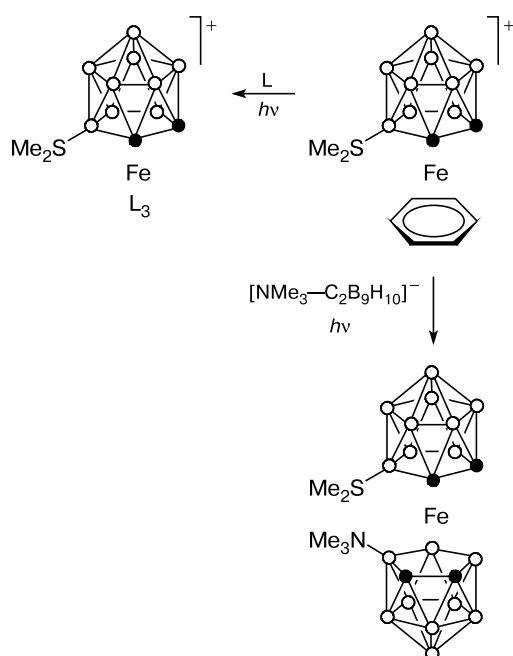
Scheme 5



M = Rh, Ir; X = Cl, Br

**Iron complexes.** The iron (cyclopentadienyl)benzene complex [CpFe( $\eta$ -C<sub>6</sub>H<sub>6</sub>)]<sup>+</sup> is a convenient equivalent of the species [CpFe]<sup>+</sup>.<sup>1,4,28</sup> In particular, the visible-light irradiation of this complex in the presence of the anion [Carb<sup>-</sup>]<sup>-</sup> affords ferracarborane CpFeCarb<sup>-</sup>.<sup>8</sup> We found that the benzene ligand in the cation [Carb<sup>-</sup>Fe(C<sub>6</sub>H<sub>6</sub>)]<sup>+</sup> is easily replaced with the two-electron ligands Bu<sup>t</sup>CN and P(OR)<sub>3</sub> to give the complexes [Carb<sup>-</sup>FeL<sub>3</sub>]<sup>+</sup> (Scheme 6). The starting benzene complex was prepared by the photochemical reaction of [( $\eta$ -C<sub>6</sub>H<sub>7</sub>)Fe( $\eta$ -C<sub>6</sub>H<sub>6</sub>)]<sup>+</sup> with [Carb<sup>-</sup>]<sup>-</sup> followed by elimination of the hydride ion from the resulting complex ( $\eta$ -C<sub>6</sub>H<sub>7</sub>)FeCarb<sup>-</sup> with the use of HCl or [Ph<sub>3</sub>C]<sup>+</sup>.<sup>29</sup> The irradiation of [Carb<sup>-</sup>Fe(C<sub>6</sub>H<sub>6</sub>)]<sup>+</sup> with the anion [9-NMe<sub>3</sub>-7,8-C<sub>2</sub>B<sub>9</sub>H<sub>10</sub>]<sup>-</sup> in a THF/MeCN mixture gives the unsymmetrical complex Carb<sup>-</sup>Fe-

Scheme 6



L = CNBu<sup>t</sup>, P(OMe)<sub>3</sub>, P(OEt)<sub>3</sub>

( $\eta$ -9-NMe<sub>3</sub>-7,8-C<sub>2</sub>B<sub>9</sub>H<sub>10</sub>) containing dicarbollide ligands with two different substituents.

To sum up, the new approach based on the use of cationic metallocarborane species is a very efficient method for the synthesis of metallocarboranes, many of which are inaccessible by other methods.

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