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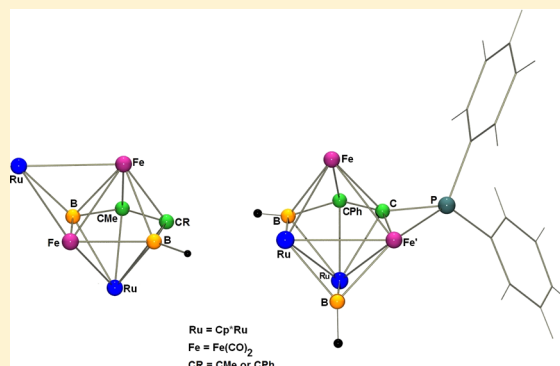
# Synthesis and Characterization of Novel Ruthenaferrocaboranes from Photoinsertion of Alkynes into a Ruthenaferrocaborane

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**S** Supporting Information

**ABSTRACT:** Photolysis of  $[(\mu_3\text{-BH})(\text{Cp}^*\text{Ru})\text{Fe}(\text{CO})_3]_2(\mu\text{-CO})$  (**1**;  $\text{Cp}^* = \eta^5\text{-C}_5\text{Me}_5$ ) in the presence of various alkynes such as 1,2-diphenylethyne, 1-phenyl-1-propyne, 2-butyne, and 1-(diphenylphosphino)-2-phenylacetylene led to the formation of four types of novel heterometallic metallacarboranes,  $[1,1,1\text{-(CO)}_3\text{-}\mu\text{-2,3-(CO)-2,3-(Cp}^*)_2\text{-4,6-Ph}_2\text{-closo-1,2,3,4,6-FeRu}_2\text{C}_2\text{BH}]$  (**2**),  $[1,8\text{-(Cp}^*)_2\text{-2,2,7,7-(CO)}_4\text{-}\mu\text{-2,8-(CO)-}\mu\text{-7,8-(CO)-4-Me-5-Ph-pileo-1,2,7,4,5-RuFe}_2\text{C}_2\text{(BH)}_2]$  (**3**),  $[1,8\text{-(Cp}^*)_2\text{-2,2,7,7-(CO)}_4\text{-}\mu\text{-2,8-(CO)-}\mu\text{-7,8-(CO)-4,5-Me}_2\text{-pileo-1,2,7,4,5-RuFe}_2\text{C}_2\text{(BH)}_2]$  (**4**), and  $[1,2\text{-(Cp}^*)_2\text{-6,6,7,7-(CO)}_4\text{-}\mu\text{-2,7-(CO)-exo-}\mu\text{-5,6-(PPh}_2\text{)-}\mu\text{-3-1,2,6-(BH)-4-Ph-pileo-1,2,6,7,4,5-Ru}_2\text{Fe}_2\text{C}_2\text{BH}]$  (**5**). Cluster compound **2** exhibits an octahedral structure with adjacent carbon atoms consistent with its skeletal electron pair (sep) count of 7. The cage geometry of **3** and **4** is based on a pentagonal bipyramid with one additional  $\{\text{Cp}^*\text{Ru}\}$  vertex capping one of its faces. The solid-state X-ray diffraction results of **5** suggest that the core geometry is a capped pentagonal bipyramid, with an Fe–C bridging  $\text{PPh}_2$  group. All the cluster compounds **2**–**5** have been characterized by IR and  $^1\text{H}$ ,  $^{11}\text{B}$ , and  $^{13}\text{C}$  NMR spectroscopy, and the geometries of the structures were unequivocally established by crystallographic analysis.



The insertion of alkynes into transition-metal–carbon bonds is a well-documented reaction and has been witnessed in nearly all of the transition metals.<sup>1–3</sup> In contrast, examples of such alkyne insertion reactions in borane or metallaborane systems are reasonably less.<sup>4,5</sup> The reaction of metallaboranes with alkynes to yield metallacarboranes was first reported by Grimes in 1974,<sup>6</sup> where it was demonstrated that the reaction of *nido*-2- $[\text{CpCoB}_4\text{H}_8]$  with acetylene yielded the *nido*-1,2,3- $[\text{CpCoC}_2\text{B}_3\text{H}_7]$ . The novel chemistry observed establishes that the electronic contributions of metal and borane fragments to the cluster structure are articulated in new types of reactivity.<sup>7,8</sup> As a result, metallaboranes provide a chemical platform to discover metal versus borane site competition for an alkyne, and they constitute an alternative route to metallacarborane compounds.<sup>9–12</sup> The conventional route to metallacarboranes proceeds in a series of steps leading from polyborane to carborane to metallacarborane.<sup>13,14</sup> Although insertion of an alkyne into a metallaborane has precedence, in the absence of efficient routes to metallaboranes, this chemistry has not been widely explored.<sup>6,15–17</sup>

The synthetic methods used for this chemistry have not, in general, explored photolytic techniques. As part of our interest in synthesizing metallaboranes containing a range of early and late transition metals,<sup>18,19</sup> we have recently described the synthesis and structure of several hybrid clusters by the reaction of *arachno*-1,2- $[(\text{Cp}^*\text{RuCO})_2\text{B}_2\text{H}_6]$  ( $\text{Cp}^* = \eta^5\text{-C}_5\text{Me}_5$ ) with  $[\text{Fe}_2(\text{CO})_9]$ : for example,  $[(\text{Cp}^*\text{Ru})_2(\mu_3\text{-CO})_2\text{B}_2\text{H}(\mu\text{-H})\{\text{Fe}(\text{CO})_2\}_2\text{Fe}(\text{CO})_3]$ <sup>20</sup> and  $[(\mu_3\text{-BH})(\text{Cp}^*\text{Ru})\text{Fe}(\text{CO})_3]_2(\mu\text{-CO})$ <sup>21</sup> (**1**). Subsequently, upon availability of **1** the chemistry was expanded by the use of alkynes under photolytic conditions. In the following, we demonstrate that a triply bridged borylene fragment facilitates the insertion of alkynes into the ruthenaferrocaborane, thereby generating the unusual ruthenaferrocaborane cages **2**–**5**.

**RESULTS AND DISCUSSION**

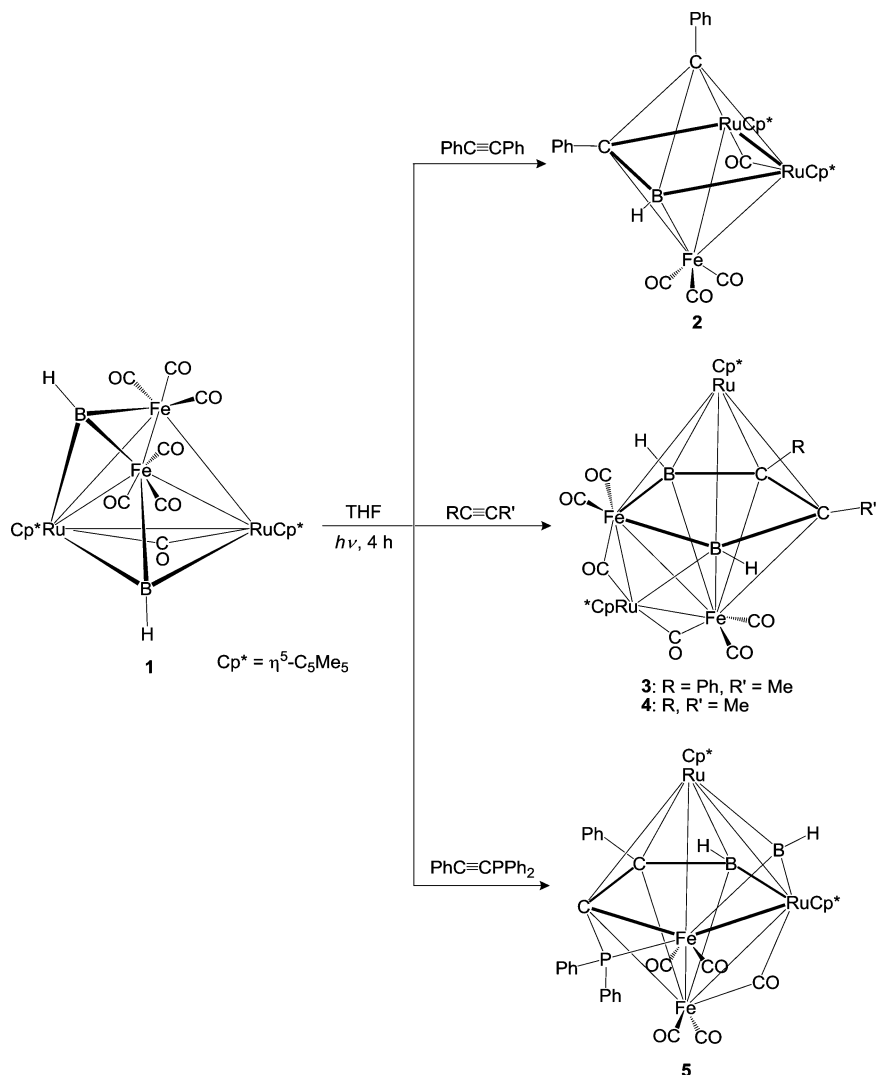
As shown in Scheme 1, photolysis of equimolar amounts of **1** and 1,2-diphenylethyne in THF for 4 h results in the formation of the metallacarborane  $[1,1,1\text{-(CO)}_3\text{-}\mu\text{-2,3-(CO)-2,3-(Cp}^*)_2\text{-4,6-Ph}_2\text{-closo-1,2,3,4,6-FeRu}_2\text{C}_2\text{BH}]$  (**2**). In a similar fashion, reaction of **1** with other alkynes, for example, 1-phenyl-1-propyne, 2-butyne, and 1-(diphenylphosphino)-2-phenylacetylene, yielded  $[1,8\text{-(Cp}^*)_2\text{-2,2,7,7-(CO)}_4\text{-}\mu\text{-2,8-(CO)-}\mu\text{-7,8-(CO)-4-Me-5-Ph-pileo-1,2,7,4,5-RuFe}_2\text{C}_2\text{(BH)}_2]$  (**3**),  $[1,8\text{-(Cp}^*)_2\text{-2,2,7,7-(CO)}_4\text{-}\mu\text{-2,8-(CO)-}\mu\text{-7,8-(CO)-4,5-Me}_2\text{-pileo-1,2,7,4,5-RuFe}_2\text{C}_2\text{(BH)}_2]$  (**4**), and  $[1,2\text{-(Cp}^*)_2\text{-6,6,7,7-(CO)}_4\text{-}\mu\text{-2,7-(CO)-exo-}\mu\text{-5,6-(PPh}_2\text{)-}\mu\text{-3-1,2,6-(BH)-4-Ph-pileo-1,2,6,7,4,5-Ru}_2\text{Fe}_2\text{C}_2\text{BH}]$  (**5**), respectively. These reactions also produced other products, which were observed during the chromatographic workup; however, due to the instability and insufficient amounts, isolation and characterization was not possible. Details of the characterization of clusters **2**–**5** using IR,  $^1\text{H}$ ,  $^{11}\text{B}$ , and  $^{13}\text{C}$  NMR, and X-ray diffraction studies follow.

## RESULTS AND DISCUSSION

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Scheme 1. Synthesis of Ruthenacarborane Clusters 2–5

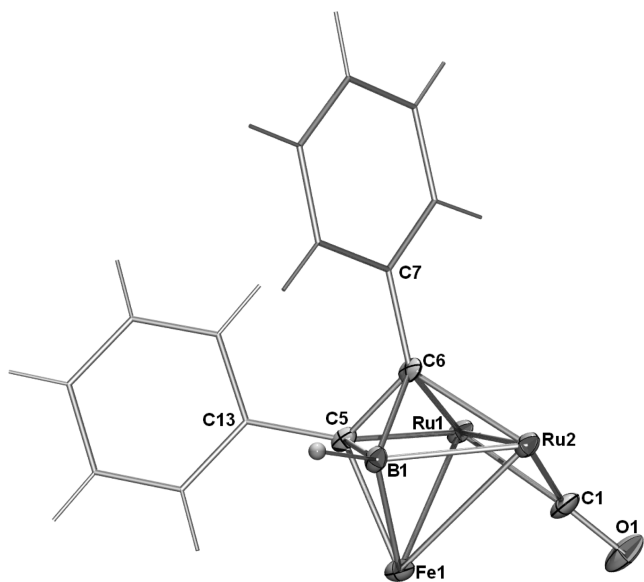


Cluster compound **2** was isolated in 9% yield as a yellow solid. The solid-state molecular structure of **2** was determined by X-ray structure analysis. The crystal structure of **2** corresponds to discrete molecule of  $[(\text{Cp}^*\text{Ru})_2(\mu\text{-CO})\text{-Ph}_2\text{C}_2\text{BHF}(\text{CO})_3]$  separated by normal van der Waals distances. The molecular structure of **2**, depicted in Figure 1, defines the structure as an octahedron. A similar octahedral geometry was previously observed for the ruthenacarborane *closo*-4-Ph-1,2- $(\text{Cp}^*\text{RuH})_2\text{-4,6-C}_2\text{B}_2\text{H}_3$ , generated from the reaction of *nido*-1,2- $[(\text{Cp}^*\text{RuH})_2\text{B}_3\text{H}_7]$  with phenylacetylene.<sup>22</sup> The cluster compound **2** appears to follow the regular electron counting rules, as it possess 7 sep's appropriate for a normal 6-vertex *closo* cluster. Cluster compound **2** has a total of 56 cluster valence electrons. In accord with the polyhedral skeletal electron pair theory (PSEPT),<sup>23,24</sup> this geometry should be associated with a total of 86 cluster valence electrons. In case of **2**, we should subtract 30 electrons from the electron count, due to the presence of three main-group elements (B1, C5, C6), which amounts to 56 valence electrons, justifying the observed geometry.

The Ru1–Ru2 distance of 2.7091(11) Å in **2** is considerably shorter than those found in  $[\text{H}_2\text{Ru}_6(\text{CO})_{18}]$ <sup>25</sup> (average 2.9105 Å). The bridging carbonyl group (C1–O1) is displaced out of the  $\text{Ru}_2\text{CB}$  square plane by 1.062 Å in a direction toward the

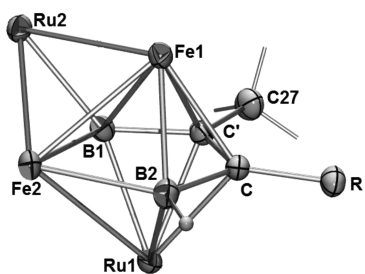
$\text{Fe}(\text{CO})_3$  group. The C5–C6 bond length of 1.487(13) Å is shorter than the C–C bond distance found in the analogous cluster  $[\text{closo-4-Ph-1,2-}(\text{Cp}^*\text{RuH})_2\text{-4,6-C}_2\text{B}_2\text{H}_3]$ .<sup>22,26</sup> The internal angles within the square plane are in the range of 73.1(2)–109.5(6)° (89.85° average), which is marginally distorted from an idealized (90°) planar structure. It should, however, be noted that a *closo*-[4-Ph-1,2- $(\text{Cp}^*\text{RuH})_2\text{-4,6-C}_2\text{B}_2\text{H}_3]$  cluster with octahedral geometry<sup>22</sup> displays an analogous trend in the deviation of the equatorial angles.

The <sup>11</sup>B NMR spectrum of **2** revealed the presence of a doublet at δ 53.7 ppm, which collapses to a sharp singlet upon broad-band <sup>1</sup>H decoupling, indicating one terminal hydrogen atom on boron. Further, the <sup>1</sup>H NMR spectrum confirms that cluster compound **2** has two types of Cp\* methyl and phenyl protons. Consistent with the <sup>1</sup>H chemical shifts, the <sup>13</sup>C NMR spectrum also shows two types of Cp\* ligands and two types of phenyl environments. In addition, two broad signals in the olefinic region can be associated with carbon atoms incorporated into the borane network. The IR spectrum revealed the presence of three absorption bands; two of them correspond to terminal and bridging carbonyl (1973 (s), 1741 cm<sup>-1</sup> (m)) and one corresponds to the terminal B–H stretches (2478 cm<sup>-1</sup> (w)).



**Figure 1.** Molecular structure and labeling diagram for **2**. Terminal carbonyl ligands are excluded for clarity. Selected bond lengths (Å) and angles (deg): Ru1–Ru2 = 2.7091(11), Ru1–Fe1 = 2.6963(14), Ru2–Fe1 = 2.7132(16), Ru1–C5 = 2.095(9), C5–B1 = 1.689(12), B1–Ru2 = 2.132(10), C5–C6 = 1.487(13), Ru1–C6 = 2.129(9), Ru2–C6 = 2.088(8); Ru1–Ru2–B1 = 78.6(3), Ru1–C5–B1 = 109.5(6), C5–B1–Ru2 = 98.2(5), C5–C6–Ru1 = 68.1(5).

Cluster compounds **3** and **4** were isolated in 29% and 34% yields, respectively, as green and relatively air-stable solids. The definitive assignment of the structures of **3** and **4** was obtained by X-ray crystallography. As shown in Figure 2, clusters



**Figure 2.** Molecular structure and labeling diagrams for **3** and **4**. Carbonyl ligands are excluded for clarity. Selected bond lengths (Å) and angles (deg) are as follows. **3** (R = Ph): Fe1–Fe2 = 2.5965(6), Ru1–Fe2 = 2.8067(5), Ru2–Fe2 = 2.6485(5), Ru2–Fe1 = 2.7035(4), B1–C' = 1.575(4), C'–C = 1.439(4), C–B2 = 1.580(4), B2–Fe2 = 2.185(3), Ru1–B2 = 2.317(3); B1–C'–C = 109.1(2), C'–C–B2 = 113.4(2), Ru1–B1–Fe1 = 107.28(13), Fe2–Ru2–Fe1 = 58.033(13). **4** (R = Me): Fe1–Fe2 = 2.5837(7), Ru2–Fe1 = 2.7018(6), Ru1–Fe2 = 2.8087(6), Ru2–Fe2 = 2.6575(6), B1–C' = 1.582(6), C–C' = 1.450(5), C–B2 = 1.568(6), B2–Fe2 = 2.035(4), Ru1–B1 = 2.328(4); B2–C–C' = 108.8(3), C–C'–B1 = 114.7(3), Ru1–B2–Fe1 = 106.62(17), Fe2–Ru2–Fe1 = 57.639(16).

compounds **3** and **4** can be viewed as monocapped pentagonal bipyramids. Following the skeletal electron-counting rules,<sup>23,27</sup> the cluster compounds **3** and **4** both have 8 sep's, appropriate for a normal capped *closo* cluster. According to the PSEP theory, a capped-pentagonal-bipyramidal cluster containing 4 main-group elements should contain 72 electrons.

The average Ru–Fe bond distance (**3**, 2.719 Å; **4**, 2.722 Å) is slightly longer than that found in **1** (2.6735 Å) (Table 1). The

Ru–B and Fe–B bond distances are slightly shorter than those observed in ruthenium and iron complexes of boron derivatives.<sup>28</sup> The internal angles within the pentagons of **3** and **4** correspond closely to the expected value (108°) for a planar structure.<sup>29</sup> The core C–C' bond lengths of 1.439(4) Å in **3** and 1.450(5) Å in **4** are typical of carbon–carbon bonds in pentagonal-bipyramidal metallacarborane clusters.<sup>30,31</sup>

Consistent with the X-ray results, the <sup>11</sup>B NMR spectra of **3** and **4** rationalize the presence of two boron resonances with equal intensity. The resonances at chemical shifts δ 26.2 and 23.5 ppm, respectively, for **3** and **4** is indicative of a low-coordinate boron atom and has been, therefore, tentatively assigned to the unique boron atom (B2) of the pentagonal plane. The other chemical shift at δ 139.7 ppm for **3** and δ 145.2 ppm for **4** is shifted considerably downfield, suggesting a greater degree of boron–metal interactions, and can be assigned to the boron B1.

Several transition-metal–carbon clusters having 8-vertex capped-pentagonal-bipyramidal (*closo*) geometry have been crystallographically characterized; among these, there are very few examples where the metal atom occupies the capping position (Chart 1). The 8-vertex organometallic species that is most relevant to the cluster described in the present paper are [Ru<sub>3</sub>Pt<sub>5</sub>(CO)<sub>12</sub>(PBU<sup>t</sup><sub>3</sub>)<sub>3</sub>]<sup>32</sup> (**I**) and [Ru<sub>6</sub>(CO)<sub>13</sub>(μ-MeC<sub>2</sub>NMe<sub>2</sub>)(MeC<sub>2</sub>NMe<sub>2</sub>)(μ<sub>4</sub>-S)<sub>2</sub>]<sup>33</sup> (**II**), in which the platinum and ruthenium metal atoms occupy capping positions, respectively. A recently reported example was the 8-vertex monocarbon metallacarborane *closo*-[2,2-(Ph<sub>3</sub>P)<sub>2</sub>-2-H-3,6,8-(MeO)<sub>3</sub>-RuCB<sub>6</sub>H<sub>4</sub>]<sup>34</sup> (**III**), with a boron-capped pentagonal-bipyramidal cage geometry. As far as we are aware, cluster compounds **3** and **4** may thus be regarded as the first metallacarboranes containing a {Cp\*M} fragment as a capping vertex in pentagonal-bipyramidal geometry.

Cluster compound **5** was isolated in 17% yield as a red-brown solid. The X-ray crystallographic data show that the PPh<sub>2</sub> fragment forms a three-membered ring with the basal iron atom and the carbon atom; thus, **5** can also be considered to possess a metallaphosphirene unit exocyclic to a capped-pentagonal-bipyramidal core (Figure 3).<sup>35</sup> The intermetallic distance of ruthenium atoms is 2.8439(5) Å, which is within the range of usual Ru–Ru single-bond lengths. The average bond length of the unbridged Fe–C edges (2.124 Å) is similar to those distances observed for [Fe(μ-η<sup>1</sup>:η<sup>2</sup>-PPh<sub>2</sub>CCPh)-Co<sub>2</sub>(CO)<sub>5</sub>{P(OMe)<sub>3</sub>}] and [(OC)<sub>4</sub>Fe(μ-η<sup>1</sup>:η<sup>2</sup>-PPh<sub>2</sub>CCPh)-Co<sub>2</sub>(CO)<sub>4</sub>{P(OMe)<sub>3</sub>}<sub>2</sub>].<sup>36</sup> The significant structural feature of **5** is the very short Fe–P bond length of 1.940(13) Å, which is much shorter than the average Fe–P bond length in related complexes.<sup>36–38</sup> The P1–C22 bond distance (1.746(4) Å) is between the average values of P–C single (1.85 Å) and P=C double bonds (1.67 Å) (Table 2).<sup>39</sup> This suggests that the formal bond order between iron, carbon, and phosphorus atoms is greater than 1. This may be due to the delocalization of electron density among the ring atoms.

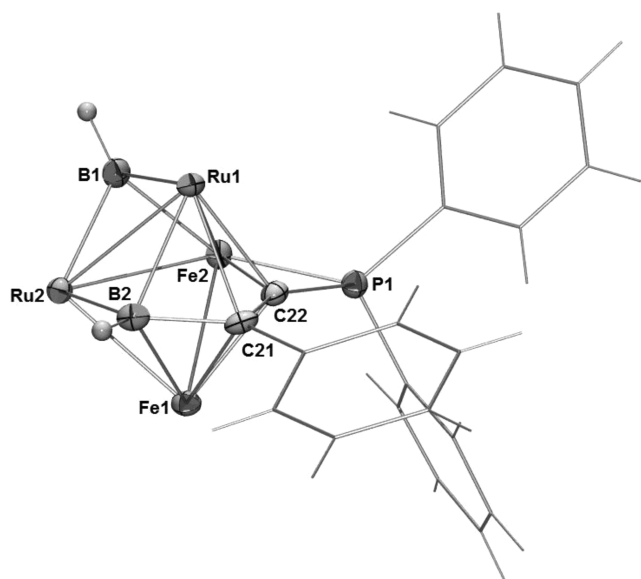
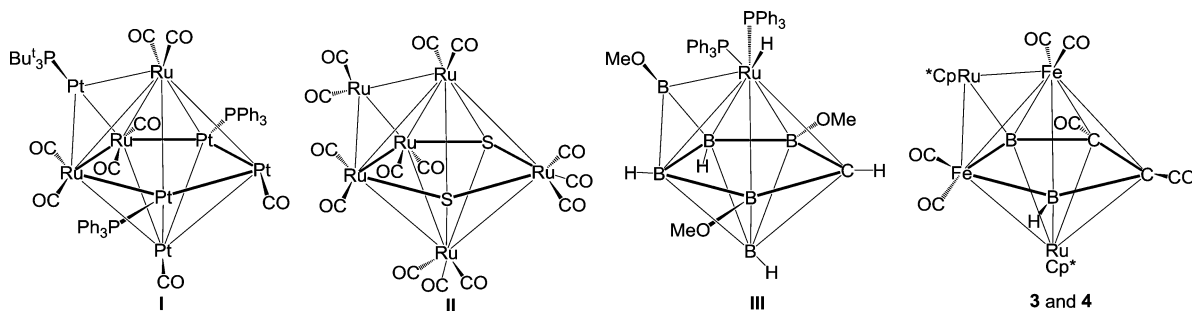
Consistent with the X-ray results, the <sup>11</sup>B NMR spectrum of **5** rationalizes the presence of two broad resonances at δ 66.93 and 119.53 ppm of relative intensity 1:1 for the basal and capped boron atoms, respectively. The large downfield chemical shift of the capped boron atom reflects the highly metallic environment. As shown in Table 1, the <sup>31</sup>P chemical shift of **5** at δ –12.9 ppm indicates the shielded nature of the phosphorus atom<sup>40</sup> and provides evidence against metal-bridged phosphido complexes which, in general, appears in the low-field region.<sup>41</sup> The IR spectrum confirms the presence

Table 1. Selected Structural Parameters of 1 and Clusters 2–5

compd	$d(\text{M}-\text{M})$ (Å) <sup>a</sup>	$d(\text{M}-\text{B})$ (Å) <sup>b</sup>	$d(\text{M}-\text{C})$ (Å) <sup>c</sup>	$d(\text{B}-\text{C})$ (Å) <sup>d</sup>
$[(\mu_3\text{-BH})(\text{Cp}^*\text{Ru})\text{Fe}(\text{CO})_3]_2(\mu\text{-CO})$ (1)	2.6668	2.092		
$[1,1,1\text{-}(\text{CO})_3\text{-}\mu\text{-}2,3\text{-}(\text{CO})\text{-}2,3\text{-}(\text{Cp}^*)_2\text{-}4,6\text{-Ph}_2\text{-closo-}1,2,3,4,6\text{-FeRu}_2\text{C}_2\text{BH}]$ (2)	2.7062	2.0915	2.0962	1.6955
$[1,8\text{-}(\text{Cp}^*)_2\text{-}2,2,7,7\text{-}(\text{CO})_4\text{-}\mu\text{-}2,8\text{-}(\text{CO})\text{-}\mu\text{-}7,8\text{-}(\text{CO})\text{-}4\text{-Me-}5\text{-Ph-pileo-}1,2,7,4,5\text{-RuFe}_2\text{C}_2(\text{BH})_2]$ (3)	2.6888	2.1531	2.1625	1.5775
$[1,8\text{-}(\text{Cp}^*)_2\text{-}2,2,7,7\text{-}(\text{CO})_4\text{-}\mu\text{-}2,8\text{-}(\text{CO})\text{-}\mu\text{-}7,8\text{-}(\text{CO})\text{-}4,5\text{-Me}_2\text{-pileo-}1,2,7,4,5\text{-RuFe}_2\text{C}_2(\text{BH})_2]$ (4)	2.6879	2.1628	2.1662	1.575
$[1,2\text{-}(\text{Cp}^*)_2\text{-}6,6,7,7\text{-}(\text{CO})_4\text{-}\mu\text{-}2,7\text{-}(\text{CO})\text{-exo-}\mu\text{-}5,6\text{-}(\text{PPh}_2)\text{-}\mu_3\text{-}1,2,6\text{-}(\text{BH})\text{-}4\text{-Ph-pileo-}1,2,6,7,4,5\text{-Ru}_2\text{Fe}_2\text{C}_2\text{BH}]$ (5)	2.7286	2.1413	2.1385	1.594

<sup>a</sup>The average M–M distance. <sup>b</sup>The average M–B distance. <sup>c</sup>The average M–C distance. <sup>d</sup>The average B–C distance.

Chart 1. Polyhedrons Containing Capped-Pentagonal-Bipyramidal Geometry



**Figure 3.** Molecular structure and labeling diagram for 5. Cp\* and carbonyl ligands are excluded for clarity. Selected bond lengths (Å) and angles (deg): Fe1–Fe2 = 2.7469(8), Ru1–B1 = 2.115(5), Ru2–Fe1 = 2.5830(7), Fe2–P1 = 1.940(13), C22–P1 = 1.746(4), Fe2–C22 = 1.992(4), Fe1–C22 = 2.147(4), Fe1–C21 = 2.101(4), C22–C21 = 1.418(5), Ru1–Ru2 = 2.8439(5); C22–Fe2–P1 = 49.03(13), C22–P1–Fe2 = 59.44(14), P1–C22–Fe2 = 71.53(15), C22–P1–C29 = 119.3(2).

of bridging and terminal carbonyl ligands and the terminal BH protons. Formally, the PPh<sub>2</sub> fragment on 5 is a one-electron ligand and it has 8 sep's, appropriate for its shape.<sup>38</sup>

## REACTION PATHWAY

Although the structural properties of the new cluster compounds obtained in this work are interesting, the reaction pathways for the formation of cluster compounds 2–5 are not fully implicit. The formation of 2 may be assumed that under photolytic conditions the alkyne is inserted into the two

tetrahedral faces of Ru<sub>2</sub>FeB associated with the elimination of one BH and one Fe(CO)<sub>3</sub> fragment. In case of 3 and 4, the major product results from addition of the alkyne followed by loss of CO. Further, formation of 5 can be explained as one of the capping BH fragment retaining its position on the Ru<sub>2</sub>Fe face as found in 1 and, presumably, the incoming alkyne placed in among the faces of the RuFe<sub>2</sub>B tetrahedron of 1 with the elimination of two CO ligands. These observations suggest a connection between the nature of the alkynes and the products observed. Electron-rich alkynes such as PhC≡CR (R = Ph, PPh<sub>2</sub>) were less reactive under the reaction conditions, resulting in smaller yields. Under the same reaction conditions, the failure to observe any alkyne insertion for bulky substituted alkynes into cluster 1 suggests that steric factors are significant in the formation of metallacarboranes.<sup>44</sup>

## CONCLUSION

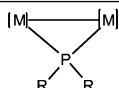
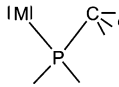
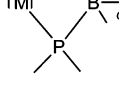
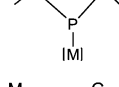
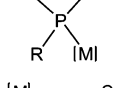
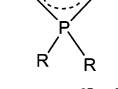
The significance of this work lies in the demonstration that group 8 metallaboranes provide a practical route to metallacarboranes. The geometries of metallacarboranes 2–5 possess an interesting test of current bonding descriptions for cluster chemistry. Both cluster compounds 3 and 4 exhibits a capped-pentagonal-bipyramidal geometry and are the first examples of {Cp\*M} fragment capped metallacarboranes. Cluster compound 5 is novel, and we are unaware of any previous characterization of metallacarboranes containing a phosphirene ring. Further, the plausible pathway for the formation of these metallacarboranes has been postulated. While carbon insertion into metallaborane cages does not qualify as a general synthetic route to metallacarboranes, it does provide a fascinating new insight into cluster chemistry.

## EXPERIMENTAL SECTION

**General Procedures and Instrumentation.** All the operations were conducted under an Ar/N<sub>2</sub> atmosphere by using standard Schlenk techniques or an inert-atmosphere glovebox. Solvents were distilled prior to use under argon. MeC≡CMe, PhC≡CMe, and PhC≡CPh (Aldrich) were used as received.  $[(\mu_3\text{-BH})(\text{Cp}^*\text{Ru})\text{Fe}(\text{CO})_3]_2(\mu\text{-CO})$ <sup>21</sup> and PhC≡CPPh<sub>2</sub><sup>45</sup> were prepared as described in



Table 2. Structural Parameters and  $^{31}\text{P}$  Chemical Shifts of Various Phosphorus Complexes and 5

Entry	Cluster	Type	$d[\text{M}-\text{C}]$ [Å]	$d[\text{P}-\text{C}]$ [Å]	$d[\text{M}-\text{P}]$ [Å]	$\delta^{31}\text{P}$ NMR	ref
1	$[(\text{Cp}^*\text{Ru})_2(\mu\text{-PMe}_2)(\mu\text{-}\eta^4\text{-B}_2\text{H}_5)]$		-	-	2.2685 <sup>b</sup>	129.6	42
2	$[(\text{OC})_4\text{Fe}(\text{PPh}_2\text{CCPh})\{\text{Co}_2(\text{CO})_6\}]$		-	1.810(3)	2.259(1)	75.6	36
3	$[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})\text{B}_3\text{H}_7(\text{P}(\text{C}_6\text{H}_5)_2)]$		-	-	2.209(1)	-11.8	37
4	$[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2(\text{PCH}(\text{SiMe}_3)\text{C}(\text{SiMe}_3)_2)]$		-	1.8665 <sup>f</sup>	2.331(2)	-59.7	38
5	$[\text{Ir}\{\text{C}(\text{tBu})\text{P}[\text{Au}(\text{Cl})](\text{Cy})\}(\text{CO})(\text{PPh}_3)_2]$		1.909(9)	1.753(9)	2.356(2)	-129.4	43
6	$[(\text{PPh}_2)(\text{Cp}^*\text{Ru})_2(\text{CO})\text{PhC}_2\text{B}_2\text{H}_2\{\text{Fe}(\text{CO})_2\}_2], \mathbf{5}$		1.992(4)	1.746(4)	1.940(13)	-12.9	This work

<sup>a</sup>[M] = Cp\*<sub>2</sub>Ru. <sup>b</sup>The average distance between metal and phosphorus. <sup>c</sup>[M] = Fe(CO)<sub>4</sub>. <sup>d</sup>[M] = (η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)Fe. <sup>e</sup>[M] = (η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)Fe. <sup>f</sup>The average distance between phosphorus and carbon. <sup>g</sup>M = Ir(PPh<sub>3</sub>)<sub>2</sub>(CO); [M] = AuCl. <sup>h</sup>[M] = Cp\*<sub>2</sub>Ru.

the literature. The external reference [Bu<sub>4</sub>N(B<sub>3</sub>H<sub>8</sub>)] for the  $^{11}\text{B}$  NMR was synthesized by the literature method.<sup>46</sup> Preparative thin-layer chromatography was performed with Merck 105554 TLC silica gel 60 F<sub>254</sub>, layer thickness 250 μm on aluminum sheets (20 × 20 cm). NMR spectra were recorded on 400 and 500 MHz Bruker FT-NMR spectrometers. Residual solvent protons were used as reference (CDCl<sub>3</sub>, δ 7.26 ppm), while a sealed tube containing [Bu<sub>4</sub>N(B<sub>3</sub>H<sub>8</sub>)] in [D<sub>6</sub>]benzene (δ<sub>B</sub> -30.07 ppm) was used as an external reference for the  $^{11}\text{B}$  NMR. The photoreactions described in this report were conducted in a Luzchem LZC-4 V photoreactor, with irradiation at 254–350 nm. Infrared spectra were recorded on a Nicolet iS10 FT spectrometer. Microanalyses for C and H were performed on a Perkin-Elmer Instruments Series II Model 2400.

**Synthetic Procedure for 2–5.** In a flame-dried Schlenk tube, a red-brown solution of **1** (0.15 g, 0.19 mmol) and 1,2-diphenylethyne (0.035 g, 0.19 mmol) in THF (20 mL) was irradiated for 4 h at room temperature. After this time, the volatile components were removed under vacuum, and the remaining dark brown residue was extracted into hexane and passed through Celite. After removal of solvent, the residue was subjected to chromatographic workup using silica gel TLC plates. Elution with a hexane/CH<sub>2</sub>Cl<sub>2</sub> (80/20 v/v) mixture yielded yellow **2** (0.014 g, 9%). In a similar fashion, reaction of **1** (0.15 g, 0.19 mmol) with 1-phenyl-1-propyne (0.024 g, 0.19 mmol), 2-butyne (0.010 g, 0.19 mmol), and 1-(diphenylphosphino)-2-phenylacetylene (0.055 g, 0.19 mmol) in THF for 4 h provided green **3** (0.048 g, 29%), green **4** (0.053 g, 34%), and reddish brown **5** (0.037 g, 17%).

**2:**  $^{11}\text{B}$  NMR (22 °C, 128 MHz, CDCl<sub>3</sub>) δ 53.7 (br, 1B);  $^1\text{H}$  NMR (22 °C, 400 MHz, CDCl<sub>3</sub>) δ 7.64–6.90 (m, 10H, 2Ph), 4.94 (partially collapsed quartet (pcq), 1BH<sub>4</sub>), 2.08 (s, 15H, Cp\*), 1.91 (s, 15H, Cp\*);  $^{13}\text{C}$  NMR (22 °C, 100 MHz, CDCl<sub>3</sub>) δ 212.0 and 196.7 (CO), 133.6, 130.2, 129.3, 128.7, 128.0, 127.1, 126.5, 125.8 (Ph), 111.1 and 100.8 (br, C–B), 96.2 and 90.1 (s, C<sub>5</sub>Me<sub>5</sub>), 10.2 and 9.6 (s, C<sub>5</sub>Me<sub>5</sub>); IR (hexane) ν/cm<sup>-1</sup> 2478 w (BH<sub>4</sub>), 1773, 1741 (CO).

**3:**  $^{11}\text{B}$  NMR (22 °C, 128 MHz, CDCl<sub>3</sub>) δ 139.7 (br, 1B), 26.2 (br, 1B);  $^1\text{H}$  NMR (22 °C, 400 MHz, CDCl<sub>3</sub>) δ 7.49 (m, 2H, Ph), 7.10 (m, 2H, Ph), 7.02 (m, 1H, Ph), 5.69 (pcq, 1BH<sub>4</sub>), 3.42 (pcq, 1BH<sub>4</sub>), 1.96 (s, 15H, Cp\*), 1.91 (s, 3H, Me), 1.84 (s, 15H, Cp\*);  $^{13}\text{C}$  NMR (22 °C, 100 MHz, CDCl<sub>3</sub>) δ 205.3 and 194.1 (CO), 131.4, 129.9, 129.0, 127.8 (Ph), 110.4 and 101.1 (br, C–B), 99.2 and 98.1 (s,

C<sub>5</sub>Me<sub>5</sub>), 21.6 (Me), 13.1 and 12.7 (s, C<sub>5</sub>Me<sub>5</sub>); IR (hexane) ν/cm<sup>-1</sup> 2501 w (BH<sub>4</sub>), 2021, 1996, 1725 (CO). Anal. Calcd for C<sub>35</sub>H<sub>40</sub>B<sub>2</sub>Fe<sub>2</sub>O<sub>6</sub>Ru<sub>2</sub>: C, 47.12; H, 4.52. Found: C, 47.41; H, 4.55.

**4:**  $^{11}\text{B}$  NMR (22 °C, 128 MHz, CDCl<sub>3</sub>) δ 145.2 (br, 1B), 23.5 (br, 1B);  $^1\text{H}$  NMR (22 °C, 400 MHz, CDCl<sub>3</sub>) δ 5.87 (pcq, 1BH<sub>4</sub>), 3.42 (pcq, 1BH<sub>4</sub>), 2.01 (s, 15H, Cp\*), 1.90 (s, 3H, Me), 1.95 (s, 3H, Me), 1.86 (s, 15H, Cp\*);  $^{13}\text{C}$  NMR (22 °C, 100 MHz, CDCl<sub>3</sub>) δ 204.8 and 198.5 (CO), 109.8 and 101.7 (br, C–B), 99.7 and 98.3 (s, C<sub>5</sub>Me<sub>5</sub>), 21.6, 20.9 (Me), 13.1 and 12.7 (s, C<sub>5</sub>Me<sub>5</sub>); IR (hexane) ν/cm<sup>-1</sup> 2501 w (BH<sub>4</sub>), 2021, 1996, 1725 (CO). Anal. Calcd for C<sub>30</sub>H<sub>38</sub>B<sub>2</sub>Fe<sub>2</sub>O<sub>6</sub>Ru<sub>2</sub>: C, 43.73; H, 4.61. Found: C, 43.41; H, 4.59.

**5:**  $^{11}\text{B}$  NMR (22 °C, 128 MHz, CDCl<sub>3</sub>) δ 121.7 (br, 1B), 69.3 (br, 1B);  $^1\text{H}$  NMR (22 °C, 400 MHz, CDCl<sub>3</sub>) δ 9.21 (br, 1BH<sub>4</sub>), 8.30–7.31 (m, 15H, Ph), 4.56 (pcq, 1BH<sub>4</sub>), 1.87 (s, 15H, Cp\*), 1.82 (s, 15H, Cp\*);  $^{31}\text{P}$  NMR (22 °C, 161 MHz, CDCl<sub>3</sub>) δ -12.8 (s, 1P);  $^{13}\text{C}$  NMR (22 °C, 100 MHz, CDCl<sub>3</sub>) δ 205.3 and 203.2 (CO), 133.6, 128.7, 127.1, 125.8 (Ph), 110.4 (br, C–B), 152.1 (br, C–P), 96.2 and 90.1 (s, C<sub>5</sub>Me<sub>5</sub>), 9.8 and 8.6 (s, C<sub>5</sub>Me<sub>5</sub>); IR (hexane) ν/cm<sup>-1</sup> 2501 w (BH<sub>4</sub>), 2021, 1996, 1725 (CO). Anal. Calcd for C<sub>45</sub>H<sub>47</sub>B<sub>2</sub>Fe<sub>2</sub>O<sub>5</sub>PRu<sub>2</sub>: C, 52.26; H, 4.58. Found: C, 52.38; H, 4.63.

**X-ray Structure Determination.** The crystal data for **2** were collected and integrated using an OXFORD DIFFRACTION XALIBUR-S CCD system equipped with graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å) at 150 K. The crystal data for **3–5** were collected and integrated using a Bruker Axs kappa apex2 CCD diffractometer, with graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å) at 298 K. The structures were solved by heavy-atom methods using SHELXS-97 or SIR92<sup>47</sup> and refined using SHELXL-97.<sup>48</sup>

**Crystal data for 2:** C<sub>38</sub>H<sub>41</sub>BF<sub>2</sub>O<sub>4</sub>Ru<sub>2</sub>, M<sub>r</sub> = 830.51 g/mol, triclinic, space group P $\bar{1}$ , a = 10.1477(9) Å, b = 11.1863(9) Å, c = 16.6034(10) Å, α = 93.754(6)°, β = 95.108(6)°, γ = 112.780(8)°, V = 1720.5(2) Å<sup>3</sup>, Z = 2, ρ<sub>calcd</sub> = 1.603 g/cm<sup>3</sup>, final R indices (I > 2σ(I)) R<sub>1</sub> = 0.1045, wR<sub>2</sub> = 0.2715, index ranges -11 ≤ h ≤ 12, -13 ≤ k ≤ 8, -19 ≤ l ≤ 19, θ range for data collection 3.34–25.00°, crystal size 0.31 × 0.27 × 0.23 mm<sup>3</sup>, 12 124 reflections collected, 6031 independent reflections, R<sub>int</sub> = 0.1248, goodness of fit on F<sup>2</sup> 1.040.

**Crystal data for 3:** C<sub>35</sub>H<sub>39</sub>B<sub>2</sub>Fe<sub>2</sub>O<sub>6</sub>Ru<sub>2</sub>, M<sub>r</sub> = 891.12 g/mol, monoclinic, space group P2<sub>1</sub>/c, a = 10.0672(3) Å, b = 17.0051(4) Å, c

= 20.5756(5) Å,  $\beta$  = 97.3530(10)°,  $V$  = 3493.45(16) Å<sup>3</sup>,  $Z$  = 4,  $\rho_{\text{calcd}}$  = 1.694 g/cm<sup>3</sup>, final  $R$  indices ( $I > 2\sigma(I)$ )  $R_1$  = 0.0255,  $wR_2$  = 0.0618, index ranges  $-11 \leq h \leq 11$ ,  $-18 \leq k \leq 19$ ,  $-24 \leq l \leq 17$ ,  $\theta$  range for data collection 1.56–25.00°, crystal size 0.25 × 0.20 × 0.12 mm<sup>3</sup>, 21 401 reflections collected, 6114 independent reflections,  $R_{\text{int}}$  = 0.0216, goodness of fit on  $F^2$  1.065.

**Crystal data for 4:** C<sub>30</sub>H<sub>37</sub>B<sub>2</sub>Fe<sub>2</sub>O<sub>6</sub>Ru<sub>2</sub>,  $M_r$  = 829.06 g/mol, monoclinic, space group  $P2_1/n$ ,  $a$  = 9.7112(5) Å,  $b$  = 18.7378(8) Å,  $c$  = 17.9279(7) Å,  $\beta$  = 105.515(2)°,  $V$  = 3143.4(16) Å<sup>3</sup>,  $Z$  = 4,  $\rho_{\text{calcd}}$  = 1.752 g/cm<sup>3</sup>, final  $R$  indices ( $I > 2\sigma(I)$ )  $R_1$  = 0.0391,  $wR_2$  = 0.1142, index ranges  $-9 \leq h \leq 13$ ,  $-25 \leq k \leq 23$ ,  $-23 \leq l \leq 23$ ,  $\theta$  range for data collection 2.17–28.70°, crystal size 0.25 × 0.15 × 0.10 mm<sup>3</sup>, 22 614 reflections collected, 7832 independent reflections,  $R_{\text{int}}$  = 0.0411, goodness of fit on  $F^2$  0.878.

**Crystal data for 5:** C<sub>45</sub>H<sub>47</sub>B<sub>2</sub>Fe<sub>2</sub>O<sub>5</sub>PRu<sub>2</sub>,  $M_r$  = 1034.26 g/mol, monoclinic, space group  $P2_1/c$ ,  $a$  = 12.4637(3) Å,  $b$  = 15.0424(3) Å,  $c$  = 22.1121(4) Å,  $\beta$  = 93.3630(10)°,  $V$  = 4138.53(15) Å<sup>3</sup>,  $Z$  = 4,  $\rho_{\text{calcd}}$  = 1.660 g/cm<sup>3</sup>, final  $R$  indices ( $I > 2\sigma(I)$ )  $R_1$  = 0.0413,  $wR_2$  = 0.1048, index ranges  $-15 \leq h \leq 16$ ,  $-12 \leq k \leq 21$ ,  $-29 \leq l \leq 31$ ,  $\theta$  range for data collection 1.64–30.03°, crystal size 0.15 × 0.10 × 0.08 mm<sup>3</sup>, 35 745 reflections collected, 11 563 independent reflections,  $R_{\text{int}}$  = 0.0523, goodness of fit on  $F^2$  0.785.

## ■ ASSOCIATED CONTENT

### ■ Supporting Information

CIF files giving crystallographic data for 2–5. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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### Notes

The authors declare no competing financial interest.

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