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Note

Reaction of *nido*-1,2-$(Cp^*RuH)_2B_3H_7$ with ethynylferrocene to yield new metallacarboranes

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Abstract

Addition of ethynylferrocene to *nido*-1,2-$(Cp^*RuH)_2B_3H_7$ (**1**) at ambient temperature leads to *nido*-1,2-$(Cp^*Ru)_2$(1,5-μ-C{Fc}Me)B_3H_7 (**2**, **3**) and *closo*-4-Fc-1,2-$(Cp^*RuH)_2$-4,6-$C_2B_2H_3$ (**4**). Compounds **2** and **3** represent a pair of geometric isomers, *nido*-species in which the regiochemistry of the alkyne reduction conforms to the Markovnikoff rule. Compound **4** is an octahedral structure in which the inserted alkyne is on an open face of the *closo* cluster.

Keywords: Boron; Metallaboranes; Metallacarboranes; Alkynes; Cluster

1. Introduction

A convenient and high-yield route to metallaboranes from the reactions of monocyclopentadienylmetal halides (groups 5–9) with monoboranes has been developed [1,2]. This provides the possibility to investigate the systematic reaction chemistries for such a type of hybrid metal-boron complexes. Traditionally, metallacarboranes were synthesized via a sequence of steps from boranes to carboranes to metallacarbones [3–6]. In fact, examples of insertion of alkynes into metallaboranes to generate metallacarboranes also had been reported [7–9], but further investigations were blocked by limited sources of the metallaboranes. Now the situation has changed with quantities of varieties of metallaboranes available. Thus, routes to prepare metallacarboranes from metallaboranes and alkynes can be explored in greater detail than before. It was observed that a metal plays a critical role. For example, the dirhodaborane leads predominantly to catalytic cyclotrimerization of alkynes [10,11]; the diiridaborane needs a molybdenum center to promote alkyne insertion [12]; and the diruthenaborane, *nido*-1,2-$(Cp^*RuH)_2B_3H_7$ (**1**) leads to diverse, unprecedented products even at ambient temperature.

Scheme 1 illustrates some of the ruthenacarborane products. If pushed, some undergo further conversions [13–17]. Relative to internal alkynes, terminal ones create novel compounds, e.g., the first M–B alkylidene complexes generated from cooperative reactivities of metal hydrides and boron hydrides of **1**. Moreover, an alkyne functionallized with CO_2Me, is involved in an unexpected chemical transformation, e.g., C=O coordination, C–O bond cleavage, and the O atom inserted into a B–H bond [16]. The large role of the alkyne substituents in the number and type of the ruthenacarboranes observed was not previously appreciated. To further explore this feather of the chemistry we now describe the reactivity of ethynylferrocene with **1**. The results provide the additional insight into the nature of the metallaborane/alkyne reactive interaction.

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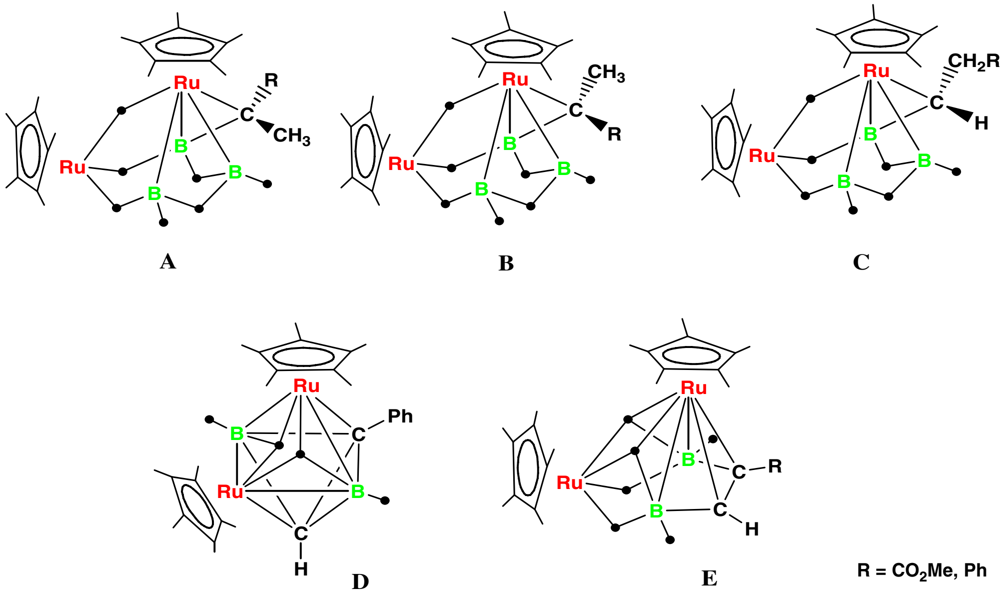

Scheme 1.

2. Results and discussion

nido-1,2-$(\mathrm{Cp^*Ru})_2(1,5\text{-}\mu\text{-C}\{\mathrm{Fc}\}\mathrm{Me})\mathrm{B_3H_7}$ (**2**) and (**3**) were isolated together in a combined yield of 16%. Attempts to separate the two compounds were not successful due to similar polarities as well as low stabilities on a silica gel column. However, both solid-state structures were successfully determined by selection of the crystals with different unit cells. They are shown in Figs. 1, 2 and Table 1. Both structures display a μ-alkylidene bridge over one Ru–B edge that arises from Markovnikoff addition of the two framework hydrogen atoms to the alkyne. Clusters **2** and **3** are geometrical isomers relative to the orientation of the methyl and ferrocenyl groups with respect to the Ru–Ru edge of the cluster. Both contain a chiral carbon center.

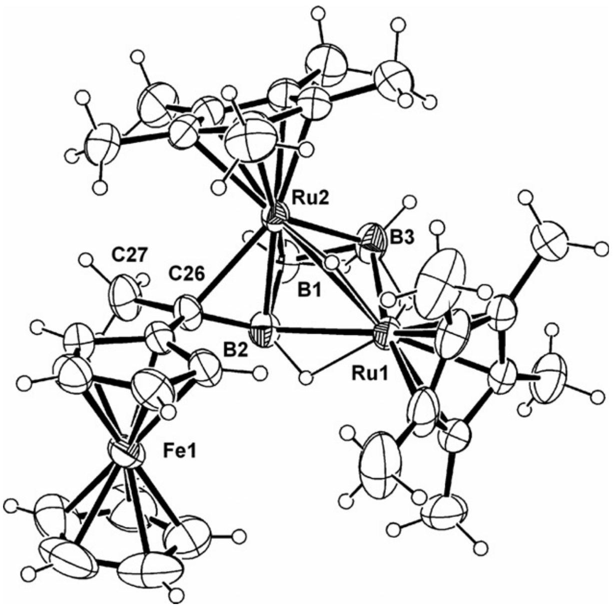

Fig. 1. Molecular structure of **2**. Selected bond length (Å). Ru(1)–B(3) 2.3000(19), Ru(1)–B(2) 2.4022(17), Ru(1)–Ru(2) 2.8889(2), Ru(2)–B(2) 2.1273(18), Ru(2)–B(1) 2.131(2), Ru(2)–B(3) 2.1694(18), Ru(2)–C(26) 2.3145(14), B(1)–B(3) 1.807(3), B(1)–B(2) 1.869(3), B(2)–C(26) 1.506(2), C(26)–C(27) 1.523(2).

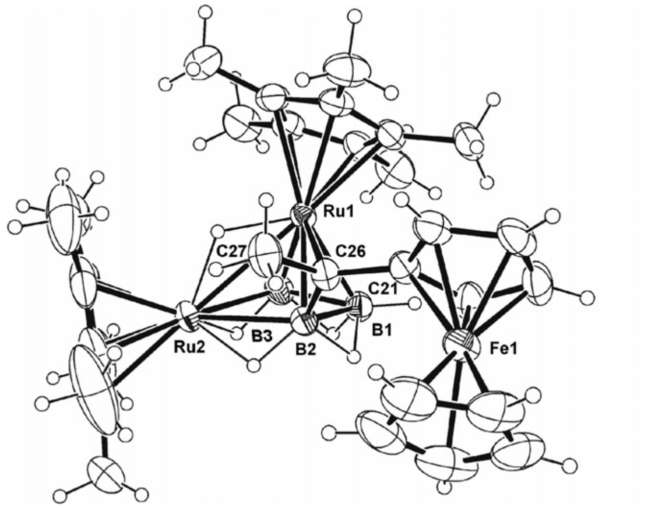

Fig. 2. Molecular structure of **3**. Selected bond length (Å). Ru(1)–B(3) 2.1714(18), Ru(1)–B(2) 2.1278(17), Ru(1)–B(1) 2.1159(18), Ru(1)–Ru(2) 2.8770(2), Ru(2)–B(2) 2.3852(17), Ru(2)–B(3) 2.3073(19), Ru(1)–C(26) 2.3304(15), B(1)–B(3) 1.820(3), B(1)–B(2) 1.845(3), B(2)–C(26) 1.503(2), C(26)–C(27) 1.522(2).

The correspondence of structures with spectroscopic data were established by measuring the solid state structure and the solution proton NMR data with the same single crystal. Notably, the two geometrical isomers show remarkable differences in chemical shifts in their ^{1}H NMR spectra. Thus, they can be readily recognized in a mixture by NMR. For example, the two methyl groups generated from the alkyne reduction are located at 1.46 ppm in **2** and