Cycloaddition

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Ruthenium-Mediated Coupling/Cycloaddition of the Cyclopentadienyl Ligand in [{η^5:σ-Me_2C-$(C_5H_4)(C_2B_{10}H_{10})$}Ru($NCCH_3)_2$] with Alkynes**

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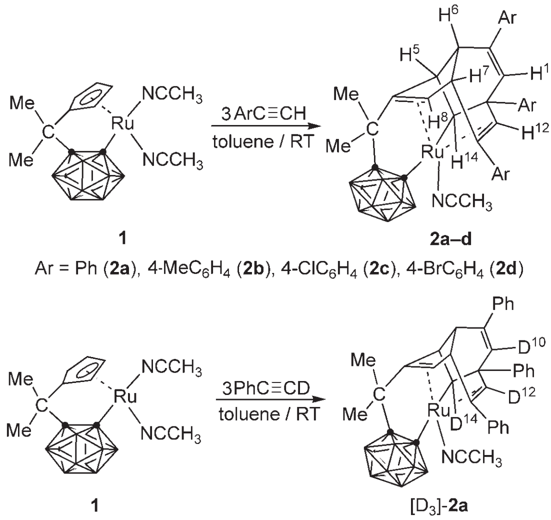
Cyclopentadienyl and its derivatives (Cp ligands) are among the most extensively utilized π ligands in organometallic chemistry. In most organometallic reactions of transition-metal complexes, the η^5-Cp ligand plays the role of a spectator that stays tightly bound in η^5 fashion to the metal center throughout the course of the reactions.[1] For example, ruthenium half-sandwich complexes [(η^5-C_5R_5)RuXL_2] (R = H, Me; X = halide; L_2 = neutral ligands) are very effective catalysts for C−C bond-forming reactions, whereby the CpRu moiety remains intact.[2] Though Cp ligands are usually considered as inert groups, a few examples of C−C activation of Cp have been reported in titanocene,[3–5] cobaltocene, and chromocene complexes.[6] We report herein an unprecedented participation of a Cp in coupling and cycloaddition reactions with alkynes to give tricyclic compounds.

Reaction of [{η^5:σ-$Me_2C(C_5H_4)(C_2B_{10}H_{10})$}Ru($NCCH_3)_2$] (**1**)[7] with 3 equiv of ArC≡CH in toluene at room temperature afforded unexpected ruthenium complexes bearing a tricyclic moiety [{η^4:σ-$Me_2C(C_{11}H_7Ar_3)(C_2B_{10}H_{10})$}Ru($NCCH_3$)] (**2a**–**d**) in 68–76 % yields of isolated compounds (Scheme 1).[8] The ^{1}H NMR spectra of **2a**–**d** were similar. In addition to multiplets for aromatic protons in the range 7.6–7.2 ppm, two singlets for the Me_2C protons at about 1.5 and 1.3 ppm, and one singlet for CH_3CN protons at about 1.7 ppm, two singlets around 6.2 and 4.9 ppm assignable to vinyl protons H10 and H12, two doublets at about 3.4 and 1.0 ppm attributable to H8 and H14, and three doublets of doublets at approximately 4.8, 3.7, and 3.3 ppm corresponding to H7, H5, and H6, respectively, were observed in all ^{1}H NMR spectra. A characteristic resonance[9] for RuC14H at about −17 ppm was found in the ^{13}C NMR spectra of **2a**–**d**. All ^{11}B NMR spectra exhibited a 1:1:3 pattern.



Scheme 1. Preparation of **2a**–**d** and [D_3]-**2a**.

When PhC≡CH was replaced by PhC≡CD in the above reaction, [{η^4:σ-$Me_2C(C_{11}H_4D_3Ph_3)(C_2B_{10}H_{10})$}Ru($NCCH_3$)] ([$D_3$]-**2a**) was isolated in 70 % yield with greater than 98 % deuterium incorporation (Scheme 1).[8] Its ^{1}H NMR spectrum showed that the resonances corresponding to H10, H12, and H14 had disappeared and one doublet attributable to H5 (instead of one doublet of doublets in **2a**) was observed, while all other signals were identical with those of **2a**. This result indicates that H10, H12, and H14 come from the alkyne.

The molecular structure of **2a** was confirmed by single-crystal X-ray analysis.[10] The Ru atom is σ-bound to C2 and C14, η^2-bound to two double bonds, and coordinated to one CH_3CN molecule in a distorted square-pyramidal geometry

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with C14 at the axial position (Figure 1). A tricycle containing a five-, a six-, and a seven-membered ring was constructed by coupling/cycloaddition of the Cp ring with three $PhC\equiv CH$ molecules. The C4–C8/C9–C10/C12–C13 distances of 1.417(8)/1.349(8)/1.387(8) Å are indicative of $C=C$ double bonds. Other C–C distances in the tricyclic framework are typical of single bonds. The Ru1–C2 distance of 2.115(6) Å falls in the range 2.10–2.26 Å observed in $[\{\eta^5{:}\sigma\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{10})\}Ru(L_2)]$ (L_2 = Lewis bases).[11] The Ru–C(14) distance of 2.100(6) Å is comparable to those observed in other ruthenium alkyl complexes, for example, 2.273(2) Å in $[(C_5Me_5)\{RuHC(PPh_2NPh)_2\}]$,[9c] 2.211(2) Å in $[(C_5Me_5)Ru(CO)\{\eta^2\text{-}HC(PPh_2NPh)_2\}]$,[9c] 2.142(9) Å in $[Ru(CO)_2\{\sigma,\eta^5\text{-}10\text{-}C(H)(PMe_2Ph)CH_2\text{-}7,8\text{-}C_2B_9H_{10}\}]$,[12a] and 2.293(16) Å in $[RuCH_3(NO)(PiPr_3)]$.[12b]

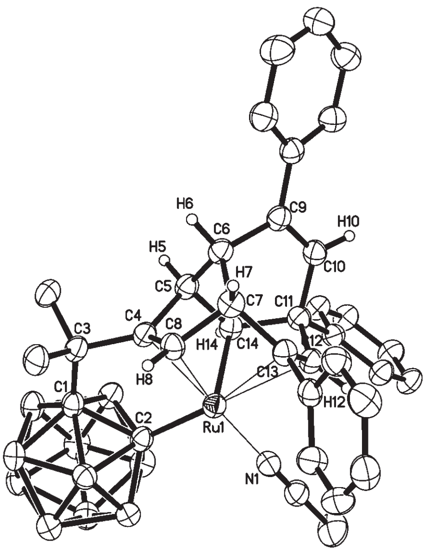
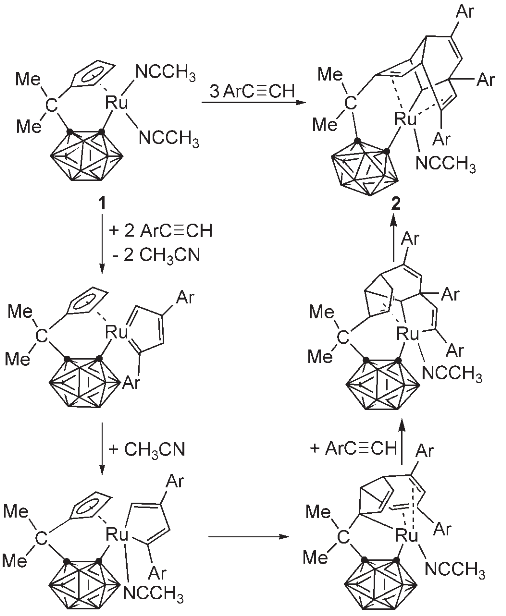


Figure 1. Molecular structure of **2a**. Selected bond lengths [Å]: Ru1–C2 2.115(6), Ru1–C4 2.200(6), Ru1–C8 2.262(8), Ru1–C12 2.337(6), Ru1–C13 2.468(6), Ru1–C14 2.100(6), Ru1–N1 2.098(6), C1–C2 1.740(8), C4–C8 1.417(8), C9–C10 1.349(8), C12–C13 1.387(8).

The formation of **2a–d** was totally unexpected, and similar reactions have not been observed before in ruthenium chemistry. Therefore, the most interesting feature of these complexes is the mechanism by which they are formed. We considered several possible reaction pathways. The most feasible (Scheme 2) is supported by DFT calculations with the B3LYP hybrid functional in which HCN and acetylene were used as model substrates. Figure 2 shows the energy profile for the pathway, which includes three stages: 1) oxidative coupling of the two acetylene ligands in **PC**, 2) stepwise migration of the newly formed diene unit in **IN2** to the Cp ring, and 3) oxidative coupling between a newly coordinated acetylene and the coordinated double bond of the cyclohexadiene unit in **IN5** followed by reductive elimination.



Scheme 2. Proposed reaction mechanism for the formation of **2**.

The first stage begins from bis-acetylene complex **PC** with a small barrier of 10.3 kcal mol^{-1} to complete the oxidative coupling step to give ruthenacycle **IN1**, which is thermodynamically very favorable with a reaction free energy of 35.4 kcal mol^{-1}. Figure 3 shows that **IN1** has a short Ru–C bond (1.924 Å), two longer C–C bonds (1.433 Å), and a shorter C–C bond (1.378 Å) in the five-membered ring. Intermediate **IN1** was commonly described as a bis-carbene species and a five-membered aromatic metallole in the literature.[13] On coordination of one nitrile molecule, **IN1** is converted to 18-electron metallacyclopentadiene intermediate **IN2**.[14] This is followed by stepwise migration of the diene unit to the Cp ring with barriers of 14.1 and 24.7 kcal mol^{-1}, respectively, to form 14-electron intermediate **IN4** bearing a five- and a six-membered ring. In the last stage, **IN4** takes up one acetylene molecule to give **IN5**, followed by oxidative coupling between the coordinated acetylene and the coordinated double bond of the cyclohexadiene ring to give **IN6**. Finally, reductive elimination with a very small barrier gives **PR** as the final product.

Our calculations suggest that coordination of a nitrile molecule to bis-carbene intermediate **IN1** to give diene species **IN2** promotes stepwise migration of the diene unit to the Cp ring (Figure 2). We examined the possibility of direct migration starting from **IN1.** The calculations give a barrier of 32.2 kcal mol^{-1}, which is 11.2 kcal mol^{-1} higher than that calculated for the conversion of **IN1** to **IN3**. Clearly, the ruthenium–carbon double-bond character in the five-membered ring of **IN1** prevents direct migration. Conversion of bis-carbene intermediate **IN1** to diene species **IN2** is necessary before migration occurs. Interestingly, a recent computational study showed that direct migration can occur in a titanocene analogue that is an intermediate derived from Cp_2Ti-mediated oxidative coupling of two coordinated acetylene molecules.[15] This is understandable because the intermediate formed is already a metallacyclopentadiene, since a Cp_2Ti fragment does not have orbitals available to make a bis-carbene structure accessible.

We also examined the possibility of acetylene trimerization to form benzene starting from **IN1** by coordinating one more acetylene molecule. Coupling between the coordinated

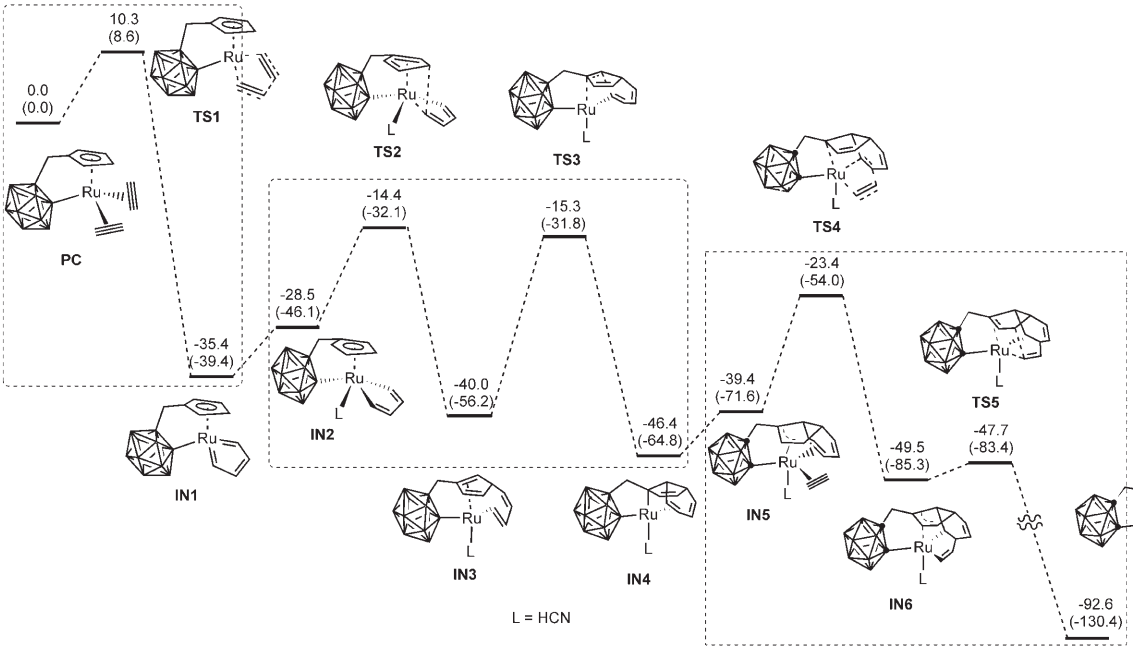


Figure 2. Energy profile of reaction pathway starting from **PC**. The relative free energies and electronic energies (in parentheses) are given in kcal mol^{-1}.

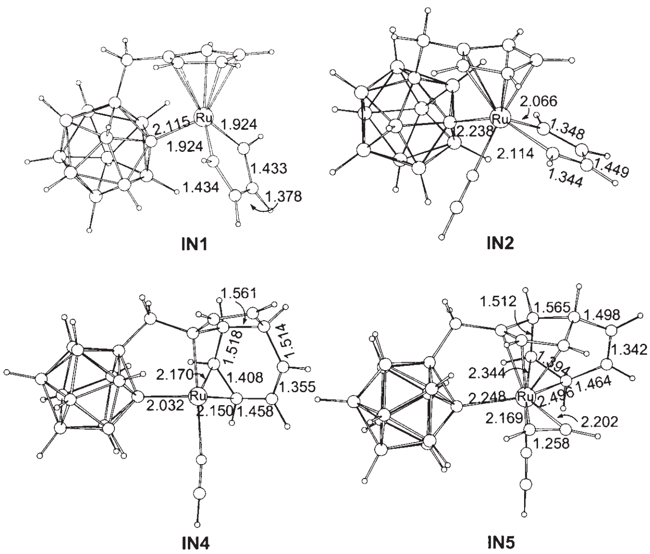


Figure 3. Selected bond lenghts [Å] calculated for intermediates.

acetylene and one of the two metal–carbene bonds was calculated to have a small barrier, consistent with those reported for CpRuCl-mediated cyclotrimerization of acetylenes.[13a,b] The transition state is higher in free energy than **IN1** + acetylene by 9.8 kcal mol^{-1}. The fact that complex **1** does not mediate cyclotrimerization of ArC≡CH can only be explained by steric arguments. Coordination of ArC≡CH to a substituted **IN1**-type intermediate is expected to be less likely in view of the sterically demanding carboranyl moiety in the current system. Even with a possible weak coordination, steric repulsion between the alkyne substituents and the bulky carboranyl moiety would make the transition state for coupling very high in energy, so that trimerization would be unlikely and the current complex differs from other CpRu systems in mediating C–C coupling of unsaturated organic substrates.[2]

The **IN4** structure shown in Figure 3 can be considered as a 14-electron seesaw structure, in which the metal center has a less crowded ligand environment than in **IN1**. Therefore, it can bind an alkyne molecule for further C–C coupling.

Reports on Cp_2Ti-mediated alkyne–Cp coupling can also be found.[3] However, the coupling products are very different from those we observed here. In a theoretical study on Ti-mediated alkyne–Cp coupling,[15] Suresh and Koga also located a Ti^{II} intermediate, which can be derived from **IN5** by replacing the acetylene, L, and carboranyl ligands with an η^5-Cp ligand, and Ru with Ti. Unlike **IN5**, which undergoes C–C coupling (Figure 2), the Ti^{II} intermediate releases a benzene molecule by C–C bond breaking. Apparently, the much greater reducing power of Ti^{II} versus Ru^{II} accounts for the different coupling products. In the cases discussed here, Ti^{II} reduces the organic ligands by breaking their C–C bonds whereas Ru^{II} reduces the organic ligands by coupling them.

In conclusion, ruthenium-mediated coupling/cycloaddition of a Cp ring with aromatic alkynes was reported for the first time and offers a facile route to tricyclic compounds.[16] A possible reaction mechanism was proposed with the help of DFT calculations. This work indicates that the sterically demanding carborane moiety plays a crucial role in regioselective dimerization of alkynes (giving head-to-tail coupling products) and prevention of alkyne trimerization.

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[10] Crystal data for **2a**: $C_{36}H_{41}B_{10}NRu$, $M_r = 696.9$, monoclinic, space group $P2_1/c$, $a = 13.734(3)$, $b = 18.414(4)$, $c = 14.171(3)$ Å, $\beta = 104.62(3)°$, $V = 3467.6(12)$ Å^3, $T = 293$ K, $Z = 4$, $\rho_{calcd} = 1.335$ g cm^{-3}, $2\theta_{max} = 50°$, $\mu(Mo_{K\alpha}) = 0.71073$ Å, absorption corrections applied by using ABSCOR,[17a] relative transmission factors in the range 1.000–0.910. A total of 8708 reflections were collected and led to 5264 unique reflections, 5264 of which with $I > 2\sigma(I)$ were considered to be observed, $R_1 = 0.071$, $wR_2(F^2) = 0.149$. The structure was solved by direct methods and refined by full-matrix least-squares techniques on F^2 by using the SHELXTL/PC crystallographic program.[17b] All non-hydrogen atoms were refined anisotropically and all hydrogen atoms were geometrically fixed by using the riding model. CCDC-605516 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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