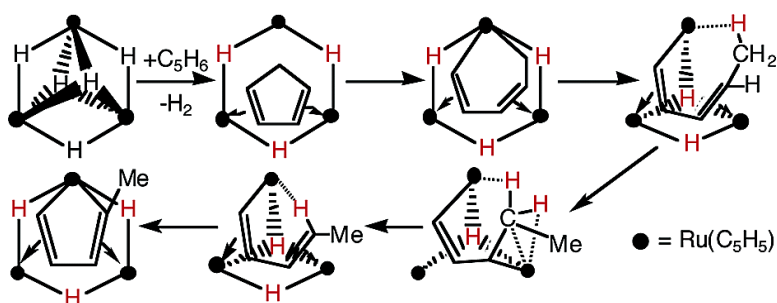


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Versatile and Cooperative Reactivity of a Triruthenium Polyhydride Cluster. A Computational Study

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Multinuclear transition metal complexes often exhibit unusual reactivities that are not found with mononuclear complexes and are attributed to the cooperativity of multiple metal centers.¹ A particular example is the diverse reactivity of multiruthenium polyhydride complexes, containing only C₅Me₅ (Cp*) as auxiliary ligands, toward a variety of substrates, which has been developed and recently reviewed by Suzuki et al.² Among the many fascinating transformations, the reaction of (Cp*)₃Ru₃H₅ with cyclopentadiene (C₅H₆) leading to formation of the trinuclear 2-methylruthenacyclopentadiene at ambient temperature^{2,3} (see Scheme 1) has attracted significant interest. It has been argued that this reaction constitutes the first example of selective C–C bond activation⁴ by three supposedly cooperating metal centers. Despite the substantial experimental effort,^{2,3} the mechanism of this reaction remains unclear. Therefore, we undertook a density functional (B3LYP)⁵ exploration of the mechanism of the reaction of a model complex (Cp)₃Ru₃H₅ (**A1** in Scheme 1) with C₅H₆. On the basis of the computational^{6,7} results, we propose a multistep mechanism for this reaction and highlight its most interesting aspects: the direct involvement of all three metal centers and two cluster hydrides, which characterizes the reactivity of this triruthenium complex as versatile and cooperative.

The proposed mechanism (Scheme 1) is divided into two parts. Part A connects the reactants, **A1** + C₅H₆, to the model of the experimentally observed intermediate, **A13** + H₂, and is slightly endothermic. This part can occur via two distinct pathways, associative and dissociative. The associative pathway begins with the C₅H₆ coordination (+C₅H₆, then –H₂); in contrast, the H₂ dissociation takes place first in the dissociative pathway (–H₂, then +C₅H₆).⁸ The dissociative pathway has two steps with high barriers: **A2** → **A3** ($\Delta G^\ddagger = +26.9$ kcal/mol, $\Delta H^\ddagger = +27.3$ kcal/mol, $\Delta S^\ddagger = +1.1$ cal/(mol K)) and **A6** + C₅H₆ → **A7** ($\Delta G^\ddagger = +25.7$ kcal/mol, $\Delta H^\ddagger = +10.8$ kcal/mol, $\Delta S^\ddagger = -50.1$ cal/(mol K)). On the other hand, the activation parameters for the rate-determining step (RDS) of the associative mechanism, **A2** + C₅H₆ → **A8**, are $\Delta G^\ddagger = +25.9$ kcal/mol, $\Delta H^\ddagger = +15.5$ kcal/mol, and $\Delta S^\ddagger = -39.6$ cal/(mol K). The comparison of these results with the experimental activation parameters² for the RDS ($\Delta G^\ddagger = +21.6$ kcal/mol, $\Delta H^\ddagger = +12.7$ kcal/mol, and $\Delta S^\ddagger = -30.0$ cal/(mol K)) does not rule out either of the two pathways.⁹ The C–C bond cleavage **A12** → **A13** step ($\Delta G^\ddagger = +19.9$ kcal/mol), which concludes Part A, is not rate-determining.

The second part (Part B, Scheme 1) of the mechanism, the conversion of the intermediate **A13** to the final product **B8**, is

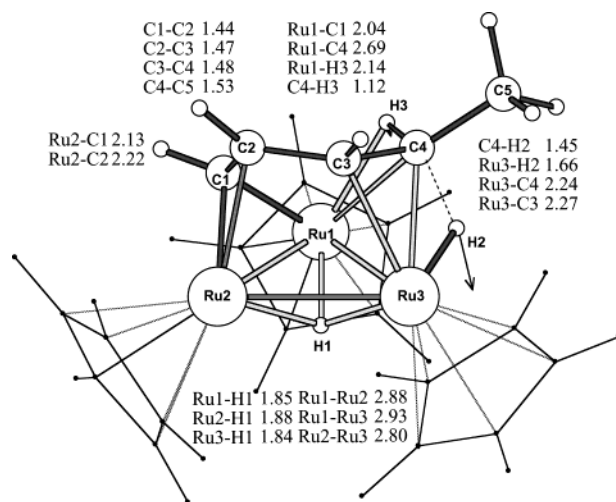


Figure 1. The optimized structure of transition state **TS-B5-B6**, and selected interatomic distances, in Å. The reaction coordinate is depicted with the arrows at the atoms. The atoms of the spectator Cp ligands are represented by dots and are connected by thin lines.

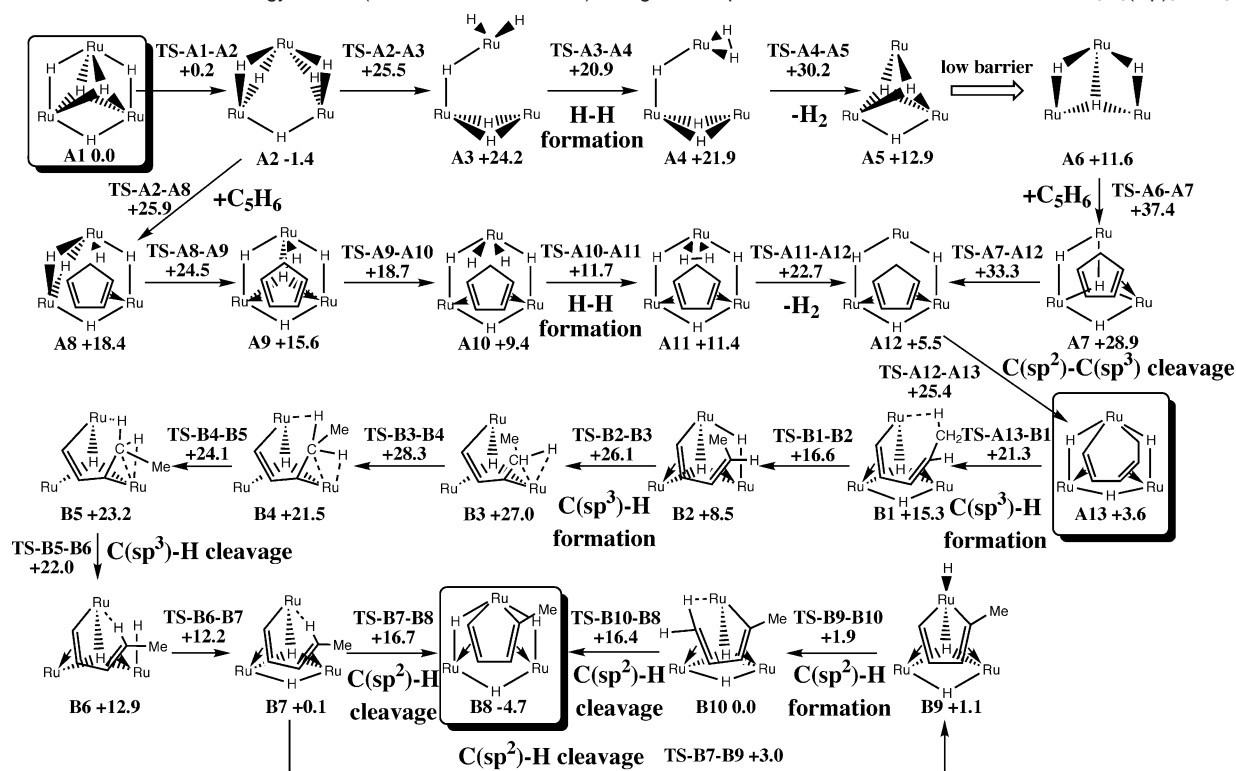
slightly exothermic. We suggest that this transformation occurs via two sequential C(sp³)–H bond formation steps (**A13** → **B1** and **B2** → **B3**) followed by C(sp³)–H and C(sp²)–H bond cleavage steps (**B5** → **B6** and **B7** → **B8**). Although the lability of C–H bonds in certain transition metal complexes is well established,¹⁰ the “catalytic” involvement of the two cluster hydrides in the transformation of the C₅H₆ moiety proposed here is novel¹¹ and quite remarkable.

Another inspiring computational result is the further support for the notion of cooperation^{2,12} between three Ru centers in a multistep transformation. For instance, in the transition state **TS-B5-B6** (Figure 1), the Ru3 center assists the C–H bond activation after the C–C bond has been cleaved on the Ru1 center. The cooperative involvement of the three Ru centers in activations of C–C and C–H bonds, as well as in agostic and π interactions with the C₅H_n fragment at various stages of Part B of our mechanism, is evident from Scheme 1.

In summary, we propose a detailed mechanism for the complex reaction of ruthenacyclopentadiene formation³ that involves direct assistance by two hydride and three Ru centers. We plan to present a more detailed discussion of our results in the near future, and we hope that our findings contribute to the understanding of multinuclear, polyhydride transition metal clusters reactivity.

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Scheme 1. The Gibbs Free Energy Profile (kcal/mol, 298 K, 1 atm) along the Proposed Mechanism for the Reaction $\text{Ru}_3\text{H}_5(\text{Cp})_3 + \text{C}_5\text{H}_6^a$ 

^a The spectator Cp ligand on each Ru is omitted. The models of the experimentally observed^{2,3} species are outlined: reactant, **A1**, intermediate, **A13**, product, **B8**. The B3LYP Gibbs free energies are in kcal/mol, relative to separated **A1** and C_5H_6 . See Supporting Information for computational details. The transition state connecting species **A5** and **A6** has not been located but is anticipated to be less than 5 kcal/mol higher than either minimum.

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Supporting Information Available: Details of the computational methods (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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