Modulating Escape Channels of Cycloheptatrienyl Rhodium Carbenes to Form Semibullvalene

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KEYWORDS**:** semibullvalene, transition-metal catalysis, density functional theory, substituent effects, rhodium-carbene, fluxional molecules, barbaralyl cation

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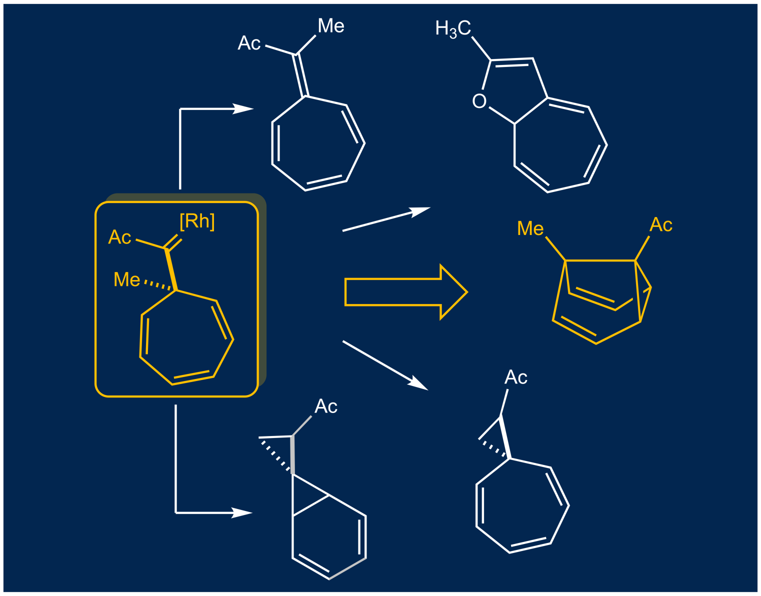


ABSTRACT. We report the various escape channels available to dirhodium carbene intermediates from cycloheptatrienyl diazo compounds with density functional theory. An intramolecular cyclopropanation would, in principle, provide a new route to semibullvalenes. A full exploration of the potential energy surface reveals that methylating carbon-7 suppresses a competing β-hydride migration pathway to heptafulvene products, giving semibullvalene formation a reasonable chance. During our explorations, we additionally discovered unusual spirononatriene, spironorcaradiene, and metal-stabilized 9-barbaralyl cation structures as local minima.

INTRODUCTION

"While it is mutually advantageous to tie theory with experiment, I still feel that theory should lead, rather than follow experiment in exploring chemistry."

— Paul von Ragué Schleyer[1]

"In my opinion, quantum mechanics can make two different contributions to chemistry. Firstly, it permits non-empirical comprehension of experimental results. However, we should not overlook another important aspect: the promotion of empirical chemistry from the theoretical side."

— Kenichi Fukui[2]

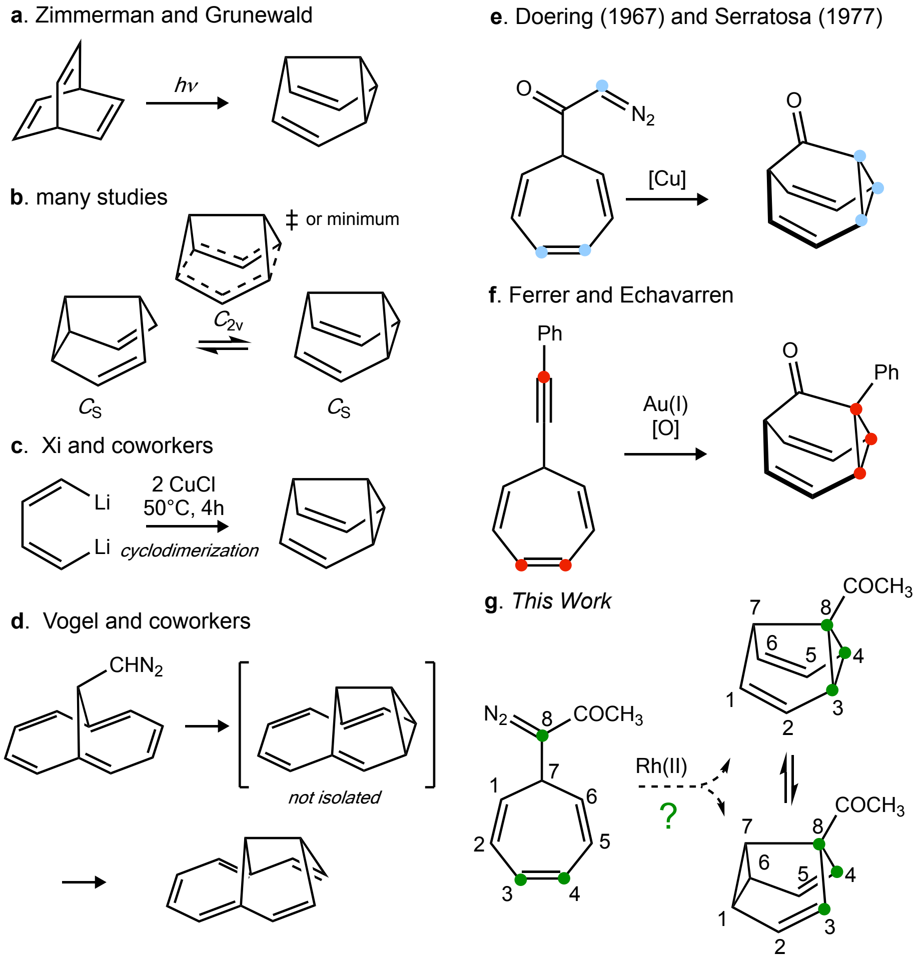
"A beautiful chemical world, of molecules waiting to be made, opens up through the ingenuity of theoretical chemists. Their predictions astound us, generate ideas, and prompt the synthesis of new structures and functions. No exaggeration, none at all, is needed to build this world."

— Roald Hoffmann, Paul von Ragué Schleyer, and Henry F. Schaefer III[3]

In 1966, by a fortunate stroke of serendipity, Zimmerman and Grunewald introduced semibullvalene (SBV) to the world of chemistry. Upon photolysis of barrelene they discovered they had synthesized SBV and its C_8H_8 isomer, cyclooctatetraene (COT, Scheme 1a).[4] In 1972, Zimmerman and Sousa then synthesized cycloheptatrienyldiazomethane and studied its thermal and photochemical rearrangement to products resulting from nitrogen loss and subsequent rearrangement of the carbene intermediate, thinking they might observe SBV among other C_8H_8 products.[5] They did not. Instead, they isolated benzene, COT, heptafulvene, and acetylene. Semibullvalene has been observed[6] as a side-product of photochemical reactions leading to COT (COT on the S_1 state is notably a photostable, Baird aromatic D_{8h} energetic sink).[7–9]

Considering advanced methods for taming carbene reactivity with transition metals (e.g., Rh),[10] we wondered whether metal carbenes might, in theory, pave an alternate way to SBV. Indeed, more than 50 years later, SBV still remains a physical organic chemist's playground,[11,12] and finding new synthetic routes to SBV and its derivatives would be synthetically useful. Here, we offer a theoretical prediction for a potential synthetic route to SBV via an intramolecular cyclopropanation of dirhodium carbenes derived from cycloheptatrienyl diazo compounds, and describe the complex mechanistic networks surrounding such reactions.

Scheme 1. Select examples of semibullvalene and barbaralone syntheses (a-f) and this work (g).



Semibullvalene in Historical Context.

Semibullvalene is one of the most important molecules in the history of physical organic chemistry. Its rapid, degenerate [3,3]-sigmatropic shift (Hardy-Cope rearrangement)[13,14] and fluxional[15] (or locked[16]) behavior have been points of sustained interest. Other work investigated SBV's electronic structure,[17–19] heavy-atom tunneling capabilities (a theoretical prediction[20] borne out by experiment),[20–25] and [3,3] rearrangement barrier height[26] with quantum calculations. Some even introduced ways to reduce,[27] eliminate,[28] interrupt,[29] and invert the activation barrier for its rearrangement to a homoaromatic minimum (Scheme 1b).[30–36] Its bromination mechanism[37] was examined in detail, as was the dynamic behavior associated with its formation via a reaction with a post-transition state bifurcation (PTSB).[38–41]

Semibullvalene is a prototypical fluxional carbon cage, a class of molecule that has gained extensive renewed interest. For instance, some have leveraged the fluxionality of related carbon cage molecules, such as bullvalene and barbaralane, for applications in materials and sensing, sparking new interest in the dynamic nature of shapeshifting molecules.[42–50] Sanchez and Maimone recently used shapeshifting anions in a total synthesis ocellatusone C, highlighting that "the barbaralyl nucleus remains an outstanding synthetic challenge".[51] Bullvalenes and SBV fit this mold as well.[52]

Efforts to synthesize SBV and SBV derivatives abound (e.g., Scheme 1c),[53–60] and some are still seemingly stumbled upon by accident.[61] Much of the work in the late twentieth century on SBV emerged out of a strong interest in homoaromaticity (Scheme 1d),[62] an interest that remains alive today.[63] With the continuous discovery of new reactions, there remains room for breathing new life into SBV synthesis. Using quantum chemical computations, we explore the viability of a new approach to synthesize monosubstituted SBVs via a dirhodium(II)-catalyzed cyclopropanation (CP) through a metal carbene intermediate (Scheme 1g), sparked by our own interest in PTSBs, i.e., could cyclopropanation lead directly to the [3,3] rearrangement transition structure (Scheme 1g)?

Targeting Semibullvalene Through the Lens of Metal-Carbene Chemistry.

Metal-carbene mediated chemistry has a long and winding history.[10] Our group has worked independently and collaborated closely with experimental groups to understand mechanisms of Rh-carbene mediated transformations, including C-H insertion[64,65] and ylide formation reactions,[66–68] with the aim of developing synthetically useful models of reactivity and selectivity. This chemistry has proven to be a playground of its own—a family of synthetically relevant organometallic reactions that display behaviors considered by some to be esoteric, but which play important roles in determining product distributions. For example, our group has shown that some C-H insertion reactions involve cryptic post-transition state bifurcations (PTSBs) that provide facile routes to unwanted side products.[69–72] Tandem processes[73] from Rh-carbene intermediates—such as CP/[3,3] rearrangements,[74–77] which have been applied in total syntheses to access (otherwise difficult to synthesize) seven-membered rings, or C-H insertion/[3,3] rearrangements[78]—also look to involve PTSBs.[70,71] Given this precedent, we additionally ask in this work whether SBV might be generated by a CP that involves a PTSB (Scheme 1g).

We are not the first to suggest a transition metal-catalyzed synthesis of fluxional molecules from cycloheptatrienes. In 1967, the Doering group discovered a synthetic route to barbaralone from a cyclohepatrien-7-yl diazomethyl ketone,[79] and building on that work in 1977, Casas and

Serratosa synthesized barbaralone with a Cu-carbene mediated CP in their synthesis of bullvalene (Scheme 1e).[80] Both methods result in products that are net cyclopropanations of the diazomethyl ketone with the central π bond of the cycloheptatriene.

Recently, Ferrer and Echavarren synthesized barbaralones by gold(I)-catalyzed intramolecular oxidative cyclization of 7-ethynyl-1,3,5-cycloheptatrienes (Scheme 1f).[81] The same group also reported generation of closely related and highly fluxional barbaralyl cations from 7-alkynyl cycloheptatrienes by gold catalysis.[82] Could Rh(II)-catalysts assist in this type of transformation? When the Echavarren group expanded on this work in 2021 they discovered that the use of Rh(II)-catalysts led to a decarbenation to alkynylcyclopropanes from 7-alkynyl cycloheptatrienes and attributed the result to a lower barrier for decarbenation ($\Delta G^{\ddagger} = 21.9$ kcal mol^{-1}) than for 6-*endo*-dig cyclization ($\Delta G^{\ddagger} = 24.4$ kcal mol^{-1}) with the use of Rh(II) catalysts.[83] Cu(I) catalysts similarly have been shown to work in a synthesis of barabaralyl-substituted allenyl acid esters from terminal alkynes and tropylium tetrafluoroborate.[84] Finally, during preparation of this manuscript, Dumele and Teichert published an intriguing synthesis of 6π and 10π neutral homoaromatics.[63] Their synthetic approach, inspired by the work of Vogel *et al.*,[62] affords homoannulene esters with a barbaralone framework through an intramolecular, dearomative Buchner reaction.

May cycloheptatrienyl diazo compounds be a reasonable starting point to synthesize semibullvalenes using Rh(II)-catalysts through an intramolecular cyclopropanation? Our computational explorations allow us to predict[1,85] that, whether or not this approach succeeds in the lab, unusual rearrangement chemistry of the metal carbene intermediate will likely reveal itself.

COMPUTATIONAL METHODS

Fluxional molecules are molecules that undergo rapid, degenerate rearrangements according to the International Union of Pure and Applied Chemistry (IUPAC; http://goldbook.iupac.org), and they generally have low activation barriers. The degenerate rearrangement of SBV is challenging to accurately predict computationally because it exists on a relatively flat surface—an experimental $\Delta G^{\ddagger}$ = 5.5 kcal mol^{-1} by ^{13}C NMR.[86] Many have considered the B3LYP[87] functional reliable for obtaining reasonable geometries, and to a certain extent, reaction barriers that are consistent with experiment.[20,88,89] In some cases, however, spurious intermediates and/or significant deviation from experimentally-derived activation barriers have clouded the consensus on the reliability of B3LYP for [3,3] rearrangements.[90–92] Recently, Karton reported that three functionals (BMK, PW6B95, and MN12-SX) outperformed other functionals in predicting accurate [3,3] barrier heights and reaction energies when compared to CCSD(T)/CBS benchmark calculations and experiment.[93] Based on Karton's benchmark work showing that PW6B95 performs accurately for systems involving SBV and for systems including Rh,[94] we selected PW6B95[95] as a functional with the def2-SVP basis set (i.e., PW6B95/def2-SVP) for geometry optimizations followed by single-point corrections to the electronic energy with a larger basis set (def2-TZVP) at those geometries. We reasoned that PW6B95/def2-TZVP//PW6B95/def2-SVP is a reasonable level of theory for reactions involving dirhodium catalysts and for qualitative investigations of this kind, which have no experimental precedent against which to compare data.[96] However, we tested PW6B95/def2-TZVP//PW6B95/def2-SVP's ability to predict the [3,3] rearrangement of SBV (experimental barrier: 5.5[86] to 6.2[97] kcal mol^{-1}) and the isomerization barrier of cycloheptatriene to norcaradiene (experimental barrier: 7.2 kcal mol^{-1}).[98] Our predicted barriers of 5.7 and 7.1 kcal mol^{-1} for the [3,3] and isomerization barriers, respectively, are within chemical accuracy (<1 kcal mol^{-1}, see Supporting Information for more details).

Geometry optimizations and frequency calculations were carried out with *Gaussian 16*.[99] Transition structures (TSs) were identified by the presence of one imaginary vibrational frequency and subsequent intrinsic reaction coordinate (IRC) calculations identified minima on the potential energy surface to which TSs are connected.[100–102] Quasi-classical *ab initio* molecular dynamics simulations were run with the Progdyn script package developed by Singleton at the PW6B95/def2-SVP level of theory.[103] Trajectories were propagated in the reactant and product directions until the C^1-C^2 and C^1-C^4 distances were greater than 2.80 Å, for which we report the trajectory as reaching the reactant well, until the C^2-C^4 is less than 1.55 Å and the C^1-C^4 and C^1-C^2 distances are less than 1.52 Å, for which we report the trajectory as reaching 'SBV product 1' (the semibullvalene product we found from the IRC calculation), or until the C^{11}-C^{13} distance is less than 1.55 Å and the C^2-C^4 distance is greater than 2.00 Å, for which we report the trajectory as reaching 'SBV product 2', the other potential product of a PTSB (Scheme 1g).

RESULTS AND DISCUSSION

Acetyl-SBV.

The simplest reaction that we envisioned might be achieved experimentally is the transformation of diazo compound **A** to acetyl-SBV **D**/**E** (Figure 1, path II in green). We chose R to be a simple acetyl (Ac = $COCH_3$) group, given the body of literature on acceptor and donor/acceptor carbenes.[104] In addition, structures similar to (diazocarbonylmethyl)cycloheptatriene (**A**), have been described in the literature.[105]

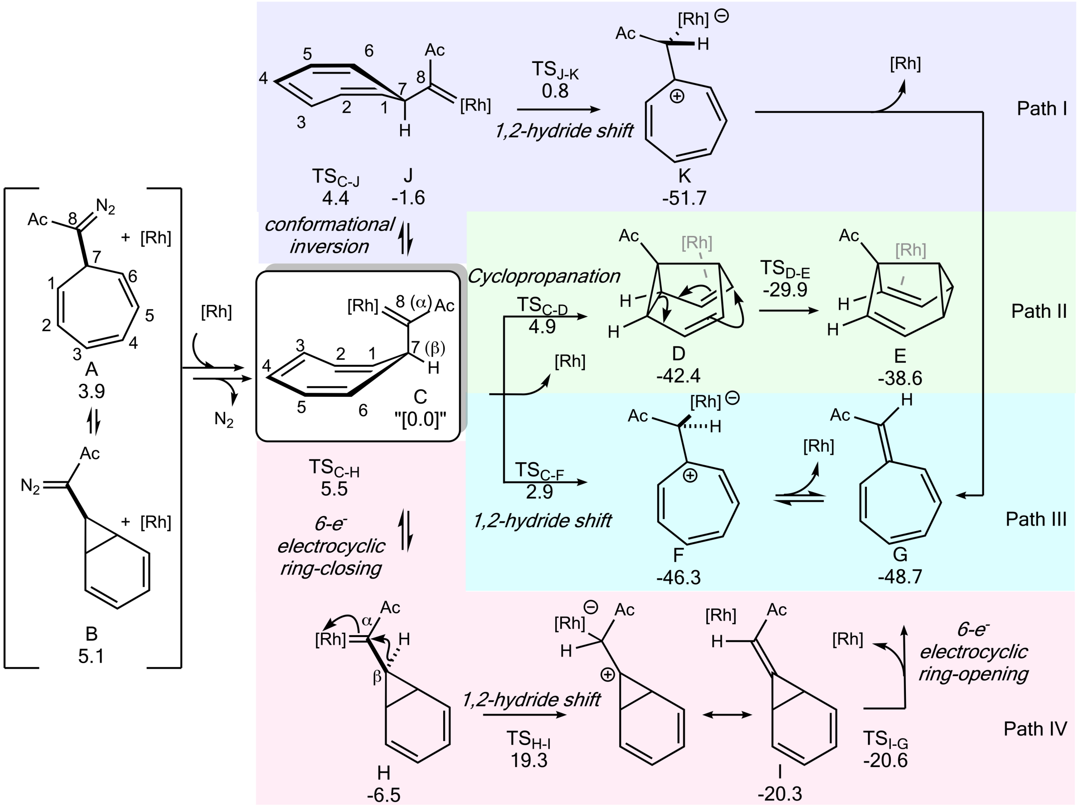


Figure 1. Possible mechanistic pathways to and from **C**. All relative free energies (PW6B95/def2-TZVP //PW6B95/def2-SVP) are in kcal mol^{-1}. (1) top, purple: conformational inversion followed by 1,2-hydride shift; (2) second to top, green: SBV formation by CP and [3,3] rearrangement; (3) second to bottom, blue: 1,2-hydride shift; (4) bottom, red: norcaradiene formation followed by 1,2-hydride shift and electrocyclic ring-opening.

Exposure of **A** to a Rh catalyst (here, we model $Rh_2(OAc)_4$ for simplicity) should lead to nitrogen extrusion to form Rh-carbene species **C**. The barrier for intramolecular CP of **C** to form Ac-SBV **D** (via **TS$_{C-D}$**) is predicted to be low (4.9 kcal mol^{-1}). Formation of **D** is also predicted to be highly exergonic (-42.4 kcal mol^{-1}), and its [3,3] rearrangement is predicted to require a 12.5 kcal mol^{-1} barrier (**TS$_{D-E}$**) to form the slightly less-favorable **E** (-38.6 kcal mol^{-1}). While these results indicate that formation of Ac-SBV would not face a large barrier, possible competing reactions must be considered.[3] For instance: (i) the cycloheptatriene–norcaradiene equilibrium (**C** ⇌ **H**) favors the norcaradiene **H** by 6.5 kcal mol^{-1}, (ii) conformational isomerization slightly favors the isomer wherein the hydrogen at C7, instead of the Rh-carbene, is positioned on the concave face of the cycloheptatriene (Figure 2), and (iii) once the Rh-carbene is formed, side-reactions (such as *β*-hydride migration to heptafulvenes, e.g., **C** → **F** → **G** or **C** → **J** → **K** → **G**)[106,107] can occur. Thus, we are unable to ignore the kinetic instability of intermediate **C**.[3] The variety of available escape channels is abundant, so these possibilities were investigated in detail.[108,109]

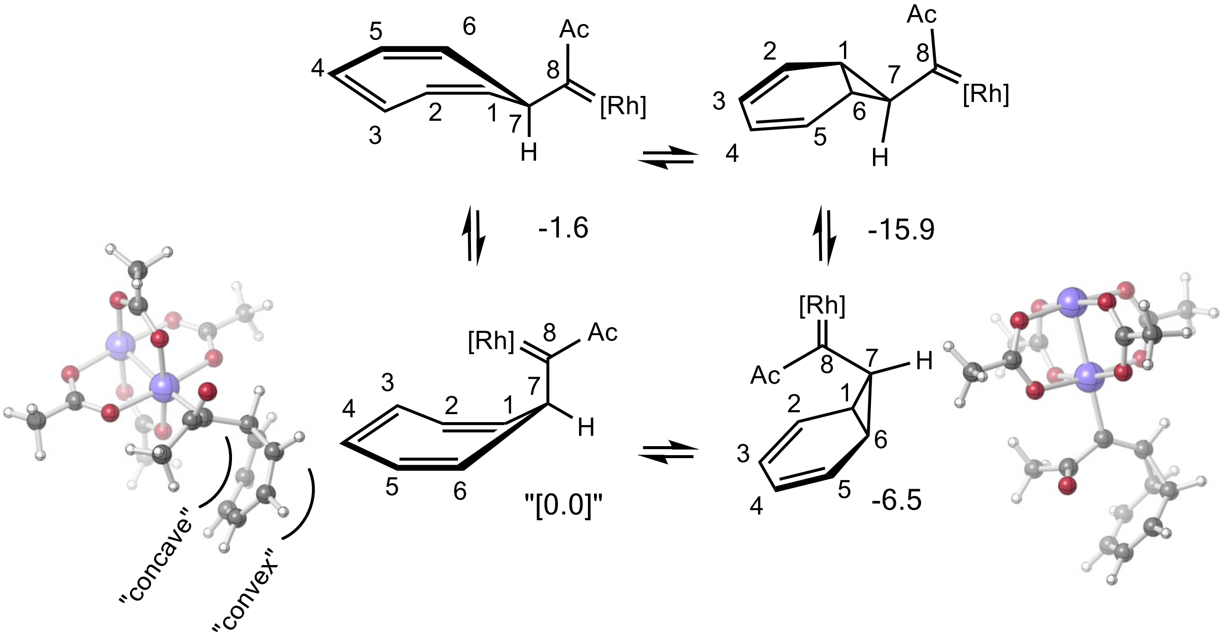


Figure 2. Cycloheptatriene-norcaradiene equilibrium. Three-dimensional depictions highlight the boat conformation of cycloheptatriene with "concave" and "convex" faces. Relative free energies (PW6B95/def2-TZVP//PW6B95/def2-SVP) are in kcal mol^{-1}.

Complications I – Electrocyclization. Cycloheptatrienes[110–112] are generally in rapid equilibrium with norcaradienes (Figure 2).[113–116] If our desired CP reaction is to predominate, either its barrier must be lower than that for **C** $\rightleftharpoons$ **H** equilibration or that equilibration must not lead to an undesired reaction that serves as a kinetic trap. In our system, a π-electron acceptor—the metal carbene group[117]—exists at the 7-position (C7), and π-electron acceptors at this position tend to favor the norcaradiene isomer.[118] We predict that **H** is lower in energy than **C** (and the **C** → **H** barrier is predicted to be 5.5 kcal mol^{-1}, comparable to the CP barrier to **D**; Figure 1). However, the subsequent 1,2-hydride migration that would lead to catalyst dissociation is associated with a TS that is much higher in energy than that for CP (a 25.8 kcal mol^{-1} barrier out of **H**; $\mathbf{TS_{H\text{-}I}}$). Therefore, the **C** → **H** → **I**… path does not appear to threaten our desired reaction.

Complications II – Conformational Bias. The π-systems of cycloheptatrienes are not flat—instead, their sp^3 carbons are bent out of plane, inducing boat like conformations (cf. Figure 2).[119] Parent tropilidene (i.e., hydrogens at C7) has a ring-inversion barrier of ca. 6 kcal mol^{-1} by low temperature ^{1}H NMR.[120–122] As a result, the environments of the two groups on its sp^3 carbon are different: one sits over the cycloheptatriene π-system, while the other points “outside”. For CP to occur, the carbene center must reside over the π-system, but the carbene center prefers to reside outside for **C** (by 1.6 kcal mol^{-1}; compare **C** vs. **J**, Figure 1, Path I). When the carbene center is outside, a 1,2-hydride shift (a *β*-hydride migration) can occur (**J** → **K**) that is predicted to be rapid and highly exergonic.[123] And our computed ring-inversion barrier ($TSS_{C\text{-}J}$) is 4.4 kcal mol^{-1}, slightly lower than that for CP, which suggests the *β*-hydride migration might indeed be a dead-end kinetic trap (Path I).

Complications III – Another β-Hydride Migration. A *β*-hydride migration may also occur directly from conformer **C** (Figure 1, Path III). While the TS for this 1,2-hydride migration is predicted to be higher in energy than that for **J** (2.9 vs. 0.8 kcal mol^{-1}), it is still lower than that for the desired CP step (4.9 kcal mol^{-1}) by 2 kcal mol^{-1}. Tendency to migrate hydride is increased for *α*-diazocarbonyl compounds—precursors to (donor/acceptor metal-carbenes)—due to their higher electrophilicity compared to donor and donor/donor metal-carbenes.[64] Indeed, in Path III, we find that the barrier for *β*-hydride migration directly from **C** is increased upon swapping out the carbonyl acyl group for a phenyl group, thereby making the donor/acceptor carbene into a donor/donor carbene (Path III, 2.9 vs. 5.9 kcal mol^{-1}; see SI Figure S.2 for donor/donor pathways). However, though the barrier for *β*-hydride migration increases upon changing the carbene from donor/acceptor to donor/donor, so does the CP barrier (Path II, 4.9 vs. 8.6 kcal mol^{-1}). Swapping the acyl group for a phenyl group does not tip the selectivity in favor of CP to SBV—the data tell us (with a $\Delta\Delta G^{\ddagger} = 2.7$ kcal mol^{-1}) that the reaction would still favor *β*-hydride migration over CP.

Thus, our metal-carbene may avoid our desired reaction through *β*-hydride migration escape channels to heptafulvene, **G**. Recall that heptafulvene was one product Zimmerman and Sousa isolated in their original report.[5] Additionally, Tomioka et al. reported heptafulvene products in the gas-phase rearrangement of phenyl carbenes, presumably through 7-membered ring intermediates.[124] Heptafulvene **G** can additionally undergo a 10-π electrocyclic ring closure to **L** (not shown in Figure 1; see SI, Figure S1) because of the acetyl group attached to C8, similar to that of the acetyl-heptafulvene reported by Houk.[125] We computed the barrier to do so and the barrier is 16.0 kcal mol^{-1} from **G** to **L**, and downhill in energy.

A Potential Antidote to β-Hydride Migration.

One way around *β*-hydride migration is to introduce a different functional group at C7 in place of the hydrogen, a group with a lower migratory aptitude (e.g., CH_3 for H). Though making this substitution in a computational study is trivial, implementing it in a synthetic campaign could be challenging. Our calculations indicate, however, that swapping out the H for a CH_3 group would switch the selectivity in favor of CP over a possible concerted, intramolecular C-H insertion (**TS$_{\mathbf{C\text{-}F}}$** vs. **TS$_{\mathbf{C\text{-}D}}$**; $\Delta\Delta G^{\ddagger} = 2.4$ kcal mol^{-1}; Figure 3) to a spirononatriene—a direct result of our attempts to locate a 1,2-methyl shift (not found)! Though small-ring spiro compounds have precedent in the literature,[126] to our knowledge, relatively few papers report structures resembling spirononatriene.[127–130] Conformational inversion of CHT (and subsequent 1,2-methyl shift to cycloheptafulvene (**G**)) is again predicted to compete with CP ($\Delta\Delta G^{\ddagger} = 0.7$ kcal mol^{-1}; compare **TS$_{\mathbf{C\text{-}J}}$** to **TS$_{\mathbf{C\text{-}D}}$**), Isomerization to norcaradiene, **H**, is also possible. The relatively high barrier for C-H insertion of **H** ($\Delta G^{\ddagger} = 23.1$ kcal mol^{-1}) makes formation of spironorcaradiene **I** unlikely here. Tricyclic spiro compounds like **I** have some literature precedent, but to our knowledge, spironorcaradienes of the sort we describe have not been reported.[131]

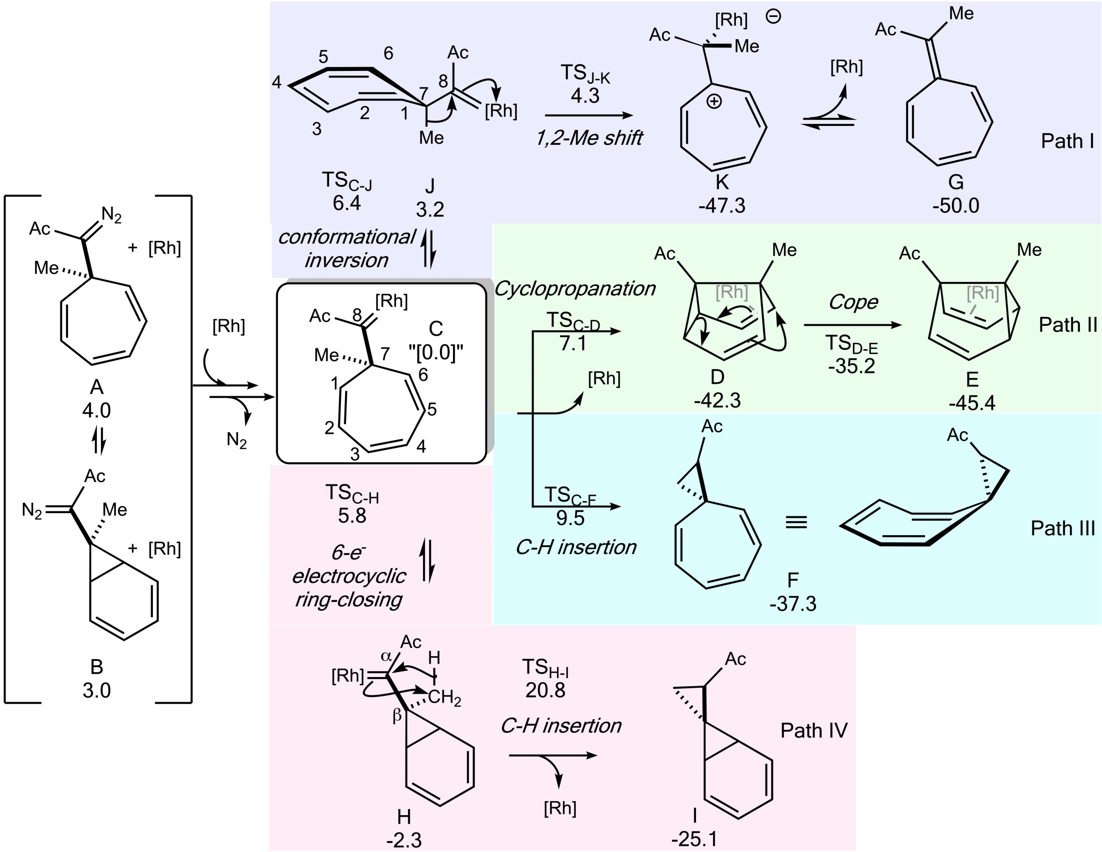


Figure 3. Possible mechanistic pathways to and from **C** for C7-methylated system. All relative free energies (PW6B95/def2-TZVP//PW6B95/def2-SVP) are in kcal mol^{-1}.

In summary, although C7 methyl substitution makes CP to form SBV more likely than in the C7 hydrogen-substituted case (Figure 1), methyl migration (Path I) could still preclude the desired chemoselectivity. We also computed the donor/donor Rh-carbene system with a methyl group at C7 and predict that selectivity for heptafulvene formation is enhanced (a $\Delta\Delta G^{\ddagger} = 2.3$ kcal mol^{-1}; see SI, Figure S4). Methyl substitution at C7 ameliorates the chemoselectivity troubles with the parent system in Figure 1, but simultaneously introduces the possibility of concerted, intramolecular C-H insertion to generate a spirononatriene (**F**).

Bifurcating Pathways

To explore whether a post-transition state bifurcation that leads to both **D** and **E** exists on the potential energy surface downhill in energy from **TS$_{\mathbf{C\text{-}D}}$**, quasi-classical dynamics trajectories were run from **TS$_{\mathbf{C\text{-}D}}$** (of Figure 3). Of trajectories that formed product (32 total), all formed **D** and none formed **E**, which suggests that a PTSB is unlikely to exist in this reaction. Rather sequential SBV formation (**D**) and subsequent [3,3] rearrangement would form **E**.

Gold(I)-catalyzed synthesis of barbaralones

How similar is our proposed reaction to published work on related fluxional molecule syntheses? For comparison, we examined Ferrer and Echavarren's gold(I)-catalyzed oxidative cyclizations[132,133] to barbaralones (Scheme 1f). In their 2016 study, the authors proposed two pathways to barbarlones—specifically, 6-*endo*-dig[134] cyclization then oxidation or *vice versa*. We examined both possible pathways (Figures 4 and 5). The predicted barrier for cyclization in the unoxidized system is higher than that for the oxidized system. The oxidized system also has a significant energetic driving force ($\Delta G = -33.2$ kcal mol^{-1}) that the unoxidized system lacks.[83] The results in Figure 5 resemble our computed CP path (Path II, Figure 1), but do not necessarily provide evidence for or against Ferrer and Echavarren's proposal that oxidation takes place on barbaralyl gold(I) intermediates *after* cyclization—further calculations would be needed.[81] Unlike their reaction, however, questions about oxidation state are irrelevant with our [Rh$_2$] catalysts. The relative energies of bare barbaralones complexed to the gold(I)-catalyst are qualitatively consistent with experimental and theoretical work by Alonso and Echavarren: in particular, the 1-phenyl-barbaralone ($\mathrm{Int_O}$ in Figure 5) is the more thermodynamically stable isomer (here, by 1.1 kcal $\mathrm{mol^{-1}}$).[135]

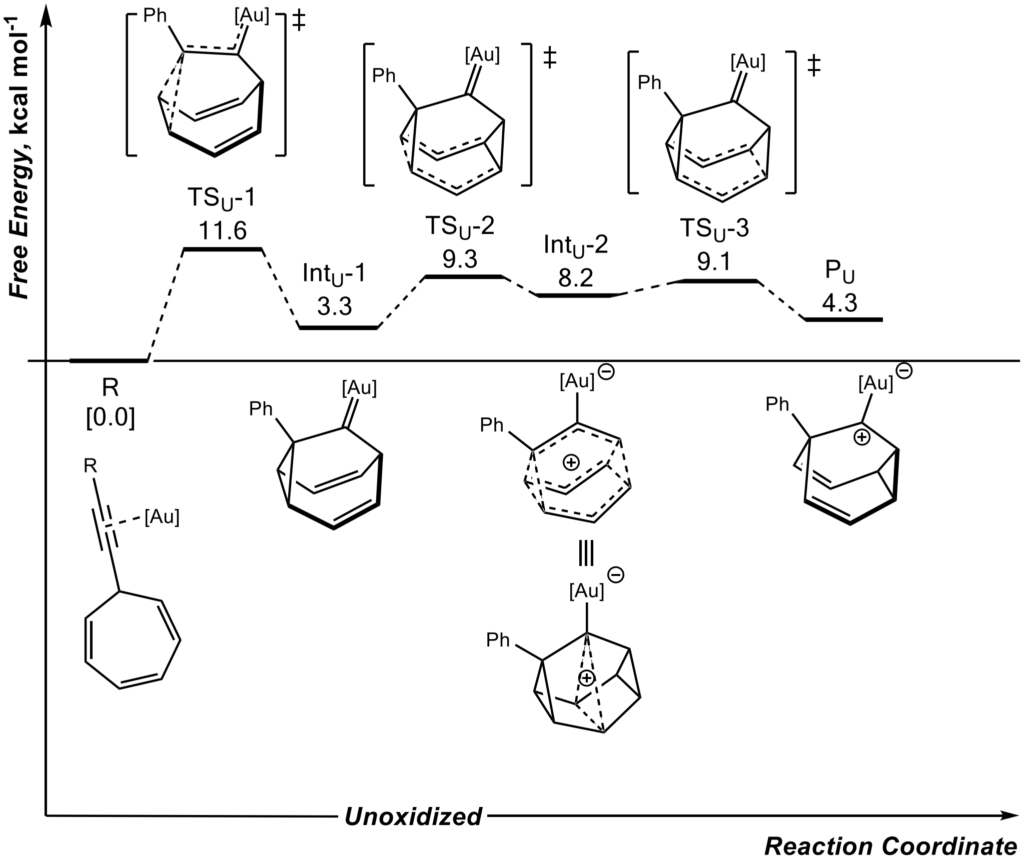


Figure 4. Potential energy surface of barbaralyl cation formation and sequential Hardy-Cope rearrangements. Relative free energies (PW6B95/def2-TZVP//PW6B95/def2-SVP) shown are in kcal $\mathrm{mol^{-1}}$ and are relative to their respective reactants, R. [Au] = $\mathrm{AuP(CH_3)_3}$.

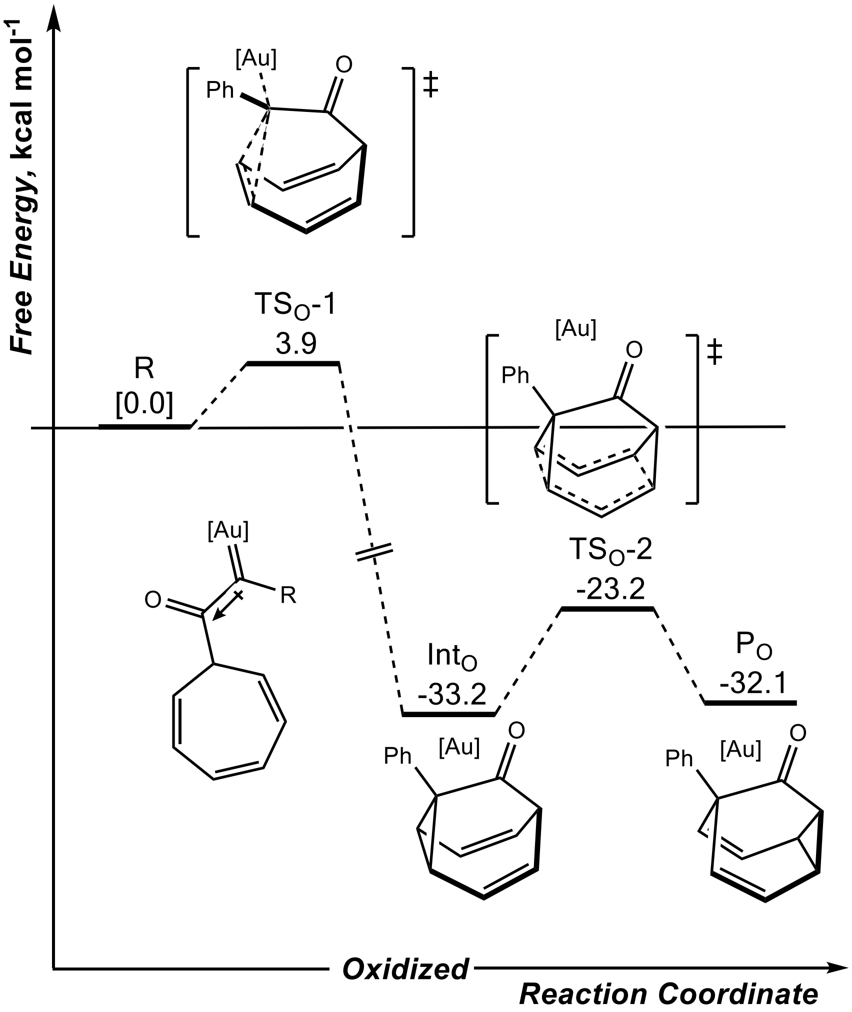
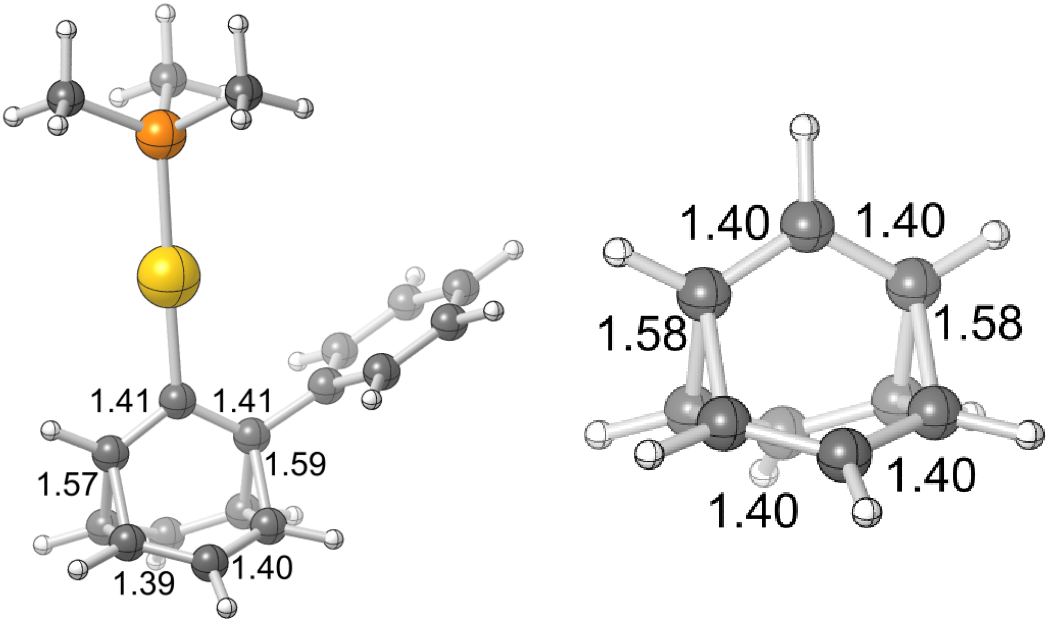


Figure 5. Potential energy surface of barbaralone cation formation and sequential [3,3] rearrangements. Relative free energies (PW6B95/def2-TZVP//PW6B95/def2-SVP) shown are in kcal mol^{-1} and are relative to their respective reactants, R. [Au] = $AuP(CH_3)_3$.

Our results in Figure 4 suggest that the [3,3] rearrangement for the unoxidized system is stepwise (not surprising given the copious studies that have discussed interrupted and aborted pathways for metal-catalyzed pericyclic reactions).[136–139] The intermediate that interrupts the rearrangement (**Int$_U$-2**) can be described as a metal-stabilized 9-barbaralyl cation.[140,141] Free of catalyst and substituents, the 9-barbaralyl cation exhibits D_{3h} symmetry and has been the focus of several studies since its description by Schleyer and coworkers (Figure 6).[142]



C_S

D_{3h}

Figure 6. Comparison of C_s (Int$_U$-2, Figure 4) and D_{3h} (9-barbaralyl cation). Bond lengths (C-C bonds) are angstrom (Å). Structures shown are optimized at the PW6B95/def2-SVP level of theory.

CONCLUSIONS

We assessed the viability of a Rh(II)-catalyzed CP strategy for the synthesis of monofunctionalized semibullvalenes from cycloheptatrienyl diazo compounds. The potential CP step was investigated by DFT calculations, the results of which indicate that CP is energetically feasible from the Rh-carbene intermediate generated after decomposition of the diazo compound. Potential side reactions and isomerizations were explored. Specifically, *β*-hydride migration is computed to compete with, and quite possibly outcompete, CP, leading to substituted heptafulvenes. While heptafulvenes are themselves potentially useful products that can be transformed further, it is possible that a particular substitution pattern would allow heptafulvene formation to be suppressed in favor of CP (a task we leave for others, given the immensity of substituent space, and the goal of this work – to demonstrate the feasibility of Rh(II)-promoted CP to form SBVs).

ASSOCIATED CONTENT

Supporting Information. Supporting Data and Figures; Energies and Frequencies of Computed Structures (PDF).

A data set collection of computational results, including geometries and structure coordinates, is available in the ioChem-BD repository[141] and can be accessed via https://iochem-bd.bsc.es/browse/handle/100/216065

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