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Alkyne Cyclotrimerization | **Hot Paper**

Ligand-Controlled Chemoselectivity in the Rhodium-Catalyzed Synthesis of Pentafulvenes via (2 + 2 + 1) Alkyne Cyclotrimerization

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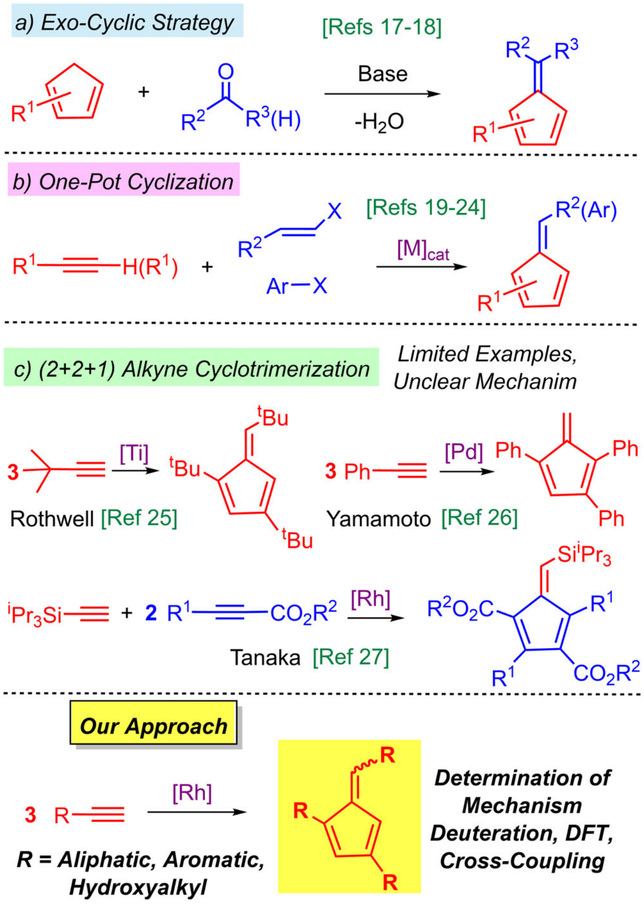
Abstract: The synthesis of pentafulvenes with varied substituents has been efficiently achieved using novel rhodium-based catalysts via (2 + 2 + 1) alkyne cyclotrimerization. A rational design of the catalyst structure, including pyridonato, NHC, and CO ligands, ensures the alkyne chemoselectivity and prevents the formation of robust rhodium-fulvene species. Furthermore, the judicious choice of acidity and steric properties of different alkynes enables the preparation of cross-coupled fulvene derivatives. Stoichiometric and deuteration experiments, as well as DFT calculations, shed light on the reaction mechanism, showing that it includes an initial alkyne deprotonation, two successive alkyne insertions, cyclization, and protonolysis, the first insertion being the rate-determining step.

Pentafulvenes constitute a versatile family of cyclic cross-conjugated organic compounds.[1] Due to their fascinating electronic properties, fulvene architectures can be found embedded in solar cells,[2] OLEDs,[3] electrochromic materials,[4,5] luminescent derivatives for bioimaging,[6] or used for forensic fingerprint detection.[7] In addition, pentafulvenes are key structural motifs in biologically relevant molecules[8] or anticancer drugs,[9] as well as useful synthetic intermediates[10–12] or multifunctional organometallic ligands.[13,14] Although some uncatalyzed cyclizations from open-chain precursors have been described,[15,16] the most common synthetic approaches exploit the exocyclic strategy, which involves the condensation of presynthesized cyclopentadienes with aldehydes or ketones (Scheme 1a).[17,18] The typically harsh alkaline conditions and a limited access to a functionalized cyclic core are major drawbacks. A versatile alternative is offered by transition metal-catalyzed C—C coupling of acyclic substrates, in which internal or terminal alkynes are the pivotal partners (Scheme 1b).[19–24] Nevertheless, a more reliable method consisting in the direct (2 + 2 + 1) alkyne cyclotrimerization can be envisaged (Scheme 1c). Pioneering work by Rothwell,[25] Yamamoto,[26] and Tanaka groups implemented this approach, but with very few alkyne substituents and scarce mechanistic information. Herein, we present an efficient catalytic system for a varied set of alkynes and delve into the reaction mechanism.



Scheme 1. Most common synthetic methods to pentafulvenes and our strategy.

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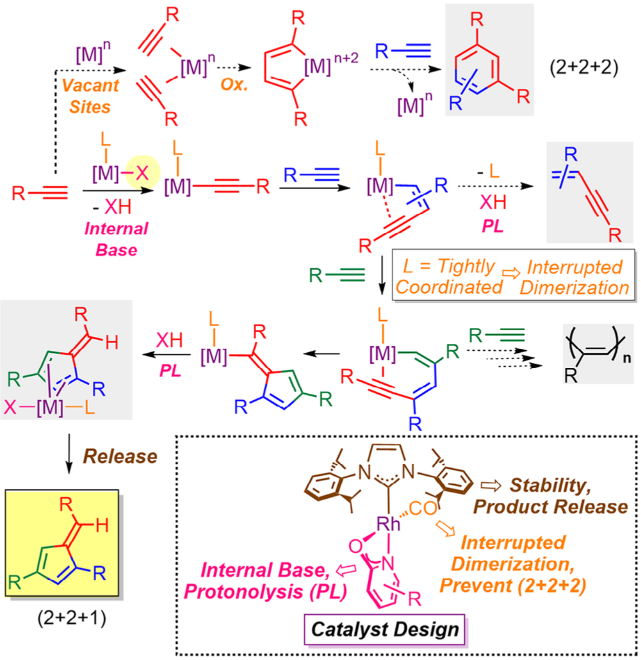
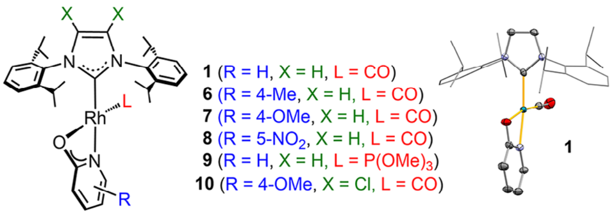


Scheme 2. Catalyst design for the control of chemoselectivity and tightly coordinated fulvene.

Efficient catalytic preparation of pentafulvenes via alkyne (2 + 2 + 1) cyclotrimerization must address two main challenges: chemoselectivity[27] and stoichiometric formation of robust fulvene complexes that thwarts the catalytic activity (Scheme 2).[28–33] Regarding chemoselectivity, (2 + 2 + 2) cycloadditions typically prevail over (2 + 2 + 1) as the formation of aromatic products is thermodynamically favored.[34] A low oxidation state of the metal center and available vacant sites are critical requirements for (2 + 2 + 2) processes. Alternatively, a feasible pathway for (2 + 2 + 1) cycloaddition entails the initial formation of metal-alkynyl species by alkyne deprotonation with an internal base, followed by two subsequent alkyne insertions, cyclization, and protonolysis (PL).[28,35] However, a part of this route is shared with the base-mediated alkyne dimerization process, namely the formation of a metal-butenynyl intermediate.[36] From this point, a protonolytic step emerges as the cornerstone for the chemo-differentiation between alkyne dimerization and (2 + 2 + 1) cycloaddition. Conceivably, a tightly coordinated ligand could hamper the protonolysis of the metal–alkenyl bond, thus interrupting the dimerization process in favor of cycloaddition. Finally, as for the fulvene release, a hindered metal environment and the presence of a high *trans*-effect ligand would be advantageous.

The following key points for an optimal catalyst design for (2 + 2 + 1) alkyne cyclotrimerization emerge from the above mechanistic analysis: i) an internal base to promote the formation of metal-alkynyl initiators, whose protonated form attacks the metal-fulvenyl species; ii) a robust electron-withdrawing ancillary ligand able to interrupt the alkyne dimerization as well as prevent (2 + 2 + 2) cycloadditions, and iii) a bulky strong electron-donating ligand to provide stability and trigger the release of the product. Regarding the built-in base, pyridonato moieties have been revealed to be very efficient proton transfer ligands,[37–39] while CO[40,41] and *N*-heterocyclic carbenes (NHCs)[42–44] are seemingly candidates for the subsequent outlined requirements.

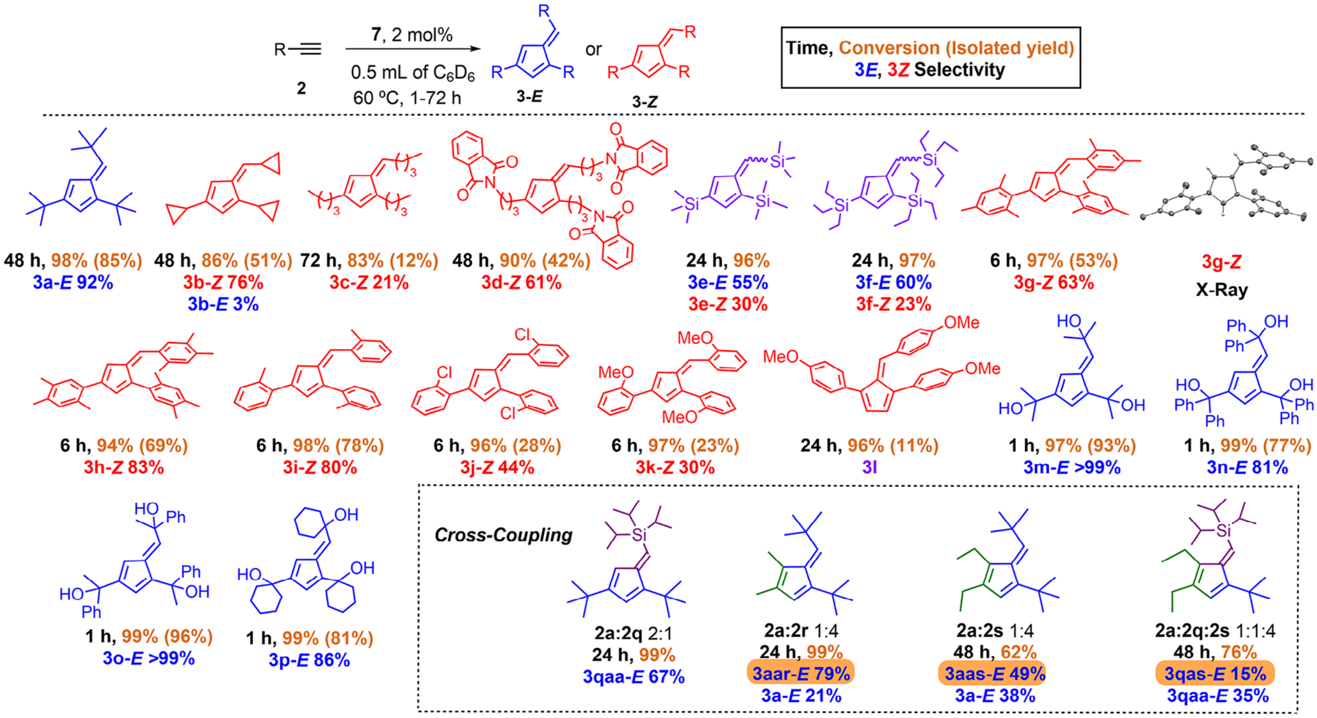


Scheme 3. New rhodium catalysts for (2 + 2 + 1) alkyne cyclotrimerization.

In the course of our studies in alkyne dimerization catalyzed by Rh-NHC-pyridonato derivatives,[45,46] we observed that the new carbonyl catalyst Rh{κ^2N,O-(Opy)}(CO)(IPr) (**1**) {IPr = 1,3-bis-(2,6-diisopropylphenyl)imidazolin-2-carbene; Opy = pyridonato} promotes a change in chemoselectivity (Scheme 3). Thus, a catalytic test with *tert*-butylacetylene (**2a**) in C_6D_6 with 5 mol% of **1** at 60 °C for 22 h, showed an 87% alkyne conversion to give (*E*)-1,3,6-tri(*tert*-butyl)fulvene (**3a-*E***) as the main product, in addition to small amounts of the dimer 1,3-di(*tert*-butyl)-but-1-yn-3-ene (**4a**) and the acyclic trimer (3*E*,5*E*)-1,3,6-tri(*tert*-butyl)-hexa-3,5-dien-1-yne (**5a**) (**3a-*E***:**4a**:**5a**, 90:7:3). Increasing of either catalyst loading or temperature spoils fulvene selectivity, while other solvents were found to be less efficient (see Table S1). Modification of the pyridonato framework within catalyst Rh{κ^2N,O-(R-Opy)}(CO)(IPr) {R = 4-Me (**6**), 4-OMe (**7**), 5-NO_2 (**8**)} shows that introduction of a 4-methoxy group (**7**) improves the catalytic activity of the parent complex **1**, allowing the catalyst loading to be reduced to 2 mol% (84% conversion after 22 h at 60 °C, **3a-*E***:**4a**:**5a**, 92:5:3) (see Table S2).

An interplay of pyridonato, CO, and IPr ligands was confirmed as the most successful combination for catalytic efficiency. Regarding the anionic ligand, the chlorido $RhCl(CO)_2(IPr)$[47] and the cationic $[Rh(CO)_2(IPr)(NCCH_3)][PF_6]$[48] complexes were found to be inactive, pointing to the need of an effective internal base. The pyridine-2-methanolato ligand in Rh{κ^2N,O-([2-(OCH_2)py]}(CO)(IPr)[40] was also inefficient, revealing the unique competence of the pyridonato framework for this catalytic transformation. Moreover, replacing CO with other acceptor ligand, such as trimethyl phosphite in Rh{κ^2N,O-(Opy)}(IPr){$P(OMe)_3$} (**9**) was also deleterious. The introduction of a more electron poor dichloro carbene, Rh{κ^2N,O-(Opy)}(CO)(IPr^{Cl}) (**10**) {IPr^{Cl} = 1,3-bis-(2,6-diisopropylphenyl)-4,5-dichloroimidazolin-2-carbene} slightly increased the catalytic activity (86%) but reduced fulvene selectivity (**3a-*E***:**4a**:**5a**, 84:8:8). Finally, Rh-CO-pyridonato catalysts without a carbene ligand, such as $[Rh(\mu\text{-}Opy)\}(CO)_2]_2$[49] or $[Rh(\mu\text{-}Opy)\}(CO)(PPh_3)]_2$[49] gave unsatisfactory results.

Next, the scope of catalyst **7** was studied (Scheme 4). Catalytic reactions were performed in C_6D_6 solutions at 60 °C using a catalyst loading of 2 mol% and monitored by ^{1}H NMR spectroscopy. The corresponding pentafulvenes (**3**) were selectively obtained, along with minor amounts of

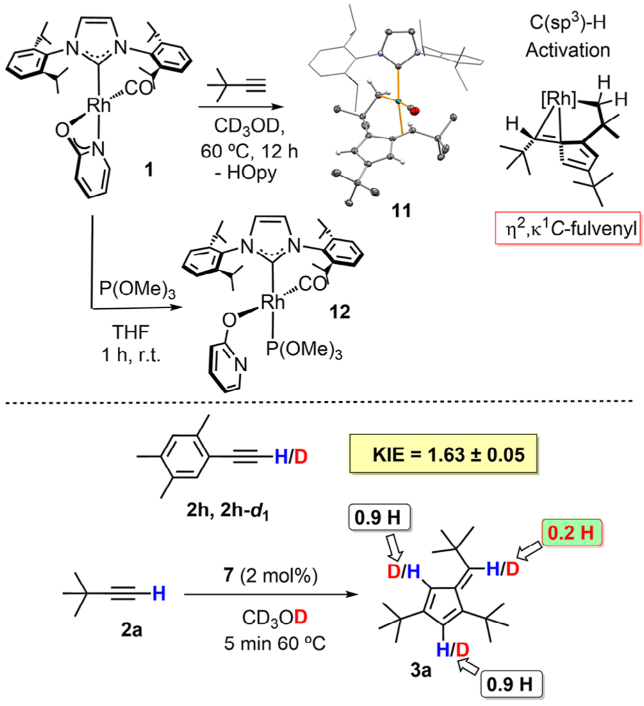


Scheme 4. Scope of the (2 + 2 + 1) alkyne cyclotrimerization catalyzed by **7**.

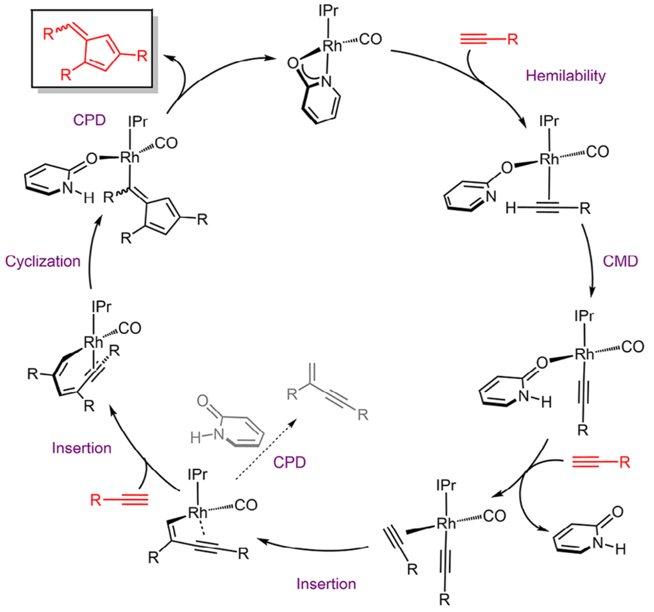
gem-dimers (**4**) and trimers (**5**), and isolated after reaching steady conversion. The steric hindrance of the substituents determines the stereochemistry of the exocyclic double bond of the aliphatic fulvenes. Hence, the bulky *tert*-butyl substituent gave rise to the staggered *E*-fulvenes (**3a**) whereas the eclipsed *Z*-fulvenes were preferentially obtained for cyclopropyl, *n*-butyl or *N*-propylphthalimide groups (**3b-d**). The thermodynamic preference for *E*-fulvenes was demonstrated by the regiodivergent preparation of cyclopropyl functionalized **3b-*E*** by using a more polar solvent such as DMA at 90 °C. Moreover, trimethylsilyl or triethylsilyl substituted alkynes, with an intermediate bulkiness, gave a mixture of both isomers (**3e-f**), that could not be separated by column chromatography. It is interesting to note that triisopropylsilylacetylene does not produce the corresponding fulvene, but only the *gem*-enyne dimer. Aromatic alkynes reacted faster than aliphatic ones, with conversions of up to 98% after 6 h (**3g-l**). In this case, the corresponding *Z*-fulvenes were selectively obtained. The structure of **3g-*Z*** has been determined by X-ray, confirming the stereochemistry of the exocyclic double bond. Substitution at the *ortho*-position of the aromatic ring favors the fulvene formation, since the parent phenylacetylene gave a complex mixture of products. However, (*Z*)-1,4,6-tri(4-methoxyphenyl)fulvene (**3l**) was isolated from the corresponding 4-ethynylanisole. Moreover, alkynols are very reactive substrates for this transformation (**3m-p**), full conversion to *E*-fulvenes being achieved in 1 h.

Incorporation of different alkynes into the fulvene structure was next attempted. Only one example of this challenging cross-trimerization reaction has previously been described by Tanaka´s group, involving silylacetylenes and internal alkynyl esters.[35] It can be anticipated that the acidity and the steric hindrance of the alkyne are relevant parameters for initial deprotonation and insertion steps, respectively. Therefore, one molecule of the more acidic and bulky triisopropylsilylacetylene (**2q**) reacts with 2 equiv of *tert*-butylacetylene (**2a**) to yield the cross-fulvene (*E*)-1,3-di(*tert*-butyl)-6-triisopropylsilyl-fulvene **3qaa**, with the silyl group in the exocyclic position, in addition to the cross-dimerization product 1-triisopropylsilyl-3(*tert*-butyl)-but-3-en-1-yne (**4qa**) (**3qaa**:**4qa** 67:33). As internal alkynes could only participate in the insertion step, 2-butyne (**2r**) or 3-hexyne (**2s**) were incorporated in the fulvene core after reaction with **2a** to afford doubly-cross fulvenes **3aar** and **3aas**, in competition with the homocoupling products (**3aar**:**3a** 79:21; **3aas**:**3a** 49:38). Even more gratifyingly, the reaction of triisopropylsilylacetylene, *tert*-butylacetylene and 3-hexyne gives access to the triple-cross fulvene **3qas** with 15% selectivity.

To shed light on the operative mechanism for (2 + 2 + 1) alkyne cyclotrimerization, some stoichiometric experiments were performed (Scheme 5). No intermediate species could be detected in the formation of fulvene **3a-*E*** by reaction of **1** with 3 equiv of *tert*-butylacetylene in toluene-d_8 at 60 °C. However, when reaction was carried out in CD_3OD, a crop of red crystals was obtained, which could be identified by X-ray diffraction analysis and multinuclear NMR spectroscopy as $\mathrm{Rh}[\eta^2,\kappa^1\overline{\mathrm{C}\{(E)\text{-}1\text{-}\{\mathrm{C(Me)_2C}}\mathrm{H_2}\}\text{-}3,6\text{-di(tert-butyl)fulvene}\}](\mathrm{CO})(\mathrm{IPr})$ (**11**), resulting from C(sp^3)-H activation of a *tert*-butyl group of a fulvene ligand coordinated through the exocyclic double bond. The formation of **11** is a demonstration of the versatile reactivity of fulvenes with transition metals



Scheme 5. Stoichiometric and deuterium-labeling experiments.



Scheme 6. Proposed catalytic cycle.

that has be claimed to hamper catalytic activity.[28–33] On another note, the hemilability of the pyridonato ligand has been demonstrated by the treatment of **1** with P(OMe)$_3$, which resulted in the formation of the tetraleptic complex Rh{κO-(Opy)}(CO)(IPr){P(OMe)$_3$} (**12**), having a κO-pyridin-2-olato moiety.[50]

Next, deuterium-labeling experiments were performed (Scheme 5). A kinetic isotope effect (KIE) of 1.63 ± 0.05 was measured by performing separate NMR experiments using 2 mol% of catalyst **7** with natural and 2,4,5-trimethylphenylacetylene-d_1 at 60 °C. This relatively small value suggests that an X—H bond cleavage or formation event is unlikely to be involved in the turnover limiting step. Moreover, a catalytic experiment using *tert*-butylacetylene in the presence of a deuterium source (CD$_3$OD) resulted in an enrichment of deuterium in the exocyclic position of the fulvene. The rationale for this fact is that the initial deprotonation of terminal alkyne by the pyridonato ligand renders 2-pyridone, which rapidly undergoes a hydrogen/deuterium exchange with CD$_3$OD and eventually transfers a deuterium atom to the rhodium-fulvenyl intermediate in the protonolytic step.

A plausible catalytic cycle is outlined in Scheme 6. It begins with an hapticity change of the pyridonato ligand from $\kappa^2 N,O$ to κO, generating a vacant coordination site that enables the first alkyne molecule to bind the metal center. Subsequently, a metal–ligand cooperative abstraction of the terminal proton of the alkyne through a concerted metalation deprotonation (CMD) process affords a rhodium alkynyl species. Following this, a second alkyne molecule displaces the neutral pyridone ligand and inserts into the metal–alkynyl bond. At this stage, the presence of the CO ligand plays a critical role by preventing protonolysis by free pyridone, which could otherwise occur via concerted protonation demetalation (CPD) to yield the *gem*-enyne. Instead, a third alkyne enters the catalytic cycle. The subsequent steps involve insertion, cyclization, and CPD, ultimately leading to the fulvene products.

DFT calculations were performed in order to highlight the pathway for the (2 + 2 + 1) cyclotrimerization of *tert*-butylacetylene to **3a-*E*** catalyzed by **1** (Figure 1). Starting from **1**, the rhodium—nitrogen bond rupture gives the unsaturated κO-pyridin-2-olato derivative **I** (+24.7 kcal mol^{-1}) which reacts with the first alkyne molecule (**II**, +6.7 kcal mol^{-1}). Thereafter, the coordination of *tert*-butylacetylene should switch from η^2-C≡C in **II** to σ-C—H in **III** (+20.5 kcal mol^{-1}).[45,46] Eventually, **III** converts into **IV** (+6.0 kcal mol^{-1}) due to the alkyne deprotonation by the nitrogen atom of the κO-pyridin-2-olato ligand.[51] Following this, the substitution reaction of 2-pyridone with the second alkyne molecule in **IV** yields the η^2-alkyne intermediate **V** (+16.0 kcal mol^{-1}). Both dissociative and associative pathways were considered and similar barriers were calculated (≈16.5 kcal mol^{-1} relative to **IV**). Next, **V** affords the rhodium butenynyl derivative **VI** (−3.3 kcal mol^{-1}) through C≡C insertion into the rhodium alkenyl bond via **TS_V-VI** (+27.9 kcal mol^{-1}), which results to be the TOF-determining transition state, **1** being the TOF-determining intermediate.[52] The subsequent reaction of **VI** with the third alkyne molecule entails the endergonic formation of the intermediate **VII** which gives rise to the hexadienynyl moiety **VIII** (−34.0 kcal mol^{-1}) through the second insertion step (**TS_VII-VIII**, +10.6 kcal mol^{-1}). Protonation of **VI** by 2-pyridone, eventually leading to 1,3-enyne, displays a higher barrier (see Figure S191). In the final stages of the catalytic process, a cyclization reaction takes place (**TS_VIII-IX**, −17.7 kcal mol^{-1}) affording the metallacyclopropene derivative **IX** (−44.0 kcal mol^{-1}),

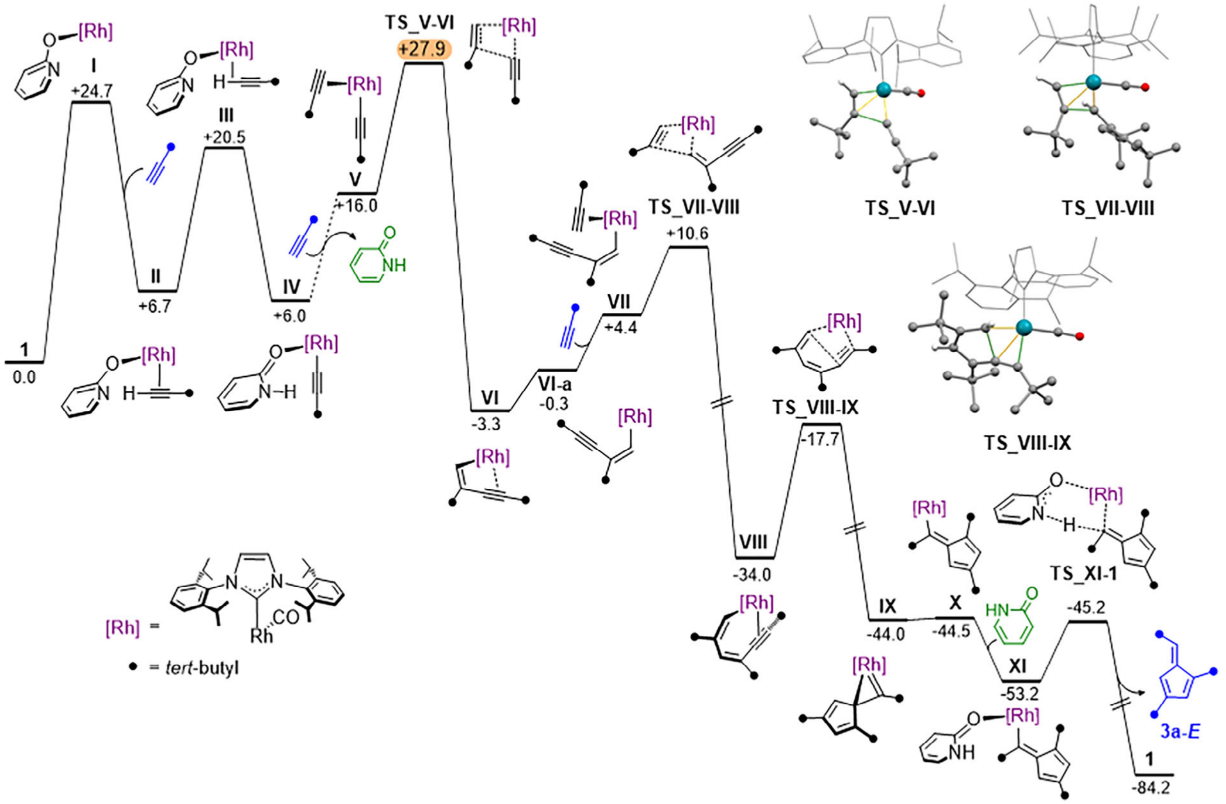


Figure 1. Relative Gibbs free energy profile (G, kcal mol^{-1}) for the (2 + 2 + 1) cyclotrimerization of *tert*-butyl acetylene to **3a-*E*** catalyzed by **1** (wB97XD/def2tzvp//B97D3/def2svp, SMD/C_6H_6, 298 K, 1 atm).

already containing the fulvene backbone. Subsequently, **IX** isomerizes to **X** that coordinates 2-pyridone. Finally, the protonation of the fulvenyl moiety (**TS_XI-1**, −45.2 kcal mol^{-1}) renders **3a-*E***. The proposed RDS is consistent with the calculated KIE (1.63 ± 0.05) and the energetic span of 27.9 kcal mol^{-1} nicely fit in with the temperature of 60 °C required for efficient conversions (see Supporting Information for further computational details).

In summary, the rational design of new rhodium-based catalysts bearing pyridonato, NHC, and CO ligands enables an efficient (2 + 2 + 1) alkyne cyclotrimerization, providing access to pentafulvenes with diverse structures and compositions, including cross-trimerization derivatives. Stoichiometric and labeling experiments, as well as DFT calculations, have shed light on the reaction mechanism showing that it consists of a metal–ligand cooperative alkyne deprotonation, two successive insertion processes, cyclization and protonolysis, with the alkyne insertion into a rhodium—alkynyl bond being the rate-determining step. The underlying principles revealed herein pave the way to the straightforward and efficient preparation of varied fulvene architectures.

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Conflict of Interests

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords: Alkyne cyclotrimerization • DFT calculations • Metal–ligand cooperation • *N*-Heterocyclic carbene • Pyridone

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Communication

Alkyne Cyclotrimerization

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Ligand-Controlled Chemoselectivity in the Rhodium-Catalyzed Synthesis of Pentafulvenes via (2 + 2 + 1) Alkyne Cyclotrimerization

Chemoselectivity Challenge: A precise catalyst design allows for chemoselectivity control over alkyne reactivity to yield pentafulvenes via (2 + 2 + 1) cyclotrimerization. Operative mechanism has been elucidated by means of stoichiometric and deuteration experiments, as well as DFT calculations.