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Photoactivated Transition-Metal Triggers for Ambient Temperature Enediyne and Dienyne Cyclization: Ruthenium-η^6-Naphthalene Complexes

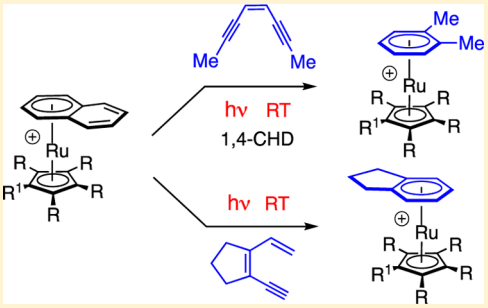
Pengjin Qin,[†] Stephen K. Cope,[†] Han Steger,[†] Kate M. Vecchiarelli,[†] Ryan L. Holland,[†] David M. Hitt,[†,§] Curtis E. Moore,[†] Kim K. Baldridge,*[,‡] and Joseph M. O'Connor*[,†]

[†]Department of Chemistry, University of California, San Diego, La Jolla, California 92093, United States

[‡]School of Pharmaceutical Science and Technology, Tianjin University, 92 Weijin Road, Nankai District, Tianjin, 300072, People's Republic of China

Supporting Information

ABSTRACT: A persistent challenge confronting potential applications of the Bergman cycloaromatization reaction is the development of methods for spatiotemporal control of diradical formation. Photochemical variants (photo-Bergman cycloaromatizations) have thus far met with limited success, failing completely in the case of acyclic enediynes. Here we describe the development of efficient photoactivated transition-metal complexes that allow for spatiotemporal control of enediyne cycloaromatization at ambient temperatures. This strategy relies on air- and moisture-stable ruthenium naphthalene complexes that undergo photochemical dissociation of the naphthalene ligand, thereby generating coordination sites for enediyne binding and cycloaromatization. The same ruthenium naphthalene complexes also trigger dienyne cyclization under photochemical conditions.



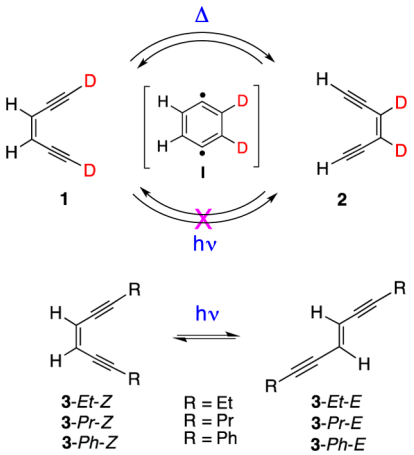
INTRODUCTION

In a now classic 1972 study, Bergman reported the gas-phase thermal equilibration of deuterium-enriched acyclic enediynes **1** and **2** and provided evidence for the intermediacy of *p*-aryne **I** (Scheme 1).[1] The thermal Bergman cycloaromatization is now the single most powerful and general method for the formation of diradicals from readily available precursors.[2] Efforts to develop photo-Bergman cycloaromatizations for spatiotemporal control of diradical formation have met with only limited success.[3] For example, Bergman and others have found that irradiation of acyclic enediynes,[4] such as **1** and **3**, results in cis–trans equilibration, with no evidence for *p*-aryne formation.[1,5,6]

Successful examples of photo-Bergman reactions typically proceed in low to moderate yield[7−11] and require a cyclic alkene in order to prevent cis–trans equilibration (eq 1).[8,10] In addition, nearly all cases reported to date require[8] the presence of conjugating substituents in order to obtain reasonable yields.[7−11] Alternative strategies for photoinitiated cycloaromatization of enediynes at ambient temperature include (a) photochemical enediyne deprotection for in situ generation of a strained-ring enediyne (eq 2),[12] (b) photochemical functional group transformation leading to increased ring strain in pre-existing enediynes (eq 3),[13,14] and (c) the use of metal-coordinated enediynes for photoinduced charge transfer cycloaromatization (eq 4).[15]

We previously demonstrated that $[Cp^*Ru(NCMe)_3]PF_6$ cycloaromatizes enediynes in the presence of a hydrogen atom donor, in the dark, to give $[Cp^*Ru(\eta^6\text{-arene})]PF_6$ complexes.[16,17] The ruthenium approach is unique in that it triggers the room-temperature cycloaromatization of *acyclic* enediynes, such as **3**-*Pr*-*Z*, which do not undergo either thermal

Scheme 1. Thermal Cycloaromatization of Acyclic Enediyne 1[a]



[a]Photolysis of **1** and **3** leads to cis–trans isomerization with no *p*-aryne formation.

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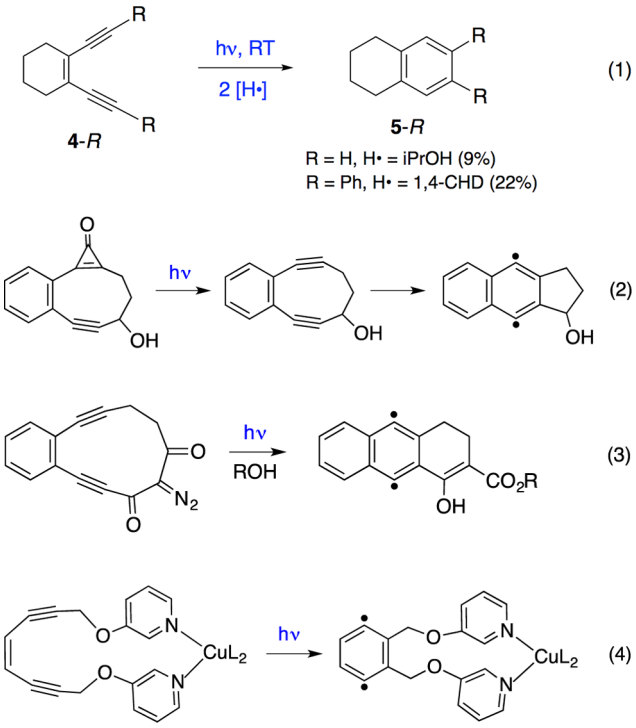
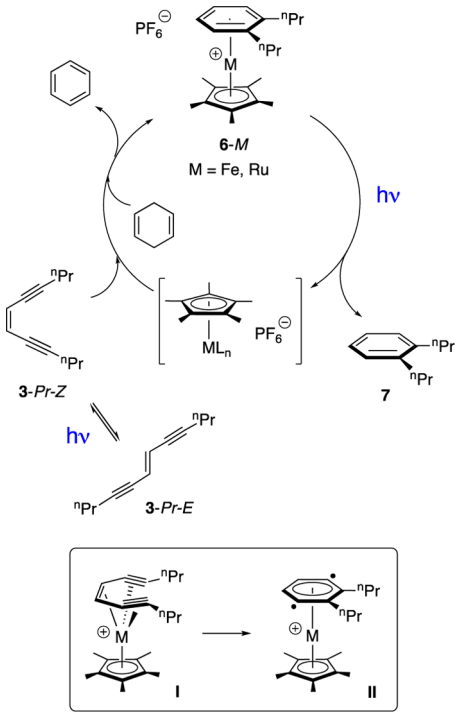


or photochemical cycloaromatization in the absence of ruthenium. The reaction was found to be catalytic in ruthenium under photochemical conditions (Scheme 2).[18] Irradiation has two functions: the first is photoisomerization of the (*E*)-enediyne to a (*Z*)-enediyne,[19] and the second is photodissociation of the arene ligand in **6**-*M*. Our current mechanistic hypothesis for this remarkable transformation involves the formation of an [Cp*Ru(η^6-enediyne)]PF_6 intermediate (**I**) which cycloaromatizes to the diradical [Cp*Ru(η^6-*p*-aryne)]PF_6 (**II**; Scheme 2). Subsequent hydrogen atom abstraction would then generate the ruthenium arene complex. A major limitation of these first-generation metal arene phototriggers is the inefficient arene photodissociation step. For example, photolysis of isolated **6**-*Ru* in acetonitrile required 48 h of irradiation to achieve 91% conversion to **7** at room temperature.[18]

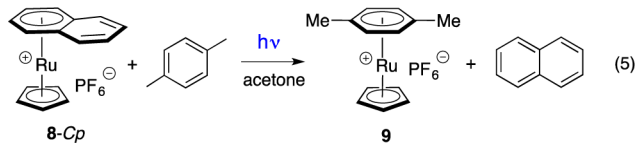
Scheme 2. Metal−Arene Complexes Serve as Photoactivated Bergman Cycloaromatization Triggers



We now report that ruthenium naphthalene complexes [(η^5-C_5H_5)Ru(η^6-naphthalene)]PF_6 (**8**-*Cp*),[20] [(η^5-C_5Me_5)Ru(η^6-naphthalene)]PF_6 (**8**-*Cp**),[21] and [(η^5-$C_5Me_4CF_3$)Ru(η^6-naphthalene)]PF_6 (**8**-*Cp*^{*CF3})[22] function as more efficient photoactivated triggers in comparison to **6**-*Ru* for ambient-temperature cycloaromatization of enediynes. The results indicate that optimal yields are obtained with a more electron rich metal center, as in **8**-*Cp**. The same complex serves as a photoactivated trigger for dienyne cyclization at ambient temperature.

RESULTS AND DISCUSSION

We were initially attracted to complexes **8**-*Cp* and **8**-*Cp** as promising candidates for photoactivated cyclization triggers by Kudinov's reports that these complexes undergo efficient photochemical exchange of the naphthalene ligand with arenes at room temperature.[23,24] For example, photolysis of acetone solutions containing **8**-*Cp* and 3 equiv of *p*-xylene led to a 95% yield of [(η^5-C_5H_5)Ru(η^6-*p*-xylene)]PF_6 (**9**) after only 6 h of irradiation (eq 5),[23a] and irradiation of an acetone solution of **8**-*Cp** and benzene (51-fold excess) for 18 h at room temperature led to a 90% isolated yield of [(η^5-C_5Me_5)Ru(η^6-benzene)]PF_6.[23d]



In order to establish the relative rates of benzene and naphthalene photodissociation from ruthenium complexes, we carried out a conversion vs time study on an NMR-tube sample containing a mixture of [(η^5-C_5Me_5)Ru(η^6-naphthalene)]PF_6 (**8**-*Cp**; 0.024 mmol), [(η^5-C_5Me_5)Ru(η^6-benzene)]PF_6 (**6**-*Ru-PhH*; 0.019 mmol), and 1,3,5-tri-*tert*-butylbenzene (internal standard) at 33−34 °C in acetonitrile-d_3. The products are naphthalene, benzene, and [Cp*Ru($NCCD_3$)$_3$]PF_6. Over the first 140 min of photolysis, the rate constant for disappearance of **6**-*Ru-PhH* was 1.54×10^{-3} min^{-1}, whereas the rate constant for disappearance of **8**-*Cp** was 6.49×10^{-3} min^{-1} (Table S2 and Figure S11 in the Supporting Information). The 5-fold faster rate for naphthalene photodissociation relative to benzene dissociation is in agreement with qualitative literature observations that naphthalene dissociation from $CpRu^+$ and Cp^*Ru^+ occurs more rapidly than does dissociation of nonbenzannulated arene ligands.[23a,c,25−27]

We chose (*Z*)-octa-4-en-2,6-diyne (**3**-*Me-Z*) as a representative acyclic enediyne substrate for preliminary studies due to the simplicity of its ^{1}H NMR spectral signature (singlets at δ 1.93 and 5.59 in $CDCl_3$) that permits convenient monitoring of reactions by ^{1}H NMR spectroscopy. Roth et al. previously prepared **3**-*Me* as a 1:1 mixture of *Z* and *E* isomers and observed equilibration of **3**-*Me* with (*Z*)- and (*E*)-4,5-diethynyl-2-butene in the gas phase, an equilibration that presumably

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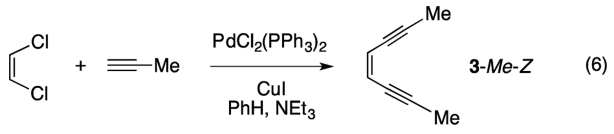
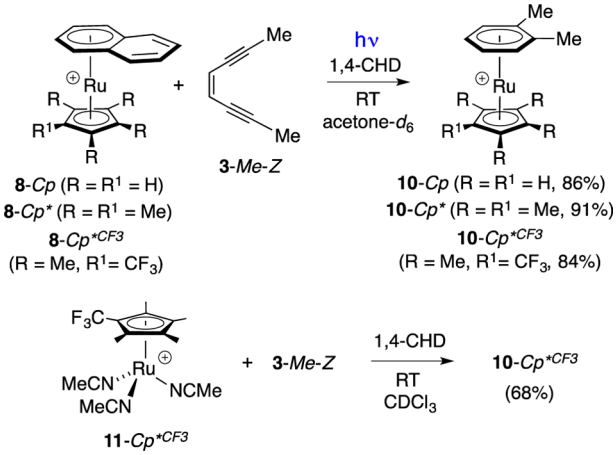
involves a *para*-aryne intermediate.[28] We prepared enediyne **3**-*Me-Z* as a single isomer in 76% isolated yield from a double-Sonogashira cross-coupling reaction between *cis*-1,2-dichloroethylene and propyne at room temperature (eq 6).



Photolysis of an acetone-d_6 solution containing **8**-*Cp* (29 μmol), **3**-*Me-Z* (29 μmol), 1,4-cyclohexadiene as a hydrogen atom donor (1,4-CHD; 60 μmol), and 1,3,5-tri-*tert*-butylbenzene (internal standard) was carried out in a Rayonett photoreactor equipped with UV broad-band lamps centered at 254 nm (Scheme 3). During the course of the reaction, the ^{1}H NMR resonances for **3**-*Me-Z* and **8**-*Cp* decreased in intensity and new resonances, attributed to $[(\eta^5\text{-}C_5H_5)Ru(\eta^6\text{-}o\text{-xylene})]PF_6$ (**10**-*Cp*), were observed at δ 2.45 (s, 6H) and 5.45 (s, 5H). After 6 h of irradiation, integration of the spectrum indicated 93% conversion of **8**-*Cp* and an 86% yield of **10**-*Cp*. In a similar fashion, **8**-*Cp** and **3**-*Me-Z* underwent conversion to the known complex $[(\eta^5\text{-}C_5Me_5)Ru(\eta^6\text{-}o\text{-xylene})]PF_6$ (**10**-*Cp**)[29] in 91% yield after 6 h of irradiation.

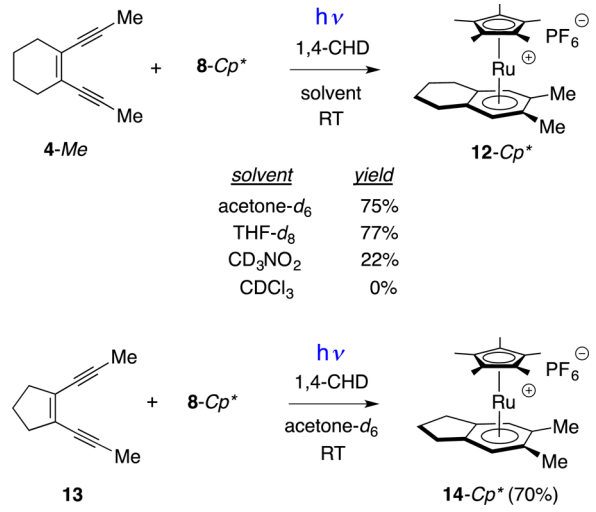
Scheme 3. Room-Temperature Photoactivated Ruthenium Enediyne Cycloaromatization Triggers (PF_6^- Counterions Not Shown)



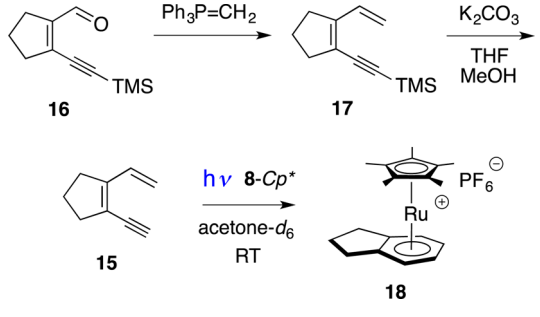
The higher yield of cycloaromatized product observed with **8**-*Cp** may be the result of either a more electron-rich metal center or larger cyclopentadienyl ligand substituents. Butenschön has noted dramatic effects for Ru-catalyzed reactions as a result of cyclopentadienyl ligand modification.[30] In order to address this classic "sterics vs electronics" question, we examined the use of $[(\eta^5\text{-}C_5Me_4CF_3)Ru(\eta^6\text{-naphthalene})]PF_6$ (**8**-*Cp*^{CF3}*)[22] as a photoactivated cyclization trigger. Gassman previously established that the 1-trifluoromethyl-2,3,4,5-tetramethylcyclopentadienyl ligand (Cp*^{CF3}) exhibits electronic properties similar to those of the Cp ligand while affording steric bulk that is similar to that of the Cp* ligand.[31] Furthermore, Mann's observation that photolysis of $[(\eta^5\text{-}C_5Me_4CF_3)Ru(\eta^6\text{-naphthalene})]PF_6$ (**8**-*Cp*^{CF3}*) in acetonitrile leads to high yields of $[(\eta^5\text{-}C_5Me_4CF_3)Ru(NCMe)_3]PF_6$ (**11**-*Cp*^{CF3}*) suggested that the Cp^{CF3} ligand would be stable under photochemical conditions. When an acetone-d_6 solution of **8**-*Cp*^{CF3}* (29 μmol), **3**-*Me-Z* (29 μmol), 1,4-CHD (60 μmol), and 1,3,5-tri-*tert*-butylbenzene (internal standard) was subjected to the same reaction conditions used for the reaction of **3**-*Me-Z* with **8**-*Cp* and **8**-*Cp**, **10**-*Cp*^{CF3}* was formed in 84% yield at 95% conversion of **8**-*Cp*^{CF3}* (Scheme 3). This result suggests that the more electron rich ruthenium center in **8**-*Cp** is responsible for the superior performance of **8**-*Cp** relative to that for **8**-*Cp*. We also examined the thermal reaction of **11**-*Cp*^{CF3}* (30 μmol) with **3**-*Me-Z* (30 μmol) in the presence of 1,4-cyclohexadiene (1,4-CHD, 30 μmol) and observed rapid conversion to $[(\eta^5\text{-}C_5Me_4CF_3)Ru(\eta^6\text{-}o\text{-xylene})]PF_6$ (**10**-*Cp*^{CF3}*), but in only 68% NMR yield.

On the basis of the superior performance of **8**-*Cp** with acyclic enediyne **3**-*Me-Z*, we next examined its use as a photoactivated trigger for the cycloaromatizations of tetrasubstituted enediyne **4**-*Me* (Scheme 4). In the dark, no reaction was observed between **8**-*Cp** and **4**-*Me* over the course of 48 h at room temperature. Under conditions similar to those employed for the reaction of **8**-*Cp** with **3**-*Me-Z*, photolysis of an acetone-d_6 solution containing **4**-*Me* and **8**-*Cp** led to a 48% yield of **12**-*Cp** after 6 h and a 75% yield after 48 h (Scheme 5). This compares with a <5% yield of cycloaromatized free arene product, **5**-*Me*, generated upon photolysis of **4**-*Me* in the absence of **8**-*Cp** (eq 1).[32] For an additional comparison, the thermal reaction of **4**-*Me* and $[(\eta^5\text{-}C_5Me_5)Ru(NCMe)_3]PF_6$ (**11**-*Cp**) in the presence of 1,4-CHD led to a 51% yield of **12**-*Cp**. The five-membered-ring

Scheme 4. Solvent Effects on Photoactivated Ruthenium Enediyne Cycloaromatization



Scheme 5. Synthesis and Cycloaromatization of Dienyne 15



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enediyne **13**, for which the critical distance[33] between the methyl-substituted sp carbons is 0.4 Å greater than in **4**-*Me*, also underwent reaction with **8**-*Cp** in acetone-d_6 to give the known arene complex[16b] **14**-Cp* in 70% yield (Scheme 4).

In order to establish the optimal reaction conditions, we examined the reaction of **4**-*Me* with **8**-*Cp** in a variety of solvents, including THF-d_8, CD_3NO_2, and $CDCl_3$ (Scheme 4). While comparable yields of **12**-*Cp** were observed in THF-d_8 and acetone-d_6, the limited solubility of **8**-*Cp** in THF was problematic. In nitromethane-d_3 the yield was only 22%, and even with a larger excess of 1,4-CHD (14 equiv) the yield was 46%. The addition of 0.3 equiv of acetone-d_6 to the nitromethane solvent failed to significantly improve the yield of **12**-*Cp**. Isopropyl alcohol is often employed as both a hydrogen atom donor and solvent for thermal enediyne cycloaromatizations; however, **8**-*Cp** exhibits very poor solubility in isopropyl alcohol. Thus, acetone proved to be the optimal solvent for the photoactivated cycloaromatization reactions of of **8**-*Cp** in comparison to $CDCl_3$, CH_3NO_2, ^{i}PrOH, and THF.

We previously observed that $[(\eta^5\text{-}C_5Me_5)Ru(NCMe)_3]PF_6$ (**11**-*Cp**) also triggered the cyclization of dienynes at ambient temperature.[16c,34] The mechanism of this reaction differs significantly from that observed for enediynes in that it is a dienyne to arene rearrangement with no H atom abstraction. Dienyne **15** was prepared from the known enynyl aldehyde **16**[35] by conversion to dienyne **17** followed by desilylation (Scheme 5). In a control experiment, photolysis of **8**-*Cp** and **15** in acetone-d_6 led to extensive decomposition of the dienyne over the course of 24 h, with no indane product observable by ^{1}H NMR spectroscopic analysis of the crude reaction mixture. We were therefore pleased to find that the use of **8**-*Cp** as a photoactivated trigger for cyclization of **15** led to formation of the arene complex $[(\eta^5\text{-}C_5Me_5)Ru(\eta^6\text{-Indane})]PF_6$ (**18**) in 60% yield after 24 h of irradiation. Complex **18** was independently prepared from the reaction of **11**-*Cp** and indane.

X-ray Crystallographic and Computational Studies. The solid-state structures of **8**-*Cp*^{CF3} and *o*-xylene complex **10**-*Cp*^{CF3} were determined by X-ray crystallography (Figure 1 and

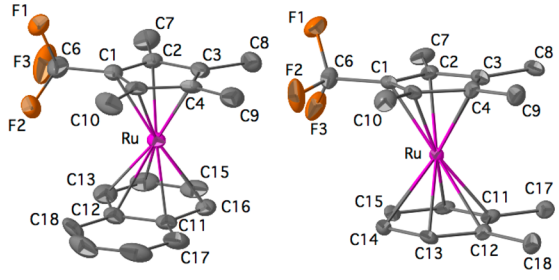

Figure 1. ORTEP drawings of the cations for **8**-*Cp*^{CF3} (left) and **10**-*Cp*^{CF3} (right). Hydrogen atoms are omitted for clarity.

Table S1 in the Supporting Information). Within the errors of the measurements the structure of **8**-*Cp*^{CF3} is nearly identical with the structures reported for **8**-*Cp**[20] and **8**-*Cp*.[23b] In order to establish the structural parameters for a series of Cp*^{CF3}, Cp*, and CpRu complexes, independent of crystal-packing forces, BP86/Def2-TZVPP(THF) computational studies were carried out on **8**-*Cp*^{CF3}-*calc*, **10**-*Cp*^{CF3}-*calc*, **10**-*Cp**-*calc*, and **10**-*Cp*-*calc* (Figure 2 and Table S1). For the three *o*-xylene complexes, the minor structural variation that exists within the

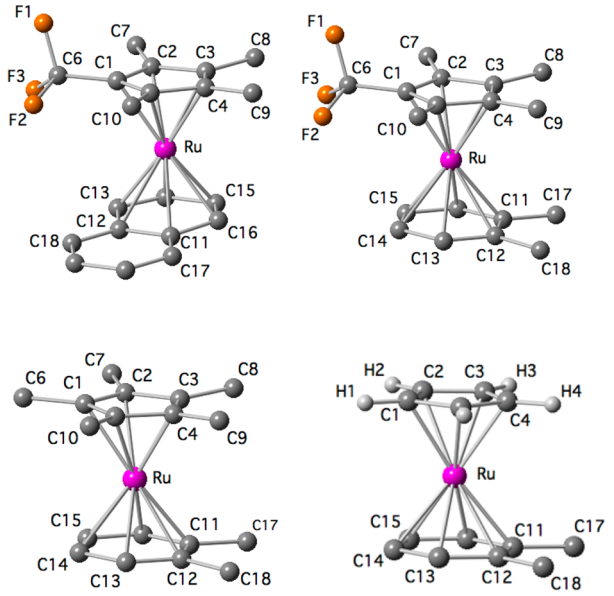

Figure 2. Calculated structures for cations of **8**-*Cp*^{CF3} (upper left) **10**-*Cp*^{CF3}-*calc* (upper right), **10**-*Cp**-*calc* (lower left), and **10**-*Cp*-*calc* (lower right). Hydrogen atoms are omitted for clarity.

series is manifested primarily in the Ru−Arene^{cnt} distances rather than the Ru−Cp^{cnt} distances. The Ru−Cp^{cnt} distances are within 0.003 Å of one another and approximately 0.1 Å longer than the Ru−Arene^{cnt} distances. Whereas **10**-*Cp*^{CF3}-*calc* and **10**-*Cp**-*calc* exhibit 1.731 and 1.730 Ru−Arene^{cnt} distances, respectively, the corresponding distance in **10**-*Cp*-*calc* is significantly shorter at 1.714 Å. This variation in metal−arene distance is attributed to less steric congestion in **10**-*Cp*-*calc* due to the absence of Cp ring substituents.

CONCLUSIONS

The ruthenium naphthalene complexes **8**-*Cp*, **8**-*Cp**, and **8**-*Cp*^{CF3} serve as convenient, readily accessible, photoactivated cycloaromatization triggers for both enediynes and dienynes. Use of the most electron rich **8**-*Cp** provides higher yields in comparison to those with either **8**-*Cp* or **8**-*Cp*^{CF3}. Advantages of the naphthalene complexes, in comparison to tris(acetonitrile) analogues such as **11**-*Cp*^{CF3} and **11**-*Cp**, include greater stability toward air and moisture, higher cyclization yields, and spatiotemporal control of diradical formation. Both disubstituted (**3**-*Me*-*Z*) and tetrasubstituted enediynes (**4**-*Me* and **13**) undergo room-temperature cycloaromatization; however, significantly lower yields and longer reaction times are observed in the case of the tetrasubstituted enediynes.

It should be noted that, while facile photodissociation of naphthalene from **8** allows for rapid reaction with enediyne substrates, it will not lead to a more efficient catalytic system than in the case of nonbenzannulated arene complexes such as **6**-*Ru* (Scheme 2). An exception to this would be ruthenium-catalyzed cycloaromatization of benzannulated enediynes, which would generate more labile benzannelated arene ligands. Beyond the development of photocatalytic enediyne cycloaromatizations, potential applications based on spatiotemporal control of diradical formation include the use of metal arene triggers in order to initiate free radical polymerization reactions[36] and spatiotemporal control of diradical formation in order to induce tumor cell death in biological systems.[2] The

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latter application will require the synthesis of ruthenium arene complexes that contain pendant enediynes.

EXPERIMENTAL SECTION

Computational Methods. The structural and energetic analyses of the molecular systems described in this study were carried out using the BP86 density functional,[37,38] with an ultrafine grid, together with the Def2-TZVPP basis set.[39] The effects of solvent were included using the continuum solvation model based on the original COSMO theory of Klamt modified for ab initio theory,[40,41] with a dielectric for THF. Full geometry optimizations were performed and uniquely characterized via second-derivative (Hessian) analysis to establish stationary points and effects of zero point energy and thermal corrections. Visualization and analysis of structures was carried out using Avogadro.[42]

General Information. All manipulations were performed using standard Schlenk techniques or in nitrogen-filled Vacuum Atmospheres or MBraun gloveboxes, unless otherwise stated. ^{1}H and ^{13}C NMR spectra were recorded on Varian Mercury 400 MHz, Varian VX 500 MHz, and JEOL ECA 500 MHz instruments. ^{1}H and ^{13}C NMR chemical shifts (δ) are reported in parts per million (ppm). Spectra were referenced to the residual solvent peak. Infrared spectra were obtained on a Nicolet iS10 FT-IR instrument. High-resolution mass spectral analyses were performed at either the mass spectrometer facility at UC San Diego or UC Riverside. Reaction solvents were dried using a solvent dispensing system equipped with two neutral alumina columns under an argon atmosphere or by the use of 3 Å activated molecular sieves. NMR-scale reactions were performed in 5 mm J. Young NMR tubes equipped with a Teflon needle valve. All literature compounds were prepared according to the indicated references or purchased from commercial suppliers and used as received.

1,2-Bis(prop-1-yn-1-yl)cyclohex-1-ene (4-*Me*). A 1 M solution of LHMDS (3.00 mL, 3.00 mmol) in THF was added to a stirred solution of 1,2-diethynylcyclohex-1-ene[43] (100 mg, 0.768 mmol) in THF (7.8 mL) at 0 °C. After 20 min at 0 °C, iodomethane (0.300 mL, 4.81 mmol) was added and the solution was warmed to room temperature over the course of 4 h. The reaction mixture was then poured over saturated aqueous NH_4Cl (20 mL) and extracted with hexanes (2 × 20 mL). The organic extracts were washed with water (20 mL)/brine (20 mL), dried over $MgSO_4$, concentrated, and purified by flash silica column chromatography (hexanes) to afford **4**-*Me* as a yellow solid (108 mg, 0.68 mmol, 89% yield). Mp: 31−34 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.53−1.62 (m, 4H, 4,5-CH_2), 2.03 (s, 6H, CH_3), 2.12−2.21 (m, 4H, 3,6-CH_2). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 4.79, 22.1, 30.4, 80.6, 89.4, 125.1. HRMS (EI) for $C_{12}H_{14}$: [M^+] calculated 158.1090; found 158.1088.

Trimethyl((2-vinylcyclopent-1-en-1-yl)ethynyl)silane (17). ^{n}BuLi (1.25 M in hexanes, 2 mL, 2.5 mmol) was added dropwise to a 0 °C suspension of methyltriphenylphosphonium bromide (890 mg, 2.5 mmol) in THF (40 mL) under N_2. The resulting red solution was stirred at 0 °C for 45 min, followed by dropwise addition of a THF solution (5 mL) of enynyl aldehyde **16**[31] (440 mg, 2.24 mmol). After the mixture was stirred at room temperature overnight, the volatiles were removed under vacuum and the residue was chromatographed on silica gel (hexanes) to give **17** as a clear oil (400 mg, 2.06 mmol, 90% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.19 (s, 9H, $SiMe_3$), 1.88 (p, $^3J_{HH}$ = 7.6 Hz, 2H, CH_2), 2.50 (t, $^3J_{HH}$ = 7.6 Hz, 2H, CH_2), 2.55 (t, $^3J_{HH}$ = 7.6 Hz, 2H, CH_2), 5.18 (d, $^3J_{HH}$ = 18.4 Hz, 1H, = CH), 5.19 (d, $^3J_{HH}$ = 9.6 Hz, 1H, = CH), 6.83 (dd, $^3J_{HH}$ = 18.4 Hz, 9.6 Hz, 1H, = CH). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 0.4, 22.5, 31.9, 37.3, 101.2, 101.8, 116.5, 122.6, 132.1, 149.4. HRMS (APCI-TOFMS) for $C_{12}H_{19}Si$: [MH^+] calculated 191.1251; found 191.1252.

1-Ethynyl-2-vinylcyclopent-1-ene (15). A solution of dienyne **17** (400 mg, 2.06 mmol) and K_2CO_3 (50 mg, 0.36 mmol) in THF/MeOH (10 mL, 1/1) was stirred at room temperature for 1 h. H_2O (50 mL) was added, and the solution was extracted with Et_2O (3 × 20 mL). The combined organic extracts were washed with brine (15 mL) and dried over $MgSO_4$, and the volatiles were removed under vacuum. The resulting residue was purified on silica gel (pentane) to give **15** as a clear oil (145 mg, 1.23 mmol, 60% yield). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 1.90 (p, $^3J_{HH}$ = 7.6 Hz, 2H, CH_2), 2.52 (t, $^3J_{HH}$ = 7.6 Hz, 2H, CH_2), 2.56 (t, $^3J_{HH}$ = 7.6 Hz, 2H, CH_2), 3.28 (s, 1H ≡CH), 5.20 (d, $^3J_{HH}$ = 17.5 Hz, 1H, = CH), 5.20 (d, $^3J_{HH}$ = 10.6 Hz, 1H, = CH), 6.84 (dd, $^3J_{HH}$ = 17.5 Hz, 10.6 Hz, 1H, = CH). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 22.4, 31.9, 37.2, 80.5, 83.6, 116.9, 121.4, 131.8, 149.7. HRMS (APCI-TOFMS) for C_9H_{11}: [MH^+] calculated 119.0855; found 119.0854.

(η^5-Cyclopentadienyl)(η^6-*o*-xylene)ruthenium(II) Hexafluorophosphate (10-*Cp*). An acetone-d_6 solution of enediyne **3**-*Me-Z* (3 mg, 29 μmol), **8**-*Cp* (12.5 mg, 29 μmol), and 1,4-CHD (6 μL, 60 μmol) was photolyzed for 6 h, at which time a ^{1}H NMR spectrum of the sample indicated 93% conversion of **8**-*Cp* and a 92% yield of **10**-*Cp*. The contents of the tube were poured into a vial, and **10**-*Cp* was precipitated by the addition of Et_2O (10 mL). The solution was filtered through a Celite pad, which was rinsed with Et_2O (2 × 2 mL) and dichloromethane (3 × 2 mL). The combined washings were evaporated under vacuum to give **10**-*Cp* as a white powder (12 mg, 25 μmol, 86% yield). ^{1}H NMR (acetone-d_6, 500 MHz): δ 2.45 (s, 6H, CH_3), 5.45 (s, 5H, C_5H_5), 6.19 (dd, $^3J_{H-H}$ = 4.3 Hz, $^4J_{H-H}$ = 2.4 Hz, 2H, aromatic CH), 6.35 (dd, $^3J_{H-H}$ = 4.3 Hz, $^4J_{H-H}$ = 2.4 Hz, 2H, aromatic CH). ^{13}C{^{1}H} NMR (acetone-d_6, 125 MHz): δ 19.0, 81.6, 85.5, 88.4, 103.0. HRMS (ESI) for $C_{13}H_{15}Ru$: [M^+] calculated 273.0217; found 273.0216.

(η^5-Trifluoromethyltetramethylcyclopentadienyl)(η^6-*o*-xylene)ruthenium(II) Hexafluorophosphate (10-*Cp^{CF3}).** A degassed solution of enediyne **3**-*Me-Z* (20 mg, 0.2 mmol) and 1,4-CHD (47 μL, 0.5 mmol) in CH_2Cl_2 (10 mL) was placed in a flask containing [(η^5-$C_5Me_4CF_3$)Ru(NCMe)$_3$]PF_6 (**11**-*Cp**^{CF3}; 110 mg, 0.2 mmol) under N_2. The resulting solution was stirred at room temperature for 2 h and then concentrated in vacuo to a volume of ca. 0.5 mL. Addition of Et_2O (10 mL) led to formation of a precipitate. The remaining suspension was filtered through a pad of Celite, which was rinsed with Et_2O (3 × 2 mL) and acetone (3 × 3 mL). The combined washings were evaporated in vacuo, and the residue was purified on a short silica gel column (2% acetone in dichloromethane) to give **10**-*Cp**^{CF3} as a colorless solid (70 mg, 0.13 mmol, 65% yield). ^{1}H NMR (acetone-d_6, 500 MHz): δ 2.07 (s, 6H, Cp ligand CH_3), 2.12 (bs, 6H, Cp ligand CH_3), 2.30 (s, 6H, arene CH_3), 6.20−6.25 (m, 4H, aromatic CH). ^{13}C{^{1}H} NMR (acetone-d_6, 125 MHz): δ 10.1, 10.4, 17.0, 85.8 (q, $^2J_{CF}$ = 36.7 Hz), 89.4, 91.3, 94.8, 98.9, 103.5, 126.3 (q, $^1J_{CF}$ = 271.6 Hz). HRMS (ESI) for $C_{18}H_{22}F_3Ru$: [M^+] calculated 397.0717; found 397.0716.

[(η^5-C_5Me_5)Ru(η^6-6,7-dimethyltetraline)][PF_6] (12-*Cp).** Enediyne **4**-*Me* (30 mg, 0.059 mmol) was added to a solution of [(η^5-C_5Me_5)Ru(NCMe)$_3$]PF_6 (**11**-*Cp**; 10 mg, 0.065 mmol) in THF (1 mL) under a N_2 atmosphere. After 14 h at 23 °C, the reaction mixture was concentrated, the residue was dissolved in minimum amount of CH_2Cl_2, and a brown solid was precipitated by addition of Et_2O. The resulting solid was purified by flash alumina column chromatography (2/8 then 7/3 EtOAc/hexanes) followed by crystallization (CH_2Cl_2/diethyl ether) to afford **12**-*Cp** as a colorless solid (2 mg, 0.004 mmol, 6%). Mp: 260 °C dec. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.60−1.86 (m, 4H, CH_2), 1.79 (s, 15H, C_5Me_5), 2.08 (s, 6H, arene CH_3), 2.32−2.43 (m, 2H, CH_2), 2.66−2.77 (m, 2H, CH_2), 5.53 (s, 2H, arene CH). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 9.8, 16.2, 21.8, 25.6, 89.2, 93.5, 98.6, 101.1. Anal. Calcd for $C_{22}H_{31}F_6PRu$: C, 48.80; H, 5.77. Found: C, 48.80; H, 5.61.

(η^5-Pentamethylcyclopentadienyl)(η^6-indane)ruthenium(II) Hexafluorophosphate (18). A solution of indane (100 μL, 0.81 mmol) in dichloromethane (5 mL) was placed in a vial containing **11**-*Cp** (100 mg, 0.2 mmol) under an argon balloon. The resulting solution was stirred at room temperature for 1 h, followed by concentration in vacuo to ca. 0.5 mL. Addition of Et_2O (10 mL) led to precipitation of **18**, and the remaining suspension was filtered through a Celite plug, which was rinsed with Et_2O (2 × 2 mL) and dichloromethane (3 × 3 mL). The combined washings were evaporated in vacuo to give additional **18** as a white powder (combined yield: 92 mg, 0.18 mmol, 92%). ^{1}H NMR (CD_2Cl_2, 500

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MHz): δ 1.68 (m, 1H, CH*H*), 1.90 (s, 15H, C_5Me_5), 2.19 (m, 1H, CH*H*), 2.53−2.58 (m, 2H, CH_2), 2.86−2.93 (m, 2H, CH_2), 5.57 (dd, $^3J_{HH}$ = 4.2 Hz, $^4J_{HH}$ = 2.3 Hz, 2H, aromatic CH), 5.72 (dd, $^3J_{HH}$ = 4.2 Hz, $^4J_{HH}$ = 2.3 Hz, 2H, aromatic CH). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 125 MHz): δ 10.6, 23.5, 29.8, 84.3, 86.0, 96.0, 107.6. HRMS (ESI-TOFMS) for $C_{19}H_{25}Ru$: [M^+] calculated 355.1000; found 355.0999.

Representative Photolysis Experiment. An acetone-d_6 solution (1.5 mL) of enediyne **4**-*Me* (4.6 mg, 29 μmol), **8**-*Cp** (14.8 mg, 29 μmol), 1,4-CHD (4.56 mg, 57 μmol), and 1,3,5-tri-*tert*-butylbenzene internal standard was maintained at room temperature for 48 h in the dark, after which time a ^1H NMR spectrum of the sample indicated that no reaction had occurred. The sample was then irradiated in a Rayonett photoreactor equipped with UV lamps centered at 254 nm, and the progress of the reaction was monitored by ^1H NMR spectroscopy. After irradiation for 24 h the yield of **12**-*Cp** was determined to be 75% by integration of the ^1H NMR spectrum. The product exhibited spectroscopic properties identical with those reported in the literature.[29]

Relative Rates of Arene Photodissociation from [(η^5-C_5Me_5)-Ru(η^6-naphthalene)]PF_6 (8-*Cp) and [(η^5-C_5Me_5)Ru(η^6-benzene)]PF_6 (6-*Ru-PhH*).** [(η^5-C_5Me_5)Ru(η^6-naphthalene)]PF_6 (**8**-*Cp**; 12.0 mg, 0.024 mmol), [(η^5-C_5Me_5)Ru(η^6-benzene)]PF_6 (**6**-*Ru-PhH*; 8.9 mg, 0.019 mmol), and 1,3,5-tri-*tert*-butylbenzene (internal standard) were placed in an oven-dried J. Young tube. Acetonitrile-d_3 (0.91 mL) was placed in the tube, and the solution was degassed via three freeze/pump/thaw/degas cycles. An initial ^1H NMR spectrum was recorded, and the tube was placed in a Rayonette photoreactor equipped with UV broad-band lamps centered at 254 nm (33−34 °C). Photolysis was initiated, and the reaction progress was monitored by interrupting the photolysis every 20 min to record a ^1H NMR spectrum. Diagnostic ^1H NMR resonances for **6**-*Ru-PhH* (δ 5.76) and **8**-*Cp** (δ 6.49) were integrated relative to internal standard. Product resonances were observed at δ 1.60 {[(η^5-C_5Me_5)Ru-($NCCD_3$)$_3$]PF_6}, δ 7.52, 7.88 (naphthalene), and δ 7.37 (benzene).

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.7b00589.

NMR spectra, crystallographic data, computational data, and kinetic data (PDF)

All computed molecule Cartesian coordinates (XYZ)

Accession Codes

CCDC 1565978−1565979 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

■ AUTHOR INFORMATION

Corresponding Authors

*E-mail for K.K.B.: kimb@tju.edu.cn.

*E-mail for J.M.O.: jmoconnor@ucsd.edu.

ORCID

Ryan L. Holland: 0000-0001-9973-4781

Kim K. Baldridge: 0000-0001-7171-3487

Joseph M. O'Connor: 0000-0001-7510-3248

Present Address

[§]Department of Chemistry and Physics, Carroll College, 1601 N. Benton Avenue, Helena, MT 59625, USA.

Notes

The authors declare no competing financial interest.

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