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Xavier Creary

J. Org. Chem., **Just Accepted Manuscript** • DOI: 10.1021/acs.joc.7b02477 • Publication Date (Web): 28 Nov 2017

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Cobalt and Silver Promoted Methylenecyclopropane Rearrangements

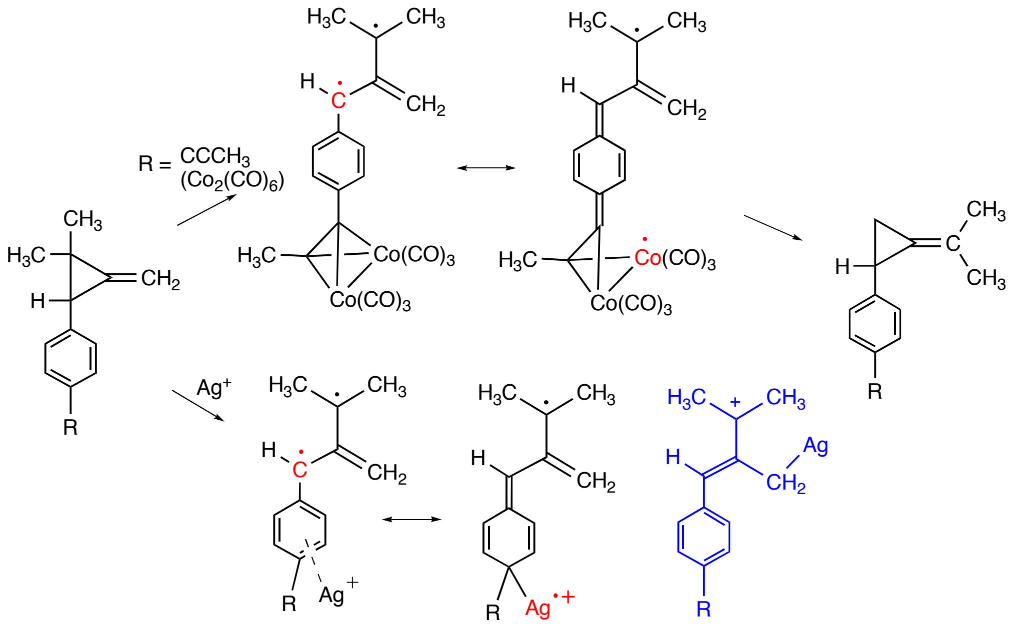
Xavier Creary

Department of Chemistry and Biochemistry

University of Notre Dame, Notre Dame, Indiana 46556

creary.1@nd.edu

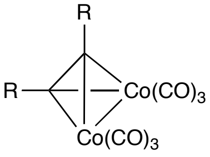
Abstract



The rate of the methylenecyclopropane rearrangement is enhanced by an alkyne-Co$_2$(CO)$_6$ complex bonded to the *para*-position of a benzene ring. This is explained by a stabilizing effect on the transition state leading to the biradical intermediate. Computational studies indicate that the benzylic type biradical intermediate is stabilized by a delocalization mechanism, where spin is delocalized onto the two cobalt atoms. Silver cation also enhances the rate of the methylenecyclopropane rearrangement. Computational studies suggest that silver cation can also stabilize a benzylic radical by spin delocalization involving silver. In the case of the silver promoted reactions, the rate enhancements in a series of aryl substituted methylenecyclopropanes correlate with σ^+ values. The question remains open as to whether the silver catalyzed methylenecyclopropane rearrangement proceeds via an argento stabilized biradical or whether the reaction involves an argento substituted allylic cation.

Introduction

Alkynes react readily with dicobalt octacarbonyl, $Co_2(CO)_8$, to give stable complexes of type **1**.[1] These complexes have been extensively studied and they contain a two cobalt atoms bonded in a tetrahedrane like structure.[2] Compounds of type **1** are likely intermediates in the Pauson-Khand reaction.[3] The carbocation stabilizing properties of these cobalt complexes have also been investigated and many carbocations of type **2** have been generated as stable molecules.[4] Alkynes can be regenerated from complexes **1** by oxidative methods, and hence the cobalt can serve as a protecting group for alkynes.[4d,e] Certain transition metal cations are also well known to coordinate with alkynes, with the Ag^+ complex **3** being a classic example.[5]



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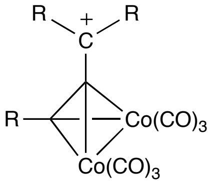

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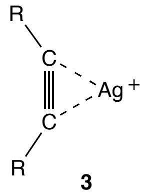

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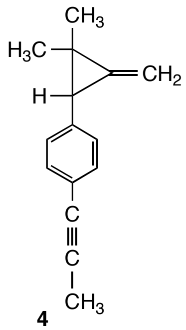

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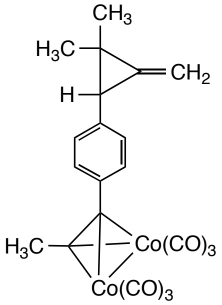

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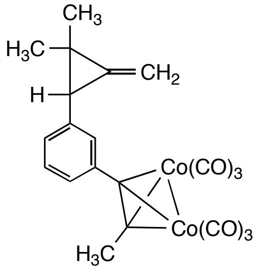

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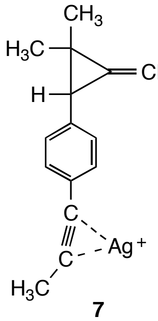
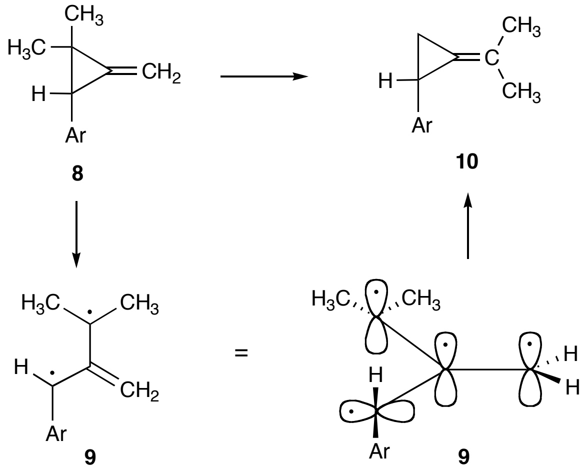


7

In view of the ability of cobalt-coordinated alkynes to stabilize carbocations, the effect of cobalt on radicals was of interest. Also of interest was the interaction of other transition metals with carbon-centered radicals. In order to investigate the effect of alkynes coordinated with cobalt on the stability of radical intermediates, the methylenecyclopropanes **4**, **5**, and **6** were prepared. Also of interest was the silver complex **7** that is potentially derived from reaction of **4** with silver cation. These substrates of general structure **8** all undergo a thermal methylenecyclopropane rearrangement to give **10** (Scheme 1).[6] This type of thermal rearrangement has been the subject of numerous investigations.[7] The generally accepted mechanism involves the formation of a short lived singlet biradical intermediate of type **9** that can close to form the product **10**.[8] This singlet biradical **9** is distinct from the parent trimethylenemethane, which is a ground state triplet diradical that can be observed by ESR spectroscopy.[9] Reported here are the results of studies designed to evaluate the effect of these transition metals on the stability of the biradical intermediates involved in the methylenecyclopropane rearrangement.

Scheme 1. Mechanism of the Thermal Methylenecyclopropane Rearrangement



Results and Discussion

Cobalt Complexes. The requisite methylenecyclopropane **4** was prepared (Scheme 2) using our standard protocol involving arylcarbene addtion to 1,1-dimethylallene.[10] Reaction of **4** with dicobalt octacarbonyl gave the isolable complex **5**. The *meta*-isomer **6** was prepared by a completely analogous method. These substrates **4-6** thermally rearrange to the corresponding isopropylidenecyclopropanes and rates can be readily monitored by ^{1}H NMR spectroscopy. Rate data for first order rearrangement processes are given in Table 1. For comparison purposes, data are also given for the parent unsubstituted substrate **13**.

Scheme 2. Synthesis and Rearrangement of Cobalt Complex 5

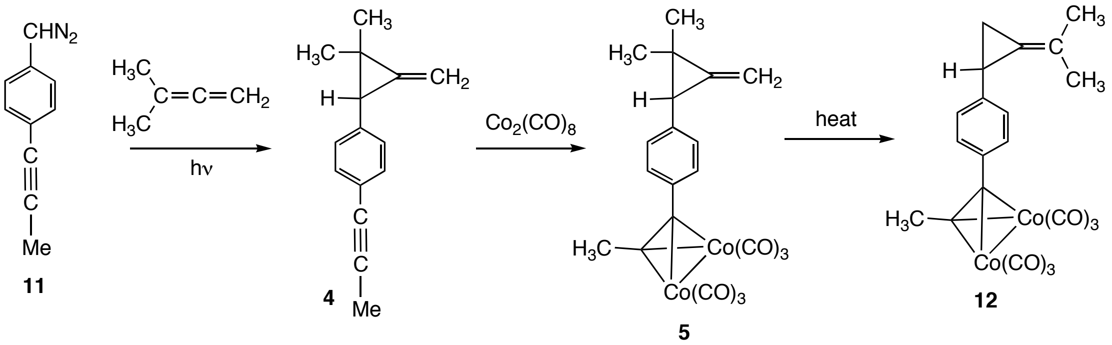
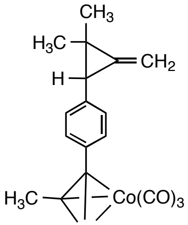
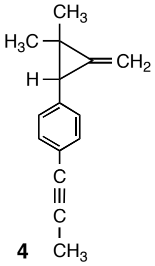
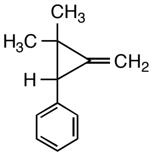
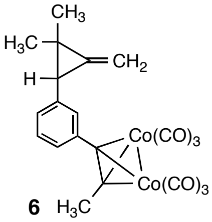
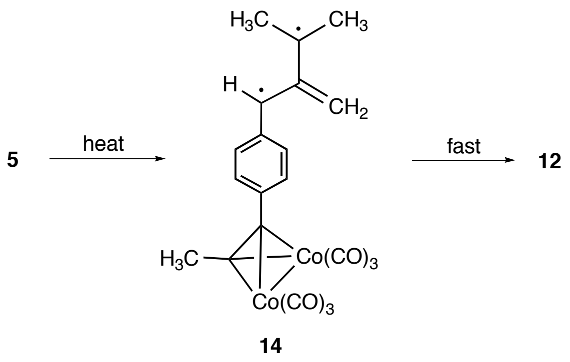


Table 1. Rearrangement Rates for Substrates 4, 5, 6, and 13 in C_6D_6

Compound	T (°C)	k (s^{-1})	k_{rel}
 **5**	80.0	3.86 x 10^{-4a}	6.93
	65.0	7.33 x 10^{-5}	
	55.0	2.20 x 10^{-5}	
	45.0	6.26 x 10^{-6}	
 **4**	80.0	2.10 x 10^{-4}	3.72
	70.0	6.93 x 10^{-5}	
	60.0	2.04 x 10^{-5}	
 **13**	80.0	5.57 x 10^{-5b}	1.00
	70.0	1.72 x 10^{-5b}	
	60.0	5.05 x 10^{-6b}	
 **6**	80.0	5.63 x 10^{-5}	1.01
	60.0	5.47 x 10^{-6}	

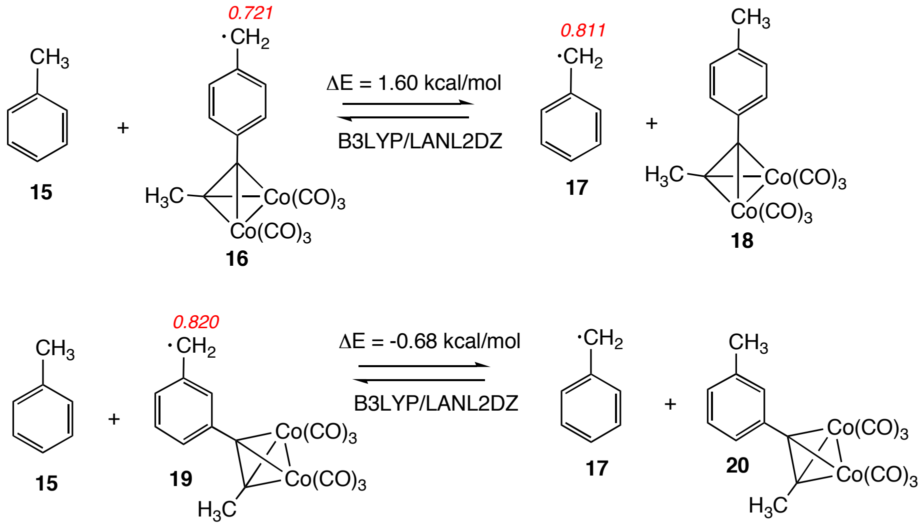
[a] extrapolated from data at lower temperatures.
[b] reference 20.

Scheme 3. Mechanism for Rearrangement of Cobalt Complex 5 to 12

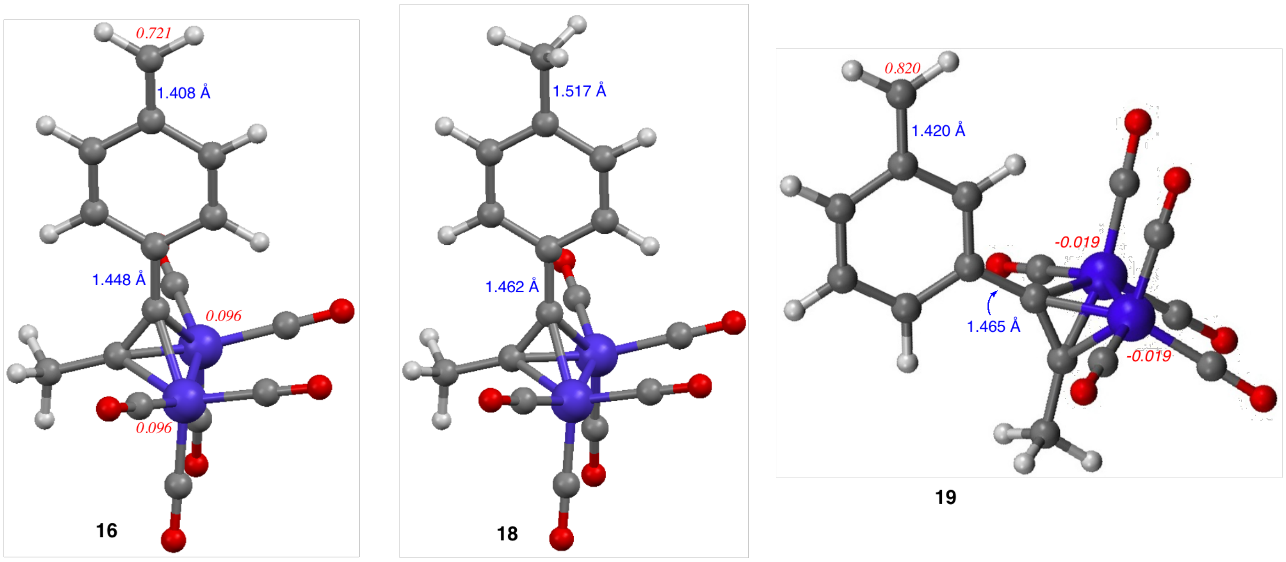


Immediately apparent is the fact that the rearrangement rate of the cobalt complex **5** is enhanced relative to the parent methylencyclopropane **13** as well as the uncomplexed alkyne **4**. This rate enhancement of 6.93 is a significant factor relative to the effect of many previously reported substituents.[6] and suggests significant stabilization of the transition state leading to the biradical intermediate **14** (Scheme 3) in the methylenecyclopropane rearrangement. This rate enhancement is not seen when the cobalt containing substituent is placed in the *meta*-position. The rate of the *m*-isomer **6** is essentially the same as that of the unsubstituted parent compound **13**.

Scheme 4. Isodesmic Reactions of Cobalt Substituted Benzylic Radicals with Toluene



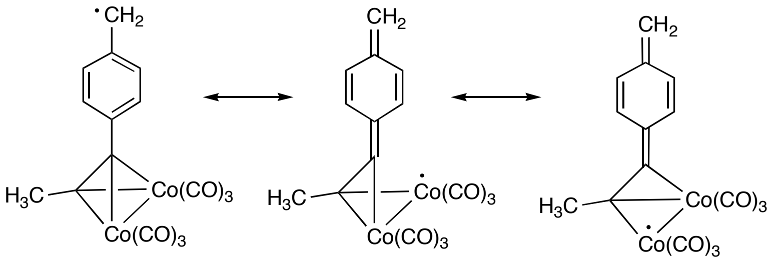
In order to further understand the effect of the cobalt complex on the stability of biradical **14**, the analogous substituted benzylic radicals **16** and **19** have been studied computationally[11a] at the B3LYP/LANL2DZ level (a common density functional method and basis set that are useful for organometallic compounds)[11b] using the isodesmic reactions shown in Scheme 4. Our previous studies have shown that radical stabilization energies calculated by this process correlate well with methylenecyclopropane rearrangement rates.[6] The calculations in Scheme 4 suggest that **16** is stabilized relative to the unsubstituted benzyl radical, **17**. Further examination of the structure of **16** (Figure 1) reveals the origin of this stabilization. Calculated spin density at the benzylic carbon of **16** (0.721) is significantly reduced relative to the unsubstituted benzyl radical **17** (0.811). On the other hand, the two cobalt atoms in **16** have accumulated some spin density (0.096). As expected, this spin delocalization leads to stabilization in **16**. Structures **16a** and **16b** (Scheme 5) display this spin delocalization in terms of contributing resonance forms. Such forms **16a** and **16b** are consistent with calculated bond lengths in **16**, where the C1-C2 bond (1.408 Å) and the C7-C8 bond (1.448 Å) are substantially shorter than the analogous bonds in the neutral molecule **18** (1.517 Å and 1.462 Å respectively). This delocalization occurs when the cobalt substituent is in the *para*-position. The *meta*-substituted benzylic radical **19** shows no such stabilization or spin delocalization. In fact, the calculation suggests that the *m*-substituted radical **19** is slightly destabilized relative to the unsubstituted benzyl radical **17**.



16 **18** **19**

Figure 1. B3LYP/LANL2DZ calculated structures of cobalt complexes **16**, **18**, and **19**.

Scheme 5. Resonance Forms of Cobalt Stabilized Benzylic Radical 16



16 **16a** **16b**

Silver Ion Promoted Reactions. There is a very large volume of literature involving the rearrangement of strained ring compounds promoted by transition metals.[12] An early example is the nickel-catalyzed rearrangement of methylenecyclopropane to butadiene.[13] The rearrangement of bicyclobutanes using silver, rhodium, and other transition metal catalysts has been one of the most intensely studied processes.[14] Transition metals are known to open methylenecyclopropane to form stable complexes of trimethylenemethane.[9,15] In light of these numerous studies, attention was next turned to silver complexes of alkynes, in particular complexes of type **7**. The question to be answered involved the ability of silver ion to promote the simple methylenecyclopropane rearrangement.

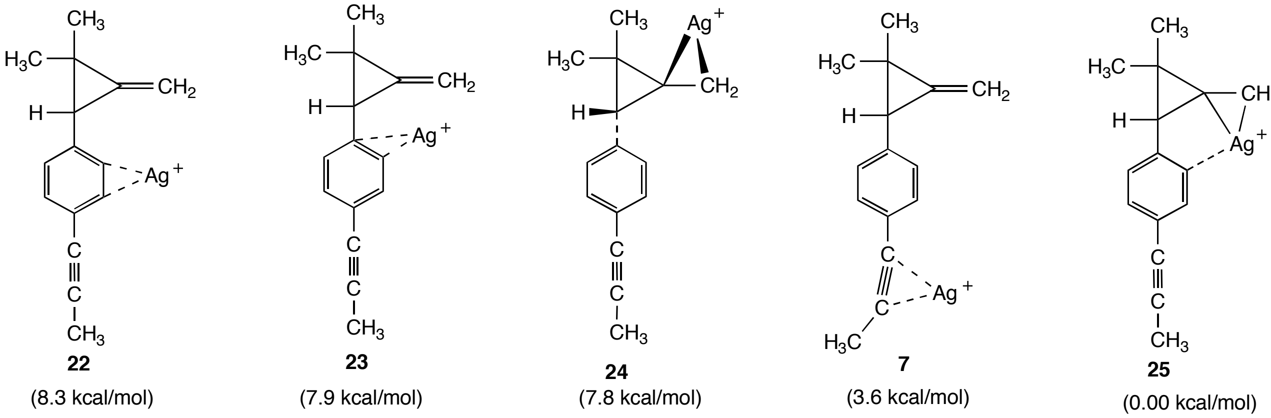
Mixing silver triflate with solutions of **4** in C_6D_6, acetone-d_6, or methanol-d_4 led to solutions of **4** in equilibrium with a silver complex. Complex formation was not complete even when four equivalents of AgOTf were added as evidenced by the fact that NMR signals continued to shift downfield even after the addition of excess AgOTf. The effect of silver triflate on the methylenecyclopropane rearrangement of **4** was next investigated in a number of solvents. Table 2 shows the results of these studies. First order rate constants for the methylenecyclopropane rearrangement are indeed enhanced when AgOTf is added to solutions of **4** in C_6D_6, acetone-d_6, and CD_3OD. In CD_3CN, there is a negligible rate enhancement. Silver perchlorate and silver trifluoroacetate in C_6D_6 also lead to rate enhancements, with the effect being smaller for silver trifluoroacetate.

Table 2. Rearrangement Rates of 4 with Added AgOTf at 60.0 °C

Solvent	Equiv of AgOTf [a]	k (s^{-1})
C_6D_6	0.00	2.04×10^{-5}
C_6D_6	0.94	3.64×10^{-5}
C_6D_6	2.03	5.35×10^{-5}
C_6D_6	4.20	7.75×10^{-5}
Acetone-d_6	0.00	1.84×10^{-5}
Acetone-d_6	1.79	3.83×10^{-5}
Acetone-d_6	3.00	5.00×10^{-5}
CD_3OD	0.00	1.59×10^{-5}
CD_3OD	1.64	6.62×10^{-5}
CD_3CN	0.00	1.92×10^{-5}
CD_3CN	1.65	2.01×10^{-5}

[a] [**4**] = 0.025 M

Silver ion is known to coordinate with alkenes,[5, 16] aromatics,[17] as well as alkynes.[5] It was therefore necessary to evaluate the nature of the silver complex with **4**, since all three functional groups are present in **4**. Five complexes of **4** with silver cation were located computationally at the B3LYP/LANL2DZ level as shown in Figure 2. Two of these complexes (**22** and **23**) involve coordination with the aromatic ring. Complex **24** has the silver complexed with the exocycic π-bond and *trans* to the aromatic ring, while **7** is an alkyne complex. Finally, silver is coordinated with both the alkene functional group and the *cis*-aromatic ring in **25**. This complex **25** has the B3LYP/LANL2DZ calculated lowest energy.



22 (8.3 kcal/mol) **23** (7.9 kcal/mol) **24** (7.8 kcal/mol) **7** (3.6 kcal/mol) **25** (0.00 kcal/mol)

Figure 2. Relative B3LYP/LANL2DZ calculated energies of Ag^+ complexes of **4**.

A number of mechanisms come to mind for the silver ion promoted methylencyclopropane rearrangement of **4**. The first involves a biradical intermediate **26** shown in Figure 3, where silver cation is coordinated with the alkyne functional group. This biradical **26** has been modeled computationally using the silver complexed benzylic radical **27**. The isodesmic reaction shown in Scheme 6 suggests that silver indeed lends stability to this benzylic radical. In addition to the calculated radical stabilization energy of 2.86 kcal/mol, the spin density at the benzylic carbon is reduced relative to the benzyl radical **17**, and there is significant spin density on the silver atom in **27**. In terms of resonance theory, form **27a** makes a significant contribution to the structure of **27**.

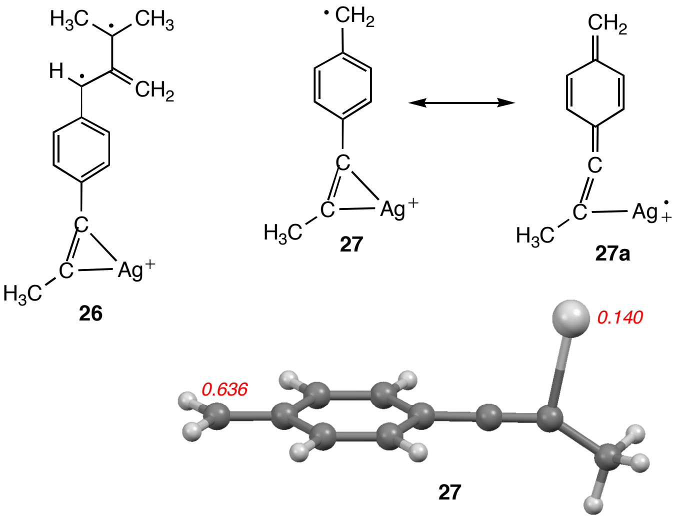
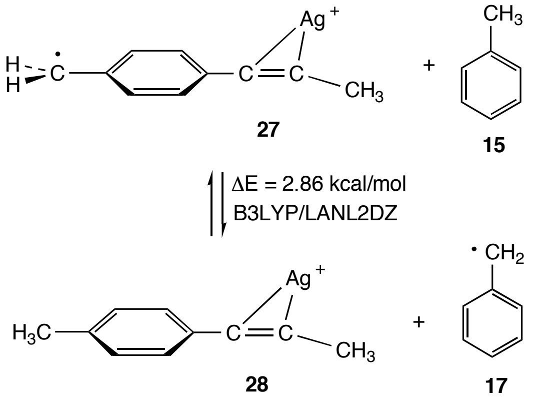


Figure 3. Structures of silver-alkyne complexed biradical and benzylic radical.

Scheme 6. Isodesmic Reaction of Silver-Alkyne Complexed Benzylic Radical with Toluene



In view of the computational structures **22** and **23** in Figure 2 that suggests that silver ion can also coordinate with the aromatic ring of **4**, alternative mechanisms must be considered. Could the rearrangement proceed via aromatic ring-coordinated biradicals such as **29**? Indeed analogous π-complexed benzylic radicals **30** and **31** (Figure 4) have been located at the B3LYP/LANL2DZ level of theory. These radicals have decreased spin density at the benzylic carbon and significant spin density is delocalized onto silver. They are presumably stabilized by silver. These intermediates suggest that the alkyne functional group would not be necessary for the silver promoted methylenecyclopropane rearrangement to occur.

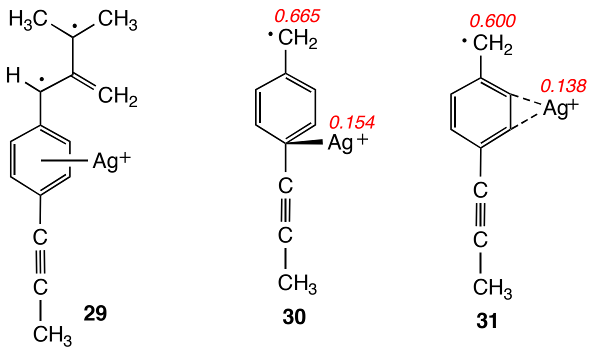
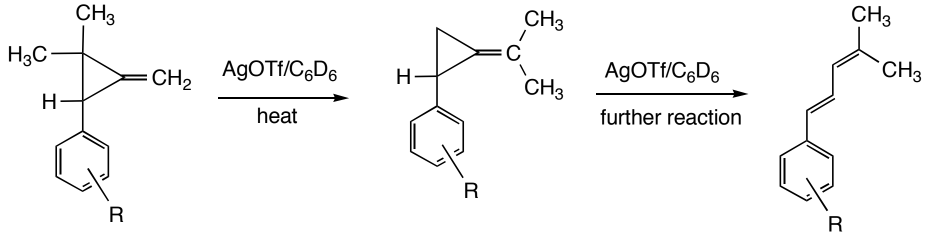


Figure 4. Structures of silver-arene complexed biradical and benzylic radical.

This hypothesis is verifiable and indeed, the substrates **13** and **32** have all been reacted thermally in the presence of silver triflate where they all rearrange to **33** as shown in Scheme 7. The rearrangements are not due to traces of triflic acid present in the reaction, since they still occur in the presence of the base 2,6-lutidine. Table 3 shows that the magnitude of the rate enhancement of the methylenecyclopropane rearrangement is substituent dependent. In fact the catalytic rate enhancement due to silver in **13**, **32b**, and **32c** is even greater than in the alkyne **4**. A Hammett plot (Figure 5) of the log of the rate enhancement versus σ^+ gives a fairly good correlation (r = 0.99). These results show that coordination of silver cation with an alkyne functional group is not a necessary condition for the silver promoted methylenecyclopropane rearrangement. Some other intermediate must be involved. Silver ion coordination with the aromatic system remains a distinct possibility. The larger rate enhancements seen in the *p*-OCH_3 and *p*-CH_3 substrates **32b** and **32c** and the smaller enhancement in the *m*-F and *p*-CF_3 substrates **32d** and **32e** might be a reflection of the increased ability of silver cation to coordinate with more electron-rich aromatic groups.

Scheme 7. Silver Ion Promoted Methylenecyclopropane Rearrangements



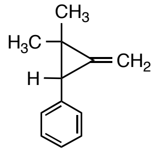
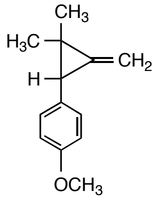
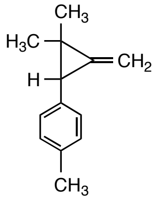
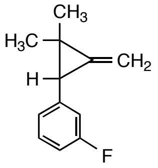
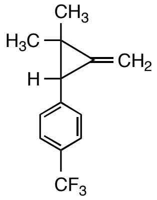
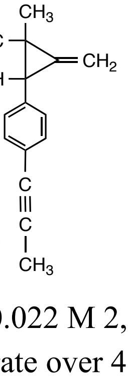
13 (R = *p*-H)
32b (R = *p*-OCH_3)
32c (R = *p*-CH_3)
32d (R = *m*-F)
32e (R = *p*-CF_3)

33a (R = *p*-H)
33b (R = *p*-OCH_3)
33c (R = *p*-CH_3)
33d (R = *m*-F)
33e (R = *p*-CF_3)

34b (R = *p*-OCH_3)

Some of the rearrangement products (especially **33b**) are not stable under the reaction conditions, but undergo further reaction to give the diene **34b** at longer times. The origin of this further rearrangement is under active investigation.

Table 3. Rearrangement Rates of substrates in C_6D_6 with added AgOTf

Compound	[AgOTf] (M)	T (°C)	k (s^{-1})	Enhancement
 **13**	0.000	70.0	1.72 x 10^{-5}	
	0.066	70.0	5.23 x 10^{-5}	3.04
	0.066[a]	70.0	4.44 x 10^{-5}	
 **32b**	0.000	60.0	1.01 x 10^{-5}	
	0.066	60.0	1.48 x 10^{-4}[b]	14.7
 **32c**	0.000	60.0	7.24 x 10^{-6}	
	0.066	60.0	4.08 x 10^{-6}	5.63
 **32d**	0.000	70.0	1.68 x 10^{-5}	
	0.066	70.0	2.99 x 10^{-5}	1.78
 **32e**	0.000	70.0	1.98 x 10^{-5}	
	0.066	70.0	2.78 x 10^{-5}	1.40
 **4**	0.000	60.0	2.04 x 10^{-5}	
	0.066	60.0	5.74 x 10^{-5}	2.81

[a] 0.022 M 2,6-lutidine added.

[b] rate over 40% reaction; product rearranges under reaction conditions.

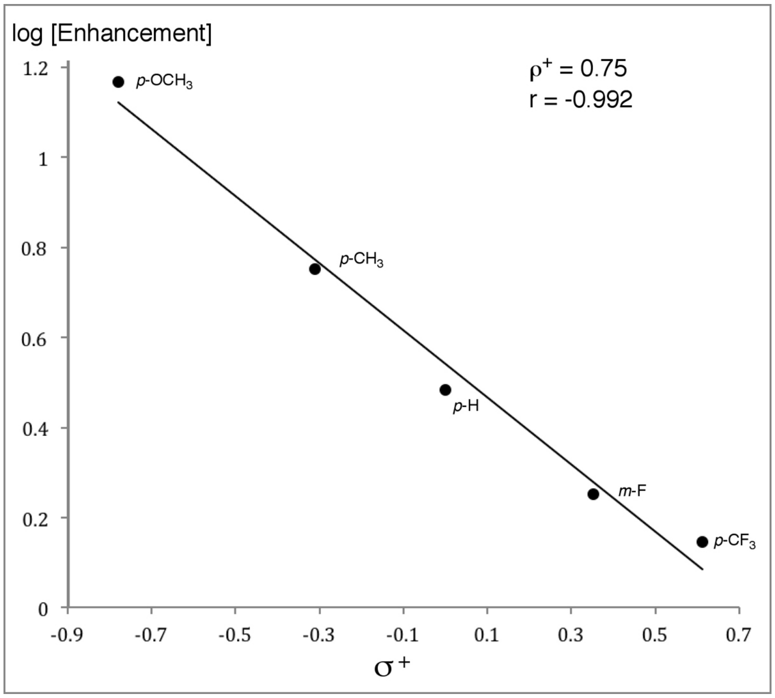


Figure 5. A plot of log [Enhancement] vs. σ^+ for the AgOTf promoted methylenecyclopropane rearrangements of **13** and **32**.

These studies suggest that intermediates such as **35** (Figure 6) might well be involved in the rearrangement of **32** as well as **4** and **13**. Spin delocalization onto silver in the benzylic analog **36** is implicated by the B3LYP/LANL2DZ calculated structure, where the spin density on silver is 0.153. This is also reflected by resonance form **36c**.

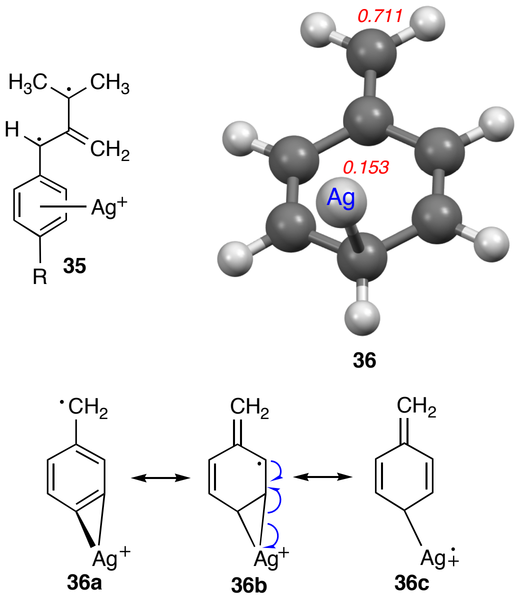
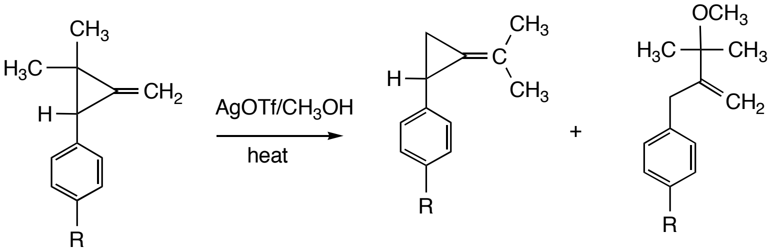


Figure 6. Structures of silver-arene complexed biradical and benzylic radical.

Scheme 8. Reactions of 4 and 13 with AgOTf in CH_3OH

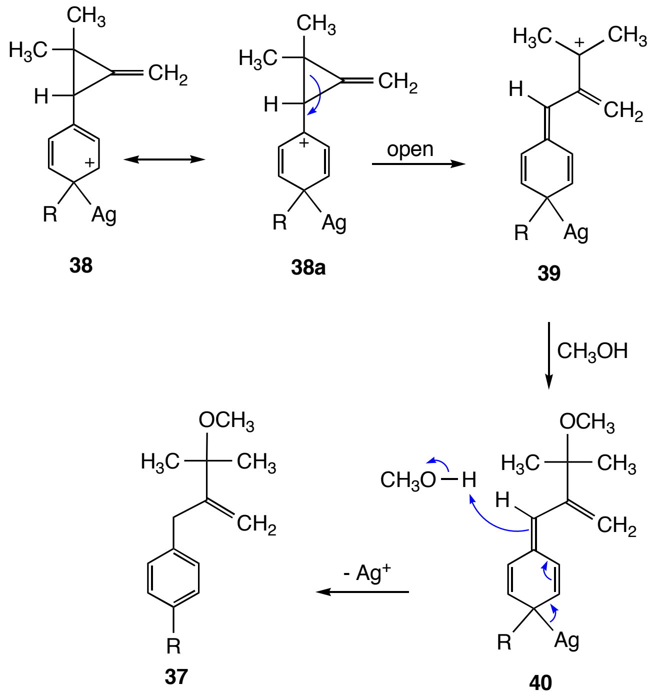


4 (R = $CCCH_3$) **33** (R = $CCCH_3$) (1 part) **37** (R = $CCCH_3$) (0.7 part)

13 (R = H) **33** (R = H) (1 part) **37** (R = H) (1.7 parts)

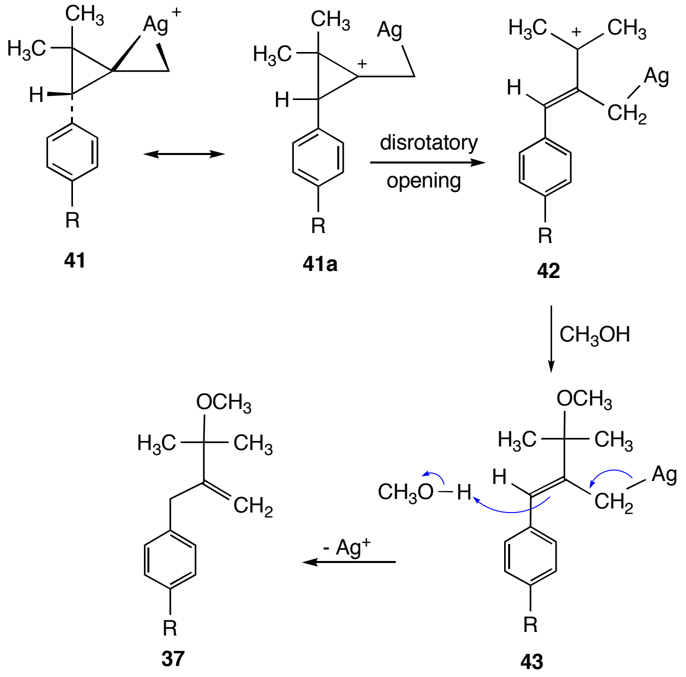
The reactions of **4** and **13** with AgOTf in CD_3OD or CH_3OH followed a somewhat different course as shown in Scheme 8. In addition to the normal methylenecyclopropane rearrangement products **33**, the methyl ethers **37** were also formed. What is the origin of the ethers **37**? It is tempting to suggest that the same silver complex is involved in the formation of both products **33** and **37**. Indeed, a reasonable mechanism for formation of **37** is shown in Scheme 9. Coordination of Ag^+ with the aromatic ring, as emphasized by form **38a**, might make the cyclopropyl ring prone to fragment in a cationic process to give allylic cation **39**. Solvent capture of this cation followed by protonation of **40** at the benzylic position would generate the product **37**.

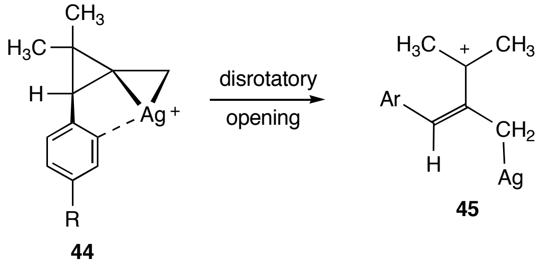
Scheme 9. Mechanism 1 for Formation of 37 in CH_3OH



Based on the ability of silver ion to coordinate with alkenes, an alternative mechanism (Scheme 10) for formation of **37** in methanol comes to mind. The cyclopropyl carbon of silver complex **41** should be electron-deficient as reflected in form **41a**. Electrocyclic ring opening of **41** would generate the allylic cation **42**, and methanol capture would give **43**. Subsequent protonation of **43** and loss of Ag^+ would yield the observed product **37**. Analogous ring opening of the related complex **44**, with silver coordinated to the exocyclic double bond as well as the *cis*-aryl group, would give the same product **37** via the allylic cation **45**.

Scheme 10. Mechanism 2 for Formation of 37 in CH_3OH





Computational studies were used to gain insight into the viability of Mechanisms 1 and 2. The relative energies of allylic cations **39**, **42**, and **45** were calculated at the B3LYP/LANL2DZ level (Figure 7). Indeed, this study suggests that allylic cation **39** in Mechanism 1 lies 30.5 kcal/mol above allylic cation **42** in Mechanism 2 and 24.2 kcal above cation **45**. This is reasonable since Mechanism 2 avoids the loss of aromaticity required in the fragmentation step of Mechanism 1. In other words, Mechanism 2 is much preferred over Mechanism 1 for the formation of addition product **37**.

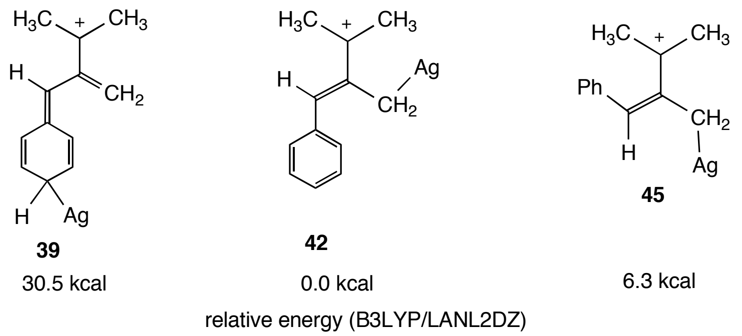
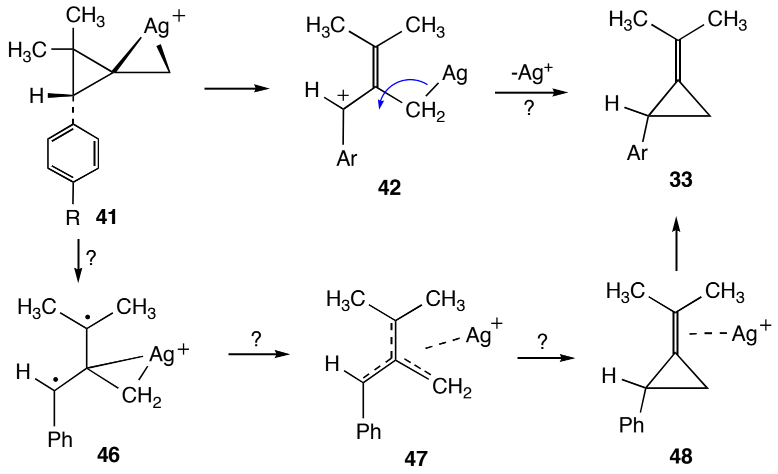


Figure 7. Structures and relative energies of potential argento-allylic cations.

While silver stabilized biradical intermediates such as **35** may be involved in the methylenecyclopropane rearrangement promoted by AgOTf, one should recall the old adage that one never proves a reaction mechanism.[18] There are other possibilities as shown in Scheme 11. Could the same alkene complex **41** (or **44**) proposed in formation of methyl ether **37** be involved in the methylenecyclopropane rearrangement? Substituent effects in Table 3 and the Hammett plot in Figure 5 are also consistent with ring opening of **41** to give an allylic cation **42**.[19] The cation **42** could cyclize with loss of silver cation to give the rearranged product **33**. Alternatively, the alkene complex **41**, with a weakened cyclopropane bond, might homolytically fragment to give biradical **46**. Could such a biradical convert to a silver coordinated trimethylenemethane **47** analogous to other transition metal coordinated trimethylenemethanes?[15] Loss of silver ion would also lead to **33**. The possibility of a concerted rearrangement of **41** to **48** also cannot be ruled out. Further studies are needed to shed more light on these silver promoted reactions.

Scheme 11. Alternative Mechanisms for the Ag^+ Promoted Methylenecyclopropane Rearrangement.



Conclusions. A dicobalt hexacarbonyl-alkyne complex in the *para*-position of a benzene ring enhances the rate of the methylenecyclopropane rearrangement. B3LYP/LANL2DZ calculations indicate that the intermediate benzylic radical is stabilized by spin delocalization involving the two cobalt atoms. Addition of silver triflate to aryl-substituted methylenecyclopropanes also leads to increased rearrangement rates that correlate with σ^+ values. In methanol solvent, a competing process involves formal addition of solvent to the strained cyclopropane bond. Computational studies indicate that silver π-complexed benzylic radical intermediates can also be stabilized by spin delocalization involving silver. The mechanism of the silver catalyzed rearrangement remains uncertain. One potential mechanism involves complexation of silver with the arene followed by fragmentation of the strained cyclopropane bond to give an argento stabilized biradical. Fragmentation to an argento substituted allylic cation followed by re-cyclization is an alternative process.

Experimental Section

General. NMR spectra were recorded on a Varian DirectDrive 600 MHz spectrometer. HRMS measurements were carried out using a Waters GCT Premier spectrometer (electron impact ionization with time-of-flight mass analyzer). Samples were run in the gas chromatography mode or using a direct insertion probe.

Preparation of 4-(prop-1-ynyl)benzaldehyde. 1-Bromo-4-(prop-1-ynyl)benzene[20] (1.47 g) was dissolved in 13 mL of anhydrous THF and the solution was cooled to -78 °C. *n*-BuLi in hexane (5.0 mL of 1.6 M) was added slowly dropwise via syringe. After 30 min at -78 °C, a solution of 0.75 g of dry *N,N*-dimethylformamide in 3 mL of ether was added slowly dropwise using an addition funnel. The mixture was then allowed to warm slowly to about -10 °C. The solution was then quenched with water and transferred to a separatory funnel using ether. The ether extract was then washed with two portions of water, saturated NaCl solution, and the dried over a mixture of Na_2SO_4 and $MgSO_4$. After solvent removal using a rotary evaporator, the residue was chromatographed on 16 g of silica gel. The column was eluted with increasing amounts of ether in pentane. The 4-(prop-1-ynyl)benzaldehyde[21] (783 mg; 72% yield), mp 54-55 °C, eluted with 5-7% ether in pentane. ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.98 (s, 1 H), 7.80 (d, J = 8.3 Hz, 2 H), 7.52 (d, J = 8.3 Hz, 2 H), 2.09 (s, 3 H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 191.5, 135.0, 132.0, 130.5, 129.5, 90.7, 79.3, 4.5.

Preparation of Methylenecyclopropane 4. Tosylhydrazine (780 mg) was suspended in 5 mL of methanol and 575 mg of 4-(prop-1-ynyl)benzaldehyde was added. The mixture was stirred for 6 h at room temperature and then 9.1 mL of 0.510 M $NaOCH_3$ in methanol was added. The methanol solvent was then removed using a rotary evaporator. The solid that formed was evacuated under aspirator pressure for an additional 8 h. Ethylene glycol (20 mL) was then added to the dry salt and the mixture was heated to about 35 °C in an oil bath until the solid dissolved. The mixture was then heated from 75-80 °C for about 10 min, cooled to room temperature, and then extracted with a 50:50 ether:pentane mixture. This heating/extraction procedure was repeated a total of three times. The combined ether/pentane extracts were washed with 2 portions of water, saturated NaCl solution and dried over a mixture of Na_2SO_4 and $MgSO_4$. The solvents were removed using a rotary evaporator to give 459 mg (74% yield) of crude unstable 1-(diazomethyl)-4-(prop-1-ynyl)benzene, **11**, as an oil that was used in the next reaction without further purification. ^{1}H NMR of **11** (600 MHz, $CDCl_3$) δ 7.30 (d, *J* = 8 Hz, 2 H), 6.81 (d, *J* = 8 Hz, 2 H), 4.94 (s, 1 H), 2.04 (s, 3 H). ^{13}C NMR of **11** (150 MHz, $CDCl_3$) δ 132.2, 129.2, 121.0, 119.2, 85.3, 79.7, 47.8, 4.4.

1-(Diazomethyl)-4-(prop-1-ynyl)benzene, **11**, prepared above (423 mg) was dissolved in 28 mL of 3-methylbuta-1,2-diene and the solution was sealed in three Pyrex tubes under argon. Each tube was individually irradiated with a Hanovia 450 watt lamp for a total of 50 min. The color changed from red orange to light brown over the course of the irradiation. The tubes were then opened and the excess 3-methylbuta-1,2-diene was removed using an aspirator vacuum. The residue was chromatographed on 12 g of silica gel and the column was eluted with pentane. The first fraction that eluted was an oil (95 mg) that contained 95% of **4** along with 5% of the isomeric 1-(prop-1-ynyl)-4-(2-(propan-2-ylidene)cyclopropyl)benzene. This was followed by fractions containing mixtures of **4** and increasing amounts of the isomeric 1-(prop-1-ynyl)-4-(2-(propan-2-ylidene)cyclopropyl)benzene. A total of 297 mg (56% yield) of products were obtained. ^{1}H NMR of **4** (600 MHz, $CDCl_3$) δ 7.29 (d, *J* = 8.2 Hz, 2 H), 7.09 (d, *J* = 8.2 Hz, 2 H), 5.57 (m, 1 H), 5.52 (m, 1 H), 2.43 (t, *J* = 2.1 Hz, 1 H), 2.04 (s, 3 H), 1.33 (s, 3 H), 0.83 (s, 3 H). ^{13}C NMR of **4** (150

MHz, $CDCl_3$) δ 145.4, 138.1, 131.1, 128.8, 121.3, 103.5, 85.4, 79.8, 32.1, 26.1, 24.1, 18.3, 4.4. HRMS (EI) (M^+) calculated for $C_{15}H_{16}$ 196.1252, found 196.1235.

Preparation of Cobalt Complex 5. A sample of $Co_2(CO)_8$ (Strem Chemical Co.) was purified by dissolving in pentane, decanting the pentane solution from the insoluble material, and removing the pentane using a rotary evaporator. The resultant orange crystals are relatively pure $Co_2(CO)_8$. A sample of $Co_2(CO)_8$ (44.8 mg; 0.131 mmol) was placed in a two mL vial and about 0.6 mL of C_6D_6 was added along with a micro stir bar. A solution of 24.2 mg (0.124 mmol) of the methylenecyclopropane **4** in about 0.2 mL of C_6D_6 was then added. After 10 h at room temperature, the solution was filtered through a small amount of silica gel in a pipette. Pentane was used to rinse the silica gel and the solvents were then removed using a rotary evaporator to give 58.3 mg (98% yield) of complex **5** as a thick dark red oil. This product was stored in pentane solution in the freezer. Traces of paramagnetic impurities can lead to broadening of NMR spectra. Samples were therefore filtered through silica gel using pentane before recording spectra. ^{1}H NMR of **5** (600 MHz, C_6D_6) δ 7.45 (d, *J* = 8.2 Hz, 2 H), 7.05 (d, *J* = 8.2 Hz, 2 H), 5.54 (m, 1 H), 5.50 (m, 1 H), 2.43 (s, 3 H), 2.33 (t, *J* = 2.1 Hz, 1 H), 1.18, (s, 3 H), 0.79 (s, 3 H). ^{13}C NMR of **5** (150 MHz, C_6D_6) δ 200.5, 146.0, 139.4, 136.0, 130.3, 129.5, 104.0, 94.7, 92.3, 33.0, 26.4, 24.8, 20.9, 18.7. HRMS (EI) (M^+) calculated for $C_{21}H_{16}Co_2O_6$ 481.9611, found 481.9603.

Preparation of an Authentic Sample of Cobalt Complex 12. A sample of $Co_2(CO)_8$ (51.8 mg; 0.151 mmol) was placed in a vial and about 0.6 mL of C_6H_6 was added. A solution of 29.6 mg (0.151 mmol) of the methylenecyclopropane **33** (R = $CCCH_3$) in 0.2 mL of benzene was then added. After 3 h at room temperature, analysis of a small sample showed about 7% unreacted methylenecyclopropane. About 5 mg of additional $Co_2(CO)_8$ was then added and after an additional

5 h, the benzene was removed using a rotary evaporator. The residue was dissolved in 2 mL of pentane and then filtered through 0.6 g of silica gel/pentane in a pipette. The pentane solvent was removed using a rotary evaporator to give 66.2 mg (91% yield) of **12** as a thick dark red oil. Samples of **12** were stored in pentane in the freezer. ^{1}H NMR of **12** (600 MHz, C_6D_6) δ 7.46 (d, *J* = 8.2 Hz, 2 H), 6.95 (d, *J* = 8.2 Hz, 2 H), 2.43 (s, 3 H), 2.38 (m, 1 H), 1.83, (m, 3 H), 1.67 (m, 3 H), 1.50 (m, 1 H), 0.98 (m, 1 H). ^{13}C NMR of **12** (150 MHz, C_6D_6) δ 200.5, 144.1, 135.5, 129.9, 128.7, 127.5, 123.4, 120.6, 94.7, 92.5, 22.6, 22.5, 21.2, 20.9, 15.9. HRMS (EI) (M^+) calculated for $C_{21}H_{16}Co_2O_6$ 481.9611, found 481.9584.

Preparation of Cobalt Complex 6. A sample of $Co_2(CO)_8$ (47.6 mg; 0.139 mmol) was placed in a two mL vial and about 0.6 mL of C_6D_6 was added. A solution of 26.2 mg (0.134 mmol) of the methylenecyclopropane **8** (Ar = *m*-$CH_3CCC_6H_4$) 0.5 mL of C_6D_6 was then added. After 26 h at room temperature, analysis of a small sample showed no unreacted methylenecyclopropane. After 2 days the C_6D_6 was removed using a rotary evaporator and the residue was taken up into 2 mL of pentane. The pentane solution was filtered through 300 mg of silica gel and the solvent was removed using a rotary evaporator to give 57 mg (79% yield) of **6** as a thick dark red oil. The product **6** was stored in pentane solution. ^{1}H NMR of **6** (600 MHz, C_6D_6) δ 7.56 (bs, 1 H), 7.34 (m, 1 H), 7.07-7.00 (m, 2 H), 5.60-5.57 (m, 2 H), 2.44 (s, 3 H), 2.39 (t, *J* = 2.1 Hz, 1 H), 1.18 (s, 3 H), 0.88 (s, 3 H). ^{13}C NMR of **6** (150 MHz, C_6D_6) δ 200.5, 145.9, 140.0, 138.2, 130.4, 129.8, 129.4, 127.1, 104.0, 94.6, 92.7, 32.6, 26.3, 24.5, 20.8, 18.7. HRMS (EI) (M^+) calculated for $C_{21}H_{16}Co_2O_6$ 481.9611, found 481.9591.

Reaction of 33b with Silver Triflate. The isopropylidenecyclopropane **33b** (11.7 mg) was dissolved in 906 mg of C_6H_6 that contained 16.1 mg of AgOTf. The solution was heated in a sealed tube at 60 °C in a water bath for 60 min. The benzene solution was taken up into three mL of pentane and then extracted with three portions of water. The benzene/pentane phase was dried over Na_2SO_4 and the solvents were removed using a rotary evaporator. The residue was filtered through a small amount of silica gel in a pipet using pentane to rinse. Removal of the solvent using a rotary evaporator gave 10.2 mg (87% yield) of **34b**[22] as a clear oil. ^1H NMR of **34b** (600 MHz, C_6D_6) δ 7.27 (d, *J* = 8.7 Hz, 2 H), 6.99 (d of d, *J* = 15.5, 11.0 Hz, 1 H), 6.77 (d, *J* = 8.7 Hz, 2 H), 6.46 (d, *J* = 15.5 Hz, 1 H), 6.05 (d, *J* = 11.0 Hz, 1 H), 3.29 (s, 1 H), 1.70 (br s, 3 H), 1.68 (br s, 3 H). ^{13}C NMR of **34b** (150 MHz, $CDCl_3$) δ 158.8, 135.3, 131.0, 129.1, 127.2, 125.5, 123.8, 114.0, 55.3, 26.2, 18.5.

Reaction of 4 with AgOTf in CH_3OH. A solution 21.1 mg of methylenecyclopropane **4** (that contained 6% of **33** (R = $CCCH_3$)) and 30.4 mg of AgOTf in 1.63 g of CH_3OH was sealed in a glass tube and heated in a water bath at 70 °C for 200 min. The CH_3OH was then removed using a rotary evaporator and the residue was taken up into water containing a drop of ammonium hydroxide and 3 mL of pentane. The pentane extract was washed with 2 portions of water and then dried over a mixture of Na_2SO_4 and $MgSO_4$. The NMR spectrum of the crude material showed methyl ether **37** (R = $CCCH_3$), rearranged product **33** (R = $CCCH_3$), and starting material **4** in a 37:56:7 ratio. After filtration the pentane volume was reduced to about 1 mL and the mixture was then chromatographed on 2.5 g of silica gel. The column was eluted with increasing amounts of ether in pentane. The unreacted starting material **4** and the rearranged product **33** (R = $CCCH_3$) eluted with pentane. The methyl ether ether **37** (R = $CCCH_3$) (7.9 mg; 37% yield based on unrecovered **4**) eluted with 3-4% ether in pentane as a clear oil. ^1H NMR of **37** (R = $CCCH_3$) (600 MHz, $CDCl_3$) δ 7.32 (d, *J* = 8.2 Hz, 2 H), 7.10 (d, *J* = 8.2 Hz, 2 H), 5.10 (m, 1 H), 4.63 (m, 1 H), 3.35 (br s, 2 H), 3.11 (s, 3 H), 2.05 (s, 3 H), 1.32 (s, 6 H). ^{13}C NMR of **37** (R = $CCCH_3$) (150

MHz, $CDCl_3$) δ 152.1, 138.9, 131.4, 129.6, 121.5, 113.8, 85.3, 79.7, 77.3, 50.3, 37.1, 25.7, 4.4. HRMS (EI) (M^+) calculated for $C_{16}H_{20}O$ 228.1514, found 228.1513.

Reaction of 13 with AgOTf in CH_3OH. A solution 22.2 mg of methylenecyclopropane **13** (that contained 4% of **33** (R = H)) and 33.9 mg of AgOTf in 2.00 g of CH_3OH was sealed in a glass tube and heated in a water bath at 70 °C for 150 min. The CH_3OH was then removed using a rotary evaporator and the residue was taken up into water containing a drop of ammonium hydroxide and 3 mL of pentane. The pentane extract 1was washed with 2 portions of water and then dried over a mixture of Na_2SO_4 and $MgSO_4$. The NMR spectrum of the crude material showed methyl ether **37** (R = H), rearranged product **33** (R = H), and starting material **13** in a 40:26:34 ratio. After filtration the pentane volume was reduced to about 1 mL and the mixture was then chromatographed on 2.6 g of silica gel. The column was eluted with increasing amounts of ether in pentane. The unreacted starting material **13** and the rearranged product **33** (R = H) eluted with pentane. The methyl ether ether **37** (R = H) (6.1 mg; 36% yield based on unrecovered **13**) eluted with 2-3% ether in pentane as a clear oil. ^{1}H NMR of **37** (R = H) (600 MHz, $CDCl_3$) δ 7.30 (t, J = 7.6 Hz, 2 H), 7.23-7.17 (m, 3 H), 5.11 (m, 1 H), 4.64 (m, 1 H), 3.38 (br s, 2 H), 3.13 (s, 3 H), 1.34 (s, 6 H). ^{13}C NMR of **37** (R = H) (150 MHz, $CDCl_3$) δ 152.4, 140.3, 129.7, 128.3, 125.9, 113.6, 77.4, 50.3, 37.2, 25.7. HRMS (CI) $(M+H)^+$ calculated for $C_{13}H_{19}O$ 191.1436, found 191.1456.

Thermal Rearrangements of Methylenecyclopropanes. Kinetics Procedures. Rates of rearrangements in Tables 1-3 were measured using our previously described ^{1}H NMR method.[6, 23] In order to avoid NMR spectral line broadening due to development of paramagnetic impurities, rearrangement rates of cobalt complex **5** were measured using freshly chromatographed samples of **5** at concentrations of about 3 mg/mL of C_6D_6 in sealed NMR tubes under nitrogen.

Rearrangement rates of cobalt complex **6** were measured using the following modified procedure. About 3 mg of the freshly chromatographed cobalt complex **6** was dissolved in 1.5 mL of C_6D_6. Portions of the solution were sealed in four tubes and the tubes were immersed in a constant temperature bath at the appropriate temperature. The tubes were periodically withdrawn from the bath and quenched at 15 °C at appropriate times. The C_6D_6 was removed from each sample using a rotary evaporator and the residue was taken up into a small amount of pentane. The pentane solution was passed through a small amount of silica gel in a pipet to remove paramagnetic impurities. After pentane removal, the residue was re-dissolved in C_6D_6 and the sample was analyzed by 600 MHz NMR. The areas due to the CH_3 group of unreacted **6** at δ 1.18 and the rearrangement product at δ 1.86 were monitored in the standard fashion.

Computational Studies. *Ab initio* molecular orbital calculations were performed at the B3LYP/LANL2DZ level using the Gaussian 09 series of programs.[11a] Structures were characterized as energy minima *via* frequency calculations that showed no negative frequencies.

Associated Content

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: xxx.

Complete reference 11a.

Computational details

^1H and ^{13}C NMR spectra of new compounds

Data used for determination of rate constants in Tables 1-3.

Author Information

Corresponding Author

creary.1@nd.edu

ORCID

Xavier Creary: 0000-0002-1274-5769

Notes

The authors declare no competing financial interest.

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