Cyclization Reactions of Rhodium Carbene Complexes. Effect of Composition and Oxidation State of the Metal†

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Received December 5, 1996⊗

Treatment of *o*-(1,7-octadiynyl)benzoyldiazoethane with rhodium(II) octanoate in pentane resulted in a double internal/internal alkyne insertion reaction producing a labile bicyclo[4.1.0]hept-1(7)-ene derivative which readily undergoes a Diels−Alder reaction with diphenylisobenzofuran. Changing the solvent from pentane to CH_2Cl_2 afforded a 2:1 mixture of *cis*- and *trans*-alkenyl-substituted indenones. Stepwise cyclization involving a set of dipolar intermediates occurs in CH_2Cl_2 whereas metallocyclobutenes are involved when pentane is used as the solvent. The rhodium(II) carboxylate catalyzed reaction of unsymmetrically substituted cyclopropenes gives substituted furans derived from cleavage of the less substituted β-bond. Thus, treatment of 3-benzoyl-3-methyl-1-(*n*-butyl)cyclopropene with Rh_2OAc_4 afforded a 26:1 mixture of 2-phenyl-3-methyl-4-(*n*-butyl)- and 2-phenyl-3-methyl-5-(*n*-butyl)furan. In contrast, the $[ClRh(CO)_2]_2$-catalyzed reaction resulted in cleavage of the more substituted σ-bond producing only 2-phenyl-3-methyl-5-(*n*-butyl)furan. Both reactions involve electrophilic attack of the rhodium metal on the less substituted carbon atom of the cyclopropene π-bond to give the most stabilized cyclopropyl carbocation. Ring opening followed by rapid electrocyclization to the furan occurs with the Rh(II) catalyst. With the Rh(I) catalyst, the ring-opened species preferentially cyclizes to a metallocyclobutene intermediate which then equilibrates with the thermodynamically more stable isomer prior to furan formation. The Rh(I)-catalyzed reaction of 3-benzoyl-1-propylcyclopropene with various terminal alkynes gives 2-alkyl-4-propyl-7-phenyloxepins in good yield. These reactions involve electrophilic attack of the rhodium metal on the more substituted carbon of the cyclopropene π-bond to give a rhodium carbene complex. This metallo carbenoid undergoes a subsequent [2 + 2] cycloaddition with terminal acetylenes. The resulting rhodacycle rearranges by a formal 1,5-sigmatropic shift, and this is followed by reductive elimination of rhodium to produce the observed oxepin.

The chemistry of transition metal carbene complexes has been the subject of intense activity over the past two decades.[1−20] Current interest in this area stems from the role of metal carbenes in alkene metathesis,[21] in alkene and alkyne polymerization,[22] in cyclopropanation chemistry,[23] and as intermediates in an impressive array of synthetic methodology.[24,25] Many transition metal carbene complexes react readily with alkynes to form vinyl carbene complexes.[1−4] The product distribution has been found to vary considerably depending on the metal employed and the nature of the functionality present on the eneyne substrate. Of special interest is the intramolecular reaction of carbene complexes with alkynes, which has inspired many variations.[20] Due to their lability, metal carbene complexes are often generated *in situ* from their corresponding precursors prior to use. Several years ago our group[26] as well as Hoye's[27] described a route for producing cycloalkenone carbenoids which involved the rhodium(II)-catalyzed decomposition of α-diazoalkynyl-substituted ketones (Scheme 1). The reaction occurs by addition of the rhodium carbenoid onto the acetylenic

† Dedicated to the memory of William G. Dauben, 1919−1997.

⊗ Abstract published in *Advance ACS Abstracts,* February 15, 1997.

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S0022-3263(96)02271-2 CCC: $14.00

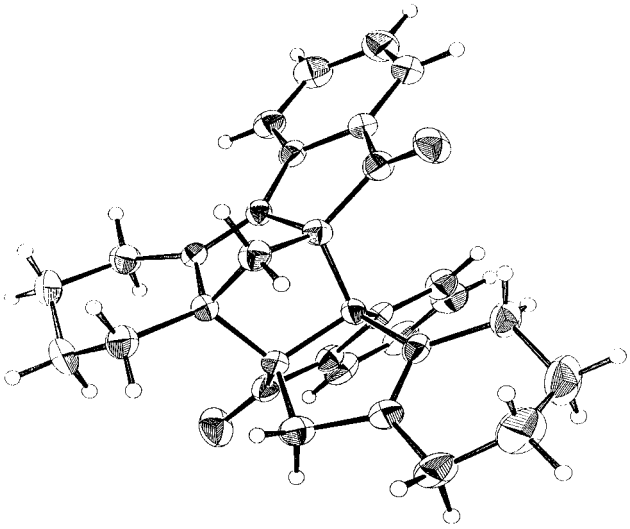
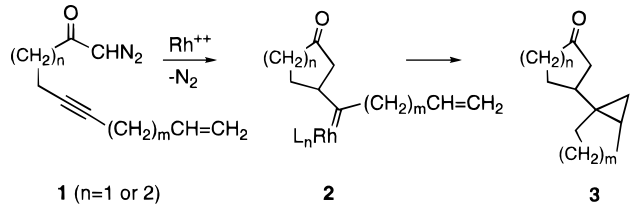


Figure 1. An ORTEP drawing of dimer **8**.

Scheme 1



π-bond to give vinyl carbenoid **2**. We have further demonstrated that the vinyl carbenoid complex can be trapped in an intramolecular fashion to give bicyclohexanes **3** in good yield when an alkene is tethered to the alkynyl group.[26] The potential for many other chemical pathways exists in the generation and further reaction of these rhodium carbenoids. For example, replacement of the alkenyl group with an alkyne should result in the formation of a bicyclic cyclopropene derivative. In this paper we detail our earlier observations[28] which show that the reaction pathway is not only highly dependent on the metal employed but is also influenced by the nature of the solvent.

Results and Discussion

Our previous findings that *o*-alkynyl-substituted α-diazoacetophenone derivatives produce vinyl carbenoids[26] suggested to us that these reactive species might undergo intramolecular addition to a neighboring acetylenic π-bond. Initial efforts focused on the rhodium(II)-catalyzed reaction of α-diazo ketone **4**. Treatment of **4** with a catalytic quantity of rhodium(II) octanoate in pentane at 25 °C afforded dimer **8** (74%), derived from a transient indenone intermediate (*i.e.*, **7**, Scheme 2). The structure of **8** was unequivocally established by an X-ray crystal structure analysis (Figure 1).[29] That the reactive indenone **7** is the primary product of reaction follows from its

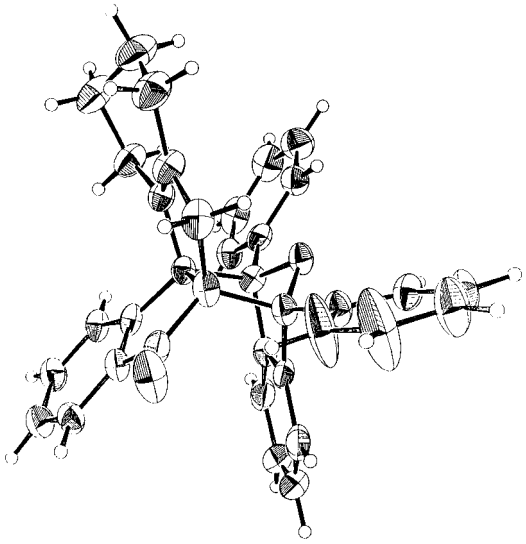
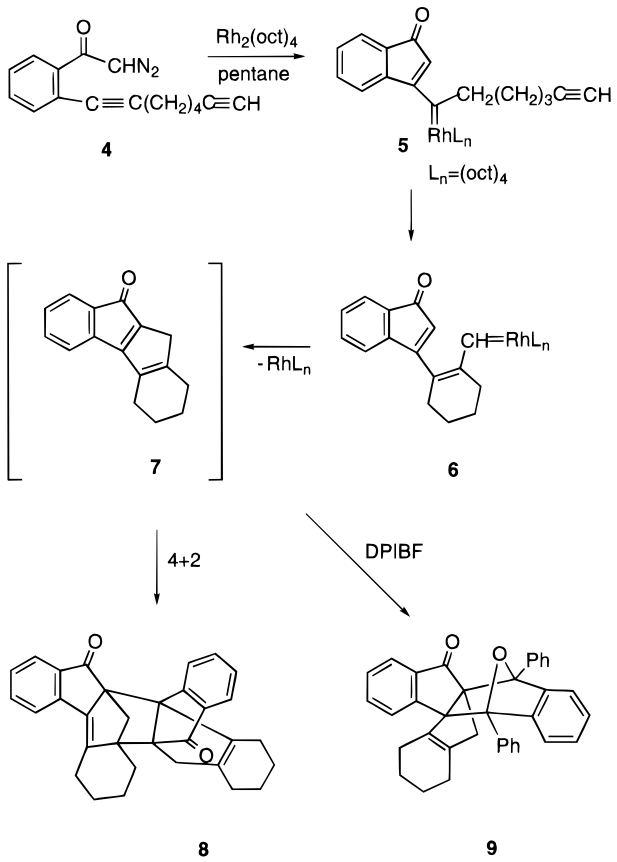


Figure 2. An ORTEP drawing of Diels−Alder cycloadduct **9**.

Scheme 2



interception by diphenylisobenzofuran (DPIBF). Cycloadduct **9** was obtained as the exclusive cycloadduct in 78% isolated yield and its structure was established by an X-ray crystal structure analysis (Figure 2).[29] As outlined in Scheme 2, formation of indenone **7** can be explained in terms of insertion of the initially formed rhodium carbenoid **5** onto the neighboring acetylenic π-bond with eventual formation of the cyclized dienyl carbenoid **6** (*vide infra*). Electrocyclization of **6** followed by reductive elimination of the rhodium(II) species produces **7** which subsequently undergoes a [4 + 2] cycloaddition to produce dimer **8**.

Extension of the carbenoid cyclization/insertion reaction to α-diazo ketone **10** was next investigated. In this case it was possible to obtain cyclopropene **12** in 80%

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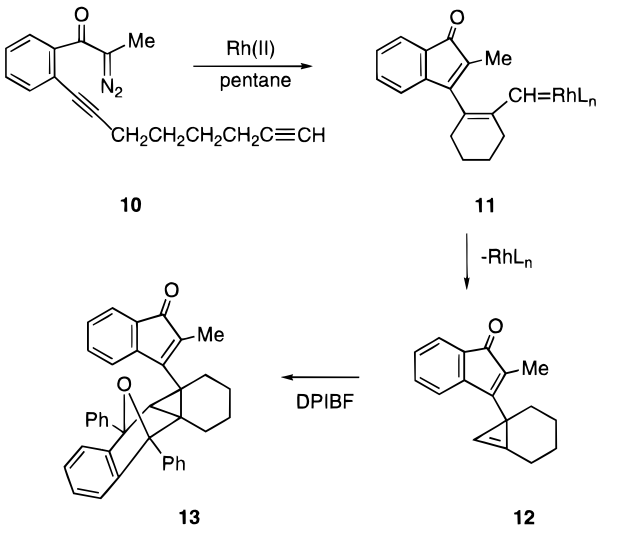
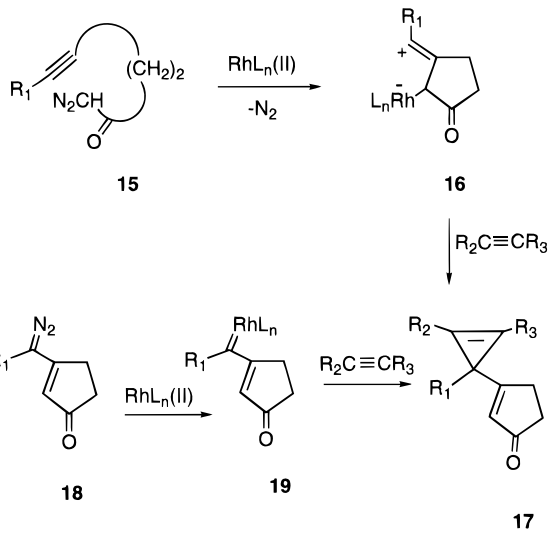
Scheme 3

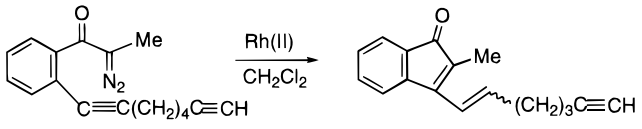


Scheme 4



yield as an isolable but reactive intermediate from the $Rh_2(oct)_4$/pentane catalyzed reaction (Scheme 3). Presumably, the reaction proceeds in an analogous fashion to produce dienyl carbenoid **11**. The presence of the methyl group on **11** significantly retards the 1,5-electrocyclization reaction and cyclopropene formation occurs instead. This highly reactive compound readily undergoes Diels−Alder cycloaddition with DPIBF to give a 1:1 *endo*/*exo* mixture of cycloadducts **13** in 78% isolated yield. Cyclopropene **12** contains significant strain which accounts for its high reactivity. Related bridged cyclopropenes have been isolated as extremely reactive substrates by Wiberg[30] and Billups[31] and have been shown to undergo facile [4 + 2] cycloadditions with diphenylisobenzofuran.

During the course of our studies, we found that the choice of solvent markedly influences the product distribution obtained from diazo ketone **10**. Thus, treatment of **10** with a catalytic quantity of rhodium(II) acetate at 25 °C in CH_2Cl_2 resulted in a 2:1 mixture of the *cis*- and *trans*-alkenyl-substituted indenones **14** (85% combined yield). No signs of cyclopropene **12** (<2%) could be detected in the crude reaction mixture by NMR spectroscopy. When $Rh_2(oct)_4/CH_2Cl_2$ was used as the catalyst/



solvent combination, a 2:3 mixture of cyclopropene **12** and indenone **14** was obtained. The use of pentane instead of dichloromethane with $Rh_2(OAc)_4$ resulted in the exclusive formation of cyclopropene **12** (80%). *What is so remarkable about these results is the degree of chemoselectivity that can be achieved by simply changing the solvent from dichloromethane to pentane.*

In an earlier publication, Hoye and Dinsmore[27] reported on the rhodium(II)-catalyzed *double internal/external alkyne insertion reaction* of an acetylenic α-diazo ketone. The initially formed rhodium carbenoid intermediate was suggested to undergo *internal insertion* into the tethered alkyne unit followed by a second *external addition* to produce a cyclopropenyl-substituted cyclopentenone derivative **17** (Scheme 4). Migration of the rhodium metal to the remote alkyne carbon *via* a [2 + 2] cycloaddition/cycloreversion path (*i.e.*, **15** → **19**) was discounted on the basis that the distribution of products derived from **15** differed significantly from those obtained from the rhodium carbenoid species **19** generated from the vinylogous diazo ketone precursor **18**. Instead, the intermediacy of zwitterion **16** was proposed.

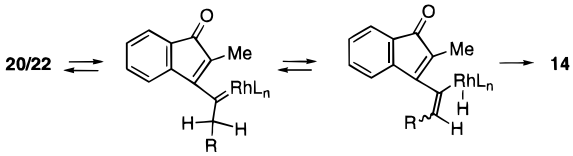
Our results dealing with the *double internal/internal alkyne insertion* of diazo ketone **10** indicate that the reaction mechanism is markedly dependent on the solvent employed. A reasonable explanation to account for the formation of indenone **14** involves stepwise cyclization of the initially formed carbenoid in accord with the Hoye−Dinsmore proposal[27] to give **20** (Scheme 5). A 1,2-hydrogen shift to form **21** is followed by collapse to **14** and regeneration of the rhodium catalyst. The intermediates involved in the formation of **14** are dipolar, which would explain why the generation of **14** is strongly inhibited in nonpolar solvents. Thus, when pentane is used as the solvent, metal migration occurs *via* the metallocyclobutene intermediates **22** and **23** so as to avoid charge buildup.[32]

Having observed the successful intermolecular alkyne insertion reaction, we next turned our attention to the *double internal/external reaction* of the related acetylenic α-diazo ketone **24** with 1-hexyne. Interestingly, stirring this mixture in the presence of 2 mol % of $Rh_2(OAc)_4$ at

(30) Wiberg, K. B.; Artis, D. R.; Bonneville, G. *J. Am. Chem. Soc.* **1991**, *113*, 7969.

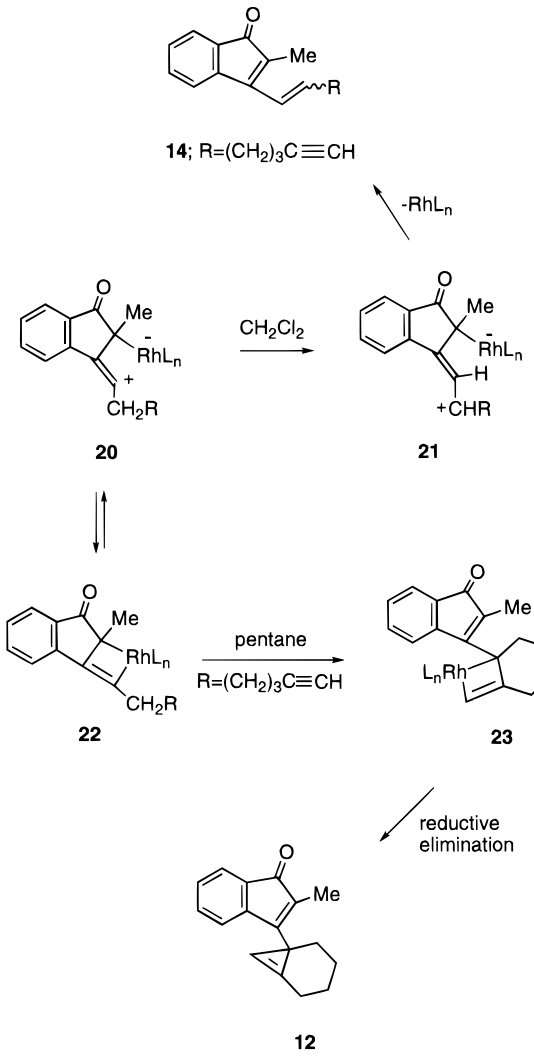
(31) Billups, W. E.; Lee, G. A.; Arney, B. E.; Whitmire, K. H. *J. Am. Chem. Soc.* **1991**, *113*, 7980.

(32) One of the reviewers has suggested an alternate mechanism for the conversion of **20**/**22** into **14** which involves rearrangement of a cyclized alkyl carbenoid (*i.e.*, **A**) to a vinyl-Rh-H intermediate **B** followed by

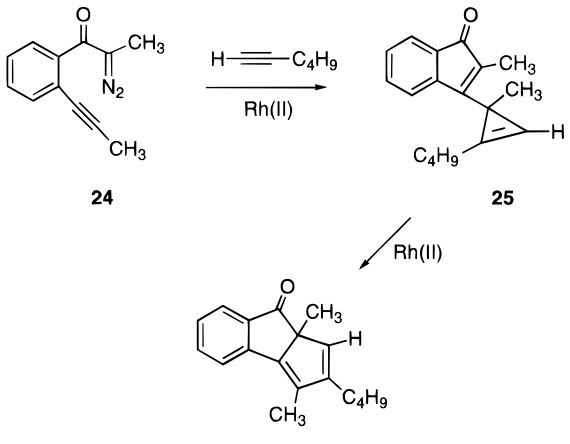


reductive elimination. However, this proposal does not account for why the change in solvent type causes the difference in reaction pathway. For other examples of product control of a rhodium-catalyzed process being influenced by solvent, see: Davies, H. M. L.; Saikali, E.; Clark, T. J.; Chee, E. H. *Tetrahedron Lett.* **1990**, *31*, 6299. Davies, H. M. L.; Saikali, E.; Young, W. B. *J. Org. Chem.* **1991**, *56*, 5696. Davies, H. M. L.; Clark, T. J.; Kimmer, G. F. *J. Org. Chem.* **1991**, *56*, 6440. Davies, H. M. L.; Hu, B.; Saikali, E.; Bruzinski, P. R. *J. Org. Chem.* **1994**, *59*, 4535.

Scheme 5

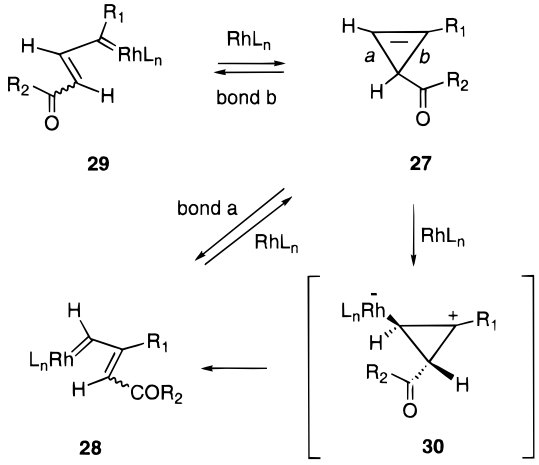


25 °C for 1 h afforded the rearranged cyclopentadiene derivative **26** in 81% yield. Control experiments established that the initial product formed was indenone **25** which is the result of the vinyl carbenoid adding across the acetylenic π-bond of 1-hexyne. Indeed, when the reaction was carried out for only 10 min at 25 °C, indenone **25** could be isolated in 85% yield. Further reaction of **25** with $Rh_2(OAc)_4$ (1 h, 25 °C) induced a subsequent rearrangement producing **26** in 92% yield.



Ring opening of cyclopropene derivatives by rhodium(II) carboxylates has been a subject of some interest[33−35] since this reaction is often highly regioselective as evidenced, for example, by the conversion of **25** to **26**. In general, the Rh(II)-catalyzed ring opening of an unsymmetrically substituted cyclopropene such as **27** may lead to two regioisomeric rhodium carbene complexes, each of which can exist as an *E*/*Z* set of stereoisomers. In all cases studied to date, the major products are always derived from cleavage of the less substituted cyclopropene bond (*i.e.*, bond a). The Doyle−Müller proposal[34] nicely accounts for these observations by invoking a preferential electrophilic attack of the bulky Rh(II) catalyst *anti* to the ketone moiety, producing the more substituted cyclopropyl cation **30** (Scheme 6). Disrotatory ring opening of **30** leads to the carbene complex **28**. Rapid equilibration among all the stereo- and regioisomeric vinyl carbenoids was also suggested to be a factor in determining the regioselectivity of bond cleavage.[34]

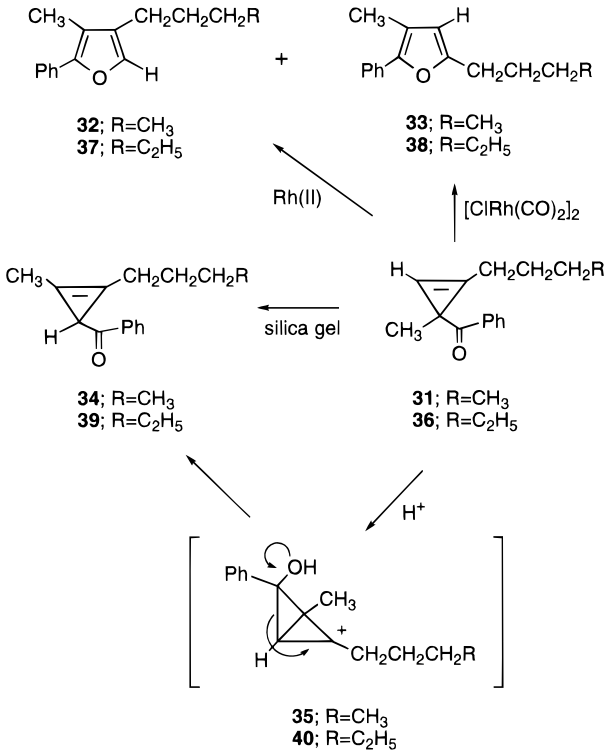
Scheme 6



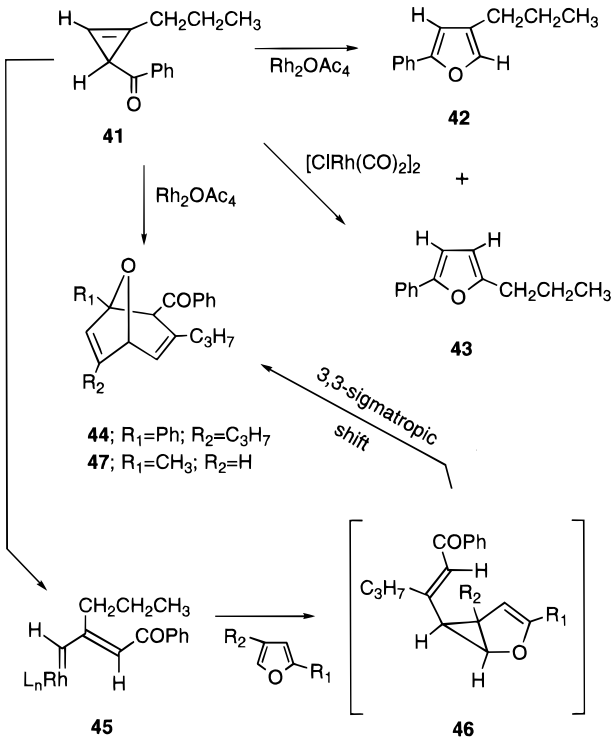
In a study related to the *double internal/external reaction* of α-diazo ketone **24** with terminal alkynes, we have found that treatment of 2-diazo-1-phenyl-1-propanone with 1-hexyne and Rh_2OAc_4 in benzene at 80 °C afforded a 26:1 mixture of furans **32** and **33** in 81% overall yield. The structural assignments rest on the chemical shift of the furanyl proton in the NMR spectra (see Experimental Section). By carrying out the reaction at 25 °C for only 15 min, it was possible to isolate the putative cyclopropene **31** in 75% yield. It is interesting to note that silica gel chromatography of **31** resulted in quantitative isomerization to cyclopropene **34**, a transformation which presumably proceeds *via* the intermediacy of the bicyclo[1.1.0]butane cation **35** (Scheme 7). Further treatment of **31** with Rh_2OAc_4 afforded furans **32** and **33** in the same ratio as encountered previously using diazo-1-phenyl-1-propanone (**30b**). The regiochemical outcome is perfectly compatible with the earlier Doyle−Müller findings.[34] Most interestingly, replacement of Rh_2OAc_4 with a rhodium(I) catalyst (*i.e.*, $[ClRh(CO)_2]_2$) resulted in a pronounced alteration in the ratio of furans produced. Thus, a solution of **31** in CH_2Cl_2 with 2 mol % of $[ClRh(CO)_2]_2$ reacted very cleanly at 25 °C to give exclusively furan **33** (86%) which corresponds to the minor product (3%) in the Rh(II)-catalyzed reaction. No signs of furan **32** (<2%) could be detected in the crude reaction mixture by NMR spectroscopy. An analogous set of results was also obtained using 1-heptyne and

(33) Davies, H. M. L.; Romines, K. R. *Tetrahedron* **1988**, *44*, 3343.
(34) Müller, P.; Pautex, N.; Doyle, M. P.; Bagheri, V. *Helv. Chim. Acta* **1990**, *73*, 1233. Müller, P.; Gränicher *Helv. Chim. Acta* **1993**, *76*, 521. Müller, P.; Gränicher *Helv. Chim. Acta* **1995**, *78*, 129.
(35) Bishop, K. C. *Chem. Rev.* **1976**, *76*, 461.

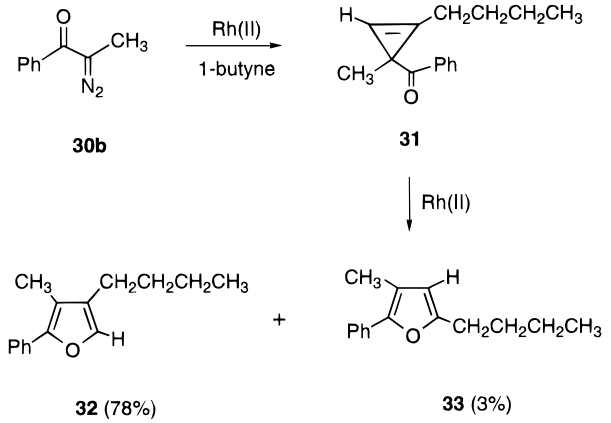
Scheme 7



Scheme 8



2-diazo-1-phenyl-1-propanone (**30b**). When Rh_2OAc was



used as the catalyst, a 22:1 mixture of furans **37** and **38** was obtained (89% overall). In contrast, the reaction of diazo ketone **30b** with 1-heptyne using $[ClRh(CO)_2]_2$ as the catalyst only produced furan **38** in 79% isolated yield. A similar finding was encountered when cyclopropene **36** was treated with catalytic quantities of $[ClRh(CO)_2]_2$, which also led to the exclusive formation of furan **38**.

When the methyl substituent of the keto cyclopropene was replaced with a hydrogen (*i.e.*, **41**, Scheme 8), a dramatic change in the course of the reaction was observed. Thus, treatment of **41** with 2 mol % of Rh_2OAc_4 in benzene at 80 °C gave furans **42** and **43** (3:1 mixture) in only 6% yield. The major product isolated (52%) corresponded to oxabicyclo[3.2.1]octadiene **44**, whose formation is easily rationalized by proposing a subsequent intermolecular addition of the expected vinyl carbenoid **45** onto the π-bond of furan **42** followed by a 3,3-sigmatropic rearrangement.[36] Supporting this hypothesis, the reaction of **41** with 1 equiv of 2-methylfuran produced the related oxabicyclic **47** in good yield. It is obvious that the presence of a hydrogen atom at the 3-position of the cyclopropene ring has dramatically affected the course of the reaction. The isolation of **44** from cyclopropene **41** can be attributed to the preferential generation of the (*E*)-vinyl carbenoid **45**, whose formation is undoubtedly related to steric factors. The *Z*-isomer is destabilized by the steric interaction of the acetate ligands of the catalyst with the large benzoyl group. The carbenoid center of **45** cannot easily cyclize onto the oxygen atom of the ketone and, therefore, either reverts back to starting material or reacts with furan **42** to give oxabicyclic **44** in high yield. More than likely, the formation of furan **42** proceeds by equilibration of the *Z* → *E* vinyl carbenoid, in analogy to the equilibration observed in related thermal and photochemical cyclopropene−vinyl carbene reactions.[37−40] Oxabicyclic ring formation was not observed with the corresponding methyl-substituted cyclopropene **31**, probably as much more of the *Z* vinyl carbenoid is formed and cyclization to the furan occurs readily from this stereoisomer. It should be noted that the *rhodium dicarbonyl chloride dimer promoted opening of **41** was extremely specific producing only furan **43** in 86% yield*. No trace of either **42** or **44** could be detected in the crude reaction mixture by NMR spectroscopy.

The rearrangement of cyclopropenes using transition metals as mediators has been extensively studied as a method for generating transition metal vinyl carbene complexes.[41−43] Despite the synthetic utility of this reaction, a complete understanding of the mechanism of the rearrangement remains ambiguous. The ring opening of cyclopropenes may be envisioned as proceeding through a stepwise sequence of cyclopropene → metal η^2-

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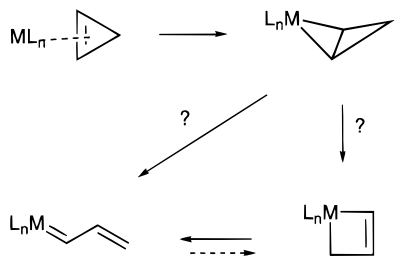
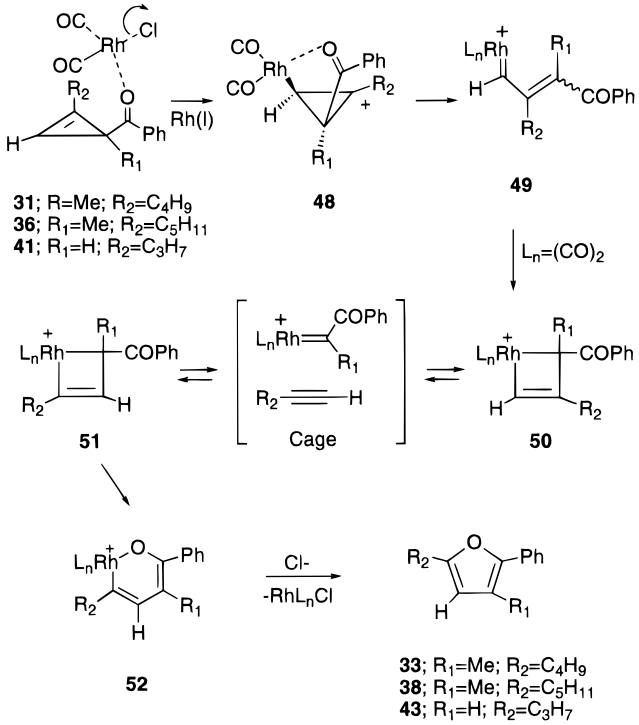
Scheme 9



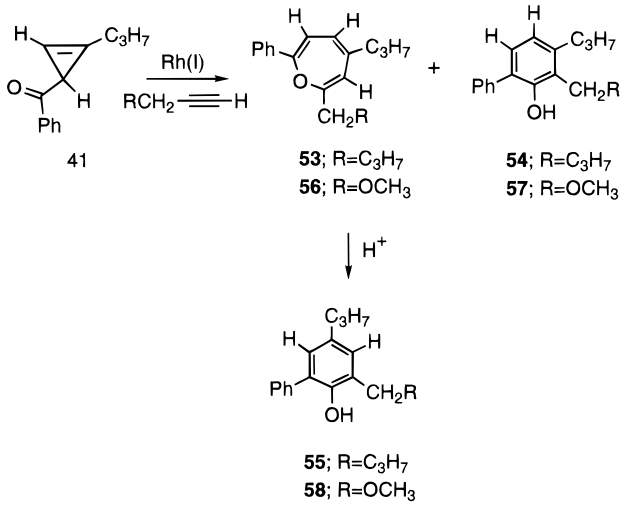
Scheme 10



cyclopropane → metallacyclobutene → metal vinyl carbene (Scheme 9). The reaction might also proceed *via* a direct π-bond insertion of the transition metal to afford the metallocyclobutene.[44] Although the intermediate metal η^2-cyclopropane,[44–46] metal vinyl carbene,[47,48] and metallacyclobutene complexes[49,50] have been independently synthesized, there have been few examples of the metal η^2-cyclopropane → metallacyclobutene conversion.[50] It is also possible that the vinyl carbene complex and the metallocyclobutene are in equilibrium with each other.

Our mechanistic rationale to account for the Rh(I)-catalyzed transformation of cyclopropenes **36** and **41** is shown in Scheme 10. Electrophilic attack of $[ClRh(CO)_2]_2$ on the less substituted carbon of the cyclopropene π-bond affords the tertiary cyclopropyl carbocation **48**. Ring opening followed by a rapid electrocyclization reaction produces the metallocyclobutene **50**. The formation of a metallocyclobutene from the metal-mediated rearrangement of cyclopropenes has good precedence in the literature.[49] Equilibration of **50** with the thermodynamically more stable 1,3-disubstituted isomer **51** proceeds *via* a cycloreversion−cycloaddition pathway.[51] Rhodium migration from carbon to oxygen followed by reductive elimination produces the observed furan. This divergent reactivity may be accounted for by the fact that the formal increase in oxidation state (*i.e.*, Rh(I) → Rh(III)) which accompanies the conversion of **49** → **50** is a much more facile process than the comparable Rh(II) → Rh(IV) formal oxidation. A closely related mechanism was suggested by Liebeskind and Cho[52] in their studies of the Rh(I)-catalyzed carbonylation reaction of cyclopropenyl-substituted ketones to α-pyrones. At the present time, however, other possibilities including a regioselective π-bond oxidative-addition process cannot be unequivocally eliminated. For example, another explanation is that Rh(I) activates the carbon−carbon double bond for nucleophilic attack by the carbonyl oxygen. In this sequence, π-coordination by Rh(I) makes the double bond susceptible to nucleophilic attack by the carbonyl group that sets in motion the electron rearrangement that results in the observed products. The π-activation mechanism is consistent with the known ability of Rh(I) to cause rearrangements of vinylcyclopropanes.[53,54]

Having established the regioselectivity of bond cleavage of unsymmetrical cyclopropenes using $[ClRh(CO)_2]_2$ as a catalyst, we next turned our attention to the application of this reaction to our alkyne−carbenoid metathesis method.[26] Stirring a sample of cyclopropene **41** with 1-hexyne in CH_2Cl_2 in the presence of 10 mol % of $[ClRh(CO)_2]_2$ afforded oxepin **53** (62%) as well as phenol **54** (8%). A related set of reactions occurred with methyl propargyl ether producing oxepin **56** (54%) and phenol **57** (7%). Treatment of oxepin **53** (or **56**) with HCl at 40 °C induced a near-quantitative rearrangement to the isomeric phenol **55** (or **58**).



These novel reactions are believed to follow the pathway outlined in Scheme 11. Electrophilic attack of $[ClRh(CO)_2]_2$ on the cyclopropene π-bond followed by ring opening eventually gives the rhodium carbene complex **59**. This carbenoid undergoes a subsequent [2 + 2] cycloaddition reaction with the terminal alkyne in a manner analogous to that encountered with its Fischer carbene counterpart.[7] Two cycloaddition products are

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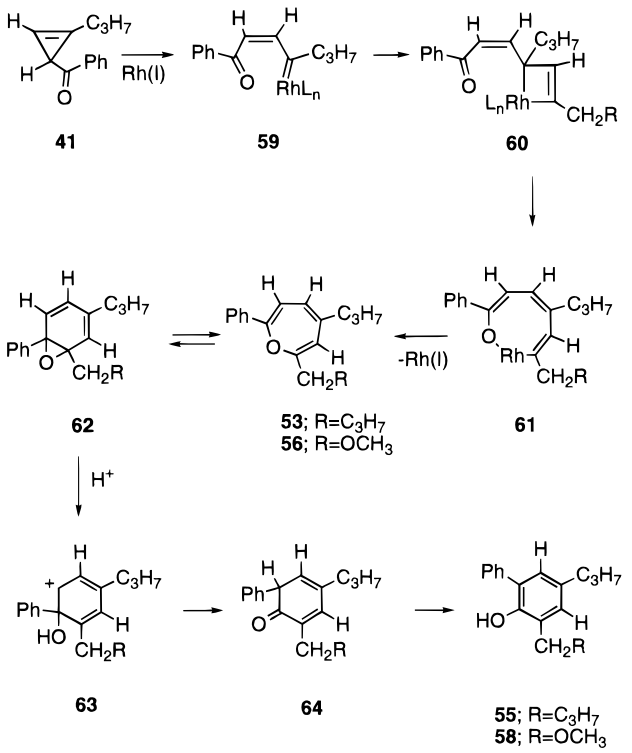
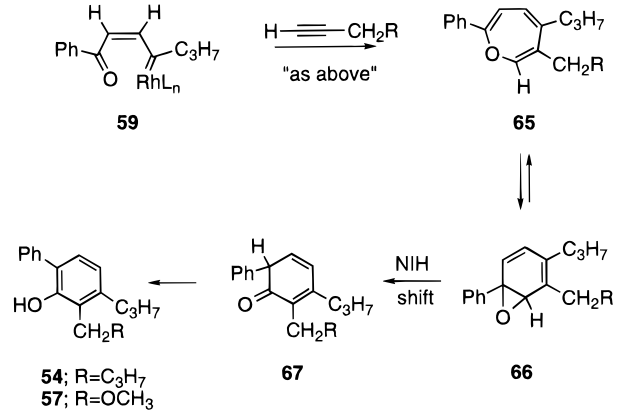
Scheme 11



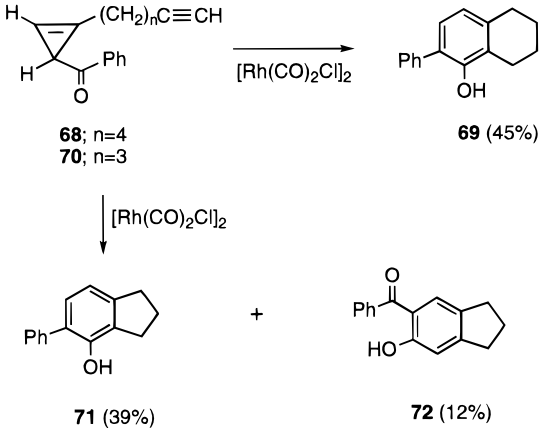
Scheme 12



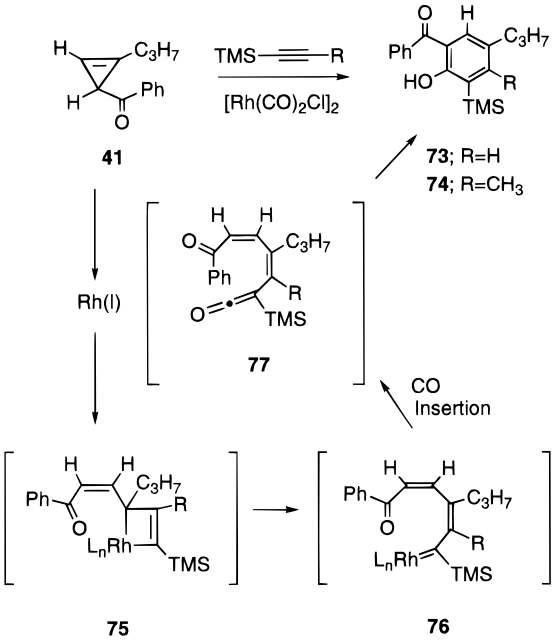
possible. The formation of **60** is favored due to a minimization of the steric interactions between the alkyl group on the carbenoid center and the substituent on the alkyne carbon. The resulting rhodacycle **60** rearranges to **61** either by a direct 1,5-sigmatropic shift or *via* a sequence involving a retro [2 + 2] ring opening followed by an 8π-electrocyclization. The transient species **61** then undergoes reductive elimination of rhodium to produce the observed oxepin **53** (or **56**). Oxepin **53** (or **56**) is in ready equilibrium with arene oxide **62**, and this transient undergoes a 1,2-phenyl shift upon treatment with acid to produce the rearranged phenol **55** (or **58**) in excellent yield.

A related sequence of reactions nicely rationalizes the formation of the minor phenol (**54** and/or **57**) (Scheme 12). Presumably a nonisolable oxepin (*i.e.*, **65**) is formed to a minor extent from the alternate 2 + 2 cycloaddition path of **59** with the terminal alkyne. Equilibration of oxepin **65** with arene oxide **66** followed by a NIH proton shift[55] eventually gives the minor phenol **54** (or **57**). Apparently, the presence of substituents on the 2- and 7-positions of oxepins **53** and **56** enhance their stability, thereby allowing for their isolation and characterization.[56]

Encouraged by the bimolecular trapping results, we decided to investigate the intramolecular annulation reaction of cyclopropene **68** with the Rh(I) catalyst. The annulated phenol **69** was isolated in 45% yield and is presumably formed by a mechanism related to that described in Scheme 11. Quite unexpectedly, treatment of cyclopropene **70** with the $[ClRh(CO)_2]_2$ catalyst not only afforded the expected phenol **71** but also produced the benzoyl phenol **72** (12%) which corresponds to an insertion of carbon monoxide (*vide infra*).



A similar CO insertion reaction was also encountered in a study of the Rh(I)-catalyzed reaction of cyclopropene **41** with trimethylsilyl-substituted alkynes. Introduction of the silyl group on the alkyne causes a significant change in the character of the reaction. Thus, when cyclopropene **41** was treated with (trimethylsilyl)acetylene in the presence of $[ClRh(CO)_2]_2$, none of the expected phenol product was observed. Instead, a low yield of phenol **73** was isolated. Carrying out the reaction under a CO atmosphere, however, afforded phenol **73** in 47% yield. A related reaction also occurred using (trimethylsilyl)-1-propyne (*i.e.*, **74**). We suspect that the reaction proceeds *via* rhodacycle **75**, which ring opens to give **76**. This transient species prefers to undergo CO insertion, and this is followed by 6π-electrocyclization and tautomerization to produce **73** (or **74**).[57] The dramatic difference which results from changing the alkyne substituent to a silyl group is not totally understood. The



steric bulk of the trimethylsilyl group present in **76** may prevent transient **76** from achieving the proper geometry necessary for cyclization to the 8-membered rhodacycle. Alternatively, the ability of a silicon atom to stabilize the ketene backbone of **77** may promote the insertion reaction.[58] It should be noted that the CO insertion reaction encountered here is significantly different from that reported by Liebeskind and Cho which provided α-pyrones.[52]

In summary, we have demonstrated that the chemoselectivity in the Rh(II)-catalyzed reaction of acetylenic α-diazo ketones can be markedly influenced by the solvent used. These substrates are also useful synthetic intermediates in that they are readily accessible, are reasonably robust, and produce vinyl carbenoids that are capable of further synthetic transformation such as alkyne insertion to produce substituted phenols. This approach to phenols nicely complements the more traditional benzannulation reaction of Fischer carbene complexes.

Experimental Section

Melting points are uncorrected. Mass spectra were determined at an ionizing voltage of 70 eV. Unless otherwise noted, all reactions were performed in flame-dried glassware under an atmosphere of dry nitrogen. Solutions were evaporated under reduced pressure with a rotary evaporator, and the residue was chromatographed on a silica gel column using an ethyl acetate−hexane mixture as the eluent unless specified otherwise.

Reaction of *o*-(1,7-Octadiynyl)-α-diazoacetophenone (4) with Rhodium(II) Octanoate. To a degassed solution containing 6.0 g (23 mmol) of methyl 2-iodobenzoate and 6.1 mL (46 mmol) of 1,7-octadiyne in 100 mL of anhydrous triethylamine was added 65 mg of *trans*-bis(triphenylphosphine)palladium(II) chloride and 100 mg of cuprous iodide. The reaction mixture was stirred at 25 °C for 12 h, and the resulting slurry was filtered through a pad of Celite. Removal of the solvent under reduced pressure followed by silica gel chromatography afforded 3.0 g (55%) of methyl 2-(1,7-octadiynyl)benzoate: IR (neat) 2232, 1733, and 1252 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.73−1.78 (m, 4H), 1.96 (t, 1H, J = 3.0 Hz), 2.24−2.29 (m, 2H), 2.49−2.54 (m, 2H), 3.92 (s, 3H), 7.31 (t, 1H, J = 7.5 Hz), 7.42 (t, 1H, J = 7.5 Hz), 7.51 (d, 1H, J = 7.0 Hz), and 7.88 (d, 1H, J = 7.0 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 17.8, 19.1, 27.4, 27.4, 51.9, 68.5, 79.4, 84.0, 95.0, 124.1, 127.1, 130.0, 131.3, 131.7, 134.0, and 166.7.

To a stirred solution containing 1.1 g (8.3 mmol) of potassium trimethylsilanolate in 100 mL of anhydrous ether was added 1.0 g (4.2 mmol) of the above benzoate. The reaction mixture was heated at reflux for 2 h under N_2 and cooled to 0 °C, then 0.64 mL (8.3 mmol) of methyl chloroformate was added, and the resulting mixture was stirred for 2 h at 25 °C. The mixture was filtered, and the filtrate was partially concentrated under reduced pressure. To this solution was added 50 mmol of an ethereal diazomethane solution at 0 °C. The resulting solution was allowed to stir at 25 °C for 16 h, and the excess diazomethane and ether were removed by evaporation in a vented hood. The residue was chromatographed on silica gel to give 0.64 g (62%) of of *o*-(1,7-octadiynyl)-α-diazoacetophenone (**4**): IR (neat) 2231, 2101, 1617, and 1356 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.68−1.83 (m, 4H), 1.97 (t, 1H, J = 2.9 Hz), 2.27 (dt, 2H, J = 6.4 and 2.9 Hz), 2.52 (t, 2H, J = 6.6 Hz), 6.28 (s, 1H), 7.32−7.45 (m, 3H), and 7.61−7.72 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 17.8, 19.1, 27.2, 27.4, 56.7, 68.7, 79.3, 83.8, 96.4, 121.2, 127.7, 130.7, 133.6, 139.0, and 187.2.

A solution of 120 mg (0.49 mmol) of α-diazo ketone **4** in 60 mL of pentane was treated with 3 mg of rhodium(II) octanoate. The resulting bright yellow solution was stirred at 25 °C for 6 h. Concentration under reduced pressure followed by silica gel chromatography gave 78 mg (74%) of dimer **8**:[30] mp 241−242 °C; IR ($CHCl_3$) 2925, 1702, 1461, 1291, and 766 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.40−2.05 (m, 13H), 2.43−2.58 (m, 5H), 2.60−2.72 (m, 2H), 6.68 (d, 1H, J = 7.6 Hz), 6.95 (d, 1H, J = 7.7 Hz), 7.00 (t, 1H, J = 7.2 Hz), 7.14 (t, 1H, J = 7.4 Hz), 7.28 (t, 1H, J = 7.2 Hz), 7.36 (t, 1H, J = 7.1 Hz), 7.59 (d, 1H, J = 7.6 Hz), and 7.78 (d, 1H, J = 7.6 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 22.0, 22.3, 22.9, 23.0, 24.1, 25.3, 26.4, 28.2, 40.3, 51.9, 61.2, 67.2, 72.4, 78.9, 123.0, 123.3, 123.7, 124.4, 127.2, 127.6, 132.7, 134.5, 134.6, 137.9, 138.6, 138.7, 139.8, 141.9, 142.7, 154.3, 203.4, and 209.2. Anal. Calcd for $C_{32}H_{28}O_2$: C, 86.45; H, 6.35. Found: C, 86.29; H, 6.23.

A solution of 100 mg (0.4 mmol) of α-diazo ketone **4** and 0.54 g (2.0 mmol) of diphenylisobenzofuran in 50 mL of pentane was treated with 3 mg of rhodium(II) octanoate. The resulting bright yellow solution was stirred at 25 °C for 3 h, concentrated under reduced pressure, and chromatographed on silica gel to give 155 mg (78%) of the [4 + 2] adduct **9**[30] as a white solid: mp 220−221 °C; IR ($CHCl_3$) 1706, 1461, and 1302 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 0.68−0.80 (m, 1H), 1.18−1.45 (m, 4H), 1.60−1.78 (m, 2H), 1.85−1.97 (m, 1H), 2.50 (d, 1H, J = 17.5 Hz), 2.63 (d, 1H, J = 17.5 Hz), 6.77−6.90 (m, 3H), 7.14−7.20 (m, 2H), 7.32 (d, 1H, J = 7.6 Hz), 7.39−7.57 (m, 8H), 7.67 (d, 1H, J = 7.7 Hz), 8.01 (d, 2H, J = 7.5 Hz), and 8.11 (s, 1H). Anal. Calcd for $C_{36}H_{28}O_2$: C, 87.77; H, 5.73. Found: C, 87.62; H, 5.78.

Reaction of *o*-(1,7-Octadiynyl)benzoyldiazoethane (10) with Rhodium(II) Octanoate. A procedure similar to that described above was utilized for the preparation of diazo ketone **10**. A solution containing 2.5 g (10 mmol) of methyl 2-(1,7-octadiynyl)benzoate in ether was converted into 1.2 g (43%) of *o*-(1,7-octadiynyl)benzoyldiazoethane (**10**): IR (neat) 2175, 2076, and 1609 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.60−1.74 (m, 4H), 1.96 (t, 1H, J = 3.0 Hz), 2.13 (s, 3H), 2.23−2.27 (m, 2H), 2.43−2.47 (m, 2H), 7.33−7.37 (m, 2H), and 7.40−7.44 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 8.5, 17.7, 18.7, 27.2, 27.3, 65.0, 68.7, 77.8, 83.7, 93.5, 120.8, 126.8, 127.7, 129.6, 132.3, 140.9, and 190.9.

A solution of 160 mg (0.6 mmol) of diazo ketone **10** and 0.33 g (1.2 mmol) of diphenylisobenzofuran in 50 mL of pentane was treated with 5 mg of rhodium(II) octanoate. The resulting yellow solution was stirred at 25 °C for 4 h, the solvent was removed under reduced pressure, and the residue was chromatographed on silica gel to give 240 mg (78%) of the [4 + 2] adduct **13** (1:1 *endo*/*exo* mixture) as a thick oil: IR (neat) 2935, 1702, 1605, and 1457 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ (isomer **13a**) 0.85 (s, 3H), 1.25−1.40 (m, 4H), 1.59−1.66 (m, 2H), 1.80−1.88 (m, 1H), 2.00 (s, 1H), 2.55−2.62 (m, 1H), 6.03 (d, 1H, J = 7.2 Hz), 6.43 (t, 1H, J = 7.4 Hz), 6.80 (t, 1H, J = 7.4 Hz), 7.00−7.20 (m, 7H), 7.34−7.40 (m, 2H), 7.43−7.50 (m, 4H), and 7.60−7.65 (m, 2H); isomer **13b** δ 0.79 (s, 3H), 1.27−1.40 (m, 4H), 1.53−1.68 (m, 2H), 1.82−1.90 (m, 1H), 1.93 (s, 1H), 2.46−2.55 (m, 1H), 6.12 (d, 1H, J = 7.2 Hz), 6.41 (t, 1H, J = 7.2 Hz), 6.81 (t, 1H, J = 7.3 Hz), 6.98−7.02 (m, 1H), 7.08−7.13 (m, 2H), 7.20 (d, 1H, J = 7.0 Hz), 7.30−7.46 (m, 9H), and 7.70 (d, 2H, J = 7.2 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ (mixture) 7.7, 7.9, 21.3, 21.4, 22.6, 23.1, 23.6, 31.5, 32.9, 35.3, 35.6, 40.8, 40.9, 41.4, 41.5, 86.7, 86.9, 89.4, 89.6, 119.2, 119.3, 120.1, 120.2, 120.3, 120.3, 120.5, 120.6, 125.6, 125.8, 126.1, 126.2, 126.8, 127.1, 127.4, 127.4, 127.5, 128.1, 128.2, 128.3, 129.1, 130.8, 131.1, 131.7, 131.7, 136.4, 136.7, 137.4, 137.7, 144.6, 145.5, 147.3, 147.8, 149.3, 149.5, 160.9, 161.0, 198.8, and 199.4; HRMS calcd for $C_{37}H_{30}O_2$ 506.2246, found 506.2229.

A solution containing 80 mg (0.3 mmol) of α-diazo ketone **10** in 5 mL of pentane was treated with 3 mg of rhodium(II) octanoate. The reaction mixture was filtered through a pad of silica gel and was concentrated under reduced pressure to give a yellow oil which was assigned by ^1H-NMR spectroscopy as cyclopropene **12** (80%): ^1H NMR (360 MHz, $CDCl_3$) δ 1.49 (s, 3H), 1.67−1.75 (m, 3H), 2.43−2.53 (m, 4H), 2.70−2.80 (m,

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1H), 6.03 (s, 1H), 7.25 (t, 1H, J = 7.7 Hz), 7.48 (d, 1H, J = 7.7 Hz), 7.61 (t, 1H, J = 7.3 Hz), and 7.76 (d, 1H, J = 7.5 Hz). Cyclopropene **12** rapidly decomposed at ambient temperature.

Reaction of *o*-(1,7-Octadiynyl)benzoyldiazoethane (10) with Rhodium(II) Acetate. A mixture containing 200 mg of α-diazo ketone **10** in 50 mL of CH_2Cl_2 was treated with 5 mg of rhodium(II) acetate at 25 °C. After the solution was stirred for 20 min, the solvent was removed under reduced pressure and the residue was chromatographed on silica gel to give 152 mg (85%) of a 2:1 mixture of *cis*- and *trans*-3-(hept-6-yn-1-enyl)-2-methylinden-1-one (**14a** and **14b**). The *cis* isomer **14a** showed the following spectral properties: IR (neat) 2119, 1706, 1457, and 1304 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.63 (quin, 2H, J = 7.2 Hz), 1.78 (d, 3H, J = 0.9 Hz), 1.86 (t, 1H, J = 2.5 Hz), 2.15−2.20 (m, 4H), 5.94 (td, 1H, J = 11.6 and 7.4 Hz), 6.16 (dd, 1H, J = 11.8 and 1.1 Hz), 6.94 (d, 1H, J = 7.5 Hz), 7.13 (t, 1H, J = 7.5 Hz), 7.28 (t, 1H, J = 7.5 Hz), and 7.38 (d, 1H, J = 7.0 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 9.2, 17.9, 27.9, 29.6, 68.8, 83.6, 119.6, 120.6, 122.0, 127.9, 130.7, 131.4, 133.3, 137.3, 146.1, 152.2, and 198.1; HRMS calcd for $C_{17}H_{16}O$ 236.1201, found 236.1200.

The *trans* isomer **14b** showed the following spectral properties: IR (neat) 2933, 1700, 1638, and 1457 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.78 (quin, 2H J = 7.3 Hz), 1.92 (s, 3H), 2.02 (t, 1H, J = 2.5 Hz), 2.30 (dt, 2H, J = 7.0 and 2.6 Hz), 2.43−2.50 (m, 2H), 6.48−6.63 (m, 2H), 7.15−7.20 (m, 1H), 7.25−7.35 (m, 2H), and 7.43 (d, 1H, J = 7.0 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 8.4, 17.9, 27.7, 33.1, 69.0, 83.7, 120.1, 122.1, 123.0, 127.9, 130.5, 131.8, 132.9, 139.6, 144.7, 150.2, and 197.8; HRMS calcd for $C_{17}H_{16}O$ 236.1201, found 236.1195.

Rhodium(I)-Catalyzed Reaction of 2-Methyl-3-(1-methyl-2-butylcyclopropenyl)inden-1-one (25). A solution containing 100 mg (0.5 mmol) of *o*-(1-propynyl)-2-diazo-1-phenylpropanone (**24**)[26] and 0.8 g of 1-hexyne in 15 mL of CH_2Cl_2 was treated with 5 mg of rhodium(II) acetate. The reaction mixture was stirred at 25 °C for 10 min and concentrated under reduced pressure, and the crude residue was chromatographed on silica gel to give 110 mg (85%) of **25** as a pale yellow oil: IR (neat) 2990, 1711, 1615, 1500, and 1465 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 0.89 (t, 3H, J = 7.5 Hz), 1.36 (m, 2H), 1.39 (s, 3H), 1.58 (m, 2H), 1.81 (s, 3H), 2.50 (t, 2H, J = 7.2 Hz), 7.09 (s, 1H), 7.06−7.20 (m, 2H), and 7.2−7.30 (m, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 7.7, 13.5, 13.6, 22.2, 24.1, 25.3, 27.5, 104.8, 107.8, 119.6, 121.5, 127.4, 130.0, 132.9, 134.3, 144.2, 155.5, and 198.8. Anal. Calcd for $C_{18}H_{20}O$: C, 85.66; H, 7.99. Found: C, 85.51; H, 7.83.

To a solution containing 50 mg (0.2 mmol) of diazo ketone **25** in 15 mL of CH_2Cl_2 was added 3 mg of rhodium(II) acetate. The reaction mixture was stirred at 25 °C for 1 h and concentrated under reduced pressure, and the residue was chromatographed on silica gel to give 46 mg (92%) of 3,8a-dimethyl-8,8a-dihydro-8-oxocyclopent[*a*]indene (**26**): IR (neat) 1710, 1610, and 1375 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 0.91 (t, 3H, J = 7.2 Hz), 1.34 (m, 2H), 1.48 (m, 2H), 1.42 (s, 3H), 2.05 (s, 3H), 2.21 (t, 2H, J = 7.5 Hz), 6.08 (s, 1H), 7.23 (m, 1H), 7.55 (m, 2H), and 7.70 (m, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 12.0, 13.7, 13.8, 22.3, 23.4, 27.9, 30.2, 69.0, 122.6, 124.8, 125.9, 131.7, 134.6, 135.1, 143.4, 144.1, 148.3, 150.3, and 197.2. Anal. Calcd for $C_{18}H_{20}O$: C, 85.66; H, 7.99. Found: C, 85.49; H, 7.91.

Rhodium(II) Acetate Catalyzed Reaction of 3-Benzoyl-1-butyl-3-methylcyclopropene (31). To a solution containing 3.0 g (21 mmol) of benzoyl chloride in 30 mL of dry ether at 0 °C was added an ethereal solution of diazoethane (60 mmol). The mixture was stirred at 0 °C for 2 h, and the excess diazoethane and ether were evaporated in a vented hood. The residue was chromatographed on silica gel to give 2.0 g (60%) of 2-diazo-1-phenylpropanone (**30**): IR (neat) 2931, 2072, 1609, and 1344 cm^{-1}; ^1H NMR ($CDCl_3$, 90 MHz) δ 2.1 (s, 3H), and 7.3−7.5 (m, 5H).

A solution containing 100 mg (0.6 mmol) of diazo ketone **30** and 0.8 g (10 mmol) of 1-hexyne in 15 mL of CH_2Cl_2 was treated with 3 mg of rhodium(II) acetate dimer. After being stirred at 25 °C for 10 min, the mixture was filtered over neutral alumina and concentrated under reduced pressure to give 115 mg (90%) of 3-benzoyl-1-butyl-3-methylcyclopropene (**31**): IR (neat) 2950, 1682, 1510, and 950 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 0.93 (t, 3H, J = 7.5 Hz), 1.26 (m, 2H), 1.51 (m, 2H), 1.45 (s, 3H), 2.42 (t, 2H, J = 7.4 Hz), 6.65 (s, 1H), and 7.34−7.55 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 9.2, 21.1, 22.0, 24.7, 28.7, 33.3, 102.3, 124.2, 127.7, 128.5, 128.6, 130.1, 134.0, 139.1, and 206.8. Anal. Calcd for $C_{15}H_{18}O$: C, 86.06; H, 8.47. Found: C, 86.13; H, 8.33.

A solution containing 100 mg (0.4 mmol) of cyclopropene **31** in 15 mL of CH_2Cl_2 was treated with 3 mg of rhodium(II) acetate dimer. The reaction mixture was heated at reflux for 30 min, cooled to rt, concentrated under reduced pressure, and chromatographed on silica gel to give 90 mg (89%) of a 26:1 mixture of 4-butyl-3-methyl-2-phenylfuran (**32**) and 5-butyl-3-methyl-2-phenylfuran (**33**). Furan **32** exhibited the following spectral properties: IR (neat) 2930, 1599, 1493, 1456, 1065, and 766 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 0.95 (t, 3H, J = 7.3 Hz), 1.42 (sex, 2H, J = 7.3 Hz), 1.50−1.60 (m, 2H), 2.19 (s, 3H), 2.39 (t, 2H, J = 7.3 Hz), 7.20 (s, 1H), 7.26−7.29 (m, 1H), 7.36−7.44 (m, 2H), and 7.58−7.66 (m, 2H); ^{13}C NMR (300 MHz, $CDCl_3$) δ 9.7, 13.9, 22.5, 23.4, 31.5, 116.3, 124.8, 125.4, 126.5, 127.8, 128.4, 132.1, and 137.4. Anal. Calcd for $C_{15}H_{18}O$: C, 86.06; H, 8.47. Found: C, 85.91; H, 8.28.

Furan **33** exhibited the following spectral properties: IR (neat) 2975, 1375, and 940 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 0.94 (t, 3H, J = 7.2 Hz),1.42 (sex, 2H, J = 7.2 Hz), 1.65 (q, 2H, J = 7.5 Hz), 2.24 (s, 3H), 2.63 (t, 2H, J = 7.5 Hz), 5.93 (s, 1H), 7.18 (m, 1H), 7.35 (m, 2H), and 7.65 (m, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 11.8, 13.7, 22.1, 27.6, 30.1, 110.4, 116.8, 124.7, 125.9, 126.0, 128.2,128.6, 132.0, and 154.7. Anal. Calcd for $C_{15}H_{18}O$: C, 86.06; H, 8.47. Found: C, 85.95; H, 8.35.

Cyclopropene **31** cleanly rearranged to 3-benzoyl-2-butyl-1-methylcyclopropene (**34**) upon silica gel chromatography: IR (neat) 1685, 1370, and 1110 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 0.95 (t, 3H, J = 7.5 Hz), 1.52 (m, 4H), 2.08 (s, 3H), 2.40 (t, 2H, J = 7.5 Hz), 3.15 (s, 1H), 7.45 (m, 3H), and 8.05 (m, 2H). Anal. Calcd for $C_{15}H_{18}O$: C, 86.06; H, 8.47. Found: C, 86.17; H, 8.24.

Rhodium(II)-Catalyzed Reaction of 3-Benzoyl-3-methyl-1-pentylcyclopropene (36). A solution containing 100 mg (0.6 mmol) of 2-diazo-1-phenylpropanone (**30**) and 0.9 g (10 mmol) of 1-heptyne in 15 mL of CH_2Cl_2 was treated with 3 mg of rhodium(II) acetate dimer. The reaction mixture was stirred at 25 °C for 10 min, filtered over neutral alumina, and then concentrated under reduced pressure to give 123 mg (91%) of 3-benzoyl-3-methyl-1-pentylcyclopropene (**36**): IR (neat) 2861, 1675, and 1449 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 0.83 (m, 3H), 1.22 (m, 2H), 1.37 (m, 2H), 1.42 (m, 2H), 1.44 (s, 3H), 2.41 (t, 2H, J = 7.5 Hz), 6.63 (s, 1H), 7.34 (m, 3H), and 7.48 (m, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 13.7, 21.1, 22.1, 25.0, 26.4, 31.0, 33.3, 102.9, 124.15, 127.5, 127.7, 128.5, 130.1, 132.9, 139.2, and 207.9. Anal. Calcd for $C_{16}H_{20}O$: C, 84.15; H, 8.83. Found: C, 84.03; H, 8.72.

A solution containing 100 mg (0.4 mmol) of cyclopropene **36** in 15 mL of benzene was treated with 5 mg of rhodium(II) acetate dimer. The reaction mixture was heated at reflux for 30 min and concentrated under reduced pressure, and the residue was chromatographed on silica gel to give 90 mg (89%) of a 22:1 mixture of 3-methyl-4-pentyl-2-phenylfuran (**37**) and 3-methyl-5-pentyl-2-phenylfuran (**38**). Furan **37** exhibited the following spectral properties: IR (neat) 2930, 2861, 1385, and 937 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 0.93 (m, 3H), 1.37 (m, 4H), 1.59 (m, 2H), 2.20 (s, 3H), 2.38 (t, 2H, J = 7.8 Hz), 7.21 (s, 1H), 7.25 (m, 1H), 7.40 (m, 2H), and 7.65 (m, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 9.6, 13.9, 22.4, 23.6 28.9, 31.5, 116.2, 125.3, 126.4, 128.3, 127.7, 132.0, 137.3, and 148.7. Anal. Calcd for $C_{16}H_{20}O$: C, 84.15; H, 8.83. Found: C, 84.11; H, 8.66.

Furan **38** exhibited the following spectral properties: IR (neat) 2930, 1600, 1449, and 1232 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 0.94 (m, 3H), 1.39 (m, 2H), 1.70 (m, 4H), 2.26 (s, 3H), 2.65 (t, 2H, J = 7.5 Hz), 5.98 (s, 1H), 7.20 (m, 2H), 7.45 (m, 2H), and 7.65 (m, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 11.9, 13.9, 22.3, 27.7, 27.9, 31.3, 110.5, 116.9, 124.7, 125.9, 128.3, 132.1, 146.6, and 154.7. Anal. Calcd for $C_{16}H_{20}O$: C, 84.15; H, 8.83. Found: C, 83.95; H, 8.62.

Cylopropene **36** rearranged to 3-benzoyl-1-methyl-2-pentylcyclopropene (**39**) when subjected to silica gel chromatography: IR (neat) 2980, 1680, 1450, and 1225 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 0.89 (m, 3H), 1.25 (m, 2H), 1.40 (m, 2H),

1.46 (m, 2H), 2.10 (s, 3H), 2.45 (t, 2H, J = 7.4 Hz), 3.15 (s, 3H), 7.45−7.50 (m, 3H), and 8.00 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 9.7, 13.7, 20.4, 26.4, 27.8, 31.0, 100.8, 105.6, 127.7, 128.1, 131.9, 138.8, and 204.4. Anal. Calcd for $C_{16}H_{20}O$: C, 84.15; H, 8.83. Found: C, 84.03; H, 8.72.

Rhodium(II)-Catalyzed Reaction of 3-Benzoyl-1-propylcyclopropene (41). To a solution of 2.9 mL (25 mmol) of benzoyl chloride in 25 mL of THF at 0 °C was added an ethereal solution of diazomethane (100 mmol). The resulting mixture was allowed to warm to 25 °C, stirred for an additional 30 min, and worked up by washing with 15 mL of water. Concentration of the solution under reduced pressure left a yellow oil which was chromatographed on silica gel to give 2.8 g (77%) of α-diazoacetophenone as a yellow solid: IR ($CHCl_3$) 2107, 1575, and 1364 cm^{-1}; ^{1}H NMR (90 MHz, $CDCl_3$) δ 5.90 (s, 1H), 7.42−7.54 (m, 3H), and 7.74−7.77 (m, 2H).

To a solution containing 6.8 mL of 1-pentyne and a catalytic amount of rhodium(II) acetate dimer in 10 mL of distilled CH_2Cl_2 was added a solution of 1.0 g of the above diazo ketone in 10 mL of CH_2Cl_2. The resulting solution was stirred at 25 °C for 20 min, concentrated under reduced pressure, and chromatographed on silica gel to give 1.0 g (79%) of cyclopropene **41** as a pale yellow oil: IR (neat) 2964, 1802, 1671, 1598, 1449, and 1225 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.97 (t, 3H, J = 7.5 Hz), 1.58−1.63 (m, 2H), 2.51 (t, 2H, J = 7.5 Hz), 3.20 (s, 1H), 6.33 (s, 1H), 7.26−7.55 (m, 3H), and 8.01−8.04 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.6, 20.2, 24.3, 26.9, 92.9, 114.4, 127.9, 128.2, 132.2, 138.3, and 203.8. Anal. Calcd for $C_{13}H_{14}O$: C, 83.82; H, 7.58. Found: C, 83.67; H, 7.41.

A solution containing 480 mg of cyclopropene **41** in 25 mL of benzene under Ar was treated with 3 mg of rhodium(II) acetate dimer. The mixture was heated at reflux for 48 h, concentrated under reduced pressure, and chromatographed on silica gel to give 249 mg of the bicyclic compound **44** as well as 30 mg of a 3:1 mixture of furans **42** and **43**. 2-Phenyl-4-propylfuran (**42**) exhibited the following spectral properties: ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.96 (t, 3H, J = 7.5 Hz), 1.62 (m, 2H), 2.42 (t, 2H, J = 7.5 Hz), 6.54 (s, 1H), 7.20−7.23 (m, 1H), 7.25 (s, 1H), 7.30−7.36 (m, 2H), and 7.60−7.70 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.8, 23.1, 27.0, 106.6, 123.6, 127.1, 127.3, 131.1, and 138.4. Anal. Calcd for $C_{13}H_{14}O$: C, 83.82; H, 7.58. Found: C, 83.75; H, 7.49.

2-Phenyl-5-propylfuran (**43**) exhibited the following spectral properties: IR (neat) 2935, 1596, 1548, 1488, and 962 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.97 (t, 3H, J = 7.5 Hz), 1.70 (m, 2H), 2.63 (t, 2H, J = 7.5 Hz), 6.03 (d, 1H, J = 3.0 Hz), 6.51 (d, 1H, J = 3.0 Hz), 7.17−7.19 (m, 1H), 7.29−7.34 (m, 2H), and 7.60−7.62 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.7, 21.4, 30.2, 105.6, 106.9, 123.3, 126.6, 128.5, 131.2, 152.1, and 156.2. Anal. Calcd for $C_{13}H_{14}O$: C, 83.82; H, 7.58. Found: C, 83.73; H, 7.56.

4-Benzoyl-3,7-di-*n*-propyl-5-phenyl-8-oxabicyclo[3.2.1]octa-2,6-diene (**44**) exhibited the following spectral properties: IR (neat) 2960, 2933, 1671, 1449, and 1202 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.79 (t, 3H, J = 7.3 Hz), 1.01 (t, 3H, J = 7.3 Hz), 1.29−1.40 (m, 2H), 1.57−1.68 (m, 2H), 1.70−1.87 (m, 2H), 2.29 (t, 2H, J = 7.3 Hz), 4.63 (s, 1H), 4.77 (d, 1H, J = 4.4 Hz), 4.90 (s, 1H), 6.18−6.24 (m, 1H), 7.14−7.22 (m, 5H), and 7.27−7.46 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.6, 13.9, 20.2, 20.8, 30.0, 36.8, 56.5, 79.9, 89.5, 120.4, 125.2, 125.2, 127.5, 128.1, 128.2, 128.3, 132.6, 138.5, 138.9, 141.8, 155.2, and 199.2. Anal. Calcd for $C_{26}H_{28}O_2$: C, 83.82; H, 7.58. Found: C, 83.94; H, 7.62.

Rhodium(II)-Catalyzed Reaction of 3-Benzoyl-1-propylcyclopropene (41) with 2-Methylfuran. A solution containing 130 mg (0.7 mmol) of cyclopropene **33** and 0.3 g (5.0 mmol) of 2-methylfuran in 15 mL of benzene was treated with 5 mg of rhodium(II) acetate dimer. The reaction mixture was heated at reflux for 24 h, concentrated under reduced pressure, and chromatographed on silica gel to give a 4:1 mixture of furans **42** and **43** in 28% yield together with 68 mg (37%) of 4-benzoyl-5-methyl-3-propyl-8-oxabicyclo[3.2.1]octa-2,6-diene (**47**): IR (neat) 2931, 1673, 1596, and 1450 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.77 (t, 3H, J = 7.3 Hz), 1.44 (m, 2H), 1.47 (s, 3H), 1.70−1.82 (m, 2H), 4.52 (s, 1H), 4.79 (m, 1H), 5.63 (d, 1H, J = 5.8 Hz), 6.07 (m, 1H), 7.40−7.52 (m, 2H), 7.55−7.60 (m, 1H), and 7.75−7.80 (m, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 13.6, 20.3, 24.6, 36.7, 54.4, 77.7, 84.8, 125.6, 128.2, 128.5, 128.7, 130.4, 133.3, 137.7, 138.5, and 198.8; HRMS calcd for $C_{18}H_{20}O_2$ 268.1463, found 268.1462.

Rhodium(I)-Catalyzed Reaction of 3-Benzoyl-1-propylcyclopropene (41) with 1-Hexyne. A solution containing 150 mg (0.81 mmol) of **41** and 1.40 mL (12 mmol) of 1-hexyne in 5 mL of CH_2Cl_2 under Ar was treated with 22 mg (0.06 mmol) of $[ClRh(CO)_2]_2$. The resulting mixture was stirred at 25 °C for 30 min and concentrated under reduced pressure, and the residue was chromatographed on silica gel to give 135 mg (62%) of 2-butyl-7-phenyl-4-propyloxepin (**53**) along with 18 mg (8%) of 2-butyl-6-phenyl-3-propylphenol (**54**). Oxepin **53** exhibited the following spectral properties: IR (neat) 2873, 1654, 1447, 1142, and 760 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.87 (t, 3H, J = 7.3 Hz), 0.94 (t, 3H, J = 7.3 Hz), 1.34 (sex, 2H, J = 7.5 Hz), 1.50−1.61 (m, 4H), 2.13−2.20 (m, 4H), 5.45 (s, 1H), 6.05 (d, 1H, J = 6.1 Hz), 6.27 (d, 1H, J = 6.1 Hz), 7.25−7.37 (m, 3H), and 7.65 (d, 2H, J = 7.4 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.8, 13.8, 22.1, 22.7, 28.9, 34.4, 40.1, 111.7, 114.4, 123.7, 125.3, 127.9, 128.2, 135.3, 143.0, 147.5, and 154.9. Anal. Calcd for $C_{19}H_{24}O$: C, 85.02; H, 9.02. Found: C, 84.96; H, 8.84.

Phenol **54** exhibited the following spectral properties: ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.96 (t, 3H, J = 7.6 Hz), 1.03 (t, 3H, J = 7.6 Hz), 1.43−1.70 (m, 6H), 2.60−2.73 (m, 4H), 5.23 (s, 1H), 6.80 (d, 1H, J = 7.8 Hz), 7.00 (d, 1H, J = 7.8 Hz), and 7.34−7.50 (m, 5H). Anal. Calcd for $C_{19}H_{24}O$: C, 85.02; H, 9.02. Found: C, 84.87; H, 8.96.

To a solution containing 100 mg (0.37 mmol) of oxepin **53** in 10 mL of CH_2Cl_2 was added 1 drop of 1 N HCl. The resulting solution was heated at reflux for 2 h, concentrated under reduced pressure, and chromatographed on silica gel to give 95 mg (95%) of 2-butyl-6-phenyl-4-propylphenol (**55**): IR (neat) 2873, 1470, 1217, and 704 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.95 (t, 6H, J = 7.3 Hz), 1.42 (sex, 2H, J = 7.8 Hz), 1.57−1.69 (m, 4H), 2.53 (t, 2H, J = 7.4 Hz), 2.65 (t, 2H, J = 7.6 Hz), 5.08 (s, 1 H), 6.89 (d, 1H, J = 2.1 Hz), 6.95 (d, 1H, J = 2.0 Hz), and 7.35−7.53 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.9, 14.0, 22.8, 24.8, 30.1, 32.1, 37.3, 127.5, 127.7, 129.0, 129.2, 129.2, 129.7, 134.3, 137.7, and 148.1. Anal. Calcd for $C_{19}H_{24}O$: C, 85.02; H, 9.02. Found: C, 84.96; H, 8.84.

Rhodium(I)-Catalyzed Reaction of 3-Benzoyl-1-propylcyclopropene (41) with Methyl Propargyl Ether. Using a procedure analagous to that described above, 150 mg (0.81 mmol) of cyclopropene **41** was converted into 138 mg (54%) of 2-(methoxymethyl)-7-phenyl-4-propyloxepin (**56**) together with 14 mg (7%) of 2-(methoxymethyl)-6-phenyl-3-propylphenol (**57**). Oxepin **56** exhibited the following spectral properties: IR (neat) 2931, 1661, 1493, 1447, 1192, and 1117 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.94 (t, 3H, J = 7.3 Hz), 1.55 (sex, 2H, J = 7.4 Hz), 2.22 (t, 2H, J = 7.3 Hz), 3.36 (s, 3H), 3.91 (s, 2H), 5.74 (s, 1H), 6.13 (d, 1H, J = 6.3 Hz), 6.31 (d, 1H, J = 6.2 Hz), 7.27−7.40 (m, 2H), and 7.66−7.68 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.7, 22.6, 39.8, 57.9, 71.9, 111.2, 116.2, 125.0, 125.2, 128.1, 128.3, 134.8, 142.3, 147.6, and 148.4. Anal. Calcd for $C_{17}H_{20}O_2$: C, 79.64; H, 7.87. Found: C, 79.51; H, 7.75.

Phenol **57** exhibited the following spectral properties: ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.00 (t, 3H, J = 7.5 Hz), 1.50−1.62 (m, 2H), 2.60 (t, 2H, J = 7.5 Hz), 3.39 (s, 3H), 3.94 (s, 2H), 6.80 (d, 1H, J = 7.4 Hz), 7.20 (d, 1H, J = 7.4 Hz), and 7.35−7.70 (m, 5H). Anal. Calcd for $C_{17}H_{20}O_2$: C, 79.64; H, 7.87. Found: C, 79.51; H, 7.73.

A sample containing 100 mg of **56** was converted into 93 mg (93%) of **58** in a manner similar to that described above. Phenol **58** exhibited the following spectral properties: IR (neat) 2960, 1478, 1233, and 1088 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.94 (t, 3H, J = 7.5 Hz), 1.62 (sex, 2H, J = 7.5 Hz), 2.53 (t, 2H, J = 7.5 Hz), 3.45 (s, 3H), 4.67 (s, 2H), 6.89 (d, 1H, J = 1.5 Hz), 7.09 (d, 1H, J = 1.7 Hz), 7.25 (s, 1H), 7.30−7.36 (m, 1H), 7.40−7.46 (m, 2H), and 7.55−7.59 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.8, 24.7, 37.1, 58.1, 73.7, 122.4, 127.0, 127.7, 128.2, 128.8, 129.3, 130.4, 138.1, and 150.6. Anal. Calcd for $C_{17}H_{20}O_2$: C, 79.64; H, 7.87. Found: C, 79.46; H, 7.92.

Rhodium(I)-Catalyzed Reaction of 3-Benzoyl-1-(5-hexynyl)cyclopropene (68). A sample of 200 mg (1.4 mmol) of α-diazoacetophenone was converted in the normal manner

into 250 mg (81%) of cyclopropene **68** by treating it with 1,7-octadiyne: IR (neat) 2939, 2117, 1667, 1632, and 1598 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.50−1.75 (m, 4H), 1.90 (t, 1H, J = 2.4 Hz), 2.15 (dt, 2H, J = 6.9 and 2.6 Hz), 2.52 (t, 2H, J = 7.1 Hz), 3.17 (s, 1H), 6.31 (s, 1H), 7.38−7.49 (m, 3H), and 7.96−7.99 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 17.9, 24.2, 24.4, 25.7, 27.6, 68.5, 83.8, 93.3, 114.0, 127.9, 128.5, 132.3, 138.2, and 203.6. Anal. Calcd for $C_{16}H_{16}O$: C, 85.67; H, 7.19. Found: C, 85.55; H, 7.04.

A solution containing 250 mg (1.1 mmol) of **68** in 20 mL of CH_2Cl_2 under Ar was treated with 108 mg (0.28 mmol) of tetracarbonyldichlorodirhodium(I). The resulting solution was stirred at 25 °C for 2 h and concentrated under reduced pressure, and the residue was chromatographed on silica gel to give 110 mg (45%) of 2-phenyl-5,6,7,8-tetrahydronaphthalene (**69**): IR (neat) 2931, 1619, 1580, 1453, and 971 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.75−1.90 (m, 4H), 2.72 (t, 2H, J = 6.1 Hz), 2.80 (t, 2H, J = 6.0 Hz), 5.26 (s, 1H), 6.75 (d, 1H, J = 7.9 Hz), 7.00 (d, 1H, J = 7.9 Hz), and 7.35−7.50 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 22.8, 22.8, 23.2, 29.6, 121.1, 124.1, 124.6, 124.6, 127.6, 129.1, 129.3, 137.5, 138.5, and 150.0; HRMS calcd for $C_{16}H_{16}O$ 224.1201, found 224.1199.

Rhodium(I)-Catalyzed Reaction of 3-Benzoyl-1-(5-pentynyl)cyclopropene (70). A sample of 0.50 g (3.4 mmol) of α-diazoacetophenone was converted in the normal manner into 0.54 g (75%) of cyclopropene **70** by treatment with 1,6-heptadiyne: IR (neat) 2119, 1669, 1449, and 1227 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.83 (quin, 2H, J = 6.8 Hz), 1.97 (t, 1H, J = 2.9 Hz), 2.29 (tt, 2H, J = 6.8 and 2.9 Hz), 2.66 (t, 2H, J = 6.5 Hz), 3.23 (s, 1H), 6.38 (s, 1H), 7.47−7.56 (m, 3H), and 8.02−8.04 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 17.8, 24.0, 24.3, 25.7, 69.0, 83.3, 93.9, 113.6, 128.0, 128.4, 132.4, 138.2, and 203.7. Anal. Calcd for $C_{15}H_{14}O$: C, 85.67; H, 6.72. Found: C, 85.49; H, 6.63.

A 180 mg (0.86 mmol) sample of **70** was converted into 70 mg (39%) of phenol **71** and 29 mg (12%) of phenol **72** in a manner similar to that described above. Phenol **71** exhibited the following spectral properties: IR (neat) 2952, 1634, 1603, and 1341 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 2.15 (quin, 2H, J = 7.5 Hz), 2.93 (t, 2H, J = 7.4 Hz), 2.96 (t, 2H, J = 7.4 Hz), 5.17 (s, 1H), 6.90 (d, 1H, J = 7.5 Hz), 7.06 (d, 1H, J = 7.6 Hz), 7.34−7.40 (m, 1H), and 7.45−7.50 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 25.3, 29.2, 33.2, 116.7, 127.5, 128.6, 129.1, 129.2, 130.1, 137.5, and 146.5; HRMS calcd for $C_{15}H_{14}O$ 210.1045, found 210.1052.

Benzoyl phenol **72** exhibited the following spectral properties: IR (neat) 2954, 1636, 1605, 1374, and 1245 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 2.07 (quin, 2H, J = 7.5 Hz), 2.79 (t, 2H, J = 6.0 Hz), 2.92 (t, 2H, J = 7.5 Hz), 6.93 (s, 1H), 7.37 (s, 1H), 7.47−7.61 (m, 3H), 7.64−7.69 (m, 2H), and 12.20 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 25.6, 31.7, 33.6, 113.8, 117.3, 128.2, 128.9, 131.5, 134.5, 138.4, 154.7, 162.8, and 201.4; HRMS calcd for $C_{16}H_{14}O_2$ 238.0994, found 238.0985.

Rhodium(I)-Catalyzed Reaction of 3-Benzoyl-1-*n*-propylcyclopropene (41) with Silyl-Substituted Alkynes. A solution containing 100 mg (0.54 mmol) of cyclopropene **41** and 1.2 mL (8.1 mmol) of (trimethylsilyl)acetylene in 5 mL of CH_2Cl_2 under a CO atmosphere was treated with 30 mg (0.08 mmol) of $[ClRh(CO)_2]_2$. The reaction mixture was stirred at 25 °C for 30 min, the solvent and excess alkyne were removed under reduced pressure, and the residue was chromatographed on silica gel to give 79 mg (47%) of 2-benzoyl-4-*n*-propyl-6-(trimethylsilyl)phenol (**73**): IR (neat) 2958, 1617, 1576, and 1420 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 0.35 (s, 9H), 0.91 (t, 3H, J = 7.2 Hz), 1.56 (sex, 2H, J = 7.2 Hz), 2.47 (t, 2H, J = 7.0 Hz), 7.36 (d, 1H, J = 2.0 Hz), 7.43 (d, 1H, J = 2.0 Hz), 7.48−7.54 (m, 2H), 7.57−7.62 (m, 1H), and 7.68 (2H, J = 7.0 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ −1.1, 13.7, 24.8, 37.1, 117.5, 128.2, 128.8, 129.1, 131.6, 132.1, 133.9, 138.4, 142.6, 166.1, and 201.9; HRMS calcd for $C_{19}H_{24}SiO_2$ 312.1546, found 312.1546.

A related reaction was carried out using 230 mg (1.2 mmol) of cyclopropene **41** and 2.7 mL (18.5 mmol) of 1-(trimethylsilyl)-1-propyne which afforded 99 mg (27%) of 2-benzoyl-5-methyl-4-propyl-6-(trimethylsilyl)phenol (**74**): IR (neat) 2960, 1611, 1447, and 1248 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 0.41 (s, 9H), 0.92 (t, 3H, J = 7.5 Hz), 1.49 (sex, 2H, J = 7.5 Hz), 2.39 (s, 3H), 2.45 (t, 2H, J = 7.5 Hz), 7.28 (s, 1H), 7.47−7.64 (m, 5H), and 12.48 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 2.6, 14.0, 20.6, 23.5, 35.5, 115.7, 128.2, 129.0, 131.4, 134.8, 138.6, 152.5, 166.9, and 201.4; HRMS calcd for $C_{19}H_{26}SiO$ (M − CO) 298.1753, found 298.1753.

Acknowledgment. We gratefully acknowledge the National Science Foundation (CHE-9509496) for generous support of this work. We also thank David J. Austin for determining the X-ray crystal structures of compounds **8** and **9**. Use of the high-field NMR spectrometer used in these studies was made possible through equipment grants from the NIH and NSF.

Supporting Information Available: ^1H-NMR and ^{13}C-NMR spectra for all compounds with high-resolution mass spectra (9 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

JO962271R