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(Alkynyl)dicobalt Hexacarbonyl-Mediated Radical Cyclizations

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This article is dedicated to Myron Rosenblum and (the late) Roland Pettit, my mentors and pioneers in the use of organometallics in organic synthesis

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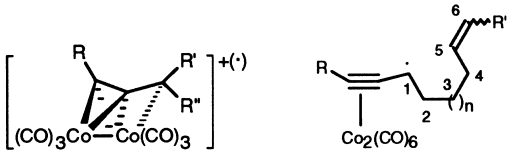
Abstract—Radicals flanked by the –(alkynyl)$Co_2(CO)_6$ unit add intramolecularly to carbon–carbon double bonds with unusual stereo- and regioselectivity. Cationic complex **13a** (R=CO_2Me) reacts with Zn to produce exclusively the *trans*-5-*exo* product **14a**. Labile propargyl bromide complexes **16a–d**, prepared from the alcohols **7a–d**, undergo cyclization with Et_3B/O_2/Ph_2SiH_2 or upon irradiation. Under the latter conditions atom transfer products (**17a–c**, **18c**,**d**) were obtained exclusively, whose regio- and stereochemistry were dependant on the olefinic acceptor. Thus, irradiation of the ester *trans*-**16a** or the phenyl derivative **16b** (*E*/*Z* mixture) gives the *trans*-cyclopentyl derivatives **17a** and **17b**; the bromide **16c** (R=Me) affords a mixture of the *trans*-cyclopentyl compound **17c** and a comparable amount of the cyclohexyl derivative **18c**; and the parent bromide **16d** (R=H) is converted exclusively to the cyclohexyl derivative **18d**. Heptenyl derivative **20d** (R=H) cyclizes exclusively to the 7-*endo* cycloheptyl derivative **21d**. Limited mechanistic experiments suggest the operation of a radical chain, atom transfer mechanism with a product-like transition state. A tandem cyclization/allylation reaction has been demonstrated in the reaction of acyclic bromide **16a** with CpFe$(CO)_2(\eta^1$-allyl). © 2000 Elsevier Science Ltd. All rights reserved.

Introduction

The modified reactivity of species coordinated to transition metals is a central paradigm of organometallic chemistry and this concept provides the basis for the myriad of stoichiometric and catalytic applications of organometallic chemistry in organic synthesis. Virtually all the examples of this concept have involved the coordination of *even electron* organic species, both neutral and charged. Indeed, the ability of transition metal fragments to dramatically alter the reactivity of species such as carbenes[1] and carbocations[2] has been widely explored fundamentally and applied synthetically.

In sharp contrast there is little known of the potential for transition metal coordination to modify the stability and reactivity of *odd electron* species, e.g. carbon-centered free radicals. There have been scattered reports of the reductive coupling of cationic metal-pi complexes, e.g. ferrocenylmethyl$^+$,[3a–c] (benzyl)$Cr(CO)_3^+$,[3c,d] (propargyl)-$Mo_2Cp_2(CO)_4^+$,[3e] and (pentadienyl)$Fe(CO)_3^+$,[3f–h] which are presumed to proceed via the intermediacy of the corresponding radicals. More recently, (benzyl)$Cr(CO)_3$ radicals have been implicated as intermediates in radical additions to double bonds flanked by the (arene)$Cr(CO)_3$ unit[4] and the structure/stability of these radicals have been examined theoretically.[5]

We recently initiated a program to systematically investigate the chemistry of carbon-centered organotransition metal radicals. In particular we seek to determine whether sterically and electronically influential organometallic units can induce extraordinary radical reactivity. Our initial efforts demonstrated that the readily accessible and synthetically useful propargyl cation complexes **1**[2b,c] undergo efficient reductive coupling, presumably via the corresponding radicals **2**, to form 1,5-diyne complexes with extraordinary diastereoselectivities when compared to dimerizations of typical organic radicals.[6,7]



1 (cation)
2 (radical)

3 (n=1)
4 (n=2)

The discovery of efficient, radical-based carbon–carbon bond-forming reactions has provided a powerful new array of tools for organic synthesis. Especially valuable are intramolecular radical additions to carbon–carbon double bonds as typified by the 5-hexenyl radical cyclization (Scheme 1).[8] A distinctive and useful feature of this reaction is the kinetically-controlled, highly regioselective formation of five-membered rings. The levels of stereoselectivity for such reactions, however, are less useful, e.g. 1-substituted 5-hexenyl radicals undergo cyclization generally with only a modest preference for *cis*-1,2-disubstituted cyclopentanes.[9]

Keywords: radical cyclization; (propargyl)$Co_2(CO_6)$; regio- and stereoselectivity.

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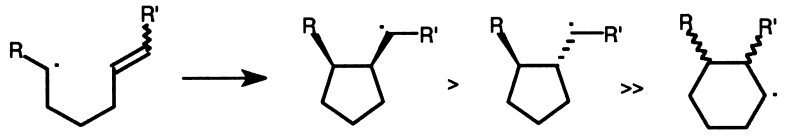


Scheme 1.

In order to further assess the reactivity and synthetic potential of (propargyl)$Co_2(CO)_6$ radicals (**2**) we have sought to engage these radicals in addition reactions to unsaturated carbon–carbon bonds. We envisioned that the regio- and stereoselectivity features of such cyclizations could provide insight into the reactivity, stability, and electronic character, e.g. nucleophilic or electrophilic, of the intermediate metal-complexed radicals. In our preliminary investigation we found that cyclizations of 1-(alkynyl)$Co_2(CO)_6$-5-hexenyl radicals (**3**) not only proceed with exceptionally high *trans*-1,2-stereoselectivity in the 5-*exo* mode, but also exhibit novel regioselectivity that is remarkably sensitive to the 6-position substituent.[10] In this report we provide a complete account of the initial study as well as investigations of the corresponding heptenyl radical cyclization, some mechanistic probes of these cyclization reactions, and an initial effort to expand their synthetic utility by trapping the intermediate cyclized radicals.

Results and Discussion

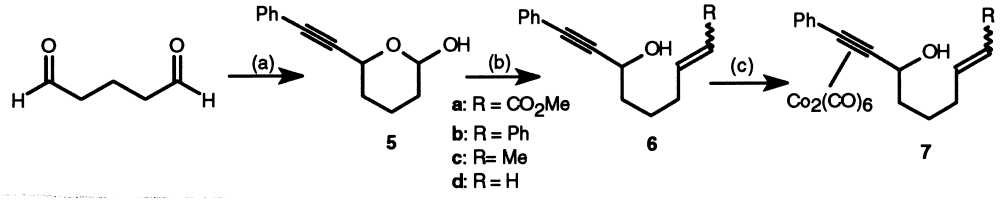
Synthesis of cyclization precursors

Substrates for the cyclization studies were prepared using conventional reactions as outlined in Schemes 2 and 3. The octen-yn-ols **6a–d** were efficiently produced by phenylacetylide addition to glutaraldehyde followed by Wittig reactions of the intermediate acetylenic hemiacetal **5**. The corresponding cobalt complexes **7a–d** were obtained in high yield upon reaction with $Co_2(CO)_8$. Compounds **7a–c** were produced as *E*/*Z* isomeric mixtures; the stereoisomers of **7a** could be separated chromatographically.

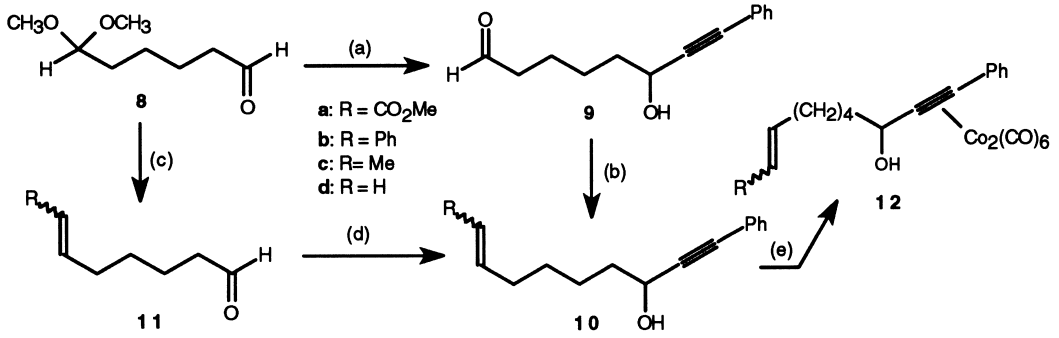
Preparation of the corresponding nonen-yn-ols **10a–d** and their cobalt complexes **12a–d** was accomplished either: (a) by acetylide addition to the monoacetal of adipaldehyde (**7**) followed by acetal hydrolysis and Wittig olefination or (b) by initial Wittig reaction of **8** and subsequent hydrolysis and acetylide addition (Scheme 3). Moderate yields of **10a–d** and **12a–d** were obtained and characterized spectroscopically.

Reductive cyclizations via the cationic complexes 13

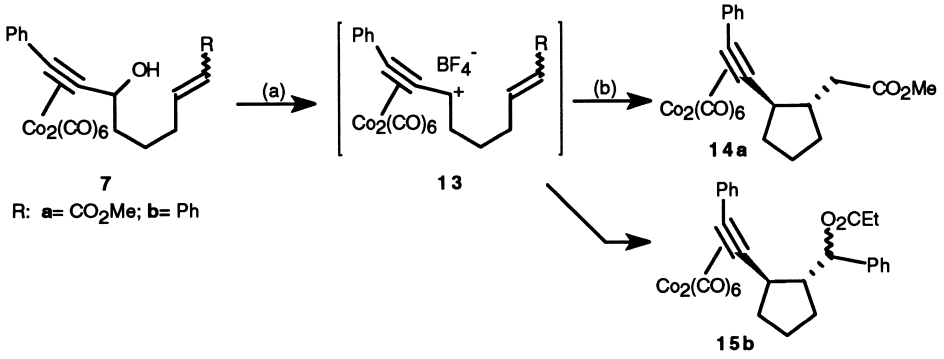
Initially, we investigated the generation of the radicals **3** by one electron reduction of the cobalt-stabilized cations **13** (Scheme 4). This unconventional approach to radical generation was initially established in our studies of reductive dimerization of the remarkably stable (and isolable) propargyl cation complexes **2**.[2b,c] Thus, treatment of alcohol complex **7a** with excess $HBF_4{\cdot}Et_2O$ at $-30°C$ in propionic anhydride followed by ether addition precipitated salt **13a** which was treated with Zn powder in CH_2Cl_2 to produce a single cyclized product **14a** (38%). NMR analysis of **14a** indicated the presence of only one isomer, established as the *trans* cyclopentane by X-ray diffraction. The yield of **14a** was primarily limited by the appreciable solubility of intermediate salt **13a** in ether, resulting in substantial losses during its isolation.



Scheme 2. (a) PhC≡CLi; (b) Ph_3PCHR; (c) $Co_2(CO)_8$.



Scheme 3. (a) i. PhC≡CLi, ii. HCl/H_2O; (b) Ph_3PCHR; (c) i. Ph_3PCHR, ii. HCl/H_2O; (d) PhC≡CLi; (e) $Co_2(CO)_8$.



Scheme 4. (a) HBF_4, $(EtCO)_2O$; (b) Zn/CH_2Cl_2, R=CO_2Me.

The successful reductive cyclization of the ester **7a** is significant in three respects: (1) the cationic complex (**13a**) itself does not cyclize under these conditions; (2) the 5-*exo* cyclization product (**14a**) is produced regioselectively; and (3) its stereochemistry is exclusively *trans*. Together, these features are consistent with a reaction occurring via a radical (i.e. **3a**) which cyclizes with typical regioselectivity but atypical stereoselectivity. That the cyclization of **13a** occurs only upon reaction with zinc supports a pathway via the radical rather than the cation and is noteworthy because the propargyl *cation* complexes are known to add to electron rich carbon–carbon double bonds.[11] Moreover, if cyclization of **13a** were to occur via the cation, the 6-*exo* product should be preferred, avoiding development of positive charge α to the electrophilic ester group. The exclusive *trans* stereoselectivity observed in the cyclization stands in contrast to that usually observed for 1-substituted-5-hexenyl radical cyclizations, which is moderately in favor of the *cis* product.[8] While bulky (e.g. *t*-butyl) groups at C-1 can tip the balance modestly towards the *trans* product,[9] the exclusive *trans* stereoselectivity found with **13a** is extraordinary.

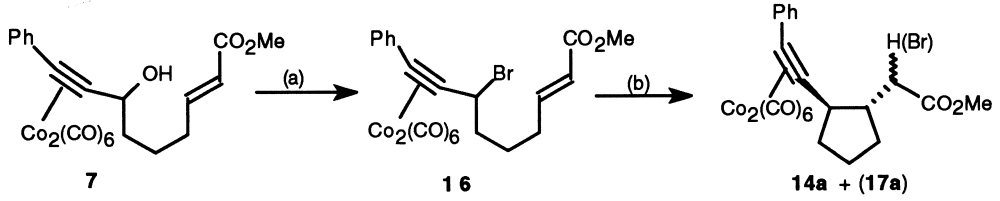
When the phenyl-substituted alcohol complex **7b** was analogously protonated, addition of pentane:ether produced a homogeneous solution (rather than precipitating the intermediate salt **13b**). Chromatography afforded the epimeric *trans* cyclopentyl propionates **15b** in good yield (Scheme 4). This product probably arises from *cationic* cyclization of the intermediate complex **13b**, facilitated by the more nucleophilic styryl double bond. The observed regio- and stereoselectivity is consistent with a late transition state favoring development of positive charge adjacent to the stabilizing phenyl group.

Atom-transfer cyclizations

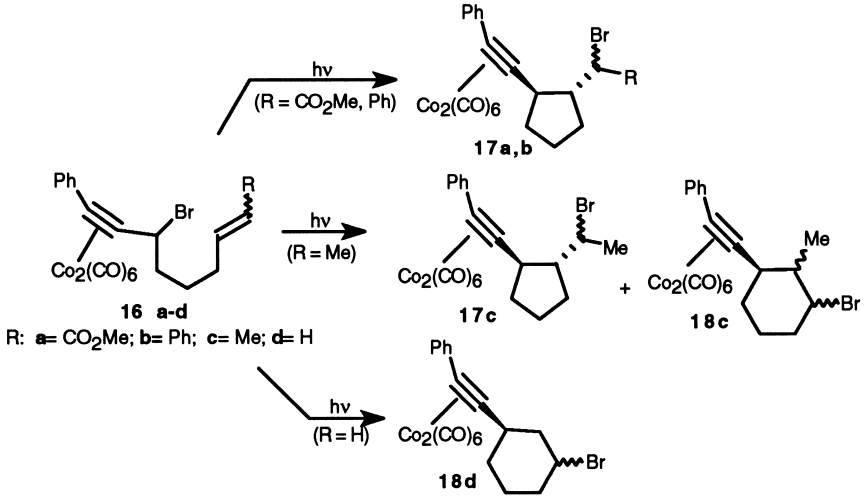
Since generation of the organometallic radicals **2** from the cationic complexes **1** generally proved inefficient, we considered more conventional radical precursors which would be more generally useful and functional group tolerant. Among the most obvious choices, (propargyl halide)$Co_2(CO)_6$, were little known species. Although a few examples of poorly characterized propargyl chloride complexes have been reported,[12a] reactions of cobalt carbonyl with propargyl halides were known to produce complex mixtures, including coupling products.[12b] Green and coworkers have recently generated metastable complexes of propargyl chlorides bearing γ-electron withdrawing groups.[13] We found a convenient route to the desired propargyl bromide derivatives **16** by treatment of the alcohol complexes **7a–d** (CH_2Cl_2, 0°C) with $2Br_2{\cdot}(Ph_2PCH_2CH_2PPh_2)$[14] (Scheme 5). The alcohol to bromide conversion was typically accompanied by substantial shifts of the ^1H and ^{13}C methine NMR absorptions. Generally these labile complexes decompose during chromatography or upon standing at room temperature so they were best stored below 0°C or used soon after preparation.

Because of the thermal instability of the bromide complexes **16**, our initial cyclization attempts utilized room temperature Et_3B/O_2 initiation,[15] together with Bu_3SnH or Ph_2SiH_2 as prospective H-atom donors. When a benzene solution of **16a** (R=CO_2Me) was treated with Et_3B and Ph_2SiH_2 at 20°C, a 1.0:1.8 separable mixture (70% yield from **7a**) of *trans* **14a** and a second compound was obtained. The latter proved to be the cyclized bromo derivative *trans*-**17a** (epimeric at C-1′) based on NMR and MS analysis. This unexpected result was confirmed by X-ray crystallographic determination of one epimer of **17a**. The bromo compound **17a** is the apparent result of a bromine atom-transfer cyclization.[16]

Subsequently, it was serendipitously discovered that neat samples (or benzene solutions) *of the propargyl bromide*



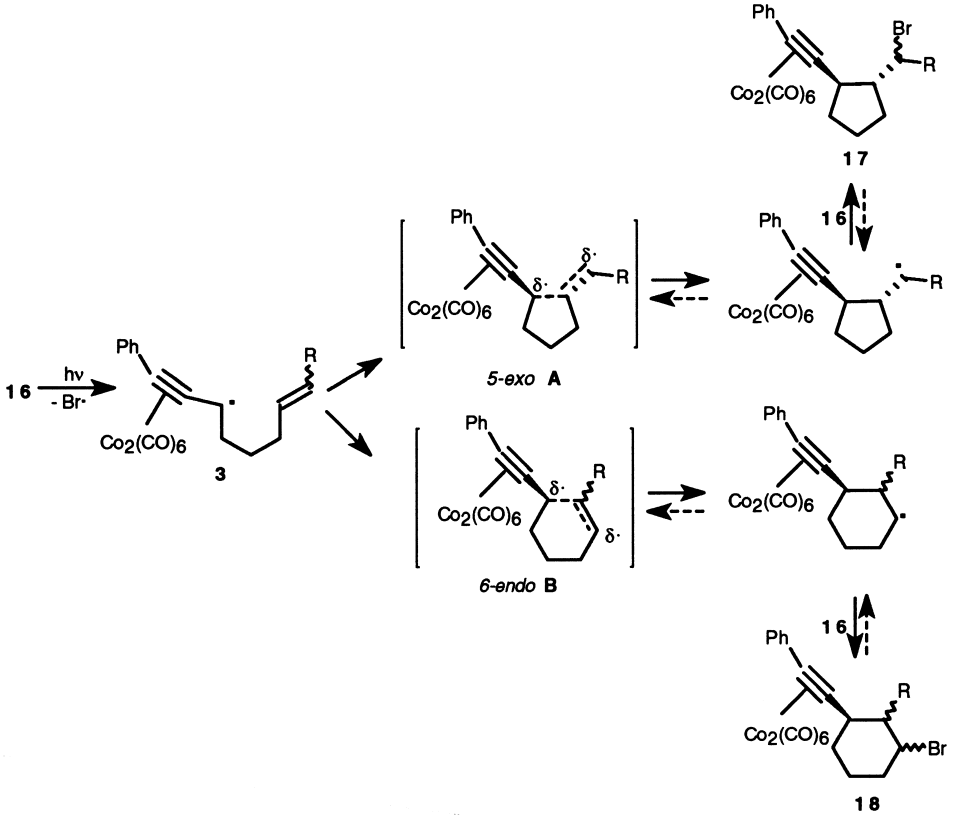
Scheme 5. (a) $2Br_2{\cdot}Ph_2CH_2CH_2PPh_2$; (b) $Et_3B/O_2/Ph_2SiH_2$.



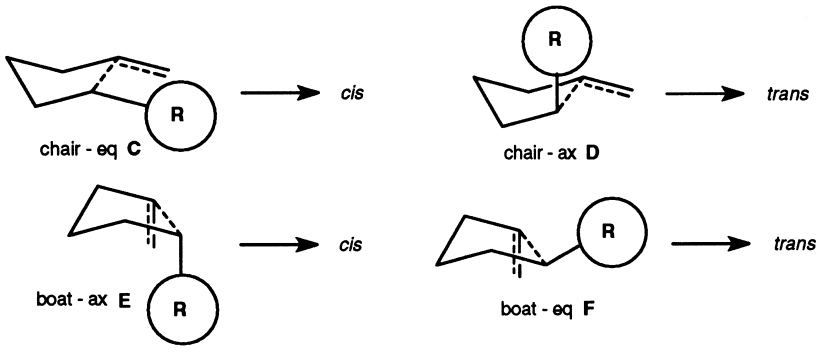
Scheme 6.

complexes **16**, *when left in direct sunlight or briefly irradiated with a 300 W sunlamp*, *were converted exclusively to atom transfer products* (Scheme 6) in good yields. Thus, irradiation of the bromoester *trans*-**16a** caused its smooth conversion to *trans*-**17a** (56% from **7a**) as the only characterizable product (epimeric mixture). The phenyl derivative **16b** (*E*/*Z* mixture) was likewise converted to *trans*-**17b** (76% from **7b**; Scheme 6). The trans stereochemical assignment for **17b** was supported by NMR comparison with the prior cyclization products and also was confirmed cystallographically.

The regiochemical course of these reactions was found to depend dramatically on the C-6 substituent. Thus, the bromide **16c** (R=Me) afforded a mixture of isomeric products (60% from **7c**), comprised of the *trans* cyclopentyl compound **16c** (2:1 stereoisomeric at C-6) and a comparable amount of the cyclohexyl derivative **18c** (isomeric mixture), the product of 6-*endo* cyclization. The latter assignment was supported by 1-D proton decoupling experiments and by X-ray diffraction analysis of the major isomer, *cis*, *cis* **18c**. The 6-*endo-trig* pathway became the exclusive one when the parent complexed bromide **16d** was irradiated;



Scheme 7.



Scheme 8.

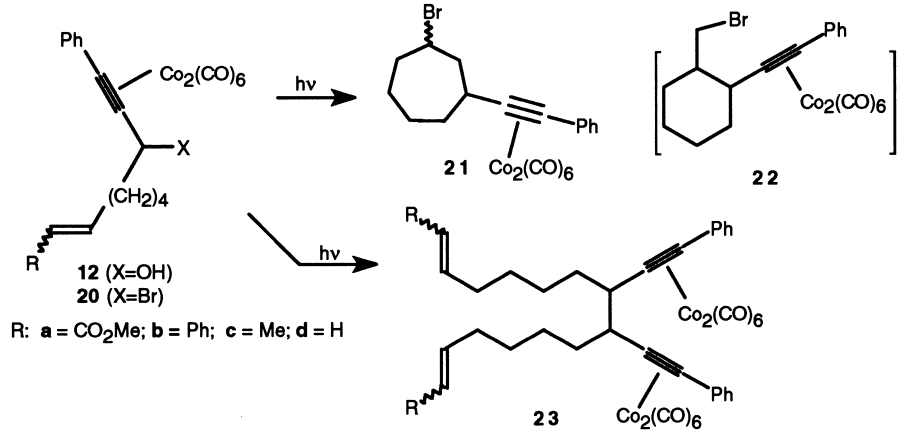
the cyclohexyl derivative **18d** was the sole regioisomer (73% from **7d**), isolated as a 2:1 mixture of stereoisomers. These assignments were based on NMR (DEPT, COSY) techniques and also confirmed by X-ray diffraction of one of the isomers.

The facile cyclizations of bromo complexes **16a–d** should be contrasted with the unreactivity of the free bromo ene-yne $PhC{\equiv}CCHBrCH_2CH_2CH_2CH{=}CH_2$ (**19d**) under similar conditions. Thus, **19d** was recovered unchanged after irradiating a neat sample or a benzene solution containing 10 mol% of Bu_6Sn_2 for 3 h.

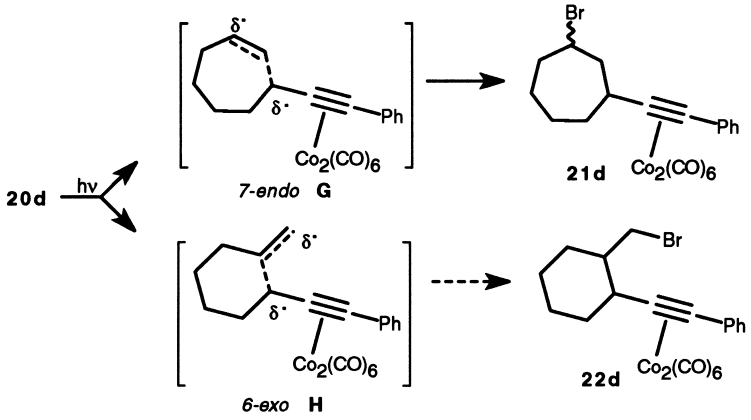
The high reactivity of the propargyl bromide complexes **16** presumably reflects a labilization of the C–Br bond by the adjacent (alkynyl)dicobalt hexacarbonyl unit which, in turn, suggests the generation of a relatively stable radical. Cyclizations of the complexes **16** are arguably the most facile of the atom transfer reactions reported to date,[17,18] which typically involve organic iodides with one or two activating groups as substrates; organic bromides generally display low reactivity. Aside from their extraordinary facility, the most unusual feature of their reactivity is the regiochemical dependence (5-*exo* vs. 6-*endo*) of cyclization on the olefinic substituent. The effect most likely is electronic in nature. The substrates possessing strongly radical stabilizing groups, **16a**,**b** (R=CO_2Me, Ph) react exclusively in the 5-*exo* mode; that bearing a weakly stabilizing Me group (**16c**) gives a mixture of 5-*exo* and 6-*endo* products; and the parent complex **16d** (R=H), lacking a radical stabilizing group, affords the 6-*endo* product exclusively. Substrates which previously have exhibited appreciable 6-*endo* selectivity either have been 5-substituted[18] (sterically blocking the 5-*exo* mode), conformationally biased[18] (e.g. α-halo carbonyl compounds), or those which produce radicals which cyclize reversibly, i.e. are under thermodynamic control.[19]

The distinctive regio- and stereoselectivity of the reactions of propargylic bromide complexes **16** can be explained in terms of an atom transfer mechanism having a late, product-like, transition state for cyclization (Scheme 7). This process is presumably initiated by cobalt-assisted photoinduced homolysis of the C–Br bond to generate radical **3** which is stabilized by metal coordination. As such, the transition states for the cyclization of **3** (**A** vs. **B**) would involve significant C–C bond making (and breaking) as well as the development of radical character at the original olefinic carbons. With a strongly radical-stabilizing group at C-6 (e.g. Ph or CO_2R) the 5-*exo* transition state **A** is favored because it allows delocalization of the developing radical at C-6. The 6-*endo* transition state **B** may be preferred for R=H since it develops secondary radical character at C-5 (vs. primary C-6 radical character as in **A**). For R=Me, the partitioning (**A** vs. **B**) is between two incipient (and similarly energetic) secondary radicals, producing significant amounts of both regioisomers.

Steric interactions between the bulky (alkyne)$Co_2(CO)_6$ unit and the –CHR group would be amplified in this later



Scheme 9.



Scheme 10.

transition state, which could account for the high *trans* stereoselectivity observed in the formation of the 5-*exo* products. The typically modest *cis* stereoselectivity of most 1-substituted hexenyl radical cyclizations is thought to reflect the composition of alternative early chair- and boat-like transition states with a long C1–C5-developing bond, the chair-equatorial conformation (**C**) being the most important (Scheme 8). The predominance of the *trans*-product for substrates bearing a bulky substituent at C1 (e.g. for R=^{t}Bu, *trans*/*cis*=85:15[20]), has been noted but is not quantitatively accounted for in the framework of the Houk[21] or Beckwith[22] force field calculational methods. Of the four likely transition states (**C**–**F**), the exclusive *trans* stereoselectivity found in the cyclizations of the 1-(alkynyl)$Co_2(CO)_6$-5-hexenyl substrates may be accommodated by having the very sterically demanding organocobalt group occupy a pseudoequatorial position in the 'boat-equatorial' transition state (**F**).

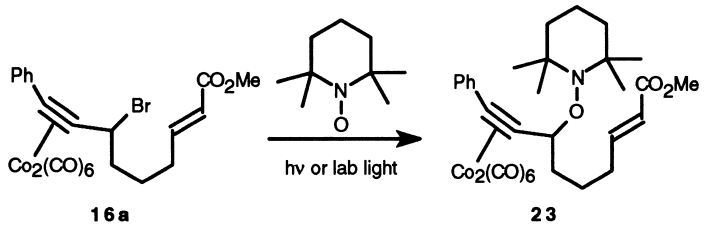
The 1-heptenyl cyclizations of the corresponding bromo complexes **20a**–**d** were also investigated (Scheme 9). These were conveniently generated from the precursor alcohol complexes **12**, again using diphos·$2Br_2$. In general, the photoinduced cyclizations of **20** proved to be much less efficient than for the above hexenyl systems. Irradiation of neat **20d** (R=H) required ca. 90 min for its complete consumption and produced several products which were separated chromatographically. Among these only one appeared to be cyclic judging by NMR and its mass spectrum indicated it to be isomeric with the starting bromide. Its structure was determined to be the 7-*endo* compound **21d** (8%) which exhibited a complex multiplet for 1H at 4.69 ppm for a –CHBr unit rather than the simple doublet expected for the $-CH_2Br$ group of the 6-*exo* derivative **22d**. This assignment was supported by homonuclear proton/proton decoupling. Photoinduced cyclization of the other heptenyl substrates **20a**–**c** proved even less efficient. In no instance was an appreciable quantity of any cyclic bromide detected. However, besides products resulting from HBr elimination from or hydrolysis of the starting materials, NMR and MS analysis indicated the formation of dimeric products, e.g. **23**, in low yield. This result provides additional evidence for the generation of radicals by C–Br bond homolysis of the propargyl bromide complexes **16** and **20**.

Lower rates and yields in heptenyl cyclizations are not unusual,[8] although the dropoff was more drastic than expected. The regioselectivity found in the case of **20d**, providing only the 7-*endo* product, is also exceptional among heptenyl radical cyclizations which, for typical organic radicals, provide a preponderance of the kinetically favored 6-*exo* products. The extraordinary regioselectivity, however, can also be rationalized by our mechanistic hypothesis involving a later cyclization transition state having significant product radical character (Scheme 10). Thus, the observed 7-*endo* pathway leading to **20d** allows development of radical character on a secondary carbon (**G**) whereas the 6-*exo* mode leads to a developing primary radical (**H**).

Mechanistic probes

Several lines of circumstantial evidence point to the involvement of a radical process for both the reductive and bromine transfer cyclizations including: (1) the reactions occur efficiently regardless of the electronic character of the olefinic acceptor; (2) the atom transfer reactions proceed in the absence of solvent or in non-polar benzene; (3) cyclization of the ester-substituted complex **16a** occurs in the 5-*exo* mode (rather than the 6-*endo* mode expected for a cationic pathway); (4) the reactions can be induced and terminated by established radical initiation methods, e.g. Et_3B/O_2 and R_3SnH/R_3SiH; and (5) dimers are produced, both in the Zn reduction of simple cation complexes (**1**)[6b,c] and in the photoreactions of the heptenyl substrates **20**.

To supplement the evidence for a radical pathway uncovered during the above reactivity studies the effect of two classical radical traps on the cyclizations was briefly examined. The photoinduced cycloisomerization of **16a** was found to be little affected by the presence of 1.5 equiv. of *meta*-dinitrobenzene; the cyclization product **17a** was still produced in moderate yield. Interestingly, irradiation of a benzene solution of **15a** in the presence of TEMPO (1 equiv.) produced the acyclic adduct **23**, judging by NMR and MS analysis, rather than cyclized products (Scheme 11). A control experiment revealed that the latter reacted with TEMPO to produce **23** even without irradiation. The failure of dinitrobenzene to significantly inhibit



Scheme 11.

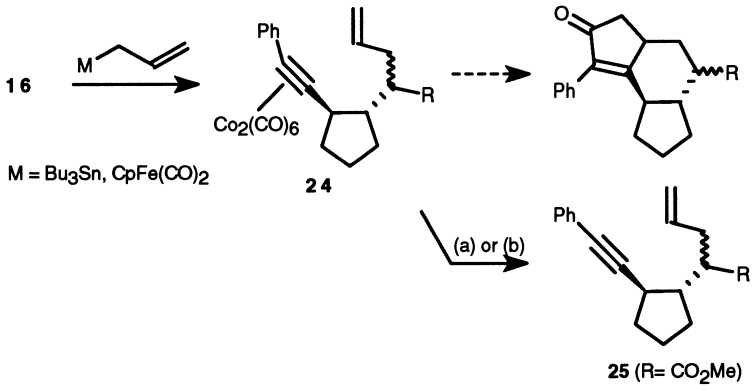
the transfer cyclizations may simply reflect a faster rate of bromine atom transfer step relative to addition of the intermediate radical to DNB. On the other hand, formation of the TEMPO adduct **24** could be the result of TEMPO trapping of low concentrations of the radical **3a** present in solutions of **16a** at room temperature in laboratory light or could be derived from a direct reaction of TEMPO with the bromide **16a** itself.

Another question of interest was whether the novel regio- and stereoselectivity associated with the hexenyl and heptenyl cyclizations of the alkynyl-cobalt complexes was the result of kinetic or thermodynamic control. Some efforts were made therefore to determine whether these reactions are reversible. Resolution of this issue is complicated by the fact that the starting bromides **16**, by virtue of the adjacent activating organocobalt unit, generate radicals under much milder conditions than the (unactivated) product bromides **17** and **18**. When cyclic bromoester **17a** (R=CO_2Me) was irradiated in the presence of the acyclic precursor **16a** as a prospective initiator, only the original cyclic product **17a** was recovered. Bromide **17a** was also irradiated together with Bu_6Sn_2 and Bu_3SnH. In this experiment a substantial quantity of the reduction product **14a** with an unaltered carbon skeleton was produced, indicating successful generation of the exocyclic radical which was trapped by tin hydride. Apparently, under these conditions ring opening is slow, i.e. essentially irreversible, relative to trapping of the cyclized radical by Bu_3SnH. Since the methyl-substituted complex **16c** cyclizes to form both 5-*exo* and 6-*endo* products, the bromocyclopentane derivative **17c** (R=Me, the presumed kinetic product) was also subjected to potentially equilibrating conditions by: (a) irradiation in the presence of Bu_6Sn_2 or (b) heating with Bu_3SnH and the radical initiators AIBN or AMVN [2,2′-azobis(2,4-dimethylvaleronitrile)]. In no instance was any cyclohexane derivative, e.g. **18c**, detected (the thermodynamic product); only products resulting from demetalation of the triple bond were isolated. Taken together, we have found no evidence for equilibrium (thermodynamic) control of the cyclizations of the cobalt complexes. We note also that the temperature at which these cyclizations proceed is far milder than those which previously have been found to be reversible.[19]

Synthetic studies

An attractive feature of atom transfer cycloadditions is the transposition of the functional halogen, which allows for subsequent synthetic elaboration at the new halogenated site.[8,16] The presence of both the bromine and the (alkynyl)-$Co_2(CO)_6$ functionalities in the cyclization products **17** and **18** offers interesting and potentially useful opportunities for further synthetic elaboration. Besides providing access to the synthetically versatile free carbon–carbon triple bond, the latter can engage directly in various cycloaddition reactions, including the Pauson–Khand conversion to cyclopentenones[23] and coupling with alkynes or nitriles to produce substituted arenes or pyridines.[24] Accordingly, we investigated a cyclization/allylation sequence of the complexes **16** to set up a subsequent Pauson–Khand cyclopentannulation (Scheme 12) to produce angular tricyclic 5–6–5 systems.

Several attempts to trap the cyclized radicals with allyltributyl tin[25] failed to provide allylated products. Thus, irradiation of either acyclic **16a** or cyclic **17a** in the presence of an excess of Bu_3Sn(allyl) (with and without Bu_6Sn_2, AIBN or vitamin B_{12}/Zn) afforded only the cyclic bromide **17a** and varying amounts of decomposition products. However, a little utilized radical allylating agent, CpFe-$(CO)_2(\eta^1$-allyl),[26] ultimately proved successful. When the acyclic bromide **16a** (R=CO_2Me) was stirred in benzene



Scheme 12.

with 5 equiv. of the latter at room temperature in normal lab light, the cyclic allylated product *trans*-**24a** (R=CO_2Me) was isolated in moderate yield as a mixture of C1′ epimers, accompanied by $CpFe(CO)_2Br$. The successful allylation of **16a** by $CpFe(CO)_2(\eta^1$-allyl), suggests that this compound could find more general use for mild allyl transfer reactions.

Without further optimization of the cyclization/allylation reaction, Pauson–Khand cyclization of **24a** was investigated. Three established protocols were tested: (1) treatment with *N*-methylmorpholine *N*-oxide,[27] (2) thermal oxidation on silica gel,[27] and (3) heating with aqueous ammonia.[27] Unfortunately, the former two reactions afforded the demetallated alkyne **25a** as the only characterizable product, while the latter produced a complex mixture of organic products. The reason for this failure is not apparent to us, but could be the result of poor proximity of the *trans*-(alkyne)cobalt carbonyl unit and the pendant alkenyl side chain or may reflect ring strain in the prerequisite intermediate metallacyle.

Conclusions

In summary, we have described facile reductive and atom transfer cyclizations of 1-[(alkynyl)$Co_2(CO)_6$]-hexenyl and -heptenyl systems. The former reactions proceed with exclusive *trans* stereoselection in the 5-*exo* mode. They also display unusual regioselectivities, favoring either 5-*exo*- or 6-*endo*-cyclization depending on the radical stabilizing ability of the alkenyl substituent. One successful -heptenyl radical cyclization proceeds exclusively in the 7-*endo* mode.

Taken together, the facility of the atom transfer cyclizations of the propargyl-cobalt complexes and their unusual regioselectivity strongly suggest that the intervening (propargyl)-$Co_2(CO)_6$ radicals are stabilized relative to typical organic radicals. Although kinetic data are not yet available, the ready cyclizations of **16** possessing either electron-rich or -poor double bonds may indicate that the (propargyl)-$Co_2(CO)_6$ radicals are ambiphilic. At this time we have no direct information on the structure of these species nor their mode of radical stabilization. However, based on studies of the related stable cations **1**,[2b,c] we anticipate that spin density in the radicals **2** can be highly delocalized onto the (alkynyl)$Co_2(CO)_6$ fragment. Studies to generate and characterize persistent derivatives of **2** are planned in order to address these issues. Our studies to date of the (propargyl)$Co_2(CO)_6$ radicals suggest that new and unusual reaction selectivity will be associated with carbon-centered organometallic radicals. Efforts to further elucidate the origin of this selectivity and to exploit it in organic synthesis are underway.

Experimental

General methods

Solvents were dried and freshly distilled before use; PE=petroleum ether, EE=diethyl ether. Organolithium reagents were standardized by titration before use. Glutaraldehyde was purchased as a 50% aqueous solution and the water was removed by freeze-drying. For all reactions the glassware was oven dried at 125°C. Acetal **7**[28] and $CpFe(CO)_2(\eta^1$-allyl)[29] were prepared by literature methods. ^{1}H NMR spectra were recorded at 300 or 400 MHz using $CDCl_3$ as solvent unless noted otherwise using residual chloroform-H (δ 7.24) as internal reference; all *J* values are in Hz. ^{13}C NMR spectra were recorded at 75 or 100 MHz and were referenced to the δ 77.0 resonance of $CDCl_3$. FT-IR spectral frequencies are given in cm^{-1}. Mass spectra were obtained either by electron impact (EI) or fast atom bombardment (FAB) methods, the latter using 3-nitrobenzyl alcohol (3-NBA) as the matrix. Elemental analyses were performed by Midwest Microlabs, Indianapolis, IN.

Preparation of hemiacetal 5

In a round bottom flask under nitrogen a solution of 0.05 mol of phenylacetylene in 70 mL of THF was cooled to −78°C, then treated dropwise with 0.05 mol of BuLi (1.6 M in hexanes) and the mixture was then stirred for 15 min. In a second round bottom flask under nitrogen, 0.050 mol of glutaraldehyde was dissolved in 50 mL of THF and then cooled to −78°C. To this solution the lithium phenylacetylide solution was transferred via cannula. The reaction was monitored by TLC (1:1 PE:EE) for the disappearance of glutaraldehyde (ca. 5 h). The reaction was quenched with 100 mL of 1 M HCl, extracted three times with 100 mL of Et_2O, the combined ether extracts dried over $MgSO_4$, filtered through Celite, and then concentrated. Purification by flash chromatography (1:1 PE/EE) afforded **5** as a light yellow oil (0.090 g, 0.44 mmol, 47%). R_f=0.43; ^{1}H NMR δ 7.44–7.41 (m, 4H), 7.29–7.26 (m, 6H), 5.35 (dd, *J*=6.9, 3.7 Hz, 1H), 5.02–4.99 (m, 1H), 4.79 (dd, *J*=6.3, 2.0 Hz, 1H), 4.46 (dd, *J*=12.0, 2.5 Hz, 1H), 2.86 (d, *J*=6.0 Hz, 1H), 2.55 (dd, *J*=3.0, 0.9 Hz, 1H), 1.98–1.24 (m, 12 H); ^{13}C NMR δ 131.8, 131.7, 128.4, 128.3, 128.2, 122.6, 122.5, 96.4, 92.3, 87.9, 87.5, 85.1, 84.5, 66.8, 62.0, 32.1, 31.5, 31.3, 30.3, 21.5, 17.7; IR (CH_2Cl_2) 3587 (m), 2952 (m), 1490 (m), 1192 (m), 1127 (m), 1071 (m), 1026 (s), 973 (s) cm^{-1}; HRMS *m/e* calcd for $C_{13}H_{15}O_2$ 203.1072, found 203.1063; 203 ($[M+H]^+$), 202 ($[M]^+$).

General preparation of ene-yne alcohols 6

In a round bottom flask under nitrogen 2.34 mmol of the appropriate phosphonium bromide was dissolved in 5 mL of THF, then 2.34 mmol of BuLi (1.3 M in hexanes) was added dropwise (in the preparation of ester **6a** the commercial ylid was used directly). The mixture was stirred 15 min before 1.17 mmol of the hemiacetal **5** dissolved in 5 mL of THF was added dropwise. The reaction was monitored by TLC (2:1 Et_2O:petroleum ether) for the disappearance of **5**. The reaction was quenched with 10 mL of 1 M HCl, then extracted three times with 50 mL of Et_2O. The combined organic extracts were dried over $MgSO_4$, filtered through Celite, and the concentrate was purified by column chromatography on silica gel (1:1 PE/EE).

6a. (*E*); light yellow oil; R_f 0.2 (10% ethyl acetate/90% PE; ^{1}H NMR δ 7.42–7.36 (m, 2H), 7.31–7.27 (m, 3H), 6.97 (dt, *J*=15.6, 6.9 Hz, 1H), 5.84, (d, *J*=15.9 Hz, 1H), 4.60 (app t, *J*=6.0 Hz, 1H), 3.71 (s, 3H), 2.27 (app q, *J*=7.2 Hz, 2H),

1.85–1.64 (m, 5H); ^{13}C NMR δ 167.1, 148.9, 131.6, 128.3, 128.2, 122.5, 121.2, 89.8, 84.9, 62.4, 51.3, 37.0, 31.7, 23.6; IR (CH_2Cl_2) 3594 (m), 3472 (m), 2950 (m), 2865 (m), 1721 (s), 1658 (s), 1490 (m), 1458 (m), 1438 (m), 1342 (m), 1316 (m), 1200 (m), 1181 (m), 1154 (m), 1100 (m), 1069 (m), 1027 (m) cm^{-1}; HRMS (FAB, 3NBA) *m/e* calcd for $C_{16}H_{18}O_3$ 258.1256, found 258.1231; 258 ([M]$^+$).

6b. (*E*/*Z*) light yellow oil; R_f 0.5 (3:1 petroleum ether:-diethyl ether); ^{1}H NMR major isomer (*E*) δ 7.43–7.16 (m, 10H), 6.40 (d, *J*=15.9 Hz, 1H), 6.22 (dt, *J*=15.9, 7.9 Hz, 1H), 4.63–4.58 (m, 1H), 2.29 (app q, *J*=7.2 Hz, 2H), 1.89–1.79 (m, 5H); minor isomer (*Z*) δ 7.43–7.16 (m, 10H), 6.43 (d, *J*=11.9 Hz, 1H), 5.66 (dt, *J*=11.9, 7.9 Hz, 1H), 4.63–4.58 (m, 1H), 2.41 (app q, *J*=7.0 Hz, 2H), 1.76–1.66 (m, 5 H); ^{13}C NMR (*E*/*Z*, $CDCl_3$,) δ 138.0, 137.9. 132.3, 131.8, 130.6, 130.4, 129.6, 128.8, 128.5, 128.4, 128.3, 128.2, 126.9, 126.6, 126.1, 122.9, 90.3, 85.2, 63.0, 62.9, 37.6, 32.6, 28.2, 25.6, 25.1; IR (CH_2Cl_2) 3595 (m), 3082 (w), 3026 (m), 2943 (m), 2862 (m), 1598 (m), 1490 (s), 1379 (m), 1070 (m), 1025 (m), 967 (s) cm^{-1}; HRMS (FAB, 3NBA) *m/e* calcd for $C_{20}H_{20}O$ 276.1514, found 276.1492; 276 ([M]$^+$).

6c. (*E*/*Z*); light yellow oil; R_f=0.8 (1:1 PE/EE); ^{1}H NMR δ 7.41–7.19 (m, 10H), 5.49–5.36 (m, 4H), 4.61–4.57 (m, 2H), 2.13–2.02 (m, 4H), 1.84–1.73 (m, 4H), 1.63–1.54 (m, 12H); ^{13}C NMR major isomer δ 131.6, 130.1, 128.3, 128.2, 124.3, 122.6, 90.1, 84.8, 62.8, 37.3, 26.4, 25.1, 12.8; minor isomer δ 131.6, 130.8, 128.3, 128.2, 125.3, 122.6, 90.1, 84.8, 62.8, 37.3, 32.1, 25.1, 17.9; IR (CH_2Cl_2) 3593 (s), 3452 (m), 3014 (m), 2938 (s), 2862 (s), 1654 (w), 1598 (m), 1490 (s), 1457 (m), 1443 (m), 1378 (s), 1069 (s), 1026 (s), 971 (s) cm^{-1}; HRMS (FAB, 3NBA) *m/e* calcd for $C_{15}H_{19}O$ 215.1436, found 215.1426; 215 ([M+H]$^+$), 214 ([M]$^+$).

6d. (light yellow oil); R_f=0.9 (3:1 PE/EE); ^{1}H NMR δ 7.45–7.41 (m, 2H), 7.32–7.26 (m, 3H), 5.83 (ddt, *J*=17.1, 10.2, 6.6 Hz, 1H), 5.04 (dd, *J*=17.1, 1.6 Hz, 1H), 4.98 (ddt, *J*=10.2, 1.6, 1.0 Hz, 1H), 4.61 (dd, *J*=12.0, 6.6 Hz, 1H), 2.14 (app q, *J*=7.2 Hz, 2H), 1.94 (d, *J*=5.4 Hz, 1H), 1.86–1.78 (m, 2H), 1.68–1.58 (m, 2H); ^{13}C NMR δ 138.4, 131.6, 128.3, 128.2, 122.5, 114.8, 90.0, 84.8, 62.7, 37.2, 33.2, 24.4; IR (CH_2Cl_2) 3594 (s), 3447 (m), 3080 (m), 2930 (s), 2863 (s), 1640 (m), 1598 (m), 1490 (s), 1379 (m), 1070 (s), 1027 (s), 997 (s), 917 (s) cm^{-1}; HRMS (FAB, 3NBA) *m/e* calcd for $C_{14}H_{17}O$ 201.1279, found 201.1265; 201 ([M+H]$^+$), 200 ([M]$^+$).

Preparation of 9

In a side-arm round bottom flask equipped with a stirring bar, 1.0 mL (9.4 mmol) of phenylacetylene was dissolved in 25 mL of THF under nitrogen. The solution was cooled to 0°C, then 5.9 mL (9.4 mmol, 1.6 M in hexanes) of BuLi was added dropwise. In a separate 250 mL side-arm round bottom flask equipped with a stirring bar, 1.51 g (9.42 mmol) of **7** was dissolved in 30 mL of THF. This flask was cooled to 0°C under nitrogen, then the phenylacetylide solution was added dropwise over 45 min. The reaction was monitored by TLC for the disappearance of **7** (about 2 h). Then 50 mL of 1 N HCl was added and the mixture stirred for another hour. The solution was then extracted with five 20 mL portions of diethyl ether, the combined extracts were washed with 50 mL $NaHCO_3$, dried over $MgSO_4$, filtered through Celite, and then concentrated. Purification by flash chromatography (1:1 PE/EE/silica gel) afforded 0.485 g (2.24 mmol, 24%) of **9** (yellow oil). ^{1}H NMR δ 9.76 (s, 1H), 7.41–7.39 (m, 2H), 7.29–7.24 (m, 3H), 4.59 (t, *J*=6.8 Hz, 1H), 2.46 (t, *J*=6.8 Hz, 2H), 1.91 (s broad, 1H), 1.83–1.73 (m, 2H), 1.72–1.66 (m, 2H), 1.59–1.53 (m, 2H). IR (CH_2Cl_2) 3598 (m), 3054 (m), 2986 (m), 2946 (m), 2865 (m), 2305 (m), 1723 (s) cm^{-1}. EIMS (12 eV) *m/z*: [M]$^+$ 216.

Preparation of 10a,d

In a side-arm round bottom flask equipped with a stirring bar under nitrogen 2.93 g (8.82 mmol) of $Ph_3PCH(CO_2CH_3)$ was dissolved in 20 mL of THF. A solution of 0.950 g (4.37 mmol) of acetylenic aldehyde **8** in 5 mL of THF was then added. The flask was equipped with a water-cooled condenser and the mixture was heated to reflux and the reaction was monitored by TLC for the disappearance of **9** (10% ethyl acetate in petroleum ether, ca. 3 h). The reaction was quenched with 20 mL of water, then extracted three times with 10 mL portions of diethyl ether. The extracts were dried over magnesium sulfate, filtered through Celite, and then concentrated. The resulting crude unsaturated acetal was then dissolved in 40 mL of acetone, 0.6 mL of water was added followed by 0.4 g of Amberlyst-15. After stirring the mixture for 24 h, the solvent was evaporated and the residue chromatographed (silica gel, 10% ethyl acetate/PE) affording **10a** (0.930 g, 3.42 mmol, 78%) as a yellow oil. ^{1}H NMR δ 7.49–7.30 (m, 2H), 7.28–7.20 (m, 3H), 6.90 (dt, *J*=15.6, 6.9 Hz, 1H), 5.76 (d, *J*=15.6 Hz, 1H), 4.57–4.86 (m, 1H), 3.64 (s, 3H), 2.21–2.15 (m, 2H), 1.82 (d, *J*=4.2 Hz, 1H), 1.78–1.67 (m, 2H), 1.54–1.40 (m, 4H); ^{13}C NMR δ 166.9, 149.2, 131.4, 128.1, 128.0, 122.4, 120.8, 90.0, 84.6, 62.5, 51.3, 37.4, 32.0, 27.6, 24.7; IR (CH_2Cl_2) 3594 (m), 3320 (m), 2940 (m), 2862 (m), 1721 (s), 1712 (s), 1657 (m) cm^{-1}; MS (FAB, 3NBA) *m/z*: 273 [M+H]$^+$.

Compound **10d** was prepared similarly from **9** and the corresponding benzyl ylid (52%, light yellow oil). ^{1}H NMR δ 7.41–7.39 (m, 2H), 7.29–7.28 (m, 3H), 5.48 (ddt, *J*=17.0, 10.3, 6.8 Hz, 1H), 4.99 (d, *J*=17.0 Hz, 1H), 4.93 (d, *J*=10.2 Hz, 1H), 4.60–4.55 (m, 1H), 2.10–2.04 (m, 2H), 1.94 (bs, 1H), 1.82–1.76 (m, 2H), 1.56–1.41 (m, 4H); ^{13}C NMR δ 138.7, 131.6, 128.3, 128.2, 122.5, 114.4, 90.0, 84.8, 62.9, 37.6, 33.6, 28.5, 24.6; IR (CH_2Cl_2) 3596 (s), 2931 (s), 2360 (m), 2228 (m), 1639 (m), 1599 (m), 1490 (s) cm^{-1}; EIMS (12 eV) *m/z*: [M]$^+$ 214.

Preparation of 10b,c

A solution of unsaturated aldehyde **11c** (1.23 g, 6.53 mmol) in 45 mL of THF was added dropwise to a solution of lithium phenylacetylide prepared by treating 0.72 mL of phenyl acetylene in 50 mL with 6.5 mL of 1.0 M butyl lithium (hexane). After stirring for 2 h TLC analysis indicated consumption of the starting aldehyde. The reaction mixture was added to aqueous ammonium chloride solution and the mixture extracted with three 50 mL portions of

ether. The combined ether extracts were dried over $MgSO_4$, filtered and concentrated. The residual oil was flash chromatographed (2:1 PE/EE) over silica gel to provide 1.89 g of **10c** (73% yield). Compound **10b** was prepared analogously from **11b** in 70% yield.

10c. (*E*/*Z*, yellow oil) ^{1}H NMR δ 7.40–7.38 (m, 4H), 7.37–7.32 (m, 6H), 5.42–5.30 (m, 4H), 4.55–4.50 (m, 2H), 2.06–1.93 (m, 6H), 1.77–1.71 (m, 4H), 1.62–1.54 (m, 6H), 1.52–1.43 (m, 4H), 1.41–1.32 (m, 4H); ^{13}C NMR (mixture) δ 131.7, 131.2, 130.4, 128.3, 128.2, 124.9, 123.9, 122.8, 90.3, 84.9, 63.0, 37.9, 32.4, 29.2, 26.7, 24.8, 24.7, 17.7, 12.6; IR (CH_2Cl_2) 3595 (m), 3052 (m), 3013 (m), 2937 (s), 2860 (s), 2305 (w), 1599 (m) cm^{-1}; HRMS-FAB (*m*/*z*): calcd. for $C_{16}H_{20}O$ 228.1514; found, 228.1552.

10b. (*E*/*Z*, yellow oil) ^{1}H NMR δ 7.41–7.11 (m, 10H), 6.38 (d, *J*=11.5 Hz, 1H), 6.36 (d, *J*=16.0 Hz, 1H), 6.18 (dt, *J*=16.0, 7.0 Hz, 1H), 5.63 (dt, *J*=11.5, 7.0 Hz, 1H), 4.61–4.52 (m, 2H), 2.36–2.31 (m, 2H), 2.34–2.19 (m, 2H), 1.95–1.91 (m, 2H), 1.82–1.76 (m, 4H), 1.57–1.52 (m, 8H); ^{13}C NMR δ 137.9, 137.8, 132.6, 131.6, 130.6, 130.1, 129.1, 128.7, 128.4, 128.3, 128.2, 128.1, 126.7, 126.4, 125.9, 122.7, 90.2, 84.9, 62.9, 37.7, 32.8, 29.6, 29.0, 28.4, 24.9, 24.7; IR (CH_2Cl_2) 2931 (s), 2862 (s), 1063 (s) cm^{-1}; HRMS-FAB (*m*/*z*): $[M+H]^+$ calcd for $C_{21}H_{22}O$ 290.1670; found 290.1655.

Preparation of complexed alcohols 7a–d and 12a–d

In a well-ventilated hood a side-arm round bottom flask was charged with 4.12 mmol of $Co_2(CO)_8$ and 75 mL of CH_2Cl_2 under nitrogen. A solution of the alcohol **6** or **10** (4.12 mmol in 5 mL of CH_2Cl_2) was then added dropwise. The reaction mixture bubbled as CO was being produced. The reaction was monitored by TLC (1:1 Et_2O:petroleum ether) for the disappearance of the starting alcohol (1–3 h). The mixture was then filtered through alumina and the filtrate concentrated. Purification was done by flash chromatography over silica gel (1:1 PE/EE).

7a. (*E*); red solid; R_f 0.45 (1:1 petroleum ether:diethyl ether); ^{1}H NMR δ 7.50 (dd, *J*=6.0, 1.5 Hz, 2H), 7.39–7.32 (m, 3H), 6.97 (dt, *J*=15.6, 6.9 Hz, 1H), 5.82 (d, *J*=15.6 Hz, 1H), 5.05–5.01 (m, 1H), 3.72 (s, 3H), 2.29 (app q, *J*=6.0 Hz, 2H), 2.13 (d, *J*= 5.1 Hz, 1H), 1.88–1.67 (m, 4H); ^{13}C NMR d 167.0, 148.6, 137.4, 129.4, 129.0, 128.0, 121.4, 101.5, 90.7, 72.1, 51.4, 38.9, 31.8, 24.8; IR (CH_2Cl_2) 2091 (s), 2058 (s), 2050 (s), 2028 (s), 1720 (m), 1716 (m) cm^{-1}.

7b. (*E*/*Z*); red solid crystallized from diethyl ether; ^{1}H NMR major isomer δ 7.52–7.48 (m, 2H), 7.35–7.20 (m, 8H), 6.39 (d, *J*=15.9 Hz, 1H), 6.20 (dt, *J*=15.9, 6.9 Hz, 1H), 5.10–5.05 (m, 1H), 2.32 (app q, *J*=6.9 Hz, 2H), 1.93 (d, *J*=5.1 Hz, 1H), 1.96–1.69 (m, 4H); minor isomer δ 7.52–7.48 (m, 2H), 7.35–7.20 (m, 8H), 6.46 (d, *J*=11.5 Hz, 1H), 5.65 (dt, *J*=11.5, 7.2 Hz, 1H), 5.03–4.97 (m, 1H), 2.43 (app q, 6.9 Hz, 2H), 1.90 (d, *J*=5.4 Hz, 1H), 1.96–1.69 (m, 4H); ^{13}C NMR δ 137.6, 137.5, 132.1, 130.5, 130.0, 129.4, 128.9, 128.7, 128.4, 128.1, 127.9, 126.9, 126.5, 125.9, 101.8, 90.7, 72.5, 72.2, 39.1, 39.0, 32.4, 28.1, 26.7, 25.9; IR (CH_2Cl_2) 2091 (s), 2058 (s), 2048 (s), 2028 (s), 1607 (w) cm^{-1}; Anal. Calcd for $C_{26}H_{20}O_7Co_2$: C, 55.54; H, 3.58; found C, 55.33; H, 3.31.

7c. (*E*/*Z*) red oil; ^{1}H NMR major isomer δ 7.53 (dd, *J*=7.8, 1.7 Hz, 2H), 7.39–7.32 (m, 3H), 5.52–5.33 (m, 2H), 5.06–5.00 (m, 1H), 2.14 (app q, *J*=6.6 Hz, 2H), 1.93 (d, *J*=5.1 Hz, 1H), 1.89–1.69 (m, 4H), 1.60 (d, *J*=6.3 Hz, 3H); minor isomer δ 7.53 (dd, *J*=7.8, 1.7 Hz, 2H), 7.39–7.32 (m, 3H), 5.52–5.33 (m, 2H), 5.06–5.00 (m, 1H), 2.09–2.04 (m, 2H), 1.92 (d, *J*=5.1 Hz, 1H), 1.89–1.69 (m, 4H), 1.64 (d, *J*=4.0 Hz, 3H); ^{13}C NMR major isomer δ 137.6, 129.8, 129.5, 128.9, 127.9, 124.5, 101.9, 90.7, 72.4, 39.2, 26.4, 26.2, 12.7; minor isomer 137.6, 130.6, 129.5, 128.9, 127.9, 125.6, 101.9, 90.7, 72.3, 39.1, 32.1, 26.1, 17.8; IR (neat) 3596 (m), 3558 (m), 3481 (br), 3078 (m), 3014 (s), 2934 (s), 2860 (s), 2090 (s), 2051 (s), 2020 (s), 1615 (m) cm^{-1}; Anal. Calcd for $C_{21}H_{18}O_7Co_2$: C, 50.42; H, 3.63; found C, 50.44; H, 3.50.

7d. (red oil) ^{1}H NMR δ 7.53 (dd, *J*=6.0, 1.5 Hz, 2H), 7.39–7.32 (m, 3H), 5.81 (ddt, *J*=17.1, 10.2, 6.7 Hz, 1H), 5.07–4.96 (m, 3H), 2.18–2.12 (m, 2H), 1.92 (d, *J*=5.1 Hz, 1H), 1.90–1.61 (m, 4H); ^{13}C NMR δ 138.1, 137.5, 129.5, 128.9, 127.9, 115.0, 101.8, 90.7, 72.2, 39.1, 33.3, 25.5; IR (CH_2Cl_2) 2091 (s) 2059 (s), 2048 (s), 2028 (s), 2015 (s) cm^{-1}.

12a. (red oil) ^{1}H NMR δ 7.52–7.48 (m, 2H), 7.39–7.29 (m, 3H), 6.95 (dt, *J*=15.6, 6.9 Hz, 1H), 5.80 (dt, *J*=15.6, 1.5 Hz, 1H), 5.02 (m, 1H), 3.72 (s, 3H), 2.55–2.52 (m, 2H), 1.95 (d, *J*=5.1 Hz, 1H), 1.88–1.65 (m, 2H), 1.60–1.52 (m, 2H). ^{13}C NMR δ 199.3, 167.0, 149.1, 137.4, 129.4, 128.9, 127.9, 121.1, 101.6, 90.7, 72.3, 51.4, 39.4, 32.0, 27.7, 26.0; IR (CH_2Cl_2) 2904 (m), 2862 (m), 2091 (S) 2026 (s), 1720 (m) cm^{-1}; MS (FAB, 3NBA) *m*/*z* 541 $[(M+H)-H_2O]^+$, 502 $[M-2(CO)]^+$.

12b. (red oil) ^{1}H NMR (*E*/*Z*) δ 7.49 (dd, *J*=6.0, 2.3 Hz, 4H), 7.37–7.26 (m, 6H), 5.45–5.29 (m, 4H), 5.03–4.97 (m, 2H), 2.03 (q, *J*=6.9 Hz, 2H), 1.91 (d, *J*=5.1 Hz, 1H), 1.89–1.34 (m, 21H); ^{13}C NMR (mixture) δ 137.6, 131.0, 130.2, 129.5, 128.9, 127.9, 125.0, 124.0, 102.0, 90.8, 72.4, 39.7, 32.4, 29.2, 26.6, 26.0, 25.9, 17.8, 12.6; IR (CH_2Cl_2) 2997 (m), 2937 (s), 2863 (s), 2090 (s), 2049 (s), 2026 (s) cm^{-1}; MS (FAB, 3NBA) *m*/*z* 497 $[(M+H)-18]^+$, 458 $[M-2(CO)]^+$.

12c. (red oil) ^{1}H NMR (*E*/*Z*) δ 7.51–7.13 (m, 20H), 6.4 (d, *J*=11.4 Hz, 1H), 6.34 (d, *J*=15.9 Hz, 1H), 6.17 (dt, *J*=15.9, 6.9 Hz, 1H), 5.62 (dt, *J*=11.4, 7.2 Hz, 1H), 5.04–4.96 (m, 2H), 2.33 (q, *J*=5.7 Hz, 2H), 2.21 (q, *J*=6.3 Hz, 2H), 1.91 (d, *J*=5.4 Hz, 1H), 1.88 (d, *J*=5.1 Hz, 1H), 1.84–1.63 (m, 6H), 1.59–1.51 (m, 6H); ^{13}C NMR (mixture) δ 137.8, 137.6, 132.5, 130.4, 130.2, 129.4, 129.2, 128.9, 128.7, 128.4, 128.1, 127.9, 126.8, 126.4, 125.9, 101.9, 90.8, 72.4, 39.7, 32.8, 29.6, 29.1, 28.4, 26.1, 26.0; IR (CH_2Cl_2) 2936 (s), 2091 (s), 2052 (s), 2025 (s) cm^{-1}; MS (FAB, 3NBA) *m*/*z* 559 $([M+H]-H_2O]^+$, 520 $[M-2(CO)]^+$.

12d. (red oil). ^{1}H NMR δ 7.45 (d, *J*=6.8 Hz, 2H), 7.36–7.29 (m, 3H), 5.76 (ddt, *J*=17.1, 10.7, 6.0 Hz, 1H), 5.02–4.90 (m, 3H), 2.04 (q, *J*=6.8 Hz, 2H), 1.90 (d, *J*=4.8 Hz, 1H), 1.85–1.42 (m, 6H); ^{13}C NMR δ 138.3, 137.6, 129.5, 128.9,

127.9, 114.6, 101.9, 90.9, 72.5, 39.7, 33.6, 28.6, 25.9; IR (CH_2Cl_2) 2935 (m), 2089 (s), 2060 (s) cm^{-1}; MS (FAB, 3NBA) *m/z* 483 $[(M+H)-18]^+$, 472 $[M-CO]^+$.

General procedure for the reductive cyclization via the salts 13

In a side-arm round bottom flask containing a stir bar, 1.00 mmol of the complexed alcohol **7a** was dissolved in 0.41 mL (3.2 mmol) of propionic acid under nitrogen and then cooled to −45°C. $HBF_4{\cdot}OEt_2$ (0.43 mL, 2.9 mmol) was then added dropwise. After stirring for 45 min the reaction mixture was triturated with 10 mL portions of cold anhydrous diethyl ether. When the ether washes were nearly colorless, the resulting dark red salt **13a** was dried under vacuum. The salt was then dissolved in 20 mL of methylene chloride and then 0.032 g (0.50 mmol) of zinc was added. After ca. 1 h TLC analysis (1:1 PE/EE) indicated the disappearance of hydrolyzed starting material. The mixture was filtered through Celite, concentrated, and the residue subjected to flash chromatography (5:1 PE/EE) to afford 0.090 g (38%) of **14a** (red solid). ^1H NMR (C_6D_6) δ 7.49 (d, J=7.8 Hz, 2H), 7.06–6.93 (m, 3H), 3.24 (s, 3H) 2.49 (app q, J=8.0 Hz, 1H), 2.53 (dd, J=15.3, 3.9 Hz, 1H), 2.30–2.20 (m, 1H), 2.07 (dd, J=15.0, 9.9 Hz, 1H), 2.05–1.89 (m, 2H), 1.68–1.29 (m, 4H); ^{13}C NMR 172.8, 138.2, 129.0, 128.8, 127.7, 103.1 92.4, 51.4, 48.4, 45.5, 39.1, 36.2, 32.8, 23.9; IR (CH_2Cl_2) 2927 (w), 2088 (s), 2051 (s), 2023 (s), 1731 (m) cm^{-1}.

Protonation of **7b** as above precipitated a salt which after stirring at 0°C for an hour dissolved upon addition of ether/pentane. Concentration of this solution followed by flash chromatography of the residue (1:1 PE/EE) afforded 0.14 g (0.26 mmol) of propionate **15b** (red oil). The epimers of **15b** could be separated by preparative TLC (1:1 PE/ether). ^1H NMR (major) δ 7.43–7.40 (m, 2H), 7.34–7.18 (m, 8H), 5.95 (d, J=4.5 Hz, 1H), 3.49–3.41 (m, 1H), 2.41 (q, J=7.8 Hz, 2H), 2.33–2.23 (m, 1H), 1.92–1.84 (m, 1H), 1.77–1.61 (m, 3H), 1.29–1.20 (m, 2H), 1.48 (t, J=1.8 Hz, 3H); IR (major) (CH_2Cl_2) 3045 (w), 2965 (w), 2087 (s), 2048 (s), 2023 (s), 1738 (m), 1605 (w) cm^{-1}; ^1H NMR (minor) δ 7.55–7.52 (m, 2H, 7.36–7.26 (m, 8H), 5.55 (d, J=10.2 Hz, 1H), 3.61–3.56 (m, 1H), 2.70–2.62 (m, 1H), 2.42–2.30 (m, 1H), 2.12 (q, J=7.2 Hz, 2H), 1.73–1.63 (m, 5H), 0.95 (t, J=7.2 Hz, 3H); IR (minor) (CH_2Cl_2) 2086 (m), 2045 (s), 2020 (s), 1734 (m) cm^{-1}; EIMS (12 eV) *m/z* 562 $[M-2(CO]^+$, 450 (20.6) $[M-6(CO)]^+$.

Cyclization of 16a,d using Ph_2SiH_2 and Et_3B

The bromide **16a**, prepared from 0.2 mmol of alcohol **7a**, was dissolved in 20 mL of benzene in a two-neck round bottom flask equipped with a stir bar under nitrogen. Ph_2SiH_2 (0.04 mL, 0.20 mmol) and Et_3B (0.04 mL, 0.04 mmol, 1 M in hexanes) were added. The valve to the flask was then closed and 0.9 mL of oxygen injected by syringe through the septum. With continued stirring the color of the reaction mixture changed from red to brown and **16a** was consumed after 1–4 h (monitored by TLC 4:1 PE/EE). The reaction mixture was filtered through Celite, then concentrated. Purification by column chromatography (10% diethyl ether in petroleum ether/silica gel) afforded **14a** and **17a** (epimers).

General preparation of the complexed bromides 16, 20

Under nitrogen a side-arm round bottom flask containing 0.21 mmol of $Ph_2PCH_2CH_2PPh_2$ dissolved in 14 mL of CH_2Cl_2 was cooled to 0°C. Bromine (2.4 mmol) in 3 mL of CH_2Cl_2 was added dropwise and the mixture stirred for an additional 15 min followed by the addition of 0.21 mmol of the alcohol complex **7** and **12** in 3 mL of CH_2Cl_2. The reaction mixture was then stirred for an hour. Addition of diethyl ether and pentane (1:2:4 CH_2Cl_2:Et_2O:pentane) produced a white precipitate. The mixture was filtered through Celite under nitrogen and concentrated under vacuum to provide the complexed bromides **16** and **20** as thermally sensitive red oils.

16a. (*E* isomer; red oil) ^1H NMR δ 7.62 (dd, J=7.6, 1.7 Hz, 2H), 7.41–7.33 (m, 3H), 6.97 (dt, J=15.7, 6.9 Hz, 1H), 5.85 (dt, J=15.7, 1.5 Hz, 1H), 5.46 (dd, J=9.3, 4.5 Hz, 1H), 3.73 (s, 3H), 2.36–2.26 (m, 2H), 2.23–2.15 (m, 2H), 2.05–1.90 (m, 1H), 1.84–1.69 (m, 1H); ^{13}C NMR ($CDCl_3$, partial) δ 148.0, 129.5, 128.8, 128.0, 121.7, 56.2, 51.4, 40.6, 31.1, 26.5.

16b. (mixture of diastereomers; red oil) ^1H NMR (*E*) δ 7.61–7.56 (m, 2H), 7.34–7.18 (m, 8H), 6.39 (d, J=15.7 Hz, 1H), 6.19 (dt, J=15.7, 6.7 Hz, 1H), 5.50 (dd, J=9.6, 3.5 Hz, 1H), 2.45–1.69 (m, 6H); (*Z*) 7.61–7.56 (m, 2H), 7.34–7.18 (m, 8H), 6.45 (d, J=13.5 Hz, 1H), 5.68–5.60 (m, 1H), 5.42 (dd, J=9.0, 4.5 Hz, 1H), 2.45–1.69 (m, 6H).

16c. (*E*,*Z*; red oil) ^1H NMR δ 7.64–7.31 (m, 10H), 5.53–5.38 (m, 6H), 2.26–2.24 (m, 8H), 6.94–1.78 (m, 2H), 1.70–1.60 (m, 8H).

16d. (red oil) ^1H NMR δ 7.61 (d, J=6.0 Hz, 2H), 7.51–7.17 (m, 3H), 5.79 (ddt, J=16.6, 10.2, 6.3 Hz, 1H), 5.46 (dd, J=9.3, 3.3 Hz, 1H), 5.02 (d overlapping, J=16.6 Hz, 1H), 4.98 (d overlapping, J=10.2 Hz, 1H), 2.28–1.64 (m, 6H).

The bromides **20a**–**d** were prepared as above and subjected to irradiation without further characterization.

General photochemical preparation of the cyclized bromides 17, 18, and 21

Irradiation of the complexed bromides **16a**–**d** as a thin film or in benzene solution was accomplished under a 300 W GE halogen floodlight (ca. 0.5 m) for 1 h. The products were purified by column chromatography over silica gel or deactivated alumina (10–20% Et_2O/petroleum ether); yields (from **7**, **12**): **17a** (56%), **17b** (76%), **17c**/**18c** (60%), **18d** (73%), **21d** (8%).

17a. (red oil); ^1H NMR major isomer δ 7.53–7.48 (m, 2H), 7.39–7.31 (m, 3H), 4.59 (d, J=3.2 Hz, 1H), 3.70 (s, 3H), 3.51 (app q, J=8.0 Hz, 1H), 2.38–2.23 (m, 3H), 2.01 (app q, J=6 Hz, 2H), 1.85–1.69 (m, 2H); minor isomer δ 7.53–7.48 (m, 2H), 7.39–7.31 (m, 3H), 4.32 (d, J=8.0 Hz, 1H), 3.77 (s, 3H), 3.63 (m, 1H), 2.76–2.68 (m,

1H), 2.38–2.23 (m, 2H), 2.14–2.06 (m, 2H), 1.85–1.69 (m, 2H); ^{13}C NMR major isomer 199.4, 169.3, 137.8, 129.0, 128.9, 127.9, 101.8, 92.8, 53.0, 52.2, 50.9, 46.5, 36.1, 28.9, 24.4; minor isomer 199.4, 169.3, 138.1, 129.1, 128.8, 127.7, 103.9, 94.4, 52.9, 52.2, 48.7, 46.9, 36.4, 30.2, 24.9; IR (CH_2Cl_2) 2089 (s), 2050 (s), 2025 (s), 1745 (m), 1738 (m) cm^{-1}; (FAB, 3NBA) *m/z* 580 $[M+2-1(CO)]^+$.

17b. (red oil, *E*/*Z*) ^{1}H NMR major isomer δ 7.54 (d, *J*=6.3 Hz, 2H), 7.41–7.30 (m, 8H), 5.30 (d, *J*=2.7 Hz, 1H), 3.66 (app q, *J*=7.5 Hz, 1H), 2.39–2.15 (m, 3H), 2.02–1.67 (m, 4H); minor isomer δ 7.53 (d, *J*=7.6 Hz, 2H), 7.33–7.27 (m, 8H), 4.89 (d, *J*=10.8 Hz, 1H), 3.90–3.88 (m, 1H), 3.06–3.01 (m, 1H), 2.41–2.35 (m, 1H), 1.83–1.59 (m, 4H), 1.42–1.36 (m, 1H); ^{13}C NMR ($CDCl_3$, partial) major isomer 199.6, 141.3, 138.1, 103.4, 93.5 61.1, 55.7, 35.7, 29.1, 24.1; minor isomer 199.6, 141.0, 138.3, 105.8, 93.0, 59.7, 55.7, 48.3, 35.4, 30.5, 25.2; IR (CH_2Cl_2) 2088 (s), 2046 (s), 2028 (s), 1605 (w) cm^{-1}; MS (FAB, 3NBA) *m/z* 598 $[M+2-1(CO)]^+$.

17c. (red oil) ^{1}H NMR δ 7.56–7.54 (m, 2H), 7.39–7.30 (m, 3H), 4.38 (dq, *J*=7.0, 2.4 Hz, 1H), 3.54 (app q, *J*=8.0 Hz, 1H), 2.29–2.21 (m, 1H), 1.97–1.69 (m, 6H), 1.65 (d, *J*=6.8 Hz, 3 H).

18c/17c′ (red oil; mixture) ^{1}H NMR **18c**: δ 7.46–7.25 (m, 5H), 4.24 (dq, *J*=6.5, 6.4 Hz, 1H), 3.41(app q, *J*=6.0 Hz, 1H), 2.31–2.60 (m, 2H), 2.07–1.52 (m, 5H), 1.68 (d, *J*=6.8 Hz, 3H); **17c**: δ 7.46–7.25 (m, 5H), 4.40 (dt, *J*=11.6, 4.4 Hz, 1H), 3.16 (dt, *J*=11.6, 3.6 Hz, 1H), 2.49–2.45 (m, 2H), 2.07–1.52 (m, 5H) 1.03 (d, 6.8 Hz, 3H); IR (CH_2Cl_2) mixture 3059 (w), 2946 (w), 2868 (w), 2088 (s), 2048 (s), 2025 (s), 2016 (s) cm^{-1}.

***cis*-18d.** (red solid, crystallized from heptane) ^{1}H NMR δ 7.45 (d app, *J*=7.6 Hz, 2H), 7.36–7.27 (m, 3H), 4.14 (app tt, *J*=11.8, 4.0 Hz, 1H), 3.02 (app tt, *J*=11.8, 3.4 Hz, 1H), 2.66 (app d, *J*=12.4 Hz, 1H), 2.38 (app d, *J*=12.8 Hz, 1H), 2.11 (app d, *J*=12.8 Hz, 1H), 1.95–1.74 (m, 3H), 1.54 (app tq, 1H), 1.37 (app dq, 1H); ^{13}C NMR 199.6, 138.0, 129.1, 128.9, 127.5, 102.8, 91.2, 49.7, 46.2, 42.6, 37.7, 33.8, 26.8; IR (CH_2Cl_2) 2089 (s), 2051 (s), 2024 (s) cm^{-1}; MS (mixture) (FAB, 3NBA) *m/z* 565 $[M+H]^+$; Anal. Calcd for $C_{20}H_{15}O_6BrCo_2$ C, 43.75; H, 2.75; found C, 44.16; H, 2.75.

***trans*-18d.** (red solid, crystallized from heptane) ^{1}H NMR δ 7.50 (app d, *J*=7.2 Hz, 2H), 7.36–7.27 (m, 3H), 4.80 (s broad, 1H), 3.60 (tt app, *J*=11.6, 3.0 Hz, 1H), 2.44 (app d, *J*=14.0 Hz, 1H), 2.15–2.01 (m, 3H), 1.85–1.74 (m, 3H), 1.38 (app dq, 1H); ^{13}C NMR δ 199.6, 138.1, 129.2, 128.9, 127.7, 104.3, 91.1, 53.6, 43.0, 36.2, 34.7, 34.0, 21.0.

Irrradiation of the bromides **21a**–**d** was carried out similarly but a longer period was needed to achieve complete consumption of the starting material. These reactions produced a number of products including the original alcohol complexes (**20**), incompletely characterized elimination products, dimeric complexes, e.g. **23a** (red solid) ^{1}H NMR δ 7.2–7.4 (bm, 10H), 6.9 (m, 1H), 6.7 (m, 1H), 5.8 (m, 1H), 5.6 (m, 1H), 3.7 (s, 6H), 2.2 (bm, 4H), 2.0 (m, 2H), 1.8 (m, 2H), 0.8–1.6 (m, 6H); MS (FAB, 3NBA) *m/z* 1082 $[M]^+$; and cyclization product **21d** (red oil) ^{1}H NMR δ 7.52 (d, *J*=6.4 Hz, 2H), 7.35–7.27 (m, 3H), 4.70–4.68 (m, 1H), 3.57 (t, *J*=6.0 Hz, 1H), 2.57 (br d, *J*=12.0 Hz, 1H), 2.68–2.19 (m, 4H), 1.85–1.71 (m, 2H), 1.62–1.40 (m, 3H); ^{13}C NMR δ 199.7, 138.1, 129.3, 128.8, 127.7, 54.6, 46.5, 39.1, 38.5, 37.3, 27.7, 24.4; IR (CH_2Cl_2) 2088 (s), 2050 (s), 2022 (s) cm^{-1}; MS (FAB, 3NBA) *m/z* 536 $[M+2-1(CO)]^+$.

Preparation of 19

In a 250 mL side-arm round bottom flask containing a stir bar under nitrogen, $Ph_2PCH_2CH_2PPh_2$ (0.501 g, 1.26 mmol) was dissolved in 12 mL of CH_2Cl_2. The reaction mixture was cooled to 0°C, then a solution of Br_2 (0.013 mL, 2.52 mmol) in 2.5 mL of CH_2Cl_2 was added dropwise. The reaction mixture was allowed to stir for 5 min, then a solution of **6d** (0.211 g, 1.05 mmol) in 2.5 mL of CH_2Cl_2 was added. The mixture was stirred at 0°C for an hour, then allowed to warm to room temperature with stirring for another 1.5 h. After **6d** had been consumed (TLC), 70 mL of pentane and 35 mL of diethyl ether was added, producing a white precipitate. The mixture was filtered through Celite, the filtrate concentrated, and the residue purified by flash chromatography (3:1 PE/EE/silica gel) affording 0.273 g (1.04 mmol, 99%) of **19** as a yellow oil. ^{1}H NMR δ 7.43–7.36 (m, 2H), 7.30–7.25 (m, 3H), 5.81 (ddt, *J*=17.1, 10.0, 6.0 Hz, 1H), 5.04 (d, *J*=17.1 Hz, 1H), 4.98 (d, *J*=10.0 Hz, 1H), 4.76 (t, *J*=6.0 Hz, 1H), 2.15–2.07 (m, 3H), 1.73–1.65 (m, 3H); ^{13}C NMR δ 137.8, 131.7, 128.7, 128.2, 122.1, 115.1, 87.9, 86.9, 39.1, 37.7, 32.7, 26.5; IR (CH_2Cl_2) 2974 (m), 2933 (m), 2867 (m), 2226 (w), 1640 cm^{-1}; MS (FAB, 3NBA) *m/z* 183 $[M-79]^+$.

Reaction of 16a with TEMPO

The bromide **16a** (prepared from 0.081 g, 0.149 mmol of alcohol **7a**) was dissolved in 6 mL of benzene under nitrogen in a side-arm round bottom flask which contained a stir bar followed by 0.056 g of TEMPO (0.24 mmol). Half of this solution was withdrawn, placed in an 25 mL side-arm round bottom flask containing a stir bar under nitrogen, and then irradiated under a 300 W halogen floodlight for 4 h. The remaining solution was stirred for 4 h without irradiation. Each reaction mixture was concentrated and then purified using column chromatography (9:1 PE/EE on activity III alumina). One fraction was isolated from each purification which was found to be **3** (17–20%, red oil). ^{1}H NMR (mixture) δ 7.39–7.37 (m, 4H), 7.31–7.25 (m, 6H), 6.98 (dt, *J*=15.7, 6.9 Hz, 1H), 6.75 (dt, *J*=15.7, 6.9 Hz, 1H), 5.84 (d, *J*=15.7 Hz, 1H), 5.51 (d, *J*=15.7 Hz, 1H), 5.18–5.16 (m, 1H), 4.64 (t, *J*=5.9 Hz, 1H), 3.70 (s, 3H), 3.67 (s, 3H), 2.76–2.70 (m, 1H), 2.26 (q, *J*=6.9 Hz, 2H), 2.15–2.02 (m, 2H), 1.87–1.81 (m, 2H), 1.77–1.66 (m, 2H), 1.55–1.80 (m, 37H), 0.87–0.49 (m, 2H); ^{13}C NMR (mixture) δ 199.7, 167.1, 166.9, 149.2, 148.6, 138.2. 131.3, 129.0, 128.7, 128.1, 127.8, 127.5, 123.3, 121.0, 120.7, 99.1, 91.3, 90.4, 86.3, 80.6, 75.0, 61.1, 60.4, 59.4, 51.3, 51.2, 40.8, 40.5, 40.0, 36.7, 34.9, 34.6, 34.4, 33.7, 32.0, 31.7, 24.8, 23.7, 20.8, 20.6, 20.4, 20.2, 17.3, 17.1; IR (CH_2Cl_2) 2933 (m), 2871 (m), 2090 (s), 2050 (s), 2026 (s), 1720 (s), 1716 (s), 1658 (m) cm^{-1}; MS (FAB, 3NBA) *m/z* 543 $[M-5(CO)]^+$, 527 $[M-TEMPO]^+$.

Allylation of 16a by $CpFe(CO)_2(\eta^1$-allyl)

The bromide **16a** (prepared from 0.411 g, 0.757 mmol of alcohol **6a**) was transferred into a side-arm round bottom flask containing a stir bar under nitrogen and then dissolved in 10 mL of benzene. A solution of 0.787 g (3.75 mmol) of $CpFe(CO)_2(\eta^1$-allyl) in 10 mL of benzene was then added via cannula. The mixture was stirred for 3 h without being irradiated. When **16a** had been consumed (TLC), the mixture was filtered through silica gel and then concentrated. Purification was performed using flash chromatography (5:1 PE/EE/silica gel). Six fractions were isolated and a proton NMR spectrum was taken of each. The first fraction contained 0.100 g (0.177 mmol, 23%) of **25a** as a dark red oil; the structures of the compounds in the other fractions were not be determined. ^{1}H NMR δ 7.47–7.43 (m, 4H), 7.34–7.26 (m, 6H), 5.62 (ddt, J=17.0, 9.9, 8.0 Hz, 2H), 5.02–4.91 (m, 4H), 3.65 (s, 3H), 3.58 (s, 3H), 3.46 (q, J=6.7 Hz, 1H), 3.36 (q, J=6.5 Hz, 1H), 2.80–2.76 (m, 1H), 3.28–2.59 (m, 1H), 2.50–2.42 (m, 2H), 2.33–2.06 (m, 6H), 1.92–1.82 (m, 4H), 1.80–1.56 (m, 6H); ^{13}C NMR δ 199.7, 175.0, 174.2, 138.4, 135.6, 135.4, 129.2, 129.1, 128.8, 128.7, 127.5, 116.6, 116.5, 104.9, 104.7, 93.4, 93.2, 51.2, 50.6, 50.1, 47.3, 47.2, 46.3, 46.0, 36.5, 36.1, 31.7, 28.4, 28.1, 24.8; IR (CH_2Cl_2) 2952 (w), 2871 (m), 2087 (s), 2047 (s), 2024 (s), 1730 (m), 1641 (w), 1605 (w) cm^{-1}; MS (FAB, 3NBA) m/z 512 $[M-2(CO)]^+$.

Attempted Pauson–Khand reaction of 24a

In a side-arm round bottom flask under nitrogen containing a stir bar 0.042 g (0.075 mmol) of **24a** was dissolved in 10 mL of CH_2Cl_2, then 0.053 g (0.045 mmol) of *N*-methyl morpholine *N*-oxide was added and the reaction mixture was stirred at room temperature. After 2 h TLC indicated a reaction had occurred, but **24a** was still present in the reaction mixture. The mixture was filtered through silica gel, concentrated, and then purified by PTLC (5:1 PE/EE). Four fractions were isolated. The first fraction was recovered **24a**. The second fraction contained 0.0070 g (0.026 mmol, 36%) of decomplexed alkyne **25a** (yellow oil) ^{1}H NMR (partial) δ 7.37–7.35 (m, 2H), 7.30–7.23 (m, 3H), 5.83–5.68 (m, 2H), 5.05 (d, J=17.4 Hz, 2H), 4.98 (d, J=9.9 Hz, 2H), 3.64 (s, 3H), 3.60 (s, 3H); MS (FAB, 3NBA) m/z 283 $[M+H]^+$.

For the reaction of **24a** with O_2 on silica gel a CH_2Cl_2 solution of **24a** (0.067 g, 0.118 mmol) was mixed with 4 g of silica gel and the solvent was removed by rotary evaporation. The flask containing the adsorbed **24a** was then heated to 45°C while being rotated on the evaporator for 2 h as oxygen was admitted to the system. The silica gel (blue) was then triturated with diethyl ether and the extracts concentrated to provide a yellow oil. Purification was performed by PTLC (5:1 PE/EE) providing one fraction (0.019 g) whose NMR spectrum indicated it to be **25a** (0.068 mmol, 57%).

X-Ray crystal structure determinations of 14a, 17b, *trans*-18d, and *cis*,*cis*-18c

Crystals were obtained by slow crystallization from pentane or heptane at −20°C. The data were collected at −70°C using monochromated MoKα (λ=0.71073 Å) radiation. The data were corrected for Lorentz and polarization effects; no absorption correction was applied since it was judged to be insignificant. The structures were solved by direct methods (for **14a**, **17b** and *cis*,*cis*-**18c**) using SHELXTL 5.0 (Siemens system) or the heavy atom method (for **18d**) and refined by full-matrix least-squares on F2 using all reflections. Hydrogen atoms were included in the idealized positions. Details of the crystal data and refinement for **14a**, **17b**, *trans*-**18d**, and *cis*,*cis*-**18c**, along with tables of fractional atomic coordinates, thermal parameters, bond lengths and angles have been deposited at the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB2 1EZ.

The methoxy group of **14a** (C22A and C22B) was disordered at two sites with unequal population. The size of the C22A and C22B atoms in the difference map, and refinement of the partial occupancy factor for these atoms, suggested 65 and 35% occupancy, respectively for these atoms. Details of the crystal data and refinement are given in the Supporting Table. Figures are drawn with 15% thermal ellipsoids. For the sake of clarity, C22B and all the hydrogens except H15A and H19A are omitted.

The crystals of **18d** appeared to be affected by internal twinning and, in general, peaks were either split or broad. Structure solution and refinement were tried both in *P*21 and *P*21/*m*. A reasonable refinement can only be obtained in the *P*21 space group. The final refined model has superimposed mirror images of the molecule and refined also as racemic twinned as suggested by the SHELXTL program. Because of this twinning problem, the refinement was poor and the accuracy of the final parameters is limited. However, the important features of the six-membered ring and the location of the bromine atom and (alkynyl)$Co_2(CO)_6$ unit are unambiguously established.

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