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REACTION OF η^5-CYCLOPENTADIENYLBIS(TRIPHENYLPHOSPHINE)-COBALT(I) WITH ALKADIYNES. PREPARATION AND REACTIONS OF BICYCLIC COBALT METALLOCYCLES AND A STABLE TRIMETHYLSILYL-SUBSTITUTED MONO-COMPLEXED ALKADIYNE. COMMENTS ON THE MECHANISM OF COBALT-CATALYZED ALKYNE COOLIGOMERIZATION

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Summary

Reactions of η^5-cyclopentadienylbis(triphenylphosphine)cobalt(I) (5) with several 2,n-alkadiynes (2) were investigated. Each of these reactions leads initially to a material in which one of the acetylene functional groups is π-coordinated to cobalt; this complex then undergoes conversion to a metallocycle. In cases where the two acetylene functions are connected by three- and four-carbon bridges (2b, 2c), metallocycles formed by intramolecular reaction of two acetylene functions in the same molecule may be isolated. In cases where the acetylene functions are joined by larger or smaller bridges, the reactions are more complex, and both inter- and intramolecular metallocycles are formed. Reactions of 5 with 1,8-bis(trimethylsilyl)-1,7-octadiyne (16) gives an isolable crystalline mono-acetylene complex (17), this material is stable in the solid state but undergoes conversion to metallocycle (18) in benzene solution. The relationship of these results to the mechanism of the $CpCo(CO)_2$-catalyzed benzocycloalkene synthesis is discussed; it is suggested that intramolecular metallocycles are intermediates in reactions leading to benzocyclopentanes and -cyclohexenes, but intermolecular metallocycles are probably involved in reactions leading to benzocyclobutenes.

Many organotransition metal complexes catalyze the conversion of alkynes to benzene derivatives [1], but the lack of selectivity observed with most

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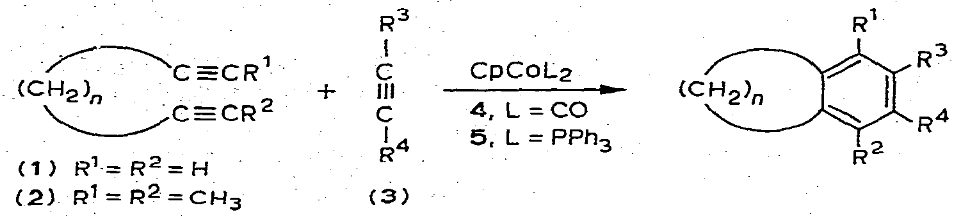
presently known alkyne oligomerization catalysts has often prevented their development as synthetically useful reagents. Recently η^5-cyclopentadienyldicarbononylcobalt (4) was found to be a useful catalyst for the cotrimerization of diynes (e.g., 1, 2) with monoacetylenes (3) [2]; Vollhardt and his co-workers



(1) $R^1 = R^2 = H$
(2) $R^1 = R^2 = CH_3$
(3)

a series: $n = 2$
b series: $n = 3$
c series: $n = 4$
d series: $n = 5$
e series: $n = 6$

have improved the yields in this reaction considerably through the use of bis(trimethylsilyl)acetylene [BTMSA; 3, $R^3 = R^4 = Si(CH_3)_3$] as the monoacetylene, and have utilized this discovery in the development of methods for the preparation of complex polycyclic ring systems [3]. Vollhardt and Funk have reported a very simple and direct steroid synthesis based on this method [4,5] *.

We recently obtained some information about the mechanism of cobalt-catalyzed trimerization of simple alkynes [6] (e.g., 2-butyne) using the related (and considerably more reactive) catalyst η^5-cyclopentadienylbis(triphenylphosphine)cobalt (5). In an effort to extend this work to the diyne-monoacetylene cotrimerization reaction, we have investigated the stoichiometric reactions of 5 with a number of disubstituted diynes (2) and have also examined some of the chemistry of the complexes formed in these reactions.

Results

I. Reactions with 2,8-decadiyne. In reactions of 5 with 2-butyne [6], we were able to prepare and isolate the cobalt-containing metallocycle 7 and detect mono-acetylene complex 6 as an intermediate in the conversion of 5 to 7 (cf. Scheme 1). We assumed we would have the best chance of observing an intramolecular analog of this reaction by employing a diacetylene capable of producing a bicyclic metallocycle containing a six-membered ring. Accordingly, we began our investigation by examining the interaction of 5 with 2,8-decadiyne (2c).

The reaction was run by adding small amounts of the diyne to a solution of 5 in benzene-d_6 (with scrupulous exclusion of air) and monitoring the progress of the transformation by NMR spectrometry. Upon mixing, the characteristic triplet at δ 4.36 ppm due to 5 was replaced by two new cyclopentadienyl signals, one at δ 4.54 ppm and the other at δ 4.80 ppm. Successive scans of

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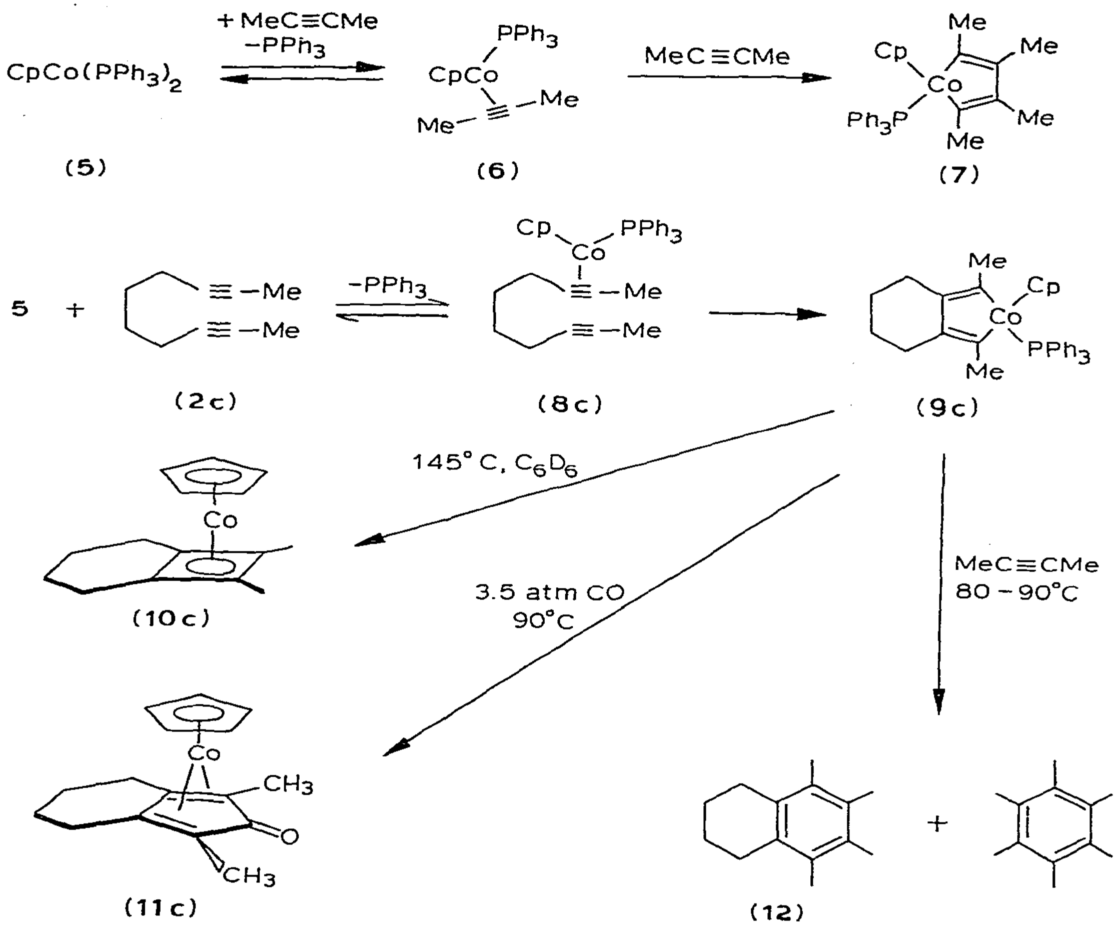
* It has also recently been reported that diynes 2 react with dicarbonyl 4 to give bicyclic cyclopentadienone complexes [5].

SCHEME 1



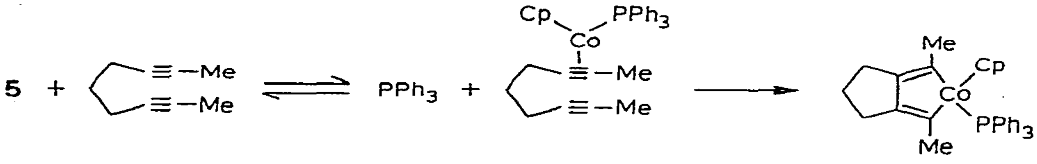
the cyclopentadienyl region after each addition showed each of these signals was due to a different complex, the complex absorbing at δ 4.54 ppm was gradually converted to that which absorbed at δ 4.80 ppm. Addition of one equivalent of diyne resulted in quantitative conversion to a solution containing only the cyclopentadienyl resonance at δ 4.80 ppm.

Concentration and addition of petroleum ether to this solution resulted in the precipitation of a brownish-yellow solid, which was characterized as metallocycle 9c. By analogy to the 2-butyne reaction [6], we assume the cyclopentadienyl resonance at δ 4.54 ppm is due to the (unisolable) mono-acetylene π-complex 8c. Metallocycle 9c is stable in anaerobic benzene for weeks, but gradually decomposes in the presence of air. It is also stable at 90°C, but when heated in solution to 145°C for 2 h, it is converted to a mixture of two unidentified compounds, one of which we assume by analogy [7] to be cyclobutadiene complex 10c.

Metallocycle 9c was stable to carbon monoxide at room temperature, up to 3.5 atm. At this pressure, reaction with CO took place at a convenient rate at 90° C, leading to cyclopentadienone complex [5] 11c in 70% yield. This material exhibits a carbonyl absorption in the IR at 1595 cm^{-1} and NMR absorptions (benzene-d_6) at δ 4.25 (s, Cp) and 1.70 (s, CH_3) ppm [lit. [5] IR ($CHCl_3$) 1545 cm^{-1}; NMR ($CDCl_3$) δ 4.64 (s), 1.72 (s) ppm].

II. Reaction with 2,7-nonadiyne. The effect of reducing the diacetylene chain length was investigated by examining the reaction of 5 with 2,7-nonadiyne (2b) (Scheme 2). Once again the intramolecular metallocycle (9b) was the ultimate product of this reaction, but in contrast to the 2,8-decadiyne case, the initial monoacetylene complex 8b could not be observed by NMR. Apparently the shorter chain length results in faster cyclization of 8b compared to 8c, as one might expect on the basis of entropic considerations. However, when the experiment was run in the presence of an eleven-fold excess of triphenylphosphine, an additional cyclopentadienyl resonance (δ 4.54 ppm) attributable to 8b was observed in addition to the metallocycle (δ 4.74 ppm) during the early stages of the reaction.

SCHEME 2

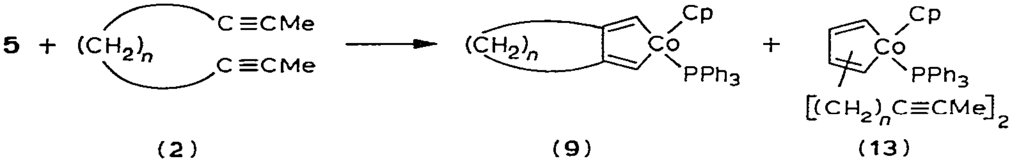


(2b) (8b) (9b)

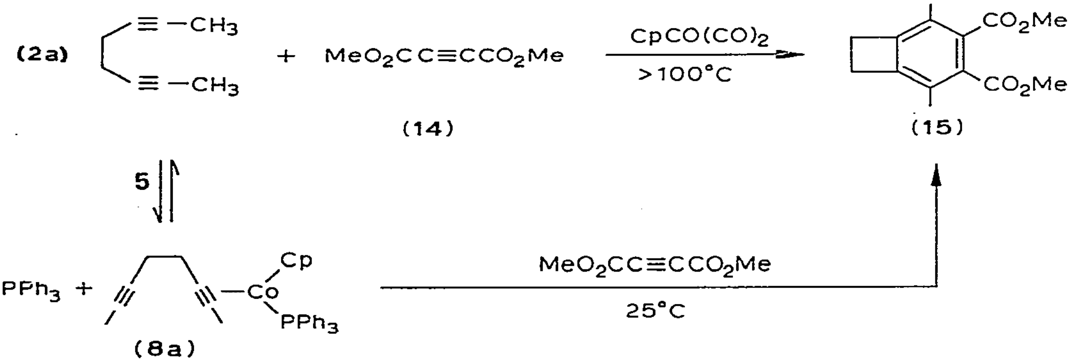
As in the previous case, concentration and addition of petroleum ether precipitated the solid metallocycle along with triphenylphosphine; the excess phosphine was removed by re-crystallization from benzene/petroleum ether. Metallocycle 9b exhibits carbonylation behavior similar to that observed for 9c. It is stable to CO (1.5 atm, 25°C) in benzene-d_6 at room temperature, but after 19.5 h at 67°C the absorptions due to 9b were replaced (35% yield) by ones characteristics of the known [5] cyclopentadienone complex 11b [IR (THF): 1597 cm^{-1}, NMR (C_6D_6): δ 4.11, 1.72 ppm; lit. [5] IR ($CHCl_3$): 1563 (sh), 1547 cm^{-1}; NMR ($CDCl_3$): δ 4.65, 1.79 ppm]. Also formed were dicarbonyl 4 (20%), (η^5-C_5H_5)Co(PPh_3)(CO) (5—10%), and free bicyclic cyclopentadienone (ca. 20%). Upon thermolysis in benzene-d_6, the metallocycle did not give a cyclobutadiene complex analogous to the one (10c) formed from 9c. Complex 9b is stable in solution at 67°C but decomposes to intractable materials at 110°C.

III. Reactions with longer- and shorter-chain diacetylenes. Several reactions with diynes 2 having chains longer and shorter than C(4) and C(3) were investigated briefly by NMR. Treatment of 2d ($n = 5$) with 5 initially gave a single new resonance at δ 4.54 ppm consistent with the formation of only the mono-acetylene η-complex. Extending the chain to this length apparently slows the rate of cyclization considerably; again, entropic factors would appear to be the cause of this retardation. Clean cyclization to intramolecular metallocycle did not occur even at longer reaction times; after 24 h at room temperature, the solution still contained 5 and the mono-acetylene complex, but along with these materials three new cyclopentadienyl resonances were observed. The largest of these signals appeared at δ 4.72 ppm; by analogy we presume this to be due to the intramolecular metallocycle 9d. The additional resonances are most likely due to isomeric "intermolecular" metallocycles 13 formed by interaction of two different diacetylene molecules. Similarly, with 2e ($n = 6$), initial reaction gave only a mixture of 5, 2e, and mono-acetylene complex. Once again several new cyclopentadienyl resonances were observed after 24 h.

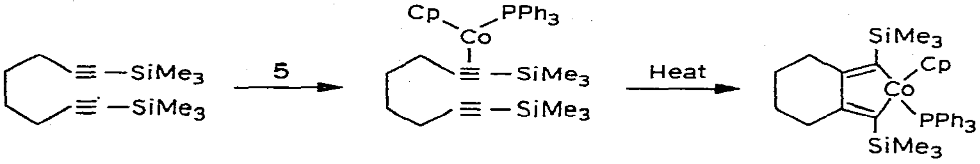
Shortening the connecting chain to 2 carbons also apparently prevents intramolecular metallocycle formation. Thus, reaction of 5 with 2a ($n = 2$) gave an NMR pattern similar to that observed with 2d. Initially only the mono-acetylene complex was formed, and further reaction at room temperature gave rise only to intermolecular metallocycle formation (13a). We were able to measure



the equilibrium constant for the formation of 8a from 5 and 2a because intermolecular metallocycle formation was slow. NMR measurement of the amounts of 5 and 8a in the presence of known amounts of added 2a and triphenylphosphine gave a value of K_{eq} (34°C) = 0.9 (±0.1) (the equilibrium constant measured [8] for the analogous reaction between 5 and 2-butyne at 33°C is 0.1). In light of this result, and considering that $CpCo(CO)_2$ provides an efficient cotrimerization reaction in the $n = 2$ case under catalytic conditions, we decided to attempt a stoichiometric cotrimerization using 5, 2a, and dimethylacetylene dicarboxylate (14). 2,6-Octadiyne (2a) was added to a solution of 5 until the production of the monoacetylene complex was maximized. To this solution was added an equivalent (based on 5) of dimethylacetylene dicarboxylate. The resulting reaction mixture was complex, but column chromotography gave 15 as the only carbonyl-containing organic product.



IV. Reaction of 5 with bis(trimethylsilyl)-1,7-octadiyne. Isolation of a stable mono-acetylene π-complex. In order to examine the effect of steric hindrance on the course of the cyclizations studied here, we examined the interaction of 5 with the bis(trimethylsilyl)-substituted diacetylene 16. The presence of the TMS groups modifies the chemistry of the system and also affects the NMR chemical shifts of the cyclopentadienyl protons in the complexes formed during the reaction. Addition of less than one equivalent of 16 to 5 immediately produced two new products. The major product exhibited a cyclopentadienyl signal at δ 5.19 ppm and a TMS signal at δ 0.67 ppm; the minor product had corresponding signals at δ 4.73 and 0.32 ppm. Addition of a full equivalent of 16 gave a solution containing >90% of the major product. Concentration and precipitation of this material gave red-orange, needle-like crystals (m.p. 117—119°C) which were characterized as the monoacetylene complex 17 (to our knowledge only one other $CpCo(PPh_3)$-monoacetylene π-complex has been isolated [7]). The monoacetylene complex 17 is stable in the solid state, but upon redissolution in benzene it begins to rearrange to the material with NMR absorptions at δ 4.73 and 0.32 ppm. Heating to 60°C completes this conversion in 10 minutes, and the product metallocycle 18 may be isolated and characterized.



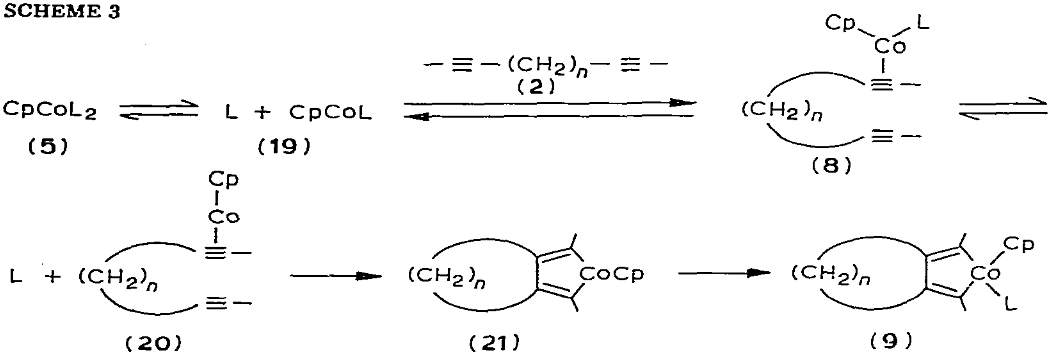
(16) (17) (18)

Discussion

The results outlined above demonstrate a number of parallels between the cobalt-induced oligomerization reactions of mono- and 1,*n*-diacetylenes. First, the metallocycles described here are all formed from acetylenes which do not bear electron-withdrawing or "activating" substituents; despite this fact, they appear to have stabilities (especially thermal stabilities) comparable to systems [9] which bear such groups. Second, it is clear the metallocycle-forming mechanism identified in the 2-butyne reaction [6], involving the intermediate formation of monoacetylene complexes which then undergo reaction with a second alkyne, is also operating in the bicyclic cases examined here. In parallel to the 2-butyne reaction, we assume the conversion of 5 to the monoacetylene complex, as well as coordination of the second acetylene function, are both dissociative in phosphine. Supporting evidence that the latter step is dissociative is provided by our observation that in the reaction of 5 with 2b, observable concentrations of the intermediate 8b build up only in the presence of excess triphenylphosphine. Thus the mechanism of metallocycle formation from 5 outlined in Scheme 3 seems well established.

The effect of diacetylene chain length on the rate of intramolecular acetylene coordination is consistent with information available in more conventional organic cyclizations. As one might expect, a stable metallocycle is easily formed from diacetylene 2c, which leads to a metallocycle fused to a six-membered ring (9c). Because a five-membered ring is only slightly more strained, metallocycle 9b is also cleanly formed. However, in this case the fewer degrees of freedom in the chain allow unsaturated intermediate 20b (*n* = 3) (Scheme 3) to cyclize more rapidly than 20c (*n* = 4), and a larger concentration of phosphine is required to force 8b to build up. As *n* gets higher, intermolecular coordination of a second molecule to the metal in 20 begins to compete with intramolecular coordination. In the case of 20a (*n* = 2), we were able to obtain no evidence for

SCHEME 3



the formation of 9a presumably because of the significantly higher strain energy of the fused four-membered ring in this metallocycle. Thus as *n* becomes small, strain energy, rather than entropic effects, tend to lower the rate of intramolecular coordination.

We believe this last observation is relevant to the mechanism of the CpCo(CO)$_2$-catalyzed benzocyclobutene synthesis [2—4]. The two most likely overall mechanisms for this transformation are outlined briefly in Scheme 4. Once the π-complex 22 (L = CO) is formed and loses CO, the unsaturated intermediate 23 has two alternatives. In path (i), it forms intramolecular metallocycle 24, which upon coordination of a second alkyne gives 25; this then leads to 26 by insertion and reductive elimination. Alternatively [path (ii)], the metal in 23 may coordinate a second alkyne, leading to 27 which can undergo a cyclization reaction not subject to the type of ring strain found in 24 (it is possible that phosphine recoordinates at this point, or alternatively the second acetylene function may complex to the metal, occupying the open coordination site as shown in 28). Insertion of the second acetylene function and reductive elimination leads to 26.

The observations that (a) 9a is not formed in the reaction of 2a with 5, and (b) treatment of 8a with dimethylacetylene dicarboxylate does lead to cooligomerization product 15, strongly suggest mechanism (ii) is operative in the CpCo(PPh$_3$)$_2$ system and, by inference, in the CpCo(CO)$_2$ reaction. In contrast, the intramolecular metallocycle route seems quite feasible for diynes in which the triply-bonded functions are connected by three- and four-carbon bridges. With longer-chain diynes, the cooligomerization may well proceed by a mixture of the two mechanisms.

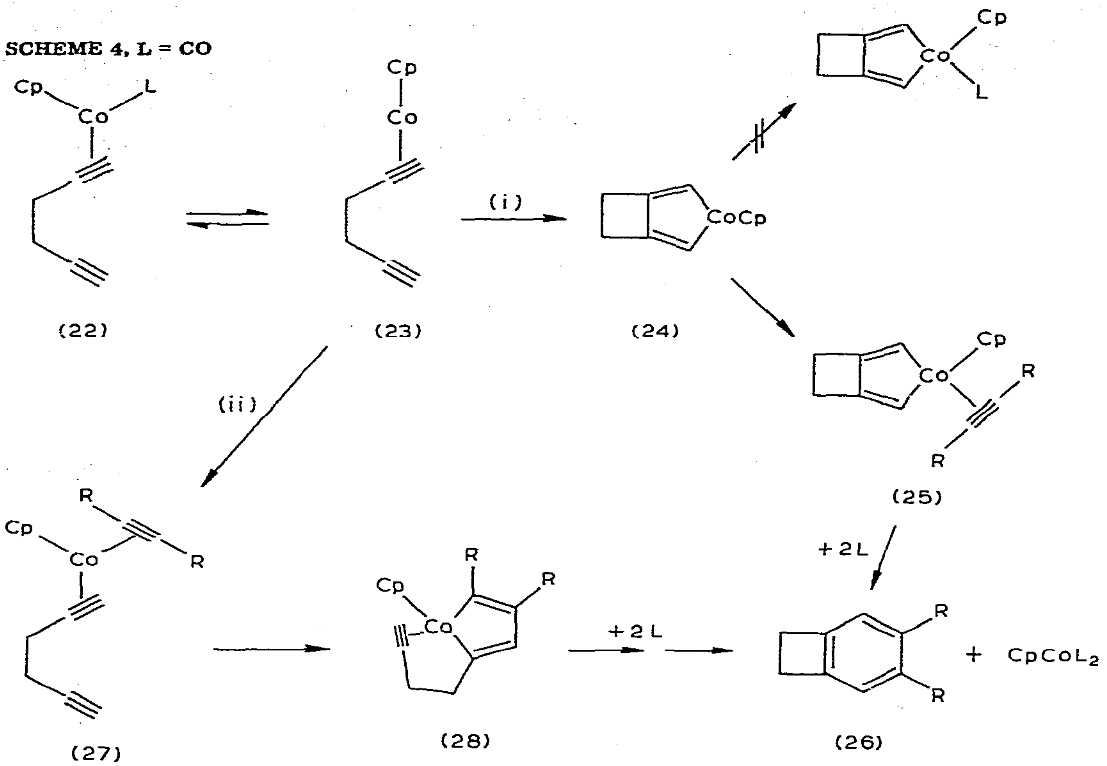
Finally, it should be mentioned that the reactions discussed here are similar to those recently developed using 1,*n*-dienes, which lead to saturated metallocycles that also may be converted to organic products upon treatment with CO and other reagents [10].

Experimental

General procedures

Infrared spectra were taken on a Perkin—Elmer Model 257 Grating Infrared Spectrophotometer and calibrated with reference to polystyrene absorptions. Nuclear magnetic resonance spectra were taken on Varian A-60, 220, and

SCHEME 4. L = CO



EM-390 NMR spectrometers. Chemical shifts are reported in δ units relative to internal tetramethylsilane. Mass spectra were obtained using a DuPont 21,492-B mass spectrometer. Data are reported as *m/e* (relative intensity >20%, 100 = base peak). Elemental analyses were performed by Schwarzkopf Microanalytical Laboratory, Inc., Woodside, New York and the Caltech Analytical Facility, Pasadena, California. Melting points (uncorrected) were taken on a Thomas Hoover capillary melting point apparatus.

Preparative gas-liquid chromatography (GLC) was performed on a Varian Aerograph Model 90-P gas chromatograph with a helium carrier gas flow (ca. 50 ml/min) and a 5 ft, 1/4" glass column packed with 8% SE-30 on acid washed Chromosorb W.

All commercial chemicals were of reagent or spectrophotometric quality unless specified otherwise, and were used without further purification. Solvents were distilled from lithium aluminum hydride. 2-Butyne (Farchan), 3-hexyne (Aldrich), diphenylacetylene (Aldrich), 1,5-hexadiyne (Chem. Samples), 1,6-heptadiyne (Chem. Samples), 1,7-octadiyne (Aldrich), 2,8-decadiyne (Chem. Samples), 2,9-undecadiyne (Farchan), and 2,10-dodecadiyne (Farchan) were used as received. Dimethylacetylenedicarboxylate (Aldrich) and η^5-cyclopentadienyldicarbonylcobalt (Ventron) were purified by bulb-to-bulb distillation. Trimethylsilyl chloride (Aldrich) was fractionally distilled from calcium hydride. Cyclopentadiene was prepared by distillation (b.p. 39°C) from dicyclopentadiene (Aldrich).

For use with organometallic complexes spectrophotometric benzene, toluene, tetrahydrofuran and anhydrous diethyl ether were vacuum transferred from sodium benzophenone ketyl. Petroleum ether (30—60°C) was washed with sulphuric acid and potassium permanganate prior to vacuum transfer from a solution containing sodium benzophenone ketyl in tetraglyme. The tetraglyme ketyl was also used for the purification of spectral grade cyclohexane. All other chemicals were degassed prior to use. All manipulations were carried out under nitrogen atmosphere unless otherwise indicated.

Preparation and characterization of diynes

1. Synthesis of 2,7-nonadiyne. Liquid ammonia (300 ml) was dried with a small amount of sodium (dry ice/acetone bath). After 20 min the reaction was quenched with ferric nitrate. Sodium amide (20 g, 0.513 mol) was added to the dry liquid ammonia. To this well-stirred suspension was added dropwise over a period of 1.5 h a solution of 1,6-heptadiyne (20 g, 0.217 mol, 0.435 equivalents) in 200 ml of anhydrous ether. The solution was stirred for an additional 2.5 h, followed by the dropwise (2 h) addition of a solution of methyl iodide (87 g, 0.613 mol) in 200 ml of anhydrous ether. The mixture was allowed to warm to room temperature while stirring overnight. After most of the ammonia had evaporated 200 ml of ice water was added dropwise and stirring was begun as soon as possible. The aqueous layer was then separated and washed with 500 ml of ether. The ether fractions were combined and washed with 5% sulfuric acid until the washings were acidic (to litmus) and then 5% sodium bicarbonate until the washings were basic. The ether was then dried over anhydrous magnesium sulfate and concentrated in vacuo.

The residue was vacuum distilled (ca. 0.6 mmHg) yielding two main fractions: (1) b.p. 30—34°C, NMR and IR show some 1,6-heptadiyne; (2) Isolated yield 40%; d: 0.8844; b.p. 34°C (ca. 0.6 mmHg); NMR: (220 MHz, CCl_4): δ 1.7 (t, 6H, CH_3), 2.15 (m, 4H, propargyl), 1.45 ppm (m, 2H, CH_2). IR: 3305 cm^{-1}; mass spectrum: *m/e*: 120(9), 119(19), 105(100), 92(21), 91(56), 79(43), 77(28), 66(39), 65(28), 53(21), 41(50). Anal. Found: C, 89.18; H, 9.97. C_9H_{12} calcd.: C, 89.94; H, 10.06%.

2. Trimethylsilylation of α,ω-diynes. General method. To a well stirred solution of magnesium turnings in dry tetrahydrofuran under nitrogen was added a small amount of bromoethane to initiate the reaction. The remaining bromoethane in 100 ml of THF was added dropwise and the solution stirred for an additional hour. To this mixture a solution of the α,ω-diyne in THF was added dropwise and the reaction mixture refluxed for 2 h (heating is necessary to keep the di-Grignard reagent in solution). Trimethylsilyl chloride (freshly distilled) was added dropwise and the solution stirred until it solidified (ca. 2 h). The solid was added to saturated ammonium chloride solution and extracted with petroleum ether. The organic fractions were dried over anhydrous magnesium sulfate and concentrated in vacuo. The residue was vacuum distilled.

a. 1,8-Bis(trimethylsilyl)-1,7-octadiyne. The di-Grignard reagent of 1,7-octadiyne was generated by treating ethyl magnesium bromide (1 mol) in THF with 1,7-octadiyne (21 g, 0.198 mol, 0.4 equivalents). To the resulting solution was added trimethylsilyl chloride (121 g, 1.1 mol). Workup and distillation (0.5 mmHg) gave 20.2 g (40%) of 16. d: 0.865; b.p. (0.5 mmHg) 74—76°C. NMR (CCl_4): δ 0.18 (s, 18H, TMS), 1.64 (m, 4H, CH_2); 2.25 ppm (m, 4H, propargyl). IR (CCl_4): 2135, 1250, 825 cm^{-1}; mass spectrum (20 eV): *m/e*: 250(1), 162(56), 161(36), 73(100). Anal. Found: C, 66.89; H, 10.24. $C_{14}H_{16}Si_2$ calcd.: C, 67.12; H, 10.46%.

b. 1,6-(Bistrimethylsilyl)-1,5-hexadiyne. The di-Grignard reagent of 1,5-hexadiyne was generated by treating ethyl magnesium bromide (1 mol) in tetrahydrofuran with 1,5-hexadiyne (25 g, 0.321 mol, 0.641 equivalents). To the resulting solution was added trimethylsilyl chloride (140 g, 1.3 mol). After workup concentration yielded a yellowish solid, which could be recrystallized from hexane. M.p. 37—38°C; NMR (C_6D_6): δ 0.1 (s, 18H, Si—Me_3), 2.21 ppm (s, 4H, CH_2). IR: 2170 cm^{-1}; *m/e*: 222(6), 207(100), 155(20), 96(25), 73(29). Anal. Found: C, 64.44; H, 9.71. $C_{12}H_{22}Si$ calcd.: C, 64.87; H, 9.91%.

General method for NMR monitored reactions of 5 and 2. A sample of 5 [11] was dissolved in benzene-d_6, and filtered into an NMR tube through a sintered glass frit or a plug of glass wool in a pipette. The tube was sealed with a rubber septum in the dry box and one equivalent of 2 was added by syringe in several portions outside the box. The NMR spectrum was monitored between additions.

Synthesis and reactions of 9c.

1. Synthesis of 9c. A sample of 5 was prepared by dissolving 121 mg (0.187 mmol) of 5 in a small amount of benzene, filtering the resulting solution through a fine sintered glass frit, and diluting the solution to a total volume of 12 ml. Neat 2c (31 μl, 0.197 mmol) was added dropwise to the stirred purple-red solution and the mixture was stirred 3 h 10 min to give a yellow-brown solution. The solvent was removed, leaving a yellow-brown oil which yielded a light brown powder when treated with 1 ml of 10% (by volume) benzene in petroleum ether. The solid was collected and the residue from the supernatent chromatographed (1 × 20 cm, Woelm neutral alumina V, 15% H_2O by weight, 20% (by volume) benzene in petroleum ether as eluent) to give additional product which was collected in a yellow band behind a pale brown forerun (composed primarily of triphenylphosphine). The chromatography fraction was combined with the crude product solid which was dissolved in THF and filtered. The solvent was removed to give 90 mg of crude product (56 mol % 9c and 44% PPh_3 by NMR, 65% yield based on starting 5). Crystallization from THF/petroleum ether gave a mixture of brown cubes of 9c and white needles of PPh_3. The PPh_3 was washed out with acetonitrile to give 27 mg (28% yield) of pure 9c, m.p. 171—173°C. NMR (C_6D_6): δ 1.2—2.8 (broad featureless m's, 8H, $(CH_2)_4$), 2.27 (broad s, 6H, CH_3), 4.80 (s, 5H, Cp), 6.9—7.15 (m, 9H, *m*- and *p*-phenyl), 7.33—7.67 (m, 6H, *o*-phenyl) ppm; Anal.: Found: C, 76.00; H, 6.46; Co, 11.37; P, 5.92. $C_{33}H_{34}CoP$ clacd.: C, 76.13; H, 6.60; Co, 11.32; P, 5.95%.

2. Reaction of 9c with 2-butyne. A sample of 9c was dissolved in benzene-d_6. To this was added a large excess of 2-butyne (350 μl, 2.42 × 10^{-1} g, 4.48 × 10^{-3} mol) and the tube was sealed. The tube was initially heated to 50°C (1 h) without any reaction being observed. Pyrolysis was continued at 80—90°C for 3 days. The solution was concentrated and the resulting brown solid washed with petroleum ether. The petroleum ether soluble fraction was collected in the dry box but chromatographed in air (20 mm × 0.8 mm Florisil/petroleum ether). The organic products were collected after 50 ml of solvent. The two products were then separated by GLC at 155°C, and identified as hexamethyl benzene and 2,3,4,5-tetramethyl tetralin [12].

3. Reaction of 9c with carbon monoxide. A sample of 9c (0.077 g, 1.48 ×

10^{-4} mol) was dissolved in 30 ml of benzene and heated at 90°C under 3.5 atm of carbon monoxide for 18.5 h. Two new absorptions were observed in the IR; 1595 cm^{-1} s and 1730 cm^{-1} w. (In a separate reaction, the yield of 11c was estimated by NMR as 70% by reference to a ferrocene internal standard.) The solution was concentrated and petroleum ether added to precipitate red needle-like crystals of 11c; m.p. 180—181°C. See text for spectral data.

Synthesis and reactions of 9b

1. Synthesis of 9b. A filtered solution of 5 (410 mg, 0.632 mmol) in 39 ml of benzene was prepared as in the synthesis of 9c. Neat 2b (100 μl, 0.675 mmol) was added dropwise to the stirred solution, which turned yellow-brown within 40 min after completing the addition. The reaction mixture was stirred for an additional 1 h 35 min, the solvent was removed and the resulting oil was treated with 3 ml of 7% (by volume) benzene in petroleum ether to give a light brown powder. The crude solid was recrystallized from THF/petroleum ether to give 81 mg (25%) of pure 9b, m.p. 150—152°C. NMR (C_6D_6): δ 1.41—2.54 [broad featureless m's, 6H, $(CH_2)_3$], 2.16 (broad s, 6H, CH_3), 4.74 (s, 5H, Cp), 6.84—7.10 (m, 9H, *m*- and *p*-phenyl), 7.23—7.67 (m, 6H, *o*-phenyl) ppm. Anal. Found: C, 75.86; H, 6.70; Co, 11.25; P, 5.73. $C_{32}H_{32}CoP$ calcd.: C, 75.87; H, 6.38; Co, 11.63; P, 6.11%.

2. Reaction of 9b with carbon monoxide. An NMR tube was charged with a solution of 9b (13 mg, 0.026 mmol) in benzene-d_6 (0.31 ml of solution) and sealed under 0.152 mmol of CO in a tube of 2.54 ml total volume. The spectrum of the solution remained unchanged after heating for 2 h 35 min at 56°C. However, after 12 h at 67°C new cyclopentadienyl absorptions were visible at δ 4.56, 4.38, and 4.11 ppm and new methyl absorptions were present at δ 2.05 and 1.72 ppm. After an additional 7 h 20 min at 67°C the absorptions from 9b had disappeared and the new cyclopentadienyl resonances were present in a ratio of approximately 1/3/6, respectively. The tube was opened and the solvent removed to give a red-orange oil which was redissolved in THF and displayed IR absorptions which were assigned to: 4 (2015, 1952 cm^{-1}), cyclopentadienylcarbonyltriphenylphosphinecobalt (1940 cm^{-1}) and 11b (1597 cm^{-1}). The NMR absorptions of the solution could be similarly assigned to: 4 (δ 4.38), cyclopentadienylcarbonyltriphenylphosphinecobalt [5] (δ 4.56 ppm), 11b [δ 4.11 (s, Cp), 1.72 (s, CH_3) ppm], and tentatively to free cyclopentadienone (δ 2.05 ppm, CH_3). After the solvent was removed and the residue pumped on for 30 min an IR spectrum of a concentrated THF solution of the remaining material showed the absence of volatile 4 and a weak absorption at 1697 cm^{-1} tentatively assigned to free dienone.

Synthesis of 17. To a solution of 5 (2.75×10^{-1} g, 4.25×10^{-4} mol) was added 16 (140 μl, 0.121 g, 4.84×10^{-4} mol). The solution was stirred for 30 min and concentrated. Addition of petroleum ether yielded reddish crystals (70 mg, 25%). M.p. 117—119°C; NMR (benzene-d_6, 220 MHz): δ 5.19 (s, 5H, Cp), 0.67 (s, 18H, Si-Me_3) ppm. Anal. Found: C, 70.13; H, 7.32. $C_{37}H_{46}CoSi_2P$ calcd.: C, 69.82; H, 7.23%.

Conversion of 17 to 18. 17 (0.0378 g, 5.94×10^{-5} mol) was dissolved in benzene-d_6 and heated at 60°C for 15 minutes. The product solution was concentrated and the product obtained (97% yield) as an oil. NMR (benzene-d_6, 220

MHz): δ 4.73 (s, 5H, Cp), 0.32 (s, 18H, $Si{-}Me_3$), 2.27, 1.91, 1.63, 1.42 (four chemically different pairs of protons, broad m) ppm. Anal. Found: C, 69.89; H, 7.35. $C_{37}H_{46}CoSi_2P$ calcd.: C, 69.82; H, 7.23%.

2,5-Dimethyl-(3,4-dicarbomethoxy)benzocyclobutene. A sample of 5 (0.077 g, 1.18×10^{-4} mol) was dissolved in benzene-d_6. To this was added 2,6-octadiyne (20 μl, 2.5×10^{-2} g, 2.36×10^{-4} mol). After shaking, dimethylacetylenedicarboxylate (17 μl, 1.96×10^{-2} g, 1.38×10^{-4} mol) was added sequentially. The products were chromatographed (air, 50 × 2 mm florisil, eluent petroleum ether/diethyl ether gradient). A single ester-containing compound (15) was isolated. IR (CCl_4): 1725 cm^{-1}; NMR (benzene-d_6): δ 3.5 (6H, CO_2CH_3), 2.5 (4H, CH_2), 2.05 (6H, CH_3) ppm; mass spectrum: *m/e* *P* 248(12), 216 (*P*—MeOH) (100).

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