

Scheme I

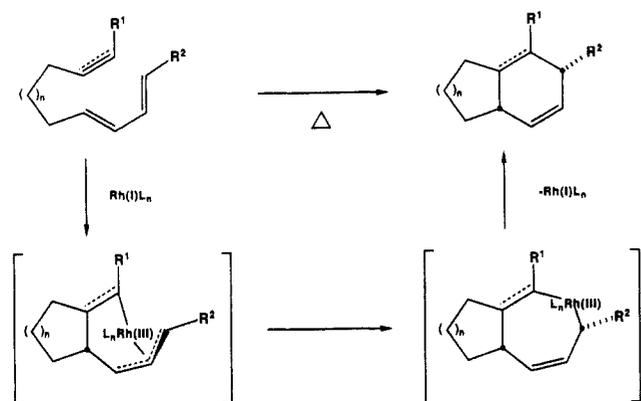


Table I. Rh(I)-Catalyzed [4 + 2] Cycloadditions

Substrate	Product	(yield %)	Reaction Conditions
		(96 %)	(Ph ₃ P) ₃ RhCl - TFE 55 °C, 15 min
		(93 %)	(Ph ₃ P) ₃ RhCl - TFE 55 °C, 45 min
		(87 %)	[(i-C ₃ H ₇ O) ₂ P] ₂ Rh* - THF ¹² 55 °C, 15 min
		(78 %)	(Ph ₃ P) ₃ RhCl - TFE 55 °C, 45 min
		(98 %)	[(i-C ₃ H ₇ O) ₂ P] ₂ RhCl - THF 25 °C, 60 h
		(61 %)	[(i-C ₃ H ₇ O) ₂ P] ₂ RhCl - THF 55 °C, 18 h

formylations⁹ results in dramatic increases in reaction efficiency. Accordingly, several new Rh(I) complexes were generated in situ by the reaction of [RhCl(cyclooctene)]₂ with various phosphite ligands (2 equiv)¹⁰ and examined for efficacy in the intramolecular [4 + 2] cycloaddition reaction. In consonance with the findings of Van Leeuwen and Roobeck,^{8,9} a significant enhancement in cyclization efficiency was observed when d⁸ rhodium complexes modified by 1,1,1,3,3,3-hexafluoro-2-propoxy bearing phosphite ligands were employed as catalysts. In addition, these highly active catalyst systems were found to be effective in THF solution at temperatures as low as 25 °C.

The generality of the rhodium-catalyzed intramolecular [4 + 2] cycloaddition reaction for the elaboration of 5/6 and 6/6 ring systems was subsequently demonstrated by its application to several representative substrates (Table I).¹¹

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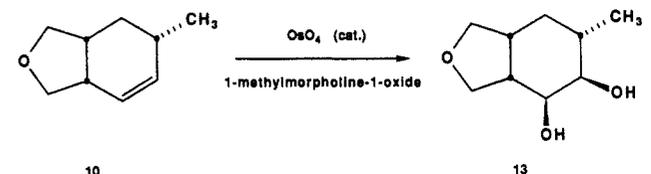
(10) Larock, R. C.; Oertle, K.; Potter, G. F. *J. Am. Chem. Soc.* **1980**, *102*, 190.

(11) In a representative experiment, a 12-cm test tube containing [(C₈-H₁₄)₂RhCl]₂ (17.9 mg, 0.025 mmol) was flushed with Ar and then charged with dry THF (4 mL). To the stirred solution was added (i-C₃H₇O)₂P (53.1 mg, 0.100 mmol) followed by **9** (276 mg, 2.000 mmol). The pale yellow solution was then allowed to stir at 25 °C for 60 h (or, alternatively, was warmed to 55 °C for 2.5 h). The reaction mixture was filtered through 3 g of alumina (30% EtOAc-C₆H₁₄ for elution), and the solvents were evaporated. Flash chromatography of the residue on silica gel followed by evaporative distillation provided **10** (270 mg, 98%).

(12) In this instance, cyclization was effected by exposure of **5** to 5 mol % of the cationic complex prepared by the sequential treatment of [(C₈-H₁₄)₂RhCl]₂ with AgO₃SCF₃ (1.0 equiv/Rh)¹³ followed by (i-C₃H₇O)₂P (2.2 equiv).

Several synthetically pertinent features serve to differentiate the reactivity profile of Rh(I) catalysts from their Ni(0) counterparts.³ Of primary interest is the observation that these cycloadditions are not confined to substrates bearing nonterminal alkynes as [4 + 2] addends. Terminal alkynes and, more importantly, alkenes readily participate in representative cyclizations to provide the corresponding bicyclic products in good to excellent yield. In addition, Rh(I)-catalyzed cycloadditions were found to proceed with excellent levels of diastereoselection. In every instance examined to date, Rh(I)-catalyzed cyclization under optimized conditions led to the formation of an exclusive cycloadduct as determined by GC as well as ¹H and ¹³C NMR.^{5,7}

In the case of **10**, rigorous proof of relative stereochemistry was provided by single-crystal X-ray diffraction analysis of the corresponding crystalline diol **13**.



The preceding examples indicate that the Rh(I)-catalyzed [4 + 2] cycloaddition reaction is an effective means for the elaboration of a range of bicyclic intermediates from acyclic precursors under exceedingly mild reaction conditions. The utilization of chiral phosphines in enantioselective variations of this novel annulation process as well as its application to problems of synthetic interest will be the topics of future reports from this laboratory.

Acknowledgment. Support for this research by grants from the Alfred P. Sloan Foundation and the National Institutes of Health are gratefully acknowledged. The authors thank Ray Larsen of the MSU X-ray facility for obtaining the crystal structure for diol **13**.

Supplementary Material Available: Spectroscopic and physical data (¹H NMR, IR, high-resolution mass spectra, and mp) for the cycloadducts **2**–**12** and the diol **13** (3 pages). Ordering information is given on any current masthead page.

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Synthesis and Crystal Structure of a Stable Hexacobalt Complex of Cyclo[18]carbon

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Recently, we reported the gas-phase formation of neutral cyclo[18]carbon (C₁₈) from a stable precursor prepared by synthesis and characterized by X-ray crystallography.^{1,2} We now report the synthesis and the structure of C₁₈, stabilized as the transition-metal complex **1** (Scheme I).

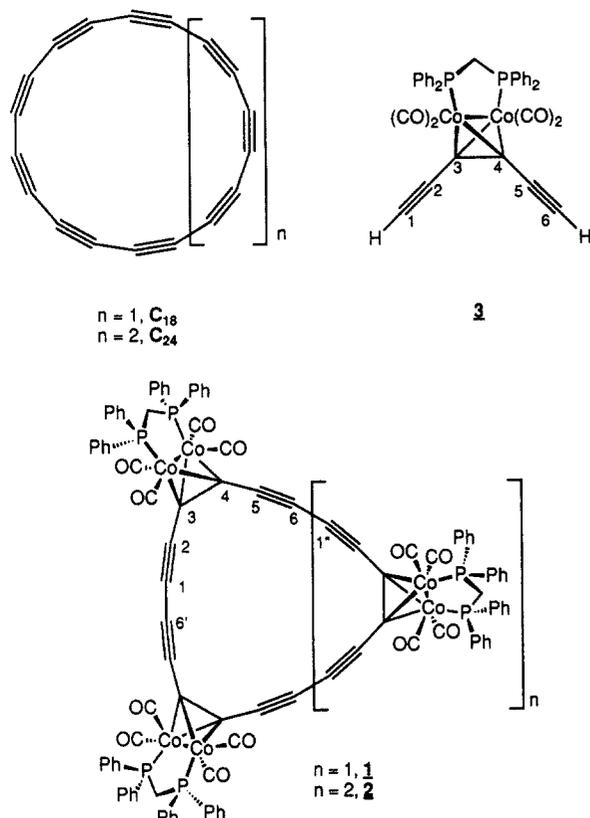
Conceptually, the synthesis of **1** originates from the ≡C—C angle bending that occurs in alkynes upon formation of (μ-acetylene)dicobalt hexacarbonyl complexes. The bending angle after complexation lies between 136.2° and 144.4° for complexes of known X-ray crystal structure.³ Dicobalt hexacarbonyl

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(2) For other precursors to the cyclo[n]carbons, see: (a) Rubin, Y.; Diederich, F. *J. Am. Chem. Soc.* **1989**, *111*, 6870–6871. (b) Rubin, Y.; Knobler, C. B.; Diederich, F. *J. Am. Chem. Soc.* **1990**, *112*, 1607–1617.

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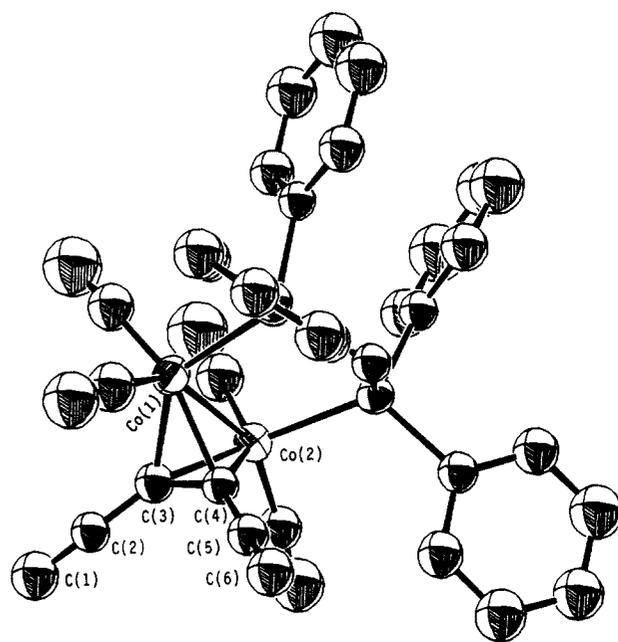
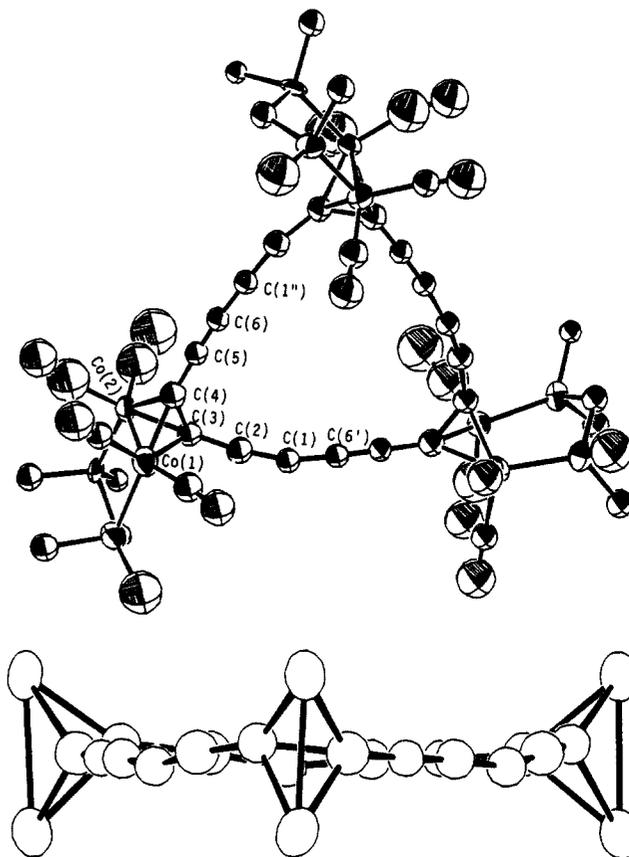
Scheme I



fragments^{4,5} have been used as protecting groups to allow geometrically disfavored cyclization reactions by bending an alkyne moiety,⁶ or to stabilize strained alkynes.⁷

Complex **5** was prepared first as a model to test the Eglinton–Glaser oxidative coupling of (μ -acetylene)dicobalt complexes bearing a free terminal alkyne unit. Ligand exchange of two carbonyls on $[(\mu\text{-bis(trimethylsilyl)butadiyne})Co_2(CO)_6]$ with bis(diphenylphosphino)methane (dppm) (benzene, reflux, 12 h, 85%) afforded **4**, which was deprotected at the alkynyl group to **5** with tetrabutylammonium fluoride (TBAF) (THF/CH₃OH, 10:1, 12 h, 97%) (Scheme II).⁹ The butadiyne complex **6** was obtained as stable, deep red crystals when stronger desilylation conditions were used (TBAF, moist THF, 25 °C, 83%). Oxidative coupling of **5**, using standard Eglinton–Glaser conditions¹⁰ (Cu(OAc)₂, pyridine, 25 °C, 24 h, 75%), furnished dimer **7**, demonstrating the applicability of this method to the coupling of (dppm)Co₂(CO)₄ derivatives like **3**.¹¹

Next, triyne **9**¹² was prepared in gram quantities by flash vacuum pyrolysis of cyclobutenedione **8**^{2b} in 69% yield.¹³ The

Figure 1. X-ray crystal structure of **3**.Figure 2. X-ray crystal structure of **1**. Above: all except the ipso carbons from the phenyl groups omitted for clarity. Below: edge view with CO and dppm ligands omitted for clarity.

reaction of **9** with Co₂(CO)₈ (*n*-hexane, 25 °C, 12 h) and subsequent ligand exchange with dppm (toluene, reflux, 2 h) furnished **10** in 75% yield (Scheme II). The bulky triisopropylsilyl groups in **9** were chosen to direct complexation toward the less hindered 3,4-triple bond. Deprotection of **10** with TBAF (moist THF, 25 °C, 5 min, 100%) gave the hexatriyne complex **3** as stable, dark

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(9) Spectroscopic data (¹H NMR, ¹³C NMR, IR, EI-MS or FAB-MS, UV-vis) and elemental analyses support the structures proposed for all new compounds.

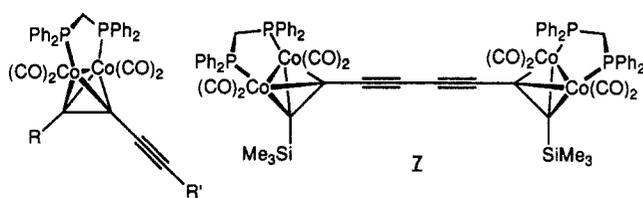
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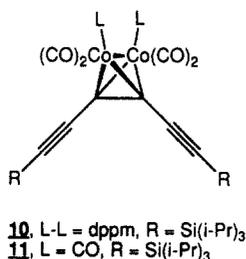
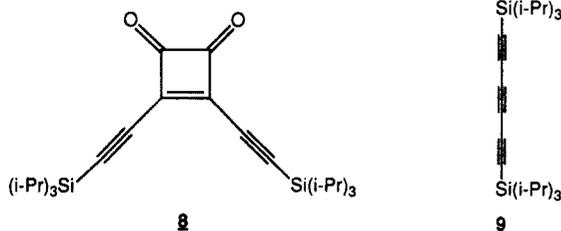
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(13) This new method for the preparation of **9** and other triynes and pentaynes will be reported later: Rubín, Y.; Knobler, C. B.; Diederich, F., unpublished results.

Scheme II



4. R = R' = SiMe₃
 5. R = SiMe₃, R' = H
 6. R = R' = H



10. L-L = dpmm, R = Si(i-Pr)₃
 11. L = CO, R = Si(i-Pr)₃

red crystals, characterized by X-ray crystallography¹⁴ (Figure 1). In contrast, attempts to deprotect the Co₂(CO)₆ complex 11, prepared in 62% yield from 9 as described above, were unsuccessful. With values of 137.7° and 138.8°, respectively, the angles C(2)–C(3)–C(4) and C(3)–C(4)–C(5) in 3 are of similar magnitude to those of previously described (μ-acetylene)Co₂(CO)₆ complexes.³ Compounds 6 and 3 provide stable, well-characterized cobalt complexes of the explosive compounds 1,3-butadiyne¹⁵ and 1,3,5-hexatriyne.^{16,17}

The oxidative cyclization of 3 (Cu(OAc)₂, pyridine, 45 °C, 48 h, [3] = 0.01 M) afforded trimer 1 (33%) and tetramer 2 (5.4%), both as air-stable shiny black needles.¹⁸ Recrystallization of 1 from 1,2-dichloroethane/methylcyclohexane provided crystals suitable for X-ray analysis¹⁹ (Figure 2). The crystal structure

(14) X-ray crystal data for 3 (C₃₅H₂₄O₄Co₂P₂CHCl₃): *M_r* = 807.8; monoclinic; space group = *P*2₁; *Z* = 2; *a* (Å) = 8.487 (2); *b* (Å) = 18.443 (3); *c* (Å) = 11.842 (2); β = 101.290 (5)°; *V* (Å³) = 1818; *D_{calc}* (g cm⁻³) = 1.26. Data were collected on a Huber diffractometer constructed by Professor C. E. Strouse, UCLA, using Mo Kα radiation, 2θ ≤ 45°, giving 2460 unique reflections; the structure was solved by direct methods (MULTAN80), yielding *R* = 0.047 and *R_w* = 0.058 for 2157 reflections with *I* > 3σ(*I*).

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(16) The preparation of a [Co₂(CO)₆]₂ complex of 1,3-butadiyne and a [Co₂(CO)₆]₃ complex of 1,3,5-hexatriyne in very low yields has been reported: Peyronel, G.; Ragni, A.; Trogu, E. F. *Gazz. Chim. Ital.* 1967, 97, 1327–1343.

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(18) Spectral data for 1, 2, and 3. Compound 3: mp > 120 °C dec; IR (CHCl₃) ν (≡CH) 3305, (C≡C) 2075, (C=O) 2053, 2047, 1993 cm⁻¹; UV (CH₂Cl₂) λ_{max} (nm) 280 (ε 26 800), 340 sh (11 100), 393 sh (2430); ¹H NMR (360 MHz, CD₂Cl₂) δ 3.76 (t, ²J_{HP} = 1.4 Hz, 1,6-H); ¹³C NMR (90.6 MHz, CD₂Cl₂, gated decoupling) δ 69.2 (br s, C-3,4), 84.5 (d, ¹J_{CH} = 252.2 Hz, C-1,6), 85.7 (d, ²J_{CH} = 49.9 Hz, C-2,5). Compound 1: IR (CH₂Cl₂) ν (C≡C) 2107, (C=O) 2057, 2042, 2000 cm⁻¹; UV (CH₂Cl₂) λ_{max} (nm) 254 sh (ε 119 500), 291 (106 000), 370 (91 400), 445 sh (36 700), 546 sh (12 400); ¹³C {¹H} NMR (90.6 MHz, CD₂Cl₂) δ 72.0 (br s, C-3,4), 84.0 (br s, C-2,5), 88.0 (s, C-1,6). Compound 2: IR (CHCl₃) ν (C≡C) 2100, (C=O) 2043, 2033, 1993 cm⁻¹; UV (CH₂Cl₂) λ_{max} (nm) 268 sh (ε 141 700), 381 (122 700), 453 sh (50 900), 560 sh (15 000); ¹³C {¹H} NMR (90.6 MHz, CD₂Cl₂) δ 70.6 (br s, C-3,4), 85.0 (br s, C-2,5), 88.0 (s, C-1,6). The highly characteristic electronic absorption spectra of 1 and 2, their similar IR and NMR spectra, and their *R_f* values (TLC, SiO₂, CH₂Cl₂/hexane, 1:1; 1, *R_f* = 0.12; 2, *R_f* = 0.08) strongly suggest that 2 is a cyclic tetramer.

shows that 1 is formally a complex of cyclo[18]carbon. The C₁₈ ring is nearly planar, the largest deviation from the least-squares plane through the 18 carbon atoms being 0.19 Å. The angles C(2)–C(3)–C(4) and C(3)–C(4)–C(5) are 131 (4)° and 134 (4)°. The diyne units show considerable deviation from linearity as a result of C≡C–C bending; the C(2)–C(1)–C(6') angle, 161 (5)°, is the smallest.

Cyclo[18]carbon is highly stabilized as a ligand in complex 1. It differs from free C₁₈ by variations in bond lengths and angles,¹ by partial deconjugation of the π-system,²⁰ and by the steric shielding provided by the three (dpmm)Co₂(CO)₄ units. Attempts to free C₁₈ of the protecting groups by mild oxidation of 1 are now under way.

Acknowledgment. We thank the National Science Foundation for support.

Supplementary Material Available: Experimental details of the crystal structure determinations for 1 and 3, fully labeled views of the two structures, and tables of their atomic coordinates, equivalent isotropic thermal parameters, bond angles, and bond lengths (18 pages); tables of observed and calculated structure factors for 1 and 3 (21 pages). Ordering information is given on any current masthead page.

(19) X-ray crystal data for 1 (C₁₀₅H₆₆O₁₂Co₆P₆): *M_r* = 2059.13; hexagonal; space group = *P*6₃; *Z* = 2; *a* (Å) = 20.922 (5); *c* (Å) = 16.385 (4); *V* (Å³) = 6211; *D_{calc}* (g cm⁻³) = 1.20; data collection as in footnote 14, 2θ ≤ 42°, 4914 unique reflections, solution by heavy-atom methods gave *R* = 0.126 and *R_w* = 0.161 for 1856 reflections with *I* > 3σ(*I*). Highly disordered solvent refinement.

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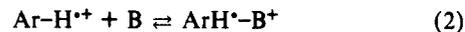
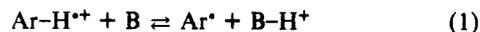
Kinetic Isotope Effects and Negative Activation Energies for Proton Transfer from 9-Phenylanthracene Cation Radical to Hindered Nitrogen-Centered Bases

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The p*K_a* of benzene cation radical in acetonitrile has been estimated to be equal to -4.¹ This suggests that reaction 1, where Ar-H^{•+} is a benzene cation radical and B is pyridine or a substituted pyridine, has an equilibrium constant of the order of 10¹⁰ or greater in acetonitrile at 298 K. Yet, there has been no



convincing evidence reported that this reaction takes place in solution. Twenty years ago it was suggested² that the primary reactions during the oxidation of benzene and biphenyl in acetonitrile consist of formation of the cation radicals followed by deprotonation to give the corresponding aryl radicals. However, no evidence was presented to support the proton transfer reactions, and subsequent work has shown that arene cation radicals undergo addition reactions 2 with nucleophiles in essentially barrier-free reactions rather than proton transfer.³⁻⁵ We now report the first evidence for reaction 1 and show that this reaction can only compete with reaction 2 when the base is rendered non-nucleophilic by steric constraints.

The reactions of 9-phenylanthracene (PAH) cation radical with 4-substituted pyridines in acetonitrile at 293 K involve nucleophilic

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