128. Synthetic Routes to the Cyclo[*n*]carbons

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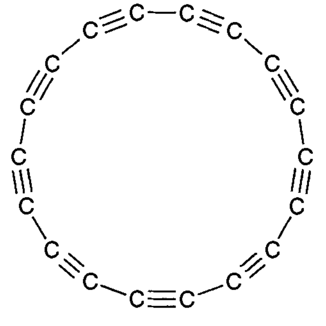
(7.VI.94)

Cyclo[*n*]carbons (*cyclo*-C_n) are *n*-membered monocyclic rings of sp-hybridized C-atoms with unique electronic structures resulting from two perpendicular systems of conjugated π-orbitals, one in-plane and one out-of-plane. Several synthetic approaches to generate *cyclo*-C_{18} from stable precursors were investigated. In a six-step sequence from anthracene, tris(anthraceno)hexadehydro[18]annulene **5** was prepared and shown by laser-desorption time-of-flight mass spectrometry to generate C_{18} in three successive *retro-Diels-Alder* reactions, together with anthracene as the by-product. The attempted preparation of C_{18} by flash-vacuum pyrolysis of **5** using solvent-assisted sublimation only afforded anthracene next to polymers. The reaction of 1,6-bis(triisopropylsilyl)hexa-1,3,5-triyne with $[Co_2(CO)_8]$ followed by exchange of two CO groups for a bridging bis(diphenylphosphino)methane (dppm) ligand gave Co complex **22** which, after removal of the silyl groups, was oxidatively cyclized to afford the very stable trimeric and tetrameric macrocycles **6** and **7**, complexes with *cyclo*-C_{18} and *cyclo*-C_{24}, respectively. An X-ray crystal structure established the identity of **6** and showed that the butadiyne units within the C_{18} core are considerably bent. Attempts to free *cyclo*-C_{18} from the coordinating metal atoms in **6** did not succeed, presumably due to the steric shielding of the Co-atoms by the dppm ligands. Low-temperature matrix isolation studies using IR and UV/VIS spectroscopy showed that irradiation of carbon oxide **2** ($C_{24}O_6$) leads to ketene intermediates and, by subsequent loss of six CO molecules, presumably to *cyclo*-C_{18}.

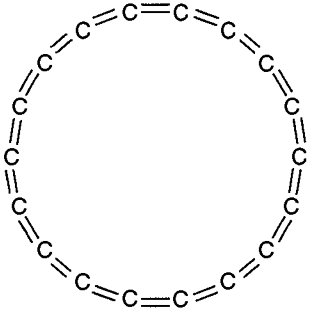
1. Introduction.

– The preparation of molecular and polymeric carbon allotropes represents a rapidly developing frontier of synthetic chemistry [1] [2]. Acetylenic scaffolding forms the basis for many of these structures [3]. In 1987, before macroscopic quantities of the fullerenes [4] became available [5], we initiated a research program aimed at preparing molecular carbon allotropes from stable, well characterized precursors [6]. The first target compound in this program was *cyclo*-C_{18}, a member of the cyclo[*n*]carbon



1a

cyclo-C_{18}

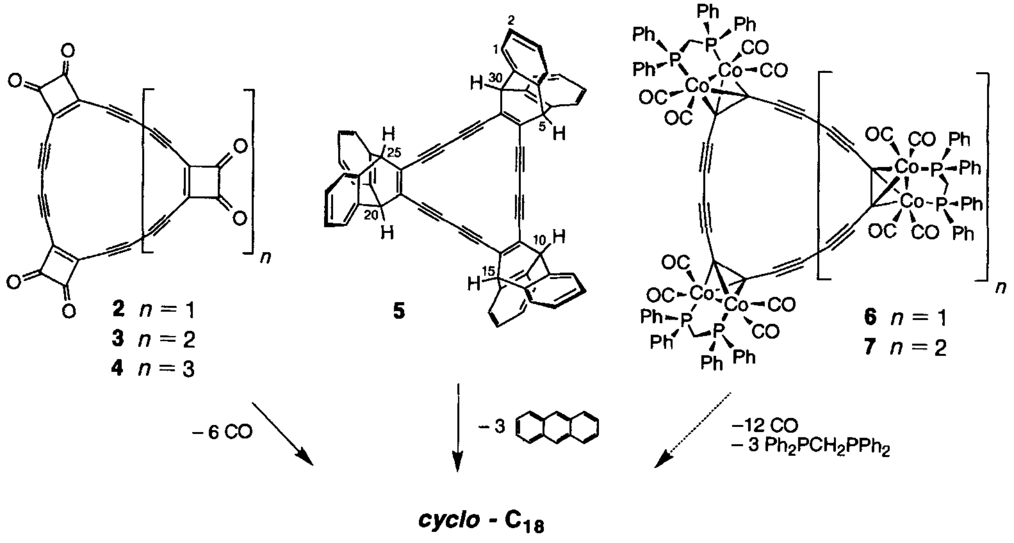


1b

family, n-membered monocyclic rings of sp-hybridized C-atoms with unique electronic structures resulting from two perpendicular systems of conjugated π-orbitals, one in-plane and one out-of-plane. Different theoretical predictions of the electronic structure exist for *cyclo*-C_{18}, which is expected to show special *Hückel*-aromatic stabilization as a result of the two orthogonal $(4n + 2)$ π-electron systems [7]. Self-consistent-field (SCF) calculations with a 3-21G or larger basis set predict that the cyclic acetylenic D_{9h} structure **1a** with alternating bond lengths represents the ground-state geometry [6]. But optimizations at the *Møller-Plesset* second-order perturbation-theory (MP2) level including valence-electron correlations [8] as well as density functional theory calculations [9] favor the cumulenic D_{18h} structure **1b** as the most stable planar monocyclic structure.

To prepare *cyclo*-C_{18} and the higher analogs *cyclo*-C_{24} and *cyclo*-C_{30}, we explored the three synthetic routes shown in *Scheme 1*. *Route 1*, *via* the carbon oxides **2**–**4** was already described in detail elsewhere [10] [11]. In unexpected developments, the positive cyclocarbon ions C_{18}^{+}, C_{24}^{+}, and C_{30}^{+} produced by exhaustive decarbonylation of **2**–**4** were shown in *Fourier*-transform mass spectrometric (FT-MS) experiments to undergo gas-phase ion-molecule coalescence reactions leading to formation of fullerene ions [11] [12].

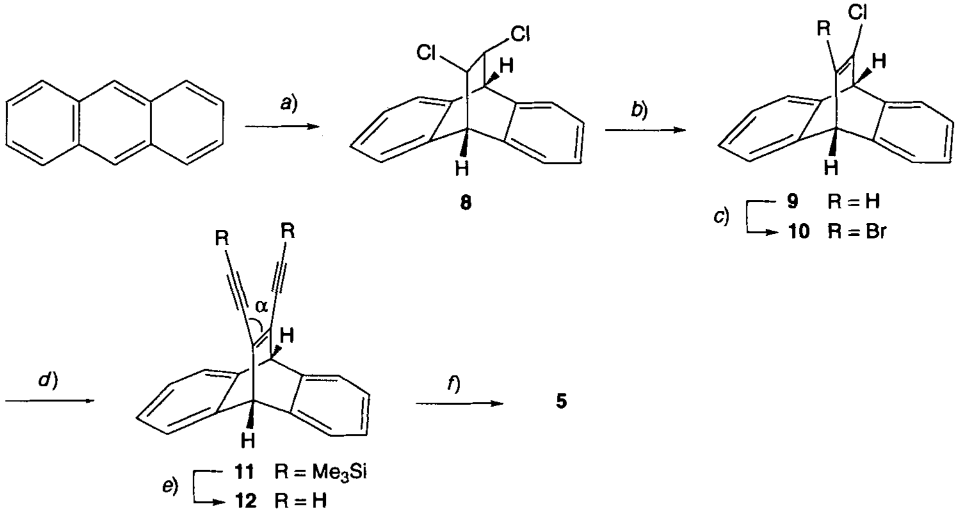
Scheme 1. *Three Synthetic Routes to* cyclo-C_{18}



Herein, we report matrix isolation experiments with **2** in attempts to prepare isolable quantities of *cyclo*-C_{18}. *Routes 2* and *3* to cyclocarbons *via* the cyclic precursors **5**–**7** were subject of preliminary communications [6] [13], and a full account of the synthetic work in these approaches is given here.

2. Results and Discussion. – 2.1. *The* retro-Diels-Alder *Route to* cyclo-C_{18}. Compound **5** was chosen as a direct precursor to *cyclo*-C_{18} since it contains the same 18-membered macrocyclic framework and should lose three anthracene molecules in a *retro-Diels-Alder* reaction under thermal conditions [6]. The synthesis of **5** (*Scheme 2*) starts with the

Scheme 2. *Synthesis of Hexadehydro[18]annulene* **5**



a) *trans*-ClHC=CHCl, 500 lbs N_2, 215°, 90%. *b*) *t*-BuOK, THF, reflux, 90%. *c*) BuLi/hexane, TMEDA, THF, −78°; then Br_2, −60°, 86%. *d*) CuI, $BuNH_2$, $[Pd(Ph_3)_4]$, $Me_3SiC{\equiv}CH$, 50°, 87%. *e*) 1.0M aq. KOH, MeOH, 20°, 98%. *f*) $Cu(OAc)_2$, pyridine/C_6H_6/MeOH, 50°, 25%.

Diels-Alder reaction of anthracene and *trans*-dichloroethene to give **8** [14]. Subsequent dehydrochlorination to the 9,10-ethenoanthracene **9** was accomplished with *t*-BuOK [15]. The bromination to **10** was best achieved by simply adding elemental Br_2 to a solution of the vinyl anion at −78°. Reacting the anion with 1,2-dibromoethane as previously described [15] was less effective and yielded only a 1:1 mixture **9**/**10**. The Pd-catalyzed alkynylation of **10** with (trimethylsilyl)acetylene in $BuNH_2$ as solvent afforded the dialkynyl derivative **11** in high yield [16]. When the alkynylation was run in benzene under conditions described by *Vollhardt* and *Winn* (3 equiv. of $BuNH_2$, 0.1 equiv. of CuI, 0.05 equiv. of $[Pd(PPh_3)_4]$) [17], an intractable mixture of starting material, mono-, and dialkynylated product was produced. Deprotection of **11** with aqueous KOH in MeOH gave the diethynyl derivative **12** quantitatively as *very unstable* crystals, which in one case ***exploded*** spontaneously.

The oxidative coupling of **12** under *Eglinton-Glaser* conditions [18] afforded the cyclic trimer **5** as the only identifiable product in 25% yield. The absence of dimer, tetramer, or pentamer can be explained by the steric matching between monomer **12** and the macrocyclic oligomer, which is found experimentally to determine largely the product distributions in *Eglinton-Glaser* couplings of enediynes to form dehydroannulenes [1] [19]. The C=C–C(sp) angle, α, in **12** (see *Scheme 2*) is calculated by MM2 (molecular mechanics 2) as 125° and by AM1 (*Austin* model 1) as 127°, values close to the average value of 123.3° found for the corresponding bond angles in the X-ray crystal structure of **5**. Whereas the parent compound 1,3,7,9,13,15-hexadehydro[18]annulene is unstable in the solid state and explodes at *ca.* 85° [20], compound **5** can be heated in a sealed tube to 250° in the solid state without appreciable decomposition and is highly stable to air. Deep-red needles of **5** suitable for X-ray analysis were obtained by recrystallization from boiling pyridine. The crystal structure [1] [6] shows a nearly perfectly planar hexadehydro[18]annulene ring which is sterically shielded by the six benzene rings and, therefore, protected with respect to bimolecular and polymerization reactions. According to both ^{1}H-NMR and electronic absorption spectroscopy, **5** is aromatic. The diatropicity of **5** is supported by the deshielding by 0.75 ppm of the bridgehead methine protons in **5** (δ 5.89) through the diamagnetic ring current of the 18 π-electron system when compared to the methine protons of **12** (δ 5.14). The UV/VIS spectrum of **5** (*Fig. 1*) shows the characteristic shape and fine structure of planar aromatic hexadehydro[18]annulenes [19] [21] with a weaker split band at λ_{max} 420 (ε = 17700 l mol^{-1}cm^{-1}) and 432 (21000) nm and a stronger band at λ_{max} 375 (87600) nm.

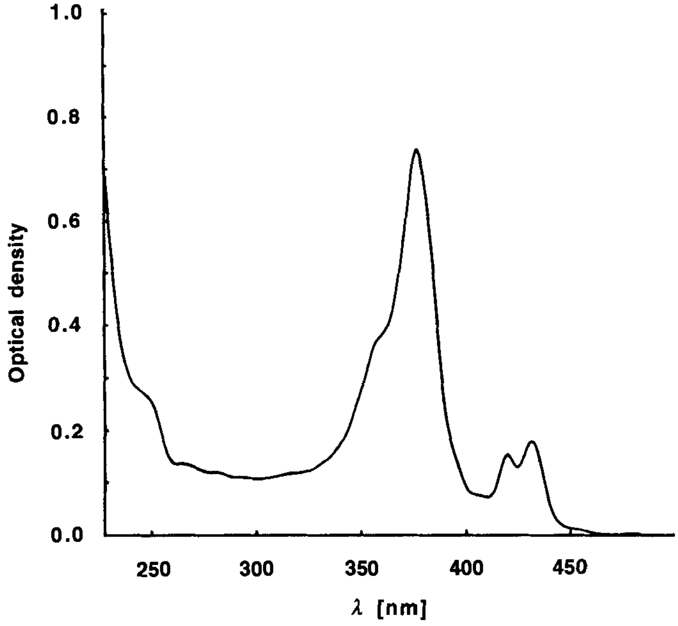
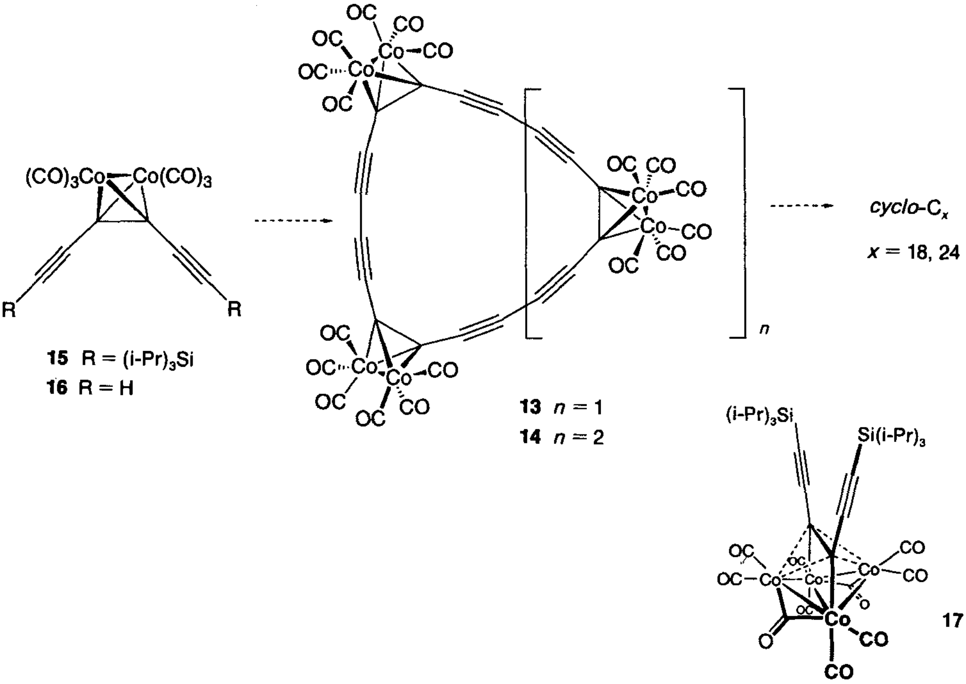


Fig. 1. *Electronic absorption spectrum of* 5 (c = 8.3 · 10^{-6} M, d = 1 cm) *in* CH_2Cl_2

Starting from **5**, *cyclo*-C_{18} was prepared in the gas phase by laser-flash heating, and the neutral product, formed by stepwise elimination of three anthracene molecules in *retro-Diels-Alder* reactions, was detected by resonant two-photon-ionization time-of-flight mass spectrometry [6]. Attempts to prepare macroscopic quantities of *cyclo*-C_{18} by flash-vacuum pyrolysis using solvent-assisted sublimation [22] only afforded anthracene and polymers.

2.2. *The Transition-Metal Complex Route to* cyclo-C_{18}. 2.2.1. *Phosphine-Free Cobalt Complexes.* Our initial efforts were directed at the preparation of the complexes **13** and **14** containing μ-(hexacarbonyl)dicobalt units, as direct precursors to *cyclo*-C_{18} and *cyclo*-C_{24} (*Scheme 3*). Conceptually, the synthesis of **13** and **14** originates from the C≡C–C angle bending that occurs in alkynes upon formation of (μ-alkyne)hexacarbonyldicobalt complexes. The bending angle after complexation lies between 136.2° and 144.4° for

Scheme 3. *Attempted Synthesis of* cyclo-C_{18} *and* cyclo-C_{24} via *the Complexes* **13** *and* **14** *Containing Hexacarbonyldicobalt Units*



complexes with known X-ray crystal structures [23]. Hexacarbonyl dicobalt fragments [24] [25] were used as protecting groups to allow geometrically disfavored cyclization reactions by bending an alkyne moiety [26] or to stabilize strained alkynes [27]. The μ-(hexacarbonyl)dicobalt units in **13** and **14** should be readily removable either by oxidation [28], alkyne-ligand exchange [29], or flash-vacuum pyrolysis [30].

From the general retrosynthetic scheme, we set out to prepare the precursor **16** from 1,6-bis(triisopropylsilyl)hexa-1,3,5-triyne *via* **15** [22] [31]. The electron density in hexa-1,3,5-triynes is highest at the central triple bond, as judged by the ^{13}C-NMR shifts for the alkyne C-atoms [22]: the most shielded C-atoms, and, therefore, the centers of highest electron density, belong to the central triple bond. This situation should disfavor the attachment of the Co-atoms to the central C-atoms, since back-donation from the Co d-orbitals to the π*-MO of an electron-poor ligand is the stabilizing factor in the bonding [29]. Accordingly, the very bulky triisopropylsilyl groups were chosen to favor the formation of the symmetrical complex **15** over the unsymmetrical complex with the $Co_2(CO)_6$ unit located next to one of the silyl substituents.

The reaction of 1,6-bis(triisopropylsilyl)hexa-1,3,5-triyne with[$Co_2(CO)_8$] in hexane first at 20° (6 h) then at reflux (3 h) under Ar afforded the symmetrical complex **15** in 11% yield in addition to a major 'by-product' (57%) which was assigned structure **17**. When the reaction was conducted at 20° for 12 h, without refluxing the solution, compound **17** was not formed and the yield of **15** greatly increased. Literature investigations showed [24] [32] that [$Co_2(CO)_8$] decomposes at 50–60° to give [$Co_4(CO)_{12}$] as a poorly soluble crystalline solid. Slow decomposition of [$Co_2(CO)_8$] during prolonged storage at room temperature also affords this compound. [$Co_4(CO)_{12}$] reacts with alkynes in solution at higher temperatures than [$Co_2(CO)_8$] to give blue-black complexes of formula [$Co_4(CO)_{10}(RC{\equiv}CR')$] [24]. Thus, we believe that the dark blue oil formed as 'by-product' has structure **17**. The analytical data support the identity of compound **17**.

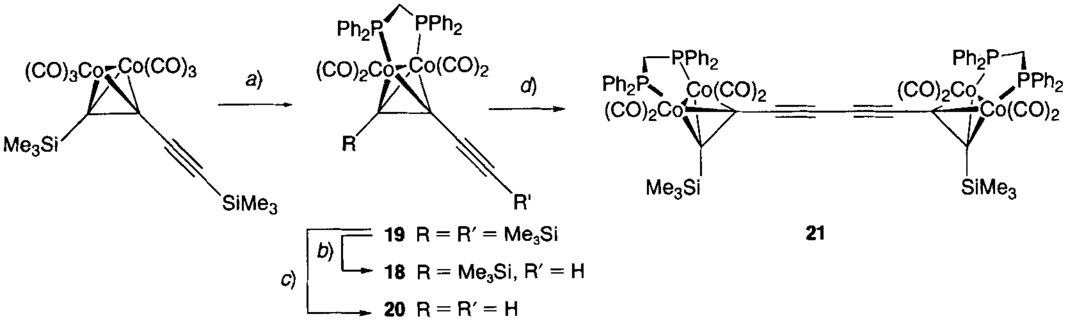
The IR spectrum of **17** shows several stretching absorptions for μ-CO groups at 2092*m*, 2042*vs*, and 2000 (sh) cm^{-1}. In addition, a resonance of medium intensity typical of a bridging CO ligand is observed at 1868 cm^{-1}. These CO absorptions are in good agreement with the ones observed for similar [$Co_4(CO)_{10}(RC{\equiv}CR')$] complexes [32]. In the ^{13}C-NMR spectrum, 2 broad CO absorptions are observed at 198.4 and 199.9 ppm, and the expected 5 absorptions for a symmetrical complex of the disilyl-protected hexatriyne are also present (δ 11.6, 18.8, 100.0, 113.9, and 134.1). Further evidence supporting structure **17** is provided by the negative-ion fast-atom-bombardment (FAB) mass spectrum. Although the parent ion itself is not present, a peak of medium intensity at *m/z* 873 corresponding to the loss of 1H and 1 CO from **17** is observed, in addition to strong fragmentation peaks at *m/z* 644 and 560 resulting from loss of $Co_2(CO)_5$ and $Co_2(CO)_8$, respectively.

Attemps to remove the $(i\text{-}Pr)_3Si$ groups in **17** with Bu_4NF in wet THF led only to decomposition. Attempted deprotection of compound **15** to obtain **16** gave the same negative result. Presumably, the two deprotection reactions did not afford the desired products due to the lability of the formed free acetylenes toward bases or nucleophiles [10] [11].

2.2.2. *Complexes Containing Bis(diphenylphosphino)methane (= Methylenebis(diphenylphosphine); dppm) as a Ligand.* The experiments described above showed that a more strongly stabilized dicobalt fragment was desirable. Hexacarbonyldicobalt complexes easily exchange two of their CO groups on neighboring Co-atoms with a number of other ligands, phosphines in particular [24]. In addition, bis(diphenylphosphino)methane (dppm) is a ligand known to strongly stabilize dinuclear transition-metal complexes by the bridging effect between two metal atoms [23a] [33]. By combining the beneficial basicity of a phosphine donor and the bridging effect of the dppm ligand, we expected to obtain a very stable dicobalt complex starting from **15**.

The butadiyne complex **18** was first prepared as a model to test the *Eglinton-Glaser* oxidative coupling of (μ-alkyne)dicobalt complexes bearing an additional free terminal alkyne group (*Scheme 4*). Ligand exchange of two CO's on [$Co_2(CO)_6$(μ-bis(trimethyl-

Scheme 4. *Synthesis of the Tetracobalt Complex* **21**

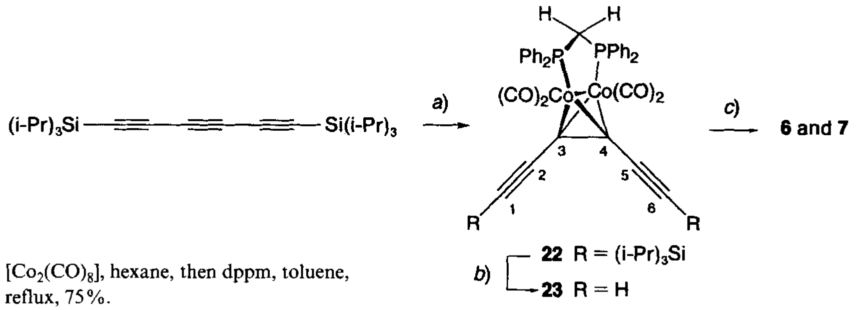


a) Dppm, benzene, reflux, 85%. *b*) Bu_4NF, THF/MeOH, 20°, 97%. *c*) Bu_4NF, THF/H_2O, 20°, 83%. *d*) $Cu(OAc)_2$, pyridine, 20°, 75%.

silyl)butadiyne)] [33] [34] with dppm afforded **19** (85%) which was deprotected almost quantitatively at the uncomplexed alkyne group with Bu_4NF in THF/MeOH 10:1 (→**18**). The butadiyne complex **20** was obtained as stable, deep red crystals when stronger desilylation conditions were used (Bu_4NF in wet THF). The oxidative coupling of **18** using standard *Eglinton-Glaser* coupling conditions [18] proceeded without any difficulty to give the dimeric compound **21**[1]).

Next, the one pot reaction of 1,6-bis(triisopropylsilyl)hexa-1,3,5-triyne with $[Co_2(CO)_8]$ and subsequent ligand exchange with dppm furnished complex **22** as the major product in 75% yield (*Scheme 5*). Deprotection with Bu_4NF in wet THF gave the hexatriyne complex **23** as very stable, dark red crystals (99%). The X-ray crystal structure of **23** [13] showed that the bond angles C(2)–C(3)–C(4) (137.7°) and C(3)–C(4)–C(5) (138.8°) are of similar magnitude to those previously described for $[Co_2(CO)_6(\mu\text{-alkyne})]$ complexes [23]. Compounds **20** and **23** constitute *stable* Co-complexes of the explosive polyynes buta-1,3-diyne and hexa-1,3,5-triyne[2]).

Scheme 5. *Synthesis of the Cobalt Complexes* **6** *and* **7** *of* cyclo-C_{18} *and* cyclo-C_{24}



a) $[Co_2(CO)_8]$, hexane, then dppm, toluene, reflux, 75%.
b) Bu_4NF, THF/H_2O, 20°, 99%.
c) $Cu(OAc)_2$, pyridine, 55°, 33% (**6**) and 5.4% (**7**).

In the ^1H-NMR spectra of **22** and **23**, the CH_2 protons of the dppm units are coupled with 2 chemically equivalent P-atoms; they appear as *t*'s broadened by the adjacent Co-atoms, with typical $^1H,^{31}P$-coupling constants of $J = 10.3$. Interestingly, the terminal alkyne protons in **23** are also coupled to the P-atoms, with $^5J(H,P) = 1.4$. The ^1H-decoupled ^{13}C-NMR spectra of **22** and **23** also show very characteristic C,P-coupling patterns. These couplings are, however, limited to the C-atoms of the Ph substituents. In the gated-decoupled ^{13}C-NMR spectrum of **23**, additional information is obtained for the 2 terminal ethynyl C-atoms, with the usual coupling constants observed for the terminal sp-C-atoms C(1) and C(6) ($^1J = 252.2$) and for the one-bond removed C-atoms C(2) and C(5) ($^2J = 49.9$).

2.2.3. *Formation and Properties of the (Cyclo[18]carbon)- and (Cyclo[24]carbon)-cobalt Complexes* **6** *and* **7**, *Respectively*. The oxidative cyclization of **23** (c = 10 mM) with $Cu(OAc)_2$ in pyridine afforded the trimer **6** (33%) and the tetramer **7** (5.4%), both as stable shiny black needles. The ^1H- and ^{13}C-NMR, as well as IR- and UV/VIS spectra of the two cycles resemble each other closely. Recrystallization of **6** from 1,2-dichloro-

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[1]) For the coupling of the anions of (alkyne)hexacarbonyldicobalt complexes, see [35].

[2]) Bis[(hexacarbonyl)dicobalt] and tris[(hexacarbonyl)dicobalt] complexes of buta-1,3-diyne and hexa-1,3,5-triyne, respectively, were prepared in very low yield, see [36]. For a bis(carbyne)tetracobalt complex of C_6, see [37]. For a mononuclear Ni complex of buta-1,3-diyne, see [38].

ethane/methylcyclohexane provided crystals for X-ray analysis which demonstrated that the trimeric cycle is formally a complex of *cyclo*-C_{18} [13]. The diyne units show striking deviations from linearity as a result of $C\equiv C-C$ bending; the C(2)–C(1)–C(6′) angle, 161 (5)°, is the smallest (*Fig. 2*). The C_{18} ring is nearly planar, the largest deviation from the least-squares plane through the 18 C-atoms being 0.19 Å. The angles C(2)–C(3)–C(4)

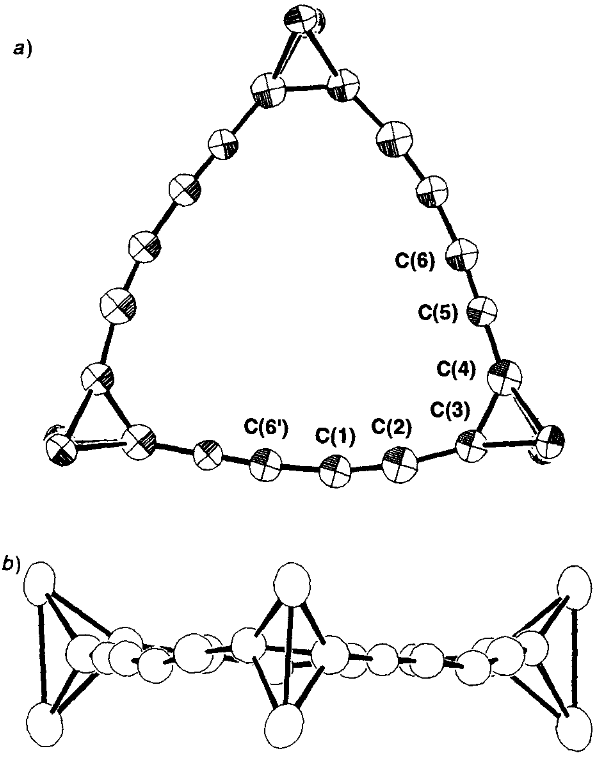


Fig. 2. a) *Partial view of the X-ray crystal structure of* **6** [13] *and* b) *side view of the* $C_{18}Co_6$ *portion.* The dppm and CO ligands are omitted.

and C(3)–C(4)–C(5) at the (μ-alkyne)dicobalt moieties are 131 (4) and 134 (4)°, respectively. Complex **6** differs from *cyclo*-C_{18} by variations in bond lengths and angles, by deconjugation of the π-system to some extent [39], and by the steric shielding provided by the three $Co_2(CO)_4$(dppm) units. Nevertheless, its considerable stability supports our expectations that *cyclo*-C_{18} is a stable, isolable compound.

The UV/VIS absorption spectra of **6** and **7** provide affirmation that partial macrocyclic conjugation exists in these compounds (*Fig. 3*). In particular, the intensities of the bands at λ_{max} 370 and 381 nm for **6** and **7**, respectively, are much higher than the triple and quadruple of the corresponding band intensity of the monomer **23** at λ_{max} 340 nm. They are also shifted to the red by 30 and 41 nm, respectively, in comparison to monomer **23**.

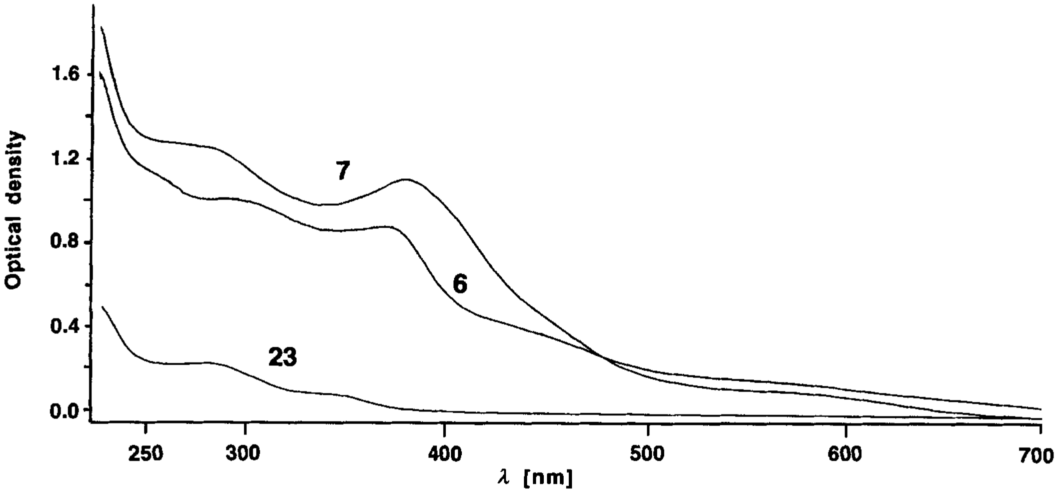


Fig. 3. *Electronic absorption spectra of the cobalt complexes* **23**, **6**, *and* **7** *in* CH_2Cl_2 ($c = 8.5 \cdot 10^{-6}$ M, $d = 1$ cm)

Decomplexation of **6** and **7** to give the free cyclocarbon has thus far been unsuccessful. Attempts to free *cyclo*-C_{18} of the protecting groups by oxidation of **6** with ceric ammonium nitrate [28], 4-methylmorpholine *N*-oxide [35], or I_2 gave only polymers. Ligand exchange with a less donating alkyne, *i.e.* dimethyl acetylenedicarboxylate, was also tried, but also failed to produce free *cyclo*-C_{18} [29]. This interesting ligand exchange happens readily with hexacarbonyldicobalt complexes, due to the energy lowering of the π^*-orbital of the alkyne, which favors back-donation from the d-orbitals of the Co-atoms. In **6** and **7**, the basic phosphine ligands presumably stabilize the complexes by increasing the electron density in the d-orbitals of the Co-atoms; thus, no ligand exchange can take place. In addition, the steric shielding of the bulky Ph substituents must hinder an efficient approach of the electron-poor alkyne near the Co-atoms. Future experiments should be directed at the preparation of the phosphine-free complexes **13** and **14**, which should undergo decomplexation more readily than **6** and **7**.

2.3. *Low-Temperature Matrix Isolation Experiments on Carbon Oxide* **2**. Laser-desorption FT-MS experiments had shown that the carbon oxides **2**–**4** readily loose all their CO groups to yield the corresponding cyclocarbon ions [11] [12]. To gain evidence for the macroscopic formation of *cyclo*-C_{18} from carbon oxide **2** ($C_{24}O_6$), we carried out low-temperature FT-IR and UV/VIS spectroscopic experiments. Carbon oxide **2** has a low volatility and explodes above 80° [11], making sublimation of the compound into an Ar matrix impractical. However, forming low-temperature glasses from solutions of **2** in organic solvents allowed for sample deposition *via* syringe, avoiding the problem of sample volatility. The solvent 2-methyltetrahydrofuran (Me-THF) proved to be excellent for electron absorption spectroscopy on $C_{24}O_6$. The carbon oxide is soluble and relatively stable in this solvent and forms an even, transparent glass upon injection onto a cold sapphire window.

Me-THF was not suitable for the FT-IR experiments on **2** since it has several significant absorption bands in the region of interest (1750–2200 cm^{-1}). A survey of other common glass-forming solvents showed that either they did not dissolve **2** or they also absorbed in the IR region of interest. In contrast, 1,2-dichloroethane worked well as solvent for the IR experiments because it forms stable solutions of **2**, and it lacks absorptions in the region of interest. As an acceptable disadvantage, it does not form a glass. Injection of the 1,2-dichloroethane solution onto a cold CsI window led to the formation of many small crystallites which did not significantly interfere with the quality of the spectra taken.

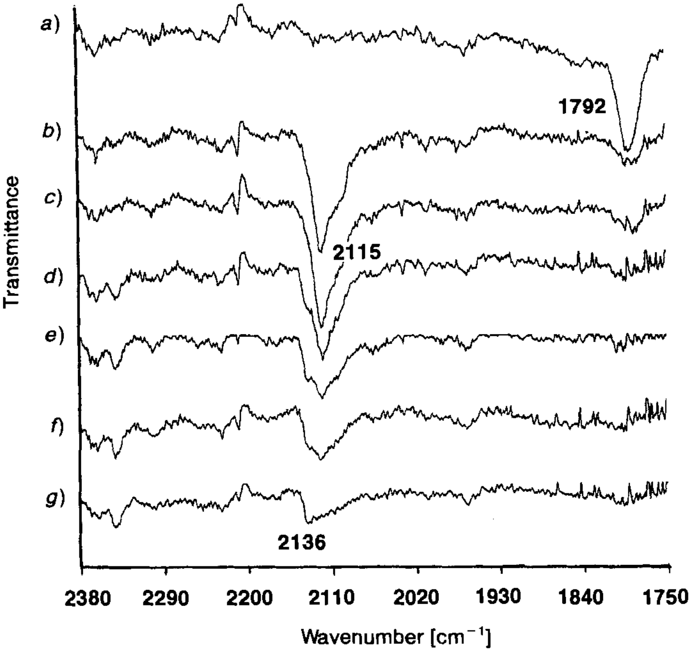
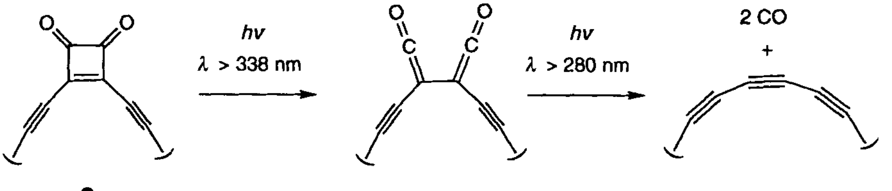


Fig. 4. *Fourier-transform IR transmittance spectra corresponding to the photolysis of* **2** *isolated in 1,2-dichloroethane at 15 K with absorbances due to solvent subtracted from each spectrum.* *a*) Initial spectrum of **2**; *b*) after 4 min irradiation at λ > 338 nm, *c*) followed by 2 min irradiation at λ > 300 nm, and *d*) 8 min, *e*) 24 min, *f*) 54 min, and *g*) 114 min irradiation at λ > 280 nm. Total irradiation time 2 h.

At 15 K, carbon oxide **2** shows a strong IR absorption at 1792 cm^{-1} (*Fig. 4*) resulting from the cyclobutenedione C=O groups. Upon irradiation of the frozen solution at λ > 338 nm, the band disappears quickly. After 6 min of irradiation (4 min at λ > 338 nm, 2 min at λ > 300 nm), the absorption at 1792 cm^{-1} is completely absent and a strong new band at 2115 cm^{-1} has appeared. The spectrum does not change with further irradiation at these wavelengths. Irradiation at λ > 280 nm, however, causes the new band at 2115 cm^{-1} to gradually decrease in intensity and to shift to higher frequency. After 2 h, the maximum intensity of this second absorption band, with significantly decreased intensity, occurs at 2136 cm^{-1}.

The IR-spectroscopy results suggest that the cyclobutenedione moieties in **2** undergo photochemical rearrangement to form diketenes, which have an expected absorption around 2100 cm^{-1} (*Scheme 6*). The diketene intermediates then extrude CO molecules

Scheme 6. *Photochemistry of* **2** *in Low-Temperature Matrices* (15 K)



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which absorb at 2138 cm^{-1}. Because the CO molecules cannot diffuse through the frozen solvent, this reaction is reversible and reaches an equilibrium.

These experiments do not provide direct evidence for the formation of *cyclo*-C_{18} from **2**, but they do give circumstantial support. C_{18} itself should have only very weak IR-active absorptions because of its high symmetry and lack of polar groups. Therefore, it is not surprising that no new IR bands corresponding to alkyne (**1a**) or cumulene (**1b**) vibrations appear.

The electronic absorption experiments provided less information than the FT-IR studies. A glass of **2** in Me-THF at 15 K showed the characteristic absorption bands in the regions λ 320–410 nm and λ 420–440 nm [11]. Upon irradiation at λ > 338 nm, these bands diminish and eventually disappear completely without any new absorption bands appearing, even at higher energy irradiation. The absence of new long-wavelength bands is best explained by the interruption of the cyclic conjugation in the intermediate diketenes and by the weakness of the symmetry-forbidden long wavelength absorptions in *cyclo*-C_{18}. Also, if C_{18} exhibits double aromaticity with macrocyclic in-plane and out-of-plane π-electron conjugation, its HOMO-LUMO gap should be quite large.

Although direct observation of *cyclo*-C_{18} was not achieved in the low-temperature experiments, the results are quite consistent with the formation of the cyclocarbon from carbon oxide **2**. Attempts to preparatively isolate *cyclo*-C_{18} by flash-vacuum pyrolysis of **2** or low-temperature photolysis of **2** in Me-THF in NMR tubes at liquid-N_2 temperature were not successful.

3. Conclusions. – Macrocyclic quantities of cyclocarbon molecules remain elusive, and the nature of their electronic structures, whether acetylenic with alternating C–C and C≡C bonds or cumulenic with C=C bonds throughout, is still uncertain. However, synthetic approaches to these all-carbon molecules *via* structurally defined precursors like **2**–**5**, which already contain the fully formed all-carbon rings, have provided unambiguous evidence for their existence in the gas phase [40] as well as exciting insight into size-specific fullerene-formation mechanisms through gas-phase ion-molecule coalescence reactions [11] [12]. In addition, the results of low-temperature matrix isolation studies with **2** are quite consistent with the photochemical formation of *cyclo*-C_{18} *via* ketene intermediates and subsequent loss of six CO molecules. Future *Raman* spectroscopic experiments should provide further clarification of the nature of the products formed upon irradiation of **2**. *cyclo*-C_{18} and *cyclo*-C_{24} are stabilized as ligands in the cobalt complexes **6** and **7**, respectively, and the electronic absorption spectra support the existence of partial cyclic conjugation in the central, all-C-atom rings. Decomplexation of **6** and **7** failed due to the particular stability of the complexes provided by the dppm ligands, and the preparation of phosphine-free complexes will be required to liberate the cyclocarbons under mild conditions. This approach, together with new ones, will be pursued in the search for a method to generate macroscopic quantities of the cyclocarbons.

This work was supported by the *U.S. Office of Naval Research*, the *U.S. National Science Foundation*, and the *Swiss National Science Foundation*. *N.S.G.* thanks the *U.S. NSF* for a graduate student fellowship 1900–1993.

Experimental Part

General. See [10]. All reactions were performed in dry standard glassware under Ar. CH_2Cl_2, pyridine, and $BuNH_2$ were distilled over CaH_2 and THF over Na/benzophenone ketyl prior to use. Benzene, hexane, and *N,N,N′,N′*-tetramethylethylenediamine (TMEDA) were stored over molecular sieves 4 Å. Anh. $MgSO_4$ was used as the drying agent after workup in all experiments. Evaporation and concentration *in vacuo* was done at water aspirator pressure. FC = Flash chromatography. Low-temperature IR spectra: *Nicolet 60SX* FT-IR, using a KBr beam splitter and a *TGS-A* detector; at 1 cm^{-1} resolution with 512 scans. Low-temperature UV/VIS spectra: *Perkin-Elmer-330* model with model *3600* data station. MS (*m/z*, %): fast-atom bombardment (FAB) matrix, 3-nitrobenzyl alcohol; DCI = desorption-chemical-ionization.

Low-Temperature Matrix Isolation Studies. The apparatus used for low-temperature spectroscopy is described in detail in [41]. A moveable cart contains the refrigeration and vacuum systems, as well as a gas-handling system not used in this study. The cooling system consists of an *Air Products* model *202* 'Displex' cryogenic refrigerator with standard instrumentation skirt and optical spectroscopy shroud (model *DMX-1A*). The bottom of the second stage of the expander connects to a 25-mm diameter × 0.5-mm thick spectrosopic window (CsI for IR experiments, sapphire for UV/VIS) in a chrome-plated high-conductivity copper holder. In all experiments, the cold window was cooled to approximately 15 K.

A conventional air-cooled diffusion pump, backed by a mechanical forepump, provides the vacuum necessary to maintain thermal insulation at the cold finger. The vacuum shroud surrounding the cold finger has four right angle ports. Two opposite ports, fitted with appropriate windows (KBr for IR studies, quartz for UV/VIS) allow spectroscopic viewing during the experiment. On one of the other sides, an injection port enables deposition of the sample soln. onto the cold finger. The final port is fitted with a quartz window for photolysis of the sample.

Carbon oxide **2** was prepared according to [10] and dissolved in 1,2-dichloroethane for IR experiments and in Me-THF for the UV/VIS studies. For each study, *ca.* 5 mg (0.01 mmol) were dissolved in 2 ml of solvent, and 200 µl of the resulting soln. were injected onto the cold window using a gas-tight syringe. An *ILC-Technology-LX300UV-300W* high-pressure xenon arc lamp acted as light source for the irradiation of the sample glass. A 10-cm path length of distilled H_2O filtered out IR irradiation to minimize heating of the cold window during photolysis. Glass cutoff filters (< 0.1 % transmittance of wavelengths shorter than the specified value) allowed for wavelength control.

trans-*11,12-Dichloro-9,10-dihydro-9,10-ethanoanthracene* [14] (**8**). Anthracene (220.9 g, 1.24 mol) and *trans*-1,2-dichloroethylene (1260 g, 1000 ml, 13 mol) were heated up to 215° for 30 h in a *Parr* autoclave under 500 lbs of N_2 gas. After cooling, the soln. was evaporated to recover excess *trans*-1,2-dichloroethylene for re-use. The solid residue was distilled under reduced pressure (b.p. 170–181°/0.25 Torr): **8** (307.7 g, 90%). Pale yellow solid which, upon recrystallization from MeOH, formed white needles. M.p. 110–112° ([14]: 113.5–114°). ^{1}H-NMR (360 MHz, $CDCl_3$): 4.16 (*dd*, *J* = 2.1, 1.3, 2 H); 4.36 (*m*, 2 H); 7.1–7.2 (*m*, 4 H); 7.22–7.27 (*m*, 2 H); 7.3–7.35 (*m*, 2 H). ^{13}C-NMR (90.6 MHz, $CDCl_3$): 52.0, 65.4; 124.3; 126.4; 127.0; 138.0; 139.3.

11-Chloro-9,10-dihydro-9,10-ethenoanthracene [15] (**9**). To **8** (257.7 g, 0.93 mol) in THF (2.5 l) at 20°, *t*-BuOK (147.1 g, 1.3 mol) was added at once. The soln. warmed up to *ca.* 40° and was then heated under reflux for 30 min. After cooling to 20°, sat. aq. NH_4Cl soln. (2 l) was added and the org. phase washed with H_2O and dried. After evaporation, recrystallization from MeOH afforded **9** (199.5 g, 90%). White needles. M.p. 127–128° ([14]: 127.5–129°). ^{1}H-NMR (360 MHz, $CDCl_3$): 4.96 (*d*, *J* = 2.2, 1 H); 5.06 (*d*, *J* = 6.4, 1 H); 6.79 (*dd*, *J* = 6.4, 2.2, 1 H); 6.9–7.0 (*m*, 4 H); 7.25–7.3 (*m*, 2 H); 7.3–7.35 (*m*, 2 H). ^{13}C-NMR (90.6 MHz, $CDCl_3$): 51.3; 58.4; 123.0; 123.3; 124.7; 125.1; 132.5; 144.6; 144.7; 145.1.

11-Bromo-12-chloro-9,10-dihydro-9,10-ethenoanthracene (**10**). At −78°, 1.6M BuLi in hexane (200 ml, 0.32 mmol) was added to TMEDA (34.86 g, 45 ml, 0.30 mol) in dry THF (2 l) under Ar. A soln. of **9** (59.68 g, 0.25 mol) in THF (200 ml) was added dropwise over 30 min and the mixture stirred further at −78° for 30 min. Br_2 (63.9 g, 21 ml, 0.40 mol) was added dropwise at −60° over 1 h, and stirring was continued for 30 min at −78°. The soln. faded from brown to yellow, and a yellow precipitate ($THF \cdot Br_2$ complex) formed at the end of the addition of Br_2. A 20% aq. sodium metabisulfite soln. (500 ml) was then added *directly* at −78° to quench the excess Br_2, and the org. phase was washed with H_2O and dried. After evaporation, the product was recrystallized from $CHCl_3$/MeOH: **10** (67.97 g, 86%). White prisms. M.p. 174–175° ([15]: 173–175°). ^{1}H-NMR (360 MHz, $CDCl_3$): 5.09 (*s*, 1 H); 5.13 (*s*, 1 H); 6.99 (*dd*, *J* = 5.3, 3.2, 4 H); 7.25–7.35 (*m*, 4 H). ^{13}C-NMR (90.6 MHz, $CDCl_3$): 59.09; 60.15; 123.25; 123.26; 125.45; 125.47; 125.63; 140.49; 143.35; 143.78. EI-MS (20 eV): 316, 318, 320 (16, 19, 6 M^+), 237, 239 (77, 31, $[M - Br]^+$), 203 (100, $[MH - Br - Cl]^+$), 178 (12, $[M - BrC{\equiv}CCl]^+$).

11,12-Bis[(trimethylsilyl)ethynyl]-9,10-dihydro-9,10-ethenoanthracene (**11**). To a degassed soln. of **10** (31.76 g, 100 mmol) and CuI (1.90 g, 10 mmol) in dry $BuNH_2$ (1 l) was added $[Pd(PPh_3)_4]$ (2.32 g, 2 mmol). After another degassing cycle, (trimethylsilyl)acetylene (24.55 g, 35 ml, 250 mmol) was added with a syringe and the mixture stirred at 50° for 14 h under Ar. The reaction was monitored by ^{1}H-NMR (H−C(9) and H−C(10) signals), since TLC ($CHCl_3$/hexane 3:7) could not show any difference in retention times (R_f 0.36) of starting material and product(s). The solvent was evaporated, the residue dissolved in Et_2O, the org. phase extracted twice with 0.1M aq. HCl, washed with H_2O and sat. aq. $NaHCO_3$ soln., dried, and evaporated and the remaining brown oil purified by gravity chromatography (SiO_2, CCl_4). Recrystallization from hexane gave **11** (34.47 g, 87%) as pale yellow platelets. Anal. pure colorless platelets were obtained by a second recrystallization from $CHCl_3$/MeOH. M.p. 209–210°. IR (CCl_4): 2150, 2130 ($C{\equiv}C$). ^{1}H-NMR (360 MHz, $CDCl_3$): 0.19 (*s*, 18 H); 5.09 (*s*, 2 H); 6.96 (*dd*, *J* = 5.3, 3.2, 4 H); 7.30 (*dd*, *J* = 5.3, 3.2, 4 H). ^{13}C-NMR (90.6 MHz, $CDCl_3$): −0.28; 55.7; 101.1; 107.3; 123.4; 125.2; 138.3; 143.6. EI-MS (70 eV): 396 (100, M^+), 381 (9, $[M - Me]^+$), 323 (14, $[M - SiMe_3]^+$), 178 (19, $C_{14}H_{10}^+$), 73 (74, $SiMe_3^+$). Anal. calc. for $C_{26}H_{28}Si_2$ (396.68): C 78.73, H 7.11; found: C 78.87, H 7.21.

11,12-Diethynyl-9,10-dihydro-9,10-ethenoanthracene (**12**). To **11** (2.05 g, 5.2 mmol) in MeOH (100 ml), 1.0M aq. KOH (1 ml, 1 mmol) was added. The soln. was stirred at 20° for 2 h and then poured into 0.1M aq. HCl/pentane, washed with H_2O and sat. aq. $NaHCO_3$ soln., and dried. Evaporation followed by FC (SiO_2, pentane) gave **12** (1.28 g, 98%) as *very unstable* colorless crystals which were redissolved immediately in benzene for the next step. IR ($CDCl_3$): 3300 (${\equiv}C{-}H$), 2250 ($C{\equiv}C$). ^{1}H-NMR (360 MHz, $CDCl_3$): 3.74 (*s*, 2 H); 5.14 (*s*, 2 H); 7.01 (*dd*, *J* = 5.3, 3.2, 4 H); 7.34 (*dd*, *J* = 5.3, 3.2, 4 H). ^{13}C-NMR (90.6 MHz, $CDCl_3$): 55.9; 79.9; 89.1; 123.4; 125.4; 138.6; 143.4. HR-MS: 252.0935 (M^+, $C_{20}H_{12}$, calc. 252.0939).

Caution: on one occasion, a sample of **12** exploded suddenly while being dried at the pump at 20° (for handling **12**, use a *safety shield*).

*6,7,8,9,16,17,18,19,26,27,28,29-Dodecadehydro-5,10,15,20,25,30-hexahydro-5,30[1′,2′]:10,15[1″,2″]:20,25-[1‴,2‴]tribenzenocyclooctadeca[1,2-*b*:7,8-*b′*:13,14-*b″*]trinaphthalene* (**5**). A soln. of **12** (5.72 g, 22.7 mmol) in benzene (100 ml) was added with a syringe-pump over 10 h to anh. $Cu(OAc)_2$ (45.0 g, 0.25 mol) in dry pyridine/MeOH 1:1 (2 l) at 50°. After stirring for 6 h, the soln. was cooled to 0° and added to a mixture of ice (2 kg), 50% aq. H_2SO_4 soln. (900 ml), and $CHCl_3$ (1.5 l). The aq. phase was extracted with $CHCl_3$ (0.5 l), the combined org. phase extracted with 1.0M aq. H_2SO_4 (2 l), washed with H_2O and sat. aq. $NaHCO_3$ soln., dried, and filtered through a plug of SiO_2 (300 g), and the filtrate concentrated *in vacuo* to 100 ml. After 12 h, **5** (1.39 g, 25%) was collected as poorly soluble red needles. M.p. > 300° (dec.; sealed tube). UV/VIS (CH_2Cl_2): 243 (sh, 30600), 248 (sh, 28700), 264 (sh, 13500), 281 (11500), 318 (sh, 11500), 359 (sh, 45000), 375 (87600), 404 (sh, 8800), 420 (17700), 432 (21000), 453 (sh, 960). IR (KBr): 2160 ($C{\equiv}C$). ^{1}H-NMR (360 MHz, $CDCl_3$): 5.89 (*s*, 6 H); 7.03 (*dd*, *J* = 5.3, 3.2, 12 H); 7.50 (*dd*, *J* = 5.3, 3.2, 12 H). ^{13}C-NMR (90.6 MHz, $CDCl_3$): 56.4; 86.2; 88.7; 124.0; 125.6; 140.0; 144.0. FAB-MS: 751 (100, MH^+), 750 (73, M^+), 572 (39, $[M - C_{14}H_{10}]^+$). HR-MS: 750.2309 (M^+, $C_{60}H_{30}$, calc. 750.2347).

Deep red single crystals of **5** for X-ray analysis were grown by recrystallization from boiling pyridine.

Hexacarbonyl[μ^2-(3,4-η:3,4-η)-1,6-bis(triisopropylsilyl)hexa-1,3,5-triyne]dicobalt (**15**) *and Decacarbonyl-[μ^2-(3,4-η:3,4-η)-1,6-bis(triisopropylsilyl)hexa-1,3,5-triyne]tetracobalt* (**17**). A soln. of 1,6-bis(triisopropylsilyl)-hexa-1,3,5-triyne [22] (413 mg, 1.07 mmol) and $[Co_2(CO)_8]$ (410 mg, 1.2 mmol) in degassed dry hexane (30 ml) was stirred for 6 h at 20° under Ar, then refluxed for an additional 3 h. TLC (hexane) before refluxing: 3 new spots at R_f 0.39 (red), 0.34 (green; bis(hexacarbonyldicobalt)), and 0.28 (red; **15**). TLC after refluxing: new spot at R_f 0.18 (dark blue; **17**), besides the two red spots present earlier. The solvent was evaporated, and FC (SiO_2, hexane) afforded a red oil (60.0 mg) which was not investigated further, **15** (79.6 mg, 11%) as a dark red oil, and **17** (280.4 mg, 57%) as a slightly unstable dark blue oil.

15: ^{1}H-NMR (360 MHz, CD_2Cl_2): 1.0–1.1 (*m*, 42 H). $^{13}C\{^1H\}$-NMR (90.6 MHz, CD_2Cl_2): 11.7 ($Me_2\mathit{C}H$); 18.8 (Me_2CH); 69.8 (C(3), C(4)); 103.8 (C(2), C(5)); 105.4 (C(1), C(6)); 198.2 (C=O).

17: IR ($CHCl_3$): 2092, 2042, 2000 ($C{\equiv}O$), 1868 (C=O). ^{1}H-NMR (360 MHz, CD_2Cl_2): 1.0–1.15 (*m*, 42 H). $^{13}C\{^1H\}$-NMR (90.6 MHz, CD_2Cl_2): 11.6 (*s*); 18.8 (*s*); 100.0 (*s*); 113.9 (*s*); 134.1 (br.); 198.4 (br.); 199.9 (br.). FAB-MS (neg. mode): 873 (12, $[M - H - CO]^-$), 818 (10, $[M - 2\,C_3H_6]^-$), 789 (3, $[M - H - CO - 2\,C_3H_6]^-$), 644 (22, $[M - Co_2(CO)_5]^-$), 560 (100, $[M - Co_2(CO)_8]^-$).

Compound **17** was not formed and the yield of **15** greatly increased when the reaction was conducted at 20° for 12 h, *without* subsequent refluxing; see preparation of **22**.

Attempted Formation of Hexacarbonyl[μ^2(3,4-η:3,4-η)-hexa-1,3,5-triyne]dicobalt (**16**). To **15** (79.2 mg, 0.12 mmol) in wet THF (10 ml) was added 1.0M Bu_4NF in THF (235 µl, 0.235 mmol). After 1 h, TLC (hexane) showed a strong baseline with a very small amount of starting material and only trace amounts of 2 more polar red spots.

*Tetracarbonyl[μ^2-(1,2-η:1,2-η)-1,4-bis(trimethylsilyl)buta-1,3-diyne][μ-methylenebis(diphenylphosphine)-*P:P'*]dicobalt* (**19**). To hexacarbonyl[μ^2-(1,2-η:1,2-η)-1,4-bis(trimethylsilyl)buta-1,3-diyne]dicobalt [34] (1.64 g, 3.4 mmol) in degassed benzene (50 ml) was added bis(diphenylphosphino)methane (dppm; 1.31 g, 3.4 mmol), and the mixture was refluxed under Ar for 12 h. Evaporation and FC (SiO_2, CH_2Cl_2/hexane 9:1 and 8:2) afforded **19** (2.34 g, 85%). Red crystals. IR ($CHCl_3$): 2115 (C≡C), 2043, 2015, 1979 (C≡O). ^{1}H-NMR (360 MHz, $CDCl_3$): 0.23 (*s*, Me_3Si); 0.36 (*s*, Me_3Si); 3.25–3.5 (*m*, *A* of ABX_2, 1 H, PCH_2P); 3.85–4.0 (*m*, *B* of ABX_2, 1 H, PCH_2P); 7.00–7.05 (*m*, 4 arom. H); 7.13–7.31 (*m*, 12 arom. H); 7.42–7.50 (*m*, 4 arom. H). $^{13}C\{^1H\}$-NMR (90.6 MHz, $CDCl_3$): 0.33 (*s*, Me_3Si); 0.45 (*t*, ^4J(C,P) = 1.6, Me_3Si); 35.8 (*t*, ^1J(C,P) = 20.3, PCH_2P); 76.3 (br. *m*, C(1)); 89.6 (*t*, ^2J(C,P) = 11.3, C(2)); 100.0 (*s*, C(4)); 108.2 (*t*, ^3J(C,P) = 4.1, C(3)); 128.0 (*t*, $^{3(5)}J$(C,P) = 4.9, C(3) of Ph); 128.2 (*t*, $^{3(5)}J$(C,P) = 4.9, C(3) of Ph); 129.1 (*s*, C(4) of Ph); 129.8 (*s*, C(4) of Ph); 130.7 (*t*, $^{2(4)}J$(C,P) = 6.1, C(2) of Ph); 132.9 (*t*, $^{2(4)}J$(C,P) = 6.6, C(2) of Ph); 133.7 (*t*, $^{1(3)}J$(C,P) = 16.7, C(1) of Ph); 138.7 (*t*, $^{1(3)}J$(C,P) = 24.4, C(1) of Ph); 201.5 (br. *s*, C=O); 207.2 (br. *s*, C=O). FAB-MS (pos. mode): 809 (88, MH^+), 808 (77, M^+), 793 (91, $[M - Me]^+$), 780 (100, $[M - CO]^+$), 753 (36, $[MH - 2\,CO]^+$), 724 (21, $[M - 3\,CO]^+$), 696 (42, $[M - 4\,CO]^+$), 502 (12, Co_2(dppm)). Anal. calc. for $C_{39}H_{40}Co_2O_4P_2Si_2$ (808.74): C 57.92, H 4.99; found: C 58.09, H 4.99.

*Tetracarbonyl[μ^2-(1,2-η:1,2-η)-1-(trimethylsilyl)buta-1,3-diyne][μ-methylenebis(diphenylphosphine)-*P:P'*]dicobalt* (**18**). To **19** (314 mg, 0.39 mmol) in THF/MeOH 10:1 (60 ml) was added 1.0M Bu_4NF in THF (0.8 ml, 0.8 mmol). The mixture was stirred under Ar at 20° for 12 h and then poured into hexane (100 ml) and sat. aq. NaCl soln. Drying of the org. phase and evaporation afforded **18** (276 mg, 97%). Dark red foam. IR ($CHCl_3$): 3300 (≡C–H), 2060 (C≡C), 2020, 1998, 1970 (C≡O). ^{1}H-NMR (360 MHz, CD_2Cl_2): 0.43 (*s*, Me_3Si); 3.37–3.47 (*m*, *A* of ABX_2, 1 H, PCH_2P); 3.72 (*s*, H–C(4)); 3.95–4.05 (*m*, *B* of ABX_2, 1 H, PCH_2P); 7.11–7.16 (*m*, 4 arom. H); 7.23–7.29 (*m*, 2 arom. H); 7.32–7.40 (*m*, 10 arom. H); 7.50–7.60 (*m*, 4 arom. H). $^{13}C\{^1H\}$-NMR (90.6 MHz, CD_2Cl_2): 0.6 (*s*, Me_3Si); 36.8 (*t*, ^1J(C,P) = 20.8, PCH_2P); 77.4 (*t*, ^2J(C,P) = 8.0, C(1)); 83.1 (*s*, C(4)); 86.7 (*t*, ^3J(C,P) = 4.1, C(3)); 89.5 (*t*, ^2J(C,P) = 11.1, C(2)); 128.5 (*t*, $^{3(5)}J$(C,P) = 4.9, C(3) of Ph); 128.7 (*t*, $^{3(5)}J$(C,P) = 4.9, C(3) of Ph); 129.7 (*s*, C(4) of Ph); 130.4 (*s*, C(4) of Ph); 131.3 (*t*, $^{2(4)}J$(C,P) = 6.2, C(2) of Ph); 133.1 (*t*, $^{2(4)}J_{(C,P)}$ = 6.5, C(2) of Ph); 134.5 (*t*, $^{1(3)}J$(C,P) = 17.5, C(1) of Ph); 138.5 (*t*, $^{1(3)}J$(C,P) = 24.0, C(1) of Ph); 202.3 (br. *s*, C=O); 207.7 (br. *s*, C=O); gated-decoupled ^{13}C-NMR: 83.1 (*d*, ^1J = 250.7). DCI-MS (CH_4^+): 737 (3, MH^+), 709 (14, $[MH - CO]^+$), 681 (5, $[MH - 2\,CO]^+$), 653 (17, $[MH - 3\,CO]^+$), 625 (20, $[MH - 4\,CO]^+$). FAB-MS (neg. mode): 735 (59, $[M - H]^-$), 708 (67, $[M - CO]^-$), 679 (13, $[M - H - 2\,CO]^-$), 651 (17, $[M - H - 3\,CO]^-$). Anal. calc. for $C_{36}H_{32}Co_2O_4P_2Si \cdot 4\,CH_3OH$ (736.5): C 57.01, H 5.04; found: C 56.66, H 5.25.

*Octacarbonylbis[μ-methylenebis(diphenylphosphine)-*P:P'*][μ^4-(1,2-η:1,2-η;7,8-η:7,8-η)-1,8-bis(trimethylsilyl)-octa-1,3,5,7-tetrayne]tetracobalt* (**21**). Anh. $Cu(OAc)_2$ (581 mg, 3.2 mmol) was added to **18** (237 mg, 0.32 mmol) in dry pyridine (10 ml) under Ar and the soln. stirred at 20° for 24 h. The solvent was evaporated, the solid extracted with CH_2Cl_2 (50 ml), and the resulting soln. filtered through a plug of SiO_2 with CH_2Cl_2. Evaporation of the filtrate and FC (SiO_2, CH_2Cl_2/hexane 1:1) followed by recrystallization from hexane/CH_2Cl_2 afforded **21** (176 mg, 75%). Dark red prisms. UV/VIS (CH_2Cl_2): 292 (sh, 52300), 321 (sh, 46900), 412 (sh, 11600), 477 (sh, 6020), 544 (sh, 4150). IR ($CHCl_3$): 2102 (C≡C), 2040, 2020, 1978 (C≡O). ^{1}H-NMR (360 MHz, CD_2Cl_2): 0.46 (*s*, 2 Me_3Si); 3.33–3.43 (*m*, *A* of ABX_2, 2 H, PCH_2P); 4.03–4.13 (*m*, *B* of ABX_2, 2 H, PCH_2P); 7.15–7.30 (*m*, 24 arom. H); 7.37–7.50 (*m*, 16 arom. H). $^{13}C\{^1H\}$-NMR (90.6 MHz, CD_2Cl_2): 0.6 (*s*, Me_3Si); 40.0 (*t*, ^1J(C,P) = 20.6, PCH_2P); 76.8 (*t*, ^2J(C,P) = 7.6, C(1), C(8)); 83.0 (*s*, C(4), C(5)); 86.8 (*t*, ^3J(C,P) = 4.0, C(3), C(6)); 91.8 (*t*, ^2J(C,P) = 11.7, C(2), C(7)); 128.6 (*t*, (*t* $^{3(5)}J$(C,P) = 4.9, C(3) of Ph); 128.7 (*t*, $^{3(5)}J$(C,P) = 4.9, C(3) of Ph); 129.9 (*s*, C(4) of Ph); 130.2 (*s*, C(4) of Ph); 131.8 (*t*, $^{2(4)}J$(C,P) = 6.3, C(2) of Ph); 132.5 (*t*, $^{2(4)}J$(C,P) = 6.3, C(2) of Ph); 135.8 (*t*, $^{1(3)}J$(C,P) = 19.4, C(1) of Ph); 136.5 (*t*, $^{1(3)}J$(C,P) = 22.2, C(1) of Ph); 202.3 (br. *s*, C=O); 207.3 (br. *s*, C=O). FAB-MS (neg. mode): 1469 (40, $[M - H]^-$), 1440 (6, $[M - CO]^-$), 153 (100). Anal. calc. for $C_{72}H_{62}Co_4O_8P_4Si_2$ (1471.1): C 58.79, H 4.25; found: C 58.92, H 4.26.

*Tetracarbonyl[μ^2-(1,2-η:1,2-η)buta-1,3-diyne][μ-methylenebis(diphenylphosphine)-*P:P'*]dicobalt* (**20**). To **19** (718 mg, 0.89 mmol) in wet THF (50 ml) was added 1.0M Bu_4NF in THF (1.8 ml, 1.8 mmol). After 10 min, the soln. was poured into hexane (100 ml) and sat. aq. NaCl soln. The org. phase was dried and evaporated: **20** (489 mg, 83%). Slightly unstable dark red crystals. M.p. > 90° (dec.). IR ($CHCl_3$): 3300 (≡C–H), 2075 (C≡C), 2025, 2000, 1972 (C≡O). ^{1}H-NMR (360 MHz, CD_2Cl_2): 3.54 (*t*, ^2J(H,P) = 10.3, 2 H, PCH_2P); 3.69 (*s*, H–C(4)); 6.01 (*s*, H–C(1)); 7.2–7.25 (*m*, 4 arom. H); 7.3–7.4 (*m*, 12 arom. H); 7.5–7.55 (*m*, 4 arom. H). $^{13}C\{^1H\}$-NMR (90.6 MHz, CD_2Cl_2): 38.8 (*t*, ^1J(C,P) = 21.6, PCH_2P); 66.7 (br. *s*, C(2)); 78.9 (br. *s*, C(1)); 82.8 (*s*, C(4)); 86.4 (*s*, C(3)); 128.6 (*t*,

$^{3(5)}J$(C,P) = 4.9, C(3) of Ph); 128.7 (*t*, $^{3(5)}J$(C,P) = 4.7, C(3) of Ph); 130.0 (*s*, C(4) of Ph); 130.3 (*s*, C(4) of Ph); 131.6 (*t*, $^{2(4)}J$(C,P) = 6.2, C(2) of Ph); 132.7 (*t*, $^{2(4)}J$(C,P) = 6.5, C(2) of Ph); 135.1 (*t*, $^{1(3)}J$(C,P) = 19.0, C(1) of Ph); 137.4 (*t*, $^{1(3)}J$(C,P) = 22.2, C(1) of Ph); 204.1 (br. *s*, C=O); 204.7 (br. *s*, C=O); gated-decoupled ^{13}C-NMR: 66.7 (br. *s*); 78.9 (*dm*, ^{1}J(C,H) = 211.0); 82.8 (*dt*, ^{1}J(C,H) = 251.3, ^{4}J(C,P) = 2.6); 86.4 (*d*, ^{2}J(C,H) = 49.6). FAB-MS: 664 (0.4, M^+), 635 (13, [MH − CO]$^+$), 607 (5, [MH − 2 CO]$^+$), 579 (45, [MH − 3 CO]$^+$), 551 (100, [MH$^+$ − 4 CO]$^+$), 502 (4, Co$_2$(dppm)), 442 (25, Co(dppm)).

*Tetracarbonyl[μ^2-(3,4-η:3,4-η)-1,6-bis(triisopropylsilyl)hexa-1,3,5-triyne][μ-methylenebis(diphenylphosphine)-*P:P′*]dicobalt* (**22**). A soln. of 1,6-bis(triisopropylsilyl)hexa-1,3,5-triyne [22] (1.79 g, 4.62 mmol) and [Co$_2$(CO)$_8$] (1.71 g, 5.00 mmol) in degassed hexane (100 ml) was stirred at 20° under Ar for 12 h. The hexane was evaporated and the residue redissolved in dry toluene. Dppm (1.81 g, 4.70 mmol) was added and the soln. refluxed for 1 h. Evaporation and FC (SiO$_2$, hexane/CH$_2$Cl$_2$ 9:1 and 8:2) afforded **22** (3.46 g, 75%). Dark red crystals. M.p. 154–156°. IR (CHCl$_3$): 2105 (C≡C), 2020, 1990 (C≡O). ^{1}H-NMR (360 MHz, CDCl$_3$): 1.09–1.11 (*m*, 42 H, i-Pr); 3.40 (*t*, ^{2}J(H,P) = 10.3, 2 H, PCH$_2$P); 7.1–7.2 (*m*, 8 arom. H); 7.2–7.3 (*m*, 4 arom. H); 7.3–7.4 (*m*, 8 arom. H). ^{13}C{^{1}H}-NMR (90.6 MHz, CDCl$_3$): 11.7 (*s*, Me$_2$CH); 18.8 (*s*, *Me*$_2$CH); 35.8 (*t*, ^{1}J(C,P) = 21.0, PCH$_2$P); 71.2 (br. *s*, C(3), C(4)); 98.7 (*t*, ^{3}J(C,P) = 2.1, C(2), C(5)); 109.5 (*s*, C(1), C(6)); 128.3 (*t*, $^{3(5)}J$(C,P) = 4.7, C(3) of Ph); 129.7 (*s*, C(4) of Ph); 131.9 (*t*, $^{2(4)}J$(C,P) = 6.2, C(2) of Ph); 135.9 (*t*, $^{1(3)}J$(C,P) = 20.2, C(1) of Ph); 202.9 (br. *s*, C=O). FAB-MS (neg. mode): 999 (43, [M − H]$^-$), 972 (100, [M − CO]$^-$), 944 (47, [M − 2 CO]$^-$), 916 (20, [M − 3 CO]$^-$), 888 (15, [M − 4 CO]$^-$), 643 (18, [M − H − dppm − CO]$^-$), 560 (68, [M − dppm − 4 CO]$^-$). Anal. calc. for $C_{53}H_{64}Co_2O_4P_2Si_2$ (1001.08): C 63.59, H 6.44; found: C 63.57, H 6.41.

*Tetracarbonyl[μ^2-(3,4-η:3,4-η)hexa-1,3,5-triyne][μ-methylenebis(diphenylphosphine)-*P:P′*]dicobalt* (**23**). To **22** (3.36 g, 3.4 mmol) in wet THF (100 ml) was added 1.0M Bu$_4$NF in THF (7.0 ml, 7.0 mmol). After 5 min, the mixture was partitioned between hexane (200 ml) and 10% aq. NH$_4$Cl soln. Drying of the org. phase, evaporation, and washing of the residue with hexane afforded **23** (2.32 g, 99%). Dark red prisms. M.p. > 120° (dec.). UV/VIS (CH$_2$Cl$_2$): 280 (26800), 340 (sh, 11100), 393 (sh, 2430). IR (CHCl$_3$): 3305 (≡C–H), 2075 (C≡C), 2053, 2047, 1993 (C≡O). ^{1}H-NMR (360 MHz, CD$_2$Cl$_2$): 3.44 (*t*, ^{2}J(H,P) = 10.3, 2 H, PCH$_2$P); 3.76 (*t*, ^{5}J(H,P) = 1.4, H–C(1), H–C(6)); 7.08–7.22 (*m*, 12 arom. H); 7.23–7.27 (*m*, 8 arom. H). ^{13}C{^{1}H}-NMR (90.6 MHz, CD$_2$Cl$_2$): 36.1 (*t*, ^{1}J(C,P) = 22.0, PCH$_2$P); 69.2 (br. *s*, C(3), C(4)); 84.5 (*s*, C(1), C(6)); 85.7 (*s*, C(2), C(5)); 128.7 (*t*, $^{3(5)}J$(C,P) = 5.0, C(3) of Ph); 130.3 (*s*, C(4) of Ph); 132.1 (*t*, $^{2(4)}J$(C,P) = 6.3, C(2) of Ph); 135.5 (*t*, $^{1(3)}J$(C,P) = 21.3, C(1) of Ph); 203.3 (br. *s*, C=O); gated-decoupled ^{13}C-NMR: 69.2 (br. *s*); 84.5 (*d*, ^{1}J(C,H) = 252.2); 86.4 (*d*, ^{2}J(C,H) = 49.9). FAB-MS: 689 (6, MH$^+$), 660 (35, [M − CO]$^+$), 632 (5, [M − 2 CO]$^+$), 604 (51, [M − 3 CO]$^+$), 576 (95, [M − 4 CO]$^+$), 154 (100). Anal. calc. for $C_{35}H_{24}Co_2O_4P_2 \cdot CHCl_3$ (688.39): C 53.53, H 3.12; found: C 53.84, H 3.10.

Crystals of **23** for X-ray crystallographic analysis were obtained by slow evaporation of a CHCl$_3$ soln. over a week.

*Dodecacarbonyltris[μ-methylenebis(diphenylphosphine)-*P:P′*][μ^6-(1,2-η:1,2-η;7,8-η:7,8-η;13,14-η;13,14-η)-cyclooctadeca-1,3,5,7,9,11,13,15,17-nonayne]hexacobalt* (**6**) *and Hexadecacarbonyltetrakis[μ-methylenebis-(diphenylphosphine)-*P:P′*][μ^8-(1,2-η;1,2-η;7,8-η;7,8-η;13,14-η;13,14-η;19,20-η;19,20-η)-cyclotetracosa-1,3,5,7,9,11,13,15,17,19,21,23-dodecayne]octacobalt* (**7**). A soln. of **23** (2.27 g, 3.29 mmol) and dry Cu(OAc)$_2$, (12.00 g, 66 mmol) in dry pyridine (450 ml) under Ar was stirred at 20° for 2 d and then at 55° for 1 d. (^{1}H-NMR monitoring: disappearance of the alkylene signals of the intermediate open oligomers.) The bulk of the pyridine was evaporated at 40°/0.1 Torr and the remaining solid dried at 10^{-2} Torr for 30 min and then suspended in CH$_2$Cl$_2$ (100 ml). Filtration of the dark mixture through a plug of SiO$_2$ with CH$_2$Cl$_2$ and evaporation of the filtrate yielded a dark brown oil. FC (SiO$_2$, hexane/CH$_2$Cl$_2$ 1:1) gave, upon recrystallization from hexane/CH$_2$Cl$_2$ by slow evaporation at 20° **6** (736 mg, 33%), and upon recrystallization from CH$_2$Cl$_2$/hexane at 20°, **7** (121 mg, 5.4%), both as shiny black needles.

6: UV (CH$_2$Cl$_2$): 254 (sh, 119500), 291 (106000), 370 (91400), 445 (sh, 36700), 546 (sh, 12400). IR (CHCl$_3$): 2107 (C≡C), 2057, 2042, 2000 (C≡O). ^{1}H-NMR (360 MHz, CD$_2$Cl$_2$): 3.47 (*t*, ^{2}J(H,P) = 10.1, 6 H, PCH$_2$P); 7.2–7.3 (*m*, 36 arom. H); 7.4–7.5 (*m*, 24 arom. H). ^{13}C{^{1}H}-NMR (90.6 MHz, CD$_2$Cl$_2$): 37.6 (*t*, ^{1}J(C,P) = 21.2, PCH$_2$P); 72.0 (br. *s*, C(1), C(2), C(7), C(8), C(13), C(14)); 84.0 (br. *s*, C(3), C(6), C(9), C(12), C(15), C(18)); 88.0 (*s*, C(4), C(5), C(10), C(11), C(16), C(17)); 128.8 (*t*, $^{3(5)}J$(C,P) = 4.9, C(3) of Ph); 130.4 (*s*, C(4) of Ph); 132.2 (*t*, $^{2(4)}J$(C,P) = 5.9, C(2) of Ph); 135.3 (*t*, $^{1(3)}J$(C,P) = 20.5, C(1) of Ph); 202.8 (br. *s*, C=O). FAB-MS (neg. mode): 2058 (M^-), 2030 ([M − CO]$^-$), 2002 ([M − 2 CO]$^-$). Anal. calc. for $C_{105}H_{66}Co_6O_{12}P_6$ (2059.13): C 61.25, H 3.23; found: C 60.92, H 3.43.

X-Ray quality single crystals were grown by slow evaporation of a soln. of **6** in 1,2-dichloroethane/methylcyclohexane 1:1 over a week.

7: UV (CH$_2$Cl$_2$): 268 (sh, 141700), 381 (122700), 453 (sh, 50900), 560 (sh, 15000). IR (CHCl$_3$): 2100 (C≡C), 2043, 2033, 1993 (C≡O). ^{1}H-NMR (360 MHz, CD$_2$Cl$_2$): 3.53 (*t*, ^{2}J(H,P) = 9.6, 8 H, PCH$_2$P); 7.2–7.3 (*m*, 48 arom.

H); 7.4–7.5 (*m*, 32 arom. H). $^{13}C\{^1H\}$-NMR (90.6 MHz, CD_2Cl_2): 38.7 (*t*, ^1J(C,P) = 21.1, PCH_2P); 70.6 (br. *s*, C(1), C(2), C(7), C(8), C(13), C(14), C(19), C(20)); 85.0 (br. *s*, C(3), C(6), C(9), C(12), C(15), C(18), C(21), C(24)); 88.0 (*s*, C(4), C(5), C(10), C(11), C(16), C(17), C(22), C(23)); 128.9 (*t*, $^{3(5)}J$(C,P) = 4.7, C(3) of Ph); 130.4 (*s*, C(4) of Ph); 132.2 (*t*, $^{2(4)}J$(C,P) = 6.0, C(2) of Ph); 135.3 (*t*, $^{1(3)}J$(C,P) = 20.8, C(1) of Ph); 203.0 (br. *s*, C=O). Anal. calc. for $C_{140}H_{88}Co_8O_{16}P_8$ (2745.51): C 61.25, H 3.23, P 9.03; found: C 61.05, H 3.58, P 8.90.

No melting or decomposition points could be observed for **6** and **7** (vacuum-sealed tube) below 360°, because the dark nature of these compounds did not allow a clear determination of any phase changes.

Attempted Formation of Cyclooctadeca-1,3,5,7,9,11,13,15,17-nonayne (*cyclo*-C_{18}) *by Deprotection of* **6**. *a) By Ligand Exchange with Dimethyl Acetylenedicarboxylate* [29]. To a soln. of **6** (20.0 mg, $9.71 \cdot 10^{-6}$ mol) in dry CH_2Cl_2 (20 ml) under Ar was added dimethyl acetylenedicarboxylate (2 ml). After stirring at 20° for 24 h and then for 48 h under reflux, no conversion could be observed by TLC (CH_2Cl_2).

b) By Oxidation with Ce(IV) [28]. To a soln. of **6** (16.6 mg, $8.06 \cdot 10^{-6}$ mol) in dry acetone (20 ml) at −78° under Ar was added dropwise a soln. of ceric ammonium nitrate (53.0 mg, $9.67 \cdot 10^{-5}$ mol, 12 equiv.) in acetone (2 ml). After 5 min, TLC (CH_2Cl_2) showed only baseline products.

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