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$(\eta^3\text{-Triphenylcyclopropenyl})\text{tricarbonsylcobalt}$

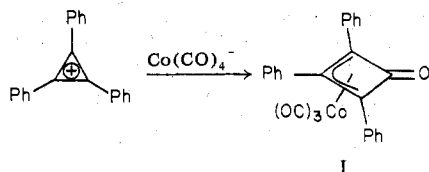
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Reaction of triphenylcyclopropenium fluoroborate with octacarbonyldicobalt gives the title compound. It is also obtained, in low yield, by using decacarbonyltricobalt anion. The compound crystallizes in the monoclinic space group $P2_1/c$ with $a = 13.343$ (3) Å, $b = 10.284$ (2) Å, $c = 14.975$ (3) Å, $\beta = 108.84$ (2)°, and $Z = 4$. The molecule has pseudo- C_{3v} symmetry with ring Co-C and C-C bond distances averaging 2.01 (1) and 1.42 (1) Å, respectively, confirming its place as the final member of the now-complete cobaltatetrahedrane family.

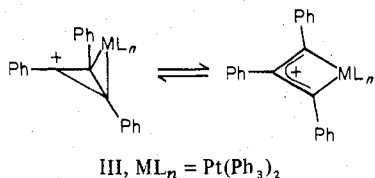
Introduction

In 1962, Coffey¹ reported the reaction of triphenylcyclopropenyl bromide with tetracarbonylcobaltate(-I) anion. The product was later shown to be the oxocyclobutenyl complex, I.^{2,3} Other reactions of cyclopropenyl compounds with

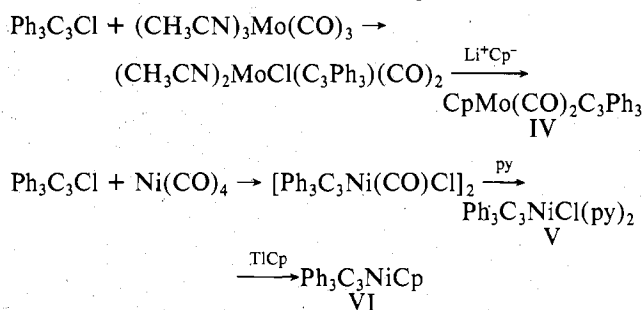


transition-metal anions have likewise failed to yield cyclopropenyl complexes: cyclopentadienyldicarbonylferrate,⁴ cyclopentadienyltricarbonsylmolybdate,⁴ and pentacarbonylmanganate⁵ anions gave products of one-electron transfer; ethylene trichloroplatinate(II)⁶ and hexacarbonylvanadate gave only saltlike precipitates. Photolysis of the triphenylcyclopropenium hexacarbonylvanadate gave, however, (triphenylcyclopropenyl)pentacarbonylvanadium,⁷ II.

Reactions of cyclopropenyl compounds with neutral transition-metal compounds, however, have resulted in a variety of complexes. Reactions of tris(dibenzylideneacetone)dipalladium⁸ and carbonylchlorotris(trimethyl phosphite)iridium⁹ gave metallacyclobutenyl systems from oxidative addition to a C-C bond. Ethylenebis(triphenylphosphine)platinum(0) gave an unsymmetrical π complex, III, with the platinum directly bonded to only two of the carbons of the three-membered ring (2.09 Å), the third distance being much longer (2.48 Å).¹⁰ This interesting structure is conceptually related to the metallacyclobutenyls by a sigmatropic ring opening:



Neutral metal carbonyls have also reacted to form cyclopropenyl complexes¹¹⁻¹⁴ ($Ph = C_6H_5$; $py = C_5H_5N$)



That V and VI are η^3 -cyclopropenyl complexes was shown by X-ray crystallography.^{15,16} II and IV may, by virtue of their stoichiometries, also be η^3 -cyclopropenyl complexes, but the unexpected structure of III should lead to caution in making structural assignments based on the available data.

Beyond the general interest in η^3 -cyclopropenyl complexes exemplified in the above studies, a cobalt tricarbonyl complex derives further interest from its membership in the cobaltatetrahedrane family, which also includes the known dodecacarbonyltetracobalt, methylnonacarbonyltricobalts,¹⁷ (alkyne)hexacarbonyldicobalts,¹⁸ and the tetrahedranes themselves, an example of which has just been reported.¹⁹ Synthesis of a cyclopropenyltricarbonsylcobalt derivative completes the family.

Experimental Section

All reactions, filtrations, and transfers were done under nitrogen with Schlenk-type glassware. Solvents were degassed with nitrogen before use. Sodium tetracarbonylcobaltate,²⁰ triphenylcyclopropenium fluoroborate,²¹ and sodium decacarbonyltricobaltate²² were prepared according to literature methods. Octacarbonyldicobalt was used as obtained from Strem Chemicals.

Reaction of Triphenylcyclopropenium Fluoroborate, VII, with Sodium Decacarbonyltricobaltate. A three-neck flask fitted with a reflux condenser and a Nujol gas-exit bubbler, nitrogen inlet, and syringe stopper was flushed with nitrogen and then charged with 0.81 g (2.28

mmol) of VII in 15 mL of acetonitrile. A solution of 1.098 g (2.28 mmol) of sodium decacarbonyltricobaltate in acetonitrile was added in one portion, whereupon a green color appeared in solution. During 3 days of stirring the solution at room temperature, the color darkened to yellow-brown, and carbonyl absorptions at ca. 2080, 2040, and 1990 cm^{-1} appeared in the infrared spectrum. Filtration of the mixture gave a brown solid (0.638 g) whose IR spectrum indicated both fluoroborate ion (ca. 1060 cm^{-1}) and metal carbonyl peaks at ca. 2080 and 2040 cm^{-1} . Evaporation of the filtrate gave 1.17 g of solid residue which was chromatographed on silica gel. Elution with hexane first gave 0.035 g of crude (diphenylacetylene)hexacarbonyldicobalt,²³ identified by IR (2090, 2056, 2028 cm^{-1}), and then 0.510 g (7%) of VIII, mp 101–103 °C. Elution with dichloromethane gave 0.42 g (43%) of I, mp 124–127 °C. Recrystallization from methanol at –30 °C gave I with mp 134–135 °C (lit.¹ mp 134–135 °C). MS (direct inlet, 70 eV) [ion, m/e (relative intensity)]: $\text{Ph}_3\text{C}_3\text{Co}(\text{CO})_4$, 438 (0.2), 410 (5), 382 (15), 354 (38), 326 (46); C_3Ph_3^+ , 267 (100); C_{15}H_6 , 189 (12); $\text{C}_7\text{H}_5\text{Co}$, 148 (15); $\text{Co}(\text{CO})_2$, 115 (8), 87 (8), 59 (7). ^{13}C NMR (CDCl_3 with $\text{Cr}(\text{acac})_3$): C(1), δ 164.9; C(2,4), δ 92.2; C(3) and phenyl C's, δ 132.3, 132.0, 130.7, 129.1, 128.9, 127.3; CO's δ 199 (br).

Reaction of VII with Octacarbonyldicobalt in Acetonitrile. The reaction was run as above, adding octacarbonyldicobalt (7.01 g, 20.5 mmol) to 7.26 g (20.5 mmol) of VII in 500 mL of acetonitrile. After 24 h the solution was filtered and the filtrate evaporated to give 15.58 g of solid. The organic-soluble portion of this material was chromatographed on silica. Hexane eluted 0.028 g of (diphenylacetylene)hexacarbonyldicobalt, and then dichloromethane eluted 7.78 g of I (87%). The insoluble material was a deep pink solid, presumably $\text{Co}(\text{CH}_3\text{CN})_x(\text{BF}_4)_2$.²⁴

Reaction of VII with Octacarbonyldicobalt in Dichloromethane. The reaction was run as above with 1.69 g of VII (4.77 mmol), 2.27 g of $\text{Co}_2(\text{CO})_8$ (6.65 mmol), and 80 mL of dichloromethane. After 2 days of stirring, the solution was filtered and evaporated, leaving 3.48 g of residue. Chromatography on neutral alumina gave 0.665 g of VIII (1.62 mmol, 34%), eluted with hexane, and then 0.692 g of I (1.58 mmol, 33%), eluted with dichloromethane. Recrystallization of VIII from methanol gave golden needles, mp 104–105 °C. Anal. Calcd for $\text{C}_{24}\text{H}_{15}\text{CoO}_3$: C, 70.2; H, 3.66; Co, 14.4. Found: C, 70.0; H, 3.95; Co, 14.1.

Photolysis of I. A solution of 1.51 g of I (3.44 mmol) in ca. 100 mL of acetonitrile was placed in a quartz photolysis tube fitted with a nitrogen-inlet tube and a glass frit at the bottom and a Nujol bubbler gas exit tube at the top. The solution was degassed by passage of nitrogen for 0.5 h and then photolyzed with 254-nm lamps in a Rayonet RPR-100 photoreactor. Gas was evolved. After 4 days, the photolysate was filtered, giving a light yellow solid (0.476 g, mp 165–168 °C) (crude IX) and a yellow filtrate, the TLC of which revealed no VIII. Evaporation of the filtrate left 0.965 g of residue which was chromatographed on neutral alumina. Hexane eluted 0.114 g of crude blue-fluorescent material which could not be separated from high molecular weight hydrocarbon contaminants. The mass spectrum showed peaks at m/e (relative intensity, ion) 562 (3, $\text{C}_6\text{Ph}_6\text{CO}$), 546 (92, C_7Ph_6), 534 (32, C_6Ph_6), 469 (40, C_7Ph_5), 148 (100), 147 (72), and 174 (60). Dichloromethane eluted 0.554 g of unreacted I (37% recovery). The yield of crude IX is thus 75%. Crude IX was recrystallized from chloroform–hexane to mp 174–175 °C. Spectroscopic data are given in the text. The ^{13}C NMR spectrum showed resonances at δ 189.0, 137.8, and 146.9 for C(1), C(2), and C(3) of the cyclobutenone rings, in good agreement with data for 4,4-dichloro-2,3-diphenylcyclobutenone.²⁵

X-ray Data Collection and Reduction. A yellow crystal of VIII with dimensions 0.15 mm \times 0.35 mm \times 0.55 mm was selected and mounted in air. All X-ray measurements were carried out with an Enraf-Nonius CAD4A diffractometer under the control of a PDP 11/45 computer system. Important features of the data collection are summarized in Table I.

Computing was carried out on the PDP 11/45 by using the Enraf-Nonius structure determination package developed chiefly by Okaya and Frenz.²⁶ The structure was solved in a straightforward manner with Patterson and difference Fourier methods. After anisotropic refinement of the heavy atoms, all hydrogen atoms could be clearly located as the principal peaks in a subsequent difference Fourier synthesis. In the final cycles of refinement, the hydrogen atom positions were varied along with their isotropic temperature factors. No absorption correction was applied since the linear absorption

Table I. Crystal Data and Data Collection Procedures for $\text{Co}(\text{CO})_3(\text{C}_3\text{Ph}_3)$, VIII

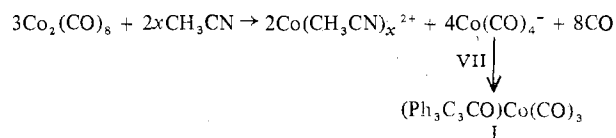
| | | | |
|----------------------------|---|-----------------------|----------------------------|
| formula | $\text{C}_{24}\text{H}_{15}\text{CoO}_3$ | β | 108.84 (2)° |
| mol wt | 410.3 | vol | 1966.6 Å ³ |
| space group | $\text{C}_2\text{h}^2\text{-P}2_1/\text{c}$ (monoclinic) | Z | 4 |
| a | 13.343 (3) Å | ρ_{calcd} | 1.385 g/cm ³ |
| b | 10.284 (2) Å | ρ_{obsd} | 1.40 (1) g/cm ³ |
| c | 14.975 (3) Å | | |
| cryst shape | 0.15 mm \times 0.35 mm \times 0.55 mm plate | | |
| radiation | Mo K α (λ 0.710 73 Å) with a graphite monochromator | | |
| linear abs coeff (μ) | 9.3 cm ⁻¹ , no cor made | | |
| temp | 22 °C | | |
| takeoff angle | 6.0° | | |
| 2 θ range | 0 < 2 θ \leq 54° | | |
| scan type | θ -2 θ | | |
| scan speed | 1.8–20°/min | | |
| scan range | symmetrical, [2 θ (Mo K α_1) – 1.0°] to [2 θ (Mo K α_2) + 1.0°], extended 25% on each end for bkgd counts | | |
| rflctns measd | $h, k \geq 0$; all l | | |
| rflctns collectd | 4869 collectd, 2022 unique with $F_o^2 > 3\sigma(F_o^2)$ | | |
| std rflctns | intensity variations within counting statistics | | |
| p | 0.04 | | |

coefficient ($\mu = 9.3 \text{ cm}^{-1}$) was small, and the crystal was of irregular shape; no evidence was found for extinction. The final refinement converged to values of R and R_w of 0.045 and 0.049, respectively, and to an error in an observation of unit weight of 1.56 electrons for the 313 variables and 2022 observations.

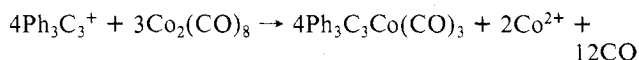
Final positional and thermal parameters are tabulated in Table II. Root-mean-square amplitudes of vibration are given in Table VII²⁷ and values of $10/F_o$ and $10/F_c$ for the 2022 reflections used in the refinement are given in Table VIII.²⁷

Results

In agreement with Coffey,¹ we find that I is formed in high yield on reaction of tetracarbonylcobaltate ion with triphenylcyclopropenium fluoroborate, VII. A particularly convenient method for preparing I is to use octacarbonyldicobalt in acetonitrile, which reacts to form tetracarbonylcobaltate.²⁴



I is also the principal product with sodium decacarbonyltricobaltate, but a small amount of (triphenylcyclopropenyl)tricarbonylcobalt, VIII, is also formed. With $\text{Co}_2(\text{CO})_8$ in CH_2Cl_2 , VIII becomes a principal product and can be isolated in 34% yield (not optimized) by column chromatography, along with 33% of I. Cobalt(II) fluoroborate is also obtained as an insoluble orchid solid. The reaction presumably occurs according to the equation



VIII is a yellow air-stable solid, mp 104–105 °C. Its IR spectrum (CCl_4) shows carbonyl peaks at 2064 and 1995 cm^{-1} , the latter being somewhat broader. Its proton NMR spectrum shows multiplets at δ 7.6 (2 H) and 7.3 (3 H). The mass spectrum (direct inlet, 70 eV) shows important peaks at m/e (relative intensity, ion) 410 (0.1, $\text{Ph}_3\text{C}_3\text{Co}(\text{CO}_3)$), 382 (2, $\text{Ph}_3\text{C}_3\text{Co}(\text{CO})_2$), 354 (18, $\text{Ph}_3\text{C}_3\text{CoCO}$), 326 (8, $\text{Ph}_3\text{C}_3\text{Co}$), and 267 (100, Ph_3C_3). The ^{13}C NMR spectrum shows resonances at δ 132.4 (α C), 129.1 and 128.8 (ortho and meta C's), 128.0 (para C), and 51.3 (cyclopropenyl C's), confirming the threefold symmetry of the η -cyclopropenyl ring. The latter value interpolates very well between the chemical shifts of the

Table II. Positional and Thermal Parameters and Their Estimated Standard Deviations^a

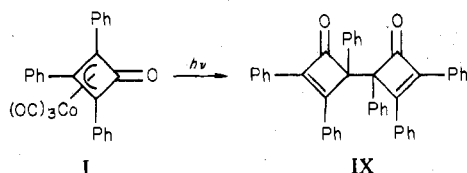
| | x | y | z | B ₁₁ | B ₂₂ | B ₃₃ | B ₁₂ | B ₁₃ | B ₂₃ |
|-------|-------------|-------------|-------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| Co | 0.11796 (4) | 0.07761 (5) | 0.26561 (4) | 4.27 (2) | 4.01 (2) | 4.93 (3) | -0.21 (2) | 1.50 (2) | -0.05 (3) |
| O(1) | 0.0266 (3) | 0.2508 (4) | 0.1078 (2) | 9.4 (2) | 7.0 (2) | 8.0 (2) | 0.7 (2) | 0.4 (2) | 2.3 (2) |
| O(2) | 0.8721 (3) | 0.3193 (3) | 0.3129 (3) | 12.5 (2) | 4.7 (2) | 13.0 (2) | 1.0 (2) | 4.8 (2) | 2.7 (2) |
| O(3) | 0.9617 (2) | 0.0503 (4) | 0.3676 (3) | 6.8 (2) | 8.8 (2) | 13.2 (2) | 1.0 (2) | 6.4 (2) | 2.2 (2) |
| C(1) | 0.0598 (3) | 0.1811 (4) | 0.1679 (3) | 5.4 (2) | 4.7 (2) | 6.2 (2) | -0.2 (2) | 1.0 (2) | -0.4 (2) |
| C(2) | 0.8791 (3) | 0.4189 (4) | 0.2837 (3) | 6.0 (2) | 5.1 (2) | 6.9 (2) | 0.8 (2) | 2.2 (2) | -0.2 (2) |
| C(3) | 0.0199 (3) | 0.0627 (4) | 0.3260 (3) | 4.6 (2) | 5.1 (2) | 8.0 (2) | 0.5 (2) | 2.2 (2) | 0.7 (2) |
| C(4) | 0.2215 (3) | 0.2035 (4) | 0.3444 (3) | 3.8 (2) | 4.3 (2) | 4.1 (2) | 0.0 (2) | 1.2 (2) | 0.1 (2) |
| C(5) | 0.2490 (3) | 0.0721 (4) | 0.3718 (2) | 4.1 (2) | 3.7 (2) | 4.6 (2) | 0.0 (2) | 1.9 (2) | -0.3 (2) |
| C(6) | 0.2709 (3) | 0.1259 (4) | 0.2920 (3) | 3.8 (2) | 3.8 (2) | 4.4 (2) | -0.4 (2) | 1.4 (2) | 0.4 (2) |
| C(41) | 0.2136 (3) | 0.3341 (4) | 0.3799 (3) | 4.4 (2) | 4.1 (2) | 4.0 (2) | 0.5 (2) | 0.9 (2) | -0.2 (2) |
| C(42) | 0.2526 (4) | 0.4400 (4) | 0.3468 (3) | 8.4 (3) | 4.7 (2) | 7.7 (3) | -1.3 (2) | 4.1 (3) | -0.9 (2) |
| C(43) | 0.2464 (4) | 0.5628 (5) | 0.3820 (4) | 9.8 (3) | 4.1 (2) | 10.0 (3) | 1.4 (2) | 3.8 (3) | 0.6 (2) |
| C(44) | 0.2019 (4) | 0.5793 (4) | 0.4512 (3) | 7.0 (2) | 4.5 (2) | 7.4 (3) | -0.7 (2) | 0.3 (2) | 2.1 (2) |
| C(45) | 0.1620 (5) | 0.4767 (5) | 0.4851 (3) | 11.1 (3) | 6.5 (3) | 6.4 (2) | 1.2 (2) | 3.6 (3) | -1.1 (2) |
| C(46) | 0.1677 (4) | 0.3536 (5) | 0.4493 (3) | 9.7 (3) | 4.8 (2) | 6.4 (2) | 0.3 (2) | 3.8 (3) | -0.1 (2) |
| C(51) | 0.2884 (3) | -0.0090 (4) | 0.4548 (2) | 4.2 (2) | 3.3 (2) | 3.9 (2) | 0.4 (2) | 1.6 (2) | 0.0 (2) |
| C(52) | 0.2372 (3) | -0.0161 (4) | 0.5234 (3) | 5.6 (2) | 4.3 (2) | 5.6 (2) | -0.6 (2) | 2.6 (2) | -0.4 (2) |
| C(53) | 0.2778 (3) | -0.0880 (4) | 0.6024 (3) | 6.7 (2) | 5.0 (2) | 4.9 (2) | -0.1 (2) | 3.1 (3) | 0.4 (2) |
| C(54) | 0.3693 (4) | -0.1555 (4) | 0.6151 (3) | 7.1 (2) | 5.0 (2) | 4.0 (2) | -0.1 (2) | 1.3 (2) | 0.9 (2) |
| C(55) | 0.4199 (3) | -0.1522 (5) | 0.5482 (3) | 5.5 (2) | 6.5 (2) | 5.7 (2) | 1.8 (2) | 1.7 (2) | 1.3 (2) |
| C(56) | 0.3796 (3) | -0.0805 (4) | 0.4681 (3) | 5.0 (2) | 5.8 (2) | 4.7 (2) | -0.5 (2) | 2.3 (2) | -0.4 (2) |
| C(61) | 0.3401 (3) | 0.1213 (4) | 0.2327 (2) | 4.0 (2) | 4.3 (2) | 3.7 (2) | -0.5 (2) | 1.2 (2) | -0.3 (2) |
| C(62) | 0.3512 (3) | 0.2299 (4) | 0.1812 (3) | 5.0 (2) | 4.6 (2) | 5.4 (2) | 0.2 (2) | 2.0 (2) | 0.7 (2) |
| C(63) | 0.4144 (3) | 0.2265 (5) | 0.1237 (3) | 6.2 (3) | 6.6 (3) | 5.5 (2) | -0.4 (2) | 2.9 (2) | 1.2 (2) |
| C(64) | 0.4674 (3) | 0.1153 (5) | 0.1169 (3) | 6.0 (3) | 8.6 (3) | 5.9 (2) | -0.7 (2) | 3.9 (2) | -0.7 (2) |
| C(65) | 0.4575 (3) | 0.0067 (5) | 0.1657 (3) | 6.8 (3) | 5.7 (2) | 6.6 (2) | 0.2 (2) | 3.8 (2) | -0.7 (2) |
| C(66) | 0.3938 (3) | 0.0097 (4) | 0.2230 (3) | 6.3 (2) | 4.3 (2) | 5.5 (2) | 0.0 (2) | 2.8 (2) | 0.2 (2) |

| | x | y | z | B, Å ² | x | y | z | B, Å ² | |
|-------|-----------|-----------|-----------|-------------------|-------|-----------|-----------|-------------------|----------|
| H(42) | 0.285 (3) | 0.425 (7) | 0.297 (2) | 5.8 (10) | H(55) | 0.519 (3) | 0.196 (4) | 0.444 (2) | 6.4 (10) |
| H(43) | 0.728 (4) | 0.132 (5) | 0.147 (3) | 11.1 (15) | H(56) | 0.585 (3) | 0.420 (4) | 0.076 (2) | 6.1 (10) |
| H(44) | 0.802 (3) | 0.161 (4) | 0.027 (2) | 5.7 (9) | H(62) | 0.318 (3) | 0.308 (3) | 0.188 (2) | 5.0 (9) |
| H(45) | 0.122 (4) | 0.017 (5) | 0.033 (3) | 9.3 (13) | H(63) | 0.425 (3) | 0.300 (4) | 0.085 (3) | 7.4 (11) |
| H(46) | 0.139 (3) | 0.285 (4) | 0.475 (3) | 7.0 (11) | H(64) | 0.502 (3) | 0.111 (3) | 0.080 (2) | 4.7 (8) |
| H(52) | 0.177 (3) | 0.036 (3) | 0.518 (2) | 4.7 (8) | H(65) | 0.503 (3) | 0.420 (4) | 0.353 (3) | 6.7 (11) |
| H(53) | 0.759 (3) | 0.093 (4) | 0.352 (2) | 6.0 (10) | H(66) | 0.613 (3) | 0.438 (3) | 0.254 (2) | 4.7 (8) |
| H(54) | 0.607 (3) | 0.198 (3) | 0.330 (2) | 4.9 (9) | | | | | |

^a The form of the anisotropic thermal parameter is $\exp[-1/4(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^{*}b^{*} + 2B_{13}hla^{*}c^{*} + 2B_{23}hkb^{*}c^{*})]$.

ring carbons of tetra-*tert*-butyltetrahedrane, 10.2,¹⁹ and (diphenylacetylene)hexacarbonylcobalt, 89.6,²⁸ in consonance with their familial relationship. The ¹³C data are also very similar to those of VI: δ 134.3 (α C), 128.8 and 128.6 (ortho and meta C's), 127.3 (para C), 53.2 (cyclopropenyl C's), and 88.8 (Cp).

One unsuccessful attempt at synthesis of VIII deserves mention. On the basis of the premise that photochemically induced decarbonylation of I would give a reactive isomer of VIII which might rearrange to VIII, we subjected I to photolysis at 254 nm. The principal product (75% yield) was an organic compound, mp 174–175 °C, whose IR [1760 (s), 1630 (m) cm⁻¹], UV [308 nm, ε 26 600], and mass [*m/e* 590 (Ph₆C₈O₂), 562 (Ph₆C₇O), 513 (Ph₅C₈O₂), 178 (Ph₂C₂), 105 (PhCO)] spectra indicated structure IX. The only other



product was an unstable blue-fluorescent compound which we were unable to purify. No VIII could be detected in the crude photolysate by TLC.

Crystal and Molecular Structures

The crystal structure of Ph₃C₃Co(CO)₃, VIII, consists of well-separated, discrete molecules with no unusual intermolecular contacts. As can be seen in Figure 1, the packing is

dominated by the phenyl rings.

The molecular structure and labeling scheme are illustrated in Figure 2, which shows a view down the pseudo-threefold axis. Important bond distances are displayed in Figure 3. A detailed list of bond distances and angles is presented in Table III.

The triphenylcyclopropenyl ligand is bound to the cobalt tricarbonyl fragment in the expected symmetrical fashion, forming an elongated tetrahedron of atoms with Co–C distances averaging 2.01 (1) Å and C–C distances averaging 1.42 (1) Å. The CO ligands are bound to the cobalt at an average distance of 1.797 (5) Å with an orientation staggered with respect to the ring carbon atoms. The angles between the CO ligands average 104.5 (8)° and are thus compressed only 5° from the values expected for a true tetrahedral, four-coordinate metal complex. As is normal, the CO ligands deviate slightly, an average of 3.4 (4)°, from linearity.

The exocyclic C–C bond distances average 1.459 (3) Å. The phenyl rings tilt back out of the plane of the three-membered ring and in addition twist about their respective axes. These tilt and twist angles are defined and given in Table III. The phenyls are otherwise normal, with C–C bond distances averaging 1.37 Å and all C atoms within 0.01 Å of the respective phenyl least-squares planes. The hydrogen atoms were easily located by difference Fourier methods and were refined, resulting in the expected range of C–H distances and angles.

The present structure is the first of a cyclopropenylcobalt complex. The structures of the free triphenylcyclopropenium cation²⁹ as well as two nickel complexes (the mixed cyclopentadienyl–triphenylcyclopropenyl sandwich compound,¹⁶ VI,

Table III. Selected Distances (Å) and Angles (deg) in $\text{Co}(\text{CO})_3(\text{C}_3\text{Ph}_3)$

| Distances | | | |
|------------|-----------|------------|-----------|
| Co-C(1) | 1.794 (5) | C(6)-C(61) | 1.456 (4) |
| Co-C(2) | 1.797 (5) | C(1)-O(1) | 1.136 (4) |
| Co-C(3) | 1.800 (4) | C(2)-O(2) | 1.128 (5) |
| Co-C(4) | 2.008 (3) | C(3)-O(3) | 1.134 (4) |
| Co-C(5) | 1.995 (3) | C(4)-C(5) | 1.428 (5) |
| Co-C(6) | 2.024 (3) | C(4)-C(6) | 1.410 (5) |
| C(4)-C(41) | 1.460 (5) | C(5)-C(6) | 1.421 (5) |
| C(5)-C(51) | 1.462 (4) | | |

| Angles | | | |
|--------------|-----------|----------------|-----------|
| C(1)-Co-C(2) | 105.0 (2) | C(4)-Co-C(6) | 40.9 (1) |
| C(1)-Co-C(3) | 104.8 (2) | C(5)-Co-C(6) | 41.4 (1) |
| C(1)-Co-C(4) | 99.1 (2) | Co-C(1)-O(1) | 176.7 (4) |
| C(1)-Co-C(5) | 137.7 (2) | Co-C(2)-O(2) | 176.6 (4) |
| C(1)-Co-C(6) | 100.8 (2) | Co-C(3)-O(3) | 176.6 (4) |
| C(2)-Co-C(3) | 103.6 (2) | C(4)-C(5)-C(6) | 59.3 (2) |
| C(2)-Co-C(4) | 137.2 (2) | C(5)-C(6)-C(4) | 60.6 (2) |
| C(2)-Co-C(5) | 100.6 (2) | C(6)-C(4)-C(5) | 60.1 (2) |
| C(2)-Co-C(6) | 99.3 (2) | Co-C(4)-C(41) | 134.2 (2) |
| C(3)-Co-C(4) | 103.6 (2) | Co-C(5)-C(51) | 135.2 (2) |
| C(3)-Co-C(5) | 101.2 (2) | Co-C(6)-C(61) | 130.9 (2) |
| C(4)-Co-C(5) | 41.8 (1) | | |

| Special Phenyl Angles | | | |
|---|-----------|--------------------------|--|
| cent ^a -C(4)-C(41) | 159.7 (3) | (20.3 (3) ^b) | |
| cent-C(5)-C(51) | 157.8 (3) | (22.2 (3) ^b) | |
| cent-C(6)-C(61) | 164.1 (3) | (15.9 (3) ^b) | |
| [cent, C(4), C(41)], [C(41), . . . , C(46)] | 13.5° | | |
| [cent, C(5), C(51)], [C(51), . . . , C(56)] | 19.2° | | |
| [cent, C(6), C(61)], [C(61), . . . , C(66)] | 2.9° | | |

^a The coordinates of the point "cent" are the average of the coordinates of C(4), C(5), and C(6). ^b Tilt angle, defined as the supplement of the preceding angle. ^c Twist, defined as the complement of the dihedral angle between the least-squares planes of the atoms indicated.

and the pyridine complex,¹⁵ V) are known (Table IV). The three-membered ring C-C bond distances and the exocyclic C-C distances show similar trends for all three complexes. The ring C-C distances increase upon coordination, from 1.375 (5) to 1.42 (1) Å consistently, while the exocyclic distances show a smaller increase from 1.436 (3) to 1.46 (1) Å. Upon complexation the phenyl rings tilt back away from the metal. In an idealized tetrahedrane molecule of T_d symmetry this tilt angle would be 19.47°. The observed angles for the three complexes approximate this value with a range of 15.9–22.2° and an average of 19 (1)°. The phenyl twist angles are variable, ranging from 2.9 to 23.5° with no particular trends observed.

It is also useful to compare the cobalt triphenylcyclopropenyl structure with the structures of analogous (η^3 -allyl)tri-

Table IV. Selected Bond Distances (Å) and Angles (deg) for the Triphenylcyclopropenyl Cation and Several Complexes

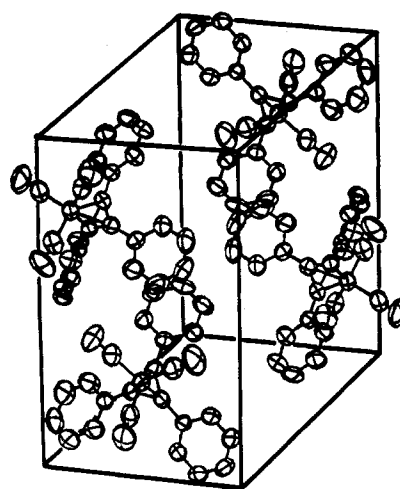
| compd | M-C(ring) ^a | C-C(ring) ^a | C-C(exo) ^a | phenyl tilt ^b | phenyl twist ^b | ref |
|---|------------------------|------------------------|-----------------------|--------------------------|---------------------------|----------|
| C_3Ph_3^+ | | 1.373 (5) | 1.436 (3) | "0" ^c | 7.6, 12.1, 21.2 | 29 |
| $\text{Co}(\text{CO})_3(\text{C}_3\text{Ph}_3)$ | 2.01 (1) | 1.42 (1) | 1.459 (3) | 2.9, 19.2, 13.5 | 15.9, 22.2, 20.3 | <i>d</i> |
| $\text{NiCp}(\text{C}_3\text{Ph}_3)$ | 1.961 (4) | 1.43 (1) | 1.45 (1) | 19.2, 19.7, 20.1 | 20.1, 23.5, 20.1 | 16 |
| $\text{NiCl}(\text{py})_2(\text{C}_3\text{Ph}_3)$ | 1.941 (5) | 1.42 (1) | 1.46 (1) | 16.7, 19.4, 20.2 | 8.4, 13.4, 18.9 | 15 |

^a Average values. ^b Defined in Table III. ^c Angles are not given, but deviations are quite small. ^d This work.

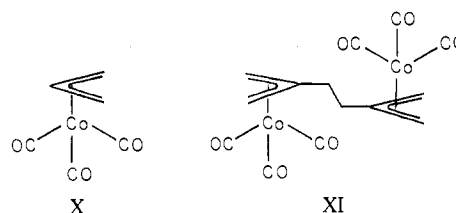
Table V. Selected Distances (Å) and Angles (deg) of Some η^3 -(CO)₃L Compounds

| compd | Co-C(CO) | Co-C(L) ^a | C-C(L) | C-Co-C(CO) | ref |
|--|------------------------|-------------------------------|-----------|---------------------------------|----------|
| $\text{Co}(\text{CO})_3(\text{C}_3\text{Ph}_3)$, VIII | 1.80 (1) | 2.01 (1) | 1.42 (1) | 105.0 (2), 104.8 (2), 103.6 (2) | <i>b</i> |
| $\text{Co}(\text{CO})_3(\text{C}_3\text{H}_5)$, X | 1.804 (3) | 2.101 (6), t 1.985 (16), c | 1.391 (9) | 101 (1), 109 (2) | 30 |
| $\text{Co}(\text{CO})_3[(\text{PhC})_3\text{CO}]$, ^c I | 1.83 | 2.11 (3), t 2.00 (3), c | 1.47 (1) | | 3 |
| $[\text{Co}(\text{CO})_3[(\text{CH}_2)_2\text{CCH}_2]]_2$, XI | 1.769 (1) 1.815 (2) | 2.095 (1), t 2.010 (2), c | 1.409 (2) | 97.0 (1), 107.4 (1) | 31 |

^a For the η^3 -allyl complexes, distances are given for terminal (t) and central (c) Co-C bond distances. ^b This work. ^c Average values of chemically equivalent distances from two independent molecules are given.

**Figure 1.** The crystal packing. The origin is at the upper left front corner. The *c* axis is vertical and the *b* axis is horizontal. The *a* axis completes the right-handed coordinate system. The hydrogen atoms are deleted for clarity.

carbonylcobalt complexes. Structures have been reported for three such compounds, including an electron diffraction study of the parent complex,³⁰ X, a preliminary X-ray study³ of I,



and a definitive study of the complex XI³¹ (Table V). The distances from the Co atom to the ligand carbon atoms are similar for all four complexes. In the cyclopropenyl complex VIII the Co-C distances average 2.01 (1) Å, which is close to the values found for the distance to the central carbon of an η^3 -allyl ligand. The terminal C atoms of the η^3 -allyl are about 0.1 Å further from the Co atom. The major structural differences between the η^3 -allyl and cyclopropenyl complexes are the angles between the CO ligands. The η^3 -allyl complexes can be considered to be pseudo-square-pyramidal complexes with the η^3 -allyl occupying two equatorial positions.³² The molecules have approximate C_3 symmetry, with the angle between the equatorial CO ligands significantly less than the angles between the equatorial CO and axial CO ligands. In the cyclopropenyl complex the symmetry is approximately C_{3v} ,

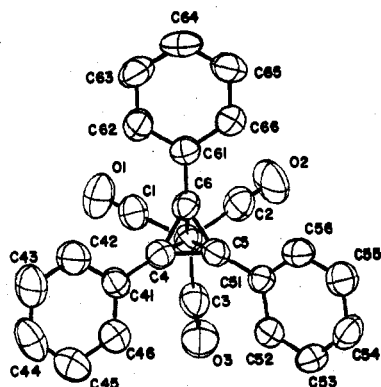


Figure 2. View of the $\text{Co}(\text{CO})_3(\text{C}_3\text{Ph}_3)$ molecule down the pseudo-threefold axis. The 50% probability ellipsoids are depicted.

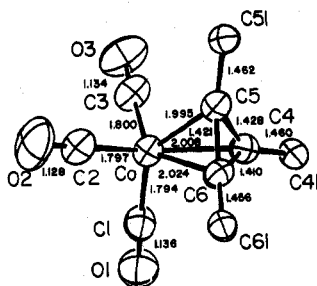


Figure 3. Important bond distances within the central portion of the $\text{Co}(\text{CO})_3(\text{C}_3\text{Ph}_3)$ molecule.

Table VI. Selected Bond Distances (Å) for the Cobaltatetrahdrene Family $[\text{Co}(\text{CO})_3]_n[\text{CR}]_{4-n}$

| n | cluster | | | C-R | ref |
|---|-----------|----------|--------------|--------------|--------------|
| | Co-Co | Co-C | C-C | | |
| 4 | 2.49 (2) | | | | 33 |
| 3 (R = CH ₃) | 2.47 (1) | 1.90 (2) | | 1.54 (1) | 34 |
| 2 (R = C(CH ₃) ₃) | 2.463 (1) | 2.00 (1) | 1.335 (6) | 1.512 (7) | 35 |
| 1 (R = C ₆ H ₅) | | 2.01 (1) | 1.42 (1) | 1.459 (3) | ^b |
| 0 (R = C(CH ₃) ₃) | | | ^a | ^a | 19 |

^a Compound has been prepared and reference made to a planned structure determination. ^b This work.

and the angles between the CO ligands are essentially equivalent.

Finally, it is of interest to compare the members of the cobaltatetrahdrene family (Table VI). Substituted derivatives of all five members have now been synthesized, and structures are available for all but the tetrahdrene. The Co-Co bond distances within the series change very little, perhaps indicating a constant mode of bonding by $\text{Co}(\text{CO})_3$ groups. While bond distances to carbon within the clusters tend to increase as the clusters become more carbon rich, the C(cluster) to C(substituent) distances tend to decrease. These changes are consistent with use by carbon of orbitals of in-

creasing p character within the cluster and s character outside it as bonds to Co are replaced by bonds to more electronegative C.

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Registry No. I, 51509-08-1; VIII, 69745-64-8; IX, 69745-17-1; $\text{NaCo}_3(\text{CO})_{10}$, 26248-46-4; $\text{Co}_2(\text{CO})_8$, 10210-68-1.

Supplementary Material Available: Tables VII and VIII, showing root-mean-square amplitudes of thermal vibration and structure factor amplitudes (10 pages). Ordering information is given on any current masthead page.

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