

Contribution from the Department of Chemistry,  
Texas A&M University, College Station, Texas 77843

## Structures and Infrared Spectra of Tricyclopentadienyltricobalt Tricarbonyl and Its Methylcyclopentadienyl Analogue

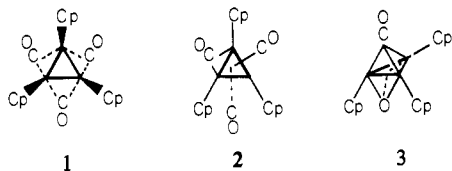
WEBB I. BAILEY, JR., F. ALBERT COTTON,\* JACKIE D. JAMERSON, and BRIAN W. S. KOLTHAMMER

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The title compounds,  $\text{Cp}_3\text{Co}_3(\text{CO})_3$  (A) and  $(\text{mCp})_3\text{Co}_3(\text{CO})_3$  (B), where Cp and mCp represent  $\eta^5\text{-C}_5\text{H}_5$  and  $\eta^5\text{-C}_5\text{H}_4\text{CH}_3$ , respectively, were prepared by photolysis of  $\text{CpCo}(\text{CO})_2$  and  $(\text{mCp})\text{Co}(\text{CO})_2$ , respectively. They were purified by chromatography and crystallized from hexane/THF. The molecular structures were determined by conventional single-crystal X-ray diffraction methods. Compound A crystallizes in space group  $P\bar{1}$  with  $Z = 2$  and unit cell dimensions of  $a = 9.128$  (4) Å,  $b = 11.691$  (5) Å,  $c = 7.948$  (4) Å,  $\alpha = 105.45$  (4)°,  $\beta = 100.70$  (4)°, and  $\gamma = 91.21$  (3)°. Compound B crystallizes in space group  $P2_1$  with  $Z = 4$  and unit cell dimensions of  $a = 7.999$  (2) Å,  $b = 13.227$  (3) Å,  $c = 18.535$  (4) Å, and  $\beta = 106.25$  (2)°. The  $\text{Cp}_3\text{Co}_3(\text{CO})_3$  and  $(\text{mCp})_3\text{Co}_3(\text{CO})_3$  molecules have essentially identical structures, in which the Co atoms form approximately equilateral triangles and there is one Cp or mCp ring attached to each. One CO group lies approximately above the center of the  $\text{Co}_3$  triangle, and the other two lie below two of the edges; neither the  $\mu_3\text{-CO}$  nor the  $\mu_2\text{-CO}$  groups are precisely symmetrical in either case. The infrared spectra show that this structure changes in solution, probably to one with one terminal CO and two  $\mu_2\text{-CO}$ 's. Both  $\text{Cp}_3\text{Co}_3(\text{CO})_3$  and  $(\text{mCp})_3\text{Co}_3(\text{CO})_3$  behave stereochemically in essentially the same way under all conditions.

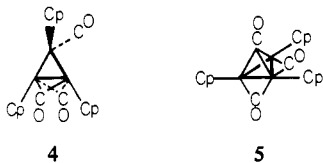
## Introduction

The first trinuclear cyclopentadienylmetal carbonyl compound with metal-metal bonds,  $\text{Cp}_3\text{Ni}_3(\text{CO})_2$  ( $\text{cp} = \eta^5\text{-C}_5\text{H}_5$ ), was reported more than 20 years ago by Fischer and Palm.<sup>1</sup> This paramagnetic species, however, is rather singular. The first member of the family of compounds with the general formula  $[\text{CpMCO}]_3$  was the cobalt compound, reported in 1964 by King,<sup>2</sup> who suggested, on the basis of solubility differences and IR and  $^1\text{H}$  NMR spectra, that two isomers were present. He proposed the formulas shown schematically as **1** and **2** to represent these.



In 1969, Dahl<sup>3</sup> made an effort to check on one of these structures by X-ray crystallography but, unfortunately, determined only the structure of what is presumably a decomposition product,  $\text{Cp}_3\text{Co}_3(\text{CO})\text{O}$  (**3**).

In the meantime, two isomeric rhodium compounds,  $[\text{CpRhCO}]_3$ , were structurally characterized<sup>4,5</sup> and shown to have structures **1** and **4**. However, the methods then available



for preparation of these isomeric rhodium compounds were so inefficient that sufficient material for follow-up studies to investigate their dynamic properties was not available. The only pertinent fact established at that time was that they did not appear to interconvert thermally at room temperature in solution, over periods of minutes to hours.

Table I. Summary of Crystallographic Data

	$[(\text{C}_5\text{H}_5)\text{-Co}(\text{CO})_3]$	$[(\text{CH}_3\text{C}_5\text{H}_4)\text{-Co}(\text{CO})_3]$
fw	456.12	498.20
space group	$P\bar{1}$	$P2_1$
<i>a</i> , Å	9.128 (4)	7.999 (4)
<i>b</i> , Å	11.691 (5)	13.227 (3)
<i>c</i> , Å	7.948 (4)	18.535 (4)
$\alpha$ , deg	105.45 (4)	90.00
$\beta$ , deg	100.70 (4)	106.25 (2)
$\gamma$ , deg	91.21 (3)	90.00
<i>V</i> , Å <sup>3</sup>	801 (1)	1883 (1)
<i>Z</i>	2	4
density (calcd), g/cm <sup>3</sup>	1.89	1.90
cryst size, mm	0.2 × 0.3 × 0.4	0.3 × 0.1 × 0.3
range of $2\theta$ , deg	0 < $2\theta$ ≤ 55	0 < $2\theta$ ≤ 45
no. of refltns collected	2738	1539
no. of refltns > $3\sigma$	2547	1388
no. of variables	217	246
<i>R</i> <sub>1</sub>	0.044	0.053
<i>R</i> <sub>2</sub>	0.060	0.068
esd of observn of unit wt	1.269	1.517

In 1975 new work involving the cobalt compound was reported.<sup>6</sup> A reaction mechanism for the formation of  $[\text{CpCoCO}]_3$  was proposed in which  $\text{CpCoCO}$ , formed by loss of CO from  $\text{CpCo}(\text{CO})_2$ , was the key intermediate, able to recombine with CO, react with another  $\text{CpCo}(\text{CO})_2$  to form a new, unstable compound,  $\text{Cp}_2\text{Co}_2(\text{CO})_3$ , or trimerize to form  $[\text{CpCoCO}]_3$ . The trinuclear product described in this new work was in some respects slightly different from both of the substances to which King had assigned such a formula but was nevertheless assumed to be "essentially the complex isolated by King". It was suggested<sup>6</sup> that the terminal carbonyl stretching frequencies reported by King were probably in error because of contamination by  $\text{Cp}_2\text{Co}_2(\text{CO})_3$ . Structure **2** was favored.

However, even as this work appeared, it was known in our laboratory that  $[\text{CpCoCO}]_3$  did exist but had none of the structures (**1**, **2**, or **4**) previously proposed for it or known for the rhodium analogue. We reported<sup>7</sup> in 1976 that crystalline  $[\text{CpCoCO}]_3$  contains molecules with structure **5**, in which none of the CO bridges is fully symmetrical, particularly the edge bridges. This structure solved the long-standing problem of

(1) Fischer, E. O.; Palm, C. *Chem. Ber.* **1958**, *91*, 1725.  
 (2) King, R. B. *Inorg. Chem.* **1966**, *58*, 2227.  
 (3) Uchtman, V. A.; Dahl, L. F. *J. Am. Chem. Soc.* **1969**, *91*, 3763.  
 (4) Mills, O. S.; Paulus, E. F. *J. Organomet. Chem.* **1967**, *10*, 331.  
 (5) Paulus, E. F. *Acta Crystallogr., Sect. B* **1969**, *B25*, 2206.

(6) Vollhardt, K. P. C.; Bercaw, J. E.; Bergman, R. G. *J. Organomet. Chem.* **1975**, *97*, 283.

(7) Cotton, F. A.; Jamerson, J. D. *J. Am. Chem. Soc.* **1976**, *98*, 1273.

**Table II.** Positional Parameters and Their Estimated Standard Deviations for  $\text{Cp}_3\text{Co}_3(\text{CO})_3$ 

atom	x	y	z	atom	x	y	z
Co(1)	0.0314 (1)	0.2388 (1)	0.2153 (1)	C(3,2)	0.2798 (7)	0.0283 (5)	0.3763 (8)
Co(2)	0.2409 (1)	0.3492 (1)	0.1647 (1)	C(3,3)	0.2936 (8)	0.1296 (6)	0.5277 (8)
Co(3)	0.2953 (1)	0.1840 (1)	0.2981 (1)	C(3,4)	0.4308 (8)	0.1928 (6)	0.5474 (8)
O(1)	0.0357 (6)	0.2081 (5)	-0.1541 (5)	C(3,5)	0.5011 (7)	0.1358 (7)	0.4114 (9)
O(2)	0.3852 (7)	0.1430 (5)	-0.0382 (7)	H(1,1)	-0.0583	0.0522	0.3302
O(3)	0.2095 (5)	0.4006 (3)	0.5341 (5)	H(1,2)	-0.0470	0.2552	0.5368
C(1)	0.0735 (7)	0.2398 (5)	0.0028 (7)	H(1,3)	-0.1678	0.3905	0.3545
C(2)	0.3351 (8)	0.1834 (6)	0.0872 (8)	H(1,4)	-0.2465	0.2629	0.0363
C(3)	0.1971 (6)	0.3346 (5)	0.3877 (7)	H(1,5)	-0.1757	0.0567	0.0259
C(1,1)	-0.0939 (9)	0.1200 (6)	0.2973 (11)	H(2,1)	0.3828	0.3667	-0.0954
C(1,2)	-0.0895 (8)	0.2315 (7)	0.4123 (9)	H(2,2)	0.5291	0.4346	0.2356
C(1,3)	-0.1561 (8)	0.3076 (6)	0.3109 (12)	H(2,3)	0.3675	0.5623	0.4059
C(1,4)	-0.1977 (8)	0.2359 (8)	0.1342 (11)	H(2,4)	0.1377	0.5719	0.2130
C(1,5)	-0.1595 (8)	0.1217 (7)	0.1291 (11)	H(2,5)	0.1444	0.4627	-0.0874
C(2,1)	0.3531 (17)	0.4156 (7)	0.0061 (15)	H(3,1)	0.4306	-0.0227	0.2037
C(2,2)	0.4323 (9)	0.4549 (9)	0.1903 (18)	H(3,2)	0.1980	-0.0309	0.3320
C(2,3)	0.3421 (13)	0.5237 (7)	0.2812 (11)	H(3,3)	0.2228	0.1508	0.6024
C(2,4)	0.2179 (13)	0.5292 (8)	0.1742 (18)	H(3,4)	0.4689	0.2634	0.6396
C(2,5)	0.2241 (16)	0.4679 (10)	0.0111 (14)	H(3,5)	0.5933	0.1615	0.3924
C(3,1)	0.4085 (8)	0.0331 (6)	0.3051 (8)				

**Table III.** Positional Parameters and Their Estimated Standard Deviations for  $(\text{mCp})_3\text{Co}_3(\text{CO})_3$ 

atom	x	y	z	atom	x	y	z
Co(1)	0.2005 (3)	0.0810 (0)	0.4238 (2)	C(2,4)	0.441 (4)	0.048 (3)	0.611 (2)
Co(2)	0.0298 (3)	-0.0730 (2)	0.4203 (2)	C(2,5)	0.304 (3)	0.044 (2)	0.646 (1)
Co(3)	0.2279 (4)	-0.0223 (3)	0.5402 (2)	C(2,6)	0.148 (4)	-0.106 (3)	0.695 (2)
Co(4)	0.2154 (3)	0.5773 (3)	0.9643 (2)	C(3,1)	0.026 (3)	-0.218 (2)	0.370 (1)
Co(5)	0.4161 (4)	0.6641 (3)	1.0676 (2)	C(3,2)	-0.029 (3)	-0.147 (2)	0.315 (1)
Co(6)	0.2392 (4)	0.5276 (3)	1.0969 (2)	C(3,3)	-0.178 (3)	-0.100 (2)	0.322 (1)
O(1)	0.396 (2)	-0.109 (1)	0.4331 (7)	C(3,4)	-0.223 (3)	-0.136 (2)	0.379 (1)
O(2)	-0.167 (2)	0.126 (1)	0.3950 (8)	C(3,5)	-0.090 (3)	-0.215 (2)	0.421 (1)
O(3)	-0.128 (2)	-0.023 (1)	0.5398 (8)	C(3,6)	0.174 (4)	-0.293 (2)	0.381 (2)
O(4)	0.048 (2)	0.712 (1)	1.0475 (7)	C(4,1)	0.167 (3)	0.599 (2)	0.849 (1)
O(5)	0.604 (2)	0.483 (2)	1.1317 (9)	C(4,2)	0.018 (3)	0.639 (2)	0.869 (1)
O(6)	0.570 (2)	0.571 (1)	0.9620 (8)	C(4,3)	-0.038 (3)	0.556 (2)	0.906 (1)
C(1)	0.282 (3)	-0.062 (2)	0.448 (1)	C(4,4)	0.055 (3)	0.468 (2)	0.899 (1)
C(2)	-0.030 (3)	0.084 (2)	0.411 (1)	C(4,5)	0.178 (3)	0.491 (2)	0.866 (1)
C(3)	-0.010 (3)	-0.031 (2)	0.517 (1)	C(4,6)	0.278 (3)	0.656 (2)	0.808 (1)
C(4)	0.164 (3)	0.655 (2)	1.042 (1)	C(5,1)	0.466 (3)	0.774 (2)	1.154 (1)
C(5)	0.468 (3)	0.522 (2)	1.112 (1)	C(5,2)	0.622 (3)	0.721 (2)	1.155 (1)
C(6)	0.448 (3)	0.587 (2)	0.984 (1)	C(5,3)	0.660 (3)	0.736 (2)	1.091 (1)
C(1,1)	0.351 (3)	0.116 (2)	0.349 (1)	C(5,4)	0.536 (3)	0.795 (2)	1.042 (1)
C(1,2)	0.202 (3)	0.181 (2)	0.337 (1)	C(5,5)	0.406 (3)	0.826 (2)	1.087 (1)
C(1,3)	0.222 (3)	0.237 (2)	0.403 (1)	C(5,6)	0.367 (5)	0.779 (4)	1.216 (2)
C(1,4)	0.374 (3)	0.202 (2)	0.455 (1)	C(6,1)	0.229 (3)	0.397 (2)	1.160 (1)
C(1,5)	0.454 (3)	0.128 (2)	0.423 (1)	C(6,2)	0.078 (3)	0.404 (2)	1.092 (1)
C(1,6)	0.386 (3)	0.042 (2)	0.292 (1)	C(6,3)	-0.011 (3)	0.491 (2)	1.099 (1)
C(2,1)	0.268 (3)	-0.057 (2)	0.656 (1)	C(6,4)	0.066 (3)	0.542 (2)	1.166 (1)
C(2,2)	0.385 (3)	-0.114 (2)	0.625 (2)	C(6,5)	0.226 (3)	0.481 (2)	1.206 (1)
C(2,3)	0.487 (3)	-0.046 (2)	0.602 (1)	C(6,6)	0.359 (3)	0.311 (2)	1.175 (1)

**Table IV.** Bond Distances (Å) in  $\text{Cp}_3\text{Co}_3(\text{CO})_3$ <sup>a</sup>

Co(1)-Co(2)	2.438 (1)	O(1)-C(1)	1.183 (7)
-Co(3)	2.519 (1)	O(2)-C(2)	1.163 (7)
-C(1)	1.803 (6)	O(3)-C(3)	1.197 (6)
-C(3)	1.939 (5)	C(1,1)-C(1,2)	1.37 (1)
-C(1,1)	2.087 (6)	C(1,2)-C(1,3)	1.42 (1)
-C(1,2)	2.094 (6)	C(1,3)-C(1,4)	1.41 (1)
-C(1,3)	2.091 (6)	C(1,4)-C(1,5)	1.38 (1)
-C(1,4)	2.067 (7)	C(1,5)-C(1,1)	1.36 (1)
-C(1,5)	2.082 (7)	C(2,1)-C(2,2)	1.45 (1)
Co(2)-Co(3)	2.457 (1)	C(2,2)-C(2,3)	1.34 (1)
-C(1)	1.984 (6)	C(2,3)-C(2,4)	1.30 (1)
-C(2)	2.123 (7)	C(2,4)-C(2,5)	1.31 (1)
-C(3)	1.936 (5)	C(2,5)-C(2,1)	1.34 (2)
-C(2,1)	2.051 (7)	C(3,1)-C(3,2)	1.40 (1)
-C(2,2)	2.065 (7)	C(3,2)-C(3,3)	1.43 (1)
-C(2,3)	2.114 (7)	C(3,3)-C(3,4)	1.40 (1)
-C(2,4)	2.102 (8)	C(3,4)-C(3,5)	1.38 (1)
-C(2,5)	2.069 (7)	C(3,5)-C(3,1)	1.42 (1)
Co(3)-C(2)	1.778 (6)		
-C(3)	2.011 (5)		
-C(3,1)	2.071 (6)		
-C(3,2)	2.085 (5)		
-C(3,3)	2.089 (5)		
-C(3,4)	2.108 (6)		
-C(3,5)	2.084 (6)		

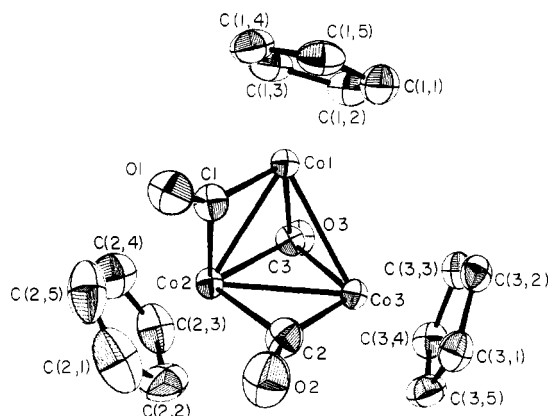
<sup>a</sup> Numbers in parentheses are estimated standard deviations in the least significant digits.**Figure 1.** Molecule of  $\text{Cp}_3\text{Co}_3(\text{CO})_3$ , showing how the atoms are numbered. Each atom is represented by its ellipsoid of thermal vibration scaled to enclose 40% of the electron density. Hydrogen atoms are omitted.

Table V. Bond Angles (Deg) in  $\text{Cp}_3\text{Co}_3(\text{CO})_3^a$ 

Co(2)–Co(1)–Co(3)	59.39 (4)	Co(3)–Co(2)–C(1)	85.1 (2)	Co(1)–C(1)–Co(2)	80.0 (2)
–C(1)	53.2 (2)	–C(2)	44.9 (1)	–O(1)	147.0 (5)
–C(3)	51.0 (1)	–C(3)	52.9 (2)	Co(2)–C(1)–O(1)	132.8 (5)
Co(3)–Co(1)–C(1)	87.1 (2)	C(1)–Co(2)–C(2)	75.2 (3)	Co(2)–C(2)–Co(3)	77.5 (2)
–C(3)	51.7 (2)	C(3)–Co(2)–C(1)	97.7 (2)	–O(2)	129.4 (5)
C(1)–Co(1)–C(3)	104.1 (3)	–C(2)	97.8 (2)	Co(3)–C(2)–O(2)	152.9 (6)
Co(1)–Co(2)–Co(3)	61.95 (3)	Co(1)–Co(3)–Co(2)	58.66 (3)	Co(1)–C(3)–Co(2)	78.0 (2)
–C(1)	46.7 (2)	–C(2)	92.6 (2)	–Co(3)	79.2 (2)
–C(2)	87.0 (2)	–C(3)	49.1 (1)	–O(3)	134.2 (4)
–C(3)	51.1 (2)	Co(2)–Co(3)–C(2)	57.5 (2)	Co(2)–C(3)–Co(3)	76.9 (2)
		–C(3)	50.1 (1)	–O(3)	134.7 (4)
		C(2)–Co(3)–C(3)	107.6 (2)	Co(3)–C(3)–O(3)	131.1 (4)
C(1,1)–C(1,2)–C(1,3)	107.5 (6)	C(2,4)–C(2,5)–C(2,1)	111.3 (10)		
C(1,2)–C(1,3)–C(1,4)	105.9 (6)	C(2,5)–C(2,1)–C(2,2)	103.0 (8)		
C(1,3)–C(1,4)–C(1,5)	108.6 (7)	C(3,1)–C(3,2)–C(3,3)	107.0 (6)		
C(1,4)–C(1,5)–C(1,1)	108.3 (7)	C(3,2)–C(3,3)–C(3,4)	108.0 (6)		
C(1,5)–C(1,1)–C(1,2)	109.7 (7)	C(3,3)–C(3,4)–C(3,5)	108.7 (6)		
C(2,1)–C(2,2)–C(2,3)	106.5 (9)	C(3,4)–C(3,5)–C(3,1)	108.1 (6)		
C(2,2)–C(2,3)–C(2,4)	109.6 (9)	C(3,5)–C(3,1)–C(3,2)	108.3 (6)		
C(2,3)–C(2,4)–C(2,5)	109.5 (10)				

<sup>a</sup> Numbers in parentheses are estimated standard deviations in the least significant digits.

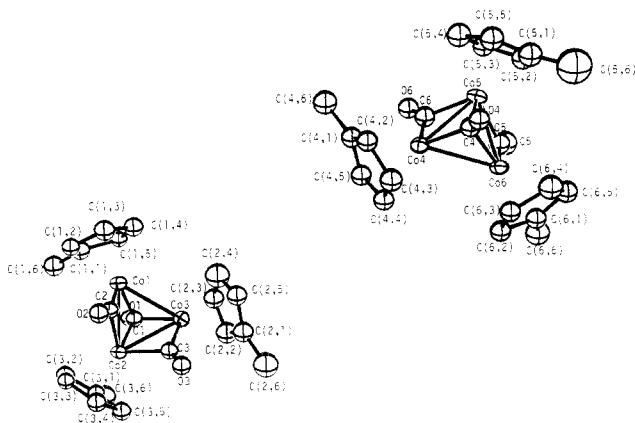


Figure 2. The two molecules comprising the asymmetric unit in the crystal of  $(\text{mCp})_3\text{Co}_3(\text{CO})_3$  with the atom-numbering scheme defined. Each atom is represented by its ellipsoidal (Co) or spherical (C, O) thermal vibration tensor, scaled to enclose 40% of its electron density.

assigning the solid-state IR spectrum since the very low frequency band at  $1673\text{ cm}^{-1}$  can be assigned to the face-bridging CO group while the other two bands, at  $1833$  and  $1775\text{ cm}^{-1}$ , can be assigned to the edge-bridging CO's.

However, it was found that in solutions the IR spectrum is greatly different. In benzene the spectrum indicates the presence (and, probably, the sole presence) of structure 4, while in THF and  $\text{CHCl}_3$  the spectra are more complex and indicate that structure 4 is probably present but accompanied by one or more additional isomers. Because of the closeness in energy of two or more structures and the apparent ease with which they can be interconverted, we proposed the designation *fictile* for this molecule, as well as others such as  $\text{Fe}_3(\text{CO})_{12}$ , that are similarly plastic or deformable.

Most recently, Lawson and Shapley<sup>8,9</sup> have found efficient preparative methods for each of the isomeric  $[\text{CpRhCO}]_3$  compounds and have studied their fluxional properties.

We have extended our work on the trinuclear cobalt compounds by preparing the methylcyclopentadienyl analogue. The idea behind this—and perhaps the preparation of other compounds containing substituted cyclopentadienyl groups—is to obtain molecules with the same essential composition but packed in different ways in the crystal. It was hoped that

different intermolecular (and intramolecular) forces might result in the stabilization of a structure other than 5. We also attempted to prepare the pentamethyl analogue,  $(\text{C}_5\text{Me}_5)_3\text{Co}_3(\text{CO})_3$ , but it appears that, because of intramolecular crowding, this is too unstable to exist, and only  $(\text{C}_5\text{Me}_5)\text{Co}(\text{CO})_2$  and  $(\text{C}_5\text{Me}_5)_2\text{Co}_2(\text{CO})_3$  were observed.

In this paper we present complete descriptions of the structures of  $\text{Cp}_3\text{Co}_3(\text{CO})_3$  and  $(\text{mCp})_3\text{Co}_3(\text{CO})_3$ , where Cp and mCp are abbreviations for  $\text{C}_5\text{H}_5$  and  $\text{CH}_3\text{C}_5\text{H}_4$  that we shall use frequently throughout this report.

## Experimental Section

All operations were carried out in an atmosphere of dry nitrogen. Solvents were dried with sodium–potassium/benzophenone and were distilled under nitrogen immediately prior to use. Infrared spectra were obtained with a Pye-Unicam 1100 spectrometer.  $\text{Co}_2(\text{CO})_8$  was obtained from Pressure Chemical Co.  $\text{CpCo}(\text{CO})_2$  and  $(\text{mCp})\text{Co}(\text{CO})_2$  were prepared by literature methods.<sup>10</sup>

$[\text{CpCo}(\text{CO})]_3$  and  $[(\text{mCp})\text{Co}(\text{CO})]_3$  were prepared by a modification of King's procedure.<sup>2</sup> Toluene solutions of the dicarbonyl monomer were photolyzed (Hanovia 450-W medium-pressure lamp) in an Ace photochemical reaction vessel at  $0^\circ\text{C}$ . A slow  $\text{N}_2$  purge was used to sweep the system of CO. Irradiation was continued for 8 h. Solvent was removed under vacuum, whereby unreacted dicarbonyl monomer was also removed. The cobalt trimers were separated from the reaction solid by chromatography on Florisil with a hexane/benzene solvent system. Crystals suitable for X-ray diffraction were obtained by cooling solutions in a mixture of hexane and THF to  $-20^\circ\text{C}$ .

**X-ray Crystallography.** Crystals were sealed in glass capillaries. Data were collected at  $21 \pm 3^\circ\text{C}$  on a Syntex P1 automated diffractometer with Mo  $K\alpha$  radiation, monochromatized with a graphite crystal in the incident beam. The automated centering and autoindexing procedures have previously been described.<sup>11</sup>  $\omega$  scans of several intense reflections had widths at half-height of  $\leq 0.25^\circ$ . The  $\theta$ – $2\theta$  scan technique was used to measure intensities, with variable scan rates of  $4.0$ – $24.0^\circ/\text{min}$ . A scan range of  $1.0^\circ$  above and below the  $K\alpha_1$  and  $K\alpha_2$  peaks was used. Background measurements were made at both limits of each scan, with equal time intervals for background and peak counting. Crystallographic data are summarized in Table I.

- King, R. B. "Organometallic Syntheses"; Academic Press: New York, 1965; Vol. I, p 115.
- Cotton, F. A.; Frenz, B. A.; Deganello, G. Shaver, A. *J. Organomet. Chem.* **1973**, *50*, 227.
- Calculations were performed on the Amdahl 470 computer at Texas A&M University and on the PDP 11/45 computer at the Molecular Structure Corp., College Station, TX, with use of the Enraf-Nonius structure determination package with local modifications.

(8) Lawson, R. J.; Shapley, J. R. *J. Am. Chem. Soc.* **1976**, *98*, 7433.

(9) Lawson, R. J.; Shapley, J. R. *Inorg. Chem.* **1978**, *17*, 772.

Table VI. Bond Distances (Å) in (mCp)<sub>3</sub>Co<sub>3</sub>(CO)<sub>3</sub><sup>a</sup>

Co(1)-Co(2)	2.442 (4)	Co(4)-Co(5)	2.416 (4)
-Co(3)	2.511 (4)	-Co(6)	2.498 (4)
-C(1)	2.00 (2)	-C(4)	1.91 (2)
-C(2)	1.79 (2)	-C(6)	1.80 (2)
-C(1,1)	2.12 (2)	-C(4,1)	2.09 (2)
-C(1,2)	2.09 (2)	-C(4,2)	2.17 (2)
-C(1,3)	2.11 (3)	-C(4,3)	2.03 (2)
-C(1,4)	2.10 (2)	-C(4,4)	2.08 (2)
-C(1,5)	2.12 (2)	-C(4,5)	2.10 (2)
Co(2)-Co(3)	2.435 (4)	Co(5)-Co(6)	2.447 (4)
-C(1)	1.94 (2)	-C(4)	1.94 (2)
-C(2)	2.12 (2)	-C(5)	2.05 (3)
-C(3)	1.98 (2)	-C(6)	1.93 (2)
-C(2,1)	2.13 (2)	-C(5,1)	2.11 (2)
-C(2,2)	2.12 (2)	-C(5,2)	2.10 (2)
-C(2,3)	2.12 (2)	-C(5,3)	2.11 (2)
-C(2,4)	2.12 (2)	-C(5,4)	2.09 (2)
-C(2,5)	2.11 (2)	-C(5,5)	2.17 (2)
Co(3)-C(1)	1.95 (2)	Co(6)-C(4)	1.98 (2)
-C(3)	1.84 (2)	-C(5)	1.77 (2)
-C(3,1)	2.12 (2)	-C(6,1)	2.10 (2)
-C(3,2)	2.10 (3)	-C(6,2)	2.06 (2)
-C(3,3)	2.09 (2)	-C(6,3)	2.07 (2)
-C(3,4)	2.06 (3)	-C(6,4)	2.14 (2)
-C(3,5)	2.08 (2)	-C(6,5)	2.14 (2)
O(1)-C(1)	1.20 (2)	O(4)-C(4)	1.22 (2)
O(2)-C(2)	1.18 (2)	O(5)-C(5)	1.16 (2)
O(3)-C(3)	1.14 (2)	O(6)-C(6)	1.17 (2)
C(1,1)-C(1,2)	1.44 (3)	C(4,1)-C(4,2)	1.44 (3)
C(1,2)-C(1,3)	1.40 (3)	C(4,2)-C(4,3)	1.43 (3)
C(1,3)-C(1,4)	1.40 (3)	C(4,3)-C(4,4)	1.40 (3)
C(1,4)-C(1,5)	1.39 (3)	C(4,4)-C(4,5)	1.33 (3)
C(1,5)-C(1,1)	1.39 (3)	C(4,5)-C(4,1)	1.46 (3)
C(1,1)-C(1,6)	1.52 (3)	C(4,1)-C(4,6)	1.52 (3)
C(2,1)-C(2,2)	1.44 (3)	C(5,1)-C(5,2)	1.42 (3)
C(2,2)-C(2,3)	1.35 (3)	C(5,2)-C(5,3)	1.33 (3)
C(2,3)-C(2,4)	1.32 (4)	C(5,3)-C(5,4)	1.37 (3)
C(2,4)-C(2,5)	1.43 (3)	C(5,4)-C(5,5)	1.55 (3)
C(2,5)-C(2,1)	1.39 (3)	C(5,5)-C(5,1)	1.38 (3)
C(2,1)-C(2,6)	1.51 (3)	C(5,1)-C(5,6)	1.58 (4)
C(3,1)-C(3,2)	1.37 (3)	C(6,1)-C(6,2)	1.49 (3)
C(3,2)-C(3,3)	1.38 (3)	C(6,2)-C(6,3)	1.38 (3)
C(3,3)-C(3,4)	1.30 (3)	C(6,3)-C(6,4)	1.39 (3)
C(3,4)-C(3,5)	1.54 (3)	C(6,4)-C(6,5)	1.51 (3)
C(3,5)-C(3,1)	1.49 (3)	C(6,5)-C(6,1)	1.39 (3)
C(3,1)-C(3,6)	1.51 (3)	C(6,1)-C(6,6)	1.51 (3)

<sup>a</sup> Numbers in parentheses are estimated standard deviations in the least significant digits.

**Solution and Refinement.**<sup>12</sup> A three-dimensional Patterson map for [CpCo(CO)]<sub>3</sub> and direct methods using the program MULTAN for [(mCp)Co(CO)]<sub>3</sub> were used to determine the positions of the cobalt atoms. For [(mCp)Co(CO)]<sub>3</sub> two independent trimers were required. The cobalt positions were refined with least squares, and subsequent difference Fourier maps revealed the approximate positions of all non-hydrogen atoms. The discrepancy factors listed in Table I are defined as

$$R_1 = \sum (||F_o| - |F_c||) / \sum |F_o|$$

$$R_2 = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}$$

The function  $\sum w(|F_o| - |F_c|)^2$  was minimized with the weighting factor,  $w$ , equal to  $4F_o/\sigma(F_o^2)$ . The structure factor calculations and least-squares refinements were executed with only those reflections for which  $F_o^2 > 3\sigma(F_o^2)$ . [CpCo(CO)]<sub>3</sub> was refined to converge by the full-matrix least-squares procedure with anisotropic temperature factors for all non-hydrogen atoms. Hydrogen positions were calculated for each cyclopentadienyl ring with the assumption of a C-H bond length of 0.95 Å. The final refinement was conducted with the hydrogen atoms held at these positions and assigned constant isotropic temperature factors. [(mCp)Co(CO)]<sub>3</sub> was refined to convergence by full-matrix least squares with the  $y$  coordinate of Co(1) held constant. Hydrogen atoms were omitted entirely. Anisotropic temperature factors were used for the cobalt atoms only. Changing the enantiomorphic specification resulted in higher discrepancy factors,

Table VII. Bond Angles (Deg) in (mCp)<sub>3</sub>Co<sub>3</sub>(CO)<sub>3</sub><sup>a</sup>

Co(2)-Co(1)-Co(3)	58.9 (1)	Co(5)-Co(4)-Co(6)	59.7 (1)
-C(1)	50.6 (6)	-C(4)	51.8 (6)
-C(2)	57.8 (8)	-C(6)	52.2 (7)
Co(3)-Co(1)-C(1)	49.6 (6)	Co(6)-Co(4)-C(4)	51.2 (6)
-C(2)	87.8 (6)	-C(6)	92.0 (7)
C(1)-Co(1)-C(2)	107 (1)	C(4)-Co(4)-C(6)	104.0 (9)
Co(1)-Co(2)-Co(3)	61.9 (1)	Co(4)-Co(5)-Co(6)	61.8 (1)
-C(1)	52.9 (7)	-C(4)	50.5 (6)
-C(2)	45.5 (5)	-C(5)	84.0 (7)
-C(3)	88.5 (6)	-C(6)	47.3 (6)
Co(3)-Co(2)-C(1)	51.3 (6)	Co(6)-Co(5)-C(4)	52.0 (7)
-C(2)	82.9 (5)	-C(5)	45.5 (6)
-C(3)	47.8 (6)	-C(6)	90.3 (7)
C(1)-Co(2)-C(2)	97.9 (9)	C(4)-Co(5)-C(5)	97.0 (9)
-C(3)	99.1 (9)	-C(6)	97.7 (9)
C(2)-Co(2)-C(3)	73.0 (8)	C(5)-Co(5)-C(6)	77 (1)
Co(1)-Co(3)-Co(2)	59.1 (1)	Co(4)-Co(6)-Co(5)	58.5 (1)
-C(1)	51.5 (7)	-C(4)	48.8 (6)
-C(3)	89.8 (6)	-C(5)	87.4 (8)
Co(2)-Co(3)-C(1)	51.1 (6)	Co(5)-Co(6)-C(4)	50.8 (6)
-C(3)	53.1 (6)	-C(5)	55.2 (8)
C(1)-Co(3)-C(3)	104.2 (9)	C(4)-Co(6)-C(5)	106 (1)
Co(1)-C(1)-Co(2)	76.5 (8)	Co(4)-C(4)-Co(5)	77.7 (7)
-Co(3)	78.9 (8)	-Co(6)	80.0 (9)
-O(1)	131 (2)	-O(4)	136 (2)
Co(2)-C(1)-Co(3)	77.6 (8)	Co(5)-C(4)-Co(6)	77.2 (7)
-O(1)	134 (2)	-O(4)	135 (2)
Co(3)-C(1)-O(1)	135 (2)	Co(6)-C(4)-O(4)	128 (2)
Co(1)-C(2)-Co(2)	76.6 (8)	Co(5)-C(5)-Co(6)	80 (1)
-O(2)	152 (2)	-O(5)	127 (2)
Co(2)-C(2)-O(2)	130 (2)	Co(6)-C(5)-O(5)	154 (2)
Co(2)-C(3)-Co(3)	79.1 (8)	Co(4)-C(6)-Co(5)	80.5 (9)
-O(3)	136 (2)	-O(6)	146 (2)
Co(3)-C(3)-O(3)	145 (2)	Co(5)-C(6)-O(6)	133 (2)
C(1,1)-C(1,2)-C(1,3)	106 (2)	C(4,1)-C(4,2)-C(4,3)	104 (2)
C(1,2)-C(1,3)-C(1,4)	107 (2)	C(4,2)-C(4,3)-C(4,4)	110 (2)
C(1,3)-C(1,4)-C(1,5)	110 (2)	C(4,3)-C(4,4)-C(4,5)	109 (2)
C(1,4)-C(1,5)-C(1,1)	106 (2)	C(4,4)-C(4,5)-C(4,1)	109 (2)
C(1,5)-C(1,1)-C(1,2)	109 (2)	C(4,5)-C(4,1)-C(4,2)	108 (2)
C(1,6)-C(1,1)-C(1,2)	125 (2)	C(4,6)-C(4,1)-C(4,2)	126 (2)
C(1,6)-C(1,1)-C(1,5)	125 (2)	C(4,6)-C(4,1)-C(4,5)	126 (2)
C(2,1)-C(2,2)-C(2,3)	106 (2)	C(5,1)-C(5,2)-C(5,3)	110 (2)
C(2,2)-C(2,3)-C(2,4)	113 (2)	C(5,2)-C(5,3)-C(5,4)	111 (2)
C(2,3)-C(2,4)-C(2,5)	107 (3)	C(5,3)-C(5,4)-C(5,5)	106 (2)
C(2,4)-C(2,5)-C(2,1)	108 (2)	C(5,4)-C(5,5)-C(5,1)	103 (2)
C(2,5)-C(2,1)-C(2,2)	106 (2)	C(5,5)-C(5,1)-C(5,2)	110 (2)
C(2,6)-C(2,1)-C(2,2)	122 (2)	C(5,6)-C(5,1)-C(5,2)	129 (2)
C(2,6)-C(2,1)-C(2,5)	131 (2)	C(5,6)-C(5,1)-C(5,5)	121 (2)
C(3,1)-C(3,2)-C(3,3)	110 (2)	C(6,1)-C(6,2)-C(6,3)	107 (2)
C(3,2)-C(3,3)-C(3,4)	111 (2)	C(6,2)-C(6,3)-C(6,4)	112 (2)
C(3,3)-C(3,4)-C(3,5)	110 (2)	C(6,3)-C(6,4)-C(6,5)	106 (2)
C(3,4)-C(3,5)-C(3,1)	99 (2)	C(6,4)-C(6,5)-C(6,1)	106 (2)
C(3,5)-C(3,1)-C(3,2)	109 (2)	C(6,5)-C(6,1)-C(6,2)	108 (2)
C(3,6)-C(3,1)-C(3,2)	129 (2)	C(6,6)-C(6,1)-C(6,2)	124 (2)
C(3,6)-C(3,1)-C(3,5)	122 (2)	C(6,6)-C(6,1)-C(6,5)	128 (2)

<sup>a</sup> Numbers in parentheses are estimated standard deviations in the least significant digits.

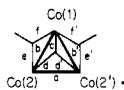
so the original structure was retained. Final difference Fourier maps were devoid of significant features for both structures.

## Results

The positional parameters for the Cp and mCp compounds are listed in Tables II and III; thermal parameters are available as supplementary material. Figure 1 is an ORTEP drawing of the molecule of Cp<sub>3</sub>Co<sub>3</sub>(CO)<sub>3</sub> showing how the atoms are labeled in all tables pertaining to this compound. The bond lengths and angles for Cp<sub>3</sub>Co<sub>3</sub>(CO)<sub>3</sub> are collected in Tables IV and V. For (mCp)<sub>3</sub>Co<sub>3</sub>(CO)<sub>3</sub>, there are two independent molecules in the asymmetric unit and these are both shown in Figure 2, where the atom labels are defined. The bond lengths and bond angles are presented in Tables VI and VII. We have examined this structure to see if it might actually be consistent with the space group  $P2_1/m$  but this is not the case.

Table VIII. Comparison of Some Interatomic Distances (Å) in the  $\text{Cp}_3\text{Co}_3(\text{CO})_3$  and  $(\text{mCp})_3\text{Co}_3(\text{CO})_3$  Molecules

type of dist <sup>a</sup>	$\text{Cp}_3\text{Co}_3(\text{CO})_3$	$(\text{mCp})_3\text{Co}_3(\text{CO})_3$		grand av
		1	2	
a	2.519 (1)	2.511 (4)	2.498 (4)	2.509 (8)
b, b'	2.438 (1), 2.457 (1)	2.442 (4), 2.435 (4)	2.416 (4), 2.447 (4)	2.439 (10)
c	1.936 (5)	1.94 (2)	1.94 (2)	1.94 (2)
d, d'	1.939 (5), 2.011 (5)	1.95 (2), 2.00 (2)	1.91 (2), 1.98 (2)	1.97 (3)
e, e'	1.803 (6), 1.778 (6)	1.84 (2), 1.79 (2)	1.80 (2), 1.77 (2)	1.80 (2)
f, f'	1.984 (6), 2.123 (7)	1.98 (2), 2.12 (2)	2.05 (2), 1.93 (2)	2.03 (7)

<sup>a</sup> Defined as

## Discussion

Even though a total of three crystallographically independent molecules,  $[\text{CpCo}(\text{CO})]_3$  and the two  $[(\text{mCp})\text{Co}(\text{CO})]_3$  molecules, have not been structurally characterized, only one type of structure, namely, **5**, has been observed. Evidently the internal preference for this general arrangement is greater than any small differences in packing forces that may prevail in the three cases, even though infrared spectra indicate that solvation energies are capable of promoting rearrangements.

In addition to being qualitatively the same, the three independent molecules are quantitatively very similar. While none of them have any imposed crystallographic symmetry, there is an approximate reflection plane in each case. In Table VIII, bond distances in the three molecules are listed and compared on this basis.

In each case the three cobalt-cobalt distances differ from one another by amounts that are statistically significant or very nearly so. Only in  $(\text{mCp})_3\text{Co}_3(\text{CO})_3$ , molecule 1, do the b and b' distances differ by a statistically insignificant amount, viz., 0.007 (6) Å. Nevertheless, these two (b, b') are in each case different from each other by only 0.007–0.037 Å while each of them differs from the other, longer, one (a) by at least 0.051 (6) Å. The average values of the a and b distances for all three structures differ by 0.070 (14) Å.

The triply bridging CO group appears to be very slightly closer to the unique cobalt atom than to the other two, but the difference is not statistically valid. It is in the arrangement of the edge-bridging CO groups that the deviation from 3-fold symmetry is unambiguously manifested, since there are but two of them and they lie on the slightly shorter edges (b, b') of the  $\text{Co}_3$  triangle. These bridges themselves are not symmetrical; in every case there is a difference of  $2.5\sigma$  or more between the largest value of e and e' and the smallest value of f or f'. The grand average values of e and f are 1.80 [2] and 2.03 [7] Å.

There is no easy way to interpret this structure in terms of the attainment of 18-electron configurations by the metal atoms. If we count electrons at each metal, neglecting for the moment the  $\mu_3$ -CO group and considering each  $\mu_2$ -CO bridge to be symmetrical, we find 18 electrons at Co(1) and 17 electrons each at Co(2) and Co(2'). It would seem natural at this point to add one more  $\mu_2$ -CO group across the a edge of the  $\text{Co}_3$  triangle to give Co(2) and Co(2') their 18-electron configurations. This would, of course, produce a structure of type 1. The  $\mu_3$  posture of the third CO group would appear to lead to excess electron density at Co(1) while not giving quite enough at Co(2) and Co(2'). This, however, could be considered to be offset by the unsymmetrical nature of the  $\mu_2$ -CO groups, which might be viewed as contributing more electron density to Co(2) and Co(2') than to Co(1).

Why the type of structure found here occurs for the cobalt compounds but not for the rhodium compounds is not easy to

say with certainty, but steric factors surely must be considered. The  $\text{Rh}_3$  triangles are appreciably larger than the  $\text{Co}_3$  triangles ( $\text{Rh-Rh}$  distances being ca. 2.65 Å). This may influence the structural preference in two ways. First, it may favor **1** by allowing more room to pack all the components in this way; it is difficult to prove or disprove the reality of this effect. Second, it may disfavor structure **5** by destabilizing the  $\mu_3$ -Co bonding because of the larger size of the  $\text{Rh}_3$  triangle.

**Infrared Spectra and Structures in Solution.** The infrared spectrum of solid  $\text{Cp}_3\text{Co}_3(\text{CO})_3$  was recorded with use of a mineral oil mull sample and found to be consistent with the solid-state structure. Three CO stretching bands are found at 1833, 1775, and 1673  $\text{cm}^{-1}$ ; the first two may be assigned to stretching of the  $\mu_2$ -CO groups and the last one to the  $\mu_3$ -CO group. For  $(\text{mCp})_3\text{Co}_3(\text{CO})_3$ , however, the use of a mineral oil mull fails because this compound is fairly soluble in the mineral oil and thus only the spectrum of the dissolved compound is observed. It has bands at 1956 (s), 1840 (m), and 1795 (s)  $\text{cm}^{-1}$ . This indicates a structural rearrangement, as will be discussed presently. By the use of a KBr pellet a solid-state spectrum of  $(\text{mCp})_3\text{Co}_3(\text{CO})_3$  (of poor quality) was obtained. It has broad, multi-peaked absorptions centered about 1820, 1770, and 1670  $\text{cm}^{-1}$ , consistent with the crystal structure.

In solution, both compounds show quite different spectra. Thus **A** in benzene has bands at 1959 (s), 1811 (s), and 1753 (m)  $\text{cm}^{-1}$  and the spectrum of **B** in mineral oil solution (vide supra) is similar. These spectra clearly rule out the retention of structure **5** and are strongly indicative of structure **2**. Lawson and Shapley<sup>9</sup> have reported that the  $\text{Cp}_3\text{Rh}_3(\text{CO})_3$  isomer with a structure of type **2** has the bands 1961–1975, 1809–1827, and 1761–1778  $\text{cm}^{-1}$  in several solvents. Moreover, they have found that this isomer of  $\text{Cp}_3\text{Rh}_3(\text{CO})_3$  is fluxional in such a way as to imply that a structure of type **5** provides a pathway for CO scrambling.

For  $(\text{mCp})_3\text{Co}_3(\text{CO})_3$  the spectrum in THF solution is also fully consistent with structure **2**, showing bands at 1957 (s), 1840 (s), and 1800 (m)  $\text{cm}^{-1}$ . For  $\text{Cp}_3\text{Co}_3(\text{CO})_3$  in THF the spectrum is ambiguous, showing the following bands: 1958 (s), 1843 (m), 1805 (s), 1760 (s), and 1702 (m)  $\text{cm}^{-1}$ . This could mean that structures **2** and **5** are both present, in equilibrium. A very similar result was obtained in  $\text{CHCl}_3$ , where bands are found at 1959 (s), 1840 (m), 1797 (m), 1750 (m), and 1710 (w)  $\text{cm}^{-1}$ .

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**Registry No.** A, 53450-15-0; B, 81846-97-1;  $\text{CpCo}(\text{CO})_2$ , 12078-25-0;  $(\text{mCp})\text{Co}(\text{CO})_2$ , 75297-02-8.

**Supplementary Material Available:** Listings of thermal parameters (Tables IIA, IIIA) and structure factors for both compounds (28 pages). Ordering information is given on any current masthead page.