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## Formation and Molecular Structure of $(\eta^5\text{-Cyclopentadienyl})(\eta^4\text{-1,3-dimesityl-2,4-diphenylcyclobutadiene})\text{cobalt}$ . A Compound with Restricted Rotation about an Aryl-Cyclobutadiene Bond

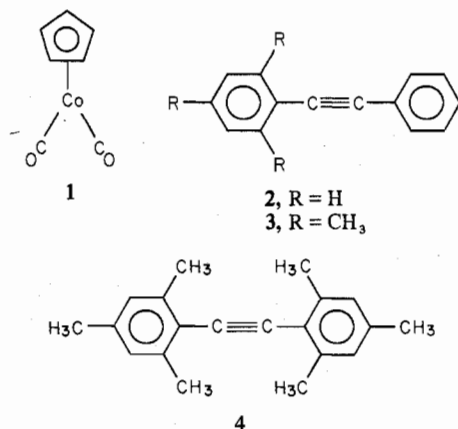
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The reaction of  $(\eta^5\text{-C}_5\text{H}_5)\text{Co}(\text{CO})_2$  (**1**) and mesitylphenylacetylene (**3**) has been found to result in the exclusive formation of a single cyclobutadiene-cobalt complex  $(\eta^5\text{-cyclopentadienyl})(\eta^4\text{-1,3-dimesityl-2,4-diphenylcyclobutadiene})\text{cobalt}$  (**6**) and a single cyclopentadienone-cobalt complex  $(\eta^5\text{-cyclopentadienyl})(\eta^4\text{-2,4-dimesityl-3,5-diphenylcyclopentadienone})\text{cobalt}$  (**8**), both of which exhibit a high degree of intramolecular steric crowding. The structures of **6** and **8** have been assigned on the basis of spectral considerations and unequivocally confirmed by means of a single-crystal X-ray crystallographic investigation of the former complex. The products **6** and **8** are those predicted on the basis of steric considerations of proposed cobaltacyclic intermediates in these types of reactions. Both <sup>1</sup>H NMR and <sup>13</sup>C NMR studies of **6** in solution indicate restricted rotation about the mesityl-cyclobutadiene bonds, and activation parameters for this process have been determined by dynamic <sup>1</sup>H NMR studies. For a quantitative measure of the degree of crowding in **6**, its crystal and molecular structures were determined by single-crystal X-ray diffraction methods. For comparison, those of **5**,  $(\eta^5\text{-C}_5\text{H}_5)\text{Co}(\text{C}_6\text{Ph}_4)$ , were determined as well. Pertinent crystallographic data for **5** are as follows: space group  $P2_1/c$ ,  $a = 10.293$  (1) Å,  $b = 19.690$  (3) Å,  $c = 12.904$  (1) Å,  $\beta = 111.42$  (1)°, volume = 2434 Å<sup>3</sup>,  $d(\text{calcd}) = 1.32$  g cm<sup>-3</sup>,  $d(\text{measd}) = 1.30$  g cm<sup>-3</sup>,  $Z = 4$ . For **6**, the space group is  $P2_1$ ,  $a = 8.573$  (4) Å,  $b = 8.951$  (7) Å,  $c = 20.324$  (7) Å,  $\beta = 97.80$  (3)°, volume = 1482.9 (2.5) Å<sup>3</sup>,  $d(\text{calcd}) = 1.265$  g cm<sup>-3</sup>,  $d(\text{measd}) = 1.25$  g cm<sup>-3</sup>, and  $Z = 2$ . Both structures were refined by standard methods to final values of  $R(F)$  and  $R_w(F)$  of 0.029 and 0.027 (**5**) and 0.041 and 0.047 (**6**). The structure of the latter is highly hindered by interactions of the *o*-methyl groups of the mesityl substituents; while in **5** no serious barriers to torsional motion are found. These results are in agreement with the solution NMR behavior of the compounds. Furthermore, we find that the steric crowding present in **6** leads to distortions of the cyclobutadiene ring which are not found in the less hindered compound **5**. Details of these steric phenomena are given in the text.

### Introduction

Recent joint studies in our laboratories have been concerned with the synthesis, mechanism of formation, and structural elucidation of products resulting from reactions of  $(\eta^5\text{-cyclopentadienyl})\text{dicarbonylcobalt}$  (**1**) with various symme-

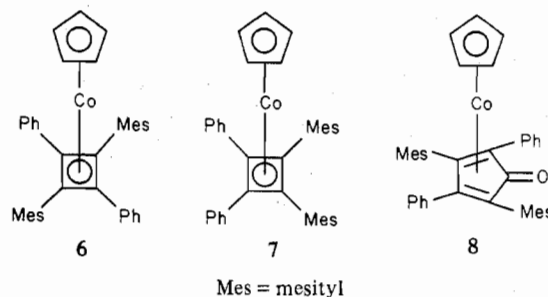


trical and unsymmetrical acetylenes.<sup>2-8</sup> In connection with this program, a reaction between **1** and  $\text{C}_6\text{H}_5\text{C}\equiv\text{CCl}_5$  was found to produce two novel cyclopentadienone-cobalt complexes which exhibited the losses of one and two chlorine atoms, respectively, from the products anticipated.<sup>9</sup> Since a pentachlorophenyl substituent might be expected to exert substantial electronic as well as steric effects on acetylene-cobalt interactions, it was of subsequent interest to examine reactions of **1** with other acetylenes in which predominantly steric factors could be examined in closer detail. In this paper, we report on the reaction of **1** with mesitylphenylacetylene (**3**) to produce both the respective cyclobutadiene- and cyclo-

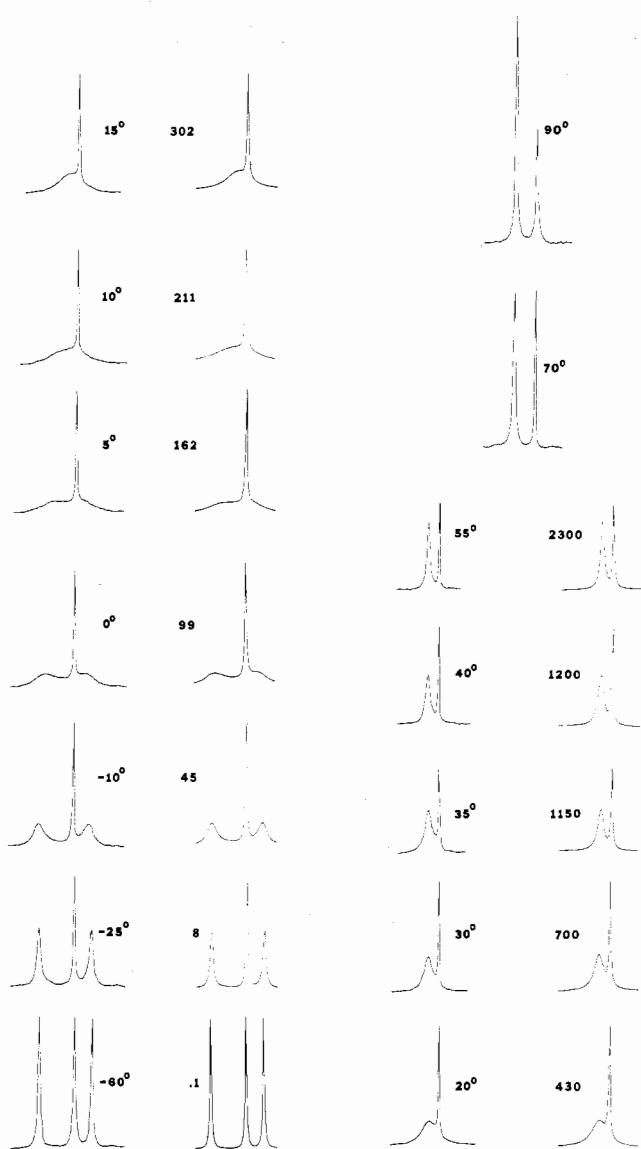
pentadienone-cobalt complexes and the results of an X-ray crystallographic analysis of the former product which unequivocally confirms its structure. Likewise described are <sup>1</sup>H NMR and <sup>13</sup>C NMR studies which demonstrate for the first time restricted rotation in solution about an aryl-cyclobutadiene bond. An attempted reaction of **1** with dimesitylacetylene (**4**) and a convenient new synthesis of the latter highly hindered acetylene are also discussed. Finally, in order to establish a "marker" to guide our interpretation of data, insofar as steric hindrance effects are concerned, we determined the crystal and molecular structure of  $(\eta^5\text{-C}_5\text{H}_5)\text{Co}(\text{C}_6\text{Ph}_4)$  (**5**). Compound **5** is a well-known product of the reaction of **1** with **2** in which steric hindrance is minimized while retaining the four phenyl substituents on the cyclobutadiene ring.<sup>2</sup>

### Results and Discussion

**Syntheses and Spectral Considerations.** As noted earlier,<sup>3-6,8</sup> the interaction of an unsymmetrical acetylene such as **3** with **1** can in principle produce two structurally isomeric cyclobutadiene-cobalt complexes, the 1,3-dimesityl isomer (**6**) and



the 1,2-dimesityl isomer (**7**). Careful examination of the reaction products from **1** and **3** following a 72-h reflux period



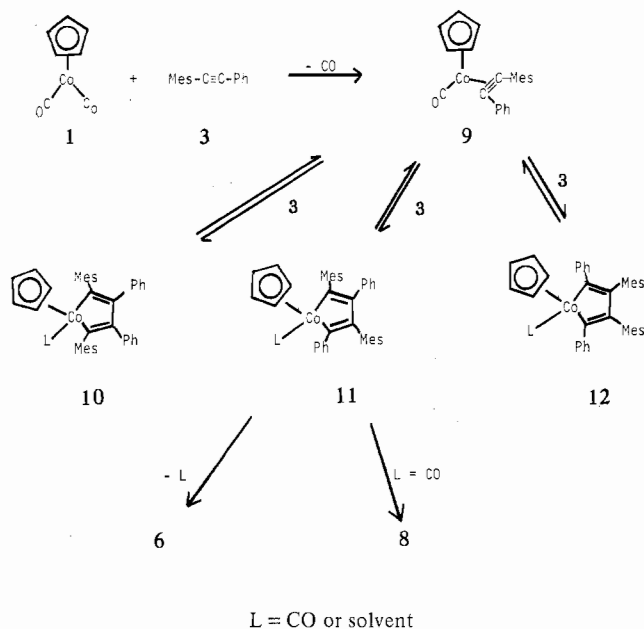
**Figure 1.** Temperature-dependent and calculated  $^1\text{H}$  NMR spectra for the methyl proton region in **6**.

in xylene, however, revealed the presence of only one cyclobutadiene-cobalt isomer, and this was tentatively assigned as **6** on the basis of examination of molecular models. Such considerations indicate severe steric crowding would occur for the 1,2-dimesityl isomer **7** as well as for the two symmetrically tetrasubstituted metallocyclic intermediates from which **7** presumably would be derived (*vide infra*).<sup>10,11</sup>

The cyclobutadiene-cobalt complex **6** was characterized by total elemental analysis and by its  $^1\text{H}$  NMR and mass spectra. The latter exhibited an intense molecular peak at  $m/e$  564, and the second most intense peak at  $m/e$  344 corresponded to an ion resulting from the loss of **3** from the molecular ion. Corresponding peaks due to losses of diphenylacetylene (**2**) and dimesitylacetylene (**4**) at  $m/e$  386 and 302, respectively, were present, although of relatively low intensity. Furthermore, a moderately intense peak at  $m/e$  220 corresponding to **3** was observed. However, peaks due to the two symmetrical acetylenes **2** and **4** were conspicuously absent. As noted in previous studies on related cyclobutadiene-cobalt complexes,<sup>5,8</sup> these results are also consistent with the cyclobutadiene-cobalt complex derived from **1** and **3** as being the 1,3-dimesityl isomer **6**.

The  $^1\text{H}$  NMR spectrum of **6** recorded at ambient temperature exhibited singlet resonances at  $\tau$  2.95, 3.12, and 5.35,

**Scheme 1**



which on the basis of relative intensities could be assigned to the phenyl, *m*-H (mesityl), and  $\eta^5$ -cyclopentadienyl protons, respectively. In the methyl proton region, on the other hand, a very broad resonance between  $\tau$  7 and 8 was observed (Figure 1). This surprising result suggested restricted rotation about the mesityl-cyclobutadiene bonds, even in the 1,3-dimesityl isomer **6**, and prompted us to undertake both variable-temperature  $^1\text{H}$  NMR studies as well as a single-crystal X-ray diffraction analysis, as are described below.

While three isomeric cyclopentadienone-cobalt complexes are theoretically possible<sup>3-6,8</sup> and have in fact been observed in reactions of **1** with certain unsymmetrical acetylenes,<sup>3,9</sup> the interaction of **1** and **3** produced only one such product. It was likewise characterized as a cyclopentadienone-cobalt complex by total elemental analysis and by mass spectrometry, the latter again exhibiting strong peaks for  $\text{M}^+$  ( $m/e$  592),  $(\text{C}_5\text{H}_5\text{CoC}_9\text{H}_{11}\text{C}_2\text{C}_6\text{H}_5)^+$  ( $m/e$  344), and an ion corresponding to **3** ( $m/e$  220). Steric considerations suggested that the product could be tentatively assigned as the unsymmetrical isomer (**8**).

The  $^1\text{H}$  NMR spectrum of the cyclopentadienone-cobalt complex, recorded at ambient temperatures, exhibited both aromatic and  $\eta^5$ -cyclopentadienyl resonances, but in addition *six* resonances in the methyl region between  $\tau$  7.0 and 8.3, corresponding to six magnetically nonequivalent types of methyl protons. This resonance pattern would result if there were a sizable energy barrier to rotation about both mesityl-cyclopentadienone bonds in this product. This result is also consistent with a structural formation of the product as **8**, as opposed to the two other symmetrically substituted isomers of **8**. In any event, it would appear that the rotational barrier for the mesityl groups in **8** is appreciably greater than in **6** under similar conditions, as might be expected from steric considerations for four bulky substituents on a cyclopentadienone vs. a cyclobutadiene ring, respectively.

A total DNMR line-shape analysis was performed for the cyclobutadiene complex **6**, and a comparison of the experimental and calculated spectra is shown in Figure 1. At  $-60^\circ\text{C}$  in  $\text{CH}_2\text{Cl}_2$  as the solvent, three singlet resonances are observed in the methyl proton region. The outer two resonances are assigned to the *o*-methyl groups on the mesityl rings, while the middle resonance is assigned to the *p*-methyl group on these rings. As the temperature is raised from  $-60$

Table I. Comparison of the Molecular Parameters of the ( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>-Co-( $\eta^4$ -C<sub>4</sub>) Fragment in Molecules 5 and 6 with Literature Values<sup>a</sup>

compd	a <sup>b</sup>	b <sub>1</sub> , b <sub>2</sub>	c	d	Co-Cp centroid	Co-Cb centroid	$\alpha$	$\beta$	ref
13	2.027 (3)	1.966 (3)	1.393 (3)	1.434 (2)	1.660	1.681	90.5 (2)	90.0 (2) <sup>d</sup>	21
	2.027 (3)	1.965 (2)	1.393 (3)	1.434 (2)					
	2.037 (3)	1.965 (2)	1.384 (3)	1.440 (2)					
	2.045 (3)	1.962 (3)	1.384 (3)	1.440 (2)					
	2.045 (3)	1.964 (2) <sup>d</sup>	1.394 (3)	1.437 (2) <sup>d</sup>					
	2.036 (9) <sup>d</sup>		1.390 (6) <sup>d</sup>						
17	2.055 (10)	1.968 (10)	1.420 (14)	1.460 (13)	1.671	1.689	88.8 (6)	90.2 (7)	22
	2.055 (10)	1.988 (8)	1.417 (15)	1.471 (11)					
	2.029 (10)	1.977 (9)	1.435 (14)	1.445 (11)					
	2.077 (10)	1.976 (8)	1.415 (17)	1.435 (13)					
	2.077 (10)	1.978 (4) <sup>d</sup>	1.379 (13)	1.453 (6) <sup>d</sup>					
	2.057 (5) <sup>d</sup>		1.412 (6) <sup>d</sup>						
5	2.049 (2)	1.984 (2)	1.396 (4)	1.458 (2)	1.679	1.692	90.1 (1)	90.4 (1)	this study
	2.041 (2)	1.982 (2)	1.382 (4)	1.467 (3)					
	2.049 (3)	1.989 (2)	1.384 (4)	1.473 (2)					
	2.061 (3)	1.983 (2)	1.384 (4)	1.474 (3)					
	2.062 (3)	1.984 (2) <sup>d</sup>	1.396 (3)	1.468 (3) <sup>d</sup>					
	2.053 (4) <sup>d</sup>		1.388 (3) <sup>d</sup>						
14	2.070 (2)	1.984 (1) <sup>c</sup>	1.371 (4)	1.460 (2)	1.682	1.694	89.8 (1)	90.4 (1)	8
	2.064 (2)	1.975 (1)	1.415 (5)	1.467 (2)					
	2.039 (2)	1.973 (2)	1.427 (4)	1.465 (2)					
	2.055 (2)	2.012 (1)	1.383 (4)	1.472 (2)					
	2.064 (2)	1.986 (5)	1.373 (4)	1.466 (5) <sup>d</sup>					
	2.058 (5)		1.394 (12) <sup>d</sup>						
6	2.065 (7)	1.994 (5)	1.392 (10)	1.463 (7)	1.692	1.698	90.8 (4)	89.1 (4)	this study
	2.043 (6)	1.964 (5)	1.418 (11)	1.470 (6)					
	2.098 (7)	1.993 (5)	1.409 (10)	1.461 (6)					
	2.102 (7)	2.002 (5)	1.442 (10)	1.455 (6)					
	2.081 (6)	1.988 (8)	1.424 (10)	1.462 (3) <sup>d</sup>					
	2.078 (10)		1.417 (8) <sup>d</sup>						
15	2.053 (4)	1.976 (3)	1.373 (6)	1.471 (4)	1.673	1.689	91.6 (2)	88.1 (2)	5
	2.057 (4)	1.968 (3)	1.408 (6)	1.463 (4)					
	2.049 (4)	1.983 (3)	1.377 (6)	1.466 (4)					
	2.042 (3)	2.002 (3)	1.407 (6)	1.466 (4)					
	2.042 (3)	1.982 (15) <sup>d</sup>	1.382 (6)	1.467 (3) <sup>d</sup>					
	2.049 (7) <sup>d</sup>		1.389 (17) <sup>d</sup>						
16	2.05 <sup>d</sup>	1.97 <sup>d</sup>	1.40 <sup>d</sup>	1.463 (11)			90.7 (7)	90.7 (7)	23
				1.477 (11)			89.3 (7)	89.4 (7)	
				1.465 (11)					
				1.435 (11)					
				1.460 (9) <sup>d</sup>					

<sup>a</sup> Distances are given in Å and angles in degrees. The molecular parameters of ( $\eta^5$ -cyclopentadienyl)( $\eta^4$ -*trans*-diphenyl-2-thienylcyclobutadienyl)cobalt were not included because of the disorder and the relatively high thermal motion exhibited by this complex [6]. <sup>b</sup> Nomenclature detailed in Figure 2. <sup>c</sup> The two b<sub>1</sub> distances are listed first. <sup>d</sup> Average value.

°C, the line separation of the two *o*-methyl resonances decreases, and the peaks broaden until coalescence is reached at ca. 5 °C. Upon continued warming, the peak for the *o*-methyl protons gradually sharpens and the intensity increases up to 55 °C, which was the upper limit for measurement in CH<sub>2</sub>Cl<sub>2</sub>. Increasing the temperature to 90 °C in C<sub>6</sub>D<sub>5</sub>Br as the solvent ultimately results in one sharp resonance for the *o*-methyl protons.

From the data in Figure 1, the activation parameters were determined to be  $E_{\text{act}} = 10.5 \pm 0.5$  kcal/mol,  $\Delta H^\ddagger = 9.9 \pm 0.4$  kcal/mol,  $\Delta S^\ddagger = -12.7 \pm 1.2$  eu, and  $\Delta G^\ddagger_{25} = 13.7 \pm 0.8$  kcal/mol. A possible mechanism for the equilibration of the *o*-methyl groups of the mesityl rings is one in which the phenyl substituents, both of which are in rapid rotation with respect to the mesityl groups, achieve a conformation in which they are essentially perpendicular to the plane of the cyclobutadiene ring. This arrangement would allow one of the mesityl groups to rotate about the aryl-cyclobutadiene bond, with only fairly weak interactions between the *o*-methyl hydrogens and the hydrogens on the  $\eta^5$ -cyclopentadienyl ring and also possibly the  $\pi$ -electron cloud of the phenyl rings. This highly ordered rotational pathway is consistent with both the high entropy of activation and the relatively low enthalpy of activation found for rotation about the mesityl-cyclobutadiene bond. Consistent with this rotational mechanism, the resonance due to the phenyl protons broadens only slightly on cooling from ambient

temperature to -60 °C, suggesting facile rotation about the phenyl-cyclobutadiene bond.

A <sup>13</sup>C NMR spectrum of the cyclobutadiene complex **6** was also obtained in CDCl<sub>3</sub> as the solvent at 35 °C. Two resonances assignable to the *p*-methyl and *o*-methyl carbon atoms of the mesityl groups were observed at 20.9 and 23.5 ppm, respectively, and two resonances assignable to the  $\eta^4$ -cyclobutadiene carbons were observed at 73.6 and 76.2 ppm. A resonance due to the  $\eta^5$ -cyclopentadienyl carbons occurred at 84.8 ppm, while peaks assignable to the aromatic carbons were observed between 125 and 141 ppm. It is noteworthy that the *o*-methyl carbon resonance was significantly broadened relative to the *p*-methyl carbon resonance under these conditions, in analogy to the <sup>1</sup>H NMR studies described above.

**Mechanistic Considerations.** It is interesting to briefly speculate on the exclusive formation of **6** and **8** from the reaction between **1** and **3**. As is illustrated in Scheme I, the first step in this process presumably involves displacement of a carbonyl ligand from **1** and substitution by **3** to form a monoacetylene complex (**9**). The next step could involve the addition of another molecule of **3** to form, in principle, the three isomeric metallocyclopentadiene complexes **10**, **11**, and **12**. Metallocycles of this general type have frequently been suggested as intermediates in the formation of cyclobutadiene-metal complexes.<sup>2-6,8,10-16</sup> Intermediates **10** and **12** would undoubtedly suffer severe steric strain due to the positioning

Table II. Hydrogen-Hydrogen Contacts of Less Than 3.0 Å

intramolecular			intermolecular		
atom 1	atom 2	dist, Å <sup>a</sup>	atom 1	atom 2	dist, Å
H1	H30	2.86	H2	H15	2.76
H1	H37A	2.76	H3	H14	2.89
H1	H39A	2.70	H3	H24C	2.76
H2	H22A	3.01	H4	H24A	2.89
H2	H22B	2.45	H4	H24B	2.86
H3	H22A	1.67	H5	H26	2.57
H3	H22B	2.50	H11	H24A	2.61
H4	H11	2.48	H11	H24C	2.62
H5	H37A	2.36	H12	H13	2.79
H5	H37B	2.64	H12	H20	2.95
H5	H37C	2.90	H12	H23A	2.93
H15	H37B	2.29	H13	H18	2.91
H22B	H26	2.57	H13	H23A	2.94
H22C	H26	2.64	H14	H20	2.93
H23C	H38B	2.22	H14	H23B	2.90
H33	H38C	2.28	H22A	H23A	2.96
H33	H39A	2.62	H22C	H38A	2.94
H33	H39B	2.78	H27	H39C	2.99
H35	H37B	2.98	H28	H30	2.68
H35	H37C	2.50	H29	H39A	2.89
H35	H39B	2.89	H30	H39A	2.93
H35	H39C	2.58	H33	H39B	2.98
			H37C	H38A	2.65
			H38A	H39B	2.73
			H38C	H39B	2.76

<sup>a</sup> Estimated standard deviations are 0.07–0.08 Å.

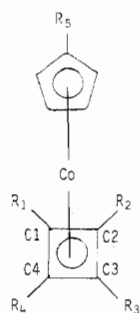
of the bulky mesityl substituents. In metallocycle **11**, however, the mesityl groups are located so as to minimize steric effects of these groups, and formation of this intermediate compared to **10** and **12** might be anticipated to be favored.

On the assumption that metallocyclic intermediates do occur in these reactions, cyclobutadiene–cobalt complex **6** can then be derived only from **11**, via loss of L and a  $\sigma$ – $\pi$  rearrangement. Likewise, cyclopentadienone–cobalt complex **8** can only be derived from **11**, by a carbonyl insertion into a carbon–cobalt bond and a  $\sigma$ – $\pi$  rearrangement. If either metallocycles **10** or **12** were formed as intermediates in the reaction of **1** and **3**, one might also expect products such as the cyclobutadiene–cobalt isomer **7** as well as either or both of the symmetrically substituted cyclopentadienone–cobalt complexes isomeric with **8**. Since none of these types of products could be detected, metallocycles **10** and **12** are apparently not formed to any appreciable extent in this reaction, in accordance with the steric arguments presented above.

It is interesting to note that, in a reaction between **1** and dimesitylacetylene (**4**) in refluxing xylene for a similar 72-h period, no organometallic products could be isolated and 90% recovery of **4** was obtained. This result again emphasizes the severe steric effects imposed by bulky mesityl groups in the formation of organometallic intermediates such as **9** and **10–12**.

**Description of the Structures.** Views of molecules **5** and **6** including the numbering systems used in the crystallographic study are given in Figures 3 and 4, respectively. The crystal structures of both compounds consist of molecules in which the cobalt atom is sandwiched between nearly parallel  $\eta^4$ -cyclobutadiene and  $\eta^5$ -cyclopentadienyl rings. In order to compare the structural characteristics of these compounds with those of related complexes, Table I was prepared. Figure 2 which gives the key to the different compounds should be used in conjunction with Table I and the discussion which follows.

**(a) The  $\eta^5$ -C<sub>5</sub>H<sub>5</sub>Co Fragment.** The  $\eta^5$ -cyclopentadienyl rings are planar (largest deviations from planarity being 0.004 and 0.006 Å for molecules **5** and **6**, respectively). The C–C distances of the five-membered rings range from 1.382 (4) to 1.396 (3) Å for compound **5** and from 1.392 (10) to 1.442 (10)



## Key to Symbols

Co–C(Cp) = a  
 Co–C(C1, C3) = b<sub>1</sub>  
 Co–C(C2, C4) = b<sub>2</sub>  
 C(Cp)–C(Cp) = c  
 C(Cb)–C(Cb) = d  
 C2–C1–C4 = C2–C3–C4 =  $\alpha$   
 C1–C2–C3 = C3–C4–C1 =  $\beta$

## Label for Compounds

R<sub>1</sub> = R<sub>2</sub> = R<sub>3</sub> = R<sub>4</sub> =  $\emptyset$  R<sub>5</sub> = H (5)  
 R<sub>1</sub> = R<sub>3</sub> =  $\emptyset$  R<sub>2</sub> = R<sub>4</sub> = Mesityl R<sub>5</sub> = H (6)  
 R<sub>1</sub> = R<sub>2</sub> = R<sub>3</sub> = R<sub>4</sub> = H R<sub>5</sub> = H (13)  
 R<sub>1</sub> = R<sub>3</sub> =  $\emptyset$  R<sub>2</sub> = R<sub>4</sub> = Ferrocenyl R<sub>5</sub> = H (14)  
 R<sub>1</sub> = R<sub>3</sub> =  $\emptyset$  R<sub>2</sub> = R<sub>4</sub> = Si(CH<sub>3</sub>)<sub>3</sub> R<sub>5</sub> = H (15)  
 R<sub>1</sub> = R<sub>4</sub> =  $\emptyset$  R<sub>2</sub> = R<sub>3</sub> = Si(CH<sub>3</sub>)<sub>3</sub> R<sub>5</sub> = H (16)  
 R<sub>1</sub> = R<sub>2</sub> = R<sub>3</sub> = R<sub>4</sub> =  $\emptyset$  R<sub>5</sub> = CN (17)

Figure 2. Definitions of the dimensions of the  $(\eta^5\text{-Cp})\text{Co}(\eta^4\text{-Cb})$  moiety and the labeling system used for various related compounds.

Å for compound **6**. The C–C(Cp) bond lengths of **5** are significantly shorter than the corresponding distances in **6**. Thus, the C–C bonds of the cyclopentadienyl ligand in **5** are close to those observed in **6** and those of **6** are similar to the corresponding bonds in **17**. Such differences in the C–C(Cp) distances were observed also by others<sup>24</sup> and may be attributed to librational motion of the ring around the metal–centroid vector.<sup>24</sup> The mean values of the internal angles of the five-membered rings of both compounds are 108.0°, as expected. In compound **5**, the Co–C(Cp) bonds range from 2.041 (2) to 2.062 (2) Å, with a Co–Cp (ring–centroid) distance of 1.679 Å. The corresponding bonds of **6** range from 2.043 (6) to 2.102 (7) Å, with a Co–Cp (ring–centroid) distance of 1.692 Å. We note that these values, which correspond to typical Co–Cp  $\pi$  interactions in diamagnetic complexes, are virtually identical with the mean Co–C(Cp) distance in the paramagnetic complex cobaltocene (2.096 (8) Å).<sup>25</sup> There is a slight increase in the Co–C(Cp) bonds and in the Co–Cp (ring–centroid) distance caused by substitution of the hydrogen atoms of the C<sub>4</sub> ring of **13** by bulky groups such as phenyl, ferrocenyl, or mesityl. Thus, the Co–C(Cp) average distance increases from 2.036 (9) Å in compound **13** to 2.057 (5), 2.053 (4), and 2.058 (5) Å in compounds **17**, **5**, and **14**, respectively. The biggest increase (2.078 (10) Å) was observed for compound **6** which has two bulky mesityl substituents. This behavior appears to be reflected also in the Co–C(Cb) bonds (Cb = cyclobutadiene) and in the Co–Cb (ring–centroid) distance. It seems that this increase in the Co–( $\eta^4$ -Cp) and Co–( $\eta^4$ -Cb) distances, when substituting the cyclobutadiene hydrogens with bulky groups, is due to the steric effects caused by overcrowding between the Cp ring and the various substituent groups. Thus, for instance, the distance between hydrogens H3 and H22A in **6** is 1.67 Å (see Table II), which is well below the van der Waals distance of 2.4 Å. As can be seen from Table I, the Co–Cp (ring–centroid) distances are characteristically shorter than the Co–Cb (ring–centroid) lengths. It seems to us that the perpendicular Co–ring centroid lengths are the main factors in controlling the Co–C (rings) distances. A similar behavior was observed by Tuggle and Weaver for the  $(\eta^5\text{-C}_5\text{H}_5)\text{Ni}(\eta^3\text{-C}_3\text{R}_3)$  system.<sup>26</sup>

**(b) The  $\eta^4$ -Cb Fragment.** The  $\eta^4$ -Cb rings of compounds **5** and **6** are planar (the deviations from planarity being 0.002 and 0.005 Å, respectively). If the plane defined by C6, C7,

**Table III.** Crystallographically Important Data Collection and Data Processing Information

compd	5	6
empirical formula	CoC <sub>33</sub> H <sub>25</sub>	CoC <sub>39</sub> H <sub>37</sub>
mol wt	480.50	564.66
cell constants <sup>a</sup>		
<i>a</i> , Å	10.293 (1)	8.573 (4)
<i>b</i> , Å	19.690 (3)	8.591 (7)
<i>c</i> , Å	12.904 (1)	20.324 (7)
α, deg	90.01 (1)	90.00
β, deg	111.42 (1)	97.80 (3)
γ, deg	89.98 (1)	90.00
unit cell vol, Å <sup>3</sup>	2434.7	1482.9 (2.5)
space group	<i>P</i> 2 <sub>1</sub> / <i>c</i>	<i>P</i> 2 <sub>1</sub>
density, g/cm <sup>3</sup>	1.32 (calcd) 1.30 (measd)	1.265 (calcd) 1.25 (measd)
absorption coeff (Mo Kα), cm <sup>-1</sup>	7.4	6.3
radiatn used for data collectn	Mo Kα (λ = 0.710 69 Å)	same
scanning range for 2θ	4.00° < 2θ < 56.0°	4.00° < 2θ < 50°
stand for intens control (every 30 reflctns)	[1̄11 and 141]	
scan width for each reflctn	[1.10 + 0.40 tan θ]°	[1.2 + 0.4 tan θ]°
max scan time, s	400	
minimum no. of counts above bkgd for each reflctn	2000	
scan technique	θ-2θ	θ-2θ
total no. of reflctns collected	6327 <sup>b</sup>	3834
no. of contributing reflctns in the last least squares	4778 <sup>c</sup>	2287
no. of variables	407	471
weighting scheme	1/σ <sup>2</sup> ( <i>F</i> <sub>o</sub> )	same
final <i>R</i> ( <i>F</i> ) <sup>d</sup>	0.029	0.041
final <i>R</i> <sub>w</sub> ( <i>F</i> ) <sup>e</sup>	0.027	0.047

<sup>a</sup> Unit cell dimensions were refined for **5** on the assumption that the cell was triclinic in order to test the precision of our values. <sup>b</sup> A total of 6327 reflections were collected for **5** of which 3102 having *I* > 3σ(*I*) were classified as "observed" with the remaining 3225 being termed "less-thans". <sup>c</sup> 3102 "observed" and 1676 "less-thans", for which |*F*<sub>c</sub>| > |*F*<sub>o</sub>|. <sup>d</sup> *R*(*F*) = Σ(|*F*<sub>o</sub>| - |*F*<sub>c</sub>||)/Σ|*F*<sub>o</sub>|. <sup>e</sup> *R*<sub>w</sub>(*F*) = [Σw(|*F*<sub>o</sub>| - |*F*<sub>c</sub>||<sup>2</sup>/Σw|*F*<sub>o</sub>|<sup>2</sup>)]<sup>1/2</sup>.

and C8 is chosen for compound **6**, then the fourth carbon is 0.02 Å out of the plane and toward the Co atom. Thus, while in **5** the Co atom is equidistant from all four carbon atoms of the cyclobutadiene ring (average 1.98 (2) Å), in molecule **6** it is closer to C9 (1.964 (5) Å) and farthest from C6 (2.002 (5) Å). The other two Co-C(Cb) distances are 1.994 (5) and 1.993 (5) Å. This distortion in **6** may be the net result of minimizing the steric effects caused by the overcrowding of H23C and H38B (2.22 Å), H15 and H37B (2.29 Å), and H5 and H37A (2.36 Å) (see Table II). The differences in the Co-C(Cb) bond lengths of **6** indicate that the ring planes (Cp and Cb) are not entirely parallel, but intersect at an angle of 7.5°, as compared to the values of 1.3, 1.1, and 1.6° observed for compounds **5**, **14**, and **15**, respectively. The four C-C bonds of the Cb rings of compounds **5** and **6** are virtually equal, with average values of 1.468 (3) and 1.462 (3) Å, respectively. These values are essentially equal to those found for compounds **14**, **15**, and **16** but are longer than the corresponding values observed for **13**. Thus, it appears that the substitution of the Cb hydrogens by bulky groups leads to a slight, but significant, increase of the Cb bonds. The four internal angles of the Cb ring of compound **5** are equal to 90° (within their estimated standard deviations). This seems to be the case whenever R<sub>1</sub> = R<sub>2</sub> = R<sub>3</sub> = R<sub>4</sub> as in compounds **13** and **17**, where the four substituents are hydrogens and phenyls, respectively. In compounds **15** and **16**, the internal angles associated with the carbons bonded to the silicon atoms are somewhat smaller than the angles at the carbons to which the phenyl rings are attached. These distortions were attributed by Kabuto et al.<sup>23</sup> to electronic and/or steric factors. The same

**Table IV.** Final Positional Parameters for Compound **5**<sup>a</sup>

atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>
Co	0.29021 (3)	0.17684 (1)	0.07782 (2)
C1	0.2832 (3)	0.1957 (1)	0.2318 (2)
C2	0.4071 (3)	0.1624 (2)	0.2423 (2)
C3	0.3742 (3)	0.1002 (1)	0.1897 (2)
C4	0.2304 (3)	0.0939 (1)	0.1471 (2)
C5	0.1739 (2)	0.1524 (1)	0.1730 (2)
C6	0.3368 (2)	0.2560 (1)	0.0029 (1)
C7	0.1921 (2)	0.2350 (1)	-0.0528 (1)
C8	0.2382 (2)	0.1709 (1)	-0.0863 (1)
C9	0.3846 (2)	0.1917 (1)	-0.0296 (1)
C10	0.4025 (2)	0.3205 (1)	0.0521 (1)
C11	0.5245 (2)	0.3226 (1)	0.1458 (2)
C12	0.5855 (3)	0.3843 (2)	0.1894 (2)
C13	0.5236 (4)	0.4438 (1)	0.1405 (2)
C14	0.4041 (3)	0.4427 (1)	0.0487 (2)
C15	0.3431 (2)	0.3814 (1)	0.0036 (2)
C16	0.0588 (2)	0.2716 (1)	-0.0766 (1)
C17	-0.0481 (2)	0.2693 (1)	-0.1811 (2)
C18	-0.1685 (2)	0.3083 (1)	-0.2025 (2)
C19	-0.1835 (2)	0.3487 (1)	-0.1217 (2)
C20	-0.0797 (2)	0.3516 (1)	-0.0176 (2)
C21	0.0409 (2)	0.3137 (1)	0.0044 (2)
C22	0.1683 (2)	0.1142 (1)	-0.1596 (1)
C23	0.2299 (2)	0.0818 (1)	-0.2255 (2)
C24	0.1644 (3)	0.0278 (1)	-0.2936 (2)
C25	0.0354 (3)	0.0058 (1)	-0.2980 (2)
C26	-0.0295 (2)	0.0385 (1)	-0.2354 (2)
C27	0.0356 (2)	0.0924 (1)	-0.1670 (2)
C28	0.5221 (2)	0.1641 (1)	-0.0188 (1)
C29	0.6283 (2)	0.2066 (1)	-0.0223 (2)
C30	0.7584 (2)	0.1803 (1)	-0.0103 (2)
C31	0.7849 (2)	0.1121 (1)	0.0065 (2)
C32	0.6807 (2)	0.0691 (1)	0.0093 (2)
C33	0.5506 (2)	0.0948 (1)	-0.0037 (2)
H1	0.274 (2)	0.238 (1)	0.259 (2)
H2	0.493 (2)	0.179 (1)	0.274 (2)
H3	0.436 (2)	0.067 (1)	0.179 (2)
H4	0.171 (2)	0.056 (1)	0.099 (2)
H5	0.078 (2)	0.164 (1)	0.158 (2)
H11	0.564 (2)	0.283 (1)	0.181 (1)
H12	0.670 (2)	0.386 (1)	0.259 (2)
H13	0.564 (2)	0.486 (1)	0.169 (2)
H14	0.358 (2)	0.486 (1)	0.010 (2)
H15	0.261 (2)	0.380 (1)	-0.066 (1)
H17	-0.036 (2)	0.240 (1)	-0.239 (1)
H18	-0.234 (2)	0.305 (1)	-0.274 (1)
H19	-0.269 (2)	0.374 (1)	-0.138 (1)
H20	-0.089 (2)	0.381 (1)	0.041 (1)
H21	0.112 (2)	0.316 (1)	0.079 (1)
H23	0.320 (2)	0.097 (1)	-0.222 (1)
H24	0.210 (2)	0.005 (1)	-0.340 (1)
H25	-0.011 (2)	-0.033 (1)	-0.347 (1)
H26	-0.122 (2)	0.026 (1)	-0.238 (1)
H27	-0.011 (2)	0.114 (1)	-0.125 (1)
H29	0.610 (2)	0.254 (1)	-0.032 (1)
H30	0.828 (2)	0.209 (1)	-0.013 (1)
H31	0.876 (2)	0.092 (1)	0.015 (1)
H32	0.700 (2)	0.021 (1)	0.023 (1)
H33	0.478 (2)	0.065 (1)	-0.005 (1)

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

behavior was observed for compound **6**, where the angles associated with the mesityl groups are smaller than the other two internal angles of the Cb ring. Since no such distortions were observed for compound **14** which has two strong electron-donating ferrocenyl substituents and since mesityl groups are only moderately electron donating, it seems to us that these changes in the internal angles of the Cb ring are due more to the steric effects of the bulky Me<sub>3</sub>Si and mesityl groups and less to electronic effects.

The four phenyl groups of **5** are bent from the cyclobutadiene plane and away from the η<sup>5</sup>-Cp-Co unit. The angles between the phenyl and cyclobutadiene rings vary from 31.6

**Table V.** Thermal Parameters ( $\times 10^3$ )<sup>a</sup> of the Nonhydrogen Atoms for Compound 5

atom	$U_{11}$	$U_{22}$	$U_{33}$	$U_{12}$	$U_{13}$	$U_{23}$
Co	36.8 (0.1)	40.9 (0.1)	33.6 (0.1)	-0.6 (0.2)	15.2 (0.1)	2.9 (0.1)
C1	102 (2)	70 (2)	35 (1)	5 (2)	31 (1)	-1 (1)
C2	52 (2)	132 (3)	42 (1)	-9 (2)	6 (1)	32 (2)
C3	112 (2)	93 (2)	79 (2)	51 (2)	62 (2)	51 (2)
C4	130 (3)	63 (2)	59 (2)	-28 (2)	47 (2)	8 (1)
C5	53 (2)	115 (2)	47 (1)	-2 (2)	29 (1)	19 (1)
C6	35 (1)	33 (1)	33 (1)	-2 (1)	13 (1)	1 (1)
C7	34 (1)	35 (1)	31 (1)	-3 (1)	13 (1)	-1 (1)
C8	31 (1)	34 (1)	33 (1)	-2 (1)	14 (1)	1 (1)
C9	34 (1)	36 (1)	34 (1)	-3 (1)	15 (1)	1 (1)
C10	41 (1)	40 (1)	39 (1)	-9 (1)	18 (1)	-5 (1)
C11	63 (2)	64 (2)	51 (1)	-19 (1)	7 (1)	-1 (1)
C12	92 (2)	92 (2)	56 (2)	-50 (2)	11 (2)	-18 (2)
C13	125 (3)	66 (2)	83 (2)	-54 (2)	54 (2)	-37 (2)
C14	90 (2)	42 (1)	91 (2)	-16 (1)	50 (2)	-8 (1)
C15	56 (1)	41 (1)	56 (1)	-9 (1)	26 (1)	-3 (1)
C16	34 (1)	35 (1)	39 (1)	-3 (1)	13 (1)	4 (1)
C17	43 (1)	54 (1)	42 (1)	-3 (1)	12 (1)	4 (1)
C18	41 (1)	63 (2)	62 (1)	-2 (1)	3 (1)	15 (1)
C19	41 (1)	47 (1)	104 (2)	5 (1)	21 (1)	8 (1)
C20	50 (2)	48 (1)	93 (2)	0 (1)	31 (1)	-16 (1)
C21	39 (1)	47 (1)	54 (1)	1 (1)	14 (1)	-8 (1)
C22	37 (1)	35 (1)	35 (1)	-3 (1)	15 (1)	1 (1)
C23	46 (1)	46 (1)	52 (1)	-6 (1)	21 (1)	-9 (1)
C24	69 (2)	56 (2)	67 (2)	-6 (1)	31 (1)	-21 (1)
C25	71 (2)	48 (2)	69 (2)	-15 (1)	18 (1)	-18 (1)
C26	49 (2)	56 (2)	75 (2)	-20 (1)	21 (1)	-4 (1)
C27	47 (1)	47 (1)	58 (1)	-10 (1)	27 (1)	-7 (1)
C28	32 (1)	43 (1)	32 (1)	-4 (1)	13 (1)	-1 (1)
C29	39 (1)	44 (1)	49 (1)	-6 (1)	20 (1)	6 (1)
C30	36 (1)	70 (2)	61 (1)	-11 (1)	24 (1)	6 (1)
C31	34 (1)	71 (2)	61 (1)	6 (1)	22 (1)	6 (1)
C32	47 (1)	51 (1)	78 (2)	6 (1)	30 (1)	5 (1)
C33	37 (1)	44 (1)	73 (2)	-5 (1)	27 (1)	1 (1)

<sup>a</sup> The form of the anisotropic thermal ellipsoid is  $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$  and  $U_{ij} = \beta_{ij}/2\pi^2 a_i^* a_j^*$ .

to 41.7°. As a consequence, there is little conjugation between these two rings as is indicated by the C(butadiene)-C(phenyl) distances (average 1.473 (2) Å) which are close to the value of 1.487 (6) Å found by Allmann and Helmer<sup>27</sup> for the C(sp<sup>2</sup>)-C(sp<sup>2</sup>) single bond. The two phenyl groups of **6** are bent, one (ring C25-C30) away from the  $\eta^5$ -Cp-Cp moiety and the other (ring C10-C15) toward it. The angles between these two phenyl planes and the cyclobutadiene ring are significantly smaller (12.9 and 17.1°) than those observed for **5**. Both mesityl groups are bent away from the cyclobutadiene plane and the angles are significantly larger (53.2 and 75.6°) than the angles between the phenyls and the cyclobutadiene rings. These changes in the dihedral angles of **6**, when compared to the corresponding angles in **5**, seem to be the result of minimizing the steric effects caused by substituting two phenyls with bulky mesityl groups. The differences in the dihedral angles of the substituent groups (phenyl and mesityl) and the cyclobutadiene ring are also reflected in the C(cyclobutadiene)-C(phenyl) vs. C(cyclobutadiene)-C(mesityl) bonds. The slightly, but significantly smaller C(cyclobutadiene)-C(phenyl) distances are probably due to a residual degree of conjugation between the phenyl and Cb groups.

The distances and internal angles of the phenyl and mesityl groups of **5** and **6** are normal.

### Experimental Section

All melting points were taken in sealed capillaries under nitrogen and are uncorrected. CAMAG neutral alumina was used for column chromatography. Columns were wrapped in aluminum foil to minimize photodecomposition. Pyridine was dried over KOH and distilled from BaO, THF was distilled from sodium-benzophenone, and xylene was stored over sodium. ( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)Co[ $\eta^4$ -C<sub>4</sub>(C<sub>6</sub>H<sub>5</sub>)<sub>4</sub>] (**5**), ( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)-

**Table VI.** Isotropic Thermal Parameters ( $\times 10^2$ ) of the Hydrogen Atoms for Compound 5

atom	$U_{iso}$	atom	$U_{iso}$	atom	$U_{iso}$
H1	9.5 (8)	H14	8.5 (7)	H24	7.8 (7)
H2	11.4 (8)	H15	6.2 (6)	H25	7.8 (7)
H3	12.9 (9)	H17	4.3 (5)	H26	8.1 (7)
H4	11.2 (8)	H18	7.2 (6)	H27	5.5 (6)
H5	9.8 (8)	H19	7.9 (7)	H29	3.8 (5)
H11	6.4 (6)	H20	8.8 (7)	H30	6.8 (6)
H12	11.0 (8)	H21	4.9 (5)	H31	6.1 (6)
H13	9.3 (7)	H23	5.8 (6)	H32	7.8 (7)
				H33	6.7 (6)

Co(CO)<sub>2</sub> (**1**),<sup>2</sup> cuprous iodide,<sup>17</sup> and cuprous phenylacetylide<sup>18</sup> were prepared according to literature procedures. Bromomesitylene, iodomesitylene, and tetrabromoethylene were obtained from Aldrich Chemical Co., K and K Laboratories, and Columbia Organic Chemicals Co., respectively. Elemental analyses were performed by the Microanalytical Laboratory, Office of Research Services, University of Massachusetts. <sup>1</sup>H NMR spectra were recorded at 90 MHz on a Perkin-Elmer R-32 instrument, <sup>13</sup>C NMR spectra on a Varian CFT-20 instrument, IR spectra on a Beckman IR-10 instrument, and mass spectra on a Perkin-Elmer Hitachi RMU-6L instrument at 70 eV. Skelly C is commercial heptane, bp 88–98 °C. Simulated <sup>1</sup>H NMR spectra were obtained by using the computer program DNMR-3, as modified by Bushweller,<sup>19</sup> on a CYBER-74 computer system.

**Preparation of Mesitylphenylacetylene (3).** In a 1000-mL, three-necked flask equipped with a magnetic stirring bar, nitrogen inlet, reflux condenser, and mercury overpressure valve were added 14.8 g (0.06 mol) of iodomesitylene and 300 mL of pyridine. The system was evacuated via water aspirator pressure and flushed with nitrogen; this process was repeated several times. Cuprous phenylacetylide (10.0 g, 0.06 mol) was then added and the reaction mixture was heated to reflux for 22 h, during which time the solution turned brown. After cooling of the mixture to room temperature, the use of nitrogen was discontinued and the reaction mixture was diluted with 600 mL of water. The mixture was extracted repeatedly with ethyl ether, the combined extracts were concentrated to ca. 500 mL, washed with 5% HCl, 5% NaHCO<sub>3</sub>, and H<sub>2</sub>O, and subsequently dried over anhydrous MgSO<sub>4</sub>. The solvent was removed to produce a brown oil which was taken up in hot methanol, decolorized with activated charcoal, and allowed to crystallize in several crops. In this manner, 7.6 g (58%) of mesitylphenylacetylene was obtained as colorless crystals, mp 37.5–38 °C.

Anal. Calcd for C<sub>17</sub>H<sub>16</sub>: C, 92.68; H, 7.32. Found: C, 92.78; H, 7.22.

The <sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>) exhibited peaks at  $\tau$  7.73 (3 H, s, *p*-CH<sub>3</sub>), 7.52 (6 H, s, *o*-CH<sub>3</sub>), 3.11 (2 H, s, *m*-H), and 2.8–2.3 (5 H, m, C<sub>6</sub>H<sub>5</sub>). The IR spectrum (CHCl<sub>3</sub>) contained a band assignable to an acetylenic stretching frequency at 2200 cm<sup>-1</sup>.

**Reaction of ( $\eta^5$ -Cyclopentadienyl)dicarbonylcobalt (1) and Mesitylphenylacetylene (3).** A mixture of 1.8 g (0.01 mol) of ( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)Co(CO)<sub>2</sub>, 4.4 g (0.02 mol) of mesitylphenylacetylene, and 150 mL of degassed xylene was heated to reflux with stirring under nitrogen in a 500-mL, three-necked flask equipped with a magnetic stirrer, nitrogen inlet, reflux condenser, and mercury overpressure valve. Reflux was continued for 72 h, after which time TLC indicated that most of the starting acetylene had been consumed. After cooling, the reaction mixture was filtered in air and a black precipitate was extracted with benzene. The combined benzene and xylene solutions were concentrated, placed on an alumina chromatography column and eluted with Skelly C. A broad brown band was collected, which after solvent removal produced 2.72 g (48%) of crude ( $\eta^5$ -cyclopentadienyl)( $\eta^4$ -1,3-dimesityl-2,4-diphenylcyclobutadiene)cobalt (**6**). An analytical sample was prepared by recrystallization of the product from benzene-hexane: golden crystals, mp 262–263 °C.

Anal. Calcd for C<sub>39</sub>H<sub>37</sub>Co: C, 82.96; H, 6.61; Co, 10.44. Found: C, 83.15; H, 6.74; Co, 10.34.

The mass spectrum exhibited principal peaks at *m/e* 564 (off scale, M<sup>+</sup>), 499 (6, M - C<sub>5</sub>H<sub>5</sub><sup>+</sup>), 386 (13, M - C<sub>6</sub>H<sub>5</sub>C<sub>2</sub>C<sub>6</sub>H<sub>5</sub><sup>+</sup>), 344 (100, M - C<sub>9</sub>H<sub>11</sub>C<sub>2</sub>C<sub>6</sub>H<sub>5</sub><sup>+</sup>), 302 (12, M - C<sub>9</sub>H<sub>11</sub>C<sub>2</sub>C<sub>9</sub>H<sub>11</sub><sup>+</sup>), 220 (30, C<sub>9</sub>H<sub>11</sub>C<sub>2</sub>C<sub>6</sub>H<sub>5</sub><sup>+</sup>), 124 (32, C<sub>5</sub>H<sub>5</sub>Co<sup>+</sup>), and 59 (8, Co<sup>+</sup>). The <sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>) recorded at ambient temperature exhibited peaks at  $\tau$  2.95 (10 H, s, C<sub>6</sub>H<sub>5</sub>), 3.12 (4 H, s, *m*-H), 5.35 (5 H, s, C<sub>5</sub>H<sub>5</sub>), and 7.2–8.0 (18 H, m, CH<sub>3</sub>).



Table VII. Bond Lengths (Å) for Compound 5

Co-C1	2.049 (2)	C22-C23	1.387 (3)
Co-C2	2.041 (2)	C23-C24	1.388 (3)
Co-C3	2.049 (3)	C24-C25	1.379 (4)
Co-C4	2.061 (3)	C25-C26	1.380 (4)
Co-C5	2.062 (3)	C26-C27	1.387 (3)
Co-C6	1.984 (2)	C27-C22	1.401 (3)
Co-C7	1.982 (2)	C28-C29	1.390 (3)
Co-C8	1.989 (2)	C29-C30	1.389 (3)
Co-C9	1.983 (2)	C30-C31	1.372 (3)
C1-C2	1.396 (4)	C31-C32	1.377 (3)
C2-C3	1.382 (4)	C32-C33	1.383 (3)
C3-C4	1.384 (4)	C33-C28	1.394 (3)
C4-C5	1.384 (4)	C1-H1	0.92 (2)
C5-C1	1.396 (3)	C2-H2	0.89 (2)
C6-C7	1.458 (2)	C3-H3	0.96 (3)
C7-C8	1.467 (3)	C4-H4	1.02 (2)
C8-C9	1.473 (2)	C5-H5	0.96 (2)
C9-C6	1.474 (3)	C11-H11	0.93 (2)
C6-C10	1.469 (2)	C12-H12	1.00 (2)
C7-C16	1.479 (3)	C13-H13	0.95 (2)
C8-C22	1.470 (2)	C14-H14	1.01 (2)
C9-C28	1.475 (3)	C15-H15	0.98 (1)
C10-C11	1.393 (2)	C17-H17	0.99 (2)
C11-C12	1.387 (4)	C18-H18	0.93 (1)
C12-C13	1.371 (4)	C19-H19	0.96 (2)
C13-C14	1.361 (4)	C20-H20	0.98 (2)
C14-C15	1.386 (3)	C21-H21	0.98 (1)
C15-C10	1.386 (3)	C23-H23	0.96 (2)
C16-C17	1.396 (2)	C24-H24	0.99 (2)
C17-C18	1.397 (3)	C25-H25	1.00 (2)
C18-C19	1.364 (4)	C26-H26	0.97 (2)
C19-C20	1.378 (3)	C27-H27	0.94 (2)
C20-C21	1.385 (3)	C29-H29	0.95 (1)
C21-C16	1.398 (3)	C30-H30	0.93 (2)
		C31-H31	0.98 (2)
		C32-H32	0.98 (2)
		C33-H33	0.95 (2)

Table VIII. Angles (deg) for Compound 5

C2-C1-C5	107.0 (2)	C29-C28-C33	117.7 (2)
C1-C2-C3	108.5 (2)	C28-C29-C30	120.7 (2)
C2-C3-C4	108.0 (3)	C29-C30-C31	120.6 (2)
C3-C4-C5	108.3 (2)	C30-C31-C32	119.6 (2)
C4-C5-C1	108.2 (2)	C31-C32-C33	120.1 (2)
C7-C6-C9	90.1 (1)	C32-C33-C28	121.3 (2)
C6-C7-C8	90.4 (1)	C17-C16-C21	118.0 (2)
C7-C8-C9	89.8 (1)	C16-C17-C18	120.2 (2)
C8-C9-C6	89.6 (1)	C17-C18-C19	120.6 (2)
C7-C6-C10	133.2 (2)	C18-C19-C20	120.3 (2)
C9-C6-C10	135.8 (2)	C19-C20-C21	119.7 (2)
C6-C7-C16	131.8 (2)	C20-C21-C16	121.2 (2)
C8-C7-C16	137.1 (1)	C23-C22-C27	118.0 (2)
C7-C8-C22	135.0 (2)	C22-C23-C24	121.0 (2)
C9-C8-C22	134.6 (2)	C23-C24-C25	120.3 (2)
C8-C9-C28	135.8 (2)	C24-C25-C26	119.6 (2)
C6-C9-C28	134.3 (2)	C25-C26-C27	120.3 (2)
		C26-C27-C22	120.7 (2)
C11-C10-C15	118.4 (2)		
C10-C11-C12	120.5 (2)		
C11-C12-C13	119.8 (2)		
C12-C13-C14	120.5 (3)		
C13-C14-C15	120.4 (2)		
C14-C15-C10	120.4 (2)		

Continued elution of the column with benzene and then 8:1 benzene-chloroform removed a dark red band, which after solvent removal gave 1.15 g (17%) of crude ( $\eta^5$ -cyclopentadienyl)( $\eta^5$ -2,4-dimesityl-3,5-diphenylcyclopentadienone)cobalt (**8**). An analytical sample was prepared by recrystallization of the product from benzene-hexane: deep red crystals, mp 240–242 °C.

Anal. Calcd for  $C_{40}H_{37}CoO$ : C, 81.06; H, 6.29; Co, 9.94; O, 2.70. Found: C, 81.25; H, 6.47; Co, 9.87; O, 2.63.

The mass spectrum exhibited principal peaks at  $m/e$  592 (off scale,  $M^+$ ), 527 (100,  $M - C_5H_5^+$ ), 468 (41,  $M - C_5H_5Co^+$ ), 344 (26,

Table IX. Least-Squares Planes (in Orthogonal A Space) and Deviations of Atoms from these Planes (in Å) for Compound 5

(a) Plane Based on C1, C2, C3, C4, and C5			
$-0.3040x - 0.4149y + 0.8576z = 0.2383$			
C1	-0.0037	C2	0.0034
C3	-0.0018	C4	0.0005
C5	0.0026	Co	-1.6786
(b) Plane Based on C6, C7, C8, and C9			
$-0.3201x - 0.4264y + 0.8460z = -3.2253$			
C6	-0.0022	C7	0.0022
C8	-0.0022	C9	0.0022
Co	1.6916	C10	-0.1863
C16	-0.1441	C22	-0.1514
C28	-0.0941		
(c) Plane Based on C10, C11, C12, C13, C14, and C15			
$-0.8097x + 0.0206y + 0.5865z = -2.6638$			
C10	0.0030	C11	0.0013
C12	-0.0045	C13	0.0034
C14	0.0010	C15	-0.0042
C6	-0.0096		
(d) Plane Based on C16, C17, C18, C19, C20, and C21			
$0.5761x + 0.7581y - 0.3056z = 4.8945$			
C16	-0.0013	C17	-0.0023
C18	0.0025	C19	0.0009
C20	-0.0046	C21	0.0048
C7	0.0903		
(e) Plane Based on C22, C23, C24, C25, C26, and C27			
$-0.1724x + 0.6394y - 0.7493z = 2.4600$			
C22	-0.0139	C23	0.0090
C24	0.0029	C25	-0.0099
C26	0.0047	C27	0.0071
C8	-0.0246		
(f) Plane Based on C28, C29, C30, C31, C32, and C33			
$-0.0649x + 0.1302y + 0.9894z = -0.1637$			
C28	0.0056	C29	0.0010
C30	-0.0070	C31	0.0065
C32	0.0001	C33	-0.0062
C9	0.0371		

## Angles between Planes

plane 1	plane 2	angle, deg
a	b	1.3
c	b	41.7
d	b	40.0
e	b	31.6
f	b	36.7

$C_5H_5CoC_9H_{11}C_2C_6H_5^+$ , 220 (30,  $C_9H_{11}C_2C_6H_5^+$ ), 124 (60,  $C_5H_5Co^+$ ), and 59 (17,  $Co^+$ ).

The  $^1H$  NMR spectrum ( $CDCl_3$ ) recorded at ambient temperature exhibited peaks at  $\tau$  8.31 (3 H, s,  $CH_3$ ), 8.27 (3 H, s,  $CH_3$ ), 7.82 (3 H, s,  $CH_3$ ), 7.75 (3 H, s,  $CH_3$ ), 7.49 (3 H, s,  $CH_3$ ), 7.05 (3 H, s,  $CH_3$ ), 5.08 (5 H, s,  $C_5H_5$ ), and 1.9–3.5 (14 H, m,  $C_6H_5$  and  $m-H$ ).

**Preparation of Dimesitylacetylene (4).** A 500-mL, three-necked flask was fitted with a nitrogen inlet, reflux condenser with mercury overpressure valve, magnetic stirring bar, and addition funnel. Under an atmosphere of nitrogen, 4.86 g (0.20 g-atom) of magnesium turnings was placed in the flask and 40 g (0.20 mol) of bromomesitylene was added to the dropping funnel. Approximately 1 mL of bromomesitylene was added and the mixture was stirred vigorously for several minutes until the magnesium was activated. Subsequently, 100 mL of THF was added to the flask and 40 mL to the addition funnel. After mixture of the THF and bromomesitylene in the funnel, the solution was added dropwise. Following the addition, the contents of the flask were heated to reflux for 3 h.

The reaction mixture was then cooled to 0 °C, and 42.0 g (0.22 mol) of cuprous iodide was added together with 50 mL of additional THF to facilitate stirring. Stirring was continued at 0 °C for 3 h. After formation of the organocopper reagent, 23.2 g (0.068 mol) of tetrabromoethylene dissolved in 70 mL of THF was slowly added to the flask. The resulting mixture was then heated to reflux for 40 h, causing a color change from orange-red to green-brown. The reaction mixture was allowed to cool to room temperature and 120 mL of water was slowly added. Most of the THF was then removed under reduced pressure and the resulting hydrolysate was extracted three times with 100-mL portions of ethyl ether. The ether extracts were combined,

Table X. Positional and Thermal Parameters and Their Estimated Standard Deviations<sup>a</sup>

atom	x	y	z	B <sub>11</sub>	B <sub>22</sub>	B <sub>33</sub>	B <sub>12</sub>	B <sub>13</sub>	B <sub>23</sub>
Co	-0.05254 (7)	-0.2500 (0)	-0.25279 (3)	0.00922 (7)	0.00842 (7)	0.00203 (1)	-0.0025 (2)	-0.00039 (5)	0.00083 (9)
C1	0.0943 (8)	-0.0726 (9)	-0.2137 (4)	0.0216 (12)	0.0175 (11)	0.0047 (2)	-0.018 (2)	-0.0005 (9)	-0.0010 (10)
C2	0.1807 (6)	-0.1915 (7)	-0.2381 (3)	0.0111 (8)	0.0150 (10)	0.0041 (2)	-0.008 (1)	-0.0008 (7)	0.0013 (7)
C3	0.1351 (7)	-0.2121 (9)	-0.3072 (3)	0.0146 (9)	0.0251 (16)	0.0042 (2)	-0.007 (2)	0.0033 (7)	0.0042 (9)
C4	0.0144 (8)	-0.1038 (8)	-0.3270 (3)	0.0223 (11)	0.0175 (11)	0.0038 (2)	-0.008 (2)	0.0028 (8)	0.0059 (8)
C5	-0.0101 (8)	-0.0156 (7)	-0.2690 (3)	0.0181 (9)	0.0116 (9)	0.0038 (2)	-0.008 (2)	0.0036 (7)	0.0026 (7)
C6	-0.2438 (6)	-0.3169 (6)	-0.2136 (2)	0.0115 (7)	0.0086 (6)	0.0017 (1)	0.001 (1)	0.0022 (5)	0.0015 (5)
C7	-0.1216 (5)	-0.4370 (6)	-0.2063 (2)	0.0101 (7)	0.0091 (7)	0.0015 (1)	-0.001 (1)	0.0003 (5)	0.0009 (5)
C8	-0.1400 (5)	-0.4596 (6)	-0.2786 (2)	0.0078 (6)	0.0093 (7)	0.0014 (1)	-0.003 (1)	-0.0005 (4)	-0.0010 (5)
C9	-0.2603 (5)	-0.3380 (6)	-0.2852 (2)	0.0075 (6)	0.0078 (6)	0.0017 (1)	0.000 (1)	0.0004 (4)	-0.0002 (5)
C10	-0.3582 (5)	-0.2624 (7)	-0.3417 (2)	0.0087 (6)	0.0093 (6)	0.0017 (1)	0.001 (1)	-0.0005 (4)	0.0000 (6)
C11	-0.3242 (7)	-0.2830 (7)	-0.4064 (2)	0.0189 (9)	0.0154 (12)	0.0021 (1)	0.010 (2)	-0.0007 (6)	-0.0007 (6)
C12	-0.4127 (8)	-0.2064 (8)	-0.4587 (2)	0.0276 (12)	0.0243 (16)	0.0015 (1)	0.010 (2)	-0.0029 (7)	-0.0013 (7)
C13	-0.5323 (7)	-0.1065 (8)	-0.4478 (3)	0.0192 (10)	0.0167 (10)	0.0030 (2)	0.000 (2)	-0.0051 (7)	0.0042 (7)
C14	-0.5659 (6)	-0.0869 (8)	-0.3846 (3)	0.0105 (8)	0.0196 (11)	0.0051 (2)	0.007 (2)	0.0018 (7)	0.0069 (9)
C15	-0.4825 (6)	-0.1662 (7)	-0.3321 (3)	0.0109 (7)	0.0167 (9)	0.0031 (1)	0.007 (2)	0.0038 (6)	0.0063 (7)
C16	-0.1014 (5)	-0.5819 (6)	-0.3256 (2)	0.0104 (7)	0.0098 (7)	0.0014 (1)	0.000 (1)	0.0008 (5)	0.0004 (5)
C17	-0.2276 (5)	-0.6630 (6)	-0.3630 (2)	0.0110 (7)	0.0111 (7)	0.0015 (1)	0.002 (1)	0.0005 (5)	0.0003 (5)
C18	-0.1977 (6)	-0.7625 (8)	-0.4143 (2)	0.0179 (8)	0.0117 (7)	0.0019 (1)	0.004 (2)	0.0005 (5)	-0.0003 (7)
C19	-0.0465 (7)	-0.7882 (6)	-0.4294 (2)	0.0235 (10)	0.0111 (10)	0.0017 (1)	0.006 (1)	0.0062 (5)	0.0003 (5)
C20	0.0750 (6)	-0.7211 (7)	-0.3883 (2)	0.0159 (8)	0.0150 (11)	0.0030 (1)	0.007 (2)	0.0070 (5)	0.0005 (7)
C21	0.0549 (6)	-0.6238 (7)	-0.3355 (3)	0.0117 (8)	0.0141 (9)	0.0028 (1)	0.002 (2)	0.0035 (5)	-0.0006 (7)
C22	0.1993 (7)	-0.5769 (9)	-0.2886 (3)	0.0133 (9)	0.0184 (12)	0.0050 (2)	0.005 (2)	0.0010 (8)	-0.0025 (9)
C23	-0.3939 (6)	-0.6527 (7)	-0.3485 (3)	0.0112 (8)	0.0144 (9)	0.0027 (1)	-0.003 (2)	-0.0007 (6)	-0.0031 (7)
C24	-0.0210 (9)	-0.8908 (10)	-0.4860 (3)	0.0317 (14)	0.0210 (13)	0.0028 (2)	0.006 (2)	0.0071 (8)	-0.0029 (8)
C25	-0.0311 (6)	-0.5115 (6)	-0.1479 (2)	0.0100 (7)	0.0103 (7)	0.0018 (1)	0.001 (1)	0.0007 (5)	0.0015 (5)
C26	0.0413 (6)	-0.6552 (7)	-0.1522 (3)	0.0166 (9)	0.0101 (8)	0.0024 (1)	0.001 (2)	-0.0034 (6)	-0.0012 (6)
C27	0.1301 (7)	-0.7194 (6)	-0.0965 (3)	0.0217 (10)	0.0073 (9)	0.0037 (2)	0.004 (1)	-0.0050 (7)	0.0034 (6)
C28	0.1434 (7)	-0.6499 (8)	-0.0379 (3)	0.0154 (9)	0.0194 (11)	0.0027 (2)	-0.002 (2)	-0.0033 (6)	0.0052 (7)
C29	0.0698 (7)	-0.5100 (9)	-0.0312 (3)	0.0183 (10)	0.0250 (13)	0.0016 (1)	-0.002 (2)	0.0009 (6)	-0.0016 (7)
C30	-0.0171 (6)	-0.4388 (8)	-0.0856 (2)	0.0158 (9)	0.0177 (10)	0.0016 (1)	0.008 (2)	0.0006 (6)	0.0018 (6)
C31	-0.3521 (5)	-0.2621 (7)	-0.1655 (2)	0.0131 (6)	0.0088 (6)	0.0017 (1)	0.005 (2)	0.0025 (4)	-0.0003 (6)
C32	-0.4416 (6)	-0.3780 (6)	-0.1389 (2)	0.0128 (7)	0.0084 (7)	0.0016 (1)	0.000 (1)	0.0015 (5)	-0.0008 (5)
C33	-0.5401 (6)	-0.3361 (7)	-0.0929 (2)	0.0120 (8)	0.0132 (8)	0.0019 (1)	-0.004 (1)	0.0015 (5)	0.0013 (6)
C34	-0.5592 (6)	-0.1848 (7)	-0.0732 (2)	0.0130 (8)	0.0185 (10)	0.0020 (1)	0.005 (2)	0.0027 (5)	-0.0028 (6)
C35	-0.4752 (7)	-0.0725 (7)	-0.1019 (3)	0.0191 (10)	0.0111 (8)	0.0034 (2)	0.006 (2)	0.0050 (7)	-0.0030 (7)
C36	-0.3739 (7)	-0.1064 (7)	-0.1467 (3)	0.0225 (11)	0.0119 (9)	0.0031 (2)	0.001 (2)	0.0057 (7)	-0.0001 (7)
C37	-0.2794 (10)	0.0251 (8)	-0.1716 (4)	0.0532 (20)	0.0068 (9)	0.0079 (3)	-0.001 (2)	0.0226 (11)	-0.0019 (9)
C38	-0.4345 (6)	-0.5461 (7)	-0.1593 (3)	0.0130 (8)	0.0117 (8)	0.0031 (2)	-0.004 (1)	0.0042 (6)	-0.0014 (6)
C39	-0.6714 (8)	-0.1443 (10)	-0.0242 (3)	0.0195 (11)	0.0272 (14)	0.0036 (2)	0.001 (2)	0.0055 (7)	-0.0080 (9)

atom	x	y	z	B, Å <sup>2</sup>	atom	x	y	z	B, Å <sup>2</sup>
H1	0.109 (5)	-0.142 (6)	-0.168 (2)	4.0000 (0)	H24A	0.070 (5)	-0.929 (6)	-0.491 (2)	4.0000 (0)
H2	0.268 (5)	-0.250 (8)	-0.215 (2)	4.0000 (0)	H24B	-0.115 (5)	-0.952 (6)	-0.513 (2)	4.0000 (0)
H3	0.187 (5)	-0.316 (6)	-0.345 (2)	4.0000 (0)	H24C	-0.037 (5)	-0.851 (6)	-0.527 (2)	4.0000 (0)
H4	-0.054 (5)	-0.083 (6)	-0.383 (2)	4.0000 (0)	H26	0.028 (5)	-0.709 (6)	-0.192 (2)	4.0000 (0)
H5	-0.090 (5)	0.067 (7)	-0.266 (2)	4.0000 (0)	H27	0.170 (5)	-0.817 (6)	-0.110 (2)	4.0000 (0)
H11	-0.216 (5)	-0.315 (6)	-0.416 (2)	4.0000 (0)	H28	0.195 (5)	-0.691 (6)	-0.007 (2)	4.0000 (0)
H12	-0.389 (5)	-0.223 (6)	-0.495 (2)	4.0000 (0)	H29	0.079 (5)	-0.453 (6)	0.001 (2)	4.0000 (0)
H13	-0.592 (5)	-0.044 (6)	-0.483 (2)	4.0000 (0)	H30	-0.062 (5)	-0.335 (6)	-0.088 (2)	4.0000 (0)
H14	-0.650 (5)	-0.041 (6)	-0.380 (2)	4.0000 (0)	H33	-0.596 (5)	-0.405 (7)	-0.075 (2)	4.0000 (0)
H15	-0.502 (5)	-0.157 (6)	-0.289 (2)	4.0000 (0)	H35	-0.497 (5)	0.015 (6)	-0.093 (2)	4.0000 (0)
H18	-0.290 (5)	-0.811 (6)	-0.436 (2)	4.0000 (0)	H37A	-0.168 (0)	0.016 (0)	-0.161 (0)	4.0000 (0)
H20	0.189 (5)	-0.740 (8)	-0.398 (2)	4.0000 (0)	H37B	-0.358 (5)	0.013 (6)	-0.219 (2)	4.0000 (0)
H22A	0.247 (5)	-0.496 (6)	-0.322 (2)	4.0000 (0)	H37C	-0.294 (5)	0.095 (7)	-0.164 (2)	4.0000 (0)
H22B	0.179 (5)	-0.512 (6)	-0.254 (2)	4.0000 (0)	H38A	-0.335 (5)	-0.605 (6)	-0.140 (2)	4.0000 (0)
H22C	0.255 (5)	-0.666 (6)	-0.266 (2)	4.0000 (0)	H38B	-0.436 (5)	-0.548 (6)	-0.207 (2)	4.0000 (0)
H23A	-0.467 (5)	-0.590 (6)	-0.379 (2)	4.0000 (0)	H38C	-0.506 (5)	-0.587 (6)	-0.142 (2)	4.0000 (0)
H23B	-0.443 (5)	-0.772 (7)	-0.361 (2)	4.0000 (0)	H39A	-0.766 (5)	-0.176 (6)	-0.039 (2)	4.0000 (0)
H23C	-0.396 (5)	-0.637 (6)	-0.306 (2)	4.0000 (0)	H39B	-0.611 (5)	-0.160 (6)	0.013 (2)	4.0000 (0)
					H39C	-0.688 (5)	-0.043 (6)	-0.008 (2)	4.0000 (0)

<sup>a</sup> The form of the anisotropic thermal parameter is  $\exp[-(B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + B_{12}hk + B_{13}hl + B_{23}kl)]$ .

dried over anhydrous magnesium sulfate, and filtered. A small amount of activated charcoal was added, and the mixture was boiled, cooled, and again filtered. The solvent was removed and the brown residue was recrystallized from ethyl ether. Three crops of off-white crystals were obtained, totaling 6.8 g (38%) of dimesitylacetylene (4). The first crop had mp 129–130 °C (lit.<sup>20</sup> mp 129–130.5 °C).

Anal. Calcd for C<sub>20</sub>H<sub>22</sub>: C, 91.55; H, 8.45. Found: C, 91.46; H, 8.26.

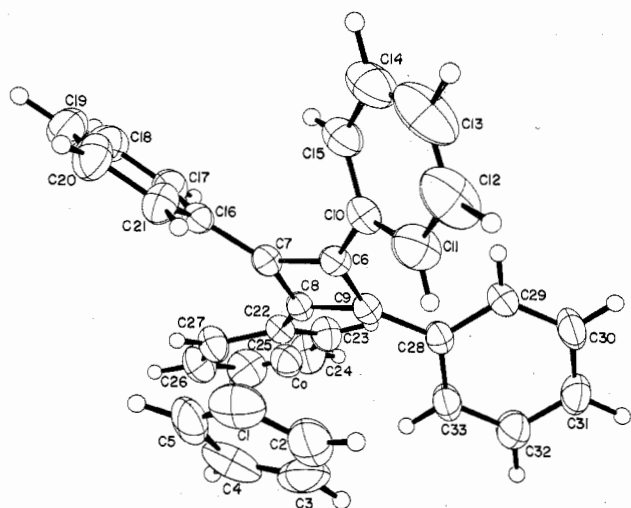
The <sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>) exhibited peaks at  $\tau$  7.72 (6 H, s, *p*-CH<sub>3</sub>), 7.50 (12 H, s, *o*-CH<sub>3</sub>), 3.13 (4 H, s, *m*-H).

**Attempted Reaction of ( $\eta^5$ -Cyclopentadienyl)dicarbonylcobalt (1) and Dimesitylacetylene (4).** A mixture of 267 mg (1.5 mmol) of

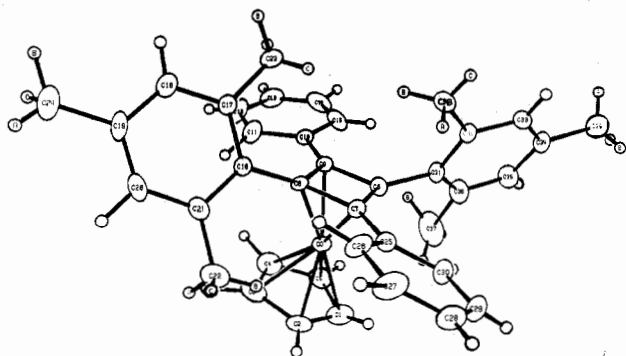
( $\eta^5$ -cyclopentadienyl)dicarbonylcobalt, 787 mg (3.0 mmol) of dimesitylacetylene, and 100 mL of degassed xylene was heated to reflux with stirring under nitrogen in a 200-mL, three-necked flask equipped with a magnetic stirrer, nitrogen inlet, reflux condenser, and mercury overpressure valve. Reflux was continued for 72 h. After cooling, the xylene solution was concentrated, placed on an alumina chromatography column, and eluted with hexane followed by benzene to give a clear band. Evaporation of this band to dryness gave 0.71 g (90% recovery) of dimesitylacetylene. Continued elution with 1:1 benzene–chloroform followed by chloroform yielded no other organic or organometallic products.

**X-ray Collection and Structure Determination for 5 and 6.** (a)





**Figure 3.** A general view of compound 5 showing the labeling system used in the crystallographic study. The numbering of the hydrogen atoms is identical with that of the carbons to which they are bonded. The thermal ellipsoids are of 50% probability for the heavy atoms and of convenient size for the hydrogen atoms.



**Figure 4.** A perspective view of compound 6 showing the labeling system used in the tables. All thermal ellipsoids are of convenient size and the methyl hydrogens are labeled with the number of the carbon atom to which they are bonded followed by a letter A, B, or C.

**Compound 5.** A crystal of irregular shape, grown from  $\text{CH}_2\text{Cl}_2$ -heptane, was mounted on a goniometer head and placed on an Enraf-Nonius CAD-4 computer-controlled diffractometer. A summary of the crystallographically important parameters for data collection and data processing is given in Table III. Accurate cell constant determination and data collection were similar to those described in detail elsewhere<sup>28</sup> and are thus not repeated here.

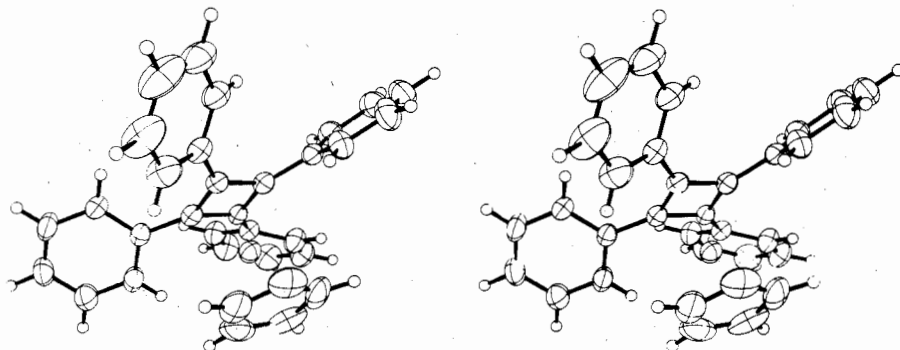
**Solution and Refinement.** Data collection was accomplished by using a locally written program (Houston). Lorentz and polarization factors were applied in converting the intensities to structure factor amplitudes,  $|F_o|$ . No absorption corrections were made due to the low value of the absorption coefficient ( $\mu = 7.4 \text{ cm}^{-1}$ ). Standard deviations of the

**Table XI.** Bond Lengths (Å) for Compound 6

Co-C1	2.065 (7)	C31-C32	1.408 (8)
Co-C2	2.043 (6)	C32-C33	1.390 (8)
Co-C3	2.098 (7)	C33-C34	1.376 (8)
Co-C4	2.102 (7)	C34-C35	1.379 (9)
Co-C5	2.081 (6)	C35-C36	1.372 (9)
Co-C6	2.002 (5)	C36-C31	1.411 (10)
Co-C7	1.994 (5)	C32-C38	1.506 (8)
Co-C8	1.993 (5)	C34-C39	1.516 (9)
Co-C9	1.964 (5)	C36-C37	1.516 (11)
C1-C2	1.392 (10)	C1-H1	1.11 (6)
C2-C3	1.418 (9)	C2-H2	0.97 (6)
C3-C4	1.409 (10)	C3-H3	1.29 (5)
C4-C5	1.442 (10)	C4-H4	1.21 (5)
C5-C1	1.424 (11)	C5-H5	0.99 (6)
C6-C7	1.463 (7)	C11-H11	1.01 (5)
C7-C8	1.470 (6)	C12-H12	0.80 (5)
C8-C9	1.461 (6)	C13-H13	0.99 (6)
C9-C6	1.455 (6)	C14-H14	0.84 (6)
C6-C31	1.511 (7)	C14-H15	0.91 (5)
C7-C25	1.473 (6)	C18-H18	0.95 (5)
C8-C16	1.486 (7)	C20-H20	1.03 (5)
C9-C10	1.477 (6)	C26-H26	0.92 (5)
C10-C11	1.397 (7)	C27-H27	0.96 (6)
C11-C12	1.385 (8)	C28-H28	0.80 (5)
C12-C13	1.377 (10)	C29-H29	0.81 (6)
C13-C14	1.365 (10)	C30-H30	0.96 (6)
C14-C15	1.381 (9)	C33-H33	0.87 (6)
C15-C10	1.383 (8)	C35-H34	0.81 (6)
C16-C17	1.418 (6)	C22-H22A	1.08 (6)
C17-C18	1.399 (8)	C22-H22B	0.93 (6)
C18-C19	1.389 (8)	C22-H22C	0.98 (6)
C19-C20	1.371 (8)	C23-H23A	0.98 (5)
C20-C21	1.389 (8)	C23-H23B	1.12 (6)
C21-C16	1.428 (7)	C23-H23C	0.88 (5)
C17-C23	1.497 (7)	C24-H24A	0.86 (6)
C19-C24	1.490 (9)	C24-H24B	1.06 (6)
C21-C22	1.511 (9)	C24-H24C	0.89 (6)
C25-C26	1.390 (7)	C37-H37A	0.95 (6)
C26-C27	1.390 (8)	C37-H37B	1.10 (5)
C27-C28	1.323 (9)	C37-H37C	0.64 (7)
C28-C29	1.373 (10)	C38-H38A	1.03 (6)
C29-C30	1.390 (8)	C38-H38B	0.96 (6)
C30-C25	1.402 (8)	C38-H38C	0.82 (6)
		C39-H39A	0.87 (5)
		C39-H39B	0.86 (5)
		C39-H39C	0.95 (6)

intensities,  $\sigma(I)$ , were estimated as  $\sigma^2(I) = I_{\text{TOT}} + 2\sum I_{\text{BC}}$ . Standard deviations in the structure factor amplitudes,  $\sigma(|F_o|)$ , were estimated as  $\sigma(|F_o|) = \sigma(I)/2(Lp)|F_o|$ . All data processing and calculations were carried out by using the X-RAY 72 system of programs.<sup>29</sup>

A three-dimensional Patterson map was computed and the position of the Co atom determined. A structure factor calculation based on the refined position of the Co atom gave an agreement factor of  $R_F = 0.45$ . All the remaining nonhydrogen atoms were easily found from successive difference Fourier maps. Full-matrix least-squares refinement with isotropic models for all the nonhydrogen atoms gave an  $R_F = 0.102$ . Hydrogen atoms were added at theoretically calculated



**Figure 5.** A stereoscopic view of compound 5.

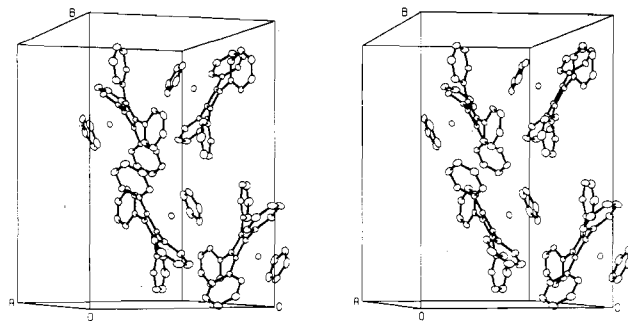


Figure 6. A packing diagram of compound 5.

Table XII. Angles (deg) for Compound 6

C2-C1-C5	106.3 (7)	C26-C25-C30	117.9 (5)
C1-C2-C3	110.8 (7)	C27-C26-C25	120.1 (6)
C2-C3-C4	107.1 (7)	C28-C27-C26	121.6 (6)
C3-C4-C5	107.3 (7)	C29-C28-C27	120.1 (6)
C4-C5-C1	108.6 (7)	C30-C29-C28	120.7 (6)
C7-C6-C9	89.1 (4)	C25-C30-C29	119.6 (6)
C6-C7-C8	90.8 (4)	C32-C31-C36	117.9 (5)
C7-C8-C9	88.6 (4)	C33-C32-C31	119.2 (5)
C8-C9-C6	91.5 (4)	C34-C33-C32	123.2 (6)
C7-C6-C31	130.4 (4)	C35-C34-C33	116.6 (6)
C9-C6-C31	134.5 (4)	C36-C35-C34	123.1 (7)
C6-C7-C25	132.8 (4)	C31-C36-C35	120.0 (6)
C8-C7-C25	136.2 (5)	C16-C21-C22	123.2 (5)
C7-C8-C16	137.1 (4)	C20-C21-C22	118.1 (5)
C9-C8-C16	131.5 (4)	C16-C17-C23	122.8 (4)
C8-C9-C10	134.9 (4)	C18-C17-C23	117.3 (5)
C6-C9-C10	133.7 (4)	C18-C19-C24	120.2 (7)
C11-C10-C15	118.2 (5)	C20-C19-C24	122.7 (7)
C10-C11-C12	120.0 (6)	C31-C36-C37	121.3 (6)
C11-C12-C13	121.0 (6)	C35-C36-C37	118.6 (7)
C12-C13-C14	119.0 (6)	C31-C32-C38	121.9 (5)
C13-C14-C15	120.9 (7)	C33-C32-C38	118.9 (6)
C14-C15-C10	120.9 (6)	C35-C34-C39	122.1 (7)
C17-C16-C21	117.5 (5)	C33-C34-C39	121.3 (7)
C16-C17-C18	119.8 (5)	C6-C31-C32	116.2 (6)
C17-C18-C19	122.1 (6)	C6-C31-C36	125.9 (6)
C18-C19-C20	117.0 (5)	C7-C25-C26	121.8 (5)
C19-C20-C21	124.1 (5)	C7-C25-C30	120.3 (5)
C20-C21-C16	118.6 (5)	C8-C16-C17	118.1 (4)
		C8-C16-C21	124.4 (4)
		C9-C10-C11	120.5 (5)
		C9-C10-C15	121.4 (4)

positions (C-H = 0.95 Å). Further anisotropic refinement of the nonhydrogen atoms and isotropic refinement of the hydrogens yielded the following final unweighted and weighted agreement factors:  $R_F = 0.029$  and  $R_{wF} = 0.027$ . The function minimized during all the least-squares refinements was  $\sum w(|F_o| - |F_c|)^2$ , where  $w$ , the weighting factors, were  $\sigma(|F_o|)^{-2}$ . The atomic scattering curves of Cromer and Mann<sup>30</sup> were used for the nonhydrogen atoms, and for the hydrogen atoms the curve of Stewart et al.<sup>31</sup> was used. Corrections for the real part of the anomalous dispersion for Co were also applied.<sup>32</sup> The estimated standard deviations were computed from the inverse matrix of the final least squares.

Final positional and thermal parameters are presented in Tables IV-VI. Bond lengths and angles are given in Tables VII and VIII. The standard deviations of the mean were calculated as  $[\sum (X_i - \bar{X})^2 / m(m-1)]^{1/2}$ . The equations of the least-squares planes through selected groups of atoms and the dihedral angles between them are given in Table IX. The stereo drawings (Figures 3-5) were obtained by using Johnson's ORTEP.<sup>33</sup>

(b) **Compound 6. Data Collection.** Well-developed, deep red parallelepiped-shaped crystals were available for crystallographic study. Several of these were examined on an Enraf-Nonius CAD-4 computer-controlled diffractometer and gave unit cell dimensions of approximately  $a = 8$ ,  $b = 8$ , and  $c = 60$  Å. Mosaic spreads on these crystals were of the order of 2-4°. A search of about 2 dozen additional crystals yielded the same results. Therefore, it was decided to proceed with the best of the examined crystals. Since it was unlikely that the  $c$  axis was actually of the order of 60 Å, indexing was carried

Table XIII. Least-Squares Planes (in Orthogonal A Space) and Deviations of Atoms from These Plane (in Å) for Compound 6

(a) Plane Based on C1, C2, C3, C4, and C5			
$0.7217x + 0.6646y - 0.1936z = 1.4285$			
C1	-0.001	C2	-0.002
C3	0.006	C4	-0.007
C5	0.004	CO	-1.692
(b) Plane Based on C6, C7, C8, and C9			
$0.7163x + 0.6947y - 0.0658z = -2.6785$			
C6	-0.005	C7	0.005
C8	-0.005	C9	0.005
CO	1.698	C10	0.041
C16	-0.342	C25	0.077
C31	-0.502		
(c) Plane Based on C6, C7, and C8			
$0.7115x + 0.6989y - 0.073z = -2.6562$			
CO	1.703	C9	0.020
(d) Plane Based on C10, C11, C12, C13, C14, and C15			
$-0.6282x - 0.7674y - 0.1284z = 3.9597$			
C10	-0.009	C11	-0.001
C12	0.015	C13	-0.009
C14	-0.011	C15	0.018
C9	-0.087		
(e) Plane Based on C16, C17, C18, C19, C20, and C21			
$0.0311x + 0.7708y - 0.6363z = 0.2631$			
C16	0.056	C17	-0.032
C18	-0.021	C19	0.043
C20	-0.011	C21	-0.052
C8	0.249	C22	-0.308
C23	-0.196	C24	0.100
(f) Plane Based on C25, C26, C27, C28, C29, and C30			
$0.8557x + 0.4736y - 0.2086z = -1.3486$			
C25	0.010	C26	-0.016
C27	0.009	C28	0.004
C29	-0.010	C30	-0.001
C7	0.032		
(g) Plane Based on C31, C32, C33, C34, C35, and C36			
$-0.6522x + 0.1145y - 0.7494z = 3.9278$			
C31	-0.017	C32	0.016
C33	-0.005	C34	-0.010
C35	0.011	C36	0.008
C6	-0.038	C37	-0.061
C38	0.082	C39	0.006

## Angles between Planes

plane 1	plane 2	angle, deg
a	b	7.5
d	b	12.9
e	b	53.2
f	b	17.1
g	b	70.2

out by using a value of one-third the measured one. Reflections with nonintegral  $l$  index were then eliminated from the data set. The remaining data were treated as for compound 5 except that both the real and imaginary terms for correction of anomalous dispersion were applied.

**Solution and Refinement.** A three-dimensional Patterson map revealed the position of the cobalt. All of the remaining nonhydrogen atoms in the molecule were found but not without some difficulty. Least-squares refinement halted at  $R_F = 0.16$ . The bond distances and angles were very poor and many extraneous peaks were visible in the difference Fourier, no doubt a reflection of the less than satisfactory data set. At this point, in desperation, a light orange irregularly shaped crystal was mounted and lo it was not twinned. The previously found positional parameters were now refined with the new data set and in two cycles  $R_F = 0.065$  whereupon all hydrogen atoms, except for several belonging to methyl groups, were located. Refinement was now continued until at least one and in some cases two hydrogens for each methyl group were found. Then the remaining hydrogens were calculated by assuming ideal positions and C-H = 0.95 Å. A temperature factor of 4.0 was assigned to the hydrogen atoms and refinement continued to convergence,  $R_F = 0.047$ . Since the space group is  $P2_1$ , either the refined structure or its mirror image is the correct one. Therefore, the signs of the positional parameters

were changed and least-squares refinement was continued.  $R_F$  and  $R_{wF}$  dropped to their final values and a better value for the error in an observation of unit weight (1.236 vs. 1.252) was obtained. Thus, the second enantiomorph was deemed to be the correct one. A final difference Fourier was now featureless. Crystallographic data for the untwinned crystal are given in Table III.

All programs used in the refinement were part of the Enraf-Nonius structure determining package.<sup>34</sup> Positional and anisotropic temperature factors for all the atoms are given in Table X; bond distances and angles in Tables XI and XII, respectively. Equations of least-squares planes are given in Table XIII. Tables of observed and calculated structure factors are available; see paragraph at end of paper and also ref 35.

**Acknowledgment.** Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for financial support. We are also indebted to Dr. John Fleming of the Perkin-Elmer Corp. for assistance in obtaining the variable-temperature <sup>1</sup>H NMR spectra. I.B. and G.M.R. thank the U.S. National Science Foundation for providing funds to purchase the diffractometer, the Robert A. Welch Foundation for research grants, and the Computer Center of the University of Houston for a generous supply of free computing time.

**Registry No.** 1, 12078-25-0; 3, 29778-31-2; 4, 5806-58-6; 5, 1278-02-0; 6, 70749-43-8; 8, 70775-26-7; iodomesitylene, 4028-63-1; cuprous phenylacetylide, 13146-23-1.

**Supplementary Material Available:** A listing of structure factor amplitudes for compound 6 (10 pages). Ordering information is given on any current masthead page.

## References and Notes

- (1) (a) University of Massachusetts. (b) University of Houston. (c) Texas A&M University. (d) Molecular Structure Corp.
- (2) M. D. Rausch and R. A. Genetti, *J. Org. Chem.*, **35**, 3888 (1970).
- (3) M. D. Rausch, Fifth International Conference on Organometallic Chemistry, Moscow, USSR, Aug. 16-21, 1971, Abstracts of Plenary & Section Lectures, Vol. III, p 10; *Pure Appl. Chem.*, **30**, 523 (1972).
- (4) I. Bernal, B. R. Davis, M. D. Rausch, and A. Siegal, *J. Chem. Soc., Chem. Commun.*, 1169 (1972).
- (5) M. D. Rausch, I. Bernal, B. R. Davis, A. Siegal, F. A. Higbie, and G. F. Westover, *J. Coord. Chem.*, **3**, 149 (1973).
- (6) A. Clearfield, R. Gopal, M. D. Rausch, E. F. Tokas, F. A. Higbie, and I. Bernal, *J. Organomet. Chem.*, **135**, 229 (1977).
- (7) M. D. Rausch, S. A. Gardner, E. F. Tokas, I. Bernal, G. M. Reisner, and A. Clearfield, *J. Chem. Soc., Chem. Commun.*, 187 (1978).
- (8) M. D. Rausch, F. A. Higbie, G. F. Westover, A. Clearfield, R. Gopal, J. M. Troup, and I. Bernal, *J. Organomet. Chem.*, **149**, 245 (1978).
- (9) S. A. Gardner, E. F. Tokas, and M. D. Rausch, *J. Organomet. Chem.*, **92**, 69 (1975).
- (10) S. A. Gardner and M. D. Rausch, *J. Organomet. Chem.*, **78**, 415 (1974).
- (11) R. G. Gastinger, M. D. Rausch, D. A. Sullivan, and G. J. Palenik, *J. Am. Chem. Soc.*, **98**, 719 (1976).
- (12) R. G. Gastinger, M. D. Rausch, D. A. Sullivan, and G. J. Palenik, *J. Organomet. Chem.*, **117**, 355 (1976).
- (13) H. Yamazaki and N. Hagihara, *J. Organomet. Chem.*, **21**, 431 (1970).
- (14) H. Yamazaki and Y. Hagihara, *J. Organomet. Chem.*, **139**, 157 (1977).
- (15) K. P. C. Vollhardt, *Acc. Chem. Res.*, **10**, 1 (1977).
- (16) W. S. Lee and H. H. Brintzinger, *J. Organomet. Chem.*, **127**, 93 (1977).
- (17) G. B. Kaufmann and R. P. Pinnell, *Inorg. Synth.*, **6**, 3 (1960).
- (18) C. E. Castro, E. J. Gaughan, and D. C. Owsley, *J. Org. Chem.*, **31**, 4071 (1966).
- (19) C. H. Bushweller, G. Bhat, L. J. Letendre, J. A. Brunell, H. S. Bilofsky, H. Ruben, D. H. Templeton, and A. Zalkin, *J. Am. Chem. Soc.*, **97**, 65 (1975).
- (20) H. E. Zimmerman and J. R. Dodd, *J. Am. Chem. Soc.*, **92**, 6507 (1970).
- (21) P. E. Riley and R. E. Davis, *J. Organomet. Chem.*, **113**, 157 (1976).
- (22) A. C. Villa, L. Coghi, A. Manfredotti, and C. Guastini, *Acta Crystallogr., Sect. B*, **30**, 2101 (1974).
- (23) C. Kabuto, J. Hayashi, H. Sakurai, and Y. Katahara, *J. Organomet. Chem.*, **43**, C23 (1972).
- (24) C. H. Saldarriaga-Molina, A. Clearfield, and I. Bernal, *Inorg. Chem.*, **13**, 2880 (1974), and references cited therein.
- (25) W. Bunder and E. Weiss, *J. Organomet. Chem.*, **92**, 65 (1975).
- (26) R. M. Tuggle and D. L. Weaver, *Inorg. Chem.*, **10**, 1504 (1971).
- (27) R. Allmann and E. Helmer, *Chem. Ber.*, **101**, 2522 (1968).
- (28) (a) G. M. Reisner, I. Bernal, H. Brunner, and J. Wachter, *J. Organomet. Chem.*, **137**, 329 (1977); (b) G. M. Reisner, I. Bernal, H. Brunner, and M. Muschiol, *Inorg. Chem.*, **17**, 738 (1978); (c) G. M. Reisner, I. Bernal, and G. R. Dobson, *J. Organomet. Chem.*, **157**, 23 (1978).
- (29) J. M. Stewart, G. Kruger, H. L. Ammon, C. Dickinson, and S. R. Hall, Eds., "The X-Ray System of Crystallographic Programs", Technical Report No. 192, Computer Science Center, University of Maryland, 1972.
- (30) D. Cromer and J. Mann, *Acta Crystallogr., Sect. A*, **24**, 321 (1968).
- (31) R. F. Stewart, E. R. Davison, and W. T. Simpson, *J. Chem. Phys.*, **42**, 3175 (1965).
- (32) "International Tables for X-Ray Crystallography", Vol. III, Kynoch Press, Birmingham, England, 1967, p 215.
- (33) C. K. Johnson, "ORTEP2, A Fortran-Ellipsoid Plot Program for Crystal Structure Illustration", ORNL-5138, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1972.
- (34) ENRAF-NONIUS, Structure Determination Package (SDP), Delft, Holland, 1975; revised 1977.
- (35) Tables of structure factors have been deposited as NAPS document No. 03512 with NAPS, c/o Microfiche Publications, P.O. Box 3513, Grand Central Station, New York, N.Y. 10017. A copy may be secured by citing the document and remitting \$3.00 for microfiche and \$5.00 for photocopies. Advance payment is required. Make checks payable to Microfiche Publications. Outside the United States or Canada, postage is \$3.00 for a photocopy or \$1.00 for a fiche.

## Notes

Contribution from the Centre de Spectroscopie Moléculaire de l'Université de Reims, Laboratoire de Chimie Minérale et Laboratoire de Chimie Organique Physique, Faculté des Sciences, Reims, France

### Fourier Transform Carbon-13 Nuclear Magnetic Resonance Study of Cyanocuprates(I) in Aqueous Solution

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Our preceding studies on copper(I) cyano complexes, based on X-ray structure determinations and on infrared and Raman

spectroscopy, showed a trigonal-planar  $\text{Cu}(\text{CN})_3^{2-}$  ion in the solid state<sup>1</sup> and in solution<sup>2</sup> whereas the  $\text{Cu}(\text{CN})_2^-$  ion was a polymer in the solid state<sup>3</sup> and a mononuclear linear ion in aqueous solution.<sup>2</sup> The vibrational study<sup>2</sup> on the three anions  $[\text{Cu}(\text{CN})_n]^{(n-1)-}$ , with  $n = 4, 3$ , and 2, led to the conclusion that in the copper-carbon bond, the  $\sigma$ -donor character of the cyanide is largely predominant over its  $\pi$ -back-bonding capacity; furthermore a comparison with metal carbonyls shows opposite correlations between CN and CO complexes. In this paper we report a reinvestigation of these results using Fourier transform carbon-13 nuclear magnetic resonance experiments in aqueous solution.