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Cobalt Metallacycles. 12.[1] Reaction of Cobaltacyclopentadiene with Nonacarbonyldiiron and Octacarbonyldicobalt. Formation of Dinuclear Metal Complexes

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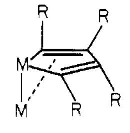
$(\eta\text{-}C_5H_5)(Ph_3P)(\overline{CoCR^1{=}CR^2CR^3{=}CR^4})$ (**4**) reacted with $Fe_2(CO)_9$ or $Co_2(CO)_8$ affording dinuclear metal complexes $[\eta\text{-}(CO)_3(\overline{FeCR^1{=}CR^2CR^3{=}CR^4})]Co(\eta\text{-}C_5H_5)$ (**5**) or $[\eta\text{-}(CO)_2(Ph_3P)(\overline{CoCR^1{=}CR^2CR^3{=}CR^4})]$-$Co(CO)_2$ (**6**) and $[\eta\text{-}(\eta\text{-}C_5H_5)(\overline{CoCR^1\cdots CR^2\cdots CR^3CHR^4})]Co(\mu\text{-}CO)(CO)_2$ (**7**). The structures of **5b** (R^1, R^4 = Ph; R^2, R^3 = COOMe) and **7a** (R^1, R^3 = Ph; R^2, R^4 = COOMe) have been unequivocally determined by single-crystal X-ray crystallography. Complex **5b** crystallizes in space group *Pbca* with $Z = 8$ and lattice constants of $a = 17.264$ (3) Å, $b = 14.966$ (2) Å, $c = 19.358$ (12) Å, and complex **7a** crystallizes in space group $P\bar{1}$ with $Z = 2$ and lattice constants $a = 9.890$ (2) Å, $b = 15.845$ (4) Å, $c = 8.793$ (3) Å, $\alpha = 104.36$ (3)°, $\beta = 82.24$ (3)°, and $\gamma = 103.56$ (2)°.

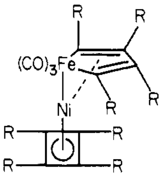
Introduction

Many homodinuclear metallacyclopentadiene complexes of the general structure **1** are known.[2] However, the corresponding heterodinuclear complexes are very rare. Maitlis[3] obtained [η-tricarbonyl(tetramethylferracylopenatadiene)] (η-tetramethylcyclobutadiene)nickel (**2**) which containd a Fe–Ni bond from the reaction between $Fe_3(CO)_{12}$ and (tetramethylcyclobutadiene)nickel dichloride; the structure was solved by Dahl[4] by means of X-ray diffraction methods. Recently Davidson[5] prepared heterodinuclear complexes **3** having Mo–Co and W–Co bonds by reaction of bis(hexafluorobut-2-yne) complexes $[M(\eta\text{-}C_5H_5)Cl(CF_3C{\equiv}CCF_3)_2]$ (M = Mo, W), with octacarbonyldicobalt.

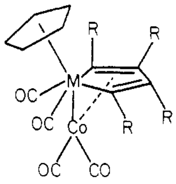
Previously, we have examined the reaction of (η-cyclopentadienyl)(triphenylphosphine)cobaltacyclopentadiene (**4**) with a variety of reagents and found that a coordinatively unsaturated species, (η-cyclopentadienyl)cobaltacyclopentadiene, is produced in the first step by unimolecular dissociation of the triphenylphosphine ligand.[6] It is of interest to attempt the reaction of the reactive unsaturated intermediate species with metal carbonyls in order to obtain new mixed-metal complexes.



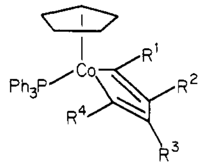
1



2, R = Me



3, M = Mo, W, R = CF_3



4a–h

a, R^1, R^3 = Ph, R^2, R^4 = COOMe
b, R^1, R^4 = Ph, R^2, R^3 = COOMe
c, R^1, R^2 = Ph, R^3, R^4 = COOMe
d, R^1, R^2, R^3, R^4 = Me
e, R^1, R^2, R^3, R^4 = Ph
f, R^1, R^3 = Ph, R^2, R^4 = H
g, R^1, R^4 = Ph, R^2, R^3 = H
h, R^1, R^2, R^3, R^4 = H

Results and Discussion

A solution of **4** in benzene was heated under reflux with $Fe_2(CO)_9$ (1:3 mole ratio) for several hours. Chromatographic separation using alumina and conventional workup gave air-stable, dark red crystals of **5**. The results are summarized in Table I. The yield of **5** largely depends on the substituents on **4** employed. In general, better yields were obtained by using electron-attracting substituents, which can be related to the stability of the intermediate cobaltacyclopentadiene complex. The extremely low yield of the tetraphenyl derivative **5e** may be due to steric reasons. Elemental and NMR analyses are consistent with those of structure **5A** in which the triphenylphosphine ligand of **4** is replaced by the tri-

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Table I. Analytical and Spectroscopic Data of $[\eta\text{-}(CO)_3(\overline{FeCR^1{=}CR^2CR^3{=}CR^4})]Co(\eta\text{-}C_5H_5)$ (5)

compd					yield,[a] %	mp, °C	C		H		IR (KBr, cm^{-1}) $\nu_{C=O}$	^1H NMR ($CDCl_3$, δ (ppm))[f]	
	R^1	R^2	R^3	R^4			calcd	found	calcd	found		$\eta\text{-}C_5H_5$	Me or H
5a	Ph	CO_2Me	Ph	CO_2Me	45 (66)	172-173	57.56	57.58	3.62	3.64	2025, 1965, 1955	5.36	3.34, 3.57
5b	Ph	CO_2Me	CO_2Me	Ph	46 (64)	163-165	57.56	57.63	3.62	3.65	2025, 1973, 1930	5.37	3.54
5c	Ph	Ph	CO_2Me	CO_2Me	27 (43)	158-159	57.56	57.56	3.62	3.60	2015, 1955	5.33	3.57, 3.77
5d	Me	Me	Me	Me	17	220-224[e]	51.65	51.77	4.61	4.60	2000, 1940 sh, 1930, 1918	4.64	2.00, 2.45
5e	Ph	Ph	Ph	Ph	<1[b]	215-217[e]					2020, 1955, 1938, 1930	5.34	
5f	Ph	H	Ph	H	10[c]	145-146[e]	61.57	61.65	3.66	3.65	2020, 1967, 1950, 1930	4.86	6.33, 7.90 (d, J = 3 Hz)
5g	Ph	H	H	Ph	9[c]	166-169[e]	61.57	61.59	3.66	3.66	2015, 1945, 1935	5.00	5.94
5h	H	H	H	H	5[d]	54-55	45.61	45.71	2.87	2.85	2020, 1940	4.95	5.95, 7.49 (AA'XX' type)[g]

[a] Yields in parentheses were calculated on the basis of 4 consumed. [b] The mass spectrum showed *m/e* 620 (M^+) followed by loss of three COs. [c] Prepared by using the 1:1 crude mixture of 3f and 3g. [d] Based on $(\eta\text{-}C_5H_5)(PPh_3)_2Co$ employed. [e] Measured in a nitrogen-filled capillary tube. [f] Phenyl protons are omitted. [g] Similar pattern was reported for $[\eta\text{-}(CO)_3(\overline{FeCH{=}CHCH{=}CH})]Fe(CO)_3$: Dettlaf, G.; Weiss, E. *J. Organomet. Chem.* **1976**, *108*, 213.

Table II. Molecular Geometry for 5b

A. Selected Bond Distances (Å) with Estimated Standard Deviations in Parentheses

Fe-Co	2.472 (2)	C(4)-C(41)	1.496 (12)
Fe-C(1)	1.807 (10)	C(5)-C(51)	1.534 (12)
Fe-C(2)	1.748 (10)	C(6)-C(61)	1.505 (13)
Fe-C(3)	1.799 (11)	C(7)-C(71)	1.505 (12)
Fe-C(4)	1.963 (8)	C(1)-O(1)	1.138 (12)
Fe-C(7)	1.957 (8)	C(2)-O(2)	1.141 (13)
Co-C(4)	2.036 (9)	C(3)-O(3)	1.140 (15)
Co-C(5)	2.019 (8)	C(51)-O(4)	1.160 (11)
Co-C(6)	2.038 (8)	C(51)-O(5)	1.348 (11)
Co-C(7)	2.065 (9)	C(52)-O(5)	1.453 (13)
C(4)-C(5)	1.396 (12)	C(61)-O(6)	1.200 (13)
C(5)-C(6)	1.435 (11)	C(61)-O(7)	1.306 (13)
C(6)-C(7)	1.415 (12)	C(62)-O(7)	1.487 (16)

B. Intramolecular Angles (deg) with Estimated Standard Deviations in Parentheses

C(1)-Fe-C(2)	98.99 (46)	C(4)-Co-C(7)	77.37 (33)
C(1)-Fe-C(3)	88.17 (45)	Fe-C(4)-Co	76.37 (30)
C(2)-Fe-C(3)	97.18 (48)	Fe-C(7)-Co	75.81 (31)
C(1)-Fe-C(7)	92.26 (41)	Fe-C(4)-C(5)	114.57 (60)
C(3)-Fe-C(4)	93.36 (42)	C(4)-C(5)-C(6)	115.02 (73)
C(2)-Fe-C(4)	98.86 (42)	C(5)-C(6)-C(7)	112.31 (73)
C(2)-Fe-C(7)	97.46 (41)	C(6)-C(7)-Fe	115.59 (61)
C(4)-Fe-C(7)	81.67 (37)		

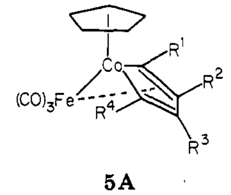
C. Least-Squares Planes and Distances of Atoms from Their Respective Planes[a]

plane		dist from the plane	
atom	dist, Å	atom	dist, Å
(1) Plane through C(4)C(5)C(6)C(7)			
$-0.6221X + 0.4995Y + 0.6029Z = 1.7655$			
C(4)	-0.004	Fe	0.204
C(5)	0.007	Co	-1.582
C(6)	-0.006	C(1)	-0.161
C(7)	0.004	C(2)	1.950
		C(3)	-0.065
(2) Plane through C(81)C(82)C(83)C(84)C(85)			
$-0.5638X + 0.5764Y + 0.5915Z = -0.7490$			
C(81)	0.007	Fe	3.287
C(82)	-0.004	Co	1.674
C(83)	0.001	C(4)	3.238
C(84)	0.004	C(5)	3.364
C(85)	-0.007	C(6)	3.334
		C(7)	3.212

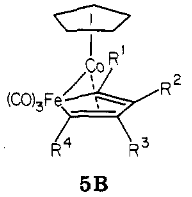
D. Dihedral Angle between the Planes 1 and 2 is 5.6°

[a] The equation of each plane is defined by $AX + BY + CZ = D$, where X, Y, and Z are the coordinates in angstroms along the a, b, and c axes, respectively.

carbonyliron moiety. However, another structure, **5B**, should be considered because [η-tricarbonyl(ferracyclopentadiene)]tricarbonyliron[7] and [η-cyclopentadienyl(cobaltacyclopentadiene)](η-cyclopentadienyl)cobalt[2k] are known to be fluxional at elevated temperatures by an intramolecular interchange of roles of the two metal moieties. An X-ray crystallographic structure determination for **5b** was undertaken to elucidate the exact



5A



5B

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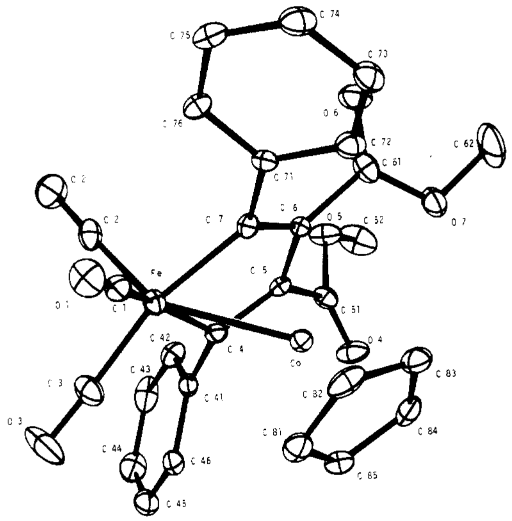
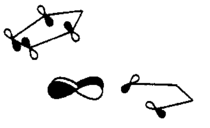


Figure 1. Molecular diagram and atom labeling scheme for **5b** (40% probability thermal ellipsoids).

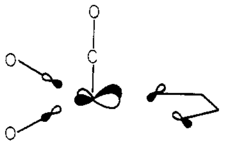
structure of **5**. A view of the molecule is presented in Figure 1, together with the labeling of the atoms. Selected bond lengths and angles are shown in Table II. The iron atom is bonded to C(4) and C(7) as a part of the metallacyclopentadiene ring and the cobalt atom is bonded to the diene moiety, thus showing that structure **5B** is the case. We can name **5** as [μ-[1-4-η-butadiene-1,4-diyl-C^1,C^4(Fe):C^1,C^2,C^3,C^4(Co)]](tricarbonyliron)cyclopentadienylcobalt(*Fe–Co*).

In order to known the reason why **5B** is preferred over **5A**, we analyzed both complexes by extended Hückel calculations. In the model calculations, C_s symmetry of the molecules with the unsubstituted metallacycle was assumed. Since **5A** is not known and X-ray analyses of the related complex **1** [M = Co(η-C_5H_5)] has not been reported, the goemetry of model **5A** was taken from **5B** as far as possible. In the model complex for **5A**, the dihedral angle between the Cp ring and the cobalt metallacycle was set as 55°, which is identical with the dihedral angle between the ferracyclopentadiene and the plane defined by the three carbonyl carbons in **5B**.

The total energy calculated using these models showed that **5B** is ca. 4 kcal/mol more stable than **5A**. The Muliken bond population analysis indicated that the stability of **5B** arises mainly from the stronger Fe–C(α) σ bond (compared to Co–C(α)). By the fragmentation analysis (C_4H_4 unit and the rest of the molecule) the strong Fe–C(α) bond, in turn, could be traced back to good overlap of the Fe d_{xy} orbital with the σ-type a″ orbital of the C_4H_4 fragment. In $(CO)_3Fe$ of **5B′**, d_{xy} is repelled by the two in-plane carbonyls and as a result of this repulsion, $4p_y$ hybridizes the d_{xy} orbital away from the carbonyls toward the C_4H_4 unit. In **5A′**, on the other hand, the antibonding character between Cp and d_{xy} of the Co atom is not strong because the Cp ring is tilted off the cobaltacyclopetadiene ring as illustrated.



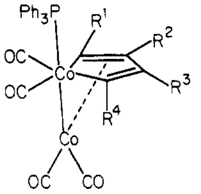
5A′



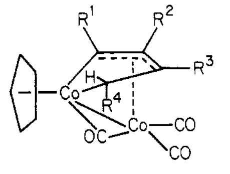
5B′

Consequently, the d_{xy} orbital of the $(CO)_3Fe$ fragment in **5B** interacts with the C_4H_4 more effectively than the CpCo orbital in **5A** does, leading to the strong Fe–C σ bond. Extended Hückel MO analysis suggested that the preference of the structure **5B** to **5A** arises mainly from the stronger M–C σ bond in **5B**.

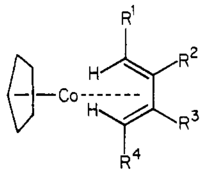
The reaction of **4a** with $Co_2(CO)_8$ (1:2 mole ratio) in benzene gave brown crystals **6a** and red brown crystals **7a**. When **4b** or **4c** was employed, only **6b** or **6c** was formed without giving any products corresponsing to **7a**. Compounds **6a–c** thus obtained are summarized in Table III. The IR elemental analysis and NMR spectra are mostly consistent with the formula $Co_2(CO)_4(PPh_3)(R^1C_2R^2)(R^3C_2R^4)$ in which the original cyclopentadienyl group has been lost. The compositions are the same as those of the known dinuclear rhodium[2v] and iridium[2x] metallacyclopentadiene complexes $[(CO)_2(Ph_3P)(\overline{MCR{=}CRCR{=}CR})]M(CO)_2$ (M = Rh, R = COOMe; M = Ir, R = COOEt), and the pattern of the metal carbonyl region in the IR spectra shows a strong similarily with those of the rhodium and iridium complexes as cited in Table III for comparison. Based on this fact, we assign **6** as [μ-[1-4-η-butadiene-1,4-diyl-C^1,C^4(Co^1):C^1,C^2,C^3,C^4(Co^2)]]tetracarbonyl(triphenylphosphine)dicobalt(*Co–Co*). The NMR spectra of **6b** and **6c** are consistent with those of this structure, but the appearance of a single resonance for the methoxy protons of **6a** should be ascribed to an accidental degeneracy.



6



7



8

The IR spectrum of **7a** shows the presence of a band due to bridging carbon monoxide at 1850 cm^{-1}, and the ^{1}H NMR spectrum shows the presence of two phenyl, one cyclopentadienyl, and two methoxy groups in different environments. However, a singlet corresponding to one proton is also observed at δ 3.27, which is difficult to assign. The structure of **7a** was determined by an X-ray crystallographic analysis. A perspective view of the molecule is given, together with the numbering of the atoms in Figure 2. Selected bond lengths and angles are shown in Table IV. One cobalt atom, Co(1), is σ bonded to C(4) and C(7), and the second cobalt atom, Co(2), is π bonded to the allylic portion, C(4), C(5), and C(6), of the cobaltacyclopentenyl moiety. There exists no bonding between Co(2) and C(7). The hydrogen atom bonded to C(7) occupies an exo position and the C(10) atm an end position to the Co(2) atom. Thus we can name the complex as [μ-[1-3-η-1,3-diphenyl-2,4-(dimethoxycarbonyl)butene-1,4-diyl-C^1,C^4(Co^1):C^1,C^3(Co^2)]](μ-carbonyl)(η-cyclopentadienyl)dicarbonyldicobalt(*Co–Co*).

In order to obtain some insight into the reaction pathway to **7**, the reaction of **4a** with $Co_2(CO)_8$ was carried out in the presence of ethanol as a sorce of the extra hydrogen. The yield of **7a** did not increase, and a new (η-butadiene)(η-cyclopentadienyl)cobalt complex (**8a**) was obtained in reasonable yield. However, the reaction of **4b** with

Table III. Analytical and Spectroscopic Data of $[(CO)_2(PPh_3)(MCR^1{=}CR^2CR^3{=}CR^4)]M(CO)_2$[6]

compd						yield, %	mp,[a] °C	C		H		IR (KBr, cm^{-1}) $\nu_{C{\equiv}O}$	${}^1H$ NMR[b] ($CDCl_3$, δ (ppm)) Me
	M	R^1	R^2	R^3	R^4			calcd	found	calcd	found		
6a	Co	Ph	CO_2Me	Ph	CO_2Me	14	152–154		61.87		3.88	2040 s, 2000 s, 1992 s, 1985 sh	3.18
6b	Co	Ph	CO_2Me	CO_2Me	Ph	41	>190 dec		62.23		3.87	2040 s, 2000 s, 1990 sh, 1938 s	3.42
6c	Co	Ph	Ph	CO_2Me	CO_2Me	32	170–173	62.08	62.12	3.85	3.87	2040 s, 2000 s, 1998 sh, 1970 s	3.28, 3.49
	Rh	CO_2Et	CO_2Et	CO_2Et	CO_2Et[c]							2072 vs, 2044 s, 2030 sh, 1998 s	
	Ir	CO_2Me	CO_2Me	CO_2Me	CO_2Me[d]							2060 s, 2040 s, 2020 sh, 1970 s	

[a] Measured in nitrogen filled capillary tube. [b] Phenyl protons are omitted. [c] Reference 2v. [d] Reference 2x.

Table IV. Molecular Geometry for **7a**

A. Selected Bond Distances (Å) with Estimated Standard Deviations in Parentheses

Co(1)–Co(2)	2.497 (1)	C(4)–C(41)	1.489 (7)
Co(1)–C(4)	1.963 (5)	C(5)–C(8)	1.512 (7)
Co(1)–C(7)	2.026 (4)	C(6)–C(61)	1.498 (5)
Co(1)–C(3)	1.949 (5)	C(7)–C(10)	1.485 (7)
Co(2)–C(1)	1.788 (6)	C(7)–H(7)	0.959 (40)
Co(2)–C(2)	1.778 (5)	C(1)–O(1)	1.131 (7)
Co(2)–C(3)	1.905 (5)	C(2)–O(2)	1.135 (6)
Co(2)–C(4)	2.009 (4)	C(3)–O(3)	1.155 (6)
Co(2)–C(5)	2.071 (4)	C(8)–O(4)	1.187 (7)
Co(2)–C(6)	2.162 (4)	C(8)–O(5)	1.331 (5)
C(4)–C(5)	1.414 (5)	C(9)–O(5)	1.448 (7)
C(5)–C(6)	1.422 (7)	C(10)–O(6)	1.204 (5)
C(6)–C(7)	1.514 (6)	C(10)–O(7)	1.349 (6)
		C(11)–O(7)	1.446 (8)

B. Intramolecular Angles (deg) with Estimated Standard Deviations in Parentheses

C(4)–Co(1)–C(7)	84.1 (2)	Co(2)–C(1)–O(1)	175.7 (5)
Co(1)–C(3)–Co(2)	80.8 (2)	Co(2)–C(2)–O(2)	178.4 (5)
C(1)–Co(2)–C(2)	97.3 (2)	Co(1)–C(3)–O(3)	139.0 (4)
Co(1)–C(4)–C(5)	113.0 (4)	Co(2)–C(3)–O(3)	140.3 (4)
C(4)–C(5)–C(6)	113.6 (4)	Co(1)–C(7)–Co(2)	60.1 (1)
Co(1)–C(7)–C(6)	104.0 (3)	Co(1)–C(7)–H(7)	100.7 (2.4)
Co(1)–C(7)–C(10)	107.7 (3)	C(6)–C(7)–H(7)	109.7 (2.9)
C(6)–C(7)–C(10)	116.8 (3)	C(10)–C(7)–H(7)	116.0 (3.2)

C. Least-Squares Planes and Distances of Atoms from Their Respective Planes[a]

plane		dist from the plane	
atom	dist, Å	atom	dist, Å
(1) Plane through C(4)C(5)C(6)			
$0.5124X + 0.3598Y - 0.7192Z = 0.0482$			
		Co(1)	0.272
		Co(2)	−1.643
		C(7)	0.755
		C(10)	0.408
		H(7)	1.690
(2) Plane through C(21)C(22)C(23)C(24)C(25)			
$0.1169X + 0.1356Y + 0.9236Z = 1.1761$			
C(21)	−0.008	Co(1)	1.726
C(22)	0.002		
C(23)	0.004		
C(24)	−0.010		
C(25)	0.013		

[a] The equation of each place is defined by $AX + BY + CZ = D$, where X, Y, and Z are the coordinates in angstroms along the a, b, and c axes, respectively.

$Co_2(CO)_8$ in benzene/ethanol gave **7b** without giving a diene complex corresponding to **8a**. On the contrary, similar treatment of **4e** gave only **8e**. Thus the formation of **7** and **8** appeared to be delicately influenced by the change of position and type of substituent. Although the mechanism of its formation is not clear, **7** may be derived from the addition of a hydridocobalt species to a coordinatively unsaturated intermediate, (η-cyclopentadienyl)cobaltacyclopentadiene.

Experimental Section

Equipment. Melting points were determined by using a Mitamura capillary melting point apparatus and were uncorrected. The ${}^1H$ NMR spectra were recorded on a Varian HA-100 spectrometer using tetramethylsilane as an internal standard. IR spectra were obtained by using a Shimadzu IR-27G spectrometer.

Reagents. For column chromatography, Sumitomo activated alumina KCG-30 was used. Complexes **4a–e** were prepared as reported previously.[8,9] $Fe_2(CO)_9$ and $Co_2(CO)_8$ were prepared

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(8) Yamazaki, H.; Waskatsuki, Y. *J. Organomet. Chem.* **1977**, *139*, 157.

(9) McAlister, D. R.; Bercaw, J. E.; Bergman, R. G. *J. Am. Chem. Soc.* **1977**, *99*, 1666.

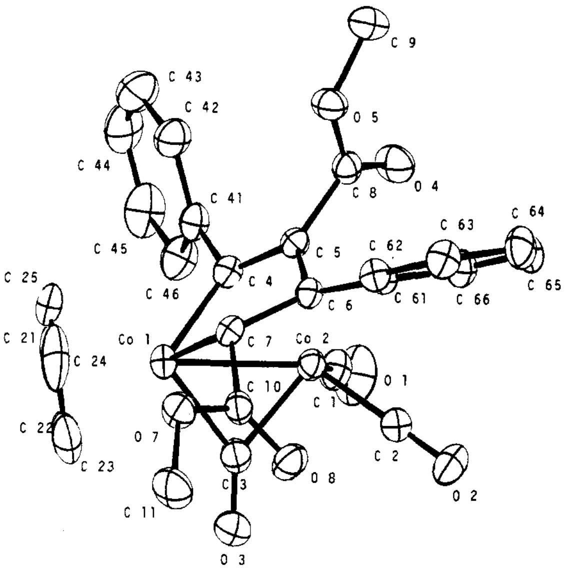

Figure 2. Molecular diagram and atom labeling scheme for **7a** (45% probability thermal ellipsoids).

by methods described in the literature.[10]

Reactions of Cobaltacyclopentadienes 4 with $Fe_2(CO)_9$. (a) Reaction of 4b. To a solution of **4b** (0.353 g, 0.5 mmol) in benzene (15 mL) was added $Fe_2(CO)_9$ (0.370 g, 1.0 mmol), and the mixture was heated at reflux for 10 h. The reaction mixture was chromatographed on Al_2O_3. The first yellow band eluted by benzene was concentrated to give $Fe(CO)_4(PPh_3)$ (0.12 g, 56%). The second red violet band, which was eluted by benzene/ethyl acetate (20:1), was concentrated, and addition of hexane gave chocolate brown crystals of **5b** (0.133 g, 46%). From the third orange band, starting **4b** was recovered (0.100 g, 28%). By similar procedures **5a**, **5c**, and **5d** were obtained.

(b) Reaction of 4e. The mixture of **4e** (0.223 g, 0.3 mmol) and $Fe_2(CO)_9$ (0.330 g, 0.1 mmol) in benzene (10 mL) was heated at reflux for 3 h. The reaction mixture was concentrated and chromatographed on Al_2O_3. The yellow to pale purple fraction eluted by benzene/hexane (1:2) and the orange fraction eluted by benzene/ethyl acetate (1:1) were collected. The first fraction was concentrated to give yellow crystals of (η-cyclopentadienyl)(η-tetraphenylcyclobutadiene)cobalt (0.093 g, 65%). The mother liquid was chromatographed again on Al_2O_3, and the red-purple fraction was separated by careful elution from the column by benzene/hexane (1:3). Evaporation of the solvent followed by crystallization using a small amount of hexane gave dark red crystals of **5e** (0.0012 g). Concentration of the second orange fraction and addition of hexane gave red crystals of (η-cyclopentadienyl)(η-tetraphenylcyclopentadienone)cobalt[11] (0.029 g, 19%).

(c) Reaction of a Mixture of 4f and 4g. To a solution of $(\eta\text{-}C_5H_5)(PPh_3)_2Co\text{-}C_6H_6$ (1.45 g, 2 mmol) in benzene (20 mL) was added phenylacetylene (1 mL), and the mixture was stirred overnight. After concentration, the reaction mixture was chromatographed on Al_2O_3 (deactivated by 5% H_2O, 2 × 15 cm). The orange-brown layer was eluted by benzene/hexane (1:2), and evaporation of the solvent under reduced pressure left a brown solid (0.65 g, 55%). The ^1H NMR spectrum showed that it consisted of a ca. 1:1 mixture of **4f** and **4g**.[12]

Table V. Crystal Data and Collection Parameters

	$CoFeC_{28}H_{21}O_7$ (**5b**)	$Co_2C_{28}H_{22}O_7$ (**7a**)
space group	*Pbca*	$P\bar{1}$
a, Å	17.264 (3)	9.890 (2)
b, Å	14.966 (2)	15.845 (4)
c, Å	19.358 (12)	8.793 (3)
α, deg		104.36 (3)
β, deg		82.24 (3)
γ, deg		103.56 (2)
M_r	584.2	588.3
V, Å^3	5001.6	1293.4
Z	8	2
ρ_{calcd}, g/cm^3	1.552	1.516
ρ_{obsd}, g/cm^3	1.54	1.52
cryst size, mm	0.06 × 0.20 × 0.47	0.40 × 0.22 × 0.18
radiatn	Mo Kα (0.710 73 Å)	
monochrometer	graphite	
scan type	$2\theta-\omega$	
scan speed	4° min^{-1}	
scan range	$2\theta \leqslant 55°$	
no. of reflctns measd	2932	4624
data used ($F_o > 3\sigma(F_o)$)	2815	3768
R_1	0.0626	0.0456
R_2	0.0447	0.0458
largest residual peak, e/Å^3	0.75	0.56

To a solution of the brown solid (0.59 g, 1.0 mmol) in benzene (30 mL) was added $Fe_2(CO)_9$ (0.74 g), and the resulting mixture was heated at reflux temperature for 1 h. After evaporation of the solvent, the residue was dissolved in hexane and chromatographed n Al_2O_3. Two red brown bands were separated on elution with benzene/hexane (1:2). The first band was collected and evaporated to dryness. Crystallization of the residue from hexane gave red brown crystals of **5f** (0.045 g, 10%). Compound **5g** (0.042 g, 9%) was obtained from the second band.

(d) Reaction of 4h. A solution of $(\eta\text{-}C_5H_5)(PPh_3)_2Co\text{-}C_6H_6$ (1.45 g, 2 mmol) in benzene (40 mL) was placed in a flask (100 mL). The flask was flushed with acetylene gas at room temperature and shook vigorously. To the the resulting dark brown solution was added $Fe_2(CO)_9$ (2 g). After being heated at reflux, the solution was concentrated and chromatographed on Al_2O_3. Treatment of the purple-red eluate with benzene/hexane (1:3) gave red crystals of **5h** (0.032 g).

Reactions of Cobaltacyclopentadienes (4) with $Co_2(CO)_8$. (a) Reaction of 4a in Benzene. To a solution of **4a** (0.353 g, 0.5 mmol) in benzene (30 mL) was added $Co_2(CO)_8$ (0.342 g, 1.0 mmol), and the mixture was heated at reflux for 30 min. The reaction mixture was chromatographed on Al_2O_3. The brown solution eluted by benzene/ethyl acetate (50:1) was evacuated almost at dryness, and addition of hexane gave pale brown crystals of **6a** (0.060 g, 14%). The second dark brown solution eluted by benzene/ethyl acetate (30:1) was evaporated to dryness, and the residue was recrystallized from hexane to give **7a** (0.028 g, 10%): mp 159–161 °C; IR (KBr) ν_{CO} 2045, 1997 (terminal), 1848 (bridge), 1722, 1680 cm^{-1} (ester); ^1H NMR ($CDCl_3$) δ 7.0–7.6 (m, 10 H, Ph), 4.60 (s, 5 H, Cp), 3.64 and 3.33 (s, 6 H, Me), 3.27 (s, 1 H, C-H). Anal. Calcd for $C_{28}H_{22}O_7Co_2$: C, 57.16; H, 3.77. Found: C, 57.14; H, 3.83. Similar procedures were used to prepare **6b** and **6c**.

(b) Reaction of 4a with $Co_2(CO)_8$ in Benzene/Ethanol. The solution of **4a** (0.353 g, 0.5 mmol) and $Co_2(CO)_8$ (0.342 g, 1.0 mmol) in benzene (30 mL) and ethanol (10 mL) was heated at reflux for 1 h. After evaporation of the solvent, the residue was chromatographed on Al_2O_3. Workup of the first wine red solution eluted by benzene/ethyl acetate (50:1) gave red brown crystals of **8a** (0.075 g, 34%): mp 135–136 °C; ^1H NMR ($CDCl_3$) δ 7.1–7.8 (m, 10 H, Ph), 4.75 (s, 5 H, Cp), 3.48 and 3.43 (s, 6 H, Me), 1.39 and 0.37 (s, 2 H, C–H). Anal. Calcd for $C_{25}H_{23}O_4Co$: C, 67.27; H, 5.19. Found: C, 67.42; H, 5.16. From the second dark brown solution was obtained **7a** (0.012 g, 4%), and from the third orange red solution was recovered **4a** (0.080 g, 23%).

(c) Reaction of 4b in Benzene/Ethanol. Similarly, reaction of **4b** (0.212 g, 0.3 mmol) with $Co_2(CO)_8$ (0.210 g) in benzene (20 mL) and ethanol (10 mL) gave **4b** (0.140 g, 66% recovery) and brown crystals of **7b** (0.009 g, 5%): mp 144–147 °C (in a N_2-filled capillary tube); IR (KBr) ν_{CO} 2050, 2000 (terminal), 1860 (bridge),

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[10] King, R. B. "Organometallic Syntheses"; Academic Press: New York, 1965; pp 93, 98.

[11] Yamazaki, H.; Hagihara, N. *J. Organomet. Chem.* **1970**, *21*, 431.

[12] Attempt to separate these isomers resulted in considerable loss of **4g** due to its relative instability. In a separate experiment, they were isolated and characterized. **4f**: mp 154–157 °C; ^1H NMR (CD_2Cl_2) δ 8.21 (t, $J_{PH} = J_{HH}$ = 3.4 Hz, 1 H, CH(α)), 6.8–7.5 (m, 25 H, Ph), 6.50 (quart, J_{PH} = 6.8 Hz, J_{HH} = 3.4 Hz, 1 H, CH(β)), 4.78 (s, 5 H, Cp). Anal. Calcd for $C_{39}H_{32}PCo$: C, 79.32; H, 5.46. Found: C, 79.34; H, 5.51. **4g**: mp 141–142 °C; ^1H NMR (CD_2Cl_2) δ 6.7–7.5 (m, 25 H, Ph), 6.14 (d, J_{PH} = 6.8 Hz, 2 H, CH(β)), 4.78 (s, 5 H, Cp). Anal. Calcd for $C_{39}H_{32}PCo$: C, 79.32; H, 5.46. Found: C, 79.60; H, 5.92%.

Table VI. Atomic Coordinates of the Non-Hydrogen Atoms (× 10^4) and the Hydrogen Atoms (× 10^3) of 5b, with Their Standard Deviations in Parentheses

atom	*x*	*y*	*z*
Fe	4228 (1)	2053 (1)	4264 (1)
Co	5499 (1)	2341 (1)	3719 (1)
O(1)	4180 (5)	273 (4)	4908 (4)
O(2)	3160 (5)	2953 (6)	5178 (5)
O(3)	3074 (6)	1349 (7)	3291 (5)
O(4)	5577 (5)	4530 (4)	3006 (3)
O(5)	5406 (5)	5095 (4)	4063 (3)
O(6)	6143 (5)	3903 (5)	5477 (4)
O(7)	6743 (4)	3899 (5)	4466 (4)
C(1)	4230 (6)	957 (6)	4655 (5)
C(2)	3574 (5)	2583 (7)	4818 (5)
C(3)	3529 (7)	1644 (7)	3651 (6)
C(4)	4511 (5)	3081 (5)	3687 (4)
C(5)	5128 (5)	3587 (5)	3940 (4)
C(6)	5517 (5)	3212 (5)	4527 (4)
C(7)	5179 (5)	2399 (6)	4745 (4)
C(41)	4016 (5)	3471 (6)	3129 (5)
C(42)	3686 (6)	4299 (7)	3231 (5)
C(43)	3182 (7)	4680 (8)	2751 (7)
C(44)	3004 (7)	4208 (9)	2157 (6)
C(45)	3328 (7)	3390 (9)	2039 (5)
C(46)	3822 (5)	3013 (7)	2529 (5)
C(51)	5411 (6)	4443 (6)	3583 (5)
C(52)	5609 (9)	5970 (7)	3793 (7)
C(61)	6170 (6)	3700 (6)	4878 (6)
C(62)	7317 (7)	4506 (10)	4793 (9)
C(71)	5547 (5)	1922 (6)	5345 (4)
C(72)	6348 (6)	1794 (6)	5390 (5)
C(73)	6668 (6)	1356 (7)	5957 (5)
C(74)	6204 (6)	1066 (7)	6481 (5)
C(75)	5419 (7)	1205 (6)	6468 (5)
C(76)	5097 (6)	1637 (6)	5897 (5)
C(81)	5511 (7)	1238 (6)	3103 (5)
C(82)	5724 (6)	1990 (7)	2708 (5)
C(83)	6388 (6)	2362 (7)	2997 (5)
C(84)	6609 (6)	1855 (8)	3569 (5)
C(85)	6079 (7)	1157 (7)	3635 (6)
H(42)	374 (6)	459 (7)	366 (5)
H(43)	276 (9)	505 (11)	279 (7)
H(44)	262 (5)	449 (6)	185 (4)
H(45)	316 (6)	307 (7)	169 (5)
H(46)	404 (5)	257 (6)	247 (5)
H(51)	582 (9)	628 (10)	423 (8)
H(52)	641 (9)	583 (10)	375 (8)
H(53)	518 (6)	624 (8)	345 (6)
H(72)	680 (7)	192 (8)	505 (6)
H(73)	728 (5)	129 (6)	596 (4)
H(74)	655 (4)	76 (5)	685 (4)
H(75)	501 (5)	102 (6)	682 (4)
H(76)	452 (5)	173 (5)	581 (4)
H(81)	505 (5)	90 (6)	300 (4)
H(82)	541 (5)	214 (6)	234 (4)
H(83)	672 (7)	285 (7)	284 (6)
H(84)	714 (6)	191 (7)	386 (5)
H(85)	627 (7)	83 (8)	405 (6)

Table VII. Atomic Coordinates of the Non-Hydrogen Atoms (× 10^4) and the Hydrogen Atoms (× 10^3) of 7a, with Their Standard Deviations in Parentheses

atom	*x*	*y*	*z*
Co1	1797 (1)	2045 (0)	2777 (1)
Co2	1506 (1)	2171 (0)	5685 (1)
O1	939 (5)	606 (3)	7037 (5)
O2	−167 (4)	3171 (3)	8147 (4)
O3	−1072 (4)	1760 (3)	4192 (4)
O4	4642 (4)	2410 (3)	7354 (4)
O5	5904 (3)	3278 (2)	5801 (4)
O6	311 (3)	3853 (2)	4716 (4)
O7	1401 (3)	4135 (2)	2433 (4)
C1	1182 (6)	1195 (3)	6462 (6)
C2	494 (5)	2792 (3)	7181 (5)
C3	126 (5)	1916 (3)	4226 (5)
C4	3112 (5)	1895 (3)	4126 (5)
C5	3609 (4)	2686 (3)	5237 (5)
C6	2908 (4)	3384 (3)	5304 (5)
C7	2445 (4)	3360 (3)	3719 (5)
C8	4743 (5)	2762 (3)	6287 (5)
C9	7149 (5)	3358 (4)	6569 (7)
C10	1276 (5)	3803 (3)	3730 (5)
C11	221 (6)	4465 (4)	2192 (7)
C21	1887 (8)	915 (4)	927 (6)
C22	593 (7)	1096 (4)	1076 (6)
C23	725 (7)	1942 (4)	836 (6)
C24	2104 (9)	2278 (4)	533 (6)
C25	2857 (7)	1655 (6)	619 (6)
C41	3814 (5)	1125 (3)	3705 (5)
C42	5237 (6)	1260 (3)	3265 (6)
C43	5909 (6)	549 (4)	2788 (8)
C44	5182 (7)	−305 (4)	2761 (7)
C45	3773 (7)	−449 (4)	3196 (7)
C46	3086 (6)	258 (3)	3650 (6)
C61	3149 (4)	4235 (3)	6537 (5)
C62	3409 (5)	5053 (3)	6122 (5)
C63	3702 (5)	5838 (3)	7255 (6)
C64	3739 (6)	5819 (3)	8819 (6)
C65	3476 (6)	5013 (4)	9234 (5)
C66	3197 (5)	4225 (3)	8103 (5)
H7	325 (4)	350 (3)	301 (5)
H21	207 (5)	42 (3)	99 (6)
H22	−27 (6)	71 (4)	132 (6)
H23	−8 (5)	226 (3)	91 (6)
H24	258 (5)	286 (3)	41 (6)
H25	375 (5)	169 (3)	40 (6)
H42	581 (5)	189 (3)	332 (5)
H43	686 (5)	68 (3)	249 (6)
H44	558 (5)	−87 (3)	240 (6)
H45	321 (5)	−106 (3)	318 (6)
H46	213 (5)	13 (3)	392 (5)
H62	331 (5)	507 (3)	504 (5)
H63	389 (5)	637 (3)	692 (5)
H64	399 (5)	639 (3)	960 (6)
H65	350 (5)	500 (3)	1037 (6)
H66	299 (5)	371 (3)	847 (5)
H91	709 (5)	369 (3)	748 (6)
H92	719 (5)	279 (3)	670 (6)
H93	793 (6)	375 (4)	606 (6)
H111	9 (5)	497 (3)	305 (6)
H112	−57 (5)	401 (3)	221 (5)
H113	43 (6)	470 (4)	115 (6)

1715, 1710 cm^{-1} (ester); ^1H NMR ($CDCl_3$) δ 7.0–7.8 (m, 10 H, Ph), 4.19 (s, 5 H, Cp), 3.59 and 3.55 (s, 6 H, Me), 3,53 (s, 1 H, C-H). Anal. Calcd for $C_{28}H_{22}O_7Co_2$: C, 57.16; H, 3.77. Found: C, 57.08; H, 3.81.

(d) Reaction of 4e in Benzene/Ethanol. The reaction mixture of **4e** (0.371 g, 0.5 mmol) and $Co_2(CO)_8$ (0.350 g) in benzene (30 mL) and ethanol (10 mL) was refluxed for 2 h. After evaporation of the solvent, the residue was chromatographed on Al_2O_3. From the yellow eluate (benzene/hexane eluent (1:5)) was obtained (η-tetraphenylbutadiene)(η-cyclopentadienyl)cobalt (0.004 g, 2%). From the orange red eluate (same eluent), red brown crystals of **8e** were obtained (0.040 g, 17%): mp 197–199 °C; ^1H NMR ($CDCl_3$) δ 6.8–7.3 (m, 20 H, Ph), 4.54 (s, 5 H, Cp), 1.55 (s, 2 H, C–H). The IR spectrum of **8e** is consistent with that of the authentic compound.[13] From the brown eluate, (benzene eluent) was recovered the starting **2e** (0.200 g, 54%).

X-ray Study. Crystals of **5b** and **7a** suitable for X-ray diffraction were grown from a benzene/hexane and a methanol solution, respectively. The diffraction data were collected on a Rigaku four-circle automatic diffractometer using Mo Kα radiation. The crystals were mounted such that the *c* axis for **5b** and the *a* axis for **7b** were nearly parallel to the ϕ axis of the diffractometer. Ten-second stationary background counts were taken at the lower and upper limits of each scan. Three standard reflections were monitored before every 100 measurements. The treatment of the intensity data has been previously described.[14]

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(13) Nakamura, A.; Hagihara, N. *Nippon Kagaku Zasshi* **1963**, *84*, 339.

(14) Aoki, K.; Yamamoto, Y. *Inorg. Chem.* **1976**, *15*, 48.

The intensities were corrected for Lorentz and polarization effects. The linear absorption coefficient of compound **5b** for Mo Kα was 13.260 cm^{-1}, and an absorption correction was made. The calculated transmission factors varied from 0.941 to 0.981. An absorption correction was not made for compound **7a**. Table V contains summary of the crystallographic data and experimental conditions under which they were obtained. The metal atoms were located by sharpened Patterson maps. The subsequent structure factor and electron density map calculations revealed the positions of all the atoms except hydrogens.

For compound **5b**, five cycles of a block-diagonal least-squares refinement of all the positional and isotropic thermal parameters resulted in the residual factors $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$ and $R_2 = [\sum\omega(|F_o| - |F_c|)^2/\sum\omega F_o^2]^{1/2}$ of 9.50 and 9.75% using unit (equal) weight, respectively. Subsequent five cycles of a refinement involving anisotropic thermal parameters converged to $R_1 = 7.25$ and $R_2 = 7.75\%$. At this stage a difference-Fourier synthesis revealed all of the 21 hydrogen atoms with isotropic thermal parameters. This refinement converged to the lower residual factors $R_1 = 6.26$ and $R_2 = 4.47\%$.

For compound **7a**, six cycles of refinement of all the positional and isotropic thermal parameters resulting in the residual factors, $R_1 = 9.05$ and $R_2 = 9.11\%$, followed by subsequent six cycles of a refinement involving anisotropic thermal parameters that converged to $R_1 = 5.64$ and $R_2 = 6.00\%$. At this stage, calculation for all hydrogen atoms of the cyclopentadienyl and two phenyl groups followed by a difference-Fourier synthesis revealed the rest of the seven hydrogen atoms bonded to C(7), C(9), and C(11) atoms. The final three cycles of a refinement converged to the lowere residual factors $R_1 = 4.56$ and $R_2 = 4.58\%$.

In these refinements the $\sum\omega(|F_o| - |F_c|)^2$ function was minimized, where the weight, ω, was 1.0. For the final refinement with anisotropic temperature factor, $\omega = 1/\sigma\,(F_o)$ was used. No unusual trends were observed in an analysis of $\sum\omega(|F_o| - |F_c|)^2$ as a function of either $(\sin\theta)/\lambda$ or $|F_o|$ for both compounds **5b** and **7a**. In the final cycles of a refinement, average shifts of positional parameter for **5b** are 0.120 and 0.400 times and the largest shift for 7a are 0.300 and 0.404 times its standerd deviation for non-hydrogen atoms and hydrogen atoms, respectively. Anomalous dispersion effects for Fe and Co were included in the calculation of F_c using $\Delta f'$ and $\Delta f''$ calculated by Cromer.[15] The atomic scattering factors used were from the usual tabulation.[16]

Tables of anisotropic temperature factors and lists of observed and calculated structure factor amplitudes are available.[17] The final atomic coordinates and thermal parameters the compounds **5b** and **7a** are listed in Tables VI and VII, respectively, and the selected bond distances and bond angles are shown in Tables II and IV, respectively.

Calculations. The parameters used in the extended Hückel calculations were taken from the work of Schilling and Hoffman.[18] In the model complex for **5B** the ferracyclopentadiene ring (C and H atoms) and the two equatorial carbonyls were placed in a plane while the third (axial) carbonyl was placed perpendicular to that plane. The planar cyclopentadienyl ring (C and H atoms) was oriented parallel to the ferracyclopentadiene ring.

The following geometries were used for **5B** (distances in Å; angles in deg): Fe–Co = 2.47, Fe–C_{Co} = 1.80, Fe–C(α) = 1.96, C(α)–C(β) = 1.40, C(β)–C(β') = 1.43, Co–(C_4H_4) = 1.58, Co–(Cp) = N 1.67, $(C–C)_{Cp}$ = 1.40, C–H = 1.0; OC–Fe–CO = 88, C(α)–Fe–C(α) = 82, Fe–C(α)–C(β) = 115, Fe–C(α)–H(α) = 126, C(α)–C(β)–H(β) = 124. To construct the model complex for **5A**, the $(CO)_3Fe$ and CpCo units were exchanged. The Cp ring was oriented so that the dihedral angle between Cp and the cobaltacyclopentadiene ring is 55°. The plane defined by the three carbonyl carbons (or oxygens) of $(CO)_3Fe$ unit was oriented parallel to the cobaltacyclopoentadiene ring with OC–Fe–CO angle of 96°.

Registry No. **4a**, 42442-00-2; **4b**, 42442-01-3; **4c**, 42441-99-6; **4d**, 62745-35-1; **4e**, 12124-09-3; **4f**, 84810-86-6; **4g**, 84810-87-7; **4h**, 84810-88-8; **5a**, 84810-89-9; **5b**, 84810-90-2; **5c**, 84810-91-3; **5d**, 84810-92-4; **5e**, 84810-93-5; **5f**, 84810-94-6; **5g**, 84810-95-7; **5h**, 83416-31-3; **6a**, 84810-96-8; **6b**, 84810-97-9; **6c**, 84810-98-0; **7a**, 84835-88-1; **7b**, 84810-99-1; **8a**, 84811-00-7; **8e**, 12119-03-8; $[(CO)_2(PPh_3)(\overline{RhCR^1{=}CR^2{=}CR^3{=}C}R^4)]Rh(CO)_2$ ($R^1 = R^2 = R^3 = R^4 = CO_2Et$), 84811-01-8; $[(CO)_2(PPh_3)$-$(\overline{IrCR^1{=}CR^2{=}Cr^3{=}C}R^4)]Ir(CO)_2$ ($R^1 = R^2 = R^3 = R^4 = CO_2Me$), 84811-02-9; $Fe_2(CO)_9$, 15321-51-4; $Co_2(CO)_9$, 10210-68-1; $Fe(CO)_4(PPh_3)$, 14649-69-5; (η-C_5H_5)$(PPh_3)_2$CO, 32993-07-0; (η-cyclopentadienyl)(η-tetraphenylcyclopentadienone)cobalt, 12119-11-8; phenylacetylene, 536-74-3; acetylene, 74-86-2.

Supplementary Material Available: Listings of anisotropic temperature factors for **5b** (Table VIII) and **7a** (Table IX) and structure amplitudes for **5b** (Table X) and of **7a** (Table XI) (36 pages). Ordering information is given on any current masthead page.

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(17) See paragraph at end of paper regarding supplementary material.

(18) Schilling, B. E. R.; Hoffmann, R. *J. Am. Chem. Soc.* **1979**, *101*, 3456.