Photochemical Reactions of a Cobaltacyclopentadiene and the Molecular Structure of (η^5-Cyclopentadienyl)(η^4-1,2,3,4-tetraphenyl-2-butene-1,4-dione-*O*,*C*,*C*′,*C*″)cobalt(I)

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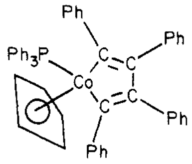
Received September 17, 1981

Ultraviolet irradiation of the cobaltacyclopentadiene complex $(\eta^5\text{-}C_5H_5)Co[C_4(C_6H_5)_4][P(C_6H_5)_3]$, **1**, in oxygenated CH_2Cl_2 or C_6H_6 solvents yields $(\eta^5\text{-}C_5H_5)Co[\eta^4\text{-}OC(C_6H_5)C(C_6H_5)C(C_6H_5)C(C_6H_5)O]$, **2**, and $(\eta^5\text{-}C_5H_5)Co[\eta^4\text{-}C_4(C_6H_5)_4]$, **3**. In the absence of O_2 only **3** forms. Complexes **2** and **3** are formed by independent photochemical pathways with low quantum efficiencies ($<5 \times 10^{-4}$ at 366 and 313 nm). The crystal structure of complex **2** at −150 °C was determined. Unusual η^4-OCCC bonding of the enedione π system of coordinated 1,2,3,4-tetraphenyl-*cis*-2-butene-1,4-dione (or (*Z*)-dibenzoylstilbene) is observed with a Co–O bond length of 1.936 (3) Å and Co–C bond lengths of 2.004 (5), 2.012 (5), and 2.066 (5) Å. There is a dihedral angle of only 10.2° between the cyclopentadiene and η^4-OCCC planes. Crystals of **2** are monoclinic, space group C_{2h}^5—$P2_1/n$ with four $C_{33}H_{25}CoO_2$ formula units in a cell of dimensions, at −150 °C, of a = 17.128 (6) Å, b = 15.893 (3) Å, c = 9.097 (2) Å, and β = 101.92 (2)°. Least-squares refinement on 177 variables led to a final value of the R index on F^2 of 0.106 for 4980 unique observations; the conventional R index on F is 0.062 for 2748 observations having $F_o^2 > 3\sigma(F_o^2)$.

Introduction

Although there has been interest in the chemistry of cobaltacyclopentadiene complexes for over two decades,[1-30] only one study[22] alluded to their photochemistry. We recently observed photochemical extrusion of N_2 from $(\eta^5\text{-}C_5H_5)Co[(Ar)NNNN(Ar)]$ complexes (Ar = C_6H_5, C_6F_5) that contain the metallotetraazadiene moiety.[31] In view of the electronic similarity between the bidentate $C_4R_4^{2-}$ and N_4R_2 groups,[32,33] we examined the photoreactivity of $(\eta^5\text{-}C_5H_5)Co(C_4Ph_4)(PPh_3)$, **1**. One of the products of the reaction with O_2, **2**, appeared to contain 1,2,3,4-tetraphenyl-*cis*-2-butene-1,4-dione (or (*Z*)-dibenzoylstilbene) coordinated to an $(\eta^5\text{-}C_5H_5)Co$ fragment. A product with similar spectral properties was observed in an earlier report.[22] In order to characterize definitively the coordination geometry of this sterically hindered enedione ligand, we undertook a single-crystal X-ray diffraction study of product **2**. This investigation reveals an unusual delo-



1, Ph = C_6H_5

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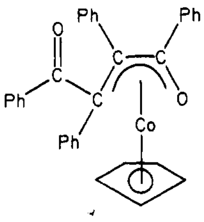

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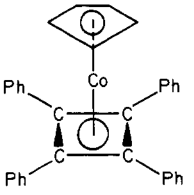
calized η^4-enone bonding mode depicted. An additional photochemical pathway, which yielded the cyclobutadiene derivative 3, was also observed.



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Experimental Section

Materials (sources) were as follows: C_6H_6, hexanes, toluene, CH_2Cl_2, cyclopentadiene dimer, PPh_3, C_2Ph_2, and $P(OMe)_3$ (Aldrich); C_6D_6, $CDCl_3$ (Merck); $(\eta^5\text{-}C_5H_5)Co(CO)_2$ (Strem); sodium (Alfa); xylenes and diethyl ether (Mallinckrodt) $CoCl_2 \cdot 6H_2O$ (Baker); O_2 (Linde). The solvents C_6H_6, C_6D_6, toluene, and hexanes were purified by distillation from Na-benzophenone or Na under a dinitrogen atmosphere. Xylenes and CH_2Cl_2 were dried over CaH_2. Cyclopentadienylcobalt dicarbonyl was vacuum distilled. Trimethyl phosphite was distilled twice from Na prior to use,[34] and PPh_3 was recrystallized from hot ethanol.

IR spectra were recorded on Perkin-Elmer 283 and Nicolet 7199 FT-IR spectrometers with the use of 0.1-mm path length NaCl cells. UV-visible spectra were obtained on a Perkin-Elmer 320 spectrophotometer; ^1H NMR spectra (60 MHz) were recorded on a Perkin-Elmer R-20B spectrometer, and a Varian CFT-20 spectrometer was used to obtain ^1H (79.54-MHz) and ^{13}C (20-MHz) NMR spectra. Chemical shifts are reported in parts per million downfield from internal Me_4Si or by using the following solvent reference peaks (C_6D_5H δ_H 7.15, δ_C 128.0; $CHCl_3$ δ_H 7.24, δ_C 77.24). Mass spectra were recorded on a Hewlett-Packard 5985 GC/MS system by Dr. D. Hung of the Northwestern University Analytical Services Laboratory. Elemental analysis were determined by H. Beck of the same laboratory or by Micro-Tech Laboratories, Skokie, IL.

$(\eta^5\text{-}C_5H_5)Co(C_4Ph_4)(PPh_3)$, 1. This complex was prepared from $CoCl(PPh_3)_3$[35] and $Na(C_5H_5)$ by a literature procedure[17] and recrystallized from benzene–hexane: ^1H NMR ($CDCl_3$) δ 4.73 ($\eta^5\text{-}C_5H_5$); $^{13}C\{^1H\}$ NMR ($CDCl_3$) 153.76, 142.35 (d, $J = 3.1$ Hz), 133.87 (d, $J = 10.0$ Hz), 129.94 (d, $J = 20.8$ Hz), 130.10 (d, $J = 5.0$ Hz), 128.27 (d, $J = 9.6$ Hz), 126.64 (d, $J = 11.3$ Hz), 123.58 (d, $J = 9.5$ Hz), 89.82 (d, $J = 1.3$ Hz, $\eta^5\text{-}C_5H_5$). Anal. Calcd for $C_{51}H_{40}CoP$: C, 82.73; H, 5.60. Found: C, 82.5; H, 5.47. A partial ^{13}C NMR spectrum of this complex was reported during the course of this work.[36] We did not observe signals from some quaternary carbons that may be found in ref 36.

Irradiation of 1 in the Presence of O_2. An O_2-saturated solution containing 0.5 g of 1 in 80 mL of freshly distilled C_6H_6 was irradiated for 4 h in a Pyrex immersion well with a 450-W medium-pressure Hanovia Hg arc lamp. The solution was filtered, the solvent removed, and the residue extracted with Et_2O–CH_2Cl_2. Mass spectrometry showed the presence of dibenzoylstilbene in the extract. Half of the dark insoluble residue was dissolved in CH_2Cl_2 and spotted on an Analtech, silica gel G (2000 μm thick) preparative TLC plate. Development with CH_2Cl_2 yielded a fast moving brown band (complex 1 and traces of 3) and a slow moving chocolate brown band (2), which was removed and extracted with methanol and dichloromethane. The second portion was treated in a similar fashion. Considerable decomposition occurred in extracting the second complex from the support to yield about 300 mg of 2, contaminated with (*Z*)-dibenzoylstilbene. Soxhlet extraction of 2 from the support with CH_2Cl_2 did not improve its yield. The organic product could be isolated by extracting the crystalline mixture with ether–CH_2Cl_2 (or by TLC) and recrystallized from benzene–hexane to yield 150 mg (58%) of (*Z*)-dibenzoylstilbene: mass spectrum (20 eV), *m/e* (relative abundance) 388.1 (199, M^+), 372.2 (41, $M^+ - O$), 360.2 (66, $M^+ - CO$), 359.2 (80, $M^+ - HCO$), 283.2 (59, $M^+ - COPh$), 255.2 (39, $M^+ - (CO)_2Ph$), 105 (55, $COPh^+$) [the ^{13}C isotope peak at *m/e* 389.2 at 32% intensity is close to the calculated value of 31%]; ^1H NMR ($CDCl_3$) δ 7.22 and 7.85 (m, C_6H_5); IR (CH_2Cl_2) 3058 (w), 1660 (s), 1598 (s), 1580 (m), 1492 (m), 1447 (m), 1444 (m), 1248 (s) cm^{-1}; mp 216–220 °C (lit.[37] 211–213 °C and lit.[38] 218–220 °C for the *Z* and lit.[37] 232–234 for the *E* isomer). The residue containing complex 2, (η^5-cyclopentadienyl)(η^4-1,2,3,4-tetraphenyl-2-butene-1,4-dione-*O,C,C′,C″*)cobalt(I), was recrystallized from benzene–hexane and washed with ether to yield 40 mg (11%): ^1H NMR ($CDCl_3$) δ 4.83 ($\eta^5\text{-}C_5H_5$), 7.25 and 8.47 (m, C_6H_5); IR (CH_2Cl_2) 1653 (s), 1599 (m), 1496 (m), 1446 (m) cm^{-1}. Anal. Calcd for $C_{33}H_{25}CoO_2$: C, 77.34; H, 4.92. Found: C, 77.6; H, 4.68. The mass spectrum of this complex could not be obtained. Heating (120 °C) led to decomposition that yielded $(\eta^5\text{-}C_5H_5)_2Co$ and OC(Ph)C(Ph)C(Ph)C(Ph)O as the only volatile species, as identified by electron impact and chemical ionization mass spectrometry (with CH_5^+).

$(\eta^5\text{-}C_5H_5)Co(\eta^4\text{-}C_4Ph_4)$, 3. This complex was prepared from $(\eta^5\text{-}C_5H_5)Co(CO)_2$ and C_2Ph_2 by the literature procedure,[4] and the ^1H NMR ($CDCl_3$) spectrum agreed with that reported.

Relative photoreactivity studies employed solutions ((5 – 8) × 10^{-3} M) of 1 in C_6D_6 solvent (vacuum distilled from Na-benzophenone) or CH_2Cl_2 (vacuum distilled from CaH_2). Aliquots (0.5 mL) were placed in identical Pyrex NMR tubes, and each was given the same dose of radiation. Product distributions were then analyzed by monitoring the $\eta^5\text{-}C_5H_5$ chemical shifts in C_6D_6 relative to Me_4Si: 1 (δ 4.81); 2 (δ 4.45); 3 (δ 4.51). A 450-W high-pressure xenon arc lamp served as the radiation source. The light was collimated, passed through 10 cm of cooled distilled water and a Corning 1-75 filter (to cut out $\lambda < \sim 300$ nm and $\lambda > \sim 800$ nm), and then focused onto the NMR tube in a holder. Quartz optics were used throughout. Quantum yield measurements employed a previously described apparatus.[39]

Crystallographic Data for 2. Preliminary precession and Weissenberg photographs showed monoclinic symmetry and the systematic absences $h0l$ ($h + l$ = odd) and $0k0$ (k = odd). These observations uniquely establish the space group as C_{2h}^5—$P2_1/n$.

A small, irregular (0.16 × 0.20 × 0.30 mm) but well-formed crystal was mounted on a Picker four-circle diffractometer. With the crystal at −150 °C[40] 14 reflections in the range 20° < 2θ(Mo Kα_1) < 24° were centered. Least-squares analysis of the resultant angular positions yielded the unit cell parameters of Table I. Details of data collection are also given in this table. The crystal showed no decomposition during data acquisition, since the intensities of six standard reflections, measured after every 100 reflections, showed only variations expected from counting statistics. Of the 5176 reflections measured 4980 are unique and 2748 of these obey the condition $F_o^2 > 3\sigma(F_o^2)$. Because of the small crystal size diffraction intensities were weak.

Heavy-atom methods were employed to solve the structure.[41] The position of the cobalt atom was located from an origin-re-

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Table I. Summary of Crystallographic Details for $(\eta^5\text{-}C_5H_5)Co[\eta^4\text{-}OC(Ph)C(Ph)C(Ph)C(Ph)O]$ (2)

formula	$C_{33}H_{25}CoO_2$
fw, g/mol	512.50
a, Å	17.128 (6)
b, Å	15.893 (3)
c, Å	9.097 (2)
β, deg	101.92 (2)
V, Å^3	2423
Z	4
d(calcd) (−150 °C), g/cm^3	1.405
d(obsd) (25 °C), g/cm^3	1.35
space group	$C_{2h}^5 - P2_1/n$
cryst faces	{100}, {011}, (13$\bar{1}$)
cryst vol, mm^3	0.014
temp, °C	−150[a]
radiation	Mo Kα [λ(Mo Kα_1) = 0.709 30 Å]
μ(Mo Kα), cm^{-1}	7.33
transmission factors	0.85–0.90
2θ range, deg	3–50
aperture	3.7 mm wide by 4.3 mm high, 32 cm from crystal
scan speed, deg/min	2 in 2θ
scan width, deg	−1.0 below Kα_1 to +0.9 above Kα_2
bkgd count time, s	20 with rescan option[a]
reflctns measd	±h,+k,+l
p	0.04
final no. of variables	177
unique data	4980
$R(F^2)$	0.106
$R_w(F^2)$	0.146
unique data ($F_o^2 > 3\sigma(F_o^2)$)	2748
$R(F, F_o^2 > 3\sigma(F_o^2))$	0.062
$R_w(F, F_o^2 > 3\sigma(F_o^2))$	0.062

[a] Reference 40.

moved, sharpened Patterson map, and the remaining nonhydrogen atoms were found from difference Fourier maps subsequent to least-squares refinement. The four phenyl groups in the molecule (denoted Ph1–Ph4) were constrained to D_{6h} symmetry and isotropic thermal motion. The other nonhydrogen atoms were allowed anisotropic motion. Refinement of this model on F led to values of R and R_w of 0.076 and 0.089. The positions of the hydrogen atoms were idealized by assuming C–H distances of 0.975 and 0.950 for the (η^5-C_5H_5) and (C_6H_6) hydrogen atoms, respectively. In the final cycles of refinement the hydrogen atoms of the η^5-C_5H_5 group were allowed to refine isotropically; however, only the temperature factors of the hydrogen atoms of the phenyl groups were permitted to vary.

Final least-squares refinement on F^2 for all 4980 unique observations (including those having $F_o^2 < 0$) led to values of R and R_w on F^2 of 0.106 and 0.146, to a value of an error in an observation of unit weight of 1.13 e^2, and to a value of R on F_o of 0.062 for the 2748 observation having $F_o^2 > 3\sigma(F_o^2)$. The largest peak in a final difference electron density map is 0.95 e/Å^3. Analysis of $\sum w(F_o^2 - F_c^2)^2$ as a function of F_o^2, setting angles, and Miller indices revealed no unusual trends. The observed and calculated structure amplitudes are available.[42]

Final positional and thermal parameters of the nongroup atoms are listed in Table II. Rigid group atomic positions and parameters are provided in Table III. Selected bond lengths and angles in 2 are presented in Tables IV and V. The atom numbering scheme for the (η^5-C_5H_5) moiety and for the skeleton of the coordinated (Z)-dibenzoylstilbene ligand are described in Figure 1. Atom C(6) of group Ph1 is bound to atom C(32), atom C(12) of group Ph2 is bound to atom C(31), atom C(18) of group Ph3 is bound to atom C(30), and atom C(24) of group Ph4 is bound to atom C(33). Hydrogen atoms H(6)–H(25) are bound to carbon atoms of groups Ph1 to Ph4 in an ascending numerical correspondence.

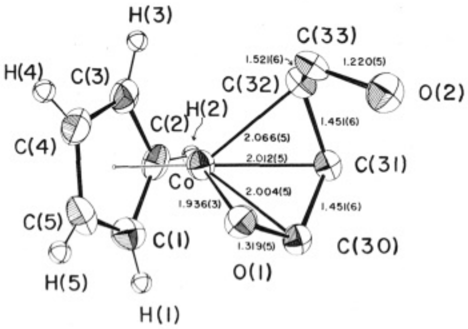
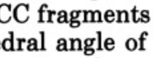


Figure 1. View of the inner coordination sphere of **2**, including atom-numbering scheme for the cyclopentadienyl ligand and the skeleton of coordinated (Z)-dibenzoylstilbene. Bond lengths (Å) are provided for the latter fragment. In this and in subsequent plots all hydrogen atoms are given isotropic thermal B values of 1.0 Å^2, and vibrational ellipsoids of other atoms are drawn at the 50% probability level.

Results and Discussion

Molecular Structure of $(\eta^5\text{-}C_5H_5)Co[\eta^4\text{-}OC(Ph)C(Ph)C(Ph)C(Ph)O]$, 2. A stereoscopic view of complex **2** (Figure 2) illustrates the helical η^4-OCCC coordination of the enedione. The planar cyclopentadienyl and nearly planar η^4-OCCC fragments (Table VI) are close to being parallel (dihedral angle of 10.2°), reminiscent of cobaltocene. The two ligand π systems are in an approximately eclipsed conformation. Other noteworthy features include the feathered phenyl groups (dihedral angles in Table VI) and the free benzoyl group that juts up and away from the η^4-OCCC plane. The long Co–C(32) bond compared with the Co–C(31), Co–C(30), and Co–O(1) bond distances may reflect steric interference by the bulky benzoyl and phenyl substituents on atom C(32). No unusual intermolecular contacts affect the molecular structure; the unit-cell contents are illustrated in Figure 3.

Coordination of the enone fragment is unusual. Several transition-metal complexes are known[43] to exhibit the metallacyclic structure **4**, a metalated enone. A cobalt complex of type **5** has also been reported.[44] Structural parameters in Figure 1 suggest to us that all the p_π orbitals of the η^4-OCCC fragment contribute to bonding with the cobalt atom. Compare (Figure 1) the long C(30)–O(1) bond with the uncoordinated C(33)–O(2) bond and the equivalence of the C(30)–C(31) and C(31)–C(32) distances. The localized enone description of bonding to cobalt, **6**, is not appropriate. Dissimilarities between the bond lengths in this coordinated dibenzoylethylene with those of the re-



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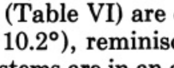

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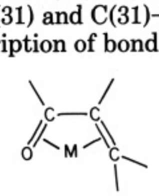

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[42] See supplementary material.

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Table II. Positional and Thermal Parameters for the Nongroup Atoms of (η^5-C_5H_5)Co[η^4-OC(Ph)C(Ph)C(Ph)C(Ph)O]

atom	x	y	z	B_{11}[b]	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Co	0.134 486 (39)	0.026 694 (41)	0.352 165 (71)	15.24 (23)	17.02 (26)	55.55 (81)	−0.91 (24)	8.02 (33)	−1.04 (44)
O(1)	0.134 22 (18)	0.074 38 (20)	0.547 90 (34)	15.0 (13)	22.7 (15)	53.1 (42)	−0.7 (11)	8.4 (19)	0.2 (20)
O(2)	0.152 58 (20)	0.251 68 (21)	0.502 76 (35)	22.2 (14)	21.3 (15)	62.8 (45)	0.3 (12)	9.0 (21)	−8.9 (22)
C(1)	0.143 31 (36)	−0.105 12 (32)	0.338 95 (64)	30.1 (26)	15.5 (21)	82.0 (78)	1.1 (19)	4.5 (36)	−4.1 (33)
C(2)	0.152 36 (32)	−0.065 34 (32)	0.203 71 (56)	20.1 (21)	24.8 (23)	67.9 (69)	−3.7 (18)	4.6 (31)	−17.3 (32)
C(3)	0.079 94 (30)	−0.019 71 (35)	0.147 54 (57)	23.4 (21)	26.1 (24)	61.3 (65)	−6.9 (20)	−0.3 (29)	−9.1 (36)
C(4)	0.028 31 (30)	−0.030 20 (36)	0.248 82 (57)	16.2 (19)	24.9 (22)	96.5 (75)	−2.0 (19)	0.2 (30)	−5.1 (37)
C(5)	0.069 21 (35)	−0.080 84 (34)	0.368 16 (67)	29.3 (25)	22.9 (23)	93.1 (82)	−9.5 (19)	20.4 (37)	−1.0 (36)
C(30)	0.209 57 (28)	0.068 09 (28)	0.536 73 (49)	16.8 (18)	17.3 (19)	45.1 (59)	−1.6 (15)	7.8 (27)	−5.0 (27)
C(31)	0.227 67 (28)	0.106 11 (28)	0.402 70 (50)	16.2 (18)	14.9 (18)	52.1 (60)	−1.2 (15)	10.8 (26)	−3.3 (27)
C(32)	0.160 25 (28)	0.150 76 (28)	0.313 95 (50)	17.1 (18)	15.0 (19)	56.4 (62)	0.5 (15)	13.7 (27)	−0.2 (28)
C(33)	0.115 37 (28)	0.208 32 (28)	0.401 39 (51)	19.8 (19)	12.9 (19)	54.1 (62)	1.1 (15)	13.4 (28)	6.6 (27)

atom	x	y	z	B, Å^2	atom	x	y	z	B, Å^2
H(1)	0.1811 (28)	−0.1366 (29)	0.3990 (52)	2.2 (11)	H(14)	0.449	0.225	0.300	3.5
H(2)	0.2006 (27)	−0.0632 (28)	0.1555 (49)	2.0 (10)	H(15)	0.320	0.228	0.351	3.3
H(3)	0.0709 (28)	0.0176 (30)	0.0626 (53)	2.5 (11)	H(16)	0.364	0.098	0.655	3.2
H(4)	−0.0239 (25)	−0.0060 (25)	0.2370 (44)	0.73 (90)	H(17)	0.446	0.038	0.868	3.4
H(5)	0.0534 (30)	−0.0943 (31)	0.4454 (55)	2.5 (12)	H(18)	0.397	−0.070	0.999	3.4
H(6)	0.201	0.077	0.074	3.2	H(19)	0.265	−0.117	0.918	3.2
H(7)	0.200	0.130	−0.167	3.6	H(20)	0.184	−0.058	0.705	3.1
H(8)	0.164	0.271	−0.223	3.3	H(21)	0.012	0.154	0.155	2.8
H(9)	0.129	0.358	−0.039	3.2	H(22)	−0.127	0.171	0.088	3.4
H(10)	0.130	0.304	0.202	2.9	H(23)	−0.194	0.224	0.249	3.4
H(11)	0.318	−0.028	0.365	3.0	H(24)	−0.123	0.298	0.477	3.4
H(12)	0.447	−0.031	0.314	3.8	H(25)	0.016	0.281	0.544	3.1
H(13)	0.513	0.095	0.282	3.5					

[a] Estimated standard deviations in the least significant figure(s) are given in parentheses in this and all subsequent tables. [b] The form of the anisotropic thermal ellipsoid is $\exp[-(B_{11}h^2 + B_{22}{}^2 + B_{33}k^2 + 2B_{12}hk + 2B_{13}hl + 2B_{23}kl)]$. The quantities given in the table are the thermal coefficients $\times 10^4$.

Table III. Derived Parameters for the Rigid-Group Atoms of (η^5-C_5H_5)Co[η^4-OC(Ph)C(Ph)C(Ph)C(Ph)O]

atom	x	y	z	B, Å^2	atom	x	y	z	B, Å^2
C(6)	0.165 64 (19)	0.185 28 (18)	0.160 49 (26)	1.58 (8)	C(18)	0.266 26 (16)	0.025 66 (19)	0.660 09 (27)	1.74 (8)
C(7)	0.186 30 (20)	0.133 77 (14)	0.050 34 (34)	2.09 (9)	C(19)	0.344 45 (17)	0.053 98 (17)	0.708 30 (32)	2.05 (9)
C(8)	0.185 60 (20)	0.165 92 (18)	−0.092 61 (30)	2.50 (10)	C(20)	0.393 13 (13)	0.018 38 (20)	0.834 94 (34)	2.30 (9)
C(9)	0.164 25 (20)	0.249 59 (19)	−0.125 41 (26)	2.40 (9)	C(21)	0.363 62 (17)	−0.045 56 (19)	0.913 37 (28)	2.30 (9)
C(10)	0.143 58 (20)	0.301 10 (14)	−0.015 26 (34)	2.18 (9)	C(22)	0.285 43 (18)	−0.073 89 (17)	0.865 16 (32)	2.22 (9)
C(11)	0.144 28 (19)	0.268 95 (17)	0.127 69 (30)	1.98 (9)	C(23)	0.236 75 (13)	−0.038 28 (19)	0.738 53 (33)	2.02 (8)
C(12)	0.307 01 (14)	0.100 01 (19)	0.362 13 (35)	1.87 (8)	C(24)	0.026 81 (13)	0.215 48 (20)	0.355 12 (33)	1.68 (8)
C(13)	0.344 75 (17)	0.023 15 (15)	0.351 39 (36)	2.07 (8)	C(25)	−0.015 76 (17)	0.182 90 (19)	0.219 73 (30)	1.93 (9)
C(14)	0.421 45 (18)	0.021 36 (16)	0.321 70 (38)	2.65 (9)	C(26)	−0.098 30 (17)	0.193 43 (20)	0.180 24 (27)	2.37 (9)
C(15)	0.460 40 (14)	0.096 43 (20)	0.302 75 (38)	2.64 (10)	C(27)	−0.138 27 (13)	0.236 54 (21)	0.276 15 (35)	2.47 (10)
C(16)	0.422 66 (18)	0.173 30 (16)	0.313 49 (39)	2.54 (10)	C(28)	−0.095 70 (17)	0.269 12 (20)	0.411 55 (32)	2.39 (9)
C(17)	0.345 96 (18)	0.175 09 (15)	0.343 18 (37)	2.21 (9)	C(29)	−0.013 16 (17)	0.258 59 (19)	0.451 03 (27)	2.04 (9)

Rigid-Group Parameters

group	x_c[a]	y_c	z_c	δ[b]	ϵ	η
Ph1	0.164 94 (12)	0.217 44 (13)	0.017 54 (23)	0.0229 (52)	1.9460 (16)	−1.2963 (53)
Ph2	0.383 71 (13)	0.098 22 (14)	0.332 44 (22)	−1.5929 (18)	2.7431 (19)	0.0355 (21)
Ph3	0.314 94 (12)	−0.009 95 (13)	0.786 73 (22)	−2.1773 (23)	−2.3628 (18)	−2.7503 (25)
Ph4	−0.055 73 (13)	0.226 01 (12)	0.315 64 (22)	1.4504 (19)	3.0933 (17)	−2.0903 (19)

[a] x_c, y_c, and z_c are the fractional coordinates of the origin of the rigid group. [b] The rigid-group orientation angles δ, ϵ, and η (radians) have been defined previously: La Placa, S. J.; Ibers, J. A. *Acta Crystallogr.* **1965**, *18*, 511–519.

Table IV. Bond Lengths within (η^5-C_5H_5)Co[(η^4-OC(Ph)C(Ph)C(Ph)C(Ph)O)] (Å)

Co-O(1)	1.936 (3)	C(1)-C(2)	1.420 (7)
Co-C(30)	2.004 (5)	C(1)-C(5)	1.404 (8)
Co-C(31)	2.012 (5)	C(2)-C(3)	1.437 (7)
Co-C(32)	2.066 (5)	C(3)-C(4)	1.412 (7)
Co-C(1)	2.106 (5)	C(4)-C(5)	1.415 (8)
Co-C(2)	2.056 (5)	av C-C	1.418 (12)[a]
Co-C(3)	2.041 (5)	C(1)-H(1)	0.91 (5)
Co-C(4)	2.074 (5)	C(2)-H(2)	1.01 (4)
Co-C(5)	2.064 (5)	C(3)-H(3)	0.96 (5)
av Co-C	2.068 (24)[a]	C(4)-H(4)	0.96 (4)
O(1)-C(30)	1.319 (5)	C(5)-H(5)	0.83 (5)
C(30)-C(31)	1.451 (6)	av C-H	0.93 (7)[a]
C(30)-C(18)	1.486 (5)		
C(31)-C(32)	1.451 (6)		
C(31)-C(12)	1.483 (6)		
C(32)-C(33)	1.521 (6)		
C(32)-C(6)	1.520 (5)		
C(33)-C(24)	1.492 (5)		
C(33)-O(2)	1.220 (5)		

[a] The number in parentheses following an average value is the standard deviation of a single observation estimated on the assumption that the values averaged are from the same population.

lated compound tetrabenzoylethylene, 7, further support the delocalized bonding model. Contrast the carbon-carbon double bond length[45] of 1.31 (1) Å in 7 with the C(32)-C(31) distance of 1.451 (6) Å in 2 and the C-C(Ph)O distance[45] of 1.52 (1) Å in 7 with that of 1.451 (6) Å for the C(31)-C(30) length in 2.

A tungsten complex of methyl vinyl ketone possesses a bent structure halfway between 5 and the present type.[46] The closest structural analogues of 2 contain the α,β-unsaturated aldehyde, cinnamaldehyde [OC(H)C(H)CHPh], coordinated to the $Fe(CO)_3$ and $Fe(CO)_2(PPh_3)$ moieties.[47,48] Bond lengths (Å) in the cinnamaldehyde skeleton complexed with $Fe(CO)_3$[47] [O-C = 1.239 (7), OC(H)-C(H)CHPh = 1.411 (8), OC(H)C(H)-CHPh = 1.412 (7)] are similar to those in 2; however, the metal-oxygen interaction appears to be weaker in the iron complex as evidenced by the 0.06 Å longer M-O and 0.08 Å shorter O-C bond lengths. Significantly similar are the increasing distances from Fe of 2.013 (3), 2.031 (5), 2.067 (4), and 2.152 (4) Å of the respective atoms in the η^4-OCCC skeleton of a bound cinnamaldehyde.[47] Again the metal-carbon bond length at the carbon end of the η^4 fragment is comparatively long.

Novel η^4 bonding of α,β-unsaturated aldehydes and ketones by the isoelectronic $Fe(CO)_3$ and (η^5-C_5H_5)Co moieties is of chemical significance. Conventional nucleophilic addition to enones generally occurs in either a [1,2] or [1,4] sense.[49] The η^4 coordination may be regarded as an *electrophilic* addition of $Fe(CO)_3$ and (η^5-C_5H_5)Co fragments to the enone π system.

Photochemistry of (η^5-C_5H_5)Co(C_4Ph_4)(PPh_3), 1. Grevels, Wakatsuki, and Yamazaki[22] observed formation of 2 when complex 1 was heated (70 °C) with O_2 in solution or treated with $^1O_2$ at room temperature. They also noted production of 2 as in eq 1 and formulated the structure of 2 as a localized enone complex 6 on the basis of spectral

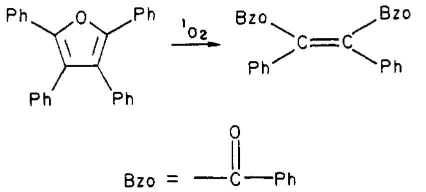
$$1 \xrightarrow[O_2]{h\nu} 2 + OPPh_3 \qquad (1)$$

data. We have monitored by ^1H FT NMR spectroscopy the photochemical reaction, as the η^5-C_5H_5 resonance provides a sensitive analytical probe. When complex 1 is irradiated in dry deoxygenated CH_2Cl_2 or C_6D_6, only 3 forms according to

$$1 \xrightarrow[CH_2Cl_2]{h\nu,\ \text{Pyrex}} 3 \qquad (2)$$

If an O_2-saturated CH_2Cl_2 solution of 1 is irradiated, both 2 and 3 form in a 4.5:1 ratio. Some decomposition also occurs and this ratio was measured by integrating the η^5-C_5H_5 resonances in a solution that was irradiated to 50% conversion. Complex 3 was identified by comparing its ^1H NMR spectrum with that of an authentic sample. Separation of 3 by TLC (benzene eluent) and mass spectral analysis (parent ion at m/e 481.2 using chemical ionization mass spectrometry with CH_5^+) further establish its identity. Irradiation of a solution of 3 containing O_2 did not produce 2. The quantum yields to form 2 and 3 are low, less than 5×10^{-4} with 366- and 313-nm excitations. This fact hampered more quantitative study of the mechanism. Added PPh_3 or $P(OCH_3)_3$ inhibits production of 3, which suggests that it forms from a coordinately unsaturated species produced by photodissociating PPh_3. When $P(OCH_3)_3$ was added in the absence of O_2, only new ^1H resonances attributable to the simple substitution product[29] were observed. Formation of 3 has also been found[25] when 1 is heated to 120 °C. This process is also thought to require dissociation of the phosphine ligand. We could not detect any products resulting from fragmentation of the cobaltacycle as has been observed for related metallotetraazadiene species.[31]

Neither added PPh_3 nor $P(OCH_3)_3$ quenched the photooxidation of 1, which implies that two independent photochemical pathways form 2 and 3. Grevels et al.[22] suggest that photooxidation occurs via the intermediacy of $^1O_2$. In this regard we note an analogy to the oxidation of the heterocycle, tetraphenylfuran,[50] which undergoes reaction 3.



(3)

Partial dissociation of the C_4Ph_4 ring and insertion of O_2 to form a peroxymetal species also should be considered, by analogy with the photochemistry of other cobalt(III) alkyls.[51] Recently, photochemical oxidation of a Pd coordinated allyl to an enealdehyde was reported;[51] however, the mechanism is unknown.

The mechanistic duality of the photoreactivity of 1 may resemble that found in thermal studies. Bergman[30] has observed both phosphine dissociation and electrophilic attack on the cobaltacycle for alkyne cyclotrimerization

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Table V. Selected Interatomic Bond Angles (Deg) within $(\eta^5\text{-}C_5H_5)Co[(\eta^4\text{-}OC(Ph)C(Ph)C(Ph)C(Ph)O)]$

O(1)-Co-C(30)	39.1 (2)	C(5)-C(1)-C(2)	107.8 (5)	O(1)-C(30)-C(18)	118.3 (4)
C(30)-Co-C(31)	42.4 (2)	H(1)-C(1)-C(2)	125 (3)	C(18)-C(30)-C(31)	127.2 (4)
C(31)-Co-C(32)	41.6 (2)	H(1)-C(1)-C(5)	127 (3)	C(30)-C(31)-C(32)	112.8 (4)
C(1)-Co-C(2)	39.9 (2)	H(2)-C(2)-C(1)	129 (3)	C(30)-C(31)-C(12)	123.2 (4)
C(2)-Co-C(3)	41.1 (2)	H(2)-C(2)-C(3)	123 (3)	C(12)-C(31)-C(32)	124.0 (4)
C(3)-Co-C(4)	40.1 (2)	H(3)-C(3)-C(2)	126 (3)	C(31)-C(32)-C(33)	115.7 (4)
C(4)-Co-C(5)	40.0 (2)	H(3)-C(3)-C(4)	125 (3)	C(31)-C(32)-C(6)	119.7 (4)
C(5)-Co-C(1)	39.3 (2)	H(4)-C(4)-C(3)	125 (3)	C(6)-C(32)-C(33)	113.4 (4)
C(1)-C(2)-C(3)	107.0 (5)	H(4)-C(4)-C(5)	128 (3)	C(32)-C(33)-O(2)	119.6 (4)
C(2)-C(3)-C(4)	108.6 (5)	H(5)-C(5)-C(4)	127 (4)	C(32)-C(33)-C(24)	119.5 (4)
C(3)-C(4)-C(5)	106.9 (5)	H(5)-C(5)-C(1)	124 (4)	C(24)-C(33)-O(2)	120.8 (4)
C(4)-C(5)-C(1)	109.6 (5)	O(1)-C(30)-C(31)	114.6 (4)		

Table VI. Least-Squares Planes in $(\eta^5\text{-}C_5H_5)Co[(\eta^4\text{-}OC(Ph)C(Ph)C(Ph)C(Ph)O)]$

plane no.	description	plane eq $Ax + By + Cz = D$[a]				dev[b] from plane (Å)
		A	*B*	*C*	*D*	
1	cyclopentadienyl carbon atoms	5.227	12.844	3.911	0.743	C(1), −0.019 (5); C(2), 0.011 (5); C(3), −0.002 (5); C(4), −0.010 (5); C(5), 0.020 (5); Co, 1.680
2	cyclopentadienyl hydrogen atoms	4.92	12.81	4.07	0.81	H(1), −0.04 (5); H(2), 0.01 (4); H(3), 0.02 (5); H(4), −0.03 (4); H(5), 0.06 (5); Co, 1.632
3	η^4-OCCC	2.267	13.289	4.489	3.761	O(1), −0.008 (3); C(30), 0.029 (4); C(31), −0.027 (4); C(32), 0.016 (4); Co, −1.520
Ph1	phenyl group bound to C(32)	−15.679	−4.357	−0.903	−3.549	
Ph2	phenyl group bound to (C31)	−3.253	−0.427	−8.379	−4.076	
Ph3	phenyl group bound to C(30)	−7.626	10.862	5.986	2.199	
Ph4	phenyl group bound to C(33)	−3.899	−13.651	4.511	1.444	

Interplanar Angles (Deg)

plane	plane	dihedral angle
1	2	1.33
1	3	10.18
3	Ph1	120.49
3	Ph2	124.76
3	Ph3	34.87
C(32)C(33)O(2)	Ph4	166.60

[a] Equations of planes are expressed in crystal coordinates as defined by: Hamilton, W. C. *Acta Crystallogr.* **1961**, *14*, 185-189. [b] Standard deviations are given for those atoms used in the definition of a particular plane.

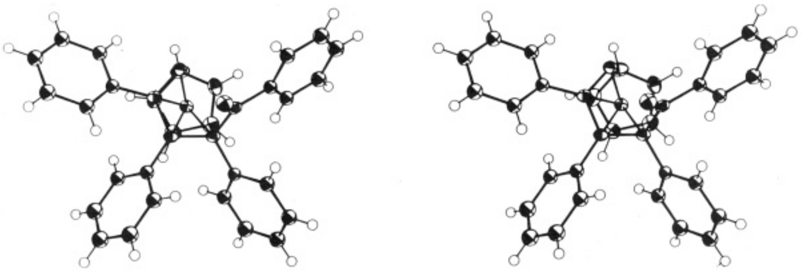


Figure 2. Stereoscopic view of **2**.

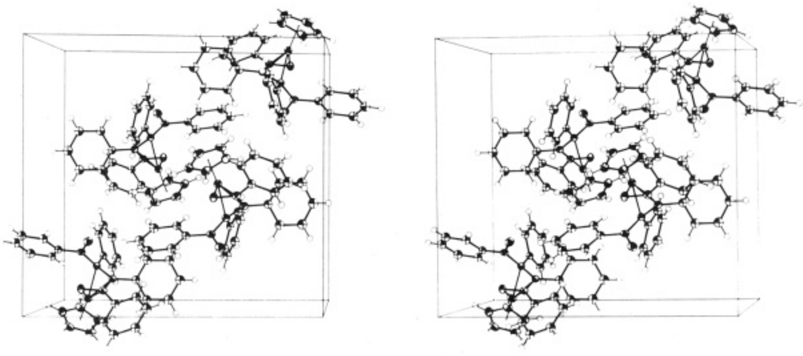
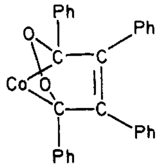


Figure 3. Stereoscopic view of the unit cell of **2**. The vertical axis is *b* and the horizontal axis is *a*.

reactions of related complexes. An excited form of 1 could add O_2 to generate an endo peroxide[50] intermediate



Further studies will be necessary to resolve the mechanism of the oxidation process.

Acknowledgment. We thank the National Science Foundation for research support (Grants CHE 78-01615 and 81-05069 to W.C.T. and Grant CHE 80-09671 to J. A.I.).

Registry No. 1, 12124-09-3; 2, 79953-72-3; 3, 1278-02-0; (*Z*)-dibenzoylstilbene, 6313-26-4.

Supplementary Material Available: A listing of observed and calculated structure amplitudes (18 pages). Ordering information is given on any current masthead page.

Organofluorosilicates in Organic Synthesis. 14.[1] Carbon–Carbon Bond Formation Promoted by Palladium Salts

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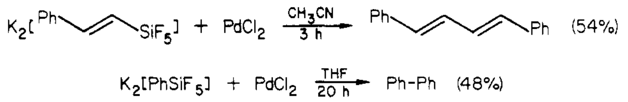
Received July 29, 1981

Five types of palladium-promoted carbon–carbon bond forming reactions have been achieved with potassium (*E*)-alkenylpentafluorosilicates which are readily available from alkynes by hydrosilylation followed by silicate formation. (1) The homocoupling reaction of styryl- and phenylsilicates gives 1,4-diphenylbutadiene and biphenyl, respectively. (2) The cross-coupling reaction with activated olefins such as methyl acrylate giving unsymmetrical 1,3-dienes is promoted by palladium acetate. (π-Allyl)palladium complexes are obtained with palladium chloride. (3) The palladium-catalyzed cross-coupling reaction with allylic halides gives (*E*)-1,4-dienes and has been applied to the synthesis of a key intermediate for total synthesis of (±)-recifeiolide. (4) A facile carbonylation occurs in methanol to give α,β-unsaturated carboxylic esters. (5) A limited number of cross-coupling reactions occur with $C(sp^2)$ halides in the presence of palladium complexes as catalysts under forced conditions. The products of these reactions may be interpreted in terms of the chemistry expected of alkenylpalladium intermediates, arising from transfer of the alkenyl group from silicon to palladium.

The formation of carbon–carbon bonds is one of the most fundamental problems in organic chemistry, and numerous selective reactions have been explored by the use of transition-metal compounds.[2] In our previous papers organopentafluorosilicates have been shown to be useful intermediates for functional group transformations.[1,3] Preliminarily we have reported several types of carbon–carbon bond forming reactions of organopentafluorosilicates under the influence of palladium,[4,5] copper,[6] and silver[7] salts. This paper describes the full details of the palladium-promoted carbon–carbon bond forming reactions. Since only the potassium salts of organopentafluorosilicates are used throughout the present study, the countercation will be omitted from the individual names of the silicates.

Results and Discussion

Homocoupling Reaction. The reaction of (*E*)-styrylpentafluorosilicate with 1 equiv of palladium chloride in acetonitrile at room temperature gave (*E*,*E*)-1,4-diphenyl-1,3-butadiene in 54% yield. The reaction was quite rapid and a black mixture resulted, probably indicating the formation of the palladium metal. Other alkenylsilicates such as 1-hexenylsilicate did not undergo a similar coupling reaction when treated with palladium chloride under various conditions but gave several minor products which were not characterized. The reason why other alkenylsilicates gave no coupling products is not clear at the present time. The phenylsilicate, however, reacted with palladium chloride to produce biphenyl in moderate yield.



The palladium-promoted homocoupling reaction may have possibly proceeded via intermediacy of the organopalladium species, arising from the metal-exchange reaction between the organosilicate and the palladium salt, by a mechanism analogous to that proposed for similar palladium-promoted coupling of alkenylmercuric chlorides[8] and styryltrimethylsilane,[9] a tetracoordinate alkenylsilane.

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[1] For part 13, see: Yoshida, J.; Tamao, K.; Kakui, T.; Kurita, A.; Murata, M.; Yamada, K.; Kumada, M. *Organometallics* 1982, *1*, 369–380.

[2] For example: (a) Noyori, R. In "Transition Metal Organometallics in Organic Synthesis"; Alper, H., Ed.; Academic Press: New York, 1976; Vol. 1, p 93. (b) Tsuji, J. "Organic Synthesis with Palladium Compounds", Springer-Verlag: Heidelberg, New York, 1980. (c) Collman, J. P.; Hegedus, L. S. "Principles and Applications of Organotransition Metal Chemistry", University Science Books: Mill Valley, CA, 1980.

[3] Tamao, K.; Yoshida, J.; Yamamoto, H.; Kakui, T.; Matsumoto, H.; Takahashi, M.; Kurita, A.; Murata, M.; Kumada, M. *Organometallics*, preceding article in this issue (part 12) and references cited therein.

[4] Yoshida, J.; Tamao, K.; Takahashi, M.; Kumada, M. *Tetrahedron Lett.* 1978, 2161.

[5] Tamao, K.; Kakui, T.; Kumada, M. *Tetrahedron Lett.* 1979, 619.

[6] Yoshida, J.; Tamao, K.; Kakui, T.; Kumada, M. *Tetrahedron Lett.* 1979, 1141.

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[8] Larock, R. C. *J. Org. Chem.* 1976, *41*, 2241.

[9] Weber, W. P.; Felix, R. A.; Willard, A. K.; Koenig, K. E. *Tetrahedron Lett.* 1971, 4701.

0276-7333/82/2301-0542$01.25/0