mp 85-87 °C; IR (hexanes) ν_{CO} 2016 (s), 1960 (s), 1638 (m) cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.76 (s, C_5H_5), 3.45 (s, CH), 7.2-7.8 (m, Ph); ^{13}C NMR ($CDCl_3$) δ 262.8 (C=O), 214.7 (C≡O), 129.70, 128.96, 128.64, 127.91 (Ph), 112.41 (PhC=C), 86.36 (C_5H_5), 47.56 (CH); mass spectrum, *m/e* 396 (P^+), 368 ($P^+ - CO$), 340 ($P^+ - 2CO$), 191 (C_3HPh_2). Anal. C, H.

Acknowledgment. We are grateful to the National Science Foundation (Grants CHE 7717877 and CHE 8022854) and the Alfred P. Sloan Foundation for financial support of this research. Helpful discussions with Professors T. A. Albright (Houston) and B. K. Carpenter (Cornell) are also acknowledged.

Registry No. 2, 79643-31-5; **3**, 79643-33-7; **5**, 79643-34-8; **6**, 79647-57-7; **7**, 79643-32-6; **8**, 79643-24-6; **10**, 82495-39-4; **11**, 69302-82-5; $[Re_2(CO)_{10}]$, 14285-68-8; $[Re(CO)_5]^-$, 14971-38-1; $Na[Mn(CO)_5]$, 13859-41-1; $Na[Fe(\eta\text{-}C_{H5})(CO)_2]$, 12152-20-4; $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_4]$, 12154-95-9; 2,3-diphenyl-2-cyclopropene-1-carbonyl chloride, 6415-58-3; 2-*tert*-butyl-2-cyclopropene-1-carbonyl chloride, 82495-40-7; 2-*tert*-butyl-3-deuterio-2-cyclopropene-1-carbonyl chloride, 82495-41-8.

Mechanism of Formation of (η^3-Oxocyclobutenyl)cobalt Compounds from $[Co(CO)_4]^-$ and Cyclopropenium Cations

William A. Donaldson and Russell P. Hughes*[1]

Contribution from the Department of Chemistry, Dartmouth College, Hanover, New Hampshire 03755. *Received November 30, 1981*

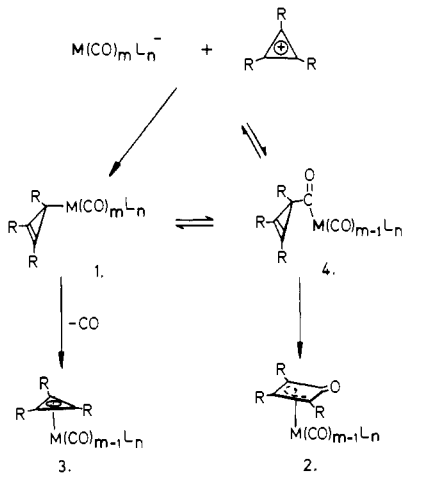
Abstract: 2-Cyclopropene-1-carbonyl chlorides **6** react with $[Co(CO)_4]^-$ in MeCN, THF, or C_6H_6 solution to afford (η^3-oxocyclobutenyl)tricarbonylcobalt complexes **7**. No η^3-cyclopropenyl compounds of cobalt are produced. The reaction is shown to proceed by initial formation of a coordinatively saturated (2-cyclopropen-1-ylcarbonyl)tetracarbonylcobalt species, which then undergoes decarbonylation to afford a coordinatively unsaturated (2-cyclopropen-1-ylcarbonyl)tricarbonylcobalt intermediate. ^2H and ^{13}C labeling studies confirm that this intermediate is the crucial precursor for ring expansion to the oxocyclobutenyl ligand. In THF or MeCN solution this intermediate is in dynamic equilibrium with a cyclopropenium cation and $[Co(CO)_4]^-$; in less polar C_6H_6 this equilibrium is insignificant. Evidence is presented that reactions of cyclopropenium cations with $[Co(CO)_4]^-$ involve direct electrophilic attack at a CO ligand rather than at cobalt; no evidence for the presence of η^1-cyclopropenyl cobalt intermediates has been obtained. In C_6H_6, chiral acyl chlorides **6** afford chiral oxocyclobutenyl compounds **7**; in THF or MeCN only racemic products are obtained due to the dissociative equilibrium mentioned above. The effects of ring substituents on the selectivity of C-C cleavage in the ring expansion step resemble those obtained in photochemical rather than thermal ring openings of cyclopropenes. A ring expansion mechanism which involves a metal-stabilized vinylcarbene transition state is proposed; this transition state collapses to a nonplanar vinylketene species which undergoes ring closure to the oxocyclobutenyl ligand. ^1H and ^{13}C NMR data for a large number of (oxocyclobutenyl)cobalt compounds are presented.

Introduction

Reactions of cyclopropenium cations with low-valent metal centers which lead to (η^3-cyclopropenyl)- and (η^1-cyclopropenyl)metal complexes have been surveyed in the preceding paper,[2] and a new synthesis of nonfluxional η^1-cyclopropenyl compounds of rhenium via the facile thermal decarbonylation of (2-cyclopropen-1-ylcarbonyl)pentacarbonyl rhenium complexes was described.[3] Curiously, reactions of cyclopropenium cations with metal carbonyl anions only rarely lead to formation of η^1-cyclopropenyl compounds **1**[4,5] but instead afford η^3-oxocyclobutenyl complexes **2**[6-9] in an intriguing reaction by which CO is incorporated into the three-membered ring.

Scheme I illustrates anticipated interconversions between η^1-cyclopropenyl compounds **1**, η^3-cyclopropenyl systems **3**, and η^3-oxocyclobutenyl complexes **2**; literature precedents for each step have been reported, though not all for the same system. The triphenylcyclopropenium cation has been shown to react with $[Fe(\eta\text{-}C_5H_5)(CO)_2]^-$ to afford the η^1-cyclopropenyl compound **1**

Scheme I



(R = Ph; M = $Fe(\eta\text{-}C_5H_5)(CO)_2$),[4,5] whereas the tri-*tert*-butylcyclopropenium cation reacts with the same anion to afford only **2** (R = *t*-Bu; M = $Fe(\eta\text{-}C_5H_5)(CO)$).[10] It was proposed that the latter reaction, for steric reasons, proceeded via direct electrophilic attack at a CO ligand rather than at the metal, to give a coordinatively unsaturated 2-cyclopropene-1-carbonyl intermediate **4** (M = $Fe(\eta\text{-}C_5H_5)(CO)$) which then underwent ring

(1) Alfred P. Sloan Research Fellow 1980-1984.
(2) DeSimone, D. M.; Desrosiers, P. J.; Hughes, R. P., preceding paper in this issue.
(3) See also: Desrosiers, P. J.; Hughes, R. P. *J. Am. Chem. Soc.* **1981**, *103*, 5593-5594.
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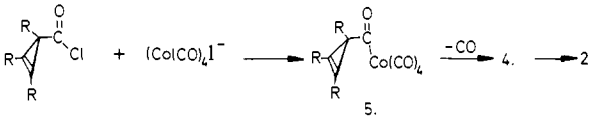
0002-7863/82/1504-4846$01.25/0

expansion to give **2**;[10] ring expansion of **4** to **2** was also proposed as a corollary to other work involving iron-promoted expansion of a four- to a five-membered ring.[11] Notably, compounds **1** (M = $Fe(\eta\text{-}C_5H_5)(CO)_2$) do not convert to the corresponding ring-expanded product **2** under thermal conditions but do under photochemical activation.[5] Interestingly, no formation of **3** (M = $Fe(\eta\text{-}C_5H_5)(CO)$) was reported.[5] Evidence for the conversion of **4** (M = $Re(CO)_4$) to **1** (M = $Re(CO)_5$), but not for the reverse reaction, has been obtained; in this case no ring expansion to produce a rhenium analogue of **2** was detected.[2,3]

It seemed reasonable to suppose that the reported formation of **2** (R = Ph, Me; M = $Co(CO)_3$, $Fe(CO)_2(NO)$)[6-9] by the reaction of $[Co(CO)_4]^-$ or $[Fe(CO)_3(NO)]^-$ with the appropriate trisubstituted cyclopropenium cation proceeded via the intermediacy of the corresponding species **1** and **4**. It is noteworthy that no η^3-cyclopropenyl derivatives **3** were observed in these reactions. However, reaction of the triphenylcyclopropenium cation (as a Br^- or PF_6^- salt) with *neutral* metal carbonyl derivatives $[Co_2(CO)_8]$ or $[Mo(CO)_4L_2]$ afforded *both* the η^3-cyclopropenyl compounds **3** (R = Ph; M = $Co(CO)_3$;[9] $MoBr(CO)_2(bpy)$[12]) and the oxocyclobutenyl compounds **2** (R = Ph; M = $Co(CO)_3$;[9] $MoBr(CO)_2(bpy)$[12]); formation of the molybdenum derivatives was proposed to involve initial formation of an unstable η^1-cyclopropenyl compound **1** which could then collapse to give **3** or rearrange to **4** followed by ring expansion to **2**.

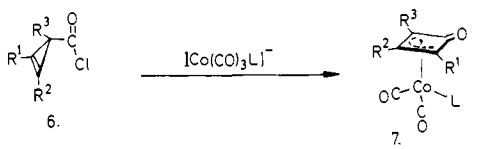
Formation of the η^3-oxocyclobutenyl ligand is a reaction which involves the net cleavage of one C–C bond and formation of two new C–C bonds. We wished to define more closely the mechanism of this novel organometallic reaction and in particular sought evidence for the proposed coordinatively unsaturated intermediate **4**. Our strategy was to approach this intermediate from another direction, by decarbonylation of the coordinatively saturated acyl compounds **5**, which could be synthesized by reaction of $[Co(CO)_4]^-$ with the appropriate acyl chlorides. A preliminary account of some of these results has appeared.[13]



5.

Results

The reaction of 2,3-diphenyl-2-cyclopropene-1-carbonyl chloride **6a** with $[Co(CO)_4]^-$ in dry THF or MeCN solution afforded, after workup, a single yellow crystalline compound in high yield. The IR (Table I), ^1H NMR (Table II), ^{13}C NMR (Table III) and microanalytical data (Table IV) indicated that the product was **7a**, containing an unsymmetrical 2,3-disubstituted cyclobutenyl ring. No evidence for any formation of the symmetrical isomeric 1-oxo-2,4-diphenylcyclobutenyl complex was obtained. The mass spectrum of **7a** exhibited a parent ion peak and daughter ions resulting from consecutive loss of *four* CO molecules; the base peak in the spectrum corresponded to the diphenylcyclopropenium cation, indicating that the ring expansion was reversible in the mass spectrometer.[14] Compound **7a** was also the exclusive product of the reaction of $[Co(CO)_4]^-$ with the 1,2-diphenylcyclopropenium cation in MeCN solution. Similarly, reaction of **6a** with the phosphine-substituted anions $[Co(CO)_3L]^-$ (L = PPh_3, PMe_2Ph, PEt_3) in THF solution led only to the corresponding unsymmetrical oxocyclobutenyl complexes **7b**, **7d**, and **7e**. Treatment of **7a** with an equimolar amount of tertiary phosphine likewise afforded **7b**, **7c**, **7d**, and **7e** by thermal displacement of CO.

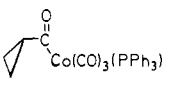


6. 7.

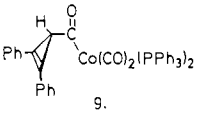
6a, R^3 = H; R^1 = R^2 = Ph
b, R^3 = H; R^1 = R^2 = Et
c, R^3 = H; R^1 = Ph; R^2 = Me
d, R^3 = Ph; R^1 = Me; R^2 = H
e, R^3 = H; R^1 = Ph; R^2 = *t*-Bu
f, R^3 = Ph; R^1 = *t*-Bu; R^2 = H
g, R^3 = H; R^1 = Ph; R^2 = *p*-$MeOC_6H_4$
6h, R^3 = H; R^1 = Me; R^2 = *p*-$MeOC_6H_4$
i, R^3 = R^2 = H; R^1 = *t*-Bu
j, R^3 = H; R^2 = D; R^1 = *t*-Bu
k, R^3 = R^2 = H; R^1 = *n*-Bu
l, R^3 = H; R^2 = D; R^1 = *n*-Bu
m, R^3 = R^2 = H; R^1 = *i*-Pr

7a, R^3 = H; R^1 = R^2 = Ph; L = CO
b, R^3 = H; R^1 = R^2 = Ph; L = PPh_3
c, R^3 = H; R^1 = R^2 = Ph; L = PPh_2Me
d, R^3 = H; R^1 = R^2 = Ph; L = $PPhMe_2$
e, R^3 = H; R^1 = R^2 = Ph; L = PEt_3
f, R^3 = H; R^2 = Et; L = CO
g, R^3 = H; R^1 = R^2 = Et; L = PPh_3
h, R^3 = H; R^1 = R^2 = *n*-Pr; L = CO
i, R^3 = H; R^1 = Ph; R^2 = Me; L = CO
j, R^3 = H; R^1 = Me; R^2 = Ph; L = CO
k, R^3 = Me; R^1 = Ph; R^2 = H; L = CO
l, R^3 = H; R^1 = Ph; R^2 = Me; L = PPh_3
m, R^3 = H; R^1 = Me; R^2 = Ph; L = PPh_3
n, R^3 = Me; R^1 = Ph; R^2 = H; L = PPh_3
o, R^3 = H; R^1 = *t*-Bu, R^2 = Ph; L = CO
p, R^3 = H; R^1 = Ph; R^2 = *t*-Bu; L = CO
q, R^3 = *t*-Bu; R^1 = Ph; R^2 = H; L = CO
7r, R^3 = H; R^1 = Ph; R^2 = *p*-$MeOC_6H_4$; L = CO
s, R^3 = H; R^1 = *p*-$MeOC_6H_4$; R^2 = Ph; L = CO
t, R^3 = H; R^1 = *p*-$MeOC_6H_4$; R^2 = Me; L = CO
u, R^3 = H; R^1 = Me; R^2 = *p*-$MeOC_6H_4$; L = CO
v, R^3 = R^2 = H; R^1 = *t*-Bu; L = CO
w, R^3 = R^1 = H; R^2 = *t*-Bu; L = CO
x, R^3 = R^2 = H; R^1 = *t*-Bu; L = PPh_3
y, R^3 = R^1 = H; R^2 = *t*-Bu; L = $PPhMe_2$
z, R^3 = H; R^2 = D; R^1 = *t*-Bu; L = CO
aa, R^3 = D; R^2 = H; R^1 = *t*-Bu; L = CO
bb, R^3 = H; R^2 = *t*-Bu; R^1 = D, L = CO
cc, R^3 = R^2 = H; R^1 = *n*-Bu; L = CO
dd, R^3 = R^1 = H; R^2 = *n*-Bu; L = CO
ee, R^3 = H; R^2 = D; R^1 = *n*-Bu; L = CO
ff, R^3 = D; R^2 = H; R^1 = *n*-Bu; L = CO
gg, R^3 = H; R^2 = *n*-Bu; R^1 = D; L = CO
hh, R^3 = R^2 = H; R^1 = *i*-Pr; L = CO

IR monitoring of the reaction of **6a** with $[Co(CO)_3(PEt_3)]^-$ in THF solution under an atmosphere of CO, showed transient ν_{CO} absorptions at 2077 (m), 2017 (s), 1969 (s), and 1651 (m) cm^{-1}, characteristic of an acyltricarbonyl(phosphine)cobalt complex. Comparative values for ν_{CO} for compound **8** are 2042 (m), 1952



8.



9.

(s), 1915 (s), and 1628 (m) cm^{-1}.[15,16] Similarly, reaction of **6a** with $[Co(CO)_2(PPh_3)_2]^-$ in THF afforded **9** (ν_{CO} 1974 (s), 1948 (s), 1653 (m) cm^{-1})[17] which only slowly dissociated a molecule of PPh_3, rather than CO, to produce ultimately **7b**. Addition of a large volume of MeOH to a THF solution of **9** did not effect any change in reaction pathway. Similarly, reaction of the diphenylcyclopropenium cation with $[Co(CO)_2(PPh_3)_2]^-$ in THF afforded only **7b**.

The reaction of **6a** with ^{13}CO-enriched $[Co(CO)_4]^-$ in MeCN afforded an enriched sample of **7a**; the ^{13}C NMR spectrum of

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(17) Comparative ν_{CO} values for $[Co(C(O)Me)(CO)_2(dppe)]$ are 1980 (s), 1923 (s), 1623 (m) cm^{-1}.[18]
(18) Heck, R. F.; Breslow, D. S. *J. Am. Chem. Soc.* **1962**, *84*, 2499–2502.

Table I. Carbonyl Infrared Stretching Frequencies of (η^3-Oxocyclobutenyl)cobalt Complexes[a]

compd	R^1	R^2	R^3	L	ν_{CO}, cm^{-1} (cyclohexane)
7a	Ph	Ph	H	CO	2088 (s), 2038 (s), 2027 (s), 1734 (m)
7b	Ph	Ph	H	PPh_3	2032 (s), 1985 (s), 1707 (m)
7c	Ph	Ph	H	PPh_2Me	2028 (s), 1981 (s), 1699 (m)
7d	Ph	Ph	H	$PPhMe_2$	2029 (s), 1980 (s), 1692 (m)
7e	Ph	Ph	H	PEt_3	2023 (s), 1977 (s), 1691 (m)
7f	Et	Et	H	CO	2085 (s), 2031 (s), 2015 (s), 1735 (m)
7g	Et	Et	H	PPh_3	2021 (s), 1973 (s), 1705 (m)
7h	*n*-Pr	*n*-Pr	H	CO	2081 (s), 2026 (s), 2010 (s), 1733 (m)
7i	Ph	Me	H	CO	2085 (s), 2035 (s), 2021 (s), 1737 (m)
7j	Me	Ph	H	CO	2085 (s), 2035 (s), 2023 (s), 1741 (m)
7k	Ph	H	Me	CO	2081 (s), 2031 (s), 2017 (s), 1729 (m)
7l	Ph	Me	H	PPh_3	2023 (s), 1976 (s), 1705 (m)
7m	Me	Ph	H	PPh_3	2023 (s), 1976 (s), 1711 (m)
7n	Ph	H	Me	PPh_3	2021 (s), 1977 (s), 1695 (m)
7o	*t*-Bu	Ph	H	CO	2085 (s), 2033 (s), 2017 (s), 1733 (m)
7p	Ph	*t*-Bu	H	CO	2085 (s), 2033 (s), 2017 (s), 1733 (m)
7q	*t*-Bu	H	Ph	CO	2085 (s), 2033 (s), 2017 (s), 1733 (m)
7r	Ph	*p*-anisyl	H	CO	2085 (s), 2035 (s), 2021 (s), 1737 (m)
7s	*p*-anisyl	Ph	H	CO	2085 (s), 2035 (s), 2021 (s), 1737 (m)
7t	*p*-anisyl	Me	H	CO	2081 (s), 2028 (s), 2016 (s), 1738 (m)
7u	Me	*p*-Anisyl	H	CO	2081 (s), 2028 (s), 2016 (s), 1738 (m)
7v	*t*-Bu	H	H	CO	2089 (s), 2029 (s), 2016 (s), 1736 (m)
7w	H	*t*-Bu	H	CO	2089 (s), 2029 (s), 2016 (s), 1736 (m)
7x	*t*-Bu	H	H	PPh_3	2027 (s), 1975 (s), 1707 (m)
7y	H	*t*-Bu	H	$PPhMe_2$	2033 (s), 1981 (s), 1697 (m)
7cc	*n*-Bu	H	H	CO	2081 (s), 2029 (s), 2018 (s), 1733 (m)
7dd	H	*n*-Bu	H	CO	2081 (s), 2029 (s), 2018 (s), 1733 (m)
7hh	*i*-Pr	H	H	CO	2085 (s), 2031 (s), 2019 (s), 1735 (m)

[a] Abbreviations: s, strong; m, medium.

Table II. 60-MHz ^1H NMR Spectral Data of (η^3-Oxocyclobutenyl)cobalt Complexes (δ (Multiplicity, Coupling in Hz))

compd	R^1	R^2	R^3	other
7a[a]	7.3–7.9 (m, 10 H)		5.09 (s, 1 H)	
7b[a]	7.1–7.7 (m, 10 H)		4.39 (d, J = 4.9,[c] 1 H)	7.1–7.7 (m, 15 H)
7c[a]	7.2–7.5 (m, 10 H)		4.80 (br, 1 H)	7.2–7.5 (m, 10 H), 1.78 (d, J = 7.8,[c] 3 H)
7d[a]	7.1–7.8 (m, 10 H)		4.42 (d, J = 2.8,[c] 1 H)	7.1–7.8 (m, 5 H), 1.61 (d, J = 8.3,[c] 3 H), 1.51 (d, J = 8.4,[c] 3 H)
7e[a]	7.2–7.8 (m, 10 H)		4.47 (d, J = 1.5,[c] 1 H)	0.6–2.0 (m, 15 H)
7f[a]	1.8–2.7 (m, 4 H), 1.23 (t, 3 H), 1.11 (t, 3 H)		4.74 (s, 1 H)	
7h[a]	0.9–2.3 (m, 14 H)		4.74 (s, 1 H)	
7i[a]	7.2–7.6 (m, 5 H)	2.41 (s, 3 H)	4.84 (s, 1 H)	
7j[a]	2.09 (s, 3 H)	7.34 (s, 5 H)	5.15 (s, 1 H)	
7k[a]	7.2–7.8 (m, 5 H)	5.72 (s, 1 H)	1.79 (s, 3 H)	
7l[a]	7.1–7.7 (m, 5 H)	1.55 (d, J = 1.3,[c] 3 H)	3.90 (d, J = 5.7,[c] 1 H)	7.1–7.7 (m, 15 H)
7m[a]	1.82 (d, J = 5.1,[c] 3 H)	7.0–7.6 (m, 5 H)	4.24 (d, J = 4.3,[c] 1 H)	7.0–7.6 (m, 15 H)
7n[a]	7.2–7.6 (m, 5 H)	5.05 (br s, 1 H)	1.35 (d, J = 4,[c] 3 H)	7.2–7.6 (m, 15 H)
7o[a]	1.31 (s, 9 H)	7.40 (s, 5 H)	4.95 (s, 1 H)	
7p[a]	7.40 (s, 5 H)	1.25 (s, 9 H)	4.69 (s, 1 H)	
7q[a]	1.26 (s, 9 H)	5.66 (s, 1 H)	7.2–7.7 (m, 5 H)	
7r[a]	7.0–7.7 (m, 5 H)	3.83 (s, 3 H) 7.0–7.8 (m, 4 H)	5.04 (s, 1 H)	
7s[a]	3.82 (s, 3 H) 7.0–7.8 (m, 4 H)	7.0–7.8 (m, 5 H)	5.08 (s, 1 H)	
7t[a]	3.81 (s, 3 H) 7.3 (ABq, 4 H)	2.39 (s, 3 H)	4.78 (s, 1 H)	
7u[a]	2.07 (s, 3 H)	3.81 (s, 3 H) 7.28 (ABq, 4 H)	5.10 (s, 1 H)	
7v[a]	1.20 (s, 9 H)	5.23 (s, 1 H)	4.55 (s, 1 H)	
7w[a]	4.65 (s, 2 H)	1.15 (s, 9 H)	...	
7x[a]	1.24 (s, 9 H)	4.28 (s, 1 H)	3.58 (d, J = 7.3,[c] 1 H)	7.3–7.5 (m, 15 H)
7y[a]	4.25 (s, 2 H)	1.17 (s, 9 H)		1.65 (d, J = 8.3,[c] 6 H), 7.2–7.8 (m, 5 H)
7cc[a]	0.91 (t, 3 H), 1.48 (m, 4 H), 1.94 (m, 2 H)	5.29 (s, 1 H)	4.54 (s, 1 H)	
7dd[a]	4.73 (s, 2 H)	1.0–2.0 (m, 9 H)	...	
7hh[a]	2.27 (m, 1 H), 1.24 (d, J = 6.7,[d] 3 H), J = 6.6,[d] 3 H)	5.27 (s, 1 H)	4.54 (s, 1 H)	

[a] $CDCl_3$ (s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet). [b] Acetone-d_6. [c] J_{P-H}. [d] J_{H-H}.

this sample indicated that ^{13}CO was present in both the terminal carbonyl and ring carbonyl positions. Comparison of ^{13}C NMR peak intensities with a natural abundance sample of **7a** run under identical conditions indicated that 13 ± 1% of the ring carbonyl carbon atoms were ^{13}C and mass spectral analysis of the sample indicated a total molecular ^{13}C enrichment of 56%; thus the ^{13}CO originally present in $[Co(CO)_4]^-$ was almost statistically distributed between the four carbonyl sites in **7a**.[19]

Table III. 15-MHz $^{13}C\{^1H\}$ NMR Spectral Data for (η^3-Oxocyclobutenyl)cobalt Complexes (δ Downfield from Me_4Si (Multiplicity, Coupling in Hz))

compd	C=O	C1	C2	C3	other
7a[a]	164.81	90.21[c]	93.88	70.84	132.35, 131.72, 128.67, 127.95, 127.71 (Ph); 198.44 (MCO)
7d[a]	163.00 (d, J_{P-C} = 10)	82.28	84.74	66.88 (d, J_{P-C} = 5)	138.05, 135.38, 135.22, 135.05, 133.67, 128.15 (Ph); 14.85 (br, PCH_3); 203.35 (br, MCO)
7e[b]	164.40	83.33	85.72	67.39	136.96, 135.67, 131.21, 129.92, 129.47, 129.23, 128.46, 128.06, 126.52 (Ph); 18.15 (d, J_{P-C} = 23.8, PCH_2); 8.22 (CH_3)
7i[a]	164.72	95.69	88.99	*d*	132.82, 129.09, 128.72, 126.53 (Ph); 14.89 (CH_3)
7j[a]	166.83	90.94	93.46	69.36	133.27, 129.33, 128.84, 126.24 (Ph); 12.09 (CH_3)
7k[a]	167.11	*d*	72.15	90.13	131.72, 129.05, 128.72, 127.02 (Ph); 11.48 (CH_3)
7v[a]	166.59	113.79	71.18	69.03	31.94 ($C(CH_3)_3$); 28.89 ($C(CH_3)_3$)
7w[a]	166.10	72.88	108.67	...	31.94 ($C(CH_3)_3$); 30.27 ($C(CH_3)_3$)
7y[b]	*d*	68.86	108.86	...	131.32, 130.63, 130.46, 130.02, 129.41 (Ph); 32.44 (d, J_{P-C} = 3.0, $C(CH_3)_3$); 31.02 (d, J_{P-C} = 4.3, $C(CH_3)_3$); 13.88 (d, J_{P-C} = 24.2, PCH_3)
7cc[a]	167.92	99.95	73.21	69.35	30.92, 27.15, 22.72, 13.63 (C_4H_9)
7hh[a]	167.40	107.38	72.19	69.27	27.43, 22.20, 20.41 ($CH(CH_3)_2$)

[a] $CDCl_3$ (d, doublet). [b] Acetone-d_6. [c] $^1J_{C=O,Cl}$ = 39.0 ± 1.2 Hz, $^1J_{Cl-H}$ = 181.3 ± 1.2 Hz. [d] Not observed.

Table IV. Melting Points and Elemental Analysis (%) of (η^3-Oxocyclobutenyl)cobalt Complexes

		elemental anal.			
		calcd		found	
compd	mp, °C	C	H	C	H
7a	100–102	63.00	3.06	62.67	2.92
7b	150–157	72.50	4.39	72.49	4.42
7d	133–140	66.11	4.69	66.19	4.70
7e	80–84	49.04	4.77	48.32	4.70
7i	82–85	56.02	3.02	56.21	3.23
7j	93–95	56.02	3.02	56.19	3.34
7k	105–107	56.02	3.02	55.98	3.08
7o	74–75	59.66	4.42	59.76	4.51
7v	78–80	49.64	4.17	49.60	4.18
7x	198	67.21	5.24	67.10	5.25
7cc	34	49.64	4.17	49.66	4.34
7hh	39–41	47.64	3.60	47.69	3.78

The reaction of the dialkyl-substituted acid chloride **6b** with $[Co(CO)_4]^-$ (THF or MeCN) likewise afforded a single product, shown by its IR and ^1H NMR spectra (Tables I and II) to be the 1-oxo-2,3-diethylcyclobutenyl complex **7f**; PPh_3 reacted with **7f** to afford **7g**. Similarly $[Co(CO)_4]^-$ reacted with the di-*n*-propylcyclopropenium cation to yield exclusively the unsymmetrical complex **7h**.

The unsymmetrically substituted acid chloride **6c** reacted with $[Co(CO)_4]^-$ (THF) to produce a 3:4 mixture of **7i** and **7j**, which could be separated by dry column chromatography. The isomers showed no tendency to interconvert in solution. The structure of the minor isomer **7i** was unambiguously determined by converting it to the cationic methoxycyclobutadiene derivative with use of $Me_3O^+PF_6^-$; the structure of this cyclobutadiene complex has been determined by X-ray crystallography.[20] The ^1H NMR spectra of an equimolar mixture of **7i** and **7j** were obtained in the presence of varying amounts of $[Eu(fod)_3]$;[21] as expected, the lanthanide-induced shift of the ring proton was essentially equal for both isomers, but the methyl group of **7j** was shifted substantially more than that of **7i**, indicating coordination of $[Eu(fod)_3]$ at the ketonic oxygen atom.[22] The reaction of **6c** with $[Co(CO)_4]^-$ in MeCN or C_6H_6 solution likewise yielded only **7i** and **7j**; the ratio of the products was somewhat dependent on the reaction solvent, being 2:3 in MeCN and 1:2 in C_6H_6. In MeCN solution the reaction of $[Co(CO)_4]^-$ with the methylphenylcyclopropenium cation afforded only an equimolar mixture of **7i** and **7j**.

An optically enriched sample of **6c** (9:1 mixture of enantiomers) reacted with $[Co(CO)_4]^-$ in MeCN to give a 2:3 mixture of **7i** and **7j**. Each product was shown to consist of a racemic mixture by ^1H NMR studies using the chiral shift reagent $Eu(facam)_3$.[23] In contrast, the reaction of an optically enriched sample of **6c** (3:1 mixture of enantiomers) with $[Co(CO)_4]^-$ in C_6H_6 solution afforded a 1:2 mixture of **7i** and **7j**, each of which was shown to consist of a 3:1 mixture of enantiomers. Reaction of racemic **6c** with ^{13}CO-enriched $[Co(CO)_4]^-$ in C_6H_6 solution likewise afforded **7i** and **7j**; ^{13}C NMR spectroscopy indicated that no enrichment in ^{13}CO had occurred at the ring carbonyl site in either of these products.

The reaction of $[Co(CO)_4]^-$ with the isomeric acid chloride **6d** in MeCN solution afforded the three products **7i**, **7j**, and **7k** in a 1.0:1.3:4.0 ratio; all three products were separated by chromatography and did not interconvert in solution. Similarly, the reaction of **6d** with ^{13}CO-enriched $[Co(CO)_4]^-$ afforded the same three products; a combination of ^{13}C NMR and mass spectrometry indicated the presence of ^{13}CO enrichment at both the terminal CO and ring CO sites in **7i** and **7j** but only at the terminal CO sites in **7k**. An optically enriched sample of **6d** (3:1 mixture of enantiomers) reacted with $[Co(CO)_4]^-$ in MeCN solution to afford the same three compounds; ^1H NMR experiments using $[Eu(facam)_3]$ indicated that **7i** and **7j** were each racemic, while **7k** comprised a 3:1 mixture of enantiomers. Compounds **7i**, **7j**, and **7k** afforded the corresponding substituted analogues **7l**, **7m**, and **7n**, respectively, on treatment with PPh_3. The reaction of **6c** with $[Co(CO)_2(PPh_3)_2]^-$ in THF solution afforded only **7l** and **7m** in a 1:1 ratio; the presence of tertiary phosphines in the coordination sphere clearly has no major effect on the selectivity of product formation.

The ^1H NMR spectra of compounds **7i–k** and **7l–n** illustrate features which are useful for assigning resonances in other compounds (vide infra). In particular a ring proton in the R^2 position (e.g., in **7k**) invariably resonates at lower field than a corresponding proton in the R^1 or R^3 sites; similarly, a proton at R^2 does not exhibit significant coupling to ^{31}P (e.g., in **7n**), whereas protons at R^1 or R^3 (e.g., **7l**, **7m**) do. Similar trends in chemical shift and in $J_{^{31}P-^1H}$ have been documented for the central and syn protons in acyclic η-allyl compounds of cobalt.[24,25]

Acid chloride **6e** reacted with $[Co(CO)_4]^-$ in MeCN solution to afford a 10:1 mixture of **7o** and **7p**. The structures were assigned by comparison of ^1H NMR chemical shift data with those of **7i** and **7j** and also by studies using $[Eu(fod)_3]$; the lanthanide-induced shift for the ring proton in both isomers was almost identical, whereas the *t*-Bu resonance in **7o** shifted to a consid-

(19) The measurement of $^1J_{^{13}C-^{13}C}$ in the four-membered ring of **7a** has already been reported: Donaldson, W. A.; Hughes, R. P. *J. Magn. Reson.* **1981**, *43*, 170–172.

(20) Donaldson, W. A.; Hughes, R. P.; Davis, R. E.; Gadol, S. M. *Organometallics* **1982**, *1*, 812–819.

(21) Tris(6,6,7,7,8,8,8-heptafluoro-2,2-dimethyl-3,5-octanedionato)europium(III).

(22) Coordination of other electrophiles in this site is discussed in detail in ref 20.

(23) Tris(3-(trifluoroacetyl)-*d*-camphorato)europium(III).

(24) Vitulli, G.; Porri, L.; Serge, A. L. *J. Chem. Soc. A* **1971**, 3246–3250.

(25) Rinze, P. V.; Muller, V. *Chem. Ber.* **1979**, *112*, 1973–1980.

erably greater extent than that of **7p**. Likewise the reaction of the isomeric acid chloride **6f** with $[Co(CO)_4]^-$ in MeCN afforded **7o**, **7p**, and the third isomer **7q** in a 3.5:1.0:5.0 ratio.

In MeCN solution, the reaction of $[Co(CO)_4]^-$ with **6g** (MeCN) afforded a 1:1 mixture of **7r** and **7s**; an analogous reaction using **6h** yielded a 2:3 mixture of **7t** and **7u**.

The reaction of the monoalkyl derivative **6i** with $[Co(CO)_4]^-$ in MeCN solution afforded a 6:1 mixture of **7v** and **7w**, which could be separated by chromatography; **7v** reacted with PPh_3 to produce **7x**, and **7w** reacted with PMe_2Ph to afford **7y**. The deuterium-labeled acid chloride **6j** likewise reacted with $[Co(CO)_4]^-$ in MeCN to yield a 3:3:1 mixture of **7z**, **7aa**, and **7bb**, respectively; the equimolar amounts of **7z** and **7aa** indicated complete scrambling of the deuterium between the R^2 and R^3 positions on the unsymmetrical oxocyclobutenyl ligand. A similar reaction of **6j** with $[Co(CO)_4]^-$ in C_6H_6 yielded a 4:1:1 mixture of **7z**, **7aa**, and **7bb**, indicating incomplete (40%) scrambling of deuterium between the R^2 and R^3 positions in this solvent, with D preferentially occupying the R^2 site; dissolution of this mixture in MeCN effected no change in the isomer ratio. The ring proton resonances in **7v** were assigned on the basis of chemical shift (vide supra); notably in the phosphine-substituted derivative **7cc**, only the higher field resonance corresponding to the proton at position R^3 exhibited coupling to ^{31}P.[26] Assignment of these proton resonances allows corresponding assignments for the deuterium-labeled analogues.

The less hindered alkyl derivative **6k** produced a 20:1 mixture of **7cc** and **7dd**, on reaction with $[Co(CO)_4]^-$ in MeCN solution. A pure sample of compound **7cc** could be separated from this mixture by dry column chromatography. The deuterium-labeled analogue **61** reacted with $[Co(CO)_4]^-$ in MeCN to yield a 12:10:1 mixture of **7ee**, **7ff**, and **7gg**, demonstrating ~91% scrambling of D between the R^2 and R^3 positions, the preferential site being R^2.

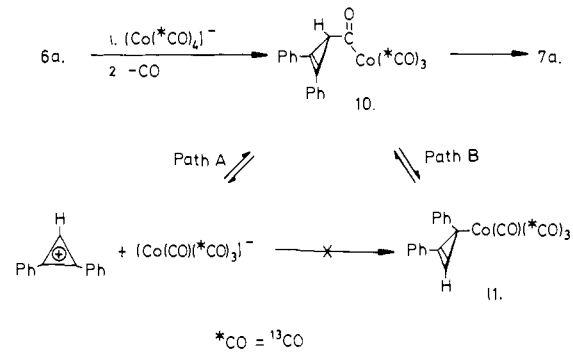
Finally the acyl chloride **6m** reacted with $[Co(CO)_4]^-$ in MeCN solution to yield exclusively the unsymmetrically substituted oxocyclobutenyl compound **7hh**.

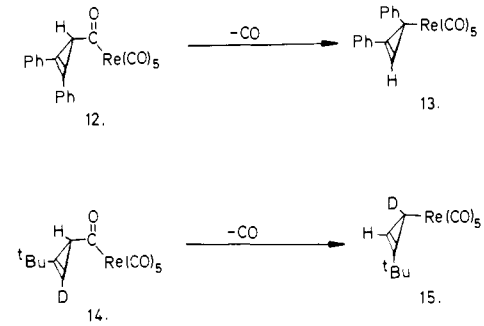
Discussion

Isolable, coordinatively saturated 2-cyclopropene-1-carbonyl compounds of rhenium, manganese, and iron are described in the preceding paper.[2] It seems clear from the results described in the preceding section that the initial products of reactions of cobalt carbonyl anions with 2-cyclopropene-1-carbonyl chlorides must also be the corresponding acylcobalt species but that these compounds are more labile toward decarbonylation than the Re, Mn, or Fe analogues.[27] The facility with which loss of a ligand can occur governs the rate at which subsequent ring expansion can occur to give the η^3-oxocyclobutenyl ligand; increasing the number of tertiary phosphine ligands suppresses CO dissociation so that in one case, an intermediate **9** can be characterized in solution. Notably **9** exhibits a preference for loss of PPh_3 rather than CO, presumably due to steric crowding, to give ultimately **7b**. Also notable is the fact that compound **8** is reported to be thermally inert toward decarbonylation, alkyl migration, or ring expansion,[15,16] indicating that an olefinic functionality within the three-membered ring is essential to subsequent reactivity.

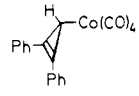
Observation that the reaction of **6a** with ^{13}CO-enriched $[Co(CO)_4]^-$ in MeCN affords **7a** in which the ^{13}C enrichment is almost statistically distributed between the terminal CO and ring CO sites clearly indicates that the mechanism in this solvent includes a step in which the acyl carbonyl and terminal CO ligands become indistinguishable. Two possible pathways might account for this result after formation of the coordinatively unsaturated intermediate **10**, as shown in Scheme II. Path A involves reversible heterolytic dissociation to give the diphenylcyclopropenium cation and $[Co(CO)(^{13}CO)_3]^-$; that such a pathway can lead ultimately to **7a** is demonstrated by the direct reaction of this cation with $[Co(CO)_4]^-$ to yield only **7a**. Path B involves reversible cyclopropenyl migration to and from the cobalt atom, with resultant scrambling of labeled and unlabeled CO. The rhenium complexes **12** and **14** have been shown to undergo facile, though irreversible, intramolecular cyclopropenyl migrations, with allylic rearrangement of the cyclopropenyl group, to give **13** and **15**, respectively.[2] Relevant to subsequent discussion is the observation

Scheme II





that the conversion of **14** to **15** is completely regiospecific, as shown, and that **15** is inert to metal migration around the cyclopropenyl ring.[2] By analogy it seems probable that Path B should also proceed to give **11** and that its microscopic reverse should afford **10**.[29] It should be noted at this stage, however, that the reaction of $[Co(CO)_4]^-$ with the diphenylcyclopropenium cation would be expected to form **16** rather than **11**, *if this reaction involved direct attack by cobalt on the three-membered ring*.[30] We shall defer discussion of this point until later.



16.

The reaction of **6i** with $[Co(CO)_4]^-$ in MeCN affords a 6:1 mixture of the isomeric complexes **7v** and **7w**, illustrating a preference for cleavage of the cyclopropene ring adjacent to *t*-Bu rather than H. Similarly the deuterium-labeled analogue **6j** affords a 3:3:1 mixture of **7z**, **7aa**, and **7bb** on reaction with $[Co(CO)_4]^-$ in MeCN but a 4:1:1 ratio of the same three isomers in C_6H_6. The complete scrambling of the deuterium label (equimolar amounts of **7z** and **7aa**) in MeCN, but incomplete scrambling (4:1 ratio of **7z** and **7aa**) in C_6H_6, is consistent with

(26) It should be noted, however, that the R^1 and R^3 protons in the symmetrical complex **7y** exhibit no observable coupling to ^{31}P; the reason for this is unclear.

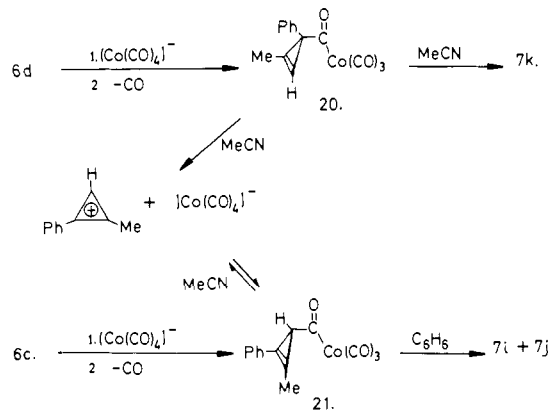
(27) Acyltetracarbonylcobalt compounds are known to decarbonylate rapidly compared to corresponding acylpentacarbonylmanganese analogues.[28]

(28) King, R. B. *Acc. Chem. Res.* **1970**, *3*, 417–427. Heck, R. F. *Adv. Organomet. Chem.* **1966**, *4*, 243–266.

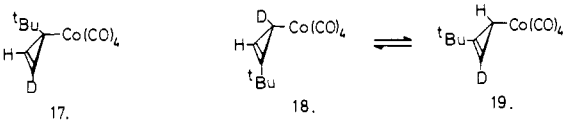
(29) Ultraviolet irradiation of **1** (R = Ph; M = $Fe(CO)_2(\eta$-$C_5H_5)$] has been reported to give **2** (R = Ph; M = $Fe(CO)(\eta$-$C_5H_5)$], although the product was only characterized spectroscopically.[5] It is possible, therefore, that a η^1-cyclopropenyl complex can serve as a precursor to a η^3-oxocyclobutenyl compound.

(30) Reaction of $[Fe(CO)_2(\eta$-$C_5H_5)]^-$ with the diphenylcyclopropenium cation has been shown to involve attack by the metal at the unsubstituted carbon atom.[4] Similarly, other nucleophiles such as Grignard reagents preferentially attack this cation at the unsubstituted site.[31,32]

Scheme III

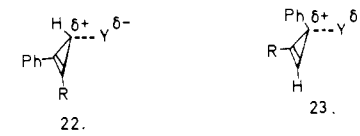


the fact that the equilibrium Path A (Scheme II) should be more facile in a polar solvent. In benzene, ring expansion occurs at a rate faster than that of heterolytic dissociation, whereas in MeCN the reverse is true. The deuterium scrambling cannot be explained by path B; in order to scramble the label this pathway must either afford directly the cyclopropenyl intermediate **17** or give **18** which would then need to equilibrate rapidly with **19** before migration of the cyclopropenyl group back to CO. Neither of these possibilities can be reconciled with the known, regiospecific conversion of **14** to *nonfluxional* **15**.[2]



The reaction of **6k** with $[Co(CO)_4]^-$ exhibits an even greater selectivity for cyclopropene cleavage adjacent to *n*-Bu rather than H, affording a 20:1 mixture of **7cc** and **7dd**. The corresponding deuterium-labeled analogue **61** does not undergo complete label scrambling, even in MeCN, as evidenced by the 1.2:1 ratio of **7ee**:**7ff**. We interpret this to mean that the smaller steric effect of *n*-Bu vs. *t*-Bu enhances the rate of ring cleavage adjacent to the alkyl group and makes this reaction more competitive with heterolytic dissociation in the former case. It is not clear why **6m** affords only **7hh**, however, since the steric effect of the *i*-Pr group is expected to be intermediate between *n*-Bu and *t*-Bu.

Further evidence of competition between heterolytic dissociation and ring expansion is provided by the reactions of isomeric acid chlorides **6c** and **6d**, with $[Co(CO)_4]^-$ in MeCN. Compound **6c** yields only the two isomeric compounds **7i** and **7j**; these isomers are also the *only* products of the reaction of the methylphenylcyclopropenium cation with $[Co(CO)_4]^-$ in MeCN. Under the same conditions **6d** yields **7i** and **7j** but also affords as the major product the third isomer **7k**. When the reaction with **6d** in MeCN is carried out by using ^{13}CO-enriched $[Co(CO)_4]^-$, products **7i** and **7j** contain ^{13}CO in the ring, whereas **7k** does not; therefore, **7k** must be formed prior to any dissociation. Similarly formation of **7i** and **7j**, with no ^{13}CO in the ring, from **6c** and ^{13}CO-enriched $[Co(CO)_4]^-$ in benzene solution indicates that no dissociation precedes ring expansion in this solvent. The most plausible explanation (Scheme III) involves partial dissociation of the coordinatively unsaturated acyl **20**, followed by recombination to give **21** (vide infra), which can lead to **7i** and **7j**; **7k** can only be formed from **20** by selective ring expansion, with ring cleavage adjacent to Me rather than H. This selectivity pattern fits that described for other alkyl substituents (vide supra). These observations require that the ring expansion of **21** be slower than that of dissociation in MeCN but that the reverse be true for **20**. This can be rationalized by considering the ease with which heterolytic dissociation can occur from two generalized species **22** and **23**. As the leaving group Y^- departs, localized partial positive charge builds up on a cyclopropenium carbon atom; a phenyl group is less able to stabilize a localized positive charge on a cyclopropenyl



ring than is H, making dissociation of **23** a higher activation energy process than **22**.[33]

An analogous series of arguments can be used to explain the observation that **6e** affords only **7o** and **7p** in MeCN solution, whereas **6f** produces **7o**, **7p**, and **7q** (major product) in the same solvent.

The absence of ^{13}CO label in the ring of **7k** unambiguously demonstrates that the actual ring expansion reaction to give the oxocyclobutenyl ligand must occur from the *acyl* compound **20**; i.e., *breakage of the cyclopropene ring C–C bond does not involve any (η^1-cyclopropenyl)cobalt intermediate.*[35] An identical conclusion concerning **21** is necessary to explain the absence of ^{13}C in the oxocyclobutenyl rings of **7i** and **7j** when the reaction of **6c** with $[Co(CO)_4]^-$ is carried out in C_6H_6.

Identical conclusions evolve from consideration of the reactions of chiral **6c** and **6d** with $[Co(CO)_4]^-$. In MeCN chiral **6c** affords only racemic **7i** and **7j**, whereas in C_6H_6 complete retention of optical activity is observed in the products. Similarly in MeCN, chiral **6d** yields racemic **7i** and **7j** but also affords chiral **7k**. These results are only consistent with loss of chirality occurring in more polar solvents via dissociation to the planar cyclopropenium cation. It is worth noting that an intramolecular path B (Scheme II) cannot account for loss of optical activity, since reversible cyclopropenyl migration should occur with retention of chirality. The most important conclusion, however, is that *under conditions where dissociation is suppressed* as evidence by absence of ^{13}CO in the oxocyclobutenyl ring, ring expansion of **20** or **21** to give the oxocyclobutenyl ligand proceeds without loss of optical activity; *a planar intermediate or transition state is thus excluded in the ring-expansion reaction.*

In Schemes II and III we have illustrated the formation of the coordinatively unsaturated acyl intermediates **10**, **20**, and **21** by direct electrophilic attack of the cyclopropenium cation on a CO ligand[39] rather than via the intermediacy of a η^1-cyclopropenyl complex formed by analgous electrophilic attack at cobalt. We have noted that path A rather than path B in Scheme II must be invoked to explain our observations. If this is so, the principle of microscopic reversibility dictates that path A should also be followed in the reverse reaction of a cyclopropenium cation with $[Co(CO)_4]^-$, *i.e. that direct electrophilic attack on carbon monoxide rather than at cobalt should be preferred.* Some supporting evidence for this is presented below.

We have already noted that in the actual ring expansion step there is a pronounced selectivity for cleavage of the cyclopropene ring adjacent to an alkyl group rather than adjacent to H, even

(31) Zimmerman, H. E.; Aasen, S. M. *J. Org. Chem.* **1978**, *43*, 1493–1506.

(32) Padwa, A.; Blacklock, T. J.; Getman, D.; Hatanaka, N.; Loza, R. *J. Org. Chem.* **1978**, *43*, 1481–1492.

(33) Resonance stabilization by phenyl of positive charge in a cyclopropenium cation serves to disrupt the aromaticity of the three-membered ring and is disfavored. Since phenyl is inductively electron withdrawing compared to H, it is less able to stabilize localized positive charge on a cyclopropenium ring carbon atom.[34] Notably, such heterolytic dissociations should be the microscopic reverse of nucleophilic attack at the three-membered ring; since nucleophilic attack occurs preferentially via a transition state corresponding to **22** rather than **23**,[31,32] it follows that **22** must be lower in energy than **23**.

(34) (a) Breslow, R.; Hover, H.; Chang, H. W. *J. Am. Chem. Soc.* **1962**, *84*, 3168–3174. (b) Breslow, R.; Ryan, G.; Groves, J. T. *Ibid.* **1970**, *92*, 988–993. (c) Breslow, R.; Sugimoto, T. *Tetrahedron Lett.* **1974**, 2437–2438. (d) Johnson, R. W.; Widlowski, T.; Breslow, R. *Ibid.* **1976**, 4685–4686.

(35) Examples of the metal-promoted ring cleavage of cyclopropenyl ligands to give mononuclear metallacyclobutadiene compounds have been reported[36,37] and have also been the subject of a theoretical investigation.[38]

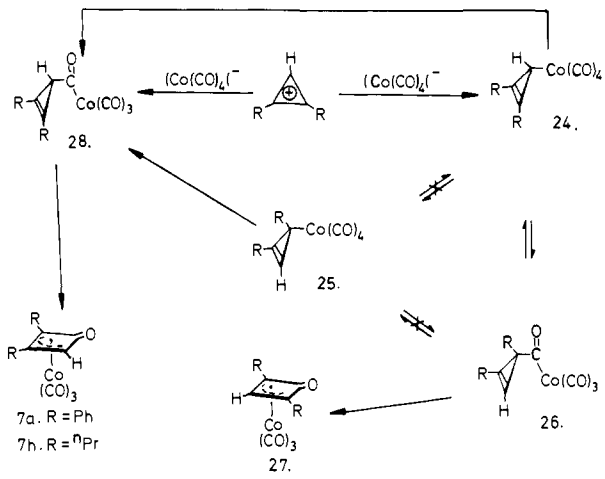
(36) Tuggle, R. M.; Weaver, D. L. *J. Am. Chem. Soc.* **1970**, *92*, 5523–5524; *Inorg. Chem.* **1972**, *11*, 2237–2242.

(37) Frisch, P. D.; Khare, G. P. *Inorg. Chem.* **1979**, *18*, 781–786.

(38) Jemmis, E. D.; Hoffmann, R. *J. Am. Chem. Soc.* **1980**, *102*, 2570–2575.

(39) This suggestion had been made previously for a system where attack at the metal was thought to be precluded by steric effects.[10]

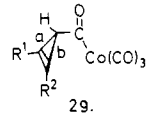
Scheme IV



when the alkyl group is as bulky as *t*-Bu. This has interesting ramifications when the mechanism of formation of **7a** and **7h** as the *exclusive* products of the respective reactions of the diphenyl- and di-*n*-propylcyclopropenium cations with $[Co(CO)_4]^-$ is considered. As discussed above and as found in practice,[4,31,32] attack by nucleophiles should occur at the unsubstituted ring position. If the nucleophilic center is the cobalt atom in this case, such attack should afford **24** as shown in Scheme IV; **24** should be non fluxional with respect to isomerization to **25**.[2] Furthermore, cyclopropenyl migration from cobalt to CO should occur with allylic rearrangement, to give the acyl **26**; notably the reverse reaction should be regiospecific and return to **24** rather than to **25**.[2] Acyl intermediate **26** should undergo selective ring cleavage adjacent to R (at least when R = *n*-Pr) to give **27** as the exclusive, or major, product, a result which is not observed. The only acyl which can afford the observed products is **28**, therefore, and we are forced to conclude either that **28** is formed directly from **24**, an unlikely prospect in view of other results,[2] or *that the site of electrophilic attack by the cation on the* $[Co(CO)_4]^-$ *anion is not at cobalt but rather at CO.* This latter path has been suggested for a related system,[39] but we feel that the results presented here provide experimental evidence for such a pathway. Notably this cannot be true for all metal carbonyl anions; for example, $[Fe(CO)_2(\eta\text{-}C_5H_5)]^-$ reacts with the diphenylcyclopropenium cation to give a product resulting from electrophilic attack at Fe.[4]

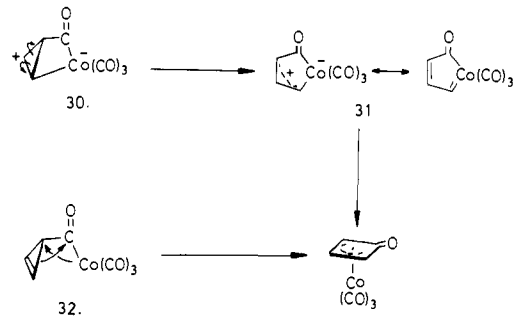
In summary, there is no evidence for the formation of η^1-cyclopropenyl intermediates in the reactions of cyclopropenium cations or 2-cyclopropene-1-carbonyl chlorides with $[Co(CO)_4]^-$; all the results described above can be explained in terms of a coordinatively unsaturated (2-cyclopropen-1-ylcarbonyl)tricarbonylcobalt complex in equilibrium with $[Co(CO)_4]^-$ and a cyclopropenium cation. Further circumstantial evidence against the intermediacy of (η^1-cyclopropenyl)cobalt compounds rests in the expectation that such complexes should collapse readily to the η^3-cyclopropenyl analogues;[40] no evidence for any of these compounds has been found here. It is interesting to speculate that the formation of both (η^3-cyclopropenyl) and (η^3-oxocyclobutenyl)cobalt compounds in the reaction of the triphenylcyclopropenium cation with neutral $[Co_2(CO)_8]$[9] may involve competition between electrophilic attack at cobalt and at CO.

Having established the coordinatively unsaturated (2-cyclopropen-1-ylcarbonyl)tricarbonylcobalt intermediates **29** as the



crucial precursors to η^3-oxocyclobutenyl products, the effects of ring substituents on the site of C–C bond cleavage in the cyclopropene ring of such species should be discussed. We have already noted that in **29** (R^1 = *t*-Bu, *n*-Bu, *i*-Pr; R^2 = H) there is a marked preference for cleavage of bond a, adjacent to the alkyl group, over bond b, adjacent to H. The products arising from **29** (R^1 = Ph; R^2 = Me) demonstrate only a slight preference for cleavage adjacent to Me (bond b) rather than adjacent to Ph (bond a); notably substitution of one CO ligand by PPh_3 in this intermediate does not effect a major change in this reaction. In a surprising contrast, intermediate **29** (R^1 = Ph; R^2 = *t*-Bu) shows a significant selectivity for cleavage at bond b rather than at bond a. Thus, there seems to be no obvious systematic steric control of reaction selectivity. Introduction of a remote electron-donating substituent on the phenyl ring also has no effect on the selectivity of bond cleavage; **29** (R^1 = Ph; R^2 = *p*-$MeOC_6H_4$) exhibits no selectivity at all, and **29** (R^1 = *p*-$MeOC_6H_4$; R^2 = Me) shows the same selectivity as **29** (R^1 = Ph; R^2 = Me) in the same solvent (vide supra).

Our results allow the exlcusion of some possible mechanisms for the ring expansion step. Generation of a zwitterionic intermediate or transition state **30** by interaction of cobalt with the



olefin should show pronounced selectivity in aryl–alkyl-substituted cyclopropenes;[41] *p*-MeO substituents should also make their presence felt. Ring opening of such a species by an allowed disrotatory process[44] would afford the achiral metallacycle **31**, destroying chirality. The concerted 1,2-shift mechanism proposed by Green,[11] and depicted as **32**, has the advantage of maintaining chirality but does not appear to require participation by the double bond. Furthermore, consideration of migratory aptitudes based on the anticipated bond strengths within the cyclopropene ring would imply that cleavage adjacent to aryl should be preferred over cleavage adjacent to alkyl.[45] In actual fact the reverse preference is observed. An alternative pathway is suggested by the known thermal, photochemical, and transition-metal chemistry of cyclopropenes.

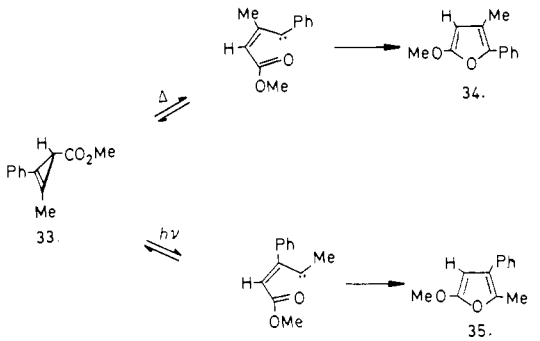
Thermal and photochemical ring openings of cyclopropenes afford vinylcarbene intermediates, in a reversible reaction, and many examples of the trapping of these species have been reported.[31,32,47-53] Substituent effects on the selectivity of vinyl-

(40) Acyclic η^1-allyl compounds of cobalt undergo extremely facile decarbonylation reactions to give the corresponding η^3-allyl analogues.[18,25]

(41) Ag^+-promoted ring-opening reactions of cyclopropenes have been shown to involve silver-stabilized carbonium ion intermediates[42,43] and exhibit pronounced selectivity for cleavage adjacent to phenyl rather than alkyl substituents.[43]

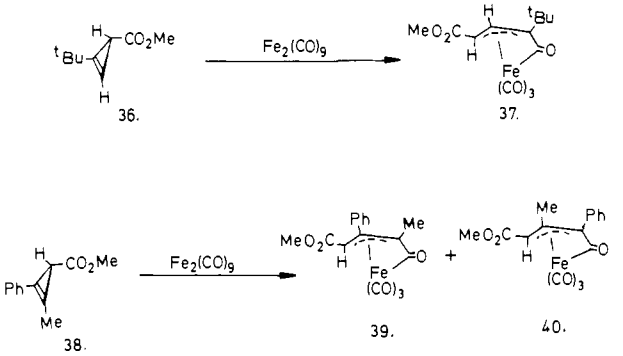
(42) Leftin, J. H.; Gil-Av, E. *Tetrahedron Lett.* **1972**, 3367–3369.
(43) Padwa, A.; Blacklock, T. J.; Loza, R. *J. Am. Chem. Soc.* **1981**, *103*, 2404–2405.
(44) Woodward, R. B.; Hoffmann, R. "The Conservation of Orbital Symmetry"; Academic Press: New York, 1970.
(45) Compilations of X-ray crystallographic data show that, compared to $C(sp^3)$ or H, a phenyl group attached to a cyclopropane ring will shorten the distal ring bond;[46] with the assumption that bond length is inversely related to bond strength for closely related compounds, this would predict that the weaker C–C bond would be adjacent to phenyl rather than opposite phenyl.
(46) Allen, F. H. *Acta Crystallogr., Sect. B* **1980**, *36*, 81–96.
(47) Battiste, M. A.; Halton, B.; Grubbs, R. H. *J. Chem. Soc., Chem. Commun.* **1967**, 907–909.
(48) Pincock, J. A.; Moutsokapas, A. *Can. J. Chem.* **1977**, *55*, 979–985.
(49) Komendantov, M. I.; Domnin, I. N.; Bulueheva, E. V. *Tetrahedron* **1975**, *31*, 2495–2497. This is a $CuSO_4$-promoted reaction, and the role of the metal is uncertain.
(50) van Tamelen, E. E.; Whitesides, T. H. *J. Am. Chem. Soc.* **1968**, *90*, 3894–3896; *Ibid.* **1971**, *93*, 6129–6140.

carbene formation depend upon whether thermal or photochemical activation is used, as exemplified by the reactions of ester **33** to give furans **34**[49] or **35**.[48] In thermal processes, the vinylcarbene



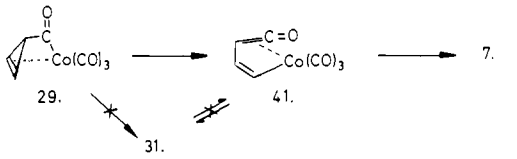
is formed by collapse of a diradical,[52] whereas the vinylcarbene formed photochemically results from collapse of the π,π^* singlet excited state of the cyclopropene.[32] The origins of the differing substituent effects in these systems remain controversial. Our cobalt-promoted C–C cleavage reactions appear to parallel the photochemical rather than thermal pathway in that cleavage adjacent to alkyl rather than aryl is obtained.

Reactions of cyclopropenes with $[Fe_2(CO)_9]$ afford η^4-vinylketene complexes,[54-56] via the probable intermediacy of vinylcarbene compounds which then insert CO.[57] We have shown that in two instances, the selectivity for C–C bond cleavage in this reaction parallels the cobalt systems described above. Ester **36** reacts with $[Fe_2(CO)_9]$ to give only **37**, resulting from cyclopropene



cleavage adjacent to *t*-Bu; **38** affords an equimolar mixture of **39** and **40** under the same conditions.[58,59] The similarities in selectivity are notable and suggest an analogous mechanism for iron- and cobalt-promoted ring openings.

We suggest that interaction of the cyclopropene olefin with cobalt in intermediate **29** leads to a transition state which resembles that for the photochemical ring openings of cyclopropenes. The developing carbene center in this transition state would be stabilized by the metal center.[60] This transition state cannot collapse to planar **31** (vide supra) but could afford a nonplanar valance isomer **41**, in which chirality is maintained. Both free[61,62]



and coordinated[63,64] vinylketenes are known to ring close to give cyclobutenones; analogous closure of **41** would afford the observed products. Attempts to trap a vinylketene intermediate by allowing the ring expansion of **9** to occur in the presence of MeOH were unsuccessful; this cannot be construed as evidence against the intermediacy of **41** because the coordinated vinylketene in **37** is unreactive toward MeOH.[58]

Concluding Remarks

Some major obstacles to a complete understanding of the mechanism of formation of oxocyclobutenyl complexes remain. The origins of ring substituent effects on C–C bond cleavage are obscure, as they are in simple cyclopropenes, although metal-promoted reactions parallel photochemical rather than thermal behavior. It is unclear why coordinatively unsaturated (2-cyclopropen-1-ylcarbonyl)cobalt compounds afford only oxocyclobutenyl compounds, with no evidence of cyclopropenyl migration to the metal, whereas the rhenium analogues follow the latter pathway exclusively. Finally, it is not apparent why cyclopropenium cations should attack $[Fe(CO)_2(\eta\text{-}C_5H_5)]^-$ at the metal, $[M(CO)_3(\eta\text{-}C_5H_5)]^-$ (M = Mo, W) at the $\eta\text{-}C_5H_5$ ring,[10] and $[Co(CO)_4]^-$ at a CO ligand. Further studies aimed at elucidating these anomalies are in progress.

Experimental Section

General Data. All IR spectra were recorded on a Perkin-Elmer 257 or 599 spectrophotometer and calibrated against the 1601-cm^{-1} peak of polystyrene. All 60-MHz ^1H NMR and 15-MHz $^{13}C\{^1H\}$ NMR spectra were recorded on either a Perkin-Elmer R-24 or a JEOL FX60Q Fourier Transform spectrometer; chemical shifts are reported in parts per million downfield from tetramethylsilane and coupling constants are reported in hertz. All 270-MHz ^1H NMR spectra were recorded on a Bruker NMR spectrometer at the Yale University NSF-NMR Regional Facility, New Haven, Conn. All routine mass spectra were recorded on a Finnegan 4023 mass spectrometer. High-resolution mass spectra were obtained from the Massachusetts Institute of Technology Regional Mass Spectroscopy Facility, Cambridge, Mass. Chemical ionization mass spectra were obtained at the Johns Hopkins Regional Mass Spectroscopy Facility, Baltimore, Md. Microanalyses were sent to Spang, Eagle Harbor, Mich. Melting points were obtained by using an electrothermal capillary melting point apparatus and are uncorrected.

Tetrahydrofuran (THF), benzene, hexanes, and diethyl ether were dried by distillation from sodium benzophenone ketyl. Methylene chloride and acetonitrile were both dried by distillation from P_4O_{10}. All organometallic reactions were run in oven-dried glassware under an atmosphere of nitrogen (Airco).

Organic Starting Materials. Ethyl diazoacetate,[65] methyl diazoacetate,[65] methylphenyl diazoacetate,[66] 1-(4-methoxyphenyl)-2-phenylacetylene,[67] 3,3-dimethyl-1-phenyl-1-butyne,[68] 3,3-dimethyl-1-(trimethylsilyl)-1-butyne,[69] and 1-(4-methoxyphenyl)-1-propyne[70] were prepared by literature procedures. 3-Hexyne, 4-octyne, 3-methyl-1-butyne, 1-(trimethylsilyl)-1-propyne, and 1-phenyl-1-propyne were obtained from Farchan Chemical Co. and were used without further purification. Methyl 2,3-diethyl-2-cyclopropene-1-carboxylate,[71] ethyl 2-methyl-3-

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(57) Mitsudo, T.; Sasaki, T.; Watanabe, Y.; Takegani, Y.; Nishigaki, S.; Nakatsu, K. *J. Chem. Soc., Chem. Commun.* **1978**, 252–254.
(58) Hughes, R. P.; Lambert, J. M. J., unpublished observations.
(59) The reaction of 1,3,3-trimethylcyclopropene with $[Fe_2(CO)_9]$ also shows selectivity for C–C cleavage adjacent to Me.[54]
(60) Even though cyclopropenes are highly strained, considerable activation energy (ca. 43 kcal·mol^{-1}) is required for ring opening, and the singlet vinylcarbene intermediate has been calculated to lie 36.6 kcal·mol^{-1} above the cyclopropene ground state.[53] Clearly, in order for the cobalt-promoted ring openings to occur at ambient temperatures, considerable transition-state stabilization by the metal must occur.
(61) Jenny, E. F.; Roberts, J. D. *J. am. Chem. Soc.* **1956**, *78*, 2005–2009.
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(70) Thigpen, A. B., Jr.; Fuchs, R. *J. Org. Chem.* **1969**, *34*, 505–509.

phenyl-2-cyclopropene-1-carboxylate,[70] methyl 2-*tert*-butyl-2-cyclopropene-1-carboxylate,[71] and methyl 2-*n*-butyl-2-cyclopropene-1-carboxylate[71] were prepared by literature methods.

Methyl 2,3-Di-*n*-propyl-2-cyclopropene-1-carboxylate. To a sample of 4-octyne (6.60 g, 60 mmol) and a catalytic amount of rhodium acetate (~0.05 g) was added dropwise a solution of 4-octyne (6.60 g, 60 mmol) and methyl diazoacetate (6.0 g, 60 mmol) over a period of 8 h at room temperature. The reaction mixture was filtered through filter-aid under positive pressure, and the resultant yellow solution was distilled under high vacuum into a cooled (−78 °C) receiver flask. The first fraction was recovered without heating and was found to be unreacted 4-octyne. Further distillation yielded the product as a clear oil: 27 °C (0.1 mmHg); 2.68 g, 16% yield; ^{1}H NMR ($CDCl_3$) δ 0.95 (t, J = 7 Hz, 6 H, CH_3), 1.55 (m, 4 H, CH_2), 2.05 (s, 1 H, CH), 2.40 (t, J = 7 Hz, 4 H, CH_2), 3.65 (s, 3 H, OCH_3).

Methyl 2-Methyl-1-phenyl-3-(trimethylsilyl)-2-cyclopropene-1-carboxylate. To a sample of 1-(trimethylsilyl)-1-propyne (6.90 g, 61.4 mmol) heated to 130 °C was added dropwise a solution of 1-(trimethylsilyl)-1-propyne (6.81 g, 60.6 mmol) and methylphenyl diazoacetate (6.97 g, 39.6 mmol) over a period of 4 h. Crystals of dimethyl stilbene-1,2-dicarboxylate (identified by ^{1}H NMR and IR spectroscopy) began to form upon slow cooling and were removed by filtration under positive pressure. The remaining brown liquid was distilled under aspirator pressure at room temperature, and a sample of 1-(trimethylsilyl)-1-propyne (5.53 g, 49.2 mmol) was recovered in a cooled (−78 °C) receiving flask. Distillation under high vacuum (82 °C (0.01 mmHg)) afforded the product as an orange oil (1.56 g, 5.99 mmol, 15% yield based on methylphenyl diazoacetate): IR (neat) 1830 ($\nu_{C=C}$), 1710 ($\nu_{C=O}$), 1250, 1200 cm^{-1} (ν_{Si-Me}); ^{1}H NMR ($CDCl_3$) δ 0.20 (s, 9 H, $SiMe_3$), 2.20 (s, 3 H, CMe), 3.53 (s, 3 H, OMe), 7.0–8.0 (m, 5 H, C_6H_5). This ester was hydrolyzed in aqueous base with cleavage of the Me_3Si group, to give 2-methyl-1-phenyl-2-cyclopropene-1-carboxylic acid (see below).

Methyl 2-*tert*-butyl-1-phenyl-3-(trimethylsilyl)-2-cyclopropene-1-carboxylate was prepared by the reaction of 3,3-dimethyl-1-(trimethylsilyl)-1-butyne with methylphenyl diazoacetate at 130 °C in a manner similar to that described above. The product was obtained from distillation (70 °C (0.02 mmHg)) of the reaction mixture as a yellow oil in 16% yield based on consumed 3,3-dimethyl-1-(trimethylsilyl)-1-butyne: IR (neat) 1825 ($\nu_{C=C}$), 1720 ($\nu_{C=O}$), 1250, 1200 cm^{-1} (ν_{Si-Me}); ^{1}H NMR ($CDCl_3$) δ 0.25 (s, 9 H, $SiMe_3$), 1.1 (s, 9 H, CMe_3), 3.60 (s, 3 H, OCH_3), 7.1–7.4 (m, 5 H, C_6H_5). This ester was hydrolyzed in aqueous base with cleavage of the Me_3Si group, to give 2-*tert*-butyl-1-phenyl-2-cyclopropene-1-carboxylic acid (see below).

Ethyl 2-*tert*-Butyl-3-phenyl-2-cyclopropene-1-carboxylate. To a sample of 3,3-dimethyl-1-phenyl-1-butyne (15.33 g, 97.0 mmol) and a catalytic amount of anhydrous copper(II) sulfate (0.05 g) heated at 120 °C was added dropwise a solution of 3,3-dimethyl-1-phenyl-1-butyne (15.00 g, 94.9 mmol) and ethyl diazoacetate (10.03 g, 88.0 mmol) over a period of 12 h. The reaction mixture was allowed to cool, filtered to remove the catalyst, and distilled under high vacuum. The first fraction (40 °C (0.02 mmHg); 27.41 g) was identified as unreacted 3,3-dimethyl-1-phenyl-1-butyne by ^{1}H NMR spectroscopy. The second fraction (80 °C (0.009 mmHg))yielded the product as a clear oil: 1.23 g, 5.02 mmol, 27% yield based on consumed 3,3-dimethyl-1-phenyl-1-butyne; IR (neat) 1880 ($\nu_{C=C}$), 1725 cm^{-1} ($\nu_{C=O}$); ^{1}H NMR ($CDCl_3$) δ 1.20 (t, J = 7 Hz, 3 H, CH_3), 1.30 (s, 9 H, CMe_3), 2.40 (s, 1 H, CH), 4.05 (q, J = 7 Hz, 2 H, OCH_2), 7.1–7.5 (m, 5 H, C_6H_5).

Methyl 2-isopropyl-2-cyclopropene-1-carboxylate was prepared from the reaction of 3-methyl-1-butyne with methyl diazoacetate in the presence of rhodium acetate catalyst in a manner similar to that described above. The reaction flask was fitted with a CCl_4/liquid N_2 slush condensor (−23 °C) to prevent loss of the volatile 3-methyl-1-butyne. Distillation of the reaction mixture at aspirator pressure, and room temperature, afforded unreacted 3-methyl-1-butyne. Distillation of the residue under high vacuum (22 °C (0.26 mmHg)) afforded the product as a clear liquid in 63% yield based on the amount of methyl diazoacetate used: ^{1}H NMR ($CDCl_3$) δ 1.20 (d, J = 7 Hz, 6 H, $CHMe_2$), 2.20 (d, J = 1 Hz, 1 H, CH), 2.85 (m, 1 H, $CHMe_2$), 3.65 (s, 3 H, OCH_3), 6.30 (dd, J = 1 Hz, 1 Hz, 1 H, C=CH).

2,3-Diphenyl-2-cyclopropene-1-carboxylic acid was prepared by the literature procedure[72] using the modifications described below.

2-(4-Methoxyphenyl)-3-phenyl-2-cyclopropene-1-carboxylic Acid. To a melt of 2-(4-methoxyphenyl)-1-phenylacetylene (26.7 g, 133.0 mmol) containing copper dust (~1.0 g) at 110 °C was added dropwise a solution of ethyl diazoacetate (7.55 g, 66.5 mmol) in cyclohexane (100 mL) over a period of 9 h. The cyclohexane was removed from the reaction mixture continuously by means of a distillation head attached to the reaction flask. The reaction was allowed to stir for an additional hour and cooled to room temperature, and the copper dust was removed by filtration through filter-aid. The filter bed was washed with ether (2 × 50 mL), the organic layers were combined, and the ether was removed under reduced pressure to afford a brown oily residue. The residue was dissolved in a solution of methanolic potassium hydroxide (200 mL of MeOH/30 g of KOH), and solution was brought to reflux for 1 h. The reaction mixture was poured into cold H_2O (300 mL) and extracted with $CHCl_3$ (3 × 10 mL) in order to recover the unreacted 2-(4-methoxyphenyl)-1-phenylacetylene. The aqueous layer was acidified with concentrated HCl to pH 4. The resultant brown precipitate was extracted with $CHCl_3$ (3 × 100 mL), the extracts were combined, and the $CHCl_3$ was removed under reduced pressure to afford a yellow solid which was recrystallized from CCl_4 (30 mL) to yield the product as white crystals: 4.05 g, 64% yield based on consumed 2-(4-methoxyphenyl)-1-phenylacetylene: mp 178–180 °C (lit.[73] mp 179.5–181.5 °C).

2-(4-Methoxyphenyl)-3-methyl-2-cyclopropene-1-carboxylic Acid. To a sample of 1-(4-methoxyphenyl)-1-propyne (9.30 g, 63.7 mmol) containing a catalytic amount of rhodium acetate (0.05 g) was added dropwise a solution of 1-(4-methoxyphenyl)-1-propyne (9.30 g, 63.7 mmol) and methyl diazoacetate (6.03 g, 60.3 mmol) over a period of 4 h. The reaction was allowed to stir overnight, and the resultant greenish yellow solution was distilled under high vacuum to recover unreacted 1-(4-methoxyphenyl)-1-propyne (40–50 °C (0.05 mmHg); 12.34 g). The residue was hydrolyzed by stirring for 24 h in 0.2 M aqueous potassium hydroxide (90 mL). The reaction mixture was neutralized with dilute HCl to pH 7, CH_2Cl_2 (50 mL) was added, and the mixture was further acidified to pH 2. The CH_2Cl_2 layer was separated, and the aqueous layer was extracted once with CH_2Cl_2 (50 mL). The methylene chloride phases were combined, dried over $MgSO_4$, and filtered, and the solvent was removed under reduced pressure to afford a crystalline product. The crystals were washed once with diethyl ether (30 mL) and dried in vacuo to afford the product as a white crystalline solid: 1.54 g, 18% yield based on consumed 1-(4-methoxyphenyl)-1-propyne; mp 117–118 °C (lit.[70] mp 116.2–117.4 °C).

2-Methyl-3-phenyl-2-cyclopropene-1-carboxylic acid was prepared by the reaction of 1-phenyl-1-propyne and methyl diazoacetate in the presence of rhodium acetate catalyst, followed by hydrolysis with 0.2 M aqueous potassium hydroxide, according to the method of Domnin et al.[74] in 18% yield based on the amount of methyl diazoacetate used. Alternatively, the same compound was prepared by the hydrolysis of ethyl 2-methyl-3-phenyl-2-cyclopropene-1-carboxylate in 46% yield (mp 132–134 °C (lit.[70] mp 137.2–137.9 °C)).

General Procedure for 2-Cyclopropene-1-carboxylate Ester Hydrolyses with 0.2 M Aqueous Potassium Hydroxide. The neat 2-cyclopropene-1-carboxylate ester (10 mmol) was added to a stirring 0.2 M aqueous potassium hydroxide solution (200 mL, 0.2 M). The reaction was allowed to stir until most of the emulsion had dissolved (1–4 days), and then the aqueous solution was extracted once with diethyl ether (100 mL). The aqueous layer was neutralized with dilute HCl to ~pH 7, CH_2Cl_2 (100 mL) was added, and the mixture was further acidified to pH 2 with dilute HCl. The CH_2Cl_2 layer was separated, and the aqueous layer was extracted once with CH_2Cl_2 (50 mL). The methylene chloride layers were combined, dried over $MgSO_4$, and filtered, and the solvent was removed under reduced pressure to yield the product.

The following were prepared in this manner.

2,3-Diethyl-2-cyclopropene-1-carboxylic acid: 88%; mp 45–46 °C (lit.[75] mp 44 °C).

2,3-Di-*n*-propyl-2-cyclopropene-1-carboxylic acid: 39%; ^{1}H NMR data identical with literature values.[76]

2-Methyl-1-phenyl-2-cyclopropene-1-carboxylic acid: 81%; mp 62–66 °C; ^{1}H NMR ($CDCl_3$) δ 2.25 (d, J = 1.5 Hz, 3 H, C=Me), 6.60 (q, J = 1.5 Hz, 1 H, C=CH), 7.0–8.0 (m, 5 H, C_6H_5). Anal. C, H.

2-*tert*-Butyl-1-phenyl-2-cyclopropene-1-carboxylic acid: 55%; mp 132–134 °C; ^{1}H NMR ($CDCl_3$) δ 1.15 (s, 9 H, CMe_3), 6.55 (s, 1 H, C=CH), 7.1–7.5 (m, 5 H, C_6H_5); high-resolution mass spectrum, m/e(calcd) 216.1150, m/e(obsd) 216.1174.

2-*tert*-Butyl-3-phenyl-2-cyclopropene-1-carboxylic acid: 65%; mp 110–111 °C from Et_2O; ^{1}H NMR ($CDCl_3$) δ 1.35 (s, 9 H, CMe_3), 2.40

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(s, 1 H, CH), 7.2–7.6 (m, 5 H, C_6H_5), 9.60 (s, 1 H, CO_2H). Anal. C, H.

2-*tert*-Butyl-2-cyclopropene-1-carboxylic acid: 92%; mp 41–42 °C (lit.[77] mp 41.5 °C).

2-*n*-Butyl-2-cyclopropene-1-carboxylic acid: 70%; pale yellow oil; ^1H NMR data identical with literature data.[78]

2-Isopropyl-2-cyclopropene-1-carboxylic acid: 81%; pale yellow oil; ^1H NMR data identical with literature data.[79]

2-*tert*-Butyl-3-deuterio-2-cyclopropene-1-carboxylic acid and **2-*n*-butyl-3-deuterio-2-cyclopropene-1-carboxylic acid** were prepared by literature procedures.[80]

Carboxylic acids were converted to acid chlorides by using thionyl chloride (method A)[81] or by stirring the neat carboxylic acid in a 2–3-fold excess of oxalyl chloride followed by pumping off excess oxalyl chloride (method B). Yields obtained by the latter method were essentially quantitative. Unless otherwise stated, products were obtained as colorless oils.

The following were prepared in this way.

2,3-Diphenyl-2-cyclopropene-1-carbonyl chloride (6a; method A): 90%; mp 101–103 °C from toluene (lit.[81] mp 101–102 °C).

2,3-Diethyl-2-cyclopropene-1-carbonyl chloride (6b; method B): ^1H NMR ($CDCl_3$) δ 1.20 (t, 6 H, CH_3), 2.50 (s, 1 H, CH), 2.50 (q, 4 H, CH_2CH_3).

2-Methyl-3-phenyl-2-cyclopropene-1-carbonyl chloride (6c; method B): ^1H NMR ($CDCl_3$) δ 2.27 (s, 3 H, CH_3), 2.82 (s, 1 H, CH), 7.38 (m, 5 H, C_6H_5).

2-Methyl-1-phenyl-2-cyclopropene-1-carbonyl chloride (6d; method B): ^1H NMR ($CDCl_3$) δ 2.25 (d, J = 1.5 Hz, 3 H, CH_3), 6.75 (q, J = 1.5 Hz, 1 H, C=CH), 7.8–8.0 (m, 5 H, C_6H_5).

2-*tert*-Butyl-1-phenyl-2-cyclopropene-1-carbonyl chloride (6e; method B): ^1H NMR ($CDCl_3$) δ 1.10 (s, 9 H, CMe_3), 6.60 (s, 1 H, C=CH), 7.15 (s, 5 H, C_6H_5).

2-*tert*-Butyl-3-phenyl-2-cyclopropene-1-carbonyl chloride (6f; method B): ^1H NMR ($CDCl_3$) δ 1.35 (s, 9 H, CMe_3), 2.90 (s, 1 H, CH), 7.2–7.4 (m, 5 H, C_6H_5).

2-(4-Methoxyphenyl)-3-phenyl-2-cyclopropene-1-carbonyl chloride (6g; method A): 83%; mp 92–96 °C; ^1H NMR ($CDCl_3$) δ 3.23 (s, 1 H, CH), 3.87 (s, 3 H, OCH_3), 7.33 (ABq, 4 H, $C_6H_4OCH_3$), 7.5 (m, 5 H, C_6H_5).

2-(4-Methoxyphenyl)-3-methyl-2-cyclopropene-1-carbonyl chloride (6h; method A): 95%; oil; ^1H NMR ($CDCl_3$) δ 2.30 (s, 3 H, C=CCH_3), 2.85 (s, 1 H, CH), 3.75 (s, 3 H, OCH_3), 7.15 (ABq, 4 H, $C_6H_4OCH_3$).

2-*tert*-Butyl-2-cyclopropene-1-carbonyl chloride (6i; method B): ^1H NMR ($CDCl_3$) δ 1.25 (s, 9 H, CMe_3), 2.65 (d, 1 H, CH), 6.40 (d, 1 H, C=CH).

2-*tert*-Butyl-3-deuterio-2-cyclopropene-1-carbonyl chloride (6j; method B): ^1H NMR ($CDCl_3$) δ 1.25 (s, 9 H, CMe_3), 2.65 (s, 1 H, CH).

2-*n*-Butyl-2-cyclopropene-1-carbonyl chloride (6k; method B): ^1H NMR ($CDCl_3$) δ 0.90 (t, 3 H, CH_3), 1.50 (m, 4 H, CH_2CH_2), 2.50 (d, 1 H, CH), 2.50 (m, 2 H, CH_2CH_2), 6.40 (d, 1 H, C=CH).

2-*n*-Butyl-3-deuterio-2-cyclopropene-1-carbonyl chloride (6l; method B): ^1H NMR ($CDCl_3$) δ 0.95 (t, 3 H, CH_3), 1.15 (m, 4 H, CH_2CH_2), 2.60 (s, 1 H, CH), 2.60 (m, 2 H, CH_2).

2-Isopropyl-2-cyclopropene-1-carbonyl chloride (6m; method B): ^1H NMR ($CDCl_3$) δ 1.15 (d, J = 7 Hz, 6 H, $CHMe_2$), 2.60 (d, 1 H, CH), 2.85 (m, 1 H, $CHMe_2$), 6.45 (m, 1 H, C=CH).

Diphenylcyclopropenium perchlorate was prepared by a modification of the literature procedure.[82] 2,3-Diphenyl-2-cyclopropene-1-carboxylic acid (1.00 g, 4.23 mmol) was treated with $HClO_4$ in Ac_2O (25 mL of a 10% solution) at 0 °C. Gas was evolved, and after 3 min the brown reaction mixture was poured into cold (0 °C) anhydrous Et_2O (700 mL). The tan precipitate was filtered and washed with cold anhydrous Et_2O (2 × 50 mL) to afford the product: 59%; mp 150 °C dec violently: (lit.[82] mp 149.5–150.5 °C dec).

Di-*n*-propylcyclopropenium perchlorate was prepared in an analogous fashion from the appropriate carboxylic acid: 41%; mp 80 °C detonates: (lit.[83] mp 79 °C).

Methylphenylcyclopropenium perchlorate was prepared in an analogous fashion from 2-methyl-3-phenyl-2-cyclopropene-1-carboxylic acid: 78%; mp 150 °C detonates; IR (Nujol) 2950 (s), 2000 (w), 1800 (m), 1080 (s), 770 (s), 680 (s), 620 (s) cm^{-1}; ^1H NMR (acetone-d_6) δ 2.00 (s, 3 H, CH_3), 7.0–8.0 (m, 5 H, C_6H_5) (ring proton not observable)].

Organocobalt Starting Materials. Octacarbonyldicobalt was obtained from the Pressure Chemical Co. Hexacarbonylbis(triethylphosphine)-dicobalt,[84] hexacarbonylbis(dimethylphenylphosphine)dicobalt,[84] hexacarbonylbis(triphenylphosphine)dicobalt,[84] and iododicarbonylbis(triphenylphosphine)cobalt[85] were prepared by literature methods. ^{13}CO-enriched octacarbonyldicobalt was prepared by a modification of the method used to prepare the ^{14}CO-enriched analogue,[86] using 90% ^{13}CO (Stohler Isotope Co). IR analysis of the product indicated that ca. 50% ^{13}CO enrichment was achieved.

Preparations of $[Co(CO)_4]^-$. Method A. A sodium amalgam was prepared by reacting sodium metal (~2.5 molar equiv) with a stirring pool of mercury under N_2. To the amalgam was added a dark brown solution of $[Co_2(CO)_8]$ (1 molar equiv) in dry THF (50–100 mL). The dimer solution was allowed to stir under N_2 for 2–4 h or until the solution had turned colorless. The excess sodium amalgam and mercury were removed by means of a stopcock attached to the reaction flask, and the anion solution was filtered through filter-aid, under N_2, into a Schlenk flask. The filter bed was washed once with dry THF (30 mL), under N_2, and the washings were filtered into the Schlenk flask. The tetracarbonylcobaltate(1−) anion was usually obtained as a pale yellow solution (~2 molar equiv).

Method B. To a stirring, dark brown solution of $[Co_2(CO)_8]$ (1 molar equiv) in dry THF (50–100 mL) under N_2 was added $Na_{2.8}K$ alloy (~2.5 molar equiv) via a syringe. The mixture was allowed to stir for 1–2 h or until the solution had turned colorless. (*Caution*! $Na_{2.8}K$ alloy is spontaneously flammable in moist air.) The anion solution was filtered through filter-aid, under N_2, into a Schlenk flask, and the filter bed was washed once with dry THF (30 mL). The tetracarbonylcobaltate(1−) anion was afforded as a pale yellow solution (2.0 molar equiv).

Method C. To a sample of solid $[Co_2(CO)_8]$ (1 molar equiv) in a dry Schlenk flask, under N_2, was added dry acetonitrile (~10 mL of CH_3CN/1 g of $[Co_2(CO)_8]$). (*Caution*! The resultant disproportionation of $[Co_2(CO)_8]$ in acetonitrile liberates carbon monoxide gas.) The dark brown, bubbling solution was allowed to stir for ca. 1 h until it had turned a dark pink color. This method afforded the tetracarbonylcobaltate(1−) anion in 1.33 molar equiv as shown by eq 1.[9]

$$3[Co_2(CO)_8] \xrightarrow{CH_3CN} 4[Co(CO)_4]^- + 2[Co(CH_3CN)_x]^{2+} + 8CO$$

Phosphine-substituted anions $[Co(CO)_3L]^-$ (L = PPh_3, PMe_2Ph, PEt_3) were obtained from the appropriate dimer by method A.

Reaction of 2,3-Diphenyl-2-cyclopropene-1-carbonyl Chloride (6a) with $[Co(CO)_4]^-$. A THF solution (100 mL) of tetracarbonylcobaltate(1−) anion (17.5 mmol) was prepared from $[Co_2(CO)_8]$ (2.99 g, 8.75 mmol) by using method A. The anion solution was cooled to −78 °C, and a solution of 2,3-diphenyl-2-cyclopropene-1-carbonyl chloride (4.35 g, 17.1 mmol) in dry THF (75 mL) was added dropwise, under N_2. The reaction mixture was allowed to warm to room temperature and stirred for 24 h. The solvent was removed under reduced pressure, and the brown oily residue was taken up in $CHCl_3$ (100 mL) and filtered through filter-aid. The solvent was again removed under reduced pressure, and the brown oily residue was taken up in a minimal amount of CH_2Cl_2 and applied to a 20 in. × 1 in. Florisil column made with hexanes. The product was eluted with Et_2O/hexanes (3:1) as a golden yellow band. The solvent was removed under reduced pressure, and the yellow residue was recrystallized from CH_2Cl_2/hexanes to afford (η^3-1-oxo-2,3-diphenylcyclobutenyl)tricarbonylcobalt(I) (**7a**) as analytically pure, yellow, air-stable crystals (2.46 g, 10.9 mmol, 64%) (physical and spectral data are given Tables I–IV).

Alternatively, a CH_3CN solution of the tetracarbonylcobaltate(1−) anion (47.5 mmol) was prepared from $[Co_2(CO)_8]$ (12.2 g, 35.7 mmol) by method C. The solution was cooled to −30 °C, and a solution of **6a** (9.07 g, 35.7 mmol) in dry CH_3CN (50 mL) was added dropwise. The reaction mixture was allowed to warm to room temperature and stir for 48 h. The dark emerald green solution was evaporated to an oily residue under reduced pressure. The residue was taken up in a minimal amount of CH_2Cl_2 and applied to a 15 in. × 1.5 in. Florisil column made in hexanes. Elution with hexanes afforded a black band which, upon evaporation of the solvent, yielded a fine, air-sensitive, black powder (2.90 g). The infrared spectrum of the black powder indicated that it was $[Co_4(CO)_{12}]$ (2061 (s), 2053 (s), 2035 (w), 2023 (w), 1865 (m) cm^{-1} (cyclohexane), identical with IR spectral data given ref 87). Elution

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with Et_2O/hexanes (3:1) afforded a yellow band which, upon evaporation of the solvent, yielded the product **7a** as a yellow crystalline compound (10.41 g, 78%). This method of preparation appears to proceed more cleanly and to give higher yield than the former reaction.

Reaction of 6a with Tricarbonyl(triethylphosphine)cobaltate(1−) Anion. A solution of $[Co(CO)_3(PEt_3)]^-$ (5.98 mmol) in dry THF (75 mL) was prepared by the reduction of $[Co_2(CO)_6(PEt_3)_2]$ (1.56 g, 2.99 mmol) with sodium amalgam in a manner similar to method A. The anion solution was cooled to −78 °C, and a solution of **6a** (1.52 g, 5.98 mmol) in dry THF (40 mL) was added dropwise under N_2. The solution was allowed to warm to room temperature and to stir for 24 h. The solvent was removed under reduced pressure, and the brown oily residue was chromatographed on a 19 in. × 1.5 in. silica gel dry column with $CHCl_3$ elution. The yellow band was cut out and eluted off of the silica gel with Et_2O and the solvent removed to afford (η^3-1-oxo-2,3-diphenylcyclobutenyl)dicarbonyl(triphenylphosphine)cobalt(I), **7e**, as a yellow, analytically pure, crystalline compound (1.54 g, 57%) (spectral and physical data are given in Tables I–IV).

Reaction of 6a with Tricarbonyl(triphenylphosphine)cobalt(1−) anion likewise afforded (η^3-1-oxo-2,3-diphenylcyclobutenyl)dicarbonyl(triphenylphosphine)cobalt(I), **7b** (50%) (physical and spectral data are given in Tables I, II, and IV.

Reaction of 6a with Tricarbonyl(dimethylphenylphosphine)cobaltate(1−) anion likewise afforded (η^3-1-oxo-2,3-diphenylcyclobutenyl)dicarbonyl(dimethylphenylphosphine)cobalt(I), 7c, in 72% yield (physical and spectral data are given in Tables I–IV).

Reaction of 6a with Tricarbonyl(triethylphosphine)cobaltate(1−) Anion in Carbon Monoxide Saturated THF. A solution of $[Co(CO)_3(PEt_3)]^-$ (1.96 mmol) in dry THF (75 mL) was prepared by the reduction of $[Co_2(CO)_6(PEt_3)_2]$ (0.26 g, 0.98 mmol) by sodium amalgam as described above. The solution was cooled to −78 °C, and carbon monoxide gas was bubbled through the solution for 3 h. While still at −78 °C, a solution of **6a** (0.25 g, 0.98 mmol) in dry THF (60 mL) was added dropwise. The solution was allowed to warm to room temperature under CO, and aliquots were sampled for IR spectroscopy at 0.5, 3, 7, and 72 h after the addition had ended. The solvent was then removed under reduced pressure and the reaction worked up in a manner similar to that above to afford exclusively **7e** (0.24 g, 55%).

General Procedure for the Reaction of 7a with Tertiary Phosphines. A sample of **7a** (1.5 mmol) was dissolved in degassed benzene (30 mL) under N_2. To the solution was added the tertiary phosphine (1.5 mmol) under N_2, and the reaction was allowed to stir at room temperature. Monitoring the carbonyl region of the infrared spectrum indicated when the reaction had proceeded to completion. After completion the solvent was removed under reduced pressure, and the residue was chromatographed on a 17 in. × 0.75 in. silica gel dry column with anhydrous diethyl ether elution. The yellow band was cut out and eluted off the silica gel with Et_2O and the solvent removed to afford the product.

The following were prepared in this fashion: **complex 7b** (63%) from **7a** (1.57 g, 4.33 mmol) and PPh_3 (1.13 g, 4.33 mmol); **complex 7c** (37%) from **7a** (0.56 g, 1.56 mmol) and $PMePh_2$ (0.31 g, 1.56 mmol), as a yellow oil (spectral data are given in Tables I and II). **complex 7d** (43%) from **7a** (0.60 g, 1.66 mmol) and PMe_2Ph (0.22 g, 1.66 mmol); **complex 7e** (44%) from **7a** (0.54 g, 1.49 mmol) and PEt_3 (0.17 g, 1.49 mmol).

Reaction of 6a with Dicarbonylbis(triphenylphosphine)cobaltate(1−) Anion. A dark brown solution of iododicarbonylbis(triphenylphosphine)cobalt (1.76 g, 1.31 mmol) in dry THF (75 mL) was reduced over a sodium amalgam, under a nitrogen atmosphere. The solution was allowed to stir for 2–4 h until it had turned an olive green. The excess amalgam and mercury were removed, and the anion solution was filtered through filter-aid under N_2. The filter bed was washed with dry THF (3 × 25 mL). The green anion solution was cooled to −78 °C, and a solution of **6a** (0.34 g, 1.33 mmol) in dry THF (10 mL) was added dropwise. The reaction was allowed to warm to room temperture. An aliquot was removed, 2 h after addition, for IR spectroscopy which indicated the formation of **9**. The reaction was allowed to stir for 48 h, and the solvent was removed under reduced pressure to afford a yellow-brown oily residue. The residue was taken up in a minimal amount of CH_2Cl_2 and applied to a 10 in. × 0.75 in. Florisil column made in hexanes. Elution with diethyl ether afforded a golden yellow band which, upon evaporation of the solvent under reduced pressure, yielded the product **7b** (0.45 g, 41%).

A similar reaction was run in which MeOH (100 mL) was added to the reaction mixture as soon as IR spectroscopy indicated complete formation of **9**. After the reaction was allowed to proceed to completion, only **7b** was recovered (39%).

The Reaction of Diphenylcyclopropenium Perchlorate with Tetracarbonylcobaltate(1−) Anion. A solution of $[Co(CO)_4]^-$ (2.18 mmol) in dry CH_3CN (5 mL) was prepared from $[Co_2(CO)_8]$ (0.56 g, 1.64 mmol) by using method C. The solution was cooled to −30 °C, and a solution of diphenylcyclopropenium perchlorate (0.65 g, 2.26 mmol) in dry CH_3CN (15 mL) was added dropwise, under N_2. The reaction was allowed to warm to room temperature and to stir for 24 h. The reaction was worked up in a manner similar to the preparation of **7a** (11 in. × 0.75 in. Florisil/hexanes column) to afford a single yellow crystalline compound. The product was determined to be **7a** by melting point and IR and ^1H NMR spectroscopy (0.54 g, 66% yield).

(η^3-1-Oxo-2,3-di-*n*-propylcyclobutenyl)tricarbonylcobalt(I) (7h) was prepared similarly by the reaction of di-*n*-propylcyclopropenium perchlorate (0.172 g, 0.77 mmol) with tetracarbonylcobaltate(1−) anion (1.16 mmol, prepared from $[Co_2(CO)_8]$ (0.30 g, 0.877 mmol) by method C) in dry CH_3CN (15 mL). The reaction was worked up by column chromatography (Florisil) to afford the product as a pale yellow oil (0.16 g, 73%) (spectral data are given in Tables I and II).

Reaction of 6a with ^{13}C-Enriched Tetracarbonylcobaltate(1−) Anion. A solution of ^{13}C-enriched tetracarbonylcobaltate(1−) anion (2.92 mmol) in dry CH_3CN (10 mL) was prepared from ^{13}C-enriched $[Co_2(CO)_8]$ (0.75 g, 2.19 mmol) by method C. The solution was cooled to −30 °C, and a solution of **6a** (0.77 g, 2.92 mmol) in dry CH_3CN (10 mL) was added dropwise, under N_2. The reaction was worked up in the usual manner to afford ^{13}C-enriched **7a** (0.42 g, 39%). The product was characterized by ^1H NMR and $^{13}C\{^1H\}$ NMR spectroscopy: IR $\nu_{^{13}CO}$ 2082 (s), 2076 (s), 2003 (s), 1981 (s), 1689 (m) cm^{-1}; chemical ionization mass spectrum, *m/e* (relative intensity) 367 (3) [$^{12}C_{15}{}^{13}C_4H_{11}O_4Co$ + H^+], 366 (14.1) [$^{12}C_{16}{}^{13}C_3H_{11}O_4Co + H^+$], 365 (49.6) [$^{12}C_{17}{}^{13}C_2{}_1O_4Co$ + H^+], 364 (100) [$^{12}C_{18}{}^{13}C_1H_{11}O_4Co + H^+$], 363 (91.7) [$^{12}C_{19}H_{11}O_4Co$ + H^+].

(η^3-2,3-Diethyl-1-Oxocyclobutenyl)tricarbonylcobalt(I) (7f) was prepared from the reaction of **6b** with tetracarbonylcobaltate(1−) anion (prepared from $[Co_2(CO)_8]$ by either method B or C). The reaction was worked up by column chromatography as described above to afford **7f** as a yellow oil (30%, method B; 79%, method C) (spectral data are given in Tables I and II).

(η^3-2,3-Diethyl-1-oxocyclobutenyl)dicarbonyl(triphenylphosphine)cobalt(I) (7g) was prepared by the reaction of **7f** (1.49 g, 5.61 mmol) with triphenylphosphine (1.47 g, 5.61 mmol) in degassed benzene (25 mL) at 45 °C. The product was afforded, after column chromatography (Florisil), as a pale yellow crystalline compound: mp 150 °C; 2.45 g, 89% (spectral data are given in Tables I and II).

Reaction of 2-Methyl-3-phenyl-2-cyclopropene-1-carbonyl Chloride (6c) with Tetracarbonylcobaltate(1−) Anion. A solution of tetracarbonylcobaltate(1−) anion (6.70 mmol) in dry THF (100 mL) was prepared from $[Co_2(CO)_8]$ (1.14 g, 3.35 mmol) according to method A. The solution was cooled to −78 °C, and a solution of **6c** (1.09 g, 6.06 mmol) in dry THF (25 mL) was added dropwise, under N_2. The reaction was allowed to warm to room temperature and to stir for 24 h. The reaction was worked up in the usual manner (Florisil/hexanes column chromatography) to afford a yellow crystalline crude product (0.49 g, 27%). The ^1H NMR spectrum indicated that this product was a mixture of **7i** and **7j** in a 3:4 ratio as determined by integration of the ring proton resonance signals. The product mixture was chromatographed on a 14 in. × 0.75 in. silica gel dry column with $CHCl_3$ elution. The resultant yellow band was cut into three equal lengths, and each section was washed with Et_2O. The middle fraction (0.20 g) was determined to be a mixture of **7i** and **7j** by ^1H NMR spectroscopy. The fraction with the greatest R_f value was determined to be pure (η^3-3-methyl-1-oxo-2-phenylcyclobutenyl)tricarbonylcobalt(I) (**7i**, 0.140 g) by ^1H NMR spectroscopy, and the fraction with the lowest R_f value was determined to be pure (η^3-2-methyl-1-oxo-3-phenylcyclobutenyl)tricarbonylcobalt(I) (**7j**, 0.145 g) by ^1H NMR spectroscopy.

Similarly, **6c** was allowed to react with tetracarbonylcobaltate(1−) anion (which had been prepared by method C) in dry CH_3CN (−30 to +23 °C). The reaction was worked up in the usual manner to afford a 2:3 mixture of **7i** and **7j** as determined by ^1H NMR spectroscopy (54% combined yield).

Likewise, a solution of tetracarbonylcobaltate(1−) anion (3.40 mmol) in dry THF (75 mL) was prepared from $[Co_2(CO)_8]$ (0.58 g, 1.70 mmol) by method A. The solvent was removed in vacuo, and the powdery residue was suspended in dry benzene (50 mL). To the suspension was added dicyclohexano-18-crown-6 (0.106 g, 0.28 mmol). A solution of **6c** (3.40 mmol) in dry benzene (30 mL) was added dropwise, and the reaction mixture was allowed to stir for 24 h. The reaction was worked up in the usual manner (Florisil column chromatography) to afford a 1:2 mixture of **7i** and **7j**, as determined by ^1H NMR spectroscopy (0.79 g, 76% combined yield).

Reaction of Methylphenylcyclopropenium Perchlorate with Tetracarbonylcobaltate(1−) Anion. A solution of tetracarbonylcobaltate(1−) anion (4.42 mmol) in dry CH_3CN (6 mL) was prepared from $[Co_2(C-$

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$O)_8$] (1.21 g, 3.31 mmol) by method C. The solution was cooled to −30 °C, and a solution of methylphenylcyclopropenium perchlorate (0.91 g, 4.42 mmol) in dry CH_3CN (10 mL) was added dropwise, under N_2. The reaction was allowed to warm to room temperature and to stir for 48 h. The reaction was worked up in the usual manner (Florisil column chromatography) to afford a 1:1 mixture of **7l** and **7j**, as determined by ^1H NMR spectroscopy (0.66 g, 50% yield).

Resolution of 2-Methyl-3-phenyl-2-cyclopropene-1-carboxylic Acid with *l*-Ephedrine. A sample of the acid (4.17 g, 25.7 mmol) was dissolved in the minimal amount of benzene (~10 mL). To the solution was added a solution of *l*-ephedrine (4.25 g, 25.7 mmol) in benzene (10 mL). The combined solutions were thoroughly mixed and allowed to stand without stirring for 5 days. The resultant fluffy white precipitate was collected by vacuum filtration and dried in vacuo (5.16 g). The precipitate was recrystallized from hot benzene (100 mL) to afford a white precipitate which was collected by vacuum filtration and dired in vacuo (0.75 g). The white precipitate was hydrolyzed in aqueous potassium hydroxide (0.2 M), in the manner described above to afford a 9:1 enantiomeric mixture of 2-methyl-3-phenyl-2-cyclopropene-1-carboxylic acid (0.36 g) as determined by ^1H NMR spectroscopy with $Eu(facam)_3$. Another sample of the acid (1.72 g, 10.6 mmol) was resolved in a similar manner into a 3:1 enantiomeric mixture (0.50 g). Both samples of optically enriched acid were converted to the acid chloride (**6c**) by treatment with oxalyl chloride.

Reaction of Optically Enriched 6c with Tetracarbonylcobaltate(1−) Anion in Acetonitrile. A solution of tetracarbonylcobaltate(1−) anion (1.87 mmol) in dry CH_3CN (10 mL) was prepared from $[Co_2(CO)_8]$ (0.48 g, 1.40 mmol) according to method C. The solution was cooled to −30 °C, and a solution of optically enriched **6c** (9:1 mixture of enantiomers; 0.238 g, 1.32 mmol) in dry CH_3CN (10 mL) was added dropwise, under N_2. The reaction mixture was allowed to warm to room temperture and to stir for 24 h. The reaction was worked up in the usual manner (Florisil column chromatography) to afford a yellow solid (0.26 g, 66% combined yield). The ^1H NMR spectrum of the product showed it to be a 2:3 mixture of **7l** and **7j**. The ^1H NMR spectra of the mixture containing varying amounts of $Eu(facam)_3$ indicated that both isomers were racemic.

Reaction of Optically Enriched 6c with Tetracarbonylcobaltate(1−) Anion in Benzene. A solution of tetracarbonylcobaltate(1−) anion (5.72 mmol) in dry THF (75 mL) was prepared from $[Co_2(CO)_8]$ (0.98 g, 2.86 mmol) according to method B. The solvent was removed in vacuo to afford a powdery residue, which was suspended in dry benzene (50 mL). The solution was cooled in an ice water bath, and a solution of optically enriched **6c** (2.47 mmol; 3:1 enantiomeric mixture) was added dropwise under N_2. The reaction was allowed to warm to room temperature and stir for 48 h. The solvent was removed in vacuo, and the residue was worked up in the usual manner (Florisil column chromatography) to afford a yellow solid (0.21 g, 28% combined yield). The ^1H NMR spectrum of the product indicated that it was a 1.0:1.1 mixture of **7l** and **7j**. The ^1H NMR spectra of the mixture containing varying amounts of $Eu(facam)_3$ indicated that each isomer was a 3:1 mixture of enantiomers.

Reaction of 6c with ^{13}CO-Enriched Tetracarbonylcobaltate(1−) Anion in Benzene. A solution of ^{13}CO-enriched tetracarbonylcobaltate(1−) anion (2.34 mmol) in dry THF (50 mL) was prepared from ^{13}CO-enriched $[Co_2(CO)_8]$ (0.40 g, 1.17 mmol). The solvent was removed in vacuo to yield a powdery residue, which was suspended in dry benzene (50 mL). To the suspension was added dropwise a solution of **6c** (1.23 mmol) in dry benzene (10 mL), and the mixtue was allowed to stir under N_2 for 24 h. The solvent was removed in vacuo, and the residue was worked up in the usual manner (Florisil column chromatography) to afford a yellow solid (0.20 g, 54% combined yield). The ^1H NMR spectrum of the product indicated that it was a 2.5:3.0 mixture of **7l** and **7j**. The $^{13}C\{^1H\}$ NMR spectrum of the mixture indicated a substantial amount of ^{13}C enrichment at the terminal carbonyl ligand carbon atoms but no ^{13}C enrichment at the cyclobutenonyl ring carbonyl carbon atom.

Reaction of 2-Methyl-1-phenyl-cyclopropene-1-carbonyl Chloride (6d) with Tetracarbonylcobaltate(1−) Anion. A solution of tetracarbonylcobaltate(1−) anion (7.99 mmol) in dry CH_3CN (20 mL) was prepared from $[Co_2(CO)_8]$ (2.05 g, 5.99 mmol) according to method C. The solution was cooled to −30 °C, and a solution of **6d** (0.85 g, 4.30 mmol) in dry CH_3CN (7 mL) was added dropwise, under N_2. The reaction was allowed to warm to room temperature and to stir for 48 h. The solvent was removed in vacuo, and the residue was worked up in the usual manner to afford a yellow solid (0.65 g, 50% combined yield). The ^1H NMR spectrum of the product indicated that it consisted of a 1.0:1.3:4.0 mixture of **7l**, **7j**, and **7k**. Two successive separations using silica gel dry column chromatography ($CHCl_3$ elution) afforded (η^3-2-methyl-1-oxo-4-phenylcyclobutenyl)tricarbonyl cobalt(I) **7k** as a pure yellow crystalline compound (0.18 g) (physical and spectral data are given in Tables I–IV). Compound **7k** had the greatest, **7l** the middle, and **7j** the lowest R_f value of the three isomeric (η^3-oxocyclobutenyl)(tricarbonyl)cobalt(I) complexes on silica gel, with $CHCl_3$ elution.

Reaction of 6d with ^{13}CO-Enriched Tetracarbonylcobaltate(1−) Anion. A solution of ^{13}CO-enriched tetracarbonylcobaltate(1−) anion (1.91 mmol) in dry CH_3CN (15 mL) was prepared from ^{13}CO-enriched $[Co_2(CO)_8]$ (0.49 g, 1.43 mmol) according to method C. The solution was cooled to −30 °C, and a solution of **6d** (0.366 g, 1.91 mmol) in dry CH_3CN (4 mL) was added dropwise, under N_2. The reaction mixture was allowed to warm to room temperature and to stir for 48 h. The solvent was removed in vacuo, and the residue was worked up in the usual manner (Florisil column chromatography) to afford a yellow solid (0.086 g, 15% combined yield). The ^1H NMR spectrum of the product indicated that it consisted of a 1.0:1.3:4.0 mixture of **7l**, **7j**, and **7k**. The mixture was separated by silica gel dry column chromatography ($CHCl_3$ elution) into pure **7k** (0.055 g) and a mixture of **7l** and **7j** (0.017 g). The $^{13}C\{^1H\}$ NMR spectrum of **7k** indicated ^{13}C enrichment in the terminal carbonyl ligand carbon atoms but no ^{13}C enrichment at the cyclobutenonyl ring carbonyl carbon atom. The $^{13}C\{^1H\}$ NMR spectrum of the mixture of **7l** and **7j** indicated ^{13}C enrichment at the terminal carbonyl ligand carbon atoms as well as at each of the oxocyclobutenyl ring carbonyl carbon atoms (**7k**, IR ($\nu_{^{13}CO}$) 2073 (s), 2067 (s), 1998 (s), 1980 (s) cm^{-1})).

Resolution of 2-Methyl-1-phenyl-2-cyclopropene-1-carboxylic Acid with *l*-Ephedrine. A sample of 2-methyl-1-phenyl-2-cyclopropene-1-carboxylic acid (0.695 g, 4.29 mmol) was dissolved in hot benzene (15 mL) and was added to a warm solution of *l*-ephedrine (0.71 g, 4.29 mmol) in benzene (10 mL). The reaction mixture was heated slightly over a steam bath and allowed to cool slowly. White crystals had formed after 7 days and were collected by vacuum filtration (0.682 g). The white crystals were hydrolyzed in aqueous KOH (0.2 M) as described above to afford 2-methyl-1-phenyl-2-cyclopropene-1-carboxylic acid (0.223 g). The 270-MHz ^1H NMR spectra of this sample containing varying amounts of $Eu(hfpc)_3$ indicated that it consisted of a 1:3 mixture of enantiomers. The sample was converted to the acid chloride **6d** by treatment with oxalyl chloride.

Reaction of Optically Enriched 6d with Tetracarbonylcobaltate(1−) Anion in Acetonitrile. A solution of tetracarbonylcobaltate(1−) anion (1.87 mmol) in dry CH_3CN (6 mL) was prepared from $[Co_2(CO)_8]$ (0.48 g, 1.40 mmol) according to method C. The solution was cooled to −30 °C, and a CH_3CN solution (3 mL) of optically enriched **6d** (1.22 mmol) was added dropwise, under N_2. The reaction was allowed to warm to room temperature and to stir for 48 h. The solvent was removed in vacuo, and the residue was worked up in the usual manner (Florisil column chromatography) to afford a yellow solid (0.20 g, 55% combined yield). The ^1H NMR spectrum of the product indicated that it consisted of a 1.0:1.0:3.5 mixture of **7l**, **7j**, and **7k**. The 270-MHz ^1H NMR spectra of the mixture containing varying amounts of $Eu(facam)_3$ indicated that isomers **7l** and **7j** were racemic while isomer **7k** consisted of a 1:3 mixture of enantiomers.

(η^3-3-Methyl-1-oxo-2-phenylcyclobutenyl)dicarbonyl(triphenylphosphine)cobalt(I) (7l) was prepared by the reaction of **7l** (0.142 g, 0.47 mmol) with triphenylphosphine (0.125 g, 0.47 mmol) in degassed benzene (5 mL) under N_2 at 45 °C. The product was purified by column chromatography (Florisil) to afford **7l** as yellow crystals: mp 145 °C dec; 0.142 g, 60% (spectral data are given in Tables I and II).

(η^3-2-Methyl-1-oxo-3-phenylcyclobutenyl)dicarbonyl(triphenylphosphine)cobalt(I) (7m) was prepared from the reaction of **7j** (0.074 g, 0.246 mmol) with triphenylphosphine (0.065 g, 0.246 mmol) in degassed benzene (5 mL) under N_2 at 45 °C. The product was purified by column chromatography (Florisil) to afford **7m**: mp 125 °C dec; 0.04 g, 33% (spectral data are given in Tables I and II).

(η^3-2-Methyl-1-oxo-4-phenylcyclobutenyl)dicarbonyl(triphenylphosphine)cobalt(I) (7n) was prepared from the reaction of **7k** (0.168 g, 0.56 mmol) with triphenylphosphine (0.145 g, 0.56 mmol) in degassed benzene (5 mL) under N_2 at 45 °C. The product was purified by column chromatography (Florisil) to afford **7n** as a yellow oil (0.133 g, 48%) (spectral data are given in Tables I and II).

Reaction of 6c with Dicarbonylbis(triphenylphosphine)cobaltate(1−) Anion. A solution of dicarbonylbis(triphenylphosphine)cobaltate(1−) anion (1.75 mmol) in dry THF (75 mL) was prepared in the manner previously described. The solution was cooled to −78 °C, and a solution of **6c** (1.75 mmol) in dry THF (10 mL) was added dropwise, under N_2. The reaction mixture was allowed to warm to room temperature and to stir for 48 h. The solvent was removed in vacuo, and the residue was worked up in the usual manner (Florisil column chromatography) to afford a yellow solid (0.24 g, 28% combined yield). The ^1H NMR spectrum of the product indicated it to consist of a 1:1 mixture of **7l** and **7m**.

Reaction of 2-*tert*-Butyl-3-phenyl-2-cyclopropene-1-carbonyl Chloride (6e) with Tetracarbonylcobaltate(1−) Anion. A solution of tetracarbonylcobaltate(1−) (3.76 mmol) in dry CH_3CN (8 mL) was prepared from $[Co_2(CO)_8]$ (0.971 g, 2.84 mmol) according to method C. The solution was cooled to −30 °C, and a solution of **6e** (0.62 g, 2.78 mmol) in dry CH_3CN (5 mL) was added dropwise, under N_2. The reaction mixture was allowed to warm to room temperature and to stir for 48 h. The solvent was removed in vacuo, and the residue was worked up in the usual manner to afford a dark yellow solid (0.59 g, 62%). The ^1H NMR spectrum of the product indicated that it consisted of a 10:1 mixture of **7o** and **7p** (see Tables I and II for spectral data). (η^3-2-*tert*-Butyl-1-oxo-3-phenylcyclobutenyl)tricarbonylcobalt(I), **7o**, could be separated from the mixture by silica gel dry column chromatography ($CHCl_3$ elution) and was found to have a greater R_f value than (η^3-3-*tert*-butyl-1-oxo-2-phenyl-cyclobutenyl)tricarbonylcobalt(I), **7p**.

Reaction of 2-*tert*-Butyl-1-phenyl-2-cyclopropene-1-carbonyl Chloride (6f) with Tetracarbonylcobaltate(1−) Anion. A solution of tetracarbonylcobaltate(1−) anion (0.858 mmol) in dry CH_3CN (4 mL) was prepared from $[Co_2(CO)_8]$ (0.22 g, 0.64 mmol) according to method C. The solution was cooled to −30 °C and a solution of **6f** (0.78 mmol) in dry CH_3CN (4 mL) was added dropwise, under N_2. The reaction mixture was allowed to warm to room temperature and stir for 48 h. The solvent was removed in vacuo, and the residue was worked up in the usual manner (Florisil column chromatography) to afford a dark yellow solid (0.10 g, 37%). The ^1H NMR spectrum of the product indicated that it consisted of a 3.0:1.5:5.0 mixture of **7o**, **7p**, and (η^3-2-*tert*-butyl-1-oxo-4-phenylcyclobutenonyl)tricarbonylcobalt(I), **7q** (spectral data are given in Tables I and II).

Reaction of 2-(4-Methoxyphenyl)-3-phenyl-2-cyclopropene-1-carbonyl Chloride (6g) with Tetracarbonylcobaltate(1−) Anion. A solution of tetracarbonylcobaltate(1−) anion (4.76 mmol) in dry CH_3CN (25 mL) was prepared from $[Co_2(CO)_8]$ (1.22 g, 3.58 mmol) according to method C. The solution was cooled to −30 °C, and a solution of **6g** (1.02 g, 3.57 mmol) in dry CH_3CN (7 mL) was added dropwise, under N_2. The reaction mixture was allowed to warm to room temperature and to stir for 48 h. The solvent was removed in vacuo, and the residue was worked up in the usual manner (Florisil column chromatography) to afford a yellow oil (0.80 g, 57%). The ^1H NMR spectrum of the product indicated that it consisted of a 1:1 mixture (η^3-2-(4-methoxyphenyl)-1-oxo-3-phenylcyclobutenyl)tricarbonylcobalt(I), **7r**, and (η^3-3-(4-methoxyphenyl)-1-oxo-2-phenylcyclobutenyl)tricarbonylcobalt(I), **7s** (spectral data are given in Tables I and II).

An analogous reaction of **6g** with $[Co(CO)_4]^-$ in dry THF gave an identical 1:1 mixture of **7r** and **7s**.

Reaction of 2-(4-Methoxyphenyl)-3-methyl-2-cyclopropene-1-carbonyl Chloride (6h) with Tetracarbonylcobaltate(1−) Anion. A solution of tetracarbonylcobaltate(1−) anion (7.64 mmol) in dry CH_3CN (5 mL) was prepared from $[Co_2(CO)_8]$ (1.96 g, 5.73 mmol) according to method C. The solution was cooled to −30 °C and a solution of **6h** (3.66 mmol) in dry CH_3CN (10 mL) was added dropwise, under N_2. The reaction mixture was allowed to warm to room temperature and to stir for 48 h. The solvent was removed in vacuo, and the residue worked up in the usual manner (Florisil column chromatography) to afford a yellow oily solid (0.39 g, 32%). The ^1H NMR spectrum of the product indicated that it consisted of a 2:3 mixture of (η^3-2-(4-methoxyphenyl)-3-methyl-1-oxocyclobutenyl)tricarbonylcobalt(I), **7t**, and (η^3-3-(4-methoxyphenyl)-2-methyl-1-oxocyclobutenyl)tricarbonylcobalt(I), **7u** (spectral data are given in Tables I and II). Recrystallization of the mixture from cold anhydrous diethyl ether afforded a golden yellow solid (0.106 g) which was found to be a 10:1 mixture of **7u** and **7t** by ^1H NMR spectroscopy.

Reaction of 2-*tert*-Butyl-2-cyclopropene-1-carbonyl Chloride (6i) with Tetracarbonyl Cobaltate(1−) Anion. A solution of tetracarbonylcobaltate(1−) anion (18.97 mmol) in dry CH_3CN (80 mL) was prepared from $[Co_2(CO)_8]$ (4.86 g, 14.23 mmol) according to method C. The solution was cooled to −30 °C, and a solution of **6i** (2.25 g, 14.26 mmol) in dry CH_3CN (15 mL) was added dropwise, under N_2. The solution was allowed to warm to room temperature and to stir for 24 h. The solvent was removed in vacuo, and the residue was worked up in the usual manner (Florisil column chromatography) to afford a pale yellow solid (2.10 g, 55%). The ^1H NMR spectrum of the product indicated that it consisted of a 6:1 mixutre of **7v** and **7w** (physical and spectral data are given in Tables I–IV). The two isomers could be separated by silica gel dry column chromatography ($CHCl_3$ elution) and (η^3-2-*tert*-butyl-1-oxocyclobutenyl)tricarbonylcobalt(I), **7v**, was found to have a greater R_f value than did (η^3-3-*tert*-butyl-1-oxocyclobutenyl)tricarbonylcobalt(I), **7w**.

(η^3-2-*tert*-Butyl-1-oxocyclobutenyl)dicarbonyl(triphenylphosphine)cobalt(I) (**7x**) was prepared from **7v** (0.15 g, 0.56 mmol) with triphenylphosphine (0.147 g, 0.56 mmol) in degassed benzene (10 mL) under N_2, at 45 °C. The product was purified by column chromatography (Florisil) to afford **7x** (0.21 g, 76%) (spectral and physical data are given in Tables I, II, and IV).

(η^3-3-*tert*-Butyl-1-oxocyclobutenyl)dicarbonyl(dimethylphenylphosphine)cobalt(I) (**7y**) was prepared from the reaction of **7w** (0.182 g, 0.684 mmol) with dimethylphenylphosphine (0.137 g, 0.684 mmol) in degassed benzene (10 mL) under N_2, at room temperature. The product was purified by column chromatography (Florisil) to afford **7y** as a pale yellow solid: mp 47–51 °C; 0.17 g, 66% (spectral data are given in Tables I–III).

Reaction of 2-*tert*-Butyl-3-deuterio-2-cyclopropene-1-carbonyl Chloride (6j) with Tetracarbonylcobaltate(1−) Anion in Dry Acetonitrile. A solution of tetracarbonylcobaltate(1−) anion (4.00 mmol) in dry CH_3CN (10 mL) was prepared from $[Co_2(CO)_8]$ (1.03 g, 3.00 mmol) according to method C. The solution was cooled to −30 °C, and a solution of **6j** (0.480 g, 3.00 mmol) in dry CH_3CN (5 mL) was added, under N_2. The reaction mixture was allowed to warm to room temperature and to stir for 48 h. The solvent was removed in vacuo, and the residue was worked up in the usual manner (Florisil column chromatography) to afford a pale yellow solid (0.43 g, 54%). The ^1H NMR spectrum of the product indicated that it consisted of a 3:3:1 mixture of (η^3-2-*tert*-butyl-3-deuterio-1-oxocyclobutenyl)tricarbonylcobalt(I), **7z**, (η^3-2-*tert*-butyl-4-deuterio-1-oxocyclobutenyl)tricarbonylcobalt(I), **7aa**, and (η^3-3-*tert*-butyl-2-deuterio-1-oxocyclobutenyl)tricarbonylcobalt(I), **7bb**.

Reaction of 6j with Tetracarbonylcobaltate(1−) Anion in Dry Benzene. A solution of tetracarbonylcobaltate(1−) anion (14.3 mmol) in dry THF (75 mL) was prepared from $[Co_2(CO)_8]$ (2.45 g, 7.16 mmol) according to method A. The solvent was removed in vacuo to afford a powdery residue, which was suspended in dry benzene (50 mL) under N_2. A solution of **6j** (13.1 mmol) in dry benzene (25 mL) was added dropwise, and the reaction was allowed to stir for 24 h. The solvent was removed in vacuo, and the residue was worked up in the usual manner (Florisil column chromatography) to afford a pale yellow solid (0.353 g, 10%). The ^1H NMR spectrum of the product indicated that it consisted of a 4:1:1 mixture of **7z**, **7aa**, and **7bb**.

Reaction of 2-*n*-Butyl-2-cyclopropene-1-carbonyl Chloride (6k) with Tetracarbonylcobaltate(1−) Anion. A solution of tetracarbonylcobaltate(1−) anion (7.64 mmol) in dry CH_3CN (20 mL) was prepared from $[Co_2(CO)_8]$ (1.96 g, 5.76 mmol) according to method C. The solution was cooled to −30 °C, and a solution of **6k** (0.874 g, 5.53 mmol) in dry CH_3CN (10 mL) was added dropwise, under N_2. The reaction mixture was allowed to warm to room temperature and to stir for 48 h. The solvent was removed in vacuo, and the residue was worked up in the usual manner (Florisil column chromatography) to afford a pale yellow solid (0.40 g, 27%). The ^1H NMR spectrum of the product indicated that it consisted of a 20:1 mixture of **7cc** and **7dd** (spectral data are given in Tables I–III). (η^3-2-*n*-Butyl-1-oxocyclobutenyl)tricarbonylcobalt(I), **7cc**, could be separated from the mixture by silica gel dry column chromatography ($CHCl_3$ elution; 0.13 g) (physical data are given in Table IV).

Reaction of 2-*n*-Butyl-3-deuterio-2-cyclopropene-1-carbonyl Chloride (6l) with Tetracarbonylcobaltate(1−) Anion. A solution of tetracarbonylcobaltate(1−) anion (8.19 mmol) in dry CH_3CN (7 mL) was prepared from $[Co_2(CO)_8]$ (2.10 g, 6.14 mmol) according to method C. The solution was cooled to −30 °C, and a solution of **6l** (0.98 g, 6.16 mmol) in dry CH_3CN (5 mL) was added dropwise, under N_2. The reaction mixture was allowed to warm to room temperature and to stir for 60 h. The solvent was removed in vacuo, and the residue was worked up in the usual manner (Florisil column chromatography) to afford a pale yellow solid (0.39 g, 24%). The ^1H NMR spectrum of the product indicated that it consisted of a 1.2:1.0 mixture of (η^3-2-*n*-butyl-3-deuterio-1-oxocyclobutenyl)tricarbonylcobalt(I), **7ee**, and (η^3-2-*n*-butyl-4-deuterio-1-oxocyclobutenyl)tricarbonylcobalt(1), **7ff**.

Reaction of 2-Isopropyl-2-cyclopropene-1-carbonyl Chloride (6m) with Tetracarbonylcobaltate(1−) Anion. A solution of tetracarbonylcobaltate(1−) anion (5.77 mmol) in dry CH_3CN (4 mL) was prepared from $[Co_2(CO)_8]$ (1.48 g, 4.32 mmol) according to method C. The solution was cooled to −30 °C, and a solution of **6m** (0.603 g, 4.17 mmol) in dry CH_3CN (2 mL) was added dropwise, under N_2. The reaction mixture was allowed to warm to room temperature and to stir for 60 h. The solvent was removed in vacuo, and the residue was worked up in the usual manner (Florisil column chromatography) to afford a pale yellow solid (0.22 g, 21%). The ^1H NMR and $^{13}C\{^1H\}$ NMR spectra of the solid indicated that (η^3-2-isopropyl-1-oxocyclobutenyl)tricarbonylcobalt(1), **7hh**, was the only product (physical and spectral data are given in Tables I–IV).

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Characterization of the Silicon-Aluminum Distribution in Synthetic Faujasites by High-Resolution Solid-State ^{29}Si NMR

M. T. Melchior,* D. E. W. Vaughan, and A. J. Jacobson

Contribution from the Exxon Research and Engineering Company, Linden, New Jersey 07036.
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Abstract: Silicon-29 NMR spectra were obtained at 11.9 MHz by using magic angle spinning and proton dipolar decoupling for a series of 14 synthetic faujasite zeolites. The isotropic ^{29}Si chemical shifts fall in the range −80 to −110 ppm (vs. Me_4Si) reported for four-coordinate silicon in solid silicates and aluminosilicates. Within this range, a regular paramagnetic shift is observed that correlates with the number (0–4) of aluminum neighbors surrounding silicon. As a consequence of the aluminum neighbor effect, the ^{29}Si NMR spectrum of a typical faujasite consists of up to five lines, the intensities of which reflect the distribution of silicon among sites having 0–4 aluminum neighbors. The details of these distributions provide evidence for a high degree of ordering in the faujasite lattice. We find that the Si,Al distribution is consistent with Lowenstein's rule, which excludes Al–O–Al linkages. Further, for a given Si/Al ratio the detailed distribution can be calculated by considering the faujasite lattice as a narrow distribution of ordered structures which minimize Al–O–Si–O–Al linkages.

Faujasite is a naturally occurring zeolite that can be readily synthesized under mild laboratory conditions over a range of Si/Al ratios. Synthetic sodium faujasites with Si/Al ratios between 1.0 and 1.5 and between 1.5 and 3.0 are conventionally called X and Y zeolites,[1,2] respectively. In practice, sodium faujasites with Si/Al ratios greater than 2.7 are difficult to obtain by direct synthesis. Directly synthesized faujasites should be distinguished from materials made by chemical dealumination of lower Si/Al compositions. Such high silica compositions are known as "stabilized" or "ultrastable" faujasites.[3] Because of the widespread use of X and Y zeolites as catalysts and sorbents, their structures have been extensively investigated by X-ray diffraction[4] and infrared spectroscopy.[5]

The structure of faujasite is illustrated in Figure 1. The structure, like that of all zeolites, is built up of SiO_4 and AlO_4 tetrahedra linked by corner sharing. Twenty-four such tetrahedra are joined to form a cubooctahedron or sodalite cage, and these secondary units are stacked tetrahedrally to form a cubic diamond lattice. The sodalite cages are joined tetrahedrally through four of the eight hexagonal faces to give hexagonal prisms. Two such sodalite cages are shown in Figure 1 together with the arrangement of atoms around the large central cavity in the structure; oxygens are omitted for clarity.

Despite an impressive body of information concerning the framework structure and the location of cations within it, the distribution of Si and Al among the framework tetrahedral sites is not generally known. The fundamental question concerns the extent of Si,Al ordering and its dependence on composition. Dempsey[6,7] calculated the Madelung energies for different ordered arrangements of Si and Al at Si/Al = 2, and some experimental evidence has been presented to support his conclusions. This evidence is based on discontinuities in the linear correlation between unit cell dimension and the aluminum content of the framework in synthetic sodium faujasites.[8] These discontinuities near Si/Al ratios of 1.4 and 2.0 are small and had not been detected in previous work on sodium Si/Al faujasites[9,10] but were later convincingly demonstrated for Ga-substituted materials.[11] A subsequent X-ray structure determination of a single crystal of zeolite X (Si/Al = 1.18)[12] showed Si,Al ordering in accordance with Loewenstein's rule,[13] which requires a regular alternation of Si and Al in the limit of Si/Al → 1.0. At high silicon content, however, it has often been assumed that Si and Al are randomly distributed among the framework tetrahedral sites.[14]

High-resolution solid-state ^{29}Si NMR spectroscopy has been shown to be sensitive to the distribution of Si and Al in solid aluminosilicates.[15,16] The technique has been applied to zeolite A.[17,18] The NMR data indicate that Si and Al are ordered in zeolite A but suggest that each silicon has three aluminum nearest neighbors in violation of Loewenstein's rule. This unusual ordered structure was subsequently confirmed by neutron diffraction.[19]

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