Inorg. Chem. **1983**, *22*, 1049-1053

Contribution from the Research Group for Petrochemistry, Hungarian Academy of Sciences, H-8201 Veszprém, Hungary, and Institute of Structural Chemistry, University of Parma, Parma, Italy

Reactivity of Acetylenes Coordinated to Cobalt. 6.[1] Preparation and Structure of (μ-$C_4O_2R^1R^2$)(μ-C=CR^3R^4)$Co_2(CO)_6$ Compounds. Unexpected 1,2-Shift of the Substituents of Coordinated Haloacetylenes[5]

ISTVÁN T. HORVÁTH,[7a,8] GYULA PÁLYI,*[7a] LÁSZLÓ MARKÓ,[7a] and GIOVANNI D. ANDREETTI[7b]

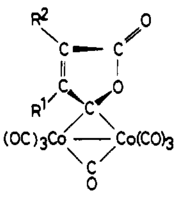
Received March 15, 1982

α-Haloacetylenes react with (μ-butenolido)(μ-carbonyl)hexacarbonyldicobalt(*Co–Co*) complexes in a reaction involving a 1,2-shift of one of the substituents of the acetylene, to yield almost quantitatively the corresponding (μ-butenolido)(μ-vinylidene)hexacarbonyldicobalt(*Co–Co*) complex. The crystal and molecular structure of a representative ((μ-C_4O_2H-*n*-Pe)(μ-CCl_2)$Co_2(CO)_6$ (*n*-Pe = *n*-pentyl)) of the new vinylidene complexes was determined by X-ray diffraction: space group $P\bar{1}$, a = 1169.7 (6) pm, b = 1130.6 (7) pm, c = 867.5 (4) pm, α = 89.09 (4)°, β = 96.33 (4)°, γ = 105.11 (5)°. The most characteristic features of the structure are the following: the six carbonyl groups are ordered almost symmetrically (C_{2v}), and the lactone ring is rectangular to the Co–Co line and is oriented with its C–C double bond toward the vinylidene ligand, the plane of which is orthogonal to the plane of the lactone ring.

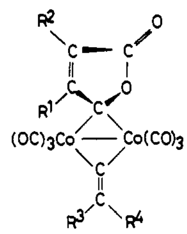
Introduction

Transition-metal cluster catalysis became the focus of interest in the last few years but well-founded examples of reactions catalyzed by at least dinuclear complexes are rare.[9,10] The catalytic synthesis of bifurandiones[3,11,12] from acetylenes, in the presence of $Co_2(CO)_8$ (aprotic, polar solvents, 20–100-MPa CO pressure, 70–110 °C), is, most probably, one of these reactions. The possibility of isolating intermediate complexes of the formation of the first ring of bifurandiones ((μ-acetylido)$Co_2(CO)_6$[13] and (μ-butenolido)(μ-CO)$Co_2(CO)_6$ (I))[14] as well as the quantitative regioselectivity observed in the formation of I[15-17] makes this problem even more attractive to further studies. Efforts have been made to prepare intermediates or models of the formation of the second lactone ring of bifurandiones by reacting complexes I with acetylenes under mild conditions. These studies with hydrocarbon acetylenes led to the formation[2,18] of a new C_5 ligand synthesized from the 4-carbon atom of the lactone ring in I and the sp carbons of two molecules of the acetylenes added. This ligand is coordinated by η^2 and η^3 bonds to two cobalt atoms in an isomeric pair of dinuclear complexes [($C_4O_2R^1R^2$)($R^3C_2R^4$)$_2$]$Co_2(CO)_5$ (II).

As an extension of these studies we examined the reaction of complexes (I) with heteroatom-containing acetylenes.



I



III

Propargyl alkyl ethers[2] gave the "regular" II complexes, propargylamines provided almost exclusively organic substances that are now under investigation, while mono- and dihaloacetylenes yielded cobalt–organic products with almost quantitative yields. These compounds (III) were found to contain the bridging lactone group of the starting I compounds and a new bridging carbene moiety formed by a 1,2-shift of one of the substituents of the acetylene, two cobalt atoms, and six terminal carbonyl ligands, as reported in a preliminary note.[6] We report here the details of the preparation and the X-ray structure determination.

Experimental Section

All operations were made under exclusion of air, under a deoxygenated Ar or CO atmosphere. Solvents distilled from sodium–ketyl were used.

$Co_2(CO)_8$ and ($C_4O_2R^1R^2$)$Co_2(CO)_7$ (I) complexes were prepared according to ref 19 and 14a, respectively. Monohaloacetylenes were made with the method of Zakharkin et al.,[20] while dihaloacetylenes were made according to the hypohalite method.[21] It should be mentioned also here that dihaloacetylenes are highly explosive in the order I << Br < Cl; therefore, C_2Br_2 and C_2Cl_2 were not isolated but transferred from the reaction mixture by an Ar stream into the solution of the I complexes. Since the dihaloacetylenes are prepared by leading a stream of C_2H_2 into the hypohalite solution, we used

---

(1) For parts 3–5, see ref 2–4.

(2) Váradi, G.; Horváth, I. T.; Pályi, G.; Markó, L.; Slovokhotov, Yu. L.; Struchkov, Yu. T. *J. Organomet. Chem.* **1981**, *206*, 119.

(3) Váradi, G.; Horváth, I. T.; Palágyi, J.; Bak, T.; Pályi, G. *J. Mol. Catal.* **1980**, *9*, 457.

(4) Váradi, G.; Galamb, V.; Palágyi, J.; Pályi, G. *Inorg. Chim. Acta* **1981**, *53*, L29.

(5) Preliminary note: ref 6.

(6) Horváth, I. T.; Pályi, G.; Markó, L.; Andreetti, G. *J. Chem. Soc., Chem. Commun.* **1979**, 1054.

(7) (a) Research Group for Petrochemistry, Hungarian Academy of Sciences. (b) Institute of Structural Chemistry, University of Parma.

(8) Institute of Chemistry, Veterinary University, Budapest, Hungary.

(9) Muetterties, E. L.; Pretzer, W. R.; Thomas, M. G.; Beier, B. F.; Thorn, D. L.; Day, V. W.; Anderson, A. B. *J. Am. Chem. Soc.* **1978**, *100*, 2090.

(10) Muetterties, E. L.; Rodin, T. N.; Band, E.; Bruckner, C. F.; Pretzer, W. R. *Chem. Rev.* **1979**, *79*, 91.

(11) Sauer, J. C. German Patent 1 054 086, 1955. Sauer, J. C.; Cramer, R. D.; Engelhardt, V. A.; Ford, T. A.; Holmquist, H. E.; Howk, B. W. *J. Am. Chem. Soc.* **1959**, *81*, 3677.

(12) Albanesi, G.; Tovaglieri, M. *Chim. Ind. (Milan)* **1959**, *41*, 189; Swiss Patent 376.900, 1964.

(13) Sternberg, H. W.; Greenfield, H.; Friedel, R. A.; Wotiz, J. H.; Markby, R.; Wender, I. *J. Am. Chem. Soc.* **1954**, *76*, 1457.

(14) (a) Sternberg, H. W.; Shukys, J. G.; Delle Donne, C.; Markby, R.; Friedel, R. A.; Wender, I. *J. Am. Chem. Soc.* **1959**, *81*, 2339. (b) Mills, O. S.; Robinson, G. *Inorg. Chim. Acta* **1967**, *1*, 61.

(15) Pályi, G.; Váradi, G.; Vizi-Orosz, A.; Markó, L. *J. Organomet. Chem.* **1975**, *90*, 85.

(16) Guthrie, D. J. S.; Khand, I. U.; Knox, G. R.; Kollmeier, J.; Pauson, P. L.; Watts, W. E. *J. Organomet. Chem.* **1975**, *90*, 95.

(17) Váradi, G.; Vecsei, I.; Ötvös, I.; Pályi, G.; Markó, L. *J. Organomet. Chem.* **1979**, *182*, 415.

(18) (a) Elder, P. A.; Guthrie, D. J. S.; Jeffreys, J. A. D.; Knox, G. R.; Kollmeier, J.; Pauson, P. L.; Symon, D. A.; Watts, W. E. *J. Organomet. Chem.* **1976**, *120*, C13. (b) Jeffreys, J. A. D. *J. Chem. Soc., Dalton Trans.* **1980**, 435.

(19) Szabó, P.; Markó, L.; Bor, G. *Chem. Tech. (Leipzig)* **1961**, *13*, 549.

(20) Zakharkin, L. I.; Gavrilenko, V. V.; Paley, B. A. *J. Organomet. Chem.* **1970**, *21*, 269.

(21) Straus, F.; Kollek, L.; Heyn, W. *Chem. Ber.* **1930**, *63*, 1868.

0020-1669/83/1322-1049$01.50/0

Table I. Infrared ν(C–O) Spectra for Compounds III, $(C_4O_2R^1R^2)(C{=}CR^3R^4)Co_2(CO)_6$

				abs max, cm^{-1}						
R^1	R^2	R^3	R^4	ν_1	ν_2	ν_3	ν_4	ν_5	ν_6	ν_{org}
H	H	*n*-Bu	Cl	2112.5	2082.7	2065.8	2054.0	2039.0		1783.6
		n-Bu	I	2110.8	2081.1	2064.8	2052.9	2037.6		1783.3
		Ph	Br	2112.9	2084.8	2066.8	2055.9	2044.1		1783.4
		Br	Br	2115.8	2088.0	2070.8	2060.3	2052.6		1785.2
		I	I	2112.4	2086.6	2070.8	2059.1	2053.4		1785.4
H	*n*-Pr	*n*-Bu	Cl	2110.4	2080.0	2062.9	2050.8	2036.4		1774.3
		n-Bu	Br	2110.0	2079.5	2062.9	2051.4	2035.9		1773.8
		Ph	Br	2110.0	2081.6	2064.1	2052.6	2041.5		1773.5
		I	I	2112.3	2084.1	2067.8	2055.8	2047.9		1784.3
H	*n*-Bu	Br	Br	2113.7	2087.3	2068.3	2057.7	2050.1	2043.5	1775.3
		I	I	2114.7	2087.0	2068.8	2058.3	2048.7		1776.3
H	*n*-Pe	I	I	2112.3	2084.5	2067.7	2056.1	2048.2		1775.4
H	Ph	*n*-Bu	Cl	2110.3	2081.6	2063.8	2052.8	2037.9		1769.9
		n-Bu	Br	2110.5	2081.5	2064.4	2053.5	2038.4		1771.2
		n-Bu	I	2108.8	2080.4	2064.0	2052.1	2036.6		1770.7
		Ph	Br	2111.3	2083.8	2065.7	2055.5	2043.5		1770.7
		I	I	2114.9	2087.9	2070.7	2058.8	2049.3		1769.2

a ~1:1 C_2H_2/Ar mixture for this purpose and a relatively slow flow rate (~50 cm^3/min) to ensure a high conversion of C_2H_2.

Infrared spectra were recorded by UR-20 and IR-75 double-beam spectrometers from Carl Zeiss (Jena, GDR) (with simultaneous DCl calibration[22]), ^{1}H NMR spectra were taken with a BS-487 (Tesla, Brno, CSSR) 80-MHz instrument, mass spectrometric measurements were performed with the direct-inlet system of an MAT-111 (Varian, Bremen, GFR) GC–MS system, and osmometric molecular weight determinations were undertaken with a Knauer vapor-phase osmometer (Darmstadt, GFR) in benzene solutions.

Separation of complexes III from the reaction mixtures was performed with use of UNI Plate 1012 silica gel G TLC plates of Anachem.

The thermogravimetric experiments were done with a Derivatograph (MOM, Budapest) thermobalance, which is capable of obtaining contemporaneously the TG, DTG, and DTA curves.

Preparation of the $(C_4O_2R^1R^2)(C{=}CR^3R^4)Co_2(CO)_6$ (III) Complexes. All complexes III were prepared in a fairly similar way; therefore, we describe only one example here.

A 1.0-g (2.25-mmol) sample of complex I (R^1 = H, R^2 = *n*-Pe) (*n*-Pe = *n*-pentyl) was dissolved in 30 cm^3 benzene. The solution was transferred to a reaction vessel, thermostated to 25 ± 5 °C and provided with a magnetic stirrer and an outlet with a Nujol bubbler, and then 0.63 g (2.26 mmol) of C_2I_2 was added. Immediately after the addition of the haloacetylene, a vigorous gas evolution occurred, which diminished after ~1 h. The solution was then stirred for a further 2 h. (In some experiments the gas valve was substituted by a thermostated gas buret and the volume of the CO evolved was measured: 0.94 ± 0.03 mol of CO/mol of starting complex was found.) The reaction mixture was then filtered, concentrated to half-volume, transferred to preparative TLC plates (~1-cm^3 pro plate), and eluted with CH_2Cl_2. Besides some fractions of very low intensity, only one colored (orange) band was observed. This was separated, eluted with Et_2O, and recrystallized two or three times from *n*-hexane/Et_2O (1:1). The orange crystalline product was analyzed to be of the formula $(C_4O_2R^1R^2)(R^3C_2R^4)Co_2(CO)_6$. Sometimes orange, powderlike, microcrystalline, moderately air-resistant substances were obtained with other combinations of the substituents. Yields were almost quantitative: 80–90%.

Infrared ν(C–O) and ^{1}H NMR spectra are shown in Tables I and II, respectively. (Table II is available as supplementary material.)

X-ray Diffraction Studies. Unit cell dimensions and other crystal data are given in Table III. Intensity data were collected at room temperature. The decay of the sample was quite limited (~10–15%), and the data were corrected by the use of a standard reflection monitored every hour. A total of 5731 reflections were collected in the range $5 \leq 2\theta \leq 58°$. Of these, 2547 had $I \geq 2.5\sigma(I)$. Two standard reflections were measured after each 60 reflections, and at the end of data collection, they showed a decrease in their intensities of about 9%. Data reduction was carried out with correction for Lorentz and polarization effects, for sample decay, and for absorption (maximum transmission coefficient 0.96, minimum 0.62).

Table III. Crystal Data for III (R^1 = H, R^2 = *n*-Pe, R^3 = R^4 = I)

mol formula	$C_{16}H_{11}O_8I_2Co_2$
mol wt	702.9
color of cryst	orange
space group	$P\bar{1}$
cell dimens^a	
a, pm	1169.7 (6)
b, pm	1130.6 (7)
c, pm	867.5 (4)
α, deg	89.09 (4)
β, deg	96.33 (4)
γ, deg	105.11 (5)
molecules/cell	2
cell vol, pm^3	110.0711 × 10^6
calcd density, g/cm^3	2.1209
radiation wavelength, pm	71.0688
linear abs coeff, cm^{-1}	43.17
cryst faces	{100}, {010}, {1,−1,0}, {011}, {−1,1,1}
cryst vol, mm^3	0.0179

^{a} At room temperature; 25 reflections.

The structure was solved by direct methods (SHELX).[23a] (The scattering factors for neutral atoms were taken from ref 23b.) The resulting *E* map revealed the two iodine and the two cobalt atoms. The subsequent Fourier map revealed the remaining atoms in the structure. Isotropic refinement followed by anisotropic refinement yielded the residuals *R* = 0.059 and R_w = 0.066. No attempts have been made to refine the hydrogen atoms of the side chain.

The "goodness of fit"in the final cycle of refinement was 2.5, and the averaged shift/standard deviation was 0.12. The ratio of observations to variables was 2547/262 = 10.

The final ΔF map showed some residual peaks about 0.8 e Å^{-3} at a distance of 0.9–1.1 Å from the iodine atoms. No other features have been observed.

Refined fractional coordinates and equivalent isotopic thermal parameters appear in Table IV. Anisotropic *U*'s are available (see supplementary material). Bond lengths and angles are displayed in Tables V and VI.

A comparison of the angles characterizing the positions of the terminal carbonyls in I (R^1 = R^2 = H) and III (R^1 = H, R^2 = *n*-Pe, R^3 = R^4 = I) was made in Table VII.

---

(22) Bor, G. *Acta Chim. Acad. Sci. Hung.* **1962**, *34*, 315.

(23) (a) Sheldrick, G. M. "SHELX, a Programme for Crystal Structure Determination"; University of Cambridge: Cambridge, U.K., 1977. (b) "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. IV, pp 99–101.

(24) Klyne, W.; Prelog, V. *Experientia* **1960**, *16*, 521.

(25) Stanford, R. H., Jr.; Waser, J. W. *Acta Crystallogr., Sect. A* **1972**, *A28*, 213.

(26) Schoemaker, W.; Waser, J.; Marsh, E. E.; Bergman, G. B. *Acta Crystallogr.* **1959**, *12*, 600.

Table IV. Atomic Coordinates for III (R^1 = H, R^2 = *n*-Pe, R^3 = R^4 = I) with Esd's in Parentheses

atom	*x*/*a*	*y*/*b*	*z*/*c*	*B*(equ), Å^2
I(1)	0.2158 (1)	0.3398 (1)	0.8838 (1)	6.12
I(2)	0.3941 (1)	0.5562 (1)	1.1581 (1)	5.92
Co(1)	0.1701 (2)	0.6384 (2)	0.6755 (2)	3.92
Co(2)	0.2909 (2)	0.7841 (2)	0.8623 (2)	4.08
O(1)	0.2008 (11)	0.4481 (12)	0.4751 (14)	6.58
O(2)	−0.0387 (11)	0.5233 (14)	0.8295 (14)	7.88
O(3)	0.0484 (11)	0.7760 (13)	0.4558 (15)	7.60
O(4)	0.5377 (11)	0.8662 (12)	0.9889 (15)	7.19
O(5)	0.1677 (14)	0.7583 (13)	1.1409 (16)	8.44
O(6)	0.2401 (12)	1.0178 (11)	0.7756 (15)	7.08
O(7)	0.3272 (9)	0.8380 (8)	0.5374 (11)	4.43
O(8)	0.4422 (10)	0.9136 (11)	0.3498 (13)	6.04
C(1)	0.1888 (14)	0.5206 (16)	0.5520 (17)	4.94
C(2)	0.0398 (14)	0.5662 (16)	0.7717 (18)	5.28
C(3)	0.0956 (14)	0.7225 (15)	0.5393 (18)	5.13
C(4)	0.4433 (15)	0.8342 (15)	0.9430 (18)	5.28
C(5)	0.2164 (16)	0.7694 (15)	1.0374 (21)	5.72
C(6)	0.2603 (14)	0.9267 (16)	0.8114 (18)	5.06
C(7)	0.3254 (12)	0.7501 (12)	0.6510 (15)	3.93
C(8)	0.4268 (11)	0.7035 (14)	0.6338 (16)	4.29
C(9)	0.4874 (12)	0.7620 (14)	0.5224 (15)	4.22
C(10)	0.4255 (13)	0.8462 (15)	0.4561 (16)	4.62
C(11)	0.6024 (14)	0.7505 (17)	0.4672 (18)	5.77
C(12)	0.7072 (17)	0.8427 (18)	0.5429 (25)	7.36
C(13)	0.7310 (21)	0.8241 (22)	0.7071 (26)	9.19
C(14)	0.8355 (27)	0.9375 (26)	0.7961 (42)	12.87
C(15)	0.9437 (24)	0.9356 (33)	0.7538 (46)	15.30
C(16)	0.2831 (13)	0.5237 (13)	0.9417 (16)	4.53
C(17)	0.2607 (11)	0.6143 (13)	0.8646 (13)	3.63

Table V. Significant Interatomic Distances in III (R^1 = H, R^2 = *n*-Pe, R^3 = R^4 = I) with Esd's in Parentheses (pm)

Bonding			
Co(1)–Co(2)	238.8 (3)	C(3)–O(3)	112.6 (22)
Co(1)–C(1)	181.6 (16)	C(4)–O(4)	109.9 (22)
Co(1)–C(2)	179.4 (18)	C(5)–O(5)	110.4 (25)
Co(1)–C(3)	179.7 (17)	C(6)–O(6)	114.6 (23)
Co(1)–C(7)	195.5 (13)	C(7)–O(7)	138.6 (16)
Co(1)–C(17)	190.8 (12)	C(7)–C(8)	144.0 (22)
Co(2)–C(4)	178.9 (16)	C(8)–C(9)	132.7 (19)
Co(2)–C(5)	181.7 (19)	C(9)–C(10)	141.8 (24)
Co(2)–C(6)	177.9 (19)	C(10)–O(7)	139.6 (19)
Co(2)–C(7)	198.4 (14)	C(10)–O(8)	118.7 (19)
Co(2)–C(17)	185.9 (15)	C(16)–C(17)	128.3 (21)
C(1)–O(1)	109.2 (22)	C(16)–I(1)	207.1 (14)
C(2)–O(2)	111.1 (23)	C(16)–I(2)	214.0 (13)
Nonbonding			
Co(1)–I(1)	393.5 (3)	C(1)–C(7)	276.2 (20)
Co(2)–I(2)	392.6 (3)	C(1)–C(17)	288.2 (19)
C(7)–C(17)	244.5 (18)	C(4)–C(7)	280.1 (19)
C(8)–C(16)	362.3 (20)	C(4)–C(17)	285.8 (19)
Co(1)–C(5)	342.0 (18)	I(1)–I(2)	352.5 (3)
Co(1)–C(6)	334.4 (17)	I(1)–C(2)	353.7 (16)
Co(2)–C(2)	333.1 (15)	O(1)–I(1)	373.3 (12)
Co(2)–C(3)	337.3 (15)	O(4)–I(2)	381.7 (13)
C(4)–I(2)	357.8 (16)	C(2)–I(1)	373.7 (19)
C(1)–I(1)	353.7 (16)		

Table VI. Significant Bond Angles in III (R^1 = H, R^2 = *n*-Pe, R^3 = R^4 = I) with Esd's in Parentheses (deg)

Co(1)–C(*n*)–O(*n*)$_{\text{av}}$ (*n* = 1–3)	179.2	C(4)–Co(2)–C(7)	95.7 (7)
Co(2)–C(*n*)–O(*n*)$_{\text{av}}$ (*n* = 4–6)	178.6	C(5)–Co(2)–C(7)	160.1 (7)
C(1)–Co(1)–C(2)	104.7 (8)	C(4)–Co(2)–C(17)	103.2 (7)
C(1)–Co(1)–C(3)	95.8 (8)	C(5)–Co(2)–C(17)	86.3 (7)
C(2)–Co(1)–C(3)	100.8 (7)	C(7)–Co(2)–C(17)	78.9 (6)
C(1)–Co(1)–C(7)	157.2 (7)	C(7)–Co(2)–Co(1)	52.1 (4)
C(2)–Co(1)–C(7)	94.8 (7)	C(17)–Co(2)–Co(1)	51.6 (4)
C(1)–Co(1)–C(17)	85.9 (6)	Co(1)–C(7)–Co(2)	74.6 (5)
C(3)–Co(1)–C(17)	155.5 (7)	Co(1)–C(17)–Co(2)	78.7 (5)
C(7)–Co(1)–C(17)	78.5 (6)	C(16)–C(17)–Co(1)	137.4 (11)
C(7)–Co(1)–Co(2)	53.3 (4)	C(16)–C(17)–Co(2)	144.0 (11)
C(17)–Co(1)–Co(2)	49.8 (4)	I(1)–C(16)–C(17)	126.5 (11)
C(4)–Co(2)–C(5)	100.6 (8)	I(2)–C(16)–C(17)	119.8 (11)
C(4)–Co(2)–C(6)	100.9 (8)	I(1)–C(16)–I(2)	113.7 (7)
C(5)–Co(2)–C(6)	93.9 (8)		

Table VII. Comparison of Angles Characterizing the Positions of the Terminal Carbonyl Groups in I (R^1 = R^2 = H)[a] and III (R^1 = H, R^2 = *n*-Pe, R^3 = R^4 = I)

torsional angles[b]			angles formed by LSQ lines[c]		
	ϑ, deg			φ, deg	
atoms	I	III	atoms[d]	I	III
C(1), Co(1), Co(2), C(4)	3.0	3.1 (1.2)	C(1), O(1)	160.3	137.3
C(2), Co(1), Co(2), C(5)	0.4	2.4 (0.8)	C(2), O(2)	104.3	104.9
C(3), Co(1), Co(2), C(6)	1.0	3.4 (0.8)	C(3), O(3)	112.8	105.9
			C(4), O(4)	135.5	138.1
			C(5), O(5)	98.4	105.8
			C(6), O(6)	114.5	104.6

[a] Calculated by using the data of ref 14b. The numbers of the atoms were changed according to this paper to facilitate comparison. [b] Calculated according to ref 24, 25. [c] Calculated according to ref 26. [d] Atoms of the respective carbonyl groups; φ refers to angle with the Co(1)–Co(2) line.

Results and Discussion

Preparative Results. Complexes I when reacted with haloacetylenes ($R^3C_2R^4$, R^3 = alkyl, aryl, Cl, Br, I; R^4 = Cl, Br, I, if both R^3 and R^4 are halogens R^3 = R^4) under atmospheric pressure (CO or Ar), at room temperature in *n*-hexane or benzene solution, were transformed into orange cobalt–organic products, which were analyzed to be $(C_4O_2R^1R^2)(R^3C_2R^4)Co_2(CO)_6$ (III) (reaction 1). The yields of compounds III were almost quantitative. The evolution of 1 mol of CO/mol of starting compound (I) could be detected if reaction 1 was followed by gas volumetry. Compounds III could be purified by TLC. During this operation the development of one intensive orange band could be observed, which could not be split into components even by repeated analytical TLC with various solvents and solvent mixtures. This result indicated that complexes III were formed in only one isomeric form, in contrast to compounds II.[2]

$$\underset{\text{I}}{(C_4O_2R^1R^2)Co_2(CO)_7} + R^3C_2R^4 \rightarrow \underset{\text{III}}{(C_4O_2R^1R^2)(R^3C_2R^4)Co_2(CO)_6} + CO \quad (1)$$

Thermogravimetric analysis and mass spectra of compounds III showed first the splitting-off of the carbonyl ligands and then *separately* the $R^3C_2R^4$ and $C_4O_2R^1R^2$ moieties. Mass spectra, however, did not show molecular ions, the highest observable fragment was $[M - 2CO]^+$ even at low (20-eV) ionization potentials. The TG and MS results thus supported the analyses and indicated that no new C–C bond was formed between the lactone and the "new" acetylene moieties of compounds III.

Destruction of compounds III by refluxing pyridine lead to the evolution of 6 mol of CO/mol of III but no free $R^3C_2R^4$ acetylene could be detected in the reaction mixture by gas chromatography. This result indicated that, although $R^3C_2R^4$ has not been bound to the lactone ring, it has probably been isomerized. The liberation of all of the CO ligands shows that neither of these has been chemically bound to either of the organic ligands as might have been expected on the basis of some analogies.[27]

---

(27) Burt, R.; Cooke, M.; Green, M. *J. Chem. Soc. A* **1970**, 2891. Dyke, A. F.; Knox, S. A. R.; Naish, P. J.; Taylor, G. E. *J. Chem. Soc., Chem. Commun.* **1980**, 409. Finnimore, S. R.; Knox, S. A. R.; Taylor, G. E. *Ibid.* **1980**, 411.

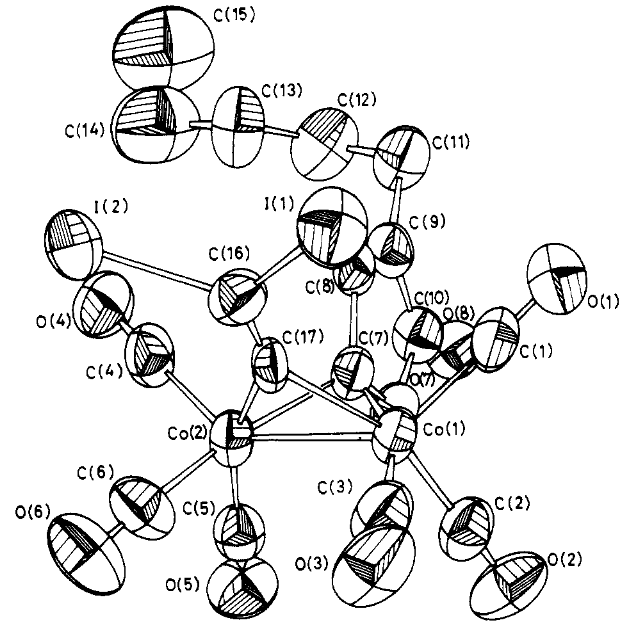


Figure 1. ORTEP drawing of the structure of III (R^1 = H, R^2 = *n*-Pe, $R^3 = R^4$ = I).

Compounds III are of remarkable stability: they can be stored under air for a couple of months and some of them could be recovered almost quantitatively unchanged after treating with concentrated H_2SO_4 at 20–40 °C.

Complexes III are orange to orange-red solids, which are very soluble in Et_2O, benzene, or CH_2Cl_2 and moderately soluble in saturated hydrocarbons. Recrystallization from Et_2O/*n*-hexane yields generally microcrystalline powders; crystals could be grown from derivatives containing at least one longer alkyl chain (e.g., R^1 = *n*-Pe, R^3 = *n*-Bu, etc.).

Spectra. In addition to the preparative and analytical results, infrared ν(C–O) (Table I) spectra indicate a $(\mu\text{-L})_2Co_2(CO)_6$ structure on the basis of the absence of bridge-CO bands. Generally five fundamentals (in one case six: a weak shoulder at the lower end of the terminal spectrum) can be observed which indicate that the C_{2v} local symmetry of the $Co_2(CO)_6$ moiety[28,29] was not (or only very slightly) perturbed by the obvious asymmetry of the bridging ligands.[30,31] These results show that the bridging ligands may be of different chemical constitution but they have similar electronic effects.[30] Another explanation of the generally low number of the bands would be that the sixth band remains hidden (most probably under the strong band system between 2070 and 2030 cm^{-1}). It is beyond the possibilities of the spectroscopic methods to choose between these explanations.

^1H NMR spectra (Table II (supplementary material)) [e.g., for III ($R^1 = R^2$ = H, $R^3 = R^4$ = I), in $CDCl_3$: 6.63 ppm, d, 1 H, J = 5 Hz, lactone 2 H (R^2); 8.27 ppm, d, 1 H, J = 5 Hz, lactone 3 H (R^1)] show that the overall structure of the lactone ring and the hydrocarbon moiety (if any) in the $R^3C_2R^4$ acetylene remained practically unaltered.

^{13}C NMR spectra could not be obtained in good quality because of low solubility and spin/quadrupole (Co) coupling problems.

The most important information obtained from the spectroscopic studies is the high similarity of the spectra showing that the overall structures of complexes III are identical. This permits the *generalization* of the *structural data* obtained for *one* representative of the new complexes.[32]

Description of the Structure. The refined structure of III (R^1 = H, R^2 = *n*-Pe, $R^3 = R^4$ = I) shows the same overall shape as reported in the preliminary note[6] with the only main difference that indications of a disorder in the C_2I_2 group disappeared upon repeated diffraction experiments on different crystal samples and further refinement.

The overall structure of compounds III can thus be deduced from that of the starting "lactone" complex I by substituting the oxygen atom in the bridging carbonyl group by the $>CR^3R^4$ moiety. Apparently the (μ-butenolido)dicobalt part of the structure remains unaltered during all the reaction steps leading to the formation of compounds III.

The new bridging ligands are doubtless novel representatives of the complexed vinylidene group. This is indicated by the C(16)–C(17) bond distance and the bonding angles around C(16) as well as by the coplanarity of the $>C{=}CI_2$ group. Even the two Co atoms fit relatively well into the plane of the $>C{=}CI_2$ moiety, indicating a real olefinic character of the $>C{=}C<$ unit.

The new ligand can formally be regarded as a bridging carbene group, which can be supposed at first sight for the bridging butenolide group too. The comparison of the geometry around the two bridging carbon atoms offers a good opportunity to compare their effective character. The geometry of the bridging lactone ring is practically the same as for I ($R^1 = R^2$ = H),[14b] for which an $sp^{2.65}$ character of the 4-C atom could be deduced on the basis of the bond angles.[15] The C(7)–C(8) and C(7)–O(7) distances in the butenolide ring agree within the experimental error with the corresponding distances of I ($R^1 = R^2$ = H) and of analogous organic[33,34] compounds where the sp^3 character of the 4-C atom of the dihydrofuranone ring is more evident than for either I or III.

Comparing the C=C distance of the vinylidene group to that in similar structures as CCH_2 (131 (1) pm),[35] CCHPh (135 (2) pm),[36] $CCPh_2$ (133 (1) pm),[37] and $CC(CN)_2$ (138 (3) pm)[38] shows that the vinilydene C–C distance in III is relatively short (128 (2) pm).

In summary, it can be concluded that the two bridging carbon atoms in III are of somewhat different character. The 4-C atom of the lactone ring (C(7)) shows a high extent of p-electron contribution to the hybrid orbitals, and thus it can be regarded as a nearly saturated carbon member of the metallacycle. The bridging carbon atom of the vinylidene group on the other hand shows a relatively high s character and can be regarded as a geminally dimetalated olefinic carbon. Obviously neither of these carbon atoms can be regarded as clear examples of sp^3 or sp^2 carbons, but the lactone 4-C atom is nearer to the sp^3 while the bridging vinylidene C is closer to the sp^2 configuration. Regarding the bonding mode of these carbon atoms to cobalt atoms, our results favor the hypothesis of Caulton et al.[35] (i.e., that the vinylidene ligand can be regarded as a geminally transition-metal-disubstituted olefin). We prefer, however, to consider the metal–bridging C bonds to be bent, i.e. to be derived from overlaps of orbitals with noncollinear orientation vectors.

The Co–Co distance (238.8 pm) in complex III can be compared with those of an already numerous series of binuclear bridged cobalt carbonyls: bridged $Co_2(CO)_8$, 252.4 pm;[39]

---

(28) Bor, G. *Chem. Ber.* **1963**, *96*, 2644.

(29) Bor, G. *J. Organomet. Chem.* **1975**, *94*, 181.

(30) Váradi, G.; Vecsei, I.; Vizi-Orosz, A.; Pályi, G.; Massey, A. G. *J. Organomet. Chem.* **1976**, *114*, 213.

(31) Bor, G.; Kettle, S. F. A.; Stanghellini, P. L. *Inorg. Chim. Acta* **1976**, *18*, L18.

(32) A similar argument could be used for complexes II,[2] too.

(33) Karle, I. L.; Karle, J. *Acta Crystallogr., Sect. B* **1969**, *B25*, 434.

(34) Karle, I. L.; Karle, J. *Acta Crystallogr., Sect. B* **1970**, *B26*, 207.

(35) Folting, K., Huffman, J. C.; Lewis, L. N.; Caulton, K. G. *Inorg. Chem.* **1979**, *18*, 3483.

(36) Aleksandrov, G. G.; Antonova, A. B.; Kolobova, N. E.; Struchkov, Yu. T. *Koord. Khim.* **1976**, 2.

(37) Mills, O. S.; Redhouse, A. D. *J. Chem. Soc. A* **1968**, 1282.

(38) Kirchner, R. M.; Ibers, J. A. *J. Organomet. Chem.* **1974**, *82*, 243.

I ($R^1 = R^2 = H$), 245 pm;[14b] (μ-$PhC_2Ph)Co_2(CO)_6$, 247 pm;[40] (μ-t-BuC_2-t-$Bu)Co_2(CO)_6$, 246.3 pm;[41] IIA ($R^1 = H$, $R^2 = Ph$, $R^3 = H$, $R^4 = n$-Bu), 247 pm;[2] IIB ($R^1 = H$, $R^2 = Ph$, $R^3 = H$, $R^4 = Me$), 247 pm;[18b] [μ-η-$(HC_2CF_3)_3]Co_2(CO)_4$, 245.9 pm;[42] [μ-η-$(HC_2H)(HC_2$-t-$Bu)_2]Co_2(CO)_4$, 243 pm;[43] and the dipnicogenic derivatives (μ-$E_2)Co_2(CO)_5(PPh_3)$ with E = P,[44] 257.4 pm, and E = As,[45] 259.4 pm. This comparison shows the Co–Co distance of III as the shortest known Co–Co bond length in bridged binuclear cobalt carbonyls.

The Co–C and C–O bond distances of the coordinated carbonyl groups are relatively long and short, respectively. This can be due to the net electron acceptor charter of the bridging substituents and the high Co–Co bond order as well. This is in agreement with the high mean ν(C–O) values observed. These distances do not show much variation (beyond the experimental error), which is in accord with the shape of the observed ν(C–O) spectra, which resembles more a C_{2v} than a C_s local symmetry situation. The array of the carbonyl groups fits quite well the idealized C_{2v} symmetry as shown in Table VII. Published data on I ($R^1 = R^2 = H$)[14b] allowed us to calculate the same orientation vectors for this compound too. The two sets of angles that are confronted in Table VII show that the reduction of the C_{2v} symmetry in the type I compounds[28,30] is reflected in the relative orientation of the coordinated carbonyl groups.

The most important of the nonbonding distances is the long C(7)–C(17) distance, which excludes the possibility that a new C–C bond had been formed as in complexes II.[2,18]

The isomerization of acetylenes coordinated to transition metals has been reported for some models in the last few years,[35,36,46–56] but these involve most probably the 1,2-shift of a terminal hydrogen atom. Reaction 1 represents the first clear example of a 1,2-shift of a non-hydrogen substituent. This type of a 1,2-shift reaction has been found recently[4] to operate also in the case of acetylenecarboxylic acid esters. The formation of $[Co_3(CO)_9C]_2$ from dihaloacetylenes and $Co_2(CO)_8$[57] may also proceed via dihalovinylidene–cobalt intermediates. We are now currently investigating the possibilities of further generalization of these 1,2-shift reactions.

The reactions involving a 1,2-shift of substituents other than H are interesting since these are much more conclusive, proving that the substituent of the acetylene has really been shifted, since hydrogen uptake of the β-carbon atom of eventual σ-acetylide intermediate(s) not only is conceivable in the generally used media but has de facto been proved preparatively too.[51]

Acknowledgment. The authors acknowledge Drs. I. Ötvös, I. Iglewski, K. Lâbdy, and A. Horvâth (Veszprêm) for help in obtaining the spectra, thermogravimetric curves, and analyses. Stimulating discussions with Prof. E. Sappa (Turin) are also acknowledged.

Registry No. I ($R^1 = R^2 = H$), 18177-59-8; I ($R^1 = H$, $R^2 = n$-Pr), 56544-39-9; I ($R^1 = H$, $R^2 = n$-Bu), 73358-21-1; I ($R^1 = H$, $R^2 = n$-Pe), 73358-22-2; I ($R^1 = H$, $R^2 = Ph$), 56385-99-0; III ($R^1 = R^2 = H$, $R^3 = n$-Bu, $R^4 = Cl$), 84583-16-4; III ($R^1 = R^2 = H$, $R^3 = n$-Bu, $R^4 = I$), 84583-17-5; III ($R^1 = R^2 = H$, $R^3 = Ph$, $R^4 = Br$), 73363-31-2; III ($R^1 = R^2 = H$, $R^3 = R^4 = Br$), 84583-18-6; III ($R^1 = R^2 = H$, $R^3 = R^4 = I$), 84583-19-7; III ($R^1 = H$, $R^2 = n$-Pr, $R^3 = n$-Bu, $R^4 = Cl$), 84583-20-0; III ($R^1 = H$, $R^2 = n$-Pr, $R^3 = n$-Bu, $R^4 = Br$), 84583-21-1; III ($R^1 = H$, $R^2 = n$-Pr, $R^3 = Ph$, $R^4 = Br$), 84583-22-2; III ($R^1 = H$, $R^2 = n$-Pr, $R^3 = R^4 = I$), 84583-23-3; III ($R^1 = H$, $R^2 = n$-Bu, $R^3 = R^4 = Br$), 73363-30-1; III ($R^1 = H$, $R^2 = n$-Bu, $R^3 = R^4 = I$), 84583-24-4; III ($R^1 = H$, $R^2 = n$-Pe, $R^3 = R^4 = I$), 73358-20-0; III ($R^1 = H$, $R^2 = Ph$, $R^3 = n$-Bu, $R^4 = Cl$), 84583-25-5; III ($R^1 = H$, $R^2 = Ph$, $R^3 = n$-Bu, $R^4 = Br$), 84583-26-6; III ($R^1 = H$, $R^2 = Ph$, $R^3 = n$-Bu, $R^4 = I$), 84583-27-7; III ($R^1 = H$, $R^2 = Ph$, $R^3 = Ph$, $R^4 = Br$), 84583-28-8; III ($R^1 = H$, $R^2 = Ph$, $R^3 = R^4 = I$), 84583-29-9; C_2Br_2, 624-61-3; C_2Cl_2, 7572-29-4; C_2I_2, 624-74-8; n-BuC_2Cl, 1119-66-0; n-BuC_2I, 1119-67-1; n-BuC_2Br, 1119-64-8; PhC_2Br, 932-87-6; Co, 7440-48-4.

Supplementary Material Available: Table II [^{1}H NMR spectra for some compounds of III, $(C_4O_2R^1R^2)(C{=}CR^3R^4)Co_2(CO)_6$], Table VIII [analyses for $(C_4O_2R^1R^2)(C{=}CR^3R^4)Co_2(CO)_6$ compounds], Table IX [anisotropic thermal parameters ($\times 10^4$) for (μ-C_4O_2H-n-Pe)(μ-$CCI_2)Co_2(CO)_6$], Table X [geometric data for (μ-C_4O_2H-n-Pe)(μ-$CCI_2)Co_2(CO)_6$], Table XI [observed and calculated structure factors for (μ-C_4O_2H-n-Pe)(μ-$CCI_2)Co_2(CO)_6$] (34 pages). Ordering information is given on any current masthead page.

---

(39) Sumner, G. G.; Klug, H. P.; Alexander, L. E. *Acta Crystallogr.* **1964**, *17*, 732.

(40) (a) Sly, W. G. *J. Am. Chem. Soc.* **1959**, *81*, 18. (b) Brown, D. A. *J. Chem. Phys.* **1960**, *33*, 1037.

(41) Cotton, F. A.; Jamerson, J. D.; Stults, B. R. *J. Am. Chem. Soc.* **1976**, *98*, 1774.

(42) Dickson, R. S.; Fraser, D. J.; Gatehouse, B. M. *J. Chem. Soc., Dalton Trans.* **1972**, 2278.

(43) Mills, O. S.; Robinson, G. *Proc. Chem. Soc., London* **1964**, 187.

(44) Campana, C. F.; Vizi-Orosz, A.; Pâlyi, G.; Markő, L.; Dahl, L. F. *Inorg. Chem.* **1979**, *18*, 3054.

(45) Foust, A. S.; Campana, C. F.; Sinclair, J. D.; Dahl, L. F. *Inorg. Chem.* **1979**, *18*, 3047.

(46) Chisholm, M. H. *Platinum Met. Rev.* **1975**, *19*, 100.

(47) Nesmeyanov, A. N.; Antonova, A. B.; Kolobova, N. E.; Anisimov, K. N. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1974**, 2873.

(48) Nesmeyanov, A. N.; Aleksandrov, G. G.; Antonova, A. B.; Anisimov, K. N.; Kolobova, N. E.; Struchkov, Yu. T. *J. Organomet. Chem.* **1976**, *110*, C36.

(49) Antonova, A. B.; Kolobova, N. E.; Petrovsky, P. V.; Loshkin, B. V., Oberyuk, N. S. *J. Organomet. Chem.* **1977**, *137*, 55.

(50) Kolobova, N. E.; Antonova, A. B.; Khitrova, O. M.; Atipin, M. Yu.; Struchkov, Yu. T. *J. Organomet. Chem.* **1977**, *137*, 69.

(51) Bruce, M. I.; Wallis, R. C. *J. Organomet. Chem.* **1978**, *161*, C1.

(52) Aime, S.; Gervasio, G.; Milone, L.; Sappa, E.; Franchini-Angela, M. *Inorg. Chim. Acta* **1978**, *27*, 145.

(53) Raverdino, V.; Aime, S.; Milone, L.; Sappa, E. *Inorg. Chim. Acta* **1978**, *30*; 9.

(54) Sappa, E.; Manotti-Lanfredi, A. M.; Tiripicchio, A. *Inorg. Chim. Acta* **1979**, *36*, 197.

(55) Sappa, E.; Tiripicchio, A.; Tiripicchio-Camellini, M. *J. Chem. Soc., Chem. Commun.* **1979**, 254.

(56) Gambino, O.; Sappa, E.; Manotti-Lanfredi, A. M.; Tiripicchio, A. *Inorg. Chim. Acta* **1979**, *36*, 189.

(57) Vâradi, G.; Pâlyi, G. *Inorg. Chim. Acta* **1976**, *20*, L33; *Magy. Kem. Foly.* **1977**, *83*, 323.