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THE REACTIVITY OF ACETYLENES COORDINATED TO COBALT

III *. REACTION OF THE BUTENE-2-OLIDE-4 COMPLEXES, ($C_4O_2R^1$, R^2)$Co_2(CO)_7$ WITH ACETYLENES; FORMATION OF NEW TYPES OF ORGANIC LIGANDS

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Summary

The "lactone" complexes, ($C_4O_2R^1$,R^2)$Co_2(CO)_7$, (μ_2-carbonyl)[μ_2-*spiro*-(2,3-substituted-2-butene-4-olide-4-ylidene)]bis(tricarbonyl-cobalt)(*Co—Co*) derivatives, were found to react with acetylenes ($R^3C_2R^4$). This reaction yields the known acetylene complexes ($R^3C_2R^4$)$Co_2(CO)_6$ and two isomeric compounds with the composition [($C_4O_2R^1$,R^2)($R^3C_2R^4$)$_2$]$Co_2(CO)_5$. Spectroscopic arguments and X-ray structure determination show that both isomers contain σ, π-C_5 ligands bonded to both Co atoms. The structures of these isomers were identified.

Introduction

Acetylenes ($R^1C_2R^2$) and $Co_2(CO)_8$, as well as the corresponding ($R^1C_2R^2$)-$Co_2(CO)_6$ complexes, react (at 70°C, 20—30 MPa) with CO in apolar solvents to form [4] the "lactone" complexes ($C_4O_2R^1$,R^2)$Co_2(CO)_7$ (I). This reaction was found to be quantitatively regiospecific [1,5,6]. The complexes I were proved

* For part II see ref. 1. The preparative and spectroscopic aspects of this work have been presented at Symposia [2,3].
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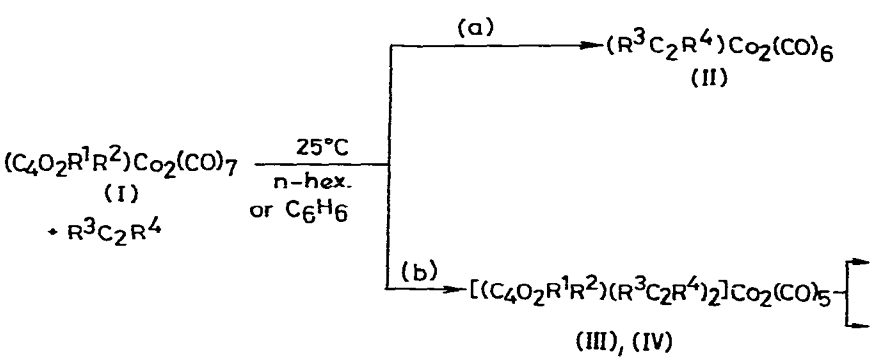
to be intermediates in the catalytic synthesis of bifurandiones [6—8]. The formation of the "second" ring of bifurandiones does not show regiospecificity [7—9]. It was believed that this latter step could be modelled by the atmospheric reaction of compounds I with acetylenes. Sternberg et al. [4] reported that the complexes I react with further amounts of acetylenes with evolution of CO and formation of some new organocobalt species, but they could not identify the latter products.

Researches carried out at the same time by an English group (c.f. refs. 10, 11 and Acknowledgement) and in our Laboratory [2,3] showed that this reaction leads to the formation of known complexes along with a pair of unknown isomeric complexes. The structure of one (IV) of the latter compounds (termed isomer B) was determined by X-ray diffraction by Pauson's group [10]. Here we report our preparative and spectroscopic observations together with X-ray diffraction results on the structure of the other isomer (A, III).

Results and discussion

Preparative results

We treated compounds I with acetylenes ($R^3C_2R^4$) and found that the main organometallic products could be resolved very laboriously by column (silica gel, 1/1 C_6H_6/Et_2O eluent) or much better by thin layer chromatography (silica gel, CH_2Cl_2 eluent) into three fractions (II, III (A) and IV (B)):



(1)

Compounds II were identified as the well-known μ-acetylene complexes [12] on the basis of their IR ν(C—O) spectra [13] as well as the analyses and ν(C—O) spectra of their monosubstituted derivatives with tertiary phosphines [14,15].

The TLC fractions III and IV were found to have the same elemental composition and molecular weight. We were unable to detect free $R^3C_2R^4$ by GLC after destruction of these compounds with aqueous acid (reflux with 10% H_2SO_4 until the brown colour disappeared) or reaction with CO (100°C, 25 MPa, 2 h, hexane — $Co_2(CO)_8$ was the only identifiable organometallic substance detected). This indicates that the two $R^3C_2R^4$ acetylene units reacted either with one of the ligands of I or with each other or both.

For a variety of terminal acetylenes and complexes I we always found the formation of compounds II, III and IV. Internal alkynes were found to react according to reaction (1) [10,11], but we observed the appearance of other probably binuclear) organocobalt carbonyl derivatives which have not yet been characterized.

The reaction of acetylene (C_2H_2) with the "lactone" complexes I leads also to the formation of the corresponding II derivative, but at least five additional complexes can be separated by TLC. The ν(C—O) spectra of the unknown products are similar to those of compounds III and IV, but neither satisfactory analyses nor well-shaped crystals (for X-ray diffraction) could be obtained.

Bistrimethylsilylacetylene and α-acetylenic alcohols reacted with compounds I, but the ν(C—O) spectra of the products were entirely different from those of compounds III and IV. These products need further study.

Haloacetylenes were found to react with complexes I in an almost quantitative reaction to give compounds which contain only one "new" acetylene unit. The product subsequently rearranged to a bridging carbene-type ligand, as reported recently [16].

The isomeric pair of compounds III and IV, A and B, were brownish-red crystalline solids, as previously reported [10]. The complexes III showed a marked tendency to form microcrystalline powders, while complexes IV crystallized much more readily to give 0.1—2 mm crystals suitable for single-crystal X-ray diffraction work. After several attempts at slow crystallization and/or recrystallization, well-formed, plate-like, dark red crystals could be obtained of the two type III complexes from a mixture (1 : 1 : 1) of n-heptane, n-octane and benzene. They were those with R^1 = H, R^2 = Ph, R^3 = H, R^4 = n-Pr and n-Bu. Here we utilized our experience that a carefully chosen "equilibrium" of rigid-polar and flexible-apolar substituents facilitates the formation of well-shaped crystals from substances of oily or powder-like appearance.

Spectra

The infrared ν(C—O) (Table 1) and ^{1}H NMR (Table 2) spectra of compounds III and IV provide several clues to the structure of the isomeric pair, but these were not enough for unambigous specification of the structure. The most important information obtained from these spectra is the large degree of similarity within both series III and IV, which allows us to generalize from the overall geometries determined by X-ray diffraction for two compounds to all the compounds of type III and IV.

X-ray diffraction studies

The English group working on the same problem succeeded in obtaining a good diffraction pattern from a crystal of IV (R^1 = H, R^2 = Ph, R^3 = H, R^4 = Me) and were able to determine the molecular structure shown in Fig. 1.

Our attempts to solve the structure of the other isomer were first focused on III (R^1 = H, R^2 = Ph, R^3 = H, R^4 = n-Pr). This compound gave well-shaped orthorombic crystals, but because of the very low intensity of reflections only the unit cell parameters could be measured: a = 2637.4(4), b = 1295.2(3), c = 1461.0(5) pm.

Compound III (R^1 = H, R^2 = Ph, R^3 = H, R^4 = n-Bu) also gave orthorombic crystals, from which 608 independent reflections could be obtained. The unit cell parameters are a = 1875.6(3), b = 1164.5(1), c = 1229.1(1) pm, V = 2684(1) $\times 10^6$ pm^3, Z = 4, d (calcd.) = 1.436 g/cm^3, space group: $P\,2_12_12_1$. The structure

TABLE 1. INFRARED ν(C—O) DATA FOR THE $[(C_4O_2R^1,R^2)(R^3C_2R^4)_2]Co_2(CO)_5$ COMPOUNDS

Lactone		Acetylene		Isomer	Absorption maxima (cm^{-1})						
R^1	R^2	R^3	R^4		ν_1	ν_2	ν_3	ν_4	$\overline{\nu_t}$	ν_5 (bridge)	ν_6 (organic)
H	H	H	n-Pr	A	2063.0	2037.7	2012.8	2008.0	2030.4	1882.4	1771.8
				B	2075.8	2043.0	2012.0	2003.9	2033.2	1880.6	1767.4
H	H	H	n-Bu	A	2062.8	2037.1	2012.8	2007.5	2027.5	1882.5	1770.2
				B	2066.1	2045.2	2017.1	2005.5	2036.2	1881.8	1768.9
H	H	H	Ph	A [a]	—	—	—	—	—	—	—
				B	2078.5	2051.6	2029.8	2015.7	2043.8	1877.5	1774.0
H	H	H	CH_2OCH_3	A	2067.6	2042.0		2014.0(br) [b]		1885.2	1768.4
				B	2079.4	2052.1	2023.9	2015.8		1887.4	1779.4
H	n-Pr	H	Ph	A	2062.1	2036.5	2012.0	2007.1	2029.4	1882.2	1770.0
				B	2075.0	2048.4	2024.5	2012.5	2040.1	1874.5	1768.5
H	n-Pr	H	CH_2OCH_3	A	2066.2	2040.9	2015.8	2007.6	2032.6	1883.8	1765.1
				B	2076.4	2050.3	2019.1	2011.3	2039.2	1884.3	1767.3
H	n-Bu	H	Me	A	2062.0	2036.5	2011.5	2005.6	2028.9	1883.7	1772.5
				B	2076.8	2045.5	2016.0	2005.2	2035.8	1880.9	1768.9
H	n-Bu	H	Ph	A	2065.1	2036.7	2013.6	2007.6	2030.7	1882.9	1769.5
				B	2076.0	2047.0	2025.2	2013.5	2040.4	1879.2	1771.2
H	n-Bu	H	CH_2OCH_3	A	2066.4	2040.5	2015.4	2008.0	2032.6	1884.5	1764.6
				B	2076.5	2050.0	2020.0	2011.5	2039.5	1886.5	1766.3
H	n-Pen	H	Me	A	2060.8	2035.5	2009.1	2004.5	2027.5	1871.0	1760.3
				B	2075.5	2047.0	2014.8	2010.5	2037.0	1870.8	1762.2
H	n-Pen	H	Ph	A	2065.1	2048.3	2017.0	2012(sh)	2035.6	1874.0	1768.2
				B	2076.0	2049.2	2024.6	2013.2	2040.8	1876.0	1769.0
H	Ph	H	Me	A [c]	2064.2	2039.5	2016.8	2009.4	2032.5	1882.8	1762.0
				B [c]	2077.6	2047.8	2022.1	2009.1	2039.2	1883.5	1765.2
H	Ph	H	n-Pr	A	2061.4	2036.9	2012.3	2007.7	2029.6	1882.7	1761.4
				B	2075.8	2044.8	2017.1	2005.9	2035.9	1883.9	1765.6
H	Ph	H	n-Bu	A	2060.8	2035.9	2011.2	2006.0	2028.5	1872.0	1760.2
				B	2075.0	2045.5	2018.5	2006.0	2036.3	1872.5	1769.8
H	Ph	H	Ph	A	2065.3	2044.0	2019.2	2015.0	2035.9	1876.0	1764.7
				B	2076.4	2050.7	2028.9	2015.1	2042.7	1877.3	1767.5
H	Ph	H	CH_2OCH_3	A	2067.5	2043.3	2018.6	2012.5	2035.5	1887.5	1763.5
				B	2077.8	2051.2	2025.9	2015.2	2042.5	1886.4	1767.1
				A	2063.1	2040.3		2014.5(br) [b]	2033.1	1871.2	1767.8
Me	Me	H	Ph								1777(sh)
				B	2077.3	2049.4	2020.0	20.15.2	2040.5	1870.3	1767.5

[a] The formation of only trace amounts of this compound prevented us obtaining a good quality IR spectrum. [b] Broad, most probably two bands in one band overlap. [c] [illegible]

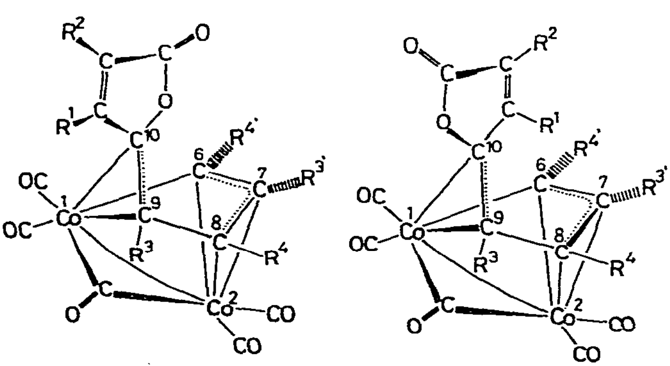
TABLE 2

^{1}H NMR SPECTRA OF SOME III AND IV ISOMERIC PAIRS

Lactone		Acetylene		Chemical shifts (ppm)		Assignment [a]
R^1	R^2	R^3	R^4	A(III)	B(IV)	
H	H	H	n-Pr	δ_1 1.10(t,6H)	1.00(t,6H)	R^4-γ-CH_3
				δ_2 1.80(sz.m,4H)	1.50(szm,4H)	R^4-β-CH_2
				δ_3 2.80(t,4H)	2.50(t,4H)	R^4-α-CH_2
				δ_4 3.42(s,1H)	4.40(s,1H)	$R^3 = H$
				δ_5 5.27(s,1H)	5.03(s,1H)	$R^3 = H$
				δ_6 6.12(d,1H)	6.12(d,1H)	$R^2 = H$
				δ_7 7.00(d,1H)	7.42(d,1H)	$R^1 = H$
H	Ph	H	n-Pr	δ_1 1.08(m,6H)	1.06(m,6H)	R^4-γ-CH_3
				δ_2 1.68(m,4H)	1.76(m,4H)	R^4-β-CH_2
				δ_3 2.60(m,4H)	2.56(m,4H)	R^4-α-CH_2
				δ_4 3.43(s,1H)	4.42(s,1H)	$R^3 = H$
				δ_5 5.20(s,1H)	5.07(s,1H)	$R^3 = H$
				δ_6 7.08(s,1H)	7.58(s,1H)	$R^1 = H$
				δ_7 7.26(m,3H)	7.30(m,3H)	$R^2 = C_6H_5$
				δ_8 7.77(m,2H)	7.78(m,2H)	$R^2 = C_6H_5$
H	Ph	H	CH_2OCH_3	δ_1 3.36(s,3H)	3.31(s,3H)	CH_2OCH_3
				δ_2 3.48(s,3H)	3.56(s,3H)	CH_2OCH_3
				δ_3 3.94(s,2H)	3.92(s,2H)	CH_2OCH_3
				δ_4 4.15(s,2H)	4.39(s,2H)	CH_2OCH_3
				δ_5 4.18(s,1H)	4.48(s,1H)	$R^3 = H$
				δ_6 5.50(s,1H)	5.40(s,1H)	$R^3 = H$
				δ_7 7.12(s,1H)	7.67(s,1H)	$R^1 = H$
				δ_8 7.20(m,3H)	7.28(m,3H)	C_6H_5
				δ_9 7.75(m,2H)	7.75(m,2H)	C_6H_5

[a] In the cases where signals belonging to the "new" acetylenes (for R^3 and $R^{3'}$ or R^4 and $R^{4'}$, notation of Fig. 1) appear separately no basis could be found to further specific assignment.

was solved by the heavy atom technique and refined by full-matrix, least-squares with anisotopic correction for the CO atoms only. We were able to obtain R = 0.098 and R_w = 0.103. Although our attempts to refine further the atomic positions failed, the overall molecular geometry and main structural features were determined unambigously.



(III) (A) (IV) (B)

Fig. 1. Schematic view of isomers A III and B IV.

A schematic view of the molecular geometry is shown in Fig. 1, an ORTEP drawing of the molecule in Fig. 2. The atomic coordinates, interatomic distances and the most important bond angles are collected in Tables 3, 4 and 5, respectively. Lists of structure factors can be obtained from the authors.

The most important features of the structure are as follows:

(i) The Co—Co distance shows a reasonably good agreement with reported X-ray data for such binuclear cobalt carbonyls as I (245 pm) [19], bridged $Co_2(CO)_8$ (252.4 pm) [20], $(\mu_2\text{-}PhC_2Ph)Co_2(CO)_6$ (247 pm) [21], $(\mu_2\text{-t-}BuC_2\text{-t-}Bu)Co_2(CO)_6$ (246.3 pm) [22] the two "flyover" complexes, $(HC_2H)(HC_2\text{-t-}Bu)_2Co_2(CO)_4$ (243 pm) [17] and $[(HC_2CF_3)_3]Co_2(CO)_4$ (245.9 pm) [18], and that of the B isomer (247 pm) [10b].

(ii) The $Co_2(CO)_4$ moiety is fairly asymmetric, as indicated by the Co—C(O) and (Co)C—O distances, and in agreement with the $\nu(C—O_t)$ spectrum.

(iii) The bonding of the bridging carbonyl is also asymmetric, similar to that in isomer B [10b]. This is also reflected by the position of the bridging ν(C—O) frequency (compare symmetrically bridged $Co_2(CO)_8$ [23] or (I) [4,5,24]. An asymmetric ("more terminal") bridging group requires a higher ν(C—O): as observed.

(iv) The coordination of the C(6)—C(7)—C(8)—C(9)—C(10) pentadiene ligand

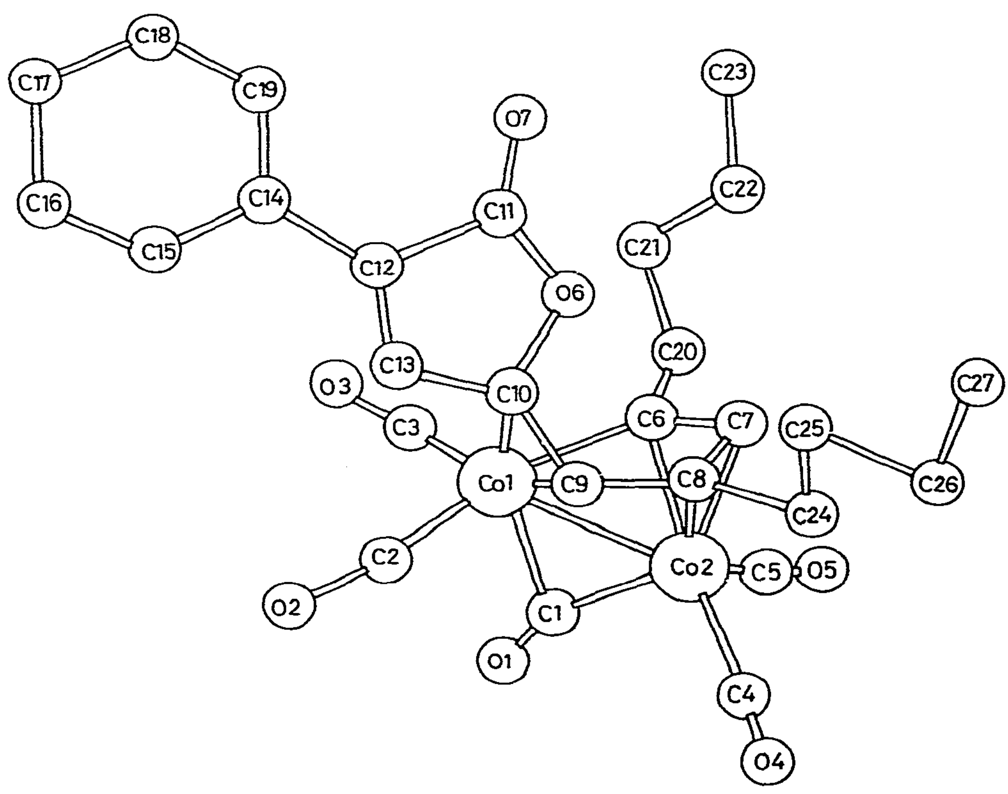


Fig. 2. ORTEP representation of the structure of isomer A III (The positions of atoms O(3), C(3) and C(8) were changed slightly for clarity).

TABLE 3. ATOMIC COORDINATES OF COMPOUND (III, R^1 = H, R^2 = Ph, R^3 = H, R^4 = n-Bu) WITH e.s.d.'s IN PARENTHESES

Atom	*g*	*x*	*y*	*z*	*b*
Co(1)	1.0	0.1873(4)	0.2588(7)	0.4607(5)	—
Co(2)	1.0	0.2787(4)	0.1102(7)	0.4258(7)	—
O(1)	1.0	0.184(2)	0.184(2)	0.605(3)	8.0(—)
O(2)	1.0	0.163(2)	0.334(3)	0.685(3)	9.6(—)
O(3)	1.0	0.037(2)	0.241(4)	0.411(3)	8.9(9)
O(4)	1.0	0.408(2)	0.074(3)	0.555(4)	8.4(—)
O(5)	1.0	0.258(2)	−0.112(4)	0.338(2)	6.1(8)
O(6)	1.0	0.218(2)	0.427(3)	0.285(2)	5.2(8)
O(7)	1.0	0.166(2)	0.554(3)	0.174(3)	6.5(9)
C(1)	1.0	0.210(3)	0.093(4)	0.538(5)	6.8(—)
C(2)	1.0	0.181(3)	0.300(4)	0.590(4)	7.6(—)
C(3)	1.0	0.094(3)	0.239(6)	0.425(5)	9.4(—)
C(4)	1.0	0.362(4)	0.077(6)	0.512(6)	11.7(—)
C(5)	1.0	0.270(2)	−0.028(5)	0.374(4)	6.1(—)
C(6)	1.0	0.214(2)	0.186(3)	0.322(3)	3.9(9)
C(7)	1.0	0.285(2)	0.214(3)	0.286(3)	2.4(9)
C(8)	1.0	0.324(2)	0.276(4)	0.362(3)	4.1(9)
C(9)	1.0	0.280(2)	0.351(3)	0.441(4)	4.6(—)
C(10)	1.0	0.229(3)	0.416(4)	0.400(4)	4.9(—)
C(11)	1.0	0.186(3)	0.524(5)	0.263(5)	7.2(—)
C(12)	1.0	0.166(2)	0.577(4)	0.374(4)	4.5(—)
C(13)	1.0	0.194(2)	0.514(4)	0.447(4)	3.2(9)
C(14)	1.0	0.123(2)	0.686(4)	0.386(4)	4.1(—)
C(15)	1.0	0.119(3)	0.742(6)	0.486(4)	8.9(—)
C(16)	1.0	0.080(3)	0.835(5)	0.513(5)	9.7(—)
C(17)	1.0	0.047(2)	0.897(4)	0.422(5)	5.7(—)
C(18)	1.0	0.062(3)	0.850(5)	0.321(4)	6.1(—)
C(19)	1.0	0.093(2)	0.743(5)	0.302(4)	5.0(—)
C(20)	1.0	0.165(2)	0.129(3)	0.240(3)	2.2(9)
C(21)	1.0	0.123(2)	0.213(3)	0.167(3)	2.7(9)
C(22)	1.0	0.179(2)	0.258(4)	0.079(4)	6.7(—)
C(23)	1.0	0.140(3)	0.316(4)	−0.015(5)	8.0(—)
C(24)	1.0	0.406(3)	0.294(5)	0.348(4)	9.0(—)
C(25)	1.0	0.414(3)	0.413(5)	0.296(4)	8.1(—)
C(26)	1.0	0.505(4)	0.398(8)	0.284(7)	17.5(—)
C(27)	1.0	0.517(4)	0.480(7)	0.198(6)	14.1(—)

TABLE 4. INTERATOMIC DISTANCES [a] (WITH e.s.d.'s) OF ISOMER AIII OF $[(C_4O_2H,Ph)(HC_2\text{-n-Bu})_2]$-$Co_2(CO)_5$

Atoms	Bond lengths (pm)	Atoms	Bond lengths (pm)
Co(1)—Co(2)	247(1)	C(4)—O(4)	101(9)
Co(1)—C(1)	219(5)	C(5)—O(5)	110(7)
Co(1)—C(2)	166(5)	C(10)—O(6)	143(6)
Co(1)—C(3)	182(6)	C(11)—O(6)	131(7)
Co(1)—C(6)	197(4)	C(11)—O(7)	121(7)
Co(1)—C(9)	206(4)	C(6)—C(7)	144(5)
Co(1)—C(10)	213(5)	C(6)—C(20)	152(5)
Co(2)—C(1)	190(6)	C(7)—C(8)	139(5)
Co(2)—C(4)	193(8)	C(8)—C(9)	155(6)
Co(2)—C(5)	174(6)	C(8)—C(24)	156(7)
Co(2)—C(6)	197(4)	C(9)—C(10)	132(7)
Co(2)—C(7)	210(4)	C(10)—C(13)	144(7)
Co(2)—C(8)	225(5)	C(11)—C(12)	154(8)
C(1)—O(1)	108(7)	C(12)—C(13)	127(7)
C(2)—O(2)	128(6)	C(12)—C(14)	151(6)
C(3)—O(3)	108(7)		

[a] Distances in the phenyl and butyl groups are omitted, mean values are 139 and 156 pm, respectively.

TABLE 5

SIGNIFICANT BOND ANGLES (WITH e.s.d.'s) IN THE STRUCTURE OF [$(C_4O_2H,Ph)(HC_2$-n-Bu$)_2$]-$Co_2(CO)_5$

Atoms	Angles (deg.)	Atoms	Angles (deg.)
Co(2)—Co(1)—C(1)	48(3)	Co(2)—C(4)—O(4)	170(10)
Co(2)—Co(1)—C(6)	51(2)	Co(2)—C(5)—O(5)	173(8)
Co(2)—Co(1)—C(9)	76(2)	Co(1)—C(6)—Co(2)	78(2)
Co(2)—Co(1)—C(10)	107(2)	Co(1)—C(6)—C(7)	114(5)
C(2)—Co(1)—C(3)	102(5)	Co(2)—C(6)—C(7)	74(4)
C(2)—Co(1)—C(6)	166(4)	Co(2)—C(6)—C(20)	127(4)
C(2)—Co(1)—C(9)	91(4)	C(7)—C(6)—C(20)	117(5)
C(2)—Co(1)—C(10)	97(4)	Co(2)—C(7)—C(6)	64(4)
Co(1)—Co(2)—C(1)	59(3)	Co(2)—C(7)—C(8)	77(4)
Co(1)—Co(2)—C(6)	51(2)	C(6)—C(7)—C(8)	113(6)
Co(1)—Co(2)—C(7)	77(2)	Co(2)—C(8)—C(7)	66(4)
Co(1)—Co(2)—C(8)	74(2)	Co(2)—C(8)—C(9)	94(4)
C(1)—Co(2)—C(4)	98(5)	C(7)—C(8)—C(9)	116(6)
C(1)—Co(2)—C(5)	96(4)	Co(1)—C(9)—C(8)	103(5)
C(1)—Co(2)—C(6)	96(4)	Co(1)—C(9)—C(10)	74(5)
C(1)—Co(2)—C(7)	134(3)	C(8)—C(9)—C(10)	118(7)
C(1)—Co(2)—C(8)	127(4)	Co(1)—C(10)—C(9)	69(5)
C(4)—Co(2)—C(5)	95(5)	Co(1)—C(10)—C(13)	112(6)
C(6)—Co(2)—C(7)	41(3)	O(6)—C(10)—C(13)	105(7)
C(6)—Co(2)—C(8)	68(3)	O(6)—C(11)—O(7)	125(9)
C(7)—Co(2)—C(8)	37(3)	O(6)—C(11)—C(12)	106(8)
C(10)—O(6)—C(11)	110(7)	O(7)—C(11)—C(12)	128(9)
Co(1)—C(1)—Co(2)	74(3)	C(11)—C(12)—C(13)	107(7)
Co(1)—C(1)—O(1)	130(8)	C(11)—C(12)—C(14)	124(7)
Co(2)—C(1)—O(1)	156(9)	C(13)—C(12)—C(14)	130(7)
Co(1)—C(2)—O(2)	169(8)	C(10)—C(13)—C(12)	111(7)
Co(1)—C(3)—O(3)	170(10)		

is of a η^3-allyl (C(6), C(7), C(8)- to Co(2)) and a η^2-olefinic (C(9), C(10)- to Co(1) type. The characteristic structural data agree fully with those published [10] for isomer B (IV). A bridging carbene behaviour of C(6) is indicated by the C(6)—Co(1) and C(6)—Co(2) distances and the Co(1)—C(6)—Co(2) angle, all of which agree very well with the corresponding parameters of similar systems [16,19].

(v) The most striking feature of the structure is its similarity to the overall geometry of the other (IV, B) isomer, the only marked difference being the orientation of the lactone ring. According to Pauson, et al. [10], in the structure of B (IV), the C=C double bond is oriented *cis* to C(6) and *trans* to the bridging carbonyl group. In our case (III(A)), the relative position of the lactonic C=C double bond to C(6) is clearly *trans* (C(6)—C(13) 413; C(6)—O(6) 284 pm) while the ring is almost symmetric to the bridging CO (O(1)—O(6) 592; O(1)—O(13) 573 pm) *. The mean planes of the butenolide ring and of the π-allyl system are inclined at 81° (79° for IV [10]) while the mean planes of the butenolide and phenyl rings are almost coplanar (5° torsion).

This structure can be rationalized by assuming terminal coordination of the

* The corresponding data calculated for IV (B) (from ref. 10b): C(6)—C(13) 405; C(6)—O(6) 556; O(1)—O(6) 549 and O(1)—C(13) 594 pm (where our numbering of the atoms was used).

"new" acetylene ($R^3C_2R^4$) as the initial step in reaction 1b, followed by an attack of the coordinated $R^3C_2R^4$ on the 4C-atom of the lactone ring. The isomer which is subsequently formed depends on which side of the lactone ring has been attacked. This picture leads to a mechanistic, stereochemical interpretation of the formation of the *cis*(Z)- and *trans*(E)-isomers [25] of the bifurandiones. It is evident that the "second" ring of the bifurandiones must originate in interaction of a (coordinated) CO with lactone-4C, likewise taking place from either the "left" of the "right" side CO group.

Experimental

Starting materials were of commercial origin, with the exception of $Co_2(CO)_8$ and the "lactone" complexes $(C_4O_2R^1,R^2)Co_2(CO)_7$, which were prepared by known methods [26] and [4,5], respectively.

IR spectra were recorded on a UR-20 (Carl Zeiss, Jena) instrument, using simultaneous DCl calibration [27], ^1H NMR spectra were recorded on a T-60 (Varian, Palo Alto) spectrometer. Osmometric molecular weight measurements were made with a Knauer Vapour Phase Osmometer.

The X-ray diffraction experiments were made using a Hilger and Watts four-circle automatic diffractometer with $I = 20$, Cu radiation, room temperature, $\theta/2\theta$ scan, $\theta = 63°$. The single crystals of the sample were sealed in a glass capillary under CO.

Reactions of $(C_4O_2R^1,R^2)Co_2(CO)_7$ complexes with acetylenes $R^3C_2R^4$

The reactions were carried out under rather similar conditions using various combinations of substitutents R^1, R^2 and R^4. A typical example is described below.

A solution of 1.5 g [3.79 mmol] $(C_4O_2H,H)Co_2(CO)_7$, 0.3 g hydroquinone and 1 ml [10.2 mmol] pentyne-1 in 25 ml benzene was kept under CO in a thermostated (25°C) reaction vessel connected to a gas burette. The mixture was stirred until CO evolution ceased (2—3 h). Subsequently, the reaction mixture was filtered and the clear reddish-brown filtrate was transferred to silica TLC plates (Anachem, Uniplate). Chromatograms developed using CH_2Cl_2 yielded five or six sharply separated bands. These were eluted from the silica gel with Et_2O. The ethereal solutions were evaporated to dryness and the residue was investigated.

The general treatment of the individual fractions (in order of elution) was as follows.

Fraction 1. This was $(R^3C_2R^4)Co_2(CO)_6$, with yields ranging between 5 and 25%. These compounds were shown by their ν(C—O) spectra in n-hexane to be identical with samples prepared independently by published methods [13]. In some cases the $(R^3C_2R^4)Co_2(CO)_5(PPh_3)$ derivatives were also prepared. These gave ν(C—O) spectra identical to these reported by others [14,15], as well as satisfactory analyses: $(n\text{-}C_3H_5C_2)Co_2(CO)_5(PPh_3)$, Found: Co, 20.9; P, 5.5; M.W., 570, $C_{28}H_{23}Co_2O_5P$ calcd.: Co, 20.03; P, 5.27%; M.W., 588.30. $(PhC_2H)Co_2(CO)_5(PPh_3)$, Found: Co, 19.3; P, 5.2; M.W., 638, $C_{31}H_{21}Co_2O_5P$ calcd.: Co, 18.94; P, 4.94%, M.W., 622.34.

Fractions 2 (A, III) and 3 (B, IV). These substances were further purified by

TABLE 6

ANALYSIS OF COMPOUNDS III AND IV

Lactone		Acetylene		Empirical formula	Iso-mer	Molecular weight		Analysis					
R^1	R^2	R^3	R^4			calcd.	found	Co		C		H	
								calcd.	found	calcd.	found	calcd.	found
H	H	H	n-Pr	$C_{19}H_{18}O_7Co_2$	A	475.97	463	24.76	23.9	47.90	—	3.82	—
					B		465		24.1		—		—
H	H	H	Ph	$C_{25}H_{14}O_7Co_2$	A	543.93	—	21.67	—	55.15	—	2.60	—
					B		538		20.8		—		—
H	H	H	CH_2OCH_3	$C_{17}H_{14}O_9Co_2$	A	479.91	—	24.56	23.9	42.51	41.92	2.95	3.16
					B		—		23.8		42.96		3.10
H	Ph	H	Me	$C_{21}H_{14}O_7Co_2$	A	495.93	—	23.75	23.2	50.80	51.4	2.86	3.00
					B	495.93	—		23.8		51.4		3.10
H	Ph	H	n-Bu	$C_{27}H_{26}O_7Co_2$	A	580.05	—	20.32	21.0	55.85	—	4.53	—
					B		568		20.1		55.6		4.71
H	Ph	H	CH_2OCH_3	$C_{23}H_{18}O_9Co_2$	A	555.95	—	21.18	21.1	49.64	49.7	3.27	3.58
					B		—		21.2		49.2		3.58

repeated TLC and/or at least twofold recrystallization from n-hexane. Yields ranged between 10 and 30% for A and between 20 and 50% for B with the exception of derivatives with R^3 = H, R^4 = Ph, where yields were ~5%. Analyses are summarized in Table 6. The remainder of the compounds were characterized by comparisons of IR ν(C—O) spectra and TLC behaviour.

Reactions with gaseous acetylenes such as C_2H_2 and MeC_2H were initiated by replacing the gas in the burette by the appropriate reactant. The CO/acetylene mixtures formed during the CO evolution replaced by pure acetylene from time to time.

Fractions 4—6. These were found to be slightly coloured organic compounds. Characterisation of these substances is in progress.

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