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ON THE REACTIVITY OF μ_2-ACETYLENES COORDINATED TO COBALT

STEREOCHEMISTRY OF THE FORMATION OF THE BUTENE-2-OLIDE-4 COMPLEXES: $Co_2(CO)_7(RR'C_4O_2)$*

GYULA PÁLYI, GYULA VÁRADI, ANNA VIZI-OROSZ and LÁSZLÓ MARKÓ

Research Group for Petrochemistry of the Hungarian Academy of Sciences, Veszprém (Hungary)

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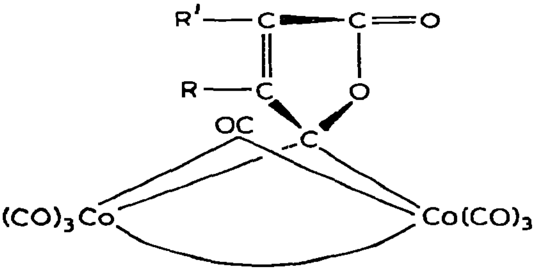
Summary

The relative positions of the R and R′ substituents in the "lactone" complexes, $Co_2(CO)_7(RR'C_4O_2)$ (μ_2-carbonyl-μ_2-*spiro*-[2,3-substituted-2-butene-4-olide-4-ylidene]-bis[tricarbonylcobalt][*Co—Co*] derivatives) was studied spectroscopically. It was found that the formation of these complexes is stereoselective and is controlled by the bulk of the substituents R and R′.

Introduction

Octacarbonyldicobalt and alkynes (RC_2R') as well as the corresponding acetylene complexes $Co_2(CO)_6(RC_2R')$ react with CO at 70° and 200-300 atm to form [2] "lactone" complexes I:



(I)

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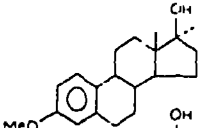
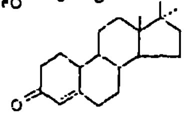
* Preliminary account of this work has been presented at symposia [1].

TABLE 1

IR SPECTRA OF $Co_2(CO)_7(C_4O_2R,R')$ (I) COMPLEXES IN THE ν(C—O) RANGE
Solvent hexane, calibration with DCl [19].

No.	R	R'	ν_1	ν_2	ν_3	ν_4	ν_5	ν_6	ν_7 (bridge)	ν_8 (organic)
Ia	H	H	2112.4	2078.3	2062.4	2051.1	2044.7	2038.7	1848.3	1784.8
Ib	H	Me	2110.9	2076.0	2059.9	2048.6	2041.9	2035.6	1846.5	1770.6 1767.5
Ic	H	Pr	2110.6	2076.8	2059.6	2048.8	2041.9	2035.3	1846.0	1778.3 1760.0
Id	H	n-C_6H_{13}	2110.2	2075.5	2059.2	2048.2	2041.3	2034.7	1846.2	1778.5
Ie	H	Ph	2110.5	2077.2	2060.9	2049.7	2046.7	2036.8	1847.1	1773.9
If	H	$SiMe_3$	2110.5	2076.1	2059.7	2055.2	2042.8	2028.7	1847.8	1780.9
Ig	H		2111.6	2076.8	2061.6	2051.6	2043.3	2035.0	1848.3	1758.0
Ih	H		2112.1	2077.5	2063.1	2052.3	2044.0	2034.9	1849.0	1742.0

These complexes are thought to be intermediates in the formation of the bifurandiones from acetylenes and CO [3]. The catalytic cocyclization of acetylenes with CO and the chemistry of the products has attracted considerable industrial [4-6] and academic [7-9] interest in the past decade, but surprisingly little attention has been given to the stereochemistry of this reaction.

The sole X-ray structure reported for this class of compounds concerns compound Ia [10]. It shows that the lactone ring is turned with its C=C double bond towards the bridging CO. If this result can be generalized a strong interaction can be expected between R and the bridge-CO. Although most of the patents cited above claim to cover all possible isomers of the bifurandiones, only one case is known [7] in which sufficient experimental evidence is presented to indicate the formation of a derivative of I with the bulkier substituent in place of R in an intermediate: this is the preparation of 2,6-dimethyl-2,4,6--octatriene-4,5-diolide from methylacetylene.

Results and discussion

Preparation of the complexes

The compounds of type I were prepared essentially by the method suggested by Sternberg et al. [2]. Either the alkyne and $Co_2(CO)_8$ or the corresponding $Co_2(CO)_6(RC_2R')$* complex can be used as the starting material. In the case of alkynes in which at least one of R and R′ is H the reaction conditions (70°/ 200-300 atm.) suggested by these authors gave good yields of I.

No reaction with CO could be observed with internal acetylenes R = R′ = Ph or $SiMe_3$ and R = Ph, R′ = Me. Even under more forcing conditions (100-130°/ 340-380 atm. for 58 h) only $Co_2(CO)_6$(alkyne) complexes were formed, in almost quantitative (85-95%) yield. It is reasonable to suppose that the steric effect of the μ_2-CO group prevents the formation of I with a bulkier R group.

The isomeric composition of the compounds I obtained was tested by elution chromatography on silica gel. The spectra were identical for different cuts from the elution bands of complexes I, indicating that, at least under the conditions used by us, only one isomer was formed.

Infrared spectra

The ν(C—O) (both coordinated and organic) spectra of complexes I are shown in Table 1. The spectrum of Ie (R = H; R′ = Pr) agrees well with the only high-resolution ν(C—O) spectrum reported for these compounds [12]. The shape of the other spectra is in good agreement with this, which is regarded as one item of proof for the structure of the new compounds reported here.

It should be noted that there is only a very slight shift in the ν(C—O) spectrum with the change of the substituents R and R′. This is important because it shows that there is no (or negligible) π-electron interaction between the $R\underset{|}{C}=\underset{|}{C}R'$ moiety of the lactone ring and the $Co_2(CO)_7$ entity of the cluster, i.e. the bridgehead 4-carbon atom behaves as an sp^3 carbon, transmitting only

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* The $Co_2(CO)_6(RC_2R')$ compounds prepared in the course of this work gave satisfactory analyses and IR spectra (cf. Experimental, Table 3).

inductive electronic effects. This is somewhat unexpected since the bond angles [10] around this carbon show considerable deviations from the sp^3 theoretical values. On the basis of the X-ray data an approximate [11] $sp^{2.65}$ formal hybridization can be calculated, which is not far from the sp^2 "carbene" configuration*. This situation is different from that which can be assumed [13, 14] at the triply bridging apical carbon atom of $Co_3(CO)_9CY$ compounds, where a partial sp^2 and/or sp character of the μ_3-C is in better agreement with the experimental observations than the formally expected sp^3 configuration. This contradiction can be resolved if we accept the following qualitative picture: the μ_2-(lactone)C in compounds I may have partially filled p-orbitals which can interact with the π-electrons of the RC=CR fragment but, as a consequence of the rigid geometry, their direction is unfavourable for significant overlap with any of the metal d (or d-containing hybrid) orbitals.

The above analysis considered along with the experimental data in Table 1 allows the subsequent assignment of the NMR spectra, which is based on the assumption that the $Co_2(CO)_7$ fragment of the molecule does not have a significant influence on the chemical environment of the substituents R and R'.

The doublet of the organic ν(C—O) band was not informative since the doublet could arise from the existence of two isomeric forms (differing in the relative position of R and R') or from a Fermi resonance, which is well known for γ-lactones [17].

The rest of the infrared spectrum could not be assigned with certainity.

TABLE 2

^1H NMR DATA FOR COMPLEXES I
CCl_4 solution, TMS internal standard

No.	^1H NMR data (ppm)	Assignment
Ia	7.70 (d, 1H, J 5 Hz)	3-H
	5.45 (d, 1H, J 5 Hz)	2-H
Ib	7.30 (s, 1H)	3-H
	1.83 (s, 3H)	2-CH_3
Ic	7.33 (s, 1H)	3-H
	0.96 (t, 3H)	γ-CH_3
	1.6 (m, 2H)[a]	β-CH_2
	2.23 (t, 2H)	α-CH_2
Id	7.35 (s, 1H)	3-H
	1.08 (t, 3H)	η-CH_3
	1.55 (br. m, 8H)	β-5-CH_2
	2.25 (t, 2H)	α-CH_2
Ie	7.75 (s, 1H)	3-H
	7.90 (br., 2H)	o-H
	7.42 (br., 3H)	m- + p-H

[a] Four observed peaks.

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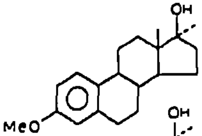
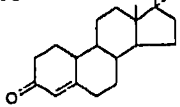
* This Co—C—Co angle is rather close to the ring C—C—C angle of a diphenylcyclopropane derivative [15] and also to the Rh—C—Rh angle of a Rh_2CPh_2 compound [16] which was described as a "carbene" complex.

TABLE 3

ANALYTICAL AND IR DATA OF SOME $Co_2(CO)_6(RC_2R')$ COMPLEXES

R	R'	Co analysis found (calcd.) (%)	ν(C—O) IR spectra in hexane (cm^{-1}) [a]				
H	Me[b]		2092.8 m	2052.9 vs	2029.1 s	2020.3 s	2011.1 m(sh)
H	n-C_6H_{13}		2092.7 m	2052.5 vs	2029.1 s	2019.8 s	2010.5 m(sh)
H	-$Si(CH_3)_3$[b]		2092.9 m	2053.2 vs	2028.5 s	2021.3 s	2010.7 m(sh)
$(CH_3)_3Si$-	-$Si(CH_3)_3$[b]		2084.5 m	2047.2 vs	2022.0 s	2014.2 s	2002.1 m(sh)
H		19.5 (19.73)	2093.8 m	2055.3 vs	2032.2 s	2023.1 s	2010.9 m(sh)
H		20.9 (20.16)	2094.2 m	2055.8 vs	2033.4 s	2028.5 s	2012.4 m(sh)

[a] Simultaneous DCl calibration was used. [b] Known compound, but no high resolution IR spectrum previously reported (cf. ref. 12).

^{1}H NMR spectra

The ^{1}H NMR data of the complexes I are shown in Table 2. Compound Ia (R = R' = H) shows two doublets at almost the values reported [18] for the corresponding free ligand, butene-2-olide-4[δ(2-H) 6.15, δ(3-H) 7.63 ppm, in $CDCl_3$ vs. TMS]. Thus if it is accepted that the organometallic part of the molecule has no significant effect on the chemical environment of the lactone-ring protons, the assignment given in Table 2 seems to be justified; then the single proton signals of the other I compounds with $R = H \neq R'$ may be assigned as shown in Table 2. These results show that the bulkier substituent is always in the 2-position of the lactone ring when the complexes I are prepared from asymmetric terminal acetylenes.

Experimental

IR spectra were recorded on a Carl Zeiss (Jena) UR-20, ^{1}H NMR spectra with a Varian T-60 and molecular weights were measured on a Knauer Dampfdruckosometer.

Starting materials were of commercial origin, with the exception of $Co_2(CO)_8$, which was prepared by the method of Szabó et al. [21], and the two ethynylsteroids, 17-ethynyl-3-methoxy-1,3,5(10)-estratrien-17β-ol and 17-ethynyl-17β-hydroxy-4-estren-3-one, which were obtained from the Research Institute for Pharmaceutical Chemistry (Budapest).

Preparation of $Co_2(CO)_6$(alkyne) complexes

The $Co_2(CO)_6$(alkyne) starting compounds were prepared by the usual method [19, 20] by treating equimolar amounts of $Co_2(CO)_8$ with the appropriate alkyne at room temperature in hexane (benzene for the two ethynylsteroids). Analyses and newly reported IR spectra of the new and some other $Co_2(CO)_6$(alkyne) complexes [19, 20] are shown in Table 3.

Preparation of complexes I

A solution of equimolar amounts of $Co_2(CO)_8$ and alkyne in hexane was kept at 70 ± 5° for 12-14 h in a stainless steel rocking autoclave under 200-300 atm. CO [2]. Benzene was used as solvent in the preparation of I derivatives

TABLE 4

ANALYTICAL DATA AND YIELDS FOR $Co_2(CO)_7(C_4O_2R,R')$ (I) COMPLEXES

No.	Co analysis found (calcd.) (%)	Mol. wt. found (calcd.) [a]	Yield[b] (%)
Ia	29.9 (29.76)	412 (396.0)	72
Ib	28.7 (28.74)	430 (410.0)	52
Ic	27.0 (26.90)	452 (438.1)	60
Id	23.8 (24.54)	496 (480.1)	72
Ie	24.0 (24.96)	482 (472.1)	48
If	24.5 (25.07)	481 (470.1)	46
Ig	16.4 (17.29)	698 (681.4)	28
Ih	17.7 (17.63)	685 (668.4)	31

[a] Osmometric, in benzene. [b] 2 × recrystallized products.

from norethysterone and ethynyloestradiol-Me-ether. Each preparation was repeated under the same conditions starting from the corresponding $Co_2(CO)_6$-(alkyne) complex. Complexes I were purified by recrystallization from Et_2O and characterized by analyses and mol. wt. measurements (Table 4). Yields are shown in Table 4.

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