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# On the reactivity of acetylenes coordinated to cobalt.

Part 8<sup>1</sup>: Carbonylation of acetylenes with bulky substituents

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(Received February 8, 1993; accepted May 5, 1993)

# Abstract

Acetylenes  $(R^1C_2R^2, R^1=H, R^2=n-Pr, i-Pr, t-Bu, neo-Pent)$  with equimolar  $Co_2(CO)_8$  or the corresponding  $(R^1C_2R^2)Co_2(CO)_6$  (1) complexes were found to undergo stoichiometric cyclocarbonylation (n-hexane, 100°C,  $p_{CO}$  27 MPa) to give almost quantitative yields of  $[\mu_2-(2-R^2-2-butene-4-olide-4-ylidene)]$   $[\mu_2$ -carbonyl] dicobalt hexacarbonyl (Co-Co) (2) complexes with nearly quantitative yields and 100% regioselectivity. The absence of the influence of the steric bulk of substituent  $R^2$  on the carbonylation is commented in terms of mechanistic speculations.

Key words: acetylenes; cobalt carbonyls; cyclocarbonylation; regioselectivity; template effect

# Introduction

The activation of acetylenes with cobalt complexes, which has become a widely used tool for the coupling of C,C (and in some cases C,O) bonds, has been reviewed extensively [2]. In spite of the several useful synthetic applications, however, factors governing the chemo-, regio- and enantioselectivity of such reactions are not yet fully understood [3].

Some years ago we performed a systematic preparative and spectroscopic



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Scheme 1. Plausible mechanism of the carbonylation of acetylenes with  $\text{Co}_2(\text{CO})_8$ . 1 and 2 are isolated compounds, A to D the supposed intermediates.

study [4] of the cyclocarbonylation of acetylenes in the presence of cobalt carbonyls [5]. It has been established that the carbonylation proceeds (Scheme 1) through complexes 1 and 2, yielding bilactones 3 with 100% regioselectivity of the first and almost random selectivity of the second lactone ring. Spectroscopic data suggested that the quantitative regioselection is decided in intermediates A and is governed by the preferred carbonylation of *that* acetylenic carbon (coordinated *sp*) atom which appears to be more shielded (lower  $\delta$ value in <sup>13</sup>C-NMR) [4a,c]. Since monocarbonylated intermediate (showing the position of the first C,C coupling) could not be isolated we attempted to obtain an additional piece of evidence by the carbonylation of acetylenes with one bulky substituent. The results of this study will be reported here.

## **Results and discussion**

Acetylenes bearing one bulky substituent reacted smoothly with  $Co_2(CO)_8$  to give intermediates 1 as expected [6]. Complexes 1 were characterized by elemental analyses, IR  $\nu$ (C–O) spectra, <sup>1</sup>H- and <sup>13</sup>C-NMR spectroscopy (Table 1,3).

Either the uncomplexed (free) acetylenes (with equimolecular  $\text{Co}_2(\text{CO})_8$ ) or complexes 1 could be carbonylated to  $\mu_2$ -butenolide complexes 2 with high

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#### TABLE 1

Spectroscopic data of complexes 1 and <sup>13</sup>C-NMR data of the corresponding free acetylenes

R <sup>1</sup> C <sub>2</sub> R <sup>2</sup>		IR $\nu$ (C-O) (cm <sup>-1</sup> ) ( <i>n</i> -hexane)	<sup>1</sup> H-NMR: $\delta$ (ppm) (J in Hz, assignment)	<sup>13</sup> C-NMR, $\delta$ (ppm) (CCl <sub>4</sub> ) <sup>a</sup>			
R1	R <sup>2</sup>			Free		Complexed	
				$\delta^1$	$\delta^2$	$\delta^1$	$\delta^2$
н	n-Pr <sup>b</sup>	2092.9 m, 2052.7 vs, 2029.1 s, 2019.6 s, 2009.7 w,sh,≈2006 vw	1.01 (t, $J=7$ , $I=3H$ , $CH_3$ ) 1.58 (m, $I=2H$ , $\beta$ - $CH_2$ ) 2.65 (t, $J=6$ , $I=2H$ , $\alpha$ - $CH_2$ ) 6.08 (s, $I=1H$ , $C_2H$ )	66.7	81.8	73.2	98.5
н	<i>i</i> -Pr	2095.8 m, 2056.9 vs, 2032 7 vs, 2025.1 s, 2014.9 w,sh,≈2003 vw	1.02 (d, $J=7$ , $I=6H$ , $CH_3$ ) 2.43 (m, $I=1H$ , <i>i</i> -Pr CH) 6.06 (s, $I=1H$ , C <sub>2</sub> H)	67.2	88.0	73.5	106.2
н	t-Bu	2092.2 m, 2052.3 vs, 2029.1 vs, 2019.9 s, 2010.2 w, sh, ≈ 2008 vw	0.98 (s, $I=9H$ , $CH_3$ ) 6.08 (s, $I=1H$ , $C_2H$ )	66.9	91.2	73.4	112.0
н	neo-Pent	2091.8 m, 2057.7 vs, 2028.1 vs, 2019.3 s, 2008.3 w, sh, 2007 vw	0.92 (s, $I=9H$ , $CH_3$ ) 2.15 (s,br; $I=2H$ ; $CH_2$ ) 6.08 (s, $I=1H$ , $C_2H$ )	66.7	85.2	73.4	100.7

<sup>a</sup>  $\delta^1$  and  $\delta^2$  correspond to the *sp* carbon atoms bearing R<sup>1</sup> and R<sup>2</sup>, respectively.

<sup>b</sup> c.f. refs [4a,c; 6b; 7b; 8a].

to excellent yields. Complexes 2 were characterized by analyses, IR  $\nu$ (C–O) and <sup>1</sup>H-NMR spectroscopy (Table 2,3).

The structure of the new 1 and 2 derivatives was straightforwardly assigned on the basis of analogy of the spectra to those of similar compounds with structure based on X-ray diffraction  $[7,8]^*$ . Our new compounds could not be studied by X-ray crystallography since most 1 derivatives were oils and the solid 1 and 2 complexes were (disordered ?) microcrystalline substances which did not give satisfactory X-ray diffraction pattern.

These results bear two additional pieces of evidence to the understanding of the quantitative regioselectivity of reaction  $1 \rightarrow 2$ .

(i) The starting acetylenes and intermediates 1 fit well into the empirical rule suggested about the carbonylation of acetylenes with Co. That is, all acetylenes carbonylated in course of this work show at least one <sup>13</sup>C-NMR band

<sup>\*</sup>Spectra for complexes 1 are given in refs. 7a-c, some crystal structures are given in refs. 7d,e. Spectra for complexes 2 are given in ref. 8a and the crystal structure of one is given in ref. 8b, and that of a derivative in ref. 8c.

TABLE 2

Spectroscopic data and yields of complexes 2

Substituents		IR $\nu$ (C-O) (cm <sup>-1</sup> )	<sup>1</sup> H-NMR: $\delta$ (ppm)	Yields (%) <sup>a</sup> from:	
R <sup>1</sup>	R <sup>2</sup>	( <i>n</i> -hexane) ( <i>J</i> in Hz, assignment) (in CCl <sub>4</sub>		Free acetylene	Complex 1
н	n-Pr <sup>b</sup>	2110.6 m, 2075.8 s, 2059.6 vs 2048.8 w, 2041.9 s, 2035.3 w 1846.9 m (bridge), 1778.3 (org.)	0.96 (t, $J = 6$ , $I = 3H$ , $\gamma$ -CH <sub>3</sub> ) 1.60 (m, $I = 2H$ , $\beta$ -CH <sub>2</sub> ) 2.23 (t, $I = 2H$ , $\alpha$ -CH <sub>2</sub> ) 7.33 (s, $I = 1H$ , 3-CH)	_	85
н	i-Pr	2110.0 m, 2075.5 vs, 2059.1 vs, 2048.1 m, 2041.3 vs, 2034.7 w, sh, 1846.5 s (bridge), 1774.5 m, 1763.6 m, sh (org.)	1.14 (d, J=7, I=6H, CH <sub>3</sub> ) 2.55 (m, I=1H, <i>i</i> -Pr CH) 7.09 (s, br, I=1H, 3-CH)	83	92
н	t-Bu	2109.8 s, 2075.2 vs, 2059.0 vs, 2048.1 m, 2040,9 vs, 2034.6 w, sh, 1846.5 s (bridge), 1773.9 m, 1754.7 m, sh (org.)	1.19 (s, <i>I</i> =9H, CH <sub>3</sub> ) 7.05 (s, <i>I</i> =1H, 3-CH)	88	92
н	neo-Pent	2110.0 s, 2075.6 vs, 2059.5 vs, 2047.3 m, 2041.4 vs, 2034.5 w, sh, 1846.7 s (bridge), 1770.3 m (org.)	0.90 (s, $I=9H$ , $CH_3$ ) 2.08 (s, br, $I=2H$ , $CH_2$ ) 7.18 (t, $J \approx 2$ , $I=1H$ , 3-CH)	84	87

<sup>&</sup>lt;sup>a</sup> Previous work [20] showed that yields of such high-pressure experiments were reproducible within  $\pm 10\%$ .

<sup>b</sup> See also ref. 4a.

for one of the sp carbons at  $\delta < 80$  ppm (free) [2b, 4c]. This behaviour confirms the validity of this rule.

(ii) The acetylenes carbonylated in course of this work bear one moreless bulky substituent. Comparison of the yields of complexes 2 obtained under strictly comparable conditions show that the bulk of the second substituent has no detectable influence on the outcome of the reaction 1 (or  $R^1C_2R^2$ )  $\rightarrow$ 2. This result provides an additional support of the mechanism depicted in Scheme 1, since it points at *sp* carbon bearing  $R^1$  (with lower <sup>13</sup>C-NMR  $\delta$ value) as starting point of the reaction (as indicated by formula A) and supports our view that the second CO insertion is not even taking place on  $C(R^2)$ , but on the acyl-O, coordinated to Co [9]\*. According to this mechanism  $C(R^2)$ 

<sup>\*</sup>The Co-O bond in low valent cobalt carbonyls instantanously inserts CO, see for example refs. 9a-d, and for a review ref. 9e.

is only forced to react in the ring closure step, similarly to analogous situation at the ring closure in the cyclotrimerization of alkynes with  $Co_2(CO)_8$  [10]\*.

This picture identifies the importance of the dinuclear template (c.f. some leading reviews [11]) mechanism in Scheme 1 in the following points: (a) The reactivity difference between  $C(R^1)$  and  $C(R^2)$  is amplified by the coordination as reflected by the increasing *difference* between the <sup>13</sup>C-NMR  $\delta$  [ $C(R^1)$ ] and  $\delta$  [ $C(R^2)$ ] by coordination [4c,7c].

(b) Enabling the O-coordination of the first acyl-carbonyl group\*\*, which leads then to the easy second insertion\*\*\*.

(c) Overcoming the steric hindrance (if any) of  $\mathbb{R}^2$  by enabling the ring closure mechanism.

It should be mentioned that the mechanism depicted in Scheme 1 gets support from some additional model experiments [13,15,16].

#### Experimental

All experiments were performed using dry, deoxygenated solvents and gases [17]. IR spectra were obtained by UR-20 (Carl Zeiss, Jena) and Philips PU 9716 instruments. <sup>1</sup>H-NMR spectra were recorded on BS-487 (Tesla, Brno) and Varian XL-200 spectrometers. <sup>13</sup>C-NMR spectra were obtained with a Varian CFT-20 instrument in the presence of  $Cr(acac)_3$  relaxation reagent (800 to 3000 transitions were collected). Osmometric molecular weights were measured by a Knauer Vapour Phase osmometer (benzene), mass spectra were measured by the direct inlet system of Varian-MAT 111 instrument.

Material were of commercial origin with the exception of  $\text{Co}_2(\text{CO})_8$  [18] and the branched-chain acetylenes [19] which were prepared according to published methods. Complexes 1 were obtained from equimolar amounts of the acetylene and  $\text{Co}_2(\text{CO})_8$  in *n*-hexane at 25°C, 1 bar Ar [6] and purified by preparative TLC (5721 DC Kieselgel 60 plates,  $20 \times 20$  cm, 0.5 mm thickness, Merck, Darmstadt; eluent:*n*-hexane). Yields ranged between 90–97%.

The standard procedure for preparation complexes 2 was as follows: dicobalt octacarbonyl,  $Co_2(CO)_8$ , 3.42 g (10 mmol) and 10 mmol of the acetylene (or 10 mmol of the corresponding  $(R^1C_2R^2)Co_2(CO)_6$ , 1, complex) were dissolved in 50 ml of *n*-hexane. This solution was charged under Ar atmosphere into a 250 ml stainless steal rocking autoclave. Then the atmosphere in the autoclave was changed for CO 2-3 times and then pressurized to 27 MPa by

<sup>\*</sup>Also in this reaction a dinuclear mechanism is operative [10a]. Ring closure from the  $\mu_2$ -C<sub>6</sub>Co<sub>2</sub>(CO)<sub>4</sub> intermediate enabled the first spectacular synthesis of *o*-di-(*t*-butyl)benzene [10b].

<sup>\*\*</sup>Direct attack of the acyl-O on the carbon of a coordinated CO also appears to be possible [12].

<sup>\*\*\*</sup>CO insertion even into otherwise very stable Co-C(alkyl) bonds is promoted by excess tertiary phosphine [14].

#### TABLE 3

Complex	Substi	tuents	Analysis results		
type	R1	R²	Measured <sup>c</sup>	Found	Calcd.
1	н	n-Pr <sup>*</sup>	Co%	33.1	33.29
1	н	<i>i</i> -Pr	C%	37.6	37.32
			<b>H%</b>	2.6	2.28
			Co%	33.0	33.29
1	н	t-Bu	C%	39.2	39.16
			Н	2.9	2.74
			Co%	32.2	32.02
1	н	neo-Pent	C%	41.1	40.86
			H%	3.3	3.17
			Co%	30.4	30.85
2	н	n-Pr <sup>a,b</sup>	Co%	27.0	26.91
_			MW.	452	438.08
2	н	<i>i</i> -Pr	C%	39.0	38.38
			H%	1.9	1.84
			Co%	27.1	26.91
			MW	$410 (M^+ - CO)$	438.08
2	н	t-Bu	C%	39.9	39.85
-		. 24	H%	2.4	2.23
			Co%	26.7	26.07
			MW	452	452.11
2	н	neo-Pent	C%	41.4	41.23
-			H%	2.7	2.59
			Co%	26.3	25.29

Analytical characterization of complexes 1 and 2

<sup>a</sup> Compare ref. [6b].

<sup>b</sup> Compare ref. [4a].

 $^{\circ}$  MW<sub>o</sub> = osmometric, MW<sub>ms</sub> = mass spectrometric molecular weights.

CO gas. The autoclave was heated to  $90 \pm 5^{\circ}$ C and rocked at this temperature for 12 h. Consumed CO was supplied in each hour. After this period the autoclave was left to cool to r.t. ( $\approx 40 \text{ min}$ ) and the CO pressure was released. The reaction mixture was filtered, concentrated to 1/3 of its volume and worked up by preparative TLC (as above). The first deep red (minor) fraction was compound 1, while a second (major) orange fraction was identified as the 2 lactone complex. This latter substance was then purified by 1–4 times recrystallization from Et<sub>2</sub>O/*n*-pentane (1:1) at  $-78^{\circ}$ C which yielded orange-red crystals. Yields and analytical data are given in Table 3.

#### Acknowledgements

Financial support is acknowledged to the Italian Ministry of University and Scientific Research (MURST). Discussions are acknowledged to Prof. L. Markò (Veszprém) and Prof. M.I. Bàn (Szeged). Help in obtaining the spectra and discussions are sincerely acknowledged to Drs. S. Iglewski (<sup>1</sup>H-NMR) and G. Szalontai (<sup>13</sup>C-NMR) (Veszprém). The authors thank for attempted Xray diffraction measurements, to Profs. G.D. Andreetti and G.L. Calestani (Parma).

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