Inorganica Chimica Acta, 53 (1981) L29–L30
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On the Reactivity of Acetylenes Coordinated to Cobalt

V[a]. Unexpected Formation of Trinuclear μ_3-Carbyne Derivatives from Acetylene Mono- and Dicarboxylic Acid Esters[b]

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Received September 8, 1980

Stoichiometric carbonylation of acetylenes ($R^1C_2R^2$) (I) with $Co_2(CO)_8$ (II) or of the corresponding (μ_2-$R^1C_2R^2$)$Co_2(CO)_6$ (III) compounds leads to the formation of the μ_2-carbene type ($C_4O_2R^1$, R^2)$Co_2(CO)_7$ complexes [3–7]. The reaction can be carried out starting from a variety of hydrocarbons and moderately polar acetylenes (*e.g.* propargyl ethers) in apolar solvents such as n-hexane at 90–100 °C under 20–40 MPa CO pressure. As an extension of our studies in this field we tested the behaviour of acetylenes with very polar substituents directly attached to the sp-carbon atom(s).

Diiodoacetylene, which forms the corresponding (III) derivative under atmospheric conditions [8], could be carbonylated neither in the free nor in the complexed form.

The reactions of acetylene mono- and dicarboxylic acid methyl esters are summarized in Scheme 1.

Compound (IV) has already been reported by Beveridge and Clark [9]. The IR ν(C–O) and ^{1}H-NMR spectra of our sample (Table I) showed reasonable* agreement with the data reported by these authors. The identity of the compound was further confirmed by satisfactory analyses and its mass spectrum: the highest observable peak was $[M-CO]^+$ and the fragmentation showed stepwise loss of all CO s, followed by the loss of COOMe, CH_2 and C; $[Co_3]^+$ was the lowest mass ion which could be assigned with certainty; the base peak was $[Co_3(CO)_3CCH_2COOCH_3]^+$.

To the best of our knowledge, compound (V) has not been previously described [10, 11]. Its suggested structure is based on satisfactory analyses, a ν(C–O) spectrum which is characteristic for $Co_3(CO)_9CY$ derivatives bearing rigid polar Y groups without three-fold symmetry [12] (Table I), ^{1}H-NMR (Table I) and mass spectrum which is very similar to that compound (IV): highest peak $[M-CO]^+$, then loss of all CO s, followed by loss of the two $COOCH_3$ and the CCH group, $[Co_3(CO)_3CCH(COOCH_3)_2]^+$ was the base peak; $[Co_3C]^+$ could not be observed.

The formation of compounds (IV) and (V) is rather unexpected. Although the behaviour of the COOMe groups can be paralleled with the halogen 1,2-shift in similar systems [13, 15], the actual

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[a] For Part IV. *cf.* ref. [1].

[b] Portions of this work were presented at Conference [2].

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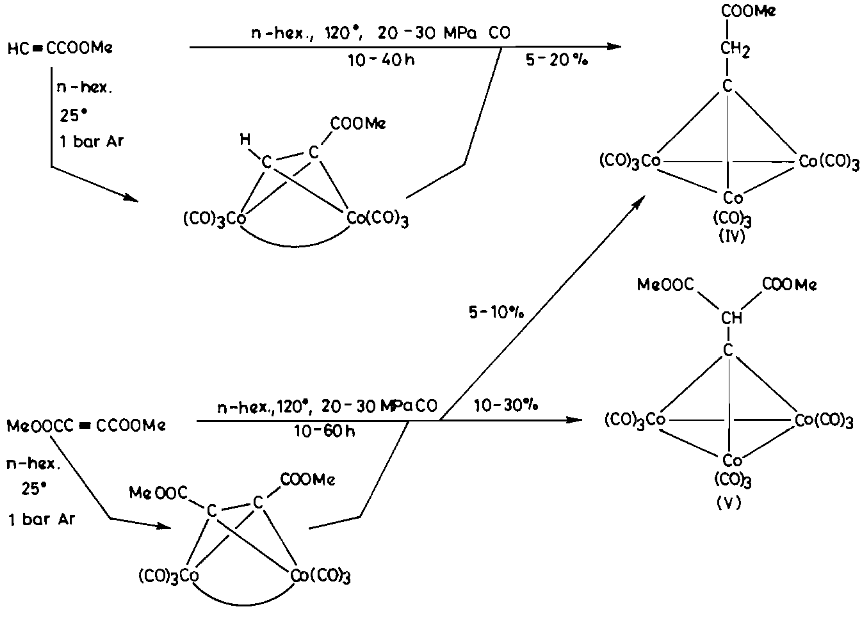
*Minor discrepancies were attributed to the choice of solvent.



source of at least one H atom is unclear* since we applied rigorously anhydrous conditions. The unexpected formation of C, H bonds in course of the earlier preparation of (IV) [9] and also of other $Co_3(CO)_9CY$ compounds [16–18] has been already reported in numerous cases and favours the hypothesis of radical pathways.

Refluxing (III), $R^1 = R^2 = COOMe$) in n-decane at 1 bar CO pressure led to the formation of $Co_4(CO)_{10}$-($MeOOCC_2COOMe$) in 20–40% yields. $Co_4(CO)_{10}$ (acetylene) complexes are known [19–20] however this particular derivative has not been previously described. It has been identified by its ν(C–O) IR spectrum (2100.5w, 2066sh, 2061.5vs, 2050.5s, 2026.0w, 2005.5m, 1885.5m, in agreement with other $Co_4(CO)_{10}$ (ac) complexes [21]) and mass spectrum (M^+ could be observed followed by loss of all CO ligands and the organic ligand).

Experimental

Atmospheric experiments were carried out with the usual inert gas technique while the high-pressure experiments were performed in stainless steel rocking autoclaves using 50 ml of the solvent and 1–5 mmol quantities of (I) + (II) or (III).

IR spectra were obtained in n-hexane with IR-75 (Carl Zeiss, Jena), ^{1}H-NMR spectra with an 80 MHz instrument (BS-487, Tesla, Brno) and mass spectra with MAT-111 (Varian, Bremen) using direct introduction and 70 eV ionization potential.

Acknowledgements

The authors are indebeted to Drs. S. Iglewski and I. Ötvös (Veszprém) for help in the ^{1}H-NMR and MS experiments, respectively.

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*Neither of the two known analogies [9, 15] are applicable to the present case.

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