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Preliminary communication

ORGANOCOBALT COMPLEXES

IX*. THE INSERTION OF ACETYLENES INTO BUTENOLIDE COMPLEXES; CRYSTAL STRUCTURE OF A DICOBALT COMPLEX WITH A NOVEL FIVE-CARBON BRIDGE

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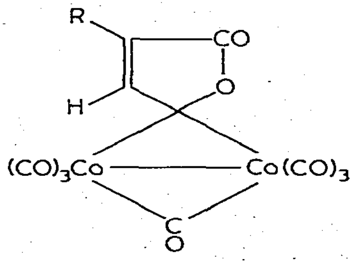
Summary

Preparative thin layer chromatography has yielded the first pure insertion products from acetylenes and butenolide dicobalt hexacarbonyls; the structure of one such product has been determined by X-ray crystallography and a related formulation is suggested for the other isomer formed in comparable amounts.

In an earlier paper [2] we showed that the butenolide cobalt complexes I are intermediates in the generation of bifurandiones which arise from them by reaction with acetylenes under carbon monoxide pressure and we commented briefly on the different pathway of reaction with acetylenes only. Examples of the latter reaction were first reported by Sternberg et al. [3] but they did not



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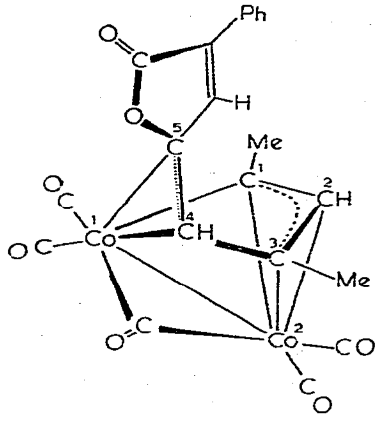
isolate pure products. Our own products, prepared from three of the butenolide complexes I (R = H, Me or Ph) and several acetylenes and isolated after column chromatography on alumina, gave reasonable elemental analyses and ^{1}H NMR spectra which showed that two acetylenes had been inserted, except that in one case (I; R = H with C_2H_2) insertion of three acetylenes appeared to have taken place. However, the products generally appeared to be amorphous and their purity remained in doubt until we observed that they could be further resolved on thin layer plates. This has now resulted in isolation of two series of well-crystallised isomeric products together with minor amounts of metal free compounds and additional organocobalt species which probably include a third isomer.

The more rapidly eluted compounds of Series A show six ν(CO) peaks at slightly lower frequencies than those of the somewhat more abundant isomers of Series B. Thus in the products from I (R = Ph) + propyne, isomer A, m.p. 164°C, shows maxima at 2063vs, 2036vs, 2014s, 2007m, 1881s and 1781s cm^{-1} while isomer B has the corresponding peaks at 2076vs, 2045vs, 2019vs, 2006vs, 1885m and ca. 1740m cm^{-1}. Both isomers show two olefinic proton and two methyl resonances supporting analytical data which show insertion of two molecules of propyne and loss of two molecules of carbon monoxide.

Formation of parallel series of compounds from insertion of symmetrical acetylenes showed that the isomers could not differ only in the ordering of the acetylene fragment and taken with the NMR evidence, appeared to rule out the more symmetrical possible formulations, but still left several reasonable alternatives. We have now established structure II for the above isomer B by X-ray analysis. The compound forms red-brown crystals, m.p. 184°C (triclinic, $P\bar{1}$, a 9.41, b 9.98, c 11.90 Å, α 97.3°. β 100.9°, γ 108.3°; Z 2, D_m 1.60, D_c 1.61); final R, with anisotropic Co atoms, 0.0197 over 946 reflections measured with a film scanner.



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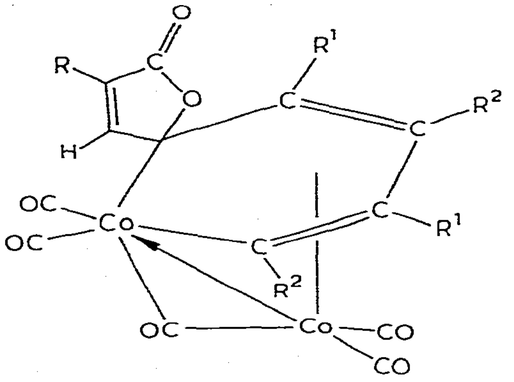
The molecule II contains two Co atoms linked directly (2.39 Å) and by a carbonyl bridge. Their bonding to the organic ligand can be described in terms of a σ-bond from Co(1) to C(1) (2.03 Å) and π-interactions between Co(1) and the formal double bond C(4)—C(5) (1.38 Å), and between Co(2) and the allyl system C(1)—C(3) (Co(1)—C(4): 2.02; Co(1)—C(5): 2.11; Co(2)—C(1); 2.04; Co(2)—C(2): 2.10; Co(2)—C(3): 2.15 Å). The mean planes of the π-allyl system and of the lactone ring are inclined at 79°. The structure represents the result of inserting two acetylene molecules (as a σ,π-butenyl unit) into one of the cobalt—butenolide bonds of the precursor I.

Although the observed structure would allow a stereoisomer differing only in the orientation of the lactone ring, we believe that a more fundamental structural change is indicated by the differences, both in the IR and in the ^{1}H NMR spectra. (Compound II shows olefinic ^{1}H NMR signals at δ 4.90s and 4.30s ppm whereas its A series isomer shows corresponding peaks (br)s at δ 5.10 and 3.48 ppm). We suggest that the most probable formulation of the A series is as represented by structure III, but as others cannot be firmly ruled out, our efforts to determine the structure of a compound of this series are continuing.



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We thank Professor L. Markó and Dr. G. Pályi for the complete exchange of information regarding their parallel studies [4], and Dr. M. Elder and his staff for scanning the X-ray films.

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