Inorganica Chimica Acta, 53 (1981) L49–L50
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The Mechanism of Formation of Cyclopentadienyl Cobalt Cyclononatetraene [1]

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Received September 3, 1980

We have recently reported [2] that photochemical reaction of bicyclo[6.1.0]nonatriene (I) with CpCo-$(CO)_2$ predominantly gives the stable complex CpCo-(1,2:5,6η-cyclononatetraene) (III), in which the nine-membered ring assumes a type of coordination not previously observed. A second isomer (II) was also formed, the structure of which we assigned on the basis of its symmetrical ^{13}C NMR spectrum as CpCo-(3-6η-cyclononatetraene). A comparison of chemical shift data of this complex II with data for a series of cobalt polyolefin complexes recently prepared by us [3], however, casts doubt on this assignment.

Re-examination of the ^{13}C-spectrum of II at higher signal-to-noise ratios revealed a previously not observed broad signal at 30.7 ppm. By a combination of ^1H and ^{13}C NMR spectroscopy the structure of II could now be fully elucidated. Mutual assignment of the ^{13}C and ^1H signals was achieved by various off-resonance decoupled spectra, whereas the assignment within the proton spectrum is based upon homo-nuclear decoupling experiments. The new signal proved to be due to a σ-bonded methylene group and is broadened by residual coupling to the adjacent cobalt nucleus. The structure of II is shown in Fig. 1.

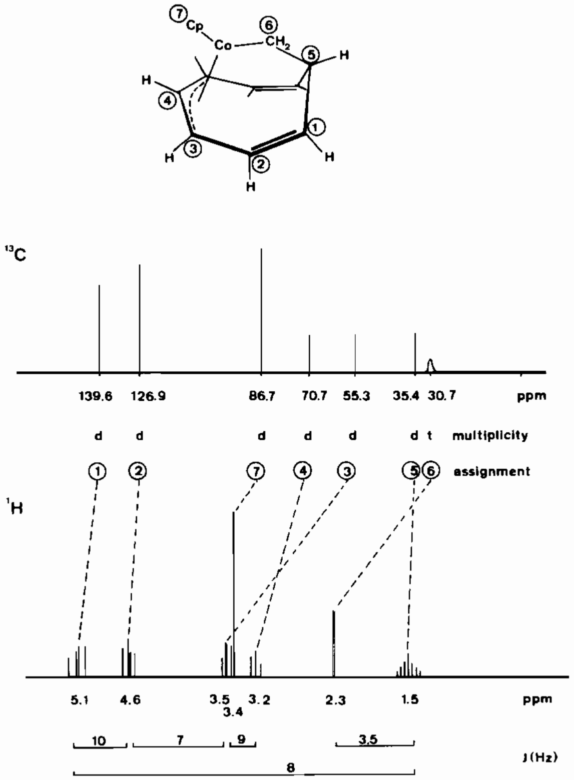
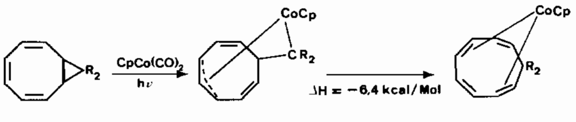


Fig. 1. ^1H and ^{13}C NMR spectra (schematic) of II in C_6D_6; chemical shifts (ppm) relative to internal TMS.

The initial reaction which occurs on irradiating $CpCo(CO)_2$ in the presence of I appears to be an insertion into the cyclopropane ring coupled with double bond shifts in the eight-membered ring. II has a symmetrical π-allyl–σ-alkyl-structure similar to previously observed iron or osmium polyolefin compounds [4]. The coordinated π-allyl group and the σ-bonded exocyclic carbon are separated in this compound by two equivalent non-coordinated double bonds and an aliphatic carbon.

Compound II is sensitive to heat and, apparently, also to further irradiation and rearranges in a clean reaction to III. In the solid state it is more stable than in solution, the rearrangement occurring shortly above melting point (70 °C), the melt then solidifying again to solid III, which melts at 95 °C. The thermodynamics of this reaction were followed by differential scanning calorimetry (DSC). As melting and recrystallisation peaks overlapped with the exothermal reaction peak, enthalpies were determined in solution, giving a reaction enthalpy ΔH = – 6.4 ± 1.0 kcal/mol in nitrobenzene solution.

A deuterium labelled olefin Ia was also reacted to determine whether proton scrambling occurred during the ring expansion.



I II III

I R= H
Ia R= D

Both deuterium atoms remain, however, at the original carbon atom as shown by ^{13}C and ^2H NMR, the deuterium isotope appearing in the σ-bonded methylene group of IIa (one ^2H signal observed) and in the methylene group of IIIa (two ^2H signals in the aliphatic region). No further deuterium signals were detectable.

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This is to our knowledge the first time that a σ, π-bonded compound has been isolated as an intermediate in a metal-catalysed ring expansion. It sheds further light on the mechanism of such organometallic rearrangements, indicating that these reactions may proceed via pathways other than the classic Woodward–Hoffmann-type.

Experimental

^{1}H, ^{13}C and ^{2}H NMR spectra were recorded on Varian EM-390 and XL-200 instruments, DSC curves on a Perkin Elmer DSC 2. 14 samples were measured and ΔH was determined by peak integration compared to a standard reference.

Acknowledgements

A gift of cyclooctatetraene by BASF Ludwigshafen is gratefully acknowledged. This work was supported by the Swiss National Science Foundation.

References

1 Part X in the series: The reactivity of complexed carbocycles; Part IX: Ref. 2. ^{13}C NMR spectroscopy, Part XXVII, Part XXVI: S. Zobl-Ruh & W. von Philipsborn, *Helv. Chim. Acta, 63,* 773 (1980).
2 A. Salzer and R. Bischof, *Transition Metal. Chem., 4,* 254 (1979).
3 P. Bigler and A. Salzer, *Inorg. Chim. Acta,* submitted.
4 G. Deganello, 'Transition Metal Complexes of Cyclic Polyolefins', Academic Press (1979).