Journal of Organometallic Chemistry
Elsevier Sequoia S.A., Lausanne
Printed in The Netherlands

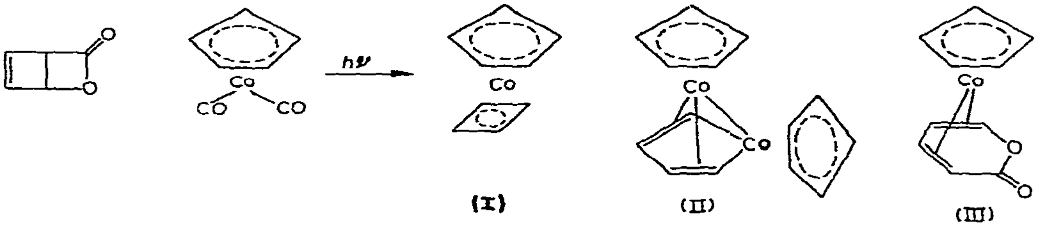
Preliminary communication

Fluxional behavior of a dicobalt complex. An example of metal-carbon $\sigma-\pi$ interconversion

M. ROSENBLUM, W.P. GIERING, B. NORTH and D. WELLS★
Edison–Lecks Laboratories, Department of Chemistry, Brandeis University, Waltham, Mass. 02154 (U.S.A.)

(Received February 5th, 1971)

We recently reported the isolation of a green complex $C_{14}H_{14}Co_2$, to which we tentatively assigned the structure II on the basis of analytical and spectroscopic data[1]. This substance is formed together with cyclobutadiene(cyclopentadienyl)cobalt (I) and α-pyrone(cyclopentadienyl)cobalt (III) when photo-α-pyrone is photolyzed in the presence of cyclopentadienylcobalt dicarbonyl. The complex II may be shown to be a terminal product in the photochemical reaction. Thus, photolysis of I alone gives II in low yield, but the conversion may be increased to 54% by carrying out the reaction in the presence of cyclopentadienylcobalt dicarbonyl. Structure (II) for the green dicobalt complex has since been confirmed by an independent X-ray study[2].



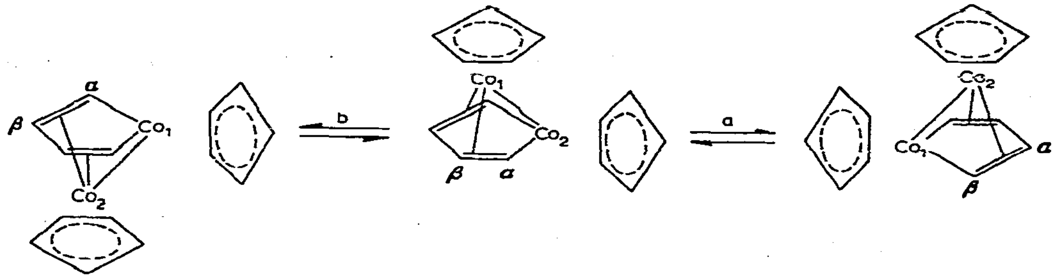
(I) (II) (III)

We now find that II exhibits novel fluxional behavior which is best interpreted as involving exchange of the two nonequivalent C_5H_5 units in the molecule concomitant with the exchange of σ and π bonding between the two cobalt atoms and the C_4H_4 unit of the cobaltacyclopentadiene ring. The exchange process is evidenced in the NMR spectrum of II★★ by broadening of the two cyclopentadienyl ring proton signals above 90° and their collapse at 142° to a broad singlet which continues to narrow up to 160°. These changes are reversible.

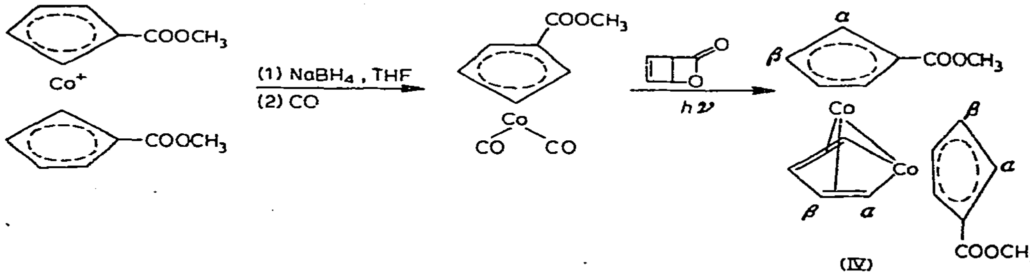
★College Teacher Summer Research Participant supported by National Science Foundation grant GY 6952. Present address, S. Carolina State University, Orangeburg, S.C. (U.S.A.)
★★Determined in *o*-dichlorobenzene solution at 60 MHz.

J. Organometal. Chem., 28 (1971) C17–C19

Three mechanisms capable of accounting for these processes need be considered. Of these, intermolecular exchange of the cyclopentadienyl rings through a dissociation process can be excluded, since the rate of exchange is independent of the concentration of II. Intramolecular exchange of the cyclopentadienyl rings may in principle be effected either by path a or b. The former, involving simultaneous exchange of cobaltacyclopentadienyl and cyclopentadienyl rings protons may be excluded since the exchange process is not accompanied by the collapse of the low field triplet resonance assigned to the β-protons of the cobaltcyclopentadiene ring★.



The dicarboxylic ester (IV), prepared from dicarbomethoxycobalticinium hexafluorophosphate by conversion to carbomethoxycyclopentadienylcobalt dicarbonyl and photolysis of this substance in the presence of photo-α-pyrone, exhibits similar behavior.



(IV)

At room temperature the NMR spectrum of this substance shows two methyl singlet signals at τ 6.12 and 6.18, a complex multiplet centered at τ 5.0 assigned to cobaltacyclopentadienyl α-protons and the two cyclopentadienyl ring β-protons, a second complex multiplet at τ 4.44 due to α-protons of the two cyclopentadienyl rings, and a triplet at τ 1.76 (J 3.8 Hz) assigned to β-protons of the cobaltacyclopentadienyl ring. Above 121°, the methyl group signals collapse to a singlet, while the multiplet at τ 4.44 is resolved into a triplet (J 2 Hz) typical of monosubstituted cyclopentadienyl systems. Over this temperature range, the signal at τ 1.76 remains unchanged.

★A second multiplet assigned to α-protons of this ring is partly obscured by the cyclopentadienyl ring proton peak at τ 5.04 and cannot therefore be examined.

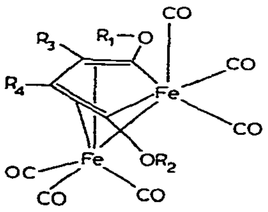
Rates for the exchange process were determined from the NMR spectra of II and IV in *o*-dichlorobenzene solution, over a 30° temperature range by a combination of line shape functions[3]. Activation parameters, calculated from least squares plots of the data, are summarized in Table 1.

TABLE 1

ACTIVATION PARAMETERS

	$\Delta H^{\neq}$(kcal/mole)	$\Delta S^{\neq}$eu
II	25.8 ± 1.8	8.6 ± 4.5
IV	24.3 ± 0.7	8.6 ± 1.8

The fluxional behavior of II and IV is closely analogous to the valence bond isomerization exhibited by the structurally related diiron complexes V formed in the reaction of acetylenes with alkaline solutions of iron carbonyl hydride. This isomerization, for which an activation energy of 29 ± 2 kcal/mole (log *A* 14.6 ± 0.6), has been determined, is demonstrated by the rapid racemization of an optically active derivative (R_1 = R_2 = Me, R_3 = t-Bu, R_4 = H) above room temperature[4].



(V)

ACKNOWLEDGEMENT

Support for this work from the National Institutes of Health (GM 16395) and from the National Science Foundation (GP-8714) is gratefully acknowledged.

REFERENCES

1 M. Rosenblum and B. North, *J. Amer. Chem. Soc.*, 90 (1968) 1060.
2 O.S. Mills, private communication.
3 L.M. Jackman and S. Sternhall, *Applications of Nuclear Magnetic Resonance Spectroscopy in organic Chemistry*, Pergamon Press, Oxford, 1969, p. 55; E. Grunwald, C.F. Jumper and S. Meiboom, *J. Amer. Chem. Soc.*, 84 (1962) 4664.
4 R. Case, E.R.H. Jones, N.V. Schwartz and M.C. Whiting, *Proc. Chem. Soc.*, (1962) 256.