than a hundred times faster in nitromethane than in tetrahydrofuran while several related Diels–Alder reactions[4] are accelerated by a factor of about two for the same solvents. If both I and II were formed from a common, rate-limiting transition state, as would be expected for an intermediate of the type proposed by Woodward for the Diels–Alder reaction collapsing in either of two possible directions, the total rate of reaction would be expected to show only the slight solvent effect which is generally characteristic of Diels–Alder reactions. Since this is not the case, it is necessary to conclude either that a change in mechanism has occurred with a change in solvent or else that I and II are formed in either solvent through separate rate-limiting transition states, quite likely involving, respectively, the *transoid* and *cisoid* configurations of the diene. Attempts at thermal interconversion as demonstrated by Woodward[5] and Roberts[7] in related systems (at the suggestion of Prof. Roberts) were thwarted by the limited thermal stability of I under conditions such that II was virtually unchanged. Decomposition appeared to be accompanied by gas evolution and formation of conjugated structures (strong absorption at 4.5, 6.1, 6.3 microns) and may be related to elimination reactions previously described for tetracyanocyclobutanes.[8]

Acknowledgments.—The author wishes to thank Dr. P. D. Bartlett, in whose laboratories several aspects of this reaction are being investigated, and Dr. J. D. Roberts for helpful discussions.

(7) R. P. Lutz and J. D. Roberts, *J. Am. Chem. Soc.*, **83**, 2199 (1961).

(8) J. K. Williams, D. W. Wiley, B. C. McKusick, 139th ACS Meeting, St. Louis, Mo. (1961) abstracts p. 9-O.

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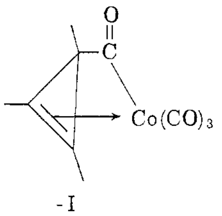
CYCLOPROPENYL COMPLEXES OF IRON AND COBALT

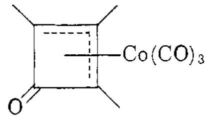
Sir:

π-Bonded metal complexes of the cyclic moieties C_nH_n are known for $n = 4, 5, 6, 7$ and 8. We attempted to prepare a complex containing a cyclopropenyl ligand π-bonded to a metal. Orgel[1] has mentioned the possibility of such complexes and noted the molecular orbitals involved. In practice, we have sought a complex of triphenylcyclopropenyl since triphenylcyclopropenyl bromide is synthesized readily[2] and is highly symmetrical.

Triphenylcyclopropenyl bromide reacted immediately with cobalt tetracarbonylate anion in acetonitrile at room temperature without gas evolution. Processing of the solution gave a 58% yield of yellow, air-stable crystals, m.p. 134–135.5°, soluble in organic solvents. *Anal.* Calcd. for $C_{25}H_{15}CoO_4$: C, 68.50; H, 3.45; Co, 13.4. Found: C, 68.26; H, 3.29; Co, 13.3. An infrared spectrum (KBr pellet) showed seven peaks in the 690–790 cm.$^{-1}$ region, an unsymmetrical doublet at 2015, 2080 cm.$^{-1}$ characteristic of the $Co(CO)_3$ group, and a band at 1710 cm.$^{-1}$ assigned to a ketonic carbonyl. The characteristic triphenylcyclopropenyl cation band at 1400 cm.$^{-1}$ was absent. These data suggest structure I or II for the product.



I



II

Similarly, $Fe(CO)_3NO^{-}$[3] reacted with triphenylcyclopropenyl bromide in methanol, producing a 14% yield of maroon crystals, m.p. 119–21°, somewhat less air-stable than the cobalt compound. *Anal.* Calcd. for $C_{24}H_{15}NFeO_4$: C, 65.94; H, 3.46; N, 3.20; Fe, 12.8. Found: C, 66.10; H, 3.99; N, 2.96; Fe, 13.3. An infrared spectrum showed a symmetrical doublet at 1950, 2005 cm.$^{-1}$ which was assigned to the carbonyl stretches in $Fe(CO)_2$, and an unsymmetrical doublet at 1720(s) and 1680 cm.$^{-1}$ (m) assigned to nitrosyl and ketonic carbonyl groups. Bands characteristic of the phenyl groups were present at 690 and 760 cm.$^{-1}$ with a shoulder at 750 cm.$^{-1}$. Structures analogous to I and II are possible for this complex, with Fe replacing Co and one CO replaced by NO.

Evidence in support of structure I was obtained by oxidizing the iron complex with 1,3-diphenylallyl chloride in hot toluene. This treatment gave yellow crystals of triphenylcyclopropenylium tetrachloroferrate (III), m.p. 253–254°, identified by comparison with the product obtained from triphenylcyclopropenyl bromide and $FeCl_3$ in ethanol. This suggests that the cyclopropene ring is intact in the complexes and therefore that structure I is correct.

These complexes are closely related to the expected π-$(C_6H_5C)_3$ complexes. In fact, the relation is the same as that existing between $RMn(CO)_5$ and $RCOMn(CO)_5$.[4] Complexes of cobalt tricarbonyl with acrylyl and 4-pentenoyl have been prepared.[5] These are similar to structure I in that bonding to cobalt occurs *via* a double bond and a bridging carbonyl.

(1) "An Introduction to Transition Metal Chemistry," L. F. Orgel, Editor, Methuen and Co., Ltd., London, 1960, pp. 153–157.

(2) R. Breslow and H. W. Chang, *J. Am. Chem. Soc.*, **83**, 2367, (1961).

(3) M. J. Hogsed, U. S. Patent 2,865,707 (1958).

(4) R. D. Closson, J. Kozikowski and T. H. Coffield, *J. Org. Chem.*, **22**, 598 (1957).

(5) R. F. Heck and D. S. Breslow, *J. Am. Chem. Soc.*, **83**, 1097 (1961).

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PHOTOCHEMICAL REACTIONS OF 1,2-DIKETONES

Sir:

The photolysis of appropriate 1,2-diketones gives 2-hydroxycyclobutanones with striking selectivity and remarkable yields. Only 2-hydroxycyclobutanones, and none of the 1-alkanoylcyclo-