Tetraphenylallene- and Tetraphenylbutatriene-Iron π-Complexes

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Although a number of organometallic π-complexes of conjugated 1, 3-diene systems have been reported,[1] no report on an example of the π-complexes of cumulene systems has been published as yet. We will now report a preparation which is believed to be the first example of the π-complexes of the cumulene systems.

The reaction of tetraphenylallene with an excess of iron pentacarbonyl in refluxing isooctane under nitrogen for 13 hr. proceeded with the evolution of a gas. After the removal of the solvent from the deep reaction mixture, a red semisolid was obtained. The semisolid crystallized from ethanol to give red crystals (I) (m. p. 102~103°C, decomp. 230°C) in 29% yield. The elemental analysis and molecular weight determination indicated the composition: (tetraphenylallene)Fe(CO)$_3$, (Found: C, 74.00; H, 4.45; mol. wt. (in benzene), 518. Calcd. for $C_{30}H_{20}FeO_3$: C, 74.39; H, 4.16%; mol. wt., 484).

Carbon monoxide (2.6 mol. equiv.) was evolved on the pyrolysis of I under nitrogen. The pyrolysis gave tetraphenylallene and 1, 1-diphenyl-3-phenylindene.[2] The infrared spectrum of I showed the presence of terminal iron carbonyl groups (2060, 1999, and 1985 cm^{-1} in carbon tetrachloride) and phenyl groups. In the visible region it showed a maximum at 468 mμ (log ε: 2.91) and had an increasing absorption towards the shorter wavelengths. The compound I was found to be diamagnetic and was quite stable in air. It was soluble in *n*-hexane, benzene and ethanol.

Tetraphenylbutatriene was allowed to react with an excess of iron pentacarbonyl in ethylcyclohexane under nitrogen for 14 hr. at reflux. The evolution of a gas was accompanied by a change in color to deep red. Red crystals mixed with a small number of yellow ones were obtained on cooling. The product was purified by repeated crystallization from a benzene-*n*-hexane mixture. Pure red crystals (II) (decomp. 200°C) were obtained in 26% yield. The product was found to have the composition: (tetraphenylbutatriene)Fe$_2$(CO)$_5$. (Found: C, 64.90; H, 3.55; mol. wt. (in benzene) 500. Calcd. for $C_{33}H_{20}Fe_2O_5$: C, 65.16; H, 3.31 %; mol. wt., 608).

The amount of carbon monoxide which evolved upon pyrolysis indicated five CO groups present in a molecule of II. The pyrolysis gave tetraphenylbutatriene and 1-diphenylmethylene-3-phenylindene.[2] The infrared spectrum of II showed the presence of terminal iron carbonyl groups (2072, 2035, 1998, and 1988 cm^{-1} in carbon tetrachloride) and phenyl groups. The visible and ultraviolet spectra showed no maxima.[3] An increasing absorption towards shorter wavelengths was observed. This spectral evidence indicates the absence of tetraphenylbutatriene chromophore, which has a strong absorption maximum at 420 mμ. Therefore, the butatriene chromophoric system is destroyed by bonding with the iron carbonyl group. The compound II was diamagnetic and was stable in air. It was soluble in benzene and slightly soluble in *n*-hexane.

It is interesting to discuss how these cumulene systems interact with iron carbonyl groups. The bonding of the iron tricarbonyl group in I through the benzene nucleus is very unlikely since no examples of benzene iron tri- or dicarbonyl type compounds are known. The bonding through one of the double bonds of the allene system and a double bond of the benzene nucleus is also less probable as a possible steric hindrance. Therefore, we are left with the possibility of the bonding through two double bonds of the allene system. We believe that cumulated double bonds in a straight chain are responsible for stable bond formation. By similar reasoning and also from the spectral evidence, we judge that the bonding in II is probably through the butatriene system. The chemical approach to the structure determination seems to be inconclusive to us. It is hoped that structure elucidation by means of X-ray will clarify the nature of the bonding in these compounds.

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[1] a) R. G. Guy and B. L. Shaw, "Advances in Inorganic Chemistry and Radiochemistry," Vol. IV, Academic Press Inc., New York (1962), p. 78; b) M. A. Bennett, *Chem. Revs.*, **62**, 611 (1962): c) E. O. Fischer and H. Werner, *Angew. Chem.*, **75**, 57 (1963).

[2] Identified by a comparison of the infrared spectra of the authentic samples.

[3] The visible and ultraviolet spectra were measured, I in ethanol, II in tetrahydrofuran.