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(2,2'-Bi-π-allylene)(hexacarbonyl)diiron. A novel example of valence tautomerism

During the course of our study on the interaction of cumulene systems with organometallic π-complexes, we obtained a compound of the composition $[C_3H_4Fe(CO)_3]_2$, from the reaction of allene with triiron dodecacarbonyl[1]. The structure of this compound was examined by use of the infrared and NMR spectra as well as the degradation with bromine. The bromine degradation at room temperature gave 2,3-bis(bromomethyl)-1,4-dibromo-2-butene[2] showing the compound has the $^{C}_{C}{>}C{-}C{<}^{C}_{C}$ unit. The infrared spectrum had strong maxima at 2068, 2030, 2003, and 1990 cm^{-1} which indicates the presence of terminal metal carbonyl groups. It is likely that the compound has a 2,2'-bi-π-allylene structure with two iron tricarbonyl groups. Similar bi-π-allylene type compounds were recently described by Emerson *et al.*[3]. If one assumes the 2,2'-bi-π-allylene structure for the compound, the NMR spectrum would have two singlets corresponding to the *syn* and *anti* protons with separation of *ca.* 1 ppm.

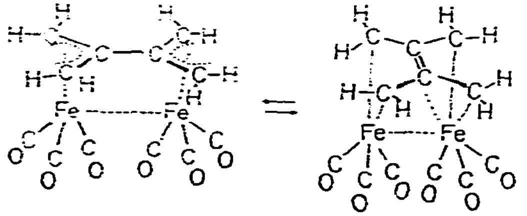

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Fig. 1. Valence tautomerism of $(C_3H_4)_2Fe_2(CO)_6$.

The actual NMR spectrum in carbon tetrachloride at 35° had two peaks separated only 0.07 ppm and centered at 8.34 τ. The separation became smaller when the temperature was lowered and finally the two peaks condensed into a sharp singlet at

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—10°. This NMR behavior can be understood by the assumption of the following valence tautomerism (Fig. 1) occurring rapidly even at —10° in the solution. This rapid tautomerism averages out all the protons and the NMR spectrum will have a single peak. The τ-value observed can be approximately calculated as follows on the assumption of the tautomerism. The calculation involves averaging out all the τ-values of the terminal protons of butadiene(tricarbonyl)iron[4] and the hypothetical τ-values for π-allyl(tricarbonyl)iron[*] and results in a value of 8.35 τ.

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[*] π-Allyltricarbonyliron is paramagnetic in solution[5]. The hypothetical τ-value was calculated by averaging the known τ-values of the terminal protons in π-allyltetracarbonylmanganese and in π-allyltricarbonylcobalt (*cf.* ref. 6).

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Solvent and concentration effects on the rate of addition of *n*-butyllithium to 1,1-diphenylethylene

Enhancement of rates of organolithium reactions by ether solvents has been recognized for many years, but quantitative knowledge is wanting. We report here measurements of the rate of reaction (1) in hydrocarbon solutions containing small amounts of tetrahydrofuran (THF)[*]. The rate increases a factor of 400–700 with a 160-fold change in THF level at each of seven *n*-butyllithium concentrations. On the other hand, with increasing amounts of *n*-butyllithium at constant THF concentrations, the rate of reaction (1) is found to decrease. Since *n*-butyllithium is one of the formal reactants, this decrease in rate is unusual. The only previously reported kinetic studies of organolithium olefin addition reactions which relate to solvent effects are the propagation reaction of *n*-butyllithium-initiated polymerization of styrene in benzene solution containing small amounts of THF[2–4] and the propagation reaction of *n*-butyllithium-initiated polymerization of dienes in hexane or THF[5] or $(C_2H_5)_2O$[6]. Initiation of these polymerizations was reported to be too fast to measure. A kinetic

$$n\text{-}C_4H_9Li + CH_2{=}C(C_6H_5)_2 \longrightarrow n\text{-}C_5H_{11}C(C_6H_5)_2Li \qquad (1)$$

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[*] See ref. 1 for a kinetic study of reaction (1) in benzene.

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