Journal of Organometallic Chemistry, 155 (1978) C13—C16

Preliminary communication

VINYLCYCLOHEXATRIENEIRON TRICARBONYL COMPLEXES OF THE DIENE TYPE VIA OLEFIN ISOMERIZATION OF ALLYL-AROMATICS

PHILIP BOUDJOUK* and SEE LIN
Department of Chemistry, North Dakota State University, Fargo, North Dakota 58102 (U.S.A.)
(Received February 17th, 1978)

Summary

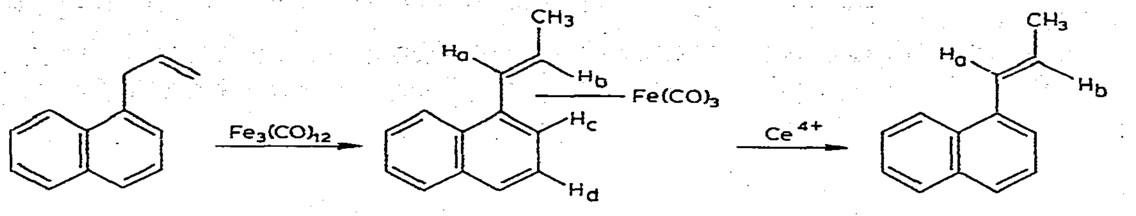
Allylnaphthalene and *m*-diallylbenzene react with iron carbonyls to form two new vinylcyclohexatrieneiron tricarbonyl complexes. The isomerization is stereospecific giving only the *trans*-β-methyl complex in each case. Allylbenzene and $Fe(CO)_5$ react only under photochemical conditions to give the known bis-iron complex, *trans*-β-methylstyrene-*trans*-bis(tricarbonyliron).

The investigation of complexes in which aromatic π-electrons are localized by one or more iron tricarbonyl groups is an active area in arene-transition metal carbonyl chemistry. The trapping of Kekulé forms of aromatic systems by iron tricarbonyl has been most successful for large condensed aromatic rings such as anthracene, benzanthracene and related heterocycles which lose only a small fraction of their delocalization energy upon coordination [1—4], and for vinyl-substituted aromatics [5—9].

The role of the vinyl group is not clearly understood but it has been suggested that it may provide a more reactive center for initial complexation to form a more stable intermediate (e.g., a vinyltetracarbonyliron) prior to diene-tricarbonyliron formation [5,8]. The coordination of vinyl-substituted aromatics to iron tricarbonyl groups is a general reaction but is very dependent on substrate and reaction conditions.

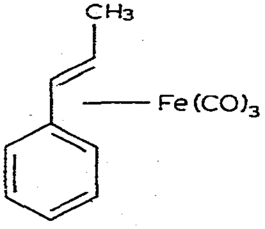
For example, α- and β-vinylnaphthalenes readily form mono-tricarbonyliron complexes when treated with iron carbonyls in refluxing solvents [5]. Styrene, however, fails to yield a tricarbonyliron complex under thermal [5,10] or photochemical conditions [10] but will form styreneiron tricarbonyl in the metal atom vaporizer [11]. Substituted styrenes, on the other hand, give mono-iron complexes only under photochemical conditions and in low yield, and some bis-iron complexes [6—8]. Introduction of a second vinyl group permits isolation of only bis(tricarbonyliron)divinylbenzenes [5].

We have found that olefin isomerization of allyl-substituted aromatics is a convenient route to β-substituted vinylcyclohexatrieneiron tricarbonyls. When α-allylnaphthalene (I) and $Fe_3(CO)_{12}$ are heated in refluxing octane for 15 h, 1-(*trans*-β-methylvinyl)naphthaleneiron tricarbonyl (II) was obtained as an orange-red solid (m.p. 92—94°C) in 58% yield. Higher yields of II (68% based on I) can be obtained by irradiating I in $Fe(CO)_5$ with 366 nm light for 2 h. Decomplexation of II using Ce^{4+} gave the new vinylnaphthalene III.

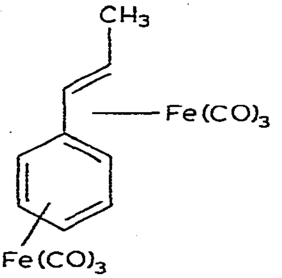


(I) (II) (III)

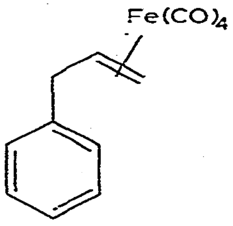
Extension of this procedure to allylbenzene in an effort to prepare the unknown IV failed, giving no isolable product. However, irradiation (366 nm, 3 h) of allylbenzene and $Fe(CO)_5$ in hexane gave the known V [6—8] in 5% yield. We also obtained infrared data (ν(CO) ~2080, ~2020, ~2005, ~1990 cm^{-1}) on an unstable yellow solution which indicated the presence of a coordinated $Fe(CO)_4$ unit suggesting the presence of VI or VII.



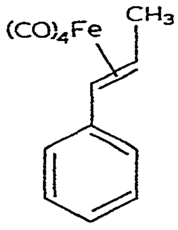
(IV)



(V)



(VI)

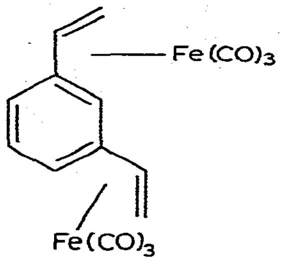


(VII)

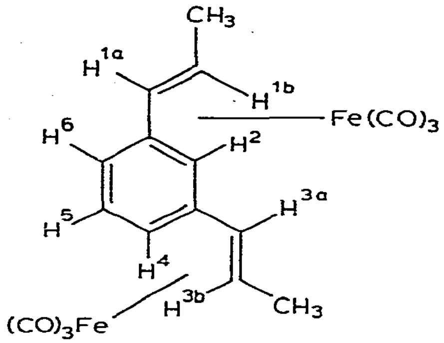
The successful coordination of two iron tricarbonyl groups to *m*-divinylbenzene to form VIII [4] prompted us to investigate *m*-diallylbenzene. We found that $Fe_3(CO)_{12}$ and *m*-diallylbenzene in refluxing benzene gave the new bis-iron complex IX, (brown-red crystals, m.p. 144—146°C). The assignment of a *trans* configuration to IX is based on its NMR spectrum which shows the *anti*-hydrogen near methyl as a multiplet above the methyl doublet as in II and V [8]. These observations are also consistent with the spectra of *cis*- and *trans*-1,3-pentadieneiron tricarbonyl [12].

While iron carbonyl-induced double-bond migration of remote dienes to form conjugated diene complexes is well known, these are the first cases where the reaction has been employed to prepare vinylcyclohexatriene tricarbonyl complexes. That allyl-aromatics are usually more readily available than the corresponding vinyl compounds indicates that they may be more useful intermediates for preparing complexes of this type.

These results also provide an interesting parallel to earlier studies on styrene systems. The complexes from allyl substrates are formed in approximately the



(VIII)



(IX)

same yield as from the related vinyl compounds under similar conditions. It is also noteworthy that *trans*-β-methylstyrene and $Fe(CO)_5$ form V in 1—8% yield when photolyzed in hexane and that attempts to detect a tetracarbonyliron intermediate failed for this and all other β-substituted styrenes [8]. This suggests that the unstable intermediate we observe in the reaction of allylbenzene with $Fe(CO)_5$ was probably VI and not VII.

The structures of II, III and IX follow from their spectroscopic and analytical properties.

II: *m/e* 308, (M^+). IR: 2050, 1996 and 1989 cm^{-1} (ν(Fe—CO)). NMR (δ in $CDCl_3$): 0.72 m (H_b); 1.32 d (CH_3, $J(H_b—CH_3)$ 3.6 Hz); 2.22 d (H_c, $J(H_c—H_d)$ 5.8 Hz); 5.94 d (H_a, $J(H_a—H_b)$ 8.2 Hz); 6.40—7.82 m (6 aromatic H's). Elemental analysis: Found: Fe, C, 62.15; H, 3.77; Fe, 17.90. $C_{15}H_{12}FeO_3$ calcd.: C, 62.33, H, 3.89; Fe, 18.18%.

III: *m/e* 168, (M^+). NMR (δ in $CDCl_3$): 1.81 dd (CH_3, $J(CH_3—H_b)$ 6.5 Hz, $J(CH_3—H_a)$ 1.5 Hz); 5.98 dq (H_b, $J(H_b—H_a)$ 14 Hz); 6.96 m (H_a).

IX: *m/e* 438, (M^+). IR: 2040, 1985, 1975 cm^{-1} (ν(Fe—CO)); 1595 cm^{-1} (endocyclic C=C). NMR (δ, in $CDCl_3$): 1.90 d (CH_3, $J(CH_3—H_b)$ 5.41); 1.26 m (H_{1b}, H_{3b}, 1.48 m); $J(H_{1a}—H_{1b}) \approx J(H_{3a}—H_{3b})$ = 9.2 Hz); 1.92 m (H_2), 1.99 m (H_4), 6.15 m ($H_{1a}—H_{3a}$), 6.42 dd (H_5), 6.58 dd (H_6). Elemental analysis: Found: C, 49.51, H, 3.36. $C_{18}H_{14}Fe_2O_6$ calcd.: C, 49.31; H, 3.20%.

Acknowledgement

We thank the Research Corporation for financial support. The authors are also grateful to Dr. V. Feil and Mr. R. Zaylskie for help in obtaining mass spectral data.

References

1 B.J. Nicholson, J. Amer. Chem. Soc., 88 (1966) 5156.
2 T.A. Manuel, Inorg. Chem., 3 (1964) 1794.
3 H. Guenther, R. Wenzel and H. Klose, Chem. Commun., (1970) 605.
4 R.A. Bauer, E.O. Fischer and C.G. Kreiter, J. Organometal. Chem., 24 (1970) 737.
5 T.A. Manuel, S.L. Stafford and F.G.A. Stone, J. Amer. Chem. Soc., 83 (1961) 3597.
6 R. Victor, R. Ben-Shoshan and S. Sarel, Tetrahedron Lett., (1970) 1680.

7 R. Victor, R. Ben-Shoshan and S. Sarel, Tetrahedron Lett., (1970) 4257.
8 R. Victor, R. Ben-Shoshan and S. Sarel, J. Org. Chem., 37 (1972) 1930.
9 R.E. Davis and R. Pettit, J. Amer. Chem. Soc., 92 (1970) 716.
10 E. Koerner von Gustorf, M.C. Henry and C. DiPietro, Z. Naturforsch. B, 21 (1966) 42.
11 J.E. Blackborow, E.R. Eady, E.A. Koerner von Gustorf, A. Scrivanti and O. Wolfbeis, J. Organometal. Chem., 111 (1976) C3.
12 R. Pettit and G.R. Emerson, Advan. Organometal. Chem., 1 (1964) 1.