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VINYLCYCLOHEXATRIENE-TYPE DIENE-IRON COMPLEXES FROM STYRENES. A NOVEL PHOTOCHEMICAL REACTION

Rae Victor, R. Ben-Shoshan and S. Sarel

Department of Pharmaceutical Chemistry, The Hebrew University School of Pharmacy, Jerusalem, Israel

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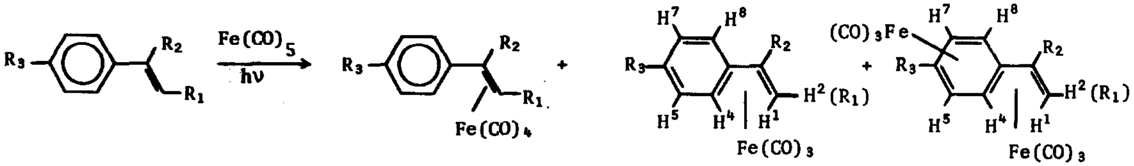
This communication is prompted following recent publications concerning bond-fixation in diene-iron carbonyl π-complexes derived from aromatic systems[1,2].

Experience shows that the aromatic double bonds in benzene derivatives exhibit little or no tendency to form diene-iron carbonyl complexes. This tendency is remarkably enhanced in the cases of divinylbenzenes[3] and isomeric vinylnaphthalenes[4]. Introduction of vinyl groups onto benzene affords a more reactive center for initial metal complexation. The metal, then, is in an advantageous position to draw electrons from the benzene system for further coordination. Clearly, the loss of benzene resonance is a prerequisite for the formation of diene-iron carbonyl-type complexes[1].

We wish to report the photochemical preparation of two novel types of iron carbonyl complexes, III and IV, in addition to tetracarbonyliron complex (II)[5], from irradiation of styrenes (I) with pentacarbonyliron. The first series (III) represents an iron tricarbonyl complex of substituted styrenes, involving two aromatic π-electrons attached to iron tricarbonyl. The second series (IV) constitutes bis-(iron tricarbonyl) complexes derived from the former series, whereby the remaining four π-electrons in III react further with iron carbonyl to form a second diene-type iron tricarbonyl complex. Complexes of series III represent the first known examples of an iron tricarbonyl complex of the eight π-electron system of styrene, whereas IV represents the only known examples of iron carbonyl complexes, prepared from benzene derivatives, in which all six aromatic π-electrons are involved in coordination to iron.

Irradiation of equimolar quantities of styrene derivative (I) and pentacarbonyliron at room temperature results in rapid formation (within 5 min.) of the mono-iron complexes of the II and III series, while the formation of the bis-iron complexes (IV) could be monitored, by infrared spectroscopy, after a period of 30-45 min. Whereas the concentration of the iron tetracarbonyl complexes (II) becomes fairly steady within a short reaction time, those of III and IV do not cease to increase until irradiation is stopped (2-3 hours). Reaction of organic substrate (Ih) with $Fe_2(CO)_9$ in the absence of uv light gives only the tetracarbonyliron complex (IIh) and $Fe(CO)_5$, suggesting that both III and IV result from photochemical processes.



I II III IV

Ia-IVa, $R_1=R_2=R_3=H$; Ib-IVb, $R_1=CH_3$; $R_2=R_3=H$; Ic-IVc, $R_1=C_6H_5$; $R_2=R_3=H$;

Id-IVd, $R_1=R_3=H$; $R_2=CH_3$; Ie-IVe, $R_1=R_3=H$; $R_2=p\text{-}CH_3OC_6H_4$; If-IVf, $R_1=R_3=H$; $R_2=C_6H_5$;

Ig-IVg, $R_1=H$; $R_2=R_3=CH_3$; Ih-IVh, $R_1=H$; $R_2=CH_3$; $R_3=Cl$; Ii-IVi, $R_1=H$; $R_2=CH_3$; $R_3=OCH_3$;

Ij-IVj, $R_1=H$; R_2=cyclopropyl; $R_3=OCH_3$

Evidence for the nature of complexes II, III and IV is given below.

II: Air-sensitive yellow complexes obtained in mixture with unconsumed organic substrate (I); ir (hexane): 2080, 2015, 2005, 1985 cm^{-1} (± 5 cm^{-1}) (C=O)[6]; mass spectrum (IIa): parent ion (m/e=272) with fragmentation in stepwise fashion of four CO units.

III: Air-sensitive red to violet complexes, generally decomposing on workup. Of these, only IIId (dec. p. 53°) and IIIh (dec. p. 80°) have been successfully isolated. Infra-red spectra: General metal carbonyl absorption (IIIa-IIIi), 2044, 1980, 1968 (± 5 cm^{-1}), and uncoordinated double bond absorptions at 751 (IIId) and 803 cm^{-1} (IIIh). The latter exhibit parent molecular-ion peaks and peaks corresponding to stepwise losses of three CO units in the mass spectra.

The main features of nmr spectra of III, as shown for the case of IIIh in the Table, are: a) the spreading of the original aromatic signal from the styrene substrate I, suggesting the destruction of aromaticity in the ligand; b) the appearance of high field signals attributed to protons now part of a coordinated diene system[7].

TABLE

		H^1	H^2	H^3	H^4	H^5	H^6	H^7	H^8
IIIh	τ	9.84	8.21	-	7.27	[$H_{5,7,8}$: 3.07 (2H), 2.36 (1H)]			
	Hz	$J_{1,2}$ 2.6			$J_{4,5}$ 5.7			$J_{7,8}$ 8.7	
IVh	τ	9.87	8.44	-	8.26	6.33	-	3.36	6.53
	Hz	$J_{1,2}$ 2.4		$J_{4,5}$ 5.3;	$J_{4,8}$ 1.5;	$J_{5,7}$ 2.1;		$J_{7,8}$ 6.5	

IV: Air-stable orange to red crystalline complexes; dec. p.: IVa, 121°; IVb, 116°; IVc, 134°; IVd, 131°; IVe, 125°[8]; IVf, 115°; IVg, 119°; IVh, 120°; IVi, 136°; IVj, 102°[9]. General properties: ir (hexane): (R_3 not Cl) 2055, 2040, 1990, 1980, 1967 (± 5 cm^{-1}); (R_3=Cl) 2060, 2044, 2000, 1990, 1983, 1972 (± 5 cm^{-1}) (C=O). There is no ir absorption due to C-C unsaturation except for those complexes with two aromatic substituents originally (Ic, Ie, If), one of which remains uncomplexed in IV. The mass spectra are characterized by successive losses of 6 CO units and 2 iron atoms from the appropriate parent ion.

Nmr: taken for all complexes IVa-j; example IVh is presented in the Table. Spectra show generally: a) a high field shift of the original aromatic protons in comparison to their values in III with qualitative separation of these chemical shifts resembling "central" and "terminal" protons of diene-iron tricarbonyl systems and b) similarity of chemical shift values and coupling constants of the high field protons in the external complex to those of complexes III and related compounds. Due to the external complex, ring proton resonances are comparatively lower than those of simple cyclic diene-tricarbonyl iron systems, though spin-spin interactions are of similar magnitude[10]. The evidence now at hand does not permit assignment of the positional orientations of the two iron atoms[11].

The chemical and spectroscopic data presented here clearly indicate that the aromaticity of the benzene ring is completely destroyed as a result of coordination to the metal, implying extensive bond-fixation of the original benzene ring, which can consequently be viewed as a cyclohexatriene ligand.

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5. Styrene tetracarbonyliron (IIa) has previously been described by E. Koerner von Gustorf, M.C. Henry and C. DiPietro, *Z. Naturforschg.*, **21b**, 42 (1966).
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7. Chemical shifts of protons H^1, H^2 and H^4 are in full agreement with the values of the corresponding protons in both 1-vinylnaphthalenetricarbonyliron (V)[4], [τ : 9,70 (H^1); 8.13 (H^2); 7.39 (H^4)] and *m*-divinylbenzene bis-(tricarbonyliron) (VI), determined by us, [τ: 9.61 and 9.77 (H^1); 8.18 and 8.29 (H^2); 7.88 and 7.48 (H^4)]. Furthermore, chemical shifts of the vinylic protons (H^5-H^8), which are lowered from values of simple monoenes or dienes, are consistent with the values of related protons in V, VI and other similar systems [See: S.R. Roth and J.D. Meier, *Tetrahedron Letters*, 2053 (1967) and G.F. Emerson, L. Watts, and R. Pettit, *J.Am.Chem.Soc.*, **87**, 131 (1965)].
8. The isomer complexed at *p*-methoxyphenyl was not isolated from starting material.
9. Complex IVj is described in the preceding paper.
10. Compare with cyclohexadienetricarbonyliron: "terminal" protons at τ 6.86, "central" protons at τ 4.78; $J_{\text{H terminal-H central}} = 6.6$ Hz ; see, R. Burton, L. Pratt and G. Wilkinson, *J.Chem.Soc.*, 594 (1961).
11. X-ray studies[1] show that for the case of *m*- and *p*-divinylbenzene bis-(tricarbonyliron), the two iron atoms assume a *trans*-relationship with respect to ligand plane.