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Preliminary communication

NEW TRICARBONYL(AMIDO-SUBSTITUTED-1,3-DIENE)IRON COMPLEXES

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Summary

X-substituded benzamides (X = H; 2-OH; 4-MeO; 3-MeO; 3,5-$(MeO)_2$; 4-Cl and 2,4-Cl_2) have been shown to add reversibly to the dienyl rings of the organometallic compounds $[(dienyl)Fe(CO)_3]BF_4$ (dienyl = C_6H_7, 2-$MeOC_6H_6$ or C_7H_9) to give the corresponding cationic tricarbonyl(substituted-diene)iron complexes.

The addition of a wide range of nucleophiles to coordinated π-hydrocarbons of the type $[(\pi\text{-hydrocarbon})M(CO)_3]^+$ have been reported to give various products depending on the nature of the metal, the π-hydrocarbon moiety, the attacking nucleophile, and of course, the reaction conditions. For example, the attack of nucleophiles such as pyridines [1], anilines [2, 3], phosphines [4, 5], and activated arenes [6—8] and aryltrimethyl-silanes and -stannanes [9, 10] on the complexes $[(dienyl)M(CO)_3]^+$ (dienyl = C_6H_7, 2-$MeOC_6H_6$ or C_7H_9; M = Fe, Ru or Os) occurs at the dienyl ring to give the corresponding 1,3-diene-substituted products. On the other hand, the attack of the iodide ion on these complexes occurs predominantly at the metal to give the carbonyl-displaced products [5, 11, 12]. Factors that govern nucleophilicity towards coordinated π-hydrocarbons are not well understood, very few kinetic studies having been carried out on such systems. The first detailed study aimed at providing a solution of this problem has only recently appeared [1].

We now wish to report that X-substituted benzamides (X = H; 2-OH; 4-MeO; 3-MeO; 3,5-$(MeO)_2$); 4-Cl and 2,4-Cl_2) add reversibly to the dienyl rings of the complexes $[(dienyl)Fe(CO)_3]BF_4$ (I, dienyl = C_6H_7, 2-$MeOC_6H_6$ or C_7H_9) to give new amido-substituted-1,3-diene products (II, eq. 1).

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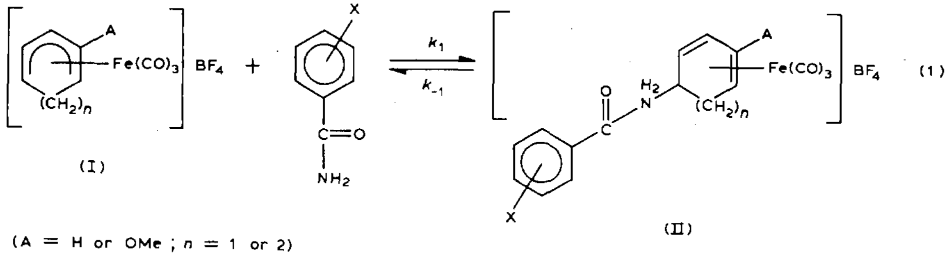


(A = H or OMe ; n = 1 or 2)

Except for II (X = 2-OH), the products II are sensitive to air in the solid state, gradually decomposing to unknown species. Solution of each of the products II in CH_3CN showed two strong IR ν(CO) bands at 2055 and 1980 cm^{-1}. In addition, the isolated stable purple solid II (X = 2-OH, A = H, n = 1) showed a strong, broad band at ca. 1060 cm^{-1} (Nujol mull) attributed to the presence of the BF_4^- anion. (Found for II (X = 2-OH, A = H, n = 1): C, 43.7; H, 3.01; N, 3.09. $C_{16}H_{14}NO_5FeBF_4$ calcd.: C, 43.4; H, 3.19; N, 3.16%). The two strong IR ν(CO) bands at 2055 and 1980 cm^{-1} found for compounds II as well as the broad band at ca. 1060 cm^{-1} (BF_4^-) are characteristic for cationic 1,3-diene-substituted iron complexes [1, 4, 7].

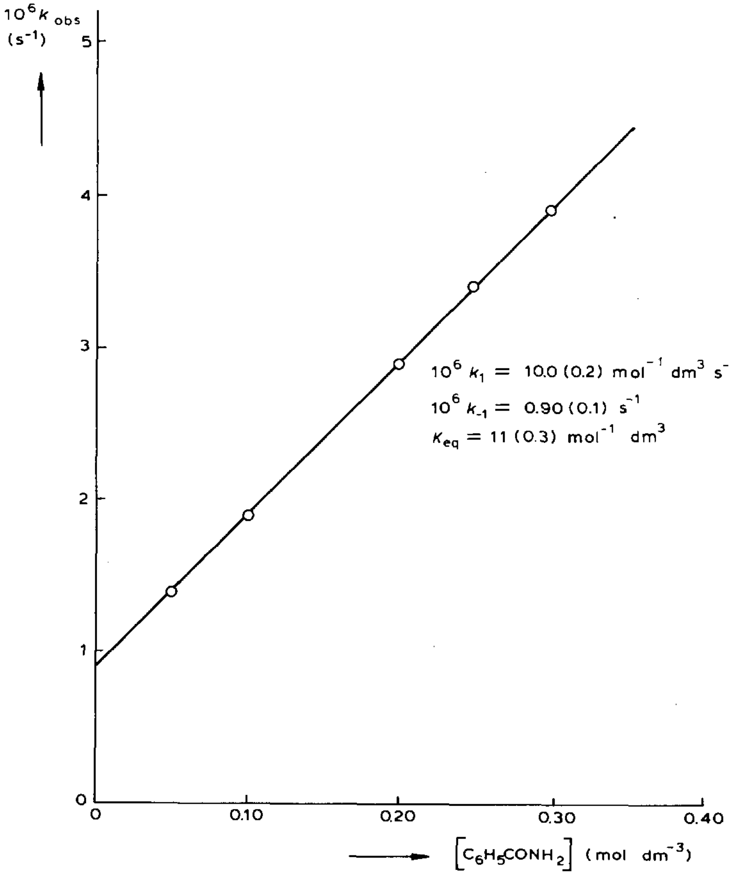
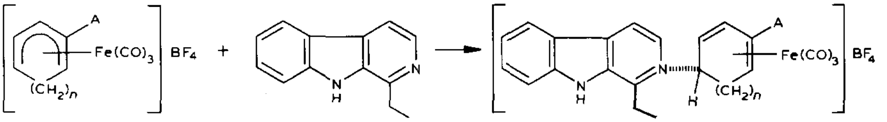


Fig. 1. Dependence of k_{obs} on [$C_6H_5CONH_2$] for the reaction of benzamide with [$Fe(CO)_3(1-5-\eta-C_6H_7)]^+$ in CH_3CN at 40°C.

A preliminary kinetic study of reactions 1 in CH_3CN indicate that they are equilibrium processes (e.g. Fig. 1). The large negative $\Delta S_1^{\ddagger}$ of -95 J mol^{-1} K^{-1} and the $\Delta H_1^{\ddagger}$ of 77 kJ mol^{-1} determined for the addition of benzamide to I ($n = 1$, A = H) in CH_3CN are consistent with an associative mechanism.

The synthetic utility of organometallic cations such as I has also been extended to β-carboline chemistry. Thus the reaction between 1-ethyl-β-carboline with cations I in CH_3NO_2 was found to proceed to completion within seconds of mixing to give the corresponding 1,3-diene-substituted products [13] (eq. 2). A solution of each of the products III in CH_3NO_2 showed two strong IR ν(CO) bands at 2055 and 1980 cm^{-1} as their analogous pyridine derivatives [1] indicating coordination of the pyridine-nitrogen of the 1-ethyl-β-carboline nucleophile to the 5-position of the dienyl rings as shown in equation 2.



(2)

(I)

(III)

(A = H or OMe ; n = 1 or 2)

The synthetic implications of reactions 1 and 2 cannot be overemphasized, particularly when it is borne in mind that careful treatment of a solution of each of the products II or III in benzene with appropriate oxidizing agents (e.g. Me_3NO [14,15]) leads to cleavage of the iron tricarbonyl unit to give new 1,3-diene-substituted organic derivatives which are otherwise inaccessible by conventional organic techniques.

We are currently carrying out detailed synthetic and mechanistic studies of reactions 1 and 2, including the cleavage of the $Fe(CO)_3$ unit.

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