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Preliminary communication

REDUCTION OF [(1—3-η-ALLYL)Fe(CO)$_2$NO] COMPLEXES WITH TRIALKYLPHOSPHINE

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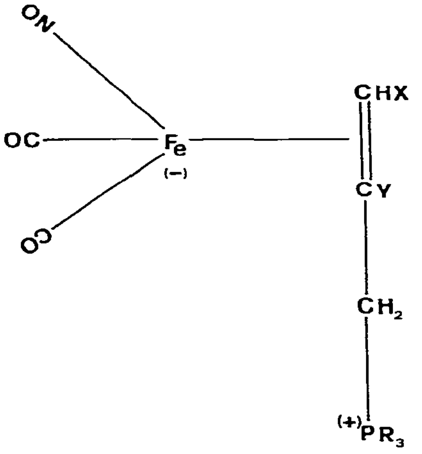
Summary

Intermediates involved in the reduction reaction of η-allyl complexes by very strong nucleophilic ligands have been isolated and characterized for the reaction of (1—3-η-allyl)dicarbonylnitrosyliron complexes with trialkylphosphine. They have dipolar ion character. Hydride ion reacts with the allyl ligand of the η-allyl complexes to form the same type of olefinic complex.

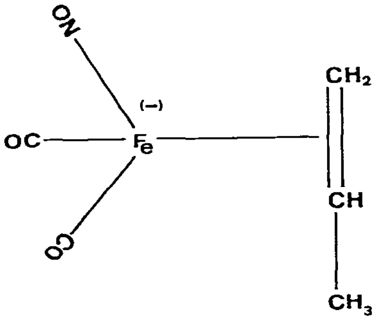
The reduction of [M(η-hydrocarbon)(CO)$_3$]$^+$ salts (M = Cr, Mo, W) [1] and of η-allyl non-ionic complexes [2] with phosphine ligands to give phosphonium adducts has been recently observed. The reaction mechanism [1] and the structure of the intermediates [2] of these reactions have also been discussed.

We describe below the preparation and characterization of intermediates having the previously proposed structure; these were obtained from the reactions of [(η-C$_3$H$_4$X)Fe(CO)$_2$NO] (I, X = H, 1-Cl, 2-Br) with very basic phosphine ligands (L = PMe$_3$, PEt$_3$, P(n-Bu)$_3$, P(cyclohexyl)$_3$). The addition of the ligands L to an ether or benzene solution of the complexes (I) results in immediate precipitation of red or yellow spongy solids, the elemental analyses of which correspond to the formula [(XH$_4$C$_3$PR$_3$)Fe(CO)$_2$NO] (II). The complexes II are decomposed by oxygen and, if dried, are pyrophoric; they are insoluble in almost all organic solvents; the most polar solvents (acetonitrile, acetone) slowly dissolve the complexes II and decompose them with formation of [Fe(CO)$_3$NO]$^-$ and allyltrialkylphosphonium ions. In tetrahydrofuran (THF) the complexes II dissolve to form the complexes I. The structure proposed for II is given in the diagram; it has a dipolar character, as indicated by IR (Table 1) and NMR spectra.

A comparison of the CO and NO stretching frequencies of II with those of [Fe(CO)$_3$NO]$^-$ and [Fe(CO)$_2$NOPPh$_3$]$^-$ ions indicates that a strong



(II)



(III)

TABLE 1

IR STRETCHING FREQUENCIES OF THE COMPLEXES (II)

X	Y	R	ν(CO) (cm^{-1})	ν(NO) (cm^{-1})	Other bands (cm^{-1})	Solvent
H	H	PR_3=H	1914, 1832	1653		CH_3CN
H	H	n-Bu	1921, 1838	1610		Nujol
H	H	C_6H_{11}	1930, 1853	1615	ν(C—H) 3082, 3000; ν(C=C) 1478	KBr
H	H	Et	1937, 1856	1630		CH_3CN
Cl	H	C_6H_{11}	1946, 1868	1627	ν(C—H) 3050, 3015; ν(C=C) 1495; ν(C-Cl) 730	KBr
H	Br	Me	1959, 1882	1639	ν(C=C) 1540	CD_3CN
H	Br	Et	1955, 1882	1645		CD_3CN

Stretching bands [4] of $[Fe(CO)_3NO]^-$ in CH_3CN: ν(CO) 1985, 1882 cm^{-1}; ν(NO) 1648 cm^{-1}
Stretching bands [3] of $[Fe(CO)_2NOPPh_3]^-$ in CH_3CN: ν(CO) 1892, 1816 cm^{-1}; ν(NO) 1598 cm^{-1}.

negative charge is localized on the iron atom; it increases with the steric hindrance by the trialkylphosphine and decreases with increasing the inductive withdrawing power of the substituent in the allyl group. The band of medium intensity in the range 1470—1550 cm^{-1}, assigned to the stretching of the C=C bond coordinated to the iron atom [5] is in accord with the proposed structure. The NMR spectra of II in CD_3CN show a phosphonium structure with localization of a positive charge on the phosphorus atom. The effect of THF on the stability of the complexes II, indicates that their formation is a reversible reaction.

The reactivity of II is similar to that observed for the intermediate observed during the chemical and electrochemical reduction of I [4], which was formulated as $[Fe(CO)_2NO]^-$. In the light of the present results this intermediate can be formulated as $[(\eta\text{-}CH_2{=}CHCH_3)Fe(CO)_2NO]^-$ (III), formed by the same mechanism as II, by addition of H^- to a terminal carbon of the allylic ligand in the complex I. This last mechanism is the same as that observed in the protonation of butadieneiron tricarbonyl complex and of its derivatives [6]; this indicates that in the organometallic carbonyl derivatives of iron either the reduction or the oxidation is localized in the organic moiety, which can act as an acid or a base.

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