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REACTIONS OF π-ALLYLTRICARBONYLHALOGENOIRON COMPLEXES AND SYNTHESIS OF NEW ORGANOIRON COMPOUNDS*

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The reactions of $[\pi\text{-}C_3H_5Fe(CO)_3\ X]$ (where, X = Cl, (1); X = Br, (2); X = I, (3)) with different chemical species are described. Thus, the reaction of (2) or (3) with $Ag[ClO_4]$ in CH_2Cl_2 yielded the perchlorate-bonded complex $[Fe(CO)_3(\pi\text{-}C_3H_5)(OClO_3)]$, (4). Complex (4) is a suitable precursor for the synthesis of the cationic complexes $[Fe(CO)_3(\pi C_3H_5)\ L][ClO_4]$ (where L = PPh_3, (6); L = $AsPh_3$, (7); L = C_5H_5N, (8)). The complex (6) reacts with univalent bidentate ligands to give the neutral complexes $[Fe(CO)_2(\sigma\text{-}C_3H_5)(PPh_3)L']$ (where L' = acetylacetonate, (9); L' = N-Phenylsalicylaldiminate, (10)); L' = 8-hydroxyquinolinate, (11); Complete de-carbonylation (10) has also been achieved to yield $[Fe(\pi\text{-}C_3H_5)(PPh_3)_2\ L']$, (12), which on protonation yielded a cationic olefinic complex [(olefin) $Fe(PPh_3)_2\ L'][BF_4]$, (13). The complex (2) or (3) reacts with Ph_2C = NLi in Et_2O to yield $[Fe(CO)_3(\pi\text{-}C_3H_5)(N = CPh_2)]$, (14), while the reaction of (1) with PhC(=S) N (Me) Li in THF yielded a novel σ-allylironcarbonyl compound (15). Ethynylmagnesium bromide, HC ≡ CMgBr reacts with (3) in THF to give π-allyltricarbonyl ethynyl complex, (16), which undergoes a dipolar cycloaddition reaction with PhC≡ N–O in Et_2O yielding a novel organoiron complex, [(μ–CO) *bis* {*bis*(σ–allyltricarbonyliron) (3-phenylisoxazole}], (17). Depending on conditions of the reactions and the value of n, the complex (2) reacts with $Ph_2P(CH_2)_n$ MgCl to yield new organoiron compounds. The reactions of $(\pi\text{-}C_3H_5)(CO)_3$ FeNa with $ClCH_2CH_2NMe_2$, $ClCH_2CH_2SCH_3$ and $ClCH_2CH_3SPh$ have also been described.

Data on elemental analyses, molar conductances, molecular weights, I. R. and ^1H NMR spectra have been used to assign structures.

Key Words : π-Allyltricarbonyliron Halides; Organoiron, Dipolar Cycloaddition

INTRODUCTION

THE allyl group $\bar{C}H_2—CH=CH_2$ can bond to metals in a σ (or η^1) fashion, or it can behave as a four-electron π-donor ligand with η^3 coordination. The VB representation indicates a delocalized π-system:

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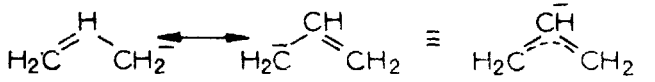
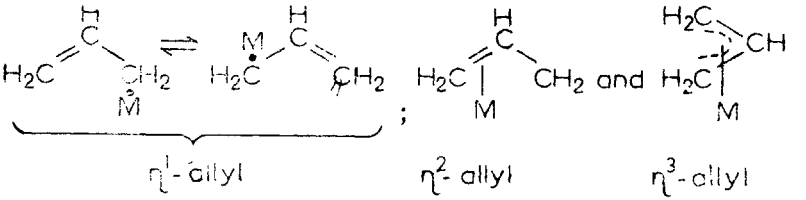
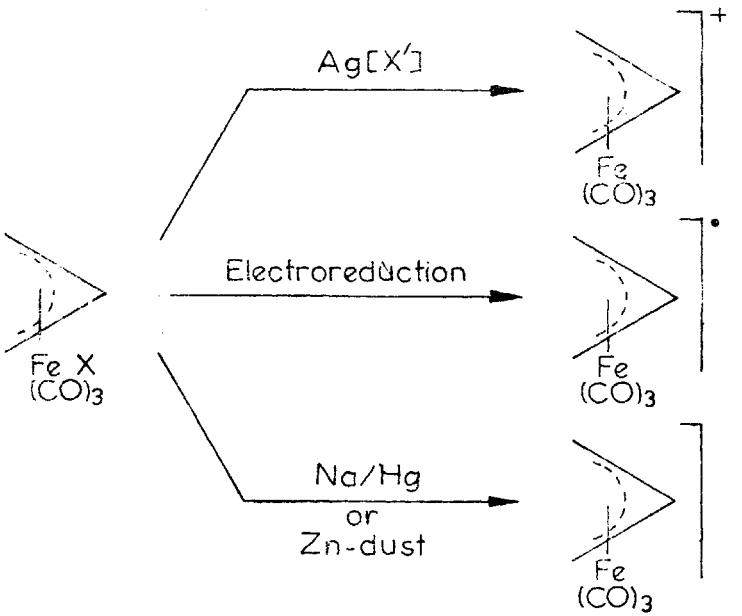


Besides, allyl group can also form bond with metal as an olefin, and thus behaving as a two-electron donor. The different modes of bonding may thus be represented as follows:



These possibilities are responsible for widespread use of allylorganometallics in many commercially useful catalytic reactions,[1] and in this sense the study of the reactivity of the π- and σ-allyltransition metal complexes is very significant. In many such reactions formation of cationic allylmetal complexes as intermediates have been proposed. As not much work is available on the synthesis and reactivity of cationic allyliron carbonyl complexes,[2,3] we have decided to synthesize and study the reactivity of such cationic and related iron complexes. In the present paper we describe the reactions of $[Fe(CO)_3(\pi\text{-}C_3H_5)X]$[4–7] [where X = Cl, (1); X = Br, (2); X = I, (3)] leading to the successful isolation of cationic and neutral π- and



Scheme I

σ-allyliron carbonyl complexes. The synthetic potential of these reactions is yet to be fully developed. One can very easily generate the following reactive species (Scheme I) from the $Fe(CO)_3$ $(\pi\text{-}C_3H_5)X$ complexes and the potential of these species as synthetic intermediates has never been exploited. In fact, iron allyl complexes have been neglected throughout the development of this fascinating field of allyltransition metal complexes.

Results and Discussion

Preparation of Complexes

The reaction [equation (i)] of (2) and (3) with $Ag[ClO_4]$ (mol ratio 1 : 1.2) in CH_2Cl_2, subsequent removal of the precipitated AgBr or AgI, and vacuum concentration of the filtrate yields $[Fe(CO)_3(\pi\text{-}C_3H_5)(OClO_3)]$, (4) as a yellow-brown powder. The complex is stable under nitrogen, but is unstable in air and moisture, and sensitive to light.

$$[Fe(CO)_3(\pi\text{-}C_3H_5)X] \underset{(2)\ \text{or}\ (3)}{} + Ag[ClO_4] \xrightarrow{CH_2Cl_2N_2} [Fe(CO)_3(\pi\text{-}C_3H_5)(OClO_3)] + AgX \quad \underset{(4)}{} \quad \ldots(i)$$

The same reaction, when carried out in acetone, produced the stoichiometric amount of silver salt [equation (ii)] and a conducting brown solution, from which no pure solid complex (5) could be isolated. However, addition of donor ligand [equation (iii)] yields the brown-red crystalline complexes $[Fe(CO)_3(\pi\text{-}C_3H_5)L]$ [L = PPh_3, (6); L = $AsPh_3$, (7); L = py (pyridine), (8)]

$$[Fe(CO)_3(\pi\text{-}C_3H_5)X] + Ag[ClO_4] \xrightarrow{Me_2CO} [Fe(CO)_3(\pi\text{-}C_3H_5)(OCMe_2)][ClO_4] + AgX \quad \underset{(5)}{} \quad \ldots(ii)$$

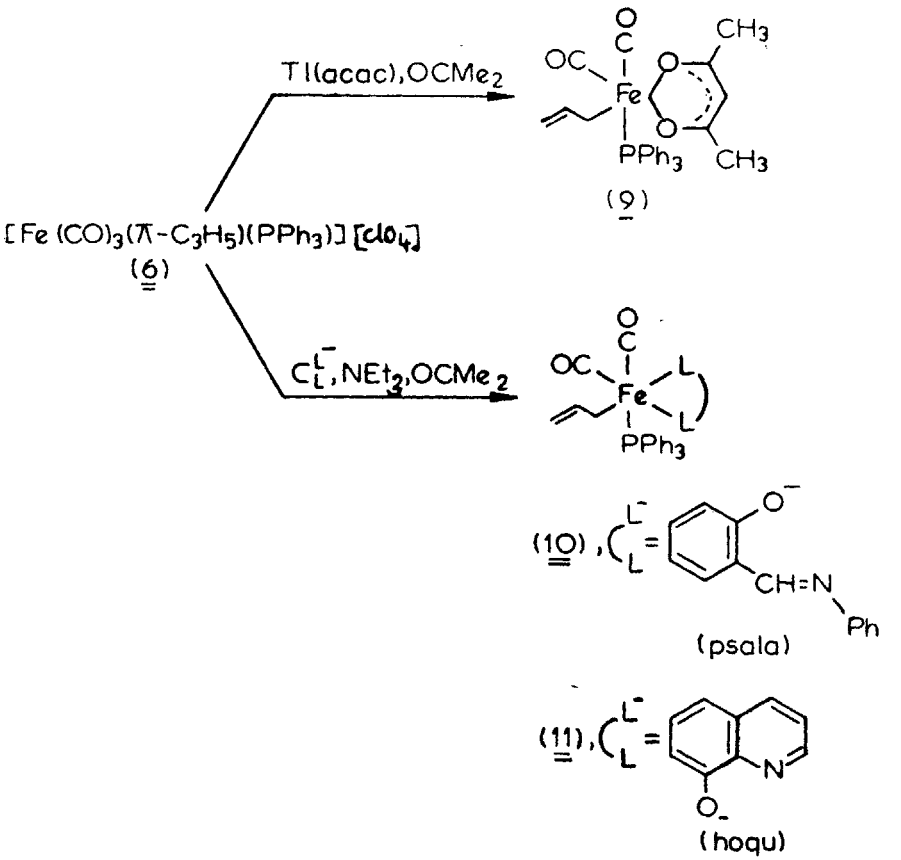
$$(5) + L \xrightarrow{Me_2CO} [Fe(CO)_3(\pi\text{-}C_3H_5)L][ClO_4] \quad \underset{(6)\ -\ (8)}{} \quad \ldots(iii)$$

The reaction of (4) with stoichiometric amounts of a ligand L in acetone also leads, according to equation (IV) (L = PPh, $AsPh_3$, or NC_5H_5), to the corresponding cationic π–allyl iron carbonyl complexes (6) – (8).

$$(4) + L \xrightarrow{MeCO} [Fe(CO)_3(\pi\text{-}C_3A_5)L][ClO_4] \quad \underset{(6)\ -\ (8)}{} \quad \ldots(iv)$$

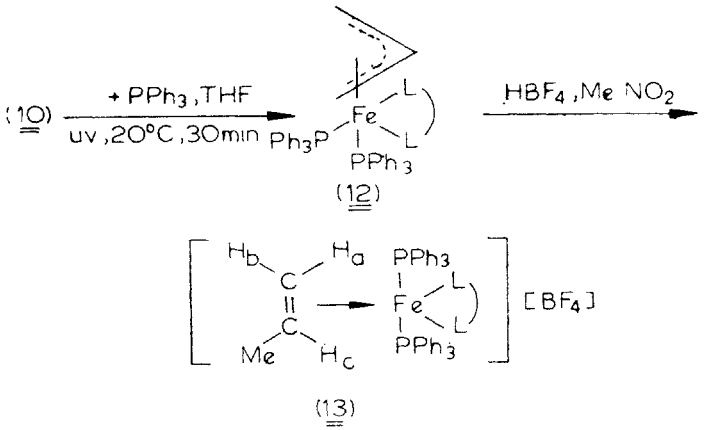
The complexes, in most cases, were isolated by concentration and cooling. The complexes are fairly stable in air and in solutions of organic solvents.

A solution of (6) is, nevertheless, a useful precursor for the synthesis of neutral σ- allyl iron complexes, (9)–(11), Scheme II (acac = acetylacetonate), which are isolated as low-melting (decomposed) powders having colours varying from yellow to brown. These complexes are not stable to air and water, but are quite stable under nitrogen, both in the solid state and in solution.



Scheme II

A tetrahydrofuran (THF) solution of complex (10), mixed with equimolar quantities of PPh_3 and then subjected to u.v. irradiation at room temperature for 30min., led to the isolation of a neutral complex (12) which, on treatment with HBF_4 in $MeNO_2$ yielded a cationic olefinic complex (13), Scheme II. In protonation of (12) we are not sure at this stage whether the η^3- allyl ligand in (12) is changed to a σ-allyl type, with the proton attacking the hydrocarbon directly, or whether it is first bonded to the metal (or whether the π-allyl ligand itself is attacked by the proton directly).

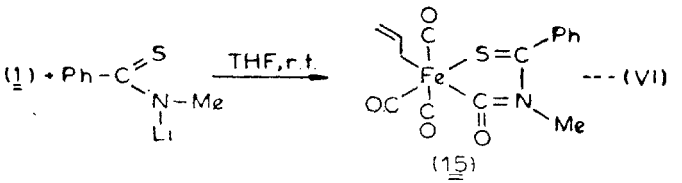


Scheme III

The reaction [equation(V)] or (2) or (3) with $Ph_2C = NLi$ (mol ratio 1 : 1) in Et_2O, subsequent removal of the precipitated Li*X*, and vacuum concentration of the filtrate yielded brown $[Fe(CO)_3 (\pi\text{-}C_3H_5) (N = CPh_2)]$, (14). The complex is stable under inert atmosphere, but unstable in air and sensitive to light. Irradiation with u.v. light gave an unidentified deep red powder.

$$(2) \text{ or } (3) + Ph_2C = NLi \xrightarrow{Et_2O,\ 0\ ^\circ C} \underset{(14)}{[Fe(CO)_3 (\pi\text{-}C_3H_5) (N = CPh_2)]} \quad \ldots(v)$$

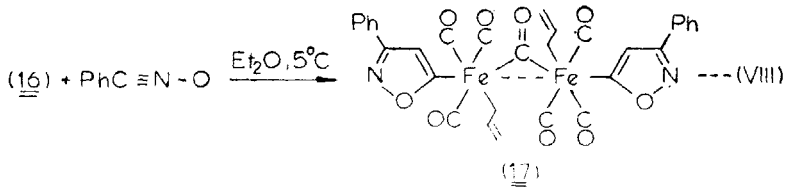
The reaction of (1) with the stoichiometric amounts of lithio-*N*-methylthiobenzamide in THF leads, according to [equation (vi)], to the novel σ-allyl complex, (15) in about 52 per cent yield.



The complex (15) is also stable only under inert atmosphere and sensitive to light. Treatment of the solution of (3) with ethynyl magnesium bromide in THF at about —10 °C yielded the π-allyltricarbonyl ethynyliron(II) complex, (16) equation (*vii*)] :

$$(3) + HC{\equiv}CMgBr \xrightarrow{THF,\ -10\ ^\circ C} \underset{(16)}{[Fe(CO)_3 (\pi\text{-}C_3H_5) (C{\equiv}CH)]} \quad \ldots(vii)$$

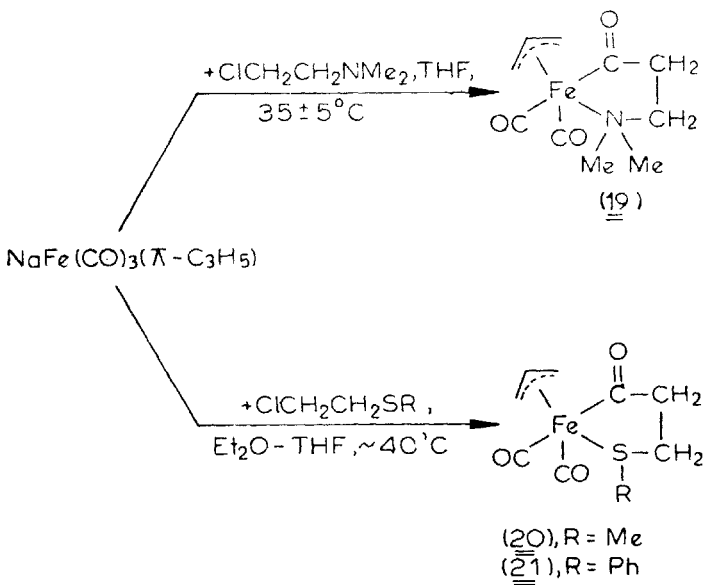
The complex (16) was found to be a good 1,3-dipolarophile, and its reaction with benzonitrile oxide in Et_2O at 5 °C proceeded to give 5(σ-allyltricarbonyliron) 3-phenylisoxazole, in the form of a carbonyl bridged dimer, (17), possibly with linkage between two iron centres, as shown in [equation (viii)] :



(17)

In the absence of X-ray crystal structure analytical data, the present structural proposition for the complex (17) may be considered as tentative.

One of the most versatile reagent for organic carbonylation is disodium tetracarbonylferrate, $Na_2Fe(CO)_4$, and many carbonylation reactions along with their potential in organic syntheses have been well documented in literature.[8] We have, therefore, decided to synthesise $NaFe(CO)_3(\pi\text{-}C_3H_5)$, (18) from $[Fe(CO)_3(\pi\text{-}C_3H_5)X]$ and to investigate its potential in synthetic chemistry. In fact, we have synthesized (18) from (2) or (3) and Na/Hg in THF. The preliminary results suggest that (18) can be induced to react with $ClCH_2CH_2NMe_2$, $ClCH_2CH_2SMe$, and $ClCH_2CH_2SPH$ to yield π-allyl complexes (19)–(21) as shown in Scheme IV.



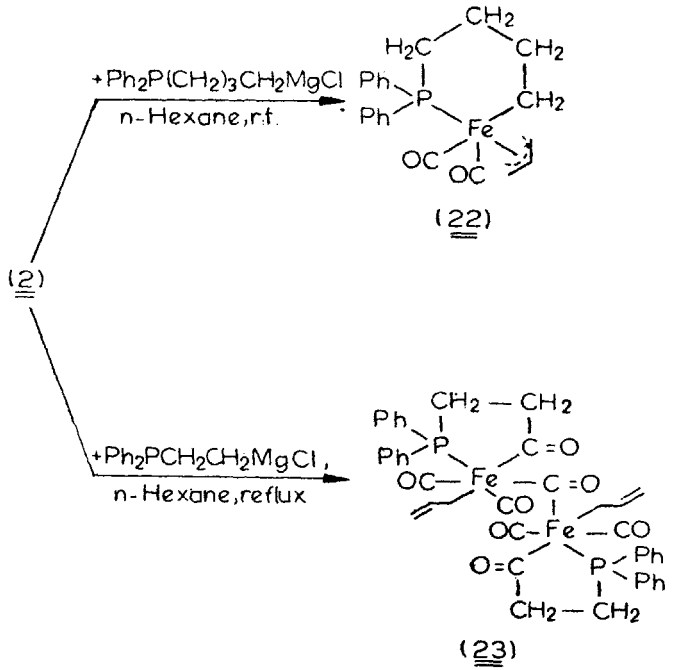
(19)

(20), R = Me
(21), R = Ph

Scheme IV

However, the reaction of (18) with alkyl/aryl halides led us to isolate products of indefinite compositions. We believe that photochemical reaction path might produce some significant results.

Interesting results were obtained when the complex (2) was allowed to react with the Grignard Reagents of ω-chloro-1-(diphenylphosphino) alkanes.[9,10] The nature of the products, to some extent, depended on the alkanes used and the reaction conditions employed (Scheme V) :



Seheme V

Nevertheless, further investigation (*X*-ray analysis) is necessary to ascertain the structure of the complexes (22) and (23), which at the moment based on elemental analyses, infrared and ^{1}H and ^{31}P NMR spectroscopic data.

Characterization of Complexes

All the complexes are coloured, stable in inert atmosphere, unstable in air and soluble in suitable organic solvents and the solutions are stable, Complexes (4) to (8) and (13) are conducting in acetone (or nitromethane) (Table I). The conductivity (Λ108-110 S cm^2 mol^{-1} in acetone, 73-80 δ cm^{2}mol^{-1} in nitromethane) are within the range expected for 1 : 1 electrolytes.[11] Most of the other complexes are non-conducting in nitromethane. Molecular weights are also in agreement with these formulae.

TABLE I

Elemental analyses and physical data for some organoiron complexes

Complex**	Colour	M.P. 0°C	Analysis (%)* C	H	N	Fe	Λ/S cm^2mol^{-1}
1	2	3	4	5	6	7	8
(4) $[Fe(CO)_3(\pi\text{-}C_3H_5)(OClO_3)]$	Yellow brown	98–99 (dec.)	25.9 (25.7)	1.5 (1.8)		20.2 (19.9)	108 (Me_2CO) 73 ($MeNO_2$)
(6) $[Fe(CO)_3(\pi\text{-}C_3H_5)(PPh_3)][ClO_4]$	Red brown	258–260 (dec.)	53.7 (53.1)	3.8 (3.7)	—	10.3 (10.3)	110 (Me_2CO) 78 ($MeNO_2$)
(7) $[Fe(CO)_3(\pi\text{-}C_3H_5)(AsPh_3)][ClO_4]$	Brown	223–228 (dec.)	49.5 (49.1)	3.6 (3.4)	—	9.6 (9.5)	80 ($MeNO_2$)
(8) $[Fe(CO)_3(\pi\text{-}C_3H_5)(py)][ClO_4]$[a]	Maroon	225–226 (dec.)	36.0 (36.8)	3.0 (2.8)	4.0 (3.9)	15.3 (15.5)	76 ($MeNO_2$)
(9) $[Fe(CO)_2(\sigma\text{-}C_3H_5)(PPh_3)(acac)]$[b]	Yellow	197–199 (dec.)	66.0 (65.9)	5.4 (5.2)	—	10.9 (10.7)	—
(10) $[Fe(CO)_2(\sigma\text{-}C_3H_5)(PPh_3)(psala)]$[c]	Red brown	200–202 (dec.)	70.4 (70.9)	5.0 (4.9)	2.8 (2.4)	9.6 (9.2)	—
(11) $[Fe(CO)_2(\sigma\text{-}C_3H_5)(PPh_3)(hoqu)]$[d]	Brown	212–214 (dec.)	70.0 (68.9)	5.1 (4.9)	2.8 (2.6)	10.8 (10.0)	—
(12) $[Fe(\pi\text{-}C_3H_5)(PPh_3)_2(psala)]$[c]	Red yellow	198–202 (de.c)	76.5 (76.4)	5.5 (5.5)	1.8 (1.7)	7.0 (6.8)	—
(13) $[Fe(CH_2{=}CHCH_3)(PPh_3)_2(psala)][BF_4]$[c]	Yellow brown	195–198 (dec.)	69.0 (68.9)	5.2 (5.1)	1.7 (1.5)	6.3 (6.1)	80.4 ($MeNO_2$)
(14) $[Fe(CO)_3(\pi\text{-}C_3H_5)(N{=}CPh_2)]$	Brown	63–65 (dec.)	63.6 (63.2)	4.7 (4.1)	4.0 (3.9)	15.4 (15.5)	—

(Continued)

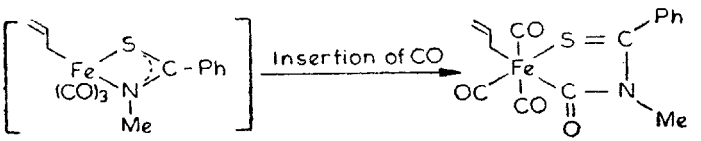
TABLE I (*Continued*)

1	2	3	4	5	6	7	8
(15) [Fe(CO)$_3$ (σ-C$_3$H$_5$) {SC(Ph) *N*(Me) CO}]	Orange red	88–91 (dec.)	49.3 (48.4)	4.0 (3.7)	4.2 (4.0)	16.6 (16.1)	—
(16) [Fe(CO)$_3$ (π-C$_3$H$_5$) ($\equiv$ CH)]	Red	—	47.0 (46.6)	2.8 (2.9)	—	27.3 (27.2)	—
(17) [{Fe(CO)$_2$ (σ-C$_3$H$_5$) (*L'*)}$_2$ μ–CO][e]	Light brown	110–112 (dec.)	55.0 (54.9)	3.7 (3.2)	4.9 (4.1)	16.8 (16.5)	—
(18) [Fe(CO)$_2$ (π-C$_3$H$_5$) {(Me$_2$) CH$_2$CH$_2$CO}]	Orange red	79–82 (dec.)	47.0 (47.5)	6.2 (5.9)	5.6 (5.5)	22.8 (22.1)	
(22) [Fe(CO)$_2$ (π-C$_3$H$_5$) {P(Ph$_2$) (CH$_2$)$_3$ CH$_2$}]$_2$	Brown	—	63.2 (63.8)	5.9 (5.8)	—	14.2 (14.7)	
(23) [{Fe(CO)$_2$ (σ-C$_3$H$_5$) {P(Ph$_2$) (CH$_2$) CO}}$_2$ μ–CO]	Light brown	—	60.6 (60.1)	4.9 (4.6)	—	13.9 (13.7)	

*Calculated values are given in parentheses, (a) py = pyridine, (b) acac = acetylacetonate anion, (c) psala = N-phenylsalicylaldiminate anion, (d) hoqu = 8-hydroxyquinolinate anion, (e) *L'* = 3-phenylisoxazole, **Molecular weights are also in agreement with these formulae.

The complex (4) shows bands in its IR spectrum at 1145vs, 1020vs, 898m, 630m, and 620br(sh) cm^{-1} which are characteristic of a metal bonded perchlorate group (C_{3v} symmetry). However, compounds (6)–(8) exhibit two bands, one in the region 1085–1100vs, br cm^{-1} and another around 625–630m cm^{-1} assignable to the $[ClO_4]^-$ anion (T_d symmetry). In some cases the assignment of the latter band is difficult, i.e. whenever the absorptions coincide either with those of the ligands or with $\nu_{(Fe\text{-}C)}$ stretching or $\delta_{(Fe\text{-}Co)}$ beinding modes.

In the IR spectra of the complexes (4), (6)-(8), (12), (14), (16) and (19)-(22) the expected π-allylic, C...C...C, bands are observed around 1510–1525cm^{-1}. The bands observed around 2018-2048vs, 2000–2010 S, and 1935-1948Scm^{-1} in the complexes (4) and (6)–(8) may be assigned to $\nu_{(C\equiv O)}$ absorptions.[12,13] However, the complexes (9)–(11) show $\nu_{(C\equiv O)}$ absorption bands in the region 2075–2080cm^{-1}. Two to three very strong bands were observed around 1930–2080cm^{-1}. In addition a medium intense band was observed around 1858cm^{-1} in the complex (17) supporting the presence of a bridging CO group. The same compound (17) also showed three infrared absorption bands around 1610, 1475 and 1385 cm^{-1}, supporting thereby the presence of substituted isoxazole moiety in the said complex.[14] The absorption 1610cm^{-1} appears as a very strong band with a shoulder at ~1600cm^{-1}. This shoulder may be considered as a ring $\nu_{(C=N)}$ absorption.[15] However, the presence of a σ-allylic group in this complex complicates this interpretation (see later discussion). The $\nu_{(C\equiv O)}$ for (16) also absorbs in $\nu_{(C\equiv O)}$ region. The complexes (15) and (19) show additional bands (for $\nu_{(C\equiv O)}$ around 1631cm^{-1} and 1625cm^{-1} respectively. These relatively low energy absorptions suggest the presence of a carbamoyl function in these complexes,[16–20] which is formed by the insertion of a CO group between Fe and N in the complex (15a), the possible intermediate species that might be formed in the synthesis of the complex (15) [see equation (iv) above]. The tricarbonyl nature of the complex is retained, the additional CO being derived from decomposed carbonyl complex. This may account for the low yield of complex (15). The low yield of the carbonyl-bridged dimeric complex (17) may be accounted for similarly. The nucleophilic attack of metal bound N to C of CO may give rise to the complex (15) with a five-membered ring.[21]



(15a) (15)

The presence of a σ-allylic group in the complexes (9)–(11), (15) and (17) is demonstrated by the appearance of IR bands for $\nu_{(C=C)}$ (allylic) in the region 1610–1600cm^{-1} region[22], while the presence of chelating acetylacetonate anion in complex (9) is demonstrated by the presence of two bands at *ca.* 1585 and 1510 cm-1[22]. The appearance of the bands $\nu_{(C=C)}$ (olefinic) *ca.* 1525 S, $\nu_{(CH_3)}$ *ca.* 1380m, and $\nu_{(=CH)}$ *ca.* 3012, 3085cm^{-1} for (13) suggests strongly the presence of an olefinic ligand in this complex[23] (Scheme 3). Two strong bands one at about 685cm^{-1} and another at about 500cm^{-1} (slightly broad) were observed in the complex (19) and may tentatively be assigned to Fe-N stretching mode, which might be coupled with the N-CH_3 stretching mode.[21,22,24] Other important chromophoric groups (e.g. C=S. C=N, C=O, etc.) present in the complexes under dicussion could easily be identified from the IR spectral bands.[24]

These structural features of the present iron complexes have also been substantiated by the ^{1}H nmr spectral data (Tables II, III)

TABLE II

Hydrogen-1 nmr data[a] *for* $[Fe(CO)_2(\sigma\text{-}C_3H_5)(PPh_3)(acac)]$, (9)*

Allyl[b]			acac[c]	
$-CH_2-$	$-CH=$	$=CH_2$	Me	$-CH=$
2.68 (dd)	5.88 (complex)	4.30 (complex)	1.55(s) 1.95(s)	5.30(s)
$J(CH_2\text{-}H) = 8$				
$J(P\text{-}H) = 4.5$				

(a) Chemical shifts (δ) in ppm, *J* in H_z; in $CDCl_3$, (b) Similar σ-allylic ligands were found to be present in complexes (10), (11), (15), (17) and (23).

(c) Phenyl and –CH = N–protons were observed at δ 6.7–7.3 and 8.62 ppm respectively.
*See Tables III and IV.

In the complexes (4), (6),–(8), (12), (16) and (19)–(22) the proton honded to C^2 appears as a complex band around δ 4-7–5.1 ppm. A pair of doublets (broad) centred at δ 2.7 and 1.8 PPm, which may be *syn* and *anti* protons bonded to C^1 and C^2, are also observed for these complexes. The spectrum cannot be further resolved at room temperature. However, the integration is approximately correct for these formulations. This supports the presence of a π-allyl ligand in these complexes.[22,25–28] The complex (16) shows an additional band at δ 3.25 (singlet) ppm showing the presence of acetylinic proton.

The synthesis, proton NMR spectral studies and X-ray crystal structure determination of σ-allyl-palladium (II) and–platinum (II) complexes have received much

TABLE III

Hydrogen-1 nmr data[a] for the σ- and π-allylic complexes[d]

Complex[c]	Ally protons[b]
(14) $Fe(CO)_3$ (π-C_3H_2) (N = CPh_2)	4.72 (m, 1H, CH), 2.80 (d, br, 2H, *syn*-CH_2), 1.90 (d, br, 2H, *anti* CH_2)
(15) [$Fe(CO)_3$ (σ-C_3H_5) {CON(Me) C(Ph) = S}]	2.80 (d, br, 2H, $-CH_2$), 6.00 (m, 1H, $-CH=$), 4.60 (m, 2H, $=CH_2$)
(16) [$Fe(CO)_3$ (π-C_3H_5) (C ≡ CH)]	4.85 (m, 1H, CH), 2.82 (d, br, 2H, *syn*-CH_2), 1–92 (d, br, 2H, *anti*-CH_2)
(17) [{$Fe(CO)_3$ (σ-C_3H_5) (L')}$_2$ (μ-CO]	2.68 (d, br, 2H, $-CH_2$), 5.98 (m, 1H, $-CH=$), 4.50 (m, 2H, $=CH_2$)
(18) [$Fe(CO)_2$ (π-C_5H_5) {N(Me_2) CH_2CH_2CO}]	5.10 (m, 1H, CH), 2.80 (d, br, 2H, *syn* $-CH_2$), 1.90 (d, br, $2H_2$ *anti* $-CH_2$)

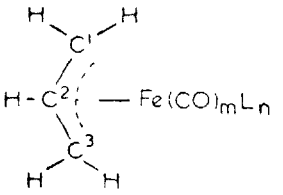
(a) Chemical shifts (δ) ppm in d_6-Acetone or $CDCL_3$ with TMS as internal reference

(b) σ-Allyl ligand for the comples (15) and (17); π-allyl ligand for the complexes (14), (16) and (18).

(c) L′ = 3-Phenylisoxazole.

(d) For (14) : 7.4–7.9 (m, 10H, Ph); (15) : 6.77–7.50 (m, 5H, Ph), 2.50 (s, 3H, N–CH_3); (16) : 3.25 (s, 1H, C ≡ CH); (17) : 7.5–7.8 (m, 5H, PH), 7.10 (br, 1H, isoxazole); (18) : 2.86 (br, 6H, N–Me_2); 2.23 ppm for NMe_2 in the free ligand.

attention in the last few years[28–33] in view of the role of these species as intermediates in the catalytic reactions of π-allyl metal complexes. Surprisingly, very few σ-allyl



(4) Where m = 3, $L_n = OClO_3$
(6) Where m = 3, $L_n = PPh_3$
(7) Where m = 3, $L_n = AsPh_3$
(8) Where m = 3 L_n = py
(14) Where m = 3, $L_n = N{=}CPh_2$
(16) Where m = 3, $L_n = C{\equiv}CH$
(19) Where m = 2, $L_n = (CO)CH_2CH_2NMe_2$

iron complexes are known[2,20] and in this sense the presence complexes (9)–(11), (15), (17) and (23) are significant, which represent some stable types of σ-allyiron complexes in solutions.[22,34,35] The chelated acetylacetonate, ligand (and other bidentate ligands) appear to be very strong by bound to iron so that the ^1H nmr spectra of the complexes (9)–(11) at room temperature can be satisfactorily interpreted in terms of rigid σ-allyliron bonding (Table III).

The elemental analyses, most aspects of the ^1H nmr spectrum in CD_3NO_2, and the IR spectrum (KBr pellet) support the formation of the olefinic complex (13) (Scheme III). In the ^1H nmr spectrum four complex bands are observed at δ 2.2, 3.7, 1.3 and 0.91 ppm, assignable to Ha, Hb, Hc and Me protons respectively [see Scheme III]. In the complex (15) the absorption of N-CH_3 and C_6H_5 protons appear as singlet and multiplets at δ 2.5 ppm and δ 6.77 ppm respectively. On the other hand, the presence of σ-allylic ligand is demonstrated by the appearance of bands[2] at δ 2.80 ppm (broad, doublets) for Fe-CH_2, at δ 4.60 ppm (complex) for $=CH_2$ and δ 6.00 ppm (complex) for –CH= species. Integrations of these bands are correct for these formulations. Similarly, the presence of the π-allyl ligand has been confirmed for the complex (19) as discussed above. Another interesting feature of the complex (19) is the high field shift of the N-Me absorption in the complex (N–Me, δ 2.80 ppm) when compared with the free ligand absorption (N-Me, δ 2.23 ppm), the reason for which may be ascribed to the donation of electrons from N to Fe.

The $\nu_{(C\equiv O)}$ absorption bands in the complexes (22) and (23) appeared around 2000-2058cm^{-1} (vs) and 1900-1980cm^{-1} (vs). Additional bands at 1850 cm^{-1} (s) and 1630cm^{-1} (s) also observed in the complex (23), which may be assigned to $\nu_{(C=O)}$ (bridging) and $\nu_{(C=O)}$ (carbamoyl) groups repectively as discussed earlier. The ^1H and ^{31}P $\{^1H\}$ nmr spectroscopic data also support these tentative structural propositions [see Scheme V], although *syn* and *anti*-proton absorption of the π-allyl ligand in the complex (22) are mixed-

up with $P(CH_2)_4$ proton absorption (Table IV), while–CH_2-proton absorption of σ-allyl ligand in the complex (23) is mixed-up with–CH_2CH_2-proton absorption (Table IV).

TABLE IV

Spectroscopic data for [*Fe(Co)₂ (π-C₃H₅) P(Ph₂) (CH₂)₂ CH₂*], (22)

and [{*Fe(CO)₂ (σ-C₃H₅) P(Ph₂) (CH₂)₂ CO*}₂ *μ–CO*], (23)

Complex		IR	¹H nmr				$^{31}P\{^1H\}$
(22)	$\nu_{(C\equiv O)}$	2058cm⁻¹ (vs) 1980cm⁻¹ (vs)	π-C_3H_5[a] 4.8–5.2 (br) 2.8 and 1.8	Fe–CH_2CH_2 1.02 (*t*)[3] J_{HH} = 7.2	$P(CH_2)_4$ 1.5–2.6 (m)	PPh_2 7.5–7.9 (m)	105.6 (s)
(23)	$\nu_{(C\equiv O)}$	2000cm⁻¹ (s) 1988cm⁻¹ (vs)	σ–C_3H_5[b]		CH_2CH_2 2.5–2.9 (m)	7.5–7.8 (m)	90.8 (d)
	$\nu_{(C=O)}$ bridging	1850cm⁻¹ (s)					
	$\nu_{(C=O)}$ carbamoyl	1630cm⁻¹ (s)					

(*a*) *syn*- and *anti* –H of π-C_3H_5 appears alongwith $P(CH_2)_4$. (*b*) –CH_2– of σ-allyl ligand mixed up with CH_2CH_2 of phosphine ligand; –CH= Observed at 6.01 (m) and $=CH_2$ at 4.5 (m).

CONCLUSION AND PROSPECTS

From the above excursion mainly through our own work on the reactions of π-allyltricarbonylhalogenoiron complexes it is evident that this embryonic field of our research investigation has opened multifaceted preparative possibilities. The cationic and neutral π–and σ-allyliron complexes, synthesized in the present investigation, can be used as precusors for further novel syntheses. Most of the reactions (excepting a few), described in this review, are metal centred leading to the syntheses of many new/novel organoiron compounds. Nevertheless, some of the reactions showed the potential of these compounds as precursors/catalysts for new/novel organic synthesis. In the future, more attention must be given to the selective ligand-centred reactions to develop new methods for organic syntheses. The knowledge gained from the photochemistry of alkyltransition metal complexes is tremendous and has paved the ways for many novel syntheses.[36,37] The σ-organyl transition metal complexes may be compared with "sleeping beauty", waiting to be awakened by uv light and thus leading to syntheses of many new/novel compounds. The knowledge gained from the alkyl complexes should also be applicable to other σ-organyl complexes, e.g. acyl or aryl coordination compounds, which have been little studied. This statement is also applicable in the present investigation, where the photochemical paths of ligand-centred reactions might produce significant results.

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