Reactions of π-Allyltricarbonylhalogenoiron Complexes and Synthesis of New Organoiron Compounds

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The reactions of $[Fe(CO)_3(\eta^3\text{-}C_3H_5)X]$ (X = Br or I) with $Ag[ClO_4]$ in dichloromethane yielded the perchlorate-bonded complex $[Fe(CO)_3(\eta^3\text{-}C_3H_5)(OClO_3)]$ (3). Complex (3) is a suitable precursor for the synthesis of the cationic complexes $[Fe(CO)_3(\eta^3\text{-}C_3H_5)L][ClO_4]$ (L = PPh_3, $AsPh_3$, and pyridine). $[Fe(CO)_3(\eta^3\text{-}C_3H_5)(PPh_3)][ClO_4]$ reacts with univalent bidentate ligands (L′ = acetylacetonate, 8-hydroxyquinolinate, and *N*-phenylsalicylaldiminate) to give the neutral complexes $[Fe(CO)(\sigma\text{-}C_3H_5)(PPh_3)L']$.

The study of the reactivity of the η^3- and σ-allyl transition-metal complexes is significant because of their involvement in many catalytic processes. Little work is available on the synthesis and reactivity of cationic allyl iron carbonyl complexes.[1,2] In the present paper we describe the reactions of $[Fe(CO)_3(\eta^3\text{-}C_3H_5)X]$ (X = Br or I) leading to the successful isolation of cationic and neutral η^3- and σ-allyl iron carbonyl complexes.

Results and Discussion

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

$$[Fe(CO)_3(\eta^3\text{-}C_3H_5)X] + Ag[ClO_4] \xrightarrow[0\text{—}5\ ^\circ C]{CH_2Cl_2,\ N_2} \underset{(3)}{[Fe(CO)_3(\eta^3\text{-}C_3H_5)(OClO_3)]} + AgX \quad \text{(i)}$$

$$[Fe(CO)_3(\eta^3\text{-}C_3H_5)X] + Ag[ClO_4] \xrightarrow{Me_2CO} \underset{(4)}{[Fe(CO)_3(\eta^3\text{-}C_3H_5)(OCMe_2)][ClO_4]} + AgX \quad \text{(ii)}$$

$$(4) + L \xrightarrow{Me_2CO} \underset{(5)\text{—}(7)}{[Fe(CO)_3(\eta^3\text{-}C_3H_5)L][ClO_4]} \quad \text{(iii)}$$

The same reaction, when carried out in acetone, produced the stoicheiometric amount of silver salt [equation (ii)] and a conducting brown solution, from which no pure solid complex (4) could be isolated. However, addition of donor ligand [equation (iii)] yields the brown-red crystalline complexes $[Fe(CO)_3(\eta^3\text{-}C_3H_5)L]$ [L = PPh_3, (5); L = $AsPh_3$, (6); L = py (pyridine), (7)].

The reaction of (3) with stoicheiometric amounts of a ligand L in acetone also leads, according to equation (iv) (L = PPh_3, $AsPh_3$, or NC_5H_5), to the corresponding cationic π-allyl iron carbonyl complexes (5)—(7).

$$(3) + L \xrightarrow{Me_2CO} \underset{(5)\text{—}(7)}{[Fe(CO)_3(\eta^3\text{-}C_3H_5)L][ClO_4]} \quad \text{(iv)}$$

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

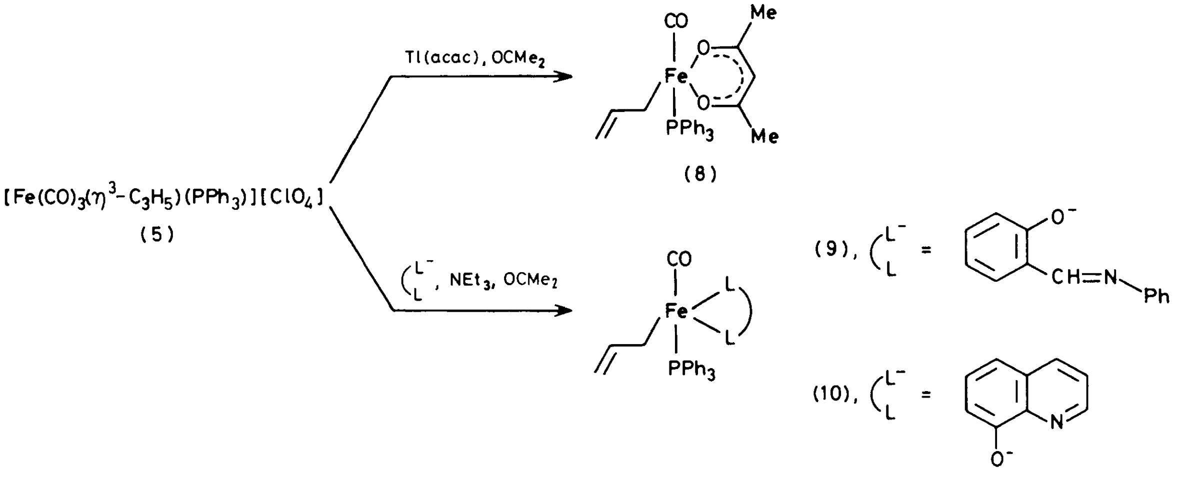
A solution of (5) is, nevertheless, a useful precursor for the synthesis of neutral σ-allyl iron complexes, (8)—(10), Scheme 1 (acac = acetylacetonate), which are isolated as low-melting (decomposed) powders having colours varying from yellow to brown. These complexes are not stable to air and water, but are quite stable under nitrogen, both in the solid state and in solution.

A tetrahydrofuran (thf) solution of complex (9), mixed with equimolar quantities of PPh_3 and then subjected to u.v. irradiation at room temperature for 30 min, led to the isolation of a neutral complex (11) which, on treatment with HBF_4 in $MeNO_2$, yielded a cationic olefinic complex (12), Scheme 2. In the protonation of (11) we are not sure at this stage whether the η^3-allyl ligand in (11) 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).

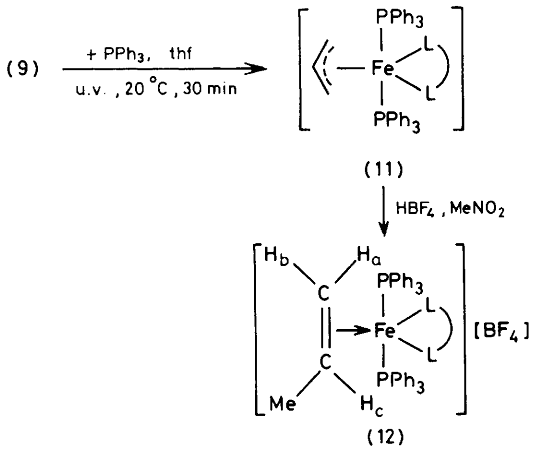
Characterization of Complexes and Spectroscopic Data.—All these complexes are coloured and are soluble in suitable organic solvents; complexes (3)—(7) are conducting in acetone (or nitromethane) (Table 1). The conductivities (Λ 108—110 S cm^2 mol^{-1} in acetone, 73—80 S cm^2 mol^{-1} in nitromethane) are within the range expected for 1 : 1 electrolytes.[3]

The complex (3) shows bands in its i.r. spectrum at 1 145vs, 1 020vs, 898m, 630m, and 620br (sh) cm^{-1} which are characteristic of a metal-bonded perchlorate group (C_{3v} symmetry). However, compounds (5)—(7) exhibit two bands, one in the region 1 085—1 100vs, 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 ν(Fe–C) stretching or δ(Fe–CO) bending modes.

In the i.r. spectra of the complexes (3), (5)—(7), and (11) the expected η^3-allylic, $C\overset{\cdots}{-}C\overset{\cdots}{-}C$, bands are observed around 1 510—1 520 cm^{-1}. The bands observed around 2 018—2 048vs, 2 000—2 010s, and 1 935—1 948s cm^{-1} in the complexes (3) and (5)—(7) may be assigned to $\nu(C\equiv O)$ absorptions.[4,5] However, the complexes (8)—(10) show $\nu(C\equiv O)$ absorption bands in the region 2 080—2 075 cm^{-1}. The presence of a σ-allylic group in the complexes (8)—(10) is demonstrated by the appearance of i.r. bands for $\nu(C{=}C)$-(allylic) in the region 1 600—1 605 cm^{-1},[6] while the presence of chelating acetylacetonate anion in complex (8) is demonstrated by the presence of two bands at *ca.* 1 585 and 1 510 cm^{-1}.[6] The appearance of the bands $\nu(C{=}C)$ (olefinic) *ca.* 1 525s,



Scheme 1.

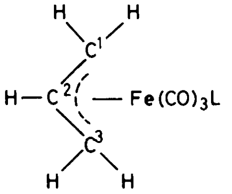


Scheme 2.

ν(CH_3) *ca.* 1 380m, and ν(=CH) *ca.* 3 012, 3 086 cm^{-1} for (12) suggests strongly the presence of an olefinic ligand in this complex [7] (Scheme 2).

These structural features of the isolated iron complexes have also been substantiated by ^1H n.m.r. spectral data (see Experimental section and Table 2). In the complexes (3), (5)—(7), and (11) the proton bonded to C^2 appears as a complex band around δ 4.8—5.0 p.p.m. A pair of doublets (broad) centred at δ 2.8 and 1.9 p.p.m., which may be *syn* and *anti* protons bonded to C^1 and C^3, are also observed for these complexes. The spectrum cannot be further resolved at room temperature. However, the integration is approximately correct. This supports the presence of a η^3-allyl ligand in these complexes.[6,8–14]

The synthesis, ^1H n.m.r. spectra, and *X*-ray crystal structure of σ-allyl palladium(II) and platinum(II) complexes have received much attention in the last few years,[15–20] in view of the role of these species as intermediates in reactions of η^3-allyl metal complexes. However, few σ-allyl iron complexes are known; complexes (8)—(10) are significant in that they are examples of stable σ-allyl iron complexes in solution.[6] The chelated acetylacetonate ligand appears to be very strongly bound to iron so that the ^1H n.m.r. spectra of the complexes (8)—(10) at room temperature can be satisfactorily interpreted in terms of rigid σ-allyl–iron bonding (see Table 2).



(3), L = $OClO_3$
(5), L = PPh_3
(6), L = $AsPh_3$
(7), L = py

The elemental analyses, most aspects of the ^1H n.m.r. spectrum in CD_3NO_2, and the i.r. spectrum (KBr pellet) support the formation of the olefinic complex (12) (Scheme 2). In the ^1H n.m.r. spectrum four complex bands are observed at δ 2.2, 3.7, 1.3, and 0.91 p.p.m., assignable to H_a, H_b, H_c, and Me protons respectively [see Scheme 2].

Experimental

Hydrogen-1 n.m.r. and i.r. spectra were recorded as described previously.[21,22] The complexes [$Fe(CO)_3(\eta^3-C_3H_5)X$] (X = Br and I) were prepared according to reported methods.[23–26] The salt Tl(acac) was prepared by treating thallium(I) ethoxide with acetylacetone in ethanol. All manipulations were carried out under nitrogen in conventional Schlenk-tube type apparatus using solvents dried by usual procedures. Microanalyses were carried out by Strathclyde University (Glasgow), Würzburg University (West Germany), Munich University, Garching (West Germany), and CDRI, Lucknow (India).

The conductivities were recorded as described previously.[21,22]

Preparations.—[$Fe(CO)_3(\eta^3-C_3H_5)(OClO_3)$] (3). A magnetically stirred solution of [$Fe(CO)_3(\eta^3-C_3H_5)Br$] (0.260 g, 0.001 mol) or [$Fe(CO)_3(\eta^3-C_3H_5)I$] (0.307 g, 0.001 mol) in dichloromethane (60 cm^3) was treated with Ag[ClO_4] (0.247 g, 0.0012 mol) for 8 h at 0—5 °C with exclusion of light. The precipitated AgBr or AgI was filtered off together with the excess of Ag[ClO_4] and the filtrate concentrated *in vacuo* to yield (3) as a yellow-brown powder (0.43 and 0.51 g respect-

Table 1. Elemental analyses and physical data for the complexes

Complex	Colour	M.p. θ_c/°C	Analysis * (%) C	H	N	Fe	Λ/S cm^2 mol^{-1}
(3) $[\text{Fe(CO)}_3(\eta^3\text{-C}_3\text{H}_5)(\text{OClO}_3)]$	Yellow-brown	98—99 (decomp.)	25.9 (25.7)	1.5 (1.8)		20.2 (19.9)	108 (Me_2CO) 73 (MeNO_2)
(5) $[\text{Fe(CO)}_3(\eta^3\text{-C}_3\text{H}_5)(\text{PPh}_3)][\text{ClO}_4]$	Red-brown	258—260 (decomp.)	53.7 (53.1)	3.8 (3.7)		10.3 (10.3)	110 (Me_2CO) 78 (MeNO_2)
(6) $[\text{Fe(CO)}_3(\eta^3\text{-C}_3\text{H}_5)(\text{AsPh}_3)][\text{ClO}_4]$	Brown	223—228 (decomp.)	49.5 (49.1)	3.6 (3.4)		9.6 (9.55)	80 (MeNO_2)
(7) $[\text{Fe(CO)}_3(\eta^3\text{-C}_3\text{H}_5)(\text{py})][\text{ClO}_4]$	Maroon	225—226 (decomp.)	36.8 (36.75)	3.0 (2.8)	4.0 (3.9)	15.3 (15.55)	76 (MeNO_2)
(8) $[\text{Fe(CO)}(\sigma\text{-C}_3\text{H}_5)(\text{PPh}_3)(\text{acac})]$	Yellow	197—199 (decomp.)	67.0 (66.85)	5.35 (5.55)		12.85 (12.75)	
(9) $[\text{Fe(CO)}(\sigma\text{-C}_3\text{H}_5)(\text{PPh}_3)(\text{psala})]$	Red-brown	200—202 (decomp.)	72.35 (72.05)	5.65 (5.15)	2.8 (2.4)	9.6 (9.6)	
(10) $[\text{Fe(CO)}(\sigma\text{-C}_3\text{H}_5)(\text{PPh}_3)(\text{hoqu})]$	Brown	212—214	70.0 (70.1)	5.1 (4.9)	2.8 (2.65)	10.8 (10.5)	
(11) $[\text{Fe}(\eta^3\text{-C}_3\text{H}_5)(\text{PPh}_3)_2(\text{psala})]$	Red-yellow	198—202 (decomp.)	76.5 (76.4)	5.5 (5.5)	1.8 (1.75)	7.0 (6.85)	
(12) $[\text{Fe}(\text{CH}_2\text{=CHCH}_3)(\text{PPh}_3)_2(\text{psala})][\text{BF}_4]$	Yellow-brown	195—198 (decomp.)	69.0 (68.95)	5.2 (5.1)	1.7 (1.55)	6.35 (6.15)	80.4 (MeNO_2)

* Calculated values are given in parentheses.

ively). ^{1}H N.m.r. $[\text{OC(CD}_3)_2]$: δ 4.8—5.0 (complex, C–H), 2.8 (d, br, *syn*-H of $-\text{CH}_2$), and *ca.* 1.9 (d, br, *anti*-H of $-\text{CH}_2$). I.r. spectrum (Nujol and hexachlorobutadiene): 1 145vs, 1 020vs, 898m, 630m, 620 (sh) (bonded ClO_4^- in C_{3v}); 2 050vs, 2 000s, 1 935s [$\nu(\text{C}\equiv\text{O})$]; 1 490s cm^{-1} [$\nu(\text{C}\overset{...}{-}\text{C}\overset{...}{-}\text{C})$, η^3-allyl ligand].

Solution of $[\text{Fe(CO)}_3(\eta^3\text{-C}_3\text{H}_5)(\text{OCMe}_2)][\text{ClO}_4]$ (4). The above reaction, when carried out in acetone instead of CH_2Cl_2, yielded a brown solution along with AgX. The resulting brown solution showed two bands, one at 630m cm^{-1} and another at 1 085vs, br cm^{-1} assignable to the ClO_4^- anion (T_d). Three more bands at *ca.* 2 048vs, 2 010s, and 1 948s cm^{-1} assignable to $\nu(\text{C}\equiv\text{O})$ were also observed along with bands at 1 598s cm^{-1} [$\nu(\text{C=O})$ ketonic bonded to iron] and at 1 520s cm^{-1} [$\nu(\text{C}\overset{...}{-}\text{C}\overset{...}{-}\text{C})$ η^3-allylic]. The conductivity of the solution (in Me_2CO) was calculated to be 110 S cm^2 mol^{-1}, supporting the presence of a 1 : 1 electrolyte.[3] Complex (4) could not be isolated, however, since concentration and cooling gave the complex (3).

$[\text{Fe(CO)}_3(\eta^3\text{-C}_3\text{H}_5)\text{L}]$ (L = PPh_3, AsPh_3, *and* py) (5)—(7). The reaction of (3) or (4) with stoicheiometric amounts of a ligand L in acetone (stirring at room temperature for 4—5 h) gave brown solutions, which on concentration and cooling gave the coloured crystalline complexes (5)—(7). ^{1}H N.m.r. ([$^2\text{H}_6$]acetone): complex bands around δ 4.9, 3.0, and 1.88 p.p.m. I.r. (Nujol): bands around 1 150vs, 1 025vs, 900m, 635m (ClO_4^-); 2 055vs, 2 010vs, 1 930s [$\nu(\text{C}\equiv\text{O})$]; 1 488s cm^{-1} [$\nu(\text{C}\overset{...}{-}\text{C}\overset{...}{-}\text{C})$].

$[\text{Fe(CO)}(\sigma\text{-C}_3\text{H}_5)(\text{PPh}_3)\text{L}']$ [L′ = *acetylacetonate* (acac), *N-phenylsalicylaldiminate* (psala), *and 8-hydroxyquinolinate* (hoqu)] (8)—(10). An equimolar (0.001 mol) mixture of (5) and Tl(acac), Hpsala, or Hhoqu in acetone was stirred at 10—15 °C for 2 h and filtered. The filtrate was concentrated under vacuum and kept in the refrigerator for 2—3 days, whereby coloured crystals of (8)—(10) were obtained. These were filtered off, washed with cold acetone, and dried *in vacuo*. Yields varied between 40 and 60%. Use of NEt_3 gave better results for the synthesis of (9) and (10). See Results and Discussion section and Table 2 for spectroscopic data.

$[\text{Fe}(\eta^3\text{-C}_3\text{H}_5)(\text{PPh}_3)_2(\text{psala})]$ (11). Complex (9) and PPh_3 in equimolar ratio were stirred in thf at room temperature for 30 min under u.v. light and then filtered. The filtrate was concentrated *in vacuo* and cooled to 0 °C for 3—4 h to give crystalline neutral complex (11) in 55% yield. The product was recrystallized from acetone–thf (50 : 50 v/v) and dried *in vacuo*. ^{1}H N.m.r. ([$^2\text{H}_6$]acetone): complex bands around δ 5.0, 2.85, and 1.90 p.p.m.; δ 8.7 p.p.m. (CH=N–). I.r. (Nujol): 1 480s [$\nu(\text{C}\overset{...}{-}\text{C}\overset{...}{-}\text{C})$], 1 605s cm^{-1} [$\nu(\text{C=N})$].

$[\text{Fe}(\text{CH}_2\text{=CHCH}_3)_2(\text{PPh}_3)(\text{psala})]$ (12). A solution of (11) in MeNO_2 was mixed with HBF_4 and stirred at 45—50 °C for 5 h and cooled. The precipitated complex (12) was filtered off, washed with hexane, and dried *in vacuo*; yield 48%. ^{1}H N.m.r. (CD_3NO_2): four complex bands around δ 2.2, 3.7, 1.3, and 0.91 p.p.m. (olefinic and methyl protons); broad band at δ 8.56 p.p.m. (CH=N protons); complex bands around δ 6.5—7.5 p.p.m. (phenyl protons). I.r. (Nujol): 1 525s [ν(C=C olefinic)], 1 380m [$\nu(\text{CH}_3)$], 3 012m, 3 086m cm^{-1} [ν(=CH)].

Table 2. Hydrogen-1 n.m.r. data [a] for $[\text{Fe(CO)}(\sigma\text{-C}_3\text{H}_5)(\text{PPh}_3)(\text{acac})]$ (8)

Allyl [b]			acac [c]	
$-\text{CH}_2-$	$-\text{CH}=$	$=\text{CH}_2$	Me	$-\text{CH}=$
2.68 (dd)	5.88 (complex)	4.30 (complex)	1.55 (s)	5.30 (s)
$J(\text{CH}_2\text{-H}) = 8$			1.95 (s)	
$J(\text{P-H}) = 4.5$				

[a] Chemical shifts (δ) in p.p.m., J in Hz; in CDCl_3. [b] Similar σ-allylic ligands were found to be present in complexes (9) and (10). [c] Phenyl and –CH=N– protons were observed at δ 6.7—7.3 and 8.62 p.p.m. respectively.

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