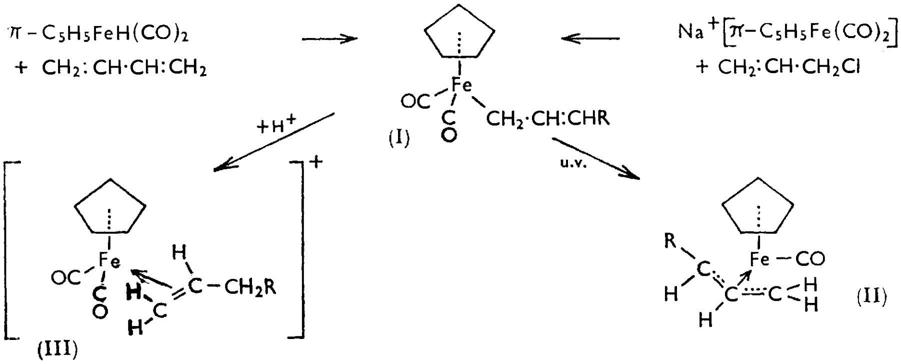
28. *Allyl and Olefin Complexes of Iron.*

By M. L. H. GREEN and P. L. I. NAGY.

The allyl complexes, $\pi\text{-}C_5H_5Fe(CO)_2\sigma\text{-}CH_2{\cdot}CH{=}CHR$ and $\pi\text{-}C_5H_5Fe(CO)\text{-}(\pi\text{-}C_3H_4R)$, where R = H or Me, are described. Reaction of the σ-allyl complexes with hydrogen chloride or aqueous mineral acids results in protonation of the allyl group, affording the π-ethylenic complexes, $[\pi\text{-}C_5H_5Fe(CO)_2\pi\text{-}C_3H_4R]^+$. Studies of the products prepared from deuterium chloride indicate that the carbon atom at position 3 is protonated. The infrared and high-resolution nuclear magnetic resonance spectra of all the compounds are given and discussed. The proposed structures are considered in the light of the chemical and spectral data.

RECENTLY, allyl complexes of nickel,[1] palladium,[2] platinum,[3] cobalt,[4] and manganese [5] have been described in which the allyl group is usually π-bonded but in a few cases σ-bonded to the metal. We now report the preparation of related complexes of iron. Reaction of the sodium salt $Na^+[\pi\text{-}C_5H_5Fe(CO)_2]^-$ with allyl chloride gives a yellow, volatile oil in high yield. Analysis and spectra described below show that the compound must be formulated as the σ-allyl complex, $\pi\text{-}C_5H_5Fe(CO)_2\sigma\text{-}CH_2{\cdot}CH{=}CH_2$. Treating the hydrido-complex $\pi\text{-}C_5H_5FeH(CO)_2$ with butadiene affords the but-2-enyl derivative, $\pi\text{-}C_5H_5Fe(CO)_2\sigma\text{-}C_4H_7$, which the evidence below shows to be an isomeric mixture. Unlike the result with pentacarbonyl-σ-allylmanganese, heating the σ-allyl iron compounds did not give π-allyl derivatives. However, as for the related σ-allylmolybdenum complexes,[6] ultraviolet irradiation affords high yields of the π-allyl compounds (II).

In these studies it was noted that the σ-allyl complexes readily dissolved in dilute mineral acids and reacted immediately with hydrogen chloride forming organometallic cations. As recently communicated,[7] these cations have been identified as the π-ethylenic complexes (III). The evidence for the formulation of the cations is given below and the products prepared from deuterium chloride have been studied.



Chemical Studies.—The compounds prepared are given in the chart, where R = H or Me. Both the σ-allyl complexes (I) are readily oxidised by atmospheric oxygen and decompose thermally above ~60°. Thermal decomposition of the σ-allyliron complexes, either in dilute solution in an inert solvent or on their being heated alone, gave, as main

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[1] Heck, Chien, and Breslow, *Chem. and Ind.*, 1961, 986, and references therein.

[2] McClellan, Hoehn, Cripps, Muetterties, and Howk, *J. Amer. Chem. Soc.*, 1961, **83**, 1601, and references therein.

[3] Shaw and Sheppard, *Chem. and Ind.*, 1961, 517, and references therein.

[4] Heck and Breslow, *J. Amer. Chem. Soc.*, 1960, **82**, 750, and references therein.

[5] Kaesz, King, and Stone, *Z. Naturforsch.*, 1960, **15**b, 682.

[6] Cousins and Green, unpublished work.

[7] Green and Nagy, *Proc. Chem. Soc.*, 1961, 378.

products, a binuclear complex, $[\pi\text{-}C_5H_5Fe(CO)_2]_2$, and unidentified hydrocarbons, and not the π-allyl derivatives. However, ultraviolet irradiation of the pure compounds in a silica vessel for 12 hours gives the π-allyl derivatives (II) in good yield. Attempts to hydrogenate the σ-allyl complex (I; R = H over Adams catalyst in ethyl acetate resulted in a slow non-stoicheiometric absorption of hydrogen and formation of the binuclear complex, $[\pi\text{-}C_5H_5Fe(CO)_2]_2$. The yellow crystalline π-allyl complex (II; R = H) is moderately unstable in air; however, in contrast, the but-2-enyl derivative (II; R = Me) is a thermally unstable oil which is oxidised very rapidly. The π-allyl complex (II; R = H) dissolved readily in dimethyl sulphoxide from which it may be recovered unchanged. The proton magnetic resonance spectrum indicates that, as reported for some π-allyl complexes of palladium,[8] there is some interaction of dimethyl sulphoxide and the complex.

Treating light petroleum solutions of the σ-allyl complexes with anhydrous hydrogen chloride results in immediate precipitation of yellow powders which are very hygroscopic and soluble in water. These are chlorides containing the cations (III). They yield diamagnetic, aqueous red-brown solutions that are comparatively stable, decomposing slowly with evolution of gas and formation of the cation, $[\pi\text{-}C_5H_5Fe(CO)_2H_2O]^+$,[9] which was identified by the infrared spectrum of the silicotungstate. Suitable non-hygroscopic precipitates of hexafluorophosphates, perchlorates, and hexachloroplatinates are readily

TABLE 1.

Infrared spectra.

π-$C_5H_5Fe(CO)_2\sigma$-C_3H_5 [a]	Note	π-$C_5H_5Fe(CO)_2\sigma$-C_4H_7 [a]	Note	π-$C_5H_5Fe(CO)\pi$-C_3H_5 [c]	Note	π-$C_5H_5Fe(CO)\pi$-C_4H_7 [a, d]	Note
3120w	*f*	3115w	*f*	3105w	*f*	3090w	*f*
3080m	*g*	3010m	*g*	3060s	*u*	3050w	
3055w	*g*	2960m	*h*	3000s	*u*	2995m	
2975m	*g*	2925s	*h*	2925m	*u*	2960m	
2925m		2860w	*h*	2850w	*u*	2940m	*g* or *u*
2865w						2895m	
2850w(sh)						2850m	
2680vw				2575vw			
2620vw				2470w			
2551vw				2400vw			
2500vw							
2010vs	*i*	2016vs	*i*	1950vs	*i*	1948vs	*i*
1948vs	*i*	1950vs	*i*				
1787w		1710vw		1805w		1503w	
1673w		1681vw		1760w		1490m	*t*
1608s	*j*	1643w	*j*?	1487s	*t*	1459m	
1485vw		1454w	*m*	1466m	*v*	1447m(sh)	
1433m	*n*	1437m	*n*	1429w	*v*	1435m	*v*
1419m	*l*	1422w	*l*	1415m	*l*	1417m	*l*
1399w	*m*	1401vw		1360w	*l*	1391m	
1358w	*l*	1377w	*m*	1261m		1363m	*l*
1291w		1363w	*l*	1211s		1300w	
1209vw		1300w		1201s		1224w	
1197m(sh)		1260vw		1112s	*l*	1195w	
1188m		1160vw		1056w		1167w	
1112w	*l*	1114vw		1011s	*l*	1114m	
1082m(sh)		1080m		1008s		1059m	
1060m(sh)		1056m		950m		1030s	
1013m	*l*	1015w	*l*	923m		1015s	*l*
998m	*l*	1000m	*l*	893s		995m	*l*
982m	*o*	960s	*q*	848w		946w	
921w		923vw		819s	*l*	910w	
875s		900vw		860m		886vw	
826s		841m				856s	
761m		826s	*l*			820s	*l*
666s		763vw				772w	
		717w	*p*				

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[8] Chien and Dehm, *Chem. and Ind.*, 1961, 745.

[9] Piper and Wilkinson, *J. Inorg. Nuclear Chem.*, 1956, **3**, 104.

TABLE 1. (*Continued.*)

$[\pi\text{-}C_5H_5Fe(CO)_2\pi\text{-}C_3H_6]^+$ $PF_6^{-\,b,\,d,\,e}$	Note	$[\pi\text{-}C_5H_5Fe(CO)_2\pi\text{-}C_3H_5D]^+$ $ClO_4^{-\,b}$	Note	$[\pi\text{-}C_5H_5Fe(CO)_2\pi\text{-}C_4H_8]^+$ $PF_6^{-\,b}$	Note	$[\pi\text{-}C_5H_5Fe(CO)_2\pi\text{-}C_4H_7D]^+$ $ClO_4^{-\,b}$	Note
3130s	*f, g, x*	3110m	*f, g*	3125s	*f, g, w*	3110m	*f, g*
				2980m		2975m	
				2945w		2940w	
				2880w		2880w	
				2850(sh)			
2082vs	*i, x*	2083vs	*i*	2088vs	*i, w*	2084vs	*i*
2053vs	*i*	2054vs	*i*	2055vs	*i*	2040vs	*i*
1533w	*k*	1525w	*k*	1785w		1522w	*k*
1466m	*m*	1461m		1522w	*k*	1455m	
1440s		1435s		1468s		1437m	
1432m		1426s		1457(sh)		1430m	
1413vw	*l*	1410(sh)	*l*	1435s		1410(sh)	*l*
1388m	*l*	1387m		1429s		1376w	*l*
1270vw		1370m	*l*	1412s	*l*	1321w	
1173vw		1300w		1390m		1095vs	*r*
1123w		1280m		1377m	*l*	1060(sh)	
1067w		1102vs	*r*	1305m		1015w	*l*
1048m		1062m		1277w		875(sh)	
1025s		1019m	*l*	1260w		869w	
1010(sh)	*l*	1005m	*l*	1120w	*l*	718w	
978s		970w		1067w			
938m		895(sh)		1036w			
837vs	*s*	877m		1018w	*l*		
722vw		829w		1006w	*l*		
		720w		960w			
				845vs	*s*		
				737w			

a, Measured on thin films. *b*, Measured as mulls in Nujol and hexachlorobutadiene. *c*, 2800—3200 cm.$^{-1}$ region separately examined with CaF_2 optics. *d*, 1400—3200 cm.$^{-1}$ region examined for D_2O solutions of the chloride. *e*, Measured in solution in CS_2 and CCl_4. *f*, C–H stretch of π-C_5H_5. *g*, Olefinic C–H stretch. *h*, Assignable to C–H stretches of ethyl group. *i*, CO stretch. *j*, Unco-ordinated C=C stretch. *k*, Co-ordinated C=C stretch. *l*, π-C_5H_5 frequencies. *m*, CH_3 deformation. *n*, CH_2 deformation. *o*, CH_2 out-of-plane deformation. *p*, *cis* =CH– out-of-plane deformation. *q*, *trans* =CH– out-of-plane deformation. *r*, ClO_4^-. *s*, PF_6^-. *t*, Co-ordinated π-allyl C–C–C stretch.[15] *u*, π-Allyl, CH stretch.[15] *v*, CH_2 or =CH–, π-allyl in-plane deformation.[15] *w*, For $PtCl_6^{2-}$ salt, C–H stretch at 3080m, CO stretches at 2075vs and 2035vs, difference measured for mixed mulls. *x*, For $PtCl_6^{2-}$ salt, C–H stretch at 3080m, CO stretches at 2072vs and 2031vs, difference measured for mixed mulls.

obtainable from the red-brown solutions and are stable under nitrogen. The hexachloroplatinates darken slowly when kept in the light. The evolution of a gas from aqueous solutions indicates ligand replacement. Treatment of the perchlorates with triphenylphosphine similarly yields gases and these were collected and identified by their infrared spectra as propene and but-1-ene for (III; R = H and Me, respectively); yellow crystals remained after this reaction and were identified as the perchlorate[10] $[\pi\text{-}C_5H_5Fe(CO)_2Ph_3P]^+ClO_4^-$. The reaction may be represented as:

$$[\pi\text{-}C_5H_5Fe(CO)_3C_3H_4R^+]ClO_4^- + Ph_3P \longrightarrow [\pi\text{-}C_5H_5Fe(CO)_3Ph_2P]^+ClO_4^- + CH_2{=}CH{\cdot}CHR$$

Thus there is strong evidence for the presence of co-ordinated olefins in the cations (III).

D_2O solutions containing the ethylenic cations (III) gave no evidence for exchange of protons, and treating the aqueous solutions with alkali resulted in immediate decomposition. Therefore, the protonation is not reversible, in contrast to protonations that form hydridometal cations.[11,12] Conductivity measurements on the perchlorates in nitrobenzene and liquid sulphur dioxide indicate that they are 1 : 1 electrolytes.[10] Analogous cations containing iron, molybdenum, or tungsten to which ethylene is co-ordinated have

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[10] Davison, Green, and Wilkinson, *J.*, 1961, 3172.
[11] Green, Pratt, and Wilkinson, *J.*, 1958, 3916.
[12] Green, McCleverty, Pratt, and Wilkinson, *J.*, 1961, 4854.

been prepared from ethylene.[13] The high solubility and stability of the salts in liquid sulphur dioxide facilitated their purification and the measurement of their proton magnetic resonance spectra.

Infrared Spectra.—The spectra and some tentative assignments are given in Table 1, down to 650 cm.$^{-1}$. The spectra of all the compounds show bands characteristic of a π-C_5H_5 metal grouping, including a sharp single C–H stretch at 3100 cm.$^{-1}$. Similarly, all spectra show very strong bands in the region 1900—2100 cm.$^{-1}$ which may be assigned to the stretching frequencies of terminal carbonyl groups. The σ-allyl complex (I; R = H) shows a strong band at 1608 cm.$^{-1}$ assignable to an unco-ordinated C=C stretch. Peaks characteristic of a vinyl group [14] are also present (see Table 1). The but-2-enyl compound (I; R = Me) has a band at 1643 cm.$^{-1}$ which likewise may be assigned to the unco-ordinated C=C stretch. In the spectra of this compound there are also bands at 717 and 960 cm.$^{-1}$ and in the region 1200—1500 cm.$^{-1}$ which are consistent with the presence of *cis*- and *trans*-isomers of the group, $-CH_2{\cdot}CH{=}CH{\cdot}CH_3$; frequencies characteristic of a terminal vinyl group are absent. The π-allyl complexes (II) show only a single carbonyl stretch; other assignments, given in Table 1, show that the spectra are consistent with the proposed formulation. The spectrum of the π-propene cation (III; R = H) shows a weak band at 1533 cm.$^{-1}$ which may be assigned to the co-ordinated C=C stretch. The 3000 cm.$^{-1}$ region is unusual in that there is only a single sharp absorption, at 3130 cm.$^{-1}$. There are only very weak bands observable for concentrated mulls and D_2O solutions in the region 2800—3000 cm.$^{-1}$. No absorption which would be expected from a methyl group is present. There are, however, bands in the region 1400 cm.$^{-1}$, assignable to C–H deformations of a methyl group. This anomaly is discussed below. The carbonyl stretches of the ethylenic cations occur about 50 cm.$^{-1}$ higher than in the neutral compounds, consistently with the higher oxidation state of the metal. The π-but-1-ene cation (III; R = Me) hexafluorophosphate shows bands of medium intensity at 2980, 2945, 2880, and 2850(sh) cm.$^{-1}$, which may be assigned to the C–H stretches of the ethyl group. There is a weak peak at 1522 cm.$^{-1}$, assignable to a co-ordinated C=C stretch.

The spectra of the deuterated cations (III) do not show marked changes in the region 2800—3200 cm.$^{-1}$; however, the anomalous nature of the spectra of the undeuterated cations has already been noted. No C–D stretches are observed, which may be due either to their absence or to their obscuration by the carbonyl peaks. There are however distinct changes in the region 1200—1500 cm.$^{-1}$ (see Table 1).

Nuclear Magnetic Resonance Spectra.—The spectra were obtained at 40 Mc./sec. and are given, with brief assignments, in Table 2. The sharpness of the lines in all spectra shows that the pure compounds are diamagnetic. In no case was a line observed where lines due to a hydrogen attached to a transition metal occur. In all spectra there is a single sharp line which may be assigned to the five equivalent protons of the π-cyclopentadienyl group. For the cationic complexes, this line occurs at lower fields, which is understandable in terms of the deshielding effect of the unipositive charge on the metal. The spectrum of the σ-allyl complex (I; R = H) is consistent with the formulation given. A comparison of the coupling constants for the H^2 proton with those of alkyl-substituted ethylenes shows that they are of the same magnitude.[16] The but-2-enyl derivative (I; R = Me) has a complex spectrum for which we can offer no complete assignment. However the spectrum can best be understood in terms of the proposed formulation (I), which leads to *cis*- and *trans*-isomers. Other isomers cannot so easily account for the observed spectrum.

The spectrum of compound (II; R = H) is entirely consistent with the π-allyl

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[13] Fischer and Fichtel, *Chem. Ber.*, 1961, **94**, 1200.

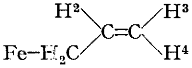
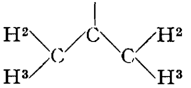
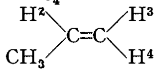
[14] Bellamy, "The Infra-red Spectra of Complex Molecules," 2nd edn., Methuen and Co., London, 1958.

[15] Fritz, *Chem. Ber.*, 1961, **94**, 1217.

[16] Pople, Schneider, and Bernstein, "High-resolution Nuclear Magnetic Resonance," McGraw-Hill Inc., New York, 1959, p. 242.

TABLE 2.

Proton magnetic resonance data.

Compound and conditions of measurement	Band posn. (τ = 10) *	Relative intensity †	Multiplicity	Sepn. between components (c./sec.) ‡	Assignment
π-$C_5H_5Fe(CO)_2$-σ-C_3H_5 as pure liq., rel. to $SiMe_4$  	7·93	2	4	app. $J_{CH_2, 2}$ = 8·4	–CH_2– split by H^2 and further by H^3 or H^4
				app. $J_{CH_2, 3 \text{ or } 4}$ = 1	
	5·45		1	—	π-C_5H_5 group
	Centre 5·31	7	Complex band (6)	—	H^3 and H^4
	Centre 3·84	1	6 or 7 with further secondary splitting	app. $J_{CH_2, 2}$ = 8·2 app. $J_{2, 3}$ = 9·2 app. $J_{2, 4}$ = 17·1	H^2 split by H^3, H^4, and –CH_2–
π-$C_5H_5Fe(CO)_2$-σ-C_4H_7 as pure liq., rel. to C_6H_{12}	8·43	3	2	app. $J_{CH_3\ H_{gem}}$ = 5	–CH_3
	7·88	2	2	app. $J_{CH_2, 2}$ = 6	–CH_2–
	5·44	5	1	—	π-C_5H_5
	Centre 4·57	2	Complex band (9)	—	olefinic protons
π-$C_5H_5Fe(CO)$-π-C_3H_5 in soln. in C_6H_6 ref. solvent  	9·32	2	2	app. $J_{3, 1}$ = 11	H^3 split by H^1
	7·33	2	2	app. $J_{2, 1}$ = 8	H^2 split by H^1
	Centre 5·84	1	Complex band (7)	—	H^1 split by H^2 and H^3
	5·94	5	1	—	π-C_5H_5
π-$C_5H_5Fe(CO)$-π-C_4H_7 in C_6H_6, rel. to $SiMe_4$	5·81	5	1	—	π-C_5H_5
	A very complex spectrum, centres at 5·94, 7·45, and 8·92.				
[π-$C_5H_5Fe(CO)_2$-π-$C_3H_6]^+ClO_4^-$ as soln. in liq. SO_2, rel. to $SiMe_4$  	8·14	3	2	app. $J_{CH_3, 2}$ = 6	CH_3 split by H^2
	6·53	1	2	app. $J_{2, 3}$ = 8	H^3 split by H^2
	6·05	1	2	app. $J_{2, 4}$ = 17	H^4 split by H^2
	Centre 5·00	1	Complex band (7)	—	H^2
	4·68	5	1	—	π-C_5H_5
[π-$C_5H_5Fe(CO)_2$-π-$C_3H_5D]^+ClO_4^-$ in soln. in liq. SO_2, rel. to $SiMe_4$	Centre 8·13	2	Complex band (8)	—	–CH_2D
	6·55	1	2	app. $J_{2, 3}$ = 8	H^3 split by H^2
	6·05	1	2	app. $J_{2, 4}$ = 16	H^4 split by H^2
	Centre 5·00	1	Complex band (11)	—	H^2
	4·38	5	1	—	π-C_5H_5
[π-$C_5H_5Fe(CO)_2$-π-$C_4H_8]^+ClO_4^-$ in soln. in liq. SO_2, rel. to $SiMe_4$	Centre 7·95	5	Complex band (27), spread 100 c./sec.	—	–$CH_2{\cdot}CH_3$
	6·57	1	2	app. $J_{2, 3}$ = 8	H^3 split by H^2
	6·05	1	2	app. $J_{2, 4}$ = 15	H^3 split by H^2
	Centre 5·10	1	Complex band (10)	—	H^2
	4·36	5	1	—	π-C_5H_5
[π-$C_5H_5Fe(CO)_2$-π-$C_4H_7D]^+ClO_4^-$ in soln. in liq. SO_2, rel. to $SiMe_4$	Centre 7·70	4	Complex band, spread 60 c./sec.	—	C_2H_4D
	6·59	1	2	app. $J_{2, 3}$ = 8	H^3 split by H^2
	6·08	1	2	app. $J_{2, 4}$ = 15	H^4 split by H^2
	Centre 5·14	1	Complex band (8)	—	H^2
	4·41	5	1	—	π-C_5H_5

* Relative to $SiMe_4$ as an internal standard, except where indicated. † Estimated to whole numbers by method of counting squares. ‡ Where multiplicities occur which may be described as first-order spin–spin couplings, the splittings are recorded as the apparent coupling constants (app. *J*).

formulation, as discussed for related complexes.[3] The but-2-enyl derivative (II; R = Me) has a very complicated spectrum and no assignment is attempted. The analogous carbonyl-π-but-2-enylcobalt compound has been shown to consist of isomers and also has a similarly complicated spectrum.[17]

The ethylenic-cation chlorides decompose sufficiently slowly for their spectra to be

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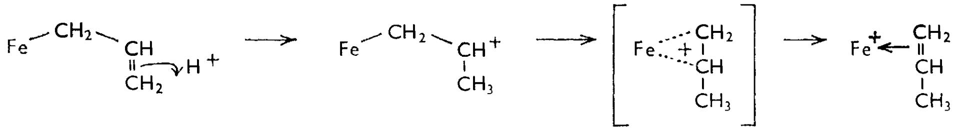
[17] Moore, Jonassen, Joyner, and Bertrand, *Chem. and Ind.*, 1960, 1304.

measured in solution in water and D_2O. However, more satisfactory spectra were obtained from solutions of the perchlorate [5] in liquid sulphur dioxide. The spectra from both solutions were almost identical. The spectrum of the cation (III; R = H) is consistent with the proposed formulation. If coupling between H^3 and H^4 is assumed to be neglible, the values obtained for the various apparent *cis*- and *trans*-coupling constants are of the right order.[16] The deuterated product shows that the doublet assigned to the methyl group of the π-propene group is replaced by a complex band of much reduced intensity. Two peaks at 8·08 and 8·21 τ correspond to the methyl doublet of the π-propene cation and indicate protonated impurities. The spectrum is complicated by H–D couplings, as shown by the band assigned to H^2. For the π-but-1-ene complex (III; R = Me) the general features of the spectrum are similar to that of (III; R = H). The complex band centred at 7·95 τ is consistent with the presence of an ethyl group. As before, the spectrum of the deuterated product shows an increased complexity and reduced intensity of the band assigned to this group.

Discussion.—The main structural features for the compounds prepared are shown in the formulæ. The actual configurations of the π-allylic and π-ethylenic groups relative to the metal in the complexes (II) and (III) are unknown, and are represented only formally. The butadienyl compound, for example, is probably an isomeric mixture of *syn*- and *anti*-forms as suggested for the related cobalt compound.[17] The analytical, proton magnetic resonance, and chemical evidence strongly supports the presence of a π-propene group in the cation (III; R = H); therefore, the absence of infrared absorption bands, which are usually characteristic of a methyl group, must be understood as a rare example of reduction by an order of magnitude of the intensity of these bands. The phenomenon has been observed for other methyl groups, for example, methoxyl and acetyl groups.[18] The cation (III; R = Me) does show bands which may be assigned to C–H stretches of the ethyl group, but they are weaker than normal. These reductions of intensity may be associated with some property of the $CH_2{=}CH^-$ co-ordinated system. The marked shift of the C–H stretching frequencies in the spectra of the cation (III; R = H) hexafluorophosphate and hexachloroplatinate is presumably due to lattice effects.

The protonation of several organometallic complexes has recently been reported. Examples are ferrocene,[19] the hydrides $(\pi\text{-}C_5H_5)_2ReH$,[11] $(\pi\text{-}C_5H_5)_2Mo(W)H_2$,[19] iron carbonyl, (substituted-phosphine)iron carbonyls, and the binuclear compounds, $[\pi\text{-}C_5H_5Mo(CO)_3]_2$ and $[\pi\text{-}C_5H_5Fe(CO)_2]_2$.[20] In these cases the metal atom is protonated, affording species containing an M–H system. Protonation of the olefin complexes (cyclo-octatetraene)-$Fe(CO)_3$,[21,22] (cycloheptatriene)$Fe(CO)_3$,[23] and $[PdCl_2\pi\text{-methylallyl}]_2$ [24] results, however, in addition of a proton to the olefinic ligand. The olefin complexes may react either by direct addition of the proton to the ligand or by formation of an intermediate hydrido-cation, followed by transfer of the hydrogen to the olefin. If for the complexes (I), the proton directly attacks the σ-allyl ligand there results an intermediate carbonium ion which may transfer the positive charge to the metal atom and finally bond to it as in other olefin cations, *viz*:



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[18] Jones and Sandorfy in Weissberger's "Techniques of Organic Chemistry," Interscience Publ. Inc., New York, 1956, Vol. IX, 341; Francis, *J. Chem. Phys.*, 1951, **19**, 942.

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[22] Davison, McFarlane, Pratt, and Wilkinson, *Chem. and Ind.*, 1961, 553.

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[24] Hüttel, Kratzer, and Bechter, *Chem. Ber.*, 1961, **94**, 766.

The stabilisation of the carbonium ion by the metal, forming the ethylenic cations (III), is comparable with the stabilisation of carbonium ions by other systems, *e.g.*, the delocalised aromatic hydrocarbon system of the triphenylmethyl cation, the non-classical delocalised system of the bicyclo[3,1,0]hexyl cation,[25] and other organometallic species such as the ferrocene derivatives.[26] The protonation may be viewed as a reversible protonation, which occurs for most olefins but in this case is carried to completion by the novel method of carbonium-ion stabilisation. That the protonation of C-3 occurs is shown by the deuteration and by the formation from compound (I; R = Me) of the butene cation (III; R = Me) rather than a but-2-ene product. A mechanism involving formation of an intermediate hydride species cannot be ruled out, so that either mechanism is possible on the basis of the present evidence.

EXPERIMENTAL

Microanalyses were carried out in the Microanalytical Laboratory, Lensfield Road, Cambridge. Preparations, reactions, and purification procedures were carried out under nitrogen or in a vacuum. Light petroleum is " AnalaR " material, b. p. 30—40°. Analytical data are given in Table 3.

σ-Allyl-π-cyclopentadienyldicarbonyliron.—Di-π-cyclopentadienyltetracarbonyldi-iron [9] (7·1 g.) in solution in tetrahydrofuran was stirred with 3% sodium amalgam for 1 hr. The resulting solution of the sodium salt, $Na^+[\pi\text{-}C_5H_5Fe(CO)_2]^-$ was slowly added to a large excess (30 ml.) of allyl chloride, and the mixture was stirred for 1 hr. The solvent and the excess of allyl chloride were removed under a vacuum, and the residue was extracted with light petroleum and the whole filtered. The filtrate was evaporated and the resulting red-brown oil was chromatographed on an acid-washed alumina column, elution being with light petroleum–ether. The yellow eluate was collected, the solvent removed under a vacuum, and the residue distilled at 45°/10^{-3} mm., to give an amber oil (*ca.* 34%), that decomposed at ~65°. The *compound* decomposed readily in air and was soluble in the common organic solvents.

σ-But-2-enyl-π-cyclopentadienyldicarbonyliron.—A solution of the compound $\pi\text{-}C_5H_5Fe(CO)_2Cl$ [9] (5·0 g.) in tetrahydrofuran, through which was passing a rapid stream of butadiene gas, was treated with an excess of sodium borohydride. After 20 min. light petroleum was added and, with care, water (50 ml.). A yellow-brown petroleum layer separated which was washed with water (3 × 50 ml.). The petroleum solution was dried ($CaCl_2$), filtered, and evaporated, giving an amber oil. Chromatography followed by distillation as before gave a deep amber-brown oil, that decomposed at ~60°. The compound has very similar properties to the σ-allyl compound (I; R = H).

TABLE 3.

	Found (%)			CO †		Required (%)			CO	
Compound	C	H	Fe *	(mole)	*M*	C	H	Fe	(mole)	*M*
$\pi\text{-}C_5H_5Fe(CO)_2\sigma\text{-}CH_2CH{=}CH_2$	55·0	4·6	24·8	—	204 ‡	54·8	4·6	25·6	—	219
$\pi\text{-}C_5H_5Fe(CO)_2\sigma\text{-}C_4H_7$	56·9	5·5	24·0	1·8	210 ‡	56·9	5·2	24·1	2·0	232
$\pi\text{-}C_5H_5Fe(CO)\pi\text{-}C_3H_5$	56·55	5·3	—	1·0	194 ‡§	56·9	5·3	—	1·0	190
$\pi\text{-}C_5H_5Fe(CO)\pi\text{-}C_4H_7$	58·9	6·2	28·2	—	—	58·6	6·3	27·5	—	—
$[\pi\text{-}C_5H_5Fe(CO)_2\pi\text{-}C_3H_6]_2{}^{2+}PtCl_6{}^{2-}$	28·2	3·2	—	—	—	28·35	2·6	—	—	—
$[\pi\text{-}C_5H_5Fe(CO)_2\pi\text{-}C_3H_6]^+ClO_4{}^-$	37·2	3·0	—	—	—	37·8	3·15	—	—	—
$[\pi\text{-}C_5H_5Fe(CO)_2\pi\text{-}C_4H_8]^+PF_6{}^-$	35·1	4·3	—	—	—	34·9	3·4	—	—	—
$[\pi\text{-}C_5H_5Fe(CO)_2\pi\text{-}C_4H_8]_2{}^{2+}PtCl_6{}^{2-}$	30·3	3·6	12·9 ¶	—	—	30·2	3·0	12·8	—	—
$[\pi\text{-}C_5H_5Fe(CO)_2PPh_3]^+Cl^-,H_2O$	60·95	4·8	—	—	—	58·6	6·3	—	—	—
$[\pi\text{-}C_5H_5Fe(CO)_2]_2Hg$	29·7	2·5	19·9	4·0	530 **	30·0	1·9	20·1	4·0	554

* By colorimetric determination of thiocyanate complex. † CO liberated by heating with I_2 at 120° and volume determined over mercury. ‡ Cryoscopic in benzene. § Isopiestic in ether. ¶ Cl: Found, 24·1. Reqd., 24·4%. ** Ebullioscopic in benzene.

π-Allyl-π-cyclopentadienylmonocarbonyliron.—(*A*) The allyl compound (I; R = H) (2 g.) contained in an evacuated silica vessel was irradiated with ultraviolet light for 6 hr. After

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[25] Winstein and Sonnenberg, *J. Amer. Chem. Soc.*, 1961, **83**, 3244.

[26] Hill and Richards, *J. Amer. Chem. Soc.*, 1961, **83**, 4216.

the evolution of gas had ceased, the product was chromatographed in light petroleum–ether on alumina as above. The eluate was collected, the solvent removed under a vacuum, and the residual solid was sublimed at 45°/10^{-3} mm. The yellow crystalline product was finally purified by resublimation (yield *ca.* 80%). It decomposes at ~65°. The *compound* is unstable both thermally and to atmospheric oxidation. It is readily soluble in the common organic solvents and is recovered unchanged from dimethyl sulphoxide. Attempts to prepare the compound by heating the σ-allyl complex, in the pure state or in dilute solution in an inert solvent, were unsuccessful. The main products were the binuclear complex $[\pi\text{-}C_5H_5Fe(CO)_2]_2$ and unidentified hydrocarbons.

(*B*) Chromatography of the reaction mixture from the preparation of the σ-allyl complex (I; R = H), as given above, gave a second yellow band on the column. The band was eluted with light petroleum–ether, the eluate collected, and the solvent removed, giving yellow crystals. The product was twice recrystallised from light petroleum and finally sublimed, giving the pure π-allyl complex in very small yield. Also isolated from the reaction mixture, as a third band on the column, was the yellow, crystalline compound, $[\pi\text{-}C_5H_5Fe(CO)_2]_2Hg$.[27]

π-Butadienyl-π-cyclopentadienylmonocarbonyliron.—The σ-but-2-enyl complex (I; R = Me) (1·5 g.) was irradiated with ultraviolet light for 24 hr. as described above. The resulting oil was chromatographed on an alumina column, first in light petroleum–ether and then in light petroleum. Removal of the solvent from the eluate gave an amber oil which was finally distilled at 40°/10^{-3} mm. (yield *ca.* 80%). The *compound* is an extremely air-sensitive oil and decomposes at ~60°. It is soluble in the common organic solvents and solutions appear stable under nitrogen. The compound is not formed by the thermal decomposition of the σ-but-2-enyl complex (I; R = Me).

π-Cyclopentadienyl-π-propenedicarbonyliron Salts.—*Chloride.* σ-Allyl-π-cyclopentadienyldicarbonyliron (2·0 g.) in light petroleum (50 ml.) was treated with dry hydrogen chloride. Immediately a pale yellow precipitate was formed, leaving a colourless petroleum layer. The petroleum was decanted and the precipitate was washed twice with petroleum and dried in vacuum (yield >90%). The chloride is very hygroscopic and soluble in water. Aqueous solutions react slowly, forming the cation $[\pi\text{-}C_5H_5Fe(CO)_2H_2O]^+$ which was identified by the infrared spectrum of the silicotungstate. In acetone solution the chloride decomposes within a few minutes, forming the neutral chloride $\pi\text{-}C_5H_5Fe(CO)_2Cl$.

Hexafluorophosphate. A concentrated aqueous solution of the chloride was treated with an aqueous solution of ammonium hexafluorophosphate. The yellow precipitate was separated by filtration, dried *in vacuo*, and recrystallised from liquid sulphur dioxide–ether (yield >90%).

The *hexachloroplatinate* was prepared from the chloride in an analogous manner by using hexachloroplatinic acid.

Perchlorate. A concentrated aqueous solution of the chloride was treated with a slight excess of silver perchlorate. The precipitate was extracted with acetone, and the solution filtered from silver chloride, concentrated, and treated with ether which precipitated the perchlorate. This was washed twice with ether and dried (yield ~60%). The perchlorate, hexachloroplatinate, and hexafluorophosphate are stable in air for short periods and decompose only slowly in acetone. They are very soluble in liquid sulphur dioxide. The perchlorate explodes violently, infrequently at room temperature but regularly at ~80°.

Conductivity Measurements.—Conductivities of the perchlorates, determined by using *ca.* 10^{-3}M-solutions in nitrobenzene at 25°, are tabulated.

Compound	Concn. (10^{-3}M)	Λ
$[\pi\text{-}C_5H_5Fe(CO)_2C_3H_6]^+ClO_4^-$	1·20	33·2
$[\pi\text{-}C_5H_5Fe(CO)_2C_4H_8]^+ClO_4^-$	1·16	33·3
$[\pi\text{-}C_5H_5Fe(CO)_2PPh_3]^+Cl^-,H_2O$	1·06	29·6

Similar results were obtained for liquid sulphur dioxide solutions at −35·6°.

High-resolution Nuclear Magnetic Resonance Spectra.—Measurements were made on a Perkin-Elmer spectrometer at 40 Mc./sec. The conditions of measurement are given in Table 2. The spectra of the cations in D_2O were unchanged after several hours and were the same as those obtained for the liquid sulphur dioxide solutions. Results are given in values with an overall estimated error of not greater than ±0·05.

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[27] Fischer and Böttcher, *Z. Naturforsch.*, 1955, **10**b, 600.

Infrared Spectra.—Measurements were made with a Perkin-Elmer model 21 spectrometer. The data and conditions of measurement are given in Table 2.

We thank Dr. C. B. Reese and Dr. L. E. Orgel for helpful discussions and Dr. N. Sheppard for assistance with the spectra. We also thank the Nickel Company (Mond) Ltd. for a generous gift of iron carbonyl, and The Hungarian Relief Fund for financial support (to P. L. I. N.).

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[*Received, May 8th*, 1962.]