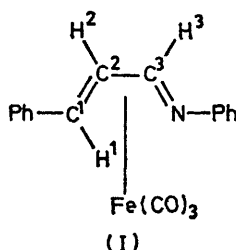


Some π -Hetero-1,3-diene Complexes of Iron Carbonyl

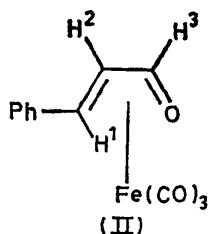
By A. M. Brodie, B. F. G. Johnson, P. L. Josty, and J. Lewis,* The Chemical Laboratory, Lensfield Road, Cambridge

Some π -(hetero-1,3-diene) complexes $\text{LFe}(\text{CO})_3$ (L = benzylideneacetone, chalcone, 2'-hydroxychalcone 2,6-dibenzylidenecyclohexanone, and *para*-substituted cinnamylideneaniline) and $\text{L}'\text{Fe}(\text{CO})_4$ (L' = chalcone, 2'-hydroxychalcone) have been synthesised. The u.v. spectra of the cinnamylideneaniline complexes are discussed. The $\text{LFe}(\text{CO})_3$ complexes (L = benzylideneacetone and cinnamylideneaniline) react with strong acid, protonation occurring on the heteroatom.

ALTHOUGH a large number of π -(1,3-diene)iron tricarbonyl complexes have been reported and their reactivity investigated^{1a} less is known of the corresponding heterodiene compounds. In such compounds, which may be regarded as derived from the basic butadiene unit by the replacement of one or more of the carbon atoms by oxygen or nitrogen, the possibility arises that the lone pair of electrons of the heteroatom is involved with the metal-ligand bond.^{1b} To date comparatively little structural information is available, although a single crystal X-ray analysis² of (cinnamylideneaniline)irontricarbonyl (I) has shown that the ligand is bonded in a manner analogous to that found for π -(1,3-diene) complexes, and that the lone pair on the nitrogen does not contribute to the bond to any significant extent. The influence of the more electronegative nitrogen (*i.e.* compared to carbon) is however quite apparent. The C²-C³ bond length of 1.36 Å is



considerably shorter than that (1.45 Å) observed for $\text{C}_4\text{H}_6\text{Fe}(\text{CO})_3$ ³ and closer to that found in $\text{C}_6\text{F}_8\text{Fe}(\text{CO})_3$ (1.37 Å).⁴ ¹H N.m.r. spectroscopic evidence for this bonding scheme in (cinnamaldehyde)irontricarbonyl⁵ (II) and (crotonaldehyde-*n*-butylamine)irontricarbonyl⁶ has also been presented.



In this paper we report the preparation and characterisation of several new iron carbonyl complexes with

¹ (a) G. E. Coates, M. L. H. Green, and K. Wade, 'Organometallic Compounds,' vol. II, Methuen, London, 1969, p. 65; (b) H. Tom Dieck and H. Bock, *Chem. Comm.*, 1968, 678.

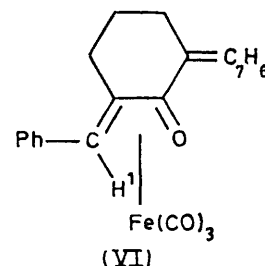
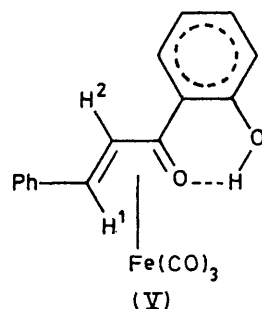
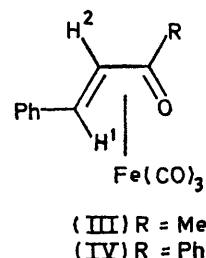
² A. de Cian and R. Weiss, *Chem. Comm.*, 1968, 348.

³ O. S. Mills and G. Robinson, *Acta Cryst.*, 1963, **16**, 758.

heterodienes involving either the $-\text{C}=\text{C}-\text{C}=\text{O}$ or $-\text{C}=\text{C}-\text{C}=\text{N}$ units and an evaluation of the importance of the heteroatom on the bonding and reactivity of these complexes. Two types of complex have been prepared: (i) those of general formula $\text{LFe}(\text{CO})_3$; (ii) those of general formula $\text{L}'\text{Fe}(\text{CO})_4$.

RESULTS AND DISCUSSION

(i) *Derivatives of the Type* $\text{LFe}(\text{CO})_3$.—Benzylideneacetone, chalcone, 2'-hydroxychalcone, and 2,6-dibenzylidenecyclohexanone all react with enneacarbonyl-di-iron in toluene under mild conditions (70–80°) to give air-stable crystalline solids of composition $\text{LFe}(\text{CO})_3$,



(III)–(VI). The molecular weights and precise molecular formulae of these compounds have been determined by the mass spectrometric method. In agreement with the formulation as iron tricarbonyl derivatives their i.r. spectra (in the region 2200–1800 cm^{-1}) show three strong $\nu(\text{C}=\text{O})$ bands (Table 1), typical of (diene)- $\text{Fe}(\text{CO})_3$ systems.⁷ Strong bands in the region 1600–1700 cm^{-1} found in the spectra of the free $\alpha\beta$ -unsaturated

⁴ M. R. Churchill and R. Mason, *Proc. Chem. Soc.*, 1964, 226.

⁵ K. Stark, J. E. Lancaster, H. D. Murdoch, and E. Weiss, *Z. Naturforsch.*, 1963, **19b**, 284.

⁶ S. Otsuka, T. Yoshida, and A. Nakamura, *Inorg. Chem.*, 1967, **6**, 20.

⁷ R. Pettit and G. F. Emerson, *Adv. Organometallic Chem.*, 1964, **1**, 10.

ketones disappear on co-ordination. Weiss *et al.*⁵ have assigned a band at 1477 cm⁻¹ in the spectrum of (cinnamaldehyde)irontricarboxyl (II) to the C—O stretching vibration of the ketonic group. Although the LFe(CO)₃ compounds show bands in this region the complexity of their spectra prevents definite assignment.

TABLE 1

Infrared spectral data for the complexes (cm⁻¹)

Compd.	$\nu(\text{C}\equiv\text{O})$ ^a	Other
(I)	2059, 2000, 1987	
(II) ^c	2073, 2015, 1994	
(III)	2065, 2005, 1985	
(IV)	2065, 2010, 1985	
(V)	2065, 2020, 1995	$\nu(\text{O—H})$ ^b 3000 wbr
(VI)	2065, 2010, 1985	
(VII)	2095, 2033, 2020, 1994	$\nu(\text{C=O})$ ^a 1655
(VIII)	2097, 2035, 2024, 1999	$\nu(\text{C=O})$ ^a 1630; $\nu(\text{O—H})$ ^b 2950 wbr
(IX)	2098, 2093, 2036, 2025, 2017, 2002, 1997	$\nu(\text{C=O})$ ^a 1694, 1686
(X)	2060, 2001, 1989	
(XI)	2061, 2003, 1990	
(XII)	2056, 1997, 1984	
(XIII)	2057, 1997, 1984	
(XIV)	2054, 1994, 1981	

^a For cyclohexane solutions. ^b For carbon disulphide solution and hexachlorobutadiene mull. ^c From ref. 5 (n-hexane).

Our main evidence for a π -bonded system is based on ¹H n.m.r. data. For typical π -(1,3-diene)irontricarboxyl complexes⁸ the *inner* protons resonate in the region τ 4–5 and the *outer* protons in the region τ 7–9. These signals are shifted upfield by about τ 0–0.5 and 2–4 respectively from the value observed for the free diene. In the spectrum of the (benzylideneacetone)-iron tricarboxyl adduct (III) (Table 2) two signals are

TABLE 2

¹H N.m.r. spectral data for the complexes (τ)

Compd.	$\text{H}^1(J_{12})$	$\text{H}^2(J_{23})$	Other ^a
(I) ^b	6.73 (9.5) ^a	4.46 (3.0)	
(II) ^{c,f}	6.87 (9.6)	4.05 (\approx 0)	H^3 2.48
(III) ^d	6.90 (9.0)	3.98	CH_3 7.50
(IV) ^d	6.54 (9.5)	3.22	
(V) ^b	6.61 (9.5)	3.43	OH 0.37 ^j
(VI) ^d	6.90		CH_2 7.30, 8.15
(VII) ^b		4.85 (11.5)	
(VIII) ^b		4.90 (11.0)	OH —2.21 ^j
(IX) ^{e,g}	4.83 (12.5)	5.25 (4.0)	H^3 0.78
(X) ^b	6.75	4.36	
(XI) ^b	6.78	4.42	
(XII) ^b	6.74	4.45	OCH_3 6.35
(XIII) ^b	6.67	4.47	OCH_3 6.28
(XIV) ^d	6.58	4.41	OCH_3 6.25

^a H (Phenyl) 2–3 τ . ^b In CS₂. ^c In CCl₄. ^d In CDCl₃. ^e In (CD₃)₂CO. ^f From ref. 5. ^g From ref. 10. ^h J values similar for *para*-substituted complexes. ⁱ H^3 obscured by H (Phenyl). ^j Free ligand value —2.64 τ .

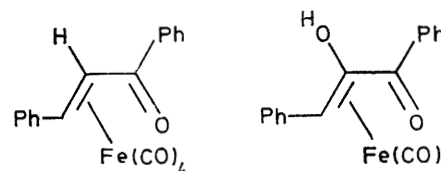
observed at τ 6.90 (doublet) and τ 3.98 (doublet); these we assign to the olefinic protons H^1 and H^2 respectively. This is reasonable since the former signal shows a significant shift ($\Delta\tau = 3.65$) and the latter little shift ($\Delta\tau = 0.74$) from those observed for the free ligand.

⁸ M. L. Maddox, S. L. Stafford, and H. D. Kaesz, *Adv. Organometallic Chem.*, 1965, **3**, 92.

⁹ Ref. 8, p. 65.

The coupling constant (J_{12}) falls from 17 Hz for the free ligand to 9 Hz in the complex. This parallels the behaviour observed for (cinnamaldehyde)irontricarboxyl (II). This effect of decreasing the *trans*-coupling constant has been observed for many other π -olefin complexes of low-valent transition metals.⁹ The spectra of the other complexes reported in this paper may be assigned similarly (see Table 2).

(ii) *Complexes of the Type L'Fe(CO)₄*.—In addition to the tricarboxyl complexes described above we have also obtained tetracarboxyl derivatives of the type L'Fe(CO)₄, (VII) and (VIII). These are produced under milder preparative conditions (toluene, *ca.* 40°). These com-

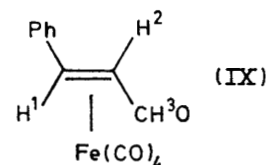


(VII)

(VIII)

plexes show typical four band spectra in the i.r. region (Table 1) and in addition a strong band at *ca.* 1630 cm⁻¹ which we assign to the vibration of the unco-ordinated ketonic double bond. As expected the ¹H n.m.r. spectra exhibit two signals (AB pair) centred at *ca.* τ 4.9 (J_{12} 11 Hz) (Table 2).

The i.r. spectrum of the previously reported¹⁰ (cinnamaldehyde)irontricarboxyl complex (IX) is of interest. We find the spectrum (cyclohexane) in the 2000 cm⁻¹ region shows seven strong absorptions assignable as $\nu(\text{C=O})$ as well as two $\nu(\text{C=O})$ bonds at 1694 and 1686 cm⁻¹ (Table 1). The i.r. data indicate the complexed aldehyde exists as two different conformers which



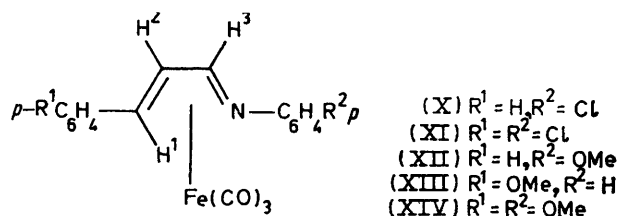
(IX)

must be in equilibrium since the aldehyde proton (H^3) resonates as the expected doublet in the n.m.r. at τ 0.78 (J_{23} 4.0 Hz). In contrast the co-ordinated chalcones show a preference for one conformation, presumably *s-trans*. We favour this conformation since if the *s-cis* form was produced conversion into the LFe(CO)₃ complex (IV) would be expected to be facilitated. This is not the case and the conversion LFe(CO)₄ (VII) into LFe(CO)₃ (IV) (L = chalcone), which may be followed by i.r., takes *ca.* 9 h (at 80° in toluene) [*cf.* for the cinnamaldehyde complex (IX) the reaction takes only 15 min under analogous conditions].

(iii) *Ultraviolet Spectra of the Complexes LFe(CO)₃*.—The u.v. spectra of the hydrocarbon polyenes are characterised by an intense absorption band in the u.v.

¹⁰ E. Weiss, K. Stark, J. E. Lancaster, and H. D. Murdoch, *Helv. Chim. Acta*, 1963, **46**, 288.

which is assigned to a $\pi \rightarrow \pi^*$ transition.¹¹ The wavelength of this absorption and its intensity are governed by the length of the conjugated polyene chain, the wavelength and intensity becoming progressively greater as the length of the conjugated chain increases. The introduction of a $-C=N-$ function into such a chain also serves to increase the wavelength and intensity values of the band.¹² The effect of co-ordination on conjugated polyenes (whether or not they contain a heteroatom) has not been examined in any detail. Birch and Fitton¹³ examined the Vitamin A aldehyde adduct of iron tricarbonyl and considered that, on the basis of the u.v. spectrum, the introduction of the $Fe(CO)_3$ unit is equivalent to the reduction of the number of double bonds by one. In this work we were able to synthesise a series of closely related derivatives (X)—(XIV). These compounds were of interest for two main reasons. First we were able to examine the effect of the $Fe(CO)_3$ moiety on the u.v. spectrum of the organic group. Secondly, the effect of change in the *para*-substituents,



R^1 and R^2 , on the spectrum of both the free ligands and the corresponding complexes could be readily studied.

The u.v. spectra of the free ligands are recorded in Table 3. The spectrum of cinnamylideneaniline in

TABLE 3

Ultraviolet spectral data for (cinnamylideneaniline)iron-tricarbonyl complexes (nm) ^a

Compd.	Ligand	Complex
(I)	296 (26.7), 330 (14.2) ^b	281 (21.7), 305 (17.2)
(X)	298 (29.7), 335 (18.5) ^b	282 (21.9), 305 (17.0) ^b
(XI)	304 (29.9), 335 (20.3) ^b	286 (25.3), 307 (22.1) ^b
(XII)	294 (26.9), 345 (19.5)	284 (21.7), 305 (17.9) ^b
(XIII)	310 (23.2), 324 (24.2), 340 (21.1) ^b	286 (20.9), 307 (20.5) ^b
(XIV) ^c	310, 322, 348	287, 310 ^b

^a In cyclohexane, molar extinction coefficients ($\times 10^{-3}$) in parentheses. ^b Inflexion. ^c Insolubility prevented measurement of extinction coefficients.

cyclohexane shows a main region of absorption centred at 296 nm ($\epsilon_{\max} = 26.7 \times 10^3$) with an inflexion at 330 nm ($\epsilon_{\max} = 14.2 \times 10^3$). In a more polar solvent (*e.g.* ethanol) the maximum at 296 nm shifts to 309 nm in agreement with assignment to a $\pi \rightarrow \pi^*$ transition. The introduction of *para*-substituents, especially *p*-OMe causes perturbation of the spectrum.

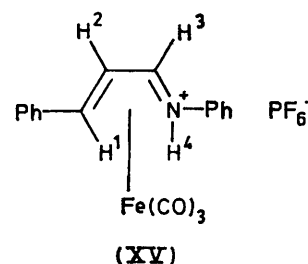
The unsubstituted (cinnamylideneaniline)iron-tricarbonyl complex (I) exhibits an absorption of 281 nm ($\epsilon_{\max} = 21.7 \times 10^3$) superimposed on an intense end

¹¹ H. H. Jaffe and M. Orchin, 'Theory and Applications of Ultraviolet Spectroscopy,' Wiley, New York, p. 228.

¹² H. C. Barany, E. A. Braude, and M. Pianka, *J. Chem. Soc.*, 1949, 1898.

absorption which extends into the visible. The u.v. spectra of (diene)irontricarbonyl complexes will be discussed in more detail in a later publication but the maxima may be assigned to essentially a $\pi \rightarrow \pi^*$ transition of the co-ordinated ligand. The observed increase in energy of this transition may be attributed to two related effects; first a change in configuration from *s-trans* in the free ligand to *s-cis* in the complex; secondly partial loss of conjugation on co-ordination (since cyclohexa-1,3-dienes which must retain their configuration on co-ordination show similar effects¹⁴). In contrast with the free ligand, introduction of the *para*-substituents causes very little change in the spectrum, suggesting that there has been a considerable interruption of conjugative effects. Charge transfer from the essentially non-bonding metal orbitals into the ligand antibonding orbitals must be significant.

(iii) *Reactivity of the Complexes* $LF_3Fe(CO)_3$.—The $LF_3Fe(CO)_3$ complexes react with strong acid, protonation occurring on the heteroatom. Thus reaction of (cinnamylideneaniline)irontricarbonyl (I) affords the moderately air stable salt (XV). Although deprotonation of



(XV) occurs in most solvents (*e.g.* water, ethanol, chloroform, and nitromethane) yielding the original neutral complex (I), the complex can be recovered unchanged from acetone. Evidence for the formulation (XV) is as follows. In the n.m.r. (Table 4) resonances at

TABLE 4

Spectral data for protonated complexes

Complex	¹ H n.m.r. (τ)	I.r. (cm^{-1})
(XV)	H ¹ 5.50 ($J_{12} = 11.0$) ^a H ² 2.97 ($J_{23} = 3.5$) H ³ 1.89	$\nu(C\equiv O)$ 2115, 2050 br ^c $\nu(N-H)$ 3235
(XVI)	H ¹ 6.39 ($J_{12} = 10.5$) ^b H ² 3.63 CH ₃ 7.37	$\nu(C\equiv O)$ 2080, 2025, 2000 ^d

^a In $(CD_3)_2CO$ solutions. ^b In conc. H_2SO_4 . ^c As Nujol mull. ^d In CF_3CO_2H .

τ 5.50 (d), 2.92 (dd), and 1.82 (d) can be assigned to the olefinic protons, H¹, H², and H³ respectively. Double-irradiation experiments show H² is coupled with both H¹ ($J_{12} = 11.0$ Hz) and H³ ($J_{23} = 3.5$ Hz) but $J_{13} \approx 0$. The spectrum is similar to that observed for the neutral complex (I) but with the olefinic protons shifted downfield ($\Delta\tau$ ca. -1). The N^+-H proton was not observed

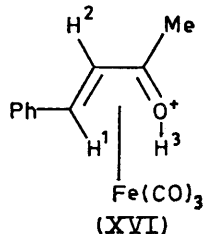
¹³ A. J. Birch and H. Fitton, *J. Chem. Soc. (C)*, 1966, 2060.

¹⁴ A. J. Birch, P. E. Cross, J. Lewis, and S. B. Wild, *J. Chem. Soc. (A)*, 1968, 332.

but would be expected to be broadened because of the electric quadrupole moment of the nitrogen nucleus. No high-field resonances indicative of protonation on the metal could be detected. The i.r. spectrum (Table 4) however, exhibits a $\nu(\text{N-H})$ frequency at 3235 cm^{-1} , pointing to protonation of the nitrogen atom, and $\nu(\text{C=O})$ bands appear at $2115(\text{s})$ and $2050\text{ cm}^{-1}(\text{s,br})$, *ca.* 50 cm^{-1} higher than for the neutral complex.

Although the $-\text{C}=\text{C}-\text{C}=\text{O}$ heterodiene complexes are recovered unchanged from HPF_6 -ether solutions they are protonated in strong acid solution. Thus (III) dissolves in concentrated sulphuric acid (from which it can be reprecipitated on addition of water) to give a red solution. The n.m.r. (Table 4) is similar to that observed for the neutral complex (III) but with the olefinic protons resonating slightly downfield ($\Delta\tau$ *ca.* -0.4). No high-field signal can be detected but the i.r. spectrum ($\text{CF}_3\text{CO}_2\text{H}$) shows the three $\nu(\text{C=O})$ bands shifted by *ca.* 20 cm^{-1} to higher frequencies (Table 4). This suggests reversible protonation of the oxygen atom occurs to give (XVI) and the proton rapidly exchanges with the solvent, although protonation of the metal cannot be entirely excluded.

Examination of the 2'-hydroxychalcone complex (V) confirms that the oxygen atom in a co-ordinated $-\text{C}=\text{C}-\text{C}=\text{O}$ π -heterodiene system can act as a basic site.



In the free ligand the hydroxy-proton is strongly intramolecularly bonded to the ketonic carbonyl group. As a consequence $\nu(\text{O-H})$ is seen as a weak broad band in the i.r. region and the hydroxy-proton resonates at $\tau -2.64$ in the n.m.r. spectrum.¹⁵ On co-ordination the possibility arises that the proton could interact with the metal atom as has been observed in ferrocenyl alcohols and arene chromium tricarbonyl compounds.¹⁶ However, in the tricarbonyl complex (V) the O-H stretching frequency is still observed as a characteristic broad weak band indicating the hydrogen bonding is essentially unaltered. In the ^1H n.m.r. spectrum of (V) the resonance of the hydroxy-proton is shifted upfield by τ *ca.* 3 (Table 2) from the value observed for the free ligand. Similar shifts are observed for the 'outer' proton in the π -(1,3-diene)irontricarbonyl complex. In the analogous iron tetracarbonyl complex (VIII) only a small shift (τ *ca.* 0.4) is observed.

Typical reactions¹⁷ show that the co-ordinated ketonic group in the $\text{LFe}(\text{CO})_3$ compounds has lost its characteristic properties as might be anticipated from

the donor character of the $\text{Fe}(\text{CO})_3$ grouping. For instance, they fail to form 2,4-dinitrophenylhydrazone derivatives. The $\alpha\beta$ -unsaturated ketone (*e.g.* benzylideneacetone) may be readily displaced under mild conditions (*ca.* 30°) by triphenylphosphine to give $(\text{Ph}_3\text{P})_2\text{Fe}(\text{CO})_3$. In contrast it has been found⁶ that for the cinnamylideneaniline complex (I) one carbon monoxide group is displaced to give an $\text{LFe}(\text{CO})_2\text{PPh}_3$ complex.

EXPERIMENTAL

^1H N.m.r. spectra were obtained on Perkin-Elmer R10 and Varian HA 100 spectrometers using tetramethylsilane as internal standard. I.r. and u.v. spectra were determined using Perkin-Elmer 257 and Unicam SP 800 machines. Mass spectra were obtained on an A.E.I. MS12 mass spectrometer at 70 eV .

All reactions were carried out under nitrogen although the complexes are moderately stable with respect to aerial oxidation. Elemental analyses (Table 5) were determined

TABLE 5
Analytical data for the complexes

Complex	Found (%)			Calc. (%)		
	C	H	N	C	H	N
(III)	54.7	3.8		54.6	3.5	
(IV)	62.7	3.9		62.1	3.5	
(V)	59.5	3.4		59.4	3.3	
(VI)	65.8	4.7		65.9	4.4	
(VII)	61.2	3.4		60.8	3.2	
(VIII)	57.9	3.3		58.2	3.1	
(X)	56.7	3.1	3.85	56.7	3.2	3.7
(XI)	51.6	2.8	3.3	52.0	2.7	3.4
(XII)	60.5	4.1	3.7	60.5	4.0	3.7
(XIII)	60.6	4.2	4.2	60.5	4.0	3.7
(XIV)	58.9	4.1	3.2	59.0	4.2	3.4
(XV) ^a	44.0	3.1	2.8	43.8	2.9	2.8

^a P, 6.2% (calc. 6.3).

by the Microanalytical Laboratory, University College. The *para*-substituted (cinnamylideneaniline)irontricarbonyl complexes were prepared according to the method described by Nakamura *et al.*⁶ for the preparation of (I).

Tricarbonyl(benzylideneacetone)iron (III).—Benzylideneacetone (1.04 g) and enneacarbonyldi-iron (2.60 g) were allowed to react in toluene (30 ml) at 60° for 4 h. On cooling, the solution was filtered through Kieselguhr, the solvent removed, and the residue chromatographed on silica (Sorbisil M60). Elution with toluene and subsequent evaporation gave the *product* as red crystals (0.61 g, 32%), m.p. $88-90^\circ$.

Tricarbonyl(chalcone)iron (IV).—Chalcone (1.38 g) and enneacarbonyldi-iron (2.33 g) were heated in toluene (30 ml) at 80° for 9 h. The mixture was then treated as above to give the *product* as red crystals (0.32 g, 14%), m.p. 90° (decomp.). A similar procedure afforded **tricarbonyl-(2'-hydroxychalcone)iron (V)** as red crystals (30%).

Tricarbonyl-(2,6-dibenzylidenecyclohexanone)iron (VI).—A mixture of the ligand (2.8 g) and the iron carbonyl (3.86 g) in benzene (25 ml) was heated at 40° for 5 h. Chromato-

¹⁵ J. C. Kotz and D. G. Pedrotty, *Organometallic Chem. Rev. (A)*, 1969, **4**, 479.

¹⁷ S. Patai, 'Chemistry of the Carbonyl Group,' Interscience, 1966, p. 375.

¹⁵ J. R. Dyer, 'Applications of Absorption Spectroscopy of Organic Compounds,' Prentice-Hall, 1965, pp. 36 and 91.

graphy on alumina (grade 'H'), with toluene as eluant gave a red fraction from which the *product* was isolated as orange crystals, m.p. 88—90°.

Tetracarbonyl(chalcone)iron (VII).—Chalcone (1.19 g) and enneacarbonyldi-iron (2.20 g) were heated in toluene (20 ml) at 40° for 1 h. Chromatography in toluene on silica afforded the *product* as yellow crystals (0.55 g, 26%), m.p. 88°. *Tetracarbonyl-(2'-hydroxychalcone)iron* (VIII) was prepared by the same method (37%).

Reaction of Compound (I) with HPF₆.—An excess of 65% HPF₆ solution was added dropwise to a stirred ether solution of (I). The orange precipitate of *tricarbonyl-(cinnamylideneaniline)iron hexafluorophosphate* (XV) which

formed was filtered off and washed with anhydrous ether. The salt can be recrystallised unchanged from acetone-ether.

Reaction of Compound (III) with Triphenylphosphine.—A mixture of the iron complex (III) (0.08 g) and triphenylphosphine (0.08 g), after stirring in benzene at 30° for 2.5 h to yield a yellow precipitate of tricarbonylbis(triphenylphosphine)iron (Found: C, 70.9; H, 4.9. C₃₉H₃₀FeO₃P₂ requires C, 70.6; H, 4.5%).

We thank the S.R.C. for scholarships (to A. M. B. and P. L. J.).

[2/216 Received, 2nd February, 1972]