Reaction of Tricarbonyl(2—6-η-hexadienium)iron with Amines, Triphenylphosphine, and Triphenylarsine: A Method for the Preparation of Triene Complexes

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Aniline and diphenylamine add to the substituted end of the diene in tricarbonyl(2—6-η-hexadienium)iron to give dienylamine complexes having *syn* geometry. Tertiary amines, PPh_3, and $AsPh_3$ add to the unsubstituted end to give quaternary adducts having *anti* geometry. The tertiary amine adducts undergo elimination when heated *in vacuo* to give the *syn*-hexatriene complex in good yield. Tricarbonyl(2–6-η-heptadienium)iron is converted directly into the *syn*-heptatriene complex on treatment with tertiary amines, but forms *anti* adducts with PPh_3. Hydrogen-2 labelled *syn*-[Fe(hexatriene)(CO)$_3$] protonates at its unco-ordinated double bond.

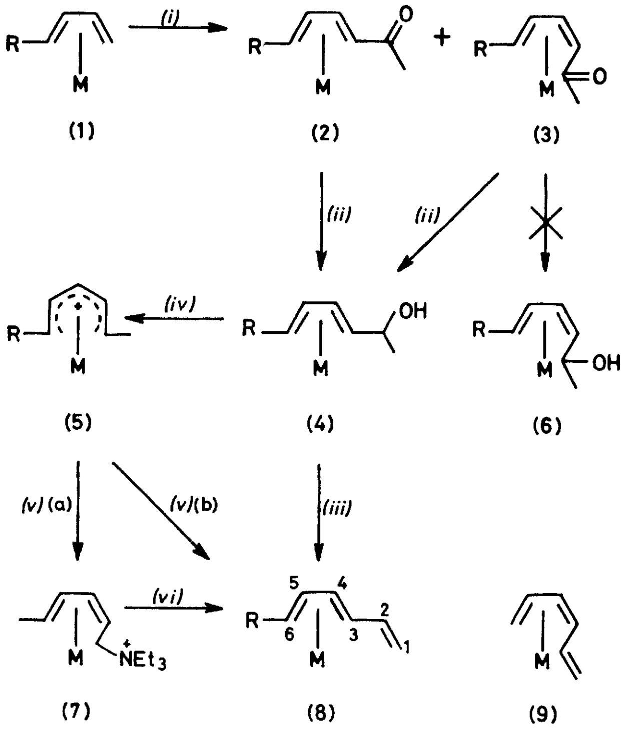
THE chemistry of conjugated diolefins bound to tricarbonyliron has expanded considerably in recent years. Complexes containing cyclic ligands have received most attention.[1] In an attempt to extend the chemistry of acyclic systems, a study of conjugated triene complexes was undertaken. Triene complexes of tricarbonyliron have been prepared by direct reaction of a triene and an iron carbonyl, and in lower yield by reaction of the tricarbonyl(hexadienium)iron cation with alumina.[2-4] It was felt that synthesis by elaboration of readily available [Fe(diene)(CO)$_3$] complexes might be more useful as it would allow production of a greater range of specifically substituted triene complexes.

RESULTS

The method outlined in Scheme 1 was used to prepare the triene complexes (8). Friedel–Crafts acylation of [Fe(diene)(CO)$_3$] has been studied in detail.[5] Initially, the trienes (8) were obtained by dehydrating the alcohols (4) on silica gel. This method was slow (4—7 d at 23 °C). Thus, as an alternative, reaction of the well known salts (5) with tertiary amines was examined. The monosubstituted salt (5a) on treatment with NMe_3 or NEt_3 gave the adducts (7). Triphenyl-phosphine and -arsine also reacted with (5a) to form adducts but no reaction was observed with triphenylstibine. The tertiary amine adducts when heated slowly *in vacuo* with the use of a condenser gave the triene (8a) in good yield. Attempts to abstract a proton from (5a) using hindered bases were not successful; 1,8-bis(dimethylamino)-naphthalene and the resin Deacidite G (SRA-99), in its NEt_2 form, both gave adducts while no reaction was observed with dicyclohexyl(ethyl)amine. The disubstituted salts (5b) and (5c), in contrast to (5a), deprotonated readily on treatment with tertiary amines. Triphenylphosphine reacted with (5b) and (5c) to form adducts but no reaction was observed with $AsPh_3$ or $SbPh_3$. The 1,1-dideuterio-derivative of (8a) was synthesised by starting with (1a) and $CD_3COCl–AlCl_3$. Hydrogen-1 n.m.r. spectroscopy demonstrated that protonation of this complex took place at the unco-ordinated ^{1,2} double bond.

DISCUSSION

The observation that (5a) formed an adduct, (7), with NEt_3 whereas (5b) gave the triene (8b) led to the suggestion that steric effects were a dominant factor in the reaction of cations (5) with tertiary amines.[6] Thus adduct formation was not observed between a secondary carbon (in a cation) and tertiary nitrogen; proton abstraction or addition at a primary carbon was observed. Since this was in contrast to the known results for



(1) (2) (3) (4) (5) (6) (7) (8) (9)

SCHEME 1 M = Fe(CO)$_3$, R = H (*a*) or Me (*b*). (*i*) MeCOCl–AlCl$_3$; (*ii*) [BH$_4$]$^-$; (*iii*) silica gel; (*iv*) HPF$_6$; (*v*) NEt$_3$; (*vi*) heat *in vacuo*

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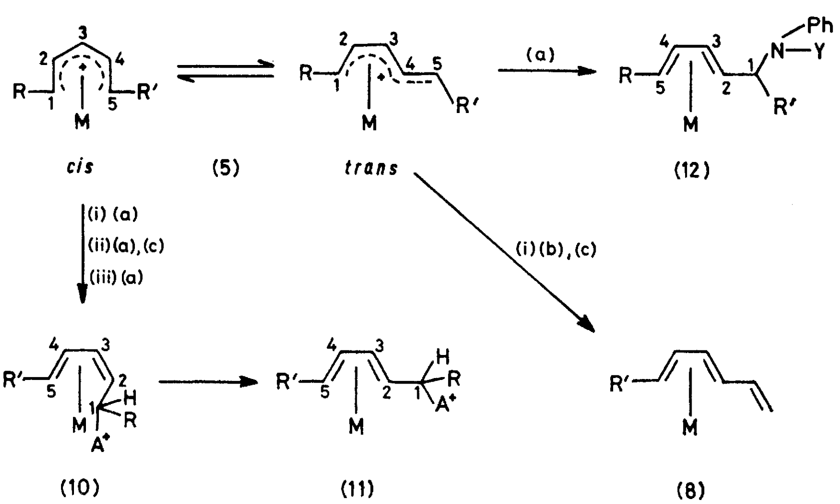
$[OH]^-$, $[OR]^-$,[7] and 1,3-dimethoxybenzene,[8] all of which add to the substituted or secondary end of (5a), it was decided to determine the structure of (7) and to examine the reaction of (5) with a range of Group 5 nucleophiles.



SCHEME 2 (a) R = H, R′ = Me; (b) R = R′ = Me; (c) R = Me, R′ = Et; A = NEt_3 (i), PPh_3 (ii), or $AsPh_3$ (iii)

Carbon-13 n.m.r. spectra at 15.03 MHz (p.p.m. from $SiMe_4$) [a]

Complex	C^1	C^2	C^3	C^4	C^5	R	R′	$\Delta(C^2,C^3)$
(10, ia) [b]	59.1 (br)	41.7	82.9	96.3	59.1		20.1	13.4
(10, iia) [b]	25.0 (42)	43.0 (10)	82.0	96.5	60.8		19.8	14.5
(10, iia) [c]	24.8 (42)	41.0 (9.8)	80.8 (2.9)	96.4	60.7		20.3	15.6
(11, iia) [d]	28.4 (46)	43.6 (8.8)	83.6 (2.9)	86.8	59.3		19.0	3.2
(11, iiia) [c]	31.4	44.8	82.9	86.9	59.2		19.0	4.0
(10, iib) [c]	28.7 (34)	53.0 (9.8)	79.9 (2.9)	96.6	60.5	17.7	19.9	16.7
(11, iib) [d]	33.6 (38)	56.5 (6.0)	83.4 (2.0)	85.3	59.6	19.7	18.8	1.9
(10, iic) [c]	29.2 (37)	51.7 (11)	79.5 (br)	95.6	69.6	17.7	28.7 [e]	16.1
(11, iic) [d]	34.8 (40)	54.7 (6.0)	82.8 (br)	84.5	68.8	19.8	27.4 [e]	1.7

[a] $J(^{31}P-^{13}C)$ values are given in parentheses. [b] In MeCN solution. [c] In $CDCl_3$ solution. [d] In $CDCl_3$ solution, after 48 h. [e] CH_2.

Structure of the Quaternary Adducts.—Hydrogen-1 n.m.r. spectra of the NMe_3 and NEt_3 adducts of (5a) were not useful, due to overlapping and the large alkyl resonances. In an attempt to simplify the latter problem an attempt was made to prepare the triphenylamine adduct. However, no reaction was observed between NPh_3 and (5a). The better known ligands PPh_3 and $AsPh_3$ did form adducts. The ^1H n.m.r. spectrum of the arsine compound contained an AB quartet with one side coupled at τ 6.28. This suggests that $AsPh_3$ has added to the unsubstituted end of (5a) to produce a methylene group. Resonances expected for the coordinated diene hydrogens were observed at τ 4.8 and 8.65. Musco and his co-workers [9] showed that the position of the latter can be used to distinguish the *syn-anti* and *syn-syn* forms (10) and (11). Thus the structure is *syn-syn*, (11, iiia), Scheme 2. The large value of ΔAB, 0.64 p.p.m., and the unequal coupling to H^2 probably means that rotation about the C^1–C^2 bond is slow. Analogous results were obtained for the phosphine compound except that here the structure was *syn-anti*, (10, iia). Due to the unsatisfactory nature of the ^1H n.m.r. spectra of the amine adducts, ^{13}C spectra were obtained for a range of compounds (Table). It was possible to fully assign the spectrum of the PPh_3 adduct of (5a) with the aid of the three observed ^{31}P–^{13}C coupling constants. In spectra obtained with either off-resonance or no ^1H decoupling the resonance at 25 p.p.m. is a triplet of doublets. This confirms the site of addition. The very close similarity of the spectra of (10, ia) and (10, iia) suggests that they have the same structure. The spectrum of the triphenylarsine compound which had structure (11, iiia) was quite different. The PPh_3 compound, initially *syn-anti*, (10, iia), slowly isomerised in $CDCl_3$ solution to the *syn-syn* form (11, iia). Since the *syn* isomer is probably less crowded and more stable, isomerisation from *anti* to *syn* is favoured. In the present case, impurities in the $CDCl_3$ may be catalysing the isomerisation.

The change from *syn-anti* to *syn-syn* is reflected in the C^3,C^4 chemical-shift difference $\Delta(C^3,C^4)$ (Table). This difference may be a useful alternative to the ^1H chemical-shift method for distinguishing *syn-syn* and *syn-anti* forms. In the reaction of (5c) with PPh_3 two products are possible. When the ^{13}C n.m.r. spectrum of the product is compared with that of (10, iib) the C^1 methyl chemical shift and its downfield shift on isomerisation is

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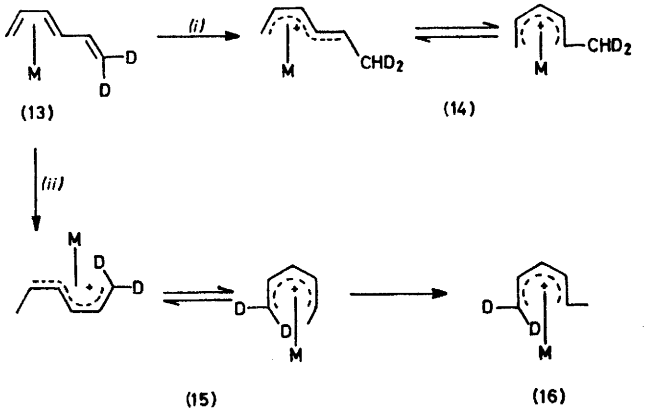
almost identical in both cases. This, together with the upfield shift observed for both C^5 substituents, R′, indicates that PPh_3 has added to the less sterically hindered C^1 end of (5c), (10, iic). Musco and his co-workers [10] examined the reaction of primary and secondary amines with (5b). Strong bases react in an *exo* manner with the *cis* form of the cation to yield *syn-anti* products. The much less basic aromatic amines react with the more active *trans* form giving *syn-syn* products. Similar results have been reported for the unsubstituted [Fe(dienium)$(CO)_3$] cation.[11] Triethylamine is a strong base and only the expected *syn-anti* isomer, the result of attack on *cis*-(5a), is observed. Since the triphenylphosphine adducts were found to have *syn-anti* geometry it appears that this nucleophile also reacts with the *cis* forms of (5a), (5b), and (5c). Triphenylphosphine, however, is not a strong base and it can only be suggested that steric factors favour attack on the *cis* isomer. The mode of triphenylarsine addition to (5a) is not clear because the reaction is slow and isomerisation during the reaction cannot be ruled out.

It was of interest to examine the reaction of the less sterically demanding primary and secondary amines aniline and diphenylamine with (5a). Hydrogen-1 n.m.r. spectra of the products clearly showed that nucleophilic attack was at the substituted end of (5a) and that the geometry was *syn-syn*. This is in contrast to the results reported here for tertiary nucleophiles but in line with those quoted above for $[OR]^-$ and the secondary C^2 carbon of 1,3-dimethoxybenzene. Thus, in the absence of steric interactions, electronic factors direct nucleophiles to the most substituted site. Not all nucleophiles show high selectivity in reactions with (5a). Sodium tetrahydroborate [7] and CdR_2 reagents (with one exception) show little selectivity.[12] For example, $CdMe_2$ and $CdPr^i_2$ were indiscriminate, each gave equal amounts of the products resulting from attack at both ends of *cis*-(5a). It appears that Na$[BH_4]$ and CdR_2 have steric requirements intermediate between those of the simpler secondary and tertiary nucleophiles, which are sufficient to prevent attack on *trans*-(5a) but not great enough to distinguish the two ends of *cis*-(5a).

Preparation of the Triene Complexes.—The cations (5b) and (5c) reacted with triethylamine to give the trienes in good yield. Hydrogen-1 n.m.r. spectra indicated that only *syn-syn* trienes were formed. This suggests that when abstracting a proton (and unlike adduct formation) NEt_3 reacted with *trans*-(5b) and -(5c). No evidence for intermediates was found when the reaction was carried out in an n.m.r. tube. The ^1H n.m.r. spectrum of (8c) contains resonances typical of a monosubstituted olefin. There are two possible isomers of *trans*-(5c), that shown in Scheme 2 and another with R and R′ interchanged. The structure of the triene (8c) suggests that it is the least sterically hindered end of the latter which reacted with NEt_3.

When the adduct (7) was heated *in vacuo* the *syn* hexatriene complex (8a) (Scheme 1) was obtained. The triene was distilled as it formed and the residue was found to contain only protonated amine, $[NEt_3H][PF_6]$. The absence of metal-containing species in the residue indicates that only the C^1–N bond is broken. This reaction is unlike the Hoffman elimination since no base was present and addition of $[OH]^-$ had no effect. It is probably a case of favoured decomposition of an unstable quaternary amine. An *anti* triene might have been the expected result of decomposition of this *syn-anti* adduct; however, it is possible that isomerisation took place during the reaction. No triene complexes were obtained when the triphenylphosphine adducts were heated *in vacuo*. Attempts to produce the *anti* triene from the *anti* ketone (3) were not successful. Reduction with Na$[BH_4]$ in ethanol at 0 °C gave only the *syn* alcohol (4) as reported by Knox and his co-workers.[5]



SCHEME 3 Protonation of unco-ordinated (*i*) and co-ordinated (*ii*) double bonds

Protonation of Tricarbonyl(3—6-η-*hexa*-1,3,5-*triene*)-*iron* (8a).—This reaction could proceed *via* addition to either the unco-ordinated, (*i*), or the co-ordinated double bond, (*ii*). This is illustrated in Scheme 3 for the 1,1-dideuterio-derivative (13). Protonation of (13) at its unco-ordinated double bond will lead to the *trans* form of the *syn* cation (14). If the co-ordinated double bond was protonated the *anti* methyl cation (15) would result. Low-temperature ^1H n.m.r. studies have shown that a closely related *anti* cation isomerises readily to the *syn* form above 0 °C.[13] If electrophilic attack takes place as illustrated in Scheme 3 then it is probably true that the unco-ordinated double bond will offer the energetically more favourable route. However, either a higher basicity at the co-ordinated double bond or *endo* protonation *via* the metal could give the opposite result. The ^1H n.m.r. spectrum of (13) in CF_3CO_2H clearly shows the presence of a CHD_2 group and therefore protonation has taken place at the unco-ordinated double bond.

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EXPERIMENTAL

Hydrogen-1 n.m.r. spectra in τ were recorded on a JEOL MH-100 spectrometer, proton-decoupled ^{13}C n.m.r. spectra (p.p.m. downfield from $SiMe_4$) on a JEOL FX-60 spectrometer. Mass spectra were obtained on an MS-20 instrument.

Tricarbonyl(2–5-η-1-*triethylammoniohexa*-2,4-*diene*)*iron Hexafluorophosphate* (7).—Triethylamine (142 mg) was added to a stirred suspension of (5a) (500 mg) in dry methylene chloride (10 cm^3). Immediate dissolution of the salt took place to give a straw-coloured solution. The adduct was precipitated using dry diethyl ether, filtered off, washed with diethyl ether, and dried *in vacuo*, yield 540 mg (85%). I.r. spectrum as Nujol mull: ν(MC–O) at 2 065 and 1 985 cm^{-1}; $\nu[PF_6]^-$ at 842 cm^{-1}. Hydrogen-1 n.m.r. in $(CD_3)_2CO$: τ 4.3 (m, 2 H, H^3 and H^4), 6.0—7.6 (m, 10 H, H^1, H^2, H^5, and NCH_2), and 8.4—9.0 (m, 12 H, H^6 and NMe). The coupling to H^3 and H^4 was removed by irradiation at τ 7.4. This indicates a *syn-anti* structure (Found: C, 38.6; H, 5.2; N, 3.1. $C_{15}H_{24}F_6FeNO_3P$ requires C, 38.55; H, 5.15; N, 3.00%).

Tricarbonyl(2—5-η-1-*trimethylammoniohexa*-2,4-*diene*)-*iron Hexafluorophosphate*.—Trimethylamine was bubbled through a stirred suspension of (5a) (500 mg) in methylene chloride (30 cm^3) until all the salt had dissolved. The product was precipitated with dry diethyl ether and dried *in vacuo*, yield 530 mg (90%) (Found: C, 34.2; H, 4.20; N, 3.40. $C_{12}H_{18}F_6FeNO_3P$ requires C, 33.1; H, 4.70; N, 3.20%).

The triphenylarsine adduct of (5a) and the triphenylphosphine adducts of (5a), (5b), and (5c) were prepared as follows using the method described for (7). A 10—15% excess of nucleophile was used and the yields were essentially quantitative.

Tricarbonyl(2—5-η-1-*triphenylarsoniohexa*-2,4-*diene*)*iron hexafluorophosphate* (11, iiia). Reaction time 14 h, solution filtered before precipitation. I.r. spectrum in Nujol: ν(MC–O) at 2 045 and 1 975 cm^{-1}; $\nu[PF_6]^-$ at 845 cm^{-1}. Hydrogen-1 n.m.r. in CD_3CN: τ 2.4 (m, 15 H, aryl), 4.8 (m, 2 H, H^3 and H^4), 5.95 (d, *J* 14, 1 H, H^1), 6.6 (t, *J* 14 Hz, 1 H, H^1), and 8.68 (m, 5 H, H^2, H^5, and Me) (Found: C, 48.5; H, 3.70. $C_{27}H_{24}AsF_6FeO_3P$ requires C, 48.25; H, 3.60%).

Tricarbonyl(2—5-η-1-*triphenylphosphoniohexa*-2,4-*diene*)-*iron hexafluorophosphate* (10, iia). I.r. spectra in Nujol mull: ν(MC–O) at 2 060 and 1 955 cm^{-1}; $\nu[PF_6]^-$ at 840 cm^{-1}. Hydrogen-1 n.m.r. in $(CD_3)_2CO$: τ 2.2 (m, 15 H, aryl), 4.65 (m, 2 H, H^3 and H^4), 6.0 (t, *J* 14, 1 H, H^1), 6.6 (t, *J* 14, H^1), 6.9—7.6 (m, 2 H, H^2 and H^5), and 8.6 (d, *J* 8 Hz, 3 H, Me) (Found: C, 51.3; H, 3.80. $C_{27}H_{24}F_6FeO_3P_2$ requires C, 51.6; H, 3.85%).

Tricarbonyl(3—6-η-2-*triphenylphosphoniohepta*-3,5-*diene*)-*iron tetrafluoroborate* (10, iib). I.r. spectrum in Nujol: ν(MC–O) at 2 060 and 1 970 cm^{-1}; $\nu[BF_4]^-$ at 1 050 cm^{-1}. Hydrogen-1 n.m.r. in $(CD_3)_2CO$: τ 2.4 (m, 15 H, aryl), 4.6 (m, 2 H, H^3 and H^4), 6.38 (m, 1 H, H^1), 7.0 (m, 1 H, H^2), 7.7 (m, 1 H, H^5), 8.44 [d of d, *J*(P–Me) 19, *J*(Me–H) 7, 3 H, R], and 8.46 (d, *J* 6 Hz, 3 H, R) (Found: C, 57.8; H, 4.60. $C_{28}H_{26}BF_4FeO_3P$ requires C, 57.55; H, 4.50%).

Tricarbonyl(3—6-η-2-*triphenylphosphonio-octa*-3,5-*diene*)-*iron hexafluorophosphate* (10, iic) (Found: C, 52.4; H, 4.30. $C_{29}H_{28}F_6FeO_3P_2$ requires C, 53.05; 4.30%).

Tricarbonyl(3—6-η-2-*phenylaminohexa*-3,5-*diene*)*iron* (12a, Y = H).—Aniline (4.28 g, a twenty-fold excess) was added to a suspension of (5a) (500 mg) in methylene chloride and the mixture was stirred for 10 min. The solvent and unchanged aniline were removed *in vacuo* and the residue was chromatographed on silica gel with light petroleum as eluant. The yellow band which developed was evaporated to give the product as a yellow oil in 60% yield. Hydrogen-1 n.m.r. in $CDCl_3$: τ 3.45 (m, 5 H, aryl), 5.1 (m, 2 H, H^3 and H^4), 6.66 (s, 1 H, br, NH), 7.41 (m, 1 H, H^2), 8.66 (d, *J* 6 Hz, 3 H, Me), and 8.6—9.2 (m, 6 H, H^1, H^3, and H^6) (Found: C, 57.0; H, 4.50; N, 4.10. $C_{15}H_{15}FeNO_3$ requires C, 57.5; H, 4.80; N, 4.50%).

Tricarbonyl(3—6-η-2-*diphenylaminohexa*-3,5-*diene*)*iron* (12a, Y = Ph).—Diphenylamine (1.1 excess) was treated with (5a) in methylene chloride. The solvent was removed *in vacuo* and the residue was chromatographed on alumina using light petroleum–diethyl ether (1.9 : 1) as eluant. The yellow band which developed was evaporated to a yellow oil. Satisfactory analyses were not obtained for C, H, and N due to the air-sensitive nature of the product. I.r. spectrum of a liquid film: ν(MC–O) at 2 050 and 1 960 cm^{-1}. Hydrogen-1 n.m.r. in $CDCl_3$: τ 3.0 (m, 10 H, aryl), 4.82 (m, 2 H, H^3 and H^4), 7.4 (m, 1 H, H^1), 8.22 [d, 1 H, H^5 (*syn*)], 8.52 (d, 3 H, Me), 8.76 (t, 1 H, H^2), and 9.62 [d, 1 H, H^5 (*anti*)].

Attempts to Effect Direct Deprotonation of (5a).—*Reaction with* 1,8-*bis*(*dimethylamino*)*naphthalene*. Treatment of (5a) with an equimolar amount of the nucleophile in methylene chloride gave a clear solution from which an adduct was precipitated in a near quantitative yield on addition of diethyl ether. I.r. spectrum in Nujol: ν(MC–O) at 2 050 and 1 970 cm^{-1}; $\nu[PF_6]^-$ at 840 cm^{-1} (Found: C, 47.6; H, 4.50; N, 5.00. $C_{23}H_{27}F_6FeN_2O_3P$ requires C, 47.6; H, 4.70; N, 4.80%).

Reaction with Deacidite G (*SRA*-99) (NEt_2 *form*). A stirred suspension of (5a) in methylene chloride was treated with a large excess of the resin. The solvent was colourless after 3 h and i.r. spectra indicated the absence of metal carbonyl species from solution. Infrared spectra of the resin were not satisfactory but it was assumed that addition had taken place.

Tricarbonyl(3—6-η-*hexa*-1,3,5-*triene*)*iron* (8a).—Slow heating (0.5 °C min^{-1}) of either the trimethyl- or the triethylamine adducts of (5a) to 80 °C *in vacuo* with the use of a condenser (5 °C) gave the triene in yields of 80%. The product was obtained pure. Hydrogen-1 n.m.r. in $CDCl_3$: 4.42 [d of t, *J*(*trans*) 17, *J*(*cis*), and *J*(H^{2}H^3) 10, 1 H, H^2], 4.89 (m, 4 H, H^1, H^4, and H^5), 8.3 [m, 2 H, H^3 and H^6 (*syn*)], and 9.55 [d of d, *J*(*trans*) 9, *J*(*gem*) 2.5 Hz, 1 H, H^6 (*anti*)] (Found: C, 49.2; H, 3.70. $C_9H_8FeO_3$ requires C, 49.15; H, 3.65%).

Tricarbonyl(3—6-η-*hepta*-1,3,5-*triene*)*iron* (8b).—A suspension of (5b) in methylene chloride was treated with excess of NEt_3 and the mixture was stirred for 5 min. Evaporation *in vacuo* at 5 °C left a residue which was distilled *in vacuo* at 50 °C to give the product in 70% yield. Hydrogen-1 n.m.r. in $CDCl_3$: τ 4.37 [d of t, *J*(*trans*) 17, *J*(*cis*) and *J*(H^{2}H^3) 9, 1 H, H^2], 4.94 [d, *J*(*trans*) 17 Hz, 1 H, H^1 (*trans* to H^2)], and 5.18 (m, 4 H, H^6 and Me) (Found: C, 51.5; H, 4.5. $C_{10}H_{10}FeO_3$ requires C, 51.3; H, 4.25%).

Tricarbonyl(3—6-η-*octa*-1,3,5-*triene*)*iron* (8c).—Complex (8c) was prepared from (5c) by the method used for the preparation of (8b). The yield was 70%. Hydrogen-1 n.m.r. in $CDCl_3$: τ 4.36 [d of t, *J*(*trans*) 17, *J*(*cis*) and *J*(H^{2}H^3) 10 Hz, 1 H, H^2), 4.60—5.2 (m, 4 H, H^1, H^4, and H^5), and 8 2—9.1 (m, 7 H, Et, H^3, and H^6).

Tricarbonyl(3—6-η-1,1-*dideuteriohexa*-1,3,5-*triene*)*iron* (13).—This complex was prepared from (1a) using CD_3COCl–$AlCl_3$ and subsequent dehydration of the alcohol produced on silica gel. The overall yield was 50%. Hydrogen-1 n.m.r. in $CDCl_3$: 4.24 (d, br, *J* 6, 1 H, H^2), 4.72 (m, 2 H, H^4 and H^5), 8.26 (m, 2 H, H^3 and H^6), and 9.5 [d of d, *J*(*trans*) 9, *J*(*gem*) 2.5 Hz, 1 H, H^6 (*anti*)].

Hydrogen-1 n.m.r. of (8a) in $CDCl_3$–CF_3CO_2H, structure (5a): τ 3.14 (t, *J* 6, 1 H, H^3), 4.15 (m, 2 H, H^2 and H^4), 6.55 [d of d, *J*(H^1H^2)(*cis*) 10, *J*(*gem*) 4, 1 H, H^1 (*syn*)], 6.8 (q, *J* 6, 1 H, H^5), 7.9 [d of d, *J*(H^1H^2)(*trans*) 12, *J*(*gem*) 4, 1 H, H^1 (*anti*)], and 9.19 (d, *J* 6 Hz, 3 H, Me). Hydrogen-1 n.m.r. of (13) in $CDCl_3$–CF_3CO_2H, similar to (8a) above, differences indicated: τ 3.14 (t, 1 H), 4.15 (m, 2 H), 6.55 (d of d, 1 H), 6.8 (m, 1 H, H^5), 7.9 (d of d, 1 H), and 9.12 (m, 1 H, CHD_2). The $[PF_6]^-$ salt was obtained on addition of HPF_6–OEt_2 (Found: C, 29.7; H, 2.7. $C_9H_7D_2F_6FeO_3P$ requires C, 29.3; H, 3.00%).

Mass spectra of (8a), (8b), (8c), and (13) contained peaks at M^+ (molecular ion), $[M - CO]^+$, $[M - 2CO]^+$, and $[M - 3CO]^+$.

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