# Organometallics in Synthesis: Alkylation of Tricarbonyldienyliron Cationic Complexes with Organocadmium Reagents

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Alkylations of tricarbonyldienyliron salts with organocadmium reagents have been achieved in high yields. The tricarbonyl-(2-methylcyclohexadienyl)iron cation reacts regioselectively mainly at the unhindered terminus and stereospecifically on the face opposite to the $Fe(CO)_3$ group. Regioselectivity is poor in the acyclic dienyl series. although the cisoid geometry of the double bond is retained in the product. The reaction of dibut-2-enylcadmium occurs at the 3-position with allylic rearrangement.

WE have recently described [1] the reaction of tricarbonyl-cyclohexadienyliron tetrafluoroborates or hexafluorophosphates (1) with organo-zinc and -cadmium reagents to give the corresponding alkylated tricarbonylcyclohexadieneiron (2). The scope of the reaction, applied to

(1) $X^- = BF_4^-$ or PF_6^- (2)
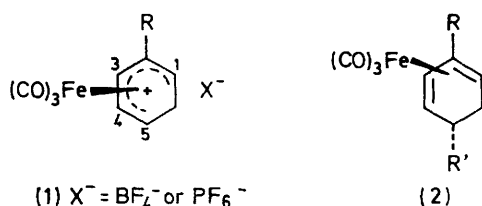
cyclic and acyclic dienyl cations, has now been further investigated and is discussed in the present paper.

RESULTS AND DISCUSSION

Tricarbonylcyclohexadienyliron Salts.—The reaction of a series of cadmium reagents (R_2Cd, with $R = Ph$, $PhCH_2$, Me_2CH, $CH_2=CH-CH_2$, $MeCH=CH-CH_2$, or $MeCH=CH$) at 0 °C and under argon or nitrogen, followed by chromatography on silica, resulted in products (2) of alkylation at the terminal carbon atom of the dienyl system. Yields and spectral characteristics are given in the Experimental section. In each case use of the corresponding Grignard reagent, RMgX, led to extensive decomposition, as evidenced by deposition of iron oxides, and reductive coupling of the cations, but no alkylation. In the case of tricarbonyl-(2-methylcyclohexadienyl)iron salts (1; R = Me) there are two non-equivalent terminal carbon atoms at which attack might occur; thus there are two possible products. Presumably owing mainly to steric factors, the product from attack at C-1, *i.e.* α to the substituted position, in all reactions formed only a minor component of the isolated mixture (≤10% from n.m.r. spectra). Thus, the reaction displays a marked regio-

selectivity leading to the tricarbonyl-(5-substituted 2-methylcyclohexadiene)iron complex. The reaction of the methyl cation with di-isopropylcadmium gave the major product formed by direct complexation of *p*-mentha-1,5-diene (n.m.r., g.l.c., and i.r.), a reaction which occurs by attachment of the $Fe(CO)_3$ group to the least hindered side of the menthadiene molecule, leading to a major product having the isopropyl group on the opposite side of the ring to the metal.[2] Therefore, addition of the organocadmium reagent occurs as expected on the least hindered face of the complex, and the reaction is stereospecific at the carbon atom undergoing attack, as is the case with other irreversible nucleophiles.[2a,3]

Reaction of the cations with diallylcadmium reagents occurs by reaction at the non-terminal point with effectual migration of the allyl double bond. Thus, the product (3) from the reaction of tricarbonylcyclohexadi-enyliron tetrafluoroborate with bis-(3-methylallyl)cad-mium showed n.m.r. signals in the vinyl region at τ 4.65 (2 H, m) due to H-2 and -3 of the diene–$Fe(CO)_3$ system, and at τ 4.4, 5.0, and 5.12 (3 H total) due to the vinyl protons of the allyl substituent; the methyl resonance occurred at τ 9.1. Had the reaction occurred directly at the terminal position the n.m.r. spectrum would have shown a total of only four protons in the vinyl region and the methyl signal would have been at τ *ca.* 8.5 [as with the product from reaction of $(MeCH=CH)_2Cd$; see Experimental section]. Therefore, allylation occurs as shown in Scheme 1, an important consideration in synthetic applications.

In the n.m.r. spectrum of compound (3) the methyl resonance appears as four closely spaced lines of approximately equal intensity; this can only be interpreted as due to the formation of a 1 : 1 mixture of diastereoisomers

[1] A. J. Birch and A. J. Pearson, *Tetrahedron Letters*, 1975, 2379.

[2] (a) A. J. Birch, K. B. Chamberlain, M. A. Haas, and D. J. Thompson, *J.C.S. Perkin I*, 1973, 1882; (b) A. J. Birch, B. Chauncy, and D. J. Thompson, unpublished work; (c) D. V. Banthorpe, H. Fitton, and J. Lewis, *J.C.S. Perkin I*, 1973, 2051.

[3] A. Pelter, K. J. Gould, and L. A. P. Kane-Maguire, *J.C.S. Chem. Comm.*, 1974, 1029.

(two asymmetric centres are formed during the reaction). Therefore, the allylcadmium reagent shows no preference for a particular orientation of the prochiral centre in the group itself during addition, the new centre being formed
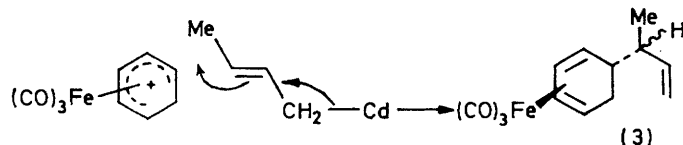
SCHEME 1

non-stereoselectively. No attempts have yet been made to vary the steric requirements or dissymmetry of the alkyl grouping which might lead to preferential orientation during the reaction.

Acyclic Tricarbonylpentadienyliron Systems.—The reaction of organocadmium reagents with the acyclic tricarbonylpentadienyliron tetrafluoroborate salts (4) has been examined under conditions identical with those used for the cyclic analogues. The yields here were variable, being greater than 60% for the reaction of diphenylcadmium with all three salts, whereas (4a) gave only 26% of alkylation product from reaction with bis-(2-methylvinyl)cadmium. Use of the same reagent with (4c) resulted only in decomposition and reductive coupling to give the corresponding dimeric hexacarbonyldi-iron complex (Experimental section). Yields of other reactions are given in the Experimental section. Thus, it appears that although in principle the alkylation is general, reaction conditions necessary for high yield in a particular synthesis would have to be established individually.

In the case of the unsymmetrical acyclic dienyl compound (4b) it was found that diphenylcadmium caused alkylation almost exclusively at the unsubstituted terminus, giving a greater than 95% yield (n.m.r.) of (6b; R = Ph); all other cadmium reagents used gave (5b) and (6b) in approximately equal amounts. The reason for the difference is not clear, though steric factors are expected to be important. This result also reflects a difference in the chemistry of acyclic and cyclic dienyl–Fe(CO)$_3$ cations; the latter show much greater regioselectivity.

The tetracarbonyl-(3-methylallyl)iron cation (7) also undergoes regioselective (>90%) addition of PhCH$_2$ from dibenzylcadmium to the unsubstituted terminus.[4] The reason for this difference probably lies in the fact that in (7) the methyl group is ' inner ' and any attack at the substituted carbon atom would lift it into a region which is occupied by Fe(CO)$_4$, thereby giving rise to unfavourable steric interactions in the transition state. This does not occur in (4b) in which the terminal methyl is ' outer ', and no such interaction occurs.

The n.m.r. spectra of phenylation products of (4a and c) indicate that the reaction occurs with retention of the

[4] A. J. Pearson, *Tetrahedron Letters*, 1975, 3617
[5] (a) J. E. Mahler, D. H. Gibson, and R. Pettit, *J. Amer. Chem. Soc.*, 1963, **85**, 3959; (b) T. H. Whitesides and J. P. Neilan, *ibid.*, 1975, **97**, 907.

cisoid geometry of the dienyl system as shown in Scheme 2, and as observed during borohydride reductions[5] of these cations and during similar alkylations of (7).[4] Thus, in the spectrum of (5a; R = Ph) irradiation of the signal at τ 8.38 caused simplification (but not complete decoupling) of the signal at τ 8.08, while the signals at τ 7.80 and 7.25 were unchanged. Irradiation at τ 4.55 caused the doublet of doublets at τ 8.38 to collapse to a distorted doublet (J 3.5 Hz) and the signal at τ 8.08 to collapse to a doublet of doublets (J 3.5 and 3 Hz), but did not change the other high-field resonances. Irradiation at τ 4.71 removed the small coupling (2 Hz) from
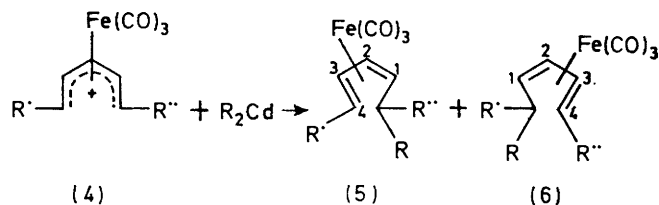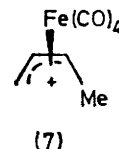

a; R' = R'' = H
b; R' = H, R'' = Me
c; R' = R'' = Me

SCHEME 2

the τ 8.03 signal, did not affect the signals at τ 7.80 and 8.38, but led to considerable simplification of the complex second-order pattern at τ 7.25.

(7)

These observations lead to the assignments given (Experimental section). The protons of the benzylic methylene group are in different chemical environments, as shown by the large difference in chemical shift (*ca.* 0.55 p.p.m.). This may be explained either by restricted rotation about the C(1)–CH$_2$ bond, due to the presence of the diene–Fe(CO)$_3$ grouping, so that the molecule exists in one conformation in which the benzylic protons are non-equivalent, or by asymmetric induction (diastereotopicity). The former explanation is more likely, since we have not observed such pronounced shift differences with benzylic protons in the cyclic compounds (Experimental section) or with similar acyclic diene–Fe(CO)$_3$ complexes in which free rotation occurs (see, for example, reference 6). This phenomenon is consistent with the *cisoid* geometry shown in (5), a conclusion supported by the low-field resonance for H-1 in both this and the methylated analogue [(5c) and (6c); see Experimental section], showing it to be ' outer '[6] (an ' inner ' proton would resonate at a field similar to H-4 inner, *i.e.* τ *ca.* 8.4; this result is obtained even with complexes having

[6] J. E. Mahler and R. Pettit, *J. Amer. Chem. Soc.*, 1963, **85**, 3955.

anisotropic deshielding substituents on the terminal carbon atom of the diene system).†

The exact stereochemistry of the reaction in this series is not known, but the alkylation most likely occurs on the face opposite to the Fe(CO)$_3$ grouping as in the tricarbonylcyclohexadienyliron cations.

This reaction is envisaged as having a general synthetic applicability. Thus, choice of a particular cyclohexadienyl complex would result, after removal of the Fe(CO)$_3$ group, in the formation of the appropriately substituted cyclohexadiene. This procedure, utilising the correct alkenylcadmium reagents, might be useful for generating trienes capable of undergoing intramolecular Diels–Alder reactions [7] to give polycyclic compounds, such as twistane derivatives.

EXPERIMENTAL

N.m.r. spectra, for solutions in carbon tetrachloride unless otherwise stated, were recorded with a JEOL Minimar or Varian HA 100 instrument. I.r. spectra were taken for liquid films unless otherwise stated with a Perkin-Elmer 257 spectrometer, and mass spectra were obtained with an A.E.I. MS9 spectrometer. Published methods were used for the preparation of both the tricarbonylcyclohexadienyliron salts [2] and the tricarbonylpentadienyliron salts.[6]

Organocadmium Reagents.—These were prepared in solution by addition of a solution of the appropriate Grignard reagent to a stirred suspension of the stoicheiometric quantity of dried cadmium chloride in ether or tetrahydrofuran under argon and at such a rate that no ebullition occurred.

Alkylation Reactions.—A slight excess of the dialkylcadmium solution was slowly added to a stirred suspension of the tricarbonyldienyliron salt (200 mg) in dry tetrahydrofuran (10 ml) at 0 °C under argon or nitrogen. In most cases reaction was instantaneous, the yellow salt disappearing into solution, but a further 5—10 mins was allowed for completion before pouring into 10% ammonium chloride (20 ml) and extracting with ether in the usual way. The dried (MgSO$_4$) extracts were chromatographed on silica, after removal of solvent. The first yellow band eluted was the alkylation products, and was followed by minor amounts of decomposition products. In the case of diphenyl- and dibenzyl-cadmium, the lower layer of biphasic tetrahydrofuran solution was used to avoid contamination with nonvolatile biphenyl and bibenzyl, formed by Wurtz coupling during preparation of the Grignard reagent and not easily removed in most of the chromatographic separations. The results and spectral characteristics of products are listed for each organocadmium reagent.

Diphenylcadmium. Tricarbonylcyclohexadienyliron tetrafluoroborate (1; R = H) gave tricarbonyl-(5-phenylcyclohexa-1,3-diene)iron (2; R = H, R' = Ph) (70—80%); $\nu_{max.}$ 2 060 and 1 970 [Fe(CO)$_3$], and 1 600, 1 580, and 1 495

† For example the n.m.r. spectrum of (A) showed signals for H$_a$ at τ 8.45 and H$_b$ at 8.74 (confirmed by decoupling).

(A)
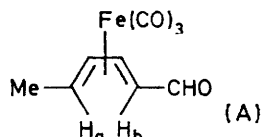
[7] A. Krantz and C. Y. Lin, *J. Amer. Chem. Soc.*, 1973, **95**, 5662.

cm^{-1} (Ph); τ 2.3—2.9 (5 H, aromatic), 4.52 (2 H, m, H-2 and -3), 6.8 (3 H, m, H-1, -4, and -5, and 7.65 (1 H, m), and 8.4 (1 H, d) (H$_2$-6, J_{gem} 16 Hz); M^+ 296.

Tricarbonyl-(2-methylcyclohexadienyl)iron tetrafluoroborate (1; R = Me) gave tricarbonyl-(2-methyl-5-phenylcyclohexa-1,3-diene)iron (2; R = Me, R' = Ph) (70%); $\nu_{max.}$ 2 050 and 1 970 [Fe(CO)$_3$] and 1 600, 1 580 and 1 495 cm^{-1} (Ph); τ 2.5—3.1 (5 H, aromatic), 4.76 (1 H, dd, H-3, $J_{3,4}$ 6, $J_{1,3}$ 1 Hz), 6.76, 6.88, and 7.08 (complex multiplets, 1 H each, H-1, -4, and -5), 7.7 (1 H, m) and 8.40 (1 H, m) (H$_2$-6, J_{gem} 14 Hz), and 7.82 (3 H, s, CH$_3$); M^+ 310.

Tricarbonylpentadienyliron tetrafluoroborate (4a) gave tricarbonyl-(1-phenylpenta-2,4-diene)iron (5a; R = Ph) (65%), $\nu_{max.}$ (Nujol) 2 055 and 1 975 [Fe(CO)$_3$] and 1 600w cm^{-1} (Ph); τ (numbering as in formula) 2.4—3.1 (5 H, aromatic), 4.55 (1 H, m, H-3), 4.73 (1 H, m, H-2), 7.25 (2 H, m, complex, H-1 and benzylic H), 7.80 (1 H, dd, benzylic H, J_{gem} 15, J_{vic} 12 Hz), 8.08 (1 H, ddd, H-4 outer, $J_{3,4'}$ 7.5, $J_{2,4'}$ 2, J_{gem} 3.5 Hz), and 8.38 (1 H, dd, H-4 inner, $J_{3,4}$ 9.5, J_{gem} 3.5 Hz); M^+ 284.

Tricarbonylhexadienyliron tetrafluoroborate (4b) gave only tricarbonyl-(1-phenylhexa-2,4-diene)iron (6b; R = Ph) (70%), $\nu_{max.}$ 2 050 and 1 965 [Fe(CO)$_3$] and 1 600, 1 585, and 1 495 cm^{-1} (Ph); τ (numbering as in formula) 2.7 (5 H, aromatic), 4.85 (2 H, m, H-2 and -3), 7.4br (3 H, complex m, H-1 and benzylic CH$_2$), 8.52 (3 H, d, J 7 Hz, CH$_3$), and 8.7 (1 H, m, H-4 inner); M^+ 298.

Tricarbonyl-(1,5-dimethylpentadienyl)iron tetrafluoroborate (4c) gave tricarbonyl-(6-phenylhepta-2,4-diene)iron (5c and 6c; R = Ph); $\nu_{max.}$ 2 040 and 1 960 [Fe(CO)$_3$] and 1 595, 1 580, and 1 480 cm^{-1} (Ph); τ [numbering as in formula (5)] 3.0 (5 H, aromatic), 4.80 (1 H, m, H-3), 5.16 (1 H, m, H-2), 7.6 (2 H, m, complex, H-1 and benzylic H), 8.48 (3 H, d, J 7 Hz, 4-CH$_3$), 8.62 {3 H, d, J 7 Hz, CH$_3$ [R'' of (5c)]}, and 8.7 (1 H, m, H-4 inner); M^+ 312.

Dibenzylcadmium. Compound (1; R = H) gave (2; R = H, R' = PhCH$_2$) (60%), $\nu_{max.}$ 2 050 and 1 960 [Fe(CO)$_3$], and 1 600, 1 580, and 1 495 cm^{-1} (Ph); τ 2.75 (5 H, aromatic), 4.67 (2 H, m, H-2 and -3), 6.96 (2 H, m, H-1 and -4), 7.54 (3 H total, singlet + underlying multiplet, benzyl CH$_2$ and H-5), and 8.08 (1 H, m) and 8.68 (1 H, dm) (H$_2$-6, J_{gem} 15 Hz), M^+ 310.

Compound (1; R = Me) gave (2; R = Me, R' = PhCH$_2$) plus a small amount (<10%) of tricarbonyl-(1-methyl-6-benzylcyclohexa-1,3-diene)iron (n.m.r.); total yield 60%; $\nu_{max.}$ 2 040 and 1 960 [Fe(CO)$_3$] and 1 600, 1 580, and 1 490 cm^{-1} (Ph); τ 2.9 (5 H, aromatic), 4.84 (1 H, m, H-3), 7.15 (2 H, m, H-1 and -4), 7.61 (3 H, singlet + underlying multiplet, benzylic CH$_2$ + H-5), 7.96 (3 H, s, CH$_3$), 8.2 (1 H, m) and 8.7 (1 H, m) (H$_2$-6), and 8.58 [<$\frac{1}{2}$ H, s, CH$_3$ of tricarbonyl-(1-methyl-6-benzylcyclohexa-1,3-diene)iron]; M^+ 324.

Compound (4a) gave (5a; R = PhCH$_2$) (55%), $\nu_{max.}$ 2 050 and 1 965 [Fe(CO)$_3$] and 1 600, 1 580, and 1 490 cm^{-1} (Ph); τ 2.9 (5 H, aromatic), 4.8 (2 H, m, H-2 and -3), 7.5 (3 H, m, complex, benzylic CH$_2$ and H-1), and 8.22 (2 H, m) and 8.60 (2 H, m) (H-4 inner, H-4 outer, and CH$_2$); M^+ 298.

Compound (4b) gave (5b; R = PhCH$_2$) and a slightly greater amount of (6b; R = PhCH$_2$); total yield 70%; $\nu_{max.}$ 2 055 and 1 965 [Fe(CO)$_3$] and 1 600, 1 580, and 1 490 cm^{-1} (Ph); τ 2.76 (5 H, aromatic), 4.9 (2 H, m, H-2 and -3 of diene), 7.6 (m), 8.18 (m), and 8.6 (m) (total 6 H, 2 × CH$_2$, H-1, and H-4 of both isomers), and 8.60 [d, J 7 Hz CH$_3$ of (6b; R = PhCH$_2$)] and 9.0 [d, J 7 Hz, CH$_3$ of (5b; R = PhCH$_2$)] (total 3 H); M^+ 312.

Compound (4c) gave (5c; R = PhCH$_2$) (50%), $\nu_{max.}$ 2 050 and 1 960 [Fe(CO)$_3$] 1 600, 1 580, and 1 490 cm^{-1} (Ph); τ 2.7 (5 H, aromatic), 4.9 (1 H, m) and 5.1 (1 H, m) (H-2 and -3), 7.6 (4 H, m, complex, benzylic CH$_2$, CHMe and H-1), 8.6 [4 H total, d, J 7 Hz, and underlying m, CH$_3$ (R') and H-4 inner], and 8.98 [3 H, d, J 6.5 Hz, CH$_3$ (R'')]; M^+ 326.

Di-isopropylcadmium. Compound (1; R = H) gave (2; R = H, R' = Me$_2$CH) (52%), $\nu_{max.}$ 2 050 and 1 960 cm^{-1} [Fe(CO)$_3$]; τ 4.42 (2 H, m, H-2 and -3), 6.8 (2 H, m, H-1 and -4), 7.9—8.65 (4 H total, H-5, H$_2$-6, and Me$_2$CH), and 9.14 (6 H, d, J 6 Hz, CMe$_2$); M^+ 262.

Compound (1; R = Me) gave (2; R = Me, R' = Me$_2$CH) together with a minor amount (<10%) of tricarbonyl-(6-isopropyl-1-methylcyclohexa-1,3-diene)iron (τ 8.40) (55%); $\nu_{max.}$ 2 050 and 1 970 cm^{-1} [Fe(CO)$_3$]; τ (CDCl$_3$) 4.44 (1 H, m, H-3), 6.9 (2 H, m, H-1 and -4), 7.82 [3 H, s, CH$_3$ of (2; R = Me, R' = Me$_2$CH)], 7.9—8.65 (4 H total, H-5, H$_2$-6, and Me$_2$CH), and 9.12 (6 H, d, J 6 Hz, CMe$_2$); M^+ 276.

Compound (4a) gave (5a; R = Me$_2$CH) (45%), $\nu_{max.}$ 2 050 and 1 960 cm^{-1} [Fe(CO)$_3$]; τ 4.65 (2 H, m, H-2 and -3), 7.5 (1 H, m, H-1), 8.1—9.1 (5 H total, H$_2$-4, CH$_2$, and Me$_2$CH), and 9.12 (6 H, d, J 7 Hz, CMe$_2$); M^+ 250.

Compound (4b) gave (5b; R = Me$_2$CH) and (6b; R = Me$_2$CH) in approximately equimolar amounts, inseparable on t.l.c. (25%); $\nu_{max.}$ 2 050 and 1 960 cm^{-1} [Fe(CO)$_1$]; τ 4.85 (2 H, m, H-2 and -3 of diene), 7.7 (1 H, m, H-1), 8.56 {d, J 6 Hz, CH$_3$ [R'' of (6b)]}, 8.94 {s, CH$_3$[R'' of (5b)]}, and 9.10 (d, J 7 Hz, CMe$_2$); further signals masked between 8.1 and 9.1 (H-4 and -4', Me$_2$CH, CHR'', and CHR'; total integral 13 H); M^+ 264.

Compound (4c) gave (5c; R = Me$_2$CH) (20%), $\nu_{max.}$ 2 050 and 1 960 cm^{-1} [Fe(CO)$_3$]; τ 4.9 (2 H, m, H-2 and -3), 7.8 (1 H, m, H-1), 8.54 (3 H, d, J 6 Hz, 4-CH$_3$), 9.02 [3 H, s, CH$_3$(R')], and 9.20 (6 H, CMe$_2$); further signals underlying 8.1—9.2 (total 3 H, H-4, CHR'', and Me$_2$CH); M^+ 278.

Diallylcadmium. Compound (1; R = H) gave (2; R = H, R' = CH$_2$=CH–CH$_2$) (82%), $\nu_{max.}$ 2 060 and 1 970 [Fe(CO)$_3$] and 1 640 cm^{-1} (C=C); τ 4.3 (1 H, m) and 5.0 (2 H, m) (vinyl H of R'), 4.67 (2 H, m, H-2 and -3), 6.9 (2 H, m, H-1 and -4), 8.0 (4 H, complex, H-5, H-6, and allyl CH$_2$), and 8.75 (1 H, m, other H-6, J_{gem} 15 Hz); M^+ 260.

Compound (1; R = Me) gave (2; R = Me, R' = CH$_2$=CH–CH$_2$) (60%), $\nu_{max.}$ 2 050 and 1 960 [Fe(CO)$_3$] and 1 635 cm^{-1} (C=C); τ 4.4 (1 H, m) and 5.1 (2 H, m) (vinyl H of R'), 4.82 (1 H, dd, H-3, $J_{3,4}$ 6 Hz), 7.08 (2 H, m, H-1 and -4), 7.90 (3 H, s, Me), 8.08 (4 H, m, H-5, H-6, and allyl CH$_2$), and 8.8 (1 H, m, other H-6, J_{gem} ca. 15 Hz); a small singlet at 8.40 (CH$_3$) shows minor formation (<5%) of tricarbonyl-(6-allyl-1-methylcyclohexa-1,3-diene)iron; M^+ 274.

Compound (4a) gave (5a; R = CH$_2$=CH–CH$_2$) (40%), $\nu_{max.}$ 2 050 and 1 970 [Fe(CO)$_3$] and 1 640 cm^{-1} (C=C); τ 4.2—5.2 (complex, total 5 H, vinyl 3 H of R, H-2, and H-3), 7.68 (1 H, m, H-1), and 7.8—8.9 (several complex

overlapping multiplets, total 6 H, 2 × CH$_2$ and H$_2$-4); M^+ 248.

Compound (4b) gave (5b; R = CH$_2$=CH–CH$_2$) and (6b; R = CH$_2$=CH–CH$_2$) in approximately equimolar amounts, inseparable on t.l.c. (25%); $\nu_{max.}$ 2 050 and 1 960 [Fe(CO)$_3$] and 1 640 cm^{-1} (C=C); τ 4.2—5.2 (complex, total 5 H, vinyl 3 H of R, H-2, and H-3), and 7.5—9.0 [complex, total 9 H, H-1, 2 × CH$_2$, H-4 of (6b), H-1, CH$_2$, CH, H$_2$-4 of (5b)]; CH$_3$ (R'') of (6b) at 8.54 (d, J 6 Hz), and of (5b) at 8.94 (s) easily distinguished; M^+ 262.

Compound (4c) gave (5c; R = CH$_2$=CH–CH$_2$) (28%), $\nu_{max.}$ 2 040 and 1 955 [Fe(CO)$_3$] and 1 640 cm^{-1} (C=C); τ 4.2—5.2 (complex, total 5 H, vinyl 3 H of R, H-2, and H-3), 7.8 (2 H, m, H-1 and CHMe), 8.1 (2 H, m, allyl CH$_2$), 8.50 [3 H, d, J 6 Hz, CH$_3$(R')], and 8.92 [4 H, s, with underlying m, CH$_3$(R'') and H-4]; M^+ 276.

Dibut-2-enylcadmium. Compound (1; R = H) gave (3) (72%), $\nu_{max.}$ 2 060 and 1 970 [Fe(CO)$_3$] and 1 640 cm^{-1} (C=C); τ (CDCl$_3$) 4.0 (m), 5.0, and 5.12 (m) (3 H total, vinyl 3 H of allyl group), 4.65 (2 H, m, H-2 and -3), 6.96 (2 H, m, H-1 and -4), 8.0 (complex, 3 H total, H-5, 1 × H$_2$-6, and allyl 1 H), 8.70 (1 H, m, H-6, J_{gem} 12 Hz), and 9.1 [3 H, 4 peaks (see Discussion section), CH$_3$]; M^+ 274.

Diprop-1-enylcadmium (cis–trans-*mixture*). Compound (1; R = H) gave (2; R = H, R' = MeCH=CH) (40%); $\nu_{max.}$ 2 050 and 1 970 [Fe(CO)$_3$] and 1 640 cm^{-1} (C=C); τ 4.2—5.0 [4 H, complex, vinyl 2 H (R'), H-2, and H-3], 6.8 (2 H, m, H-1 and -4), 7.3 (1 H, m, H-5), 7.88 (1 H, m, H-6), 8.36 (3 H, d, J 7 Hz, vinyl CH$_3$), and 8.68 (1 H, m, other H-6, J_{gem} 16 Hz); M^+ 260.

Compound (1; R = Me) gave (2; R = Me, R' = MeCH=CH) (60%); no tricarbonyl-[1-methyl-6-(prop-1-enyl)cyclohexa-1,3-diene]iron was detected from the n.m.r. spectrum; $\nu_{max.}$ 2 050 and 1 960 [Fe(CO)$_3$] and 1 640w cm^{-1} (C=C); τ 4.4—5.3 [3 H, complex, vinyl 2 H (R'), H-3], 7.1 (2 H, m, H-1 and -4), 7.3 (1 H, m, H-5), 7.88 (3 H, s, and 1 H, m, 2-Me and 6-H), 8.43 (3 H, d, J 6 Hz, vinyl CH$_3$), and 8.7 (1 H, m, other H-6); M^+ 274.

Compound (4a) gave (5a; R = MeCH=CH) (26%), $\nu_{max.}$ 2 050 and 1 960 [Fe(CO)$_3$] and 1 660w (C=C); τ 4.7 [4 H, m, vinyl 2 H (R), H-2, and H-3], 7.48 (1 H, m, H-1), and 7.9 (1 H, m), 8.16 (2 H, m), and 8.4 (4 H, complex) (CH$_2$, Me, and H$_2$-4); M^+ 248.

Compound (4b) gave (5b; R = MeCH=CH) and (6b; R = MeCH=CH), unresolved in n.m.r. and inseparable on t.l.c. (18%); $\nu_{max.}$ 2 050 and 1 960 [Fe(CO)$_3$] and 1 660w cm^{-1} (C=C); τ 4.8 [4 H, m, vinyl 2 H(R), H-2, and H-3]. 7.68 (2 H, m) and 8.16 (2 H, m) [H-1 and CH$_2$(6b)], 8.3—8.6 (6 H total, complex, 2 × Me), and 8.9 [<1 H, m, H-4 of (6b)]; M^+ 262.

Compound (4c) gave only the product of reductive dimerisation (10%), M^+ 470 {loss of 6 × CO indicates [Fe(CO)$_3$]$_2$ and therefore dimeric material}.