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(η^5-1-SUBSTITUTED-PENTADIENYL)(TRICARBONYL)IRON(+1) CATIONS: REACTIVITY WITH MALONATE NUCLEOPHILES

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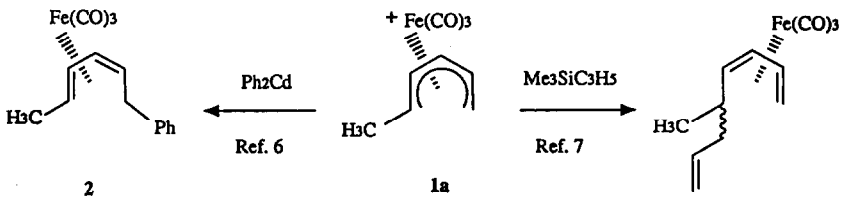
SUMMARY: The title compounds react with malonate anions by attack at both the substituted and unsubstituted terminii, to afford the *trans-cis* substituted diene products.

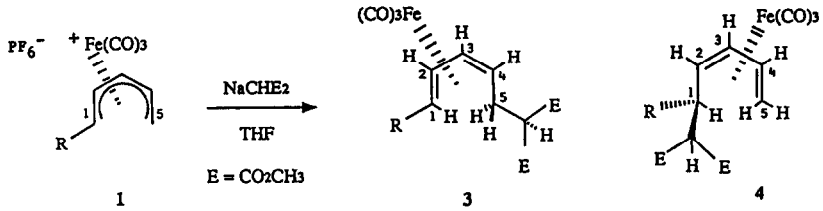
(η^5-Cyclohexadienyl)- and (η^5-cycloheptadienyl)iron(+1) cations are important synthetic precursors due to their regio- and stereoselective reaction with carbon and heteroatom nucleophiles.[1,2] Although open (η^5-pentadienyl)iron(+1) cations have been known for more than 20 years,[3] the reactivity of these cations with carbon nucleophiles has not been as throughly examined.[4] Reaction of (pentadienyl)iron cations with Grignard reagents generally gives reductive coupling products. By comparison, reaction with organocadmium reagents affords the addition products with poor regioselectivity.[5] The exception is diphenylcadmium which reacts with *1a* exclusively by attack at the unsubstituted terminus to give the *trans,cis* product *2*. More recently, the reaction of *1a* with allyl trimethylsilane has been reported to proceed via attack at the more substituted terminus.[6]



2 1a

Only two isolated reactions of (pentadienyl)(tricarbonyl)iron(+1) cations with malonate anions have been reported.[7,8] These recent accounts of the reactivity of (η^5-pentadienyl)iron cations with carbon nucleophiles as well as the recent interest in η^1- and η^3-pentadienyl metal complexes[9] prompts us to report our inital results on the reactivity of cations *1* with stabilized carbon nucleophiles.

The preparation of cations *1a-d* have been reported elsewhere.[10,11] The cation *1e* was prepared from methyl 5-phenylpentadienoate by *i)* coordination to iron tricarbonyl, *ii)* reduction with DIBAL and *iii)* protonation with HPF_6.[12] Reaction of the alkyl substituted cations *1a-c* with stabilized carbon nucleophiles proceeded by attack at both the C1 and C5 termini[13] as shown in Scheme 1.



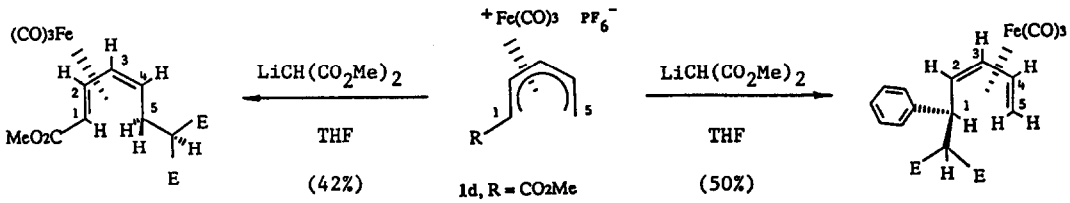
Scheme 1.

1 3 4

				total yield
a,	R = methyl	1 :	1.8	53%
b,	= ethyl	1 :	1	35%
c,	= *n*-propyl	1 :	1	32%

The products *3* and *4* are separable by careful column chromatography and their structural assignments are based on their ^{1}H and ^{13}C NMR spectral data.[14] Notably, the $RC\underline{H}E_2$ methine proton appears as a doublet of doublets and a simple doublet for *3a* and *4a* respectively. Complex *3a* is obtained as the coordinated *cis,trans*-diene as evidenced by a small J_{cis} coupling (~7 Hz) for H3-H4 and a larger J_{trans} coupling (~10 Hz) for H1-H2. Likewise complex *4a* is assigned the *cis* geometry based on coupling data. The relative stereochemistry of *4a* at C1 is assumed to be that as shown in Scheme 1 based on *exo*-attack of stabilized carbon nucleophiles on (cyclohexadienyl)iron(+1) cations.[1]

Scheme 2.



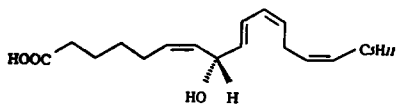
3d 1d, R = CO_2Me 1e, R = phenyl 4e

In comparison, the reaction of (pentadienyl)iron(+1) cations *1d* and *1e* with malonate anion afforded a single product in each case (Scheme 2). The structural assignment for product *3d* is based on ^{1}H and ^{13}C NMR spectral data. In particular, the ^{1}H NMR doublet at δ 2.80 ppm (J = 11 Hz) was assigned to the proton on C1; the large coupling constant being characteristic of a *trans* geometry (*vide supra*). In addition, the ^{13}C NMR resonances of *3d* may be compared with those of *3a*, with concomitant downfield shifts due to the C1 carbomethoxy substituent. The structural assignment for *4e* is based on comparison of its $^{13}C\{^{1}H\}$ NMR spectral data with that for *4a*. In particular, the peak at δ 41 corresponds to the unsubstituted coordinated diene terminus and the peaks at δ 92.4 and 85.1 correspond to the C3 and C4 carbons of a *cis* diene complex. It is interesting to note that the two diastereotopic carbomethoxy groups of *4e* appear as two clearly distinct singlets in its 60 MHz ^{1}H NMR spectrum. The relatively large difference in chemical shift (Δδ 0.4 ppm) may be attributed to the anisotropic effects of the neighboring phenyl substituent.

Pearson has indicated that site selectivity for nucleophilic attack on (cyclohexadienyl)(tricarbonyl)iron(+1) cations (ie. C1, C5 vs. C2, C4) is due to overall frontier orbital control, while the regioselectivity for attack at the C1 terminus versus C5 may be

subject to additional charge and steric effects.[15] While the site of nucleophilic attack (ie. C1 vs C5) for the 1-alkyl substituted cations (*1a-c*) is disappointingly nonregioselective, nucleophilic attack on the carbomethoxy and phenyl substituted cations (*1d* and *1e*) proceeds with high regioselectivity.[16] These results strongly suggest that the site of attack by malonate anion on substituted (pentadienyl)iron(+1) cations is largely the result of charge control; ie. attack at the pentadienyl terminus which is better able to stabilize the "δ+" charge. The lack of regioselectivity for malonate attack at the 1-alkyl pentadienyl cations may be rationalized on the basis of off setting weak steric and electronic influences.

We are currently exploring applications of the reactivity of (pentadienyl)iron(+1) cations, in particular *1d*, to the synthesis of the biologically interesting leukotrienes[17] (cf. 8-HETE and 5,6-LTA_4, *5* and *6*).



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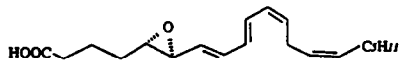

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12) The tetrafluoroborate salt of *1e* has previously been prepared by a different route.[4]

13) Recently, nucleophilic attack at the internal position (C2) of the (pentadienyl)-tris(trimethylphosphine)iron(+1) cation has been reported to afford a π-allyl-σ-alkyl complex: J.R. Bleeke, M.K. Hays, *Organometallics* (1987) 6, 1367.

14) **Selected spectral data:**

3a: IR (CH_2Cl_2, cm^{-1}) 2051s, 1977s, 1736s; 250 MHz ^1H NMR ($CDCl_3$) δ 5.22 (dd, *J* = 5.2, 9.4, *H2*), 5.04 (dd, *J* = 5.2, 7.6, *H3*), 3.7 (s, 6H, OCH_3), 3.27 (dd, *J* = 6.2, 8.5, $CH(CO_2Me)_2$), 2.36 (dq, *J* = 9.4, 6.2, H1), 2.29 (ddd, *J* = 4.7, 7.6, 10.4, *H4*), 2.15 (ddd, *J* = 4.7, 6.2, 14.2, CH_2CHE_2), 1.62 (ddd, *J* = 8.5, 10.4, 14.2, CH_2CHE_2), 1.43 (d, *J* = 6.2, CH_3); 15 MHz $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 210.8 (M-C=O), 168.7 (CO_2Me), 95.1, 81.7 (*C2, C3*), 58.0 (*C1*), 54.3, 54.0 (*C4, CHE*$_2$), 52.3 (OCH_3), 29.2 (*C5*), 20.3 (CH_3).

4a: IR (CH_2Cl_2, cm^{-1}) 2050s, 1977s, 1734s; 250 MHz ^1H NMR ($CDCl_3$) δ 5.42 (ddd, *J* = 5.0, 7.0, 11.0, *H4*), 5.08 (dd, *J* = 5.0, 7.0, *H3*), 3.7 (s, 6H, OCH_3), 3.12 (d, 7.5, $CH(CO_2Me)_2$), 2.37 (dd, *J* = 7.0, 11.0, *H2*), 1.94 (dd, *J* = 2.0, 7.0, H_5*exo*), 1.80 (ddq, *J* = 7.5, 11.0, 6.5, *H1*), 1.41 (dd, *J* = 2.0, 11.0, *H5endo*), 1.11 (d, *J* = 6.5, CH_3); 15 MHz $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 210.3, 168.2 (M-C=O, CO_2Me), 92.2, 85.2 (*C3, C4*), 64.3, 61.0 (*C2,* CHE_2), 52.3 (OCH_3), 41.8 (*C5*), 34.4 (*C1*), 20.2 (CH_3).

3b: 60 MHz ^1H NMR (CCl_4) δ 5.4-4.9 (m, 2H, *H2, H3*), 3.70 (s, 6H, OCH_3), 3.3 (m, 1H, $CH(CO_2Me)_2$), 2.5-1.0 (m, 6H), 1.15 (t, *J* = 7, 3H, CH_2CH_3); 15 MHz $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 210.6, 168.6 (M-C=O, CO_2Me), 93.6, 81.7 (*C2, C3*), 66.9 (*C1*), 54.3, 54.0 (*C4,* CHE_2), 52.3 (OCH_3), 29.0 (*C5*), 28.5, 16.3 (CH_2CH_3).

3c: 60 MHz ^1H NMR (CCl_4) δ 5.4-4.8, (m, 2H, *H2, H3*), 3.7 (s, 6H, OCH_3), 3.1 (dd, *J* = 5, 8, 1H, $CH(CO_2Me)_2$), 2.6-0.8 (m, 11H); 15 MHz $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 211.3, 169.1 (M-*C*=O, CO_2Me), 94.1, 82.0 (*C2, C3*), 64.8 (*C1*), 54.6, 54.1 (*C4,* CHE_2), 52.6 (OCH_3), 37.7 (CH_2Et), 29.2 (*C5*), 25.3, 13.9 (CH_2CH_3).

3d: 60 MHz ^1H NMR ($CDCl_3$) δ 4.50 (m, 1H, *H3*), 4.25 (dd, *J* = 6, 11, *H2*), 3.65, 3.57, and 3.48 (s, 9H, OCH_3), 2.80 (d, *J* = 11, *H1*), 2.35 (m, 2H, *H4, H5*), 1.7 (m, 1H, *H5'*); 15 MHz $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 203.3 (M-C=O), 179.5, 167.4, 166.9 (CO_2Me), 97.9 (*C2*), 62.5, 60.2 (*C1, C4*), 54.5 (CHE_2), 52.5, 51.4 (OCH_3's), 38.5 (*C5*).

4e: 60 MHz ^1H NMR (CCl_4) δ 7.3-7.0 (m, 5H, C_6H_5), 5.6-5.0 (m, 2H, *H2, H3*), 3.70 (s, 3H, OCH_3), 3.5 (m, 1H, $CH(CO2Me)_2$), 3.35 (s, 3H, OCH_3), 2.75 (m, 2H, *H1, H2*), 2.1-1.5 (m, 2H, *H5's*); 15 MHz $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 209.6 (M-C=O), 168.0, 167.2 (CO_2Me), 141.3, 128.5, 127.7 (C_5H_6), 92.4, 85.1 (*C3, C4*), 62.2, 60.2 (*C2,* CHE_2), 52.6 (OCH_3), 44.1 (*C1*), 41.2 (*C5*).

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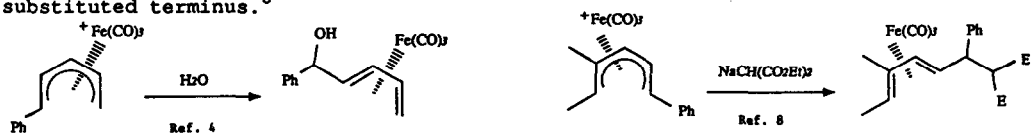
16) It should be noted that the regioselectivity for attack by malonate on cations *1d* and *1e* parallels the regioselectivity for the reaction of these cations with water.[4,12] However, the reaction of *1e* with water gives the *trans* diene product. It should also be noted that the reaction of (1,2-dimethyl-5-phenylpentadienyl)(tricarbonyl)iron(+1) cation with malonate anion also proceeds via exclusive attack at the phenyl substituted terminus.[8]



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