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CONCERNING THE REACTION OF (η^5-1-METHOXYCARBONYLPENTADIENYL)(TRICARBONYL) IRON(+1) WITH MALONATE ANION: A STRUCTURAL CORRECTION

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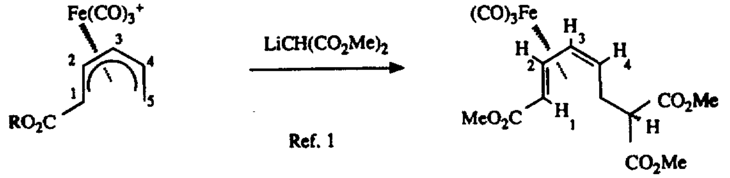
SUMMARY: The title reaction was originally reported to afford the E,Z-η^4-diene complex. Reexamination of the spectral data and decomplexation of the ligand indicates that the product is a σ-π-allyl complex.

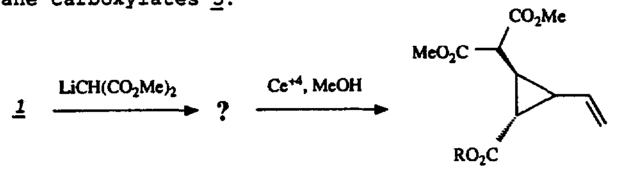
As part of our overall program on the application of organoiron chemistry to organic synthesis, we recently reported on the reactivity of a series of (1-substituted-pentadienyl)-(tricarbonyl)iron(+1) cations (1) with malonate nucleophiles.[1] In particular, the reaction of (1-methoxycarbonylpentadienyl)(tricarbonyl)iron(+1) (1a) with dimethyl malonate anion was originally reported to afford the E,Z-diene complex 2. As a result of our further studies on the reactivity of cation 1a with nucleophiles[2], and from the decomplexation of the product, we now wish to correct this erroneous structural assignment.

1a, R = Me
1b, = Et



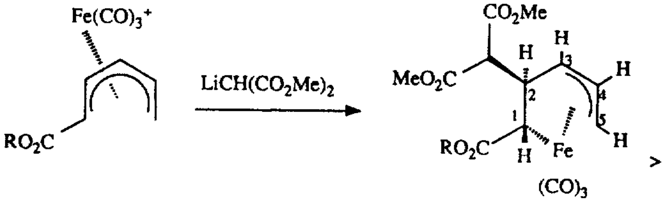
2

In general, the oxidative decomposition of (η^4-diene)(tricarbonyl)iron complexes simply affords the liberated ligand.[3] In comparison, decomplexation (Ce^{+4}, MeOH) of the chromatographed product from the reaction of 1a or 1b with dimethyl malonate anion gave the 3-substituted-2-vinylcyclopropane carboxylates 3.[4]



3a, R = Me (39%)
3b, = Et (76%)

A comparison of the ^{1}H NMR spectral data for the product[5] from the reaction of 1a with malonate anion with that of known E,Z- or E,E-(1-methoxycarbonyldiene)iron complexes[2,6] indicates that the original structural assignment (an η^4-diene complex) is incorrect. Moreover, the spectral data more closely matches that reported for a variety of σ,π-allyl complexes.[7] In specific, the upfield signal at δ 0.08 (obscured in the original study by internal TMS) is characteristic of protons on carbon σ-bound to a metal. *Thus, we would like to reassign 4 as the major product.* The 300 MHz NMR spectrum of the crude product also indicated that 2[8] was formed as a very minor product (<5%).



4 + 2

> 20 : 1

To our knowledge, attack by malonate nucleophile at an internal position on a (dienyl)-(tricarbonyl)iron(+1) cation is *unprecedented.*[9] Attack on 1a at C2 is probably due to coulombic interactions as a result of increased electronic demand by methoxycarbonyl substitutent at C1.[10] The ^{1}H and ^{13}C NMR spectra of 1a[11] are consistent with this proposal. Notably, the *C1* and *H2* signals of 1a appear at ~δ66 and δ6.73 respectively, while the *C1* and *H2* signals for (1-alkyl-pentadienyl)iron(+1) cations appear at ~δ94 and 6.2 respectively (CD_3NO_2 solvent).[12]

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REFERENCES AND NOTES

1) W.A. Donaldson, M. Ramaswamy, *Tetrahedron Lett.* (1988) 1343.
2) W.A Donaldson, M. Ramaswamy, *Tetrahedron Lett.* preceeding communication in this issue.
3) J.E. Mahler, R. Pettit, *J. Am. Chem. Soc.* (1963) *85*, 3955; R. Gree, M. Laabassi, P. Mouset, R. Carrie, *Tetrahedron Lett.* (1984) 3693; A.J. Pearson, T. Ray, *Tetrahedron* (1985) *41*, 5765.
4) 3b: 250 MHz ^{1}H NMR ($CDCl_3$) δ 5.32 (m, 1H), 5.20 (d, *J* = 15.5, 1H), 5.16 (d, *J* = 9.0, 1H), 4.12 (q, *J* = 7.0, 2H), 3.72 (s, 6H), 3.02 (d *J* = 10.2, 1H), 2.3-2.1 (m, 2H), 1.73 (t, *J* = 4.7, 1H), 1.24 (t, *J* = 7.0, 3H); 15 MHz ^{13}C{1H} NMR ($CDCl_3$) δ 171.7, 168.7, 132.0, 118.7, 60.8, 52.6, 50.4, 28.7, 26.0, 25.6, 14.2; GC/MS (m/z) 270 (1.2), 139 (100).
5) 4a: 300 MHz ^{1}H NMR ($CDCl_3$) δ4.6-4.5 (m, *H3,4*), 3.78 (m, *H2*), 3.72, 3.66, 3.57 (s, 10H, OMe & $H5_{syn}$), 2.84 (d, *J* = 11, C*HE*$_2$), 2.45 (dd, *J* = 2.5, 11, $H5_{anti}$), 0.08 (d, *J* = 9, *H1*).
6) J.P. Lellouche, P. Breton, J.P. Beaucort, L. Toupet, R. Gree, *Tetrahedron Lett.* (1988) 2449; J. Morey, D. Gree, P. Mosset, L. Toupet, R. Gree, *Ibid.* (1987) 2959; R. Gree, M. Laabassi, P. Mosset, R. Carrie, *Ibid.* (1985) 2317.
7) T.H. Whitesides, J.P. Neilan, *J. Am. Chem. Soc.* (1976) *98*, 63; J.R. Bleeke, M.K. Hays, *Organometallics* (1987) *6*, 1367; P. Pinsard, J.P. Lellouche, J.P. Beaucort, L. Toupet, L. Schio, R. Gree, *Organometallics*, submitted for publication.
8) 2a: 300 MHz ^{1}H NMR ($CDCl_3$) δ 6.06 (dd, *J* = 5.5, 9.1, *H2*), 5.28 (dd, *J* = 5.5, 7.5, *H3*), 3.75, 3.69 (s's, OCH_3), 3.34 (dd, *J* = 6.5, 8.1, $CH(CO_2Me)_2$), 2.60 (m, *H4*), 2.31 (m, *H5*), 2.21 (d, *J* = 9.1, *H1*), 1.65 (m, *H5'*).
9) Attack by 2,4-dimethylpentadienyl anion at the internal position of (pentadienyl)tris(trimethylphosphine)iron(+1) and attack of $NaBH_3CN$ at the internal position of (1,5-diphenylpentadienyl)(tricarbonyl)iron(+1) have been reported. In addition, the reaction of 1a with trimethylphosphite proceeds via attack at C2 and C5 (2:3 ratio).[7]
10) In general, the regioselectivity of attack by "soft" nucleophiles on (cyclohexadienyl)(tricarbonyl)iron(+1) cations has been attributed to frontier orbital control: A.J. Pearson, T.R. Perrior, D.C. Rees, *J. Organometal. Chem.* (1982) *226*, C39.
11) 1a: 60 MHz ^{1}H NMR δ 7.30 (t, *J* = 7, *H3*), 6.73 (dd, *J* = 7, 11, *H2*), 6.40 (m, *H4*), 4.07 (dd, *J* = 3, 9, $H5_{exo}$), 3.87 (s, OCH_3), 2.60 (d, *J* = 11, *H1* & $H5_{endo}$); ^{13}C{^{1}H} NMR δ195.2 (M-C=O), 168.1 (CO_2Me), 106.2, 105.8 (*C2* & *C4*), 97.9 (*C3*), 68.5, 64.9 (*C1* & *C5*), 52.8 (OMe).
12) W.A. Donaldson, M. Ramaswamy, *Syn. React. Inorg. Met.-Org. Chem.* (1987) *17*, 49.

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