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

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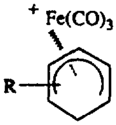
SUMMARY: The title compounds react with alkynyl cuprates via attack at the unsubstituted terminus to afford (η^4-*trans,cis*-1,3,6-dienyne)Fe(CO)$_3$ complexes. The regioselectivity of this attack appears to be sterically controlled.

The application of (η^5-cyclohexadienyl)iron(+1) cations (1) to the synthesis of cyclohexane containing natural products is well documented.[1] In comparison, although the corresponding *open* (η^5-pentadienyl)iron(+1) cations (2)[2] have been known for nearly as long, there are few examples of the application of these compounds to the synthesis of linear polyenes.[3] This is due largely to the fact that little is known of the reactivity of 2 with carbon nucleophiles.[4,5] Recently we reported upon the reactivity of cations 2 with malonate nucleophiles and noted that the site of attack was dependent on the nature of the substitutent R.[6] As part of our continuing interest in the application of cations 2 to organic synthesis, we have investigated the reactivity of these cations with alkynyl nucleophiles.



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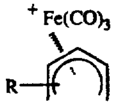
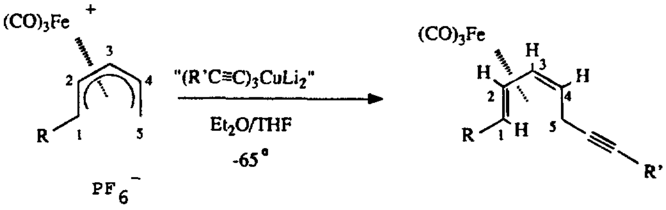


2

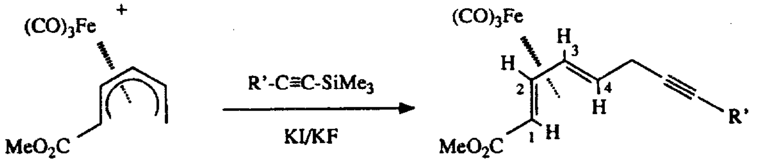
The reaction of cations 3a-c with lithio phenylacetylene resulted in products which were extremely sensitive to decomposition, and could not be isolated or characterized. In contrast, the reaction of cations 3a-c with alkynyl cuprates gave the (diene)iron complexes 4a-d, in good to modest yield after column chromatography.[7] The products isolated are those which arise via attack of the nucleophile regiospecifically at the unsubstituted pentadienyl terminus. In addition each of the dienes was assigned the E,Z stereochemistry on the basis of their characteristic ^{1}H NMR spectral data. In particular, complexes 4c and d exhibit a signal at ~δ6.0 (dd, J = 5, 10) for H_2 and a signal at ~δ5.3 (dd, J = 5, 6) for H_3.[8,9]

3a, R = CH_3
3b, R = Ph
3c, R = CO_2Me



	R	R'	yield
4a	CH_3	Ph	64%
4b	Ph	Ph	32%
4c	CO_2Me	Ph	27%
4d	CO_2Me	C_5H_{11}	59%

While the reaction of (cyclohexadienyl)iron cations with *alkyl cuprates* is known,[10] the present results represent the first examples of the reactivity of *alkynyl cuprates* with dienyl iron cations. It has previously been noted that alkynyl cuprates are considerably more stable and therefore less reactive than the corresponding alkyl cuprates.[11] Thus the facile reactivity of *3a-c* with alkynyl cuprates indicates that these cations are *extremely* good organometallic electrophiles. It should be noted that the attack of alkynyl cuprate on cation *3a* is regiospecific while the attack of malonate anion on *3a* is non-selective. In addition, cations *3b* and *3c* undergo reaction with alkynyl cuprates at a completely different pentadienyl carbon than attack by malonate anion (*C1* and *C2* respectively).[6] This is perhaps not surprising. The regioselectivity for nucleophilic attack of alkyl cuprates on (cyclohexadienyl)iron(+1) cations[10] is greater than that observed for malonate nucleophile.[12] The regioselectivity for this latter C-C bond formation has previously been attributed to steric effects.[10] The results reported herein are consistent with attack at the less sterically hindered pentadienyl terminus.

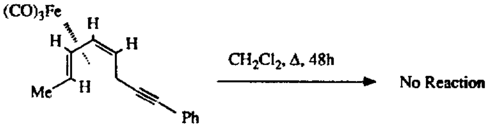


3c PF_6^-

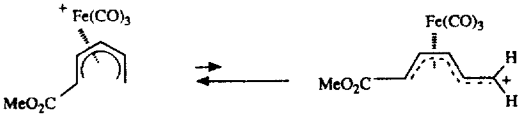
5 R' = Ph (56%)

6 R' = C_5H_{11} (46%)

In comparison, the reaction of cation *3c* with 1-trimethylsilylphenylacetylene or 1-trimethylsilyl-1-heptyne in refluxing methylene chloride in the presence of KF/KI gave the complexed dienoates *5* and *6* respectively.[13] The products are assigned the *E,E* stereochemistry on the basis of their characteristic ^{1}H NMR spectral data. In contrast to complexes *4c* and *4d*, complexes *5* and *6* exhibit signals at ~δ5.7 (dd, *J* = 5, 9) for H_2 and ~δ5.3 (dd, *J* = 5, 9) for H_3.[14] While the isomerization of *cis*-diene iron complexes to the more stable *trans*-diene iron complexes is known to occur thermally, we do not believe that the products *5* and *6* arise via initial formation of *trans,cis* complexes *4c* and *4d* followed by isomerization. In general, this isomerization process requires considerably higher temperatures (~75-100°C)[9] than that achieved under the present reaction conditions. For example, heating complex *4a* in CH_2Cl_2 at reflux for 48h gave only unchanged *trans,cis* *4a*. However, while it is clear that *5* and *6* do not arise via attack on the "U" pentadienyl cation, the exact mechanism for their formation is not unambigous. One possibility is attack of a weak nucleophile on the "S" or *trans* pentadienyl cation.[15]

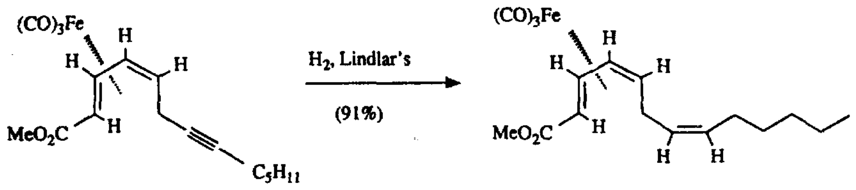


4a



"U" "S"

The reduction of complexed 1,3,6-dienyne 4d with H_2 in the presence of Lindlar's catalyst gave the complexed (E,Z,Z)-1,3,6-triene 7 in excellant isolated chemical yield.[16] While the ^1H NMR signal for H_2 appeared as a distinct signal (δ6.04, dd, J = 5, 9) the signal for H_3 was obscured by the peaks due to the new olefinic protons. However, the stereochemistry could be assigned on the basis of ^{13}C NMR spectral data.[17] Notably, the only major difference between the two spectra is the appearance of the *cis*-olefinic peaks for 7 (δ130.9, 128.8) instead of the alkynyl peaks of 4d (δ82.2, 78.6); the remainder of the signals are nearly identical. This compound might serve as an intermediate for the synthesis of the leukotriene 8-HETE or 5,6-LTA_4.[18]



4d 7

In summary, these results demonstrate that the (1-substituted-pentadienyl)iron(+1) cations may serve as precursors for the stereoselective synthesis of (E,Z)-1,3,6-dienynes via their reaction with alkynyl cuprates. The regioselectivity of this reaction appears to be controlled by steric influence.

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5) Recently, the reactivity of the *trans*-pentadienyl iron cation, generated *in situ*, with allyl silanes has been reported: M. Uemura, T. Miniami, Y. Yamashita, *Tetrahedron Lett.* (1987) 641.

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7) A typical experimental procedure follows: A solution of lithio phenylacetylene (1.50 mmol prepared from phenylacetylene and *n*-butyl lithium) in diethyl ether (20 mL) was added to $CuBr{\cdot}Me_2S$ (100 mg, 0.45 mmol) in ether (20 mL) at -65°C under N_2. After stirring (1/2 h) a homogeneous solution was obtained. To the cold alkynyl cuprate solution was added (tricarbonyl)(1-methylpentadienyl)iron(+1) hexafluorophosphate (180 mg, 0.49 mmol). The reaction mixture was stirred at -65°C (2 h), warmed to 23°C (1 h) and treated successively with 28%

aqueous NH_4OH (2 mL) and saturated aqueous NH_4Cl (30 mL). The mixture was extracted with ether (40 mL) and washed 3X with H_2O. The organic layer was dried over $MgSO_4$, filtered and the solvent removed under reduced pressure. The residue was chromatographed on silica gel using hexanes:benzene as eluant. The yellow fraction was concentrated to give the product 4a (100 mg, 0.31 mmol, 64%).

8) 4a: IR (CH_2Cl_2, cm^{-1}) 2046s, 1972s; 60 MHz ^1H NMR ($CDCl_3$) δ 7.6-7.1 (m, Ar*H*), 5.3-5.0 (m, *H2* and *H3*), 2.5-1.0 (m, *H1, H4, H5*), 1.42 (d, *J* = 6, CH_3); 15 MHz ^{13}C NMR ($CDCl_3$) δ 211.1 (M-*C*=O), 132.5, 131.5, 128.7, 127.7 (Ar), 95.5 (*C2*), 89.6 (*C*≡C), 81.2 (*C3*), 78.9 (C≡*C*), 57.6 (*C1*), 55,0 (*C4*), 20.3, 19.0 (CH_3, *C5*).

4b: IR (CH_2Cl_2, cm^{-1}) 2049s, 1980s; 60 MHz ^1H NMR ($CDCl_3$) δ 7.6-6.9 (m, Ar*H*, 10H), 5.95 (dd, *J* = 5, 10, *H2*), 5.30 (t, *J* = 5, *H3*), 3.29 (d, *J* = 10, *H1*), 2.9-2.4 (m, *H4, H5*); 15 MHz ^{13}C NMR ($CDCl_3$) δ 210.4 (M-*C*=O), 140.0, 132.5, 131.6, 128.7, 127.8, 126.7, 126.1 (*Ar*), 89.8 (*C2*), 89.1 (*C*≡C), 81.6 (*C3*), 80.6 (C≡*C*), 60.7 (*C1*), 54.7 (*C4*), 19.4 (*C5*).

4c: IR (CH_2Cl_2, cm^{-1}) 2064s, 2001s, 1718s; 60 MHz ^1H NMR ($CDCl_3$) δ 7.4-7.0 (m, Ar*H*), 5.97 (dd, *J* = 5, 9, *H2*), 5.27 (dd, *J* = 5, 6, *H3*), 3.57 (s, OCH_3), 2.8 (m, *H4*), 2.3 (m, *H5*), 2.07 (d, *J* = 9, *H1*), 1.3 (m, *H5'*); 15 MHz ^{13}C NMR ($CDCl_3$) δ 210.4 (M-*C*=O), 172.9 (*C*OOR), 131.6, 128.1, 127.9 (*Ar*), 93.7 (*C2*), 88.3 (*C*≡C), 85.0 (*C3*), 80.6 (C≡*C*), 56.4 (*C1*), 51.8 (OCH_3), 45.9 (*C4*), 19.2 (*C5*).

4d: IR (CH_2Cl_2, cm^{-1}) 2062s, 1998s, 1715s; 60 MHz ^1H NMR ($CDCl_3$) δ 6.05 (dd, *J* = 5, 9, *H2*), 5.32 (dd, *J* = 5, 6, *H3*), 3.60 (s, OCH_3), 2.85 (m, *H4*), 2.3-1.9 (m, 5H), 1.6-1.2 (m, 6H), 0.9 (br t, CH_3); 15 MHz ^{13}C NMR ($CDCl_3$) δ 208.7 (M-*C*=O), 173.1 (*C*OOR), 93.6 (*C2*), 85.1 (*C3*), 82.2 (*C*≡C), 78.6 (C≡*C*), 57.8 (*C1*), 51.8 (OCH_3), 45.9 (*C4*), 18.7 (*C5*), 31.2, 28.6, 22.2, 18.7, 14.0.

9) For comparison, see: J. Morey, D. Gree, P. Mosset, L. Toupet, R. Gree, *Tetrahedron Lett.* (1987) 2959; R. Gree, M. Laabassi, P. Mosset, R. Carrie, *Ibid.* (1985) 2317; T.H. Whitesides, J.P. Neilan, *J. Am. Chem. Soc.* (1976) 98, 63.

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14) 5: IR (CH_2Cl_2, cm^{-1}) 2062s, 1991s, 1712s; 60 MHz ^1H NMR ($CDCl_3$) δ 7.4-7.0 (m, Ar*H*), 5.70 (dd, *J* = 5, 9, *H2*), 5.30 (dd, *J* = 5, 9, *H3*), 3.52 (s, OCH_3), 2.7 (m, 2H, *H5*), 1.3 (m, *H4*), 0.90 (d, *J* = 9, *H1*); 15 MHz ^{13}C NMR ($CDCl_3$) δ 209.4 (M-*C*=O), 172.5 (*C*OOR), 131.6, 128.3, 128.0 (*Ar*), 87.0 (*C*≡C), 86.7 (*C2*), 83.4 (*C3*), 59.9 (*C1*), 51.5 (OCH_3), 46.0 (*C4*), 24.0 (*C5*). The signal for the other alkyne carbon is obscured by one of the peaks for $CDCl_3$ (79.1).

6: IR (CH_2Cl_2, cm^{-1}) 2062s, 1998s, 1712s; 60 MHz ^1H NMR ($CDCl_3$) δ 5.72 (dd, *J* = 5, 9, *H2*), 5.30 (dd, *J* = 5, 9, *H3*), 3.64 (s, OCH_3), 2.5 (m, 2H), 2.1 (m, 2H), 1.36 (m, 7H), 0.9 (m, 4H); 15 MHz ^{13}C NMR ($CDCl_3$) δ 209.9 (M-*C*=O), 172.6 (*C*OOR), 86.7 (*C2*), 83.1 (*C3*), 61.3 (*C1*), 51.7 (OCH_3), 45.8 (*C4*), 23.5 (*C5*), 31.2, 28.6, 22.3, 18.7, 14.0. One of the alkynyl carbon signals overlaps with *C3* (83.1) and the other is obscured by $CDCl_3$ (79.1).

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17) 7: IR (CH_2Cl_2, cm^{-1}) 2059s, 1981s, 1712s; 60 MHz ^1H NMR ($CDCl_3$) δ 6.04 (dd, *J* = 5, 9, *H2*), 5.3 (m, 3H, *H3, H6, H7*), 3.65 (s, OCH_3), 2.7 (m, *H4*), 2.20 (d, *J* = 9, *H1*), 1.9 (br m, 4H), 1.2 (br m, 6H), 0.90 (br t, 3H); 15 MHz ^{13}C NMR ($CDCl_3$) δ 209.2 (M-*C*=O), 173.1 (*C*OOR), 130.9 (*C*=*C*), 128.8 (*C*=*C*), 92.8 (*C2*), 85.5 (*C3*), 58.6 (*C1*), 51.6 (OCH_3), 46.0 (*C4*), 31.5, 29.2, 27.3, 26.7, 22.6, 14.0.

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