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Synthesis and reactivity of tricarbonyl(η^5-4-triethylsilyl-1-methylpentadienyl)iron(+1) cation

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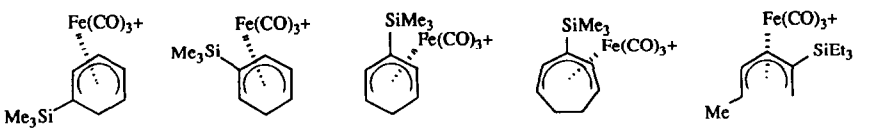
Abstract

Tricarbonyl(η^5-4-triethylsilyl-1-methylpentadienyl)iron(+1) hexafluorophosphate was prepared by the protonation of *Ψ-endo* tricarbonyl(η^4-5-triethylsilyl-3,5-hexadien-2-ol)iron with hexafluorophosphoric acid. The cation reacts with H_2O, CH_3OH, $NaBH_3CN$, PPh_3, sodium dimethylmalonate and dimethyl cuprate in a regiospecific fashion by nucleophilic attack at C1. The regioselectivity for nucleophilic attack appears to be predominantly the result of steric control.

Introduction

Silyl-substituted dienes have shown utility in organic synthesis owing to their ability to participate in Diels–Alder reactions [1] as well as their ability to react as vinyl silanes [2]. As part of our efforts on the stereospecific synthesis of 1,3-dienes we have investigated the regioselectivity of nucleophilic attack on substituted tricarbonyl(pentadienyl)iron cations [3]. While there are no reported syntheses of silyl-substituted (pentadienyl)$Fe(CO)_3$ cations, the preparation of 1-, 2-, and 3-trimethylsilyl-substituted (*cyclohexadienyl*)$Fe(CO)_3$ cations (**1**, **2**, **3**) [4] and (3-trimethylsilyl*cycloheptadienyl*)-$Fe(CO)_3$ cation **4** [5] have been reported. However, **1** and **2** were obtained as an inseparable mixture [4a] and the substitution pattern present in **3** and **4** is not suitable for delineating the regiochemical directing effect of a trialkylsilyl substituent.



1 **2** **3** **4** **5**

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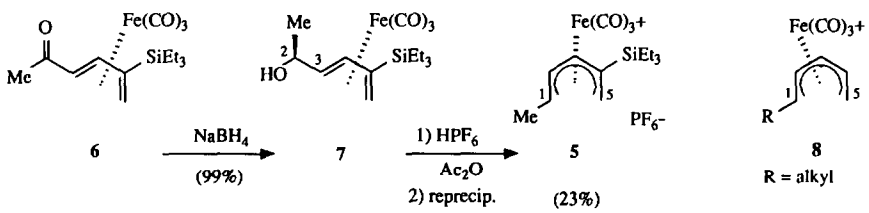
We herein report on the synthesis of tricarbonyl (η^5-4-triethylsilyl-1-methylpentadienyl)iron(+1) hexafluorophosphate (**5**) and the regiospecific reaction of **5** with a variety of carbon and heteroatom nucleophiles.

Results and discussion [6*]

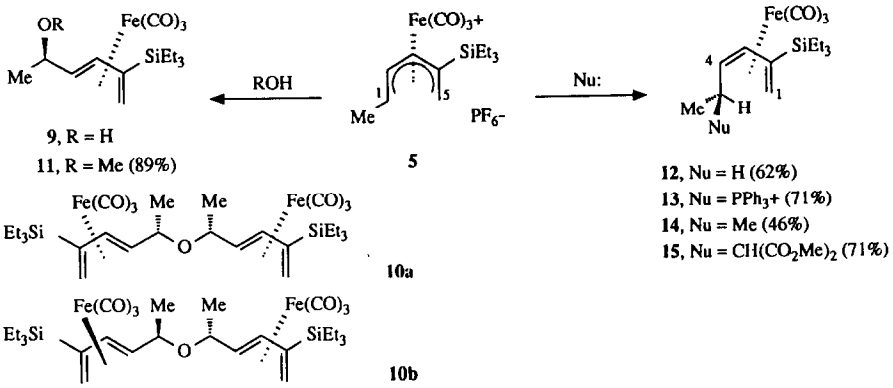
Tricarbonyl[(*E*)-5-triethylsilyl-3,5-hexadien-2-one]iron (**6**) was prepared according to the literature procedure by acylation of tricarbonyl(2-triethylsilyl-1,3-butadiene)iron, followed by isomerization and separation [7]. Reduction of **6** with sodium borohydride gave a single dienol product **7**. The *E* stereochemistry was assigned to **7** on the basis of its ^{1}H NMR spectral data. Notably, the signal corresponding to H4 appears at δ 5.12 as a doublet (J 8.8 Hz) and the signal for H6*endo* appears far upfield at δ 0.22 ppm. Furthermore, this compound was assigned the *Ψ-endo* relative stereochemistry [8*] by analogy to the reduction of other complexed dienyl–methyl ketones [9] and by spectral comparison with the *Ψ-exo* isomer (*vide infra*).

Treatment of **7** with HPF_6–Ac_2O–Et_2O, followed by reprecipitation from CH_3NO_2–Et_2O—0°C gave the cation **5** as a pale yellow solid. The pentadienyl ligand was assigned the *cis* ("U") geometry on the basis of its ^{1}H NMR coupling data [10]. The ^{13}C NMR chemical shifts for the signals corresponding to C1 and C5 of **5** (δ 97.7 and 63.7) are relatively similar to those for C1 and C5 of other (η^5-1-alkyl-pentadienyl)iron(+1) cations **8** (*ca.* δ 96 and 64) [9]. This might be interpreted to indicate that the triethylsilyl substituent at C4 has no significantly electronic effect on the terminal carbons [11*].



The results of the reactions of **5** with water, methanol, sodium cyanoborohydride, triphenylphosphine, lithium dimethylcuprate and sodium dimethylmalonate appear in Scheme 1. The reaction of **5** with water gave a mixture of the *trans Ψ-exo* alcohol **9** and two diastereoisomeric ethers **10a** and **10b** (*ca.* 1:2:2 ratio). Portions of the NMR spectral data for **9** are conspicuously different from those of **7**. Notably, the relative chemical shifts of the alcohol methine proton (δ 3.78 and δ 3.60, **7** and **9** respectively) are consistent with the pattern empirically observed for the alcohol methine signals of complexed dienols (*i.e. Ψ-endo* downfield of *Ψ-exo*) [12]. The *trans-Ψ-exo* configuration for **9** is consistent with attack by water on the *transoid* ("S") form of the pentadienyl cation [13]. The ethers **10a** and **10b** arise via reaction of the cation **5** with alcohol **9** at a competitive rate to reaction with water [14*]. Since the cation **5** and therefore the alcohol **9** are both racemic mixtures of enantiomers (with respect to the coordination of the diene) then two diastereoiso-

* Reference number with asterisk indicates a note in the list of references.



Scheme 1.

meric ethers are formed. Therefore, each iron diene *subunit* of the dimers is assigned the *Ψ-exo* relative stereochemistry. In comparison, the reaction of **5** with methanol gave a single methyl ether **11**. The *Ψ-exo* relative configuration was assigned to **11** by analogy to the reaction of **5** with water.

The reaction of **5** with $NaBH_3CN$, triphenylphosphine, $(CH_3)_2CuLi$, or sodium dimethylmalonate gave a single isolable product in each case (**12**, **13**, **14**, and **15** respectively). The structure of each was assigned on the basis of ^1H NMR spectral data. The presence of only a single internal diene proton (H3, δ 4.8–5.0) and the relatively downfield chemical shifts of the signals for H1*endo* and H4 (δ 1.25–1.45 and δ 2.3–2.7 respectively) are characteristic of a (*Z*)-2,4-disubstituted diene complex [3d, 15*].

In all cases examined, nucleophilic attack occurs regiospecifically at C1 of the cation **5**. The electronic character at C1 and C5 of **5** is not greatly different from that of **8**. Thus it is illustrative to compare the reactivity of **5** with the reactivity of **8**. The reactions of **8** (R = Me) with water [13], $NaBH_3CN$ [16], triphenylphosphine [17], sodium dimethylmalonate [3a] and cuprates [3b, 18] have been reported. The reactions of **5** with triphenylphosphine and dimethyl cuprate proceed with the opposite regiospecificity as compared to the reactions of **8** with the same types of nucleophiles. Thus, for these nucleophiles, the regiochemical directing effect of the 4-triethylsilyl substituent is opposite to, and greater than, the directing effect of a 1-methyl substituent. It has been proposed that the regioselectivity for attack on the pentadienyl ligand by cyanoborohydride, PPh_3 and cuprates is the result of steric control [3b, 16, 17]. It is perhaps not surprising that the considerable bulk of the triethylsilyl substituent is able to reverse the steric influence of the methyl substituent. A molecular mechanics generated structure [19] for **5**, which illustrates this hindrance, appears in Fig. 1.

The 1-methyl substituent shows a slight regiodirecting effect for attack by malonate anion at the substituted terminus. This effect has been rationalized as a subtle counter-balancing of opposing steric and electronic effects [3a]. For malonate anion as the nucleophile, the 4-triethylsilyl substituent augments the directing effect of the 1-methyl substituent. Presumably, the additional hindrance for attack at C5 causes the combined steric effects to be coincident with the electronic effects for **5**.

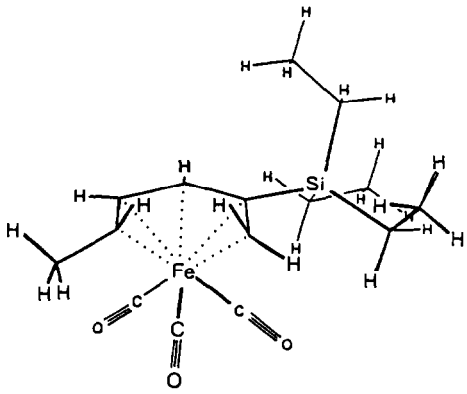
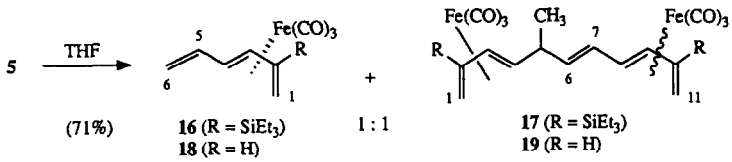


Fig. 1.

The regiospecificity of nucleophilic attack of water–alcohol nucleophiles with **5** and with **8** is identical. Thus for this nucleophile it is not possible to compare the directing effects of the 4-triethylsilyl and the 1-methyl substituents.

Finally, the cation **5** is somewhat unstable in THF solution. Upon dissolution of **5** in THF-d_8, the formation of triene complex **16** could be observed by ^{1}H NMR spectroscopy. Monitoring the reaction by TLC indicated the formation of **16** as well as the dimeric species **17**. The structural assignments for **16** and **17** are based upon comparison of their NMR spectral data with that reported for **18** and **19** [20]. Presumably, the 4-triethylsilyl substituent activates **5** toward deprotonation under mild conditions. Reaction of the triene **16** with the transoid form of cation **5**, followed by deprotonation affords **17**. As in the case of ethers **10**, the dimers **17** are obtained as a mixture of diastereomers since the precursor **5** is racemic.



In summary, it has been shown that the bulky 4-triethylsilyl substituent can influence, and for certain nucleophiles reverse, the regiochemical directing effect of a 1-methyl substituent.

Experimental section [21*]

Tricarbonyl(5-triethylsilyl-3,5-hexadien-2-ol)iron (7)

To a solution of tricarbonyl[(*E*)-5-triethylsilyl-3,5-hexadien-2-one]iron (**6**, 4.20 g, 12.0 mmol) in anhydrous EtOH (50 mL) was added solid sodium borohydride (0.23 g, 6.3 mmol) in small portions. The mixture was stirred for 1 h. A second portion of $NaBH_4$ (0.22 g, 6.0 mmol) was added and the mixture stirred for an additional 1 h. The volume of the solution was reduced, followed by cautious addition of H_2O (70 mL). The mixture was filtered through filter-aid, extracted with ether (2 × 50 mL) and the combined organic layers were dried (Na_2SO_4) and the solvent removed

under reduced pressure. The residue was purified by chromatography on SiO_2 using 7% EtOAc–hexanes as eluant. Evaporation of the product fractions gave a yellow oil: 4.20 g, 11.9 mmol, 99%. **7**: ^1H NMR ($CDCl_3$) δ 5.12 (d, J 8.8, H4), 3.78 (pent, J 6.5, H2), 1.69 (br s, H6*exo*), 1.61 (br s, OH), 1.35 (d, J 6.3, CH_3), 0.98 (m, H3), 0.22 (br s, H6*endo*), 1.05 (t, $J = 7.5$) and 0.76 (q, J 7.5, $Si(CH_2CH_3)_3$); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 89.3 (C5), 84.8 (C4), 74.6 (C2), 69.9 (C3), 43.2 (C6), 26.0 (C1), 7.5 and 3.6 ($SiEt_3$); IR (neat) 3410, 2043, 1971 cm^{-1}; EI-HRMS, m/z 352.0809 [$C_{15}H_{24}O_4FeSi$ calcd.: 352.0789].

Tricarbonyl(η^5-2-triethylsilylhexadienyl)iron(+1) hexafluorophosphate (5)

To a cold solution of HPF_6 (1.7 mL, 60% in H_2O) in acetic anhydride (1.8 mL) was added a solution of **7** (2.20 g, 6.25 mmol) in acetic anhydride (1.1 mL) and ether (7 mL). The solution was slowly added dropwise to a large excess of ether (250 mL). The ether was decanted and the resultant precipitate was collected by vacuum filtration. The crude product was dissolved in a minimal amount of nitromethane and was reprecipitated by dropwise addition to excess ether (250 mL). The resultant light yellow precipitate was collected by vacuum filtration and dried *in vacuo*: 0.68 g, 1.41 mmol, 23%. **5**: m.p. 90–94°C (dec.); ^1H NMR (CD_3NO_2) δ 6.78 (d, J 6.8, H3), 5.86 (dd, J 6.8, 12.1, H4), 3.81 (dq, J 12.1, 6.0, H5), 3.39 (d, J 3.6, H1*exo*), 2.14 (d, J 3.6, H1*endo*), 1.91 (d, J 6.0, CH_3), 1.11 (t, J 7.8) and 0.97 (q, J 7.8, $Si(CH_2CH_3)_3$); $^{13}C\{^1H\}$ NMR (CD_3NO_2) δ 120.2 (C2), 107.3 (C4), 99.9 (C3), 97.7 (C5), 63.7 (C1), 21.8 (C6), 7.7 and 4.0 ($Si(CH_2CH_3)_3$); IR (KBr) 2114, 2062, 1979 cm^{-1}; Anal. Found: C, 35.62; H, 4.76. $C_{15}H_{23}O_3SiFePF_6$ calcd.: C, 35.50; H, 4.79%.

Reaction of 5 with water

A sample of **5** (70 mg, 0.15 mmol) was added to water–THF (1:1, 15 mL) and the suspension was vigorously stirred for 1 h. The reaction mixture was extracted with ether (2 × 50 mL) and the combined ethereal extracts were washed with brine (25 mL). The organic layer was dried ($MgSO_4$), and the solvent evaporated, and dried *in vacuo* to afford a yellow oil: 40 mg. This was identified as a mixture of alcohol **9** and the diastereomeric ethers **10a** and **10b** (1:2:2). **9**: ^1H NMR ($CDCl_3$, partial) δ 5.19 (d, J 8.3, H5), 3.80 (m, H2), 1.38 (d, J 6.6, CH_3); **10a/b**: ^1H NMR ($CDCl_3$) δ 5.09 (d, J 9.2) and 4.99 (d, J 9.2, diastereomeric H4), 3.32 (m, H2), 1.70 (br s, H6*exo*), 1.33 (d, J 6.2, CH_3), 1.18 (m H3), 1.05 (t, J 7.5) and 1.03 (t, J 7.5) and 0.75 (q, J 7.5, $Si(CH_2CH_3)_3$), 0.32 (br s, H6*endo*).

Reaction of 5 with methanol

A sample of **5** (50 mg, 0.10 mmol) was added to methanol (10 mL) and the mixture was stirred for 1 h. The mixture was diluted with water (10 mL) and worked up in a fashion similar to the reaction of **5** with water. The crude product was purified by chromatography (SiO_2) using 10% EtOAc–hexanes as eluant to give a yellow oil: 30 mg, 0.089 mmol, 89%. **11**: ^1H NMR ($CDCl_3$) δ 5.14 (d, J 8.5, H4), 3.32 (s, OCH_3), 3.09 (dq, J 8.0, 6.2, H2), 1.70 (br s, H6*exo*), 1.35 (d, J 6.2, CH_3), 1.14 (t, J 8.3, H3), 0.31 (br s, H6*endo*), 1.06 (t, J 7.9) and 0.77 (q, J 7.9, $Si(CH_2CH_3)_3$); EI-HRMS, m/z 338.1006 [$C_{15}H_{26}O_3FeSi$ ($M - CO$) calcd.: 338.0996].

Reaction of 5 with $NaBH_3CN$

To a solution of **5** (0.10 g, 0.21 mmol) in THF (10 mL) at 0°C was added solid $NaBH_3CN$ (13.1 mg, 0.21 mmol) and the mixture was stirred for 1 h. The clear yellow solution was diluted with water (10 mL) and extracted with petroleum ether (2 × 25 mL). The combined extracts were dried ($MgSO_4$), and the solvent evaporated, and dried *in vacuo* to afford a yellow oil: 44 mg, 0.13 mmol, 62%. **12**: ^1H NMR ($CDCl_3$) δ 5.03 (d, *J* 7.9, H3), 2.70 (dt, *J* 5.5, 8.0, H4), 1.70 (d, *J* 2.0, H1*exo*), 1.64 (m, H5), 1.44 (d, *J* 2.0, H1*endo*), 1.21 (m, H5'), 0.94 (t, *J* 7.3, CH_3), 1.05 (t, *J* 7.6) and 0.75 (q, *J* 7.6, $Si(CH_2CH_3)_3$; EI-HRMS, *m/z* 336.0847 [$C_{15}H_{24}O_3FeSi$ calcd.: 336.0840].

Reaction of 5 with triphenylphosphine

To a solution of **5** (0.10 g, 0.21 mmol) in CH_2Cl_2 (10 mL) was added triphenylphosphine (60.0 mg, 0.23 mmol). The golden yellow solution was stirred for 18 h. The solvent was evaporated to afford a glassy solid which was washed several times with ether and dried *in vacuo* to give a light-yellow solid: 0.11 g, 0.15 mmol, 71%. **13**: mp 92–96°C; ^1H NMR ($CDCl_3$) δ 7.85–7.61 (m, 15H, PPh_3), 4.80 (d, *J* 6.9, H3), 3.32 (m, H5), 2.25 (br s, H1*exo*), 2.07 (dt, *J* 7.3, 11.6), 1.98 (br s, H1*endo*), 1.53 (dd, *J* 6.4, 19.3, CH_3), 0.95 (t, *J* 7.6) and 0.63 (q, *J* 7.6, $Si(CH_2CH_3)_3$); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 209.5 (M-C=O), 135.0 (d, *J*(PC) 2.4), 133.8 (d, *J*(PC) 5.5), 130.6 (d, *J*(PC) 12.2), 117.6 (d, *J*(PC) 81.2) (4 aryl C's), 101.2 (C2), 89.3 (d, *J*(PC) 2.4, C3), 55.6 (d, *J*(PC) 9.8, C4), 46.0 (C1), 28.7 (d, *J*(PC) 37.2, C5), 18.2 (C6), 7.5 and 3.4 ($SiEt_3$); Anal. Found: C, 52.41; H, 5.17. $C_{33}H_{38}O_3P_2F_6SiFe \cdot 1/2H_2O$ calcd.: C, 52.74; H, 5.23%.

Reaction of 5 with dimethylcuprate

To a suspension of $CuBr \cdot Me_2S$ (63.4 mg, 0.31 mmol) in ether (2 mL) at −78°C was added an ethereal solution of methyl lithium (0.44 mL, 1.4 *M*, 0.62 mmol) and the mixture was stirred for 1 h. To the cold solution was added solid **5** (123.4 mg, 0.28 mmol) in one portion and the mixture was stirred at −78°C for an additional 2 h. The solution was warmed to room temperature diluted with saturated aqueous NH_4Cl (10 mL) and H_2O (10 mL), and extracted with ether (2 × 20 mL). The combined extracts were washed with H_2O (25 mL), followed by brine (25 mL), dried (Na_2SO_4) and the solvent evaporated under reduced pressure. The crude product was purified by chromatography over SiO_2 using hexane as eluant to give a yellow oil: 47.0 mg, 0.13 mmol, 46%. **14**: ^1H NMR ($CDCl_3$) δ 4.90 (d, *J* 8.1, H3), 2.60 (dd, *J* 8.1, 9.0, H4), 1.81 (br d, *J* 1.9, H1*exo*), 1.51 (m, H5), 1.33 (d, *J* 1.9, H1*endo*), 1.06 (t, *J* 7.8) and *ca.* 1.03 (d, 12H, $Si(CH_2CH_3)_3$ and $CHCH_3$), 0.80 (d, *J* 6.4) and 0.76 (br q, *J ca.* 7.8, 9H, $Si(CH_2CH_3)_3$ and $CHCH_3$); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 211.8 (M-C=O), 99.0 (C2), 90.2 (C3), 74.6 (C4), 43.9 (C1), 29.2, 29.0, 24.5 (C5, C6, C6'), 7.5 and 3.5 ($SiEt_3$); IR (neat) 2043, 1969, 1462 cm^{-1}; EI-HRMS, *m/z* 350.1006 [$C_{16}H_{26}O_3FeSi$ calcd.: 350.0996].

Reaction of 5 with sodium dimethylmalonate

To a solution of **5** (47.9 mg, 0.1 mmol) in THF (2.5 mL) cooled to 0°C was added sodium dimethylmalonate (0.13 mmol, freshly prepared from excess NaH and dimethylmalonate) in THF (4 mL). The reaction mixture was stirred for 1 h and then poured into ice–water (75 mL). The solution was poured into a separatory

funnel, ether (5.0 mL) was added, followed by 1N HCl (5 mL) and saturated aqueous NaCl. The layers were separated and the aqueous layer was extracted with ether (2 × 50 ml). The combined ethereal extracts were dried (Na_2SO_4) and concentrated. The residue was chromatographed over SiO_2 using hexanes: EtOAc (2:1) as eluant to give a yellow oil: 33 mg, 0.071 mmol, 71%. **15**: ^1H NMR ($CDCl_3$) δ 4.89 (d, *J* 7.9, H3), 3.71, 3.70 (2 s, OCH_3), 3.02 (d, *J* 6.8, CHE_2), 2.51 (dd, *J* 7.9, 10.3, H4), 2.05 (m, H5), 1.88 (br d, *J* 2.5, H1*exo*), 1.39 (d, *J* 2.5, H1*endo*), 1.19 (d, J = 6.4, CH_3), 1.06 (t, *J* 7.8) and 0.76 (br q, *J* 7.8, $Si(CH_2CH_3)_3$); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 211.1 (M − C=O), 168.3, 168.2 (COOR), 98.4 (C2), 90.2 (C3), 68.2 (C4), 60.8 (CHE_2), 52.3, 52.1 (OCH_3), 44.2 (C1), 34.6 (C5), 19.5 (CH_3), 7.5 and 3.6 ($SiEt_3$); EI-HRMS *m/z* 382.1269 [calculated for $C_{17}H_{30}O_4FeSi$ (M-3CO) 382.1257].

Deprotonation and dimerization of 5

A sample of **5** (0.11 g, 0.23 mmol) was dissolved with stirring in THF (5 mL). After 0.5 h the solvent was evaporated and the residue chromatographed (SiO_2) using hexanes as eluant, to give a yellow oil: 54.9 mg. This was determined to be a mixture of **16** and **17** (*ca.* 1:1) by NMR spectroscopy. Further chromatography of this mixture (SiO_2 230–400 mesh) using petroleum ether as eluant gave **16** (12.6 mg) followed by **17** (20.8 mg). **16**: ^1H NMR ($CDCl_3$) δ 5.77 (dt, *J* 16.9, 10.0, H5), 5.27 (br d, *J* 16.9, H6), 5.16 (d, *J* 8.8, H3), 4.98 (br d, *J* 10.3, H6′), 2.03 (t, *J* 10.0, H4), 1.74 (br s, H1*exo*), 0.47 (br s, H1*endo*), 1.06 (t, *J* 8.0) and 0.76 (br q, *J* 8.0, $Si(CH_2CH_3)_3$); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 211.9 (M − C=O), 138.7 (C5), 114.9 (C6), 90.9 (C2), 84.9 (C3), 66.4 (C4), 42.9 (C1), 7.6 and 3.6 ($SiEt_3$); EI-HRMS *m/z* 334.0700 [$C_{15}H_{22}O_3FeSi$ calcd.: 334.0681]. **17**: ^1H NMR ($CDCl_3$) δ 5.73 and 5.63 (dd, *J* 6.5, 15.1, H6), 5.43 (dd, *J* 10.0, 15.4, H7), 5.11 and 4.94 (2 d, *J* 8.8, H3 & H9), 2.08 (t, *J* 9.5, H8), 1.95 (m, H5), 1.70 and 1.66 (2 br s, H1*exo* & H11*exo*), 0.43 (br s, H11*endo*), 0.21 (br s, H1*endo*), 1.06 (t, *J* 8.0) and 0.76 (br q, *J* 8.0. $[Si(CH_2CH_3)_3]_2$); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 212.1 (M-C=O), 137.3 and 137.0 (diastereomeric C6), 129.5 and 129.4 (dia. C7), 91.8, 90.5, and 90.4 (dia. C3 & C10), 85.0, 84.5, and 84.2 (dia. C3 & C9), 73.0 and 72.9 (dia. C4), 66.7 and 66.6 (dia. C8), 43.0 and 42.9 (dia. C11), 42.4 and 41.5 (dia. C5), 22.4 and 21.7 (dia. CH_3), 7.6 and 3.6 ($SiEt_3$); FAB-HRMS *m/z* 667.1317 ($M^+ - H$) [$C_{30}H_{43}O_6Fe_2Si_2$ calcd.: 667.1303].

Acknowledgments

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6 All compounds described are racemic mixtures of enantiomers. Only one enantiomer has been diagrammed for clarity.

7 M. Franck-Neumann, M. Sedrati and M. Mokhi, J. Organomet. Chem., 326 (1987) 389.

8 The *Ψ-exo* and *Ψ-endo* nomenclature was first used by Lillya [9a].

9 (a) N.A. Clinton and C.P. Lillya, J. Am. Chem. Soc., 92 (1970) 3058; (b) M. Franck-Neumann, in A. de Meijere and H. tom Dieck (Eds.), Organometallics in Organometallic Synthesis, Springer-Verlag, Berlin, 1987, pp. 247–264.

10 W.A. Donaldson and M. Ramaswamy, Synth. React. Inorg. Met.-Org. Chem., 17 (1987) 49.

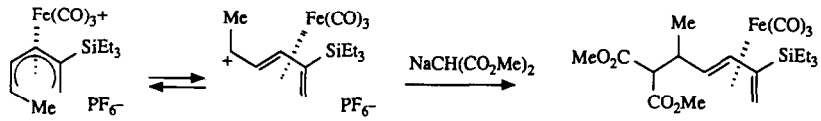
11 In contrast, a methoxy substituent at C2 of a cyclohexadienyl exerts significant electronic influence upon the terminal dienyl carbons as evidenced by ^{13}C NMR spectroscopy; *cf.* A.J. Birch, P.W. Westerman and A.J. Pearson, Aust. J. Chem., 29 (1976) 1671.

12 For further examples see W.A. Donaldson, C. Tao, D.W. Bennett and D. Grubisha, J. Org. Chem., 56 (1991) 4563, and references therein.

13 R.S. Bayoud, E.R. Biehl and P.C. Reeves, J. Organomet. Chem., 150 (1978) 75; J.E. Mahler, D.H. Gibson and R. Pettit, J. Am. Chem. Soc., 85 (1963) 3959.

14 Formation of ethers from the reaction of relatively insoluble (cyclohexadienyl)$Fe(CO)_3$ cations with water has previously been observed; A.J. Birch and D.H. Williamson, J. Chem. Soc., Perkin Trans. I, (1973) 1892.

15 If the solid generated by treatment of **7** with HPF_6 is not reprecipitated, an alternative outcome ensues. Reaction of this solid with sodium dimethylmalonate affords a *trans*-diene complex *i* (72%). It should be noted that the *cis* adduct **15** does not isomerize to *i* under the reaction conditions or with base (NaOMe) or thermally (C_6H_6, reflux). We have tentatively identified this solid as *ii*, the *endo*-methyl isomer of **5**, however, dissolution of this solid in CD_3NO_2, appears to effect isomerization to the *exo*-methyl isomer **5**.



ii *i*

i: ^1H NMR ($CDCl_3$) δ 5.01 (d, *J* 8.7, H3), 3.75, 3.74 (2 s, OCH_3), 3.57 (d, *J* 4.0, CHE_2), 2.10 (m, H5), 1.66 (s, H1*exo*), 1.50 (t, *J* 8.8, H4), 1.25 (d, *J* 6.8, CH_3), 1.05 (t, *J* 7.6) and 0.75 (br q, *J* 7.6, $Si(CH_2CH_3)_3$), 0.21 (s, H1*endo*); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 211.7 (M−C=O), 169.0, 168.5 (COOR), 92.1 (C2), 85.1 (C3), 70.9 (C4), 56.8 (CHE_2), 52.4, 52.1 (OCH_3), 43.4 (C1), 38.8 (C5), 19.6 (CH_3), 7.5 and 3.6 ($SiEt_3$); EI-HRMS *m/z* 382.1260 [$C_{17}H_{30}O_4FeSi$ (M−3CO) calcd.: 382.1257].

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