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An Unprecedented Hydride Abstraction from Tricarbonyl[ethyl *exo*-3-[1-4-η-1,3-cyclohexadien-5-yl]propionate]iron Complex

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Abstract: The addition of triphenylcarbenium hexafluorophosphate to the title complex gives tricarbonyl(η^5-cyclohexadienylium)iron hexafluorophosphate with a side chain at the C-1 position of the ring. Intramolecular cyclization of the cation using sodium- or calcium- hydride generates a hetero spiro[4.5]decane derivative.

Tricarbonyl(η^5-cyclohexadienylium)iron cations are promising intermediates for organic synthesis.[1] Recently, we reported that sequential additions of nucleophiles to tricarbonyl(η^5-cyclohexadienylium)iron cations afforded fused bicyclic skeletons.[2] In general, the cations can be obtained by direct hydride abstraction from neutral (η^4-cyclohexadiene)$Fe(CO)_3$ complexes using triphenylcarbenium hexafluorophosphate (trityl cation) in refluxing dichloromethane. However, steric effects can be important in determining the outcome of the hydride abstraction reaction. Particularly this is vexing in cases where an alkyl substituent is present at the sp^3 carbon of the cyclohexadiene complex. For example, treatment of complex such as **1a** with the trityl cation failed to produce cation **2a**.[3] It is assumed that the methyl group in complex **1a** is *exo* to the tricarbonyl moiety, then abstraction of the sole *exo*-hydrogen at the C-6 position of the ring would be hindered by the methyl group. An alternative route to the synthesis of the cation salt with a 6-*exo* substituent on the dienylium ligand was developed by Pearson.[4] The method involved intramolecular oxidative cyclization of complexes containing an alcohol moiety by thallium (III) trifluoroacetate. However, the study found in the Paquette group indicated a profound effect of a trimethylsilyl group at the internal position of the diene ligand. Treatment of **1b** with triphenylcarbenium hexafluorophosphate resulting in the abstraction of the *exo*-hydrogen at the C-5 position of the cyclohexadiene ring produced **2b** in 66% yield.[5] However, prior to our study, there is no report on the hydride abstraction reaction at the *endo* 5-H of the C-5 substituted (η^4-cyclohexadiene)$Fe(CO)_3$ complexes. Here we report for the first time that treatments of the title complex **3a** with triphenylcarbenium hexafluorophsphate in acetonitrile result in the abstraction of the most hindered *endo* 5-H to afford tricarbonyl[ethyl 3-[1-5-η-cyclohexadienylium-1-yl]propionate]iron hexafluorophosphate (**4a**).

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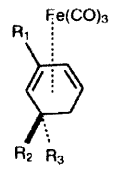
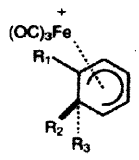
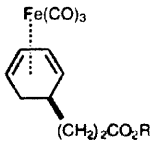


1



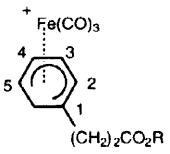
2

a : $R_1 = R_3 = H$, $R_2 = Me$
b : $R_1 = SiMe_3$, $R_2 = R_3 = Me$
c : $R_1 = R_2 = R_3 = H$



3

a : R = Et
b : R = H



4

a : R = Et
b : R = H

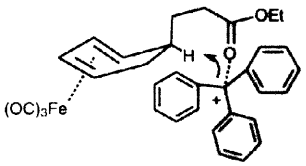
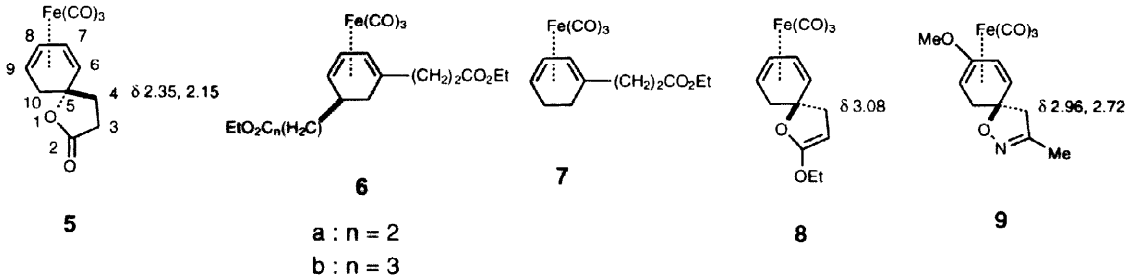


Figure 1

The title complex **3a** was prepared from (η^5–cyclohexadienylium)$Fe(CO)_3$ (**2c**) and $CO_2Et(CH_2)_2Cu(CN)ZnI$ in 83% yield according to the literature procedure.[2] Finally, our synthesis of the C-1-substituted tricarbonyl(η^5-cyclohexadienylium)iron cation **4a** involved the slow addition of a acetonitrile solution of triphenylcarbenium hexafluorophosphate (1.5 equiv.) to complex **3a** in acetonitrile at 25 °C under nitrogen. The addition was carried out for 8 h at 25 °C. The resulting solution was concentrated on rotary evaporator followed by ether added at 0 °C. The yellow solid obtained after filtration was dried under vacuum to give cation salt **4a** as a yellow powder in 84% yield. Cation salt **4a** is a air stable compound and decomposes at 230 °C. The ^1H NMR spectroscopic data of **4a** is consistent with those found for the cation **2c**; particular noteworthy are the downfield shift signals at δ 7.41 (triplet), 6.28 (triplet), 6.03 (doublet) and 4.60 (broad triplet), corresponding to the protons at C-3, C-4, C-2, and C-5, respectively. The reason for the hydride abstraction from the most hindered *endo* hydrogen at C-5 of complex **3a** is suggested as follows. It was assumed that the trityl cation may attach to the carbethoxy functional group and the *endo*-5-H would be in proximity for the abstraction as depicted in Figure 1. To further prove the unusual hydride abstraction at the C-5 position of the ring, ester complex **3a** was hydrolyzed using KOH in MeOH-THF-H_2O at 25 °C to afford the corresponding acid **3b** in 95% yield. However, hydride abstraction of **3b** using 1.5 molar equiv. of the trityl cation in acetonitrile at 25 °C gave an unstable solid. Nevertheless, hydride abstraction followed by addition of 1.0 molar equiv. of triethylamine produced a yellow crystalline compound in 70% yield after flash column chromatagraphy and recrystallization from hexane and CH_2Cl_2. The yellow stable compound (mp 90.0–90.5 °C) was assigned as tricarbonyl[6-9-η-1-oxa-spiro[4.5]deca-6,8-dien-2-one]iron (**5**)[6] on the basis of the following considerations. The ^{13}C NMR spectrum of complex **5** exhibited a signal at δ 210.5 assigned to the carbonyl of the $Fe(CO)_3$ moiety, a signal at δ 176.2 assigned to C-2 (carbonyl of the lactone functionality) and a signal at δ 83.9 assigned to C-5 (quaternary carbon center). The high resolution mass spectrum showed the molecular ion peak at *m/z* 289.9886. The formation of complex **5** presumably started from hydride abstraction of **3b** with the trityl cation to give cation **4b**. Deprotonation of **4b** with triethylamine followed by addition of the resulting carboxylate at the hindered C-1 position of the ring generated the spiro[4.5]decane ring skeleton **5**. Attempts to confirm the relative stereochemistry of **5** using NOSEY (nuclear Overhauser enhancement spectroscopy) measurements were unsuccessful. Rigorous proof of the structure of **5** was finally accomplished by X-ray diffraction analysis. To our surprise, complex **5** has

been derived from *endo* addition of the carboxylate at the C-1 position of cation **4b**. This result contradicts to intermolecular additions of most nucleophiles, including alkoxides, hydroxide, amines, enols,[6] aromatic amines,[7] organo-copper and -zinc reagents,[8] to the (cyclohexadienylium)iron cation occurring exclusively from the opposite site of tricarbonyliron moiety (*exo* addition). Moreover, intramolecular *exo* addition of keto ester groups onto the (cyclohexadienylium)iron cation system to produce spiro[4.5]decane ring systems was also observed by Pearson group.[9] Therefore, it is reasonable to suggest that the carboxylate anion generated by treatment of **4b** with triethylamine could attach the iron center or a carbonyl ligand before the addition at the dienyl ligand. The initial coordination would result in the unusual "*endo*" addition of the carboxylate anion at the hindered C-1 position of the ring to give **5**.



5 **6** **7** **8** **9**

a : n = 2
b : n = 3

Further manipulation of the cation **4a** was demonstrated as follows. Addition of 1.2 molar equiv. of the functionalized zinc–copper reagent [IZn(CN)Cu$(CH_2)_nCO_2Et$, n = 2 or 3] to **4a** in THF at 25 °C generated complexes **6a** (77%) and **6b** (56%), respectively. Complexes **6a-b** were derived from *anti* addition of the zinc–copper reagents at the less hindered C-5 position of **4a**. Furthermore, cation **4a** had also shown to undergo reaction with a variety of hydrides, these usually gave mixtures of complexes **7** and **3**. The ratios of these products appeared to be dependent on the hydride. For a simple hydride such as sodium borohydride, the ratio of **7/3** was 6 : 1 and in 72% yield. However, with bulky hydrides, such as K-selectride or Red-Al, the addition occurred at the less hindered C-5 position of the dienylium ligand to give predominantly complex **7** (75% and 34% yield, respectively). A third mode of action was also noted in the cases of calcium-, and sodium- hydride and 9-BBN, which led to the spiro complex **8** as a single stereoisomer isolated in moderate yields (43%, 73%, and 48% yield, respectively). The relative stereochemistry of **8** was tentatively assigned as depicted on the basis of *exo* addition of the ester enolate to the hindered C-1 position of the dienylium ligand and agreed with the result found in the literature.[9] The distinguished stereochemical outcome between the ester **4a** (*exo* addition) and the acid **4b** (*endo* addition) may be explained by the difficuty of the bulkier ester enolate (compared to the carboxylate) to coordinate at the $Fe(CO)_3$ before addition at the dienyl ligand. Moreover, the ^1H NMR study provided the evidence for support of the structural assignments. The ^1H NMR spectrum of complex **8**[10] exhibited a multiplet , centered at δ 3.08, assigned to the two diastereotopic methylene protons at C-4, whereas the C-4 diastereotopic methylene protons of complex **5** showed at a higher field of δ 2.35 and 2.15. The relative lower value (δ 3.08) of the chemical shifts for the C-4 diastereotopic methylene protons of **8** is

consistent with the deshielding effect caused by the $Fe(CO)_3$ group and agrees closely with the data (δ 2.96 and 2.72) found for the corresponding C-4 methylene protons of the hetero spiro[4.5]decane derivative **9**.[11] Moreover, treatment of **4a** with sodium ethoxide or sodium t-butoxide also gave **8** as the major product in 71% and 52% yield, respectively.

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10. Spectroscopic data for **8**: ^1H NMR ($CDCl_3$) δ 5.45 (1H, t, *J* 5.86 Hz), 5.38 (1H, t, *J* 3.89 Hz), 4.91 (1H, t, *J* 7.55 Hz), 4.13 (2H, q, *J* 7.32 Hz), 3.77 (1H, d, *J* 6.35 Hz), 3.29 (1H, m), 3.08 (2H, m),2.41 (2H, dd, *J* 17.1, 8.8 Hz) and 1.27 (3H, t, *J* 7.36 Hz) ; ^{13}C NMR ($CDCl_3$) δ 211.2, 138.0, 110.0, 96.1, 84.4, 83.7, 60.9, 60.6, 59.0, 33.1, 30.2, and 14.1; IR (CH_2Cl_2, solution) ν/cm^{-1} 3032w, 2990m, 2930w, 2046s, 1971s, 1728m, 1606m, 1099m, 9190m, 875w and 852w; mass (EI) *m/z* 318 (M^+, 4%), 290 (8), 262 (84), 234 (100); high resolution, calc. for $C_{14}H_{14}O_5Fe$ 318.0286; found*m/z* 318.0188.

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