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Solvolysis reactions at the 13th carbon of 1-aryl organoiron complexes

Caroline Roe, Elizabeth J. Sandoe, G. Richard Stephenson *

School of Chemistry, University of East Anglia, Norwich, NR4 7TJ, UK

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ABSTRACT

Acid-catalysed solvolysis procedures exchange protecting groups on benzyl alcohol derivatives in the synthesis of η^5 1-arylcyclohexadienyliron building blocks for alkaloid synthesis. The reaction proceeds via a carbocation intermediate which can also be intercepted by intramolecular electrophilic addition to the tricarbonyl(η^4-diene)iron(0) moiety to provide a novel and high-yielding cyclisation reaction forming a 5aα-cyanomethyl-5a,8a-dihydrofluorene tricarbonyliron complex in 96% yield.

Our synthetic strategy[1–5] introduces the '13th' benzylic carbon atom (Fig. 1) early in our organoiron-mediated[6,7] routes to *Amaryllidaceae* alkaloids.[8,9] In many alkaloid syntheses this carbon is added much later[10] by a Pictet–Spengler reaction. In comparison, our routes are more convergent, and hence potentially more efficient. However, the advantage has been somewhat offset by the need to employ relatively bulky protecting groups on the benzylic alcohol.[3] The choice of a *1,1* iterative strategy[2,11] to elaborate **1** by repeated use of the metal lies at the heart of this application of arylcyclohexadienyliron complexes (e.g., **2a**) as key building blocks, and we have shown[2,12–14] that when the 1-aryl group bears an *ortho* substituent, it is important that the arene can adopt a relatively flat conformation aligned with the dienyl ligand to allow nucleophiles to add *ipso*. Large protecting groups on the CH_2O at this *ortho* position are more likely to hinder the approach of the nucleophile next to the aromatic ring, and so complicate the optimisation of synthetic routes because of the need to balance performance and selectivity in two separate areas: the fundamental issue of *i* versus ω nucleophile addition,[12] and practical issues concerning the introduction, stability and removal of protecting groups.

Our preferred method[1,15–18] to prepare 1-aryl-cyclohexadienyliron electrophiles uses the removal of an allylic OMe group next to the η^4-diene complex. TFA followed by the addition of ammonium hexafluorophosphate,[15] aqueous hexafluorophosphoric acid in acetic anhydride,[16] triphenylcarbenium ion reagents[17] and Meerwein's reagent[18] are all procedures that we have employed successfully in a wide variety of reactions. However, when the hexafluorophosphoric acid method was used with the methyl ether **4** (Scheme 1), the product, isolated in 83% yield, was the acetate **5**, which was clearly identified by the replacement of the OMe ^1H and ^{13}C resonances at 4.34 and 73.0 ppm with signals at 4.94 and 64.5 ppm for the CH_3CO_2 group, and the presence of an additional stretching vibration at 1728 cm^{-1} in the IR spectrum of the product. This structure was confirmed by FAB high resolution mass spectrometry which gave the expected ion for $C_{21}H_{21}FeO_8PF_6$. The two additional OMe groups on the arene are clearly sufficiently electron-donating to activate the CH_2OMe group for an efficient S_N1 solvolysis reaction[19] with acetic acid generated by mixing aqueous hexafluorophosphoric acid and acetic anhydride. This observation led us to examine the possibility that S_N1 conditions might provide a way to use the simple (and small) CH_2OMe substituent in synthetic routes that later required a free OH group at this position, by employing an S_N1 process to replace OMe by OH during other acid-catalysed reactions in the closing stages of the synthesis. In the course of this work, we have discovered an unexpected intramolecular C–C bond formation that gives rise to a dihydrofluorene-derived cyclohexadieneiron complex.

Addition of the 2-methoxymethyl-4,5-dimethoxyarene to tricarbonyl(η^5-2-methoxycylohexadienyl)iron(1+) hexafluorophosphate (**7**)[20] (Scheme 1) was performed[21,22] by generating a diarylcuprate **6** from our normal[5] aryllithium reagent **3** by reaction with copper(I) iodide in THF at −78 °C over a period of 90 min. The electrophile **7** was then added, and after a further 2 h at −78 °C, the reaction mixture was warmed to room temperature overnight and worked up to give the methoxybenzyl ether complex **8** in 56% yield. A simple S_N1 hydrolysis procedure with dilute aqueous HCl was then employed to evaluate the practicality of replacing

* Corresponding author.
E-mail address: g.r.stephenson@uea.ac.uk (G.R. Stephenson)

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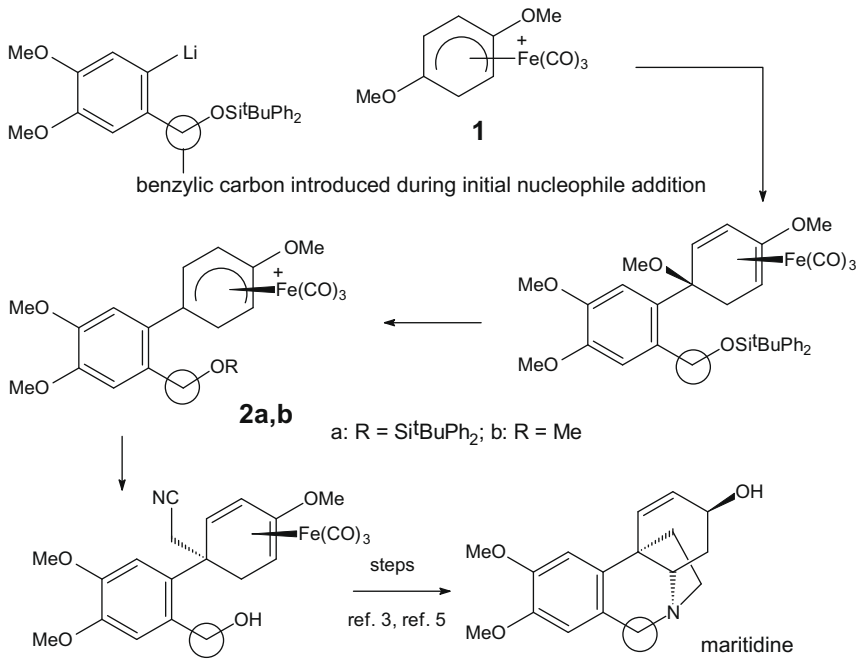
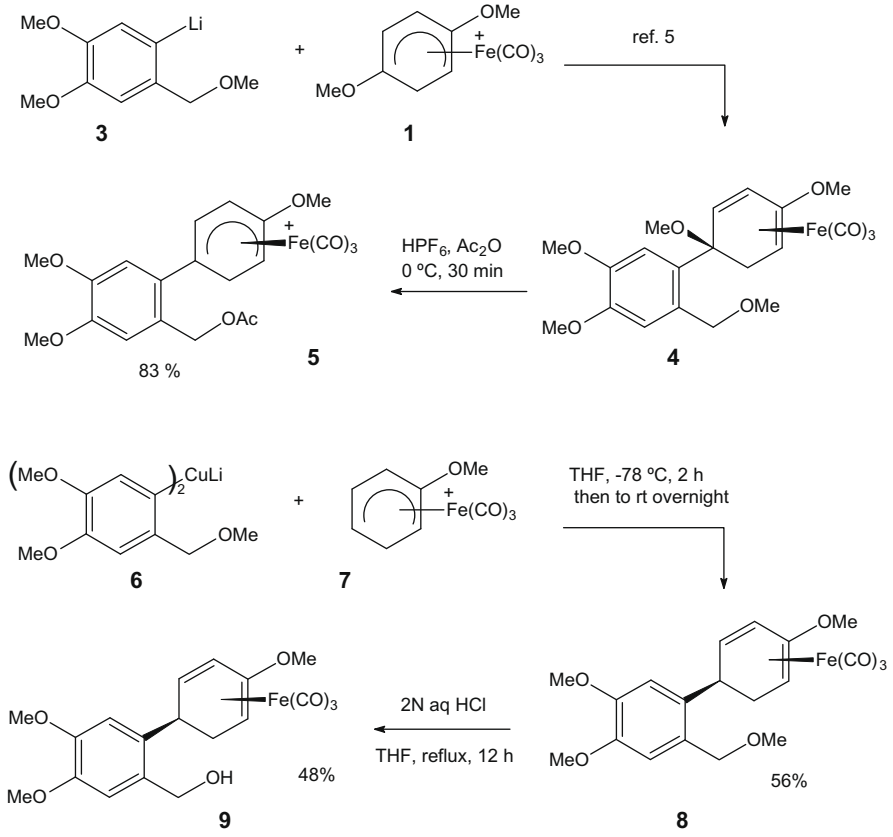
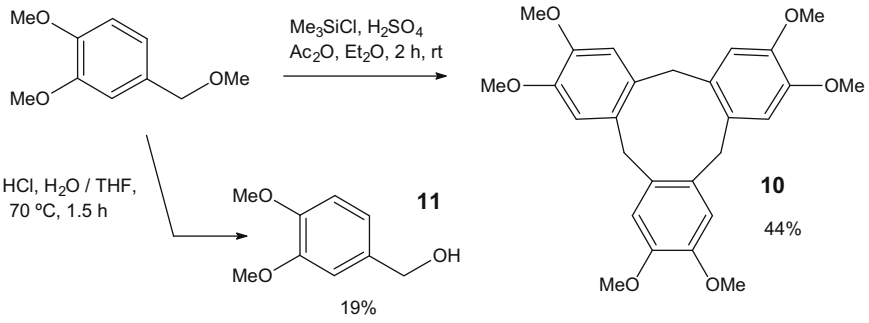


Figure 1. Use[3] of an aryllithium reagent with an *ortho* $CH_2OTBDPS$ substituent to extend our 'C_{12} building block'[1–5] approach in a formal total synthesis of the *Amaryllidaceae* alkaloid maritidine (the '13th carbon' is ringed).

the OMe group by OH. Despite quite vigorous reaction conditions (overnight at reflux), the desired benzyl alcohol product **9** was obtained in 48% yield. Using methyl 3,4-dimethoxybenzyl ether itself as a simple model compound (Scheme 2), a range of milder reaction conditions were tried (Table 1). The conditions used successfully with **4** to form the acetate, followed by saponification with aqueous sodium hydroxide gave only traces of the expected 3,4-dimethoxybenzyl alcohol[23] (**11**). The use of aqueous HCl worked better, and with a longer reaction time would probably give the most efficient procedure, as was the case (Scheme 1) with the tri-



Scheme 1. Solvolysis reactions in the synthesis of cationic η^5 and neutral η^4 aryl-substituted organoiron complexes.



Scheme 2. Cyclisation and solvolysis of methyl 3,4-dimethoxybenzyl ether (see Table 1).

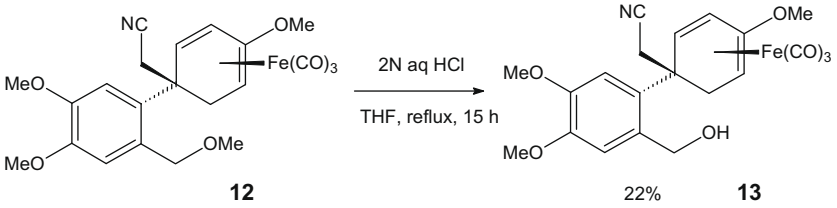
Table 1
Solvolysis reactions of the model compound methyl 3,4-dimethoxybenzyl ether

Entry	Conditions	
1	HPF_6 (aq), Ac_2O, 0 °C, 90 min, then NaOH (aq)	Trace of product **11**
2	*p*-TSA,[a] THF, H_2O (3:2)	No reaction
3	*p*-TSA,[a] AcOH, Ac_2O (1:1)	Trace of product **11**
4	TMSCl,[b] H_2SO_4, Ac_2O, Et_2O, 2 h	44% yield of trimer **10**
5	HCl, H_2O, THF (10:1), 70 °C, 1.5 h	19% yield of product **11**

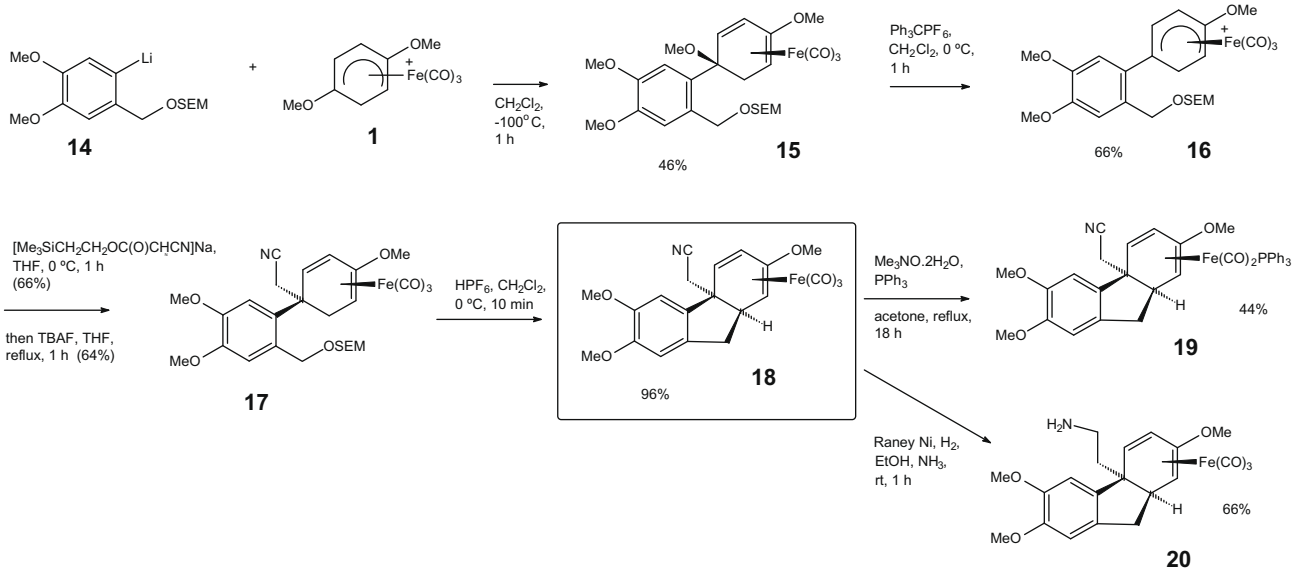
[a] *para*-Toluene sulfonic acid.
[b] Trimethylsilyl chloride.

carbonyliron complex **5**. Sarma has described[24] rather unusual S_N1 conditions (trimethylsilyl chloride and concd sulfuric acid), and with methyl 3,4-dimethoxybenzyl ether this formed cyclotriveratrylene **10**[25] in 44% yield. This is a known[26] product from the benzyl alcohol, formed by reaction with glacial acetic acid containing a few drops of concd sulfuric acid. This trimerisation reaction would give an interesting product in the case with the tricarbonyliron complex attached, but when **7** was treated with trimethylsilyl chloride and concd sulfuric acid, decomposition of the more sensitive organometallic substrate was observed.

Reaction of $[Me_3SiCH_2CH_2OC(O)CHCN]Na$[27] with **2b** was followed by desilylative dealkylation/carboxylation promoted by adding TBAF to the reaction mixture and heating at reflux for 90 min, to give an efficient one-pot formation of the nitrile **12** which is the methyl ether analogue of the silyl ethers used[3] (Fig. 1) in our maritidine work. Reaction of **12** with dilute aqueous HCl overnight (Scheme 3) afforded the benzyl alcohol **13** in 22% yield. Addition of the SEM-protected aryllithium reagent **14** to



Scheme 3. Access to the benzyl alcohol **13**.



Scheme 4. Synthetic route to the novel cyclisation product **18** (box) and preparation of the dicarbonyltriphenylphosphine and alkylamine derivatives.

the 1,4-dimethoxy salt **1** gave **15** in 46% yield (Scheme 4). The product was converted in 66% yield into the 1-arylcyclohexadienyliron salt **16** using triphenylcarbenium hexafluorophosphate in dichloromethane. Addition of $[Me_3SiCH_2CH_2OC(O)CHCN]Na$ followed by reaction with TBAF gave the nitrile **17** in 64% yield. The intention had originally been to perform both the deprotection of the benzyl alcohol and the desilylative dealkylation/decarboxylation in a single step, but unexpectedly, the SEM-protecting group proved resistant to TBAF in this example. Lipshutz had reported[28] an improved desilylation method using dry TBAF. When **17** was heated at 40 °C in THF with TBAF and 4 Å molecular sieves, traces of an unexpected product were observed by TLC. This was clearly not the desired benzyl alcohol because it had a higher R_f value than the starting material. Consequently, we examined this problem further (Table 2) in our survey of S_N1 procedures. In an earlier model study[29] for lycoramine, decomposition had been observed[30] when deprotection of a phenolic MOM ether had been attempted using 2 N HCl, so we chose alternative reaction conditions for use with compound **17**. Interestingly, we discovered that the less polar compound observed with dry TBAF now became the major product under S_N1 conditions. This reaction was performed at 40 °C with aqueous hexafluorophosphoric acid in THF, and gave a 67% yield of **18**. This was improved[31] to 96% yield by dropping the reaction temperature to 0 °C and using dichloromethane instead of THF. The product from these reactions had only two OMe groups, and since these had signals at the position in the ^{1}H NMR spectrum expected for methyl aryl ethers, it was clear that the reaction had been partially successful in the sense that the benzylic OMe group had been removed. The typical 4.72 ppm 7 Hz doublet for the resonance of the benzylic CH_2O methylene group was also replaced by two doublet of doublet resonances at 3.29 and 2.69 ppm (Table 3), each integrating for a single hydrogen, which, in view of the shift to higher field, ruled out the possibility that the product contained a CH_2O group adjacent to the arene.[32] Although **18** was crystalline, X-ray quality crystals could not be obtained, and when the product was converted into the $Fe(CO)_2PPh_3$ derivative **19** the product failed to crystallise at all. The nitrile in **18** was reduced with Raney nickel in ethanol saturated with ammonia to afford the primary amine **20** which again had the pair of doublet of doublet 1H signals, this time at 3.14 and 2.62 ppm. All three products had very similar features in their ^{1}H NMR spectra for the CH_2 group originating from the benzyl ether. On this basis, the identity of the product was finally established. The larger coupling in each doublet of doublets is clearly the geminal coupling between the two hydrogens, showing that the CH_2 group remains intact. The smaller couplings of about 10 Hz and 4 Hz indicate the presence of a CH adjacent to the CH_2, indicating that a C–C bond-formation reaction had been caused by the hexafluorphosphoric acid. The initial product was thus assigned as the dihydrofluorene **18**, produced by intramolecular electrophilic C–C bond formation between the carbocation formed in the S_N1 process and the η^4-dieneiron complex. The *cis* ring junction is structurally the most reasonable and is consistent with the normal[33] *endo* addition of electrophiles to tricarbonyl(η^4-cyclohexadiene)iron complexes.

In conclusion, we have shown that S_N1 conditions can cause efficient replacement of benzylic ethers during the preparation of cationic cyclohexadienyliron(1+) complexes, that this same procedure works for the deprotection of neutral η^4-cyclohexadiene complexes, though in lower yield, and, when performed in less polar non-nucleophilic solvents, provides an efficient method to effect a novel stereoselective intramolecular cyclisation reaction. The mild conditions (0 °C) and high yield (96%) of this reaction indicate that it will be suitable to gain access to a new class of tricyclic η^4-dieneiron complexes with fused cyclopentane ring systems.

Table 2
Solvolysis reaction conditions to form **18**

Entry	Conditions	Yield (%)
1	TBAF,[a] THF, 4 Å sieves, 40 °C	Trace[b]
2	HPF_6, THF, H_2O, 40 °C	67
3	HPF_6, CH_2Cl_2, 0 °C	96

[a] Tetrabutylammonium fluoride.
[b] Observed by TLC.

Table 3
Selected ^{1}H NMR signals for **18**, **19** and **20** correspond to consistent dihedral angles between hydrogens in the rigid 8a,9 section of a dihydrofluorene

Compound	δ (ppm)	Dd J (Hz)	δ (ppm)	Dd J (Hz)
18	3.29	16.8,[a] 9.6[b]	2.69	16.8,[a] 3.8[c]
19	3.28	16.5,[a] 9.9[b]	3.02	16.5,[a] 4.3[c]
20	3.14	16.5,[a] 9.9[b]	2.62	16.5,[a] 3.3[c]

[a] $J_{9Hexo,9Hendo}$.
[b] $J_{8aHexo,9Hexo}$.
[c] $J_{8aHexo,9Hendo}$.

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31. *Experimental procedure:* the SEM ether **17** (21 mg, 0.036 mmol) was dissolved in CH_2Cl_2 (5 ml) at 0 °C. Hexafluorophosphoric acid (75% in water) (2 drops) was added. The reaction mixture was stirred for 10 min, then quenched with H_2O (5 ml) and Et_2O (5 ml) and extracted with Et_2O (3 × 10 ml). The combined organic extracts were dried over $MgSO_4$, filtered and evaporated to leave a yellow gum which was purified by column chromatography on silica, eluting with Et_2O/40–60 bp petroleum ether (20:80) to give tricarbonyl[(5,6,7,8-η)-5aα-cyanomethyl-2,3,7-trimethoxy-5a,8a-dihydrofluorene]iron(0) **18** as a pale yellow powder (15 mg, 0.034 mmol) in 96% yield. ^{1}H NMR (270 MHz, $CDCl_3$): δ 2.54 (m, 3H, CH_2CN and H-8a); 2.69 (dd, *J* 16.8, 3.8, 1H, H-8); 2.78 (d, *J* 6.3, 1H, H-5); 3.29 (dd, *J* 16.8, 9.6, 1H, CH_2); 3.30 (m, 1H, H-8); 3.85 (s, 3H, Ar-OMe); 3.90 (s, 3H, Ar-OMe); 5.17 (dd, *J* 6,3, 2.3, 1H, H-6); 6.66 (s, 1H, H-1); 6.69 (s, 1H, H-4); ^{13}C NMR (67.5 MHz, $CDCl_3$): δ 32.8, 38.5, 46.2, 54.6, 56.0, 56.1, 56.5, 58.0, 59.0, 65.9, 104.9, 109.5, 118.3, 134.0, 137.3, 138.8, 149.0, 150.0, 209.7; ν_{max} (CH_2Cl_2) 2307, 2049, 1974, 1609, 1507, 1423, 1266, 1112, 896 cm^{-1}; *m/z* (EI) 409 (M^+–CO, 4), 381 (8), 353 (24), 234 (23), 206 (47), 178 (61), 150 (100%); Elemental Anal. Calcd for $C_{21}H_{19}FeNO_6$: C, 57.7; H, 4.4, N, 3.2. Found: C, 57.7; H, 4.2; N, 3.0.
32. The MOM ether can be removed with $MgBr_2$ to give the alcohol **13** which was shown to be different (TLC) from the product **18**.
33. Franck-Neumann, M.; Sedrati, M.; Mokhi, M. *New J. Chem.* **1990**, *14*, 471–480; Rivera, A. V.; Sheldrick, G. M. *Acta Crystallogr., Sect. B* **1978**, *B34*, 1716–1718.