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Preliminary communication

Trimethylaluminum mediated halomethylation of $[(\text{arene})_2\text{Fe}]^{2+}$ cations

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Abstract

The arene salts $[(\text{arene})_2\text{Fe}](\text{PF}_6)_2$ (arene = mesitylene, **1a**, and hexamethylbenzene, **1c**) react readily with AlMe_3 in dichloromethane or dibromomethane to produce the novel *exo*-halomethyl-η^5-cyclohexadienyl salts $[(\eta^5\text{-}exo\text{-CH}_2\text{XC}_6\text{H}_3\text{Me}_3)(\eta^6\text{-C}_6\text{H}_3\text{Me}_3)\text{Fe}]\text{PF}_6$ (X = Cl, **2d**; X = Br, **2e**) and $[(\eta^5\text{-}exo\text{-CH}_2\text{XC}_6\text{Me}_6)(\eta^6\text{-C}_6\text{Me}_6)\text{Fe}]\text{PF}_6$ (X = Cl, **2f**; X = Br, **2g**) which have been characterized spectroscopically and, in the case of **2f**, crystallographically.

Stereospecific arene functionalization via complexation to transition metals and subsequent reaction is a well established facet of organometallic chemistry. Susceptibility towards nucleophilic addition, perhaps the most widely utilized mode of activation, is exemplified by addition of carbanionic moieties to complexed arenes, and has been investigated with numerous substrates by a number of groups [1–5]. Unfortunately, lack of availability of appropriate nucleophilic reagents has tended to limit the cyclohexadienyl products to those containing alkyl or aryl substituents, a problem that is not present when cyclohexadienyl complexes are formed via complexed dienes [6].

We recently communicated [7] details of a convenient, one step, high yield synthesis of the [(*exo*-ethylcyclohexadienyl)(arene)Fe]PF_6 complexes **2a–2c** from the reaction of AlEt_3 with the salts $[(\text{arene})_2\text{Fe}](\text{PF}_6)_2$ (**1a–1c**). **2a–2c** are synthetically useful [8*] products but, except for **2a** [9*], cannot otherwise be synthesized via direct carbanion addition. In this communication we report the unexpected results of an investigation into the reactivity of AlMe_3 with **1a** and **1c**.

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* Reference numbers with asterisks indicate notes in the list of references.

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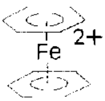
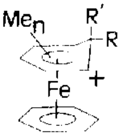
Under the same conditions utilized for $AlEt_3$, $AlMe_3$ surprisingly yields the chloromethylated cyclohexadienyl complexes $[(\eta^5\text{-}exo\text{-}CH_2ClC_6H_3Me_3)(\eta^6\text{-}C_6H_3Me_3)Fe]PF_6$ (**2d**) and $[(\eta^5\text{-}exo\text{-}CH_2ClC_6Me_6)(\eta^6\text{-}C_6Me_6)Fe]PF_6$ (**2f**) rather than the corresponding methyl adducts **2h** and **2i**. When dichloromethane is replaced by dibromomethane as the solvent the corresponding bromomethylated cyclohexadienyl complexes $[(\eta^5\text{-}exo\text{-}CH_2BrC_6H_3Me_3)(\eta^6\text{-}C_6H_3Me_3)Fe]PF_6$ (**2e**) and $[(\eta^5\text{-}exo\text{-}CH_2BrC_6Me_6)(\eta^6\text{-}C_6Me_6)Fe]PF_6$ (**2g**) are isolated. Preparation of **2d** was effected by first suspending 1.00 g (1.71 mmol) of **1a** [10 *] in 75 ml of dichloromethane in an Erlenmeyer flask inside an inert atmosphere glove box. A 4-fold excess of $AlMe_3$ (Texas Alkyls, 0.65 ml, 6.82 mmol) was added and a purple solution formed within one minute. The solution was stirred at room temperature for 24 h. The reaction vessel was then taken from the glove box, cooled to 0 °C, and quenched with excess ice water under air. Filtration, separation of the CH_2Cl_2 layer, and removal of CH_2Cl_2 under reduced pressure afforded orange/red solids which were subsequently recrystallized from acetonitrile/water, washed with hexanes, and dried under vacuum. 0.21 g of **2d** (25%) was obtained: ^1H NMR $((CD_3)_2(CO)$: δ 5.87(s, 3H), 4.45(s, 2H), 3.03(t, 1H), 2.76(s, 3H), 2.60(d, 2H), 2.50(s, 9H), 1.80(s, 6H); ^{13}C NMR $((CD_3)_2CO)$: δ 103.8s, 97.0s, 94.0d, 85.4d, 59.7s, 49.1d, 45.7t, 23.3q, 19.8q, 19.0q. **2d** was shown via NMR spectroscopy to contain 5–10% of **2h** and could only be purified by fractional crystallization. **2e**–**2g** were prepared in a manner similar to that outlined for **2d** utilizing the appropriate salts and solvents. **2e** was obtained in 34% yield and was shown via ^1H NMR to contain 20% of **2h**; ^1H NMR $((CD_3)_2CO)$: δ 5.88(s, 3H), 4.46(s, 2H), 3.05(t, 1H), 2.75(s, 3H), 2.50(s, 9H), 2.09(d, 2H), 1.83(s, 6H): ^{13}C NMR $((CD_3)_2(CO)$: δ 103.8s, 97.5s, 93.9d, 85.1d, 60.2s, 48.7d, 33.2t, 23.3q, 19.8q, 19.0q. **2f** was obtained pure in 50% yield: ^1H NMR



(**1a**, arene = 1,3,5-$C_6H_3Me_3$;

1b, arene = C_6HMe_5;

1c, arene = C_6Me_6)



(**2a**: arene = $C_6H_3Me_3$, R = H, R′ = Et, Me_n = 1,3,5-Me_3;
2b: arene = C_6HMe_5, R = H, R′ = Et, Me_n = 1,2,3,4,5-Me_5;
2c: arene = C_6Me_6, R = Me, R′ = Et, Me_n = 1,2,3,4,5-Me_5;
2d: arene = $C_6H_3Me_3$, R = H, R′ = CH_2Cl, Me_n = 1,3,5-Me_3;
2e: arene = $C_6H_3Me_3$, R = H, R′ = CH_2Br, Me_n = 1,3,5-Me_3;
2f: arene = C_6Me_6, R = Me, R′ = CH_2Cl, Me_n = 1,2,3,4,5-Me_5;
2g: arene = C_6Me_6, R = Me, R′ = CH_2Br, Me_n = 1,2,3,4,5-Me_5;
2h: arene = $C_6H_3Me_3$, R = H, R′ = Me, Me_n = 1,3,5-Me_3;
2i: arene = C_6Me_6, R = Me, R′ = Me, Me_n = 1,2,3,4,5-Me_5)

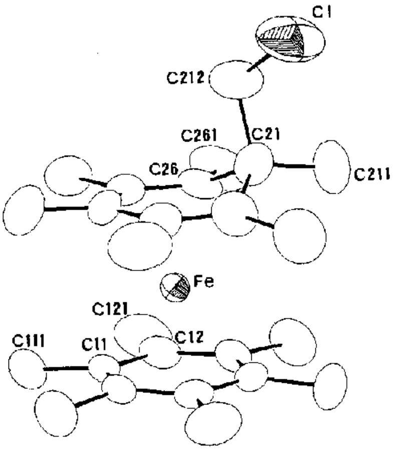
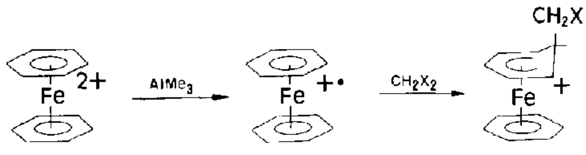


Fig. 1. ORTEP perspective view of **2f**. Important bond distances (Å): Fe–C(22), 2.133(7); Fe–C(23), 2.091(7); Fe–C(24), 2.096(7); Fe–C(25), 2.107(7); Fe–C(26), 2.166(8); Fe–C(arene), 2.155 average.

($CDCl_3$): δ 2.42(s, 3H), 2.19(s, 18H), 1.97(s, 2H), 1.80(s, 6H), 1.42(s, 3H), 1.29(s, 6H); ^{13}C NMR ($(CD_3)_2CO$): δ 101.5s, 93.4s, 92.3s, 53.3s, 52.6t, 45.5s, 20.8q, 16.0q, 15.5q, 14.5q, 14.2q. Anal: Found: C, 52.01; H, 6.74. $C_{25}H_{38}ClF_6FeP$ calcd.: C, 52.24; H, 6.66%) and **2g** was also obtained pure in 70% yield: ^1H NMR ($(CD_3)_2CO$): δ 2.52(s, 3H), 2.33(s, 18H), 2.14(s, 2H), 1.93(s, 6H), 1.51(s, 3H), 1.46(s, 6H); ^{13}C NMR: δ 101.6s, 93.3s, 92.4s, 52.8s, 44.7s, 42.4t, 21.8q, 16.0q, 15.4q, 14.5q, 14.3q. **2f** was characterized by single crystal X-ray crystallography in order to determine the stereochemistry of CH_2Cl addition.

Crystal data. $[(\eta^5\text{-}exo\text{-}CH_2ClC_6Me_6)(\eta^6\text{-}C_6Me_6)Fe]PF_6$ (**2f**) crystallized in the monoclinic space group $C2/c$ ($Z = 8$) with a 34.164(3), b 10.344(1), c 16.219(2) Å, β 115.680(7)°, V 5165.3 Å^3, D_c 1.478 g cm^{-3}, and $R = 0.058$ ($R_2 = 0.066$) for 2286 unique reflections with $I \geq 2.5\sigma(I)$ and 348 least squares parameters. The ORTEP [11] perspective view of **2f** (Fig. 1) indicates that *exo* addition of the CH_2Cl fragment has occurred. **2f**PF_6 is isostructural with **2c**PF_6 [7], and therefore also exhibits several manifestations of steric strain, including staggering of the two rings, non-planarity in the ring carbon atoms, and pointing away from the metal by the methyl carbon atoms of the η^6-ring.

A plausible mechanism for the formation of **2d**–**2g** would involve initial one electron reduction of **1a** and **1c** via an outer sphere electron transfer (ET) from $AlMe_3$. Cyclohexadienyl formation would subsequently occur via slow reaction of the known [12*] 19-electron complexes with CH_2X_2 (Scheme 1). Several observations from this study lend support to an ET mechanism: (1) the purple solution



Scheme 1.

formed upon addition of $AlMe_3$ is indicative of the 19-electron cation $[(arene)_2Fe]^+$ [12*]; (2) no double addition occurs, an observation that can be correlated with the expected increase in reduction potential between **1a**, **1c** and **2a–2i** [13*]; (3) if the reaction of **1a** is conducted in benzene and the products are extracted with CH_2Cl_2 **2h** is the only isolable salt [14*]; (4) $AlMe_3$ retains its integrity in CH_2X_2 in the absence of **1a** and **1c** [15*]. The halomethylated addition species are therefore formed during the initial reaction before aqueous quenching. Also, addition of CH_2Cl to reduced organometallic species via reaction with dichloromethane has been reported in the literature [16] and trialkylaluminum compounds have been shown to give reduction products, presumably via ET reactions, with $[(arene)Mn(CO)_3]PF_6$ [17*] salts and with organic substrates [18].

In addition to opening up routes to halomethylated arenes this work demonstrates how critical choice of solvent is when treating carbanionic reagents with organometallic substrates. We are presently seeking routes to further functionalize **2d**–**2g** via the halomethyl moieties.

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and, although the cyclohexadienyl cations **2a–2i** have not been investigated electrochemically, the related cyclopentadienyl $[(C_5H_5)Fe(arene)]^+$ cations have reduction potentials in the range −1.37 to −1.67v vs. SCE (D. Astruc, Acc. Chem. Res., 19 (1986) 377).

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15 This was determined following the suggestion of a referee. A solution of $AlMe_3$ in CH_2X_2 was prepared in the dry box in the same proportion utilized in the reactions described in the text. The solution was monitored via ^1H NMR spectroscopy over a 24 h period and no evidence of conversion to, for example, $AlCH_2Cl$ moieties was noted.

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