Pseudoferrocenes

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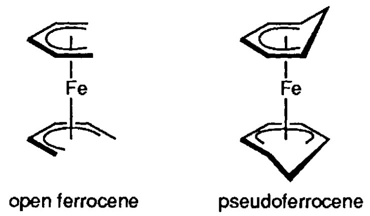
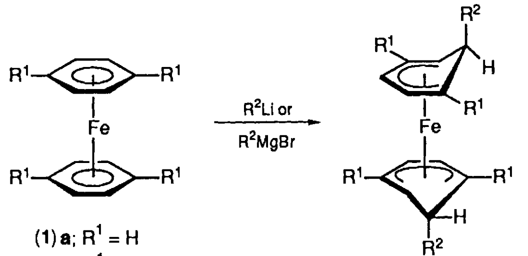
Dichloromethane facilitates clean high-yield double addition of carbanions to $[(\eta^6\text{-arene})_2\text{Fe}]^{2+}$ dications affording bis(η^5-cyclohexadienyl)iron or 'pseudoferrocene' compounds in accord with the Davies, Green, and Mingos rules; the crystal structure of one example has been determined.

Since its discovery over four decades ago the prototypical organometallic sandwich complex, ferrocene, has attracted considerable interest.[1] In more recent years bis(pentadienyl)-iron complexes or 'open ferrocenes,' have been detailed by Ernst[2] but bis(cyclohexadienyl)iron complexes or 'pseudoferrocenes,' although first reported in 1970,[3] have attracted relatively little attention. This is in spite of the fact that cyclohexadienyl moieties offer greater synthetic potential as precursors to synthetically useful cyclohexadienes and substituted arenes.[4] The relatively low level of interest in pseudofer-





(**1**)**a**; $R^1 = H$
b; $R^1 = Me$

(**2**) $R^2 = Ph$
(**3**) $R^2 = Bu^t$
(**4**) $R^2 = PhCH_2$

rocenes may be due to the fact that double addition to the readily accessible $[(arene)_2Fe]^{2+}$ series of dications (**1**) has hitherto only been accomplished for $[(mesitylene)_2Fe](PF_6)_2$.[3] Furthermore, recent work by Astruc *et al.* suggests that addition of nucleophiles to (**1**) often affords intractable reduction products and that if double H^- or R^- addition does occur, [(arene)(cyclohexadiene)Fe] complexes are isolated.[5—9] The latter observation is in violation of the Davies, Green, and Mingos rules[10] for addition of nucleophiles to unsaturated hydrocarbon ligands. In this communication we report that use of dichloromethane rather than tetrahydrofuran as solvent for net addition of carbanions to (**1**) may facilitate clean, high-yield formation of pseudoferrocenes for arenes other than mesitylene, and present the first crystallographic characterization of a prototypical pseudoferrocene compound with unsubstituted dienyl moieties.

In a typical experiment $[(benzene)_2Fe](PF_6)_2$ (**1a**) or $[(p\text{-xylene})_2Fe](PF_6)_2$ (**1b**) (1.00 g) was stirred in CH_2Cl_2 (30 ml) at −90 °C under dinitrogen. A four-fold excess of the appropriate lithium (R^2 = Ph or Bu^t) or Grignard (R^2 = $PhCH_2$ or Bu^t) reagent was added *via* syringe, resulting in an immediate darkening of the slurry. Following warming of the mixture to 25 °C and quenching with H_2O (5 ml) the solvent was removed under reduced pressure. The orange air-stable products (**2a**), (**3a**), (**3b**), (**4a**), and (**4b**) were extracted into dried, distilled hexanes (50 ml) and recrystallized to give final yields of 63—94%.† The identity of the products was confirmed by elemental analysis, 360 MHz ^1H and 91 MHz ^{13}C NMR spectroscopy,‡ and, in the case of (**3a**), *X*-ray crystallography. For arene = C_6Me_5H or C_6Me_6 only single addition occurs for Bu^tLi thereby affording $[(cyclohexadienyl)(arene)Fe]PF_6$ salts. However, yields are high and no reduction products are isolated, as we recently observed for ethylation using $AlEt_3$.[12] A crystal structure of the 1,3,5-trimethyl analogue has been reported.[13]

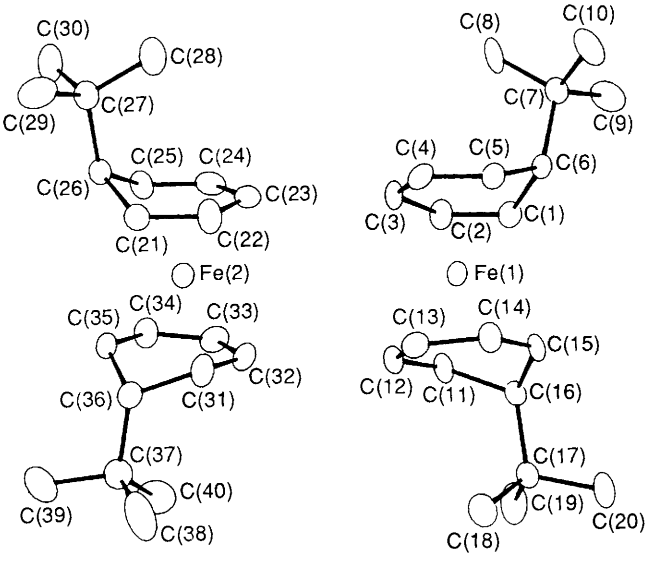


Figure 1. ORTEP[18] perspective view of the two independent molecules of (**3a**). The average Fe–C and Fe–dienyl plane distances are 2.06(3) and 1.556(3) Å, respectively. Average Fe–C and Fe–dienyl plane distances for ferrocene and open ferrocenes are 2.05(2) and 1.66 Å, and 2.088(1) and 1.46 Å, respectively.

The *X*-ray structure of (**3a**)§ (Figure 1) represents only the second crystallographic characterization of a pseudoferrocene, and the first with unsubstituted dienyl ring atoms.[13] The solid-state conformation of pseudoferrocenes in the absence of intramolecular steric effects may therefore now be ascertained. Complex (**3a**) adopts a *gauche* eclipsed conformation with the dienyl moieties twisted by 59.5 and 57.5° for the two independent molecules. Such a conformation is expected from *X*-ray structural observations[14,15] and EHMO calculations[16] on bis(η^5-pentadienyl) iron complexes.

In conclusion, our results demonstrate that double addition of carbanions to (**1**) takes place readily and is general, thereby

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† Compound (**2b**) was not isolated as a clean product as reaction of (**1b**) with PhLi affords a red oil that decomposes quickly in solution. The ^1H NMR spectrum of this oil is complex and suggests the presence of two or more neutral products. Astruc has reported that the same reaction in tetrahydrofuran affords the (cyclohexadiene)(arene)Fe complex.[9] Deprotonation of the cyclohexadienyl-methyl is another possible reaction pathway, thereby yielding a methylene–cyclohexadiene species similar to that reported by Davies *et al.* for hydroxide removal from methoxy-substituted chromium cyclohexadienyls.[11] The products may be recrystallized *via* slow evaporation of acetone–water solutions or cooling concentrated solutions in hexanes: yields (%): (**2a**), 63; (**3a**), 94 (R^2Li), 81 (R^2MgX); (**3b**), 82 (R^2Li), 71 (R^2MgX); (**4a**), 75; (**4b**), 80.

‡ The NMR spectra are typical of co-ordinated cyclohexadienyl moieties. Complexes (**3b**) and (**4b**) are diastereoisomeric and, although the isomers may be separated by fractional crystallization, NMR studies of the crude products indicate no diastereoselectivity during addition of the second carbanion. One of each pair of diastereoisomers is fluxional and we are currently investigating the variable-temperature NMR behaviour of these complexes. No temperature dependence between −60 and +40 °C was observed for (**2a**), (**3a**), and (**4a**).

§ *Crystal data*: $C_{20}H_{30}Fe$, M = 326.304, triclinic, space group $P\bar{1}$, a = 6.421(1), b = 14.916(2), c = 19.282(3) Å, α = 99.36(1), β = 91.92(1), γ = 92.40(1)°, U = 1819.04 Å^3, Z = 4, D_c = 1.191 g cm^{-3}, crystal size = 0.2 × 0.3 × 0.9 mm, Mo-K_α (λ = 0.70930 Å), T = 298 K, $F(000)$ = 704, μ = 0.82 mm^{-1}, R = 0.041, R_w = 0.046 for 3257 unique observed reflections with $I \geqslant 2.5\sigma(I)$. Enraf-Nonius CAD-4 diffractometer, Lorentz, polarization, and absorption corrections applied. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

providing ready access to a wide range of novel pseudoferrocene compounds. Our results, particularly the effect of solvent, pose questions about the mechanism of carbanion addition to co-ordinated arenes, an issue we have raised earlier.[12,17] In terms of synthetic utility, removal of the *endo*-hydride at C-6 or decomplexation with concurrent loss of the *endo*-hydride are critical objectives. We are currently investigating methods of effecting such reactions.

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