

Benzyl anion abstraction from a ( $\beta$ -diiminato)Fe(II) benzyl complex†

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The 3-coordinate 12 VE iron(II) benzyl complex [(nacnac)-Fe(CH<sub>2</sub>Ph)] reacts with B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> to yield a paramagnetic contact ion pair with an  $\eta^2$ -(*o,m*)-[PhCH<sub>2</sub>B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>] anion, which was characterised by X-ray diffraction.

Iron(II) 2,6-diimine pyridine complexes have been found to be highly efficient catalysts for the polymerisation of olefins when activated with methyl alumoxane (MAO) cocatalyst.<sup>1</sup> The nature of the catalytically active species is still unproven, though calculations have suggested it to be a 14 valence electron (VE) cationic alkyl species.<sup>2</sup> So far, well-defined dialkyl derivatives of this system have not been reported, which precludes generation of the proposed alkyl cations by alkyl abstraction.‡ In fact, relatively little is known about the reactivity of electron-deficient iron alkyl species.<sup>3</sup> In order to obtain information on alkyl abstraction behaviour and cation–anion interactions in electron-deficient iron complexes, we have been studying ways to generate and study representative model systems.

One way to generate well-defined electron-deficient transition metal complexes is the use of sterically demanding ancillary ligands.  $\beta$ -Diketiminato (nacnac) ligands with 2,6-disubstituted aryl groups on the nitrogens have been shown to serve this purpose particularly well,<sup>4,5</sup> and  $\beta$ -diketiminato ligands have been used as ancillary ligand for olefin polymerisation catalysts based on trivalent Ti, V, Cr and Sc.<sup>6</sup>

In order to study the stability of electron deficient alkyl complexes of iron(II) and their reactivity towards commonly used borane and borate activators, we have synthesised a 12 VE iron(II) benzyl complex by alkylation of the ferrate [Li(THF)<sub>2</sub>][(nacnac)FeCl<sub>2</sub>] (nacnac = ArNCMeCHCMeNAr; Ar = 2,6-diisopropylphenyl) reported recently by Holland.<sup>5</sup> Reaction of this ferrate (generated *in situ*) with benzylmagnesium bromide in THF cleanly affords the benzyl derivative, obtained as paramagnetic air sensitive red crystals with composition [(nacnac)Fe(CH<sub>2</sub>Ph)]·0.5C<sub>5</sub>H<sub>12</sub> (**1**) after recrystallisation from pentane.§

The molecular structure of **1** was determined by X-ray diffraction (Fig. 1).¶ The unit cell contains two independent molecules which do not differ significantly. The iron atom lies in the plane defined by the three coordinating atoms, with the sum of the angles around Fe equalling 360°. The same coordination geometry was found for [(CH(C(*t*Bu)NAr)<sub>2</sub>FeCH<sub>3</sub>] (Ar = 2,6-*i*Pr-C<sub>6</sub>H<sub>3</sub>), which contains a sterically more demanding  $\beta$ -diiminato ligand.<sup>7</sup> Despite the formal electron deficiency (12 VE) of the 3-coordinate iron atom, no secondary interaction between the arene part of the benzyl group and the iron atom is present: Fe(11)–C(130)–C(131) = 113.18(11)°. This is in contrast to the usual observation in electron-deficient group 4 metal benzyl complexes of  $\eta^2$ -benzyl bonding to the metal centre.<sup>8</sup> This absence of  $\eta^2$ -interaction in **1** is probably related to the high-spin configuration of the metal centre in (nacnac)FeR<sup>7</sup> and the consequent lack of empty valence orbitals on the metal centre.

† Electronic supplementary information (ESI) available: experimental data. See <http://www.rsc.org/suppdata/cc/b2/b204454d/>

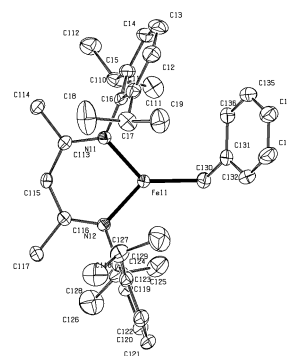
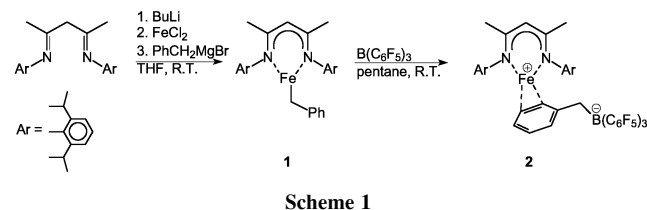


Fig. 1 Molecular structure of **1** (hydrogens not shown) with thermal ellipsoids at 50% probability. Selected bond lengths (Å) and angles (°): Fe(11)–N(11) 1.9831(11), Fe(11)–N(12) 1.9807(11), Fe(11)–C(130) 2.0414(18), Fe(11)–C(130)–C(131) 113.18(11).

Reaction of **1** with the strong Lewis acid B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> in toluene, benzene or pentane results in selective abstraction of the benzyl anion from the metal centre (Scheme 1). The ionic compound [(nacnac)Fe][PhCH<sub>2</sub>B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>] (**2**), precipitates from solution, and single crystals were obtained by recrystallisation from bromobenzene. The molecular structure of **2** (Fig. 2)§ reveals a contact ion pair in which the anion is  $\eta^2$ -coordinated to the iron centre *via* the benzyl *o*- and *m*-carbons.

The distances of the iron centre to C(30) and C(31) are at least 0.25 Å shorter than the distances to the other ring carbons, but



Scheme 1

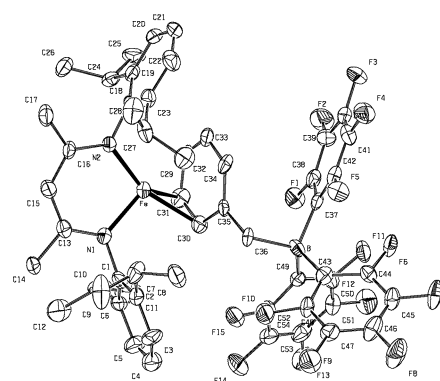


Fig. 2 Molecular structure of **2** (hydrogens not shown) with thermal ellipsoids at 50% probability. Selected bond lengths (Å) and angles (°): Fe–N(1) 1.970(6), Fe–N(2) 1.973(6), Fe–C(30) 2.344(8), Fe–C(31) 2.340(8), Fe–C(32) 2.592(7), Fe–C(33) 2.741(7), Fe–C(34) 2.716(8), Fe–C(35) 2.604(7), N(1)–Fe–N(2) 95.9(2), C(35)–C(36)–B 114.0(6).

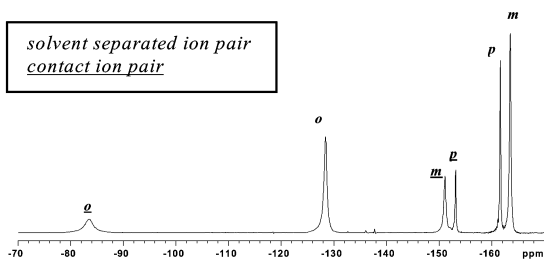
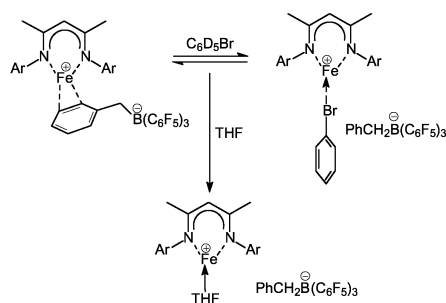


Fig. 3  $^{19}\text{F}$  NMR spectrum of **2** (470 MHz,  $\text{C}_6\text{D}_5\text{Br}$ , 253 K).

the arene C–C bond lengths do not show significant deviations from aromaticity, ranging from 1.383(12) Å (C(30)–C(31)) to 1.42(1) Å (C(30)–C(35)). The plane through C(30), C(31) and Fe makes an angle of 69.1(5)° with the diiminate coordination plane and an angle of 37.2(6)° with the plane perpendicular to the diiminate coordination plane and bisecting N(1)–Fe–N(2). To the best of our knowledge, this coordination mode is unprecedented for the  $\text{PhCH}_2\text{B}(\text{C}_6\text{F}_5)_3$  anion, for which coordination in  $\eta^3$ - and  $\eta^6$ -fashion has been reported.<sup>9</sup> For the  $\text{BPh}_4^-$  anion  $\eta^2$ -(*m,p*)-coordination to  $[\text{Cp}^*\text{ZrMe}]^+$  has been proposed based on  $^1\text{H}$  NMR data<sup>10</sup> and  $\eta^2$ -(*o,m*)-coordination of  $[\text{BPh}_4]^-$  to  $[(\text{en})\text{Cu}(\text{CO})]^+$  has been established by X-ray diffraction.<sup>11</sup>

In  $\text{C}_6\text{D}_5\text{Br}$  solution, low temperature  $^{19}\text{F}$  NMR spectroscopy (Fig. 3) shows resonances for two  $[\text{PhCH}_2\text{B}(\text{C}_6\text{F}_5)_3]$  species: one with chemical shifts normal for the free anion (71%) and one in which the *o*-F and (to a lesser extent) *m*-/*p*-F resonances are considerably downfield shifted and broadened due to coordination to the paramagnetic Fe(II) ion (29%). Apparently there is an equilibrium between the contact ion pair and a species where the  $[\text{nacnac}]\text{Fe}$ -cation is solvated by bromobenzene.

Addition of THF to this solution results in a colour change from red–brown to bright yellow. The resulting  $^{19}\text{F}$  NMR spectrum of the THF adduct displays sharp resonances for the free  $[\text{PhCH}_2\text{B}(\text{C}_6\text{F}_5)_3]$  anion, indicating that the Lewis base THF has completely displaced the anion from the metal centre (Scheme 2).



Scheme 2

In conclusion, the present study has shown that alkyl groups from electron-deficient iron species can be conveniently abstracted by a Lewis acid commonly used to activate early transition-metal polymerisation catalyst precursors, and a new coordination mode of the common  $[\text{PhCH}_2\text{B}(\text{C}_6\text{F}_5)_3]$ -counterion was observed. Interaction of fluorinated borate anions with paramagnetic transition-metal centres was seen to result in large shifts in the  $^{19}\text{F}$  NMR spectrum, suggesting that paramagnetic complexes may be used to probe even weaker cation–anion interactions in solution. We are presently investigating this possibility.

## Notes and references

‡ Olefin adducts of the corresponding Ru(II) and Rh(III) alkyl cations have been synthesised.<sup>12</sup> For Mn(II) and Co(II), alkylation is complicated by

reduction to lower oxidation states yielding monoalkyl species, indicating that, at least for Co, a Co(II) alkyl cation may not be the actual active species.<sup>13,14</sup>

§ **1**: Yield 71% based on diimine. Anal.  $\text{C}_{36}\text{H}_{48}\text{N}_2\text{Fe}\cdot 0.5\text{C}_5\text{H}_{12}$  requires C 76.98, H 9.06, N 4.66, Fe 9.30, found C 77.47, H 9.31, N 4.74, Fe 9.00%.  $^1\text{H}$  NMR (300 MHz, THF-*d*<sub>8</sub>, rt)  $\delta$  (Δ*v*<sub>2</sub>) 36.8(70), 12.1(35), –19.7(897), –25.0(217), –29.0(290), –43.6(39), –50.4(40), –56.2(166) ppm (Hz).

¶ **Crystal data** for **1**,  $\text{C}_{36}\text{H}_{48}\text{N}_2\text{Fe}\cdot 0.5\text{C}_5\text{H}_{12}$ ,  $M = 600.72$ , monoclinic,  $a = 15.3319(9)$ ,  $b = 20.652(1)$ ,  $c = 22.408(1)$  Å,  $U = 7094.5(6)$  Å<sup>3</sup>,  $T = 125$  K, space group  $P2_1/c$  (no. 14),  $Z = 8$ ,  $\mu = 4.52$  cm<sup>–1</sup>,  $\lambda(\text{Mo-K}\alpha) = 0.71073$  Å, 44924 reflections measured, 18149 unique ( $R_{\text{int}} = 0.0276$ ),  $wR(F^2) = 0.1134$  for 18149 reflections and 1181 parameters,  $R(F) = 0.0430$  for 13810 reflections obeying  $F_o \geq 4.0 \sigma(F_o)$ .

‖ **2**: Yield 72% based on **1**. Anal.  $\text{C}_{54}\text{H}_{48}\text{N}_2\text{FeBF}_{15}$  requires C 60.24 H 4.49 N 2.60, found C 60.00, H 4.58 N 2.59%.  $^{19}\text{F}$  NMR (470 MHz,  $\text{C}_6\text{D}_5\text{Br}$ , 253.3 K):  $\delta$  –82.6 (*o*-F), –128.4 (*o*-F), –150.7 (*m*-F), –152.8 (*p*-F), –161.5 (*p*-F), –163.4 (*m*-F).  $^{19}\text{F}$  NMR (188 MHz, THF-*d*<sub>8</sub>, rt):  $\delta$  –131.8 (d,  $J_{\text{FF}} = 21.45$  Hz, 6F, *o*-F), –167.3 (t,  $J_{\text{FF}} = 19.66$  Hz, 3F, *p*-F), 169.5 (m, 6F, *m*-F).

CCDC 185601 and 185603. See <http://www.rsc.org/suppdata/cc/b2/b204454d/> for crystallographic data in .cif or other electronic format.

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