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Half-pseudoferrocene cations from nucleophilic addition of *o*-carboranyl anions to the $[(\eta^6\text{-mesitylene})_2\text{Fe}]^{2+}$ dication[†]

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Reactions between the mesitylene (mes) dication $[(\eta^6\text{-mes})_2\text{Fe}]^{2+}$ (1a) $[(\text{PF}_6^-)_2 \text{ salt}]$ and lithium *o*-carboranes Li[1-R-1,2-C₂B₁₀H₁₁] (2) (R = H, 2a; Me, 2b; Ph, 2c) at low temperature (-60 °C, 1 h, followed by stirring for 2 h at r.t.) in THF resulted in a clean addition of the corresponding carborane anions to one of the unsubstituted arene sites in 1a, forming a series of orange monocations of general structure $[(\eta^5\text{-mes}-exo-6-\{2\text{-R}-1,2\text{-}C_2\text{B}_{10}\text{H}_{11}\})\text{Fe}(\eta^6\text{-mes})]^+$ (3) (R = H, 3a; Me, 3b; Ph, 3c) which were isolated as PF₆⁻ salts (3PF₆) in yields ranging 50–75%. Individual complexes were obtained on purification by LC or preparative TLC on a silica gel substrate, using MeCN–CH₂Cl₂ mixtures as the mobile phase. Interestingly, the room-temperature reaction between 2a (threefold excess) and 1a(PF₆)₂ with a reverse order of addition of the reaction components yielded an orange salt $[(\eta^5\text{-mes}-exo-6-\{1,2-C_2B_{10}H_{11}\})\text{Fe}(\eta^6\text{-mes})]^+[closo-nido-H_{11}B_{10}C_2\text{-}C_2B_{10}H_{12}]^-$ (3acCA) (cCA = conjucto-carborane anion = [closo-nido-H₁₁B₁₀C₂-C₂B₁₀H₁₂]⁻) as a sole product in 71% yield. The formation of this conjucto anion can be taken as a strong support for the participation of a radical-chain mechanism in the ostensible nucleophilic addition which we suppose to be initiated by the formation of the [(mes)₂Fe⁺]⁻ radical cation. The structures of both 3PF₆ and 3acCA have been established by X-ray diffraction and the constitution of all compounds isolated is in agreement with elemental analyses, multinuclear NMR data, and MS spectra.

Introduction

We have just recently entered the area of the $[(Me_nC_6H_{6-n})_2 Fe^{2^+}$ dications (1) by exploring their reactions with the dicarbollide anion $[7,8-C_2B_9H_{11}]^{2-}$ that generated a complete series of polymethylated arene ferradicarbaboranes $[1-(\eta^6 Me_nC_6H_{6-n}$)-closo-1,2,3-FeC₂B₉H₁₁] with the number of arene methyls n = 1-6^{1,2} These reactions resulted in the displacement of one of the arene ligands² in **1** by the π -donating dicarbollide dianion and not in nucleophilic addition to the arene ring. Addition reactions of nucleophiles (Nu⁻) to iron dications generally proceed at the unsubstituted arene site (see Scheme 1) and have never been observed with uncomplexed arenes. These types of reactions have been reported mostly for carbanions and other strong nucleophiles (for example, H⁻) and are known to be strongly affected and restricted by the nature of the nucleophile, arene, and solvent used.³ Although nucleophilic addition reactions of the $[2-Me-1,2-C_2B_{10}H_{10}]^-$ anion to the cyclopentadiene ring in $[RuCl(Cp)(PPh_3)_2]$ and to the arene ring in $[(\eta^{\hat{6}}\mbox{-}arene)Cr\mbox{-}$ $(CO)_3$ have been reported^{4,5} no addition reactions of σ -bonding



Scheme 1 General scheme of a single addition of a nucleophilic anion to $[(Me_nC_6H_{6-n})_2Fe]^{2+}$ dications.

carborane anions to iron-complexed arenes have surprisingly been examined. Therefore we believe that this paper will represent the first successful attempt in the area of iron-arene chemistry.

Results and discussion

Syntheses

In order to examine the scope of possible addition reactions, we have started investigating reactions between the mesitylene (mes) dication $[(\eta^6\text{-mes})_2\text{Fe}]^{2+}$ (1a) and Li⁺ salts of monofunctional σ -bonding carboranyl anions, Li[1-R-1,2-C₂B₁₀H₁₁] (2) (R = H, 2a; Me, 2b; Ph, 2c), in THF solvent. Scheme 2 shows that successive addition of lithium carboranes 2 to 1a(PF₆)₂ at low temperature (-60 °C, 1 h, followed by stirring for 2 h at r.t.) in THF

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Scheme 2 The main *exo*-mode of nucleophilic addition of lithium *o*-carboranes (2) to the $[(\eta^6\text{-mes})_2\text{Fe}]^{2+}$ (1a) dication.

resulting in a clean addition of the corresponding carborane anions to one of the unsubstituted arene sites in 1a upon formation of the exocyclic C-C bond. This entirely regioselective reaction mode generated a series of three orange monocations of general structure $[(\eta^5 - mes - exo - 6 - \{2 - R - 1, 2 - C_2 B_{10} H_{11}\})Fe(\eta^6 - 4)$ $[mes)]^+$ (3) (R = H, 3a; Me, 3b; Ph, 3c) which were isolated as PF_6 salts (3PF₆) in good yields ranging from 50 to 75%. Individual complexes were obtained on purification by LC or preparative TLC on a silica gel substrate, using MeCN-CH2Cl2 mixtures as the mobile phase. No double addition, as reported, *e.g.*, for lithium alkyls LiR (R = tBu, Ph, CH=CH₂),^{3a,d} or signs of addition to the Me-substituted site were observed. It should be also noted, however, that similar reactions with $[(\eta^6-p$ xylene)₂Fe]²⁺ and $[(\eta^6$ -durene)₂Fe]²⁺ dications gave only intractable and rather complex product mixtures, which is in agreement with the rules previously formulated by Astruc *et al.*^{3b}

The room-temperature reaction between a threefold excess of 2a and the mesitylene dication $1a(PF_6)_2$ using a reverse order of addition of the reaction components (addition of $1a(PF_6)_2$ to 2a). The reaction yielded an orange species formulated as the mono- $[(\eta^{5}\text{-mes-exo-6-}\{2\text{-R-1},2\text{-}C_{2}B_{10}H_{11}\})Fe(\eta^{6}\text{-mes})]^{+}$ cationic $[closo-nido-H_{11}B_{10}C_2-C_2B_{10}H_{12}]^-$ (3acCA) (cCA = conjuctocarborane anion = $[conjucto closo-nido-H_{11}B_{10}C_2-C_2B_{10}H_{12}]^-)$ as a sole product in 71% yield. The cationic part of this compound is the same as in $3aPF_6$, but the original PF_6^- counteranion has now been replaced by cCA⁻. The cCA⁻ anion has been isolated earlier by Xie et al.⁶ in the form of salts with two lanthanide counter cations $[LnCl_2(THF)_5]^+$ (Ln = Er and Y) which were characterized structurally. However, this last report formulates the species as [µ-CH-(closo-C₂B₁₀H₁₁)-nido-CB₁₀H₁₁]⁻.

The formation of **3a***c*CA from **1a** seems to be in agreement with the overall stoichiometry as in eqn (1) and (2) and the double-cage nature of cCA^- (see also Fig. 2) constitutes a direct structural support for a radical-chain ET (electron transfer) mechanism^{3b,c,h} of the nucleophilic addition process. Some of the possible steps of this radical mechanism are outlined in eqn (3)–(6). The mechanism may be triggered by the formation of the 19-electron radical cation $[(ms)_2Fe^+]^-$ (eqn (3)). This may generate a carb⁻ radical (carb = $C_2B_{10}H_{11}$)

$$[\operatorname{carb} - \operatorname{carb}]^{2-} + H_2 O \rightarrow [\operatorname{carb} - \operatorname{carb} H]^- + OH^- _{cCA^-}$$
(2)

Possible alternations of a radical mechanism:

$$[(\text{mes})_2 \text{Fe}]^{2+} + [\text{carb}]^- \rightarrow [(\text{mes})_2 \text{Fe}^+]^+ + [\text{carb}]^-$$
 (3)

$$[(\text{mes})_2 \text{Fe}^+]^{\bullet} + [\text{carb}]^{\bullet} \rightarrow [(\text{mes}) \text{Fe}(\text{mes-exo-6-carb})]^+$$

3a

$$2 [carb] \rightarrow carb-carb \tag{5}$$

$$2 \ [(mes)_{2}Fe^{+}]^{\bullet} + carb - carb \rightarrow \\ [(mes)_{2}Fe]^{2+}[carb - carb]^{2-} + [(mes)_{2}Fe]^{2+}$$
(6)

that can either combine with $[(\text{mes})_2\text{Fe}^+]^{-1}$ to form cation **3a** (eqn (4)) or undergo C–C coupling to form the neutral carb–carb dimer (eqn (5)). Its polyhedral expansion *via* addition of two electrons onto one of the carborane subclusters (eqn (6)) would then lead to the $[\text{carb-carb}]^{2-}$ dianion,⁷ from which the resulting $c\text{CA}^-$ (or $[\text{carb-carbH}]^-$) anion is formed on hydrolysis (eqn (2)).

From the viewpoint of B-cluster chemistry, the cCA^- anion can be regarded as a derivative of a new $[nido-C_2B_{10}H_{13}]^$ isomer, in which the skeletal CH₂ vertex is *exo*-substituted by the 1-*o*-carboranyl group. The isomerism of the *nido* subunit in cCA^- consists in *m*-positioning of the two cage carbon vertexes in comparison to *p*-arrangement in the known isomer of the $[nido-C_2B_{10}H_{13}]^-$ anion.⁸

Structural studies

NMR spectroscopy

The ¹¹B NMR spectra of cations 3 (Table 1) consist of 1:1:2:2:2:2 patterns of doublets (with coincidental overlaps of the B4,5/7,11 resonances) as expected for 1,2-disubstituted o-carboranes with two different substituents at carbon sites.⁹ Also the corresponding ¹H NMR spectra (Table 2) are in agreement with C_s symmetry, exhibiting two 3:9 resonances due to mes-H and mes-Me, two 2:1 resonances assigned to cyclohexadiene (chd) H2,4 and endo-H6 hydrogens, and two 3:6 resonances due to chd 3- and 1,5-methyls. The C-H, C-Me, and C-Ph protons of the exo-carboranyl cage can be also clearly distinguished. In contrast to the previously reported ¹H NMR spectra of the neutral doubly substituted $[(\eta^5-6-R-mes)_2Fe]$ (pseudoferrocene) complexes (R = tBu and Ph),^{3a} the corresponding spectra of cations 3 are temperature independent. No significant cross-peaks have been found in the [¹H-¹H]-COSY NMR spectra of cations 3 because of non-adjacency of all C-H positions. The ${}^{13}C-{}^{1}H$ NMR spectrum of $3aPF_6$ (see

$$[(\text{mes})_2 \text{Fe}]^{2+} + 3 [\text{carb}]^- \rightarrow [(\text{mes}) \text{Fe}(\text{mes}\text{-}\text{exo-6-\text{carb}})]^+ [\text{carb} - \text{carb}]^{2-}$$

$$1b \qquad 3a \qquad (1)$$

Compd	B12	B9	B8,10	B4,5,7,11	B3,6
3a PF ₆	-4.9^{a}	-3.3	-10.4	-12.9	-13.3
3b PF ₆	-7.7	-10.0	-10.0	-11.8	-13.9
3c PF ₆	-1.3	-2.7	-10.5	-12.9	-10.5

^{*a*} δ (¹¹B) in ppm relative to BF₃·OEt₂, assignments by [¹¹B–¹¹B]-COSY experiments, measured at 128.3 MHz in CD₃CN (296 K) with broadband ¹H decoupling; for *o*-carborane numbering system see ref. 9.

Table 2 Chem. shifts $\delta({}^{1}\text{H})$ for cations of structure **3**

Compd	mes-H	chd-H2,4	chd-H6	mes-Me	chd-3-Me	chd-1,5-Me ₂
$\begin{array}{c} \textbf{3aPF}_{6}^{a,b} \\ \textbf{3acCA}^{a,c} \\ \textbf{3bPF}_{6}^{a,d} \\ \textbf{3cPF}_{6}^{a,e} \end{array}$	5.63(3)	4.29(2)	3.45	2.38(9)	2.57(3)	1.78(6)
	5.54(3)	4.25(2)	3.41	2.34(9)	2.53(3)	1.73(6)
	5.43(3)	3.97(2)	2.83	2.27(9)	2.42(3)	1.38(6)
	5.44(3)	4.23(2)	2.17	2.21(9)	2.51(3)	1.37(6)

^{*a*} δ (¹H) in ppm relative to TMS, measured at 400 MHz in CD₃CN (296 K), intensities other than 1 in parentheses. ^{*b*} δ (¹H) (carb. cage): 3.67(CH). ^{*c*} δ (¹H) (carb. cage): 3.62(CH), 3.54(CH), 2.85(2 H,CH). ^{*d*} δ (¹H) (carb. cage): 2.18(3 H,Me). ^{*e*} δ (¹H) (carb. cage): 7.73–7.75(5 H, Ph).

Experimental) exhibits all resonances for mes and chd ring carbons and methyls expected from C_s symmetry.

The ¹¹B NMR spectrum of **3a***c*CA is very complex, consisting of a severely overlapped area (29 B) between -3.2 and -20.6 ppm, in which the ¹¹B resonances due to the **3a** cation can be identified. The ¹H NMR spectrum of the *c*CA⁻ anion contains four 1 : 1 : 2 resonances due to the three different cage-CH environments. The ESI-MS spectrum of **3a***c*CA exhibits the molecular-ion envelope identical with the **3a** cation (*m*/*z*_{max} 439.30).

X-ray diffraction analyses

The structures of **3a**PF₆·CH₂Cl₂ and **3a***c*CA were established by an X-ray diffraction study and are shown in Fig. 1 and 2. It is seen that the pseudoferrocene ligand in the cationic part adopts configuration similar to that found for structurally established pseudoferrocene compounds [Fe(η^5 -mes-*exo*-6-*t*Bu)₂]⁷ and [(η^6 -(mes)Fe(η^5 -mes-*exo*-6-Y](PF₆) (where Y = CH₂Cl and CHCl₂),³ⁱ with the central Fe atom sandwiched between η^6 -mesitylene and η^5 -trimethylcyclohexadienyl ligands. The carborane substituted *nido* subcluster in the *c*CA⁻ anion contains two *m*-positioned open-face CH vertexes with two extra long C31–B33 (1.990(3) Å) and C31–B36 (2.002(2) Å) distances (marked by dotted lines) associated with the carbon interconnecting the *closo* and *nido* subclusters.

Conclusions

The isolation of the *o*-carboranyl-trimethylcyclohexadienyl cations of type **3** surely opens a new, broader area of carboranyl-substituted pseudoferrocene chemistry. For example, reactions of the **1a** dication with the isomeric Li[*closo*-1,7 and 1,10-



Fig. 1 ORTEP representation of the crystallographically determined molecular structure of $[(\eta^5\text{-mes}-exo-6-\{2\text{-R}-1,2\text{-}C_2B_{10}H_{11}\})\text{Fe}(\eta^6\text{-mes})]^+$ (PF₆⁻)·CH₂Cl₂ (**3**PF₆) (crystallographic numbering) at 50% probability level. The CH₂Cl₂ molecule was omitted for clarity. Selected bond lengths (Å) and angles (°): arene ring: mean C–C 1.4115(12): mean Fe–C 2.1124(13), Fe–arene (ring centroid) 1.572(3), mean C–C–C 119.99(10); chd ring: C1–C2 1.401(6), C1–C6 1.507(6), C2–C3 1.423(6), C3–C4 1.416(7), C4–C5 1.411(7), Fe–chd (ring centroid) 1.571(3), C6–C(carb) 1.560(6), C2–C1–C6 118.8(4), C2–C3–C4 116.1(4), C1–C6–C(carb) 116.8(4), H6–C6–C19 107.2; carborane cluster: C19–C20 1.676(7), mean C19–B 1.711(3), mean C20–B 1.712(3), C6–C19–C20 114.5(4), C6–C19–B22 126.6(4).



Fig. 2 ORTEP representation of the crystallographically determined molecular structure of $[(\eta^5\text{-mes-}exo\text{-}6\text{-}\{2\text{-}R\text{-}1,2\text{-}C_2B_{10}H_{11}\})\text{Fe}(\eta^6\text{-}mes)]^+(cCA)^-$ (**3***ac*CA) (crystallographic numbering). Bond lengths (Å) and angles (°) in the cationic part are very similar to those in **3***a*PF₆ (Fig. 1). The *c*CA anion: *nido*-carborane subcluster, open face: C31–C34 2.581(3), mean C31–B 2.075(4), mean C34–B 1.642(4), mean B32–B 1.773(5), mean B–B (other) 1.756(5), C43–C31–H31 106.5(3), C31–B32–C34 64.6(4); bond lengths in the *-*1-*closo*-1,2-C₂B₁₀H₁₁ subcluster are similar to those in **3***a*PF₆ (Fig. 1).

 $C_2B_{10}H_{11}$] carboranes should generate cations near structure **3** with a modified carborane functionality. Similar reactions, for example with monocarbaborane $Li_2[closo-CB_nH_n]$ compounds, may be expected to lead to neutral monocarbaborane analogs of **3**. Moreover, boron-removal reactions on the carborane part of **3**,

followed by metal complexation, are expected to provide bimetallic sandwich assemblies of designed molecular shape, and decomplexation procedures applied to structures of type **3** should generate aryl or cyclohexadienyl carboranes with unusual substituents. Relevant experiments are currently underway in our laboratories.

Experimental

General

All reactions were carried out with the use of standard vacuum or inert-atmosphere techniques as described by Shriver and Drezdzon,¹⁰ although some operations, such as column LC, were carried out in air. The starting dication 1a was prepared according to the literature.¹¹ Dichloromethane and hexane were dried over CaH₂ and freshly distilled before use, THF was dried with sodium diphenyl ketyl and distilled. Other chemicals were of reagent or analytical grade and were used as purchased. Analytical TLC was carried out on ®Silufol (silica gel on aluminum foil; detection by I₂ vapor, followed by 2% aqueous AgNO₃ spray). Column chromatography was performed on silica gel (Aldrich, 250-350 mesh). Mass spectra were recorded on a Thermo Finnigan LCQ Fleet Ion Trap mass spectrometer. ¹H, ¹¹B and ¹³C NMR spectroscopy was performed on a Varian Mercury 400 instrument. The ¹¹B NMR spectra (referenced to $BF_3 \cdot OEt_2$ standard) were assigned by $[^{11}B^{-11}B]$ -COSY measurements.12

General synthesis of $[(\eta^5 \text{-mes}\text{-}exo\text{-}6-\{2\text{-}R\text{-}1,2\text{-}C_2B_{10}H_{11}\})Fe(\eta^6 \text{-}mes)]^+(PF_6)^-$ (3PF₆) (R = H, Me, and Ph) complexes

A solution of lithium carboranes $Li[1-R-1,2-C_2B_{10}H_{10}]$ (2) (R = H, 2a; Me, 2b; Ph, 2c) (1.1 mmol reaction scale) in THF (50 ml) was cooled to *ca*. -60 °C and treated with solid $[(\eta^6-\text{mes})_2\text{Fe}]$ - $(PF_6)_2$ (1aPF₆) (530 mg, 1 mmol). The mixture was stirred at -40 to -60 °C for 1 h and then for an additional 2 h at ambient temperature. Water (ca. 1 ml, dropwise) was carefully added and the bulk of THF rotary evaporated. The residue was digested with 30 ml-portions of CH₂Cl₂ and water and the orangecoloured bottom layer was separated, dried over MgSO₄, filtered, and subjected to LC separation on a silica gel substrate. Elution with a CH₂Cl₂-MeCN mixture (ca. 10:1) developed the main orange bands (anal. R_F ca. 0.30–0.35) which were evaporated to dryness to isolate cations 3a, 3b and 3c as PF_6^- salts in unoptimized yields 70, 60, and 75%, respectively. Individual complexes can be crystallized by adding carefully excess Et₂O onto the surface of acetone solutions. Anal. (calcd/found): 3aPF₆·CH₂Cl₂: 37.01/36.40%C, 5.48/5.51%H. 3bPF₆: 42.13/ 43.53%C, 6.24/6.12%H. 3cPF₆: 47.26/48.12%C, 5.96/6.02%H. ESI-MS: *m*/*z* (100%) (calcd/found): **3a**: 439.31/439.28 [M⁺]; **3b**: 452.32/452.30 [M⁺]; **3c**: 515.40/515.40. δ (¹³C)-{¹H} (100.6 MHz, CD₃CN) for 3aPF₆: 104.9 (1C, chd-3-ring), 94.9 (3C, mes-C1,3,5-ring), 84.8 (2C, chd-C1,5-ring), 66.1 (3C, mes-C2,4,6-ring), 60.4 and 57.2 (2C, carb C), 49.7 (1C, chd-C6), 24.7 (1C, chd-3-Me), 19.0 (2C, chd-1,5-Me)15.4 (3C, mes-1,3,5-Me).

Synthesis of $[(\eta^5 - mes - exo - 6 - \{1, 2 - C_2 B_{10} H_{11}\})Fe(\eta^6 - mes)]^+ - (B_{10}H_{11}C_2 - C_2 B_{10}H_{12})^- (3acCA)$

Solid $[(\eta^6\text{-mes})_2\text{Fe}](\text{PF}_6)_2$ (1aPF₆) (530 mg, 1 mmol) was added in several portions to a solution of Li[1,2-C₂B₁₀H₁₁] (2a) (451 mg, 3 mmol) in THF (50 ml) at room temperature and the mixture was stirred 3 h. Further work up as in the preceding experiment gave 516 mg (71%) of orange 3acCA upon crystallization from a CH₂Cl₂ solution onto the surface of which a layer of hexane was carefully added. Anal. (calcd/found): 39.64/ 38.41%C, 8.04/8.12%H. ESI-MS: *m/z* (100%) (calcd/found): 439.31/439.28 [M⁺ corresponding to 3a].

X-ray crystallography

The X-ray data for orange crystals of compounds 3aPF₆·CH₂Cl₂ and 3acCA were obtained at 150 K using an Oxford Cryostream low-temperature device and a Nonius KappaCCD diffractometer with MoK_{α} radiation ($\lambda = 0.71073$ Å), a graphite monochromator, and the ϕ and χ scan mode. Data reductions were performed with DENZO-SMN.13 The absorption was corrected by integration methods.¹⁴ Structures were solved by direct methods $(Sir92)^{15}$ and refined by full matrix least-squares based on F^2 (SHELXL97).¹⁶ Hydrogen atoms could be mostly localized on a difference Fourier map. However, to ensure uniformity of treatment of crystal structures, they were recalculated into idealized positions (riding model) and assigned temperature factors $U_{\rm iso}({\rm H}) = 1.2 \ U_{\rm eq}({\rm pivot \ atom})$ or of 1.5 $U_{\rm eq}$ for the methyl moieties with C-H = 0.96 Å, 0.97, and 0.93 Å for the methyl, methylene, and aromatic hydrogen atoms, respectively, and 1.1 Å for B-H and C-H bonds in the carborane cage.

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