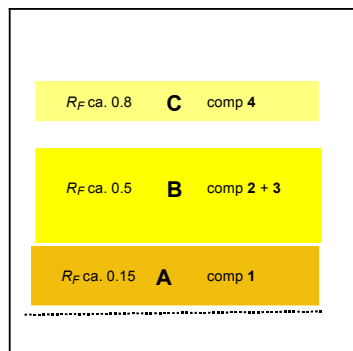


Supplementary Information

Experimental section

General. All thermolyses were carried out under argon atmosphere, but subsequent operations, such as column LC, were carried out in air. The starting complexes **1** and the $[\text{Ar}_2](\text{PF}_6)_2$ salts were prepared according to the literature.¹ Dichloromethane and hexane were dried over CaH_2 and freshly distilled before use. Other chemicals were of reagent or analytical grade and were used as purchased. Preparative TLC was carried out on 200 x 250 mm-glass plates coated with Fluka silica gel H and 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 and ^{11}B NMR spectroscopy was performed on a Varian Mercury 400 instrument inclusive of standard ^{11}B - ^{11}B -COSY and ^1H - $\{^{11}\text{B}(\text{selective})\}$ NMR experiments leading to complete assignments of all resonances due to cage BH units. ^1H and ^{11}B NMR chem. shifts are in Table S1, melting points, ESI-MS, and elemental analyses are in Table S2 below.



Thermolysis of $[\text{1-(}\eta^6\text{-Ar)-closo-1,2,3-FeC}_2\text{B}_9\text{H}_{11}]$ (Ar = mes, **1a and pmb, **1b**) ferradicalbollides at 350 °C.** A suspension of compounds **1a** and **1b** (309 and 337 mg, 1 mmol) in mineral oil (20 ml) was heated under stirring for 2 h. The mixture was then extracted with hexane (2 x 30 ml) and dichloromethane. The residual orange solution was divided into three parts, of which each was subjected to a long lasting 10-fold preparative TLC procedure, using a 5% dichloromethane-hexane mixture as a mobile phase. The resulting chromatographic pattern, shown in the left figure, consisted of three bands A, B, and C. Band A, the front part (ca.1/3) of band B, and band C were removed and extracted with CH_2Cl_2 . Vacuum evaporation of individual combined extracts gave recovered compounds **1a** (263 mg, 85%) and **1b** (302 mg, 81%) together with complexes **3a** (19 mg, 6%) and **3b** (20 mg, 6%) and **4a** (19 mg, 6%) and **4b** (30 mg, 9%). The same isolation procedure was applied to the rest of the band B which contained a mixture of compounds **2** and **3**, from which additional amounts of compounds **3** can be isolated by repeated chromatography. Crystals of complexes **3** (light orange) and **4** (yellow-orange) can be grown by slow

diffusion of hexane vapors into CH_2Cl_2 solutions or by vacuum sublimation at ca. 150 °C.

Thermolysis of $[\text{1-(}\eta^6\text{-Ar)-closo-1,2,3-FeC}_2\text{B}_9\text{H}_{11}]$ (Ar = mes, **1a and pmb, **1b**) ferradicalbollides at 500 °C.** Compounds **1a** and **1b** (154 and 169 mg, 0.5mmol) were heated in an evacuated Pyrex ampoule (ca. 10ml) at ca. 500 °C for 2 h. The ampoule was then cooled by dry ice, opened and the contents were extracted by CH_2Cl_2 (ca. 20 ml). Chromatography in a 10%-hexane- CH_2Cl_2 developed a single orange fraction, which was evaporated to give compounds **4a** (31 mg, 20%) and **4b** (39 mg, 23%) which were identified by ^{11}B NMR.

$[\text{1-(}\eta^6\text{-Ar)-closo-1,2,4-FeC}_2\text{B}_9\text{H}_{11}]$ (Ar = mes, **2a and pmb, **2b**) ferradicalbollides.** A mixture of the dicationic compounds $[(\text{mes})_2\text{Fe}](\text{PF}_6)_2$ (586 mg, 1 mmol) or $[(\text{pmb})_2\text{Fe}](\text{PF}_6)_2$ (642 mg, 1 mmol) and 1,2-dichloroethane (20 ml) was treated with $\text{Ti}_2[7,9\text{-C}_2\text{B}_9\text{H}_{11}]$ (540 mg, 1 mmol). The mixture was heated at reflux under stirring for 6 h. Upon cooling to ambient temperature, silica gel (~10 g) was added, the solvent was evaporated and the remaining solid residue was mounted onto a silica gel column (2.5 x 35 cm), which was eluted with a 10 % hexane- CH_2Cl_2 mixture to collect the front orange band. The eluted solution was evaporated to dryness and the residual crude product washed by hexane, which was then removed by a syringe. Crystals of **2a** (93 mg, 30%) and **2b** (54 mg, 16%) were grown from concentrated CH_2Cl_2 or CHCl_3 solutions, onto the top of which a layer of hexane of equal volume was carefully added. Both products can be also purified by vacuum sublimation at ca. 150 °C.

X-ray crystallography. The X-ray data for orange crystals of compounds **2a** and **2b** were obtained at 150K using Oxford Cryostream low-temperature device and a Nonius KappaCCD diffractometer with Mo $\text{K}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$), a graphite monochromator, and the ω and ϕ scan mode. Data reductions were performed with DENZO-SMN.² The absorption was corrected by integration methods.³ Structures were solved by direct methods (Sir92)⁴ and refined by full matrix least-squares based on F^2 (SHELXL97).⁵ 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 $U_{\text{iso}}(\text{H}) = 1.2 U_{\text{eq}}(\text{pivot atom})$ or of $1.5 U_{\text{eq}}$ for the methyl moieties with C-H = 0.96 Å, 0.97, and 0.93 Å for the methyl and aromatic hydrogen atoms, respectively, and 1.1 Å for B-H and C-H bonds in the carborane cage.

Crystallographic data for **2a**: $\text{C}_{11}\text{H}_{23}\text{B}_9\text{Fe}$, $M = 308.43$, orthorhombic, $Pna2_1$, red block, $a = 12.6261(6)$, $b = 9.6201(5)$, $c = 12.6258(14) \text{ \AA}$, $V = 1533.58(12) \text{ \AA}^3$, $Z = 4$, $T = 150(1) \text{ K}$, 13537 total reflections, 3053 independent ($R_{\text{int}} = 0.029$), $R1$ (obs. data) = 0.0271, $wR2$ (all data) = 0.0601, GOF = 1.119. For **2b**: $\text{C}_{13}\text{H}_{27}\text{B}_9\text{Fe}$, $M = 336.49$, orthorhombic, $Pbca$, red block, $a = 10.7301(7)$, $b = 12.0972(12)$, $c = 26.5778(14) \text{ \AA}$, $V = 3449.8(4) \text{ \AA}^3$, $Z = 8$, $T = 150(1) \text{ K}$, 50955 total reflections, 2898 independent ($R_{\text{int}} = 0.0306$), $R1$ (obs. data) = 0.0452, $wR2$ (all data) = 0.0961, GOF = 1.078.

There is a slight positional disorder in the structure of **2b** which we tried to solve by splitting of the arene as well as methyl carbon atoms into two positions but the result obtained is of lower quality than the initial dataset.

Crystallographic data for structural analyses have been deposited with the Cambridge Crystallographic Data Centre, CCDC deposition nos 810293 and 810292 for **2a** and **2b**, respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EY, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk

Table S1. ¹¹B and ¹H NMR chemical shifts (CDCl₃) for [(mes and pmb)FeC₂B₉H₁₁] isomers^a

isomer	δ(¹¹ B) and δ(¹ H) chem. shifts ^a
1-(mes)-1,2,4-FeC ₂ B ₉ H ₁₁ 2a	-3.6 (d, 140, B12), -6.7 (d, 149, B5/6), -12.9 (d, 162, B3), -15.1 (d, 150, B9/11), -15.1 (d, 150, B10), -20.7 (d, 156, B7/8); B7/8-B9/11 cross-peak unobserved ^b 5.65 (s, 3 H, mes-H), 3.95 (s, 1 H, H3), 2.70 (s, 1 H, H12), 2.77 (s, 2 H, H5/6), 2.41 (s, 9 H, mes-Me), 1.75 (s, 2 H, H2/4), 1.58 (s, 1 H, H10), 1.43 (s, 2 H, H7/8), 1.34 (s, 2 H, H9/11)
1-(pmb)-1,2,4-FeC ₂ B ₉ H ₁₁ 2b	-4.7 (d, ~140, B12), -5.9 (d, 147, B5/6), -11.6 (d, 155, B3), -14.9 (d, 143, B9/11), -15.6 (d, -, B10), -20.8 (d, 156, B7/8); B10-B12 cross-peak unobserved ^b 5.67 (s, 1 H, pmb-H), 3.56 (s, 1 H, H3), 2.64 (s, 1 H, H12), 2.52 (s, 2 H, H5/6), 2.31 (s, 6 H, pmb-Me), 2.24 (s, 3 H, pmb-Me), 2.20 (s, 6 H, pmb-Me), 1.51 (s, 2 H, H2/4), 1.51 (s, 1 H, H10), 1.40 (s, 2 H, H7/8), 1.34 (s, 2 H, H9/11)
1-(mes)-1,2,7-FeC ₂ B ₉ H ₁₁ 3a	5.0 (d, 138, B5), -3.0 (d, 134, B4), -7.6 (d, 140, B12), -9.5 (d, -, B6 or B8 or B9), -10.2 (d, -, B6 or B8 or B9), -10.8 (d, -, B6 or B8 or B9), -15.7 (d, 141, B10), -19.1 (d, 161, B3), -20.9 (d, 174, B11); B11-B12 cross-peak unobserved ^b 5.44 (s, 3 H, mes-H), 2.72 (s, 1 H, H12), 2.57 (s, 1 H, H5), 2.50 (s, 1 H, H2 or 7), 2.47 (s, 1 H, H2 or 7), 2.41 (s, 1 H, H9), 2.33 (s, 9 H, mes-Me), 2.19 (s, 1 H, H4), 1.74 (s, 1 H, H11), 1.58 (s, 2 H, H3 and 8) ^c
1-(pmb)-1,2,7-FeC ₂ B ₉ H ₁₁ 3b	5.7 (d, 138, B5), -2.4 (d, 131, B4), -9.0 (d, -, B12), -9.3 (d, -, 3 B, B6/8/B9), -15.9 (d, 143, B10), -19.3 (d, 165, B3), -20.9 (d, ~175, B11) 5.50 (s, 1 H, pmb-H), 2.64 (s, 1 H, H12), 2.43 (s, 2 H, H2/7), 2.34 (s, 1 H, H5), 2.24 (s, 6 H, pmb-Me), 2.20 (s, 3 H, pmb-Me), 2.15 (s, 6 H, pmb-Me), 1.95 (s, 1 H, H4), 1.64 (s, 1 H, H11), 1.58 (s, 2 H, H3 and 8) ^c
1-(mes)-1,2,8-FeC ₂ B ₉ H ₁₁ 4a	-3.3 (d, 141, B9/12), -6.7 (d, ~135, B4), -7.2 (d, ~135, B6), -11.8 (d, ~150, B3), -12.9 (d, ~145, B5), -16.2 (d, 141, B10), -21.0 (d, ~165, B11), -22.6 (d, ~165, B7); B7-B12 cross-peak unobserved ^b 5.48 (s, 3 H, mes-H), 2.85 (s, 2 H, H3/12), 2.77 (s, 2 H, H6), 2.32 (s, 9 H, mes-Me), 2.15 (s, 1 H, H9), 2.09 (s, 1 H, H2 or 8), 1.96 (s, 1 H, H7), 1.88 (s, 1 H, H4), 1.77 (s, 1 H, H2 or 8), 1.62 (s, 1 H, H5), 1.52 (s, 1 H, H10), 1.42 (s, 1 H, H11)
1-(pmb)-1,2,8-FeC ₂ B ₉ H ₁₁ 4b	-1.9 (d, ~135, B12), -3.0 (d, ~130, B9), -6.2 (d, 152, B4), -8.2 (d, 156, B6), -10.7 (d, 159, B3), -12.8 (d, 152, B5), -16.5 (d, 144, B10), -20.9 (d, 161, B11), -22.6 (d, ~165, B7); B7-B12 cross-peak unobserved ^b 5.47 (s, 1 H, pmb-H), 2.73 (s, 1 H, H6), 2.55 (s, 2 H, H3/12), 2.25 (s, 6 H, pmb-Me), 2.20 (s, 3 H, pmb-Me), 2.15 (s, 6 H, pmb-Me), 2.04 (s, 1 H, H2 or 8), 1.93 (s, 2 H, H7/9), 1.68 (s, 1 H, H4), 2.33 (s, 9 H, mes-Me), 1.65 (s, 1 H, H5), 1.51 (s, 1 H, H2 or 8), 1.47 (s, 1 H, H10), 1.40 (s, 1 H, H11)

^aGiven in ppm relative to BF₃·OEt₂ and TMS, respectively; ordered as δ(¹¹B) (multiplicity, ¹J(BH/Hz), assignment) and δ(¹H) (multiplicity, intensity, assignment); assignments by [¹¹B-¹H]-COSY and ¹H{¹¹B(selective)} experiments. ^b Other theoretical [¹¹B-¹H]-COSY cross-peaks observed. ^cOther resonances of cage-BH units could not be determined satisfactorily due to peak overlap.

Table S2. Other properties of [(mes and pmb)FeC₂B₉H₁₁] isomers

comp	m. p. (°C) ^a	m/z(%) (calcd/found) ^b	elem. anal. (calcd/found) ^c
2a	255-256	311.20(8)/ 311.21 (6)	42.82/43.03 7.51/7.64
2b	274-276	339.23(8)/ 339.26(8)	42.82/42.94 7.51/7.58
3a	158-160	311.20(8)/ 311.21(7)	42.82/43.13 7.51/7.62
3b	171-172	339.23(8)/ 339.24 (9)	42.82/42.41 7.51/7.58
4a	160-162	311.20(8)/ 311.22 (8)	42.82/43.15 7.51/7.67
4b	168-169	339.23(8)/ 339.24(9)	42.82/42.13 7.51/7.81

^aUncorrected. ^bMolecular cut-off peak in the parent envelope. ^c%C followed by %H.

References

1 Štíbr, B.; Bakardjiev, M.; Holub, J.; Růžicka, A.; Kvičalová M. *Inorg. Chem.* **2009**, *48*, 10904.
2 Otwinowski, Z.; Minor W. *Method Enzymol.* **1997**, *276*, 307.
3 Coppens P. In *Crystallographic Computing*; Ahmed F. R., Hall S. R., Huber C. P., Eds.; Munksgaard: Copenhagen, 1970, pp. 255 – 270.
4 Altomare, A.; Cascarano, G.; Giacovazzo, C.; Guagliardi, A. *J. Appl. Crystallogr.* **1993**, *26*, 343.
5 Sheldrick, G. M.; SHELXL-97, University of Göttingen: Göttingen, 1997.