

Supporting Information for:

**1,2-Halosilane vs. 1,2-Alkylborane Elimination from (Boryl)(Silyl) Complexes of Iron:
Switching Between Borylenes and Silylenes just by Changing the Alkyl Group**

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Experimental Section

General considerations: All syntheses were performed either under an atmosphere of dry argon or *in vacuo* using standard Schlenk line or glovebox techniques. Solvents were purified by distillation under dry argon from alkali metals (P₂O₅ in the case of halogenated solvents) and stored under the same inert gas over molecular sieves. C₆D₆ and CD₂Cl₂ were degassed by three freeze-pump-thaw cycles and stored over molecular sieves. NMR spectra were acquired on a Bruker Avance 400 (¹H: 400.1 MHz, ¹¹B: 128.4 MHz, ¹³C{¹H}: 100.6 MHz, ³¹P{¹H}: 162.0 MHz) or a Bruker Avance 500 (¹H: 500.1 MHz, ¹¹B{¹H}: 160.5 MHz, ¹³C{¹H}: 125.8 MHz, ³¹P{¹H}: 202.5 MHz, ²⁹Si: 99.36 MHz) NMR spectrometer. NMR spectra were referenced to external SiMe₄ (¹H, ¹³C, ²⁹Si), BF₃·OEt₂ (¹¹B), and 85% H₃PO₄ (³¹P). Microanalyses (C, H) were performed on a Elementar Vario MICRO cube instrument. GC/MS analyses were performed on an Agilent Technologies GC/MS system (GC 7890A, EI-MS 5975C). [Fe(CO)₄(PMe₃)],¹ [Fe(CO)₃H(PMe₃)(SiR₃)]² (R = Me, Et), K[Fe(CO)₃(PMe₃)(SiR₃)]² (R = Me, Et), DurBr,³ DurLi,⁴ and DurBX₂⁵ (X = Br, Cl) were prepared according to published literature procedures.

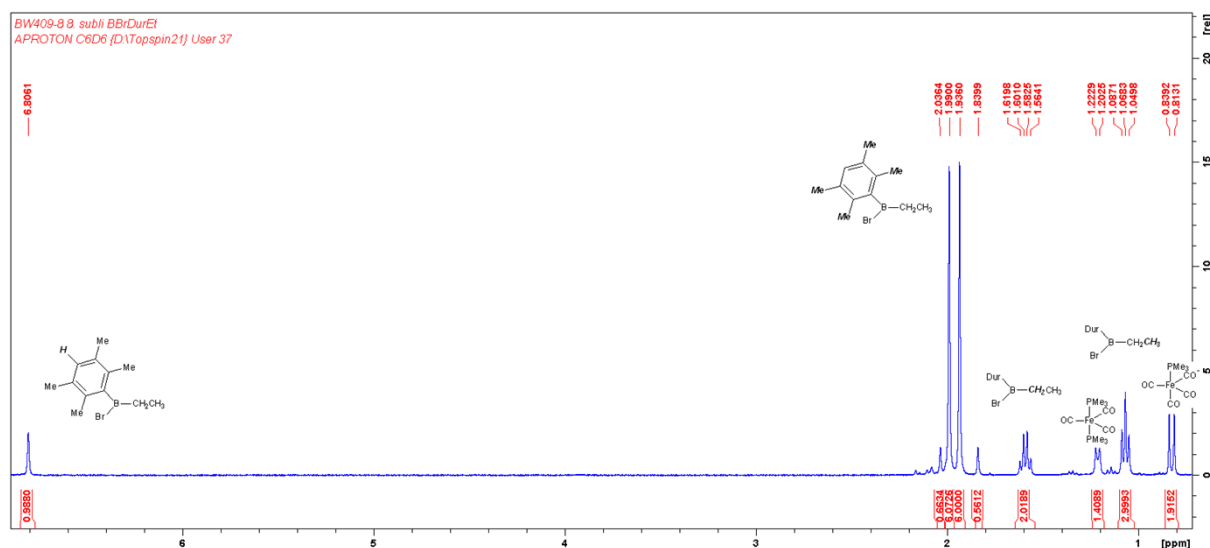
Synthesis of *mer*-[Fe(BCIDur)(CO)₃(PMe₃)(SiMe₃)] (3a): A toluene solution (30 mL) of Cl₂BDur (**2a**) (42 mg, 0.20 mmol) was transferred to a grey suspension of K[Fe(CO)₃(PMe₃)(SiMe₃)] (**1a**) (66 mg, 0.20 mmol) in 3 mL of hexane at rt. The reaction mixture was stirred for 2 h at ambient temperature and was subsequently filtered. All volatile components were removed *in vacuo*. The pale brown residue was extracted with ca. 1.5 mL hexane and stored at -30 °C overnight, yielding **3a** as colourless crystals (46 mg, 0.09 mmol, 45%). ¹H NMR (400.1 MHz, C₆D₆): δ = 0.65 (s, 9H, SiMe₃), 0.81 (m, 9H, PMe₃), 2.10 (s, 6H, Me of Dur), 2.30 (s, 6H, Me of Dur), 6.81 (s, 1H, *p*-H of Dur); ¹¹B{¹H} (128.4 MHz, C₆D₆): δ = 114.20 (bs); ³¹P{¹H} NMR (162.0 MHz, C₆D₆): δ = 2.45 (s); ²⁹Si NMR (99.4 MHz, tol-d₈):

$\delta = 16.66$ (d, $^2J_{PC} = 12.07$ Hz); IR (solid): 1946 (br, C \equiv O), 2025 (s, C \equiv O); elemental analysis calcd. [%] for C₁₉H₃₁BClFeO₃PSi: C 48.70, H 6.67; found: C 48.64, H 6.75. Due to the instability in aromatic solvents no ¹³C NMR data could be obtained. **Crystal data for 3a:** C₁₉H₃₁BClFeO₃PSi, $M_r = 468.61$, orange block, 0.260×0.120×0.110 mm³, monoclinic space group $P21/n$, $a = 8.606(2)$ Å, $b = 18.251(10)$ Å, $c = 14.997(7)$ Å, $\beta = 91.994(15)^\circ$, $V = 2354.3(18)$ Å³, $Z = 4$, $\rho_{calcd} = 1.322$ g·cm⁻³, $\mu = 0.889$ mm⁻¹, $F(000) = 984$, $T = 99(2)$ K, $R_1 = 0.0320$, $wR^2 = 0.0691$, 4598 independent reflections [$2\theta \leq 51.966^\circ$] and 254 parameters. CCDC-1061921.

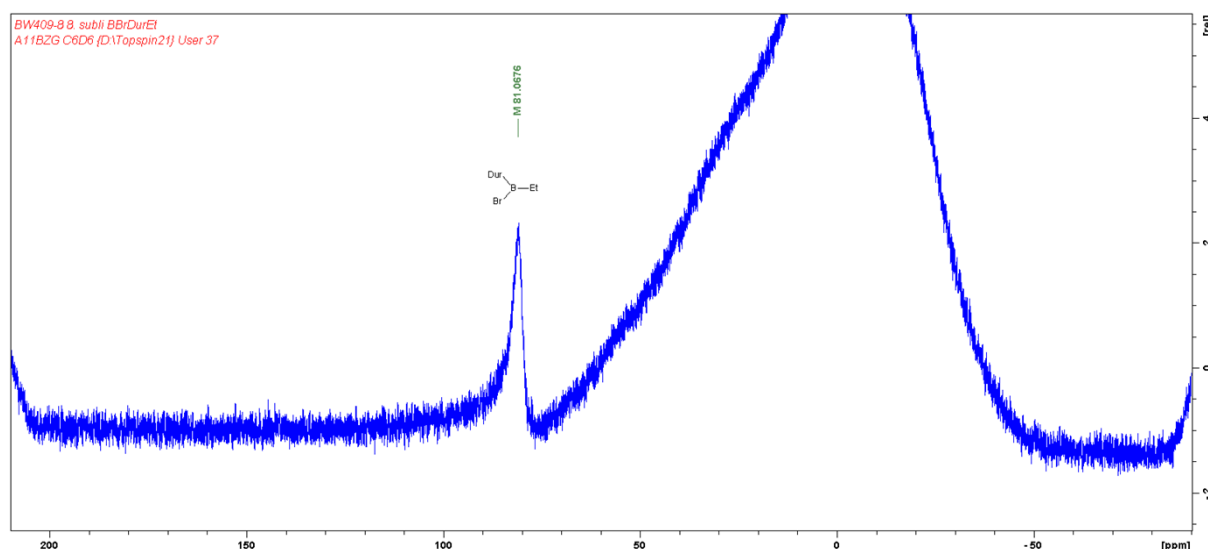
Synthesis of [Fe₂(CO)₆(PMe₃)₂(μ -SiEt₂)₂] (6c): A hexane solution (20 mL) of Br₂BDur (**2b**) (820 mg, 2.70 mmol) was transferred to a pale yellow suspension of K[Fe(CO)₃(PMe₃)(SiEt₃)] (**1b**) (1.00 g, 2.70 mmol) in 5 mL of hexane at rt. The reaction mixture was stirred for 6 h at ambient temperature and was subsequently filtered. The solution was concentrated to about 10 mL and stored at -30 °C overnight. The obtained residue was recrystallized from hexane, yielding **6c** as yellow crystals (205 mg, 0.68 mmol, 25%). ¹H NMR (500.1 MHz, C₆D₆): $\delta = 0.99$ (d, $^2J_{HH} = 8.35$ Hz, 18H, PMe₃), 1.42 (t, $^3J_{HH} = 7.70$ Hz, 12H, SiCH₂CH₃), 1.97 (q, $^3J_{HH} = 7.80$ Hz, 8H, SiCH₂CH₃); ³¹P{¹H} NMR (202.5 MHz, C₆D₆): $\delta = 9.42$ (s); ¹³C{¹H} NMR (125.8 MHz, C₆D₆): $\delta = 11.55$ (s, SiCH₂CH₃), 17.28 (s, SiCH₂CH₃), 20.67–20.91 (m, P(CH₃)₃), 213.71–213.87 (m, CO); ²⁹Si NMR (99.4 MHz, C₆D₆): $\delta = 29.77$ (bs); IR (solid): 1913 (br, C \equiv O), 1975 (s, C \equiv O); elemental analysis calcd. [%] for C₂₀H₃₈Fe₂O₆P₂Si₂: C 39.75, H 6.34; found: C 40.32, H 6.38. **Crystal data for 6c:** C₂₀H₃₈Fe₂O₆P₂Si₂, $M_r = 604.32$, yellow plate, 0.14×0.10×0.03 mm³, monoclinic space group $P21/n$, $a = 10.1597(16)$ Å, $b = 12.900(2)$ Å, $c = 10.7901(18)$ Å, $\beta = 105.385(5)^\circ$, $V = 1363.5(4)$ Å³, $Z = 2$, $\rho_{calcd} = 1.472$ g·cm⁻³, $\mu = 1.301$ mm⁻¹, $F(000) = 632$, $T = 100(2)$ K,

$R_1 = 0.0292$, $wR^2 = 0.0660$, 2785 independent reflections [$2\theta \leq 52.73^\circ$] and 150 parameters. CCDC-1061922.

Synthesis of BBrEtDur: The mother liquor from the synthesis of **6c** was reduced to dryness in vacuo, leaving a black residue. Through sublimation in vacuo (10^{-3} mbar, 60°C) a mixture of substances was obtained as a pale yellow solid (231 mg), consisting of the zerovalent iron complexes $[\text{Fe}(\text{CO})_4(\text{PMe}_3)]$ and $[\text{Fe}(\text{CO})_3(\text{PMe}_3)_2]$ as well as the borane BBrEtDur (approx. 85% determined by ^1H NMR). Although cocrystallization and cosublimation impeded the isolation of analytically pure BBrEtDur, GC-MS data for hydrolyzed BEtDurOH was obtained and the ^1H , ^{11}B NMR for BBrEtDur could be assigned as follows: ^1H NMR (400.1 MHz, C_6D_6): $\delta = 1.07$ (t, $^3J_{\text{HH}} = 7.48$ Hz, 3H, BCH_2CH_3), 1.59 (q, $^3J_{\text{HH}} = 7.44$ Hz, 2H, BCH_2CH_3), 1.94 (s, 6H, Me of Dur), 1.99 (s, 6H, Me of Dur), 6.81 (s, 1H, *para*-H of Dur); $^{11}\text{B}\{^1\text{H}\}$ (128.4 MHz, C_6D_6): $\delta = 81.15$ (bs); EI-MS (BEtDurOH): $m/z = 190$ [M^+].



^1H NMR spectrum of the mixture



^{11}B NMR spectrum of the mixture

Attempts to independently synthesize BBrEtDur: (Attempt A) A hexane solution (100 mL) of Br_2BDur (1.00 g, 3.29 mmol) was cooled to $-78\text{ }^\circ\text{C}$. A cyclohexane solution of EtLi (6.6 mL, 0.5 M, 3.3 mmol) was added dropwise. The reaction mixture was allowed to warm to rt overnight. Reduction of the solvent in vacuo and sublimation of the white residue (10^{-3} mbar, rt) gave a white solid containing the disubstituted borane BEt_2Dur and the desired BBrEtDur as main products determined by NMR data. The ^1H and ^{11}B NMR signals of the latter compound matched those of the borane product of the above reaction. Several attempts to separate the products by crystallization or sublimation were unsuccessful. **(Attempt B)** A diethyl ether solution of BrMgEt (1.6 mL, 2.0 M, 3.2 mmol) were added dropwise to a hexane solution (100 mL) of Br_2BDur (1.00 g, 3.29 mmol) at $-78\text{ }^\circ\text{C}$. The reaction mixture was stirred for 3 h at $-78\text{ }^\circ\text{C}$, at which point the solvent was reduced in vacuo at $-30\text{ }^\circ\text{C}$. According to ^1H NMR spectra, this white residue did not contain any of the desired BBrEtDur, only BEt_2Dur and typical signals for ether cleavage products.

Synthesis of $[\text{Fe}_2(\text{CO})_4(\mu\text{-CO})(\text{PMe}_3)_2(\mu\text{-SiEt}_2)_2]$ (7c**):** $[\text{Fe}_2(\text{CO})_6(\text{PMe}_3)_2(\mu\text{-SiEt}_2)_2]$ (**6c**) (50.0 mg, 82.7 μmol) was transferred into a J. Young NMR tube and dissolved in 1 mL of toluene. After 3 h of UV irradiation the solvent was removed in vacuo and the yellow residue was dissolved in hexane (5 mL). The solution was stored at $-30\text{ }^\circ\text{C}$ overnight, yielding **6c** as yellow crystals (39.0 mg, 67.7 μmol , 82%). ^1H NMR (500.1 MHz, C_6D_6): $\delta = 1.15$ (d, $^2J_{\text{HH}} = 8.35$ Hz, 18H, PMe_3), 1.30 (t, $^3J_{\text{HH}} = 7.50$ Hz, 12H, SiCH_2CH_3), 1.57 (br, 8H, SiCH_2CH_3); $^{31}\text{P}\{^1\text{H}\}$ NMR (202.5 MHz, C_6D_6): $\delta = 10.01$ (s); $^{13}\text{C}\{^1\text{H}\}$ NMR (125.8 MHz, C_6D_6): $\delta = 10.30$ (s, SiCH_2CH_3), 15.92 (bs, SiCH_2CH_3), 19.88 (d, $^1J_{\text{PC}} = 28.62$ Hz, $\text{P}(\text{CH}_3)_3$), 215.46 (br, CO); ^{29}Si NMR (99.4 MHz, C_6D_6): $\delta = 190.44$ (br s); IR (solid): 1900 (s, $\text{C}\equiv\text{O}$), 1914 (s, $\text{C}\equiv\text{O}$), 1942 (br, $\text{C}\equiv\text{O}$); elemental analysis calcd. [%] for $\text{C}_{19}\text{H}_{38}\text{Fe}_2\text{O}_5\text{P}_2\text{Si}_2$: C 39.60, H 6.65; found: C 39.60, H 6.79. **Crystal data for **7c**:** $\text{C}_{19}\text{H}_{38}\text{Fe}_2\text{O}_5\text{P}_2\text{Si}_2$, $M_r = 576.31$, yellow plate, $0.20\times 0.15\times 0.04\text{ mm}^3$, monoclinic space group $P21$, $a = 9.1382(6)\text{ \AA}$, $b = 12.4474(8)\text{ \AA}$, $c = 11.8729(8)\text{ \AA}$, $\beta = 96.852(2)^\circ$, $V = 1340.86(15)\text{ \AA}^3$, $Z = 2$, $\rho_{\text{calcd}} = 1.427\text{ g}\cdot\text{cm}^{-3}$, $\mu = 1.316\text{ mm}^{-1}$, $F(000) = 604$, $T = 100(2)\text{ K}$, $R_I = 0.0202$, $wR^2 = 0.0429$, 5701 independent reflections [$2\theta \leq 53.748^\circ$] and 281 parameters. CCDC-1061923.

Crystal structure determination: The crystal data were collected on Bruker X8-APEX II with an area detector and multi-layer mirror monochromated $\text{MoK}\alpha$ radiation. The structures were solved using the intrinsic phasing method (ShelXT), refined with ShelXL. All non-hydrogen atoms were refined anisotropically (except disordered solvent molecules, *vide infra*).⁶ Hydrogen atoms were included in structure factor calculations. ShelXL was interfaced with ShelXLe GUI⁶ for most of the refinement steps. The pictures of molecules were prepared using POV-RAY 3.6.2.⁷ Crystallographic data have been deposited with the Cambridge Crystallographic Data Center. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

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