

Tuning the Strain and Polymerizability of Organometallic Rings: The Synthesis, Structure, and Ring-Opening Polymerization Behavior of [2]Ferrocenophanes with C-Si, C-P and C-S Bridges

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Supporting Information

Materials. Iron (II) chloride, platinum chloride (PtCl_2), potassium trimethylsilanoate (KOSiMe_3), dichlorodimethylsilane Cl_2SiMe_2 , dichlorophenylphosphine (Cl_2PPh), 2,6-di-*t*-butylpyridine, methyl trifluoromethanesulfonate ($\text{CF}_3\text{SO}_3\text{Me}$), lithium trifluoromethanesulfonate ($\text{Li}[\text{O}_3\text{SCF}_3]$), boron trifluoride ($\text{BF}_3 \cdot \text{Et}_2\text{O}$), N,N,N',N'',N' -pentamethyldiethylenetriamine (PMDETA), 1.6 M butyllithium in hexanes, 1.8 M phenyllithium in hexanes, dicyclopentadiene and pentamethylcyclopentadiene were purchased from Aldrich Chemical Co. Bis(phenylsulfonylsulfide) $\text{S}(\text{SO}_2\text{Ph})_2$,¹ Cl_2PMes ,² 1,2,3,4,5-pentamethylferrocene³ and $[(\eta\text{-C}_5\text{H}_4\text{Li})\text{Fe}(\eta\text{-C}_5\text{Me}_4)\text{CH}_2\text{Li}] \cdot x \text{ PMDETA}$ ⁴ were prepared according to literature procedures. Solvents were dried by standard methods, distilled, and stored under nitrogen over activated molecular sieves prior to use.

Reaction stoichiometries were determined based on $[(\eta\text{-C}_5\text{H}_4\text{Li})\text{Fe}(\eta\text{-C}_5\text{Me}_4)\text{CH}_2\text{Li}] \cdot 0.66 \text{ PMDETA}$. ^1H NMR analysis of reactions of $[(\eta\text{-C}_5\text{H}_4\text{Li})\text{Fe}(\eta\text{-C}_5\text{Me}_4)\text{CH}_2\text{Li}] \cdot x \text{ PMDETA}$ with Me_3SiCl suggested that $x = 1$, however, it was found that by employing a coefficient of $x = 0.66$ the overall yields were improved. **NOTE:** The yields of reactions using $[(\eta\text{-C}_5\text{H}_4\text{Li})\text{Fe}(\eta\text{-C}_5\text{Me}_4)\text{CH}_2\text{Li}] \cdot x \text{ PMDETA}$ were determined by adopting a coefficient of $x = 1$.

Equipment. All reactions and manipulations were carried out under an atmosphere of prepurified nitrogen using either Schlenk techniques or an inert-atmosphere glove box (Vacuum Atmospheres or MBraun). The 400 MHz ^1H NMR spectra, 100 MHz ^{13}C NMR

spectra, 375 MHz ^{19}F NMR and 79.4 MHz ^{29}Si NMR spectra were recorded on a Varian XL 400. 120.5 MHz ^{31}P NMR spectra were recorded on a Varian Gemini 300. ^1H NMR and ^{13}C NMR were referenced to residual protonated solvent. The ^{29}Si NMR spectra were referenced externally to SiMe_4 (TMS) and were collected utilizing a normal (proton decoupled) pulse sequence. The ^{19}F NMR spectra were referenced externally to CFCl_3 . Solid state NMR spectra were obtained on a Bruker DSX-400 (^{13}C at 100.6 MHz) spectrometer and were referenced to adamantane (^{13}C , 38.4 ppm vs. TMS). UV-Visible spectra were obtained using a Perkin Elmer Lambda 900 UV-Vis/near IR spectrophotometer in hexanes or THF. Molecular weights were estimated by gel permeation chromatography (GPC) using a Waters Associates liquid chromatograph equipped with a 510 HPLC pump, U6K injector, ultrastyrigel columns with a pore size between 10^3 - 10^5 Å, and a Waters 410 differential refractometer. A flow rate of 1.0 mL/min was used and the eluent was a solution of 0.1% tetra-*n*-butylammonium bromide in THF. Polystyrene standards were used for calibration purposes. Mass spectra were obtained with the use of a VG 70-250S mass spectrometer operating in electron impact (EI), electrospray, or pyrolysis mode. The calculated isotopic distribution for each ion was in agreement with experimental values. The thermal behavior of compounds 7 - 9 was studied using a Perkin Elmer DSC-7 differential scanning calorimeter equipped with a TAC-7 instrument controller. Thermograms were calibrated with the melt transitions of cyclohexane and indium and were obtained at a heating rate of 10 °C/min under a nitrogen atmosphere. Thermogravimetric analyses (TGA) were performed using a Perkin-Elmer TGA-7 analyzer under nitrogen at a heating rate of 10 °C/min. Elemental analyses were performed by Quantitative Technologies Inc., Whitehouse, NJ. X-ray powder diffraction data were obtained using a Siemens D500 diffractometer employing Ni filtered $\text{Cu K}\alpha$ ($\lambda = 1.54178$ Å) radiation. Samples were scanned at step widths of 0.040° with 1.0 s per step in the Bragg angle range of 10° - 70° . Samples were prepared by spreading finely ground powder on grooved glass slides. Cyclic voltammograms were recorded with a BAS model CV-50W potentiostat and a BAS model C3 Cell Stand. A platinum disc (0.07 cm^2) working electrode was used in conjunction with a platinum wire counter electrode. A Ag/AgCl electrode was used as a reference electrode. All potentials are relative to the ferrocene/ferrocenium ion couple at 0.00 V which was used as an

internal reference. Methylene chloride (solvent) was freshly distilled from P_2O_5 . Anhydrous grade $[NBu_4][PF_6]$ (Aldrich) dried under high vacuum at 40 °C for 24 h was used as the supporting electrolyte and the analyses were carried out under nitrogen after rigorous deoxygenation of the analyte solutions. Solutions analyzed by CV were 0.1 M in $[NBu_4][PF_6]$ and 0.001 M in analyte.

Synthesis of the [2]Carbosilaferrocenophane 7. To a suspension of $[(\eta-C_5H_4Li)Fe(\eta-C_5Me_4)CH_2Li] \cdot 0.66$ PMDETA (2.0 g, 5.2 mmol) in Et_2O (40 mL), Cl_2SiMe_2 (575 μ L, 5.4 mmol) was added dropwise at -78 °C. The reaction mixture was stirred at this temperature for 3 h and was then allowed to warm up to room temperature over a 12 h period. Following solvent removal in vacuo, orange crystals of **7** were isolated and purified by vacuum sublimation (80 °C, 10 mmHg). Yield 0.81 g (57 %). 1H NMR (400 MHz, C_6D_6): δ = 4.12 (m, 2H, C_5H_4), 3.95 (m, 2H, C_5H_4), 2.16 (s, 6H, C_5Me_4), 2.03 (s, 2H, CH_2), 1.80 (s, 6H, C_5Me_4), 0.39 (s, 6H, Si-Me) ppm. ^{13}C NMR (100 MHz, C_6D_6): δ = 82.0 (ipso- C_5Me_4), 80.8 (C_5Me_4), 80.5 (C_5Me_4), 80.3 (C_5H_4), 73.4 (C_5H_4), 70.5 (ipso- C_5H_4), 19.2 (CH_2), 13.0 (C_5Me_4), 12.1 (C_5Me_4), 1.9 (Si-Me) ppm. ^{29}Si NMR (79.5 MHz, C_6D_6) δ = 9.1 ppm. MS (70 eV): m/z (%): 312 (100) [M^+], 297 (55) [$M^+ - Me$]. HR-MS $C_{17}H_{24}SiFe$, Calculated mass: 312.0997, Found mass: 312.0992. EA Calculated for $C_{17}H_{24}SiFe$: C, 65.4; H, 7.8. Found: C, 65.5; H, 8.1. UV/Vis (hexanes): λ_{max} = 458 nm (ϵ = 120 $M^{-1}cm^{-1}$).

Synthesis of the [2]Carbophosphaferrocenophanes 8a and 8b. For 8a: To a suspension of $[(\eta-C_5H_4Li)Fe(\eta-C_5Me_4)CH_2Li] \cdot 0.66$ PMDETA (2.0 g, 5.2 mmol) in Et_2O (200 mL) at -78 °C was added dropwise a solution of Cl_2PPh (780 μ L, 5.74 mmol) in 50 mL of Et_2O kept at -78 °C. The reaction mixture was stirred at this temperature for 2 hours and was then allowed to warm up to room temperature at which point the reaction mixture was extracted with 3 x 100 mL aliquots of water. The separated organic layer was dried over anhydrous $MgSO_4$ for one hour after which the deep red solution was filtered and dried under vacuum. Recrystallization from minimal hexanes at -55 °C afforded **8a** as a light red powder. Yield: 0.43 g (26 %). 1H NMR (400 MHz, C_6D_6): δ =

7.41 - 7.38 (m, 2H, C₆H₅), 7.14 - 7.12 (m, 1H, C₆H₅), 7.10 - 6.99 (m, 2H, C₆H₅), 4.53 (br, 1H, C₅H₄), 4.33 (br, 1H, C₅H₄), 4.00 (br, 1H, C₅H₄), 3.72 - 3.68 (dd, 1H, CH₂, ²J_{PH}, J_{HH} = 7 Hz, 16Hz), 3.67 (br, 1H C₅H₄), 3.28 - 3.17 (dd, 1H, CH₂, ²J_{PH}, J_{HH} = 29 Hz, 16 Hz), 2.57 (br, 3H, C₅Me₄), 1.88 (s, 3H, C₅Me₄), 1.75 (s, 3H, C₅Me₄), 1.57 (s, 3H, C₅Me₄) ppm. ¹³C NMR (100 MHz, C₆D₆): δ = 144.5 (d, ipso-C₆H₅, ¹J_{PC} = 15 Hz), 129.6 (d, ortho-C₆H₅, ²J_{PC} = 14 Hz), 128.4 (d, meta-C₆H₅, ³J_{PC} = 4 Hz), 126.8 (para-C₆H₅), 85.7 (d, C₅H₄, ^{2/3}J_{PC} = 46 Hz), 83.8 (C₅Me₄), 83.6 (C₅Me₄), 83.0 (s, C₅Me₄), 81.8 (d, ipso-C₅Me₄, ²J_{PC} = 4 Hz), 80.5 (C₅Me₄), 80.4 (d, C₅H₄, ^{2/3}J_{PC} = 8 Hz), 74.7 (br, ipso-C₅H₄), 74.6 (C₅H₄), 71.1 (d, C₅H₄, ^{2/3}J_{PC} = 12 Hz), 35.2 (d, CH₂, ¹J_{PC} = 18 Hz), 13.6 (d, C₅Me₄, ⁴J_{PC} = 12Hz), 12.1 (C₅Me₄), 11.4 (C₅Me₄), 11.3 (C₅Me₄) ppm. ³¹P NMR (120.5 MHz, C₆D₆): δ = 7.5 (CH₂P) ppm. MS (70 eV): m/z (%): 362 (100) [M⁺], 347 (6) [M⁺ - Me]. HR-MS C₂₁H₂₃PFe. Calculated mass: 362.0887, Found mass: 362.0895. EA Calculated for C₂₁H₂₃PFe: C, 69.6; H, 6.4. Found: C, 69.5; H, 6.5. UV/Vis (hexanes): λ_{max} = 472 nm (ε = 280 M⁻¹cm⁻¹).

1). For 8b: To a suspension of [(η-C₅H₄Li)Fe(η-C₅Me₄)CH₂Li]· 0.66 PMDETA (3.0 g, 7.8 mmol) in Et₂O (200 mL) at -78 °C was added 1.1 equivalent (1.9 g, 8.6 mmol) of Cl₂PMes. The reaction mixture was stirred at this temperature for 2 h and was then allowed to warm up to room temperature at which point the reaction mixture was extracted with 3 x 100 mL aliquots of water. The separated organic layer was dried over MgSO₄ for one hour after which the deep red solution was filtered and dried under vacuum. Recrystallization from minimal hexanes at -55 °C afforded **8b** as a light red powder. Yield: 1.3 g (47 %). ¹H NMR (400 MHz, C₆D₆) δ = 6.71 (s, 1H, C₆H₂Me₃), 4.42 (br, 1H, C₅H₄), 4.19 (br, 1H, C₅H₄) 4.01-3.94 (dd, 1H, CH₂, ²J_{PH}, J_{HH} = 7 Hz, 15 Hz), 3.72 (br, 1H, C₅H₄), 3.57 (br, 1H, C₅H₄), 3.54 - 3.40 (dd, 1H, CH₂, ²J_{PH}, J_{HH} = 29 Hz, 15 Hz), 2.62 (br, 3H, C₅Me₄), 2.29 (s, 6H, ortho-C₆H₂Me₃), 2.11 (s, 3H, para-C₆H₂Me₃), 1.85 (s, 3H, C₅Me₄), 1.80 (s, 3H, C₅Me₄), 1.62 (s, 3H, C₅Me₄) ppm. ¹³C NMR (100 MHz, C₆D₆): δ = 138.7 (d, ortho-C₆H₂Me₃, ²J_{PC} = 11 Hz), 138.1 (d, ipso-C₆H₂Me₃, ¹J_{PC} = 26 Hz), 136.3 (para-C₆H₂Me₃), 130.1 (meta-C₆H₂Me₃), 84.1 (d, C₅H₄, ^{2/3}J_{PC} = 47 Hz), 84.4 (C₅Me₄), 83.7 (C₅Me₄), 83.0 (C₅Me₄), 81.0 (C₅Me₄), 80.0 (br, ipso-C₅Me₄), 79.8 (d, C₅H₄, ^{2/3}J_{PC} = 8 Hz), 79.4 (ipso-C₅H₄) 74.1 (C₅H₄), 70.4 (d, C₅H₄, ^{2/3}J_{PC} = 12 Hz), 35.0 (d, CH₂, ²J_{PC} = 12 Hz), 25.0 (d, ortho-C₆H₂Me₃, ³J_{PC} = 8 Hz), 20.7 (para-C₆H₂Me₃), 13.7 (d, C₅Me₄, ⁴J_{PC} = 15 Hz), 11.9 (C₅Me₄), 11.5 (C₅Me₄), 11.4 (C₅Me₄) ppm. ³¹P NMR

(120.5 MHz, C_6D_6): $\delta = 3.8$ (CH_2P) ppm. MS (70 eV): m/z (%): 404 (100) [M^+], 389 (61) [$M^+ - Me$]. EA Calculated for $C_{24}H_{29}PFe$: C, 71.3; H, 7.23. Found: C, 71.1; H, 7.23. UV/Vis (hexanes): $\lambda_{max} = 465$ nm ($\epsilon = 310$ $M^{-1}cm^{-1}$).

Synthesis of the [2]Carbothiaferrocenophane 9. To a suspension of $[(\eta-C_5H_4Li)Fe(\eta-C_5Me_4)CH_2Li] \cdot 0.66$ PMDETA (4.0 g, 10.4 mmol) in Et_2O (200 mL) at -78 °C was added dropwise a solution of $S(SO_2Ph)_2$ (3.6 g, 11.5 mmol) in 50 mL of THF kept at -78 °C. The reaction mixture was stirred at this temperature for 2 h and was then allowed to warm up to room temperature. Following solvent removal in vacuo, the crude material was purified by column chromatography (hexanes, basic Alumina, 2 cm x 10 cm). Red crystals of **9** were isolated by recrystallization at -55 °C from a concentrated hexanes solution. Yield: 1.34 g (52 %). 1H NMR (400 MHz, C_6D_6): $\delta = 4.69$ (m, 2H, C_5H_4), 4.18 (s, 2H, CH_2S), 3.64 (m, 2H, C_5H_4), 2.41 (s, 6H, C_5Me_4), 1.65 (s, 6H, C_5Me_4) ppm. ^{13}C NMR (100 MHz, C_6D_6): $\delta = 93.7$ (ipso- C_5H_4), 84.7 (C_5Me_4), 84.6 (C_5H_4), 83.8 (ipso- C_5Me_4), 71.2 (C_5H_4), 42.6 (CH_2-S), 12.3 (C_5Me_4), 11.2 (C_5Me_4) ppm. MS (70 eV): m/z (%): 286 (100) [M^+], 194 (8) [$M^+ - 4$ Me, -S], 126 (11) [$M^+ - 4$ Me, $-CH_2-S$, -Fe]. HR-MS $C_{15}H_{18}SFe$ Calculated mass: 286.0479, Found mass: 286.0478. EA Calculated for $C_{15}H_{18}SFe$: C, 62.9; H, 6.3. Found: C, 63.1; H, 6.1. UV/Vis (hexanes): $\lambda_{max} = 475$ nm ($\epsilon = 240$ $M^{-1}cm^{-1}$).

Attempted ROP of the [2]Carbosilaferrocenophane 7. (a) Samples of **7** (ca. 0.15 g, 0.5 mmol) were heated in evacuated, sealed Pyrex glass tubes at increasing temperatures of i) $150^\circ C$, ii) $200^\circ C$, iii) $250^\circ C$, and iv) $350^\circ C$ for up to 7 days. No increase in melt viscosity was observed and the tube contents (dissolved in $CDCl_3$) were found to contain only unreacted **7** by 1H NMR. In addition, analysis of the tube contents by mass spectrometry and GPC in THF showed that no high molecular weight ($M_w > 1,000$ $g \cdot mol^{-1}$) oligomeric or polymeric material was present. (b) Samples of **7** (ca. 0.2 g, 0.64 mmol) together with ca. 1 mg (1 mol %) of $K[OSiMe_3]$ were heated in evacuated sealed Pyrex glass tubes at i) $150^\circ C$ for 1.5 h, and ii) $160^\circ C$ for 1.5 h. In all cases no increase in melt viscosity was observed and the tube contents (dissolved in $CDCl_3$) were subsequently found to contain only unreacted **7** by 1H NMR. In addition, analysis by

mass spectrometry and GPC showed that no high molecular weight ($M_w > 1,000 \text{ g}\cdot\text{mol}^{-1}$) material was present. (c) Samples of **7** (ca. 0.05 g, 0.16 mmol) together with a stoichiometric amount of 1.31 M PhLi (120 mL, 0.16 mmol) were dissolved in 0.5 ml THF and stirred for 24 h, at which point the reaction mixture was quenched with ClSiMe_3 . After solvent removal in vacuo, analysis of the reaction mixture by ^1H NMR (dissolved in CDCl_3) only revealed resonances for unreacted **7**. In addition, analysis by mass spectrometry and GPC showed that no high molecular weight material ($M_w > 1,000 \text{ g}\cdot\text{mol}^{-1}$) was present. (d) Samples of **7** (ca. 0.05 g, 0.16 mmol) were treated with ca. 2 mg (0.2 mmol) of $[(\text{cyclooctene})_2\text{RhCl}]_2$ in 0.5 ml of benzene and stirred for 24 h. No increase in solution viscosity was observed and after solvent removal in vacuo, the reaction mixture (dissolved in CDCl_3) was subsequently found to contain only unreacted **7** by ^1H NMR. Analysis of the reaction mixture by mass spectrometry and GPC showed that no high molecular weight ($M_w > 1,000 \text{ g}\cdot\text{mol}^{-1}$) material was present.

Thermal ROP of 8a; Synthesis of Polycarbophosphaferrocene 11. A sample of **8a** (ca. 0.095 g, 0.28 mmol) was heated in an evacuated, sealed Pyrex tube at 250°C . After ca. 8 h of heating, the melt viscosity was noticed to increase. After an additional 8 h of heating, the tube contents were extracted into THF (2 mL) and precipitated into hexanes (200 mL). The resulting yellow fibrous material was washed with 3 x 100 mL aliquots of hexanes and dried under vacuum. Yield: 0.04 g (42 %). ^1H NMR (400 MHz, C_6D_6): $\delta = 7.42\text{--}7.02$ (br, m, 5H, C_6H_5), 3.93–3.67 (br, m, 4H, C_5H_4), 3.22 – 3.10 (br, m, 2H, CH_2), 2.21 – 1.26 (br, m, 12H, C_5Me_4) ppm. ^{13}C NMR (100 MHz, C_6D_6): $\delta = 140.2$ (br, m, ipso- C_6H_5), 134.7 (br, m, ortho- C_6H_5), 128.7 (br, m, meta- C_6H_5 ; para- C_6H_5), 81.7 – 80.5 (br, m, C_5H_4 , C_5Me_4 , ipso- C_5Me_4), 74.7 – 72.4 (br, m, ipso- C_5H_4 , C_5H_4), 29.5 (br, m, CH_2), 12.6 – 11.1 (br, m, C_5Me_4) ppm. ^{31}P NMR (120.5 MHz, C_6D_6): $\delta = -31.7$ (CH_2P) ppm. EA Calculated for $\text{C}_{21}\text{H}_{23}\text{PFe}$: C, 69.6; H, 6.4. Found: C, 68.9; H, 6.7. UV/Vis (THF): $\lambda_{\text{max}} = 443 \text{ nm}$ ($\epsilon = 148 \text{ M}^{-1}\text{cm}^{-1}$). WAXS: ($10^\circ \leq 2_\theta \leq 70^\circ$); amorphous halo, centered at $d = 6.08 \text{ \AA}$.

Sulfurization of 11; Synthesis of Polycarbophosphaferrocene 12. To a solution of **11** (0.3 g) in CH_2Cl_2 was added a large excess of sublimed S_8 . After stirring for 24 hours,

the reaction mixture was filtered and pumped dry under vacuum. Residual sulfur was removed by high vacuum sublimation at 60 °C. Yield: 0.32 g (98%). GPC (Polystyrene Standards, THF): $M_w = 1.2 \times 10^4 \text{ g} \cdot \text{mol}^{-1}$, PDI = 1.6. ^1H NMR (400 MHz, C_6D_6): $\delta = 7.99 - 7.09$ (br, m, 5H, C_6H_5), 3.89 - 3.48 (br, m, 4H, C_5H_4), 2.30 - 1.31 (br, m, 14H, CH_2 , C_5Me_4) ppm. ^{13}C NMR (100 MHz, C_6D_6): $\delta = 132.7$ (br, m, ortho- C_6H_5), 130.9 (br, m, meta- C_6H_5 , para- C_6H_5), 84.5 - 80.0 (br, m, C_5H_4 , C_5Me_4 , ipso- C_5Me_4), 78.0 - 71.5 (br, m, ipso- C_5H_4 , C_5H_4), 30.8 (br, m, CH_2), 11.6 - 10.8 (br, m, C_5Me_4) ppm. ^{31}P NMR (120.5 MHz, C_6D_6): $\delta = 39.5$ (CH_2P) ppm. UV/Vis (THF): $\lambda_{\text{max}} = 434 \text{ nm}$ ($\epsilon = 133 \text{ M}^{-1}\text{cm}^{-1}$).

Attempted Anionic ROP of the [2]Carbophosphaferrocenophane 8a. (a) To a solution of **8a** (0.1 g, 0.28 mmol) in 5 mL of THF was added one equivalent (175 μL) of $n\text{BuLi}$ (1.6 M in hexanes). ^1H NMR analysis of reaction mixture after 48 hours revealed only the presence of unreacted **8a**. (b) To a solution of **8a** (0.1 g, 0.28 mmol) in 5 mL of THF was added one equivalent (175 μL) of $n\text{BuLi}$ (1.6 M in hexanes). This mixture was heated at 60 °C for 48 hours. Analysis of the resulting reaction mixture by ^1H NMR revealed only the presence of unreacted **8a**.

Methylation of 8a with $\text{CF}_3\text{SO}_3\text{Me}$; Synthesis of the Methylated [2]Carbophosphaferrocenophane 13. To a solution of **8a** (0.3 g, 0.83 mmol) in 100 mL of hexanes was added one equivalent (94 μL) of $\text{CF}_3\text{SO}_3\text{Me}$. After 6 hours, the resulting fine orange precipitate was collected by filtration and washed with 3 x 200 mL aliquots of hexanes. Compound **13** was isolated as fine orange powder after drying in vacuo. Yield: 0.4 g (92 %). ^1H NMR (400 MHz, C_6D_6): $\delta = 7.85 - 7.80$ (m, 2H, C_6H_5), 7.29 - 7.15 (m, 3H, C_6H_5), 5.34 (br, 1H, C_5H_4), 5.05 - 4.98 (dd, 1H, CH_2 , $^2J_{\text{PH}}$, $J_{\text{HH}} = 10 \text{ Hz}$, 17 Hz), 4.58 - 4.51 (dd, 1H, CH_2 , $^2J_{\text{PH}}$, $J_{\text{HH}} = 11 \text{ Hz}$, 17 Hz), 3.99 (br, 1H, C_5H_4), 3.79 (br, 1H, C_5H_4), 3.56 (br, 1H, C_5H_4), 2.58 (d, 3H, $\text{P}(\text{C}_6\text{H}_5)\text{Me}$, $^2J_{\text{PH}} = 14 \text{ Hz}$), 2.53 (s, 3H, C_5Me_4), 1.72 (s, 3H, C_5Me_4), 1.51 (s, 3H, C_5Me_4), 1.36 (s, 3H, C_5Me_4) ppm. ^{13}C NMR (100 MHz, C_6D_6): $\delta = 149.2$ (d, ipso- C_6H_5 , $^1J_{\text{PC}} = 15 \text{ Hz}$), 134.2 (d, ortho- C_6H_5 , $^2J_{\text{PC}} = 3 \text{ Hz}$), 132.0 (d, meta- C_6H_5 , $^3J_{\text{PC}} = 15 \text{ Hz}$), 130.0 (para- C_6H_5), 123.3 (q, CF_3 , $^1J_{\text{FC}} = 74 \text{ Hz}$), 86.1 (C_5H_4), 84.6 (C_5Me_4), 84.2 (C_5Me_4), 84.1 (d, ipso- C_5Me_4 , $^2J_{\text{PC}} = 3 \text{ Hz}$), 80.8 (d, C_5Me_4 , $^{2/3}J_{\text{PC}} = 15 \text{ Hz}$), 79.8 (d, C_5H_4 , $^{2/3}J_{\text{PC}} = 13 \text{ Hz}$), 76.1 (C_5H_4), 76.0 (C_5Me_4), 75.5 (d,

C_5H_4 , $^{2/3}J_{PC} = 12$ Hz), 72.1 (d, ipso- C_5H_4 , $^1J_{PC} = 11$ Hz), 56.7 (d, $P(C_6H_5)Me$, $^2J_{PC} = 96$ Hz), 34.5 (d, CH_2 , $^2J_{PC} = 67$ Hz), 14.4 (C_5Me_4), 13.9 (C_5Me_4), 11.9 (C_5Me_4), 10.6 (C_5Me_4) ppm. ^{19}F NMR (375.7 MHz, C_6D_6): $\delta = -77.9$ (CF_3) ppm. ^{31}P NMR (120.5 MHz, C_6D_6): $\delta = 48.3$ (CH_2P) ppm. MS (electrospray): m/z (%): [cation]: 377 (100), [anion]: 149 (100). UV/Vis (THF): $\lambda_{max} = 465$ nm ($\epsilon = 120$ M $^{-1}$ cm $^{-1}$).

Attempted Thermal ROP of 13. Samples of **13** (0.05 g, 0.09 mmol) were heated in evacuated, sealed Pyrex tubes at temperatures of i) 250 °C and ii) 280 °C. After 24 h, no increase in melt viscosity was observed in either case and analysis of the tube contents by 1H and ^{31}P NMR revealed only the presence of unreacted **13**.

Attempted Transition Metal Catalyzed ROP of 13. (a) To a solution of **13** (0.1 g, 0.19 mmol) in 5 mL of THF was added 5 mol % (2.5 mg) of $PtCl_2$. 1H and ^{31}P NMR analysis of the reaction mixture after 48 h revealed only the presence of unreacted **13**. (b) To a solution of **13** (0.1 g, 0.19 mmol) in 5 mL of THF was added 0.1 % by weight of a 3 % by weight solution of Karstedt's catalyst in xylenes (3.7 μ L). 1H and ^{31}P NMR analysis of the reaction mixture after 48 h revealed only the presence of unreacted **13**.

Thermal ROP of 9; Synthesis of Polycarbothiaferrocene 14. A sample of **9** (0.1 g, 0.35 mmol) was heated in an evacuated, sealed Pyrex tube at 200 °C. After 2 h at this temperature the melt viscosity increased. After an additional 3h of heating, the tube contents were found to be predominantly insoluble in common organic solvents. A small soluble portion was extracted into C_6D_6 . 1H NMR (400 MHz, C_6D_6): $\delta = 3.70$ (br, m, 6H, (C_5H_4), CH_2-S), 1.64 (br, s, 12H, C_5Me_4) ppm. GPC (Polystyrene Standards, THF): $M_w = 6000$ g $\cdot$ mol $^{-1}$, PDI = 1.1.

Attempted Anionic ROP of 9. (a) To a solution of **9** (0.1 g, 0.35 mmol) in 5 mL of THF was added one equivalent (218 μ L) of $nBuLi$ (1.6 M in hexanes). 1H NMR analysis of the reaction mixture after 48 h revealed only the presence of unreacted **9**. (b) To a solution of **9** (100 mg, 0.35 mmol) in 5 mL of THF was added one equivalent (218 μ L) of

nBuLi (1.6 M in hexanes). This mixture was refluxed at 60 °C for 48 h. Analysis of the reaction mixture by ^1H NMR revealed only the presence of unreacted **9**.

Attempted Transition Metal Catalyzed ROP of 9. (a) To solutions of **9** (0.1 g, 0.35 mmol) in 5 mL of THF at i) 25 °C and ii) 60 °C, was added 5 mol % (4.6 mg) of PtCl_2 . ^1H NMR analysis of the reaction mixtures after 48 h revealed in both cases only the presence of unreacted **9**. (b) To a solution of **9** (100 mg, 0.35 mmol) in 5 mL of THF was added 0.1 % by weight of a 3 % by weight solution of Karstedt's catalyst in xylenes (3.7 μL). ^1H NMR analysis of the reaction mixture after 48 h revealed only the presence of unreacted **9**.

Cationic ROP of 9. Synthesis of Polycarbothiaferrocene 14. (a) $\text{CF}_3\text{SO}_3\text{Me}$: To a solution of **9** (0.1 g, 0.35 mmol) in toluene (2 mL) was added 5 mol% of $\text{CF}_3\text{SO}_3\text{Me}$ (2.0 μL). Immediately after the addition of $\text{CF}_3\text{SO}_3\text{Me}$, the deep red reaction mixture turned a light orange, followed by precipitation of fine yellow powder (**14**). Further reaction resulted in slight oxidation of the final product. Yield: 0.08 g (80 %). ^1H NMR (400 MHz, C_6D_6 , soluble fraction): δ = 3.65 (br, m, 6H, (C_5H_4) , CH_2S), 1.61 (br, s, 12H, C_5Me_4) ppm. (b) $\text{BF}_3\cdot\text{Et}_2\text{O}$: To a solution of **9** (0.1 g, 0.35 mmol) in toluene (2 mL) was added 5 mol % of $\text{BF}_3\cdot\text{Et}_2\text{O}$ (2.2 μL). Shortly after the addition of $\text{BF}_3\cdot\text{Et}_2\text{O}$, the reaction solution underwent a color change from deep red to light orange which was immediately followed by the precipitation of fine yellow powder identified as **14**. Yield: 0.09 g (90 %). ^1H NMR (400 MHz, C_6D_6 , soluble fraction): δ = 3.67 (br, m, 6H, (C_5H_4) , CH_2S), 1.67 (br, s, 12H C_5Me_4) ppm. ^{13}C CP-MAS NMR (400 MHz, 8 kHz spin rate): δ = 83.6 - 72.1 (br, m, (C_5Me_4) , (C_5H_4)), 35.9 (br, s, CH_2), 10.4 (br, s, C_5Me_4) ppm. DSC: T_g = 60 °C. MS (pyrolysis): m/z (%): 794 (25) [$\text{M}_3 - 4\text{Me}$], 540 (68) [$\text{M}_2 - \text{S}$], 286 (100) [M^+]. WAXS: ($10^\circ \leq 2_\theta \leq 70^\circ$); d-spacings: 6.91, 5.86, 5.28 Å. EA Calculated for $\text{C}_{15}\text{H}_{18}\text{SFe}$: C, 62.9; H, 6.3. Found: C, 62.3; H, 6.6.

Treatment of 9 with excess $\text{CF}_3\text{SO}_3\text{Me}$; Attempted isolation of a ring-opened intermediate. A solution of **9** (0.05 g, 0.17 mmol) in 5 mL of toluene was treated with 5 equivalents of $\text{CF}_3\text{SO}_3\text{Me}$ (100 μL , 0.85 mmol). Immediately after the addition of

$\text{CF}_3\text{SO}_3\text{Me}$, a fine yellow precipitate formed which was found to be mainly insoluble in common organic solvents. ^1H NMR analysis (C_6D_6) of the mother liquor showed no evidence for the formation of a ring-opened intermediate. ^1H NMR analysis (C_6D_6) of the soluble fraction showed it to contain **14**. Similar results were obtained when a solution of **9** (0.05 g, 0.17 mmol) in 5 mL of toluene was added to 5 equivalents of $\text{CF}_3\text{SO}_3\text{Me}$ (100 μL , 0.85 mmol) in 5 mL of toluene.

Treatment of 9 with excess $\text{CF}_3\text{SO}_3\text{Me}$ in the presence of excess $\text{Li}[\text{O}_3\text{SCF}_3]$; Attempted isolation of a ring-opened intermediate. A solution of **9** (0.05 g, 0.17 mmol) and 10 equivalents of $\text{Li}[\text{O}_3\text{SCF}_3]$ (0.27 g, 1.75 mmol) in 5 mL of CH_2Cl_2 was treated with 5 equivalents of $\text{CF}_3\text{SO}_3\text{Me}$ (100 μL , 0.85 mmol). Similar results were obtained to the experiment without added $\text{Li}[\text{O}_3\text{SCF}_3]$.

Treatment of 9 with $\text{CF}_3\text{SO}_3\text{Me}$ in the presence of $[\text{NBu}_4]\text{Cl}$; Attempted isolation of a ring-opened intermediate. To a solution of 0.05 g (0.17 mmol) of **9** and 0.05 g (0.17 mmol) of $[\text{NBu}_4]\text{Cl}$ in 5.0 mL of CH_2Cl_2 was added 10 mol % of $\text{CF}_3\text{SO}_3\text{Me}$ (ca. 2 μL). ^1H NMR analysis of the resulting solution after 48 h revealed the presence of unreacted **9**.

Attempted Cationic ROP of 9 with $\text{BF}_3\cdot\text{Et}_2\text{O}$ in the Presence of 2,6-di-*t*-butylpyridine. A solution of **9** (0.05 g, 0.17 mmol) and 5 equivalents (0.167 g, 0.87 mmol) of 2,6-di-*t*-butylpyridine in 10 mL of toluene was treated with 0.20 molar equivalents (4.3 μL) of $\text{BF}_3\cdot\text{Et}_2\text{O}$. After 48 hours, analysis of the reaction mixture by ^1H NMR revealed only the presence of unreacted **9**.

Cationic ROP of 9 with $\text{CF}_3\text{SO}_3\text{Me}$ in the Presence of 2,6-di-*t*-butylpyridine. A solution of **9** (0.05 g, 0.17 mmol) and 5 equivalents (0.167 g, 0.87 mmol) of 2,6-di-*t*-butylpyridine in 10 mL of toluene was treated with 0.20 mol. equiv. (3.8 μL) of $\text{CF}_3\text{SO}_3\text{Me}$. Immediately after the addition of $\text{CF}_3\text{SO}_3\text{Me}$, a fine yellow precipitate formed which was mainly insoluble in common organic solvents. ^1H NMR analysis of a soluble fraction showed it to contain **14**.

Attempted Cationic Copolymerization of 9 with (CH₂)₃S. (a) To a solution of **9** (0.1 g, 0.35 mmol) and (CH₂)₃S (0.26 g, 0.35 mmol) in 10 mL of toluene was added 5 mol % of BF₃·Et₂O (2 μL). Shortly after the addition of BF₃·Et₂O a fine yellow precipitate formed which was mainly insoluble in common organic solvents. ¹H NMR analysis of a soluble fraction of this yellow precipitate revealed it to be polyferrocene **14**. ¹H NMR analysis of the reaction solution revealed it to contain poly(trimethylene sulfide) [(CH₂)₃S]_n. ¹H NMR (400 MHz, C₆D₆): δ = 2.42 (br, 4H, CH₂CH₂CH₂S), 1.74 (br, 2H, CH₂CH₂CH₂S) ppm. (b) To a solution of **9** (0.1 g, 0.35 mmol) and (CH₂)₃S (0.013 g, 0.17 mmol) in 10 mL of toluene was added 5 mol % (based on **9**) of BF₃·Et₂O (2 μL). Shortly after the addition of BF₃·Et₂O a fine yellow precipitate formed which was mainly insoluble in common organic solvents. ¹H NMR analysis of the mother liquor indicated that poly(trimethylene sulfide), [(CH₂)₃S]_n, was formed. ¹H NMR analysis of the soluble fraction of the yellow precipitate showed the presence of polyferrocene **14**.

Thermal Copolymerization of 9 with (CH₂)₃S. Synthesis of Polycarbothiaferrocene/Poly(trimethylene sulfide) Random Copolymer 15. A sample of **9** (0.1 g, 0.35 mmol) and (CH₂)₃S (0.18 g, 2.43 mmol) was heated in an evacuated, sealed Pyrex tube at 180 °C. After 2 h at this temperature, the melt viscosity was observed to increase. After an additional 16 h, the tube contents were allowed to cool to 25 °C and were extracted into THF (3 mL) and precipitated into a 10 % N₂H₄ solution in MeOH (250 mL). The hydrazine was used to ensure that all of the iron centers in the final product were in the reduced state. The resulting yellow fibrous material (**15**) was washed with 3 x 150 mL of MeOH and dried under vacuum. Yield: 170 mg (60 %). GPC (Polystyrene Standards, THF): M_w = 3.0 x 10⁵ g·mol⁻¹, PDI = 2.6. ¹H NMR (400 MHz, C₆D₆): δ = 3.60 (br, m, C₅H₄, CH₂S), 2.42 (br, m, (CH₂)₃S), 1.74 (br, C₅Me₄) ppm. ¹³C NMR (100 MHz, C₆D₆): δ = 82.0 (br, C₅Me₄, C₅H₄), 81.4 (br, C₅Me₄, C₅H₄), 77.1 (br, C₅Me₄, C₅H₄), 76.4 (br, C₅Me₄, C₅H₄), 73.4 (br, C₅Me₄, C₅H₄), 37.4 - 34.3 (br, m, C₅Me₄CH₂-S-(CH₂)₃S), 31.0 (br, CH₂CH₂CH₂S), 29.7 (br, CH₂CH₂CH₂S), 11.1 (br, C₅Me₄) ppm. UV/Vis (THF): λ_{max} = 436 nm (ε = 124 M⁻¹cm⁻¹). MS (pyrolysis): m/z (%) [x,y] (x and y are the coefficients in the general formula, [(η-C₅Me₄)(η-C₅H₄)FeCH₂S]_x[(CH₂)₃S]_y): 1218 (< 1) [4,1], 1144 (< 1) [4,0], 1080 (1) [3,3],

1006 (1) [3,2], 932 (< 1) [3,1], 878 (< 1) [1,8], 858 (< 1) [3,0], 804 (2) [1,7], 794 (2) [2,3], 720 (7) [2,2], 646 (13) [2,1], 572 (7) [2,0], 508 (13) [1,3], 434 (15) [1,2], 286 (100) [1,0].

X-ray Structural Characterization. A summary of selected crystallographic data are given in Table 2. For compounds **8a**, **8b** & **13** data were collected on a Nonius KappaCCD diffractometer using graphite monochromated MoK α radiation ($\lambda = 0.71073\text{\AA}$). A combination of 1° phi and omega (with kappa offsets) scans were used collect sufficient data. The data frames were integrated and scaled using the Denzo-SMN package.⁵ For compounds **7** and **9** data were collected on a Bruker P4 diffractometer using graphite monochromated MoK α radiation ($\lambda = 0.71073\text{\AA}$) and data were integrated using XSCANS.⁶

The structures were solved and refined using the SHELXTL\PC V5.1⁷ package. Refinement was by full-matrix least-squares on F^2 using all data (negative intensities included). For **8a**, **8b** and **13** hydrogen atoms were included in calculated positions and for **7** & **9** hydrogen atoms were refined with isotropic thermal parameters.

References

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Supp. Material for Compound 7

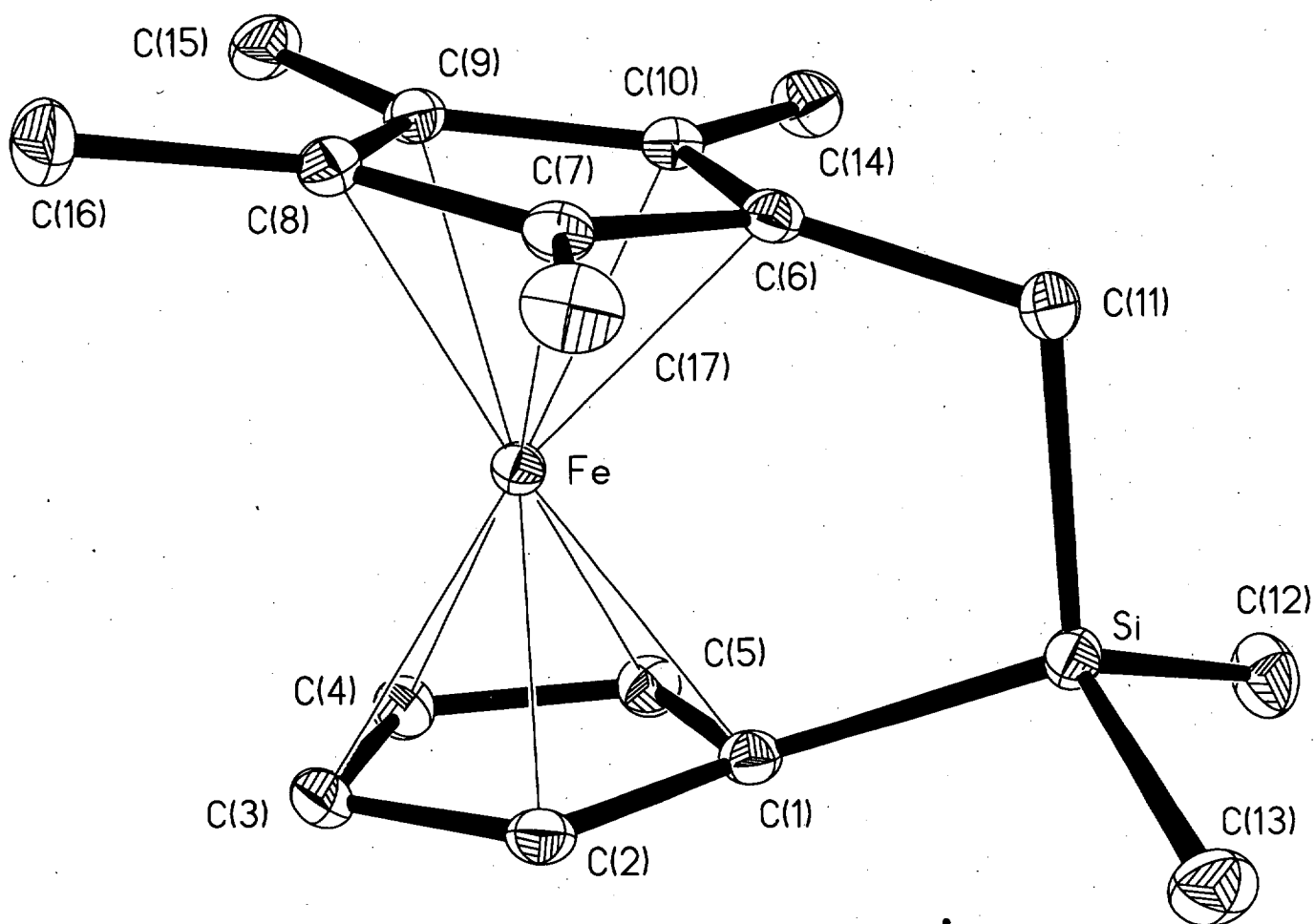


Table 1. Crystal data and structure refinement for S9543.

Identification code	s9543	
Empirical formula	C17 H24 Fe Si	
Formula weight	312.30	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 7.347(1) Å	$\alpha = 74.90(1)^\circ$
	b = 8.464(1) Å	$\beta = 89.57(1)^\circ$
	c = 14.190(1) Å	$\gamma = 66.41(1)^\circ$
Volume	776.06(15) Å ³	
Z	2	
Density (calculated)	1.336 Mg/m ³	
Absorption coefficient	1.034 mm ⁻¹	
F(000)	332	
Crystal size	0.24 x 0.21 x 0.19 mm ³	
Theta range for data collection	2.72 to 27.50°	
Index ranges	0 ≤ h ≤ 9, -9 ≤ k ≤ 10, -18 ≤ l ≤ 18	
Reflections collected	3813	
Independent reflections	3539 [R(int) = 0.0344]	
Completeness to theta = 27.50°	99.1 %	
Max. and min. transmission	0.8278 and 0.7895	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	3539 / 0 / 268	
Goodness-of-fit on F ²	1.065	
Final R indices [I > 2σ(I)]	R1 = 0.0426, wR2 = 0.1059	
R indices (all data)	R1 = 0.0520, wR2 = 0.1117	
Largest diff. peak and hole	0.788 and -0.876 e.Å ⁻³	

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for S9543. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Fe	613(1)	161(1)	7550(1)	15(1)
Si	3476(1)	-3453(1)	7131(1)	18(1)
C(1)	807(4)	-2133(3)	7290(2)	19(1)
C(2)	26(4)	-2001(4)	8213(2)	21(1)
C(3)	-1776(4)	-406(4)	8051(2)	23(1)
C(4)	-2159(4)	457(4)	7026(2)	23(1)
C(5)	-596(4)	-596(4)	6559(2)	22(1)
C(6)	3539(3)	-344(3)	7477(2)	17(1)
C(7)	2984(4)	-111(3)	8419(2)	19(1)
C(8)	1408(4)	1648(3)	8265(2)	20(1)
C(9)	998(4)	2506(3)	7230(2)	19(1)
C(10)	2336(4)	1272(3)	6743(2)	18(1)
C(11)	4932(4)	-2085(4)	7287(2)	22(1)
C(12)	3620(5)	-3777(5)	5876(2)	31(1)
C(13)	4481(5)	-5676(4)	8074(2)	30(1)
C(14)	2466(5)	1648(4)	5661(2)	26(1)
C(15)	-507(4)	4371(4)	6737(2)	29(1)
C(16)	450(5)	2487(5)	9054(2)	30(1)
C(17)	3917(5)	-1452(4)	9391(2)	29(1)

Table 3. Bond lengths [Å] and angles [°] for S9543.

Fe-C(1)	2.019(2)
Fe-C(6)	2.024(2)
Fe-C(5)	2.030(2)
Fe-C(2)	2.037(3)
Fe-C(10)	2.041(2)
Fe-C(7)	2.042(2)
Fe-C(9)	2.050(2)
Fe-C(8)	2.053(2)
Fe-C(4)	2.069(3)
Fe-C(3)	2.072(3)
Si-C(13)	1.862(3)
Si-C(12)	1.867(3)
Si-C(1)	1.875(3)
Si-C(11)	1.914(3)
C(1)-C(2)	1.439(3)
C(1)-C(5)	1.440(4)
C(2)-C(3)	1.429(4)
C(3)-C(4)	1.419(4)
C(4)-C(5)	1.425(4)
C(6)-C(10)	1.429(3)
C(6)-C(7)	1.434(3)
C(6)-C(11)	1.512(3)
C(7)-C(8)	1.435(4)
C(7)-C(17)	1.495(4)
C(8)-C(9)	1.432(4)
C(8)-C(16)	1.502(4)
C(9)-C(10)	1.441(3)
C(9)-C(15)	1.498(4)
C(10)-C(14)	1.495(4)
C(1)-Fe-C(6)	96.07(10)
C(1)-Fe-C(5)	41.65(10)
C(6)-Fe-C(5)	115.02(10)
C(1)-Fe-C(2)	41.55(10)

C(6)-Fe-C(2)	115.59(10)
C(5)-Fe-C(2)	68.67(11)
C(1)-Fe-C(10)	113.91(10)
C(6)-Fe-C(10)	41.16(10)
C(5)-Fe-C(10)	103.06(10)
C(2)-Fe-C(10)	151.23(10)
C(1)-Fe-C(7)	114.80(10)
C(6)-Fe-C(7)	41.30(10)
C(5)-Fe-C(7)	151.60(11)
C(2)-Fe-C(7)	104.46(10)
C(10)-Fe-C(7)	69.18(10)
C(1)-Fe-C(9)	153.83(10)
C(6)-Fe-C(9)	69.49(10)
C(5)-Fe-C(9)	123.78(11)
C(2)-Fe-C(9)	164.51(10)
C(10)-Fe-C(9)	41.25(10)
C(7)-Fe-C(9)	69.11(10)
C(1)-Fe-C(8)	154.77(11)
C(6)-Fe-C(8)	69.38(10)
C(5)-Fe-C(8)	163.29(11)
C(2)-Fe-C(8)	125.32(10)
C(10)-Fe-C(8)	69.09(10)
C(7)-Fe-C(8)	41.03(10)
C(9)-Fe-C(8)	40.86(10)
C(1)-Fe-C(4)	69.67(10)
C(6)-Fe-C(4)	154.46(11)
C(5)-Fe-C(4)	40.66(10)
C(2)-Fe-C(4)	68.09(11)
C(10)-Fe-C(4)	124.27(11)
C(7)-Fe-C(4)	164.04(11)
C(9)-Fe-C(4)	114.22(11)
C(8)-Fe-C(4)	131.08(10)
C(1)-Fe-C(3)	69.74(10)
C(6)-Fe-C(3)	155.15(11)
C(5)-Fe-C(3)	68.24(10)
C(2)-Fe-C(3)	40.67(11)

C(10)-Fe-C(3)	163.28(11)
C(7)-Fe-C(3)	125.30(11)
C(9)-Fe-C(3)	131.02(10)
C(8)-Fe-C(3)	115.14(10)
C(4)-Fe-C(3)	40.09(11)
C(13)-Si-C(12)	109.85(15)
C(13)-Si-C(1)	109.78(13)
C(12)-Si-C(1)	109.37(13)
C(13)-Si-C(11)	110.55(14)
C(12)-Si-C(11)	110.19(14)
C(1)-Si-C(11)	107.05(11)
C(2)-C(1)-C(5)	105.7(2)
C(2)-C(1)-Si	125.55(19)
C(5)-C(1)-Si	124.98(19)
C(2)-C(1)-Fe	69.89(14)
C(5)-C(1)-Fe	69.58(14)
Si-C(1)-Fe	107.85(11)
C(3)-C(2)-C(1)	109.3(2)
C(3)-C(2)-Fe	70.99(15)
C(1)-C(2)-Fe	68.55(14)
C(4)-C(3)-C(2)	107.6(2)
C(4)-C(3)-Fe	69.83(14)
C(2)-C(3)-Fe	68.34(14)
C(3)-C(4)-C(5)	108.1(2)
C(3)-C(4)-Fe	70.09(15)
C(5)-C(4)-Fe	68.20(14)
C(4)-C(5)-C(1)	109.3(2)
C(4)-C(5)-Fe	71.14(14)
C(1)-C(5)-Fe	68.77(14)
C(10)-C(6)-C(7)	108.1(2)
C(10)-C(6)-C(11)	125.7(2)
C(7)-C(6)-C(11)	125.6(2)
C(10)-C(6)-Fe	70.06(14)
C(7)-C(6)-Fe	70.04(13)
C(11)-C(6)-Fe	118.92(16)
C(6)-C(7)-C(8)	108.0(2)

C(6)-C(7)-C(17)	125.9(2)
C(8)-C(7)-C(17)	126.1(2)
C(6)-C(7)-Fe	68.67(13)
C(8)-C(7)-Fe	69.90(13)
C(17)-C(7)-Fe	128.01(19)
C(9)-C(8)-C(7)	108.1(2)
C(9)-C(8)-C(16)	125.9(3)
C(7)-C(8)-C(16)	125.9(2)
C(9)-C(8)-Fe	69.43(14)
C(7)-C(8)-Fe	69.07(13)
C(16)-C(8)-Fe	130.04(19)
C(8)-C(9)-C(10)	107.8(2)
C(8)-C(9)-C(15)	126.3(2)
C(10)-C(9)-C(15)	125.8(2)
C(8)-C(9)-Fe	69.71(14)
C(10)-C(9)-Fe	69.05(13)
C(15)-C(9)-Fe	128.04(18)
C(6)-C(10)-C(9)	108.0(2)
C(6)-C(10)-C(14)	126.3(2)
C(9)-C(10)-C(14)	125.7(2)
C(6)-C(10)-Fe	68.78(13)
C(9)-C(10)-Fe	69.70(14)
C(14)-C(10)-Fe	128.20(18)
C(6)-C(11)-Si	110.10(17)

Symmetry transformations used to generate equivalent atoms:

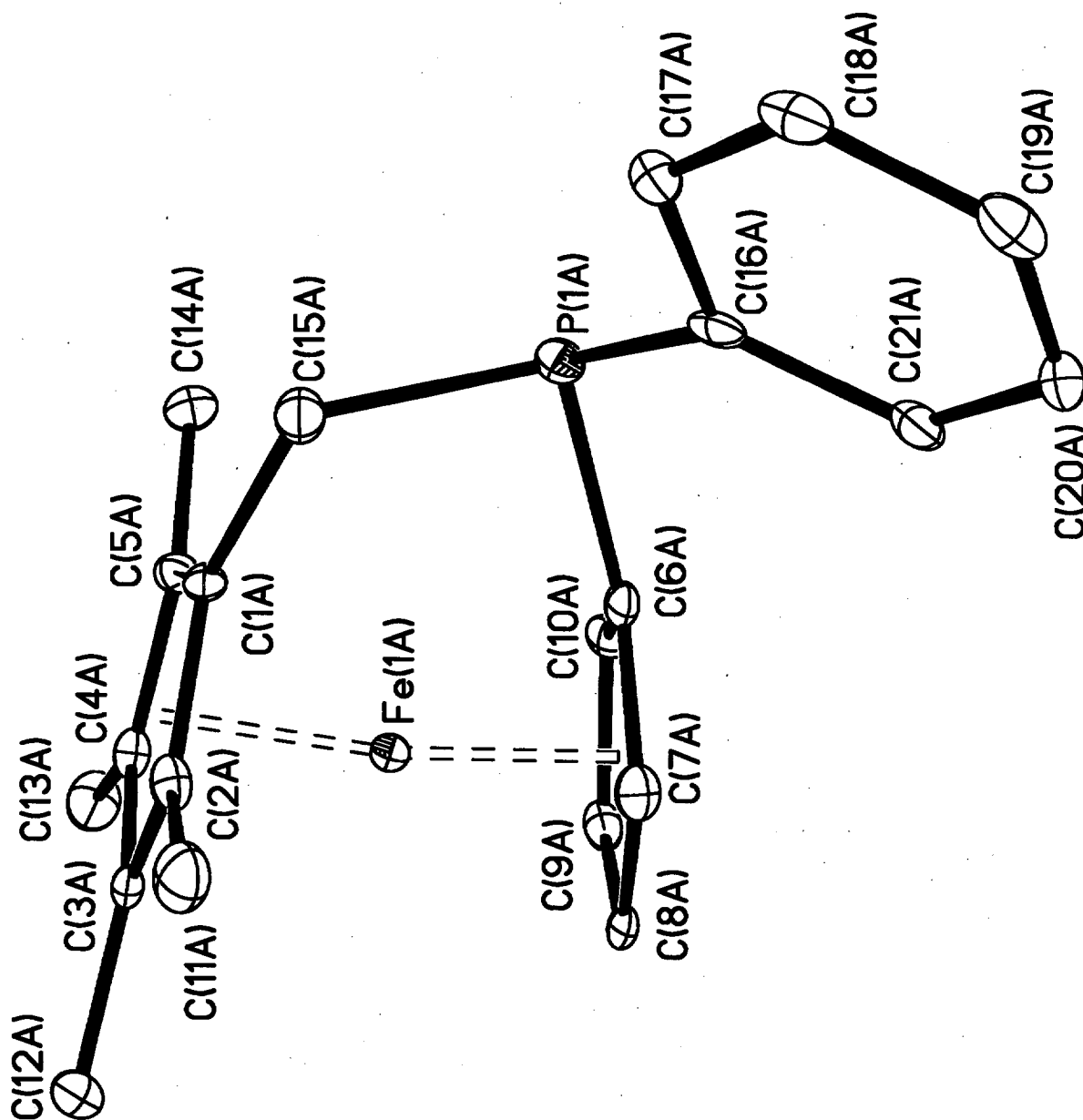
Table 4. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for S9543. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U^{11} + \dots + 2 h k a^* b^* U^{12}]$

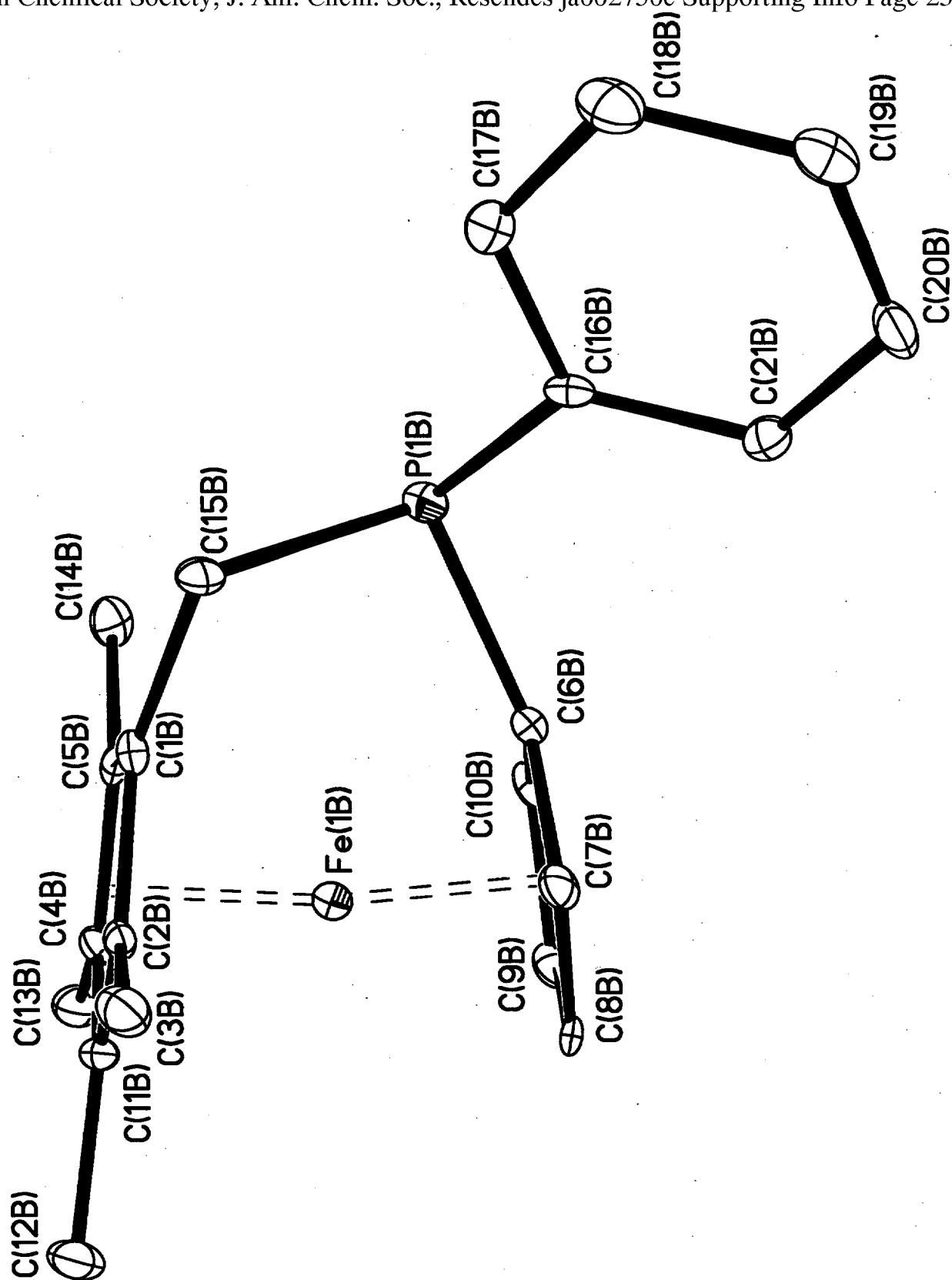
	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Fe	14(1)	15(1)	15(1)	-4(1)	1(1)	-7(1)
Si	19(1)	16(1)	19(1)	-5(1)	3(1)	-6(1)
C(1)	21(1)	20(1)	19(1)	-7(1)	3(1)	-12(1)
C(2)	25(1)	21(1)	21(1)	-5(1)	5(1)	-14(1)
C(3)	22(1)	28(1)	28(1)	-12(1)	10(1)	-15(1)
C(4)	14(1)	25(1)	32(1)	-11(1)	0(1)	-7(1)
C(5)	21(1)	25(1)	21(1)	-8(1)	0(1)	-11(1)
C(6)	14(1)	18(1)	21(1)	-4(1)	1(1)	-8(1)
C(7)	17(1)	22(1)	18(1)	-5(1)	-1(1)	-10(1)
C(8)	21(1)	22(1)	21(1)	-9(1)	4(1)	-11(1)
C(9)	18(1)	16(1)	24(1)	-5(1)	1(1)	-8(1)
C(10)	19(1)	18(1)	19(1)	-4(1)	1(1)	-10(1)
C(11)	16(1)	19(1)	30(1)	-8(1)	3(1)	-5(1)
C(12)	30(2)	41(2)	27(2)	-18(1)	7(1)	-14(1)
C(13)	31(2)	22(1)	33(2)	1(1)	0(1)	-11(1)
C(14)	33(2)	29(1)	19(1)	-4(1)	6(1)	-16(1)
C(15)	27(1)	16(1)	40(2)	-5(1)	1(1)	-7(1)
C(16)	30(2)	38(2)	31(2)	-21(1)	11(1)	-15(1)
C(17)	31(1)	34(2)	20(1)	-1(1)	-5(1)	-15(1)

Table 5. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^{-3}$) for S9543.

	x	y	z	U(eq)
H(2A)	620(50)	-2810(50)	8810(30)	27(8)
H(3A)	-2570(50)	-20(40)	8570(20)	27(8)
H(4A)	-3240(50)	1530(50)	6700(20)	27(8)
H(5A)	-390(50)	-320(40)	5850(20)	21(8)
H(11A)	5570(60)	-1840(50)	6730(30)	41(10)
H(11B)	5930(50)	-2770(40)	7790(20)	25(8)
H(12A)	3000(60)	-4570(60)	5820(30)	52(12)
H(12B)	3020(70)	-2700(70)	5390(40)	66(14)
H(12C)	5090(70)	-4280(60)	5770(30)	57(12)
H(13A)	3890(60)	-6390(60)	8010(30)	52(12)
H(13B)	5920(60)	-6320(50)	8000(30)	35(9)
H(13C)	4360(60)	-5550(50)	8730(30)	49(11)
H(14A)	3230(60)	2290(60)	5470(30)	52(12)
H(14B)	3030(60)	510(60)	5450(30)	50(11)
H(14C)	1230(60)	2340(50)	5290(30)	38(10)
H(15A)	-120(60)	5220(50)	6710(30)	41(10)
H(15B)	-1060(70)	4420(60)	6090(30)	58(12)
H(15C)	-1700(50)	4670(50)	7090(30)	34(9)
H(16A)	1220(60)	3040(50)	9290(30)	49(11)
H(16B)	-810(70)	3300(60)	8820(30)	52(12)
H(16C)	280(60)	1660(60)	9580(30)	52(12)
H(17A)	4980(60)	-1290(50)	9640(30)	45(10)
H(17B)	2940(60)	-1390(50)	9880(30)	51(11)
H(17C)	4320(70)	-2640(60)	9330(30)	58(13)

Supp. Material for Compound Ba.





Least-squares planes (x,y,z in crystal coordinates) and deviations from them
 (* indicates atom used to define plane)

$$5.7951 (0.0204) x + 10.2534 (0.0197) y + 11.7957 (0.0186) z = 10.5592 (0.0116)$$

- * 0.0061 (0.0029) C1A
- * -0.0080 (0.0029) C2A
- * 0.0068 (0.0028) C3A
- * -0.0031 (0.0029) C4A
- * -0.0019 (0.0029) C5A

Rms deviation of fitted atoms = 0.0057

$$4.5480 (0.0217) x + 11.9315 (0.0127) y + 9.9136 (0.0219) z = 12.1929 (0.0171)$$

Angle to previous plane (with approximate esd) = 14.75 (0.28)

- * -0.0157 (0.0028) C6A
- * 0.0100 (0.0028) C7A
- * -0.0004 (0.0028) C8A
- * -0.0095 (0.0027) C9A
- * 0.0157 (0.0027) C10A

Rms deviation of fitted atoms = 0.0117

$$- 7.2224 (0.0187) x + 3.5870 (0.0304) y + 4.7974 (0.0316) z = 1.2110 (0.0480)$$

Angle to previous plane (with approximate esd) = 69.12 (0.18)

- * -0.0100 (0.0029) C1B
- * 0.0065 (0.0029) C2B
- * -0.0005 (0.0030) C3B
- * -0.0057 (0.0030) C4B
- * 0.0096 (0.0029) C5B

Rms deviation of fitted atoms = 0.0073

$$- 5.4931 (0.0217) x + 6.7790 (0.0267) y + 5.3459 (0.0306) z = 1.0422 (0.0476)$$

Angle to previous plane (with approximate esd) = 15.03 (0.38)

- * 0.0093 (0.0030) C6B

- * -0.0077 (0.0029) C7B
- * 0.0032 (0.0029) C8B
- * 0.0027 (0.0029) C9B
- * -0.0075 (0.0030) C10B

Rms deviation of fitted atoms = 0.0066

Table 1. Crystal data and structure refinement for k99167.

Identification code	k99167	
Empirical formula	C ₂₁ H ₂₃ Fe P	
Formula weight	362.21	
Temperature	100.0(1) K	
Wavelength	0.71220 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 10.6721(11) Å	α = 71.687(5)°
	b = 13.2867(9) Å	β = 70.138(4)°
	c = 14.1653(15) Å	γ = 69.365(6)°
Volume	1724.2(3) Å ³	
Z	4	
Density (calculated)	1.395 Mg/m ³	
Absorption coefficient	0.964 mm ⁻¹	
F(000)	760	
Crystal size	0.12 x 0.09 x 0.06 mm ³	
Theta range for data collection	3.14 to 25.11°	
Index ranges	0 ≤ h ≤ 12, -14 ≤ k ≤ 15, -15 ≤ l ≤ 16	
Reflections collected	16353	
Independent reflections	6078 [R(int) = 0.139]	
Completeness to theta = 25.11°	99.5 %	
Absorption correction	multi-scan (Denzo-SMN)	
Max. and min. transmission	0.9444 and 0.8931	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	6078 / 0 / 416	
Goodness-of-fit on F ²	0.922	
Final R indices [I > 2σ(I)]	R1 = 0.0534, wR2 = 0.0941	
R indices (all data)	R1 = 0.1220, wR2 = 0.1104	
Extinction coefficient	0.0005(6)	
Largest diff. peak and hole	0.436 and -0.404 e.Å ⁻³	

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for k99167. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	$U(\text{eq})$
Fe(1B)	8334(1)	3652(1)	8939(1)	15(1)
P(1B)	8190(1)	1240(1)	9850(1)	17(1)
C(1B)	6493(5)	3406(3)	9732(4)	15(1)
C(2B)	6327(5)	4294(3)	8852(4)	14(1)
C(3B)	6808(5)	5131(3)	8937(4)	16(1)
C(4B)	7252(5)	4789(3)	9850(4)	16(1)
C(5B)	7039(5)	3711(3)	10367(4)	14(1)
C(6B)	9282(5)	2073(3)	8875(4)	16(1)
C(7B)	9146(5)	2728(3)	7872(4)	18(1)
C(8B)	9857(5)	3546(3)	7587(4)	17(1)
C(9B)	10461(5)	3400(3)	8391(4)	20(1)
C(10B)	10120(5)	2493(3)	9172(4)	17(1)
C(11B)	5745(5)	4365(4)	8012(4)	22(1)
C(12B)	6779(5)	6229(3)	8182(4)	25(1)
C(13B)	7804(5)	5444(4)	10236(4)	26(1)
C(14B)	7316(5)	3064(4)	11385(4)	22(1)
C(15B)	6419(5)	2248(3)	9852(4)	19(1)
C(16B)	8210(5)	226(3)	9204(4)	16(1)
C(17B)	7156(5)	-298(4)	9611(4)	22(1)
C(18B)	7194(6)	-1132(4)	9209(4)	27(1)
C(19B)	8298(5)	-1472(4)	8402(4)	22(1)
C(20B)	9339(5)	-958(4)	8017(4)	24(1)
C(21B)	9311(5)	-124(3)	8407(4)	17(1)
Fe(1A)	5374(1)	1530(1)	6357(1)	15(1)
P(1A)	4306(1)	3930(1)	5105(1)	18(1)
C(1A)	4497(5)	1706(3)	5265(4)	15(1)
C(2A)	3971(5)	955(4)	6164(4)	19(1)
C(3A)	5125(5)	49(3)	6397(4)	19(1)
C(4A)	6344(5)	239(4)	5624(4)	18(1)
C(5A)	5973(5)	1258(4)	4922(4)	17(1)
C(6A)	4910(5)	3132(3)	6261(4)	17(1)

C(7A)	4173(5)	2619(3)	7242(4)	18(1)
C(8A)	5150(5)	1812(4)	7755(4)	19(1)
C(9A)	6492(5)	1823(3)	7117(4)	20(1)
C(10A)	6346(5)	2655(3)	6208(4)	17(1)
C(11A)	2493(5)	1078(4)	6771(4)	29(1)
C(12A)	5054(6)	-943(4)	7250(4)	29(1)
C(13A)	7790(5)	-544(4)	5574(4)	30(1)
C(14A)	6935(5)	1748(4)	4002(4)	28(1)
C(15A)	3665(5)	2878(3)	4880(4)	24(1)
C(16A)	2654(5)	4894(3)	5573(4)	18(1)
C(17A)	1681(5)	5338(4)	4989(4)	20(1)
C(18A)	477(5)	6153(4)	5252(4)	24(1)
C(19A)	206(5)	6542(4)	6126(4)	26(1)
C(20A)	1154(5)	6117(3)	6706(4)	22(1)
C(21A)	2377(5)	5312(3)	6439(4)	20(1)

Table 3. Bond lengths [Å] and angles [°] for k99167.

Fe(1B)-C(1B)	1.988(5)
Fe(1B)-C(6B)	1.998(4)
Fe(1B)-C(7B)	2.016(5)
Fe(1B)-C(5B)	2.032(5)
Fe(1B)-C(10B)	2.038(4)
Fe(1B)-C(2B)	2.039(4)
Fe(1B)-C(8B)	2.055(5)
Fe(1B)-C(3B)	2.063(4)
Fe(1B)-C(4B)	2.065(5)
Fe(1B)-C(9B)	2.073(5)
P(1B)-C(6B)	1.829(5)
P(1B)-C(16B)	1.842(5)
P(1B)-C(15B)	1.892(5)
C(1B)-C(2B)	1.434(6)
C(1B)-C(5B)	1.437(6)
C(1B)-C(15B)	1.522(5)
C(2B)-C(3B)	1.429(6)
C(2B)-C(11B)	1.483(6)
C(3B)-C(4B)	1.413(6)
C(3B)-C(12B)	1.511(6)
C(4B)-C(5B)	1.448(6)
C(4B)-C(13B)	1.510(6)
C(5B)-C(14B)	1.496(6)
C(6B)-C(10B)	1.429(6)
C(6B)-C(7B)	1.439(6)
C(7B)-C(8B)	1.421(6)
C(8B)-C(9B)	1.422(6)
C(9B)-C(10B)	1.417(6)
C(16B)-C(21B)	1.384(6)
C(16B)-C(17B)	1.394(6)
C(17B)-C(18B)	1.380(6)
C(18B)-C(19B)	1.390(7)
C(19B)-C(20B)	1.373(6)
C(20B)-C(21B)	1.373(6)

Fe(1A)-C(6A)	1.979(4)
Fe(1A)-C(1A)	1.982(4)
Fe(1A)-C(7A)	2.012(5)
Fe(1A)-C(5A)	2.021(5)
Fe(1A)-C(10A)	2.025(4)
Fe(1A)-C(2A)	2.029(4)
Fe(1A)-C(9A)	2.049(5)
Fe(1A)-C(8A)	2.050(5)
Fe(1A)-C(4A)	2.056(5)
Fe(1A)-C(3A)	2.058(4)
P(1A)-C(16A)	1.827(5)
P(1A)-C(6A)	1.835(5)
P(1A)-C(15A)	1.904(4)
C(1A)-C(2A)	1.430(6)
C(1A)-C(5A)	1.440(6)
C(1A)-C(15A)	1.526(6)
C(2A)-C(3A)	1.433(6)
C(2A)-C(11A)	1.496(7)
C(3A)-C(4A)	1.430(7)
C(3A)-C(12A)	1.487(6)
C(4A)-C(5A)	1.422(6)
C(4A)-C(13A)	1.519(6)
C(5A)-C(14A)	1.486(6)
C(6A)-C(10A)	1.423(6)
C(6A)-C(7A)	1.433(7)
C(7A)-C(8A)	1.415(6)
C(8A)-C(9A)	1.413(7)
C(9A)-C(10A)	1.423(6)
C(16A)-C(17A)	1.399(6)
C(16A)-C(21A)	1.402(6)
C(17A)-C(18A)	1.382(6)
C(18A)-C(19A)	1.392(7)
C(19A)-C(20A)	1.375(7)
C(20A)-C(21A)	1.388(6)
C(1B)-Fe(1B)-C(6B)	95.09(18)

C(1B)-Fe(1B)-C(7B)	107.23(19)
C(6B)-Fe(1B)-C(7B)	42.00(18)
C(1B)-Fe(1B)-C(5B)	41.86(17)
C(6B)-Fe(1B)-C(5B)	108.58(19)
C(7B)-Fe(1B)-C(5B)	142.25(18)
C(1B)-Fe(1B)-C(10B)	121.13(18)
C(6B)-Fe(1B)-C(10B)	41.46(17)
C(7B)-Fe(1B)-C(10B)	69.0(2)
C(5B)-Fe(1B)-C(10B)	105.4(2)
C(1B)-Fe(1B)-C(2B)	41.71(17)
C(6B)-Fe(1B)-C(2B)	119.05(18)
C(7B)-Fe(1B)-C(2B)	101.57(19)
C(5B)-Fe(1B)-C(2B)	69.84(18)
C(10B)-Fe(1B)-C(2B)	158.82(16)
C(1B)-Fe(1B)-C(8B)	144.95(19)
C(6B)-Fe(1B)-C(8B)	69.78(18)
C(7B)-Fe(1B)-C(8B)	40.83(17)
C(5B)-Fe(1B)-C(8B)	172.19(19)
C(10B)-Fe(1B)-C(8B)	68.1(2)
C(2B)-Fe(1B)-C(8B)	117.80(19)
C(1B)-Fe(1B)-C(3B)	69.21(17)
C(6B)-Fe(1B)-C(3B)	159.80(18)
C(7B)-Fe(1B)-C(3B)	128.87(19)
C(5B)-Fe(1B)-C(3B)	68.62(18)
C(10B)-Fe(1B)-C(3B)	158.29(18)
C(2B)-Fe(1B)-C(3B)	40.77(17)
C(8B)-Fe(1B)-C(3B)	115.67(18)
C(1B)-Fe(1B)-C(4B)	69.91(18)
C(6B)-Fe(1B)-C(4B)	147.4(2)
C(7B)-Fe(1B)-C(4B)	168.89(19)
C(5B)-Fe(1B)-C(4B)	41.38(17)
C(10B)-Fe(1B)-C(4B)	121.86(19)
C(2B)-Fe(1B)-C(4B)	68.94(18)
C(8B)-Fe(1B)-C(4B)	137.73(18)
C(3B)-Fe(1B)-C(4B)	40.05(18)
C(1B)-Fe(1B)-C(9B)	161.42(18)

C(6B)-Fe(1B)-C(9B)	69.42(18)
C(7B)-Fe(1B)-C(9B)	68.53(19)
C(5B)-Fe(1B)-C(9B)	131.91(19)
C(10B)-Fe(1B)-C(9B)	40.30(18)
C(2B)-Fe(1B)-C(9B)	155.38(19)
C(8B)-Fe(1B)-C(9B)	40.29(18)
C(3B)-Fe(1B)-C(9B)	128.11(17)
C(4B)-Fe(1B)-C(9B)	117.66(18)
C(6B)-P(1B)-C(16B)	104.7(2)
C(6B)-P(1B)-C(15B)	100.1(2) θ
C(16B)-P(1B)-C(15B)	102.2(2)
C(2B)-C(1B)-C(5B)	108.5(4)
C(2B)-C(1B)-C(15B)	125.3(4)
C(5B)-C(1B)-C(15B)	124.8(4)
C(2B)-C(1B)-Fe(1B)	71.1(3)
C(5B)-C(1B)-Fe(1B)	70.7(3)
C(15B)-C(1B)-Fe(1B)	113.8(3)
C(3B)-C(2B)-C(1B)	107.0(4)
C(3B)-C(2B)-C(11B)	125.4(4)
C(1B)-C(2B)-C(11B)	127.6(4)
C(3B)-C(2B)-Fe(1B)	70.5(3)
C(1B)-C(2B)-Fe(1B)	67.2(2)
C(11B)-C(2B)-Fe(1B)	128.2(3)
C(4B)-C(3B)-C(2B)	109.6(4)
C(4B)-C(3B)-C(12B)	125.9(4)
C(2B)-C(3B)-C(12B)	124.5(4)
C(4B)-C(3B)-Fe(1B)	70.1(3)
C(2B)-C(3B)-Fe(1B)	68.7(2)
C(12B)-C(3B)-Fe(1B)	129.7(4)
C(3B)-C(4B)-C(5B)	107.6(4)
C(3B)-C(4B)-C(13B)	126.3(4)
C(5B)-C(4B)-C(13B)	126.1(4)
C(3B)-C(4B)-Fe(1B)	69.9(3)
C(5B)-C(4B)-Fe(1B)	68.1(2)
C(13B)-C(4B)-Fe(1B)	128.8(3)
C(1B)-C(5B)-C(4B)	107.3(4)

C(1B)-C(5B)-C(14B)	127.3(4)
C(4B)-C(5B)-C(14B)	125.5(4)
C(1B)-C(5B)-Fe(1B)	67.4(3)
C(4B)-C(5B)-Fe(1B)	70.5(3)
C(14B)-C(5B)-Fe(1B)	128.3(3)
C(10B)-C(6B)-C(7B)	106.5(4)
C(10B)-C(6B)-P(1B)	120.0(4)
C(7B)-C(6B)-P(1B)	129.9(4)
C(10B)-C(6B)-Fe(1B)	70.7(2)
C(7B)-C(6B)-Fe(1B)	69.7(2)
P(1B)-C(6B)-Fe(1B)	107.8(2)
C(8B)-C(7B)-C(6B)	108.4(4)
C(8B)-C(7B)-Fe(1B)	71.0(3)
C(6B)-C(7B)-Fe(1B)	68.3(3)
C(7B)-C(8B)-C(9B)	108.2(4)
C(7B)-C(8B)-Fe(1B)	68.1(3)
C(9B)-C(8B)-Fe(1B)	70.5(3)
C(10B)-C(9B)-C(8B)	107.7(4)
C(10B)-C(9B)-Fe(1B)	68.5(3)
C(8B)-C(9B)-Fe(1B)	69.2(3)
C(9B)-C(10B)-C(6B)	109.2(4)
C(9B)-C(10B)-Fe(1B)	71.2(3)
C(6B)-C(10B)-Fe(1B)	67.8(2)
C(1B)-C(15B)-P(1B)	109.5(3)
C(21B)-C(16B)-C(17B)	118.8(4)
C(21B)-C(16B)-P(1B)	122.3(3)
C(17B)-C(16B)-P(1B)	118.5(4)
C(18B)-C(17B)-C(16B)	120.5(5)
C(17B)-C(18B)-C(19B)	120.3(5)
C(20B)-C(19B)-C(18B)	118.6(4)
C(21B)-C(20B)-C(19B)	121.7(5)
C(20B)-C(21B)-C(16B)	120.1(4)
C(6A)-Fe(1A)-C(1A)	94.59(18)
C(6A)-Fe(1A)-C(7A)	42.09(19)
C(1A)-Fe(1A)-C(7A)	109.38(19)
C(6A)-Fe(1A)-C(5A)	108.96(19)

C(1A)-Fe(1A)-C(5A)	42.15(18)
C(7A)-Fe(1A)-C(5A)	144.51(19)
C(6A)-Fe(1A)-C(10A)	41.60(18)
C(1A)-Fe(1A)-C(10A)	118.65(18)
C(7A)-Fe(1A)-C(10A)	69.16(19)
C(5A)-Fe(1A)-C(10A)	103.23(19)
C(6A)-Fe(1A)-C(2A)	117.84(19)
C(1A)-Fe(1A)-C(2A)	41.76(18)
C(7A)-Fe(1A)-C(2A)	102.6(2)
C(5A)-Fe(1A)-C(2A)	70.25(19)
C(10A)-Fe(1A)-C(2A)	156.71(18)
C(6A)-Fe(1A)-C(9A)	70.01(18)
C(1A)-Fe(1A)-C(9A)	159.44(18)
C(7A)-Fe(1A)-C(9A)	68.67(19)
C(5A)-Fe(1A)-C(9A)	128.7(2)
C(10A)-Fe(1A)-C(9A)	40.87(17)
C(2A)-Fe(1A)-C(9A)	158.0(2)
C(6A)-Fe(1A)-C(8A)	69.98(19)
C(1A)-Fe(1A)-C(8A)	147.8(2)
C(7A)-Fe(1A)-C(8A)	40.74(18)
C(5A)-Fe(1A)-C(8A)	169.02(19)
C(10A)-Fe(1A)-C(8A)	68.43(19)
C(2A)-Fe(1A)-C(8A)	120.3(2)
C(9A)-Fe(1A)-C(8A)	40.32(19)
C(6A)-Fe(1A)-C(4A)	147.8(2)
C(1A)-Fe(1A)-C(4A)	69.47(18)
C(7A)-Fe(1A)-C(4A)	169.0(2)
C(5A)-Fe(1A)-C(4A)	40.82(18)
C(10A)-Fe(1A)-C(4A)	121.34(19)
C(2A)-Fe(1A)-C(4A)	68.95(19)
C(9A)-Fe(1A)-C(4A)	116.45(19)
C(8A)-Fe(1A)-C(4A)	136.78(19)
C(6A)-Fe(1A)-C(3A)	158.81(19)
C(1A)-Fe(1A)-C(3A)	69.76(18)
C(7A)-Fe(1A)-C(3A)	128.4(2)
C(5A)-Fe(1A)-C(3A)	69.40(18)

C(10A)-Fe(1A)-C(3A)	159.05(19)
C(2A)-Fe(1A)-C(3A)	41.06(18)
C(9A)-Fe(1A)-C(3A)	128.39(18)
C(8A)-Fe(1A)-C(3A)	115.74(19)
C(4A)-Fe(1A)-C(3A)	40.67(18)
C(16A)-P(1A)-C(6A)	104.8(2)
C(16A)-P(1A)-C(15A)	100.3(2)
C(6A)-P(1A)-C(15A)	100.0(2)
C(2A)-C(1A)-C(5A)	108.6(4)
C(2A)-C(1A)-C(15A)	124.4(4)
C(5A)-C(1A)-C(15A)	126.0(4)
C(2A)-C(1A)-Fe(1A)	70.9(3)
C(5A)-C(1A)-Fe(1A)	70.4(3)
C(15A)-C(1A)-Fe(1A)	115.3(3)
C(1A)-C(2A)-C(3A)	107.6(4)
C(1A)-C(2A)-C(11A)	127.0(4)
C(3A)-C(2A)-C(11A)	125.4(4)
C(1A)-C(2A)-Fe(1A)	67.4(2)
C(3A)-C(2A)-Fe(1A)	70.5(3)
C(11A)-C(2A)-Fe(1A)	127.1(3)
C(4A)-C(3A)-C(2A)	107.7(4)
C(4A)-C(3A)-C(12A)	126.1(4)
C(2A)-C(3A)-C(12A)	126.1(5)
C(4A)-C(3A)-Fe(1A)	69.6(2)
C(2A)-C(3A)-Fe(1A)	68.4(2)
C(12A)-C(3A)-Fe(1A)	130.3(3)
C(5A)-C(4A)-C(3A)	109.0(4)
C(5A)-C(4A)-C(13A)	126.5(5)
C(3A)-C(4A)-C(13A)	124.5(4)
C(5A)-C(4A)-Fe(1A)	68.3(3)
C(3A)-C(4A)-Fe(1A)	69.7(3)
C(13A)-C(4A)-Fe(1A)	128.7(3)
C(4A)-C(5A)-C(1A)	107.0(4)
C(4A)-C(5A)-C(14A)	126.0(4)
C(1A)-C(5A)-C(14A)	127.0(4)
C(4A)-C(5A)-Fe(1A)	70.9(3)

C(1A)-C(5A)-Fe(1A)	67.5(3)
C(14A)-C(5A)-Fe(1A)	127.5(3)
C(10A)-C(6A)-C(7A)	106.7(4)
C(10A)-C(6A)-P(1A)	121.3(4)
C(7A)-C(6A)-P(1A)	129.8(4)
C(10A)-C(6A)-Fe(1A)	71.0(2)
C(7A)-C(6A)-Fe(1A)	70.2(2)
P(1A)-C(6A)-Fe(1A)	110.9(2)
C(8A)-C(7A)-C(6A)	108.5(4)
C(8A)-C(7A)-Fe(1A)	71.1(3)
C(6A)-C(7A)-Fe(1A)	67.7(3)
C(9A)-C(8A)-C(7A)	108.3(4)
C(9A)-C(8A)-Fe(1A)	69.8(3)
C(7A)-C(8A)-Fe(1A)	68.2(3)
C(8A)-C(9A)-C(10A)	107.8(4)
C(8A)-C(9A)-Fe(1A)	69.9(3)
C(10A)-C(9A)-Fe(1A)	68.6(3)
C(6A)-C(10A)-C(9A)	108.7(4)
C(6A)-C(10A)-Fe(1A)	67.4(2)
C(9A)-C(10A)-Fe(1A)	70.5(2)
C(1A)-C(15A)-P(1A)	110.7(3)
C(17A)-C(16A)-C(21A)	117.7(5)
C(17A)-C(16A)-P(1A)	119.4(4)
C(21A)-C(16A)-P(1A)	122.5(4)
C(18A)-C(17A)-C(16A)	121.8(5)
C(17A)-C(18A)-C(19A)	119.7(5)
C(20A)-C(19A)-C(18A)	119.2(5)
C(19A)-C(20A)-C(21A)	121.5(5)
C(20A)-C(21A)-C(16A)	120.1(5)

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for k99167. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U^{11} + \dots + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Fe(1B)	16(1)	13(1)	16(1)	-3(1)	-4(1)	-4(1)
P(1B)	19(1)	14(1)	19(1)	-2(1)	-6(1)	-4(1)
C(1B)	12(3)	15(2)	16(3)	-7(2)	-2(2)	0(2)
C(2B)	12(3)	14(2)	11(3)	-3(2)	-3(2)	2(2)
C(3B)	19(3)	11(2)	13(3)	0(2)	-1(2)	-3(2)
C(4B)	17(3)	11(2)	19(3)	-6(2)	-4(2)	-2(2)
C(5B)	9(3)	19(2)	11(3)	-4(2)	-1(2)	-1(2)
C(6B)	15(3)	11(2)	17(3)	-2(2)	-2(2)	-1(2)
C(7B)	23(3)	14(2)	17(3)	-8(2)	-4(2)	-2(2)
C(8B)	13(3)	13(2)	14(3)	-4(2)	6(2)	1(2)
C(9B)	17(3)	15(2)	30(3)	-9(2)	-4(3)	-6(2)
C(10B)	12(3)	14(2)	26(3)	-9(2)	-8(2)	1(2)
C(11B)	21(3)	18(2)	27(3)	-2(2)	-9(3)	-3(2)
C(12B)	35(3)	15(3)	23(3)	1(2)	-10(3)	-5(2)
C(13B)	34(3)	21(3)	23(3)	-4(2)	-6(3)	-9(2)
C(14B)	23(3)	24(3)	20(3)	-10(2)	-6(3)	-3(2)
C(15B)	20(3)	13(2)	24(3)	-2(2)	-3(2)	-8(2)
C(16B)	20(3)	11(2)	15(3)	3(2)	-6(2)	-6(2)
C(17B)	18(3)	22(3)	23(3)	-5(2)	-3(2)	-5(2)
C(18B)	29(3)	21(3)	36(4)	-6(3)	-11(3)	-11(2)
C(19B)	32(3)	18(3)	25(3)	-7(2)	-15(3)	-8(2)
C(20B)	26(3)	15(2)	24(3)	-8(2)	-5(3)	3(2)
C(21B)	16(3)	18(2)	17(3)	-3(2)	-3(2)	-7(2)
Fe(1A)	20(1)	12(1)	14(1)	-2(1)	-6(1)	-4(1)
P(1A)	19(1)	15(1)	19(1)	-2(1)	-7(1)	-2(1)
C(1A)	21(3)	11(2)	14(3)	0(2)	-12(2)	-1(2)
C(2A)	21(3)	19(3)	24(3)	-8(2)	-7(3)	-7(2)
C(3A)	32(3)	13(2)	15(3)	-4(2)	-10(3)	-7(2)
C(4A)	18(3)	20(3)	21(3)	-10(2)	-6(3)	-5(2)
C(5A)	20(3)	19(2)	15(3)	0(2)	-5(2)	-11(2)
C(6A)	22(3)	15(2)	18(3)	-6(2)	-9(2)	-6(2)

C(7A)	13(3)	18(3)	23(3)	-10(2)	-2(2)	0(2)
C(8A)	34(3)	15(2)	15(3)	-4(2)	-11(3)	-9(2)
C(9A)	23(3)	15(2)	26(3)	-7(2)	-12(3)	-3(2)
C(10A)	18(3)	16(2)	18(3)	-3(2)	-2(2)	-9(2)
C(11A)	30(3)	34(3)	32(4)	-11(3)	-8(3)	-14(3)
C(12A)	44(4)	22(3)	24(3)	1(2)	-12(3)	-16(3)
C(13A)	29(3)	26(3)	35(4)	-11(3)	-15(3)	2(3)
C(14A)	39(4)	28(3)	17(3)	-2(2)	-4(3)	-15(3)
C(15A)	30(3)	18(3)	26(3)	-5(2)	-16(3)	-1(2)
C(16A)	22(3)	14(2)	17(3)	5(2)	-5(2)	-11(2)
C(17A)	23(3)	16(2)	21(3)	-4(2)	-5(3)	-5(2)
C(18A)	25(3)	18(3)	27(3)	5(2)	-11(3)	-9(2)
C(19A)	23(3)	15(3)	33(4)	-3(2)	-4(3)	-3(2)
C(20A)	28(3)	16(2)	21(3)	-8(2)	-4(3)	-3(2)
C(21A)	25(3)	12(2)	24(3)	0(2)	-10(3)	-6(2)

Table 5. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^{-3}$) for k99167.

	x	y	z	U(eq)
H(7BA)	8628	2631	7452	21
H(8BA)	9906	4135	6940	20
H(9BA)	11000	3871	8413	24
H(10A)	10391	2210	9838	20
H(11A)	4745	4716	8188	34
H(11B)	5916	3622	7923	34
H(11C)	6190	4804	7371	34
H(12A)	5899	6769	8402	38
H(12B)	6868	6146	7497	38
H(12C)	7549	6482	8159	38
H(13A)	7030	5918	10650	39
H(13B)	8309	5901	9648	39
H(13C)	8430	4938	10659	39
H(14A)	6491	3270	11938	33
H(14B)	8098	3222	11468	33
H(14C)	7541	2274	11415	33
H(15A)	6104	2226	9279	23
H(15B)	5743	2039	10506	23
H(17A)	6406	-80	10171	26
H(18A)	6462	-1475	9484	32
H(19A)	8332	-2047	8123	27
H(20A)	10099	-1187	7467	28
H(21A)	10048	214	8128	21
H(7AA)	3143	2788	7511	22
H(8AA)	4928	1301	8439	23
H(9AA)	7386	1325	7271	24
H(10B)	7124	2846	5615	20
H(11D)	2059	720	6510	44
H(11E)	1995	1863	6703	44
H(11F)	2457	731	7497	44

H(12D)	4927	-1510	7012	43
H(12E)	4272	-744	7831	43
H(12F)	5917	-1230	7468	43
H(13D)	7956	-1073	5165	46
H(13E)	7869	-941	6272	46
H(13F)	8477	-123	5253	46
H(14D)	7034	1465	3412	42
H(14E)	7843	1551	4138	42
H(14F)	6564	2552	3848	42
H(15C)	2673	2972	5246	28
H(15D)	3756	3003	4136	28
H(17B)	1853	5073	4395	24
H(18B)	-163	6446	4838	28
H(19B)	-624	7096	6319	31
H(20B)	968	6381	7304	26
H(21B)	3027	5044	6843	24
