Electronic Supplementary Information

A sodium ferrocenyl-phosphanide polymer based on racemic primary aminoalkyl(bisphosphanyl)ferrocene

Carolin Limburg, [a] Santiago Goméz Ruiz [b] and Evamarie Hey-Hawkins *[a]

[a] Institut für Anorganische Chemie, Universität Leipzig, Johannisallee 29, 04103 Leipzig, Germany. Fax: +49 341 9739319; Tel: +49 341 9736151; Email: hey@rz.uni-leipzig.de
[b] New address: Departamento de Química Inorgánica y Analítica, E.S.C.E.T., Universidad Rey Juan Carlos, 28933 Móstoles, Madrid, Spain. Fax: +34 914888143; Tel: +34 914888527; E-mail: santiago.gomez@urjc.es

Experimental Section

General Considerations

All manipulations were carried out using standard Schlenk techniques under an atmosphere of dry high-purity nitrogen or argon. THF was distilled from sodium/benzophenone and stored over a potassium mirror. *N*,*N*,*N'*,*N'*-Tetramethylethylenediamine (TMEDA) was distilled from sodium and stored over molecular sieves (4 Å). Diethyl ether and *n*-hexane were taken from an MBRAUN Solvent Purification System MB SPS-800 and stored over a potassium mirror. Water was degassed in a nitrogen stream in an ultrasonic bath. ^{1}H, ^{13}C and ^{31}P NMR spectra were recorded on a Bruker Avance DRX 400 spectrometer and referenced to tetramethylsilane (TMS).[1] Mass spectra were recorded on a ZAB-HSQ-VG12-520 Analytical Manchester spectrometer or a MASPEC II spectrometer. FT-IR spectra were recorded on a Perkin-Elmer Spectrum 2000 spectrometer. The signals of some ^{1}H, ^{13}C and ^{31}P NMR spectra were assigned by ^{1}H-^{1}H-COSY-, APT, ^{1}H-^{13}C-HMQC, ^{1}H-^{31}C-HMBC, ^{1}H-^{31}P-HMQC experiments and several ^{13}C{^{31}P} experiments with various decoupling power. *N*,*N*-dimethylaminomethyl ferrocene (**1a**)[2] and (*S*)-*N*,*N*-dimethyl-1-ferrocenylethylamine (**1b**)[3] were synthesised according to literature procedures. Other chemicals were obtained from commercial sources and used as supplied.

Synthetic Procedures

2-(*N*,*N*-dimethylaminomethyl)-1,1’bis(diethoxyphosphanyl)ferrocene (2a)

A solution of *n*-BuLi (25.00 ml; 61.26 mmol; 2.45 M in *n*-hexane) and TMEDA (7.12 g; 61.26 mmol) in 15 ml diethyl ether was slowly added to a solution of **1** (6.77 g; 27.84 mmol) in diethyl ether (50 ml). After stirring for 20 h, the reaction mixture was cooled to –78 °C and diethyl chlorophosphite (10.03 g; 64.04 mmol) was added. The reaction mixture was warmed to room temperature overnight and filtered. The solvent was evaporated and the residue dried *in vacuo* for 1 h at 50 °C. The orange oil was then re-dissolved in *n*-hexane and filtered once more. After evaporation of the solvent a crude, oily product was obtained, which consisted mainly of the desired product and the monosubstituted compound 2-(*N*,*N*-dimethylaminomethyl)-1-(diethoxyphosphanyl)ferrocene. This by-product was removed by bulb-to-bulb distillation at 80 °C bath temperature *in vacuo* (*ca.* $5 \cdot 10^{-6}$ mbar). The distillation residue was then dissolved in diethyl ether (*ca.* 5 ml) and filtered over neutral alumina. After evaporation of the solvent and drying *in vacuo*, **2a** was obtained as an orange oil. Yield: 6.97 g (52 %).

^{1}H NMR (+20 °C, 400.13 MHz, C_6D_6/TMS): δ = 1.12 (m, 9H, OCH_2CH_3), 1.22 (m, 3H, OCH_2CH_3), 2.18 (s, 6H, $N(CH_3)_2$), 3.32 (d, $^2J_{HH}$ = 12.7 Hz, 1H, CH_2N), 3.62-4.08 (br. m, 9H, CH_2N and OCH_2CH_3), 4.34 (br. m, 3H, C_5H_4 and C_5H_3 *m* to P), 4.45 (br. s, 1H, C_5H_4), 4.49 (br. s, 1H, C_5H_3 *m* to P), 4.52 (br. s, 1H, C_5H_4 *o* to P), 4.64 (br. s, 1H, C_5H_3 *o* to P) ppm. ^{13}C NMR (+20 °C, 100.6 MHz, C_6D_6/TMS): δ = 16.7 (d, $^3J_{CP}$ = 3.6 Hz, OCH_2CH_3), 16.9 (d, $^3J_{CP}$ = 5.2 Hz, OCH_2CH_3), 17.1 (d, $^3J_{CP}$ = 5.6 Hz, OCH_2CH_3), 17.3 (d, $^3J_{CP}$ = 6.0 Hz, OCH_2CH_3), 44.9 (s, $N(CH_3)_2$), 57.8 (d, $^3J_{CP}$ = 6.5 Hz, CH_2N), 59.8 (s, OCH_2CH_3 at C_5H_3), 61.0 (d, $^2J_{CP}$ = 7.4 Hz, OCH_2CH_3 at C_5H_4), 61.6 (d, $^2J_{CP}$ = 10.0 Hz, OCH_2CH_3 of C_5H_4), 63.6 (d, $^2J_{CP}$ = 20.9 Hz, OCH_2CH_3 at C_5H_3), 70.0 (s, C_5H_3 *m* to P or C_5H_4), 70.9 (d, $^2J_{CP}$ = 3.2 Hz, C_5H_3 *o* to P), 71.1 (d, $^2J_{CP}$ = 18.0 Hz, C_5H_4 *o* to P), 71.8[*] (C_5H_4), 71.9[*] (C_5H_3 *m* to P or C_5H_4), 72.4 (s, C_5H_3 *m* to P or C_5H_4), 74.2 (s, C_5H_3 *m* to P), 80.2 (d, $^1J_{CP}$ = 24.4 Hz, $C_{Fc}P(OEt)_2$ of C_5H_3), 80.4 (d, $^1J_{CP}$ = 20.3 Hz, $C_{Fc}P(OEt)_2$ of C_5H_4), 89.6 (d, $^2J_{CP}$ = 21.9 Hz, $C_{Fc}CH_2N$) ppm. ^{31}P{^{1}H} NMR (+20 °C, 161.98 MHz, C_6D_6/TMS): δ = 156.2, 156.3 ppm. FT-IR $\tilde{\nu}$*/in cm*$^{-1}$ (KBr): 3426 (m), 3096 (m), 2973 (s), 2933 (s), 2876 (s), 2813 (m), 2765 (s), 2722 (w), 2485 (w), 2169 (w), 2079 (w), 1941 (w), 1645 (w), 1454 (m), 1442 (m), 1384 (s), 1360 (m), 1332 (w), 1313 (w), 1260 (m), 1234 (m), 1194 (m), 1178 (w), 1164 (s), 1137 (m), 1096 (s), 1029 (s), 923 (s), 832 (m), 818 (m), 738 (s), 651 (w), 593 (w), 534 (m), 458 (m). MS (EI pos. 14 eV): 483 [M^+] (100%), 454 [$(M - CH_2CH_3)^+$] (13.3%), 438 [$(M - OCH_2CH_3)^+$] (1.5%), 410 [$(M - N(CH_3)_2 - CH_2CH_3)^+$] (3.0%), 362 [$(M - P(OCH_2CH_3)_2)^+$] (2.6%). Elemental analysis for $C_{21}H_{35}FeNO_4P_2$(%): Calc: C 52.19, H 7.30, N 2.90; Found: C 52.22, H 7.20, N 3.05.

---

[*] chemical shift read off ^{13}C{^{31}P} NMR spectra; multiplicity and coupling constant could not be determined due to overlap of several signals

N,*N*-dimethyl-1-[1',2-bis(diethoxyphosphanyl)ferrocenyl]ethylamine (2b)

The procedure for the preparation and purification of **2a** was followed using **1b** (6.47 g, 25.16 mmol), *n*-BuLi (22.59 ml; 55.35 mmol; 2.45 M in *n*-hexane), TMEDA (6.43 g; 55.35 mmol) and diethyl chlorophosphite (6.72 g; 57.87 mmol). Yield: 6.76 g (54 %). The product consists of 96% (*S*,*R*)-**2b** and 4% (*S*,*S*)-**2b**.
^{1}H NMR (+20 °C, 400.13 MHz, C_6D_6/TMS): δ = 1.11 (m, 9H, OCH_2CH_3, [*S*,*R*-**2b**]), 1.25 (m, 6H, OCH_2CH_3 and $CHCH_3$, [*S*,*R*-**2b**]), 2.13 (s, 6H, $N(CH_3)_2$, [*S*,*R*-2**b**]), 2.24 (s, 0.25H, $N(CH_3)_2$, [*S*,*S*-2**b**]), 3.63-3.99 (br. m, 8H, OCH_2CH_3, [*S*,*R*-**2b**]), 4.21 (q, $^3J_{HH}$ = 5.9 Hz, 1H, $CHCH_3$, [*S*,*R*-**2b**]), 4.32 (br. s, 2H, C_5H_4 and C_5H_3 *m* to P, [*S*,*R*-**2b**]), 4.37 (br. s, 1H, C_5H_3 *m* to P, [*S*,*R*-**2b**]), 4.40 (br. s, 2H, C_5H_4 *m* to P, [*S*,*R*-**2b**]), 4.57 (br. s, 1H, C_5H_4 *o* to P, [*S*,*R*-**2b**]), 4.73 (br. s, 1H, C_5H_3 *o* to P, [*S*,*R*-**2b**]) ppm. ^{13}C NMR (+20 °C, 100.6 MHz, C_6D_6/TMS): δ = 9.3 (d, $^4J_{CP}$ = 2.1 Hz, $CHCH_3$, [*S*,*R*-**2b**]), 16.3 (s, OCH_2CH_3, [*S*,*S*-**2b**]), 16.6 (s, OCH_2CH_3, [*S*,*S*-**2b**]), 16.8 (d, $^3J_{CP}$ = 4.1 Hz, OCH_2CH_3 at C_5H_3) [*S*,*R*-**2b**]), 17.0 (d, $^3J_{CP}$ = 4.5 Hz, 2C, OCH_2CH_3 at C_5H_4, [*S*,*R*-**2b**]), 17.4 (d, $^3J_{CP}$ = 6.5 Hz, OCH_2CH_3 at C_5H_3, [*S*,*R*-**2b**]), 39.3 (s, $N(CH_3)_2$, [*S*,*R*-**2b**]), 41.6 (s, $N(CH_3)_2$, [*S*,*S*-**2b**]), 56.8 (d, $^3J_{CP}$ = 5.4 Hz, $CHCH_3$ [*S*,*R*-**2b**]), 58.9 (s, OCH_2CH_3, [*S*,*S*-**2b**]), 59.1 (s, OCH_2CH_3, [*S*,*S*-**2b**]), 59.9 (d, $^2J_{CP}$ = 1.2 Hz, OCH_2CH_3 at C_5H_3, [*S*,*R*-**2b**]), 61.2 (d, $^2J_{CP}$ = 8.5 Hz, OCH_2CH_3 at C_5H_4, [*S*,*R*-**2b**]), 61.4 (d, $^2J_{CP}$ = 9.4 Hz, OCH_2CH_3 at C_5H_4, [*S*,*R*-**2b**]), 63.5 (d, $^2J_{CP}$ = 22.1 Hz, OCH_2CH_3 at C_5H_3, [*S*,*R*-**2b**]), 68.9* (C_5H_3, [*S*,*R*-**2b**]), 69.5* (C_5H_3 [*S*,*S*-**2b**]), 70.1* (C_5H_3, [*S*,*R*-**2b**]), 70.6* (C_5H_3 or C_5H_4, [*S*,*S*-**2b**]), 71.0*(C_5H_3 or C_5H_4, [*S*,*S*-**2b**]), 71.1* (C_5H_3 or C_5H_4, [*S*,*R*-**2b**]), 71.2* (C_5H_3 or C_5H_4, [*S*,*R*-**2b**]), 71.9* (C_5H_4, [*S*,*S*-**2b**]), 72.0* (C_5H_4, [*S*,*R*-**2b**]), 72.1* (C_5H_4, [*S*,*R*-**2b**]), 72.6* (C_5H_4, [*S*,*R*-**2b**]), 72.8* (C_5H_4, [*S*,*S*-**2b**]), 80.1 (d, $^1J_{CP}$ = 20.4 Hz, $C_{Fc}P(OEt)_2$ of C_5H_3, [*S*,*R*-**2b**]), 80.4 (d, $^1J_{CP}$ = 24.9 Hz, $C_{Fc}P(OEt)_2$ of C_5H_4, [*S*,*R*-**2b**]), 96.2 (d, $^2J_{CP}$ = 21.8 Hz, $C_{Fc}CH_2N$, [*S*,*R*-**2b**]) ppm. ^{31}P{^{1}H} NMR (+20 °C, 161.98 MHz, C_6D_6/TMS): δ = 154.1 (*S*,*S*-**2b**), 156.0 (*S*,*R*-**2b**), 156.5 (*S*,*R*-**2b**) ppm. FT-IR $\tilde{\nu}$/*in cm*$^{-1}$ (KBr): 3934 (m), 3098 (s), 2972 (s), 2932 (s), 2817 (s), 2773 (s), 2617 (w), 2452 (w), 2254 (w), 2216 (w), 2079 (w), 1945 (m), 1650 (m), 1444 (s), 1384 (s), 1313 (m), 1265 (m), 1243 (m), 1193.7 (m), 1164 (s), 1096 (s), 1032 (s), 973 (w), 923 (s), 830 (m), 734 (s), 650 (m), 612 (w), 591 (w), 565 (w), 536 (s), 459 (s). MS (EI pos. 14 eV): 497 [M^+] (100%), 482 [$(M - CH_3)^+$] (12.5%), 468 [$(M - CH_2CH_3)^+$] (7.8%), 422 [$(M - 2CH_3 - OCH_2CH_3)^+$] (11.7%), 407 [$(M - (OCH_2CH_3)_2)^+$] (7.9%). Elemental analysis for $C_{22}H_{37}FeNO_4P_2$(%): Calc: C 53.13, H 7.50, N 2.82; Found: C 52.95, H 7.58, N 2.83.

2-(*N*,*N*-dimethylaminomethyl)-1,1'bis(phosphanyl)ferrocene (3a)

A solution of **2a** (3.4 g; 7.04 mmol) in diethyl ether (30 ml) was added dropwise to a suspension of $LiAlH_4$ (0.53 g; 14.07 mmol) in diethyl ether (10 ml) at 0 °C. The reaction mixture was stirred over night at room temperature and carefully hydrolysed with slightly basic water (one KOH pellet in 25 ml) at 0 °C. After stirring for 2 h at room temperature, the organic layer was separated and dried over $MgSO_4$. After filtration, the solvent was removed to give **3a** as a brown-red high-boiling-point liquid with a typical phosphane odour, which

was dried *in vacuo*. **3a** could be further purified by bulb-to-bulb distillation at 95 °C bath temperature *in vacuo* (*ca.* $1\cdot10^{-3}$ mbar). Yield: 1.4 g (65%).
^{1}H NMR (+20 °C, 400.13 MHz, C_6D_6/TMS): δ = 2.09 (s, 6H, $N(CH_3)_2$), 3.04 (d, $^2J_{HH}$ = 12.7 Hz, 1H, CH_2N), 3.60 (d, $^2J_{HH}$ = 12.7 Hz, 1H, CH_2N), 3.69 (dd, $^2J_{HH}$ = 12.3 Hz, $^1J_{PH}$ = 201.1 Hz, 1H, PH_2 at C_5H_3), 3.72 (d, $^1J_{PH}$ = 199.8 Hz, 2H, PH_2 at C_5H_4), 3.81 (dd, $^2J_{HH}$ = 12.3 Hz, $^1J_{PH}$ = 201.1 Hz, 1H, PH_2 at C_5H_3), 3.91 (br. s, 2H, C_5H_4 *m* to P), 3.96 (br. s, 2H, C_5H_3 *m* to P and C_5H_4 *o* to P), 3.99 (br. s, 1H, C_5H_4 *o* to P), 4.03 (br. s, 1H, C_5H_3 *o* to P), 4.10 (br. s, 1H, C_5H_3 *m* to P) ppm. ^{13}C NMR (+20 °C, 100.6 MHz, C_6D_6/TMS): δ = 44.7 (s, $N(CH_3)_2$), 57.7 (s, CH_2N), 65.1 (d, $^1J_{CP}$ = 7.2 Hz, $C_{Fc}PH_2$ of C_5H_4), 66.9 (d, $^1J_{CP}$ = 8.7 Hz, $C_{Fc}PH_2$ of C_5H_3), 70.3 (d, $^3J_{CP}$ = 2.5 Hz, C_5H_3 *m* to P), 72.7 (d, $^3J_{CP}$ = 4.2 Hz, 2C, C_5H_4 *m* to P), 74.0 (d, $^3J_{CP}$ = 1.9 Hz, C_5H_3 *m* to P), 76.8 (d, $^2J_{CP}$ = 7.6 Hz, C_5H_4 *o* to P), 76.9 (d, $^2J_{CP}$ = 6.8 Hz, C_5H_4 *o* to P), 77.3 (d, $^2J_{CP}$ = 9.0 Hz, C_5H_3 *o* to P), 90.0 (d, $^2J_{CP}$ = 12.8 Hz, $C_{Fc}CH_2N$) ppm. ^{31}P NMR (+20 °C, 161.98 MHz, C_6D_6/TMS): δ = –147.0 (td, $^1J_{PH}$ = 199.9 Hz, $^4J_{PP}$ = 5.3 Hz, PH_2 of C_5H_4), –152.6 (td, $^1J_{PH}$ = 201.1 Hz, $^4J_{PP}$ = 5.3 Hz, PH_2 of C_5H_3) ppm. FT-IR $\tilde{\nu}$/in cm^{-1} (KBr): 3924 (w), 3428 (m), 3080 (m), 2966 (m), 2938 (s), 2853 (m), 2813 (s), 2766 (s), 2264.7 (s), 1647 (m), 1454 (s), 1402 (w), 1383 (w), 1354 (m), 1317 (w), 1260 (m), 1235 (m), 1201 (s), 1180.4 (s), 1165.2(s), 1137 (m), 1076 (s), 1022 (s), 890 (w), 840 (s), 812 (s), 754 (w), 713 (w), 625 (w), 593 (w), 518 (m), 495 (m), 454 (m). MS (EI pos. 14 eV): 307 [M^+] (11.2%), 262 [$(M - HN(CH_3)_2)^+$] (100%). Elemental analysis for $C_{13}H_{19}FeNP_2$(%): Calc: C 50.84, H 6.24, N 4.56; Found: C 50.80, H 6.20, N 4.61.

***N*,*N*-dimethyl-1-[1’,2-bis(phosphanyl)ferrocenyl]ethylamine (3b)**

The procedure for the preparation and purification of **3a** was followed using **2b** (3.43 g, 6.89 mmol) and $LiAlH_4$ (0.47 g; 12.38 mmol). Yield: 1.82 g (87 %). The product consists of 96% (*S*,*R*)-**3b** and 4% (*S*,*S*)-**3b**.
^{1}H NMR (+20 °C, 400.13 MHz, C_6D_6/TMS): δ = 1.16 (d, $^3J_{HH}$ = 6.7 Hz, 3H, CH*H*$_3$, [*S*,*R*-**3b**]), 1.46 (d, $^3J_{HH}$ = 6.7 Hz, 0.13H, CH*H*$_3$, [*S*,*S*-**3b**]), 2.04 (s, 6H, $N(CH_3)_2$, [*S*,*R*-**3b**]), 2.10 (s, 0.25H, $N(CH_3)_2$, [*S*,*S*-**3b**]), 3.70 (dd, $^2J_{HH}$ = 11.9 Hz, $^1J_{PH}$ = 199.7 Hz, 1H, PH_2 at C_5H_3, [*S*,*R*-**3b**]), 3.74 (d, $^1J_{PH}$ = 199.6 Hz, 2H, PH_2 at C_5H_4, [*S*,*R*-**3b**]), 3.77 (d, $^1J_{PH}$ = 200.1 Hz, 0.1H, PH_2 at C_5H_4, [*S*,*S*-**3b**]), 3.85 (dd, $^2J_{HH}$ = 11.9 Hz, $^1J_{PH}$ = 199.8 Hz, 1H, PH_2 at C_5H_3, [*S*,*R*-**3b**]), 3.92 (br. m, 2H, C_5H_4 *m* to P, [*S*,*R*-**3b**]), 3.97 (br. s, 3H, C_5H_3 *m* to P and C_5H_4 *o* to P, [*S*,*R*-**3b**]), 4.01 (br. s, 1H, C_5H_4 *o* to P, [*S*,*R*-**3b**]), 4.04 (br. s, 1H, C_5H_3 *o* zu P, [*S*,*R*-**3b**]) ppm. ^{13}C NMR (+20 °C, 100.6 MHz, C_6D_6/TMS): δ = 10.1 (s, CH*C*H$_3$, [*S*,*R*-**3b**]), 17.5 (d, $^4J_{CP}$ = 8.4 Hz, CH*C*H$_3$, [*S*,*S*-**3b**]), 39.5 (s, $N(CH_3)_2$, [*S*,*R*-**3b**]), 42.0 (s, $N(CH_3)_2$, [*S*,*S*-**3b**]), 56.8 (d, $^3J_{CP}$ = 3.4 Hz, *C*HCH$_3$, [*S*,*R*-**3b**]), 59.4 (s, *C*HCH$_3$, [*S*,*S*-**3b**]), 64.4 (d, $^1J_{CP}$ = 10.7 Hz, $C_{Fc}PH_2$ of C_5H_4, [*S*,*S*-**3b**]), 64.8 (d, $^1J_{CP}$ = 7.3 Hz, $C_{Fc}PH_2$ of C_5H_4, [*S*,*R*-**3b**]), 65.0 (d, $^1J_{CP}$ = 6.9 Hz, $C_{Fc}PH_2$ of C_5H_3, [*S*,*S*-**3b**]), 67.2 (d, $^1J_{CP}$ = 7.7 Hz, $C_{Fc}PH_2$ of C_5H_3, [*S*,*R*-**3b**]), 69.4 (s, C_5H_3 *m* to P, [*S*,*R*-**3b**]), 69.7 (s, C_5H_3 *m* to P, [*S*,*S*-**3b**]), 69.9 (d, $^3J_{CP}$ = 3.1 Hz, C_5H_3 *m* to P, [*S*,*R*-**3b**]), 72.9 (d, $^3J_{CP}$ = 3.8 Hz, C_5H_4 *m* to P, [*S*,*R*-**3b**]), 73.0 (d, $^3J_{CP}$ = 3.4 Hz, C_5H_4 *m* to P, [*S*,*R*-**3b**]), 73.1 (d, $^3J_{CP}$ = 3.1 Hz, C_5H_4 *m* to P, [*S*,*S*-**3b**]), 73.2 (d, $^3J_{CP}$ = 2.7 Hz, C_5H_4 *m* to P, [*S*,*S*-**3b**]), 76.6 (d, $^2J_{CP}$ = 14.5 Hz, C_5H_4 *o* to P, [*S*,*R*-**3b**]), 76.7 (d, $^2J_{CP}$ = 13.8 Hz, C_5H_4 *o* to P,

[*S*,*S*-**3b**]), 77.1 (d, $^2J_{CP}$ = 7.2 Hz, C_5H_4 *o* to P, [*S*,*R*-**3b**]), 77.2 (d, $^2J_{CP}$ = 5.2 Hz, C_5H_3 *o* to P, [*S*,*R*-**3b**]), 77.3 (s, C_5H_4 or C_5H_3 *o* to P, [*S*,*S*-**3b**]), 77.7 (s, C_5H_4 or C_5H_3 *o* to P, [*S*,*S*-**3b**]), 96.0 (d, $^2J_{CP}$ = 15.3 Hz, $C_{Fc}CH_2N$, [*S*,*R*-**3b**]), 96.6 (d, $^2J_{CP}$ = 13.8 Hz, $C_{Fc}CH_2N$, [*S*,*S*-**3b**]) ppm. ^{31}P NMR (+20 °C, 161.98 MHz, C_6D_6/TMS): δ = –142.9 (td, $^1J_{PH}$ = 200.1 Hz, $^4J_{PP}$ = 6.0 Hz, PH_2 of C_5H_4 [*S*,*S*-**3b**]), –146.6 (td, $^1J_{PH}$ = 200.1 Hz, $^4J_{PP}$ = 6.0 Hz, PH_2 of C_5H_3 [*S*,*S*-**3b**]), –146.8 (td, $^1J_{PH}$ = 199.9 Hz, $^4J_{PP}$ = 6.1 Hz, PH_2 of C_5H_4 [*S*,*R*-**3b**]), –149.1 (td, $^1J_{PH}$ = 199.7 Hz, $^4J_{PP}$ = 6.1 Hz, PH_2 of C_5H_3 [*S*,*R*-**3b**]) ppm. FT-IR *ṽ/in cm^{-1}* (KBr): 3926 (m), 3360 (w), 3086 (s), 2968 (s), 2933 (s), 2817 (s), 2774 (s), 2267 (s), 1891 (w), 1666 (m), 1452 (s), 1364 (s), 1317 (m), 1262 (m), 1244 (m), 1199 (s), 1165 (s), 1071 (s), 1024 (s), 974.6 (m), 931 (m), 815 (s), 728 (w), 631 (w), 596 (w), 498 (s). MS (EI pos. 70 eV): 321 [M^+] (15.2%), 276 [$(M – HN(CH_3)_2)^+$] (100%), 243 [$(M – 2PH_2 – CH_3)^+$] (63.2%). Elemental analysis for $C_{14}H_{21}FeNP_2$(%): Calc: C 52.36, H 6.59, N 4.36; Found: C 52.23, H 6.79, N 4.39.

[{Na(thf)-1-PH-2-$CH_2N(CH_3)_2C_5H_3$}Fe{Na(thf)-1'-PH-C_5H_4}]$_\infty$ (5)

A solution of NaHMDS (9.00 ml; 5.41 mmol; 0.6 M in toluene) was slowly added to a solution of **3a** (0.83 g; 2.70 mmol) in *n*-hexane (15 ml) at –78 °C. The reaction mixture was slowly warmed to room temperature overnight, filtered and the orange, highly pyrophoric powder was dried *in vacuo*. Yield: 0.94 g (99%).

^{31}P NMR (+20 °C, 161.98 MHz, C_6D_6/TMS): δ = –178.8 (d, $^1J_{PH}$ = 159.7 Hz), –195.0 (d, $^1J_{PH}$ = 154.4 Hz) ppm. FT-IR *ṽ/in cm^{-1}* (KBr): 3369 (m), 3082 (m), 2945 (s), 2858 (m), 2820 (s), 2776 (s), 2253 (s), 1655 (w), 1458 (s), 1394 (m), 1323 (w), 1259 (s), 1169 (s), 1133 (m), 1068 (s), 1009 (s), 985 (s), 932 (m), 811 (s), 694 (w), 516 (m).

Orange crystalline plates of **4**, suitable for X-ray crystallography, formed at room temperature within a few days, after dissolving the isolated orange powder in thf. The obtained crystals were not soluble in any solvent.

FT-IR *ṽ/in cm^{-1}* (KBr): 3400 (m), 3079 (m), 2943 (s), 2868 (s), 2818 (s), 2773 (s), 2256 (s), 1654 (w), 1458 (s), 1391 (w), 1313 (w), 1248 (s), 1169 (s), 1032 (s), 810 (s), 616 (w), 517 (m). Mp: 153 °C (decomposition)

X-ray Crystallography

Suitable crystals were obtained as described above and mounted in perfluoropolyalkyl ether. Crystallographic measurements were made using an Oxford Diffraction Xcalibur S diffractometer. The structures were solved by direct methods and refined on F^2 by full-matrix least-squares techniques (SHELX97).[4] All non-hydrogen atoms were refined anisotropically, hydrogen atoms H1p and H2p were located and refined isotropically, all other hydrogen atoms were included in a riding mode.

CCDC 773632 contains the supplementary crystallographic data for this paper that can be obtained free of charge from the Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif

Crystal Data and Structure Refinement

Empirical formula	$C_{13}H_{17}FeNNa_2P_2 \cdot 2(C_4H_8O)$	
Formula weight	495.25	
Temperature	130(2) K	
Wavelength	71.073 pm	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 1038.12(4) pm	α= 74.681(3)°
	b = 1091.69(3) pm	β= 69.882(3)°
	c = 1227.37(4) pm	γ= 70.925(3)°
Volume	1.21621(7) nm^3	
Z	2	
Density (calculated)	1.352 Mg/m^3	
Absorption coefficient	0.804 mm^{-1}	
F(000)	520	
Crystal size	0.30 x 0.15 x 0.10 mm^3	
Theta range for data collection	2.91 to 28.28°	
Index ranges	-13<=h<=13, -14<=k<=14, -16<=l<=16	
Reflections collected	28818	
Independent reflections	6032 [R(int) = 0.0445]	
Completeness to theta = 28.28°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1 and 0.97692	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6032 / 20 / 262	
Goodness-of-fit on F^2	1.001	
Final R indices [I>2σ(I)]	R1 = 0.0507, wR2 = 0.1209	
R indices (all data)	R1 = 0.0867, wR2 = 0.1308	
Largest diff. peak and hole	1.690 and -0.364 $eÅ^{-3}$	

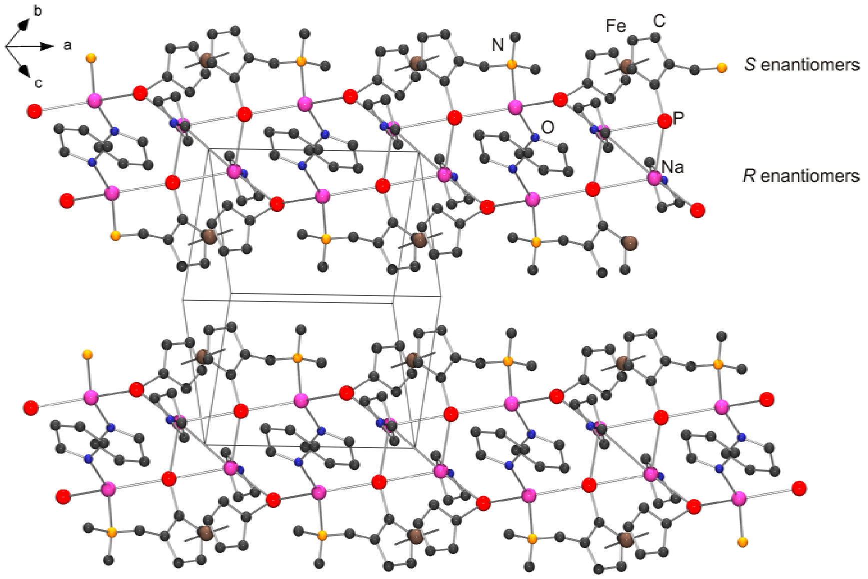

Figure 1: Polymeric structure of **4**

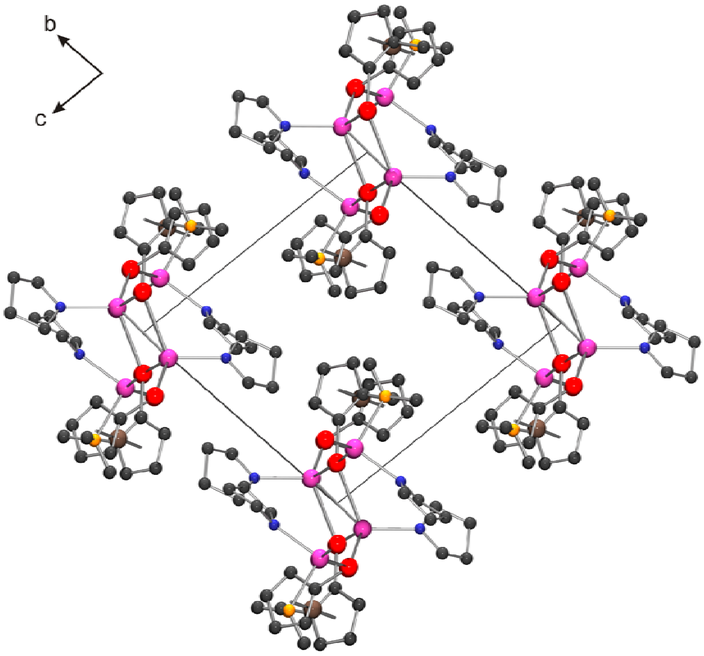

Figure 2: Polymeric structure of **4** (view along the a axis)

---

[1] R. K. Harris, E. D. Becker, S. M. Cabral de Menezes, R. Goodfellow and P. Granger, *Pure Appl. Chem.*, 2001, **73**, 1795

[2] J. K. Lindsay and C. R. Hause, *J. Org. Chem.*, 1957, **22**, 355

[3] D. Marquading, H. Klusacek, G. W. Gokel, P. Hoffman and I. K. Ugi, *J. Am. Chem. Soc.*, 1970, **92**, 5389

[4] SHELX97 (Includes SHELXS97, SHELXL97, SHELXH97): G. M. Sheldrick, (1997); *SHELX97. Programs for Crystal Structure Analysis (Release97-2)*, University of Göttingen, Germany