

Redox-active iron-containing polymers: synthesis and anionic polymerization of a *C*-ferrocenyl-substituted phosphalkene

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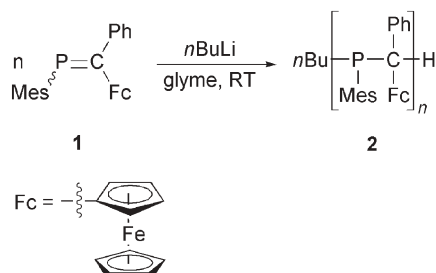
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The addition polymerization of a ferrocenyl-substituted P=C bond leads to new redox-active polymers with functional ferrocene and phosphine moieties.

Macromolecules containing transition metals are known to possess unique redox, magnetic, optical and electronic properties and are attractive for use as ceramic precursors and catalyst supports.¹ The ferrocenyl moiety has played an integral role in the growth of metal-containing polymer science. Macromolecules are known where ferrocene is incorporated into the main chain, side-chain and even into dendrimers.² The earliest ferrocene-containing polymers were prepared from the addition polymerization of the C=C bond in vinyl ferrocene.^{3,4}

We have recently reported that P=C bonds, like C=C bonds, can be polymerized to afford macromolecules containing functional phosphine moieties.⁵ Interestingly, copolymerizations of phosphalkenes and olefins afford either random copolymers or block copolymers depending on the method of initiation.^{6,7} The chemical functionality of poly(methylenephosphine)s is demonstrated by their effectiveness as polymeric ligands in Pd-catalyzed reactions. The preparation of macromolecules composed of both phosphines and ferrocenes is particularly attractive due to the prospect of accessing bimetallic polymers with interesting electronic, magnetic or catalytic properties. Primarily a consequence of the lack of effective synthetic routes to phosphine-ferrocene hybrid polymers, only a few examples have been reported.^{8–10} Herein we describe the synthesis and addition polymerization of *C*-ferrocenyl phosphalkene **1** to afford a new redox active bifunctional poly(methylenephosphine) (**2**).



Although metalla-phosphalkenes are quite common,^{11–13} the target monomers, ferrocenyl-substituted phosphalkenes, are not widely available. Becker-type phosphalkenes [*i.e.* RP=C(OSiMe₃)R'] possessing C-Fc and P-Fc substituents are

known,¹⁴ however very few non-heteroatom-substituted P=C systems have been reported. A rare example, ^tBuP=CHFc, was detected in solution but dimerized upon attempted isolation.^{14c} For polymerization studies, isolable monomers with no heteroatoms directly attached to the P=C bond are desired to avoid possible side reactions during initiation. Consequently, methods to access new ferrocene-substituted phosphalkenes are needed. The phospho-Peterson reaction is a general and convenient route to phosphalkenes.^{15,16} This convenient reaction involves the condensation of a silyl phosphide Li[RP(SiMe₃)] with a ketone and affords phosphalkenes with a variety of substituents provided that suitably bulky substituents are employed to protect the P=C bond.

The precursor to *C*-ferrocenyl phosphalkene (**1**), benzoylferrocene, was prepared according to a modified literature procedure.¹⁷ A THF solution of *in situ* prepared Li[MesP(SiMe₃)] was treated with benzoylferrocene at 60 °C. Analysis of an aliquot removed from the deep red reaction mixture using ³¹P NMR spectroscopy revealed that Li[MesP(SiMe₃)] (δ -187) had been completely consumed. Two new signals were observed downfield at 218 and 211 ppm (70 : 30 ratio) which are consistent with the formation of *E/Z*-**1**.† Crystals suitable for X-ray diffraction were obtained from the slow evaporation of a hexanes solution of *E/Z*-**1**.‡ The molecular structure of the *C*-ferrocenyl-substituted phosphalkene is shown in Fig. 1 and, interestingly, the Fc substituent is *cis* to the bulky P-Mes substituent (*i.e.* *Z*-**1**). The ³¹P NMR spectrum of a C₆D₆ solution of the crystals of *Z*-**1** shows signals consistent with

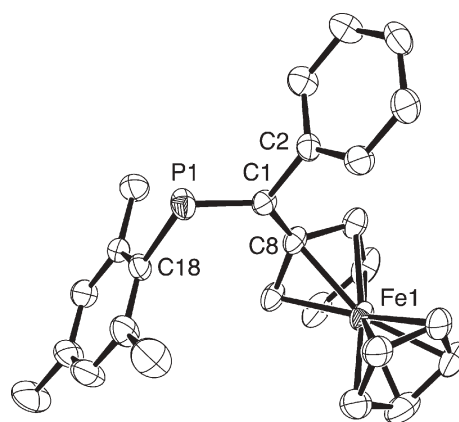
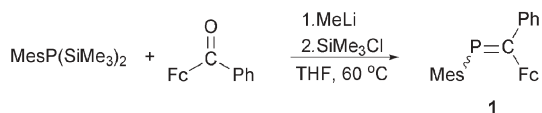


Fig. 1 Molecular structure of *Z*-**1** (hydrogen atoms omitted for clarity). Thermal ellipsoids at 30% probability. Selected bond lengths (Å) and angles (°): P1–C1 1.697(2), P1–C(18) 1.842(2), C1–C(2) 1.512(2), C1–C(8) 1.468(2); C(8)–C(1)–C(2) 114.95(13), C(8)–C(1)–P(1) 130.69(11), C(2)–C(1)–P(1) 114.16(11), C(1)–P(1)–C(18) 107.31(7).

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both *E*-**1** and *Z*-**1** isomers (*ca.* 85 : 15 ratio) and suggests facile *E*, *Z* isomerization in solution. Selective ^1H NMR NOE experiments provided confirmation that the major isomer in solution is *Z*-**1**. In particular, irradiating at the resonance frequency of the *ortho* CH_3 groups on the mesityl ring (δ 2.30) leads to enhancement of signals assigned to the *ortho* hydrogens of the substituted Cp ring (δ 4.61). This signal enhancement is consistent with the Mes and Fc substituents being *cis* configured and therefore the *Z*-**1** isomer was concluded to be the major isomer in solution.



The molecular structure of *Z*-**1** is shown in Fig. 1. The P=C bond length in **1** (1.697(2) Å) is in the long end of the range typical for phosphalkenes (1.61–1.71 Å), however is similar to the P=C bond length in $\text{MesP}=\text{CPh}_2$ (1.692(3) Å).¹⁸ Interestingly, the *cis*-Fc substituent shows a larger angle to the P=C bond than the ideal sp^2 angle ($\angle\text{P}=\text{C}-\text{C}_{\text{Fc}}$ 130.69(11) $^\circ$) and is greater than the typical *cis* aryl substituent of P-mesityl phosphalkenes ($\angle\text{P}=\text{C}-\text{C}_{\text{cis}}$ 125–128 $^\circ$).¹⁶ We speculate that this is a consequence of increased steric repulsion between the *cis* configured Fc and Mes moieties in *Z*-**1**. Remarkably, the angle between the best planes of the C_5H_4 moiety and the P=C bond is just 13.2(1) $^\circ$. For comparison, the analogous angle in the only other crystallographically characterized C-ferrocenyl phosphalkene ($\text{Me}_3\text{SiP}=\text{C}(\text{OSiMe}_3)\text{Fc}$) is 36.6 $^\circ$,^{14d} whilst that in $\text{MesP}=\text{CPh}_2$ is 42.9 $^\circ$.^{18,19} This data suggests that significant π -conjugation is present between the Fc substituent and the P=C bond in *Z*-**1**. Additional support for π -conjugation in *Z*-**1** is provided by the shortening of C(1)–C(8) bond (1.468(2) Å) with respect to the typical C–C single bond length which is 1.54 Å and by the intense red colour of **1** compared with pale yellow $\text{MesP}=\text{CPh}_2$.

To determine whether anionic initiation of a C-ferrocenyl phosphalkene was feasible, monomer **1** was treated with *n*BuLi (1 equiv) in glyme (1,2-dimethoxyethane). The ^{31}P NMR spectrum of the reaction mixture showed only a singlet at –18.7 ppm which is consistent with the formation of $\text{Li}[\text{Mes}(\text{Bu})\text{PC}(\text{Fc})\text{Ph}]$. Once the feasibility of anionic initiation had been demonstrated, a solution of monomer **1** in 1,2-dimethoxyethane (glyme) was treated with *n*BuLi (5 mol%) as the anionic initiator. The progress of the polymerization was monitored by ^{31}P NMR spectroscopy and, after seven days, 50–60% of monomer **1** had been cleanly converted to polymer **2** (δ –5 br). Due to facile isomerization in solution, the isomer ratio in monomer *E/Z*-**1** (85 : 15) does not change during the polymerization reaction. The polymerization was terminated by quenching with methanol and polymer **2** was separated from **1** by reprecipitation from THF into methanol ($\times 4$). The golden coloured polymer was analyzed by triple detection GPC and an absolute number average molecular weight (M_n) was determined to be 9500 with a polydispersity index (PDI) of 1.21. The identical experiment was repeated and the same M_n was achieved with a PDI of 1.18. Further studies are underway to ascertain whether this polymerization may be conducted in a living fashion.

In order to investigate the electronic properties of **1** and **2**, both were analyzed by UV-Vis spectroscopy (Fig. 2). Previous studies on phosphalkenes have demonstrated that P=C bonds are

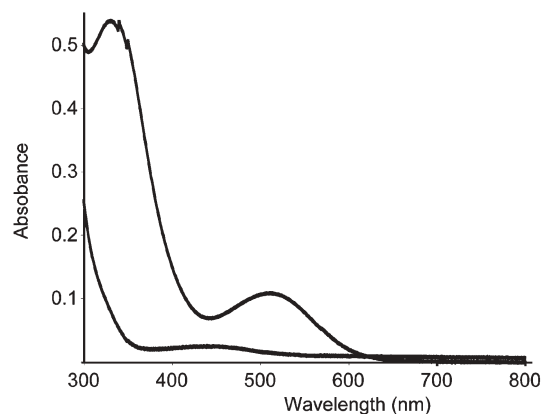


Fig. 2 UV/Vis spectra of monomer **1** (top) and polymer **2** (bottom) (0.1 mM in toluene).

capable of electronic communication through π conjugation.²⁰ The deep red solution of **1** exhibited two broad absorbances at $\lambda_{\text{max}} = 512$ and 331 nm which are assigned to the d-d transition of the ferrocenyl moiety and the $\pi-\pi^*$ transition for the P=C bond, respectively. Interestingly, the absorbance maximum at 512 nm is significantly red-shifted when compared to that for vinylferrocene ($\lambda_{\text{max}} = 442$ nm) and ferrocene ($\lambda_{\text{max}} = 440$ nm).^{4,21} The dramatic bathochromic shift is most likely attributable to a favourable electronic interaction between the ferrocene group and the P=C bond. The second transition at 331 nm, assigned to the $\pi-\pi^*$ transition of the P=C bond, is similar to that observed for $\text{MesP}=\text{CPh}_2$ ($\lambda_{\text{max}} = 324$ nm).²² In contrast, the gold coloured macromolecule **2** exhibits only a weak transition at 448 nm, which is very similar to the d-d transition for ferrocene (440 nm).

The electrochemical properties of poly(methylenephosphine) **2** were analyzed by cyclic voltammetry. The observed reversible one electron oxidation of **2** is consistent with the expected ferrocene–ferrocenium couple. The detection of a single wave suggests that the Fc moieties are electronically isolated; analogous to the case of poly(vinylferrocene). The half-cell potential (*vs.* SCE) for polymer **2** is ($\Delta E_{1/2} = 0.41$ V) is slightly lower than that for poly(vinylferrocene) ($\Delta E_{1/2} = 0.44$ –0.48 V).²³ For comparison, $\text{FcCH}_2\text{PPh}_2$, a possible model compound for polymer **2**, similarly exhibits a reversible oxidation slightly lower than that for ferrocene ($\Delta E = -0.04$ V).²⁴

In summary, a phosphalkene analogue of vinyl ferrocene has been prepared and polymerized anionically to afford new bifunctional redox active polymers. This development opens the door to the synthesis of bimetallic polymers possessing both Fc moieties and phosphine–metal complexes which may have interesting optoelectronic, magnetic and preceramic properties.

Notes and references

† *Synthesis* of $\text{MesP}=\text{C}(\text{Fc})\text{Ph}$ (**1**): To a stirred solution of $\text{MesP}(\text{SiMe}_3)_2$ (5.03 g, 17 mmol) in THF was added MeLi in Et_2O (12.2 mL, 1.4 M, 17 mmol) at 25 $^\circ\text{C}$. The reaction mixture was heated to 60 $^\circ\text{C}$ for *ca.* 1 h and analysis of an aliquot by ^{31}P NMR spectroscopy suggested total conversion to $\text{MesP}(\text{SiMe}_3)\text{Li}$ (δ –187). Subsequently, benzoylferrocene (4.94 g, 17 mmol) was added and the reaction mixture was stirred at 60 $^\circ\text{C}$ for *ca.* 30 min. The ^{31}P NMR spectrum showed signals at 218 and 211 ppm (70 : 30 ratio) assigned to *Z*-**1** and *E*-**1**, respectively. To the solution was added Me_3SiCl (2.15 mL, 17 mmol) to quench the LiOSiMe_3 . The volatiles were removed *in vacuo*, the residue was extracted into hexanes (3 \times 50 mL),

filtered through Celite, and the solvent removed *in vacuo*. Single crystals of **1** (4.16 g, 58%) were obtained from slow evaporation of a hexanes solution of the crude product. ^{31}P NMR (C_6D_6) δ (ppm): 218 (Z, 85%), 211 (E, 15%). ^1H NMR (CD_2Cl_2) δ (ppm): 7.5 (m, 5H, *E-o,m,p*-Ph), 7.10 (m, 5H, *Z-o,m,p*-Ph), 6.98 (s, 2H, *E-m*-Mes), 6.69 (s, 2H, *Z-m*-Mes), 4.61 (t, 2H, $^2J_{\text{H-H}} = 1.2$ Hz, *Z-o*-Fc), 4.45 (s, 2H, *Z-m*-Fc), 4.23 (m, 5H, *Z-Cp*-Fc, 2H, *E-m*-Fc), 4.10 (s, 5H, *E-Cp*-Fc), 3.79 (s, 2H, *E-o*-Fc), 2.44 (s, 6H, *E-o*-CH₃), 2.37 (s, 3H, *E-p*-CH₃), 2.30 (s, 6H, *Z-o*-CH₃), 2.17 (s, 3H, *Z-p*-CH₃). MS (EI, 70 eV): 424 [8, 36; M⁺]. UV/Vis (C_7H_9): $\lambda_{\text{max}}/\text{nm}$ ($\epsilon/\text{M}^{-1}\text{cm}^{-1}$) = 331 (4600), 512 (930). Anal. Calc. for $\text{C}_{26}\text{H}_{25}\text{PFe}$: C, 73.60; H, 5.94. Found: C, 73.30; H, 6.04%.

‡ Crystal data for **1**: $\text{C}_{26}\text{H}_{25}\text{PFe}$, $M = 424.30$, triclinic, space group $P\bar{1}$ (no. 2), $a = 8.0754(8)$, $b = 8.4767(7)$, $c = 16.382(2)$ Å, $\alpha = 101.647(3)$, $\beta = 96.033(4)$, $\gamma = 96.270(4)^\circ$, $U = 2547.2(5)$ Å³, $T = 173(2)$ K, $Z = 2$, $\mu(\text{Mo-K}\alpha) = 7.79$ cm⁻¹, $D_c = 1.302$ g cm⁻³, 23518 reflections measured, 5083 unique reflections ($R_{\text{int}} = 0.032$) which were used in all calculations. The final $R_1(F)$ was 0.034, wR_2 (on F_2) was 0.095. CCDC 642679. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b704967f

§ Synthesis of $[\text{P}(\text{Mes})\text{C}(\text{Fc})(\text{Ph})]_n$ (**2**): A typical polymerization procedure is described. To a stirred solution of $\text{MesP}=\text{CPh}(\text{Fc})$ (1.00 g, 2.3 mmol) at room temperature in glyme (7 mL) was added *n*BuLi (1.5 M, 80 μL , 0.12 mmol). The reaction mixture was stirred at room temperature and monitored by ^{31}P NMR spectroscopy. The growth of a broad signal in the ^{31}P NMR spectrum was observed over 7 days and, subsequently, the reaction mixture was removed from the glovebox, quenched and precipitated using methanol (3×100 mL). Residual solvent was removed *in vacuo*. Yield = 250 mg (25%). ^{31}P NMR (C_6D_6) δ (ppm): -5 ppm. ^1H NMR (C_6D_6) δ (ppm): 8–6.5 (br, 7H, aryl-H), 4.5–3.5 (br, 9H, Fc-H), 3–1.5 (br, H, Mes-H). GPC-LLS (THF): $M_n = 9500$, PDI = 1.21, $R_h = 1.5$ nm. UV/Vis (C_7H_9): $\lambda_{\text{max}}/\text{nm}$ ($\epsilon/\text{M}^{-1}\text{cm}^{-1}$) = 448 (210). Anal. Calc. for $\text{C}_{26}\text{H}_{25}\text{PFe}$: C, 73.60; H, 5.94. Found: C, 73.50; H, 6.29%.

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