New phosphonates containing a π-conjugated ferrocenyl unit

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A new class of phosphorus compounds containing a ferrocenyl unit are obtained from vinylferrocene and phosphono-substituted aromatic halides by using palladium-catalyzed Heck-type reactions. The crystal structure of compound 3a confirms the *trans* planar geometry of the π-conjugated system. The electrochemistry and electronic absorption spectra of phosphorus esters 3a,b and acids 4a,b are investigated.

Compounds with a ferrocene unit are well known for their numerous applications in organic synthesis, homogeneous catalysis, non-linear optics and materials science.[1] There is also considerable recent interest in the synthesis of new materials containing organometallic vinylferrocenes, since the vinylferrocene moiety has been used as a π-electron donor in potential non-linear optical (NLO) materials.[2] Moreover, the specific properties of ferrocenyl redox centers can be enhanced with aromatic substituents, by transmission of their effects through π-electron conjugated systems.[3] Optical and electrical properties of conjugated materials are strongly dependent on the coplanarity of the π-conjugated system and on the general organization of the material. The conformation of the delocalized fragment directly affects the electronic states of the species and any conformational change may induce variations in UV-vis spectra, luminescence, redox potentials and conductivity. We planned to combine the properties of the π-conjugated ferrocenes with phosphonates, phosphonate derivatives also being well-known for their applications in materials science and sol–gel chemistry.[4] Our idea relied on the well-known efficiency of self-assembled monolayers (SAMS) to serve as models for surface molecular materials. The formation of SAMS is based on the anchoring of functional substituents on the surface. Thiol derivatives and organofunctional silanes have been exploited in detail.[5] The use of such precursors with various supports, colloids, membranes or microdomains is growing with potential applications as new sensors or light-emitting devices.[6] The emergence of phosphonate groups as efficient agents, especially with mixed oxides,[7] incited us to develop the synthesis of new precursors incorporating that functionality.

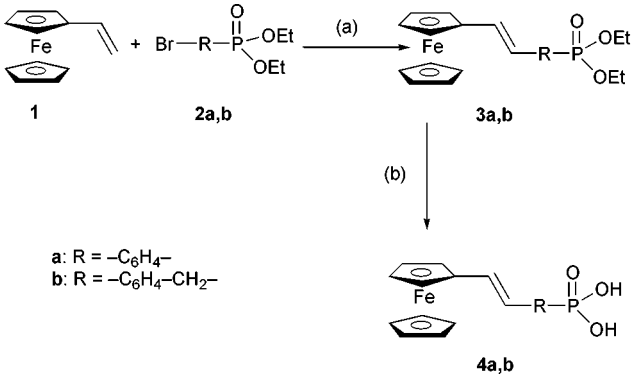
A general synthetic route to (ferrocenylvinyl)arenes is based on the Wittig reaction of ferrocenecarboxaldehyde with ylides[8a] or (ferrocenylmethyl)triphenylphosphonium iodide with aldehydes.[8b] The *E* configuration of the double bond in π-conjugated systems is necessary to ensure planarity and to provide for the transmission of the electronic effects. Unfortunately, stereochemical control of the double bond using the Wittig reaction is sometimes difficult and cumbersome procedures are required for the separation of *E* and *Z* isomers.[9] Furthermore, the presence of a benzylphosphonate group makes the use of the Wittig reaction particularly difficult. We therefore turned to the Heck reaction, the mild conditions of which tolerate functionalized phosphonates. Little is known about the palladium-catalyzed Heck reaction[10] of vinylferrocene with various aromatic halides; two examples have been reported[11] under Jeffery's phase transfer conditions.[12] In these two cases the *E* configuration of the double bond was obtained. We decided to use the homogeneous conditions of the Heck reaction[13] to prepare new phosphonates containing a *trans* π-conjugated ferrocenyl unit.

Standard Heck reaction [$Pd(OAc)_2$, tris(*o*-tolyl)phosphine (TOP), Et_3N, PhMe] of commercially available vinylferrocene **1** with bromoaryl phosphonates **2a** and **2b**[14] gave **3a** (57% yield) and **3b** (83% yield) (Scheme 1). In these two reactions, the ^1H NMR spectrum of the crude mixture indicated that only one isomer was obtained, with a *trans* configuration of the double bond ($^3J_{HH} = 16$ Hz).

The crystal structure of **3a** was determined by X-ray analysis;[15] the compound crystallizes in the centrosymmetric triclinic space group $P\bar{1}$. An ORTEP drawing of the complex **3a** is shown in Fig. 1, which confirms the *trans* configuration of the double bond. We observe two independent molecules in the asymmetric unit. The Fe–C bond distances found for the substituted Cp rings [Fe1–C ave. 2.042(1) and Fe2–C ave. 2.032(8) Å] are similar to those found in the literature.[16] The length of the double bond in the two molecules is 1.289(5) (C37–C38) and 1.337(4) Å (C47–C48), respectively. These distances are of the same order as those reported in the literature[17] for *trans* π-conjugated systems. The values of the dihedral angles formed by the substituted phenyl group and the cyclopentadienyl ring (C31–C36–C1–C5: 13.9 and C41–C46–C11–C15: 9.4°) give a high degree of coplanarity in the system in the solid state.[18] Thus our molecule possesses the chemical functions and stereochemistry necessary for electronic transfer devices.

Treatment of the phosphonate functionality with bromotrimethylsilane[19] and hydrolysis of the silylated intermediate gave the corresponding phosphonic acids. These mild conditions furnished **4a** (78%) and **4b** (75%) in good yields (Scheme 1).

The electronic absorption spectra of compounds **3a**, **3b**, **4a**



Scheme 1 *Reagents and conditions*: (a) $Pd(OAc)_2$ [4 mol% of **1**], tris(*o*-tolyl)phosphine (TOP) [15 mol% of **1**], 6 equiv. Et_3N, toluene, 115 °C, 48 h. (b) (1) 3 equiv. Me_3SiBr, CH_2Cl_2, RT; (2) 16.5 equiv. H_2O, RT.

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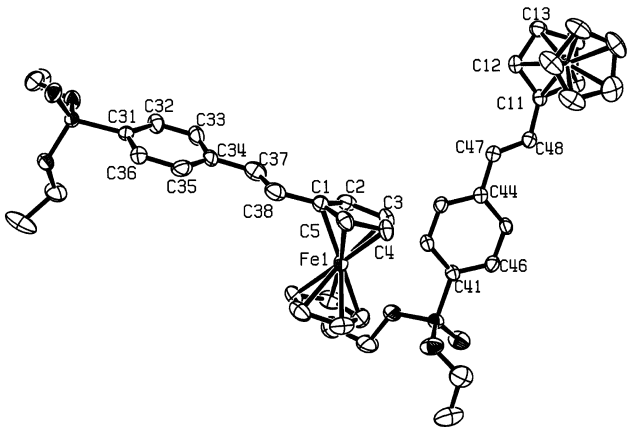

Fig. 1 Molecular structure (ORTEP drawing) of the two independent molecules of **3a**. Hydrogen atoms are omitted for clarity. Selected bonds (Å) and angles (°). Fe1–C (mean) 2.050(3); Fe2–C (mean) 2.053(3); C1–C38 1.496(5); C11–C48 1.465(4); C37–C38 1.289(5); C47–C48 1.337(4); C34–C37 1.506(5); C44–C47 1.467(4); C34–C37–C38 125.9(4); C44–C47–C48 127.0(3); C37–C38–C1 123.0(4); C47–C48–C11 124.8(3). Angle of the Cp plane [C1–C5] to the phenyl plane [C31–C36] 13.9°; Cp plane [C11–C15] to phenyl plane [C41–C46] 9.4°.

and **4b** have been investigated (Fig. 2). The low-energy spectrum of ferrocene is dominated by two weak bands at 327 and 442 nm, assignable respectively to π–π* and d–d transitions of the ferrocene unit.[20] As expected, the π–π* and the d–d transitions of iron in the present ferrocene derivatives are shown to progressively shift to longer wavelength with increasing conjugation, with respective maxima for the π–π* transition at 369 nm for **3b**, 376 nm for **3a**, 365 nm for **4b** and 375 nm for **4a**. The d–d transition shifts to 457 nm for **3b**, 467 nm for **3a**, 456 nm for **4b** and 463 nm for **4a**.[21–24]

The electrochemical properties of phosphonates **3a** and **3b**, and their corresponding phosphonic acids **4a** and **4b**, have been investigated by cyclic votammetry in dimethylsulfoxide (Fig. 3) and compared to ferrocene (E_{pa} = 455; ΔE = 110 mV). The reversible oxidation wave assigned to the Fe^{II}/Fe^{III} couple occurs at 505 mV for **3a** (475 mV for **3b**). Under the same conditions the phosphonic acid **4a** was oxidized at 501 mV (470 mV for **4b**). The oxidation peak potentials (E_{pa}) are in the expected range of values for ferrocene analogs of stilbene (*vs.* SCE).[21] No variation of the E_{pa} values is observed if we compare the phosphonates and their corresponding phosphonic acids, a specificity already noted for carboxylate/carboxylic acid[22] substituted ferrocenes. The easier oxidation of **3b** compared to **3a** could be due to the presence of the $-CH_2-$ group, which reduces the electron-withdrawing effect of the phosphonate substituent.[25]

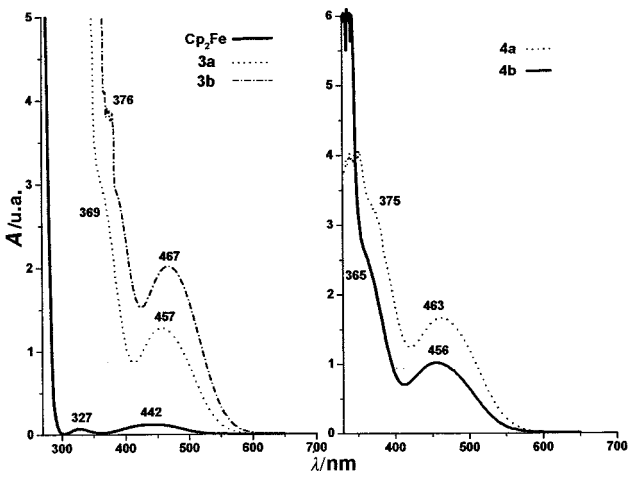

Fig. 2 Absorption spectra of **3a**, **3b**, **4a** and **4b** (10^{-3} M in DMSO).

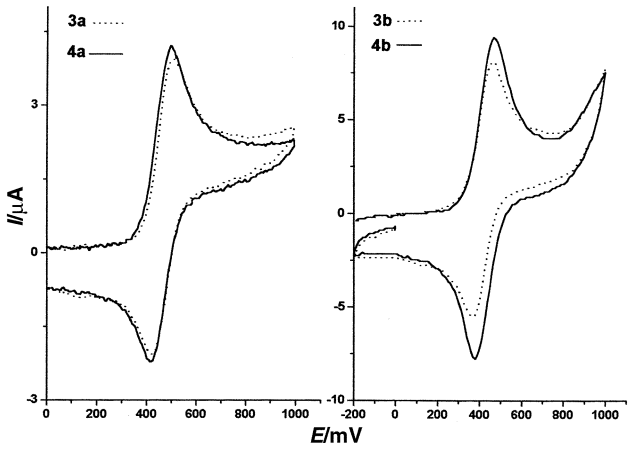

Fig. 3 Cyclic voltammograms of **3a, 4a** and **3b**, **4b**. Experimental conditions: Pt electrode in 0.1 mol L^{-1} solution of Bu_4NPF_6 in DMSO, complex concentration at 10^{-3} M, scan rate 0.1 V s^{-1}, *vs.* SCE.

The efficiency of the Heck reaction has been applied to the rapid and easy synthesis of new ferrocenylarylenevinylene conjugated phosphonates and phosphonic acids. The stereochemical control of the reaction is excellent, leading to *trans* coplanar π-conjugated systems, as emphasized by their structural and electro-optical characterizations. The interesting properties of compounds **3a**,**b** and **4a**,**b** will be exploited in the synthesis of new materials, especially for modification of the behavior of metal oxides.

Experimental

Vinylferrocene was purchased from Lancaster, bromotrimethylsilane and palladium acetate were purchased from Avocado, and these products were used without further purification. 4-Bromophenylphosphonic acid diethyl ester and 4-bromobenzylphosphonic acid diethyl ester were synthesized according to literature procedures.[14] All reactions and manipulations were carried out under an atmosphere of argon. Solvents were dried by standard methods and were distilled prior to use. ^1H, ^{13}C and ^{31}P NMR spectra were obtained on a Bruker AC-200 spectrometer. IR spectra were recorded on a Perkin–Elmer 1600 FT spectrometer with 4.0 cm^{-1} resolution. Mass spectra were recorded on a Jeol JMS-DX300 instrument using FAB^+ mode with a glycerol–thioglycerol (GT) matrix. UV-visible spectra were recorded on an Anthelie Advanced Secomam spectrophotometer.

General procedure for the Heck reaction

A mixture of 1 equiv. of **2a** (**2b**) (4.5 mmol), 1.05 equiv. of **1** (4.72 mmol), palladium acetate (0.19 mmol), tris(*o*-tolyl)phosphine (0.71 mmol) and 6 equiv. of triethylamine (28.3 mmol) in toluene (20 mL) was heated at 115 °C. After stirring for 48 h at 115 °C, the solution was cooled to room temperature, filtered and the solvent was evaporated. The product was purified by column chromatography on silica (eluent: diethyl ether) and collected as an orange fraction. After evaporation of the solvent, compound **3a** was obtained as red crystals (1.1 g, 57% yield) and compound **3b** was obtained as orange crystals (1.64 g, 83% yield).

Compound 3a. Mp = 100.5–101.0 °C. ^1H NMR (200 MHz, $CDCl_3$, 293 K): δ 1.40 (t, $^3J_{HH}$ = 6.5, 6H, CH_3); 4.16 (m, $^3J_{HH}$ = 7.1, 4H, CH_2O); 4.20 (s, 5H, C_5H_5); 4.36, 4.52 (each t, $^3J_{HH}$ = 1.8, 4H, C_5H_4); 6.72 (d, $^3J_{trans}$ = 16, 1H, vinyl); 7.05 (d, $^3J_{trans}$ = 16.2 Hz, 1H, vinyl); 7.5–7.9 (m, 4H, C_6H_4). ^{13}C NMR (200 MHz, $CDCl_3$, 293 K): δ 16.7 (d, $^3J_{PC}$ = 6.5, CH_3); 62.4 16.7 (qd, $^3J_{PC}$ = 6.5, CH_3); 62.4 (td, $^2J_{PC}$ = 5.3, CH_2); 67.6 (d, 2C, C_5H_4); 69.7 (d, 2C, C_5H_4); 69.9 (d, 5C, C_5H_5); 82.3 (s, C_5H_4); 125.1 (dd, $^5J_{PC}$ = 0.6, CH=); 126.0 (dd, 2C, $^2J_{PC}$ = 15.4,

C_6H_4); 126.2 (sd, $^1J_{PC}$ = 190.4, C_6H_4); 130.5 (d, CH=); 132.6 (dd, 2C, $^3J_{PC}$ = 10.2, C_6H_4); 142.3 (sd, $^4J_{PC}$ = 3.3 Hz, C_6H_4). ^{31}P NMR (200 MHz, $CDCl_3$, 293 K): δ 20.6 (s). IR (CCl_4) ν/cm^{-1}: 3094, 2977, 2905 (C–H), 1631, 1599 (C=C), 1250 (P=O), 1124 (P–C), 1053, 1027 (P–O). HRMS (FAB$^+$, GT): 425.0868 (calc. for MH$^+$); 425.0969 (obs.): Anal. calc. for $C_{22}H_{25}FePO_3$: C 62.23; H 5.89%. Found: C 62.55; H 6.05%. UV-vis (DMSO): λ_{max}/nm (ε/L mol^{-1} cm^{-1}) = 376 (3500), 467 (1840).

Compound 3b. Mp = 52.1–53.0 °C. ^{1}H NMR (200 MHz, $CDCl_3$, 293 K): δ 1.30 (t, $^3J_{HH}$ = 7.1, 6H, CH_3); 3.18 (d, $^2J_{PH}$ = 21.7, 2H, CH_2–P); 4.10 (m, $^3J_{HH}$ = 7, 4H, CH_2–O); 4.17 (s, 5H, C_5H_5); 4.30, 4.50 (t, $^3J_{HH}$ = 1.8, 4H, C_5H_4); 6.70 (d, $^3J_{trans}$ = 16.2, 1H, vinyl); 6.89 (d, $^3J_{trans}$ = 16.3 Hz, 1H, vinyl); 7.30–7.43 (m, 4H, C_6H_4). ^{13}C NMR (200 MHz, $CDCl_3$, 293 K): δ 16.7 (q, CH_3); 33.9 (td, $^1J_{PC}$ = 138.2, CH_2–P); 62.5 (t, CH_2–O); 67.2 (d, 2C, C_5H_4); 69.4 (d, 2C, C_5H_4); 69.6 (s, 5C, C_5H_5); 83.7 (s, C_5H_4); 126.0 (dd, $^6J_{PC}$ = 2.3, CH=); 126.3 (dd, 2C, $^4J_{PC}$ = 3.3, C_6H_4); 127.2 (dd, $^7J_{PC}$ = 1.9, CH=); 130.3 (s, C_6H_4); 130.4 (dd, 2C, $^3J_{PC}$ = 6.7, C_6H_4); 137 (sd, $^5J_{PC}$ = 4.1 Hz, C_6H_4). ^{31}P NMR (200 MHz, $CDCl_3$, 293 K): δ 27.5 (s). IR (CCl_4) ν/cm^{-1}: 3094, 2986, 2905 (C–H), 1636 (C=C), 1252 (P=O), 1053, 1026 (P–O), 958 (P–O–C). HRMS (FAB$^+$, GT): 438.1086 (calc. for M$^+$); 438.1047 (obs.). Anal. calc. for $C_{23}H_{27}FePO_3$: C 63.00; H 6.16%. Found: C 62.48; H 6.19%. UV-vis (DMSO): λ_{max}/nm (ε/L mol^{-1} cm^{-1}) = 369 (2500), 457 (1140).

General procedure for the synthesis of 4a and 4b

To a solution of 1 equiv. of phosphonate **3a** (**3b**) (2.36 mmol) in 50 mL of dichloromethane was added in a single portion 3 equiv. of bromotrimethylsilane (7.08 mmol). After stirring at room temperature for 2 h, volatiles were evaporated to isolate the silyl ester. The oil obtained was hydrolyzed with 16.5 equiv. of water (37.8 mmol) to give the product as a red precipitate. This wet precipitate was dissolved in MeOH at 65 °C and, after cooling to room temperature, coded to −20 °C. The solid was filtered, washed three times with diethyl ether and then air dried to give **4a** (680 mg, 78% yield) and **4b** (650 mg, 75% yield) as orange powders.

Compound 4a. Mp = 235 °C (dec). ^{1}H NMR (200 MHz, DMSO-d^6, 293 K): δ 4.10 (s, 5H, C_5H_5); 4.30, 4.60 (each t, $^3J_{HH}$ = 1.8, 4H, C_5H_4); 6.79 (d, $^3J_{trans}$ = 16.2, 1H, vinyl); 7.10 (d, $^3J_{trans}$ = 16.2 Hz, 1H, vinyl); 7.48–7.87 (m, 4H, C_6H_4). ^{13}C NMR (200 MHz, DMSO-d^6, 293 K): δ 67.8 (d, 2C, C_5H_4); 70.0 (d, 2C, C_5H_4); 69.9 (s, 5C, C_5H_5); 83.5 (s, C_5H_4); 125.6 (d, CH=); 126.0 (dd, 2C, $^3J_{PC}$ = 14.5, C_6H_4); 130.0 (d, CH=); 131.8 (dd, 2C, $^3J_{PC}$ = 10.1, C_6H_4); 132.7 (sd, $^1J_{PC}$ = 183, C_6H_4); 140.9 (sd, $^4J_{PC}$ = 3.1 Hz, C_6H_4). ^{31}P NMR (200 MHz, DMSO-d^6, 293 K): δ 14.2 (s). IR (KBr) ν/cm^{-1}: 1632 (C=C), 2765, 2300 (PO–H), 922 (P–OH). HRMS (FAB$^+$, GT): 368.0286 (calc. for M$^+$); 368.0265 (obs.). UV-vis (DMSO): λ_{max}/nm (ε/L mol^{-1} cm^{-1}) = 375 (2840), 463 (1480).

Compound 4b. Mp = 206 °C (dec). ^{1}H NMR (200 MHz, DMSO-d^6, 293 K): δ 2.90 (d, $^2J_{PH}$ = 21.6, 2H, CH_2–P); 4.10 (s, 5H, C_5H_5); 4.31, 4.59 (t, $^3J_{HH}$ = 1.7, 4H, C_5H_4); 6.74 (d, $^3J_{trans}$ = 16.3, 1H, vinyl); 6.94 (d, $^3J_{trans}$ = 16.2 Hz, 1H, vinyl); 7.13–7.42 (m, 4H, C_6H_4). ^{13}C NMR (200 MHz, DMSO-d^6, 293 K): δ 36.1 (td, $^1J_{PC}$ = 132.2, CH_2–P); 67.5 (d, 2C, C_5H_4); 69.6 (d, 2C, C_5H_4); 69.8 (s, 5C, C_5H_5); 84.2 (s, C_5H_4); 126.2 (dd, 2C, $^4J_{PC}$ = 5.4, C_6H_4); 126.3 (d, CH=); 127.1 (d, CH=); 130.9 (dd, 2C, $^3J_{PC}$ = 6.4, C_6H_4); 133.7 (sd, $^2J_{PC}$ = 9.7, C_6H_4); 136.2 (sd, $^5J_{PC}$ = 3.7 Hz, C_6H_4). ^{31}P NMR (200 MHz, DMSO-d^6, 293 K): δ 22.1 (s). IR (KBr) ν/cm^{-1}: 1634 (C=C), 2775, 2299 (PO–H), 941 (P–OH). HRMS (FAB$^+$, GT): 382.0355 (calc. for M$^+$); 382.0421 (obs.). UV-vis (DMSO): λ_{max}/nm (ε/L mol^{-1} cm^{-1}) = 365 (3100), 456 (1520).

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Notes and references

1 A. Togni and T. Hayashi, *Ferrocenes*, VCH, Weinheim, Germany, 1995 and references therein.

2 (*a*) M. L. H. Green, S. R. Marder, M. E. Thompson, J. A. Brandy, D. Bloor, P. V Kolinsky and R. J. Jones, *Nature* (*London*), 1987, **330**, 360; (*b*) D. F. Eaton, *Science*, 1991, **253**, 281; (*c*) J. C. Calabrese, L.-T. Cheng, J. C. Green, S. R. Marder and W. Tam, *J. Am. Chem. Soc.*, 1991, **113**, 7227; (*d*) S. R. Marder, J. W. Perry, B. G. Tiemann and W. P. Schaefer, *Organometallics*, 1991, **10**, 1896.

3 P. D. Beer, C. Blackburn, J. F. McAleer and H. Sikanyika, *Inorg. Chem.*, 1990, **29**, 378.

4 (*a*) G. Alberti, in *Comprehensive Supramolecular Chemistry*, ed. J. M. Lehn, J. L. Atwood, J. E. D. Davies, D. D. Macnicol and F. Vögtle, Elsevier Science, Oxford, UK, 1996, vol. 7, pp. 151–187; (*b*) A. Clearfield, *Chem. Mater.*, 1998, **10**, 2801; (*c*) R. J. P. Corriu and D. Leclercq, *Angew. Chem. Int. Ed. Engl.*, 1996, **35**, 1420; (*d*) A. Vioux, *Chem. Mater.*, 1997, **9**, 2292.

5 A. Ulman, *Chem. Rev.*, 1996, **96**, 1533.

6 S. Flink, F. C. J. M. van Veggel and D. N. Reinhoudt, *Adv. Mater.*, 2000, **12**, 1315.

7 (*a*) H.-G. Hong, D. D. Sackett and T. E. Mallouk, *Chem Mater.*, 1991, **3**, 521; (*b*) I. Lukes, M. Borbaruah and L. D. Quin, *J. Am. Chem. Soc.*, 1994, **116**, 1737; (*c*) W. Gao, L. Dickinson, C. Grozinger, F. G. Morin and L. Reven, *Langmuir*, 1996, **12**, 6428; (*d*) P. Bonhôte, J.-E. Moser, R. Humphry-Baker, N. Vlachopoulos, S. M. Zakeeruddin, L. Walder and M. Grätzel, *J. Am. Chem. Soc.*, 1999, **121**, 1324.

8 (*a*) J. M. Osgerby and P. L. Pauson, *J. Chem. Soc.*, 1961, 4604; (*b*) P. L. Pauson and W. E. Watts, *J. Chem. Soc.*, 1963, 2990.

9 J. A. Mata, S. Uriel, R. Llusar and E. Peris, *Organometallics*, 2000, **19**, 3797.

10 R. F. Heck, *Palladium Reagents in Organic Synthesis*, Academic Press, London, 1985.

11 (*a*) B. König, H. Zieg, P. Bubenitschek and P. G. Jones, *Chem. Ber.*, 1994, **127**, 1811; (*b*) K.-Y. Kay, Y. G. Baek, D. W. Han and S. Y. Yen, *Synthesis*, 1997, 35.

12 T. Jeffery, *Tetrahedron Lett.*, 1985, **26**, 2667; T. Jeffery, *Tetrahedron Lett.*, 1990, **31**, 6641.

13 A. De Meijeire and F. E. Meyer, *Angew. Chem., Int. Ed. Engl.*, 1994, **53**, 2379.

14 (*a*) T. Hirao, T. Masunaga, Y. Ohshiro and T. Agawa, *Synthesis*, 1981, 56; (*b*) G. Kennedy and A. D. Perboni, *Tetrahedron Lett.*, 1996, **37**, 7611; (*c*) B. Iorga, F. Eymery and P. Savignac, *Tetrahedron*, 1999, **55**, 2671.

15 Crystallographic data for **3a**: $C_{22}H_{25}FeO_3P$: M = 424.24, triclinic, space group $P\bar{1}$, a = 9.708(3), b = 10.855(2), c = 20.083(5) Å, α = 82.78(2), β = 86.35(2), γ = 77.90(2)°, U = 2051.5(9) Å^3, Z = 4, T = 166 K, μ = 8.32 cm^{-1}, 5157 observed reflections, R_1 [for 729 $F_0 > 4\sigma(F_0)$] = 0.0421; wR_2 = 0.1120. CCDC reference number 440/245. See http://www.rsc.org/suppdata/nj/b0/b008937k/ for crystallographic files in .cif format.

16 (*a*) J. G. Rodriguez, A. Oñate, R. I. Martin-Villamil and I. Fonseca, *J. Organomet. Chem.*, 1996, **513**, 71; (*b*) J. G. Rodriguez, M. Gayo and I. Fonseca, *J. Organomet. Chem.*, 1997, **534**, 35.

17 M. R. Buchmeiser, N. Schuler, G. Kaltenhauser, K. H. Ongania, I. Lagoja, K. Wurst and H. Schottenberger, *Macromolecules*, 1998, **31**, 3175.

18 M. E. Wright and B. B. Cochran, *Organometallics*, 1993, **12**, 3873.

19 (*a*) C. E. McKenna and J. Schmidhauser, *J. Chem. Soc., Chem. Commun.*, 1979, 739; (*b*) L. Wozniak and J. Chojnowski, *Tetrahedron*, 1989, **45**, 2465 and references therein.

20 T. Yamamoto, T. Morikita and T. Maruyama, *Macromolecules*, 1997, **30**, 5390.

21 (*a*) A. G. Nagy and S. Toma, *J. Organomet. Chem.*, 1985, **282**, 267; (*b*) W. E.Geiger, in *Organometallic Radical Processes*, ed. W. C. Trogler, Elsevier Science, Amsterdam, The Netherlands, 1990, vol. 22, pp. 142–172.

22 D. Naskas, S. Kumar Das, L. Giribabu, B. G. Maiya and S. Roy, *Organometallics*, 2000, **19**, 1464.

23 B. Delavaux-Nicot and S. Fery-Forgues, *Eur. J. Inorg. Chem.*, 1999, 1821.

24 A. Hradsky, B. Bildstein, N. Schuler, H. Schottenberger, P. Jaitner, K. H. Ongania, K. Wurst and J. P. Launay, *Organometallics*, 1997, **16**, 392.

25 M. G. Hutchings, P. F. Gordon, P. J. Duggan, I. Ledoux, G. Puccetti and J. Zyss, *Tetrahedron Lett.*, 1994, **35**, 9073.