ELSEVIER

www.elsevier.nl/locate/jorganchem

Journal of Organometallic Chemistry 601 (2000) 293–298

Journal of Organometallic Chemistry

Synthesis and solvatochromism of some dipolar aryl-phosphonium and -phosphine oxide systems

David W. Allen * , Josephine P. Mifflin, Peter J. Skabara

Division of Chemistry, Sheffield Hallam University, Pond Street, Sheffield S1 1WB, UK

Received 13 December 1999; received in revised form 26 January 2000

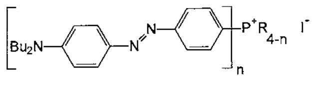
Abstract

The synthesis is reported of a series of dipolar arylphosphonium salts bearing ferrocenylethenyl, 2-thienylethenyl, 4-dimethylaminophenylethenyl, or (4-dimethylaminophenyl)butadienyl electron-donor centres, together with a study of their course of alkaline hydrolysis, which provides a convenient synthetic route to related dipolar phosphine oxides. The phosphonium salts exhibit a modest degree of negative solvatochromism, whereas the related phosphine oxides show a small positive solvatochromic effect. In the case of the ferrocenyl systems, the electronic effects of the phosphorus acceptor group on the ferrocene unit have been studied by cyclic voltammetry. © 2000 Elsevier Science S.A. All rights reserved.

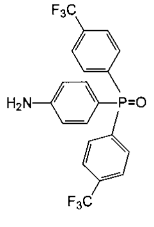
Keywords: Phosphonium salt; Phosphine oxide; Solvatochromism; Ferrocenyl; Cyclic voltammetry

1. Introduction

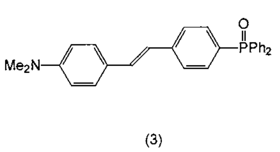
There is growing interest in the opto-electronic properties of organic derivatives of the heavier Main Group 15 elements, notably those of phosphorus. Recent papers have reported the synthesis of the dipolar systems **1** [1], **2** [2,3], **3** [4], and **4** [5], which have proved to be of interest in connection with their non-linear and other optical properties. All of these systems involve either a phosphonium or phosphine oxide moiety as the electron-deficient centre, to which is bonded a polarisable π-system that carries an electron-donating substituent.



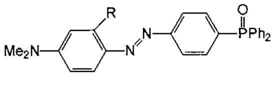
(1) (R = Me or Ph)



(2)

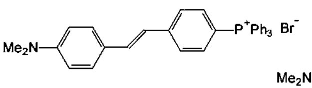


(3)

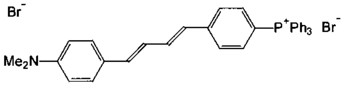


(4) (R = H or Me)

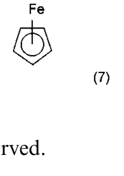
We have embarked on a study of the solvatochromism of dipolar compounds of the heavier Main Group 15 elements. Compounds that are solvatochromic are also of potential interest in that they may also exhibit non-linear optical properties under appropriate circumstances. In recent papers, we have described the synthesis and solvatochromic properties of a series of phosphonioaryl-imidazolide and phosphonioaryl-phenolate betaines [6,7], and an extension of these studies to the analogous compounds of arsenic and antimony [8]. In this paper, we report the synthesis of a series of dipolar phosphonium salts **5**–**8**, and a study of their course of alkaline hydrolysis, which provides a convenient synthetic route to the related



(5)



(6)



(7)

(8)

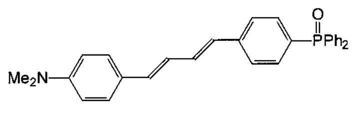
---

* Corresponding author. Tel.: + 44-114-2253000; fax: + 44-144-2253066.

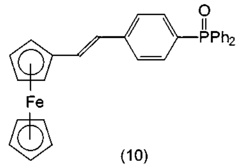
E-mail address: d.w.allen@shu.ac.uk (D.W. Allen)

PII: S0022-328X(00)00085-1

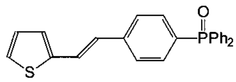
dipolar phosphine oxides **3**, **9**, **10** and **11**. The solvatochromism of the phosphonium salts and phosphine oxides has also been investigated, and, in the case of the ferrocenyl systems **7** and **10**, the electronic effects of the phosphorus acceptor group on the ferrocene unit have been studied by cyclic voltammetry.



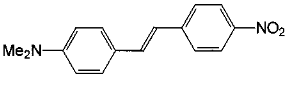
(9)



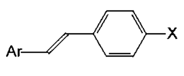
(10)



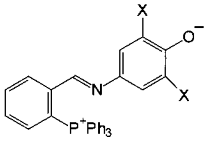
(11)



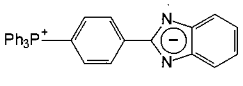
(12)



(13)



(14)



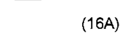
(15)

2. Results and discussion

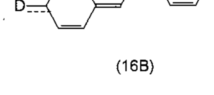
The discovery of the non-linear optical properties of 4-dimethylamino-4′-nitrostilbene (DANS) (**12**) [9,10] has stimulated a wide range of studies of related polarisable dipolar systems that bear a potential donor centre linked to an electron-withdrawing group, via a polarisable π-system. Following our earlier work on solvatochromic heavier Group 15 compounds, we decided to explore the synthesis and solvatochromism of a series of molecules related to DANS, in which the electron-withdrawing group is either a phosphonium cation or a phosphine oxide moiety, and the electron-donating systems include ferrocenyl and 2-thienyl groups.

The arylphosphonium salts **5**–**8** were prepared by the Horner reaction [11] in which the appropriate bromoarene (**13**, X = Br) was heated with triphenylphosphine and anhydrous nickel(II) bromide in benzonitrile. Conversion of the phosphonium salts to the phosphine oxides **3**, **9**, **10** and **11** was achieved by alkaline hydrolysis, a well-established reaction that proceeds with cleavage of the group most stable as a developing carbanion, which is then protonated to form the related hydrocarbon [12–14]. In the case of the above salts, there is clearly a choice of potential aryl carbanion between phenyl and arylethenyl substituted phenyl (**13**, X = lone pair), which could result in a mixture of products. However, in these reactions, it is clear that the remote electron-donating substituent must destabilise the forming carbanion relative to phenyl such that loss of phenyl is favoured. There is clearly a statistical effect here as well in that three phenyl groups are available for cleavage in relation to the single substituted phenyl group. Traces of the competitive cleavage products, triphenylphosphine oxide and the hydrocarbons (**13**, X = H) were detected, but the desired phosphine oxides were isolated cleanly and in good yield.

As expected, introduction of the phosphonium centre shifted the visible absorption bands of the stilbene-like systems (**13**, X = Br) towards longer wavelength, the colour of the salt depending on the nature of the donor group present. Whereas the thienylethenyl salt **8** was isolated as a pale yellow powder, the dimethylaminoaryl salts **5** and **6** were orange and bright red, respectively, and were noticeably fluorescent in solution in dichloromethane. The ferrocenyl salt **7** was also red. The phosphonium salts exhibited negative solvatochromism, but to a much smaller extent than the phosphonioiminophenolate betaines (**14**, X = Cl, Br, or Ph) [7], or the phosphoniobenzimidazolide **15** [6]. Thus, the ferrocenylethenyl system **7** showed $\lambda_{\max} = 336$ and 486 nm in methanol compared with 340 and 498 nm in dichloromethane. A similar range was observed for the dimethylaminophenyl systems **5** and **6**, the stilbene **5** having $\lambda_{\max} = 406$ nm in methanol and 422 nm in dichloromethane, and the dienyl system **6** having $\lambda_{\max} = 422$ nm in methanol and 442 nm in dichloromethane. The 2-thienylethenyl salt **8** showed an even smaller solvatochromic effect, having $\lambda_{\max} = 352$ nm in methanol and 358 nm in dichloromethane. The extent of negative solvatochromism observed in these salts is consistent with a small degree of intramolecular charge transfer from the donor centre through the π-system to the ring bearing the phosphonium group, as in **16**, the less polar excited states, e.g. **16B**, being of higher energy in the more polar solvents, which tend to stabilise the more polar ground state (**16A**) to a greater extent. Clearly, the extent of charge transfer is smaller for the thienyl system than for ferrocenyl and 4-dimethylaminophenyl.



(16A)



(16B)

In contrast, the related phosphine oxides **3** and **10** show a small degree of positive solvatochromism, reflecting the lack of formal positive charge (and smaller electron-withdrawing power) of the diphenylphosphinyl group compared with the formally positive triphenylphosphonio group. The solvatochromic properties of **3** have been described previously [4], this compound exhibiting a small degree of positive solvatochromism, having $\lambda_{max} = 367$ nm in cyclohexane and 383 nm in DMSO. This is consistent with charge transfer from nitrogen to the phosphorus centre in the excited state, which is then more polar than the ground state. This compound has also been shown to exhibit a significant second-order non-linear optical effect [4]. The ferrocenylethenyl phenylphosphine oxide **10** also exhibited a small degree of positive solvatochromism, exhibiting a long-wavelength band at 439 nm in cyclohexane, at 466 nm in dichloromethane, and at 472 nm in DMSO, consistent with electron transfer from the ferrocenyl system to the phosphorus group. In contrast, the solvatochromic properties of the related dienyl system **9**, and the thienyl system **11** were almost non-existent, implying that the extent of charge displacement towards the phosphine oxide unit is much smaller. Thus, the dienyl system **9** showed a visible absorption band at 396 nm in both dichloromethane and DMSO. Similarly, the thienyl system **11** absorbed at 338 nm in dichloromethane, and 340 nm in DMSO. Solubility problems precluded the use of less polar solvents for these compounds. The similarity in solvatochromic properties of compound **10** to those of **3** would suggest that the former might also display significant non-linear optical properties. The synthetic route reported in this paper provides a simple approach to a range of dipolar π-bridged systems which provides scope for considerable variation in the nature of the phosphorus-containing electron-withdrawing group, including chiral centres, which would enhance the likelihood of encountering significant solid state non-linear optical properties.

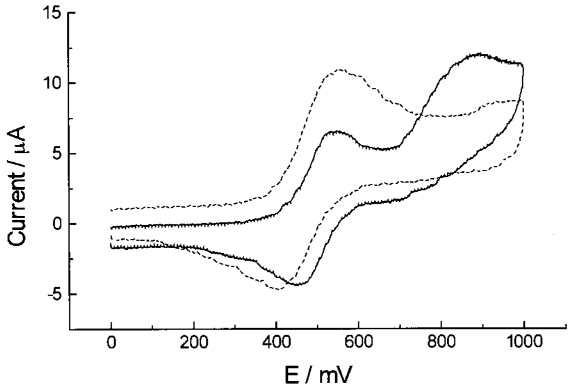


Fig. 1. Cyclic voltammograms of compounds **7** (—) and **10** (- - -) in MeCN vs. Ag/AgCl, Pt wire counter electrode, Pt disk working electrode, at 20°C, 0.1 M Bu_4NPF_6 supporting electrolyte, ca. 0.001 M substrate, 200 mV s^{-1} scan rate with *iR* compensation.

Table 1
Cyclic voltammetric data for ferrocene, **7**, **10**, **17** and **18**, and electronic absorption maxima (obtained in dichloromethane) corresponding to intramolecular charge transfer

Compound	$E_1^{1/2}$ (mV)	E_2 (mV)	$E_1^{1/2}$ shift from FcH	λ_{max} (nm)
Ferrocene (FcH)	443 [a]	–	–	–
7	499 ep	885 [a]	56	498
10	482 [a]	–	39	466
17 [17]	306 [b]	–	42	480
18 [17]	334 [b]	–	70	535

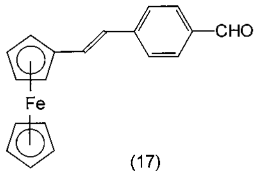
[a] Obtained in acetonitrile.

[b] Obtained in dichloromethane.

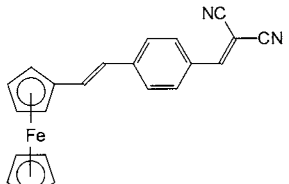
2.1. Electrochemistry

The redox properties of ferrocenyl compounds **7** and **10** were studied by cyclic voltammetry in acetonitrile solution, using unsubstituted ferrocene as internal standard (see Fig. 1 and Table 1). In each case, a reversible oxidation process is observed, which represents the transformation of the ferrocene unit to the ferrocenium species. The voltammogram for the salt **7** shows an additional irreversible peak at + 885 mV; this process represents the oxidation of the bromide species and is irreversible due to coupling of the radical species to form bromine.

In comparison to ferrocene, both $E_1^{1/2}$ processes are shifted anodically (56 mV for **7** and 39 mV for **10**), due to the electron-withdrawing nature of the phosphorus-containing substituents that decrease the electron releasing ability of the ferrocene unit. Notably, the shift is greater in derivative **7**, which bears the stronger electron-withdrawing unit. However, if we consider the nucleophilic constants (σ_p) of the phosphonium and phosphine oxide groups (0.53 for $P(O)Ph_2$ and 1.18 for $P^+(Me)Ph_2$) [15], we would expect the oxidation of the ferrocene moiety in **7** to occur at an even higher potential. This hypothesis can be made on the basis of a similar study utilising more 'traditional' electron withdrawing groups, in which ferrocene derivatives **17** [16] and **18** [17], bearing formyl and dicyanovinyl groups, respectively, have been investigated for their solvatochromic and electrochemical properties (in dichloromethane, with ferrocene as internal reference; see Table 1) [17].



(17)



(18)

From the values of the nucleophilic constants for the substituents CHO ($\sigma_p = 0.42$) and $CH=C(CN)_2$ ($\sigma_p = 0.84$), it is not surprising that the greater anodic shift for the ferrocene/ferrocenium redox couple is observed in compound **18**. The same analogy can be made in the electronic absorption spectra of the two compounds —

relative to the formyl derivative **17**, the longest wavelength maximum (corresponding to intramolecular charge-transfer) is shifted bathochromically in **18** by 55 nm.

Clearly, the dicyanovinyl group is a powerful electron-withdrawing species; however, σ_p for a phosphonium group is greater than that of the former [15]. Since the difference in the nucleophilic constants for the formyl and phosphine oxide groups is quite small ($\Delta\sigma_p = 0.11$), we would expect $\Delta\lambda_{max}$ and $\Delta\sigma_p$ between derivatives **7** and **10** to be greater than the corresponding values for **17** and **18**. Remarkably, the reverse is true, showing that under the experimental conditions, the phosphonium species is a weaker electron-withdrawing group than the dicyanovinyl fragment. These results are in direct contrast with the values of the nucleophilic constants for the respective acceptor groups and may be explained by the inability of the phosphonium centre to act as a π-acceptor as a result of the now recognised minimal d-orbital involvement in the bonding in potentially five-covalent, four-coordinate Main Group 15 compounds [18].

3. Experimental

^{31}P- and ^{1}H-NMR studies were carried out using a Bruker AC 250 FTNMR spectrometer. Low-resolution mass spectra were recorded on a VG Micromass 7070F instrument. High-resolution FABMS determinations were carried out by the EPSRC Mass Spectrometry Service, University of Wales, Swansea. Cyclic voltammetry was performed on a BAS CV50W voltammetric analyser, with *iR* compensation, using anhydrous acetonitrile as the solvent, Ag/AgCl as the reference electrode and platinum wire and disk as the counter and working electrodes, respectively. All solutions were degassed (N_2) and contained the substrate in concentrations of ca. 10^{-3} M, together with Bu_4NPF_6 (0.1 M) as the supporting electrolyte. The scan rate was 300 mV s^{-1}.

*3.1. 1-Ferrocenyl-2-(4-bromophenyl)ethene (**13**, Ar = ferrocenyl, X = Br)*

This was prepared as described in the literature [19].

*3.2. 1-Ferrocenyl-2-(4-triphenylphosphoniophenyl)ethene bromide (**7**)*

The bromophenylalkene (**13**, Ar = ferrocenyl, X = Br) (1.57 g, 0.0043 mol) was heated under reflux with triphenylphosphine (1.69 g, 0.0065 mol) and nickel(II) bromide (0.47 g, 0.0021 mol) in benzonitrile (37 ml) for 4 h under nitrogen. The solution remained a deep red in colour instead of turning the usual bottle green. Once cooled, solvent extraction was carried out with dichloromethane and aqueous KBr (10%). The organic layer was dried ($MgSO_4$) and the solvent was evaporated in vacuo. The remaining benzonitrile mixture was poured into diethyl ether and the solid precipitated was triturated many times with fresh diethyl ether. On filtering, the solid was found to be very hygroscopic and, therefore, the salt was purified and isolated as a red crystalline solid by column chromatography with an eluting solvent of dichloromethane–methanol. The solid was dried under reduced pressure. Yield: 0.38 g (14%); m.p. > 75°C (dec.). ^{31}P NMR ($CDCl_3$): 22.42 ppm. ^{1}H-NMR ($CDCl_3$): 4.16 (s, 5H), 4.39 (s, 2H), 4.53 (s, 2H) (cyclopentadienyl), 7.0 (centre of AB pattern, $J_{AB} = 16.1$ Hz, CH=CH), 7.52–7.92 (m, 19H, aromatic) ppm. FABMS: Calc. for $C_{36}H_{30}FeP$ cation: 549.09376. Found: 549.09369 (0.00 ppm).

*3.3. 1-(4-Bromophenyl)-2-(2-thienyl)ethene (**13**, Ar = 2-thienyl, X = Br)*

To a solution of (2-thienylmethyl)triphenylphosphonium bromide (9.79 g, 0.022 mol) and 4-bromobenzaldehyde (4 g, 0.022 mol) in dry THF (100 ml) was added potassium tertiary butoxide (3.4 g, 0.03 mol), and the reaction mixture stirred for 4 h. The reaction mixture was poured into water (200 ml) and extracted with diethyl ether (3 × 50 ml). The yellow organic layer was dried ($MgSO_4$). The crude solid was washed with methanol until the washings went from pale yellow to colourless to afford a pale yellow solid. Yield: 1.66 g (28.5%); m.p. 144–146°C. ^{1}H-NMR ($CDCl_3$): 6.83–7.49 (m, 9H, aromatic and olefinic) ppm. MS (EI) [M^+] 264 and 266. Anal. Calc. for $C_{12}H_9BrS$: C, 54.36; H, 3.42. Found: C, 54.52; H, 3.50%.

*3.4. 1-(2-Thienyl)-2-(4-triphenylphosphoniophenyl)-ethene bromide (**8**)*

The bromo compound (**13**, Ar = 2-thienyl, X = Br) (1.5 g, 0.0057 mol) was heated under reflux in benzonitrile (50 ml) with triphenylphosphine (3 g, 0.01 mol) and nickel(II) bromide (0.63 g, 0.0029 mol) for 8 h under nitrogen to form a bottle green reaction mixture. The mixture was poured into aqueous KBr (10%) (200 ml) and the product extracted with dichloromethane (3 × 50 ml). The yellow organic layer was dried ($MgSO_4$) and the solvent was evaporated in vacuo. The remaining benzonitrile mixture was poured into diethyl ether and triturated several times with fresh diethyl ether. The solid was filtered to afford a pale yellow powder. Yield: 1.18 g (60%); m.p. 310–312°C (dec.). ^{31}P-NMR ($CDCl_3$): 22.35 ppm. ^{1}H-NMR ($CDCl_3$): 6.50–8.30 (m, 24H, aromatic and olefinic) ppm. FABMS: Calc. for $C_{30}H_{24}PS$ [M^+] cation): 447.133636. Found 447.133450 (0.4 ppm). Anal. Calc. for

$C_{30}H_{24}BrPS$: C, 68.31; H, 4.59. Found: C, 68.02; H, 4.60%.

*3.5. 1-(4-Bromophenyl)-2-(4-dimethylaminophenyl)-ethene (**13**, Ar = 4-dimethylaminophenyl, X = Br)*

This was prepared as described by Lequan et al. [20].

*3.6. 1-(4-Dimethylaminophenyl)-2-(4-phenylphosphoniophenyl)ethene bromide (**5**)*

The bromostilbene (**13**, Ar = 4-dimethylaminophenyl, X = Br) (3 g, 0.01 mol) was heated under reflux with triphenylphosphine (3.93 g, 0.015 mol) and nickel(II) bromide (1.09 g, 0.005 mol) in benzonitrile (70 ml) for 4 h under nitrogen. The cooled reaction mixture was poured into aqueous KBr (10% w/v) (200 ml) and extracted with dichloromethane (3 × 50 ml). The combined organic layers were washed with KBr (aq), dried ($MgSO_4$), and the solvent was evaporated in vacuo. After repeated trituration of the oil with diethyl ether, a rusty–orange solid was obtained, which was dried under vacuum. Yield: 4.54 g (94%); m.p. > 70°C (dec.). ^{31}P-NMR ($CDCl_3$): 22.25 ppm. ^{1}H-NMR ($CDCl_3$): 2.95 (s, 6H, NMe_2), 6.65–7.86 (m, 25H, aromatic and olefinic) ppm. ^{13}C-NMR ($CDCl_3$): 40.55, 112.13, 112.43, 117.53, 118.96, 121.1, 124.2, 127.76, 127.76, 127.96, 129.02, 130.32, 131.04, 131.23, 134.54, 134.69, 135.31, 136.06, 146.34, 151.35 ppm. FABMS: Calc. for [M^+] cation: $C_{34}H_{31}NP$: 484.219414. Found: 484.218048 (2.8 ppm). Anal. Calc. for $C_{34}H_{31}BrNP\cdot 2H_2O$: C, 68.00; H, 5.87; N, 2.33. Found: C, 67.84; H, 5.30; N, 2.32%.

*3.7. 1-(4-Bromophenyl)-4-(4-dimethylaminophenyl)-1,3-butadiene (**13**, Ar = 4-dimethylaminophenylethenyl, X = Br)*

To a solution of (4-bromobenzyl)triphenylphosphonium bromide (16.6 g, 0.032 mol) and 4-dimethylaminocinnamaldehyde (5.68 g, 0.032 mol) in dry THF (120 ml) at room temperature was added potassium tertiary butoxide (4 g, 0.035 mol), and the resulting solution left to stir overnight. The reaction mixture was poured into a large volume of water, and the solid filtered under suction. The crude solid was recrystallised from dichloromethane, and washed with a small amount of cold acetone to afford a pale yellow solid (one isomer only, from GC–MS, assumed to be *trans–trans*). Yield: 2.1 g (20%); m.p. 239–240°C. ^{1}H-NMR ($CDCl_3$): 2.99 (s, 6H, NMe_2), 6.46–6.95 (m, 4H, olefinic), 7.28–7.45 (m, 8H, aromatic) ppm. MS (EI) required for [M^+] $C_{18}H_{18}\,^{79}BrN$: 327.06226. Found: 327.06000 (6.9 ppm). Anal. Calc. for $C_{18}H_{18}BrN$: C, 65.86; H, 5.53; N, 4.27. Found: C, 65.74; H, 5.53; N, 4.21%.

*3.8. 1-(4-Dimethylaminophenyl)-4-(4-triphenylphosphoniophenyl)-1,3-butadiene bromide (**6**)*

The diene (**13**, Ar = 4-dimethylaminophenylethenyl, X = Br) (2 g, 0.006 mol) was heated under reflux in benzonitrile (40 ml) with triphenylphosphine (2.36 g, 0.009 mol) and nickel(II) bromide (0.066 g, 0.003 mol) for 4 h under nitrogen. The cooled reaction mixture was poured into aqueous potassium bromide (10% w/v) (200 ml) and extracted with dichloromethane (3 × 50 ml). The combined organic layers were washed with aqueous potassium bromide, dried ($MgSO_4$) and the solvent was removed in vacuo. After repeated trituration of the oil with diethyl ether, the filtered solid was found to be hygroscopic, and so was purified by flash chromatography using MeOH–CH_2Cl_2 (1:9) as the eluting solvent. A bright red crystalline solid was obtained. Yield: 3.43 g (97%); m.p. > 330°C (dec.). ^{31}P-NMR ($CDCl_3$): 22.29 ppm. ^{1}H-NMR ($CDCl_3$): 2.95 (s, 6H, NMe_2), 6.62–6.80 (m, 4H, olefinic), 7.34–7.92 (m, 23H, aromatic) ppm. ^{13}C-NMR ($CDCl_3$): 40.59, 112.93, 118.93, 128.54, 131.04, 131.25, 134.57, 134.72, 136.07 ppm. FABMS: required for [M^+] cation $C_{36}H_{33}NP$: 510.235064. Found: 510.235002 (0.1 ppm). Anal. Calc. for $C_{36}H_{33}BrNP\cdot H_2O$: C, 71.05; H, 5.80; N, 2.30. Found: C, 70.86; H, 5.72; N, 2.21%.

*3.9. 1-(4-Diphenylphosphinoylphenyl)-2-(ferrocenyl)ethene (**10**)*

Phosphonium salt **7** (0.81 g, 1.6 mmol) was heated under reflux in ethanol (3 ml) for 3 h with sodium hydroxide (1 M, 1.5 ml). After several hours the colour of the reaction mixture turned from red to orange–brown. The cooled reaction mixture was poured into water and extracted with dichloromethane (3 × 20 ml) and washed with water. The combined organic layers were dried ($MgSO_4$), and the solvent evaporated in vacuo to afford the crude phosphine oxide as an orange powder. Yield: 0.4 g (52%); m.p. 154–157°C. ^{31}P-NMR ($CDCl_3$): 29.02 ppm. ^{1}H-NMR ($CDCl_3$): 4.11 (s, 5H), 4.33 (s, 2H), 4.49 (s, 2H) (cyclopentadienyl), 6.86 (centre of AB pattern, $J_{AB} = 16.25$ Hz, CH=CH), 7.40–8.2 (m, 14H, aromatic) ppm. MS (EI) Calc. for $C_{30}H_{25}\,^{54}FeOP$: 486.10391. Found: 486.10211 (3.7 ppm, 7.19%). Calc. for $C_{30}H_{25}\,^{56}FeOP$: 488.09924. Found: 488.10001 (−1.6 ppm, 100%). Calc. for $C_{30}H_{25}\,^{57}FeOP$: 489.09970. Found: 489.10274 (−6.2 ppm, 35.97%).

*3.10. 1-(4-Diphenylphosphinoyl)-2-(2-thienyl)ethene (**11**)*

Analogously to the procedure for **10**, salt **8** (0.5 g, 0.95 mmol) was heated under reflux in ethanol with sodium hydroxide (1 M, 2 ml) for 2 h. No colour change was observed during the reaction. After solvent extraction a pale yellow solid was obtained. Yield: 0.14 g (27%); m.p. 156–160°C. ^{31}P-NMR ($CDCl_3$): 28.63 ppm. ^{1}H-NMR ($CDCl_3$): 6.95–7.73 (m, 17H, aromatic), 7.18 (CH=CH, $J_{AB} = 16.1$ Hz) ppm. MS (EI) Calc. for $C_{24}H_{19}OPS$: 386.08942. Found: 386.08705 (6.1 ppm).

*3.11. 1-(4-Dimethylaminophenyl)-2-(4-diphenylphosphinoylphenyl)ethene (**3**)*

Analogously to the procedure for **10**, salt **5** (0.11 g, 0.195 mmol) was heated under reflux in ethanol with sodium hydroxide (1 M, 0.5 ml) for 2 h. No colour change was observed during the reaction and a pale orange solid was obtained. The phosphine oxide **3** was isolated by column chromatography as a yellow solid. Yield: 0.05 g (70%); m.p. 253–254°C (lit. [4], 255°C). ^{31}P-NMR ($CDCl_3$): 29.17 ppm. ^{1}H-NMR ($CDCl_3$): 2.87 (s, 6H, NMe_2), 6.4–8.1 (m, 18H, aromatic), 7.04 (centre of AB pattern, $J_{AB} = 15.9$ Hz, CH=CH) ppm. MS (EI) Calc. for $C_{28}H_{26}NOP$: 423.17520. Found: 423.17500 (0.5 ppm).

*3.12. 1-(4-Dimethylaminophenyl)-4-(4-diphenylphosphinoylphenyl)-1,3-butadiene (**9**)*

Analogously to the procedure for **10**, salt **6** (0.5 g, 0.85 mmol) was treated with sodium hydroxide (1 M, 4 ml) under refluxing ethanol (3 ml). As soon as the base was added, a bright yellow solid precipitated, which was left stirring under reflux for a further hour. A bright yellow waxy solid was obtained from which the phosphine oxide **9** was isolated by column chromatography as a bright yellow waxy solid. Yield: 0.2 g (53%); m.p. 202–205°C. ^{31}P-NMR ($CDCl_3$): 28.80 ppm. ^{1}H-NMR ($CDCl_3$): 3.12 (s, 6H, NMe_2), 6.3–8.0 (m, 22H, aromatic and olefinic) ppm. MS (EI) Calc. for $C_{30}H_{28}NOP$: 449.19086. Found: 449.19026 (1.3 ppm).

3.13. Solvatochromism studies

UV–vis studies were carried out on the salts **5**–**8** and the phosphine oxides **3**, **9**, **10** and **11** at room temperature and pressure using analytical grade (Aldrich) solvents, at concentrations of ca. 1×10^{-4} M.

References

[1] C. Lambert, E. Schmälzlin, K. Meerholz, C. Brauchle, Chem. Eur. J. 4 (1998) 512.
[2] C.M. Whitaker, K.L. Kott, R.J. McMahon, J. Org. Chem. 60 (1995) 3499.
[3] K.L. Kott, C.M. Whitaker, R.J. McMahon, Chem. Mater. 7 (1995) 426.
[4] K. Chane-Ching, M. Lequan, R.-M. Lequan, C. Runser, M. Barzoukas, A. Fort, J. Mater. Chem. 5 (1995) 649.
[5] M. Lequan, R.-M. Lequan, K. Chane-Ching, P. Bassoul, G. Bravic, Y. Barrans, D. Chasseau, J. Mater. Chem. 6 (1996) 5.
[6] D.W. Allen, J. Hawkrigg, H. Adams, B.F. Taylor, D.E. Hibbs, M.B. Hursthouse, J. Chem. Soc. Perkin Trans. 1 (1998) 335.
[7] D.W. Allen, X. Li, J. Chem. Soc. Perkin Trans. 2 (1997) 1099.
[8] D.W. Allen, J.P. Mifflin, S. Coles, Chem. Commun. (Cambridge) (1998) 2115.
[9] J.L. Oudar, J. Chem. Phys. 67 (1977) 446.
[10] A. Dulcic, C. Flytzanis, C.L. Tang, D. Pépin, M. Fétizon, Y. Hoppiliard, J. Chem. Phys. 74 (1981) 1559.
[11] L. Horner, G. Mummenthey, H. Moser, P. Beck, Chem. Ber. 99 (1966) 2782.
[12] M. Zanger, C.A. VanderWerf, W.E. McEwen, J. Am. Chem. Soc. 81 (1959) 3806.
[13] W.E. McEwen, K.F. Kumli, A. Blade-Font, M. Zanger, C.A. VanderWerf, J. Am. Chem. Soc. 86 (1964) 2378.
[14] W.E. McEwen, G. Axelrad, M. Zanger, C.A. VanderWerf, J. Am. Chem. Soc. 87 (1965) 3948.
[15] C. Hansch, A. Leo, R.W. Taft, Chem. Rev. 91 (1991) 165. This reference does not include the σ_p value for P^+Ph_3; however, we suspect that the value for this substituent should be at least, if not greater than, 1.18 (σ_p for $P^+(Me)Ph_2$), since the substitution of methyl groups for phenyl groups has an increasing effect on the value of σ_p ($P^+Me_3 = 0.73$).
[16] H.E. Bunting, M.L.H. Green, S.R. Marder, M.E. Thompson, D. Bloor, P.V. Kolinsky, C.J. Jones, Polyhedron 11 (1992) 1489.
[17] K.R.J. Thomas, J.T. Lin, Y.S. Wen, J. Organomet. Chem. 575 (1999) 301.
[18] D.G. Gilheaney, Chem. Rev. 94 (1994) 1339.
[19] K.L. Kott, R.J. McMahon, J. Org. Chem. 57 (1992) 3097.
[20] M. Lequan, R.M. Lequan, K. Chane-Ching, J. Mater. Chem. 1 (1991) 997.