Synthesis, reactivity and X-ray crystal structure of an uncomplexed 1-phosphabarrelene: application to the synthesis of 1,1′-bis(dimethylsilylphosphinine)ferrocenes

Sebastien Welfelé, Nicolas Mézailles, Nicole Maigrot, Louis Ricard, François Mathey* and Pascal Le Floch*

Laboratoire Hétéroéléments et Coordination (CNRS UMR 7653), Ecole Polytechnique, 91128 Palaiseau cedex, France. E-mail: lefloch@poly.polytechnique.fr

Received (in Montpellier, France) 26th April 2001, Accepted 27th June 2001
First published as an Advance Article on the web 4th September 2001

The 5,6-diphenyl-3-tertiobutyl-1,2-azaphosphinine **3** reacts with bis(phenylethynyldimethylsilyl)ferrocene, **2**, to afford a mixture of the phosphinine **4**, resulting from the cycloaddition of **3** with one alkynyl group of **2**, and 1-phosphabarrelene, **5**, whose formation results from an intramolecular [4 + 2] cycloaddition between the remaining alkynyl group of the ferrocenyl ligand and the 1,4-phosphabutadienic system of **4**. The X-ray structure of compound **5** was obtained and shows no particular strain in the molecule. Competitive experiments have shown that, at high temperature, phosphinine **4** equilibrates with barrelene **5**. Synthesis of a bidentate ligand **6**, incorporating two dimethylsilyl-substituted phosphinines, was achieved by reacting the azaphosphinine **3** with half an equivalent of the ferrocene derivative **2**. The mixed ligand **8**, incorporating two different phosphinine subunits, was also prepared using a two-step sequence by reacting a mixture of **4** and **5** with diazaphosphinine **1**. This reaction first produced an intermediate azaphosphinine-phosphinine ligand **7**, which was then trapped with trimethylsilylacetylene to afford ligand **8**.

It has been shown that the delocalized structure of phosphinines[1,2] is very sensitive towards the substitution pattern of the ring. Thus, the replacement of a CH unit by a nitrogen atom,[3] the inclusion of the ring in a fused system containing a more aromatic neighbor,[4] or the complexation of the phosphorus atom lone pair[5] have been shown to reinforce the dienic and/or the dienophilic character of the ring. Various types of adducts resulting from [4 + 2] cycloaddition of 1,3-dienes at the P=C double bond or of alkynes at the 1-phosphabutadienyl skeleton of phosphinines have thus been characterized.[5,6] Reactions involving unactivated phosphinines in such [4 + 2] cycloaddition processes are very rare. To the best of our knowledge, the unique known example was provided by the groups of Märkl and Ashe who reported the successful synthesis of 1-phosphabarrelenes from the reaction of 2,6-disubstituted-4-phenylphosphinines or from the parent compound C_5H_5P with the highly electron-deficient alkynes hexafluoro-2-butyne and dicyanoethylene (Scheme 1).[7]

Herein we will demonstrate that intramolecular constraints can be exploited to favor the reversible formation of 1-phosphabarrelenes from unactivated phosphinines. Additionally, we also report on the synthesis of a new type of phosphinine-based bidentate ligand incorporating a ferrocenyl spacer.

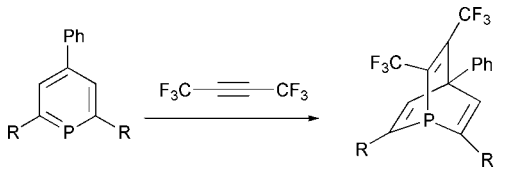
Results and discussion

We recently reported some synthetic strategies allowing the preparation of phosphinine-based bi- and tridentate ligands and macrocycles.[8] All these approaches rely on the reactivity of 1,3,2-diazaphosphinines and 1,2-azaphosphinines such as **1** towards alkynes and diynes. Being substantially less aromatic than phosphinines (see discussion above),[2] these compounds behave as 1,4-dipoles through their 1,2-phosphaazabutadiene skeleton to give phosphinines *via* a [4 + 2] cycloaddition/cyloreversion sequence. The general scheme of these syntheses is summarized in Scheme 2.

As part of a program aimed at exploring the elaboration of sophisticated phosphinine-based bidentate ligands, we recently expanded our studies to the synthesis of 1,1′-substituted ferrocenyl derivatives. 1,1′-Bis(phosphino)substituted ferrocenes are indeed a class of phosphorus bidentate ligands that has found a very wide range of applications in the field of homogeneous catalysis.[9] As previously noted in our works, the use of silyl-substituted alkynes is a determining factor that allows regioselective cycloaddition processes onto diazaphosphinine **1**. Therefore, we first turned our attention toward the synthesis of the 1,1′-bis(phenylethynyl)ferrocene **2**.[10] Its preparation was readily achieved by reacting the 1,1′-dilithioferrocene with two equivalents of (phenylethynyl)chlorodimethylsilane (Scheme 3).[11]

In order to test the reactivity of **1** towards diyne **2**, our first experiments focused on the synthesis of a monodentate ligand. Reaction of equimolar amounts of monoazaphosphinine **3**, and precursor **2** led to a quite unexpected result. Contrary to what was expected, the phosphinine **4**, resulting from the cycloaddition of **3** with one alkyne function of **2**, was not exclusively formed (Scheme 4). In addition to the very characteristic signal of **4** at low field ($\delta = 244.0$ in toluene), the ^{31}P-NMR spectrum of the crude reaction mixture indicated the presence of a second compound **5** whose signal appeared at high field (−43.0 ppm in toluene) with a comparable intensity. Whatever the conditions used (concentration, duration) further heating of this mixture did not modify the ratio between **4** and **5**. Whereas the formulation of **4** could be unambiguously confirmed on the basis of NMR data, that of **5** remained unclear. The two most significant pieces of data were obtained from the mass spectrum, which indicated that compound **5** has the same molecular weight as phosphinine **4**, and by the ^{1}H-NMR spectrum, which reveals the presence of

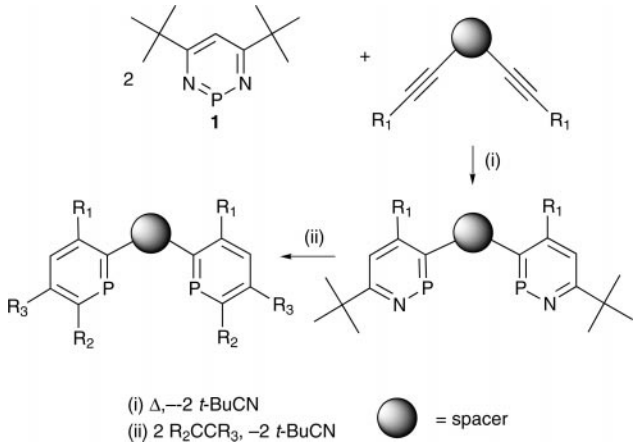
 DOI: 10.1039/b103779j



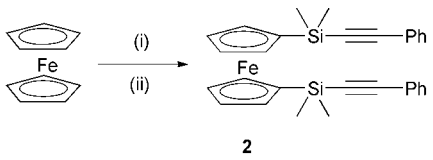
Scheme 1 Synthesis of phosphabarrelenes from phosphinines and hexafluoro-2-butyne.

four sets of magnetically inequivalent cyclopentadienyl protons (see Experimental).

The formulation of **5** was definitively established by an X-ray crystal structure analysis. The structure of one molecule of **5** is shown in Fig. 1; crystallographic data are collected in Table 1. As can be seen, compound **5** is a 1-phosphabarrelene resulting from the intramolecular [4 + 2] cycloaddition of phosphinine **4** with the second alkyne function of the ferrocenyl substituent. Contrary to what might be thought at first sight, the structure of **5** is not particularly strained. Thus, in the ferrocenyl unit, which adopts an eclipsed conformation, the two cyclopentadienyl ligands are roughly coplanar ($\Theta = 4°$). Moreover, in the phosphabarrelene backbone, P–C bond distances are nearly equivalent (average 1.863 Å).

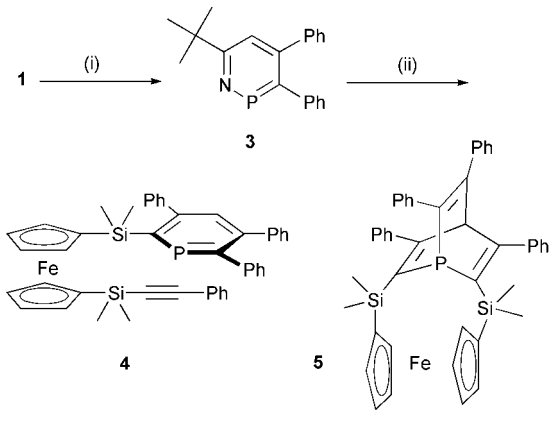


Scheme 2 General scheme describing the synthetic approach towards phosphinine-based bidentate ligands.



(i) 2 BuLi/TMEDA/hexane; (ii) 2 PhCCSiMe$_2$Cl

Scheme 3



(i) PhCCPh, toluene, 110 °C, 15 h
(ii) **2**, 110 °C, 30 h

Scheme 4

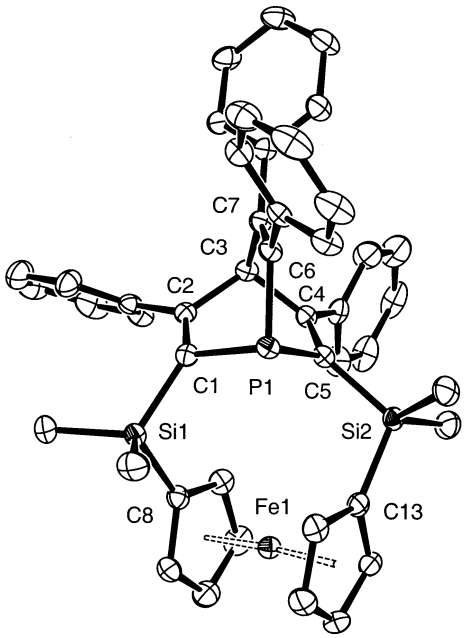


Fig. 1 ORTEP view of one molecule of phosphabarrelene **5**. Displacement ellipsoids are shown at the 50% probability level. The numbering is arbitrary and different from that used in the NMR spectra. Selected bond distances (Å) and angles (°) are as follows. P1–C1, 1.864(2); P1–C5, 1.868(2); P1–C6, 1.860(2); C1–C2, 1.342(2); C2–C3, 1.538(2); C3–C4, 1.544(2); C4–C5, 1.335(2); C6–C7, 1.345(2); C3–C7, 1.533(2); C1–Si1 1.877(2); Si1–C8, 1.865(2): C1–P1–C5, 95.62(6); P1–C1–C2, 112.9(1); P1–C5–C4, 113.4(1); C1–C2–C3, 118.0(1); C2–C3–C4, 108.5(1); C4–C3–C7, 108.4(1); P1–C6–C7, 115.0(1); C6–P1–C5, 96.41(6); C6–P1–C1, 96.86(7); C6–C7–C3, 115.8(1); P1–C1–Si1, 116.03(8); C1–Si1–C8, 104.30(7).

Finally, bond lengths and bond angles in the two dimethylsilyl linkers fall in the usual range.

The formation of **5** thus raises several questions. First of all, it appears that **5** is the unique example of a stable phosphabarrelene resulting from the reaction of an unactivated phosphinine and alkyne. Indeed, whatever the conditions used (temperature, amount of reagents), additional experiments carried out by heating a series of 2-trimethylsilyl-substituted phosphinines with various phenyl- and silyl-substituted alkynes exclusively led to the recovery of the starting compounds. This tends to show that the formation of **5** is favored by geometrical factors. A second important point concerns the isolation of phosphinine **4**, which is the "open" form of **5**. Competitive experiments showed that **4** and **5** equilibrate in solution. Variable temperature ^{31}P-NMR experiments allowed us to extract the thermodynamic values $\Delta S°$ and $\Delta H°$ associated with this equilibrium. The transition state between

Table 1 Crystallographic data and data collection details for compound **5**

Empirical formula	$C_{45}H_{41}FePSi_2 \cdot C_6H_{12}$
Formula weight	808.93
T/K	150.0(1)
Crystal system	Triclinic
Space group	$P\bar{1}$
a/Å	11.197(5)
b/Å	12.256(5)
c/Å	16.462(5)
α/°	83.370(5)
β/°	80.060(5)
γ/°	67.750(5)
U/Å^3	2056.4(14)
Z	2
μ/cm^{-1}	0.500
Total reflect.	16 825
Indep. Reflect.	11 913
R_{int}	0.0298
Final R_1, wR_2 [$I > 2\sigma(I)$]	0.0399, 0.1107

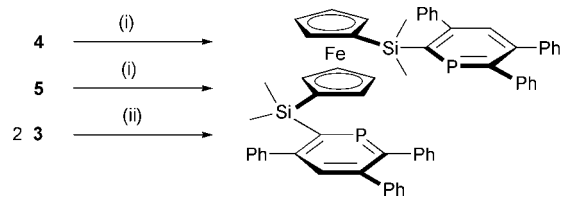
$K° = 0.52$

Scheme 5

4 and **5** being highly ordered, a high negative value of -35 e.u. was calculated, as expected. A $\Delta H°$ of -8.9 kJ mol^{-1} was found, leading to an equilibrium constant $K°$ of 0.52 (Scheme 5). As additional evidence, confirming the equilibrium between **4** and **5**, we found that 1-phosphabarrelene **5** could be used as a precursor for the synthesis of the bis-phosphinine **6** upon reaction with an equivalent of monoazaphosphinine **3**. Following a more straightforward route, compound **6** can also be prepared by reacting two equivalents of azaphosphinine **3** with one equivalent of **2** as depicted in Scheme 6.

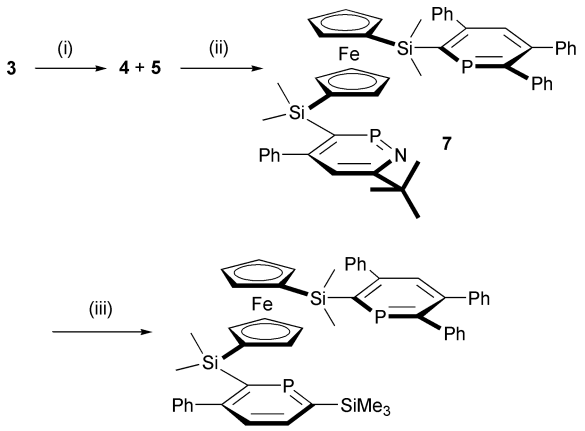
Characterization of **6** was achieved by ^{1}H and ^{13}C-NMR spectroscopy, elemental analysis and mass spectrometry. In order to expand the scope of this study, we also investigated the synthesis of mixed ferrocenyl ligands incorporating two different phosphinine subunits. Following our discovery, synthesis of the bis(phosphinine) **8**, including 2-dimethylsilyl-3,5,6-triphenylphosphinine and 2,6-bis-silylated-3-phenylphosphinine subunits, could be achieved using a one-pot sequence. Reaction of a mixture of **4** and **5**, prepared as described above, with one equivalent of diazaphosphinine **1** yielded intermediate **7** whose formulation was unambiguously established on the basis of the ^{31}P-NMR spectrum. The presence of the azaphosphinine unit is evidenced by a strongly deshielded singlet at 304.0 ppm whereas the chemical shift of the phosphinine subunit is identical to that recorded for compound **4** ($\delta = 244.0$ in toluene). Further heating of this mixture with trimethylsilylacetylene cleanly afforded the expected bis(phosphinine) **8** (Scheme 7) which was characterized by NMR techniques, mass spectroscopy and elemental analyses.

In conclusion, we have shown that proximity effects can overcome the energetic barrier provided by the aromaticity of phosphinines. This led to the isolation and structural characterization of a stable 1-phosphabarrelene. Though in this case



(i) **3**, 110 °C, toluene, 50 h
(ii) **2**, 110 °C, toluene, 50 h

Scheme 6



(i) **2**, 110 °C, toluene, 30 h
(ii) **1**, 110 °C, toluene, 25 h
(iii) $HCCSiMe_3$, 90 °C, 24 h

Scheme 7

the geometry of the diyne employed is particularly well suited to achieve an intramolecular [4 + 2] cycloaddition, it is probable that many other types of functional diynes could display the same behavior. Additionally, we also synthesized a new type of bis-phosphinine ligand including a ferrocenyl spacer. Studies aimed at exploring their coordination chemistry as well as their use in homogeneous catalysis are currently underway in our laboratory.

Experimental

General procedures

All reactions were routinely performed under an inert atmosphere of nitrogen by using Schlenk techniques and dry deoxygenated solvents. Dry THF, hexanes and toluene were obtained by distillation from Na/benzophenone. Dry Celite was used for filtration. Nuclear magnetic resonance spectra were recorded on a Bruker AC-200 SY spectrometer. Chemical shifts are expressed in parts per million downfield from external TMS (^{1}H and ^{13}C) and 85% H_3PO_4 (^{31}P), and coupling constants are given in hertz. Mass spectra were obtained at 70 eV with an HP 5989 B spectrometer coupled with an HP 5890 chromatograph by the direct inlet method. The following abbreviations are used: s, singlet; d, doublet; t, triplet; m, multiplet; v, virtual. Elemental analyses were performed by the "Service d'Analyse du CNRS", Gif sur Yvette, France.

Syntheses

Bis(phenylethynyldimethylsilyl)ferrocene, 2. A solution of butyllithium (38.4 mL, 54 mmol, 1.6 mol L^{-1} in hexane) was added at room temperature to a solution of ferrocene (5.0 g, 27 mmol) in hexane (100 mL) and TMEDA (8.05 mL, 54 mmol). The reaction mixture was then heated at 60 °C for 1 h. A small volume of THF (10 mL) was then added to solubilize a part of the dilithio derivative and the mixture was the cooled to -80 °C. Phenylethynyldimethylchlorosilane (10.5 g, 54 mmol) was added and the resulting mixture was then slowly warmed to room temperature. After 1 h stirring at 25 °C, Celite (5.0 g) was added to the mixture and the solvents were evaporated. The coated Celite was then loaded onto the top of a silica gel packed flash column for chromatography. A first fraction eluted with hexane yielded unreacted ferrocene. A second fraction eluted with a mixture of hexane–toluene (90 : 10) yielded compound **2**, which was recovered as an orange solid. Yield: 9.50 g (70%). ^{1}H-NMR (200 MHz, $CDCl_3$): δ 0.51 (s, 12H, $SiMe_2$), 4.31 (vt, AA′BB′, 4H, $\Sigma J_{HH} = 14.3$, C_5H_4), 4.31 (vt, AA′BB′, 4H, $\Sigma J_{HH} = 14.3$, C_5H_4), 7.34–7.58 (m, 10H, C_6H_5). ^{13}C-NMR (50 MHz, $CDCl_3$): δ -0.7 (s, $SiMe_2$), 69.3 (s, C_{ipso} of C_5H_4), 73.0 (s, CH of C_5H_4), 74.3 C_5H_4), 93.9 (s, C of alkyne), 106.2 (s, C–Si of alkyne), 123.8 (s, C_{ipso} of C_6H_5), 128.9, 129.2, 132.6 (s, CH of C_6H_5). MS m/z (ion, relative intensity): 502 (M $-$ 10), 401 (M $-$ CCPh, 100). Anal. calc. for $C_{30}H_{30}FeSi_2$, MW = 502.5: C, 71.69; H, 6.02; found: C, 71.75; H, 6.08%.

Phosphinine, 4, and phosphabarrelene, 5. Diazaphosphinine **1** (1 mmol) in toluene (20 mL) was reacted with diphenylacetylene (0.178 g, 1 mmol) at 110 °C for 15 h. A ^{31}P-NMR control indicated the complete formation of azaphosphinine **3**. Diyne **2** (0.50 g, 1 mmol) was then added to the reaction mixture and the resulting solution was heated at 110 °C for 30 h. Celite (2 g) was then added and the solvent was evaporated, yielding a brown powder that was then deposited onto the top of a silica gel column. A first fraction eluted with a mixture of hexane–toluene (90 : 10) yielded traces of unreacted diyne **2** and phosphabarrelene **5**. Compound **5** was easily separated from unreacted diyne by washing with methanol. A second fraction eluted with the same solvent yielded a mixture of barrelene **5** phosphinine **4**. Finally, a last fraction eluted with a mixture of hexane–toluene (85 : 15) yielded traces of bis(phosphinine) **6**. Washing

with hexanes (3 × 25 mL) allowed separation of barrelene **5** and phosphinine **4** (only **4** is soluble in hexanes). Following this procedure, compounds **4** and **5** were recovered as orange powders.

4. Yield: 255 mg (35%). ^{31}P-NMR (81 MHz, $CDCl_3$): δ 242.0. ^{1}H-NMR (200 MHz, $CDCl_3$): δ 0.38 (d, 6H, $^4J_{PH} = 1.8$, $SiMe_2$), 0.43 (s, 6H, $SiMe_2$), 4.08 (vt, AA′BB′, 2H, $\Sigma J_{HH} = 3.4$, C_5H_4), 4.18 (vt, AA′BB′, 2H, $\Sigma J_{HH} = 3.4$, C_5H_4), 4.30 (vt, AA′BB′, 2H, $\Sigma J_{HH} = 3.4$, C_5H_4), 4.43 (vt, AA′BB′, 2H, $\Sigma J_{HH} = 3.4$, C_5H_4), 7.12–7.35 (m, 25H, C_6H_5). ^{13}C-NMR (50 MHz, $CDCl_3$): δ 0.7 (s, $SiMe_2$), 1.5 (s, $^3J_{PC} = 11.4$, $SiMe_2$), 72.5 (s, C_5H_4), 72.6 (s, C_5H_4), 74.1 (s, C_5H_4), 74.9 (s, C_5H_4), 93.9 (s, **3**C–Si), 106.3 (s, ≡C); 127.2–137.2 (m, C_6H_5), 135.4 (d, $^3J_{PC} = 16.5$, C4), 142.5 (s, C_{ipso} of C_6H_5), 142.7 (s, C_{ipso} of C_6H_5), 143.2 (s, C_{ipso} of C_6H_5), 146.1 (d, $^2J_{PC} = 9.6$, C_3 or C_5), 153.4 (s, $^2J_{PC} = 12.6$, C_3 or C_5), 168.0 (d, $^1J_{PC} = 73.7$, C_2 or C_6), 168.2 (d, $^1J_{PC} = 72.1$, C_2 or C_6). MS *m*/*z* (ion, relative intensity): 726 (M − 100). Anal. calc. for $C_{45}H_{41}FePSi_2$, MW = 724.8: C, 74.57; H, 5.70; found: C, 74.68; H, 5.71.

5: Yield: 255 mg (35%). ^{31}P-NMR (81 MHz, $CDCl_3$): δ −42.0. ^{1}H-NMR (200 MHz, $CDCl_3$): δ −0.37 (s, 6H, $SiMe_2$), 0.54 (s, 6H, $SiMe_2$), 3.86 (m, 2H, C_5H_4), 4.27 (m, 2H, C_5H_4), 4.38 (m, 2H, C_5H_4), 4.84 (m, 2H, C_5H_4), 5.74 (d, 1H, $^4J_{PH} = 1.5$, C_4 of phosphinine), 7.08–7.31 (m, 20H, C_6H_5). ^{13}C-NMR (50 MHz, $CDCl_3$): δ −0.4 (d, $^3J_{PC} = 7.2$, $SiMe_2$), 1.7 (d, $^3J_{PC} = 7.2$, $SiMe_2$), 55.4 (d, $^3J_{PC} = 3.0$, C_4 of barrelene), 70.5 (s, C_5H_4), 71.9 (s, C_5H_4), 75.3 (s, C_5H_4), 75.5 (s, C_5H_4) 75.6 (s, C_5H_4), 126.8–130.5 (m, CH of C_6H_5), 141.0 (s, C_{ipso} of C_6H_5), 141.4 (d, $^1J_{PC} = 64.4$, C_7 of barrelene), 141.6 (d, $^1J_{PC} = 92.3$, $C_{2,6}$ of barrelene), 144.0 (d, $^2J_{PC} = 2.8$, $C_{3,5}$ of barrelene), 144.7 (d, $^2J_{PC} = 30.6$, C_8 of barrelene), 155.1 (s, C_{ipso} of C_6H_5), 170.9 (d, $J_{PC} = 2.7$, C_{ipso} of C_6H_5). MS *m*/*z* (ion, relative intensity): 725 (M − 1, 100). Anal. calc. for $C_{45}H_{41}FePSi_2$, MW = 724.8: C, 74.57; H, 5.70; found: C, 74.75; H, 5.82%.

Bis(phosphinine), 6. A solution of azaphosphinine **3** (1 mmol), prepared as described above, was reacted with diyne **2** (0.25 g, 0.5 mmol) at 110 °C for 50 h. After this period, a ^{31}P NMR spectrum of the reaction mixture showed formation of bis(phosphinine) **6**. Celite (2 g) was then added to the reaction mixture. The resulting mixture was evaporated to dryness, yielding a brown powder that was deposited onto the top of a silica gel column for chromatography. A first fraction eluted with a mixture of hexane–toluene (90 : 10) yielded bis(phosphinine) **6**, which was recovered as an orange solid. Yield: 310 mg (65%). ^{31}P-NMR (81 MHz, $CDCl_3$): δ 242.0. ^{1}H-NMR (200 MHz, $CDCl_3$): δ 0.45 (d, 12H, $^4J_{PH} = 1.7$, $SiMe_2$), 4.10 (pt, AA′BB′, 4H, $\Sigma J_{HH} = 3.4$, C_5H_4), 4.35 (pt, AA′BB′, 4H, $\Sigma J_{HH} = 3.4$, C_5H_4), 7.21–7.47 (m, 32H, H_4 and C_6H_5). ^{13}C-NMR (50 MHz, $CDCl_3$): δ 2.1 (d, $^3J_{PC} = 11.4$, $SiMe_2$), 72.2 (s, C_5H_4), 74.0 (s, C_5H_4), 127.0–131.0 (m, C_6H_5), 135.5 (d, $^3J_{PC} = 16.5$, C_4), 142.2 (s, C_{ipso} of C_6H_5), 142.5 (s, C_{ipso} of C_6H_5), 143.0 (s, C_{ipso} of C_6H_5), 146.1 (d, $^2J_{PC} = 9.2$, C_3 or C_5 of phosphinine), 153.4 (d, $^2J_{PC} = 12.3$, C_5 or C_3 of phosphinine), 168.0 (d, $^1J_{PC} = 73.7$, C_2 or C_6 of phosphinine), 168.2 (d, $^1J_{PC} = 72.0$, C_6 or C_2 of phosphinine). MS *m*/*z* (ion, relative intensity): 948 (M − 30). Anal. calc. for $C_{60}H_{52}FeP_2Si_2$, MW = 947.02: C, 76.10; H, 5.53; found: C, 76.40; H, 5.68%.

Bis(phosphinine), 8. A solution of azaphosphinine **3** (1 mmol) in toluene (10 mL), prepared as described above, was heated with diyne **2** (0.50 g) at 110 °C in toluene. After 30 h, the ^{31}P NMR spectrum of the crude mixture showed the formation of phosphinine **4** and phosphabarrelene **5** in equal amounts. A solution of diazaphosphinine **1** (1 mmol) in toluene (10 mL) was then added to this mixture and the resulting solution was heated at 110 °C. After 25 h, the reaction was complete and the ^{31}P NMR spectrum showed the presence of intermediate **7**, which is characterized by two singlets at δ ^{31}P 304.0 (azaphosphinine subunit) and 244.0 (phosphinine subunit). Additional traces of unreacted diazaphosphinine **1** could also be detected. Trimethylsilylacetylene (0.28 mL, 2 mmol) was then added to the reaction mixture and the resulting solution was heated at 90 °C for 24 h. The solvent was then evaporated in the presence of Celite (2 g). The brown solid obtained was deposited onto the top of a silica gel column for chromatography. A fraction eluted with hexane allowed the separation of traces of the 2,6-bis(trimethylsilyl)phosphinine formed by reaction of **1** with excess trimethylsilylacetylene. A second fraction eluted with a mixture of hexane–toluene (60 : 40) allowed isolation of the bis(phosphinine) **8**, which was recovered as an orange solid. Yield: 460 mg (55%). ^{31}P-NMR (81 MHz, $CDCl_3$): δ 261.0 (disilyl-substituted phosphinine) and 242.0. ^{1}H-NMR (200 MHz, $CDCl_3$): δ 0.40 (d, 12H, $^4J_{PH} = 1.7$, $SiMe_2$), 0.45 (d, 9H, $^3J_{PH} = 2.8$, $SiMe_3$), 3.99 (pt, AA′BB′, 2H, $\Sigma J_{HH} = 3.4$, C_5H_4), 4.04 (pt, AA′BB′, 2H, $\Sigma J_{HH} = 3.4$, C_5H_4), 4.27 (pt, AA′BB′, 2H, $\Sigma J_{HH} = 3.4$, C_5H_4); 4.30 (pt, AA′BB′, 2H, $\Sigma J_{HH} = 3.4$, C_5H_4), 7.16–7.45 (m, 22H, H_4 of phosphinines and C_6H_5), 8.01 (d, $J_{PH} = 1.2$, H_5 of bis(silyl)phosphinine). MS *m*/*z* (ion, relative intensity): 868 (M − 100). Anal. calc. for $C_{51}H_{52}FeP_2Si_2$, MW = 838.92: C, 73.02; H, 6.25; found: C, 73.30; H, 6.15%.

X-Ray crystallography

Single crystals of compound **5** suitable for X-ray crystallography were obtained by diffusing cyclohexane into a dichloromethane solution of the compound in a tube. Data were collected on a Nonius Kappa CCD diffractometer using an Mo-Kα ($\lambda = 0.710\,70$ Å) X-ray source and a graphite monochromator. Experimental details are described in Table 1. The crystal structures were solved using SIR 97[12] and SHELXL-97.[13] ORTEP drawings were made using ORTEP III for Windows.[14]

CCDC reference number 168236. See http://www.rsc.org/suppdata/nj/b1/b103779j/ for crystallographic data in CIF or other electronic format.

Acknowledgements

This work was supported by the Centre National de la Recherche Scientifique and by the Ecole Polytechnique.

References

1 For general reviews on phosphinine chemistry, see: (*a*) G. Märkl, in *Multiple Bonds and Low Coordination in Phosphorus Chemistry*, ed. M. Regitz and O. J. Scherer, Georg Thieme Verlag, Stuttgart, 1990, p. 220; (*b*) K. B. Dillon, F. Mathey and J. F. Nixon, *Phosphorus: The Carbon Copy*, Wiley, Chichester, 1998; (*c*) N. Mézailles, F. Mathey and P. Le Floch, *Prog. Inorg. Chem.*, 2001, **49**, 455.

2 For articles discussing the aromatic behavior of phosphinines, see: (*a*) J. Waluk, H.-P. Klein, A. J. Ashe III and J. Michl, *Organometallics*, 1989, **8**, 2804; (*b*) G. Frison, A. Sevin, N. Avarvari, F. Mathey and P. Le Floch, *J. Org. Chem.*, 1999, **64**, 5524.

3 (*a*) G. Märkl and G. Dorfmeister, *Tetrahedron Lett.*, 1987, **28**, 1093; (*b*) G. Märkl, C. Dörges, T. Riedl, F. G. Klärner and C. Lodwig, *Tetrahedron Lett.*, 1990, **31**, 4589; (*c*) G. Märkl and S. Dorsch, *Tetrahedron Lett.*, 1995, **36**, 3839; (*d*) G. Märkl and C. Dörges, *Angew. Chem., Int. Ed. Engl.*, 1991, **30**, 106; (*e*) N. Avarvari, P. Le Floch and F. Mathey, *J. Am. Chem. Soc.*, 1996, **118**, 11978.

4 (*a*) G. Märkl and K. H. Heier, *Tetrahedron Lett.*, 1974, **49–50**, 4369; (*b*) G. Märkl, F. Lieb and C. Martin, *Tetrahedron Lett.*, 1971, **17**, 1249.

5 (*a*) J.-M. Alcaraz and F. Mathey, *Tetrahedron Lett.*, 1984, **25**, 4659; (*b*) S. Holand, J.-M. Alcaraz, L. Ricard and F. Mathey, *Heteroatom. Chem.*, 1990, **1**, 37; (*c*) J.-M. Alcaraz and F. Mathey, *Tetrahedron Lett.*, 1984, **25**, 207; (*d*) G. Märkl and H.-J. Beckh, *Tetrahedron Lett.*, 1987, **28**, 3475; (*e*) G. Märkl, H.-J. Beckh, M. L. Ziegler and B. Nuber, *Angew. Chem., Int. Ed. Engl.*, 1987, **26**, 1134; (*f*) N. Mézailles, L. Ricard, F. Mathey and P. Le Floch, *Eur. J. Inorg. Chem.*, 1999, 2233.

6 J. C. Tebby, in *Comprehensive Heterocyclic Chemistry II*, ed. A. R. Katritsky, C. W. Rees and E. F. V. Scriven, Pergamon Press, New York, 1996, vol. 8, p. 863.
7 (*a*) G. Märkl and F. Lieb, *Angew. Chem., Int. Ed. Engl.*, 1968, **7**, 733; (*b*) A. J. Ashe III and M. D. Gordon, *J. Am. Chem. Soc.*, 1972, **94**, 7596.
8 (*a*) N. Avarvari, P. Le Floch, L. Ricard and F. Mathey, *Organometallics*, 1997, **16**, 4089; (*b*) N. Avarvari, N. Mézailles, L. Ricard, P. le Floch and F. Mathey, *Science*, 1998, **280**, 1587; (*c*) N. Avarvari, N. Maigrot, L. Ricard, F. Mathey and P. Le Floch, *Chem. Eur. J.*, 1999, **5**, 2109; (*d*) U. Rhörig, N. Mézailles, N. Maigrot, L. Ricard, F. Mathey and P. Le Floch, *Eur. J. Inorg. Chem.*, 2000, 2565; (*e*) N. Mézailles, N. Maigrot, S. Hamon, L. Ricard, F. Mathey and P. Le Floch, *J. Org. Chem.*, 2001, **66**, 1054.
9 A. Togni, in *Metallocenes*, ed. A. Togni and R. L. Halterman, Wiley-VCH, Weinheim, 1998, vol. 2, p. 685.
10 R.-J. de Lang, J. van Soolingen, H. D. Verkruijsse and L. Brandsma, *Synth. Commun.*, 1995, **25**, 2989.
11 H. Lang and U. Lay, *Z. Anorg. Allg. Chem.*, 1991, **596**, 7.
12 A. Altomare, M. C. Burla, M. Camalli, G. Cascarano, C. Giacovazzo, A. Guagliardi, A. G. G. Moliterni, G. Polidori and R. Spagna, *J. Appl. Crystallogr.*, 1999, **32**, 115.
13 G. M. Sheldrick, SHELXL-97, Universität Göttingen, Germany, 1998.
14 L. J. Farrugia, ORTEP III, University of Glasgow, UK, 2000.