PAPER www.rsc.org/njc | New Journal of Chemistry

Experimental and theoretical study of phosphinine sulfides†

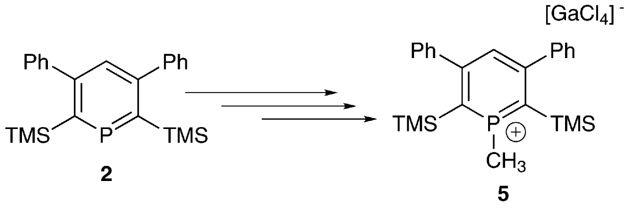
Audrey Moores, Thibault Cantat, Louis Ricard, Nicolas Mézailles and Pascal Le Floch*

Received (in Montpellier, France) 26th February 2007, Accepted 24th April 2007
First published as an Advance Article on the web 15th May 2007
DOI: 10.1039/b702851b

The first examples of phosphinine sulfides (**3** and **4**) were prepared by sulfuration of the corresponding phosphinines (**1** and **2**). These new compounds have been fully characterised by NMR spectroscopy and X-ray diffraction analysis. The precise electronic structure of the parent phosphinine oxide (**III**) and sulfide (**IV**) was investigated at the DFT level and compared to the parent phosphinine (**I**) and 1-methylphosphininium cation (**II**). According to this computational study, the phosphinine sulfide and oxide are aromatic compounds. In the phosphinine sulfide the sulfur lone pairs are efficiently stabilized by two σ*(P–C) orbitals and the phosphinine π* system. Oxidation of the phosphinine leads to a complete reorganisation of the P hybridization state. The variations observed across the series follow Bent's rule and are in excellent agreement with the experimental data.

Introduction

Since their first synthesis in 1966, phosphinines have attracted attention because of their peculiar properties: they are aromatic compounds in which the π* system is rather low in energy and they feature an accessible, though diffuse, lone pair at the phosphorus.[1] Although η[1]-coordinated complexes of phosphinine, whose lone pair is implicated in a bond with various metal centers, are numerous,[1,2] the product of sulfurization of this lone pair has so far eluded isolation and thus complete characterisation. Phosphinine sulfides have been claimed as reactive intermediates in Diels–Alder reactions with 1,3-dienes yielding bicyclic phosphine sulfides[3] and rare derivatives have been characterised by ^{31}P NMR spectroscopy exclusively.[3a,4] Recently in our group, the first 1-methylphosphininium cation was isolated (Scheme 1).[5] This molecule, the phosphorus analog of the well known pyridinium salts, features interesting properties: its aromaticity is comparable to that of phosphinine and both species react as dienes in Diels–Alder reaction. This study also revealed that, unlike as commonly thought, aromaticity and reactivity in Diels–Alder reaction are not incompatible. It was also shown that the phosphorus center in phosphinines may accommodate efficiently important alterations of its environment, because of an easy rehybridization at the P. From this early work, it seemed interesting to reconsider the synthesis of the highly reactive phosphinine sulfide.



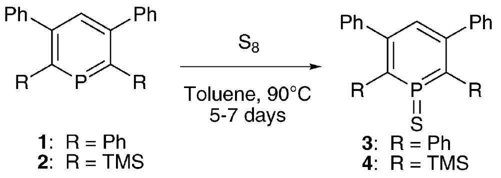
Scheme 1 Synthesis of the phosphininium cation **5**.

Our goal here is fourfold. First, we wish to present the first full characterisation, including X-ray diffraction analysis, of two phosphinine sulfide derivatives. Secondly, in depth electronic analysis of these species is reported, in light of the results of DFT calculations. Thirdly, comparison of the aromaticity between a phosphinine derivative, its sulfide, oxide and cation, is made. And finally, the energy profile of the Diels–Alder reaction, between these derivatives and an alkyne, is calculated and compared to the experimental results.

Results and discussion

Synthesis

Phosphinines **1** and **2** were chosen for their availability. Phosphine **2** is of particular interest as the phosphinium cation was also synthesised from that molecule. Both molecules were heated in toluene for several days at 90 °C with a slight excess of sulfur (Scheme 2). Phosphinine sulfide **3** and **4** were obtained with good yields by simple concentration of the reaction medium, from which they precipitated. They were fully characterised by ^{31}P, ^{1}H and ^{13}C NMR spectroscopy.



Scheme 2 Synthesis of phosphinine sulfides **3** and **4**.

Laboratoire Hétéroéléments et Coordination, École Polytechnique, CNRS, Palaiseau, France. E-mail: lefloch@poly.polytechnique.fr; Fax: (0033)16 933 3990; Tel: (0033)16 933 4575

† Electronic supplementary information (ESI) available: Tables of crystal data, atomic coordinates and equivalent isotropic displacement parameters, bond lengths and bond angles, anisotropic displacement parameters and hydrogen coordinates, ORTEP view of one molecule of compounds **2**, **3** and **4**; a listing of coordinates for all computed structures. See DOI: 10.1039/b702851b

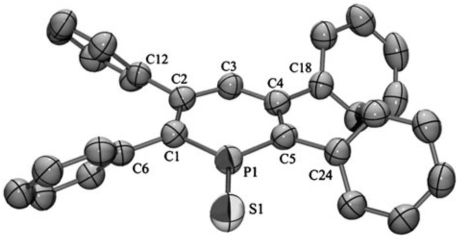


Fig. 1 ORTEP view of one molecule of **3**. Ellipsoids are scaled to enclose 50% of the electron density. The numbering is arbitrary and different from that used in the assignment of NMR spectra.

Table 1 Relevant distances (Å) and angles (°) for **2**, **3**, **4** and **5**

X	**3** S1	**4** S1	**2** —	**5**[5] Me$^+$
P1–X	1.916(1)	1.929(1)	—	1.790(3)
P1–C1	1.724(2)	1.718(2)	1.744(1)	1.697(2)
P1–C5	1.713(2)	1.720(2)	1.745(1)	1.697(2)
C1–C2	1.400(3)	1.417(2)	1.410(2)	1.415(3)
C2–C3	1.396(3)	1.400(2)	1.394(2)	1.407(2)
C3–C4	1.402(3)	1.397(2)	1.397(2)	1.407(2)
C4–C5	1.404(3)	1.412(2)	1.410(2)	1.415(3)
C1–P1–C5	110.2(1)	113.5(1)	106.3(1)	117.7(1)
C1–P1–X	124.9(1)	124.4(1)	—	120.8(1)
C5–P1–X	124.8(1)	122.2(1)	—	120.8(1)

The phosphorus chemical shift is upfield shifted very significantly ($\Delta\delta \sim -60$ ppm) from 206.0 ppm in **1**[6] to 159.4 in **3**, and from 269.4 ppm in **2**[7] to 194.0 ppm in **4**. However, these values remain typical of sp^2 hybridised phosphorus in an aromatic nucleus. ^{1}H and ^{13}C NMR spectra also provided interesting information. The H_4 proton in **3** resonates at 7.11 ppm (6.69 for **4**) compared to the 7.70 ppm measured for **1** (7.34 for **2**). The same upfield shift was recorded for all the carbon centers of the ring when comparing the phosphinine sulfide to the phosphinine derivative, with different magnitude however. Indeed, the shift is very large for the C_2 carbon atom: $\Delta\delta \sim -30$ ppm (169.6 ppm for **1**[6] *vs.* 139.2 ppm for **3**, 166.5 ppm for **2**[7] *vs.* 134.9 ppm for **4**), but much smaller for C_3 and C_4 atoms: $\Delta\delta$ up to -10 ppm. This high field shift can be interpreted as an increase of the electron density on the C2–C6 backbone of the molecule.

Single crystals of **3** and **4** were grown in toluene and analyzed by X-ray diffraction (Fig. 1 and 2). The most interesting metric parameters are presented in Table 1 and compared with the values of the neutral phosphinine **2** and the phosphininium cation **5**.[5] The values of the P–S bond are 1.916(1) and 1.929(1) Å, respectively. Both P–S distances were found to be shorter than in S=PPh$_3$ (1.952 Å),[8] suggesting that the sulfur atom lone pairs interact with the σ* and π* system of the phosphinine nucleus. Noteworthy, the sum of the angles at phosphorus atom are 359.92 and 359.99° in **3** and **4**, respectively, showing that both atoms are perfectly planar. The C–C bond distances inside the ring are intermediate between simple and double bonds distances and thus typical of aromatic compounds. The values of the P1–C1 bond distances and the C1–P1–C5 angle also deserve some comments because they can also be regarded as a probe of the hybridization state of the phosphorus center. In **5**, the P1–C1 bond was found shorter (1.697(2) Å) than in **2** (1.744(1) Å) and the C1–P1–C5 angle larger in **5** (117.7(1)°) than in **2** (106.3(1)°). For **3** and **4** the values are intermediate (1.724(2) and 1.718(2) Å for the P1–C1 distance and 110.2(1) and 113.5(1)° for the C1–P1–C5 angle, respectively). All these geometrical differences suggest that the phosphorus atom has undergone a rehybridization upon sulfuration, but this phenomenon is not as marked as in the case of the phosphininium cation.

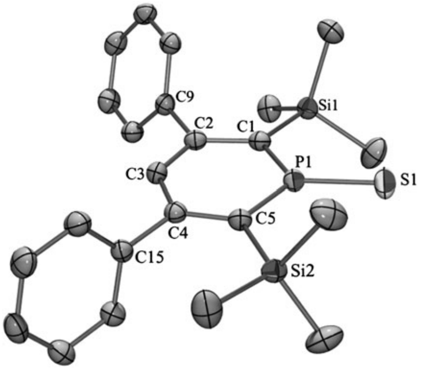
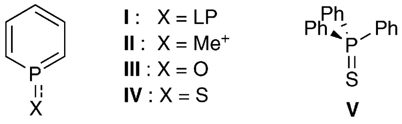


Fig. 2 ORTEP view of one molecule of **4**. Ellipsoids are scaled to enclose 50% of the electron density. The numbering is arbitrary and different from that used in the assignment of NMR spectra.

Theoretical study

DFT calculations were performed on model systems (at the B3LYP/6-311+G(d,p) level of theory) to fully rationalize the variations in geometrical parameters between phosphinine (**I**), 1-methylphosphininium (**II**), phosphinine oxide (**III**), phosphinine sulfide (**IV**) and triphenylphosphine sulfide (**V**). These calculations allow us to present a detailed electronic structure for the oxidation products of phosphinine (Scheme 3). First, phosphinine sulfide **IV** and the well known triphenylphosphine sulfide **V** have been computed to compare how the phosphinine and the phosphine accommodate the effects of oxidation. **IV** was optimized within the C_{2v} point group and **V** within the C_3 point group. No significant difference was noted with the C_1 structures in terms of energy (<1 kcal mol^{-1}) and geometrical parameters. The optimized geometries for **IV** and **V** are in excellent agreement with the experimental structures (Tables 1 and 2). In particular, the shortening of the P–S bond between the phosphine sulfide (1.977 Å in **V**) and the phosphinine sulfide (1.944 Å in **IV**) is well reproduced.

A natural bond orbital (NBO) analysis was performed on optimized geometries in order to get some insight on their electronic structure.[9] Filled NBOs describe the different bonds or lone pairs that correspond to an idealized "strictly" localized Lewis structure. The real system deviates from this hypothetical structure because of donor–acceptor interactions



Scheme 3 Computed molecules.

Table 2 Geometrical parameters for **I**, **II**, **III**, **IV** and **V**

	X	P–X/Å	P–C/Å	C–P–C/°
I	LP	—	1.743	100.04
II	Me$^+$	1.809	1.698	110.66
III	O	1.489	1.708	107.47
IV	S	1.944	1.719	106.13
V	S	1.977	1.842	—

Table 3 NBO analysis of selected donor–acceptor interactions in **IV** and **V**

	Orbital				
	Donor	Acceptor	E(2)/kcal mol^{-1}	E_{ij}/au	F_{ij}/au
IV	LP1(S)	σ*(P–C)	11.6	0.49	0.069
	LP1(S)	σ* (P–C)	11.6	0.49	0.069
	LP2(S)	π*(P–C)	37.7	0.15	0.071
V	LP1(S)	σ*(P–C)	14.6	0.40	0.069
	LP2(S)	σ*(P–C)	11.0	0.40	0.060
	LP2(S)	σ*(P–C)	11.0	0.40	0.060

between filled and empty NBOs. It thus provides a measure of the energetics of delocalization/hyperconjugation. The NBO analysis points to a Lewis structure which involves in **IV** and **V** three lone pairs on the sulfur atom. In both compounds, two sulfur lone pairs (LP1(S) and LP2(S)) are involved in donor–acceptor interactions: *i.e.* donation from the filled LP1(S) and LP2(S) to the three vacant vicinal antibonding P–C NBOs. (The third sulfur lone pair is oriented along the P–S axis and does not overlap with vicinal vacant NBOs). The resulting interaction energy can be estimated *via* a standard second-order perturbation approach (that affords a E(2) energy). The magnitude of the donor–acceptor interaction is mainly controlled by (i) the energy gap (ΔE_{ij}) between the donor (i) and acceptor (j) orbitals (ii) the corresponding Fock matrix element F_{ij} and (iii) the occupation of the donor orbital n_i. As shown in Table 3, **IV** and **V** strongly differ by the nature of their acceptor orbitals. Thus, whereas the sulfur lone pairs are stabilized by three equivalent σ*(P–C) orbitals in **V**, they are stabilized by two equivalent σ*(P–C) and one π*(P–C) orbitals in **IV**. Therefore, in **V**, LP1(S) is stabilized by one vicinal σ*(P–C) NBO (E(2) = 14.6 kcal mol^{-1}) and LP2(S) is stabilized by two vicinal σ*(P–C) NBOs (E(2) = 11.0 kcal mol^{-1} each). In **IV**, LP1(S) is also stabilized by the two vicinal σ*(P–C) NBOs of the phosphinine cycle (11.6 kcal mol^{-1}, Fig. 3 and Table 3) with a similar magnitude than in **V**. However the presence of the low lying π*(P–C) orbital leads to a strong stabilisation of LP2(S) (37.7 kcal mol^{-1}, Fig. 3 and Table 3). Finally, the stabilisation of the sulfur atom lone pairs is almost twice as high in phosphinine sulfide ($\sum E(2)$ = 60.9 kcal mol^{-1} in **IV**) than in the phosphine sulfide ($\sum E(2)$ = 36.6 kcal mol^{-1} in **V**). This results nicely accounts for the shortening of the P–S bond distance observed in phosphinine sulfides **3** and **4**.

Upon oxidation, the phosphinine ring undergoes several structural modifications such as a shortening of the P–C bond and a concomitant widening of the C–P–C internal angle. We will show in this part that these trends are in straight line with the modification of hybridization state at phosphorus. For this purpose we compared phosphinine (**I**) with the oxidized 1-methylphosphininium cation (**II**) and the phosphinine sulfide (**IV**). Even though phosphinine oxides have never been isolated so far,[10] we considered it interesting to include **III** in the series. The geometry of **I** and **III** were optimized within the C_{2v} point group and the geometry of **II** within the C_1 point group. As shown in Table 2, the P–C bond distance is reduced and the C–P–C angle widened in the following order: **I** (X = LP), **IV** (X = S), **III** (X = O), **II** (X = Me$^+$). As the oxidation occurs at the phosphorus center, the hybridization state of this atom was investigated (Table 4).

In the parent phosphinine **I**, the 3s character of the lone pair is large (62.2%) whereas the contribution of the phosphorus in the P–C bond exhibits an important 3p character (79.6%).[11] On the contrary, in the phosphininium salt **II** the three P–C bonds are, with respect to phosphorus, almost perfect sp^2 bonds. The situation in **IV** is intermediate between the phosphinine **I** and the phosphininium cation **II**: the phosphorus atom directs a sp$^{1.85}$ hybrid orbital towards the sulfur atom and sp$^{2.23}$ hybrid orbitals towards the two carbon atoms. In **III**, the hybridization state at the phosphorus atom is very close to what is observed in phosphininium **II**. These results should be analyzed in light of Bent's rule.[12] According to Bent's rule "*a central atom tends to direct hybrids of higher p character toward more electronegative substituents*" so that the

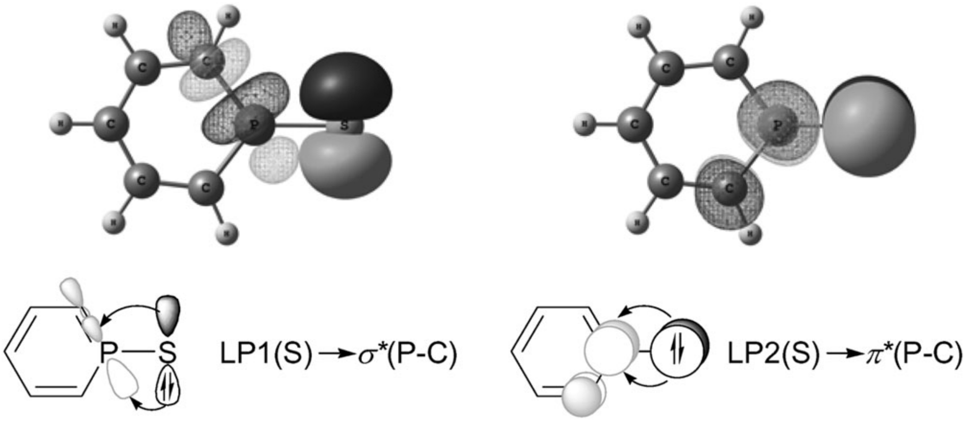


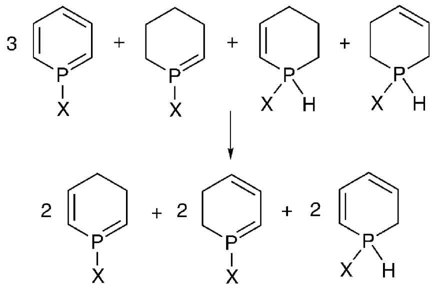
Fig. 3 NBO plots of selected donor–acceptor interactions in **IV**. Empty acceptor NBOs are represented by a mesh surface and filled donor NBOs by a solid surface.

Table 4 Phosphorus hybridization state

	P–C bond			P–X bond		
	s Character (%)	p Character (%)	sp^{λ}	s Character (%)	p Character (%)	sp^{λ}
I (X=LP)	19.6	79.6	$\mathrm{sp}^{4.06}$	62.2	37.8	$\mathrm{sp}^{0.61}$
II (X=Me$^+$)	33.3	66.1	$\mathrm{sp}^{1.98}$	33.2	66.3	$\mathrm{sp}^{2.00}$
III (X=O)	33.5	65.6	$\mathrm{sp}^{1.96}$	32.9	66.0	$\mathrm{sp}^{2.00}$
IV (X=S)	32.4	66.8	$\mathrm{sp}^{2.23}$	34.9	64.4	$\mathrm{sp}^{1.85}$

low energy s orbital is reserved for electron pairs that are concentrated on the central atom (P here). The phosphinine (**I**) obviously follows this rule and the maximum 3s character is found in the phosphorus lone pair (62.2% *vs.* 19.6% in the P–C bonds). Oxidation of the P lone pair leads to a reorganisation of the phosphorus hybridization state in **II**, **III** and **IV**. Analysis of the phosphorus hybrid orbital in the P–X bond indicates that the 3p character increases in the order: **I** (X = LP), **IV** (X = S), **III** (X = O), **II** (X = Me$^+$). Considering that the Me$^+$ cation is a stronger electron withdrawing group than an oxygen atom or a sulfur atom, respectively, the variations observed in the hybridization of the P atom across the series follow nicely Bent's rule. An increase of the phosphorus 3p character in the P–X bond is clearly concomitant with a decrease of the 3p character in the P–C bond of the phosphinine ring that therefore results in a widening of the C–P–C angle and a shortening of the P–C bond. This trend correlates very well with the observed structural parameters (*cf.* Table 1).

Phosphinines and phosphininium cations were proven to be aromatic species,[5] and for the sake of comparison, the aromaticity of both the oxide **III** and the sulfide **IV** was calculated by two independent methods. First, the ASE (aromatic stabilization energy) using the equation depicted in Scheme 4 was calculated.[13] Results obtained for **III** and **IV** are presented in Table 5 alongside those for **I** and **II**, which had been previously reported. According to this criterion, the phosphinine sulfide and the phosphinine oxide are more aromatic than the parent phosphinine and phosphininium cation. Secondly, the NICS (nuclear independent chemical shift) values at 1 Å above the ring were calculated.[14] In contrast with the results of the ASE, the NICS values show that compounds **III** and **IV** are less aromatic than both **I** and **II**.[5] A contradiction between the trends observed for the NICS and the ASE has already been observed for the same type of molecules.[5] Nevertheless, this series of calculation ascertains a strong aromaticity of the studied molecules.



Scheme 4 Aromatic stabilization energy (ASE) equation.

Finally, the reactivity of these molecules as diene in Diels–Alder reactions with alkynes was rationalized by DFT calculations. Experimentally, whereas phosphinines react at high temperature only with activated alkynes,[15] the phosphininium cation yields phosphabarrelenium with electron-rich alkyne at room temperature.[5] It appears that phosphinine sulfides possess intermediate reactivity, and may provide sulfurated phosphabarrelene upon mild heating, as shown by Alcaraz and Mathey.[3a,b] The reaction path of the [4 + 2] cycloaddition process was modelled for the phosphinine sulfide **IV** and acetylene. The reaction profile is presented in Scheme 5. First, the activation energy of 25.3 kcal mol^{-1} is clearly consistent with the need of mild heating. The thermodynamic balance in favor of the barrelene derivative by 11.9 kcal mol^{-1} points to a non-reversible reaction under the experimental conditions. Therefore, in this case again, the sulfide derivative features a behavior which is intermediate between that of the phosphinine and the cation.

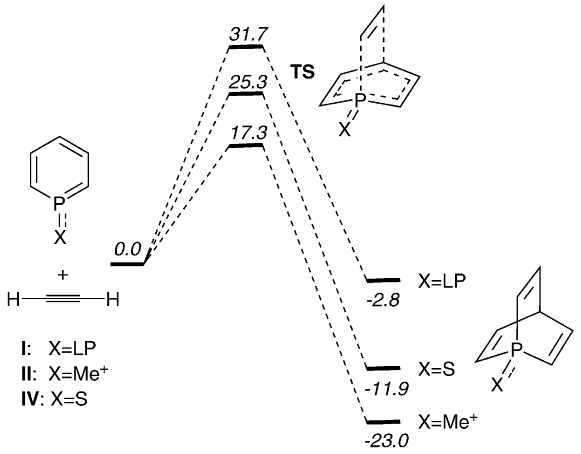
Conclusions

Two phosphinine sulfides were synthesised and fully characterised by NMR spectroscopy and for the first time by X-ray crystallography. DFT calculations have shown that the sulfur lone pairs in these sulfides are strongly stabilized by the two σ^*(P–C) orbitals and the phosphinine π^* system. A comparison between phosphinine, phosphininium cation, phosphinine oxide and phosphinine sulfide has also clearly established that upon oxidation, a modification of the hybridization state at phosphorus takes place. The experimental observation of the stability of the phosphinine, the sulfide and the cation, shows that the phosphorus center accommodates very efficiently the changes in the hybridization. Variations observed across the series were shown to follow Bent's rule. Further calculations of ASE and NICS values showed that these molecules are aromatic compounds, although reactive toward alkynes. The reactivity of phosphinine sulfide in Diels–Alder reactions, compared to that of phosphininium cation, was also fully rationalized by DFT calculations.

Table 5 Calculated aromatic stabilization energy of compounds **I**, **II**, **III** and **IV**

X	**I**[a] LP	**II**[a] Me$^+$	**III** O	**IV** S
ASE/kcal mol^{-1}	28.09	27.87	29.42	29.22
NICS (1 Å)	−10.78	−11.47	−10.04	−9.87

[a] See ref. 5.



Scheme 5 Calculated reaction profile of Diels–Alder reaction on phosphinine sulfide **IV** (energies, zero-point energy (ZPE) corrected, are in kcal mol^{-1}).

Experimental

General remarks

All reactions were routinely performed under an inert atmosphere of argon or nitrogen by using Schlenk and glove-box techniques and dry deoxygenated solvents. Dry toluene was distilled over metallic Na. Nuclear magnetic resonance spectra were recorded on a Bruker AC-200 SY spectrometer operating at 300.0 MHz for ^{1}H, 75.5 MHz for ^{13}C and 121.5 MHz for ^{31}P. Solvent peaks were used as internal reference relative to Me_4Si for ^{1}H and ^{13}C chemical shifts (ppm); ^{31}P chemical shifts are relative to a 85% H_3PO_4 external reference. Coupling constants are given in Hertz. The following abbreviations are used: s, singlet; d, doublet; t, triplet; m, multiplet; bs, broad singlet. Phosphinines **1** and **2** were prepared following procedures described in refs. 6 and 7. Elemental analyses were performed by the "Service d'analyses du CNRS" at Gif sur Yvette.

Syntheses

Synthesis of 2,3,5,6-tetraphenylphosphinine-1-sulfide (3). A slight excess of sulfur (24 mg, 1.5 eq.) was added to a solution of phosphinine **1** (200 mg, 0.5 mmol) in toluene (4 mL). This solution was heated for 1 week at 100 °C. Completion of the reaction was confirmed by ^{31}P NMR spectroscopy. Upon cooling the resulting yellow mixture to room temperature, a pale yellow solid precipitated. Solvent was removed and the yellow solid was washed with hexanes (3 × 5 mL). The compound was isolated as a pale yellow powder (203 mg, 94%). δ_H (300.0 MHz, $CDCl_3$; Me_4Si) 7.11 (d, $^{4}J_{H-P}$ = 7.4 Hz, 1 H, H_4), 7.13–7.29 (m, 20 H, CH of phenyls). δ_C (75.5 MHz, $CDCl_3$; Me_4Si) 124.56 (d, J_{P-C} = 27.8 Hz, CH of phenyls), 127.65 (s, CH of phenyls), 127.75 (d, J_{P-C} = 2.6 Hz, CH of phenyls), 128.07 (s, CH of phenyls), 128.23 (d, J_{P-C} = 1.19 Hz, CH of phenyls), 129.47 (s, CH of phenyls), 131.65 (d, J_{P-C} = 9.0 Hz, C_4H), 135.00 (d, J_{P-C} = 5.3 Hz, C_3), 139.15 (d, J_{P-C} = 76.6 Hz, C_2), 141.15 (d, J_{P-C} = 13.9 Hz, C_{ipso} of *ortho* phenyls), 151.34 (s, C_{ipso} of *meta* phenyls). δ_P (121.5 MHz, $CDCl_3$; H_3PO_4 85% as external reference) 159.37 (s). Anal. Found: C, 80.81; H, 4.97. Calc. for $C_{29}H_{21}PS$: C, 80.53; H, 4.89%.

Synthesis of 3,5-diphenyl-2,6-bistrimethylsilylphosphinine-1-sulfide (4). A slight excess of sulfur (24 mg, 1.5 eq.) was added to a solution of phosphinine **2** (200 mg, 0.51 mmol) in toluene (2 mL). This solution was heated for 5 days at 90 °C. Completion of the reaction was confirmed by ^{31}P NMR spectroscopy. Solvent was removed and the yellow solid obtained was washed with hexanes (3 × 5 mL). **4** was isolated as a pale yellow powder (197 mg, 91%). δ_H (300.0 MHz, $CDCl_3$; Me_4Si) 0.162 (s, 18 H, $Si(CH_3)_3$), 6.69 (d, $^{4}J_{H-P}$ = 3.9 Hz, 1 H, H_4), 7.24–7.28, 7.35–7.37 (m, 10 H, CH of phenyls). δ_C (75.5 MHz, $CDCl_3$; Me_4Si) 1.50 (d, $^{3}J_{P-C}$ = 3.2 Hz, $Si(CH_3)_3$), 124.45 (d, $^{3}J_{P-C}$ = 43.0 Hz, C_4H), 128.16, 128.19, 128.65 (3 s, phenyls CH), 134.90 (d, J_{P-C} = 19.4 Hz, C_2-TMS), 145.04 (d, J_{P-C} = 5.3 Hz, C_3-Ph), 159.87 (d, J_{P-C} = 9.3 Hz, C_{ipso} of phenyls). δ_P (121.5 MHz, $CDCl_3$; H_3PO_4 85% as external reference) 191.61 ppm (s). Anal. Found: C, 64.81; H, 6.99. Calc. for $C_{23}H_{29}PSSi_2$: C, 65.05; H, 6.88%.

X-Ray crystallographic study

Crystals of **3** and **4** were obtained by cooling at −20 °C a solution of the corresponding phosphinine sulfide in toluene. Data were collected on a Nonius Kappa CCD diffractometer using a Mo-Kα (λ = 0.71070 Å) X-ray source and a graphite monochromator at 150 K. The crystal structures were solved using SIR 97 [16] and SHELXL-97.[17] ORTEP drawings were made using ORTEP III for Windows.[18] CCDC reference numbers 637688 (**2**), 637689 (**3**) and 637690 (**4**). For crystallographic data in CIF or other electronic format see DOI: 10.1039/b702851b

Crystal data for 3. $C_{29}H_{21}PS$, M = 432.49, orthorhombic, space group $P2_12_12_1$, a = 6.240(1), b = 12.986(1), c = 27.663(1) Å, U = 2241.6(4) $Å^3$, T = 150.0 K, Z = 4, μ(Mo-Kα) = 0.230 cm^{-1}, 5058 reflections measured, 5058 unique, 4217 used; R_1 = 0.0384, wR_2 = 0.0990.

Crystal data for 4. $C_{23}H_{29}PSSi_2$, M = 3397.46, orthorhombic, space group $Pbcn$, a = 17.932(1), b = 12.292(1), c = 20.981(1) Å, U = 4624.6(5) $Å^3$, T = 150.0 K, Z = 8, μ(Mo-Kα) = 0.3190 cm^{-1}, 19 073 reflections measured, 5271 unique, 4326 used; R_1 = 0.0332, wR_2 = 0.0998.

Computational details

Geometrical optimisations, as well as the [4 + 2] cycloaddition energetic pathways were computed at the B3LYP/6-311+G(d,p) level of theory[19] within the DFT framework using the Gaussian 03 program package.[20] A vibrational analysis was done to characterise stationary points and transition structures and thereby estimate their zero-point vibrational energies (ZPEs). The aromatic stabilisation energy (ASE) of compounds **III** and **IV** was calculated by optimising each reactant and product of the reaction presented in Scheme 4 at the B3LYP/6-311+G(d,p). This ASE equation, which considers the different isomers of dihydro- and tetrahydrophosphinine compounds, compensates for ring strain.[13] The values calculated were ZPE corrected. The aromatic character was also evaluated for **III** and **IV** by computing the nucleus independent chemical shift 1 Å above the ring center according to the method developed by Schleyer (NICS, RHF/6-311+G**).[14]

Acknowledgements

The CNRS and the Ecole Polytechnique are acknowledged for supporting this work. We thank IDRIS (Orsay, Paris XI, project No. 71616) for the allowance of computer time. This research was partially supported by the Improving Human Potential Programme, Access to Research Infrastructures under contract HPRI-1999-00071, "Access to CESCA and CEPBA Large-Scale Facilities" established between the European Community and CESCA-CEPBA. The Spanish "Dirección General de Investigación" (Project BQU2002-04110-CO2-02) is also acknowledged.

References

1 (*a*) N. Mezailles and P. Le Floch, *Curr. Org. Chem.*, 2006, **10**, 3–25; (*b*) N. Mézailles, F. Mathey and P. Le Floch, *Prog. Inorg. Chem.*, 2001, **49**, 455.
2 (*a*) P. Le Floch, *Coord. Chem. Rev.*, 2006, **250**, 627–681; (*b*) P. Le Floch, D. Carmichael and F. Mathey, in *Synthetic Methods of Organometallic and Inorganic Chemistry, Hermann/Bramuer*, ed. W. A. Hermann, Georg Thieme Verlag, New York, 1996, vol. 3, p. 167; (*c*) H. Trauner, P. Le Floch, J. M. Lefour, L. Ricard and F. Mathey, *Synthesis*, 1995, 717–726; (*d*) P. Rosa, N. Mezailles, F. Mathey and P. Le Floch, *J. Org. Chem.*, 1998, **63**, 4826–4828; (*e*) X. Sava, N. Mezailles, N. Maigrot, F. Nief, L. Ricard, F. Mathey and P. Le Floch, *Organometallics*, 1999, **18**, 4205–4215; (*f*) F. Mathey, in *Phosphorus–Carbon Heterocyclic Chemistry: The Rise of a New Domain*, ed. F. Mathey, Pergamon, Palaiseau, 2001, pp. 753–772.
3 (*a*) J. M. Alcaraz and F. Mathey, *J. Chem. Soc., Chem. Commun.*, 1984, 508–509; (*b*) J. M. Alcaraz and F. Mathey, *Tetrahedron Lett.*, 1984, **25**, 4659–4662; (*c*) J. M. Alcaraz and F. Mathey, *Tetrahedron Lett.*, 1984, **25**, 4659–4662; (*d*) P. Le Floch, D. Carmichael and F. Mathey, *Organometallics*, 1991, **10**, 2432–2436; (*e*) P. Le Floch, D. Carmichael and F. Mathey, *Phosphorus, Sulfur Silicon Relat. Elem.*, 1993, **76**, 293–296; (*f*) P. Le Floch, D. Carmichael, L. Ricard and F. Mathey, *J. Am. Chem. Soc.*, 1991, **113**, 667–669; (*g*) P. Le Floch, D. Carmichael, L. Ricard, F. Mathey, A. Jutand and C. Amatore, *Organometallics*, 1992, **11**, 2475–2479.
4 (*a*) D. G. Holah, A. N. Hughes and K. L. Knudsen, *J. Chem. Soc., Chem. Commun.*, 1988, 493–495; (*b*) S. Holand, J. M. Alcaraz, L. Ricard and F. Mathey, *Heteroat. Chem.*, 1990, **1**, 37.
5 A. Moores, L. Ricard and P. Le Floch, *Angew. Chem., Int. Ed.*, 2003, **42**, 4940–4944.
6 M. Doux, N. Mézailles, L. Ricard and P. Le Floch, *Eur. J. Inorg. Chem.*, 2003, 687.
7 (*a*) A. Moores, L. Ricard, P. Le Floch and N. Mézailles, *Organometallics*, 2003, **22**, 1960–1966; (*b*) N. Avarvari, P. Le Floch and F. Mathey, *J. Am. Chem. Soc.*, 1996, **118**, 11978–11979; (*c*) N. Avarvari, P. Le Floch, L. Ricard and F. Mathey, *Organometallics*, 1997, **16**, 4089–4098.
8 P. W. Codding and K. A. Kerr, *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.*, 1978, **34**, 3785.
9 A. E. Reed, L. A. Curtiss and F. Weinhold, *Chem. Rev.*, 1988, **88**, 899–926.
10 (*a*) K. Dimroth, O. Schaffer and A. Chatzida, *Angew. Chem., Int. Ed. Engl.*, 1972, **11**, 506; (*b*) K. Dimroth, K. Vogel and U. Schoeler, *Angew. Chem., Int. Ed. Engl.*, 1968, **7**, 371; (*c*) A. Hettche and K. Dimroth, *Chem. Ber./Recl.*, 1973, **106**, 1001–1011.
11 G. Frison, A. Sevin, N. Avarvari, F. Mathey and P. Le Floch, *J. Org. Chem.*, 1999, **64**, 5524–5529.
12 H. A. Bent, *Chem. Rev.*, 1961, **61**, 275–311.
13 (*a*) P. V. Schleyer, H. Freeman, J. Jiao and B. Goldfuss, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 337–340; (*b*) L. Nyulaszi, *Chem. Rev.*, 2001, **101**, 1229–1246; for comparison benzene exhibits an ASE of 32.2 kcal mol^{-1}.
14 P. V. Schleyer, C. Maerker, A. Dransfeld, H. J. Jiao and N. J. Hommes, *J. Am. Chem. Soc.*, 1996, **118**, 6317–6318.
15 (*a*) N. Mezailles, L. Ricard, F. Mathey and P. Le Floch, *Eur. J. Inorg. Chem.*, 1999, 2233–2241; (*b*) S. Welfele, N. Mezailles, N. Maigrot, L. Ricard, F. Mathey and P. Le Floch, *New J. Chem.*, 2001, **25**, 1264–1268; (*c*) O. Piechaczyk, M. Doux, L. Ricard and P. le Floch, *Organometallics*, 2005, **24**, 1204–1213.
16 *SIR97*, an integrated package of computer programs for the solution and refinement of crystal structures using single crystal data: A. Altomare, M. C. Burla, M. Camalli, G. L. Cascarano, C. Giacovazzo, A. Guagliardi, A. G. G. Moliterni, G. Polidori and R. Spagna, *J. Appl. Crystallogr.*, 1999, **32**, 115.
17 G. M. Sheldrick, *SHELXL-97*, Universität Göttingen, Göttingen, Germany, 1997.
18 L. J. Farrugia, *ORTEP-3*, Department of Chemistry, University of Glasgow.
19 (*a*) M. M. Francl, W. J. Pietro, W. J. Hehre, J. S. Binkley, M. S. Gordon, D. J. Defrees and J. A. Pople, *J. Chem. Phys.*, 1982, **77**, 3654–3665; (*b*) J. P. Perdew, *Phys. Rev. B*, 1986, **33**, 8822–8832; (*c*) A. D. Becke, *Phys. Rev. A: At., Mol., Opt. Phys.*, 1988, **38**, 3098–3108.
20 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. G. Johnson, W. Chen, M. W. Wong, C. Gonzalez and J. A. Pople, *GAUSSIAN 03 (Revision C.02)*, Gaussian, Inc., Wallingford, CT, 2004.