

Phosphininium Compounds

A 1-Methyl-Phosphininium Compound: Synthesis, X-Ray Crystal Structure, and DFT Calculations**

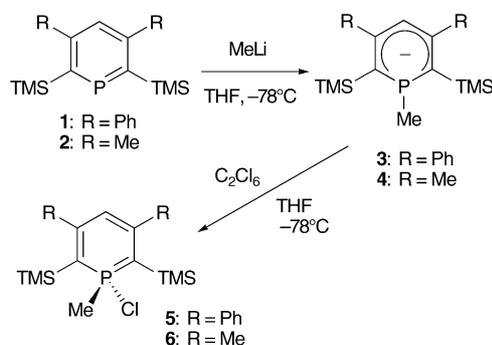
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It is well established that the replacement of nitrogen by phosphorus in aromatic structures results in profound modifications of electronic properties.^[1] One of the most representative examples is provided by phosphinines, the phosphorus equivalent of pyridines. In these heterocycles, the lone pair at the phosphorus center, which features a significant amount of 3s character (63.8% vs 29.1% in pyridine), is only weakly basic.^[2] Conversely, phosphinines are relatively inert towards electrophilic attacks at the phosphorus atom. An illustration of this peculiar electronic situation is given by several unsuccessful attempts to produce 1-R-phosphininium (R = alkyl, aryl, or H). For example, direct protonation of phosphorus with CF₃SO₃H did not yield the expected 1-H-phosphininium and the gas-phase proton affinity of phosphinine, determined by ion-cyclotron resonance techniques, was found to be slightly higher than that of PH₃.^[3,4]

Though phosphininiums were thought to be involved as intermediates in many transformations leading to λ⁵-phosphinines, only a few data are available on their structure, reactivity, and electronic properties.^[5] In 1984, Dimroth and co-workers reported the successful preparation of a 1-phenylphosphininium, from the reaction of AlCl₃ with a λ⁵-1-phenyl-1-fluorophosphinine, but this compound was only partially characterized (³¹P and ¹H NMR spectroscopy).^[6] In view of the potential synthetic utility of phosphininium compounds in heterocyclic phosphorus chemistry, we reinvestigated their

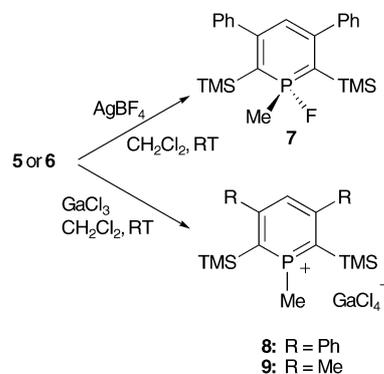
synthesis. Herein, we report the characterization by NMR spectroscopy and X-ray crystallography of a 1-methylphosphininium gallium tetrachloride adduct and its electronic structure.

λ⁵-1-methyl-1-chlorophosphinines **5** and **6** were chosen as starting precursors for this study. Their syntheses rely on the oxidation of anions **3** and **4** that were conventionally produced by treating methyllithium with phosphinines **1**^[7] and **2**,^[8] respectively (Scheme 1).^[9]


Scheme 1. Synthesis of compounds **5** and **6**. TMS = SiMe₃.

We tried to duplicate the strategy reported by Dimroth and co-workers, and therefore compounds **5** and **6** were treated with AlCl₃ in CH₂Cl₂ at room temperature. In both cases, a reaction took place and the ³¹P NMR spectrum showed broad signals at δ = 133.5 and 137.0 ppm, respectively. Suspecting that an exchange could occur between the counterion AlCl₄⁻ and the phosphininium, we investigated the use of different reagents as chloride abstractor (AgBF₄, AgBPh₄, TIBPh₄ and GaCl₃). Whereas no reaction occurred when **5** or **6** were treated with tetraphenylborate salts, treatment of **5** with AgBF₄ resulted in the exchange of the halogen atom at phosphorus to afford the fluoro derivative **7**. More convincing results were obtained when **5** and **6** were treated with GaCl₃ in CH₂Cl₂ at room temperature. In both cases, a clean reaction took place to produce 1-methylphosphininium compounds **8** and **9** which were isolated as moisture sensitive powders (Scheme 2).

Both compounds were successfully characterized by NMR spectroscopy and elemental analysis. The formation of the


Scheme 2. Synthesis of compounds **7**, **8**, and **9**.

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phosphininium is evidenced by a strong downfield shift in ^{31}P NMR (from $\delta = 63.7$ in **5** to $\delta = 160.2$ ppm for **8** and from $\delta = 64.7$ in **6** to $\delta = 156.9$ ppm for **9**). The aromaticity of the ring is also apparent in the ^{13}C NMR spectra from the chemical shifts of the C2 and C4 carbon atoms that are strongly deshielded (from $\delta = 88.8$ in **5** to $\delta = 140.3$ in **8** for C2 and from $\delta = 117.4$ to $\delta = 134.7$ for C4). The formulation of **8** was definitively established by an X-ray crystal-structure analysis.^[10] A view of one molecule of **8** is presented in Figure 1. The structure consists of two discrete units contain-

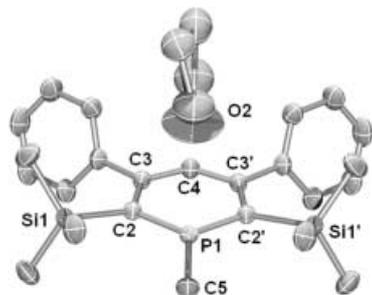
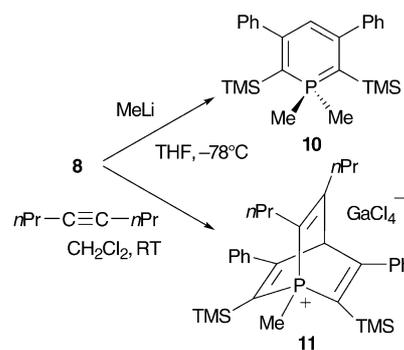


Figure 1. Molecular structure of **8** without hydrogen atoms. Selected bond lengths [Å] and angles [°]: P1-C2 1.697(2), C2-C3 1.415(3), C3-C4 1.407(2), Si1-C2 1.921(2), P1-C5 1.790(3); C2-P1-C2' 117.7(1), C2-P1-C5 120.80(6), P1-C2-C3 113.1(1), C2-C3-C4 24.7(2), C3-C4-C3' 126.5(2).

ing the phosphininium cation, the GaCl_4^- ion and two molecules of THF. One THF molecule is located far away above the ring (P–O separation: 3.174(5) Å), the oxygen atom pointing in the direction of the phosphorus atom. The phosphinine ring is not rigorously planar and both phosphorus and the C4 carbon atoms escape from the mean plane (C2-C3-C3'-C2') by 3.8° and 1.7°, respectively. But, the most significant data are given by the internal bond distances which are significantly modified in comparison to those of a λ^3 -phosphinine: the two internal P–C bond lengths are significantly shortened from 1.734(5) Å in the reference compound^[11] to 1.697(2) Å in **8**,^[12] whilst the internal C2-P1-C2' angle changes from 106.3(2)° to 117.7(1)°. These two pieces of data clearly suggest that the phosphorus atom has gained a significant amount of sp^2 character. This result is peculiar as it has always been believed that phosphorus could not undergo such a rehybridization within a six-membered ring, which accounted for the low basicity of phosphinine moieties.^[4,13]

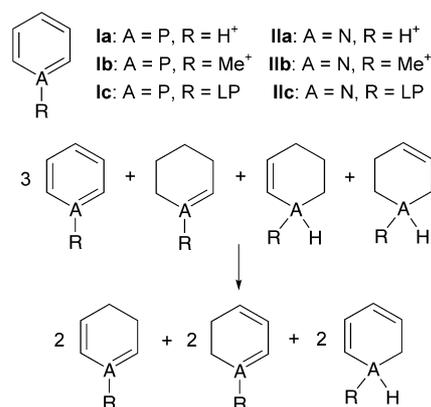
Phosphininium intermediates are known to be highly reactive towards nucleophiles and we found that compound **8** rapidly reacts with methyllithium in THF at low temperature to afford the λ^5 -dimethylphosphinine **10** (Scheme 3). We also found that the dienic character of the ring is significantly enhanced compared to λ^3 -phosphinines. Reaction of **8** with 4-octyne at room temperature for 24 h cleanly yielded the phosphabarrelenium salt **11** which was isolated as beige solid and fully characterized by NMR spectroscopy and elemental analysis (Scheme 3).

A theoretical study was undertaken; calculations were carried out on the unsubstituted 1-H **Ia** and 1-Me- **Ib** derivatives by using a combination of the B3LYP functional with the 6-311 + G(d,p) basis set.^[14] The calculated geometry



Scheme 3. Reactivity of phosphoninium **8**.

of **Ib** was found to be close to that of the experimental structure. The shortening of the two P=C bonds (1.698 Å in **Ib** vs 1.743 Å in the parent phosphinine **Ic**; Scheme 4) as well as the widening of the internal angle C2-P1-C2' angle (110.67° in **Ib** vs 100.02° in **Ic**) are reproduced.^[15] An NBO analysis^[16] reveals that the phosphorus atom bears a significant positive charge (1.017 in **Ia** and 1.285 in **Ib** vs 0.642 in **Ic**) and has gained a substantial sp^2 character. Thus the contribution of



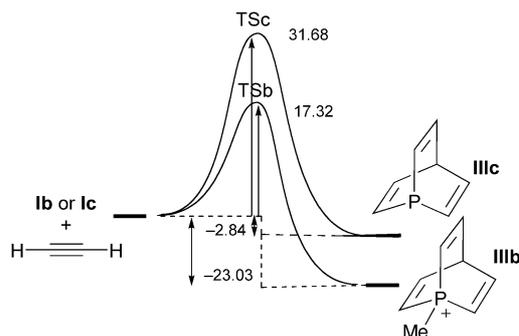
Scheme 4. Structures used as the basis for calculations and the aromatic stabilization energy equation; LP = lone pair.

the 3s orbital in a P–C bond changes from 19.42% in **Ic** to 33.30% in **Ib**. Useful data were obtained by calculating the ASE (aromatic stabilization energy) using the equation depicted in Scheme 4.^[17] To draw an efficient comparison, similar calculations were also carried out on the 1-H **IIa**, 1-Me **IIb** pyridinium cations and pyridine **IIc**. Nuclear independent chemical shift (NICS; *N*-iodosuccinimide) at 1 Å above the ring were calculated at the 6-311 + G** level (Table 1).^[18] The aromaticity of the phosphininium is close to that of the free phosphinine (94.3% in **Ia** and 99.2% in **Ib**). On the contrary, the two pyridiniums were found to be slightly more aromatic than pyridine (109.3% in **IIa** and 105.9% in **IIb**). NICS values do not reproduce exactly the same trends, but confirm the strong aromaticity of the six molecules. In view of these data, it seems evident that the high reactivity of **8** towards 4-octyne does not result from a disruption of aromaticity within the ring. Therefore, the reaction paths of the [4+2] cycloaddition

Table 1: Calculated aromatic stabilization energy of compound **Ia–c**, **IIa–c**.

Compound	Ia	Ib	Ic	IIa	IIb	IIc
ASE [kcal mol ⁻¹] ZPE corrected	26.5	27.87	28.09	32.29	31.29	29.55
NICS (1 Å)	-11.6128	-11.4749	-10.7827	-10.7212	-10.7446	-11.1321

process of **Ib** and **Ic** with acetylene (to give **IIIb** and **IIIc**) were modeled (Figure 2). These calculations which were conducted at the B3LYP6-311 + G(d,p) level of theory indicate that the formation of the phosphabarrelene is strongly exothermic (-23.03 kcal mol⁻¹ and only requires a weak activation energy


Figure 2. Calculated reaction profile of Diels–Alder reaction on phosphinine or phosphinium (energies, zero-point energy (ZPE) corrected, are in kcal mol⁻¹).

($E_{\text{TSb}} = 17.32$ kcal mol⁻¹; TS = transition state). In good agreement with experimental data, the formation of the phosphabarrelene from **Ic** is only weakly exothermic and involves a high activation barrier ($E_{\text{TSc}} = 31.68$ kcal mol⁻¹).

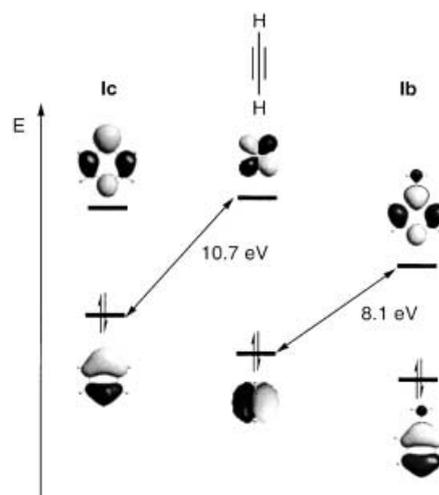
These results are fully consistent with the relative energies of frontier orbitals in **Ib** and **Ic** (calculated at the MP2/6-311 + G(d,p) level of theory using B3LYP geometries). As expected, the introduction of a methyl group at the phosphorus atom does not modify the shape of frontier orbitals, which, having a π symmetry, can not interact with methyl group molecular orbitals (MOs). On the contrary, energies of the MOs are significantly lowered because of orbital contraction. As can be seen in Figure 3, reaction of **Ic** with acetylene is a classical [4+2] cycloaddition process in which the phosphinine acts as the diene and reacts through its HOMO. On the contrary, in phosphinium **Ib** its low-lying LUMO reacts with the HOMO of the alkyne (inverse electron demand process).

In conclusion, we have established the existence of 1-methyl-phosphinium compounds. We believe that these cations will find interesting applications in the synthesis of new phosphorus heterocycles.

Experimental Section

All work was carried out under nitrogen or argon using Schlenk techniques. The solvents used were freshly distilled, dried, and saturated with nitrogen or argon.

5: A solution of MeLi in diethyl ether (80 μ L, 0.127 mmol, 1.6 M) was added to a solution of 50 mg of phosphinine (**1** or **2**, 0.127 mmol)


Figure 3. Shape and level of frontier orbitals of phosphinine, phosphinium, and acetylene.

in THF (2 mL) at -78°C . The solution turned from colorless to red and was warmed to room temperature. Completion of the reaction was checked by ^{31}P NMR spectroscopy. Hexachloroethane (30 mg, 0.127 mmol) was added at -78°C . The solution was warmed to room temperature, solvent was removed in vacuo, and the resulting brown solid was extracted with hexane (3×2 mL). The product was recovered as a yellow oil, yield 49 mg (87%); **5** was too air sensitive to give satisfactory elemental data. Selected data: ^1H NMR (300 MHz, C_6D_6 , 25°C): $\delta = 0.14$ (s, 18H, $\text{Si}(\text{CH}_3)_3$), 2.51 (d, $^2J(\text{H,P}) = 15.7$ Hz, 3H, PCH_3), 6.07 (d, $^4J(\text{H,P}) = 4.7$ Hz, 1H, H4), 7.01–7.30 ppm (m, 10H, Ph); ^{31}P NMR (121.5 MHz, C_6D_6 , 25°C , 85% H_3PO_4 as external standard): $\delta = 63.7$ ppm (s).

6: A solution of MeLi in diethyl ether (100 μ L; 0.149 mmol, 1.6 M) was added to a solution of phosphinine (40 mg 0.149 mmol) in hexane (2 mL) at -78°C . The solution turned from colorless to bright yellow. The solution was warmed to room temperature and completion of the reaction was checked by ^{31}P NMR spectroscopy. Hexachloroethane (35 mg, 0.149 mmol) was added at -78°C . The solution was warmed to room temperature, solvent was removed in vacuo, and the solution filtered to remove the salts. The product was recovered from the filtrate as a yellow oil, yield 38 mg (80%); **6** was too air sensitive to give satisfactory elemental data. Selected data: ^1H NMR (300 MHz, C_6D_6 , 25°C): $\delta = 0.39$ (s, 18H, $\text{Si}(\text{CH}_3)_3$), 2.12 (d, $^4J(\text{H,P}) = 0.9$ Hz, 6H, C3- CH_3), 2.24 (d, $^2J(\text{H,P}) = 16.3$ Hz, 3H, PCH_3), 5.67 ppm (d, $^4J(\text{H,P}) = 5.0$ Hz, 1H, H4); ^{31}P NMR (121.5 MHz, C_6D_6 , 25°C , 85% H_3PO_4 as external standard): $\delta = 64.69$ ppm (s).

7: AgBF_4 (22 mg, 0.111 mmol) was added to a solution of **5** (0.111 mmol, 49 mg) in THF (2 mL) at room temperature. This solution was stirred for 24 h. Completion of the reaction was checked by ^{31}P NMR spectroscopy. Solvent was removed in vacuo and the resulting brown solid was extracted with hexane (3×2 mL). The product was recovered as a pale brown oil, yield 35 mg (74%); **7** was too air sensitive to give satisfactory elemental data. Selected data: ^1H NMR (300 MHz, C_6D_6 , 25°C): $\delta = 0.11$ (s, 18H, $\text{Si}(\text{CH}_3)_3$), 1.96 (d, $^2J(\text{H,P}) = 14.7$ Hz, 3H, PCH_3), 5.90 (dd, $^4J(\text{H,P}) = 7.0$ Hz, $^5J(\text{H,P}) = 0.6$ Hz, 1H, H4), 7.04–7.31 ppm (m, 10H, Ph); ^{31}P NMR (121.5 MHz,

THF, 25°C 85% H₃PO₄ as external standard): δ = 80.09 ppm (d, ¹J(P,F) = 1043.2 Hz).

8: A solution of GaCl₃ (21 mg, 0.119 mmol) in CH₂Cl₂ (1 mL) was added to a solution of **5** (48 mg, 0.108 mmol) in CH₂Cl₂ (2 mL) room temperature. After stirring for 5 min, solvent was removed and, the product was recovered as a beige powder, yield 62 mg (93%). Crystallization of **8** at -18°C in a mixture of CH₂Cl₂ and hexane afforded colorless crystals. Elemental analysis (%) calcd: C 46.55, H 5.21; found: C 46.53, H 5.22; ¹H NMR (300 MHz, C₆D₆, 25°C): δ = 0.21 (s, 18H, Si(CH₃)₃), 3.20 (d, ²J(H,P) = 20.8 Hz, 3H, PCH₃), 7.32–7.48 (m, 10H, Ph), 7.63 ppm (d, ⁴J(H,P) = 6.1 Hz, 1H, H4); ¹³C NMR (75.5 MHz, C₆D₆, 25°C): δ = 1.68 (d, ³J(C,P) = 3.4 Hz, Si(CH₃)₃), 12.77 (d, ¹J(C,P) = 51.5 Hz, PCH₃), 128.46 (s, *o*-C of Ph), 128.54 (s, *m*-C of Ph), 129.40 (s, *p*-C of Ph), 134.72 (d, ³J(C,P) = 51.3 Hz, C4), 140.34 (d, ¹J(C,P) = 22.4 Hz, C2-TMS), 142.29 (d, ²J(C,P) = 18.9 Hz, C3), 162.45 ppm (d, ³J(C,P) = 14.9 Hz, C_{ipso} of Ph); ³¹P NMR (121.5 MHz, THF, 25°C, 85% H₃PO₄ as external standard): δ = 160.23 ppm (s).

9: A solution of GaCl₃ (23 mg, 0.131 mmol) in CH₂Cl₂ (1 mL) was added to a solution of **6** (38 mg, 0.119 mmol) in CH₂Cl₂ (2 mL) at room temperature. After stirring for 5 min, solvent was removed and the product was recovered as a light brown powder, yield 52 mg (88%). Elemental analysis (%) calcd: C 33.97; H 5.70; found: C 33.93, H 5.68; ¹H NMR (300 MHz, C₆D₆, 25°C): δ = 0.55 (s, 18H, Si(CH₃)₃), 2.71 (d, ²J(H,P) = 2.4 Hz, 3H, PCH₃), 3.03 (d, ²J(H,P) = 20.9 Hz, 3H, PCH₃), 7.50 ppm (d, ⁴J(H,P) = 6.1 Hz, 1H, H4); ¹³C NMR (75.5 MHz, C₆D₆, 25°C): δ = 0.97 (d, ³J(C,P) = 3.7 Hz, Si(CH₃)₃), 10.91 (d, ¹J(C,P) = 53.6 Hz, PCH₃), 26.92 (d, ¹J(C,P) = 17.1 Hz, PCH₃), 134.72 (d, ³J(C,P) = 53.2 Hz, C4), 136.46 (d, ²J(C,P) = 30.2 Hz, C2), 158.94 ppm (d, ²J(C,P) = 15.4 Hz, C3); ³¹P NMR (121.5 MHz, THF, 25°C, 85% H₃PO₄ as external standard): δ = 156.86 ppm (s).

10: MeLi in diethyl ether (70 μ L; 0.111 mmol, 1.6 M) was added to a crude solution of **8** (0.111 mmol) in THF at -78°C. The solution was stirred for 10 min, then allowed to warm to room temperature, solvent was removed in vacuo, and the product extracted in hexane (2 \times 2 mL) and recovered as a pale yellow powder, yield 41 mg (88%). Selected data: elemental analysis (%) calcd for: C 71.04, H 8.35; found: C 71.07, H 8.36; ¹H (300 MHz, C₆D₆, 25°C): δ = -0.06 (s, 18H, Si(CH₃)₃), 1.29 (d, ²J(H,P) = 12.1 Hz, 6H, PCH₃), 5.57 (d, ⁴J(H,P) = 1.5 Hz, 1H, H4), 7.02–7.35 ppm (m, 10H, Ph); ³¹P (121.5 MHz, C₆D₆, 25°C 85% H₃PO₄ as external standard): δ = 10.5 ppm (s).

11: An equimolar amount of dried 4-octyne (17 μ L, 0.111 mmol) was added to a crude solution of **8** (0.111 mmol) in CH₂Cl₂. The resulting mixture was stirred at room temperature in the glove box for 24 h. After removing of the solvent in vacuo, the product was recovered as a beige powder, yield 71 mg (86%). Selected data: elemental analysis (%) calcd for: C 53.32, H 6.51; found: C 53.28, H 6.51; ¹H NMR (300 MHz, CD₂Cl₂, 25°C): δ = 0.04 (s, 18H, Si(CH₃)₃), 0.78 (t, ³J(H,H) = 7.3 Hz, 3H, CH₃ of propyl), 0.92 (t, ³J(H,H) = 7.3 Hz, 3H, CH₃ of propyl), 1.12–1.23 (m, 2H, CH₂ of propyl), 1.41–1.50 (m, 2H, CH₂ of propyl), 2.34–2.39 (m, 2H, CH₂ of propyl), 2.45–2.58 (m, 2H, CH₂ of propyl), 2.70 (d, ²J(H,P) = 13.9 Hz, 3H, PCH₃), 5.52 (d, ⁴J(H,P) = 6.0 Hz, 1H, H4) 6.93–7.00 (m, 5H, Ph), 7.32–7.48 ppm (m, 5H, Ph); ³¹P (121.5 MHz, CD₂Cl₂, 25°C 85% H₃PO₄ as external standard): δ = 4.36 ppm (s).

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Keywords: aromaticity · density functional calculations · Diels–Alder reactions · phosphinium compounds · phosphorus

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