

Phosphorus Lone Pairs Stabilization of Carbocations: the Synthesis and Dynamics of Unsymmetrical Methylene Phosphonium Ions

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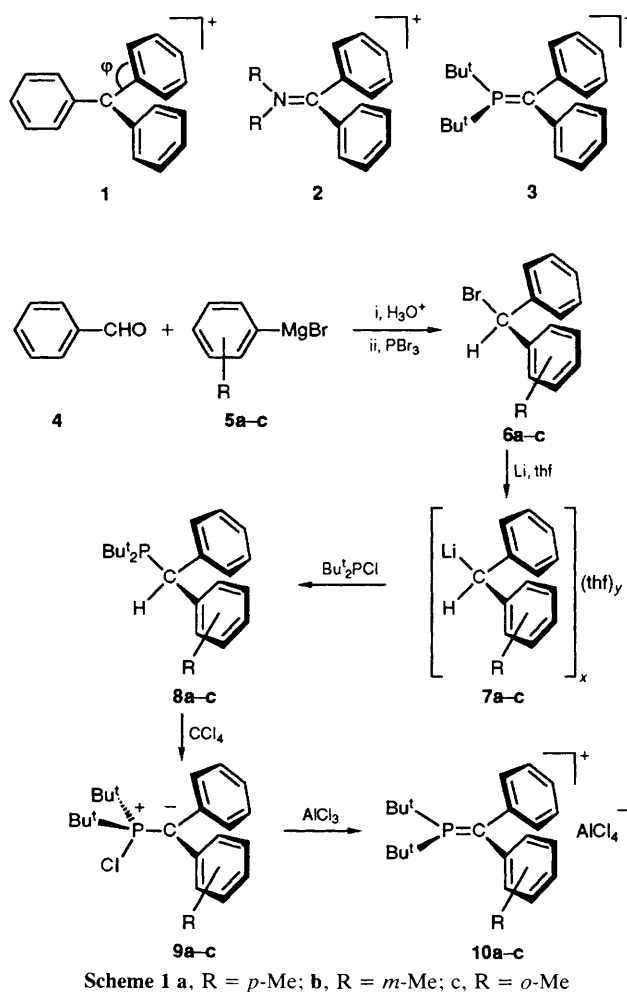
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Halide abstractions from P-chlorinated phosphorus ylides **9a–c** either by AlCl_3 or SnCl_2 yield unsymmetrical methylene phosphonium ions **10a–c** in which energy barriers $> 83 \text{ kJ mol}^{-1}$ for the rotation around the $\text{P}=\text{C}$ have been estimated by NMR techniques. The salts with AlCl_4^- counteranions are stable, but compounds with SnCl_3^- anions decompose stereoselectively to unsymmetrical methylene phosphanes, SnCl_2 , and Bu^tCl .

As early as 1901 the first stable carbocation, the triphenylmethyl cation **1** was described.¹ Its unusual stability—compared with other carbocations²—is due to delocalization of charge over 19 trigonal planar carbon atoms. Perfect conjugation is diminished by rotation of the three phenyl rings (by 30° in the solid state) against the central plane.³ Heteroatoms with a lone pair of electrons 'stabilize' carbocations by transfer of π -electron density.⁴ This is best documented for amino groups as donors; e.g. iminium ions such as **2** are versatile building blocks in organic synthesis.⁵ Methylene phosphonium ion **3**, a heavier homologue of **2**, was recently characterized.⁶ It is related to **1** by substitution of one phenyl ring for a Bu_2P group. In this new type of unsaturated organo phosphorus compound, a phosphorus atom with formal oxidation state +5 is double bonded to its neighbouring atom without violating the octet rule.⁷ In order to estimate the barrier for rotation around the $\text{P}=\text{C}$ we have now synthesized unsymmetrical methylene phosphonium salts.

The phosphanes **8a–c** were prepared in good yield using standard procedures (Scheme 1).[‡] Subsequent oxidation with CCl_4 ⁸ gives the phosphorus ylides **9a–c**. However, the reaction leading to **9c** (tetrahydrofuran, 10 equiv. CCl_4 , -78°C to room temp., 2 h) has to be controlled carefully (^{31}P NMR) in order to avoid decomposition. The attempted synthesis of the

even more sterically congested ylide $\text{Bu}_2\text{P}(\text{Cl})=\text{CPh}(\text{Mes})$ (Mes = mesityl) failed and $\text{Bu}_2\text{P}(\text{Cl})$ is obtained as the main product resulting from $\text{P}-\text{C}$ bond cleavage.⁹ The methylene phosphonium salts **10a–c** were synthesized by abstraction of chloride from ylides **9a–c** by AlCl_3 powder (10% excess) in CH_2Cl_2 at low temperatures (-78°C). After rapid filtration of the reaction mixtures below -30°C and evaporation of all volatiles in vacuum (1×10^{-3} Torr; 1 Torr = 133.32 Pa), the compounds **10a–c** were isolated as highly sensitive orange oils that crystallized slowly at -30°C . Single crystals suitable for an X-ray structure analysis§ were obtained from **10c**. A plot



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‡ Selected physical data for **8a–c**, **9a–c**, **10a–c** and **11c**: **8a**: m.p. 109–110 °C; ^{31}P NMR (CDCl_3): δ 44.9; ^1H NMR (CDCl_3): δ 1.04 (d, $^3J_{\text{PH}}$ 10.0 Hz, CH_3), 1.06 (d, $^3J_{\text{PH}}$ 9.9 Hz, CH_3), 2.28 (s, *p*- CH_3), 4.45 (d, $^2J_{\text{PH}}$ 5.0 Hz, CH), 7.05–7.607 (m, arom. CH); ^{13}C NMR (CDCl_3): δ 49.5 (d, $^1J_{\text{CP}}$ 29.3 Hz, CH). **8b**: m.p. 89–90 °C; ^{31}P NMR (CDCl_3): δ 47.9; ^1H NMR (CDCl_3): δ 1.04 (d, $^3J_{\text{PH}}$ 10.0 Hz, CH_3), 1.05 (d, $^3J_{\text{PH}}$ 10.0 Hz, CH_3), 2.34 (s, *m*- CH_3), 4.44 (d, $^2J_{\text{PH}}$ 5.1 Hz, CH), 6.80–7.70 (m, arom. CH); ^{13}C (CDCl_3): δ 50.1 (d, $^1J_{\text{CP}}$ 29.3 Hz, CH). **8c**: m.p. 73–74 °C; ^{31}P NMR (CDCl_3): δ 48.6; ^1H NMR (CDCl_3): δ 1.00 (d, $^3J_{\text{PH}}$ 10.2 Hz, CH_3), 1.04 (d, $^3J_{\text{PH}}$ 9.8 Hz, CH_3), 2.47 (s, *o*- CH_3), 4.71 (d, $^2J_{\text{PH}}$ 5.1 Hz, CH), 7.01–7.56 (m, arom. CH); ^{13}C NMR (CDCl_3): δ 43.6 (d, $^1J_{\text{CP}}$ 29.3 Hz, CH).

9a: m.p. 90–91 °C; ^{31}P NMR (CDCl_3): δ 90.4; ^1H NMR (CDCl_3): 1.35 (d, $^3J_{\text{PH}}$ 16.5 Hz, CH_3), 2.27 (s, *p*- CH_3), 7.01–7.49 (m, arom. CH); ^{13}C NMR (CDCl_3): δ 72.6 (d, $^1J_{\text{CP}}$ 104 Hz, C_{ylid}). **9b**: m.p. 91–93 °C; ^{31}P NMR (CDCl_3): δ 91.8; ^1H NMR (CDCl_3): 1.38 (d, $^3J_{\text{PH}}$ 16.4 Hz, CH_3), 2.33 (s, *m*- CH_3), 6.90–7.60 (m, arom. CH); ^{13}C NMR (CDCl_3): δ 72.8 (d, $^1J_{\text{CP}}$ 97 Hz, C_{ylid}). **9c**: m.p. 101–102 °C; ^{31}P NMR (CDCl_3): δ 85.0; ^1H NMR (CDCl_3): δ 1.36 (d, $^3J_{\text{PH}}$ 16.6 Hz, CH_3), 2.42 (d, $^5J_{\text{PH}}$ 1.7 Hz, *o*- CH_3), 7.07–7.19 (m, arom. CH); ^{13}C NMR (CDCl_3): δ 70.6 (d, $^1J_{\text{CP}}$ 104 Hz, C_{ylid}).

10a: oil; ^{31}P NMR (CD_2Cl_2): δ 179.1; ^1H NMR (CD_2Cl_2): δ 1.56 (d, $^3J_{\text{PH}}$ 18.9 Hz, CH_3), 1.58 (d, $^3J_{\text{PH}}$ 19.0 Hz, CH_3), 2.43 (d, $^7J_{\text{PH}}$ 3.6 Hz, *p*- CH_3), 7.20–7.53 (m, arom. CH); ^{13}C NMR (CD_2Cl_2): δ 179.2 (d, $^1J_{\text{PH}}$ 72 Hz, C=P). **10b**: m.p. 116–117 °C; ^{31}P NMR (CD_2Cl_2): δ 179.7; ^1H NMR (CD_2Cl_2): δ 1.58 (d, $^3J_{\text{PH}}$ 18.9 Hz), 2.40 (s, CH_3 , *m*- CH_3), 7.11–7.53 (m, arom. CH); ^{13}C NMR (CD_2Cl_2): 179.9 (d, $^1J_{\text{CP}}$ 72 Hz, C=P). **10c**: m.p. 121–122 °C; ^{31}P NMR (CD_2Cl_2): δ 184.7; ^1H NMR (CD_2Cl_2): δ 1.53 (d, $^3J_{\text{PH}}$ 18.7 Hz, CH_3), 1.62 (d, $^3J_{\text{PH}}$ 19.0 Hz, CH_3), 1.89 (d, $^5J_{\text{PH}}$ 1.9 Hz, *o*- CH_3), 7.29–7.66 (m, arom. CH); ^{13}C NMR (CD_2Cl_2): δ 180.6 (d, $^1J_{\text{CP}}$ 70 Hz, C=P).

11c: yellow oil; ^{31}P NMR (CDCl_3): δ 288.5; ^1H NMR (CDCl_3): δ 1.10 (d, $^3J_{\text{PH}}$ 10.6 Hz, CH_3), 2.12 (s, *o*- CH_3), 7.18–7.54 (aromat. CH), ^{13}C NMR (CDCl_3): δ 192.5 (d, $^1J_{\text{PH}}$ 52 Hz, C=P).

§ Crystal data for **10c**: space group $P2_1/n$, $a = 11.313(9)$, $b = 14.129(9)$, $c = 16.438(15)$ Å, $\beta = 95.34(7)^\circ$, $V = 2616$ Å³, $Z = 4$, 1631 observed reflections [$I > \sigma(I)$], four-circle diffractometer (Mo-K α radiation, ω -scan), Al, Cl, P, C anisotropic, hydrogen atoms in calculated positions, $R = 0.070$, $R_w = 0.064$. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

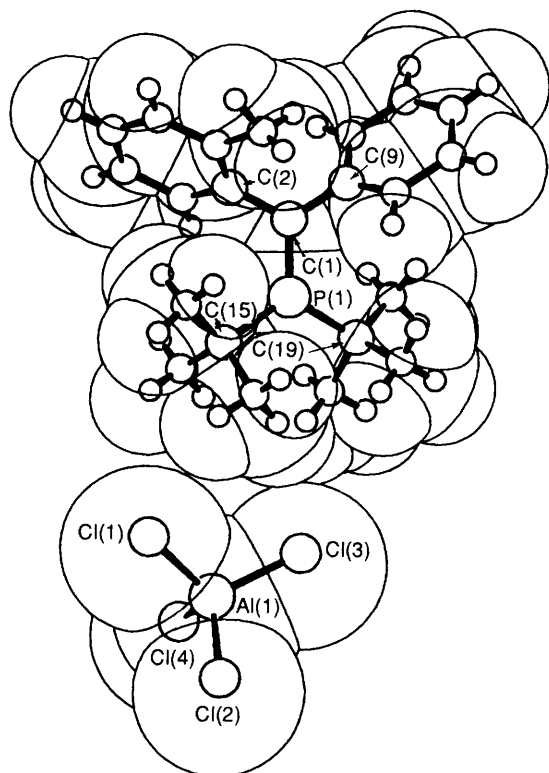
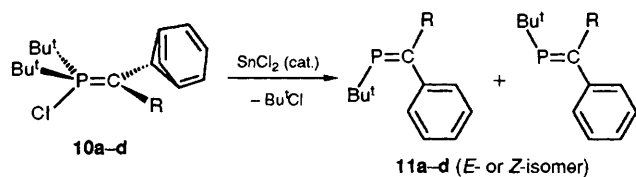


Fig. 1 Plot of the molecular structure of **10c**. Selected bond length (Å) and angles (°): P(1)–C(1) 1.680(8), P(1)–C(15) 1.870(9), P(1)–C(19) 1.868(9), C(1)–C(2) 1.464(11), C(1)–C(9) 1.470(11); C(1)–P(1)–C(15) 120.6(4), C(1)–P(1)–C(19) 120.3(4), C(19)–P(1)–C(15) 119.1(4), C(2)–C(1)–P(1) 119.4(6), C(9)–C(1)–P(1) 121.4(6), C(9)–C(1)–C(2) 119.2(7); shortest anion cation contact Cl–H 2.83 Å.

generated using van der Waals radii is shown in Fig. 1.¹⁰ The P=C is 1.680(8) Å, in good agreement with bond lengths determined previously.⁶ The trigonal planar molecular fragments [$\Sigma^\circ(\text{P}) = 360.0^\circ$; $\Sigma^\circ(\text{C}) = 360.0^\circ$] are twisted by 22° against each other. Compared with the carbocation **1**, the planes formed by the aryl rings in **10c** are more steeply orientated against the central plane [**10c**: $\phi = 56.9, 53.3^\circ$; **1**: $\phi = 33^\circ$]. Moreover, in the methylene phosphonium ion **10c**, the aryl rings are arranged almost perpendicular to each other (91.1 vs. 54° in **1**); no significant deviations of bond angles within the aryl rings as found in **1** are observed.^{2,3} The structural data already indicate that loss of resonance energy caused by the aryl ring twist in the ions must be efficiently counterbalanced by the phosphorus lone pair. This is further supported by the ^1H NMR spectra of **10a–c** at 60°C in CDCl_3 where no equilibrations of the inequivalent Bu^t groups are observed; in **10b** the resonances are not well-resolved. Above a temperature at 60°C , rapid decomposition of **10a–c** occurred. Therefore, only a lower limit of the energy barrier ΔG^\ddagger (333 K) $> 83\text{ kJ mol}^{-1}$ for rotation around the P=C can be estimated. Calculations predict rotation barriers of $\Delta G^\ddagger = 128\text{ kJ mol}^{-1}$.¹¹ These NMR experiments show that although high inversion barriers in R_2P groups (*i.e.* PH_3 : 155.6 , NH_3 : 22.3 kJ mol^{-1}) hamper π -donation, the lone pairs at the phosphorus atoms stabilize carbocations to a considerable extent.

Table 1

11	R	E-isomer (%)	^{31}P NMR/ δ	Z-isomer (%)	^{31}P NMR/ δ
a	<i>p</i> -Me- C_6H_4	50	284.5	50	289.2
b	<i>m</i> -Me- C_6H_4	56	288.0	44	28.5
c	<i>o</i> -Me- C_6H_4	97	288.5	3	292.5
d	Me_3Si	>97	329.2^a	—	—

^a Ref. 13.

P-chlorinated phosphorus ylides **10a–c** are cleanly decomposed to methylene phosphanes, $\text{Bu}^t\text{P}=\text{CR}_2$, and Bu^tCl in a first-order process ($t_{1/2}$ 3–20 min) by a catalytic amount of SnCl_2 (Scheme 3). This new method to generate methylene phosphanes involves methylene phosphonium ions as detectable intermediates (^{31}P NMR). While the stereochemical induction of *para* and *meta* methyl groups in **10a–b** is poor, methyl substitution in the *ortho* position (Fig. 1) of one phenyl group makes the reaction stereoselective (Table 1). For the ylide **10d**,¹² long reaction times are necessary to convert the ylide into **11d** (*ca.* 7 d, 75% isolated yield) but only one isomer is detected by NMR. Note that conventional methods give a much smaller excess of one isomer (*E*-isomer 75%; *Z*-isomer 25%).¹³ We are currently investigating the mechanism and scope of this promising simple way to produce low coordinated phosphorus compounds.

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