

Phosphocations with Co-ordination Number 2 and 3: Phosphenium- iminophosphonium Bisphosphocations

Marie-Rose Marre, Michel Sanchez, and Robert Wolf

Laboratoire des hétérocycles de l'azote et du phosphore, Equipe de Recherche Associée au C.N.R.S. n° 926,
Université Paul Sabatier, 31062 Toulouse Cedex, France

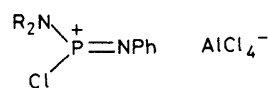
New phosphocations containing phosphorus with co-ordination number 2 and 3 and deriving from $\text{Cl}-\overset{+}{\text{P}}-\text{NR}_2 \text{AlCl}_4^-$ have been obtained: chloroiminophosphonium compounds (**2**) and the bisphosphocations (phosphenium-iminophosphoniums) (**3**).

In a prior investigation^{1a} we have shown that azides RN_3 react with the bis(dialkylamino)phosphenium compound $(\text{R}_2\text{N})_2\text{P}^+ \text{AlCl}_4^-$ to give the corresponding bis(dialkylamino)iminophosphonium $(\text{R}_2\text{N})_2\overset{+}{\text{P}}=\text{NR}$. Five cations of this latter type were described. Several experiments show that this extension of the Staudinger reaction actually occurs by reaction of the phosphenium cation and not the initial chlorophosphine $\text{Cl}-\text{P}(\text{NR}_2)_2$ which was used to prepare $(\text{R}_2\text{N})_2\text{P}^+$ by Cl^- abstraction.

To determine the scope of this new reaction, we have explored the reactivity of the chlorophospheniums $\text{Cl}-\overset{+}{\text{P}}-\text{NR}_2$ (**1**). Few such entities are known² and we used $\text{Pr}^i_2\text{N}-\overset{+}{\text{P}}-\text{Cl}$ (**1a**) and $\text{Me}_2\text{N}-\overset{+}{\text{P}}-\text{Cl}$ (**1b**). In the traditional Staudinger reaction, the replacement of the R_2N group by Cl on the trivalent phosphorus usually strongly decreases and even

inhibits the formation of iminophosphine,³ so the reaction of (**1**) with azides (RN_3) seems worthy of study.

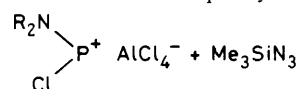
The reaction of phenyl azide on chlorophospheniums (**1**) in stoichiometric amounts, gives the expected evolution of N_2 and leads to the chloroiminophosphoniums (**2**). In the absence of accurate kinetic data, we noted qualitatively that the reaction occurs as quickly as with $(\text{R}_2\text{N})_2\text{P}^+$ cations. Com-



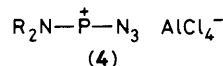
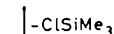
(2)

a; R = Prⁱ

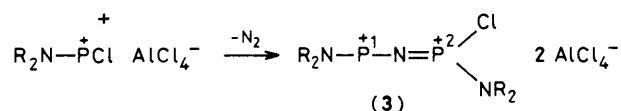
b; R = Me



(1)



(4)



(3)

a; R = Prⁱ

b; R = Me

Scheme 1

compound (**2a**) has been isolated as a solid and the structure has been well established by n.m.r. spectroscopy: ^{31}P (36.44 MHz) $\delta + 34.6$ p.p.m. (t, $^3J_{\text{P-H}}$ 25.5 Hz); ^1H (60 MHz) $\delta 1.33$ (6H, d, $^3J_{\text{H-H}}$ 7 Hz, Me_2C), 4.1 [2H, hept. d, $^3J_{\text{H-H}}$ 7, $^3J_{\text{H-P}}$ 26 Hz, $\text{N}(\text{CHMe}_2)_2$].

The course of the reaction is the same for (**1b**), giving (**2b**) which has been identified by ^{31}P n.m.r. [$\delta 43.8$ p.p.m. (hept., $^3J_{\text{P-H}}$ 15.5 Hz)], but the adduct $\text{Cl}_2(\text{Me}_2\text{N})\text{P}=\text{N}-\text{Ph}, \text{AlCl}_3$ is also present in the solution ($\delta 46$ p.p.m.).^{1b}

With trimethylsilylazide (Me_3SiN_3) the reaction of (**1**) is not predictable due to the fact that the Staudinger reaction is in competition with possible elimination of ClSiMe_3 .⁴

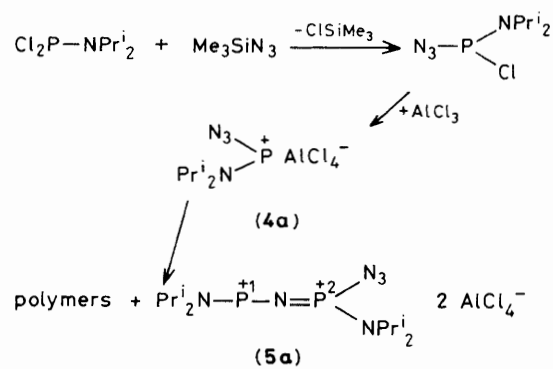
Several experiments have been performed; at room temperature, addition of Me_3SiN_3 to (**1a**) in solution (CH_2Cl_2) leads to an unexpected result: isolation of a solid and stable phosphonium-iminophosphonium cation (**3a**).

The structure of this first bisphosphocation is consistent with ^{31}P n.m.r. signals for the two kinds of P atoms [$\delta \text{P}(1)$ 311.3, $\text{P}(2)$ 27 p.p.m., $^2J_{\text{P-N-P}}$ 111.8 Hz]. Furthermore the trico-ordinated $\text{P}(2)^+$ nucleus is coupled with the CH isopropyl group (t, $^3J_{\text{P(2)-H}}$ 29 Hz). The other n.m.r. data confirm the unique dicationic structure: ^{27}Al (23.47 MHz) $\delta 104.9$ p.p.m. (narrow singlet characteristic of AlCl_4^- anion); ^1H (90.00 MHz) ($\text{Me}_2\text{CH})_2\text{N}-\text{P}(1)^+$ group $\delta 3.48$ (2H, hept., $^3J_{\text{H-H}}$ 6.9 Hz, CH) and 1.48 (6H, d, $^3J_{\text{H-H}}$ 6.9 Hz, Me), ($\text{Me}_2\text{CH})_2\text{N}-\text{P}(2)^+$ group $\delta 3.73$ and 3.89 (2H, 2 hept. d, $^3J_{\text{H-H}}$ 6.8, $^3J_{\text{H-P}}$ 29.0 Hz, CH); ^{13}C (22.63 MHz) ($\text{Me}_2\text{CH})_2\text{N}-\text{P}(1)^+$ group $\delta 48.74$ (2C, s, CH) and 19.43 (4C, s, Me), ($\text{Me}_2\text{CH})_2\text{N}-\text{P}(2)^+$ group $\delta 50.3$ (1C, d, $^2J_{\text{C-P}}$ 8.8 Hz, CH) 49.5 (1C, d, $^2J_{\text{C-P}}$ 7.4 Hz, CH), and 21.6 p.p.m. (4C, s, Me). The bisphosphocation (**3b**) can be unambiguously detected in solution [$\delta \text{P}(1)$ 293.5, $\text{P}(2)$ 30 p.p.m., $^2J_{\text{P-N-P}}$ 90.8, $^3J_{\text{P(2)-H}}$ 15.6 Hz]. However this compound is less stable than (**3a**) and we were unable to isolate it in pure form.

Production of biscation (**3**) can be explained by the route shown in Scheme 1. We have some experimental arguments to support the pathway. We have tried to obtain (**4a**) by a traditional method according to Scheme 2.

The phosphonium azide intermediate (**4a**) reacting upon itself gives the bisphosphocation (**5a**) [$\delta \text{P}(1)$ 301.4, $\text{P}(2)$ 20.5 p.p.m., $^2J_{\text{P-N-P}}$ 93, $^3J_{\text{P(2)-H}}$ 23.8 Hz; $\nu(\text{N}_3)$ 2160 cm^{-1}] and polymers.

Note that (**5a**) is different from (**3a**) only by the replacement



Scheme 2

of Cl by an N_3 group. So Schemes 1 and 2 demonstrate the ability of the phosphonium cations ($\text{R}_2\text{N}-\text{P}^+-\text{Cl}$ or $\text{R}_2\text{N}-\text{P}^+-\text{N}_3$) to react with the phosphonium azide (**4**). Furthermore when the reaction in Scheme 1 is made unfavourable by changing the order of addition: *i.e.* (**1a**) is added to Me_3SiN_3 , both bisphosphocations (**3a**) and (**5a**) are present in the reaction mixture.

In conclusion this communication proves that the extension of the Staudinger reaction to the chlorophosphonium cation is feasible; in the case of trimethylsilylazide, a bisphosphocation has been prepared for the first time and the particular phosphonium azides (**4**) appear as interesting intermediate sources of polyphosphocations.

Received, 29th December 1983; Com. 1688

References

- (a) M. R. Marre, M. Sanchez, and R. Wolf, *Phosphorus Sulfur*, 1982, **13**, 327; (b) M. Sanchez, M. R. Marre, J. F. Brazier, J. Bellan, and R. Wolf, *ibid.*, 1983, **14**, 331.
- M. G. Thomas, C. W. Schultz, and R. W. Parry, *Inorg. Chem.*, 1977, **16**, 994.
- Y. G. Gololobov, I. N. Zhmurova, and L. F. Kasukhin, *Tetrahedron Report 102, Tetrahedron*, 1981, **37**, 437.
- I. Yu. Boudilova, H. I. Gusar, and Yu. G. Gololobov, *Zh. Obshch. Khim.*, 1980, **50**, 1201.