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Intramolecular Donor-Stabilized Phosphanylium Salts via λ^3Functionalized -Iminophosphanes

Michel Sanchez*[a], Frédéric Cosledan[a], Jean Marc Sotiropoulos[a], Lydia Lamandé[a], Andrei B. Drapailo[b], Andrei O. Gudima[b] and Vadim D. Romanenko*[a,b]

[a]Laboratoire Synthèse, Structure et Réactivité de Molécules Phosphorées,
(ER 76), Université Paul Sabatier, 31062 Toulouse - France
[b]Institute of Organic Chemistry of the National Academy of Sciences,
Murmanskaya st. 5, 253660, Kiev-94 Ukraine

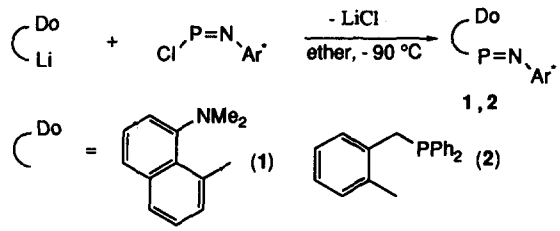
Abstract: λ^3-Iminophosphanes,R-P=NAr*(Ar*=2,4,6-tri-tBuC$_6$H$_2$),containing intramolecularly coordinating substituents at the dicoordinate phosphorus atom (R= 8-NMe$_2$ C$_{10}$H$_6$ or 2-Ph$_2$PCH$_2$ C$_6$H$_4$ have been synthesized and used for generation of the isolable phosphanylium salts stabilized by a donor P→ P bond.

Over the last two decades there has been considerable interest in the preparation and characterization of phosphanylium salts .[1] Most of this interest comes from the fact that studies of species containing a formally electron deficient cationic phosphorus center gives a new dimension to phosphorus chemistry in terms of structure, bonding, and reactivity.[2] Nevertheless, the structural diversity of the known phosphanylium cations remains to date very scarce. Moreover,whilst many examples of bis(amino)phosphanylium salts have been described, only a few isolable phosphanylium derivatives containing other types of organic substituents are known .[3]

So far, the most widely used method to synthezise phosphanylium ions involves chloride ion abstraction from chlorophosphane precursors.[1,2] Very recently, we have shown that the reaction of aminoiminophosphanes, R$_2$N-P=NAr* (Ar* = 2,4,6-tri-tBuC$_6$H$_2$) with CF_3SO_3H or Lewis acids ($AlCl_3$, $GaCl_3$) leads in high yield to isolable phosphanylium derivatives.[4] The potentiality of this strategy was demonstrated by the preparation and structural characterization of the first stable compounds containing primary amino ligands (e.g., [(Ar*NH)$_2$P]$^+$ [CF_3SO_3]$^-$). As part of current efforts to prepare structurally well-defined, isolable highly reactive organyl-substituted phosphanylium ions, we describe here the application of this approach to the synthesis of intramolecularly base-stabilized aryl(arylamino)phosphanylium salts. Efficiency of intramolecular base coordination in stabilizing unusual oxydation and coordination states and also isolation of reactive intermediates, has been widely demonstrated both in main group [5] and transition metals chemistry.[6] However all the examples using this methodology in cationic phosphorus chemistry are based on the generation of an electron deficient center by phosphorus-halogen heterolysis. [2d,7]

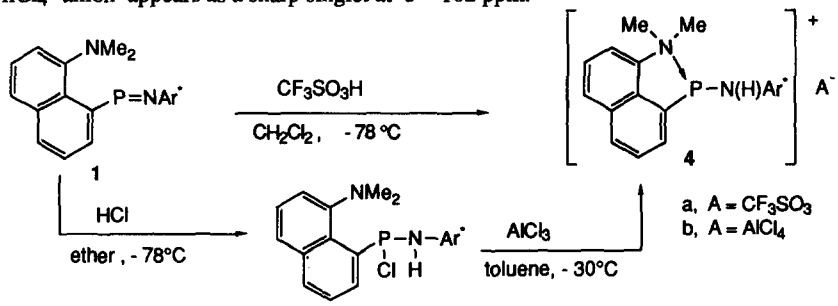
Iminophosphanes **1** and **2** were conveniently prepared by reaction of 8-dimethylamino-1-naphthyllithium [8] or of 2-diphenylphosphinomethylphenyllithium [9] with a stoichiometric amount of P-chloro-N-(2,4,6-tritBu-C$_6$H$_2$)iminophosphane [10] in diethylether at -78 °C (yields 56 % and 42%) (scheme 1). Both compounds were isolated as dark blue, extremely air- and moisture sensitive crystalline solids, soluble in hydrocarbon solvents. They gave satisfactory C, H, N analyses, showed parent ions in their mass spectra (FAB MS) and exhibited ^{31}P signals in the characteristic field of λ^3 iminophosphanes (350-425 ppm) .[11] In each case, these

resonances (**1**, δP = 379; **2**, δP = 394 ppm) were shifted slightly towards high field from those of non-functionalized iminophosphanes R-P=NAr* (R = Ph, δP = 415; R = Mes, δP = 456 ppm) [12] indicating that only weak donor-acceptor interaction exists between the donor group (Me_2N or Ph_2P) and the PπNπ-bonded dicoordinate phosphorus atom. This conclusion is supported by the relatively low value of the phosphorus-phosphorus coupling constant through space of 62 Hz in the $^{31}P\{1H\}$ NMR spectrum of **2** and by the fact that in the ^1H NMR spectrum of **1** the Me_2N group appears as a singlet at 2.28 ppm.[13]



Scheme 1

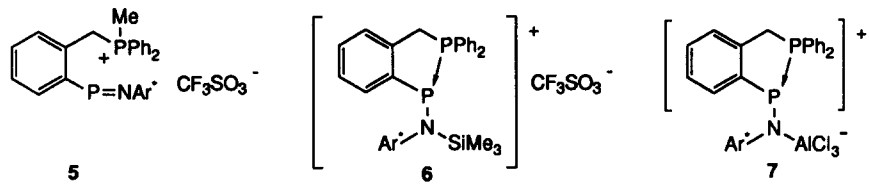
Treatment of the iminophosphine **1** with a stoichiometric amount of CF_3SO_3H in dichloromethane leads with 62% yield to a colourless, thermally stable solid, analyzed as **1**.CF_3SO_3H (scheme 2). The spectroscopic data indicate that the solid is the donor-stabilized phosphanylium salt **4a** . The formation of the five membered cationic heterocycle in **4a** can be deduced from the NMR spectra. The resonance of the NMe_2 group in the ^1H NMR spectrum shows two signals which correspond to two diastereotopic methyl groups resulting from the coordination of the nitrogen atom to the phosphorus atom. The ^{31}P NMR resonance of **4a** is substantially shifted towards high field (δP = 167 ppm) as compared to that of **1**; however, it is located downfield from the resonance corresponding to the tricoordinate phosphorus in chlorophosphane **3** (δP = 110 ppm) obtained by treatment of **1** with an ether solution of hydrogen chloride. The ^1H and ^{31}P NMR parameters of the salt **4b** prepared by the reaction of **3** with $AlCl_3$ are similar to those of **4a.** In the ^{27}Al NMR spectrum of **4b** the $AlCl_4^-$ anion appears as a sharp singlet at δ = 102 ppm.



Scheme 2

Three electrophilic reagents were chosen for generation of cationic phosphorus species starting from **2** : CF_3SO_3Me, $CF_3SO_3SiMe_3$ and $AlCl_3$. As expected (cf.[14]), when methyltrifluoromethanesulfonate was allowed to react with **2** , quaternization of the tricoordinate phosphorus atom occurs. The formation of **5** can be explained, taking into account the higher nucleophilicity of a $\sigma^3\lambda^3$-P centre in **2** compared with the $\sigma^2\lambda^3$-P centre and the imino nitrogen atom. The ^{31}P NMR spectrum of **5** shows two downfield-shifted doublets (δP =

409 and 22 ppm) in comparison to those of **2**, it is important to note that the phosphorus-phosphorus coupling constant in **2** (J_{PP} = 62 Hz) is greater than in **5** (J_{PP} = 20 Hz).



5 **6** **7**

In contrast, treatment of **2** with an excess of $CF_3SO_3SiMe_3$ (1:10, toluene, 3h, 25 °C) produced phosphanylium salt **6** in almost quantitative yield. Electrophilic attack of the Me_3Si cation on the PPh_2 group in this case seems to be unfavorable, due to a very low energy of the P-Si bond compared to that of N-$SiMe_3$. Similarly, the iminophosphane **2** reacts with $AlCl_3$ at -30 °C in toluene to give the zwitterionic complex **7**. Compounds **6** and **7** are stable at room temperature under dry argon and show satisfactory elemental analysis. Their ^{31}P NMR spectra exhibited AX pattern in the expected range for the postulated structures [**6**, δP = 29 (PPh_2), 47 (PN) ; **7**, δP = 38.5 (PPh_2), 119 (PN)] The strongest evidence for a P -> P^+ donor-acceptor interaction comes from the phosphorus-phosphorus coupling constants (J_{PP} = 327 Hz **6**, 525 Hz **7**) which are higher than the typical $^1J_{PP}$ value for a single phosphorus-phosphorus bond (200-300 Hz) .[15]

In conclusion, we predict that in view of their ready availability and high reactivity, both the functionalized iminophosphanes **1**, **2** and the stabilized phosphanylium salts **4**, **6** and **7** are likely to be versatile ligands for coordination chemistry. Further studies in that direction are now currently under way in our laboratories.

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13. Representative NMR spectra: **1**, ^{1}H NMR (C_6D_6) δ 1.43 (s, 9H, p-But), 1.66 (s, 18H, o-But), 2.28 (s, 6H, Me_2N), 7.4-8.1 (m, 8H, H arom); ^{31}P (C_6D_6) 379 ppm. **2**, ^{1}H NMR (C_6D_6) δ 1.44 (s, 9H, p-But), 1.62 (s, 18H, o-But), 3.77 (s, 2H, CH_2), 7.0-7.6 (m, 6H, H arom); ^{31}P{^{1}H} NMR (C_6D_6) δ 8.4 (d, J_{PP} = 62 HZ, PPh_2), 394.5 (d, J_{PP} = 62 Hz, P=N). **3**, ^{31}P NMR (C_6D_6) δ 110.5 ppm. **4a**, ^{1}H NMR ($CDCl_3$) δ 1.27 (s, 9H, p-But), 1.27 (s, 18H, o-But), , 3.10 (s, 3H, MeN), 3.16 (s, 3H, MeN), 5.84 (d, J_{HP} = 11.3 Hz, 1H, NH), 7.4-8.1 (m, 8H, H arom); ^{31}P NMR ($CDCl_3$) δ 167 ppm. **5**, ^{1}H NMR (C_6D_6) d 1.32 s, 18H, o-But), 1.37 (s, 9H, p-But), 2.40 (d, J_{HP} = 13.4 Hz, 3H, MeP), 5.11 (d, J_{HP} = 15.6 Hz, 2H, CH_2), 7.4-7.8 (m, 14H, H arom); ^{31}P NMR (C_6D_6), δ 22.2 (d, J_{PP} = 20 Hz, PPh_2), 409.3 (d, J_{PP} = 20Hz, PN). **6**, ^{31}P NMR($CDCl_3$) δ 28.8 (d, J_{PP} = 327 Hz, PPh_2), 46.7 (d, J_{PP} = 327 Hz, PN). **7**, ^{31}P NMR ($CDCl_3$) δ 38.5 (d, J_{PP} = 525 Hz, PPh_2), 119 (d, J_{PP} = 525 Hz, PN).

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