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Crystalline, Lewis Base-Free, Cationic Phosphoranimines (Iminophosphonium Salts)

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Supporting Information

ABSTRACT: Cationic phosphoranimines have been postulated as intermediates in phosphazene polymerization chemistry. However, the high electrophilicity of the phosphorus center has so far prevented their characterization. Here, we report the synthesis of two Lewis base-free iminophosphonium salts, obtained by reaction of a stable phosphinonitrene with methyl trifluoromethanesulfonate and trifluoromethanesulfonic acid. These cationic species were characterized by NMR spectroscopy and single-crystal X-ray diffraction analysis. Using 4-(dimethylamino)pyridine, a corresponding Lewis-base adduct has also been isolated.

For several decades, trigonal planar phosphorus cations **I** have been the subject of intense investigations (Figure 1).[1]

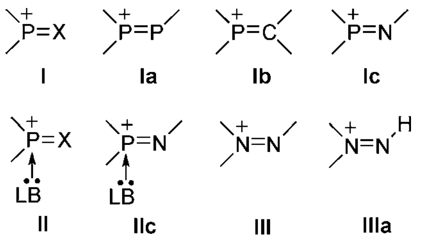


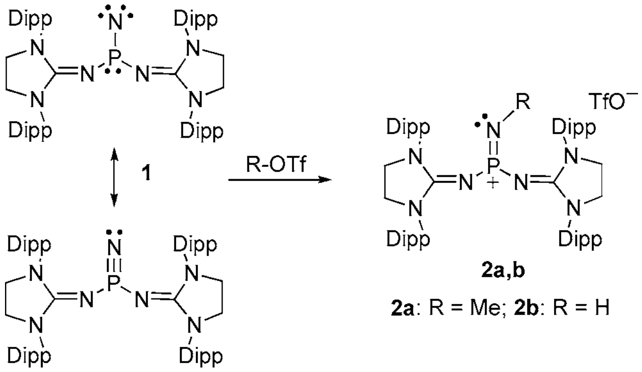
Figure 1. Trigonal planar phosphorus cations **I**, their corresponding Lewis-base adducts **II**, and diazeniums **III**.

However, apart from a phosphanylphosphenium (**Ia**)[2] and a few methylenephosphonium salts (**Ib**),[3] none of these low-coordinate phosphorus cations have been isolated and structurally characterized. Iminophosphonium salts **Ic**, also named phosphoranimine cations, deserve special attention since they have been shown to play an integral role in phosphazene polymerization chemistry.[4,5] The difficulty in isolating cations of type **I** is mainly due to the strong electrophilicity of the phosphorus center, which usually covalently binds to the counteranion. To overcome this difficulty, Lewis bases have been utilized. A variety of adducts of type **II**, including **IIc**[5] and even the most electrophilic oxophosphonium salts,[6] have recently been prepared. On the other hand, a few nitrogen analogues of **Ic**, namely iminoammonium salts (diazeniums) **III** have been isolated.[7] Although the non-substituted end-on derivatives **IIIa** can be generated *in situ* and used in organic synthesis,[8] they have never been crystallographically characterized.

Herein we report the synthesis and single-crystal X-ray diffraction study of two Lewis base-free iminophosphonium salts of type **Ic**, including an N-hydrogeno-substituted derivative, which readily reacts with a Lewis base to form the corresponding adduct of type **IIc**.

The recent preparation of the stable phosphinonitrene **1**,[9,10] which is the monomer corresponding to polyphosphazenes, gave us a straightforward entry to the desired salt. Alkylation of **1** in toluene at −78 °C with methyl trifluoromethanesulfonate proceeded cleanly (Scheme 1). After the solution warmed to room temperature, **2a** was isolated in 79% yield as a white solid. The ^{31}P NMR signal appears as a quartet (J_{PH} = 40.1 Hz), indicating the presence of a methyl group at nitrogen. This signal (+48.4 ppm) is downfield shifted with respect to the nitrene precursor **1** (+7.7 ppm), suggesting that the triflate anion is not covalently bonded to the phosphorus. To prove the ionic nature of the product, single crystals were grown by slow diffusion of hexane into a $CHCl_3$ solution of **2a**. Although the systematic disorder of **2a** in the solid state does not allow for an accurate discussion of bond lengths and angles, the data show that the triflate anion is located over 7.4 Å away from the phosphorus center (Figure 2).

Scheme 1



As indicated in the introduction, hydrogeno diazenium salts **IIIa** are too reactive to be isolated. Because of the higher electropositivity of phosphorus, we reasoned that the nitrogen center of iminophosphonium salts **Ic** should be less susceptible to nucleophilic attack, and could be stable. Indeed, when a toluene solution of trifluoromethanesulfonic acid was added to

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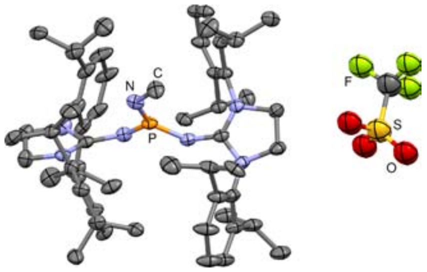


Figure 2. Solid-state structure of **2a**; hydrogen atoms are omitted for clarity. The triflate anion and large parts of the cationic molecule are disordered (see SI for more details). Thermal ellipsoid plot at the 30% level of probability.

1 at −78 °C, an instantaneous reaction occurred. The protonation was apparent from the ^{31}P and ^{1}H NMR spectra, which showed doublets at +72.9 and 2.46 ppm (J_{PH} = 7.2 Hz), respectively. Single crystals were obtained by vapor diffusion of pentane into a saturated $CHCl_3$ solution of **2b** (50% yield).

The crystallographic study clearly demonstrates the ionic nature of **2b** (Figure 3). The oxygen atoms of the triflate anion are over 6.4 Å away from the phosphorus center, and the shortest contact between the anion and the cation, i.e. the F··· H(N1) distance, is close to 2.8 Å. Additionally, the phosphorus is in a planar environment (sum of the angles: 360°). The P−N1 bond [1.526(2) Å] is significantly lengthened compared to that of the starting material **1** [1.457(8) Å] and is in the range reported for PN double bonds (1.50−1.60 Å).[11] Also of note are the shortening of the P−N2 and C1−N4 bonds and the lengthening of the N2−C1 bond compared to those of **1** [**2b**: 1.553(2), 1.330(3), 1.326(3) Å; **1**: 1.629(8), 1.374(11), 1.282(11) Å]. These geometric parameters indicate that electron donation from the imidazolidin-2-iminato substituents is even stronger for **2b** than for **1**, which is a consequence of the increased electron deficiency of the phosphorus center.

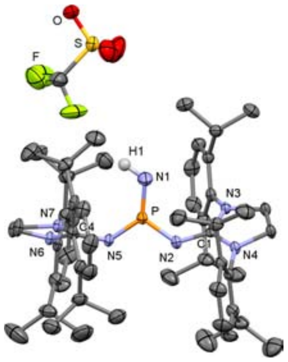
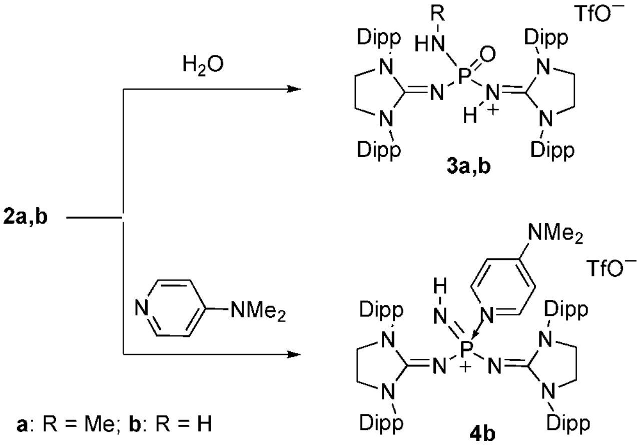


Figure 3. Solid-state structure of **2b** with thermal ellipsoid plot at the 50% levels of probability. Hydrogen atoms, except the imino-H atom, are omitted for clarity. Selected bond lengths (Å) and angles (°): P−N1, 1.526(2); P−N2, 1.553(2); P−N5, 1.559(2); C1−N2, 1.326(3); C1−N3, 1.349(3); C1−N4, 1.330(3); N1−P−N2, 120.5(1); N1−P−N5, 130.5(1); N2−P−N5, 108.9(1).

Although salts **2a,b** are thermally stable, they are extremely sensitive to moisture. Water adds across the PN double bond, leading to **3a,b**, which features a proton on the basic nitrogen of an iminato substituent (Scheme 2).

To check further the iminophosphonium behavior of **2**, we reacted **2b** with 4-(dimethylamino)pyridine (DMAP), and we observed the instantaneous formation of the Lewis base adduct **4b** (Scheme 2). The ^{31}P NMR signal (−0.8 ppm) is strongly upfield shifted with respect to that of **2b** (+72.9 ppm) and appears as a triplet (J_{PH} = 7.0 Hz) due to the coupling with the *ortho*-H atoms of DMAP. Two sets of signals are observed in the ^{1}H and ^{13}C NMR spectra for the 2,6-diisopropylphenyl substituents and for the methylene H atoms, indicating the presence of a tetracoordinated phosphorus center. In the ^{1}H NMR spectrum, the imino-H signal (−0.65 ppm) is upfield shifted compared to that of **2b** (+2.46 ppm), which could be a result of the magnetic shielding by the pyridine ring.

Scheme 2



a: R = Me; **b**: R = H

These results demonstrate further the efficiency of the imidazolidin-2-iminato substituent[12] for the stabilization of highly electrophilic centers. This group has found many applications as a ligand for transition metal centers,[13] but its use in main group chemistry is still in its infancy.[14] We are currently investigating the possibility of isolating oxo- and thioxo-phosphonium salts, as well as other group 13 and 14 diamagnetic and paramagnetic highly electron-deficient species.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Full experimental details, and X-ray crystallographic data for **2a**, **2b**, and **3a**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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