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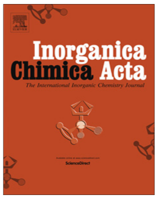

Research paper

Phosphoranimines containing cationic N-imidazolinium moieties

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ABSTRACT

Three new monomeric phosphoranimines (PAs; R′—N=PR$_3$) were synthesized by the Staudinger route using 2-azido-1,3-dimethylimidazolinium hexafluorophosphate [ADMImPF] and various phosphines to form their respective PA salts of triphenylphosphine (**1**), tri(*n*-octyl)phosphine (**2**), and tris(2,2,2-trifluoroethoxy)phosphite (**3**). These PA salts have a cationic imidazolinium moiety attached to nitrogen. Interestingly, **2** is a room temperature ionic liquid (RTIL) with a melting point around −5 °C and a viscosity of 740cP at 25.5 °C. **1** and **2** show stability to moisture exposure and atmosphere for weeks whereas **3** is not stable toward atmospheric moisture undergoing decomposition to form 2-amino-1,3-dimethylimidazolinium phosphate (**4**). Thermal analyses reveal that **1** and **2** are stable to 90 °C under nitrogen, but **3** undergoes degradation by exposure to moisture and/or elevated temperature. All compounds exhibit similar multinuclear NMR chemical shifts as compared to their corresponding phosphine oxide counterparts. However, their respective X-ray structure determinations indicate that **2** has an open structure with the octyl groups that avoid the ionic charges, whereas **1** and **3** have tighter structural packing of the hexafluorophosphate to their pendant groups.

1. Introduction

Phosphoranimines (PAs; Fig. 1) are small molecule phosphorus-nitrogen compounds that are common building blocks to make polyphosphazenes or cyclic phosphazenes [1–4]. These materials have unique properties that range in a variety of membrane, biological, and electronic applications [5–8], and recently PAs were shown that they could be used as an additive battery electrolyte in lithium-ion batteries [9]. Traditional PA chemistry has been used to generate polymeric phosphazenes, where the PAs contain a trimethylsilyl-group at nitrogen (Fig. 1) and different phosphorus pendant groups, such as directly bound alkyl/aryl groups and a good leaving group (chloro-, trifluoroethoxy- or phenoxy-) [3,7,10–12]. Generally, heating these PAs to 180–200 °C results in condensation polymerization, and recent literature has shown that some of their oligomeric intermediates can be isolated as ionic moieties even at ambient temperatures in the presence of Lewis acid catalysts (e.g., PCl$_5$) [13–16]. This polymerization has been studied to determine the reactive intermediate compound (ionic PA) that sustains the living polymerization at ambient temperatures [15,16]. Several different ionic PA intermediates were characterized; however, the resulting ionic PAs are not stable towards atmospheric moisture and will tend to degrade. Other PA compounds with a reactive imide ligand (hydrogen, halogen or organosilane) can be transformed into a reactive intermediate that builds larger PA structured compounds and metal complexes, such as the aza-Wittig reagents [17–23]. Interestingly, recent research has shown similar ionic and non-ionic PA compounds can be used for polymerization and depolymerization catalysts/co-catalysts of various organic condensation polymers, e.g. depolymerization of polyesters using sterically hindered, strong PA Lewis bases [24–26,21].

Most PAs without a P=N-P backbone (only P=N) structure are made by two common synthetic strategies: Neilson method or Staudinger reaction [3,11,27–30]. The Neilson method is the preferred synthetic route in making PA precursors, as it avoids the use of hazardous organic azides, as well as the creation of unwanted by-products through P=N cyclization, and limits phosphite or PA rearrangement products, such as alkyl phosphoramidates ((RO)$_2$P(=O)NH$_2$) [11,30,31]. The disadvantage of the Neilson method is that it requires several reaction steps followed by vacuum distillation to achieve a pure PA product. Also, because the method produces products that tend to polymerize to yield polyphosphazenes, the Neilson method is limited to producing moisture sensitive PAs with organosilanes at nitrogen. As the

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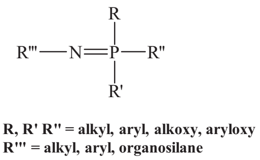


Fig. 1. *N*-organophosphoranimine (PA) structure.

oldest synthetic route to PAs, the Staudinger route comprises of a single step reaction between an azide and phosphine where a variety of N and P pendant groups can be utilized to make unique PA compounds.

Over the past decade, new interest in the Staudinger reaction has re-emerged through "click" chemistries, such as azide fluorescent markers on biological materials or attachments to polymer pendant groups [32–35]. Several new organic azides from commercial sources not only can be utilized for the Staudinger 3+2 "click" reactions, but they can also be used with phosphines to make new PAs. In some cases, these organic azides are stable as purified solids, e.g. 2-Azido-1,3-dimethylimidazolinium hexafluorophosphate [ADMImPF] [36–38]. ADMImPF can be used directly in the Staudinger reaction without needing to employ rigorous safety precautions during the synthesis. The added azide stability is essential to the Staudinger method and introduces new PA compounds which are not easily accessible by the Neilson method. We report three cationic N-imidazolinium PA compounds that were synthesized from the reactions of triphenylphosphine (TPP), trioctylphosphine (TOP) or tris(2,2,2-trifluoroethoxy)phosphite (TTFP) with ADMImPF. All isolated PA products were characterized by multinuclear NMR and single crystal X-ray diffraction, and the thermal properties and reactivity towards the atmosphere and moisture were also characterized.

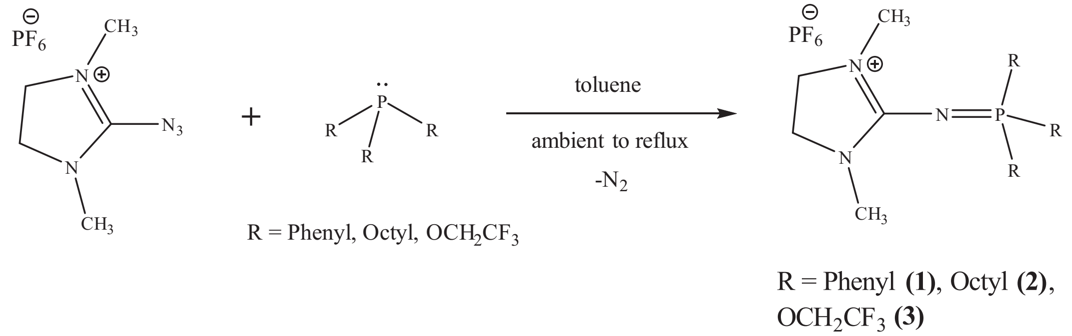
2. Results and discussion

A series of monomeric PA salt products (Scheme 1 and Fig. 2) with an organophosphine (TPP, TOP or TTFP) and ADMImPF were synthesized by the Staudinger method: P,P,P-triphenylphosphoraniminyl-N-1,3-dimethylimidazolinium hexafluorophosphate [**1**], P,P,P-trioctylphosphoraniminyl-N-1,3-dimethylimidazolinium hexafluorophosphate [**2**], and P,P,P-tris(2,2,2-trifluoroethoxy)phosphoraniminyl-N-1,3-dimethylimidazolinium hexafluorophosphate [**3**]. These PA compounds can be a solid or liquid at room temperature, depending on the pendant groups at phosphorus. PA **2** was the most interesting due to it being an atmospherically stable room temperature ionic liquid (RTIL) with a viscosity of 740cP (25.5 °C). Previous PA compounds by the Neilson and Staudinger synthetic methods focused on attaching or creating ionic moieties at the phosphorus position, such as imidazolium halides, organophosphines, and 4-dimethylaminopyridine [39–42]; however, their PA products are not commonly stable under atmospheric conditions for extended periods. Also, there are a limited number of usable organic azide compounds, and the syntheses of PA compounds with a cationic pendant group at nitrogen have not been explored by the Staudinger method. In the literature, atmospherically stable PA compounds are formed as either (large) sterically encumbered alkyl/aromatic PA compounds [11,43,44] or as various forms of ionic aromatic structures of $Ph_3P{=}N^+{=}PPh_3\ X^-$ ([PPN]Cl) with halogen anions [20,42,45], giving the [*PPN*]Cl structure its stability and its charge distribution across the compound. Hence, the reported compounds **1**–**3** have the ability to distribute the charge across the PA structure through electron resonance structures (Fig. 3), which can enhance their stability for extended periods.

ADMImPF is a commercial product that is available as a white powder. It is stable to brief exposure to the atmosphere at room temperature. Thus, it is relatively simple to handle in the laboratory and a good candidate for the Staudinger reaction. Even though, ADMImPF is not completely soluble in toluene (as reported in the literature), the reported phosphines were able to react with the azide in toluene without issues. In addition, toluene allowed for easier workup and has a useful temperature range for these reactions.

All three new PAs form a yellow colored intermediate during reaction. 1 and 2 show distinct color changes that dissipated over time as the azide reacted with the phosphine. It is interesting that all three reactions do not proceed at room temperature do not immediately react as the phosphine was added, but further heating was required to yield PA products, such as **2** and **3**. All PA products were not completely soluble in toluene and tend to precipitate or oil out of solution upon cooling to room temperature. Also, these compounds do not show water solubility. The toluene solution was decanted or pipetted away from the products, where they were washed and isolated from hexane solutions. The PAs that are solids could be purified further by common recrystallization methods. In the instance of synthesizing compound **2**, isolation was carried out using hexanes, and the compound remained as an oily liquid at room temperature after solvent removal. This product was placed in a freezer (−30 °C), where prismatic crystals were generated. All of the reported PA products were isolated and analyzed by multi-nuclear NMR, thermal analysis, and single-crystal X-ray diffraction.

In Table 1, the multi-nuclear P-31 NMR spectra of **1**–**3** show that CF_3CH_2O— groups contribute more electron density to phosphorus than the phenyl or octyl groups. When comparing compounds **1**–**3** to their phosphine oxide precursors [46], all compounds follow similar trends in the chemical shifts; however, PAs **1**–**3** have slightly more electron density at phosphorus resulting in a 12–17 ppm upfield shift. No differences in chemical shifts are observed among the P-31 NMR spectra of the PF_6^- counter ion to compounds **1**–**3**, which would be expected due to the over-



Scheme 1. Staudinger reaction of 2-azido-1,3-dimethylimidazolinium hexafluorophosphate (ADMImPF) and phosphines to form PA compounds **1**–**3**.