

Anionic ring-opening polymerization of a strained phosphirene: A route to polyvinylenephosphines†

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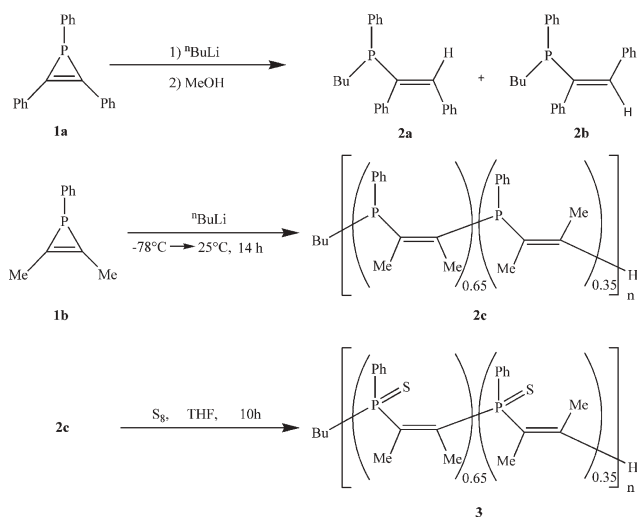
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A strained 1-phenyl-2,3-dimethylphosphirene undergoes anionic ring-opening polymerization upon initiation with *n*-butyl lithium at ambient temperature to yield polyvinylenephosphine, an unsaturated organophosphorus polymer.

Functional polymers that incorporate inorganic elements in their main chain are of current interest due to their unique properties and potential applications.¹ Phosphorus-containing polymers are attracting particular current attention as self-assembled materials,² π -conjugated materials³ and catalyst supports.⁴ Until recently, they have been mainly accessible only by traditional condensation polymerization and thermal ring-opening polymerization (ROP) routes.¹ Over the past decade, a variety of new and versatile synthetic routes to these materials have been described, including chain growth and metal-catalyzed polycondensation, Lewis acid-catalyzed and anionic ROP at ambient temperature, and addition polymerization.⁵ In this communication, we report the successful anionic polymerization of a strained three-membered organophosphorus heterocycle, which provides a convenient ambient temperature route to a novel class of unsaturated vinylenephosphine polymers.

Phosphirenes are interesting organophosphorus three-membered rings containing a C=C double bond.⁶ These species contain considerable ring-strain, as demonstrated by their ability to undergo stoichiometric ring-opening reactions.⁷ This suggests that they are potentially useful as monomers in the synthesis of vinylenephosphine polymers *via* ROP, but no successful polymerization has been reported to date.⁸ Treatment of triphenylphosphirene (**1a**) (Scheme 1) with a stoichiometric amount of *n*-butyl lithium (ⁿBuLi) has previously been shown to result in attack at the phosphorus center, with concurrent ring-opening, to afford a mixture of phosphine isomers (*cis* and *trans*).⁷ The resulting products could be readily sulfurized and oxidized, and were isolated as their air-stable sulfide and oxide derivatives, respectively. Ring-opening of **1a** was also reported in the presence of hydrogen peroxide, however the products were difficult to isolate due to oligomerization.⁷ Apart from these studies, the polymerization of phosphirenes remains, to our knowledge, unexplored.



Scheme 1

In order to induce the ROP of **1a**, we treated this species with sub-stoichiometric quantities of an anionic initiator. The reaction of **1a** with 0.1 equiv. of ⁿBuLi followed by quenching with MeOH resulted in *ca.* 10% yield of a ring-opened product, as detected by ³¹P NMR spectroscopy. Signals at δ -2.1 and -26.7 closely matched values reported for the corresponding *cis*- and *trans*-protonated alkenyl phosphines (**2a** and **2b**).⁷ Unfortunately, the ring-opening reaction did not propagate beyond the ring-opened vinylphosphine. We attribute this to the steric bulk of the phenyl groups (and possibly electronic effects), which renders chain propagation kinetically, and perhaps also thermodynamically, unfavourable. We anticipated that phosphirenes which possess smaller ring substituents might function as more suitable monomers. The less sterically encumbered 1-phenyl-2,3-dimethylphosphirene monomer (**1b**) was therefore reacted with ⁿBuLi (0.1 equiv.) at -78 °C and allowed to gradually warm to room temperature. New signals, assigned to anionic ring-opened products, were observed by ³¹P NMR at δ -4.9 and -14.4, in addition to those of the starting material. As a general rule, Duncan and Gallager have noted that more sterically compressed

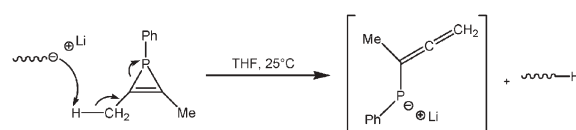
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Scheme 2

Table 1 Summary of results for the polymerization of **1b** with ⁿBuLi initiator

| Trial | Initiator (I)/mmol | Monomer (M)/mmol | [M]/[I] ₀ | Calculated MW (M _n)/g mol ^{-1a} | Experimental MW (M _n)/g mol ^{-1a} | Polydispersity index | Degree of polymerization ^c | Percentage yield by ³¹ P NMR (Percentage isolated yield) |
|-------|--------------------|------------------|----------------------|--|--|----------------------|---------------------------------------|---|
| 1 | 0.06 | 0.6 | 10/1 | 2000 | 1700 | 1.42 | 11 | 63 (17) ^b |
| 2 | 0.09 | 2.2 | 24/1 | 4700 | 8000 | 1.35 | 50 | 87 (84) |
| 3 | 0.09 | 2.2 | 24/1 | 4700 | 8200 | 1.45 | 51 | 84 (81) |
| 4 | 0.09 | 2.2 | 24/1 | 4700 | 8600 | 1.58 | 53 | 87 (83) |
| 5 | 0.12 | 6.2 | 51/1 | 9900 | 18 000 | 1.23 | 111 | 85 (84) |

^a Of sulfurized polymer **3**. ^b The low isolated yield is a result of difficulties in precipitating this low molecular weight polymer. ^c DP_n

isomers show more shielded ³¹P nuclei.⁹ Consequently, the more shielded signal at δ -14.4 was assigned to the *trans* isomer, while that at δ -4.9 was attributed to the *cis* isomer. Upon further reaction for 14 h, the ³¹P NMR signal of monomer **1b** was no longer observed, while two broad signals were detected at δ -5.1 and -9.6, consistent with successful chain propagation and polymer formation.‡ The polymer product **2c** was isolated by concentration of the THF solution and subsequent precipitation into hexanes as a beige solid in 17% yield. The ¹H and ¹³C NMR spectra of **2c** were also consistent with the assigned structure. The material was rendered air-stable through sulfurization with elemental sulfur in THF to afford the corresponding sulfide **3**. This resulted in the downfield shift of the ³¹P NMR resonances, as well as an overlap of the signals from each isomer, as the chemical shift difference was reduced. The sulfurization step also permitted analysis of the molecular weight by gel permeation chromatography (GPC) in THF, as polymers containing uncoordinated phosphorus(III) centers often adsorb to size exclusion columns.^{5e} The weight-average molecular weight (M_w) was found to be 2000 g mol⁻¹ and the number-average molecular weight (M_n) was 1400 g mol⁻¹ vs. polystyrene standards. These values correspond to a number-average degree of polymerization (DP_n) of ca. 10 repeat units, as might be expected for a 1 : 10 initiator to monomer ratio.

To generate higher molecular weight materials, polymerizations were performed with decreased amounts of initiator. Reactions using 0.04 equiv. of ⁿBuLi relative to **1b** were performed. After 14 h, the ³¹P NMR spectrum showed the same broad peaks at δ -5.1 and -9.6 associated with the polymer (87%), but also showed some unreacted **1b** (13%). Further reaction resulted in no change in these signals, and can possibly be attributed to side reactions quenching the propagating anionic species. One likely possibility is a "chain transfer to monomer" reaction, where the propagating anion abstracts a proton from one of the methyl substituents on the phosphirene ring. Rearrangement of the resulting compound may afford a stable allenylphosphine structure, which would be unreactive towards **1b** (Scheme 2). Such a mechanism has been reported for the nucleophilic attack of 1-mesityl-2,3-dimethylphosphirene, where the bulky mesityl group prevents nucleophilic attack at the phosphorus.^{7b} Despite the possible occurrence of this chain transfer reaction, this procedure has been used to repeatedly and controllably prepare polymeric **3** with molecular weights of M_w = ca. 8000–8600 g mol⁻¹. This corresponds to a DP_n of 24. In preliminary experiments, polymers with molecular weights as high as M_w = 18 000 g mol⁻¹ have been obtained by using smaller quantities of initiator (Table 1).

In summary, we have demonstrated a facile route to high molecular weight polyvinylphosphines through the anionic ring-opening polymerization of 1-phenyl-2,3-dimethylphosphirene.

We anticipate that ROP should be generally possible for strained rings of this type, providing that the steric encumbrance is not too severe. Experiments aimed at testing this assertion, and exploring properties and applications are underway.

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Notes and references

‡ We tentatively assign the peak at δ -5.1 to P atoms flanked by *cis* and *trans* C=C bonds, and that at δ -9.6 to those in a *trans-trans* environment. Tacticity effects, which provide an alternative explanation for the environment of two peaks, cannot be disproved at this stage.

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