Inorg. Chem. **2002**, *41*, 1690–1691

A New High-Yield Synthesis of $Cl_3P{=}NSiMe_3$, a Monomeric Precursor for the Controlled Preparation of High Molecular Weight Polyphosphazenes

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Received October 31, 2001

The phosphoranimine, $Cl_3P{=}NSiMe_3$, was prepared using a new, high-yield (>80%), one-pot synthesis via oxidation of the chlorophosphine, $Cl_2PN(SiMe_3)_2$ with SO_2Cl_2 in ether. $Cl_3P{=}NSiMe_3$ is a valuable monomeric precursor in the synthesis of well-defined polyphosphazenes.

The phosphoranimine $Cl_3P{=}NSiMe_3$[1] has attracted attention in our group[2,3] as a precursor to perhalogenated phosphoraniminato complexes. In 1995 we showed in collaboration with Allcock and co-workers that this species could be polymerized at ambient temperatures via a living cationic procedure in the presence of Lewis acid initiators such as PCl_5 providing poly(dichlorophosphazene) with controlled molecular weights and narrow polydispersities.[4] This polymerization strategy represents a significant advance over the most commonly utilized pre-existing route, which involves thermal (250 °C) ring-opening polymerization of $[NPCl_2]_3$. The latter procedure allows no control over the degree of polymerization and affords broad molecular weight distributions.[5] In addition, $Cl_3P{=}NSiMe_3$ can be polymerized in various solvents, and the living nature of this route has been exploited to synthesize a variety of polymer architectures (e.g., di- and triblock, graft, star, and random copolymers) incorporating both organic and inorganic components.[6,7] Aryl/alkyl,[8] alkoxy,[9] and halogenated[10] polyphosphazenes with broad molecular weight distributions have also been prepared at elevated temperature by the chain growth condensation polymerization of related phosphoranimine monomers.

Trichloro(trimethylsilyl)phosphoranimine, $Cl_3P{=}NSiMe_3$, was first synthesized by Niecke and Bitter from PCl_5 and $LiN(SiMe_3)_2$ in 1973.[1] The reaction was carried out at 10 °C, and a yield of 20% was reported. We later discovered that lowering the reaction temperature to −78 °C reproducibly improved the yield to 20−40%, with occasional yields of 60%.[2] However there are problems associated with this synthesis which have limited the use of this potentially versatile reagent. For example, PCl_5 is known to initiate the polymerization of $Cl_3P{=}NSiMe_3$; hence the formation of significant amounts of oligomeric and polymeric byproducts {e.g., $[NPCl_2]_3$ and $[NPCl_2]_n$} during the synthesis is unavoidable. Another side product, $ClN(SiMe_3)_2$, is also routinely produced and cannot be separated from $Cl_3P{=}NSiMe_3$ by distillation. The chloroamine, $ClN(SiMe_3)_2$, drastically inhibits polymerization, and additional purification steps have to be performed before the phosphoranimine can be used as a polymer precursor.[11] Allcock and co-workers have recently described an alternate synthesis of $Cl_3P{=}NSiMe_3$ from PCl_5 and $N(SiMe_3)_3$ and report a 40% yield after removal of the above-mentioned byproducts.[11]

Wisian-Neilson and Neilson have reported the facile synthesis of related phosphoranimines $BrR_2P{=}NSiMe_3$ via halogenation of phosphorus(III) precursors, $R_2PN(SiMe_3)_2$, using bromine.[12] Motivated by this work, we decided to explore whether a similar strategy could be used to synthesize

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10.1021/ic011125n CCC: $22.00 © 2002 American Chemical Society
Published on Web 03/09/2002

$Cl_3P{=}NSiMe_3$, thus eliminating the need for PCl_5. Initial attempts to chlorinate $Cl_2PN(SiMe_3)_2$ (made in situ from PCl_3 and $LiN(SiMe_3)_2$) with hexachloroethane, $Cl_3C{-}CCl_3$, failed to produce any observable reaction. However, when we chose the stronger chlorinating agent SO_2Cl_2,[13] a smooth reaction with the phosphine occurred to give quantitative formation of $Cl_3P{=}NSiMe_3$ (by $^{31}P\{^1H\}$ NMR: $\delta = -53.0$ ppm), $ClSiMe_3$ and gaseous SO_2 as a byproduct.

$$PCl_3 + LiN(SiMe_3)_2 \xrightarrow[0\ ^\circ C]{Et_2O} Cl_2P{-}N(SiMe_3)_2 + LiCl \qquad (1)$$

$$Cl_2P{-}N(SiMe_3)_2 + SO_2Cl_2 \xrightarrow[-ClSiMe_3]{\substack{Et_2O \\ 0\ ^\circ C}} Cl_3P{=}N{-}SiMe_3 + SO_2 \qquad (2)$$

All reaction procedures,[14] including the in situ formation of $Cl_2PN(SiMe_3)_2$, can be performed within the mild temperature regime of 0 °C to room temperature, and the use of volatile ether as a solvent facilitates the removal of large amounts of solvent (and $ClSiMe_3$) without significant loss of less volatile $Cl_3P{=}NSiMe_3$ (bp = 24 °C, 0.1 $mmHg^2$). Provided the workup of $Cl_3P{=}NSiMe_3$ is performed within the same day as its synthesis, isolated yields greater than 80% are routinely obtained with only trace amounts of $ClSiMe_3$ as the sole impurity (<2% by ^1H NMR). This reaction has been carried out on a large scale affording over 60 g of pure phosphoranimine in less than 1 day using common Schlenk techniques.

In summary, we report a promising new method for the preparation of $Cl_3P{=}NSiMe_3$ starting with PCl_3. As PCl_5 is not used, losses in yield due to subsequent cationic polymerization are minimized. In addition, no chloroamine impurities are formed; these are difficult to remove and hinder subsequent polymerization. Furthermore, low reaction temperatures (<0 °C) are unnecessary. We anticipate that this new procedure will facilitate further development of the living cationic polymerization route to polyphosphazenes and other chemistry involving this species.

Acknowledgment. This research was supported by the Natural Sciences and Engineering Research Council of Canada (NSERC). E.R. thanks NSERC for a Postgraduate Fellowship (1999−2003), and I.M. would like to thank the University of Toronto for a McLean Fellowship (1997−2003), the Ontario Government for a PREA Award (1997−2003), and the Canadian Government for a Canada Research Chair (2001). We also acknowledge Dr. Y. Chang in the group of Prof. H. R. Allcock at Penn State University for testing the unoptimized procedure.

Supporting Information Available: Text giving complete synthetic details of an alternate preparation of $Cl_3P{=}NSiMe_3$ using pentane as the solvent. This material is available free of charge via the Internet at http://pubs.acs.org.

IC011125N

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(14) All manipulations were carried out under anaerobic and anhydrous conditions. A pale yellow suspension of $LiN(SiMe_3)_2$ (55.4 g, 0.33 mol) in 900 mL of Et_2O was cooled to 0 °C, and freshly distilled PCl_3 (29.0 mL, 0.33 mol) was then added dropwise over 30 min. The resulting mixture was warmed to room temperature and stirred for 1 h, giving a white suspension. Freshly distilled SO_2Cl_2 (26.6 mL, 0.33 mol) was then added dropwise (over 35 min) to the above-mentioned suspension cooled to 0 °C. The reaction was allowed to proceed for 1 h at 0 °C, followed by 30 min at room temperature, and the mixture was then filtered through a 1 cm layer of Celite. The volatiles were removed from the pale yellow filtrate by distillation under reduced pressures (100 mmHg, Et_2O; 25 mmHg, $ClSiMe_3$; temperature of filtrate, 0 °C). $Cl_3P{=}NSiMe_3$, a colorless liquid, was isolated in high yield (62.0 g, 84%) by distilling the remaining residue under static vacuum (ca. 25 °C, ca. 0.1 mmHg). The resulting product gave a clean $^{31}P\{^1H\}$ NMR spectrum [−53.0 ppm (s), $CDCl_3$] and contained trace quantities of $ClSiMe_3$ ($\delta = 0.44$ ppm, <2%) as determined by ^1H NMR spectroscopy [δ for $Cl_3P{=}NSiMe_3$, 0.18 ppm (d, $^4J_{HP} = 1.1$ Hz), $CDCl_3$]. Trace amounts of $ClSiMe_3$ could be removed by redistilling the product as described above or as in ref 2. The reaction can also be carried out in pentane with similar results. For further details, see Supporting Information.