Supporting Information

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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Experimental Section

Materials and Equipment. $LiN(SiMe_3)_2$ (Aldrich, 97 %) was used as received. SO_2Cl_2 (Aldrich, 97 %) and PCl_3 (BDH, 98 %) were distilled before use. Pentane was stirred over CaH_2 overnight and distilled prior to use. All glassware was flame dried under vacuum before use. The reactions were performed using standard Schlenk techniques or in a glove box (Innovative Technology) under an atmosphere of prepurified nitrogen (Matheson).

$^{31}P\{^1H\}$ and ^1H spectra (in $CDCl_3$) were recorded on a Varian Mercury 300 NMR spectrometer operated at 121.4 and 300.0 MHz, respectively. ^1H NMR spectra were referenced to protio impurities in the solvent, while ^{31}P NMR chemical shifts were externally referenced to 85 % phosphoric acid.

Alternate Procedure for the Preparation of $Cl_3P{=}NSiMe_3$ in Pentane. $LiN(SiMe_3)_2$ (4.94 g, 29.5 mmol) was dissolved in 100 mL of pentane and the solution was cooled to 0 °C. PCl_3 (2.5 mL, 29 mmol) was then added dropwise over 10 min. The resulting mixture was stirred for 30 min at the same temperature giving a white suspension. $^{31}P\{^1H\}$ NMR revealed complete conversion of PCl_3 (δ = 221 ppm) to $Cl_2PN(SiMe_3)_2$ (δ = 189 ppm). SO_2Cl_2 (2.5 mL, 31 mmol) was then added dropwise over 10 min to the above mentioned suspension at 0 °C. The reaction was allowed to proceed for 30 min at 0 °C and $Cl_3P{=}NSiMe_3$ (δ = -53.0 ppm) was the only product present by $^{31}P\{^1H\}$ NMR. The mixture was then filtered through Celite (dried at ~120 °C for > 48 h prior to use), which was then washed with pentane (2 x 20 mL). The volatiles from the resulting pale yellow filtrate were removed under reduced pressure (20 mm Hg, 0 °C)[1] to give a yellow liquid. $Cl_3P{=}NSiMe_3$ was isolated (5.49 g, 85 %) as a colorless liquid by distilling the remaining residue under static vacuum (*ca.* 25 °C, *ca.* 0.1 mm Hg). The

resulting product contained trace quantities of $ClSiMe_3$ (δ = 0.44 ppm, < 1 %) as determined by ^1H NMR spectroscopy [δ for $Cl_3P{=}NSiMe_3$, 0.18 ppm (d, $^4J_{HP}$ = 1.1 Hz)].

References:

(1) For a reduced pressure set-up, please refer to: Krell, E. *Handbook of Laboratory Distillation*; Lumb, E. C., Ed.; Elsevier Publishing Company: New York, 1963; Fig. 381, page 470.