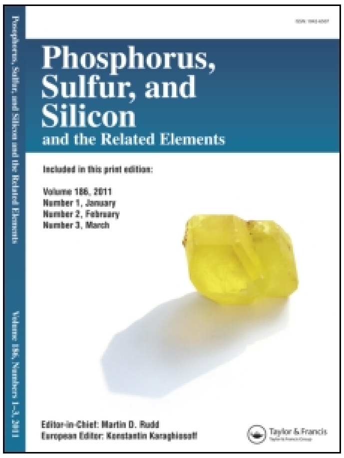

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TELLURADIAZAPHOSPHETIDINES: PREPARATION AND SPECTROSCOPIC CHARACTERIZATION OF THE PN_2Te RING

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Communication

TELLURADIAZAPHOSPHETIDINES: PREPARATION AND SPECTROSCOPIC CHARACTERIZATION OF THE PN_2Te RING

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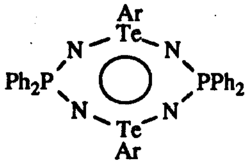
The reactions of $Ph_2PN_2(SiMe_3)_3$ with $ArTeCl_3$ (Ar = C_6H_5, C_6H_4OMe-4, mesityl) in acetonitrile at 23°C produce $Ph_2P(NSiMe_3)_2TeCl_2Ar$, which are formulated as four-membered rings on the basis of analytical and NMR (^1H, ^{31}P and ^{125}Te) spectroscopic data.

Key words: Telluradiazaphosphetidines; ^{125}Te NMR, PN_2Te ring.

INTRODUCTION

Eight-membered rings of the type 1,5-$Ph_4P_2N_4Se_2R_2$ can be prepared by the reaction of $Ph_2PN_2(SiMe_3)_3$ with $RSeCl_3$ (R = Ph, Me, Et)[1] or three molar equivalents of PhECl (E = S, Se).[2] The sulfur analogues, 1,5-$Ph_4P_2N_4S_2R_2$, may also be obtained by the latter method in the case of R = Ph[2] or by treatment of the anions $Ph_4P_2N_4S_2Me^-$ or $Ph_4P_2N_4S_2^{2-}$ with methyl iodide for R = Me.[3] Although the selenium-containing rings are structurally similar to their sulfur counterparts, the former are more reactive. For example, 1,5-$Ph_4P_2N_4Se_2R_2$ derivatives are converted to the corresponding 1,3 isomers either in methylene chloride at 23°C for 3–4 days (R = Me, Et) or at reflux in toluene (1-2h, R = Me, Et; 2 days, R = Ph).[4] In an attempt to prepare the hitherto unknown $P_2N_4Te_2$ ring system **1**, we have investigated the reaction of $Ph_2PN_2(SiMe_3)_3$ with aryltellurium trichlorides. We find that these cyclocondensation reactions produce the four-membered rings $Ph_2P(NSiMe_3)_2TeCl_2Ar$, **2**, rather than **1**, as determined by analytical and spectroscopic data (^1H, ^{31}P and ^{125}Te NMR), for **2a** and ^{31}P and ^{125}Te NMR data for **2b** and **2c**.



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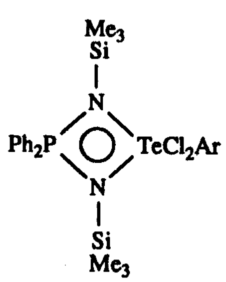
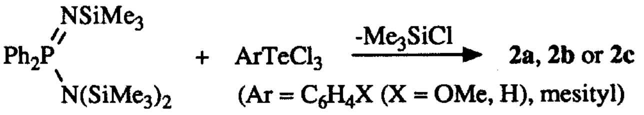


2a, Ar = C_6H_4OMe-4
2b, Ar = C_6H_5
2c, Ar = mesityl

RESULTS AND DISCUSSION

The reaction of $Ph_2PN_2(SiMe_3)_3$ with aryltellurium trichlorides in CH_2Cl_2, CCl_4 or CH_3CN at various temperatures were monitored by ^{31}P NMR spectroscopy and shown to yield one major product together with a complex mixture of minor phosphorus-containing products. The separation and purification of the major product was extremely difficult because of (a) moisture- and oxygen-sensitivity, (b) decomposition to Te metal in warm solutions or on long standing, and (c) contamination with by-products. However, in the case of $4\text{-}MeOC_6H_4TeCl_3$, highly moisture-sensitive white crystals, which showed only one resonance in the ^{31}P NMR spectrum [$\delta(^{31}P)$ + 33.2 ppm] were isolated. The C, H, N analytical data for this product indicated the formation of **2a** rather than **1** (Ar = $4\text{-}MeOC_6H_4$) in the cyclocondensation reaction Equation (1). The ^1H NMR spectrum of **2a** confirmed that two Me_3Si groups had been retained for each Ph_2P or $MeOC_6H_4$ unit. The ^{125}Te NMR spectrum exhibited a doublet [$^2J(^{125}Te\text{-}^{31}P)$ = 84.5 Hz] demonstrating unambiguously that the tellurium is coupled to a single phosphorus atom rather than two equivalent phosphorus atoms. The structure **2a**, containing the novel four-membered PN_2Te ring, is uniquely consistent with these spectroscopic data. Unfortunately, the thin needles of **2a** were unsuitable for an X-ray structural determination. We note, however, that the four-membered CN_2Te ring, prepared from the reaction of $PhCN_2(SiMe_3)_3$ and $TeCl_4$, has been structurally characterized.[5] The reaction of $Ph_2PN_2(SiMe_3)_3$ with $TiCl_4$ also produces several heterocycles that were shown to contain the four-membered PN_2Ti ring.[6]



$$Ph_2P(=NSiMe_3)N(SiMe_3)_2 + ArTeCl_3 \xrightarrow{-Me_3SiCl} \textbf{2a, 2b or 2c} \quad (Ar = C_6H_4X\ (X = OMe, H), \text{mesityl}) \qquad (1)$$

The ^{31}P and ^{125}Te NMR data for **2a–c** are summarized in Table I. The similarity between the NMR parameters of **2b** and **2c** and those of **2a** suggests that these derivatives are structurally similar to **2a**. The ^{31}P NMR chemical shifts fall in the narrow range +33 to +34 ppm, while the $\delta(^{125}Te)$ occurs in the region 1281 to 1331 ppm with $^2J(^{125}Te\text{-}^{31}P)$ = 85–116 Hz. For comparison, we note that the ^{125}Te NMR spectrum of the six-membered ring $\overline{NP(Ph_2)CH_2(Ph_2)PNTeCl_2}$ consists of

TABLE I

^{31}P and ^{125}Te NMR data for $Ph_2PN_2(SiMe_3)_2TeCl_2Ar$[a] (**2a–c**)

Ar	$\delta(^{31}P)$[b]	$\delta(^{125}Te)$[c]	$^2J(^{31}P\text{-}^{125}Te)$ (Hz)
$4\text{-}CH_3OC_6H_4$	33.2	1298.0(d)	84.5
C_6H_5	33.8	1280.7(d)	85.4
Mesityl	33.5	1330.7(d)	116.0

a. In CH_2Cl_2.
b. In ppm relative to external 85% H_3PO_4.
c. In ppm relative to external K_2TeO_3 in D_2O; d = doublet.

an unresolved triplet centered at 1530.7 ppm with a value for $^2J(^{31}P\text{-}^{125}Te) = 132$ Hz.[7]

A solution of **2a** in CH_2Cl_2 slowly gives rise to new resonances at +31.5 ppm and 1288.3 ppm [$^2J(^{31}P\text{-}^{125}Te) = 70.4$ Hz] in the ^{31}P and ^{125}Te NMR spectra, respectively. In view of the similarity of these NMR parameters to those of **2a**, it seems likely that these new resonances can be assigned to the hydrolysis product of **2a** in which $>$N-SiMe$_3$ groups have been converted to $>$NH groups.

EXPERIMENTAL

The reagent $Ph_2PN_2(SiMe_3)_3$[8] and the diaryl ditellurides ArTeTeAr[9] were prepared by literature procedures. Analytically pure aryl tellurium trichlorides were obtained by the treatment of the appropriate ditelluride with an excess of SO_2Cl_2 at 23°C in CCl_4. Solvents were dried with the appropriate drying agent and distilled before use. All reactions and the manipulation of moisture-sensitive products were carried out under an atmosphere of dry nitrogen.

^1H NMR spectra were recorded on a Bruker ACE 200 spectrometer and chemical shifts are reported relative to Me_4Si in $CDCl_3$. ^{31}P and ^{125}Te NMR spectra were obtained by use of a Bruker AM-400 spectrometer and chemical shifts are reported with reference to external 85% H_3PO_4 and K_2TeO_3 in D_2O, respectively.

A solution of $Ph_2PN_2(SiMe_3)_3$ (1.27 g, 2.94 mmol) in CH_3CN (40 mL) was added slowly (1h) to a stirred solution of 4-$MeOC_6H_4TeCl_3$ (1.0 g, 2.93 mmol) in CH_3CN (30 mL) at 23°C. After 3h a ^{31}P NMR spectrum of the reaction mixture showed a major product at +33.6 ppm and weak resonances at +48.2, +18.5 and +2.5 ppm. After 20h, solvent was removed under vacuum to give a foamy solid, which was redissolved in CH_2Cl_2 (10 mL). This solution was added dropwise to vigorously stirred pentane (60 mL) to give a pale yellow oil. Solvents were removed by transfer needle and the oil solidified under dynamic vacuum to give $Ph_2PN_2(SiMe_3)_2TeCl_2(C_6H_4OMe\text{-}4)$, **2a** (0.6 g). An additional 0.4 g of **2a** was obtained as highly, moisture-sensitive white needles from the pentane/CH_2Cl_2 solution, which had been stored at −20°C for 30 days. The total yield of **2a** was 53%. Anal. Calcd. for $C_{25}H_{35}PN_2Si_2TeCl_2O$: C, 45.73; H, 5.31; N, 4.21. Found: C, 46.15; H, 5.17; N, 4.22. ^1H NMR (in $CDCl_3$): 7.07–8.15 (m, C_6H_5 and C_6H_4, 10H + 4H), 3.87 (s, OCH_3, 3H), 0.07 (s, $Si(CH_3)_3$, 18H).

The other derivatives $Ph_2PN_2(SiMe_3)_2TeCl_2Ar$ (**2b**, Ar = C_6H_5; **2c**, Ar = mesityl) were prepared in a similar way from $Ph_2PN_2(SiMe_3)_3$ and $C_6H_5TeCl_3$ or mesitylTeCl$_3$, respectively. The ^{31}P and ^{125}Te NMR data for **2a**, **2b** and **2c** are summarized in Table I.

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