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Preparations and X-ray Structures of Compounds Containing the Four-Membered PN_2Te Ring

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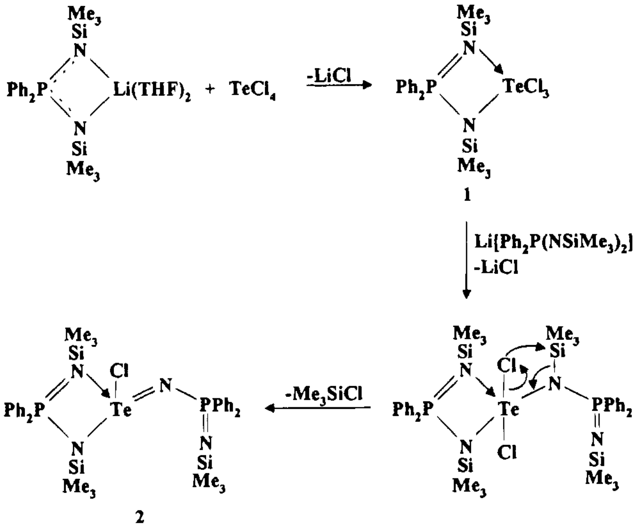
The reaction of $Li[Ph_2P(NSiMe_3)_2]$ with $TeCl_4$ in a 1:1 molar ratio in CH_2Cl_2 at −78 °C, followed by warming to 23 °C, produces $Ph_2P(NSiMe_3)_2TeCl_3$ (**1**) in essentially quantitative yield. An X-ray analysis shows **1** to contain a four-membered PN_2Te ring with Te−N bond distances of 2.056(3) and 2.185(3) Å. When the same reaction is carried out in a 2:1 molar ratio, the product is $Ph_2P(NSiMe_3)_2Te(Cl)NPPh_2NSiMe_3$ (**2**), which consists of a PN_2Te ring with Te−N bond distances of 2.108(3) and 2.275(4) Å and a short exocyclic tellurium−nitrogen bond of 1.922(4) Å. Crystals of **1** are monoclinic, of space group $P2_1/n$, with $a = 15.494(7)$ Å, $b = 11.580(9)$ Å, $c = 15.823$, $\beta = 96.46(3)°$, $V = 2820(2)$ Å^3, and $Z = 4$. The final R and R_w values were 0.024 and 0.027, respectively. Crystals of **2** are triclinic, of space group $P\bar{1}$, with $a = 12.372(7)$ Å, $b = 17.040(6)$ Å, $c = 11.648(4)$ Å, $\alpha = 108.11(2)°$, $\beta = 109.32(4)$, $\gamma = 88.76(4)°$, $V = 2193(2)$ Å^3, and $Z = 2$. The final R and R_w values were 0.036 and 0.037, respectively.

Introduction

The development of the chemistry of inorganic tellurium−nitrogen (Te−N) heterocycles is in its infancy.[1−4] However, the early indications suggest that tellurium will form significantly different structural types in nitrogen-containing ring systems than either of the smaller chalcogens, sulfur or selenium. For example, the reaction of $PhCN_2(SiMe_3)_3$ with $TeCl_4$ gives $PhC(NSiMe_3)_2TeCl_3$, which contains the four-membered CN_2Te ring,[5] whereas the corresponding reaction with sulfur or selenium halides produces the five-membered rings $PhCN_2E_2^+$ (E = S, Se)[6,7] and/or the eight-membered ring $Ph_2C_2N_4S_2$[6] depending on the reaction conditions. Secondly, the reaction of $Ph_2PN_2(SiMe_3)_3$ with $RSeCl_3$ (R = Me, Et, Ph) yields the eight-membered rings 1,5-$Ph_4P_2N_4Se_2R_2$[8] while treatment of the same reagent with $ArTeCl_3$ [Ar = C_6H_4X (X = OMe, H), mesityl] produces derivatives of the type $Ph_2P(NSiMe_3)_3TeCl_2Ar$.[9] In a preliminary communication, these products were assigned a four-membered PN_2Te ring structure on the basis of the observation of a doublet [$^2J(^{125}Te-^{31}P) = 84-116$ Hz] in the solution ^{125}Te NMR spectrum,[9] but the solid-state structures were not determined.

In this article, we report the preparations and spectroscopic characterizations of $Ph_2P(NSiMe_3)_2TeCl_3$ (**1**) and $Ph_2P(NSiMe_3)_2Te(Cl)NPPh_2NSiMe_3$ (**2**) (see Scheme 1), both of which are shown to contain a four-membered PN_2Te ring (telluradiazaphosphetines) by X-ray crystallography. Compound **2** also exhibits a short exocyclic tellurium−nitrogen bond distance, which is of the same order of magnitude (*ca.* 1.92 Å) as the shortest known Te−N bonds.[10,11]

Scheme 1. Preparation of $[Ph_2P(NSiMe_3)_2]TeCl_3$ (**1**) and $Ph_2P(NSiMe_3)_2Te(Cl)NPPh_2NSiMe_3$ (**2**) from $Li[Ph_2P(NSiMe_3)_2]$ and $TeCl_4$



Experimental Section

The reagent $Ph_2P(NHSiMe_3)(NSiMe_3)$ was prepared from Ph_2PH and trimethylsilyl azide (Aldrich) by the literature procedure.[12] $TeCl_4$ (Alfa) was used as received. Solvents were dried with the appropriate drying agents and distilled immediately 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. Infrared spectra were obtained as Nujol mulls on a Mattson 4030 FTIR spectrophotometer. Elemental analyses were provided by Analytical Services Laboratory, Department of Chemistry, The University of Calgary.

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Table 1. Crystallographic Data for $Ph_2P(NSiMe_3)_2TeCl_3{\cdot}CH_2Cl_2$ and $Ph_2P(NSiMe_3)_2Te(Cl)NPPh_2NSiMe_3{\cdot}0.5C_7H_8$

formula	$C_{19}H_{30}PN_2Si_2Cl_5Te$	$C_{33}H_{47}N_4P_2ClTeSi_3{\cdot}0.5C_7H_8$
fw	678.67	855.09
space group	$P2_1/n$ (No. 14)	$P\bar{1}$ (No. 2)
a, Å	15.494(7)	12.372(7)
b, Å	11.580(9)	17.040(6)
c, Å	15.823(6)	11.648(4)
α, deg		108.11(2)
β, deg	96.46(3)	109.32(4)
γ, deg		88.76(4)
V, Å^3	2820(2)	2193(2)
T, °C	−123	23
λ, Å	0.710 69	0.710 69
ϱ_{calcd}, g cm^{-3}	1.597	1.295
μ, mm^{-1}	1.68	9.22
R^a	0.024	0.036
$R_w{}^b$	0.027	0.037

^{a} $R = \sum||F_o| - |F_c||/\sum|F_o|$ ^{b} $R_w = [\sum w\Delta^2/\sum wF_o{}^2]^{1/2}$

Preparation of $Ph_2(NSiMe_3)_2TeCl_3$ (1). A cold (−78 °C) solution of $Li[Ph_2P(NSiMe_3)_2]$ (5.104 g, 13.92 mmol) [prepared from ^nBuLi and $Ph_2P(NHSiMe_3)(NSiMe_3)$]^{13} in CH_2Cl_2 (40 mL) was added, via cannula, to a stirred slurry of $TeCl_4$ (3.751 g, 13.92 mmol) in CH_2Cl_2 (40 mL) at −78 °C. The reaction mixture was then allowed to reach room temperature. After 30 min, the pale yellow solution was separated from the white precipitate of lithium chloride by filtration through a layer of dry Celite and sea sand. Removal of solvent under vacuum produced $Ph_2P(NSiMe_3)_2TeCl_3$ (8.22 g, 13.85 mmol, 99% yield) as a very moisture-sensitive white solid, which was recrystallized from CH_2Cl_2−hexanes at 0 °C. Anal. Calc for $C_{19}H_{30}PN_2Si_2Cl_5Te$: C, 33.63; H, 4.47; N, 4.13. Found: C, 33.61; H, 4.48; N, 4.36. ^1H NMR (in CD_2Cl_2): δ 7.57−8.16 (PC_6H_5, 10H), 0.14 ($SiCH_3$, 18H). $^{31}P\{^1H\}$ NMR (in THF): δ 44.2 [s, $^2J(^{31}P{-}^{125}Te)$ = 144 Hz]. ^{125}Te NMR (in THF): δ 1317.3 [d, $^2J(^{31}P{-}^{125}Te)$ = 144 Hz]. The infrared spectrum (CsI windows) of **1** showed bands at 1252 s, 1115 s, 986 m, 839 s, 794 w, 746 m, 691 m, 648 m, 596 w, 525 s, 245 s, and 233 s cm^{-1}.

Preparation of $Ph_2P(NSiMe_3)_2Te(Cl)NPPh_2NSiMe_3$ (2). The above reaction was carried out in a 2:1 molar ratio using $Li[Ph_2P(NSiMe_3)_2]$ (1.05 g, 2.86 mmol) and $TeCl_4$ (0.385 g, 1.43 mmol). The reaction mixture was stirred vigorously and allowed to reach 23 °C. The progress of the reaction was monitored by ^{31}P NMR spectroscopy and, after 4 h, workup was carried out according to the procedure described for **1** to give white block-shaped crystals of $Ph_2P(NSiMe_3)_2Te(Cl)NPPh_2NSiMe_3$ (1.05 g, 1.24 mmol, 87% yield) after recrystallization from a 1:1 toluene−hexane mixture (20 mL). Anal. Calc for $C_{33}H_{47}ClN_4P_2Si_3Te{\cdot}0.5C_7H_8$: C, 46.35; H, 5.33; N, 6.55. Found: C, 46.92; H, 5.72; N, 6.22. NMR samples were recrystallized from CH_2Cl_2−diethyl ether. ^1H NMR (CD_2Cl_2): δ 7.9−8.8 (m, 20H, Ph), 0.64 (s, 18H, $SiMe_3$), 0.60 (s, 9H, $SiMe_3$). $^{31}P\{^1H\}$ NMR (in THF): δ 38.0 [s, $^2J(^{31}P{-}^{125}Te)$ = 104 Hz], 22.6 [s, $^2J(^{31}P{-}^{125}Te)$ = 107 Hz]. ^{125}Te NMR (in THF): δ 1635.4 [t, $^2J(^{31}P{-}^{125}Te)$ = 102 Hz]. The ^{125}Te NMR resonance appears as a 1:2:1 triplet as a result of the overlap of two doublets with nearly equal $^2J(^{31}P{-}^{125}Te)$ coupling constants.

X-ray Analysis of 1. A suitable colorless crystal of $Ph_2P(NSiMe_3)_2TeCl_3{\cdot}CH_2Cl_2$ (**1**$\cdot CH_2Cl_2$) with dimensions 0.42 × 0.33 × 0.56 mm was obtained at 5 °C from CH_2Cl_2 solutions layered with hexanes. Accurate cell dimensions and a crystal orientation matrix were determined on a Rigaku AFC6S diffractometer by a least-squares fit of the setting angles of 19 reflections with 2θ in the range 40−50°. Intensity data were collected by the $\omega/2\theta$ method using a scan speed of 4.0°/min, scan width of $(1.52 \pm 0.35 \tan\theta)°$, and monochromatic Mo K$\alpha$ radiation in the range $4 < 2\theta < 50°$. Three reflections were monitored every 100 min of exposure time and showed insignificant variations. The intensities of 5252 reflections were measured of which 4010 had $I > 3\sigma(I)$. Data were corrected for Lorentz, polarization, and absorption effects.^{14} Crystal data are given in Table 1, and the positional parameters are given in Table 2.

Table 2. Positional Parameters and B(eq) Values for **1**$\cdot CH_2Cl_2$

atom	x	y	z	B(eq), Å^2
Te(1)	0.10978(1)	0.09971(2)	0.57010(1)	1.218(7)
Cl(1)	0.06036(5)	0.08726(8)	0.41110(5)	2.08(4)
Cl(2)	−0.00435(5)	0.24852(8)	0.58068(6)	2.42(4)
Cl(3)	0.15256(6)	0.11998(9)	0.72627(5)	2.31(4)
Cl(4)	0.00735(7)	−0.0723(1)	0.10325(7)	3.26(5)
Cl(5)	0.15801(6)	0.00266(9)	0.21623(7)	3.12(4)
P(1)	0.27912(5)	0.14268(7)	0.52915(5)	1.12(3)
Si(1)	0.18463(6)	0.38158(8)	0.54456(6)	1.64(4)
Si(2)	0.26204(6)	−0.12455(8)	0.55303(6)	1.45(4)
N(1)	0.1953(2)	0.2270(2)	0.5440(2)	1.3(1)
N(2)	0.2354(2)	0.0228(2)	0.5530(2)	1.2(1)
C(1)	0.3763(2)	0.1771(3)	0.5972(2)	1.3(1)
C(2)	0.3787(2)	0.1573(3)	0.6845(2)	1.7(1)
C(3)	0.4515(2)	0.1863(3)	0.7389(3)	2.3(2)
C(4)	0.5227(2)	0.2359(3)	0.7065(3)	2.1(2)
C(5)	0.5215(2)	0.2547(3)	0.6213(3)	2.0(2)
C(6)	0.4492(2)	0.2271(3)	0.5659(2)	1.7(1)
C(7)	0.3074(2)	0.1474(3)	0.4217(2)	1.4(1)
C(8)	0.3749(2)	0.0770(3)	0.4000(2)	1.9(2)
C(9)	0.3970(3)	0.0766(4)	0.3180(2)	2.6(2)
C(10)	0.3529(3)	0.1471(4)	0.2565(2)	2.6(2)
C(11)	0.2862(3)	0.2164(3)	0.2777(2)	2.3(2)
C(12)	0.2624(2)	0.2164(3)	0.3597(2)	1.7(1)
C(13)	0.1576(3)	0.4325(4)	0.6496(3)	2.9(2)
C(14)	0.2934(3)	0.4403(4)	0.5288(3)	2.8(2)
C(15)	0.1051(3)	0.4286(4)	0.4540(3)	2.7(2)
C(16)	0.3766(3)	−0.1429(4)	0.6015(3)	2.4(2)
C(17)	0.2472(3)	−0.1808(4)	0.4424(3)	2.3(2)
C(18)	0.1857(3)	−0.1954(4)	0.6184(3)	2.5(2)
C(19)	0.0522(3)	−0.0555(4)	0.2102(3)	2.8(2)

The structure was solved by direct method (SIR88)^{15} and expanded using Fourier techniques.^{16} The non-hydrogen atoms were refined anisotropically, and hydrogen atoms were refined isotropically. Refinement was by full-matrix least squares to $R = 0.024$ [$R = \sum(|F_o| - |F_c|)/\sum|F_o|$], $R_w = 0.027$ [$R_w = [\sum w(|F_o| - |F_c|)^2/\sum_w F_o{}^2]^{1/2}$]. In the refinement cycles, weights were derived from the counting statistics. Scattering factors were those of Cromer and Waber,^{17} and allowance was made for anomalous dispersion.^{18} The maximum and minimum residual electron densities in the final ΔF map were 0.66 and −0.94 e Å^{-3}. All calculations were performed using the teXsan^{19} crystallographic software package.

X-ray Analysis of 2. A colorless, block-shaped crystal of $Ph_2P(NSiMe_3)_2Te(Cl)NPPh_2NSiMe_3{\cdot}0.5C_7H_8$ (**2**$\cdot 0.5C_7H_8$) with dimensions 0.63 × 0.65 × 0.30 mm was grown from a toluene−hexane solution at 5 °C. Accurate cell dimensions and a crystal orientation matrix were determined on a Rigaku AFC6S diffractometer by a least-squares fit of the setting angles of 25 reflections with 2θ in the range 20−40°. Intensity data were collected by the $\omega/2\theta$ method using a scan speed of 8.0°/min, scan width of $(1.73 + 0.34 \tan\theta)°$, and monochromatized Mo Kα radiation in the range $4 < 2\theta < 50°$. The intensities of 7771 reflections were measured, of which 5873 had $I > 3\sigma(I)$. Data were corrected for Lorentz, polarization, and absorption effects.^{14} Crystal data are given in Table 1, and positional parameters are reported in Table 3. The structure was solved by the Patterson method^{20} and expanded using Fourier techniques.^{21} The non-hydrogen

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Table 3. Atomic Coordinates and B_{eq} Values for **2**·0.5C_7H_8

atom	x	y	z	B_{eq},[a] Å^2
Te(1)	0.01116(3)	0.18493(2)	0.17325(3)	3.142(8)
Cl(1)	0.1252(1)	0.1956(1)	0.0298(1)	5.83(4)
P(1)	−0.1972(1)	0.25790(8)	0.1810(1)	3.45(3)
P(2)	0.1995(1)	0.22375(8)	0.4041(1)	3.22(3)
Si(1)	−0.0930(1)	0.3363(1)	0.0278(2)	4.47(4)
Si(2)	−0.1909(2)	0.1166(1)	0.2967(2)	5.40(5)
Si(3)	0.2573(1)	0.0459(1)	0.2820(2)	4.88(4)
N(1)	−0.1057(3)	0.2669(2)	0.1093(3)	3.15(10)
N(2)	−0.1447(3)	0.1849(2)	0.2356(4)	3.4(1)
N(3)	0.1031(3)	0.2721(2)	0.3232(3)	3.09(9)
N(4)	0.1848(3)	0.1292(2)	0.3298(4)	3.8(1)
C(1)	−0.3414(4)	0.2312(3)	0.0708(6)	4.5(1)
C(2)	−0.3628(5)	0.1974(4)	−0.0600(6)	5.9(2)
C(3)	−0.4732(7)	0.1697(4)	−0.1452(7)	8.5(2)
C(4)	−0.5617(7)	0.1747(6)	−0.100(1)	10.5(3)
C(5)	−0.5441(6)	0.2062(5)	0.029(1)	8.9(3)
C(6)	−0.4338(5)	0.2346(4)	0.1150(7)	6.4(2)
C(7)	−0.1990(4)	0.3510(3)	0.3057(5)	3.4(1)
C(8)	−0.2818(4)	0.4075(3)	0.2923(5)	4.3(1)
C(9)	−0.2750(5)	0.4780(4)	0.3934(6)	5.1(2)
C(10)	−0.1877(6)	0.4941(4)	0.5066(6)	5.5(2)
C(11)	−0.1036(5)	0.4403(4)	0.5233(5)	6.0(2)
C(12)	−0.1103(5)	0.3693(3)	0.4233(6)	4.6(1)
C(13)	0.1812(4)	0.2451(3)	0.5587(4)	3.3(1)
C(14)	0.1738(5)	0.3244(3)	0.6285(5)	4.9(2)
C(15)	0.1576(6)	0.3418(4)	0.7457(6)	6.2(2)
C(16)	0.1454(5)	0.2790(5)	0.7903(5)	5.7(2)
C(17)	0.1492(5)	0.1997(4)	0.7213(6)	5.3(2)
C(18)	0.1679(5)	0.1817(3)	0.6047(5)	4.4(1)
C(19)	0.3404(4)	0.2748(3)	0.4457(5)	3.6(1)
C(20)	0.4315(5)	0.2664(4)	0.5441(6)	6.5(2)
C(21)	0.5417(6)	0.3008(6)	0.5715(7)	9.1(3)
C(22)	0.5584(6)	0.3473(5)	0.5026(8)	8.1(3)
C(23)	0.4699(6)	0.3581(4)	0.4054(7)	6.9(2)
C(24)	0.3602(5)	0.3223(4)	0.3763(6)	4.9(2)
C(25)	−0.2065(6)	0.4089(4)	0.0353(7)	7.9(2)
C(26)	−0.1195(5)	0.2776(4)	−0.1448(5)	6.6(2)
C(27)	0.0476(5)	0.3986(4)	0.1074(6)	6.1(2)
C(28)	−0.0820(6)	0.0421(4)	0.3195(7)	8.0(2)
C(29)	−0.212(1)	0.1742(6)	0.4469(9)	15.8(5)
C(30)	−0.3261(6)	0.0564(5)	0.180(1)	12.9(3)
C(31)	0.1606(6)	−0.0237(4)	0.1267(7)	9.6(2)
C(32)	0.3870(6)	0.0734(5)	0.2544(9)	11.4(3)
C(33)	0.2941(8)	−0.0110(5)	0.3968(9)	12.4(4)
C(34)	0.565(2)	0.547(3)	0.947(6)	23(1)
C(35)	0.540(2)	0.570(2)	1.066(7)	25(1)
C(36)	0.484(5)	0.534(4)	1.127(3)	33(1)

[a] $B_{eq} = {}^8/_3\pi^2[U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{12}aa^*bb^* \cos \gamma + 2U_{13}aa^*cc^* \cos \beta + 2U_{23}bb^*cc^* \cos \alpha]$.

atoms were refined anisotropically. Hydrogen atoms were included but not refined. A molecule of toluene was located in the lattice on a special position and is disordered; the methyl C atom could not be located successfully and was assumed to be disordered over six sites and, therefore, the contribution of the methyl group was included at the sites in the benzene ring along with hydrogen atoms. Refinement was carried out in a manner similar to that described for **1**·CH_2Cl_2 and converged with $R = 0.036$ and $R_w = 0.037$.

Results and Discussion

Syntheses of $Ph_2P(NSiMe_3)_2TeCl_3$ (1) and $Ph_2P(NSiMe_3)_2Te(Cl)NPPh_2NSiMe_3$ (2). The reaction of $Li[Ph_2P(NSiMe_3)_2]$ with $TeCl_4$ in a 1:1 molar ratio in dichloromethane proceeds cleanly to give $Ph_2P(NSiMe_3)_2TeCl_3$ (**1**) in essentially quantitative yields as highly moisture-sensitive, colorless crystals (see Scheme 1). The ^1H NMR spectrum of **1** indicates the presence of two equivalent $Si(CH_3)_3$ groups per $P(C_6H_5)_2$ unit, and the ^{125}Te NMR spectrum exhibits a doublet centered at 1317.3 ppm with $^2J(^{31}P-^{125}Te) = 144$ Hz, implying the presence of a four-membered PN_2Te ring. The ^{125}Te NMR chemical shift falls within the range (1298−1331 ppm) previously observed for derivatives of the type $Ph_2P(NSiMe_3)_2TeCl_2Ar$, but the two-bond ^{31}P-^{125}Te coupling constant is significantly larger than those found for other PN_2Te rings, which were in the range 84−116 Hz.[9] For comparison, the six-membered ring $\overline{NP(Ph_2)CH_2(Ph_2)PNTeCl_2}$ has a value of $^2J(^{31}P-^{125}Te) = 132$ Hz.[22]

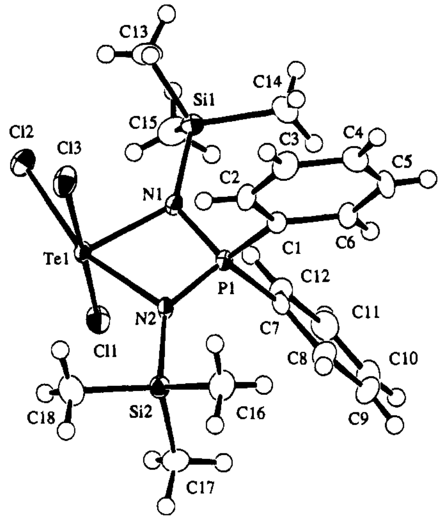

Figure 1. ORTEP diagram and atomic numbering scheme for $[Ph_2P(NSiMe_3)_2]TeCl_3$ (**1**).

The reaction of $Li[Ph_2P(NSiMe_3)_2]$ with $TeCl_4$ in dichloromethane in a 2:1 molar ratio occurs via the formation of **1**, which was detected by ^{31}P NMR spectroscopy, to give a product identified as $Ph_2P(NSiMe_3)_2Te(Cl)NPPh_2NSiMe_3$ (**2**), which was isolated as moisture-sensitive, colorless crystals in 87% yield. The ^1H NMR spectrum reveals that **2** contains three Me_3Si groups, two of which are in indistinguishable environments, and two Ph_2P groups. The ^{31}P NMR spectrum of **2** in THF consists of two singlets at 38.0 and 22.6 ppm, both of which show ^{125}Te satellites with coupling constants of 104 and 107 Hz, respectively, corresponding to two-bond $^{31}P-^{125}Te$ interactions. The ^{125}Te NMR spectrum of **2** in THF consists of an apparent 1:2:1 triplet centered at 1635.4 ppm, which is the result of two overlapping doublets with nearly equal $^2J(^{31}P-^{125}Te)$ coupling constants. Thus it is evident that the 2:1 reaction results in the elimination of Me_3SiCl from the initial product, but the NMR data do not unambiguously establish the structure of **2** depicted in Scheme 1. An alternative spirocyclic structure in which the terminal $=NSiMe_3$ is coordinated (through nitrogen) to tellurium cannot be ruled out. For comparison, it is interesting to note that the reaction of $Ph_2PN_2(SiMe)_3$ with $TiCl_4$ in a 2:1 molar ratio gives $Ph_2P(NSiMe_3)_2TiCl_2NPPh_2N(SiMe_3)_2$.[23]

X-ray Structures of $Ph_2P(NSiMe_3)_2TeCl_3$ (1) and $Ph_2P(NSiMe_3)_2Te(Cl)NPPh_2NSiMe_3$ (2). An X-ray analysis of **1**·CH_2Cl_2 confirmed the presence of a four-membered PN_2Te ring. An ORTEP diagram of **1** is shown in Figure 1, and pertinent bond lengths and bond angles are given in Table 4. The conformation of the PN_2Te ring is almost planar with the nitrogen atoms N(1) and N(2) lying out of the best plane by 0.053(3) and 0.051(3) Å, respectively. The Te−N distances of 2.056(3) and 2.185(3) Å can be compared with the cor-

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Table 4. Selected Bond Lengths (Å) and Bond Angles (deg) in $\mathbf{1}\cdot CH_2Cl_2$ and $\mathbf{2}\cdot 0.5C_7H_8$

$\mathbf{1}\cdot CH_2Cl_2$		$\mathbf{2}\cdot 0.5C_7H_8$	
Te(1)−N(1)	2.056(3)	Te(1)−Cl(1)	2.564(2)
Te(1)−N(2)	2.185(3)	Te(1)−N(1)	2.108(3)
P(1)−N(1)	1.662(3)	Te(1)−N(2)	2.275(4)
P(1)−N(2)	1.608(3)	Te(1)−N(3)	1.922(4)
Te(1)−Cl(1)	2.550(1)	P(1)−N(1)	1.648(1)
Te(1)−Cl(2)	2.488(1)	P(1)−N(2)	1.598(4)
Te(1)−Cl(3)	2.496(1)	P(2)−N(3)	1.638(4)
Si(1)−N(1)	1.798(3)	P(2)−N(4)	1.555(4)
Si(2)−N(2)	1.756(3)	Si(1)−N(1)	1.769(4)
		Si(2)−N(2)	1.733(4)
		Si(3)−N(4)	1.706(4)
N(1)−Te(1)−N(2)	70.3(1)	N(1)−Te(1)−N(2)	68.7(1)
N(1)−P(1)−N(2)	96.8(1)	N(1)−P(1)−N(2)	99.4(2)
Te(1)−N(1)−P(1)	98.0(1)	Te(1)−N(1)−P(1)	98.2(2)
Te(1)−N(2)−P(1)	94.7(1)	Te(1)−N(2)−P(1)	93.2(2)
Te(1)−N(1)−Si(1)	130.6(1)	Te(1)−N(3)−P(2)	104.1(2)
Te(1)−N(2)−Si(2)	127.5(1)	Te(1)−N(1)−Si(1)	129.5(2)
P(1)−N(1)−Si(1)	131.3(2)	Te(1)−N(2)−Si(2)	129.8(2)
P(1)−N(2)−Si(2)	137.2(2)	P(1)−N(1)−Si(1)	131.5(2)
Cl(1)−Te(1)−Cl(2)	88.21(3)	P(1)−N(2)−Si(2)	136.3(2)
Cl(1)−Te(1)−Cl(3)	177.05(3)	Cl(1)−Te(1)−N(1)	92.0(1)
Cl(1)−Te(1)−N(1)	88.33(8)	Cl(1)−Te(1)−N(2)	157.5(1)
Cl(1)−Te(1)−N(2)	91.56(7)	Cl(1)−Te(1)−N(3)	95.9(1)
Cl(2)−Te(1)−Cl(3)	88.85(3)	N(1)−Te(1)−N(3)	92.6(3)
Cl(2)−Te(1)−N(1)	89.78(8)	N(2)−Te(1)−N(3)	96.3(1)
Cl(2)−Te(1)−N(2)	160.11(7)	N(3)−P(2)−N(4)	110.8(2)
Cl(3)−Te(1)−N(1)	91.50(8)	P(2)−N(4)−Si(3)	143.8(3)
Cl(3)−Te(1)−N(2)	91.16(7)		

responding values of 2.096(4) and 2.192(4) Å in $PhC(NSiMe_3)_2$-$TeCl_3$. The P−N distances in $\mathbf{1}\cdot CH_2Cl_2$ also exhibit a marked inequality [1.608(2) and 1.662(3) Å]. Pairwise bond inequalities are also observed in the samarium(III) complex $[Ph_2P(NSiMe_3)_2]_2$-$Sm(\mu\text{-}I)_2Li(THF)_2$.[24] By contrast, the four-membered PN_2M rings in derivatives of the type $Ph_2P(NSiMe_3)_2ML_n$ (where ML_n = $TiCl_3$,[23] $Li(THF)_2$,[24] and $K(THF)_4$[25]) have more symmetrical structures with P−N distances that are equal within experimental error. The endocyclic angle at phosphorus in **1** is 96.8°; cf. 109.4(2)° in $Ph_2P(NSiMe_3)_2Li(THF)_2$.[24] The geometry at the two nitrogen atoms is essentially planar with $\sum\hat{N}(1) = 359.9°$ and $\sum\hat{N}(2) = 359.4°$. Apart from the small bite angle of the ligand [$\angle N(1)-Te(1)-N(2) = 70.3(1)°$], the pseudooctahedral geometry is not significantly distorted by the lone pair on the tellurium(IV) center with bond angles in the range 88.2−91.6°.

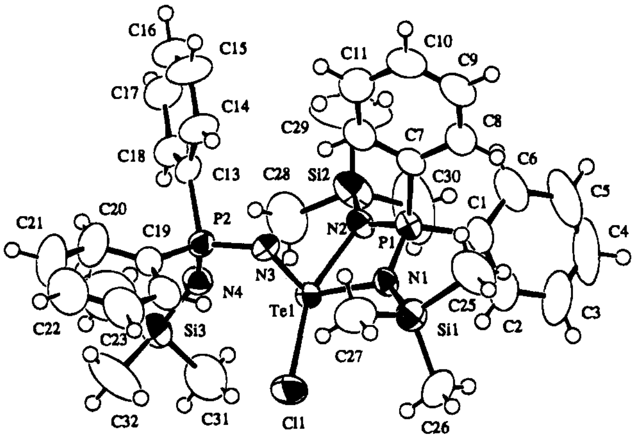

Figure 2. ORTEP diagram and atomic numbering scheme for $Ph_2P(NSiMe_3)_2Te(Cl)NPPh_2NSiMe_3$ (**2**).

Table 5. Tellurium−Nitrogen Bond Lengths for Compounds Containing Short Te−N Bonds

compound	*d*(Te−N), Å	ref
$(Ph_3PN)_2TeCl_2$	1.912(2), 1.923(3)	10
$(Ph_3PN)TeCl_2(C_6H_4OMe\text{-}4)$	1.918(2)	10
$Ph_2P(NSiMe_3)_2Te(Cl)NPPh_2NSiMe_3$	1.922(4)	this work
$(Ph_2SN)TeCl_3\cdot pyridine$	1.951(7)	11
$(Ph_2SN)_2TeCl_2$	1.951(3), 1.956(3)	11
$(4\text{-}MeOC_6H_4)_2Te{=}NSO_2C_6H_4CH_3\text{-}4$	1.98	25
$(Ph_2CN)_2TeF_2\cdot 0.5CH_3CN$	1.989(3), 1.995(3)	11

An ORTEP diagram of **2** is illustrated in Figure 2, and selected bond lengths and bond angles are summarized in Table 4. The X-ray structural determination confirmed the structure of **2** depicted in Scheme 1. This inorganic heterocycle consists of a PN_2Te ring with unequal Te−N bond distances of 2.108(3) and 2.275(4) Å and a short exocyclic tellurium−nitrogen bond of 1.922(4) Å. As indicated in Table 5, this value is among the shortest for a Te−N bond reported in the literature. However, although Te(1)−N(3) is formally a double bond in **2**, the bond distance is significantly longer than the predicted value of 1.83 Å,[11] suggesting dipolar contributions to the bond, which may also account for the shorter-than-expected P(2)−N(3) bond [1.638(4) Å]. The P(2)−N(4) distance of 1.555(4) Å corresponds to a double bond. The P−N bond lengths in the PN_2Te ring are unequal [1.648(1) and 1.598(4) Å], with the longer one associated with the shorter Te−N bond. The endocyclic bond angle of 99.4(2)° at phosphorus in **2** is slightly larger than that observed for **1**, while the bite angle of 68.7(3)° at tellurium is smaller. The other bond angles around tellurium fall within the range 92.6−96.3°, indicating a distorted pseudo-square-pyramidal geometry with a lone pair occupying a basal site. There is a remarkable difference in the bond angles at the two-coordinate nitrogen atoms N(3) and N(4) [104.1(2) *vs* 143.8(3)°].

In summary, the reaction of $Li[Ph_2P(NSiMe_3)_2]$ with $TeCl_4$ in a 1:1 molar ratio provides a high-yield route to $Ph_2P(NSiMe_3)_2$-$TeCl_3$, which contains a four-membered TeN_2P ring. When this reaction is carried out in a 2:1 molar ratio, the elimination of Me_3SiCl from the initial product occurs spontaneously to give $Ph_2P(NSiMe_3)_2Te(Cl)NPPh_2NSiMe_3$. These telluradiazaphosphetidines should be useful reagents for the development of TeNP chemistry.

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Supplementary Material Available: Tables listing X-ray experimental details, bond distances, bond angles, torsion angles, anisotropic thermal parameters, and parameters for hydrogen atoms (21 pages). Ordering information is given on any current masthead page.

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