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Synthesis and Characterization of New Heterocyclic Compounds of Tungsten, Selenium, and Tellurium

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The bis-silylated phosphorane $Me_3SiNP(Ph_2)CH_2(Ph_2)PNSiMe_3$ (**1**) reacts with WF_6, WCl_6, $SeOCl_2$ and $TeCl_4$ to form new heterocyclic compounds containing tungsten [$NP(Ph_2)CH_2(Ph_2)PNWF_4$ (**2**), $NP(Ph_2)CH_2(Ph_2)PNWCl_4$ (**3**)], selenium [$NP(Ph_2)CH_2(Ph_2)PNSeCl_2$ (**5**)], and tellurium [$NP(Ph_2)CH_2(Ph_2)PNTeCl_2$ (**6**)], respectively. The reaction of the unsaturated heterocyclic compound **3** with the base DBU leads to the formation of a conjugated heterocyclic compound, $NP(Ph_2)CH(Ph_2)PNWCl_3$ (**4**), through the elimination of DBU·HCl. ^1H, ^{31}P, ^{19}F, ^{77}Se, and ^{125}Te NMR spectroscopic investigations confirm the structures of compounds **2**–**6**.

Introduction

Cyclophosphazene chemistry continues to be an important area of research in inorganic heterocyclic systems. The synthesis of (a) transition-metal-bound phosphazenes,[1-3] (b) phosphazene derivatives with biologically active side groups,[4,5] and (c) organofunctional phosphazene polymers possessing unusual properties[6-8] are some of the noteworthy advances in this field in the last few years. A majority of these investigations are concerned with the substitution reactions of the halogenocyclophosphazenes; in contrast, synthesis of phosphazene compounds incorporating an additional (new) heteroatom within the ring skeleton remains relatively unexplored. The synthesis of cyclophospha(thia)zenes[9,10] has stimulated renewed interest in discovering different inorganic heterocyclic systems using "phosphazene" as the basic ring skeleton.

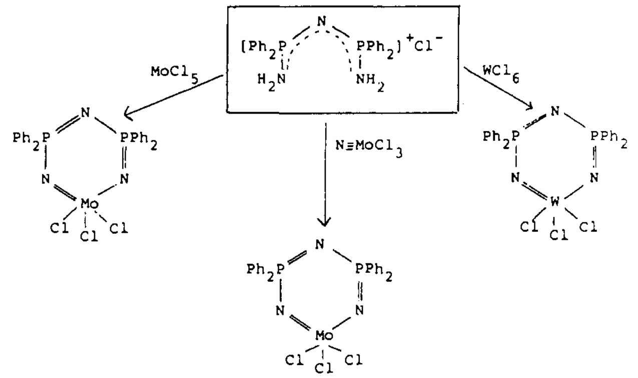
Recently, new synthetic strategies (Scheme I) have been developed in our laboratory that led to the preparation of cyclometallaphosphazenes: cyclophosphazenes containing transition metals as part of the ring skeleton.[11-13] These cyclometallaphosphazenes have provided valuable information about the bonding within the phosphazene ring and also have shown promise as potential precursors for the synthesis of transition-metal-incorporated phosphazene polymers.[14]

In this paper, we report synthetic routes to new heterocyclic compounds of tungsten, tellurium, and selenium (Scheme II). We also show that the bis-silylated phosphorane **1**, which is a building unit for these new heterocyclic compounds, has important chemical implications in view of its dual phosphazene and phosphorane characteristics.

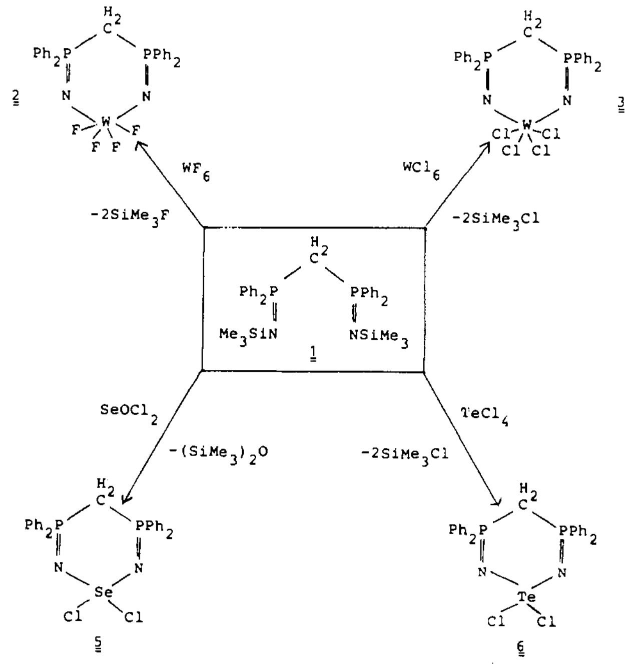
Experimental Section

Materials. All experimental manipulations were performed under an atmosphere of dry nitrogen. Solvents were dried and distilled prior to use. The silylated phosphorane **1** was prepared by using the method described previously.[15] WCl_6, WF_6, $SeOCl_2$ and $TeCl_4$ were commercial products obtained from Fluka chemicals.

Scheme I



Scheme II



Equipment. ^{19}F, ^{31}P, ^{77}Se, and ^{125}Te NMR spectra were obtained by means of a Bruker AM 250 instrument using an internal standard of $CFCl_3$ and 85% H_3PO_4, $(CH_3)_2Se$, and $(CH_3)_2Te$ as external standards, respectively. ^1H NMR spectra were obtained by means of a Bruker 60 E spectrometer with $SiMe_4$ as internal standard. C_6D_6 or $CDCl_3$ was used as an internal lock. The chemical shifts are quoted on the δ scale

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Table I. ^{31}P and ^{1}H NMR Spectroscopic Data

compd	^{31}P NMR[a] δ [J, Hz]	^{1}H NMR[b]		
		δ(PCHP)	δ($P(C_6H_5)$)	^2J(P–C–H), Hz
$(SiMe_3)_2N(Ph_2)PCH_2P(Ph_2)N(SiMe_3)_2$ (**1**)	−3.8 (s)	3.35 (t)	7.32 (m)	14
$\overline{NP(Ph_2)CH_2(Ph_2)PNW}F_4$ (**2**)	29.7 (m) [$^2J(^{31}P–^{183}W)$ = 78; $^3J(^{31}P–^{19}F)$ = 3.5]	3.90 (t)	7.55 (m)	12.5
$\overline{NP(Ph_2)CH_2(Ph_2)PNW}Cl_4$ (**3**)	32.6 (s)	3.85 (t)	7.55 (m)	12
$\overline{NP(Ph_2)N(Ph_2)PNW}Cl_3$[c]	39.2 (s) [$^2J(^{31}P–^{183}W)$ = 63]			
$\overline{NP(Ph_2)CH(Ph_2)PNW}Cl_3$ (**4**)	49.2 (s) [$^2J(^{31}P–^{183}W)$ = 70]	1.90 (br)	7.50 (m)	
$\overline{NP(Ph_2CH_2(Ph_2)PNSe}Cl_2$ (**5**)	15.5 (s) [$^2J(^{31}P–^{77}Se)$ = 49]	3.65 (t)	7.40 (m)	13.3
$\overline{NP(Ph_2)CH_2(Ph_2)PNTe}Cl_2$ (**6**)	13.3 (s) [$^2J(^{31}P–^{125}Te)$ = 132]	3.65 (t)	7.40 (m)	13

[a] All spectra recorded in DMF with C_6D_6 as lock and referenced to external 85% H_3PO_4. Key: s = singlet; m = multiplet. [b] All spectra recorded in $CDCl_3$ with $SiMe_4$ as an internal reference. Key: t = triplet; br = broad; m = multiplet. [c] From ref 11.

with positive shifts downfield of the standard. Infrared spectra were obtained on a Perkin-Elmer 180 spectrophotometer. Mass spectrometric analysis were performed on a Finnigan MAT 8230 instrument. The elemental microanalyses were carried out by Beller Laboratory, Göttingen, FRG.

Synthesis of $\overline{NP(Ph_2)CH_2(Ph_2)PNW}F_4$ (2). **1** (3.90 g, 7 mmol) dissolved in dry dichloromethane (100 mL) was added dropwise (30 min) to a stirred solution of WF_6 (2.10 g, 7 mmol) in dichloromethane (50 mL) at −78 °C. The mixture was allowed to warm up to room temperature and was heated at reflux for 3 h. The white precipitate was filtered off at ambient temperature and dried in vacuo. The ^{31}P and the ^{19}F NMR spectra of this solid indicated **2** along with considerable amounts of impurities. The crude product was washed with dry chloroform (4 × 50 mL) and recrystallized twice from dry DMF (yield of **2** 2.15 g, 45%); mp 235 °C.

Anal. Calcd for $C_{25}H_{22}F_4N_2P_2W$: C, 44.65; H, 3.27; N, 4.16; F, 11.31; P, 9.22. Found: C, 44.39; H, 3.17; N, 4.20; F, 11.27; P, 9.17; IR (Nujol), cm^{-1}: 1200 vs, br, 1185 vs, br, 1150 m, 1115 vs, br, 1055 s, 1030 m, 780 s, 740 s, br, 680 s, 635 s, 605 s, 595 s, 565 s, 500 s, 445 s. ^{19}F NMR (DMF, C_6D_6; internal $CFCl_3$): $\delta(F_A)$ −0.7 (t), $\delta(F_B)$ −26.0 (t) [$^2J(^{19}F_A–^{19}F_B)$ = 70 Hz; $^3J(^{19}F–^{31}P)$ = 3.5 Hz; $^1J(^{19}F–^{183}W)$ = 50 Hz].

Synthesis of $\overline{NP(Ph_2)CH_2(Ph_2)PNW}Cl_4$ (3). **1** (5.62 g, 10 mmol) dissolved in dry chloroform (100 mL) was added dropwise (30 min) to a stirred solution of WCl_6 (4.08 g, 10 mmol) in dry chloroform (100 mL) at 0 °C. The mixture was allowed to warm up to room temperature and was heated under reflux for 24 h. The pale-yellow precipitate was filtered at ambient temperature and dried in vacuo. The crude product was recrystallized from DMF (yield of **3** 6.15 g, 80%); mp 250–252 °C.

Anal. Calcd for $C_{25}H_{22}Cl_4N_2P_2W$: C, 40.50; H, 2.97; N, 3.78; Cl, 19.18. Found: C, 40.43; H, 2.69; N, 3.75; Cl, 20.0. IR (Nujol), cm^{-1}: 1185 m, 1155 m, 1110 vs, br, 1055 s, 990 s, 850 s, 780 m, 745 vs, br, 730 s, 690 vs, 605 s, 545 s, 495 s, 420 s, 400 s. MS: *m/z* calcd 739, found 739.

Synthesis of $\overline{NP(Ph_2)CH(Ph_2)PNW}Cl_3$ (4). DBU (1.02 g, 6.6 mmol) dissolved in toluene (50 mL) was added dropwise (30 min) to a stirred solution of **3** (4.55 g, 6 mmol) in toluene (100 mL). The reaction mixture was heated under reflux for 10 h and filtered at ambient temperature. The dark brown precipitate was washed with chilled (5 °C) acetonitrile (4 × 25 mL) and dried in vacuo. This crude product was recrystallized from DMF–chloroform (yield of **4** 2.87 g, 66%); mp 190–192 °C.

Anal. Calcd for $C_{25}H_{21}Cl_3N_2P_2W$: C, 42.78; H, 2.93; N, 3.99; Cl, 15.16. Found: C, 42.51; H, 3.04; N, 3.96; Cl, 15.25. IR (Nujol), cm^{-1}: 1210 s, 1190 s, br, 1160 m, 1135 s, br, 1080 s, br, 1050 m, 980 s, 880 s, br, 790 m, 760 s, 710 vs, 610 s, 560 s, 500 s, br, 420 s, 400 s. MS: *m/z* calcd 703, found 703.

Synthesis of $\overline{NP(Ph_2)CH_2(Ph_2)PNSe}Cl_2$ (5). A solution of **1** (8.42 g, 15 mmol) in dry chloroform (150 mL) was added dropwise to a stirred solution of $SeOCl_2$ (2.50 g, 15 mmol). The reaction mixture was stirred at 25 °C for 24 h. The pale yellow precipitate was filtered off and washed with dry chloroform (2 × 25 mL). The crude product was recrystallized from DMF–chloroform (yield of **5** 5.58 g, 65%); mp 140 °C.

Anal. Calcd for $C_{25}H_{22}Cl_2N_2P_2Se$: C, 53.39; H, 3.91; Cl, 12.62; Se, 14.04. Found: C, 53.50; H, 4.01; Cl, 12.39; Se, 13.96. IR (Nujol), cm^{-1}: 1265 m, 1115 vs, 1090 vs, 1035 m, 1010 s, 990 s, 797 s, 735 s, 690 s, 650 m, 560 m, 500 w, 480 m, br. ^{77}Se NMR (DMF, C_6D_6; external $(CH_3)_2Se$): δ 1336 (t, br).

Synthesis of $\overline{NP(Ph_2)CH_2(Ph_2)PNTe}Cl_2$ (6). A solution of **1** (8.36 g, 15 mmol) in dry toluene (150 mL) was added dropwise (45 min) to a stirred solution of $TeCl_4$ (4.15 g, 15 mmol) in toluene (100 mL) at 0 °C. The reaction mixture was stirred at 25 °C for 4 h and then heated under reflux for 12 h. The white shiny solid was filtered off and dried in vacuo. It was recrystallized from DMF–chloroform (yield of **6** 7.27 g, 80%); mp 150–152 °C.

Anal. Calcd for $C_{25}H_{22}Cl_2N_2P_2Te$: C, 49.14; H, 3.60; N, 4.58; Cl, 11.61; Te, 20.90. Found: C, 48.97; H, 3.63; N, 4.49; Cl, 12.10; Te, 21.01. IR (Nujol), cm^{-1}: 1110 s, 1065 m, 1040 m, 1025 s, 1000 m, 780 s, 760 s, 745 s, 730 s, 695 s. ^{125}Te NMR (DMF, C_6D_6; external $(CH_3)_2Te$): δ 1530 (s, br). MS: *m/z* calcd 610, found 577 (M^+ − Cl).

Results and Discussion

General Reaction. The silylated phosphorane **1** reacts with WF_6, WCl_6, $SeOCl_2$, and $TeCl_4$ to yield a new class of heterocyclic compounds **2**, **3**, **5**, and **6**, respectively (Scheme II). A key feature in all these reactions involves the reactivity of the Si–N bond in **1**. A similar approach has led to the synthesis of a number of P–N compounds[15,16] and P–N polymers.[16]

Synthesis of 2. Compound **1** reacts with WF_6 in CH_2Cl_2 to give **2** in up to 45% yield. This low yield can be attributed to nucleophilic cleavage of the P–C–P linkage in **1** by WF_6 as evidenced by the ^{19}F and ^{31}P NMR spectra of the reaction mixture. In fact, the yield of **2** decreased drastically when forcing conditions like rapid addition of reactants and refluxing for more than 12 h were employed. The procedure described in the Experimental Section is a result of several experiments to obtain **2** in maximum yields.

Compound **2** is a hydrolytically stable white solid. Alkylaminotungsten(VI) fluorides are known in the form of air-sensitive viscous oils.[17] The stability of **2** can be understood in terms of the stability of the acyclic analogue $(Ph_3P{=}N)_2WF_4$.[18] The W–N bond length in this acyclic compound corresponds to some multiple-bonding character and the consequent neutralization of the high nuclear charge of tungsten can account for the high kinetic stability of such compounds.[18]

The ^{19}F NMR spectrum of **2** shows two triplets centered at −0.7 and −26.0 ppm with ^{183}W satellites and with fine structures attributable to the coupling with ^{31}P nucleus across three bonds. The data are summarized in the Experimental Section. The ^{31}P NMR spectrum of **2** shows an unresolved multiplet centered at 29.7 ppm. However, the ^{183}W satellites and the $^3J(^{31}P–^{19}F)$ couplings can be easily seen (Table I). NMR measurements at low temperatures were not possible because of the poor solubility of **2**. From the interpretation of the ^{19}F NMR spectrum of **2**, it can be concluded that the fluorine atoms occupy the cis positions in the tungsten octahedron. This observation indicates a high trans influence of the ligand **1**. The acyclic compound $(Ph_3P{=}N)_2WF_4$

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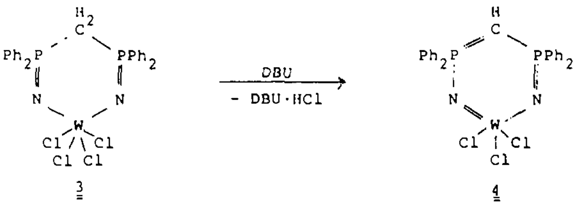
Scheme III



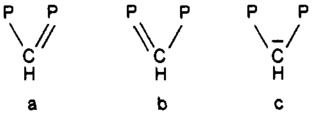
showed ^{19}F NMR spectroscopic patterns similar to those of **2**, and it was confirmed to be a cis isomer by X-ray crystallography.[18] The structure of **2** is further confirmed by ^{1}H NMR spectroscopy (Table I).

Synthesis of 3. The reaction of **1** with WCl_6 in refluxing chloroform resulted in the formation of the heterocyclic compound **3** in 80% yield. **3** is a brown moisture-sensitive solid. The ^{31}P NMR spectrum of **3** consisted of a singlet at 32.6 ppm with unresolved ^{183}W satellites. The ^{1}H NMR spectrum of **3** (Table I) fully confirms its structure. The electron-impact mass spectrum of **3** showed the parent ion (m/z 739), which is compatible with structure **3**.

The unsaturated ring **3** can be converted into a conjugated heterocyclic compound **4** by intermolecular abstraction of HCl from **3**. This was accomplished by treating **3** with a base, 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) (Scheme III). Compound **4** is a brown moisture-sensitive solid.

The ^{31}P NMR spectrum of **4** consisted of a singlet at 49.2 ppm with ^{183}W satellites ($^{2}J(^{31}\mathrm{P}-^{183}\mathrm{W})$ = 70 Hz). These ^{31}P NMR parameters can be compared with that of the corresponding cyclometallaphosphazene, $\overline{\mathrm{NP(Ph_2)N(Ph_2)PNW}}\mathrm{Cl_3}$, which resonates at 39.2 ppm.[11]

The unequivocal evidence for the conjugated structure of **4** comes from ^{1}H NMR spectroscopy. The CH proton in **4** resonates at 1.90 ppm as a broad signal even at −30 °C, instead of an expected triplet. This value of the chemical shift is rather uncharacteristic of a vinyl proton and rules out the possibility of resonance restructures a and b for the P-C-P group in **4**. However, the CH proton seems to have the ylide character with a free electron pair on the carbon atom as depicted in structure c. The ylide type of CH proton in **4** would be expected to have an intermolecular exchange and therefore resonates as a broad signal at low temperatures also. Appel et al. have made a similar observation on an analogous conjugated heterocyclic compound, $\overline{\mathrm{NP(Ph_2)CH(Ph_2)PNS}}\mathrm{CH_3}$.[19] Bestmann et al. have observed a similar ^{31}P–^{1}H coupling effect in a phosphorus ylide.[20] The electron-impact mass spectrum of **4** showed the parent ion (m/z 703) to be compatible with the structure **4**.



Attempts to regenerate **3** by reacting **4** with HCl gas were unsuccessful. However, a partial decomposition of **4** occurred to give a mixture of products as revealed by ^{31}P and ^{1}H NMR spectroscopy.

Synthesis of 5 and 6. The silylated phosphorane **1** reacts with $SeOCl_2$ and $TeCl_4$ to give **5** and **6**, respectively, in good yields. The selenium heterocyclic compound **5** is a white crystalline solid, sensitive to light and moisture whereas the tellurium analogue is a hydrolytically stable white solid. The ^{31}P NMR spectra of **5** and **6** showed single resonances at 15.5 and 13.3 ppm with ^{77}Se and ^{125}Te satellite signals, respectively. The ^{77}Se and ^{125}Te NMR spectra for **5** and **6** consisted of unresolved triplets centered at 1336 and 1530.7 ppm, respectively. It may be noted that the selenium atom in **5** resonates at much lower field compared to Se in the acyclic compound $Ph_3P{=}N{-}SeCl_3$.[21] The ^{1}H NMR spectroscopic parameters for **5** and **6** (Table I) give further evidence for their structures. The electron-impact mass spectrum of **5** did not show meaningful fragmentations. However, the elemental microanalysis was compatible with structure **5**. The electron-impact mass spectrum of **6** showed the parent ion minus one chlorine atom. Satisfactory elemental microanalysis confirmed structure **6**.

Conformation of the Six-Membered Rings in 2–6. ^{1}H NMR spectroscopy of **2–6** reveals that the phenyl and the methylene protons in these heterocyclic compounds are magnetically equivalent. It therefore appears that these six-membered ring systems are planar. It may be noted that the six-membered rings of the cyclometallaphosphazenes $\overline{\mathrm{NP(Ph_2)N(Ph_2)PNM}}\mathrm{Cl_3}$ (M = W or Mo) are also planar as indicated by X-ray crystallography.[11,12] Because of the low solubility of the metallacyclic compounds (**2–6**) in common organic solvents, we assume that their solid-state structures will have extensive halogen bridges.

Conclusions

The versatality of the silylated phosphorane **1** for synthesis of new inorganic heterocyclic compounds is demonstrated. The convenient synthetic route to the selenium heterocyclic compound **5** is particularly important because of its relevance to selenium–nitrogen-based polymers. The synthesis of cyclometallaphosphazenes,[11-13] cyclometallathiazenes,[10,22,23] and the cyclometalladiazadiphosphoranes **2–4** has opened up a new topic of research in transition-metal-based inorganic heterocyclic chemistry.

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Supplementary Material Available: ^{19}F NMR spectrum of **2** (1 page). Ordering information is given on any current masthead page.

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