An unconventional route to [(Me₃Si)₂HCPCl₂W(CO)₅] and its conversion to the structurally characterized *P*-chalcogenides (Me₃Si)₂HCP(X)Cl₂ [X = S, Se]

Arif Ali Khan, Cathleen Wismach, Peter G. Jones and Rainer Streubel*

Institut für Anorganische und Analytische Chemie der Technischen Universität Braunschweig, Postfach 3329, D-38023 Braunschweig, Germany. E-mail: r.streubel@tu-bs.de

Heating a solution of 2*H*-azaphosphirene complex **1** in CCl₄ at 75 °C for 2 h yields selectively [(Me₃Si)₂HCPCl₂W(CO)₅] (**6**). Attempts to convert this cleanly to the corresponding *P*-oxide [(Me₃Si)₂HCP(O)Cl₂] (**7**) were unsuccessful and even the reaction of (Me₃Si)₂HCPCl₂ (**9**) with the urea–H₂O₂ adduct in toluene led only to the formation of the hydrolysis product [(Me₃Si)₂HCP(O)(OH)Cl] (**8**). However, **9** could be selectively converted to **7** by the use of DMSO. In contrast, the related chalcogenides [(Me₃Si)₂HCP(S)Cl₂] (**10**) and [(Me₃Si)₂HCP(Se)Cl₂] (**11**) could be synthesized from either **6** or **9** with elemental sulfur and selenium, respectively. All products were characterized by NMR and MS and, additionally **6**, **8**, **10** and **11** by single crystal X-ray studies. Compound **10** represents the first example of a structurally characterized thiophosphonic dihalide.

Introduction

Recently, we demonstrated the versatile use of 2*H*-azaphosphirene complexes **I** in P-heterocycle synthesis.[1] For example, thermal P–C bond cleavage reactions of the three-membered ring of **I** generated short-lived nitrilium phosphane–ylide complexes[2] **II** or electrophilic terminal phosphinidene complexes **III** that could both be trapped by various π-systems *via* [3 + 2] or [2 + 1] cycloaddition reactions, thus furnishing **IV** and **V**, respectively (Scheme 1).
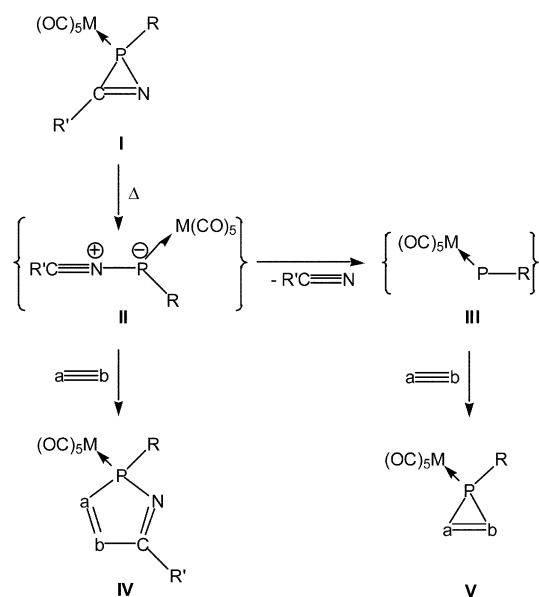
Scheme 1 Known thermal reactions of 2*H*-azaphosphirene complexes with π-systems.

So far, the only ring cleavage reactions of 2*H*-azaphosphirene complex **1** in which no π-system was involved (at one stage or another) were reactions with triethylammonium chloride, giving complex **3**,[3] or water, thus yielding complex **4**[4] *via* reaction of the transiently formed phosphinidene complex **2**; the pathway of the latter reaction was not elucidated (Scheme 2). Although the reactivity of electrophilic terminal phosphinidene complexes **III** was studied in the past twenty years in some depth,[5,6] no example of a reaction of an electrophilic terminal phosphinidene complex with a main group halide has been described until now that results in a halogen transfer from
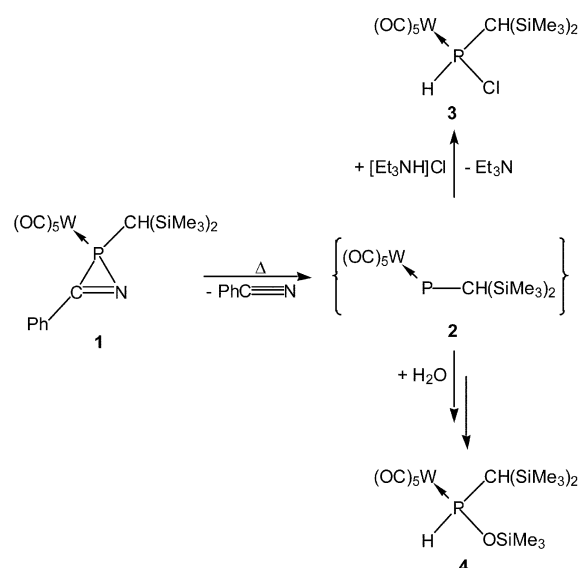
Scheme 2 Ring cleavage reactions of 2*H*-azaphosphirene complexes using compounds with polar element–hydrogen bonds.

carbon to phosphorus. On the other hand, organophosphorus compounds containing P–Cl bonds such as RPCl₂ and RP(X)Cl₂ (X = O, S, Se; R = aryl or alkyl groups) are considered as very important in view of their synthetic utility. It is then remarkable that very few X-ray structures of compounds RP(X)Cl₂ (X = O, S, Se; R = aryl or alkyl groups) are known. 1-Adamantyl selenophosphonic dichloride is one of the rare examples characterized by single crystal X-ray studies.[7] The chemistry and reactivity of various chalcogenophosphonic dichlorides have been reviewed by Fild and Schmutzler.[8] It is noteworthy that some of these compounds, *e.g.* phosphonic dichlorides, can serve as precursors for biologically active compounds.[9] Surprisingly, the organodichlorophosphine (Me₃Si)₂-HCPCl₂[10] has been used as precursor for the synthesis of various organophosphorus compounds,[11] but no chalcogenophosphonic derivatives derived from **9** have been described, so far.

Here we report the thermal reaction of complex **1** in CCl₄ solution at 75 °C, which led to [(Me₃Si)₂HCPCl₂W(CO)₅] (**6**) as sole phosphorus-containing product; the fate of dichlorocarbene, which can be formally regarded as the other product, could not be elucidated. Furthermore, synthesis and characterization

of the complex **6** and corresponding *P*-chalcogenides are described in this paper.

Results and discussion

The formation of complex **6** from the 2*H*-azaphosphirene complex **1** can be regarded as a very unusual reaction of the transiently formed electrophilic terminal phosphinidene complex **2** with CCl₄. It seems plausible that complex **2** reacts with CCl₄ *via* a Lewis acid/Lewis base adduct **5** giving complex **6** *via* an unknown decomposition pathway (Scheme 3). The isolated yield of complex **6** was also surprisingly low. There are a few examples in the literature, which show that CCl₄ is able to perform oxidative 1,1-addition of organophosphorus compounds, *e.g.*, with P=N double bond systems the formation of $\sigma^4\lambda^5$-iminophosphorane derivatives was reported.[12] Somewhat similar to our case are the reactions of Ph₃P and other substituted phosphines with CCl₄.[13]
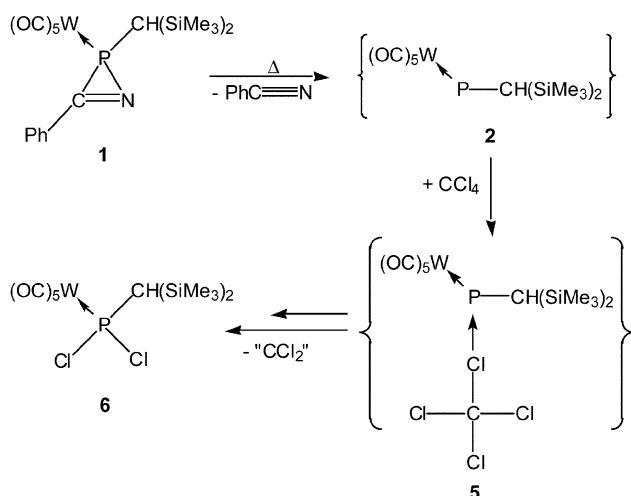
**Scheme 3** Ring cleavage reactions of 2*H*-azaphosphirene complexes using CCl₄.

Unfortunately, the related reaction of **6** with the urea–H₂O₂ adduct as oxidizing agent was unselective. Therefore and because of the lack of the *P*-oxide derivative of (Me₃Si)₂-HCPCl₂, we became interested in investigating the reactivity of **6** towards oxygen-transfer agents. There are a few reports that involve direct oxidation of organodichlorophosphines to the corresponding oxophosphonic dichlorides.[14] The attempt to prepare [(Me₃Si)₂HCP(O)Cl₂] (**7**) by reaction of **9** with the urea–H₂O₂ adduct in toluene resulted only in the isolation of the hydrolysis product [(Me₃Si)₂HCP(O)(OH)Cl] (**8**) (Scheme 4). Nevertheless, the reaction of **9** with DMSO in dichloromethane was successful and furnished the *P*-oxide derivative **7** (Scheme 4).

Preliminary studies on the reactivity of complex **6** towards oxidizing agents such as elemental sulfur and selenium showed that the corresponding *P*-chalcogenide derivatives **10** and **11** are
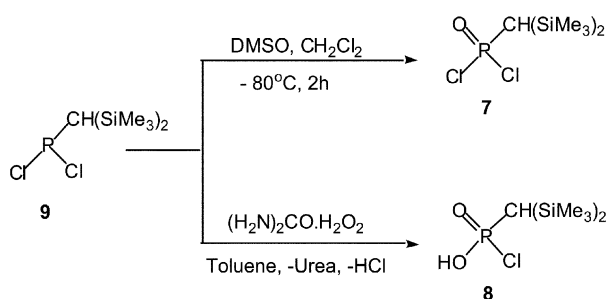
Scheme 4 Preparation of compound **7** and **8** using DMSO and urea–H₂O₂.

easily accessible, which was also achieved in a more straightforward manner using (Me₃Si)₂HCPCl₂ (**9**) as starting material (Scheme 5).
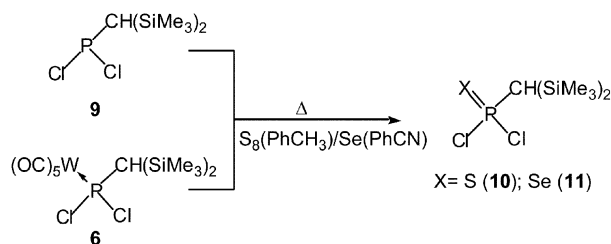
Scheme 5 Synthesis of compounds **10** and **11** using different starting materials under oxidative conditions.

Discussion of selected NMR and X-ray data

Compounds **6**–**11**, except **8**, show ¹H NMR resonances at low field compared to (Me₃Si)₂HCPCl₂ (**9**) (δ ¹H = 0.27 ppm (d, 18H, ^4J(P,H) = 1.1 Hz, Si(CH₃)₃); 1.3 ppm (d, 1H, ^2J(P,H) = 13.5 Hz, PCH) with a singlet for the methyl protons and a doublet for the methyne proton. The ¹H NMR spectrum of compound **8** is almost identical to that of **9** with an additional broad signal at 12.4 ppm for the OH proton resonance. The values of the ^2J(P,H) coupling constants increase from compounds **7** to **11** (25.6–27.3 Hz) and is higher than those of **9** (13.5 Hz); compound **6** has only a value of 8.3 Hz.

The ¹³C NMR spectra of compounds **6**–**11** show also no surprises as compared to (Me₃Si)₂HCPCl₂ (δ ¹³C = 2.4 (d, ^3J(P,C) = 5.9 Hz, Si(CH₃)₃), 33.3 (d, ^1J(P,C) = 79.1 Hz, PCH)) but the signals for the methyl carbon atoms are high field-shifted compared to **9**, except those of **6**, whereas the methyne carbon atom resonances are observed at lower field, except those of **8**. All compounds **6**–**11** (3.8–5.0 Hz) show smaller values for the ^3J(P,C) coupling constants than **9** (5.9 Hz), whereas the ^1J(P,C) coupling constants are very low for all compounds (13.4–55.4 Hz) compared to **9** (79.1 Hz), except those of **8** (87.4 Hz).

The ³¹P NMR spectrum of complex **6** shows a signal at 157.6 ppm (^1J(P,W) = 330.8 Hz; d, ^2J(P,H) = 8.2 Hz) which is significantly high field-shifted compared to the free ligand (Me₃Si)₂-HCPCl₂ (δ ³¹P = 225 ppm, d, ^2J(P,H) = 13.5 Hz). The value of the phosphorus–tungsten coupling constant is as expected for complexes of organophosphorus ligands containing P–Cl bonds.[15] ³¹P NMR spectra of compounds **7** and **8** show a signal at 50.5 (d, ^2J(P,H) = 25.6 Hz) and 52.6 (d, ^2J(P,H) = 26.3 Hz), respectively, and are high field-shifted compared to all other compounds. Compound **10** shows a signal at 91.7 ppm (d, ^2J(P,H) = 27.2 Hz), which is similar to other thiophosphonic dichlorides.[16] For compound **11** a resonance at 68.2 ppm (d, ^2J(P,H) = 27.3 Hz, ^1J(P,Se) = 893.7 Hz)) is observed, which is high field-shifted to 1-adamantyl selenophosphonic dichloride[7] (105.5 ppm, ^1J(P,Se) = 910 Hz) and low field-shifted compared to tertiary phosphine selenides[17] with $\sigma^4\lambda^5$ phosphorus nuclei (−26.1 to −47.7 ppm). The ⁷⁷Se resonance of **11** is observed at very low field (292.1 ppm) compared to 1-adamantyl[7] (60.65 ppm) and phenyl[18] selenophosphonic dichlorides (149 ppm). Most probably, the presence of two chlorine atoms at phosphorus leads to a strong deshielding of the selenium atom. The high coupling constant ^1J(P,Se) = 894.9 Hz also shows the presence of electronegative elements at phosphorus, thus increasing the ^1J(P,Se) coupling constant.[18] According to the literature, it can be concluded that the magnitude of ^1J(P,Se) = 894.9 Hz indicates that there is an almost negligible contribution of ylidic bonding of the type R¹R²₂P⁺–Se⁻ (R¹ = CH(SiMe₃)₂, R²₂ =Cl).[18]

A comparison of the most important molecular parameters of the crystal structure of complex **6** (Fig. 1 and Tables 1 and 2) with W(PCl₃)(CO)₅ [19] reveals for **6** a W–P bond length of 2.459 Å, which is longer than in W(PCl₃)(CO)₅ (2.378 Å) but

Table 1 Crystal data and structure refinement of complexes **6**, **8**, **10** and **11**

Compound	6	8	10	11
Formula	$C_{12}H_{19}Cl_2O_5PSi_2W$	$C_7H_{20}ClO_2PSi_2$	$C_7H_{19}Cl_2PSSi_2$	$C_7H_{19}Cl_2PSeSi_2$
M_r	596.96	257.82	293.33	340.23
Crystal system	monoclinic	triclinic	monoclinic	monoclinic
Space group	$P2_1/n$	$P(-1)$	$P2_1/c$	$P2_1/c$
a/Å	14.8271(8)	6.7903(6)	8.619(4)	8.6576(10)
b/Å	9.6096(6)	8.7696(8)	14.482(7)	14.5623(16)
c/Å	14.8458(8)	12.5541(10)	12.031(6)	12.1849(14)
a/°	90	75.307(3)	90	90
β/°	100.063(3)	77.234(3)	105.926(10)	106.019(3)
γ/°	90	72.823(3)	90	90
V/Å³	2082.7(2)	682.19(10)	1444.1(12)	1476.6(3)
Z	4	2	4	4
T/°C	−140	−140	−140	−140
Refl. measured	38893	9764	23211	17609
Refl. unique	6084	3379	4504	3665
R_{int}	0.082	0.022	0.168	0.048
R^a ($F > 4\sigma(F)$)	0.031	0.030	0.061	0.033
wR^b(F^2, all refl.)	0.083	0.087	0.161	0.093

[a] $R(F) = \Sigma \ ||F_o| - |F_c||/\Sigma \ |F_o|$. [b] $wR(F^2) = [\Sigma\{w(F_o^2 - F_c^2)^2\}/\Sigma\{w(F_o^2)^2\}]^{0.5}$; $w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP$, where $P = [F_o^2 + 2F_c^2]/3$ and a and b are constants adjusted by the program. [c] $S = [\Sigma\{w(F_o^2 - F_c^2)^2\}/(n-p)]^{0.5}$, where n is the number of data and p the number of parameters.

Table 2 Selected bond lengths (Å) and angles (°) in complex **6**

Bond lengths		Bond angles	
W–P	2.4589(7)	Cl(1)–P–Cl(2)	96.96(4)
P–C(6)	1.804(3)	C(6)–P–Cl(1)	106.70(9)
P–Cl(1)	2.0584(9)	C(6)–P–Cl(2)	103.30(9)
P–Cl(2)	2.0598(9)	C(3)–W–P	176.00(9)
W–C(2)	2.070(3)	C(1)–W–C(4)	178.02(12)
W–C(3)	2.012(3)	C(2)–W–C(5)	175.82(11)
Si(1)–C(6)	1.943(3)	O(4)–C(4)–W	179.4(3)
Si(2)–C(6)	1.919(3)	C(6)–P–W	119.57(9)

Table 3 Selected bond lengths (Å) and angles (°) in complex **8**

Bond lengths		Bond angles	
P–O(1)	1.5452(11)	O(1)–P–O(2)	114.46(6)
P–O(2)	1.4912(10)	O(1)–P–C(1)	107.72(6)
P–C(1)	1.7557(14)	O(2)–P–C(1)	114.49(6))
P–Cl	2.0375(5)	O(1)–P–Cl	104.50(5)
Si(1)–C(1)	1.9280(13)	O(2)–P–Cl	105.55(5)
Si(2)–C(1)	1.9150(13)	C(1)–P–Cl	109.58(5)

Table 4 Selected bond lengths (Å) and angles (°) in complex **10**

Bond lengths		Bond angles	
P–S	1.9176(10)	C(1)–P–S	118.08(7)
P–C(1)	1.7744(18)	C(1)–P–Cl(1)	105.95(7)
P–Cl(1)	2.0374(10)	C(1)–P–Cl(2)	107.69(7)
P–Cl(2)	2.0336(10)	Cl(1)–P–S	112.93(5)
Si(1)–C(1)	1.9304(19)	Cl(2)–P–S	112.11(3)
Si(2)–C(1)	1.9394(19)	Cl(1)–P–Cl(2)	98.03(3)

Table 5 Selected bond lengths (Å) and angles (°) in complex **11**

Bond lengths		Bond angles	
P–Se	2.0659(7)	C(1)–P–Se	117.99(8)
P–C(1)	1.778(2)	C(1)–P–Cl(1)	107.91(8)
P–Cl(1)	2.0495(9)	C(1)–P–Cl(2)	106.04(8)
P–Cl(2)	2.0531(9)	Cl(1)–P–Se	112.16(3)
Si(1)–C(1)	1.932(2)	Cl(2)–P–Se	112.85(4)
Si(2)–C(1)	1.944(2)	Cl(1)–P–Cl(2)	97.85(4)

Fig. 1 Molecular structure of **6** in the crystal (ellipsoids represent 50% probability levels, hydrogen atoms are omitted for clarity).

shorter than in $W(PMe_3)(CO)_5$ (2.516 Å).[19] Complex **6** has a slightly longer P–Cl bond (2.058 Å) than in $W(PCl_3)(CO)_5$ (2.028 Å), probably due to a weaker π-acceptor ability of $(Me_3Si)_2HCPCl_2$ than PCl_3. The P–Cl bonds in complex **6** are also longer than those in the corresponding chalcogenides **10** (Table 4) and **11** (Table 5). The Cl(1)–P–Cl(2) angle in complex **6** (96.9°) is smaller than those in the corresponding chalcogenides **10** (98.0°) and **11** (97.9°) and is appreciably more narrow than in $W(PCl_3)(CO)_5$ (100.0°), probably due to the presence of the bulky $(SiMe_3)_2CH$ group at the phosphorus atom.

Attempts to grow suitable crystals for single crystal X-ray analysis of **7** in different solvents were unsuccessful. The crystal structure of **8** was established and represents, to the best of our knowledge, the first example of a single crystal X-ray structure of a chlorophosphonic acid. The molecular structure of **8** (Fig. 2 and Table 3) shows that the P=O bond (1.491 Å) is slightly longer than the P=O bond (1.433 Å) reported

for 2-chloro-3-isopropyl-4-methyl-5-phenyl-1,3,2-oxazaphospholidine 2-oxide [O–C(Ph)H–C(Me)H–N(iPr)–P(O)Cl)],[20] which has a similar environment at the phosphorus atom.

The crystal structure of **10** was also established and represents also the first example of a structurally characterized thiophosphonic dihalide. The molecular structure of **10** (Fig. 3 and Table 4) can be compared with $[PPh_3Me][PS_2Cl_2]$[21] as both compounds possess similar moieties, *i.e.* $P(S)Cl_2$, although the latter is an ionic compound, which has to be kept in mind. The P=S bond in **10** (1.917 Å) is slightly shorter than in $[PPh_3Me][PS_2Cl_2]$ (1.948 Å) whereas the Cl(1)–P–Cl(2) bond angle in **10** (98.03°) is narrower by 5°. Tertiary phosphine sulfides[22] also show slightly longer P=S bond lengths (range: 1.9360–1.9660 Å) than in compound **10** (1.917 Å).

The crystal structure of **11** (Fig. 4 and Table 5) shows a P=Se bond length (2.066 Å) that is slightly shorter than the P=Se
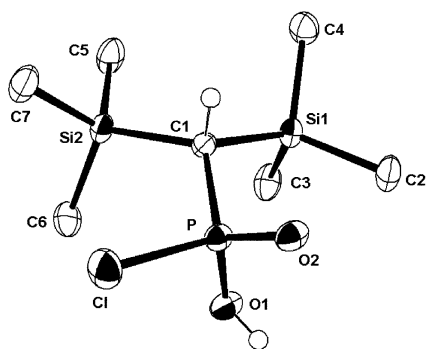
Fig. 2 Molecular structure of **8** in the crystal (ellipsoids represent 50% probability levels, hydrogen atoms except OH are omitted for clarity).
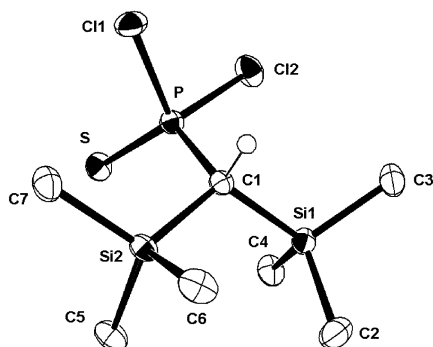
Fig. 3 Molecular structure of **10** in the crystal (ellipsoids represent 50% probability levels, hydrogen atoms except the CH group are omitted for clarity).
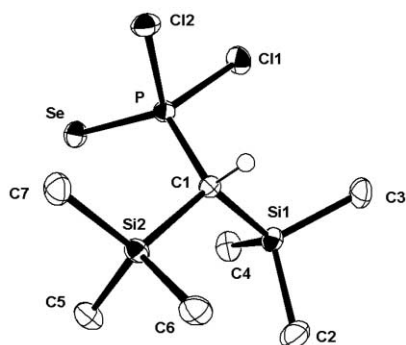
Fig. 4 Molecular structure of **11** in the crystal (ellipsoids represent 50% probability levels, hydrogen atoms are omitted for clarity).

bond (2.068 Å) in 1-adamantylselenophosphonic dichloride,[7] which is the only example of a structurally characterized compound of this type. Compound **11** has a small Cl(1)–P–Cl(2) bond angle (97.85°) compared to 1-adamantylselenophosphonic dichloride[7] (103.13°).

The P–C and C–Si bond of the compounds **6**–**11** can be compared with those of the recently reported diphosphane[23] RPH–PHR (R = CH(SiMe₃)₂). The compounds **6**–**11** have P–C bond lengths in the range of 1.756–1.804 Å, whereas the diphosphane has very long P–C bonds (1.868/1.868 Å) probably due to steric interactions between the bulky silyl groups. However, the situation for C–Si bonds is reverse, the diphosphane has shorter C–Si bonds (1.882/1.889 Å), than compounds **6**–**11** (range: 1.915–1.944 Å).

It is noteworthy that in the structure of compound **10** are intermolecular contacts between the atom hydrogen and chlorine of (2.87 Å); the bond angle C–H ⋯ Cl is 137.7°. Similar intermolecular contacts between hydrogen and chlorine (2.94 Å) are also found in the structure of compound **11**; the bond angle C–H ⋯ Cl is 133.7°. These contacts were generated by symmetry operators x, $-y + 1/2$, $z - 1/2$.

Experimental

Materials

All reactions and manipulations were carried out under an inert atmosphere of deoxygenated dry nitrogen with the use of standard schlenk-line techniques. All solvents were dried by conventional methods and distilled over nitrogen. 2H-azaphosphirene complex **1**,[1] $(Me_3Si)_2HCPCl_2$ [10,11] were prepared according to the references.

Physical measurements

All reactions were monitored by ^{31}P-NMR spectroscopy. The ^{1}H, ^{13}C and ^{31}P NMR spectra were recorded on a Bruker AC-200 spectrometer (200 M Hz for ^{1}H; 50.3 M Hz for ^{13}C and 81.0 M Hz for ^{31}P) using (D)chloroform as solvent and internal standard; shifts are given relative to ext. tetramethylsilane (^{1}H, ^{13}C) or 85% H_3PO_4 (^{31}P). Mass spectra were recorded on a Finnigan Mat 8430 (70 eV, EI); apart from the molecule ions, only the m/z-values having intensities of more than 20% are given. Infrared spectra were recorded on a Biorad FT-IR 165 spectrometer (selected data given). Melting points were obtained on a Büchi 535 capillary apparatus. Elemental analyses were performed using a Carlo Erba analytical gas-chromatograph.

Preparation of $[(Me_3Si)_2HCPCl_2W(CO)_5]$ (6)

A solution of 2H-azaphosphirene complex **1** (0.617 g, 1 mmol) in CCl_4 was heated at 75 °C for 2–3 h. The resulting dark purple solution was concentrated and the product was separated by low-temperature column chromatography (SiO₂, −10 °C, n-pentane). Evaporation of the solvents of the second fraction and recrystallization from n-pentane at −20 °C yielded **5** as pale yellow crystals. Yield: 0.234 g (40%). Anal. Calcd. $C_{12}H_{19}Cl_2O_5$-PSi_2W: C, 24.63; H, 3.27%. Found: C, 24.78; H, 3.41%. Mp 73–75 °C. ^{1}H NMR (CDCl₃): δ 0.41 (s, 18H, SiMe₃), 2.24 (d, ^2J(P,H) = 8.3 Hz, 1H, PCH). ^{13}C NMR: δ 3.0 (d, ^3J(P,C) = 3.8 Hz, SiMe₃), 43.8 (d, ^1J(P,C) = 22.3 Hz, PCH), 196.3 (d, ^2J(P,C) = 7.8 Hz, cis-CO), 198.9 (d, ^2J(P,C) = 44.5 Hz, trans-CO). ^{31}P{^{1}H} NMR: δ 157.6 (^1J(P,W) = 330.8 Hz, ^2J(P,H) = 8.2 Hz). MS (70 eV, EI, ^{184}W): m/z 584 (5) (M⁺), 73 (100) ((SiMe₃)⁺), 117 (21) ((PCHSiMe₃)⁺). IR (KBr) data (cm⁻¹): v(CO) 1936, 1949, 1957, 1991 and 2084.

Preparation of $[(Me_3Si)_2HCP(O)Cl_2]$ (7)

To a precooled CH_2Cl_2 solution of $(Me_3Si)_2HCPCl_2$ (0.520 g, 2 mmol) at −80 °C a DMSO (0.240 g, 3.0 mmol) solution in CH_2Cl_2 was added dropwise and stirring was continued for 2 h at −80 °C. The solvent was removed in vacuo and the product was separated by low-temperature column chromatography (SiO₂, −10 °C, diethyl ether : petrol ether = 1 : 9). Evaporation of the solvents of the second fraction and recrystallization from n-pentane at −20 °C yielded **7** as colourless needles. Yield: 0.480 g (87%). Anal. Calcd. $C_7H_{19}Cl_2OPSi_2$: C, 30.32; H, 6.91%. Found: C, 30.30; H, 6.98%. Mp 73–75 °C. ^{1}H NMR (CDCl₃): δ 0.31 (s, 18H, SiMe₃), 1.8 (d, ^2J(P,H) = 25.6 Hz, 1H, PCH). ^{13}C NMR: δ 1.6 (d, ^3J(P,C) = 4.8 Hz, SiMe₃), 36.6 (d, ^1J(P,C) = 55.4 Hz, PCH). ^{31}P{^{1}H} NMR: δ 50.5 (^2J(P,H) = 25.6 Hz). MS (70 eV, EI, ^{32}S): m/z 276 (15) (M⁺), 261 (100) ((M)⁺–CH₃), 187 (50) (PCl₂C(SiMe₃)⁺), 167 (70) ((C₄H₉ClOPSi)⁺), 73 (35) ((SiMe₃)⁺). IR (KBr) data (cm⁻¹): $v_{P=O}$ 1252.

Preparation of $[(Me_3Si)_2HCP(O)(OH)Cl]$ (8)

A mixture of $(Me_3Si)_2HCPCl_2$ (0.261 g, 1 mmol) and urea–H_2O_2 adduct (0.094 g, 1 mmol) was stirred in toluene at 0 °C for 2 h. The solvent was removed in vacuo and the product was obtained after purification of the residue, by washing with n-pentane, as white solid. Suitable crystals for X-ray analysis were obtained from a CDCl₃ solution kept overnight at −20 °C.

Yield: 0.176 g (60%). Anal. Calcd. $C_7H_{20}ClO_2PSi_2$ (**7**): C, 32.48; H, 7.79%. Found: C, 32.51; H, 7.84%. Mp 111–115 °C. ^{1}H NMR (CDCl$_3$): δ 0.27 (s, 18H, SiMe$_3$), 1.18 (d, ^2J(P,H) = 26.4 Hz, 1H, PC*H*), 12.4 (br, 1H, OH). ^{13}C NMR: δ 1.5 (d, ^3J(P,C) = 4.2 Hz, SiMe$_3$), 25.9 (d, ^1J(P,C) = 87.4 Hz, PCH). ^{31}P{^{1}H} NMR: δ 52.6 (^2J(P,H) = 26.3 Hz). MS (70 eV, EI): m/z 258 (5) (M$^+$), 243 (40) (M$^+$ –CH$_3$), 227 (30) (($C_6H_{17}ClOPSi_2$)$^+$), 207 (40) (($C_6H_{16}O_2PSi_2$)$^+$), 167 (25) (($C_4H_9ClOPSi$)$^+$), 133 (95) (($C_4H_{10}OPSi$)$^+$), 73(100) ((SiMe$_3$)$^+$). IR (KBr) data (cm^{-1}): ν(P=O) 684, ν(O–H) 1638 and 3442.

Preparation of [(Me$_3$Si)$_2$HCP(S)Cl$_2$] (10)

Method 1. A solution of 2*H*-azaphosphirene **1** (0.617 g, 1 mmol) in 3 mL CCl$_4$ was heated for 2 h at 75 °C; elemental sulfur (0.32 g, 10 mmol) was then added and the mixture heated at the same temperature for 24 h. The resulting dark brown solution was concentrated and the product was separated by low-temperature column chromatography (SiO$_2$, −10 °C, diethyl ether : petrol ether = 1 : 9). Evaporation of the solvents of the second fraction and recrystallization from *n*-pentane at −20 °C yielded **10** as colourless needles. Yield: 0.124 g (42%). Anal. Calcd. $C_7H_{19}Cl_2PSSi_2$: C, 28.66; H, 6.53%. Found: C, 27.72; H, 5.76%. Mp 57–59 °C. ^{1}H NMR (CDCl$_3$): δ 0.36 (s, 18H, SiMe$_3$), 2.22 (d, ^2J(P,H) = 27.2 Hz, 1H, PC*H*). ^{13}C NMR: δ 2.2 (d, ^3J(P,C) = 5 Hz, Si*Me*$_3$), 44.3 (d, ^1J(P,C) = 28.1 Hz, PC*H*). ^{31}P{^{1}H} NMR: δ 91.7 (^2J(P,H) = 27.2 Hz). MS (70 eV, EI, ^{32}S): m/z 292 (5) (M$^+$), 277 (78) (($C_6H_{16}Cl_2SPSi_2$)$^+$), 141 (39) (?), 121 (26) (?), 93 (42) ((C_2H_6ClSi)$^+$), 73 (100) ((SiMe$_3$)$^+$). IR (KBr) data (cm^{-1}): $\nu_{P–S}$ 673.

Method II. A mixture of (Me$_3$Si)$_2$HCPCl$_2$ (0.261 g, 1 mmol) and elemental sulfur (0.32 g, 0.01 mol) in 3 mL toluene was heated at 95 °C for 24 h. The product was separated as above. Yield: 0.202 g (69%).

Preparation of [(Me$_3$Si)$_2$HCP(Se)Cl$_2$] (11)

Method I. A solution of 2*H*-azaphosphirene **1** (0.617 g, 1 mmol) in 3 mL CCl$_4$ was heated for 2 h at 75 °C. Then selenium powder (0.79 g, 10 mmol) was added to it and heated at the same temperature for 24 h. The resulting dark brown solution was filtered to remove excess Se powder and the solution was concentrated. The product was separated by low-temperature column chromatography (SiO$_2$, −20 °C, petrol ether). Evaporation of the solvents of the first fraction and recrystallization from *n*-pentane at −20 °C yielded **11** as colourless crystals. Yield: 0.154 g (45%). Anal. Calcd. $C_7H_{19}Cl_2PSeSi_2$: C, 24.71; H, 5.63%. Found: C, 24.72; H, 5.76%. Mp 61–62 °C. ^{1}H NMR (CDCl$_3$): δ 0.40 (s,18H, SiMe$_3$), 2.63 (d, ^2J(P,H) = 27.3 Hz, 1H, PC*H*). ^{13}C NMR: δ 2.3 (d, ^3J(P,C) = 4.9 Hz, Si*Me*$_3$), 46.1 (d, ^1J(P,C) = 13.4 Hz, PC*H*). ^{31}P{^{1}H} NMR: δ 68.2 (^1J(P,Se) = 893.7 Hz, ^2J(P,H) = 27.3 Hz). ^{77}Se NMR: 292.1 (d, ^1J(P,Se) = 894.9 Hz) MS (70 eV, EI, ^{79}Se): m/z 342 (3)/340 (5) (M$^+$), 93 (100) (?), 73 (95) ((SiMe$_3$)$^+$). IR (KBr) data (cm^{-1}): ν(P=Se) 574.

Method II. A mixture of (Me$_3$Si)$_2$HCPCl$_2$ (0.261 g, 1 mmol) and selenium powder (0.79 g, 10 mmol) in 3 mL benzonitrile was heated at 95 °C for 24 h. The product was separated as above. Yield: 0.280 g (82%).

X-ray crystallographic studies

Details of crystallographic data collection and refinement for [(Me$_3$Si)$_2$HCPCl$_2$W(CO)$_5$] (**6**), [(Me$_3$Si)$_2$HCP(O)(OH)Cl] (**8**), [(Me$_3$Si)$_2$HCP(S)Cl$_2$] (**9**) and [(Me$_3$Si)$_2$HCP(Se)Cl$_2$] (**11**) are summarized in Table 1. Data were collected on a Bruker Smart 1000 CCD area detector with graphite monochromated Mo Kα radiation (λ = 0.71073Å); ω- and ϕ-scan techniques. The structures **8**, **10**, **11** were solved by direct methods, structure **6** by the heavy-atom method. Structures were refined anisotropically on F^2 using the program SHELXL-97.[24] Hydrogen atoms were included using a riding model or rigid methyl groups (exception: hydroxyl H of **8** refined freely with bond length restraint). Compounds **10** and **11** are isostructural.

CCDC reference numbers 197414 (**6**), 197415 (**8**), 197416 (**10**), 197417 (**11**).

See http://www.rsc.org/suppdata/dt/b3/b301775c/ for crystallographic data in CIF or other electronic format.

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