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LETTERS

A Novel Synthetic Route to Chalcogen Substituted Diphospholes

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Abstract: The reaction of $[Li(TMEDA)_2][1,2,4\text{-}SbP_2C_2Bu^t{}_2]$ **1** with $E(S_2CNEt_2)_2$ (E = Se or Te) leads to the chalcogen substituted diphospholes $[1,2,4\text{-}EP_2C_2Bu^t{}_2]$ (E = Se **2**, E = Te **3**). Compound **3** represents the first example of a tellurium substituted diphosphole. © 1999 Elsevier Science Ltd. All rights reserved.

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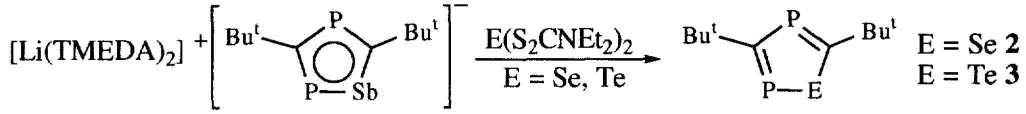
Hetero-diphospholes are an important class of compounds containing low coordinate phosphorus centres. A range of cycloaddition and condensation reactions have been used to prepare examples containing sulphur[1-4] or nitrogen[5-7] as the heteroatom. More recently, a new group of compounds of this type has emerged, *viz.* the 1,2,4-selenadiphospholes. The synthesis of 3,5-di-*tert*-butyl-1,2,4-selenadiphosphole **2** has been achieved in low yield by two alternative routes. The first involves the thermolysis of the phosphaalkyne $P{\equiv}CBu^t$ with 1,2,3-selenadiazole in a sealed tube with no solvent.[8] The second synthetic route is based on the treatment of the triphosphole, $1,2,4\text{-}PC(Bu^t)PC(Bu^t)P\{CH(SiMe_3)_2\}$, with elemental selenium.[9] In this paper we describe a novel and higher yielding route to compound **2** and show how this method can also be used to prepare **3**, the first example of a telluradiphosphole.

Treatment of two equivalents of $[Li(TMEDA)_2][1,4,2\text{-}P_2SbC_2Bu^t{}_2]$, **1**,TMEDA = N,N,N',N'-tetramethylethylenediame, with $E(S_2CNEt_2)_2$ (E = Se, Te) leads to the formation of **2** or **3** in yields of 60 % and 32 % respectively (Scheme 1). The spectroscopic data recorded for compound **2** are in good agreement with those previously reported.[8,9]



Scheme 1

The $^{31}P\{^1H\}$ NMR spectrum of the telluradiphosphole **3** is similar to that of **2** and consists of two doublets at 299 ppm and 302 ppm with a typical $^2J_{PP}$ coupling of 50.6 Hz. ^{125}Te satellites are visible on both resonances and indicate $^1J_{P\text{-}Te}$ and $^2J_{P\text{-}Te}$ couplings of 1028 Hz and 151 Hz respectively which is in accord with the generalisation that spin-spin couplings involving tellurium are approximately two to three times greater than the same coupling involving selenium[10] [*cf.* $^1J_{P\text{-}Se}$ = 443 Hz and $^2J_{P\text{-}Se}$ = 61 Hz in **2**]. The one bond phosphorus-tellurium coupling is markedly higher than expected [e.g. = $^1J_{P\text{-}Te}$ 451 Hz in $(Bu^t{}_2P)_2Te]$[11], and is closer to the value of 1600 Hz in $Bu^t{}_3P{=}Te$[11]. This, perhaps suggests that the tellurium-phosphorus bond in **3** has appreciable double bond character. This is consistent with the parent tellurophene which shows properties typical of a 6π electron aromatic system. The ^{125}Te chemical shift of **3** is 1383 ppm which is somewhat higher than those seen in tellurophenes (generally 750-1000 ppm).

It is difficult to be sure of the mechanism of formation of **2** and **3** but in both cases elemental antimony deposited from the reaction mixture which suggests that a redox process is occurring. However, despite

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repeated efforts we have not yet obtained experimental data to confirm the exact mechanism.

We are currently examining the organic and organometallic chemistry of compounds **2** and **3**, the results of which will be reported in forthcoming publications.[12]

Syntheses:

Compound 2: The salt $[\mathrm{Li(TMEDA)_2}][1,2,4\text{-}\mathrm{SbP_2C_2Bu^t{}_2}]$[13] (1.0 g, 1.78 mmoles) was added as a solution in THF (5 ml) to a stirred suspension of $\mathrm{Se(S_2CNEt_2)_2}$[14] (0.334 g, 0.89 mmoles) in THF (5 ml) at -78°C. The resulting solution was warmed to room temperature and stirred for 24 hours during which time a metallic mirror formed on the inside of the reaction vessel. Volatiles were removed *in vacuo* and the residue extracted with hexane and filtered. The filtrate was chromatographed (florisil/hexane) to yield **2** as a pale yellow oil (yield 60%). Spectroscopic data were consistent with the literature values.[8,9]

Compound 3: The salt $[\mathrm{Li(TMEDA)_2}][1,2,4\text{-}\mathrm{SbP_2C_2Bu^t{}_2}]$[13] (1.00 g, 1.78 mmoles) was added as a solution in DME (10 ml) to a stirred suspension of $\mathrm{Te(S_2CNEt_2)_2}$[14] (0.377 g, 0.83 mmoles) in DME (10 ml) at -50°C. The resulting solution was warmed to room temperature and stirred for 18 hours in the absence of light. Volatiles were removed *in vacuo* and the residue extracted with hexane and filtered. The filtrate was run through a pad of florisil and evaporated to yield **3** as a yellow oil (0.092g, 32 %) NMR ($\mathrm{C_6D_6}$, 298K): ^{1}H (250 MHz) δ 1.48 (d, 9H, $\mathrm{Bu^t}$, $^4J_{\mathrm{PH}} = 0.61$ Hz), 1.66 (d, 9H, $\mathrm{Bu^t}$, $^4J_{\mathrm{PH}} = 2.4$ Hz); ^{13}C (100.6 MHz) δ 29.9 (dd, $\mathrm{C(\underline{C}H_3)_3}$, $^3J_{\mathrm{PC}} = 10.4$ Hz and 13.7 Hz), 31.8 (d, $\mathrm{C(\underline{C}H_3)_3}$, $^3J_{\mathrm{PC}} = 13.7$ Hz), 34.5 (d, $\mathrm{\underline{C}(CH_3)_3}$, $^2J_{\mathrm{PC}} = 15.3$ Hz), 37.9 (dd, $\mathrm{\underline{C}(CH_3)_3}$, $^2J_{\mathrm{PC}} = 19.8$ Hz and 22.9 Hz), 204 (dd, $\mathrm{P\underline{C}Te}$, $^1J_{\mathrm{PC}} = 65.6$ Hz, $^2J_{\mathrm{PC}} = 8$ Hz), 223 (dd, $\mathrm{P\underline{C}P}$, $^1J_{\mathrm{PC}} = 77.8$ Hz and 87.0 Hz); ^{125}Te (78.87 MHz) δ 1383 (dd, $^1J_{\mathrm{P\text{-}Te}} = 1035$ Hz, $^2J_{\mathrm{P\text{-}Te}} = 140$ Hz); $^{31}\mathrm{P}\{^1\mathrm{H}\}$ (101.4 MHz) δ 299 (d, $\mathrm{C\underline{P}C}$, $^2J_{\mathrm{PP}} = 50.8$ Hz, $^2J_{\mathrm{P\text{-}Te}} = 151.3$ Hz), 302 (d, $\mathrm{C\underline{P}Te}$, $^2J_{\mathrm{PP}} = 50.4$ Hz, $^1J_{\mathrm{P\text{-}Te}} = 1028$ Hz); IR: υ / $\mathrm{cm^{-1}}$ 1361 (s), 1250 (m), 1261 (m).

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