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A Stabilized Phosphinothioylidene Generated by Deselenation of a Selenoxothioxophosphorane

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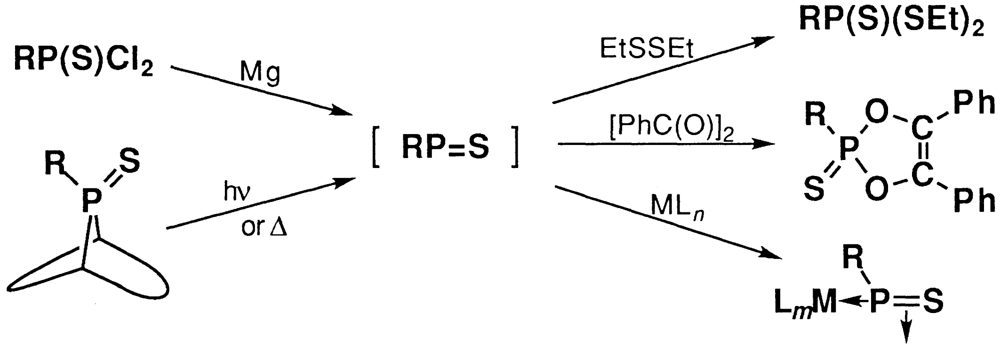
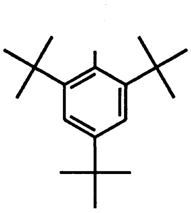
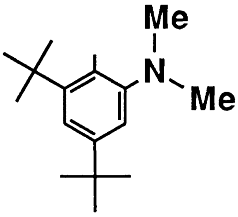
Selenoxothioxo(2,4-di-*t*-butyl-6-dimethylaminophenyl)phosphorane was prepared and was deselenated with tris(dimethylamino)phosphine to give the corresponding phosphinothioylidene (thioxophosphine, thionophosphine, or phosphinidene sulfide), for the first time, as a thermally stable compound, which is considered to be stabilized with the lone pair electrons of the *o*-dimethylamino group.

Compounds with a low-coordinated heavier main group element such as phosphorus can be sterically protected by a built-in bulky substituent (kinetic protection).1) The 2,4,6-tri-*t*-butylphenyl group (hereafter abbreviated to Ar) is one of the typical bulky protecting groups2) and by utilizing this substituent we and others have successfully prepared various types of low-coordinated trivalent phosphorus compounds such as diphosphenes, phosphaalkenes, phosphacumulenes, phosphaalkynes, and so forth. Low coordinate organophosphorus compounds of chalcogenophosphine type ($\sigma^2\lambda^3$-coordination state such as in R-P=O) or monomeric metaphosphate type ($\sigma^3\lambda^5$-coordination state such as in $\mathrm{R\text{-}P(=O)_2}$) are of current interest.1) The latter species are particularly important with respect to the ATP hydrolysis. Using the Ar group, some $\sigma^3\lambda^5$-coordinated phosphorus species such as dithioxophosphorane of the type $\mathrm{ArP(=S)_2}$3) and diselenoxophosphorane of the type $\mathrm{ArP(=Se)_2}$4) have been isolated as thermally stable compounds, although they are rather sensitive to moisture and/or air. Since we postulated the generation of phosphinothioylidenes (thioxophosphines, thionophosphines, or phosphinidene sulfides, R-P=S) as an intermediate in the reactions of phosphonothioic dichlorides with magnesium in the presence of trapping reagents such as diethyl disulfide and benzil,5) there have been several reports on the generation and trapping of phosphinothioylidenes,6,7) including the formations and the X-ray structures of manganese8) and molybdenum8,9) complexes of RP=S.



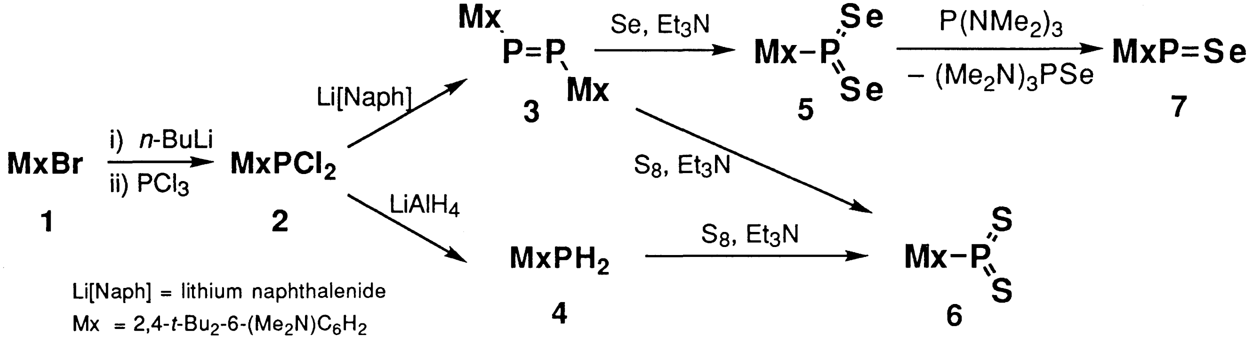


(Ar)



(Mx)

We recently reported that the 2,4-di-*t*-butyl-6-dimethylaminophenyl group (hereafter abbreviated to Mx group), starting from the corresponding bromobenzene **1**,[10)] can be utilized to stabilize low coordinate organophosphorus compounds such as diphosphene **3**, dithioxophosphorane **6**, and diselenoxophosphorane **5**, as well as phosphonous dichloride **2** and primary phosphine **4**.[11)] We have also described that deselenation reaction of the diselenoxophosphorane **5** with tris(dimethylamino)phosphine gave phosphinoselenoylidene (selenoxophosphine, selenonophosphine, or phosphinidene selenide, **7**).[11)] We now report generation of phosphinothioylidene from selenoxothioxophosphorane.

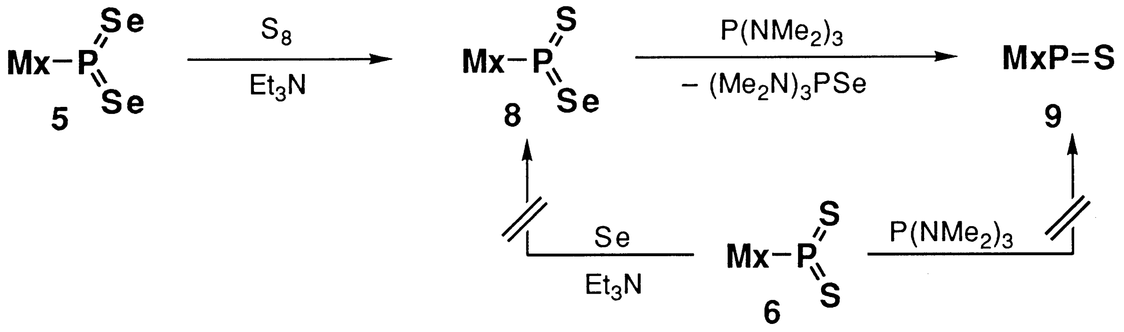


Li[Naph] = lithium naphthalenide
Mx = 2,4-*t*-Bu_2-6-(Me_2N)C_6H_2

In an attempt to desulfurize dithioxophosphorane with a phosphine, **6** was allowed to react with tris(dimethylamino)phosphine. But the reaction was unsuccessful, indicating that the thioxo sulfur in **6** resists desulfurization in contrast to the case of deselenation of the selenoxo selenium of **5**. Therefore we tried to prepare a selenoxothioxophosphorane as a precursor of thioylidene, but the reaction of selenium with dithioxophosphorane **6** gave neither diselenoxophosphorane **5** nor selenoxothioxophosphorane **8**, indicating that the sulfur atoms of the dithioxophosphorane **6** are not labile.

The selenium-sulfur exchange reaction of **5**, however, occurred to give the selenoxothioxo derivative **8** in the presence of organic base such as triethylamine. Thus, diselenoxophosphorane **5** was prepared from diphosphene **3** and selenium in triethylamine as reported previously.[11)] Under an atmosphere of argon, the diselenoxophosphorane (**5**, 190.5 mg, 0.452 mmol) was allowed to react with sulfur (115.9 mg, 3.61 mmol) in triethylamine (20 mL) at refluxing for 1 h to afford 102.5 mg of a mixture of the corresponding selenoxothioxophosphorane (**8**; δ_P 162) and dithioxophosphorane (**6**; δ_P 171), together with the starting diselenoxophosphorane (**5**; δ_P 150) in a molar ratio of 56 : 19 : 25 as estimated by ^{31}P NMR. After flush column chromatographic separation on silica gel (Fuji-Davison BW-300, dichloromethane as eluant), the mixture of phosphoranes was subjected to HPLC over reversed phase (ODS) with 70% aqueous acetonitrile to afford the first selenoxothioxophosphorane (**8**; 25.7 mg, 0.0686 mmol) in pure state in 15% yield. **8**: mp 243–244 °C; ^1H NMR (200 MHz, $CDCl_3$); δ = 1.33 (9H, s, Bu^t), 1.56 (9H, s, Bu^t), 3.21 (3H, d, $^5J_{PH}$ = 7.03 Hz, NMe), 3.26 (3H, d, $^5J_{PH}$ = 7.90 Hz, NMe), 7.09 (1H, dd, $^4J_{PH}$ = 2.22 Hz and $^4J_{HH}$ = 1.47 Hz, arom.), and 7.52 (1H, dd, $^4J_{PH}$ = 8.12 Hz and $^4J_{HH}$ = 1.41 Hz, arom.); $^{13}C\{^1H\}$ NMR (50 MHz, $CDCl_3$) δ = 31.3 (s, $C\underline{Me}_3$), 31.4 (s, $C\underline{Me}_3$), 35.9 (s, $\underline{C}Me_3$), 36.4 (s, $\underline{C}Me_3$), 46.5 (s, NMe), 47.5 (s, NMe), 111.6 (d, $^3J_{PC}$ = 10.1 Hz, *m*-

arom.), 126.7 (d, $^3J_{PC}$ = 12.8 Hz, *m*'-arom.), 140.0 (d, $^1J_{PC}$ = 76.4 Hz, *ipso*-arom.), 147.9 (d, J_{PC} = 2.41 Hz, arom.), 151.7 (d, J_{PC} = 3.32 Hz, arom.), and 157.8 (d, J_{PC} = 2.87 Hz, arom.); ^{31}P{^{1}H} NMR (81 MHz, $CDCl_3$) δ = 162.1, satellite d, $^1J_{PSe}$ = 837.9 Hz; UV (CH_2Cl_2) 273 nm (log ε 3.71); IR (KBr) 694 cm^{-1}; MW (C_6H_6) 440; MS (70 eV) *m/z* (rel intensity) 375 (M^+; 98), 294 (M^+–Se; 89), and 263 (MxP^+; 100); Found: *m/z* 375.0688. Calcd for $C_{16}H_{26}NPSSe$: M, 375.0689. The ^{31}P{^{1}H} NMR of **8** appeared as a singlet accompanied by a satellite doublet signal with ^{77}Se. Furthermore, in the ^{1}H NMR, the methyl protons on the nitrogen atom appeared as magnetically non-equivalent.

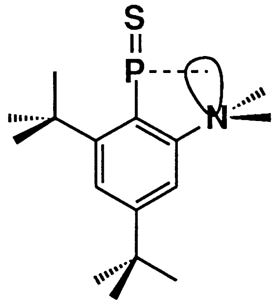


The selenoxothioxophosphorane (**8**; 4.7 mg, 0.013 mmol) thus obtained was then allowed to react with tris(dimethylamino)phosphine in THF-d_8 (0.4 mL) in an NMR tube (ϕ = 5 mm) at room temperature under argon to give almost exclusively phosphinothioylidene (**9**; δ_P 382) together with tris(dimethylamino)phosphine selenide (δ_P 85) by the NMR studies. **9**: ^{1}H NMR (200 MHz, THF-d_8) δ = 1.31 (9H, s, Bu^t), 1.37 (9H, s, Bu^t), 2.76 (3H, s, NMe), 3.05 (3H, d, $^5J_{PH}$ = 5.18 Hz, NMe), 7.14 (1H, dd, $^4J_{PH}$ = $^4J_{HH}$ = 1.49 Hz, arom.), and 7.40 (1H, dd, $^4J_{PH}$ = $^4J_{HH}$ = 1.68 Hz, arom.); ^{31}P{^{1}H} NMR (81 MHz, THF-d_8) δ = 382.0; MS (70 eV) *m/z* (rel intensity) 295 (M^+; 93), 280 (M^+–Me; 100), and 262 (MxP^+–1; 48); Found: *m/z* 295.1488. Calcd for $C_{16}H_{26}NPS$: M, 295.1524. It should be mentioned that one of the methyl groups on the nitrogen atom (which non-equivalently resonated at the lower chemical shift in the ^{1}H NMR) appeared as a doublet due to spin-spin coupling with the phosphorus nucleus. These results suggest that the nitrogen lone-pair electrons interact with the P=S moiety, as shown in the following scheme, to permit us observation of a phosphinothioylidene for the first time at room temperature. Table 1 shows the ^{31}P NMR chemical shifts of some of the chalcogenophosphines and phosphoranes carrying an Mx group. It should be noted that the chemical shift of either phosphinothioylidene or phosphinoselenoylidene of the $\sigma^2\lambda^3$ type appears at considerably lower field than those for dithioxo derivatives of the $\sigma^3\lambda^5$ type.[12)] The compound **9** thus formed, however, slowly decomposed to give unidentified materials, probably because of the reaction with aerial moisture and oxygen, and attempted reactions of **9** with either benzil or diethyl disulfide have been failed so far. Further studies on the detailed structure and the reactivities of **9** are in progress.

Table 1. ^{31}P NMR Data of Some Chalcogenophosphines and Phosphoranes Carrying the Mx Group

Compound	$MxPS_2$[a,c)]	MxPSSe[b,c)]	$MxPSe_2$[a,c)]	MxP=S[b,d)]	MxP=Se[a,d)]
	6	**8**	**5**	**9**	**7**
Chemical shift/ δ_P	170.6	162.1	149.6	382.0	399.0
$^1J_{PSe}$ / Hz	—	837.9	819.6	—	708.7

a) Data taken from Ref. 11. b) This work. c) In $CDCl_3$. d) In THF-d_8.



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