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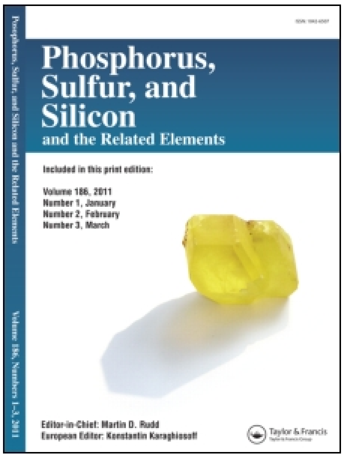

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Synthesis of the First Stable Pentaco-Ordinate 1,2-Thiaphosphetene

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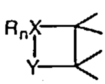
Pentacoordinate 1,2-thiaphosphetenes bearing the Martin ligand were synthesized by the reaction of the corresponding phosphorus ylide with isothiocyanates. Their mass and NMR spectral data showed that they have 1:2 adducts of the phosphorus ylide and isothiocyanates, which have a distorted trigonal bipyramid with oxygen and sulfur atoms at the apical positions. Thermolysis of the phenyl isothiocyanate adduct gave the corresponding cyclic thiophosphinate as a phosphorus-containing product in almost quantitative yield.

Keywords: pentacoordinate 1; 2-thiaphosphetenes; Wittig reaction; the Martin ligand; thermolysis

INTRODUCTION

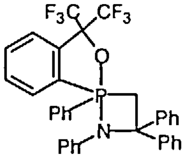
In the course of our study on heteracyclobutanes **1**[1] bearing highly coordinate main group elements at the position adjacent to the heteroatom we have reported the syntheses and isolation of intermediates of the Wittig and Peterson-type reactions.[2] We also reported the synthesis of pentacoordinate 1,2-azaphosphetidines **2**, i.e., intermediates of the Wittig reaction with Schiff's bases, and the first observation of their *C*-apical *N*-equatorial pseudorotamers.[1c] On the other hand, Erker and coworkers reported the first observation of pentacoordinate 1,2-thiaphosphetane **3**, i.e., an intermediate of the

Wittig reaction of a phosphorus ylide with thiobenzophenone, and its unique reactivity.[3] From our interest in the synthesis and isolation of such species we studied the generation and reactions of the phosphorus ylide **4** bearing the Martin ligand. In its reaction with an isothiocyanate we succeeded in the synthesis of the first stable 1,2-thiaphosphetene **5**.[4] Here we wish to report the results.



1

X= P, Si⁻, Ge⁻, Sn⁻,
S, Se
Y= O, NPh



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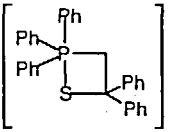

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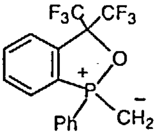

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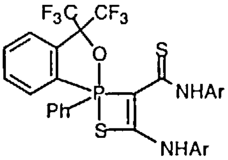
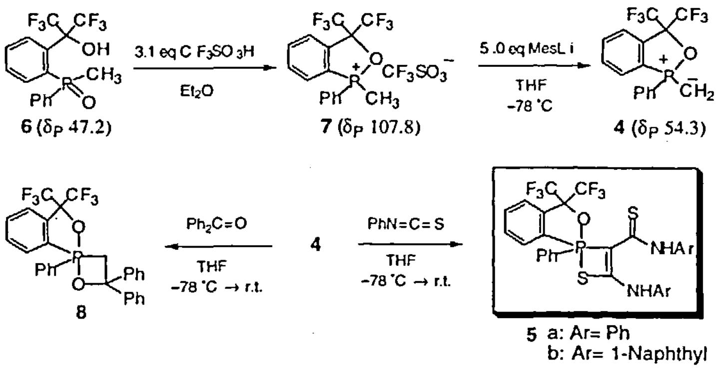


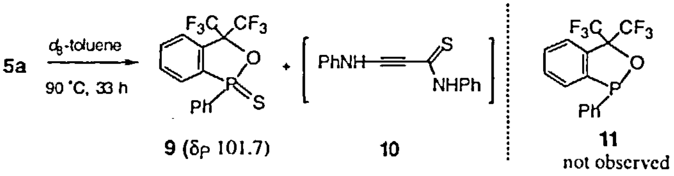
5

RESULTS AND DISCUSSION

The phosphorus ylide **4** having the Martin ligand,[5] which was prepared by acid-catalyzed cyclization of phosphine oxide **6**[1b] with 3.1 equiv of trifluoromethanesulfonic acid in Et_2O, followed by deprotonation of the resulting phosphonium salt **7** with 5.0 equiv of 2,4,6-trimethylphenyllithium (MesLi), was allowed to react with excess benzophenone in THF to give the corresponding pentacoordinate 1,2-oxaphosphetane **8**[1b] in 72% yield. Similarly, the reactions with phenyl and 1-naphthyl isothiocyanates gave the corresponding 1,2-thiaphosphetenes **5a**[6] and **5b** as 1:2 adducts of **4** with isothiocyanates isothiocyanates in 28% and 11% yields, respectively. In the ^{31}P NMR spectra the signals were observed at δ –40.7 and –39.9, respectively, indicating that they have a pentacoordinate phosphorus. Low filed shift was observed for the ortho-proton of the Martin ligand of **5a,b**, supporting that they have a trigonal bipyramid structure with oxygen and sulfur atoms at the apical positions.



Since the monitor of thermolysis of **5a** by ^{31}P NMR spectroscopy showed almost quantitative formation of the corresponding cyclic thiophosphinate **9**, instead of the cyclic phosphinite **11** which would be formed via a decomposition pathway similar to that reported by Erker and coworkers,[3] it is likely that **5a** has the Wittig-type reactivity, although the product **10** without a phosphorus has not been identified yet.



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Education, Science, Sports and Culture, Japan. We thank Central Glas and Tosoh Akzo Co. Ltd. for gifts of hexafluoroacetone trihydrate an alkyllithiums, respectively.

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[4] For stable 1,3,2-thiazaphosphetanes, see: M. Fulde, W. Ried, and J. W. Bats, *Helv. Chim. Acta,* **72,** 139 (1989).

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[6] **5a:** ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.18–7.52 (m, 15H, arom), 7.81–7.84 (m, 3H, arom), 8.63–8.67 (m, 1H, *o*-H), 10.5 (s, 1H, NHPh), 13.7 (s, 1H, NH'Ph); $^{31}P\{^1H\}$ NMR (36 MHz, $CDCl_3$) δ –40.7; ^{19}F NMR (254 MHz, $CDCl_3$) δ –73.7 (q, $^4J_{F,F}$= 9.3 Hz), –74.1 (q, $^4J_{F,F}$= 9.3 Hz); HRMS (70 eV) *m/z* 634.0720, calcd for $C_{30}H_{21}F_6N_2OPS_2$ 634.0737.