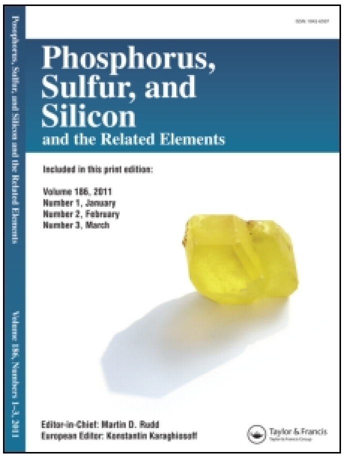

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

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To cite this Article Ogawa, Satoshi , Sato, Soichi , Masutomi, Yutaka and Furukawa, Naomichi(1992) 'Generation and Reactions of Hypervalent Organic Selenium and Tellurium Compounds Having Aryl Ligands', Phosphorus, Sulfur, and Silicon and the Related Elements, 67: 1, 99 — 102

To link to this Article: DOI: 10.1080/10426509208045824

URL: http://dx.doi.org/10.1080/10426509208045824

Phosphorus, Sulfur, and Silicon, 1992, Vol. 67, pp. 99–102
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GENERATION AND REACTIONS OF HYPERVALENT ORGANIC SELENIUM AND TELLURIUM COMPOUNDS HAVING ARYL LIGANDS

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Abstract The evidence for the formation of tetraaryl selenuranes as intermediates was presented in the ligand coupling reaction of triarylselenonium or diaryl selenoxide with phenyllithium (PhLi) by NMR studies. Triaryl telluranes were also formed as intermediates in the ligand exchange and disproportionation reactions of diaryl tellurides with PhLi.

As hypervalent chalcogenide compounds bearing four carbon ligands tetraphenyl selenurane and tellurane have been prepared.[1] Recently, the structure of tetraphenyl tellurane has been determined by X-ray crystallographic analysis.[2] The reactions of triphenyl selenonium salts with organometallic reagents have long been believed to proceed via an initial formation of σ-selenurane.[3] Therefore, we reinvestigated the reactions of triaryl selenonium salts and selenoxides with PhLi and found the first crucial evidence for formation of tetraphenyl selenuranes [10-Se-4(C4)] by low temperature NMR experiments. On the other hand, diaryl selenides and tellurides react readily with organometallic reagents suggesting the possible formation of ate complexes of triaryl selenuranes or telluranes bound to three carbon ligands. Recently, Reich and his co-workers have reported the lithium-tellurium exchange reactions by ^{13}C and ^{7}Li NMR and disclosed the formation of triphenyl tellurium ate complex.[4] In the course of the study of the reactions on chalcogenide atoms, we also found that the hypervalent ate complexes [10-Te-3(C3)]$^{-}$Li^{+} were formed in the reactions of diaryl tellurides with phenyllithium by low temperature NMR experiments.

FORMATION OF TETRAARYL SELENURANES

When an equimolar amount of PhLi was added to a suspension of triphenylselenonium bromide (**1**) in THF under N_2 at -78 °C, the mixture became yellowish homogeneous solution. Subsequently, the mixture was treated with 1N aqueous HBr solution to give the recovered **1** quantitatively. Similarly, diphenyl selenoxide (**2**) was treated with two equivalents of PhLi, then with 1N aqueous HBr solution at -78 °C afforded the same selenonium salt **1**. Further treatment of **1** and **2** with PhLi led to the ligand coupling products, diphenyl selenide (**3**) and biphenyl (**4**) in 85 and 87% yields respectively at elevating temperature suggesting that a stable intermediate like σ-selenurane **A** should be formed at low temperature. In order to confirm the formation of this σ-selenurane as a discrete intermediate, ^{77}Se, ^{1}H, and ^{13}C NMR spectra of the reaction mixture were measured at -100 °C. A new ^{77}Se NMR signal of **A** appeared at 373.7 ppm and no other signals were observed at all. By elevating the temperature of the solution to 22 °C, the ^{77}Se NMR signal shifted significantly to the downfield as a new singlet peak at 414.2 ppm which was consistent with that of diphenyl selenide (**3**) at 22 °C (the chemical shift of **3** observed at 401.6 ppm in THF at -100 °C). On similar treatment of diphenyl selenoxide (**2**) with PhLi in THF at -100 °C, the ^{77}Se NMR signal appeared initially at 827.0 ppm shifted also to 373.7 ppm corresponding to that of the intermediate **A**, which was shifted again to 414.2 ppm as a sharp singlet suggesting the formation of **3** at 22 °C. In order to confirm further the formation of selenurane **A**, temperature dependent ^{1}H and ^{13}C NMR experiments were carried out in anhydrous THF-d_8. New sets of the ^{1}H and ^{13}C NMR chemical shifts due to the phenyl group were assigned to the corresponding ortho, meta, and para-hydrogens and carbons. The ^{1}H and ^{13}C NMR chemical shifts of **A** were determined by the cross peaks observed in the CH-COSY spectrum. Both ^{1}H and ^{13}C spectra of the reaction mixture at 22 °C were consistent with that of nearly 1:1 mixture of **3** and **4**. Interestingly, the four phenyl groups in the selenurane formed should have an equivalent state suggesting that the

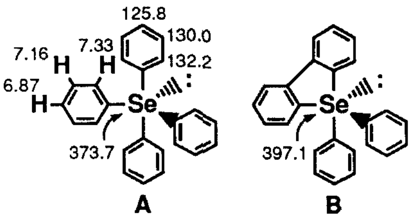
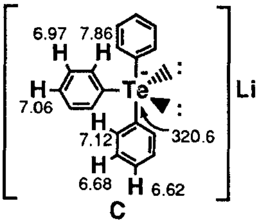


Figure 1. NMR data δ (ppm) in THF at -100 °C

pseudorotation takes place rapidly even under low temperature as -100 °C. Furthermore, we also tried to detect (2,2'-biphenylylene)diphenyl selenurane (**B**) of which structure should be fixed by a five membered ring and hence be more stable than the selenurane **A**. Upon similar treatment of (2,2'-biphenylylene)phenylselenonium chloride (**5**) and dibenzoselenophene 5-oxide (**6**) with PhLi and after work-up, phenyl o-terphenyl selenide (**7**) was obtained in 80% yield. A sharp singlet peak due to the selenurane **B** was also observed at 397.1 ppm by ^{77}Se NMR which is nearly identical with that of **A** but different chemical shifts from either that of the starting compounds or that of the corresponding coupling products **7** (390.0 ppm) and dibenzoselenophene (**8**) (445.9 ppm) at -100 °C.

FORMATION OF TRIARYL TELLURANES

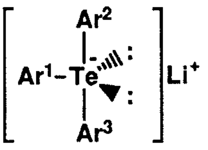
When diaryl tellurides were treated with an equimolar amount of phenyllithium and HMPA in THF at -78 °C, facile ligand exchange reaction took place to give a mixture of three tellurides. The exchange reactions proceeded readily even with 0.2 equimolar amount of phenyllithium. The low temperature NMR studies were performed in order to obtain a reliable evidence for the formation of the intermediate, triaryl ate complex in the reaction. The ^{125}Te NMR chemical shift of diphenyl telluride appeared at 670.4 ppm at -100 °C. Upon careful addition of PhLi at -100 °C to this solution the peak at 670.4 ppm disappeared at once to shift enormously to the upfield at 320.6 ppm. This dramatic shift of ^{125}Te NMR reveals that the ate complex **C** is formed as an intermediate in this exchange reaction. This large upfield shift of the ^{125}Te NMR is explained rationally in terms of the increase of the electron density at the central tellurium atom formed by hypervalent ate complex. This peak shifts to 694.7 ppm at room temperature, which is assigned as that of diphenyl telluride. The ^{13}C NMR spectrum of this ate complex **C** in THF-d_8 was measured and the results were satisfactory agreement with the values reported by Reich[4] within experimental error. The ^{1}H NMR data reveal the aromatic protons and their coupling constants of the ate complex **C**. The chemical shifts of the ^{13}C and ^{1}H NMR signals



C

Figure 2. NMR data δ (ppm) in THF at -100 °C

were assigned by the cross peaks obtained in CH-COSY spectrum. Both the ^1H and ^{13}C NMR spectra indicate that the pseudorotation does not take place at -100 °C due to the stability of the present rotamer in which the equatorial positions are occupied by one phenyl group and two lone electron pairs while the apical positions are occupied by two electronegative phenyl groups. Furthermore, we tried to confirm the formation of other ate complexes as intermediates in the reactions of p-substituted diaryl tellurides and phenyllithium. The ^{125}Te NMR spectra of these reactions were measured similarly as described above. Indeed the six peaks in ^{125}Te NMR spectra were obtained from a 1:1 mixture of phenyl p-tolyl telluride (or di-p-tolyl telluride) and phenyllithium with an equivalent HMPA in THF at -100 °C. This reveals that the ate complexes (C-H) were formed as a consequence of the rapid ligand exchange reaction between the telluride and phenyllithium. These peaks shift to the downfield at room temperature and hence they are assigned as the corresponding disproportionated three tellurides (diphenyl, phenyl p-tolyl, and di-p-tolyl telluride at 695.6, 680.6, and 667.8 ppm, respectively) by comparison with those of the authentic samples.



	Ar^1	Ar^2	Ar^3	δ, ppm
C	Ph	Ph	Ph	319.6
D	p-Tol	Ph	Ph	317.4
E	Ph	p-Tol	Ph	315.2
F	p-Tol	p-Tol	Ph	301.6
G	Ph	p-Tol	p-Tol	299.4
H	p-Tol	p-Tol	p-Tol	297.2

Figure 3. ^{125}Te NMR data in THF at -100 °C

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