

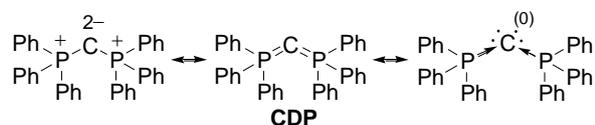
Synthesis and Structure of E=C=S(VI) Heteroallenes (E = S(IV), S(VI))

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Introduction

Carbodiphosphanes (CDPs) are heteroallene compound bearing phosphorus atoms. According to computational studies by Frenking and co-workers, CDPs should be more adequately described as *coordination complexes* of the type $L \rightarrow C^{(0)} \leftarrow L$ ($L = PPh_3$) rather than heteroallene and called “carbone” (Scheme 1)¹. Carbone compounds consist of two phosphine ligands coordinated to a central carbon atom, which keeps its four valence electrons in the form of two orthogonal lone pairs and hence gains formally zero-valent character. Strong σ - and π -donor ability of the CDPs attributed to the both electron pairs of the central zero-valent carbon were demonstrated by the proton affinity calculation and geminally dimetallated complexes^{1,2}.

Recently, we have first succeed in the synthesis and characterization of the stable and isolable carbodi- λ^6 -sulfane (CDS, Figure 1)³. From our theoretical and experimental results, CDS could be considered as “carbone” compounds, consist of two sulfur (VI) ligand, and which was coordinated to the Ag (I) ion⁴. We have also been revealed that the electron density of the central carbon atom in CDS is decreased by strong $n-\sigma^*$ interaction of methylimino moieties⁵. Thus, $Ph_2S=C=SPh_2(=NMe)$ (**1**) having an S(IV) ligand instead of an S(VI) ligand would be expected that the central carbon atom has an enhanced strong nucleophilic character by weakened $n-\sigma^*$ interaction. Herein, we present the synthesis of heteroallene **1** using the synthetic method of precursors which were previously reported⁶ and its structural comparison of heteroallene **1** and CDS.



Scheme 1

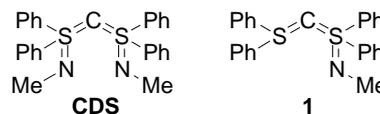
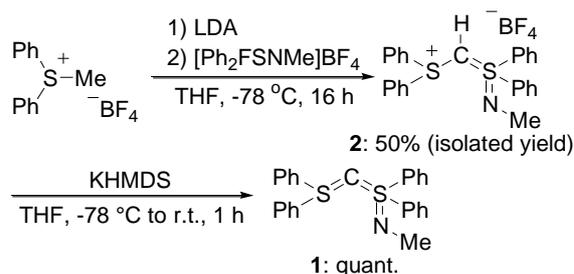


Figure 1

Results and Discussion

Heteroallene **1** was synthesized from the corresponding carbon-atom-protonated cationic salts **2**, which are obtained by the reaction of $[Ph_2FS=NMe]BF_4$ with diphenyl sulfonium methylide (Scheme 2). Deprotonation of **2** using potassium hexamethyldisilazane (KHMDS) results in the clean formation of heteroallene **1**, which were successfully isolated in almost quantitative yield.

The central carbon of heteroallene **1** appears at $\delta = 36.9$ ppm in the ^{13}C NMR spectrum, which is in the range of CDP' ($\delta = 12.3$ ppm)⁷ to CDS ($\delta = 39.9$ ppm)³. Thus, heteroallene **1** should be considered as a carbone compound, which has higher electron density at central carbon than CDS.



Scheme 2

The molecular structure of both **1** and **2** were confirmed by X-ray crystallography. The S(VI)-C bond of **1** (1.648(2) Å) is shorter compared to the precursor **2** (1.673(3) Å). In contrast, the S(IV)-C bond (1.707(2) Å) is slightly longer compared to the **2** (1.695 Å) ($\Delta_{S-C} = 0.012$). This observation is in contrast to the trend in CDPs and CDS. Generally, the bond distances between the coordinated atom and the central carbon atom

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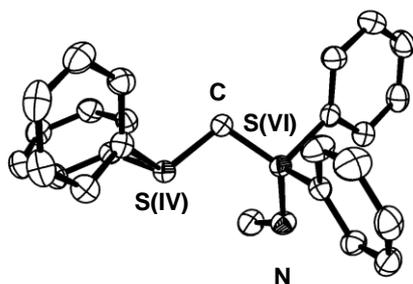
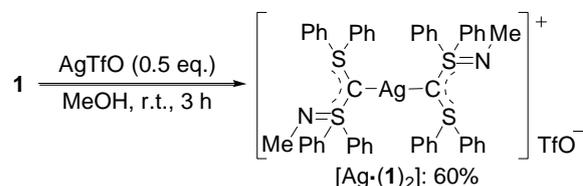


Figure 2 ORTEP drawing of **1** (50% probability thermal ellipsoids omitted hydrogen.)

tends to become shorter upon deprotonation, because short distances allows the efficient stabilization of the electron pairs at the central carbon atom through the $n\text{-}\sigma^*$ interaction. In the case of heteroallene **1**, to minimize the electronic repulsion, lone pair at the S(IV) atom favored the antiperiplanar relationship between the electron pairs at the central carbon. Therefore, the orbital overlap between the electron pairs at the central carbon atom and the σ^* orbital on the S(IV) atom is greatly reduced. This explains the small elongation of S(IV)-C bond length compared to that shortening of the other heteroallenes after the deprotonation (Figure 2)^{2,3,5,8}

The angle at the central carbon decreases significantly from the salt **2** ($116.76(17)^\circ$) to heteroallene **1** ($106.67(14)^\circ$) ($\Delta_{\text{S-C-S}} = 10.1^\circ$). This observation is similar to the **CDS**, which become acute upon deprotonation. While the angle of **CDS** ($116.8(2)^\circ$) indicating its hybridization close to sp^2 , the value of heteroallene **1** means sp^3 . In fact, the S(IV)-C-S(VI) fragment is so strongly bent that it nearly matches that of the highly strained five-membered cyclic **CDP** (105°) (Table 2)⁸.

Addition of 0.5 eq. of AgTfO to a solution of heteroallene **1** in MeOH gave C-coordinated Ag(I) complex $[\text{Ag}\cdot(\mathbf{1})_2]\text{TfO}$, which was fully characterized, including by X-ray diffraction analysis (Scheme 3).



Scheme 3

Conclusion

We succeeded in the synthesis, complexation, and characterization of a heteroallene **1** and suggested its C(0) character. Further investigation of reactivities of heteroallene **1** to H_2O , electrophiles, and transitionmetal ions are now in progress.

References

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Table 1 Selected bond lengths (\AA) and angles ($^\circ$) of **1**, **2**, **CDS** and **CDSH**

	1	2	CDS	CDSH
S(IV)-C	1.707(2)	1.695(3)	-	-
S(VI)-C	1.648(2)	1.673(3)	1.636(2)	1.695(2)
S-N	1.556(2)	1.528(3)	1.550(8)	1.531(2)
S-C-S	106.67(14)	116.76(17)	116.8(2)	118.0(1)