# Chalcogen atom transfer reactions. Kinetics of terminal bonded sulfur atom transfer between main group metal centers

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**The first comprehensive investigation of S atom transfer between two different metal centers is presented using the reaction of the terminal chalcogen atom bearing complex [CyNC($^t$Bu)NCy]$_2$SnS with [CyNC($^t$Bu)NCy]$_2$Ge$^{II}$; this multielectron redox reaction between Ge$^{II}$ and Sn$^{IV}$ proceeds *via* a second-order process with an inner sphere mechanism involving a μ-S intermediate as the proposed pathway; results of S and Se atom transfer between [CyNC($^t$Bu)NCy]$_2$Ge and PPh$_3$ are also presented.**

Atom transfer reactions are an active area of fundamental investigation that have attracted considerable attention in large part due the manifest role of oxygen atom transfer in many oxidation processes and in several biological processes.[1,2] The oxygen atom transfer reactions that have been studied are dominated by metal–oxo donor reactions with a non-metal acceptor. In comparison, transfer of heavier group 16 elements and/or complete inter-metal transfer of a multivalent atom are less established.[3,4] Some chalcogen complexes of Ti(IV) are known to function as effective sources of chalcogen atoms. However, the atom transfer reactivity of Cp$_2$TiE$_5$ (E = S, Se)[5] and of (OEP)TiE$_2$ (OEP = octaethylporphyrinato; E = O, S, Se)[6] are based on ligand reduction and are therefore categorized as secondary atom transfer reactions. When attention is focussed on main group metal complexes the number of clear examples of this class of reaction dwindles to a single detailed investigation.[7] In fact this example, shown by eqn. (1), represents the sole comprehensive study for inter-metal two electron transfer mediated by heavy elements of group 16 (*i.e.* S or Se) and involved the reversible transfer of sulfur and selenium atoms between tin porphyrin complexes of *meso*-tetraphenylporphyrinato (TPP) and *meso*-tetra-*p*-tolylporphyrinato (TTP) ligands.

$$\mathrm{(TTP)Sn^{II} + (TPP)Sn{=}S \rightleftarrows (TTP)Sn{=}S + (TPP)Sn^{II}} \qquad (1)$$

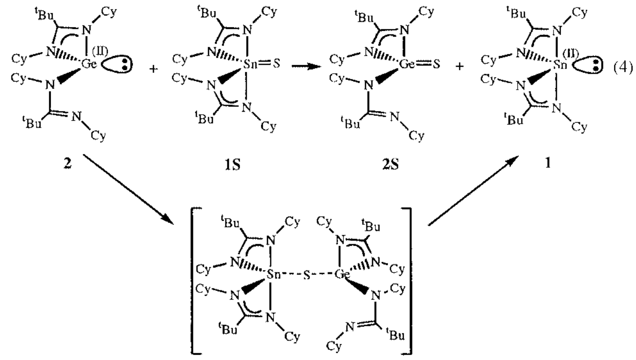
The limited examples of primary atom transfer reactions involving sulfur and selenium atoms include the exchange between the terminal chalcogenido complexes [η$^4$-Me$_8$taa]SnE (E = S, Se; Me$_8$taa = octamethyldibenzotetraazaannulene) and the Ge(II) species [η$^4$-Me$_8$taa]Ge [eqn. (2)].[8] More recently the preparation of terminal selenido complexes of gallium and indium supported by tris(3,5-di-*tert*-butylpyrazolyl)hydroborato ($^{tBu}$Tp) ligation allowed for the observation of selenium atom transfer from indium to gallium [eqn. (3)].[9] Kinetic parameters have not been established for either of these systems.

$$\mathrm{[\eta^4\text{-}Me_8taa]SnE + [\eta^4\text{-}Me_8taa]Ge^{II} \rightarrow [\eta^4\text{-}Me_8taa]Sn^{II} + [\eta^4\text{-}Me_8taa]GeE} \qquad (2)$$

$$\mathrm{[^{tBu}Tp]InSe + [^{tBu}Tp]Ga^{I} \rightarrow [^{tBu}Tp]In^{I} + [^{tBu}Tp]GaSe} \qquad (3)$$

Our interest in the formation of multiple bonds between main group elements and the subsequent reactivity of these unusual species led us to prepare a family of amidinato complexes of Ge and Sn [CyNC($^t$Bu)NCy]$_2$ME [M = Sn, E = S (**1S**); M = Ge, E = S (**2S**), Se (**2Se**)] that possess terminal chalcogenido functions.[10,11] These compounds were prepared by oxidative addition of styrene sulfide or elemental selenium to the corresponding M(II) precursors, [CyNC($^t$Bu)NCy]$_2$M [M = Sn (**1**), Ge(**2**)]. These results now allow us to report the first comprehensive study of heteronuclear inter-metal sulfur atom transfer reactions.

When the bis(amidinato)tin(IV) sulfide species **1S** and bis(amidinato)germanium(II) complex **2** are mixed at room temperature complete sulfur atom exchange between these complexes can be achieved according to eqn. (4) in Scheme 1.



**Scheme 1**

At room temperature this reaction proceeded smoothly over several days and could be conveniently monitored by $^1$H NMR in C$_6$D$_6$. The $^t$Bu groups for the four different amidinate complexes provided an excellent spectroscopic handle to monitor this reaction. For example, as the reaction progresses, the $^t$Bu resonances of **1S** at $\delta$ 1.17 continuously decrease in intensity concomitant with the appearance of new $^t$Bu resonances at $\delta$1.35, signifying the formation of **1**.

The corresponding $^t$Bu resonances for the germanium complexes are slightly more complicated. Instead of having both amidinate ligands bidentate and equivalent as with compounds **1** and **1S**, both **2** and **2S** are known to exhibit one bidentate and one monodentate ('dangling') ligand as shown in Scheme 1. This feature has been demonstrated through structural and spectroscopic characterization for both **2** and **2S** and is a general feature for a number of other germanium amidinate complexes that we have prepared.[12] As a result, the two amidinate ligands in the Ge complexes are inequivalent and two separate $^t$Bu signals are observed for **2** and for **2S**. Thus, during the progress of the reaction, two new $^t$Bu resonances appear at $\delta$ 1.70 and 1.07 signifying the formation of **2S** while the two resonances for the $^t$Bu groups of **2** ($\delta$1.61, 1.16) simultaneously decrease in intensity.

The progress of S atom transfer between **1S** and **2** can be monitored by following the changes in integration of the $^t$Bu resonance of any of the four complexes in Scheme 1. In all kinetic runs, the data for this transfer reaction was found to obey an integrated rate law for second-order reactions.† Plots of reciprocal concentration *vs.* time were linear for more than two half lives. In all cases the data indicated a complete, non-reversible transfer of a terminally bonded sulfur atom from Sn to Ge.

Rate constants for this reaction could be determined over a temperature range of 40 °C and a summary of this data is given in

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Table 1. Measurements from 25 to 65 °C resulted in $k$ values that ranged from $1.18 \times 10^{-3}$ to $2.14 \times 10^{-2}$ $M^{-1} s^{-1}$ with resulting half-lives of 18 h to 31 min. The thermal decomposition of **2S** precluded studies at higher temperatures. An Eyring plot of these results indicated a linear relationship with associated activation parameters of $\Delta H^{\ddagger} = 17.6 \pm 0.2$ kcal mol$^{-1}$ and $\Delta S^{\ddagger} = -14.4 \pm 0.3$ cal K$^{-1}$ mol$^{-1}$.

The first-order dependence of the reactants was confirmed by imposing pseudo-first-order conditions on the reaction by having **1S** in large excess compared to **2**. Under these circumstances the disappearance of **2** and subsequent formation of **2S** exhibited first order behavior.

The only comparable system for which kinetic information is available is given by eqn. (1). In this case the kinetic analysis was consistent with a reversible second-order reaction.[7] The equilibrium constant for this reaction was near unity between −40 and −10 °C in toluene-d$_8$. Kinetic measurements for eqn. (1) at temperatures ranging from 30 to 60 °C resulted in $k_f$ values from 0.40 to 2.39 $M^{-1} s^{-1}$.

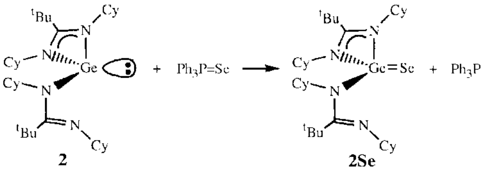
The rate law and activation parameters that we obtained for eqn. (4) in Scheme 1 support an inner-sphere mechanism which likely proceeds *via* interaction of the chalcogen atom on tin and the Ge(II) center resulting in a sulfur bridged intermediate (Scheme 1). While this species was not observed in our experiments, the negative entropy of activation ($\Delta S^{\ddagger} = -14.4$ cal K$^{-1}$ mol$^{-1}$) is consistent with an associative type reaction involving a μ-sulfido intermediate. This observation is in line with the value of $\Delta S^{\ddagger}$ (−24.1 cal K$^{-1}$ mol$^{-1}$) determined for eqn. (1) for which a similar μ-S species was suggested.[7] Consistent with this proposition is the low $\Delta H^{\ddagger}$ value, which suggests that significant bond formation between Ge and the bridging sulfido ligand that offsets the energy are required for the cleavage of the Sn=S during the transfer. Again the $\Delta H^{\ddagger}$ value obtained for eqn. (4) is similar to that obtained for the homonuclear exchange reaction shown in eqn. (1) ($\Delta H^{\ddagger} = 10.9 \pm 0.9$ kcal mol$^{-1}$).[7]

The direction of this sulfur atom exchange reaction demonstrates the thermodynamic stability of the terminal GeS bond relative to the corresponding SnS bond. This is consistent with the notions that both the tendency to engage in multiple bonding and the stability of M(IV) *vs.* M(II)[13] decreases for the heavier congeners of the group 14 elements (Ge > Sn > Pb). This is further supported by the fact that the π-bond energy associated with the Sn=S bond has been estimated to be 31.8 kcal mol$^{-1}$ which is considerably lower than that of the Ge=S bond (40.0 kcal mol$^{-1}$).[14]

Keeping in mind that the common acceptors for oxygen atom transfer reactions are tertiary phosphines[1,2] we also examined the chalcogen atom exchange reactions between the germanium complexes **2**, **2S** and **2Se** and $Ph_3PE/Ph_3P$ (E = S, Se). This should also provide some indication of the relative bond strengths for these species. Complex **2** reacts with 1 equiv. of triphenylphosphine selenide‡ in $C_6D_6$ according to eqn. (5). $^1H$ NMR spectroscopy indicated a complete conversion of $Ph_3P{=}Se$ to $Ph_3P$ while germylene **2** was converted to **2Se**. Under these conditions complete selenido atom exchange was achieved from the phosphorus to the germanium in < 4 min at room temperature with no indication of remaining starting materials. However, when the same reaction was performed with $Ph_3PS$ in place of the $Ph_3PSe$, no reaction with **2** was observed even at elevated temperatures.

**Table 1** Rate constants for eqn. (4) in $C_6D_6$

| $T$/°C | $k$ $M^{-1} s^{-1}$ |
|---|---|
| 25 | $(6.28 \pm 0.84) \times 10^{-4}$ |
| 35 | $(1.46 \pm 0.13) \times 10^{-3}$ |
| 45 | $(4.19 \pm 0.06) \times 10^{-3}$ |
| 55 | $(1.08 \pm 0.04) \times 10^{-2}$ |
| 60 | $(1.53 \pm 0.06) \times 10^{-2}$ |
| 65 | $(2.14 \pm 0.05) \times 10^{-2}$ |



(5)

We have found complete primary sulfur atom exchange between tin and germanium amidinates can be achieved and the kinetic parameters of this reaction have been fully determined. This represents the first comprehensive study of a heteronuclear inter-metal two-electron sulfur atom transfer. The data indicate an inner-sphere mechanism with μ-S formation. Chalcogen atom exchange between $PPh_3$ and **2** provide results that are consistent with increasing strength of interaction for the terminal sulfido species in the order $[CyNC(^tBu)NCy]_2SnS$ **1S** < $[CyNC(^tBu)NCy]_2GeS$ **2S** < $Ph_3PS$ while for terminal selenido species the order appears to be $Ph_3PSe$ < $[CyNC(^tBu)NCy]_2GeSe$ **2Se**. Our current efforts are directed at extending this investigation of inter-metal chalcogen atom transfer and exploring transfer to non-metal acceptors.

## Notes and references

† All kinetic measurements were carried out in duplicate and were monitored by NMR spectroscopy using a Bruker 500 MHz or a Gemini 200 MHz spectrometer. Benzene-d$_6$ was distilled from Na/K alloy and used as solvent and internal standard. $[CyNC(^tBu)NCy]_2Sn{=}S$ **1S** and $[CyNC(^tBu)NCy]_2Ge$ **2** were prepared according to literature procedures.[10,11]

Solutions of **1S** and **2** were prepared at concentrations ranging from 0.011 to 0.075 M and in ratios from 1:1 to 7:1. Samples were monitored in a temperature controlled NMR probe for at least two half lives. During remote $^1H$ NMR experiments, spectra were obtained at regular intervals that varied with temperature (*e.g.* 45 min at 35 °C and 3 min at 65 °C). For measurements at 25 °C, a temperature controlled water bath set at 25.0 °C was used and spectra were recorded manually every 2 h. Pseudo-first-order conditions were investigated at 35 °C where the initial concentrations were: $[(CyNC(^tBu)NCy)_2Sn{=}S] = 0.075$ M and $[(CyNC(^tBu)NCy)_2Ge] = 0.011$ M.

‡ $Ph_3P{=}Se$ was prepared by dissolving triphenylphosphine (2.038 g, 7.78 mmol) in 35 ml THF followed by addition of excess elemental selenium (1.023 g, 13 mmol). The mixture was stirred for 24 h and filtered. The product was subsequently recrystallized from THF in 66% yield (1.66 g).

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