

**PRF#:** 56705-ND3

**Project Title:** *Development of the Synthesis of Mixed Oxysulfidometalates and of a New, General Methodology for the Preparation of Terminal Disulfide Complexes*

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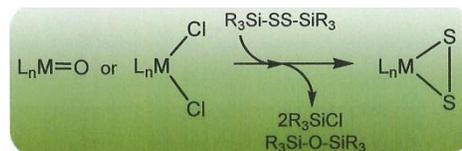
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The central goal of this project has been the development of a facile and general methodology for the synthesis of terminal disulfide complexes,  $M(\eta^2-S_2)$ . The probable importance of this functional group along the reactive edges of bulk inorganic sulfides has brought attention and interest to well-defined coordination complexes having this moiety.

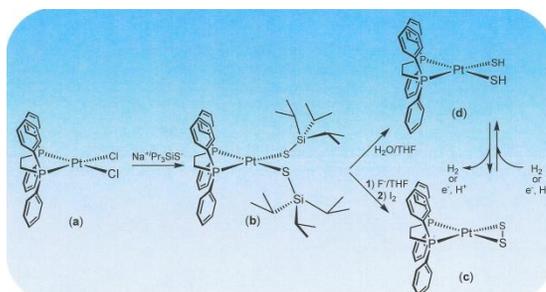
The initial approach that was proposed was a one-step ligand exchange with bis(trialkylsilyl) disulfide complexes, as exemplified in **Scheme 1**. However, a lack of ready access to  $R_3Si-SSiR_3$  complexes that are sufficiently reactive (*i.e.*, having R relatively small, as Me) has hampered progress. The sterically encumbered disulfide  ${}^iPr_3Si-SSi{}^iPr_3$ , for example, is accessible from commercially available  ${}^iPr_3SiSH$  but has been unreactive in reactions of the type shown in **Scheme 1**.

Our revised approach to the general proposition that silylthiolates might be useful, masked forms of inorganic sulfide or disulfide has been to introduce  $Na^+SSiR_3^-$  ligands and then to assess whether the  $R_3Si$  group might be deliberately and cleanly removed. We have restricted our attention to Group 10 compounds with ancillary bis(phosphine) ligands because of their general stability and ease of handling. Substitution of chloride by  $Na^+SSiR_3^-$  (**Scheme 2, Figure 1**) does work and appears to depend on the rapid precipitation of NaCl from the mixture. Unsurprisingly, the triisopropylsilanethiolate complexes show greater stability against atmospheric moisture than do the trimethylsilylthiolate versions. On the other hand, the triisopropylsilyl group is more difficult to unmask. We have found that commercially available samples of  $Bu_4N^+F^-$  (whose concentrations of  $F^-$  we have to measure by  ${}^{19}F$  NMR), do indeed lead to removal of the  $R_3Si-$  group and, following protonation, to the metallodithiol. **Figure 2** shows the  $-SH$  signals in the  ${}^1H$  NMR spectrum of  $[(dppe)Pt(SH)_2]$ , which reveal a distinctive pattern of coupling to  ${}^{195}Pt$  and the *cis* and *trans*  ${}^{31}P$ . The interconversion between metallodithiol and metallodisulfide has not, to our knowledge ever been examined and is currently under study in our lab as an aspect of the fundamental properties of  $M(\eta^2-S_2)$  complexes.

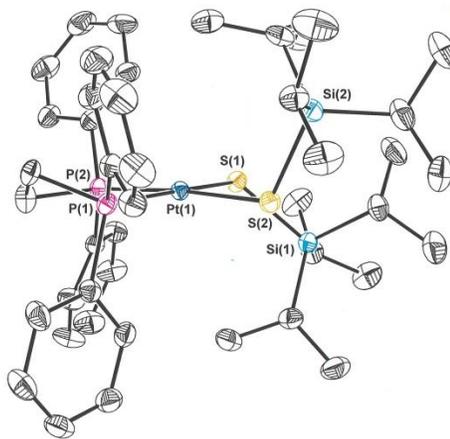
In ongoing work, we intend to return to  $Me_3SiSSSiMe_3$  as a reagent, which should be makeable in three steps from  $Me_3SiCl$ . Although highly malodorous,  $Me_3SiSSSiMe_3$  is the



**Scheme 1.** A proposed general methodology to terminal disulfide complexes.



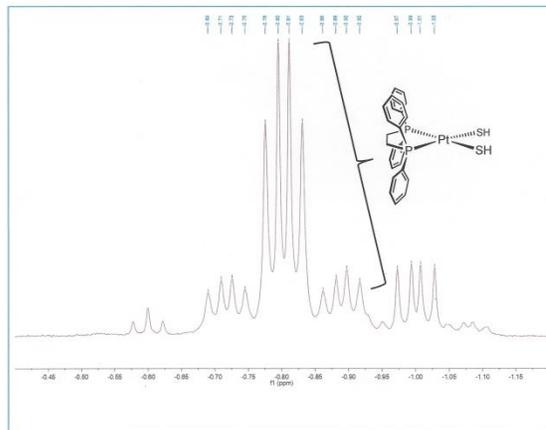
**Scheme 2.** Synthesis of terminal disulfide and metallodithiol complexes in the Donahue Lab.



**Figure 1.** Thermal ellipsoid plot of  $[(dppe)Pt(SSi{}^iPr_3)_2]$  (50%). All H atoms are omitted for clarity.

compound best suited to react according to **Scheme 1**. Other variants, such as  $\text{PhMe}_2\text{SiSSSiMe}_2\text{Ph}$  warrant some consideration, as they may be solids but not so sterically encumbered as to suppress all interesting reactivity. Finally, we will in parallel pursue the direct synthesis of known dithiols as an independent route to the terminal disulfides with the aim of developing greater familiarity with their properties and behavior while the chemistry of **Scheme 1** is under study.

This funded project has been very impactful upon the direction of research in the Donahue Group. A decisive turn in theme has been toward the synthesis, properties and reactivity of inorganic sulfide and disulfide complexes, both mononuclear and multi-metallic. The Donahue lab now is deeply invested in this area, as we see a variety of areas that are either under-developed or unexplored. The change in direction has brought our group into unanticipated collaborations wherein we use our cumulative experience with synthesis to provide samples to others for studies of their own or identify new targets for synthesis. This project has been in transition between two students, having supported one at the tail end of her studies and a new student at the beginning of his Ph.D. work. Both of these students have enjoyed accelerated progress toward their degrees because of this support.



**Figure 2.**  $^1\text{H}$  NMR spectrum of  $[(\text{dppe})\text{Pt}(\text{SH})_2]$  showing  $-\text{SH}$  signal with its distinctive coupling to  $^{195}\text{Pt}$  and  $^{31}\text{P}$ , *cis* and *trans*.