

New Compositions Containing Carbon and Sulfur

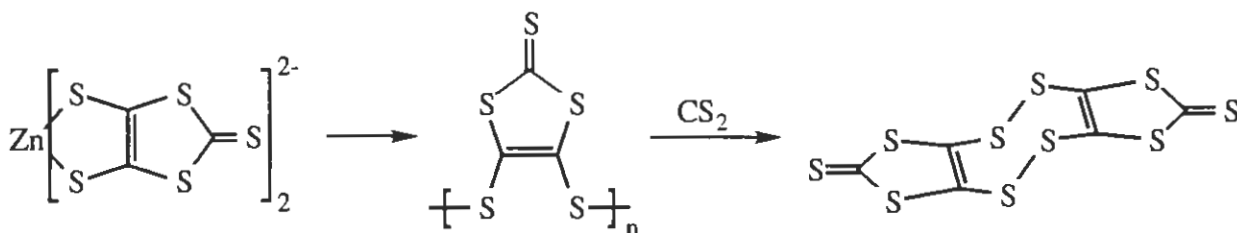
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Because binary phases are particularly fundamental to chemistry and materials science, most have been rather heavily studied, especially those that might afford molecular species. Nonetheless, compositions of the type C_nS_m have been overlooked and remain a promising source of new binary molecular and polymeric materials [1]. The known molecular architectures based on carbon and sulfur are quite varied although they are constructed from only C=C, C=S, and S-S bonds [2].

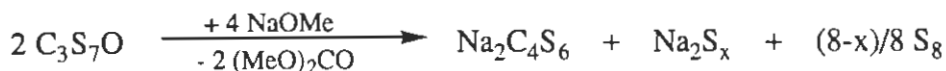
Using the zinc salt $(NBu_4)_2[Zn(\alpha-C_3S_5)_2]$, pure $[C_3S_5]_n$ was prepared via its oxidation with sulfonyl chloride [3]. Raman and reactivity studies indicate that $[C_3S_5]_n$ is probably polymeric although it can be converted to the dimer C_6S_{10} by treatment with CS_2 [4].



Treatment of the above $[Zn(\alpha-C_3S_5)_2]^{2-}$ with HCl gave the dithiol, $C_3S_5H_2$. Like cis-dimercaptoethylene [5], this alkene dithiol is unstable with respect to loss of H_2S . Thermolysis of the dithiol afforded the new binary carbon sulfide C_6S_8 as an insoluble red-brown powder.

Both C_6S_{10} and C_6S_8 were converted to dicarbonyl derivatives through an Hg^{2+} promoted O for S exchange of the thiocarbonyl groups. For C_6S_{10} , this reaction was accompanied by a skeletal rearrangement of the central 1,2,5,6- S_4C_4 ring to a 1,2,3,6 isomer as shown by single crystal X-ray diffraction. When a mixture of the previously reported [6] carbon sulfides C_6S_{12} and C_6S_8 was subjected to the same O for S exchange conditions, only the compound C_3S_7O was isolated. Analysis of this compound by X-ray diffraction showed that the C_2S_5 ring adopts a conformation similar to cyclo- S_7 .

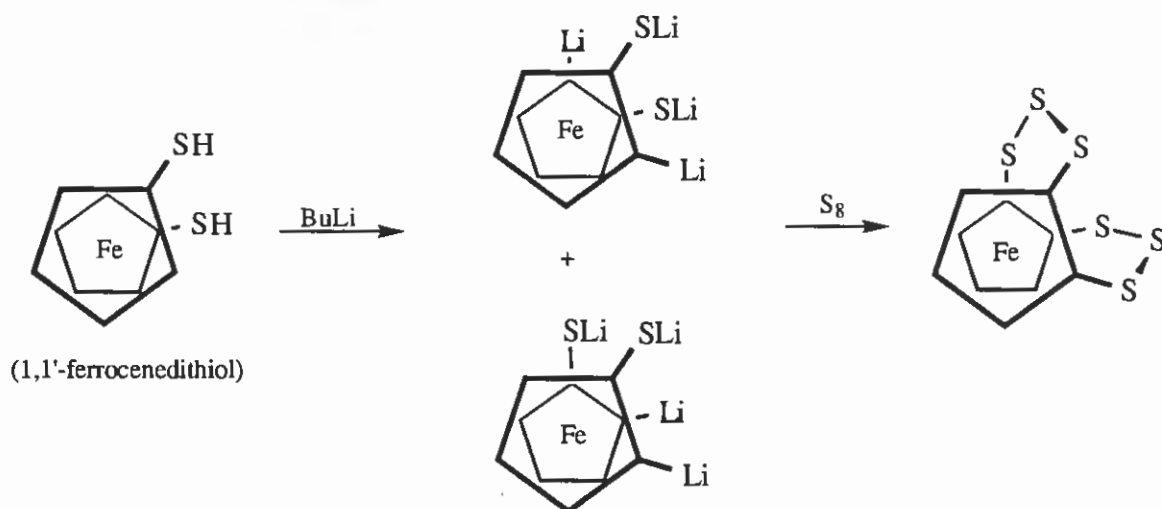
Base promoted decarbonylation of C_3S_7O does not give $C_2S_7^{2-}$ but instead affords the dianion $C_4S_6^{2-}$. Crystallographic analysis showed that this anion adopts a nonclassical structure with 1,1- and 1,2-dithiolate termini. This analysis, in conjunction with an EHMO calculation, indicates that the $C_4S_6^{2-}$ anion is a π delocalized species. Preliminary studies show that it forms the 1:1 polymer $[Ni(C_4S_6)]_n$. This complex displayed two point conductivity values of $> 10^{-2} S cm^{-1}$ which are similar to the conductivities of other thiocarbon metal complexes.



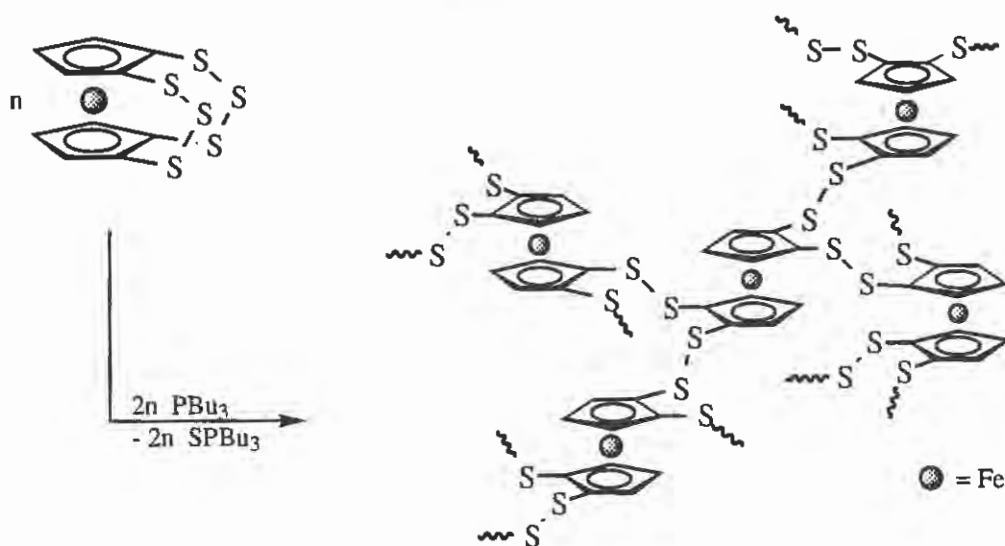
Following the success of other organotitanium group transfer reagents [6,7] such as $(C_5H_5)_2TiS_5$, two new organometallic thiocarbon adducts were prepared and used in the synthesis of carbon sulfides. The oxidative addition of C_4S_6 to $(MeC_5H_4)_2Ti(CO)_2$ afforded the

compound $(\text{MeC}_5\text{H}_4)_2\text{TiC}_4\text{S}_6$. The titanocene complex $[(\text{C}_5\text{H}_5)_2\text{Ti}]_3\text{C}_6\text{S}_6$ was prepared in good yield from the reaction of the hexathiol $\text{C}_6(\text{SH})_6$ with $(\text{C}_5\text{H}_5)_2\text{TiCl}_2$. These transfer agents, $(\text{MeC}_5\text{H}_4)_2\text{TiC}_4\text{S}_6$ and $[(\text{C}_5\text{H}_5)_2\text{Ti}]_3\text{C}_6\text{S}_6$, were converted to C_5S_7 [8] and C_6S_9 by treatment of the former with thiophosgene and the latter with sulfur dichloride.

While the binary carbon sulfides are attractive for their simplicity and synthetic versatility, they suffer from very low solubility. In order to prepare soluble polymeric materials based on C-S and S-S bonds, the incorporation of other elements is necessary. Thus, the ferrocene polysulfides $\text{Fe}(\text{C}_5\text{H}_3)(\text{S}_3)_2$ and $\text{Fe}(\text{t-BuC}_5\text{H}_2)(\text{C}_5\text{H}_3)_2(\text{S}_3)_2$ were prepared from ferrocene and t-butylferrocene using a stepwise lithiation-sulfurization methodology [9].



Like the known ferrocene trisulfides [10], the hexasulfides display conformational isomerism in solution. This isomerism arises from the relative orientations of the central sulfur atoms of the trisulfide bridges. Upon addition of tributylphosphine to solutions of the hexasulfides, desulfurization occurred concomitant with polymerization to yield network polymers. In the case of $\text{Fe}(\text{t-BuC}_5\text{H}_2)(\text{C}_5\text{H}_3)_2(\text{S}_3)_2$, the polymer was soluble. Characterization of the polymer by gel permeation chromatography showed that it had high molecular weights.



References

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