

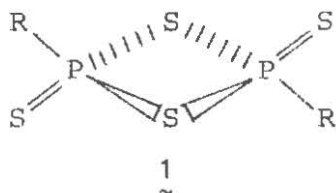
Sulfur Rich Transition Metal-Main Group Heterocycles and Cages

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The reactivity of elemental sulfur homocycles has long been postulated to occur via highly reactive thiopolysulfide (S=S) ring intermediates [1,2]. The existence of these S=S linkages has been supported by matrix infrared studies [3]. Consistent with the reactivity associated with these postulated S=S intermediates is that observed for the organoperthiophosphinic acid anhydrides, 1.



These anhydrides are one of the most efficient reagents known for the thiation of organic carbonyl compounds (eq. 1) [4,5].



In an effort to enhance the reactivity of the well studied Cp_2TiS_5 system we sought to incorporate $RP(S)$ fragments into the pentasulfide ring. As a result of this study a new class of phosphorus sulfide chelates has been prepared, which show a lability analogous to many heterocumulene systems [6]. The transition metal complexes of these phosphorus sulfide chelates were found to have a similar reactivity toward organic substrates as 1, but unlike 1 reacted readily with dioxygen. It is not unusual for titanium complexes to be oxophilic [7], but this reactivity was traced to the lability associated with the particular phosphorus sulfide chelate. The investigation into the reactivity of these transition metal complexes has lead to a better understanding of the reactivity of the parent anhydrides themselves. A kinetics study of the sulfur transfer reactivity of 1 indicated RPS_2 fragments as the reactive species.

Replacement of the organic group of these organothiophosphoryl (RPS_2) ligands with sulfide affords, formally, condensed anions of trithiophosphite (PS_3^{2-}). Divalent metal salts of these dianions (MES_3 , $E=P,As$) have been employed as intercalation hosts [8,9], while mono- and divalent metal salts of the ES_3^{3-} trianion form a large class of minerals termed Sulfosalts [10]. In an effort to produce molecular transition metal complexes of these ES_3 anions, the reactions of two binary arsenic sulfide minerals, Orpiment (As_2S_3) and Realgar (As_4S_4), with nucleophiles were investigated. These minerals were found to dissolve in the presence of sulfide which followed by metathesis with organotransition metal halides or through the use of nucleophilic transition metal sulfides has lead to the isolation of molecular compounds. These transition metal compounds can be viewed as molecular Sulfosalts in that they contain AsS_3^{3-} or catenates of these trigonal pyramids as ligands.

One of these molecular Sulfosalts ($Cp_3Ti_2OAsS_3$) structurally resembles the E_4S_3 ($E=P,As$) cages wherein a Cp_2Ti fragment occupies a divalent site (S) and a $CpTi$ moiety a trivalent one (E). This observation suggested the possibility of preparing $(CpTi)_4S_x$ cages from mono(cyclopentadienyl)titanium trichloride and lithium sulfides. The two isolated complexes from this reaction were $Cp_4Ti_4S_8O_x$ ($x=1,2$) which like the E_4S_3 cages are comprised of a tetrahedral array of trivalent atoms. Unlike the main group cages these Ti_4 compounds contained μ_4 -oxides and bridging disulfides.

References

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