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Preliminary communication

CATENATED POLYSULFUR LIGANDS: THE PENTASULFIDES OF DI-η^5-CYCLOPENTADIENYL-ZIRCONIUM(IV) AND -HAFNIUM(IV)

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Summary

The thiols $Cp_2M(SH)_2$, where M = Ti and Zr, react to form the complexes Cp_2MS_5 when treated with mono- and di-sulfur transfer reagents. Treatment of Cp_2MCl_2 with Li_2S_2 and sulfur gave Cp_2MS_5, M = Ti, Zr and Hf, in better yield. The new Zr and Hf complexes have a six-membered MS_5 ring in a chair conformation similar to that previously observed for M = Ti. Variable temperature NMR studies show that the barriers to MS_5 ring inversion decrease in the order Ti > Hf > Zr.

Elemental sulfur has been intensively studied; however, the factors that determine chain length and ring size are surprisingly poorly understood [1]. A few transition metal complexes containing a catenated polysulfur metallocycle, MS_x, where $x = 4$ or 5, have been reported [2]. Interest in these complexes arises from the expectation that they will provide insight concerning synthetic and theoretical aspects of sulfur chemistry. In addition there is great interest in metal—sulfur interactions because of the catalyst poisoning properties of sulfur compounds. The reaction of recently developed sulfur transfer reagents with Group IVB metal compounds has resulted in the isolation of the new complexes Cp_2MS_5, where M = Zr and Hf, and Cp = η^5-C_5H_5.

Sulfur transfer reagents of the type $>N—S_n—N<$, where $>N$ = benzimidazole, $n = 1,2$, react with thiols to give tri- and tetra-sulfides, respectively [3]. Thus, the complex $Cp_2Ti(SH)_2$ (I) was chosen as a possible precursor to Cp_2TiS_x where $x = 3$, and 4; the compound with $x = 5$ being previously known [2a]. The reported preparation [4] of I did not work in our hands. However, treatment of Cp_2TiCl_2 in dry THF under nitrogen with excess H_2S in the presence of Et_3N gave a precipitate of $Et_3NH \cdot Cl$ which was removed by filtration under nitrogen, thus eliminating the need for the destructive washing with H_2O as originally reported. Stripping the filtrate to dryness gave the dithiol (95% yield) which was sufficiently pure for our purposes. Application of a similar procedure to

Cp_2ZrCl_2 using dry THF as the crystallizing solvent resulted in the isolation of the new dithiol $Cp_2Zr(SH)_2$ (II)* in up to 46% yield** as yellow crystals (dec. 145°C without melting). However, $Cp_2Hf(SH)_2$ could not be isolated by this technique. Both complexes I and II react with $>N{-}S_n{-}N<$ to give as the exclusive isolated products Cp_2TiS_5 (III, $n = 1, 2$) and Cp_2ZrS_5 (IV, $n = 2$), respectively. Variations in the reaction conditions did not produce additional isolated products. The yields of III and IV were low reflecting the deficiency of sulfur in the reaction stoichiometry. No evidence could be found for other Cp containing complexes in the NMR spectra of the isolated product.

Another type of sulfur transfer reagent, Li_2S_2, reacts with alkyl chlorides to give disulfides [5]. Treatment of Cp_2MCl_2 under N_2in THF with $Li_2S_2/3S$ followed by CH_2Cl_2 extraction and filtration under N_2, concentrating the filtrate and cooling resulted in the isolation of Cp_2MS_5 (M = Ti, Zr) and Hf (V) in 50—60% yield. This latter method is the preferred method of synthesis. The new complexes IV (orange, dec. 160—170°C) and V (yellow, dec. 150—155°C) were isolated as large air stable crystals. Their infrared spectra are very similar to that for III. Preliminary X-ray studies [6] on IV have shown that it has a cyclohexane-like ring with an axial and an equatorial Cp group very similar to that found for III [7] (Fig. 1).

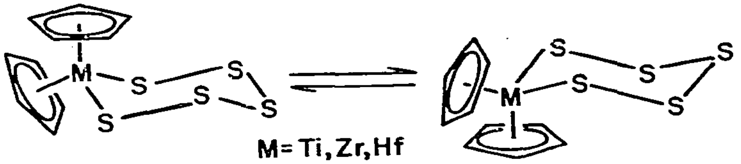

Fig. 1. The interconversion of Cp_2MS_5 species.

Thus a series of catenated polysulfur complexes are available for study. Like cyclohexane, III, IV and V undergo chair-to-chair ring flipping which when slow on the NMR time scale causes two peaks due to the axial and equatorial Cp rings to be observed. As the temperature is raised the flipping becomes more rapid causing the two peaks to collapse and coalesce. At room temperature ring-flipping in III is slow and the sample must be heated to 120°C [2a, 8] in order to observe the one peak of the fast exchange limit. However, IV and V are flipping rapidly at room temperature since only one peak due to the Cp groups is observed. IV and V must be cooled to −80 and −50°C, respectively, to freeze out the motion and observe sharp peaks for the axial and equatorial groups. Approximate free energies of activation for the inversion process were calculated from the observed coalescence temperatures and signal separations in the low-temperature limiting spectra (Table 1). The values decrease in the order $Ti > Hf > Zr$.

The dicyclopentadienyls of the Group IVB metals form only six membered rings, MS_5, even under conditions designed to favour the formation of MS_3 and MS_4 species. The latter are observed in the mass spectra of III, IV and V. MS_4

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*Satisfactory elemental, infrared, mass spectroscopic and NMR analyses were obtained for all new complexes reported.

**An additional complex, $Cp_4Zr_2S_2$, can also be isolated, the details of which will be described in a subsequent report.

TABLE 1

^{1}H NMR PARAMETERS FOR Cp_2MS_5

Complex	T_c(K)^a	Δ(Hz)^b	$\Delta G^{\ddagger}$ (kJ mol^{-1})^c
Ti	361±0.5	10.0 (16.5±0.1)^e	76.3^d
Zr	227±0.5	13.7±0.05	48.6^e
Hf	257±1.0	4.0±0.05	58.0^e

[a] T_c = coalescence temperature. [b] Δ = separation of signals due to axial and equatorial Cp groups at low temperature. [c] Ref. 10. [d] At room temperature in toluene-d_8, ref. 8. [e] In CD_2Cl_2, this work.

species such as Cp_2MoS_4 [2c, 9] and $(PPh_3)_2PtS_4$ [2g] have been reported; thus the predominance of the six-membered ring is not absolute. Moreover, the factors which cause the observed variation of the ring-flip activation energies for III—V are not readily apparent. Additional synthetic and structural studies are planned.

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