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Preliminary Communication

Synthesis of the novel bifunctional ligand, dicyclopentadienylsulfide $(C_5H_5)_2S$, and its dilithium salt

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Abstract

The dicyclopentadienylsulfide ligand $(C_5H_5)_2S$ (**1**) was synthesized via reaction of CpTl with SCl_2. The dilithium salt $Li_2[(C_5H_4)_2S]$ (**2**) was obtained by the reaction of **1** with ^nBuLi and was characterized spectroscopically.

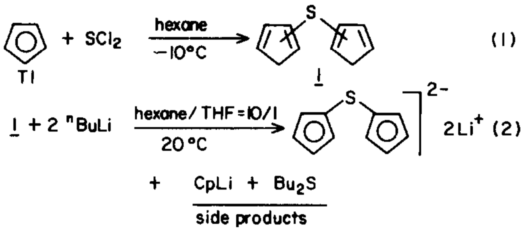
Key words: Iron; Cyclopentadienyl; Sulfur; Lithium

Dicyclopentadienes with a one-membered bridge are extensively used in the synthesis and investigation of a wide variety of mono- and binuclear metallocenes [1]. Syntheses of dicyclopentadienes (and their salts) with a bridge other than carbon or silicon are rare, but several examples with germanium and phosphorus containing fragments have been described [2–6]. These dicyclopentadienes are of peculiar interest because they are the starting materials for synthesis of the ansa-metallocenes, derivatives of early transition metals, which have a specific activity as components of Ziegler–Natta polymerization catalysts.

In the present work we report the synthesis of the dicyclopentadienylsulfide **1** and its dilithium salt **2** (see Scheme 1).

An equimolar amount of SCl_2 (5% hexane solution) was mixed with a suspension of CpTl in hexane under continuous stirring. The reaction was carried out for 3 h at −10°C. The resulting dicyclopentadienylsulfide **1** is a chromatographically pure (TLC-test), readily decomposed pale-yellow oil (yield ≈ 100%).

It should be particularly emphasized that all solvents were purified by standard methods and freshly distilled prior to use [7]. CpTl was obtained by a routine procedure [8] and was vacuum sublimed. SCl_2 was distilled twice in a Cl_2 current and twice with a small amount of PCl_3 to remove the traces of Cl_2 [9].



Scheme 1.

Owing to the fast elementotropic migration process the NMR spectra of **1** are unduly difficult to interpret and are thus of no use for this study.

We have found that dicyclopentadienylsulfide (**1**) instantaneously reacts with ^nBuLi [10] in a hexane/tetrahydrofuran 10/1 mixture forming a white microcrystalline precipitate of the dilithium salt **2** (see Eq. (2), Scheme 1). The latter was isolated using sealed Schlenk-type vessels.

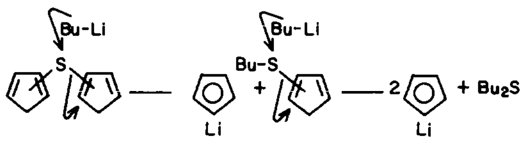
^1H- and ^{13}C-NMR spectra were recorded in tetrahydrofuran-d_8 with a Varian VXR-400 (^1H: 400 MHz; ^{13}C: 100 MHz) NMR spectrometer.

The ^1H-NMR spectrum of **2** is the AA′BB′ system of signals of the monosubstituted Cp-anion ($J(AB) = 2.8$ Hz). The ^{13}C-NMR spectrum shows three types of carbon atoms (δ 114.247, 103.422, 103.358).

The NMR data show that the salt **2** is slightly contaminated with CpLi (^1H-NMR: δ 5.695; ^{13}C-NMR: δ 109.254, see Figs. 1 and 2).

This fact is explained by the proximity of the rates of the nucleophilic attack of ^nBuLi upon the sulfur atom and of the deprotonating process of **1** (see Eq. (2), Schemes 1 and 2).

The salt **2** is extremely sensitive to oxygen and/or water; when dry it ignites spontaneously in air.



Scheme 2.

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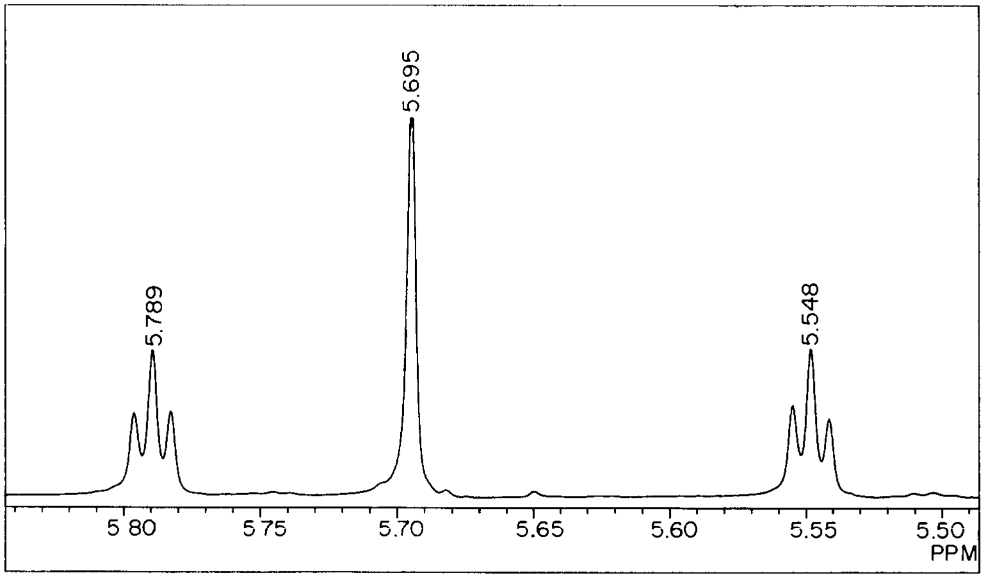

Fig. 1. ^{1}H-NMR data for **2**.

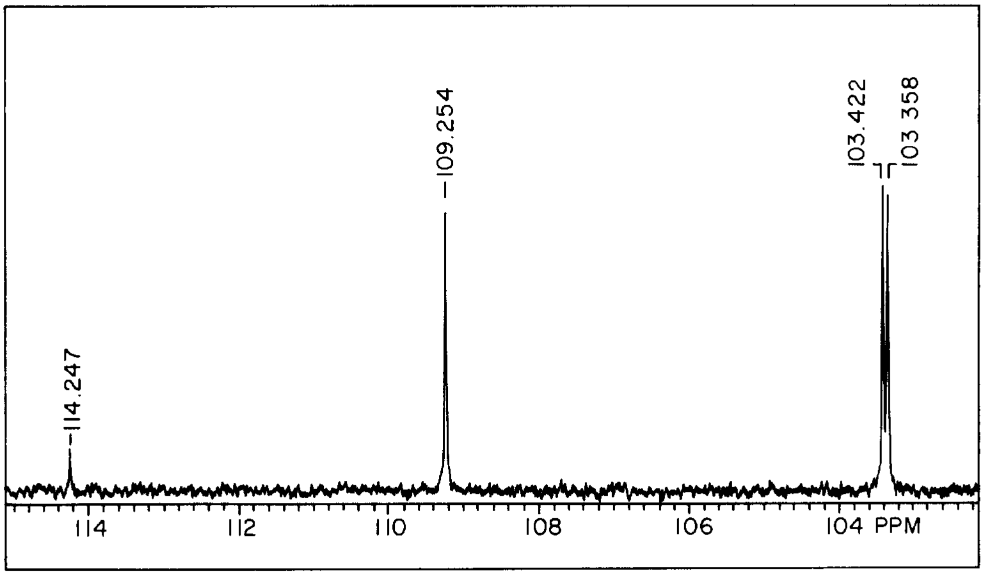

Fig. 2. ^{13}C-NMR data for **2**.

In subsequent papers we plan to present data on the syntheses of metal complexes with this dicyclopentadienylsulfide bifunctional ligand.

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