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Propylthiocyclopentadiene: a new synthetic route to complexes of iron and group 4 transition metals. Molecular structure of $(C_5H_4SCH_2CH_2CH_3)_2ZrCl_2$

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Summary — The use of the propylthio-substituted cyclopentadienylsodium salt leads to 1,1′-bis(propylthio)ferrocene and dichlorobis(propylthiocyclopentadienyl)zirconium, titanium or hafnium(IV). The structure of $(C_5H_4SCH_2CH_2CH_3)_2ZrCl_2$ has been established by X-ray analysis (orthorhombic, *Pbcn*, a = 11.943(1) Å, b = 6.883(2) Å, c = 22.412(2) Å, V = 1842.4(2) Å^3, Z = 4, $R(F)$ = 0.027). The complexes have been characterized by ^1H and ^{13}C NMR and electrochemical studies. The physicochemical properties of 1,1′-bis(propylthio)ferrocene are discussed by a molecular approach at the extended Hückel level.

cyclopentadienyl / sulfur / ferrocene / zirconium / titanium / hafnium

Résumé — Propylthiocyclopentadiène : nouvelle voie d'accès à des complexes du fer et des métaux de transition du groupe 4. Structure moléculaire de $(C_5H_4SCH_2CH_2CH_3)_2ZrCl_2$. *À partir du sel de sodium du cyclopentadiène substitué par un groupe propylthio, nous avons préparé le 1,1′-bis(propylthio)ferrocène et les dichlorobis(propylthiocyclopentadiényl)-zirconium, titane, hafnium IV. La structure de $(C_5H_4SCH_2CH_2CH_3)_2ZrCl_2$ a été établie par une analyse aux rayons X (orthorhombique,* Pbcn, a *= 11,943(1) Å,* b *= 6,883(2) Å,* c *= 22,412(2) Å,* V *= 1842,4(2) Å^3,* Z *= 4,* R(F) *= 0,027). Les complexes ont été caractérisés par une analyse en RMN ^1H et ^{13}C et par des études électrochimiques. Les propriétés physicochimiques du 1,1′-bis(propylthio)ferrocène sont discutées par une approche théorique en Hückel étendue.*

cyclopentadiényle / soufre / ferrocène / zirconium / titane / hafnium

Introduction

Alkyl or arylthiocyclopentadienes and their lithium or thallium salts are not common and their use in the construction of organometallic complexes is quite limited. It has been shown that the action of sulfenyl chlorides on thallium cyclopentadienide leads to the unstable alkyl or arylthio-cyclopentadienes [1], which upon the deprotonation with thallium ethanolate give the corresponding thallium salts $(C_5H_4SR)Tl$. The use of these salts for subsequent substitutions on C5 ring with alkylating reagents R′X gives the *S*-alkylated cyclopentadienes (C_5H_4SRR') instead of the expected *C*-substituted ones $(C_5H_{4-n}R'_nSR)$. This is probably the major limitation of application of the thallium salts in the synthesis of polysubstituted cyclopentadienyl rings intended for building of transition metal complexes. Recently, Rufanov and coworkers [2], described the reactivity of alkyllithium salt with dicyclopentadienyl sulfide. They found that both nucleophilic attack upon the sulfur atom and a deprotonation process occur. Thus the specific availability of lithium salts and their use also appears rather limited.

Complexes containing cyclopentadienyl ligands substituted with functional groups are an interesting class of compounds [3, 4]. An abundant number of substituted ferrocenes and bent metallocenes are now available, but standard protocols used for preparation of iron or early transition metal derivatives are not the same. In general, an electrophilic substitution of group R for H may be used for the synthesis of substituted ferrocenes, while the substituted bent cyclopentadienyls of group 4 transition metals (Ti, Zr and Hf) have so far been obtained only when the appropriate cyclopentadienyl salts are already avalaible. Thus, a large number of ferrocenes containing heteroelements (like the chalcogens) have been described [3], while no report treats similar ring substitutions in bent metallocene chemistry [5].

In this paper we describe the formation and properties of the first alkylthiocyclopentadienyl derivatives of the transition metals, together with the crystal structure of the dichloride of di(propylthiocyclopentadienyl)-zirconium.

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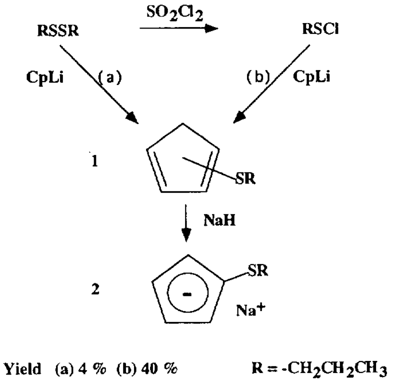
* Correspondence and reprints

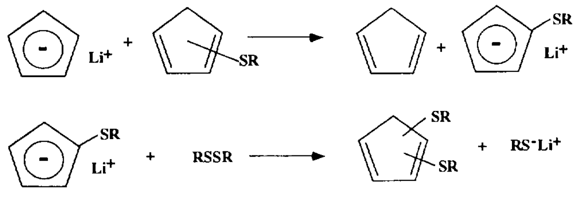
Results and discussion

In the light of chemistry of thiolato-substituted cyclopentadienides presented above, we attempted the synthesis of the sodium thiolatocyclopentadienide starting from dipropyl disulfide. The expected chemistry is shown in scheme 1.



Scheme 1

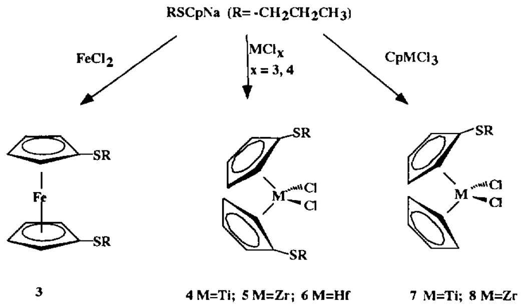
Strategy (a) (scheme 1) consists of the reaction of an appropriate commercial disulfide with cyclopentadienyllithium. The resulting propylthiocyclopentadiene **1** is further deprotonated by sodium hydride giving the sodium salt $(CH_3CH_2CH_2SC_5H_4)Na$ **2**. We have observed that during the preparation of **1** in this way some byproducts, mainly cyclopentadiene and polyalkylthiocyclopentadienes (scheme 2), are formed. Consequently, purification of the crude product **1** is difficult and the final yield is very low (4%). Attempts to synthesize other alkylthiocyclopentadienylsodium salts (R = CH_3, *t*-Bu, $PhCH_2$) in this way failed.



Scheme 2

Strategy (b) (scheme 1) consists of the preparation of an alkanesulfenyl chloride as intermediate by addition of sulfuryl chloride to a solution of disulfide in dichloromethane cooled to −50 °C. The less volatile material is then isolated and immediately treated with C_5H_5Li, yielding **1** with no byproducts. Based on ^1H NMR studies we observe that **1** is a 1:1 mixture of two isomers identified as 1-(propylthio)cyclopenta-1,3-diene and 1-(propylthio)cyclopenta-1,4-diene. No changes in the ^1H NMR spectra are observed over a period of at least 1 week. Further reduction of **1** leads to $CH_3CH_2CH_2SC_5H_4Na$ **2** in 40% overall yield.

The coordinating ability of the $(CH_3CH_2CH_2SC_5H_4)^-$ ligand was checked through its reaction with transition metal chlorides (scheme 3) .



Scheme 3

The reaction of two equivalents of **2** with iron(II) chloride in tetrahydrofuran (0 °C) results in the formation of 1,1′-di(propylthio)ferrocene $(C_5H_4SCH_2CH_2CH_3)_2Fe$ **3** as a red oily product. This ferrocenyl compound, which is formally a derivative of the ferrocene-1,1′-dithiol, may also be obtained by the alternative thiolate route ($(C_5H_4SLi)_2Fe$ + $CH_3CH_2CH_2Cl$).

Likewise, the sodium reagent **2** is a convenient precursor for substituted dicyclopentadienyl complexes of group 4 transition metals which are not available through an electrophilic substitution on the parent compounds Cp_2MCl_2. Treatment of MCl_x ($x = 4$: M = Zr, Hf; $x = 3$: M = Ti) with two equivalents of **2**, followed by the usual work-up procedure, such as addition of carbon tetrachloride to oxidize Ti(III) species, leads to a new family of substituted bent metallocenes with sulfide functional group $(C_5H_4SCH_2CH_2CH_3)_2MCl_2$ (**4** M = Ti, **5** M = Zr, **6** M = Hf, scheme 3).

Reaction of the sodium salt with $CpMCl_3$ (M = Ti, Zr) at 0 °C in THF affords the expected mixed metallocene dichlorides **7** and **8**.

All the complexes **4**–**8** were isolated as air stable solids, light yellow for M = Zr, Hf and green for M = Ti. The zirconium complexes may be purified by sublimation, those of titanium by column chromatography, while the crystallization is a sole methode to reach a pure hafnium complex **6**.

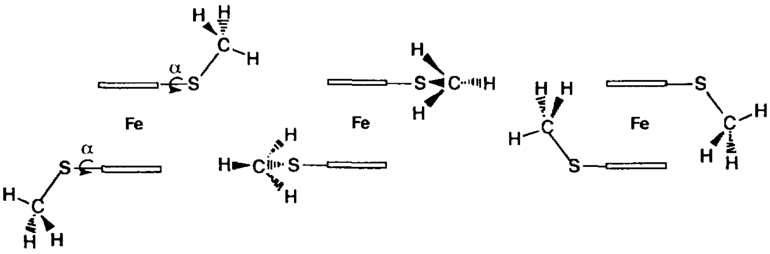
Room temperature ^1H NMR spectra of complexes **3**–**8** exhibit two CH resonances corresponding to the cyclopentadienyl protons. The morphology is that of A_2B_2 system with $\Delta v/J$ decreasing in the sequence **3** > **5**, **6**, **8** > **4**, **7**. The ^1H resonances of propyl substituent vary little from one complex to another (see *Experimental section*).

The electronic properties of substituted ferrocenes may be evaluated from electrochemical and from ^{13}C NMR [6] data. Previous statements concerning the effect of the methylthio group on the iron center in substituted ferrocenes on the basis of electrochemical studies seem contradictory. This effect has been described as either electron withdrawing [7] or electron-donating [8]. In order to estimate correctly the shifts of $E_{1/2}$ potentials we recorded the cyclic voltammograms for $(C_5H_5)_2Fe$ and **3** in different solvents. These voltammo-

Table I. Electrochemical and ^{13}C NMR data ($R = CH_2CH_2CH_3$).

	$E_{1/2} = (E_{pa} + E_{pc})/2$, *(V/ESC)*	^{13}C *NMR* $\{^1H\}$ *Cp ring (ppm)*			
Cp_2Fe	0.52^a; 0.44^b; 0.39^c	68.6			
$(RSCp)_2Fe$	0.51^a; 0.44^b; 0.37^c	71.3	75.4	81.9	
Cp_2TiCl_2	-0.73^a	120.9			
$(RSCp)_2TiCl_2$	-0.71^a	119.5	120.7	133.9	122.9^d
Cp_2ZrCl_2	-1.61^a	116.7			
$(RSCp)_2ZrCl_2$	-1.52^a	116.5	118.5	125.5	119.1^d
Cp_2HfCl_2	-1.94^a	115.2			
$(RSCp)_2HfCl_2$	-1.84^a	114.9	118.0	122.7	117.7^d

[a] THF; [b] CH_2Cl_2; [c] CH_3CN; [d] $\delta^{13}C$, average of five Cp carbon atoms.



α = 0° out-of-plane *exo*

α = 90° in-plane

α = 180° out-of-plane *endo*

Scheme 4

grams agree with the expected reversible one-electron oxidation. The oxidation potential is slightly lower for **3** than for $(C_5H_5)_2Fe$ (table I) suggesting that the propylthio group behaves as a weak electron donor towards the iron atom (assuming that the oxidation process involves principally the metallic center).

On the other hand, the ^{13}C NMR data (table I) show a deshielding of the ring carbon atoms in **3** with respect to the values observed for ferrocene. Thus, the propylthio group withdraws the electron density from the ring and consequently from the metal. It is worth noting that the ring protons are also deshielded in the substituted ferrocene **3**.

The electron-attracting or electron-donating effects in $(C_5H_4ZMe)_2Fe$ (Z = O, S) have already been discussed qualitatively by Sato et al [6]. The electron-withdrawing property was assigned to the activation of the sulfur symmetry-adapted *d* atomic orbital, while the donor properties involve its *p* atomic orbital interacting through space with an iron atomic orbital. Even if such a qualitative description seems plausible, we decided to check its validity by carrying out the calculations on a model (methyl instead of propylthiolate) at the extended Hückel level [9]. A staggered conformation of Cp rings was chosen because the ferrocene itself (D_{5d}) and its symmetrically substituted derivatives (C_i) exhibit this ring conformation in the solid state [10]. On the other hand, different conformations of substituent on Cp ring may be expected in solution (conditions for electrochemical and ^{13}C NMR measurements). Some of these are depicted in scheme 4 as the out-of-plane *exo* ($\alpha = 0°$), the in-plane ($\alpha = 90°$) and the out-of-plane *endo* ($\alpha = 180°$, with the carbon atoms of the thiolate alkyl groups placed between the C_5H_4 rings). The C_i point molecular symmetry has been accepted for all possible conformations.

In order to estimate the influence of substituent conformation on the total molecular energy, and on that of some valence molecular orbitals, we varied the α parameter from 0° (*exo* structure) to 180° (*endo* structure). The results are given in figure 1. One states that the total energy curve is rather flat from $\alpha = 0°$ to about $\alpha = 70°$, shows a weak minimum near 90–100°

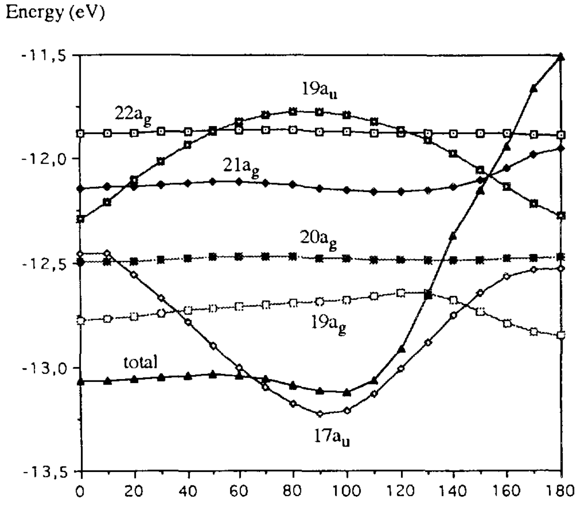


Fig 1. Evolution of the total molecular energy and of the energies of highest molecular orbitals as a function of α (see scheme 4) for $(C_5H_4SMe)_2Fe$.

Table II. Atomic charges calculated for $(C_5H_4SMe)_2Fe$ at $\alpha = 90°$.

Atom	*Without* d*(S) AOs* *standard EH [9a]*	*With* d*(S) AOs* *Standard EH [9a]*	 *With charge iteration [9b]*
Fe	+0.009	+0.150	+0.136
Cα	+0.132	+0.158	+0.151
Cβ	−0.086	+0.004	+0.006
Cβ	−0.085	−0.013	−0.014
Cγ	−0.049	−0.030	−0.029
Cγ	−0.050	−0.031	−0.029
S	−0.063	−0.516	−0.497
C(Me)	+0.030	−0.017	+0.015

Reference (staggered $(C_5H_5)_2Fe$): +0.085 (Fe) and −0.041 (C).

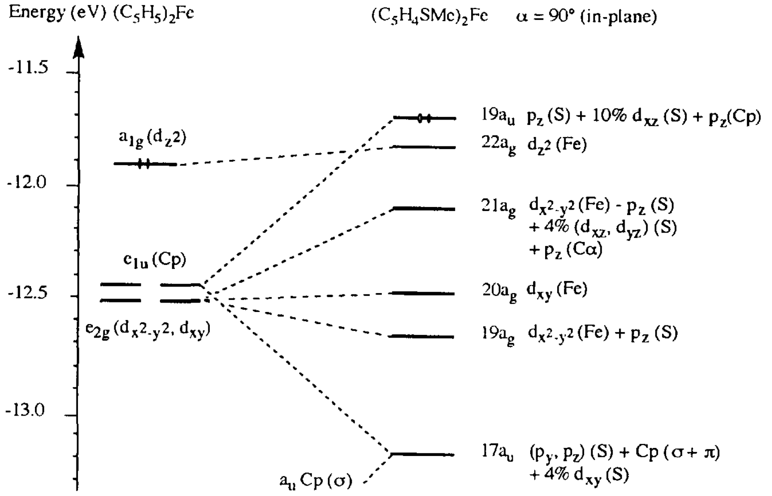


Fig 2. Energy correlation between $(C_5H_5)_2Fe$ and $(C_5H_4SMe)_2Fe$ for $\alpha = 90°$ (see scheme 4).

and increases on going from 100° to 180°, thus rendering the *endo* structure less stable.

The energies of two molecular orbitals of a_u symmetry are strongly dependent on the conformation. That of $19a_u$ increases from $\alpha = 0°$ to 90° and this increase is apparently compensated by a decrease in the energy of $17a_u$. The energies of other molecular orbitals, in particular those of four valence symmetrical (a_g) orbitals in a model of **3** are little affected by the out-of-plane or in-plane conformations.

Figure 2 shows the relative energies of the analogous molecular orbitals for the SMe-substituted and the parent ferrocene molecules [11]. The in-plane ($\alpha = 90°$) conformation of SMe group is represented in this figure, because it corresponds to the geometry observed for $C_5H_4SCH_2CH_2CH_3$ ligand in the structure of **5** (see below) and agrees well with the conformational diagram of figure 1. The $19a_u$ orbital (the HOMO in this conformation) is strongly destabilized by antibonding $p\pi(S) - p\pi(C)$ interaction. This orbital (fig 3) contains some contribution from the d_{xz} atomic orbital of sulfur atoms which are also responsible for the electron density fluctuation from the Cp rings to the sulfur atoms via a $d\pi(S) - p\pi(C)$ interaction. Such a description of bonding corresponds well to the calculated atomic charges given in table II. The reported values indicate the influence of the sulfur *d* atomic orbitals. When their contribution is neglected, only the C_α atoms of the Cp rings bear a significantly lower electron density with respect to the unsubstituted ferrocene, while the C_β and C_γ atoms seem to increase it. In the presence of the *d* atomic orbitals of sulfur all carbon atoms of the Cp rings are less negative than in the ferrocene, leading to a good correlation between charge on the C atom and ^{13}C NMR chemical shift.

The a_{1g} molecular orbital of ferrocene, mostly built of the d_{z^2} atomic orbital of iron, is little affected by the substitution, while the degenerated e_{2g} ferrocene level ($d_{x^2-y^2}$, d_{xy}) leads under substitution of SMe group for H to three well-defined high energy molecular orbitals $21a_g - 19a_g$. The $21a_g$ molecular orbital is destabilized by an antibonding $p_z(S) - [p_z(C); d_{x^2-y^2}(Fe)]$ interaction (fig 3), while the $19a_g$ contains a stabilizing $p_z(S) - d_{x^2-y^2}(Fe)$ effect. The overall electronic interaction thus consists of a slight increase in energy of the orbitals derived from d_{z^2} and $d_{x^2-y^2}$ iron orbitals. In the light of the above discussion of electronic properties of substituted ferrocene, and because the electrochemical data show only a very small decrease of $E_{1/2}$ oxidation potentials for **3** with respect to the ferrocene molecule, we believe that this oxidation process involves principally the d_{z^2} ($22a_g$) orbital of iron (slight destabilization, fig 1) and that the effects consisting of $p_z(S) - d_{x^2-y^2}(Fe)$ interactions are not important, contrasting with the interpretation of Sato et al [6].