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η^5-Complexes of cyclopentadienylsilylethers ($C_5H_4OSiR_3$) and hydroxycyclopentadiene (C_5H_4OH) with titanium and zirconium chlorides

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Abstract

The reactions of the lithiated trialkylsiloxy-cyclopentadienyl ethers ($C_5H_4OSiR_3$; $R_3 = Et_3$, $Me_2{}^tBu$, $^iPr_3$) with $TiCl_4$, $ZrCl_4$, Cp^*ZrCl_3 or $CpTiCl_3$ result in the formation of the respective metallocene dichlorides [$(C_5H_4OSiR_3)_2TiCl_2$, $(C_5H_4OSiR_3)_2ZrCl_2$, $(C_5H_4OSiR_3)(C_5H_5)TiCl_2$, $(C_5H_4OSiR_3)(C_5Me_5)ZrCl_2$)] in moderate to good yields. The reaction of $Li(C_5H_4OSiEt_3)$ with Cp^*TiCl_3 in toluene produced, in addition to the expected complex $(C_5H_4OSiEt_3)(C_5Me_5)TiCl_2$, the hydroxytitanocene dichloride $(C_5H_4OH)(C_5Me_5)TiCl_2$ in a yield of 21%. The half-sandwich complex $C_5H_4(OSiMe_2{}^tBu)TiCl_3$ was formed with $C_5H_4(OSiMe_2{}^tBu)(SiMe_3)$ and $TiCl_4$. © 1997 Elsevier Science S.A.

Keywords: Cyclopentadienylsilylether; Hydroxycyclopentadiene; Titanium chloride; Zirconium chloride

1. Introduction

Cyclopentadienyls continue to be among the most important ligands in organometallic chemistry because they form a wide range of stable metal complexes whose steric and electronic properties can be easily tailored by varying the substituents at the five-membered ring [1,2]. Consequently a steady stream of cyclopentadienes with novel side groups keeps emerging from the chemistry literature [3–10]. In most cases the synthesis of substituted cyclopentadienes follows a general scheme in which a nucleophilic reagent (typically lithium or sodium cyclopentadienide) is reacted with an electrophile (e.g. alkyl halide). This allows the synthesis of a wide variety of carbon-functionalized cyclopentadienes. However, this approach is not very successful for the synthesis of cyclopentadienes or metallocenes with more electronegative substituents like oxygen or nitrogen, since the required electrophilic synthons R_2N^+ or RO^+ are not very convenient [11–13,40]. This as well as the diminished oxidative stability of the resulting metal complexes may be the reason for the relative scarcity of amino- and hydroxy-substituted metallocenes or half-sandwich complexes [14].

However, instead of using nucleophilic cyclopentadienyl reagents for the synthesis of substituted cyclopentadienes we [15–17] and others [18] have been quite successful with an electronically inverse route using cyclopentenones as electrophilic reagents. Consequently we were able to demonstrate the utility of the enamine reaction of 3,4-diphenylcyclopentenone with sec. amines for the facile synthesis of numerous aminocyclopentadienes and aminoferrocenes [19,20,39], -cobaltocenes [21], -cymantrenes [22] and -zirconocene dichlorides [23].

More recently we have also described a very simple synthesis of siloxy-substituted ferrocenes [24,25] and cymantrenes [26], again by using cyclopentenones as starting materials, which were treated with trialkylsilyltriflates in the presence of base, resulting in the formation of the corresponding silyl-enolethers (= cyclopentadienyl-silylethers) in almost quantitative yields (Scheme 1) [27].

Deprotonation with strong bases and reaction with metals salts provides access to various metal complexes, which is quite significant since examples of oxygen substituted metallocenes and half-sandwich complexes are still rare [28–31] and a systematic access to this compounds had not been described up to our work.

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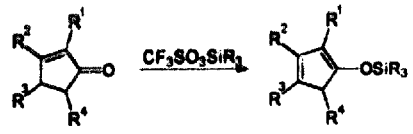


Scheme 1.

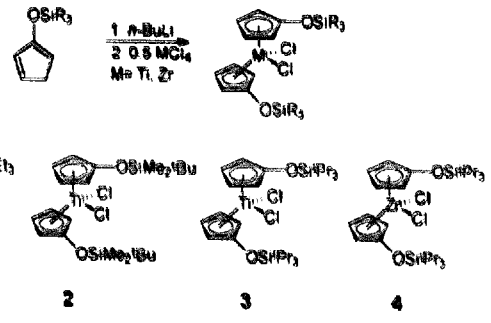
Here we wish to report on the use of lithiated cyclopentadienyl-silylethers for the synthesis of previously unknown metallocene dichlorides of the early transition metals titanium and zirconium.

2. Results and Discussion

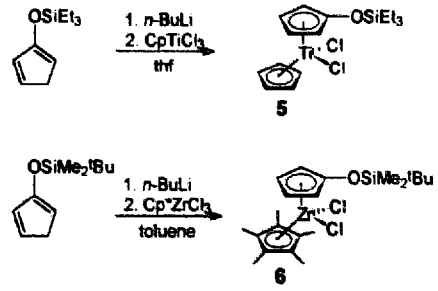
For the synthesis of 1,1'-bis(trialkylsiloxy)-substituted metallocene dichlorides, the respective trialkylsiloxy-cyclopentadienes were deprotonated at low temperatures with *n*-BuLi and then reacted with $TiCl_4*2$ THF or $ZrCl_4$. The titanocene dichlorides **1**, **2** and **3** were obtained in poor to moderate yields (15–40%), the corresponding zirconium complex **4** in a good yield of 52% (Scheme 2).

In contrast to **2**, **3** and **4**, the triethylsiloxy-substituted complex **1** is air- and moisture sensitive, reflecting the lower stability of the $-SiEt_3$ protective group. The reaction of lithiated trialkylsiloxycyclopentadienes with $CpTiCl_3$ and Cp^*ZrCl_3 results in the formation of the respective metal complexes **5** and **6** (Scheme 3) and again the $-SiEt_3$-protected complex **5** was only formed in low yield (13%), whereas $-SiMe_2{}^tBu$ protected **6** was obtained in 71% yield.

Since the $-SiEt_3$-protected ether can be cleaved much more easily than the $-SiMe_2{}^tBu$-ethers, we were interested in synthesizing other triethylsiloxy-cyclopentadienyl-titanocene dichlorides, hoping that the stabilizing effect of the pentamethylcyclopentadienyl group Cp^* would be useful. Consequently Cp^*TiCl_3 was reacted with $Li(C_5H_4OSiEt_3)$, which led to the unexpected formation of two products (Scheme 4). In THF solvent — besides the expected product **7** (yield 14%) — some $(C_5H_4OH)Cp^*TiCl_2$ **8** was isolated in 10% yield. Flash chromatographic purification of the reaction mixture gave **7** as a red solid and **8** as a violet microcrystalline



Scheme 2.



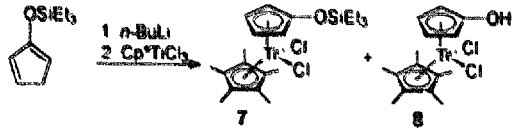
Scheme 3.

powder. Since the yields of this reaction were rather poor, we anticipated that changing the solvent would lead to better yields of one or both products. After testing several solvents of different polarity the best results were obtained in toluene producing **7** in a 20% yield and the hydroxide **8** in 23%.

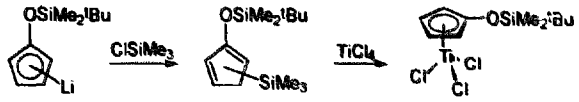
All attempts to produce single crystals of the latter complex were, however, unsuccesful since the hydroxide **8** is not very stable in solution. This is not too surprising because this complex has two functional groups of opposing reactivity (nucleophilic OH and an electrophilic metal center). This instability may explain why we were not succesful in cleaving the $SiEt_3$-protected ether in **7** to produce the hydroxide **8** under controlled conditions. It remains unclear what leads to the predominant formation of the hydroxide **8** in toluene. The isolation of the hydroxide **8** may also help to explain why the related reaction of $CpTiCl_3$ only gave such small yields of **5** (Scheme 3), since there the formation of a very unstable, violet by-product was also observed (presumably $(C_5H_4OH)CpTiCl_2$).

We were immediately intrigued by the idea of reacting the hydroxyl group with acids, organic or inorganic halides or to attach the hydroxy metallocene to an oxidic surface to synthesize new types of supported catalysts. However, up until now our efforts were frustrated, since reactions of **8** with for example CH_3COCl, $SiCl_4$ or $TiCl_4$ did not result in tractable products.

Recently, Rausch et al. had attempted the synthesis of a methoxy-substituted (indenyl)$TiCl_3$ complex [32]. We were therefore interested if it was possible to obtain related complexes like $(C_5H_4OSiR_3)TiCl_3$, since in the presence of MAO this type of compounds can be used to effect the stereo specific polymerisation of styrene [33,34]. $CpTiCl_3$ half-sandwich complexes are available in high yields in the reaction of $CpSiMe_3$ with $TiCl_4$ [35] and it was possible to generate the related compound **10** in the same manner (Scheme 5).



Scheme 4.



Scheme 5.

In conclusion it can be stated that the reactions of lithiated or silylated trialkylsiloxycyclopentadienyl ethers with titanium and zirconium chlorides provide facile access to previously unknown η^5-complexes of cyclopentadienylsilylethers ($C_5H_4OSiR_3$) and hydroxy-cyclopentadiene (C_5H_4OH) with these metals, while it remains to be seen whether functionalisation reactions of the hydroxyl group can be succesful.

3. Experimental section

All reactions were performed under dry nitrogen using standard Schlenk techniques. Commercially available solvents and reagents were purified according to literature procedures. NMR spectra were recorded at 300 K with a Bruker AC200 F (^{1}H-NMR 200 MHz, ^{13}C-NMR 50 MHz). ^{1}H-NMR was referenced to residual hydrogen in the deuterated solvents and ^{13}C-NMR to the signals of $CDCl_3$ (7.26, 77.0 ppm). IR-spectra: Bruker IFS 25. Elemental analyses were performed at the Mikroanalytisches Laboratorium der Chemischen Laboratorien, Universität Freiburg. Starting materials were commercially available or synthesized according to literature procedures: Trialkylsiloxy-cyclopentadienes [24–26], $CpTiCl_3$ [36], Cp^*TiCl_3 [37], Cp^*ZrCl_3 [38].

3.1. Bis-η^5-(triethylsiloxy-cyclopentadienyl)titanium-dichloride (1)

A solution of triethylsiloxy-cyclopentadiene (653 mg, 3.32 mmol) in THF (40 ml) was cooled to 0°C and treated with *n*-BuLi (1.45 ml, 3.65 mmol, 2.5 M in hexane). After stirring for 1h the reaction mixture was cooled to −40°C and $TiCl_4$ * 2 THF (555 mg, 1.66 mmol) added, whereupon a color change to red was observed. The solution was slowly allowed to room temperature and the volatiles were removed in vacuo. The residue was extracted with toluene, the extract filtered, the solvent removed in vacuo and the residue recrystallized from petroleum ether 30/50 three times, whereupon a red, moisture sensitive solid was obtained. Yield: 234 mg (14%), mp. 64°C. ^{1}H NMR (C_6D_6): δ 0.74 (q, J = 7.4 Hz, 12H, CH_2), 0.99 (t, J = 7.4 Hz, 18H, CH_3), 5.44 (t, J = 2.8 Hz, 4H, CpH), 6.13 (t, J = 2.8 Hz, 4H, CpH). ^{13}C NMR (C_6D_6): δ 5.48, 6.84, 104.14, 116.62, 157.06.

3.2. Bis-η^5-(tert.-butyldimethylsiloxy-cyclopentadienyl)titanium-dichloride (2)

Same procedure as for (1): *tert.*-butyldimethylsiloxy-cyclopentadiene (1.52 g, 7.73 mmol), THF (50 ml), *n*-BuLi (3.4 ml, 8.5 mmol, 2.5 M in hexane), $TiCl_4$ * 2THF (1.29 g, 3.86 mmol). Yield: 0.42 g (21%) orange-colored, airstable powder, mp. 149°C. ^{1}H NMR ($CDCl_3$): δ 0.28 (s, 12H, $Si(CH_3)_2$), 0.98 (s, 18H, C_4H_9), 5.52 (t, J = 2.8 Hz, 4H, CpH), 6.32 (t, J = 2.8 Hz, 4H, CpH). ^{13}C NMR ($CDCl_3$): δ −4.05, 18.37, 25.62, 104.02, 117.84, 157.30. Analysis calc. for $C_{22}H_{38}Cl_2O_2Si_2Ti$ (509.50) C 51.86, H 7.52, found: C 51.31, H 7.35.

3.3. Bis-η^5-(triisopropylsiloxy-cyclopentadienyl)titanium-dichloride (3)

Same procedure as for (1): triisopropylsiloxy-cyclopentadiene (815 mg, 3.42 mmol), THF (40 ml), *n*-BuLi (1.5 ml, 3.76 mmol, 2.5 M in hexane), $TiCl_4$ * 2THF (571 mg, 1.71 mmol). Recrystallization from pentane gave a red, airstable solid. Yield: 398 mg (40%), mp. 109°C. ^{1}H NMR ($CDCl_3$): δ 1.10 (d, J = 6.6 Hz, 36H, CH_3), 1.16–1.32 (m, 6H, CH), 5.57 (t, J = 2.7 Hz, 4H, CpH), 6.38 (t, J = 2.7 Hz, 4H, CpH). ^{13}C NMR ($CDCl_3$): δ 12.39, 17.68, 104.86, 118.67, 157.15.

3.4. Bis-η^5-(triisopropylsiloxy-cyclopentadienyl)zirconium-dichloride (4)

A solution of triisopropylsiloxy-cyclopentadiene (839 mg, 3.52 mmol) in toluene (40 ml) was treated with *n*-BuLi (1.53 ml, 3.87 mmol, 2.5 M in hexane). After stirring for 1h $ZrCl_4$ (410 mg, 1.76 mmol) was added and the reaction mixture heated under reflux for 3d. Afterwards the hot solution was filtered, the volatiles were removed in vacuo and the residue recrystallized from petroleum ether 60/70. Yield: 583 mg (52%) pale-yellow crystals, mp. 70°C. ^{1}H NMR ($CDCl_3$): δ 1.05–1.29 (m, 42H, $CH(CH_3)_2$), 5.54 (t, J = 2.9 Hz, 4H, CpH), 6.14 (t, J = 2.9 Hz, 4H, CpH). ^{13}C NMR($CDCl_3$): δ 12.33, 17.69, 101.35, 112.89, 153.55.

3.5. η^5-(Triethylsiloxy-cyclopentadienyl)-η^5-cyclopentadienyl-titanium-dichloride (5)

A solution of lithium-(triethylsiloxy-cyclopentadienide) (323 mg, 1.60 mmol) in THF (40 ml), prepared from the cyclopentadiene and BuLi, was cooled to −40°C and $CpTiCl_3$ (350 mg, 1.60 mmol) added. The reaction mixture was slowly warmed to room temperature and stirring continued for another 3 h. Finally the volatiles were removed in vacuo and the remaining solid extracted with toluene. The red solution was filtered, the toluene removed in vacuo and the residue

recrystallized from petroleum ether 60/70. Yield: red crystals 80 mg (13%), mp. 93°C. ^{1}H NMR ($CDCl_3$): δ 0.72–0.88 (m, 6H, CH_2), 0.99–1.08 (m, 9H, CH_3), 5.52 (t, J = 2.8 Hz, 2H, CpH), 6.48 (t, J = 2.8 Hz, 2H, CpH), 6.53 (s, 4H, CpH). ^{13}C NMR ($CDCl_3$): δ 5.01, 6.53, 103.42, 119.71, 120.91, 156.40.

3.6. η^5-(tert.-Butyldimethylsiloxy-cyclopentadienyl)-η^5-(pentamethylcyclopentadienyl)-zirconium-dichloride (6)

A solution of *tert.*-butyldimethylsiloxy-cyclopentadiene (0.95 g, 4.84 mmol) in toluene (50 ml) was treated with *n*-BuLi (2.13 ml, 5.3 mmol, 2.5 M in hexane). After stirring for 1h Cp^*ZrCl_3 (1.58 g, 4.84 mmol) was added and the reaction mixture heated under reflux for 3d. The hot solution was filtered and reduced to approx. 1/3 in volume. Upon slowly cooling the solution to −30°C the product precipitated as pale yellow crystals, which were filtered off and dried in vacuo. Yield: 1.71 g (71%), mp. 112°C. ^{1}H NMR ($CDCl_3$): δ 0.23 (s, 6H, CH_3), 0.94 (s, 9H, C_4H_9), 2.03 (s, 15H, $C_5(CH_3)_5$), 5.46 (t, J = 2.9 Hz, 4H, CpH), 5.72 (t, J = 2.9 Hz, 4H, CpH). ^{13}C NMR ($CDCl_3$): δ −4.10, 12.29, 18.30, 25.65, 102.26, 109.19, 123.84, 153.89.

3.7. η^5-(Triethylsiloxy-cyclopentadienyl)-η^5-(pentamethylcyclopentadienyl)titanium-dichloride (7) and η^5-(Hydroxy-cyclopentadienyl)-η^5-(pentamethylcyclopentadienyl)-titanium-dichloride (8)

A solution of triethylsiloxycyclopentadiene (626 mg, 3.19 mmol) in toluene (50 ml) was treated with *n*-BuLi (1.40 ml, 3.51 mmol, 2.5 M in hexane) and after 1h Cp^*TiCl_3 (923 mg, 3.19 mmol) added. After 3h the volatiles were removed in vacuo and the remaining solid purified by flash chromatography on silica with cyclohexane/ethyl acetate = 20:1 to elute (7) and finally cyclohexane/ethyl acetate 2:1 to elute (8). The volatiles were evaporated from each of the two separate solutions and the remaining solids dried in vacuo. (7) Yield: 284 mg (20%) red solid, mp. 88°C. ^{1}H NMR ($CDCl_3$): δ 0.72–0.83 (m, 6H, CH_2), 0.94–1.04 (m, 9H, CH_3), 2.04 (s, 15H, $C_5(CH_3)_5$), 5.42 (t, J = 2.8 Hz, 2H, CpH), 5.74 (t, J = 2.8 Hz, 2H, CpH). ^{13}C NMR ($CDCl_3$): δ 5.28, 6.63, 13.31, 106.45, 113.16, 128.76, 158.05. (8) Yield: 250 mg (23%) violet powder, mp. 150°C (dec.). ^{1}H NMR ($CDCl_3$): δ 2.06 (s, 15H, $C_5(CH_3)_5$), 5.56 (t, J = 2.8 Hz, 2H, CpH), 5.67 (br, 1H, OH), 5.87 (t, J = 2.8 Hz, 2H, CpH). ^{13}C NMR ($CDCl_3$): δ 13.38, 108.67, 114.71, 129.64, 154.50. IR (KBr): ν 1262 (s, C–O), 3317 (br, O–H) cm^{-1}. Analysis calcd. for $C_{15}H_{20}Cl_2OTi$ (335.11) C 53.76, H 6.02, found: C 53.96, H 6.07.

3.8. η^5-(tert.-Butyldimethylsiloxy-cyclopentadienyl)-titanium-trichloride (10)

To a solution of lithium *tert.*-butyldimethylsiloxy-cyclopentadienide (1.89 g, 7.93 mmol) in THF (20 ml) at 0°C was slowly added $ClSiMe_3$ (1.01 ml, 7.93 mmol) in THF (10 ml). After 2h the volatiles were evaporated in vacuo, the residue dissolved in petroleum ether 30/50 and the LiCl precipitate filtered off. The solvent was stripped from the filtrate to yield 1.38 g (65%) *tert.*-butyldimethylsiloxy-cyclopentadienyl-trimethylsilane (9) which was used without further purification. A solution of (9) (1.30 g, 4.84 mmol) in toluene (20 ml) was slowly added to a solution of $TiCl_4$ in toluene (50 ml) and stirring continued for another 2h. After removal of the volatiles in vacuo, the residue was recrystallized twice from petroleum ether 30/50. Yield: 0.18 g (11%), red crystals, mp. 69°C. ^{1}H NMR ($CDCl_3$): δ 0.34 (s, 6H, $Si(CH_3)_2$), 0.99 (s, 9H, C_4H_9), 6.27 (t, J = 2.9 Hz, 2H, CpH), 6.71 (t, J = 2.9 Hz, 2H, CpH). ^{13}C NMR ($CDCl_3$): δ −4.16, 18.26, 25.42, 110.83, 118.76, 159.52. Analysis calcd. for $C_{11}H_{19}Cl_3OSiTi$ (349.4) C 37.79, H 5.48; found: C 37.80, H 5.49.

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