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Stereoselective Access to the Three Diisodicyclopentadienyltitanium Dichlorides[†]

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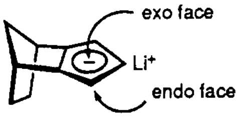
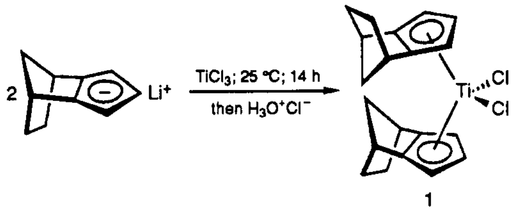
Summary: Two of the three possible diisodicyclopentadienyltitanium dichlorides were obtained with a high degree of selectivity by reacting titanium trichloride with the isodicyclopentadienide anion either at 25 °C (for exo,exo) or at −64 °C (for endo,endo). *exo*-isodicyclopentadienyltitanium trichloride, synthesized from lithium isodicyclopentadienide (isodiCpLi), trimethylsilyl chloride, and titanium tetrachloride, reacts at −78 °C with isodiCpLi to form the endo,exo isomer selectively. All three diastereoisomers have been unambiguously identified by ^{1}H NMR and mass spectroscopy.

As determined in our recent studies relating to the complexation of the isodicyclopentadienide anion to group 4 transition metals, *exo,exo*-diisodicyclopentadienyltitanium chloride (1) is selectively produced upon reaction of titanium trichloride with lithium isodicyclopentadienide at room temperature for 14 h[1] (eq 1).





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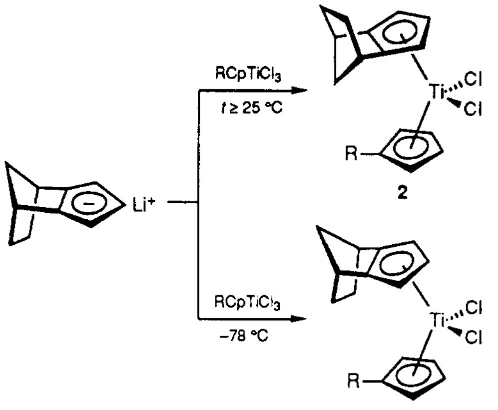
(1)

In related work, the pronounced influence of reaction temperature on stereoselectivity was also demonstrated during the formation of cyclopentadienyl–isodicyclopentadienyl complexes.[2,3] Whereas complexation on the exo face to give **2** is largely preferred at or above room temperature, endo isomer **3** is obtained nearly exclusively at −78 °C (eq 2). The same temperature effect has proven effective for controlling the stereoselectivity of complexation to a chiral cyclopentadienide anion.[4] This striking behavior is very likely related to the large temperature dependence of the monomer–dimer equilibrium of lithium isodicyclopentadienide in THF solution.[5]



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(2)

Subsequently, Farona and co-workers[6] reported on the complexation of group 4 transition metals to tricyclo[5.2.1.0^{2,6}]deca-2,5,8-trienyl and tricyclo[5.2.1.0^{2,6}]deca-2,5-dienyl (isodicyclopentadienyl)anions. Their product distributions determined by NMR analysis were notably different from ours. In the titanocene series of immediate interest, for example, we isolated the exo,exo isomer in 49% yield after recrystallization.[1] In contrast, Farona's group experiments led to a mixture of exo,exo (40.4%), exo,endo (58.6%), and endo,endo (1%) isomers (overall yield of 45%), which was not separated.

In the present paper, our previous results are confirmed and highly stereoselective syntheses of the endo,endo and endo,exo isomers are described.

Results and Discussion

A solution of lithium isodicyclopentadienide in THF was added to TiCl$_3$ at −78 °C, and the temperature was quickly increased to 25 °C. After 14 h of stirring and the customary work up, the 400-MHz ^{1}H NMR spectrum of the crude residue showed the presence of more than 98% of the exo,exo (**1**), somewhat less than 2% of the endo,exo (**6**), and only traces of the endo,endo isomer (**4**). This result is in contradiction to that reported by Farona;[6] the observed discrepancy could be the result of several differences in the synthetic processes that were used:[7] (1) Farona's results were obtained with concentrations 10–20 times greater than ours. (2) His solvent was a mixture of THF/hexane/benzene whereas ours is THF or THF/hexane. (3) We replaced TiCl$_4$ by TiCl$_3$·3THF, which led to a better stereoselectivity at low temperature.

Among these differences, the concentration seems to play a prominent role. It has been shown recently[5] that the equilibrium dimer ⇄ monomer observed for isodiCpLi at low temperature is greatly dependent on the concentration. The very high concentration used by Farona (near

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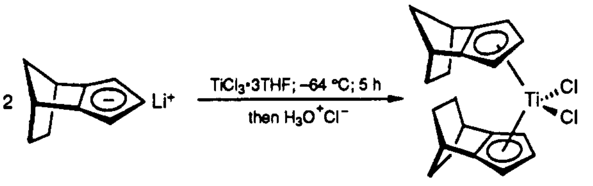
1 mol·dm^{-3}) probably results in a large dimer proportion and consequently causes the isomer's distribution to be oriented toward the endo,exo and endo,endo complexes.

When Farona's experiments were tentatively reproduced from isodiCpH (2.5 mmol) and $TiCl_4$ in strictly stoichiometric quantities to form the complex, we were forced to use double the volume of solvent recommended in the original paper to obtain a clear solution. After 20 min of stirring, the reaction mixture was seen to contain more than 95% of the exo,exo stereoisomer. Increasing the reaction time had no significant effect on the proportions observed.

All the isomers are configurationally stable, but an isomerization cannot be excluded in the presence of a slight excess of isodiCp anion and close attention must be payed to the stoichiometry. Some additional experiments in this area are presently being investigated.

Since an important temperature effect on stereoselectivity was suspected, the decision was made to undertake additional experiments involving isodicyclopentadienide anion–Ti(III) complexation. Thus, a mixture containing endo,endo (**4**, 91%), endo,exo (**6**, 9%), and exo,exo (**1**, traces) was produced when lithium isodicyclopentadienide (2 equiv) was reacted with $TiCl_3{\cdot}3THF$ (1 equiv) at −64 °C for 5 h. Recrystallizations from CH_2Cl_2/hexane afforded pure endo,endo stereoisomer **4** (eq 3). ^1H NMR (400 MHz, $CDCl_3$): δ 6.35 (d), 5.80 (t), 3.32 (s), 1.89 (d), 1.82 (m), 1.69 (d). MS: *m/e* 380 (M^+).

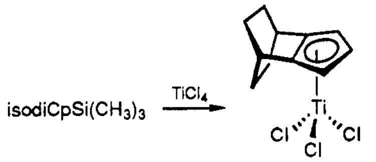


(3)

4

As we indicated for other complexes,[2,3] the endo,endo stereoisomer is kinetically favored at low temperature, probably as a consequence of the great amount of dimeric lithium isodicyclopentadienide present at this temperature.[5]

From our results, it can assumed that the endo,exo isomer is coproduced when the operating temperature ranges from ambient to −64 °C. However, all attempts to separate **6** from these reaction mixtures have systematically failed. Pure endo,exo isomer can, however, be obtained in a very different way[8] (eq 4).



(4)

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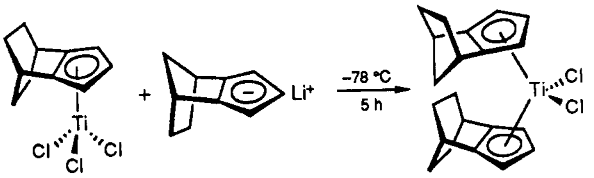
In the first step, *exo*-isodiCp$TiCl_3$ (**5**) was quantitatively prepared from reaction of isodiCpSi$(CH_3)_3$[9] with $TiCl_4$. ^1H NMR (400 MHz, C_6D_6): δ 6.47 (t), 5.64 (d), 3.03 (s), 2.00 (m), 1.17 (m), 0.51 (m). The features of the NMR spectrum of **5** as well as its reaction form the basis for the indicated exo complexation to the titanium atom. Interestingly, the endo isomer was not formed over an appreciable temperature range.

endo,exo-Diisodicyclopentadienyltitanium dichloride (**6**) was stereospecifically obtained by reaction of **5** with lithium isodicyclopentadienide at −78 °C (eq 5). ^1H NMR (400 MHz, $CDCl_3$): δ 6.32 (d), 6.20 (d), 6.13 (t), 5.90 (t), 3.35 (s), 3.31 (s), 1.93 (d), 1.86 (m), 1.76 (m), 1.33 (d), 1.19 (d), 1.09 (dd). MS: *m/e* 380 (M^+).



(5)

6

Of the three stereoisomeric dichlorides, only the exo,exo stereoisomer has been examined by X-ray diffraction.[1] The other structural assignments have been advanced on the basis of NMR chemical shift analysis.[2,3] Of course, the symmetry apparent in the spectrum of **4** precludes an endo,exo structure; in addition, the sequence observed in the chemical shifts of its cyclopentadienyl protons, where the peripheral proton doublet is more deshielded than the central proton triplet, is notably characteristic of endo complexation.[2,3]

The spectral characteristics of **6** clearly reveal the superpositioning of signals typical for both types of complexation (endo and exo). The appearance of two doublets and two triplets is consistent with distinctive pairs of cyclopentadienyl protons. The two singlets in evidence correspond to the two sets of bridgehead protons. The ethano bridge protons in the endo component appear in the range 1.8–1.9 ppm, while the corresponding protons in the exo component are split into signals near 1.8 and 1.2 ppm.

Following upon precedent, the ^1H NMR spectrum of **6** should logically exhibit an exo triplet that is more deshielded than the exo doublet. To the contrary, the two endo,exo doublets are more deshielded than the two endo,exo triplets. This characteristic feature can be attributed to simultaneous complexation to both stereoisomeric faces of the isodicyclopentadienyl ligand within the same molecule.

Conclusions

We have shown that stereospecific synthesis of the three possible diisodicyclopentadienyltitanium dichlorides is highly dependent upon experimental conditions. We are currently attempting to prepare single crystals in order to establish unambigously by X-ray methods the precise conformations of these complexes in the solid state. Extensions of these observations to other transition-metal systems as well as elucidation of the chemical reactivity of **1**, **4**, and **6** will be reported in due course.

Experimental Section

Reactions were carried out in an argon atmosphere by using Schlenk type glassware. Solvents were dried and freshly distilled from sodium/benzophenone under argon prior to use.

A typical experiment was conducted as follows: Isodicyclopentadienyllithium (THF solution) was added at the appropriate temperature to a suspension of $TiCl_3$ or $TiCl_3{\cdot}3THF$ in THF at the same temperature. At the end of the reaction, the mixture was treated with hydrochloric acid and extracted with chloroform. The combined organic layers were dried, and the solvent was evaporated. The solid residue was recrystallized from dichloromethane/hexane.

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