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Cobalt(I) and cobalt(III) cyclopentadienyl complexes with new silicon-branched fluorous tags

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ABSTRACT

Two new fluorous tags based on omega-[tris(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)silyl]alkyl substituents (alkyl = ethyl, propyl) were synthesized from 3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl iodide as the fluorine-containing component. Cyclopentadienes (the mixtures of 1- and 2-substituted isomers) which bore the tags were prepared, cyclopentadienyl cobalt(I) dicarbonyl complexes were subsequently obtained from the reactions of the cyclopentadienes with dicobalt octacarbonyl. Oxidative additions of 1-iodoperfluoroalkanes on the cobalt(I) complexes provided cobalt(III) complexes with one of their four ponytails bonded directly to the metal and with a stereocenter at the metal.

1. Introduction

Fluorous chemistry, first introduced in 1994 in a seminal paper by Rábai and Horváth [1], has developed into a useful instrument in organic and organometallic chemistry including catalysis [2]. Over time long linear per- or polyfluoroalkylated substituents have been partly replaced by more sophisticated fluorous tags [3], the attachment of which, either reversible or irreversible, have made organic compounds of interest or ligands in metal complexes compatible with fluorous phases. Reports of syntheses of such new tags continue to appear [4]. Examples of catalysis in fluorous biphase systems [5] and in supercritical carbon dioxide [6] have also been reported.

We have been particularly interested in fluorous cyclopentadienyl ligands for transition metal complexes [7] since reportedly [8] cyclopentadienyl ligands are found in about 80% of all organometallic complexes. Several types of cyclopentadienes and cyclopentadienyl metal complexes have been synthesized (see a brief review of literature up to 2005 [9]). However, in our opinion the intended target – synthesis of highly fluorophilic and easily accessible cyclopentadienyl ligand – has not yet been reached.

Here we report the synthesis of a new fluorous tag based on silicon as a branching atom which we believe can be used as a general tool for fluorophilization of molecules [10]. The new tag was attached to cyclopentadiene and cyclopentadienyl cobalt(I) dicarbonyl complexes were prepared. Oxidative addition of perfluoroalkyl iodides to the latter complexes provided cobalt(III) complexes with fluorous ponytails attached both to the ligand and to the metal directly.

2. Results and discussion

2.1. Fluorous tags and polyfluoroalkylated cyclopentadienes

Our previous results concerning the synthesis of synthons $HSi(CH_2CH_2R_f)_3$ (R_f = perfluoroalkyl) and $BrSi(CH_2CH_2R_f)_3$ opened the way to cyclopentadienes tri- and hexasubstituted with fluorous ponytails and their titanium(IV) complexes [7b]. Despite being highly fluorous, principal shortcomings of the latter cyclopentadienes are their moisture sensitivity and characterization hampered both by complex regioisomer composition and dynamic behaviour at room temperature.

In our renewed effort, a recent approach for insulation of Si–H group from the ring in a series of titanocene dichloride derivatives [11] inspired us to removing the above mentioned shortcomings by insertion of a carbon spacer between the cyclopentadiene ring and the silicon branching atom. The fluorous reagents containing a reactive group at the end of the spacer were expected to react with

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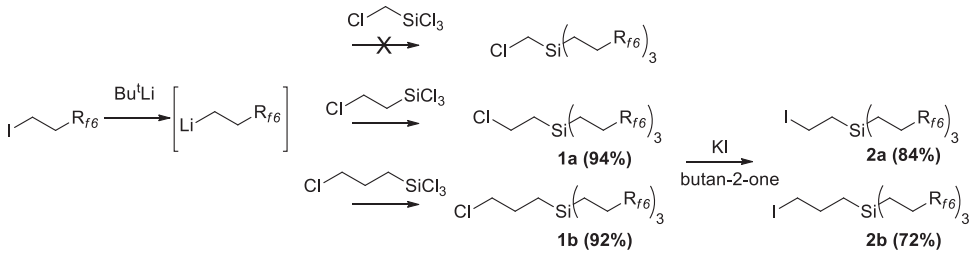


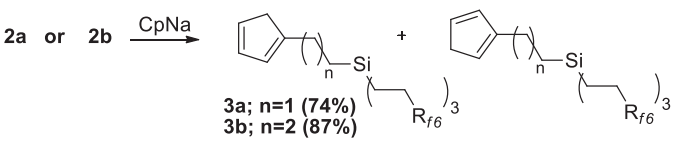
Scheme 1. Synthesis of fluorous tags.

cyclopentadienyl anion to produce cyclopentadienes. At first, insertion of only one CH_2 group between cyclopentadiene ring and silicon atom was attempted. (Chloromethyl)trichlorosilane was used as a starting material and $LiCH_2CH_2R_{f6}$, formed in situ at low temperature from the corresponding iodide and *tert*-butyllithium in a 1:1.1 ratio [12], as an alkylation reagent. However, the required product was obtained only in about 15% yield (according to NMR) and the presence of many side products was detected. This was probably caused by the two protons of the carbon spacer which are easily deprotonable with strongly basic reagents owing to their increased acidity caused by the proximity of both geminal chlorine atom and chlorines on silicon. The attempts to prepare the bromine analogue by radical bromination [13] of $CH_3Si(CH_2CH_2R_f)_3$, easily accessible by an alkylation of methyltrichlorosilane, also failed.

The preparation of a derivative containing two methylene groups according to the same protocol was also attempted (Scheme 1). Substitution of chlorine atoms on silicon in (chloroethyl)trichlorosilane with a carbanionic polyfluorinated chain prepared in situ led somewhat surprisingly to product **1a** in good yield. The chlorine can be substituted by iodine in the Finkelstein reaction. Cyclopentadiene **3a** substituted by a moiety containing three fluorinated ponytails was then prepared (Scheme 2) by reaction of the iodide with $Na(C_5H_5)$. NMR spectroscopy of the product revealed the presence of two vinylic isomers (2-substituted/1-substituted) in the ratio 1/0.7, respectively, as determined by integrating the signals of protons in positions 5 on cyclopentadiene rings in ^1H NMR spectra. The 2-substituted isomer was identified through a characteristic five-bond interaction, observed in gCOSY and gHMBC spectra between methylene hydrogens on the ring and the first (alpha) methylene group of the substituent. The interaction is possibly facilitated by W-shape arrangement of bonds one of them being the double bond. Similar (^4J) interaction was not observed in case of 1-isomer where the double bond is not in between.

It should be noted that there could be no interference here of long-range coupling from fluorines as shown previously for isomers of 2-(perfluoroalkyl)ethylcyclopentadienes [14]. The intended use of **1a** or **2a** as general fluorous tag precursors, however, seems to be prevented by their decomposition in basic conditions when some water is present. Under the latter conditions ethylene extrusion supported by a hyperconjugation effect and stabilization of the silylcarbonium intermediate [15] to form siloxane as the end product was observed.

Therefore, finally, a higher homolog **1b** with three methylene groups between silicon atom and chlorine was synthesized. The spacer of this length effectively isolated the halogen or other functional group from the influence of electronegative fluorine



Scheme 2. Synthesis of cyclopentadienes bearing three fluorous ponytails.

atoms as well as from the branching silicon atom. Thus, the chemical behaviour of the reactive functional group was as usually expected in organic chemistry and common procedures could be applied. The reagent could be prepared from commercially available precursors in a one-pot reaction in yields of around 90%. Cyclopentadiene **3b** was prepared in analogy to the synthesis of **3a**, here 2-substituted isomer predominated over 1-substituted isomer in ratio 1/0.65, respectively. The same assignment method as for **3a** was employed. In addition to that, the assignment was confirmed by 2D INADEQUATE. In the 1-isomer methylene carbon at 42.98 ppm was next to the quarternary carbon at 148.57 ppm whereas in the 2-isomer methylene carbon at 41.16 had two methine carbon neighbours at 127.42 and 134.87 ppm.

2.2. Cobalt(I) dicarbonyl complexes containing cyclopentadienyls with three ponytails

Three general ways to incorporate a perfluorinated chain into the cyclopentadienyl organocobalt compounds were reported. Historically, the first method was the oxidative addition of R_fI to $Cp'Co(CO)_2$ (Cp′ = cyclopentadienyl, indenyl) to produce Co(III) complexes with perfluorinated chains bonded directly to the metal [16]. Recently Baker et al. have shown that such compounds can be used as starting materials for syntheses of cobalt fluorocarbene complexes [17]. In the second approach fluorous cobalt cyclobutadiene complexes were prepared by cyclodimerization of polyfluorinated alkynes to give cobalt cyclobutadiene aducts [18]. The third possibility which affects the central metal in a minimal way compared to the previous two possibilities is the attachment of a poly- or perfluorinated chain to cyclopentadiene and subsequent complexation. With this objective Hughes prepared a series of cobalt dicarbonyl complexes bearing one poly- or perfluorinated ponytail [19]. The latter method, which involved the reaction of $Co_2(CO)_8$ with cyclopentadiene derivatives **3a** and **3b** in the presence of cyclohexadiene as a hydrogen acceptor [19,20], was first chosen in our work. The resulting dicarbony1 complexes **4a** and **4b** were obtained as red oils in good yields (75–80%), their air-sensitivities being comparable with that of $CpCo(CO)_2$.

2.3. Perfluoroalkyl cobalt(III) complexes

As shown in Scheme 3, the compounds **4a** and **4b** were used as starting compounds for syntheses of compounds **5a–c** bearing two different types of fluoroalkyl chains thus combining two principal approaches for the incorporation of perfluorinated chains into cyclopentadienyl cobalt complexes. The procedure used by King et al. [16a] was adopted and slightly modified. Carbonyl compounds **4a** or **4b** were heated with an excess of perfluoroalkyl iodides at 50 °C in toluene for 10–15 h. Products were generally black viscous liquids which in solution gave a deep green colour.

Since there is a stereocenter on the metal in complexes **5a–c**, hydrogens and carbons of cyclopentadienyl rings as well as fluorines of perfluorinated chains are diastereotopic. Signals of each nucleus belonging to the two pairs of diastereotopic protons