Notes

A Surprising Solvent Effect on the Crystal Structure of an Anionic Lanthanide Sandwich Complex[†]

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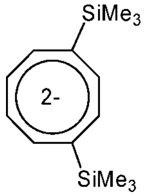
*Summary: An unusual solvent effect on the crystallization of an anionic lanthanide sandwich complex has been discovered, demonstrating how small changes can make big differences when crystallizing organometallic compounds. Crystallization of Li(DME)Tb(COT″)$_2$ (**1**) from toluene leads to the formation of supramolecular [Li(DME)Tb(COT″)$_2$]$_n$ (**1a**), while monomeric Li(DME)Tb(COT″)$_2$ (**1b**) is formed upon crystallization from pentane, which is intercalated in the crystal structure of the latter.*

In organometallic chemistry, crystallization of new compounds from organic solvents is the method of choice for growing X-ray quality single crystals. However, given the vast range of organic solvents with different polarity, the right choice is not always easy. When typical donor solvents such as THF or 1,2-dimethoxyethane (= DME) are employed, coordinative interaction with a metal center is frequently encountered. Thus, it is generally accepted that in such cases different crystal structures could arise as compared to crystallization from nonpolar solvents. In the case of nonpolar hydrocarbon solvents, especially hydrocarbons, there are of course significant differences between aromatic and aliphatic hydrocarbons. Quite frequently, one type of hydrocarbon solvent (e.g., toluene) yields suitable crystals while the other (e.g., *n*-pentane) does not or vice versa. However, one would not expect the formation of different crystalline forms when switching between these different nonpolar hydrocarbon solvents. We report here such an unusual solvent effect on the crystallization of an anionic lanthanide sandwich complex. The work reported here provides a fascinating example of how small changes can have big effects on crystal structure and coordination mode.

The compound in question is Li(DME)Tb(COT″)$_2$ (**1**), a formally anionic lanthanide sandwich complex containing bulky cyclooctatetraenyl ligands. The organometallic chemistry of the rare earth elements continues to be a highly attractive field of research, in particular due to the numerous applications of organolanthanides in catalysis[1] and organic synthesis.[2] An increasingly important area focuses on the development of noncyclopentadienyl organolanthanide complexes.[3] Here, cyclooctatetraenyl ligands (= COT) play an important role because the large, flat COT dianions are ideally suited to form sandwich complexes of the rare earth metals.[4] Long known and well established are the anionic lanthanide(III) sandwich complexes M[Ln(COT)$_2$] (M = alkaline metal).[4a,5] More recently, bulky organosilyl-substituted COT ligands such as the 1,4-bis(trimethylsilyl)cyclooctatetraenyl dianion (= COT″) have become increasingly popular.[6]

Scheme 1. COT″ Ligand



Anionic sandwich complexes of the type [Li(THF)$_4$]-[Ln(COT″)$_2$] (Ln = Ce, Pr, Sm, Y) are formed upon treatment

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[†] Dedicated to Professor Rudolf Hoppe on the occasion on his 85th birthday.

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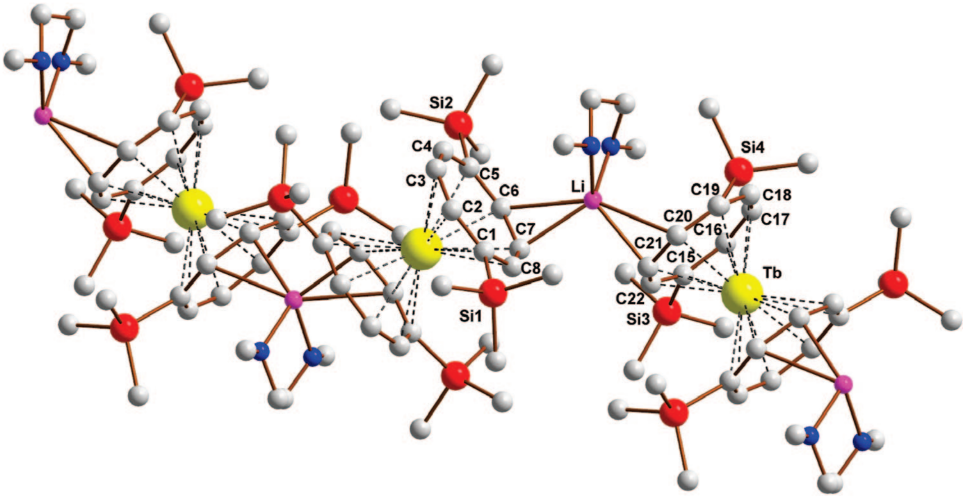

Figure 1. Supramolecular structure of **1a**. Selected bond lengths (Å) and angles (deg): Tb−C 2.645(5)−2.674(5), Tb−$\mathrm{X_{COT''}}$ 1.912(2)−1.919(2), C−C (COT″) 1.401(7)−1.439(8), Li−C6 2.683(10), Li−C7 2.377(10), Li−C20 2.764(11), Li−C21 2.364(11), Li−O 1.97(2), $\mathrm{X_{COT''}}$−Tb−$\mathrm{X_{COT''}}$ 179.0(2) ($\mathrm{X_{COT''}}$ = COT″ ring centroid).

of anhydrous $\mathrm{LnCl_3}$ with 2 equiv of $\mathrm{Li_2(COT'')}$.[7] The solid-state structure of $\mathrm{[Li(THF)_4][Sm(COT'')_2]}$ was found to consist of separated ions and thus displayed no unexpected structural features.[7] The same reactions carried out in DME solution led to DME-solvated lithium salts of the anionic $\mathrm{[Ln(COT'')_2]^-}$ sandwich complexes. Here, the influence of the ionic radius of the respective lanthanide element becomes evident. While the large $\mathrm{Ce^{3+}}$ ion affords $\mathrm{[Li(DME)_3][Ce(COT'')_2]}$, monosolvated $\mathrm{Li(DME)Tb(COT'')_2}$ (**1**) is formed with the "middle lanthanide element" terbium. An unusual solvent effect was encountered when the molecular structure of the terbium species **1** was elucidated by X-ray methods. Crystallization by slow cooling of a saturated toluene solution of **1** yielded bright yellow, needle-like single crystals suitable for X-ray diffraction. The crystal structure of this modification (**1a**, $\mathrm{[Li(DME)Tb(COT'')_2]}_n$) consists of polymeric, one-dimensional zigzag chains, in which $\mathrm{[Tb(COT'')_2]^-}$ anions are alternatingly bridged by $\mathrm{[Li(DME)]^+}$ units. The COT″ rings are η^8-coordinated to terbium, while the coordination to the bridging Li atoms can be best described as μ-η^2:η^2-bridging (Figure 1). The Li−C bond lengths are in the range of 2.364(10)−2.683(10) Å. π-Coordination of Li to a COT sandwich has several precedents in organolanthanide chemistry. Well-characterized examples include $\mathrm{Li(THF)_3}$(μ-η^2:η^8-COT)Sm(COT),[6e] $\mathrm{Li(THF)_3}$(μ-η^2:η^8-COT)Tm(COT),[8] $\mathrm{Li(THF)_2}$(μ-η^4:η^4-COT)Sc(COT),[9] and $\mathrm{Li(THF)_2}$(μ-η^2:η^8-COT)$\mathrm{Sm[CH(SiMe_3)_2]_2}$.[10] In these compounds, Li−C distances in the range between 2.258(9) and 2.762(10) Å have been found, and an unambigous decision about the hapticity of the Li−COT coordination cannot always be made.

When **1** was crystallized from pentane, more compact, bright yellow prisms were obtained, which were also structurally characterized by an X-ray analysis. Surprisingly, the X-ray diffraction study revealed the presence of a monomeric modification of $\mathrm{Li(DME)Tb(COT'')_2}$ (**1b**) (Figure 2). While the η^8-coordination of the two COT″ rings to Tb remains unchanged, the Li(DME) unit is now significantly more centered above a COT″ ligand. In this case, the bonding of Li to the COT″ ring approaches an η^5-pentadienyl-type coordination with Li−C distances ranging from 2.367(8) to 2.785(10) Å.

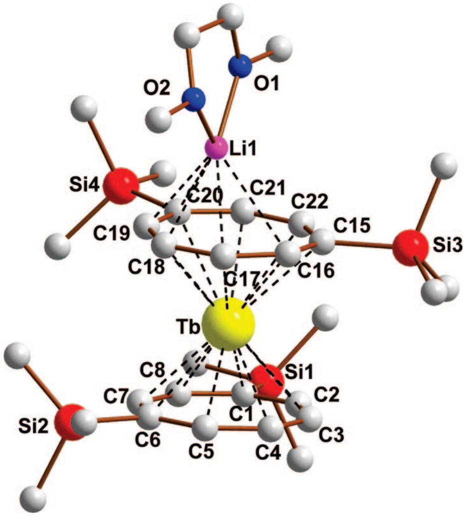

Figure 2. Monomeric structure of **1b**. Selected bond lengths (Å) and angles (deg): Tb−C 2.603(3)−2.695(3), Tb−$\mathrm{X_{COT''}}$ 1.865(2)−1.966(2), C−C (COT″) 1.407(4)−1.435(4), Li−O 1.893(7)−1.914(8), Li−C16 2.785(10), Li−C17 2.532(8), Li−C18 2.367(8), Li−C19 2.372(8), Li−C20 2.601(8), $\mathrm{X_{COT''}}$−Tb−$\mathrm{X_{COT''}}$ 176.62(9) ($\mathrm{X_{COT''}}$ = COT″ ring centroid).

A closer inspection of the crystal structures of **1a** and **1b** revealed the presence of intercalated pentane in the crystal lattice of **1b**. This is clearly seen in Figure 3. Thus, switching between the two hydrocarbon solvents toluene and pentane is the only subtle difference guiding the formation of the different forms of **1**. An attempt to interconvert the two forms by recrystallizing monomeric **1b** from toluene did not lead to the formation of supramolecular **1a** again. In all cases, there is little deviation from the parallel orientation of the η^8-coordinated COT″ rings with X−Ln−X angles (X = COT″ ring centroid) of 179.0(2)° in **1a** and 176.62(9)° in **3b**. Significant changes in the coordination mode are observed mainly for the Li−COT″ interaction (vide supra). It should be noted here that mass spectrometry was used to ascertain that the terbium compound was investi-

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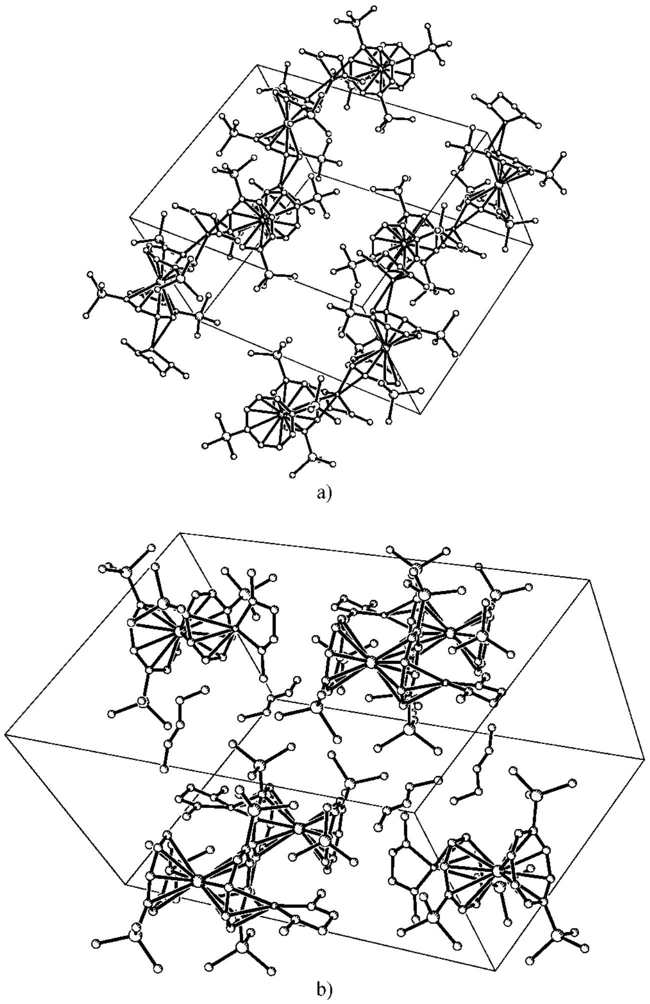

Figure 3. (a) Crystal structure of supramolecular **1a**. (b) Crystal structure of monomeric **1b** showing the intercalated pentane molecules.

gated in both cases and that no misidentification of the lanthanide element had occurred.

In summarizing these results, we have demonstrated that the outcome of the seemingly trivial reactions of anhydrous lanthanide trichlorides with $Li_2(COT'')$ in DME solution critically depends not only on the ionic radius of the lanthanide element, but also on the solvents employed. Minor changes in the workup procedure, i.e. switching between the two inert and noncoordinating solvents toluene and pentane, is sufficient to achieve formation of either supramolecular **1a** or monomeric **1b**. Without investigating both crystalline forms of **1**, the structure of this compound would have been published as either supramolecular or monomeric. Regardless of the fact that **1** is a somewhat "exotic" organolanthanide sandwich complex, the results reported here give a fascinating example of how small changes can make big differences when crystallizing organometallic compounds. Researchers in all fields of organometallic chemistry may wish to keep this in mind when using these solvents for growing single crystals of new compounds.

Experimental Section

General Techniques and Materials. All reactions were conducted in oven-dried or flame-dried glassware under an inert atmosphere of dry argon employing standard Schlenk and glovebox techniques. DME, *n*-pentane, and THF were distilled from sodium/benzophenone under nitrogen atmosphere. All glassware was oven-dried at 140 °C for at least 24 h, assembled while hot, and cooled under high vacuum prior to use. The starting materials 1,4-$(Me_3Si)_3C_8H_8$[6] and $TbCl_3(THF)_3$[11] were prepared according to literature procedures. IR spectra were recorded using KBr pellets on a Perkin-Elmer FT-IR spectrometer system 2000 between 4000 and 400 cm^{-1}. Microanalyses of the compounds were performed using a Leco CHNS 923 apparatus.

[Li(DME)Tb(COT″)₂]*ₙ* (1a): $TbCl_3(THF)_3$ (2.80 g, 5.81 mmol) was added to a stirred DME (150 mL) solution of in situ prepared $Li_2(COT'')$ [from 15 mL of 1.6 M *n*-butyllithium solution (24 mmol) in hexane and 3.00 g (12 mmol) of 1,4-$(Me_3Si)_3C_8H_8$] at room temperature. The reaction mixture was stirred for 30 h, and the solvents were evaporated in vacuum. The solid residue was extracted with boiling toluene (ca. 80 mL). One third of the toluene was evaporated in vacuum. $[Li(DME)Tb(COT'')_2]_n$ (**1a**) precipitated at room temperature as yellow needles (3.05 g, 70%), which were suitable for X-ray crystallography. Anal. Calcd for $C_{32}H_{58}LiO_2Si_4Tb$: C, 51.04; H, 7.76. Found: C, 51.21; H, 7.44. IR (KBr disk): ν = 3030w, 2951s, 2895m, 2833w, 1772vw, 1542w, 1474w, 1448w, 1401w, 1366w, 1245s, 1212w, 1193vw, 1114m, 1079m, 1051s, 996m, 981m, 934m, 908w, 832vs, 783w, 732s, 682m, 636m, 550w, 510w, 408w cm^{-1}. NMR: Because of the paramagnetic nature of the Tb^{3+} ion, it was impossible to obtain interpretable NMR data. Mass spectrum (EI): *m*/*z* 656 (10%) $[\{C_8H_6(SiMe_3)_2\}_2Tb]$, 407 (40%) $[\{C_8H_6(SiMe_3)_2\}Tb]$, 248 (22%) $[C_8H_6(SiMe_3)_2]$, 207 (70%), 161 (35%), 145 (45%), 135 (45%), 89 (20%), 73 (100%) $[SiMe_3]$. The isotope patterns of the peaks at *m*/*z* 656 and 407 are in good agreement with those calculated for $[\{C_8H_6(SiMe_3)_2\}_2Tb]$ and $[\{C_8H_6(SiMe_3)_2\}Tb]$.

Li(DME)Tb(COT″)₂ (1b). This crystalline form of **1** was made in the same manner as described above except that *n*-pentane (ca. 120 mL) was used to extract and crystallize the product. After 1 week at room temperature, prism-like crystals, also suitable for X-ray crystallography, were formed in comparable yield. Anal. Calcd for $C_{32}H_{58}LiO_2Si_4Tb \cdot$ *n*-pentane: C, 53.86; H, 8.55. Found: C, 52.89; H, 9.93.

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Supporting Information Available: ORTEP drawings and CIF files giving X-ray structural data for **1a** and **1b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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