A Partially Demethylated Donor-Functionalized Terphenyl Lanthanide Compound

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Summary: The synthesis and structural characterization of an unsolvated lanthanide half-sandwich compound of composition [DanipOSmCp]$_2$ (**1**) is reported featuring a novel dianionic partially demethylated donor-functionalized terphenyl ligand [DanipO = 2-(o-anisyl)-6-(o-2-phenoxide)phenyl].*

There is much current interest in the chemistry of terphenyl-based compounds.[1−3] We have focused on the synthesis of such compounds of the f-elements and previously reported the synthesis of a number of lanthanide compounds (Ln = Sm−Lu) stabilized by the donor-functionalized terphenyl ligand Danip [Danip = 2,6-di(*o*-anisyl)phenyl].[4] For example, reaction of DanipLi[5] with $LnCl_3$ in THF produces cage-like compounds that are comprised of THF-solvated lithium chloride adducts of $DanipLnCl_2$ fragments.[6] Additionally, the one-pot synthesis of DanipLi, $LnCl_3$, and 2 equiv of several potassium amide or aryloxide reagents yields complexes of general composition $DanipLnX_2$ (X = $N(SiMe_3)_2$, $N(SiHMe_2)_2$, O(2,6-diisopropyl)phenyl).[7] In all of these compounds the terphenyl ligand adopts the chiral (racemic) *d,l* conformation. The analogous one-pot synthesis of DanipLi, $SmCl_3$, and K_2COT produces DanipSm(THF)COT, with the Danip moiety adopting the *meso* conformation.[8]

Organometallic rare-earth metal compounds supported by bis(cyclopentadienyl) frameworks are excellent catalysts for a variety of transformations.[9,10] We were therefore interested in probing the accessibility of Danip-based half-sandwich or metallocene compounds employing different anionic Cp-type ligands as well as their potential applications in homogenious catalysis. Compared with numerous structurally characterized metallocenes of the f-elements, a considerably smaller number of half-sandwich compounds is known,[11,12] which is in part due to the possibility of ligand scrambling, resulting in formation of bis(cyclopentadienyl) complexes.

Reaction of equimolar amounts of DanipLi and $SmCl_3$ in THF (30 min) followed by addition of 1 or 2 equiv of KCp* (14−18 h), however, does not produce the targeted heteroleptic DanipSm(Cp*)Cl or a terphenyl-based metallocene. After standard workup procedures, washing with hexanes, and subsequent extraction of the crude product with warm hexanes a yellow half-sandwich compound of composition [DanipOSmCp*]$_2$ (**1**) crystallizes in an approximate yield of 20% [DanipO = 2-(*o*-anisyl)-6-(*o*-2-phenoxide)phenyl].[13] We found that typically a better yield is obtained when using 2 equiv of KCp* instead of one. After crystallization the product is insoluble in hexanes, but readily soluble in arene solvents. Additionally, an amorphous, red material of unknown composition is isolated from the toluene cut of the crude product, which slowly precipitates and then is no longer soluble in arene solvents.

The molecular structure of **1** (Figure 1)[14] features an unsolvated dimeric half-sandwich compound and a dianionic partially demethylated donor-functionalized mixed arylether/aryloxide terphenyl ligand (=DanipO). As the methyl group acceptor Danip-Me was identified by ^{1}H NMR spectroscopy (two sets of signals in an approximate 2:1 ratio: 2.23 and 2.19 ppm, −Me; 3.20 and 3.25 ppm, −OMe), by GC/MS, and also by a single-crystal X-ray diffraction study.[15] We also investigated the same reaction using YCl_3 and $YbCl_3$ and obtained significant amounts of Danip-Me in both cases from the hexane cut of the crude products. Unfortunately, our attempts to crystallize the metal-containing component employing rare-earth cations smaller than samarium have not been successful so far. Still, formation of Danip-Me is indicative that an ether-cleavage reaction occurs.

Formation of compound **1** can be rationalized in terms of a Cp*-induced ether-cleavage reaction through a concerted intermolecular methyl-group-transfer reaction (Scheme 1). Alternatively, a flexible coordination mode of the terphenyl moiety

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(13) Characterization data for **1**: ^{1}H NMR (C_6D_6): δ 1.26 (s, 30H, Cp*), 4.48 (s, 6H, OMe) plus several sets of signals ranging from 4.83 to 8.32 ppm corresponding to aromatic protons of the terphenyl moiety. ^{13}C NMR (C_6D_6): δ 15.3 (C-Me), 66.5 (O-Me), 114.8, 116.1, 117.6, 118.5, 121.6, 123.3, 124.5, 125.4, 126.7, 127.1, 130.2, 131.3, 131.9, 133.8, 138.1, 145.1, 149.2, 152.6. Anal. Calcd for $C_{58}H_{58}O_4Sm_2$: C, 62.2; H, 5.2. Found: C, 61.9; H, 5.0. Mp > 210 °C (dec).

(14) Crystal data for **1**·methylcyclopentane: monoclinic, $P2_1/c$, a = 16.5266(16) Å, b = 15.5034(15) Å, c = 21.809(2) Å, β = 106.7030(10)°, V = 5352.1(9) Å^3, Z = 4, T = 100(2) K, D_{calc} = 1.524 g cm^{-3}, $R(F)$ = 2.26% for 10 266 observed independent reflections (3.68° < 2θ < 55.06°). Crystal data for **2**: monoclinic, $P2_1/c$, a = 10.477(3) Å, b = 31.172(9) Å, c = 8.232(3) Å, β = 107.430(6)°, V = 2565.1(14) Å^3, Z = 2, T = 100(2) K, D_{calc} = 1.642 g cm^{-3}, $R(F)$ = 5.54% for 5079 observed independent reflections (4.08° < 2θ < 56.86°).

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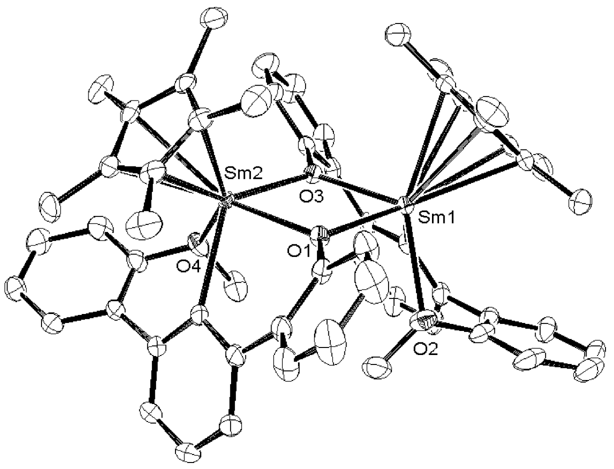
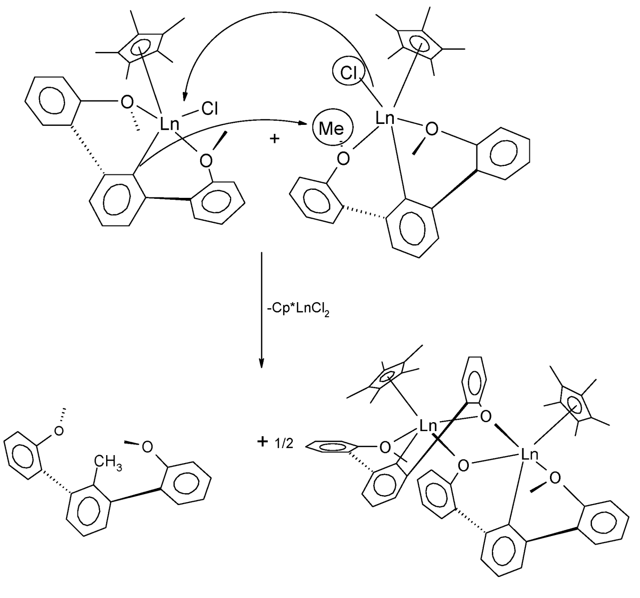


Figure 1. Molecular structure of **1**.

Scheme 1



can be discussed as a first step of the ether-cleavage reaction; that is, one of the anisyl moieties of one Danip ligand rotates away from the metal atom and a methoxy group from a neighboring terphenyl unit coordinates to both metals at the same time.

We note that in our previous reports on the above-mentioned DanipLnX$_2$-type compounds formation of small amounts of Danip-Me is also observed, particularly after prolonged time periods in THF at ambient temperature. However, in all of these reactions the ether-cleavage reaction appears to be only a minor side product, and we have not been able yet to isolate and characterize the metal-containing components.

In the molecular structure of dimeric **1** the Sm−C(Cp*) distances range from 2.6924(19) (C2) to 2.7472(19) Å (C5) (av 2.72 Å) and fall into the range of other Cp*-based half-sandwich compounds of samarium.[11] They can be compared, for example, with those in the monomeric bis(aryloxide) compound Cp*Sm[O(2,6-di-*tert*-butyl)phenyl]$_2$(THF) (av 2.76 Å).[16] Both Cp* rings are on the same side of the Sm$_2$O$_2$ plane; so are the two central phenyl rings of the DanipO moiety. The dihedral angles between the central phenyl ring and the rings in the 2,6-positions are 47° (O2) and 35° (O3) for Sm1 and 48° (O4) and 37° (O1) for Sm2, respectively. The terphenyl moiety coordinated to Sm1 is slightly tilted with Sm−C−C angles of 119.16(14)° and 124.09(13)° (C−C−C: 115.77(17)°), while the other ligand exhibits Sm−C−C angles of 121.72(14)° and 121.19(14)° (C−C−C: 115.89(18)°). The Sm−C(ipso) distances of 2.4687(19) Å (Sm1) and 2.4821(19) Å (Sm2) can favorably be compared with the corresponding distance in the five-coordinate Danip samarium compound DanipSm[N(SiHMe$_2$)$_2$]$_2$ (2.484(4) Å)[7] or seven-coordinate [DanipSm(μ_2-Cl)$_2$(μ_2-Cl)Li(THF)$_2$]$_2$ (2.489(3) Å)[6] exhibiting as well *d,l*-coordinated terphenyl ligands, but are noticeably shorter than the one in DanipSm(THF)COT (2.543(3) Å),[8] showing the Danip moiety in the *meso* conformation and a higher formal coordination number at the samarium atom. The bridiging Sm−O distances (2.2817(14) and 2.3812(14) Å for Sm1; 2.2879(14) and 2.3664(14) Å for Sm2) are shorter than the coordinating Sm−O(OMe) separations of 2.4584(14) and 2.4546(13) Å. As one would expect for bridiging atoms, they are significantly longer than the terminal Sm−O separations in Cp*Sm[O(2,6-di-*tert*-butyl)phenyl]$_2$(THF) of 2.133(6) and 2.188(6) Å. The Sm−O(OMe) distances are slightly shorter than those in DanipSm[N(SiHMe$_2$)$_2$]$_2$ (2.496(3) and 2.512(3) Å) and are considerably shorter than the corresponding separations in DanipSm(THF)COT (2.5436(19) and 2.576(2) Å).

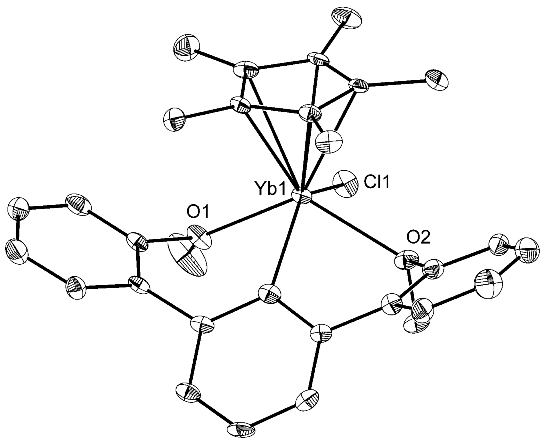


Figure 2. Molecular structure of **2**.

We were interested in investigating whether or not a postulated intermediate of composition DanipLnCp*Cl can be isolated. In the case of Ln = Yb we managed to obtain single crystalline material of DanipYbCp*Cl (**2**), however, in relatively poor yield after standard workup of the reaction mixture approximately 2 h after addition of the KCp* reagent and subsequent extraction with hexanes. Isolation of **2**, even in low yield, is in principle in support of the postulated mechanism for the formation of **1**.

The molecular structure of **2** (Figure 2)[14] features another unsolvated half-sandwich compound that is comprised of a Cp* ligand, a terminal chloride atom (Yb−Cl = 2.5781(18) Å), and a Danip ligand, which adopts here the *meso* conformation, as was previously found in the case of the mixed COT/Danip compound of the lanthanide element samarium.[8] The Yb−C(ipso) (2.415(7) Å) as well as the Yb−O distances (2.335(5) and 2.340(6) Å) in **2** are in relatively good agreement with, for example, those in DanipYb[O(2,6-diisopropylphenyl)]$_2$ (Yb−C = 2.379(3) Å; Yb−O = 2.3172(13) Å).[7] The O−Yb−O angle of 124.1(2)° in the *meso*-type bonded Danip in **2** differs considerably, for example, from the same angle found in the *d,l*-type bonded terphenyl moiety in DanipYb[N(SiMe$_3$)$_2$]$_2$ (152.8(2)°).[7] Further comparisons can be made with the O−Sm−O angle of 103.56(6)° in the *meso*-type bonded

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[16] Butcher, R. J.; Clark, D. L.; Gordon, J. C.; Watkin, J. G. *J. Organomet. Chem.* **1999**, *577*, 228.

DanipSm(THF)COT.[8] The Yb−C(Cp*) distances range from 2.588(7) (C2) to 2.618(7) Å (C5) (av 2.60 Å). The Yb−C−C angles of the terphenyl moiety are 122.7(5)° and 121.8(5)°, respectively (C−C−C: 114.5(6)°). The dihedral angles between the central phenyl ring and the rings in the 2,6-positions are 43° (O1) and 45° (O2).

In summary, use of the Cp* anion allows for the kinetic stabilization, isolation, and structural characterization of a metal-containing component of an ether-cleavage reaction, i.e., **1**, thereby giving detailed insight into the reaction mechanism. Additionally, the presence of the heteroleptic intermediate **2** is documented.

In the course of our studies we were also interested in investigating whether or not a more simplified synthetic procedure for the preparation of Danip-I is feasible. So far the easiest way to prepare Danip-I in relatively high yield is by a one-pot synthesis using 3.5 equiv of the Grignard reagent (prepared from 1-bromo-2-methoxybenzene) and 1 equiv of 1,3-dichloro-2-iodobenzene in THF at ambient temperature via a two aryne sequence followed by addition of 1.5 equiv of iodine.[17] We were able to demonstrate that this procedure can be simplified using even more inexpensive starting materials. Reaction of 3.5 equiv of 1-lithium-2-methoxybenzene (prepared from *n*-butyllithium and 1-bromo-2-methoxybenzene in hexanes) with 1 equiv of 1,3-dichlorobenzene followed by addition of 1.5 equiv of iodine yields the targeted Danip-I in good yield after standard workup procedures. The reaction can be carried out in the absence of THF or diethyl ether as a a one-pot synthesis in a 2 L flask starting from a 1 L bottle of 1.6 M *n*-butyllithium in hexanes, which serves as the exclusive solvent for this synthesis.

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Supporting Information Available: X-ray structural data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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