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Helicate tris(aryl)carbinolates bearing pendant NR_2 donors – a new family of supporting ligands for the synthesis of Sc^{3+} alkyl complexes

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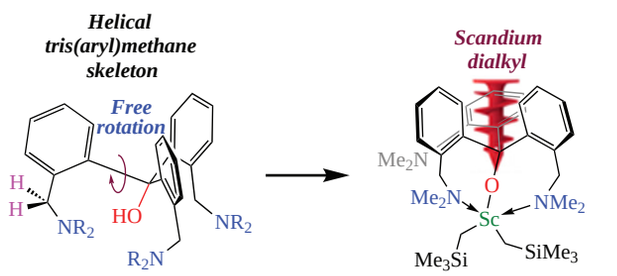
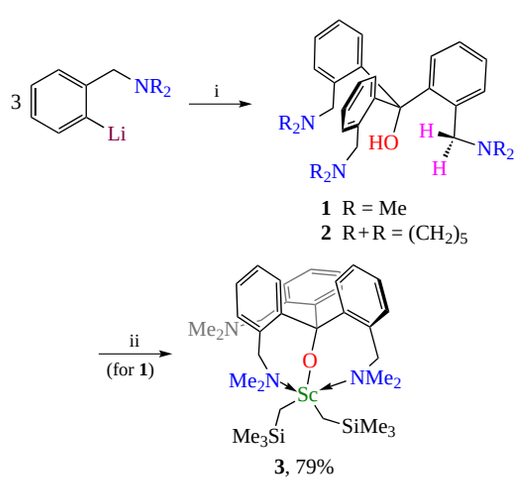
The reactions of aryllithium reagents *o*-$LiC_6H_4CH_2NR_2$ with $(MeO)_2CO$ afford two new tris(aryl)carbinols bearing pendant-NR_2 donor groups in the side chain $[o\text{-}R_2NCH_2C_6H_4]_3COH$ [R = Me, R + R = $(CH_2)_5$]. These alcohols feature helical chirality due to differently inclined aromatic fragments and are presented in a crystalline cell as two M and P enantiomers. Carbinol (R = Me) readily reacts with $(Me_3SiCH_2)_3Sc(THF)_2$ to give a scandium bis(alkyl) complex $[(o\text{-}C_6H_4CH_2NMe_2)_3CO]Sc(CH_2SiMe_3)_2$ featuring rigid binding of the alkoxy anion through a κ^1-O, κ^2-N chelating coordination mode.



Keywords: alkoxide anion, rare-earth metals, scandium complexes, bis(alkyl) complexes, carbinol, helical chirality, donor ligand.

Highly reactive Group 3 metal hydrocarbyl complexes present one of the most promising and intriguing objects in the organometallic chemistry.[1] The past two decades have clearly witnessed the enormous potential of rare-earth alkyl complexes not only in a number of fundamentally important stoichiometric reactions[1(*c*)–(*j*)] but also in a variety of catalytic applications involving multiple C=C bonds.[2] Among the rare-earth elements, scandium has the smallest ionic radius,[3] the highest electrophilicity[4] and high-energy d-orbitals, that provides its compounds with unique properties. The first reported[5] example of methane CH-bond activation by Sc^{3+} alkyl complex marked the beginning of varied and fruitful application of scandium compounds in C–C bond formation reactions,[2(*c*),6–17] associated with selective activation of normally inert sp^3- and sp^2-hybridized CH-bonds of substrates with acidic proton.[18] It should be noted that bis(alkyl) complexes of the smallest scandium are the key precursors to poorly explored highly reactive imide derivatives which can act as intermediates in hydroamination reactions.[1(*e*),19–23] However, in most cases, in order to achieve the desired effect, the introduction of 'supporting' ligands into the metal coordination sphere is required to provide fine tuning of the stereo-electronic properties of the metal center which proved to be a key tool for controlling the reactivity and catalytic performance. It is hard to overestimate the role of cyclopentadienyl ligands in rare-earth chemistry, especially that of C_5Me_5, whose employment gave a powerful impetus to the progress of the field.[24] The tertiary alkoxide anion R_3CO^- due to its electron donating nature and rigid binding to the oxophilic metallocenter can act as an excellent easily modifiable alternative to Cp ligands. However, despite the hidden potential, only a few examples of rare-earth metal alkyl complexes with a monoanionic tertiary alkoxide group are known so far and none based on sterically demanding triarylmethane framework.[25–28] Herein we report on the synthesis and structures of two tertiary alcohols featuring triarylmethane skeleton and bearing various pendant NR_2-groups [R = Me, R + R = $(CH_2)_5$], as well as scandium bis(alkyl) complex $[(o\text{-}C_6H_4CH_2NMe_2)_3CO]Sc(CH_2SiMe_3)_2$.

Assembling of a key triarylmethanol skeleton was achieved using standard protocol based on the reaction of the corresponding aryllithium reagents *o*-$LiC_6H_4CH_2NR_2$ with dimethyl carbonate (3 : 1 molar ratio, Scheme 1). After hydrolysis of lithium alkoxides Ar_3COLi with NH_4Cl, toluene extraction and recrystallization from hot hexane, products **1** and **2** were isolated in 74 and 61% yields. Their structures have been established by NMR in different solvents and



Scheme 1 *Reagents and conditions*: i, $(MeO)_2CO$, Et_2O, room temperature, then NH_4Cl/H_2O; ii, $(Me_3SiCH_2)_3Sc(THF)_2$, hexane, 0 °C (–Me_4Si, –THF).

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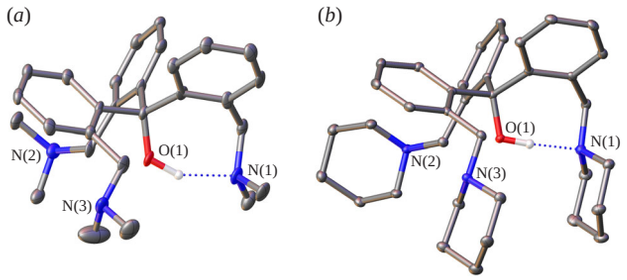

Figure 1 General view of (*a*) alcohol **1** and (*b*) alcohol **2** in representation of atoms *via* thermal ellipsoids at 30% probability level. All hydrogen atoms except those of OH groups are omitted for clarity, and labels are given for heteroatoms only.

X-ray analysis (Figure 1, see also Online Supplementary Materials).†

The single crystal X-ray diffraction studies revealed that alcohols **1** and **2** crystallize in the monoclinic space groups $P2_1/n$ (**1**) and $C2/c$ (**2**) with two propeller-like M and P enantiomeric forms (left and right screws, respectively).[29,30] The angles between the planes of the aromatic rings are 77.67(18), 78.1(2) and 80.76(19)° for **1** and 75.48(7), 76.89(7) and 79.77(7)° for **2**. Unfortunately, due to the low enantiomerization barrier, caused by free rotation of aryl rings around the C–C bond, it is not possible to separate the enantiomers. However, the complete blocking of the *ortho*-positions of the aryl rings by bulky groups sufficiently increases the barrier.[31] The hydroxy group is located in the cavity formed by the substituents of the side chains and is linked by an intramolecular hydrogen bond O–H···N with an amino group. The C–O bond lengths are rather similar in **1** and **2** [1.435(7) and 1.433(2) Å], while the hydrogen bond O···N distances are 2.714(8) and 2.638(2) Å.

In solution ($CDCl_3$, 25 °C), ^{1}H and $^{13}C\{^1H\}$ NMR spectra of compounds **1** and **2** are somewhat broadened, thus indicating the occurrence of dynamic processes. A likely scenario is the relatively slow intramolecular transposition of the hydrogen bonding between different amino groups at room temperature. Lowering the temperature to 223 K (for compound **1**) leads to sharpening the signals, which is consistent with a C_3-symmetric molecule (see Online Supplementary Materials, Figure S4). The diastereotopic CH_2 protons emerge as two well-resolved doublets at 3.78 and 3.05 ppm ($^2J_{HH}$ = 14.5 Hz). The similar pattern for the methylene CH_2 protons in the ^{1}H NMR spectrum of carbinol **2** appears already at 293 K if C_6D_5N is used as a solvent (Figure S8). The signal corresponding to the hydroxyl proton appears as a downfield singlet at 9.84 (**1**) and 9.91 ppm (**2**) ($CDCl_3$, 298 K). Intramolecular character of this bonding is evidenced by the concentration independence of the OH proton chemical shift (9.81 ppm; at 0.12, 0.24 and 0.35 M) in the ^{1}H NMR spectra (Figure S11).

Reaction of compound **1** with an equimolar amount of $(Me_3SiCH_2)_3Sc(THF)_2$ in hexane affords a THF-free bis(alkyl) complex **3** in high yield 79% (see Scheme 1). According to X-ray analysis (Figure 2), the alkoxide ligand is coordinated to the Sc^{3+} ion in a κ^1-O, κ^2-N-fashion while the third donor group does not participate in the bonding and is bent aside. The Sc–O bond length in compolex **3** [1.953(2) Å] is in a good agreement with the values previously reported for five-coordinate Sc^{3+} alkoxy complexes.[25,26] Two coordination bonds between Sc^{3+} and NMe_2 units have similar lengths [2.368(3) and 2.411(3) Å] and are in line with the values reported for Sc^{3+} β-diketiminate complexes.[20,29] The Sc–C bond lengths in **3** [2.242(4) and 2.285(4) Å] fall into the range of values typical for Sc^{3+} bis(alkyl) complexes.[25,29]

In solution (C_6D_6), in contrast to the parent alcohol **1**, the ^{1}H NMR spectrum of complex **3** due to the rigid chelating bonding of the ligand to the metal already at room temperature gives an evidence for non-equivalence of all three aryl fragments. In view of chirality, the signals of methylene as well as NMe_2 groups appear as six doublets and six singlets in the range of 4.59–2.00 ppm. The alkyl groups are also non-equivalent and resonate as two singlets belonging to Me_3Si groups and four doublets belonging to methylene $–CH_2SiMe_3$ protons (Figure S9). Complex **3** proved to be rather thermally stable and can be safely stored in a benzene solution at room temperature for more than one week without visible signs of decomposition. However, increasing the temperature to 60 °C leads to decomposition into unidentifiable products with a half-life time of 24 h. The rigid chelating κ^1-O, κ^2-N coordination mode of ligand, together with the donor character of the $R_3CO^–$ anion and

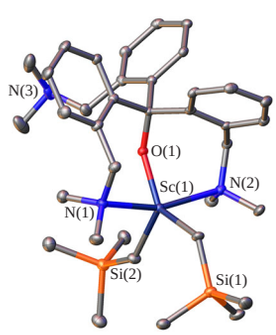

Figure 2 General view of complex **3** in representation of atoms *via* thermal ellipsoids at 30% probability level. All hydrogen atoms are omitted for clarity, and labels are given for heteroatoms only.

† *Crystal data for* **1**. $C_{28}H_{37}N_3O$, M = 431.60, monoclinic, space group $P2_1/n$, at 120 K, a = 10.36(2), b = 14.18(3) and c = 17.82(4) Å, β = 105.79(4)°, V = 2518(10) Å^3, Z = 4, d_{calc} = 1.139 g cm^{-3}, $F(000)$ = 936. Intensities of 22621 reflections were measured with a Bruker APEX2 DUO CCD diffractometer, λ(MoKα) = 0.71073 Å, μ(MoKα) = 0.69 cm^{-1}, ω-scans, $2\theta < 54°$, and 5496 independent reflections (R_{int} = 0.3965) were used for the structure solution and refinement. Final R factors: R_1 = 0.1037 for 1715 observed reflections with $I > 2\sigma(I)$, wR_2 = 0.2490 and GOF = 0.872 for all the independent reflections.

Crystal data for **2**. $C_{37}H_{49}N_3O$, M = 551.79, monoclinic, space group $C2/c$, at 120 K, a = 22.095(2), b = 18.6709(16) and c = 18.428(3) Å, β = 123.964(2)°, V = 6305.0(12) Å^3, Z = 8, d_{calc} = 1.163 g cm^{-3}, $F(000)$ = 2400. Intensities of 22182 reflections were measured with a Bruker APEX2 DUO CCD diffractometer, λ(MoKα) = 0.71073 Å, μ(MoKα) = 0.69 cm^{-1}, ω-scans, $2\theta < 54°$, and 6895 independent reflections (R_{int} = 0.0680) were used for the structure solution and refinement. Final R factors: R_1 = 0.0484 for 4423 observed reflections with $I > 2\sigma(I)$, wR_2 = 0.1135 and GOF = 1.012 for all the independent reflections.

Crystal data for **3**. $C_{36}H_{54}N_3OScSi_2$, M = 645.96, monoclinic, space group $C2/c$, at 120 K, a = 31.801(5), b = 20.422(3) and c = 13.143(2) Å, β = 108.147(3)°, V = 8111(2) Å^3, Z = 8, d_{calc} = 1.058 g cm^{-3}, $F(000)$ = 2784. Intensities of 42814 reflections were measured with a Bruker APEX2 DUO CCD diffractometer, λ(MoKα) = 0.71073 Å, μ(MoKα) = 2.68 cm^{-1}, ω-scans, $2\theta < 54°$, and 8848 independent reflections (R_{int} = 0.1709) were used for the structure solution and refinement. Final R factors: R_1 = 0.0589 for 4621 observed reflections with $I > 2\sigma(I)$, wR_2 = 0.1665 and GOF = 0.953 for all the independent reflections.

Using Olex2,[32] the structures were solved with the ShelXT[33] structure solution program using Intrinsic Phasing and refined with the XL[34] refinement package using Least-Squares minimization. Hydrogen atoms of the OH group in **1** and **2** were found in difference Fourier synthesis while positions of other hydrogen atoms were calculated, and they all were refined in the isotropic approximation within the riding model.

CCDC 2172172 (**1**), 2172173 (**2**) and 2172174 (**3**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* http://www.ccdc.cam.ac.uk.

saturation of the scandium coordination sphere due to Sc–NMe_2 interactions, makes this complex an excellent starting agent for other highly reactive scandium derivatives, including terminal imides.

In summary, two new tertiary tris(aryl)carbinols [*o*-$R_2NCH_2C_6H_4]_3COH$ [R = Me (**1**), R + R = $(CH_2)_5$ (**2**)] have been synthesized and characterized. Compounds **1** and **2** feature helical chirality and are present in the crystalline state in the form of two enantiomers, namely, left (M) and right (P) propellers. The hydroxyl groups in **1** and **2** form hydrogen bonds with one of the pendant NR_2 groups. Compound **1** readily reacts with $(Me_3SiCH_2)_3Sc(THF)_2$ to afford a THF-free alkoxy bis(alkyl) complex **3** in which the alkoxide anion adopts a κ^1-O, κ^2-N-coordination mode.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2022.11.023.

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