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Homoleptic yttrium and lanthanide complexes of aminotroponiminates and aminotroponates: experimental and theoretical studies

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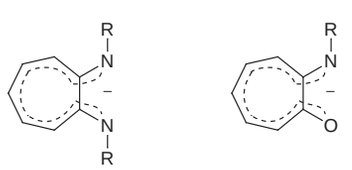
Density functional theory (DFT) calculations were performed for the homoleptic aminotroponiminate complexes $[Ln\{C_7H_5(NPr^i)_2\}_3]$ (Ln = Y or Sm) in order to get structural and energetic information about the possible isomers. The calculations predict a propeller-shaped chiral isomer of D_3 symmetry as lowest in energy. Two less stable isomers turned out to be stationary points of higher order. One is likely to be close to a structure acting as intermediate in the mechanism of rapid racemisation observed by NMR studies. Based on these results experimental and DFT computational studies of homoleptic lanthanide complexes with the new ligand system aminotroponate $C_7H_5(NPr^i)O^-$ were carried out. This related but asymmetric ligand results in a slower isomerisation and thus detection of the concerned species: ^{1}H NMR experiments showed an equilibrium of several $[Y\{C_7H_5(NPr^i)O\}_3]$ isomers in solution, in agreement with the computational results.

Recently there has been a significant activity in early transition-metal chemistry to replace cyclopentadienyl (or related systems) by other ligands for generating a similar steric and electronic environment.[1] For example, a number of metal complexes of the lanthanides and Group 3 elements has been synthesized in which cyclopentadienyl is replaced by anionic bidentate ligands such as amides,[2] benzamidinates,[3] diazadienes[4] or (alkoxydimethylsilyl)amides.[5] The benzamidinates in particular, which have been used for catalytic applications,[6] have steric properties similar to those of the cyclopentadienyl ligands. As a new alternative to these systems the aminotroponiminates $C_7H_5(NR)_2^-$ **A** have been introduced as cyclopentadienyl replacements for Group 3,[7] 4[8] and the lanthanide elements.[7] Lately, it was shown that yttrium aminotroponiminate amides, $[Y\{C_7H_5(NPr^i)_2\}\{N(SiMe_3)_2\}_2]$ and $[Y\{C_7H_5(NPr^i)_2\}_2\{N(SiMe_3)_2\}]$ are active as catalysts in hydroamination/cyclisation reactions.[9] Aminotroponiminate is a bidentate monoanion which features a 10π-electron backbone. Upon coordination it forms a five-membered metallacycle. Recently, we discovered that the homoleptic complexes $[Ln\{C_7H_5(NPr^i_2)_2\}_3]$ (Ln = Y, La or Sm) show a diastereotopic splitting of the isopropyl CH_3 signals in the ^{1}H and ^{13}C NMR spectra, confirming a chiral co-ordination sphere.[7] In order to obtain a better understanding of the structure and stability of the possible isomers in these systems we now report density functional theory (DFT) calculations of homoleptic $[Ln\{C_7H_5(NMe)_2\}_3]$ (Ln = Y or Sm). Based on these results we experimentally and theoretically investigated the related new system, aminotroponate $C_7H_5(NR)O^-$ **B** as a ligand for homoleptic lanthanide complexes. Again, the experimentally used ligand carried isopropyl groups at the nitrogen donor centre for better solubility, leading to $[Ln\{C_7H_5(NPr^i)O\}_3]$ (Ln = Y or Lu). Methyl groups were employed for the ensuing DFT investigations on the yttrium complexes, namely $[Y\{C_7H_5(NMe)O\}_3]$.



A **B**

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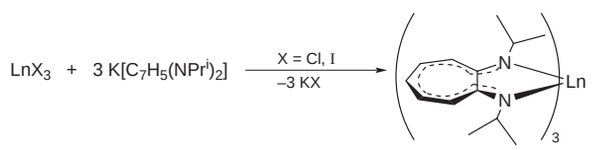


Scheme 1 Ln = Y **1a**, La **1b** or Sm **1c**

Results and Discussion

Aminotroponiminates

As we reported earlier, the homoleptic compounds $[Ln\{C_7H_5(NPr^i)_2\}_3]$ (Ln = Y **1a**, La **1b** or Sm **1c**) were obtained by transmetallation of $K[C_7H_5(NPr^i)_2]$ with anhydrous lanthanide trichlorides/triiodides in thf in a 3:1 molar ratio (Scheme 1).[7] Their ^{1}H and ^{13}C NMR spectra show a diastereotopic splitting of the isopropyl CH_3 signals, confirming chiral co-ordination around the metal centre. Since attempts to separate the ^{1}H NMR signals of the enantiomers of **1a** by addition of stoichiometric amounts of the chiral shift reagent $[Eu(hfc)_3]$ {hfc = 3-(heptafluoropropyl)hydroxymethylene-(+)-camphorate; camphor = 1,7,7-trimethylbicyclo[2.2.1]heptan-2-one} failed at room temperature and at −60 °C it is obvious that **1** have a stereochemical non-rigid structure in solution.

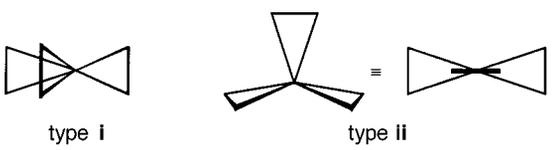
Density functional theoretical investigations have been carried out in order to determine the structure of the chiral product as well as to find an explanation for the fluxional behaviour observed in the NMR spectra. As an example, the trivalent ions Y^{3+} (f^0 electronic configuration) and Sm^{3+} (f^5 electronic configuration) have been used. Besides the molecular structures, the energy differences between the isomers of the yttrium- and samarium-centred complexes, respectively, could be evaluated. The $C_7H_5(NMe)_2^-$ ligand was substituted for the $C_7H_5(NPr^i)_2^-$ of **1** throughout the calculations in order to reduce the computational effort. The investigations were performed with the TURBOMOLE program system[10] by using the RIDFT program[11,12] with the Becke–Perdew (BP) functional[13] and the gridsizes m3 (Y) and m5 (Sm)[14] (see Theoretical).

The arrangement of three $C_7H_5(NMe)_2^-$ ligands around a central atom leads to the design of propeller-shaped molecules with either parallel wings (type **i**) or with one wing perpendicular to the two others (type **ii**). Both types are sketched in Scheme 2. A regular octahedron is prohibited by the 'bite' of

Table 1 Total energies E, energy differences ΔE and Ln–N distances (Ln = Y or Sm) of the calculated isomers **I**–**III** with yttrium or samarium trivalent central ions

Species	Central ion	Symmetry	Type	Ln–N/pm	E^a/au	ΔE^b/kJ mol^{-1}
Ia	Y^{3+}	D_3	**i**	238.7	−1414.762 970	0
IIa		C_{2v}	**ii**	238.3, 240.3	−1414.755 974	18.4
IIIa		C_{3h}	**i**	242.1	−1414.745 618	45.6
Ib	Sm^{3+}	D_3	**i**	247.9	−1411.141 647	0
IIb		C_{2v}	**ii**	246.9, 249.6	−1411.136 657	13.1
IIIb		C_{3h}	**i**	250.4	−1411.130 947	28.1

^{a} 1 au = 1 hartree = 2625.47 kJ mol^{-1}. ^{b} Energy difference with respect to the most stable isomer (**I**, D_3 symmetry).



Scheme 2 Representation of the two types of possible arrangements of three bidentate ligands around a metal centre. Type **i**: three parallel propeller wings. Type **ii**: one wing perpendicular to the two others

the bidentate ligand (2.62 Å); O_h symmetry cannot be achieved due to the low ligand symmetry anyway.

The DFT structure optimisations yielded three independent isomers with the optimised structures **I**, **II** or **III**, respectively (Fig. 1): **I** and **III** are of type **i**, **II** is of type **ii**. Only **I** (D_3 symmetry) has a chiral molecular structure, whereas **II** (C_{2v} symmetry) and **III** (C_{3h} symmetry) contain mirror planes disturbing chirality. Therefore, the last two were certainly not detected in the NMR investigations but could still be less stable structural isomers.

Table 1 contains the total energies E and energy differences ΔE of the three resulting isomers **I**–**III** for the yttrium complexes **Ia**–**IIIa**, and the analogous samarium complexes **Ib**–**IIIb**. Additionally, Y–N and Sm–N distances are given that increase (in average) with increasing values of the total energy. The propeller wings of **I** are rotated by $\varphi = 30.7°$ around the axis $Y–C_{apical}$. Therefore, the arrangement represents an intermediate position between trigonal prismatic ($\varphi = 0°$) and trigonal antiprismatic (octahedral, $\varphi = 60°$). The structure is lowest in energy and represents a local minimum on the energy hyperface.

As one result, we claim **I** to be the experimentally observed molecule. Another question to be answered is whether the two less stable isomers, **II** and **III**, play any role in the system. They show two imaginary frequencies each when performing second derivatives (see Theoretical), thus being stationary points of higher order. We are in no position to tell how far both structures are away from eventually existing transition states§ represented by exactly one imaginary frequency. However, for structural reasons mentioned below, we believe that they are fairly close to the structures of possible transition states. Therefore we would like to treat them as models for the unknown intermediate(s) of somewhat lower energy than **II** or **III**. Owing to the fact that racemisation takes place very rapidly compared to the NMR timescale, it is obviously not possible to resolve the NMR signals of the different isomers occurring during the inversion from one enantiomer to the other. Thus, the non-chiral species **II** or **III** (*i.e.* corresponding transition states) could represent non-detectable intermediates during the racemisation. Actually, both structures, a C_{3h} type and a C_{2v} type, are in principle known as transition states for the racemisation of tris(chelate) complexes, the occurrence of one of them being selected by the bite of the ligand.[15] Isomer **III** would be formed through the simultaneous −30.7° rotation of all propeller wings. Continuation of this movement would end up with the mirror image of **I**. The appearance of **II** is conceivable

§ There does not exist an algorithm for searching C_1 transition states in TURBOMOLE yet.

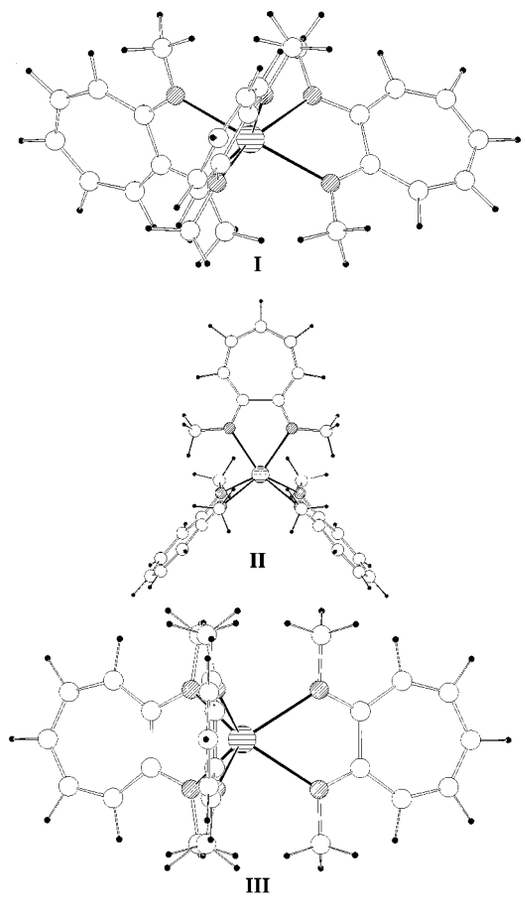


Fig. 1 Molecular structures of the calculated aminotroponiminate ligated isomers **I**–**III**, shown for the Y-centred compounds (**I** and **III**, type **i**; **II**, type **ii**). Y, Horizontal hatching; N, sloping hatching; C, open circles; H, filled circles. Isomer **I** is lowest in energy (see Table 1) and represents a local minimum on the energy hyperface; **II** and **III** represent stationary points of higher order

considering another pathway: one propeller wing is rotated about 59.3° into a horizontal position while the two others are vertical upon a 30.7° rotation in the opposite direction. Again, continuing these rotations, the mirror image of **I** is obtained.

However, for bidentate ligands with a bite of the reported value (2.62 Å), it cannot be predicted *a priori* which of the inversion mechanisms will be observed.[15] In order to discriminate between these pathways, the corresponding inversions of the yttrium complex **IIa** or **IIIa** were initialised through a very slight distortion in the desired direction. An optimisation run was performed afterwards, leading to a structure of **Ia** in either case. Since the initial distortions corresponded to the modes belonging to the imaginary frequencies, the significant part of the energy hyperface was analysed for both complexes. The course of the energy dependence on the rotation angle φ is given for both pathways in Fig. 2.

The distortions do not show an energy barrier in both cases,

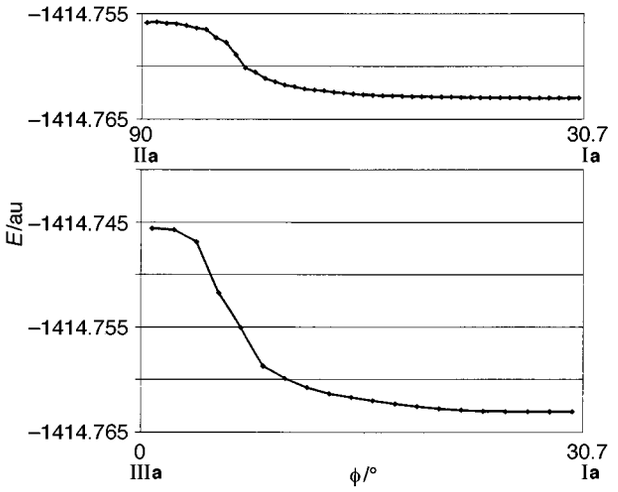
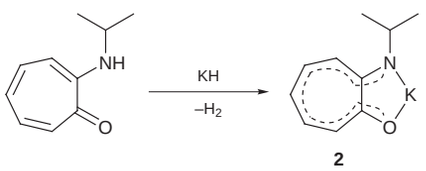


Fig. 2 Dependence of the total energy of yttrium complexes on the angle φ representing the rotation of one aminotroponiminate ligand. Top: inversion from **IIa** to **Ia**. Bottom: inversion from **IIIa** to **Ia**. For the transition **IIa** ⟶ **Ia** the φ values represent rotation of the ligand orientated perpendicular to the two others



Scheme 3

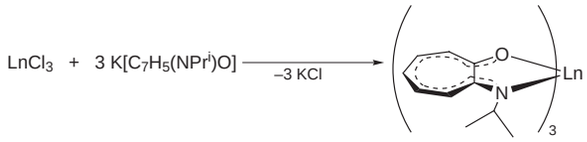
explaining the rapid racemisation. Obviously, the interaction of the methyl groups around the metal centre is sufficiently high for the less stable isomers that they immediately disappear after (potential) formation. From these results it seems to be more likely that the racemisation goes through an intermediate like **II** due to the lower energy difference to be surmounted throughout the rotations of the propeller wings.

Furthermore, it can be seen from the theoretical investigations that the energy differences of the respective isomers decrease with increasing ionic radius (Y^{3+}, 90; Sm^{3+}, 96 pm).[16] As one cannot expect to resolve signals caused by isomers separated by gross energy differences of less than 20 kJ mol^{-1} at room temperature,[17] it should be even more difficult to resolve the analogous NMR signals when going from yttrium (**1a**) to samarium (**1c**) or even lanthanum (**1b**).

Aminotroponates

Since tropones[18] and aminotroponiminates are known in organolanthanide chemistry, we were interested in the missing link between these two compounds, the aminotroponates, as ligands in organolanthanide chemistry. The potassium salt $K[C_7H_5(NPr^i)O]$ **2** was synthesized by treating the neutral ligand with an excess of KH in thf (Scheme 3). It was obtained as a very air-sensitive yellow powder characterized by ^1H and ^{13}C NMR spectroscopy. The spectra indicate the alkali-metal cation of **2** to be co-ordinated by one molecule of thf. This is in contrast to the analogous $K[C_7H_5(NPr^i)_2]$ compound in which no thf is co-ordinated.[7] In comparison to the neutral ligand,[8] the NMR signals of **2** show a slight upfield shift. The isopropyl C*H* resonance (δ 3.61) is shifted 0.19 ppm upfield upon metallation.

In order to investigate the co-ordination behaviour of $C_7H_5(NPr^i)O^-$ with yttrium and lutetium, the homoleptic compounds with three ligands attached to the metal centre were desired. Transmetallation of compound **2** with anhydrous lanthanide trichlorides in thf in a 3:1 molar ratio followed by work-up in toluene afforded the complex $[Ln\{C_7H_5(NPr^i)O\}_3]$ **3**



Scheme 4 Ln = Y **3a** or Lu **3b**

as pure crystalline solids in fairly good yield (Scheme 4). The products were characterized by mass, IR, ^1H and ^{13}C NMR spectroscopy and elemental analysis. For **3a** and **3b** molecular peaks were observed in the EI mass spectra.

Unlike the clear spectra of complexes **1**, the ^1H NMR spectra of **3a** and **3b** both show a broad multiplet (δ 0.8–1.5) for the isopropyl CH_3 signals indicating the presence of various energetically fairly well separated isomers. At higher temperatures (80 °C) the multiplet starts to merge into broad signals at δ 1.00 and 1.24, respectively. In contrast to the spectroscopic results for **1** (one fluctuating species), one observes two areas of coalescence in this case. This suggests the occurrence of two pairs of isomers that convert into each other through a fluxional behaviour of the ligand in solution. It is evident from the NMR spectra that an equilibrium between facial (*fac*) and meridional (*mer*) isomers is observed.[15,19] We performed DFT calculations for **3** better to understand the equilibrium properties of the isomers.

The molecular structures of the $[Y\{C_7H_5(NMe)_2\}_3]$ isomers **Ia**–**IIIa** were used as starting points for the calculation of the $[Y\{C_7H_5(NMe)O\}_3]$ compounds. For this, three O atoms were substituted for NCH_3 groups in the respective molecules. Owing to the two types of donor centres in the $C_7H_5(NR)O^-$ ligand, each of the three $C_7H_5(NR)_2^-$ ligated structures was so modified into two different $C_7H_5(NR)O^-$ starting compounds: one *fac* and one *mer* isomer (for type **ii** structures this nomenclature is used with respect to the two ligands orientated parallel). The less symmetric $C_7H_5(NR)O^-$ ligand caused a reduction of symmetry. Thus, the two derivatives of **III** show C_3 or C_1 symmetry, respectively, all other compounds had to be optimised in C_1.

Three independent isomers, **IV**–**VI** (Fig. 3), result from the DFT calculations: **IV** is of type **i**, **VI** corresponds to type **ii** and **V** shows a ligand arrangement inbetween. The respective energies and selected interatomic distances are given in Table 2. Owing to the size of the $C_7H_5(NR)O^-$ systems investigated, the calculation of second derivatives was not possible.

Species **IV** (*fac*) results from the structure optimisations of complexes derived from the type **i** compounds **I** or **III**, when the three remaining NCH_3 groups in the molecules are situated on one side of the propeller. The calculations in the point group C_3 or C_1 lead to the same isomer. The exchange of the O and the NCH_3 donor centre of one ligand causes convergence into a second isomer, **V** (*mer*), that is about 13 kJ mol^{-1} lower in energy. The (typical) energetic preference of the *mer vs.* the *fac* isomer[15] can in this case be rationalised by the position of the three methyl groups: in **IV** the steric interaction is higher, thus destabilising the structure. Isomer **V** is also obtained as the *mer* isomer when the starting compound was derived from the type **ii** molecular structure of **II**; **VI** (*fac*) represents the corresponding *fac* $C_7H_5(NR)O^-$ ligated species, being about 32 kJ mol^{-1} energetically disadvantaged.

Interestingly, two different *fac* isomers exist for the two complex types while one obtains only one and the same *mer* isomer, **V**. Accordingly, in **V**, the ligand arrangement does not unambiguously correspond to one of the types: the ligands are neither parallel nor perpendicular, but twisted by about three different values of φ, 2.7, 7.0 and 14.7°. The optimum orientation of the NCH_3 groups, two in *trans* positions and the remaining one pointing between them, permits one to rationalise the overall energetic preference of this 'hybrid' structure. The very fact that **V** results from three different starting structures

Table 2 Total energies E, energy differences ΔE and Y–N as well as Y–O distances of the calculated isomers **IV**–**VI** with an yttrium trivalent central ion

Species	Symmetry	Type	Y–N/pm	Y–O/pm	E/au	ΔE*/kJ mol^{-1}
IV	C_3	**i**	242.7	224.6	−1356.581 723	12.8
V	C_1	**i/ii**	238.5, 240.6, 241.8	225.1, 225.8, 226.3	−1356.586 577	0
VI	C_1	**ii**	240.7, 240.8, 244.4	224.2, 225.7, 227.0	−1356.574 519	31.7

* Energy difference with respect to the most stable isomer (**V**).

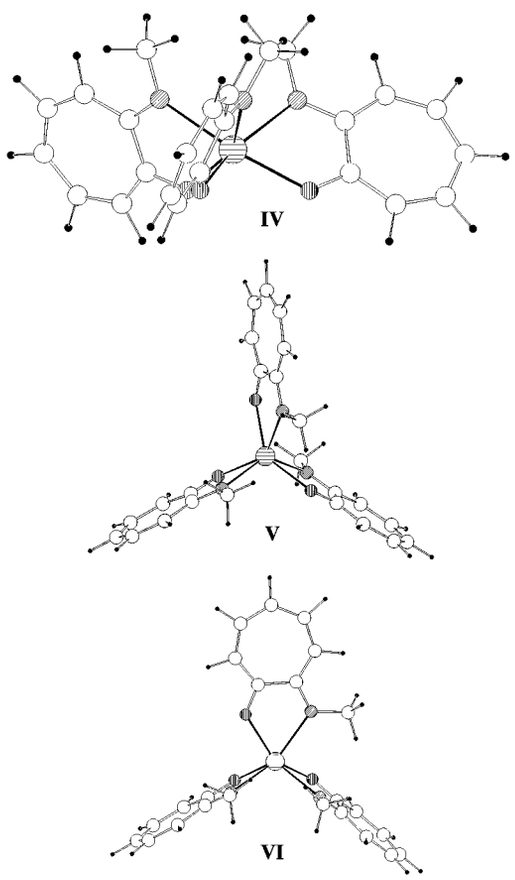


Fig. 3 Molecular structures of the calculated aminotroponate ligated isomers **IV**–**VI** (**IV**, type **i**; **VI**, type **ii**; **V**, 'hybrid'). Key as in Fig. 1 except: O, vertical hatching. Isomer **V** is lowest in energy (see Table 2)

(two corresponding to point group C_1)¶ can be taken as evidence that the compound represents a local minimum on the energy hyperface.

In contrast to the $C_7H_5(NR)_2^-$ complex system, the distortion of **VI** through the asymmetric ligand or even a distortion along the 'critical angles' analogous to the slight distortion of **II** does not cause ligand reorientation to give type **i** isomer **IV**. Owing to the presence of only three methyl groups (instead of six in **II**) at the metal centre, the isomer remains of type **ii** even without symmetry restraints. This result strongly indicates **VI** to be a minimum structure.

On the other hand, like the $C_7H_5(NR)_2^-$ complexes, the removal of the mirror plane in the species derived from **III**, as a consequence of the lower ligand symmetry, causes convergence into species **IV** (or **V**) derived from **I**. This possibly indicates a local minimum for **IV**. The steric demand of even three methyl groups (in the respective starting compounds) seems to be too large for the given arrangement of the ligands. The non-existence of a pseudo-C_{3h} symmetric isomer is in accordance with the fact that compound **III** is not a minimum and of relatively high energy. Thus, these (*pseudo*) C_{3h} symmetric species are obviously of minor or even no importance for both systems.

The observation of a multiplet in the room temperature NMR spectrum of compound **3** is consistent with several (three) chiral isomers representing local minima on the energy hyperface. Even though their total energies differ by only about 13 or 32 kJ mol^{-1} (see Table 2; compare to Table 1) the species can probably all be detected in the NMR experiment (*i.e.* 'slow' or stereochemically rigid[19] complexes). The reason for this will be energy barriers that separate the isomers well enough. After coalescence at 80 °C two domains of isomerising complexes remain. There are various possibilities of concerted isomerisations between species **IV**, **V** and **VI** or, if definite rotations are carried out twice, the respective enantiomers. Therefore we are not in a position to assign the signals in detail with confidence. Furthermore, at 80 °C, bond rupture processes are also conceivable, again increasing the number of possible isomerising pairs.[19]

Experimental

General

All manipulations of air-sensitive materials were performed with the rigorous exclusion of oxygen and moisture in flamed Schlenk-type glassware either on a dual-manifold Schlenk line, or interfaced to a high vacuum (10^{-4} Torr, *ca.* 1.33×10^{-2} Pa) line, or in an argon-filled Braun Atmospheres glove-box. Ether solvents (tetrahydrofuran and diethyl ether) were predried over sodium wire and distilled under nitrogen from Na/K alloy benzophenone. Hydrocarbon solvents (toluene and pentane) were distilled under nitrogen from sodium wire. All solvents for vacuum-line manipulations were stored *in vacuo* over Na/K alloy in resealable flasks. Deuteriated solvents were obtained from Aldrich Inc. (all 99 atom % D) and were degassed, dried, and stored *in vacuo* over Na/K alloy in resealable flasks. The NMR spectra were recorded on a Bruker AC 250 spectrometer. Chemical shifts are referenced to internal solvent resonances and reported relative to tetramethylsilane. The IR spectra were performed on a Bruker IFS 28, mass spectra at 70 eV ($\approx 1.12 \times 10^{-17}$ J) on a Varian MAT 711 spectrometer. Elemental analyses were performed in the microanalytical laboratory of the author's institute (S. Ariman).

Preparations

K[$C_7H_5(NPr^i)O$] 2. To a suspension of KH (610 mg, 15.3 mmol) in thf (20 cm^3) was slowly added $C_7H_5(NHPr^i)O$ (1.25 g, 7.7 mmol) in thf (30 cm^3) at −78 °C. The mixture was warmed to room temperature and stirred for 6 h. Then the remaining KH was filtered off and the solvent of the filtrate was removed in vacuum. The remaining yellow residue was washed with diethyl ether (3 × 50 cm^3) and dried in vacuum. Yield: 1.1 g (69%). ^{1}H NMR ([$^2H_8$]thf, 250 MHz, 25 °C): δ 1.07 [d, 6 H, CH_3, J(HH) = 6.2], 1.76 (m, thf), 3.57 (m, thf), 3.61 [m, 1 H, CH(CH_3)$_2$], 5.67 [t, 1 H, H^5, J(HH) = 9.0 Hz], 6.11–6.28 (dd, 2 H, H^{3,7}) and 6.38–6.52 (m, 2 H, H^{4,6}). ^{13}C-{^{1}H} NMR ([$^2H_8$]thf, 62.9 MHz, 25 °C): δ 23.9 (CH_3), 25.2 (thf), 49.1 [CH(CH_3)$_2$], 67.3 (thf), 112.7 (C^5), 114.2 (C^3), 114.8 (C^7), 132.6 (C^4), 134.1 (C^6), 164.5 (C^2) and 180.2 (C^1).

¶ The structure relaxation procedure implemented in TURBOMOLE is designed strictly to locate local minima in C_1 symmetry.

$[Ln\{C_7H_5(NPr^i)O\}_3]$ (Ln = Y 3a or Lu 3b) (general synthesis). Tetrahydrofuran (25 cm^3) was syringed at room temperature on to a mixture of $LnCl_3$ (0.5 mmol) and compound **2** (302 mg, 1.5 mmol) and stirred for 16 h at room temperature. The solvent was evaporated in vacuum and toluene added. Then the solution was filtered and the solvent removed. This procedure was repeated twice. The remaining solid was washed with pentane (10 cm^3) and recrystallised from thf–pentane (1 : 5).

Compound **3a**. Yield: 204 mg (71%). IR (KBr, cm^{-1}): 2964vs, 1602vs, 1569vs, 1508vs, 1439m, 1407vs, 1347m, 1265vs, 1222vs, 1166vs, 981vs, 877m and 721vs. ^{1}H NMR (C_6D_6, 250 MHz, 25 °C): δ 0.77–1.45 (m, 18 H, CH_3), 3.89 [m, 3 H, C*H*$(CH_3)_2$], 6.04 [d, 3 H, H^5, *J*(HH) = 11.2 Hz], 6.20–6.47 (m, 6 H, $H^{3,7}$) and 6.64–6.76 (m, 6 H, $H^{4,6}$). ^{13}C-{^{1}H} NMR (C_6D_6, 62.9 MHz, 25 °C): δ 22.5 (CH_3), 50.9 [*C*H$(CH_3)_2$], 118.3 (C^5), 118.7 (C^3), 120.0 (C^7), 135.4 (C^4), 136.2 (C^6), 167.5 (C^2) and 178.6 (C^1). EI mass spectrum: *m*/*z* 575 (M^+, 7), 413 ($[M - C_{10}H_{12}NO]^+$, 9) and 163 ($[C_{10}H_{13}NO]^+$, 100%) (Found: C, 61.98; H, 6.53; N, 6.91. Calc. for $C_{30}H_{36}N_3O_3Y$: C, 62.61; H, 6.30; N, 7.30%).

Compound **3b**. Yield: 212 mg (64%). IR (KBr, cm^{-1}): 2965vs, 1602vs, 1570vs, 1508vs, 1470s, 1407vs, 1437st, 1266vs, 1222vs, 1166s, 982vs, 845s and 722vs. ^{1}H NMR (C_6D_6, 250 MHz, 25 °C): δ 0.81–1.47 (m, 18 H, CH_3), 3.88 [m, 3 H, C*H*$(CH_3)_2$], 6.05 (m, 3 H, H^5), 6.20–6.25 (m, 6 H, $H^{3,7}$) and 6.65–6.74 (m, 6 H, $H^{4,6}$). ^{13}C-{^{1}H} NMR (C_6D_6, 62.9 MHz, 25 °C): δ 22.5 (CH_3), 50.9 [*C*H$(CH_3)_2$], 118.5 (C^5), 119.7 (C^3), 121.4 (C^7), 135.8 (C^4), 136.6 (C^6), 167.3 (C^2) and 175.3 (C^1). EI mass spectrum: *m*/*z* 661 (M^+, 100), 499 ($[M - C_{10}H_{12}NO]^+$, 98) and 163 ($[C_{10}H_{13}NO]^+$, 35%) (Found: C, 54.31; H, 5.99; N, 5.98. Calc. for $C_{30}H_{36}LuN_3O_3$: C, 54.46; H, 5.84; N, 6.35%).

Theoretical

The use of the DFT method has been tested on the $[Y\{C_7H_5(NMe)_2\}(NMe_2)_2]$ model compound in comparison to the $[Y\{C_7H_5(NPr^i)_2\}\{N(SiMe_3)_2\}_2]$ complex which was recently structurally determined by X-ray crystallography.[9] The deviation of the Y–N bond length to the $C_7H_5(NR)_2^-$ ligand amounted to 1.9 pm. As could be expected, the Y–N bond length to the more simplified ligand NMe_2 [*vs.* $N(SiMe_3)_2$] was calculated too short (Δ = 4.1 pm). The RIDFT program has been developed based on the DFT program,[11] approximating the coulomb part of the two-electron interactions.[12] Basis sets were of SVP quality[20] (split valence plus polarisation). For Y and Sm, relativistic corrected effective core potentials (ECPs) have been used to approximate inner electrons: Y, 28 core electrons (ECP-28);[21] Sm, 51 core electrons (ECP-51).[22] An ECP-51 contains all f electrons, thus treating no f electrons explicitly. This turned out to be appropriate for ionogene complexes. The calculations of the samarium-centred complexes are the first calculations of f-element compounds within the program system TURBOMOLE. Second derivatives were calculated from the reoptimised SCF structures using the program AOFORCE implemented in TURBOMOLE.

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