Potential Precursors for Terminal Methylidyne Rare-Earth-Metal Complexes Supported by a Superbulky Tris(pyzrazolyl)borato Ligand

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Abstract: A series of solvent-free heteroleptic terminal rare-earth-metal alkyl complexes stabilized by a superbulky tris(pyzrazolyl)borato ligand with the general formula \([\text{Tp}^\text{Bu,Me}_{\text{Ln}}\text{Me}]\) have been synthesized and fully characterized. Treatment of the heterobimetallic mixed methyl/tetramethylaluminate compounds \([\text{Tp}^\text{Bu,Me}_{\text{Ln}}\text{Me}][\text{MeAlMe}_4]\) \((\text{Ln} = \text{Y}, \text{Lu})\) with two equivalents of the mild halogenido transfer reagents \(\text{SiMe}_3\text{X} \quad (X = \text{Cl}, \text{I})\) gave \([\text{Tp}^\text{Bu,Me}_{\text{Ln}}\text{Me}]\) in high yields. The addition of only one equivalent of \(\text{SiMe}_3\text{Cl}\) to \([\text{Tp}^\text{Bu,Me}_{\text{Lu}}\text{Me}][\text{MeAlMe}_4]\) selectively afforded the desired mixed methyl/chloride complex \([\text{Tp}^\text{Bu,Me}_{\text{Lu}}\text{Me}]\). Further reactivity studies of \([\text{Tp}^\text{Bu,Me}_{\text{Lu}}\text{Me}]\) with \(\text{LiR}\) or \(\text{KR} \quad (R = \text{CH}_2\text{Ph}, \text{CH}_2\text{SiMe}_3)\) through salt metathesis led to the monomeric mixed-alkyl derivatives \([\text{Tp}^\text{Bu,Me}_{\text{Lu}}\text{Me}]\text{Me}(\text{CH}_2\text{SiMe}_3)\) and \([\text{Tp}^\text{Bu,Me}_{\text{Lu}}\text{Me}]\text{Me}(\text{CH}_2\text{Ph})\), respectively, in good yields. The \(\text{SiMe}_4\) elimination protocols were also applicable when using \(\text{SiMe}_3\text{X}\) featuring more weakly coordinating moieties (here \(X = \text{OTf}, \text{NTf}_2\)). X-ray structure analyses of this diverse set of new \([\text{Tp}^\text{Bu,Me}_{\text{Ln}}\text{Me}]\text{Me}\) compounds were performed to reveal any electronic and steric effects of the varying monoanionic ligands \(R\) and \(X\), including exact cone-angle calculations of the tridentate tris(pyrazolyl)borato ligand. Deeper insights into the reactivity of these potential precursors for terminal alkylidene rare-earth-metal complexes were gained through NMR spectroscopic studies.

Introduction

Terminal transition-metal carbene and alkylidene complexes are of fundamental importance in organometallic chemistry/catalysis and organic synthesis.\(^{[1]}\) In contrast, discrete terminal rare-earth-metal (Ln) alkylidene complexes of the type \(\text{LLn}[\text{R}]\) \((\text{R} = \text{H} \text{or hydrocarbon substituent}; \text{L} = \text{monoaionic ancillary ligand})\) have remained elusive,\(^{[2]}\) which is mainly attributed to the dominance of \(\text{Ln} = \text{C}\) [ionic bonding and hence pronounced tendency for intermetallic bridging.\(^{[3]}\) Nonetheless, such bridging alkylidene moieties were accessed in mixed methyl/methylidene,\(^{[4]}\) methyl/chloride,\(^{[5]}\) cubane-like methylidene complexes,\(^{[6]}\) and the first four-coordinate methandiide alkyl lutetium complex.\(^{[7]}\) Also, Lewis acid-stabilized\(^{[8]}\) or pincer-like rare-earth-metal alkylidene complexes\(^{[9]}\) have been reported. Recent advances in the latter areas are represented by the syntheses of the first bridged bis-alkylidene scandium complex,\(^{[10]}\) a non-pincer-type mononanionic phosphinoalkylidene scandium complex,\(^{[11]}\) and silyl-thiophosphinoyl alkylidene as well as phosphinomethylidene rare-earth-metal compounds.\(^{[12]}\) By nature, higher-valent transition-metal chemistry draws upon alternative approaches to access terminal alkylidynes. For example, in 2017, Mündola and co-workers isolated the first terminal titanium methylidene complex \(\text{[PN]}\text{Ti}(-\text{CH}_2\text{H})\) by treating \(\text{[PN]}\text{Ti}(-\text{CH}_2\text{H})\text{OTf}\) \((\text{I, PN} = \text{N}(2-(\text{diisopropylphosphino})-4\text{-methylphenyl})-2,6\text{-trimethylphenanilide})\) with the Wittig reagent \(\text{H}_2\text{CP}_2\text{H}_3\). This protocol involves the abstraction of the weakly coordinating OTf group \((\text{OTf} \equiv \text{CF}_3\text{SO}_{3})\) and formation of the reactive \(\text{Ti}(-\text{CH}_2\text{H})\text{OTf}\) (Scheme 1, path A). Another prominent example in transition-metal methylidene chemistry is the reaction behavior of \(\text{[CR}_2\text{Ti}(-\text{CH}_2\text{R})_2]\) \((\text{II}, \text{CP} = \text{C}_2\text{H}_5, \text{R} = \text{H}, \text{SiMe}_3, \text{Ph})\) during thermolysis.\(^{[13]}\) Petasis et al. found this compound to be an olefination agent for carboxylic derivatives. Therefore, terminal alkylidyres \(\text{[CR}_2\text{Ti}(-\text{CHR})]\) were proposed as reaction intermediates (Scheme 1, path B), similar to the effective metathesizing species \(\text{Tebbe reagent.}\(^{[14]}\) Although Petasis et al. could not confirm their proposal by X-ray diffraction analysis (neither did Tebbe et al.), methane elimination during thermolysis and further reactivity studies substantiated their proposal of an intermediate methylidene moiety. Additionally, mixed alkyl titanocene, for example, \(\text{[CR}_2\text{Ti}(-\text{CH}_2\text{SiMe}_3)]\)\(^{[15]}\) showed the abili-
Results and Discussion

In search of potential precursors for terminal Ln(III) alkylidene chemistry we focused on monomeric compounds \([\text{Tp}^\text{Bu,Me} \text{LnMe}](\text{AlMe}_3)]\) \((\text{Ln} = \text{Y}, \text{Lu})\) and \([\text{Tp}^\text{Bu,Me} \text{LuMe}_2]\) supported by the superbulky scorpionate ligand \(\text{Tp}^\text{Bu,Me}\) (hydrotris(3-tert-butyl-5-methylpyrazolyl)borato). Importantly, Piers et al. and Takats and co-workers reported similar complexes featuring \([\text{Tp}^\text{L-indenyl} \text{Sc}(\text{CH}_3\text{SiMe}_3)\text{yr}(\text{THF})]\) \((\text{R} = \text{Me}, \text{R}_2 = \text{H}; \text{R} = \text{Bu}, \text{R}_2 = 0)\). Importantly, Piers et al. and Takats and co-workers reported similar complexes featuring \([\text{Tp}^\text{L-indenyl} \text{Sc}(\text{CH}_3\text{SiMe}_3)\text{yr}(\text{THF})]\) \((\text{R} = \text{Me}, \text{R}_2 = \text{H}; \text{R} = \text{Bu}, \text{R}_2 = 0)\). These complexes showed a broadened signal at \(\delta = 0.26\) ppm for the terminal methyl moiety, not indicative of any \(\text{Y}-\text{H}\) coupling. To further investigate this behavior, a low-temperature \(^1\text{H}\) NMR spectroscopy study was carried out (Figure S2 in the Supporting Information).

“Half-sandwich” triflate complexes

In accordance to Scheme 1/path A/complex I, we anticipated the introduction of trifluoromethanesulfonamide (OTf) or the even weaker coordinating trifluoromethanesulfonimido (N(SO\(_2\)CF\(_3\))\(_2\)) or NTf\(_2\) ligands to be feasible through mild trimethylsilyl-based transfer reagents SiMe\(_3\)X (X = OTf, NTf). Therefore, the scorpionate-supported hydrocarbonyl complexes \([\text{Tp}^\text{Bu,Me} \text{YMe}(\text{AlMe}_3)]\) and \([\text{Tp}^\text{Bu,Me} \text{LuMe}_2]\) were treated with one or two equivalents of SiMe\(_3\)X, respectively, in toluene (Scheme 2).

In particular, given that the yttrium derivatives are extremely temperature sensitive, careful adjustment of the reaction conditions was required to afford complexes \([\text{Tp}^\text{Bu,Me} \text{LnMe}(\text{OTf})]\) \((\text{Ln} = \text{Y}, \text{Lu})\), \([\text{Tp}^\text{Bu,Me} \text{Lu}(\text{OTf})]\) \((2-\text{Lu})\), \([\text{Tp}^\text{Bu,Me} \text{LuMe}(\text{NTf})]\) \((3-\text{Lu})\), and \([\text{Tp}^\text{Bu,Me} \text{Lu}(\text{NTf})]\) \((4-\text{Lu})\). The ambient-temperature \(^1\text{H}\) NMR spectra of the diamagnetic compounds 1–4 showed only one set of signals for the pyrazolyl groups of the \(\text{Tp}^\text{Bu,Me}\) ligand with chemical shifts similar to those of the starting compounds (spectral data are presented in the Supporting Information). This indicates a highly fluxional behavior, which is in accordance with previous studies on complex \([\text{Tp}^\text{Bu,Me} \text{LuMe}(\text{AlMe}_3)]\). However, these previous studies also reported that similar complexes behave differently at lower temperatures, with the pyrazolyl rings revealing a 2:1 splitting in the \(^1\text{H}\) NMR spectra in accordance with the \(C_5\) symmetry of these complexes in the solid state. For 1-\text{Lu} and 3-\text{Lu}, the Lu-bound Me groups gave sharp singlets at \(\delta = 0.39\) and 0.14 ppm, respectively.

The ambient-temperature \(^1\text{H}\) NMR spectrum of 1-\text{Y} in \(\text{C}_6\text{D}_6\) showed a broadened signal at \(\delta = 0.26\) ppm for the terminal methyl moiety, not indicative of any \(\text{Y}-\text{H}\) coupling. To further investigate this behavior, a low-temperature \(^1\text{H}\) NMR spectroscopy study was carried out (Figure S2 in the Supporting Information).
mation). Due to solubility issues in toluene at temperatures below 20 °C and rapid decomposition of complex 1-Y in [D₆]toluene. Remarkably, the chosen NMR solvent “mixture” showed a strong influence on the chemical shift of the Y–Me moiety at low temperature, revealing a doublet at δ = 0.13 ppm (J(Y–C) = 1.5 Hz) markedly shifted to higher fields compared with 1-Y in [D₆]benzene (δ = 0.26 ppm, Figure S1, Supporting Information). The ¹H–¹⁹F HSQC NMR spectrum of 1-Y at 0 °C shows a cross peak at δ = 515 ppm on the ¹⁹F NMR scale (Figure 1), which is shifted to higher field in comparison to precursor [TpᵗBu,MeLuMe(AlMe₄)] (δ = 798 ppm). The ¹H–¹⁹Y HSQC NMR spectrum of 1-Y at 0 °C shows a cross peak at δ = 515 ppm on the ¹⁹Y NMR scale (Figure 1), which is shifted to higher field in comparison to precursor [TpᵗBu,MeLuMe(AlMe₄)]. The fluorine-containing complexes 1-Ln, 2-Lu, 3-Lu, and 4-Lu showed one set of signals for the TpᵗBu,Me ligand but ¹³C resonances of the CF₃ groups could not be detected, which is consistent with already reported compounds. Notwithstanding, the presence of OTf and NTf₂ moieties was unambiguously evidenced by ¹⁹F NMR spectroscopy revealing one sharp resonance at δ = −78.0, −78.1, −77.5, −77.9, and −76.9 ppm each for complexes 1-Y, 1-Lu, 2-Lu, 3-Lu, and 4-Lu, respectively.

X-ray crystallographic structure determinations were performed on 1-Lu, 3-Lu, and 4-Lu (Figure 2, Table 1). The five-fold-coordinated lutetium centers of the methyl complexes [TpᵗBu,MeLuMeX] (X = OTf, 1-Lu; NTf₂, 3-Lu) adopt a distorted trigonal-bipyramidal coordination geometry. Moreover, the typically observed κ⁴ coordination of the ancillary ligand is adopted. In comparison with the reactant [TpᵗBu,MeLuMe₂][24], the Lu–O₁ distances for 1-Lu (2.191(3) Å) are significantly shorter than those reported before for eightfold-coordinated [CpLu(OTf₂)₂(THF)]₃[26] (2.237(4), 2.213(4) Å) and [Lu(OTf)₃(OPPh₃)₄][25a] (2.202(6), 2.232(5) Å) featuring likewise monodentate triflato ligands. Similarly, the Lu–O₁ distance in bidentate eightfold-coordinated complex [(bmpyr)Lu(NTf₂)₂][27] (bmpyr = 1-butyl-1-methylpyrrolidinium) (av. 2.30 Å) is elongated compared with that in 3-Lu (2.243(1) Å). The presence of the electron-withdrawing triflato moieties implies also slightly shorter Lu–C(Me) distances of 1-Lu (2.327(4) Å) and 3-Lu (2.323(2) Å) than those in the precursor [TpᵗBu,MeLuMe₂][24] (2.364(3)/2.375(2) Å). Despite several achievements on the structural characterization of various Tp-supported Ln–OTf complexes,[28] mixed Me/OTf and Me/NTf₂ structural motifs have not yet been identified. So far, the structurally authenticated complexes comprise “sandwich complexes” exclusively.
sandwich complexes of the type \((\text{C}5\text{Me}_4\text{SiMe}_3)\text{LnMe}_2\)\(_3\) were HR analog to Petasis (see Scheme 1/path intramolecular elimination of either methane or the respective aged alkylidene species following a thermal or donor-induced dehydration and bidentate NTf\(_2\) ligand (Figure 2, right). The Lu–O(triflato) distances range from 2.2213(1) to 2.2885(1) Å.

To target the envisaged LnMeX to Ln = CH\(_2\) transformation (see Scheme 1/path A) complexes [Tp\(_{Bu,Me}\)MeLuMeX] (X = OTf, Lu; Tnf\(_{Bu,Me}\), 3-Lu) were treated with one equivalent of H\(_2\)CPPh\(_3\) in D\(_2\)benzene. Unfortunately, no reactivity was observed at ambient temperature. Further heating the reaction mixture to 50 °C led to methane elimination through C–H bond activation involving the \(\text{Bu}\) methyl groups of the ancillary ligand and the Lu–CH\(_2\) moiety, as observed previously.\(^{[17]}\) This intramolecular C–H bond activation could not be prevented by addition of N- or O-donors like 4-dimethylaminopyridine (DMAP) and tetrahydrafuran (THF).

Generation of di(halogenido) and mixed methyl/halogenido and methyl/alkyl complexes

Further efforts to generate Ln\(^{11}\) alkylidenes led to the idea of targeting mixed methyl/alkyl (Me/R) complexes [Tp\(_{Bu,Me}\)LuMeR]. The latter might be convertible to the envisaged alkylidene species following a thermal or donor-induced intramolecular elimination of either methane or the respective HR analog to Petasis (see Scheme 1/path B). Note that half-sandwich complexes of the type \([\text{C}_n\text{Me}_6\text{SiMe}_3\text{LnMe}_2]\)\(_3\) were previously shown to undergo such reactions affording tetrametallic cuboid clusters \([\text{C}_n\text{Me}_6\text{SiMe}_3\text{Ln}(\text{Me}_1\text{CH}_2)]_n\) (Ln = Tm, Lu),\(^{[30]}\) Preliminary NMR-scale reaction studies probing the olefination capability of [Tp\(_{Bu,Me}\)LuMe\(_2\)] toward 9-fluorenone at 50 °C (according to Petasis) indicated the exclusive formation of the respective alkoxide species. Therefore, to evade such preferential nucleophilic attack of the methyl moiety at the carbonyl functionality, the initial formation of an alkylidene species was envisaged. To provide a more versatile platform for further derivatization reactions, the above-mentioned precursors [Tp\(_{Bu,Me}\)MeLuMe\(_2\)] and [Tp\(_{Bu,Me}\)LuMe\(_2\)] were treated with one equivalent of SiMe\(_3\)X (here X = Cl, I) in toluene for the generation of mixed alkyl/halogenido compounds as depicted in Scheme 3.

| Ln | 1-Lu (X = Me, X' = O) | 2-Lu (X = Me, X' = O) | 3-Lu (X = X' = Cl) | 4-Lu (X = X' = Cl) | 5-Lu (X = Me, X' = Cl) | 6-Lu (X = X' = I) | 7-Lu (X = Me, X' = Cl) | 8-Lu (X = Me, X' = CH\(_3\)) | 9-Lu (X = Me, X' = CH\(_3\)) |
|---|---|---|---|---|---|---|---|---|---|
| Lu–N2 | 2.376(3) | 2.376(3) | 2.311(2) | 2.391(6) | 2.298(3) | 2.313(9) | 2.352(2) | 2.310(2) | 2.310(2) |
| Lu–N4 | 2.299(3) | 2.299(3) | 2.260(2) | 2.306(3) | 2.293(3) | 2.413(1) | 2.353(2) | 2.323(2) | 2.323(2) |
| Lu–N5/6' | 2.309(4) | 2.309(4) | 2.3108(2) | 2.306(3) | 2.378(3) | 2.313(9) | 2.487(2) | 2.466(2) | 2.466(2) |
| Lu–X | 2.374(7) | 2.323(2) | 2.2820(1) | 2.4916(2) | 2.4867(4) | 2.393(1) | 2.343(2) | 2.343(2) | 2.343(2) |

Unfortunately, for yttrium and the combination Lu/I only the di(halogenido) derivatives [Tp\(_{Bu,Me}\)YCl\(_2\)] (5-Y), [Tp\(_{Bu,Me}\)YI\(_2\)] (6-Y), and [Tp\(_{Bu,Me}\)LuI\(_2\)] (6-Lu) could be isolated, evidencing extensive ligand redistribution. It is noteworthy that the synthesis and isolation of such di(halogenido) “half-sandwich” complexes has been formerly assessed as problematic because of the occurrence of ligand redistribution reactions and B–N bond cleavage (formation of pyrazole adducts), in particular for complexes derived from Tp\(_{Bu,Me}\)[29]. The few monomeric complexes [Tp\(_{Bu,Me}\)Ln(halogenido)]\(_2\) authenticated by X-ray structure analysis include THF adducts [Tp\(_{Bu,Me}\)LnCl\(_2\)(THF)] and [Tp\(_{Bu,Me}\)LnI\(_2\)(THF)], as well as N-donor stabilized [Tp\(_{Bu,Me}\)LnCl\(_2\)(dpmpz\(_2\))],\(^{[30]}\) [Tp\(_{Bu,Me}\)YCl\(_2\)](dpmpz\(_2\)) (dpmpz\(_2\): dimethylpyrazole, 1,10-phen: 1,10-phenanthroline, bipyy: 2,2'-bipyridine),\(^{[31]}\)

MUCH to our delight, the combination Lu/Cl gave the desired mixed methyl/chloride complex [Tp\(_{Bu,Me}\)LuMeCl] (7-Lu), in addition to the (chlorido) derivative [Tp\(_{Bu,Me}\)LuCl\(_2\)] (5-Lu, two-equivalent reaction). All halide complexes exhibit low solubility which facilitated their isolation through crystallization (5-Y, 6-Y, 6-Lu, 7-Lu) or precipitation (5-Lu) from toluene solutions. Single crystals of 6-Lu and 7-Lu were grown from saturated toluene solutions at −35 °C, whereas 5-Lu was crystallized from THF at −35 °C. The \(^1\)H and \(^{13}\)C NMR spectroscopic data for all compounds clearly showed only one set of signals for the pyrazolyl groups of the ancillary ligand. In comparison with 1-Lu and 3-Lu, the proton NMR spectrum of 7-Lu shows a sharp singlet of the Lu–Me moiety located at δ = 0.29 ppm, and hence shifted slightly to lower field. Overall, the Lu–N(pz)
Lu

than in C(methyl) bond length of 2.393(1)/C138 in 7-Lu/C0

respectively, reflecting the size of the halogenido anion. The Lu

vents, all subsequent reactions were carried out in toluene.

solvents and unintended C

7-Lu

Scheme 4). Due to the low solubility of

metathesis reactions with different alkali-metal alkyls

7-Lu

methyl/chloride lutetium complex

caused by the presence of the methyl ligand.

bond of 2.526(4)/C138 in 3-Lu/C0

are comparable to those found for 1-Lu, 3-Lu, and 4-Lu. The

Lu–X distances in the di(halogenido) derivatives [Tp

Bu,MeLuCl2] (5-Lu) and [Tp

Bu,MeLuMe] (6-Lu) average 2.493 and 2.873 Å, respectively, reflecting the size of the halogenido anion. The Lu–

C(methyl) bond length of 2.393(1) Å in 7-Lu is slightly longer than in [Tp

Bu,MeLuMe]2[24] (2.364(3)/2.375(2) Å) and complexes 1-Lu and 3-Lu (see Table 1). Striking is the elongated Lu–Cl

bond of 2.526(4) Å in 7-Lu compared with 5-Lu, apparently caused by the presence of the methyl ligand.

Aiming at mixed methyl/alkyl compounds, the mixed

methyl/chloride lutetium complex 7-Lu was examined in salt-

metathesis reactions with different alkali-metal alkyls

(Scheme 4). Due to the low solubility of 7-Lu in other nonpolar solvents and unintended C–H bond activation in donor solvents, all subsequent reactions were carried out in toluene.

The mixed alkyl complex [Tp

Bu,MeLuMe(CH2SiMe3)] (8-Lu) was obtained by reacting 7-Lu with LiCH2SiMe3. Due to the thermal lability of 8-Lu, the reaction was performed at temperatures below 0 °C. Such low temperatures are also beneficial to the

use of Li salts because conducting the involved metathesis re-

actions at ambient temperature favors the formation of

LiTp

Bu,Me[20] in contrast, the mixed methyl/benzyl complex

[Tp

Bu,MeLuMe(CH2Ph)] (9-Lu) is thermally stable, but a pro-

longed reaction time is crucial when reacting 7-Lu with potassium benzyl. For both mixed bis(alkyl) complexes 8-Lu and 9-

Lu, the 1H and 13C NMR spectra show only one set of signals for the pyrazolyl groups. The Ln-bound methyl groups appeared as narrow singlets at δ = 0.19 (8-Lu) and 0.39 ppm (9-

Lu). In agreement with literature reports, the methylene moieties of the neosilyl and benzyl ligand feature distinctly shifted

signals at δ = −0.71 and 1.63 ppm, respectively, attributable to a strong electronic influence of the SiMe3/Ph groups.

Complexes 8-Lu and 9-Lu were crystallized from saturated toluene solutions at −35 °C and their solid-state structures ana-

lyzed by X-ray crystallography (Figure 4). As commonly ob-

served for LnIII-Tp

Bu,Me complexes with coordination number 5, both complexes adopt a distorted trigonal-bipyramidal geometry. The pyrazolyl nitrogen atoms N2 and N4 and the methyl carbon C25 reside in the equatorial plane, whereas the methyl-

carbon atom C26 and the pyrazolyl nitrogen atom N6 occupy the axial positions. In comparison with complexes 1-Lu and 3-Lu the Lu–N(pz) bond lengths are slightly elongated for the mixed alkyl compounds 8-Lu (2.352(2)/2.487(2) Å) and 9-

Lu (2.310(2)/2.466(2) Å).

Furthermore, the Lu–C(Me) distances of 8-Lu (2.343(2) Å) and 9-Lu (2.349(3) Å) lie in between those of 1-Lu/3-Lu and 7-

Lu (Table 1). In accordance with literature, the Lu–C(neosilyl)

bond length of 8-Lu of 2.372(2) Å is in the same range as de-

dected for Lu(CH2SiMe3)2(THF)3[32] (2.314(18)/2.344(18) Å) and Tp

Me,MeLu(CH2SiMe3)2(THF) (2.373(2)/2.379(2) Å).[21] Other rare solid-state structures of monomeric but heteroleptic Tp-based rare-earth-metal complexes as [Tp

Lu(Danip)(CH2SiMe3)] (R = Me or R = H, Ln = Yb, Danip = 2,6-di(o-anisole)phenyl) display similar bond lengths (Yb–C

= 2.414(3)/2.438(4)/2.402(4).

Figure 3. ORTEP representation of the molecular structures of 5-Lu (left), 6-Lu (middle), and 7-Lu (right) with atomic displacement parameters set at the 50

level. Hydrogen atoms except for BH and solvent THF are omitted for clarity. Selected bond lengths are given in Table 1.
Hydrogen atoms except for BH and CH2 are omitted for clarity. For 9-Lu (bottom) with atomic displacement parameters set at the 50% level. Chem. Eur. J. 2019 (2.380(3)–2.404(3)/C138) but is slightly elongated compared with 2.435(5)/C138; Yb/C0.

Figure 4. ORTEP representation of the molecular structures of 8-Lu (top) and 9-Lu (bottom) with atomic displacement parameters set at the 50% level. Hydrogen atoms except for BH and CH2 are omitted for clarity. For 9-Lu the disorder in one tBu group and toluene are omitted for clarity. Selected bond lengths are given in Table 1.

The Cp*Lu(CH2Ph)2(THF) (2.378(2)–2.386(2)/C138; Cp* = C5Me5). Fur-[Tp Me,MeYCl2(THF)2] was obtained through salt metathesis of N- or O-donor molecules such as DMAP or THF, but failed kylidenes through intramolecular deprotonation led to the use of N- or O-donor molecules such as DMAP or THF, but failed kylidenes through intramolecular deprotonation led to the use of various donors. In accordance with other already reported degradation processes, we assume C–H-bond activation of one tert-butyl group or B–N bond cleavage to be responsible for the formation of multiple unidentified metal complexes in these reaction mixtures. It is also noteworthy, that the di(chlorido) derivative [TpBuMe5LuCl2] (5-Lu) does not undergo any “Tebbe-like” reaction with AlMe3 at ambient temperature, but leads to unidentified complicated reaction mixtures (ancillary ligand degradation) at elevated temperatures (T = 50°C).

In spite of these sobering findings, the successful isolation of mixed alkyl complexes 8-Lu and 9-Lu spurred our interest in the evaluation of the steric effects on the ancillary TpBuMe ligand caused by the distinct triflato, halogenido, or alkyl co-ligands. According to a method recently reported by our group, we calculated the exact ligand cone angles Θ for the procedure is given in the Supporting Information. According to Allen and co-workers, the term “exact” refers to the acute mathematical solution and does not reflect the accuracy of the input structure itself. As a prerequisite for meaningful interpretations, the metal centers should have the same coordination number (CN, here 5) and the same overall charge. A general overview of the determined cone angles is summarized in Table 2.

Next, we examined whether complexes 8-Lu and 9-Lu are capable of intramolecular deprotonation and alkane elimination (see Scheme 1/path B). As mentioned before, [TpBuMe5LuMe(CH2SiMe3)] is temperature-sensitive. After one day at ambient temperature, a solution of complex 8-Lu in [D8]benzene turned from colorless to yellow. Monitoring this behavior with 1H NMR spectroscopy revealed degradation of the ancillary ligand as indicated by different new pyrazolyl signals and methane evolution. Further attempts at generating alkyldienes through intramolecular deprotonation led to the use of N- or O-donor molecules such as DMAP or THF, but failed for the same reasons. Although compound 9-Lu is stable in solution in [D8]benzene at ambient temperature, heating to 40°C for 4 h also led to degradation of the ancillary ligand, as did the utilization of various donors. In accordance with other already reported degradation processes, we assume C–H-bond activation of one tert-butyl group or B–N bond cleavage to be responsible for the formation of multiple unidentified metal complexes in these reaction mixtures. It is also noteworthy, that the di(chlorido) derivative [TpBuMe5LuCl2] (5-Lu) does not undergo any “Tebbe-like” reaction with AlMe3 at ambient temperature, but leads to unidentified complicated reaction mixtures (ancillary ligand degradation) at elevated temperatures (T = 50°C).

Conclusions

Aiming at new synthesis protocols for terminal rare-earth metal alkyldiene complexes, we gained access to unprecedented mono-tris(pyrazolyl)borate complexes. Following TMS-elimination protocols by applying complexes [TpBuMe5Me][AlMe3]

| 1-Lu | 3-Lu | 6-Lu | 7-Lu | 8-Lu | 9-Lu |
|------|------|------|------|------|------|
| 280.9 | 280.4 | 278.2 | 278.9 | 277.1 | 277.3 |

[a] directly determined from atomic positions.

The TpBuMe5 ligand engages in an exclusive trigonal-bipyramidal coordination geometry at the Lu complexes under study, and hence, very similar cone angles (Θ = 277.1 to 280.9° for CN = 5) were calculated. For 1-Lu, two different cone angles are displayed due to the respective disorder in one tert-butyl group. Nonetheless, the noticeable trend makes complexes with mixed alkyl co-ligands the least sterically demanding, followed by the di(halide) complexes, whereas the weakly coordinating triflato or triflimido moieties allow for the largest cone angles. Another important finding is that the mathematically exact method determines cone angles distinctly higher than those reported for TpBuMe5 complexes in the literature (Θ = 244°). Therefore, further efforts should be expended to build up a library for better comparison.

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and [Tp\textsubscript{Bu,Me}LuMe\textsubscript{2}] along with SiMe\textsubscript{3}X (X = OTf, NTF\textsubscript{2}), the superbulky ligand Tp\textsubscript{Bu,Me} supports the formation of mixed methyl triflate and mixed methyl triffimide complexes of yttrium and lutetium as new structural motif in rare-earth-metal chemistry. Moreover, similar reactions employing SiMe\textsubscript{3}X (X = Cl, I) afforded not only unsolvated d(halide) complexes Tp\textsubscript{Bu,Me}LnX\textsubscript{2} but also the mixed methyl/chloride complex [Tp\textsubscript{Bu,Me}LuMeCl]. The latter gave efficient access to mixed alkyl complexes [Tp\textsubscript{Bu,Me}LuMe(CH\textsubscript{2}Ph)] and through salt-metathesis reactions with different alkali-metal salts. Unfortunately, neither reactivity studies utilizing the Wittig reagent nor the attempted thermally-induced intramolecular deprotonation afforded rare-earth-metal alkylidene compounds. It seems that terminal alkylidene devoid of Lewis acid stabilization are not accessible/isolable in the presence of this very Tp\textsubscript{Bu,Me} ligand, which engages preferably in intramolecular B–N- and C–H-bond activation processes. Ongoing research focuses on tripodal ancillary ligand systems which are less prone to degradation and C–H-bond activation.

**Experimental Section**

All operations were performed under rigorous exclusion of air and water by using standard Schlenk, high-vacuum, and glovebox techniques (MBraun 2008; <0.1 ppm O\textsubscript{2}, <0.1 ppm H\textsubscript{2}O). Solvents were purified by using Grubbs-type columns (MBraun SPV, solvent purification system) and stored inside a glovebox. [D\textsubscript{6}]Benzene was dried over NaK alloy for two days and [D\textsubscript{8}]toluene was obtained from Sigma–Aldrich, stirred over NaK alloy, and distilled. [D\textsubscript{8}]Benzene was dried over NaK alloy for two days and [D\textsubscript{8}]toluene was obtained from Sigma–Aldrich, stirred over NaK alloy, and distilled. SiMe\textsubscript{3}Cl, trimethylsilyl trifluoromethanesulfonate (Me\textsubscript{3}SiOTf), and (trimethylsilyl)methyllithium (LiCH\textsubscript{2}SiMe\textsubscript{3}) solutions were purchased from Sigma Aldrich, stirred over NaK alloy, and distilled. 

**Synthesis and characterization**

[TP\textsubscript{Bu,Me}YMe\textsubscript{OTf}] (1-Y): A solution of Me\textsubscript{3}SiOTf (18.0 mg, 0.0814 mmol) in toluene (2 mL) was added to a solution of [TP\textsubscript{Bu,Me}LuMe\textsubscript{2}] (50.0 mg, 0.0788 mmol) in toluene (5 mL) at ambient temperature. The reaction mixture was allowed to stir for 2 h. The solution was concentrated in vacuo and stored at −35 °C. Crystallization yielded compound 1-Y (48.0 mg, 0.0630 mmol, 80%) as colorless crystals. 1H NMR (250 MHz, [D\textsubscript{6}]benzene, 26 °C): \(\delta = 0.0814 \text{ ppm} \) (vs, CH\textsubscript{2}), 1.36 (s, 27 H, 4-pz-CH\textsubscript{3}), 2.01 (s, 9 H, pz-CH\textsubscript{3}), 2.07 (s, 9 H, pz-CH\textsubscript{3}). 13C{1H} NMR (63 MHz, [D\textsubscript{6}]benzene, 26 °C): \(\delta = 29.6 \text{ ppm} \) (vs, CH\textsubscript{2}). 19F{1H} NMR (376 MHz, [D\textsubscript{6}]benzene, 26 °C): \(\delta = 5.64 \text{ ppm} \) (s, 3 H, 4-pz-CH\textsubscript{3}), 1.40 ppm (s, 27 H, pz-C(C\textsubscript{H\textsubscript{3}}\textsubscript{3})), 1.44 (s, 27 H, pz-C(CH\textsubscript{3})), 0.39 ppm (s, 3 H, Lu-CH\textsubscript{3}).

11B{1H} NMR (80 MHz, [D\textsubscript{6}]benzene, 26 °C): \(\delta = 78.1 \text{ ppm} \) (vs, Z-BBu,MeC). The latter gave efficient access to mixed alkyl complexes [TP\textsubscript{Bu,Me}LuMe(CH\textsubscript{2}Ph)] and through salt-metathesis reactions with different alkali-metal salts. Unfortunately, neither reactivity studies utilizing the Wittig reagent nor the attempted thermally-induced intramolecular deprotonation afforded rare-earth-metal alkylidene compounds. It seems that terminal alkylidene devoid of Lewis acid stabilization are not accessible/isolable in the presence of this very Tp\textsubscript{Bu,Me} ligand, which engages preferably in intramolecular B–N- and C–H-bond activation processes. Ongoing research focuses on tripodal ancillary ligand systems which are less prone to degradation and C–H-bond activation. **Experimental Section**

All operations were performed under rigorous exclusion of air and water by using standard Schlenk, high-vacuum, and glovebox techniques (MBraun 2008; <0.1 ppm O\textsubscript{2}, <0.1 ppm H\textsubscript{2}O). Solvents were purified by using Grubbs-type columns (MBraun SPV, solvent purification system) and stored inside a glovebox. [D\textsubscript{6}]Benzene and [D\textsubscript{6}]toluene were obtained from Sigma–Aldrich and degassed, [D\textsubscript{6}]benzene was dried over NaK alloy for two days and [D\textsubscript{6}]toluene was stored over Na. Both were filtered prior to use. [D\textsubscript{6}]THF was obtained from Sigma–Aldrich, stirred over NaK alloy, and distilled. SiMe\textsubscript{3}Cl, trimethylsilyl trifluoromethanesulfonate (Me\textsubscript{3}SiOTf), and (trimethylsilyl)methyllithium ([CH\textsubscript{3}SiCH\textsubscript{2}]Li) solutions were purchased from Sigma Aldrich, SiMe\textsubscript{3}I and N-(trimethylsilyl)bis(trifluoromethyl)methyllide (Me\textsubscript{3}SiNTf\textsubscript{2}) were purchased from ABCR and all chemicals were used as received. Potassium benzyl (KBn), [41] AVII were recorded by using J. Young valve NMR tubes on a Bruker 400 spectrometer (1H, 400.13; 13C, 100.61; 19F, 376.31 MHz), or a Bruker Avilion 600 spectrometer (1H, 600.13; 13C, 150.99; 19F, 376.31 MHz), on a Bruker Avilion 500 spectrometer (1H, 500.00; 13C, 125.76; 19F, 24.51 MHz), and on a Bruker Avilion 250 spectrometer (1H, 250.00; 13C, 80.21; 19F, 62.86 MHz). IR spectra were recorded on a Thermo Fisher Scientific Nicolet 6700 FTIR spectrometer using a DRIFT chamber with dry KBr/sample mixture and KBr windows; IR (DRIFT) data were converted by using the Kubelka–Munk refinement. Elemental analyses were performed on an Elementar Vario MICRO Cube.

**Synthesis and characterization**

[TP\textsubscript{Bu,Me}YMe\textsubscript{OTf}] (1-Y): A chilled solution of Me\textsubscript{3}SiOTf (18.1 mg, 0.0814 mmol) in toluene (2 mL) was added to a solution of [TP\textsubscript{Bu,Me}LuMe\textsubscript{2}] (50.0 mg, 0.0788 mmol) in toluene (5 mL) at ambient temperature. The reaction mixture was allowed to stir for 2 h. The solution was concentrated in vacuo and stored at −35 °C. Crystallization yielded compound 1-Y (48.0 mg, 0.0630 mmol, 80%) as colorless crystals. 1H NMR (250 MHz, [D\textsubscript{6}]benzene, 26 °C): \(\delta = 5.56 \text{ ppm} \) (s, 3 H, 4-pz-CH\textsubscript{3}), 4.42 (br v d, J(\textsubscript{BH}) = 355 Hz, CH\textsubscript{3}), 2.01 (s, 9 H, pz-CH\textsubscript{3}), 1.36 (s, 27 H, pz-C(CH\textsubscript{3})). 13C NMR resonances for the trifluoroborate groups were not detected. 19F{1H} NMR (376 MHz, [D\textsubscript{6}]benzene, 26 °C): \(\delta = 7.75 \text{ ppm} \) (s, 3 H, 4-pz-CH\textsubscript{3}), 1.40 ppm (s, 27 H, pz-C(CH\textsubscript{3})).
A precooled solution of Me₅SiNT₄ (56.0 mg, 0.158 mmol) in toluene (5 mL) was added to a precooled solution of [TpBLuMe₅] (300 mg, 0.158 mmol) in toluene (5 mL) at −35 °C. The reaction mixture was allowed to stir for 3 h at −35 °C. The solution was concentrated in vacuo and stored at −35 °C. Crystallization yielded compound 2-Lu (80 mg, 0.00895 mmol, 57%) as colorless crystals. ¹H NMR (250 MHz, [D₆]benzene, 26 °C): δ = 5.56 (1 H, 4-pz-H), 4.47 (4 br v, J(BH) = 355 Hz, 1 H, Bh), 1.95 ppm (9 H, pz-CH₃), 1.50 ppm (10 H, 8-pz-(CH₃)₃), 1.10 ppm (3 H, 4-pz-(CH₃)₃). ¹³C{¹H} NMR (63 MHz, [D₆]benzene, 26 °C): δ = 166.4 (13C=C), 147.1 (3-pz-C), 104.0 (4-pz-C), 32.6 (pz-C(CH₃)₃), 31.5 (pz-C(CH₃)₃), 13.1 ppm (pz-CH₃). ¹¹B{¹H} NMR (80 MHz, [D₆]benzene, 26 °C): δ = −0.79 ppm. IR (KBr): ν = 2963 (s), 2928 (w), 2859 (w), 2577 (vB-H), 1538 (vs), 1471 (w), 1463 (m), 1435 (s), 1382 (w), 1360 (m), 1346 (s), 1346 (s), 1332 (w), 1241 (w), 1192 (s), 1173 (vs), 1133 (w), 1121 (w), 1067 (m), 1064 (m), 1029 (m), 1014 (w), 989 (w), 847 (vB-H), 810 (w), 804 (w), 787 (m), 777 (w), 765 (s), 729 (w), 683 (w), 677 (w), 659 (w), 645 (m), 515 cm⁻¹ (vw); elemental analysis calc (%) for C₂₄H₅₂BF₆Lu₂N₄O₁₂S₄: C 29.03, H 5.21, N 9.95; found C 24.11, H 3.94, N 12.39. A precooled solution of Me₅SiNT₄ (56.0 mg, 0.158 mmol) in toluene (5 mL) was added to a precooled solution of [TpBLuMe₅] (50.0 mg, 0.0788 mmol) in toluene (5 mL) at −35 °C. The reaction mixture was allowed to stir for 4 h at 0 °C. The solution was concentrated in vacuo and stored at −35 °C. Crystallization yielded compound 4-Lu (65.0 mg, 0.0561 mmol, 71%) as colorless crystals. ¹H NMR (250 MHz, [D₆]benzene, 26 °C): δ = 5.57 (1 H, 4-pz-H), 4.52 (4 br v, J(BH) = 340 Hz, 1 H, Bh), 2.06 (s, 9 H, pz-CH₃), 1.31 ppm (27 H, 8-pz-(CH₃)₃), 1.05 ppm (3 H, 3-pz-C), 106.9 (4-pz-C), 32.3 (pz-C(CH₃)₃), 30.9 (pz-C(CH₃)₃) ppm. ¹³C NMR resonances for the triflato groups could not be detected. ¹¹B{¹H} NMR (80 MHz, [D₆]benzene, 26 °C): δ = −7.6 ppm. ¹³C{¹H} NMR (376 MHz, [D₆]benzene, 26 °C): δ = −76.9 ppm. IR (KBr): ν = 3149 (vW), 2974 (w), 2956 (w), 2873 (vW), 2569 (vB-H), 1544 (m), 1482 (w), 1464 (w), 1422 (w), 1358 (m), 1338 (s), 1324 (m), 1259 (vs), 1218 (vs), 1193 (vs), 1134 (s), 1119 (s), 1100 (vs), 1055 (m), 1035 (m), 1017 (w), 982 (w), 928 (vW), 847 (vW), 838 (vW), 824 (w), 806 (w), 767 (w), 743 (w), 681 (vW), 661 (w), 653 (m), 605 (m), 579 (m), 531 (m), 512 (m), 441 (vW), 426 (vW), 419 (vW); elemental analysis calc (%) for C₂₄H₅₂BF₆Lu₂N₄O₁₂S₄: C 29.03, H 3.48, N 9.67; found C 30.12, H 3.49, N 9.27. Due to the high 5 and F contents no better elemental analysis could be obtained.
A precooled solution of SiMe₃Cl (34.2 mg, 0.154 mmol) in toluene (5 mL) was added to a precooled solution of [TpAu(κ3-P)(κ5-P)]. The reaction mixture was stirred for 3 h at ambient temperature. The solvent was evaporated under reduced pressure to afford a pale green solid. The solid was dried in vacuo to afford [TpAu(κ3-P)(κ5-P)].

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Conflict of interest

The authors declare no conflict of interest.

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