

A Rare-Earth Metal Variant of the Tebbe Reagent**

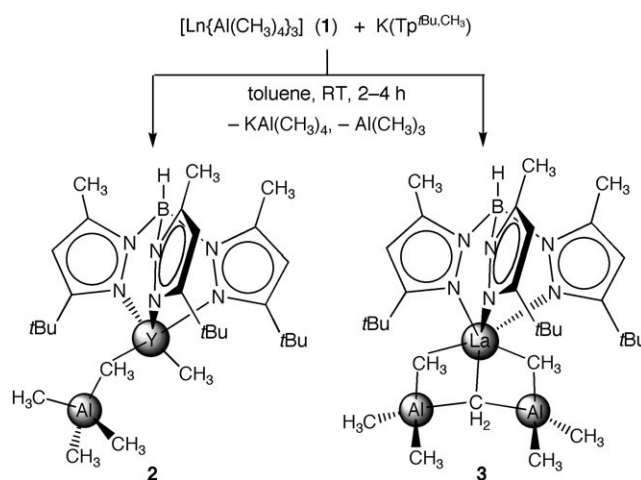
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Tebbe reagent $[\text{Cp}_2\text{Ti}\{(\mu\text{-CH}_2)(\mu\text{-Cl})\text{Al}(\text{CH}_3)_2\}]$ (**A**; Cp = cyclopentadienyl) belongs to the most enigmatic organometallic compounds.^[1] Its successful synthesis, resulting from the careful investigation of the reaction of $[\text{Cp}_2\text{TiCl}_2]$ with two equivalents $\text{Al}(\text{CH}_3)_3$, was triggered by important discoveries in two fundamentally different areas of homogeneous catalysis. Indeed, the initial studies of methane (and methylidene) formation from $[\text{Cp}_2\text{TiCl}_2]/\text{Al}(\text{CH}_3)_3$ mixtures were conducted in the context of Ziegler–Natta polymerization catalysis,^[2] but the methylene unit was structurally characterized by X-ray crystallography for the first time in tantalum alkylidene complexes, such as $[\text{Cp}_2\text{Ta}(\text{CH}_2)(\text{CH}_3)]$,^[3] and tungsten methylene compounds, related to proposed catalysts for olefin metathesis.^[4] Although catalytically active in olefin metathesis,^[5] the Tebbe reagent is currently used for efficient carbonyl methylenation reactions.^[6] In his initial studies, Tebbe also commented on the synthesis of the structurally similar all-methyl derivative $[\text{Cp}_2\text{Ti}\{(\mu\text{-CH}_2)(\mu\text{-CH}_3)\text{Al}(\text{CH}_3)_2\}]$ (**B**) from the labile $[\text{Cp}_2\text{Ti}(\text{CH}_3)_2]$ and $\text{Al}(\text{CH}_3)_3$, suggesting $[\text{Cp}_2\text{Ti}(\text{CH}_3)_2\{\text{Al}(\text{CH}_3)_3\}]$ (**B**⁺) as a stabilized intermediate.^[1] Although the structures of the bis(neopentyl) derivative $[\text{Cp}_2\text{Ti}\{(\mu\text{-CH}_2)(\mu\text{-Cl})\text{Al}(\text{CH}_2\text{C}(\text{CH}_3)_3)_2\}]$ and a zirconium analogue $[\text{Cp}_2\text{Zr}\{(\mu\text{-CHCH}_2\text{C}(\text{CH}_3)_3)(\mu\text{-Cl})\text{Al}(\text{CH}_2\text{CH}(\text{CH}_3)_2)_2\}]$ ^[8] have been reported, there are no X-ray structures of the Tebbe reagent nor of discrete metallacycles of the type $[\text{M}(\mu\text{-CH}_2)(\mu\text{-R})\text{Al}(\text{CH}_3)_2]$ (R = Cl, CH₃).^[9,10]

Previous studies from our laboratories on rare-earth-metal(III) tetramethylaluminate complexes $[\text{L}_x\text{Ln}\{\text{Al}(\text{CH}_3)_4\}_y]$ (y = 1, 2, 3; x + y = 3, L = monovalent ancillary ligand, Ln = lanthanides and Sc, Y, La) as polymerization catalysts^[11,12] led to the isolation of Ln^{III} clusters with methylene,^[13,14] methine,^[15] and carbide functionalities.^[16] We also found that complex $[\text{Cp}^*_3\text{Y}_3(\mu\text{-Cl})_3(\mu_3\text{-Cl})(\mu_3\text{-CH}_2)(\text{thf})_3]$ (Cp* = C₅(CH₃)₅) displayed Tebbe-like reactivity.^[13] Herein, we report that the bulky hydrotris(pyrazolyl)borate ligand $\text{Tp}^{\text{tBu,Me}}$ (cone angle: 244°; Trofimenko's scorpionate) provides a unique ligand environment for the stabilization

and isolation of discrete rare-earth metal methyl–methylene species.^[17] Such compounds are structurally similar to the Tebbe reagent and display Tebbe-like reactivity.

Recently we reported the synthesis of $[(\text{Tp}^{\text{tBu,Me}})\text{Y}\{\text{Al}(\text{CH}_3)_4(\text{CH}_3)\}]$ (**2**) by protonolysis of $[\text{Y}\{\text{Al}(\text{CH}_3)_4\}_3]$ (**1a**) with $\text{H}(\text{Tp}^{\text{tBu,Me}})$.^[14] We have now succeeded in obtaining single crystals of complex **2** using salt metathesis as an alternative synthesis approach (Scheme 1).^[18,19] No visual changes were



Scheme 1. Ln^{III} -size-dependent salt metathesis reaction pathways of $[\text{Ln}\{\text{Al}(\text{CH}_3)_4\}_3]$ and $[\text{K}(\text{Tp}^{\text{tBu,Me}})]$.

observed when $[\text{Y}\{\text{Al}(\text{CH}_3)_4\}_3]$ (**1a**)^[20] was added to a white suspension of $\text{K}(\text{Tp}^{\text{tBu,Me}})$ in toluene. However, extraction of the product from the precipitated $\text{KAl}(\text{CH}_3)_4$ and subsequent evaporation of the solvent afforded a powdery white solid, the ¹H NMR spectrum of which is identical to that of complex **2**.^[14] X-ray structure analysis performed on colorless crystals (the crude compound was recrystallized from a toluene/hexane mixture)^[21] confirmed the molecular structure proposed by variable-temperature (VT) ¹H NMR spectroscopic studies^[14] (Figure 1). Consistent with the high mobility of the CH₃ ligands, **2** can be viewed as $[(\text{Tp}^{\text{tBu,Me}})\text{Y}(\text{CH}_3)_2\{\text{Al}(\text{CH}_3)_3\}]$, hence representing a structural analogue of the previously postulated Tebbe intermediate **B**⁺.^[1]

Complex **2** adopts a distorted trigonal-bipyramidal coordination geometry; the terminal CH₃ group (C25) and N3 and N5 from two of the pyrazolyl rings occupy the equatorial plane, and the bridging methyl group (C26) of the $\text{Al}(\text{CH}_3)_4$ ligand and N1 of the third pyrazolyl ring are in the apical positions. The $\text{Tp}^{\text{tBu,Me}}$ ligand coordinates to the yttrium center in a κ^3 fashion with Y–N bond lengths ranging from 2.361(2) to 2.418(2) Å; the longest distance (Y–N1) belongs

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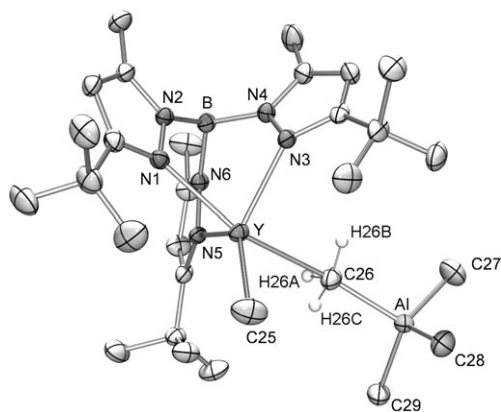


Figure 1. Molecular structure of **2** (thermal ellipsoids are set at the 50% probability level). One of the *t*Bu groups is rotationally disordered, only the major part is shown. Selected bond lengths [Å] and angles [°]: Y–C25 2.382(3), Y–C26 2.715(3), Y–N1 2.418(2), Y–N3 2.361(2), Y–N5 2.357(2), Al–C26 2.057(3), Al–C27 2.002(3), Al–C28 1.999(3), Al–C29 1.994(3), Y–C26–Al 161.0(1), C25–Y–C26 89.1(1), N1–Y–C26 153.22(8).

to the pyrazolyl ring *trans* to the bridging CH₃ group. The Al(CH₃)₄ moiety shows the unusual η^1 -coordination previously observed in the solid-state structure of [(NNN)La{(μ -CH₃)Al(CH₃)₃}(thf)] (NNN = 2,6-[(2,6-*i*Pr₂C₆H₃)NC(CH₃)₂]₂C₅H₃N).^[22] The presence of this η^1 -coordinated Al(CH₃)₄ ligand in addition to the terminal CH₃ group clearly demonstrates the sterically saturated environment imposed on yttrium by the bulky Tp^{*t*Bu,Me} ligand and its tendency to produce metal complexes with low coordination numbers.^[23] The Y–C bond lengths differ markedly: Y–C(CH₃) is quite short (2.382(3) Å), while Y–C [(μ -CH₃)Al(CH₃)₃] (2.715(3) Å) is relatively long. For comparison, the Y–C bonds in the five-coordinate complex [(Tp^{*t*Bu,Me})Y(CH₂Si(CH₃)₃)₂] and in the alkyl-alkylidene complex [Y{CH₂Si(CH₃)₃}{C(PPh₂)=NSi(CH₃)₃}(thf)] are 2.393(2) and 2.421(2) Å,^[24] and 2.406(3) and 2.408(3) Å,^[25] respectively.

Interestingly, when the same salt metathesis protocol was applied to the larger rare-earth metal center lanthanum (radii: La³⁺ 1.032, Y³⁺ 0.900 Å for six-coordination),^[26] the new complex [(Tp^{*t*Bu,Me})La{(μ -CH₂){(μ -CH₃)Al(CH₃)₂}] (**3**) was obtained from [La{Al(CH₃)₄}] (**1b**)^[27] and K(Tp^{*t*Bu,Me}) (Scheme 1). Separation of KAl(CH₃)₄, evaporation of the solvent, and washing with a small amount of cold hexane gave a white powder of **3** in more than 50% yield.^[19] The molecular composition of complex **3** could be assigned on the basis of a VT NMR spectroscopic study and an X-ray structure analysis.^[21]

The ambient-temperature ¹H NMR spectrum of **3** in C₆D₆ was not particularly informative, showing only one set of signals for the 39 protons of the pyrazolyl groups of the Tp^{*t*Bu,Me} ligand (δ = 5.60, 1.85, and 1.33 ppm) and a BH resonance at δ = 4.43 ppm. Two signals were observed for metal-bound CH protons: one broad singlet at δ = 0.97 ppm accounting for two protons, and one singlet at δ = –0.02 ppm with an integral intensity of 18. This result excluded the formation of the anticipated bis(tetramethylaluminate) complex [(Tp^{*t*Bu,Me})La{Al(CH₃)₄}] (CH integral intensity of 24). A

VT ¹H NMR spectroscopic study eventually unraveled the structural composition of complex **3** (Figure 2).

At –60 °C all of the proton signals, except that of the BH proton, have decoalesced. For the Tp^{*t*Bu,Me} ligand, the

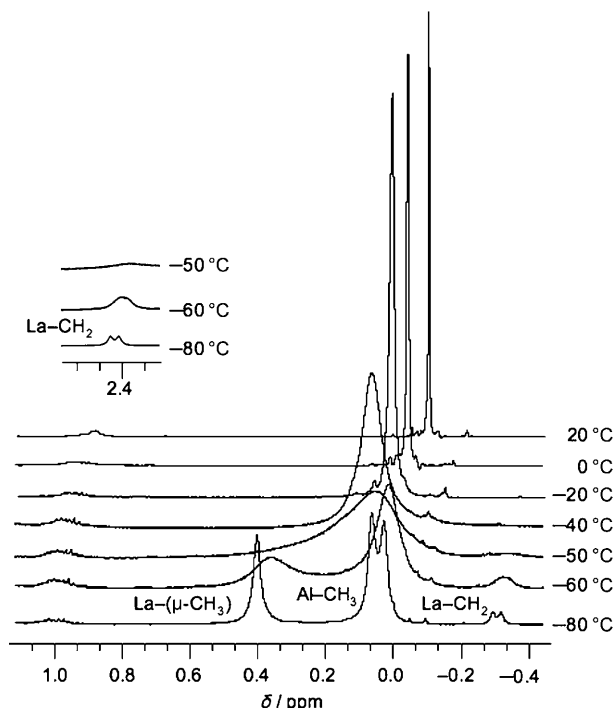


Figure 2. Variable-temperature ¹H NMR spectra (500.13 MHz) of **3**, in the region of metal-bonded CH, in [D₈]toluene.

pyrazolyl protons now appear as two sets of signals in a 2:1 ratio, implying two different environments for the pyrazolyl rings. The signal at δ = 0.97 ppm, assigned to CH₂ protons, splits into two broad singlets at δ = 2.39 and –0.35 ppm. Upon further cooling to –80 °C these two peaks resolve into doublets with a geminal coupling constant of ²J_{H,H} ≈ 12 Hz. The large chemical shift difference for the methylene protons suggests rather different orientations with respect to the lanthanum center; the downfield signal indicates a close La⋯H contact (cf. X-ray structure analysis).^[28] At –60 °C, the signal for metal-bonded CH₃ groups at δ = –0.02 ppm splits into two broad singlets at 0.35 and 0.00 ppm (2:4 ratio), which can be assigned to two bridging and four terminal CH₃ groups, respectively. At –80 °C, the latter peak decoalesces further into two singlets, consistent with distinct terminal Al–CH₃ environments as revealed by the X-ray structure analysis of **3**.

Colorless single crystals of **3** were obtained by recrystallization from a toluene/hexane mixture (Figure 3). The lanthanum center in complex **3** is in a distorted octahedral coordination environment. As in the yttrium complex **2**, the Tp^{*t*Bu,Me} ligand coordinates to the lanthanum center in a κ^3 fashion; the La–N bond lengths range from 2.567(2) to 2.608(2) Å. The butterfly-shaped Tebbe-like [(μ -CH₂){(μ -CH₃)Al(CH₃)₂}] moiety (dihedral angle 39.28(8)°) features a relatively short La–C(methylene) bond of 2.519(2) Å, matching the La–C(σ) separations in homoleptic three-

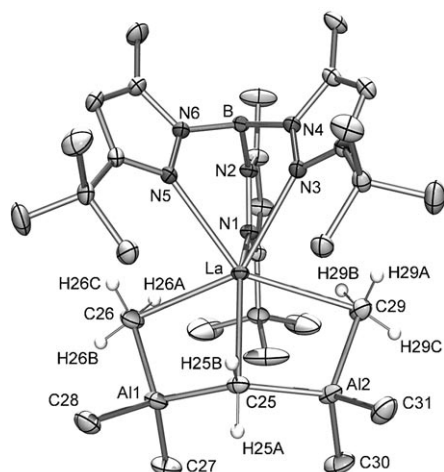
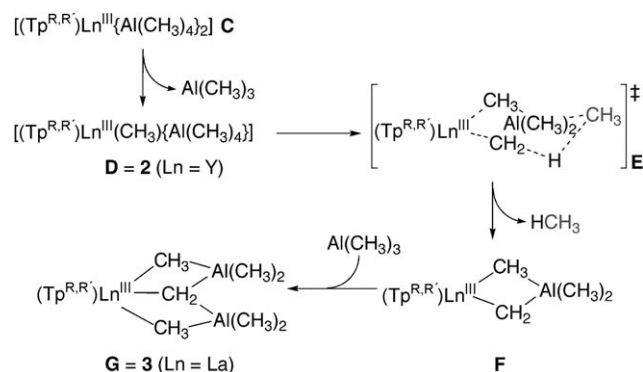


Figure 3. Molecular structure of **3** (thermal ellipsoids are set at the 50% probability level). Selected bond lengths [Å] and angles [°]: La–C25 2.519(2), La–H25B 2.60(3), La–C26 2.809(2), La–C29 2.833(2), La–N1 2.567(2), La–N3 2.595(2), La–N5 2.608(2), Al1–C25 2.073(2), Al1–C26 2.074(2), Al1–C27 1.990(2), Al1–C28 1.989(2), Al2–C25 2.075(2), Al2–C29 2.085(2), Al2–C30 1.983(2), Al2–C31 1.988(2); La–C25–H25B 84(2), La–C25–H25A 171(4), La–C25–Al1 90.1(1), La–C25–Al2 89.9(1), La–C26–Al1 82.5(1), La–C29–Al2 81.5(1).

coordinate [La{CH[Si(CH₃)₃]₂}₃] (2.515(9) Å).^[29] One of the methylene protons points toward the lanthanum center, reminiscent of La–(HC) α-agostic interactions (La–H25B 2.60(3) Å and La–C25–H25B 84(2)°).^[30] The only other known La–C(methylene) moieties have been found in the dodecanuclear molecular clusters [La₄Al₈(CH)₄(CH₂)₂(CH₃)₂₀{P(CH₃)₃}] (La–CH₂ 2.588(4) and 2.629(4) Å) and [La₄Al₈(C)(CH)₂(CH₂)₂(CH₃)₂₂(toluene)] (2.549(7)–2.889(7) Å)^[16] as well as in [Cp*₃La₃(μ-Cl)₃(μ₃-Cl)(μ₃-CH₂)-(thf)₃] (2.537(3)–2.635(3) Å).^[13] The two La–(μ-CH₃) bond lengths in **3** (La–C26 2.809(2), La–C29 2.833(2) Å) fall in the expected range.^[22,27]

Given the structures of complexes **2** and **3**, it is tempting to speculate about the reaction sequence leading to their formation (Scheme 2). Apparently, the high steric demand of the Tp^{tBu,Me} ligand prevents the formation of a stable bis(tetramethylaluminate) derivative **C**, well known for a series of other monovalent ancillary ligands.^[12,18,22] Elimination of a molecule of Al(CH₃)₃ results in **D**, which is stable in the case of yttrium only (**D** = 2). Owing to steric constraints or to rapid side reactions of the released Al(CH₃)₃, a cyclic transition state **E**—proposed for the formation of the Tebbe reagent on the basis of kinetic studies^[31]—seems to be disfavored for the yttrium complex **2**.^[32] The six-membered heterobimetallacycle **E** would then lead to the Ln analogue of the Tebbe reagent **F** by extrusion of CH₄.^[33] However, the latter would render a sterically unsaturated lanthanum center, which therefore re-associates with Al(CH₃)₃ to form **G** (complex **3**).^[34]

Contrary to complex **2**, which at ambient temperature acts as an exclusively alkylating reagent toward fluorenone,^[14] preliminary NMR spectroscopy experiments revealed that compound **3** is capable of performing carbonyl methylenation



Scheme 2. Proposed activation sequence for the formation of the Tebbe moieties [Ln(μ-CH₂){(μ-CH₃)Al(CH₃)₂}_n] (*n* = 1, 2; Tp^{R,R'} = Tp^{tBu,Me}).

reactions. When **3** was reacted with 9-fluorenone in C₆D₆, its conversion into the methylenated derivative 9-methylenefluorene (ca. 50%) and the 1,2-addition product 9-CH₃-fluorenoxy-dimethylaluminum, [(CH₃)₂Al(OC₁₄H₁₁)] (ca. 50%)^[35] was complete after approximately 2 h. Formation of the latter alkylation product could be suppressed by addition of diethyl ether as a scavenger for the released Al(CH₃)₃.

In conclusion, we have shown that the sterically crowded, monoanionic Tp^{tBu,Me} scorpionate ligand provides a unique environment for the isolation of discrete rare-earth metal complexes with Y–(CH₃)₂Al(CH₃)₂ and La–(CH₂) moieties. Ongoing studies are aimed at fine-tuning the steric influence by varying the size of the rare-earth metal and the substitution pattern of the ancillary Tp^{R,R'} ligand, for a comprehensive understanding of the feasibility and reactivity of such rare-earth-metal methylene functionalities.

Experimental Section

Synthesis of 3: In a glovebox, [La{Al(CH₃)₄}₃] (**1b**; 140 mg, 0.35 mmol) was dissolved in toluene (3 mL) and added to a stirred suspension of K(Tp^{tBu,Me}) (162 mg, 0.35 mmol) in toluene (3 mL). The resulting white suspension was stirred another 4 h at ambient temperature. The supernatant solution was decanted, and the solid residue (product and KAl(CH₃)₄) was extracted with additional toluene (3 × 3 mL). The combined extracts were dried under vacuum to yield **3** contaminated by a small amount of decomposition material. Washing with a small amount of cold hexane and drying under vacuum left **3** as a white powdery solid (128 mg, 0.18 mmol, 51%).
¹H NMR (600 MHz, C₆D₆, 25 °C): δ = 5.60 (s, 3H, 4-pz-H), 4.43 (v br d, ¹J_{B-H} ≈ 90 Hz, 1H, BH), 1.85 (s, 9H, pz-CH₃), 1.33 (s, 27H, pz-C(CH₃)₃), 0.97 (br s, 2H, La(CH₂)), –0.02 ppm (s, 18H, Al(CH₃)).
¹H NMR (500 MHz, [D₈]Tol, –80 °C): δ = 5.40 (s, 1H, 4-pz-H), 5.25 (s, 2H, 4-pz-H), 4.28 (v br s, 1H, BH), 2.41 (br d, ²J_{H-H} ≈ 12 Hz, 1H, La(CH₂)), 1.90 (s, 3H, pz-CH₃), 1.58 (s, 6H, pz-CH₃), 1.34 (br s, 18H, pz-C(CH₃)₃), 1.29 (br s, 9H, pz-C(CH₃)₃), 0.39 (br s, 6H, Al(μ-CH₃)), 0.05 (br s, 6H, Al(CH₃)), 0.01 (br s, 6H, Al(CH₃)), –0.33 ppm (br d, ²J_{H-H} ≈ 12 Hz, 1H, La(CH₂)).
¹³C NMR (126 MHz, C₆D₆, 25 °C): δ = 166.0 (3-pz-C), 149.0 (5-pz-C), 104.9 (4-pz-C), 50.9 (La(CH₂)), 32.9 (pz-C(CH₃)₃), 31.5 (pz-C(CH₃)₃), 13.3 (pz-CH₃), 0.3 ppm (Al(CH₃)).
¹³C NMR (126 MHz, [D₈]Tol, –60 °C): δ = 165.9 (3-pz-C), 164.4 (3-pz-C), 148.8 (5-pz-C), 147.5 (5-pz-C), 105.3 (4-pz-C), 104.4 (4-pz-C), 48.9 (La(CH₂)), 32.7 (pz-C(CH₃)₃), 31.5 (pz-C(CH₃)₃), 31.0 (pz-C(CH₃)₃),

13.6 (pz-CH₃), 13.2 (pz-CH₃), −5.0 ppm (br, Al(CH₃)). ²⁷Al{¹H} NMR (130 MHz, C₆D₆, 25°C): δ = 167 ppm (br s, Al(CH₃/CH₂)). ¹¹B{¹H} NMR (161 MHz, C₆D₆, 25°C): δ = 22.1 ppm (br s, BH). Elemental analysis (%) calcd for C₃₁H₆₀N₆Al₂BLa (720.54 g mol^{−1}): C 51.67, H 8.39, N 11.66; found: C 51.30, H 7.85, N 11.02.

Full experimental and analytical details are available in the Supporting Information.

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- [1] F. N. Tebbe, G. W. Parshall, G. S. Reddy, *J. Am. Chem. Soc.* **1978**, *100*, 3611.
- [2] For an example, see: E. Heins, H. Hinck, W. Kaminsky, G. Oppermann, P. Paulinat, H. Sinn, *Makromol. Chem.* **1970**, *134*, 1.
- [3] a) L. J. Guggenberger, R. R. Schrock, *J. Am. Chem. Soc.* **1975**, *97*, 6578; b) R. R. Schrock, *Acc. Chem. Res.* **1979**, *12*, 98.
- [4] N. Calderon, E. A. Ofstead, W. A. Judy, *Angew. Chem.* **1976**, *88*, 433; *Angew. Chem. Int. Ed. Engl.* **1976**, *15*, 401.
- [5] F. N. Tebbe, G. W. Parshall, D. W. Ovenall, *J. Am. Chem. Soc.* **1979**, *101*, 5074.
- [6] For reviews, see: a) R. C. Hartley, G. J. McKiernan, *J. Chem. Soc. Perkin Trans. 1* **2002**, 2763; b) K. C. Rana, *Synlett* **2007**, 1795.
- [7] U. Klabunde, F. N. Tebbe, G. W. Parshall, R. L. Harlow, *J. Mol. Catal.* **1980**, *8*, 37; metrical parameters on the crucial heterobimetallic fragment are lacking due to a disordering of the respective bridging chloride and methylidene group.
- [8] F. M. Hartner, Jr., S. M. Clift, J. Schwartz, T. H. Tulip, *Organometallics* **1987**, *6*, 1346.
- [9] For related X-ray structurally characterized Ti–Al heterobimetallic methylidene/alkylidene complexes, see: a) J. E. Kickham, F. Guérin, D. W. Stephan, *J. Am. Chem. Soc.* **2002**, *124*, 11486; [(*t*Bu₃PN)Ti(μ₂-*t*Bu₃PN(μ₃-CH₂)₂[Al(CH₃)₂][Al(CH₃)₃]); b) B. C. Bailey, A. R. Fout, H. Fan, J. Tomaszewski, J. C. Huffman, D. J. Mindiola, *Angew. Chem.* **2007**, *119*, 8394; *Angew. Chem. Int. Ed.* **2007**, *46*, 8246; [(PNP)Ti{C(*t*Bu)Al(CH₃)₃}] (PNP = [2-(*P*iPr₂-4-methylphenyl)₂N[−]]).
- [10] For a structurally similar Ti–Rh heterobimetallic methylidene complex, see: J. W. Park, P. B. Mackenzie, W. P. Schaefer, R. H. Grubbs, *J. Am. Chem. Soc.* **1986**, *108*, 6402; [Cp₂Ti(μ-CH₂)(μ-CH₃)Rh(cod)] (cod = 1,5-cyclooctadiene).
- [11] For a review, see: A. Fischbach, R. Anwender, *Adv. Polym. Sci.* **2006**, *204*, 155.
- [12] For examples, see: a) A. Fischbach, M. G. Klimpel, M. Widenmeyer, E. Herdtweck, W. Scherer, R. Anwender, *Angew. Chem.* **2004**, *116*, 2284; *Angew. Chem. Int. Ed.* **2004**, *43*, 2234; b) A. Fischbach, F. Perdihi, E. Herdtweck, R. Anwender, *Organometallics* **2006**, *25*, 1626; c) C. Meermann, K. W. Törnroos, W. Nerdal, R. Anwender, *Angew. Chem.* **2007**, *119*, 6628; *Angew. Chem. Int. Ed.* **2007**, *46*, 6508; d) M. Zimmermann, K. W. Törnroos, R. Anwender, *Angew. Chem.* **2008**, *120*, 787; *Angew. Chem. Int. Ed.* **2008**, *47*, 775; e) M. Zimmermann, H. Sitzmann, K. W. Törnroos, R. Anwender, *Chem. Eur. J.* **2008**, *14*, 7266.
- [13] H. M. Dietrich, K. W. Törnroos, R. Anwender, *J. Am. Chem. Soc.* **2006**, *128*, 9298.
- [14] M. Zimmermann, J. Takats, G. Kiel, K. W. Törnroos, R. Anwender, *Chem. Commun.* **2008**, 612.
- [15] H. M. Dietrich, H. Grove, K. W. Törnroos, R. Anwender, *J. Am. Chem. Soc.* **2006**, *128*, 1458.
- [16] L. C. H. Gerber, E. Le Roux, K. W. Törnroos, R. Anwender, *Chem. Eur. J.* **2008**, DOI: 10.1002/chem.200801175.
- [17] a) The formation of polymeric Ln alkylidene complexes of type {[Ln(=CHSi(CH₃)₃)(CH₂Si(CH₃)₃)_n] (Ln = Er, Lu) by slow thermal decomposition of {[Ln(CH₂Si(CH₃)₃)₂(thf)₂]} has been proposed but not confirmed by X-ray structure analysis: K. A. Rufanow, D. M. M. Freckmann, H.-J. Kroth, S. Schutte, H. Schumann, *Z. Naturforsch. B* **2005**, *60*, 533, and references therein; b) methylidene species of the type [(CH₂)LnH₂] (Ln = Sc, Y, La) were produced by methane activation of the laser-ablated metals and characterized by matrix IR spectroscopy: H.-G. Cho, L. Andrews, *Organometallics* **2007**, *26*, 633.
- [18] E. Le Roux, F. Nief, F. Jaroschik, K. W. Törnroos, R. Anwender, *Dalton Trans.* **2007**, 4866.
- [19] A detailed discussion of the advantages and drawbacks of the different reaction protocols addressing crucial factors, such as reaction time and temperature as well as the effect of released trimethylaluminum, and the spectroscopic characterization and structural chemistry byproducts with activated C–H and B–N bonds, will be presented in an upcoming full paper.
- [20] W. J. Evans, R. Anwender, J. W. Ziller, *Organometallics* **1995**, *14*, 1107.
- [21] Compound **2** (C₂₉H₅₅AlBN₆Y, *M*_r = 614.49) crystallizes from a toluene/hexane mixture in the monoclinic space group *P*₂₁/*n* with *a* = 13.4920(4), *b* = 16.8964(5), *c* = 15.2229(4) Å, β = 90.293(1), *V* = 3470.26(17) Å³, and *d*_{calc} = 1.176 g cm^{−3} for *Z* = 4. Data were collected at 100(2) K on a BRUKER-AXS SMART 2K CCD system. The structure was solved by direct methods, and least-squares refinement of the model based on 6615 (all data) and 5462 reflections (*I* > 2.0σ(*I*)) converged to final *R*1 = 0.0327 and *wR*2 = 0.0811, respectively. Compound **3** (C₄₅H₇₆Al₂BLaN₆, *M*_r = 904.80) crystallizes with two toluene solvent molecules from a toluene/hexane mixture in the monoclinic space group *P*₂₁/*n* with *a* = 13.1926(4), *b* = 9.9430(3), *c* = 37.0228(12) Å, β = 98.396(1), *V* = 4804.4(3) Å³, and *d*_{calc} = 1.251 g cm^{−3} for *Z* = 4. Data were collected at 100(2) K on a BRUKER-AXS SMART 2K CCD system. The structure was solved by direct methods, and least-squares refinement of the model based on 16015 (all data) and 13845 reflections (*I* > 2.0σ(*I*)) converged to a final *R*1 = 0.0358 and *wR*2 = 0.0695, respectively. CCDC-696636 and 696637 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.
- [22] M. Zimmermann, K. W. Törnroos, R. Anwender, *Angew. Chem.* **2007**, *119*, 3187; *Angew. Chem. Int. Ed.* **2007**, *46*, 3126.
- [23] a) S. Trofimenko, *J. Am. Chem. Soc.* **1967**, *89*, 3170; b) S. Trofimenko, *Scorpionates: The Coordinational Chemistry of Polypyrazolylborate Ligands*, Imperial College Press, London, **1999**; c) N. Marques, A. Sella, J. Takats, *Chem. Rev.* **2002**, *102*, 2137.
- [24] J. Cheng, K. Saliu, G. Y. Kiel, M. J. Ferguson, R. McDonald, J. Takats, *Angew. Chem.* **2008**, *120*, 4988; *Angew. Chem. Int. Ed.* **2008**, *47*, 4910.
- [25] S. T. Liddle, J. McMaster, J. C. Green, P. L. Arnold, *Chem. Commun.* **2008**, 1747.
- [26] R. D. Shannon, *Acta Crystallogr. Sect. A* **1976**, *32*, 751.
- [27] M. Zimmermann, N. Å. Frøystein, A. Fischbach, P. Sirsch, H. M. Dietrich, K. W. Törnroos, E. Herdtweck, R. Anwender, *Chem. Eur. J.* **2007**, *13*, 8784.
- [28] M. Zimmermann, F. Estler, E. Herdtweck, K. W. Törnroos, R. Anwender, *Organometallics* **2007**, *26*, 6029.
- [29] P. B. Hitchcock, M. F. Lappert, R. G. Smith, R. A. Bartlett, P. P. Power, *J. Chem. Soc. Chem. Commun.* **1988**, 1007.
- [30] W. Scherer, G. S. McGrady, *Angew. Chem.* **2004**, *116*, 1816; *Angew. Chem. Int. Ed.* **2004**, *43*, 1782.
- [31] K. C. Ott, E. J. M. deBoer, R. H. Grubbs, *Organometallics* **1984**, *3*, 223.
- [32] ¹H NMR spectroscopic investigations of the equimolar reaction of pure **2** and Al(CH₃)₃ indicate the formation of various yttrium methylene species; see also references [19] and [28].

- [33] Alternatively, deprotonation of **D** could proceed by formation of an intermediate ion pair $\{[(\text{Tp}^{\text{tBu,Me}})\text{Ln}(\text{CH}_3)][\text{Al}(\text{CH}_3)_4]\}$ and subsequent removal of a methyl proton by a basic methyl group in $[\text{Al}(\text{CH}_3)_4]^-$; such a scenario has been suggested for the synthesis of $[\text{Cp}_2\text{Ta}\{\text{CH}_2\text{Al}(\text{CH}_3)_3\}(\text{CH}_3)]$ from $[\text{Cp}_2\text{Ta}(\text{CH}_3)_3]$ and $\text{Al}(\text{CH}_3)_3$: R. R. Schrock, P. R. Sharp, *J. Am. Chem. Soc.* **1978**, *100*, 2389.
- [34] It is noteworthy that Tebbe-like products are not observed when $[\text{Cp}_2\text{Zr}(\text{CH}_3)_2]$ is treated with $\text{Al}(\text{CH}_3)_3$; in this case, only the scrambling of methyl groups occurs: A. R. Siedle, R. A. Newmark, J. N. Schroepfer, P. A. Lyon, *Organometallics* **1991**, *10*, 400.
- [35] H. M. Dietrich, C. Meermann, K. W. Törnroos, R. Anwender, *Organometallics* **2006**, *25*, 4316.
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