Ln(III) methyl and methylidene complexes stabilized by a bulky hydrotris(pyrazolyl)borate ligand†

Melanie Zimmermann,[a] Josef Takats,[b] Gong Kiel,[b] Karl W. Törnroos[a] and Reiner Anwander*[a]

The reaction of Ln(AlMe$_4$)$_3$ with bulky hydrotris(pyrazolyl)-borate (Tp^{tBu,Me})H proceeds *via* a sequence of methane elimination and C–H bond activation, affording unprecedented rare-earth metal ligand moieties including Ln(Me)[(μ-Me)-AlMe$_3$] and X-ray structurally characterized "Tebbe-like" Ln[(μ-CH$_2$)$_2$AlMe$_2$].

Bulky ancillary ligands give access to low-coordinate organolanthanide complexes with small ligands of exceptional reactivity and relevance for olefin polymerization.[1] For example, highly substituted cyclopentadienyl (Cp) and tris(pyrazolyl)borate (Tp) ligands allowed for the isolation and structural characterization of low-molecular hydrido species such as monomeric (1,3,4-tBu$_3$C$_5$H$_2$)$_2$Ce^{III}H[2] and dimeric [(Tp^{tBu,Me})Yb^{II}(μ-H)]$_2$,[3] respectively. Cp-based ligands have also largely dominated the field of Ln^{III} hydrocarbyl chemistry,[4] where in particular the [Ln^{III}–CH$_3$] moiety has demonstrated exceptional reactivity as evidenced by methane activation,[5] multiple hydrogen abstraction[6] and α-olefin polymerization.[7] However, careful design of alternative spectator ligands gave access to a prolific non-cyclopentadienyl organolanthanide chemistry.[8] Anionic tris(3-R-5-R′-pyrazolyl)borate ligands (Tp$^{R,R'}$), formally isoelectronic to the Cp anions, displayed unique versatility as ancillary ligands since their first preparation by Trofimenko 40 years ago.[9] The steric demand of the Tp$^{R,R'}$ ligands can effectively be adjusted by variation of the substituents in the 3-position of the pyrazolyl group (cone angles: Tp^{H,H} 184°, Tp^{Me,Me} 224°, Tp^{tBu,Me} 244°; *cf.*, C$_5$Me$_5$ 142°).[10] Given the current high impact of half-sandwich Ln^{III} hydrocarbyl complexes,[11] trivalent Tp analogues remain scarce.[12,13] Only two examples of half-sandwich (Tp) Ln^{III} hydrocarbyls have been reported so far.[14–16] Long and Bianconi described the synthesis of (Tp^{Me,Me})Y(CH$_2$SiMe$_3$)$_2$(thf) according to a salt metathesis reaction using (Tp^{Me,Me})YCl$_2$(thf) and LiCH$_2$SiMe$_3$.[14] Piers *et al.* employed the alternative alkane elimination protocol to obtain scandium compounds (Tp^{Me,Me})Sc(CH$_2$SiMe$_3$)$_2$(thf) and (Tp^{tBu,Me})Sc(CH$_2$-SiMe$_3$)$_2$ from Sc(CH$_2$SiMe$_3$)$_3$(thf)$_2$ and (Tp$^{R,R'}$)H.[15]

Homoleptic tris(tetramethylaluminate) complexes Ln(AlMe$_4$)$_3$ are versatile precursors for the synthesis of heterobimetallic Ln–Al complexes.[17] Protonolysis reaction of such "alkyls in disguise" has been described for a variety of ancillary ligands including cyclopentadienyl, alkoxo and amido ligands.[18–20] Stimulated by

the potential of these precursors to form highly active Ln–methyl moieties we set out to explore their reactivity toward the acid form of the sterically demanding hydrotris(3-*tert*-butyl-5-methyl-pyrazolyl)borate, (Tp^{tBu,Me})H.

Ln(AlMe$_4$)$_3$ (Ln = Lu (1a) and Y (1b)) react with (Tp^{tBu,Me})H in hexane according to an alkane elimination reaction as evidenced by instant gas evolution and precipitation of a white solid material (Scheme 1). Separation of the precipitate from the supernatant afforded white powdery compounds identified as (Tp^{tBu,Me})Ln(AlMe$_4$)(Me) (Ln = Lu (2a), Y (2b)). The IR spectra of complexes 2 exhibit ν(B–H) stretching vibrations at 2561 (2a) and 2566 cm^{-1} (2b), respectively, indicative of tridentate Tp^{tBu,Me} ligands.[21] ^{1}H NMR and ^{13}C NMR spectra at ambient temperature display one set of resonances for the H-4, the C-5 methyl, and the C-3 tBu groups of the pyrazolyl ligand. The resonances assignable to the [AlMe$_4$] and [Me] moieties appear as broad singlets (Fig. 1). Variable temperature (VT) ^{1}H NMR studies gave conclusive insight into the exchange processes of the highly fluxional compounds 2. At 50 °C (decomposition at 60 °C), the ^{1}H NMR spectrum of lutetium derivative 2a in toluene-d_8 shows only one singlet in the metal alkyl region (−0.15 ppm) accounting for 15 protons of the very fast exchanging AlMe$_4$ and Me ligands (Fig. 1). Signal decoalescence into two broad singlets at 0.45 ppm (Me, 3H) and −0.23 ppm (AlMe$_4$, 12H) occurred at approximately ambient temperature.

Upon cooling to −10 °C the high-field signal decoalesced further and appeared as two distinct singlets in a 3 : 9 ratio. These
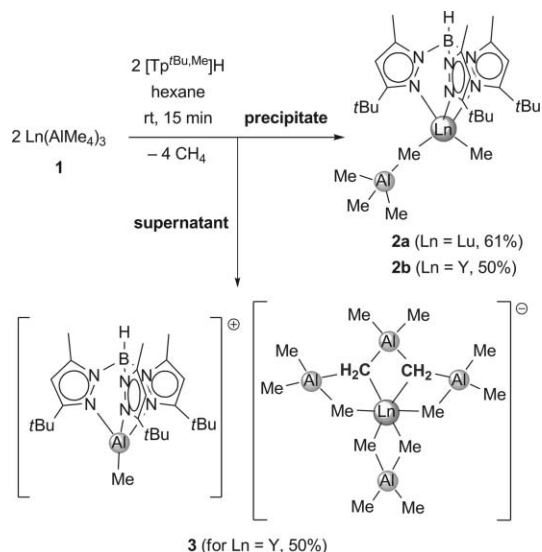
[a]Department of Chemistry, University of Bergen, Allégaten 41, 5007 Bergen, Norway. E-mail: reiner.anwander@kj.uib.no; Fax: +47 55589490
[b]Department of Chemistry, University of Alberta, Edmonton, Alberta, Canada T6G 2G2. E-mail: joe.takats@ualberta.ca; Fax: +1 780 4928231

Scheme 1
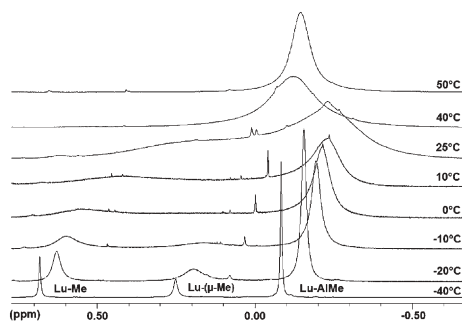
Fig. 1 Variable temperature ^{1}H NMR spectra (500.13 MHz) of (Tp^{tBu,Me})Lu(AlMe$_4$)(Me) (**2a**) dissolved in toluene-d_8.
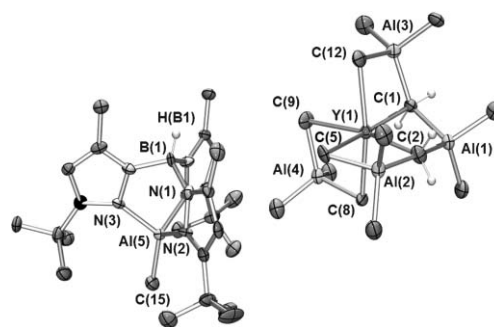

Fig. 2 Molecular structure of **3** (atomic displacement parameters are set at the 50% level). Hydrogen atoms (except for H(B1), H(1A), H(1B), H(2A) and H(2B)) are omitted for clarity. Selected bond distances [Å] and angles [°]: Y(1)–C(1) 2.344(8), Y(1)–C(2) 2.411(9), Y(1)–C(5) 2.582(9), Y(1)–C(8) 2.563(7), Y(1)–C(9) 2.654(8), Y(1)–C(12) 2.589(8), Y(1)···Al(1) 2.993(3), Y(1)···Al(2) 3.046(2), Y(1)···Al(3) 3.031(3), Y(1)···Al(4) 3.122(3), Al(1)–C(1) 2.097(7), Al(1)–C(2) 2.093(1), Al(2)–C(2) 2.05(1), Al(2)–C(5) 2.10(1), Al(3)–C(1) 2.068(8), Al(3)–C(12) 2.076(8), Al(4)–C(8) 2.044(8), Al(4)–C(9) 2.06(1), Al(5)–N(1) 1.927(7), Al(5)–N(2) 1.912(6), Al(5)–N(3) 1.909(7), Al(5)–C(15) 1.948(8); N(1)–Al(5)–N(2) 96.4(3), N(1)–Al(5)–N(3) 97.8(3), N(2)–Al(5)–N(3) 97.2(3), N(1)–Al(5)–C(15) 119.4(3), B(1)···Al(5)···C(15) 179.1(4), C(2)–Y(1)–C(9) 170.2(3), C(1)–Y(1)–C(9) 100.4(3), C(5)–Y(1)–C(9) 90.0(3), C(8)–Y(1)–C(9) 81.4(3), C(9)–Y(1)–C(12) 88.1(3), C(1)–Y(1)–C(2) 85.9(3), C(1)–Al(1)–C(2) 101.4(3), Y(1)–C(1)–Al(3) 86.5(3), Y(1)–C(12)–Al(3) 80.2(3), Y(1)–C(2)–Al(2) 85.8(4), Y(1)–C(5)–Al(2) 80.5(3), C(8)–Al(4)–C(9) 112.0(3).

findings suggest a [(μ-Me)AlMe$_3$] coordination mode of the tetramethylaluminate ligand in complexes **2** which demonstrates the tendency of the bulky Tp^{tBu,Me} ligand to give rise to low coordination numbers.[10] The existence of such η^1-coordinated tetramethylaluminate ligands was recently confirmed by the solid-state structure of (NNN)La[(μ-Me)AlMe$_3$](thf) (NNN = 2,6-[(2,6-iPr$_2$C$_6$H$_3$)NCMe$_2$]$_2$C$_5$H$_3$N).[22] The proton resonances of the pyrazolyl ligand showed progressive broadening at lower temperature. The H-4 proton signal already decoalesced well above −40 °C into two signals in a 2 : 1 ratio, consistent with a C_s symmetric structure (ESI, Fig. S1–S4†).

Yttrium complex **2b** showed analogous dynamic behaviour. Decoalescence of the AlMe$_4$ proton signals, however, occurred at lower temperatures (−60 °C) consistent with the increasing steric unsaturation at the larger yttrium centre and therefore more rapid methyl group exchange.[17] Attempted crystallization of compounds **2** was hampered by their insolubility in aliphatic solvents and their reactivity toward aromatic solvents (toluene, benzene).

The exceptional formation of rare-earth metal hydrocarbyls **2**, comprising [Ln(AlMe$_4$)] and [Ln(Me)] moieties, is assumed to originate from a sequence of fast processes. A mechanistic proposal could include the initial formation of a transient bis(tetramethylaluminate) species (Tp^{tBu,Me})Ln(AlMe$_4$)$_2$, followed by intra- (from a κ^2-coordinated Tp^{tBu,Me} ligand)[23] or intermolecular (by (Tp^{tBu,Me})H) N-donor cleavage of one tetramethylaluminate ligand, producing a terminal methyl group under concomitant release of one equivalent of AlMe$_3$.[24] Owing to the steric protection by the bulky Tp^{tBu,Me} ligand the highly reactive methyl group is kinetically protected and stable complexes **2** can be isolated (Scheme 1).

Cooling the hexane supernatant of the reaction between Y(AlMe$_4$)$_3$ (**1b**) and (Tp^{tBu,Me})H to −30 °C reproducibly yielded colourless single crystals of **3** suitable for X-ray structural analysis (Fig. 2).‡ The X-ray diffraction study revealed an unprecedented salt-like compound consisting of a [(Tp^{tBu,Me})AlMe]$^+$ cation and a [Y(AlMe$_4$){(μ-CH$_2$)(μ-Me)AlMe$_2$}$_2$(AlMe$_2$)]$^-$ anion (Scheme 1). While the detailed mechanistic scenario leading to this extraordinary mixed metal compound remains obscure, several reactivity patterns can be recognized. The cationic unit most likely originates from the reaction of (Tp^{tBu,Me})H with one equivalent AlMe$_3$ released in the acid–base reaction of (Tp^{tBu,Me})H and Y(AlMe$_4$)$_3$ or donor cleavage of [AlMe$_4$] (*vide supra*) to form the transient neutral aluminium complex (Tp^{tBu,Me})AlMe$_2$.[22] Looney and Parkin previously reported the analogous alkyl aluminium compound (Tp^{tBu,H})AlMe$_2$ with the *t*Bu substituted pyrazole

ligand coordinated in a κ^2 fashion. Coordination of the third pyrazolyl ring is prevented by steric constraints.[25] However, this becomes feasible by elimination of one methyl ligand and concomitant cationization as revealed by the formation of the four-coordinate [(Tp^{tBu,Me})AlMe]$^+$ cation in **3**. The Al(5)–N bond distances (av. 1.916(7) Å) differ only slightly, substantiating a κ^3 coordination of the pyrazolylborate ligand in the solid-state. Besides for steric reasons the release of a methyl group might further be driven by the observed C–H bond activation (CH$_4$ formation) at a [AlMe$_4$] unit of unreacted Y(AlMe$_4$)$_3$ producing the anionic part of salt **3**. The two methylidene-containing [(μ-CH$_2$)(μ-Me)AlMe$_2$] moieties are strong reminders of the prominent Tebbe reagent Cp$_2$Ti[(μ-CH$_2$)(μ-Cl)AlMe$_2$] and its derivative Cp$_2$Ti[(μ-CH$_2$)(μ-Me)AlMe$_2$] which can be obtained by reaction of [Cp$_2$TiMe$_2$] and AlMe$_3$.[26] It was only recently that rare-earth metal complexes containing such nucleophilic methylidene moieties were obtained as products of C–H bond activation processes.[27,28] While a more detailed understanding of the reaction pathways leading to compound **3** remains elusive, the reaction stoichiometry comes out even considering the reproducible 50% yield of yttrium complex **2b** and salt **3**. The coordination geometry of the yttrium metal centre in **3** is best described as distorted octahedral with C(2) and C(9) occupying the apical positions (C(2)–Y(1)–C(9), 170.2(3)°). All hydrogen atoms of coordinating C atoms could be located and refined, unequivocally proving the formation of two bridging methylidene groups (μ$_3$-CH$_2$) (Fig. 2). Compared to the Y–C(μ-CH$_3$) bond distances in the same molecule the Y–C(μ-CH$_2$) bonds are significantly shortened (av. 2.378(9) Å *vs.* 2.597(9) Å). These yttrium methylidene carbon distances are even shorter than the ones found for the trinuclear yttrium cluster [Cp*$_3$Y$_3$(μ-Cl)$_3$(μ$_3$-Cl)(μ$_3$-CH$_2$)(thf)$_3$] (2.424(2)– 2.450(2) Å).[27] ^{1}H and ^{13}C NMR spectra of **3** suggest a large

barrier for the exchange of pyrazolyl groups implying a local C_s symmetry of the cationic unit. Signal assignment for the methylidene (^{1}H: 0.35 and 0.25 ppm; ^{13}C: 31.3 and 31.0 ppm) and methyl groups (^{1}H: -0.02–-0.25, 0.64 ppm; ^{13}C: -0.4–2.5 ppm) of the anionic unit was feasible, albeit complex signal patterns made a more detailed interpretation difficult. (ESI, Fig. S5†).

Nucleophilic addition of [M–CH$_3$] moieties to carbonyl functionalities are routine reactions in organic synthesis.[29] To test the methylating capability of compounds **2**, reactions with 1–3 eq. of 9-fluorenone in C$_6$D$_6$ at ambient temperature were monitored by ^{1}H NMR spectroscopy. The investigations revealed instant bleaching of the yellow reaction mixture for the addition of 1 and 2 eq. of the ketone, while the addition of a third equivalent led to yellow reaction mixtures containing ill-defined Ln species. Preliminary investigations of the reactivity of **2** toward secondary amines (HNEt$_2$) evidenced protonolysis of the [Me] and [(μ-Me)AlMe$_3$] moieties (formation of CH$_4$ and Ln–NEt$_2$) accompanied by competitive formation of (Tp^{tBu,Me})H. Furthermore, instant gas evolution was observed when **2** was treated with SiMe$_4$ in accord with the occurrence of C–H bond activation.

In conclusion, we have demonstrated that protonolysis between Ln(AlMe$_4$)$_3$ and the sterically demanding (Tp^{tBu,Me})H provides a convenient strategy for the synthesis of highly reactive mixed metal Ln^{III} hydrocarbyl complexes, (Tp^{tBu,Me})Ln(AlMe$_4$)(Me). The formation of salt-like [(Tp^{tBu,Me})AlMe]$^+$[Y(AlMe$_4$){(μ-CH$_2$)(μ-Me)AlMe$_2$}$_2$(AlMe$_2$)]$^-$ substantiates the high potential of tetramethylaluminate-containing reaction mixtures to activate C–H bonds. Preliminary reactivity studies revealed highly efficient methylation of carbonylic functionalities and promising reactivity in alkane elimination reactions.

Notes and references

‡ Crystal structure determination of complex **3**
Crystal data. C$_{39}$H$_{83}$N$_6$Al$_5$BY, M = 870.73, orthorhombic, a = 29.6427(17), b = 9.5879(6), c = 18.0884(11) Å, V = 5140.9(5) Å^3, d_{calc} = 1.125 g cm^{-3}, T = 123 K, space group P$na2_1$, Z = 4. The structure was solved by Patterson methods, and least-square refinement of the model based on 7423 reflections (all data) and 4683 reflections (I > 2.0$\sigma(I)$) converged to a final $R1$ = 0.0520 and w$R2$ = 0.1244, respectively. CCDC 656616. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b713378b

1 For reviews, see: H. Yasuda, *Top. Organomet. Chem.*, 1999, **2**, 255; R. Anwander, in *Applied Homogeneous Catalysis with Organometallic Compounds*, ed. B. Cornils and W. A. Herrmann, Wiley-VCH, Weinheim, 2002, p. 974.
2 L. Maron, E. V. Werkema, L. Perrin, O. Eisenstein and R. A. Andersen, *J. Am. Chem. Soc.*, 2005, **127**, 279.
3 G. M. Ferrence, R. McDonald and J. Takats, *Angew. Chem., Int. Ed.*, 1999, **38**, 2233; G. M. Ferrence and J. Takats, *J. Organomet. Chem.*, 2002, **647**, 84.
4 W. J. Evans and B. L. Davis, *Chem. Rev.*, 2002, **102**, 2119.
5 P. L. Watson, *J. Am. Chem. Soc.*, 1983, **105**, 6491.
6 H. M. Dietrich, H. Grove, K. W. Törnroos and R. Anwander, *J. Am. Chem. Soc.*, 2006, **128**, 1458.

7 Z. Hou and Y. Wakatsuki, *Coord. Chem. Rev.*, 2002, **231**, 1; J. Gromada, J.-F. Carpentier and A. Mortreux, *Coord. Chem. Rev.*, 2004, **248**, 397; P. M. Zeimentz, S. Arndt, B. R. Elvridge and J. Okuda, *Chem. Rev.*, 2006, **106**, 2404.
8 F. T. Edelmann, D. M. M. Freckmann and H. Schumann, *Chem. Rev.*, 2002, **102**, 1851; W. E. Piers and D. J. H. Emslie, *Coord. Chem. Rev.*, 2002, **233–234**, 131.
9 S. Trofimenko, *J. Am. Chem. Soc.*, 1967, **89**, 3170; S. Trofimenko, *Scorpionates: The Coordination Chemistry of Polypyrazolylborate Ligands*, Imperial College Press, London, 1999.
10 I. Santos and N. Marques, *New J. Chem.*, 1995, **19**, 551; N. Marques, A. Sella and J. Takats, *Chem. Rev.*, 2002, **102**, 2137; S. Trofimenko, J. C. Calabrese and J. S. Thompson, *Inorg. Chem.*, 1987, **26**, 1507; E. Frauendorfer and H. Brunner, *J. Organomet. Chem.*, 1982, **240**, 371; C. E. Davies, I. M. Gardiner, J. C. Green, M. L. H. Green, N. J. Hazel, P. D. Grebenik, V. S. B. Mtetwa and K. Prout, *J. Chem. Soc., Dalton Trans.*, 1985, 669.
11 S. Arndt and J. Okuda, *Chem. Rev.*, 2002, **102**, 1953; Z. Hou, Y. Luo and X. Li, *J. Organomet. Chem.*, 2006, **691**, 3114.
12 J. L. Galler, S. Goodchild, J. Gould, R. McDonald and A. Sella, *Polyhedron*, 2004, **23**, 253; A. Sella, S. E. Brown, J. W. Steed and D. A. Tocher, *Inorg. Chem.*, 2007, **46**, 1856.
13 For Ln^{II} hydrocarbyls, see: L. Hasinoff, J. Takats, X. W. Zhang, P. H. Bond and R. D. Rogers, *J. Am. Chem. Soc.*, 1994, **116**, 8833.
14 D. P. Long and P. A. Bianconi, *J. Am. Chem. Soc.*, 1996, **118**, 12453.
15 J. A. Blackwell, C. Lehr, Y. Sun, W. E. Piers, S. D. Pearce-Batchilder, M. J. Zaworotko and V. G. J. Young, *Can. J. Chem.*, 1997, **75**, 702.
16 The synthesis of a wide range of (Tp$^{R,R'}$)Ln(CH$_2$SiMe$_2$R″)$_2$(thf)$_{1/0}$ (R″= Me, Ph) complexes has been achieved *via* a combination of protonolysis and Tl-hydrocarbyl elimination: J. Cheng, K. Saliu and J. Takats, unpublished results.
17 A. Fischbach and R. Anwander, *Adv. Polym. Sci.*, 2006, **204**, 155; M. Zimmermann, N. Å. Frøystein, A. Fischbach, P. Sirsch, H. M. Dietrich, K. W. Törnroos, E. Herdtweck and R. Anwander, *Chem.–Eur. J.*, 2007, **13**, 8784.
18 H. M. Dietrich, C. Zapilko, E. Herdtweck and R. Anwander, *Organometallics*, 2005, **24**, 5767.
19 A. Fischbach, M. G. Klimpel, M. Widenmeyer, E. Herdtweck, W. Scherer and R. Anwander, *Angew. Chem., Int. Ed.*, 2004, **43**, 2234.
20 M. Zimmermann, K. W. Törnroos and R. Anwander, *Organometallics*, 2006, **25**, 3593.
21 M. Akita, K. Ohta, Y. Takahashi, S. Hikichi and Y. Moro-oka, *Organometallics*, 1997, **16**, 4121.
22 M. Zimmermann, K. W. Törnroos and R. Anwander, *Angew. Chem., Int. Ed.*, 2007, **46**, 3126.
23 X. Zhang, R. McDonald and J. Takats, *New J. Chem.*, 1995, **19**, 573; A. C. Hillier, X. W. Zhang, G. H. Maunder, S. Y. Liu, T. A. Eberspacher, M. V. Metz, R. McDonald, A. Domingos, N. Marques, V. W. Day, A. Sella and J. Takats, *Inorg. Chem.*, 2001, **40**, 5106.
24 Donor-induced cleavage of tetramethylaluminates (O-donors, N-donors) offers a convenient synthesis approach toward highly reactive [Ln–Me] moieties: J. Holton, M. F. Lappert, D. G. H. Ballard, R. Pearce, J. L. Atwood and W. E. Hunter, *J. Chem. Soc., Dalton Trans.*, 1979, 54.
25 A. Looney and G. Parkin, *Polyhedron*, 1990, **9**, 265; D. J. Darensbourg, E. L. Maynard, M. W. Holtcamp, K. K. Klausmeyer and J. H. Reibenspies, *Inorg. Chem.*, 1996, **35**, 2682.
26 F. N. Tebbe, G. W. Parshall and G. S. Reddy, *J. Am. Chem. Soc.*, 1978, **100**, 3611.
27 H. M. Dietrich, K. W. Törnroos and R. Anwander, *J. Am. Chem. Soc.*, 2006, **128**, 9298.
28 M. Zimmermann, F. Estler, E. Herdtweck, K. W. Törnroos and R. Anwander, *Organometallics*, 2007, **26**, 6029.
29 J. J. Eisch, in *Comprehensive Organometallic Chemistry II*, ed. G. Wilkinson, F. G. A. Stone and E. W. Abel, Pergamon Press, Oxford, UK, 1995, vol. 11, ch. 6; T. Imamoto, *Pure Appl. Chem.*, 1990, **62**, 747; T. Imamoto, *Lanthanides in Organic Synthesis*, Academic Press, London, 1994.