ChemComm

Cite this: *Chem. Commun.*, 2011, **47**, 11441–11443

www.rsc.org/chemcomm

COMMUNICATION

Allyl complexes of scandium: synthesis and structure of neutral, cationic and anionic derivatives†

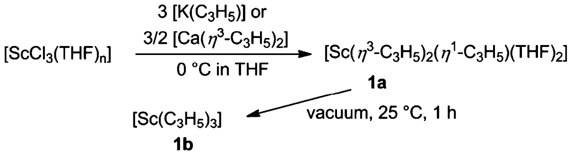
Sabine Standfuss, Elise Abinet, Thomas P. Spaniol and Jun Okuda*

Received 12th July 2011, Accepted 12th September 2011
DOI: 10.1039/c1cc14180e

Neutral, cationic and anionic allyl compounds of scandium contain highly fluxional allyl ligands in solution, whilst in the solid state both η^1- and η^3-binding modes are detected.

Allyl complexes of the rare earth metals are initiators for the homogeneous stereoselective polymerization of dienes.[1–3] Although tris(allyl) complexes of the rare earth metals [Ln(η^3-C_3H_5)$_3$(L)] (L = THF, 1,4-dioxane) are a versatile source for neutral and cationic allyl derivatives,[1–12] peculiarly the parent tris(allyl) complex of scandium has remained elusive so far. Only cyclopentadienyl-supported allyl complexes of scandium have been reported: [Cp_2Sc(η^3-C_3H_5)] (Cp = C_5Me_5,[13a] C_5H_5[13b,14] or C_5Me_4H[15]), [{$SiMe_2$(η^5-C_5H_4)$_2$}Sc(η^3-C_3H_5)],[13c] [Cp*Sc(η^3-C_3H_5)$_2$] (Cp* = η^5-C_5Me_5),[2] [Cp′Sc(η^3-C_3H_5)$_2$]^{2a,b} and [Cp′Sc(η^3-C_3H_5)(THF)$_2$]$^+$ (Cp′ = η^5-$C_5Me_4SiMe_3$).[2a] Recent theoretical studies of homoleptic bis(allyl)- and tris(allyl)scandium using DFT calculations showed η^3-binding mode for all allyl ligands.[4] We report here that starting from the neutral compound tris(allyl)scandium [Sc(C_3H_5)$_3$(THF)$_n$] (**1a**: n = 2; **1b**: n = 0) both cationic (**2**) and anionic (**3**) derivatives are accessible which contain η^3- and η^1-allyl ligands in the solid state.

Tris(allyl)scandium compounds [Sc(C_3H_5)$_3$(THF)$_n$] (**1a**: n = 2; **1b**: n = 0) were obtained by the reaction of anhydrous $ScCl_3$ with three equivalents of allylpotassium[16] or with 1.5 equivalents of bis(allyl)calcium[5] in THF at 0 °C in 70% yield (Scheme 1). The ^{1}H NMR spectrum of **1** in THF-d_8 indicates highly fluxional behavior of all three allyl ligands in solution on the NMR time scale with one doublet for the terminal allyl protons at δ = 2.97 ppm and one quintet for the methine proton at δ = 6.18 ppm. Below −80 °C, broadening of the signal for the terminal protons is observed (Fig. S1c, ESI†). At −95 °C, the signal is broad (2.2–3.5 ppm) but decoalescence was not observed (Fig. S1d, ESI†). The coordinated THF ligands in **1a** are lost by drying *in vacuo* for 1 h. The crystalline product slowly changed into a yellow powder of **1b** and its ^{1}H NMR spectrum shows only traces of THF beside a doublet and a quintet for the allyl ligands, consistent with the homoleptic compound [Sc(C_3H_5)$_3$] (Fig. S2, ESI†).



Scheme 1 Synthesis of [Sc(η^1-C_3H_5)(η^3-C_3H_5)$_2$(THF)$_2$] (**1a**) and [Sc(C_3H_5)$_3$] (**1b**).

Single crystals of **1a** were obtained by slow crystallization from a THF solution at −40 °C within five days. X-Ray diffraction study‡ revealed two crystallographically independent molecules in the unit cell. Both show trigonal bipyramidal configuration with two THF ligands in the axial positions (O1–Sc1–O2 177.82(11)°). Two allyl ligands are η^3- and one allyl ligand is η^1-coordinated consistent with the formula [Sc(η^1-C_3H_5)(η^3-C_3H_5)$_2$(THF)$_2$] (**1a**) (Fig. 1). The manganese complex [Li(THF)$_4$][Mn{η^3-$(Me_3Si)_2C_3H_3$}{η^1-$(Me_3Si)_2C_3H_3$}$_2$]^{17a} contains

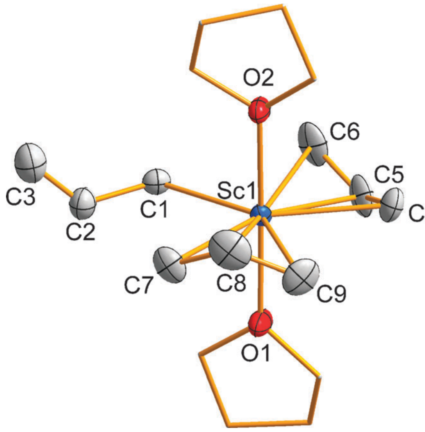


Fig. 1 Molecular structure of [Sc(η^1-C_3H_5)(η^3-C_3H_5)$_2$(THF)$_2$] (**1a**). Displacement ellipsoids are shown at 50% probability; hydrogen atoms are omitted for clarity. Selected interatomic distances [Å] and angles [°]: Sc1–C1 2.373(4), Sc1–C4 2.434(4), Sc1–C5 2.479(4), Sc1–C6 2.557(4), Sc1–C7 2.493(4), Sc1–C8 2.485(4), Sc1–C9 2.447(4), Sc1–O1 2.225(3), Sc1–O2 2.208(3), C1–C2 1.477(5), C2–C3 1.310(6), O1–Sc1–O2 177.82(11), C1–Sc1–O1 89.46(11), C1–Sc1–O2 90.85(11).

Institute of Inorganic Chemistry, RWTH Aachen University, Landoltweg 1, 52056 Aachen, Germany
E-mail: jun.okuda@ac.rwth-aachen.de; Fax: +49 241 8092644

† Electronic supplementary information (ESI) available: Synthesis and characterization of **1a–b**, **2a–c**, **3a–c** and **4**. CCDC 832188 (**1a**), 832189 (**2a**), 832190 (**3c**). For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c1cc14180e.

two η^1- and one η^3-coordinated allyl fragments ($r(Mn^{2+})$ = 0.66 Å, CN = 4; $r(Sc^{3+})$ = 0.745 Å, CN = 6).[18]

The metal atom only deviates by 0.040(3) Å from the plane formed by C2, C5 and C8. The Sc1–C1 bond length is 2.373(4) Å for the η^1-allyl ligand and the average distance from Sc1 to the carbon atoms of the η^3-allyl ligands of 2.48 Å (ranging from 2.434(4) to 2.557(4) Å) is within the expected range.[4] The interatomic distance C2–C3 of 1.310(6) Å is as expected in the range of a C–C double bond[12] and the C–C distances within the η^3-coordinated fragments of 1.38 Å (ranging from 1.359(6) to 1.421(6) Å) are as expected for η^3-allyl ligands.[3–6]

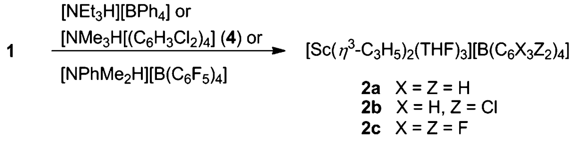
The related compounds with larger metal centers $[Ln(\eta^3\text{-}C_3H_5)_3(THF)_2]$, (Ln = Ce, Pr),[3] $[Nd(\eta^3\text{-}C_3H_5)_3(\mu\text{-}C_4H_8O_2)]_n$[6a] and $[Ca(\eta^3\text{-}C_3H_5)_2(triglyme\text{-}\kappa^4)]$[5] contain η^3-coordinated allyl ligands in the solid state. The tris(allyl)indium compound $[In(\eta^1\text{-}C_3H_5)_3(\mu\text{-}C_4H_8O_2)]_n$ with a smaller ionic radius ($r(In^{3+})$ = 0.62 Å, CN = 4)[18] and a more covalent character displays η^1-coordinated allyl ligands in the solid state.[12]

The neutral compound **1a** was protonated by the Brønsted acids $[NEt_3H][BPh_4]$, $[NMe_3H][B(C_6H_3Cl_2)_4]$ (**4**) and $[NPhMe_2H][B(C_6F_5)_4]$ in THF to give the bis(allyl) cation $[Sc(\eta^3\text{-}C_3H_5)_2(THF)_3]^+$ in **2a–c**. These compounds precipitated within 5 min at room temperature as yellow powder in 68–80% isolated yield (Scheme 2).

The ^{1}H NMR spectrum of **2a** in THF-d_8 shows two signals for both allyl ligands: a doublet for the terminal protons at δ = 3.10 ppm and a quintet for the methine protons at δ = 5.99 ppm. The CH_2 resonances are shifted towards lower field as compared to **1a** and the dynamic behavior is comparable to **1a**. Similar behavior is found for the cations in $[Sc(C_3H_5)_2(THF)_3][B(C_6H_3Cl_2)_4]$ (**2b**) and in $[Sc(C_3H_5)_2(THF)_3][B(C_6F_5)_4]$ (**2c**).

By cooling the filtered reaction mixture of **2a** to −40 °C, single crystals suitable for X-ray diffraction were obtained. The cation $[Sc(\eta^3\text{-}C_3H_5)_2(THF)_3]^+$ contains a five-coordinate scandium center. Both allyl ligands are within the equatorial plane (Fig. 2). As in **1a**, the axial positions are occupied by two THF ligands (O1–Sc1–O3 175.44(4)°). The average distance from the scandium center to the carbon atoms of the η^3-allyl ligands is 2.47 Å (ranging from 2.3854(16) to 2.5870(17) Å) and similar to that in **1a**. The C–C distances within the η^3-coordinated fragments of 1.37 Å (ranging from 1.257(7) to 1.434(8) Å) are as expected for η^3-allyl ligands.[3–6] Cationic lanthanide bis(allyl) and mono(allyl) complexes $[Ln(\eta^3\text{-}C_3H_5)_2(THF)_4]^+$ (Ln = La, Ce, Nd)[3] and $[Cp'Sc(\eta^3\text{-}C_3H_5)(THF)_2]^+$[2a] contain η^3-coordinated allyl ligands in the solid state.

When **1a** was treated with one equivalent of allylpotassium in THF at 0 °C, the ate complex $K[Sc(C_3H_5)_4]$ (**3a**) was obtained. Compound **3a** was also synthesized directly by treating $ScCl_3$ with four equivalents of allylpotassium. With bis(allyl)calcium,[5] $[Ca(THF)_6][Sc(C_3H_5)_4]_2$ (**3b**) was obtained in THF at 0 °C (Scheme 3).



Scheme 2 Synthesis of $[Sc(\eta^3\text{-}C_3H_5)_2(THF)_3][BPh_4]$ (**2a**), $[Sc(C_3H_5)_2(THF)_3][B(C_6H_3Cl_2)_4]$ (**2b**) and $[Sc(C_3H_5)_2(THF)_3][B(C_6F_5)_4]$ (**2c**).

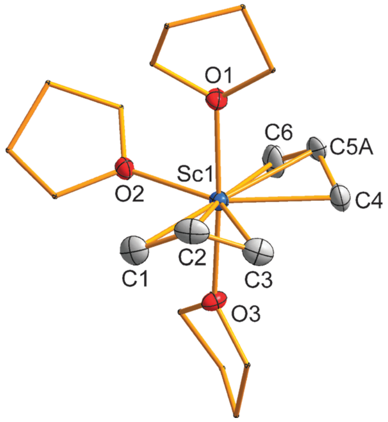
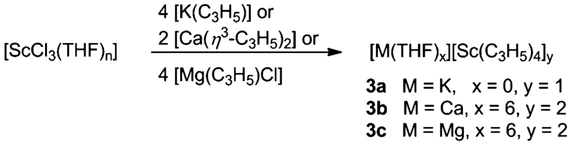


Fig. 2 Molecular structure of the cationic part of $[Sc(\eta^3\text{-}C_3H_5)_2(THF)_3][B(C_6H_5)_4]$ (**2a**). Displacement ellipsoids shown at 50% probability; hydrogen atoms and the anion $[BPh_4]^-$ are omitted for clarity; only one of the two split positions of C5 is shown. Selected interatomic distances [Å] and angles [°]: Sc1–C1 2.5071(16), Sc1–C2 2.4662(16), Sc1–C3 2.4117(16), Sc1–C4 2.3854(16), Sc1–C5a 2.474(2), Sc1–C5b 2.486(6), Sc1–C6 2.5870(17), C1–C2 1.378(2), C2–C3 1.382(2), C4–C5a 1.417(3), C5a–C6 1.331(3), C4–C5b 1.434(8), C5b–C6 1.257(7), Sc1–O1 2.1814(10), Sc1–O2 2.2379(10), Sc1–O3 2.2071(10), O1–Sc1–O3 175.44(4), O1–Sc1–O2 85.96(4), O2–Sc1–O3 89.48(4), C2–Sc1–C5a 136.54(7), C2–Sc1–C5b 141.14(18).



Scheme 3 Synthesis of $K[Sc(C_3H_5)_4]$ (**3a**), $[Ca(THF)_6][Sc(C_3H_5)_4]_2$ (**3b**) and $[Mg(THF)_6][Sc(C_3H_5)_4]_2$ (**3c**).

The ^{1}H NMR spectra of **3a** and **3b** in THF-d_8 show a doublet and a quintet for the allyl groups at δ = 2.70 ppm (CH_2) and δ = 6.09 ppm (CH), indicating fluxional behavior in solution. The resonances for the methylene protons are shifted towards higher field compared to **1a**. At −95 °C, all signals retain their multiplicity and are slightly shifted to higher field (Fig. S7b, ESI†).

When $ScCl_3$ was reacted with $[Mg(C_3H_5)Cl]$,[19] single crystals of $[Mg(THF)_6][Sc(C_3H_5)_4]_2$ (**3c**) suitable for X-ray diffraction precipitated from a THF/*n*-pentane solution at −40 °C. The molecular structure in the solid state shows that two allyl ligands are η^1- and two ligands are η^3-coordinated to the scandium center (Fig. 3). The geometry around the metal center is best described as distorted tetrahedral. The angle C7–Sc1–C10 of 96.1(2)° between the η^1-coordinated allyl ligands is less than expected for tetrahedral geometry and reflects this distorted geometry. The average distance between the scandium center and the carbon atoms of the η^3-coordinated allyl ligands is 2.45 Å (ranging from 2.424(5) to 2.488(5) Å) and very similar to the neutral **1a** and the cationic **2a**. The distances to the η^1-coordinated allyl ligands of 2.271(5) and 2.277(5) Å are smaller than in **1a** explained by the smaller coordination number in **3c**. In comparison, $[Mg(THF)_6][Sm(\eta^3\text{-}C_3H_5)_4]_2$,[7] $[Li_2(\mu\text{-}C_3H_5)(C_4H_8O_2)_3][Ce(\eta^3\text{-}C_3H_5)_4]$[20] and $[Li(\mu\text{-}C_4H_8O_2)_{3/2}][La(\eta^3\text{-}C_3H_5)_4]$[6b] with the larger atoms samarium, cerium and lanthanum contain four η^3-coordinated allyl fragments. The anionic parts in $[K(15\text{-}crown\text{-}5)_2][Al(\eta^1\text{-}C_3H_5)_4]_2$[21]

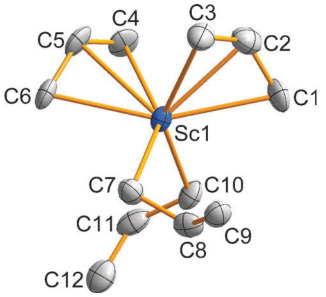


Fig. 3 Molecular structure of the anionic part of $[Mg(THF)_6]$-$[Sc(\eta^1\text{-}C_3H_5)_2(\eta^3\text{-}C_3H_5)_2]_2$ (**3c**). Displacement ellipsoids shown at 50% probability; hydrogen atoms and cation $[Mg(THF)_6]^{2+}$ are omitted for clarity. Selected interatomic distances [Å] and angles [°]: Sc1–C1 2.450(5), Sc1–C2 2.436(6), Sc1–C3 2.450(6), Sc1–C4 2.488(5), Sc1–C5 2.453(5), Sc1–C6 2.424(5), Sc1–C7 2.271(5), Sc1–C10 2.277(5), C1–Sc1–C7 110.2(2), C6–Sc1–C10 109.6(2), C7–Sc1–C10 96.1(2).

and $[\{MgCl(THF)_2\}_3(\mu_3\text{-}C_3H_5)_2]_2[Mg(\eta^1\text{-}C_3H_5)_4]$[17b] contain four η^1-coordinated allyl fragments to the smaller metal centers aluminium and magnesium. The anion in $[Li(TMEDA)_2]$-$[Ni(\eta^1\text{-}C_3H_5)_2(\eta^3\text{-}C_3H_5)]$ with the smaller nickel(II) center contains one η^3- and two η^1-coordinated allyl ligands.[22]

The neutral (tris)allyl compound **1** was also observed as only product from **2a** with one equivalent of **3a** containing the cationic as well as the anionic fragment in a ^1H NMR experiment (Fig. S3, ESI†). Furthermore, **3a** reacted with two equivalents of the Brønsted acid $[NEt_3H][BPh_4]$ to give **2a**.

Cationic allyl compounds are known to catalyze the polymerization of olefins.[1–3] Since **2c** is better soluble in organic solvents than **2a** and **2b**, this compound was tested for the polymerization of styrene and 1,3-butadiene in toluene.[3,23] Atactic polystyrene was isolated in modest yield after 1 h at 50 °C. Polymerization of 1,3-butadiene gave a mixture of 1,4-polybutadiene (*cis*/*trans* ratio = 2 : 1) and 1,2-polybutadiene in moderate yield after 15 min at 25 °C. This is comparable to the reported polymerizations of 1,3-butadiene using the analogous neodymium catalyst $[Nd(\eta^3\text{-}C_3H_5)_2(THF)_3][BPh_4]$.[3]

In conclusion, we have structurally characterized the neutral, cationic and anionic allyl compounds of scandium **1–3**. Fluxional behavior of the coordination manner of the allyl ligands is found in solution. Even at −95 °C the ^1H NMR spectra of **1a** and **3a** do not show decoalescence. The crystal structure of the anionic part of **3c** contains two η^1- and two η^3-coordinated allyl ligands, the scandium atom in the neutral compound **1a** is bonded to one η^1- and two η^3-coordinated allyl ligands and the cationic part in **2a** contains two η^3-coordinated allyl ligands. The smallest rare earth metal scandium represents a borderline case for η^3-coordination of allyl ligands that is common for all larger, less electronegative metals.[1–8,11,13–15,20,24] The high activity of some scandium complexes in polymerizations may be correlated with the propensity to both η^1- and η^3-allyl binding modes in the reactive intermediate prior to olefin insertion.[13b]

We are grateful to the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie for financial support.

Notes and references

‡ Crystal data for **1a**: $C_{17}H_{31}O_2Sc$, M = 312.38 g mol^{-1}, monoclinic, $P2_1/c$, a = 14.341(6), b = 21.027(9), c = 11.963(5) Å, β = 104.738(7)°, V = 3489(3) Å^3, Z = 8, $\mu(MoK_\alpha)$ = 0.422 mm^{-1}, T = 100(2) K, $2\theta_{max}$ = 53.42°, 41 084 reflections measured, 7333 unique, R_{int} = 0.1140, GoF = 0.974, R_1 [$I > 2\sigma(I)$] = 0.0753, wR_2 (all data) = 0.2238. Crystal data for **2a**: $C_{18}H_{34}O_3Sc{\cdot}C_{24}H_{20}B$, M = 662.62 g mol^{-1}, monoclinic, $C2/c$, a = 31.6886(18), b = 9.9269(6), c = 23.1586(13) Å, β = 93.9940(10)°, V = 7267.3(7) Å^3, Z = 8, $\mu(MoK_\alpha)$ = 0.240 mm^{-1}, T = 100(2) K, $2\theta_{max}$ = 60.98°, 53 345 reflections measured, 10 704 unique, R_{int} = 0.0840, GoF = 0.947, R_1 [$I > 2\sigma(I)$] = 0.0475, wR_2 (all data) = 0.1134. Crystal data for **3c**: $C_{24}H_{48}MgO_6{\cdot}2(C_{12}H_{20}Sc){\cdot}2(C_4H_8O)$, M = 1019.62 g mol^{-1}, monoclinic, $P2_1/n$, a = 13.0491(12), b = 11.3146(10), c = 20.4870(18) Å, β = 97.444(4)°, V = 2999.3(5) Å^3, Z = 2, $\mu(MoK_\alpha)$ = 0.284 mm^{-1}, T = 130(2) K, $2\theta_{max}$ = 52.98°, 43 819 reflections measured, 6000 unique, R_{int} = 0.2219, GoF = 0.841, R_1 [$I > 2\sigma(I)$] = 0.0670, wR_2 (all data) = 0.1759.

1 (*a*) L. Friebe, O. Nuyken and W. Obrecht, *Adv. Polym. Sci.*, 2006, **204**, 1; (*b*) S. M. Guillaume, E. Kirillov, Y. Sarazin and J.-F. Carpentier, *C. R. Chim.*, 2010, **13**, 608.

2 (*a*) N. Yu, M. Nishiura, X. Li, Z. Xi and Z. Hou, *Chem.–Asian J.*, 2008, **3**, 1406; (*b*) Z. Jian, D. Cui, Z. Hou and X. Li, *Chem. Commun.*, 2010, **46**, 3022; (*c*) L. Zhang, T. Suzuki, Y. Luo, M. Nishiura and Z. Hou, *Angew. Chem., Int. Ed.*, 2007, **46**, 1909.

3 D. Robert, E. Abinet, T. P. Spaniol and J. Okuda, *Chem.–Eur. J.*, 2009, **15**, 11937.

4 M. P. Pu, Q. Li, Y. Xie, R. B. King and H. F. Schaefer, *J. Phys. Chem. A*, 2011, **115**, 4491.

5 P. Jochmann, T. Dols, T. P. Spaniol, L. Perrin, L. Maron and J. Okuda, *Angew. Chem., Int. Ed.*, 2009, **48**, 5715.

6 (*a*) R. Taube, *J. Organomet. Chem.*, 1996, **513**, 49; (*b*) R. Taube, H. Windisch, F. H. Görlitz and H. Schumann, *J. Organomet. Chem.*, 1993, **445**, 85; (*c*) R. Taube, S. Maiwald and J. Sieler, *J. Organomet. Chem.*, 2001, **621**, 327.

7 L. F. Sánchez-Barba, D. L. Hughes, S. M. Humphrey and M. Bochmann, *Organometallics*, 2005, **24**, 5329.

8 E. Abinet, T. P. Spaniol and J. Okuda, *Chem.–Asian J.*, 2011, **6**, 389.

9 S. C. Chmely, C. N. Carlson, T. P. Hanusa and A. L. Rheingold, *J. Am. Chem. Soc.*, 2009, **131**, 6344.

10 E. G. Hoffmann, R. Kallweit, G. Schroth, K. Seevogel, W. Stempfle and G. Wilke, *J. Organomet. Chem.*, 1975, **97**, 183.

11 N. Yue, E. Hollink, F. Guérin and D. W. Stephan, *Organometallics*, 2001, **20**, 4424.

12 I. Peckermann, G. Raabe, T. P. Spaniol and J. Okuda, *Chem. Commun.*, 2011, **47**, 5061.

13 (*a*) M. E. Thompson, S. M. Baxter, A. R. Bulls, B. J. Burger, M. C. Nolan, B. D. Santarsiero, W. P. Schaefer and J. E. Bercaw, *J. Am. Chem. Soc.*, 1987, **109**, 203; (*b*) M. B. Abrams, J. C. Yoder, C. Loeber, M. W. Day and J. E. Bercaw, *Organometallics*, 1999, **18**, 1389; (*c*) J. C. Yoder, M. W. Day and J. E. Bercaw, *Organometallics*, 1998, **17**, 4946.

14 R. Coutts and P. C. Wailes, *J. Organomet. Chem.*, 1970, **25**, 117.

15 (*a*) S. Demir, S. E. Lorenz, M. Fang, F. Furche, G. Meyer, J. W. Ziller and W. J. Evans, *J. Am. Chem. Soc.*, 2010, **132**, 11151; (*b*) S. Demir, E. Montalvo, J. W. Ziller, G. Meyer and W. J. Evans, *Organometallics*, 2010, **29**, 6608; (*c*) S. Demir, T. J. Mueller, J. W. Ziller and W. J. Evans, *Organometallics*, 2011, **30**, 3083.

16 J. B. Wilkes, *J. Org. Chem.*, 1967, **32**, 3231.

17 (*a*) R. A. Layfield and S. M. Humphrey, *Angew. Chem., Int. Ed.*, 2004, **43**, 3067; (*b*) T. H. Bullock, F. García, S. M. Humphrey, P. Schüler and R. A. Layfield, *Chem. Commun.*, 2006, 2039.

18 R. D. Shannon, *Acta Crystallogr., Sect. A: Cryst. Phys., Diffr., Theor. Gen. Crystallogr.*, 1976, **32**, 751.

19 S. O'Brien, M. Fishwick, B. McDermott, M. G. H. Wallbridge and G. A. Wright, *Inorg. Synth.*, 1971, **13**, 73.

20 Z. Huang, M. Chen, W. Qiu and W. Wu, *Inorg. Chim. Acta*, 1987, **139**, 203.

21 C. Lichtenberg, T. P. Spaniol and J. Okuda, *Organometallics*, 2011, **30**, 4409.

22 D. Alberti, R. Goddard, A. Rufińska and K.-R. Pörschke, *Organometallics*, 2003, **22**, 4025.

23 General conditions for polymerization: m(**2c**) = 15 mg; [monomer]/[**2c**] = 1000; $[Al(CH_2CHMe_2)_3]$/[**2c**] = 5; V_{total} = 20 mL; styrene: 50 °C, 1 h; 1,3-butadiene: 25 °C, 15 min.

24 Metrical parameters for allyl bonds for **1a**,**b** and the anion of **3a–c** are in good agreement with those obtained by DFT calculations; Prof. L. Maron, personal communication.