DALTON COMMUNICATION

A facile access to *rac ansa*-lanthanocene alkyl complexes with an ether-bridged indenyl ligand and crystal structure of *rac*-$[O(CH_2CH_2C_9H_6)_2]YCH_2SiMe_3$

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Pure *rac ansa*-lanthanocene alkyl complexes $[O(CH_2CH_2C_9H_6)_2]LnCH_2SiMe_3$ (Ln = Y 1, Lu 2) are stereoselectively formed dictated by the nonbonded interactions between the six-membered portion of the indenyl moiety and the alkyl group.

Racemic *ansa*-lanthanocene alkyls have proved to be efficient single component catalysts (pre-catalysts) for stereospecific polymerization of α-olefins, modeling the well-known homogenous Ziegler–Natta systems based on chiral Group 4 *ansa*-metallocene complexes.[1] However, lack of efficient procedures to stereoselectively provide the desired *rac ansa*-lanthanocene complexes hampers an extensive investigation. A problem encountered in the synthesis of the *ansa*-metallocene complexes is that the undesired *meso* isomer is normally formed along with the *rac* isomers, so a subsequent tedious separation is required to remove the *meso* isomer. A stereoselective approach to *rac ansa*-yttrocene complexes with silylene bridged ligands requires incorporation of two bulkyl substituents (especially the α-substituents) on the bridged cyclopentadienyl (Cp) rings,[2] *e.g.* $[Me_2Si(C_5H_2SiMe_3\text{-}2\text{-}CMe_3\text{-}4)_2]^{2-}$. The α-substituents appear to be the key since the stereoselectivity would be inverted without them on the Cp rings, that is the *meso* isomer is favorably formed,[3] although more sterically demanding substituents such as (−)-menthyl [(1*R*,2*S*,5*R*)-(−)-C_6H_3Me-5-Pr^i-2] or (+)-neomenthyl [(1*S*,2*S*,5*R*)-(+)-C_6H_3Me-5-Pr^i-2] and *tert*-butyl can be introduced on the linked Cp rings,[4] *e.g.* $\{Me_2Si(Bu^tC_5H_4)[(1S,2S,5R)\text{-}(+)\text{-}C_6H_3Me\text{-}5\text{-}Pr^i\text{-}2\text{-}C_5H_3]\}^{2-}$. Recently, Anwander and co-workers have reported their isolation of the pure *rac ansa*-yttrocene silylamide $Me_2Si(C_9H_5Me\text{-}2)_2YN(SiHMe_2)_2$ after recrystallization of the *rac*/*meso* mixture (3 : 1) in hydrocarbon solvents.[5] We have isolated solvated *rac ansa*-lanthanocene chlorides $[O(CH_2CH_2C_9H_6)_2]LnCl(thf)$, featuring a rigid and unsymmetric structure, but isomerisation occurred upon dissolving in coordinative solvents such as THF leading to a equilibrium of the *rac*/*meso* (6 : 1) mixture.[6] Here we report a facile stereoselective access to solvent-free pure *rac ansa*-lanthanocene alkyl complexes by direct alkylation of the corresponding lanthanocene chlorides and insight into the stereoselectivities of the formation of these types of complexes.

Alkylation of solvated *ansa*-lanthanocene chlorides $[O(CH_2CH_2C_9H_6)_2]LnCl(thf)$ (Ln = Y, Lu) with $LiCH_2SiMe_3$ in toluene provided the *rac ansa*-lanthanocene alkyls **1** and **2** in modest yields [eqn. (1)].† These complexes are very soluble in toluene

$$[O(CH_2CH_2C_9H_6)_2]LnCl(thf) + LiCH_2SiMe_3 \xrightarrow[0\ ^\circ C,\ -thf,\ -LiCl]{toluene} [O(CH_2CH_2C_9H_6)_2]Ln(CH_2SiMe_3) \quad (1)$$

Ln = Y **1** 53%, Lu **2** 48%

and benzene, and sparingly soluble in hexane. Spectroscopic data and elemental analyses are consistent with the replacement of THF in the alkyl complexes. The ^{1}H NMR spectra of **1** and **2** show a similar pattern, implying that their structures should be essentially identical. The observation of only one set of resonances in the ^{1}H NMR (C_6D_6) of complexes **1** and **2** clearly indicates the presence of solely *rac*-isomers in solution. All the protons of the ancillary ligand appear to be inequivalent in the ^{1}H NMR spectra of the alkyl complexes, indicating an unsymmetric structure is assumed similar to their precursor chlorides. 2D ^{1}H NMR studies (NOESY and COSY) of complex **2** have allowed ^{1}H NMR assignments (Fig. 1). The presence of cross peaks between H^1 and aromatic protons $H^{6'}$ *etc.* and the absence of cross peaks between $H^{1'}$ and aromatic protons confirm the unsymmetric structure of the *rac ansa*-lanthanocene alkyl. Additionally, the exchange connectivities of the two groups of protons of the ancillary ligand 'separated' by the oxygen atom, such as H^1–$H^{1'}$, H^2–$H^{2'}$, aromatic protons H^3–$H^{3'}$ *etc.* and methylene protons H^a–$H^{a'}$ *etc.* imply an oscillation between the two parts of the ancillary ligand. The two methylene protons of CH_2SiMe_3 show different chemical shifts probably due to the hindered rotation around the Ln–C axis. The $^2J_{Y-H}$ (3.3 and 3.6 Hz) coupling constants agree well with direct bonding of the CH_2SiMe_3 moiety to yttrium in complex **1**.

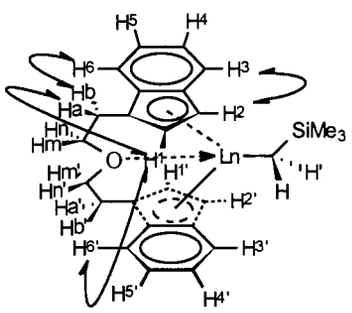

Fig. 1 The numbering scheme for the ^{1}H NMR of **2** with important NOEs.

An X-ray single crystal structure analysis‡ of **1** unambiguously confirmed the unsymmetric structure (Fig. 2). Although the bond distance ranges of the two bridged indenyl rings, 2.592(9)–2.731(8) Å (Δ = 0.14 Å) and 2.633(9)–2.713(9) Å (Δ = 0.08 Å), in molecule **1**(**A**) are evidently different, there is a similar feature, 2.59(1)–2.74(1) Å (Δ = 0.15 Å) and 2.623(8)–2.726(8) Å (Δ = 0.10 Å) in molecule **1**(**B**); both indenyl groups are typically η^5-coordinated to the metal ion. The Y(1)–C(23) bond length in molecule **A** and the Y(2)–C(49) bond length in molecule **B** are 2.376(8) and 2.35(1) Å respectively, which are a little shorter than those in the more crowded yttrocene alkyls with a terminal σ Y–C bond such as $(C_5Me_5)_2YCH(SiMe_3)_2$ 2.468(7)[7] and $(C_5Me_5)_2YMe(thf)$ 2.44(2) Å,[8] but agree well with that in (*S*)-$Me_2SiC_5Me_4[(1S,2S,5R)\text{-}(+)\text{-}C_6H_3Me\text{-}5\text{-}Pr^i\text{-}2\text{-}C_5H_3]YCH(SiMe_3)_2$ 2.36(1) Å, whose shorter σ Y–C bond distance was attributed to the minimization of the nonbonded interactions between the bulky substituents and the alkyl group due to their special spatial arrangements.[4] Indeed, in its (*R*)–epimers

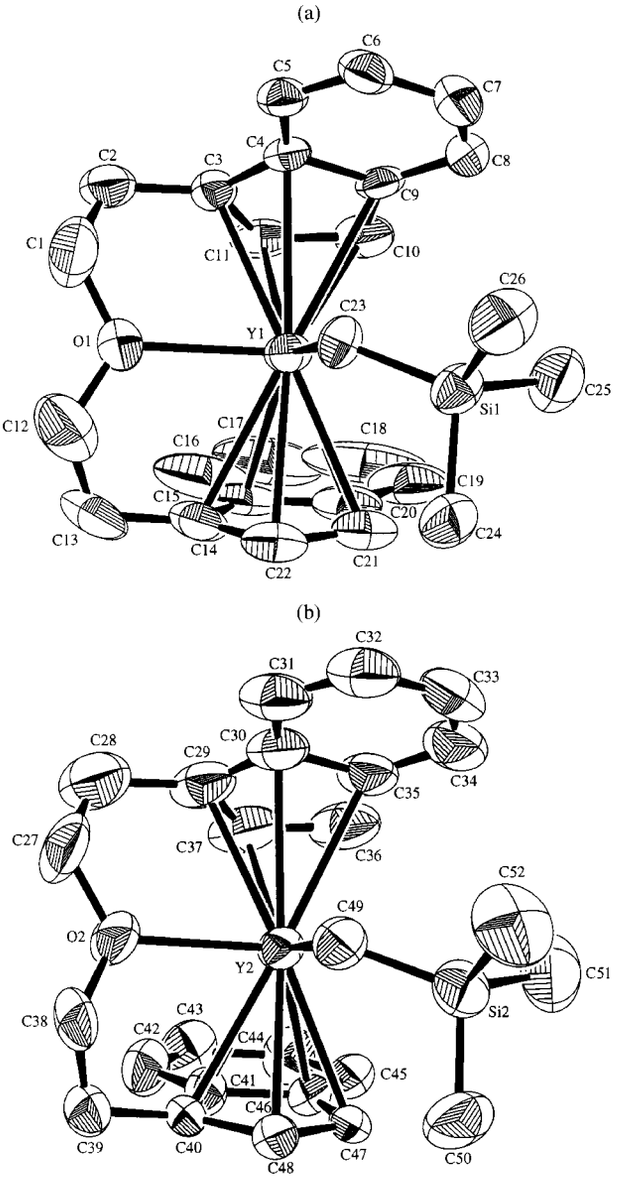

Fig. 2 (a) ORTEP[9] drawing of **1**(**A**) (one of the two independent molecules, **A** and **B**, with the same configuration in the unit cell). Selected bond lengths, bond length ranges for η^5-indenyl (Å) and angles (°) of molecule **A**: Y(1)–C(23) 2.376(8), Y(1)–O(1) 2.323(6) Y(1)–C(3) 2.641(8) to Y(1)–C(11) 2.592(9), Y(1)–C(14) 2.653(9) to Y(1)–C(22) 2.633(9); O(1)–Y(1)–C(23) 100.4(3), C(1)–O(1)–C(12) 118.9(9), C(1)–O(1)–Y(1) 119.3(6), C(12)–O(1)–Y(1) 120.8(7). Dihedral angle of the two indenyl planes, 46.38°. (b) ORTEP[9] drawing of **1**(**B**). Corresponding selected bond lengths, bond length ranges for η^5-indenyl (Å) and angles (°) of molecule **B**: Y(2)–C(49) 2.35(1), Y(2)–O(2) 2.337(6), Y(2)–C(29) 2.623(10) to Y(2)–C(37) 2.59(1), Y(2)–C(40) 2.658(8) to Y(2)–C(48) 2.623(8); O(2)–Y(2)–C(49) 97.4(3), C(27)–O(2)–C(38) 118.4(8), C(27)–O(2)–Y(2) 122.3(6), C(38)–O(2)–Y(2) 115.2(5). Dihedral angle of the two indenyl planes, 44.54°.

the corresponding bond length is significantly longer 2.49(1) Å. It is noteworthy that the O(1)–Y(1)–C(23) and O(2)–Y(2)–C(49) angles in molecule **1**(**A**) and **1**(**B**) are 100.4(3) and 97.4(3)° respectively. This means, that in contrast to the silylene bridged bis(indenyl) yttrocene amide $Me_2Si(C_9H_5Me\text{-}2)_2YN(SiHMe_2)_2$,[5] the orientation of the alkyl group parallels the bridged indenyl planes, *syn* to the six-membered portion of one of the bridged indenyl rings, and *anti* to that of the other indenyl ring. This interesting arrangement is perhaps adopted to avoid the repulsion between the CH_2SiMe_3 and the edges of the indenyl planes since the 'wide portion' of the *ansa*-metallocene is significantly narrowed by the rigid five-atom bridge. It is evident that efficient minimization of the nonbonded repulsion could be achieved in the *rac* isomers since the alkyl group could not only avoid simultaneous interactions with the six-membered portions of the two bridged indenyl rings but also further minimize the nonbonded repulsion by orienting away from the *syn* indenyl plane. However, a strong repulsion could be anticipated in the *meso* isomer whether the alkyl group orients to the narrow or wide portion of the *ansa*-metallocene wedge. Based on these structural analyses, the *rac*/*meso* stereoselectivty should be dictated by the nonbonded interactions between the indenyl planes and the alkyl group, instead of the two bridged indenyl rings themselves. Since there is no isomerisation observed in hydrocarbon solution, it is reasonable to expect that a catalysis system stereoselective in polymerization of α-olefins could be developed based on these *rac ansa*-lanthanocene alkyls although further investigations are needed.

Acknowledgements

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Notes and references

† Preparation of complex **1**. To a suspension of 1.70 g (3.42 mmol) yttrocene chloride $[O(CH_2CH_2C_9H_6)_2]YCl(thf)$ in 50 ml toluene was added 0.31 g (3.30 mmol) $LiCH_2SiMe_3$ at about 0 °C. The resulting suspension was allowed to warm to ambient temperature and stirred overnight under argon. The precipitate was separated by centrifugation and the clear solution was concentrated. The residue was extracted with toluene–hexane (1 : 15, v/v). The hexane extract was cooled to −30 °C and 0.83 g (53% yield) of **1** was obtained as a colourless crystalline solid (Found: C, 65.58; H, 6.55. Calc. for $C_{26}H_{31}OSiY$: C, 65.55; H, 6.51%). ^{1}H NMR (300 MHz, C_6D_6, 25 °C): δ 7.55 (m, 1H, aromatic), 7.40 (m, 1H, aromatic), 7.25 (m, 2H, aromatic), 7.10 (m, 4H, aromatic), 6.85 (d, J = 2.7, 1H, H$^{1'}$), 6.15 (d, J = 3.2, 1H, H$^{2'}$), 5.00 (s, 2H, H^1, H^2), 3.80 (m, 1H, OCH^{n}H$^{n'}$), 3.50 (m, 1H, OCH$^{n}H^{n'}$), 3.25 (m, 1H, OCH^{m}-$H^{m'}$), 3.05 (m, 1H, OCH^{m}H$^{m'}$), 2.60 (m, 1H, C$H^{b'}$H$^{a'}$), 2.40 (m, 2H, CH^{b}H^{a}, C$H^{a'}$H^{a}), 2.20 (m, 1H, CH$^{b}H^{a}$), 0.30 [s, 9H, Si(CH$_3$)$_3$], −1.65 (dd, 1H, $^2J_{H-H}$ = 10.6, $^2J_{Y-H}$ = 3.6, CHH′SiMe$_3$), −2.00 (dd, 1H, $^2J_{H-H}$ = 10.6, $^2J_{Y-H}$ = 3.3 Hz, CHH'SiMe$_3$).

For **2**. A similar procedure was adopted to provide **2** as colorless crystals (48%) (Found: C, 55.43; H, 5.65. Calc. for $C_{26}H_{31}OSiLu$: C, 55.52; H, 5.52%). ^{1}H NMR: δ 7.60 (m, 1H, H$^{3'}$, aromatic), 7.45 (m, 1H, H^3, aromatic), 7.30 (m, 1H, H$^{6'}$, aromatic), 7.20 (m, 5H, H^6, H^4, H$^{4'}$, H^5, H$^{5'}$, aromatic), 6.85 (d, J = 3.2, 1H, H$^{1'}$), 6.10 (d, J = 3.2, 1H, H$^{2'}$), 5.15 (d, J = 3.2, 1H, H^2), 4.90 (d, J = 3.2, 1H, H^1), 3.85 (m, 1H, OCH^{n}-H^{m}), 3.50 (m, 1H, OC$H^{n'}$H$^{m'}$), 3.35 (m, 1H, OCH$^{n'}H^{m'}$), 3.10 (m, 1H, OCH$^{n}H^{m}$), 2.60 (m, 1H, C$H^{b'}$H$^{a'}$), 2.40 (m, 2H, CH$^{b'}H^{a'}$, CH^{b}H^{a}), 2.20 (m, 1H, CH$^{b}H^{a}$) 0.35 [s, 9H, Si(CH$_3$)$_3$], −1.85 (d, 1H, $^2J_{H-H}$ = 10.8, CHH′SiMe$_3$), −2.20 (d, 1H, $^2J_{H-H}$ = 10.8 Hz, CH'HSiMe$_3$).

‡ Crystal data for *rac*-**1**: $C_{26}H_{31}OSiY$, M = 476.52, monoclinic, space group $P2_1/n$, a = 24.24(1), b = 8.394(7), c = 24.46(1) Å, β = 102.35(3)°, V = 4862(5) Å^3, Z = 8, D_c = 1.302 g cm^{-3}, F(000) = 1984.00, μ(Mo-Kα) = 24.65 cm^{-1}, T = 293 K, no. reflections: total 9417, unique 9189, observations 3988 [$I > 2.00\sigma(I)$], variables 524, R = 0.063, R_w = 0.057. CCDC reference number 186/1300. See http://www.rsc.org/suppdata/dt/1999/519/ for crystallographic files in .cif format.

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