C_3-Chiral Tripodal Amido Complexes

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Dedicated to Professor Guy Ourisson on the occasion of his 75th birthday

Abstract: A comprehensive study into the coordination chemistry of two C_3-chiral tripodal amido ligands has been carried out. The amido ligands contain a trisilylmethane backbone and chiral peripheral substituents. The amine precursors, $HC\{SiMe_2NH[(S)\text{-1-phenylethyl}]\}_3$ (**1**) and $HC\{SiMe_2NH[(R)\text{-1-indanyl}]\}_3$ (**2**) were found to be in equilibrium in solution with the cyclic diamines $HC\{SiMe_2N[(S)\text{-1-phenylethyl}]_2\}\{SiMe_2NH[(S)\text{-1-phenylethyl}]\}$ (**3**) and $HC\{SiMe_2NH[(R)\text{-1-indanyl}]\}\{SiMe_2NH[(R)\text{-1-indanyl}]\}$ (**4**), which are generated upon ejection of one molecule of the chiral primary amine. Reaction of these equilibrium mixtures with three molar equivalents of butyllithium instantaneously gave the trilithium triamides $HC\{SiMe_2N(Li)[(S)\text{-1-phenylethyl}]\}_3$ (**5**) and $HC\{SiMe_2N(Li)[(R)\text{-1-indanyl}]\}_3$ (**6**), both of which were characterised by an X-ray diffraction study. Both lithium compounds possess a central heteroadamantane core, in which the two-coordinate Li atoms are additionally weakly solvated by the three aryl groups of the chiral peripheral substituents, the Li–C contacts being in the range of 2.65–2.73 Å. Reaction of **5** and **6** with $[TiCl_4(thf)_2]$ and $ZrCl_4$ gave the corresponding amido complexes $[TiCl\{HC\{SiMe_2N[(S)\text{-1-phenylethyl}]\}_3\}]$ (**7**), $[TiCl\{HC\{SiMe_2N[(R)\text{-1-indanyl}]\}_3\}]$ (**8**), $[ZrCl\{HC\{SiMe_2N[(S)\text{-1-phenylethyl}]\}_3\}]$ (**9**) and $[ZrCl\{HC\{SiMe_2N[(R)\text{-1-indanyl}]\}_3\}]$ (**10**), respectively. Of these, compound **7** was structurally characterised by X-ray structure analysis and was shown to possess a C_3-symmetrical arrangement of the tripod ligand. The chiral anionic dinuclear complex $[Li(OEt_2)_4][Zr_2Cl_3\{HC\{SiMe_2N[(S)\text{-1-phenylethyl}]\}_3\}_2]$ (**11**) was isolated from reaction mixtures leading to **9**. An X-ray diffraction study established its dimeric structure, in which the chiral amido ligands cap the two metal centres, which are linked through three symmetrically arranged, bridging chloro ligands. Reaction of **9** and **10** with a series of alkyl Grignard and alkyllithium reagents yielded the corresponding alkylzirconium complexes. X-ray structure analyses of $[Zr(CH_3)\{HC\{SiMe_2N[(S)\text{-1-phenylethyl}]\}_3\}]$ (**12**) and $[Zr(CH_3)\{HC\{SiMe_2N)[(R)\text{-1-indanyl}]\}_3\}]$ (**20**) established their detailed molecular arrangements. While the reaction of **12** with the aryl ketones PhC(O)R (R = CH=CHPh, *i*Pr, Et) gave the corresponding C–O insertion products, which contain an additional chiral centre in the alkoxy group, with low stereoselectivity (0–40% *de*). The corresponding conversions with several aryl aldehydes yielded the alkoxo complexes with high stereoselectivity. Upon hydrolysis, the chiral alcohols were isolated and shown to have enantiomeric excesses between 68 and 82%. High stereodiscrimination was also observed in the insertion reactions of several chiral ketones and aldehydes. However, this was shown to originate primarily from the chirality of the substrate. In analogous experiments with carbonyl compounds, the ethyl- and butyl-zirconium analogues of **12** did not undergo CO insertion into the metal–alkyl bond. Instead, β-elimination and formal insertion into the metal-hydride bond occurred. It was found that the elimination of the alkene was induced by

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Introduction

Molecular symmetry is a leading principle in the development of new stereoselective reagents and catalysts.[1–3] In coordination chemistry, this is most often achieved by employing polydentate ligands containing local symmetry elements,[4] which are then retained upon coordination to a metal centre. An important argument in favour of ligand symmetry in chiral reagents and catalysts is the reduction of the number of possible diastereomeric intermediates or transition states by

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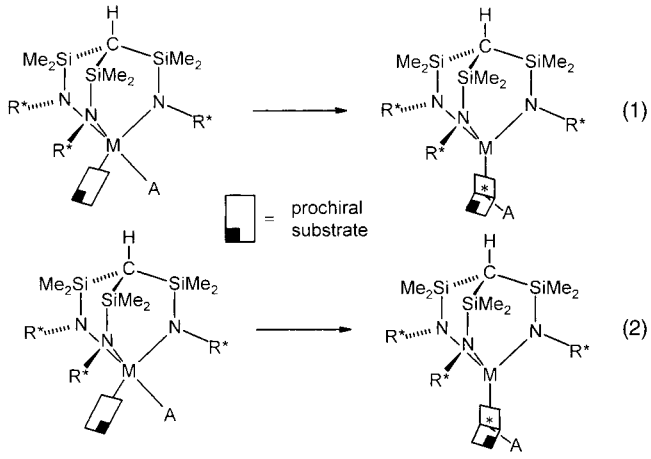
the rotational symmetry element. This may give improved stereoselectivity and in addition facilitates the rationalisation of the observed stereocontrol, which is important in the systematic optimisation of a reagent.

While twofold rotational symmetry has been successfully employed in a large number of chiral reagents and catalysts,[5] there is still comparatively little known about the efficiency of systems of higher rotational symmetry. Currently, there is a burgeoning interest in C_3-chiral complexes and their application in catalysis.[6–8] The majority of the systems studied to date are coordination compounds of the late transition metals.[9] In contrast, stereoselective transformations of C_3-chiral early transition metal complexes are barely explored. These require highly charged ligands, such as alkoxo or amido ligands, in order to stabilise the formally high-valent metal centres.[10] Several examples of C_3-chiral alkoxo ligands, in which three chiral centres are located in the ligand backbone, have been studied in Nugent's group as well as by Knochel and co-workers.[11]

To date, there are two different strategies for the synthesis of C_3-chiral amido tripods. The first involves the introduction of chirality in the peripheral groups of the amido ligand at close proximity to the donor functions as first shown by us.[12] An alternative approach has been the generation of a chiral ligand tripod-backbone as pursued by Moberg and co-workers in their synthesis of chiral triamidoamine ligands.[13] In a landmark contribution to the field, they demonstrated that the titanium complexes containing these ligands may be used in the catalytic asymmetric alkylation, albeit with only moderate stereoselectivity.

The conceptual background and the choice of the model system: In the same way as C_2-symmetrical bidentate ligands in square-planar and tetrahedral complexes render the two remaining coordination sites homotopic, an octahedral complex containing a C_3-symmetrical tripodal ligand will have three stereochemically identical remaining binding sites, as was first pointed out by Burk and Harlow.[14] Although the equivalence of the three remaining coordination sites induced by a C_3 tripod in an octahedral complex simplifies the analysis of such systems, there remain several possibilities of the relative orientation of prochiral ligands in stoichiometric transformations or in elementary steps of catalytic cycles.[14] This may limit the conceptual usefulness of the approach.

The possible reduction in selectivity-determining alternatives in stoichiometric conversions involving threefold symmetrical chiral ligands is by no means restricted to the octahedral case. A similar situation is expected to arise in fivefold coordinate complexes, or reaction intermediates bearing such a chiral tripod and in which the two remaining ligands are arranged symmetrically on either side of the molecular axis. Such a coordination geometry has been postulated by Ugi et al. for the transition state in the turnstile rearrangement of five-coordinate molecules.[15] We have found such an arrangement as the ground-state geometry of several five-coordinate zirconium complexes bearing tripodal amido ligands.[16] If one of these two monodentate ligands were a planar prochiral molecule and the other ligand a molecular fragment to be coupled with the prochiral unit to give a new stereo-element, the C_3-symmetrical tripod renders all possible arrangements essentially identical. Therefore the stereochemical alternatives would be reduced to the two possible orientations of the prochiral faces with respect to the attacking ligand [Eqs. (1) and (2)].



The C_3-symmetrical tripod renders all possible isomers, distinguished only by the relative rotation of the {(tripod)M} and the {M(L)(L′)} units, essentially stereochemically identical. A reaction that represents this situation exactly, and which therefore permits the practical evaluation of this conceptual approach, is the stoichiometric insertion of an *O*-coordinated prochiral carbonyl compound into a metal–alkyl bond.[17] If the three stereocentres in the ligand periphery of the tripodal ligand adopt a similar orientation, thus generating real threefold symmetry, this in turn defines a helicoidal environment for the remaining ligands and will, therefore, favour one of the two possible orientations of the carbonyl compound vis-à-vis the alkyl ligand. This stereodiscrimination will be greatest in carbonyl compounds that contain two very different substituents at the CO function, which is why we chose to investigate primarily aryl aldehydes as substrates.

In this paper, the scope of the conceptual considerations will be judged by the results of a study of the stoichiometric stereoselective alkylation reactions with aldehydes as well as several chiral ketones by alkyltitanium and -zirconium complexes bearing two different chiral tripodal ligands. The synthesis and chemical behaviour of the two C_3-chiral amine precursors (containing a trisilylmethane ligand frameworks), their lithiated derivatives and the structures of key complexes are also reported.

Results and Discussion

Synthesis, solution dynamics and structures of the C_3-chiral triamines and lithium triamides: The choice of the ligand backbone was dictated by the ease with which chiral substituents are introduced in tripodal amines. The synthesis of the amine-ligand precursors was achieved as previously described for related systems in a one-step transformation.[18] Reaction of $HC(SiMe_2Br)_3$ with three molar equivalents of (*S*)-1-phenylethylamine and (*R*)-1-indanylamine in the pres-

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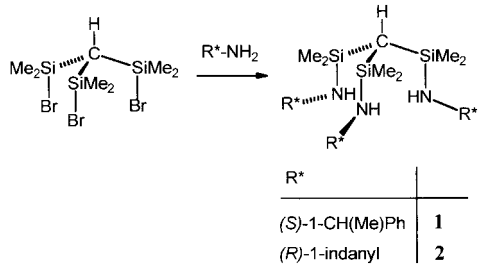
ence of three equivalents of triethylamine, yielded the tripodal amines HC{$SiMe_2NH$[(*S*)-1-phenylethyl]}$_3$ (**1**) and HC{$SiMe_2NH$[(*R*)-1-indanyl]}$_3$ (**2**) (Scheme 1).



Scheme 1. Synthesis of the C_3-chiral triamines **1** and **2**.

The spectrocopic and analytical data of both compounds are in accord with the postulated structures. A single-crystal X-ray structure analysis as well as a NOESY study in solution of **1**, which we published previously,[12a] established a molecular arrangement that may be related to a heteroadamantane cage, the base of which is formed by a loosely aggregated $(N{-}H)_3$ unit stabilised by $N{-}H\cdots N$ hydrogen bonds. This hydrogen bonding was also reflected in the infrared vibrational N–H stretching frequency of 3343 cm^{-1}, which is significantly lower than those of non-hydrogen bonded analogues ($\tilde{\nu}$(N–H) ca. 3400 cm^{-1}). The indanyl-substituted compound **2** displays very similar spectroscopic characteristics ($\tilde{\nu}$(N–H) ca. 3339 cm^{-1}), and a preliminary X-ray diffraction study of the weakly diffracting crystals of **2** confirm a molecular arrangement that is similar to that of **1**. Although the poor quality of the data do not permit a detailed discussion of the the metric parameters of **2**, the overall molecular arrangement is well established and represented in Figure 1.

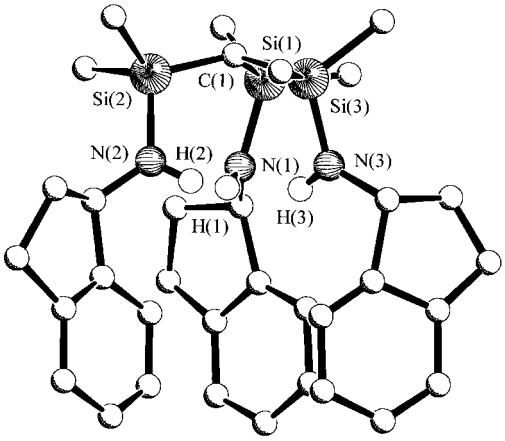
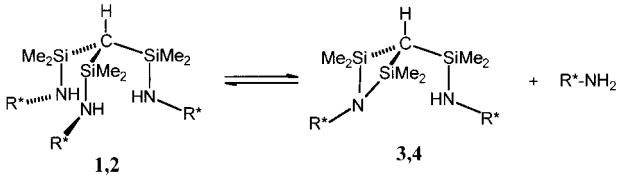


Figure 1. Molecular structure of the triamine **2**, showing the clawlike arrangement of the tripodal molecule.

As can be readily seen, the ligand is effectively "pre-arranged", even in the form of its amine precursor, and the potential binding site for the metal is clearly evident. The chiral centres in the 1-indanyl groups would be arranged at close proximity to the "reactive" site in a complex.

Whereas the amines **1** and **2** are readily isolated as crystalline solids in good yields, they are unstable in solution. ^1H and ^{13}C NMR spectroscopy established an equilibrium between the triamines **1** and **2** and the cyclic diamines **3** and **4**, which are generated by elimination of one molecule of (*S*)-1-phenylethylamine and (*R*)-1-indanylamine, respectively (Scheme 2). We previously reported the isolation and characterisation of a similar azadisilacyclobutane species, PhC-{$(SiMe_2)_2NtBu$}{$SiMe_2NHtBu$}.[18]

At 295 K, the equilibra between **1** and **3** and between **2** and **4** lies almost entirely on the side of the tripodal amines. As can be seen in the variable temperature series of ^1H NMR spectra of **2** displayed in Figure 2, the equilibrium may be almost completely shifted towards the cyclic product **4** and the free primary amine upon raising the temperature of a solution in toluene to 355 K. It should be pointed out that, upon



Scheme 2. Equilibrium in solution between the triamines **1** and **2** and the cyclic aminosilanes **3** and **4**, respectively.

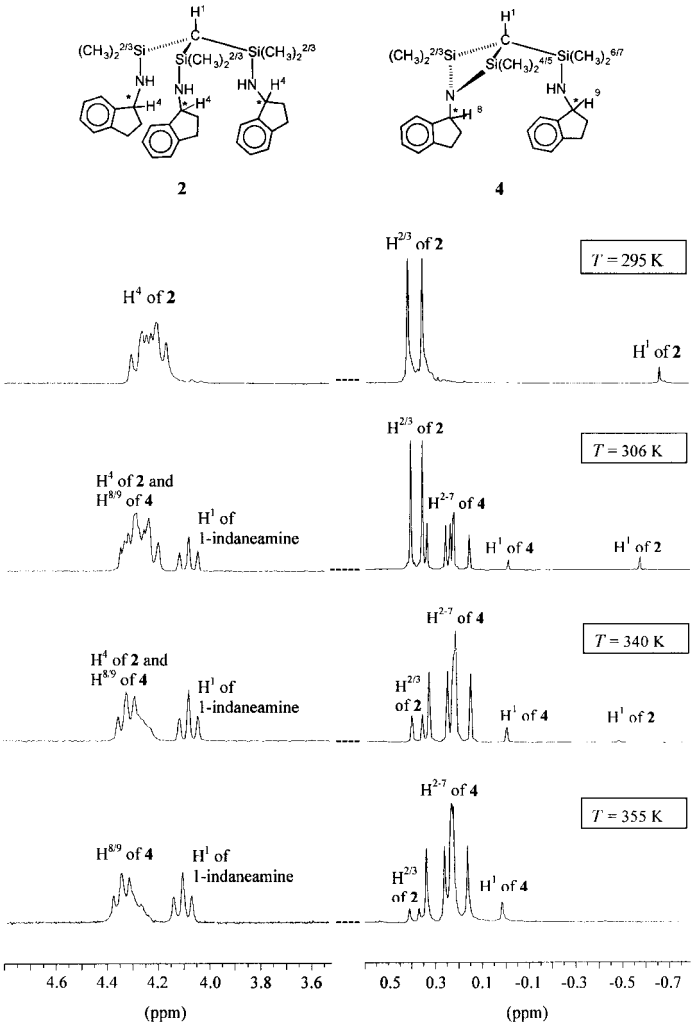
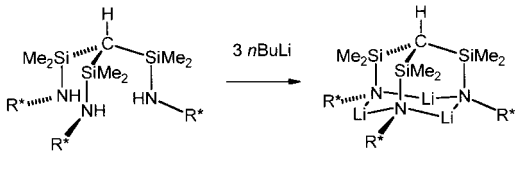


Figure 2. Variable-temperature NMR spectra of a solution of **2** in toluene between 295 and 355 K, showing the almost complete conversion to the cyclic product **4** at high temperatures.

dissociation of (*R*)-1-indanylamine, the threefold molecular symmetry is lost, rendering all hydrogen positions in the ligand framework nonequivalent. The equilibrium constants at the various temperatures could be determined by integration of the singlet resonances due to the apical CH protons, which are observed at $\delta = -0.66$ (**2**) and -0.10 (**4**).

An analysis of the temperature dependence of this equilibrium yielded a standard reaction enthalpy of $\Delta H = +49.9 \pm 0.5\ \mathrm{kJ\,mol^{-1}}$ and a reaction entropy of $\Delta S = +162.1 \pm 2.0\ \mathrm{J\,mol^{-1}\,K^{-1}}$. The dissociation of the tripodal amine is thus an entropy driven process. Its endothermic nature is thought to be due to the greater molecular strain in the cyclic product, with the total number of element–element bonds remaining unchanged. Additional intramolecular stabilisation through the N–H···N hydrogen-bond network discussed above may also contribute to the relative stability of the triamines.

The amido ligand transfer reagents used in this study are the corresponding lithium amides HC{$SiMe_2N(Li)$[(*S*)-1-phenylethyl]}$_3$ (**5**) and HC{$SiMe_2N(Li)$[(*R*)-1-indanyl]}$_3$ (**6**), which are readily obtained by reaction of the amine precursors with three equivalents of *n*-butyllithium (Scheme 3).



R*	
(*S*)-1-CH(Me)Ph	**1**
(*R*)-1-indanyl	**2**

R*	
(*S*)-1-CH(Me)Ph	**5**
(*R*)-1-indanyl	**6**

Scheme 3. Synthesis of the C_3-chiral trilithium triamides **5** and **6**.

It is notable that the result of this metalation is the same whether the reaction is carried out with the essentially pure tripodal amines **1** and **2**, or mixtures of the triamines and the cyclic products **3** and **4** in the presence of the dissociated primary amines. Since in the latter case the deprotonation of the N–H groups occurs much more rapidly than the reformation of the triamine, the generation of the lithium amides is thought also to occur "indirectly" by attack of a lithiated primary amine upon the azasilacyclobutane.

Both compounds were isolated as highly crystalline, colourless solids, which were used as such in the subsequent conversions. Although a large number of lithium amides have been structurally characterised,[19] very few chiral systems have been investigated.[20] In addition, it was of interest to establish how the ligand periphery in **5** and **6** would arrange itself with respect to the $(Li–N)_3$ unit. Single crystal diffraction studies of both lithium amides have established their molecular structures, which are represented in Figure 3.

Compounds **5** and **6** crystallise in the space groups *R*3 and $P2_12_12_1$, respectively. For **5**, the molecular threefold axis coincides with the threefold crystallographic axis (Figure 3, top), thus rendering this compound exact C_3 symmetry in the solid. The indanyl-substituted derivative **6** (Figure 3, middle) deviates only slightly from an ideal C_3-symmetrical arrangement, so that both lithium amides may be directly compared.

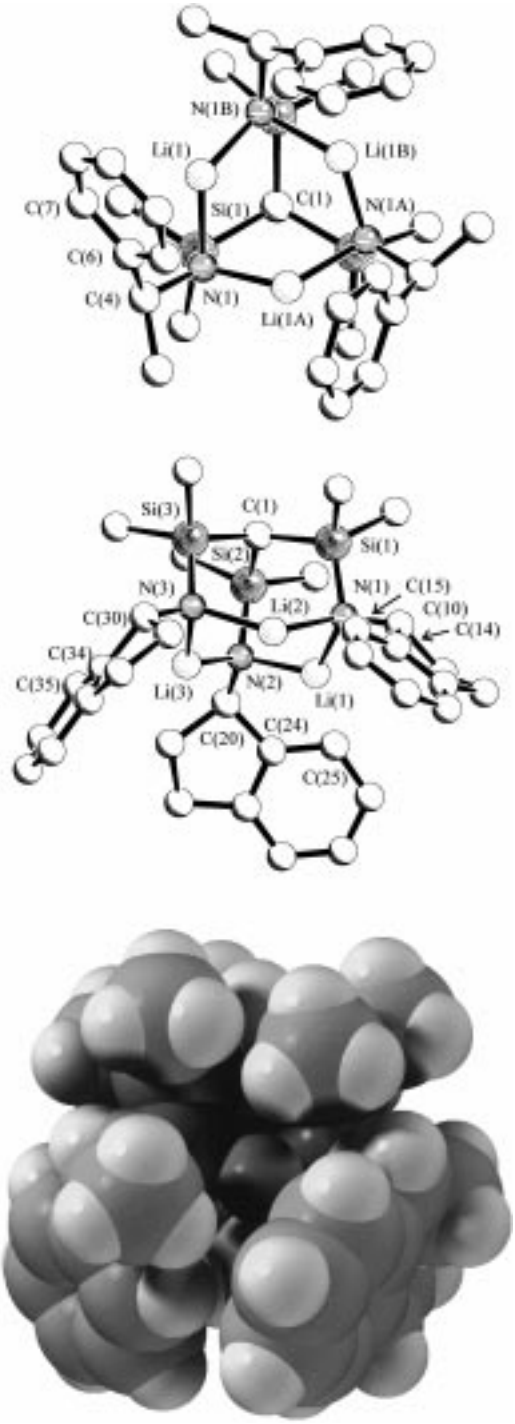


Figure 3. Top: molecular structure of HC{$SiMe_2N(Li)$[(*S*)-1-phenylethyl]}$_3$ (**5**) viewed along the threefold crystallographic axis. Principal bond lengths (Å) and interbond angles (°): Si(1)–N(1) 1.678(8), Si(1)–C(1) 1.901(5), Si(1)–C(2) 1.88(1), Si(1)–C(3) 1.89(1), N(1)–C(4) 1.50(1), N(1)–Li(1) 1.98(2), N(1)–Li(1A) 1.87(2); N(1)-Si(1)-C(1) 107.6(6), Si(1)-N(1)-C(4) 119.5(7), Si(1)-N(1)-Li(1) 99.5(7), Si(1)-N(1)-Li(1A) 117.2(8), C(4)-N(1)-Li(1) 102.2(8), Li(1)-N(1)-Li(1A) 94(1), N(1)-Li(1)-N(1A) 120(1). Middle: molecular structure of HC{$SiMe_2N(Li)$[(*R*)-1-indanyl]}$_3$ (**6**) viewed orthogonal to the virtual molecular axis. Principal bond lengths (Å) and interbond angles (°): Si(1)–N(1) 1.711(6), Si(1)–C(1) 1.854(8), Si(1)–C(2) 1.899(8), Si(1)–C(3) 1.891(8), N(1)–C(10) 1.455(10), N(1)–Li(1) 1.945(19), N(1)–Li(2) 1.951(17); N(1)-Si(1)-C(1) 109.2(4), Si(1)-N(1)-C(10) 112.9(6), Si(1)-N(1)-Li(1) 112.2(6), Si(1)-N(1)-Li(2) 101.6(6), C(10)-N(1)-Li(1) 123.0(7), Li(1)-N(1)-Li(2) 91.0(7), N(1)-Li(1)-N(2) 120.1(8). Bottom: space-filling model of compound **5**, showing the intramolecular "solvation" of the $(LiN)_3$ core by the peripheral arene groups.

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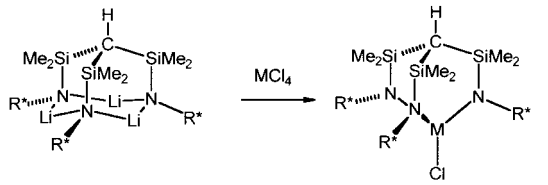
As with all previously characterised tripodal lithium amides of this type, the structural centre piece in this molecules is the adamantane-derived cage composed of the trisilylmethane and the triamidolithium units.[18, 21] The most interesting structural aspect, which sets **5** and **6** apart from previously studied compounds of this type, is the "internal solvation" of the two-coordinate lithium atoms by the peripheral aryl groups. This structural feature in lithium amides was first discovered by Snaith and co-workers in the trimeric structure of dibenzyllithium.[22] The distance between Li(1) and C(7) in **5** of 2.69(2) Å and the corresponding interatomic distances in **6** (Li(1)–C(25) 2.83, Li(2)–C(15) 2.73, Li(3)–C(35) 2.66 Å) are within the range of the aryl–Li contacts found in dibenzyllithium (average d(Li–C): 2.80 Å; shortest contact: 2.70 Å). The intramolecular π-arene solvation leads to an almost complete encapsulation of the primarily ionic $(LiN)_3$ core, as can be seen in a space-filling model of **5** (Figure 3, bottom).

There are several other examples in the literature of aryl π-coordination of alkali metal compounds (particularly the heavier ones).[23] A secondary effect of the interaction of the Li centres with the aryl groups is the more pronounced puckering of the $(LiN)_3$ unit [average torsion angles ∢(Li-N-Li′-N′) 66° (**5**), 59° (**6**)] in comparison, for example, to $HC\{SiMe_2N(Li)tBu\}_3$ [∢(Li-N-Li′-N′) 53–56°].[18]

Synthesis and structures of C_3-chiral amido complexes of the Group 4 metals: Reaction of the tripodal lithium amides **5** and **6** with $[TiCl_4(thf)_2]$ in pentane and with $ZrCl_4$ in toluene or diethyl ether gave the corresponding C_3-chiral titanium and zirconium complexes $[TiCl\{HC\{SiMe_2N[(S)\text{-1-phenylethyl}]\}_3\}]$ (**7**), $[TiCl\{HC\{SiMe_2N[(R)\text{-1-indanyl}]\}_3\}]$ (**8**), $[ZrCl\{HC\{SiMe_2N[(S)\text{-1-phenylethyl}]\}_3\}]$ (**9**), and $[ZrCl\{HC\{SiMe_2N[(R)\text{-1-indanyl}]\}_3\}]$ (**10**) (Scheme 4).



R*	
(S)-1-CH(Me)Ph	**5**
(R)-1-indanyl	**6**

R*	M	
(S)-1-CH(Me)Ph	Ti	**7**
(R)-1-indanyl	Ti	**8**
(S)-1-CH(Me)Ph	Zr	**9**
(R)-1-indanyl	Zr	**10**

Scheme 4. Synthesis of the chlorotitanium and zirconium complexes **7**–**10**.

Conversion to the titanium complexes is complete after stirring the reaction mixture at ambient temperature for six days. Both compounds are highly soluble in hydrocarbon solvents, which leads to some losses in yield upon their isolation as yellow crystalline solids. The reaction giving the zirconium analogues proceeds at a much slower rate. Complete conversion, with almost quantitative yield, is achieved for compound **9** after a reaction time of 18 days in diethyl ether. Similar conditions may be used in the synthesis of **10**; however, a superior and almost quantitative yield of this complex is obtained upon heating of the reaction mixture at 60 °C for 7 h. After separation from the LiCl generated in these reactions and washing with cold pentane, both complexes **9** and **10** are obtained as analytically pure, colourless microcrystalline solids.

A single-crystal X-ray structure analysis of **7** has established the details of its molecular structure (Figure 4). The tripodal ligand-metal [2,2,2]bicyclooctane-related cage structure at the

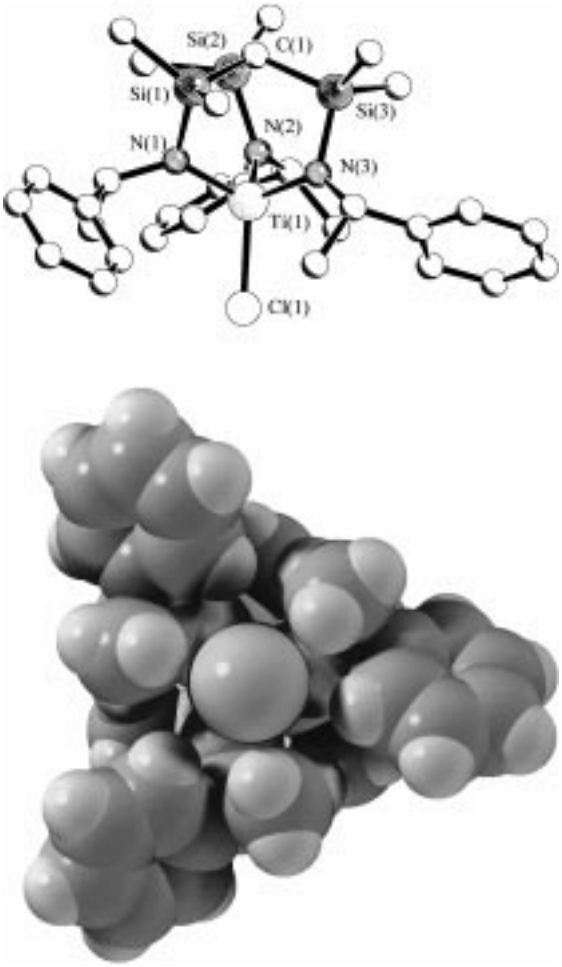


Figure 4. Top: molecular structure of $[TiCl\{HC\{SiMe_2N[(S)\text{-1-phenylethyl}]\}_3\}]$ (**7**). Principal bond lengths (Å) and interbond angles (°): Si(1)–N(1) 1.749(6), Si(1)–C(1) 1.906(7), Si(1)–C(2) 1.851(8), Si(1)–C(3) 1.842(9), N(1)–Ti(1) 1.886(5), N(2)–Ti(1) 1.905(5), N(3)–Ti(1) 1.898(6), Ti(1)–Cl(1) 2.250(2); N(1)-Si(1)-C(1) 101.0(3), Si(1)-N(1)-C(8) 116.6(5), Si(1)-N(1)-Ti(1) 113.6(3), N(1)-Ti(1)-Cl(1) 115.3(2), C(8)-N(1)-Ti(1) 129.7(5), N(1)-Ti(1)-N(2) 102.3(2), N(1)-Ti(1)-N(3) 103.4(3). Bottom: space-filling model of **7** viewed along the molecular threefold axis.

centre of this molecule is similar to those found in other tripod-metal compounds.[18, 24] However, the chiral ligand periphery and its arrangement deserve particular attention (Figure 4, bottom). As can be seen in the space-filling model of the complex viewed along its molecular threefold axis, the "reactive" coordination site occupied by the chloro ligand—while appearing accessible for incoming reactants—is intimately embedded in the chiral ligand periphery of the tripod. The three (*S*)-1-phenylethyl groups adopt the same relative orientation, generating the C_3-chiral structure. This situation

precisely represents the helicoidal environment postulated in the introduction, which is thought to favour stereoselectivity in conversions via turnstile-type five-coordinate intermediates.

Whereas the tetracoordinate structures established for **7**–**10** represent the only structural type to have been observed for titanium complexes, zirconium readily forms compounds with a higher coordination number. We have previously isolated and structurally characterised several LiCl adducts of tripodal amidozirconium complexes, in which the central metal atom adopts five- or sixfold coordination.[25] If, in the preparation of **9**, the separation of the LiCl and the extraction of the final product with a hydrocarbon solvent is not carried out, but isolation attempted directly from the reaction mixture in diethyl ether, such a formal LiCl adduct may be isolated. Such an aggregate, $[Li(OEt_2)_4][Zr_2Cl_3\{HC\{SiMe_2N[(S)\text{-1-phenylethyl}]\}_3\}_2]$ (**11**), was obtained in the form of single crystals and was characterised by an X-ray diffraction study. In this compound, two tripodal amidozirconium units are linked by three chloro bridges to give the monoanionic dinuclear C_3-chiral complex shown in Figure 5, top.

The coordination geometry of the zirconium atoms is highly distorted octahedral with an average N-Zr-N′ angle of 102.5° and an average Cl-Zr-Cl′ angle of 74.6°. This structural situation is mainly imposed by the dimensions of the binding site of the tridentate amido ligand, as well as a mutual repulsion of the two opposite tripodal amides. The latter also induces somewhat longer Zr–Cl bonds (2.674(2) – 2.725(2) Å) than previously observed by us for related systems.

The counterion is the ether-solvated lithium cation $[Li(OEt_2)_4]^+$. While there are a large number of structures containing the tetrakis(tetrahydrofuran) solvate,[26] there is only one report by Bau et al. of a structurally characterised salt containing the corresponding four-coordinate lithium/diethyl ether complex.[27] However, due to severe disorder along a threefold crystallographic axis, Bau and co-workers were not able to solve the complete molecular structure of the complex cation. The Li – O distances in this first fully characterised $[Li(OEt_2)_4]^+$ cation lie between 1.82(3) and 2.04(3) Å, and are thus in the usual range for ether-lithium compounds.[26]

There are two crystallographically independent molecules of the complex per asymmetric unit. In addition, one formula unit of $[Li(OEt_2)_4][ZrCl_5(OEt_2)]$, which co-crystallised together with complex **11**, was found with half-occupancy per asymmetric unit (Figure 5, bottom). The analogous, slightly distorted, octahedral pentachloro(tetrahydrofuran)zirconium anion has been previously reported in the literature.[28]

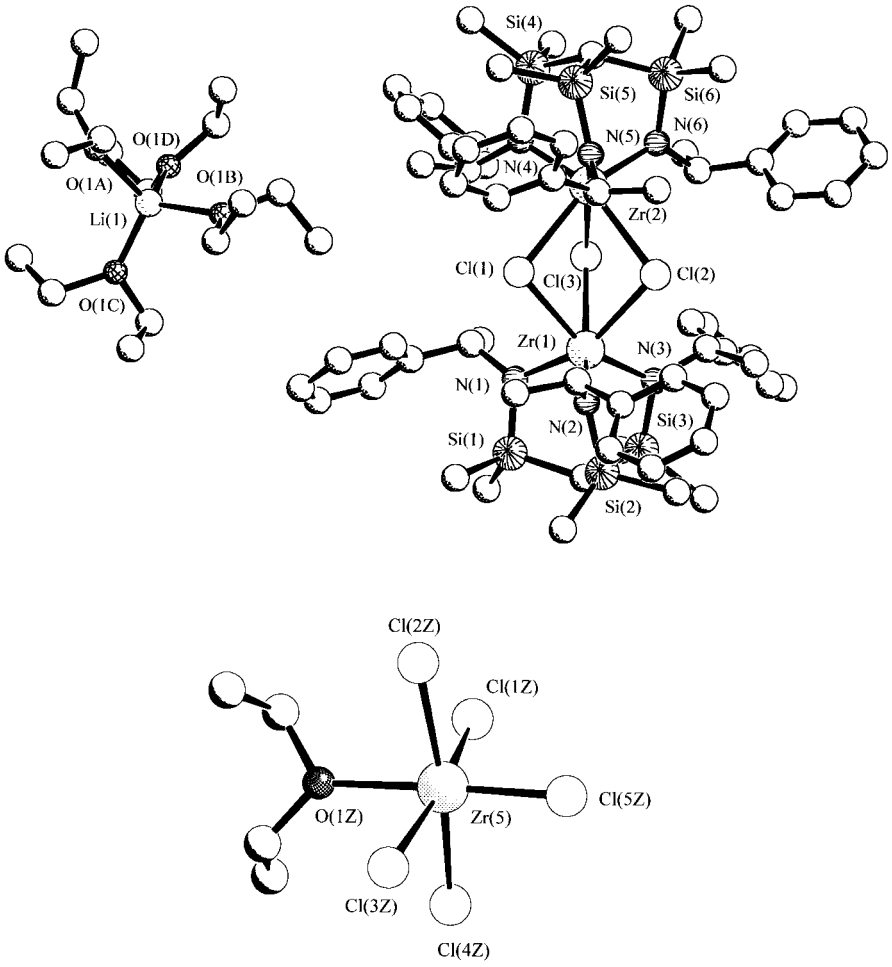


Figure 5. Top: Molecular structure of $[Li(OEt_2)_4][Zr_2Cl_3\{HC(SiMe_2N[(S)\text{-1-phenyl-ethyl}])_3\}_2]$ (**11**). Principal bond lengths (Å) and interbond angles (°): Si(1)–N(1) 1.750(6), Si(1)–C(1) 1.877(9), Zr(1)–N(1) 2.087(5), Zr(1)–N(2) 2.078(5), Zr(1)–N(3) 2.088(5), Zr(1)–Cl(1) 2.725(2), Zr(1)–Cl(2) 2.707(2), Zr(1)–Cl(3) 2.674(2); N(1)-Si(1)-C(1) 104.4(3), Si(1)-N(1)-Zr(1) 111.6(3), N(1)-Zr(1)-N(2) 102.4(3), N(1)-Zr(1)-N(3) 103.0(2), N(1)-Zr(1)-Cl(1) 90.14(16), N(1)-Zr(1)-Cl(2) 158.72(15), Cl(1)-Zr(1)-Cl(2) 72.47(6), Zr(1)-Cl(1)-Zr(2) 91.57(7). Bottom: molecular structure of the anionic complex $[ZrCl_5(Et_2O)]^-$.

Synthesis and structural characterisation of C_3-chiral alkyl amido complexes: Reaction of complexes **9** and **10** with a series of alkyllithium and Grignard reagents gave the corresponding alkylzirconium complexes **12**–**20** (Scheme 5). All complexes possess ^1H and ^{13}C NMR signal patterns for their tripod ligands, which are very similar to those of the chloro complexes. Their most characteristic spectroscopic feature is the ^1H NMR chemical shift of the α-C–H protons of the zirconium-bonded alkyl groups, which ranges from $\delta = -0.13$ for **13** to $\delta = -1.66$ for **20**; the only exception being the benzylzirconium complex, for which the $PhCH_2$ signals are observed at $\delta = 2.11$. The ^{13}C NMR chemical shifts of the metal-bonded carbon nuclei are found between $\delta = 52.2$ (**20**) and $\delta = 83.4$ (**16**).

In order to gain insight into the detailed structural environment of the metal-coordinated

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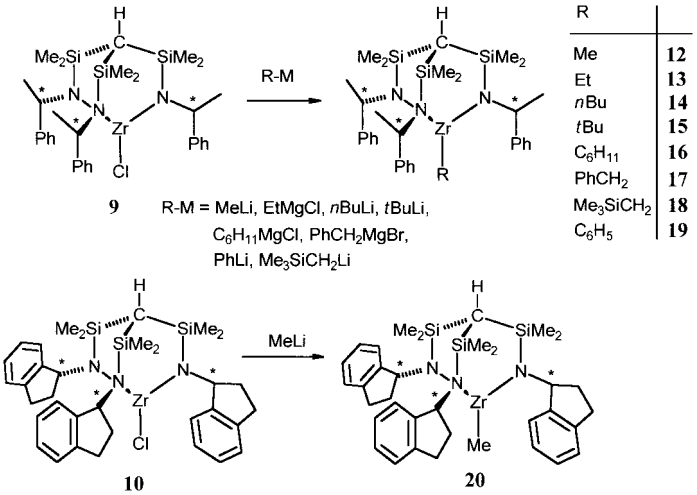


R	
Me	**12**
Et	**13**
*n*Bu	**14**
*t*Bu	**15**
C_6H_{11}	**16**
$PhCH_2$	**17**
Me_3SiCH_2	**18**
C_6H_5	**19**

Scheme 5. Synthesis of the alkylzirkonium complexes **12**–**20**.

alkyl groups in these chiral compounds, single-crystal X-ray structure analyses of **12** and **20**, which were to be used in the carbonyl alkylation reactions described below, were carried out. The molecular structures of both complexes are displayed in Figure 6; the principal bond lengths and angles are given in the legend.

The structural centre piece in both complexes is the amido-metal cage, which is distorted with respect to the ideal threefold symmetrical structure. This is probably due to the irregular arrangement of the peripheral (*S*)-1-phenylethyl groups in **12** and the (*R*)-1-indanyl groups in **20**. In the former, two of the aryl groups are arranged fairly closely to the Zr-CH_3 unit—the ipso-carbon atoms being located 3.29 and 3.46 Å from the metal centre—while the third is pointing away, almost horizontally, to the virtual molecular axis. This distortion of the ligand periphery is less pronounced in **20**; however, there is an even closer contact of an "ipso"-C atom of one of the aryl units and the zirconium atom (3.19 Å). A possible reason for this unequal arrangement of the three chiral N-bonded groups is the coordinative unsaturated nature of the central atom. It is well known in amidozirconium chemistry of, in particular, low-coordinate cationic species, that intra or intermolecular π-interactions with aryl units stabilise these complexes.[29] However, metal–carbon contacts in these cases lie in the range of 2.5–2.9 Å, and are thus significantly shorter than those observed in **12** and **20**. In the latter, the geometric arrangement of the aryl units is severely constrained by the ligand structure as a whole, and thus effectively prevented from further approach of the central metal atom. As a consequence of the orientation close to the zirconium centre of one or two of the aryl units in **20** and **12**, respectively, the remaining peripheral unit(s) is(are) pushed away due to steric overcrowding, giving the overall unsymmetrical arrangement of the ligand. If the coordination number in these complexes is greater than four, as is the case for the dinuclear complex anion **11**, all three peripheral groups are expected to be rotated to point away from the central atom. This restores the threefold symmetry of the system in its thermodynamic ground state, as is indeed found in the crystal structure of **11**. There is no spectroscopic

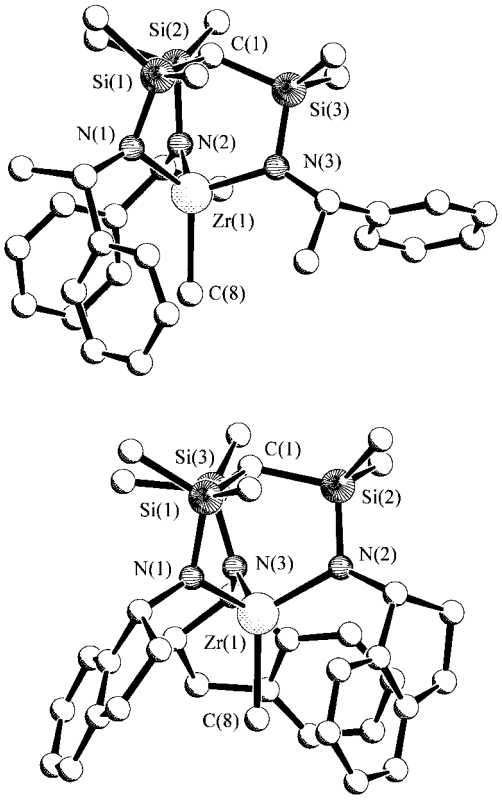
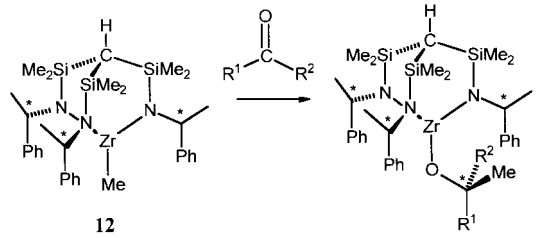


Figure 6. Top: molecular structure of $[Zr(CH_3)\{HC\{SiMe_2N[(S)\text{-1-phenylethyl}]\}_3\}]$ (**12**). Principal bond lengths (Å) and interbond angles (°): Si(1)–N(1) 1.730(3), Si(1)–C(1) 1.896(3), Zr(1)–N(1) 2.086(2), Zr(1)–N(2) 2.053(2), Zr(1)–N(3) 2.059(3), Zr(1)–C(8) 2.268(3); N(1)-Si(1)-C(1) 104.7(1), Si(1)-N(1)-Zr(1) 111.3(1), N(1)-Zr(1)-N(2) 101.42(8), N(1)-Zr(1)-N(3) 104.2(1), N(1)-Zr(1)-C(8) 125.7(1), N(2)-Zr(1)-C(8) 108.74(9), N(3)-Zr(1)-C(8) 110.6(1). Btoom: molecular structure of $[Zr(CH_3)\{HC\{SiMe_2N[(R)\text{-1-indanyl}]\}_3\}]$ (**20**). Principal bond lengths (Å) and interbond angles (°): Si(1)–N(1) 1.739(3), Si(1)–C(1) 1.895(3), Zr(1)–N(1) 2.067(2), Zr(1)–N(2) 2.074(3), Zr(1)–N(3) 2.060(3), Zr(1)–C(8) 2.227(3); N(1)-Si(1)-C(1) 104.55(12), Si(1)-N(1)-Zr(1) 111.52(12), N(1)-Zr(1)-N(2) 101.60(10), N(1)-Zr(1)-N(3) 102.22(10), N(1)-Zr(1)-C(8) 115.48(11), N(2)-Zr(1)-C(8) 120.38(12), N(3)-Zr(1)-C(8) 111.49(12).

evidence of a lower than threefold symmetry for all the alkyl complexes **12**–**20** in $[D_8]$toluene solution, even at 180 K. The interconversion of the different conformers is thus a rapid process with an activation barrier of less than 10 kcal mol^{-1}.

Insertion of prochiral ketones and aryl aldehydes into the Zr–CH_3 units of compounds 12 and 20: In a first attempt to test the chiral induction effected by the C_3-chiral environment of the tripodal amido ligands, the zirconium complex **12** was treated at −70 °C with several aryl ketones PhC(O)R (R=CH=CHPh, *i*Pr, Et) (Scheme 6). In all cases, immediate insertion of the ketone into the metal–carbon bond took place, generating the corresponding alkoxyzirconium complexes **21**–**23**.

The NMR spectroscopic analysis of the product mixtures indicated a low stereoselectivity of these insertion reactions. Whereas no appreciable chiral induction is observed in the reaction with benzylideneacetophenone (≈0 % *de*), the other two products were obtained with diastereomeric excesses of 12 % (for **22**) and 40 % (for **23**). The chiral environment of the

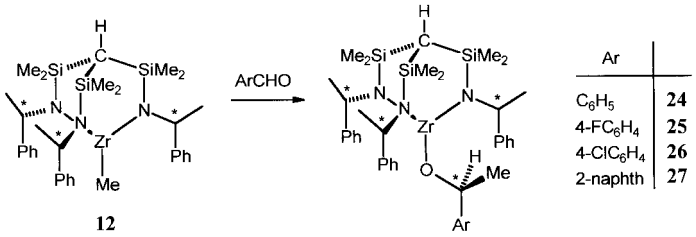


R^1	R^2	
PhCH=CH	Ph	**21**
*i*Pr	Ph	**22**
Et	Ph	**23**

Scheme 6. Insertion of ketones into the Zr–C bond of compound **12**.

metal centre does not strongly discriminate between the carbonyl substituents of almost similar size.

Chiral recognition, and thus stereoselectivity of the conversion, was significantly greater in insertion reactions performed with several aryl aldehydes (Scheme 7). In this



Ar	
C_6H_5	**24**
4-FC_6H_4	**25**
4-ClC_6H_4	**26**
2-naphth	**27**

Scheme 7. Insertion of aryl aldehydes into the Zr–C bond of compounds **12** and **20**.

case, the difference in size of the two CO substituents is maximised. The most characteristic spectroscopic features of the alkoxy complexes **24**–**27** are the quartet resonances in the ^{1}H NMR spectra of the methine CH proton adjacent to the coordinated oxygen atom, which are observed between $\delta =$ 4.64 and 4.98, as well as the OCH(Ar)CH_3 methyl doublet at $\delta = 0.99 - 1.20$. The corresponding ^{13}C NMR resonances are found between $\delta = 79.8$ and 80.9 and in the range of $\delta = 26.3 -$ 26.5, respectively.

Hydrolysis of the zirconium complexes with dilute HCl, and isolation of the secondary alcohol by distillation, allowed the determination of the enantiopurity of the chiral alcohols by chiral gas chromatography (GC). Comparison with authentic enantiomerically pure samples indicated that insertion into the methyl–zirconium bond of complex **12**, in which the 1-phenylethyl groups have *S* configuration, yielded the *S*-configured alcohols as major products. Their enantiomeric excess ranged from 68 % for (*S*)-1-(4-chlorophenyl)ethanol to 80 % for (*S*)-2-naphthylethanol (Table 1). The relatively high selectivity in the generation of the latter is not surprising, since the inserted ketone has a maximum difference in size of the carbonyl substituents.

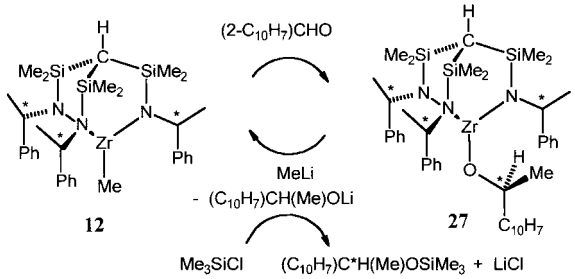
Reaction of the (*R*)-1-indanyl-substituted complex **20** with 2-naphthaldehyde yielded the corresponding insertion product **28** (Scheme 7). After hydrolysis and work up, (*R*)-2-naphthylethanol was isolated in an enatiomeric excess of

Table 1. Enantiopurity of the chiral secondary alcohols obtained after hydrolysis of the insertion products **24**–**28**.

Alcohol	*ee* [%]
$C_6H_5CH(CH_3)OH$	76
4-$FC_6H_4CH(CH_3)OH$	74
4-$ClC_6H_4CH(CH_3)OH$	68
(2-naphth)$CH(CH_3)OH$ (from **27**)	80
(2-naphth)$CH(CH_3)OH$ (from **28**)	82

82 %. The more rigid ligand periphery in **20**, in comparison to **12**, and thus the reduced conformational degrees of freedom in the alkylating agent, apparently do not translate into a significant increase in the stereoselectivity of the transformation.

The high chemoselectivity of the reaction with aryl aldehydes, and the observation that the alkoxo complex reacts cleanly with methyllithium to generate **12**, led us to perform repeated cycles of insertions and alkylations with benzaldehyde. In order to avoid side reactions of the lithium alkoxide generated in this process, a silylation step with Me_3SiCl was introduced to remove the product from the reactive cycle as the silyl ether (Scheme 8). Up to 4 cycles could be performed without decrease of selectivity.



Scheme 8. Cycle of benzaldehyde insertion into **12** and methylation of **24** with methyl lithium to regenerate **12**. The alcoholate is trapped as silylether with Me_3SiCl.

The limits of C_3-chiral recognition

Insertion of chiral carbonyl compounds into the Zr–CH_3 units of chiral and nonchiral complexes: As described above, good chiral induction was achieved in the alkylation of aryl aldehydes, while the methylation of ketones occured with relatively low stereoselectivity. This was explained by invoking the difference in size of the CO substituents, and consequently the degree of the stereochemical discrimination with respect to the orientation of the two prochiral faces of the metal-coordinated ketones vis-à-vis the methyl group. A complementary approach to testing the effectiveness of the C_3-chiral ligand periphery in the alkylamidozirconium complexes was their reaction with chiral carbonyl compounds, including ketones. This allowed the assessment of the degree to which chiral discrimination stems from the chirality in the substrate or the chiral ligand of the alkylating agent. As chiral carbonyl compounds, we chose (*S*)-(+)-carvone (**I**), (*R*)-myrtenal (**II**), (*S*)-(−)-perillaldehyde (**III**) and (*S*)-citronellal (**IV**).

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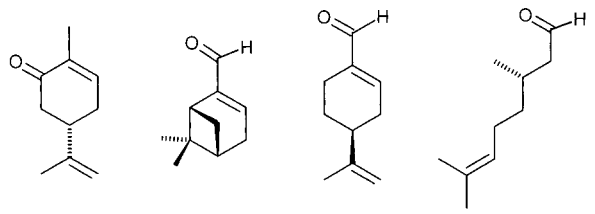
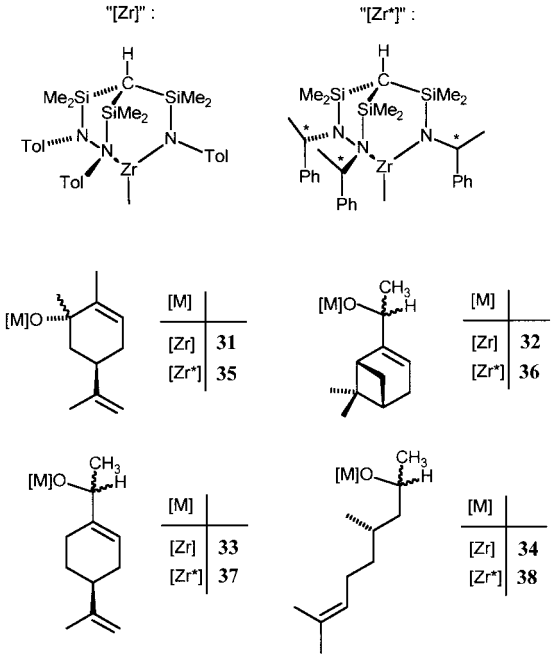


I **II** **III** **IV**

As alkylating agents, we compared the chiral zirconium complex **12** and the nonchiral complex [Zr(CH_3){HC[SiMe_2N(*p*-Tol)]$_3$}] (**30**), which was obtained—similar to the alkylations described above—by reaction of [ZrCl{HC[SiMe_2N(*p*-Tol)]$_3$}] (**29**) with methyllithium. Reaction of **30** and **12** with the chiral ketone and aldehydes **I**–**IV** gave the alkoxo complexes **31**–**34** and **35**–**38**, respectively (Scheme 9).



Scheme 9. Compounds **31**–**34** from the reaction of **12** and compounds **35**–**38** from the reaction **30** with (*S*)-(+)-carvone (**I**), (*R*)-myrtenal (**II**), (*S*)-(−)-perillaldehyde (**III**), and (*S*)-citronellal (**IV**), respectively.

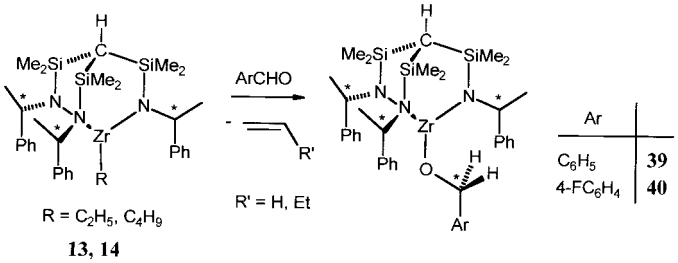
Subsequent hydrolysis of the zirconium alcoholates and work up gave the free alcohols, the stereopurity of which was determined by chiral GC. The results of the alkylations with **30** and **12** are summarised in Table 2. As is evident from these results, the alkylation with the the achiral zirconium complex occurs with diastereomeric excesses ranging from 0% (for **IV**) to 58% (for **I**). For all four carbonyl compounds, the selectivity increases significantly upon use of the chiral complex **12**, leading to diastereomeric excesses up to 94% (for **I**). However, this increased stereoselectivity does not appear to be due to the chirality of the alkylating agent, but originates from the stereoinformation encoded in the chiral substrate. This is highlighted by the observation that the reaction of **12** with the enantiomer of **I**, (*R*)-(−)-carvone, gives the corresponding alcohol in a diastereomeric excess of 93%, which is essentially identical to the selectivity in the reaction with **I**, and a "match/mismatch" effect is thus not found. The increased stereoselectivity in the methylations with **12** is probably a consequence of the greater steric shielding of the reactive site in the 1-phenylethyl-substituted complex in comparison to the tolyl-substituted species **30**. This slows down the reaction and favours alkyl transfer from one of the two diastereotopic faces of the carbonyl group. NMR tube experiments with both enatiomers of **II**–**IV** indicate essentially similar diasteromeric excesses and are, therefore, consistent with this interpretation.

Table 2. Diastereoselectivity of the insertion of the chiral carbonyl compounds **I**–**IV** into the Zr–C bonds in **30** and **12**. Diastereopurity of the alcohols after hydrolysis.

Complex	Substrate	*de* [%]	Complex	Substrate	*de* [%]
30	**I**	58	**12**	**I**	94
30	**II**	32	**12**	**II**	60
30	**III**	8	**12**	**III**	38
30	**IV**	0	**12**	**IV**	16

The limits of the chiral recognition in the C_3-symmetrical complex **12** (and **20**) are readily apparent. While the chirality of the alkylation reagent induces fairly high enantioselectivities in aryl aldehydes, neither achiral nor chiral ketones are suitable substrates. For these compounds, the threefold chirality of the complex is almost "invisible", and the diastereoselectivity in the alkylation of the chiral substrates is mainly due to the stereochemistry of the substrate.

Carbonyl insertion versus β-elimination in long chain alkylzirconium complexes: In view of the high selectivity found in the methylation of aryl aldehydes, it was of interest to see whether this approach could be extended to the transfer of other alkyl groups. While the reactions of **15**–**19** lead to complicated product mixtures and apparent degradation of the zirconium complex, the conversions studied with the ethyl and *n*-butyl derivatives **13** and **14** occurred cleanly. However, the products of the reactions with benzaldehyde and 4-fluorobenzaldehyde were not the results of an alkyl, but of a hydride transfer (Scheme 10).

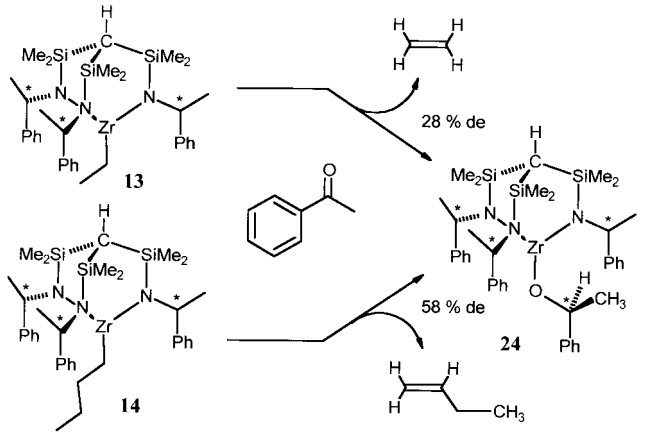


Scheme 10. β-Eliminations in the reaction of **13** and **14** with benzaldehyde and 4-fluorobenzaldehyde.

In both cases, the corresponding benzyloxo complex was isolated, while the quantitative formation of ethene and 1-butene was detected by ^{1}H NMR spectroscopy. The long-chain alkyl compounds **13** and **14**, which are thermally stable in the absence of the substrate, therefore undergo β-elimi-

nation upon its coordination to the Lewis acidic zirconium centre, and the aldehyde immediately inserts into the zirconium hydrido complex. Such a hydrido complex was recently reported by Jia, who treated the butyl complex $[HC\{SiMe_2N(p\text{-}Tol)\}_3Zr(CH_2Ph)]$ with H_2.[30] In the case at hand, the rapid insertion of the aldehyde does not permit the detection of such an intermediate.

The β-elimination observed in the reactions of **13** and **14** allowed an alternative synthesis of the 1-phenylethoxyzirconium complex **24** by using acetophenone as a substrate. In both cases, olefin elimination occurred immediately and complex **24** was formed (Scheme 11). However, the stereoselectivity of the conversions with the ethyl and butyl complexes **13** and **14** differ markedly, as is manifested by the enantiomeric excesses of the isolated alcohol of 28% and 58%, respectively. Two possible mechanistic conclusions can be derived from this. The stereoselectivity is either due to the orientation of the carbonyl group vis-à-vis the alkyl unit before β-elimination takes place, with this preorientation appearing to pertain in the insertion reaction into the Zr–H bond which follows. The insertion thus occurs more rapidly than a possible reorientation of the *O*-coordinated aldehyde at the zirconium centre. The higher stereoselectivity in the reaction with the *n*-butyl complex is thought to be due to the greater steric demand of this long-chain alkyl ligand, which in turn induces increased stereodiscrimination on the coordination of the aldehyde to the metal centre. An alternative plausible pathway would be the direct β-H transfer to the coordinated aldehyde, in analogy with the low-energy chain transfer mechanism in olefin polymerisation.



Scheme 11. Alternative synthesis of **24** by reaction of **13** and **14** with acetophenone. The stereoselectivity of the insertion into the transient Zr–H bond is dependant on the eliminated alkyl group.

Conclusion

We have shown in this first study of the coordination chemistry of tripodal amido ligands which contain chiral substituents in the ligand periphery, that the alkyl complexes may act as asymmetric alkylation agents for aryl aldehydes. Stereoselectivities are high for carbonyl derivatives that contain substituents of very different size at the carbonyl function. The ketones studied by us do not sufficiently meet this requirement and are thus unsuitable substrates for the C_3-chiral alkyl complexes. This aspect has been additionally substantiated in the reactions with chiral carbonyl compounds, in which the stereoselectivity was induced almost entirely by the shape of the substrate. The chosen method appears to be confined to methyl transfer, since long-chain alkyl ligands undergo β-elimination upon coordination of the carbonyl substrate.

A particular advantage of this approach is the facile accessibility of the enantiomerically pure chiral ligand in a one-step reaction; this allows the preparation of large quantities of these materials. It also readily enables the variation of the peripheral substituents in the tripodal amido ligands, and thus an optimisation of the stereoselectivity in reactions that involve these complexes. Furthermore, it has been possible to obtain detailed structural information about the ligands, the lithium amides and the C_3-chiral metal complexes well beyond the previous level of knowledge attained in this field.[31]

Compared with Moberg's C_3-symmetric catalytic amidotitanium system,[13] the enantioselectivity of the stoichiometric reaction presented in this paper is significantly greater. Current and future activities in this area are directed towards the development of a catalytic system by using the alkyltitanium derivatives and alkylzinc reagents.

Experimental Section

General: All manipulations were performed under purified argon in standard (Schlenk) glassware, which was flame dried with a Bunsen burner in vacuo prior to use. Separation of solids from suspensions occured by centrifugation only, thus avoiding all filtration procedures. The centrifuge employed was a Rotina 48 (Hettich Zentrifugen, Tuttlingen, Germany), which was equipped with a specially designed Schlenk-tube rotor.[32] Solvents were dried according to standard procedures. The deuterated solvents used for the NMR spectroscopic measurements were degassed by three successive "freeze-pump-thaw" cycles and dried over 4 Å molecular sieves.

The ^1H, ^7Li, ^{13}C, ^{19}F and ^{29}Si NMR spectra were recorded on a Bruker AC200 equipped with a B-VT-2000 variable temperature unit (at 200.13, 77.77, 50.32, 188.31 and 39.76 MHz, respectively) and a Bruker AMX400 spectrometer (at 400.14, 155.51, 100.62, 376.45 and 79.50 MHz, respectively) with tetramethylsilane (^{29}Si NMR), LiI (1M in H_2O, ^7Li NMR) and $CFCl_3$ (^{19}F NMR) as references. Infrared spectra were recorded on a Bruker Vector22 spectrometer. Elemental analyses were carried out in the microanalytical laboratory of the chemistry deptartment at Würzburg. Compound **1**, $HC(SiMe_2Br)_3$ and $HC\{SiMe_2NH(4\text{-}CH_3C_6H_4)\}_3$ were prepared as reported previously by us.[12a] All other chemicals used as starting materials were obtained commercially and used without further purification.

Preparation of $HC\{SiMe_2NH[(R)\text{-}1\text{-}indanyl]\}_3$ (2): A solution of $HC(SiMe_2Br)_3$ (2.00 g, 4.68 mmol) in diethyl ether (20 mL) was added to a stirred solution of (*R*)-1-aminoindane (1.80 mL, 14.04 mmol) and triethylamine (2.10 mL, 15.15 mmol) in diethyl ether (30 mL)diethyl etherat 0 °C. After stirring for 14 h at room temperature, the triethylammonium bromide was separated by centrifugation and the precipitate was washed with diethyl ether (40 mL). The solvent of the combined ether solutions and the excess of triethylamine were removed in vacuo. Upon storing at 4 °C in diethyl ether for 24 h, compound **2** was obtained as a colourless, highly crystalline solid. Yield 1.74 g, 3.00 mmol (64%); m.p. 102 °C; ^1H NMR (400.14 MHz, C_6D_6, 295 K): $\delta = -0.66$ (s, 1H; *H*C(Si…)$_3$), 0.36 (s, 9H; Si(C*H*$_3$)$_2$), 0.42 (s,

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9H; Si(CH_3)$_2$), 1.52 (ddt, ^2J(H^a,H^e) = 12.0 Hz, ^3J(H^2,H^3) = 9.9 Hz, J(H^2,H$^{1/3}$) = 8.6 Hz, 3H; H^2 of indanyl), 1.75 (d, ^3J(HC,NH) = 12.0 Hz, 3H; NH), 2.24 (ddt, ^2J(H^a,H^e) = 12.0 Hz, ^3J(H^2,H$^{1/3}$) = 7.2 Hz, ^3J(H^2,H^3) = 2.1 Hz, 3H; H^2 of indanyl), 2.50 (ddd, ^2J(H^a,H^e) = 15.4 Hz, ^3J(H^3,H^2) = 9.9 Hz, ^3J(H^3,H^2) = 7.6 Hz, 3H; H^3 of indanyl), 2.65 (ddd, ^2J(H^a,H^e) = 15.4 Hz, ^3J(H^3,H^2) = 8.6 Hz, ^3J(H^3,H^2) = 2.1 Hz, 3H; H^3 of indanyl), 4.22 (dt, ^3J(HC,NH) = 12.0 Hz, ^3J(H^1,H^2) = 7.9 Hz, 3H; H^1 of indanyl), 6.91 (dt, ^3J(H,H) = 7.6 Hz, ^3J(H,H) = 2.1 Hz, 3H; H^{arom} of indanyl), 7.05 – 7.16 (m, 9H; H^{arom} of indanyl); {^{1}H}^{13}C NMR (100.62 MHz, C_6D_6, 295 K): δ = 3.8, 4.8 (Si(CH_3)$_2$), 5.5 (HC(Si…)$_3$), 30.2, 40.3 (C^{2,3} of indanyl), 58.0 (C^1 of indanyl), 124.4, 124.6, 126.9, 127.0 (C$^{4-7}$ of indanyl), 142.6, 148.4 (C^{3a,7a} of indanyl); {^{1}H}^{29}Si NMR (79.50 MHz, C_6D_6, 295 K): δ = 1.24; IR (benzene): $\tilde{\nu}$ = 3339 (s), 3070 (s), 3022 (s), 2950 (vs), 2850 (s), 1473 (m), 1458 (m), 1410 (s), 1252 (vs), 1138 (m), 1124 (s), 1079 (s), 1007 (s), 882 (vs), 832 (vs), 823 (vs), 801 (s), 763 (vs), 742 (s), 673 cm^{-1} (m); elemental analysis calcd (%) for $C_{34}H_{49}N_3Si_3$ (584.04): C 69.92, H 8.46, N 7.20; found C 69.15, H 7.85, N 7.35.

Spectroscopic characterisation of HC{SiMe$_2$NH[(*S*)-1-phenylethyl]}-{(SiMe$_2$)$_2$N[(*S*)-1-phenylethyl]} (3): Upon storing a solution of (**1**) in benzene for 24 h at room temperature, formation of the equilibrium of **1** and HC{SiMe$_2$NH[(*S*)-1-phenylethyl]}{(SiMe$_2$)$_2$N[(*S*)-1-phenylethyl]} (**3**) and (*S*)-1-phenylethylamine was observed. At 330 K, only compound **3** and the primary amine were detected in the ^{1}H NMR experiment. Spectroscopic data of **3**: ^{1}H NMR (200.13 MHz, C_6D_6, 330 K): δ = −0.11 (s, 1H; HC(SiMe$_2$)$_3$), 0.07, 0.09, 0.12, 0.19, 0.21, 0.24 (s, 6 × 3H; Si(CH_3)$_2$), 1.29 (d, ^3J(H,H) = 6.9 Hz, 3H; HCCH_3), 1.33 (d, ^3J(H,H) = 7.3 Hz, 3H; HCCH_3), 3.97 – 4.09 (m, 2H; $HCCH_3$), 7.01 – 7.28 (m, 15H; C_6H_5); {^{1}H}^{13}C NMR (50.32 MHz, C_6D_6, 330 K): δ = 2.6, 2.7, 3.5, 4.0, 4.8, 4.8 (Si(CH_3)$_2$), 7.7 (HC(Si…)$_3$), 25.4, 28.4 (HCCH_3), 51.6, 54.3 (HCCH_3), 126.1, 126.3, 126.4, 127.2, 128.3, 128.4, (*o*, *m*, *p*-C of C_6H_5), 148.1, 149.8 (*i*-C of C_6H_5); {^{1}H}^{29}Si NMR (39.76 MHz, C_6D_6, 330 K): δ = −0.4 (SiMe$_2$N(H)(…)), 5.7, 5.8 ((SiMe$_2$)$_2$N(…)).

Spectroscopic characterisation of HC{SiMe$_2$NH[(*R*)-1-indanyl]}{(SiMe$_2$)$_2$N[(*R*)-1-indanyl]} (4): A solution of **2** in toluene was studied at variable temperature between 295 – 355 K. The equilibrium between **2** and HC{SiMe$_2$NH[(*R*)-1-indanyl]}{(SiMe$_2$)$_2$N[(*R*)-1-indanyl]} (**4**) and (*R*)-1-indaneamine was monitored by NMR spectroscopy, and the ratio between **2** and **4** determined by integration of the signals assigned to the apical CH groups. Spectroscopic data of **4**: ^{1}H NMR (200.13 MHz, C_6D_6, 330 K): δ = 0.01 (s, 1H; HC(SiMe$_2$)$_3$), 0.16, 0.23, 0.24, 0.24, 0.26, 0.34 (s, 6 × 3H; Si(CH_3)$_2$), 1.79 (ddt, 2H; H^2 of indanyl), 2.50 – 2.98 (m, 6H; H^{2,3} of indanyl), 4.28 – 4.38 (m, 2H; H^1 of indanyl), 7.07 – 7.39 (m, 6H; H^{arom} of indanyl), 7.40 (d, ^3J(H,H) = 6.9 Hz, 2H; H^{arom} of indanyl); {^{1}H}^{13}C NMR (100.62 MHz, C_6D_6, 330 K): δ = 2.9, 3.1, 3.5, 4.1, 4.9, 5.0 (Si(CH_3)$_2$), 8.1 (HC(Si…)$_3$), 30.3, 30.5, 37.4, 39.9 (C^{2,3} of indanyl), 58.2, 59.3 (C^1 of indanyl), 124.6, 124.6, 125.3, 126.4, 127.1, 127.2, 127.2, 128.2 (C$^{4-7}$ of indanyl), 142.7, 142.8, 147.4, 149.2 (C^{3a,7a} of indanyl); {^{1}H}^{29}Si NMR (39.76 MHz, C_6D_6, 330 K): δ = −0.1 (SiMe$_2$N(H)(…)), 5.7, 5.9 ((SiMe$_2$)$_2$N(…)).

Preparation of HC{SiMe$_2$NLi[(*S*)-1-phenylethyl]}$_3$ (5): A solution of *n*BuLi (2.5 M) in *n*-hexane (2.20 mL, 5.50 mmol) was added to a stirred solution of **1** (1.00 g, 1.83 mmol) in *n*-pentane (40 mL)at −78 °C. After stirring for 1 h at room temperature and concentrating to 20 mL, the white precipitate was separated by centrifugation. Upon storing at 4 °C in *n*-pentane for 24 h, the product was obtained as a colourless, highly crystalline solid. Yield 0.81 g (78 %); ^{1}H NMR (400.14 MHz, C_6D_6, 295 K): δ = −0.93 (s, 1H; HC(Si…)$_3$), 0.31, 0.38 (s, 2 × 9H; Si(CH_3)$_2$), 0.94 (d, ^3J(H,H) = 6.4 Hz, 3H; HCCH_3), 4.06 (q, ^3J(H,H) = 6.4 Hz, 3H; $HCCH_3$), 6.92 – 7.21 (m, 15H; C_6H_5); {^{1}H}^{13}C NMR (100.62 MHz, C_6D_6, 295 K): δ = 5.9, 7.0 (Si(CH_3)$_2$), 10.6 (HC(Si…)$_3$), 27.9 (HCCH_3), 55.7 (HCCH_3), 124.1 (C^{2,6} of C_6H_5), 126.6 (C^4 of C_6H_5), 130.9 (C^{3,5} of C_6H_5), 154.0 (C^1 of C_6H_5); {^{1}H}^{7}Li NMR (155.51 MHz, C_6D_6, 295 K): δ = −0.4; elemental analysis calcd (%) for $C_{31}H_{46}Li_3N_3Si_3$ (565.93): C 65.79, H 8.19, N 7.43; found C 65.64, H 7.89, N 7.35.

Preparation of HC{SiMe$_2$NLi[(*R*)-1-indanyl]}$_3$ (6): A solution of *n*BuLi (2.5 M) in *n*-hexane (8.01 mL, 20.03 mmol) was added to a stirred solution of **2** (3.90 g, 6.68 mmol) in *n*-pentane (40 mL) at 0 °C. After stirring for 14 h at room temperature and concentrating to 20 mL, the white precipitate was separated by centrifugation. Upon storing at 4 °C in *n*-pentane for 24 h, the product was obtained as a colourless, highly crystalline solid. Yield 3.53 g, 5.86 mmol (88 %); m.p. 32 °C; ^{1}H NMR (400.14 MHz, [D$_8$]toluene, 295 K): δ = −0.69 (s, 1H, HC(Si…)$_3$), 0.51 (s, 18H, Si(CH_3)$_2$), 0.69 (ddt, ^2J(H^a,H^e) = 11.7 Hz, ^3J(H^2,H^3) = 7.8 Hz, ^3J(H^2,H^1) = 7.0 Hz, 3H; H^2 of indanyl), 2.26 (dddd, ^2J(H^a,H^e) = 11.7 Hz, ^3J(H^2,H^1) = 7.0 Hz, ^3J(H^2,H^3) = 7.8, 3.9 Hz, 3H; H^2 of indanyl), 2.36 (ddd, ^2J(H^a,H^e) = 15.7 Hz, ^3J(H^3,H^2) = 7.8 Hz, ^3J(H^3,H^2) = 3.9 Hz, 3H; H^3 of indanyl), 2.51 (dt, ^2J(H^a,H^e) = 15.7 Hz, ^3J(H^3,H^2) = 7.8 Hz, 3H; H^3 of indanyl), 4.57 (t, ^3J(H^1,H^2) = 7.0 Hz, 3H; H^1 of indanyl), 6.93 – 6.99 (m, 6H; H^{arom} of indanyl), 7.03 – 7.08 (m, 3H; H^{arom} of indanyl), 7.09 – 7.13 (m, 3H; H^{arom} of indanyl); {^{1}H}^{13}C NMR (100.62 MHz, [D$_8$]toluene, 295 K): δ = 5.9, 8.8 (Si(CH_3)$_2$), 10.9 (HC(Si…)$_3$), 30.2, 42.9 (C^{2,3} of indanyl), 62.0 (C^1 of indanyl), 120.0, 126.3, 126.8, 128.1 (C$^{4-7}$ of indanyl), 142.7, 154.4 (C^{3a,7a} of indanyl); {^{1}H}^{29}Si NMR (79.50 MHz, [D$_8$]toluene, 295 K): δ = −0.7; {^{1}H}^{7}Li NMR (155.51 MHz, [D$_8$]toluene, 295 K): δ = 2.3; elemental analysis calcd (%) for $C_{34}H_{46}Li_3N_3Si_3$ (601.84): C 67.85, H 7.70, N 6.98; found C 67.64, H 7.50, N 7.20.

Preparation of [TiCl{HC{SiMe$_2$N[(*S*)-1-phenylethyl]}$_3$}] (7): A solution of *n*BuLi (2.5 M) in *n*-hexane (6.49 mL, 16.23 mmol) was added to a stirred solution of HC{SiMe$_2$NH[(*S*)-1-phenylethyl]}$_3$ (2.96 g, 5.40 mmol) in *n*-pentane (100 mL) at −50 °C. After warming to room temperature over a period of 30 min and stirring for 1 h, the solution was cooled down again to −50 °C. Solid [TiCl$_4$(thf)$_2$] (1.85 g, 5.54 mmol) was added, and the reaction mixture was warmed to room temperature over a period of 20 h. The solid LiCl was separated by centrifugation after stirring for 5 days, and the yellow solution was concentrated to 30 mL. Upon storing at −40 °C the product was obtained as a yellow, highly crystalline solid; Yield 1.18 g (33 %); m.p. 86 °C; ^{1}H NMR (200.13 MHz, C_6D_6, 295 K): δ = −0.45 (s, 1H; HC(Si…)$_3$), 0.05 (s, 9H; Si(CH_3)$_2$), 0.10 (s, 9H; Si(CH_3)$_2$), 1.98 (d, ^3J(H,H) = 6.9 Hz, 9H; HCCH_3), 4.68 (q, ^3J(H,H) = 6.9 Hz, 3H; $HCCH_3$), 7.05 – 7.51 (m, 15H; C_6H_5); {^{1}H}^{13}C NMR (50.32 MHz, C_6D_6, 295 K): δ = 3.4, 4.6 (Si(CH_3)$_2$), 9.9 (HC(Si…)$_3$), 27.8 (HCCH_3), 64.4 (HCCH_3), 127.2 (C^{2,6} of C_6H_5), 127.5 (C^4 of C_6H_5), 128.6 (C^{3,5} of C_6H_5), 147.7 (C^1 of C_6H_5); {^{1}H}^{29}Si NMR (39.76 MHz, C_6D_6, 295 K): δ = 5.5; IR (toluene): $\tilde{\nu}$ = 1585 (s), 1366 (s), 1243 (m), 1167 (m), 1064 (s), 1029 (vs), 1018 (vs), 884 (m), 829 (s), 668 cm^{-1} (m); elemental analysis calcd (%) for $C_{31}H_{46}ClN_3Si_3Ti$ (627.33): C 59.35, H 7.39, N 6.70; found C 59.20, H 7.41, N 6.84.

Preparation of [TiCl{HC{SiMe$_2$N[(*R*)-1-indanyl]}$_3$}] (8): [TiCl$_4$(thf)$_2$] (0.28 g, 0.83 mmol) was added to a stirred solution of HC{SiMe$_2$NLi[(*R*)-1-indanyl]}$_3$ (**6**) (0.50 g, 0.83 mmol) in *n*-pentane (20 mL)at −78 °C. The solution was warmed to room temperature over a period of 12 h. The solid LiCl was separated by centrifugation after stirring for 6 days. After removal of the solvent in vacuo, the product was obtained as a light brown powder, which was washed twice with 2 mL of cold pentane. Yield 0.48 g, 0.72 mmol (87 %); ^{1}H NMR (200.13 MHz, [D$_8$]toluene, 295 K): δ = −0.49 (s, 1H; HC(Si…)$_3$), 0.37 (s, 9H; Si(CH_3)$_2$), 0.38 (s, 9H; Si(CH_3)$_2$), 2.30 – 2.92 (m, 18H; H^{2,3} of indanyl), 4.75 (t, ^3J(H^1,H^2) = 7.7 Hz, 3H; H^1 of indanyl), 6.92 – 7.19 (m, 9H; H^{arom} of indanyl), 7.52 (d, ^3J(H,H) = 7.3 Hz, 3H; H^{arom} of indanyl); {^{1}H}^{13}C NMR (50.32 MHz, [D$_8$]toluene, 295 K): δ = 3.2 (HC(Si…)$_3$), 4.3, 4.6 (Si(CH_3)$_2$), 30.3, 40.1 (C^{2,3} of indanyl), 68.9 (C^1 of indanyl), 124.8, 126.2, 127.4, 129.1 (C$^{4-7}$ of indanyl), 143.0, 148.5 (C^{3a,7a} of indanyl); {^{1}H}^{29}Si NMR (79.50 MHz, [D$_8$]toluene, 295 K): δ = 3.3; elemental analysis calcd (%) for $C_{34}H_{46}ClN_3Si_3Ti$ (664.35): C 61.47, H 6.98, N 6.33; found C 61.71, H 7.14, N 6.03.

Preparation of [ZrCl{HC{SiMe$_2$N[(*S*)-1-phenylethyl]}$_3$}] (9): A solution of *n*BuLi (2.5 M) in *n*-hexane (12.24 mL, 30.06 mmol) was added to a stirred solution of **1** (4.96 g, 9.05 mmol) in *n*-pentane (40 mL) at −78 °C. The solution was slowly warmed to room temperature and stirred for 15 h. The solid lithium amide was separated by centrifugation and re-dissolved in diethyl ether (40 mL).Solid ZrCl$_4$ (2.11 g, 9.05 mmol) was added to the stirred solution at −78 °C. The solution was again slowly warmed up to room temperature and stirred for 3 weeks. After concentrating to 15 mL, a small amount of precipitated salts were separated by centrifugation. Storage of the solution at −25 °C yielded colourless crystals. The crude product was recrystallised from *n*-pentane to obtain compound **9**. Yield 5.98 g, 8.90 mmol (98 %); m.p. 87 °C; ^{1}H NMR (400.13 MHz, C_6D_6, 295 K): δ = −0.62 (s, 1H; HC(Si…)$_3$), 0.10 (s, 9H; Si(CH_3)$_2$), 0.16 (s, 9H; Si(CH_3)$_2$), 1.74 (d, ^3J(H,H) = 6.8 Hz, 9H; HCCH_3), 4.37 (q, ^3J(H,H) = 6.8 Hz, 3H; $HCCH_3$), 7.10 (t, ^3J(H,H) = 7.2 Hz, 3H; *p*-C of C_6H_5), 7.24 (t, ^3J(H,H) = 7.2 Hz, 6H; *m*-C of C_6H_5), 7.49 (d, ^3J(H,H) = 7.2 Hz, 6H; *o*-C of C_6H_5); {^{1}H}^{13}C NMR (100.62 MHz, C_6D_6, 295 K): δ = 2.1 (HC(Si…)$_3$), 3.9, 4.4 (Si(CH_3)$_2$), 28.1 (HCCH_3), 59.2 (HCCH_3), 127.0 (C^{2,4,6} of C_6H_5), 128.7 (C^{3,5} of C_6H_5), 148.1 (C^1 of C_6H_5); {^{1}H}^{29}Si NMR (39.76 MHz, C_6D_6, 295 K): δ = 0.2; IR (pentane): $\tilde{\nu}$ = 3070 (w), 3045 (w), 3012 (w), 1595 (w), 1484 (w), 1433

(w), 1365 (m), 1245 (vs), 1192 (m), 1074 (vs), 1055 (m), 1025 (w), 1013 (m), 944 (vs), 860 (vs), 815 (br s), 755 (br s), 691 cm^{-1} (s); elemental analysis calcd (%) for $C_{31}H_{46}ClN_3Si_3Zr$ (671.66): C 55.44, H 6.90, N 6.26; found C 55.28, H 6.45, N 6.13.

Preparation of [ZrCl{HC{SiMe$_2$N[(*R*)-1-indanyl]}$_3$}] (10): $ZrCl_4$ (0.19 g, 0.83 mmol) was added to a stirred solution of **3** (0.50 g, 0.83 mmol) in toluene (20 mL)at $-78\,^{\circ}C$. The solution was slowly warmed to room temperature and stirred 8 h at $60\,^{\circ}C$. After separation of the LiCl by centrifugation, the solvent was removed in vacuo, and the product was obtained as a light-brown powder. Yield 0.53 g, 0.75 mmol (90%); m.p. $32\,^{\circ}C$; ^1H NMR (400.14 MHz, [D$_8$]toluene, 295 K): $\delta = -0.46$ (s, 1H; *H*C(Si…)$_3$), 0.39 (s, 9H; Si(C*H*$_3$)$_2$), 0.49 (s, 9H; Si(C*H*$_3$)$_2$), 1.91 (dq, $^2J(H^a,H^e) = 12.3$ Hz, $^3J(H^2,H^3) = 8.7$ Hz, 3H; H^2 of indanyl), 2.40 (ddt, $^2J(H^a,H^e) = 12.3$ Hz, $^3J(H^2,H^1)_{/3} = 7.6$ Hz, $^3J(H^2,H^3) = 2.7$ Hz, 3H; H^2 of indanyl), 2.56 (dt, $^2J(H^a,H^e) = 15.8$ Hz, $^3J(H^3,H^2) = 8.2$ Hz, 3H; H^3 of indanyl), 2.80 (ddd, $^2J(H^a,H^e) = 15.8$ Hz, $^3J(H^3,H^2) = 8.7$ Hz, $^3J(H^3,H^2) = 2.7$ Hz, 3H; H^3 of indanyl), 4.22 (t, $^3J(H^1,H^2) = 7.6$ Hz, 3H; H^1 of indanyl), 6.92–7.19 (m, 9H; H^{arom} of indanyl), 7.53 (d, $^3J(H,H) = 7.2$ Hz, 3H; H^{arom} of indanyl); {^1H}^{13}C NMR (100.62 MHz, [D$_8$]toluene, 295 K): $\delta = 1.4$ (*H*C(Si…)$_3$), 3.8, 5.8 (Si(*C*H$_3$)$_2$), 30.6, 41.3 (C^{2,3} of indanyl), 64.4 (C^1 of indanyl), 123.8, 125.4, 126.8, 127.8 (C$^{4-7}$ of indanyl), 143.2, 148.6 (C^{3a,7a} of indanyl); {^1H}^{29}Si NMR (79.50 MHz, [D$_8$]toluene, 295 K): $\delta = 0.6$; IR (toluene): $\tilde{\nu} = 3070$ (m), 3044 (w), 3022 (m), 2949 (vs), 2850 (s), 1476 (m), 1458 (s), 1252 (vs), 1105 (vs), 1074 (vs), 960 (vs), 895 (vs), 840 (vs), 811 (vs), 676 (w), 633 cm^{-1} (w); elemental analysis calcd (%) for $C_{34}H_{46}ClN_3Si_3Zr$ (707.69): C 57.70, H 6.55, N 5.94; found C 57.64, H 6.68, N 5.72.

Preparation of [Li(Et$_2$O)$_4$][Zr$_2$Cl$_3${HC{SiMe$_2$N[(*S*)-1-phenylethyl]}$_3$}$_2$] (11): The preparation and reaction conditions were analogous to those of **9**. Workup: Storage of the solution at $-25\,^{\circ}C$ yielded the product **11** as colourless crystals which were not recrystallised from *n*-pentane. Yield 2.81 g, 1.44 mmol (32%); m.p. $30\,^{\circ}C$ (decomp). ^1H, ^{13}C, and ^{29}Si NMR spectra in solution could not be obtained due to rapid disintegration of the compound yielding compound **9**. Rapid loss of diethyl ether prevented elemental analysis of the compound which is solely characterised by X-ray diffraction.

General procedure for the preparation of [ZrR{HC{SiMe$_2$N[(*S*)-1-phenylethyl]}$_3$}] (12–19): To a stirred solution of compound **9** in diethyl ether, a solution of the equimolar amount of Grignard or organolithium compound was added at $-78\,^{\circ}C$. The solution was slowly warmed up to room temperature and stirred for 15 h. After removing the solvent in vacuo and redissolving the residue in *n*-pentane, the white precipitates were separated by centrifugation. The products were obtained as off-white powders after removal of the solvent in vacuo and washing with cold pentane.

[Zr(CH$_3$){HC{SiMe$_2$N[(*S*)-1-phenylethyl]}$_3$}] (12): Yield 85%; m.p. $61\,^{\circ}C$; ^1H NMR (200.13 MHz, C_6D_6, 295 K): $\delta = -0.71$ (s, 1H; *H*C(Si…)$_3$), -0.42 (s, 3H; ZrC*H*$_3$), 0.20 (s, 9H; Si(C*H*$_3$)$_2$), 0.30 (s, 9H; Si(C*H*$_3$)$_2$), 1.65 (d, $^3J(H,H) = 6.7$ Hz, 9H; HCC*H*$_3$), 4.42 (q, $^3J(H,H) = 6.7$ Hz, 3H; *H*CCH$_3$), 7.08–7.55 (m, 15H; C$_6$*H*$_5$); {^1H}^{13}C NMR (50.32 MHz, C_6D_6, 295 K): $\delta = 2.5$ (*H*C(Si…)$_3$), 4.3, 4.7 (Si(*C*H$_3$)$_2$), 27.7 (HC*C*H$_3$), 52.8 (Zr*C*H$_3$), 57.2 (H*C*CH$_3$), 126.9 (C^{2,4,6} of C_6H_5), 128.7 (C^{3,5} of C_6H_5), 148.8 (C^1 of C_6H_5); {^1H}^{29}Si NMR (39.76 MHz, C_6D_6, 295 K): $\delta = -0.5$; IR (pentane): $\tilde{\nu} = 3070$ (w), 3050 (w), 3010 (w), 1595 (w), 1485 (w), 1248 (s), 1195 (w), 1143 (br), 945 (s), 845 (s), 815 (vs), 755 (m), 695 $^{cm-1}$ (s); elemental analysis calcd (%) for $C_{32}H_{49}N_3Si_3Zr$ (651.23): C 59.02, H 7.58, N 6.45; found C 58.62, H 7.53, N 6.42.

[Zr(CH$_2$CH$_3$){HC{SiMe$_2$N[(*S*)-1-phenylethyl]}$_3$}] (13): Yield 64%; m.p. $56\,^{\circ}C$; ^1H NMR (400.14 MHz, C_6D_6, 295 K): $\delta = -0.73$ (s, 1H; *H*C(Si…)$_3$), -0.13 (m, 2H; ZrC*H*$_2$CH$_3$), 0.20 (s, 9H; Si(C*H*$_3$)$_2$), 0.25 (s, 9H; Si(C*H*$_3$)$_2$), 0.81 (t, $^3J(H,H) = 7.8$ Hz, 3H; ZrCH$_2$C*H*$_3$), 1.71 (d, $^3J(H,H) = 7.0$ Hz, 9H; HCC*H*$_3$), 4.50 (q, 3H; *H*CCH$_3$), 7.05–7.30 (m, 9H; C$_6$*H*$_5$), 7.58 (d, 6H; C$_6$*H*$_5$); {^1H}^{13}C NMR (100.62 MHz, C_6D_6, 295 K): $\delta = 2.9$ (H*C*(Si…)$_3$), 4.8 (Si(*C*H$_3$)$_2$), 11.7 (ZrCH$_2$*C*H$_3$), 27.6 (HC*C*H$_3$), 57.1 (H*C*CH$_3$), 66.9 (Zr*C*H$_2$CH$_3$), 126.9 (C^4 of C_6H_5), 127.0 (C^{2,6} of C_6H_5), 128.6 (C^{3,5} of C_6H_5), 148.8 (C^1 of C_6H_5); {^1H}^{29}Si NMR (79.50 MHz, C_6D_6, 295 K): $\delta = -0.7$; IR (benzene): $\tilde{\nu} = 3060$ (w), 3025 (w), 2961 (vs), 2926 (s), 2859 (s), 1492 (m), 1451 (m), 1252 (vs), 1100 (vs), 1019 (m), 963 (m), 949 (vs), 866 (vs), 831 (vs), 821 (vs), 699 cm^{-1} (s); elemental analysis calcd (%) for $C_{33}H_{51}N_3Si_3Zr$ (665.27): C 59.58, H 7.73, N 6.32; found C 59.66, H 7.91, N 6.04.

[Zr(*n*-C$_4$H$_9$){HC{SiMe$_2$N[(*S*)-1-phenylethyl]}$_3$}] (14): Yield 72%; m.p. $36\,^{\circ}C$; ^1H NMR (200.13 MHz, C_6D_6, 295 K): $\delta = -0.71$ (s, 1H; *H*C(Si…)$_3$), -0.26 – -0.10 (m, 2H; ZrC*H*$_2$(…) of *n*C$_4$H$_9$), 0.22 (s, 9H; Si(C*H*$_3$)$_2$), 0.26 (s, 9H; Si(C*H*$_3$)$_2$), 0.70–1.52 (m, 7H; *n*C$_4$*H*$_9$), 1.71 (d, $^3J(H,H) = 6.9$ Hz, 9H; HCC*H*$_3$), 4.48 (q, $^3J(H,H) = 6.9$ Hz, 3H; *H*CCH$_3$), 7.05–7.29 (m, 9H; C$_6$*H*$_5$), 7.56 (br d, 6H; C$_6$*H*$_5$); {^1H}^{13}C NMR (50.32 MHz, C_6D_6, 295 K): $\delta = 2.8$ (H*C*(Si…)$_3$), 4.7, 4.8 (Si(*C*H$_3$)$_2$), 27.5 (HC*C*H$_3$), 28.5, 29.6 (CH$_2$ of *n*C$_4$H$_9$), 56.9 (H*C*CH$_3$), 76.8 (ZrCH$_2$(…) of *n*C$_4$H$_9$), 126.8 (C^4 of C_6H_5), 127.0 (C^{2,6} of C_6H_5), 128.6 (C^{3,5} of C_6H_5), 148.8 (C^1 of C_6H_5); {^1H}^{29}Si NMR (39.76 MHz, C_6D_6, 295 K): $\delta = -0.7$; elemental analysis calcd (%) for $C_{35}H_{55}N_3Si_3Zr$ (693.32): C 60.63, H 8.00, N 6.06; found C 60.65, H 7.92, N 5.79.

[Zr{C(CH$_3$)$_3$}{HC{SiMe$_2$N[(*S*)-1-phenylethyl]}$_3$}] (15): Yield 68%; m.p. $53\,^{\circ}C$; ^1H NMR (200.13 MHz, C_6D_6, 295 K): $\delta = -0.93$ (s, 1H; *H*C(Si…)$_3$), -0.09 (s, 9H; Si(C*H*$_3$)$_2$), 0.26 (s, 9H; Si(C*H*$_3$)$_2$), 0.99 (s, 9H; ZrC(C*H*$_3$)$_3$), 1.73 (d, $^3J(H,H) = 6.8$ Hz, 9H; HCC*H*$_3$), 4.93 (q, 3H; *H*CCH$_3$), 7.09–7.59 (m, 15H; C$_6$*H*$_5$); {^1H}^{13}C NMR (50.32 MHz, C_6D_6, 295 K): $\delta = 4.4$ (H*C*(Si…)$_3$), 5.9, 7.0 (Si(*C*H$_3$)$_2$), 25.1 (ZrC(*C*H$_3$)$_3$), 25.5 (HC*C*H$_3$), 54.7 (H*C*CH$_3$), 58.4 (Zr*C*(CH$_3$)$_3$), 127.0 (C^4 of C_6H_5), 128.1 (C^{2,6} of C_6H_5), 128.6 (C^{3,5} of C_6H_5), 149.5 (C^1 of C_6H_5); {^1H}^{29}Si NMR (39.76 MHz, C_6D_6, 295 K): $\delta = -1.1$; IR (benzene): $\tilde{\nu} = 3045$ (w), 3010 (w), 2948 (s), 2810 (s), 1593 (w), 1483 (m), 1439 (m), 1361 (w), 1245 (s), 1192 (w), 1091 (s), 1055 (m), 1030 (w), 1013 (w), 956 (s), 940 (s), 855 (vs), 815 (br vs), 762 (m), 695 cm^{-1} (m); elemental analysis calcd (%) for $C_{35}H_{55}N_3Si_3Zr$ (693.32): C 60.63, H 8.00, N 6.06; found C 61.01, H 8.19, N 5.83.

[Zr(C$_6$H$_{11}$){HC{SiMe$_2$N[(*S*)-1-phenylethyl]}$_3$}] (16): Yield 74%; m.p. $29\,^{\circ}C$; ^1H NMR (200.13 MHz, C_6D_6, 295 K): $\delta = -0.76$ (s, 1H; *H*C(Si…)$_3$), -0.70 (tt, $^3J(H,H) = 12.1$ Hz, $^4J(H,H) = 2.5$ Hz, 1H; CH of ZrC$_6$*H*$_{11}$), 0.10–0.16 (m, 2H; C$_6$*H*$_{11}$), 0.19 (s, 9H; Si(C*H*$_3$)$_2$), 0.25 (s, 9H; Si(C*H*$_3$)$_2$), 0.60–0.82 (m, 3H; ZrC$_6$*H*$_{11}$), 0.85–0.99 (m, 3H; ZrC$_6$*H*$_{11}$), 1.50 (br t, 2H; ZrC$_6$*H*$_{11}$), 1.76 (d, $^3J(H,H) = 6.7$ Hz, 9H; HCC*H*$_3$), 4.68 (q, $^3J(H,H) = 6.7$ Hz, 3H; *H*CCH$_3$), 7.08–7.32 (m, 9H; C$_6$*H*$_5$), 7.63 (br d, 6H; C$_6$*H*$_5$); {^1H}^{13}C NMR (50.32 MHz, C_6D_6, 295 K): $\delta = 3.5$ (H*C*(Si…)$_3$), 5.2, 5.5 (Si(*C*H$_3$)$_2$), 26.7 (HC*C*H$_3$), 27.2, 28.7, 29.3, 29.8, 30.1 (CH$_2$ of ZrC$_6$H$_{11}$), 56.3 (H*C*CH$_3$), 83.4 (CH of Zr*C*$_6$H$_{11}$), 126.8 (C^4 of C_6H_5), 127.2 (C^{2,6} of C_6H_5), 128.5 (C^{3,5} of C_6H_5), 148.3 (C^1 of C_6H_5); {^1H}^{29}Si NMR (39.76 MHz, C_6D_6, 295 K): $\delta = -0.6$; IR (benzene): $\tilde{\nu} = 3083$ (w), 3062 (w), 3025 (w), 2961 (m), 2924 (s), 2850 (m), 1583 (w), 1492 (m), 1448 (m), 1369 (w), 1252 (s), 1198 (w), 1099 (s), 1062 (m), 965 (m), 946 (s), 863 (vs), 809 (vs), 741 (w), 700 cm^{-1} (s); elemental analysis calcd (%) for $C_{37}H_{57}N_3Si_3Zr$ (719.36): C 61.78, H 7.99, N 5.84; found C 62.31, H 7.84, N 5.57.

[Zr(CH$_2$C$_6$H$_5$){HC{SiMe$_2$N[(*S*)-1-phenylethyl]}$_3$}] (17): Yield 99%; m.p. $34\,^{\circ}C$; ^1H NMR (200.13 MHz, C_6D_6, 295 K): $\delta = -0.79$ (s, 1H; *H*C(Si…)$_3$), 0.15 (s, 9H; Si(C*H*$_3$)$_2$), 0.23 (s, 9H; Si(C*H*$_3$)$_2$), 1.62 (d, $^3J(H,H) = 6.7$ Hz, 9H; HCC*H*$_3$), 2.11 (s, 2H; ZrC*H*$_2$C$_6$H$_5$), 4.42 (q, $^3J(H,H) = 6.7$ Hz, 3H; *H*CCH$_3$), 6.33 (d, 2H; ZrCH$_2$C$_6$*H*$_5$), 6.55–7.35 (m, 12H; ZrCH$_2$C$_6$*H*$_5$ and C$_6$*H*$_5$), 7.51 (d, 6H; C$_6$*H*$_5$); {^1H}^{13}C NMR (50.32 MHz, C_6D_6, 295 K): $\delta = 2.9$ (H*C*(Si…)$_3$), 5.2 (Si(*C*H$_3$)$_2$), 26.8 (HC*C*H$_3$), 56.5 (H*C*CH$_3$), 78.9 (Zr*C*H$_2$C$_6$H$_5$), 122.0 (C^4 of ZrCH$_2$*C*$_6$H$_5$), 125.7, 128.5 (C^{2,3,5,6} of ZrCH$_2$*C*$_6$H$_5$), 126.7 (C^4 of C_6H_5), 127.3 (C^{2,6} of C_6H_5), 128.8 (C^{3,5} of C_6H_5), 146.0 (C^1 of CH$_2$*C*$_6$H$_5$), 148.1 (C^1 of C_6H_5); {^1H}^{29}Si NMR (39.76 MHz, C_6D_6, 295 K): $\delta = -0.6$; IR (benzene): $\tilde{\nu} = 3060$ (w), 3025 (s), 2971 (vs), 2897 (m), 2865 (m), 1595 (m), 1491 (s), 1448 (m), 1369 (m), 1252 (vs), 1199 (m), 1100 (br s), 1068 (s), 1030 (s), 1020 (s), 949 (s), 866 (vs), 809 (vs), 744 (m), 700 cm^{-1} (s); elemental analysis calcd (%) for $C_{38}H_{53}N_3Si_3Zr$ (727.34): C 62.75, H 7.35, N 5.78; found C 63.07, H 7.32, N 5.69.

[Zr{CH$_2$Si(CH$_3$)$_3$}{HC{SiMe$_2$N[(*S*)-1-phenylethyl]}$_3$}] (18): Yield 74%; m.p 34 $^{\circ}C$; ^1H NMR (200.13 MHz, C_6D_6, 295 K): $\delta = -0.73$ (s, 1H; *H*C(Si…)$_3$), -0.35 (d, $^2J(H,H) = 11.2$ Hz, 1H; ZrC*H*$_2$SiMe$_3$), -0.14 (s, 9H; ZrCH$_2$Si(C*H*$_3$)$_3$), -0.04 (d, $^2J(H,H) = 11.2$ Hz, 1H; ZrC*H*$_2$SiMe$_3$), 0.21 (s, 9H; Si(C*H*$_3$)$_2$), 0.28 (s, 9H; Si(C*H*$_3$)$_2$), 1.73 (d, $^3J(H,H) = 6.7$ Hz, 9H; HCC*H*$_3$), 4.58 (q, 1H; *H*CCH$_3$), 7.07–7.58 (m, 15H; C$_6$*H*$_5$); {^1H}^{13}C NMR (50.32 MHz, C_6D_6, 295 K): $\delta = 1.3$ (H*C*(Si…)$_3$), 2.8 (ZrCH$_2$Si(*C*H$_3$)$_3$), 4.8, 5.1 (Si(*C*H$_3$)$_2$), 27.8 (HC*C*H$_3$) 56.4 (H*C*CH$_3$), 71.9 (Zr*C*H$_2$SiMe$_3$), 126.8 (C^4 of C_6H_5), 127.2 (C^{2,6} of C_6H_5), 128.5 (C^{3,5} of C_6H_5), 148.6 (C^1 of C_6H_5); {^1H}^{29}Si NMR (39.76 MHz, C_6D_6, 295 K): $\delta = -0.4$; IR (toluene): $\tilde{\nu} = 1363$ (w), 1246 (s), 1098 (s), 1060 (w), 1015 (w), 945 (m), 865 (s), 815 (vs), 758 cm^{-1} (w); elemental analysis calcd (%) for $C_{35}H_{57}N_3Si_4Zr$ (723.42): C 58.11, H 7.94, N 5.80; found C 57.77, H 7.54, N 5.42.

[Zr(C$_6$H$_5$){HC{SiMe$_2$N[(*S*)-1-phenylethyl]}$_3$}] (19): Yield 55%; ^1H NMR (200.13 MHz, C_6D_6, 295 K): $\delta = -0.64$ (s, 1H; *H*C(Si…)$_3$), 0.25 (s, 9H; Si(C*H*$_3$)$_2$), 0.27 (s, 9H; Si(C*H*$_3$)$_2$), 1.63 (d, $^3J(H,H) = 6.8$ Hz, 9H; HCC*H*$_3$),

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4.67 (q, 3H; $HCCH_3$), 6.95–7.51 (m, 20H; C_6H_5); $\{^1H\}^{13}C$ NMR (50.32 MHz, C_6D_6, 295 K): $\delta = 3.0$ ($HC(Si\ldots)_3$), 5.2, 5.3 ($Si(CH_3)_2$), 26.9 ($HCCH_3$), 57.2 ($HCCH_3$), 126.7 (*o*-C of ZrC_6H_5), 127.1 (C^4 of C_6H_5), 127.2 ($C^{2,6}$ of C_6H_5), 128.5 ($C^{3,5}$ of C_6H_5), 129.3 (*p*-C of ZrC_6H_5), 132.1 (*m*-C of ZrC_6H_5), 147.9 (C^1 of C_6H_5), 154.0 (*i*-C of ZrC_6H_5); $\{^1H\}^{29}Si$ NMR (39.76 MHz, C_6D_6, 295 K): $\delta = -0.2$; IR (benzene): $\tilde{\nu} = 3060$ (w), 3018 (w), 2950 (m), 2890 (w), 1595 (w), 1485 (m), 1440 (m), 1365 (m), 1250 (s), 1195 (m), 1090 (br s), 1055 (m), 1030 (m), 957 (s), 945 (s), 862 (vs), 815 (br vs), 718 (m), 697 cm^{-1} (s).

Preparation of [Zr(CH$_3$){HC{SiMe$_2$N[(*R*)-1-indanyl]}$_3$}] (20): A solution of MeLi (1.6 M) in diethyl ether (0.47 mL, 0.75 mmol) was added to a stirred solution of **10** (0.48 mg, 0.68 mmol) in diethyl ether (10 mL), diethyl etherat $-78\,^\circ C$. The solution was slowly warmed up to room temperature and stirred for 15 h. After removing the solvent in vacuo and re-dissolving in *n*-pentane, the LiCl was separated by centrifugation. Upon storing at $-25\,^\circ C$, compound **12** was obtained as a colourless, highly crystalline solid. Yield 0.41 mg, 0.60 mmol (88%); m.p. 55 °C; ^1H NMR (200.13 MHz, [D$_8$]toluene, 295 K): $\delta = -1.66$ (s, 3H; $ZrCH_3$), -0.54 (s, 1H; $HC(Si\ldots)_3$), 0.41 (s, 9H; $Si(CH_3)_2$), 0.51 (s, 9H; $Si(CH_3)_2$), 1.85–2.05 (m, 3H; $H^{2,3}$ of indanyl), 2.38–2.88 (m, 9H; $H^{2,3}$ of indanyl), 4.62 (t, $^3J(H^1,H^2) = 7.3$ Hz, 3H; H^1 of indanyl), 6.84–7.21 (m, 9H; H^{arom} of indanyl), 7.70 (d, $^3J(H,H) = 7.3$ Hz, 3H; H^{arom} of indanyl); $\{^1H\}^{13}C$ NMR (50.32 MHz, [D$_8$]toluene, 295 K): $\delta = 2.8$ ($HC(Si\ldots)_3$), 3.5, 5.9 ($Si(CH_3)_2$), 30.7, 41.6 ($C^{2,3}$ of indanyl), 52.2 ($ZrCH_3$), 63.4 (C^1 of indanyl), 124.0, 125.2, 126.9, 127.6 (C^{4-7} of indanyl), 143.0, 149.4 ($C^{3a,7a}$ of indanyl); $\{^1H\}^{29}Si$ NMR (39.76 MHz, [D$_8$]toluene, 295 K): $\delta = 0.6$; IR (toluene): $\tilde{\nu} = 3069$ (m), 3022 (m), 2946 (vs), 2898 (m), 2849 (s), 1475 (m), 1458 (m), 1251 (vs), 1109 (vs), 1075 (m), 965 (m), 894 (vs), 834 (vs), 811 (vs), 743 cm^{-1} (m); elemental analysis calcd (%) for $C_{35}H_{49}N_3Si_3Zr$ (687.27): C 61.17, H 7.19, N 6.11; found C 61.34, H 7.27, N 5.93.

General procedure for the preparation of [Zr{O(Me)R^{1}R^2}{HC{SiMe$_2$N[(*S*)-1-phenylethyl]}$_3$}] (21–23): One equivalent of the ketone was added to a stirred solution of compound **12** in toluene (0.5 mL), at $-70\,^\circ C$. After 30 min, the solution was slowly warmed up to room temperature. Removal of the solvent in vacuo and washing with cold pentane yielded the products as yellow powders.

[Zr{OC(Me)(Ph)(HC=CHPh)}{HC{SiMe$_2$N[(*S*)-1-phenylethyl]}$_3$}] (21): Yield 88%; ^1H NMR (400.14 MHz, [D$_8$]toluene, 295 K), (diastereomeric mixture): $\delta = -0.49$, -0.49 (s, 1H; $HC(Si\ldots)_3$), 0.14 (s, 9H; $Si(CH_3)_2$), 0.25, 0.25 (2 × s, 9H; $Si(CH_3)_2$), 1.39, 1.47 (2 × s, 3H; $ZrOC(CH_3)(C_6H_5)(\ldots)$), 1.69 (d, $^3J(H,H) = 6.8$ Hz, 9H; $HCCH_3$), 4.50, 4.52 (2 × q, $^3J(H,H) = 6.6$ Hz, 3H; $HCCH_3$), 6.16, 6.29 (2 × AB-spin system, $^3J(H,H) = 6.1$ Hz, 2H; *HC*=*CH*), 6.82–7.30 (m, 19H; C_6H_5 and $ZrOC(CH_3)(C_6H_5)$-(HC=CHC_6H_5)), 7.50 (d, $^3J(H,H) = 7.2$ Hz, 6H; C_6H_5); $\{^1H\}^{13}C$ NMR (100.62 MHz, [D$_8$]toluene, 295 K), (diastereomeric mixture): $\delta = 1.5$, 1.7 ($HC(Si\ldots)_3$), 4.6, 4.8, 4.9 ($Si(CH_3)_2$), 29.1, 29.3 ($HCCH_3$), 30.4, 30.7 ($ZrOC(CH_3)(C_6H_5)(\ldots)$), 58.0, 58.1 ($HCCH_3$), 85.8 ($ZrOC(CH_3)$-($C_6H_5$)(…)), 125.7, 126.3, 126.6, 126.7, 126.7, 126.8, 126.9, 127.2, 127.4, 127.8, 127.9, 127.9, 128.3, 128.3, 136.9, 138.1 ($ZrOC(CH_3)(C_6H_5)$-(HC=CHC_6H_5)), 126.2 (C^4 of C_6H_5), 126.7 ($C^{2,6}$ of C_6H_5), 128.1 ($C^{3,5}$ of C_6H_5), 147.3, 146.4 (*i*-C of $ZrOC(CH_3)(C_6H_5)(HC$=CHC_6H_5), 149.2, 149.3 (C^1 of C_6H_5); $\{^1H\}^{29}Si$ NMR (39.76 MHz, [D$_8$]toluene, 295 K), (diastereomeric mixture): $\delta = -0.7$; IR (toluene): $\tilde{\nu} = 3083$ (w), 3060 (m), 3026 (m), 2968 (s), 2896 (w), 2864 (w), 1492 (s), 1446 (s), 1252 (vs), 1103 (vs), 1069 (vs), 950 (vs), 865 (vs), 831 (vs), 763 (m), 739 (m), 700 cm^{-1} (vs).

[Zr{OC(Me)(CHMe$_2$)(Ph)}{HC{SiMe$_2$N[(*S*)-1-phenylethyl]}$_3$}] (22): Yield 93%; ^1H NMR (200.13 MHz, [D$_8$]toluene, 295 K), (diastereomer 1): $\delta = -0.58$ (s, 1H; $HC(Si\ldots)_3$), 0.14, 0.17 (s, 2 × 9H; $Si(CH_3)_2$), 0.35 (d, $^3J(H,H) = 7.1$ Hz, 3H; $ZrOC(Me)(CH(CH_3)_2)(Ph)$), 0.80 (d, $^3J(H,H) = 6.6$ Hz, 3H; $ZrOC(Me)(CH(CH_3)_2)(Ph)$), 1.21 (s, 3H; $ZrOC(CH_3)(CHMe_2)(Ph)$), 1.62 (d, $^3J(H,H) = 6.6$ Hz, 9H; $HCCH_3$), 1.87–2.08 (m, $^3J(H,H) = 6.64$ Hz, 1H; $ZrOC(CH_3)(CHMe_2)(Ph)$), 4.60 (q, 3H; $HCCH_3$), 6.80–7.52 (m, 20H; C_6H_5 and $ZrOC(Me)(CHMe_2)(C_6H_5)$); ^1H NMR (200.13 MHz, [D$_8$]toluene, 295 K), (diastereomer 2): $\delta = -0.59$ (s, 1H; $HC(Si\ldots)_3$), 0.13, 0.14 (s, 2 × 9H; $Si(CH_3)_2$), 0.44 (d, $^3J(H,H) = 6.6$ Hz, 3H; $ZrOC(Me)(CH(CH_3)_2)(Ph)$), 0.87 (d, $^3J(H,H) = 6.6$ Hz, 3H; $ZrOC(Me)(CH(CH_3)_2)(Ph)$), 1.19 (s, 3H; $ZrOC(CH_3)(CHMe_2)(Ph)$), 1.67 (d, $^3J(H,H) = 6.6$ Hz, 9H; $HCCH_3$), 1.87–2.08 (m, $^3J(H,H) = 6.64$ Hz, 1H; $ZrOC(Me)(CHMe_2)(Ph)$), 4.69 (q, 3H; $HCCH_3$), 6.80–7.61 (m, 20H; C_6H_5 and $ZrOC(Me)(CHMe_2)(C_6H_5)$); $\{^1H\}^{13}C$ NMR (50.32 MHz, [D$_8$]toluene, 295 K), (diastereomer 1): $\delta = 1.8$ ($HC(Si\ldots)_3$), 5.1, 5.3 ($Si(CH_3)_2$), 17.7, 18.6, 22.1 ($ZrOC(CH_3)(CH(CH_3)_2)(C_6H_5)$), 27.8 ($HCCH_3$), 57.8 ($HCCH_3$), 88.8 ($ZrOC(Me)(CHMe_2)(Ph)$), 126.5 ($C^4$ of C_6H_5), 127.2 ($C^{2,6}$ of C_6H_5), 126.3, 126.8 (*o*, *p*-C of $ZrOC(Me)(CHMe_2)(C_6H_5)$), 128.1 (*m*-C of $ZrOC(Me)(CHMe_2)(C_6H_5)$), 128.2 ($C^{3,5}$ of C_6H_5), 148.1 (*i*-C of $ZrOC(Me)(CHMe_2)(C_6H_5)$), 148.7 (C^1 of C_6H_5); $\{^1H\}^{13}C$ NMR (50.32 MHz, [D$_8$]toluene, 295 K), (diastereomer 2): $\delta = 2.1$ ($HC(Si\ldots)_3$), 4.9, 5.7 ($Si(CH_3)_2$), 18.3, 18.5, 23.8 ($ZrOC(CH_3)(CH(CH_3)_2)(C_6H_5)$), 28.4 ($HCCH_3$), 58.2 ($HCCH_3$), 88.9 ($ZrOC(Me)(CHMe_2)(Ph)$), 126.5 ($C^4$ of C_6H_5), 127.1 ($C^{2,6}$ of C_6H_5), 126.3, 126.7 (*o*, *p*-C of $ZrOC(Me)(CHMe_2)(C_6H_5)$), 128.0 (*m*-C of $ZrOC(Me)(CHMe_2)(C_6H_5)$), 128.3 ($C^{3,5}$ of C_6H_5), 147.7 (*i*-C of $ZrOC(Me)(CHMe_2)(C_6H_5)$), 148.7 (C^1 of C_6H_5); $\{^1H\}^{29}Si$ NMR (39.76 MHz, [D$_8$]toluene, 295 K): $\delta = -1.0$; IR (toluene): $\tilde{\nu} = 3084$ (w), 3060 (m), 3025 (m), 2963 (vs), 2898 (w), 2873 (w), 1492 (s), 1448 (s), 1349 (m), 1252 (vs), 1198 (m), 1128 (m), 1101 (vs), 1066 (s), 1033 (s), 1022 (m), 953 (vs), 862 (s), 821 (br vs), 774 (m), 700 cm^{-1} (vs).

[Zr{OC(Me)(Et)(Ph)}HC{SiMe$_2$N[(*S*)-1-phenylethyl]}$_3$}] (23): Yield 91%; ^1H NMR (200.13 MHz, [D$_8$]toluene, 295 K), (diastereomer 1): $\delta = -0.51$ (s, 1H; $HC(Si\ldots)_3$), 0.15 (s, 9H; $Si(CH_3)_2$), 0.19 (s, 9H; $Si(CH_3)_2$), 0.45 (t, 3H; $ZrOC(Me)(CH_2CH_3)(Ph)$), 1.18 (s, 3H; $ZrOC(CH_3)(Et)(Ph)$), 1.21–1.29 (m, 2H; $ZrOC(Me)(CH_2CH_3)(Ph)$), 1.55 (d, $^3J(H,H) = 6.8$ Hz, 9H; $HCCH_3$), 4.50 (q, 3H; $HCCH_3$), 6.97–7.53 (m, 20H; C_6H_5 and $ZrOC(Me)$-(Et)(C_6H_5)); ^1H NMR (200.13 MHz, [D$_8$]toluene, 295 K), (diastereomer 2): $\delta = -0.50$ (s, 1H; $HC(Si\ldots)_3$), 0.17 (s, 9H; $Si(CH_3)_2$), 0.23 (s, 9H; $Si(CH_3)_2$), 0.39 (t, 3H; $ZrOC(Me)(CH_2CH_3)(Ph)$), 1.21 (s, 3H; $ZrOC(CH_3)(Et)(Ph)$), 1.21–1.29 (m, 2H; $ZrOC(Me)(CH_2CH_3)(Ph)$), 1.65 (d, $^3J(H,H) = 6.8$ Hz, 9H; $HCCH_3$), 4.58 (q, 3H; $HCCH_3$), 6.97–7.53 (m, 20H; C_6H_5 and $ZrOC(Me)(Et)(C_6H_5)$); $\{^1H\}^{13}C$ NMR (50.32 MHz, [D$_8$]toluene, 295 K), (diastereomer 1): $\delta = 1.9$ ($HC(Si\ldots)$, 4.8, 5.1 ($Si(CH_3)_2$), 9.5 ($ZrOC(Me)$-(CH_2CH_3)(Ph)), 27.7 ($ZrOC(CH_3)(Et)(Ph)$), 28.9 ($HCCH_3$), 38.5 ($ZrOC$-(Me)(CH_2CH_3)(Ph)), 58.2 ($HCCH_3$), 86.5 ($ZrOC(Me)(Et)(Ph)$), 126.2, 128.0 (*o*, *m*-C of $ZrOC(Me)(Et)(C_6H_5)$), 126.6 (C^4 of C_6H_5), 127.0 ($C^{2,6}$ of C_6H_5), 128.3 ($C^{3,5}$ of C_6H_5), 128.5 (*p*-C of $ZrOC(Me)(Et)(C_6H_5)$), 146.2 (*i*-C of $ZrOC(Me)(Et)(C_6H_5)$), 149.6 (C^1 of C_6H_5); $\{^1H\}^{13}C$ NMR (50.32 MHz, [D$_8$]toluene, 295 K) (diastereomer 2): $\delta = 1.6$ ($HC(Si\ldots)$, 4.6, 4.8 ($Si(CH_3)_2$), 9.5 ($ZrOC(Me)(CH_2CH_3)(Ph)$), 28.3 ($ZrOC(CH_3)(Et)(Ph)$), 28.6 ($HCCH_3$), 39.0 ($ZrOC(Me)(CH_2CH_3)(Ph)$), 57.9 ($HCCH_3$), 86.5 ($ZrOC(Me)(Et)(Ph)$), 126.0, 128.0 (*o*, *m*-C of $ZrOC(Me)(Et)(C_6H_5)$), 126.4 (C^4 of C_6H_5), 127.0 ($C^{2,6}$ of C_6H_5), 128.3 ($C^{3,5}$ of C_6H_5), 128.4 (*p*-C of $ZrOC(Me)(Et)(C_6H_5)$), 146.5 (*i*-C of $ZrOC(Me)(Et)(C_6H_5)$), 149.1 (C^1 of C_6H_5); $\{^1H\}^{29}Si$ NMR (39.76 MHz, [D$_8$]toluene, 295 K), (diastereomers 1 and 2): $\delta = 4.2$, 4.3; IR (toluene): $\tilde{\nu} = 3045$ (w), 3010 (w), 2950 (s), 1610 (br w), 1485 (m), 1440 (m), 1361 (w), 1246 (s), 1192 (w), 1095 (s), 946 (s), 860 (vs), 812 (vs), 695 cm^{-1} (s).

General procedure for the hydrolysis, work up and analysis of the chiral alcohols: The product complex (60–100 mg) derived from the insertion of a carbonyl compound into the Zr–C bond was dissolved in diethyl ether (ca. 5 mL). Dilute aqueous HCl (1 M) was slowly added to the stirred solution, until the initially formed white precipitate was redissolved. After neutralisation with $NaHCO_3$, the organic phase was separated, and the aqueous phase extracted with diethyl ether (3 × 10 mL). The combined organic extracts were dried over Na_2SO_4, the solvent removed and the oily residue purified by Kugelrohr distillation. Analysis of the product was carried out by gas chromatorgraphy by using a Siemens Sichromat 2 instrument or a Fisons GC 8000 instrument equipped with an FID detector. Stationary phases used in the analysis were 30% 2,6-dimethyl-3-pentyl-β-cyclodextrin in OV 1701, 30% 2,3-diethyl-6-*tert*-butyldimethyl-β-cyclodextrin in PS 086 or Cyclodex B commercialised by J&W Scientific.

General procedure for the preparation of [Zr{O(H)(CH$_3$)R}{HC{SiMe$_2$N[(*S*)-1-phenylethyl]}$_3$}] (24–27): One equivalent of the aldehyde was added to a stirred solution of compound **12** in toluene, at $-70\,^\circ C$. After 30 min, the solution was slowly warmed up to room temperature. Removal of the solvent in vacuo and washing with cold pentane yielded the products as yellow powders.

[Zr{OC(H)(Me)(C_6H_5)}{HC{SiMe$_2$N[(*S*)-1-phenylethyl]}$_3$}] (24): Yield 96%, m.p. 93 °C; *de*: 76%; ^1H NMR (200.13 MHz, C_6D_6, 295 K): $\delta = -0.48$ (s, 1H; $HC(Si\ldots)_3$), 0.11, 0.26 (s, 2 × 9H; $Si(CH_3)_2$), 1.12 (d, 3H; $^3J(H,H) = 6.4$ Hz, $ZrOC(CH_3)(H)(Ph)$), 1.62 (d, $^3J(H,H) = 6.7$ Hz, 9H; $HCCH_3$), 4.33 (q, $^3J(H,H) = 6.7$ Hz, 3H; $HCCH_3$), 4.80 (q, $^3J(H,H) = 6.4$ Hz, 1H; ZrO (CH_3)(*H*)(Ph)), 6.87–7.28 (m, 14H; C_6H_5, $ZrO(C(CH_3)(H)(C_6H_5))$, 7.44 (d, $^3J(H,H) = 7.5$ Hz, 6H; C_6H_5); $\{^1H\}^{13}C$ NMR (50.32 MHz, C_6D_6, 295 K): $\delta = 1.5$ ($HC(Si\ldots)_3$), 4.4, 4.5 ($Si(CH_3)_2$), 26.4 ($ZrOC(CH_3)(H)(Ph)$), 29.5 ($HCCH_3$), 58.5 ($HCCH_3$), 80.9

(ZrO*C*(CH_3)(H)(Ph)), 126.4 (C^4 of C_6H_5), 126.5 (*p*-C of ZrOC(CH_3)(H)(C_6H_5)), 126.7 ($C^{2,6}$ of C_6H_5), 126.7, 128.4 (*o*, *m*-C of ZrOC(CH_3)(H)(C_6H_5)), 128.3 ($C^{3,5}$ of C_6H_5), 145.5 (*i*-C of ZrOC(CH_3)(H)(C_6H_5)), 149.8 (C^1 of C_6H_5); {^{1}H}^{29}Si NMR (39.76 MHz, C_6D_6, 295 K): $\delta = -0.7$; IR (pentane): $\tilde{\nu} = 3092$ (w), 3061 (m), 3025 (m), 1648 (w), 1605 (w), 1492 (m), 1370 (m), 1256 (vs), 1202 (m), 1100 (br vs), 1025 (s), 955 (s), 865 (br vs), 825 (br vs), 705 cm^{-1} (s); elemental analysis calcd (%) for $C_{39}H_{55}N_3OSi_3Zr$ (757.36): C 61.85, H 7.31, N 5.54; found C 61.39, H 7.52, N 5.09.

[Zr{OC(H)(Me)(*p*-FC_6H_4)}{HC{$SiMe_2$N[(*S*)-1-phenylethyl]}$_3$}] (25): Yield 97%; ^{1}H NMR (200.13 MHz, [D_8]toluene, 295 K): $\delta = -0.48$ (s, 1H; *H*C(Si…)$_3$), 0.11, 0.25 (s, 2 × 9H; Si(C*H*$_3$)$_2$), 1.02 (d, ^3J(H,H) = 6.6 Hz, 3H; ZrOC(C*H*$_3$)(H)(*p*-FC_6H_4)), 1.59 (d, ^3J(H,H) = 6.6 Hz, 9H; HCC*H*$_3$), 4.32 (q, ^3J(H,H) = 6.6 Hz, 3H; *H*CCH$_3$), 4.69 (q, ^3J(H,H) = 6.6 Hz, 1H; ZrOC(CH_3)(*H*)(*p*-FC_6H_4)), 6.52 – 7.47 (m, 19H; C_6H_5, ZrOC(CH_3)(H)(*p*-FC_6H_4)); {^{1}H}^{13}C NMR (50.32 MHz, [D_8]toluene, 295 K): $\delta = 1.3$ (*H*C(Si…)$_3$), 4.2, 4.4 (Si(*C*H$_3$)$_2$), 26.4 (ZrOC(*C*H$_3$)(H)(*p*-F*C*$_6$H$_4$)), 29.5 (HC*C*H$_3$), 58.4 (H*C*CH$_3$), 79.8 (ZrO*C*(CH_3)(H)(*p*-F*C*$_6$H$_4$)), 115.2 (d, ^2J(C,F) = 21.7 Hz; *m*-C of ZrOC(CH_3)(H)(*p*-F*C*$_6$H$_4$)), 126.4 (C^4 of C_6H_5), 126.6 ($C^{2,6}$ of C_6H_5), 128.0 (d, ^3J(C,F) = 8.1 Hz; *o*-C of ZrOC(CH_3)(H)(*p*-F*C*$_6$H$_4$)), 128.3 ($C^{3,5}$ of C_6H_5), 141.3 (d, ^4J(C,F) = 3.0 Hz; *i*-C of ZrOC(CH_3)(H)(*p*-F*C*$_6$H$_4$)), 149.7 (C^1 of C_6H_5), 162.2 (d, ^1J(C,F) = 244.9 Hz; *p*-C of ZrOC(CH_3)(H)(*p*-F*C*$_6$H$_4$); {^{1}H}^{29}Si NMR (39.76 MHz, [D_8]toluene, 295 K): $\delta = -0.7$; {^{1}H}^{19}F NMR ([D_8]toluene, 295 K): $\delta = -110.1$; IR (toluene): $\tilde{\nu} = 3059$ (m), 3022 (s), 2961 (vs), 2920 (w), 2889 (w), 2861 (w), 1602 (s), 1491 (s), 1445 (s), 1405 (m), 1366 (m), 1250 (vs), 1221 (s), 1199 (m), 1120 (br vs), 1091 (br vs), 1018 (br m), 947 (vs), 855 (br vs), 812 (br vs), 757 (br m), 693 cm^{-1} (s); elemental analysis calcd (%) for $C_{39}H_{54}FN_3OSi_3Zr$ (775.39): C 60.41, H 7.02, N 5.42; found C 60.09, H 6.81, N 5.39.

[Zr{OC(H)(Me)(*p*-ClC_6H_4)}{HC{$SiMe_2$N[(*S*)-1-phenylethyl]}$_3$}] (26): Yield 89%; ^{1}H NMR (200.13 MHz, [D_8]toluene, 295 K): $\delta = -0.48$ (s, 1H; *H*C(Si…)$_3$), 0.11, 0.26 (s, 2 × 9H; Si(C*H*$_3$)$_2$), 0.99 (d, ^3J(H,H) = 6.6 Hz, 3H; ZrOC(C*H*$_3$)(H)(*p*-ClC_6H_4)), 1.59 (d, ^3J(H,H) = 6.6 Hz, 9H; HCC*H*$_3$), 4.32 (q, ^3J(H,H) = 6.6 Hz, 3H; *H*CCH$_3$), 4.64 (q, ^3J(H,H) = 6.6 Hz, 1H; ZrOC(CH_3)(*H*)(*p*-ClC_6H_4)), 6.62 – 7.54 (m, 19H; C_6H_5 and ZrOC(CH_3)(H)(*p*-ClC_6H_4)); {^{1}H}^{13}C NMR (50.32 MHz, [D_8]toluene, 295 K): $\delta = 1.3$ (*H*C(Si…)$_3$), 4.2, 4.5 (Si(*C*H$_3$)$_2$), 26.4 (ZrOC(*C*H$_3$)(H)(*p*-ClC_6H_4)), 29.5 (HC*C*H$_3$), 58.3 (H*C*CH$_3$), 79.8 (ZrO*C*(CH_3)(H)(*p*-ClC_6H_4)), 126.5 (C^4 of C_6H_5), 126.6 ($C^{2,6}$ of C_6H_5), 127.7, 128.5 (*o*, *m*-C of ZrOC(CH_3)(H)(*p*-ClC_6H_4)), 128.4 ($C^{3,5}$ C_6H_5), 133.0 (*p*-C of ZrOC(CH_3)(H)(*p*-ClC_6H_4)), 144.0 (*i*-C of ZrOC(CH_3)(H)(*p*-ClC_6H_4)), 149.7 (C^1 of C_6H_5); {^{1}H}^{29}Si NMR (39.76 MHz, [D_8]toluene, 295 K): $\delta = -0.8$; IR (toluene): $\tilde{\nu} = 3056$ (w), 3021 (m), 2958 (vs), 2855 (w), 1486 (s), 1443 (s), 1411 (s), 1346 (m), 1248 (vs), 1195 (s), 1088 (br vs), 1011 (m), 939 (vs), 855 (br vs), 812 (br vs), 758 (m), 734 (m), 691 cm^{-1} (s); elemental analysis calcd (%) for $C_{39}H_{54}ClN_3OSi_3Zr$ (791.81): C 59.16, H 6.87, N 5.31; found C 59.40, H 6.97, N 5.22.

[Zr{OC(H)(Me)(2-$C_{10}H_7$)}{HC{$SiMe_2$N[(*S*)-1-phenylethyl]}$_3$}] (27): Yield 97%; ^{1}H NMR (200.13 MHz, [D_8]toluene, 295 K): $\delta = -0.49$ (s, 1H; *H*C(Si…)$_3$), 0.11, 0.25 (s, 2 × 9H; Si(C*H*$_3$)$_2$), 1.20 (d, ^3J(H,H) = 6.4 Hz, 3H; ZrOC(C*H*$_3$)(H)($C_{10}H_7$)), 1.63 (d, ^{3}J(H,H) = 6.5 Hz, 9H; HCC*H*$_3$), 4.34 (q, 3H; *H*CCH$_3$), 4.98 (q, 1H; ZrOC(CH_3)(*H*)($C_{10}H_7$)), 6.93 – 7.58 (m, 22H; C_6H_5 and naphthyl); {^{1}H}^{13}C NMR (50.32 MHz, [D_8]toluene, 295 K): $\delta = 3.6$ (*H*C(Si…)$_3$), 4.2, 4.5 (Si(*C*H$_3$)$_2$), 26.4 (ZrOC(*C*H$_3$)(H)($C_{10}H_7$)), 29.5 (HC*C*H$_3$), 58.5 (H*C*CH$_3$), 80.9 (ZrO*C*(CH_3)(H)($C_{10}H_7$)), 126.4 (C^4 of C_6H_5), 126.6 ($C^{2,6}$ of C_6H_5), 124.8, 125.1, 125.7, 126.0, 127.9, 128.2, 128.6 ($C^{1,3-8}$ of naphthyl), 128.3 ($C^{3,5}$ of C_6H_5), 133.3, 133.6 ($C^{4a,8a}$ of naphthyl), 142.8 (C^2 of naphthyl), 149.7 (C^1 of C_6H_5); {^{1}H}^{29}Si NMR (39.76 MHz, [D_8]toluene, 295 K): $\delta = -0.7$; IR (toluene): $\tilde{\nu} = 3082$ (w), 3060 (s), 3025 (s), 2966 (vs), 2924 (s), 2896 (s), 2863 (s),1602 (m), 1508 (m), 1491 (vs), 1450 (vs), 1368 (s), 1251 (vs), 1198 (m), 1173 (m), 1129 (s), 1103 (br vs), 1031 (m), 1020 (s), 950 (br vs), 862 (br vs), 821 (br vs), 748 (s), 700 (vs), 672 cm^{-1} (m); elemental analysis calcd (%) for $C_{43}H_{57}N_3OSi_3Zr$ (807.43): C 63.97, H 7.12, N 5.20; found C 63.73, H 6.95, N 4.78.

Preparation of [Zr{OC(H)(Me)(2-$C_{10}H_7$)}{HC{$SiMe_2$N[(*R*)-1-indanyl]}$_3$}] (28): A solution of 2-naphtaldehyde (18.2 mg, 0.12 mmol) in toluene (0.2 mL) was added to a stirred solution of **20** (80.0 mg, 0.12 mmol) in toluene (0.3 mL) at −70 °C. After 30 min the solution was slowly warmed to room temperature and the product was obtained as a yellow powder after removal of the solvent in vacuo. Yield: 92.5 mg, 0.11 mmol (91%); ^{1}H NMR (200.13 MHz, [D_8]toluene, 295 K): $\delta = -0.32$ (s, 1H; *H*C(Si…)$_3$), 0.23 (d, ^3J(H,H) = 6.1 Hz, 3H; ZrOC(C*H*$_3$)(H)($C_{10}H_7$)), 0.44, 0.55 (s, 2 × 9H; Si(C*H*$_3$)$_2$), 1.63 – 1.88 (m, 3H; H^{2,3} of indanyl), 2.42 – 2.62 (m, 9H; H^{2,3} of indanyl), 3.57 (q, ^3J(H,H) = 6.9 Hz, 1H; ZrOC(CH_3)(*H*)($C_{10}H_7$)), 4.46 (dd, ^3J(H^1,H^2) = 10.3, 6.4 Hz, 3H; H^1 of indanyl), 6.38 (d, ^3J(H,H) = 9.9 Hz, 1H; naphthyl), 6.71 (d, ^3J(H,H) = 7.8 Hz, 3H; H^{arom} of indanyl), 6.79 – 7.33 (m, 11H; H^{arom} of indanyl and naphthyl), 7.49 (d, ^3J(H,H) = 7.9 Hz, 3H; H^{arom} of indanyl), 7.49 – 7.63 (m, 1H; naphthyl); {^{1}H}^{13}C NMR (50.32 MHz, [D_8]toluene, 295 K): $\delta = 0.7$ (*H*C(Si…)$_3$), 4.1, 6.0 (Si(*C*H$_3$)$_2$), 26.0 (ZrOC(*C*H$_3$)(H)($C_{10}H_7$)), 30.4, 43.0 ($C^{2,3}$ of indanyl), 64.0 (C^1 of indanyl), 79.3 (ZrO*C*(CH_3)(H)($C_{10}H_7$)), 123.5, 123.6, 125.4, 125.6, 127.8, 128.3, 129.1 ($C^{1,3-8}$ of naphthyl), 123.7, 124.7, 126.5, 126.9 (C^{4-7} of indanyl), 133.3, 133.8 ($C^{4a,8a}$ of naphthyl), 143.4 (C^2 of naphthyl), 142.5, 150.6 ($C^{3a,7a}$ of indanyl); {^{1}H}^{29}Si NMR (39.76 MHz, [D_8]toluene, 295 K): $\delta = -0.3$; IR (toluene): $\tilde{\nu} = 3040$ (m), 3021 (m), 2975 (s), 2947 (vs), 2853 (m), 1458 (w), 1417 (m), 1351 (m), 1251 (s), 1116 (vs), 1077 (s), 956 (m), 894 (vs), 834 (vs), 809 (vs), 746 (s), 631 cm^{-1} (w); $C_{46}H_{57}N_3OSi_3Zr$ (843.46): C 65.50, H 6.81, N 4.98; found C 65.46, H 6.93, N 5.16.

Preparation of [ZrCl{HC{$SiMe_2$N(4-$CH_3C_6H_4$)}$_3$}] (29): To a stirred solution of HC{$SiMe_2$NH(4-$CH_3C_6H_4$)}$_3$ (5.63 g, 11.13 mmol) in diethyl ether (40 mL) a 2.5 M solution of *n*BuLi in *n*-hexane (14.69 mL, 36.73 mmol) was added at −78 °C. The solution was slowly warmed up to room temperature and stirred for 24 h. The solid lithium amide was separated by centrifugation and redissolved in diethyl ether (40 mL). Solid $ZrCl_4$ (2.59 g, 11.13 mmol) was added at −78 °C to the stirred solution. The solution was again slowly warmed up to room temperature and stirred for 2 weeks. After concentrating to 15 mL, the precipitated salts were separated by centrifugation. Storage of the solution at −25 °C yielded colourless crystals. The crude product was recrystallised from *n*-pentane to obtain the product as a white powder. Yield: 5.72 g, 9.09 mmol (82%); m.p. 28 °C; ^{1}H NMR (200.13 MHz, C_6D_6, 295 K): $\delta = -0.26$ (s, 1H; *H*C(Si…)$_3$), 0.45 (s, 18H; Si(C*H*$_3$)$_2$), 0.80 (t; (C*H*$_3$CH$_2$)$_2$O), 2.15 (s, 9H; $C_6H_4CH_3$), 3.21 (q; (CH$_3$C*H*$_2$)$_2$O), 6.95 – 7.13 (m, 12H; $C_6H_4CH_3$); {^{1}H}^{13}C NMR (50.32 MHz, C_6D_6, 295 K): $\delta = 4.5$ (Si(*C*H$_3$)$_2$), 5.3 (H*C*(Si…)$_3$), 14.6 ((*C*H$_3$CH$_2$)$_2$O), 20.9 ($C_6H_4CH_3$), 66.2 ((CH$_3$*C*H$_2$)$_2$O), 124.8 ($C^{2,6}$ of $C_6H_4CH_3$), 130.3 ($C^{3,5}$ of $C_6H_4CH_3$), 130.9 (C^4 of $C_6H_4CH_3$), 149.3 (C^1 of $C_6H_4CH_3$); {^{1}H}^{29}Si NMR (39.76 MHz, C_6D_6, 295 K): $\delta = 1.1$; IR (benzene): $\tilde{\nu} = 3016$ (w), 2975 (vs), 2922 (s), 2866 (s), 1606 (m), 1512 (vs), 1499 (vs), 1444 (w), 1381 (w), 1368 (w), 1288 (m), 1252 (vs), 1222 (vs), 1118 (s), 1016 (s), 970 (s), 848 (br vs), 808 (vs), 704 (m), 521 cm^{-1} (m).

Preparation of [Zr(CH_3){HC{$SiMe_2$N(4-$CH_3C_6H_4$)}$_3$}] (30): A 1.6 M solution of MeLi in diethyl ether (0.49 mL, 0.78 mmol) was added to a stirred solution of **29** (0.49 mg, 0.78 mmol) in diethyl ether (30 mL) at −78 °C. The solution was warmed up to room temperature over a period of 1 h and stirred for a further 15 h. After removal of the solvent in vacuo and redissolving the residue in *n*-pentane, the LiCl was separated by centrifugation. Removal of the solvent in vacuo yielded a grey powder. Yield: 0.39 mg, 0.63 mmol (81%); m.p. 39 °C; ^{1}H NMR (200.13 MHz, C_6D_6, 295 K): $\delta = -0.54$ (s, 1H; *H*C(Si…)$_3$), 0.38 (s, 3H; ZrC*H*$_3$), 0.43 (s, 18H; Si(C*H*$_3$)$_2$), 2.12 (s, 9H; $C_6H_4CH_3$), 6.96 – 7.09 (m, 12H; $C_6H_4CH_3$); {^{1}H}^{13}C NMR (50.32 MHz, C_6D_6, 295 K): $\delta = 3.9$ (H*C*(Si…)$_3$), 4.5 (Si(*C*H$_3$)$_2$), 20.9 ($C_6H_4CH_3$), 48.7 (Zr*C*H$_3$), 124.7 ($C^{2,6}$ of $C_6H_4CH_3$), 130.8 ($C^{3,5}$ of $C_6H_4CH_3$), 131.5 (C^4 of $C_6H_4CH_3$), 145.6 (C^1 of $C_6H_4CH_3$); {^{1}H}^{29}Si NMR (39.76 MHz, C_6D_6, 295 K): $\delta = -0.3$; IR (benzene): $\tilde{\nu} = 3071$ (w), 3014 (m), 2972 (s), 2948 (s), 2921 (s), 1606 (m), 1501 (vs), 1252 (br vs), 1105 (m), 969 (s), 937 (m), 917 (s), 856 (br vs), 804 (m), 741 (s), 706 (s), 679 cm^{-1} (m); elemental analysis calcd (%) for $C_{29}H_{43}N_3Si_3Zr$ (609.16): C 57.18, H 7.12, N 6.90; found C 56.81, H 6.79, N 6.82.

General procedure for the insertion of the chiral ketones/aldehydes into the Zr–C bond of 30: One equivalent of the chiral ketone/aldehyde was added to a stirred solution of compound **30** (400 mg, 0.7 mmol) in toluene (5 mL), at −70 °C. After 30 min the solution was slowly warmed up to room temperature, and the product was obtained as a yellow powder after removal of the solvent in vacuo.

[Zr{(5*R*)-1-methylcarveolate}{HC{$SiMe_2$N(4-$CH_3C_6H_4$)}$_3$}] (31): ^{1}H NMR (400.14 MHz, [D_8]toluene, 295 K): $\delta = -0.29$ (s, 1H; *H*C(Si…)$_3$), 0.44 (s, 18H; Si(C*H*$_3$)$_2$), 0.89 (s, 3H; C*H*$_3$), 1.37 (m, 3H; C*H*$_3$), 1.56 (s, 3H; C*H*$_3$), 1.58 – 1.75 (m, 3H; C*H* and C*H*$_2$), 1.92 – 1.96 (m, 2H; C*H*$_2$), 2.18 (s, 9H; C*H*$_3$C$_6$H$_4$), 4.64 (m, 1H; =C*H*$_2$), 4.73 (m, 1H; =C*H*$_2$), 4.95 (m, 1H; =C*H*), 6.98 (s, 12H; C_6H_4); {^{1}H}^{13}C NMR (100.62 MHz, [D_8]toluene, 295 K): $\delta = 2.9$ (H*C*(Si…)$_3$), 4.6 (Si(*C*H$_3$)$_2$), 17.6 (*C*H$_3$), 20.6 (*C*H$_3$), 20.7 (*C*H$_3$C$_6$H$_4$), 28.4 (*C*H$_3$), 31.4 (*C*H$_2$), 40.8 (*C*H), 45.6 (*C*H$_2$), 84.3 (−*C*(OZr…)(CH$_3$)−),

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108.8 (=CH_2), 117.1 (=*C*H), 124.6 ($C^{2,6}$ of C_6H_4), 129.9 ($C^{3,5}$ of C_6H_4), 130.3, 139.6 (2 × =*C*), 144.4 (C^4 of C_6H_4), 149.1 (C^1 of C_6H_4); $\{^1H\}^{29}Si$ NMR (79.50 MHz, [D$_8$]toluene, 295 K): $\delta = -1.2$; IR (toluene): $\tilde{\nu} = 3072$ (w), 3015 (m), 2972 (vs), 2947 (s), 2920 (vs), 2864 (s), 1607 (m), 1512 (m), 1500 (vs), 1445 (m), 1367 (m), 1260 (s), 1245 (vs), 1122 (w), 1093 (m), 1016 (w), 963 (w), 937 (m), 915 (s), 895 (s), 865 (vs), 840 (br vs), 810 (vs), 776 (w), 710 cm^{-1} (m).

[Zr{(1*R*,5*S*)-1-(6,6-dimethylbicyclo[3.1.1]hept-2-en-2-yl)ethanolate}{HC{SiMe$_2$N(4-CH$_3$C$_6$H$_4$)}$_3$}] (32): ^{1}H NMR (400.14 MHz, [D$_8$]toluene, 295 K), (diastereomer 1): $\delta = -0.29$ (s, 1H; *H*C(Si…)$_3$), 0.48 (s, 18H; Si(C*H*$_3$)$_2$), 0.75 (s, 3H; C*H*$_3$), 1.05 (d, ^3J(H,H) = 6.6 Hz, 3H; ZrOC(H)(…)(C*H*$_3$)), 1.16–1.27 (m, 2H; C*H*$_2$), 1.28 (s, 3H; C*H*$_3$), 1.87–1.95 (m, 2H; C*H*$_2$), 1.99–2.06 (m, 2H; 2 × C*H*), 2.21 (s, 9H; C*H*$_3$C$_6$H$_4$), 4.27 (m, 1H; ZrOC(*H*)(…)(CH$_3$)), 5.23 (s, 1H; =C*H*), 6.92–7.04 (m, 12H; C$_6$*H*$_4$); $\{^1H\}^{13}C$ NMR (100.62 MHz, [D$_8$]toluene, 295 K), (diastereomer 1): $\delta = 2.9$ (H*C*(Si…)$_3$), 4.8 (Si(*C*H$_3$)$_2$), 20.8 (*C*H$_3$C$_6$H$_4$), 21.3 (*C*H$_3$), 23.3 (*C*H$_3$), 26.5 (*C*H$_3$), 31.3 (*C*H$_2$), 32.4 (*C*H$_2$), 38.0 (*C*), 41.4 (*C*H), 44.1 (*C*H), 78.3 (ZrO*C*(H)(…)), 123.8 (=*C*H), 124.2 ($C^{2,6}$ of C_6H_4), 129.7 ($C^{3,5}$ of C_6H_4), 144.4 (C^4 of C_6H_4), 150.0 (C^1 of C_6H_4), 150.2 (=C); $\{^1H\}^{29}Si$ NMR (79.50 MHz, [D$_8$]toluene, 295 K): $\delta = -1.5$, -1.6; IR (toluene): $\tilde{\nu} = 3013$ (m), 2974 (vs), 2949 (vs), 2918 (vs), 2831 (w), 1513 (vs), 1500 (vs), 1365 (s), 1245 (vs), 1103 (m), 967 (m), 917 (s), 897 (s), 864 (s), 840 (vs), 811 (vs), 705 cm^{-1} (m).

[Zr{1-[(4*S*)-4-(prop-1-en-2-yl)cyclohex-1-en-1-yl]ethanolate}{HC{SiMe$_2$N(4-CH$_3$C$_6$H$_4$)}$_3$}] (33): ^{1}H NMR (400.14 MHz, [D$_8$]toluene, 295 K), (diastereomers 1 and 2): $\delta = -0.32$, -0.32 (2 × s, 1H; *H*C(Si…)$_3$), 0.47 (s, 18H; Si(C*H*$_3$)$_2$, 1.08 (t, ^3J(H,H) = 6.8 Hz, 2H; C*H*$_2$), 1.69 (s, 3H; C*H*$_3$), 1.74–2.28 (m; 2 × C*H*$_2$ and C*H*), 2.20 (s, 9H; C*H*$_3$C$_6$H$_4$), 4.07, 4.19 (2 × q, ^3J(H,H) = 6.2 Hz, 1H; ZrOC(*H*)(…)(CH$_3$)), 4.78, 4.80 (2 × s, 2H; =C*H*$_2$), 5.32, 5.36 (2 × m, 1H; =C*H*), 6.93–7.04 (s, 12H, C$_6$*H*$_4$); $\{^1H\}^{13}C$ NMR (100.62 MHz, [D$_8$]toluene, 295 K), (diastereomers 1 and 2): $\delta = 2.9$ (H*C*(Si…)$_3$), 4.8, 4.9 (Si(*C*H$_3$)$_2$), 20.8, 20.8 (*C*H$_3$C$_6$H$_4$), 28.1, 30.8, 30.9 (*C*H$_2$), 20.9, 20.9, 23.3, 23.4 (*C*H$_3$), 41.8, 41.8 (*C*H), 80.4, 81.1 (ZrO*C*H(CH$_3$)(…)), 108.9, 108.9 (=*C*H$_2$), 117.6 (=*C*H), 124.1, 124.2 ($C^{2,6}$ of C_6H_4), 129.8, 129.8 ($C^{3,5}$ of C_6H_4), 141.7, 141.9, 149.9, 149.9 (=*C*), 144.4 (C^4 of C_6H_4), 150.0, 150.1 (C^1 of C_6H_4); $\{^1H\}^{29}Si$ NMR (79.50 MHz, [D$_8$]toluene, 295 K), (two diastereomers): $\delta = -1.6$, -1.6; IR (toluene): $\tilde{\nu} = 3071$ (w), 3013 (m), 2972 (s), 2920 (s), 2863 (m), 1607 (s), 1500 (vs), 1451 (m), 1287 (s), 1245 (vs), 1073 (m), 966 (m), 917 (vs), 895 (s), 840 (vs), 705 cm^{-1} (m).

[Zr{(4*S*)-4,8-dimethylnon-7-en-2-olate}{HC{SiMe$_2$N(4-CH$_3$C$_6$H$_4$)}$_3$}] (34): ^{1}H NMR (200.13 MHz, [D$_8$]toluene, 295 K) (diastereomers 1 and 2): $\delta = -0.33$, -0.32 (2 × s, 1H; *H*C(Si…)$_3$), 0.47 (s, 18H; Si(C*H*$_3$)$_2$), 0.81–0.94, 1.02–1.15, 1.98–2.30 (3 × m; C*H*$_3$, C*H*$_2$ and C*H* of dimethylnonenolate), 1.60, 1.61 (2 × s, 3H; C*H*$_3$), 1.69 (s, 6H; 2 × C*H*$_3$), 2.20, 2.21 (2 × s, 9H; C*H*$_3$C$_6$H$_4$), 3.78 (m, 1H; ZrOC*H*(Me)(…)), 5.18–5.27 (m, 1H; *H*C=CMe$_2$), 6.94–7.05 (m, 12H; C$_6$*H*$_4$); $\{^1H\}^{13}C$ NMR (100.62 MHz, [D$_8$]toluene, 295 K) (diastereomers 1 and 2): $\delta = 2.9$ (H*C*(Si…)$_3$), 4.8, 4.9 (Si(*C*H$_3$)$_2$), 17.7, 19.5, 20.0, 24.4, 25.8, 25.8, 25.9, 30.8 (*C*H$_3$), 20.8 (*C*H$_3$C$_6$H$_4$), 25.5, 38.0, 47.8 (*C*H$_2$), 29.6, 29.8 (CH), 75.3, 75.6 (ZrO*C*H(Me)(…)), 117.1 (HC=*C*Me$_2$), 124.1, 124.2 ($C^{2,6}$ of C_6H_4), 129.8 ($C^{3,5}$ of C_6H_4), 130.3 (HC=*C*Me$_2$), 144.4 (C^4 of C_6H_4), 150.1, 150.2 (C^1 of C_6H_4); $\{^1H\}^{29}Si$ NMR (79.50 MHz, [D$_8$]toluene, 295 K) (diastereomers 1 and 2): $\delta = -1.5$, -1.6.

Preparation of [Zr{(5*R*)-1-methylcarveolate}{HC{SiMe$_2$N[(*S*)-1-phenylethyl]}$_3$}] (35): (*R*)-(−)-Carvone (0.26 mL, 1.69 mmol) was added to a stirred solution of compound **12** (1.10 g, 1.69 mmol) in toluene (15 mL)at −70 °C. After 30 min, the solution was slowly warmed to room temperature, and the product was obtained as a yellow powder after removal of the solvent in vacuo. Yield 1.32 g, 1.64 mmol (97%); *de*: 94%; ^{1}H NMR (200.13 MHz, [D$_8$]toluene, 295 K): $\delta = -0.52$ (s, 1H; *H*C(Si…)$_3$), 0.11, 0.21 (2 × s, 2 × 9H; Si(C*H*$_3$)$_2$), 1.09 (s, 3H; ZrOC(C*H*$_3$)(…)(…)), 1.45 (s, 3H; C*H*$_3$), 1.62 (s, 3H; C*H*$_3$), 1.70–1.85 (m, 5H; C*H* and 2 × C*H*$_2$), 1.80 (d, ^3J(H,H) = 6.8 Hz, 9H; HCC*H*$_3$), 4.44 (s, 1H; =C*H*$_2$), 4.58 (q, 3H; *H*CCH$_3$), 4.60 (s, 1H; =C*H*$_2$), 5.02 (s, 1H; =C*H*), 6.98–7.63 (m, 15H; C$_6$*H*$_5$); $\{^1H\}^{13}C$ NMR (50.32 MHz, [D$_8$]toluene, 295 K): $\delta = 1.8$ (H*C*(Si…)$_3$), 4.6, 4.9 (Si(*C*H$_3$)$_2$), 18.5 (*C*H$_3$), 20.6 (*C*H$_3$), 28.9 (*C*H$_3$), 29.6 (HC*C*H$_3$), 31.5 (*C*H$_2$), 47.3 (*C*H$_2$), 41.1 (*C*H), 58.4 (H*C*CH$_3$), 84.7 (−*C*(OZr…)(CH$_3$)−), 109.3 (=*C*H$_2$), 123.2=*C*H), 126.5 (C^4 of C_6H_5), 126.9 ($C^{2,6}$ of C_6H_5), 128.3 ($C^{3,5}$ of C_6H_5), 138.3 (−*C*(CH$_3$)(=CH$_2$)), 148.4 (−(CH$_3$)*C*=C(H)−), 149.3 (C^1 of C_6H_5); $\{^1H\}^{29}Si$ NMR (39.76 MHz, [D$_8$]toluene, 295 K): $\delta = -0.8$; IR (toluene): $\tilde{\nu} = 3083$ (m), 3061 (m), 3025 (s), 2968 (vs), 2924 (s), 2863 (m), 1644 (s), 1491 (s), 1449 (vs), 1367 (m), 1251 (vs), 1197 (m), 1126 (s), 1102 (br vs), 1069 (s), 1034 (s), 1029 (s), 949 (vs), 866 (br vs), 821 (br vs), 757 (br m), 700 cm^{-1} (s); elemental analysis calcd (%) for $C_{42}H_{63}N_3OSi_3Zr$ (801.46): 62.94, H 7.92, N 5.24; found C 62.60, H 8.18, N 5.01.

Characterisation of [Zr{(5*S*)-1-methylcarveolate}{HC{SiMe$_2$N{(*S*)-1-phenylethyl}}$_3$}] (35a): Preparative procedure analogous to **35**, but with (*S*)-(+)-carvone. ^{1}H NMR (400.14 MHz, [D$_8$]toluene, 295 K): $\delta = -0.50$ (s, 1H; *H*C(Si…)$_3$), 0.15, 0.25 (2 × s, 2 × 9H; Si(C*H*$_3$)$_2$), 0.94 (s, 3H; ZrOC(C*H*$_3$)(…)(…)), 1.44 (t, ^4J(H,H) = 1.4 Hz, 3H; C*H*$_3$), 1.56 (s, 3H; C*H*$_3$), 1.46–1.62 (m, 2H; C*H*$_2$), 1.70 (m, 1H; C*H*), 1.77 (d, ^3J(H,H) = 6.8 Hz, 9H; HCC*H*$_3$), 1.90 (m, 2H; C*H*$_2$), 4.53 (q, 3H; *H*CCH$_3$), 4.66 (s, 1H; =C*H*$_2$), 4.73 (s, 1H; =C*H*$_2$), 5.06 (m, 1H; =C*H*), 6.98–7.31 (m, 9H; C$_6$*H*$_5$), 7.56 (d, 6H; C$_6$*H*$_5$); $\{^1H\}^{13}C$ NMR (100.62 MHz, [D$_8$]toluene, 295 K): $\delta = 1.6$ (H*C*(Si…)$_3$), 4.8, 4.9 (Si(*C*H$_3$)$_2$), 18.0 (*C*H$_3$), 20.9 (*C*H$_3$), 28.5 (*C*H$_3$), 28.8 (HC*C*H$_3$), 31.4 (*C*H$_2$), 47.4 (*C*H$_2$), 41.0 (*C*H), 58.0 (H*C*CH$_3$), 84.7 (−*C*(OZr…)(CH$_3$)−), 109.2 (=CH$_2$), 123.0 (=*C*H), 126.5 (C^4 of C_6H_5), 126.9 ($C^{2,6}$ of C_6H_5), 128.3 ($C^{3,5}$ of C_6H_5), 138.4 (−*C*(CH$_3$)(=CH$_2$)), 148.7 (−(CH$_3$)*C*=C(H)−), 149.3 (C^1 of C_6H_5); $\{^1H\}^{29}Si$ NMR (79.50 MHz, [D$_8$]toluene, 295 K): $\delta = -0.7$; IR (toluene): $\tilde{\nu} = 3083$ (m), 3061 (m), 3025 (s), 2969 (vs), 2924 (s), 2864(m), 1644 (m), 1491 (s), 1450 (vs), 1367 (m), 1251 (vs), 1197 (m), 1126 (s), 1102 (br vs), 1069 (m), 1035 (m), 1021 (s), 950 (vs), 864 (br vs), 831 (vs), 816 (vs), 770 (m), 740 (m), 700 cm^{-1} (vs).

Preparation of [Zr{(1*R*,5*S*)-1-(6,6-dimethylbicyclo[3.1.1]hept-2-en-2-yl)-ethanolate}{HC{SiMe$_2$N[(*S*)-1-phenylethyl]}$_3$}] (36): (*R*)-(−)-Myrtenal (7.0 μL, 0.05 mmol) was added to a stirred solution of compound **12** (30 mg, 0.05 mmol) in toluene (0.5 mL) at −70 °C. After 30 min, the solution was slowly warmed up to room temperature, and the product was obtained as a yellow powder after removal of the solvent in vacuo. ^{1}H NMR (400.14 MHz, [D$_8$]toluene, 295 K): $\delta = -0.46$ (s, 1H; *H*C(Si…)$_3$), 0.13, 0.28 (2 × s, 2 × 9H; Si(C*H*$_3$)$_2$), 0.71 (s, 3H; C*H*$_3$), 0.91 (d, ^3J(H,H) = 6.5 Hz, 3H; ZrOC(H)(…)(C*H*$_3$)), 1.12 (s, 3H; C*H*$_3$), 1.04–1.16 (m, 2H; C*H*$_2$), 1.77 (d, ^3J(H,H) = 6.8 Hz, 9H; HCC*H*$_3$), 1.77–1.89 (m, 2H; C*H*$_2$), 2.09–2.22 (m, 2H; 2 × C*H*), 4.17 (m, 1H; ZrOC(*H*)(…)(CH$_3$)), 4.45 (q, 3H; *H*CCH$_3$), 5.28 (s, 1H; =C*H*), 6.96–7.58 (m, 15H; C$_6$*H*$_5$); $\{^1H\}^{13}C$ NMR (100.62 MHz, [D$_8$]toluene, 295 K): $\delta = 1.5$ (H*C*(Si…)$_3$), 4.4, 4.7 (Si(*C*H$_3$)$_2$), 21.4 (*C*H$_3$), 23.3 (*C*H$_3$), 26.3 (*C*H$_3$), 29.5 (HC*C*H$_3$), 30.7 (*C*H$_2$), 31.8 (*C*H$_2$), 37.9 (*C*), 41.2 (*C*H), 44.1 (*C*H), 58.5 (H*C*CH$_3$), 80.0 (ZrO*C*(H)(…)), 115.3 (*C*H), 126.4 (C^4 of C_6H_5), 126.8 ($C^{2,6}$ of C_6H_5), 128.3 ($C^{3,5}$ of C_6H_5), 149.8 (C^1 of C_6H_5), 150.7 (=C); $\{^1H\}^{29}Si$ NMR (79.50 MHz, [D$_8$]toluene, 295 K): $\delta = -1.1$; IR (toluene): $\tilde{\nu} = 3060$ (w), 3024 (m), 2968 (vs), 2922 (s), 2866 (m), 2833(w), 1491 (s), 1449 (s), 1367 (s), 1251 (vs), 1197 (m), 1171 (m), 1137 (s), 1103 (br vs), 1070 (m), 1032 (m), 1021 (m), 951 (vs), 866 (vs), 832 (vs), 821 (vs), 764 (m), 741 (w), 700 (vs), 673 (w), 625 cm^{-1} (w).

Preparation of [Zr{1-[(4*S*)-4-(prop-1-en-2-yl)cyclohex-1-en-1-yl]ethanolate}{HC{SiMe$_2$N[(*S*)-1-phenylethyl]}$_3$}] (37): (*S*)-(−)-Perillaldehyde (6.9 mg, 7.0 μL, 0.05 mmol) was added to a stirred solution of compound **12** (30 mg, 0.05 mmol) in toluene (0.5 mL), at −70 °C. After 30 min, the solution was slowly warmed to room temperature and the product was obtained as a yellow powder after removal of the solvent in vacuo. ^{1}H NMR (400.14 MHz, [D$_8$]toluene, 295 K), (diastereomer 1): $\delta = -0.46$ (s, 1H; *H*C(Si…)$_3$), 0.13, 0.28 (2 × s, 2 × 9H; Si(C*H*$_3$)$_2$), 0.98 (d, ^3J(H,H) = 6.7 Hz, 3H; ZrOC(H)(…)(C*H*$_3$)), 1.27–1.95 (m; 3 × C*H*$_2$ and C*H*), 1.50 (s, 3H; =CC*H*$_3$), 1.76 (d, ^3J(H,H) = 6.6 Hz, 9H; HCC*H*$_3$), 4.31 (q, ^3J(H,H) = 6.7 Hz, 1H; ZrOC(*H*)(…)(CH$_3$)), 4.42 (q, ^3J(H,H) = 6.6 Hz, 3H; *H*CCH$_3$), 4.71–4.75 (m, 2H; =C*H*$_2$), 5.36 (m, 1H; =C*H*), 7.08–7.13 (m, 3H; C$_6$*H*$_5$), 7.23–7.29 (m, 6H; C$_6$*H*$_5$), 7.50–7.54 (m, 6H; C$_6$*H*$_5$); ^{1}H NMR (400.14 MHz, [D$_8$]toluene, 295 K), (diastereomer 2): $\delta = -0.47$ (s, 1H; *H*C(Si…)$_3$), 0.13, 0.27 (2 × s, 2 × 9H; Si(C*H*$_3$)$_2$), 0.99 (d, ^3J(H,H) = 6.7 Hz, 3H; ZrOC(H)(…)(C*H*$_3$)), 1.27–1.95 (m; 3 × C*H*$_2$ and C*H*), 1.58 (s, 3H; =CC*H*$_3$), 1.73 (d, ^3J(H,H) = 6.6 Hz, 9H; HCC*H*$_3$), 4.22 (q, ^3J(H,H) = 6.7 Hz, 1H; ZrOC(*H*)(…)(CH$_3$)), 4.38 (q, ^3J(H,H) = 6.6 Hz, 3H; *H*CCH$_3$), 4.71–4.75 (m, 2H; =C*H*$_2$), 5.30 (m, 1H; =C*H*), 7.08–7.13 (m, 3H; C$_6$*H*$_5$), 7.23–7.29 (m, 6H; C$_6$*H*$_5$), 7.50–7.54 (m, 6H; C$_6$*H*$_5$); $\{^1H\}^{13}C$ NMR (100.62 MHz, [D$_8$]toluene, 295 K), (diastereomer 1): $\delta = 1.5$ (H*C*(Si…)$_3$), 4.2, 4.5 (Si(*C*H$_3$)$_2$), 20.9 (*C*H$_3$), 23.6 (*C*H$_3$), 23.4 (*C*H$_2$), 27.6 (*C*H$_2$), 30.3 (*C*H$_2$), 29.9 (HC*C*H$_3$), 40.8 (*C*H), 58.5 (H*C*CH$_3$), 83.1 (ZrO*C*(H)(…)), 108.8 (=CH$_2$), 122.3 (=*C*H), 126.4 (C^4 of C_6H_5), 126.7 ($C^{2,6}$ of C_6H_5), 128.3 ($C^{3,5}$ of C_6H_5), 140.3 (=C), 149.6 (=C), 149.8 (C^1 of C_6H_5); $\{^1H\}^{13}C$ NMR (100.62 MHz, [D$_8$]toluene, 295 K), (diastereomer 2): $\delta = 1.4$ (H*C*(Si…)$_3$), 4.2, 4.5 (Si(*C*H$_3$)$_2$), 20.7 (*C*H$_3$), 23.4 (*C*H$_3$), 23.5 (*C*H$_2$), 27.8 (*C*H$_2$), 30.7 (*C*H$_2$), 29.5 (HC*C*H$_3$), 41.7 (*C*H), 58.5 (H*C*CH$_3$), 83.2 (ZrO*C*(H)(…)), 108.9 (=CH$_2$), 122.8 (=*C*H), 126.4 (C^4 of C_6H_5), 126.7 ($C^{2,6}$ of C_6H_5), 128.3

($C^{3,5}$ of C_6H_5), 140.4 (=C), 149.6 (=C), 149.8 (C^1 of C_6H_5); $\{^1H\}^{29}Si$ NMR (79.50 MHz, [D$_8$]toluene, 295 K), (diastereomer 1): $\delta = -1.1$; $\{^1H\}^{29}Si$ NMR (79.50 MHz, [D$_8$]toluene, 295 K), (diastereomer 2): $\delta = -1.2$; IR (toluene): $\tilde{\nu} = 3061$ (w), 3024 (m), 2967 (vs), 2922 (s), 2864 (m), 1645 (m), 1491 (s), 1450 (s), 1368 (m), 1251 (vs), 1103 (vs), 1075 (s), 951 (vs), 866 (vs), 821 (vs), 700 cm^{-1} (vs).

[Zr{(*4S*)-4,8-Dimethylnon-7-en-2-olate}{HC{SiMe$_2$N[(*S*)-1-phenylethyl]}$_3$}] (38): Compound **38** was prepared by the method described for compound **37**, but with (*S*)-citronellal. ^1H NMR (400.14 MHz, [D$_8$]toluene, 295 K), (diastereomer 1): $\delta = -0.46$ (s, 1H; *H*C(Si…)$_3$), 0.14, 0.27 (2 × s, 2 × 9H; Si(C*H*$_3$)$_2$), 0.66, 0.83 (2 × d, ^3J(H,H) = 6.4 Hz, 2 × 3H; 2 × C*H*$_3$), 0.85 – 0.94, 1.01 – 1.35, 1.57 – 1.92 (3 × m; C*H*$_2$ and C*H* of dimethylnonenolate), 1.55, 1.67 (2 × s, 2 × 3H; HC=(C*H*$_3$)$_2$), 1.73 (d, ^3J(H,H) = 6.9 Hz, 9H; HCC*H*$_3$), 4.01 (m, 1H; ZrOC*H*(CH$_3$)(…)), 4.39 (q, ^3J(H,H) = 6.9 Hz, 3H; *H*CCH$_3$), 5.10 (q, ^3J(H,H) = 8.2 Hz, 1H; *H*C=CMe$_2$), 7.09 (tt, ^3J(H,H) = 7.2 Hz, ^4J(H,H) = 1.4 Hz, 3H; H^4 of C$_6$*H*$_5$), 7.26 (t, ^3J(H,H) = 7.5 Hz, 6H; H^{3,5} of C$_6$*H*$_5$), 7.51 (d, ^3J(H,H) = 7.2 Hz, 6H; H^{2,6} of C$_6$*H*$_5$); ^1H NMR (400.14 MHz, [D$_8$]toluene, 295 K), (diastereomer 2): $\delta = -0.45$ (s, 1H; *H*C(Si…)$_3$), 0.14, 0.28 (2 × s, 2 × 9H; Si(C*H*$_3$)$_2$), 0.64, 0.82 (2 × d, ^3J(H,H) = 6.4 Hz, 2 × 3H; 2 × C*H*$_3$), 0.85 – 0.94, 1.01 – 1.35, 1.57 – 1.92 (3 × m; C*H*$_2$ and C*H* of dimethylnonenolate), 1.55, 1.67 (2 × s, 2 × 3H; HC=(C*H*$_3$)$_2$), 1.73 (d, ^3J(H,H) = 6.9 Hz, 9H; HCC*H*$_3$), 4.01 (m, 1H; ZrOC*H*(CH$_3$)(…)), 4.33 (q, ^3J(H,H) = 6.9 Hz, 3H; *H*CCH$_3$), 5.10 (q, ^3J(H,H) = 8.2 Hz, 1H; *H*C=CMe$_2$), 7.09 (tt, ^3J(H,H) = 7.2 Hz, ^4J(H,H) = 1.4 Hz, 3H; H^4 of C$_6$*H*$_5$), 7.26 (t, ^3J(H,H) = 7.5 Hz, 6H; H^{3,5} of C$_6$*H*$_5$), 7.51 (d, ^3J(H,H) = 7.2 Hz, 6H; H^{2,6} of C$_6$*H*$_5$); $\{^1H\}^{13}C$ NMR (100.62 MHz, [D$_8$]toluene, 295 K), (diastereomers 1 and 2): $\delta = 1.3$, 1.4 (*H*C(Si…)$_3$), 4.3, 4.3, 4.4, 4.5 (Si(*C*H$_3$)$_2$), 17.7, 19.3, 20.1, 23.8, 25.0, 25.8, 29.6, 29.8 (*C*H$_3$), 29.5 (*C*H), 29.6 (HC*C*H$_3$), 25.7, 25.8, 36.8, 38.4, 48.1, 48.4 (*C*H$_2$), 58.2 (H*C*CH$_3$), 76.9, 77.0 (ZrO*C*H(CH$_3$)(…)), 125.1, 125.2 (H*C*=CMe$_2$), 126.1, 126.4, 126.4 ($C^{4,2,6}$ of C$_6$H$_5$), 128.0 ($C^{3,5}$ of C$_6$H$_5$), 130.7 (HC=*C*Me$_2$), 149.8, 149.9 (C^1 of C$_6$H$_5$); $\{^1H\}^{29}Si$ NMR (79.50 MHz, [D$_8$]toluene, 295 K), (diastereomers 1 and 2): $\delta = -0.8$, -0.7; IR (toluene): $\tilde{\nu} = 3060$ (w), 3025 (m), 2964 (vs), 2925 (vs), 2865 (s), 1491 (m), 1450 (s), 1251 (vs), 1134 (s), 1103 (vs), 1070 (s), 952 (vs), 867 (vs), 821 (vs), 700 cm^{-1} (s).

Reaction of [Zr(CH$_2$CH$_3$){HC{SiMe$_2$N[(*S*)-1-phenylethyl]}$_3$}] (13) with benzaldehyde and 4-fluorobenzaldehyde: One equivalent of benzaldehyde or 4-fluorobenzaldehyde (46 μL, 0.5 mmol) was added to a stirred solution of compound **13** (300 mg, 0.5 mmol) in benzene (5 mL), at room temperature. ^1H NMR spectra of samples taken from the reaction mixture indicated rapid generation of ethene. After 30 min stirring at this temperature, and subsequent removal of the solvent in vacuo, the products **39** and **40** were obtained, respectively, as yellow powders.

[Zr{OCH$_2$(C$_6$H$_5$)}{HC{SiMe$_2$N[(*S*)-1-phenylethyl]}$_3$}] (39): ^1H NMR (400.14 MHz, C$_6$D$_6$, 295 K): $\delta = -0.51$ (s, 1H; *H*C(Si…)$_3$), 0.13, 0.26 (s, 9H; Si(C*H*$_3$)$_2$), 1.56 (d, ^3J(H,H) = 6.5 Hz, 9H; HCC*H*$_3$), 4.30 (q, ^3J(H,H) = 6.5 Hz, 3H; *H*CCH$_3$), 4.70 (AB-spin system, $J_{AB} = 12.4$ Hz, 2H; ZrOC(*H*)$_2$(C$_6$H$_5$)), 5.25 (s, ethene), 6.92 – 7.27 (m, 14H; C$_6$*H*$_5$ and ZrOC(H)$_2$(C$_6$*H*$_5$)), 7.44 (d, ^3J(H,H) = 7.9 Hz, 6H; C$_6$*H*$_5$); $\{^1H\}^{13}C$ NMR (100.62 MHz, C$_6$D$_6$, 295 K): $\delta = 1.0$ (*H*C(Si…)$_3$), 4.2, 4.4 (Si(*C*H$_3$)$_2$), 29.2 (HC*C*H$_3$), 58.5 (H*C*CH$_3$), 75.1 (ZrO*C*(H)$_2$(C$_6$H$_5$)), 126.4 (C^4 of C_6H_5), 126.7 ($C^{2,6}$ of C_6H_5), 126.2, 128.1, 128.4 (*o*, *m*, *p*-C of ZrOC(H)$_2$(C$_6$H$_5$)), 128.4 ($C^{3,5}$ of C_6H_5), 140.8 (*i*-C of ZrOC(H)$_2$(C$_6$H$_5$)),150.0 (C^1 of C_6H_5); $\{^1H\}^{29}Si$ NMR (79.50 MHz, C$_6$D$_6$, 295 K): $\delta = -1.2$; IR (benzene): $\tilde{\nu} = 3062$ (m), 3027 (s), 2963 (vs), 2824 (s), 2898 (m), 2864 (m), 1493 (m), 1451 (m), 1369 (m), 1252 (vs), 1201 (m), 1128 (s), 1106 (vs), 1021 (m), 952 (vs), 867 (vs), 821 (vs), 757 (m), 700 cm^{-1} (vs).

[Zr{OCH$_2$(4-FC$_6$H$_4$)}{HC{SiMe$_2$N[(*S*)-1-phenylethyl]}$_3$}] (40): ^1H-NMR (200.13 MHz, [D$_8$]toluene, 295 K): $\delta = -0.50$ (s, 1H; *H*C(Si…)$_3$), 0.12, 0.26 (2 × s, 2 × 9H; Si(C*H*$_3$)$_2$), 1.51 (d, ^3J(H,H) = 6.7 Hz, 9H; HCC*H*$_3$), 4.27 (q, ^3J(H,H) = 6.7 Hz, 3H; *H*CCH$_3$), 4.52 (AB-spin system, $J_{AB} = 12.8$ Hz, 2H; ZrOC(*H*)$_2$(*p*-FC$_6$H$_4$)), 6.89 – 7.27 (m, 13H; C$_6$*H*$_5$ and *p*-FC$_6$*H*$_4$), 7.40 (d, ^3J(H,H) = 7.5 Hz, 6H; C$_6$*H*$_5$); $\{^1H\}^{13}C$ NMR (50.32 MHz, [D$_8$]toluene, 295 K): $\delta = 0.9$ (*H*C(Si…)$_3$), 4.2, 4.3 (Si(*C*H$_3$)$_2$), 29.1 (HC*C*H$_3$), 58.3 (H*C*CH$_3$), 74.1 (ZrO*C*(H)$_2$(*p*-FC$_6$H$_4$)), 114.8 (d, ^2J(C,F) = 21.3 Hz, *m*-C of *p*-FC$_6$H$_4$), 126.2 (C^4 of C_6H_5), 126.3 ($C^{2,6}$ of C_6H_5), 128.1 ($C^{3,5}$ of C_6H_5), 129.5 (d, ^3J(C,F) = 8.3 Hz; *o*-C of *p*-F*C*$_6$H$_4$), 147.7 (*i*-C of *p*-FC$_6$H$_4$), 149.9 (C^1 of C_6H_5), 162.7 (d, ^1J(C,F) = 251.6 Hz; *p*-C of *p*-F*C*$_6$H$_4$); $\{^1H\}^{29}Si$ NMR (39.76 MHz, [D$_8$]toluene, 295 K): $\delta = -1.0$; $\{^1H\}^{19}F$ NMR (77.77 MHz, [D$_8$]toluene, 295 K): $\delta = -115.0$; IR (toluene): $\tilde{\nu} = 3061$ (m), 3025 (s), 2962 (vs), 2925 (s), 2898 (m), 2862 (s), 1602 (m), 1509 (s), 1449 (s), 1251 (vs), 1222 (s), 1128 (vs), 1103 (br vs), 1092 (br vs), 1033 (br s), 952 (vs), 868 (vs), 834 (vs), 821 (vs), 700 (s), 603 cm^{-1} (m).

Reaction of [Zr(*n*-C$_4$H$_9$){HC{SiMe$_2$N[(*S*)-1-phenylethyl]}$_3$}] (14) with benzaldehyde and with 4-fluorobenzaldehyde: One equivalent of benzaldehyde or 4-fluorobenzaldehyde was added to a stirred solution of

Table 3. Crystal data and structure refinement for compounds **2**, **5**, **6**, **7**, **11**, **12** and **20**.

	2	**5**	**6**	**7**	**11**	**12**	**20**
formula	$C_{34}H_{49}N_3Si_3 \cdot 0.5(Et_2O)$	$C_{31}H_{46}Li_3N_3Si_3$	$C_{34}H_{46}Li_3N_3Si_3$	$C_{31}H_{46}ClN_3Si_3Ti$	$\{[C_{31}H_{46}Cl_{1.5}N_3Si_3Zr][Li(OEt_2)_4]\} \cdot 0.25\{[ZrCl_5(OEt_2)][Li(OEt_2)_4]\} \cdot 1.5(Et_2O)$	$C_{32}H_{49}N_3Si_3Zr$	$C_{35}H_{49}N_3Si_3Zr$
M_r	621.09	565.8	601.83	628.33	1954.85	651.23	687.26
crystal system	monoclinic	trigonal	orthorhombic	monoclinic	monoclinic	monoclinic	monoclinic
space group	$P2_1$	$R\bar{3}$	$P2_12_12_1$	$P2_1$	$P2_1$	$C2$	$P2_1$
a [Å]	9.5750(10)	17.004(3)	13.349(2)	11.011(3)	20.715(4)	17.121(5)	12.681(2)
b [Å]	17.4014(10)	–	20.625(3)	8.791(3)	19.423(4)	11.6921(18)	10.4993(11)
c [Å]	22.1276(10)	10.108(3)	25.736(5)	18.253(4)	28.535(6)	17.981(5)	13.416(2)
β [°]	92.497(10)	–	–	90.621(5)	110.91(3)	107.313(12)	92.532(7)
V [Å^3]	3683.4(5)	2528.3(1)	7085.9(19)	1762.2(5)	10725(4)	3436.3(14)	1784.5(4)
Z	4	3	8	2	4	4	2
ρ_{calcd} [g cm^{-3}]	1.120	1.11	1.128	1.18	1.211	1.259	1.279
μ [mm^{-1}]	0.158	0.159	0.160	0.439	0.439	0.445	0.436
$F(000)$	1348	912	2576	668	4158	1376	724
crystal size [mm]	0.60 × 0.50 × 0.40	0.40 × 0.20 × 0.15	0.48 × 0.48 × 0.46	0.70 × 0.40 × 0.20	0.75 × 0.40 × 0.30	0.60 × 0.50 × 0.50	0.60 × 0.40 × 0.40
θ range [°]	2.13 – 21.00	2 – 25.00	1.82 – 21.00	2 – 25	1.83 – 19.00	2.14 – 29.00	2.16 – 25.00
reflections collected	4488	1649	8480	3428	53084	5816	7753
independent reflections (R_{int})	4104 (0.1350)	603(0.053)	7598 (0.0599)	3320(0.028)	17250 (0.0769)	5641 (0.0122)	6294 (0.0345)
data/restraints/parameters	4104/259/415	603/0/65	7598/0/775	2256/0/351	17250/1019/1040	5641/1/362	6294/1/386
S on F^2[a]	1.348	1.67	0.910	1.93	1.025	1.043	1.024
R_1[b] [$I > 2\sigma(I)$]	0.0969	0.0578	0.0748	0.044	0.0623	0.0280	0.0308
wR_2[b] [$I > 2\sigma(I)$]	0.2667	0.1277	0.1001	0.0820	0.1652	0.0723	0.0751
max/min $\Delta\rho$ [e Å^{-3}]	0.544/ – 0.712	0.660/ – 0.592	0.175/ – 0.180	0.520/ – 0.350	0.727/ – 0.807	0.709/ – 0.360	0.480/ – 0.399

[a] $S = [\Sigma w(F_o^2 - F_c^2)^2/(n-p)]^2$, where n = number of reflections and p = total number of parameters. [b] $R_1 = \Sigma \| F_o \| - | F_c \| / \Sigma | F_o |$, $wR_2 = \Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]^2$, $w^{-1} = [R^2(F_o)^2 + (aP)^2 + bP]$, $P = [\max(F_o^2, 0) + 2(F_c^2)]/3$.

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compound **14** (500 mg, 0.7 mmol) in toluene (5 mL)at room temperature. Monitoring of the reaction by ^{1}H NMR spectroscopy revealed the rapid formation of 1-butene. After 30 min at this temperature, the product was obtained as a yellow powder after removal of the solvent in vacuo. The ^{1}H, ^{13}C and ^{29}Si NMR spectra established the identity of the reaction products as **39** and **40**, respectively.

X-ray crystallographic studies of 2, 5, 6, 7, 11, 12 and 20: Data was collected by using an Enraf-Nonius CAD4 diffractometer at a temperature of 173(2) K (**2**, **12**), 296(2) K (**5**, **7**) and 193(2) K (**20**), or a Stoe IPDS at a temperature of 173(2) K (**11**) with oil-coated shock-cooled crystals[33–35] mounted under nitrogen. Data of **6** was collected by using a Siemens *P*4 diffractometer at a temperature of 301(2) K with an oil-coated crystal mounted in a Lindemann capillary under argon.

Crystal data and experimental details for the crystals of **2**, **5**, **6**, **7**, **11**, **12** and **20** are given in Table 3. The data for the structures **12** and **20** were corrected for absorption using ψ-scans. The structures of **2**, **6**, **11**, **12** and **20** were solved by direct methods (**2**, **6**, **11**, **20**: SHELXS-97; **12**: SHELXS-86) and refined on F^2 (**2**, **6**, **11**, **20**: SHELXL-97; **12**: SHELXL-93).[36–39] Both structures **5** and **7** were solved and refined on F^2 using the Texsan software package.[40]

In the case of **2**, one solvent molecule (diethyl ether) was found in the asymmetric unit and due to a shortage of data, caused mainly by poor diffraction, only the silicon and nitrogen atoms were refined with anisotropic displacement parameters. In the asymmetric unit of **11**, two independent monoanionic Zr dimers with $[Li(Et_2O)_4]^+$ counterions were initially located (some disorder of the ethyl carbon atoms of counterions was observed and some being resolved into two components of 50:50% occupancy). A large volume of residual electron density was, with difficulty, identified as due to a half occupancy $[ZrCl_5(Et_2O)]^-$ anionic complex, apparently disordered with its counterion, a half occupancy $[Li(Et_2O)_4]^+$ cation (not all atoms of the counterion could be located). In addition, two full occupancy and two half occupancy diethyl ether solvate molecules were located. For **11**, the zirconium, chlorine, silicon, nitrogen and full occupancy oxygen atoms were refined with anisotropic displacement parameters. In the final cycles of refinement, all non-hydrogen atoms of **5**, **6**, **7**, **12** and **20** were assigned anisotropic displacement parameters. Hydrogen atoms were included in idealised positions riding on the parent atoms and were assigned isotropic displacement parameters of 1.2 U_{eq} (=CH, CH, CH_2) and 1.5 U_{eq} (CH_3) of the parent atom; for **11** only the hydrogen atoms of the anionic Zr dimers were included.

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 151773–151779. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223–336–033; e-mail: deposit@ccdc.cam.ac.uk).

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