Construction of C_1-symmetric zirconium complexes by the design of new Salan ligands. Coordination chemistry and preliminary polymerisation catalysis studies†

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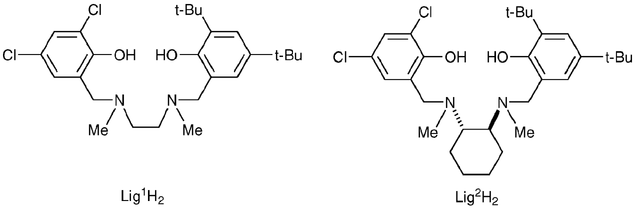
The first synthesis of achiral and chiral [ONNO′]-type Salan ligands featuring two different phenol arms, and the diastereoselective formation of the corresponding octahedral C_1-symmetric zirconium complexes is described; the activity and isospecificity induction of the [ONNO′]Zr(bn)$_2$ complexes in 1-hexene polymerisation reflected those of the parent symmetric compounds.

The Salans, sequential tetradentate dianionic diamine bis(phenolate) ligands, have drawn considerable attention since their introduction to the group 4 metal realm in the year 2000.[1–4] Their tendency to wrap in a *fac–fac* manner around octahedral metal centres resulted in C_2-chiral (racemic) complexes in which the two labile groups are in *cis*-geometry, rendering them able to serve as isospecific polymerisation catalysts. Their coordination to other metals and their applications are constantly expanding.[5] Chiral Salan ligands constructed around the *trans*-1,2-diaminocyclohexane skeleton may wrap in two *fac–fac* modes (Δ and Λ) and lead to two C_2-symmetric diastereomers. The deciphering of factors that control the diastereoselectivity in chiral Salan wrapping has allowed the introduction of enantiomerically-pure catalysts of predetermined chirality-at-the metal, that afforded asymmetric catalysis (Ti)[6] and chiral cyclopolymerisation (Zr).[7] All Salan ligands reported to date have featured identical phenolate rings. Herein we report, for the first time, the synthesis of achiral and chiral [ONNO′]-type Salan ligands featuring two different phenolate rings, their C_1-symmetric zirconium complexes, and the preliminary application of these complexes in olefin polymerisation catalysis.[8]



The character of the phenolate substituents of the symmetric Salan ligands (both achiral and chiral) was found to influence dramatically the performance of the resulting zirconium catalysts in α-olefin polymerisation. Thus, electron-withdrawing substituents (*e.g.*, chloro) led to highly active aspecific catalysts, whereas bulky substituents (*e.g.*, *tert*-butyl) led to mildly active highly isospecific catalysts.[1,2,7] In designing the non-symmetric hybrid-Salan ligands, we aimed at ligands whose two arms are markedly different. The two ligands studied in this work each feature a 2,4-dichlorophenolate arm and a 2,4-di(*tert*-butyl)phenolate arm and are based on either the diaminoethane skeleton, Lig^{1}H$_2$, or the *trans*-1,2-diaminocyclohexane skeleton, Lig^{2}H$_2$.

The most convenient entry to the symmetric Salan ligands relies on the Mannich condensation between the *N*,*N*′-dimethyl-diamines, formaldehyde and the substituted phenols. The attempt to form a 2 : 1 : 1 statistical mixture of the asymmetric ligand and the two symmetric ligands by Mannich condensation of *N*,*N*′-dimethyl-diaminoethane, formaldehyde, and 2,4-di(*tert*-butyl)phenol and 2,4-dichlorophenol gave instead a 1 : 1 mixture of the two known symmetric ligands with no trace of the desired asymmetric ligand. The selective formation of a mono-dichlorophenolate adduct was accomplished by condensation of the diamines with the corresponding salicylaldehyde followed by NaBH$_4$ reduction. However, exposing the monophenolate adduct to Mannich conditions in the presence of the other phenol yielded again only the 1 : 1 mixture of symmetric ligands, apparently because of a retro-Mannich–Mannich reaction sequence. Eventually, reacting the two intermediates with the bromomethyl derivative of 2,4-di(*tert*-butyl)phenol[9] gave the two desired ligands Lig^{1}H$_2$ and Lig^{2}H$_2$ (either enantiomerically pure or racemic) with no traces of the symmetric ligands, as supported by ^{1}H NMR and mass spectra (Scheme 1, see the ESI†).

Lig^{1}H$_2$ and *rac*-Lig^{2}H$_2$ reacted with zirconium(IV) *tert*-butoxide to give the zirconium complexes Lig^{1,2}Zr(O-*tert*-Bu)$_2$ as white solids in practically quantitative yields. ^{1}H NMR characterisation of Lig^{1}Zr(O-*tert*-Bu)$_2$ indicated the formation of a single stereoisomer of C_1-symmetry, as expected for a *fac–fac* wrapping of a non-symmetric [ONNO′]-type ligand.[10] The ^{1}H NMR spectrum of *rac*-Lig^{2}Zr(O-*tert*-Bu)$_2$ indicated the formation of a single stereoisomer of C_1-symmetry as well. Based on the wrapping tendencies of the symmetric C_2-chiral Salan ligands, we presume that a single *fac–fac* diastereomer out of the possible two had formed.

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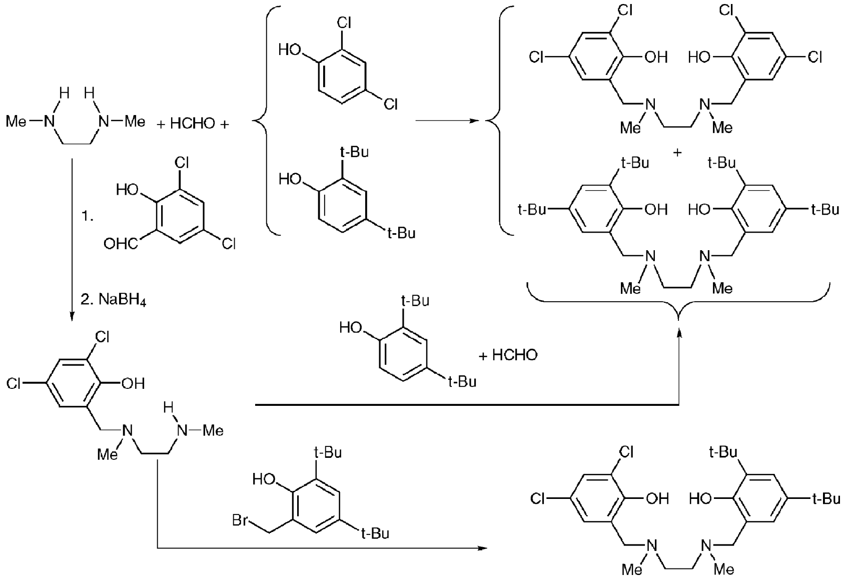

Scheme 1 Synthetic attempts towards the asymmetric ligands.

Crystals of $Lig^1Zr(O\text{-}tert\text{-}Bu)_2$ suitable for X-ray analysis were grown from cold pentane and the structure was solved.[11] Two independent molecules were found in the asymmetric unit, both featuring the predicted wrapping mode of the asymmetric Salan ligand around the zirconium, giving a *cis* relationship between the two monodentate alkoxo groups (O4–Zr1–O5 = 107.8°; O47–Zr44–O48 = 108.0°). A slightly longer O(dichlorophenolate)–Zr relative to O(di(*tert*-butyl)-phenolate)–Zr bond length in the two molecules (2.085 *vs.* 2.044, and 2.055 *vs.* 2.019 Å) is consistent with the electron deficiency of the former. Beyond that, the overall structure is very similar to that found in the C_2-symmetric [ONNO]–$Zr(O\text{-}tert\text{-}Bu)_2$ complex of the parent Salan ligand with *tert*-butyl phenolate substituents.[12]

The X-ray structure of *rac*-$Lig^2Zr(O\text{-}tert\text{-}Bu)_2$ was solved as well, revealing the predicted *fac–fac* wrapping. Most notably, the same diastereoselectivity found for the C_2-chiral ligands was demonstrated here as well, *i.e.*, the (*R*,*R*)-ligand enantiomer twists in a Δ-mode around the zirconium centre.[6a,7] The bond lengths and angles around the metal are similar to those found in $Lig^1Zr(O\text{-}tert\text{-}Bu)_2$ (Fig. 1).

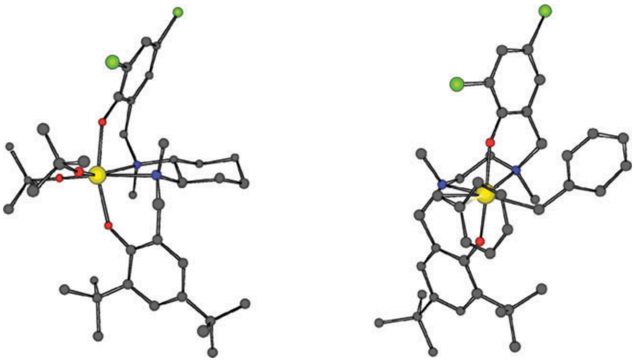

Fig. 1 X-Ray structures of $Lig^2Zr(O\text{-}tert\text{-}Bu)_2$ (left) and Lig^1ZrBn_2 (right).

Dibenzylzirconium complexes of the two ligands, Lig^1ZrBn_2 and *rac*-Lig^2ZrBn_2, were obtained in high yields as yellow solids by direct reactions between the ligands and tetrabenzylzirconium. ^1H NMR characterisation of the two complexes supported the formation of single stereoisomers of C_1-symmetry. Crystals of Lig^1ZrBn_2 were grown from cold ether and its X-ray structure was solved, revealing the expected *fac–fac* ligand wrapping. This is the first structure of a dibenzylzirconium complex featuring a non-bulky electron-poor Salan phenolate arm. Notably, one of the benzyl groups is acutely bent towards the metal (Zr–C–C = 89.2°) signifying a substantial η^2-binding character. We attribute this bending to the combined effects of electron-deficiency and an open site on the metal centre (Fig. 1).

Upon activation with $B(C_6F_5)_3$ at room temperature, the two complexes Lig^1ZrBn_2 and *rac*-Lig^2ZrBn_2 were found to be active for 1-hexene polymerisation catalysis. Lig^1ZrBn_2 led to a high activity of 1300 g $mmol^{-1}$ h^{-1}, and to a relatively high molecular weight of 47 000 g mol^{-1} of poly(1-hexene) (PDI = 1.6). The activity of Lig^2ZrBn_2 was lower (53 g $mmol^{-1}$ h^{-1}) and the molecular weight of the polymer was higher: *ca.* 240 000 g mol^{-1} (PDI = 1.9). These activities are intermediate between the high activities of the electron-deficient C_2-symmetric Salan zirconium complexes and the low activities of the sterically-congested C_2-symmetric Salan complexes. The higher molecular weight obtained for the more rigid Lig^2ZrBn_2 is consistent with the values found for its parent symmetric complexes.[7a]

More intriguing is the stereocontrol aspect of these catalysts. As one of the two parent C_2-symmetric complexes induces highly isospecific polymerisation and the other induces aspecific polymerisation, several directing modes may be envisioned for these hybrid C_1-symmetric complexes.[13,14] If the two sites have independent directing abilities, and if no site-epimerisation takes place, then consecutive insertions will occur in different steric environments, leading to a *hemi*-isotactic polymer. However, if each insertion is affected by both environments, (*e.g.*, by the growing polymer chain from one quadrant *and* the phenolate substituents from another quadrant), or if, alternatively, fast site-epimerisation takes place, then an intermediate tacticity may result. These possibilities may be distinguished by pentad-analysis.[15] The ^{13}C NMR spectra of the poly(1-hexene) samples produced by both catalysts appeared very similar, indicating a similar stereocontrol (see the ESI†). In both spectra, the dominant C3-peak is the mmmm pentad at 34.73 ppm (*ca.* 40%), corresponding to a low-to-medium degree of isotacticity. A perfect *hemi*-isotactic polymer requires a ratio of 1 : 1 between the mmmm pentad and the rrrr pentad.[16] As the rrrr pentad (at 34.00 ppm), is considerably less abundant, we conclude that a *hemi*-isotactic polymer had not formed. It would therefore seem that a combined effect of both sites occurs in every insertion event.

In conclusion, the first Salan ligands featuring different phenolate groups have led to well-defined C_1-symmetric complexes. Preliminary polymerisation studies indicated that the tendencies of the parent catalysts are reflected in the activities of the hybrid catalysts. The expansion of the range of achiral and chiral asymmetric Salans and exploration of their catalytic potential in polymerisation, copolymerisation, and asymmetric transformations is currently under way.

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