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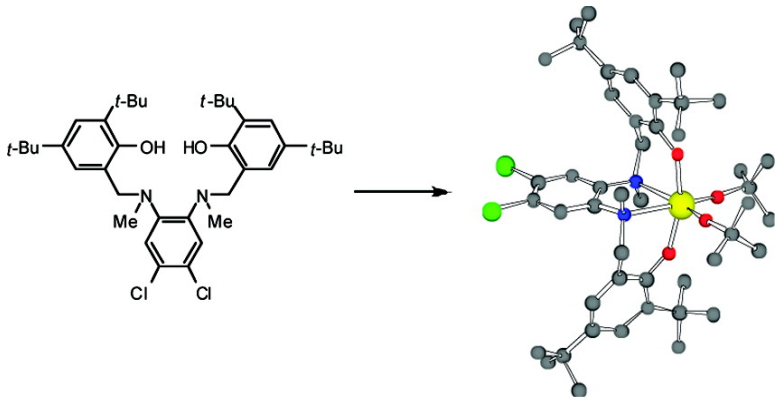

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Titanium and Zirconium Complexes of Robust Salophan Ligands. Coordination Chemistry and Olefin Polymerization Catalysis

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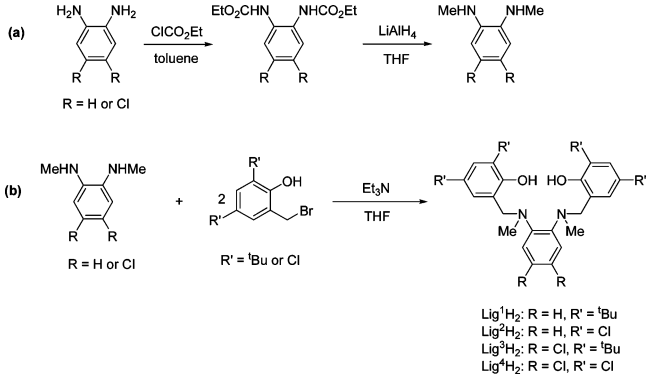
Salans are [ONNO]-type linear tetradentate diamine−diphenolate ligands having an aliphatic bridge between the two amine donors. They tend to wrap around group 4 metals in a *fac*−*fac* mode yielding C_2-symmetric octahedral complexes in which the two labile groups are of *cis* geometry.[1] These features make the Salan complexes suitable for olefin polymerization catalysis and especially for isospecific polymerization (the actual degree of isotacticity is determined by the combined effects of the phenolate ring substituents, the size of the metal, and the bulk of the monomer).[2] Salophan ligands are close analogues of the Salans in which the aliphatic spacer has been replaced by an aromatic one.[3] The aromatic spacer is expected to enhance the rigidity of the ligand backbone and to enable fine-tuning of the electronic character of the *N*-donors by ring substitutions, thus broadening the possible activities. Yet, while complexes of Salan ligands have attracted considerable attention recently in polymerization catalysis and beyond,[4−8] complexes of Salophan ligands remain almost unexplored. The Salophan ligands reported to date featured non-substituted secondary *N*-donors. Therefore, they could act as either tetra-anionic ligands by losing the acidic *N*-protons (forming complexes of aluminum and gallium alkyls of varying nuclearity)[3a,b] or as dianionic ligands featuring neutral *N*-donors (forming mononuclear group 4 alkoxides).[9] The attempted preparation of dialkylzirconium Salophan complexes that may serve in olefin polymerization catalysis, by reacting of the ligand precursors with tetrabenzylzirconium, led to unidentified products. Broadening the scope beyond coordination chemistry requires more robust Salophan ligands, that is, those featuring tertiary *N*-donors. Herein we describe the synthesis of such *N*-Me Salophan ligands, their coordination chemistry around titanium and zirconium, and their preliminary application in olefin polymerization catalysis.

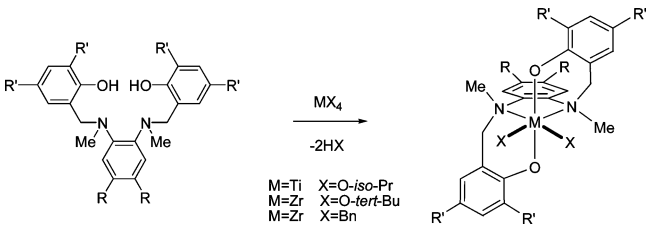
The synthesis of the Salophan ligands featuring secondary *N*-donors relies on condensation between diaminobenzene and salicylaldehyde, followed by reduction with $NaBH_4$. The *N*-Me Salophan ligands proved more elusive. The attempted methylation of the *N*-H Salophan ligands either by methyl iodide or by condensation with formaldehyde followed by reduction[10] was unsuccessful. The attempted Mannich condensation between *N*,*N*′-dimethyl-1,2-diaminobenzene (see below), formaldehyde, and a substituted phenol failed, as well. Finally, nucleophilic substitution of bromomethylated phenols with the *N*,*N*′-methylated diaminobenzenes yielded the desired Salophans. To explore electronic effects on the aromatic bridge, two diamine precursors were used: 1,2-diaminobenzene and its electron-poor analogue—the 4,5-dichloro derivative (no significant steric influence is expected from substituents in the remote 4,5-positions).

The two *N*,*N*′-disubstituted diamines were obtained through condensation of the parent diamines with ethylchloroformate to give the bis(ethylcarbamate) intermediates followed by $LiAlH_4$ reduction (Scheme 1a; see the Supporting Information). Both disubstituted

Scheme 1. Ligand Synthesis



Scheme 2. Complexes Synthesis



diamines were found to be unstable, so they were reacted immediately with the bromomethylated phenols to yield the corresponding *N*-Me Salophan ligands for the first time (Scheme 1b; see the Supporting Information). Altogether, four ligands were prepared featuring either sterically demanding *tert*-butyl or electron-withdrawing chloro substituents on the phenolate rings. Notably, even though the aniline nitrogens are poor nucleophiles (especially those of the 4,5-dichloro-substituted ring), all the synthetic attempts led to the desired Salophans in decent yields.

While the non-substituted Salophans were found to wrap around group 4 metals in the desired *fac*−*fac* mode,[8] the rigid backbone combined with increased crowdedness of substituted Salophans might impede their coordination ability or favor different binding modes. We therefore addressed their coordination chemistry first. Reacting all four Salophan ligands with titanium(IV) isopropoxide at room temperature led cleanly to the complexes $Lig^{1-4}Ti(O\text{-}iso\text{-}Pr)_2$. NMR characterization indicated that single isomers of C_2-symmetry had formed in all cases. The reaction of the ligand precursor Lig^1H_2 with $Zr(O\text{-}tert\text{-}Bu)_4$ yielded the complex $Lig^1Zr(O\text{-}tert\text{-}Bu)_2$ as a mixture of two (kinetic and thermodynamic) isomers in ca. 1:1 ratio that coalesced to a single isomer on heating to 75 °C.[11] The other ligand precursors yielded each a single isomer of $Lig^{2-4}Zr(O\text{-}tert\text{-}Bu)_2$ at room temperature. NMR characterization revealed that all the zirconium complexes were of C_2-symmetry, as well (Scheme 2). Single crystals of $Lig^1Zr(O\text{-}tert\text{-}Bu)_2$ were grown from cold pentane, and its X-ray structure was solved. The

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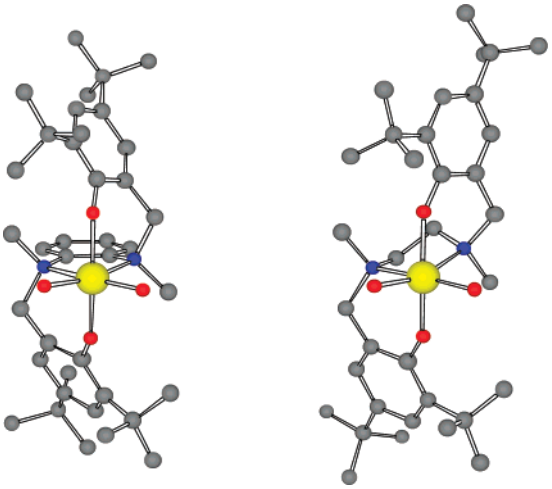

Figure 1. Crystal structure of Lig^{1}Zr(O-*tert*-Bu)$_2$ (left) and its analogous Salan complex (right). For clarity, only the O atoms of the *tert*-Bu−O labile groups are shown.

crystal structure is shown in Figure 1 next to the structure of the analogous Salan complex that was previously published.[12]

The structure reveals an octahedral complex in which the Salophan ligand wraps around the zirconium in the desired *fac*−*fac* mode typical of the Salan ligands. The zirconium atom lies within the N−C−C−N bridge forming a practically planar diazametallacyclopentane (0.034 Å deviation from plane), unlike the puckered Salan complex. The Salophan and Salan complexes share similar N−Zr−N bite angles of 69.2 and 71.4°, respectively, identical O−Zr−O angle between the labile groups (107.7°) and Zr−O bond lengths (1.93 Å), and similar Zr−O−C bond angles (ca. 165°), indicating that the labile groups in the two complexes reside in similar environments. Yet, the Salophan complex appears more compact, with the phenolate groups pulled back from the labile groups and bent toward the aromatic bridge. The diminished protrusion of the *ortho*-*tert*-Bu groups might impair their stereoregulating induction. The crystal structure of the complex Lig^{3}Zr(O-*tert*-Bu)$_2$ was solved, as well (see the Supporting Information), and featured practically identical bond lengths and angles around the zirconium. Namely, the electron deficiency of this ligand is not apparent in its bonding parameters to the metal.

To explore the activity of the new Salophan systems in polymerization, we attempted the synthesis of dibenzylzirconium complexes by reacting the ligand precursors with $ZrBn_4$. All reactions gave undefined products at room temperature that converted to C_2-symmetric dibenzyl complexes upon heating to 75 °C, according to their ^{1}H NMR spectra. These are the first alkyl complexes of dianionic Salophan ligands reported with any metal.

Upon activation with $B(C_6F_5)_3$, all four dibenzylzirconium complexes led to active 1-hexene polymerization catalysts. Lig^{2}ZrBn$_2$ and Lig^{4}ZrBn$_2$, the two complexes that include chloro substituents on the phenolate rings, led to ultrahigh activities of ca. 20 000 g mmol^{-1} h^{-1}, which are considerably higher than those exhibited by the most active Salan complexes (also featuring chloro substituents on the phenolate rings).[2,7] No significant effects of the 4,5-dichlorophenylene bridge substituents on activity or polymer characteristics were observed, and the polymers obtained were atactic. Lig^{1}ZrBn$_2$ and Lig^{3}ZrBn$_2$ that feature *tert*-butyl phenolate groups were less active—1.0 and 5.6 g mmol^{-1} h^{-1}, respectively. Namely, withdrawing electron density from the *N*-donors causes a significant increase in reactivity in this case. The ^{13}C NMR spectra indicated that these two polymers were mildly isotactic (mmmm of ca. 65%) and supported an enantiomorphic-site control mechanism (see the Supporting Information). In comparison, the isotacticity of the poly(1-hexene) derived from the corresponding zirconium Salan complex was much higher.[1] It is not clear, at this stage, whether the lower stereocontrol results from the Salophan backbone rigidity or from the slight geometrical differences between the Salan and Salophan wrapping around the zirconium.

In conclusion, we have introduced the first Salophan ligands that retain their dianionic character in different environments and are amenable to fine-tuning of the electronic character of the *N*-donors. These ligands have led to promising catalysts for polymerization of α-olefins.

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Supporting Information Available: Details of the synthesis and characterization of the ligands and complexes, crystallographic data in text format for Lig^{1}Zr(O-*tert*-Bu)$_2$ and Lig^{3}Zr(O-*tert*-Bu)$_2$, polymerization procedures, and polymer characterization. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) Tshuva, E. Y.; Goldberg, I.; Kol, M. *J. Am. Chem. Soc.* **2000**, *122*, 10706.
(2) Segal, S.; Goldberg, I.; Kol, M. *Organometallics* **2005**, *24*, 200.
(3) (a) Atwood, D. A.; Rutherford, D. *Organometallics* **1995**, *14*, 2880. (b) Atwood, D. A.; Remington, M. P.; Rutherford, D. *Organometallics* **1996**, *15*, 4763. (c) Singer, A. L.; Atwood, D. A. *Inorg. Chim. Acta* **1998**, *227*, 157. (d) Gheller, S. F.; Hambley, T. W.; Snow, M. R.; Murray, K. S.; Wedd, A. G. *Aust. J. Chem.* **1984**, *37*, 911.
(4) (a) For isospecific polymerization of propene and co-polymerization of propene and ethene, see: Busico, V.; Cipullo, R.; Pellecchia, R.; Ronca, S.; Roviello, G.; Talarico, G. *Proc. Natl. Acad. Sci. U.S.A.* **2006**, *103*, 15321. (b) See also: Corradini, P.; Guerra, G.; Cavallo, L. *Accounts Chem. Res.* **2004**, *37*, 231.
(5) For lactide polymerization by aluminum Salan complexes, see: Hormnirum, P.; Marshall, E. D.; Gibson, V. C.; White, A. J. P.; Williams, D. J. *J. Am. Chem. Soc.* **2004**, *126*, 2688.
(6) For titanium complexes of chiral Salan ligands in asymmetric catalysis, see: (a) Yeori, A.; Groysman, S.; Goldberg, I.; Kol, M. *Inorg. Chem.* **2005**, *44*, 4466. (b) Sawada, Y.; Matsumoto, K.; Kondo, S.; Watanabe, H.; Ozawa, T.; Suzuki, K.; Saito, B.; Katsuki, T. *Angew. Chem., Int. Ed.* **2006**, *45*, 3478.
(7) For zirconium complexes of chiral Salan ligands, see: Yeori, A.; Goldberg, I.; Shuster, M.; Kol, M. *J. Am. Chem. Soc.* **2006**, *128*, 13062.
(8) For biological activity of titanium Salan complexes, see: Shavit, M.; Peri, D.; Manna, C. M.; Alexander, J. S.; Tshuva, E. Y. *J. Am. Chem. Soc.* **2007**, *129*, 12098.
(9) Groysman, S.; Sergeeva, E.; Goldberg, I.; Kol, M. *Eur. J. Inorg. Chem.* **2005**, 2480.
(10) Balsells, J.; Carroll, P. J.; Walsh, P. J. *Inorg. Chem.* **2001**, *40*, 5568.
(11) The kinetic isomer appeared as C_2- or C_s-symmetric by ^{1}H NMR.
(12) Gendler, S.; Segal, S.; Goldberg, I.; Goldschmidt, Z.; Kol, M. *Inorg. Chem.* **2006**, *45*, 4783.

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