

# Syntheses of Allyl- and 3-Silylpropyl-substituted Salen-like Tetradentate Ligands *via* Hypercoordinate Silicon Complexes

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The reaction of allylchlorosilanes ( $\text{AllSiCl}_3$ ,  $\text{AllSiPhCl}_2$ ) with the tetradentate salen-like ligand **1**, *o*-HO-*p*-MeO-C<sub>6</sub>H<sub>3</sub>-C(Ph)=N-(CH<sub>2</sub>)<sub>2</sub>-N=C(Ph)-C<sub>6</sub>H<sub>3</sub>-*p*-OMe-*o*-OH, yields pentacoordinate silicon complexes of an allyl-substituted ligand system (*o*-O-*p*-MeO-C<sub>6</sub>H<sub>3</sub>-C(Ph)=N-(CH<sub>2</sub>)<sub>2</sub>-N-C(Ph,All)-C<sub>6</sub>H<sub>3</sub>-*p*-OMe-*o*-O)SiR (**2a**: R = Ph, **3**: R = Cl). The allyl shift step involved in the formation of **2a** and **3** probably occurs *via* an intermediate hexacoordinate silicon complex. This reaction is diastereoselective. The missing diastereomer of **2** (**2b**) was prepared using an alternative synthesis route, which starts from the trimethylsilyl derivative of ligand **1** *o*-Me<sub>3</sub>SiO-*p*-MeO-C<sub>6</sub>H<sub>3</sub>-C(Ph)=N-(CH<sub>2</sub>)<sub>2</sub>-N=C(Ph)-C<sub>6</sub>H<sub>3</sub>-*p*-OMe-*o*-OSiMe<sub>3</sub>. The diastereomers of **2** obtained from modified reaction pathways give rise to suggestions about the mechanism of formation of these complexes.

Further functionalization of the allyl-substituted ligand system of **3** was carried out by hydrosilylation with  $\text{HSiCl}_3$  to yield complex **4** (*o*-O-*p*-MeO-C<sub>6</sub>H<sub>3</sub>-C(Ph)=N-(CH<sub>2</sub>)<sub>2</sub>-N-C(Ph)[(CH<sub>2</sub>)<sub>3</sub>-SiCl<sub>3</sub>]-C<sub>6</sub>H<sub>3</sub>-*p*-OMe-*o*-O)SiCl.

*Key words:* Allyl, Chelate, Hypercoordination, Rearrangement, Silicon