University of Victoria | Graduate Studies

Notice of the Final Oral Examination for the Degree of Doctor of Philosophy

of

PETER LEE

MASc (Saint Mary's University, 2009)
BSc (Simon Fraser University, 2006)

"B(C6F5)3-Catalyzed Reductions with Hydrosilanes: Scope and Implications to the Selective Modification of Poly(phenylsilane)"

Department of Chemistry

Wednesday, September 2, 2015
10:00 A.M.
Engineering and Computer Science Building
Room 130

Supervisory Committee:
Dr. Lisa Rosenberg, Department of Chemistry, University of Victoria (Supervisor)
Dr. Jeremy Wulff, Department of Chemistry, UVic (Member)
Dr. Frank van Veggel, Department of Chemistry, UVic (Member)
Dr. Real Roy, Department of Biology, UVic (Outside Member)

External Examiner:
Dr. Daniel Foucher, Department of Chemistry and Biology, Ryerson University

Chair of Oral Examination:
Dr. Anthony Quas, Department of Math, UVic

Dr. David Capson, Dean, Faculty of Graduate Studies

Abstract

New complex silicon-containing molecules were made by B(C6F5)3-catalyzed hydrosilation, dehydrocoupling, and dealkylative coupling reactions starting from Si-H reagents. The scope of reactions starting from disilane was expanded to include the formation of silicon-sulfur1, silicon-oxygen and silicon-alkyl side-chains. Substrate-catalyst complexation showed reaction inhibition, which was expected based on the proposed mechanism (Chapter 2). B(C6F5)3 was found to be selective for Si-H activation in reactions of disilane and no competing Si-Si bond cleavage side-reactions were observed. This result will guide future studies and application of B(C6F5)3-catalyzed reactions with polysilanes.

Competing B(C6F5)3-catalyzed over-reduction was found and classified into two distinct cases: alkyl groups for which over-reduction reactions were observed with some functional groups was classified into two distinct cases: alkyl groups for which over-reduction was dependent on the steric bulk of the alkyl group, and benzylic groups for which over-reduction was dependent on an α-aryl group. These reactions are consistent with the proposed Piers-Oestreich mechanism (see Chapter 3) and suggest the rate-determining step for over-reduction is the nucleophilic attack of the alkoxysilane (R′-O-SiR3) to the R3Si•••H•••B(C6F5)3 complex.2 Benzylic side-chains were over-reduced regardless of the steric bulk of the aryl groups. Literature precedents suggest that benzyl over-reductions must undergo an alternative mechanism to the Piers-Oestreich mechanism. A number of mechanisms have been proposed in the literature and in Chapter 3, suggesting conventional substrate-borane or silane-borane complexation.2 Furthermore, over-reduction of benzylic sulfur-containing side-chains was found and this reaction was exploited in the B(C6F5)3-catalyzed synthesis of unique silicon-sulfur-silicon-containing products. These over-reduction reactions highlighted the role of the silane for over-reduction and the challenges associated with th post-polymerization modification of poly(phenylsilane).

The advances in B(C6F5)3-catalyzed synthesis of small silane molecules suggested reaction conditions and gave spectroscopic benchmarks that were applied

to the post-polymerization modification of poly(phenylsilane) (Chapter 4). New X-modified poly(phenylsilane) derivatives with thiolato (sulfur), alkoxy/aryloxy (oxygen), amido (nitrogen) and alkyl (carbon) side-chains were prepared with 10-40% incorporation of the 'X' group into poly(phenylsilane). These new polysilanes were characterized by the following methods: 1H/13C/29Si NMR, IR, MALS-GPC, EA, and UV-vis absorption spectroscopy. Together, these characterization methods showed that the polysilane had not undergone Si-Si cleavage and thus demonstrated the utility of B(C6F5)3 for the selective activation of Si-H bonds. Thermal decomposition of X-modified poly(phenylsilane) derivatives and parent poly(phenylsilane) showed interesting redistribution pathways (Chapter 5). The thermal decomposition products of poly(phenylsilane) were identified: volatile monosilanes, a structurally complex not-yet-identified phenylsilicon-containing material generated at 500 °C, and a mixture of silicon carbide (SiC) and elemental carbon generated at 800 °C.

The B(C6F5)3-catalyzed post-polymerization method (Chapter 4) was evaluated based on the substitution percentage for X-functionalized poly(phenylsilane) derivatives. Reactions of highly electron-donating substrates gave a low amount of X incorporation (10%, e.g. aryloxy side-chains derived from phenol). Aryloxy groups were alternatively introduced via demethanative coupling, which gave a polymer with a greater substitution percentage (25%). The overall impact of the H-to-X substitution reactions was gauged by UV-vis absorption spectra and desirable UV absorption properties would require the modified poly(phenylsilane) to have a high degree of substitution.