

## Electrophilic Substitution on Phenylsilsesquioxanes

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Phenylsilsesquioxanes,  $[\text{PhSiO}_{1.5}]_{8,10,12}$  undergo a surprising number of novel electrophilic reactions that cannot be directly correlated with traditional concepts of electrophilic substitution at functionalized benzene. Although the  $T_8$ ,  $T_{10}$  and  $T_{12}$   $[-\text{SiO}_{1.5}]_x$  cages exhibit strongly electron withdrawing character equal to a traditional  $-\text{CF}_3$  group the phenyl rings can undergo electrophilic substitution at the ortho, meta or para positions depending on the reactants.

Thus, nitration, sulfonylation or acetylation give traditional meta substitution, whereas bromination goes almost exclusively ortho and iodination goes almost exclusively para providing diverse starting materials for a wide variety of hybrid materials applications. In this study we examine the mechanisms involved that strongly suggest electronic effects not anticipated by the simple structures.

Theoretical modeling studies combined with extensive studies on the effects of electrophilic substitution on the title cage compounds, their photonic properties in particular indicate that the cage structures themselves strongly influence the electronic character of the transition state in the noted electrophilic reactions. A detailed understanding of the processes that transpire offers a facile new route to two faced (Janus) cages of potentially significant value for multiple fields of study.