The understanding and the manipulation of silicon surfaces\(^1\) are key aspects of silicon-based technologies. Stable molecular siliconoids are unsaturated neutral silicon clusters that exhibit typical features of silicon nanoparticles and surfaces,\(^2\) in particular the presence of one or more unsubstituted vertices.\(^3\) Evidently, functionalised vertices are a prerequisite for the embedding of siliconoids in extended supramolecular assemblies. However, only unfunctionalized siliconoids have been reported so far, severely limiting further developments in this regard.

Here we report the site-selective reductive cleavage of aryl groups of cluster-like hexasilabenzene isomers (Figure 1). As demonstrated by reactions with representative electrophiles of Groups 13 to 15, these anionic siliconoids efficiently transfer the \(\text{Si}_6\) motif to various substrates, while maintaining the integrity of the unsaturated cluster scaffold in most cases. On the other hand, with suitable substrates a targeted stepwise expansion of the cluster scaffold can be achieved.

