

[20]Silafulleranes: Regioselective Derivatization Supported by ^{35}Cl NMR Spectroscopy

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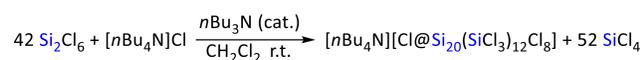
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Syntheses

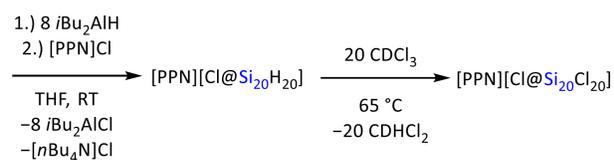
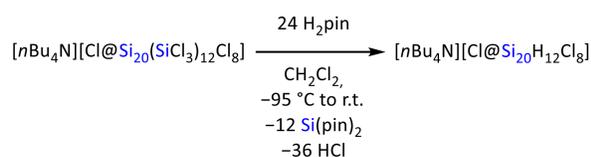
One-Step Synthesis from Si_2Cl_6 ^[1,2]



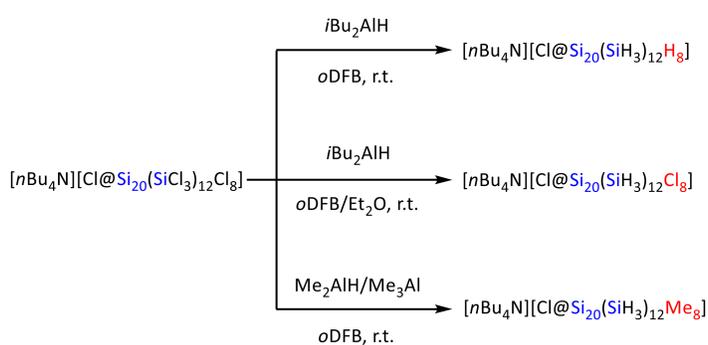
$[n\text{Bu}_4\text{N}][\text{Cl}@_{\text{Si}_{20}}(\text{SiCl}_3)_{12}\text{Cl}_8]$ can be isolated by harvesting large single crystals in yields up to 30%!



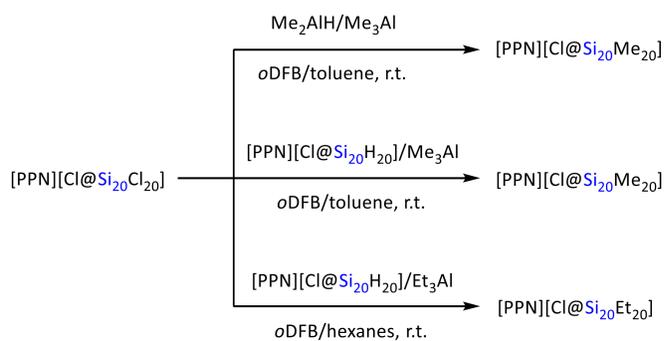
Desilylation^[3]



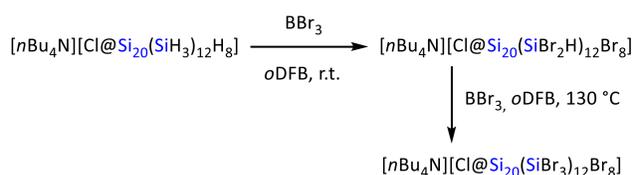
Regioselective Hydrogenation



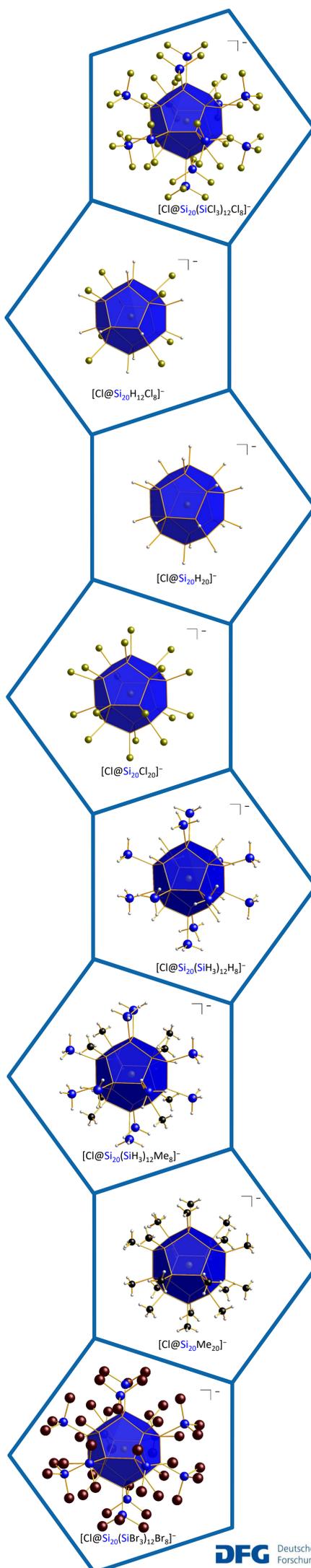
Core Alkylation



Stepwise Bromination



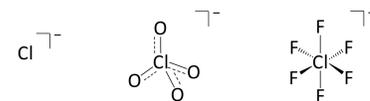
Crystal Structures



^{35}Cl NMR Spectroscopy

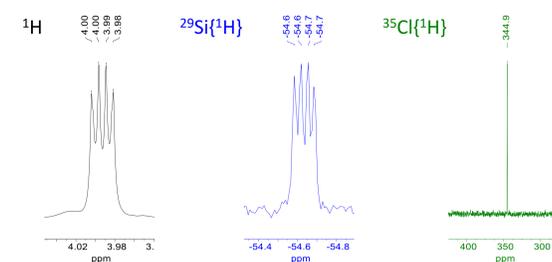
Background

^{35}Cl (and ^{37}Cl) NMR experiments ($S(^{35}\text{Cl}) = S(^{37}\text{Cl}) = 3/2$) normally suffer from extreme line broadening as a result of rapid quadrupolar relaxation.^[4] Only in highly symmetric environments, this is not the case. Thus, Cl^- (used as the external standard for ^{35}Cl NMR), ClO_4^- , and ClF_6^- ions exhibit narrow ^{35}Cl resonances.



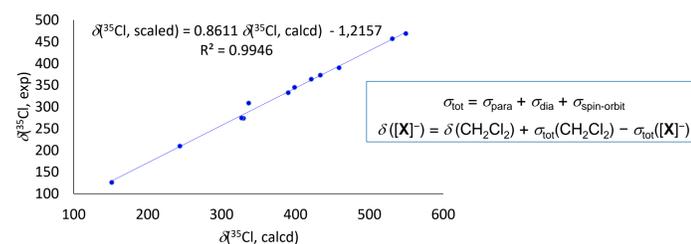
NMR Spectra of $[\text{Cl}@_{\text{Si}_{20}}\text{H}_{20}]^-$

Quadrupolar relaxation is not a problem in the I_h and T_h symmetric environments of our endohedral Cl^- ions! Therefore, 1:1:1:1 quartets caused by coupling to the endohedral ^{35}Cl or ^{37}Cl nuclei are observed in the ^1H and $^{29}\text{Si}\{^1\text{H}\}$ NMR spectra of $[\text{PPN}][\text{Cl}@_{\text{Si}_{20}}\text{H}_{20}]$: $J(\text{H},\text{Cl}) = 3.3 \text{ Hz}$; $J(\text{Si},\text{Cl}) = 3.0 \text{ Hz}$.^[3]



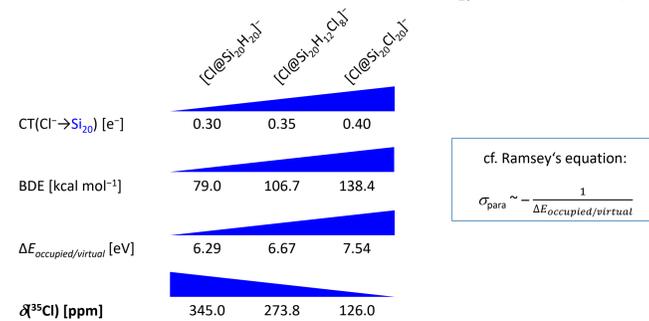
Quantum-Chemical Prediction

The quantum-chemical prediction of $\delta(^{35}\text{Cl})$ values is achieved efficiently at the SO-ZORA-PBE0(COSMO(CH_2Cl_2))/ZORA/TZP/PBEh-3c(COSMO(CH_2Cl_2)) level of theory. A linear-scaling approach gives an almost perfect match with the experimentally determined values!



Probing the $\text{Cl} \rightarrow \text{Si}_{20}$ Interaction

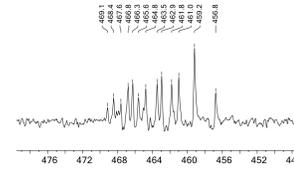
$\delta(^{35}\text{Cl})$ is a useful spectroscopic probe for the $\text{Cl} \rightarrow \text{Si}_{20}$ interaction strength!



Symmetry Influences

The endohedral Cl^- ions in H/Cl-substituted Si_{20} clusters only give rise to narrow ^{35}Cl NMR signals when perfect T_h or I_h symmetry is fulfilled. In contrast, the endohedral Cl^- ions in H/Me-substituted Si_{32} clusters ($[\text{Cl}@_{\text{Si}_{32}}(\text{SiH}_3)_{12}\text{Me}_8]^-$ and its derivatives) are much more tolerant towards symmetry breaking!

Therefore, some ^{35}Cl NMR spectra recorded during the synthesis development of $[\text{Cl}@_{\text{Si}_{20}}(\text{SiH}_3)_{12}\text{Me}_8]^-$ showed many signals.



References:

- J. Tillmann, J. H. Wender, U. Bahr, M. Bolte, H.-W. Lerner, M. C. Holthausen and M. Wagner, *Angew. Chem. Int. Ed.*, 2015, **54**, 5429–5433.
- Invited review: J. Teichmann and M. Wagner, *Chem. Commun.*, 2018, **54**, 1397–1412.
- M. Bamberg, M. Bursch, A. Hansen, M. Brandl, G. Sentis, L. Kunze, M. Bolte, H.-W. Lerner, S. Grimme and M. Wagner, *J. Am. Chem. Soc.*, 2021, **143**, 10865–10871.
- J. W. Akitt, The Quadrupolar Halides. In *Multinuclear NMR*; J. Mason, Ed.; Springer: Boston, 1987, pp. 447–461.