

Siladodecahedrane $[\text{Cl}@Si_{20}H_{20}]^-$ and its Chlorinated Derivatives

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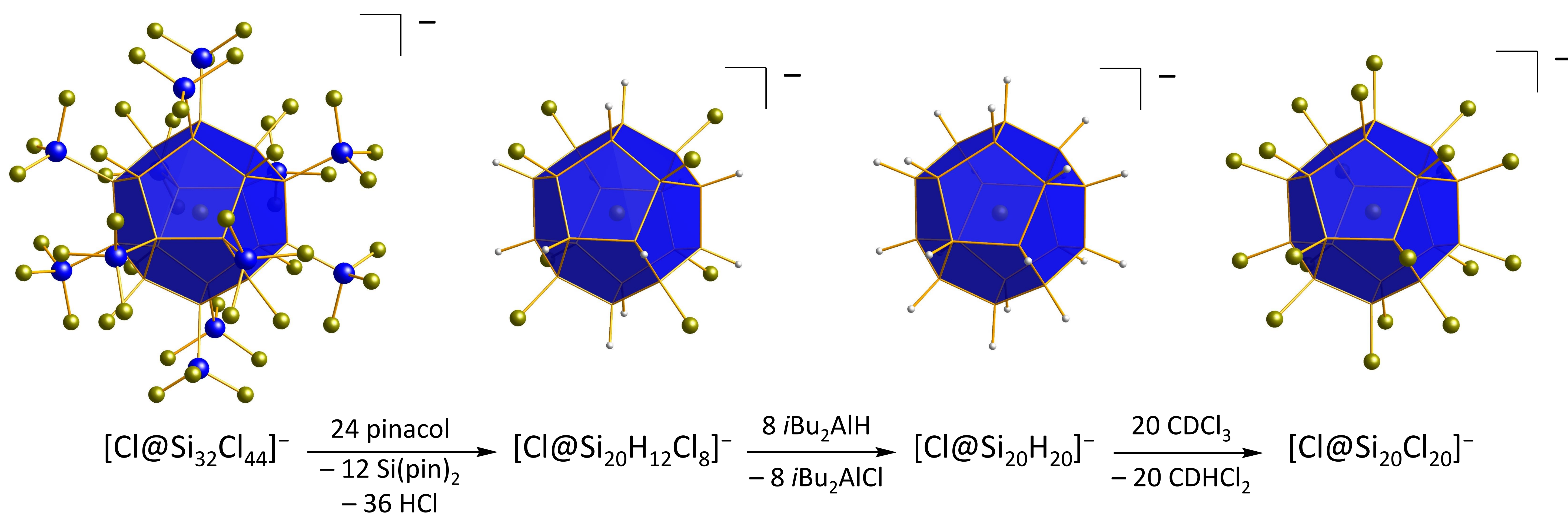
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Introduction

Compared to their carbonaceous analogues, silafullerenes (Si_n) and their saturated derivatives, silafulleranes (Si_nH_n), represent an almost untouched area of synthetic chemistry. Nevertheless, the smallest possible silafullerane cage, $Si_{20}H_{20}$, has been considered an attractive subject for quantum-chemical research over decades. Just recently, we have proven its existence by the synthesis of salts containing the endohedrally chloride-doped cluster $[\text{Cl}@Si_{20}H_{20}]^-$. Our efficient protocol builds on the previously published synthesis of the T_h -symmetric [20]silafullerane $[\text{Cl}@Si_{32}Cl_{44}]^-$ as the first of three steps.^[1] $[(nBu_4N)][\text{Cl}@Si_{32}Cl_{44}]$ can be prepared from Si_2Cl_6 , $[(nBu_4N)Cl]$, and catalytic amounts of nBu_3N in a one-pot procedure and crystallizes in yields up to 30%.^[2,3]

Syntheses and Molecular Structures in the Solid State (SC-XRD)

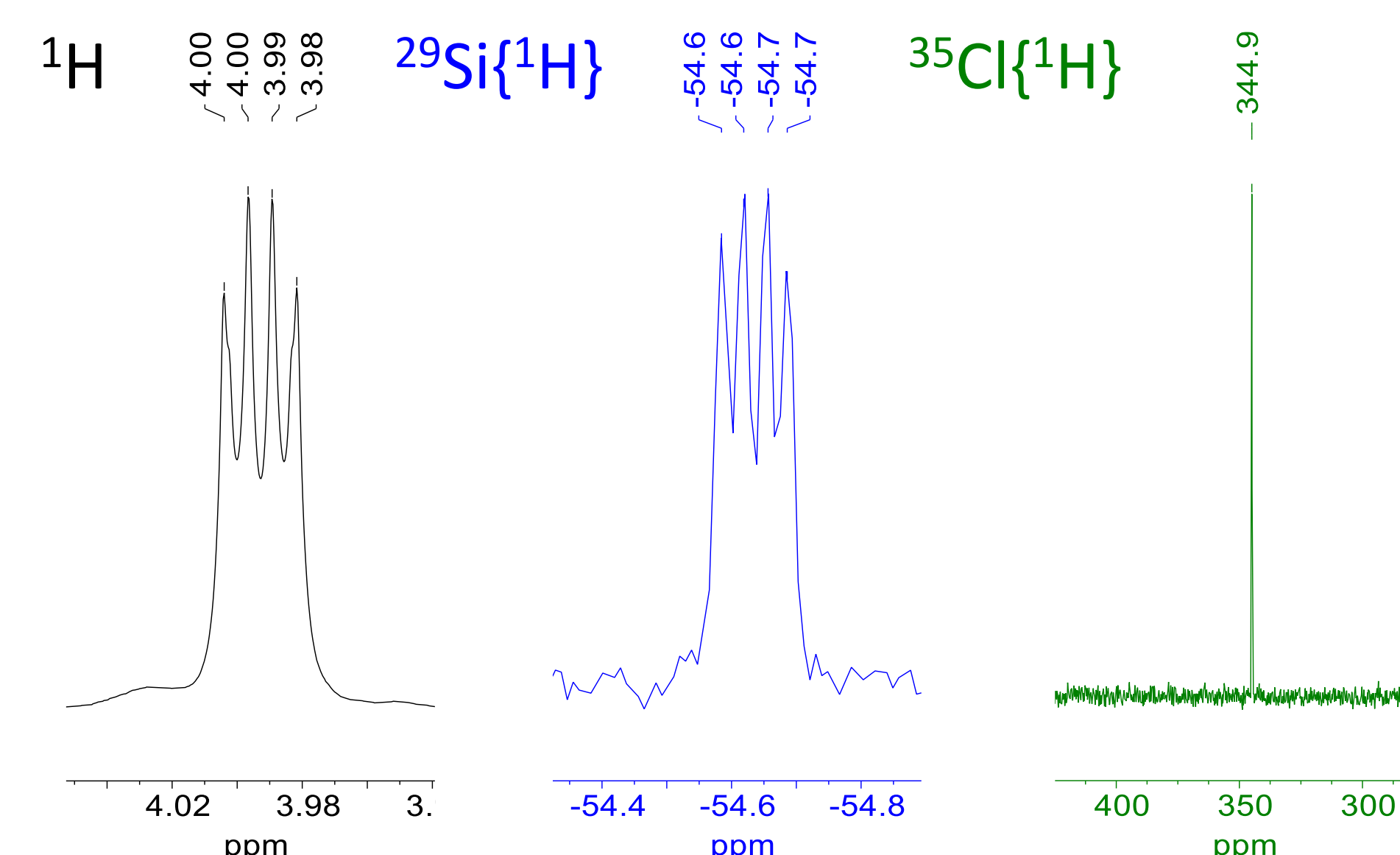


Note: The cations ($[(Et_4N)^+]$, $[(nBu_4N)^+]$, or $[(Ph_3P)_2N]^+$) have been omitted for clarity.

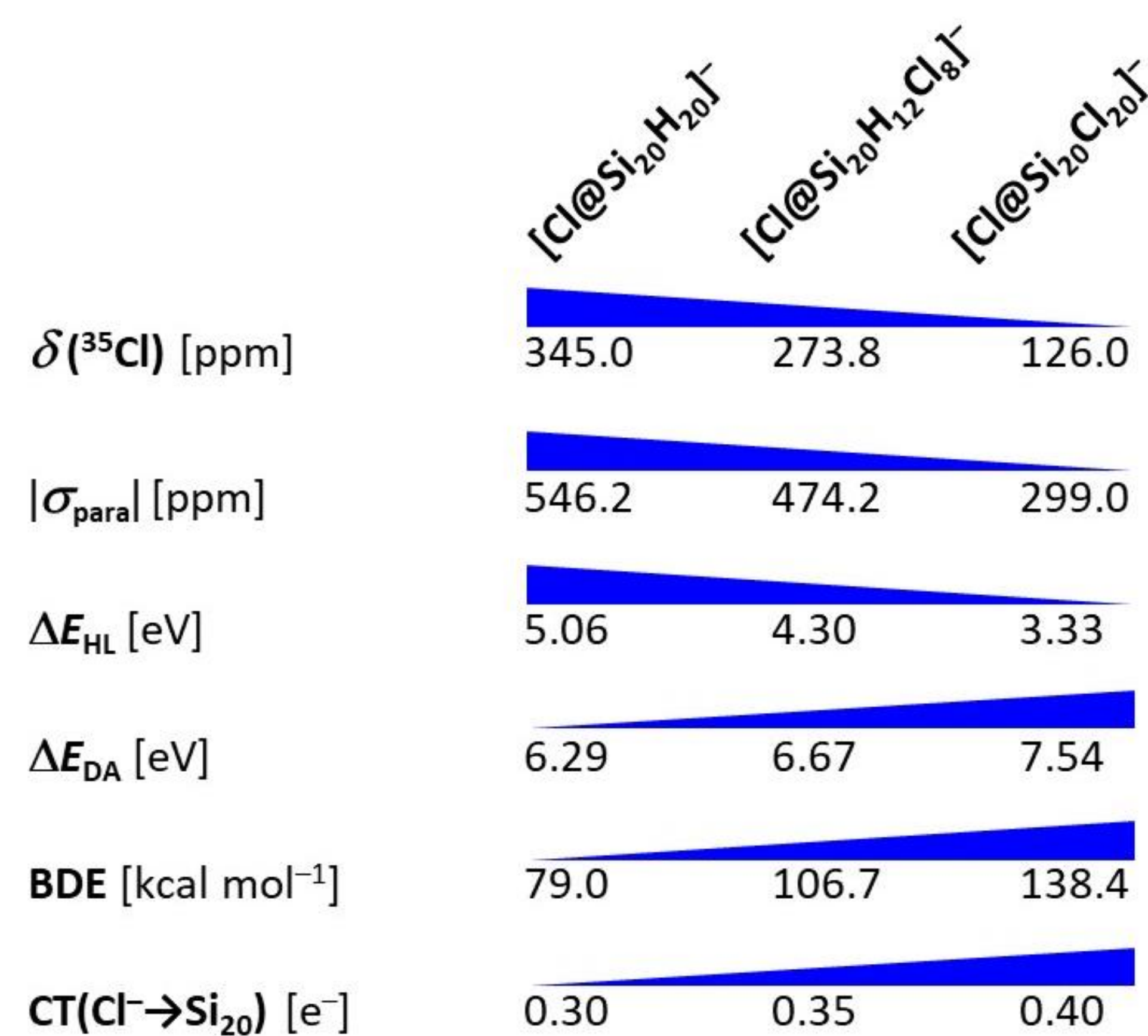
³⁵Cl NMR Spectroscopy

³⁵Cl (and ³⁷Cl) NMR experiments ($S(^{35}Cl) = S(^{37}Cl) = 3/2$) normally suffer from extreme line broadening as a result of rapid quadrupolar relaxation.^[4] This 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 ³⁵Cl or ³⁷Cl nucleus are observed in the ¹H and ²⁹Si{¹H} NMR spectra of $[(Ph_3P)_2N][\text{Cl}@Si_{20}H_{20}]^-$: $J(H,Cl) = 3.3 \text{ Hz}$; $J(Si,Cl) = 3.0 \text{ Hz}$.



Probing the Endohedral $Cl^- \rightarrow Si_{20}$ Interaction



A higher number of Cl substituents on the Si_{20} cluster surface...

- ... increases the charge transfer (CT) from the endohedral Cl^- ion to its Si_{20} host.
- ... leads to a larger bond-dissociation energy (BDE) between host and guest.
- ... decreases the HOMO-LUMO gap (ΔE_{HL}).
- ... causes a stronger magnetic shielding of the endohedral Cl^- ion!

Major theoretical achievements:

- ✓ Application of DLPNO-CCSD(T1)/*VeryTightPNO*/ $\delta^{CCSD(T)/aug-cc-pVTZ}$ MP2/CBS(aug-cc-pVTZ/aug-cc-pVQZ) for the calculation of accurate BDE and CT values.
- ✓ Calculation of NMR-spectroscopic parameters and analysis of shielding components at the SO-ZORA-PBE0/TZP(COSMO(THF))/B3LYP-D4/def2-TZVPP level of theory.
- ✓ Rationalization of the inverse correlation between $\delta(^{35}Cl)$ and BDE / CT($Cl^- \rightarrow Si_{20}$) by perturbation theory.

References:

- [1] 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.
 [2] 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.
 [3] Invited review: J. Teichmann and M. Wagner, *Chem. Commun.*, 2018, **54**, 1397–1412.
 [4] J. W. Akitt, The Quadrupolar Halides. In *Multinuclear NMR*; J. Mason, Ed.; Springer: Boston, 1987, pp. 447–461.