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Keywords: neutron, hydride, cluster

MS.61.3

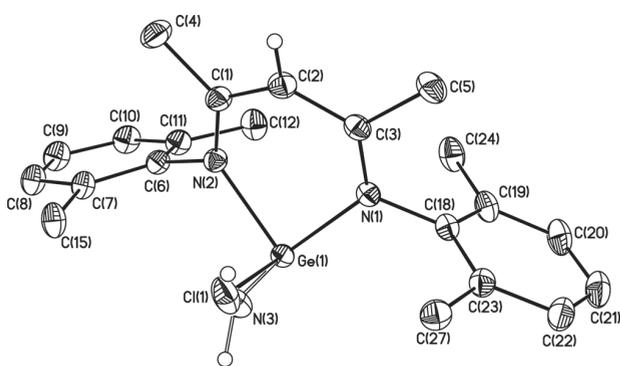
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Germynes: high resolution X-ray data for unambiguous ligand identification

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Despite the long-term chemical interest in low-valent germanium compounds, they are difficult to synthesize and even more difficult to crystallize. Roesky et al. successfully prepared a series of germynes, LGeX (X = OH (**1**), NH₂ (**2**), H (**3**); L = CH{(CMe)(2,6-Pr₂C₆H₃N)}₂) [1-3] and studied their fascinating reactivity. Group 14 carbene analogues are known to activate chemically inert entities and therefore represent potent catalysts. [3-5]

Single crystals of the entire germylene series were successfully obtained and their structure determination gave first insights into the bonding of the Ge(II) entity. For a deeper understanding of the catalytic properties it is inevitably important to clarify the nature of the substituents at Ge(II) and exclude any ambiguity in the crystallographic model. Catalytic reactions at the low valent metal atoms are often non-stoichiometric and may be initiated by traces of by-products, with a different chemical environment at the metal atom. Initial data collections were carried out on a sealed tube with modern optics and a microfocus source. [6] The more thorough investigation involved the most powerful rotating anode generator with confocal multilayer optics. The final high resolution data set revealed crystallographic details which are the key to understand some of the chemical features inherent to compounds.



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Keywords: germylene, single crystal x-ray data comparison, high resolution data

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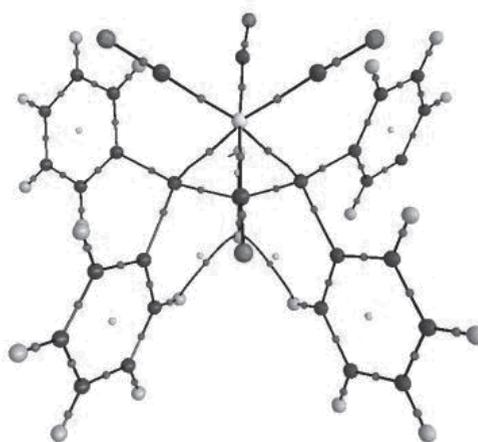
Theoretical QTAIM study on S- and Se-bridged polynuclear Mn complexes

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Starting from the standard X-ray diffraction experimental geometries of [(CO)₄Mn{(PPh₂)₂CH-S-S-CH(PPh₂)₂}Mn(CO)₄][ClO₄]₂·CH₂Cl₂·HClO₄·5H₂O [1] and [(CO)₄Mn{(PPh₂)₂CH-Se-Se-CH(PPh₂)₂}Mn(CO)₄][ClO₄]₂·2CH₂Cl₂ [2], theoretical electron density calculations have been performed in order to explain the interesting and anomalous features observed in the NMR spectra of such compounds, as compared with their mono- and poly-(S,Se)-bridged counterparts.

Preliminary DFT calculations on the simplified cation model [(CO)₄Mn{(PH₂)₂CH-S-S-CH(PH₂)₂}Mn(CO)₄]²⁺ could not fully explain the observed facts, although large basis sets and different hybrid functionals were used [3]. However, further QTAIM studies on the same model, as well as on [(CO)₄Mn{(PH₂)₂CH-Se-Se-CH(PH₂)₂}Mn(CO)₄]²⁺ showed the existence of non-bonding interactions involving CH-X-X-CH (X = S, Se) central groups, as evidenced from their delocalization indexes and other topological parameters [2].

The most recent QTAIM calculations, performed on the theoretically optimized geometries of [(CO)₄Mn{(PPh₂)₂CH-S-S-CH(PPh₂)₂}Mn(CO)₄]²⁺ and [(CO)₄Mn{(PPh₂)₂CH-Se-Se-CH(PPh₂)₂}Mn(CO)₄]²⁺ show the presence of additional small interactions between CH groups and phenyl hydrogen atoms, as reflected in the bond critical points and bond paths detected (see Figure). Such bonding interactions, together with the non-bonding ones, could easily explain the anomalous ¹H-NMR displacements observed for the CH groups.



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Keywords: topological analysis, theoretical electron density, organometallic compounds.