Microsymposia

MS.61.3

Germylenes: 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 germylenes, LGeX (X = OH (1), NH (2), H (3); L = CH(CMe)(2,6-Pr_{2}C_{6}H_{4}N=)) [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 first insights into the bonding of the Ge(II) entity. For a deeper understanding of the catalytic properties it is inevitable to clarify the nature of the bonding of the Ge(II) entity. For a deeper understanding of the catalytic properties it is inevitable to clarify the nature of the bonding of the Ge(II) entity. [1,2,3-5]

Keywords: neutron, hydride, cluster

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)_{4}Mn{(PPh)}_{2}CH-S-S-CH{(PPh)}_{2}Mn{(CO)}_{4}][ClO_{4}], CH_{2}Cl_{2}, CHCl_{3} and 2H_{2}O [1] and [(CO)_{4}Mn{(PPh)}_{2}CH-Se-Se-CH{(PPh)}_{2}Mn{(CO)}_{4}][ClO_{4}], CH_{2}Cl_{2}, the 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 of [(CO)_{4}Mn{(PPh)}_{2}CH-S-S-CH{(PPh)}_{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)_{4}Mn{(PPh)}_{2}CH-Se-Se-CH{(PPh)}_{2}Mn{(CO)}_{4}]^{2+} showed the existence of non-bonding interactions involving CH-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)_{4}Mn{(PPh)}_{2}CH-S-S-CH{(PPh)}_{2}Mn{(CO)}_{4}]^{2+} and [(CO)_{4}Mn{(PPh)}_{2}CH-Se-Se-CH{(PPh)}_{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.

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


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