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Patterns in the bonding of the phenalenyl radical with groups 2 and 12 metals

Abstract: The singly occupied molecular orbital SOMO of the phenalenyl radical ($C_{13}H_9$) is exceptionally interesting from a purely electronic standpoint. The MO has a node on the central atom and on alternating terminal atoms. The molecule is therefore more likely to form edge bonding structures, rather than bond through the central atom. Interested in probing the limits of the bonding possibilities for this high symmetry (D_{3h}) and particularly stable radical, we investigate the bonding between pairs of phenalenyl radicals and the divalent 2 and 12 metals (Be, Mg, Ca, Sr, Ba, Zn, Cd, and Hg). The pure dimer of the phenalenyl radical is known, but we have been surprised to find that its organometallic chemistry has received little attention in the literature. Theoretical calculations at the B3LYP computational level have uncovered exceptional bonding patterns for the series of molecules including an intriguing nonsymmetrical η^1 - η^3 bis(phenalenyl)Be complex. The Ca, Sr and Ba systems are bent slip sandwiches with the metal between overlapping regions of one of the six-membered rings of the two radicals. The most stable bis(phenalenyl)Mg complex is a slip sandwich structure as well, but very unusual electronically: a molecular orbital and population analyses suggest that Mg is in a promoted state but hardly involved in the bonding, which is primarily an interaction of the radicals. The group 12 metals prefer an η^1 structure with the two phenalenyl radicals trans to each other, and bonded via a single C site to s(p) hybrid orbitals on Zn, Cd and Hg.