Hypervalent *versus* Nonhypervalent Carbon. Disk-between-Balls Model

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Silicon in $[Cl–SiH_3–Cl]^-$ is hypervalent whereas carbon in $[Cl–CH_3–Cl]^-$ is not. We have recently shown how this can be understood in terms of the ball-in-a-box model according to which silicon fits perfectly into the box that is constituted by the five substituents, while carbon is too small and, in a sense, "drops to the bottom" of the box (see illustration, lower). But how does carbon acquire hypervalency in the isostructural and isoelectronic noble gas–methyl cation complexes $[Ng–CH_3–Ng]^+$, which feature a delocalized D_{3h} symmetric structure with two equivalent C–Ng bonds? That is, for Ng = He and Ne. From Ng = Ar, the $[Ng–CH_3–Ng]^+$ complex acquires again a propensity to localize one of its axial C–Ng bonds and to largely break the other one, and this propensity increases along Ng = Ar, Kr, Xe and Rn. The behavior of the helium and neon complexes violates the ball-in-a-box principle! Why does this happen? The purpose of this study is to answer these questions and to understand why carbon can become truly hypervalent under certain conditions (see illustration, upper).