

Strained Rings and Sandwiches: Theoretical Analysis of Conjoined Metallocene Complexes

Matt Bober Kelling Donald

Exploring new molecular motifs that possess unusual patterns of bonding are attractive because they may yield intriguing synthetic targets. This is potentially interesting chemistry as we investigate a series of tri-sandwich complexes involving hexalphenyl benzene and the d_6 metals (Cr, Mo, and W). The metals in group 6 are known to form so-called sandwich complexes that satisfy the 18-electron rule. Bis(benzene)chromium is a well studied example of these complexes in which each of the benzene rings, situated one above and one below the metal, donate six π -electrons each to the chromium metal that is situated between them. We investigate the influence of strain on the stability of these complexes by an assessment of the relative stability of the group six bis(benzene)metal complexes and a novel series of $M_3C_6(Ph)_6$ tri-sandwich complex in which three bis(benzene)metal complexes are linked via the Ph rings to a central benzene fragment. This arrangement imposes a degree of strain on the sandwich complexes enforcing a set of intriguing compromises in the sandwiches themselves and the central benzene ring. The bond orders, binding energies of the and minimum energy tri-sandwich and bis(benzene) complex has been studied at the B3PW91 level of theory determined and compared. The tri-sandwich complexes are surprisingly stable, relative to the unstrained systems and the bond orders are comparable, suggesting that these systems may be experimentally accessible. We look forward extending our investigation to include further assessments of the electronic and thermodynamic properties of these and other poly-sandwich complexes.