Ab initio investigation of metal-ring bonding in the sandwich-like benzene complexes of group VI transition metals.

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The metal-ligand bonding in the sandwich-like benzene complexes $M(C_6H_6)_2$ (M=Cr, Mo, W) of group VI transition metals has been studied by ab initio methods of quantum chemistry. The metal-benzene and C-C distances were optimized and the average binding energies were calculated. The metal-benzene systems were investigated by different approaches taking into account electron correlation effects at the MP2, CCSD and CCSD(T) levels with different atomic basis sets. The calculation results were compared to the thermochemical experimental data as well as to previuos calculatons by King et al.[1]

The critical dependence of the binding energies on the treatment of correlation contributions, especially on the including of triples excitations was confirmed. A modified scaling procedure was suggested for the extrapolation of correlation energy estimates to larger basis sets, comprising polarization functions on all atoms. The triple excitation contributions were estimated on the base of CCSD/CCSD(T) correlaton energy ratio in smaller basis set with a subsequent scaling. This extrapolation scheme was tested in a single point calculation for the $W(C_6H_6)_2$ complex. This allowed us to simulate the CCSD(T) results with an accuracy of 0.003 A for the bond lengths, 0.5 kcal/mol for binding energies and 1.7 kcal/mol for the total energies. The calculations overestimated the binding energy up to 11 kcal/mol with respect to experimental results related to the solution.

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1. King W.A. et.al. J.Am.Chem.Soc.,v.118,p.627(1996)