Structural and Electronic Properties of Carbenes as Ligands

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In developing the basis for a ligand knowledge base (LKB), we have studied a test group of ligands, carbenes, in order to gauge their electronic, structural and steric properties when complexed to a metal centre. Data is collected from mining structural databases, from structural studies of new complexes determined and from computational studies, and then organised using informatics methods.

Forty different carbenes, chosen to span a range of electronic and steric properties, were optimised using density functional theory (DFT) at the BP86/6-31G* level of theory, both as the free carbene and as a ligand attached to a number of metal fragments. Various geometric, electronic and steric parameters were calculated for each of the carbenes and their complexes.

These data were analysed using principal component analysis (PCA) and the data scrutinised in order to remove highly correlated parameters and parameters for which there was insignificant variation. About 75% of the variance in the data could be represented by 5 principal components. Rated by their factor scores against a particular principal component, carbenes of a similar nature cluster together in ligand space (LS). Apparently unrelated carbenes which mimic one another may be identified by their similar positions in LS.

Carbenes may be characterised by objective LS parameters. This approach may offer opportunities to design new catalysts with specific and desirable properties.

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