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Computationally Synthesised Inorganic and Organometallic Complexes

A thesis presented in partial fulfilment of the requirements of the degree of

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Muhammad Arif Sajjad

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Dedicate to my late father and brother

Abstract

Catalytic aromatic ring C–H bond functionalisations by transition metal cyclometallation reactions are important for organic transformation reactions. The cyclometallated product, which contains a new metal–carbon bond is formed as a consequence of different types of carbon–hydrogen···metal (C–H···M) interactions. These C–H···M interactions have been known as anagostic, preagostic and agostic interactions. By nature, the anagostic interaction has mainly electrostatic components, the preagostic interaction has electrostatic components with some back-bonding from metal to C–H antibonding orbital involved and the agostic interaction has mainly covalent components when the C–H bond donates electron density to the partially occupied metal centre. Prior to the current thesis work, an in-depth study that addresses the influence of steric and electronic factors on the anagostic, preagostic and agostic carbon–hydrogen···metal interaction was missing. In this thesis, the influence of both the steric and electronic factors on the anagostic, preagostic and agostic C–H···M interactions has been studied. It is seen that the electronic and steric influences play differently for different ligand systems as with the flexible tetralone ligand, a maximum of steric and electronic influence results into another type of anagostic interaction named as the ‘C-anagostic’ interaction. It is also seen that a stronger steric and electronic effect can trigger agostic covalency at the anagostic stage of the reaction. The inflexible ligand ensures the short anagostic approach, which has some back-bonding character and the nature of the interaction lies into the preagostic category. Finally, the aromatic ring agostic interactions have more complexity as new donations named as ‘syndetic’ from C–C pi bond to metal antibonding orbitals were recognised which shares the same antibonding acceptor orbitals as the agostic donation does. The recognition of new bonding situations in C–H···M interactions can have significant implications for C–H bond functionalisation reactions.

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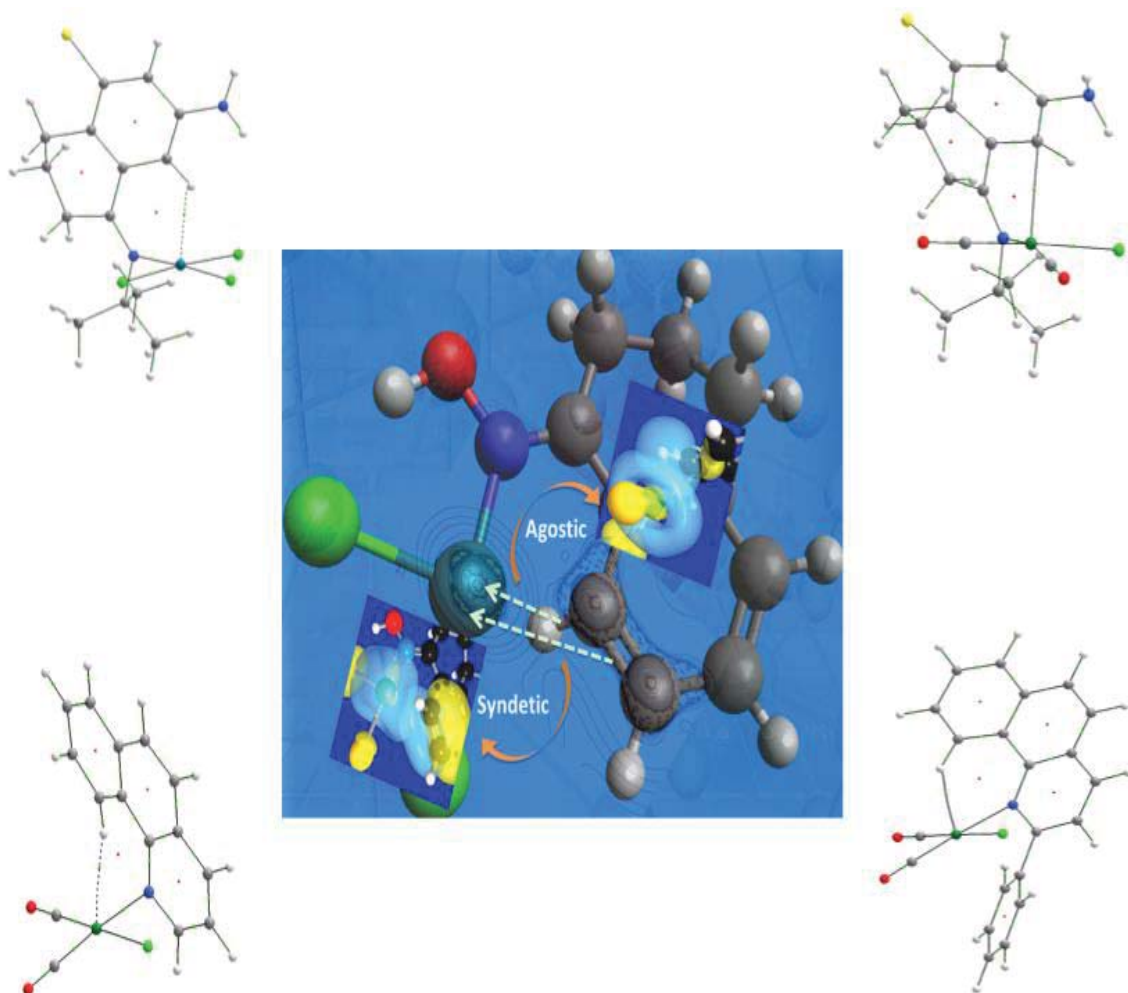
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Abbreviations

DFT	density functional theory
PBE-D3	Perdew–Burke–Ernzerhof exchange-correlation functional with D3 version of Grimme’s dispersion parameters
B3LYP	Becke’s 3-parameter hybrid functional with the correlation functional of Lee, Yang, and Parr
BP86	Becke’s 1988 exchange and Perdew 86 correlation functional
CAM-B3LYP	a new hybrid exchange-correlation functional B3LYP modified by Coulomb- attenuating method
CAM-B3LYPD3	CAM-B3LYP functional with D3 version of Grimme’s dispersion parameters
Aug	augmented
cc-pVDZ	correlation-consistent polarised valence double-zeta
cc-pVTZ	correlation-consistent polarised valence triple-zeta
EHT	extended Hückel theory
QTAIM	quantum theory of atoms in molecules
NBO	natural bond orbital
LP	lone pair
NCI	non-covalent interaction
RDG	reduced density gradient
2D	two-dimensional
3D	three-dimensional
IR	infra-red
NMR	nuclear magnetic resonance
BCP	bond critical point
RCP	ring critical point

Reference Chart of C–H···M Interactions



Publications and Thesis Structure

Publications relevant to this thesis

1. **M. A. Sajjad**, K. E. Christensen, N. H. Rees, P. Schwerdtfeger, J. A. Harrison, A. J. Nielson, *Chem. Comm.*, 2017, **53**, 4187–4190.
2. A. J. Nielson, J. A. Harrison, **M. A. Sajjad**, P. Schwerdtfeger, *Eur. J. Inorg. Chem.*, 2017, 2255–2264.
3. J. A. Harrison, A. J. Nielson, **M. A. Sajjad**, G. C. Saunders, P. Schwerdtfeger, *Eur. J. Inorg. Chem.*, 2016, 64–77.

Additional publications

4. J. A. Harrison, **M. A. Sajjad**, P. Schwerdtfeger, A. J. Nielson, *Cryst. Growth Des.*, 2016, **16**, 4934–4942.

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