

X-ray Spectroscopy Unveils Unusually Strong Agostic Methyl-Nickel Bonding in Linear Ni(I) Complexes

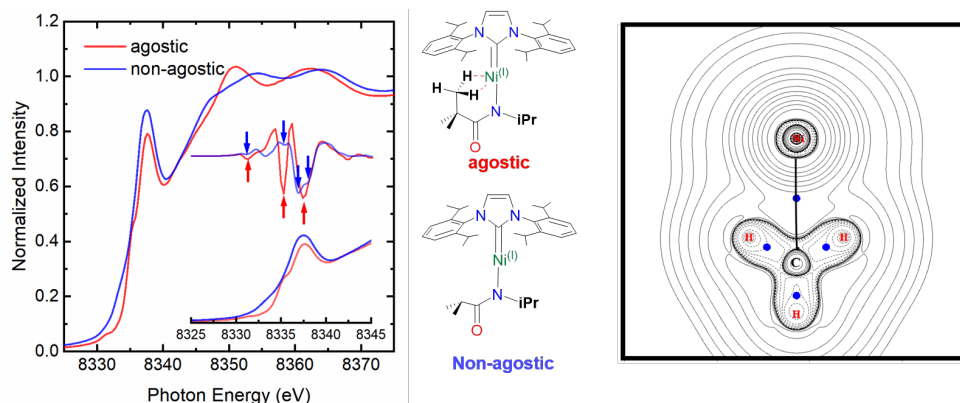
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Agostic interactions play an important role in transition metal catalyzed C-H activation. These interactions are typically dominated by charge donation from the σ_{CH} bond into empty valence metal d orbitals.¹ Herein, we report an unusual bis(CH) agostic interaction in electron rich linear $3d^9$ Ni(I) complexes.^{2,3} Ni K-edge X-ray absorption spectroscopy (XAS) show that the agostic interaction has an unexpectedly dramatic influence on the empty valence states with very little contribution from the valence metal 3d orbitals.

Our experimental findings are supported by DFT results, which reveal an unconventional covalent agostic interaction with donation into the metal 4p orbitals with both σ and π charge donation from two C-H σ bonds into the 4p orbitals of the metal center. The primary interaction involves primarily C 2p donor contributions to the corresponding collinear empty 4p orbital. In this geometry, the bis(CH) ligand is both a σ and π donor leading to a surprisingly strong (50-80 kJ/mol) stabilization. The implications of this unusual bonding mode are discussed and contrasted with more typical agostic interactions.



References

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