The name is Bond; non-covalent “Bond”: Non-covalent Axial Interactions in d8 metal complexes

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Abstract

Square planar d8 transition metal complexes provide unique opportunities for reactivity

and solid-state properties that are employed in catalysis, nanoscale devices, and crystal

engineering amongst others. Open coordination sites provide sites for “weak” inter- and

intramolecular interactions that can radically alter physical properties of d8 metal

complexes in solution and/or the solid state. Macrocycles including the thiacrown 1,3,7-trithiacyclononane (9S3) with facial coordination preferences are mismatched with d8 metals preference for square planar structures, leading to M…S axial interactions consistently longer than M-S bonds

but shorter than van der Waals radii. Strategies to modulate these “weak” interactions

will be presented, including counter ligands, metal-metal dative bonding, donor atom

modifications, and macrocycle ring size. A variety of behaviors comparing solution and

solid-state structures including persistent, hemilabile, and non-persistent axial

interactions will be described. Recent developments including a temperature induced

reversible single-crystal-to-single-crystal transformation with axial interaction changes

accompanied by striking color changes and theoretical studies to elucidate these changes will be presented.