

Contents

| | | |
|----------|--|-----------|
| 1 | Introduction | 11 |
| 1.1 | Theoretical Chemistry | 11 |
| 1.2 | Oxidative Addition | 12 |
| 1.3 | Hydrogen Bonds and Halogen Bonds | 15 |
| 2 | Theories, Models and Methods | 23 |
| 2.1 | Semantics | 23 |
| 2.2 | Quantum Chemistry | 24 |
| 2.3 | Density Functional Theory | 25 |
| 2.4 | Computational Details | 27 |
| 2.5 | Activation Strain Model of Chemical Reactivity | 30 |
| 2.6 | Molecular Orbital Theory & Interaction Energy Decomposition | 33 |
| 3 | Nonlinear d^{10}-ML_2 Complexes | 39 |
| 3.1 | Introduction | 39 |
| 3.2 | Structures and Energetics | 40 |
| 3.3 | General Bonding Mechanism | 44 |
| 3.4 | Bonding Mechanism: Variation of Ligands | 46 |
| 3.5 | Bonding Mechanism: Variation of Metals | 49 |
| 3.6 | Walsh Diagrams | 51 |
| 3.7 | Conclusions | 53 |
| 4 | Steric Attraction and Steric Repulsion: The Effect of Bulky Ligands | 57 |
| 4.1 | Introduction | 57 |
| 4.2 | $Pd(PR_3)_2$ Geometries and $Pd-PR_3$ Bond Analyses | 59 |
| 4.3 | The Effect of Steric Attraction on Oxidative Addition | 65 |
| 4.4 | Conclusions | 70 |

| | | |
|----------|---|------------|
| 5 | Electronic and Steric Effects on Bite-Angle Flexibility and Nonlinearity | 73 |
| 5.1 | Introduction | 73 |
| 5.2 | Pd(PX ₃) ₂ Geometries and Pd-PX ₃ Bond Analyses | 74 |
| 5.3 | Reactivity of Pd(PX ₃) ₂ Towards the Methane C-H Bond | 77 |
| 5.4 | Conclusions | 81 |
| 6 | New Design Concepts for d¹⁰-ML_n Catalysts | 83 |
| 6.1 | Introduction | 83 |
| 6.2 | General Reaction Profiles and Exceptions | 85 |
| 6.3 | Metal Variation from Group 9 to Group 11 | 88 |
| 6.4 | Metal Variation from Row 1 to Row 3 | 92 |
| 6.5 | Variation from σ -Donating to π -Accepting Ligands | 94 |
| 6.6 | Alternative Reaction Pathways for M(NH ₃) ₂ Catalysts | 96 |
| 6.7 | Catalyst Design Principles: d Regime versus s Regime | 98 |
| 6.8 | Conclusions | 102 |
| 7 | Rational Catalyst Design: Selective C-H and C-C Bond Activation | 105 |
| 7.1 | Introduction | 105 |
| 7.2 | General Energy Profiles for Ethane C-H and C-C Activation | 106 |
| 7.3 | Trends in Reaction Barriers for Ethane C-H Activation | 110 |
| 7.4 | Trends in Reaction Barriers for Ethane C-C Activation | 113 |
| 7.5 | Selective C-C or C-H Bond Activation | 115 |
| 7.6 | Selective Methane C-H versus Ethane C-H Bond Activation | 118 |
| 7.7 | Ethane C-C Activation via Ethane C-H Activation | 120 |
| 7.8 | Conclusions | 122 |
| 8 | Halogen Bonding versus Hydrogen Bonding: A Molecular Orbital Perspective | 125 |
| 8.1 | Introduction | 125 |
| 8.2 | Hydrogen Bonds: Strength and Structure | 126 |
| 8.3 | Halogen Bonds: Strength and Structure | 128 |
| 8.4 | Bond Analyses: Variation of the Accepting Halide | 130 |
| 8.5 | Bond Analyses: Variation of the Donating Group | 135 |
| 8.6 | Bond Analyses: Variation of the Central Atom | 137 |
| 8.7 | Conclusions | 139 |
| 9 | Resonance Assistance and Cooperativity in Halogen-Bonded Complexes | 143 |
| 9.1 | Introduction | 143 |
| 9.2 | Bond Analyses: B-DNA Base Pairs | 145 |
| 9.3 | Bond Analyses: G-DNA Quadruplexes | 147 |
| 9.4 | The Origin of Cooperativity in G ₄ and X-G ₄ Quartets | 151 |
| 9.5 | Conclusions | 158 |

| | |
|--------------------------------|------------|
| 10 Summary | 161 |
| 11 Samenvatting | 169 |
| 12 References | 177 |
| 13 Acknowledgements | 189 |
| 14 List of Publications | 191 |

