

Table of Contents

1. Introduction	1
1.1 White Phosphorus, Other Main Group Elements and Cage Compounds	1
1.2 Substituent-Free P_n Ligand Complexes	3
1.3 Reactivity of P_n Ligand Complexes	6
1.4 Cp^R Ligands with High Steric Demand	9
1.5 References	13
2. Research Objectives	17
3. The Highly Sterically Demanding Cp^{BIG} Ligand	19
3.1 Solubility	19
3.2 Geometrical Considerations	20
3.3 The Cp^{BIG} Ligand in Crystal Structures	21
3.4 References	23
4. Intact P_4 Tetrahedra as Terminal and Bridging Ligands in Neutral Complexes of Manganese	24
4.1 Introduction	25
4.2 Results and Discussion	26
4.3 Experimental Part	32
4.4 Additional Notes	34
4.5 References	35
4.6 Supplementary Information	37
5. Synthesis of the Heterocubane Cluster $[(CpMn)_4(\mu_3-P)_4]$ as a Starting Material for the Formation of Polymeric Coordination Compounds	54
5.1 Introduction	55
5.2 Results and Discussion	55
5.3 Experimental Part	60

5.4	References.....	64
5.5	Supplementary Information.....	66
6. Synthesis and Characterization of Manganese Triple-Decker		
Complexes.....		84
6.1	Introduction	85
6.2	Results and Discussion.....	86
6.3	Experimental Part.....	91
6.4	References.....	93
6.5	Supplementary Information.....	94
7. Activation of Coordinated P₄ Tetrahedra with 14 Valence		
Electron {Cp^{'''}Co} Fragments.....		104
7.1	Introduction	105
7.2	Results and Discussion.....	106
7.3	Experimental Part.....	110
7.4	References.....	112
7.5	Supplementary Information.....	114
8. Low Temperature Activation of S₈, Se_{red} and α-Te with		
[Cp^{BIG}Fe(CO)₂] Radicals.....		120
8.1	Introduction	121
8.2	Results and Discussion.....	121
8.3	Experimental Part.....	126
8.4	References.....	129
8.5	Supplementary Information.....	131
9. Activation of Group 15 Based Cage Compounds by		
[Cp^{BIG}Fe(CO)₂] Radicals.....		143
9.1	Introduction	144
9.2	Results and Discussion.....	145

9.3 Experimental Part	149
9.4 References	152
9.5 Supplementary Information	153
10. Differences in the Reaction Behaviour of the Butterfly Complexes $[\{\text{Cp}^{\text{BIG}}\text{Fe}(\text{CO})_2\}_2(\mu, \eta^{1:1}\text{-E}_4)]$ (E = P, As) – Irradiation and Thermolysis.....	161
10.1 Introduction	162
10.2 Results and Discussion	162
10.3 Experimental Part	169
10.4 References	171
10.5 Supplementary Information	172
11. Selective Functionalization of P_4 by Metal-Mediated C–P Bond Formation	184
11.1 Introduction	185
11.2 Results and Discussion	186
11.3 Experimental Part	193
11.4 References	196
11.5 Supplementary Information	198
12. Novel Polymeric Aggregates of Pentaphosphaferrocenes and Monocationic Coinage Metal Salts – Synthesis of $[\{\text{Cp}^{\text{BIG}}\text{Fe}(\eta^5\text{-P}_5)\}\text{Ag}]_n[\text{Al}(\text{OC}(\text{CF}_3)_3)_4]_n$ and $[\{\text{Cp}^*\text{Fe}(\eta^5\text{-P}_5)\}\{\text{Cu}(\text{GaCl}_4)_2\}]_n$.....	204
12.1 Introduction	205
12.2 Results and Discussion	205
12.3 Experimental Part	211
12.4 References	213
12.5 Supplementary Information	215

13. The Superbulky Pentaphosphaferrocene [Cp^{BIG}Fe(η⁵-P₅)] as Building Block for the Formation of Macromolecules with Lens-Shaped Scaffolds	221
13.1 Introduction	222
13.2 Results and Discussion.....	222
13.3 Experimental Part.....	226
13.4 References.....	228
13.5 Supplementary Information.....	230
14. A Giant Spherical Cluster with <i>I</i>-C₁₄₀ Fullerene Topology ..	237
14.1 Introduction	238
14.2 Results and Discussion.....	239
14.3 Experimental Part.....	242
14.4 References.....	244
14.5 Supplementary Information.....	246
15. Conclusion.....	252
15.1 Synthesis of P _n Ligand Complexes of Manganese	252
15.2 Activation of Small Molecules with [Cp ^{BIG} Fe(CO) ₂] ₂ and {Cp ^{BIG} }• Radicals	254
15.3 Formation of Supramolecular Assemblies using P _n Ligand Complexes and Coinage Metal Salts	257
16. Zusammenfassung	259
16.1 Darstellung von P _n -Ligandkomplexen des Mangans	259
16.2 Aktivierung kleiner Moleküle mit [Cp ^{BIG} Fe(CO) ₂] ₂ und {Cp ^{BIG} }• Radikalen	261
16.3 Bildung Supramolekularer Aggregate unter Verwendung von P _n -Ligandkomplexen und Münzmetallsalzen.....	264
17. Appendices.....	267
17.1 Alphabetic List of Abbreviations.....	267
17.2 List of Used Programs	269
17.3 Addresses of Cooperation Partners	270

17.4 Acknowledgments 271