



Table of Contents

1. Introduction	1
1.1 Metal complexes	1
1.2 Multinuclear metal complexes	1
1.2.1 Multinuclear complexes with direct metal-metal bond(s)	2
1.2.2 Multinuclear complexes <i>via</i> bridging ligands	4
1.3 Divalent lanthanides	5
1.3.1 General	5
1.3.2 Lanthanide-Transition metal carbonyl complexes	9
1.4 Pentaphosphaferrocene	11
1.4.1 Coordination chemistry of pentaphosphaferrocene	11
1.4.2 Reactivity of the <i>cyclo</i> -P ₅ ring of pentaphosphaferrocene	12
1.5 Low-valent main group compounds	15
1.5.1 <i>N</i> -Heterocyclic carbenes	15
1.5.2 <i>N</i> -Heterocyclic silylenes	16
1.5.3 Mono-valent aluminium	16
2. Aim of the Project	19
3. Results and Discussion	21
3.1 Heterometallic complexes of Zn and Au	21
3.1.1 Introduction	21
3.1.2 Synthesis of a rigid zinc-metalloligand bearing terminal phosphines	22
3.1.3 Synthesis of a nonanuclear Zn-Au heterometallic complex	23
3.1.4 Synthesis of a flexible zinc-metalloligand bearing terminal phosphines	25
3.1.5 Synthesis of nonanuclear Zn-Au heterometallic complex featuring aurophilic interactions	27
3.2 Lanthanide-TM carbonyl complexes	29
3.2.1 Introduction	29
3.2.2 Synthesis of Ln-TM carbonyl complexes by using bulky amidinates as ligands on Ln ^{II}	30
3.2.3 Synthesis of Ln-TM carbonyl complexes by using cyclopentadienyl as a ligand on Ln ^{II}	42
3.2.4 Theoretical calculations of complex 10 and 11	48
3.3 Reactivity of pentaphosphaferrocene with low-valent main group compounds	51
3.3.1 Introduction	51
3.3.2 Reactivity of [Cp*Fe(η^5 -P ₅)] with <i>N</i> -heterocyclic carbenes	53
3.3.3 Reactivity of [Cp*Fe(η^5 -P ₅)] with <i>N</i> -heterocyclic silylenes	57



3.3.4 Reactivity of [Cp*Fe(η^5 -P ₅)] with chloro-germylenes	65
3.3.5 Reactivity of [Cp*Fe(η^5 -P ₅)] with di-silylene and di-germylene	67
3.3.6 Reactivity of [Cp*Fe(η^5 -P ₅)] with mono-valent magnesium complex	79
3.3.7 Reactivity of [Cp*Fe(η^5 -P ₅)] with monovalent aluminium complexes.....	82
4. Experimental Section	92
4.1 General Methods	92
4.2 Synthesis of Starting Materials	93
4.3 Synthesis and analytical data	93
4.3.1 Synthesis of [(Bipy)Zn(ρ -O ₂ C(C ₆ H ₄)PPh ₂) ₂] (1)	93
4.3.2 Synthesis of [(Bipy)Zn(ρ -O ₂ C(C ₆ H ₄)PPh ₂ (AuCl)) ₂] (2a) and [(Bipy) ₂ Zn ₃ { ρ -O ₂ C(C ₆ H ₄)PPh ₂ (AuCl)} ₆] (2)	94
4.3.3 Synthesis of [(Bipy)Zn(O ₂ C(C ₂ H ₄)PPh ₂) ₂] (3)	95
4.3.4 Synthesis of [(Bipy) ₂ Zn ₃ {O ₂ C(C ₂ H ₄)PPh ₂ (AuCl)} ₆] (4)	96
4.3.5 Synthesis of [{(DippForm) ₂ Sm ^{III} }] ₂ {(μ_3 -CO) ₂ (CO) ₉ Fe ₃ }] (5)	96
4.3.6 Synthesis of [{(DippForm) ₂ Sm ^{III} (thf)}] ₂ {(μ -CO) ₂ (CO) ₂ Co ₂ }] (6)	97
4.3.7 Synthesis of [{(DippForm) ₂ Yb ^{III} (thf)}] ₂ {(μ -CO)(CO) ₃ Co} (7)	97
4.3.8 Synthesis of [{(DippForm) ₂ Sm ^{III} (thf)}] ₂ {(μ -CO)(CO) ₄ Mn} (8)	98
4.3.9 Synthesis of [{(DippForm) ₂ Yb ^{III} (thf)}] ₂ {(μ -CO)(CO) ₄ Mn} (9)	98
4.3.10 Synthesis of [{(DippForm) ₂ Sm ^{III} (thf)}] ₂ {(μ - η^2 -CO) ₂ (μ - η^1 -CO) ₂ (CO) ₄ Re ₂ }] (10)	99
4.3.11 Synthesis of [{(Cp*) ₂ Sm ^{III} }] ₃ {(Cp*) ₂ Sm ^{III} (thf)}] ₂ {(μ -O ₄ C ₄)(μ - η^2 -CO) ₂ (μ - η^1 -CO)(CO) ₅ Re ₂ }] (11)	99
4.3.12 Synthesis of [{(Cp*) ₂ Sm ^{III} (thf)}] ₂ {(μ -CO) ₂ (CO) ₃ Mn}] _n (12)	100
4.3.13 Synthesis of complex [ITMe(η^4 -P ₅)FeCp*] (13)	100
4.3.14 Synthesis of complexes [(η^4 -P ₅ SiL)FeCp*] (14) and [LSi(Cl)=P-SiL(Cl) ₂] (15)	101
4.3.15 Synthesis of complex [(LSi(N(SiMe ₃) ₂))(η^4 -P ₅)FeCp*] (16)	103
4.3.16 Synthesis of complex [(η^4 -P ₅ (SiL) ₂)FeCp*] (17)	104
4.3.17 Synthesis of [(LGe) ₂ {(μ - η^4 -P ₅)FeCp*}] (18)	105
4.3.18 Isomerization of [(LGe) ₂ {(μ - η^4 -P ₅)FeCp*}] (18) to [(LGe){(μ - η^3 -P ₅)(η^1 -GeL)FeCp*}] (19) by 1,2-migration of germylene moiety	105
4.3.19 Synthesis of [(Mes-BDI-Mg ^{II}) ₂ (μ - η^4 - η^4 -P ₁₀)(FeCp*) ₂] (20)	106
4.3.20 Synthesis of [Dipp-BDI-Al ^{III} (μ - η^4 -P ₅)FeCp*] (21)	107
4.3.21 Synthesis of [(P)(Cp*Al ^{III}) ₃ (μ - η^2 - η^2 - η^4 -P ₄)(FeCp*)] (22)	108
4.3.22 Synthesis of [(Cp*Al ^{III}) ₄ (P ₁₀)(Cp*Fe) ₂] (23) and [(Cp*Al ^{III}) ₆ (P ₆)] (24)	108
5. Crystal Structure Measurements	109



5.1 Data Collection and Refinement	109
5.2 Crystal Data	110
5.2.1 [(Bipy)Zn(<i>p</i> -O ₂ C(C ₆ H ₄)PPh ₂) ₂] (1)	110
5.2.2 [(Bipy) ₂ Zn ₃ { <i>p</i> -O ₂ C(C ₆ H ₄)PPh ₂ (AuCl)} ₆] (2)	111
5.2.3 [(Bipy)Zn(O ₂ C(C ₂ H ₄)PPh ₂) ₂] (3)	112
5.2.4 [(Bipy) ₂ Zn ₃ {O ₂ C(C ₂ H ₄)PPh ₂ (AuCl)} ₆] (4)	113
5.2.5 [{(DippForm) ₂ Sm ^{III} }] ₂ {(μ ₃ -CO) ₂ (CO) ₉ Fe ₃ } (5)	114
5.2.6 [{(DippForm) ₂ Sm ^{III} (thf)}] ₂ {(μ-CO) ₂ (CO) ₂ Co ₂ } (6)	115
5.2.7 [{(DippForm) ₂ Yb ^{III} (thf)}] ₂ {(μ-CO)(CO) ₃ Co} (7)	116
5.2.8 [{(DippForm) ₂ Sm ^{III} (thf)}] ₂ {(μ-CO)(CO) ₄ Mn} (8)	117
5.2.9 [{(DippForm) ₂ Yb ^{III} (thf)}] ₂ {(μ-CO)(CO) ₄ Mn} (9)	118
5.2.10 [{(DippForm) ₂ Sm ^{III} (thf)}] ₂ {(μ-η ² -CO) ₂ (μ-η ¹ -CO) ₂ (CO) ₄ Re ₂ } (10)	119
5.2.11 [{(Cp*) ₂ Sm ^{III} }] ₃ {(Cp*) ₂ Sm ^{III} (thf)} ₂ {(μ-O ₄ C ₄)(μ-η ² -CO) ₂ (μ-η ¹ -CO)(CO) ₅ Re ₂ } (11)	120
5.2.12 [{(Cp*) ₂ Sm ^{III} (thf)}] ₂ {(μ-CO) ₂ (CO) ₃ Mn} _n (12)	121
5.2.13 [ITMe{(η ⁴ -P ₅)FeCp*}] (13)	122
5.2.14 [(η ⁴ -P ₅ SiL)FeCp*] (14)	123
5.2.15 [LSi(Cl)=P-SiL(Cl) ₂] (15)	124
5.2.16 [{LSi(N(SiMe ₃) ₂)}{(η ⁴ -P ₅)FeCp*}] (16)	125
5.2.17 [{(η ⁴ -P ₅ (SiL) ₂)FeCp*}] (17)	126
5.2.18 [(LGe) ₂ {(μ-η ⁴ -P ₅)FeCp*}] (18)	127
5.2.19 [(LGe){(μ-η ³ -P ₅)(η ¹ -GeL)FeCp*}] (19)	128
5.2.20 [(Mes-BDI-Mg ^{II}) ₂ (μ-η ⁴ -η ⁴ -P ₁₀)(FeCp*) ₂] (20)	129
5.2.21 [Dipp-BDI-Al ^{III} (μ-η ⁴ -P ₅)FeCp*] (21)	130
5.2.22 [(P)(Cp*Al ^{III}) ₃ (μ-η ² -η ² -η ⁴ -P ₄)(FeCp*) ₂] (22)	131
5.2.23 [(Cp*Al ^{III}) ₄ (P ₁₀)(Cp*Fe) ₂] (23)	132
5.2.24 [(Cp*Al ^{III}) ₆ (P ₆)] (24)	133
6. Summary (Zusammenfassung)	134
6.1 Summary	134
6.2 Zusammenfassung	140
7. References	146
8. Appendix	154
8.1 Directory of Abbreviations	154
8.2 NMR Abbreviations	155



8.3 IR Abbreviations	155
8.4 Directory of Compounds	156
9. Curriculum Vitae	157
10. Acknowledgements.....	159