



INDEX

Index of compounds discussed in this dissertation	11
1. Introduction	17
1.1 Heavy group 14 element analogues of alkenes	17
1.2 Heavy group 14 element analogues of alkynes	21
1.3 Heavy group 14 element analogues of alkylidene (carbene) complexes	24
1.4 Heavy group 14 element analogues of alkylidyne (carbyne) complexes	27
1.4.1 Fischer and Schrock type carbyne complexes	27
1.4.2 Heavy group 14 analogues of Fischer type alkylidyne complexes	28
1.5 Statement of Goals and Objectives	32
2. Results and Discussion	33
2.1 Reactivity of ECIR (E = Ge, R = 2,6-Trip ₂ -C ₆ H ₃ ; E = Sn, R = 2,6-Mes ₂ -C ₆ H ₃) towards group 10 metal complexes	33
2.1.1 Insertion of ECIR (E = Ge, R = 2,6-Trip ₂ -C ₆ H ₃ ; E = Sn, R = 2,6-Mes ₂ -C ₆ H ₃) into Pd–Cl bonds of square planar Pd(II) complexes.	34
2.1.2 Insertion of ECl ₂ (E = Ge, Sn) into Pd–Cl bonds of square planar Pd(II) complexes	39
2.1.3 Reactivity of [SnCl(η ⁵ -C ₅ Me ₅)] 2-Sn with 1-Pd : Cp* transfer to Pd	43
2.2 Reactivity of [ECIR] ₂ (E = Ge, R = 2,6-Trip ₂ -C ₆ H ₃ ; E = Sn, R = 2,6-Mes ₂ -C ₆ H ₃) towards a d ⁸ configured group 9 complex: [Rh(η ² -C ₂ H ₄) ₂ Cl] ₂ : tetrel insertion into the Rh–Cl bond and C ₂ H ₄ elimination	49
2.3 Reactivity of stannylenes, germylenes and plumbylens, of the type [EXR] (E = Ge, Sn, R = 2,6-Mes ₂ -C ₆ H ₃ or 2,6-Trip ₂ -C ₆ H ₃ , X = Cl; E = Pb, R = 2,6-Trip ₂ -C ₆ H ₃ , X = Br) towards iron complexes	58
2.3.1 Reactions of [Fe(depe) ₂ (N ₂)] towards [ECIR] (E = Ge and Sn, R = 2,6-Mes ₂ -C ₆ H ₃ or 2,6-Trip ₂ -C ₆ H ₃ , X = Cl)	58
2.3.1.1 Double bonding between Fe and Sn: The first example of an iron halostannylidene complex and the first structurally characterised transition metal haloylidene complex.	60
2.3.1.2: Triple bonding between Fe and Sn: The first examples of transition metal complexes outside group 6 bearing triple bonds to tin.	64
2.3.1.3: Triple bonding between Fe and Ge: The first transition metal complexes outside group 6 bearing a triple bond to germanium.	71
2.3.2 Reactivity of [Fe(depe) ₂ (N ₂)] towards [PbXR] (X = Br, R = 2,6-Trip ₂ -C ₆ H ₃ ; X = Cl, R = C(tms) ₃): Formation of Fe(I) complexes	82



2.3.2.1 Excursion into Fe(I) chemistry: Facile synthesis and isolation of the first Fe(I) alkyl complex.	83
2.3.3 Complexes featuring double and triple bonding between Fe and Ge or Sn atoms: Facile access by phosphane elimination	90
2.3.4: Reactivity of C,H activated iron complexes towards 1-Sn: insertion, reverse CH activation, and redox chemistry.	103
2.3.4.1 Insertion of 1-Sn into $[\text{FeH}\{\eta^2\text{-CH}_2\text{PMe}_2\}(\text{PMe}_3)_3]$ 18-Fe	103
2.3.4.2 Reactivity of 1-Sn towards $[\text{FeH}(\eta^3\text{-MeCHPEtC}_2\text{H}_4\text{PEt}_2)(\text{depe})]$	107
2.3.4.3 Reactivity of 1-Sn towards $[\text{FeH}(\text{dppe})[\eta^3\text{-Ph}_2\text{PCH}_2\text{CH}_2\text{PPhC}_6\text{H}_4\text{}}]$	112
2.3.5: Some reactions of iron stannylidenes	116
2.3.5.1 Reactivity of the iron stannylidene complex 3-Fe	116
(a) Reaction of 3-Fe with MeLi	117
(b) Reaction of 3-Fe with Na[BHET ₃]: Access to the first example of a hydridostannylidene complex of iron	120
(c) Reaction of 3-Fe with HCl	123
2.3.6 ⁵⁷ Fe Mößbauer spectroscopic investigations	135
2.3.6.1 ⁵⁷ Fe Mößbauer spectra of some of our investigated Fe(0) complexes	136
2.3.6.2 Mößbauer spectra of Fe(I) complexes	145
2.3.6.3 Mößbauer spectrum of 20-Fe	147
2.3.7 UV/Vis Studies	148
2.4 A brief excursion into ruthenium chemistry: attempted photochemical access to ruthenium germylidyne and stannylidyne complexes	152
2.4.1 Synthesis of the precursor complex 1-Ru	152
2.4.2 Photolytic reactions of 1-Ru with 1-Ge and 1-Sn	153
2.5 An excursion into low valent germanium chemistry: synthesis and characterisation of base stabilised germylenes of the type GeRCl(L), where R = aryl, L = Lewis base.	157
2.5.1 Synthesis and characterisation of GeRX(L), where R = aryl, X = Cl, I; L = Lewis base.	158
2.5.2 UV/Vis spectroscopic investigations	165
3. Summary, conclusion and outlook	168
3.1 Summary	168
3.2 Conclusion	175
3.3 Outlook	176
3.2.1 Ylidyne complexes of other late transition metal elements	176
The preparation of Ru ylidyne complexes	176

4. Experimental Section	179
4.1 General section	179
4.2 Analytical methods	181
4.2.1 Nuclear Magnetic Resonance (NMR) spectroscopy	181
4.2.2 Infra-red spectroscopy	182
4.2.3 UV-Vis Spectrometry	182
4.2.4 Mößbauer Spectroscopy	183
4.2.5 Melting Point determinations	183
4.2.6 Elemental analysis	184
4.2.7 Electron paramagnetic resonance spectroscopy (EPR)	184
4.2.9 X-ray diffraction analysis	185
4.3 Starting materials prepared according to literature procedures	186
4.4 Commercially available starting materials	187
4.5 Synthesis and full characterisation of new compounds	188
4.5.1 [PdCl{SnCl ₂ (2,6-Mes ₂ -C ₆ H ₃)}(cod)] (3-Pd)	188
4.5.2 [PdCl{SnCl ₂ (2,6-Mes ₂ -C ₆ H ₃)}(dppe)] (4-Pd)	189
4.5.3 [PdCl(SnCl ₃)(cod)] (6-Pd)	191
4.5.4 [PdCl(GeCl ₃)(cod)] (7-Pd)	192
4.5.6 [(depe) ₂ Fe=SnCl(2,6-Mes ₂ -C ₆ H ₃)] (3-Fe)	193
4.5.7 [(depe) ₂ Fe≡Sn(2,6-Mes ₂ -C ₆ H ₃)] [SnCl ₂ (2,6-Mes ₂ -C ₆ H ₃)] (4-Fe)	195
4.5.8 [(depe) ₂ Fe≡Sn(2,6-Mes ₂ -C ₆ H ₃)] [BCl(C ₆ F ₅) ₃] (5-Fe)	198
4.5.9 [(depe) ₂ Fe≡Sn(2,6-Mes ₂ -C ₆ H ₃)] [B(3,5-(CF ₃) ₂ -C ₆ H ₃) ₄] (6-Fe)	199
4.5.10 [(depe) ₂ Fe≡Ge(2,6-Trip ₂ -C ₆ H ₃)] [GeCl ₂ (2,6-Trip ₂ -C ₆ H ₃)] (8-Fe)	201
4.5.11 [(depe) ₂ Fe≡Ge(2,6-Mes ₂ -C ₆ H ₃)] [GeCl ₂ (2,6-Mes ₂ -C ₆ H ₃)] (9-Fe)	203
4.5.12 [FeCl(depe) ₂] (10-Fe)	206
4.5.13 [Fe(CH ₃)(depe) ₂] (12-Fe)	208
4.5.14 [(dmpe) ₂ Fe=SnCl(2,6-Mes ₂ -C ₆ H ₃)] (16-Fe)	209
4.5.15 [Fe(dmpe) ₂ (PMe ₃)] (17-Fe)	211
4.5.16 [(PMe ₃) ₃ FeH{SnCl(2,6-Mes ₂ -C ₆ H ₃)(CH ₂ PMe ₂)}] (20-Fe)	212
4.5.17 [(depe)Fe=Sn(CH ₃)(2,6-Mes ₂ -C ₆ H ₃)] (26-Fe)	214
4.5.18 [(depe) ₂ Fe=SnH(2,6-Mes ₂ -C ₆ H ₃)] (27-Fe)	215
4.5.19 <i>trans</i> -[FeH(SnCl ₃)(depe) ₂] (28-Fe)	216
4.5.20 <i>trans</i> -[FeCl(SnCl ₃)(depe) ₂] (29-Fe)	218
4.5.21 <i>trans</i> -[FeCl(GeCl ₃)(depe) ₂] (31-Fe)	219
4.5.22 <i>trans</i> -[FeH(GeCl ₃)(depe) ₂] (32-Fe)	220
4.5.23 [GeCl ₂ (IME ₂ Me ₂)] (5-Ge)	221

4.5.25 [GeI(2,6-Mes ₂ -C ₆ H ₃)(IMe ₂ Me ₂)] (7-Ge)	224
4.5.26 [GeCl(2,6-Mes ₂ -C ₆ H ₃)(PMe ₃)] (8-Ge)	225
4.5.27 [Rh{SnCl ₂ (C ₆ H ₃ -2-Mes-6-η ⁶ -Mes)}(η ² -C ₂ H ₄)] (2-Rh)	227
4.5.28 [Rh{GeCl ₂ (C ₆ H ₃ -2-Trip-6-η ⁶ -Trip)}(η ² -C ₂ H ₄)] (3-Rh)	228
4.6 Starting materials, not commercially available prepared by modified literature procedures	231
4.6.1 [GeCl ₂ (PMe ₃)] (4-Ge)	231
4.6.2 [SnCl(2,6-Mes ₂ -C ₆ H ₃)] (1-Sn)	231
4.6.3 [Rh(C ₂ H ₄) ₂ Cl] ₂ (1-Rh)	233
4.6.4 [Fe(depe) ₂ (N ₂)] (1-Fe)	234
4.6.5 [FeCl ₂ (depe) ₂] (2-Fe)	235
4.6.6 [FeCl ₂ (dmpe) ₂] (14-Fe)	236
4.6.7 [{Fe(dmpe) ₂ } ₂ (μ-dmpe)] (15-Fe)	236
4.6.8 [FeCl ₂ (PMe ₃) ₂] (19-Fe)	238
4.6.9 Synthesis of [FeH(η ³ -Et ₂ PCH ₂ CH ₂ PET{CHCH ₃ })(depe)] (22-Fe)	239
4.6.10 [FeH(dppe){η ³ -Ph ₂ PCH ₂ CH ₂ PPhC ₆ H ₄ }] (24-Fe)	239
4.6.11 <i>trans</i> -[FeClH(depe) ₂] (30-Fe)	241
4.6.12 [FeCl ₂ (dppe)] (25-Fe)	243
4.7 New partially characterised compounds	244
4.7.1 [Pd(η ⁵ -C ₅ Me ₅)(cod)][SnCl ₃] (8-Pd) and its derivative (8-Pd-b)	244
4.7.2 16 [(PMe ₃) ₃ FeH{=Sn(2,6-Mes ₂ -C ₆ H ₃)(CH ₂ PMe ₂)}][ClB(C ₆ F ₅) ₃] (21-Fe)	245
4.7.3 Reaction of SnCl(2,6-Mes ₂ -C ₆ H ₃) with [FeH(dppe){η ³ -Ph ₂ PCH ₂ CH ₂ PPhC ₆ H ₄ }] resulting in [FeCl(dppe)] 25-Fe	246
4.7.4 Reaction of [FeH(η ³ -Et ₂ PCH ₂ CH ₂ PET{CHCH ₃ })(depe)] (22-Fe) with 1-Sn to yield a mixture of 3-Fe and [FeH(η ³ -Et ₂ PCH ₂ CH ₂ PET{CHCH ₃ SnCl(2,6-Mes ₂ -C ₆ H ₃)})(depe)] (23-Fe)	246
4.7.5 Reaction of Fe(N ₂)(depe) ₂ with [Pb(Ctms ₃)Cl]	247
4.7.6 [(dmpe) ₂ Fe=Sn(2,6-Mes ₂ -C ₆ H ₃)Cl] (16-Fe-2)	248
4.7.7 [(dmpe) ₂ Fe≡Ge(2,6-Mes ₂ -C ₆ H ₃)][ClB(C ₆ F ₅) ₃] (16-Fe-3)	249
4.7.8 <i>trans</i> -[RuH(SnCl ₂ (2,6-Mes ₂ -C ₆ H ₃)(depe) ₂] (5-Ru)	250
5. Appendices	251
5.1 Appendix A: Crystallographic Data	251
5.2 Appendix B: Commonly Used Abbreviations	279
5.3 Scientific Contributions from this work	282
5.4 Curriculum Vitae	283
6. References	287
7. Oath of compliance with academic integrity	303