Acknowledgements

Firstly, I would like to thank my supervisor Dr Eva Hevia for everything she has done for me over the last few years. I have really enjoyed working with her on some fantastic projects, and couldn’t have asked for a better PhD supervisor. I’m extremely grateful for all the work she has put in to help me during the last few years, and to get so many of these results published. I particularly want to thank her for all the help in proof reading this thesis, which I think has caused her more stress than it has me.

Special thanks also go to all the members of the Hevia group - Zoe, Sharon, Vicki and Thomas. Particularly to Zoe, who has had to put up with working next to me in the lab for the last few years (maybe she’ll start keeping the glove box a bit tidier now that I’m gone!), and Sharon for helping me out many times while I was writing up and putting up with my driving on our road trip to Oxford. It’s been great to work with such nice people every day, and they have both given me a lot of laughs during the last few years. Although they’ll pretend not to, I’m sure they will miss me. I would also like to mention two of my project students, Jonathan Chua and Lorraine Nuttall, for their important contributions to the magnesium-zincate work.

I am extremely thankful for all of the help and advice I have received from Professor Robert Mulvey and Dr Charlie O’Hara, their input and suggestions have been greatly appreciated. Equally important has been everyone else in the lab who I have had the chance to work with over the last three and a half years, who have all contributed to this thesis in some way. Special mentions have to go to Pablo, my second favourite Spaniard, for all his help in the lab and some hilarious but un-repeatable stories, to Stuart for in-depth discussions on the important things in life (TV and football), although some of his jokes need some work, and also the “fun gang” (Jan, Ross and Stuart) for occasionally letting me join them for a few drinks on a Friday night. These acknowledgments wouldn’t be complete without mentioning the important contribution of Ross, the ridiculous things he said every day provided a welcome distraction from chemistry. Finally to Ben, for constantly getting terrible songs stuck in my head all day, and being the only person in the lab who loves the Borders more than I do.

The thing I’ll remember most from this PhD is all the fantastic people I have had the chance to work with, and all the great memories of trips to Rothesay, the conference in Hawaii, the Retro Bar in Manchester, being part of the worst football team ever to play in the University of Strathclyde 5-a-side league, and being pushed to the limits of diabetes by eating more cake than I realised existed.

I would also like to take this opportunity to thank the following people; Dr Alan Kennedy, Dr Jan Klett, Dr Pablo Garcia-Álvarez, Dr Luca Russo and Prof. William Clegg (X-ray crystallography), Dr Dave Armstrong (DFT calculations), Dr John Parkinson and Craig Irving (NMR spectroscopy), Dr Pamela Alan (atomic absorption analysis), Pat Keating (GC/MS) and Denise Gilmour (Elemental analysis). I cannot thank them enough for giving up their time to help me, and I can only apologies to the X-ray crystallographers who have had to deal with numerous samples of my nemesis [(THF)4MgCl2] that I have sent their way.

A huge thank you to my Mum and Dad for all their guidance and support over the last 26 years. Even though they have no idea exactly what it is that I do, they still make the effort to appear interested in it (although I doubt they’ll ever read past this page).

Finally, and most importantly I want to say thank you to my girlfriend Kirsty, who even after all this time still manages to put up with me. Her support over the last few years has been so important, and I definitely couldn’t have done this without her. She’s the one who has to put up with me when things aren’t going so well, and always manages to get me smiling again. She has also been very understanding of me turning our kitchen into a make-shift office for the last few months. I promise we’ll go back to Hawaii sometime soon!

**Abstract**

Building on recent advances in zincate chemistry, but going beyond the state-of-the-art, this project sought to advance the understanding of the mechanisms involved in alkali metal-mediated zincation (AMM*Zn*), as well as design a new type of mixed-metal reagent, magnesium-zinc hybrids, focussing on their applications in nucleophilic additions to ketones and direct zinc-iodine exchange reactions.

Unveiling two new applications of the alkali metal TMP-zincates [(THF)Li(TMP)ZntBu2] (**1**) and [(TMEDA)Na(TMP)ZntBu2] (**3**), reaction with trimethyl(phenoxy)silane (**12**) allowed the isolation of the first intermediates of direct lateral zincation (D*l*Zn) of an aromatic substrate, while the reaction of **3** with benzoylferrocene (**17**) has shown that two competing pathways are available: (i) remote 1,6-nucleophilic addition of a *tert*-butyl group to the phenyl ring of **17** and (ii) simultaneous α-deprotonation of the substituted cyclopentadienyl ring and 1,2-addition of a *tert*-butyl anion to the carbonyl group of the ketone.

Shedding new light on the mechanism by which these alkali metal TMP-zincates react, the proposed intermediate species of the two-step mechanism (previously proposed by theoretical studies) [(THF)2Li(*o*-C6H4OMe)ZnMe2] (**26**) and [(THF)3Li(*o*-C6H4OMe)ZntBu2] (**29**) were prepared. Reactivity studies of **26** and **29** with TMP(H) provided the first tangible experimental evidence that the AMM*Zn* of anisole by **1** proceeds via a two-step mechanism, which is greatly influenced by both the nature of the alkyl groups of the zincate (Me vs. tBu) and the polarity of the solvent in which the reaction is performed (hexane/benzene vs. THF).

In addition, investigations into the seemingly simple stoichiometric salt metathesis reactions of Grignard reagents with ZnCl2 led to the isolation of a series of magnesium-zinc hybrid species [(THF)Mg(µ-Cl)2Zn(tBu)(Cl)] (**34**) and [(THF)Mg(µ-Cl)3ZnR}2] (R = tBu (**36**), nBu (**37**), Et (**38**), *o*-C6H4OMe (**39**)), formed via metathetical co-complexation. Altering the stoichiometry of these reactions (from 1:1 to 3:1) to mimic the conditions employed in ZnCl2 catalysed reactions of Grignard reagents led to the formation of the alkyl-rich Mg-Zn hybrids [{Mg2Cl3(THF)6}+{ZntBu3}-] (**40**) and [{Mg2Cl3(THF)6}+{Zn2Et5}-] (**41**).

Probing the possible applications of these Mg-Zn hybrid species in various key synthetic methodologies revealed that **41** can be employed both stoichiometrically, and catalytically in the presence of an excess of EtMgCl, to perform the chemoselective alkylation of ketones. In contrast, the analogous 1st generation Mg-Zn hybrid **38** displayed diminished reactivity even towards activated ketones, although the addition of LiCl resulted in improved reactivity, hinting at the existence of trimetallic Li-Mg-Zn hybrid species in solution. Furthermore, **40** can readily undergo direct Zn-I exchange reactions with a wide range of functionalised aryl iodide substrates, demonstrating high atom economy, with the subsequent aryl-zincate species proving to be valuable precursors for Pd-catalysed Negishi cross-coupling reactions.

**Publications**

1. “*Assessing the Reactivity of Sodium Zincate [(TMEDA)Na(TMP)ZntBu2] Towards Benzoylferrocene: Deprotonative Metalation vs Alkylation Reactions*”; E. Hevia, A. R. Kennedy and **M. D. McCall**, *Dalton Trans.,* **2012**, 41, 98.

2. “*Expanding Mg-Zn hybrid chemistry: Inorganic salt effects in addition reactions of organozinc reagents to trifluoromethyl acetophenone and implications for a synergistic lithium-magnesium-zinc activation"*; D. R. Armstrong, W. Clegg, P. García-Alvarez, A. R. Kennedy, **M. D. McCall**, L. Russo and E. Hevia, *Chem. Eur. J.*, **2011**,17, 8333.

3. *“Shedding New Light on ZnCl2-Mediated Addition Reactions of Grignard Reagents to Ketones: Structural Authentication of Key Intermediates and Diffusion-Ordered NMR Studies"*; D. R. Armstrong, W. Clegg, P. García-Alvarez, **M. D. McCall**, L. Nuttall, A. R. Kennedy, L. Russo and E. Hevia, *Chem. Eur. J.*, **2011**, 17, 4470.

4. “*Hidden Complexity of Stoichiometric and Catalytic Metathesis Reactions: Synthesis and Structural Elucidation of Mg-Zn hybrids”*; J. Z. Chua, P. García-Álvarez, E. Hevia, A. R. Kennedy and **M. D. McCall**, *Procd. Natl. Acad. Sci. USA*, **2010**, 107, 5294.

5. “*New Insights into Addition Reactions of Dialkylzinc Reagents to Trifluoromethyl Ketones: Structural Authentication of a β-hydride Elimination Product Containing a Tetranuclear Zinc Chain*”; E. Hevia, A. R. Kennedy, J. Klett, Z. Livingstone and **M. D. McCall**, *Dalton Trans.*, **2010**, 39, 520.

6. “*Donor-dictated Interlocking Co-complexation Reactions of LiNHDipp with Dimethylzinc: Synthesis and Structures of New Methyl(amido)zincates*”; W. Clegg, D. V. Graham, E. Herd, E. Hevia, A. R. Kennedy, **M. D. McCall** and L. Russo, *Inorg. Chem.*, **2009**, *48*, 5320.

7. “*Direct Lateral Metallation using Alkali-Metal Mediated Zincation (AMMZn): SiC-H vs Si-O Bond Cleavage*”; E. Hevia, A. R. Kennedy, J. Klett and M. D. McCall, *Chem. Commun.*, 2009, 3240.

8. “*Closer Insight into the Reactivity of TMP-dialkyl Zincates in Directed ortho-Zincation of Anisole: Experimental Evidence of Amido Basicity and Structural Elucidation of Key Reaction Intermediates*”; W. Clegg, B. Conway, E. Hevia, **M. D. McCall**, L. Russo and R. E. Mulvey, *J. Am. Chem. Soc.*, **2009**, *131*, 2375.

Conference Oral Presentations

1. “*Exposing the Hidden Complexity of Metathesis Reactions: Applications of Mg-Zn Hybrids*”; International Congress of the Pacifichem Societies, Hawaii, USA, December 2010.

2. “*Organozinc Reagents: Structural Tailoring for Mixed-Metal Applications*”; University of Strathclyde Postgraduate Awards lecture, October 2010.

3. “*New Insights into Direct Zincation of Aromatic Molecules*”; Universities of Scotland Inorganic Conference, Heriot-Watt University, Edinburgh, September 2009.

4. “*New Insights into Direct Zincation of Aromatic Molecules*”; University of Strathclyde, Inorganic Section Research Day, June 2009.

5. “*New Insights into Direct Zincation of Aromatic Molecules*”; 4th WestChem Research Day, University of Glasgow, June 2009.

Conference Poster Presentations

1. “*Expanding Magnesium-Zinc Hybrid Chemistry*”; Universities of Scotland Inorganic Conference, Glasgow University, July 2011.

2. “*Exposing the Hidden Complexity of Stoichiometric and Catalytic Metathesis Reactions: Elucidation and Applications of Mg-Zn Hybrids*”; Universities of Scotland Inorganic Conference, Durham University, July 2010.

3. “*Hidden Complexity of Salt Metathesis Reaction*”; RSC Dalton Division Meeting on Main Group Chemistry, University of Manchester, September 2009. Awarded 1st prize in poster competition.

4. “*Hidden Complexity of Salt Metathesis Reaction*”; 42nd IUPAC Congress, Scottish Exhibition and Conference Centre, Glasgow, July 2009.

5. “*Unveiling the Reactivity of TMP-dialkyl Zincates in Directed ortho-Zincation of Anisole*”; Universities of Scotland Inorganic Conference, University of Strathclyde, Glasgow, September 2008.

Table of Common Abbreviations

acac Acetylacetonate

AMM*Zn* Alkali metal mediated zincation

CCDB Cambridge crystallographic database

CDDE Cyclododecene

CIP Contacted ion-pair

COSY 1H-1H correlated spectroscopy

Cp Cyclopentadiene anion (C5H5)-

Cp’ Substituted cyclopentadiene ring of benzoylferrocene

CSI-MS Cold-spray ionization - mass spectroscopy

DA Diisopropylamide

DFT Density functional theory

Dl*Zn* Direct lateral zincation

DMG Direct metallating group

D*o*L Directed *ortho* lithiation

D*o*M Directed *ortho* metallation

DOSY Diffusion ordered NMR spectroscopy

dppf 1,1’-bis(diphenylphosphino)ferrocene

ee Enantiomeric excess (%)

ESI-MS Electrospray ionization - mass spectroscopy

FAAS Flame atomic absorption spectroscopy

GC-FID Gas chromatography - flame ionization detector

HSQC Heteronuclear single quantum correlation spectroscopy

LDA Lithium diisopropylamide

(-)-MIB (2*S*)-3-*exo*-(Morpholino)isoborneol

MOM ethers Methoxymethyl ethers

MVK Methyl vinyl ketone

NMR Nuclear magnetic resonance

ODE 1-octadiene

PGSE Pulsed gradient spin echo

PhN Phenylnaphthalene

PMDETA *N*,*N*,*N*',*N*",*N*"-pentamethyldiethylenetriamine

SSIP Solvent separated ion-pair

TEEDA *N*,*N*,*N*’,*N*’-tetraethylethylenediamine

TEMPO (2,2,6,6-Tetramethylpiperidin-1-yl)oxyl

THF Tetrahydrofuran

THP Tetrahydropyran

TMEDA *N*,*N*,*N*',*N*'-tetramethylethylenediamine

TMP 2,2,6,6-tetramethylpiperidide

TMP(H) 2,2,6,6-tetramethylpiperidine

TMS Trimethylsilyl or tetramethylsilane

TPhN 1,2,3,4-tetraphenylnaphthalene

TSǂ Transition state

Table of Contents

Acknowledgements I

Abstract III

Publications V

Oral Presentations VI

Poster Presentations VII

Table of Common Abbreviations VIII

Table of Contents X

Table of Compounds XIV

Chapter 1: Introduction to organozinc chemistry and recent advances in alkali metal zincates

1.1 Organozinc reagents 1

1.2 Alkali metal zincates 4

1.2.1 Preparation of alkali metal zincates 6

1.2.2Applications of alkali metal zincates in 1,4-conjugate addition and 1,2-addition 7

1.2.3 Applications of alkali metal zincates in metal-halogen exchange 9

# 1.3 Alkali metal TMP-zincates in directed *ortho* metallation (D*o*M) 15

1.3.1 Directed *ortho* metallation (D*o*M) 15

1.3.2 Recent developments in alkali metal TMP-zincates 16

1.3.3 Zinc modified turbo-Hauser bases 29

Chapter 2: Unveiling new reactivity patterns in AMM*Zn* 32

2.1 Direct lateral metallation using alkali metal-mediated zincation (AMM*Zn*):

SiC-H vs. Si-O bond cleavage 32

2.1.1 Investigating the reactivity of trimethyl(phenoxy)silane (12) with 1 and 3 34

2.1.2 Investigating the regioselectivity of the Dl*Zn* of **12** by **1** 42

2.1.3 Applications of Dl*Zn* to other silyl-substituted substrates 46

2.1.4 Conclusions 48

2.2 Assessing the reactivity of sodium TMP-zincate (3) towards benzoylferrocene:

deprotonative metallation vs. alkylation reactions 49

2.2.1 Investigating the reactivity of benzoylferrocene (17) with sodium TMP-zincate (3) 52

2.2.2 Electrophilic quenching studies 57

2.2.3 Further investigation into the two-fold activation of ZntBu2 in **3** 61

2.2.4 Conclusions 63

**2.3 Summary** 64

Chapter 3: Closer insight into the mechanisms of AMM*Zn* of anisole by TMP-dialkyl zincates 65

**3.1 Theoretical studies on D*o*M of anisole using lithium TMP-zincates** 66

**3.2 Theoretical studies on metallation of benzene using sodium TMP-zincates** 69

**3.3 New insight into the reactivity of lithium TMP-zincates in D*o*M of anisole** 72

3.3.1 Co-complexation of [(THF)2Li4(*o*-C6H4OMe)4] (25) with ZnMe2 74

3.3.2 Co-complexation of [(THF)2Li4(*o*-C6H4OMe)4] (25) with ZntBu2 78

3.3.3 Investigating the reactivity of [(THF)2Li(*o*-C6H4OMe)ZnMe2] (26) with TMP(H) 83

3.3.4 Investigating the reactivity of [(THF)3Li(*o*-C6H4OMe)ZntBu2](29) with TMP(H) 87

3.3.5 Disproportionation process of 26 and 29 to [(THF)2Li2Zn(*o*-C6H4OMe)4](27) 97

3.4 Conclusions 101

Chapter 4: Investigating metathesis reactions of Grignard reagents with ZnCl2 104

4.1 Investigating the salt metathesis reaction of tBuMgCl and ZnCl2 108

4.2 Further studies on the metathesis reaction Grignard reagents with ZnCl2 115

**4.3 Applications of ZnCl2 catalysed reactions of Grignard reagents** 123

**4.4 Investigating the salt metathesis reaction of tBuMgCl with substoichiometric**

**amounts of ZnCl2** 128

**4.5 Investigating the salt metathesis reaction of EtMgCl with substoichiometric**

**amounts of ZnCl2** 134

**4.6 Conclusions** 146

Chapter 5: Expanding Mg-Zn hybrid chemistry: nucleophilic alkylation reactions of ketones 148

5.1 Investigating the reactivity of [{Mg2Cl3(THF)6}+{Zn2Et5}-] (41) in stoichiometric alkylation reactions of benzophenone 149

5.2 Investigating the catalytic activity of [{Mg2Cl3(THF)6}+{Zn2Et5}-] (41) in alkylation

reactions of benzophenone by EtMgCl 157

5.3 Insight into the constitution of the reduction products 160

5.4 Assessing the reactivity of 1st generation magnesium-zinc hybrid reagents in nucleophilic

addition reactions: salt effects 163

5.5 Conclusions 169

Chapter 6: Applying magnesium-zinc hybrid chemistry to direct Zn-I exchange and Pd-catalysed

Negishi cross-coupling reactions 171

**6.1 Investigating the reactivity of [{Mg2Cl3(THF)+{Zn*t*Bu3}-] (40) in Zn-I exchange and**

**Pd-catalysed Negishi cross-coupling Reactions** 172

**6.2 Expanding the scope of Zn-I exchange and Negishi cross-coupling reactions of**

**[{Mg2Cl3(THF)6}+{Zn*t*Bu3}-] (40) to 2-Iodotolune and 3-Iodotoluene** 178

**6.3 Investigating Zn-I Exchange and Negishi cross-coupling reactions of 40 with**

**iodoanisole substrates** 180

**6.4 Investigating Zn-I exchange and Negishi Cross-coupling reactions of 40 with**

**iodobenzonitrile substrates** 184

6.5 Conclusions 196

Chapter 7: General experimental techniques & procedures 198

7.1 General experimental techniques 198

7.1.1 Schlenk techniques 198

7.1.2 Glove box 199

7.1.3 Solvent purification 200

7.1.4 Standardisation of organometallic reagents 200

7.1.5 Analytical procedures 201

7.2 Synthesis of common starting materials 201

7.2.1 Synthesis of ZntBu2 201

7.2.2 Synthesis of BuNa 201

7.2.3 Synthesis of [(THF)Li(TMP)ZntBu2] (1) 202

7.2.4 Synthesis of [(TMEDA)Na(TMP)ZntBu2] (3) 202

7.3 Synthesis of Products 202

7.3.1 Synthesis of [(THF)Li(TMP){PhOSi(CH3)2CH2}ZntBu] (13) 202

7.3.2 Synthesis of [(TMEDA)Na(TMP){PhOSi(CH3)2CH2}ZntBu] (14) 203

7.3.3 Synthesis of [(PhOSiMe3)Li(TMP){PhOSi(CH3)2CH2}ZntBu] (16) 203

7.3.4 Synthesis of [(TMEDA)Na(μ-TMP)Zn{OC(tBu)(*η*5-C5H3)Fe(*η*5-C5H5)}] (18) 204

7.3.5 Synthesis of [PhC(OH)(*t*Bu)(*η*5-C5H3I)Fe(*η*5-C5H5)] (19) and

[4-*t*Bu-C6H4C(=O)(*η*5-C5H4)Fe(*η*5-C5H5)] (21) 205

7.3.6 Synthesis of [C6H5C(OH)tBu(*η*5-C5H3D)Fe(*η*5-C5H5)] (23) and

[tBu-C6H4CO(*η*5-C5H4)Fe(*η*5-C5H5)] (21) 206

7.3.7 Synthesis of [C6H5C(OH)tBu(*η*5-C5H4)Fe(*η*5-C5H5)] (24) and

[tBu-C6H4CO(*η*5-C5H4)Fe(*η*5-C5H5)] (21) 207

7.3.8 Synthesis of [Li4(*o*-C6H4OMe)4(THF)2] (25) 207

7.3.9 [(THF)2Li(*o*-C6H4OMe)ZnMe2] (26) 208

7.3.10 Synthesis of [(THF)2Li2Zn(*o*-C6H4OMe)4] (27) 209

7.3.11 Synthesis of [(TMEDA)Li(*o*-C6H4OMe)ZnMe2] (28) 209

7.3.12 Synthesis of [(THF)3Li(*o*-C6H4OMe)ZntBu2] (29) 210

7.3.13 [(PMDETA)Li(*o*-C6H4OMe)ZntBu2] (30) 210

7.3.14 Synthesis of [(THF)Li(TMP)ZnMe2] (32) 211

7.3.15 Synthesis of [(THF)4Mg(μ-Cl)2Zn(tBu)(Cl)](34) 211

7.3.16 Synthesis of [{(THF)2Mg(μ-Cl)3ZnR}2](36-39) 212

7.3.17 Synthesis of [{Mg2Cl3(THF)6}+{ZntBu3}-](40) 213

7.3.18 Synthesis of [{Mg2Cl3(THF)6}+{Zn2Et5}-] (41) 214

7.3.19 Synthesis of [{Mg3(OEt)2Br3(THF)6}+{Zn2Et5}‒] (42) 215

7.3.20 Synthesis of [{Mg2Cl3(THF)6}+{Mg2(OC(Et)Ph2)2Cl3(THF)}‒] (44) 215

7.3.21 Synthesis of [{(THF)5Mg3Cl4{OC(H)Ph(CF3)}2] (50) 216

7.3.22 General procedure for alkylation studies of 2,2,2-trifluoroacetophenone (47) 216

7.3.23 Synthesis of [{Mg2Cl3(THF)6}+{Zn(*p*-C6H4Me) 3}-](52) 217

7.3.24 Cross-coupling reaction of 52 with iodobenzene 217

7.3.25 General procedure for monitoring Zn-I exchange reactions of 40 with functionalised

aryl iodide substrates in d8-THF 218

7.3.26 General procedure for Zn-I exchange reactions of 40 with functionalised aryl iodide

substrates followed by Negishi cross-coupling with iodobenzene 218

(a) 4-methylbiphenyl (53) 219

(b) 3-methylbiphenyl (56) 219

(c) 2-methylbiphenyl (57) 220

(d) 2-methoxybiphenyl (61) 220

(e) 3-methoxybiphenyl (62) 221

(f) 4-methoxybiphenyl (63) 221

(g) 2-cyanobiphenyl (70) 221

(h) 3-cyanobiphenyl (71) 222

(i) 4-cyanobiphenyl (72) 222

7.3.27 Synthesis of [{Mg(THF)6}2+{Zn(*o*-C6H4OMe)3}2-](64) 222

7.3.28 Synthesis of [(THF)4MgCl{N≡C-C6H4}ZnI(C6H4CN)(THF)] (68) 223

Chapter 8: Overview, conclusions and outlook 224

Bibliography 230

CD-ROM: Appendices (X-ray crystallographic data, DOSY studies, DFT studies and publications)

Table of Compounds

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| **Number** | **Compound** | **Number** | **Compound** | |
| **1** |  | **2** |  | |
| **3** |  | **4** |  | |
| **5** |  | **6** |  | |
| **7** |  | **8** |  | |
| **9** |  | **10** |  | |
| **11** |  | **12** |  | |
| **13** |  | **14** |  | |
| **Number** | **Compound** | **Number** | **Compound** | |
| **15** |  | **16** |  | |
| **17** |  | **18** |  | |
| **19** |  | **20** |  | |
| **21** |  | **22** |  | |
| **23** |  | **24** |  | |
| **25** |  | **26** |  | |
| **27** |  | **28** |  | |
| **Number** | **Compound** | **Number** | **Compound** |
| **29** |  | **30** |  | |
| **31** |  | **32** |  | |
| **33** |  | **34** |  | |
| **35** |  | **36** |  | |
| **37** |  | **38** |  | |
| **39** |  | **40** |  | |
| **41** |  | **42** |  | |
| **43** |  | **44** |  | |
| **Number** | **Compound** | **Number** | **Compound** |
| **45** |  | **46** |  | |
| **47** |  | **48** |  | |
| **49** |  | **50** |  | |
| **51** |  | **52** |  | |
| **53** |  | **54** |  | |
| **55** |  | **56** |  | |
| **57** |  | **58** |  | |
| **59** |  | **60** |  | |
| **61** |  | **62** |  | |
| **63** |  | **64** |  | |
| **65** |  | **66** |  | |
| **Number** | **Compound** | **Number** | **Compound** | |
| **67** |  | **68** |  | |
| **69** |  | **70** |  | |
| **71** |  | **72** |  | |