The Development of
Gold-Catalysed Reactions

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Degree of Doctor of Philosophy

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May, 2012

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Abstract

This thesis describes the research carried out in the development of novel homogeneous gold(I)-catalysed reactions. It is written in such a format as to describe chronologically the process in which the study and our understanding evolved.

- Chapter one provides an introduction to homogeneous gold catalysis and in particular the development and reactivity of gold(I) catalysts as powerful activators of unsaturated carbon-carbon species towards nucleophilic attack.

- Chapter two describes our initial work in this area and how we were able to show that gold(I) can catalyse the intramolecular rearrangements of cyclopropenes with ester functionalities.

- Chapter three presents the intermolecular addition of alcohol to 3,3-dialkyl and aryl cyclopropenes catalysed by gold(I).

- Chapter four describes how we were able to utilise our knowledge of gold(I)-catalysed reactions with cyclopropenes to completely switch the regiochemistry of gold(I)-catalysed hydroalkoxylation of allenes from producing primary alkyl allylic ethers to tertiary alkyl allylic ethers. We were also able to show that by trapping the vinyl gold intermediate we could further functionalise the tertiary allylic ether.

- Chapter five describes the results of the addition of furan to cyclopropenes catalysed by gold(I) to produce functionalised conjugated trienes.

- Chapter six presents initial work into the gold(I) catalysed addition of indoles to cyclopropenes. Also described in this chapter are the attempted reactions with a variety of alternative nucleophiles.
This thesis is dedicated to my father Henry Gordon Hadfield.
Acknowledgements

I would firstly like to thank Ai-Lan for her belief in me, support and energy during my time in the lab, but even more so her patience and guidance while writing up. I could not have wished for a better supervisor and I feel the relationship we quickly developed lead to a fantastic and productive working environment.

Dr. Alan Boyd provided fantastic support with “his” NMR especially with some difficult “crude” analysis and even more so for his help with the characterisation of our clean products.

I would like to acknowledge the moral support and friendship of Alan (Big Dawg) McComb, who made the monotony of countless columns seem a great deal less monotonous. I would also like to show my gratitude to Paul Young who took over from where I left off and is flying with the scraps he was left with. Ross McLaren and Amellie Heuer-Jungemann for their work on the vinyl gold trapping and Jurgen Bauer’s work in the alcohol addition to cyclopropenes aided our research a great deal.

I acknowledge ScotCHEM for their funding towards my PhD and, Heriot-Watt University along with the Alumni for helping fund my trip to the ACS meeting in Boston. It was an amazing opportunity to present my work on a prestigious global stage.

I would also like to thank my family and in particular Diane for her support and understanding of why most weekends in the past year or so have been dominated by a PC screen and a mound of papers, books and spectra.

Finally, a big thank you to my mum and dad who gave me the confidence and financial support to get me through my studies, without their love and belief I would not be in the position I am today.
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School/PGI: Engineering and Physical Sciences

Version: Final

Degree Sought: Degree of Doctor of Philosophy in Chemistry

Declaration

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2) where appropriate, I have made acknowledgement of the work of others and have made reference to work carried out in collaboration with other persons
3) the thesis is the correct version of the thesis for submission and is the same version as any electronic versions submitted*
4) my thesis for the award referred to, deposited in the Heriot-Watt University Library, should be made available for loan or photocopying and be available via the Institutional Repository, subject to such conditions as the Librarian may require
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Date Submitted:

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Received in the SSC by (name in capitals): 

Method of Submission
(Handed in to SSC; posted through internal/external mail):

E-thesis Submitted (mandatory for final theses)

Signature: Date:
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Abbreviations

\( \delta \)  
NMR chemical shift

\( \text{Å} \)  
Angstrøm

\( p\text{-ABSA} \)  
\emph{para}-acetamidobenzenesulfonyl azide

\begin{center}
\includegraphics[width=0.2\textwidth]{abse.png}
\end{center}

Ac  
acetyl

AgOTf  
silver triflate

approx.  
approximately

app.  
an apparent

aq.  
aqueous

Ar  
aryl

Bu  
butyl

\( ^{13}\text{C NMR} \)  
carbon nuclear magnetic resonance

cat.  
catalyst

Cl  
chemical ionisation

Cy  
cyclohexyl

d  
doublet

DBU  
1,8-diazabicyclo[5.4.0]undec-7-ene

\begin{center}
\includegraphics[width=0.2\textwidth]{dbu.png}
\end{center}

DCE  
dichloroethane

DCM  
dichloromethane

DEPT  
distortionless enhancement by polarisation transfer

\( ^{\circ}\text{C} \)  
degrees Celsius

DFT  
density functional theory

DMF  
dimethylformamide

DNBA  
2,4-dinitrobenzenesulfonic acid

dr  
diasteromeric ratio

DTBM-Segphos  
5,5'-bis[di(3,5-di-\emph{tert}-butyl-4-methoxyphenyl) phosphino]-4,4'-bi-1,3-benzodioxole

ee  
enantiomeric excess
equiv.     equivalents
ESI     electrospray ionisation
Et     ethyl
EtOH     ethanol
der     diethyl ether
g     gram(s)
h     hour(s)
HBr     hydrobromic Acid
HPLC     high pressure liquid chromatography
HSbF$_6$     fluoroantimonic Acid
$^1$H NMR     proton nuclear magnetic resonance
Hz     Hertz
IPA     isopropyl Alcohol
$^3$Pr     isopropyl
IPr     2,6-diisopropylphenyl imidazolium
IR     infra red spectroscopy
$J$     NMR coupling constant
KMnO$_4$     potassium permanganate
KOH     potassium hydroxide
l     litre(s)
M     molar (moles/litre)
m     multiplet
md     medium
Me     methyl
MeCN     acetonitrile
MeOH     methanol
mg     milligrams
MgSO$_4$     magnesium sulfate
MHz     mega Hertz
min(s)     minute(s)
ml     millilitre(s)
mmol     millimoles
moly dip     aqueous ammonium molybdate-sulfuric acid solution
m/z     mass/charge ratio
<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Full Form</th>
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<tbody>
<tr>
<td>aBuOH</td>
<td>nonyl butanol</td>
</tr>
<tr>
<td>NHC</td>
<td>N-heterocyclic carbene</td>
</tr>
<tr>
<td>NH₄Cl</td>
<td>ammonium chloride</td>
</tr>
<tr>
<td>NMR</td>
<td>nuclear magnetic resonance</td>
</tr>
<tr>
<td>NU</td>
<td>nucleophile</td>
</tr>
<tr>
<td>o</td>
<td>ortho</td>
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<td>methoxy</td>
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<td>para</td>
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<tr>
<td>R</td>
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</tr>
<tr>
<td>RT</td>
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</tr>
<tr>
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<td>retention time</td>
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<td>starting material</td>
</tr>
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</tr>
<tr>
<td>t</td>
<td>triplet</td>
</tr>
<tr>
<td>tBuOH</td>
<td>tertiary butanol</td>
</tr>
<tr>
<td>Temp.</td>
<td>temperature</td>
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<tr>
<td>Tf</td>
<td>trifluoromethane sulfonate (triflate)</td>
</tr>
<tr>
<td>TfOH</td>
<td>triflic acid</td>
</tr>
<tr>
<td>TFA</td>
<td>trifluoroacetic acid</td>
</tr>
<tr>
<td>THF</td>
<td>tetrahydrofuran</td>
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<td>TLC</td>
<td>thin layer chromatography</td>
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<td>toluene</td>
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<tr>
<td>UV</td>
<td>ultraviolet</td>
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