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Maximilian Joost

Synthesis and Original Reactivity of Copper and Gold Complexes

σ -Bond Coordination, Oxidative
Addition, Migratory Insertion



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Synthesis and Original Reactivity of Copper and Gold Complexes

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Doctoral Thesis accepted by
the Paul Sabatier University, Toulouse, France

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M. Joost, L. Estévez, S. Mallet-Ladeira, K. Miqueu, A. Amgoune, D. Bourissou, *Angew. Chem. Int. Ed.* **2015**, *54*, 5236–5240.

“Enhanced π -Backdonation from Gold(I): Isolation of Original Carbonyl and Carbene Complexes”

M. Joost, L. Estévez, S. Mallet-Ladeira, K. Miqueu, A. Amgoune, D. Bourissou, *Angew. Chem. Int. Ed.* **2014**, *53*, 14512–14516.

“Facile Oxidative Addition of Aryl Iodides to Gold(I) by Ligand Design: Bending Turns on Reactivity”

M. Joost, A. Zeineddine, L. Estévez, S. Mallet-Ladeira, K. Miqueu, A. Amgoune, D. Bourissou, *J. Am. Chem. Soc.* **2014**, *136*, 14654–14657.

“Mechanisms of *syn*-Insertion of Alkynes and Allenes into Gold-Silicon Bonds: a Comprehensive Experimental/Theoretical Study”

M. Joost, L. Estévez, S. Mallet-Ladeira, K. Miqueu, A. Amgoune, D. Bourissou, *J. Am. Chem. Soc.* **2014**, *136*, 10373–10382.

“Direct Evidence for Intermolecular Oxidative Addition of σ (Si-Si) Bonds to Gold”

M. Joost, P. Gualco, Y. Coppel, K. Miqueu, C. E. Kefalidis, L. Maron, A. Amgoune, D. Bourissou, *Angew. Chem. Int. Ed.* **2014**, *53*, 747–751.

“Direct *syn* Insertion of Alkynes and Allenes into Au-Si Bonds”

M. Joost, P. Gualco, S. Mallet-Ladeira, A. Amgoune, D. Bourissou, *Angew. Chem. Int. Ed.* **2013**, *52*, 7160–7163.

“ σ -SiH Complexes of Copper: Experimental Evidence and Computational Analysis”

M. Joost, S. Mallet-Ladeira, K. Miqueu, A. Amgoune, D. Bourissou, *Organometallics* **2013**, *32*, 898–902.

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For my family

Supervisors' Foreword

Transition metal complexes occupy a forefront position in homogeneous catalysis thanks to their ability to promote a wide range of unique reactions in a selective manner, allowing the synthesis of sophisticated organic molecules and materials. These important achievements have been made possible thanks to intensive and constant fundamental organometallic research seeking to understand how metal complexes work and how to tailor their electronic and geometric properties to a specific need.

In striking contrast, the development of gold complexes in homogeneous catalysis was lagging well behind for a long time. Gold was long considered as chemically inert and thus synthetically useless. This situation changed dramatically a few decades ago and the 2000s have witnessed a real “gold rush” in catalysis. However, all the catalytic applications of gold complexes are essentially based on a unique reactivity, namely the electrophilic activation of CC multiple bonds, meaning that gold behaves as a soft Lewis acid. This noble metal was considered inappropriate to promote the key elementary reactions involved in transition metal catalytic cycles, in particular oxidative addition and migratory insertion processes.

When Dr. Maximilian Joost started his Ph.D. in 2011, very little was known about the reactivity of gold complexes towards these elementary reactions. Maximilian carried out fundamental organometallic studies to gain comprehensive knowledge into the properties of gold complexes, in particular into the parameters governing their reactivity. Thanks to a rational ligand design approach, he showed for the first time that the oxidative addition of aryl halides as well as carbon–carbon bonds is possible with gold, and also evidenced an unprecedented *syn* insertion process with gold.

The experimental work combined with computational investigations has provided valuable information on the bonding, structure and reactivity of new gold complexes. Key parameters controlling the reactivity of gold towards oxidative addition reactions have been precisely identified. This thesis highlights novel reactivity patterns of gold complexes that may guide and inspire the development of new catalytic transformations.

Toulouse, France
March 2015

Dr. Abderrahmane Amgoune
Dr. Didier Bourissou

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In numerous parts of this thesis, the experimental data is accompanied by theoretical calculations to contribute to the analysis and understanding. I am thankful to Dr. Karinne Miqueu and Dr. Laura Estévez, as well as to Prof. Dr. Laurent Maron and Dr. Christos Kefalidis for these important contributions.

I acknowledge the support of all of the analytical and technical staff of the Institut de Chimie de Toulouse, and I am especially grateful for help and assistance by the members of the NMR and the X-Ray crystallography services.

Furthermore, I am grateful to all the staff at the Laboratoire Hétérochimie Fondamentale et Appliquée for providing a well-honed, efficient research environment. I would like to thank Dr. Ghenwa Bouhadir, Prof. Dr. Blanca Martin-Vaca, Olivier Thillaye de Boullay, Dr. Julien Monot, Dr. Tsuyoshi Kato, Dr. Noel Nebra and Dr. Nicolas Mézailles for valuable scientific discussions, as well as my fellow coworkers in the lab for stimulating and inspiring exchange. Among many, I am especially indebted to Dr. Marc Devillard, Dr. Yannick Escudie, Dr. Johannes Guenther, Feriel Rekhroukh and Dr. Amos Rosenthal. Abdallah Zeineddine is thanked for valuable experimental contributions.

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Abbreviations

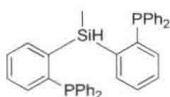
Ad	2-Adamantyl group
Alk	Generic alkyl group
Ar	Generic aryl group
BArF ₂₀	Tetrakis(pentafluorophenyl)borate
BArF ₂₄	Tetrakis(bis(3,5-trifluoromethyl)phenyl)borate
CMD	Concerted metallation/deprotonation
cod	Cyclooctadiene
CSA	Camphersulfonic acid
Cy	Cyclohexyl group
deg	Degree
DFT	Density functional theory
Dipp	(2,6-diisopropyl)phenyl group
DMAD	Dimethyl acetylenedicarboxylate
E	Main group element
Elt. Anal.	Elemental analysis
EPR	Electron paramagnetic resonance
eq.	Equivalent
ESI	Electrospray ionization
EWG	Electron-withdrawing group
FT	Fourier transformed
GIAO	Gauge-including atomic orbital
HOMO	Highest occupied molecular orbital
HRMS	High resolution mass spectrometry
IGLO	Individual gauge for localized orbitals
IMes	<i>N,N'</i> -bis(2,4,6-trimethylphenyl)imidazol-2-ylidene
IPr	<i>N,N'</i> -bis(2,6-diisopropylphenyl)imidazol-2-ylidene
IR	Infrared
L	Generic neutral, 2-electron donor ligand
LUMO	Lowest unoccupied molecular orbital
M	Transition metal
Mes	Mesityl group

Mp	Melting point
NBO	Natural bond orbital
NHC	<i>N</i> -heterocyclic carbene
NLMO	Natural localized molecular orbital
NMR	Nuclear magnetic resonance
NPA	Natural population analysis
PCM	Polarizable continuum model
PES	Potential energy surface
pin	Pinacol
RC	Reaction coordinate
RECP	Relativistic effective core potential
Selectfluor	1-Chloromethyl-4-fluoro-1,4-diazoniabicyclo[2.2.2]octane bis (tetrafluoroborate)
SMD	Universal solvation model based on solute electron density
TEMPO	(2,2,6,6-Tetramethyl-piperidin-1-yl)oxyl
THF	Tetrahydrofuran
THT	Tetrahydrothiophene
Tol	<i>p</i> -Tolyl group
TPA	1,3,5-triaza-7-phospha-adamantane
TS	Transition state
Ts	Tosyl (<i>p</i> -toluenesulfonyl) group
vdW	van der Waals
X	F, Cl, Br or I
Xanthphos	4,5-Bis(diphenylphosphino)-9,9-dimethylxanthene
XRD	X-ray diffraction

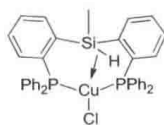
List of Compounds

Chapter 2: σ -SiH Coordination to Cu(I)

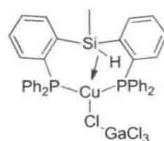
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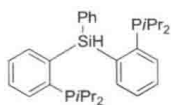
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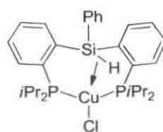
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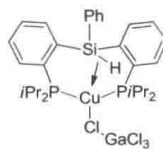
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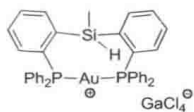
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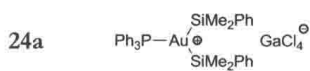
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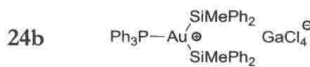
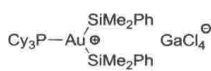
Chapter 4: Migratory Insertion at Au(I)

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|---------|--|----|--|
| 8 | $\text{Ph}_3\text{P}-\text{Au}-\text{Si}^t\text{BuPh}_2$ | 15 | |
| 9 | | 16 | |
| 9-Sn | | 17 | |
| 9-Allyl | | 18 | |
| 9-Aryl | | 19 | $\text{Me}_3\text{P}-\text{Au}-\text{Si}^t\text{BuPh}_2$ |
| 10 | | 20 | |
| 11 | | 21 | |
| 12 | | 22 | |
| 13 | | 23 | |
| 14 | $\text{Ph}_3\text{P}-\text{Au}-\text{SiPh}_3$ | | |

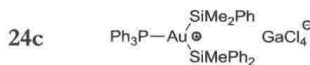
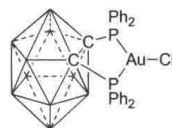
Chapter 5: Oxidative Addition at Gold(I)



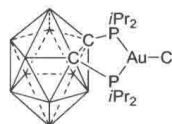
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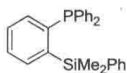
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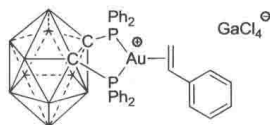
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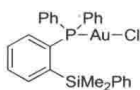
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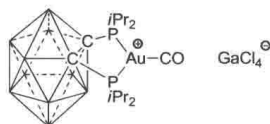
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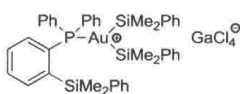
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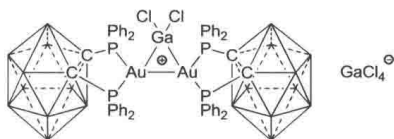
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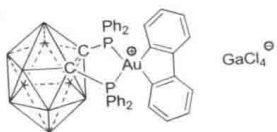
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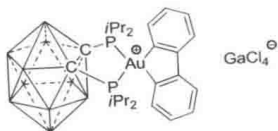
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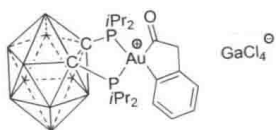
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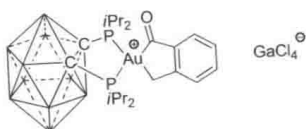
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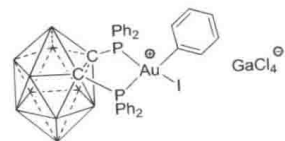
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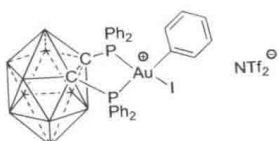
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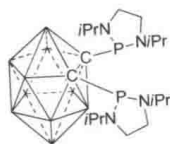
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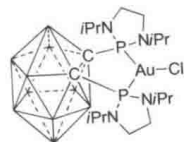
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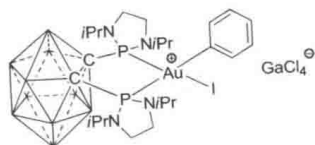
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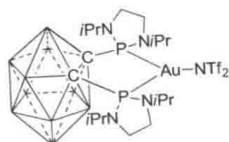
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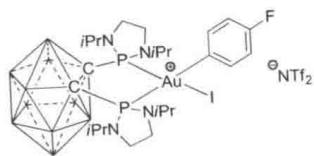
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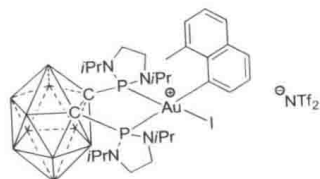
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General Remarks

The work presented in this dissertation was carried out in the Laboratoire Hétérochimie Fondamentale et Appliquée at the Université de Toulouse III—Paul Sabatier under the guidance of Dr. Abderrahmane Amgoune and Dr. Didier Bourissou from October 2011 to May 2014. Computational studies accompanying this work were carried out by Dr. Karinne Miqueu and coworkers at the Institut des Sciences Analytiques et de Physicochimie pour l'Environnement et les Matériaux (Université de Pau et des pays de l'Adour) and Prof. Dr. Laurent Maron and coworkers at the Laboratoire de Physique et Chimie de Nano-Objets (Université de Toulouse III—Paul Sabatier).

General Procedures

The reactions and manipulations reported in this manuscript were carried out under an atmosphere of dry argon using standard Schlenk techniques or in an argon-filled glovebox, if not otherwise stated. Dichloromethane, diethyl ether, pentane, tetrahydrofuran and toluene were dried by passage through activated molecular sieves (3 Å), using an mBraun solvent purification system. Fluorobenzene and hexamethyldisiloxane were dried by stirring with activated powdered molecular sieves (3 Å) for at least 24 h and subsequent filtration. Solvents were degassed by multiple freeze-pump-thaw cycles. Deuterated solvents were dried by stirring with activated powdered molecular sieves (3 Å) for at least 24 h and subsequent filtration.

o-Lithiated triphenylphosphine, *o*-lithiated phenyldiisopropylphosphine [1], chloro [1,3-bis(2,6-diisopropyl)phenyl]imidazol-2-ylidene)gold(I) [2], 1-bromo-2-diphenylphosphinobenzene [3], 1,1,2-trimethyl-1,2,2-triphenyldisilane [4], 1,2-bis(diphenylphosphino)-1,2-dicarba-*closo*-dodecaborane [5], 1,2-bis(diisopropylphosphino)-1,2-dicarba-*closo*-dodecaborane [6], chloro-[1,2-bis(diphenylphosphino)-1,2-dicarba-*closo*-dodecaborane- $\kappa^2 P, P'$]gold(I) [7], biphenylene [8], benzocyclobutenone [9], dilithio-1,2-dicarba-*closo*-dodecaborane [10], 2-chloro-1,3-diisopropyl-1,3,2-diazaphospholidine [11] were prepared according to reported procedures. [AuCl(THT)] was obtained from Umicore (Brussels, Belgium) as a generous gift. 1,2-Dicarba-*closo*-dodecaborane was purchased from KatChem (Prague, Czech Republic). All other starting materials were purchased from Aldrich (Saint-Quentin Fallavier, France),