COINAGE METAL(I) HALIDE COMPLEXES STABILIZED THROUGH GERMYLENES AND GERMANECHALCOGENONES

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by

DHIRENDRA YADAV

Department of Chemistry

Submitted

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Dedicated to My Parents

Certificate

This is to certify that the thesis entitled "**Coinage Metal(I) Halide Complexes Stabilized through Germylenes and Germanechalcogenones**" being submitted by **Mr. Dhirendra Yadav** (Entry No.: 2009CYZ8173) to **Indian Institute of Technology Delhi**, for the award of the degree of **Doctor of Philosophy**, is a record of bonafide research work carried out by him. **Mr. Dhirendra Yadav** has worked under my supervision and has fulfilled all the requirements for the submission of his PhD thesis, which to my knowledge has reached the requisite standard and is worthy of consideration for the award of PhD degree.

The work embodied in this thesis has not been submitted, in part or full, to other University or Institute for the award of any degree or diploma.

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Abstract

The thesis entitled *"Coinage Metal(I) Halide Complexes Stabilized through Germylenes and Germanechalcogenones"* presents the details about the study of various aminotroponiminate (ATI) ligand stabilized Ge(II) and Ge(IV) compounds as ligands for the group 11 metal(I) halides. The thesis is divided into the six chapters. A brief description about each chapter is given below:

***Chapter 1*:** This chapter gives a brief overview about metallylenes, their isolation, and reactivity. Under the reactivity, the use of metallylenes as ligands for the stabilization of metal complexes is focussed. Subsequently, the aim of the thesis is mentioned.

***Chapter 2*:** In this chapter, methods of drying solvents used in synthesis and NMR spectroscopic studies are mentioned. Commercial sources and synthetic methodology for various starting materials are provided. Details regarding the synthetic techniques, apparatus, instruments used for analyses, crystallographic software, structure visualization software, chemical structure drawing program, and theoretical studies are also discussed.

***Chapter 3*:** The use of aminotroponiminato(chloro)germylene [(*i*-Bu)$_2$ATIGeCl] (**3a**) (ATI = aminotroponiminate) as a ligand to stabilize copper(I) iodide complexes is presented. The reaction of compound **3a** with CuI in acetonitrile, afforded an aminotroponiminato (chloro)germylene stabilized copper(I) iodide complex [{(*i*-Bu)$_2$ATIGeCl}$_2$(Cu$_4$I$_4$)(CH$_3$CN)$_2$] (**3b**) with a tetrameric distorted cubane type Cu$_4$I$_4$ core. The reaction of compound **3a** in dichloromethane with CuI in the presence of two equivalents of pyridine resulted in the first germylene stabilized copper(I) iodide complex [{(*i*-Bu)$_2$ATIGeCl}(CuI)(C$_5$H$_5$N)$_2$] (**3c**) with a monomeric CuI core. A reaction of compound **3a** with equimolar amounts of CuI and pyridine in

dichloromethane resulted in a copper(I) iodide complex [{(*i*-Bu)$_2$ATIGeCl}$_2$(Cu$_2$I$_2$)(C$_5$H$_5$N)$_2$] (**3d**) with a dimeric Cu$_2$I$_2$ core. Interestingly, an interconversion between compounds **3c** and **3d** and conversion of compound **3b** to compounds **3c** and **3d** under suitable conditions are also reported. The compounds **3b**–**3d** have been characterized by multinuclear NMR spectroscopy and single-crystal X-ray diffraction studies. The copper atoms in all these complexes are tetracoordinate and the Ge(II)-Cu(I) bond lengths in complexes **3b**, **3c**, and **3d** are 2.341(1), 2.308(1), and 2.345(1) Å, respectively. Compound **3c** was tested for its catalytic activity towards C-S coupling reactions and found to be an efficient catalyst.

***Chapter 4*:** Reaction of an aminotroponiminato(chloro)germylene [(*t*-Bu)$_2$ATIGeCl] (**4a**) (ATI = aminotroponiminate) with phenyllithium afforded phenyl germylene [(*t*-Bu)$_2$ATIGePh] (Ph = phenyl) (**4b**) which is used as a ligand to isolate various germylene stabilized copper(I) halide complexes. Reactions of phenyl germylene **4b** with CuX (X = Cl, Br·SMe$_2$, I) in a 2:1 ratio afforded germylene stabilized mononuclear copper(I) halide complexes [{(*t*-Bu)$_2$ATIGePh}$_2$CuX] (X = Cl **4c**, Br **4d**, I **4e**). Further, the reaction of compound **4b** with CuCl in a 1:1 ratio resulted in germylene stabilized trinuclear copper(I) chloride complex [{(*t*-Bu)$_2$ATIGePh}$_3$(CuCl)$_3$] (**4f**). Single crystal X-ray diffraction studies reveal the planar arrangement of copper atoms in these germylene copper complexes (**4c**-**4f**). These copper-germylene complexes efficiently catalyze the regioselective cycloaddition of alkynes and benzyl azide.

***Chapter 5*:** Use of a digermylene oxide as a ligand is demonstrated through the isolation of a series of group 11 metal(I) iodide complexes. Accordingly, the reactions of a digermylene oxide [{(*i*-Bu)$_2$ATIGe}$_2$O] (ATI = aminotroponiminate) (**5a**) with CuI under different conditions afforded [({(*i*-Bu)$_2$ATIGe}$_2$O)$_2$(Cu$_4$I$_4$)] (**5b**) with a Cu$_4$I$_4$ octahedral core, [({(*i*-

Bu)$_2$ATIGe}$_2$O)$_2$(Cu_3I_3)] (**5c**) with a Cu_3I_3 core, and [{(*i*-Bu)$_2$ATIGe}$_2$O(Cu_2I_2)(C_5H_5N)$_2$] (**5d**) with a butterfly type Cu_2I_2 core. The reactions of compound **5a** with AgI and AuI produced [({(*i*-Bu)$_2$ATIGe}$_2$O)$_2$(Ag_4I_4)] (**5e**) with a Ag_4I_4 octahedral core and [{(*i*-Bu)$_2$ATIGe}$_2$O(Au_2I_2)] (**5f**) with a Au_2I_2 core, respectively. The presence of metallophilic interactions in these compounds is shown through the single crystal X-ray diffraction and Atoms in Molecules (AIM) studies.

***Chapter 6*:** The potential of germanechalcogenones [ATI(Ge=E)(Ph)] (E = S **6a**, Se **6b**) to function as ligands has been demonstrated through the isolation of their coinage metal(I) iodide complexes [{(*t*-Bu)$_2$ATIGe(E)Ph}$_2$(M_2I_2)] (E = S, M = Cu **6c**; E = Se, M = Cu **6d**; E = S, M = Ag **6e**; E = Se, M = Ag **6f**; E = Se, M = Au **6g**). Crystallographic studies reveal the presence of cuprophilic (**6c**, **6d)**, argentophilic (**6f)** interactions in these complexes. Crystallographic data reveals the presence of a strong argentophilic interaction (2.950(1) Å) in complex **6f**, but is inconclusive in complex **6e** (3.470(1) Å). Using theoretical studies, proof for the presence and absence of argentophilic interactions in complexes **6f** and **6e** was obtained, respectively. Further, it is disclosed that the donor ability of the chalcogen atoms in the Ge=E→Ag-I moieties dictate the Ag···Ag interaction in the complexes **6e**-**f**.

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List of Symbols and Abbreviations

ATI	aminotroponiminate
%	percentage
°	degree
°C	degree centigrade
Å	angstrom
AIM	atoms in molecules
Anal	analysis
au	atomic unit
bcp	bond critical point
bs	broad singlet
Calcd	calculated
cm	centimeter
Cp*	pentamethylcyclopentadienyl
Cp	cyclopentadienyl
DCM	dichloromethane
dd	double doublet
deg	degree
DFT	density functional theory
Et	ethyl
Me	methyl
Ph	phenyl
n-Pr	*normal*-propyl
h	hour
HOMO	highest occupied molecular orbital
Hz	Hertz
i-Bu	*iso*-butyl
i-Pr	*iso*-propyl
K	kelvin
Kcal	kilocalorie
LUMO	lowest unoccupied molecular orbital
m/*z*	mass-to-charge ratio
Me	methyl
mg	milligram
MHz	megahertz
min.	minute
mL	milliliter
mmol	mill mole
MO	molecular orbital
Mp	melting point
NBO	natural bond orbital
NHC	*N*-heterocyclic carbene
nm	nanometer
NMR	nuclear magnetic resonance
NPA	natural population analysis
J	coupling constant
NHGe	*N*-heterocyclic germylene
g	gram
Ph	phenyl
ppm	parts per million
Py	pyridyl
Pz	pyrazolyl
rcp	ring critical point
rt	room temperature
t-Bu	*tertiary*-butyl

THF	tetrahydrofuran
TLC	thin layer chromatography
NRT	natural resonance theory
OTf	triflate
TMS	trimethylsilyl

WBI	Wiberg bond index
δ	(delta) chemical shift
ΔG	change in free energy
ΔH	change in enthalpy
λ	(lambda) wavelength