Coinage Metal Complexes of Germylene and Stannylene

Moushakhi Ghosh, † Nilanjana Sen, † and Shabana Khan *

ABSTRACT: Group 11 metal (M = Cu, Ag, Au) complexes of heavier tetrylenes (namely, germylene and stannylene) have been studied for several years now. However, the field is mainly unexplored for their potential application either in homogeneous catalysis or in photophysical properties regardless of how the current reports allude to the rich and fascinating chemistry of group 14 elements. In this mini-review, we attempted to summarize the recent advances of heavier tetrylene-stabilized coinage metal complexes, which are majorly dominated by structure elucidation studies. This comprehensive summary intends to help researchers design and fine-tune the tetrylene ligand framework that can lead to coinage metal complexes for future applications as photoemitters in organic light-emitting diode fabrication and efficient catalysts in homogeneous catalysis.

1. INTRODUCTION
The carbene-stabilized coinage metal complexes have exhibited excellent catalytic and photophysical properties.1 However, the coinage metal complexes of heavier congeners of carbene, namely, silylene, germylene, and stannylene, are still in their infancy. They have been mainly used in small-molecule activation, coordination to low valent species, and, nowadays, in homogeneous catalysis.2,3 Recently, we have summarized N-heterocyclic silylene coordinated coinage metal complexes and their potential application in homogeneous catalysis.4 However, a compilation of the germylene and stannylene coordinated coinage metal complexes remains to be addressed. This motivated us to revisit their existing literature to compile their unique bonding scenario with coinage metals, which demand more investigation. We have covered the literature since 2010 and segregated the content based on germylene/stannylene supported copper(I), silver(I), and gold(I) complexes.

2. TETRYLENE-SUPPORTED COINAGE METAL COMPLEXES

2.1. Germylene—Copper(I) Complexes. The behavior of tetrylenes as Lewis bases is characteristic of their coordination chemistry, enabling them to form various metal complexes. In 2012, Fulton and co-workers utilized the Lewis basicity of a germanium alkoxide \([\text{LGeO} \text{Bu}] (\text{L} = \text{HC}[\text{C}(\text{Me})\text{N}-2,6-\text{iPr}_2\text{C}_6\text{H}_3])\) and prepared dimeric germanium(II)—copper(I) iodide adduct 1 (Chart 1) with a four-membered bridged rhomboidal Cu$_2$I$_2$ core.5 This was the first structurally isolated three-coordinate copper(I) complex possessing a Cu$_2$I$_2$ ring attached to the germylene center. Similarly, Zhao and co-workers also reported two different types of copper(I) complexes, 2 and 3 (Chart 1), via the reaction of LGeMe (L = HC[C(\text{Me})N-2,6-\text{iPr}_2\text{C}_6\text{H}_3]) and (CuC$_6$F$_5$)$_4$.6 2 displays a bridged (CuC$_6$F$_5$)$_2$ unit, while 3 has a chain-like aggregation of (CuC$_6$F$_5$)$_4$ with the Cu—Cu bond distance ranging from 2.3819(11) to 2.4919(8) Å. Due to these cuprophilic interactions (d$^{10}$—d$^{10}$), 2 and 3 exhibit photoluminescence properties. The photophysical properties of 2 and 3 were also studied in DCM at room temperature. The copper complex 2 exhibits green luminescence ($\lambda_{\text{em}} = 497$ nm) upon excitation at $\lambda_{\text{ex}} = 336$ nm, whereas 3 shows a blue luminescence ($\lambda_{\text{em}} = 458$ nm) upon excitation at $\lambda_{\text{ex}} = 340$ nm. Stahl and co-workers reported an N-heterocyclic germylene—copper(I) complex 4 consisting of a four-step ladder-type structure. The ladder steps of 4 comprise Ge—Cu and Cu—Cl bonds alternatively, where Ge and copper centers adopt terminal and bridging binding modes (Chart 1).7 The quick shuttling of germylenes (between the terminal and bridging copper(I) centers) makes them magnetically and chemically equivalent. An example of β-diketiminate ligand stabilized (phenylethylnyl) germylene \([\text{LGe}(\text{C} \equiv \text{CPh})\text{CuC}_6\text{F}_5] (\text{L} = \text{HC}[\text{C}(\text{Me})\text{N}-2,6-\text{Pr}_2\text{C}_6\text{H}_3])\) was utilized by Roesky and co-workers with 0.25 equiv of...
Chart 1. Germylene and Stannylene Supported Copper(I) and Silver(I) Complexes
CuC₆F₅)₄, which led to the formation of \( \text{LGe(CōCPh)}\)-CuC₆F₅ (L = \text{HC[C(Me)N-2,6-iPr₂C₆H₃]₂})⁸, displaying an open coordination site at the Ge(II) center.

Hence, the authors treated it further with another equivalent of (CuC₆F₅)₄, which afforded complex 5.⁸ Complex 5 features a germylene coordinated to the copper(I), where the copper possesses a Lewis acidic C₆F₅ group.

The chemistry of aminotroponiminato chloro germylene \([\text{(iBu)}₂\text{ATI} \text{GeCl}, (\text{ATI} = \text{aminotroponiminate})]\) as a ligand was explored by Nagendran and co-workers in 2014.⁹ They performed various reactions with CuI by varying the stoichiometry and solvents to afford complexes 6–8 (Chart 1). In 6, the germylene center bears a tetrameric cubane of Cu₄I₄ with \( \mu^3 \)-bridging of iodine with three copper atoms, while 7 displays a dimeric Cu₂I₂ core. In continuation with the previous report in 2015, Nagendran and co-workers investigated the reactivity of a spacer-arranged di(germylene)oxide \([\text{(iBu)}₂\text{ATI} \text{Ge})₂\text{O}]\) with 2 equiv CuI for the synthesis of coinage metal complexes, reporting complex 9 with a Cu₄I₄ octahedral core and complex 10 with a trinuclear Cu₃I₃ core (Chart 1).¹⁰ Further addition of pyridine produced a structurally unique germylene- and pyridine-bound dimeric copper(I) complex, 11 (Chart 1).

Cabeza and co-workers utilized a benzamidinate-germylene \([\text{PhC(NtBu)}₂\text{GeBu}]\) and prepared copper(I) complexes, 12 and 13, upon treatment with 1 equiv of CuCl and 0.5 equiv of [Cu(MeCN)]₄[BF₄] respectively (Chart 1). Complex 12 attained a pseudocubane-type Cu₄(\( \mu^3\)-Cl)₄ core, while 13 (Chart 1) remained monomeric.¹¹ The authors also noted that benzamidinato tert-butyl germylene failed to stabilize any transition metal complexes, unlike silicon derivatives. Hence, the sterically demanding tert-butyl group plays an important role in stabilizing metal complexes. A half pincer-based germylene \([\text{(2-Et₂NCH₂-4,6-tBu₂-C₆H₂)} \text{GeCl}]\) was employed by Jambor and co-workers to treat with CuCl and CuI, which afforded the dimeric complexes 14 and 15 (Chart 1). Both complexes display a four-membered Cu₂X₂ moiety comprising Cu(\( \mu-X\)) (X = Cl, I) bridges.¹² They also isolated the mononuclear complexes, 16 and 17, via the reaction of 14 and 15 with 1 equiv of the corresponding germylene, respectively (Chart 1).¹³ Complexes 18 and 19 were prepared by reacting 17 with AgOAc and AgOTf, respectively.¹³ Complexes 16–19 have a tricoordinate central Cu atom attached with two chlorides and one Ge(II) atom. Interestingly, 16 and 17 were found to be catalytically active for the ring-opening polymerization of f-lactide.¹² This study explores the brighter future of germylene-supported coinage metal complexes, a new milestone in homogeneous catalysis.

2.2. Germylene–Silver(I) Complexes. The examples of germylene supported silver(I) complexes are comparatively

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Chart 2. Germylene and Stannylene Stabilized Gold(I) Complexes

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(CuC₆F₅)₄, which led to the formation of \( \text{LGe(CōCPh)}\)-CuC₆F₅ (L = \text{HC[C(Me)N-2,6-iPr₂C₆H₃]₂})⁸, displaying an open coordination site at the Ge(II) center.

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2.2. Germylene–Silver(I) Complexes. The examples of germylene supported silver(I) complexes are comparatively
limited. Heterobimetallic complex 20 was also synthesized by reacting pentafluorophenyl silver with LGe(C≡CPh)CuC6F5 (L = HC[C(Me)N-2,6-(Pr2NCH2)2]2), analogous to 5 (Chart 1).8 Another cationic complex ([LGe(C≡CPh)Ag][Ag(CF3OH)]2−) (Chart 1) was also formed with the addition of one more equivalent of pentafluorophenyl silver. For the silver compounds, 20 and 21, the persistence of Ge−Ag donor−acceptor bonding in solution is proved by the appearance of the blue luminescence band at 460 nm for 20 and green luminescence band at 526 nm for 21. Similarly, silver complexes 22 and 23, which are analogous to 12 and 13, were also reported (Chart 1) by Cabeza et al.11 Nagrendran and co-workers also investigated the reaction of bisgermylene [((Bu)2ATIGe)2O] with silver iodide to afford 24 (Chart 1), which contains a Ag4I4 octahedral core.30 Recently, the nucleophilic cationic Ge(II) center was utilized by the group of Majumdar toward the coordination with coinage metals.31 They isolated a biscoordinated cationic Ag(I) complex 25, which acquires a barbell-shaped structure (Chart 1). For 25, the trflate moiety is weakly coordinated to the Ag center. In line with this, So and co-workers reported the synthesis of the bis(germylimidylidene)silver(I) complex dication, 26a (Chart 1),15 which upon treatment with an N-heterocyclic carbene, IMe [IMe = :C{N(Me)C(Me)}2], afforded a bis(germylimidylidene)silver(I) complex dication 26b. Germilyimidene cations generally possess the ambiphilic nature of germylene and the high Lewis acidic character of the germacyl cation.

2.3. Stannylene–Silver(I) Complexes. To our surprise, there are no reports of stannylene-supported copper(I) complexes after 2010, and the examples of silver(I) complexes are also minimal. As an ongoing investigation on heavier tetraylene's coordination chemistry, we also performed a reaction of benzamidinato-stannylene [PhC(NtBu)2SnN(TMS)] with Ag2SbF6, which led to the formation of cationic silver complex 27, displaying weak Ag(I)······F interactions (Chart 1).16 This weak noncovalent interaction indicates a lower σ-donation of stannylene than its lighter congeners. Jambor and co-workers utilized the intermolecularly stabilized SnNS ligand and explored the coordination with different silver(I) salts (Chart 1).17 Complexes 28 and 29 were isolated from the reaction of (2,6-(Me2NCH2)2C6H3)SnCl with AgOAc and Ag(acac), respectively. Both structures comprise a central cubane core of Ag3Cl2. Further, the reaction of the SnNS ligand with (COD)Ag(Hfac) resulted in a monomeric complex 30 (Chart 1).17 However, the reaction with [(THF)Ag{(3,5-(CF3)2Pz)}2] produced 31, where stannylene acts as a donor ligand only. In a very recent report by Majumdar and co-workers, intermolecularly (ene-amide) stabilized stannylene was used to coordinate with coinage metal salts, producing complexes 32 and 33 (Chart 1). These complexes feature a mononuclear cationic silver(I) center, which is coordinated with two homoleptic stannylene molecules.18

2.4. Germylene–Gold(I) Complexes. NHC-stabilized gold(I) complexes are well-known for their catalytic application and photophysical properties due to Au······I interactions. However, tetraylene-supported gold(I) complexes are still not well explored. To begin with, Saffon and co-workers demonstrated the coordination of phosphaalkenyl germylene [([NHC]Ge(C≡CPh)CuC6F5)2; NHC = tPr2MeN(1,3-di-iso-propyl-4,5-dimethyl-imidazolin-2-ylidene)] with gold(I) salts19 and isolated 34 and 35 upon reaction with Au and AuCl-Me2S, respectively. Both possess similarly Ge······Au bonded adducts displaying a near-linear geometry (Chart 2). Following this, Cabeza and co-workers isolated 36 (Chart 2) by reacting 2 equiv of [Ge(N(SiMe3)2)2] with AuCl(THT). Compound 36 is formed via the insertion of one of the Ge(II) centers into the Au−Cl bond, and the gold center remains linearly attached to both the germanium centers of the ligand,20 where substitution of the THF ligand with Ge(N-(SiMe3)2)2 at the gold center is evident. In 2013, Roesky and co-workers isolated a mononuclear discordinate gold(I) complex 37 (Chart 2) from the reaction of (phenylethynyl)germylene and AuC6F5-SC6H4.21 However, the reaction of LGe(C≡CPh)CuC6F5 with AuC6F5-SC6H4 yielded 38 (Chart 2), a trimetallic Ge−Cu−Au compound with terminally bonded AuC6F5 at the Ge(II) center. Contemporarily, Cabeza et al. employed [PhC(NtBu)2GeBu] in the same context and prepared 39 (Chart 2).11 39 exhibits mononuclear nature, and the Au−Cl bond is linearly coordinated to the Ge(II) center. Similarly, digermylene oxide [((Bu)2ATIGe)2O] reaction with AuI afforded 40, which has a Au2I2 core with the Au−Au distance of 3.1562 Å, indicating the presence of an aurophilic interaction.9 The emission spectrum of 40 displays four peaks of the same intensity at 486, 460, 431, and 407 nm (λex = 360 nm), suggesting d9−d9 interaction. In 2016, Marschner and his team used an acyclic NHC (IMe4) stabilized Ge(HMDS)2 and performed a reaction with AuCN, which led to the formation of complex 41 (Chart 2).21 Here, instead of the NHC unit, the tris(trimethylsilyl) unit moves to the gold center, and the cyanide group gets attached to the germanium atom. In continuation of the previous discussion, the gold(I) analogue of 25 was also prepared via the reaction of the Ge(II) dication and AuCl-Me2S and led to the isolation of a biscoordinated Au(I) complex 42.14 In this case, the Ge−Au−Ge moiety is almost linear with two [LGe::]2+ units. Campos and co-workers used the GeCl2-dioxane complex and reacted it with cationic gold(I) complexes ([PMe2Ar5(H)]AuNTBu), generating germyl gold complexes. During halide abstraction with GaCl3 and NaBArF from germyl gold complexes,22 complexes 43−46 (Chart 2) were isolated. Subsequently, the electrophilicity of the Ge(II) center in 43−46 was tested by reacting them with 4-DMAP (4-dimethylaminopyridine), which resulted in 4-DMAP-coordinated complexes 47−50 (Chart 2). Recently, we have isolated [PhC(NtBu)2GeN(TMS)]-stabilized cationic gold(I) complexes, where benzene (51) and toluene (52) are present in η2 binding fashion.23 Complexes 51 and 52 were further used as efficient catalysts for glycosidation reaction. Moreover, 52 was found to be equally efficient like a silylene counterpart for the disaccharide formation. This study indicates that germylene-stabilized coinage metal complexes can be potential catalysts for various organic transformations.

2.5. Stannylene–Gold(I) Complexes. In contrast to silver and copper complexes, stannylene-supported gold complexes are comparatively more explored. As mentioned in the previous section, Cabeza and co-workers reported a similar reactivity with Sn(HMDS)2 and isolated 53, which is analogous to 36; only one THF group remains attached to one of the tin centers (Chart 2).20 Upon substituting the chloride ligand of 53 with LiBu and Li(HMDS), complexes 54 and 55 were obtained (Chart 2). On the same note, Marschner and his team utilized the NHC adduct of disilylated acyclic stannylene and reacted it with AuCN to afford 56 (Chart 2).21 Complex 56 bears three tris(trimethylsilyl)silyl ligands attached to the
tin and gold centers. Furthermore, Kira and co-workers reported adduct formation. A cyclic trigold anionic salt S7 (Chart 2) was isolated using the same cyclic dialkyl stannylene as the ligand backbone and Et3PAuCl followed by reduction with KC8, where the Au8 ring presents a regular triangle with the average Au−Au bond lengths of 2.9343(4) Å.24 Jambor and co-workers have also utilized the pincer-type N,C,N-coordinated stannylene as a ligand to synthesize the Sn(II)−Au(I) complex.17 The reaction of LSnCl [L = 2,6-(Me3NCH2)2C6H3] with AuCl-SMe2 provided the desired adduct S8 (Chart 2), displaying a linear Sn−Au−Cl bond and a weak aurophilic interaction of 3.0878(3) Å. Majumdar and co-workers recently reported the coordination toward Au(I) centers with pyridine-ene-amine stabilized stannylene.18 They isolated the ionic distannylene−gold complex S9 by utilizing the above-mentioned ligand and 0.5 equiv of AuCl and trimethylsilyl trifluoromethanesulfonate, where the stannylene center remains coordinated to the Au cation from both sides, forming an Sn−Au−Sn linear geometry.

3. SUMMARY AND FUTURE OUTLOOK

The availability of a lone pair of electrons and a vacant p-orbital makes tetrylenes an attractive class of donor ligands for the transition metals, which is very clear from the significant contributions in this area in the past decade. Among transition metals, coinage metals have a very special place due to their interesting catalytic and photophysical properties. The N-heterocyclic carbenes have a tunable singlet−triplet energy gap that offers exclusive electrophilicity and could show faster radiative decay. Also, nowadays, carbene-metal-amides (CMAs) (metal = Cu, Ag, Au) are gaining popularity as they provide strong photoluminescence properties because of the extended donor−acceptor systems. These aspects are missing for the heavier tetrylenes, which could be a fascinating area of research. However, it requires a systematic study to design efficient phospholuminescent complexes that can be utilized in OLED fabrication.

Similarly, homogeneous catalysis with heavier tetrylene-coordinated coinage metals is another gap in this area. Although many heavier tetrylene-stabilized coinage metal complexes have been isolated, only two reports prevail for their catalytic application. This mini-review mainly focuses on the coinage metal complexes of various germynes and stannynes and their associated structural properties. This discussion indicates that there is certainly much scope for tetrylene-ligated coinage metal complexes, majorly in the area of photophysical properties, as d10−d10 interactions are often responsible for attractive luminescent materials. We sincerely hope that due to their unique physical and chemical properties tetrylene coinage metal complexes will develop from academic curiosities to commercially important materials.

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Notes
The authors declare no competing financial interest.

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Nilanjan Sen obtained her B.Sc. degree from Scottish Church College, Calcutta University in 2014 and completed her M.Sc. from National Institute of Technology, Durgapur in 2016. Currently, she is working as a doctoral student under the supervision of Dr. Shabana Khan at Indian Institute of Science Education and Research, Pune. Her area of interest is synthesis of low valent p-block element based ligands and catalysis.

Shabana Khan obtained her Ph.D. degree from the Indian Institute of Technology, Delhi in 2008. Subsequently, she joined the research group of Prof. Herbert W. Roesky as a postdoctoral fellow, followed by a second post doc with Dr. Manuel Alcarazo at the Max Planck Institute for Coal Research. She joined IISER Pune in 2013. Currently, she is working as an associate professor in the Department of Chemistry, Indian Institute of Science Education and Research, Pune (IISER Pune), India.

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