

Coinage Metal Complexes of Germylene and Stannylene

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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 carbenes, 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 [LGeOtBu (L = HC[C(Me)N-2,6-*i*-Pr₂C₆H₃]₂)] and prepared dimeric germanium(II)–copper(I) iodide adduct **1** (Chart 1) with a four-membered bridged rhomboidal Cu₂I₂ core.⁵ This was the first structurally isolated three-coordinate copper(I) complex possessing a

Cu₂I₂ 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(Me)N-2,6-*i*-Pr₂C₆H₃]₂) and (CuC₆F₅)₄.⁶ **2** displays a bridged (CuC₆F₅)₂ unit, while **3** has a chain-like aggregation of (CuC₆F₅)₄ with the Cu–Cu bond distance ranging from 2.3819(11) to 2.4919(8) Å. Due to these cuprophilic interactions (d¹⁰–d¹⁰), **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 (λ_{em} = 497 nm) upon excitation at λ_{ex} = 336 nm, whereas **3** shows a blue luminescence (λ_{em} = 458 nm) upon excitation at λ_{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-diketiminato ligand stabilized (phenylethynyl) germylene [LGe(C≡CPh)CuC₆F₅ (L = HC[C(Me)N-2,6-*i*-Pr₂C₆H₃]₂)] was utilized by Roesky and co-workers with 0.25 equiv of

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Chart 1. Germylene and Stannylene Supported Copper(I) and Silver(I) Complexes

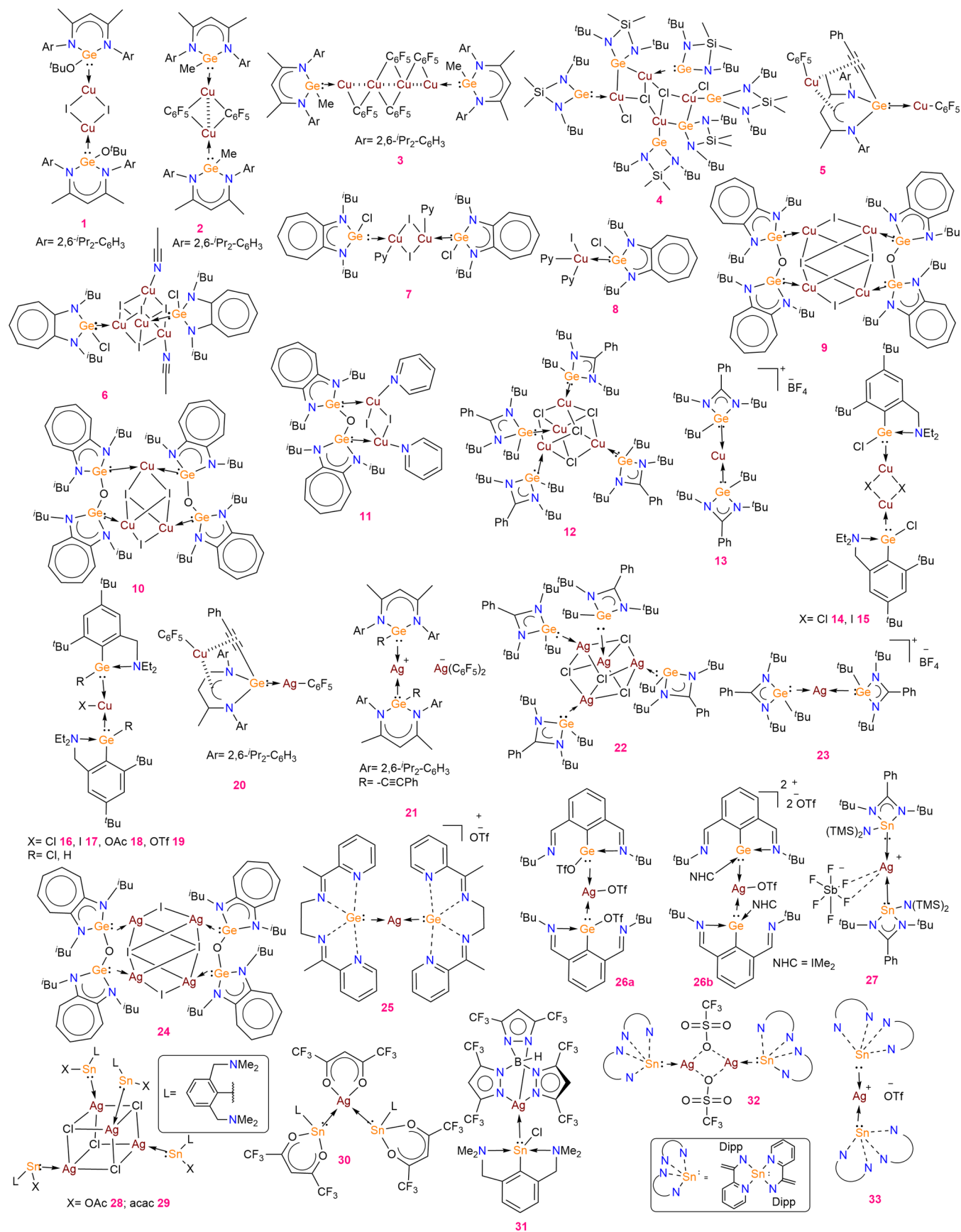
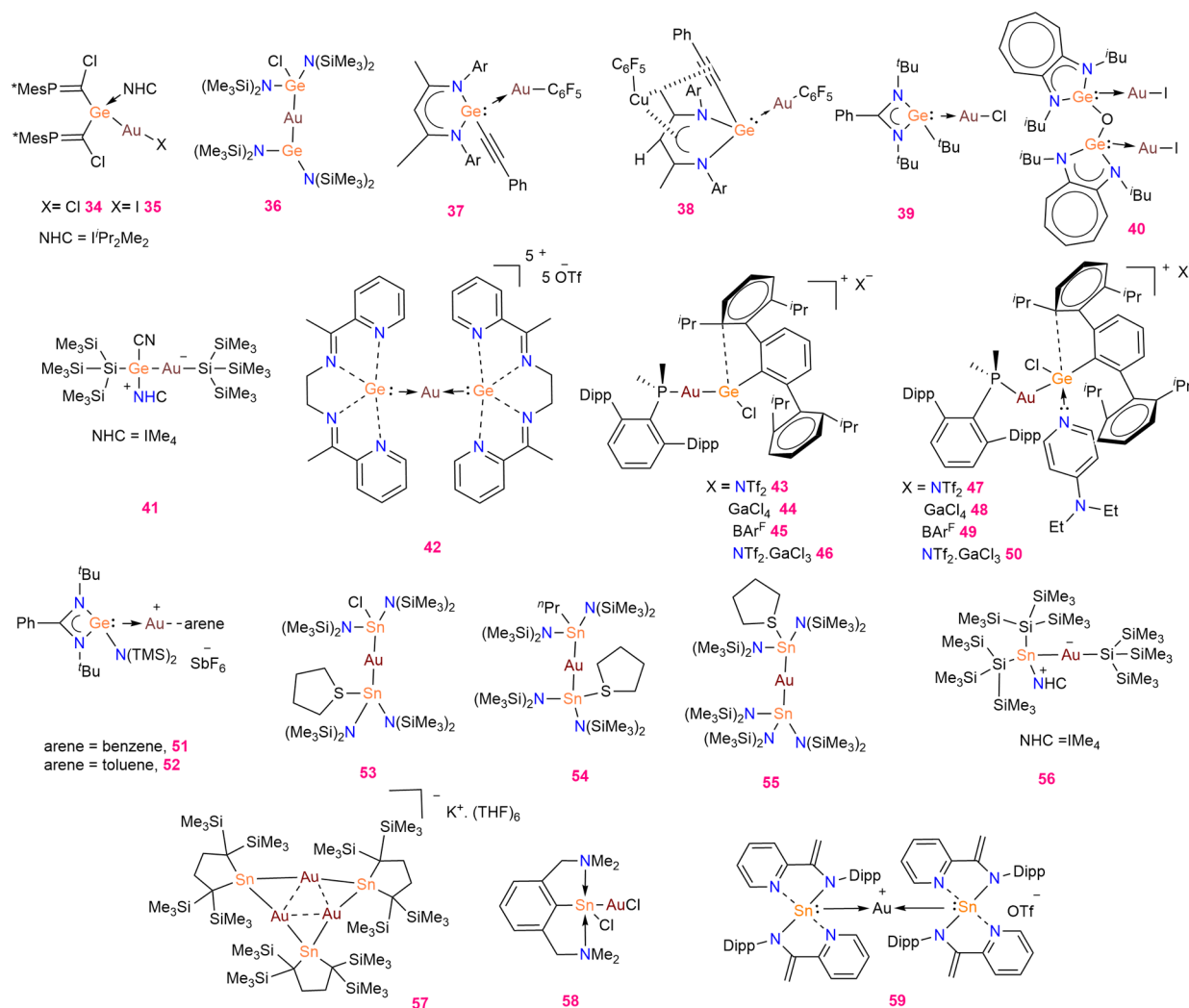


Chart 2. Gernylene and Stannylene Stabilized Gold(I) Complexes



(CuC_6F_5)₄, which led to the formation of $\text{LGe}(\text{C}\equiv\text{CPh})\text{-CuC}_6\text{F}_5$ ($\text{L} = \text{HC}[\text{C}(\text{Me})\text{N}-2,6\text{-iPr}_2\text{C}_6\text{H}_3]_2$),⁸ displaying an open coordination site at the Ge(II) center.

Hence, the authors treated it further with another equivalent of (CuC_6F_5)₄, which afforded complex **5**.⁸ Complex **5** features a gerylene coordinated to the copper(I), where the copper possesses a Lewis acidic C_6F_5 group.

The chemistry of aminotroponimato chloro gerylene [(*i*Bu)₂ATI₂GeCl, (ATI = aminotroponimato)] 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 gerylene center bears a tetrameric cubane of Cu_4I_4 with μ^3 bridging of iodine with three copper atoms, while **7** displays a dimeric Cu_2I_2 core. In continuation with the previous report in 2015, Nagendran and co-workers investigated the reactivity of a spacer-arranged di(gerylene)oxide [(*i*Bu)₂ATI₂Ge]₂O with 2 equiv CuI for the synthesis of coinage metal complexes, reporting complex **9** with a Cu_4I_4 octahedral core and complex **10** with a trinuclear Cu_3I_3 core (Chart 1).¹⁰ Further addition of pyridine produced a structurally unique gerylene- and pyridine-bound dimeric copper(I) complex, **11** (Chart 1).

Cabeza and co-workers utilized a benzamidinate-gerylene [$\text{PhC}(\text{NtBu})_2\text{Ge}(\text{tBu})$] and prepared copper(I) complexes, **12**

and **13**, upon treatment with 1 equiv of CuCl and 0.5 equiv of [$\text{Cu}(\text{MeCN})_4$][BF_4], respectively (Chart 1). Complex **12** attained a pseudocubane-type $\text{Cu}_4(\mu^3\text{-Cl})_4$ core, while **13** (Chart 1) remained monomeric.¹¹ The authors also noted that benzamidinato *tert*-butyl gerylene 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 gerylene [(2-Et₂NCH₂-4,6-*t*Bu₂-C₆H₂)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 Cu_2X_2 moiety comprising $\text{Cu}(\mu\text{-X})$ ($\text{X} = \text{Cl}, \text{I}$) bridges.¹² They also isolated the mononuclear complexes, **16** and **17**, via the reaction of **14** and **15** with 1 equiv of the corresponding gerylene, 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 *L*-lactide.¹² This study explores the brighter future of gerylene-supported coinage metal complexes, a new milestone in homogeneous catalysis.

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

limited. Heterobimetallic complex **20** was also synthesized by reacting pentafluorophenyl silver with $\text{LGe}(\text{C}\equiv\text{CPh})\text{CuC}_6\text{F}_5$ [$\text{L} = \text{HC}[\text{C}(\text{Me})\text{N}-2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3]_2$], analogous to **5** (Chart 1).⁸ Another cationic complex $[(\text{LGeC}\equiv\text{CPh})_2\text{Ag}]^+[\text{Ag}(\text{C}_6\text{F}_5)_2]^-$ (**21**) (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 Nagendran and co-workers also investigated the reaction of bisgermylene $[(^i\text{Bu})_2\text{ATiGe}_2\text{O}]$ with silver iodide to afford **24** (Chart 1), which contains a Ag_4I_4 octahedral core.¹⁰ Recently, the nucleophilic cationic Ge(II) center was utilized by the group of Majumdar toward the coordination with coinage metals.¹⁴ They isolated a biscoordinated cationic Ag(I) complex **25**, which acquires a barbell-shaped structure (Chart 1). For **25**, the triflate moiety is weakly coordinated to the Ag center. In line with this, So and co-workers reported the synthesis of the bis(germyliumylidene)silver(I) complex, **26a** (Chart 1),¹⁵ which upon treatment with an N-heterocyclic carbene, IME [$\text{IME} = \text{:C}\{\text{N}(\text{Me})\text{C}(\text{Me})\}_2$], afforded a bis(germyliumylidene)silver(I) complex dication **26b**. Germyliumylidene cations generally possess the ambiphilic nature of germylene and the high Lewis acidic character of the germyl cation.

2.3. Stannylyene–Silver(I) Complexes. To our surprise, there are no reports of stannylyene-supported copper(I) complexes after 2010, and the examples of silver(I) complexes are also minimal. As an ongoing investigation on heavier tetrylene's coinage metal chemistry, we also performed a reaction of benzamidinato-stannylyene $[\text{PhC}(\text{N}^i\text{Bu})_2\text{SnN}(\text{TMS})_2]$ with AgSbF_6 , which led to the formation of cationic silver complex **27**, displaying weak $\text{Ag}(\text{I})\cdots\text{F}$ interactions (Chart 1).¹⁶ This weak noncovalent interaction indicates a lower σ -donation of stannylyene than its lighter congeners. Jambor and co-workers utilized the intermolecularly stabilized NSnN ligand and explored the coordination with different silver(I) salts (Chart 1).¹⁷ Complexes **28** and **29** were isolated from the reaction of $(2,6\text{-}(\text{Me}_2\text{NCH}_2)_2\text{C}_6\text{H}_3)\text{SnCl}$ with AgOAc and $\text{Ag}(\text{acac})$, respectively. Both structures comprise a central cubane core of Ag_4Cl_4 . Further, the reaction of the NSnN ligand with $[(\text{COD})\text{Ag}(\text{Hfac})]$ resulted in a monomeric complex **30** (Chart 1).¹⁷ However, the reaction with $[(\text{THF})\text{Ag}\{\text{HB}(3,5\text{-}(\text{CF}_3)_2\text{Pz})_3\}]$ produced **31**, where stannylyene acts as a donor ligand only. In a very recent report by Majumdar and co-workers, intermolecularly (ene-amide) stabilized stannylyene 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 stannylyene 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 $\text{Au}\cdots\text{Au}$ interactions. However, tetrylene-supported gold(I) complexes are still not well explored. To begin with, Saffon and co-workers demonstrated the coordination of phosphalkenyl germylene $[(\text{NHC})\text{Ge}(\text{CCl} = \text{PMes}^*)_2]$; $\text{NHC} = \text{I}^i\text{Pr}_2\text{Me}_2$ (1,3-di-*iso*-propyl-4,5-dimethyl-imidazolin-2-ylidene)] with gold(I) salts¹⁹ and isolated **34** and **35** upon reaction with

AuI and $\text{AuCl}\cdot\text{Me}_2\text{S}$, respectively. Both possess similarly $\text{Ge} \rightarrow \text{Au}$ bonded adducts displaying a near-linear geometry (Chart 2). Following this, Cabeza and co-workers isolated **36** (Chart 2) by reacting 2 equiv of $[\text{Ge}(\text{N}(\text{SiMe}_3)_2)_2]$ with $\text{AuCl}(\text{THT})$. 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 THT ligand with $\text{Ge}(\text{N}(\text{SiMe}_3)_2)_2$ at the gold center is evident. In 2013, Roesky and co-workers isolated a mononuclear dicoordinate gold(I) complex **37** (Chart 2) from the reaction of (phenylethynyl) germylene and $\text{AuC}_6\text{F}_5\cdot\text{SC}_4\text{H}_8$.⁸ However, the reaction of $\text{LGe}(\text{C}\equiv\text{CPh})\text{CuC}_6\text{F}_5$ with $\text{AuC}_6\text{F}_5\cdot\text{SC}_4\text{H}_8$ yielded **38** (Chart 2), a trimetallic Ge–Cu–Au compound with terminally bounded AuC_6F_5 at the Ge(II) center.

Contemporarily, Cabeza et al. employed $[\text{PhC}(\text{N}^i\text{Bu})_2\text{Ge}^i\text{Bu}]$ 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 $[(^i\text{Bu})_2\text{ATiGe}_2\text{O}]$ reaction with AuI afforded **40**, which has a Au_2I_2 core with the Au–Au distance of 3.1562 Å, indicating the presence of an aurophilic interaction.¹⁰ The emission spectrum of **40** displays four peaks of the same intensity at 486, 460, 431, and 407 nm ($\lambda_{\text{ex}} = 360$ nm), suggesting $d^{10}\text{--}d^{10}$ interaction. In 2016, Marschner and his team used an acyclic NHC (IME4) stabilized $\text{Ge}(\text{HMDS})_2$ 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 $\text{AuCl}\cdot\text{Me}_2\text{S}$ 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 $[\text{LGe}]^{2+}$ units. Campos and co-workers used the GeCl_2 -dioxane complex and reacted it with cationic gold fragments $[(\text{PMe}_2\text{Ar}^{\text{Dipp}2})\text{AuNTf}_2]$, generating germyl gold complexes. During halide abstraction with GaCl_3 and NaBAR^{F} 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 $[\text{PhC}(\text{N}^i\text{Bu})_2\text{GeN}(\text{TMS})_2]$ -stabilized cationic gold(I) complexes, where benzene (**51**) and toluene (**52**) are present in η^2 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. Stannylyene–Gold(I) Complexes. In contrast to silver and copper complexes, stannylyene-supported gold complexes are comparatively more explored. As mentioned in the previous section, Cabeza and co-workers reported a similar reactivity with $\text{Sn}(\text{HMDS})_2$ and isolated **53**, which is analogous to **36**; only one THT group remains attached to one of the tin centers (Chart 2).²⁰ Upon substituting the chloride ligand of **53** with LiBu and $\text{Li}(\text{HMDS})$, complexes **54** and **55** were obtained (Chart 2). On the same note, Marschner and his team utilized the NHC adduct of disilylated acyclic stannylyene 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 **57** (Chart 2) was isolated using the same cyclic dialkyl stannylene as the ligand backbone and Et_3PAuCl followed by reduction with KC_8 , where the Au_3 ring presents a regular triangle with the average Au–Au bond lengths of $2.9343(4)\text{Å}$.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 [$\text{L} = 2,6\text{-(Me}_2\text{NCH}_2)_2\text{C}_6\text{H}_3$] with AuCl-SMe_2 provided the desired adduct **58** (Chart 2), displaying a linear Sn–Au–Cl bond and a weak aurophilic interaction of $3.0878(3)\text{Å}$. Majumdar and co-workers recently reported the coordination toward Au(I) centers with pyridine-ene-amide stabilized stannylene.¹⁸ They isolated the ionic distannylene–gold complex **59** 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 photoluminescent 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 germylenes and stannylenes 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 $d^{10}\text{--}d^{10}$ 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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Author Contributions

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Notes

The authors declare no competing financial interest.

Biographies

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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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