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Reactivity Studies of (Phenylethynyl)germylene LGeC≡CPh (L = HC[C(Me)N-2,6-*i*Pr$_2$C$_6$H$_3$]$_2$) toward Pentafluorophenylcopper(I), -silver(I), and -gold(I) Complexes

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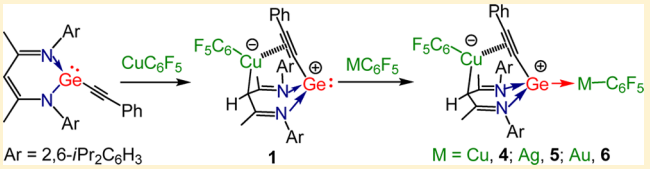
Supporting Information

ABSTRACT: Reactions of (phenylethynyl)germylene LGeC≡CPh (L = HC[C(Me)N-2,6-*i*Pr$_2$C$_6$H$_3$]$_2$) with 0.25 equiv of $(CuC_6F_5)_4$, 1 equiv of AgC_6F_5·MeCN, and 1 equiv of AuC_6F_5·SC_4H_8, respectively, yielded LGe(C≡CPh)CuC_6F_5 (**1**), $[(LGeC{\equiv}CPh)_2Ag]^+[Ag(C_6F_5)_2]^-$ (**2**), and LGe(C≡CPh)AuC_6F_5 (**3**). Complexes **1**−**3** were characterized by IR and NMR spectroscopy and X-ray crystallography. Compound **1** shows a bonding pattern of the CuC_6F_5 entity by both the phenylethynyl C≡C linkage and the L ligand backbone of the γ-C atom, while **3** exhibits a bonding mode of the AuC_6F_5 entity at the germylene center. Compound **2** is an ionic derivative featuring the Ge−Ag donor−acceptor bond formed under redistribution of the AgC_6F_5 entity. Further reactions of **1** with $(CuC_6F_5)_4$, AgC_6F_5·MeCN, and AuC_6F_5·SC_4H_8 afforded the complexes LGe(C≡CPh)$(CuC_6F_5)(MC_6F_5)$ (M = Cu (**4**), Ag (**5**), Au (**6**)). Compounds **4**−**6** were characterized by IR and NMR spectroscopy, and **5** and **6** were further investigated by X-ray crystallography. Compounds **4**−**6** all show an additional bonding of the respective MC_6F_5 moiety at the germylene center of **1**. These studies reveal a multiple donor reactivity of LGeC≡CPh. The slightly different Lewis acidic properties of the congeneric pentafluorophenylcopper(I), -silver(I), and -gold(I) complexes as acceptors are thus disclosed.



INTRODUCTION

A monoanionic N,N′-chelate ligand (L = HC[C(Me)N-2,6-*i*Pr$_2$C$_6$H$_3$]$_2$) has been extensively employed for synthesizing the heteroleptic germylene compound LGeR due to a kinetic intramolecular donor stabilization.[1] The R substituent has been tuned in a number of compounds with a germylene center.[2−4] The germylene center contains a lone pair of electrons capable of bonding to transition metals.[2c,f−i,5−7] Transition-metal−germylene chemistry has attracted special attention due to addition reactions of small molecules across the M−Ge bond.[2f,h,8−10] The group 10 and 11 metal germylene complexes have been found to activate small molecules such as H_2, CO_2,[8b] O_2,[8c,9] and COS.[8d] Recently, we and others have prepared complexes of the LGeR type with R = halide, alkyl, aryl, alkoxide, amide, phosphide, where L is a β-diketiminato,[3b,11] guanidinato,[2g] or pyrrolylaldiminato ligand.[12] We also prepared and structurally characterized complexes $[LGeMe(CuC_6F_5)_n]_2$ (*n* = 1, 2), LGe[C(SiMe$_3$)N$_2$]AgC_6F_5, and {LGe[C(SiMe$_3$)N$_2$]$(AgC_6F_5)_2$}$_2$ (L = HC[C(Me)N-2,6-*i*Pr$_2$C$_6$H$_3$]$_2$) with a M−Ge bond.[13] The incorporation of the R donor functionality at the germylene center provides a further bonding site for different metal fragments. It appears intriguing to see whether the donor R could collaborate or compete with the adjacent germylene center. During subsequent investigations by altering the R on the alkynyl functionality, we found multiple donor reactivities of such germylene species LGeC≡CPh toward pentafluorophenylcopper(I), -silver(I), and -gold(I) complexes. Different types of group 11 metal(I)−germylene complexes were generated to reveal the interaction of either the phenylethynyl donor or the germylene site. Herein, we report on these reactions and isolation and characterization of a series of new group 11 metal(I)−germylene complexes.

RESULTS AND DISCUSSION

The β-Diketiminato ligand-stabilized (phenylethynyl)-germylene LGeC≡CPh (L = HC[C(Me)N-2,6-*i*Pr$_2$C$_6$H$_3$]$_2$) has been reported as one of the products from the addition reaction of phenylacetylene with the ylide-like germylene L′Ge (L′ = HC[C(CH$_2$)N-2,6-*i*Pr$_2$C$_6$H$_3$][C(Me)N-2,6-*i*Pr$_2$C$_6$H$_3$]) in a low yield (16%).[14] For a preparation perspective, we used a convenient route to LGeC≡CPh by a one-pot synthesis through multiple-step metathesis reactions without isolation of the intermediate LGeCl. As summarized in Scheme 1, LH reacted with *n*BuLi to form LLi, which was directly used for the reaction with $GeCl_2$·(dioxane) to produce LGeCl. Subsequently, LGeCl reacted by chloride−phenylacetylide exchange

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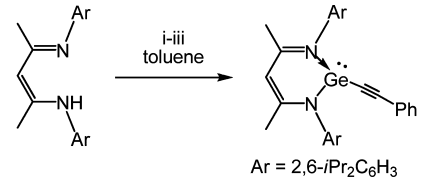
Scheme 1. One-Pot Synthesis of LGeC≡CPh



i. *n*BuLi, -30 °C-r.t., 12 h; ii. $GeCl_2$·dioxane, -30 °C-r.t., 12 h; iii. PhC≡CLi, -30 °C-r.t., 20 h.

with PhC≡CLi to afford LGeC≡CPh as a yellowish crystalline solid in high yield (90%).

Using LGeC≡CPh as the precursor, we first carried out the reaction with the pentafluorophenylcopper(I) complex. The reaction of LGeC≡CPh with 0.25 equiv of $(CuC_6F_5)_4$ proceeded smoothly in toluene at room temperature, and compound LGe(C≡CPh)CuC_6F_5 (**1**) was produced (Scheme 2). Compound **1** was isolated as light yellow crystals in a yield of 71%. It has been fully characterized by IR and NMR (^{1}H, ^{13}C, and ^{19}F) spectroscopy, X-ray crystallography, and elemental analysis. The structural analysis reveals that the formation of **1** may involve strong interactions of the CuC_6F_5 entity with both the phenylethynyl C≡C linkage and the L ligand backbone of the γ-CH group. This result is remarkably different from that of the previously reported copper(I)–germylene bonding reactions.[1h,9,13] The ^{1}H and ^{13}C NMR spectra display the L ligand backbone of the γ-CH proton resonance at δ 5.75 ppm and that of the carbon at δ 88.79 ppm. Both of these chemical shifts are significantly different in comparison to those of LGeC≡CPh (δ 5.10, 100.1 ppm)[14] and the related Ge–Cu-bound complexes $[LGe(Me)CuC_6F_5]_2$ (δ 4.76, 98.5 ppm) and $[LGe(Me)(CuC_6F_5)_2]_2$ (δ 4.73, 99.2 ppm).[13] The phenylethynyl C≡C carbon atoms resonate at a lower field (δ 121.18, 115.58 ppm) in comparison with those of LGeC≡CPh (δ 113.0, 103.3 ppm).[14] The IR spectrum shows the C≡C absorption band at $\tilde{\nu}$ 1957 cm^{-1}, which is red-shifted by ca. 160 cm^{-1} relative to that in LGeC≡CPh ($\tilde{\nu}$ 2117 cm^{-1}). These data indicate a π complexation between the CuC_6F_5 moiety and the C≡C linkage. In addition, the ^{19}F NMR spectrum exhibits resonances at δ −111.38 (*o*-*F*), −160.097 (*p*-*F*), and −161.51 ppm (*m*-*F*) with an integral intensity ratio of 2:1:2, similar to those typical of strong donor-molecule-interacting pentafluorophenylcopper(I) complexes.[15−18] The $\Delta\delta(^{19}F_{m,p})$ value of δ 1.42 ppm is indicative of a terminally bound C_6F_5 group at the Cu center.[18]

The crystal structure of **1** shows a bridging of the F_5C_6Cu–η^2-C≡CPh part over the central C_3N_2Ge ring by the γ-C and the Ge atom as a result of the strong interactions of the CuC_6F_5 entity with the C≡C linkage and the γ-CH group (Figure 1). The Cu–$C_{C\equiv C}$ bond lengths of 1.982(3) and 2.074(3) Å and the $C_{C\equiv C}$–Cu–$C_{C\equiv C}$ angle of 35.47(14)° are both in the range typical of those found in the copper(I)–η^2-alkynyl complexes (1.935(7)–2.201(5) Å, 35.4(2)–36.7(3)°).[19] Correspondingly, the C≡C bond length (1.234(4) Å) appears slightly longer than that in LGeC≡CPh (1.219(5) Å),[14] although the difference is negligible. These structural data evidence a Cu–η^2-C≡C π-complexation in agreement with the results from IR and NMR spectroscopy. The Cu···$C_{\gamma\text{-CH}}$ separation is 2.236(3) Å, which is longer than the Cu–$C_{C\equiv C}$ bond distance but distinctly shorter than the corresponding van der Waals radii (3.10 Å), indicating a strong Cu···$C_{\gamma\text{-CH}}$ interaction. Due to this interaction, the $C_{\gamma\text{-CH}}$ atom is in a tetrahedral geometry similar to those found in the P_{PCl_2}–$C_{\gamma\text{-CH}}$ bond compound $LPCl_2$[20] and the bicyclo[2.2.2]octane-type complex L″Ge (L″ = HC[C(CH_2)N-2,6-*i*$Pr_2C_6H_3$][C(Me)N-2,6-*i*$Pr_2C_6H_3$][C(R)=CH], R = H, Ph).[14] This suggests that a Cu–$C_{\gamma\text{-CH}}$ covalent bond is formed. However, we noted that within the C_3N_2Ge ring in **1** the C_{CN}–$C_{\gamma\text{-CH}}$ bond lengths (1.427(4) and 1.418(4) Å) and the C–N distances (1.326(4) and 1.319(4) Å) have changed slightly in comparison with those in LGeC≡CPh (C_{CN}–$C_{\gamma\text{-CH}}$ = 1.390(3) Å, C–N = 1.345(3) Å).[14] We also noted that in $LPCl_2$ a C_{CN}–$C_{\gamma\text{-CH}}$ single bond (1.514(5) and 1.532(5) Å) and a C–N double bond (1.281(5) and 1.284(5) Å) are formed.[20] Furthermore, in the compound $(L'''CpZrCl)_2[B(C_6F_5)_3]_2$ (L‴ = HC[C(Me)NC_6H_5]$_2$), the central C_3N_2 part

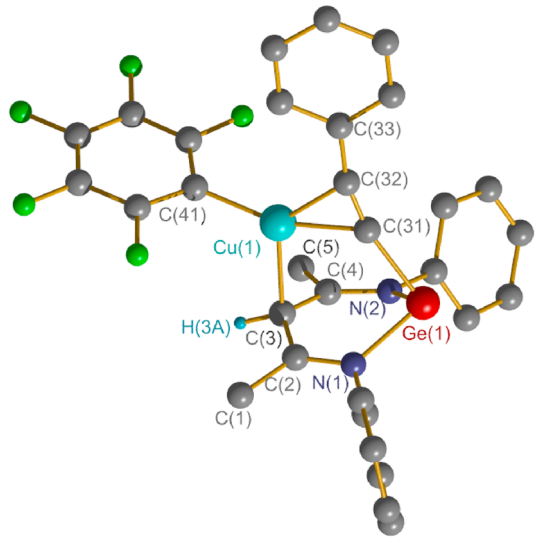
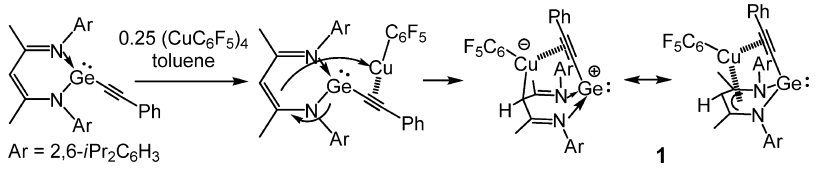


Figure 1. X-ray crystal structure of **1** with *i*Pr of the Ar at L omitted for clarity. Selected bond lengths (Å) and angles (deg): Ge(1)–N(1) = 1.994(2), Ge(1)–N(2) = 1.994(2), Ge(1)–C(31) = 2.043(3), Cu(1)–C(31) = 1.982(3), Cu(1)–C(32) = 2.074(3), Cu(1)–C(3) = 2.233(3), Cu(1)–C(41) = 1.943(3), N(1)–C(2) = 1.324(4), N(2)–C(4) = 1.320(4), C(1)–C(2) = 1.498(5), C(2)–C(3) = 1.416(5), C(3)–C(4) = 1.432(5), C(4)–C(5) = 1.502(5), C(31)–C(32) = 1.239(5); N(1)–Ge(1)–N(2) = 91.05(12), N(1)–Ge(1)–C(31) = 90.03(13), N(2)–Ge(1)–C(31) = 90.44(13), Ge(1)–C(31)–C(32) = 164.2(3), C(31)–C(32)–C(33) = 164.4(3), C(31)–Cu(1)–C(32) = 35.47(14).

Scheme 2. Plausible Bond Rearrangement Formation of 1



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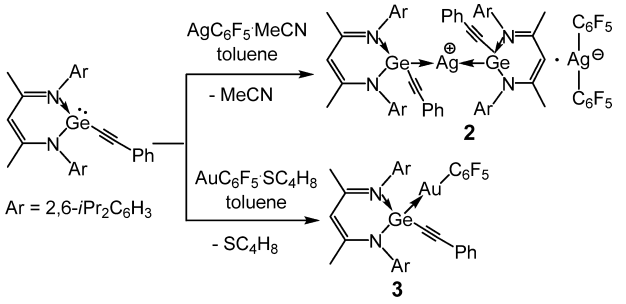
of the L‴ is found to be in a σ,π ligation at the Zr atom due to steric hindrance. The $C_{CN}-C_{\gamma\text{-}CH}$ bond lengths are 1.422(3) and 1.410(4) Å, and the C−N distances are 1.342(4) and 1.325(4) Å.[21] Obviously it can be seen, by focusing on the structural parameters of the C_3N_2Ge ring, that the $C_{CN}-C_{\gamma\text{-}CH}$ and C−N bond lengths in **1** are intermediate between those of conjugated and nonconjugated systems of other comparable complexes. However, small differences of the related parameters are indicated due to the different coordination environments. Therefore, we can argue that the formation of **1** might involve an initial bonding of the CuC_6F_5 entity at the phenylethynyl C≡C linkage followed by a nucleophilic attack of the C=C bond from the C_3N_2Ge skeleton to the Cu center, giving zwitterionic **1**, which largely resonates to a C_3N_2Ge ring···CuC_6F_5 π-complexation mode (Scheme 2).

Further reactions of LGeC≡CPh were performed with the pentafluorophenylsilver(I) and -gold(I) complexes, and as a result, different types of products were formed. Treatment of LGeC≡CPh with 1 equiv of AgC_6F_5·MeCN in toluene at room temperature in the absence of light resulted in the formation of $[(LGeC{\equiv}CPh)_2Ag]^+[Ag(C_6F_5)_2]^-$ (**2**). The reaction with 1 equiv of $AuC_6F_5{\cdot}SC_4H_8$ in toluene at room temperature produced $LGe(C{\equiv}CPh)(AuC_6F_5)$ (**3**) (Scheme 3). Compound **2** was isolated as yellow crystals in 65% yield

Scheme 3. Formation of 2 and 3



and **3** as colorless crystals in 71% yield. Both compounds have been confirmed by IR and NMR (^1H, ^{13}C, and ^{19}F) spectroscopy and X-ray crystallography. The IR spectra display the C≡C absorption band at $\tilde{\nu}$ 2145 for **2** and 2135 cm^{-1} for **3**. The ^{13}C NMR spectra record the C≡C carbon atom resonances at δ 123.55 and 104.72 ppm for **2** and at δ 104.83 and 101.37 ppm for **3**, respectively. These data suggest a free phenylethynyl C≡C linkage without any π bonding, which is different from that in **1**. Meanwhile, the combined ^1H and ^{13}C NMR spectra show the L ligand backbone of the γ-CH proton and the carbon resonances at δ 4.98 and 100.30 ppm for **2** and at δ 4.96 and 100.39 ppm for **3**, respectively, which are close to those of LGeC≡CPh,[14] indicating no further bonding of the γ-CH group by the AgC_6F_5 or AuC_6F_5 fragment.

The X-ray structural analysis clearly discloses **2** as an ionic compound with one Ag^+ bound by two LGeC≡CPh molecules to form a cation while the other Ag^+ coordinates to the two C_6F_5 groups constituting the anionic counterpart. In contrast, compound **3** forms the coordinated F_5C_6Au−germylene complex. The crystal structures of **2** and **3** are depicted in Figures 2 and 3. The structure of **2** can be compared with that of $[Ag(NHC)_2]^+[AgX_2]^-$ (NHC = N-heterocyclic carbene, X = halide). The latter compound is considered to be formed by redistribution of the AgX under interaction with the strong NHC donor.[22−25] However, the donor reactivity of the N-heterocyclic germylenes (NHGes) have been discussed to be relatively weak.[1d] Therefore, the formation of **2** is mostly attributed to the Lewis acidity of the AgC_6F_5 that causes a strong interaction with the germylene. Compound **2** represents, to our knowledge, the first example as a result of a redistribution of the organosilver(I) species under interaction with the NHGe. The Ge−Ag bond lengths are 2.4731(10) and 2.4732(10) Å and are nearly comparable to those in the complex $(R_2ATI)(X)GeAg\{HB[3,5\text{-}(CF_3)_2Pz]_3\}$ (2.4116(10)−2.4215(9) Å; R_2ATI = *N*-alkyl-2-(methylamino)troponiminate, R = *n*Pr, X = Cl;[4] R = Me, X = Cl, O_3SCF_3;[6a] R = *n*Pr, X = N_3[6b]) and the calculated complex $[HC(H)N]_2GeAgCl$ (2.448 Å).[26] The small differences might be due to steric hindrance from the bulky L ligand at the Ge center. The geometry of the coordinated Ag whether in the cation (176.23(2)°) or in the anion (179.4(2)°) is almost linearly arranged. In the structure of **3**, the Ge−Au bond length is 2.3683(6) Å (2.3641(7) Å for another molecule) and can be compared to that in R′(Cl)-GeAuI (2.346(2) Å, R′ = $(2\text{-}C_5H_4N)C(Me_3Si)C(Ph)N(Me_3Si)$).[2f] In the germaaurate compounds $Ph_3PAuGeCl_3$ (2.406(1) Å), $(Ph_3P)_3AuGeCl_3$ (2.536(1) Å),[27] $(Ph_4P)[MeC(CH_2NSiMe_3)_3Ge]_2Au$ (2.423(2) Å),[28] and $LAuGeX[N(SiMe_3)_2]_2$ (2.4085(3)−2.4169(5) Å; X = Cl, L = PPh_3, PCy_3, PEt_3; X = F, L = PPh_3),[29] the Ge−Au distances appear slightly longer. The Au atom adopts a nearly linear geometry (Ge(1)−Au(1)−C(41) = 176.64(14)°; 174.30(17)° for another molecule).

The interaction of the AgC_6F_5 and AuC_6F_5 moieties with the germylene in **2** and **3** is significantly different from that of **1**. This might be due to the different Lewis acidic properties of CuC_6F_5, AgC_6F_5, and AuC_6F_5, although they contain the same C_6F_5 group. Compound **1** still carries an unreacted germylene donor site. This prompted us to examine further reactions of **1** with $(CuC_6F_5)_4$, AgC_6F_5·MeCN, and $AuC_6F_5{\cdot}SC_4H_8$, respectively. The reactions of **1** with 0.25 equiv of $(CuC_6F_5)_4$ or 1 equiv of AgC_6F_5·MeCN or $AuC_6F_5{\cdot}SC_4H_8$ were accomplished under conditions similar to those when LGeC≡CPh was used as the precursor. The additional F_5C_6M−germylene donor−acceptor bound compounds $LGe(C{\equiv}CPh)(CuC_6F_5)(MC_6F_5)$ (M = Cu (**4**), Ag (**5**), Au (**6**)) were generated as expected (Scheme 4). In comparison, **2** and **3** both have a free phenylethynyl group. However, no reaction was observed when **2** and **3** were reacted with AgC_6F_5·MeCN or $AuC_6F_5{\cdot}SC_4H_8$. Compounds **5** and **6** were isolated as yellow crystals in 72% and 57% yields, respectively. Compound **4** was produced as a yellow solid in 43% yield. Compound **4** is almost insoluble in organic solvents. Its ^1H and ^{19}F NMR spectral data were only obtained by an in situ measurement of the NMR tube reaction in C_6D_6, and the related ^{13}C NMR data were not available. Compounds **5** and **6** have been fully characterized by NMR (^1H, ^{13}C, and ^{19}F) and IR spectroscopy and X-ray crystallography. Due to the limited solubility of **5**, its ^{13}C NMR spectrum did not give clear resonances whether in aromatic (C_6D_6) or in chlorinated ($CDCl_3$ or CD_2Cl_2) hydrocarbons after a long time of spectral acquisition.

The IR spectra display the phenylethynyl C≡C absorption band at $\tilde{\nu}$ 1956 cm^{-1} for **4**, 1952 cm^{-1} for **5**, and 1962 cm^{-1} for **6**, respectively. These IR bands are close to that found in **1**, indicating a M−(η^2-C≡C) bonding mode in all three complexes. The ^1H NMR spectra show the γ-CH proton resonance at δ 5.57 ppm for **4**, δ 5.57 ppm for **5**, and δ 5.00 ppm for **6**. Note that the ^{19}F NMR spectra display two groups of resonance data for the respective compounds **4**−**6**. This

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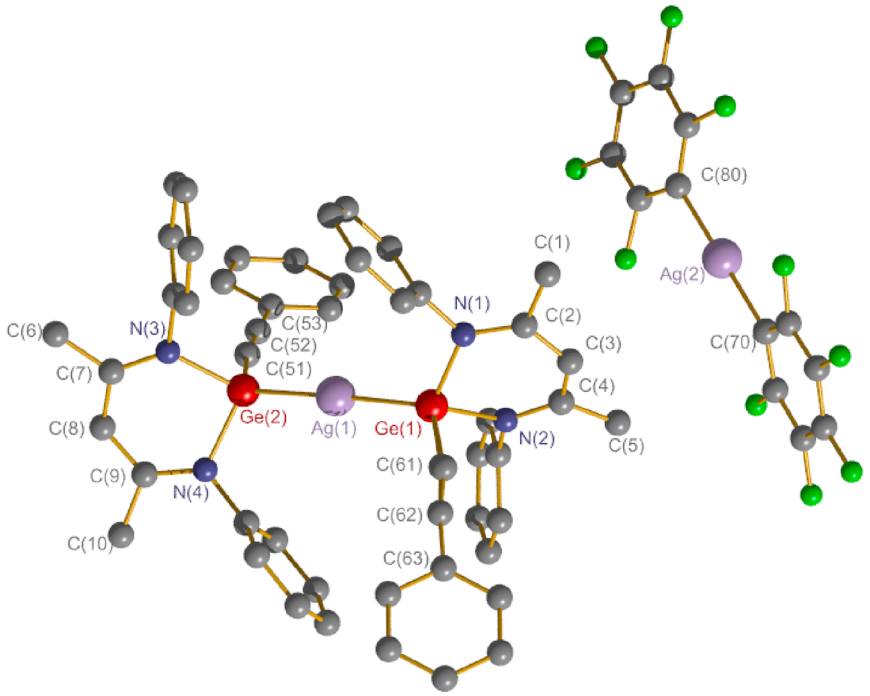

Figure 2. X-ray crystal structure of **2** with *i*Pr of the Ar at L omitted for clarity. The disordered phenylethynyl group C(61)C(62)C(63)C(64)-C(65)C(66)C(67)C(68) is shown with an occupation of 0.51796 and the related Ge(1)−C(61) and C(61)−C(62) bond lengths are given as average values. Selected bond lengths (Å) and angles (deg): Ge(1)−N(1) = 1.927(4), Ge(1)−N(2) = 1.928(4), Ge(1)−C(61) = 1.93(3) (average value), Ge(2)−N(3) = 1.927(4), Ge(2)−N(4) = 1.937(4), Ge(2)−C(51) = 1.929(6), Ge(1)−Ag(1) = 2.4732(10), Ge(2)−Ag(1) = 2.4731(10), Ag(2)−C(70) = 2.101(6), Ag(2)−C(80) = 2.103(6), C(51)−C(52) = 1.202(7), C(61)−C(62) = 1.20(3) (average value); N(1)−Ge(1)−N(2) = 95.42(15), N(3)−Ge(2)−N(4) = 95.21(16), Ge(1)−Ag(1)−Ge(2) = 176.23(2), C(70)−Ag(2)−C(80) = 179.4(2).

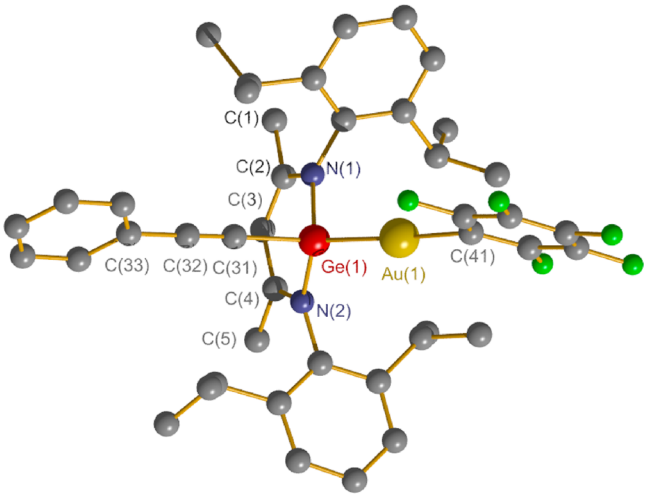

Figure 3. X-ray crystal structure of **3**. Selected bond lengths (Å) and angles (deg) (the data in brackets are for another independent molecule): Ge(1)−N(1) = 1.919(4) [1.919(4)], Ge(1)−N(2) = 1.926(5) [1.926(4)], Ge(1)−C(31) = 1.926(5) [1.932(6)], Ge(1)−Au(1) = 2.3683(6) [2.3461(7)], Au(1)−C(41) = 2.069(6) [2.058(7)], C(31)−C(32) = 1.196(6) [1.215(8)]; N(1)−Ge(1)−N(2) = 95.48(19) [95.05(17)], Au(1)−Ge(1)−C(31) = 120.43(18) [117.37(16)], Ge(1)−C(31)−C(32) = 173.3(6) [165.8(6)], C(31)−C(32)−C(33) = 178.2(7) [179.7(8)], Ge(1)−Au(1)−C(41) = 176.64(14) [174.30(17)].

Scheme 4. Formation of Compounds 4−6

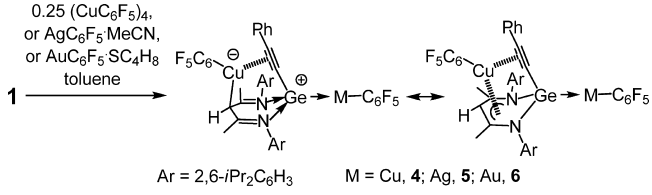

Table 1. Summary of the ^{19}F NMR Data for the MC_6F_5 (M = Cu, Ag, Au) Entity in 1−6

	^{19}F NMR (δ, ppm)		
compd	CuC_6F_5	AgC_6F_5	AuC_6F_5
1	−111.38, −160.09, −161.51		
2		−107.48, −159.58, −161.88	
3			−115.25, −159.92, −162.78
4	−111.83, −159.03, −161.11[a]		
	−105.01, −152.53, −157.45[b]		
5	−112.40, −159.22, −161.91	−107.49, −157.88, −161.91	
6	−114.79, −159.92, −162.74		−116.38, −123.31, 150.31, −159.08, 161.87

[a]Phenylethynyl group π-complexed CuC_6F_5 entity. [b]Germylene-bound CuC_6F_5 entity.

implies that the original CuC_6F_5 species and a newly bound MC_6F_5 fragment actually exhibit different fluorine resonances. On the basis of the ^{19}F NMR data for **1**−**3**, we were able to give a reasonable assignment. As summarized in Table 1, for **4** one group of resonances at δ −111.83, −159.03, and −161.11 ppm is close to that for **1** and should correspond to the π-complexed CuC_6F_5 species. Another group of resonances at δ −105.01, −152.53, and −157.45 ppm is thus of the Ge-bound CuC_6F_5

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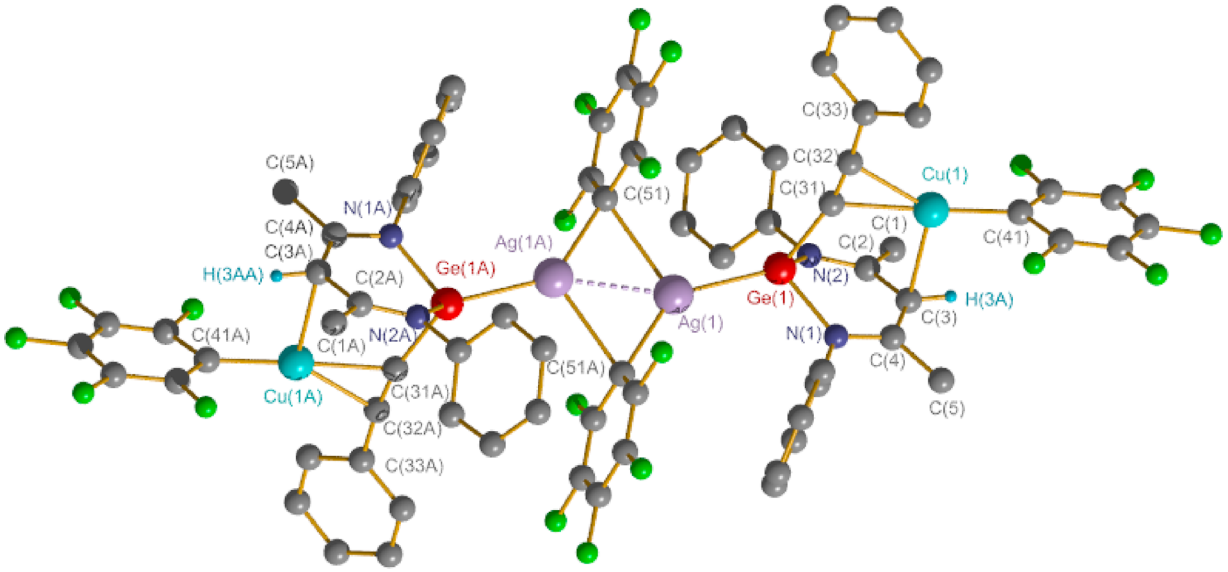

Figure 4. X-ray crystal structure of **5** with *i*Pr of the Ar at L omitted for clarity. Selected bond lengths (Å) and angles (deg): Ge(1)−N(1) = 1.930(5), Ge(1)−N(2) = 1.944(5), Ge(1)−C(31) = 1.963(6), Ge(1)−Ag(1) = 2.4551(8), Ag(1)···Ag(1A) = 2.7073(9), Ag(1)−C(51) = 2.543(6), Ag(1)−C(51A) = 2.237(7), Cu(1)−C(31) = 2.180(8), Cu(1)−C(32) = 2.316(10), Cu(1)···C(3) = 2.617, Cu(1)−C(41) = 1.925(10), N(1)−C(4) = 1.330(8), N(2)−C(2) = 1.321(8), C(1)−C(2) = 1.512(9), C(2)−C(3) = 1.417(9), C(3)−C(4) = 1.392(9), C(4)−C(5) = 1.510(9), C(31)−C(32) = 1.207(10); N(1)−Ge(1)−N(2) = 94.2(2), Ge(1)−C(31)−C(32) = 164.5(3), C(31)−C(32)−C(33) = 164.7(3), C(31)−Cu(1)−C(32) = 35.35(12), Ge(1)−Ag(1)−C(51) = 109.48(16), Ge(1)−Ag(1)−C(51A) = 138.76(17), C(51)−Ag(1)−C(51A) = 111.34(18). Symmetry code (A): $-x, -y + 2, -z + 1$.

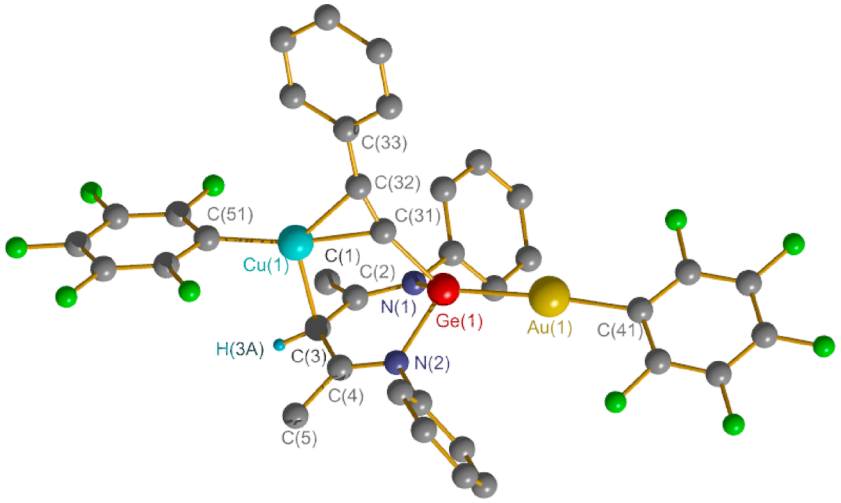

Figure 5. X-ray crystal structure of **6** with *i*Pr of the Ar at L omitted for clarity. Selected bond lengths (Å) and angles (deg): Ge(1)−N(1) = 1.924(3), Ge(1)−N(2) = 1.921(1), Ge(1)−C(31) = 1.955(4), Ge(1)−Au(1) = 2.3625(4), Au(1)−C(41) = 2.056(4), Cu(1)−C(31) = 1.973(4), Cu(1)−C(32) = 2.080(4), Cu(1)−C(3) = 2.343(3), Cu(1)−C(51) = 1.931(4), N(1)−C(2) = 1.329(5), N(2)−C(4) = 1.321(5), C(1)−C(2) = 1.506(5), C(2)−C(3) = 1.409(5), C(3)−C(4) = 1.417(5), C(4)−C(5) = 1.504(5), C(31)−C(32) = 1.221(5); N(1)−Ge(1)−N(2) = 94.80(12), N(1)−Ge(1)−C(31) = 94.92(14), N(2)−Ge(1)−C(31) = 95.82(14), Ge(1)−Au(1)−C(41) = 175.21(11), Ge(1)−C(31)−C(32) = 164.4(3), (31)−C(32)−C(33) = 164.2(4), C(31)−Cu(1)−C(32) = 34.94(14).

part. Similarly, in the spectrum of **5**, the group of the resonances at δ −112.40, −159.22, and −161.91 ppm is assigned to the π-complexed CuC_6F_5 species, whereas another group of resonances at δ −107.49, −157.88, and −161.91 ppm is attributed to the Ge-bound AgC_6F_5 part. However, broad resonances are observed for the latter group. This suggests an aggregation of the AgC_6F_5 entity, as has been discussed in the ^{19}F NMR spectrum of the compound $\{LGe[C(SiMe_3)N_2]\text{-}(AgC_6F_5)_2\}_2$ due to the formation of an equilibrium by fast transformation of the AgC_6F_5 species in solution.[13] In the spectrum of **6**, the three resonances δ −114.78 (*o-F*), −159.91 (*p-F*), and −162.76 ppm (*m-F*) can be assigned to the CuC_6F_5 part. However, five resonances (δ −116.42 (*o-F*), −123.35 (*o-F*), −150.31 (*p-F*), −159.08 (*m-F*), and −161.87 ppm (*m-F*)) were observed, which correspond to the Ge-bound AuC_6F_5 species due to hindered rotation probably induced by the bulky *i*Pr groups of the NAr substituents. However, this resonance mode is quite different from the three resonances found in **3**–**5**. Although we performed VT NMR spectral measurements on **6** in CD_2Cl_2 from 20 to −50 °C, almost no change of this resonance mode was found. Thus, we conclude that the spectroscopic behavior of **6** in solution is not clear.

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The X-ray structural analysis of **5** clearly shows a novel GeCuAg trimetallic hexanuclear compound with an additional bonding of the AgC_6F_5 species at the germylene center (Figure 4). The AgC_6F_5 part aggregates to form a centrosymmetric $(AgC_6F_5)_2$ core. The Ag−$C_{C_6F_5}$ bond lengths are 2.237(7) and 2.543(6) Å and are longer than those of the terminal bond distances in **2** (2.101(6) and 2.103(6) Å). In the similar compound $\{LGe[C(SiMe_3)N_2](AgC_6F_5)_2\}_2$, the bridged Ag−$C_{C_6F_5}$ bond lengths are 2.155(5) and 2.264(4) Å.[13] These Ag−$C_{C_6F_5}$ bond lengths are remarkably longer than the Cu−$C_{C_6F_5}$ bond length (1.925(10) Å). The Ge−Ag bond length is 2.4551(8) Å and is comparable to those in **2**. However, the bound AgC_6F_5 species at the Ge atom appears to give rise to a significant change of the bond parameters around the Cu atom, and longer Cu−$C_{C\equiv C}$ (2.180(8) and 2.316(10) Å) as well as remarkably longer Cu−$C_{\gamma\text{-}C}$ (2.617 Å) bond lengths are observed in comparison to those in **1**. This indicates that in **5** the aforementioned C_3N_2Ge ring···CuC_6F_5 π complexation is mainly adopted.

The structure of **6** shows a GeCuAu trimetallic compound with a terminally bound AuC_6F_5 species at the Ge center (Figure 5). The Au−$C_{C_6F_5}$ bond length (2.056(4) Å) can be compared with those in **3** (2.058(7)−2.069(6) Å), but it is longer than the Cu−$C_{C_6F_5}$ bond length (1.931(4) Å). The Ge−Au bond length (2.3625(4) Å) is similar to that in **3**. This Ge−AuC_6F_5 bound part seems to have no great effect on the bonding parameters around the Cu center. Cu−$C_{C_6F_5}$ (1.931(4) Å), Cu−$C_{C\equiv C}$ (1.973(4) and 2.080(4) Å), and Cu−$C_{\gamma\text{-}C}$ (2.343(3) Å) bond lengths close to those found in **1** suggest a relatively strong F_5C_6Cu−γ-CH interaction.

CONCLUSION

In summary, we have presented reactions of the β-diketiminato ligand stabilized (phenylethynyl)germylene LGeC≡CPh with pentafluorophenylcopper(I), -silver(I), and -gold(I) complexes. We isolated and structurally characterized a series of group 11 metal(I)−germylene complexes $LGe(C\equiv CPh)CuC_6F_5$ (**1**), $[(LGeC\equiv CPh)_2Ag]^+[Ag(C_6F_5)_2]^-$ (**2**), $LGe(C\equiv CPh)$-AuC_6F_5 (**3**), and $LGe(C\equiv CPh)(CuC_6F_5)(MC_6F_5)$ (M = Cu (**4**), Ag (**5**), Au (**6**)). The formation of compounds **1**−**3** reveals routes of the MC_6F_5 species at the different donor sites of LGeC≡CPh. This is obviously due to slightly different Lewis acidic species of the pentafluorophenylcopper(I), -silver(I), and -gold(I) complexes as acceptors. The donor molecule coordination dependent properties of these complexes imply the difference in their Lewis acidities.[15−18,31,32] However, detailed studies on this chemistry have been reported to a much lesser extent.[33] Compound **4** shows a bound CuC_6F_5 species not only at the germylene center but also at the phenylethynyl group where the central C_3N_2Ge ring donor site is also involved. However, the generation of **2**, **3**, **5**, and **6** may indicate a specific reactivity of the AgC_6F_5 or AuC_6F_5 species at the germylene center.

EXPERIMENTAL SECTION

Materials and Methods. All syntheses and manipulations were carried out on a Schlenk line or in an argon-filled MBraun glovebox (typically oxygen and moisture were controlled at less than 1.2 ppm). Toluene and *n*-hexane were dried by refluxing with sodium/potassium benzophenone under N_2 prior to use. The deuterated solvent C_6D_6 was degassed and dried over sodium/potassium alloy. $CDCl_3$ and CD_2Cl_2 were degassed and dried over CaH_2. ^{1}H (400 MHz), ^{13}C (100 MHz), and ^{19}F NMR spectra (376 MHz) were recorded on a Bruker Avance II 400 MHz spectrometer. Melting points of compounds were measured in sealed glass tubes using a Büchi-540 instrument. Elemental analysis was performed on a Thermo Quest Italia SPA EA 1110 instrument. Commercial reagents were purchased from Aldrich, Acros, or Alfa-Aesar and used as received. $(CuC_6F_5)_4$,[15] AgC_6F_5·MeCN,[31] and AuC_6F_5·SC_4H_4[32] were prepared according to published procedures. LGeC≡CPh was synthesized using a one-pot method, detailed as follows.

LGeC≡CPh. *n*BuLi (2 mL, 5 mmol, 2.5 M solution in *n*-hexane) was added to a solution of LH (2.091 g, 5 mmol) in toluene (60 mL) at −30 °C. The mixture was warmed to room temperature and stirred for 12 h. After workup, the solution was cooled to −30 °C and then slowly added to a precooled (−30 °C) suspension of $GeCl_2$·(dioxane) (1.160 g, 5 mmol) in toluene (30 mL) with stirring. After the mixture was warmed to room temperature and stirred for an additional 12 h, the orange-yellow suspension that formed was cooled to −30 °C again before addition of LiC≡CPh which was freshly prepared from the reaction of PhC≡CH (0.511 g, 5 mmol) with *n*BuLi (2 mL, 5 mmol, 2.5 M) in *n*-hexane (15 mL) at −30 °C to room temperature within 3 h. After the mixture was stirred for 20 h, all volatiles were removed under reduced pressure and the residue was extracted with toluene. The toluene extract was evaporated to dryness under reduced pressure and further washed with cold *n*-hexane (2 × 1 mL) to give LGeC≡CPh as a golden yellow crystalline solid (2.66 g, 90%). The ^{1}H NMR spectral data are the same as those obtained from the reaction of L′Ge (L′ = HC[C(CH_2)N-2,6-*i*$Pr_2C_6H_3$][C(Me)N-2,6-*i*$Pr_2C_6H_3$] with PhC≡CH.[14] IR (KBr plate, Nujol mull, cm^{-1}): $\tilde{\nu}$ 2117 (w, C≡C).

LGe(C≡CPh)CuC_6F_5 (1). In a glovebox, a solution of $(CuC_6F_5)_4$ (0.115 g, 0.125 mmol) in toluene (10 mL) was added to a stirred solution of LGeC≡CPh (0.30 g, 0.5 mmol) in toluene (15 mL) at room temperature. A quick color change from golden yellow to light yellow was observed. The mixture was stirred for an additional 4 h. After concentration to ca. 5 mL the solution was stored at −20 °C. Two days later, X-ray-quality, light yellow crystals of **1**·(toluene) were formed and collected by filtration (0.35 g, 74%). Mp: 164 °C. ^{1}H NMR (400 MHz, C_6D_6, 298 K, ppm): δ 7.67−6.93 (m, 16 H, C_6H_3, C_6H_5, Me*Ph*), 5.75 (s, 1 H, γ-C*H*), 3.40 (br, 2 H), 3.17 (br, 2 H) (C*H*Me_2), 2.11 (s, 3 H, Ph*Me*), 1.71 (s, 6 H, C*Me*), 1.24, 1.21 (d, overlapped, 18 H), 0.96 (d, 6 H) (CH*Me*$_2$). ^{13}C NMR (100 MHz, C_6D_6, 298 K, ppm): δ 173.05 (*C*N), 145.77, 142.58, 139.53, 137.64, 132.14, 129.08, 128.87, 128.57, 128.31, 129.19, 127.92, 127.68, 125.44, 125.13, 124.06 (C_6H_3, C_6H_5, C_6F_5, *Ph*Me), 121.18, 115.58 (*C*≡CPh), 88.79 (γ-*C*), 29.45, 29.31, 27.37, 24.33, 24.08, 22.96, 22.88, 21.18 (*C*Me, *CH*Me_2, Ph*Me*). ^{19}F NMR (376 MHz, C_6D_6, 298 K, ppm): δ −111.38 (m, 2 F, *o-F*), −160.09 (m, 1 F, *p-F*), −161.51 (m, 2 F, *m-F*). IR (KBr plate, cm^{-1}): $\tilde{\nu}$ 1957 (w, C≡C). The crystalline solid of **1** was used for elemental analysis. Anal. Calcd for $C_{43}H_{46}CuF_5GeN_2$ (M_r = 822.02): C, 62.83; H, 5.64; N, 3.41. Found: C, 62.56; H, 5.43; N, 3.39.

$[(LGeC\equiv CPh)_2Ag]^+[Ag(C_6F_5)_2]^-$ (2). In a glovebox, LGeC≡CPh (0.12 g, 0.2 mmol) and AgC_6F_5·MeCN (0.06 g, 0.2 mmol) were mixed in a brown vial and toluene (2.5 mL) was added. The mixture was stirred for 0.5 h, and then toluene (1 mL) was added until all solids had dissolved. After it was stirred for an additional 1 h, the solution was filtered to remove a small amount of precipitate. The filtrate was layered with *n*-hexane (1 mL) and stored at −20 °C. Two days later, yellow crystals of **2**·2(toluene) were formed and collected by filtration (0.12 g, 65%). Mp: 174 °C dec. ^{1}H NMR (400 MHz, C_6D_6, 298 K, ppm): δ 7.42−7.00 (m, 22 H, C_6H_3, C_6H_5), 4.98 (s, 2 H, γ-C*H*), 3.73 (sept, $^3J_{HH}$ = 6.8 Hz, 4 H), 3.30 (sept, $^3J_{HH}$ = 6.8 Hz, 4 H) (CH*Me*$_2$), 1.47 (s, 12 H, C*Me*), 1.52 (d, $^3J_{HH}$ = 6.8 Hz, 12 H), 1.39 (d, $^3J_{HH}$ = 6.8 Hz, 12 H), 1.16 (d, $^3J_{HH}$ = 6.8 Hz, 12 H), 1.02 (d, $^3J_{HH}$ = 6.8 Hz, 12 H) (CH*Me*$_2$). ^{13}C NMR (100 MHz, C_6D_6, 298 K, ppm): δ 168.90 (*C*N), 146.38, 143.34, 138.31, 131.94, 128.89, 128.59, 128.45, 127.82, 127.68, 125.29, 124.75 (C_6H_3, C_6H_5, C_6F_5), 123.55, 104.72 (*C*≡CPh), 100.30 (γ-C), 29.72, 28.65, 27.68, 24.62, 24.49, 23.81, 23.11 (*C*Me, *CH*Me_2). ^{19}F NMR (376 MHz, C_6D_6, 298 K, ppm): δ −107.48 (m, 4 F, *o-F*), −159.58 (m, 2 F, *p-F*), −161.88 (m, 4 F, *m-F*). IR (KBr plate,

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Nujol mull, cm^{-1}): $\tilde{\nu}$ 2145 (w, C≡C). The crystalline solid of **2** was used for elemental analysis. Anal. Calcd for $C_{86}H_{92}Ag_2F_{10}Ge_2N_4$ (M_r = 1732.68): C, 59.61; H, 5.35; N, 3.23. Found: C, 59.38; H, 5.23; N, 3.32.

LGe(C≡CPh)AuC$_6$F$_5$ (3). In a glovebox, a solution of $AuC_6F_5{\cdot}SC_4H_8$ (0.18 g, 0.40 mmol) in toluene (5 mL) was added to a stirred solution of LGeC≡CPh (0.24 g, 0.40 mmol) in toluene (5 mL) at room temperature. A quick color change from golden yellow to light yellow was observed. The mixture was stirred for an additional 4 h, filtered, and stored at −20 °C. One week later, X-ray-quality, colorless crystals of **3**·0.75(toluene) were formed and collected by filtration (0.29 g, 71%). Mp: 176 °C. ^{1}H NMR (400 MHz, C_6D_6, 298 K, ppm): δ 7.40−6.96 (m, 14.8 H, C_6H_3, C_6H_5, *Ph*Me), 4.96 (s, 1 H, γ-C*H*), 3.74 (sept, $^3J_{HH}$ = 6.8 Hz, 2 H), 3.41 (sept, $^3J_{HH}$ = 6.8 Hz, 2 H) (C*H*Me$_2$), 2.11 (s, 2.2 H, Ph*Me*), 1.46 (s, 6 H, C*Me*), 1.60 (d, $^3J_{HH}$ = 6.8 Hz, 6 H), 1.43 (d, $^3J_{HH}$ = 6.8 Hz, 6 H), 1.16 (d, $^3J_{HH}$ = 6.8 Hz, 6 H), 1.05 (d, $^3J_{HH}$ = 6.8 Hz, 6 H) (CH*Me*$_2$). ^{13}C NMR (100 MHz, C_6D_6, 298 K, ppm): δ 169.63 (*C*N), 146.23, 143.70, 138.02, 132.03, 129.07, 128.98, 128.73, 128.44, 128.30, 127.91, 127.68, 125.43, 125.15, 124.71, 123.27 (C_6H_3, C_6H_5, C_6F_5, *Ph*Me), 104.83, 101.37 (*C*≡CPh), 100.39 (γ-*C*), 29.83, 28.73, 27.64, 24.44, 23.75, 23.23, 21.16 (C*Me*, CH*Me*$_2$, Ph*Me*). ^{19}F NMR (376 MHz, C_6D_6, 298 K, ppm): δ −115.25 (m, 2 F, *o*-*F*), −159.92 (m, 1 F, *p*-*F*), −162.78 (m, 2 F, *m*-*F*). IR (KBr plate, Nujol mull, cm^{-1}): $\tilde{\nu}$ 2135 (w, C≡C). Anal. Calcd for $C_{48.25}H_{52}AuF_5GeN_2$ (**3**·0.75(toluene), M_r = 1024.54): C, 56.56; H, 5.12; N, 2.73. Found: C, 56.24; H, 5.18; N, 2.67.

LGe(C≡CPh)(CuC$_6$F$_5$)$_2$ (4). In a glovebox, a solution of LGeC≡CPh (0.12 g, 0.20 mmol) in toluene (5 mL) was cooled to −20 °C and added to a precooled (−20 °C) solution of $(CuC_6F_5)_4$ (0.09 g, 0.10 mmol) in toluene (5 mL). The mixture was stirred for 5 min, and a quick color change from golden yellow to light yellow was observed. The solution was stored at −20 °C. Two days later, a light yellow solid of **4** was formed and collected (0.09 g, 43%). Mp: 154 °C dec. Due to the very poor solubility of **4** in organic solvents, the ^{1}H and ^{19}F NMR data were only obtained from in situ measurement of the NMR-tube reaction of LGeC≡CPh with 1 equiv of $(CuC_6F_5)_2{\cdot}$(dioxane) in C_6D_6. The ^{13}C NMR data were not available. ^{1}H NMR (400 MHz, C_6D_6, 298 K, ppm): δ 7.88−6.93 (m, 11 H, C_6H_3, C_6H_5), 5.57 (s, 1 H, γ-C*H*), 3.35 (s, 8 H, dioxane-*H*), 2.84 (br, 4 H, C*H*Me$_2$), 1.49 (s, 6 H, C*Me*), 1.36 (d, $^3J_{HH}$ = 6.4 Hz, 6 H), 1.07 (d, $^3J_{HH}$ = 6.4 Hz, 12 H), 0.74 (d, $^3J_{HH}$ = 6.4 Hz, 6 H) (CH*Me*$_2$). ^{19}F NMR (376 MHz, C_6D_6, 298 K, ppm): δ −111.87 (m, 2 F, *o*-*F*), −159.03 (t, 1 F, *p*-*F*), −161.10 (m, 2 F, *m*-*F*) (π-complexed CuC_6F_5), −105.06 (m, 2 F, *o*-*F*), −152.52 (t, 1 F, *p*-*F*), −157.45 (m, 2 F, *m*-*F*) (Ge−CuC_6F_5). IR (KBr plate, cm^{-1}): $\tilde{\nu}$ 1956 (w, C≡C). Anal. Calcd for $C_{49}H_{46}Cu_2F_{10}GeN_2$ (M_r = 1052.62): C, 55.91; H, 4.40; N, 2.66. Found: C, 55.62; H, 4.48; N, 2.61.

LGe(C≡CPh)(CuC$_6$F$_5$)(AgC$_6$F$_5$) (5). In a glovebox, **1** (0.16 g, 0.2 mmol) and $AgC_6F_5{\cdot}$MeCN (0.06 g, 0.2 mmol) were mixed in a brown vial and toluene (2.5 mL) was added. The mixture was stirred for 0.5 h, and then toluene (1 mL) was added until all solids had dissolved. After it was stirred for an additional 1 h, the solution was filtered to remove a small amount of precipitate. The filtrate was layered with *n*-hexane (1 mL) and stored at −20 °C. Two days later, light yellow crystals of **5**·(toluene) were formed and collected by filtration (0.17 g, 72%). Mp: 147 °C dec. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K, ppm): δ = 7.55−7.17 (m, 27 H, C_6H_3, C_6H_5, *Ph*Me), 5.57 (br, 2 H, γ-C*H*), 3.59 (br, 2 H), 3.10 (br, 6 H) (CH*Me*$_2$), 2.36 (s, 3 H, Ph*Me*), 1.96 (s, overlapped, 12 H, C*Me*), 2.09 (br, 12 H), 1.37 (d, $^3J_{HH}$ = 6.4 Hz, 12 H), 1.27 (d, $^3J_{HH}$ = 6.4 Hz, 12 H), 1.13 (d, $^3J_{HH}$ = 6.4 Hz, 12 H) (CH*Me*$_2$). The ^{13}C NMR spectrum did not give reliable data due to limited solubility. ^{19}F NMR (376 MHz, C_6D_6, 298 K, ppm): δ −107.50 (br, 4 F, *o*-*F*), −157.78 (br, 2 F, *p*-*F*), −161.58 (br, 4 F, *m*-*F*) (AgC_6F_5), −112.44 (m, 4 F, *o*-*F*), −159.22 (br, 2 F, *p*-*F*), −161.58 (br, 4 F, *m*-*F*) (CuC_6F_5). IR (KBr plate, cm^{-1}): $\tilde{\nu}$ 1952 (w, C≡C). The crystalline solid of **5** was used for elemental analysis. Anal. Calcd for $C_{49}H_{46}AgCuF_{10}GeN_2$ (M_r = 1096.94): C, 53.65; H, 4.23; N, 2.55. Found: C, 53.53; H, 4.28; N, 2.47.

LGe(C≡CPh)(CuC$_6$F$_5$)(AuC$_6$F$_5$) (6). In a glovebox, a solution of **1** (0.25 g, 0.30 mmol) in toluene (15 mL) was cooled to −20 °C and then added to a precooled (−20 °C) solution of $AuC_6F_5{\cdot}SC_4H_8$ (0.14 g, 0.30 mmol) in toluene (10 mL) with stirring. A quick color change from golden yellow to light yellow was observed. The mixture was warmed to room temperature and stirred for an additional 1 h. After concentration to ca. 5 mL the solution was stored at −20 °C. One week later, X-ray-quality, light yellow crystals of **6**·0.5(toluene) were formed and collected by filtration (0.21 g, 57%). Mp: 184 °C. ^{1}H NMR (400 MHz, C_6D_6, 298 K, ppm): δ 7.53−6.80 (m, 11 H, C_6H_3, C_6H_5), 5.00 (s, 1 H, γ-C*H*), 3.50 (sept, $^3J_{HH}$ = 6.8 Hz, 2 H), 2.36 (sept, $^3J_{HH}$ = 6.8 Hz, 2 H) (C*H*Me$_2$), 1.37 (s, 6 H, C*Me*), 1.72 (d, $^3J_{HH}$ = 6.8 Hz, 6 H), 1.02 (d, $^3J_{HH}$ = 6.8 Hz, 6 H), 0.83 (d, $^3J_{HH}$ = 6.8 Hz, 6 H), 0.42 (d, $^3J_{HH}$ = 6.8 Hz, 6 H) (CH*Me*$_2$). ^{13}C NMR (100 MHz, C_6D_6, 298 K, ppm): δ 170.47 (*C*N), 145.27, 144.16, 137.38, 129.38, 129.07, 128.83, 128.72, 128.60, 128.43, 128.30, 127.14, 127.07, 125.43, 125.02 (C_6H_3, C_6H_5, C_6F_5), 125.18, 124.73 (*C*≡CPh), 100.08 (γ-C), 31.71, 30.25, 28.11, 24.68, 24.64, 24.17, 23.85, 23.59, 22.79 (C*Me*, CH*Me*$_2$). ^{19}F NMR (376 MHz, C_6D_6, 298 K, ppm): δ −114.78 (br, 2 F, *o*-*F*), −159.91 (br, 1 F, *p*-*F*), −162.76 (br, 2 F, *m*-*F*) (AuC_6F_5), −116.42 (m, 1 F, *o*-*F*), −123.35 (m, 1 F, *o*-*F*), −150.31 (m, 1 F, *p*-*F*), −159.08 (m, 1 F, *m*-*F*), −161.87 (m, 1 F, *m*-*F*) (CuC_6F_5). IR (KBr plate, cm^{-1}): $\tilde{\nu}$ 1962 (w, C≡C). Anal. Calcd for $C_{52.5}H_{50}AuCuF_{10}GeN_2$ (**6**·0.5(toluene), M_r = 1232.11): C, 51.18; H, 4.09; N, 2.27. Found: C, 50.82; H, 4.13; N, 2.37.

X-ray Crystallographic Analyses of Complexes 1−3, 5, and 6. Crystallographic data for **1**·(toluene,) **3**$_2$·1.5(toluene), **5**·(toluene), and **6**·0.5(toluene) were collected on an Oxford Gemini S Ultra system, and the data for **2**·2(toluene) was obtained on a Rigaku R-Axis Spider IP system. In all cases graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) was used. Absorption corrections were applied using the spherical harmonics program. Structures were solved by direct methods (SHELXS-96)[34] and refined against F^2 using SHELXL-97.[35] In general, the non-hydrogen atoms were located by difference Fourier synthesis and refined anisotropically, and hydrogen atoms were included using the riding model with U_{iso} tied to the U_{iso} values of the parent atoms unless otherwise specified. In **1**·(toluene), the two toluene molecules were located and refined isotropically with respective occupations of 0.5. In **2**·2(toluene), one of the phenylethynyl groups was disordered, treated in a splitting mode, and refined isotropically. In addition, three toluene molecules were located, one of which was disordered, treated in a splitting mode, and refined isotropically, while the other two toluene molecules were refined isotropically, both with the respective occupations of 0.5. In **3**$_2$·1.5(toluene), two independent molecules of **3** were disclosed, in which one of the isopropyl groups of the aryl substituent was disordered, treated in a splitting mode, and refined isotropically. Furthermore, the two toluene molecules were located and refined isotropically, one of which with an occupation of 0.5 was seriously disordered and refined isotropically. It was not possible to realize hydrogen atom addition. In **5**·(toluene), the toluene molecule was seriously disordered and could not be treated upon hydrogen atom addition. In **6**·0.5(toluene), the toluene molecule was disordered, treated in a splitting mode, and refined isotropically. For this toluene molecule, it was not possible to realize hydrogen atom addition. Cell parameters, data collection, and structure solution and refinement details are given in Table 1s (Supporting Information).

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

CIF files and a table giving crystallographic data for **1**−**3**, **5**, and **6** and figures giving NMR spectra of **1**−**6**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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