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β-Diketiminate Germylene-Supported Pentafluorophenylcopper(I) and -silver(I) Complexes $[LGe(Me)(CuC_6F_5)_n]_2$ (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 = $HC[C(Me)N\text{-}2,6\text{-}iPr_2C_6H_3]_2$): Synthesis and Structural Characterization

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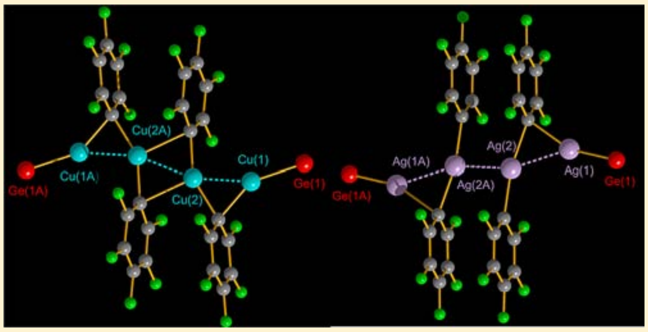
Supporting Information



ABSTRACT: Reactions of LGeMe (L = $HC[C(Me)N\text{-}2,6\text{-}iPr_2C_6H_3]_2$) with 0.25 or 0.5 equiv of $(CuC_6F_5)_4$ gave the products $[LGe(Me)CuC_6F_5]_2$ (**1**) and $[LGe(Me)(CuC_6F_5)_2]_2$ (**2**), respectively. In situ formed **1** reacted with 0.5 equiv of $(CuC_6F_5)_4$ to give **2** on the basis of NMR (^1H and ^{19}F) spectral measurements. Conversely, **2** was converted into **1** by treatment with 2 equiv of LGeMe. Reactions of $LGeC(SiMe_3)N_2$ with 1 or 2 equiv of $AgC_6F_5\cdot MeCN$ produced the corresponding compounds $LGe[C(SiMe_3)N_2]AgC_6F_5$ (**3**) and $\{LGe[C(SiMe_3)N_2](AgC_6F_5)_2\}_2$ (**4**). Similarly, **3** was converted into **4** by treatment with 1 equiv of $AgC_6F_5\cdot MeCN$ and **4** converted into **3** by reaction with 2 equiv of $LGeC(SiMe_3)N_2$. X-ray crystallographic studies showed that **1** contains a rhombically bridged $(CuC_6F_5)_2$, while **2** has a chain-structurally aggregated $(CuC_6F_5)_4$, both supported by LGeMe. Correspondingly, **3** showed a terminally bound AgC_6F_5 and **4** a chain-structurally aggregated $(AgC_6F_5)_4$, both supported by $LGeC(SiMe_3)N_2$. Photophysical studies proved that the Ge−Cu metal−metalloid donor−acceptor bonding persists in solutions of **1** and **2** and Ge−Ag donor−acceptor bonding in solutions of **3** and **4** as a result of the clear migration of their emission bands compared to those of the corresponding starting materials. Low-temperature (−50 °C) ^{19}F NMR spectral measurements detected dissociation of **1**, **2**, and **4** by the aggregation part of the CuC_6F_5 or AgC_6F_5 entities in solution. These results provide good support for pentafluorophenylcopper(I) or -silver(I) species having β-diketiminate germylene as a donor because of its remarkably electronic and steric character.

INTRODUCTION

N-Heterocyclic carbenes (NHCs) have been well developed and used widely as strong donor ligands in organometallic and catalytic chemistry in the past 20 years.[1−3] The N-heterocyclic germylenes (NHGes) have also been studied extensively.[4] However, the reactivity of the NHGes as donors has been described to a rather lesser extent.[4h] Some NHGes have been reported to show the Lewis acidic reactivity[5] as well as the reductive activity of the singlet electron lone pair at the Ge^{II} center.[5b,6] As a donor ligand in incorporating the group 11 metal(I) species, Boehme and Frenking have calculated that the metal−carbene bond dissociation energy of NHC → MCl (M = Cu, Ag, Au) appears generally to be greater than that of a metal−germylene NHGe → MCl.[7] This suggests a distinctive degree of interaction between NHC and NHGe with the group 11 metal(I) complexes as a result of their different electronic properties.[8] Nonetheless, a number of group 11 metal(I) NHC complexes have been prepared,[1j,9] and some related NHGe complexes have also been synthesized. The Ge−Ag complexes $(R_2ATI)(X)GeAg\{HB[3,5\text{-}(CF_3)_2Pz]_3\}$ [R_2ATI = N-alkyl-2-(methylamino)troponiminate; R = Me, X = Cl or OSO_2CF_3; R = nPr, X = Cl or N_3] were reported by Dias et al. in the early 2000s.[10] The Ge−Cu complex $[HC(Mes)N]_2GeCuL'$ (L′ = $HC[C(Me)N\text{-}2,6\text{-}Me_2C_6H_3]_2$) was prepared by Tolman and co-workers,[11] and the Ge−Cu and Ge−Au complexes $[R'(Cl)GeCuI]_4$ and $R'(Cl)GeAuI$ [R′ = $N(SiMe_3)C(Ph)C(SiMe_3)(C_5H_4N\text{-}2)$] were synthesized by Leung and co-workers[12] in 2006. In 2009, Mochida and co-workers reported complexes $L''(R'')GeCuL''$ (L″ = $HC[C(Me)NiPr]_2$; R″ = Cl, Me, or H) and found that the Ge−Cu bonding could tolerate a further metathesis reaction at the Ge center.[13]

We recently reported on the use of an NHC, imidazol-2-ylidene, as the donor ligand not only to support the copper(I) aryls in conjugate addition to the organic azide[14a] but also to investigate stepwise the reaction of the NNP−ligand copper(I) compound $[o\text{-}N{=}CH(C_4H_3N){-}PPh_2C_6H_4]_2Cu$ with elemental sulfur.[14b] We now show the use of NHGe as the donor ligand to complex group 11 organometallic species. To our knowledge, such compounds have not been reported

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hitherto.[15] An initial reaction was attempted between an N-heterocyclic LGeMe (L = HC[C(Me)N-2,6-iPr$_2$C$_6$H$_3$]$_2$)[6c] and (CuMes)$_4$ (Mes = 2,4,6-Me$_3$C$_6$H$_2$). Surprisingly, no reaction was observed on the basis of the ^{1}H NMR spectral measurements.[16] However, when the copper(I) species was changed to (CuC$_6$F$_5$)$_4$,[17] the reaction occurred smoothly. Not only [LGe(Me)CuC$_6$F$_5$]$_2$ (**1**) but also [LGe(Me)(CuC$_6$F$_5$)$_2$]$_2$ (**2**) was isolated, depending on the molar ratio of the two starting materials used. Further investigation of the reaction of LGeC(SiMe$_3$)N$_2$[18] with AgC$_6$F$_5$·MeCN[19] in various molar ratios resulted in LGe[C(SiMe$_3$)N$_2$]AgC$_6$F$_5$ (**3**) and {LGe[C(SiMe$_3$)N$_2$](AgC$_6$F$_5$)$_2$}$_2$ (**4**), respectively. **1**−**4** have been structurally characterized to show novel aggregation forms of (MC$_6$F$_5$)$_n$ (M = Cu, n = 2, 4; M = Ag, n = 1, 4) supported by the respective germylenes, which are different from those using organic donor molecules.[15b,19−24] Herein, we present the synthesis and characterization of **1**−**4**. Photophysical studies are carried out to detect the Ge−Cu or Ge−Ag interactions, and variable-temperature ^{1}H and/or ^{19}F NMR measurements are performed to disclose the nature of the CuC$_6$F$_5$ or AgC$_6$F$_5$ aggregation under the germylene support.

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, n-hexane, tetrahydrofuran, and diethyl ether were predried over fine sodium wires and then refluxed with sodium/potassium benzophenone under a nitrogen atmosphere prior to use. CH$_2$Cl$_2$ and CHCl$_3$ were refluxed with CaH$_2$ for 3 days before use. ^{1}H (400 MHz), ^{13}C (100 MHz), ^{19}F (376 MHz), and ^{29}Si (99 MHz) NMR spectra 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 analyses were performed on a Thermo Quest Italia SPA EA 1110 instrument. Commercial reagents were purchased from Aldrich, Acros, Alfa-Assar, or Lvyin Chemical Co. and used as received. LGeMe,[6c] (CuMes)$_4$,[16] (CuC$_6$F$_5$)$_4$,[17] and AgC$_6$F$_5$·MeCN[19] were prepared according to published procedures. The synthesis of LGeC(SiMe$_3$)N$_2$[18] was modified using a one-pot method as detailed.

Fluorescence spectra were measured on a Hitachi F-7000 FL spectrophotometer and UV−vis spectra on a Shimadzu UV-2550 spectrophotometer with solution samples in CH$_2$Cl$_2$ (2 mL) at concentrations of 1.0×10^{-3} mol L^{-1} for the former and of 1.0×10^{-5} mol L^{-1} for the latter. For fluorescence measurements, excitation (xenon lamp)/emission slit widths of 10/10 nm were used with a scan speed of 240 nm min^{-1}. For UV measurements, a slit width (D$_2$ lamp) of 2.0 nm was used with a moderate scan speed.

LGeC(SiMe$_3$)N$_2$. nBuLi (1 mL, 2.5 mmol, 2.5 M solution in n-hexane) was added to a solution of LH (1.045 g, 2.5 mmol) in toluene (40 mL) at −30 °C. The mixture was allowed to warm to room temperature and stirred for 12 h. The solution was cooled to −30 °C and then slowly added to a precooled (−30 °C) suspension of GeCl$_2$·dioxane (0.580 g, 2.5 mmol) in toluene (20 mL) with stirring. The mixture was warmed to room temperature and stirred for 12 h. An orange-yellow suspension was formed and cooled to −30 °C before the addition of LiC(SiMe$_3$)N$_2$, freshly prepared by the reaction of N$_2$CH(SiMe$_3$) (2.5 mL, 2.5 mmol, 1.0 M solution in n-hexane) and nBuLi (1 mL, 2.5 mmol, 2.5 M solution in n-hexane) in n-hexane (15 mL) at −30 °C to room temperature within 3 h. The mixture was stirred for 20 h, all volatiles then removed under vacuum, and the residue extracted into toluene. The extract was evaporated under vacuum and further washed with cold n-hexane (2 × 1 mL) to give LGeC(SiMe$_3$)N$_2$ as an orange-yellow crystalline solid (1.267 g, 84%). The melting point (mp) and ^{1}H NMR data identify the compound as that prepared from the reaction of L′Ge (L′ = HC[C(CH$_2$)N-2,6-iPr$_2$C$_6$H$_3$][C(Me)N-2,6-iPr$_2$C$_6$H$_3$] with N$_2$CHSiMe$_3$.[18]

[LGe(Me)CuC$_6$F$_5$]$_2$ (1). In a glovebox, a solution of (CuC$_6$F$_5$)$_4$ (0.115 g, 0.125 mmol) in toluene (5 mL) was added to a solution of LGeMe (0.253 g, 0.5 mmol) in toluene (5 mL). A quick color change from orange red to light yellow was observed. The mixture was stirred for 2 h and filtered, and the filtrate was kept at −20 °C. After 5 days, X-ray-quality light-yellow crystals of **1**·2toluene were collected by filtration (0.34 g, 81%). Mp: 206 °C. ^{1}H NMR (400 MHz, C$_6$D$_6$, 298 K, ppm): δ 0.35 (s, 6 H, GeMe), 1.01 (d, $^3J_{HH}$ = 6.8 Hz, 12 H), 1.13 (d, $^3J_{HH}$ = 6.8 Hz, 12 H), 1.20 (d, $^3J_{HH}$ = 6.8 Hz, 12 H), 1.45 (d, $^3J_{HH}$ = 6.8 Hz, 12 H) (CHMe_2), 1.36 (s, 12 H, CMe), 3.09 (sept, $^3J_{HH}$ = 6.8 Hz, 4 H), 3.60 (sept, $^3J_{HH}$ = 6.8 Hz, 4 H) (CHMe$_2$), 4.76 (s, 2 H, γ-CH), 7.00−7.15 (m, 12 H, C$_6$$H_3$). ^{13}C NMR (100 MHz, C$_6$D$_6$, 298 K, ppm): δ 4.5 (br, GeMe), 21.2, 22.7, 24.29, 24.98, 25.94, 28.23, 29.58 (CMe and CHMe_2), 98.5 (γ-C), 124.3, 125.1, 125.4, 129.1, 137.6, 137.9, 144.1, 145.1 (C_6H$_3$ and C_6F$_5$), 169.0 (CN). ^{19}F NMR (376 MHz, C$_6$D$_6$, 298 K, ppm): δ −161.74 (br, 4 F, m-F), −159.17 (br, 2 F, p-F), −111.01 (br, 4 F, o-F). Anal. Calcd for C$_{72}$H$_{88}$Cu$_2$F$_{10}$Ge$_2$N$_4$ (M_r = 1471.85): C, 58.75; H, 6.03; N, 3.81. Found: C, 59.41; H, 6.62; N, 3.82.

[LGe(Me)(CuC$_6$F$_5$)$_2$]$_2$ (2). The preparation of **2** was performed similarly to that for **1** using (CuC$_6$F$_5$)$_4$ (0.231 g, 0.25 mmol) and LGeMe (0.253 g, 0.5 mmol). X-ray-quality light-yellow crystals of **2**·0.5toluene were obtained after the final solution was kept at −20 °C for 5 days (0.44 g, 89%). Mp: 110 °C (dec). ^{1}H NMR (400 MHz, C$_6$D$_6$, 298 K, ppm): δ 0.38 (s, 6 H, GeMe), 0.96 (d, $^3J_{HH}$ = 6.8 Hz, 12 H), 1.07 (d, $^3J_{HH}$ = 6.8 Hz, 12 H), 1.16 (d, $^3J_{HH}$ = 6.8 Hz, 12H), 1.27 (d, $^3J_{HH}$ = 6.8 Hz, 12 H) (CHMe_2), 1.28 (s, 12 H, CMe), 2.11 (s, 12 H, PhMe), 2.90 (sept, $^3J_{HH}$ = 6.8 Hz, 4 H), 3.27 (sept, $^3J_{HH}$ = 6.8 Hz, 4 H) (CHMe$_2$), 4.73 (s, 2 H, γ-CH), 6.90−7.16 (m, 32 H, C$_6$$H_3$ and PhMe). ^{13}C NMR (100 MHz, C$_6$D$_6$, 298 K, ppm): δ 4.28 (GeMe), 21.18, 22.64, 24.11, 24.19, 25.25, 25.58, 28.09, 29.65 (CMe, CHMe_2, and PhMe), 99.20 (γ-C), 124.58, 124.97, 125.45, 127.81, 128.31, 129.08, 137.43, 137.65, 144.39, 144.45 (C_6H$_3$, C_6F$_5$, and PhMe), 169.41 (CN). ^{19}F NMR (376 MHz, C$_6$D$_6$, 298 K, ppm): δ −160.71 (br, 8 F, m-F), −153.60 (br, 4 F, p-F), −107.77 (br, 8 F, o-F). Anal. Calcd for C$_{87.5}$H$_{92}$Cu$_4$F$_{20}$Ge$_2$N$_4$ (**2**·0.5toluene, M_r = 1979.13): C, 53.10; H, 4.69; N, 2.83. Found: C, 53.86; H, 4.77; N, 2.72.

LGe[C(SiMe$_3$)N$_2$]AgC$_6$F$_5$ (3). In a glovebox, LGeC(SiMe$_3$)N$_2$ (0.121 g, 0.2 mmol) and AgC$_6$F$_5$·MeCN (0.063 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 (ca. 1 mL) added until all solids had dissolved. After stirring for 0.5 h, the solution was filtered and the filtrate was overlayered with n-hexane (1 mL) and then kept at −20 °C. After 2 days, light-yellow crystals of **3** were collected by filtration (0.125 g, 71%). Mp: 156 °C (dec). ^{1}H NMR (400 MHz, CDCl$_3$, 298 K, ppm): δ −0.07 (s, 9 H, SiMe_3), 1.10 (d, $^3J_{HH}$ = 6.8 Hz, 6 H), 1.28 (d, $^3J_{HH}$ = 6.8 Hz, 6 H), 1.41 (d, $^3J_{HH}$ = 6.8 Hz, 6 H), 1.52 (d, $^3J_{HH}$ = 6.8 Hz, 6 H) (CHMe_2), 2.01 (s, 6 H, CMe), 3.15 (sept, $^3J_{HH}$ = 6.8 Hz, 2 H), 3.37 (sept, $^3J_{HH}$ = 6.8 Hz, 2 H) (CHMe$_2$), 5.13 (s, 1 H, γ-CH), 7.23−7.35 (m, 6 H, C$_6$$H_3$). ^{13}C NMR (100 MHz, CDCl$_3$, 298 K, ppm): δ 0.59 (SiMe_3), 24.20, 24.50, 25.30, 25.40, 27.58, 30.45 (CMe and CHMe_2), 97.38 (γ-C), 125.05, 125.20, 128.81, 137.94, 143.36, 146.14 (C_6H$_3$ and C_6F$_5$), 169.54 (CN); the GeC carbon resonance was not observed. ^{19}F NMR (376 MHz, CDCl$_3$, 298 K, ppm): δ −162.16 (m, 2 F, m-F), −159.68 (t, 1 F, p-F), −107.75 (m, 2 F, o-F). ^{29}Si NMR (99 MHz, CDCl$_3$, ppm): δ 0.05 (s, SiMe$_3$). Anal. Calcd for C$_{39}$H$_{50}$AgF$_5$GeN$_4$Si (M_r = 878.38): C, 53.32; H, 5.74; N, 6.38. Found: C, 53.57; H, 5.68; N, 6.45.

{LGe[C(SiMe$_3$)N$_2$](AgC$_6$F$_5$)$_2$}$_2$ (4). The preparation of **4** was performed similarly to that for **3** using LGeC(SiMe$_3$)N$_2$ (0.091 g, 0.15 mmol) and AgC$_6$F$_5$·MeCN (0.095 g, 0.300 mmol). X-ray-quality light-yellow crystals of **4** were obtained (0.095 g, 55%). Mp: 145 °C (dec). ^{1}H NMR (400 MHz, CDCl$_3$, 298 K, ppm): δ −0.06 (s, 9 H, SiMe_3), 1.12 (d, $^3J_{HH}$ = 6.8 Hz, 12 H), 1.30 (d, $^3J_{HH}$ = 6.8 Hz, 12 H), 1.42 (d, $^3J_{HH}$ = 6.8 Hz, 12 H), 1.49 (d, $^3J_{HH}$ = 6.8 Hz, 12 H) (CHMe_2), 2.04 (s, 12 H, CMe), 3.16 (sept, $^3J_{HH}$ = 6.8 Hz, 4 H), 3.29 (sept, $^3J_{HH}$ = 6.8 Hz, 4 H) (CHMe$_2$), 5.21 (s, 2 H, γ-CH), 7.18−7.34 (m, 12 H, C$_6$$H_3$). ^{13}C NMR (100 MHz, CDCl$_3$, 298 K, ppm): δ 0.57 (SiMe_3), 24.22, 24.48, 25.24, 25.38, 27.71, 30.27 (CHMe_2 and CMe), 97.88 (γ-C), 124.98, 125.28, 128.89, 137.39, 143.21, 146,12 (C_6H$_3$ and C_6F$_5$),

Table 1. Summary of Crystal Data and Structure Refinement for 1·2toluene, 2·0.5toluene, 3, and 4[a]

	1·2 toluene	2·0.5 toluene	3	4
formula	$C_{86}H_{104}Cu_2F_{10}Ge_2N_4$	$C_{87.5}H_{92}Cu_4F_{20}Ge_2N_4$	$C_{39}H_{50}AgF_5GeN_4Si$	$C_{90}H_{100}Ag_4F_{20}Ge_2N_8Si_2$
fw	1655.99	1978.99	878.38	2306.62
cryst syst	monoclinic	monoclinic	monoclinic	monoclinic
space group	$C2/c$	$P2(1)/c$	$P2(1)/c$	$P2(1)/n$
a/Å	21.0177(8)	13.638(3)	11.3442(3)	13.8783(6)
b/Å	16.8869(7)	21.394(4)	17.0271(5)	21.7083(7)
c/Å	22.5197(9)	16.103(3)	21.5490(5)	16.1356(8)
α/deg				
β/deg	92.657(3)	105.49(3)	102.671(2)	102.470(4)
γ/deg				
V/Å^3	7984.2(6)	4527.7(16)	4061.01(19)	4746.6(3)
Z	4	2	4	2
ρ_{calcd}/g cm^{-3}	1.378	1.452	1.437	1.614
μ/mm^{-1}	1.341	1.663	1.307	1.547
$F(000)$	3440	2010	1800	2312
cryst size/mm^3	0.44 × 0.40 × 0.38	0.34 × 0.30 × 0.24	0.22 × 0.21 × 0.20	0.20 × 0.20 × 0.10
θ range/deg	2.71−26.00	3.10−26.00	2.65−26.00	2.75−26.00
index ranges	$-25 \leq h \leq 22$ $-20 \leq k \leq 20$ $-27 \leq l \leq 27$	$-16 \leq h \leq 16$ $-26 \leq k \leq 26$ $-19 \leq l \leq 19$	$-13 \leq h \leq 13$ $-18 \leq k \leq 21$ $-26 \leq l \leq 26$	$-14 \leq h \leq 17$ $-26 \leq k \leq 25$ $-19 \leq l \leq 19$
collected data	31718	53752	31073	28650
unique data	7817 (R_{int} = 0.0432)	8845 (R_{int} = 0.0462)	7953 (R_{int} = 0.0510)	9310 (R_{int} = 0.0921)
completeness to θ/%	99.6	99.4	99.9	99.8
data/restraints/param	7817/0/452	8845/0/553	7953/0/473	9310/0/581
GOF on F^2	1.118	0.999	0.795	0.636
final R indices [$I > 2\sigma(I)$]	R1 = 0.0584, wR$_2$ = 0.1490	R1 = 0.0410, wR2 = 0.1266	R1 = 0.0316, wR2 = 0.0519	R1 = 0.0415, wR2 = 0.0339
R indices (all data)	R1 = 0.0743, wR2 = 0.1531	R1 = 0.0548, wR2 = 0.1350	R1 = 0.0626, wR2 = 0.0552	R1 = 0 0.1102, wR2 = 0.0465
largest diff peak/hole (e Å^{-3})	1.108/−0.921	1.004/−0.442	0.333/−0.419	0.577/−0.404

[a] All data were collected at 173(2) K. $R1 = \sum(||F_o| - |F_c||)/\sum|F_o|$, $wR2 = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$, $GOF = \{\sum[w(F_o^2 - F_c^2)^2]/(N_o - N_p)\}^{1/2}$.

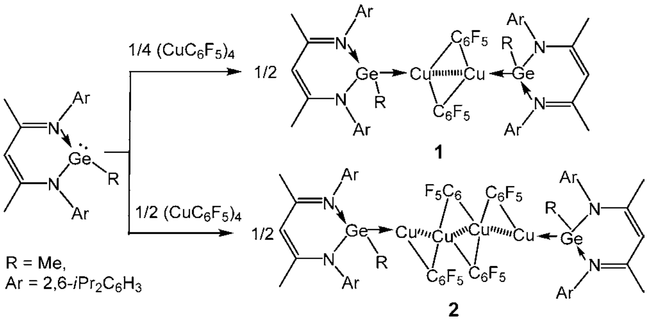
169.87 (CN); the Ge*C* carbon resonance was not observed. ^{19}F NMR (376 MHz, CDCl$_3$, 298 K, ppm): δ −160.79 (br, 8 F, *m-F*), −152.66 (br, 4 F, *p-F*), −104.25 (br, 8 F, *o-F*). ^{29}Si NMR (99 MHz, CDCl$_3$, 298 K, ppm): δ 0.30 (s, *Si*Me$_3$). Anal. Calcd for $C_{97}H_{108}Ag_4F_{20}Ge_2N_8Si_2$ (4· toluene, M_r = 2398.84): C, 48.57; H, 4.54; N, 4.67. Found: C, 49.30; H, 4.74; N, 4.46.

X-ray Crystallographic Analyses of Complexes 1−4. Crystallographic data of compounds **1**·2toluene, **2**·0.5toluene, **3**, and **4** were collected on an Oxford Gemini S Ultra system. In all cases, graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) was used. Absorption corrections were applied using the spherical harmonics program (multiscan type). Structures were solved by direct methods (*SHELXS-96*)[25a] and refined against F^2 using *SHELXL-97*.[25b] In general, non-H atoms were located by difference Fourier synthesis and refined anisotropically and H atoms were included using the riding model with U_{iso} tied to U_{iso} of the parent atoms unless otherwise specified. In **1**·2toluene, **1** was disclosed as a half-moiety and toluene molecules were found in disorder. Toluene was treated in a splitting mode and refined isotropically. In **2**·0.5toluene **2** was determined by a half-moiety also, in which one of the *i*Pr groups in the *N*-aryl substituent of the L ligand was disordered, treated in a splitting mode, and refined isotropically. The 0.5toluene was seriously disordered and refined isotropically without the geometric hydrogen addition. Compound **4** was determined as a half-moiety. The complete molecules of **1**, **2**, and **4** were obtained by a symmetric operation. Cell parameters, data collection, and structure solution and refinement are given in Table 1.

■ RESULTS AND DISCUSSION

Synthesis and Characterization of 1 and 2. The reaction of LGeMe (L = HC[C(Me)N-2,6-*i*Pr$_2$C$_6$H$_3$]$_2$) with 0.25 equiv of (CuC$_6$F$_5$)$_4$ proceeded smoothly in toluene at room temperature and gave light-yellow crystals of **1**·2toluene in good yield (81%). Similarly, the reaction of LGeMe with 0.5 equiv of (CuC$_6$F$_5$)$_4$ also yielded light-yellow crystals of **2**·0.5toluene (89%; Scheme 1). Compounds **1** and **2** are both air-sensitive and change color to dark green and finally to black when exposed to air in the solid state or in solution. **1** is thermally stable (mp 206 °C), whereas **2** is unstable and decomposes at ca. 110 °C. Both of them have been fully characterized by NMR (^{1}H, ^{13}C, and ^{19}F), elemental, and single-crystal X-ray structural analysis.

Scheme 1. Synthesis of 1 and 2



The ^{1}H NMR spectrum of **1** recorded in C$_6$D$_6$ shows distinct signals for the L ligand and the methyl group at the Ge center. Two septets at δ 3.60 and 3.09 and four doublets at δ 1.45, 1.20, 1.13, and 1.01 correspond to the typical C*HMe*$_2$ methine and methyl protons in the ligand *N*-aryl substituents. A high-field singlet at δ 0.35 is assigned to the Ge*Me* protons. The ^{19}F

NMR spectrum shows resonances at δ −110.77, −159.17, and −161.74 with an integral intensity ratio of 2:1:2, corresponding to *o*-, *p*-, and *m*-F atoms, respectively. All of these fluorine signals are broad, indicating that the CuC_6F_5 entities are aggregated in **1**, in which a fast equilibrium is established for the C_6F_5 groups in solution at room temperature. ^1H and ^{19}F NMR spectra of **2** show resonance patterns similar to those of **1** but with different chemical shifts for the protons [δ 3.27 and 2.90 (C*H*Me$_2$), 1.27, 1.16, 1.07, and 0.96 (CH*Me*$_2$), and 0.38 (Ge*Me*)] and fluorines [δ −107.77 (*o*-F), −153.60 (*p*-F), and −160.71 (*m*-F)]. $\Delta\delta(^{19}F_{m,p})^{26}$ is δ 2.57 for **1** but δ 7.11 for **2**, suggesting different CuC_6F_5 aggregation forms in **1** and **2**.

The X-ray structural analysis clearly shows for **1** and **2** the 1:0.25 and 1:0.5 molar ratio products of the two reactants. **1** contains a bridged $(CuC_6F_5)_2$ and **2** a chain-structurally aggregated $(CuC_6F_5)_4$, both supported by LGeMe in general centrosymmetry. Either $(CuC_6F_5)_2$ or $(CuC_6F_5)_4$ shows a new type of aggregation significantly different from the known square-ring one in $(CuC_6F_5)_4$[20,22] and the puckered-ring ones in $[(CuC_6F_5)_4{\cdot}D_m]_n$ (m = 2, n = 0, D = toluene,[20] pyridine,[21] naphthalene, and 2,2′-bithiophene;[23] m = 1, n = ∞, D = naphthalene and 2,2′-bithiophene[22]).

The structure of **1** (Figure 1) shows that the Ge center has tetrahedral geometry due to formation of the Ge−CuC_6F_5 bonding. The Ge−Cu bond length, 2.3228(7) Å, falls in the range for those of Ge−Cu metal−metalloid donor−acceptor bonding complexes [2.2138(4)−2.359(2) Å].[11−13] The Ge−N bond lengths, 1.968(4) and 1.973(4) Å, and the Ge−C distance, 1.972(5) Å, are a little shorter than the corresponding ones in the LGeMe precursor [Ge−N, 2.008(2) and 2.038(2) Å; Ge−C, 2.002(4) Å].[6c] This can be interpreted as a result of a σ donation of the s-orbital electron pair at the Ge center to form the Ge−Cu bond, which increases the s character of the bond between the Ge center and the adjacent coordinating groups.[10c] The Cu center is three-coordinate in nearly triangular geometry (periphery angle, 358.74°). Each C_6F_5 group bridges Cu(1) and Cu(1A) with Cu−$C_{C_6F_5}$ bond lengths of 2.127(5) and 2.130(5) Å, constituting a perfectly rhombic Cu_2C_2 ring.

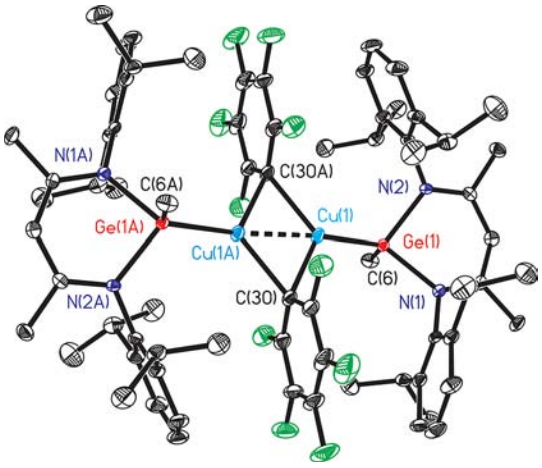


Figure 1. Thermal ellipsoid (50%) drawing of **1**. Selected bond lengths [Å] and angles [deg]: Ge(1)−N(1) 1.973(4), Ge(1)−N(2) 1.968(4), Ge(1)−C(6) 1.972(5), Ge(1)−Cu(1) 2.3228(7), Cu(1)−C(30) 2.127(5), Cu(1)−C(30A) 2.130(5), Cu(1)···Cu(1A) 2.3819(11); N(1)−Ge(1)−N(2) 92.43(15), Cu(1)−Ge(1)−C(6) 120.98(17), Ge(1)−Cu(1)···Cu(1A) 169.56(5), Cu(1)−C(30)−Cu(1A) 68.03(15), Ge(1)−Cu(1)−C(30) 122.58(13), Ge(1)−Cu(1)−C(30A) 124.19(13). Symmetry code: A, −*x* + 0.5, −*y* + 0.5, −*z* + 1.

The Cu_2C_2 ring plane can be extended to the two Ge atoms (mean deviation from the plane, $\Delta_{Ge_2Cu_2C_2}$ = 0.0574 Å), and along the $Ge_2Cu_2C_2$ plane, the two C_6F_5 groups at the Cu atoms are orthogonally arranged, both locating well within the L ligand *N*-aryls. The ipsilateral $(C_6F_5)_{centriod}\cdots aryl_{centroid}$ distances are 3.794 and 3.821 Å with respective dihedral angles of 18.2 and 20.9°, indicating π-stacking interactions between the C_6F_5 groups and the L ligand aryls. Similar strong interactions are observed in $(CuC_6F_5)_4{\cdot}toluene_2$ by parallel arrangement of the toluene molecules to the C_6F_5 groups at a distance of 3.3 Å.[20] In phenyl and pentafluorophenyl esters of benzene-1,2-dicarboxylic acid and tetrafluorobenzene-1,2-dicarboxylic acid, such interactions are indicated by arene···arene separations of 3.70−4.85 Å with corresponding dihedral angles of 5−21°.[27] It is reasonable that the steric and electronic character of LGeMe leads to the lowest $(CuC_6F_5)_2$ aggregate so far observed among organocopper(I) complexes.[28] Therefore, the Cu(1)···Cu(1A) contact of 2.3819(11) Å appears to be the shortest among the $(CuC_6F_5)_4$ aggregates [2.4301(3)−2.6779(8) Å],[20,21] suggestive of a strong $Cu^I\cdots Cu^I$ d^{10}−d^{10} interaction. Theoretical calculations have proved that such interactions should be weakly attractive with respect to the relative contraction of the 4s orbital by admixture with 3d states. That effectively reduces the population of the 3d valence shell,[29] although there is a controversy as to the degree of such interplays under the ligand support.[30]

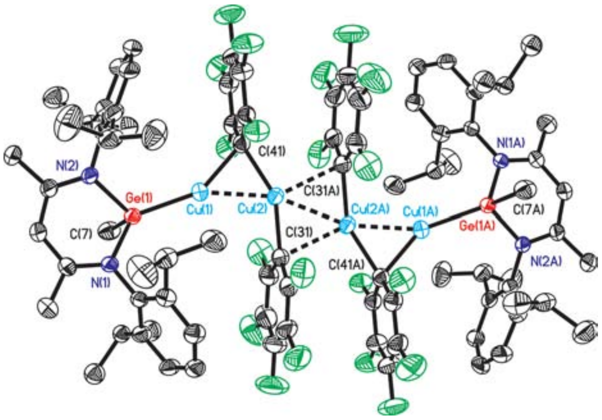


Figure 2. Thermal ellipsoid (50%) drawing of **2**. Selected bond lengths [Å] and angles [deg]: Ge(1)−N(1) 1.955(3), Ge(1)−N(2) 1.943(2), Ge(1)−C(7) 1.969(3), Ge(1)−Cu(1) 2.2867(7), Cu(1)−C(41) 2.039(3), Cu(2)−C(41) 2.005(3), Cu(2)−C(31) 1.953(3), Cu(2A)···C(31) 2.392(3), Cu(1)···Cu(2) 2.4157(7), Cu(2)···Cu(2A) 2.4919(8); N(1)−Ge(1)−N(2) 94.09(11), Cu(1)−Ge(1)−C(7) 124.82(12), Ge(1)−Cu(1)−C(41) 149.01(9), Cu(1)−C(41)−Cu(2) 73.35(11), C(31)−Cu(2)−C(41) 151.81(13), C(31)−Cu(2)−C(31A) 110.85(10), C(41)−Cu(2)−C(31A) 97.04(12), Ge(1)−Cu(1)···Cu(2) 155.64(2), Cu(1)···Cu(2)···Cu(2A) 162.09(3). Symmetry code: A, −*x* + 1, −*y*, −*z* + 1.

The structure of **2** (Figure 2) shows that a Ge−Cu bond length, 2.2867(7) Å, is comparable to that in **1**. However, the Cu(1) center is two-coordinate with the Ge(1)−Cu(1)−C(41) bond angle of 149.01(9)°, significantly nonlinear, whereas the Cu(2) atom appears three-coordinate in triangular geometry (periphery angle, 359.70°). The $(C_6F_5)_{C(41)}$ group bridges Cu(1) and Cu(2) with Cu(1)−C(41) and Cu(2)−C(41) bond lengths of 2.039(3) and 2.005(3) Å. It vectorially splits the

Cu(1)−C(41)−Cu(2) angle by unequal 45.6° and 27.8° amounts. In sharp contrast, the $(C_6F_5)_{C(31)}$ group bonds to Cu(2) and Cu(2A) with a shorter Cu(2)−C(31) bond length of 1.953(3) Å versus a longer Cu(2A)−C(31) bond length of 2.392(3) Å. The $Cu(2)(C_6F_5)_{C(31)}$ moiety is planar (Δ = 0.0422 Å), while the Cu(2A) atom lies out of this plane [Cu(2)−C(31)−Cu(2A), 69.15(10)°]. The Ge(1)Cu(1)-Cu(2)Cu(2A)Cu(1A)Ge(1A)C(31)C(41)C(31A)C(41A) core is observed to be closely planar (Δ = 0.0589 Å), while the four C_6F_5 groups at the respective Cu atoms are arranged orthogonally along the core, residing among the L ligand aryls with ipsilateral $(C_6F_5)_{\text{centriod}}\cdots\text{aryl}_{\text{centroid}}$ distances of 3.881 and 4.014 Å and a $(C_6F_5)_{\text{centriod}}\cdots(C_6F_5)_{\text{centroid}}$ separation of 3.523 Å. This indicates that arene−arene π-stacking interactions are present in **2** also. The Cu(2)···Cu(2A) separation [2.4919(8) Å] is longer than the Cu(1)···Cu(2) distance [2.4157(7) Å]. Both of these two distances are longer than that for **1** [2.3819(11) Å].

Solution Interconversion of 1 and 2. The formation of the dimeric $(CuC_6F_5)_2$ aggregate in **1** and the tetrameric $(CuC_6F_5)_4$ in **2** is due to the use of different molar ratios of the two starting materials. This suggests that production of these two aggregates could be adjustable under the LGeMe support. As shown in Figures 16s and 17s (see the Supporting Information), monitoring of the reaction by ^1H and ^{19}F NMR spectra showed the formation of **1** (see Figures 1s and 3s in the Supporting Information) upon mixing LGeMe with 0.25 equiv of $(CuC_6F_5)_4$ in C_6D_6. The further addition of 0.25 equiv of $(CuC_6F_5)_4$ into this reaction resulted in **2** (see Figures 4s and 6s in the Supporting Information). Interestingly, the addition of 1 equiv of LGeMe to this reaction system at room temperature resulted in the re-formation of **1**. Thus, **1** and **2** can be readily interconverted in solution as follows:

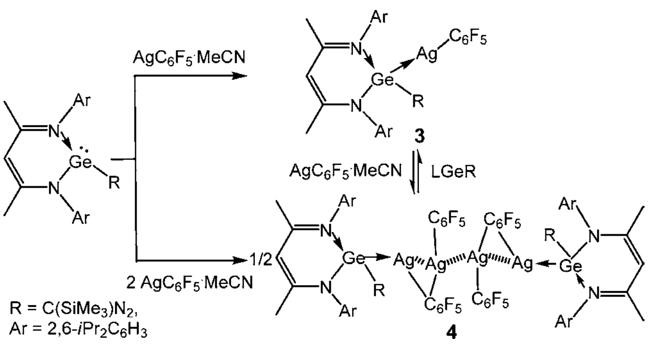
$$\mathbf{1} \xrightleftharpoons[2\ \text{LGeR}]{0.5\ (\text{CuC}_6\text{F}_5)_4} \mathbf{2}$$

The room temperature reactions of LGeMe with $(CuC_6F_5)_4$ in molar ratios of 1:0.75, 1:1, and even 1:2.5 were continuously monitored by NMR spectra to see if highly aggregated $(CuC_6F_5)_n$ (*n* = 6, 8, or 20) could be formed under the support of LGeMe, owing to its steric and electronic character. The respective ^1H and ^{19}F NMR spectra displayed only one set of resonances for each reaction, resembling those for the respective 1:0.25 and 1:0.5 molar ratio reactions (see Figures 16s and 17s in the Supporting Information). The corresponding proton and fluorine resonances showed a gradual migration and then became more and more close, until the fluorine chemical shifts appeared close to those of the starting material $(CuC_6F_5)_4$. Moreover, in all cases, broad fluorine resonances were exhibited.

Low-temperature (−50 °C) ^{19}F NMR spectral measurements were performed on **1** and **2** as well as on the 1:0.75, 1:1, and 1:2.5 molar ratio reactions of LGeMe and $(CuC_6F_5)_4$, all in C_7D_8. First, one set of sharp resonances was seen for **1** (Figure 21s in the Supporting Information), which appeared similar to those in the breakdown $CuC_6F_5 \cdot D'$ (D′ = pyridines or substituted ones),[21] implying that **1** dissociated to give monomeric $LGe(Me)CuC_6F_5$ at low temperature. Second, more than one set of broad resonances were observed for **2**, in which one group of the resonances at δ −105.06 (*o*-F), −145.46 (*p*-F), and −158.72 (*m*-F) was assignable to free $(CuC_6F_5)_4$ [δ −104.65 (*o*-F), −145.71 (*p*-F), and −158.46 (*m*-F); see Table 1s in the Supporting Information] whereas another group of resonances at δ −106.37 (*o*-F), −153.07 (*p*-F), and −160.14 (*m*-F) seemed close to the LGeMe-supported CuC_6F_5 species rather than to the monomeric LGe(Me)-CuC_6F_5 (Figure 22s in the Supporting Information). Meanwhile, the overall integral intensities for the former resonances appeared much lower than those for the latter. All of these results suggest a partial dissociation of the CuC_6F_5 entity from **2** to form free $(CuC_6F_5)_4$. Similar results were also observed for the 1:0.75, 1:1, and 1:2.5 molar ratio reactions (Figures 23s−25s in the Supporting Information), in which the overall integral resonance intensity for the free $(CuC_6F_5)_4$ appeared to increase compared to that for **2**. Accordingly, the observation of one set of the respective ^1H and ^{19}F resonances at room temperature reasonably indicates a fast equilibrium on the NMR time scale between the LGeMe-complexed CuC_6F_5 and uncomplexed $(CuC_6F_5)_4$ for **2** as well as for the 1:0.75, 1:1, and 1:2.5 molar ratio reactions. The formation of highly aggregated $(CuC_6F_5)_n$ (*n* > 4) under the LGeMe support ought to be impossible. Indeed, preparative-scale reactions of LGeMe with $(CuC_6F_5)_4$ in the molar ratio of 1:0.75 or 1:1 were carried out, and only **2** was formed on the basis of NMR (^1H and ^{19}F) spectra and X-ray diffraction analysis of the crystals isolated.

Synthesis and Characterization of 3 and 4. Encouraged by the syntheses of **1** and **2**, we investigated the reaction of the germylene with pentafluorophenylsilver(I). The reaction of $LGeC(SiMe_3)N_2$ with $AgC_6F_5 \cdot MeCN$ was performed as before but in the dark because of the photosensitivity of the silver species. Compounds **3** (71% yield) and **4** (55% yield) were obtained as light-yellow crystals according to the molar ratios of 1:1 and 1:2 of the two starting materials used (Scheme 2). A pentafluorophenylsilver(I) compound was prepared early in the 1970s.[19a] Probably because of the strong solvent dependence, the solid-state structure of this compound has not yet been disclosed, although it has been suggested to have a tetrameric, square-ring structure similar to that of related arylsilver(I) complexes.[31] When treated with organic donors, infinitely long, chainlike structure complexes $AgC_6F_5 \cdot RCN$ (R = Me, Et) and $Au(C_6F_5)_2Ag \cdot SC_4H_8$ were reported.[19b,c] Apparently, both **3** and **4** represent a new type of AgC_6F_5 aggregation supported by the diketiminate germylene.

Scheme 2. Synthesis of 3 and 4



These two compounds are sensitive to air but only a little to light. They are both thermally unstable. **3** decomposes at 156 °C and **4** at 145 °C. The ^1H NMR spectra recorded in $CDCl_3$ show one set of proton resonances for the L ligand and the $C(SiMe_3)N_2$ group at Ge for **3** and **4**. The ^{29}Si NMR spectra show the silicon resonance at δ 0.05 for **3** and at δ 0.30 for **4**. ^{19}F NMR spectra exhibit fluorine resonances for the C_6F_5

group(s) with sharp signals present in **3** [δ −162.16 (*m-F*), −159.68 (*p-F*), and −107.75 (*o-F*)] but much broader ones in **4** [δ −160.79 (*m-F*), −152.66 (*p-F*), −104.25 (*o-F*); Figures 9s and 13s in the Supporting Information] compared to those in **1** and **2** (Figures 9s and 13s in the Supporting Information).

The X-ray structural analysis shows **3** as a monomeric compound with AgC_6F_5 terminally bound to $LGeC(SiMe_3)N_2$ (Figure 3). The Ge−Ag bond length is 2.4480(3) Å, comparable to those in complexes $(R_2ATI)(X)GeAg\{HB[3,5\text{-}(CF_3)_2Pz]_3\}$ [2.4116(10)−2.4215(9) Å; R_2ATI = *N*-alkyl-2-(methylamino)troponiminate, R = Me, X = Cl or OSO_2CF_3; R = *n*Pr, X = Cl or N_3],[10] and fits well to the predicted one in $[HC(H)N]_2GeAgCl$ (2.448 Å).[7] The Ge−Ag metal−metalloid donor−acceptor bonding also results in the shorter Ge−N and Ge−C bond lengths around the Ge center compared with those in $LGeC(SiMe_3)N_2$.[18] The $(C_6F_5)_{C(30)}$ bonds to Ag(1) in a perfect plane (Δ = 0.0143 Å) with a Ag(1)−C(30) bond distance of 2.122(3) Å and a $Ge{-}Ag{-}C_{C_6F_5}$ angle of 173.16(10)°. This structural feature may suggest free rotation of the C_6F_5 group in **3** in solution, therefore giving sharp resonances in the ^{19}F NMR spectrum.

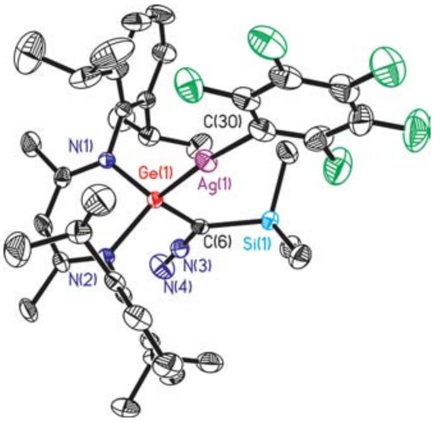


Figure 3. Thermal ellipsoid (50%) drawing of **3**. Selected bond lengths [Å] and angles [deg]: Ge(1)−N(1) 1.944(2), Ge(1)−N(2) 1.944(2), Ge(1)−C(6) 1.945(3), Ge(1)−Ag(1) 2.4480(3), Ag(1)−C(30) 2.122(3); N(1)−Ge(1)−N(2) 94.19(9), Ag(1)−Ge(1)−C(6) 111.46(8), Ge(1)−Ag(1)−C(30) 173.16(10).

The structure of **4** is very similar to that of **2** apart from the $C(SiMe_3)N_2$ group replacing the Me and the Ag atom replacing Cu both at the Ge atom (Figure 4). However, the $(AgC_6F_5)_4$ array presents differences in the geometry compared to $(CuC_6F_5)_4$ in **2** due to the different metal centers. The $(C_6F_5)_{C(30)}$ bridges Ag(1) and Ag(2) with a Ag(1)−C(30) bond length of 2.264(4) Å and Ag(2)−C(30) of 2.155(5) Å and a Ag(1)−C(30)−Ag(2) angle of 76.21(15)° [$(C_6F_5)_{C(30)}$ vector bisection angles, 54.4° and 21.9°]. $(C_6F_5)_{C(40)}$ should be considered terminally bound to Ag(2) because Ag(2)-$(C_6F_5)_{C(40)}$ is almost planar (Δ = 0.0510 Å), while the Ag(2)−C(40) bond length [2.091(5) Å] appears close to the terminal bond in **3**. Furthermore, the Ag(2A)···C(40) separation is much greater (3.619 Å) and is even longer than the corresponding van der Waals radii (3.42 Å).[32] Such a Ag(2)−$(C_6F_5)_{C(40)}$···Ag(2A) bonding mode also is remarkably different from those found in infinite chainlike complexes $AgC_6F_5{\cdot}RCN$ [R = Me,[19c] 2.147(2) and 2.381(2) Å; R = Et,[19b] 2.128(5) and 2.387(5) Å]. All of these features suggest that there is almost no interaction between the Ag(2A) atom and the $(C_6F_5)_{C(40)}$ group. Thus, the Ag(2)···Ag(2A) contact is formed by 3.0627(7) Å on the basis of the centrosymmetric operation. This distance is much longer than the Ag(1)···Ag(2) one [2.7264(5) Å] but relates to those in ligand-unsustained nonorganometallic silver(I) complexes [3.0228(5)−3.431(4) Å].[33] This indicates that the Ag(2)···Ag(2A) $d^{10}{-}d^{10}$ interaction is actually attractive but without ligand support. Similar cases have only been found in silver(I)-involved infinite chainlike complexes $AuC_6F_5{\cdot}SC_4H_8$ [$Au^I{\cdots}Au^I$, 3.128(2)−3.306(1) Å][34a] and $Au(C_6F_5)_2Ag{\cdot}SC_4H_8$ [$Au^I{\cdots}Au^I$, 2.889(2) Å; $Au^I{\cdots}Ag^I$, 2.717(2)−2.726(2) Å].[34b] It should therefore be concluded that the adjacent Ag(1)···Ag(2) and Ag(1A)···Ag(2A) interplays are attractive because of the considerably shorter distances, although they are supported by the C_6F_5 groups. The Cu···Cu distances in **1** and **2** are much shorter than those of unsupported complexes [2.5790(4)−4.7230(5) Å],[33] similarly indicating that the $Cu^I{\cdots}Cu^I$ interactions are also attractive. In addition, the four C_6F_5 groups locate among the L ligand aryls with the ipsilateral $(C_6F_5)_{centriod}{\cdots}aryl_{centroid}$ of 4.043 and 5.221 Å and $(C_6F_5)_{centriod}{\cdots}(C_6F_5)_{centroid}$ of 3.548 Å, all demonstrating arene−arene π-stacking interactions.

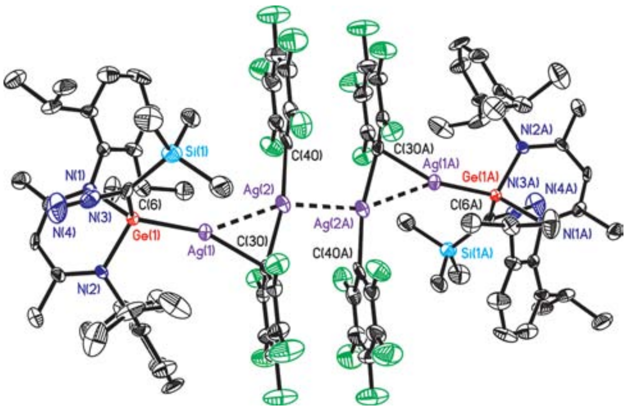


Figure 4. Thermal ellipsoid (50%) drawing of **4**. Selected bond lengths [Å] and angles [deg]: Ge(1)−N(1) 1.953(3), Ge(1)−N(2) 1.924(4), Ge(1)−C(6) 1.947(4), Ge(1)−Ag(1) 2.4258(5), Ag(1)−C(30) 2.264(4), Ag(2)−C(30) 2.155(5), Ag(2)−C(40) 2.091(5), Ag(2A)···C(40) 3.619, Ag(1)···Ag(2) 2.7264(5), Ag(2)···Ag(2A) 3.0627(7); N(1)−Ge(1)−N(2) 94.57(15), Ag(1)−Ge(1)−C(6) 114.70(12), Ge(1)−Ag(1)−C(30) 156.04(12), Ag(1)−C(30)−Ag(2) 76.21(15), C(30)−Ag(2)−C(40) 167.32(15), Ge(1)−Ag(1)···Ag(2) 149.41(2), Ag(1)···Ag(2)···Ag(2A) 153.19(2). Symmetry code: A, −*x* − 1, −*y*, −*z*.

The ^1H and ^{19}F NMR spectral-monitored reactions were also carried out, revealing interconversion between **3** and **4** (Scheme 2 and Figures 18s−20s in the Supporting Information). Although this appeared relatively complex compared to the $LGeMe/(CuC_6F_5)_4$ reaction system, a fast equilibrium on the NMR time scale should be established between the $LGeC(SiMe_3)N_2$-complexed and uncomplexed AgC_6F_5 species for **4** as well as for the 1:3, 1:4, and 1:10 molar ratio reactions by the related ^1H and ^{19}F NMR at room temperature as well as by low-temperature (−50 °C) ^{19}F NMR measurements (Figures 26s−30s in the Supporting Information). It is noteworthy that the sharp fluorine resonance data pattern was maintained at −50 °C for **3**, which indirectly proves dissociation of **1** into its monomeric form at low temperature.

Photoluminescence Studies of 1−4. We carried photophysical studies of **1**−**4** with starting materials LGeR [R = Me and $C(SiMe_3)N_2$], $(CuC_6F_5)_4$, and $AgC_6F_5{\cdot}MeCN$ for comparison. All samples were measured in a CH_2Cl_2 solution at room temperature. The absorption, excitation, and emission spectra of each compound are shown in Figures 31s–39s (see the Supporting Information). The emission spectra for the LGeMe/$(Cu_6F_5)_4$ reaction system complexes are shown in Figure 5(I) and for the LGeC$(SiMe_3)N_2$/$AgC_6F_5\cdot$MeCN system compounds in Figure 5(II). Complex **1** displays green luminescence (λ_{em} = 497 nm) upon excitation at λ_{ex} = 336 nm and **2** blue luminescence (λ_{em} = 458 nm) at λ_{ex} = 340 nm. These two emission bands are significantly red-shifted compared to those of the starting materials LGeMe and $(CuC_6F_5)_4$ (both at λ_{em} = 404 nm) under the same conditions. This is due to the strong Ge−Cu metal−metalloid donor−acceptor bonding present in **1** and **2** in solution. Tolman and co-workers have discussed the Cu → Ge$[N(SiMe_3)_2]_2$/Ge$[(NMes)_2(CH)_2]$ charge-transfer (MLCT) transitions by observation of the weaker shoulder bands in the UV−vis spectra.[11] The fact that coordination of metal ions by external organic donor(s) often results in significant emission band changes is well-known.[35]

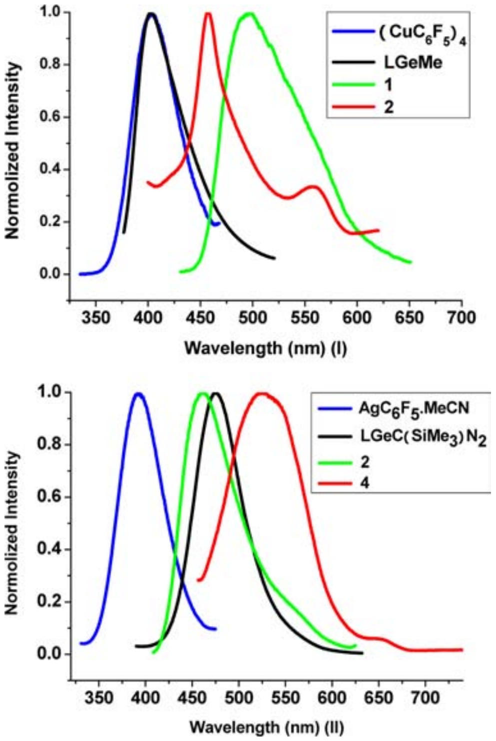


Figure 5. Luminescence spectra recorded in a CH_2Cl_2 solution at room temperature by irradiation with a UV−vis lamp (λ_{em}, nm): (I) LGeMe (404), $(CuC_6F_5)_4$ (402), **1** (497), and **2** (458 and 558); (II) LGeC$(SiMe_3)N_2$ (476), $AgC_6F_5\cdot$MeCN (392), **3** (460), and **4** (526 and 648).

Correspondingly, Figure 5(II) proves the persistence of the Ge−Ag metal−metalloid donor−acceptor bonding in solution from the presence of the blue luminescence band at 460 nm for **3** and the green one at 526 nm for **4** because these two bands are both clearly shifted relative to those of LGeC$(SiMe_3)N_2$ (λ_{em} = 476 nm) and $AgC_6F_5\cdot$MeCN (λ_{em} = 392 nm).

CONCLUSIONS AND REMARKS

In summary, we have shown the use of the N-heterocyclic β-diketiminate germylene in the formation of the pentafluorophenylcopper(I) and -silver(I) complexes **1**−**4**. These were clearly characterized by NMR (^1H, ^{13}C, ^{19}F, and/or ^{29}Si) spectroscopy and X-ray crystallography. The reactions were successful for germylene with $(CuC_6F_5)_4$ rather than with $(CuMes)_4$.[16] This implies a requirement of enhanced Lewis acidity for the organocoinage metal(I) species in forming the Ge−Cu metal−metalloid donor−acceptor bond. The formation of $(CuC_6F_5)_n$ (n = 2, 4) or $(AgC_6F_5)_4$ under germylene support reflects the strong aggregation nature of the CuC_6F_5 or $(AgC_6F_5)_4$ entity, although these aggregations are affected by the temperature in solution. However, the exhibition of the weakly attractive $Cu^I\cdots Cu^I$ or $Ag^I\cdots Ag^I$ d^{10}−d^{10} interactions with or without ligand support as well as the arene−arene π stackings among C_6F_5 and the L ligand aryls truly reveals the electronic and steric properties of the N-heterocyclic β-diketiminate germylene in character.[36] In addition, structural differences between **1** and **3** as well as between **2** and **4** clearly show the disparity between the CuC_6F_5 and AgC_6F_5 species, resulting from their different metal radii and the electronic properties. Further work is in process on the use of the germylene-supported CuC_6F_5 or AgC_6F_5 compounds for organic molecule transformation reactions and synthesis of the germylene-sustained organogold(I) complexes.

ASSOCIATED CONTENT

Ⓢ Supporting Information

CIF data, NMR spectra, and photophysical (absorption, excitation, and emission) spectra for **1**−**4**. 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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REFERENCES

(1) Selected examples and reviews: (a) Kuhn, N.; Kratz, T. *Synthesis* **1992**, 561−562. (b) Arduengo, A. J., III; Dias, H. V. R.; Calabrese, J. C.; Davidson, F. *Organometallics* **1993**, *12*, 3405−3409. (c) Bourissou, D.; Guerret, O.; Gabbai, F. P.; Bertrand., G. *Chem. Rev.* **2000**, *100*, 39−92 and references cited therein. (d) Herrmann, W. A. *Angew. Chem., Int. Ed.* **2002**, *41*, 1290−1309 and references cited therein. (e) Carrison, J. C.; Youngs, W. J. *Chem. Rev.* **2005**, *105*, 3978−4008. (f) Arduengo, A. J.; Bertrand, G. *Chem. Rev.* **2009**, *109*, 3209−3210 and references cited therein. (g) Öfele, K.; Tosh, E.; Taubmann, C.; Herrmann, W. A. *Chem. Rev.* **2009**, *109*, 3408−3444 and references cited therein. (h) Arnold, P. L.; Casely, I. J. *Chem. Rev.* **2009**, *109*, 3599−3611. (i) Lin, J. C. Y.; Huang, R. T. W.; Lee, C. S.; Bhattacharyya, A.; Hwang, W. S.; Lin, I. J. B. *Chem. Rev.* **2009**, *109*, 3561−3598. (j) Díez-González, S.; Marion, N.; Nolan, S. P. *Chem. Rev.* **2009**, *109*, 3612−3676. (k) Vougioukalakis, G. C.; Grubbs, R. H. *Chem. Rev.* **2010**, *110*, 1746−1787.

(2) Selected examples: (a) Pineda, L. W.; Jancik, V.; Roesky, H. W.; Magull, J. *Angew. Chem., Int. Ed.* **2004**, *43*, 1419−1421. (b) Jancik, V.; Pineda, L. W.; Pinkas, J.; Roesky, H. W.; Neculai, D.; Neculai, A. M.; Herbst-Irmer, R. *Angew. Chem., Int. Ed.* **2004**, *43*, 2141−2145. (c) Zhu, H.; Chai, J.; He, C.; Bai, G.; Roesky, H. W.; Jancik, V.; Schmidt, H.-G.; Noltemeyer, M. *Organometallics* **2005**, *24*, 380−384. (d) Roesky, H. W.; Singh, S.; Jancik, V.; Chandrasekhar, V. *Acc. Chem. Res.* **2004**, *37*, 969−981. (e) Roesky, H. W.; Singh, S.; Yusuff, K. K. M.; Maguire, J. A.; Hosmane, N. S. *Chem. Rev.* **2006**, *106*, 3813−3843. (f) Ghadwal, R. S.; Roesky, H. W.; Merkel, S.; Henn, J.; Stalke, D. *Angew. Chem., Int. Ed.* **2009**, *48*, 5683−5686. (g) Cui, H.; Shao, Y.; Li, X.; Kong, L.; Cui, C. *Organometallics* **2009**, *28*, 5191−5195. (h) Sen, S. S.; Roesky, H. W.; Stem, D.; Henn, J.; Stalke, D. *J. Am. Chem. Soc.* **2010**, *132*, 1123−1126. (i) Filippou, A. C.; Chernov, O.; Blom, B.; Stumpf, K. W.; Schnakenburg, G. *Chem.—Eur. J.* **2010**, *16*, 2866−2872.

(3) Selected reviews and examples: (a) Enders, D.; Niemeier, O.; Henseler, A. *Chem. Rev.* **2007**, *107*, 5606−5655. (b) Zhang, Y.; Miyake, G. M.; Chen, E. Y.-X. *Angew. Chem., Int. Ed.* **2010**, *49*, 10158−10162. (c) Biju, A. T.; Kuhl, N.; Glorius, F. *Acc. Chem. Res.* **2011**, *44*, 1182−1195. (d) Boddaert, T.; Coquerel, Y.; Rodriguez, J. *Chem.—Eur. J.* **2011**, *17*, 2266−2271.

(4) (a) Pfeiffer, J.; Noltemeyer, M.; Meller, A. *Z. Anorg. Allg. Chem.* **1989**, *572*, 145−150. (b) Dias, H. V. R.; Wang, Z.; Jin, W. *Coord. Chem. Rev.* **1998**, *176*, 67−86. (c) Jutzi, P.; Keitemeyer, S.; Neumann, B.; Stammler, H.-G. *Organometallics* **1999**, *18*, 4778−4784. (d) Kühl, O. *Coord. Chem. Rev.* **2004**, *248*, 411−427. (e) Nagendran, S.; Roesky, H. W. *Organometallics* **2008**, *27*, 457−492. (f) Mizuhata, Y.; Sasamori, T.; Tokitoh, N. *Chem. Rev.* **2009**, *109*, 3479−3511. (g) Mandal, S. K.; Roesky, H. W. *Chem. Commun.* **2010**, *46*, 6016−6041. (h) Asay, M.; Jones, C.; Driess, M. *Chem. Rev.* **2011**, *111*, 354−396. (i) Yao, S.-L.; Xiong, Y.; Driess, M. *Organometallics* **2011**, *30*, 1748−1767. (j) Mandal, S. K.; Roesky, H. W. *Acc. Chem. Res.* **2012**, *45*, 298−307.

(5) (a) Gehrhus, B.; Hitchcock, P. B.; Lappert, M. F. *J. Chem. Soc., Dalton Trans.* **2000**, 3094−3009. (b) Yao, S.; Xiong, Y.; Driess, M. *Chem. Commun.* **2009**, 6466−6468.

(6) (a) Pfeiffer, J.; Noltemeyer, M.; Meller, A. *Chem. Ber.* **1989**, 245−252. (b) Contel, M.; Hellmann, K. W.; Gade, L. H.; Scowen, I. J.; McPartlin, M.; Laguna, M. *Inorg. Chem.* **1996**, *35*, 3713−3715. (c) Ding, Y.; Ma, Q.; Roesky, H. W.; Herbst-Irmer, R.; Usón, I.; Noltemeyer, M.; Schmidt, H.-G. *Organometallics* **2002**, *21*, 5216−5220. (d) Ding, Y.; Ma, Q.; Usón, I.; Roesky, H. W.; Noltemeyer, M.; Schmidt, H.-G. *J. Am. Chem. Soc.* **2002**, *124*, 8542−8543. (e) Ding, Y.; Ma, Q.; Roesky, H. W.; Usón, I.; Noltemeyer, M.; Schmidt, H.-G. *Dalton Trans.* **2003**, 1094−1098. (f) Mcheik, A.; Katir, N.; Castel, A.; Gornitzka, H.; Massou, S.; Riviere, P.; Hamieh, T. *Eur. J. Inorg. Chem.* **2008**, 5397−5403.

(7) D_e = 61.2−88.6 at the MP2 level and 56.5−82.8 kcal mol^{-1} at the CCSD(T) level for NHC → MCl (M = Cu, Ag, Au) and D_e = 33.0−53.5 at the MP2 level and 29.9−49.4 kcal mol^{-1} at the CCSD(T) level for NHGe → MCl. See: Boehme, C.; Frenking, G. *Organometallics* **1998**, *17*, 5801−5809.

(8) The NHC has been well-known as a strong σ donor but a weak π acceptor. Comparably, the NHGe is thought to be a poor σ donor and a good π acceptor. See: Ullah, F.; Kühl, O.; Bajor, G.; Veszprémi, T.; Jones, P. G.; Heinicke, J. *Eur. J. Inorg. Chem.* **2009**, 221−229.

(9) Selected examples: (a) Niemeyer, M. *Z. Anorg. Allg. Chem.* **2003**, *629*, 1535−1540. (b) Mankad, N. P.; Gray, T. G.; Laitar, D. S.; Sadighi, J. P. *Organometallics* **2004**, *23*, 1191−1193. (c) Mankad, N. P.; Laitar, D. S.; Sadighi, J. P. *Organometallics* **2004**, *23*, 3369−3371. (d) Goj, L. A.; Blue, E. D.; Munro-Leighton, C.; Gunnoe, T. B.; Petersen, J. L. *Inorg. Chem.* **2005**, *44*, 8647−8649. (e) Goj, L. A.; Blue, E. D.; Delp, S. A.; Gunnoe, T. B.; Cundari, T. R.; Petersen, J. L. *Organometallics* **2006**, *25*, 4097−4104. (f) Goj, L. A.; Blue, E. D.; Delp, S. A.; Gunnoe, T. B.; Cundari, T. R.; Pierpont, A. W.; Petersen, J. L.; Boyle, P. D. *Inorg. Chem.* **2006**, *45*, 9032−9045. (g) Ren, H.; Zhao, X.; Xu, S.; Song, H.; Wang, B. *J. Organomet. Chem.* **2006**, *691*, 4109−4113.

(10) (a) Dias, H. V. R.; Wang, Z. *Inorg. Chem.* **2000**, *39*, 3890−3893. (b) Dias, H. V. R.; Ayers, A. E. *Polyhedron* **2002**, *21*, 611−618. (c) Ayers, A. E.; Dias, H. V. R. *Inorg. Chem.* **2002**, *41*, 3259−3268.

(11) York, J. T.; Young, V. G., Jr.; Tolman, W. B. *Inorg. Chem.* **2006**, *45*, 4191−4198.

(12) Leung, W.-P.; So, C.-W.; Chong, K.-H.; Kan, K.-W.; Chan, H.-S.; Mak, T. C. W. *Organometallics* **2006**, *25*, 2851−2858.

(13) (a) Arii, H.; Nakadate, F.; Mochida, K. *Organometallics* **2009**, *28*, 4909−4911. (b) During the revision of this manuscript, one of the germanium(II) → copper(I) compounds was reported: Faaerro, L.; Hitchcock, P. B.; Coles, M. P.; Fulton, J. R. *Inorg. Chem.* **2012**, *51*, 1544−1551.

(14) (a) An, D.; Wang, J.; Dong, T.; Yang, Y.; Wen, T.; Zhu, H.; Lu, X.; Wang, Y. *Eur. J. Inorg. Chem.* **2010**, 4506−4512. (b) Tan, G.; Zhu, H. *Inorg. Chem.* **2011**, *50*, 6979−6986.

(15) (a) van Koten, G. *J. Organomet. Chem.* **1990**, *400*, 283−301. (b) Jäkle, F. *Dalton Trans.* **2007**, 2851−2858.

(16) The ^{1}H NMR spectral data of a mixture of LGeMe and 0.25 equiv of (CuMes)$_4$ in C_6D_6 at room temperature showed no change in the proton resonances compared to those of starting materials LGeMe and (CuMes)$_4$. (CuMes)$_4$ was prepared according to the following references: (a) Meyer, E. M.; Gambarotta, S.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *Organometallics* **1989**, *8*, 1067−1079. (b) Eriksson, H.; Håkansson, M. *Organometallics* **1997**, *16*, 4243−4244.

(17) Cairncross, A.; Sheppard, W. A.; Wonchoba, E.; Guilford, W. J.; House, C. B.; Coates, R. M. *Org. Synth.* **1980**, *59*, 122−127.

(18) Jana, A.; Objartel, I.; Roesky, H. W.; Stalke, D. *Inorg. Chem.* **2009**, *48*, 7645−7649.

(19) (a) Sun, K. K.; Miller, W. T. *J. Am. Chem. Soc.* **1970**, *92*, 6985−6987. (b) Tyrra, W.; Wickleder, M. S. *Z. Anorg. Allg. Chem.* **2002**, *628*, 1841−1847. (c) Kuprat, M.; Lehmann, M.; Schulz, A.; Villinger, A. *Organometallics* **2010**, *29*, 1421−1427.

(20) Sundararaman, A.; Lalancette, R. A.; Zakharov, N. L.; Rheingold, A. L.; Jäkle, F. *Organometallics* **2003**, *22*, 3526−3532.

(21) Doshi, A.; Sundararaman, A.; Venkatasubbaiah, K.; Zakharov, L. N.; Rheingold, A. L.; Myahkostupov, M.; Piotrowiak, P.; Jäkle, F. *Organometallics* **2012**, *31*, 1546−1558.

(22) (a) Cairncross, A.; Sheppard, W. A. *J. Am. Chem. Soc.* **1968**, *90*, 2186−2187. (b) Cairncross, A.; Omura, H.; Sheppard, W. A. *J. Am. Chem. Soc.* **1971**, *93*, 248−249.

(23) Doshi, A.; Venkatasubbaiah, K.; Rheingold, A. L.; Jäkle, F. *Chem. Commun.* **2008**, 4264−4266.

(24) Sundarararman, A.; Zakharov, L. N.; Rheingold, A. L.; Jäkle, F. *Chem. Commun.* **2005**, 1708−1710.

(25) (a) *SHELXS-90, Program for Structure Solution*: Sheldrick, G. M. *Acta Crystallogr., Sect. A* **1990**, *46*, 467−473. (b) Sheldrick, G. M. *SHELXL-97, Program for Crystal Structure Refinement*; University of Göttingen: Göttingen, Germany, 1997.

(26) Jäkle and co-workers have discussed that $\Delta\delta(^{19}\mathrm{F}_{m,p})$ could be used to reflect the degree of aggregation of CuC_6F_5 interacting with different donors; see refs 20 and 21.

(27) Bacchi, S.; Benaglia, M.; Cozzi, F.; Demartin, F.; Filippini, G.; Gavezzotti, A. *Chem.—Eur. J.* **2006**, *12*, 3538−3546.

(28) (a) He, X.; Olmstead, M. M.; Power, P. P. *J. Am. Chem. Soc.* **1992**, *114*, 9668−9670. (b) Niemeyer, M. *Organometallics* **1998**, *17*, 4649−4656.

(29) (a) Mehrotra, P. K.; Hoffmann, R. *Inorg. Chem.* **1978**, *17*, 2187−2189. (b) Merz, K. M., Jr.; Hoffmann, R. *Inorg. Chem.* **1988**, *27*, 2120−2127. (c) Pyykkö, P. *Chem. Rev.* **1997**, *97*, 597−636. (d) Ford., P. C.; Cariati, E.; Bourassa, J. *Chem. Rev.* **1999**, *99*, 597−636. (e) Kölmel, C.; Ahlrichs, R. *J. Phys. Chem.* **1990**, *94*, 5536−5542. (f) Hermann, H. L.; Boche, G.; Schwerdtfeger, P. *Chem.—Eur. J.* **2001**, *7*, 5333−5342.

(30) Cotton, F. A.; Feng, X.; Matus, M.; Poli, R. *J. Am. Chem. Soc.* **1988**, *110*, 7077−7083.

(31) (a) Gambarotta, S.; Floriani, C.; Chiesa-Villa, A.; Guastini, C. *J. Chem. Soc., Chem. Commun.* **1983**, 1087−1088. (b) Edwards, D. A.; Harker, R. M.; Mahon, M. F.; Molloy, K. C. *J. Chem. Soc., Dalton Trans.* **1997**, 3509−3514. (c) Voelker, H.; Labahn, D.; Bohnen, F. M.; Herbst-Irmer, R.; Roesky, H. W.; Stalke, D.; Edelmann, F. T. *New J. Chem.* **1999**, *23*, 905−909.

(32) Bondi, A. *J. Phys. Chem.* **1964**, *68*, 441−451.

(33) (a) Singh, K.; Long, J. R.; Stavropoulos, P. *J. Am. Chem. Soc.* **1997**, *119*, 2942−2943. (b) Zhang, J.-P.; Wang, Y.-B.; Huang, X.-C.; Lin, Y.-Y.; Chen, X.-M. *Chem.—Eur. J.* **2005**, *11*, 552−561.

(34) (a) Coetzee, J.; Gabrielli, W. F.; Coetzee, K.; Schuster, O.; Nogai, S. D.; Cronje, S.; Raubenheimer, H. G. *Angew. Chem., Int. Ed.* **2007**, *46*, 2497−2500. (b) Usón, R.; Laguna, A.; Laguna, M. *J. Chem. Soc., Chem. Commun.* **1981**, 1097−1098.

(35) Schulman, S. G. *Fluorescence and Phosphorescence Spectroscopy: Physicochemical Principles and Practice*; Pergamon Press: Oxford, U.K., 1977.

(36) This L ligand feature has been extensively applied in the synthesis of mononuclear complexes involving most elements in the periodic table. See selected examples: (a) Cui, C.; Roesky, H. W.; Schmidt, H.-G.; Noltemeyer, M.; Hao, H.; Cimpoesu, H. *Angew. Chem., Int. Ed.* **2000**, *39*, 4274−4276. (b) Hardman, N. J.; Eichler, B. E.; Power, P. P. *Chem. Commun.* **2000**, 1991−1992. (c) Hardman, N. J.; Power, P. P.; Gorden, J. D.; Macdonald, C. L. B.; Cowley, A. H. *Chem. Commun.* **2001**, 1866−1867. (d) Bourget-Merle, L.; Lappert, M. F.; Severn, J. R. *Chem. Rev.* **2002**, *102*, 3031−3065 and references cited therein. (e) Hardman, N. J.; Wright, R. J.; Philips, A. D.; Power, P. P. *J. Am. Chem. Soc.* **2003**, *125*, 2667−2679. (f) Roesky, H. W. *Inorg. Chem.* **2004**, *43*, 7284−7293 and references cited therein. (g) Kempter, A.; Gemel, C.; Fischer, R. A. *Inorg. Chem.* **2005**, *44*, 163−165. (h) Chai, J.; Zhu, H.; Stückl, A. C.; Roesky, H. W.; Magull, J.; Bencini, S.; Caneschi, A.; Gatteschi, D. *J. Am. Chem. Soc.* **2005**, *127*, 9201−9206. (i) Yao, Y.; Zhang, Z.; Peng, H.; Zhang, Y.; Shen, Q.; Lin, J. *Inorg. Chem.* **2006**, *45*, 2175−2183. (j) Li, X.; Cheng, X.; Song, H.; Cui, C. *Organometallics* **2007**, *26*, 1039−1043. (k) Nagendran, S.; Roesky, H. W. *Organometallics* **2008**, *27*, 457−492 and references cited therein.