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Synthesis and Complexation of a Free Germanide Bearing a Tridentate N-Heterocyclic Substituent

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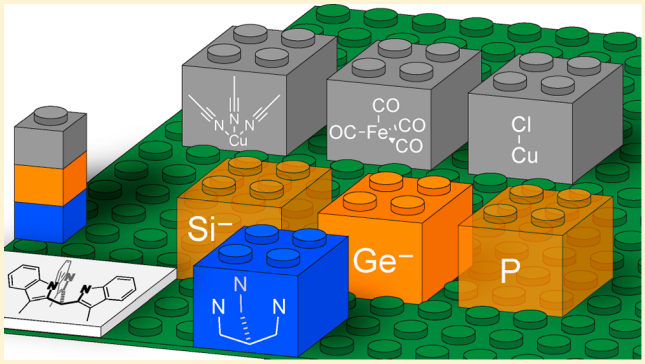
Supporting Information

ABSTRACT: The tris-N-heterocycle germanide (tmim)Ge$^-$ (**1**) (tmimH$_3$ = tris(3-methylindol-2-yl)methane) was synthesized by nucleophilic substitution for the tmim^{3-} trianion on GeCl$_2$·dioxane. In combination with the previously reported (tmim)Si$^-$ and (tmim)P analogues, it provides a convenient model for investigating the influence of the central atom on the properties of isoelectronic ligands. Complexation of the germanide (tmim)Ge$^-$ to CuCl resulted in the dimeric chloro cuprate [(tmim)GeCu(μ-Cl)]$_2^{2-}$, which is prone to dissociation in MeCN to form the neutral, solvated germylcopper (tmim)GeCu(NCMe)$_3$. The reaction of **1** with Fe$_2$(CO)$_9$ afforded the germyl iron tetracarbonyl [(tmim)GeFe(CO)$_4$]$^-$. Analysis of the $\tilde{\nu}$(CO) infrared absorption bands in this complex indicates that the combined electron donating and accepting properties of **1** are found in between those of (tmim)P and (tmim)Si$^-$. In contrast to (tmim)Si$^-$, (tmim)Ge$^-$ is reluctant to coordinate to FeCl$_2$, likely because of its softer Lewis base character. Key structural features of the ligands and complexes reflect changes in their electronic properties. In particular, the N−Ge−N angles increase upon coordination to a metal fragment, suggesting increasing hybridization of the Ge s- and p-orbitals. These findings will be useful in further understanding low-valent heavier group 14 complexes in organometallic chemistry.



INTRODUCTION

Ligands based on the heavier analogues of carbenes have received considerable interest in recent years.[1−3] A large fraction of known Si(II) and Ge(II) species are base-stabilized silylenes or germylenes, i.e., compounds featuring two anionic and at least one donating, neutral substituent. Such compounds can serve as ligands for a broad range of transition metals, and transition-metal complexes of silylene[4−11] and germylene[5,6,10] ligands are finding applications in catalysis. Ge(II) compounds are generally less reducing than their Si(II) counterparts and hence more easily accessible, largely because Ge(II) precursors such as GeCl$_2$·dioxane are readily available.

Because of their similar covalent radii (Si: 1.11(2) Å and Ge: 1.20(4) Å),[12] Si(II) and Ge(II) often give rise to similar structures and parallel reactivity, but instructive differences are known. For example, Aquino et al. investigated the electronic properties, e.g., Brønsted acidity, of zwitterionic silyl-substituted methanides, silanides, and germanides (R$_3$E(II) anions), showing that basicity decreases down group 14 (Scheme 1, A).[13] They also note that the methanides are markedly different from the silanides and germanides, both structurally and electronically, mainly due to significant hyperconjugation of the lone pair into the adjacent silyl groups. The decreased basicity also translates in increased stability of E(II) compounds going down group 14. For example, the mere existence of compounds of type X$_2$E (X = halo, N(SiMe$_3$)$_2$) for E = Ge(II), Sn(II) illustrates this difference, as the Si(II) homologues decompose well below ambient temperature. The stability of these germylenes and stannylenes is due to the increasing energy separation of the central atom's s- and p-orbitals, descending group 14.[14−18]

Another illustrative example is the addition of small molecules over the β-diketiminato silylene or germylene (Scheme 1, B). Despite their structural resemblance, the silylene showed a thermodynamic preference for 1,1-addition and formal oxidation of Si(II) to Si(IV), whereas, in the germylene, 1,4-addition was preferred, transforming the diamido-germylene center in a base-stabilized amido(triflate)-germylene.[19−21] Finally, the catalytic activity of homologous silylene and germylene complexes has been compared. In hydroformylation catalysis, a rhodium complex of a ferrocene-

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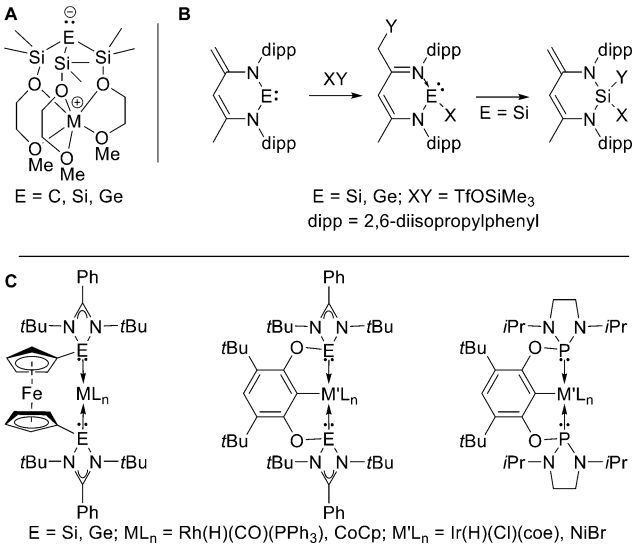
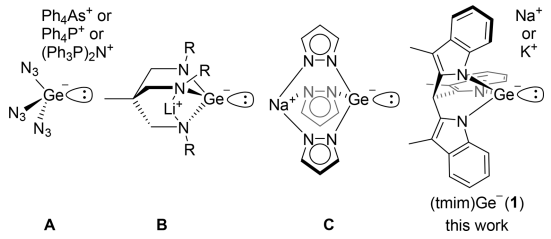
Scheme 1. (A) Group 14 Anions Used for Brønsted Acidity Determination.[13] (B) Contrasting Reactivity between Structurally Similar Silylene and Germylene.[19−21] (C) Catalytically Active Complexes of Silylene and Germylene Ligands and of a Related Phosphine Ligand[5a,6,10,22]



bridged disilylene ligand (Scheme 1, C) proved to be much more active than its germylene analogue.[22] This difference was attributed to the enhanced σ-donor strength of the silylene. The same trend was observed in the cyclotrimerization reaction of phenylacetylene catalyzed by the analogous CoCp complex.[6] The decreased reactivity of the germylene complex is in this case attributed to a stronger coordination of Ge to Co, hampering the creation of an active site. Interestingly, in the C−H borylation of arenes catalyzed by an iridium SiCSi pincer complex featuring two silylene donor moieties (Scheme 1, C), the yield was only slightly higher compared to the germylene (90% and 80%), but significantly higher compared to the related phosphine complex (64%).[10] The increased reactivity of the Si and Ge complexes is thought to arise from stronger σ-donor properties compared to P. Complexes of these ligands with NiBr showed similar reactivity for the silylene and phosphine in a Sonogashira coupling. Interestingly, the germylene complex showed an increased yield from 40% to 53% compared to the silylene complex.[5a]

In recent work from our group, the synthesis and coordination chemistry of an unusual Si(II) anion supported by the tmim scaffold ($tmimH_3$ = tris(3-methylindol-2-yl)-methane) by substitution on a Si(II) precursor was reported.[23] The introduction of electron-withdrawing groups to delocalize the negative charge and the tight cage structure are thought to enhance the stability of the anion by lowering the energy of the lone pair. To gain understanding on the influence of this cage design on ligand properties, the analogous germanide **1** (Chart 1) was investigated. All-nitrogen substituted germanides similar to **1** have received some attention, examples including triazidogermanide **A**, bicyclo triamidogermanide **B**, and the zwitterionic tripyrazolyl germanide **C** (Chart 1).[24−30] Their coordination chemistry is scarce, and structurally characterized complexes are limited to a tungsten(II) complex derived from structure **A**, a gold(I) complex derived from structure **B**, and iron(II) complexes of a tetradentate triphosphinogermyl ligand.[24−26] In the current work, the synthesis of compound **1** and its complexation to soft Lewis-acidic metal fragments

Chart 1. Naked Tri-nitrogen Substituted Germanides

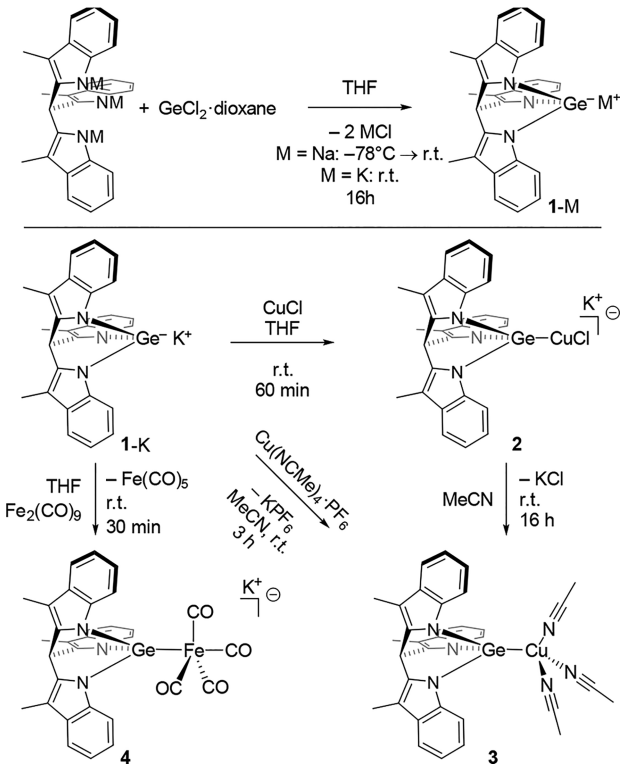


(CuCl, $Cu(NCMe)_3$, and $Fe(CO)_4$) is reported. In contrast to the silanide, coordination to the harder Lewis acid $FeCl_2$ results in at most a weak interaction with a small association constant in solution. The properties of **1** as a ligand are compared with those of (tmim)Si^- as well as the neutral P(III) analogue previously reported by Barnard and Mason,[31] showing that its donor ability is situated between those. Analysis of the N−E−N angles, N−E, and E−M distances provides insight in the electronic nature of the ligands.

RESULTS AND DISCUSSION

The substituent $(tmim)H_3$ was synthesized and deprotonated according to published procedures.[23,32] Subsequently, the germanide **1** was synthesized by nucleophilic substitution of chloride for the $tmim^{3-}$ trianion on $GeCl_2$·dioxane (Scheme 2), which is a common approach to synthesize germanides.[24−29,33,34] The germanide was obtained either as its sodium salt **1**-Na or as its potassium salt **1**-K. The synthesis of **1**-Na requires an excess of $GeCl_2$·dioxane to reach completion, which is tentatively attributed to formation of insoluble $NaGeCl_3$. In contrast, a stoichiometric amount of $GeCl_2$·

Scheme 2. Synthesis of 1-M by Nucleophilic Substitution of Cl for tmim in $GeCl_2$·Dioxane and Synthesis of Transition-Metal Complexes 2−4



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dioxane was sufficient for the synthesis of **1**-K. Therefore, the potassium salt **1**-K was used for complexation studies.

A single set of ^{1}H resonances in the aromatic region indicates that **1** possesses three-fold symmetry, as expected for a bicyclo[2.2.2]octane topology. The presence of **1** was detected by ESI-MS as the molecular anion (M^- (**1**-K) = measured: 474.1060 a.u., calcd: 474.1031 a.u.). Crystals of **1**-Na suitable for X-ray diffraction were grown by storing a concentrated sample of **1**-Na in THF at −35 °C for 2 days. The molecular structure shows the presence of a free tricoordinate germanide with a solvated sodium counterion (Figure 1). The N−Ge−N angles provide a crude measure for the extent of hybridization of the Ge valence orbitals (s,p).[35] Ideally, the sum of angles is 270° in nonhybridized and 328.5° in sp^3 hybridized systems. The sum of the N−Ge−N angles (263.5(3)°) suggests negligible hybridization of the Ge valence orbitals, with the lone pair located in the s-orbital. Angles close to 90° are commonly found in germanides, also in the absence of a cage structure enforcing them, as for example in compound **A** (Chart 1).[27,28,36−38] This is a consequence of the generally low propensity of heavier elements to undergo orbital hybridization, i.e., the inert pair effect.[14−18]

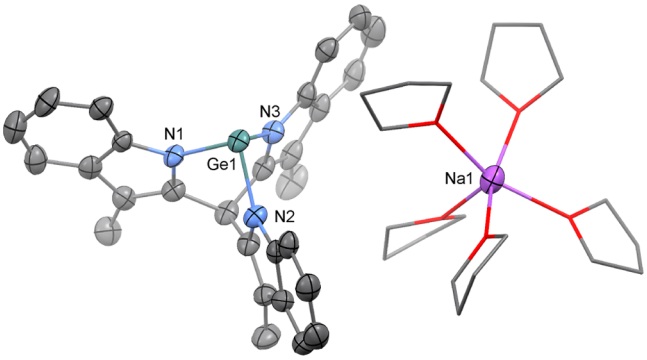

Figure 1. Molecular structure of **1**-Na in the crystal. Ellipsoids are drawn at the 50% probability level. Only the major component of the disordered THF is shown. Hydrogen atoms are omitted for clarity. Selected bond distances [Å] and angles [deg]: N1−Ge1 1.956(4), N2−Ge1 1.969(4), N3−Ge1 1.970(4), N1−Ge1−N2 87.98(18), N2−Ge1−N3 88.02(18), N1−Ge1−N3 87.47(18).

The coordination chemistry of the synthesized germanide was investigated with first-row transition-metal synthons (Scheme 2). Germanide **1**-K was complexed to 1 equiv of CuCl in THF at ambient temperature to form the chloro cuprate **2**. A single set of ^{1}H resonances in the aromatic region shows retention of three-fold symmetry. In solution, the chloro cuprate exists as a monomer as was evidenced by the identical diffusion coefficients observed in DOSY NMR for **1** and **2** in C_4D_8O. Crystals suitable for X-ray diffraction were grown from a concentrated THF solution at −35 °C. In the solid state, complex **2** has two independent dimeric Cu complexes in the asymmetric unit which are both located on general positions without symmetry. Consequently, there are four independent germanide ligands. The dimers are characterized by Cu_2Cl_2 diamond cores, similar to the (tmim)Si chloro cuprate.[23] Unlike the silicon analogue, the structure of **2** is slightly bent: the Cl−Cu−Cl planes form angles of 21.2(2)° and 20.6(2)° for the two independent dimers. The sum of the N−Ge−N angles in the four independent germanide ligands are 273.0(6), 272.7(6), 272.6(6), and 272.3(6)°. This suggests a slight rehybridization in the direction of sp^3 compared to the free germanide **1**, for which the sum of the N−Ge−N angles is 263.5(3)°. Compound **2** constitutes only the second structurally characterized example of a germyl cuprate, next to bis(triphenylgermyl)copper as reported by Orlov et al.[39] Diamond core dimeric structures (Cu_2X_2; X = C_6F_5, I) related to **2** were previously observed for germylene complexes bearing nacnac- and aminotroponiminate ligands.[40−42] This diamond core is generally planar; it is bent only in a Cu_2I_2 complex bearing a bidentate digermylene ligand, forcing the bent geometry.[43] The Ge−Cu bond lengths of 2.2557(17)−2.2611(17) Å in **2** are remarkably short, shorter distances being found only in germylene complexes of copper 1,3-diketimines.[44]

The chloride in anionic cuprate **2** can be replaced by acetonitrile to form a neutral copper germanide, similarly to what is observed for the silicon analogue.[23] A saturated solution of **2** in acetonitrile produces crystals within 16 h (Figure 2). The solid-state structure of **3** shows a monomeric, tris-acetonitrile complex. This complex is one of a few neutral monodentate germyl copper complexes.[45−48] The Ge−Cu distance in **3** (Ge1−Cu1 2.2921(3) Å) is the shortest observed for such complexes.[45,46] To determine whether the chlorocuprate dissociates in acetonitrile and THF solution, an authentic sample of neutral **3** was synthesized by complexation of **1**-K to $Cu(MeCN)_4{\cdot}PF_6$. The ^{1}H NMR spectrum of the resulting complex is identical to that of **2** in CD_3CN, whereas a significant difference can be seen in the chemical shift of the indole-H7 between both samples in THF (7.62, 7.94 ppm for **3** and **2**, respectively). This suggests that complex **2** exists as a molecular chlorocuprate in THF but dissociates to the neutral complex **3** in acetonitrile.

The synthesis of an $Fe(CO)_4$ derivative of compound **1** is of interest as a way to investigate its electronic properties as a ligand. Reaction of **1**-K with $Fe_2(CO)_9$ in THF at room temperature afforded very cleanly the $Fe(CO)_4$ complex **4** (Figure 2) with loss of $Fe(CO)_5$. Retention of the three-fold symmetry is indicated by a single set of ^{1}H NMR resonances in the aromatic region. Crystals suitable for X-ray diffraction were grown by diffusion of hexane into a concentrated THF solution of **4**. The structure is very similar to that of the neutral phosphine analogue (tmim)PFe$(CO)_4$ reported by Barnard and Mason.[49] The distinct axial and equatorial CO resonances of **4** in ^{13}C NMR were observed in a 1:3 ratio at −40 °C (δ = 222.57, 212.16 ppm) and 1 coalesced resonance at 70 °C (δ = 215.53 ppm). One broad resonance at room temperature (δ = 215.15 ppm, fwhm = 125 Hz) suggests that this is above the coalescence temperature. In (tmim)PFe$(CO)_4$, similar fluxional behavior was ascribed to hindered axial−equatorial exchange of the carbonyl ligands caused by steric repulsion of the indole rings on the carbonyls in the square pyramidal intermediate of plausible Berry pseudorotation[50] as well as turnstile rotation.[49] For the phosphine complex, the coalescence temperature is estimated to be 97 °C, albeit not observed.[31] The lower coalescence temperature for the germanium analogue suggests a lower energy barrier for the carbonyl exchange, which can be ascribed to the longer Ge−Fe (2.2978(16) Å) bond with respect to the P−Fe bond (2.1539(5) Å), reducing steric congestion around the iron center.

Whereas copper chloride and iron carbonyl give well-defined complexes with germanide **1**, it binds only weakly to $FeCl_2$ (Scheme 3). In the ^{1}H NMR of an equimolar solution of **1**-K

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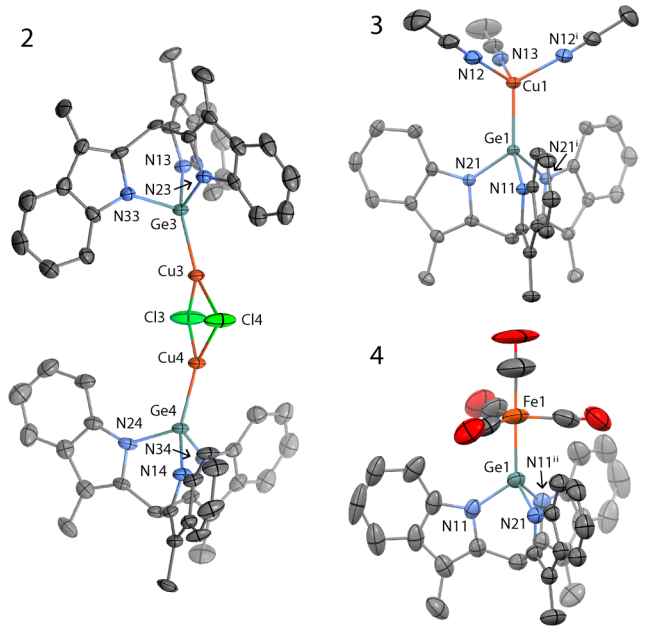
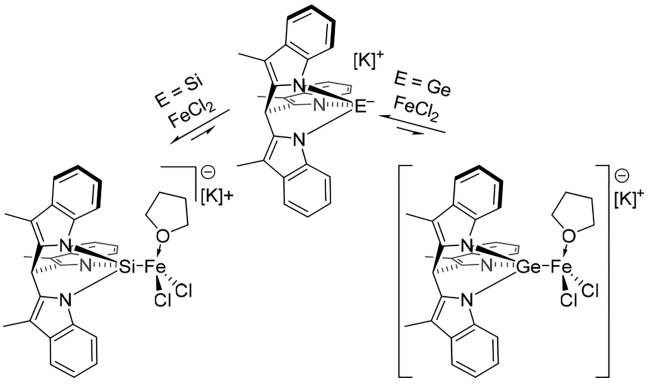


Figure 2. Molecular structure of the dianion of **2**, neutral **3**, and the anion of **4** in the crystal. Ellipsoids are drawn at the 50% probability level. Hydrogen atoms, THF solvated potassium cations, and cocrystallized, non-coordinated MeCN are omitted for clarity. Atom labels marked with ^{i} or ^{ii} arise from mirror symmetry. The asymmetric unit of **2** contains two independent molecules of which one is shown. Selected bond distances [Å] and angles [deg]: **2**: Molecule 1: Ge1−Cu1 2.2591(17), Ge2−Cu2 2.2557(17), Ge1−N11 1.899(8), Ge1−N21 1.898(8), Ge1−N31 1.906(9), Ge2−N12 1.911(8), Ge2−N22 1.906(9), Ge2−N32 1.918(8), N11−Ge1−N21 90.3(3), N21−Ge1−N31 91.4(4), N31−Ge1−N11 91.3(3), N12−Ge2−N22 90.6(4), N22−Ge2−N32 91.3(4), N32−Ge2−N12 90.8(3), angle between planes Cl1−Cu1−Cl2 and Cl1−Cu2−Cl2: 21.2(2). Molecule 2: Ge3−Cu3 2.2611(17), Ge4−Cu4 2.2604(16), Ge3−N13 1.907(8), Ge3−N23 1.902(9), Ge3−N33 1.901(8), Ge4−N14 1.909(8), Ge4−N24 1.917(9), Ge4−N34 1.898(9), N13−Ge3−N23 90.6(4), N23−Ge3−N33 91.4(4), N33−Ge3−N13 90.6(3), N14−Ge4−N24 90.3(3), N24−Ge4−N34 91.9(4), N34−Ge4−N14 90.1(4), angle between planes Cl3−Cu3−Cl4 and Cl3−Cu4−Cl4: 20.6(2); **3**: Ge1−Cu1 2.2921(3), Ge1−N11 1.9110(16), Ge1−N21 1.9162(11), N11−Ge1−N21 90.19(5), N21−Ge1−N21^{i} 88.69(7) (symmetry code *i*: *x*, 1 − *y*, *z*); **4**: Ge1−Fe1 2.2978(16), Ge1−N11 1.890(5), Ge1−N21 1.902(6), N11−Ge1−N21 92.57(18), N11−Ge1−N11^{ii} 92.4(3) (symmetry code *ii*: 1 − *x*, *y*, *z*).

Scheme 3. Coordination of the Silanide and Germanide Ligands to Iron Dichloride[a]



[a] $[K]^+$ = K(18-crown-6)$^+$ for E = Si and K^+ for E = Ge.

and $FeCl_2$ in THF, the indole-H7 peak broadens (fwhm, from 2.8 to 40 Hz) and shifts 0.50 ppm to low field (Figure 3).

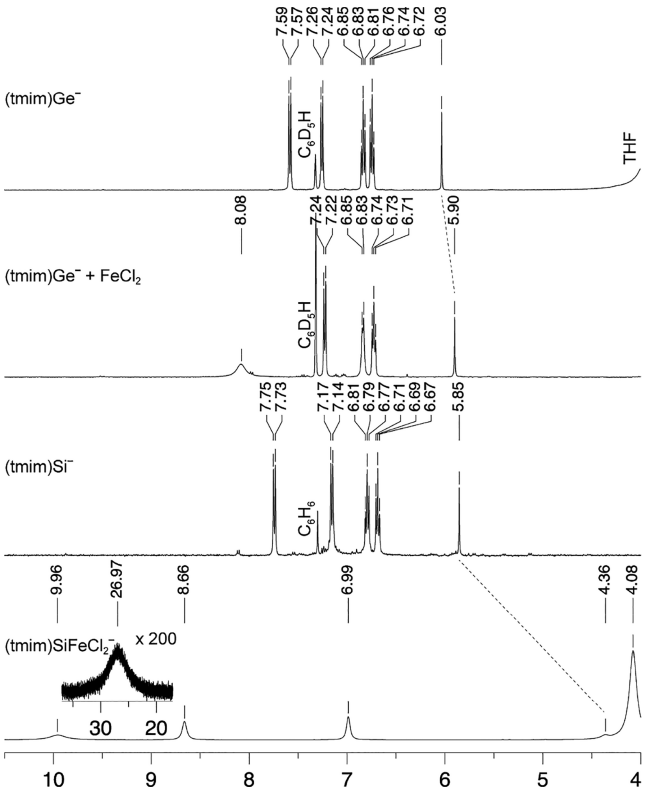


Figure 3. ^{1}H NMR spectra of (tmim)E$^-$ compounds (E = Ge, Si, $SiFeCl_2$) and an equimolar mixture of **1**-K and $FeCl_2$ in THF-H_8 + C_6D_6 (Ge) or THF-d_8 (Si).

Concomitantly, the R_3CH signal shifts 0.13 ppm to high field. This is in contrast with (tmim)Si$^-$, which binds to $FeCl_2$ to form (tmim)$SiFeCl_2$·THF, causing a low-field shift of 20 ppm for the indole-H7 and a high-field shift of 1.5 ppm for the R_3CH signal.[23] The weaker affinity of **1** for $FeCl_2$ with respect to (tmim)Si$^-$ can be understood in terms of Hard and Soft Acids and Bases (HSAB), the germanide being a softer Lewis base than the silanide.

The series of Ge compounds described herein provide a rare opportunity to compare side by side the properties of isostructural ligands featuring three different central elements, namely, P(III),[31,49] Si(II),[23] and Ge(II). Key geometrical and spectroscopic parameters are collected in Table 1. In the solid state, the anions (tmim)Ge$^-$ and (tmim)Si$^-$ possess rather acute N−E−N angles ($\sum$(N−Si−N) = 272.58(9)°, $\sum$(N−Ge−N) = 263.5(3)°), with respect to the phosphine analogue ($\sum$(N−P−N) = 285.30(12)°, Table 1).[31,49] The more acute angles in (tmim)Ge$^-$ compared to (tmim)Si$^-$ likely arise from the larger atomic radius of germanium, because the through-space N···CH···N angles are larger in (tmim)Ge$^-$, indicating that the tmim scaffold needs to open up to accommodate the larger Ge$^-$ anion. This is also reflected in the N−E distances being larger in (tmim)Ge$^-$, but does not appear to result in substantial cage strain. The strain energy estimated computationally for (tmim)Ge$^-$ according to the homodesmotic reaction depicted in Scheme 4 is very low (ΔH = −1.0 kcal/mol), similarly to those calculated for (tmim)Si$^-$ (−1.6 kcal/mol) and (tmim)P (1.2 kcal/mol; Supporting Information, Table S2).[23] The difference in N−E−N angles between Si and

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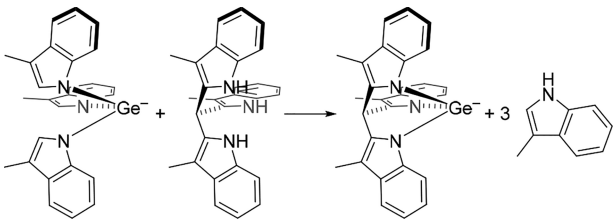
Table 1. Sum of Angles, Distances, and $\tilde{\nu}$(CO) in tmimE Compounds (E = P, Si^-, Ge^-) and Their Complexes

E =	P	Si^-	Ge^-
tmimE			
∑N−E−N/deg	285.30(12)	272.58(9)	263.5(3)
⟨N−E⟩/Å	1.7084(8)	1.8416(6)	1.965(2)
⟨N···CH···N⟩/deg	62.3	64.7	67.40(12)
$[(tmimE)Cu(\mu\text{-}Cl)]_2^{2-}$			
Cu−E/Å		2.1906(10)	2.2557(17)−2.2611(17)[b]
∑N−E−N/deg		280.8(2)	272.3(3)−273.0(6)[b]
⟨N−E⟩/Å		1.8010(17)	1.901(5)−1.912(5)[b]
$(tmimE)Cu(NCMe)_3$			
Cu−E/Å		2.2106(8)	2.2921(3)
∑N−E−N/deg		278.73(12)	269.07(12)
⟨N−E⟩/Å		1.8063(10)	1.9145(7)
$(tmimE)Fe(CO)_4$			
Fe−E/Å	2.1539(5)		2.2978(16)
∑N−E−N/deg	292.56(12)		277.5(4)
⟨N−E⟩/Å	1.7085(8)		1.894(3)
$\tilde{\nu}$(CO)/cm^{-1} exp	2076 2006 1977	2029[a] 1920	2037 1954 1933
$\tilde{\nu}$(CO)/cm^{-1} calcd	2074 2012 1990	2026 1956 1939	2032 1961 1948

[a]Tentative assignment from a spectrum measured on a mixture of components. [b]Four independent germanide ligands.

Scheme 4. Homodesmotic Reaction Used for Strain Calculations[23]



P is likely a combined effect of the slightly larger P radius and the absence of a negative charge on phosphorus, i.e., less repulsion for the anionic indole moieties.

The solid-state structures of the complexes presented herein correlate with changes in orbital hybridization at the central atom. Upon complexation, the N−E−N angles increase in all ligands, which can be explained by an increasing p-character of the lone pair upon binding to a Lewis acid and a consequent decrease in the p-character of the E−N bonding orbitals. This is in agreement with Bent's rule: increased electronegativity of a substituent (from a lone pair to a metal fragment) results in increased p-character of the bonding orbitals.[35] The E−N distances decrease upon complexation for both (tmim)Si and **1** to CuCl and $Cu(MeCN)_3$, but the E−N distances in (tmim)P remain unchanged within the error bounds upon complexation to $Fe(CO)_4$. This difference can be interpreted as a consequence of the stronger electron-donor character of the anionic ligands as compared with (tmim)P, which results in a higher degree of charge transfer upon complexation, causing a shortening of the N−E bonds as the electron density at the central element is depleted.

In the cuprates derived from (tmim)Ge^- and (tmim)Si^-, the E−Cu distances are very short and congruent (Δd(E−Cu) = 0.0686(13) Å) if one takes into account the difference in covalent radii between Si and Ge (0.09(4) Å).[12] The metal fragment in the acetonitrile complexes is somewhat less electron-withdrawing as is reflected in tightening of the N−E−N angles and a slight increase in E−N distance from $LCuCl^-$ to $LCu(NCMe)_3$, correlating with slightly longer Cu−E bonds. This can be taken to indicate that the increase in coordination number in the acetonitrile complex outweighs the loss of the more electron-rich, anionic chloride ligand.

For comparison with **4**, complexation of (tmim)Si^- to $Fe(CO)_4$ was investigated. It affords a mixture of two major components of which one is tentatively assigned to $[(tmim)\text{-}SiFe(CO)_4]^-$ on the basis of ESI-MS and IR (in combination with DFT-calculated $\tilde{\nu}$(CO), Table 1). Isolation of the silyl iron complex was unsuccessful. The vibrational frequency of the carbonyls in $(tmim)EFe(CO)_4$ (E = Si^-, Ge^-, P; Table 1) indicates that the silanide is the strongest electron donor, the germanide is somewhat weaker, and the phosphine is a significantly weaker donor.

■ CONCLUSIONS

The free germanide (tmim)Ge^- (**1**, $(tmim)H_3$ = tris(3-methylindol-2-yl)methane) was synthesized through nucleophilic substitution on $GeCl_2$·dioxane by the trianion $tmim^{3-}$. Germanide **1** was shown to coordinate to Cu(I) and Fe(0) fragments, affording the chloro cuprate $[(tmim)GeCuCl]^-$ and the iron carbonyl complex $[(tmim)GeFe(CO)_4]^-$. The chloro cuprate was shown to dissociate in acetonitrile to give the neutral acetonitrile solvated complex $(tmim)GeCu(NCMe)_3$. Contrasting with the reactivity of the analogous silanide, coordination of **1** to $FeCl_2$ results in at most a weak interaction. With the existence of the analogous (tmim)P and (tmim)Si^-, and complexes thereof, a rare opportunity arose of comparing the properties of isostructural ligands featuring different central elements, namely, P(III), Si(II), and Ge(II). The relative electron donor strength was interrogated from the observed $\tilde{\nu}$(CO) in IR spectroscopy, showing that the donor strength follows the trend $P < Ge < Si$. Analysis of the N−E−N angles, N−E, and E−M distances provides insight in the electronic nature of the ligands, suggesting increased hybridization of the Ge s- and p-orbitals upon complexation to a metal fragment. The findings presented here contribute to the understanding of low-valent heavier group 14 ligands and their complexes and may provide important insights necessary for further development of this promising class of ligands.

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EXPERIMENTAL SECTION

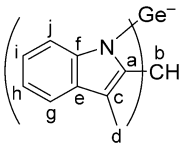
All reactions involving air-sensitive compounds were conducted under a N_2 atmosphere by using standard glovebox or Schlenk techniques. Acetonitrile and *n*-hexane were dried with an MBRAUN MB SPS-79 system; THF was distilled from benzophenone/Na. All solvents were degassed by bubbling with N_2 for 30 min, and stored over molecular sieves in a glovebox. Deuterated acetonitrile and THF were degassed by four freeze−pump−thaw cycles and stored over molecular sieves in a glovebox. Skatole, NaH (60 wt % in mineral oil), KH (30 wt % in mineral oil), and $FeCl_2$ were purchased from Sigma-Aldrich. Triethyl orthoformate, $Fe_2(CO)_9$, and CuCl were purchased from Acros. $GeCl_2$·dioxane was purchased from ABCR. All commercially obtained chemicals were used as received, except for CuCl. From CuCl, copper oxides and hydroxides were removed with hydrochloric acid as described in the literature, and the resulting solid was azeotropically dried with acetonitrile until $\tilde{\nu}$(C≡N) in the IR spectrum disappeared.[51] All NMR measurements were performed on a Varian VNMRS400 or Varian MRF400 spectrometer; shifts are reported relative to TMS with the residual solvent signal as internal standard.[52] All NMR experiments involving air-sensitive compounds were conducted in J-Young NMR tubes under a N_2 atmosphere. Salts of solvated sodium or potassium cations generally yielded unreliable elemental analysis data due to partial desolvation. Their purity was established by NMR spectroscopy. In particular, the THF content determination for purity purposes was done by NMR; the acquisition time was chosen so that the full FID was recorded. Additionally, the relaxation time was set to 7 times the longest T_1, determined by an individual T_1 measurement. IR spectra were recorded on a PerkinElmer Spectrum Two FT-IR spectrometer. ESI-MS measurements were performed on a Waters LCT Premier XE KE317 spectrometer; the Waters software was used for simulations. Elemental analysis was conducted by the Mikroanalytisches Laboratorium Kolbe (**3**, **4**) or Medac Ltd. (**2**). The experimental methods and parameters of the X-ray crystal structure determinations are detailed in the Supporting Information. The compounds (tmim)H_3,[32] (tmim)Na_3,[23] (tmim)K_3,[23] and (tmim)Si^-[23] were prepared according to reported procedures.

Computational Methods. Calculations were performed using Gaussian 09, Revision D.01.[53] The absence of negative eigenvalues was confirmed for all structures. All structures were optimized using the TPSS functional with the TZVP basis set.

Syntheses. *Synthesis of Na[(tmim)Ge] (**1**-Na).* Solutions of (tmim)Na_3 (501 mg, 27 wt % THF, 0.78 mmol) in THF (10 mL) and $GeCl_2$.dioxane (337 mg, 1.46 mmol) in THF (6 mL) were cooled to −78 °C. The $GeCl_2$·dioxane solution was added to the stirred tmim solution, resulting in a suspension. This was allowed to warm to r.t. over 16 h. Filtration and removal of the solvent, followed by recrystallization from THF at −35 °C and drying *in vacuo*, afforded a yellow powder (190 mg, 34 wt % THF, 0.405 mmol, 32%). ^{1}H NMR (400 MHz, CD_3CN, 25 °C) δ = 7.56 (dt, ^3J(H,H) = 8.3 Hz, ^4J(H,H) = 0.8 Hz, ^5J(H,H) = 0.8 Hz, 3H, Indole-H7), 7.32 (dt, ^3J(H,H) = 7.8 Hz, ^4J(H,H) = 1.1 Hz, ^5J(H,H) = 1.1 Hz, 3H, Indole-H4), 6.92 (ddd, ^3J(H,H) = 8.1 Hz, ^3J(H,H) = 7.0 Hz, ^4J(H,H) = 1.3 Hz, 3H, Indole-H6), 6.83 (ddd, ^3J(H,H) = 7.9 Hz, ^3J(H,H) = 7.0 Hz, ^4J(H,H) = 1.1 Hz, 3H, Indole-H5), 6.01 (s, 1H, R_3CH), 2.43 ppm (s, 9H, CH_3). ^{13}C NMR (101 MHz, CD_3CN, 25 °C) δ = 141.9 (2x ^{Ar}qC), 131.2 (^{Ar}qC), 119.9 (^{Ar}CH), 118.6 (^{Ar}CH), 117.7 (^{Ar}CH), 112.2 (^{Ar}CH), 103.4 (^{Ar}qC), 34.2 (R_3CH), 8.9 ppm (CH_3). Satisfactory elemental analysis could not be obtained, likely due to THF solvation.

*Synthesis of (tmim)GeK (**1**-K).* A solution of $GeCl_2$·dioxane (203 mg, 0.875 mmol) in THF (6 mL) was added over 20 min at room temperature to an orange, green luminescent solution of (tmim)K_3 (500 mg, 10 wt % THF, 0.869 mmol) in THF (15 mL) and stirred for 16 h. The resulting yellow suspension was diluted to 40 mL with THF and centrifuged for 10 min at 2000 rpm. The decanted supernatant was concentrated to 6 mL, during which precipitation occurred. Decanting and washing with THF (4 × 0.5 mL) yielded a white microcrystalline powder (297 mg). Repeated storing of the combined THF fractions at −35 °C for 16 h, decanting, and washing with cold THF yielded two more crops (m_{total} = 506 mg, 37 wt % THF, 0.62 mmol, 71%). ^{1}H NMR (400 MHz, CD_3CN, 25 °C) δ = 7.58 (dt, ^3J(H,H) = 8.1 Hz, ^4J(H,H) = 0.9 Hz, ^5J(H,H) = 0.9 Hz, 3H, Indole-H7), 7.34 (dt, ^3J(H,H) = 7.8 Hz, ^4J(H,H) = 1.0 Hz, ^5J(H,H) = 1.0 Hz, 3H, Indole-H4), 6.94 (ddd, ^3J(H,H) = 8.1 Hz, ^3J(H,H) = 6.9 Hz, ^4J(H,H) = 1.3 Hz, 3H, Indole-H6), 6.85 (ddd, ^3J(H,H) = 7.9 Hz, ^3J(H,H) = 7.0 Hz, ^4J(H,H) = 1.1 Hz, 3H, Indole-H5), 6.03 (s, 1H, R_3CH), 2.46 ppm (s, 9H, CH_3). ^{1}H NMR (400 MHz, C_4H_8O + C_6D_6, 25 °C) δ = 7.54 (d, ^3J(H,H) = 8.0 Hz, 3H, Indole-H7), 7.21 (d, ^3J(H,H) = 7.7 Hz, 3H, Indole-H4), 6.79 (t, ^3J(H,H) = 7.5 Hz, 3H, Indole-H6), 6.70 (t, ^3J(H,H) = 7.3 Hz, 3H, Indole-H5), 5.99 (s, 1H, R_3CH), 2.41 ppm (s, 9H, CH_3). ^{13}C NMR (Chart 2 gives a graphical depiction of the assignment) (101 MHz, CD_3CN, 25 °C) δ = 142.0 (C_f), 141.9 (C_a), 131.2 (C_e), 120.0 (C_i), 118.6 (C_g), 117.7 (C_h), 112.2 (C_j), 103.4 (C_c), 34.2 (C_b), 8.9 ppm (C_d). DOSY NMR (400 MHz, C_4D_8O, 25 °C): D = 7 × 10^{-18} m^2/s; ESI-MS $C_{28}H_{22}N_3Ge^-$: exp: 474.1060, sim: 474.1031 a.u.. Satisfactory elemental analysis could not be obtained, likely due to THF solvation.

Chart 2. Assignment of ^{13}C NMR Signals of (tmim)Ge$^-$ (1)



*Synthesis of K[(tmim)GeCuCl] (**2**).* To the combined solids **1**-K (30 mg, 40 wt % THF, 35 μmol) and CuCl (3.5 mg, 35 μmol) was added THF (2 mL), and the suspension was stirred for 60 min, during which the amount of solid increased. The resulting suspension was freed of solvent *in vacuo*, affording a white powder (29 mg, 27 wt % THF, 35 μmol, 99%). ^{1}H NMR (400 MHz, C_4D_8O, 25 °C) δ = 7.96 (d, ^3J(H,H) = 8.1 Hz, 3H, Indole-H7), 7.26 (d, ^3J(H,H) = 7.7 Hz, 3H, Indole-H4), 6.90 (t, ^3J(H,H) = 7.5 Hz, 3H, Indole-H6), 6.77 (t, ^3J(H,H) = 7.4 Hz, 3H, Indole-H5), 6.05 (s, 1H, R_3CH), 2.43 ppm (s, 9H, CH_3). ^{13}C NMR (101 MHz, C_4D_8O, 25 °C) δ = 140.5 (^{Ar}qC), 139.8 (^{Ar}qC), 130.6 (^{Ar}qC), 118.9 (^{Ar}CH), 117.3 (^{Ar}CH), 116.8 (^{Ar}CH), 111.5 (^{Ar}CH), 102.8 (^{Ar}qC), 32.7 (R_3CH), 7.8 ppm (CH_3); DOSY NMR (400 MHz, C_4D_8O, 25 °C): D = 7 × 10^{-18} m^2/s; ESI-MS $C_{28}H_{22}N_3ClGeCu^-$: exp: 572.0092, sim: 572.0009 a.u. Satisfactory elemental analysis could not be obtained, likely due to THF solvation.

*Solvolysis of **2** To Form (tmim)GeCu(MeCN)$_3$ (**3**).* A solution of **2** (∼10 mg) in CD_3CN (0.4 mL) was allowed to stand for 16 h, during which crystals of **3** suitable for X-ray diffraction grew. ^{1}H NMR (400 MHz, CD_3CN, 25 °C) δ = 7.78 (d, ^3J(H,H) = 8.1 Hz, 3H, Indole-H7), 7.34 (ddd, ^3J(H,H) = 7.7 Hz, ^4J(H,H) = 1.3 Hz, ^5J(H,H) = 0.7 Hz, 3H, Indole-H4), 6.94 (t, ^3J(H,H) = 7.5 Hz, 3H, Indole-H6), 6.87 (ddd, ^3J(H,H) = 7.9 Hz, ^3J(H,H) = 6.9 Hz, ^4J(H,H) = 1.1 Hz, 3H, Indole-H5), 6.04 (s, 1H, R_3CH), 2.42 ppm (s, 9H, CH_3); ^{13}C NMR (101 MHz, CD_3CN, 25 °C) δ = 141.4 (^{Ar} qC), 140.8 (^{Ar} qC), 131.1 (^{Ar}qC), 120.7 (^{Ar}CH), 118.9 (^{Ar}CH), 118.5 (^{Ar}CH), 112.5 (^{Ar}CH), 104.7 (^{Ar}qC), 33.6 (R_3CH), 8.7 ppm (CH_3).

*Synthesis of (tmim)GeCu(MeCN)$_3$ (**3**) from Cu(MeCN)$_4$·PF$_6$.* A solution of **1**-K (32 mg, 38 wt % THF, 39 μmol) in acetonitrile (0.5 mL) was added to a stirred solution of Cu(MeCN)$_4$·PF_6 (14 mg, 39 μmol) in acetonitrile (0.5 mL). The vial was rinsed with acetonitrile (2 × 0.5 mL), and the solution was added to the mixture. Within 5 min, a white solid precipitated. After 3 h, the mixture was filtered and the white residue was washed with acetonitrile (2 × 0.5 mL) and freed of solvent *in vacuo* (21 mg, 32 μmol, 83%). ^{1}H NMR (400 MHz, C_4H_8O + C_6D_6, 25 °C) δ = 7.62 (d, ^3J(H,H) = 8.0 Hz, 3H, Indole-H7), 7.28 (d*, Indole-H4), 6.86 (t, ^3J(H,H) = 7.5 Hz, 3H, Indole-H6), 6.79 (t, ^3J(H,H) = 7.3 Hz, 3H, Indole-H5), 6.04 (s, 1H, R_3CH), 2.42 ppm (s, 9H, CH_3). *doublet overlaps with C_6D_5H. ^{1}H NMR (400 MHz, CD_3CN, 25 °C) δ = 7.77 (d, ^3J(H,H) = 8.1 Hz, 3H, Indole-H7), 7.34 (d, ^3J(H,H) = 7.7 Hz, 3H, Indole-H4), 6.94 (t, ^3J(H,H) = 7.5 Hz, 3H, Indole-H6), 6.87 (t, ^3J(H,H) = 7.3 Hz, 3H,

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Indole-H5), 6.04 (s, 1H, R_3CH), 2.42 ppm (s, 9H, CH_3). ^{13}C NMR (101 MHz, CD_3CN, 25 °C) δ = 141.4 (^{Ar}qC), 140.8 (^{Ar}qC), 131.1 (^{Ar}qC), 120.7 (^{Ar}CH), 118.9 (^{Ar}CH), 118.5 (^{Ar}CH), 112.4 (^{Ar}CH), 104.7 (^{Ar}qC), 33.6 (R_3CH), 8.7 ppm (CH_3). Satisfactory elemental analysis could not be obtained, likely due to loss of coordinated MeCN.

Synthesis of K[(tmim)GeFe(CO)$_4$] (4). A solution of **1**-K (122 mg, 62 wt % THF, 0.15 mmol) in THF (13 mL) was added to an orange suspension of $Fe_2(CO)_9$ (54 mg, 147 μmol) in THF (5 mL) and stirred for 30 min. The solution was freed of solvent *in vacuo* to a burgundy solid, which was dissolved in THF (1.5 mL) and cooled to −35 °C. Cold hexane (15 mL) was added, and after 16 h at −35 °C, the suspension was filtered and the white solid was dried in vacuo (105 mg, 15 wt % THF, 0.13 mmol, 88%). ^1H NMR (400 MHz, CD_3CN, 70 °C) δ = 8.00 (d, ^3J(H,H) = 8.2 Hz, 3H), 7.41 (d, ^3J(H,H) = 7.8 Hz, 3H), 7.04 (ddd, ^3J(H,H) = 8.3 Hz, ^3J(H,H) = 6.8 Hz, ^4J(H,H) = 1.5 Hz, 3H), 6.96 (t, ^3J(H,H) = 7.4 Hz, 3H), 6.17 (s, 1H), 2.49 ppm (s, 8H). ^1H NMR (400 MHz, CD_3CN, 25 °C) δ = 7.96 (dt, ^3J(H,H) = 8.3 Hz, ^4J(H,H) = 0.9 Hz, 3H, Indole-H7), 7.40 (ddd, ^3J(H,H) = 7.8 Hz, ^4J(H,H) = 1.3 Hz, ^5J(H,H) = 0.7 Hz, 3H, Indole-H4), 7.04 (ddd, ^3J(H,H) = 8.3 Hz, ^3J(H,H) = 7.0 Hz, ^4J(H,H) = 1.3 Hz, 3H, Indole-H6), 6.95 (ddd, ^3J(H,H) = 7.9 Hz, ^3J(H,H) = 7.0 Hz, ^4J(H,H) = 1.1 Hz, 3H, Indole-H5), 6.15 (s, 1H), 2.46 ppm (s, 9H). ^1H NMR (400 MHz, CD_3CN, −40 °C) δ = 7.94 (dt, ^3J(H,H) = 8.3 Hz, ^4J(H,H) = 0.9 Hz, 3H), 7.40 (ddd, ^3J(H,H) = 7.8 Hz, ^4J(H,H) = 1.3 Hz, ^5J(H,H) = 0.7 Hz, 3H), 7.04 (ddd, ^3J(H,H) = 8.3 Hz, ^3J(H,H) = 7.0 Hz, ^4J(H,H) = 1.3 Hz, 3H), 6.95 (ddd, ^3J(H,H) = 7.9 Hz, ^3J(H,H) = 7.0 Hz, ^4J(H,H) = 1.1 Hz, 3H), 6.15 (s, 1H), 2.45 ppm (s, 9H). ^{13}C NMR (101 MHz, CD_3CN, −40 °C): δ = 222.6 (^{ax}CO), 212.2 (^{eq}CO), 140.3 (^{Ar}qC), 139.0 (^{Ar}qC), 130.4 (^{Ar}qC), 121.3 (^{Ar}CH), 119.0 (2 ^{Ar}CH), 112.2 (^{Ar}CH), 105.6 (^{Ar}qC), 32.4 (R_3CH), 8.4 ppm (CH_3). ^{13}C NMR (101 MHz, CD_3CN, 25 °C): δ = 215.1 (fwhm = 125 Hz, CO), 141.0 (^{Ar}qC), 139.9 (^{Ar}qC), 131.2 (^{Ar}qC), 121.5 (^{Ar}CH), 119.3 (^{Ar}CH), 119.2 (^{Ar}CH), 112.9 (^{Ar}CH), 105.6 (^{Ar}qC), 33.1 (R_3CH), 8.6 ppm (CH_3). ^{13}C NMR (101 MHz, CD_3CN, 70 °C): δ = 215.5 (CO), 141.6 (^{Ar}qC), 140.5 (^{Ar}qC), 131.8 (^{Ar}qC), 121.6 (^{Ar}CH), 119.5 (^{Ar}CH), 119.4 (^{Ar}CH), 113.3 (^{Ar}CH), 105.7 (^{Ar}qC), 33.7 (R_3CH), 8.8 ppm (CH_3); ESI-MS $C_{32}H_{22}O_4GeN_3Fe^-$: exp: 642.0437, sim: 642.0180 a.u.; IR (THF): $\tilde{\nu}$ = 2037, 1954, 1933 cm^{-1}. Satisfactory elemental analysis could not be obtained, likely due to THF solvation.

Interaction between 1 and FeCl$_2$. The combined solids **1**-K (30 mg, 40 wt % THF, 35 μmol) and $FeCl_2$ (4.6 mg, 36 μmol) were dissolved in THF (2 mL) and stirred for 60 min. ^1H NMR (400 MHz, C_4H_8O + C_6D_6, 25 °C) δ* = 8.08 (br s, 3H), 7.23 (d, ^3J(H,H) = 7.6 Hz, 3H), 6.83 (br d, ^3J(H,H) = 6.8 Hz, 3H), 6.73 (t, ^3J(H,H) = 7.1 Hz, 3H), 5.90 (s, 1H), 2.40 ppm (s, 9H). * relative to C_6D_5H in THF (7.32 ppm).

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.8b00630.

Crystallographic data, spectroscopic data, and computational details (PDF)

Coordinates of the computed structures (XYZ)

Accession Codes

CCDC 1848178−1848181 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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