ORGANOMETALLICS

Article

pubs.acs.org/Organometallics

Synthesis and Reactivity of Intramolecularly NHC-Stabilized Germylenes and Stannylenes

Daniel Paul,[†] Frederik Heins,[‡] Sergei Krupski,[‡] Alexander Hepp,[‡] Constantin G. Daniliuc,[†] Kevin Klahr,[†,§] Johannes Neugebauer,[†,§] Frank Glorius,*[,†] and F. Ekkehardt Hahn*[,‡]

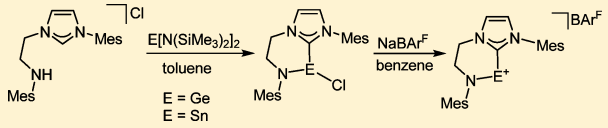
[†]Organisch-Chemisches Institut, Westfälische Wilhelms-Universität Münster, Corrensstraße 40, 48149 Münster, Germany

[‡]Institut für Anorganische und Analytische Chemie, Westfälische Wilhelms-Universität Münster, Corrensstraße 28−30, 48149 Münster, Germany

[§]Center for Multiscale Theory and Computation, Westfälische Wilhelms-Universität Münster, Corrensstraße 40, 48149 Münster, Germany

Supporting Information

ABSTRACT: The HOMO−LUMO energy gap of germylenes bearing C_{NHC}^N_{amido} chelate ligands has been calculated in order to find suitable candidates for the activation of small molecules. Identified as promising structures, intramolecularly NHC-stabilized three-coordinate germylenes and stannylenes of type [E(C_{NHC}^N_{amido})Cl] (E = Ge and Sn) were synthesized and characterized by NMR spectroscopy and X-ray crystallography. Chlorido substitution at the E^{II} center for *tert*-butoxido or hexamethyl disilazide ligands was also performed. Chlorido abstraction with $NaBAr^F$ gave rise to cationic two-coordinate germylenes and stannylenes.



INTRODUCTION

Tetrylenes are compounds of general formula R_2E, where E is an electron-deficient, divalent group 14 element with only six electrons in the valence shell. The isolation of the first free *N*-heterocyclic carbenes (NHCs) in 1991[1] triggered not only intensive research on these compounds[2] but also caused renewed interest in the heavier NHC analogs, the *N*-heterocyclic silylenes (NHSi), germylenes (NHGe), stannylenes (NHSn), and plumbylenes (NHPb),[3] generically named tetrylenes. Some of the heavier tetrylenes have actually been known long before the chemistry of stable carbenes developed.[4] The first *N*-heterocyclic stannylene (NHSn), for example, was reported by Veith in 1975,[5] and the first isolable and stable acyclic diamido tetrylenes were reported even earlier by the group of Lappert in 1974 and by others.[6]

The nitrogen atoms of the cyclic (NHEs) and acyclic diamido tetrylenes significantly contribute to the stability of the molecules. They cause a positive mesomeric effect by electron donation to the vacant p_π orbital of the divalent group 14 element. At the same time the nitrogen atoms cause a negative inductive effect by withdrawing electron density from the group 14 element.[3] The heterocyclic NHEs are bent at the group 14 element and exclusively exist in the singlet ground state. In this bent geometry, the σ-orbital of the divalent group 14 atom is best described to contain two electrons, while its p_π orbital remains vacant, leading to a characteristic ambiphilic reactivity as nucleophiles and electrophiles. This situation has been described early on for selected tetrylenes by others[3b,c,7,8] and later by us.[3a,7,8]

The ambiphilic reactivity of tetrylenes has already been used for the activation of small molecules (Scheme 1).[9] As early as 2007, Bertrand and co-workers showed that the substitution of one nitrogen atom adjacent to the carbene carbon atom in NHCs for another carbon atom leads to the cyclic(alkyl)(amino)carbenes (CAACs). Due to the reduced stabilization of the carbene center from the single nitrogen atom, the HOMO−LUMO gap observed for CAACs is also reduced and both, nucleophilicity and electrophilicity are increased. These effects allowed the activation of elemental hydrogen (Scheme 1A).[10] Sterically shielded diarylgermylenes and -stannylenes are also able to activate dihydrogen and ammonia, as shown by Power and co-workers (Scheme 1B).[11] In 2014, Tobita et al. presented the cationic germylene tungsten complex $[Cp^*(CO)_3WGe(IPr)](BAr^F{}_4)$,[12] and one year later, the same group demonstrated the insertion of this complex into X−H bonds, where X is H (Scheme 1C), B, or Si.[13] The activation of the latter two bonds was found to be reversible.

Density functional theory (DFT) calculations on the insertion of different silylenes and germylenes into the H−H bond showed that the energy difference between the HOMO and LUMO of these tetrylenes determines the course of the reaction. For NHGe, the activation energy for the insertion reaction drops significantly at a HOMO−LUMO gap of 3.4−3.6 eV or lower.[14] These findings initiated various studies regarding the activation of elemental hydrogen by tetrylenes including the present one.

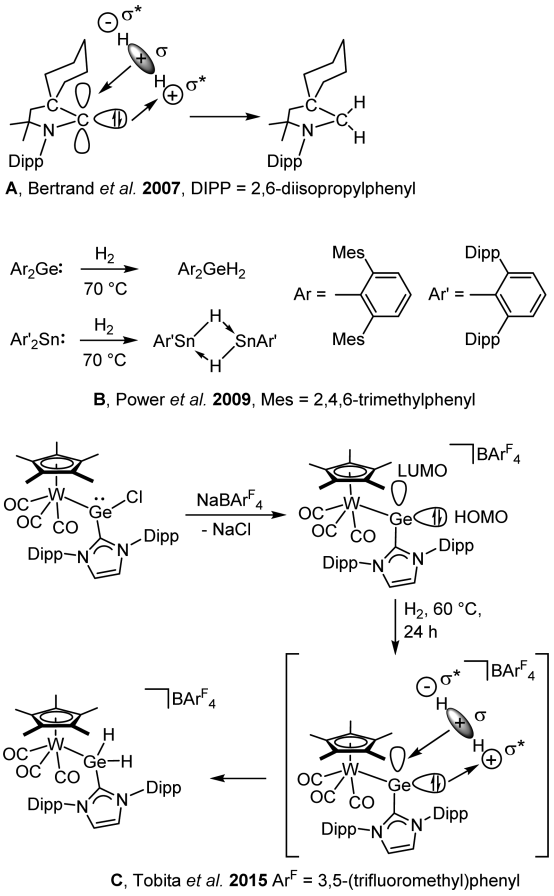
In an attempt to identify suitably substituted tetrylenes for the insertion into the H−H bond, we have calculated the HOMO−LUMO energy differences for a number of these

Received: December 13, 2016

 © XXXX American Chemical Society

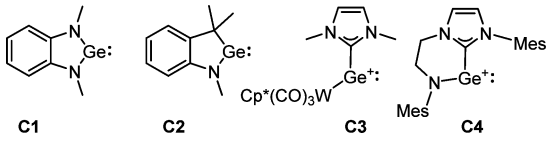
DOI: 10.1021/acs.organomet.6b00925
Organometallics XXXX, XXX, XXX−XXX

Scheme 1. Activation of Dihydrogen with Tetrylenes



derivatives and compared these to the known tetrylene **C3** (Table 1) which is known to insert into the H−H bond. Based on these results, we designed and prepared a novel intramolecularly stabilized cationic tetrylene featuring an amido and an NHC donor and studied its reaction with elemental hydrogen. Few related heavier tetrylenes stabilized by C- and N-donors have previously been described.[15−17]

Table 1. Calculated HOMO−LUMO Energy Gaps for Different NHGe Structures[a]



compound	HOMO−LUMO energy gap[b]
C1	4.038
C2	3.808
C3	2.780
C4	3.214

[a]Cp* = η^5-C_5M_5, Mes = 2,4,6-trimethylphenyl. [b]Values are given in eV.

RESULTS AND DISCUSSION

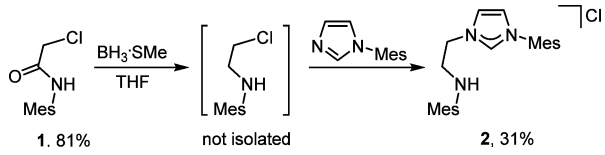
In our initial studies we have focused on Arduengo-type NHGes and NHSns.[7c,e,18] Unfortunately, these tetrylenes appear not suitable for the actvation of small molecules by simultaneous action of the nucleophilic sp^2 and the electrophilic p_π orbital at the E^{II} center. The calculated HOMO−LUMO energy difference of 4.038 eV for simplified *N*,*N*′-dimethyl substituted NHGe **C1** is too large for an insertion into the H−H bond of elemental hydrogen (Table 1). Related HOMO−LUMO energy gaps were found for NHGes featuring an unsaturated imidazolin or a saturated imidazolidin skeleton.[14,19]

Substituting one NMe group of the heterocycle in **C1** for a CMe_2 group leads to CAAC analogue **C2**. CAACs featuring a C^{II} atom have been successfully employed for the activation of elemental hydrogen.[10] The HOMO−LUMO energy gap of 3.808 eV calculated for the Ge^{II} CAAC derivative is smaller than the value calculated for NHC analogue **C1**. The calculated value for **C2** is close to the threshold value of 3.4−3.6 eV previously calculated for dihydrogen activation by germylenes.[14] Tobita et al. and our group also calculated the HOMO−LUMO gap for compound **C3**: ref 13, 2.780 eV; this work, 2.715 eV. The difference is probably due to slightly different structures/computational settings, which has been demonstrated to activate elemental hydrogen.

Based on these calculations, we concluded that a C- and N-substituted germylene similar to **C2** might be suitable for the activation of elemental hydrogen. Considering the reactivity of germylene **C3**, it was decided that the carbon substituent for the desired germylene should be an NHC. An R,R′,N-amido group, as is found in germylenes **C1** and **C2**, was selected as the second substituent for the gemanium(II) center. These considerations led us to compound **C4** bearing a C_{NHC}^N_{amido} chelate ligand, which we envisaged to be a suitable germylene for the activation of dihydrogen. We calculated a HOMO−LUMO energy gap of 3.214 eV for **C4**, which is lower than the equivalent value calculated for germylene **C2**. While some examples of donor-stabilized tetrylenes have been described,[20] no intramolecularly NHC-stabilized cationic germylens are known, which makes the synthesis of compounds of type **C4** also an interesting synthetic target.

The compound 1-mesityl-3-[2-(mesitylamino)ethyl]-1*H*-imidazol-3-ium chloride (Scheme 2) was prepared utilizing a modified version of a described procedure[21a] to give imidazolium salt **2** in moderate yield. This compound has been prepared previously by Fryzuk et al.[21b] and was used as ligand precursor for transition metal NHC complexes.[21c] Compound **2** was characterized by NMR spectroscopy and mass spectrometry. The ^{1}H NMR spectrum features the characteristic resonances for the C2 and NH protons at δ 10.50 and 4.12 ppm, respectively. The resonance for the C2 carbon atom was found at δ 139.7 ppm in the $^{13}C\{^1H\}$ NMR spectrum.

Scheme 2. Synthesis of Imidazolium Salt 2

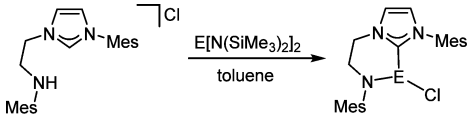


The reaction of compound **2** with equimolar amounts of $E[N(SiMe_3)_2]_2$ (E = Ge and Sn) in toluene afforded tetrylenes **3a** and **3b** in good yields (Scheme 3). No external base was needed for the deprotonation of the C2 carbon atom of the imidazolium group or the secondary amine function. Compounds **3a** and **3b** are stable under argon over weeks both as solids and in THF solution.

The ^{1}H NMR spectra of **3a** and **3b** no longer feature any resonances for C2 and NH protons, and we take the absence of

DOI: 10.1021/acs.organomet.6b00925
Organometallics XXXX, XXX, XXX−XXX

Scheme 3. Synthesis of Tetrylenes 3a and 3b



these resonances as an indication for the double deprotonation of **2** and the coordination of the resulting C^N chelate ligand. This conclusion is corroborated by the observation of diastereotopic protons at the ethylene bridge in accord with previous observations for complexes bearing donor-functionalized NHCs with an ethylene linker.[22] Based on these observations, we assumed that compounds **3a** and **3b** did form according to Scheme 3. The $^{13}C\{^1H\}$ NMR resonances for the C_{NHC} carbon atoms were detected at δ 171.4 (**3a**) and δ 178.6 ppm (**3b**). A signal at δ −149 ppm in the ^{119}Sn NMR spectrum confirms the formation of electron-rich tin(II) compound **3b**.

X-ray diffraction analyses with crystals of compositions **3a**·0.5THF and **3b**·0.5THF confirmed that the E^{II} atoms in tetrylenes **3a** and **3b** are surrounded by the neutral NHC donor and one anionic amido and a chlorido ligand (Figure 1).

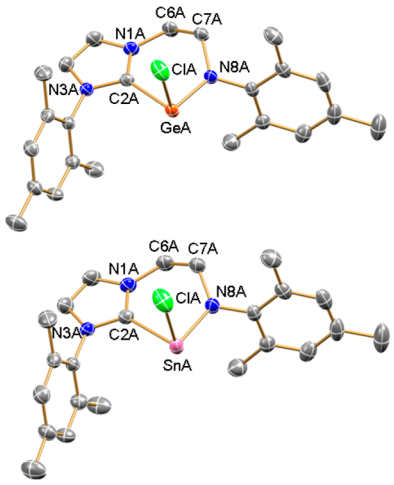
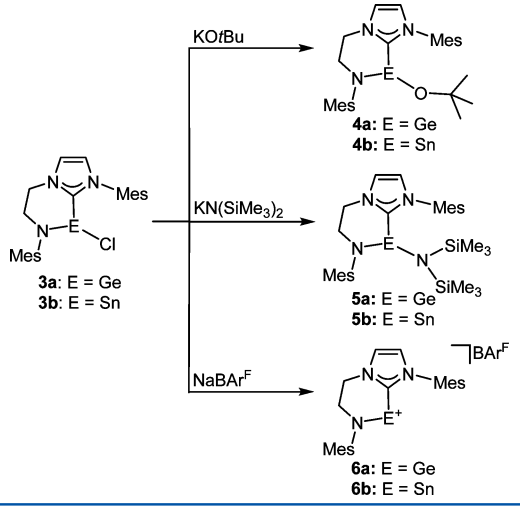


Figure 1. Molecular structure of one molecule of **3a** in **3a**·0.5THF (top) and **3b** in **3b**·0.5THF (bottom). Only one of the two essentially identical molecules in the asymmetric unit for both compounds is depicted (50% probability displacement ellipsoids; hydrogen atoms have been omitted for clarity). Selected bond lengths (Å) and angles (deg) for **3a** [**3b**]: EA−ClA 2.03708(8) [2.5069(10)], EA−N8A 1.891(2) [2.088(2)], EA−C2A 2.062(2) [2.249(3)], N1A−C2A 1.343(3) [1.350(4)], N3A−C2A 1.350(3) [1.348(4)]; ClA−EA−N8A 99.07(7) [96.51(8)], ClA−EA−C2A 90.82(7) [89.66(8)], N8A−EA−C2A 88.27(9) [83.37(10)], N1A−C2A−N3A 105.4(2) [105.3(2)].

The E−Cl bonds are oriented almost perpendicular relative to the C2−E−N8, which constitutes a typical geometric situation for chlorido-substituted germylenes.[20g,i] The plane of the ring incorporating the E^{II} atom deviates significantly from planarity in accord with previous observations.[20g] This arrangement of bonds would indicate an sp^2-hybridized E^{II} atom featuring an empty p-orbital for interaction with the chlorido ligand. The metric parameters in the two tetrylenes vary with the atomic radius of the E^{II} atom. Consequently, the E−Cl, E−N8, and E−C2 distances in germylene **3a** are significantly shorter than those in stannylene **3b**. The bond angles in the two tetrylenes are rather similar to the exception of the inner-ring N8−E−C2 angle in **3b** (83.37(10)°) which is in accord with the longer E−N8 and E−C2 bond distances in this tetrylene being smaller than those in **3a** (88.27(9)°).

Next, we studied the substitution of the chlorido ligand of the tetrylenes for other monodentate anionic ligands (Scheme 4).

Scheme 4. Ligand Substitution and Ligand Abstraction at Tetrylenes 3a and 3b



The reaction products were completely characterized by NMR spectroscopy. Treatment of tetrylenes **3a** or **3b** with potassium *tert*-butoxide in benzene resulted in the exchange of the chlorido ligand for a *tert*-butoxido ligand. The $^{13}C\{^1H\}$ NMR spectrum of germylene **4a** features the resonance for the C2 carbon atom at δ 173.7 ppm only slightly downfield shifted ($\Delta\delta$ 2.3 ppm) compared to the resonance for the C2 carbon atom in **3a** (δ 171.4 ppm). A slightly different behavior was found for stannylene **4b**. The C2 carbon atom resonance for the chlorido stannylene **3b** was observed at δ 178.6 ppm. Upon substitution of the chloride ligand to give stannylene **4b**, this resonance is shifted downfield to δ 207.5 ppm ($\Delta\delta$ 28.9 ppm). The reasons for this strong downfield shift are not completely clear at this time. The chemical shift for the C_{NHC} atom in **4b** falls in the range observed for free imidazolin-2-ylidenes (δ 211−220 ppm),[2b] but dissociation of the NHC as part of a chelate ligand from the metal center is not very likely. We are currently investigating reasons for the observed downfield shift such as fluxionality of the Sn−C_{NHC} bond.

Germylene **4a** was crystallized from the C_6D_6 solution used for NMR spectroscopy to give crystals of composition **4a**·0.5C_6D_6. The X-ray diffraction analysis with these crystals revealed the expected molecular structure for germylene **4a** composed of a germanium atom surrounded by the NHC donor and anionic amido and *t*-butoxido ligands (Figure 2). The Ge−O bond, as previously observed for the Ge−Cl bond in **3a**, is oriented almost perpendicular to the C2−Ge−N8 plane, and the germanium containing heterocycle is not planar. Comparable metric parameters in chlorido germylene **3a** and *t*-butoxido germylene **4a** are rather similar, confirming an essentially identical influence of the anionic ligands on the molecular structures. The Ge−O bond length in **4a** compares well to the Ge−OH bond length observed for a related three-coordinate Ge^{II} hydroxide (Ge−O 1.8249(18) Å)[20f] but is significantly longer than the Ge=O bond in a four-coordinate germanones (about 1.67 Å).[20d]

DOI: 10.1021/acs.organomet.6b00925
Organometallics XXXX, XXX, XXX−XXX

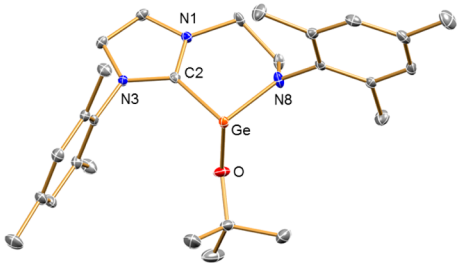


Figure 2. Molecular structure of **4a** in **4a**·0.5C_6H_6 (50% probability displacement ellipsoids, hydrogen atoms have been omitted for clarity). Selected bond lengths (Å) and angles (deg): Ge−O 1.8832(10), Ge−N8 1.9123(11), Ge−C2 2.0673(13), N1−C2 1.348(2), N3−C2 1.352(2); O−Ge−N8 100.25(5), O−Ge−C2 87.71(5), N8−Ge−C2 87.30(5), N1−C2−N3 105.22(11).

Next, the reactivity of **3a**/**3b** toward potassium bis(trimethylsilyl)amide was investigated (Scheme 4). In contrast to *tert*-butoxido tetrylenes **4a** and **4b**, HMDS tetrylenes **5a** (E = Ge) and **5b** (E = Sn) do not show significant differences of the C_{NHC} resonances in the $^{13}C\{^1H\}$ NMR spectra (δ 174.3 ppm for **5a**, δ 178.5 ppm for **5b**). The C_{NHC} resonances observed for **5a** and **5b** are also very similar to those observed for chloride tetrylenes **3a** and **3b**.

Tobita et al. demonstrated that cationic germylenes such as **C3** (Table 1)[13] obtained by chlorido abstraction from a three-coordinate germylene leads to cationic derivatives which are capable of activating elemental hydrogen. Based on our calculation of the HOMO−LUMO energy gap for compound **C4** (Table 1), we decided to prepare cationic tetrylenes by chlorido abstraction from **3a**/**3b**. Reaction of **3a** and **3b** with $NaBAr^F$ (BAr^F = *tetrakis*[3,5-bis(trifluoromethyl)phenyl]-borate, Scheme 4) gave tetrylenes **6a** (E = Ge) and **6b** (E = Sn). Evidence for the formation of the cationic tetrylenes comes from the NMR spectra of the compounds. Upon removal of the chlorido ligand from **3a** to give **6a**, the C_{NHC} resonace shifts from δ 171.4 to 166.0 ppm. The upfield shift of the H4 and H5 protons of the NHC-ring backbone is also significant, shifting from δ 7.25 and 7.52 ppm for **3a** to δ 5.84 and 5.97 ppm for **6a**. Similar observations were made for stannylene **3b** and its cationic derivative, **6b**. Formation of cationic stannylene **6b** is most clearly demonstrated by the chemical shift difference observed in the ^{119}Sn NMR spectra for **3b** (δ −149 ppm) and **6b** (δ −60 ppm). Related cationic two-coordinate germylenes of type [(β-diketiminate)Ge]$^+$ have been obtained from the three-coordinate chloride compounds by chloride removal with $B(C_6F_5)_3$.[23]

The cationic germylenes and stannylenes were tested in the activation of elemental hydrogen. For these studies, a sample of the tetrylene was dissolved in toluene, and this solution was submitted to a hydrogen pressure of 1 bar under vigorous stirring. Analysis of the reaction products was performed by ^1H NMR spectroscopy. The results were, however, not conclusive. For the compounds of types **3**−**5**, no reaction or decomposition of the tetrylene was observed. Even the cationic tetrylenes of type **6** did not react with elemental hydrogen. Apparently, the calculated HOMO−LUMO gap of 3.214 eV is still to large for the hydrogen activation to proceed.

CONCLUSIONS

We succeeded in preparing several novel intramolecularly stabilized three-coordinate germylenes and stannylenes of type **3** bearing NHC^amido chelate and chlorido ligands. The chlorido ligand in these tetrylenes can be substituted for monodentate anionic *t*-butoxido or bis(trimethylsilyl)amido ligands. Removal of the chlorido ligand leads to cationic tetrylenes **6a**/**6b** bearing only the bidentate NHC^amido chelate ligand. DFT calculations indicated that germylene **6a** features a HOMO−LUMO energy gap which might make germylenes of this type potentially suitable for the activation of elemental hydrogen. However, no such hydrogen activation was observed so far.

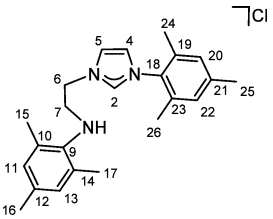
EXPERIMENTAL SECTION

All reactions were carried out under an inert argon atmosphere using standard Schlenk techniques or in a glovebox if not stated otherwise. Solvents were dried and freshly distilled by standard procedures prior to use. NMR spectra were recorded at ambient temperature (unless stated otherwise) using Bruker AVANCE I 400, Bruker AVANCE III 400, Varian 500 MHz INOVA or Varian 600 unity plus spectrometers. Chemical shifts (δ) are expressed in ppm downfield from tetramethylsilane using the residual protonated solvent (^1H NMR) or Me_4Sn (^{119}Sn NMR) as an internal standard. EI mass spectra were recorded on a MicroTof spectrometer (Bruker Daltronics, Bremen) with loop injection, using the nanospray technique and sodium formate cluster for calibration. Di[bis(trimethylsilyl)amido]tin(II) and di[bis(trimethylsilyl)amido]germanium(II) were prepared by published procedures.[6a]

Synthesis of 2-Chloro-*N*-mesitylacetamid 1.

Compound **1** was prepared following a procedure described by Grubbs et al.[21a] Mesitylamine (2.71 g, 2.82 mL, 20.0 mmol) and K_2CO_3 (5.53 g, 40.0 mmol) were suspended in acetonitrile (50 mL). Chloroacetyl chloride (2.27 g, 1.60 mL, 20.0 mmol) was added dropwise, and the reaction mixture was stirred at ambient temperature for 48 h. Subsequently, the mixture was filtered through a pad of silica, and hexane was added to the concentrated MeCN solution leading to the formation of crystalline **1**. The colorless crystals were isolated by filtration and washed with cold hexane (10 mL). Yield: 3.45 g (16.3 mmol, 82%). R_F (pentane/EtOAc 8:2): 0.08. ^1H NMR (300 MHz, $CDCl_3$, δ) 7.83 (s, 1H, NH), 6.92 (s, 2H, Mes−H), 4.26 (s, 2H, CH_2Cl), 2.28 (s, 3H, Mes−CH_3), 2.19 (s, 6H, Mes−CH_3). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, δ) 164.9 (C=O), 137.7, 135.0, 129.9, 129.1 (Mes−C), 42.7 (CH_2Cl), 21.0, 18.2 (Mes−CH_3). HRMS (ESI, positive ions): m/z = 234.0656 (calcd for [**1** − Na]$^+$, [$C_{11}H_{14}ClNONa$]$^+$ 234.0661).

Synthesis of 1-Mesityl-3-(2-(mesitylamino)ethyl)-1*H*-imidazol-3-ium Chloride 2.



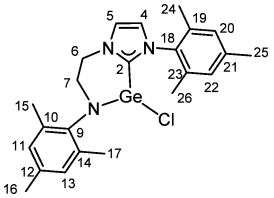
A sample of 2-chloro-*N*-mesitylacetamid **1** (4.23 g, 20.0 mmol) was dissolved in dry THF (50 mL), and the solution was cooled to 0 °C. At this temperature, borane dimethylsulfide complex (5.36 mL, 4.29 g, 56.6 mmol) was added slowly. After stirring at ambient temperature for 24 h, the reaction mixture was quenched with MeOH until gas evolution ceased. Subsequently, brine (50 mL) was added, and the mixture was extracted with pentane (50 mL). The solvent from the pentane solution was removed *in vacuo* to give a light yellow oil which was used for the next reaction. Under neat conditions, the obtained chloroamine was mixed with mesitylimidazole (3.70 g, 20.0 mmol), and the mixture was stirred at 140 °C for 15 h. A white solid was obtained which was purified by column chromatography (SiO_2, CH_2Cl_2/MeOH 9:1) to give **2** as a colorless solid. Yield: 2.367 g

DOI: 10.1021/acs.organomet.6b00925
Organometallics XXXX, XXX, XXX−XXX

(6.165 mmol, 31%). R_F (CH_2Cl_2/MeOH 9:1): 0.21. ^{1}H NMR (400 MHz, $CDCl_3$, δ) 10.50 (s, 1H, H2), 8.03 (s, 1H, H5), 7.09 (s br, 1H, H4), 6.93 (s, 2H, H20 and H22), 6.70 (s, 2H, H11 and H13), 5.06 (t, 2H, J = 5.4 Hz, H6), 4.12 (br, 1H, NH), 3.24 (t, 2H, J = 5.4 Hz, H7), 2.30 (s, 3H, H25), 2.15 (s, 3H, H16), 2.09 (s, 6H, H15 and H17), 2.01 (s, 6H, H24 and H26). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, δ) 142.1 (C9), 141.2 (C21), 139.7 (C2), 134.3 (C19 and C23), 132.4 (C12), 131.4 (C10 and C14), 130.9 (C18), 129.9 (C20 and C22), 129.3 (C11 and C13), 123.6 (C5), 122.4 (C4), 49.9 (C6), 47.6 (C7), 21.1 (C25), 20.6 (C16), 18.3 (C15 and C17), 17.6 (C24 and C26). HRMS (ESI, positive ions): m/z = 348.2436 (calcd for [**2** − Cl]$^+$, $[C_{23}H_{30}N_3]^+$ 248.2434.

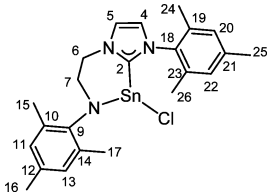
General Procedure for the Preparation of Germylene 3a and Stannylene 3b. Di[bis(trimethylsilyl)amido]germanium(II) $Ge[N(SiMe_3)_2]_2$ (393 mg, 1.0 mmol) or di[bis(trimethylsilyl)amido]-tin(II) $Sn[N(SiMe_3)_2]_2$ (439 mg, 1.0 mmol) and **2** (384 mg, 1.0 mmol) were suspended in toluene (15 mL) in a Schlenk flask. After stirring of the reaction mixture at 110 °C for 48 h, the solvent and volatile $HN(SiMe_3)_2$ were removed *in vacuo*. The solid residue was washed with hexane (3 × 5 mL) to give the germylene (as a yellow solid) and the stannylene (as an orange solid), respectively. The tetrylenes were further recrystallized from THF to give single crystals of composition **3a**·0.5THF and **3b**·0.5THF, respectively.

Germylene 3a.



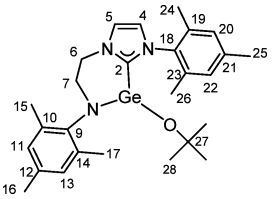
Yield: 391 mg (0.86 mmol, 86%). ^{1}H NMR (400 MHz, THF-d_8, δ) 7.52 (d, ^3J = 1.8 Hz, 1H, H5), 7.25 (d, ^3J = 1.8 Hz, 1H, H4), 6.99 (s br, 1H, H22), 6.97 (s br, 1H, H20), 6.75 (s br, 1H, H11), 6.72 (s br, 1H, H13), 4.48−4.44 (m, 1H, H6a), 4.32−4.22 (m, 2H, H6b, H7a), 3.22−3.18 (m, 1H, H7b), 2.35 (s br, 3H, H15 or H17), 2.30 (s, 3H, H25), 2.21 (s br, 3H, H17 or H15), 2.16 (s br, 3H, H24), 2.15 (s, 3H, H16), 2.04 (s br, 3H, H26). ^{13}C{^{1}H} NMR (100 MHz, THF-d_8, δ) 171.4 (C2), 151.0 (C9), 140.4 (C21), 137.4 (C19 or C23), 136.9 (C23 or C19), 135.4 (C10 or C14), 135.2 (C14 or C10), 134.2 (C18), 132.3 (C12), 130.3 (C22), 129.6 (C20), 128.8 (C13), 123.8 (C5), 122.3 (C4), 52.7 (C6), 50.5 (C7), 21.1 (C25), 20.9 (C16), 20.5 (C15 or C17), 20.3 (C17 or C15), 18.5 (C24), 17.8 (C26). MS (EI): m/z (%) 455 (100) [**3a**]$^+$, 419 (87), [**3a** − HCl] $^+$. Anal. Calcd for ($C_{23}H_{28}$-$ClGeN_3$)·0.5THF: C, 61.20; H, 6.58; N, 8.57. Found: C, 61.15; H, 6.44; N, 8.58.

Stannylene 3b.



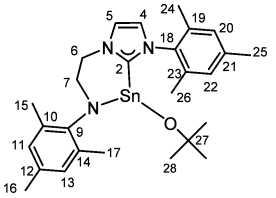
Yield: 451 mg (0.90 mmol, 90%). ^{1}H NMR (400 MHz, THF-d_8, δ) 7.53 (d, ^3J = 1.7 Hz, 1H, H5), 7.29 (d, ^3J = 1.7 Hz, 1H, H4), 7.03 (s br, 1H, H20), 7.01 (s br, 1H, H22), 6.76 (s br, 1H, H11), 6.72 (s br, 1H, H13), 4.72−4.66 (m, 1H, H6a), 4.31−4.18 (m, 2H, H6b and H7a), 3.46−3.38 (m, 1H, H7b), 2.36 (s, 3H, H15), 2.32 (s, 3H, H25), 2.21 (s, 3H, H17), 2.14 (s br, 6H, H16, H26), 2.04 (s, 3H, H24). ^{13}C{^{1}H} NMR (101 MHz, THF-d_8, δ) 178.6 (C2), 152.7 (C9), 140.6 (C21), 137.4, 136.9, 135.1, 135.0 (C10, C14, C19 and C23), 134.8 (C18), 131.5 (C12), 130.4 (C20), 130.3 (C11), 129.8 (C22), 128.9 (C13), 124.5 (C5), 122.3 (C4), 54.5(C6), 53.2 (C7), 21.2 (C25), 20.9 (C16), 20.4 (C15 or C17), 20.3 (C17 or C15), 18.3 (C26), 17.8 (C24). ^{119}Sn NMR (149 MHz, THF-d_8, δ) −149. MS (EI): m/z (%) 501 (46) [**3b**]$^+$.

Germylene 4a.



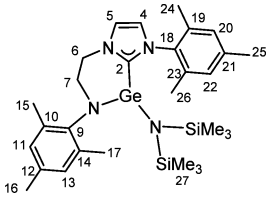
In the glovebox, a sample of germylene **3a** (20 mg, 0.044 mmol) was suspended in C_6D_6 (0.6 mL), and solid KO*t*Bu (5 mg, 0.045 mmol) was added. The resulting solution was characterized using NMR spectroscopy. Single crystals of **4a**·0.5C_6D_6 were obtained from a C_6D_6 solution. ^{1}H NMR (500 MHz, C_6D_6, δ) 7.04 (s, 1H, H13), 6.99 (s, 1H, H11), 6.78 (s, 1H, H20), 6.68 (s, 1H, H22), 5.97 (s, 1H, H5), 5.87 (s, 1H, H4), 4.66−4.54 (m, 1H, H7a), 3.55−3.48 (m, 1H, H6a), 3.23 (d, 1H, J = 13.1 Hz, H6b), 2.99 (d, 1H, J = 13.1 Hz, H7b), 2.72 (s, 3H, H17), 2.58 (s, 3H, H15), 2.27 (s, 3H, H16), 2.15 (s, 3H, H25), 2.06 (s, 3H, H24), 2.03 (s, 3H, H26), 1.30 (s, 9H, H28). ^{13}C{^{1}H} NMR (126 MHz, C_6D_6, δ) 173.7 (C2), 152.2 (C9), 139.5 (C19), 136.5 (C21), 134.9 (C23), 134.2 (C18), 130.3 (C10 and C14), 130.3 (C12 and C13), 129.4 (C22), 129.2 (C11 and C20), 121.7 (C5), 120.1 (C4), 69.4 (C27), 52.5 (C6), 48.6 (C7), 33.6 (C28), 21.5 (C15), 21.0 (C16 or C24), 21.0 (C16 or C24), 20.8 (C17), 18.6 (C25), 17.9 (C26).

Stannylene 4b.



In the glovebox, a sample of stannylene **3b** (20 mg, 0.04 mmol) was suspended in C_6D_6 (0.6 mL), and solid KO*t*Bu (10 mg, 0.09 mmol) was added. The resulting solution was characterized using NMR spectroscopy. ^{1}H NMR (500 MHz, C_6D_6, δ) 7.03 (s, 2H, H11 and H13), 6.75 (s, 2H, H20 and H22), 6.02 (s, 1H, H4), 5.97 (s, 1H, H5), 4.31−4.21 (m, 2H, H6), 3.91−3.83 (m, 2H, H7), 2.69 (s, 6H, H15 and H17), 2.26 (s, 3H, H16), 2.08 (s, 3H, H25), 1.85 (s, 6H, H24 and H26), 1.36 (s, 9H, H28). ^{13}C{^{1}H} NMR (126 MHz, C_6D_6, δ) 207.5 (C2), 153.2 (C9), 139.2 (C18), 137.8 (C19, C23 and C21), 136.8 (C10 and C14), 130.0 (C12), 129.5 (C11 and C13), 128.9 (C20 and C22), 120.3 (C5), 119.2 (C4), 69.8 (C27), 56.3 (C7), 55.7 (C6), 35.7 (C28), 21.4 (C15 and C17), 21.1 (C16), 20.9 (C25), 17.8 (C24 and C26). ^{119}Sn NMR (224 MHz, C_6D_6, δ) −148.

Germylene 5a.

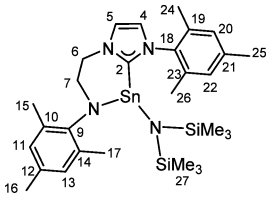


In the glovebox, germylene **3a** (20 mg, 0.044 mmol) was suspended in C_6D_6 (0.6 mL), and $KN(SiMe_3)_2$ (9 mg, 0.045 mmol) was added. The resulting solution was characterized using NMR spectroscopy. ^{1}H NMR (500 MHz, C_6D_6, δ) 7.02 (s, 1H, H11), 6.98 (s, 1H, H13), 6.75 (s, 1H, H20), 6.67 (s, 1H, H22), 5.97 (d, 1H, J = 1.8 Hz, H5), 5.87 (d, 1H, J = 1.8 Hz, H4), 4.38 (ddd, 1H, J = 14.3, 12.5, 3.1 Hz, H7a), 3.52 (m, 1H, H6a), 3.21 (ddd, 1H, J = 12.5, 3.1, 1.9 Hz, H6b), 3.01 (ddd, 1H, J = 14.3, 4.5, 1.9 Hz, H7b), 2.65 (s, 3H, H15), 2.48 (s, 3H, H17), 2.24 (s, 3H, H16), 2.14 (s, 3H, H24), 2.08 (s, 3H, H25), 1.92 (s, 3H, H26), 0.23 (s, 18H, H27). ^{13}C{^{1}H} NMR (126 MHz, C_6D_6, δ) 174.3 (C2), 152.6 (C9), 139.6 (C21), 136.6 (C10), 135.9 (C23), 135.0 (C14), 134.7 (C19), 133.9 (C18), 131.1 (C12), 130.0 (C11), 129.8 (C22), 129.4 (C20), 128.9 (C13), 122.2 (C5), 121.5 (C4), 52.7 (C6), 48.8 (C7), 21.6 (C17), 21.2 (C15), 21.1 (C16), 20.9 (C25),

DOI: 10.1021/acs.organomet.6b00925
Organometallics XXXX, XXX, XXX−XXX

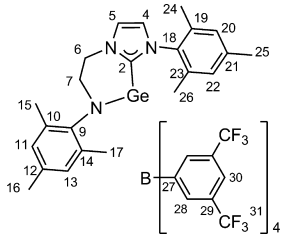
19.4 (C24), 18.4 (C26), 6.6 (C27). ^{29}Si NMR (99 MHz, C_6D_6, δ) −2.83 ppm.

Stannylene 5b.



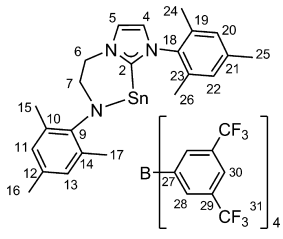
In the glovebox, a sample of stannylene **3b** (20 mg, 0.04 mmol) was suspended in toluene-d_8 (0.6 mL), and $KN(SiMe_3)_2$ (8 mg, 0.04 mmol) was added. The resulting solution was characterized using NMR spectroscopy. ^{1}H NMR (500 MHz, toluene-d_8, 253 K, δ) 7.02 (s, 1H, H13), 6.92 (s, 1H, H11), 6.68 (s, 1H, H22), 6.56 (s, 1H, H20), 5.85 (s, 1H, H4 or H5), 5.73 (s, 1H, H4 or H5), 4.70 (t, 1H, J = 12.6 Hz, H7a), 3.41−3.29 (m, 2H, H6a and H7b), 3.24 (d, 1H, J = 12.6 Hz, H6b), 2.66 (s, 3H, H17), 2.37 (s, 3H, H15), 2.28 (s, 3H, H16), 2.04 (s, 3H, H24), 2.01 (s, 3H, H25), 1.93 (s, 3H, H26), 0.11 (s, 18H, H27). ^{13}C{^{1}H} NMR (126 MHz, toluene-d_8, 253 K, δ) 178.5 (C2), 152.8 (C9), 139.5 (C21), 135.1 (C23), 134.9 (C14), 134.8 (C19), 134.3 (C18), 133.6 (C10), 130.4 (C13), 129.9 (C20), 129.5 (C22), 129.3 (C12), 129.0 (C11), 123.0 (C4 or C5), 121.8 (C4 or C5), 52.9 (C6), 49.3 (C7), 21.8 (C15), 21.1 (C17), 20.9 (C16), 20.8 (C25), 18.8 (C26), 18.7 (C24), 2.5 (C27). ^{29}Si NMR (99 MHz, toluene-d_8, 253 K, δ) −3.53. ^{119}Sn NMR (186 MHz, toluene-d_8, 253 K, δ) −124.3.

Germylene 6a.



In the glovebox, a sample of germylene **3a** (20 mg, 0.044 mmol) was suspended in C_6D_6 (0.6 mL), and $NaBAr^F$ (9 mg, 0.045 mmol) was added. The resulting solution was characterized using NMR spectroscopy. ^{1}H NMR (600 MHz, C_6D_6, δ) 8.35 (s, 8H, H28), 7.65 (s, 4H, H30), 6.72 (s, 2H, H11 and H13), 6.57 (s, 2H, H20 and H22), 5.97 (s, 1H, H5), 5.84 (s, 1H, H4), 3.16 (t, 2H, J = 5.5 Hz, H6), 2.75−2.68 (m, 2H, H7), 2.08 (s, 3H, H16), 1.98 (s, 3H, H25), 1.80 (s, 6H, H15 and H17), 1.49 (s, 6H, H24 and 26). ^{13}C{^{1}H} NMR (151 MHz, C_6D_6, δ) 166.0 (C2), 163.3−162.0 (q, J = 49.8 Hz, C27), 144.6 (C9), 142.1 (C21), 137.7 (C12), 135.4 (C28), 133.8 (C19 and C23), 133.2 (C10 and C14), 130.2 (C11, C13, C20 and C22), 129.0 (m, C29) 125.2 (q, J = 272.6 Hz, C31), 123.4 (C4), 122.5 (C5), 118.1 (C30), 52.2 (C7), 50.3 (C6), 20.8 (C25), 20.7 (C16), 18.4 (C15 and C17), 16.7 (C24 and C26). ^{11}B NMR (192 MHz, C_6D_6, δ) −6.03. ^{19}F NMR (564 MHz, C_6D_6, δ) −62.23.

Stannylene 6b.



In the glovebox, stannylene **3b** (20 mg, 0.04 mmol) was suspended in C_6D_6 (0.6 mL), and $NaBAr^F$ (9 mg, 0.045 mmol) was added. The resulting solution was characterized using NMR spectroscopy. ^{1}H NMR (600 MHz, C_6D_6, δ) 8.39 (s, 8H, J = 2.1 Hz, H28), 7.67 (s, 4H, H30), 6.89 (s, 2H, H11 and H13), 6.45 (s br, 2H, H20 and H22), 6.01 (d, 1H, J = 1.6 Hz, H4 or H5), 5.86 (d, 1H, J = 1.6 Hz, H4 or H5), 3.43 (m br, 2H, H6 or H7), 3.28 (m br, 2H, H6 or H7), 2.22 (s, 3H, H16), 2.14 (s, 6H, H15 and H17), 2.02 (s, 3H, H25), 1.60 (s, 6H, H24 and H26). ^{13}C{^{1}H} NMR (151 MHz, C_6D_6, δ) 162.7 (q, J = 49.9 Hz, C27), 149.3 (C9), 141.0 (C21), 135.5 (C28), 134.3 (C12, together with C10, C14, C19, and C23), 132.7 (C18), 129.9 (s, C11, C13, C20, and C22), 129.0 (m, C29) 125.3 (q, J = 272.6 Hz, C31), 123.2 (C4 or C5), 122.1 (C4 or C5), 118.1 (p, J = 4.3 Hz, C30), 53.6 (C6 or C7), 53.6 (C6 or C7), 20.8 (C16), 20.8 (C25), 19.8 (C15 and C17), 17.1 (C24 and C26). The resonance for the C2 carbon atom was not detected. ^{11}B NMR (192 MHz, C_6D_6, δ) −5.97. ^{19}F NMR (564 MHz, C_6D_6, δ) −62.21. ^{119}Sn NMR (149 MHz, THF-d_8, δ) −60.

Computational Details. All calculations were carried out using the Gaussian09 program.[24] Structural optimizations were carried out with the B3LYP[25] hybrid exchange-correlation functional, a 6-31G(d,p)[26] basis set for all atoms except W, and a LanL2DZ[27] effective core potential/basis set for W atoms. HOMO−LUMO gaps were calculated with the same method for the optimized structures. The threshold values in ref 14 were calculated with the larger 6-311+G** basis. Test calculations carried out here for compounds **C1** and **C2** indicate that this leads to slightly lower (∼0.1 eV) HOMO−LUMO gaps compared to the 6-31G(d,p) data.

X-ray Diffraction Studies. X-ray diffraction data for compounds **3a**·0.5THF, **3b**·0.5THF, and **4a**·0.5C_6D_6 were recorded with graphite monochromated Mo Kα radiation (λ = 0.71073 Å) at T = 100(2) K for **4a**·0.5C_6D_6 and at T = 153(2) for **3a**·0.5THF and **3b**·0.5THF. Diffraction data were collected over the full sphere and were corrected for absorption. Structure solutions were found with the SHELXS[28] package using direct methods and were refined with SHELXL[28] against $|F^2|$ using first isotropic and later anisotropic thermal parameters for all non-hydrogen atoms. Hydrogen atoms were added to the structure models on calculated positions and refined as riding atoms. If not noted otherwise, then no hydrogen positions were calculated for disordered atoms (see the individual refinement details).

Crystal Data and Structure Refinement Details for 3a·0.5THF. $C_{23}H_{28}N_3ClGe{\cdot}0.5C_4H_8O$, M_r = 490.58 g·mol^{-1}, colorless block, 0.42 × 0.25 × 0.25 mm^3, monoclinic, space group $P2_1/n$, Z = 8, a = 8.21160(10) Å, b = 12.2330(2) Å, c = 48.3211(6) Å, β = 94.3080(10)°, V = 4840.36(12) Å^3, ρ_{calcd} = 1.346 g·cm^{-3}, μ = 1.395 mm^{-1}, ω- and φ-scans, 64 438 measured intensities (1.7° ≤ 2θ ≤ 59.1°), semiempirical absorption correction (0.645 ≤ T ≤ 0.746), 13 573 independent (R_{int} = 0.0368) and 11 367 observed intensities ($I \geq 2\sigma(I)$), refinement of 562 parameters against $|F^2|$ of all measured intensities with hydrogen atoms on calculated positions. R = 0.0481, wR = 0.1134, R_{all} = 0.0616, wR_{all} = 0.1193. The asymmetric unit contains two formula units of **3a** and one THF molecule. The THF molecule is disordered over two positions (SOF = 0.62/0.28). The positional parameters of the THF molecule were refined with isotropic thermal parameters, and no hydrogen positions were calculated for the THF molecule.

Crystal Data and Structure Refinement Details for 3b·0.5THF. $C_{23}H_{28}N_3Cl_2OSn$, M_r = 536.68 g·mol^{-1}, colorless block, 0.16 × 0.15 × 0.12 mm^3, monoclinic, space group $P2_1/n$, Z = 8, a = 8.2740(4) Å, b = 12.2320(6) Å, c = 49.393(2) Å, β = 94.8040(10)°, V = 4981.4(4) Å^3, ρ_{calcd} = 1.431 g·cm^{-3}, μ = 1.152 mm^{-1}, ω- and φ-scans, 143 770 measured intensities (4.2° ≤ 2θ ≤ 61.1°), semiempirical absorption correction (0.746 ≤ T ≤ 0.677), 15 264 independent (R_{int} = 0.0630) and 11 310 observed intensities ($I \geq 2\sigma(I)$), refinement of 557 parameters against $|F^2|$ of all measured intensities with hydrogen atoms on calculated positions. R = 0.0485, wR = 0.1022, R_{all} = 0.0771, wR_{all} = 0.1113. The asymmetric unit contains two formula units of **3b** and one THF molecule. The THF molecule is disordered.

Crystal Data and Structure Refinement Details for 4a·0.5C_6D_6. $C_{30}H_{37}D_3N_3GeO$, M_r = 534.26 g·mol^{-1}, colorless prism, 0.26 × 0.18 × 0.09 mm^3, monoclinic, space group $P2_1/c$, Z = 4, a = 13.0226(4) Å, b = 15.0573(5) Å, c = 14.4071(5) Å, β = 96.067(1)°, V = 2809.2(2) Å^3, ρ_{calcd} = 1.263 g·cm^{-3}, μ = 1.117 mm^{-1}, ω- and φ-scans, 65 178 measured intensities (4.8° ≤ 2θ ≤ 55.1°), semiempirical absorption correction (0.86 ≤ T ≤ 0.90), 6460 independent (R_{int} = 0.0457) and 5712 observed intensities ($I \geq 2\sigma(I)$), refinement of 325 parameters against $|F^2|$ of all measured intensities with

DOI: 10.1021/acs.organomet.6b00925
Organometallics XXXX, XXX, XXX−XXX

hydrogen atoms on calculated positions. R = 0.0247, wR = 0.0563, R_{all} = 0.0311, wR_{all} = 0.0592. The asymmetric unit contains one formula unit **4a**·0.5C_6D_6.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.6b00925.

NMR spectra for all compounds (PDF)

X-ray crystallographic data for **3a**·0.5THF, **3b**·0.5THF, and **4a**·0.5C_6D_6 (CIF)

■ AUTHOR INFORMATION

Corresponding Authors

*E-mail: glorius@uni-muenster.de.

*E-mail: fehahn@uni-muenster.de.

ORCID

Alexander Hepp: 0000-0003-1288-925X

Frank Glorius: 0000-0002-0648-956X

F. Ekkehardt Hahn: 0000-0002-2807-7232

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We gratefully acknowledge financial support from the Deutsche Forschungsgemeinschaft (SFB 858 and IRTG 2027).

■ REFERENCES

(1) Arduengo, A. J., III; Harlow, R. L.; Kline, M. *J. Am. Chem. Soc.* **1991**, *113*, 361−363.

(2) (a) Hopkinson, M. N.; Richter, C.; Schedler, M.; Glorius, F. *Nature* **2014**, *510*, 485−496. (b) Hahn, F. E.; Jahnke, M. *Angew. Chem., Int. Ed.* **2008**, *47*, 3122−3172.

(3) (a) Zabula, A. V.; Hahn, F. E. *Eur. J. Inorg. Chem.* **2008**, *2008*, 5165−5179. (b) Mizuhata, Y.; Sasamori, T.; Tokitoh, N. *Chem. Rev.* **2009**, *109*, 3479−3511. (c) Asay, M.; Jones, C.; Driess, M. *Chem. Rev.* **2011**, *111*, 354−396.

(4) (a) Davidson, P. J.; Lappert, M. F. *J. Chem. Soc., Chem. Commun.* **1973**, 317a. (b) Davidson, P. J.; Harris, D. H.; Lappert, M. F. *J. Chem. Soc., Dalton Trans.* **1976**, 2268−2274.

(5) Veith, M. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 263−264.

(6) (a) Harris, D. H.; Lappert, M. F. *J. Chem. Soc., Chem. Commun.* **1974**, 895−896. (b) Schaeffer, C. D., Jr.; Zuckerman, J. J. *J. Am. Chem. Soc.* **1974**, *96*, 7160−7162.

(7) (a) Boehme, C.; Frenking, G. *J. Am. Chem. Soc.* **1996**, *118*, 2039−2046. (b) Hahn, F. E.; Wittenbecher, L.; Kühn, M.; Lügger, T.; Fröhlich, R. *J. Organomet. Chem.* **2001**, *617*−*618*, 629−634. (c) Zabula, A. V.; Hahn, F. E.; Pape, T.; Hepp, A. *Organometallics* **2007**, *26*, 1972−19809. (d) Zabula, A. V.; Pape, T.; Hepp, A.; Schappacher, F. M.; Rodewald, U. C.; Pöttgen, R.; Hahn, F. E. *J. Am. Chem. Soc.* **2008**, *130*, 5648−5649. (e) Krupski, S.; Dickschat, J. V.; Hepp, A.; Pape, T.; Hahn, F. E. *Organometallics* **2012**, *31*, 2078−2084.

(8) (a) Driess, M.; Grützmacher, H. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 828−856. (b) Power, P. P. *Chem. Rev.* **1999**, *99*, 3463−3503. (c) Hahn, F. E.; Wittenbecher, L.; Le Van, D.; Zabula, A. V. *Inorg. Chem.* **2007**, *46*, 7662−7667. (d) Zabula, A. V.; Pape, T.; Hepp, A.; Hahn, F. E. *Organometallics* **2008**, *27*, 2756−2760. (e) Zabula, A. V.; Pape, T.; Hepp, A.; Hahn, F. E. *Dalton Trans.* **2008**, 5886−5890. (f) Hahn, F. E.; Zabula, A. V.; Pape, T.; Hepp, A.; Tonner, R.; Haunschild, R.; Frenking, G. *Chem. - Eur. J.* **2008**, *14*, 10716−10721. (g) Heitmann, D.; Pape, T.; Hepp, A.; Mück-Lichtenfeld, C.; Grimme, S.; Hahn, F. E. *J. Am. Chem. Soc.* **2011**, *133*, 11118−11120.

(9) Power, P. P. *Nature* **2010**, *463*, 171−177.

(10) Frey, D. D.; Lavallo, V.; Donnadieu, B.; Schoeller, W. W.; Bertrand, G. *Science* **2007**, *316*, 439−441.

(11) Peng, Y.; Guo, J.-D.; Ellis, B. D.; Zhu, Z.; Fettinger, J. C.; Nagase, S.; Power, P. P. *J. Am. Chem. Soc.* **2009**, *131*, 16272−16282.

(12) Inomata, K.; Watanabe, T.; Tobita, H. *J. Am. Chem. Soc.* **2014**, *136*, 14341−14344.

(13) Inomata, K.; Watanabe, T.; Miyazaki, Y.; Tobita, H. *J. Am. Chem. Soc.* **2015**, *137*, 11935−11937.

(14) Wang, Y.; Ma, J. *J. Organomet. Chem.* **2009**, *694*, 2567−2575.

(15) Schmidt, H.; Keitemeyer, S.; Neumann, B.; Stammler, H.-G.; Schoeller, W. W.; Jutzi, P. *Organometallics* **1998**, *17*, 2149−2151.

(16) Rivard, E.; Fischer, R. C.; Wolf, R.; Peng, Y.; Merrill, W. A.; Schley, N. D.; Zhu, Z.; Pu, L.; Fettinger, J. C.; Teat, S. T.; Nowik, I.; Herber, R. H.; Takagi, N.; Nagase, S.; Power, P. P. *J. Am. Chem. Soc.* **2007**, *129*, 16197−16208.

(17) Su, B.; Ganguly, R.; Li, Y.; Kinjo, R. *Chem. Commun.* **2016**, *52*, 613−616.

(18) (a) Piel, I.; Dickschat, J. V.; Pape, T.; Hahn, F. E.; Glorius, F. *Dalton Trans.* **2012**, *41*, 13788−13790. (b) Krupski, S.; Pöttgen, R.; Schellenberg, I.; Hahn, F. E. *Dalton Trans.* **2014**, *43*, 173−181.

(19) Wang, L.; Lim, Y. S.; Li, Y.; Ganguly, R.; Kinjo, R. *Molecules* **2016**, *21*, 990−1000.

(20) (a) Akkari, A.; Byrne, J. B.; Saur, I.; Rima, G.; Gornitzka, H.; Barrau, J. *J. Organomet. Chem.* **2001**, *622*, 190−198. (b) Leung, W.-P.; So, C.-W.; Chong, K.-H.; Kan, K.-W.; Chan, H.-S.; Mak, T. C. W. *Organometallics* **2006**, *25*, 2851−2858. (c) Rupar, P. A.; Jennings, M. C.; Ragogna, P. J.; Baines, K. M. *Organometallics* **2007**, *26*, 4109−4111. (d) Yao, S.; Xiong, Y.; Driess, M. *Chem. Commun.* **2009**, 6466−6468. (e) Katir, N.; Matioszek, D.; Ladeira, S.; Escudié, J.; Castel, A. *Angew. Chem., Int. Ed.* **2011**, *50*, 5352−5355. (f) Wang, W.; Inoue, S.; Yao, S.; Driess, M. *Organometallics* **2011**, *30*, 6490−6494. (g) Siwatch, R. K.; Kundu, S.; Kumar, D.; Nagendran, S. *Organometallics* **2011**, *30*, 1998−2005. (h) Matioszek, D.; Kocsor, T.-G.; Castel, A.; Nemes, G.; Escudié, J.; Saffon, N. *Chem. Commun.* **2012**, *48*, 3629−3631. (i) Álvarez-Rodríguez, L.; Cabeza, J. A.; García-Álvarez, P.; Polo, D. *Organometallics* **2013**, *32*, 3557−3561. (j) Ochiai, T.; Franz, D.; Wu, X.-N.; Inoue, S. *Dalton Trans.* **2015**, *44*, 10952−10956. (k) Chorley, R. W.; Hitchcock, P. B.; Jolly, B. S.; Lappert, M. F.; Lawless, G. A. *J. Chem. Soc., Chem. Commun.* **1991**, 1302−1303. (l) Pu, L.; Olmstead, M. M.; Power, P. P.; Schiemenz, B. *Organometallics* **1998**, *17*, 5602−5606. (m) Ding, Y.; Roesky, H. W.; Noltemeyer, M.; Schmidt, H.-G.; Power, P. P. *Organometallics* **2001**, *20*, 1190−1194.

(21) (a) Thomas, R. M.; Keitz, B. K.; Champagne, T. M.; Grubbs, R. H. *J. Am. Chem. Soc.* **2011**, *133*, 7490−7496. (b) Jong, H.; Patrick, B. O.; Fryzuk, M. D. *Can. J. Chem.* **2008**, *86*, 803−810. (c) Jong, H.; Patrick, B. O.; Fryzuk, M. D. *Organometallics* **2011**, *30*, 2333−2341.

(22) (a) Hahn, F. E.; Naziruddin, A. R.; Hepp, A.; Pape, T. *Organometallics* **2010**, *29*, 5283−5288. (b) Naziruddin, A. R.; Hepp, A.; Pape, T.; Hahn, F. E. *Organometallics* **2011**, *30*, 5859−5866.

(23) Stender, M.; Phillips, A. D.; Power, P. P. *Inorg. Chem.* **2001**, *40*, 5314−5315.

(24) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, O.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. *Gaussian 09*, revision D.01; Gaussian, Inc.: Wallingford, CT, 2009.

DOI: 10.1021/acs.organomet.6b00925
Organometallics XXXX, XXX, XXX−XXX

(25) (a) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648−5652. (b) Stephens, P. J.; Devlin, F. J.; Chabalowski, C. F.; Frisch, M. J. *J. Phys. Chem.* **1994**, *98*, 11623−11627.
(26) (a) Hariharan, P. C.; Pople, J. A. *Theoret. Chim. Acta* **1973**, *28*, 213−222. (b) Francl, M. M.; Pietro, W. J.; Hehre, W. J.; Binkley, J. S.; Gordon, M. S.; DeFrees, D. J.; Pople, J. A. *J. Chem. Phys.* **1982**, *77*, 3654−3665. (c) Rassolov, V.; Pople, J. A.; Ratner, M.; Windus, T. L. *J. Chem. Phys.* **1998**, *109*, 1223−1229. (d) Rassolov, V.; Pople, J. A.; Ratner, M.; Redfern, P. C.; Curtiss, L. A. *J. Comput. Chem.* **2001**, *22*, 976−984.
(27) (a) Hay, P. J.; Wadt, W. R. *J. Chem. Phys.* **1985**, *82*, 270−283. (b) Wadt, W. R.; Hay, P. J. *J. Chem. Phys.* **1985**, *82*, 284−298. (c) Hay, P. J.; Wadt, W. R. *J. Chem. Phys.* **1985**, *82*, 299−310.
(28) SHELXS-97, SHELXL-97: Sheldrick, G. M. *Acta Crystallogr., Sect. A: Found. Crystallogr.* **2008**, *64*, 112−122.

DOI: 10.1021/acs.organomet.6b00925
Organometallics XXXX, XXX, XXX−XXX