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Synthesis and Structural Characterization of Base-Stabilized Oligomeric Heterovinylidenes

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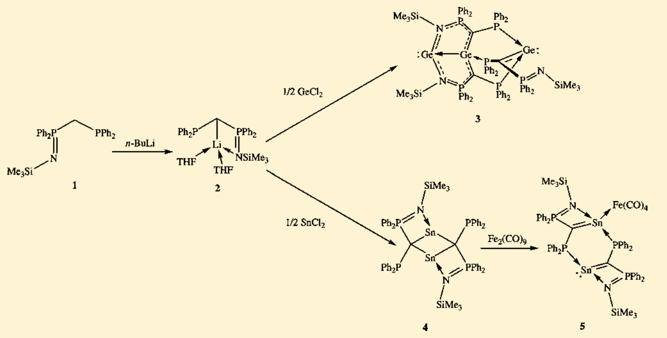
Supporting Information

ABSTRACT: Metalation of the (iminophosphoranyl)phosphine $PPh_2CH_2(PPh_2{=}NSiMe_3)$ (**1**) with an equimolar amount of *n*-BuLi afforded the monolithium salt $[Li\{CH(PPh_2)(PPh_2{=}NSiMe_3)\}(THF)_2]$ (**2**). The reaction of **2** with $GeCl_2{\cdot}1,4$-dioxane has led to the formation of a germavinylene moiety, which trimerized to form a new heterocyclic cage compound, $[\{(PPh_2{=}NSiMe_3)(PPh_2)C{=}Ge{:}\}\{(PPh_2{=}NSiMe_3)(PPh_2)C\}_2Ge{\rightarrow}Ge{:}]$ (**3**). A similar reaction of the lithium methanide complex **2** with $SnCl_2$ afforded the stannavinylidene moiety, which underwent a "head-to-tail" cycloaddition to form a stable 1,3-distannacyclobutane, **4**. A trapping reaction of **4** with diiron nonacarbonyl gave the novel iron stannavinylidene complex **5**. The solid-state structure analysis of **5** reveals that it contains two stannavinylidene moieties bonded in a Sn−P "head-to-tail" fashion, with one of the tin(II) centers coordinating to a $Fe(CO)_4$ moiety. The X-ray structures of **2**−**5** have been determined by X-ray crystallography. In addition, the dynamic behavior of **5** has been studied by means of variable-temperature ^{31}P and ^{119}Sn NMR spectroscopy.



INTRODUCTION

The chemistry of base-stabilized methanediide metal complexes has been extensively studied in the past decades since the report of a dilithium bis(iminophosphoranyl)methanediide complex by Cavell et al. and Ong and Stephan.[1−3] After that, bis(iminophosphoranes) bearing tetramethylsilane,[4] $P(X)(OR)_2$,[5] and sterically hindered aryl groups were synthesized.[6] In particular, bis(iminophosphoranyl)methane $CH_2(PPh_2{=}NSiMe_3)_2$[4] has been used as a ligand precursor for the synthesis of main-group,[7] transition-metal,[8] and lanthanide-metal[9] methanediide complexes. By varying both the electronic and steric properties of bis(phosphoranyl)methanes, Le Floch and co-workers recently reported the direct synthetic routes to mixed P−N ligands[10] of the general formula (R_2P−spacer−$PR_2{=}N{-}R$) that incorporate both a phosphino group and an iminophosphorane moiety. Cavell and co-workers have also demonstrated that the controlled Staudinger reaction[11] of diphosphines with 1 equiv of azide can lead to the formation of heterobifunctional phosphinophosphoranoimines $PPh_2CH_2(PPh_2{=}NR)$.[12] Meanwhile, the (iminophosphoranyl)phosphine $PPh_2CH_2(PPh_2{=}NSiMe_3)$ (**1**) was employed by P. Roesky in the synthesis of potassium and samarium phosphine(phosphinimino)methanide complexes.[13] The closely related hemilabile ligands of the general composition $(Ph_2P{=}E)CH_2(PPh_2{=}NSiMe_3)$ (E = S, Se) have been reported by individual research groups of So and Cadierno in the synthesis of some metal complexes.[14,15] Despite the recent advances in ligand development and the coordination chemistry of base-stabilized metal methanide complexes, stable heavier main group 14 vinylidene analogues (:M=C<) are still scarcely known. This is due to the high reactivity of the C=M: bond. In general, they are expected to undergo oligomerization more readily. Until now, there are only two examples of structurally characterized heavier group 14 metallavinylidene analogues (:M=C<). The first example of a bis(germavinylidene) was reported in 2001, which contains a weak Ge−Ge interaction (Figure 1).[7b] So and co-workers recently reported the synthesis of a tin(II) (iminophosphinoyl)(thiophosphinoyl)methanediide complex, $[(PPh_2NSiMe_3)(PPh_2S)C{=}Sn{:}]_2$ (Figure 1).[16]

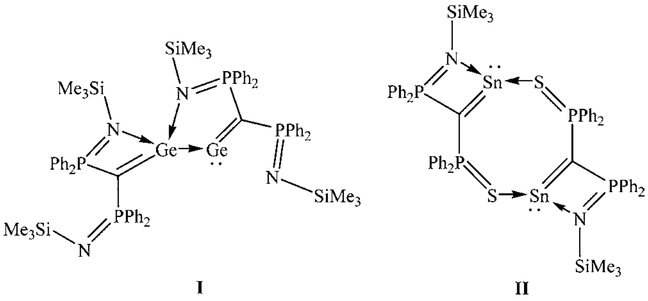


Figure 1. Existing examples of base-stabilized germavinylidene and stannavinylidene.

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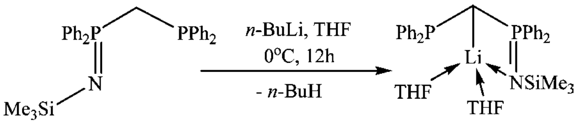
Here we report the synthesis and structural characterization of a heterocyclic cage compound, [{(PPh$_2$=NSiMe$_3$)(PPh$_2$)-C=Ge:}{(PPh$_2$=NSiMe$_3$)(PPh$_2$)C}$_2$Ge→Ge:] (**3**), which contains a phosphine-stabilized germavinylidene moiety. In addition, the synthesis of a 1,3-distannacyclobutane, [Sn{μ^2-C(PPh$_2$=NSiMe$_3$)(PPh$_2$)}]$_2$ (**4**), and its trapping reaction with Fe$_2$(CO)$_9$ to give a novel iron stannavinylidene complex, [{(PPh$_2$=NSiMe$_3$)(PPh$_2$)C=Sn:}{(PPh$_2$=NSiMe$_3$)(PPh$_2$) C=Sn→Fe(CO)$_4$}] (**5**), are described.

■ RESULTS AND DISCUSSION

Synthesis of Germavinylidene. The treatment of **1** with *n*-BuLi in tetrahydrofuran (THF) at 0 °C afforded the lithium phosphine(phosphinimino)methanide [Li{CH(PPh$_2$)(PPh$_2$=NSiMe$_3$)}(THF)$_2$] (**2**; Scheme 1).

Scheme 1. Synthesis of 2



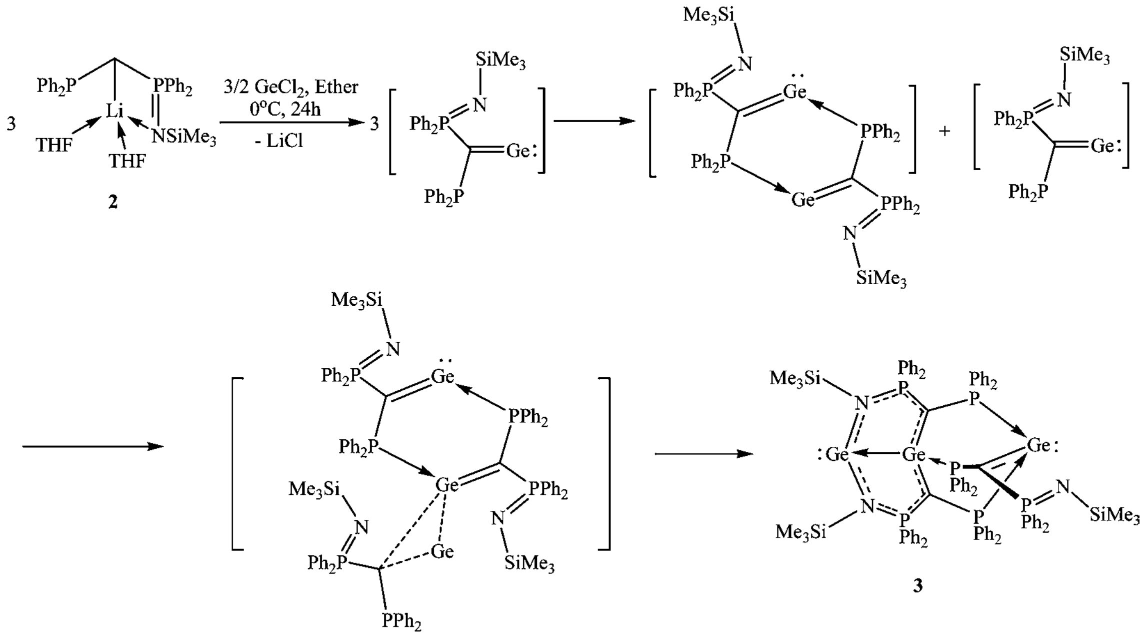
1 **2**

The reaction of **2** with 0.5 equiv of GeCl$_2$·1,4-dioxane afforded a fused tricyclic germanium(II) methanediide complex, **3** (Scheme 2). The formation of **3** is proposed to involve three molecules of unstable germavinylidene generated from reaction with a lithium salt. Two of the germavinylidenes formed a dimer via the Ge−P "head-to-tail" fashion. The other germavinylidene transferred one methanediide ligand to one of the germanium atoms, followed by rearrangement to form **3**. Delocalization of charge within the cyclic ring is based on the structural data. The lithium salt **2** acted both as a ligand-transfer reagent and as a base for dehydrochlorination. Formation of the byproduct (iminophosphoranyl)phosphine was confirmed by a ^{31}P NMR study. Similar dehydrochlorination has been reported in the synthesis of bis(germavinylidene) from the reaction of GeCl$_2$·1,4-dioxane with [Li{CH(PPh$_2$=NSiMe$_3$)$_2$}(THF)].[7b]

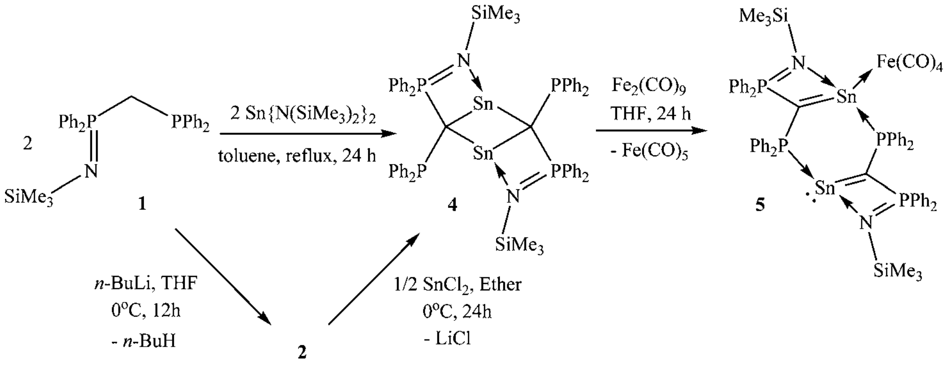
Synthesis of an Iron Stannavinylidene Complex. The reaction of **2** with SnCl$_2$ afforded a 1,3-distannacyclobutane, **4**, with a "steplike" structure (Scheme 3). A similar reaction of the lithium methanide complex [Li{CH(PPh$_2$=NSiMe$_3$)$_2$}-(THF)] with SnCl$_2$ also afforded 1,3-distannacyclobutane but with an "open-box" structure.[7b] We have reported the synthesis of a series of 1,3-distannacyclobutanes derived from different ligands and proposed that the formation of these compounds involves the "head-to-tail" cycloaddition of a highly reactive stannavinylidene intermediate.[17] However, attempts to trap the transient stannavinylidene had been unsuccessful. We have learned that several groups have used the donor−acceptor strategy for stabilization of a highly reactive species in the coordination spheres of transition metals or by formation of a stable adduct with both Lewis acid or Lewis base.[18] Inspired by the results derived from this donor−acceptor stabilization strategy, we anticipated isolating the unstable stannavinylidene by the addition of 1 equiv of Fe$_2$(CO)$_9$ with **4**. We have successfully isolated the iron stannavinylidene complex **5**. Compound **5** represents the first example of a transition-metal stannavinylidene complex. The solid-state structure of **5** reveals that each molecule of **5** contains two stannavinylidene moieties bonded in a Sn−P "head-to-tail" fashion with one of the tin(II) centers coordinating to a Fe(CO)$_4$ moiety. The other tin(II) center remains with a stereoactive lone-pair electron uncoordinated.

Spectroscopic Properties. Compounds **2**−**5** were isolated as yellow or dark-red crystalline solids, which decompose readily upon contact with air or moisture. They are soluble in THF, ether, and toluene but sparingly soluble in hexane. The ^{1}H NMR spectrum of **2** shows one doublet of doublets for the methanide proton at δ 1.39 ($^2J_{P'-H}$ = 11.6 Hz and $^2J_{P-H}$ = 5.6 Hz) due to the coupling of the methanide proton to two nonequivalent phosphorus nuclei. The ^{31}P{^{1}H} NMR spectrum displays two doublets at δ −19.3 and +25.8 ($^2J_{P-P'}$ = 129.6 Hz), which is consistent with the presence of two different

Scheme 2. Synthesis of 3



Scheme 3. Synthesis of 4 and 5



phosphorus environments. The ^1H NMR spectrum of **3** displays two singlets with an intensity ratio of 1:2 due to the three $SiMe_3$ groups within the molecule. The ^{31}P NMR spectrum of **3** shows four signals and is consistent with the structure that contains four different phosphorus environments.

The ^1H NMR spectra of **4** and **5** display signals due to the $SiMe_3$ and phenyl protons. Similar to bis(germavinylidene)[7b] and the tin(II) bis(phosphinoyl)methanediide complex,[16] the ^{13}C NMR signal for the carbenic carbon in **4** or **5** was not observed. The $^{31}P\{^1H\}$ NMR spectrum of **4** displayed two doublets at δ −13.6 and +32.2 ($^2J_{P-P'}$ = 24.3 Hz) due to two different phosphorus environments. The ^{119}Sn NMR spectrum of **4** displays a signal at δ 284.6, which is consistent with the solid-state structure. However, the ^{31}P and ^{119}Sn NMR spectra of **5** at room temperature are not consistent with the solid-state structure. There are two signals at δ 36.6 and 42.3 ($^2J_{P-P'}$ = 39.9 Hz), and one broad signal was observed at δ 2.5 in the ^{31}P NMR spectrum. In addition, the ^{119}Sn NMR spectrum showed a signal at δ 79.6 and a broad signal at δ 88.2. To get insight into the structure of **5** in solution, we have carried out a variable-temperature ^{31}P NMR experiment of **5** (Figure 2). We found that eight signals at δ −21.7, −19.4, +4.1, +6.1, +33.8, +35.2, +39.5, and +45.5 were recorded at −80 °C. The $^{31}P-^{31}P$ COSY and variable-temperature ^{119}Sn NMR spectra were also recorded. At −80 °C, the ^{119}Sn NMR spectrum of **5** showed four signals at δ 89.4, 100.7, 297.1, and 345.5. We propose that in solution compound **5** is subjected to a dynamic equilibrium that involves the breaking of the tin−phosphorus dative interactions to give monomers **6** and **7** in a reversible manner (Scheme 4). At room temperature, interconversion is at a moderate rate and so broad signals were observed in the room temperature ^{31}P and ^{119}Sn NMR spectra. At −80 °C, the exchange rate slows down and the eight signals observed in the ^{31}P NMR spectrum correspond to the eight different phosphorus environments. The four signals observed in the ^{119}Sn NMR spectrum at −80 °C are also consistent with the proposed solution-state dynamic equilibrium. It is noteworthy that the breaking of the Ge−Ge interaction in bis(germavinylidene) and the existence of monomeric germavinylidene in the solution state have been demonstrated by the trapping reactions of bis(germavinylidene).[19]

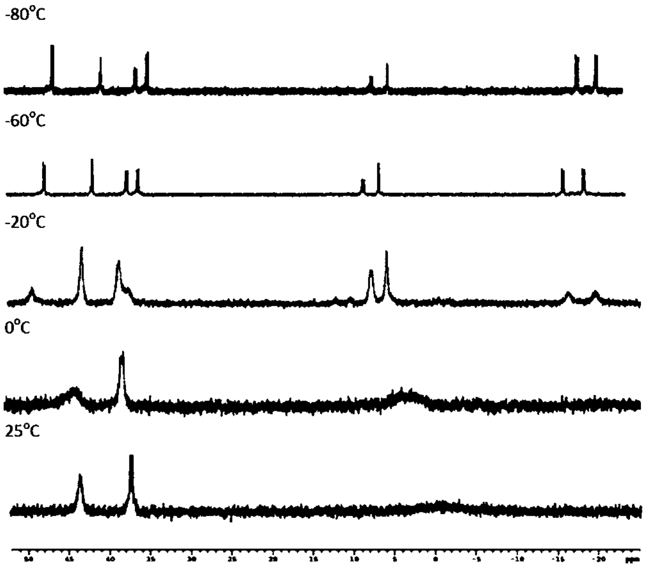
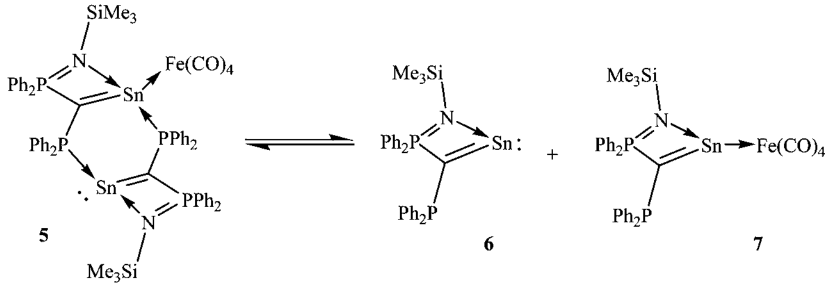


Figure 2. Variable-temperature $^{31}P\{^1H\}$ NMR spectra (THF-d_8) of **5**.

X-ray Structures. The molecular structures of **2**−**5** are shown in Figures 3−6, respectively. Selected bond distances (Å) and angles (deg) can be found in Tables 1−4 in the Supporting Information. Compound **2** is a monomeric compound containing a four-membered metallacycle Li(1)−C(1)−P(1)−N(1). The anionic $[Ph_2PCH(PPh_2{=}NSiMe_3)]^-$ ligand coordinates via the N−P−C backbone in a heteroallylic fashion onto the lithium atom. The C(1)−Li(1) distance of 2.321(1) Å is shorter than that of 2.560(8) Å in the lithium methanide complex $[Li\{CH(PPh_2{=}NSiMe_3)_2\}(THF)]$[20] and comparable to the $C-Li_{avg}$ distance of 2.386 Å in the dilithium methanediide complex $[Li_2C(PPh_2{=}NSiMe_3)_2]$.[2,3] The C(1)−P bond distances of 1.715(6) and 1.753(6) Å are comparable to those of the potassium methanide complex $[K\{CH(Ph_2P)(PPh_2{=}NSiMe_3)\}]_n$ [1.724(6) and 1.739(7) Å].[13]

The molecular structure of **3** is significantly different from that of bis(germavinylidene) (Figure 1), which comprises of two germavinylidenes $[(Ph_2P{=}NSiMe_3)_2C{=}Ge{:}]$ bonded together in a "head-to-head" manner.[7b] Compound **3** consists of a germavinylidene $[(PPh_2{=}NSiMe_3)(PPh_2)C{=}Ge{:}]$ moiety on one side of the molecule stabilized by two other phosphorus donor atoms from a germaallene moiety. The eight-membered heterocyclic ring contains two germanium atoms with a germanium(II)−germanium(II) donor−acceptor interaction. The structure of compound **3** is symmetrical; it has three different germanium environments. Ge(1) is three-coordinate, and the sum of the bond angles at the Ge(1) atom is 281.9°, which is consistent with the presence of a stereoactive lone-pair electron at the germanium(II) center. The Ge(3) atom is bonded with one methanediide carbon, C(72), and two phosphorus atoms, P(2) and P(4), from the other two ligands. The sum of the bond angles at the Ge(3)

Scheme 4. Equilibrium of 5 in the Solution State



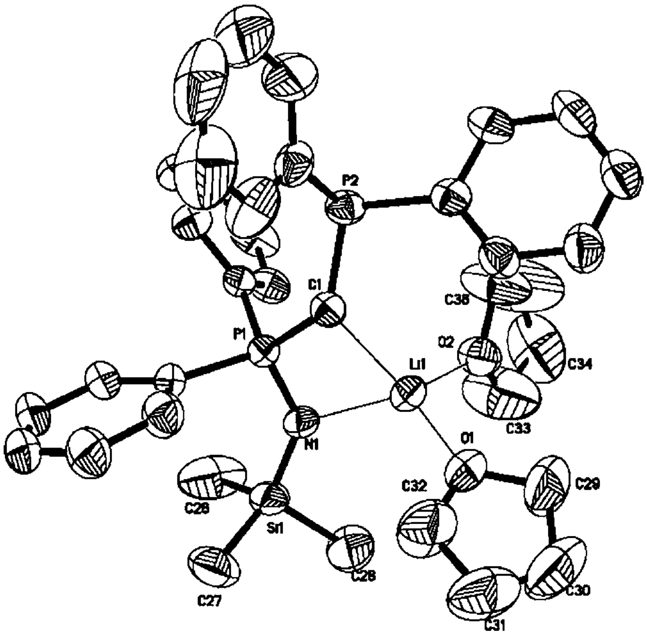


Figure 3. Molecular structure of **2**. Hydrogen atoms are omitted for clarity. 30% thermal ellipsoids are shown. Selected bond distances (Å) and angles (deg): Li(1)−C(1) = 2.321(1), Li(1)−N(1) = 2.027(1), P(1)−C(1) = 1.715(6), P(2)−C(1) = 1.753(6); P(1)−C(1)−Li(1) = 79.2(4), P(2)−C(1)−Li(1) = 123.0(4), P(1)−C(1)−P(2) = 123.1(4), P(1)−N(1)−Li(1) = 123.0(4).

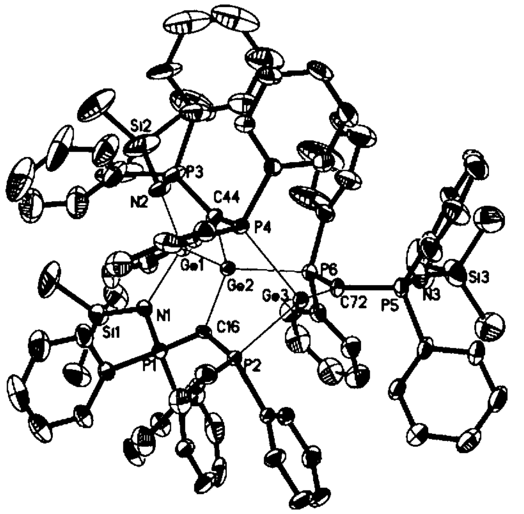


Figure 4. Molecular structure of **3**. Hydrogen atoms are omitted for clarity. 30% thermal ellipsoids are shown. Selected bond distances (Å) and angles (deg): Ge(1)−Ge(2) = 2.427(1), Ge(2)−C(44) = 1.913(5), Ge(2)−C(16) = 1.943(5), Ge(3)−C(72) = 1.975(5), Ge(2)−P(6) = 2.363(1), Ge(3)−P(2) = 2.526(1); N(1)−Ge(1)−Ge(2) = 84.7(1), N(2)−Ge(1)−Ge(2) = 85.9(1), N(2)−Ge(1)−N(1) = 111.3(2), C(16)−Ge(2)−Ge(1) = 106.0(1), C(44)−Ge(2)−Ge(1) = 104.4(2), C(16)−Ge(2)−P(6) = 109.4(1), C(72)−Ge(3)−P(4) = 102.1(2), C(72)−Ge(3)−P(2) = 100.2(2).

atom is 292.4°, which is consistent with a stereoactive lone pair at the germanium(II) center.

The Ge(2)−C(16), Ge(2)−C(44), and Ge(3)−C(72) bond distances of 1.943(5), 1.913(5), and 1.975(5) Å are comparable to the Ge−C double-bond distances of 1.908(7) and 1.905(8) Å in bis(germavinylidene)[7b] and significantly shorter than the Ge−C single-bond distances in the 1,3-digermacyclobutane 1,3-$[\mathrm{Ge}\text{-}\{\mathrm{C}(\mathrm{Pr^i{}_2P{=}NSiMe_3})(2\text{-}\mathrm{Py})\}]_2$ [2.107(3) and 2.132(3) Å][17a] and those in the germanium(II) methanediide complexes $[(\mathrm{Me_3SiN{=}PPh_2})_2\mathrm{C}\text{-}\mathrm{GeW(CO)_3(M(CO)_5)}]$ [2.046(4) Å] and $[(\mathrm{Me_3SiN{=}PPh_2})_2\{(\mathrm{cod})\mathrm{Rh}\}\mathrm{C}\text{-}\mathrm{GeCl}]$ [2.076(3) Å].[19] In addition, the Ge−C bond distances of **3** are slightly longer than the Ge−C double-bond distance in the germanium(IV) bismethanediide complex [1.882(2) Å][21] because of the lower oxidation state of germanium in **3**. A rare germanium(II)−germanium(II) donor−acceptor interaction is also observed in compound **3**. The Ge(1)−Ge(2) bond distance of 2.427(1) Å in the eight-membered heterocyclic ring is comparable to the Ge−Ge bond distance of 2.483(1) Å in bis(germavinylidene).[7b] It is shorter than the Ge−Ge single-bond distances reported for germanium(I) dimers [2.506(1)−2.709(1) Å][22] but longer than the Ge−Ge double bond in the NHC-stabilized digermanium(0) complex [2.349(1) Å][23] and much longer than the Ge−Ge triple bonds found in digermynes [2.206(1)−2.285(1) Å].[24] The Ge−$\mathrm{P_{avg}}$ distance of 2.460(1) Å in **3** is in the range of 2.314(2)−2.526(1) Å observed for some reported phosphinegermylene compounds.[25]

Compound **4** consists of two metal atoms bridged by two methanediide carbon atoms, forming a 1,3-$\mathrm{Sn_2C_2}$ four-membered ring. Each imino nitrogen atom of the ligand coordinates to the tetrahedral metal center to form a SnCPN four-membered ring. In each molecule, the two SnCPN rings together with the $\mathrm{Sn_2C_2}$ ring form a "steplike" structure, which is different from the "open-box" structure found in the 1,3-distannacyclobutane $[\mathrm{Sn}\{\mu^2\text{-}\mathrm{C}(\mathrm{PPh_2{=}NSiMe_3})_2\}]_2$.[7b] Notably, the phosphorus atom of the diphenylphosphine group remains uncoordinated. The C(1)−Sn(1) bond distance of 2.364(2) Å in **4** is comparable to the distance of 2.376 Å in the 1,3-distannacyclobutane $[\mathrm{Sn}\{\mu^2\text{-}\mathrm{C}(\mathrm{PPh_2{=}NSiMe_3})_2\}]_2$[7b] and the Sn−C single-bond distances of 2.373(4) and 2.362(2) Å reported in the bis(phosphorus-stabilized)methanediide tin(II) complexes.[26]

The molecular structure of compound **5** shows that it is unsymmetrical and comprised of two stannavinylidene $[(\mathrm{PPh_2{=}NSiMe_3})(\mathrm{PPh_2})\mathrm{C{=}Sn{:}}]$ moieties bonded together

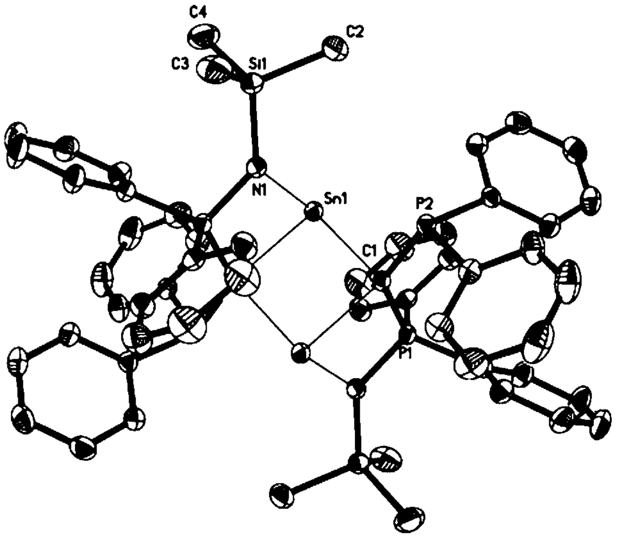


Figure 5. Molecular structure of **4**. Hydrogen atoms are omitted for clarity. 30% thermal ellipsoids are shown. Selected bond distances (Å) and angles (deg): Sn(1)−C(1) = 2.364(2), Sn(1)−N(1) = 2.247(2); C(1)#1−Sn(1)−C(1) = 87.1(1), Sn(1)#1−C(1)−Sn(1) = 93.0(1), P(1)−C(1)−Sn(1) = 107.2(1), P(2)−C(1)−Sn(1) = 101.9(1), P(1)−C(1)−P(2) = 130.4(1), N(1)#1−P(1)−C(1) = 102.2(1).

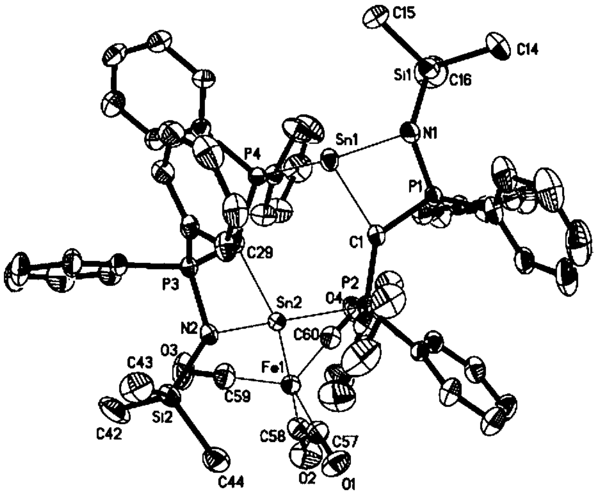


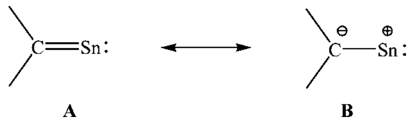
Figure 6. Molecular structure of **5**. Hydrogen atoms are omitted for clarity. 30% thermal ellipsoids are shown. Selected bond distances (Å) and angles (deg): Fe(1)−Sn(2) = 2.505(1), Sn(1)−C(1) = 2.207(5), Sn(2)−C(29) = 2.134(4), Sn(1)−N(1) = 2.252(4), Sn(2)−N(2) = 2.188(4), Sn(1)−P(4) = 2.690(1); C(29)−Sn(2)−Fe(1) = 132.4(1), Fe(1)−Sn(2)−P(3) = 138.8(3), C(29)−Sn(2)−P(2) = 103.9(1), P(2)−Sn(2)−P(3) = 108.2(1), C(1)−Sn(1)−N(1) = 70.0(2), C(1)−Sn(1)−P(4) = 91.3(1), P(3)−C(29)−P(4) = 129.6(3), P(4)−C(29)−Sn(2) = 131.3(2).

in a Sn−P "head-to-tail" manner, with one of the tin(II) centers coordinated to a Fe(CO)$_4$ moiety. In addition to the iron atom Fe(1), the tin atom Sn(2) is bonded to the methanediide carbon atom C(29), one nitrogen atom, and one phosphorus atom of each ligand. Therefore, the geometry around Sn(2) is tetrahedral. As for the Sn(1) atom, it is bonded to the methanediide carbon atom C(1), one nitrogen atom, and one phosphorus atom of each ligand. The geometry around the Sn(1) center is trigonal-pyramidal. The sum of the bond angles at the tin atom is 272.0°, which is consistent with the presence of a stereoactive lone-pair electron at the tin(II) center.

The C(1)−Sn(1) bond distance of 2.207(5) Å and the C(29)−Sn(2) bond distance of 2.134(4) Å in **5** are both significantly shorter than the Sn−C single-bond distances of 2.364(2) Å in **4** and the distance of 2.376 Å in the 1,3-distannacyclobutane [Sn{μ^2-C(PPh$_2$=NSiMe$_3$)$_2$}]$_2$.[7b] Although the C(1)−Sn(1) bond distance of 2.207(5) Å and the C(29)−Sn(2) bond distance of 2.134(4) Å in **5** are comparable to the Sn−C distances of 2.234(5) and 2.205(3) Å in the four- and three-coordinate tin(II) complexes recently reported by Jurkschat et al. and Růžička et al.,[27,28] they are significantly shorter than the Sn−C single-bond distances of 2.373(4) and 2.362(2) Å reported for the bis(phosphorus-stabilized)methanediide tin(II) complexes.[26] In addition, the Sn−C bond distances in **5** are comparable to the distance of 2.2094(9) Å for the reported Sn−C double-bond distance of the stannavinylidene derivative [(PPh$_2$NSiMe$_3$)(PPh$_2$S)C=Sn:]$_2$.[16] This demonstrates that some double-bond character exists in both of the C(1)−Sn(1) and C(29)−Sn(2) bonds. The Sn−C distances in **5** are longer than those of the stannaethene [{(Me$_3$Si)$_2$CH}$_2$Sn=C{(B*t*-Bu)$_2$C(SiMe$_3$)$_2$}] [2.025(4) Å],[29] the 6-stannapentafulvene [(Tbt)(Mes)Sn=CR$_2$] [2.016(5) Å],[30] and the 2-stannaallene [Sn{C(PPh$_2$=S)$_2$}$_2$] [2.063(2) Å][31] because of the lower oxidation state (+2) of the tin atoms in **5**.

Density functional theory calculations and natural bond orbital analysis have been carried out in a similar stannavinylidene complex, [(PPh$_2$NSiMe$_3$)(PPh$_2$S)C=Sn:]$_2$ (Figure 1). It was found that the electron densities of the σ and π bonds are mostly occupied by the methanediide carbon atom (85.3% electron density of the σ bond and 96.9% electron density of the π bond).[16] Topological analysis of the electron densities shows that the Sn−C bond is polar and covalent and can be viewed as between the resonance forms **A** and **B** (Scheme 5).

Scheme 5. Resonance Forms A and B of the Sn−C Bonds in Stannavinylidene Complexes



Meanwhile, the comparison of the Sn−C bond distances in compound **5** also supports that the Sn−C bond in **5** can be between the resonance forms **A** and **B** (Scheme 5). That the C(29)−Sn(2) bond [2.134(4) Å] in **5** is shorter than the C(1)−Sn(1) bond [2.207(5) Å] can be explained by the fact that the Sn(2) atom forms a dative bond with Fe(1) and so the electron density at Sn(2) is lowered, thereby making it more electrophilic. The resonance form of the C(29)−Sn(2) bond lies more to **A** form; hence, shortening of the Sn−C bond is observed. The Sn(1)−N(1) [2.252(4) Å] and Sn(2)−N(2) [2.188(4) Å] bonds are comparable to that of **4** [2.2469(19) Å]. The Sn(1)−P(4) [2.6899(12) Å] and Sn(2)−P(2) [2.6167(12) Å] bonds are comparable to the reported dative Sn−P distances.[32−34]

■ CONCLUSIONS

To summarize, we have prepared the lithium methanide complex **2** from the (iminophosphoranyl)phosphine **1**. Compound **2** serves as a ligand-transfer and dehydrochlorination reagent in the synthesis of a cyclic germanium(II)

Table 1. Crystallographic Data for Compounds **2**−**5**

	2	**3**	**4**	**5**
formula	$C_{36}H_{46}LiNO_2P_2Si$	$C_{84}H_{87}Ge_3N_3P_6Si_3$	$C_{56}H_{58}N_2P_4Si_2Sn_2$	$C_{60}H_{58}FeN_2O_4P_4Si_2Sn_2$
M_r	621.71	1626.43	1176.48	1344.37
color	pale yellow	yellow	yellow	red
cryst syst	triclinic	triclinic	monoclinic	monoclinic
space group	$P\bar{1}$	$P\bar{1}$	$P2_1/c$	$P2_1/n$
a (Å)	10.7296(19)	16.6973(8)	10.4080(3)	22.6265(13)
b (Å)	10.880(2)	22.7980(11)	12.8655(4)	12.3720(7)
c (Å)	16.270(3)	23.5002(12)	20.8788(7)	25.1730(15)
α (deg)	95.857(4)	86.2080(10)	90	90
β (deg)	100.286(3)	78.4490(10)	101.6420(10)	108.4570(10)
γ (deg)	96.741(3)	89.7510(10)	90	90
V (Å^3)	1841.1(6)	8745.0(7)	2738.24(15)	6684.3(7)
Z	2	4	2	4
d_{calcd} (g cm^{-3})	1.121	1.235	1.427	1.336
μ (mm^{-1})	0.180	1.217	1.110	1.129
$F(000)$	664	3360	1192	2712
cryst size (mm)	0.40 × 0.30 × 0.20	0.50 × 0.40 × 0.30	0.40 × 0.30 × 0.20	0.50 × 0.40 × 0.30
2θ range (deg)	1.28−25.00	0.89−25.25	1.87−27.97	1.90−25.25
index range	$-12 \leq h \leq 12, -12 \leq k \leq 12, -16 \leq l \leq 19$	$-20 \leq h \leq 19, -27 \leq k \leq 27, -28 \leq l \leq 28$	$-13 \leq h \leq 13, -16 \leq k \leq 15, -27 \leq l \leq 27$	$-27 \leq h \leq 26, -14 \leq k \leq 14, -30 \leq l \leq 30$
no. of rflns collected	10061	97744	34465	54315
no. of indep rflns	6450	31621	6588	12002
R1, wR2 [$I > 2(\sigma)I$]	0.0845, 0.2129	0.0608, 0.1453	0.0275, 0.0613	0.0603, 0.1609
R1, wR2 (all data)	0.2043, 0.3062	0.1097, 0.1623	0.0439, 0.0687	0.0712, 0.1721
GOF, F^2	0.989	0.899	1.023	1.042
no. of data/restraints/param	6450/0/389	31621/0/1783	6588/0/298	12002/0/676
largest diff peaks, e Å^{-3}	+0.377, −0.336	+1.895, −0.981	+0.399, −0.298	+1.434, −0.769

methanediide complex, **3**, which also comprises a rare germanium(II)−germanium(II) donor−acceptor interaction. The reaction of **2** with $SnCl_2$ has led to the formation of a 1,3-distannacyclobutane, **4**. The trapping reaction of **4** with $Fe_2(CO)_9$ afforded the first iron stannavinylidene complex, **5**, which contains two different stannavinylidene moieties, with one of the tin(II) centers coordinating to a $Fe(CO)_4$ moiety.

■ EXPERIMENTAL SECTION

General Procedures. All manipulations were carried out under an inert atmosphere of dinitrogen gas by standard Schlenk techniques. Solvents were dried over and distilled from $CaCl_2$ (hexane and CH_2Cl_2) and/or Na (Et_2O, toluene, and THF). $Ph_2PCH_2(PPh_2{=}NSiMe_3)$[12,13] and $Sn\{N(SiMe_3)_2\}_2$[35] were prepared according to literature procedures. *n*-BuLi (1.6 M solution in hexane), $GeCl_2$·1,4-dioxane, $SnCl_2$, and $Fe_2(CO)_9$ were purchased from Aldrich Chemical Co. and used without further purification. The proton-decoupled NMR spectra were recorded on Bruker 400 spectrometers in THF-d_8. The chemical shifts δ are relative to $SiMe_4$ for ^1H and $^{13}C\{^1H\}$ NMR, 85% H_3PO_4 and $SnMe_4$ for $^{31}P\{^1H\}$ NMR, and $^{119}Sn\{^1H\}$ NMR, respectively. Elemental analyses (duplicate trials) were performed by MEDAC Ltd., United Kingdom. Electronic spectra of compounds **3**−**5** were recorded on a Varian Cary 5G UV−vis spectrophotometer. General procedures of preparing samples in a drybox involved weighing of the corresponding compound (**3**, 0.017 g; **4**, 0.020 g; **5**, 0.018 g), subsequent dissolution with 6 mL of THF, and the transfer of 0.1 mL of the solution to a 1 cm cell. The solution was made up to 3 mL by adding 2.9 mL of THF.[36] The electronic spectra of **3**−**5** can be found in Figures 12−14 in the Supporting Information. For measurement of the melting points, samples were sealed in glass tubes under nitrogen, and their melting points were measured by an electrochemical melting point apparatus and were uncorrected.

Synthesis of $C_{36}H_{46}LiNO_2P_2Si$ (2). *n*-BuLi (2.50 mL, 1.6 M in hexane, 4.0 mmol) was added dropwise to a solution of $PPh_2CH_2(PPh_2{=}NSiMe_3)$ (**1**; 1.89 g, 4.01 mmol) in THF (30 mL) at 0 °C. The resultant yellow mixture was raised to ambient temperature and stirred for 12 h. Volatiles from the mixture were removed under reduced pressure, and the residue was then extracted with diethyl ether (30 mL). The mixture was then filtered and concentrated to 10 mL to give pale-yellow crystals of **2**. Yield: 1.77 g (71%). Mp: 87 °C. Anal. Calcd for $C_{36}H_{46}LiNO_2P_2Si$: C, 69.55; H, 7.46; N, 2.25. Found: C, 69.23; H, 7.47; N, 2.63. ^1H NMR (THF-d_8): δ −0.25 (s, 9H, $SiMe_3$), 1.39 (dd, 1H, P_2CH, $^2J_{P'-H}$ = 11.6 Hz, $^2J_{P'-H}$ = 5.6 Hz), 7.01−7.08 (m, 4H, Ph), 7.19−7.27 (m, 6H, Ph), 7.36−7.40 (m, 4H, Ph), 7.65−7.70 (m, 6H, Ph). $^{13}C\{^1H\}$ NMR (THF-d_8): δ 1.26 ($SiMe_3$), 20.46 (dd, PCP′, $^2J_{P-C}$ = 89.2 and 112.8 Hz), 24.13 (THF), 68.35 (THF), 123.4−136.9 (m, Ph). $^{31}P\{^1H\}$ NMR (THF-d_8): δ −19.3, 25.8 ($^2J_{P-P'}$ = 129.6 Hz).

Synthesis of $C_{84}H_{87}Ge_3N_3P_6Si_3$ (3). A solution of **2** (0.62 g, 1.00 mmol) in diethyl ether (30 mL) was added slowly to a stirring suspension of $GeCl_2$·1,4-dioxane (0.12 g, 0.52 mmol) in diethyl ether (10 mL) at 0 °C. The resultant orange suspension was warmed to room temperature and stirred for another 24 h. The volatiles were then removed under reduced pressure, and the residue was extracted with toluene (20 mL). The extract was then added with 10 mL of THF, and subsequent concentration of the extract to 4 mL of the solution afforded yellow crystals of **3**. Yield: 0.15 g (53%). Mp: 202 °C. Anal. Calcd for $C_{84}H_{87}Ge_3N_3P_6Si_3$: C, 62.02; H, 5.39; N, 2.58. Found: C, 61.80; H, 5.55; N, 3.12. ^1H NMR (THF-d_8): δ −0.53 (s, 9H, $SiMe_3$), −0.07 (s, 18H, $SiMe_3$), 6.32−6.36 (m, 4H, Ph), 6.50−6.58 (m, 10H, Ph), 6.69−6.73 (m, 8H, Ph), 6.85−7.08 (m, 14H, Ph), 7.26−7.40 (m, 20H, Ph), 8.33−8.37 (m, 4H, Ph). $^{13}C\{^1H\}$ NMR (THF-d_8): δ 3.91, 5.98 ($SiMe_3$), 127.2−132.9 (m, Ph). $^{31}P\{^1H\}$ NMR (THF-d_8): δ 3.3, 11.1, 14.1, 38.4 (m).

Synthesis of $C_{56}H_{58}N_2P_4Si_2Sn_2$ (4). A solution of **1** (0.94 g, 1.99 mmol) in toluene (30 mL) was added slowly to a stirring solution of

$Sn\{N(SiMe_3)_2\}_2$ (0.88 g, 2.00 mmol) in toluene (30 mL) at room temperature. The resultant yellow mixture was refluxed for 1 day. The mixture was filtered and then concentrated to 10 mL of the solution to give yellow crystals of **4**. Yield: 0.64 g (54%). Mp: 243 °C. Anal. Calcd for $C_{56}H_{58}N_2P_4Si_2Sn_2$: C, 57.17; H, 4.97; N, 2.38. Found: C, 56.87; H, 5.05; N, 2.71. ^{1}H NMR (THF-d_8): δ −0.25 (s, 9H, SiMe$_3$), 7.04−7.20 (m, 10H, Ph), 7.36−7.40 (m, 8H, Ph), 7.67−7.72 (m, 2H, Ph). ^{13}C{^{1}H} NMR (THF-d_8): δ 1.79 (SiMe$_3$), 126.4−134.9 (m, Ph). ^{31}P{^{1}H} NMR (THF-d_8): δ −13.6, 32.2 ($^2J_{P-P'}$ = 24.3 Hz). ^{119}Sn{^{1}H} NMR (THF-d_8): δ 284.6.

Synthesis of 4 from $SnCl_2$. A solution of **2** (0.98 g, 1.58 mmol) in diethyl ether (40 mL) was added slowly to a stirring suspension of $SnCl_2$ (0.15 g, 0.79 mmol) in diethyl ether (15 mL) at 0 °C. The resultant orange suspension was warmed to room temperature and stirred for another 24 h. The volatiles were then removed under reduced pressure, and the residue was extracted with toluene (20 mL). The extract was then filtered and concentrated to 10 mL to give yellow crystals. Yield: 0.28 g (56%).

Synthesis of $C_{60}H_{58}FeN_2O_4P_4Si_2Sn_2$ (5). A solution of **4** (1.41 g, 1.20 mmol) in THF (40 mL) was added slowly to a stirring suspension of diiron nonacarbonyl (0.44 g, 1.21 mmol) in THF (30 mL) at 0 °C. The resultant orange-red solution was warmed to room temperature and stirred for another 24 h. The volatiles were then removed under reduced pressure and extracted with toluene (20 mL). The extract was then added with 5 mL of THF and 5 mL of ether. Concentration of the extract to 8 mL of the solution afforded **5** as red crystals. Yield: 0.82 g (51%). Mp: 252 °C. Anal. Calcd for $C_{60}H_{58}FeN_2O_4P_4Si_2Sn_2$: C, 53.60; H, 4.35; N, 2.08. Found: C, 52.83; H, 4.96; N, 2.33. ^{1}H NMR (THF-d_8): δ −0.23 (s, 9H, SiMe$_3$), −0.15 (s, 9H, SiMe$_3$), 6.44−7.15 (m, 16H, Ph), 7.16−7.49 (m, 20H, Ph), 7.94−8.14 (m, 4H, Ph). ^{13}C{^{1}H} NMR (THF-d_8): δ 2.81, 2.92 (SiMe$_3$), 128.0−135.5 (m, Ph), 216.6 (CO). ^{31}P{^{1}H} NMR (THF-d_8, −80 °C): δ −21.7 (d, $^2J_{P-P'}$ = 33.5 Hz), −19.4 (d, $^2J_{P-P'}$ = 40.5 Hz), 4.1 (t, $^3J_{P-P'}$ = 8.1 Hz), 6.1 (dt, $^3J_{P-P'}$ = 6.2 Hz, $^2J_{P-P'}$ = 38.9 Hz), 34.0 (d, $^2J_{P-P'}$ = 40.5 Hz), 35.2 (dt, $^3J_{P-P'}$ = 6.2 Hz, $^2J_{P-P'}$ = 38.9 Hz), 39.5 (t, $^3J_{P-P'}$ = 8.1 Hz), 45.5 (d, $^2J_{P-P'}$ = 34.0 Hz). ^{119}Sn{^{1}H} NMR (THF-d_8, −80 °C): δ 89.4, 100.7, 297.1, 345.5.

X-ray Crystallography. Single crystals were sealed in Lindemann glass capillaries under nitrogen. X-ray data of **2**−**5** were collected on a Rigaku R-AXIS II imaging plate using graphite-monochromatized Mo Kα radiation (λ = 0.71073 Å) from a rotating-anode generator operating at 50 kV and 90 mA. Crystal data are summarized in Table 1. The structures were solved by direct phase determination using the computer program *SHELXTL-PC*[37] on a PC 486 and refined by full-matrix least squares with anisotropic thermal parameters for the non-hydrogen atoms. Hydrogen atoms were introduced in their idealized positions and included in structure factor calculations with assigned isotropic temperature factor calculations.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

X-ray crystallographic files in CIF format for the structure determinations of **2**−**5**, NMR and electronic spectra, and selected bond distances and angles. 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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