ORGANOMETALLICS

Reactivity of Pyridyl-1-azaallyl Germanium(I) Dimer: Synthesis of a Digermahydrazine Derivative and an Iron-Coordinated Germanium(I) Dimer

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Supporting Information

ABSTRACT: Reactivity of the pyridyl-1-azaallyl germanium(I) dimer LGeGeL (**2**; L = N(SiMe₃)C(Ph)C(SiMe₃)(C₅H₄N-2)) has been investigated. Treatment of germanium(I) dimer **2** with 1 equiv of azobenzene afforded the pyridyl-1-azaallyl digermahydrazine derivative [LGeNPh]₂ (**3**). The reaction of **2** with 1 and 2 equiv of diiron nonacarbonyl, Fe₂(CO)₉, afforded the novel unsymmetric germanium(I) complex [LGeGe(Fe(CO)₄)L] (**4**) and the diiron Lewis acid—base adduct [LGe(Fe(CO)₄)]₂ (**5**). The solid-state structure of **4** reveals that the two germanium(I) centers within the same molecule have different coordinating geometries. Compound **4** can also be prepared by the facile reaction of the pyridyl-1-azaallyl germanium(II) chloride LGeCl (**1**) with Collman's reagent, Na₂Fe(CO)₄.

INTRODUCTION

The chemistry of the heavier group 14 alkyne analogues (or ditetrelynes) $RE \equiv ER$ (E = Si, Ge, Sn, Pb; R = bulky terphenyl, silyl, aryl substituents) has attracted much attention in the past two decades.¹ In 2000, Power and co-workers reported the first diplumbyne analogue, RPbPbR, with a trans-bent structure.² Subsequently, they also isolated the first stable digermyne³ and distannyne.⁴ The series of alkyne analogues was completed when Sekiguchi reported the structural characterization of a stable disilyne in 2004.5 Furthermore, Jones and co-workers have reported the isolation of the first amido-digermyne, which possesses a short Ge-Ge multiple bond.¹ⁿ Recently, the chemistry of low-valent group 14 elements has extended to a series of group 14 element(I) dimers⁶ following the pioneering result reported by Jones in 2006.7 These group 14 metal(I) dimers, comprising a metal-metal single bond and a lone pair of electrons on each metal atom, can be considered as intramolecular base-stabilized examples of the doubly or triply bonded heavier group 14 alkyne analogues. The chemistry of the silicon analogue has been extensively explored by Roesky and co-workers.⁸ Furthermore, preliminary reactivity studies of the intramolecularly donor-stabilized germanium(I) dimers have been reported^{6e,g,9} in which the digermylene nature of these species is demonstrated. For example, Roesky and coworkers have communicated the reactivity of a gauche-bent germanium(I) dimer with 2 equiv of diiron nonacarbonyl to yield a unique diiron complex that employs both of the germanium(I) centers as Lewis bases.9ª Recently, So and coworkers have described the reduction chemistry of germanium-(I) dimers supported by 2,6-diiminophenyl and 2-imino-5,6methylenedioxylphenyl ligands.^{6g}



Our group has reported the synthesis of the chlorogermylene 1 (Figure 1) supported by a pyridyl-1-azaallyl ligand,¹⁰ and its



Figure 1. Pyridyl-1-azaallyl germanium(II) chloride 1.

reactivity has been explored.¹¹ Recently, we have also carried out investigations on its reduction chemistry and communicated the synthesis of the pyridyl-1-azaallyl germanium(I) dimer **2**, which adopts a *trans*-bent germanium(I) dimer recently reported by Roesky,^{9a} we intended to carry out investigations to compare the reactivity between germanium(I) dimers adopting a *trans*-bent and a *gauche*-bent geometry. In addition, the reaction of germanium(I) dimer with Fe₂(CO)₉ to give a

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novel germanium(I) complex with one iron-coordinated germanium center is also described.

RESULTS AND DISCUSSION

Synthesis of [PhNGe{N(SiMe₃)C(Ph)C(SiMe₃)($C_5H_4N_2$)]₂ (3). The reaction of germanium(I) dimer 2 with 1 equiv of azobenzene afforded compound 3 (Scheme 1). Compound 3 was formed from the cleavage of the Ge(I)–Ge(I) bond followed by the insertion of the N=N moiety of the azobenzene between the germanium(I) centers. The formal oxidation state of both germanium atoms in 3 has changed from +1 to +2. Similar reactions of a terphenyl-stabilized digermyne and an amidinate-stabilized germanium(I) dimer with azobenzene have been reported by the groups of Power¹² and Roesky,^{9a} respectively.

Synthesis of $[{N(SiMe_3)C(Ph)C(SiMe_3)(C_5H_4N-2)(Fe-(CO)_4)GeGe{N(SiMe_3)C(Ph)C(SiMe_3)(C_5H_4N-2)]}]$ (4) and $[{N(SiMe_3)C(Ph)C(SiMe_3)(C_5H_4N-2)Ge(Fe(CO)_4)]_2}$ (5). Reaction of 2 with 1 equiv of diiron nonacarbonyl afforded compound 4, which was isolated as a dark red crystalline solid. Alternatively, compound 4 can also be prepared by the reaction of chlorogermylene 1 with Collman's reagent, Na₂FeCO₄ (Scheme 1).

Upon the addition of compound 1 to $Na_2Fe(CO)_4$, compound 1 was first reduced by $Na_2Fe(CO)_4$ to give dimer 2, while the $[Fe(CO)_4]^{2-}$ ion was oxidized to $Fe(CO)_4$. A 1:1 mixture of the germanium(I) dimer 2 and a $Fe(CO)_4$ moiety was formed. The $Fe(CO)_4$ moiety is coordinated to one of the germanium(I) centers in 2, leading to the formation of the unsymmetric germanium(I) dimer 4 with different coordination numbers at the two germanium(I) centers. In compound 4, one of the germanium(I) centers coordinates to a $Fe(CO)_4$ moiety. A tin(I) dimer with two differently coordinated tin atoms (one is three-coordinated and the other is four-coordinated) was recently reported by Roesky,^{6h} while Driess has documented the synthesis of a unsymmetric digermylene supported by two different ligands.^{6d} The reaction of germanium(I) dimer **2** with $Fe_2(CO)_9$ differs from a previous reaction with azobenzene, where cleavage of the Ge(I)-Ge(I) interaction was observed.

When compound 2 was treated with 2 equiv of $Fe_2(CO)_{9}$, the corresponding Lewis acid-base adduct 5, with two $Fe(CO)_4$ moieties coordinating to the two germanium(I) atoms, was isolated as a dark red crystalline solid (Scheme 1). The elemental analysis for 5 is consistent with the proposed structure of 5. Both the ¹H and ¹³C NMR spectra and IR spectrum of 5 are consistent with the structure of compound 5. However, attempts to isolate good-quality crystals of 5 for Xray structural determination have been unsuccessful. It is noteworthy that compound 5 can also be obtained from the addition of the unsymmetric germanium(I) dimer 4 to 1 equiv of $Fe_2(CO)_{q}$. This indicates that the stereoactive lone pair on the three-coordinated germanium(I) center in 4 can function as a base to react with another $Fe(CO)_4$ moiety. The existence of compound 5 in the product mixture was confirmed by NMR and IR studies.

Spectroscopic Properties. Compounds 3–5 were isolated as orange or dark red crystalline solids which decompose readily upon contact with air or moisture. They are soluble in THF, diethyl ether, and toluene but sparingly soluble in hexane.



Figure 2. Molecular structure of $[PhNGe{N(SiMe_3)C(Ph)C(SiMe_3)(C_5H_4N-2)}]_2$ (3). Hydrogen atoms are omitted for clarity, and 30% probability thermal ellipsoids are shown. Selected bond distances (Å) and angles (deg): Ge(1)-N(1) = 2.079(3), Ge(1)-N(2) = 1.945(3), Ge(1)-N(3) = 1.953(3), Ge(2)-N(4) = 1.961(3), Ge(2)-N(5) = 2.081(3), Ge(2)-N(6) = 1.967(3), N(3)-N(4) = 1.454(4), N(1)-C(5) = 1.351(5), N(2)-C(10) = 1.403(5), N(3)-C(20) = 1.388(4); N(2)-Ge(1)-N(3) = 99.8(1), N(2)-Ge(1)-N(1) = 87.1(1), N(3)-Ge(1)-N(1) = 102.4(1), N(4)-Ge(2)-N(6) = 106.2(1), N(4)-Ge(2)-N(5) = 103.1(1), N(6)-Ge(2)-N(5) = 87.5(1), C(20)-N(3)-N(4) = 116.3(3), C(20)-N(3)-Ge(1) = 134.3(2), N(4)-N(3)-Ge(1) = 98.0(2), N(3)-N(4)-Ge(2) = 107.7(2).

The ¹H NMR spectrum of 3 displays two singlets at δ –0.32 and –0.21 ppm due to the protons in the two different SiMe₃ groups. Signals due to the pyridyl and phenyl protons are observed at δ 6.55–7.67 ppm. The ¹³C NMR spectrum of 3 displays two sharp singlets at δ 1.63 and 2.24 ppm for the two different carbons in each of the azaallyl ligands. Both the ¹H and ¹³C NMR spectra are consistent with the solid-state structure. The ¹H NMR spectrum of 5 shows two singlet signals at δ –0.05 and –0.02 ppm due to the two SiMe₃ groups within the symmetric molecule. In addition, the ¹H NMR spectrum of 4 displays four singlet signals at δ –0.20, –0.13, –0.11, and –0.06 ppm for the protons in the four different SiMe₃ groups due to the unsymmetrical nature of 4. In both spectra, signals are also observed due to the pyridyl and phenyl protons (δ 6.80–8.49 ppm for 4, δ 7.38–8.82 ppm for 5).

Both compounds have also been characterized by infrared spectroscopy. The CO stretching frequencies of 2006 (s), 1923 (s), and 1900 (s) cm⁻¹ in 4 and 2032 (s), 1987 (s), and 1912 (s) cm⁻¹ in 5 are similar to those reported for LGe[Fe(CO)₄]-Ge[Fe(CO)₄]L (2029 (m), 1974 (s), and 1920 (s) cm⁻¹; L = PhC(NBu¹)₂)^{9a} and [HC(CMeNAr)₂Ge(OH)Fe(CO)₄] (2039 (s), 1956 (s), and 1942 (s) cm⁻¹).¹³ In these compounds, the iron atoms adopt a trigonal-bipyramidal geometry while the iron-coordinated germanium atoms adopt a distorted-tetrahedral geometry.

X-ray Structures. The molecular structure of 3 is depicted in Figure 2. Selected bond distances and angles are also given in the figure caption. Both of the germanium(II) centers in compound 3 adopt a trigonal-pyramidal geometry, with the germanium atom Ge(1) bonded to the three nitrogen atoms N(1), N(2), and N(3). The Ge(1)–N(1) dative bond distance of 2.079(3) Å is slightly longer than the Ge(1)–N(2) and the Ge(1)–N(3) distances of 1.945(3) and 1.953(3) Å, respectively. Similarly, the Ge(1)–N(5) coordinate bond distance of 2.081(3) Å is slightly longer than the other two Ge–N singlebond distances of 1.961(3) and 1.967(3) Å. These distances are comparable to other dative bond distances found in the germanium(I) dimer 2 (2.057(3) and 1.955(4) Å). They are also similar to those reported for amidinate-stabilized and terphenyl-stabilized germanium(II) hydrazine derivatives $(1.905 \text{ Å} (av) \text{ for } [PhC(NBu^{t})_{2}Ge(Ph)NN(Ph)Ge (NBu^{t})_{2}CPh]_{3}^{9a}$ 1.879 Å (av) for $[(2,6-Trip_{2}C_{6}H_{3})Ge(Ph)-NN(Ph)Ge(2,6-Trip_{2}-C_{6}H_{3})])^{12}$ The N–N bond distance in compound 3 is 1.454(4) Å. The bond distance is consistent with a single N–N bond $(1.46 \text{ Å for } (H_3 \text{Si})_2 \text{NN}(\text{SiH}_3)_2)^{14}$ and agrees with the bond distances of 1.436(4) Å in [PhC-(NBu^t)₂Ge(Ph)NN(Ph)Ge(NBu^t)₂CPh]^{9a} and 1.45(3) Å in $[(2,6-Trip_2C_6H_3)Ge(Ph)NN(Ph)Ge(2,6-Trip_2C_6H_3)]$.¹² The comparison of the N-N bond distance in compound 3 with those observed in the analogous species $[PhC(NBu^{t})_{2}Ge(Ph)_{2}]$ $NN(Ph)Ge(NBu^{t})_{2}CPh$ and $[(2,6-Trip_{2}C_{6}H_{3})Ge(Ph)NN (Ph)Ge(2,6-Trip_2C_6H_3)$ is indicative of the presence of a single N–N bond in 3. In compound 3, both of the germanium atoms are three-coordinated. The sum of bonding angles $(293.1^{\circ} (av))$ at the germanium(II) centers is consistent with the presence of a stereoactive lone pair. Hence, the reaction of 2 with 1 equiv of azobenzene can be regarded as an oxidative insertion reaction with simultaneous Ge(I)-Ge(I) bond cleavage.

The molecular structure of 4 is depicted in Figure 3. Selected bond distances and angles are given in the figure caption. The Ge(2) atom, which is coordinated with a Fe(CO)₄ moiety, adopts a tetrahedral geometry with the germanium atom Ge(2) bonding to the Ge(1) atom, the Fe(1) atom, and the two nitrogen atoms N(3) and N(4). A similar coordination geometry is also observed for the amidinate-stabilized germanium(I)-iron complex LGe[Fe(CO)₄]Ge[Fe(CO)₄]L (L = PhC(NBu^t)₂).^{9a} The other Ge(1) center is threecoordinated and adopts a trigonal-pyramidal geometry. The Ge(1) atom is bonded to a Ge(2) atom and the two nitrogen atoms N(1) and N(2). The sum of bonding angles at Ge(1) is 292.7(1)°, which is consistent with the presence of a stereoactive lone pair. The Ge(1)-Ge(2) bond distance of 2.611(1) Å in 4 is within the range of Ge-Ge single-bond





N(4)-Ge(2)-N(3) = 89.4(1), N(4)-Ge(2)-Fe(1) = 119.4(1),N(3)-Ge(2)-Fe(1) = 105.5(1), N(4)-Ge(2)-Ge(1) = 106.6(1),N(3)-Ge(2)-Ge(1) = 87.8(1), C(41)-Fe(1)-Ge(2) = 86.2(1).

distances reported for other germanium(I) dimers (2.506(1)-2.709(1) Å),^{6,7} supporting the Ge–Ge single-bond character in compound 4. In comparison, it is slightly shorter than that of 2.7093(7) Å reported for Jones' amido-digermyne with a Ge-Ge single bond (LGeGeL: $L = N(SiMe_3)(Ar^*)$; $Ar^* =$ $C_6H_2Me\{C(H)Ph_2\}_2-4,2,6\}$.¹⁵ In addition, the Ge-Ge single-bond distance is slightly longer than the Ge-Ge donoracceptor bond distance of 2.427(1) Å in the phosphinestabilized heterocyclic germavinylidene complex.¹⁶ It is also longer than the Ge-Ge double bond in the NHC-stabilized digermanium(0) complex $(2.349(1) \text{ Å})^{17}$ and much longer than the Ge–Ge triple bonds found in digermynes (2.206(1) - 2.285(1) Å).^{3a,18} These further support the presence of singlebond character of the Ge-Ge interaction in compound 4. It is also noteworthy that the Ge-Ge bond of 2.611(1) Å in 4 is similar to that of 2.602(8) Å in 2, showing that the addition of a $Fe(CO)_4$ moiety to the germanium(I) center has little effect on the Ge(I)-Ge(I) bond distance. The iron atom adopts a trigonal-bipyramidal geometry: four of the coordinating sites are occupied by carbonyl groups and one by the Ge(2) atom. The Ge(2)-Fe(1) bond distance of 2.400(1) Å is similar to that of 2.340(1) Å in LGe[Fe(CO)₄]Ge[Fe(CO)₄]L (L = $PhC(NBu^{t})_{2}$).^{9a} It is also comparable to other reported examples where the $Fe(CO)_4$ moiety is attached to a germanium atom in the formal oxidation state of +2. The Ge(2)-Fe(1) bond distance of 2.400(1) Å in compound 4 is similar to that of 2.33(1) Å in [HC(CMeNAr)₂Ge(OH)Fe- $(CO)_4]^{13}$ and that of 2.348(1) Å in $[(\eta^3 - (\mu - Bu^tN)_2(SiMeNBu^t)_2)GeFe(CO)_4]^{19}$ but it is slightly longer in comparison with that of 2.29(2) Å in $[HC(CMeNAr)_2Ge (Cl)Fe(CO)_4]^{20}$ The Ge–Fe coordinate bond distance of 2.400(1) Å in compound 4 is also comparable to the Ge-Fe single-bond distance of 2.496(2) Å in the iron-germylene

complex LGeFe(η^5 -C₅H₅)(CO)₂ (L = CH{CMe(NAr)}₂, Ar = $2,6^{-i}Pr_2C_6H_3).^2$

CONCLUSIONS

In conclusion, we have synthesized the digermahydrazine derivative $[LGeNPh]_2$ (3) from the reaction of LGeGeL (2) with azobenzene. The reaction of dimer 2 with 2 equiv of diiron nonacarbonyl afforded the diiron complex $[LGe(Fe(CO)_4)]_2$ (5); whereas the reaction of 2 with 1 equiv of diiron nonacarbonyl yielded a novel unsymmetric germanium(I) dimer with two different germanium(I) centers.

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 CaCl₂ (hexane and CH₂Cl₂) and/or Na (Et₂O, toluene, and THF). The pyridyl-1-azaallyl germanium(II) chloride 1 was prepared according to the literature procedure.¹⁰ Azobenzene and diiron nonacarbonyl were purchased from Aldrich Chemical Co. and used without further purification. The NMR spectra were recorded on Brüker 400 MHz spectrometers and recorded in THF- d_8 . The chemical shifts δ are relative to SiMe₄ for ¹H and ¹³C{¹H}.

Synthesis of $[PhNGe\{N(SiMe_3)C(Ph)C(SiMe_3)(C_5H_4N-2)\}]_2$ (3). A solution of $[N(SiMe_3)C(Ph)C(SiMe_3)(C_5H_4N-2)]_2Ge_2$ (2; 0.80 g, 0.97 mmol) in THF (25 mL) was added slowly to a stirred solution of azobenzene (0.18 g, 0.99 mmol) in THF (10 mL) at 0 °C. The resultant dark green mixture was warmed to ambient temperature and stirred for 24 h. The solution was filtered, and the volatiles were removed under reduced pressure. The dark red residue was extracted with toluene. After filtration, concentration of the filtrate afforded red crystals. Yield: 0.16 g (21%). Mp: 201–204 °C. Anal. Found: C, 58.98; H, 6.61; N, 8.11. Calcd for C₅₀H₆₄Ge₂N₆Si₄: C, 59.65; H, 6.41; N, 8.35. ¹H NMR (THF- d_8): δ -0.32 (s, 9H, SiMe₃), -0.21 (s, 9H, SiMe₃), 6.55–6.61 (m, 1H, 5-py), 6.84–6.90 (m, 5H, Ph), 7.12–7.20 (m, 5H, NPh), 7.31–7.35 (m, 1H, 3-py), 7.38–7.42 (m, 1H, 4-py), 7.67 (d, 1H, 6-py, ${}^{2}J_{H-H'} = 6.3$ Hz). ${}^{13}C{}^{1}H{}$ NMR (THF- d_{8}): δ 1.63, 2.24 (SiMe₃), 118.7 (CSiMe₃), 120.3–152.6 (Ph and Py), 161.0 (NCPh).

Synthesis of [{N(SiMe₃)C(Ph)C(SiMe₃)(C₅H₄N-2)(Fe(CO)₄)- $GeGe{N(SiMe_3)C(Ph)C(SiMe_3)(C_5H_4N-2)}]$ (4). A solution of [N- $(SiMe_3)C(Ph)C(SiMe_3)(C_5H_4N-2)]_2Ge_2$ (2; 0.75 g, 0.91 mmol) in THF (20 mL) was added slowly to a stirred solution of diiron nonacarbonyl (0.33 g, 0.91 mmol) in THF (10 mL) at 0 °C. The resultant mixture was warmed to ambient temperature and stirred for 24 h. The solution was filtered, and the volatiles were removed under reduced pressure. The dark red residue was extracted with 30 mL of toluene. The solution was then filtered. Addition of 5 mL of THF followed by concentration of the filtrate afforded dark red crystals. Yield: 0.42 g (47%). Mp: 182-184 °C. Anal. Found: C, 50.11; H, 6.17; N, 6.28. Calcd for C42H54FeGe2N4O4Si4: C, 50.83; H, 5.48; N, 5.65. ¹H NMR (THF- d_8): δ -0.20 (s, 9H, SiMe₃), -0.13 (s, 9H, SiMe₃), -0.11 (s, 9H, SiMe₃), -0.11 (s, 9H, SiMe₃), -0.06 (s, 9H, SiMe₃), 6.80-7.18 (m, 2H, 5-py), 7.22-7.55 (m, 10H, Ph), 7.60-7.68 (m, 2H, 3-py), 7.71-7.92 (m, 2H, 4-py), 8.20-8.49 (m, 2H, 6-py). ¹³C{¹H} NMR (THFd₈): δ 1.55, 1.60, 1.63, 2.04 (SiMe₃), 111.0, 112.2 (CSiMe₃), 120.3-152.6 (Ph and Py), 159.0, 161.1 (NCPh), 202.5, 205.7 (CO). IR (KBr, cm⁻¹): ν (CO) 2006 (s), 1923 (s), 1900 (s).

Synthesis of 4 from 1 and Na₂Fe(CO)₄. A solution of $[{N(SiMe_3)C(Ph)C(SiMe_3)(C_5H_4N-2)}GeCl]$ (1; 0.47 g, 1.05 mmol) in THF (25 mL) was added slowly to a stirring solution of Na₂Fe(CO)₄ (0.11 g, 0.51 mmol) in THF (20 mL) at -90 °C. The resultant dark red mixture was warmed to ambient temperature and stirred for 12 h. The solution was filtered, and the volatiles were removed under reduced pressure. The red residue was extracted with 20 mL of toluene. After filtration, addition of 5 mL of THF and concentration of the filtrate afforded dark red crystals. Yield: 0.31 g (61%).

Synthesis of [{N(SiMe₃)C(Ph)C(SiMe₃)(C₅H₄N-2)(Fe(CO)₄)Ge]₂ (5). A solution of $[N(SiMe_3)C(Ph)C(SiMe_3)(C_5H_4N-2)]_2Ge_2$ (2; 0.88 g, 1.07 mmol) in THF (20 mL) was added slowly to a stirred solution of diiron nonacarbonyl (0.78 g, 2.14 mmol) in THF (20 mL) at 0 °C. The resultant mixture was warmed to ambient temperature and stirred for 24 h. The volatiles were then removed under reduced pressure. The dark red residue was extracted with 30 mL of ether. The solution was filtered, and concentration of the filtrate afforded a dark red crystalline solid. Yield: 0.06 g (48%). Mp: 195-199 °C. Anal. Found: C, 48.18; H, 4.88; N, 5.21. Calcd for C₄₆H₅₄Fe₂Ge₂N₄O₈Si₄: C, 47.62; H, 4.69; N, 4.83. ¹H NMR (THF- d_8): δ –0.05 (s, 9H, SiMe₃), -0.02 (s, 9H, SiMe₃), 7.38-7.46 (m, 5H, Ph), 7.58-7.61 (m, 1H, 5py), 7.70 (d, 1H, 3-py, ${}^{2}J_{H-H'} = 6.5$ Hz), 8.00 (t, 1H, 4-py, ${}^{2}J_{H-H'} = 6.5$ Hz), 8.82 (d, 1H, 6-py, ${}^{2}J_{H-H'} = 6.5$ Hz). ${}^{13}C{}^{1}H{}$ NMR (THF- d_{8}): δ 2.43, 3.44 (SiMe₃), 112.1 (CSiMe₃), 121.3-157.0 (Ph and Py), 161.9 (NCPh), 201.5, 203.1 (CO). IR (KBr, cm⁻¹): ν (CO) 2032 (s), 1987 (s), 1912 (s).

Synthesis of 5 from 4. A solution of $[{N(SiMe_3)C(Ph)C-(SiMe_3)(C_5H_4N-2)(Fe(CO)_4)GeGe{N(SiMe_3)C(Ph)C(SiMe_3)-(C_5H_4N-2)}]$ (4; 0.42 g, 0.42 mmol) in THF (20 mL) was added slowly to a stirred solution of diiron nonacarbonyl (0.16 g, 0.44 mmol) in THF (10 mL) at 0 °C. The resultant mixture was warmed to ambient temperature and stirred for 24 h. The volatiles were removed under reduced pressure. The dark red residue was extracted with 30 mL of ether. The solution was filtered, and concentration of the filtrate afforded a dark red crystalline solid. Yield: 0.32 g (66%).

X-ray Crystallography. Single crystals were sealed in Lindemann glass capillaries under nitrogen. X-ray data of **3** and **4** were collected on a Rigaku R-AXIS II imaging plate using graphite-monochromated Mo K α radiation ($\lambda = 0.71073$ Å) from a rotating-anode generator operating at 50 kV and 90 mA. Crystal data are summarized in Table 1 in the Supporting Information. The structures were solved by direct phase determination using the computer program SHELXTL-PC²² 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.

ASSOCIATED CONTENT

Supporting Information

CIF files and a table giving X-ray crystallographic data for the structure determinations of **3** and **4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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REFERENCES

(1) Selected reviews: (a) Bourget-Merle, L.; Lappert, M. F.; Severn, J. R. Chem. Rev. 2002, 102, 3031–3066. (b) Kühl, O. Coord. Chem. Rev. 2004, 248, 411–427. (c) Power, P. P. Organometallics 2007, 26, 4362–4372. (d) Leung, W.-P.; Kan, K.-W.; Chong, K.-H. Coord. Chem. Rev. 2007, 251, 2253–2265. (e) Nagendran, S.; Roesky, H. W. Organometallics 2008, 27, 457–492. (f) Mizuhata, Y.; Sasamori, T.; Tokitoh, N. Chem. Rev. 2009, 109, 3479–3511. (g) Power, P. P. Nature 2010, 463, 171–177. (h) Fischer, R. C.; Power, P. P. Chem. Rev. 2010, 110, 3877–3923. (i) Mandal, S. K.; Roesky, H. W. Chem. Commun. 2010, 6016–6041. (j) Asay, M.; Jones, C.; Driess, M. Chem.

Rev. 2011, 111, 354–396. (k) Lee, V. Y.; Sekiguchi, A. Inorg. Chem.
2011, 50, 12303–12314. (l) Yao, S.; Xiong, Y.; Driess, M. Organometallics 2011, 30, 1748–1767. (m) Sen, S. S.; Khan, S.; Nagendran, S.; Roesky, H. W. Acc. Chem. Res. 2012, 45, 578–587. (n) Hadlington, T. J.; Hermann, M.; Li, J.; Frenking, G.; Jones, C. Angew. Chem., Int. Ed. 2013, 52, 10199–10203.

(2) Pu, L.; Twamley, B.; Power, P. P. J. Am. Chem. Soc. 2000, 122, 3524–3525.

(3) (a) Stender, M.; Phillips, A. D.; Wright, R. J.; Power, P. P. Angew. Chem., Int. Ed. 2002, 41, 1785–1787. (b) Power, P. P. Chem. Commun. 2003, 2091–2101. (c) Pu, L. H.; Phillips, A. D.; Richards, A. F.; Stender, M.; Simons, R. S.; Olmstead, M. M.; Power, P. P. J. Am. Chem. Soc. 2003, 125, 11626–11636.

(4) Phillips, A. D.; Wright, R. J.; Olmstead, M. M.; Power, P. P. J. Am. Chem. Soc. 2002, 124, 5930–5931.

(5) Sekiguchi, A.; Kinjo, R.; Ichinohe, M. Science 2004, 305, 1755–1757.

(6) (a) Jambor, R.; Kasna, B.; Kirschner, K. N.; Schürmann, M.; Jurkschat, K. Angew. Chem., Int. Ed. 2008, 47, 1650–1653.
(b) Nagendran, S.; Sen, S. S.; Roesky, H. W.; Koley, D.; Grubmüller, H.; Pal, A.; Herbst-Irmer, R. Organometallics 2008, 27, 5459–5463. (c) Sen, S. S.; Jana, A.; Roesky, H. W.; Schulzke, C. Angew. Chem., Int. Ed. 2009, 48, 8536–8538. (d) Wang, W.; Inoue, S.; Yao, S.; Driess, M. Chem. Commun. 2009, 2661–2663. (e) Leung, W.-P.; Chiu, W.-K.; Chong, K.-H.; Mak, T. C. W. Chem. Commun. 2009, 6822–6824. (f) Jones, C.; Bonyhady, S. J.; Holzmann, N.; Frenking, G.; Stasch, A. Inorg. Chem. 2011, 50, 12315–12325. (g) Chia, S.-P.; Yeong, H.-X.; So, C.-W. Inorg. Chem. 2012, 51, 1002–1010. (h) Khan, S.; Michel, R.; Dieterich, J. M.; Mata, R. A.; Roesky, H. W.; Demers, J.-P.; Lange, A.; Stalke, D. J. Am. Chem. Soc. 2011, 133, 17889–17994. (i) Chia, S.-P.; Ganguly, R.; Li, Y.; So, C.-W. Organometallics 2012, 31, 6415–6419.

(7) Green, S. P.; Jones, C.; Junk, P. C.; Lippert, K.-A.; Stasch, A. Chem. Commun. 2006, 3978–3980.

(8) (a) Sen, S. S.; Khan, S.; Nagendran, S.; Roesky, H. W. Acc. Chem. Res. 2012, 45, 578–587. (b) Sen, S. S.; Khan, S.; Samuel, P. P.; Roesky, H. W. Chem. Sci. 2012, 3, 659–682. (c) Blom, B.; Stoelzel, M.; Driess, M. Chem. Eur. J. 2013, 19, 40–62.

(9) (a) Sen, S. S.; Kratzert, D.; Stern, D.; Roesky, H. W.; Stalke, D. Inorg. Chem. 2010, 49, 5786–5788. (b) Zhang, S.-H.; So, C.-W. Organometallics 2011, 30, 2059–2062.

(10) Leung, W.-P.; So, C.-W.; Wu, Y.-S.; Li, H.-W.; Mak, T. C. W. Eur. J. Inorg. Chem. 2005, 3, 513–521.

(11) (a) Leung, W.-P.; Chong, K.-H.; Wu, Y.-S.; So, C.-W.; Chan, H.-S.; Mak, T. C. W. *Eur. J. Inorg. Chem.* **2006**, 808–812. (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) Leung, W.-P.; Chiu, W.-K.; Mak, T. C. W. *Organometallics* **2012**, *31*, 6966–6971.

(12) Cui, C.; Olmstead, M. M.; Fettinger, J. C.; Spikes, G. H.; Power, P. P. J. Am. Chem. Soc. 2005, 127, 17530–17541.

- (13) Pineda, L. W.; Jancik, V.; Colunga-Valladares, J. F.; Roesky, H. W.; Hofmeister, A.; Magull, J. Organometallics **2006**, *25*, 2381–2383.
- (14) Glidewell, C.; Rankin, D. W. H.; Robiette, A. G.; Sheldrick, G. M. J. Chem. Soc. A **1970**, 318–320.

(15) Li, J.; Schenk, C.; Goedecke, C.; Frenking, G.; Jones, C. J. Am. Chem. Soc. 2011, 133, 18622–18625.

(16) Leung, W.-P.; Chiu, W.-K.; Mak, T. C. W. Inorg. Chem. 2013, 52, 9479–9486.

(17) Sidiropoulos, A.; Jones, C.; Stasch, A.; Klein, S.; Frenking, G. Angew. Chem., Int. Ed. 2009, 48, 9701–9704.

(18) Sugijama, Y.; Sasamori, T.; Hosoi, Y.; Furukawa, Y.; Takagi, N.; Nagase, S.; Tokitoh, N. J. Am. Chem. Soc. **2006**, *128*, 1023–1031.

(19) Saur, I.; Rima, G.; Miqueu, K.; Gornitzka, H.; Barrau, J. J. Organomet. Chem. 2003, 672, 77–85.

(20) Veith, M.; Becker, S.; Huch, V. Angew. Chem., Int. Ed. 1990, 29, 216–218.

(21) Inoue, S.; Driess, M. Organometallics 2009, 28, 5032-5035.

(22) Sheldrick, G. M. In Crystallographic Computing 3: Data Collection, Structure Determination, Proteins, and Databases; Sheldrick,

G. M., Kruger, C., Goddard, R., Eds.; Oxford University Press: New York, 1985; pp 175–189.