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Synthesis and Characterization of an Amidinate-Stabilized Bisgermylene Oxide and Sulfide

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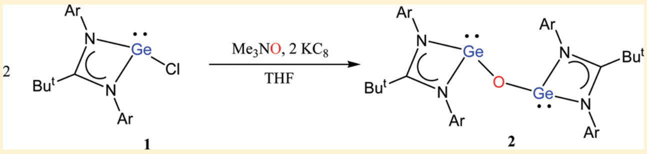
S *Supporting Information*

ABSTRACT: The synthesis and characterization of the amidinate-stabilized bisgermylene oxide and sulfide $[L^2Ge{-}E{-}GeL^2]$ (E = O (**2**), S (**3**); $L^2 = Bu^tC(NAr)_2$, Ar = 2,6-$Pr^i{}_2C_6H_3$) are described. Compound **2** was prepared by the reaction of two equivalents of $[L^2GeCl]$ (**1**) with Me_3NO and two equivalents of KC_8 in THF. It is proposed that the reaction proceeds through an $[L^2Ge^I]$ intermediate, which then reacts with Me_3NO to form **2**. Similarly, the reaction of two equivalents of **1** with elemental sulfur and two equivalents of KC_8 in THF afforded **3**. Compounds **2** and **3** have been characterized by NMR spectroscopy and X-ray crystallography.



Stable heavier group 14 dicarbene analogues of composition $R\ddot{E}{-}\ddot{E}R$ (R = supporting ligand; E = low valent Si, Ge, Sn, Pb) have attracted much attention in the past few years. These compounds comprise an $\ddot{E}{-}\ddot{E}$ single bond and a lone pair of electrons at each E atom.[1] The formal oxidation state of each E atom is +1. They can be synthesized successfully by incorporating sterically hindered substituents at the heavier group 14 elements. For example, the amidinate-stabilized disilylene and digermylene $[L\ddot{E}{-}\ddot{E}L]$ (E = Si, Ge, $L = L^1 = PhC(NBu^t)_2$; E = Ge, $L = L^2 = Bu^tC(NAr)_2$, Ar = 2,6-$Pr^i{}_2C_6H_3$),[1a,c,d] *N*-heterocyclic carbene-stabilized dichlorodisilylene $[L^3{\rightarrow}(Cl)Si{-}Si(Cl){\leftarrow}L^3]$ (L^3 = :C{N(Ar)CH}$_2$),[1e] pyridyl-1-azaallyl digermylene $[L^4Ge{-}GeL^4]$ ($L^4 = N(SiMe_3)C(Ph)C(SiMe_3)(C_5H_4N\text{-}2)$),[1b] and diaryldistannylene $[L^{Ar}Sn{-}SnL^{Ar}]$ [L^{Ar} = 2,6-$(Me_2NCH_2)_2C_6H_3$] were synthesized and structurally characterized.[1g] The reactions of stable heavier group 14 dicarbene analogues were reported.[2] Recently, Roesky et al. showed that $[L^1Si{-}SiL^1]$ reacted with N_2O in toluene to afford $[L^1Si(\mu\text{-}O){-}O{-}Si(\mu\text{-}O)L^1]_2$, which contains two four-membered disiloxane rings bridged by two oxygen atoms.[2d] The reaction appears to proceed through an insertion of $[L^1Si{-}SiL^1]$ with N_2O to form an $[L^1Si{-}O{-}SiL^1]$ intermediate. The $[L^1Si{-}O{-}SiL^1]$ intermediate undergoes an oxidation with N_2O to form $[L^1Si(O){-}O{-}Si(O)L^1]$, which then dimerizes to afford $[L^1Si(\mu\text{-}O){-}O{-}Si(\mu\text{-}O)L^1]_2$. It is noteworthy that $[L^1Si{-}O{-}SiL^1]$ was not isolated from the reaction mixture. In contrast, the reaction of $[L^1Si{-}SiL^1]$ with elemental selenium afforded the di(silaneselone) $[L^1Si(Se){-}Si(Se)L^1]$.[3] Selenium does not insert into the $Si^I{-}Si^I$ bond. Jambor et al. reported that $[L^{Ar}Sn{-}SnL^{Ar}]$ reacted with excess elemental selenium in toluene/hexane to form $[L^{Ar}Sn{-}Se{-}SnL^{Ar}]$.[2h] Similar reaction for a longer reaction time gave $[L^{Ar}Sn(Se){-}Se{-}Sn(Se)L^{Ar}]$. Leung et al. showed that the reaction of the digermylene $[L^4Ge{-}GeL^4]$ with excess elemental sulfur afforded $[L^4Ge(S){-}S{-}Ge(S)L^4]$.[1b] The reaction is proposed to proceed through an insertion of $[L^4Ge{-}GeL^4]$ with sulfur to form an $[L^4Ge{-}S{-}GeL^4]$ intermediate, which then undergoes an oxidation with elemental sulfur to form $[L^4Ge(S){-}S{-}Ge(S)L^4]$. However, $[L^4Ge{-}S{-}GeL^4]$ was not isolated from the reaction mixture. To the best of our knowledge, bisgermylene chalcogenides [RGe−E−GeR] have not been reported and structurally characterized.

Recently, we reported the synthesis and characterization of the first isolable silylsilylene $[L^1SiSi(Cl)\{(NBu^t)_2C(H)Ph\}]$.[4] It is stable at room temperature under anaerobic conditions because it benefits from electronic stabilization and steric protection by the amidinate ligand. It is anticipated that the amidinate ligand is capable of stabilizing low-valent germanium chalcogenides. Herein, we report the synthesis and characterization of an amidinate-stabilized bisgermylene oxide and sulfide $[L^2Ge{-}E{-}GeL^2]$ (E = O (**2**), S (**3**); $L^2 = Bu^tC(NAr)_2$, Ar = 2,6-$Pr^i{}_2C_6H_3$).

The novel bisgermylene oxide $[L^2Ge{-}O{-}GeL^2]$ (**2**) was synthesized by the reaction of two equivalents of $[L^2GeCl]$ (**1**) with Me_3NO and two equivalents of KC_8 in THF (Scheme 1). The reaction was stirred at room temperature for 12 h. After removal of THF *in vacuo*, the crude product was characterized by ^1H NMR spectroscopy. The spectrum shows that a mixture of **2** (major product) and the digermylene $[L^2Ge{-}GeL^2]$[1a] (minor product) was formed. The crude product was extracted with Et_2O to give compound **2** as colorless crystals. An attempt to isolate $[L^2Ge{-}GeL^2]$ by recrystallization failed. However, the reaction of $[L^2Ge{-}GeL^2]$ with one equivalent of Me_3NO in THF did not afford compound **2**, confirmed by NMR spectroscopy. The results suggest that the reaction of **1** with Me_3NO and KC_8 proceeds through the formation of a germanium(I) $[L^2Ge^I]$ intermediate. The intermediate then reacts with Me_3NO to form **2**, or it dimerizes to form $[L^2Ge\text{-}GeL^2]$. Moreover, there is no

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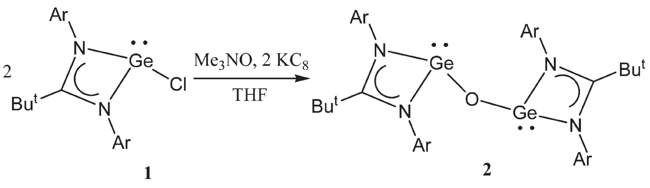
reaction between **1** and Na_2O in THF. The results suggest that the reaction of **1** with Me_3NO and KC_8 may not proceed through a substitution reaction of **1** and the K_2O intermediate. The lighter congener $[L^1Si{-}O{-}SiL^1]$ can be synthesized by the reaction of $[L^1SiH(Cl){-}O{-}SiH(Cl)L^1]$ with $LiN(SiMe_3)_2$, and the structure of $[L^1Si{-}O{-}SiL^1]$ has been characterized by X-ray crystallography.[5] The heavier congeners $[R\ddot{E}{-}O{-}\ddot{E}R]$ (E = Sn, Pb) are still unknown. Power et al. showed that the reaction of $[Ar'EEAr']$ ($Ar' = C_6H_3$-2,6-Ar_2, E = Ge, Sn) with N_2O in hexane or toluene afforded $[Ar'\ddot{E}(\mu\text{-}OH)]_2$.[6]

Similarly, the reaction of two equivalents of **1** with elemental sulfur and two equivalents of KC_8 in THF afforded $[L^2Ge{-}S{-}GeL^2]$ (**3**, Scheme 2). $[L^2Ge{-}GeL^2]$ cannot be observed in the crude product. The reaction of $[L^2Ge{-}GeL^2]$ with one equivalent of elemental sulfur in THF afforded **3** and a mixture of inseparable products, confirmed by NMR spectroscopy. However, an attempt to isolate **3** by recrystallization failed. It is proposed that the reaction of **1** with KC_8 and elemental sulfur proceeds through the $[L^2Ge^I]$ intermediate, which then reacts with elemental sulfur to form **3**. The $[L^2Ge^I]$ intermediate can also dimerize to form $[L^2Ge{-}GeL^2]$, which then reacts with elemental sulfur to form **3**. Thus, $[L^2Ge{-}GeL^2]$ was not observed in the crude product. Moreover, **1** did not react with Na_2S in THF to form **3**. The results suggest that the reaction of **1** with elemental sulfur and KC_8 may not proceed through a substitution reaction of **1** and the K_2S intermediate. The heavier congener, $[L^{Ar}Sn{-}S{-}SnL^{Ar}]$, was synthesized by the reaction of $[L^{Ar}Sn{-}SnL^{Ar}]$ with elemental sulfur.[2g]

Compounds **2** and **3** were isolated as highly air- and moisture-sensitive colorless crystalline solids that are soluble in THF and Et_2O. They are stable in solution or the solid state at room temperature in an inert atmosphere. They have been characterized by elemental analysis, spectroscopic methods, and X-ray crystallography. The ^1H and ^{13}C NMR spectra of **2** and **3** display resonances due to the amidinate ligand.

The molecular structure of **2** with an atomic numbering scheme is shown in Figure 1. Selected bond distances (Å) and angles (deg) are given in Table 1. There is a substantial disorder of the Ge—O—Ge skeleton. The amidinate ligands are bonded in a *N*,*N*′-chelate fashion to the germanium centers, which adopt a trigonal-pyramidal geometry. The sum of the bond angles at the Ge(1) and Ge(2) atoms are 269.20° and 250.93°, respectively. They are comparable with that of the three-coordinated chlorogermylene $[L^2GeCl]$ (265.29°).[1a] This geometry is consistent with a stereoactive lone pair at the germanium centers. The lone pair electrons at the germanium centers have a *trans* conformation. The Ge(1)—O(1)—Ge(2) angle (147.2(3)°) in **2** is significantly smaller than the Si—O—Si angle in $[L^1Si{-}O{-}SiL^1]$ (159.88(15)°).[5] The Ge—O bonds (1.733(4), 1.766(5) Å) are comparable with typical Ge—O single bonds (1.75−1.85 Å),[7] but they are shorter than that in $MamxGeOPr^i$ (Mamx = methylaminomethyl-*m*-xylyl, 1.856(2) Å).[8] The C—N bond lengths (C(13)—N(1): 1.330(3) Å, C(13)—N(2): 1.343(3) Å) are approximately between the C—N double and C—N(sp^2) single bond lengths. This geometry shows considerable delocalization throughout the NCN backbone of the ligand.

Scheme 1. Synthesis of 2



The molecular structure of **3** with an atomic numbering scheme is shown in Figure 2. Compound **3** crystallizes in the triclinic space group $P\bar{1}$ incorporating disordered THF molecules in the asymmetric unit. Disordered THF molecules are omitted for clarity in Figure 2. Selected bond distances (Å) and angles (deg) are given in Table 1. The amidinate ligands are bonded in a *N*,*N*′-chelate fashion to the germanium centers, which adopt a trigonal-pyramidal geometry. The sum of the bond angles at the Ge(1) and Ge(2) atoms are 256.96° and 255.41°, respectively. This geometry is consistent with a stereoactive lone pair at the germanium centers. The structure of compound **3** is different from that of **2**. The lone pair electrons at the germanium centers have a *cis* conformation. A similar structure can be found in $[L^4Ge(S){-}S{-}Ge(S)L^4]$, which is comprised of two Ge═S bonds in a *cis* conformation.[1b] It is suggested that the electronic repulsion of lone pair electrons on the Ge—E—Ge skeleton and the steric hindrance between the amidinate ligands determine the

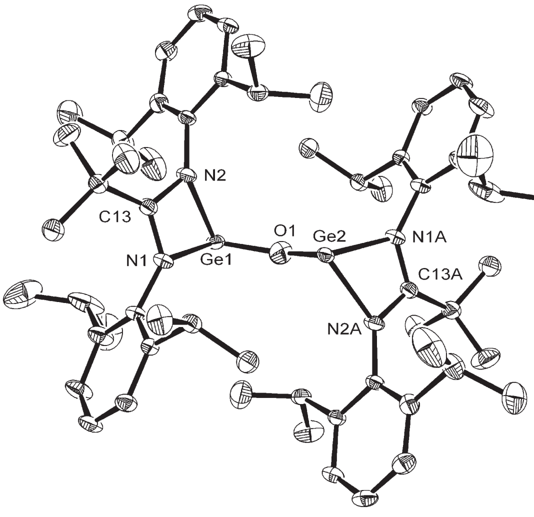


Figure 1. Molecular structure of **2** with thermal ellipsoids at the 50% probability level. Hydrogen atoms are omitted for clarity.

Scheme 2. Synthesis of 3

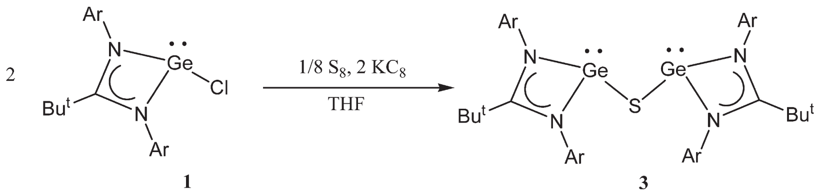


Table 1. Selected Bond Distances (Å) and Bond Angles (°) for Compounds 2 and 3

2			
Ge(1)−O(1)	1.733(4)	Ge(2)−O(1)	1.766(5)
Ge(1)−N(1)	2.026(2)	Ge(1)−N(2)	2.055(2)
N(1)−C(13)	1.330(3)	N(2)−C(13)	1.343(3)
Ge(2)−N(1A)	2.077(2)	Ge(2)−N(2A)	2.097(2)
Ge(1)−O(1)−Ge(2)	147.2(3)	N(1)−Ge(1)−O(1)	103.00(16)
N(2)−Ge(1)−O(1)	102.47(16)	N(1A)−Ge(2)−O(1)	92.80(16)
N(2A)−Ge(2)−O(1)	95.98(15)	N(1)−Ge(1)−N(2)	63.73(9)
Ge(1)−N(1)−C(13)	93.72(16)	N(1)−C(13)−N(2)	107.4(2)
C(13)−N(2)−Ge(1)	92.06(15)	N(1A)−Ge(2)−N(2A)	62.15(8)
3			
Ge(1)−S(1)	2.2512(14)	Ge(2)−S(1)	2.2626(14)
Ge(1)−N(1)	2.048(4)	Ge(1)−N(2)	2.019(4)
C(13)−N(1)	1.331(7)	C(13)−N(2)	1.338(6)
Ge(2)−N(3)	2.039(4)	Ge(2)−N(4)	2.032(4)
N(3)−C(42)	1.333(6)	N(4)−C(42)	1.343(6)
Ge(1)−S(1)−Ge(2)	101.37(6)	N(1)−Ge(1)−S(1)	100.63(13)
N(2)−Ge(1)−S(1)	92.52(13)	N(1)−Ge(1)−N(2)	63.81(16)
Ge(1)−N(1)−C(13)	93.6(3)	N(1)−C(13)−N(2)	107.3(4)
C(13)−N(2)−Ge(1)	94.7(3)	N(3)−Ge(2)−S(1)	100.24(13)
N(4)−Ge(2)−S(1)	91.22(13)	N(3)−Ge(2)−N(4)	63.95(16)
Ge(2)−N(3)−C(42)	94.0(3)	N(3)−C(42)−N(4)	107.3(4)
C(42)−N(4)−Ge(2)	94.0(3)		

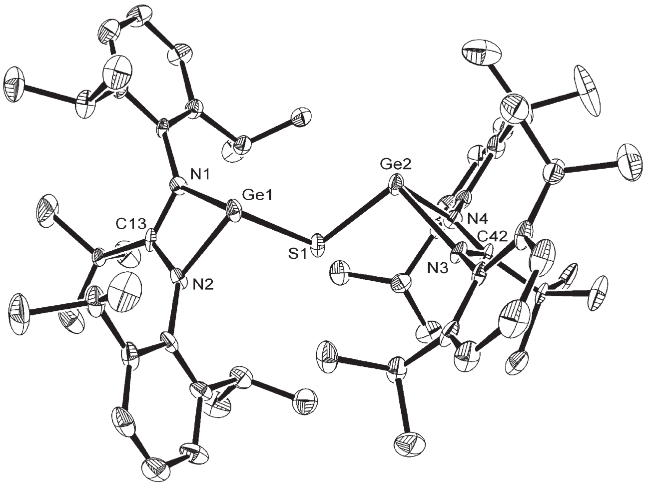


Figure 2. Molecular structure of **3** with thermal ellipsoids at the 50% probability level. Disordered THF molecules and hydrogen atoms are omitted for clarity.

conformation of the Ge−E−Ge skeleton in **2** and **3**. The Ge(1)−S(1)−Ge(2) angle (101.37(6)°) in **3** is significantly smaller than the Ge−O−Ge angle in **2**, and it is similar to that in [L^{4}Ge(S)−S−Ge(S)L^4] (101.4(1)°).[1b] The Ge−S bonds (2.2512(14) and 2.2626(14) Å) are comparable to typical Ge−S single bonds (2.21−2.29 Å)[7] and the Ge−S single bond in [L^{4}Ge(S)−S−Ge(S)L^4] (2.222(3), 2.226(3) Å).[1b] The Ge(1)···Ge(2) distance (3.492 Å) is longer than typical Ge−Ge single bonds (average 2.61 Å), which indicates there is no bonding between the germanium centers.

■ EXPERIMENTAL SECTION

All manipulations were carried out under an inert atmosphere of argon gas using standard Schlenk techniques. Solvents were dried over and distilled over Na/K alloy prior to use. **1** was prepared as described in the literature.[1a] The ^{1}H and ^{13}C NMR spectra were recorded on a JEOL ECA 400 spectrometer. The NMR spectra were recorded in C_6D_6. The chemical shifts δ are relative to SiMe$_4$ for ^{1}H and ^{13}C. Elemental analyses were performed by the Division of Chemistry and Biological Chemistry, Nanyang Technological University. Melting points were measured in sealed glass tubes and were not corrected.

Synthesis of 2. THF (15 mL) was added to a mixture of **1** (1.58 g, 2.99 mmol), Me$_3$NO (0.13 g, 1.69 mmol), and KC$_8$ (0.55 g, 4.01 mmol) at −78 °C. The reaction mixture was stirred at room temperature for 12 h. Volatiles were removed by vacuum, and the residue was extracted with Et$_2$O. The resulting green-red solution was filtered, and the filtrate was concentrated to a volume of approximately 10 mL. Storage of the solution at room temperature for 1 day afforded colorless block crystals of **2**. Yield: 0.16 g (11%). Mp: 308.9 °C. Anal. Calcd for $C_{58}H_{86}Ge_2N_4O$: C, 69.60; H, 8.67; N, 5.60. Found: C, 69.43; H, 8.52; N, 5.43. ^{1}H NMR (395.9 MHz, 21.2 °C): δ 0.91 (s, 18 H, Bu^t), 1.07 (d, $^3J_{H-H}$ = 6.3 Hz, 12 H, CH(*CH*$_3$)$_2$), 1.32 (br s, 24 H, CH(*CH*$_3$)$_2$), 1.37 (d, $^3J_{H-H}$ = 6.3 Hz, 12 H, CH(*CH*$_3$)$_2$), 3.63 (sept, $^3J_{H-H}$ = 6.3 Hz, 4 H, *CH*(CH$_3$)$_2$), 3.82 (sept, $^3J_{H-H}$ = 6.3 Hz, 4 H, *CH*(CH$_3$)$_2$), 7.04−7.10 ppm (m, 12 H, Ph). ^{13}C NMR (99.5 MHz, 21.4 °C): δ 23.4 (C*Me*$_3$), 27.6 (CH(*CH*$_3$)$_2$), 28.4 (CH(*CH*$_3$)$_2$), 29.5 (CH(*CH*$_3$)$_2$), 29.6 (CH(*CH*$_3$)$_2$), 30.6 (CH(*CH*$_3$)$_2$), 42.3 (*C*Me$_3$), 123.8, 124.3, 141.1, 144.7, 145.7 (Ph), 175.4 ppm (NCN).

Synthesis of 3. THF (15 mL) was added to a mixture of **1** (1.57 g, 2.98 mmol), S$_8$ (0.0497 g, 0.194 mmol), and KC$_8$ (0.53 g, 3.92 mmol) at −78 °C. The reaction mixture was stirred at room temperature for 12 h and filtered. The resulting red-brown solution was concentrated to a volume of approximately 10 mL. Storage of the solution at room temperature for 1 day afforded colorless block crystals of **3**·2THF. Yield: 0.25 g (15%). Mp: 312.7 °C. Anal. Calcd for **3**·2THF, $C_{66}H_{102}Ge_2N_4O_2S$: C, 68.27; H, 8.86; N, 4.83. Found: C, 67.91; H, 8.52; N, 4.57. ^{1}H NMR for **3**·2THF (395.9 MHz, 21.6 °C): δ 0.91 (s, 18 H, Bu^t), 1.19 (d, $^3J_{H-H}$ = 6.8 Hz, 12 H, CH(*CH*$_3$)$_2$), 1.28 (d, $^3J_{H-H}$ = 4.1 Hz, 12 H, CH(*CH*$_3$)$_2$), 1.29 (d, $^3J_{H-H}$ = 4.1 Hz, 12 H, CH(*CH*$_3$)$_2$), 1.39 (d, $^3J_{H-H}$ = 6.8 Hz, 12 H, CH(*CH*$_3$)$_2$), 1.42 (m, 8 H, THF), 3.57 (m, 8 H, THF), 3.63 (sept, $^3J_{H-H}$ = 6.8 Hz, 4 H, *CH*(CH$_3$)$_2$), 4.03 (sept, $^3J_{H-H}$ = 6.8 Hz, 4 H, *CH*(CH$_3$)$_2$), 7.00−7.01 (d, 1 H, Ph), 7.02−7.03 (d, 2 H, Ph), 7.07−7.11 (t, 4 H, Ph), 7.12−7.13 (d, 3 H, Ph), 7.14−7.15 (d, 2 H, Ph). ^{13}C NMR for **3**·2THF (99.5 MHz, 21.7 °C): δ 23.0 (CH(*CH*$_3$)$_2$), 23.7 (CH(*CH*$_3$)$_2$), 26.2 (THF), 28.5 (CH(*CH*$_3$)$_2$), 28.6 (CH(*CH*$_3$)$_2$), 28.7 (CH(*CH*$_3$)$_2$), 29.4 (C*Me*$_3$), 29.6 (CH(*CH*$_3$)$_2$), 42.4 (*C*Me$_3$), 68.2 (THF), 123.7, 124.6, 128.2, 140.1, 145.1, 146.4 (Ph), 172.4 ppm (NCN).

X-ray Data Collection and Structural Refinement. Intensity data for compounds **2** and **3** were collected using a Bruker APEX II diffractometer. The crystals of **2** and **3**·2THF were measured at 103(2) K. The structures were solved by direct phase determination (SHELXS-97) and refined for all data by full-matrix least-squares methods on F^2.[9] All non-hydrogen atoms were subjected to anisotropic refinement. The hydrogen atoms were generated geometrically and allowed to ride on their respective parents atoms; they were assigned appropriate isotopic thermal parameters and included in the structure-factor calculations. Selected X-ray crystallographic data of **2** and **3**·2THF are summarized in Table 2. The largest diffraction peak and hole values for compound **3**·2THF are high because of the disordered THF molecules in the

Table 2. Crystallographic Data for Compounds **2** and **3**·2THF

	2	**3**·2THF
formula	$C_{58}H_{86}Ge_2N_4O$	$C_{66}H_{102}Ge_2N_4O_2S$
M	1000.49	1160.76
color	colorless	colorless
cryst syst	monoclinic	triclinic
space group	$P2(1)/c$	$P\bar{1}$
a/Å	12.1248(7)	13.4937(15)
b/Å	19.2482(12)	13.5639(10)
c/Å	13.3429(6)	19.802(2)
α/deg	90	98.213(5)
β/deg	119.477(4)	100.902(5)
γ/deg	90	109.631(3)
V/Å^3	2710.9(3)	3267.6(6)
Z	2	2
d_{calcd}/g cm^{-3}	1.226	1.180
μ/mm^{-1}	1.150	0.995
$F(000)$	1068	1244
cryst size/mm	0.40 × 0.04 × 0.04	0.40 × 0.40 × 0.10
index range	$-17 \leq h \leq 9$	$-15 \leq h \leq 17$
	$-27 \leq k \leq 27$	$-17 \leq k \leq 16$
	$-15 \leq l \leq 19$	$-14 \leq l \leq 25$
no. of rflns collected	41 399	14 916
R_1, wR_2 ($I > 2(\sigma)I$)	0.0589, 0.1446	0.0885, 0.2153
R_1, wR_2 (all data)	0.1193, 0.1844	0.1469, 0.2387
goodness of fit, F^2	1.061	1.076
no. of data/restraints/params	8312/0/318	14 916/274/783
largest diff peak, hole/e Å^{-3}	0.709, −0.777	2.199, −1.713

asymmetric unit. The large $U_{eq}(\max)/U_{eq}(\min)$ ratio for compound **3**·2THF is due to the Pr^i groups, which usually show large atomic displacement parameters.

ASSOCIATED CONTENT

Supporting Information. CIF files giving X-ray data for **2** and **3**·2THF. This material is available free of charge via the Internet at http://pubs.acs.org.

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REFERENCES

(1) (a) Green, S. P.; Jones, C.; Junk, P. C.; Lippert, K.-A.; Stasch, A. *Chem. Commun.* **2006**, 3978. (b) Leung, W.-P.; Chiu, W.-K.; Chong, K.-H.; Mak, T. C. W. *Chem. Commun.* **2009**, 6822. (c) Nagendran, S.; Sen, S. S.; Roesky, H. W.; Koley, D.; Grubmüller, H.; Pal, A.; Herbst-Irmer, R. *Organometallics* **2008**, *27*, 5459. (d) Sen, S. S.; Jana, A.; Roesky, H. W.; Schulzke, C. *Angew. Chem., Int. Ed.* **2009**, *48*, 8536. (e) Wang, Y.; Xie, Y.; Wei, P.; King, R. B.; Schaefer, H. F., III; Schleyer, P. v. R.; Robinson, G. H. *Science* **2008**, *321*, 1069. (f) Fischer, R. C.; Pu, L.; Fettinger, J. C.; Brynda, M. A.; Power, P. P. *J. Am. Chem. Soc.* **2006**, *128*, 11366. (g) Jambor, R.; Kašná, B.; Kirschner, K. N.; Schürmann, M.; Jurkschat, K. *Angew. Chem., Int. Ed.* **2008**, *47*, 1650. (h) Pu, L.; Twamley, B.; Power, P. P. *J. Am. Chem. Soc.* **2000**, *122*, 3524. (i) Wang, W.; Inoue, S.; Yao, S.; Driess, M. *Chem. Commun.* **2009**, 2661.

(2) (a) Yeong, H.-X.; Lau, K.-C.; Xi, H.-W.; Lim, K. H.; So, C.-W. *Inorg. Chem.* **2010**, *49*, 371. (b) Yeong, H.-X.; Xi, H.-W.; Lim, K. H.; So, C.-W. *Chem.—Eur. J.* **2010**, *16*, 12956. (c) Sen, S. S.; Roesky, H. W.; Meindl, K.; Stern, D.; Henn, J.; Stückl, A. C.; Stalke, D. *Chem. Commun.* **2010**, 5873. (d) Sen, S. S.; Tavčar, G.; Roesky, H. W.; Kratzert, D.; Hey, J.; Stalke, D. *Organometallics* **2010**, *29*, 2343. (e) Tavčar, G.; Sen, S. S.; Roesky, H. W.; Hey, J.; Kratzert, D.; Stalke, D. *Organometallics* **2010**, *29*, 3930. (f) Sen, S. S.; Kratzert, D.; Stern, D.; Roesky, H. W.; Stalke, D. *Inorg. Chem.* **2010**, *49*, 5786. (g) Bouška, M.; Dostál, L.; Růžička, A.; Beneš, L.; Jambor, R. *Chem.—Eur. J.* **2011**, *17*, 450. (h) Bouška, M.; Dostál, L.; de Proft, F.; Růžička, A.; Lyčka, A.; Jambor, R. *Chem.—Eur. J.* **2011**, *17*, 455.

(3) Zhang, S.-H.; Yeong, H.-X.; So, C.-W. *Chem.—Eur. J.* **2011**, *17*, 3490.

(4) Zhang, S.-H.; Yeong, H.-X.; Xi, H.-W.; Lim, K. H.; So, C.-W. *Chem.—Eur. J.* **2010**, *16*, 10250.

(5) Wang, W.; Inoue, S.; Yao, S.; Driess, M. *J. Am. Chem. Soc.* **2010**, *132*, 15890.

(6) Spikes, G. H.; Peng, Y.; Fettinger, J. C.; Steiner, J.; Power, P. P. *Chem. Commun.* **2005**, 6041.

(7) Baines, K. M; Stibbs, W. G. *Coord. Chem. Rev.* **1995**, *145*, 157.

(8) Jutzi, P.; Keitemeyer, S.; Neumann, B.; Stammler, H.-G. *Organometallics* **1999**, *18*, 4778.

(9) Sheldrick, G. M. *SHELXL-97*; Universität Göttingen: Göttingen, Germany, 1997.