

Bis(amidinato)germylenerhodium Complexes: Synthesis, Structure, and Density Functional Theory Calculations

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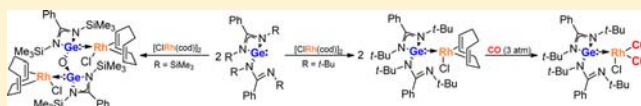
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S Supporting Information

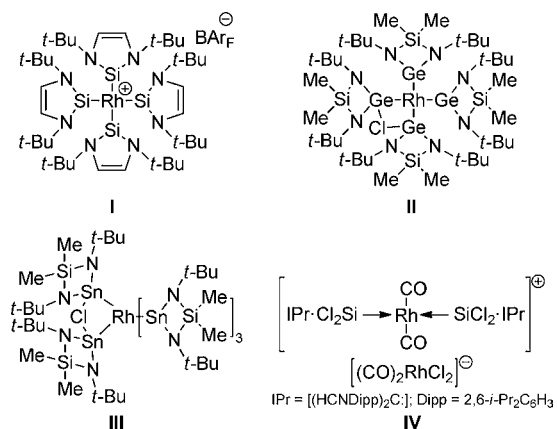
ABSTRACT: The first monogermylenerhodium complexes stabilized by bulky amidinato ligands on the divalent germanium center have been synthesized and characterized by NMR spectroscopy and X-ray crystallography. Their stability strongly depends on the steric hindrance of the amidinato ligand. With trimethylsilyl groups on the nitrogen atoms of the amidinato ligand, only the germylene oxide rhodium complex could be obtained; by contrast, with *t*-Bu groups, the germylenerhodium complex was isolated. In both cases, the formation of amidinorhodium complexes was observed. The donating ability of the germylene ligand has been assessed from the CO stretching frequency of the corresponding dicarbonylrhodium complex and was confirmed by density functional theory calculations.



INTRODUCTION

The investigation of the transition-metal chemistry of the heavier analogues of carbenes, particularly the group 14 diaminomethylenes (Si, Ge, Sn, and Pb), has attracted considerable interest¹ since the first isolation of germylenes and stannylenes by Lappert and co-workers.² The ability of these compounds to coordinate to transition metals is due to the presence of a stereochemically active lone pair of electrons, allowing the formation of a coordinative donor bond. However, despite their early discovery, the use of these aminometalylenes as σ -donor ligands to transition metals^{1,3} is less developed than that of the N-heterocyclic carbenes (NHCs).⁴ In (NHC)-M derivatives, one of the most used transition metals (M) is rhodium because of multiple applications of its complexes in catalytic processes.⁵ The activity of the latter is highly dependent on the σ -donor ability of the carbenic unit L, which can be easily determined from LRhCl(CO)₂ by IR experiments.⁶ To date, the replacement of the carbene by one of its heavier analogues (silylene, germylene, or stannylene) has not been reported, and it would be interesting to prepare such complexes and to evaluate their σ -donor character using the same method. However, there are few examples of rhodium complexes (Chart 1) containing two or four aminometalylenes. In the silicon series, cationic tetrasilylenerhodium(I) complexes (I) have been prepared using various NHSi and [Rh(cod)]₂-BAR_F {cod = 1,5-cyclooctadiene; BAR_F = tetrakis[3,5-bis-(trifluoromethyl)phenyl]borate}.⁷ The formation of mono-nuclear complexes II and III has also been reported using bis(amino)germylenes⁸ and -stannylenes.⁹ More recently, the bis(silylene)rhodium complex IV was isolated and structurally

Chart 1. Metallylenerhodium Complexes



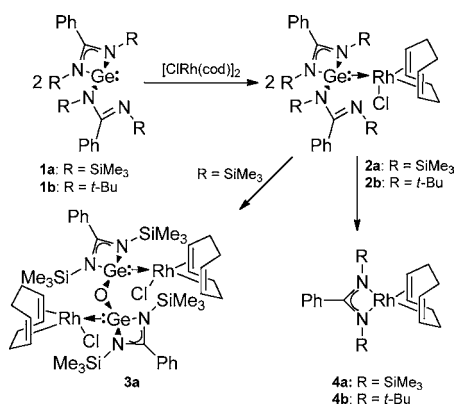
characterized.¹⁰ In our part, we showed that the chloroamidinatogermanium(II) compound {Me₃SiNC(Ph)-NSiMe₃}GeCl easily coordinated to transition-metal moieties such as W(CO)₄ or Mo(CO)₄.¹¹ This prompted us to investigate the reactivity of amidinogermylenes toward [RhCl(cod)]₂. In this paper, we describe the straightforward synthesis of the first monogermylenerhodium complexes, their structural characterization, and density functional theory (DFT) calculations, allowing us to gain further insight into their bonding.

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RESULTS AND DISCUSSION

Attempted reaction of the amidinato(chloro)germylene $\{\text{Me}_3\text{SiNC}(\text{Ph})\text{NSiMe}_3\}\text{GeCl}$ with $[\text{RhCl}(\text{cod})]_2$ failed; only a mixture of unidentified products was obtained, and the expected germylene complex could not be evidenced. By contrast, when using the bis(amidinato)germylene $\{\text{Me}_3\text{SiNC}(\text{Ph})\text{NSiMe}_3\}_2\text{Ge}$ (**1a**),¹¹ a rapid reaction takes place, leading to a mixture of the bis(rhodium germylene) oxide **3a** and the amidinatorhodium complex **4a** (Scheme 1). The formation of

Scheme 1. Synthesis of Compounds 2–4^a

^aCompound **2a** could not be isolated.

3a can only be explained by the preliminary formation of the germylenerhodium complex $\{\text{Me}_3\text{SiNC}(\text{Ph})\text{NSiMe}_3\}_2\text{GeRhCl}(\text{cod})$ (**2a**), which is very sensitive and further reacts with traces of moisture in solution.

Because it is well-known that stabilization of the amidinato group 14 low-valent species is generally governed by the nature of the substituents on the nitrogen atoms of the ligand, we tested the bis(amidinato)germylene **1b**¹² having a *t*-Bu group on the nitrogen atoms instead of a trimethylsilyl group with the view to obtain stable and isolable monogermylenerhodium complexes. Indeed, the addition of compound **1b** to $[\text{RhCl}(\text{cod})]_2$ at -78°C in diethyl ether led to the sole formation of the expected germylenerhodium complex **2b**, which could be isolated as air- and moisture-sensitive orange crystals in 49% yield (Scheme 1).

Complex **2b** was stable in the solid state under an inert atmosphere but slowly decomposed in solution, leading to the amidinatorhodium complex **4b**. Both compounds **4a** and **4b** correspond to the transfer of the amidinato ligand to the rhodium center. Such a transfer has been previously observed in the reaction of bis(germavinylidene) $[(\text{Me}_3\text{SiN}=\text{PPh}_2)_2\text{C}=\text{Ge}=\text{Ge}=\text{C}(\text{PPh}_2=\text{NSiMe}_3)_2]$ with a carbonylmolybdenum complex.¹³ Derivatives **4a** and **4b** could be easily prepared in 75–78% yield by reacting the corresponding lithium amidinate salts^{1c,14} with $[\text{RhCl}(\text{cod})]_2$ (Scheme 2). The coordination of amidinates toward metals from all blocks of the periodic table has been extensively examined,¹⁵ but despite this, there are few examples of structurally characterized rhodium(I) complexes incorporating an *N,N'*-chelating amidinato ligand.¹⁶

Single crystals of **2b** and **3a** suitable for X-ray diffraction analyses were grown in diethyl ether and pentane, respectively. **2b** crystallizes in the triclinic space group $P\bar{1}$ and complex **3a** in the monoclinic space group $P2_1/n$ (Figures 1 and 2).¹⁷ In both structures, the coordination sphere is square-planar at the rhodium(I) center. The rhodium–olefin bond lengths

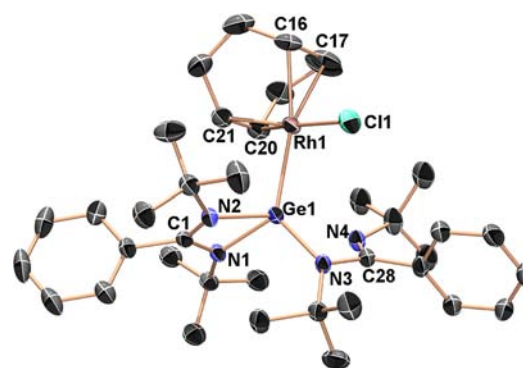
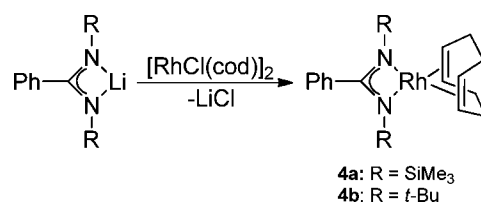
Scheme 2. Synthesis of Amidinatorhodium Complexes **4a** and **4b**

Figure 1. Molecular structure of compound **2b** in the solid state (ellipsoids set at 50% probability). For clarity, hydrogen atoms, the crystallization solvent (diethyl ether), and disorder on the two *t*-Bu groups of *N4* and *N2* atoms are omitted. Selected bond distances [Å] and bond angles [deg]: Ge1–N1 1.991(2), Ge1–N2 2.043(2), Ge1–N3 1.898(2), Ge1...N4 2.568(2), N1–C1 1.335(3), N2–C1 1.320(3), Ge1–Rh1 2.445(1), Cl1–Rh1 2.355(1), Rh1–C16 2.188(2), Rh1–C17 2.171(2), Rh1–C20 2.123(2), Rh1–C21 2.108(2); N1–Ge1–N2 65.12(7), N1–Ge1–Rh1 121.80(5), N2–Ge1–Rh1 106.75(5), N3–Ge1–Rh1 127.58(5), Cl1–Rh1–Ge1 86.934(17).

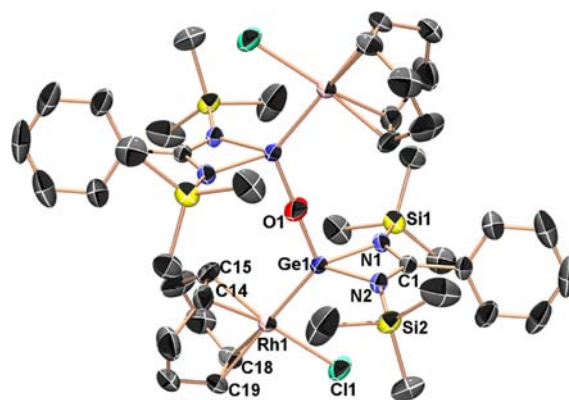


Figure 2. Molecular structure of compound **3a** in the solid state (ellipsoids set at 50% probability). For clarity, hydrogen atoms are omitted. Selected bond distances [Å] and bond angles [deg]: Ge1–N1 1.971(3), Ge1–N2 1.979(3), O1–Ge1 1.734(1), Rh1–Ge1 2.351(1), N1–C1 1.330(4), N2–C1 1.328(4), Rh1–Cl1 2.357(1), Rh1–C14 2.099(4), Rh1–C15 2.107(4), Rh1–C18 2.200(4), Rh1–C19 2.219(4); N1–Ge1–N2 68.02(11), N1–Ge1–Rh1 121.71(8), N2–Ge1–Rh1 124.23(8), O1–Ge1–N1 102.13(8), O1–Ge1–N2 103.80(8), O1–Ge1–Rh1 123.154(18), N1–C1–N2 112.4(3). Symmetry code: (i) $-x, -y, -z$.

[2.188(2), 2.171(2) and 2.108(2), 2.123(2) Å for **2b**; 2.099(4), 2.107(4) and 2.200(4), 2.219(4) Å for **3a**] are in the normal range as in analogous rhodium complexes.^{4i,18} In the cyclic amidinato moiety, the N–C bond distances [1.320(3) and 1.335(3) Å in **2b** and 1.328(4) and 1.330(4)

in **3a**] are similar and between the expected ones for single and double bonds, in agreement with a significant degree of π -electron delocalization along the N–C–N moiety.^{11,16} The germanium atoms adopt a tetrahedral arrangement in both cases; the most remarkable difference between these two structures probably lies in their torsion angles N–Ge–Rh–Cl. The amidinato ring is almost perpendicular to the coordination plane in **3a** (89.28°), while the torsion angle is smaller (79.67°) in **2b**. These values remain in the range of those often observed in NHC rhodium complexes.^{41,18} The Ge–Rh bond distance [$2.445(1)$ Å] in **2b** is slightly longer than that in **3a** [$2.351(1)$ Å] and than those observed in the tetragermylenerhodium complex [$2.3366(9)$ and $2.3368(7)$ Å]⁸ but shorter than the value reported for the Ge–Rh covalent bond in $\text{Ph}_3\text{GeRh}(\text{CO})_4$ (**6**) [$2.5061(4)$ Å].¹⁹ The Ge–O bond [$1.734(1)$ Å] is comparable to those found in the bis(amidinato)germylene oxide [$[\text{Bu}^t\text{C}(\text{NAr})_2\text{Ge}]_2\text{O}$ [$1.733(4)$ and $1.766(5)$ Å]²⁰ and in the lower range of Ge–O single-bond lengths (1.75 – 1.85 Å).²¹ The value of the Ge–O–Ge bond angle is exactly 180° because of the presence of an inversion center located on the oxygen atom.

The X-ray crystal structures of the two amidinatorhodium(**I**) **4a** (Figure 3) and **4b** (Figure 4) are similar to those described

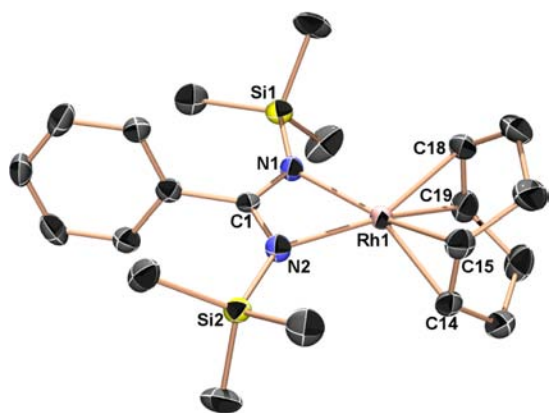


Figure 3. Molecular structure of compound **4a** in the solid state (ellipsoids set at 50% probability). For clarity, only one of the two independent molecules of the asymmetric unit is shown and hydrogen atoms are omitted. Selected bond distances [Å] and bond angles [deg]: N1–C1 1.341(5), N2–C1 1.318(4), Rh1–N1 2.110(3), Rh1–N2 2.108(3), Rh1–C14 2.101(3), Rh1–C15 2.136(4), Rh1–C18 2.118(4), Rh1–C19 2.130(4); N1–C1–N2 114.4(3), N1–Rh1–N2 63.98(11).

for amidinato-^{16a} and guanidinatorhodium^{16b} complexes. The asymmetric unit of **4a** contains two chemically identical but crystallographically different molecules. In each compound, the amidinato ligand is bonded in a $\text{N,N}'$ -chelate fashion to the rhodium atom, which adopts a distorted square-planar geometry with Rh–N distances close to those previously observed. The C–N bond distances [$1.318(4)$, $1.341(5)$ and $1.323(4)$, $1.325(4)$ Å in **4a** and $1.336(2)$ Å, identical because of a mirror in **4b**] are in agreement with a significant degree of delocalization on the NCN fragment.

In order to gain more insight into the σ -donor character of such germylenes, the rhodium complex derivative **2b** was converted into the corresponding dicarbonyl compound **5** with carbon monoxide (CO; 3 atm) in tetrahydrofuran (THF) at -80°C (Scheme 3). The ^1H NMR spectrum showed the complete replacement of cod by CO in less than 10 min.

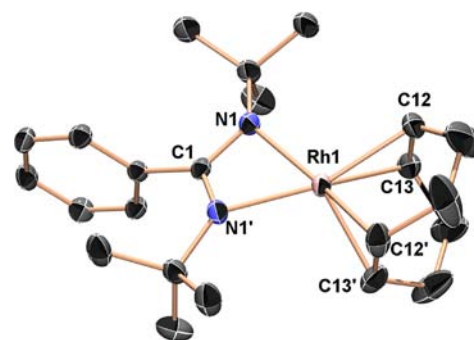
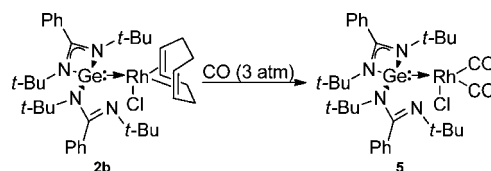


Figure 4. Molecular structure of compound **4b** in the solid state (ellipsoids set at 50% probability). For clarity, hydrogen atoms are omitted. Selected bond distances [Å] and bond angles [deg]: N1–C1 1.336(2), Rh1–N1 2.103(2), Rh1–C12 2.138(2), Rh1–C13 2.118(2), C12–C13 1.391(3); N1–Rh1–N1' 63.14(9).

Scheme 3. Synthesis of the Germylenedicarbonylrhodium(**I**) Complex **5**



Nonequivalent CO carbon atoms were observed in the ^{13}C NMR spectrum at 185.55 ppm ($^1J_{\text{C-Rh}} = 62.4$ Hz) and 188.50 ppm ($^1J_{\text{C-Rh}} = 72.1$ Hz). Complexes of the general formula $[\text{LRh}(\text{CO})_2\text{Cl}]$ ($\text{L} = 2e^-$ donor) are often used to gauge the relative electron-donating ability by comparing the values of the $\nu(\text{CO})$ stretching frequencies.⁴¹ The IR spectroscopy of complex **5** showed two CO vibrations of similar intensities (1971 and 2058 cm^{-1}) with a low average CO stretching frequency [$\nu_{\text{AV}}(\text{CO}) = 2015\text{ cm}^{-1}$]. Using the average $\nu_{\text{AV}}(\text{CO})$ frequencies of *cis*- $[\text{LRh}(\text{CO})_2\text{Cl}]$, Bertrand et al.²² reported that the donor strength of the carbenic ligands follows the order cyclic carbodiphosphoranes (2001 cm^{-1}) > (amino)-(ylidic) carbenes (2009 – 2017 cm^{-1}) > NHCs (2039 – 2049 cm^{-1}).⁶ Compared with these values, the germylene **1b** presents a strong electron-donor character probably because of the intramolecular coordination of the nitrogen atom. All attempts to isolate this complex led to its fast decomposition.²³

DFT calculations were performed with compounds **2b**, **5**, and **6**¹⁹ at the B3LYP/SDD (Rh) and 6-31G** (other atoms) levels coupled with natural bond orbital (NBO) calculations. The optimized geometries nicely match those determined by X-ray studies in particular for the Ge–Rh bond length in **2b** (2.494 Å). These calculations show a short Ge–Rh distance involving a strong donor–acceptor interaction. A polarized $\sigma_{\text{Ge-Rh}}$ bond with 32.9% electron density on the germanium atom and 67.1% on the rhodium one is localized at the first order in NBO analysis. These results are close to those found for **6**, a complex involving a strongly polarized Ge–Rh covalent bond (26.9% Ge and 73.1% Rh). Moreover, atoms-in-molecules (AIM) analyses for **2b** and **6** show that a bond critical point exists between the germanium and rhodium atoms with an electron density [$\rho(r)$] of the same magnitude [$\rho(r) = \sim 7 \times 10^{-2}\text{ e}^- \text{ bohr}^{-3}$; Figure 5].

Compound **5** was analyzed in the same way, and the results from NBO and AIM calculations are close to those calculated for compounds **2b** and **6**. The calculated Ge–Rh bond length

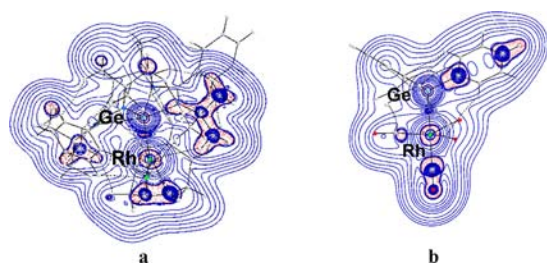


Figure 5. Laplacian plot of the electron density $\nabla^2 \rho(r)$ with charge accumulation [$\nabla^2 \rho(r) < 0$] printed in blue and charge depletion [$\nabla^2 \rho(r) > 0$] printed in red for complexes **2b** (a) and **6** (b).

(2.400 Å) is found to be shorter than that for **2b**, and the electron density $\rho(r)$ slightly higher [$\rho(r) \approx 8.3 \times 10^{-2} \text{ e}^- \text{ bohr}^{-3}$], with a less polarized $\sigma_{\text{Ge-Rh}}$ bond (57.2% Ge and 42.8% Rh), coherent with the π -acceptor character of the CO substituents. The description of the bonding situation in complexes **2b** and **6** is similar: the same nature of the Ge \rightarrow Rh interaction (localization of the $\sigma_{\text{Ge-Rh}}$ bond in the NBO calculations at the first order) and the same value of the electron density $\rho(r)$ using AIM analysis. Nevertheless, polarization of the Ge–Rh bond is found to be slightly different in **2b** compared to **6**. It means that the Ge–Rh bond in **2b** presents a slightly less polarized covalent character than **6**.

CONCLUDING REMARKS

In summary, two monogermylenerhodium(I) complexes, **2b** and **3a**, have been prepared via a one-step route from bis(amidinato)germylenes **1a** and **1b** and $[\text{RhCl}(\text{cod})]_2$; they were fully characterized by NMR spectroscopy and X-ray crystallography. Their stability strongly depends on the nature of the ligand and particularly on the steric hindrance of the substituent on the nitrogen atoms. Whereas with trimethylsilyl groups on the nitrogen atom only the germylene oxide rhodium complex could be obtained, with *t*-Bu groups on the amidinato ligand, the germylene rhodium complex was stable and isolable. In both cases, the formation of amidinatorhodium complexes was also observed. Complex **2b** was completely converted to the corresponding dicarbonyl compound **5**. The IR study showed that the starting germylene **1b** is a strong electron donor comparable with the strongest electron-donating NHC. DFT calculations confirm that complexes **2b** and **5** present a polarized covalent bond Ge–Rh, which leads to a short Ge–Rh distance.

EXPERIMENTAL SECTION

General Procedures. All manipulations with air-sensitive materials were performed in a dry and oxygen-free atmosphere of argon by using standard Schlenk-line and glovebox techniques. Solvents were purified with the MBRAUN SBS-800 purification system. NMR spectra were recorded in C_6D_6 or $\text{THF-}d_8$ on a Bruker Avance II 300 [^1H (300.13 MHz), ^{13}C (74.48 MHz), and ^{29}Si (59.63 MHz) at 298 K] or on a Bruker Avance II 400 [^1H (400.13 MHz) and ^{13}C (100.61 MHz) at 193 K]. Chemical shifts are expressed in parts per million with residual solvent signals as the internal reference (^1H and $^{13}\text{C}\{^1\text{H}\}$). Mass spectrometry (MS) spectra were measured with a Hewlett-Packard 5989A in electron impact mode (70 eV). High-resolution MS (HR-MS) spectra were measured with a GCT Premier Waters in DCI mode (CH_4). IR spectra were measured on a Varian 640-IR FT-IR spectrometer. Melting points were measured with a sealed capillary using the Stuart automatic melting point SMP40 apparatus. The germanium(II) derivatives **1a**¹¹ and **1b**¹² and the lithium amidinato salts^{1c,14} were prepared according to literature procedures.

2b. A cooled (-78°C) solution of **1b** (0.14 g, 0.26 mmol) in diethyl ether (4 mL) was added to a solution of $[\text{RhCl}(\text{cod})]_2$ (0.07 g, 0.14 mmol) in diethyl ether (4 mL) at -78°C . After 45 min, the solution was raised to room temperature and then stirred for a further 45 min. After filtration, the solvent was concentrated under reduced pressure to incipient crystallization. **2b** was obtained as yellow crystals (0.10 g, 49%). Mp: 91°C . ^1H NMR ($\text{THF-}d_8$, 400.13 MHz, 193 K): δ 1.22, 1.24, 1.42, 1.45 (4s, $4 \times 9\text{H}$, CH_3), 1.74–1.89 (m, 4H, CH_2), 2.30–2.46 (m, 4H, CH_2), 3.58, 4.15, 4.86, 4.94 (4s, $4 \times 1\text{H}$, $\text{CH}=\text{C}$), 7.33–7.40 (m, 5H, C_6H_5), 7.45–7.48 (m, 5H, C_6H_5). ^{13}C NMR ($\text{THF-}d_8$, 100.61 MHz, 193 K): δ 29.44, 29.55 (CH_2); 32.80, 32.88, 33.65, 33.89 (CH_3), 54.63, 55.04, 55.26, 57.34 ($\text{C}(\text{CH}_3)_3$), 93.73, 94.02 ($\text{CH}=\text{C}$), 127.22, 128.17, 128.44, 128.92, 129.01, 129.49, 129.87, 130.56, 130.66, 130.77 (C_o , C_m , C_p), 136.07, 139.53 (C_i), 166.29, 166.86 ($\text{C}_6\text{H}_5\text{C}$). MS: m/z 551 (1%) ($[\text{M} - \text{C}_6\text{H}_5\text{C}[\text{N}t\text{-Bu}]_2]^+$), 536 (1%) ($[\{\text{C}_6\text{H}_5\text{C}[\text{N}t\text{-Bu}]_2\}_2\text{Ge}\}^+$), 57 (100%) ($[t\text{-Bu}]^+$). Anal. Calcd for $\text{C}_{38}\text{H}_{58}\text{ClGeN}_4\text{Rh}$: C, 58.37; H, 7.48; N, 7.17. Found: C, 57.62; H, 7.06; N, 6.55.

3a. A solution of **1a** (0.20 g, 0.33 mmol) in toluene (1.5 mL) at -70°C was slowly added to a suspension of $[\text{RhCl}(\text{cod})]_2$ (0.08 g, 0.17 mmol) in toluene (1.5 mL) at -70°C . After 2 h, the solution was raised to room temperature and then stirred for a further 1 h. The solvent was removed under reduced pressure and the residue treated with pentane. After filtration, the solution was cooled at 4°C to yield crystals of **4a** (80% NMR yield) and **3a** (20% NMR yield). **3a** was not isolated from the reaction mixture; the reaction was performed several times, leading to reproducible results. ^1H NMR (C_6D_6 , 300.13 MHz): δ -0.15 (36H, SiCH_3), 1.35 (s, 8H, CH_2), 2.19–2.21 (m, 8H, CH_2), 5.51 (s, 8H, $\text{CH}=\text{C}$), 6.88–7.07 (m, 10H, C_6H_5). ^{13}C NMR (C_6D_6 , 75.48 MHz): δ 2.45 (SiCH_3), 33.61 (CH_2), 96.03 ($\text{CH}=\text{C}$), 126.43 (C_o), 128.14 (C_m), 128.62 (C_p), 139.03 (C_i), 163.42 ($\text{C}_6\text{H}_5\text{C}$). ^{29}Si NMR (C_6D_6 , 59.63 MHz): δ 2.70. IR (C_6D_6): 839 cm^{-1} ($\nu_{\text{Ge-O}}$).

4a. A solution of $[\{\text{Me}_3\text{SiNC}(\text{Ph})\text{CNSiMe}_3\}\text{Li}]$ (0.41 mmol) in diethyl ether was added to a solution of $[\text{Rh}(\text{cod})\text{Cl}]_2$ (0.10 g, 0.20 mmol) in diethyl ether (5 mL) at -78°C . After 10 min, the solution was raised to room temperature and stirred for 2 h. The volatiles were removed under reduced pressure, and the residue was treated with 8 mL of toluene. After filtration, the filtrate was concentrated under reduced pressure to incipient crystallization. **4a** was obtained as yellow crystals at -24°C (0.11 g, 77%). Mp: 91°C (dec). ^1H NMR (C_6D_6 , 300.13 MHz): δ -0.15 (s, $^2J_{\text{H-Si}} = 6.6 \text{ Hz}$, 18H, SiCH_3), 1.50–1.57 (m, 4H, CH_2), 2.27–2.31 (m, 4H, CH_2), 4.42 (s, 4H, $\text{CH}=\text{C}$), 6.85–6.94 (m, 3H, C_6H_5), 7.03–7.06 (m, 2H, C_6H_5). ^{13}C NMR (C_6D_6 , 75.48 MHz): δ 2.45 ($^1J_{\text{C-Si}} = 56.6 \text{ Hz}$, SiCH_3), 31.11 (CH_2), 76.46 (d, $^1J_{\text{C-Rh}} = 12.6 \text{ Hz}$, $\text{CH}=\text{C}$), 126.34 (C_o), 128.02 (C_m), 128.32 (C_p), 142.68 (d, $^3J_{\text{C-Rh}} = 2.5 \text{ Hz}$, C_i), 187.84 (d, $^2J_{\text{C-Rh}} = 5.0 \text{ Hz}$, $\text{C}_6\text{H}_5\text{C}$). ^{29}Si NMR (C_6D_6 , 59.63 MHz): δ 2.70 ($^2J_{\text{Si-Rh}} = 0.9 \text{ Hz}$). MS: m/z 474 (58%) ($[\text{M}]^+$), 459 (29%) ($[\text{M} - \text{CH}_3]^+$), 73 (100%) ($[\text{Si}(\text{CH}_3)_3]^+$). HR-MS for $\text{C}_{21}\text{H}_{35}\text{N}_2\text{RhSi}_2$ ($[\text{M}]^+$): calcd mass, 474.1394; measd mass, 474.1374.

4b. A solution of $[\{t\text{-BuNC}(\text{Ph})\text{CN}t\text{-Bu}\}\text{Li}]^{1c}$ (0.40 mmol) was added to a solution of $[\text{Rh}(\text{cod})\text{Cl}]_2$ (0.10 g, 0.20 mmol) in diethyl ether (5 mL) at -78°C . After 10 min, the solution was raised to room temperature and stirred for 1 h and 30 min. The volatiles were removed under reduced pressure, and the residue was treated with 8 mL of toluene. After filtration, the filtrate was evaporated under vacuum to yield **4b** (0.13 g, 75%) as a yellow powder. Yellow crystals were obtained from a saturated solution of toluene at room temperature. Mp: 185°C (dec). ^1H NMR (C_6D_6 , 300.13 MHz): δ 0.92 (s, 18H, CH_3), 1.56–1.64, 2.30–2.35 (2m, $2 \times 4\text{H}$, CH_2), 4.66 (s, 4H, $\text{CH}=\text{C}$), 6.86–6.94 (m, 3H, C_6H_5), 7.21–7.25 (m, 2H, C_6H_5). ^{13}C NMR (C_6D_6 , 75.48 MHz): δ 31.11 (CH_2), 33.17 (CH_3), 55.34 (d, $^2J_{\text{C-Rh}} = 1.8 \text{ Hz}$, $\text{C}(\text{CH}_3)_3$), 75.35 (d, $^1J_{\text{C-Rh}} = 12.4 \text{ Hz}$, $\text{CH}=\text{C}$), 126.74 (C_o), 128.05 (C_p), 130.37 (C_m), 139.67 (d, $^3J_{\text{C-Rh}} = 2.0 \text{ Hz}$, C_i), 179.76 (d, $^2J_{\text{C-Rh}} = 1.0 \text{ Hz}$, $\text{C}_6\text{H}_5\text{C}$). MS: m/z 442 (46%) ($[\text{M}]^+$), 328 (22%) ($[\text{M} - t\text{-Bu}]^+$), 57 (100%) ($[t\text{-Bu}]^+$). HR-MS for $\text{C}_{23}\text{H}_{35}\text{N}_2\text{Rh}$ ($[\text{M}]^+$): calcd mass, 442.1855; measd mass, 442.1874.

NMR-Scale Synthesis of 5. A solution of **2b** (0.04 g, 0.05 mmol) in $\text{THF-}d_8$ was placed under an atmosphere of CO (3 atm, J. Young

Table 1. Crystallographic Data of Compounds 2b, 3a, 4a, and 4b

	2b	3a	4a	4b
empirical formula	C ₃₈ H ₅₈ ClGeN ₄ Rh, C ₄ H ₁₀ O	C ₄₂ H ₇₀ Cl ₂ Ge ₂ N ₄ ORh ₂ Si ₄	C ₂₁ H ₃₅ N ₂ RhSi ₂	C ₂₃ H ₃₅ N ₂ Rh
fw (g/mol)	855.95	1181.28	474.60	442.44
temperature (K)	193(2)	193(2)	193(2)	193(2)
λ (Mo K α) (Å)	0.71073	0.71073	0.71073	0.71073
cryst syst	triclinic	monoclinic	monoclinic	monoclinic
space group	$P\bar{1}$	$P2_1/n$	Pn	$P 2_1/m$
<i>a</i> (Å)	11.7561(5)	10.9112(4)	6.6791(2)	6.8114(6)
<i>b</i> (Å)	13.3498(6)	15.7314(5)	9.7861(4)	13.7680(13)
<i>c</i> (Å)	13.6919(6)	15.2579(6)	34.6517(13)	11.0049(9)
α (deg)	87.584(2)	90	90	90
β (deg)	86.103(2)	92.178(2)	94.379(2)	92.509(3)
γ (deg)	87.405(2)	90	90	90
volume (Å ³)	2140.02(16)	2617.10(16)	2258.30(14)	1031.04(16)
<i>Z</i>	2	2	4	2
density calcd (g cm ⁻³)	1.328	1.499	1.396	1.425
abs coeff (mm ⁻¹)	1.185	1.985	0.870	0.837
<i>F</i> (000)	900	1204	992	464
cryst size (mm)	0.28 × 0.08 × 0.06	0.26 × 0.04 × 0.03	0.40 × 0.18 × 0.12	0.22 × 0.08 × 0.04
θ range (deg)	5.15 - 26.37	5.11 - 28.28	5.11 - 30.51	5.36 - 28.28
index ranges <i>hkl</i>	-14 ≤ <i>h</i> ≤ 14 -16 ≤ <i>k</i> ≤ 16 -17 ≤ <i>l</i> ≤ 17	-8 ≤ <i>h</i> ≤ 14 -20 ≤ <i>k</i> ≤ 20 -20 ≤ <i>l</i> ≤ 20	-9 ≤ <i>h</i> ≤ 9 -13 ≤ <i>k</i> ≤ 13 -49 ≤ <i>l</i> ≤ 49	-9 ≤ <i>h</i> ≤ 8 -18 ≤ <i>k</i> ≤ 18 -14 ≤ <i>l</i> ≤ 14
reflns collected/unique	37198/8662	22484/6439	34029/13075	10898/2639
<i>R</i> (int)	0.0252	0.0530	0.0406	0.0314
completeness to θ (%)	98.9	99.0	99.1	99.1
data/restraints/param	8662/151/532	6439/0/265	13075/2/481	2639/0/133
GOF	1.050	1.010	1.024	1.056
<i>R</i> ₁ , w <i>R</i> ₂ [<i>I</i> > 2(σ)]	0.0261, 0.0680	0.0384, 0.0789	0.0382, 0.0681	0.0273, 0.0679
<i>R</i> ₁ , w <i>R</i> ₂ (all data)	0.0307, 0.0709	0.0733, 0.0913	0.0491, 0.0715	0.0319, 0.0709
largest diff peak and hole (e Å ⁻³)	0.718, -0.471	0.684, -0.491	0.543, -0.764	0.571, -0.545

Valve NMR tube) at -80 °C. Ligand exchange was monitored using ¹H NMR spectroscopy; the reaction was completed in less than 10 min. ¹H NMR (THF-*d*₈, 400.13 MHz, 193 K): δ 1.27, 1.31, 1.35, 1.37 (4s, 4 × 9H, CH₃), 7.31–7.54 (m, 10H, C₆H₅). ¹³C NMR (THF-*d*₈, 100.61 MHz, 193 K): δ 32.63, 32.74, 33.46, 33.98 (CH₃), 55.04, 55.19, 56.32, 56.97 (C(CH₃)₃), 127.77, 128.42, 128.53, 128.83, 129.94, 130.46, 130.89, 130.96, 131.55 (C_o, C_m, C_p), 135.80, 136.37 (C_i), 166.97, 168.92 (C₆H₅C), 185.55 (d, ¹J_{C-Rh} = 62.4 Hz, CO), 188.50 (d, ¹J_{C-Rh} = 72.1 Hz, CO). IR (THF): 1971, 2058 cm⁻¹ (ν _{CO}). Concentration of the reaction mixture resulted in decomposition of the expected product.²³

Computational Information. Calculations were performed with the *Gaussian 03* suite of programs,²⁴ using the DFT method.²⁵ The hybrid exchange functional B3LYP set²⁶ was used. B3LYP is a three-parameter functional developed by Becke that combines the Becke gradient-corrected exchange functional and the Lee–Yang–Parr and Vosko–Wilk–Nusair correlation functionals with part of the exact Hartree–Fock exchange energy. The SDD basis set was used for rhodium and the 6-31G(d) basis set for other atoms.²⁷ Geometry optimizations were carried out without any symmetry restrictions. The electron density of the optimized structures was subjected to AIM analysis (QTAIM analysis)²⁸ using *AIMAll* software.²⁹

X-ray Structure Determinations. The data of the structures for compounds 2b, 3a, 4a, and 4b were collected on a Bruker-AXS APEX II diffractometer using a 30 W air-cooled microfocus source (ImS) with focusing multilayer optics at a temperature of 193(2) K, with graphite-monochromated Mo K α radiation (wavelength = 0.71073 Å) by using ϕ and ω scans. The data were integrated with *SAINT*, and an empirical absorption correction with *SADABS* was applied.³⁰ The structures were solved by direct methods using *SHELXS-97*³¹ and refined using the least-squares method on *F*².³² All non-hydrogen atoms were treated anisotropically. The hydrogen atoms were fixed

geometrically and refined with a riding model. The hydrogen atoms were located by difference Fourier maps and refined with a riding model. Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Center as CCDC 848154 (2b), 892930 (3a), 892931 (4a), and 848155 (4b). These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K., fax (+44) 1223-336-033, or e-mail deposit@ccdc.cam.ac.uk). See also the Supporting Information.

Structural data are summarized in Table 1.

■ ASSOCIATED CONTENT

● Supporting Information

Crystallographic data in CIF format for 2b, 3a, 4a, and 4b and details of calculations for 2b, 5, and 6. Computational Information. 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) (a) Asay, M.; Jones, C.; Driess, M. *Chem. Rev.* **2011**, *111*, 354–396. (b) Mandal, S. K.; Roesky, H. W. *Chem. Commun.* **2010**, 6016–6041. (c) Nagendran, S.; Sen, S. S.; Roesky, H. W.; Koley, D.; Grubmüller, H.; Pal, A.; Herbst-Irmer, R. *Organometallics* **2008**, *27*, 5459–5463. (d) Zabula, A. V.; Hahn, F. E. *Eur. J. Inorg. Chem.* **2008**, 5165–5179. (e) Kühn, O. *Coord. Chem. Rev.* **2004**, *248*, 411–427. (f) Lappert, M. F.; Rowe, R. S. *Coord. Chem. Rev.* **1990**, *100*, 267–292. (g) Petz, W. *Chem. Rev.* **1986**, *86*, 1019–1047.
- (2) Davidson, F.; Harris, D. H.; Lappert, M. F. *J. Chem. Soc., Chem. Commun.* **1976**, 2268–2274.
- (3) (a) Cabeza, J. A.; Fernandez-Colinas, J. M.; Garcia-Alvarez, P.; Polo, D. *Inorg. Chem.* **2012**, *51*, 3896–3903. (b) Mansell, S. M.; Herber, R. H.; Nowik, I.; Ross, D. H.; Russell, C. A.; Wass, D. F. *Inorg. Chem.* **2011**, *50*, 2252–2263. (c) Ullah, F.; Kühn, O.; Bajor, G.; Veszpremi, T.; Jones, P. G.; Heinicke, J. *Eur. J. Inorg. Chem.* **2009**, 221–229. (d) Yang, W.; Fu, H.; Wang, H.; Chen, M.; Ding, Y.; Roesky, H. W.; Jana, A. *Inorg. Chem.* **2009**, *48*, 5058–5060. (e) Saur, I.; Rima, G.; Miqueu, K.; Gornitzka, H.; Barrau, J. *J. Organomet. Chem.* **2003**, *672*, 77–85. (f) Bazinet, P.; Yap, G. P. A.; Richeson, D. S. *J. Am. Chem. Soc.* **2001**, *123*, 11162–11167. (g) Schmedake, T. A.; Haaf, M.; Paradise, B. J.; Millevolte, A. J.; Powell, D. R.; West, R. J. *Organomet. Chem.* **2001**, *636*, 17–25. (h) Jutzi, P.; Keitemeyer, S.; Neumann, B.; Stammler, H.-G. *Organometallics* **1999**, *18*, 4778–4784. (i) Hitchcock, P. B.; Lappert, M. F.; Thomas, S. A.; Thorne, A. J. *J. Organomet. Chem.* **1986**, *315*, 27–44.
- (4) (a) Köcher, C.; Herrmann, W. A. *J. Organomet. Chem.* **1997**, *532*, 261–265. (b) Bildstein, B.; Malaun, M.; Kopacka, H.; Ongania, K.-H.; Wurst, K. *J. Organomet. Chem.* **1999**, *572*, 177–187. (c) Huang, J.; Stevens, E. D.; Nolan, S. P.; Petersen, J. L. *J. Am. Chem. Soc.* **1999**, *121*, 2674–2678. (d) Weskamp, T.; Kohl, F. J.; Herrmann, W. A. *J. Organomet. Chem.* **1999**, *582*, 362–365. (e) Chianese, A. R.; Li, X.; Janzen, M. C.; Faller, J. W.; Crabtree, R. H. *Organometallics* **2003**, *22*, 1663–1667. (f) Cattoën, X.; Gornitzka, H.; Bourissou, D.; Bertrand, G. *J. Am. Chem. Soc.* **2004**, *126*, 1342–1343. (g) Dorta, R.; Stevens, E. D.; Nolan, S. P. *J. Am. Chem. Soc.* **2004**, *126*, 5054–5055. (h) Arnold, P. L.; Pearson, S. *Coord. Chem. Rev.* **2007**, *251*, 596–609. (i) Khranov, D. M.; Lynch, V. M.; Bielawski, C. W. *Organometallics* **2007**, *26*, 6042–6049. (j) Pugh, D.; Danopoulos, A. A. *Coord. Chem. Rev.* **2007**, *251*, 610–641. (k) Hahn, F. E.; Jahnke, M. C. *Angew. Chem., Int. Ed.* **2008**, *47*, 3122–3172. (l) Song, G.; Zhang, Y.; Li, X. *Organometallics* **2008**, *27*, 1936–1943. (m) Jacobsen, H.; Correa, A.; Poater, A.; Costabile, C.; Cavallo, L. *Coord. Chem. Rev.* **2009**, *253*, 687–703. (n) Melaimi, M.; Soleilhavoup, M.; Bertrand, G. *Angew. Chem., Int. Ed.* **2010**, *49*, 8810–8849. (o) Bierenstiel, M.; Cross, E. D. *Coord. Chem. Rev.* **2011**, *255*, 574–590.
- (5) (a) Gil, W.; Trzeciak, A. M.; Ziółkowski, J. *J. Organometallics* **2008**, *27*, 4131–4138. (b) Gil, W.; Trzeciak, A. M. *Coord. Chem. Rev.* **2011**, *255*, 473–483. (c) Gülcemal, S.; Daran, J.-C.; Çetinkaya, B. *Inorg. Chim. Acta* **2011**, *365*, 264–268. (d) Türkmen, H.; Çetinkaya, B. *Appl. Organomet. Chem.* **2011**, *25*, 226–232.
- (6) (a) Lavallo, V.; Mafhouz, J.; Canac, Y.; Donnadiou, B.; Schoeller, W. W.; Bertrand, G. *J. Am. Chem. Soc.* **2004**, *126*, 8670–8671. (b) Martin, D.; Baceiredo, A.; Gornitzka, H.; Schoeller, W. W.; Bertrand, G. *Angew. Chem., Int. Ed.* **2005**, *44*, 1700–1703. (c) Türkmen, H.; Çetinkaya, B. *J. Organomet. Chem.* **2006**, *691*, 3749–3759. (d) Iglesias, M.; Beetstra, D. J.; Stasch, A.; Horton, P. N.; Hursthouse, M. B.; Coles, S. J.; Cavell, K. J.; Dervisi, A.; Fallis, I. A. *Organometallics* **2007**, *26*, 4800–4809. (e) Iglesias, M.; Beetstra, D. J.; Kariuki, B.; Cavell, K. J.; Dervisi, A.; Fallis, I. A. *Eur. J. Inorg. Chem.* **2009**, 1913–1919. (f) Scarborough, C. C.; Guzei, I. A.; Stahl, S. S. *Dalton Trans.* **2009**, 2284–2286. (g) Tonner, R.; Frenking, G. *Organometallics* **2009**, *28*, 3901–3905. (h) Wolf, S.; Plenio, H. *J. Organomet. Chem.* **2009**, *694*, 1487–1492. (i) Dröge, T.; Glorius, F. *Angew. Chem., Int. Ed.* **2010**, *49*, 6940–6952.
- (7) Neumann, E.; Pfaltz, A. *Organometallics* **2005**, *24*, 2008–2011.
- (8) Veith, M.; Müller, A.; Stahl, L.; Nötzel, M.; Jarczyk, M.; Huch, V. *Inorg. Chem.* **1996**, *35*, 3848–3855.
- (9) Veith, M.; Stahl, L.; Huch, V. *Inorg. Chem.* **1989**, *28*, 3278–3280.
- (10) Al-Rafia, S. M. I.; Malcolm, A. C.; McDonald, R.; Ferguson, M. J.; Rivard, E. *Chem. Commun.* **2012**, *48*, 1308–1310.
- (11) Matioszek, D.; Katir, N.; Saffon, N.; Castel, A. *Organometallics* **2010**, *29*, 3039–3046.
- (12) Yeong, H.-X.; Zhang, S.-H.; Xi, H.-W.; Guo, J.-D.; Lim, K. H.; Nagase, S.; So, C.-W. *Chem.—Eur. J.* **2012**, *18*, 2685–2691.
- (13) Leung, W.-P.; So, C.-W.; Wang, J.-Z.; Mak, T. C. W. *Chem. Commun.* **2003**, 248–249.
- (14) Edelmann, F. T. *Coord. Chem. Rev.* **1994**, *137*, 403–481.
- (15) (a) Junk, P. C.; Cole, M. L. *Chem. Commun.* **2007**, 1579–1590. (b) Edelmann, F. T. *Adv. Organomet. Chem.* **2008**, *57*, 183–352. (c) Jones, C. *Coord. Chem. Rev.* **2010**, *254*, 1273–1289.
- (16) (a) Lahoz, F. J.; Tiripicchio, A.; Tiripicchio Camellini, M.; Oro, L. A.; Pinillos, M. P. *J. Chem. Soc., Dalton Trans.* **1985**, 1487–1493. (b) Jones, C.; Mills, D. P.; Stasch, A. *Dalton Trans.* **2008**, 4799–4804.
- (17) CCDC 848154 (2), 892930 (3a), 892931 (4a), and 848155 (4b) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif.
- (18) Herrmann, W. A.; Elison, M.; Fischer, J.; Köcher, C.; Artus, G. R. *J. Chem.—Eur. J.* **1996**, *2*, 772–780.
- (19) Adams, R. D.; Trufan, E. *Inorg. Chem.* **2010**, *49*, 3029–3034.
- (20) Zhang, S.-H.; So, C.-W. *Organometallics* **2011**, *30*, 2059–2062.
- (21) Baines, K. M.; Stibbs, W. G. *Coord. Chem. Rev.* **1995**, *145*, 157–200.
- (22) Melaimi, M.; Soleilhavoup, M.; Bertrand, G. *Angew. Chem., Int. Ed.* **2010**, *49*, 2–42.
- (23) Sanderson, M. D.; Kamplain, J. W.; Bielawski, C. W. *J. Am. Chem. Soc.* **2006**, *128*, 16514–16515.
- (24) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian 03*, revision E.01; Gaussian, Inc.: Pittsburgh, PA, 2003.
- (25) Parr, R. G.; Yang, W. *Functional Theory of Atoms and Molecules*; Breslow, R., Goodenough, J. B., Eds.; Oxford University Press: New York, 1989.
- (26) (a) Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098–3100. (b) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648–5652. (c) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785–789.
- (27) Hariharan, P. C.; Pople, J. A. *Theor. Chim. Acta* **1973**, *28*, 213–222.
- (28) (a) Bader, R. F. W. *Atoms in Molecules: A Quantum Theory*; Oxford University Press: New York, 1990. (b) Bader, R. F. W. *Chem. Rev.* **1991**, *91*, 893–928.
- (29) Keith, T. A. *AIMAll*, version 10.10.11; TK Gristmill Software: Overland Park, KS, 2010.
- (30) (a) SAINT-NT; Bruker AXS Inc.: Madison, WI, 2000. (b) SADABS; Program for data correction; Bruker AXS Inc.: Madison, WI, 2000.
- (31) Sheldrick, G. M. *Acta Crystallogr.* **1990**, *A46*, 467–473.
- (32) SHELXL-97; Program for Crystal Structure Refinement; Sheldrick, G. M. *Acta Crystallogr., Sect. A* **2008**, *64*, 112–122.