Inorganic Chemistry

Article

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Amidinate-Stabilized Group 9 Metal−Silicon(I) Dimer and −Silylene Complexes

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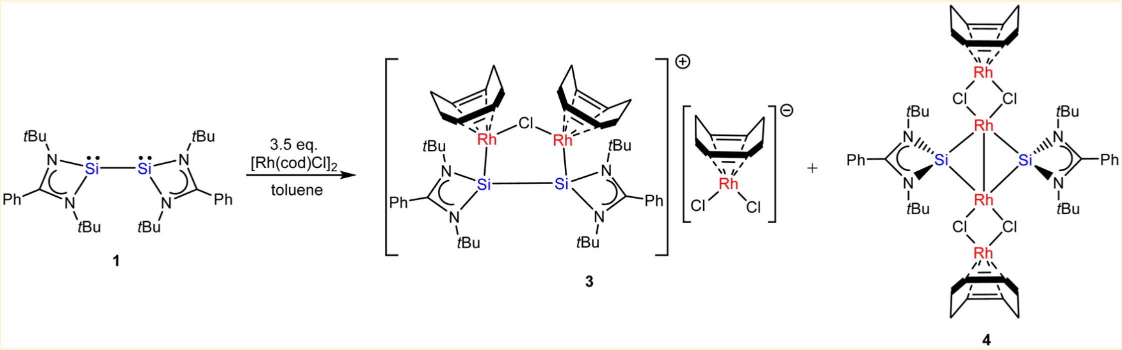
Supporting Information



ABSTRACT: The coordination chemistry of the amidinate-stabilized silicon(I) dimer toward group 9 metal complexes is described. The reaction of $[LSi:]_2$ (**1**, L = PhC(N*t*Bu)$_2$) with $[Ir(cod)Cl]_2$ (cod = 1,5-cyclooctadiene) in toluene at ambient temperature afforded the base-stabilized silicon(I) dimer-iridium complex $[LSi\{Ir(cod)\text{-}\mu\text{-}Cl\text{-}Ir(cod)\}SiL][(cod)IrCl_2]$ (**2**). In contrast, the reaction of **1** with $[Rh(cod)Cl]_2$ in toluene at ambient temperature afforded a mixture of the amidinate-stabilized silicon(I) dimer-rhodium complex $[LSi\{Rh(cod)\text{-}\mu\text{-}Cl\text{-}Rh(cod)\}SiL]$ (**3**) and the dimeric amidinate-stabilized rhodosilylene $[(LSi)\mu\text{-}\{Rh(\mu\text{-}Cl)_2Rh(cod)\}]_2$ (**4**). Moreover, the latter reacted with PPh_3 to afford a mixture of the Wilkinson's catalyst $[(PPh_3)_3RhCl]$ and the dimeric rhodosilylene complex $[(LSi)\mu\text{-}\{RhCl(PPh_3)\}]_2$ (**5**), which underwent a rearrangement to form the rhodosilylene-phosphidorhodium dimer $(LSi)[\mu\text{-}\{RhCl(PPh_3)\}\mu\text{-}\{RhCl(LSiPh)\}](PPh_2)$ (**6**). Compounds **2**−**6** were characterized by NMR spectroscopy and X-ray crystallography. In addition, DFT calculations of compound **4** were performed to understand its electronic structure.

■ INTRODUCTION

Silylenes of composition $[L_2Si:]$ (L = supporting ligand) have attracted much attention in the past two decades due to their unique structures and reactivities.[1] They comprise a lone pair of electrons and vacant p orbital on the low valent silicon atoms, which enable them to be both donors and acceptors. As a result, they can serve as an ancillary ligand in transition metal complexes in which there are synergy electron transfers between the low valent silicon atoms and transition metals.[2] The resulting transition metal−silylene complexes were found to be catalytic intermediates[3] or to be capable of activating small molecules.[4] Moreover, the chemistry of transition metal−silylene complexes has been extended to the stabilization of otherwise highly reactive silylene species within the coordination sphere of transition metal fragments.[5]

Recently, a series of base-stabilized silicon(I) dimers $[LSi:]_2$ was synthesized.[6] They comprise a Si−Si single bond and a lone pair of electrons on each Si atom. Their reactivity showed that they are powerful reagents for the activation of small molecules, unsaturated substrates, etc.[7] Because they comprise two low valent silicon centers, their coordination chemistry toward transition metals could be different from that of silylenes due to different concerted effort between the silicon(I) and transition metal centers. However, until now, base-stabilized silicon(I) dimer-transition metal complexes are still unknown.

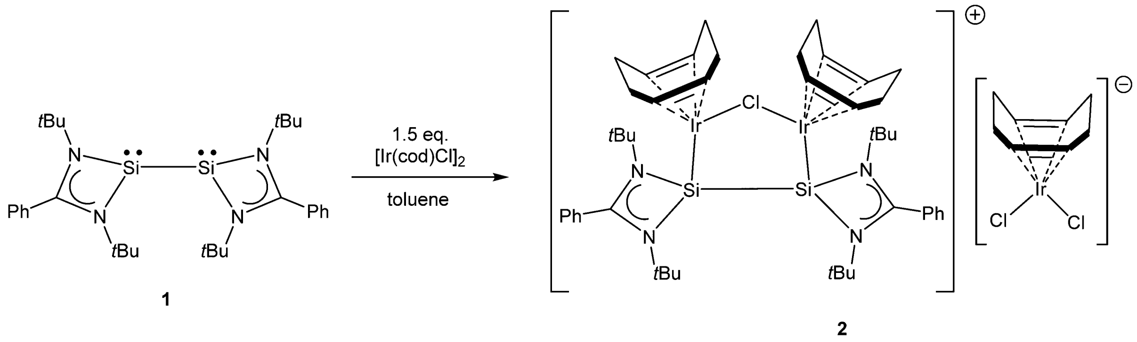
Our group has been utilizing heavier group 14 element(I) dimers as building blocks for the construction of complex molecules such as the germatrisilacyclobutadiene, 2,4-diimino-1,3-disilacyclobutanediyl, and digermadistannacyclobutadiene.[8] Because the heavier group 14 element(I) dimer-transition metal complex is rare and only one example was reported,[9] this prompted our interest in investigating the coordination chemistry of heavier group 14 element(I) dimers toward transition metals. In this Article, we report the reactivity of a base-stabilized silicon(I) dimer toward iridium(I) and rhodium(I) complexes leading to the formation of base-stabilized group 9 metal−silicon(I) dimer and −silylene complexes.

Received: August 3, 2015
Published: October 1, 2015

ACS Publications

DOI: 10.1021/acs.inorgchem.5b01759
Inorg. Chem. 2015, 54, 9968−9975

Scheme 1. Synthesis of 2



RESULTS AND DISCUSSION

The reaction of the amidinate-stabilized silicon(I) dimer [LSi:]$_2$ (**1**, L = PhC(N*t*Bu)$_2$)[6b] with [Ir(cod)Cl]$_2$ (cod = 1,5-cyclooctadiene) in toluene at ambient temperature afforded the base-stabilized silicon(I) dimer-iridium complex [LSi{Ir(cod)-μ-Cl-Ir(cod)}SiL][(cod)IrCl$_2$] (**2**, Scheme 1), in which the Si$^{\mathrm{I}}$ atoms act as a 2-electron donor coordinating to the Ir$^{\mathrm{I}}$ atom and Ir$^{\mathrm{I}}$ cation, respectively. The Ir centers are bridged by the Cl atom. The reaction appears to proceed through the coordination of the Si$^{\mathrm{I}}$ atoms to "(cod)IrCl" moieties, followed by the displacement of the Cl$^-$ anion, which may be due to steric hindrance, to form [LSi{Ir(cod)-μ-Cl-Ir(cod)}SiL]$^+$ cation. The Cl$^-$ anion then reacts with another molecule of [Ir(cod)Cl]$_2$ to form [(cod)IrCl$_2$]$^-$ anion. The results are different from the reaction of the β-diketiminato chlorosilylene with [Ir(cod)Cl]$_2$ to form the silylene-iridium complex [HC{C(Me)NAr}$_2$](Cl)SiIrCl(cod), in which the iridium cation [(cod)Ir]$^+$ and anion [(cod)IrCl$_2$]$^-$ were not generated.[4g]

Compound **2** was isolated as a highly air- and moisture-sensitive red crystalline solid (yield: 29%), which is soluble in toluene and THF. It was characterized by NMR spectroscopy. The ^{1}H and ^{13}C{^{1}H} NMR spectra display one set of resonances due to the amidinate and cod ligands. The ^{29}Si{^{1}H} NMR resonance (δ = 73.5 ppm) is slightly upfield shifted as compared to that of **1** (δ = 76.3 ppm),[6b] but it is downfield shifted as compared to that of [HC{C(Me)NAr}$_2$](Cl)SiIrCl(cod) (δ = 0.79 ppm).[4g]

Compound **2** was characterized by X-ray crystallography (Figure 1). There are two independent molecules in the asymmetric unit with slightly different bond lengths and angles. Only one independent molecule is discussed here for clarity. The molecular structure of **2** shows that the Si1/2 atoms coordinate to the Ir1/2 atoms, which adopt a distorted tetrahedral geometry. Each Ir1/2 atom adopts a square planar geometry by coordinating with the bidentate cod molecule, bridging Cl1 atom, and Si1/2 atom, respectively. The Si1–Si2 bond (2.376(5) Å) is comparable to that of **1** (2.413(2) Å).[6b] The Si1–Ir1 (2.334(4) Å) and Si2–Ir2 (2.307(4) Å) bonds are comparable to [HC{C(Me)NAr}$_2$](Cl)SiIrCl(cod) (2.3164(8) Å).[4g] They are also similar to other silyl iridium complexes (2.264(2)–2.437(1) Å).[10]

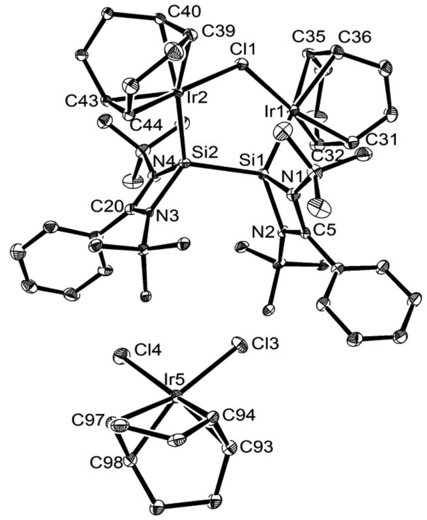
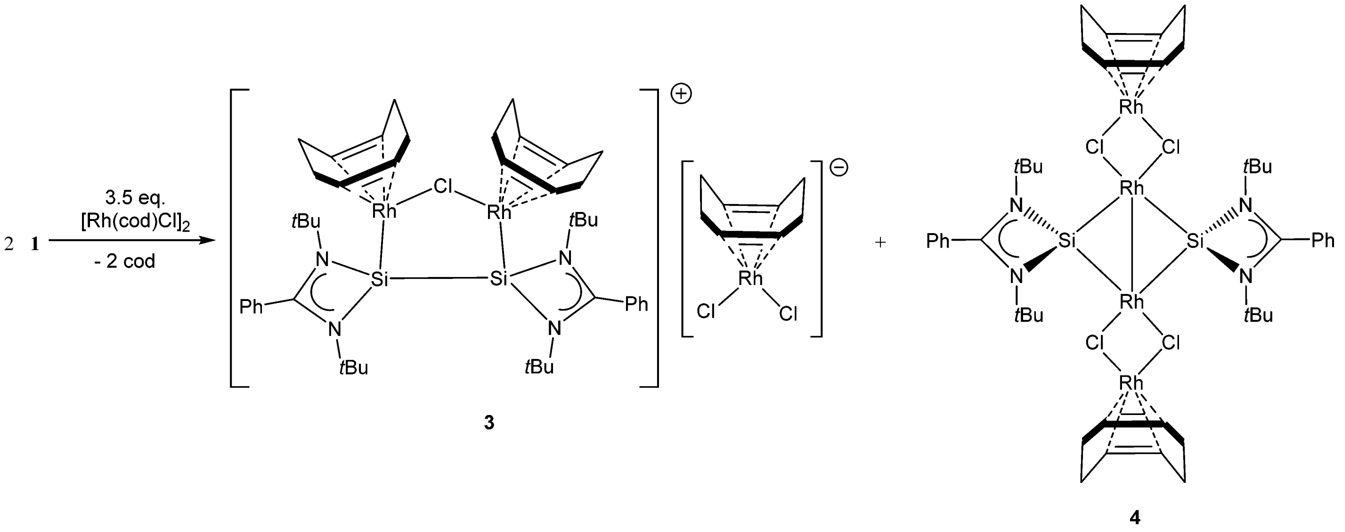


Figure 1. Molecular structure of **2** with thermal ellipsoids at the 30% probability level. There are two independent molecules in the asymmetric unit with slightly different bond lengths and angles. Only one independent molecule is discussed here for clarity. Hydrogen atoms and solvent molecules are also omitted for clarity. Selected bond lengths (Å) and bond angles (deg): Ir1–Si1 2.334(4), Ir1–Cl1 2.373(3), Ir2–Si2 2.307(4), Ir2–Cl1 2.387(3), Si1–Si2 2.376(5), N1–Si1 1.838(11), N2–Si1 1.836(11), N3–Si2 1.832(11), N4–Si2 1.823(11), C5–N1 1.345(16), C5–N2 1.318(15), Ir5–Cl4 2.355(4), Ir5–Cl3 2.370(3); Si1–Ir1–Cl1 89.92(12), Si2–Ir2–Cl1 92.03(12), Ir1–Cl1–Ir2 123.76(15), Ir1–Si1–Si2 109.55(18), Ir2–Si2–Si1 105.62, N2–Si1–N1 71.1(5), N1–Si1–Ir1 115.1(4), N2–Si1–Si2 118.2(4), N4–Si2–N3 71.1(5), Cl4–Ir5–Cl3 89.50(13).

The reaction of **1** with [Rh(cod)Cl]$_2$ in toluene at ambient temperature afforded a mixture of the silicon(I) dimer-rhodium complex [LSi{Rh(cod)-μ-Cl-Rh(cod)}SiL] (**3**) and the dimeric rhodosilylene [(LSi)μ-{Rh(μ-Cl)$_2$Rh(cod)}]$_2$ (**4**, Scheme 2). The reaction mixture was filtered, and the filtrate was concentrated to afford compound **3** as an air- and moisture-sensitive yellow crystalline solid (yield: 76%). The mother liquor was filtered and then further concentrated to afford **4** as an air- and moisture-sensitive dark red crystalline solid (yield: 19%). The formation of **3** is similar to that of **2**. Compound **4** is formed by the insertion of [Rh(cod)Cl]$_2$ with the Si–Si bond in **1**, along with the displacement of two cod molecules. The results are different from those of the reaction of [Ir(cod)Cl]$_2$ with **1**. This could be attributed to the reduction potential of [Rh(cod)Cl]$_2$ and [Ir(cod)Cl]$_2$ by which the former enables one to cleave the Si–Si bond in compound **1**.

Compound **3** was characterized by NMR spectroscopy. The ^{1}H and ^{13}C{^{1}H} NMR spectra show one set of resonances for the amidinate and cod ligands. The ^{29}Si{^{1}H} NMR spectrum displays a resonance at δ = 76.8 ppm (d, $J_{\mathrm{Si-Rh}}$ = 76.6 Hz) with coupling to the adjacent rhodium atom. It falls within the range of the cationic silylene-rhodium adducts (δ = 27.9–134.5

Scheme 2. Synthesis of 3 and 4



ppm).[11] It is also downfield shifted as compared to that of the neutral silylene-rhodium adducts (δ = −1.03−66.4 ppm).[4c,g]

Compound **3** is isostructural to compound **2** (Figure 2). The Si−Si bond (2.388(2) Å) in **3** is comparable to that in **2** (2.376(5) Å). The Rh−Si bonds in **3** (2.2984(17), 2.2951(17) Å) are comparable to that of [HC{C(Me)NAr}$_2$](Cl)SiRhCl(cod) (2.295(1) Å).[4g] They are shorter than typical Si−Rh single bonds (average 2.32 Å)[12] and that in the cationic silylene-rhodium complex $[(\text{IPr} \rightarrow \text{SiCl}_2)_2\text{Rh(CO)}_2]^+$ (2.3605(8) Å, IPr = {HCN(Ar)}$_2$C:).[11a] These indicate that there is some π-back bonding from the rhodium to silicon atoms.

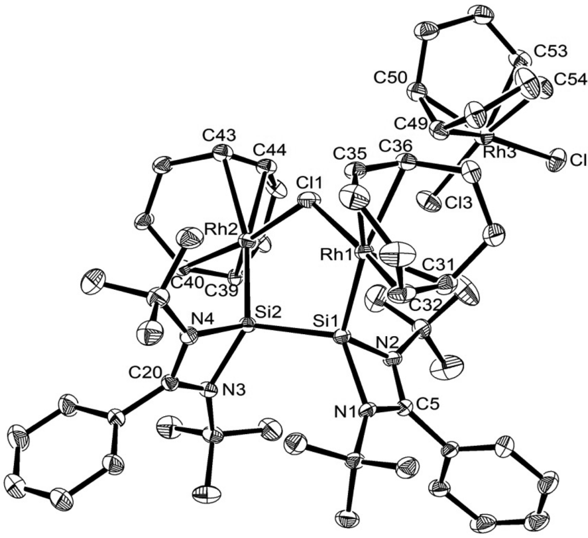


Figure 2. Molecular structure of **3** with thermal ellipsoids at the 30% probability level. Hydrogen atoms and solvent molecules are omitted for clarity. Selected bond lengths (Å) and bond angles (deg): Rh1−Si1 2.2984(17), Rh2−Si2 2.2951(17), Si1−Si2 2.388(2), Cl1−Rh1 2.3862(17), Cl1−Rh2 2.3871(17), Cl2−Rh3 2.3822(18), Cl3−Rh3 2.381(2); Si1−Rh1−Cl1 88.38(6), Si2−Rh2−Cl1 88.26(6), Rh1−Cl1−Rh2 126.34(7), Rh1−Si1−Si2 107.57(7), Rh2−Si2−Si1 108.04(7), N1−Si1−N2 71.3(2), N2−Si1−Rh1 118.04(16), N1−Si1−Si2 118.55(17), N3−Si2−N4 70.8(2), Cl3−Rh3−Cl2 92.00(7).

Compound **4** was characterized by NMR spectroscopy. Its ^{1}H and ^{13}C NMR spectra display resonances attributable to the amidinate and cod ligands. The ^{29}Si NMR spectrum of **4** exhibits a triplet at δ 195 ppm ($J_{\text{Si−Rh}}$ = 68.9 Hz) with coupling to the two rhodium atoms in the Si$_2$Rh$_2$ ring. It is downfield shifted as compared to that of **3** and the dinuclear transition metal bridged-silylene complexes (δ = 60−160 ppm).[13]

The molecular structure of **4** (Figure 3) shows that the Si$_2$Rh$_2$ ring is planar and rhombic. The Si1 and Si1A atoms, which adopt a distorted tetrahedral geometry, are coordinated with two nitrogen atoms of the amidinate ligands and two rhodium (Rh2 and Rh2A) atoms. The latter are also bonded to two bridging chlorine atoms to adopt a distorted planar geometry (the dihedral angle of Si1−Si1A−Rh2−Cl2, 172.74°; Si1−Si1A−Rh2A−Cl1A, 175.12°). The Si1−Rh2A (2.2001(5)

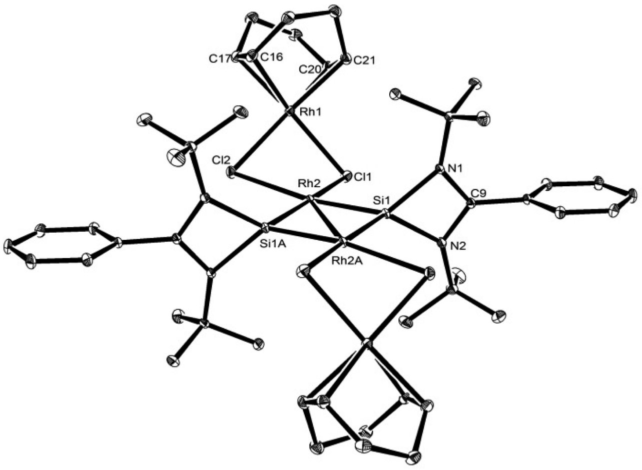
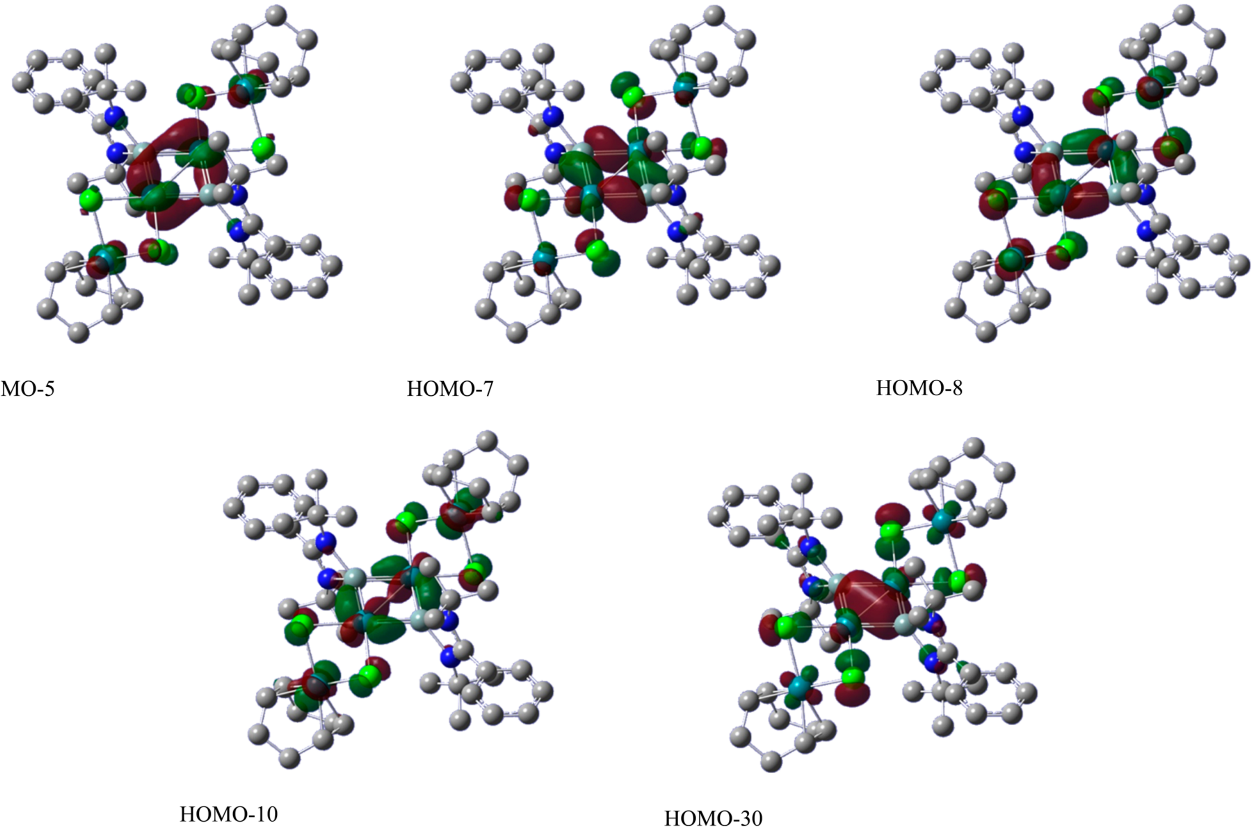


Figure 3. Molecular structure of **4** with thermal ellipsoids at the 50% probability level. Hydrogen atoms and solvent molecules are omitted for clarity. Selected bond lengths (Å) and angles (deg): Si1−Rh2 2.1792(5), Si1−Rh2A 2.2001(5), Rh2−Cl1 2.4346(4), Rh2−Cl2 2.4612(5), Rh1−Cl1 2.4015(5), Rh1−Cl2 2.4143(4), Si1−N1 1.8283(15), Si1−N2 1.8314(15), C9−N1 1.334(2), C9−N2 1.337(2); Si1−Rh2−Si1A 96.450(17), Rh2−Si1−Rh2A 83.552(17), Cl1−Rh2−Cl2 85.362(16), Si1−Rh2−Cl1 90.815(18), Si1A−Rh2−Cl2 88.065(17), N1−Si1−N2 71.19(7).

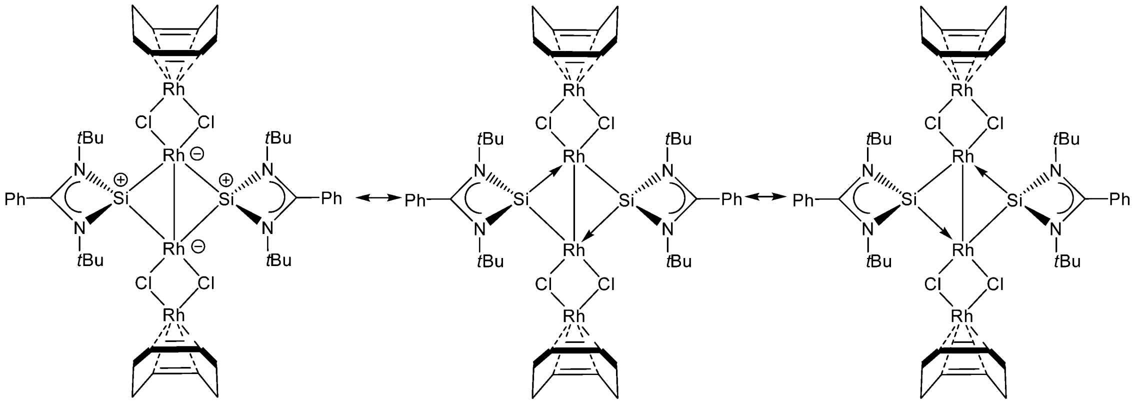


HOMO-5 HOMO-7 HOMO-8

HOMO-10 HOMO-30

Figure 4. Selected molecular orbitals of **4** (isovalue = 0.04).

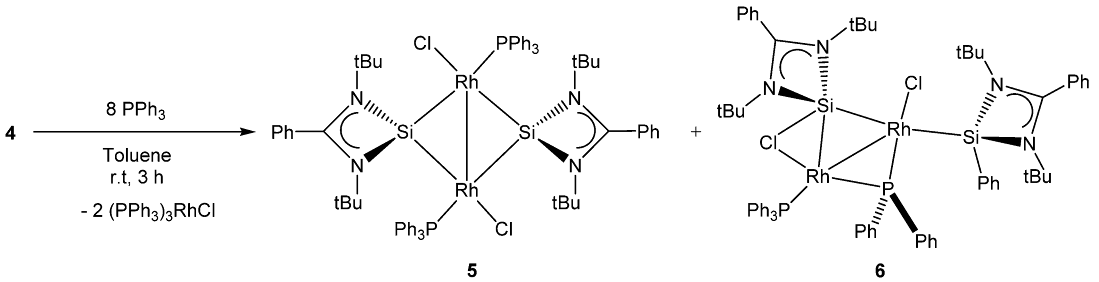
Scheme 3. Resonance Structures of Compound 4



Å) and Si1−Rh2 (2.1792(5) Å) bonds are almost identical, which are shorter than that of **3**. The results indicate that there is a significant π-back bonding from the Rh2/2A atoms to the Si1/1A atoms. Moreover, the Rh2−Rh2A bond length (2.9176(3) Å) indicates that it is a single bond.[14] Furthermore, the Si−N and C−N bonds of the amidinate ligands are comparable to those in **1** (Si−N, 1.866(4), 1.874(4); C−N, 1.331(6) Å).[6b]

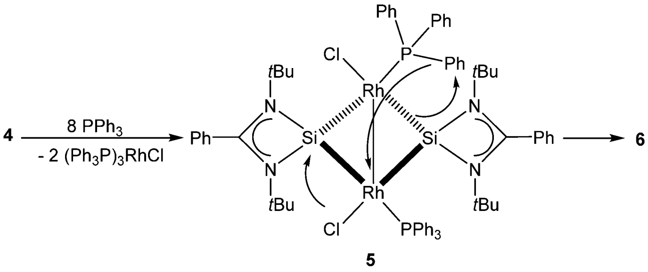
To understand the bonding nature in compound **4**, density functional theory (DFT) calculations were performed to characterize the chemical bonding.[15] The HOMO−30 (Figure 4) shows the lone pair electrons on the Si1/1A atoms donating to the Rh2/2A atoms. The HOMO−10 displays the Rh2−Rh2A interaction. The HOMO−7 and HOMO−8 demonstrate the Rh−Si σ orbitals. The HOMO−5 illustrates the π-back bonding from the Rh2/2A atoms to the Si1/1A atoms, which shortens the Si−Rh bonds. The large difference in NPA charges of the Rh2/2A and Si1/1A atoms (Rh, −0.85 e; Si, +1.64 e) implies that the Si−Rh bonds are highly polar. The Wiberg bond indices (WBI) of the Rh−Si bonds (0.728, 0.769) are slightly larger than that of the silyl rhodium(III) complex [$H_3Si-RhH_2$] (Si−Rh, 2.256 Å; WBI, 0.7103),[15] which imply that the Si−Rh bonds in **4** are single bonds. The Wiberg bond index of the Rh2−Rh2A bond (WBI: 0.229) implies that there is an interaction between the Rh2 and Rh2A atoms. These results illustrate that compound **4** is a dimer of two rhodosilylene complexes, which is illustrated in Scheme 3.

Scheme 4. Synthesis of 5 and 6



The reaction of **4** with excess PPh_3 afforded a mixture of the Wilkinson's catalyst $[(PPh_3)_3RhCl]$, the dimeric rhodosilylene complex $[(LSi)\mu\text{-}\{RhCl(PPh_3)\}]_2$ (**5**), and the rhodosilylene-phosphidorhodium dimer $(LSi)[\mu\text{-}\{RhCl(PPh_3)\}\mu\text{-}\{RhCl(LSiPh)\}](PPh_2)$ (**6**, Scheme 4). Volatiles were removed under vacuum. Extraction of the residue with Et_2O and hexane afforded a mixture of an orange crystalline solid of $[(PPh_3)_3RhCl]$ and a few pieces (ca. 3–7 pieces) of red crystals of **5**. An attempt to isolate pure compound **5** from the mixture by recrystallization failed. The mother liquor was filtered and further concentrated to obtain **6** as orange-red crystals (yield: 43%). The reaction appears to proceed through the displacement of "Rh(cod)Cl" moieties in **4** by PPh_3 to form **5** and $[(PPh_3)_3RhCl]$, respectively (Scheme 5). One of the silicon atoms in **5** undergoes a substitution reaction with PPh_3, which results in forming the phenylsilylene "LSiPh" and phosphido "Ph_2P^{-}" ligands. They coordinate to the Rh atoms, along with the coordination of the Cl atom to the Si^{II} atom, which lead to the formation of **6**. The mechanism was monitored by ^{31}P NMR spectroscopy. A mixture of **5** (δ = 53.0 ppm), $[(PPh_3)_3RhCl]$ (δ = 31.4, 48.2 ppm), and PPh_3 (δ = −4.77 ppm) was dissolved in C_6D_6 in a NMR tube. Upon standing overnight, ^{31}P NMR signals at δ = 28.8 and 223.4 ppm for compound **6** were observed.

Scheme 5. Proposed Mechanism for the Formation of 6



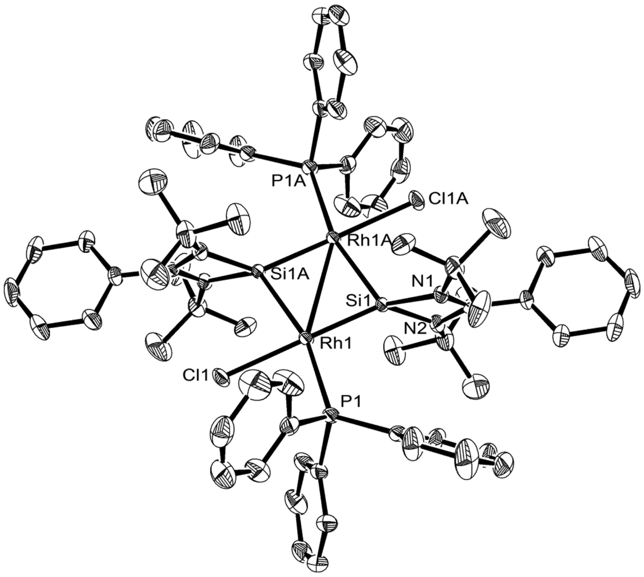


Figure 5. Molecular structure of **5** (50% thermal ellipsoids). Hydrogen atoms, the disordered *t*Bu substituents, and phenyl rings on P1 and P1A are omitted for clarity. Selected bond lengths (Å) and angles (deg): Si1−N1 1.824(3), Si1−N2 1.831(2), Si1−Rh1 2.1797(8), Si1−Rh1A 2.3046(8), Rh1−Rh1A 2.9294(4), Rh1−P1 2.3025(8), Rh1−Cl1 2.4224(8); N1−Si1−N2 71.51(11), Rh1A−Si1−N2 118.04(9), Rh1−Si1−Rh1A 81.52(3), Rh1−Si1−N1 135.84(9), Si1−Rh1−Si1A 98.48(3), Si1−Rh1−P1 98.51(3), P1−Rh1−Cl1 82.83(3), Si1A−Rh1−Cl1 80.60(3).

A mixture of $[RhCl(PPh_3)_3]$ and **5** was characterized by ^{31}P NMR spectroscopy. Because a few pieces of red crystals of **5** were isolated by recrystallization, its ^{29}Si and ^{13}C NMR spectroscopic signal cannot be obtained. On the basis of the ^{31}P NMR resonances of $[RhCl(PPh_3)_3]$ (δ = 48.1 and 31.2 ppm),[16] the ^{31}P NMR resonance of **5** (δ = 53.0 ppm, J_{P-Rh} = 195.08 Hz) can be identified in the spectrum.

The molecular structure of **5** (Figure 5) shows that the Si_2Rh_2 core is planar and rhombic, with the Si1−Rh1−Si1A and Rh1−Si1−Rh1A angles being 98.48(3)° and 81.52(3)°, respectively. The sum of the internal bond angles is 360.0°. The Si1 and Si1A atoms are tetracoordinated, each coordinated with two nitrogen atoms of the amidinate ligand and the two Rh atoms. The Rh1 and Rh1A atoms adopt an almost square planar geometry (the dihedral angle of Si1−Si1A−Cl1−Rh1/Si1A−Si1−Cl1A−Rh1A: 2.65°), with the sum of bond angles around the Rh1 atom being 360.42°. Each Rh atom is bonded to a PPh_3 ligand, a chloride atom, and two Si atoms. The Si1−Rh1 bond (2.1797(8) Å) is comparable to that of compound **4** (2.2001(5), 2.1792(5) Å). Because of the trans-influence of the PPh_3 ligand, the Si1−Rh1A bond (2.3046(8) Å) is elongated as compared to the above-mentioned.

Compound **6** exhibits poor solubility in hydrocarbon solvents and decomposes in polar solvents like pyridine and DCM. It is stable in the solid state at room temperature under an inert atmosphere. Compound **6** was characterized by spectroscopic methods and X-ray crystallography. The ^{1}H NMR spectrum of **6** displays two singlets (δ = 1.17 and 1.54 ppm) and multiplets (δ = 6.82–8.42 ppm) for the *t*Bu and phenyl substituents, respectively. The ^{29}Si CP-MAS NMR spectrum exhibits a doublet at δ = 60.3 ppm (d, J_{Si-Rh} = 72.7 Hz) for the LSiPh moiety, which is comparable to the amidinate-stabilized *tert*-butylsilylene [LSi*t*Bu] (δ = 61.5 ppm).[17] It also shows a broad signal (δ = 71.4 ppm) for the Si atom in the $SiPRh_2$ ring, which is significantly upfield shifted as compared to that of **4** due to the increment in the coordination number from four to five. The ^{31}P NMR spectrum exhibits resonances for PPh_3 (δ = 28.8 ppm) and the bridging phosphido substituent (δ = 223 ppm). The latter is comparable with those of dirhodium(I) complexes containing two bridging diphenylphosphido ligands and a Rh−Rh bond, for example, $[(Ph_3P)_2Rh(\mu\text{-}PPh_2)_2Rh(cod)]$ (δ = 216 ppm), and $[(Et_3P)_2Rh(\mu\text{-}PPh_2)_2Rh(cod)]$ (δ = 217 ppm).[18]

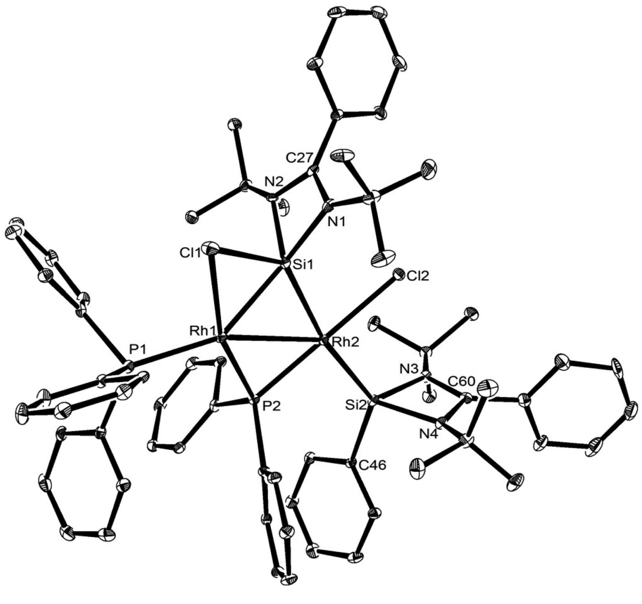


Figure 6. Molecular structure of **6** with thermal ellipsoids at the 30% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Si1−Rh1 2.2999(17), Si1−Rh2 2.3585(17), P2−Rh1 2.1806(15), P2−Rh2 2.1848(16), Rh1−Cl1 2.4611(16), Rh1−P1 2.2670(16), Si1−Cl1 2.384(2), Rh2−Si2 2.3090(16), Rh2−Cl2 2.4311(15), Si2−C46 1.900(6), Si1−N1 1.834(5), Si1−N2 1.825(5), Si2−N3 1.859(5), Si2−N4 1.844(5); Rh1−Si1−Rh2 74.80(5), Si1−Rh1−P2 102.48(6), Si1−Rh2−P2 100.49(6), Rh1−P2−Rh2 80.81(5), Cl1−Si1−Rh1 63.36(6), Rh1−Cl1−Si1 56.65(5), Cl1−Rh1−Si1 60.00(6), P1−Rh1−Si1 148.59(6), P1−Rh1−P2 102.81(6), P1−Rh1−Cl1 94.77(6), Cl2−Rh2−Si1 82.40(5), Cl2−Rh2−P2 174.56(6), Cl2−Rh2−Si2 86.65(6), N1−Si1−N2 71.3(2), N1−Si1−Cl1 91.03(17), N2−Si1−Cl1 97.07(17), N1−Si1−Rh1 148.18(18), N1−Si1−Rh2 122.45(17), N2−Si1−Rh1 127.24(18), N2−Si1−Rh2 118.40(17), N3−Si2−C46 98.1(2), N3−Si2−N4 71.3(2), N4−Si2−C46 101.0(2), Rh2−Si2−C46 130.91(19).

The molecular structure of **6** (Figure 6) shows that the $SiRh_2P$ ring is puckered (dihedral angle of Rh1−Si1−Rh2−P2: 8.87°). The amidinate ligand is bidentate bonded to the Si1 atom, which adopts a distorted trigonal bipyramidal geometry with the Cl1 and Rh2 atoms at the axial positions and the N1, N2, and Rh1 atoms at the equatorial positions. The Rh1 and Rh2 atoms adopt a distorted planar geometry with the Si1 atom at the trans position with respect to the LSiPh and PPh_3 moieties. The different extents of trans influences of LSiPh and PPh_3 moieties hinder the π-back bonding from the filled d orbitals at the Rh atoms to the empty p orbital at the Si1 atom. As a result, the Si1−Rh bonds (2.2999(17), 2.3585(17) Å) are lengthened and slightly unequal as compared to those in **4**. The Si1−Cl1 bond length of 2.384(2) Å, which is longer than that of [LSiCl] (2.156(1) Å), indicates a coordinative covalent bond between the Si1 and Cl1 atoms.[19] Such interaction is absent in compound **4**. Moreover, the P2 atom adopts a tetrahedral geometry. The P2−Rh bonds are equal (2.1806(15) and 2.1848(15) Å). They are also shorter than the Rh−P single bond (2.205(1)−2.392(1) Å) in the dirhodium(I) complex comprising bridging diphenylphosphido ligand and a Rh−Rh bond $[(Et_3P)_2Rh(\mu\text{-}PPh_2)_2Rh(cod)]$.[18] This indicates that the P2−Rh bonds in **6** have some multiple bond characters, which could be due to the π-back bonding from the Rh1 and Rh2 atoms to the P2 atom. The Rh1−Rh2 bond (2.8297(7) Å) is significantly shorter than the Rh−Rh bond in **4**.

In conclusion, the amidinate-stabilized silicon(I) dimer **1** can be a Lewis base to coordinate with "(cod)MCl" and "(cod)M$^+$" (M = Ir, Rh) moieties to form the base-stabilized silicon(I) dimer-iridium **2** and -rhodium **3** complexes, respectively. In case of rhodium, the Si−Si bond in **1** can also undergo an insertion reaction to form the dimeric rhodosilylene complex **4**. Its further reaction with PPh_3 afforded the rhodosilylene-phosphidorhodium dimer **6**. Their catalytic studies are under investigation.

■ EXPERIMENTAL SECTION

General Procedure. All manipulations were carried out under an inert atmosphere of argon gas using standard Schlenk techniques. THF, hexane, diethyl ether, and toluene were dried and distilled over NaK alloy prior to use. **1** was prepared as described in the literature.[6b] The ^{1}H, ^{13}C, and ^{29}Si spectra were recorded on a JEOL ECA 400 spectrometer. The chemical shifts (δ) are relative to $SiMe_4$ for ^{1}H, ^{13}C, and ^{29}Si. 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. Toluene (10 mL) was added to a mixture of **1** (0.103 g, 0.199 mmol) and $[Ir(cod)Cl]_2$ (0.134 g, 0.199 mmol) at ambient temperature. The mixture was allowed to stir for 16 h. After filtration, the filtrate was concentrated yielding red crystals of compound **2**. Yield: (0.0866 g, 29%). Mp 163 °C (dec). Anal. Calcd for $C_{54}H_{82}Cl_3Ir_3N_4Si_2$: C, 42.50; H, 5.41; N, 3.67. Found: C, 42.30; H, 5.19; N, 3.63. ^{1}H NMR (399.5 MHz, C_6D_6, 24.7 °C): δ = 1.59 (s, 36H, *t*Bu), 1.96−2.60 (br, 24H, CH_2), 3.48 (br, 4H, =CH), 4.28 (br, 4H, =CH), 5.37 (br, 4H, =CH), 6.96−7.13 (m, 8H, Ar−H), 8.67−8.69 ppm (m, 2H, Ar−H). ^{13}C{^{1}H} NMR (100.5 MHz, C_6D_6, 24.7 °C): δ = 31.62 (CMe_3), 32.11−32.82 (br, CH_2), 37.32 (=CH), 42.87 (=CH), 47.09 (=CH), 54.50 (=CH), 61.73 (CMe_3), 125.38, 129.98, 130.45, 131.99, 133.17 (Ph), 170.19 ppm (NCN). ^{29}Si{^{1}H} NMR (79.4 MHz, C_6D_6, 24.4 °C): δ = 73.53 ppm.

Synthesis of 3 and 4. Toluene (10 mL) was added to a mixture of **1** (0.103 g, 0.199 mmol) and $[Rh(cod)Cl]_2$ (0.0986 g, 0.200 mmol) at ambient temperature. The mixture was allowed to stir for 16 h. After filtration, the filtrate was concentrated yielding yellow crystals of compound **3**. The mother liquor was filtered and further concentrated to afford dark red crystals of compound **4**.

3: Yield, (0.095 g, 76%). Mp 135 °C (dec). Anal. Calcd for $C_{54}H_{82}Cl_3Rh_3N_4Si_2$: C, 51.55; H, 6.57; N, 4.45. Found: C, 51.45; H, 6.48; N, 4.34. ^{1}H NMR (399.5 MHz, C_6D_6, 24.7 °C): δ = 1.63 (s, 18H, *t*Bu), 1.70 (s, 18H, *t*Bu), 2.05−2.34 (br, 24 H, CH_2), 3.64 (br d, $^2J_{H-Rh}$ = 105.7 Hz, 4H, =CH), 4.32 (br, 4H, =CH), 5.88 (br d, $^2J_{H-Rh}$ = 41.6 Hz, 4H, =CH), 6.93−7.05 (m, 8H, Ar−H), 8.83−8.85 (m, 2H, Ar−H). ^{13}C{^{1}H} NMR (100.5 MHz, C_6D_6, 24.6 °C): δ = 30.62 (CMe_3), 31.90 (CMe_3), 33.23 (br, CH_2), 54.14 (br, CMe_3), 76.81 (d, J_{C-Rh} = 13.4 Hz, =CH), 78.30 (d, J_{C-Rh} = 14.4 Hz, =CH), 125.38, 129.94, 132.21, 133.19, 137.58 (Ph), 168.84 ppm (NCN). ^{29}Si{^{1}H} NMR (78.7 MHz, C_6D_6, 25.2 °C): δ 76.82 ppm (d, J_{Si-Rh} = 76.6 Hz).

4: Yield, (0.024 g, 19%). Mp 195.2 °C. Anal. Calcd for $C_{46}H_{70}Cl_4N_4Rh_4Si_2$: C, 42.88; H, 5.48; N, 4.35. Found: C, 42.61; H, 5.33; N, 4.01. ^{1}H NMR (395.9 MHz, C_6D_6, 24.5 °C): δ = 1.50 (s, 36H, *t*Bu), 1.56−1.60 (m, 8H, CH_2), 2.29−2.32 (m, 8H, CH_2), 4.67 (br s, 8H, =CH), 6.81−6.94 (m, 6H, Ph), 7.27−7.31 ppm (m, 4H, Ph). ^{13}C NMR (99.55 MHz, C_6D_6, 24.8 °C): $\delta = 30.92$ (C*Me*$_3$), 31.26 (CH_2), 32.22 (CH_2), 54.46 (CMe_3), 77.13 (d, $J_{C-Rh} = 13.4$ Hz, $=$CH), 78.55 (d, $J_{C-Rh} = 14.3$ Hz, $=$CH), 125.70, 128.85, 130.13, 131.65 (Ph), 172.75 ppm (NCN). ^{29}Si{^{1}H} NMR (79.52 MHz, C_6D_6, 25.0 °C): $\delta = 195.1$ ppm (t, $J_{Si-Rh} = 68.9$ Hz). UV/vis (DME): λ_{max} (ε) = 410 (2922), 634 (472 mol^{-1} dm^3 cm^{-1}) nm.

Synthesis of 5 and 6. A solution of PPh_3 (0.224 g, 0.852 mmol) in toluene (7.9 mL) was added dropwise at room temperature to the stirring solution of **4** (0.137 g, 0.107 mmol) in toluene (15.8 mL). The resultant reaction solution was stirred for an additional 3 h. Volatiles were removed under vacuum. Extraction of the residue with a mixture of Et_2O and hexane afforded **5** as red crystals. **5** was isolated as a mixture with $[Rh(PPh_3)_3Cl]$, which precipitated out as an orange solid. Attempts to obtain a pure sample of **5** by recrystallization failed. On the basis of the ^{31}P NMR resonances of $[RhCl(PPh_3)_3]$, the NMR resonances of **5** can be identified in the spectrum. ^{31}P{^{1}H} NMR (162 MHz, C_6D_6, 24.5 °C): $\delta = 53.00$ ppm (d, $J_{P-Rh} = 195.08$ Hz).

After crystallization of **5**, the mother liquor was filtered and further concentrated to obtain **6** as orange-red crystals. Yield: (0.061 g, 43%). Mp 213.5 °C (dec). Anal. Calcd for $C_{66}H_{76}Cl_2N_4P_2Rh_2Si_2$: C, 60.05; H, 5.80; N, 4.24. Found: C, 59.75; H, 5.63; N, 4.15. ^{1}H NMR (399.5 MHz, C_6D_6, 24.7 °C): $\delta = 1.17$ (s, 18H, *t*Bu), 1.54 (s, 18H, *t*Bu), 6.82–6.98 (m, 18H, Ph), 7.08–7.12 (m, 7H, Ph), 7.41–7.50 (m, 5H, Ph), 7.61–7.66 (m, 8H, Ph), 8.13–8.15 (m, 1H, Ph), 8.40–8.42 ppm (m, 1H, Ph). ^{13}C NMR (99.55 MHz, C_6D_6, 24.9 °C): $\delta = 31.37$, 31.59 (C*Me*$_3$), 53.78, 54.80 (CMe_3), 126.70, 126.83, 127.08, 127.38, 127.52, 127.69, 128.76, 128.86, 128.93, 129.73, 130.14, 130.64, 132.19, 132.98, 133.69, 133.88, 134.00, 134.94, 135.28, 135.44, 136.68, 137.03 (Ph), 169.81, 174.06 ppm (NCN). ^{31}P{^{1}H} NMR (162 MHz, C_6D_6, 24.5 °C): $\delta = 28.77$ (br d, $J_{P-Rh} = 200.8$ Hz, PPh_3), 223.40 ppm (t, $J_{P-Rh} = 149.5$ Hz, PPh_2). ^{29}Si CP-MAS: $\delta = 60.31$ (d, $J_{Si-Rh} = 72.7$ Hz, Si(Ph)), 71.43 (br, Si) ppm. No detectable signal was observed in the solution ^{29}Si NMR spectrum.

X-ray Data Collection and Structural Refinement. Intensity data for compounds **2–6** were collected using a Bruker APEX II diffractometer. Their crystals were measured at 103(2) K. The structures were solved by a direct phase determination (SHELXS-97) and refined for all data by full-matrix least-squares methods on F^2.[20] All non-hydrogen atoms were subjected to anisotropic refinement. The hydrogen atoms were generated geometrically and allowed to ride on their respective parent atoms; they were assigned appropriate isotopic thermal parameters and included in the structure-factor calculations.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorgchem.5b01759.

Table S2 giving crystallographic data of compounds **2–6**, and details of DFT calculations of compound **4** (PDF)

X-ray data for compounds **2–6** (CIF)

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work is supported by ASTAR SERC PSF Grant.

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DOI: 10.1021/acs.inorgchem.5b01759
Inorg. Chem. 2015, 54, 9968−9975