

Organocalcium Complex-Catalyzed Selective Redistribution of ArSiH_3 or $\text{Ar}(\text{alkyl})\text{SiH}_2$ to Ar_3SiH or $\text{Ar}_2(\text{alkyl})\text{SiH}$

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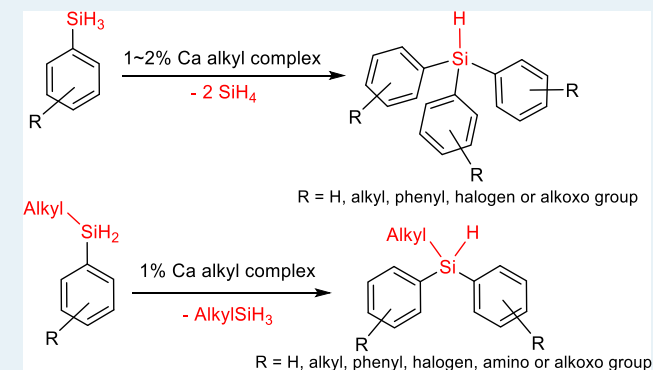
Supporting Information

ABSTRACT: Calcium is an abundant, biocompatible, and environmentally friendly element. The use of organocalcium complexes as catalysts in organic synthesis has had some breakthroughs recently, but the reported reaction types remain limited. On the other hand, hydrosilanes are highly important reagents in organic and polymer syntheses, and redistribution of hydrosilanes through C–Si and Si–H bond cleavage and reformation provides a straightforward strategy to diversify the scope of such compounds. Herein, we report the synthesis and structural characterization of two calcium alkyl complexes supported by β -diketiminato-based tetradentate ligands. These two calcium alkyl complexes react with PhSiH_3 to generate calcium hydrido complexes, and the stability of the hydrido complexes depends on the supporting ligands. One calcium alkyl complex efficiently catalyzes the selective redistribution of ArSiH_3 or $\text{Ar}(\text{alkyl})\text{SiH}_2$ to Ar_3SiH and SiH_4 or $\text{Ar}_2(\text{alkyl})\text{SiH}$ and alkylSiH_3 , respectively. More significantly, this calcium alkyl complex also catalyzes the cross-coupling between the electron-withdrawing substituted $\text{Ar}(\text{R})\text{SiH}_2$ and the electron-donating substituted $\text{Ar}'(\text{R})\text{SiH}_2$, producing $\text{ArAr}'(\text{alkyl})\text{SiH}$ in good yields. The synthesized $\text{ArAr}'(\text{alkyl})\text{SiH}$ can be readily transferred to other organosilicon compounds such as $\text{ArAr}'(\text{alkyl})\text{SiX}$ (where $\text{X} = \text{OH}, \text{OEt}, \text{NEt}_2$, and CH_2SiMe_3). DFT investigations are carried out to shed light on the mechanistic aspects of the redistribution of $\text{Ph}(\text{Me})\text{SiH}_2$ to $\text{Ph}_2(\text{Me})\text{SiH}$ and reveal the low activation barriers (17–19 kcal/mol) in the catalytic reaction.

KEYWORDS: calcium, catalysis, DFT, hydrosilane, redistribution

INTRODUCTION

Calcium is an abundant, biocompatible, and environmentally friendly element. The organocalcium chemistry has attracted researchers' attention for more than a century since, for example, Beckmann reported his attempts on the synthesis of a calcium aryl complex in 1905.^{1,2} However, although calcium has the advantages of low cost and environmentally benign nature, the use of organocalcium complexes as catalytic reagents in organic synthesis did not gain momentum until recently. The development of calcium catalysts has lagged far behind that of transition-metal catalysts, which is mainly associated with the following features: (1) the divalent calcium ion lacks the d-electrons, which are perceived as crucial for catalytic reactions and (2) the calcium alkyl and hydrido complexes, which are the best candidates for catalysis, are rare.^{3–5} The groups of Harder, Hill, Okuda, and others have made some pioneer contributions in developing organocalcium complexes as catalysts. They synthesized several calcium alkyl, hydrido, and amido complexes and demonstrated their efficiency as catalysts in organic synthesis.^{3–9} However, the reported reaction types catalyzed by organocalcium complexes remain limited and are mainly focused on the hydrogenation or



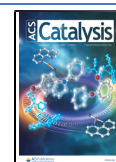
hydroelementation of alkenes (or alkynes), dehydrocoupling of aminoboranes, and dehydrocoupling of silanes with terminal alkynes (or amines).

Hydrosilanes are highly important reagents in organic and polymer syntheses.¹⁰ The redistribution of hydrosilanes is a straightforward strategy to diversify the scope of such compounds.¹¹ However, the poor selectivity and low efficiency severely hindered the application of this synthetic protocol.¹² First, the hydrosilanes can undergo dehydrocoupling to give oligo- or polysilanes, where the redistribution is, in fact, a side reaction.¹³ Second, the redistribution reactions usually provide a mixture of primary, secondary, tertiary, and quaternary silanes.¹⁴ Examples of highly selective hydrosilane redistribution are quite rare (Scheme 1). Tanaka and co-workers briefly reported that $\{\text{RuCl}_2[\text{P}(\text{C}_6\text{H}_4\text{Me-}p)_3]_3\}$ catalyzes the selective

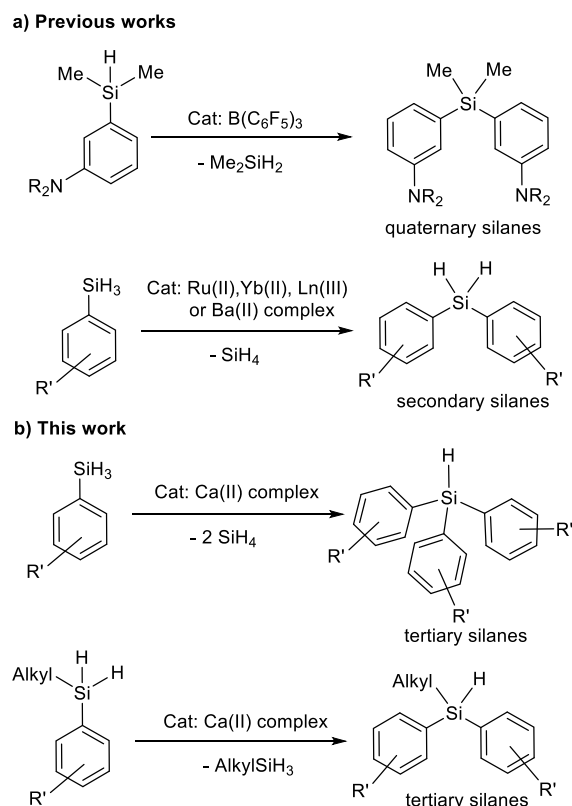
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Scheme 1. Selective Redistribution of Arylsilanes

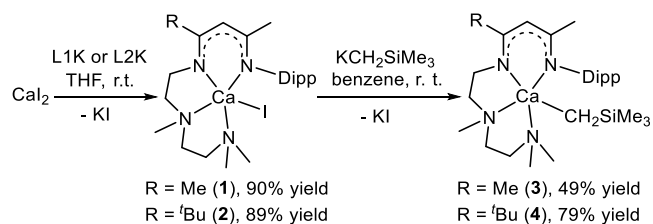


redistribution of trihydrophenylsilane and trihydro(*p*-tolyl)silane to dihydrodiphenylsilane and dihydrodi(*p*-tolyl)silane, respectively, with the elimination of SiH_4 .¹⁵ Hou and co-workers reported that $\text{B}(\text{C}_6\text{F}_5)_3$ catalyzes the redistribution of tertiary silanes containing electron-rich aromatic substituents to quaternary silanes with good selectivity.¹⁶ Recently, we found that a divalent ytterbium alkyl complex catalyzes the redistribution of primary arylsilanes to selectively provide a series of secondary arylsilanes as well as the cross-coupling between the electron-withdrawing substituted primary arylsilanes and electron-donating substituted primary arylsilanes to secondary arylsilanes containing two different aryls.¹⁷ After our report, Luo and co-workers reported that the hybrid materials $\text{Ln}(\text{CH}_2\text{C}_6\text{H}_4\text{-NMe}_2\text{-o})_3@ \text{SBA-15}$ ($\text{Ln} = \text{La}, \text{Y}$) are also able to catalyze the selective redistribution of primary arylsilanes to secondary arylsilanes, although the catalytic activity is much lower than that of the divalent ytterbium alkyl complex.¹⁸ Very recently, Cheng and co-workers reported the selective redistribution of primary arylsilanes to secondary arylsilanes catalyzed by a heteroleptic barium aminobenzyl complex.¹⁹ However, the selective redistribution of primary arylsilanes to tertiary arylsilanes as well as aryl- and alkyl-substituted secondary silanes $\text{Ar}(\text{R})\text{SiH}_2$ to tertiary silanes $\text{Ar}_2(\text{R})\text{SiH}$ remain challenging. There was a report that shows that alkali-metal complexes and $\text{Ba}(\text{OC}_8\text{H}_{17})_2$ catalyze the redistribution of trihydrophenylsilane to hydrotriphenylsilane, but the yields were not ideal.²⁰ The radius of calcium(II) ion is very close to that of the ytterbium(II) ion [Ca^{2+} (1.00 Å) and Yb^{2+} (1.02 Å) for the coordination number of 6],²¹ and recent studies showed that the catalytic properties of organocalcium complexes are somewhat similar to those of divalent organoytterbium complexes. Therefore, after we disclosed the selective redistribution of primary arylsilanes to secondary

arylsilanes catalyzed by a divalent ytterbium alkyl complex, we investigated the synthesis of the related calcium alkyl complex and its catalytic properties toward the redistribution of primary arylsilanes. Interestingly, the synthesized calcium alkyl complex catalyzes the redistribution of primary arylsilanes to provide tertiary arylsilanes in excellent yields with the elimination of SiH_4 (Scheme 1). More significantly, the calcium alkyl complex is also able to catalyze the redistribution of $\text{Ar}(\text{alkyl})\text{SiH}_2$ to $\text{Ar}_2(\text{alkyl})\text{SiH}$ as well as the cross-coupling between the electron-withdrawing substituted $\text{Ar}(\text{alkyl})\text{SiH}_2$ and electron-donating substituted $\text{Ar}'(\text{alkyl})\text{SiH}_2$ to $\text{ArAr}'(\text{alkyl})\text{SiH}$ with the elimination of alkylSiH_3 .

RESULTS AND DISCUSSION

Synthesis and Structural Characterization of Calcium Complexes. Reactions of CaI_2 with the potassium salt L1K $\{\text{L1} = [\text{MeC}(\text{NDipp})\text{CHC}(\text{Me})\text{NCH}_2\text{CH}_2\text{N}(\text{Me})\text{-CH}_2\text{CH}_2\text{NMe}_2]^-\}$, Dipp = 2,6-(*i*-Pr)₂C₆H₃} or L2K $\{\text{L2} = [\text{MeC}(\text{NDipp})\text{CHC}(\text{tBu})\text{NCH}_2\text{CH}_2\text{N}(\text{Me})\text{CH}_2\text{CH}_2\text{NMe}_2]^-\}$ in tetrahydrofuran (THF) at room temperature provide calcium iodides, **1** and **2**, with 90 and 89% yields, respectively (Scheme 2). The desired calcium alkyl complexes, **3** and **4**, are

Scheme 2. Synthesis of Calcium Alkyl Complexes **3** and **4**

subsequently synthesized from the reaction of calcium iodides, **1** and **2**, with $\text{KCH}_2\text{SiMe}_3$ in benzene at room temperature with 49 and 79% yields. Complexes **1**–**4** are characterized by NMR spectroscopy [^1H , ^{13}C (^1H)] and elemental analysis, the structures of **3** and **4** are further confirmed by single-crystal X-ray diffraction. The molecular structure of **4** is shown in Figure 1, while that of **3** is given in the Supporting Information. The structural features of **3** and **4** are very similar, and **4** is taken as the example. In **4**, the calcium adopts a distorted square pyramidal geometry according to the τ value of 0.14, with the four nitrogen atoms of L2 forming the basal plane and a carbon

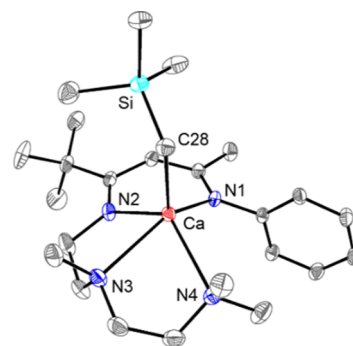
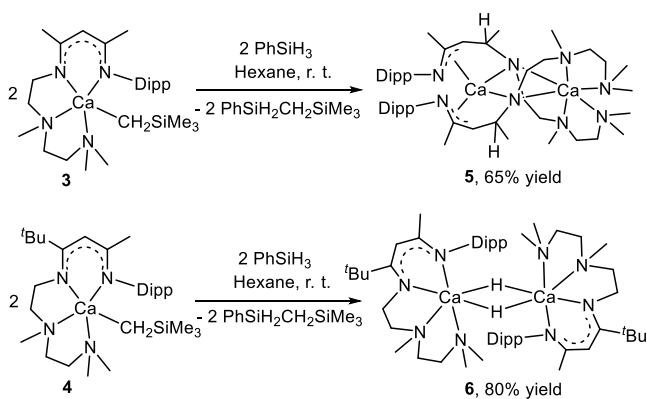


Figure 1. Molecular structure of complex **4** with ellipsoids set at 30% probability level. Dipp isopropyl groups and hydrogen atoms are omitted for clarity. Selected bond distances [Å]: Ca–N1 2.3643(11), Ca–N2 2.3719(12), Ca–N3 2.5371(12), Ca–N4 2.5998(12), and Ca–C28 2.5079(14).

atom of the alkyl group in the apical position. The bond lengths of Ca–N3 and Ca–N4 [2.5371(12) and 2.5998(12) Å, respectively] are significantly longer than those of Ca–N1 and Ca–N2 [2.3643(11) and 2.3719(12) Å, respectively], as the N3 and N4 atoms are the neutral donors, while the N1 and N2 atoms act as the anionic ones. The Ca–C bond length is 2.5079(14) Å, which is similar to that in a calcium terminal alkyl complex {Ca[CH(SiMe₃)₂](THF)₂} [2.4930(18) Å].²² This bond length is also close to that reported for a divalent ytterbium alkyl complex (L1YbCH₂SiMe₃) [2.510(4) Å],¹⁷ which is reasonable as the Ca²⁺ and Yb²⁺ ions have very similar ion radii. In the ¹H NMR spectra of **3** and **4** recorded in C₆D₆, the Ca–CH₂ appears as two broad signals at $\delta = -1.18$ and -1.48 ppm for **3** and $\delta = -1.23$ and -1.39 ppm for **4**, indicating that the rotation of –CH₂SiMe₃ group in the complexes is hindered. The ¹³C(¹H) NMR spectra of **3** and **4** show the appearance of Ca–CH₂ signals at $\delta = 6.4$ ppm for **3** and 6.5 ppm for **4**.

Complex **3** reacts with PhSiH₃ at room temperature to yield complex **5** (Scheme 3), which is formed from an addition of

Scheme 3. Reactions of Calcium Alkyl Complexes **3** and **4** with PhSiH₃



the Ca–H bond of the initially formed calcium hydride to one C=N bond of ligand L1. A similar addition has been previously observed in the reaction of an yttrium dimethyl complex containing the same supporting ligand [LYMe₂] with PhSiH₃.²³ On the other hand, the reaction of complex **4** with PhSiH₃ gives a calcium hydride **6**, indicating that the presence of a bulky *tert*-butyl group inhibits the addition of the Ca–H bond to C=N. Single crystals of **5** and **6** are obtained and analyzed by X-ray crystallography. The molecular structure of **5** is shown in Figure S2 in the Supporting Information, and the structural parameters of **5** are in line with the addition of H[−] to the monoanionic ligand L1, which forms a dianionic ligand. Complex **6** exists as a dimer, in which each of the calcium ions is coordinated by four nitrogen atoms of L2 and two bridging hydrides (Figure 2). The Ca–H bond lengths, 2.25(3) and 2.21(3) Å, are comparable to those in a dimeric calcium hydride supported by the bulky bidentate ketiminato ligand [(Dipp-nacnac)CaH(THF)]₂ {Dipp-nacnac = [MeC(NDipp)CHC(NDipp)Me][−], Dipp = 2,6-(ⁱPr)₂C₆H₃}, 2.09(4)–2.21(3) Å.²⁴ The ¹H NMR spectrum of **6** in C₆D₆ at 25 °C shows two sets of signals, indicating that there are two isomers in the solution. Some signals are broad and overlapped, but increasing the temperature from 25 to 75 °C results in the broadening and coalescence of the resonances followed by sharpening of the resulting coalesced signals. The Ca–H signal

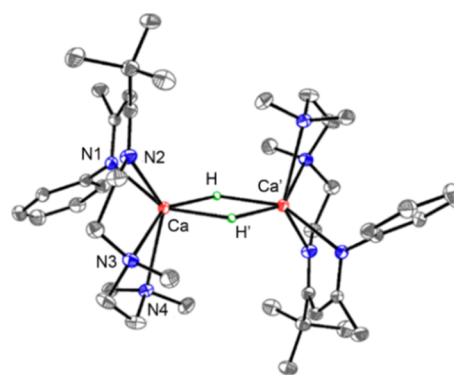
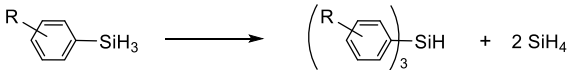
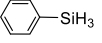
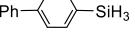
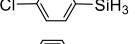
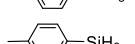
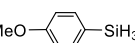
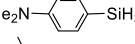
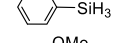
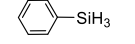
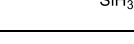
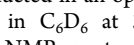


Figure 2. Molecular structure of complex **6** with ellipsoids at 30% probability level. Dipp isopropyl groups and hydrogen atoms (except CaH and CaH') are omitted for clarity. Selected bond distances [Å]: Ca–N1 2.417(2), Ca–N2 2.402(2), Ca–N3 2.607(2), Ca–N4 2.650(2), Ca–H 2.25(3), Ca–H' 2.21(3), and Ca⋯Ca' 3.574(1).

appears at $\delta = 4.74$ ppm at 65 °C, close to that in [(Dipp-nacnac)CaH(THF)]₂ (4.45 ppm). The ¹H DOSY NMR experiments in C₆D₆ at 25 °C reveals that these two isomers are both dimers, which have the hydrodynamic radii of 6.75 Å (see the Supporting Information for details).

Catalytic Activity of Calcium Complexes. Although the divalent ytterbium alkyl complex [L1YbCH₂SiMe₃] and the calcium alkyl complex **3** catalyze the redistribution of PhSiH₃ to produce diarylsilane Ph₂SiH₂ as the main product by eliminating one SiH₄ molecule, the calcium alkyl complex **4** efficiently catalyzes the redistribution of PhSiH₃ to triarylsilane Ph₃SiH by eliminating two SiH₄ molecules (Table 1, entry 3 vs entries 1 and 2). When the reaction with 1 mol % of **4** is conducted in an open system under argon at 37 °C and stirred rapidly to facilitate the dissipation of SiH₄ gas, >99% of PhSiH₃ is consumed in 40 min and Ph₃SiH and Ph₂SiH₂ are produced in 57 and 41% yields, respectively. As the redistribution is reversible, the dissipation of volatile SiH₄ promotes the conversion of PhSiH₃ into products.¹⁷ Upon increasing the reaction time to 2 h, the generated Ph₂SiH₂ mostly converts into Ph₃SiH, and the yield of Ph₃SiH increases to 92%. The calcium hydride **6** shows a similar reactivity (slightly higher reactivity at the beginning), indicating that the hydride, which is generated from the reaction of the alkyl complex with arylsilane, is the real catalytic species in the catalytic cycle. Complex **4** can also efficiently catalyze the conversion of *p*-Ph-C₆H₄SiH₃ into triarylsilane (*p*-Ph-C₆H₄)₃SiH, with the yield of (*p*-Ph-C₆H₄)₃SiH being 84% in 2 h. Under the same reaction conditions, the electron-withdrawing –Cl- or –F-substituted arylsilanes rapidly undergo the redistribution reaction to give the triarylsilanes (95% yield for the –Cl-substituted substrate and 91% yield for the –F-substituted one in 40 min, Table 1, entries 6 and 7). The redistribution of *p*-Me-C₆H₄SiH₃ or *p*-OMe-C₆H₄SiH₃ is slower than that of PhSiH₃, which is related to the electronic effect of –Me and –OMe. Reactivity decrease induced by the electron-donating group at the para-position had also been observed in the divalent ytterbium complex-catalyzed arylsilane redistribution.¹⁷ This reactivity can be increased by increasing the reaction temperature as the reactions at 50 °C provide (*p*-Me-C₆H₄)₃SiH and (*p*-OMe-C₆H₄)₃SiH in 96 and 93% yields, respectively, in 3 h using 2 mol % of **4** as the catalyst (Table 1, entries 8 and 9). The reactivity of these arylsilanes follows the order Cl > F > H > Ph > Me > OMe, which is in line with that of their Hammett

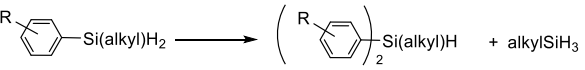
Table 1. Redistribution of ArSiH₃ to Ar₃SiH and SiH₄^a


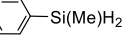
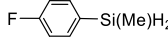
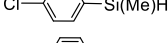
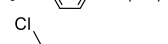
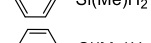
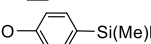
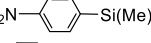
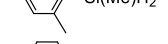
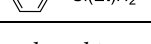
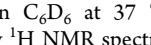
entry	cat	ArSiH ₃	40 min		2 h	
			conv. (%) ^b	yield (%) ^b	conv. (%) ^b	yield (%) ^b
1	[Yb] (1%) ^c		99	25(73) ^d	99	42(56) ^d
2	3 (1%)		99	9(89) ^d	99	21(77) ^d
3	4 (1%)		>99	57(41) ^d	>99	92
4	6 (0.5%) ^e		>99	68(31) ^d	>99	95
5	4 (1%)		-	-	>99	84(16) ^d
6	4 (1%)		>99	95	>99	97
7	4 (1%)		>99	91(8) ^d	>99	94
8 ^f	4 (2%)		>99 ^g	89 ^g (11) ^d	>99 ^h	96 ^h
9 ^f	4 (2%)		>99 ^g	83 ^g (16) ^d	>99 ^h	93 ^h
10 ^f	4 (2%)		>99 ^g	6 ^g (93) ^d	>99 ^h	10 ^h (89) ^d
11 ^f	4 (2%)		>99 ^g	95 ^g	>99 ^h	99 ^h
12	4 (1%)		99	43(53) ^d	>99	90
13	4 (1%)		0	0	0	0

^aReactions are conducted in an open system under argon with 1 or 2 mol % of catalyst in C₆D₆ at 37 °C, [ArSiH₃] = 1.36 mol/L. ^bDetermined by ¹H NMR spectroscopy using 1,3,5-trimethylbenzene as the internal standard. ^c[Yb] = [LYbCH₂SiMe₃]. ^dThe value in parenthesis is the yield of diarylsilane. ^eComplex **6** is a dimer; therefore, 0.5 mol % of **6** is used. ^fReaction temperature is 50 °C. ^gReaction time is 120 min. ^hReaction time is 180 min.

constants Cl (0.23) > F (0.06) > H (0) > Ph (−0.01) > Me (−0.17) > OMe (−0.27).²⁵ When *p*-NMe₂-C₆H₄SiH₃ is the substrate, the reaction produces diarylsilane (*p*-NMe₂-C₆H₄)₂SiH₂ as the main product (Table 1, entry 10). The low reactivity of *p*-NMe₂-C₆H₄SiH₃ can be ascribed to the strong electron-donating property of −NMe₂, and the −NMe₂ group may also form a coordinate bond with the metal center and reduce the reactivity of the metal catalyst. Complex **4** also efficiently catalyzes the conversion of *m*-Me-C₆H₄SiH₃ and *o*-OMe-C₆H₄SiH₃ into corresponding triarylsilanes, (*m*-Me-C₆H₄)₃SiH and (*o*-OMe-C₆H₄)₃SiH (Table 1, entries 11 and 12). Under the same reaction conditions, alkylsilanes such as *n*-C₆H₁₃SiH₃ do not undergo the redistribution reaction to give the dialkylsilane or trialkylsilane (Table 1, entry 13).

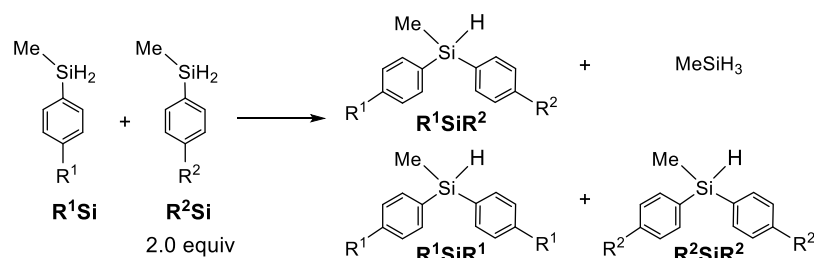
The selective redistribution of aryl- and alkyl-substituted secondary silanes Ar(alkyl)SiH₂ to tertiary silanes Ar₂(alkyl)SiH by eliminating alkylSiH₃ has not been reported before. Interestingly, calcium alkyl complex **4** is able to catalyze this reaction, and its catalytic activity is much higher than those of [LYbCH₂SiMe₃] and calcium alkyl complex **3** (Table 2, entry 3 vs entries 1 and 2). In the presence of 1 mol % of **4**, 92% of Ph(Me)SiH₂ is consumed and Ph₂(Me)SiH is produced in 91% yield in 2 h when the reaction is conducted in an open system under an argon atmosphere at 37 °C and stirred rapidly to facilitate the dissipation of MeSiH₃ gas. The elimination of

Table 2. Redistribution of Ar(alkyl)SiH₂ to Ar₂(alkyl)SiH and AlkylSiH₃^a


Entry	Cat	Ar(alkyl)SiH ₂	40 min		2 h	
			conv. (%) ^b	yield (%) ^b	conv. (%) ^b	yield (%) ^b
1	[Yb]		28	27	37	36
2	3		13	12	18	17
3	4		59	58	92	91
4	4		85	84	94	93
5	4		78 ^c	77 ^c	91 ^d	89 ^d
6	4		90 ^c	89 ^c	94 ^d	93 ^d
7	4		97	94	99	96
8	4		36	35	86 ^e	85 ^e
9	4		34	33	83 ^e	82 ^e
10 ^f	4		60 ^g	59 ^g	75 ^e	74 ^e
11 ^f	4		51 ^g	50 ^g	67 ^e	65 ^e
12	4		50	48	84	82

^aReactions are conducted in an open system under argon with 1 mol % of catalyst in C₆D₆ at 37 °C, [Ar(alkyl)SiH₂] = 1.36 mol/L. ^bDetermined by ¹H NMR spectroscopy using 1,3,5-trimethylbenzene as the internal standard. ^cReaction time is 10 min. ^dReaction time is 20 min. ^eReaction time is 180 min. ^fReaction temperature is 50 °C and 5 mol % of catalyst is used. ^gReaction time is 120 min.

MeSiH₃ from the reaction is confirmed by the ¹H NMR spectral monitoring of the reaction in a sealed NMR tube (δ = 3.58 ppm, 3H, MeSiH₃; δ = −0.12 ppm, 3H, MeSiH₃). Similar to that observed in the redistribution of ArSiH₃ to Ar₃SiH, introducing electron-withdrawing substituents, such as −F, −Cl, or −CF₃, at the para-position of Ar group increases the reactivity of Ar(Me)SiH₂ (Table 2, entries 4–6). The reaction of (*p*-F-C₆H₄)₂(Me)SiH₂ gives (*p*-F-C₆H₄)₂(Me)SiH in 84% yield in 40 min and 93% yield in 2 h. For the substrates with a −Cl or −CF₃ substituent, the reactions are even faster [89% yield of (*p*-Cl-C₆H₄)₂(Me)SiH and 93% yield of (*p*-CF₃-C₆H₄)₂(Me)SiH in 20 min]. (*m*-Cl-C₆H₄)₂(Me)SiH₂ also rapidly undergoes the redistribution reaction, providing 94% yield of (*m*-Cl-C₆H₄)₂(Me)SiH in 40 min. On the other hand, the substrates containing electron-donating substituents display lower reactivity (Table 2, entries 8–10), even though the redistribution of the substrates with −Me or −OMe substituent in the para-position provides the corresponding Ar₂(Me)SiH in 85 and 82% yields, respectively, in 3 h. For (*p*-NMe₂-C₆H₄)₂(Me)SiH₂, using an increased amount of **4** (5 mol %) and performing the reaction at an elevated temperature (50 °C), the tertiary silane can be obtained with 74% yield. The introduction of a methyl substituent at the ortho-position of Ar decreases the reactivity [with 5 mol % of **4**, the reaction of (*o*-Me-C₆H₄)₂(Me)SiH₂ at 50 °C provides (*o*-Me-C₆H₄)₂(Me)SiH in 65% yield in 3 h]. In the presence of **4** (1 mol %), Ph(Et)SiH₂ also undergoes redistribution to

Table 3. Cross-Coupling between Ar(Me)SiH₂ and Ar'(Me)SiH₂^{a,b}

entry	substrate	time (min)	yield (%)		
			R ¹ SiR ²	R ¹ SiR ¹	R ² SiR ²
1	R ¹ = CF ₃ , R ² = H	30	89	<2	18
2	R ¹ = CF ₃ , R ² = F	30	82	17	45
3	R ¹ = CF ₃ , R ² = Me	30	84	<2	9
4	R ¹ = CF ₃ , R ² = OMe	30	81	<2	7
5	R ¹ = CF ₃ , R ² = NMe ₂	30	59	35	<2
6	R ¹ = CF ₃ , R ² = NMe ₂	70	96	<2	<2
7	R ¹ = Cl, R ² = H	70	81	16	49
8	R ¹ = Cl, R ² = F	70	72	28	65
9	R ¹ = Cl, R ² = Me	70	78	18	26
10	R ¹ = Cl, R ² = OMe	70	73	19	22
11	R ¹ = Cl, R ² = NMe ₂	70	58	41	<2
12	R ¹ = Cl, R ² = NMe ₂	140	73	15	<2
13	R ¹ = F, R ² = Me	140	62	38	36
14	R ¹ = F, R ² = OMe	140	61	35	34

^aReactions are conducted in an open system under argon with 2 mol % of catalyst [related to Ar(Me)SiH₂] in C₆D₆ for 30, 70, or 140 min at 37 °C, [Ar(Me)SiH₂] = 0.5 mol/L, [Ar'(Me)SiH₂] = 1.0 mol/L. ^bThe yields are determined by ¹H NMR spectroscopy using 1,3,5-trimethylbenzene as the internal standard; the yields of R¹SiR² and R¹SiR¹ are calculated based on the amount of R¹Si used, while those of R²SiR² are based on the amount of R²Si used.

produce Ph₂(Et)SiH by eliminating EtSiH₃ in 82% yield in 2 h at 37 °C (Table 2, entry 12).

Compared to the homo-coupling of Ar(R)SiH₂, the cross-coupling between two different Ar(R)SiH₂ is more challenging due to the easy homo-coupling side reactions. Fascinatingly, complex 4 is able to catalyze the cross-coupling of the electron-withdrawing -CF₃- or -Cl-substituted Ar(Me)SiH₂ with -H-, -F-, -Me-, -OMe-, or -NMe₂-substituted Ar(Me)SiH₂ to give the corresponding tertiary silanes, containing one alkyl and two different aryl groups, in good yields (72–96% yields) (Table 3, one of the substrates is used in 2.0 equiv). The cross-coupling of (*p*-CF₃-C₆H₄)(Me)SiH₂ with Ar(R)SiH₂ containing -H-, -F-, -Me-, or -OMe at the para-position of Ar is also fast (with 2 mol % of 4 as the catalyst, the reactions at 37 °C provide the cross-coupling products in 81–89% yields in 30 min). On the other hand, the reaction of (*p*-CF₃-C₆H₄)(Me)SiH₂ with (*p*-NMe₂-C₆H₄)(Me)SiH₂ is slower, as (*p*-CF₃-C₆H₄)(*p*-NMe₂-C₆H₄)Si(Me)H is obtained in only 59% yield in 30 min. The slower reaction is in line with the lower reactivity of (*p*-NMe₂-C₆H₄)(Me)SiH₂, being similar to that observed in the homocoupling of (*p*-NMe₂-C₆H₄)(Me)SiH₂. A high yield of (*p*-CF₃-C₆H₄)(*p*-NMe₂-C₆H₄)Si(Me)H can be achieved by increasing the reaction time to 70 min, which gives the product in 96% yield. The yield of the homo-coupling product (*p*-CF₃-C₆H₄)₂Si(Me)H decreases from 35% to <2%; this is reasonable as the Si-C_{Ar} bond of (*p*-CF₃-C₆H₄)₂Si(Me)H can be easily cleaved that enables (*p*-CF₃-C₆H₄)₂Si(Me)H to react with excess (*p*-NMe₂-C₆H₄)(Me)SiH₂ in the system to yield (*p*-CF₃-C₆H₄)(*p*-NMe₂-C₆H₄)Si(Me)H. The cross-coupling reactions of (*p*-Cl-C₆H₄)(Me)SiH₂ with -H-, -F-, -Me-, or -OMe-substituted Ar(Me)SiH₂ afford the

cross-coupling products in 72–81% yields in 70 min, and with -NMe₂-substituted Ar(Me)SiH₂ in 73% yield in 140 min. The selectivity for the cross-coupling of the -F-substituted Ar(Me)SiH₂ with -Me- or -OMe-substituted Ar(Me)SiH₂ is not high, providing the cross-coupling products in 62 and 61% yields in 140 min. This is reasonable as the difference in the electronic properties between -F and -Me or -OMe is not significant; the Hammett constants of -F, -Me, and -OMe are 0.06, -0.17, and -0.27, respectively.²⁵ The cross-coupling products (*p*-CF₃-C₆H₄)PhSi(Me)H, (*p*-CF₃-C₆H₄)(*p*-Me-C₆H₄)Si(Me)H, (*p*-CF₃-C₆H₄)(*p*-OMe-C₆H₄)Si(Me)H, (*p*-CF₃-C₆H₄)(*p*-NMe₂-C₆H₄)Si(Me)H, (*p*-Cl-C₆H₄)PhSi(Me)H, (*p*-Cl-C₆H₄)(*p*-Me-C₆H₄)Si(Me)H, (*p*-Cl-C₆H₄)(*p*-OMe-C₆H₄)Si(Me)H, (*p*-Cl-C₆H₄)(*p*-NMe₂-C₆H₄)Si(Me)H, (*p*-F-C₆H₄)(*p*-Me-C₆H₄)Si(Me)H, and (*p*-F-C₆H₄)(*p*-OMe-C₆H₄)Si(Me)H are isolated and characterized by NMR spectroscopy (¹H, ¹³C, ¹⁹F, and ²⁹Si) and high-resolution mass spectrometry (see the Supporting Information for details).

Further Transformation of the Cross-Coupling Product. The cross-coupling product has one reactive Si-H bond and therefore may react further. To demonstrate this possibility, the cross-coupling of (*p*-CF₃-C₆H₄)(Me)SiH₂ with (*p*-NMe₂-C₆H₄)(Me)SiH₂ is scaled up to gram scale, and (*p*-CF₃-C₆H₄)(*p*-NMe₂-C₆H₄)Si(Me)H is obtained and tested for further transformation. First, (*p*-CF₃-C₆H₄)(*p*-NMe₂-C₆H₄)Si(Me)H is treated with H₂O in THF at room temperature using 0.3 mol % of [RhCl(CO)₂]₂ as a catalyst. After 30 min, (*p*-CF₃-C₆H₄)(*p*-NMe₂-C₆H₄)Si(Me)OH is obtained in 91% yield, in which -H is selectively replaced by -OH (Scheme 4). Accordingly, treatment of (*p*-CF₃-

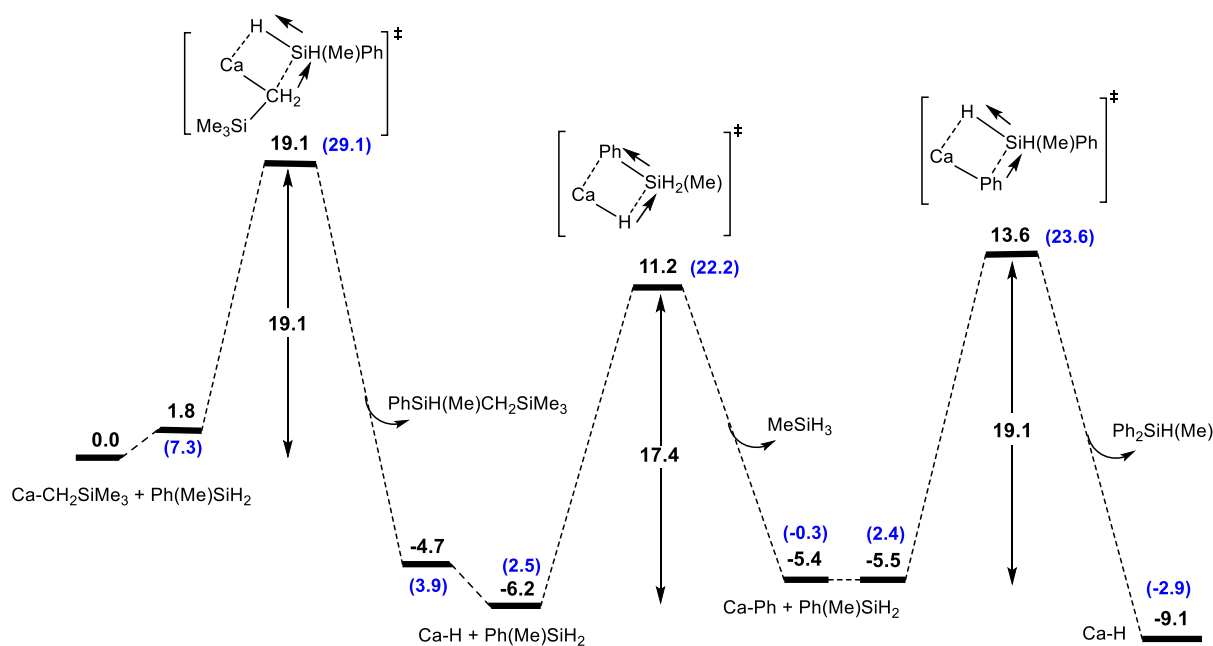
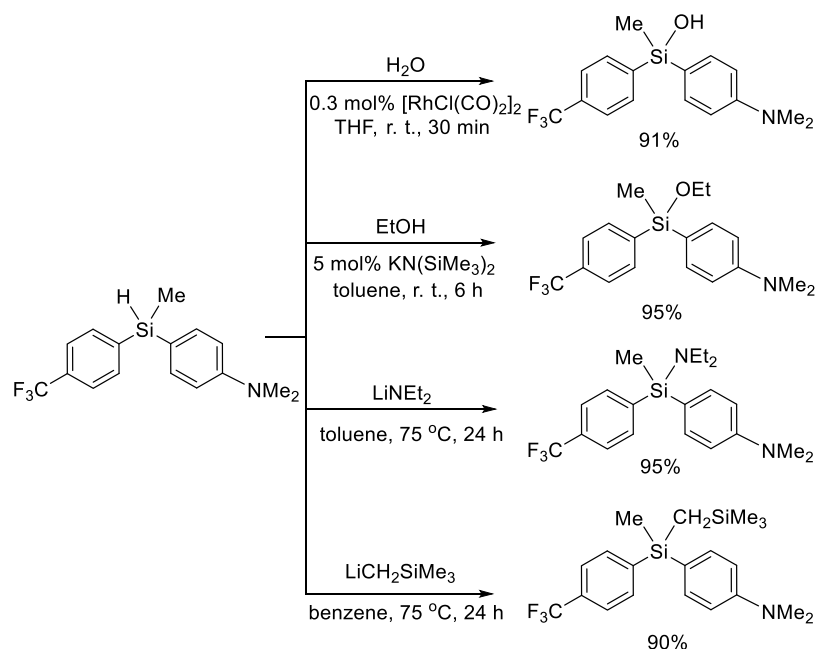
Scheme 4. Transformation of $(p\text{-CF}_3\text{-C}_6\text{H}_4)(p\text{-NMe}_2\text{-C}_6\text{H}_4)\text{Si}(\text{Me})\text{H}$ into Other Organosilicon Compounds

Figure 3. Computed enthalpy profile at the DFT (B3PW91) level for the redistribution reaction of $\text{Ph}(\text{Me})\text{SiH}_2$ catalyzed by **4**. Energy values are shown in kcal/mol. Gibbs free energy is given within brackets.

$\text{C}_6\text{H}_4)(p\text{-NMe}_2\text{-C}_6\text{H}_4)\text{Si}(\text{Me})\text{H}$ with EtOH in toluene for 6 h in the presence of 5 mol % of $\text{KN}(\text{SiMe}_3)_2$ produces $(p\text{-CF}_3\text{-C}_6\text{H}_4)(p\text{-NMe}_2\text{-C}_6\text{H}_4)\text{Si}(\text{Me})\text{OEt}$ in 95% yield. $(p\text{-CF}_3\text{-C}_6\text{H}_4)(p\text{-NMe}_2\text{-C}_6\text{H}_4)\text{Si}(\text{Me})\text{H}$ also reacts with LiNEt_2 in toluene at 75 °C to give $(p\text{-CF}_3\text{-C}_6\text{H}_4)(p\text{-NMe}_2\text{-C}_6\text{H}_4)\text{Si}(\text{Me})\text{NEt}_2$ in 95% yield in 24 h. It also reacts with $\text{LiCH}_2\text{SiMe}_3$ in benzene at 75 °C to provide $(p\text{-CF}_3\text{-C}_6\text{H}_4)(p\text{-NMe}_2\text{-C}_6\text{H}_4)\text{Si}(\text{Me})\text{CH}_2\text{SiMe}_3$ in 90% yield in 24 h.

DFT Calculations. In order to get insights into the reaction mechanism, DFT calculations (B3PW91) were carried out on the redistribution reaction of a typical secondary silane $\text{Ph}(\text{Me})\text{SiH}_2$ in the presence of complex **4** (Figure 3). The redistribution process begins by Si–H activation of $\text{Ph}(\text{Me})\text{SiH}_2$ by complex **4**.

The other transition states were computed, namely, Si–H activation with silicon at the α position and Si–C activation with silicon at the β position (see Figures S167 and S168 in the Supporting Information) and are found to be higher in energy by 5.6 and 36.6 kcal/mol, respectively, so that they can be discarded. After the formation of a silane adduct (almost athermic, 1.8 kcal/mol), a Si–H σ -bond metathesis transition state with silicon at the β position is achieved. The associated activation barrier is 19.1 kcal/mol, indicating a kinetically accessible step. The geometry around the silicon is a slightly distorted trigonal bipyramid (TBP) with the exchanged hydrogen and alkyl groups occupying the equatorial and apical positions, respectively. Interestingly, the alkyl group is

reoriented with an elongated Ca–C bond (2.58 Å) in order to have the lone pair pointing toward the calcium atom, and the interaction between the calcium and the alkyl group is ensured by a strong α -agostic interaction. The Ca–H bond is not yet formed (2.49 Å) and the activated Si–H one is elongated (from 1.49 to 1.59 Å) as the hydrogen interacts with Ca (Ca–H distance, 2.27 Å). Following the intrinsic reaction coordinate, it yields the calcium hydride (whose dimerization is computed to be favorable by 13.2 kcal/mol, but that is quite unlikely to occur under catalytic conditions due to the low concentration of the formed hydride and also because the dimerization barrier is computed to be 15.5 kcal/mol) with the release of the tertiary silane $(\text{Ph})(\text{Me})\text{Si}(\text{H})(\text{CH}_2\text{SiMe}_3)$ that is observed experimentally. This step is exothermic by 4.7 kcal/mol. The formed hydride can thus react with another molecule of $\text{Ph}(\text{Me})\text{SiH}_2$ (see also Figure S169). The reaction begins by the formation of a stable silane adduct (–6.2 kcal/mol). Rather than the unproductive Si–H activation (H/H exchange), the system undergoes a Si–C activation reaction. Such a reaction was also reported to be kinetically accessible and favored over Si–H activation with the silicon at the α position by Perrin et al. in their study of hydrosilylation of alkene catalyzed by Cp_2^*SmH .²⁶ The associated transition state is again an σ -bond metathesis one with the silicon at the β position. The geometry is also a slightly distorted TBP around the silicon where the hydride lies in the equatorial plane and the phenyl ring is in the apical position. The Si–H bond almost formed (1.67 Å), while the Ca...C distance remains long (3.04 Å). However, the *ipso* carbon of the phenyl ring is bent in the direction of the calcium indicating that although small, an interaction exists between the two centers. The barrier is slightly lower than the first one (17.4 kcal/mol) in line with a kinetically accessible step. The system further evolves with the formation of a calcium phenyl complex and the liberation of MeSiH_3 that is observed experimentally, and whose formation is exothermic by 5.4 kcal/mol from the entrance channel (almost athermic +0.8 kcal/mol from calcium hydride formation). Finally, the calcium phenyl complex reacts with a molecule of silane $\text{Ph}(\text{Me})\text{SiH}_2$. After weak coordination of silane (0.1 kcal/mol), the system reaches a Si–H activation transition state (TS) with silicon at the β position. This TS has similar features as those of the Si–C activation one which was just described above. Indeed, the hydrogen lies in the equatorial plane, whereas the phenyl is in the apical position. The Si–H bond is elongated to 1.63 Å allowing a Ca–H interaction at 2.26 Å. The Ca–phenyl distance has also been strongly elongated to 2.93 Å (2.47 Å in the calcium phenyl complex) but remains bent toward Ca. The second phenyl ring lies in the equatorial plane, whereas the methyl is in the apical position. The associated barrier is 19.1 kcal/mol, which is similar to the first barrier, indicating that the hydride formation, which is the actual catalyst, is the rate-determining step of the reaction. Following the intrinsic reaction coordinate, it yields the silane distribution product $\text{SiH}(\text{Me})(\text{Ph})_2$ and regenerates the calcium hydride. The overall redistribution reaction is exothermic by 9.1 kcal/mol. The substituent effect has been investigated by computing the redistribution reaction for $(p\text{-CF}_3\text{-C}_6\text{H}_4)(\text{Me})\text{SiH}_2$ (Table 2, entry 6). The computed reaction profile (Figure S170) is quite similar to that reported for $\text{PhSi}(\text{Me})\text{H}_2$ (Figure 3), but the energies are found to be lower. Following the Curtin–Hammett principle, since the rate-determining step of the reaction is the last step (redistribution TS), the difference in the activity of the two substrates only depends on the TS

energies (13.6 for $R' = p\text{-H}$ vs 9.5 kcal/mol for $R' = p\text{-CF}_3$) so that the activity for the latter is greater than that of the former.

CONCLUSIONS

In summary, organocalcium complexes supported on a β -diketiminato-based tetradentate ligand (L1 or L2) are synthesized and structurally characterized, and their application as catalysts for the redistribution of hydrosilanes is explored. The supporting ligands L1 and L2 can both stabilize the calcium alkyl complex, while for calcium hydride, only the one with L2 which contains a bulky *tert*-butyl group is obtained. The calcium alkyl complex supported by L2 efficiently catalyzes the redistribution of ArSiH_3 or $\text{Ar}(\text{alkyl})\text{SiH}_2$ to Ar_3SiH and SiH_4 or $\text{Ar}_2(\text{alkyl})\text{SiH}$ and alkylSiH_3 , respectively, and its catalytic performance is much better than those of the calcium alkyl complex supported by L1 and a reported divalent ytterbium alkyl complex. This calcium alkyl complex also catalyzes the cross-coupling between the electron-withdrawing, substituted $\text{Ar}(\text{R})\text{SiH}_2$ and the electron-donating, substituted $\text{Ar}'(\text{R})\text{SiH}_2$ to provide $\text{ArAr}'(\text{alkyl})\text{SiH}$ in good yields, and the synthesized $\text{ArAr}'(\text{alkyl})\text{SiH}$ can be easily transferred to other organosilicon compounds based on its Si–H bond transformation. Therefore, this protocol provides new opportunities to synthesize various arylsilanes. Both experimental and theoretical studies indicate that calcium hydride is the real catalytic species in the catalytic cycle. The reaction sequence is demonstrated to involve three steps (catalyst formation, Ca–Ph formation, and catalyst regeneration) which exhibit similar low activation barriers (17–19 kcal/mol) in line with a facile reaction.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acscatal.1c00463>.

Experimental and computational details and X-ray crystallography structure data (PDF)

Crystallographic information on complex 3 (CCDC 2043282) (CIF)

Crystallographic information on complex 4 (CCDC 2043283) (CIF)

Crystallographic information on complex 5 (CCDC 2043284) (CIF)

Crystallographic information on complex 6 (CCDC 2043285) (CIF)

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

Caution: SiH₄ and MeSiH₃ are pyrophoric.

Crystallographic data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK; fax: +44 1223336033.

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