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Unexpected Formation of Polydentate Phosphinoalkyl−Silyl and −Germyl Ligands from Reaction of [$MoH_4(Ph_2PCH_2CH_2PPh_2)_2$] with Organosilanes and Organogermanes: Novel Activation of Mo−H, E−H (E = Si, Ge), and C−H Bonds in the Same System

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Reaction of [$MoH_4(Ph_2PCH_2CH_2PPh_2)_2$] (**1**) with $PhEH_3$ (E = Si, Ge) in refluxing toluene yielded the novel complexes [$MoH_3\{[Ph_2PCH_2CH_2P(Ph)C_6H_4\text{-}o]_2(Ph)E\text{-}P,P,P,P,E\}$] (E = Si (**2**), Ge (**3**)) with a quinquidentate ligand comprised of a P−P−E−P−P framework as a result of the oxidative addition involving E−H bond cleavage with concomitant selective activation of the ortho C−H bonds of the two dppe ligands. When secondary Ph_2SiH_2 was employed in a similar reaction with **1**, a trihydrido complex with a tridentate ligand ([$Ph_2PCH_2CH_2P(Ph)C_6H_4\text{-}o]Ph_2Si\text{-}P,P,Si$) comprised of a P−P−Si framework was isolated. On the other hand, the reaction between Ph_2GeH_2 and **1** proceeded with accompanying evolution of 1 mol of benzene to give **3**; that is, in addition to the Ge−H and C−H activation, Ge−C(Ph) bond cleavage took place. It is concluded that the reaction path includes the intermediacy of silylene or germylene metal complexes via an α-migration process on the basis of deuterium-labeling studies.

Introduction

Compounds that contain an interelement linkage[1] of M−E (M = transition metals; E = group 14 elements) have a longstanding history in the field of organometallic chemistry. They are highly important as active species in catalytic addition of the linkage to unsaturated organic substrates. Most of the effort in this area has been focused on the synthesis of silicon complexes.[2] A metal−silicon single bond is unique and often displays unusual properties, such as unexpectedly short bond distances or high bond energies, which are not yet fully understood.[3] In addition, the electron-releasing properties and strong trans influence of silyl ligands may alter or enhance the catalytic performance of transition-metal catalysts.[4]

The oxidative addition of organosilanes or organogermanes to transition-metal complexes and their reductive elimination from the silyl− or germyl−hydridometal complexes are generally accepted to be reversible; they involve η^2-E−H (E = Si, Ge) σ complexes as the common intermediates. Recently Kubas and co-workers have examined the reaction of molybdenum complexes, $Mo(CO)(R_2PCH_2CH_2PR_2)_2$ (R = Ph or Et), with silanes[5] and germanes.[6] They observed the formation of σ-silane or σ-germane complexes, which are in tautomeric equilibrium with their oxidative addition products in solution. They pointed out that studies of the interaction between such $Mo(PP)_2$ (PP = diphosphine) complexes and the E−H bond may provide valuable insight into the factors that influence catalytic transformations of organosilanes and organogermanes.

We have reported versatile reactivities of the coordinatively unsaturated intermediate $MoH_n(dppe)_2$ ($n = 2$, 0; dppe = $Ph_2PCH_2CH_2PPh_2$), which is generated photochemically or thermally from [$MoH_4(dppe)_2$] (**1**),[7]

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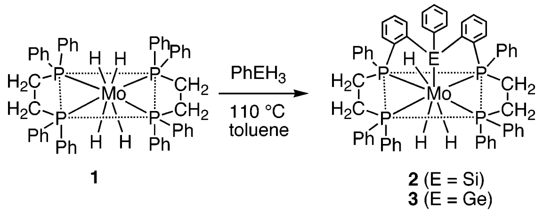
10.1021/om0401298 CCC: $30.25

Scheme 1



toward various substrates involving the selective C−H, C−O, O−H, or N−H bond cleavage.[8] On the basis of these studies, we have studied the reactivity of **1** toward organosilanes and organogermanes. To our surprise, the resulting polyhydrido complexes possess unusual quintuply chelated ligands comprised of a P−P−E−P−P framework. Preliminary accounts have been published.[9]

Results and Discussion

Reaction of 1 with 1 Equiv of Primary Silanes and Germane in Toluene. Heating a toluene solution of **1** under reflux in the presence of 1 equiv of PhEH$_3$ for 3 h afforded the unanticipated complexes **2** (E = Si) and **3** (E = Ge) as yellow solids (Scheme 1).

In the solid state, the complexes are stable indefinitely under an inert atmosphere; in organic solvents, they are also stable in the absence of oxygen. It is well-known that polyhydrido silyl-containing transition-metal complexes are often not isolated but, instead, lose dihydrogen to afford transition-metal silyl products. As a consequence, relatively few polyhydrido transition-metal silyl complexes have been characterized.[10]

Complexes **2** and **3** exhibited very similar spectroscopic features and will be described and discussed together. The IR spectra of these complexes showed ν(Mo−H) at 1714 cm^{-1} for **2** and at 1808 cm^{-1} for **3**. We could not observe the characteristic E−H absorptions[11] at around 2100 cm^{-1}, suggesting that these bonds are absent in the resulting complexes.

The ^{1}H NMR spectra of the complexes in benzene-d_6 at room temperature showed multiplet signals between δ −3.9 and −4.7 ppm for **2** and between δ −3.7 and −4.6 ppm for **3**. These signals in the high-field region are assignable to Mo−H protons; they are analyzed as a set of a broad triplet (**2**, δ −4.15; **3**, δ −3.90) with apparent coupling constant values of 33 (**2**) and 48 Hz (**3**) and a broad quintet (**2**, δ −4.45; **3**, δ −4.40) with apparent coupling constant values of 35 (**2**) and 29 Hz (**3**). The integration ratio of the former and the latter was found to be 1:2. In addition, the ratio of the total intensity of these signals to that of the CH$_2$CH$_2$ signals in the dppe ligand was found to be 3:8. Low-temperature ^{1}H NMR (−50 °C, toluene-d_8) only led to broadening of the hydrido groups. However, we observed that, on raising the temperature, these signals gradually coalesced and finally became a simple quintet (**2**, 90 °C; **3**, 105 °C). Upon cooling of the samples to room temperature, the signals returned to their original multiplet patterns.

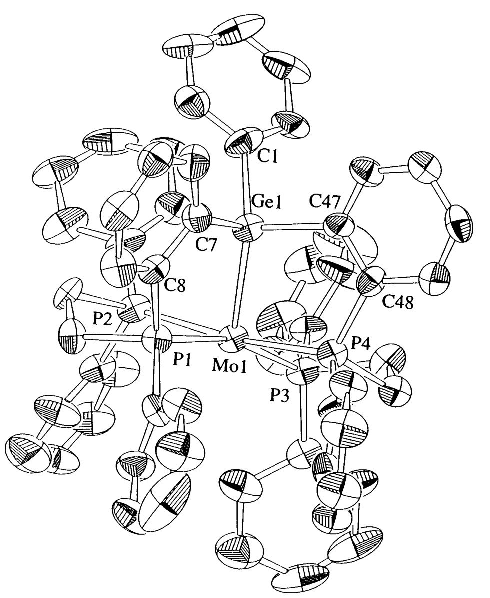


Figure 1. ORTEP drawing of the molecular structure of **3**.

T_1 measurements in ^{1}H NMR are a useful method for distinguishing classical from nonclassical structures in transition-metal polyhydrides.[12] In complex **2**, the T_1 values measured at room temperature at 400 MHz were found to be 90 ms for the signal at δ −4.45 ppm and 96 ms for the signal at δ −4.15 ppm. These values seem to be consistent with a coordinate classical polyhydride.[12c] The ^{31}P{^{1}H} NMR spectra of **2** and **3** revealed two doublets (**2**, δ 81.4, 110.2; **3**, δ 83.8, 113.8) with coupling constant values of 61 (**2**) and 55 Hz (**3**), indicating the presence of two chemically different P nuclei. There were virtually no changes in the ^{31}P{^{1}H} NMR spectra of **2** in toluene-d_8 measured at room temperature and at 90 °C.

To determine the bonding pattern for the new complex **3**, a single-crystal X-ray analysis was carried out (Figure 1). Yellow crystals of **3** suitable for the analysis were obtained by recrystallization from toluene/hexane at 0 °C. Selected bond lengths and angles are listed in Table 1. Although the hydride ligands were not able to be located directly in the molecular structure, their presence was confirmed by means of ^{1}H NMR spectroscopy (vide supra). As shown in Figure 1, the structure reveals a striking feature, in which the phenylgermanium group and the two dppe ligands are now linked by new carbon−germanium bonds. Thus, complex **3** contains bonds between the germanium atom and the ortho carbons of the phenyl groups in the dppe ligands constructing a novel quinquidentate ligand. The formation of complex **3** is itself very novel, because activation

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[11] The IR spectra of PhEH$_3$ showed ν(E−H) at 2157 cm^{-1} (E = Si) and at 2072 cm^{-1} (E = Ge).

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Table 1. Interatomic Distances (Å) and Angles (deg) for 3

	Distances		
Mo1−P1	2.456(4)	Mo1−P2	2.457(5)
Mo1−P3	2.449(5)	Mo1−P4	2.436(5)
Ge1−Mo1	2.587(2)	Ge1−C1	2.03(2)
Ge1−C7	1.96(2)	Ge1−C47	2.03(2)
	Angles		
P1−Mo1−P2	80.6(2)	P2−Mo1−P3	102.0(2)
P3−Mo1−P4	80.8(2)	P1−Mo1−P4	98.8(2)
Ge1−Mo1−P1	76.8(1)	Ge1−Mo1−P2	111.6(6)
Ge1−Mo1−P3	119.1(1)	Ge1−Mo1−P4	93.9(1)
Mo1−Ge1−C1	125.5(7)	Mo1−Ge1−C7	78.8(1)
Mo1−Ge1−C47	106.6(5)	C1−Ge1−C7	106.8(9)
C7−Ge1−C47	101.4(8)	C47−Ge1−C1	101.9(9)

of not only the Ge−H bonds but also two ortho C−H bonds takes place in the same system.

The total of the bond angles P1−Mo1−P2, P2−Mo1−P3, P3−Mo1−P4, and P4−Mo1−P1 is 362.2°, which confirms the planarity of the P−P−Mo−P−P moiety. A survey of the Cambridge Crystallographic Database revealed that the Mo1−Ge1 bond distance of 2.587(2) Å lies in the usual region for Mo−Ge single-bond lengths in molybdenum−germyl complexes (2.5−2.7 Å). The most intriguing aspect of the structure of **3** is that the Mo1−P1 bond length (2.456(4) Å) is nearly equal to that of the Mo1−P2 bond (2.457(5) Å), indicating that the resultant germanium−carbon linkages do not affect these bonds, although P1−Mo1−P4 is slightly compressed (98.8(2)°) and P2−Mo1−P3 is slightly enlarged (102.0(2)°).

The structure can be compared with that of the parent complex **1**[13] and the closely related molybdenum−germanium complex MoH(GeH$_2$Ph)(CO)(Et$_2$PCH$_2$CH$_2$PEt$_2$)$_2$ (**A**).[6] The Ge1−C1 bond distance of 2.03(2) Å is similar to that of 1.998(3) Å in **A**. On the other hand, the Mo1−Ge1 bond distance of 2.587(2) Å is considerably shorter than that of 2.6693(5) Å in **A**. Presumably this is due to the chelating constraint imposed by the P−P−Ge−P−P framework. The P2−Mo1−P3 bond angle of 102.0(2)° is nearly identical with that found in **1** (101.56(2)°). In addition, the mean Mo−P bond length of 2.450 Å in **3** is only slightly longer than that exhibited by **1** (2.420 Å).

Subsequently, the reactivity of **1** toward a series of primary silanes was studied. Various kinds of primary silanes containing ortho-hindered (**2b**), electron-withdrawing (**2c**), electron-donating (**2d**), and even aliphatic substituents (**2e**,**f**) reacted with **1** to give the corresponding complexes similar to **2**. Preparative and selected spectroscopic data are compiled in Tables 2 and 3.

In ^{1}H NMR, the hydride resonances for the C$_6$F$_5$ compound **2c** are shifted to lower field by about 0.2 ppm, while those for the 4-Me$_2$NC$_6$H$_4$ compound **2d** are shifted to higher field by about 0.05 ppm versus the corresponding resonances for the phenyl compound **2**. A higher field shift compared to **2** is also observed in the pair **2e**,**f**. Taking into account the electronic effect of these substituents, the present results are expected.

Table 2. Preparation of [MoH$_3${[Ph$_2$PCH$_2$CH$_2$P(Ph)C$_6$H$_4$-*o*]$_2$(R)E-*P*,*P*,*P*,*P*,*E*}]

	substrate			
compd	amt of **1**, mmol	RSiH$_3$ (R)/ amt, mmol	amt of toluene, mL	yield, %
2a	0.251	*p*-CH$_3$C$_6$H$_4$/0.254	20	75
2b	0.224	*o*-CH$_3$C$_6$H$_4$/0.896	20	83
2c	0.570	C$_6$F$_5$/0.860	15	85
2d	0.334	4-(CH$_3$)$_2$NC$_6$H$_4$/0.502	15	85
2e	0.580	*n*-C$_6$H$_{13}$/0.860	40	75
2f	0.223	cyclo-C$_6$H$_{11}$/0.334	40	79
3	0.301	PhGeH$_3$/0.301	30	60

At present, the structure of **2** remains somewhat ambiguous, as no crystals suitable for X-ray diffraction are available and combustion analyses have been repeatedly unsatisfactory, except for **2f**.[14] However, the similarity of the ^{1}H and ^{31}P{^{1}H} NMR spectra of **2** and **3**, along with the results of the following section, strongly suggests that **2** and **3** have similar structures.

Reaction of 1 with Excess Primary Silanes in Toluene. When the reaction was carried out in the presence of more than 2 equiv of PhSiH$_3$, a yellow solid of **4** was obtained in 78% yield (Scheme 2). We found that **4** is also derived from **2** by its reaction with excess PhSiH$_3$ in refluxing toluene. The fact that **4** and **2** were obtained in a stepwise manner starting from **1** strongly suggests that **4** is formed via oxidative addition of the second molecule of PhSiH$_3$ to **2**.

X-ray-quality crystals of **4** were successfully grown from a toluene/hexane solution. The molecular structure is depicted in Figure 2; selected bond distances and angles are listed in Table 4. There are two Si atoms in the molecule: one (Si1) is present in the usual terminal SiH$_2$Ph ligand and another (Si2) contains bonds between the silyl atom and the ortho carbons of the phenyl groups in the dppe ligands, constructing a novel quinquidentate ligand.

The coordination environment of the molybdenum atom is found to be entirely analogous to that of **3**. Hence, the reaction proceeded in a manner similar to that in the case of the PhGeH$_3$ system. Combustion analysis data for the diffraction-quality crystals were in accord with the formulation of the complex determined by the diffraction study. Although the hydride ligands were not able to be located directly in the molecular structure, their presence was confirmed by means of ^{1}H NMR spectroscopy (vide infra). It is noteworthy that the Mo−Si1 bond distance of 2.620(2) Å is slightly elongated relative to that of Mo−Si2 by 0.06 Å, suggestive of the exceptional character of the silyl group as a trans-influencing ligand.[15] The structure can be compared and contrasted with that of the parent complex **1** and the germanium complex **3**. The P1−Mo−P3 bond angle of 101.39(7)° is nearly identical to that found in **1** (101.56(2)°). In addition, the mean Mo−P bond length of 2.471 Å in **4** is only slightly longer than that exhibited by **1** (2.420 Å). These observations indicate that the formation of the new bonds between the silicon and the ortho carbons of the phenyl groups

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[14] Microanalyses were performed, but none of the products, except for **2f** (Anal. Calcd for C$_{58}$H$_{60}$P$_4$MoSi: C, 69.31; H, 6.02. Found: C, 69.56; H, 6.10), could be analyzed properly; carbon percentage values were found to be approximately 2−4% below their calculated values, and reproducibility was poor on samples that were clean as determined by ^{1}H NMR. In silicon compounds, carbon contents are occasionally too low due to formation of silicon carbide. See: Söldner, M.; Sandor, M.; Schier, A.; Schmidbaur, H. *Chem. Ber.* **1997**, *130*, 1671.

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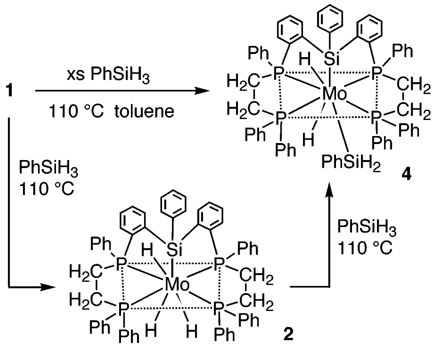
Table 3. Selected Spectroscopic Data for [MoH$_3${[Ph$_2$PCH$_2$CH$_2$P(Ph)C$_6$H$_4$-*o*]$_2$(R)E-*P,P,P,P,E*}]

compd	IR^a/cm^{-1} ν(Mo−H)	^{1}H NMR (J, Hz) δ(Mo−H)	^{1}H NMR (J, Hz) δ(other)	^{31}P NMR (J, Hz)
2	1714	−4.45 (br quint, 2H, J_{HP} = 35)	1.6−2.6 (m, 8H, C$_2H_4$)	81.4 (d, 2P, J_{PP} = 61)
		−4.15 (br t, 1H, J_{HP} = 33)	6.6−7.8 (m, 43H, Ph protons)	110.2 (d, 2P, J_{PP} = 61)
2a	1705	−4.38 (br quint, 2H, J_{HP} = 29)	1.6−2.6 (m, 8H, C$_2H_4$), 2.2 (s, 3H, *p*-CH_3-C$_6$H$_4$)	83.6 (d, 2P, J_{PP} = 58)
		−4.05 (br t, 1H, J_{HP} = 31)	6.6−7.9 (m, 42H, Ph protons)	112.8 (d, 2P, J_{PP} = 58)
2b	1718	−4.38 (br quint, 2H, J_{HP} = 22)	1.6−2.6 (m, 8H, C$_2H_4$), 2.1 (s, 3H, *o*-CH_3-C$_6$H$_4$)	76.9 (dd, 1P, J_{PP} = 25, 48)
		−3.95 (dt. 1H, J_{HP} = 46, 22)	6.6−7.8 (m, 42H, Ph protons)	87.1 (dd, 1P, J_{PP} = 33, 65)
				108.0 (dd, 1P, J_{PP} = 25, 48)
				109.0 (dd, 1P, J_{PP} = 33, 65)
2c	1736	−4.22 (br quint, 2H, J_{HP} = 27)	1.6−2.4 (m, 8H, C$_2H_4$)	82.0 (d, 2P, J_{PP} = 61)
		−4.03 (br t, 1H, J_{HP} = 27)	6.6−7.8 (m, 38H, Ph protons)	109.0 (d, 2P, J_{PP} = 61)
2d	1743	−4.50 (br quint, 2H, J_{HP} = 27)	1.8−2.4 (m, 8H, C$_2H_4$), 2.7 (s, 6H, NCH_3)	82.0 (d, 2P, J_{PP} = 59)
		−4.20 (br t, 1H, J_{HP} = 31)	6.8−7.8 (m, 42H, Ph protons)	110.0 (d, 2P, J_{PP} = 59)
2e	1704	−4.50 (br quint, 2H, J_{HP} = 24)	0.6−1.6 (m, 13H, C$_6H_{13}$), 2.1−2.4 (m, 8H, C$_2H_4$)	80.4 (d, 2P, J_{PP} = 61)
		−4.40 (br t, 1H, J_{HP} = 30)	6.5−7.5 (m, 38H, Ph protons)	110.2 (d, 2P, J_{PP} = 61)
2f	1774	−4.55 (br quint, 2H, J_{HP} = 25)	0.9−1.9 (m, 11H, C$_6H_{11}$), 2.0−2.5 (m, 8H, C$_2H_4$)	80.1 (d, 2P, J_{PP} = 63)
		−4.45 (br t, 1H, J_{HP} = 30)	6.5−7.5 (m, 38H, Ph protons)	109.5 (d, 2P, J_{PP} = 63)
3	1808	−4.40 (br quint, 2H, J_{HP} = 29)	1.6−2.6 (m, 8H, C$_2H_4$)	83.8 (d, 2P, J_{PP} = 55)
		−3.90 (br t, 1H, J_{HP} = 48)	6.6−8.0 (m, 43H, Ph protons)	113.8 (d, 2P, J_{PP} = 55)

Scheme 2



does not impose a significant effect upon the equatorial plane defined by the four phosphorus atoms. The Mo1−Si2 bond distance is 2.559(2) Å, which is slightly shorter than that of the Mo−Ge bond in **3** by ca. 0.03 Å. On the other hand, the mean Mo−P distance of 2.471 Å in **4** is slightly longer than that found in **3** (2.450 Å). The Si2−C7 bond distance of 1.899(8) Å is shorter than that of Ge1−C1 in **3** (2.03(2) Å), reflecting a difference in their covalent radii (Ge = 1.23 Å and Si = 1.17 Å).

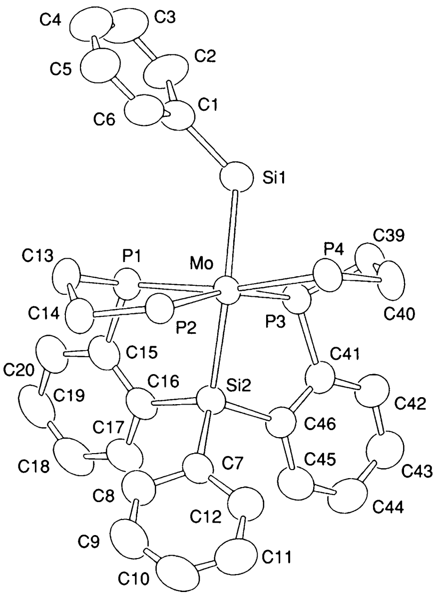


Figure 2. ORTEP drawing of the molecular structure of **4**.

Table 4. Interatomic Distances (Å) and Angles (deg) for 4

Distances			
Mo1−P1	2.455(2)	Mo1−P2	2.490(2)
Mo1−P3	2.451(2)	Mo1−P4	2.487(2)
Si1−Mo1	2.620(2)	Si2−Mo1	2.559(2)
Si1−C1	1.898(9)	Si2−C7	1.899(8)
Si2−C16	1.913(3)	Si2−C46	1.913(8)
Angles			
P1−Mo1−P2	81.08(7)	P2−Mo1−P4	100.67(7)
P1−Mo1−P3	101.39(7)	P3−Mo1−P4	79.44(7)
Si1−Mo1−Si2	143.91(5)	Mo1−Si1−C1	124.4(3)
Mo1−Si2−C7	126.2(2)	C16−Si2−C46	106.6(3)

The spectroscopic data for **4** are consistent with the solid-state structure. The high-field ^{1}H NMR spectrum for **4** is informative; it exhibited a complex multiplet centered at δ −4.50 ppm and a broad quintet at −5.40 ppm for the Mo−H resonances due to coupling to ^{31}P nuclei. The integration ratio of the former and the latter was found to be 1:1. No change was observed for the signals on lowering the temperature in toluene-d_8 to −60 °C. The presence of two sets of hydride signals of identical intensities at least at and below room temperature may indicate that these two hydrides are located separately in both sides of the pseudoequatorial plane comprised of four phosphorus atoms of the dppe ligands. The ^{31}P{^{1}H} NMR spectrum of **4** revealed two doublets at δ 94.1 and at 72.5 ppm with a coupling constant value of 70 Hz.

Reactions of **1** with excess C$_6$F$_5$SiH$_3$ and 4-Me$_2$NC$_6$H$_4$SiH$_3$ provided the analogous disilyl type complexes [MoH$_2$(Ar){[Ph$_2$PCH$_2$CH$_2$P(Ph)C$_6$H$_4$-*o*]$_2$(Ar)-Si-*P,P,P,P,Si*}] (Ar = C$_6$F$_5$ (**4a**), 4-Me$_2$NC$_6$H$_4$ (**4b**)). In contrast to these silanes, treatment of **1** with excess *p*-CH$_3$C$_6$H$_4$SiH$_3$, *o*-CH$_3$C$_6$H$_4$SiH$_3$, and PhGeH$_3$ did not allow the synthesis of the corresponding disilyl and digermyl type complexes, due to the highly unstable nature of the products.

Reaction of 1 with Ph$_2$EH$_2$ in Toluene. When the secondary silane Ph$_2$SiH$_2$ was employed in a similar reaction with **1**, the trihydride complex **5** with a tridentate P−P−Si ligand was isolated in 87% yield (Scheme 3).

X-ray-quality crystals of **5** were successfully grown from a benzene/hexane solution. The molecular structure is depicted in Figure 3; selected bond distances and

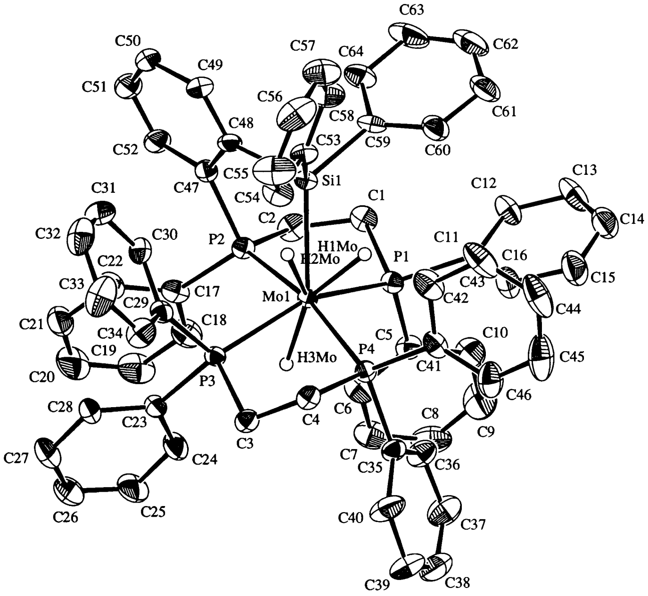
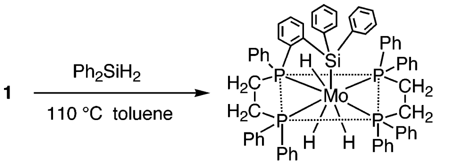


Figure 3. ORTEP drawing of the molecular structure of **5**.

Scheme 3



5

Table 5. Interatomic Distances (Å) and Angles (deg) for 5

	Distances		
Mo1–P1	2.503(4)	Mo1–P2	2.418(5)
Mo1–P3	2.477(2)	Mo1–P4	2.460(5)
Si1–Mo1	2.541(2)	Mo1–C48	1.909(6)
Si1–C53	1.919(7)	Si1–C59	1.917(6)
Mo1–H(1Mo)	1.70(6)	Mo1–H(2Mo)	1.76(6)
Mo1–H(3Mo)	1.72(6)		
	Angles		
P1–Mo1–P2	79.2(2)	P2–Mo1–P3	95.4(1)
P1–Mo1–P4	100.5(2)	P3–Mo1–P4	79.1(1)
Mo1–Si1–C53	121.6(2)	C48–Si1–C59	100.9(3)

angles are listed in Table 5. The structure is well-resolved, and the hydride atoms are clearly identified. The ORTEP drawing shows that complex **5** contains a new bond between the silyl atom and the ortho carbon of the phenyl group in one of the dppe ligands. Accordingly, even in the case of the secondary silane system, activation of the Si–H bond and the ortho C–H bond takes place.

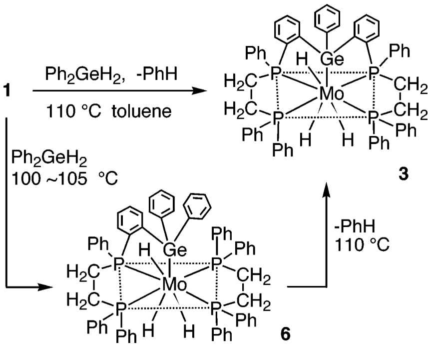
The Mo1–Si1 bond length (2.541(2) Å) is remarkably similar to that exhibited by **4** (2.559(2) Å). The Mo–P bond length of **5** (2.465 Å (average)) is also similar to that of **4** (2.471 Å (average)). The hydrides are located on both sides of the pseudoequatorial plane comprised of four phosphorus atoms of the dppe ligands.

Table 6. Comparison of Structural Parameters for Compounds 1 and 3–5

compd	Mo–P bond dist, Å	P–Mo–P bond angle, deg			
1[13]	2.421[a]	82.30(2)		101.56(2)	
3	2.450[b]	80.6(2)	80.8(2)	102.0(2)	98.8(2)
4	2.471[b]	81.08(7)	79.44(7)	100.67(7)	101.39(7)
5	2.465[b]	79.1(1)	79.2(2)	100.5(2)	95.4(1)

[a] Mean value of the two Mo–P distances. [b] Mean value of the four Mo–P distances.

Scheme 4



To compare the coordination environment of the molybdenum atom of **5** with those of **1**, **3**, and **4**, Table 6 presents a selected list of structural parameters for the four compounds. As is evident from the data, these parameters do not change significantly among the four structures, indicating that the formation of the new bond between the E atom and the phenyl group has very little impact on the bond lengths and the angles to the resulting ligands.

The $^{31}P\{^{1}H\}$ NMR spectrum of **5** consisted of four signals at δ 84.1, 85.1, 91.7, and 109.1 ppm with a 1:1:1:1 peak area ratio, indicating the presence of four inequivalent P nuclei, which is fully in accord with the X-ray diffraction data. At room temperature, the ^{1}H NMR spectrum of **5** exhibited one broad shielded resonance at δ −5.20 ppm due to the hydride ligands; it is analyzed as a doublet of quartets with coupling constant values of 16 and 29 Hz. This is in stark contrast to complexes **2** and **4**, in which the corresponding hydride ligands were found to be inequivalent at room temperature. However, at temperatures below −70 °C, three resonances (δ −2.0, −6.3, and −6.7) were observed in the hydride region, indicating the non-equivalence of the three hydride groups in **5**.

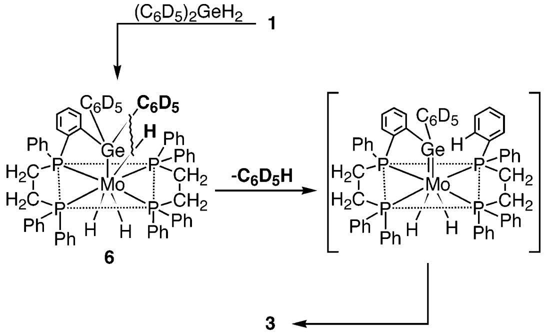
Using methylphenylsilane ($PhMeSiH_2$) as a reagent, the methylated congener **5a** was obtained in 73% yield. The structural assignment is based upon comparing spectroscopic data with those for **5** (see Experimental Section).

Noteworthy is the reaction of **1** with the secondary species Ph_2GeH_2, which resulted in the formation of **3** (85% yield). We confirmed that the reaction proceeds with accompanying evolution of 1 mol of benzene (Scheme 4).

The result is in contrast to that found in a similar reaction employing Ph_2SiH_2, in which the only isolated product was complex **5**, as described above. The reaction between **1** and Ph_2GeH_2 was found to be very sensitive to the reaction temperatures. At temperatures of 100–105 °C, the intermediary **6** with tridentate ligand, which is analogous to the silyl complex **5**, was formed (96%). We observed that **6** is converted easily into **3** by heating the former in toluene at 110 °C.

To obtain some insights into the mechanism of the formation of **3**, we attempted the reaction of **1** with selectively deuterium-labeled $(C_6D_5)_2GeH_2$ at 110 °C

Scheme 5



(Scheme 5). It was hoped that this reagent could be used to determine whether the resulting benzene is derived from the phenyl group in the dppe ligand[16] or from the phenyl group in diphenylgermane.

GC-MS analysis of the volatile products showed a peak at *m/z* 83, which was ascribed to pentadeuterated benzene, C_6D_5H, suggesting a cleavage of the Ge−C(Ph) bond. This α-elimination reaction of **1** with Ph_2GeH_2 is proposed to occur via intervention of the germylene intermediate. The silyl complex **5** was found to be stable to prolonged heating in toluene; similar transformation into **2** did not take place at all. It is quite difficult to rationalize these differences in the reactivity between Ph_2GeH_2 and Ph_2SiH_2, because the strengths of chemical bonds in Ge−C(Ph) and Si−C(Ph) are similar.[17] In organogermanium compounds, intramolecular coordination between a germanium atom and a substituent (halogen, O, S, etc.) in a position α to the germanium has been known to favor a homolytic cleavage of the Ge−C bond.[18] Hence, the Mo(dπ)−GeC(Ph)(σ^*) interaction might have induced a weakening of the Ge−C bond. In the case of the silyl−molybdenum complex **5**, we may suppose that such an interaction between the d electron and antibonding orbital is weak, since the Si−C(σ^*) orbital lies much higher in energy than the Ge−C(σ^*) orbital. Similar reaction patterns in which a germyl−metal complex suffers Ge−C bond cleavage by α-migration whereas the corresponding silyl−metal complex does not have been observed for ruthenium systems of the type L_3Ru-ER_3.[19] However, to the best of our knowledge, the present results show the first example for the molybdenum system.

Consideration of the Formation Mechanism of the Complexes 2 and 5. The reaction is a very complex one, where Mo−H, Si−H, and C−H bond cleavage/formation all occurs in the same system. There are two possible mechanisms.[9a] The most plausible is a route that incorporates a sequence of reactions involving oxidative addition of the ortho C−H bond of the phenyl group in the dppe ligand to the 16-electron reactive intermediate $MoH_2(dppe)_2$ formed by H_2 loss to give the ortho-metalated species, oxidative addition of $RR'SiH_2$, reductive elimination to generate a new Si−C bond, and intramolecular oxidative addition of the Si−H bond. A similar reaction process in which a coordinatively unsaturated species is first converted into the ortho-metalated intermediate through the ortho C−H bond scission in the dppe ligand was observed by Hidai and co-workers.[20] They reported that the thermal reaction of *trans*-$[M(N_2)_2(dppe)_2]$ (M = Mo, W) with dppe resulted in the formation of the tetradentate phosphine ligand *o*-$C_6H_4(PPhCH_2CH_2PPh_2)$. One proposed pathway for this novel transformation involves cleavage of the P−Ph bond in one dppe ligand and the ortho C−H bond of one Ph group in the other dppe ligand. Although their results add weight to the present mechanism, it must be remembered that, in the reaction between **1** and Ph_2GeH_2, intervention of the germylene intermediate was postulated. Therefore, an analogous path that includes the intermediacy of silylene metal complexes via α-migration of hydrogen cannot be ruled out.[21] In an effort to determine which pathway is operative here, a study with deuterium-labeled Ph_2SiD_2 was performed (Scheme 6). If formation of **5** were to proceed via the ortho-metalated intermediate, two deuterium atoms would be incorporated in the final product (**i**), as shown by path A of Scheme 6. On the other hand, if the silylene intermediate were involved in the mechanism (path B), complex **i** or monodeuterated **ii** would be obtained, depending on whether H_2 or DH is released. Thus, in this case, the final product seems to be a 1:2 mixture of **i** and **ii** on the basis of statistical considerations.

Detailed analysis of the reaction product using ^1H NMR revealed that the ratio of the total intensity of hydrido signals to that of the CH_2CH_2 signals in the dppe ligand was found to be 1.00:4.54. When the reaction proceeds via the silylene pathway to yield a 1:2 mixture of **i** and **ii**, this ratio would be 1.00:4.80. Therefore, we favor the silylene mechanism as a plausible explanation of the present system. Presumably, in the case of the primary silane $RSiH_3$, the process repeats to attach Si to the phenyl group in the other dppe ligand to give the final products **2**.

Conclusion

Reaction of $[MoH_4(dppe)_2]$ (**1**) with a series of primary silanes and germanes REH_3 in refluxing toluene yielded the novel complexes $[MoH_3\{[Ph_2PCH_2CH_2P(Ph)$-$C_6H_4$-*o*$]_2$(R)E-*P,P,P,P,E*$\}]$ (E = Si (**2**), Ge (**3**)) with a quinquidentate ligand comprised of a P−P−E−P−P framework. Despite the difference in the electronic properties and the steric requirements of the starting silanes and germanes, the resulting complexes exhibit similar structural features, as determined by NMR spectroscopy. When the secondary silane Ph_2SiH_2 was employed in a similar reaction with **1**, the trihydrido complex **5** with a tridentate ligand ($[Ph_2PCH_2CH_2P(Ph)C_6H_4$-*o*$]$-$Ph_2Si$-*P,P,Si*) comprised of a P−P−Si framework was

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[16] Hidai and co-workers reported that thermal reaction of the related molybdenum N_2 complex *trans*-$[Mo(N_2)_2(dppe)_2]$ resulted in condensation of two dppe ligands with concurrent liberation of benzene; see: Arita, C.; Seino, H.; Mizobe, Y.; Hidai, M. *Bull. Chem. Soc. Jpn.* **2001**, *74*, 561.

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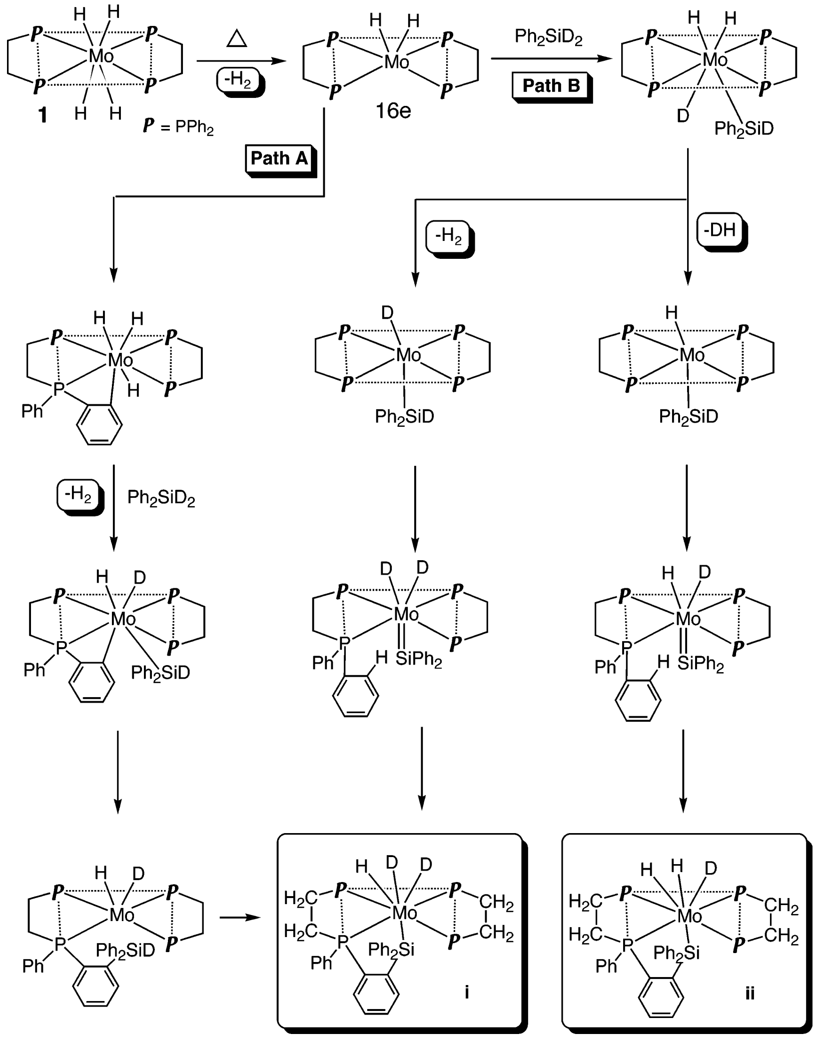
Scheme 6



isolated. On the other hand, the reaction between Ph_2GeH_2 and **1** proceeded with accompanying evolution of 1 mol of benzene to give **3**. We have observed evidence to suggest that the reaction path includes the intermediacy of silylene or germylene metal complexes via an α-migration process. We believe that these new complexes possess rich reaction chemistry. The properties of the complexes and a range of further reactions are currently being investigated in our laboratory.

Experimental Section

General Procedures and Reagent Syntheses. Unless otherwise noted, all manipulations were performed using standard Schlenk techniques under purified argon or nitrogen. Commercially available reagent grade chemicals were used as such without any further purification. All solvents were dried by standard methods and were stored under argon. Complex **1**, organosilanes, and organogermanes were prepared by literature procedures or modifications of these.[7,22] Selectively deuterium-labeled $(C_6D_5)_2GeH_2$ was prepared by reduction of $(C_6D_5)_2GeCl_2$ (prepared from C_6D_5MgBr and $GeCl_4$) with $LiAlH_4$ by a standard method.[23] Ph_2SiD_2 was prepared by reaction of Ph_2SiCl_2 with $LiAlD_4$. All NMR spectra were recorded on a JEOL-JNM-270 spectrometer. $^{31}P\{^1H\}$ NMR peak positions were referenced to external H_3PO_4 or PPh_3.

X-ray Crystallography. Single crystals were mounted on a Rigaku AFC7R four-circle diffractometer equipped with graphite-monochromated Mo Kα radiation and a rotating anode generator. All diffraction studies were performed at 23 °C. The parameters used during the collection of diffraction data are given in Table 7. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined.

Reaction of 1 with 1 Equiv of Primary Silanes and Germanes in Toluene. A solution of **1** (1.153 g, 1.286 mmol) and phenylsilane (160 μl, 1.286 mmol) in toluene (90 mL) was heated with stirring at 110 °C for 3 h. The solution was initially yellow but gradually darkened to brown. The resulting solution was concentrated to a volume of 45 mL under reduced pressure. Hexane (25 mL) was then added, and the mixture was allowed to stand for 12 h at 0 °C, whereupon yellow precipitates separated. The product was collected by filtration, washed with hexane (10 mL × 3), and then dried in vacuo to give **2** (0.858 g, 66%). This procedure is also applicable to the synthesis of the other complexes (**2a**−**f** and **3**). Experiments listed in Table 2 were carried out under essentially the same conditions. A crystal of **3** suitable for X-ray crystallographic analysis could be obtained by recrystallization from toluene/hexane solution.

Reaction of 1 with Excess $ArSiH_3$ in Toluene. A solution of **1** (0.208 g, 0.232 mmol) and phenylsilane (173 μl, 1.39 mmol) in toluene (20 mL) was heated with stirring at 110 °C for 3 h.

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Table 7. Crystal Data for Complexes 3−5

	3	4	5
chem formula	$C_{58}H_{54}GeMoP_4$	$C_{78}H_{74}MoP_4Si_2$	$C_{64}H_{60}MoP_4Si$
fw	1043.49	1287.45	1077.10
cryst syst	monoclinic	orthorhombic	monoclinic
space group	*Pn* (No. 7)	*Pbca* (No. 61)	$P2_1/n$ (No. 14)
Z	2	8	4
a, Å	12.465(3)	44.862(5)	10.07(1)
b, Å	12.111(3)	23.072(4)	23.07(1)
c, Å	16.631(6)	12.859(5)	23.06(2)
β, deg	94.90(3)		93.0(2)
V, Å^3	2501(1)	13309(4)	5351(6)
F(000)	1072.00	5376.00	2240.00
d(calcd), g cm^{-3}	1.385	1.285	1.337
μ(Mo Kα), cm^{-1}	10.16	3.72	4.27
cryst size, mm	0.35 × 0.20 × 0.02	0.30 × 0.24 × 0.24	0.30 × 0.25 × 0.20
2θ range, deg	22 (28.7−29.9)	23.34−29.36	20 (29.9−30.6)
scan rate, deg min^{-1}	16.0	16.0	32, 16, 8,4
no. of rflns measd	6368	9544	0
no. of unique rflns	6024	9542	12 606
no. of rflns obsd	2863 ($I > 2\sigma(I)$)	4646 ($I > 3\sigma(I)$)	7286 ($I > 3\sigma(I)$)
R	0.082	0.045	0.053
R_w	0.246	0.047	0.083
GOF	1.34	1.47	1.31

The solution was initially yellow but gradually darkened to brown. The resulting solution was concentrated to a volume of 10 mL under reduced pressure. Hexane (20 mL) was then added, and the mixture was allowed to stand for 12 h at 0 °C, whereupon yellow crystals in the form of flat plates suitable for X-ray crystallographic analysis separated. The product was collected by filtration and then dried in vacuo to give **4** (0.233 g, 78%). Similar experiments employing $C_6F_5SiH_3$ and 4-$Me_2NC_6H_4SiH_3$ gave **4a** (81%) and **4b** (89%), respectively.

4. ^{1}H NMR (C_6D_6, ppm): 4.20 (s, 2H, SiH_2), −4.50 (br m, 1H, MoH), −5.40 (br quint, 1H, MoH). ^{31}P NMR (THF-d_8, ppm): 94.1 (br d, 2P, J_{PP} = 70 Hz), 72.5 (br d, 2P, J_{PP} = 70 Hz). IR (KBr): ν(Si−H) 2083 cm^{-1}, ν(Mo−H) 1742 cm^{-1}. Anal. Calcd for $C_{78}H_{76}P_4MoSi_2$ (**4**·2(toluene)): C, 72.65; H, 5.94. Found: C, 72.85; H, 5.93.

4a. ^{1}H NMR (C_6D_6, ppm): 6.0−8.0 (m, 38H, Ph protons), 3.9−4.0 (br, 2H, SiH_2), 1.6−2.8 (br, 8H, C_2H_4), −4.10 (br m, 1H, MoH), −5.20 (br m, 1H, MoH). ^{31}P NMR (C_6D_6, ppm): 102.0 (br d, 2P, J_{PP} = 63 Hz), 71.0 (br d, 2P, J_{PP} = 63 Hz). IR (KBr): ν(Si−H) 2142 cm^{-1}, ν(Mo−H) 1711 cm^{-1}.

4b. ^{1}H NMR (C_6D_6, ppm): 6.0−8.0 (m, 46H, Ph protons), 3.9−4.0 (br, 2H, SiH_2), 2.8 (br, 12H, NCH_3), 1.8−2.8 (br, 8H, C_2H_4), −4.10 (br m, 1H, MoH), −5.30 (br m, 1H, MoH). ^{31}P NMR (C_6D_6, ppm): 100.0 (br d, 2P, J_{PP} = 71 Hz), 79.0 (br d, 2P, J_{PP} = 71 Hz). IR (KBr): ν(Si−H) 2132 cm^{-1}, ν(Mo−H) 1712 cm^{-1}.

Reaction of 1 with PhRSiH$_2$ in Toluene. A solution of **1** (0.229 g, 0.255 mmol) and Ph_2SiH_2 (283 μl, 1.53 mmol) in toluene (20 mL) was heated with stirring at 110 °C for 5 h. The solution was initially yellow but gradually darkened to brown. The resulting solution was concentrated to dryness, and the crude product was extracted with benzene (10 mL). Hexane (25 mL) was then added, and the mixture was allowed to stand for 12 h at room temperature, whereupon yellow precipitates separated. The product was collected by filtration, washed with hexane (5 mL × 3), and then dried in vacuo to give **5** (0.239 g, 87%). A yellow crystal suitable for X-ray crystallographic analysis could be obtained by recrystallization from benzene/hexane solution. A similar experiment employing $PhMeSiH_2$ gave **5a** in 70% yield.

5. ^{1}H NMR (C_6D_6, ppm): 1.6−2.6 (br, 8H, C_2H_4), −5.20 (d quart, 3H, J_{HP} = 16, 29 Hz, MoH_3). ^{31}P NMR (THF-d_8, ppm): 109.1 (m, 1P), 91.7 (m, 1P), 85.1 (m, 1P), 84.1 (m, 1P). IR (KBr): ν(Mo−H) 1732 cm^{-1}. Anal. Calcd for $C_{64}H_{60}MoSiP_4$: C, 71.37; H, 5.62. Found: C, 70.68; H, 5.49.

5a. ^{1}H NMR (THF-d_8, ppm): 1.6−2.6 (br, 8H, C_2H_4), 0.43 (s, 3H, SiCH_3), −4.80 (d quart, J_{HP} = 16, 29 Hz, 3H, MoH_3). ^{31}P NMR (THF-d_8, ppm): 115.8 (m, 1P), 92.6 (m, 3P). IR (KBr): ν(Mo−H) 1714 cm^{-1}.

Reaction of 1 with Ph$_2$GeH$_2$ in Toluene. A solution of **1** (1.09 g, 1.220 mmol) and Ph_2GeH_2 (359 μl, 1.820 mmol) in toluene (100 mL) was heated with stirring at 110 °C for 6 h. The solution was initially yellow but gradually darkened to brown. The resulting solution was concentrated to a volume of 50 mL under reduced pressure. Hexane (50 mL) was then added, and the mixture was allowed to stand for 12 h at 0 °C, whereupon yellow precipitates separated. The product was collected by filtration, washed with hexane (10 mL × 3), and then dried in vacuo to give **3** (1.08 g, 85%). In this reaction, GC analysis of the volatiles revealed the formation of benzene (83%, based on **1**). A similar experiment employing $(C_6D_5)_2GeH_2$ gave C_6D_5H, which was identified by GC−MS spectrometry (EI, 70 eV).

When the reaction was conducted at temperatures of 100−105 °C, complex **6**, which is analogous to the silyl complex **5**, was formed (96%).

6. ^{1}H NMR (C_6D_6, ppm): 1.5−2.7 (br, 8H, C_2H_4), −4.30 (br quint, 3H, MoH_3). ^{31}P NMR (C_6D_6, ppm): 115.5 (br d, 1P, J_{PP} = 46 Hz), 94.2 (m, 1P), 76.9 (m, 2P). IR (KBr): ν(Mo−H) 1812 cm^{-1}.

Acknowledgment. We are grateful to Prof. K. Osakada of the Tokyo Institute of Technology, Dr. M. Yamasaki of Rigaku Corp., and Dr. Y. Yamaguchi of Yokohama National University for X-ray structure analyses. We also thank Prof. K. Mochida of Gakushuin University for a generous gift of $GeCl_4$. We gratefully acknowledge Dr. T. Koizumi of the Tokyo Institute of Technology for T_1 measurements and for helpful discussion. We wish to thank Dr. M. Tanaka of the Tokyo Institute of Technology and Dr. T. Fujiwara and Professor A. Nagasawa of Saitama University for the elemental analyses.

Supporting Information Available: Listings of atomic coordinates, anisotropic thermal parameters, and extensive interatomic distances and angles for **5**. This material is available free of charge via the Internet at http://pubs.acs.org. This data and the data for **3**, **4** have also been deposited with the Cambridge Crystallographic Data Centre, as CCDC Nos. 270366, 183312, and 100496, respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. (fax, +44-1223-336033; e-mail, deposit@ccdc.cam.ac.uk; web, http://www.ccdc.cam.ac.uk).

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