Reaction of Ruthenium Complexes Having both a Phosphite and a Group 14 Element Ligand with a Lewis Acid

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Reactions of Cp(CO)(ER_3)Ru{PN(Me)CH_2CH_2NMe(OMe)} having an alkyl group (ER_3 = Me (**1a**), CH_2SiMe_3 (**2a**)), a silyl group (ER_3 = $SiMe_3$ (**3a**), $SiMe_2SiMe_3$ (**4a**)), a germyl group (ER_3 = $GeMe_3$ (**5a**)), or a stannyl group (ER_3 = $SnMe_3$ (**6a**), Sn^nBu_3 (**7a**), $SnPh_3$ (**8a**)) with a Lewis acid ($BF_3\cdot OEt_2$ or $Me_3SiOSO_2CF_3$ (TMSOTf)) have been examined. In the reactions with $BF_3\cdot OEt_2$, in any case except for **8a**, an OMe abstraction as an anion uniformly takes place at the first stage to give the corresponding cationic phosphenium complex [Cp(CO)(ER_3)Ru{PN(Me)CH_2CH_2NMe}]BF_4 (**1b**−**7b**). The successive reaction depends on the type of ER_3 group. Alkyl complexes (**1b** and **2b**) immediately undergo migratory insertion of the phosphenium ligand into the Ru−C bond, and a subsequent reaction with PPh_3 gives the cationic complex [Cp(CO)(PPh_3)Ru{PN(Me)CH_2CH_2NMe(ER_3)}]BF_4 (ER_3 = Me (**1c**), CH_2SiMe_3 (**2c**)). Silyl and germyl complexes (**3b**−**5b**) are stable with the Ru−Si and Ru−Ge bonds intact. In contrast, stannyl complexes (**6b** and **7b**) undergo migration of one of the R groups on Sn to give the stannylene complex [Cp(CO){PN(Me)CH_2CH_2NMe(R)}Ru=SnR_2]BF_4 (R = Me (**6e**), ^{n}Bu (**7e**)). The reactions with another Lewis acid, TMSOTf, exhibit reactivities similar to those with $BF_3\cdot OEt_2$, except when ER_3 is a stannyl group. In the reaction of **6a**, **7a**, or **8a** with TMSOTf, one of the R groups on Sn is directly abstracted to give the corresponding stannylene complex [Cp(CO){PN(Me)CH_2CH_2NMe(OMe)}Ru=SnR_2]OTf (R = Me (**6f**), ^{n}Bu (**7f**), Ph (**8f**)). **8f** has been determined to be a doubly base stabilized stannylene complex by single-crystal X-ray diffraction.

Introduction

There is growing interest in the chemistry of transition-metal complexes having a cationic phosphenium as a ligand, because it can serve both as a strong π-acceptor due to its empty p orbital and as a σ-donor and is regarded as isolobal to a singlet carbene.[1] In comparison with the extensive development of the chemistry of carbene complexes,[2] little had been achieved in the chemistry of the cationic phosphenium complexes until the first report of Parry's group in 1978.[3a,b] After that, many such complexes were reported for several kinds of transition metals regarding the syntheses and structures,[3c,4−11] but little has been studied with regard to the reactivities of cationic phosphenium complexes.

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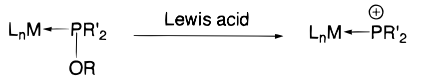
We have recently developed a new method for the preparation of cationic phosphenium transition-metal complexes of Cr,[7] Mo,[7−9] W,[7,9] and Fe,[10,11] where an OR group on a coordinating phosphorus compound is abstracted by a Lewis acid such as $BF_3{\cdot}OEt_2$ or TMSOTf ($Me_3SiOSO_2CF_3$) (eq 1).



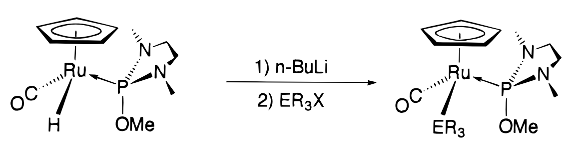
(1)

We also found some interesting facts that the cationic phosphenium complexes thus formed exhibit the different reactivities depending on the kind of the group 14 element ligand on the transition metal.[9,10] For example, in the reaction of the iron complex $Cp(CO)(ER_3)Fe\{PNN(OMe)\}$ (E = group 14 element; PNN(OMe) stands for $\overline{PN(Me)CH_2CH_2N}Me(OMe)$ in this paper) with a Lewis acid such as $BF_3{\cdot}OEt_2$ or TMSOTf, OMe abstraction as an anion by a Lewis acid uniformly takes place at the first stage to give the cationic phosphenium iron complex $[Cp(CO)(ER_3)Fe\{PNN\}]^+$. When E is a carbon atom, migratory insertion of the phosphenium ligand into the Fe−C bond or, more simply, alkyl migration from Fe to phosphenium P occurs to give the 16-electron cationic complex $[Cp(CO)Fe\{PNN(CR_3)\}]^+$.[10a,b] When E is a silicon or a germanium atom, the cationic phosphenium complex is stable and the Fe−Si or an Fe−Ge bond remains unreacted.[10a,b,d] In contrast, when E is a tin atom, not SnR_3 itself but one of its alkyl groups migrates to the phosphenium P to give the stannylene complex $[Cp(CO)\{PNN(R)\}Fe{=}SnR_2]^+$.[10b,c]

As an extension of our studies, we report here the comparative reactions of Ru complexes $Cp(CO)(ER_3)Ru\{PNN(OMe)\}$ (E = group 14 element) with a Lewis acid such as $BF_3{\cdot}OEt_2$ or TMSOTf together with the reactivity of the cationic ruthenium phosphenium complexes.

Results and Discussion

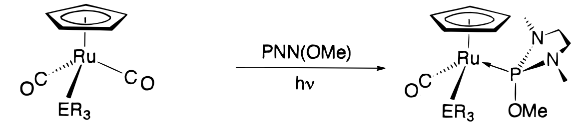
Ruthenium complexes having a group 14 element ligand (ER_3) and a diamino-substituted phosphite (PNN(OMe)) were prepared from the reaction of a ruthenium−hydride complex with ^{n}BuLi and then the corresponding ER_3X (E = C, Si, Ge, Sn) reagent (eq 2).



(2)

1a: $ER_3 = Me$
2a: $ER_3 = CH_2SiMe_3$
3a: $ER_3 = SiMe_3$
4a: $ER_3 = SiMe_2SiMe_3$
5a: $ER_3 = GeMe_3$
6a: $ER_3 = SnMe_3$
7a: $ER_3 = Sn^nBu_3$
8a: $ER_3 = SnPh_3$

(Trimethylsilyl)methyl complex **2a** was obtained in only 5% yield. Thus, we attempted an alternative synthesis based on a photoreaction of $Cp(CO)_2RuCH_2SiMe_3$ with PNN(OMe) (eq 3), resulting in an improved yield (65%).

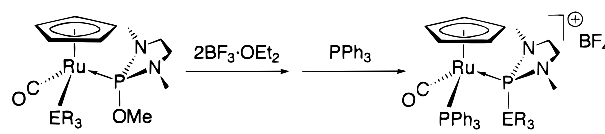


(3)

2a: $ER_3 = CH_2SiMe_3$

These complexes were characterized by IR and ^{1}H, ^{13}C, ^{29}Si, ^{31}P, and ^{119}Sn NMR spectra as well as elemental analysis. They were subjected to reaction with a Lewis acid such as $BF_3{\cdot}OEt_2$ or TMSOTf ($Me_3SiOSO_2CF_3$).

Reaction of Alkyl Complexes with a Lewis Acid. A ruthenium−alkyl complex, Cp(CO)(Me)Ru{PNN(OMe)} (**1a**), was treated with 2 equiv of $BF_3{\cdot}OEt_2$ at room temperature and then with PPh_3 at −78 °C in CH_2Cl_2 to afford the cationic complex $[Cp(CO)Ru(PPh_3)\{PNN(Me)\}]BF_4$ (**1c**) (eq 4). Complex **1c** was characterized by NMR and IR spectroscopy as well as elemental analysis. In the IR spectrum, the absorption band assigned to the CO stretching vibration was observed at 1981 cm^{-1}, which was 47 cm^{-1} higher in frequency than that for the starting complex **1a**, indicative of the formation of the cationic complex. The ^{1}H and ^{13}C NMR spectra of **1c** showed no resonance due to an OMe group on the phosphorus atom. Instead, a new resonance was observed at 1.58 ppm ($^2J_{PH}$ = 6.6 Hz) in the ^{1}H NMR spectrum and at 25.6 ppm ($^1J_{PC}$ = 13.1 Hz) in the ^{13}C NMR spectrum, suggesting the formation of a P−Me direct bond. The ^{31}P NMR spectrum showed two resonances at 44.2 and 137.5 ppm as doublets ($^2J_{PP}$ = 44.1 Hz), which were assigned to PPh_3 and PNN(Me), respectively, indicating that both phosphine ligands coordinate to the same ruthenium atom.



(4)

1a: $ER_3 = CH_3$
2a: $ER_3 = CH_2SiMe_3$

1c: $ER_3 = CH_3$
2c: $ER_3 = CH_2SiMe_3$

In the above reaction, it is considered that an Me group on the phosphorus comes from the ruthenium atom. In fact, the migration of an alkyl group from the Ru to the P is proved by a parallel reaction of **2a**, which has a CH_2SiMe_3 group in place of an Me group on the Ru in **1a** (eq 4). The product, $[Cp(CO)Ru(PPh_3)\{PNN(CH_2SiMe_3)\}]BF_4$ (**2c**), clearly shows that the OMe group on the P is eliminated and the CH_2SiMe_3 group on the Ru migrates to the P coordinating to the Ru.

Considering the products in the reactions of **1a** and **2a**, the reaction process shown in Scheme 1 could be postulated. The cationic phosphenium complex **b** is produced as an intermediate at the first stage in these reactions, where an OMe group on the phosphorus ligand is abstracted as an anion by $BF_3{\cdot}OEt_2$. However, **b** is so reactive that an alkyl group on the ruthenium atom immediately migrates to the phosphenium phos-

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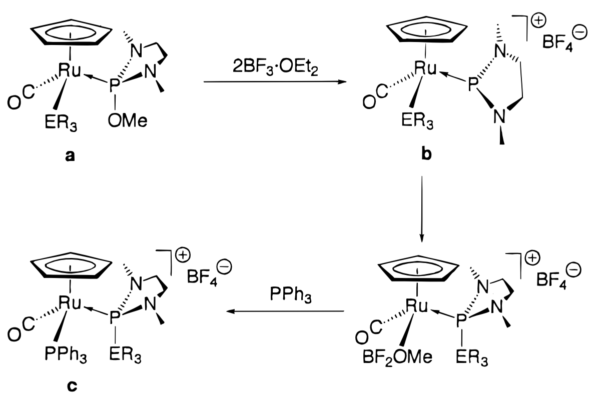
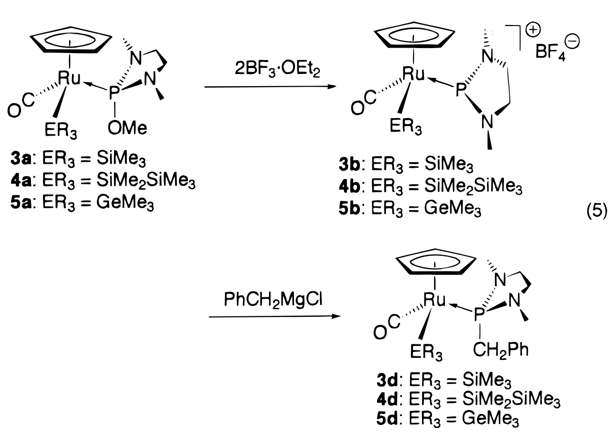
Scheme 1



phorus to give the 16-electron cationic complex [Cp(CO)-Ru{PNN(ER_3)}]$^+$. It is stabilized presumably by the coordination of BF_2OMe via oxygen present in the solution.[10a] Such a species was observed in the ^{31}P NMR spectrum at 179.6 ppm as a singlet, but several attempts to isolate it were not successful due to its instability. BF_2OMe is readily replaced by a stronger base such as PPh_3 to give the stable complex **c**. These results obtained here were, as expected, similar to those for the iron analogues.[10a,b]

It is generally accepted that a bond between a transition metal and a main-group element becomes stronger on going down the periodic table for transition metals in the same group. With an expectation of obtaining or detecting the cationic phosphenium complex, we attempted the above reactions at −78 °C. However, the resonance due to the cationic phosphenium complex was not observed at all in the ^{31}P NMR spectrum. These results suggest that when a group 14 element ligand coordinated to Ru is a carbon atom, the phosphenium complex as a whole is very reactive and the further reaction proceeds immediately; i.e., migratory insertion of the phosphenium ligand into the Ru−C bond or, more simply, alkyl migration from the Ru to the phosphenium P occurs to give a 16-electron cationic complex. Similar results were obtained when TMSOTf was used as a Lewis acid.

Reaction of Silyl Complexes with a Lewis Acid. In contrast to the reaction of alkyl complexes, the reaction of a silyl complex, Cp(CO)($SiMe_3$)Ru{PNN-(OMe)} (**3a**), with BF_3·OEt_2 resulted in the formation of the cationic phosphenium complex [Cp(CO)($SiMe_3$)-Ru{PNN}]BF_4 (**3b**) (eq 5). In the ^{31}P NMR spectrum, a



singlet was observed at 286.6 ppm, which was at 135.0 ppm lower magnetic field than that of the starting complex. This large downfield shift strongly suggests the formation of the cationic phosphenium complex.[7,8,10] For example, the corresponding cationic phosphenium complex of Fe, [Cp(CO)($SiMe_3$)Fe{PNN}]BF_4, the structure of which was determined by X-ray analysis, exhibits a resonance in the ^{31}P NMR spectrum at 309.9 ppm, which is 132.7 ppm lower than that of the starting complex, Cp(CO)($SiMe_3$)Fe{PNN(OMe)}.[10a] In the ^1H and ^{13}C NMR spectra, a doublet assigned to an OMe group on the phosphorus in **3a** disappeared, indicating that the OMe group was abstracted by a Lewis acid. The ^{29}Si NMR spectrum showed a doublet at 25.8 ppm (25.2 ppm for the starting complex), indicating that the $SiMe_3$ ligand remains intact.

The cationic phosphenium complex **3b** thus formed is fairly stable in the reaction mixture, but several attempts to isolate **3b** as a solid have not been successful to date. However, **3b** could be converted, by the reaction with $PhCH_2MgCl$, into the isolable Cp(CO)($SiMe_3$)Ru-{PNN(CH_2Ph)} (**3d**), which was fully characterized and was shown to have the $PhCH_2$ group bound to the phosphorus atom (eq 5). This is further evidence that **3b** is a cationic phosphenium complex.

The reaction of the ruthenium disilane complex **4a** with BF_3·OEt_2 was also carried out. Ogino et al. have reported for transition-metal disilane complexes with CO ligands that photolysis initiates a loss of CO, and then a terminal silyl group migrates to a coordinatively unsaturated metal center with an Si−Si bond cleaved.[12] Since a cationic phosphenium complex is also considered to have an unsaturated site on the P, the migration of the silyl group to the phosphenium P atom may well be expected when the cationic phosphenium complex is formed in the reaction of **4a**.

In the reaction of **4a** at −78 °C, the cationic phosphenium complex **4b** was formed quantitatively, but a further reaction involving the cleavage of the Si−Si bond was not observed at all. Warming the reaction mixture to room temperature led to the formation of unassignable products. The cationic phosphenium complex **4b** is stable enough in the reaction mixture at −78 °C, but the attempts to isolate it as a solid were all in vain because of the accompanying decomposition. Instead, the subsequent reaction with $PhCH_2MgCl$ gave the stable neutral complex **4d** (eq 5).

In the reaction of **3a** or **4a**, the silyl or methyl migration product as found in the reaction of **1a** or **2a** was not observed at all, even when PPh_3 was added to the reaction mixture. These results suggest that when a group 14 element ligand coordinated to Ru is a silicon atom, the phosphenium complex formed is comparatively stable, probably due to the Ru−Si bond being stronger than the Ru−C bond. Similar results were obtained when TMSOTf was used as a Lewis acid.

Reaction of a Germyl Complex with a Lewis Acid. The reaction of the germyl complex Cp(CO)-($GeMe_3$)Ru{PNN(OMe)} (**5a**) with BF_3·OEt_2 or TMSOTf gave a homogeneous solution, which showed spectroscopic data similar to those of the silyl complex **3a**. When BF_3·OEt_2 is used, for example, a higher wave-

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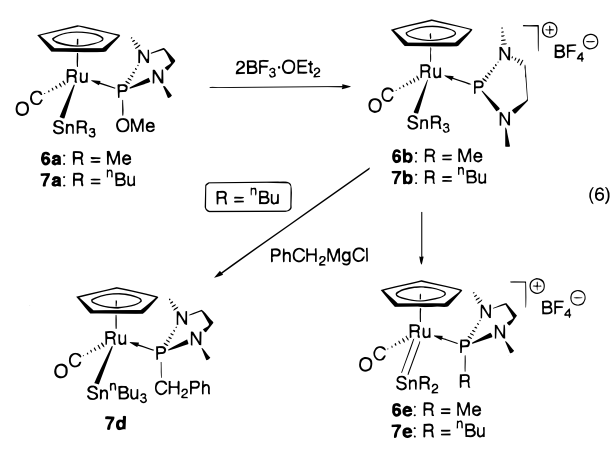
number shift by 53 cm^{-1} is observed for ν_{CO} in the IR spectrum compared with the starting complex **5a**, the ^{31}P NMR spectrum exhibits a singlet at 289.10 ppm which is at more than 100 ppm lower magnetic field than that of **5a**, and the ^{1}H and ^{13}C NMR spectra show the absence of an OMe group and the presence of a $GeMe_3$ group. Therefore, the product of the reaction is strongly suggested to be a cationic phosphenium complex, [Cp(CO)($GeMe_3$)Ru{PNN}]BF_4 (**5b**) (eq 5).

Complex **5b** is stable at room temperature in the reaction mixture and does not undergo germyl migration from Ru to the phosphenium P. The subsequent reaction with $PhCH_2MgCl$ gave the isolable complex **5d**, which was fully characterized.

Reaction of Stannyl Complexes with $BF_3 \cdot OEt_2$. The product in the reaction of stannyl complexes depends on the kind of Lewis acid used. In the reaction of the $SnMe_3$ complex Cp(CO)($SnMe_3$)Ru{PNN(OMe)} (**6a**) with 2 equiv of $BF_3 \cdot OEt_2$, the ^{31}P NMR spectrum showed singlet signals at 286.2 and 185.0 ppm at the beginning of the reaction. The former resonance, which is at 134.3 ppm lower magnetic field than that of the starting complex **6a**, can be assigned to a cationic phosphenium complex where an OMe group on the P is eliminated as an anion (vide supra). This signal disappeared within 30 min, and only the signal at 185.0 ppm was left. At the same time, the ^{119}Sn NMR spectrum showed a broad signal at 664.4 ppm, which is at considerably lower field than that (58.4 ppm) of **6a**. This very low chemical shift strongly suggests the formation of an Ru=Sn fragment.[10b,c,13,14] For example, the stannylene complex [Cp(CO){PNN(Me)}Fe=$SnMe_2$]OTf exhibits a resonance in the ^{119}Sn NMR spectrum at 495.8 ppm[10b,c] and $(CO)_5Cr=Sn(SCH_2CH_2)_2N^tBu$ at 622.8 ppm.[14] On the basis of these results and the formation of a stannylene complex in the reaction of the corresponding iron complex,[10c] the product would be best formulated as [Cp(CO){PNN(Me)}Ru=$SnMe_2$]BF_4 (**6e**), where one of the methyl groups on the Sn migrates to the phosphenium P atom (eq 6). However, **6e** has proved too reactive to isolate as a solid to date.



(6)

The reaction of the Sn^nBu_3 complex **7a** with $BF_3 \cdot OEt_2$ was also carried out. It has been reported that an Sn−^{n}Bu bond is less reactive than an Sn−Me bond in electrophilic cleavage reactions.[15] Therefore, it is expected that a cationic phosphenium complex with an Sn^nBu_3 group is more stable than that with an $SnMe_3$ group, since the stronger Sn−^{n}Bu bond retards the ^{n}Bu migration from Sn to P.

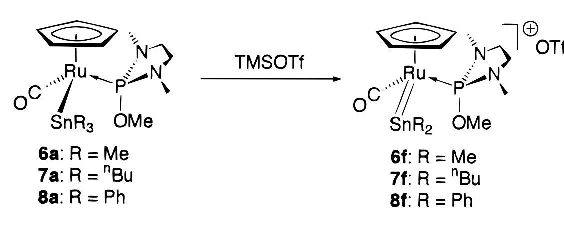
As expected, in the reaction of **7a** at −78 °C, the cationic phosphenium complex **7b** was cleanly formed and was stable in the reaction mixture at −78 °C. Although **7b** could not be isolated as a solid, the spectroscopic data were fully obtained and they confirmed **7b** to be a cationic phosphenium complex. The treatment of **7b** with $PhCH_2MgCl$ at −78 °C yielded **7d** quantitatively, which was isolated and fully characterized (eq 6). This is another evidence that **7b** is a cationic phosphenium complex.

When **7b** was gradually warmed to room temperature in the reaction mixture, the ^{31}P and ^{119}Sn NMR spectra showed the disappearance of the resonance due to **7b**. Instead, a new resonance probably due to a stannylene complex **7e** appeared at 194.8 ppm in the ^{31}P NMR spectrum and at 674.67 ppm in the ^{119}Sn NMR spectrum. However, several attempts to isolate **7e** were also unsuccessful due to its instability.

Similarly, reaction of the $SnPh_3$ complex **8a** with $BF_3 \cdot OEt_2$ was also attempted. In this case, the ^{31}P and ^{119}Sn NMR measurements revealed the formation of several kinds of complexes. The Sn−C bond[15] for **8a** is the weakest among **6a**−**8a**, which may cause the complicated reactions involving Sn−Ph bond cleavage (vide infra). We did not analyze the products in detail.

In the reaction of stannyl complexes **6a** and **7a** with $BF_3 \cdot OEt_2$, it is clearly shown that an OMe group on the phosphorus is first abstracted as an anion to give a cationic phosphenium complex. Then it undergoes alkyl migration from Sn to P to give a stannylene complex.

Reaction of Stannyl Complexes with Trimethylsilyl Triflate (TMSOTf). In contrast to the reaction with $BF_3 \cdot OEt_2$, the reaction of stannyl complexes with TMSOTf gave a different product. In the reaction of the $SnMe_3$ complex **6a** in hexane, the stannylene complex [Cp(CO){PNN(OMe)}Ru=$SnMe_2$]OTf (**6f**) was obtained as a white powder (eq 7), which was characterized by



(7)

NMR and IR spectroscopy as well as elemental analysis. The IR spectrum of **6f** showed a CO stretching absorption at 1939 cm^{-1}, which is 22 cm^{-1} higher than that of the starting complex **6a**, suggesting that the product has cationic character. In the ^{119}Sn NMR spectrum, a doublet was observed at 494.1 ppm (J_{PSn} = 311.2 Hz), which is at 435.7 ppm lower magnetic field than that of **6a**. This large downfield shift suggests the formation of the stannylene complex (vide supra).[10b,c,13,14] The ^{31}P NMR spectrum did not exhibit any significant change in the chemical shift, indicating that the phosphite ligand coordinated to Ru remained intact in the reac-

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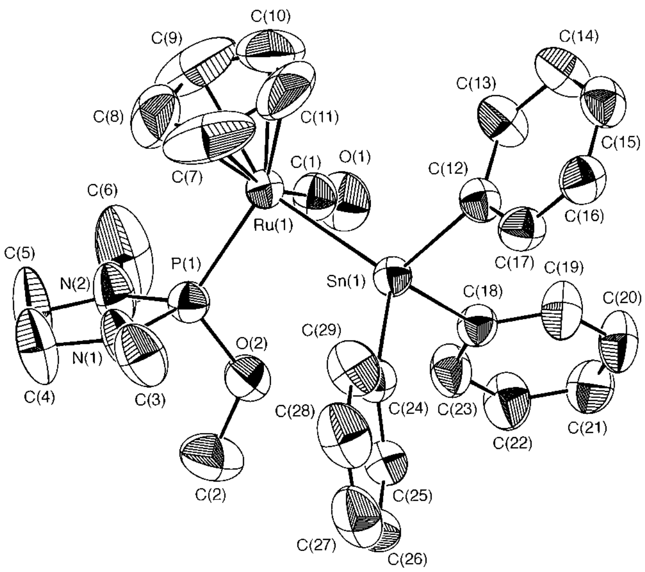


Figure 1. ORTEP drawing of **8a** showing the atom-numbering scheme. The thermal ellipsoids are drawn at the 50% probability level.

tion, which was also confirmed by the ^{1}H and ^{13}C NMR spectra. In the ^{1}H NMR spectrum, it was confirmed that one of methyl groups on Sn was eliminated. Similar results were obtained in the reactions of **7a** and **8a** to give the corresponding stannylene complexes **7f** and **8f**, respectively (eq 7), and the X-ray analysis established the structure for **8f**, which is found to be a stannylene complex stabilized by both an OTf anion and an OMe oxygen (vide infra).

In solution, there may be an equilibrium for these stannylene complexes obtained here between a base-stabilized stannylene form and a base-free one. For example, the ^{1}H and ^{13}C NMR spectra of **6f** show that the two Me groups on Sn are magnetically equivalent, indicating that when an OTf anion is freed from the Sn, fast rotation of the $SnMe_2$ group takes place around the Ru−Sn bond.

In the reaction with TMSOTf, an OMe elimination reaction observed on treatment with $BF_3{\cdot}OEt_2$ was not observed at all; however, one of the R groups on Sn is selectively abstracted. Although it is not easy to elucidate where the selectivity comes from, it should be noted that an OTf anion can encourage the cleavage of an Sn−R bond, as is shown in the following example. Addition of NaOTf to a solution containing a cationic phosphenium iron complex, [Cp(CO)(Sn^{n}Bu$_3$)Fe{PNN}]-BF_4, promotes a migration of one ^{n}Bu group from the Sn to the phosphenium P to give a stannylene complex, [Cp(CO){PNN(^{n}Bu)}Fe=Sn^{n}Bu$_2$]OTf.[10b] Coordination of the OTf oxygen to the Sn to give a five-coordinated Sn (hypervalent Sn) may trigger an R migration from Sn to P. Therefore, it may be considered that the coordination ability of OTf$^-$ is responsible for the interesting selectivity found here.

In the reaction of Cp(CO)(SnR_3)M{PNN(OMe)} with TMSOTf, an R group is abstracted from a stannyl group for the ruthenium complex, whereas an OMe group is abstracted from a phosphite ligand for the iron complex.[10b,c] This may be explained from the following differences between the Fe and Ru complexes: (i) in the O atom basicity of an OMe group, (ii) in the strength of an Sn−R bond, (iii) in the thermodynamic stability of the product, and (iv) in the energy of the transition state of the reaction, for example. However, where the difference in the reactivity comes from is not clear at present.

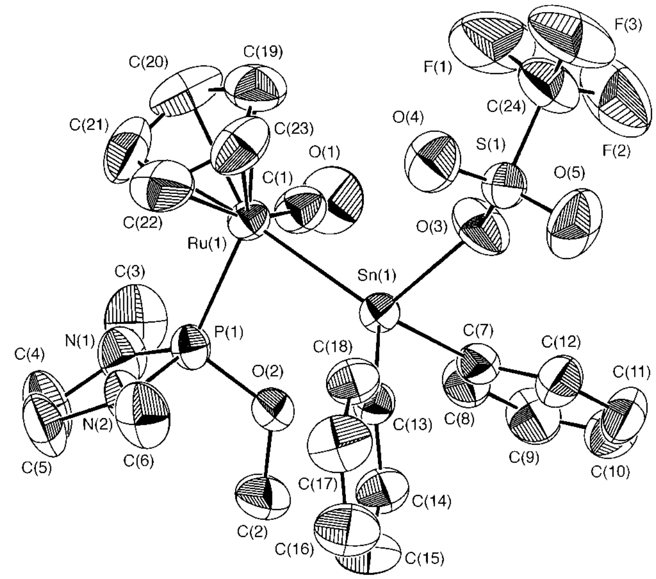


Figure 2. ORTEP drawing of **8f** showing the atom-numbering scheme. The thermal ellipsoids are drawn at the 50% probability level.

Table 1. Summary of Crystal Data for 8a and 8f

	8a	8f
formula	$C_{29}H_{33}N_2O_2RuPSn$	$C_{24}H_{28}F_3N_2O_5RuPSSn$
fw	692.30	764.31
cryst syst	monoclinic	monoclinic
space group	$P2_1/n$	$P2_1/n$
a, Å	18.024(7)	18.487(8)
b, Å	15.546(6)	12.007(6)
c, Å	10.621(5)	13.997(5)
β, deg	101.50(3)	105.56(3)
V, Å^3	2916(2)	2993(2)
Z	4	4
D_{calcd}, g cm^{-3}	1.58	1.80
μ, cm^{-1}	14.5	14.9
cryst size, mm	0.37 × 0.37 × 0.20	0.30 × 0.30 × 0.25
radiation (λ, Å)	Mo Kα (0.710 73)	Mo Kα (0.710 73)
scan technique	$\omega-2\theta$	$\omega-2\theta$
scan range, deg	$3 < 2\theta < 57$	$3 < 2\theta < 53$
no. of unique data	9358	7533
no. of unique data with $F_o > 3\sigma(F_o)$	5269	5098
R	0.034	0.031
R_w	0.041	0.032

Crystal Structures of 8a and 8f. X-ray structure analyses of **8a** and **8f** were undertaken. The ORTEP drawings of **8a** and **8f** are displayed in Figures 1 and 2, respectively. Crystal data and selected bond distances and angles are summarized in Tables 1−3.

These complexes have normal piano-stool configurations; the ruthenium has a cyclopentadienyl ligand bonded in an η^5 fashion, a terminal CO ligand, a diamino-substituted phosphite ligand, and a tin ligand.

Comparison of the structures of **8a** and **8f** reveals that the Ru−Sn bond is ca. 0.04 Å shorter for **8f** than for **8a**. However, the Ru−Sn bond (2.577 Å) for **8f** is not shortened in comparison with various Ru−SnR_3 complexes previously reported, where Ru−Sn single-bond lengths between 2.55 and 2.69 Å have been measured.[16]

(16) Holt, M. S.; Wilson, W. L.; Nelson, J. H. *Chem. Rev.* **1989**, *89*, 11.

Table 2. Selected Bond Distances (Å) and Angles (deg) for 8a

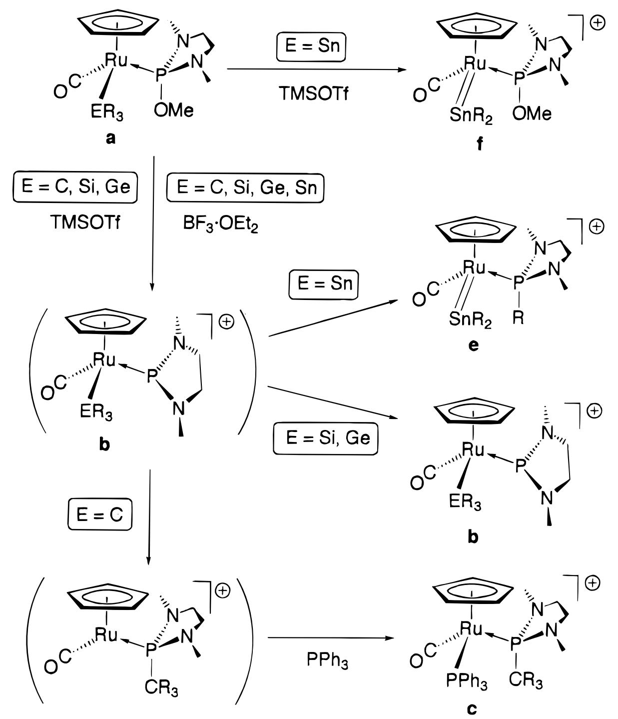
	Bond Distances		
Sn(1)−Ru(1)	2.617(1)	P(1)−N(2)	1.662(3)
Sn(1)−C(12)	2.177(2)	O(1)−C(1)	1.148(4)
Sn(1)−C(18)	2.181(3)	O(2)−C(2)	1.438(2)
Sn(1)−C(24)	2.164(3)	N(1)−C(3)	1.421(5)
Ru(1)−P(1)	2.239(1)	N(1)−C(4)	1.447(5)
Ru(1)−C(1)	1.858(3)	N(2)−C(5)	1.423(6)
P(1)−O(2)	1.612(3)	N(2)−C(6)	1.440(6)
P(1)−N(1)	1.665(3)	C(4)−C(5)	1.447(6)
	Bond Angles		
Ru(1)−Sn(1)−C(12)	111.6(1)	O(2)−P(1)−N(2)	105.0(2)
Ru(1)−Sn(1)−C(18)	117.5(1)	N(1)−P(1)−N(2)	92.0(2)
Ru(1)−Sn(1)−C(24)	121.0(1)	P(1)−O(2)−C(2)	121.0(3)
C(12)−Sn(1)−C(18)	99.0(1)	P(1)−N(1)−C(3)	125.2(3)
C(12)−Sn(1)−C(24)	101.1(1)	P(1)−N(1)−C(4)	114.5(3)
C(18)−Sn(1)−C(24)	103.3(1)	C(3)−N(1)−C(4)	120.1(3)
Sn(1)−Ru(1)−P(1)	93.3(1)	P(1)−N(2)−C(5)	114.6(3)
Sn(1)−Ru(1)−C(1)	85.1(1)	P(1)−N(2)−C(6)	124.4(3)
P(1)−Ru(1)−C(1)	88.9(1)	C(5)−N(2)−C(6)	119.2(4)
Ru(1)−P(1)−O(2)	111.4(1)	Ru(1)−C(1)−O(1)	177.5(3)
Ru(1)−P(1)−N(1)	119.0(2)	N(1)−C(4)−C(5)	108.4(4)
Ru(1)−P(1)−N(2)	118.9(2)	N(2)−C(5)−C(4)	109.9(4)
O(2)−P(1)−N(1)	108.3(2)		

Table 3. Selected Bond Distances (Å) and Angles (deg) for 8f

	Bond Distances		
Sn(1)−Ru(1)	2.577(1)	P(1)−N(2)	1.649(3)
Sn(1)···O(2)	2.711(2)	O(1)−C(1)	1.144(5)
Sn(1)−O(3)	2.253(3)	O(2)−C(2)	1.443(5)
Sn(1)−C(7)	2.147(3)	N(1)−C(3)	1.434(6)
Sn(1)−C(13)	2.147(3)	N(1)−C(4)	1.450(6)
Ru(1)−P(1)	2.251(1)	N(2)−C(5)	1.445(5)
Ru(1)−C(1)	1.841(4)	N(2)−C(6)	1.444(5)
P(1)−O(2)	1.632(2)	C(4)−C(5)	1.463(6)
P(1)−N(1)	1.653(3)		
	Bond Angles		
Ru(1)−Sn(1)···O(2)	71.9(1)	O(2)−P(1)−N(2)	108.1(2)
Ru(1)−Sn(1)−O(3)	108.2(1)	N(1)−P(1)−N(2)	92.5(2)
Ru(1)−Sn(1)−C(7)	128.6(1)	Sn(1)···O(2)−P(1)	92.2(1)
Ru(1)−Sn(1)−C(13)	121.9(1)	Sn(1)···O(2)−C(2)	140.7(2)
O(2)···Sn(1)−O(3)	168.8(1)	P(1)−O(2)−C(2)	122.4(2)
O(3)−Sn(1)−C(7)	87.4(1)	P(1)−N(1)−C(3)	124.7(3)
O(3)−Sn(1)−C(13)	97.2(1)	P(1)−N(1)−C(4)	114.3(3)
C(7)−Sn(1)−C(13)	103.2(1)	C(3)−N(1)−C(4)	120.9(4)
Sn(1)−Ru(1)−P(1)	83.3(1)	P(1)−N(2)−C(5)	115.5(3)
Sn(1)−Ru(1)−C(1)	86.1(1)	P(1)−N(2)−C(6)	125.6(3)
P(1)−Ru(1)−C(1)	91.4(2)	C(5)−N(2)−C(6)	118.8(3)
Ru(1)−P(1)−O(2)	105.1(1)	Ru(1)−C(1)−O(1)	177.5(3)
Ru(1)−P(1)−N(1)	121.6(2)	N(1)−C(4)−C(5)	108.8(3)
Ru(1)−P(1)−N(2)	120.7(1)	N(2)−C(5)−C(4)	107.7(4)
O(2)−P(1)−N(1)	107.9(2)		

For **8f**, the tin atom is five-coordinate with a geometry described best as distorted trigonal bipyramidal, with two oxygens (O(2) and O(3)) occupying the axial sites: the Ru(1)Sn(1)C(7)C(13) unit is nearly planar (the sum of angles around Sn amounts to 353.7°), and the O(2)−Sn(1)−O(3) angle is 168.8°. In comparison with the structures of O-base-stabilized stannylene complexes reported previously,[10c,14,17] the Sn(1)−O(2) bond length (2.253 Å) is reasonable, whereas the Sn(1)−O(3) bond is slightly longer (2.711 Å) but significantly shorter than the sum of van der Waals radii (3.70 Å).[18] Therefore, **8f** is best described as a doubly base stabilized stannylene complex of ruthenium. These results are very similar to those of an iron analogue, [Cp(CO){PNN(Me)}Fe═SnMe$_2$]OTf,[10c] except in the manner of stabilization of the stannylene Sn by a base, where one of the nitrogen atoms on P acts as a donor in place of an OMe oxygen in **8f**.

Scheme 2



Conclusion

The results in reactions of ruthenium complexes Cp(CO)(ER$_3$)Ru{PNN(OMe)} (**a**) (E = group 14 element) with a Lewis acid are summarized in Scheme 2. When BF$_3$·OEt$_2$ is used, a cationic phosphenium complex (**b**) is obtained with an OMe group abstraction in the initial step irrespective of the kind of E. However, the successive reaction depends on the kind of E. When E is a carbon atom, migratory insertion of the phosphenium ligand into the Ru−C bond takes place, and a subsequent reaction with PPh$_3$ gives **c**. When E is a silicon or a germanium atom, the cationic phosphenium complex (**b**) is comparatively stable and an Ru−Si or an Ru−Ge bond remains unreacted. When E is a tin atom, one of R groups on the Sn migrates to the phosphenium P to give a stannylene complex (**e**). These observations are very similar to those of the iron analogues. The reactions with another Lewis acid, TMSOTf, exhibit reactivities similar to those with BF$_3$·OEt$_2$, except when E is a tin atom. In the reaction of a stannyl complex of Ru with TMSOTf, one of the R groups on the Sn is directly abstracted to give another stannylene complex (**f**). This result is quite different from that of the iron case.

Experimental Section

General Remarks. All reactions were carried out under an atmosphere of dry nitrogen by using standard Schlenk tube techniques. All solvents were purified by distillation: ether, THF, and benzene were distilled from sodium/benzophenone,

(17) For example: (a) Balch, A. L.; Oram, D. E. *Organometallics* **1988**, *7*, 155. (b) Almedia, J. F.; Dixon, K. R.; Eaborn, C.; Hitchcock, P. B.; Pidcock, A.; Vinaixa, S. *J. Chem. Soc., Chem. Commun.* **1982**, 1315.

(18) Huheey, J. E. In *Inorganic Chemistry*; Harper & Row: New York, 1983.

heptane, hexane, and pentane were distilled from sodium metal, and CH_2Cl_2 and $ClCH_2CH_2Cl$ were distilled from P_2O_5. All solvents were stored under a nitrogen atmosphere. $BF_3 \cdot OEt_2$ and TMSOTf were distilled prior to use. PNN(OMe) was prepared according to the literature method.[19] Other reagents employed in this research were used as received. Column chromatography was carried out quickly in the air on Merck aluminum oxide 90 (No. 1.01097).

IR spectra were recorded on a Shimadzu FTIR-8100A spectrometer. A JEOL LA-300 multinuclear spectrometer was used to obtain ^{1}H, ^{13}C, ^{29}Si, ^{31}P, and ^{119}Sn NMR spectra. The reference was as follows: for ^{1}H and ^{13}C NMR data, $Si(CH_3)_4$ as an internal standard; for ^{29}Si NMR data, $Si(CH_3)_4$ as an external standard; for ^{31}P NMR data, 85% H_3PO_4 as an external standard; for ^{119}Sn NMR data, $SnMe_4$ as an external standard. Elemental analyses were performed on a Perkin-Elmer 2400CHN elemental analyzer.

Preparation of Cp(CO)(H)Ru{PNN(OMe)}. $Ru_3(CO)_{12}$ (1000 mg, 1.56 mmol) was added to a solution of CpH (1.30 mL, 15.8 mmol) in heptane (100 mL) in a Schlenk tube, and the reaction mixture was heated under reflux for 2 h. The initial deep red solution became a clear yellow solution, indicating the formation of $Cp(CO)_2RuH$.[20] To this solution, which was cooled to room temperature, was added PNN(OMe) (0.69 mL, 4.69 mmol), and the reaction mixture was heated to 100 °C for 10 min to complete the reaction. After filtration to remove insoluble materials, the filtrate was concentrated to ca. 10 mL under reduced pressure to give a yellow suspension. The supernatant was removed by cannula, and the resulting residue was washed with pentane and dried in vacuo to yield a yellow powder of the title compound (1157 mg, 3.37 mmol, 72%). Although the ^{1}H NMR spectrum showed that the product includes a small amount of impurity probably due to cyclopentadiene, it was used for the following reactions as a starting complex without further purification.

It is possible to obtain the title compound as a pure form. The yellow powder obtained above was loaded on an alumina column, the colorless band eluted with benzene/hexane (1/1) was collected, and the solvents were removed in vacuo to give a white powder. Crystallization from a hot hexane solution gave a colorless crystal of the title compound. Yield: <10%. Anal. Calcd for $C_{11}H_{19}N_2O_2PRu$: C, 38.48; H, 5.58; N, 8.16. Found: C, 38.65; H, 5.49; N, 8.08. IR (ν_{CO}, cm^{-1}, in benzene): 1935. ^{1}H NMR (δ, in C_6D_6): −11.67 (d, J_{PH} = 33.3 Hz, 1H, RuH), 2.54 (d, J_{PH} = 12.1 Hz, 3H, NCH_3), 2.62 (d, J_{PH} = 12.1 Hz, 3H, NCH_3), 2.64 (m, 2H, NCH_2), 2.88 (m, 2H, NCH_2), 3.07 (d, J_{PH} = 11.7 Hz, 3H, OCH_3), 4.99 (d, J_{PH} = 0.7 Hz, 5H, C_5H_5). ^{13}C NMR (δ, in C_6D_6): 33.86 (d, J_{PC} = 11.8 Hz, NCH_3), 34.21 (d, J_{PC} = 13.1 Hz, NCH_3), 50.72 (s, NCH_2), 50.79 (s, NCH_2), 51.16 (d, J_{PC} = 9.9 Hz, OCH_3), 83.08 (d, J_{PC} = 2.5 Hz, C_5H_5), 205.10 (d, J_{PC} = 24.2 Hz, CO). ^{31}P NMR (δ, in C_6D_6): 163.44.

Preparation of Cp(CO)(ER$_3$)Ru{PNN(OMe)} (ER$_3$ = Me (1a), CH$_2$SiMe$_3$ (2a), SiMe$_3$ (3a), SiMe$_2$SiMe$_3$ (4a), GeMe$_3$ (5a), SnMe$_3$ (6a), Sn^{n}Bu$_3$ (7a), SnPh$_3$ (8a)) from Cp(CO)(H)Ru{PNN(OMe)}. In a typical procedure, ^{n}BuLi (0.63 mL, 1.57 M of hexane solution, 0.99 mmol) was added to a solution of Cp(CO)(H)Ru{PNN(OMe)} (340 mg, 0.99 mmol) in THF (5 mL) at −78 °C. The solution was stirred for 20 min, and then MeI (0.062 mL, 0.99 mmol) was added. The reaction mixture was warmed to room temperature and stirred for 3 h. After the volatiles were removed under reduced pressure, the residue was loaded on an alumina column and the column eluted with CH_2Cl_2. The yellow band developed was collected and was reloaded on an alumina column. The colorless band eluted with CH_2Cl_2/hexane (1/4) was collected, and the solvents were removed in vacuo to give a colorless crystal of **1a** (251 mg, 0.70 mmol, 71%). Anal. Calcd for $C_{12}H_{21}N_2O_2PRu$: C, 40.33; H, 5.92; N, 7.84. Found: C, 40.35; H, 5.82; N, 7.82. IR (ν_{CO}, cm^{-1}, in CH_2Cl_2): 1924. ^{1}H NMR (δ, in $CDCl_3$): 0.13 (d, J_{PH} = 3.9 Hz, 3H, $RuCH_3$), 2.65 (d, J_{PH} = 11.0 Hz, 3H, NCH_3), 2.68 (d, J_{PH} = 10.5 Hz, 3H, NCH_3), 3.08 (m, 2H, NCH_2), 3.28 (d, J_{PH} = 11.6 Hz, 3H, OCH_3), 3.33 (m, 2H, NCH_2), 4.98 (s, 5H, C_5H_5). ^{13}C NMR (δ, in $CDCl_3$): −33.18 (d, J_{PC} = 13.7 Hz, $RuCH_3$), 33.25 (d, J_{PC} = 11.8 Hz, NCH_3), 33.89 (d, J_{PC} = 12.4 Hz, NCH_3), 51.23 (s, NCH_2), 51.39 (d, J_{PC} = 1.3 Hz, NCH_2), 51.48 (d, J_{PC} = 9.4 Hz, OCH_3), 85.67 (d, J_{PC} = 3.1 Hz, C_5H_5), 207.07 (d, J_{PC} = 28.7 Hz, CO). ^{31}P NMR (δ, in $CDCl_3$): 152.10 (s).

2a was obtained from $ClCH_2SiMe_3$ as a colorless crystal. Yield: 5%. Anal. Calcd for $C_{15}H_{29}N_2O_2PRuSi$: C, 41.94; H, 6.81; N, 6.52. Found: C, 42.22; H, 7.03; N, 6.23. IR (ν_{CO}, cm^{-1}, in CH_2Cl_2): 1914. ^{1}H NMR (δ, in $CDCl_3$): −0.65 (dd, J_{PH} = 12.1 Hz, J_{HH} = 2.9 Hz, 1H, $RuCH_2$), −0.04 (s, 9H, $SiCH_3$), 0.04 (dd, J_{PH} = 12.1 Hz, J_{HH} = 2.4 Hz, 1H, $RuCH_2$), 2.65 (d, J_{PH} = 10.4 Hz, 3H, NCH_3), 2.71 (d, J_{PH} = 10.6 Hz, 3H, NCH_3), 3.11 (m, 2H, NCH_2), 3.32 (d, J_{PH} = 11.6 Hz, 3H, OCH_3), 3.35 (m, 2H, NCH_2), 4.97 (s, 5H, C_5H_5). ^{13}C NMR (δ, in $CDCl_3$): −30.11 (d, J_{PC} = 10.0 Hz, $RuCH_2$), 2.49 (s, $SiCH_3$), 33.39 (d, J_{PC} = 11.2 Hz, NCH_3), 33.81 (d, J_{PC} = 13.0 Hz, NCH_3), 51.36 (s, NCH_2), 51.50 (d, J_{PC} = 9.3 Hz, OCH_3), 51.52 (s, NCH_2), 85.38 (d, J_{PC} = 3.1 Hz, C_5H_5), 207.38 (d, J_{PC} = 29.2 Hz, CO). ^{29}Si NMR (δ, in $CDCl_3$): 8.49 (s). ^{31}P NMR (δ, in $CDCl_3$): 151.33 (s).

3a was obtained from $ClSiMe_3$ as a white powder. Yield: 72%. Anal. Calcd for $C_{14}H_{27}N_2O_2PRuSi$: C, 40.47; H, 6.55; N, 6.74. Found: C, 40.53; H, 6.38; N, 6.75. IR (ν_{CO}, cm^{-1}, in CH_2Cl_2): 1917. ^{1}H NMR (δ, in $CDCl_3$): 0.25 (s, 9H, $SiCH_3$), 2.63 (d, J_{PH} = 11.6 Hz, 3H, NCH_3), 2.71 (d, J_{PH} = 11.0 Hz, 3H, NCH_3), 3.08 (m, 2H, NCH_2), 3.22 (d, J_{PH} = 11.9 Hz, 3H, OCH_3), 3.33 (m, 2H, NCH_2), 4.95 (d, J_{PH} = 0.6 Hz, C_5H_5). ^{13}C NMR (δ, in $CDCl_3$): 9.36 (s, $SiCH_3$), 33.70 (d, J_{PC} = 11.8 Hz, NCH_3), 33.71 (d, J_{PC} = 11.8 Hz, NCH_3), 50.69 (d, J_{PC} = 1.2 Hz, NCH_2), 50.95 (d, J_{PC} = 12.4 Hz, OCH_3), 51.43 (d, J_{PC} = 1.9 Hz, NCH_2), 84.92 (d, J_{PC} = 2.5 Hz, C_5H_5), 206.32 (d, J_{PC} = 24.2 Hz, CO). ^{29}Si NMR (δ, in $CDCl_3$): 25.21 (d, J_{PSi} = 17.3 Hz). ^{31}P NMR (δ, in $CDCl_3$): 153.64 (s).

4a was obtained from $ClSiMe_2SiMe_3$ as a colorless crystal. Yield: 66%. Anal. Calcd for $C_{16}H_{33}N_2O_2PRuSi_2$: C, 40.57; H, 7.02; N, 5.91. Found: C, 40.59; H, 6.88; N, 5.98. IR (ν_{CO}, cm^{-1}, in CH_2Cl_2): 1922. ^{1}H NMR (δ, in $CDCl_3$): 0.05 (s, 9H, $RuSiSiCH_3$), 0.28 (s, 3H, $RuSiCH_3$), 0.38 (s, 3H, $RuSiCH_3$), 2.65 (d, J_{PH} = 11.6 Hz, 3H, NCH_3), 2.71 (d, J_{PH} = 11.2 Hz, 3H, NCH_3), 3.08 (m, 2H, NCH_2), 3.23 (d, J_{PH} = 11.9 Hz, 3H, OCH_3), 3.34 (m, 2H, NCH_2), 4.97 (d, J_{PH} = 0.6 Hz, 5H, C_5H_5). ^{13}C NMR (δ, in $CDCl_3$): −0.29 (s, $RuSiSiCH_3$), 3.46 (s, $SiCH_3$), 5.26 (s, $SiCH_3$), 33.69 (d, J_{PC} = 12.8 Hz, NCH_3), 33.81 (d, J_{PC} = 13.1 Hz, NCH_3), 50.75 (s, NCH_2), 50.93 (d, J_{PC} = 12.4 Hz, OCH_3), 51.43 (s, NCH_2), 84.72 (d, J_{PC} = 2.5 Hz, C_5H_5), 205.46 (d, J_{PC} = 25.5 Hz, CO). ^{29}Si NMR (δ, in $CDCl_3$): −11.54 (s, RuSi*Si*), −0.84 (d, J_{PSi} = 15.5 Hz, Ru*Si*Si). ^{31}P NMR (δ, in $CDCl_3$): 151.26 (s).

5a was obtained from $ClGeMe_3$ as a white powder. Yield: 78%. Anal. Calcd for $C_{14}H_{27}GeN_2O_2PRu$: C, 36.55; H, 5.92; N, 6.09. Found: C, 36.75; H, 5.84; N, 5.96. IR (ν_{CO}, cm^{-1}, in CH_2Cl_2): 1917. ^{1}H NMR (δ, in $CDCl_3$): 0.33 (s, 9H, $GeCH_3$), 2.64 (d, J_{PH} = 10.6 Hz, 3H, NCH_3), 2.68 (d, J_{PH} = 10.1 Hz, 3H, NCH_3), 3.07 (m, 2H, NCH_2), 3.21 (d, J_{PH} = 11.9 Hz, 3H, OCH_3), 3.30 (m, 2H, NCH_2), 4.92 (d, J_{PH} = 0.8 Hz, 5H, C_5H_5). ^{13}C NMR (δ, in $CDCl_3$): 7.93 (s, $GeCH_3$), 33.64 (d, J_{PC} = 13.7 Hz, NCH_3), 33.69 (d, J_{PC} = 13.5 Hz, NCH_3), 50.66 (s, NCH_2), 50.87 (d, J_{PC} = 12.4 Hz, OCH_3), 51.34 (d, J_{PC} = 2.5 Hz, NCH_2), 83.88 (d, J_{PC} = 2.5 Hz, C_5H_5), 206.14 (d, J_{PC} = 25.5 Hz, CO). ^{31}P NMR (δ, in $CDCl_3$): 153.26 (s).

6a was obtained from $ClSnMe_3$ as a white powder. Yield: 78%. Anal. Calcd for $C_{14}H_{27}N_2O_2PRuSn$: C, 33.22; H, 5.38; N, 5.53. Found: C, 33.21; H, 5.46; N, 5.43. IR (ν_{CO}, cm^{-1}, in CH_2Cl_2): 1917. ^{1}H NMR (δ, in $CDCl_3$): 0.15 (s, with Sn satellites,

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J_{SnH} = 42.9, 41.3 Hz, 9H, $SnCH_3$), 2.63 (d, J_{PH} = 10.6 Hz, 3H, NCH_3), 2.67 (d, J_{PH} = 11.7 Hz, 3H, NCH_3), 3.03 (m, 2H, NCH_2), 3.21 (d, J_{PH} = 11.9 Hz, 3H, OCH_3), 3.34 (m, 2H, NCH_2), 4.91 (d, J_{PH} = 0.4 Hz, 5H, C_5H_5). ^{13}C NMR (δ, in $CDCl_3$): −4.34 (s, with Sn satellites, J_{SnC} = 210.1, 201.4 Hz, $SnCH_3$), 33.73 (d, J_{PC} = 13.7 Hz, NCH_3), 33.86 (d, J_{PC} = 13.1 Hz, NCH_3), 50.67 (s, NCH_2), 51.06 (d, J_{PC} = 11.8 Hz, OCH_3), 51.34 (d, J_{PC} = 1.9 Hz, NCH_2), 82.28 (d, J_{PC} = 2.5 Hz, C_5H_5), 205.74 (d, J_{PC} = 24.9 Hz, CO). ^{31}P NMR (δ, in $CDCl_3$): 151.92 (s, with Sn satellites, J_{SnP} = 200.5, 191.6 Hz). ^{119}Sn NMR (δ, in $CDCl_3$): 58.39 (d, J_{PSn} = 202.3 Hz).

7a was obtained from $ClSn^nBu_3$ as a white powder. Yield: 79%. Anal. Calcd for $C_{23}H_{45}N_2O_2PRuSn$: C, 43.68; H, 7.17; N, 4.43. Found: C, 43.91; H, 7.41; N, 4.34. IR (ν_{CO}, cm^{-1}, in CH_2Cl_2): 1915. ^{1}H NMR (δ, in $CDCl_3$): 0.88 (m, 6H, $SnCH_2CH_2CH_2CH_3$), 0.90 (t, J_{HH} = 7.3 Hz, 9H, $SnCH_2CH_2CH_2CH_3$), 1.32 (sext, J_{HH} = 7.3 Hz, 6H, $SnCH_2CH_2CH_2CH_3$), 1.48 (m, 6H, $SnCH_2CH_2CH_2CH_3$), 2.64 (d, J_{PH} = 11.2 Hz, 3H, NCH_3), 2.67 (d, J_{PH} = 11.7 Hz, 3H, NCH_3), 3.05 (m, 2H, NCH_2), 3.21 (d, J_{PH} = 11.7 Hz, 3H, OCH_3), 3.34 (m, 2H, NCH_2), 4.94 (s, 5H, C_5H_5). ^{13}C NMR (δ, in $CDCl_3$): 13.66 (s, with Sn satellites, J_{SnC} = 217.5, 208.8 Hz, $SnCH_2CH_2CH_2CH_3$), 13.82 (s, $SnCH_2CH_2CH_2CH_3$), 27.94 (s, with Sn satellites, J_{SnC} = 54.7 Hz, $SnCH_2CH_2CH_2CH_3$), 30.37 (s, with Sn satellites, J_{SnC} = 16.8 Hz, $SnCH_2CH_2CH_2CH_3$), 33.81 (d, J_{PC} = 12.4 Hz, NCH_3), 33.89 (d, J_{PC} = 12.4 Hz, NCH_3), 50.78 (s, NCH_2), 50.97 (d, J_{PC} = 13.1 Hz, OCH_3), 51.44 (d, J_{PC} = 1.9 Hz, NCH_2), 81.89 (d, J_{PC} = 2.5 Hz, C_5H_5), 205.97 (d, J_{PC} = 24.9 Hz, CO). ^{31}P NMR (δ, in $CDCl_3$): 154.76 (s, with Sn satellites, J_{SnP} = 182.7, 173.8 Hz). ^{119}Sn NMR (δ, in $CDCl_3$): 75.15 (d, J_{PSn} = 181.7 Hz).

8a was obtained from $ClSnPh_3$ as a colorless crystal. Yield: 74%. Anal. Calcd for $C_{29}H_{33}N_2O_2PRuSn$: C, 50.31; H, 4.80; N, 4.05. Found: C, 50.44; H, 4.69; N, 4.03. IR (ν_{CO}, cm^{-1}, in CH_2Cl_2): 1929. ^{1}H NMR (δ, in $CDCl_3$): 2.34 (d, J_{PH} = 11.2 Hz, 3H, NCH_3), 2.55 (d, J_{PH} = 11.7 Hz, 3H, NCH_3), 2.82 (m, 2H, NCH_2), 2.97 (d, J_{PH} = 12.2 Hz, 3H, OCH_3), 3.12 (m, 2H, NCH_2), 4.97 (s, 5H, C_5H_5), 7.19 (m, 9H, C_6H_5), 7.54 (m, 6H, C_6H_5). ^{13}C NMR (δ, in $CDCl_3$): 33.34 (d, J_{PC} = 12.4 Hz, NCH_3), 33.55 (d, J_{PC} = 12.4 Hz, NCH_3), 50.64 (s, NCH_2), 51.15 (d, J_{PC} = 12.4 Hz, OCH_3), 51.18 (d, J_{PC} = 1.2 Hz, NCH_2), 82.78 (d, J_{PC} = 2.5 Hz, C_5H_5), 126.67 (s, with Sn satellites, J_{SnC} = 8.8 Hz, *p*-C_6H_5), 127.21 (s, with Sn satellites, J_{SnC} = 38.5 Hz, *m*-C_6H_5), 137.23 (s, with Sn satellites, J_{SnC} = 36.0 Hz, *o*-C_6H_5), 137.23 (s, with Sn satellites, J_{SnC} = 303.3 Hz, 289.6 Hz, ϵ-C_6H_5), 205.44 (d, J_{PC} = 24.2 Hz, CO). ^{31}P NMR (δ, in $CDCl_3$): 149.63 (s, with Sn satellites, J_{SnP} = 231.7, 220.5 Hz). ^{119}Sn NMR (δ, in $CDCl_3$): 10.11 (d, J_{PSn} = 229.7 Hz).

Alternative Preparation of Cp(CO)(CH_2SiMe_3)Ru{PNN(OMe)} (2a). Cp(CO)$_2$RuCH$_2$SiMe$_3$ (151 mg, 0.49 mmol), benzene (10 mL), and PNN(OMe) (0.080 mL, 0.54 mmol) were placed in a Pyrex Schlenk tube, and the solution was irradiated with a 400 W medium-pressure mercury arc lamp at 0 °C for 4 h. After the solvent was removed under reduced pressure, the resulting residue was loaded on an alumina column and eluted with CH_2Cl_2. The yellow band developed was collected and was reloaded on an alumina column. The colorless band eluted with CH_2Cl_2/hexane (1/9) was collected, and the solvents were removed in vacuo to give a white powder of **2a** (137 mg, 0.32 mmol, 65%).

Typical Preparation of [Cp(CO)(ER_3)Ru{PNN}]BF_4 (ER_3 = $SiMe_3$ (3b), $SiMe_2SiMe_3$ (4b), $GeMe_3$ (5b), Sn^nBu_3 (7b)). In a typical procedure, a solution of **3a** (147 mg, 0.38 mmol) in CH_2Cl_2 (1.5 mL) was cooled to −78 °C, and then BF_3·OEt_2 (0.096 mL, 0.76 mmol) was added. After the solution was warmed to room temperature, it was directly subjected to spectroscopic measurements, which confirmed the formation of **3b**. IR (ν_{CO}, cm^{-1}, in CH_2Cl_2): 1971. ^{13}C NMR (δ, in CH_2Cl_2): 9.43 (d, J_{PC} = 1.9 Hz, $SiCH_3$), 33.96 (d, J_{PC} = 13.1 Hz, NCH_3), 52.13 (s, NCH_2), 88.40 (s, C_5H_5), 201.26 (d, J_{PC} = 20.5 Hz, CO). ^{29}Si NMR (δ, in CH_2Cl_2): 25.78 (d, J_{PSi} = 18.4 Hz). ^{31}P NMR (δ, in CH_2Cl_2): 286.63 (s).

Similarly, the formations of **4b**, **5b**, and **7b** were confirmed when **4a**, **5a**, and **7a** were respectively used as starting complexes. **4b**: IR (ν_{CO}, cm^{-1}, in CH_2Cl_2) 1967. ^{13}C NMR (δ, in CH_2Cl_2): −1.67 (s, $RuSiSiCH_3$), 3.90 (s, $RuSiCH_3$), 5.04 (s, $RuSiCH_3$), 33.74 (d, J_{PC} = 14.3 Hz, NCH_3), 51.67 (s, NCH_2), 87.58 (d, J_{PC} = 3.7 Hz, C_5H_5), 200.54 (d, J_{PC} = 19.9 Hz, CO); ^{29}Si NMR (δ, in CH_2Cl_2) −13.03 (s, RuSi*Si*), −3.46 (d, J_{PSi} = 16.7 Hz, Ru*Si*Si); ^{31}P NMR (δ, in CH_2Cl_2) 286.13 (s). **5b**: IR (ν_{CO}, cm^{-1}, in CH_2Cl_2) 1970; ^{1}H NMR (δ, in CH_2Cl_2) 0.43 (s, 9H, $GeCH_3$), 2.89 (d, J_{PH} = 13.2 Hz, 6H, NCH_3), 3.71 (m, 4H, NCH_2), 5.39 (s, 5H, C_5H_5); ^{13}C NMR (δ, in CH_2Cl_2) 8.26 (s, $GeCH_3$), 33.62 (d, J_{PC} = 14.3 Hz, NCH_3), 51.79 (s, NCH_2), 87.36 (s, C_5H_5), 200.86 (d, J_{PC} = 21.8 Hz, CO); ^{31}P NMR (δ, in CH_2Cl_2) 289.10 (s). **7b**: IR (ν_{CO}, cm^{-1}, in CH_2Cl_2) 1962; ^{13}C NMR (δ, in CH_2Cl_2) 14.66 (s, with Sn satellites, J_{SnC} = 273.5, 260.4 Hz, $SnCH_2CH_2CH_2CH_3$), 15.23 (s, $SnCH_2CH_2CH_2CH_3$), 27.57 (s, with Sn satellites, J_{SnC} = 66.5 Hz, $SnCH_2CH_2CH_2CH_3$), 30.02 (s, with Sn satellites, J_{SnC} = 19.9 Hz, $SnCH_2CH_2CH_2CH_3$), 33.96 (d, J_{PC} = 14.9 Hz, NCH_3), 51.92 (s, NCH_2), 85.47 (d, J_{PC} = 2.5 Hz, C_5H_5), 200.86 (d, J_{PC} = 19.9 Hz, CO); ^{31}P NMR (δ, in CH_2Cl_2) 287.64 (s, with Sn satellites, J_{SnP} = 182.7 Hz); ^{119}Sn NMR (δ, in CH_2Cl_2) 88.46 (d, J_{PSn} = 185.2 Hz).

Preparation of [Cp(CO)(PPh_3)Ru{PNN(Me)}]BF_4 (1c). BF_3·OEt_2 (0.023 mL, 0.18 mmol) was added to a solution of **1a** (33 mg, 0.092 mmol) in CH_2Cl_2 (1.5 mL) at room temperature, and the solution was stirred for 30 min. After it was cooled to −78 °C, the solution was treated with PPh_3 (48 mg, 0.18 mmol), warmed to room temperature, stirred for 2 h, and then loaded on an alumina column. After elution with CH_2Cl_2, the colorless band eluted with CH_2Cl_2/acetone (4/1) was collected and dried in vacuo to give a white powder. Crystallization from a CH_2Cl_2/ether layer gave a colorless crystal of **1c** (25 mg, 0.037 mmol, 40%). Anal. Calcd for $C_{29}H_{33}BF_4N_2OP_2Ru$: C, 51.57; H, 4.92; N, 4.15. Found: C, 51.55; H, 4.87; N, 4.12. IR (ν_{CO}, cm^{-1}, in CH_2Cl_2): 1981. ^{1}H NMR (δ, in $CDCl_3$): 1.58 (d, J_{PH} = 6.6 Hz, 3H, PCH_3), 2.25 (d, J_{PH} = 12.5 Hz, 3H, NCH_3), 2.52 (d, J_{PH} = 12.1 Hz, 3H, NCH_3), 2.60 (m, 1H, NCH_2), 2.84 (m, 3H, NCH_2), 5.23 (s, 5H, C_5H_5), 7.34 (s, 6H, C_6H_5), 7.45 (s, 9H, C_6H_5). ^{13}C NMR (δ, in $CDCl_3$): 25.57 (d, J_{PC} = 13.1 Hz, PCH_3), 32.93 (d, J_{PC} = 8.1 Hz, NCH_3), 33.52 (d, J_{PC} = 7.5 Hz, NCH_3), 50.73 (s, NCH_2), 51.13 (s, NCH_2), 89.16 (s, C_5H_5), 128.65 (d, J_{PC} = 11.2 Hz, *m*-C_6H_5), 131.05 (d, J_{PC} = 2.5 Hz, *p*-C_6H_5), 133.24 (d, J_{PC} = 11.2 Hz, *o*-C_6H_5), 134.18 (d, J_{PC} = 51.0 Hz, ϵ-C_6H_5), 202.10 (dd, J_{PC} = 19.9, 18.0 Hz, CO). ^{31}P NMR (δ, in $CDCl_3$): 47.05 (d, J_{PP} = 34.0 Hz, PPh_3), 137.20 (d, J_{PP} = 33.9 Hz, PNN(Me)).

Preparation of [Cp(CO)(PPh_3)Ru{PNN(CH_2SiMe_3)}]BF_4 (2c). Complex **2c** was prepared from **2a**, BF_3·OEt_2, and PPh_3 in the same manner as that of **1c**. Yield: 46%. Anal. Calcd for $C_{32}H_{41}BF_4N_2OP_2RuSi$: C, 51.41; H, 5.53; N, 3.75. Found: C, 51.20; H, 5.66; N, 3.73. IR (ν_{CO}, cm^{-1}, in CH_2Cl_2): 1971. ^{1}H NMR (δ, in $CDCl_3$): −0.03 (s, 9H, $SiCH_3$), 1.13 (dd, J_{PH} = 15.6 Hz, J_{HH} = 6.2 Hz, 1H, PCH_2), 1.38 (dd, J_{PH} = 15.6 Hz, J_{HH} = 6.2 Hz, 1H, PCH_2), 2.35 (d, J_{PH} = 11.9 Hz, 3H, NCH_3), 2.50 (d, J_{PH} = 11.9 Hz, 3H, NCH_3), 2.90 (m, 1H, NCH_2), 3.07 (m, 3H, NCH_2), 5.22 (s, 5H, C_5H_5), 7.44 (m, 15H, C_6H_5). ^{13}C NMR (δ, in $CDCl_3$): 0.16 (s, $SiCH_3$), 33.57 (d, J_{PC} = 9.3 Hz, NCH_3), 34.21 (d, J_{PC} = 9.4 Hz, NCH_3), 35.30 (d, J_{PC} = 11.2 Hz, PCH_2), 50.71 (s, NCH_2), 50.85 (s, NCH_2), 89.40 (s, C_5H_5), 128.77 (d, J_{PC} = 10.5 Hz, *m*-C_6H_5), 131.10 (s, *p*-C_6H_5), 133.30 (d, J_{PC} = 11.2 Hz, *o*-C_6H_5), 134.50 (d, J_{PC} = 49.6 Hz, ϵ-C_6H_5), 203.04 (t, J_{PC} = 19.2 Hz, CO). ^{29}Si NMR (δ, in $CDCl_3$): −0.62 (d, J_{PSi} = 12.5 Hz). ^{31}P NMR (δ, in $CDCl_3$): 47.23 (d, J_{PP} = 29.2 Hz, PPh_3), 139.39 (d, J_{PP} = 29.2 Hz, PNN(CH_2SiMe_3)).

Preparation of Cp(CO)($SiMe_3$)Ru{PNN(CH_2Ph)} (3d). BF_3·OEt_2 (0.13 mL, 1.04 mmol) was added to a solution of **3a** (235 mg, 0.57 mmol) in CH_2Cl_2 (5.0 mL) at −78 °C, and the solution was stirred for 30 min. The solution was treated with $PhCH_2MgCl$ (0.40 mL, 2.0 M of THF solution, 0.80 mmol) at −78 °C, warmed to room temperature, and stirred for 1 h. After the volatiles were removed in vacuo, the residue was extracted with pentane (10 mL × 4). After the pentane extract was evaporated to dryness under reduced pressure, the resulting residue was loaded on an alumina column. The colorless band eluted with CH_2Cl_2 was collected and dried in vacuo. Crystallization from hexane gave a colorless crystal of **3d** (131 mg, 0.28 mmol, 49%). Anal. Calcd for $C_{20}H_{31}N_2OPRuSi$: C, 50.51; H, 6.57; N, 5.89. Found: C, 50.24; H, 6.54; N, 5.88. IR (ν_{CO}, cm^{-1}, in CH_2Cl_2): 1910. ^{1}H NMR (δ, in $CDCl_3$): 0.34 (s, 9H, $SiCH_3$), 2.34 (m, 2H, NCH_2), 2.70 (m, 2H, NCH_2), 2.70 (d, J_{PH} = 11.2 Hz, 3H, NCH_3), 2.73 (d, J_{PH} = 11.2 Hz, 3H, NCH_3), 3.07 (dd, J_{PH} = 14.7 Hz, J_{HH} = 2.2 Hz, 1H, PCH_2), 3.27 (dd, J_{PH} = 14.7 Hz, J_{HH} = 2.2 Hz, 1H, PCH_2), 4.97 (s, 5H, C_5H_5), 7.02 (m, 2H, C_6H_5), 7.19 (m, 3H, C_6H_5). ^{13}C NMR (δ, in $CDCl_3$): 9.92 (s, $SiCH_3$), 34.18 (d, J_{PC} = 12.4 Hz, NCH_3), 34.52 (d, J_{PC} = 11.2 Hz, NCH_3), 50.51 (s, NCH_2), 50.96 (d, J_{PC} = 10.6 Hz, PCH_2), 51.16 (s, NCH_2), 85.56 (s, C_5H_5), 125.58 (s, *p*-C_6H_5), 127.76 (s, *m*-C_6H_5), 129.87 (d, J_{PC} = 3.1 Hz, *o*-C_6H_5), 137.02 (d, J_{PC} = 10.0 Hz, ϵ-C_6H_5), 206.90 (d, J_{PC} = 20.5 Hz, CO). ^{29}Si NMR (δ, in $CDCl_3$): 22.89 (d, J_{PSi} = 14.9 Hz). ^{31}P NMR (δ, in $CDCl_3$): 153.55 (s).

Preparation of Cp(CO)($SiMe_2SiMe_3$)Ru{PNN(CH_2Ph)} (4d). Complex **4d** was prepared from **4a**, $BF_3{\cdot}OEt_2$, and $PhCH_2MgCl$ in the same manner as that of **3d**. The crude product was purified by alumina column chromatography. The colorless band eluted with CH_2Cl_2/hexane (1/1) was collected and dried in vacuo. Crystallization from hexane gave a colorless crystal of **4d**. Yield: 46%. Anal. Calcd for $C_{22}H_{37}N_2OPRuSi_2$: C, 49.51; H, 6.99; N, 5.25. Found: C, 49.71; H, 6.95; N, 5.00. IR (ν_{CO}, cm^{-1}, in CH_2Cl_2): 1913. ^{1}H NMR (δ, in $CDCl_3$): 0.08 (s, 9H, $RuSiSiCH_3$), 0.36 (s, 3H, $RuSiCH_3$), 0.45 (s, 3H, $RuSiCH_3$), 2.33 (m, 2H, NCH_2), 2.69 (m, 2H, NCH_2), 2.69 (d, J_{PH} = 11.0 Hz, 3H, NCH_3), 2.73 (d, J_{PH} = 11.0 Hz, 3H, NCH_3), 3.07 (dd, J_{PH} = 14.7 Hz, J_{HH} = 3.5 Hz, 1H, PCH_2), 3.27 (dd, J_{PH} = 14.7 Hz, J_{HH} = 3.5 Hz, 1H, PCH_2), 4.97 (s, 5H, C_5H_5), 7.01 (m, 2H, C_6H_5), 7.18 (m, 3H, C_6H_5). ^{13}C NMR (δ, in $CDCl_3$): −0.04 (s, $RuSiSiCH_3$), 4.37 (s, $RuSiCH_3$), 5.02 (s, $RuSiCH_3$), 34.13 (d, J_{PC} = 12.4 Hz, NCH_3), 34.72 (d, J_{PC} = 11.2 Hz, NCH_3), 50.61 (s, NCH_2), 50.69 (d, J_{PC} = 10.6 Hz, PCH_2), 51.17 (s, NCH_2), 85.43 (d, J_{PC} = 0.9 Hz, C_5H_5), 125.65 (d, J_{PC} = 2.5 Hz, *p*-C_6H_5), 127.80 (d, J_{PC} = 1.9 Hz, *m*-C_6H_5), 129.90 (d, J_{PC} = 3.7 Hz, *o*-C_6H_5), 136.97 (d, J_{PC} = 10.6 Hz, ϵ-C_6H_5), 206.20 (d, J_{PC} = 21.8 Hz, CO). ^{29}Si NMR (δ, in $CDCl_3$): −11.03 (s, PSi*Si*), 22.89 (d, J_{PSi} = 13.7 Hz, P*Si*Si). ^{31}P NMR (δ, in $CDCl_3$): 152.45 (s).

Preparation of Cp(CO)($GeMe_3$)Ru{PNN(CH_2Ph)} (5d). Complex **5d** was prepared from **5a**, $BF_3{\cdot}OEt_2$, and $PhCH_2MgCl$ in the same manner as that of **3d**. The crude product was purified by alumina column chromatography. The colorless band eluted with CH_2Cl_2/hexane (1/1) was collected and dried in vacuo. Crystallization from hexane gave a white powder of **5d**. Yield: 35%. Anal. Calcd for $C_{20}H_{31}GeN_2OPRu$: C, 46.18; H, 6.01; N, 5.39. Found: C, 46.44; H, 6.02; N, 5.15. IR (ν_{CO}, cm^{-1}, in CH_2Cl_2): 1911. ^{1}H NMR (δ, in $CDCl_3$): 0.36 (s, 9H, $GeCH_3$), 2.28 (m, 2H, NCH_2), 2.60 (m, 2H, NCH_2), 2.63 (d, J_{PH} = 11.2 Hz, 3H, NCH_3), 2.64 (d, J_{PH} = 11.2 Hz, 3H, NCH_3), 3.00 (dd, J_{PH} = 14.7 Hz, J_{HH} = 2.6 Hz, 1H, PCH_2), 3.15 (dd, J_{PH} = 14.7 Hz, J_{HH} = 2.6 Hz, 1H, PCH_2), 4.97 (s, 5H, C_5H_5), 6.95 (m, 2H, C_6H_5), 7.14 (m, 3H, C_6H_5). ^{13}C NMR (δ, in $CDCl_3$): 8.45 (s, $GeCH_3$), 34.27 (d, J_{PC} = 12.4 Hz, NCH_3), 34.56 (d, J_{PC} = 12.4 Hz, NCH_3), 50.52 (d, J_{PC} = 9.3 Hz, PCH_2), 50.58 (s, NCH_2), 51.17 (s, NCH_2), 84.66 (d, J_{PC} = 1.9 Hz, C_5H_5), 125.60 (d, J_{PC} = 2.5 Hz, *p*-C_6H_5), 127.78 (d, J_{PC} = 1.9 Hz, *m*-C_6H_5), 129.91 (d, J_{PC} = 3.7 Hz, *o*-C_6H_5), 137.03 (d, J_{PC} = 10.6 Hz, ϵ-C_6H_5), 206.90 (d, J_{PC} = 20.5 Hz, CO). ^{31}P NMR (δ, in $CDCl_3$): 152.58 (s).

Preparation of Cp(CO)(Sn^nBu_3)Ru{PNN(CH_2Ph)} (7d). Complex **7d** was prepared from **7a**, $BF_3{\cdot}OEt_2$, and $PhCH_2MgCl$ in the same manner as that of **3d**. The crude product was purified by alumina column chromatography. The colorless band that eluted with CH_2Cl_2/hexane (1/1) was collected and dried in vacuo. Crystallization from hexane gave a white powder of **7d**. Yield: 45%. Anal. Calcd for $C_{29}H_{49}N_2OPRuSn$: C, 50.30; H, 7.13; N, 4.05. Found: C, 50.13; H, 7.28; N, 3.75. IR (ν_{CO}, cm^{-1}, in CH_2Cl_2): 1907. ^{1}H NMR (δ, in $CDCl_3$): 0.89 (t, J_{HH} = 7.2 Hz, 9H, $SnCH_2CH_2CH_2CH_3$), 0.95 (m, 6H, $SnCH_2CH_2CH_2CH_3$), 1.33 (sext, J_{HH} = 7.2 Hz, 6H, $SnCH_2CH_2CH_2CH_3$), 1.50 (m, 6H, $SnCH_2CH_2CH_2CH_3$), 2.26 (m, 2H, NCH_2), 2.64 (m, 2H, NCH_2), 2.66 (d, J_{PH} = 11.4 Hz, 3H, NCH_3), 2.73 (d, J_{PH} = 11.4 Hz, 3H, NCH_3), 3.13 (m, 2H, PCH_2), 4.92 (s, 5H, C_5H_5), 7.00 (m, 2H, C_6H_5), 7.17 (m, 3H, C_6H_5). ^{13}C NMR (δ, in $CDCl_3$): 13.71 (s, with Sn satellites, J_{SnC} = 211.7, 202.5 Hz, $SnCH_2CH_2CH_2CH_3$), 13.79 (s, $SnCH_2CH_2CH_2CH_3$), 27.92 (s, with Sn satellites, J_{SnC} = 53.1 Hz, $SnCH_2CH_2CH_2CH_3$), 30.43 (s, with Sn satellites, J_{SnC} = 18.3 Hz, $SnCH_2CH_2CH_2CH_3$), 34.34 (d, J_{PC} = 12.8 Hz, NCH_3), 34.73 (d, J_{PC} = 12.8 Hz, NCH_3), 50.57 (s, NCH_2), 51.18 (s, NCH_2), 51.81 (d, J_{PC} = 13.7 Hz, PCH_2), 82.66 (s, C_5H_5), 125.63 (d, J_{PC} = 2.8 Hz, *p*-C_6H_5), 127.79 (d, J_{PC} = 2.8 Hz, *m*-C_6H_5), 129.94 (d, J_{PC} = 3.7 Hz, *o*-C_6H_5), 137.15 (d, J_{PC} = 11.0 Hz, ϵ-C_6H_5), 206.77 (d, J_{PC} = 20.2 Hz, CO). ^{31}P NMR (δ, in $CDCl_3$): 154.76 (s, with Sn satellites, J_{SnP} = 151.5 Hz). ^{119}Sn NMR (δ, in $CDCl_3$): 63.38 (d, J_{PSn} = 154.3 Hz).

Preparation of [Cp(CO){PNN(Me)}Ru=$SnMe_2$]BF_4 (6e). A solution of **6a** (89 mg, 0.18 mmol) in CH_2Cl_2 (1.0 mL) was cooled to −78 °C, and then $BF_3{\cdot}OEt_2$ (0.088 mL, 0.70 mmol) was added. After the solution was warmed to room temperature, it was directly subjected to spectroscopic measurements. ^{31}P NMR (δ, in CH_2Cl_2): 184.95 (s, with Sn satellites, J_{SnP} = 230.6 Hz). ^{119}Sn NMR (δ, in CH_2Cl_2): 664.1 (br).

Preparation of [Cp(CO){PNN(^{n}Bu)}Ru=Sn^nBu_2]BF_4 (7e). A solution of **7a** (232 mg, 0.37 mmol) in CH_2Cl_2 (1.5 mL) was cooled to −78 °C, and then $BF_3{\cdot}OEt_2$ (0.093 mL, 0.74 mmol) was added. After the solution was warmed to room temperature, it was directly subjected to spectroscopic measurements. ^{31}P NMR (δ, in CH_2Cl_2): 194.78 (s, with Sn satellites, J_{SnP} = 195.6 Hz). ^{119}Sn NMR (δ, in CH_2Cl_2): 674.67 (br).

Preparation of [Cp(CO){PNN(OMe)}Ru=$SnMe_2$]OTf (6f). TMSOTf (0.043 mL, 0.24 mmol) was added to a solution of **6a** (120 mg, 0.24 mmol) in hexane (5.0 mL), and the solution was stirred for 2 days at room temperature to give a white suspension. The supernatant was removed by cannula, and the residue was washed with ether and pentane and dried in vacuo to give a white powder of **6f** (97 mg, 0.15 mmol, 64%). Anal. Calcd for $C_{14}H_{24}F_3N_2O_5PRuSSn$: C, 26.27; H, 3.78; N, 4.38. Found: C, 26.29; H, 3.43; N, 4.33. IR (ν_{CO}, cm^{-1}, in CH_2Cl_2): 1939. ^{1}H NMR (δ, in $CDCl_3$): 0.77 (s, with Sn satellites, J_{SnH} = 38.1 Hz, 6H, $SnCH_3$), 2.66 (d, J_{PH} = 11.4 Hz, 3H, NCH_3), 2.68 (d, J_{PH} = 12.5 Hz, 3H, NCH_3), 3.10 (m, 2H, NCH_2), 3.21 (d, J_{PH} = 11.7 Hz, 3H, OCH_3), 3.36 (m, 2H, NCH_2), 5.13 (s, C_5H_5). ^{13}C NMR (δ, in $CDCl_3$): 7.15 (s, with Sn satellites, J_{SnC} = 174.4 Hz, $SnCH_3$), 33.22 (d, J_{PC} = 12.5 Hz, NCH_3), 33.75 (d, J_{PC} = 12.4 Hz, NCH_3), 50.86 (s, NCH_2), 51.09 (s, NCH_2), 52.21 (d, J_{PC} = 11.8 Hz, OCH_3), 83.23 (s, C_5H_5), 119.15 (q, J_{FC} = 317.8 Hz, CF_3), 203.43 (d, J_{PC} = 22.3 Hz, CO). ^{31}P NMR (δ, in $CDCl_3$): 150.18 (s, with Sn satellites, J_{SnP} = 313.5, 300.1 Hz). ^{119}Sn NMR (δ, in $CDCl_3$): 494.06 (d, J_{PSn} = 311.2 Hz).

Preparation of [Cp(CO){PNN(OMe)}Ru=Sn^nBu_2]OTf (7f). TMSOTf (0.085 mL, 0.47 mmol) was added to a solution of **7a** (297 mg, 0.47 mmol) in $ClCH_2CH_2Cl$ (10 mL). The solution was heated to 60 °C and stirred for 12 h. After the reaction mixture was concentrated to ca. 2 mL, it was directly subjected to spectroscopic measurements, which confirmed the formation of **7f**. ^{1}H NMR (δ, in $ClCH_2CH_2Cl$): 2.53 (d, J_{PH} = 11.6 Hz, 3H, NCH_3), 2.58 (d, J_{PH} = 12.5 Hz, 3H, NCH_3), 3.00 (m, 2H, NCH_2), 3.10 (d, J_{PH} = 11.7 Hz, 3H, OCH_3), 3.24 (m, 2H, NCH_2), 5.07 (s, 5H, C_5H_5). Detailed assignments of the Sn^nBu_2 resonances were not possible, due to interference by resonances of the ^{n}Bu protons abstracted by a Lewis acid present in the solution. ^{13}C NMR (δ, in $ClCH_2CH_2Cl$): 8.85 (s, with Sn satellites, J_{SnC} = 312.6, 299.0 Hz, $SnCH_2CH_2CH_2CH_3$), 13.71 (s, $SnCH_2CH_2CH_2CH_3$), 27.57 (s, with Sn satellites, J_{SnC}

= 52.2 Hz, $SnCH_2CH_2CH_2CH_3$), 29.41 (s, with Sn satellites, J_{SnC} = 19.3 Hz, $SnCH_2CH_2CH_2CH_3$), 33.07 (d, J_{PC} = 12.4 Hz, NCH_3), 33.60 (d, J_{PC} = 12.4 Hz, NCH_3), 50.94 (s, NCH_2), 51.25 (s, NCH_2), 51.98 (d, J_{PC} = 11.8 Hz, OCH_3), 83.31 (d, J_{PC} = 2.5 Hz, C_5H_5), 204.10 (d, J_{PC} = 22.4 Hz, CO). The CF_3 carbon was not observed. ^{31}P NMR (δ, in $ClCH_2CH_2Cl$): 150.89 (s, with Sn satellites, J_{SnP} = 284.1, 276.2 Hz). ^{119}Sn NMR (δ, in $ClCH_2$-CH_2Cl): 532.09 (d, J_{PSn} = 281.2 Hz).

Preparation of [Cp(CO){PNN(OMe)}Ru=SnPh$_2$]OTf (8f). TMSOTf (0.051 mL, 0.28 mmol) was added to a solution of **8a** (197 mg, 0.28 mmol) in CH_2Cl_2 (10 mL) at −78 °C. The solution was warmed to room temperature and stirred for 12 h. The solution was then concentrated to ca. 2 mL under reduced pressure. After slow addition of hexane (10 mL), it was kept in a refrigerator to give colorless crystals, which were collected by filtration, washed with ether and hexane, and dried in vacuo, yielding **8f** (104 mg, 0.14 mmol, 48%). Anal. Calcd for $C_{24}H_{28}F_3N_2O_5PRuSSn$: C, 37.72; H, 3.69; N, 3.67. Found: C, 37.70; H, 3.51; N, 3.66. IR (ν_{CO}, cm^{-1}, in CH_2Cl_2): 1950. ^1H NMR (δ, in $CDCl_3$): 2.28 (d, J_{PH} = 11.4 Hz, 3H, NCH_3), 2.69 (d, J_{PH} = 12.5 Hz, 3H, NCH_3), 3.01 (m, 2H, NCH_2), 3.03 (d, J_{PH} = 11.7 Hz, 3H, OCH_3), 3.22 (m, 2H, NCH_2), 5.35 (d, J_{PH} = 1.5 Hz, 5H, C_5H_5), 7.36 (m, 6H, C_6H_5), 7.65 (m, 4H, C_6H_5), ^{13}C NMR (δ, in $CDCl_3$): 32.73 (d, J_{PC} = 11.8 Hz, NCH_3), 33.58 (d, J_{PC} = 12.4 Hz, NCH_3), 50.85 (s, NCH_2), 51.03 (s, NCH_2), 52.07 (d, J_{PC} = 11.8 Hz, OCH_3), 83.45 (d, J_{PC} = 2.5 Hz, C_5H_5), 128.14 (s, with Sn satellites, J_{SnC} = 44.3 Hz, *m*-C_6H_5), 128.73 (s, with Sn satellites, J_{SnC} = 10.0 Hz, *p*-C_6H_5), 135.50 (s, with Sn satellites, J_{SnC} = 47.9 Hz, *o*-C_6H_5), 150.18 (s, ϵ-C_6H_5), 203.48 (d, J_{PC} = 21.8 Hz, CO). The CF_3 carbon was not observed. In principle, satellite peaks due to ^{117}Sn and ^{119}Sn for the ϵ-C_6H_5 carbon should be observed. However, they were not observed due to the low concentration of the sample. ^{31}P NMR (δ, in $CDCl_3$): 148.04 (s, with Sn satellites, J_{SnP} = 329.7 Hz). ^{119}Sn NMR (δ, in $CDCl_3$): 306.96 (d, J_{PSn} = 332.6 Hz).

X-ray Structure Determination for 8a and 8f. Crystallographic and experimental details of X-ray crystal structure analysis for **8a** and **8f** are given in Table 1. The suitable crystals of **8a** and **8f** were individually mounted on a Mac Science MXCκ diffractometer and irradiated with graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å). Unit-cell dimensions were obtained by least squares from the angular setting of 29 accurately centered reflections with 32° < 2θ < 35° for **8a** and from that of 24 such reflections with 32° < 2θ < 35° for **8f**. $P2_1/n$ was selected as the space group for both **8a** and **8f**, which led to successful refinements. Reflection intensities were collected in the usual manner at 25 ± 1 °C, and 3 reflections checked after every 200 reflections showed no decrease in intensity.

The structures were solved by a direct method with the program SIR92.[21] The positions of the hydrogen atoms were calculated by assuming idealized geometries. Absorption and extinction corrections were then applied,[22,23] and several cycles of full-matrix least-squares refinement with anisotropic temperature factors for non-hydrogen atoms led to final values of R = 0.034 and R_w = 0.041 for **8a** and R = 0.031 and R_w = 0.032 for **8f**. All calculations were performed on an SGI Indy R5000 computer using the program system CRYSTAN-GM[24] with neutral atom scattering factors from Cromer and Waber.[25]

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Supporting Information Available: Tables giving positional and thermal parameters for **8a** and **8f**. This material is available free of charge via the Internet at http://pubs.acs.org.

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