Reversible Cycloaddition of Isocyanates to Ruthenium Silylene Complexes

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Abstract: Reactions of ruthenium silylene complexes of the type [Cp*(PMe$_3$)$_2$Ru=SiR$_2$]$^+$ with unsaturated compounds were investigated. Nonpolar, unsaturated substrates such as ethylene, acetylene, and 2-butyne do not react with [Cp*(PMe$_3$)$_2$Ru=SiR$_2$]B(C$_6$F$_5$)$_4$ (**1a**, R = Me; **1b**, R = Ph). However, methyl isocyanate inserts into an Si−S bond of the silylene complex [Cp*(PMe$_3$)$_2$Ru=Si(STol)$_2$][BPh$_4$] (**5**) to give the 1,2-dipolar addition product {Cp*(PMe$_3$)$_2$RuSi(STol)[η^2−O(MeN)C(STol)]}[BPh$_4$] (**6a**) in 87% yield. This product was characterized by X-ray crystallography as possessing a base-stabilized silylene ligand with thiolate and thiocarbamate substituents. Compound **1a** reacts with methyl and phenyl isocyanate to give the 2 + 2 cycloaddition products [Cp*(PMe$_3$)$_2$RuSiMe$_2$NRC=O][B(C$_6$F$_5$)$_4$] (**7**, R = Me; **8**, R = Ph). The analogous triflate complexes [Cp*(PMe$_3$)$_2$RuSiR$_2$NMeC=O][OTf] (**9**, R = Ph; **10**, R = Me) were prepared by reaction of the appropriate ruthenium silyls Cp*(PMe$_3$)$_2$RuSiR$_2$OTf with methyl isocyanate. Heating **9** to 100 °C in toluene resulted in dissociation of the isocyanate and regeneration of the triflate Cp*(PMe$_3$)$_2$RuSiPh$_2$OTf. Competition reactions of various para-substituted phenyl isocyanates with **1b** show that the rate of cycloaddition increases with the electron-donating ability of the incoming isocyanate. This is consistent with a stepwise cycloaddition mechanism involving initial coordination of the isocyanate nitrogen atom to the Lewis acidic silylene silicon atom.

Introduction

Transition metal silylene complexes have been the target of numerous synthetic investigations over many years since these compounds are expected to mediate useful transformations of organosilicon species.[1,2] In fact, a number of stoichiometric and catalytic reactions based on transition metal reagents appear to involve silylene complexes as intermediates.[1−3] Considerable progress toward understanding the properties of silylene com-

plexes has been made in recent years. In 1987, closely related base adducts containing tetrahedral silicon centers, of the type L$_n$MSiR$_2$(donor), were described.[4] Since then, numerous base-stabilized silylene complexes have been reported, and in 1990 we were able to isolate the first examples of base-free silylene complexes (with sp^2 silicon), [Cp*(PMe$_3$)$_2$Ru=Si(SR)$_2$]BPh$_4$ (Cp* = η^5-C$_5$Me$_5$).[5] Subsequently, we described the synthesis and structural characterizations of the transition metal substituted silylene complex (CO)$_4$OsSi(STol-*p*)[RuCp*(PMe$_3$)$_2$],[6] hetero-atom-stabilized [*trans*-(Cy$_3$P)$_2$(H)Pt=Si(SEt)$_2$]BPh$_4$,[7] and [Cp*(PMe$_3$)$_2$Ru=SiR$_2$]B(C$_6$F$_5$)$_4$ (**1a**, R = Me; **1b**, R = Ph).[8] Silylene complexes have also been obtained by coordination of the remarkably stable free silylene :SiN(^{t}Bu)CH=CHN(^{t}Bu) to nickel.[9]

Reactivity studies for directly observed L$_n$M=SiR$_2$ complexes are so far quite limited. The pronounced Lewis acid character for such compounds is well documented,[10,11] and we recently described redistributions at silicon which occur by a bimolecular mechanism mediated by silylene complexes.[12] By analogy with transition metal carbene complexes,[13] cycloaddition reactions

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(1) (a) Tilley, T. D. In *The Silicon−Heteroatom Bond;* Patai, S., Rappoport, Z., Eds.; Wiley: New York, 1991; Chapters 9 and 10, pp 245 and 309. (b) Tilley, T. D. In *The Chemistry of Organic Silicon Compounds;* Patai, S., Rappoport, Z., Eds.; Wiley: New York, 1989; Chapter 24, p 1415. (c) Tilley, T. D. *Comments Inorg. Chem.* **1990**, *10,* 37. (d) Zybill, C. *Top. Curr. Chem.* **1991**, *160,* 1. (e) Lickiss, P. D. *Chem. Soc. Revs.* **1992**, 271. (f) Corey, J. In *Advances in Silicon Chemistry;* Larson, G., Ed.; JAI Press, Inc.: Greenwich, CT, 1991; Vol. 1, p 327. (g) Pannell, K. H.; Sharma, H. K. *Chem. Rev.* **1995**, *95,* 1351. (h) Schubert, U. *Angew. Chem.*, *Int. Ed. Engl.* **1994**, *33,* 419.

(2) (a) Curtis, M. D.; Epstein, P. S. *Adv. Organomet. Chem.* **1981**, *19,* 213. (b) Choe, S. B.; Sanai, H.; Klabunde, J. *J. Am. Chem. Soc.* **1989**, *111,* 2875. (c) Okinoshima, H.; Yamamota, K.; Kumada, M. *J. Am. Chem. Soc.* **1972**, *94,* 9273. (d) Kobayashi, T.; Hayahi, T.; Yamahita, H.; Tanaka, M. *Chem. Lett.* **1988**, 1411. (e) Okinoshima, H.; Yamamota, K.; Kumada, M. *J. Organomet. Chem.* **1971**, *27,* C31. (f) Ishikawa, M.; Sakamoto, H.; Kanetani, F. *Organometallics* **1989**, *8,* 2767.

(3) (a) Seyferth, D.; Shannon, M. L.; Vick, S. C.; Lim, T. F. O. *Organometallics* **1985**, *4,* 57. (b) Clarke, M. P.; Davidson, I. M. T. *J. Organomet. Chem.* **1991**, *408,* 149. (c) Pannell, K. H.; Cervantes, J.; Hernandez, C.; Cassias, J.; Vincenti, S. *Organometallics* **1986**, *5,* 1056. (d) Pannell, K. H.; Rozell, J. M, Jr.; Hernandez, C. *J. Am. Chem. Soc.* **1989**, *111,* 4482. (e) Pannell, K. H.; Wang, L.-J.; Rozell, J. M. *Organometallics* **1989**, *8,* 550. (f) Tobita, H.; Ueno, K.; Ogino, H. *Bull Chem. Soc. Jpn.* **1988**, *61,* 2797. (g) Ueno, K.; Tobita, H.; Ogino, H. *Chem. Lett.* **1990**, 369. (h) Haynes, A.; George, M. W.; Haward, M. T.; Poliakoff, M.; Turner, J. J.; Boag, N. M.; Green, M. *J. Am. Chem. Soc.* **1991**, *113,* 2011. (i) Ueno, K.; Hamasima, N.; Shimoi, M.; Ogino, H. *Organometallics* **1991**, *10,* 959. (j) Pestana, D. C.; Koloski, T. S.; Berry, D. H. *Organometallics* **1994**, *13,* 4173. (k) Yamashita, H.; Tanaka, M.; Goto, M. *Organometallics* **1992**, *11,* 3227. (l) Tanaka, Y.; Yamashita, H.; Tanaka, M. *Organometallics* **1995**, *14,* 530. (m) Tamao, K.; Sun, G.-R.; Kawachi, A. *J. Am. Chem. Soc.* **1995**, *117,* 8043.

(4) (a) Straus, D. A.; Tilley, T. D.; Rheingold, A. L.; Geib, S. J. *J. Am. Chem. Soc.* **1987**, *109,* 5872. (b) Zybill, C.; Müller, G. *Angew. Chem., Int. Ed. Engl.* **1987**, *26,* 669.

(5) Straus, D. A.; Grumbine, S. D.; Tilley, T. D. *J. Am. Chem. Soc.* **1990**, *112,* 7801.

(6) Gumbine, S. D.; Tilley, T. D.; Rheingold, A. L. *J. Am. Chem. Soc.* **1993**, *115,* 358.

(7) Grumbine, S. D.; Tilley, T. D.; Arnold, F. P.; Rheingold, A. L. *J. Am. Chem Soc.* **1993**, *115,* 7884.

(8) Grumbine, S. K.; Tilley, T. D.; Arnold, F. P.; Rheingold, A. L. *J. Am. Chem. Soc.* **1994**, *116,* 5495.

(9) Denk, M.; Hayashi, R. K.; West, R. *J. Chem. Soc., Chem. Commun.* **1994**, 33.

(10) Nakatsuji, H.; Hada, M.; Kondo, K. *Chem. Phys. Lett.* **1992**, *196,* 404.

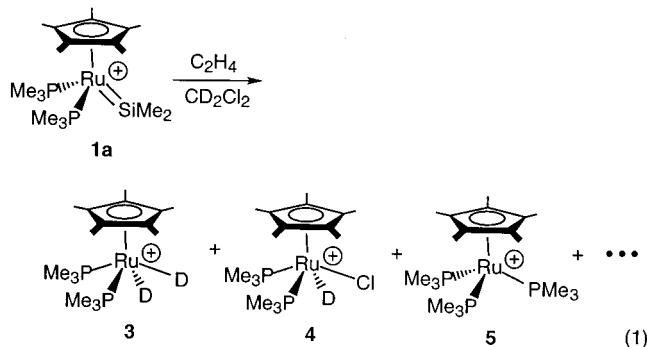(11) Grumbine, S. K.; Straus, D. A.; Tilley, T. D.; Rheingold, A. L. *Polyhedron* **1995**, *14,* 127.

(12) Grumbine, S. K.; Tilley, T. D. *J. Am.Chem. Soc.* **1994**, *116,* 6951.

of silylene complexes with unsaturated substrates might be expected to provide important silicon-element bond-forming processes. Here we report our observations on the interaction of unsaturated compounds with silylene complexes of the type $[Cp^*(PMe_3)_2Ru{=}SiR_2]^+$ (R = Me, Ph, S-*p*-Tol), and the first directly observed cycloaddition reactions for silylene complexes.

Results and Discussion

Transition metal silylene complexes are in general highly reactive, due primarily to their very electron-deficient silicon centers.[8,11] These complexes may, however, be stabilized by π-donation from a heteroatom substituent, or via coordination of a Lewis base to silicon.[5–9,11,12] The non-heteroatom-stabilized silylene complexes that are known do not form stable solutions at room temperature, making them somewhat difficult to study.[8] Fortunately, the triflate complexes Cp*(PMe₃)₂-RuSiR₂OTf may be used as convenient, stable precursors for generating silylene complexes *in situ*. In this investigation, dichloromethane solutions of the silylene complexes **1a** and **1b** were generated quantitatively by reaction of the corresponding triflate complexes with $(Et_2O)LiB(C_6F_5)_4$.[8] The precipitated LiOTf was then removed by filtration, giving a light yellow (**1a**) or orange (**1b**) solution of the desired silylene complex. Compounds **1a** ($t_{1/2}$ = 7 h at 298 K) and **1b** ($t_{1/2}$ = 3 h at 298 K) were typically generated at 0 °C immediately before use. On the other hand, the heteroatom-stabilized complex [Cp*-(PMe₃)₂RuSi(S-*p*-Tol)₂]BPh₄ (**2**) is stable enough to be stored for long periods at room temperature.[5]

Attempted Reactions with Nonpolar Unsaturated Substrates. Initial reactivity studies with **1a** and **1b** focused on nonpolar, unsaturated hydrocarbons. Under 1 atm of ethylene at −78 °C, a solution of **1a** in dichloromethane-d_2 converted to a complex mixture of products over 4 days (by NMR spectroscopy). During the reaction, the SiMe₂ ¹H NMR resonances of **1a** were replaced by multiple peaks in the region from 0.0 to 0.2 ppm, which presumably represent species derived from the silylene fragment. The ³¹P NMR spectrum contained three primary resonances, assigned to the cations Cp*(PMe₃)₂RuD₂⁺ (**3**),[14] Cp*(PMe₃)₂RuCl(D)⁺ (**4**),[14,15] and Cp*(PMe₃)₃Ru⁺ (**5**),[14] and other unidentified signals (eq 1). However, no hydride

(1)

resonances were observed in the ¹H NMR spectrum, indicating that deuteride ligands were derived from the solvent. Since these same decomposition products are observed when **1a** is allowed to decompose in dichloromethane solution, we conclude that **1a** does not react with ethylene.

Complexes **1a** and **1b** also did not react over 4 days at −78 °C with acetylene or 2-butyne in dichloromethane, as nearly the same mixture of decomposition products was eventually observed by ¹H and ³¹P NMR spectroscopy. Also, no reaction was observed between **1a** and CO₂ at 0 °C in dichloromethane after 6 h. In contrast, azobenzene reacts with **1a** over a 12-h period to produce a dark orange oil, which could not be purified by crystallization. However, an NMR analysis of the crude reaction mixture revealed that it was composed of a major product, formed in 50% yield. In the ³¹P NMR spectrum, this product gave rise to two doublets at 3.11 and −3.54 ppm (J_{PP} = 46.8 Hz), and inequivalent ¹H resonances for the SiMe₂ group, at 0.44 and 0.43 ppm, were also observed. Although it was not possible to isolate and fully characterize this product, its spectroscopic properties suggested that it might be a metallacycle, formed via a 2 + 2 cycloaddition with the Ru=Si double bond.

Reactions with Polar Unsaturated Substrates. Given the lack of reactivity of **1a** and **1b** toward nonpolar substrates and the polar nature of the Ru=Si double bond, we turned our attention to reactions of silylene complexes with polar multiple bonds. Methyl isocyanate reacted cleanly with the heteroatom-stabilized silylene complex [Cp*(PMe₃)₂Ru=Si(STol)₂][BPh₄] (**2**) to form one product (**6a**), isolated in 85% yield from dichloromethane. In a similar manner, the analogous triflate salt **6b** was prepared from the corresponding triflate Cp*-(PMe₃)₂RuSi(STol)₂OTf.[5,11] The ¹H NMR spectra of **6a** and **6b** indicate the presence of inequivalent thiolate and phosphine groups, and the ³¹P NMR spectra contain a set of doublets corresponding to inequivalent phosphorus atoms. Although the spectroscopic data did not allow an unambiguous assignment of structures for **6a** and **6b**, they appeared to be consistent with 2 + 2 cycloaddition products. Subsequently, a single crystal structure determination for **6b** (vide infra) revealed the structure depicted in eq 2. These reactions may therefore be described

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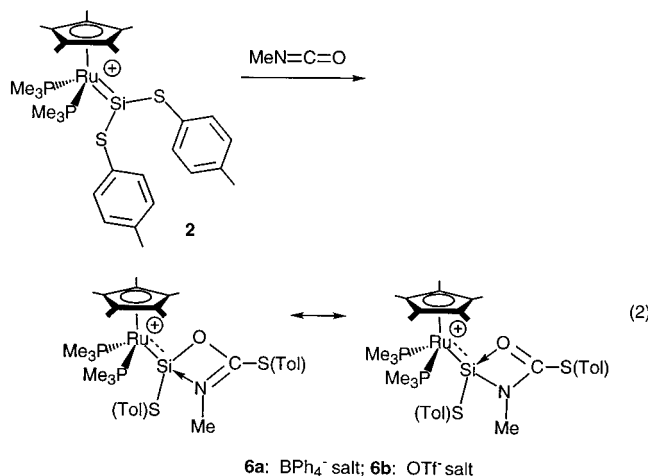
as 1,2-dipolar additions of an Si–S bond to the isocyanate. The products may be regarded as base-stabilized silylene complexes, with a chelating thiocarbamate group bound to silicon. A similar process has been observed for addition of an isocyanate to a Fischer-type carbene complex,[16a] and related 1,2-dipolar additions of M–OR derivatives to isocyanates are also known.[16b,c] This reaction probably occurs in a stepwise manner, via initial coordination of the isocyanate nitrogen atom to silicon, followed by migration of the thiolate group to the carbonyl carbon atom.

(13) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G.; *Principles and Applications of Organotransition Metal Chemistry*; University Science: Mill Valley, CA, 1987; Chapter 16.

(14) Grumbine, S. K. Ph.D. Thesis, University of California, San Diego, 1993.

(15) Tilley, T. D.; Grubbs, R. H.; Bercaw, J. E. *Organometallics* **1984**, *3*, 274.

(16) (a) Fischer, H.; Schlageter, A.; Bidell, W.; Früh, A. *Organometallics* **1991**, *10*, 389. (b) Gibson, V. C.; Redshaw, C.; Clegg, W.; Elsegood, M. R. J. *J. Chem. Soc., Chem. Commun.* **1994**, 2635. (c) Braunstein, P.; Nobel, D. *Chem. Rev.* **1989**, *89*, 1927.
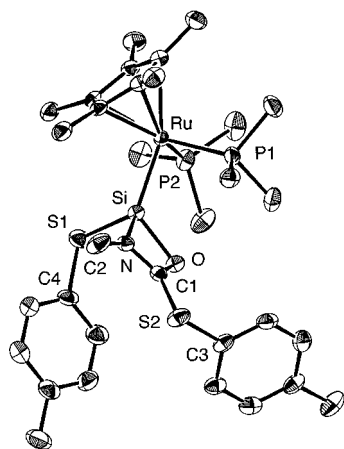
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Figure 1. ORTEP drawing of the cation in **6b**.

Table 1. Selected Bond Distances (Å) and Angles (deg) for **6b·0.5C₇H₈**

(a) Bond Distances							
Ru−P1	2.299(1)	Si−O	1.838(3)	C1−S2	1.734(4)
Ru−P2	2.291(1)	Si−S1	2.158(2)	N−C2	1.458(5)
Ru−Si	2.249(1)	C1−N	1.308(5)	S1−C4	1.790(4)
Si−N	1.866(3)	C1−O	1.305(5)	S2−C3	1.781(4)

| (b) Bond Angles				
P1−Ru−P2	93.71(4)	Si−O−C1	90.6(2)
P1−Ru−Si	90.88(4)	Si−N−C1	89.2(3)
P2−Ru−Si	88.74(4)	Si−N−C2	145.5(3)
Ru−Si−N	128.0(1)	C1−N−C2	125.2(4)
Ru−Si−O	123.7(1)	S2−C1−O	125.6(3)
Ru−Si−S1	118.59(6)	S2−C1−N	124.6(3)
S1−Si−O	103.1(1)	O−C1−N	109.7(3)
S1−Si−N	102.3(1)	Si−S1−C4	105.3(1)
O−Si−N	70.4(1)	C1−S2−C3	100.7(2)

An attempt to observe intermediates in the formation of **6a** by monitoring the reaction at −60 °C by ^{31}P NMR spectroscopy was not successful.

The structure of **6b** is shown in Figure 1, and relevant bond distances and angles are listed in Table 1. The geometry about ruthenium may be described as a fairly regular three-legged piano stool, with L−Ru−L angles (L = P, Si) close to 90°. The silicon is in a pseudotetrahedral environment, with Si−O and Si−N bond lengths of 1.838(3) and 1.866(3) Å, respectively. These distances are relatively long compared to typical single bond distances of 1.63 (Si−O) and 1.74 Å (Si−N).[17] On the other hand, bonds to the three-coordinate carbon atom C(1) are significantly shortened with respect to normal single bond distances. The C(1)−O, C(1)−N, and C(1)−S(2) distances of 1.304(5), 1.308(5), and 1.734(4) Å are considerably shorter than typical single bond lengths of 1.41, 1.47, and 1.81 Å, respectively.[18] The sum of the angles about C(1) (359.9°) reflects planarity and sp[2] hybridization. Internal angles in the Si−O−C(1)−N ring vary greatly, ranging from an O−Si−N angle of 70.4(1)° to an O−C(1)−N(1) angle of 109.7(3)°, with the Si−O−C(1) (90.6(2)°) and Si−N−C(1) (89.2(3)°) angles being intermediate.

Considerable delocalization of electron density in the silicon-based ligand is indicated both by the observed metrical parameters and by the number of resonance structures that can be drawn for **6b** (Scheme 1). In particular π-donation from oxygen, nitrogen, and sulfur, as evidenced by the short bond distances, results in partial double bond character in the bonds to C(1). The ^{13}C NMR chemical shift of 177.72 ppm for C(1)
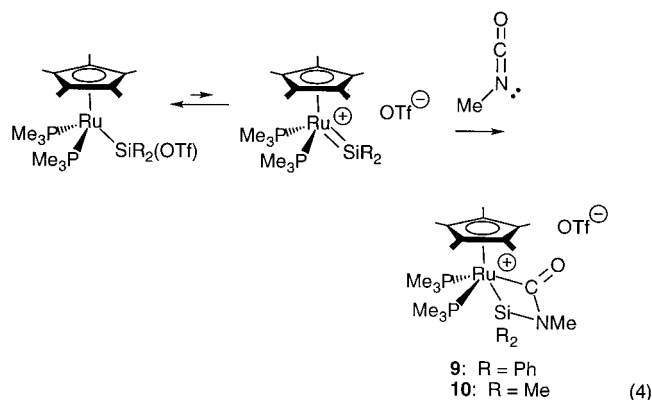
is consistent with carbamate character for the OC(NMe)S(Tol) group,[19] and strong contributions from resonance structures **A** and **B**. This picture is also supported by the IR spectrum of **6a**, which displays an absorption at 1625 cm^{−1} attributed to the carbamate group.[19] The Ru−Si distance of 2.249(1) Å is quite short, inviting description of the compound as a base-stabilized silylene complex. For comparison, the acetonitrile-stabilized complex [Cp*(PMe₃)₂Ru=Si(STol)₂(NCMe)]BPh₄[4a] has a Ru−Si distance of 2.284(1) Å, and the base-free dimethylsilylene complex **1a** possesses a Ru−Si bond length of 2.238(2) Å.[8]

The reactivity mode described above for **2** is not available to silylene complexes **1a** and **1b**, which possess relatively strong Si−C bonds. Compound **1a** reacts rapidly and quantitatively with methyl isocyanate (MeN=C=O) in dichloromethane to form a new product (**7**) that possesses inequivalent phosphine ligands (by ^{31}P NMR spectroscopy) and silicon methyl groups (by ^{1}H NMR spectroscopy). The combustion analysis for **7** confirmed formation of a silylene−isocyanate adduct, and the infrared spectrum of this complex contains an absorption at 1643 cm^{−1}, which indicated the presence of a carbon−heteroatom double bond. To obtain more structural information for **7**, a 2D ^{1}H/[29]Si correlation experiment was used to measure the Si−N−C−H ($^3J_{HSi}$ = 2.9 Hz) and Si−C−H (average $^2J_{HSi}$ = 6.0 Hz) coupling constants. The similar coupling constants $^3J_{HSi}$ = 3.3 Hz and $^2J_{HSi}$ = 6.6 Hz reported for Me₂Si(NMe₂)₂[20] suggested the structure given in eq 3, which was later confirmed
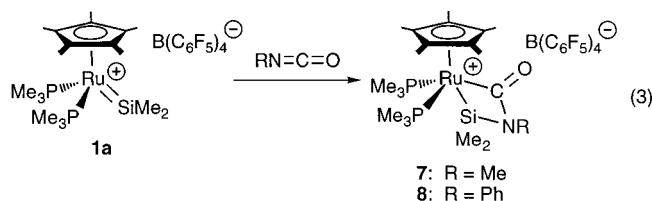
by X-ray crystallography (vide infra). Reaction of **1a** with phenyl isocyanate (PhN=C=O) in dichloromethane at 0 °C rapidly produced a similar product (**8**; eq 3). Inequivalent phosphine and SiMe groups (by NMR spectroscopy) indicate that **8** has a structure analogous to that for **7**.

Interestingly, isocyanates also react with the complexes Cp*-(PMe₃)₂RuSiR₂OTf (R= Me, Ph) to displace triflate and produce the corresponding cycloaddition products. Reactions with methyl isocyanate occur instantly at room temperature to afford the metallacycles **9** (R = Ph) and **10** (R = Me). We attribute this reactivity to the equilibrium shown in eq 4, involving triflate

(17) Sheldrick, W. S. In *The Chemistry of Organic Silicon Compounds;* Patai, S., Rappoport, Z., Eds.; Wiley: New York, 1989; Chapter 3, p 227.
(18) March, J. *Advanced Organic Chemistry,* 3rd ed.; Wiley-Interscience: New York, 1985; p 19.

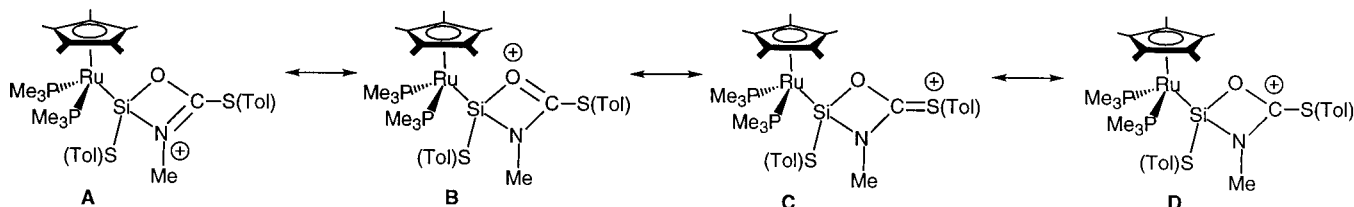(19) Silverstein, R. M.; Bassler, G. C.; Morrill, T. C., *Spectroscopic Identification of Organic Compounds,* 4th ed.; Wiley: New York, 1981; Chapter 5.
(20) Van Der Kelen, G. P.; Van Den Berghe, E. V. *J. Organomet. Chem.* **1976**, *122*, 329.

Scheme 1

Table 2. Selected Bond Distances (Å) and Angles (deg) for
9·2CH₂Cl₂

(a) Bond Distances					
Ru−P1	2.374(1)	Ru−C1	2.171(5)	O−C1	1.216(5)
Ru−P2	2.362(1)	Si−N	1.752(4)	N−C1	1.351(6)
Ru−Si	2.483(1)	Si−C3	1.894(5)	N−C2	1.460(6)
		Si−C4	1.901(5)		

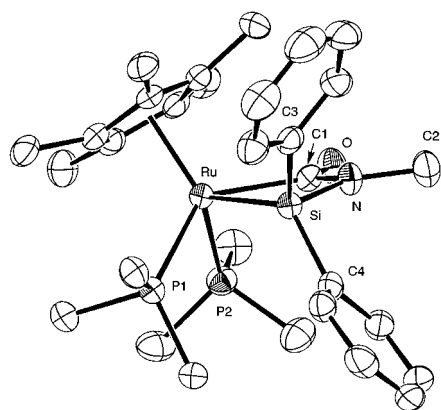| (b) Bond Angles			
P1−Ru−P2	85.59(5)	Ru−Si−N	85.6(1)
P1−Ru−Si	81.22(5)	Ru−Si−C3	120.5(2)
P1−Ru−C1	129.3(1)	Ru−Si−C4	129.6(2)
P2−Ru−Si	110.86(5)	N− Si−C3	109.1(2)
P2−Ru−C1	77.1(1)	N− Si−C4	104.1(2)
Si−Ru−C1	62.1(1)	C3−Si−C4	102.9(2)
Ru−C1−O	126.4(4)	Si−N−C1	101.4(3)
Ru−C1−N	110.3(3)	Si−N−C2	136.9(3)
O−C1−N	123.3(4)	C1−N−C2	121.0(4)

Figure 2. ORTEP drawing of the cation in **9**.

dissociation to produce a transient ruthenium silylene complex, which is then rapidly trapped by isocyanate.[11] It is difficult at this time to entirely rule out an S_N2 substitution mechanism. Attempts to determine the effect of added [ⁿBu₄N][OTf] on the rate for the reaction of Cp*(PMe₃)₂RuSiPh₂OTf with PhNCO were unsuccessful due to the extremely rapid reaction at low temperature.

The cycloaddition products **7−10** exhibit fluxional behavior (by variable-temperature ¹H NMR spectroscopy). At room temperature, one of the PMe₃ groups of **7** appears as a sharp doublet at 1.54 ppm ($^2J_{HP}$ = 9.3 Hz), while the other phosphine ligand gives rise to a broad singlet at 1.65 ppm. Heating a sample of **7** in toluene-d_8 to 50 °C resulted in sharpening of the latter resonance to a well-defined doublet, and cooling to −30 °C resolved this peak into three distinct doublets for each methyl group of the PMe₃ ligand. We attribute this behavior to hindered rotation about one of the Ru−P bonds. The coalescence temperatures are insensitive to the nature of the group bound to nitrogen (Me or Ph). However as expected, substituents at silicon play a strong role in determining the coalescence temperature. The difference in coalescence temperatures for **7** and **9**, −20 and 40 °C, reflects a greater activation barrier for rotation in **9** (by ca. 2 kcal mol⁻¹).[21]

The molecular structure of **9** was unequivocally established by X-ray crystallography (Figure 2). Selected bond distances and angles are listed in Table 2. The coordination geometry for ruthenium may be described as a four-legged piano stool. The Ru−P(1) and Ru−P(2) distances are 2.374(1) and 2.362-(1) Å, respectively, while the P(1)−Ru−P(2) angle is 85.59-(5)° and the C(1)−Ru−Si angle is only 62.1(1)°. The metallacycle ring is nearly planar, with the largest deviation from the least-squares plane being 0.068(5) Å (for C(1)), but it is also highly asymmetric, with bond lengths of 1.351(6) (C(1)−N), 1.752(4) (Si−N), 2.171(5) (Ru−C(1)), and 2.483(1) Å (Ru−Si). The C(1)−N distance of 1.351(6) Å is greater than the N=C distance of 1.168(5) Å in free methyl isocyanate,[22] but still significantly less than the N−C(2) single bond distance of 1.460(6) Å.

Compounds **7−10** are relatively stable and show no signs of decomposition at room temperature after 3 days in dichloromethane-d_2. However, we were intrigued by the possibility that these metallacycles might undergo ring opening to give a silaimine (e.g., Me₂Si=NMe) and the carbonyl complex Cp*(PMe₃)₂RuCO⁺. It seemed that a potentially strong driving force for this reaction might be extrusion of the strongly π-accepting carbonyl ligand from the metallacycle, which would greatly stabilize the electron-rich Cp*(PMe₃)₂Ru⁺ fragment. Of course, the silaimine would be a high-energy species which would dimerize to more stable structures containing tetrahedral silicon centers.[23] To investigate this possibility, we examined the pyrolytic decomposition of complex **9**. Heating **9** in toluene-d_8 at 100 °C for 1 day produced predominately one product, which was identified by ¹H and ³¹P NMR spectroscopy as the triflate Cp*(PMe₃)₂RuSiPh₂OTf. Similar results were obtained with compounds **7** and **8**, although the starting silylene complexes were not recovered cleanly (presumably because of their thermal instability). Additionally, a solid sample of **9** heated to 150 °C under vacuum produced methyl isocyanate, trapped at −196 °C and identified by GC/ MS, as the only volatile thermal decomposition product. The cycloaddition reactions are therefore reversible, as indicated in eq 5.

This chemistry suggests that these metallacyles might be characterized by weak Ru−C and Si−N bonds. However, analysis of the bond distances in **9** does not support this view. For comparison, the Ru−C(1) distance of 2.171(5) Å in **9** is slightly longer than the corresponding Ru−C bond (2.084(7) Å) in the complex CpRu(CO)₂CONH₂.[24] In addition, the C=O and C−N bond lengths of 1.216(5) and 1.351(6) Å in **9** are close to the corresponding values of 1.244(8) and

(21) This estimate is based on a two-site exchange formula: Sandström, J.; *Dynamic NMR Spectroscopy*, Academic Press: London, 1982; Chapter 7.

(22) Anderson, D. W. W.; Rankin, D. W. H.; Robertson, A. *J. Mol. Struct.* **1972**, *14*, 385.

(23) (a) Parker, D. R.; Sommer, L. H. *J. Organomet. Chem.* **1976**, *110*, C1. (b) Zigler, S.; Johnson, L. M.; West, R. *J. Organomet. Chem.* **1988**, *341*, 187. (c) Wiberg, N.; Schurz, K. *J. Organomet. Chem.* **1988**, *341*, 145. (d) Tamao, K.; Nakagawa, Y.; Ito, Y. *J. Am. Chem. Soc.* **1992**, *114*, 218.

(24) Wagner, H.; Jungbauer, A.; Thiele, G.; Behrens, H. *Z. Naturforsch., Teil B* **1979**, *34*, 1487.

(5)

Scheme 2

Figure 3. Hammett plot. Open points represent rates relative to phenyl isocyanate. Solid points represent rates relative to *p*-chlorophenyl isocyanate, adjusted to phenyl isocyanate. Averaged results are as follows: *p*-MeOPhNCO/PhNCO (1.86:1), *p*-ClPhNCO/PhNCO (0.30:1), *p*-CF$_3$Ph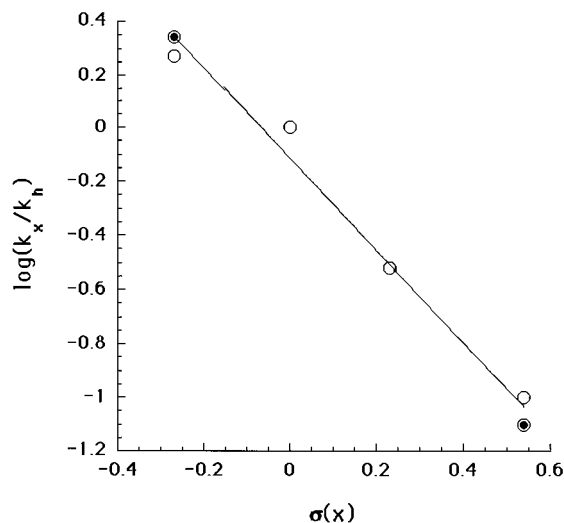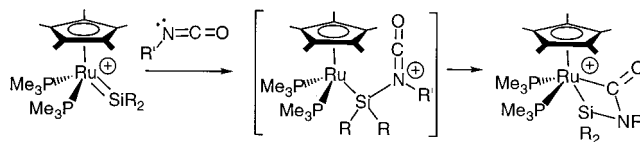NCO/PhNCO (0.11:1), *p*-MeOPhNCO/*p*-ClPhCNO (7.33:1), *p*-CF$_3$PhNCO/*p*-ClPhCNO (0.32:1). Slope = −1.7, R^2 = 0.98.

1.336(10) Å observed for CpRu(CO)$_2$CONH$_2$. Also, the Si−N distance of 1.752(4) Å in **9** is not unusual, as seen by comparison to the average Si−N distance of 1.73 Å in [Me$_2$-SiNMe]$_4$.[25]

A possible mechanism for these cycloaddition reactions is shown in Scheme 2. Given the strong Lewis acidic nature of the silylene complexes under consideration,[11] we favor initial coordination of the isocyanate to silicon via the nitrogen lone pair. This produces an intermediate that may be considered a base-stabilized silylene complex, or a Ru(II) silyl complex with the positive charge localized principally on nitrogen. In the final step of this mechanism, the electron rich Ru(II) center adds to the carbonyl carbon atom to form the metallacycle. This reaction could therefore be described as a stepwise cycloaddition involving polar intermediates.[26] So far, we have not been able to detect an intermediate (by ^{31}P NMR spectroscopy) in these extremely rapid cycloadditions.

For cycloadditions involving rate-determining coordination to silicon, the rates should scale with the nucleophilicity of the incoming isocyanate. To investigate this possibility, a series of competition reactions between pairs of *para*-substituted phenyl isocyanates and the diphenylsilylene complex **1b** were examined. Rates for *p*-methoxyphenyl isocyanate, *p*-chlorophenyl isocyanate, and *p*-(trifluoromethyl)phenyl isocyanate were determined relative to the rate for phenyl isocyanate. Additionally, rates for *p*-methoxyphenyl isocyanate and *p*-(trifluoromethyl)phenyl isocyanate were determined relative to that for *p*-chlorophenyl isocyanate. For each reaction, 10 equiv of each isocyanate were combined and then added to a solution of the silylene complex in 0.5 mL of dichloromethane-*d*$_2$. The relative rates of reaction were then determined by integration of the ^{31}P NMR spectra, with each competition being examined twice. The product ratios were measured within 0.5 h of initiation of reaction, and are assumed to represent kinetically determined product distributions. The validity of this assumption was supported by the competition reaction involving *p*-methoxyphenyl and phenyl isocyanate. This competition resulted in a product ratio of 1.86:1 in favor of the *p*-methoxyphenyl isocyanate adduct. After standing at room temperature for 1 day the ratio of products did not change, but heating the sample to 60 °C for 8 h resulted in an altered ratio of 1.5:1, still in favor of the *p*-methoxyphenyl isocyanate adduct. Continued heating resulted in no further change in the product ratio, indicating that a thermodynamic distribution had been reached.

Unlike methyl isocyanate, isocyanates with electron-withdrawing substituents do not react with the silyl triflate complexes. When *p*-chlorophenyl isocyanate or *p*-(trifluoromethyl)-

phenyl isocyanate was added to Cp*(PMe$_3$)$_2$RuSiPh$_2$OTf, no reaction occurred after 30 min in dichloromethane-*d*$_2$, or after heating to 80 °C for 1 day in toluene-*d*$_8$. However, when the triflate was precipitated from these reaction solutions by addition of (Et$_2$O)LiB(C$_6$F$_5$)$_4$, the solution immediately turned from very light yellow to the bright orange color of **1b**, then back to pale yellow within a span of a few seconds. NMR spectroscopy confirmed clean conversion to the corresponding cycloaddition products. As expected, [Cp*(PMe$_3$)$_2$RuSiPh$_2$N-(*p*-ClC$_6$H$_4$)C=O]B(C$_6$F$_5$)$_4$ reacts with [^{n}Bu$_4$N][OTf] in toluene-*d*$_8$ at 80 °C to regenerate the silyl triflate complex Cp*(PMe$_3$)$_2$-RuSiPh$_2$OTf and the isocyanate. Presumably, the electron withdrawing effect of the *p*-chloro and *p*-CF$_3$ substituents reduces the nucleophilicity of the isocyanate nitrogen such that these isocyanates do not compete effectively with triflate for binding to the silicon center. As a consequence, all competition studies were performed with the free silylene complex **1b** to prevent interference from the triflate counterion.

The averaged results from the competition reactions are compiled in the Hammett plot of Figure 3. The linearity of this plot indicates that the same mechanism is involved in each reaction, and the negative ρ value of −1.7 describes the accelerating effect of electron-donating groups in the *para* position. These data are therefore consistent with the mechanism of Scheme 2 involving initial nucleophilic attack of the isocyanate at the silylene silicon atom.

Conclusions

Given the very limited availability of transition metal silylene complexes, little is known concerning their reactivity. In this contribution, we describe the first direct observation of cycloaddition reactions involving silylene complexes. These reactions occur in a stepwise manner via a mechanism that

(25) Edwards, B. P. E.; Harrison, W.; Nowell, I. W.; Post, M. L.; Shearer, H. M. M.; Trotter, J. *Acta Crystallogr., Sect. B* **1976**, *32*, 648.

(26) (a) Lim, D.; Jorgensen, W. L. *J. Phys. Chem.* **1996**, *100*, 17490. (b) Huisgen R. *Pure Appl. Chem.* **1980**, *52*, 2283. (c) Huisgen R. *Acc. Chem. Res.* **1977**, *10*, 117. (d) Huisgen R. *Acc. Chem. Res.* **1977**, *10*, 199.

(27) Massey, A. G.; Park, A. J. *J. Organomet. Chem.* **1964**, *2*, 245.

involves nucleophilic attack onto the electrophilic silicon center. The ruthenium silylene complexes discussed here are unreactive toward nonpolar multiple bonds which do not bind initially to the silylene ligand. This lack of reactivity is probably also associated with the inert nature of the metal's coordination sphere, which does not allow the binding of alkene or alkyne substrates. Future investigations on cycloaddition reactions of silylene complexes will focus on 16-electron platinum centers,[7] which should more readily bind (and activate) unsaturated substrates.

Experimental Section

All manipulations were performed under an inert atmosphere with standard Schlenk techniques. Dry, oxygen-free solvents were employed throughout. Diethyl ether, pentane, and benzene-d_6 were distilled from sodium/benzophenone and stored under nitrogen. Dichloromethane was distilled from CaH_2 and degassed with two freeze−pump−thaw cycles prior to use. The compounds $Cp^*(PMe_3)_2RuSiMe_2OTf$,[11] $Cp^*(PMe_3)_2RuSiPh_2OTf$,[4a] $(Et_2O)LiB(C_6F_5)_4$,[27] and $[Cp^*(PMe_3)_2Ru=Si(STol)_2][BPh_4]$[5] were prepared according to known procedures. All isocyanates were purchased from Aldrich. Methyl isocyanate, *p*-methoxyphenyl isocyanate, and *p*-(trifluoromethyl)phenyl isocyanate were used as received. Phenyl isocyanate was distilled prior to use, and *p*-chlorophenyl isocyanate was recrystallized prior to use. Elemental analyses were performed by Desert Microanalytical Laboratories or in the Microanalytical Laboratory in the College of Chemistry at the University of California, Berkeley. All IR samples were prepared as Nujol mulls on CsI plates, and all absorptions are reported in cm⁻¹. All NMR spectra were recorded at room temperature in dichloromethane-d_2, unless otherwise noted. All ¹H NMR spectra were obtained at 300 MHz, unless otherwise stated. The compounds $Cp^*(PMe_3)_2RuD_2^+$ (**3**), $Cp^*(PMe_3)_2RuCl(D)^+$ (**4**), and $Cp^*(PMe_3)_3Ru^+$ (**5**) were identified by their ³¹P{¹H} NMR chemical shifts of δ 10.10, 8.26, and 1.98, respectively.[14]

{Cp*(PMe₃)₂RuSi(STol)[η²−O(MeN)C(STol)]}[BPh₄] (6a). To a solution of $[Cp^*(PMe_3)_2Ru=Si(STol)_2][BPh_4]$ (0.200 g, 0.201 mmol) in 15 mL of dichloromethane was added MeNCO (16 μL, 0.27 mmol) via syringe. After the solution was stirred for 5 min, the volatile materials were removed under reduced pressure and the resulting yellow residue was crystallized from 15 mL of 1:1 dichloromethane/diethyl ether at −40 °C. Yield 87% (0.181 g). Anal. Calcd for $C_{56}H_{66}S_2P_2BNORuSi$: C, 64.98; H, 6.43. Found: C, 64.72; H, 6.13. Mp 162−165 °C. ¹H NMR (400 MHz) δ 1.31 (d, $^2J_{HP}$ = 8.4 Hz, 9 H, PMe₃), 1.40 (d, $^2J_{HP}$ = 8.8 Hz, 9 H, PMe₃), 1.89 (s, 15 H, Cp*), 2.41 (s, 3 H, STol), 2.43 (s, 3 H, STol), 2.80 (s, 3 H, NMe), 6.88 (t, $^3J_{HH}$ = 14.4 Hz, 4 H, BPh₄), 7.03 (t, $^3J_{HH}$ = 14.8 Hz, 4 H, BPh₄), 7.14−7.28 (m, 16 H, BPh₄), 7.30−7.34 (m, 8 H, STol). ¹³C{¹H} NMR (100 MHz) δ 11.97 (s, Cp*), 21.38 (s, STol), 21.58 (s, STol), 23.20 (d, $^1J_{CP}$ = 24 Hz, PMe₃), 23.50 (d, $^1J_{CP}$ = 23 Hz, PMe₃), 32.48 (s, NMe), 96.20 (s, ring Cp*), 117.72 (s, BPh₄), 125.75 (s, BPh₄), 127.21 (s, BPh₄), 128.67 (s, ring STol), 129.48 (s, ring STol), 130.52 (s, ring STol), 131.05 (s, ring STol), 134.95 (s, ring STol), 135.73 (s, ring STol), 138.46 (s, BPh₄), 138.65 (s, ring STol), 142.82 (s, ring STol), 177.72 (s,*C*STol). ³¹P-{¹H} NMR (162.0 MHz) δ 2.52 (d, $^2J_{PP}$ = 35 Hz), 4.24 (d, $^2J_{PP}$ = 35 Hz). IR: 1754 m, 1625 s, 1312 m, 1075 s, 992 w, 793 m, 750 m, 726 m, 654 w.

{Cp*(PMe₃)₂RuSi(STol)[η²−O(MeN)C(STol)]}[OTf] (6b). To a solution of $Cp^*(PMe_3)_2RuSi(STol)_2OTf$ (0.300 g, 0.369 mmol) in 10 mL of dichloromethane was added MeNCO (40 μL, 0.668 mmol) via syringe. After the solution was stirred for 15 min, the volatile materials were removed under reduced pressure and the resulting green-yellow residue was crystallized from 20 mL of toluene at −80 °C. Yield 90% (0.289 g). Anal. Calcd for $C_{33}H_{50}RuO_4F_3S_3P_2NSi$: C, 45.61; H, 5.80. Found: C, 45.42; H, 5.94. mp 158−160 °C. ¹H NMR (400 MHz) δ 1.31 (d, $^2J_{HP}$ = 8.4 Hz, 9 H, PMe₃), 1.40 (d, $^2J_{HP}$ = 8.8 Hz, 9 H, PMe₃), 1.89 (s, 15 H, Cp*), 2.41 (s, 3 H, STol), 2.43 (s, 3 H, STol), 2.80 (s, 3 H, NMe), 7.30−7.34 (m, 8 H, STol). ¹³C{¹H} NMR (100 MHz) δ 11.97 (s, Cp*), 21.38 (s, STol), 21.58 (s, STol), 23.20 (d, $^1J_{CP}$ = 24 Hz, PMe₃), 23.50 (d, $^1J_{CP}$ = 23 Hz, PMe₃), 32.48 (s, NMe), 96.20 (s, ring Cp*), 128.67 (s, ring STol), 129.48 (s, ring STol), 130.52 (s, ring

STol), 131.05 (s, ring STol), 134.95 (s, ring STol), 135.73 (s, ring STol), 138.65 (s, ring STol), 142.82 (s, ring STol), 177.72 (s, *C*STol). ³¹P-{¹H} NMR (162.0 MHz) δ 2.52 (d, $^2J_{PP}$ = 35 Hz), 4.24 (d, $^2J_{PP}$ = 35 Hz). IR: 1754 m, 1625 s, 1260 m, 1144 s, 926 w, 793 m, 750 m, 726 m, 654 w.

[Cp*(PMe₃)₂RuSiMe₂NMeC=O][B(C₆F₅)₄] (7). A 50-mL round-bottom Schlenk flask was charged with $Cp^*(PMe_3)_2RuSiMe_2OTf$ (0.150 g, 0.252 mmol) and $(Et_2O)LiB(C_6F_5)_4$ (0.192 g, 0.252 mmol). Dichloromethane (5 mL) was added after the flask was cooled to 0 °C, and the mixture was stirred until all reactants had dissolved. A cloudy yellow solution formed within 30 s, indicating the formation of **1a**. The solution was then filtered into a precooled (0 °C) flask and MeNCO (21 μL, 0.356 mmol) was added via syringe. The reaction mixture was stirred for 5 min, after which the volatile material was removed under reduced pressure. The crude product was crystallized from 1:1 dichloromethane/diethyl ether (10 mL) at −40 °C. Yield 85% (0.298 g). Anal. Calcd for $C_{44}H_{42}F_{20}P_2BNORuSi$: C, 44.68; H, 3.58; N, 1.18. Found: C, 44.39; H, 3.57; N, 1.33. Mp 150−155 °C dec. ¹H NMR: δ 0.55 (s, 3 H, SiMe₂), 0.59 (s, 3 H, SiMe₂), 1.54 (d, $^2J_{HP}$ = 9.3 Hz, 9 H, PMe₃), 1.65 (br s, 9 H, PMe₃), 1.77 (s, 15 H, Cp*), 2.74 (s, 3 H, NMe). ¹³C{¹H} NMR (100 MHz) δ 5.26 (s, SiMe₂), 10.06 (s, SiMe₂), 11.21 (s, Cp*), 19.70 (d, $^1J_{CP}$ = 40 Hz, PMe₃), 23.40 (br s, PMe₃), 29.78 (s, NMe), 104.35 (s, ring Cp*), 113.10 (m, C₆F₅), 137.7 (dm, $^1J_{CF}$ = 258 Hz, C₆F₅), 145.15 (dm, $^1J_{CF}$ = 243 Hz, C₆F₅), 148.44 (dm, $^1J_{CF}$ = 249 Hz, C₆F₅), 163.9 (dd, $^2J_{CPcis}$ = 5.2 Hz, $^2J_{CPtrans}$ = 49 Hz). ³¹P{¹H} NMR (121.5 MHz) δ −4.75 (d, $^2J_{PP}$ = 55 Hz), 4.94 (d, $^2J_{PP}$ = 55 Hz). ²⁹Si{¹H} NMR (59.6 MHz) δ 14.16 (dd, $^2J_{SiPcis}$ = 3.0 Hz, $^2J_{SiPtrans}$ = 33 Hz). IR: 1643 m, 1616 s, 1512 m, 1294 s, 1261 m, 1216 w, 1087 s, 978 s, 831 m, 773 w, 758 m, 683 w, 663 w, 575 w.

[Cp*(PMe₃)₂RuSiMe₂NPhC=O][B(C₆F₅)₄] (8). The procedure employed was identical with that used to synthesize **7**, with the following quantities: $Cp^*(PMe_3)_2RuSiMe_2OTf$ (0.140 g, 0.235 mmol), $(Et_2O)LiB(C_6F_5)_4$ (0.179 g, 0.235 mmol) and PhNCO (45 μL, 0.435 mmol). Yield 70% (0.205 g). Anal. Calcd for $C_{49}H_{44}F_{20}P_2$-BNORuSi: C, 47.28; H, 3.56; N, 1.13. Found: C, 45.28; H, 3.82; N, 1.05. Mp 147−150 °C. ¹H NMR: δ 0.65 (s, 3 H, SiMe₂), 0.82 (s, 3 H, SiMe₂), 1.63 (d, $^2J_{HP}$ = 9.6 Hz, 9 H, PMe₃), 1.72 (br s, 9 H, PMe₃), 1.83 (s, 15 H, Cp*), 7.25−7.33 (m, 5 H, NC₆H₅). ¹³C{¹H} NMR (100 MHz) δ 6.60 (s, SiMe₂), 10.50 (s, SiMe₂), 11.20 (s, Cp*), 19.60 (d, $^1J_{CP}$ = 40 Hz, PMe₃), 22.50 (br s, PMe₃), 104.8 (s, ring Cp*), 123.2 (s, NC₆H₅), 125.7 (s, NC₆H₅), 129.4 (s, NC₆H₅), 164.7 (dd, $^2J_{CPcis}$ = 5.1 Hz, $^2J_{CPtrans}$ = 50 Hz). The *ipso* carbon was not observed. ³¹P{¹H} NMR (121.5 MHz) δ −5.29 (d, $^2J_{PP}$ = 56 Hz), 4.03 (d, $^2J_{PP}$ = 56 Hz). IR: 1643 m, 1622 s, 1269 s, 1086 m, 978 s, 739 m, 683 w, 660 m.

[Cp*(PMe₃)₂RuSiPh₂NMeC=O][OTf] (9). MeNCO (24 mL, 0.400 mmol) was added via syringe to a solution of $Cp^*(PMe_3)_2RuSiPh_2OTf$ (0.220 g, 0.306 mmol) in dichloromethane (5 mL). After the reaction mixture was stirred for approximately 5 min, the volatiles were removed *in vacuo* to leave a light green residue that was then crystallized from 1:1 dichloromethane/diethyl ether (20 mL) at −40 °C. Yield 82% (0.195 g). Anal. Calcd for $C_{31}H_{46}O_4F_3P_2NSSiRu$: C, 47.93; H, 5.97; N, 1.80. Found: C, 46.78; H, 6.19; N, 1.70. Mp 120−125 °C. ¹H NMR: δ 0.81 (br s, 3 H, PMe₃), 1.57 (s, 15 H, Cp*), 1.64 (d, $^2J_{HP}$ = 9.6 Hz, 12 H, PMe₃), 1.97 (br s, 3 H, PMe₃), 3.07 (s, 3 H, NMe), 7.38−7.41, 7.49−7.52, 7.70−7.73 (m, 10 H, C₆H₅). ¹³C{¹H} NMR (100 MHz) δ 10.74 (s, Cp*), 20.31 (d, $^1J_{CP}$ = 31 Hz, PMe₃), 32.38 (s, NMe), 104.3 (s, ring Cp*), 129.0, 129.3, 130.2, 130.6, 134.4, 135.7, 136.7, 139.1 (all s, C₆H₅), 162.1 (dd, $^2J_{CPcis}$ = 5.2 Hz, $^2J_{CPtrans}$ = 52 Hz). ³¹P{¹H} NMR (161.98 MHz) δ −2.04 (d, $^2J_{PP}$ = 57 Hz), 4.80 (d, $^2J_{PP}$ = 57 Hz). IR: 1614 s, 1269 s, 1221 m, 1142 m, 1030 m, 943 w, 825 m, 752 m, 714 w, 685 w, 634 m, 571 m, 507 w.

[Cp*(PMe₃)₂RuSiMe₂NMeC=O][OTf] (10). The procedure employed was identical with that used for **9**, with $Cp^*(PMe_3)_2RuSiMe_2$-OTf (0.300 g, 0.504 mmol) and MeNCO (40 μL, 0.667 mmol). Yield 90% (0.296 g). Anal. Calcd for $C_{21}H_{42}O_4F_3P_2NSRuSi$: C, 38.64; H, 6.49; N, 2.15. Found: C, 38.69; H, 6.81; N, 2.34. Mp 138−140 °C. ¹H and ³¹P{¹H} NMR spectra are identical with those for **7**. The ¹³C-{¹H} spectrum is identical with that for **7**, except for the absence of B(C₆F₅)₄⁻ resonances. IR: 1614 m, 1260 s, 1144 m, 1030 m, 964 m, 944 w, 825 m, 636 s, 517 m.

Table 3. Crystal and Data Collection Parameters for **6b**·0.5C$_7$H$_8$ and **9**·2CH$_2$Cl$_2$

	6b·0.5C$_7$H$_8$	**9**·2CH$_2$Cl$_2$
	(a) Crystal Parameters	
formula	RuO$_4$F$_3$S$_3$P$_2$NSiC$_{36.5}$H$_{54}$	RuSP$_2$SiF$_3$O$_4$NC$_{33}$Cl$_4$H$_{50}$
formula weight	915.11	946.73
crystal color, habit	colorless block	colorless, columnar
crystal size, mm	0.20 × 0.20 × 0.30	0.15 × 0.30 × 0.30
crystal system	monoclinic	orthorhombic
space group	$P2_1$/c (No. 14)	P*bca* (No. 61)
a, Å	12.1313(3)	14.5771(1)
b, Å	18.7362(3)	18.4240(1)
c, Å	19.2248(4)	31.1253(3)
β, deg	100.599(1)	
V, Å^3	4295.1(1)	8359.27(9)
Z	4	8
D(calc), g cm^{-3}	1.415	1.504
μ(Mo Kα), cm^{-1}	6.59	8.35
temp, K	151	158
	(b) Data Collection	
diffractometer	Siemens SMART	Siemens SMART
radiation	Mo Kα (λ = 0.71069 Å)	Mo Kα (λ = 0.71069 Å)
scan type	ω (0.30° per frame)	ω (0.30° per frame)
scan rate, s per frame	10.0	30.0
total no of reflcns collected	18051	33799
no of unique reflcns	6614 (R_{int} = 0.032)	6646 (R_{int} = 0.032)
no. of observations	4992 ($I > 3.00\sigma(I)$)	4843 ($I > 3.00\sigma(I)$)
	(c) Refinement	
reflection/parameter ratio	10.76	10.64
$R(F)$, %	3.6	4.5
$R(wF)$, %	4.7	5.9
goodness of fit indicator	1.80	2.84
max peak in final diff map, e$^-$/Å^3	0.92	0.90
min peak in final diff map, e$^-$/Å^3	−0.73	−0.81

Competition Experiments. Adducts were generated in solution via reaction of silylene **1b**, generated from Cp*(PMe$_3$)$_2$RuSiR$_2$OTf (0.015 g, 0.021 mmol) and (Et$_2$O)LiB(C$_6$F$_5$)$_4$ (0.016 g, 0.021 mmol), with the appropriate isocyanate. Addition of *p*-ClC$_6$H$_4$NCO (0.005 g, 0.030 mmol) to a solution of **1b** in 0.5 mL of dichloromethane-*d$_2$* yielded the adduct Cp*(PMe$_3$)RuSiPh$_2$N(*p*-ClC$_6$H$_4$)C=O][B(C$_6$F$_5$)$_4$] exclusively (by ^{1}H and ^{31}P NMR spectroscopy): ^{1}H NMR (400 MHz) δ 0.71 (br s, 3 H, PMe$_3$), 1.59 (s, 15 H, Cp*), 1.64 (d, $^2J_{HP}$ = 9.6 Hz, 12 H, PMe$_3$), 1.94 (br s, 3 H, PMe$_3$), 7.00−7.07 (m, 5 H, SiC$_6$H$_5$), 7.25−7.31, (m, 5 H, SiC$_6$H$_5$), 7.42 (m, 2 H, p-ClPh), 7.61 (m, 2 H, p-ClPh). ^{31}P{^{1}H} NMR (162.0 MHz) δ −3.82 (d, $^2J_{PP}$ = 59 Hz), 1.54 (d, $^2J_{PP}$ = 59 Hz). Other adducts were generated analogously.

Cp*(PMe$_3$)$_2$RuSiPh$_2$N(*p*-MeOC$_6$H$_4$)C=O][B(C$_6$F$_5$)$_4$]: ^{1}H NMR (400 MHz) δ 0.70 (br s, 3 H, PMe$_3$), 1.62 (s, 15 H, Cp*), 1.71 (d, $^2J_{HP}$ = 9.6 Hz, 12 H, PMe$_3$), 1.92 (br s, 3 H, PMe$_3$), 7.12−7.16 (m, 5 H, SiC$_6$H$_5$), 7.22−7.28 (m, 5 H, SiC$_6$H$_5$), 7.40 (m, 2 H, p-MeOPh), 7.58 (m, 2 H, p-MeOPh). ^{31}P{^{1}H} NMR (162.0 MHz) δ −3.54 (d, $^2J_{PP}$ = 59 Hz), 1.68 (d, $^2J_{PP}$ = 59 Hz). Cp*-(PMe$_3$)$_2$RuSiPh$_2$N(*p*-CF$_3$C$_6$H$_4$)C=O][B(C$_6$F$_5$)$_4$]: ^{1}H NMR (400 MHz) δ 0.75 (br s, 3 H, PMe$_3$), 1.63 (s, 15 H, Cp*), 1.68 (d, $^2J_{HP}$ = 9.6 Hz, 12 H, PMe$_3$), 1.98 (br s, 3 H, PMe$_3$), 6.98−7.02 (m, 5 H, SiC$_6$H$_5$), 7.15−7.21 (m, 5 H, SiC$_6$H$_5$), 7.45 (m, 2 H, p-CF$_3$Ph), 7.58 (m, 2 H, p-CF$_3$Ph). ^{31}P{^{1}H} NMR (162.0 MHz) δ −3.84 (d, $^2J_{PP}$ = 58 Hz), 1.77 (d, $^2J_{PP}$ = 58 Hz). Cp*(PMe$_3$)$_2$RuSiPh$_2$N(Ph)C=O][B(C$_6$F$_5$)$_4$]: ^{1}H NMR (400 MHz) δ 0.82 (br s, 3 H, PMe$_3$), 1.65 (s, 15 H, Cp*), 1.67 (d, $^2J_{HP}$ = 9.6 Hz, 12 H, PMe$_3$), 2.01 (br s, 3 H, PMe$_3$), 7.05−7.12 (m, 5 H, SiC$_6$H$_5$), 7.19−7.28 (m, 5 H, SiC$_6$H$_5$), 7.49 (m, 2 H, NPh), 7.63 (m, 2 H, NPh). ^{31}P{^{1}H} NMR (162.0 MHz) δ −3.66 (d, $^2J_{PP}$ = 59 Hz), 1.58 (d, $^2J_{PP}$ = 59 Hz).

In a glovebox, a well-mixed solid mixture of Cp*(PMe$_3$)$_2$RuSiPh$_2$-OTf (0.027 g, 0.037 mmol) and (Et$_2$O)LiB(C$_6$F$_5$)$_4$ (0.028 g, 0.037 mmol) was dissolved in 0.5 mL of dichloromethane-*d$_2$* to generate the silylene complex **1b**. The orange solution was then added to a mixture of *p*-chlorophenyl isocyanate (0.060 g, 0.39 mmol) and phenyl isocyanate (0.047 g, 0.39 mmol), resulting in immediate formation of a light-yellow solution. The ratio of cycloaddition products for each sample was then determined by integration of the ^{31}P NMR spectra, and the results of

two experiments were averaged. An identical procedure was employed for the other experiments, but with the following quantities: *p*-methoxyphenyl isocyanate (0.057 g, 0.38 mmol)/phenyl isocyanate (0.045 g, 0.37 mmol), *p*-(trifluoromethyl)phenyl isocyanate (0.072g, 0.38 mmol)/phenyl isocyanate (0.048 g, 0.40 mmol), *p*-methoxyphenyl isocyanate (0.057 g, 0.38 mmol)/*p*-chlorophenyl isocyanate (0.061 g, 0.39 mmol), *p*-(trifluoromethyl)phenyl isocyanate (0.074 g, 0.39 mmol)/*p*-chlorophenyl isocyanate (0.059 g, 0.38 mmol).

X-ray Crystal Structure Determinations. Crystals were mounted on a glass fiber with Paratone N hydrocarbon oil. All X-ray data were collected on a Siemens SMART diffractometer with a CCD area detector. Preliminary orientation matrices and unit cell parameters were determined by collecting 60 10-s frames. Frame data were integrated by using SAINT and corrected for Lorentz and polarization effects.

(a) 6b·0.5C$_7$H$_8$: A colorless blocklike crystal with approximate dimensions of 0.20 × 0.20 × 0.30 mm was mounted and placed under a cold stream of nitrogen on the diffractometer. A hemisphere of data was collected at a temperature of −121 ± 1 °C with ω scans of 0.30° and a collection time of 10 s per frame. An absorption correction was applied by using XPREP (μR = 0.05, T_{max} = 0.90, T_{min} = 0.82). The 18051 reflections which were integrated were averaged in point group 2/*m* to yield 6614 unique reflections (R_{int} = 0.032). No correction for decay was necessary. The structure was solved by using direct methods (SIR92) and refined by full matrix least-squares methods with use of teXsan software. The non-hydrogen atoms were refined anisotropically, except for the disordered toluene methyl carbon, which was modeled at half occupancy and refined isotropically. Hydrogen atoms were included at calculated positions but not refined. The number of variable parameters was 464, giving a data/parameter ratio of 10.76. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.92 and −0.73 e$^-$/Å^3: R = 0.036, R_w = 0.047, GOF = 1.80.

(b) 9·2CH$_2$Cl$_2$: A colorless columnar crystal with approximate dimensions of 0.15 × 0.30 × 0.30 mm was mounted and placed under a cold stream of nitrogen on the diffractometer. A hemisphere of data was collected at a temperature of −115 ± 1 °C with ω scans of 0.30° and a collection time of 30 s per frame. Analysis of the redundant data with the program XPREP indicated that there was no significant

absorption by the crystal and no correction was applied. The 33799 reflections which were integrated were averaged in point group *mmm* to yield 6646 unique reflections (R_{int} = 0.032). No correction for decay was necessary. The structure was solved using direct methods (SAPI91), expanded with Fourier techniques (DIRDIF92), and refined by full matrix least-squares methods with use of teXsan software. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included at calculated positions but not refined. The number of variable parameters was 455, giving a data/parameter ratio of 10.64. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.90 and −0.81 e⁻/Å³: R = 0.045, R_w = 0.059, GOF = 2.84.

Supporting Information Available: Tables of crystal, data collection, and refinement parameters, bond distances and angles, and anisotropic displacement parameters (27 pages). See any current masthead page for ordering and Internet access instructions.

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