Silyl Migration of Me₃SiCCPh Coordinated to [RuH(CO)(PᵗBu₂Me)₂]BAr′₄ Can Be Reversed: Synthesis and Structure of [Ru(CH=C(SiMe₃)(Ph))(CO)(PᵗBu₂Me)₂]BAr′₄

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Abstract: Reaction of 14-electron $RuH(CO)L_2^+$ (L = P^tBu_2Me, anion = $B[C_6H_3(CF_3)_2]_4^-$) with $Me_3SiC{\equiv}CPh$ gives the silyl-migrated product $Ru[CH{=}C(SiMe_3)Ph](CO)L_2^+$, in which the ortho H on phenyl syn to Ru is agostic to the metal, to give a square-pyramidal coordination geometry augmented by an agostic interaction with a ᵗBu methyl group. These interactions, from X-ray diffraction, persist in solution. Reaction at lower temperature reveals (NMR studies) one detectable species which, however, is unlikely to be an intermediate. Under 1 atm of CO, this cation adds *three* CO's to give $Ru(CO)_2[CO{-}CH{=}C(SiMe_3)Ph]L_2^+$, which is shown ($^{13}CO$ labeling) to add an additional CO. In the absence of excess CO, this acyl complex forms $RuH(CO)_3L_2^+$ with release of $Me_3SiC{\equiv}CPh$; Me_3Si migration is thus reversed.

Introduction

There is a plethora of reports on isomerization of terminal alkynes on late transition metal centers to give metal vinylidene complexes,[1] which have found some applications in organic synthesis.[2] Less frequent is the isomerization of silyl alkynes on 14-electron fragments (i.e., $RhClL_2$, $IrClL_2$, and $RuCl_2L_2$; L = phosphine) to corresponding vinylidenes (eq 1).[3] Computa-

$$L_nM + G{-}C{\equiv}CR \longrightarrow L_nM{=}C{=}C{\diagup}{\diagdown}{\genfrac{}{}{0pt}{}{R}{G}} \qquad (1)$$

$$G = H, SiR_3, SnR_3$$
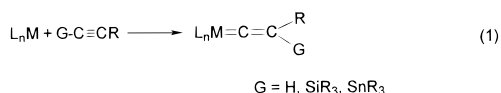
tional studies suggested that a 1,2-H (or SiR_3) shift is energetically very costly, and it has been proposed that bimolecular H transfer is an alternative.[4] In contrast, isomerization of terminal alkynes on unsaturated *hydride* complexes is not well studied until recently.[5] That report reveals that the 14-electron transient $RuHClL_2$ reacts with Me_3SiCCH to give a vinylidene but by

an unconventional mechanism, which involves insertion of the $C{\equiv}C$ triple bond into the M−H bond to give a metal vinyl complex as an intermediate. The 14-electron intermediate then undergoes α-H migration to give the vinylidene complex. The mechanism is supported by DFT calculations and by a deuterium labeling study. In sharp contrast, less π-basic but isoelectronic $[RuH(CO)L_2]BAr′_4$ (L = P^tBu_2Me) reacts with *two* molecules of Me_3SiCCH to give, instead of a vinylidene, an alkyne-coupled η^3-butadienyl complex.[6] We report here that $[RuH(CO)L_2]^+$ also reacts with an internal silyl alkyne, $Me_3SiCCPh$, to give the silyl-migrated product, $[Ru(CH{=}C(SiMe_3)(Ph))(CO)L_2]^+$. Reported here are the structure and solution spectra of this complex and its reaction with CO, which remarkably regenerates $Me_3SiCCPh$ and $RuH(CO)_3L_2^+$.

Results

Reaction of [RuH(CO)L₂]BAr′₄ with Me₃SiCCPh. Within the time of mixing at room temperature, $[RuH(CO)L_2]BAr′_4$ reacts with $Me_3SiCCPh$ in methylene chloride or fluorobenzene to give a silyl-migrated product (**1**) quantitatively (eq 2). Sterically more demanding $Me_3SiCCSiMe_3$, however, does not

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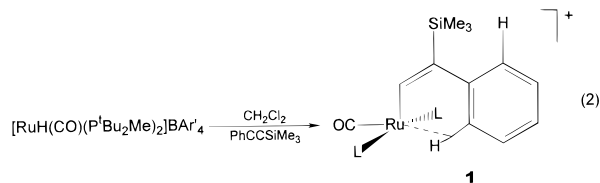(2) Bruneau, C.; Dixneuf, P. H. *Acc. Chem. Res.* **1999**, *32*, 311.

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(2)

Figure 1. ORTEP drawing of $[Ru[CHC(SiMe_3)(Ph)](CO)(P^tBu_2Me)_2]^+$ (**1**). The agostic methyl hydrogens shown are placed in idealized positions.

react; no spectroscopic change is observed on combination of these reactants. **1** is isolated as red crystals from fluorobenzene/pentane. The solid-state structure of **1** is determined by X-ray crystallography (Figure 1). The determination reveals a unit cell containing two crystallographically independent molecules, which can represent a distinct advantage since it serves to test the reality of weak interactions (by their replication or nonreplication). In the present case, a least-squares fit of the two independent cations shows deviations of less than 0.1 Å, except for the carbonyl oxygen (0.18 Å), Si (0.25 Å), and the two phosphine nuclei (0.22 and 0.33 Å); the only major differences arise from CH₃(Si) and CH₃(P) orientations. Bond lengths and angles (Tables 1 and 2) show no significant differences. The following description deals with features found in *both* independent cations. The structure shows a sawhorse (i.e., nonplanar, SF₄ type) coordination geometry (2P, carbonyl, and vinyl carbon), augmented by a short ortho agostic donation from the phenyl C7 hydrogen (Figure 1). A sixth coordination site (trans to the vinyl carbon C4) is more distantly (i.e., weakly) occupied by one ᵗBu methyl hydrogen. The Ru−C24 distance, 3.049(1) Å (3.090(13) Å in the second cation), while long, shows a consistency between independent molecules, suggesting a real attraction with a well-defined energetic minimum. The ortho phenyl hydrogen-to-Ru distance is 1.74 Å (1.70), with a Ru−H−C angle of 131.6° (131.6°). The associated Ru/C distances are 2.588 and 2.551 Å. The agostic interaction also twists the Ph ring away from coplanar with the C=C bond. Esteruelas and co-workers reported the presence of relatively strong agostic interaction between vinyl C−H and Os(II) in a formally 16-electron complex, OsH{C₆H₄-2-(*E*-CH=CH_{agostic}Ph)}(CO)(PⁱPr₃)₂. This agostic hydrogen is crystallographically located 2.05(7) Å away from Os.[7] It is typical of strong C−H metal interactions that they become nonlinear (i.e., the M−C distance becomes shorter).[8] The reality of the agostic ᵗBu interaction in **8** is supported by the Ru−P−C (quaternary carbon) angle being 6−9° smaller than that of the corresponding ᵗBu on the nonagostic PᵗBu₂Me in the same cation and 18−20° smaller than that of the second ᵗBu within the same (agostic) ᵗBu. Finally, the Ru−P distance involving the agostic ᵗBu is 0.036 (12 esd's) and 0.046 Å (15 esd's) shorter than that to the "ordinary" PᵗBu₂Me. This pattern has been seen before.[6]

Spectroscopic Evidence for Agostic Interactions of 1 in Solution. Ionic **1** is not soluble in nonpolar solvents such as benzene or alkanes but is highly soluble in methylene chloride and fluorobenzene. In either solvent, there is no evidence for solvent coordination since the CO stretching frequencies remain the same in both solvents. Therefore, we carried out the following spectroscopic study of **1** in CD₂Cl₂. At 20 °C, the ¹H NMR spectrum reveals two virtual triplets for the ᵗBu protons, indicative of two mutually trans phosphines with diastereotopic ᵗBu groups. A singlet at 8.35 ppm is found for the α-proton of the Ru-vinyl group, and the phenyl region shows two multiplets at 7.75 and 7.43 ppm with an integration ratio of 2:1, accounting
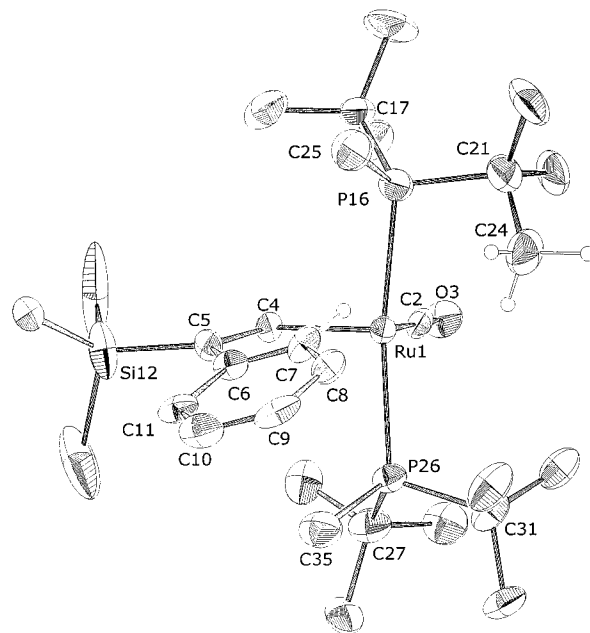
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Table 1. Crystallographic Data for $[Ru(CH=C(SiMe_3)(Ph))(CO)(P^tBu_2Me)_2]BAr'_4$

formula	$C_{62}H_{69}BF_{24}OP_2RuSi$	space group	$P2_1/c$
a, Å	17.762(5)	T, °C	−168
b, Å	19.337(5)	λ, Å	0.710 69
c, Å	39.838(10)	ρ_{cald}, g/cm^{-3}	1.456
β, deg	97.21(1)	μ(Mo Kα), cm$^{-1 a}$	4.00
V, Å^3	13 574.65 Å^3	R^b	0.085
Z	8	$R_w{}^c$	0.073
formula wt	1488.10		

^{a} Graphite monochromator. ^{b} $R = \sum||F_o| - |F_c||/\sum|F_o|$. ^{c} $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$, where $w = 1/\sigma^2(|F_o|)$.

for only three protons. The other two phenyl protons are located as a very broad peak ($w_{1/2} = 300$ Hz) at 6.00 ppm, which, upon cooling to −70 °C, decoalesces to two peaks, a multiplet at 7.65 ppm, and a broad singlet at 3.98 ppm. The higher field peak is due to the agostic ortho hydrogen. Apparently, the phenyl group is rotating fast enough to coalesce the two ortho protons at higher temperatures. Also, at low temperature, decoalescence of the two meta (Ph) protons is observed, and the ¹³C{¹H} NMR spectrum of **1** gives six distinct signals for the phenyl carbons of the cation. Compared to the other phenyl carbon chemical shifts (128−135 ppm), the agostic carbon resonance is shifted to higher field (110 ppm), with $^1J(CH) = 132$ Hz, i.e., much smaller than the normal $^1J(CH)$ value of 160−170 Hz for sp² C−H of other phenyl carbons. This is a rare example of agostic interaction which can be decoalesced on the NMR time scale. By analyzing the variable-temperature ¹³C spectra of the phenyl carbons, we obtained $\Delta G^{\ddagger}$ for phenyl rotation of 8.6 kcal·mol⁻¹ at 273 K. Because the hydrogen exchange is an intramolecular process, the entropy change should be close to zero. This energy, however, reflects the upper limit of agostic bond strength since the barrier has several major contributions: the agostic interaction itself, a steric preference for Ph in the mirror plane, *and* the conjugation of Ph π-electrons with the vinyl. The weaker agostic interaction from the phosphine methyl group of **1** could not be decoalesced, as was also the case of the formally 16-electron d⁶ Re(I) and Mo(0)/W(0) complexes and [RuR(CO)-L₂]BAr′₄.[9] Nonetheless, the weak agostic interaction with the

Table 2. Selected Geometric Parameters of [Ru(CH=C(SiMe$_3$)(Ph))(CO)(P^{t}Bu$_2$Me)$_2$]BAr$'_4$

	molecule 1	molecule 2		molecule 1	molecule 2		molecule 1	molecule 2
			Bond Lengths (Å)					
Ru(1)−P(16)	2.416(3)	2.465(3)	Ru(1)−C(4)	2.018(9)	2.026(10)	C(4)−C(5)	1.376(12)	1.343(12)
Ru(1)−P(26)	2.452(3)	2.419(3)	Ru(1)−C(7)	2.588(9)	2.551(8)	C(5)−C(6)	1.475(13)	1.462(12)
Ru(1)−C(2)	1.802(10)	1.803(10)	O(3)−C(2)	1.182(10)	1.193(11)	C(6)−C(7)	1.373(14)	1.427(13)
			Bond Angles (deg)					
P(16)−Ru(1)−P(26)	171.31(10)	165.31(10)	C(2)−Ru(1)−C(7)	168.5(4)	163.7(4)	Ru(1)−C(2)−O(3)	178.6(8)	173.4(8)
P(16)−Ru(1)−C(2)	91.4(3)	87.4(3)	C(4)−Ru(1)−C(7)	75.5(3)	75.7(3)	Ru(1)−C(4)−C(5)	121.2(7)	120.8(7)
P(16)−Ru(1)−C(4)	95.51(28)	99.3(3)	Ru(1)−P(16)−C(17)	122.6(4)	118.7(4)	C(4)−C(5)−C(6)	117.6(9)	119.6(9)
P(16)−Ru(1)−C(7)	92.24(24)	97.18(22)	Ru(1)−P(16)−C(21)	102.0(4)	110.6(4)	C(5)−C(6)−C(7)	121.5(8)	118.7(8)
P(26)−Ru(1)−C(2)	89.7(3)	91.7(3)	Ru(1)−P(16)−C(25)	112.0(4)	108.3(4)	C(5)−C(6)−C(11)	121.8(10)	124.3(9)
P(26)−Ru(1)−C(4)	93.03(28)	95.3(3)	Ru(1)−P(26)−C(27)	116.6(4)	121.6(3)	Ru(1)−C(7)−C(6)	100.0(6)	100.3(5)
P(26)−Ru(1)−C(7)	88.34(23)	87.76(22)	Ru(1)−P(26)−C(31)	108.4(4)	101.4(4)	Ru(1)−C(7)−C(8)	130.5(7)	131.3(7)
C(2)−Ru(1)−C(4)	93.4(4)	88.1(4)	Ru(1)−P(26)−C(35)	114.0(4)	114.5(3)			

Scheme 1^a

^{a} All the complexes have 1+ charge.

Scheme 2^a
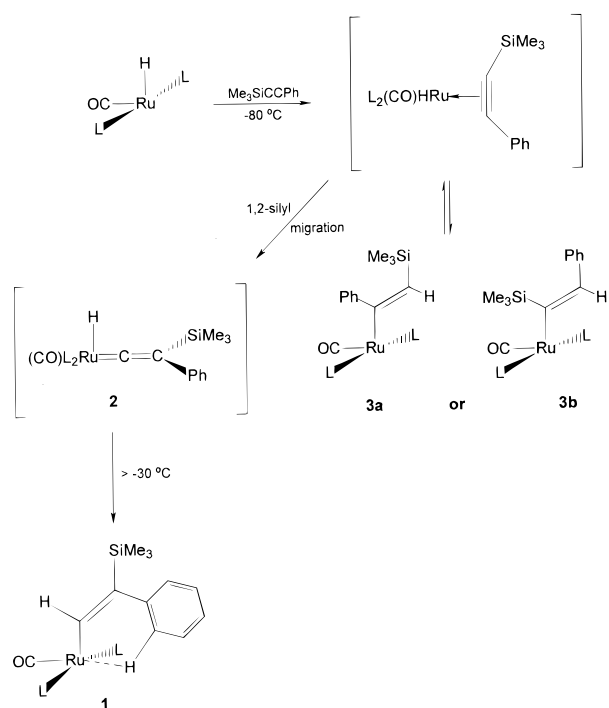
^{a} All the complexes have 1+ charge.

CH$_3$ is not likely due to the weaker ligating ability of the C−H bond of CH$_3$. This is well demonstrated in the formally 14-electron Ir(III) complex, [IrH$_2$(P^{t}Bu$_2$Ph)$_2$]BAr$'_4$,[10] in which the ^{t}Bu is superior to Ph as an agostic donor.

Search for Reaction Intermediates. Apparently (Scheme 1), formation of **1** goes through a vinylidene intermediate, **2**, formed by 1,2-silyl migration. **2** then undergoes α-H migration to give **1**. To gather spectroscopic evidence for **2**, a low-temperature NMR study was carried out. Combining equimolar [RuH(CO)L$_2$]BAr$'_4$ and PhCCSiMe$_3$ in a 1:1 mixture of C$_6$H$_5$F and toluene-d_8 at −80 °C causes an immediate color change from light orange to bright orange. The ^{31}P{^{1}H} NMR spectrum at this temperature reveals a product with a sharp singlet at 40.6 ppm. Correspondingly, the ^{1}H NMR spectrum shows a peak at 3.65 ppm; no hydride signal is detected. These spectral features do not support **2**, which should have an upfield hydride signal. The peak at 3.65 ppm is assigned as a vinyl H on a β carbon,

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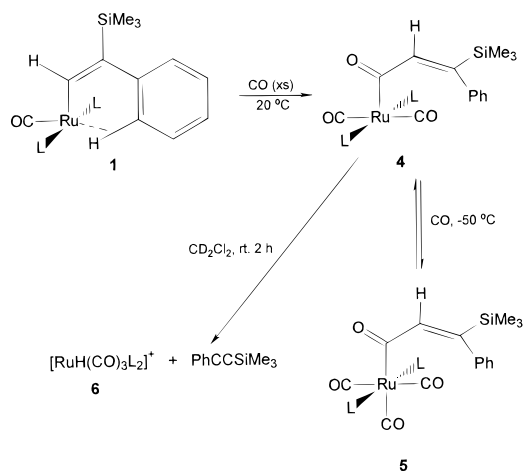
due to either **3a** or **3b**. η^2-Vinyl structures cannot be excluded for **3**. Upon warming to −30 °C, **1** begins to form and after 10 min at room temperature is the only observed product. Because the structure of **3a(b)** is counterproductive for the formation of **1**, we propose that the kinetic product **3a(b)** reverts to undetected [RuH(η^2-Me$_3$SiCCPh)(CO)L$_2$]$^+$, which then isomerizes to unobserved **2** before the hydride migrates to give **1**. In general, the striking feature of this reaction is that, due to high mobility of silyl and hydrogen, thermodynamic product **1** is formed so readily. Product **1** has the least steric repulsion among the ligands, and it fills more metal orbitals than does intermediate **3a/b**.

Reaction of 1 with CO. Addition of 1 atm of CO to CD$_2$Cl$_2$ solution of **1** at 25 °C causes an immediate color change from red to bright yellow. Spectroscopic analysis of the solution reveals (Scheme 2) formation of [Ru(CO)$_2$[(CO−CH=C(SiMe$_3$)-(Ph)]L$_2$]$^+$ (**4**). The C=O stretching frequency of **4** is normal (1645 cm^{-1}) for η^1-acyl. The large intensity difference (8:2) of two CO stretching peaks (1996 and 2087 cm^{-1}) suggests they are approximately trans. The vinyl proton of **4** is at much higher field (6.85 ppm) than that of **1**, in accord with the CO-inserted product. Remarkably, at room temperature, the ^{13}C{^{1}H} NMR shows no resonances for coordinated CO. Below 10 °C, two broad peaks appear at 203 and 197 ppm with a 1:1 ratio, indicating that the two metal-bound CO's are inequivalent at this temperature. This is likely due to the hindered rotation of the acyl group, a very common feature for RuXY(CO)(P^{t}Bu$_2$-Me)$_2$ complexes.[11] The C(=O) resonance is found at 225 ppm as a triplet. Moreover, there are two ^{t}Bu (CH$_3$) chemical shifts, indicating the ^{t}Bu groups on phosphines are diastereotopic,
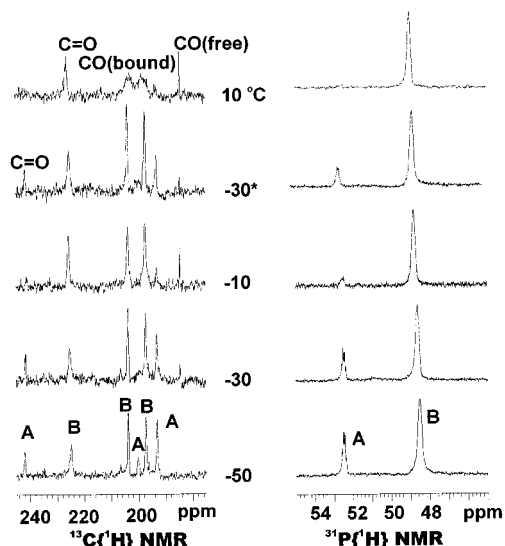
Figure 2. Variable-temperature NMR spectra of **1** + ¹³CO (excess). Solvent: CD₂Cl₂. Peaks labeled A are assigned to **5**; peaks marked B are assigned to **4** (see Scheme 2). The spectrum marked with an asterisk was recorded after cooling from −10 °C. It is similar to that recorded at −30 °C, revealing the reversibility of the process.

consistent with slow rotation of the acyl group. If ¹³CO is used, similar resonances are observed. It is also evident that ¹³CO incorporates to the acyl group, since the integration of the ¹³C(=O) peak is comparable to that of coordinated CO signals (Figure 2). Since **4** is a 16-electron complex, it could coordinate another CO. Indeed, upon cooling (−50 °C) the solution under excess ¹³CO, [Ru(¹³CO)₃(¹³C(O)CH=C(SiMe₃)(Ph))L₂⁺] (**5**) is formed, and the free CO peak disappears (Figure 2). Strong evidence for **5** is the ³¹P{¹H} NMR spectrum, which shows an apparent quartet due to the coupling with three ¹³CO's (J_{CP} = 10 Hz; coupling with the acyl ¹³C is not resolved). It seems contradictory that five-coordinated **4** shows hindered rotation and give rise to two different CO's, while **5** has only two CO peaks (200.3 and 193.1 ppm). One reason for this may be that **5** has a longer Ru−C(=O) bond (trans to CO) than that (trans to vacant site) of **4**;[12] as a consequence, the acyl group in **5** can rotate faster. At higher temperature (>−10 °C), only **4** and free ¹³CO are observed.
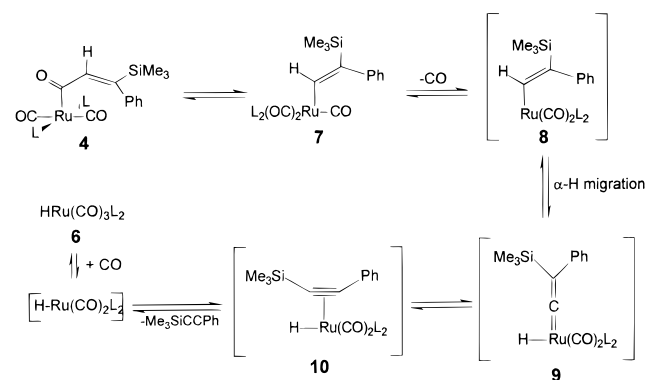
Isomerization of 4. 4 is not persistent in solution. At 20 °C and in CD₂Cl₂, it transforms over 2 h to RuH(CO)₃L₂⁺ (**6**) and PhCCSiMe₃, which is confirmed by comparison of the ¹H NMR data with those of authentic Me₃SiCCPh. **6** shows a characteristic hydride peak at −7.58 ppm and one ᵗBu proton virtual triplet. To strengthen the assignment, **6** was synthesized independently from [RuH(CO)L₂]⁺ and excess CO. The X-ray structure of an analogous complex, [RuH(CO)₃(PPh₃)₂][CH-(OTf)₂], reveals an octahedral geometry around Ru(II).[13] Although the transformation from **4** to **6** should involve many elementary steps, no intermediates are detected by ¹H and ³¹P{¹H} NMR spectra. We thus speculate that it goes through the stepwise transformation depicted in Scheme 3. **4** undergoes CO deinsertion to give saturated **7**. This intramolecular process should be independent of free CO concentration. The fact that

Scheme 3[a]

[a] All the complexes have 1+ charge.

7 is not observed indicates the equilibrium favors **4**. Loss of CO from **7** produces unsaturated **8**. α-H migration of **8** gives vinylidene **9**, which isomerizes to alkyne adduct **10**. The alkyne then dissociates, and the 16-electron intermediate [RuH-(CO)₂L₂]⁺ is trapped by CO to form **6**. The transformation does not happen under 1 atm of CO; compound **4** is persistent. Therefore, CO dissociation from **7** is likely to be the rate-determining step. The reaction illustrates the high mobility of silyl and hydride in this complex.

Discussion

The conversion shown in eq 1 is a very common reaction, but only for the mobile groups G = H or SiR₃. The rate of these reactions is highly variable, but, most significantly, there are no generalizations or predictive principles concerning these rates. A corollary ignorance is that of mechanism of this reaction. Often the reaction for G = H occurs on a cationic metal center, and the possibility that the conventional mechanisms[4b] might be replaced by base-catalyzed processes (polar solvent, counterion, or adventitious Brønsted basic impurity) remains to be clearly evaluated. The fact that silyl groups can be unexpectedly hydrolyzed off (i.e., R₃Si → H)[3c] emphasizes the *availability* of potential nucleophilic catalysts. In contrast, when neutral complexes are involved, base catalysis is less likely. Indeed, it has been observed recently[14] that "The most remarkable feature is that . . . the metal-assisted isomerization of HC≡CR to C=CHR takes place considerably *faster* in the coordination sphere of a four-coordinate *cationic* than of a related *neutral d⁸* metal center." The adduct between (arene)M-(CO)ₙ and Me₃SiC≡CSiMe₃ has been shown[15] to be an equilibrium mixture of η²-alkyne and vinylidene, C=C(SiMe₃)₂, isomers. The equilibrium is established in 1 h when n = 0 but essentially instantly for the analogous radical cation (n = 1+). The mechanism whereby a Me₃Si group can migrate without the aid of nucleophilic catalysis and in arene solvent is unknown.

In general, we have demonstrated here silyl migration of a silyl alkyne on the highly electron deficient Ru(II) hydride, [RuH(CO)L₂]⁺, to give, instead of an 16-electron vinylidene, a vinyl complex in which *two* agostic interactions avoid a 14-electron count. The thermodynamic preference of the product is in sharp contrast with the reaction product of RuHClL₂ with terminal alkyne, which is a 16-electron vinylidene.[5] From this result, we conclude that less π-basic [RuH(CO)L₂]⁺ cannot provide enough back-donation to stabilize the unobserved

(11) It is well established that the rotation of Ru−Ph bond in Ru(Ph)-Cl(CO)(PᵗBu₂Me)₂ is slow even at room temperature, so there are five distinct Ph proton resonances, see: Notheis, J. U.; Heyn, R. H.; Caulton, K. G. *Inorg. Chim. Acta* **1995**, *229*, 187.
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vinylidene, $[RuH(=C=CR_2)(CO)L_2]^+$, while π-electron-rich RuHClL$_2$ favors forming a π-acidic vinylidene ligand. Similarly, RuHClL$_2$ isomerizes ethyl vinyl ether to give a carbene complex $[RuCl(C(OEt)(CH_3))L_2]$,[16] while $[RuH(CO)L_2]^+$ inserts[17] the C=C bond to give $[Ru(\eta^2\text{-}CH_2CH_2OEt)(CO)L_2]^+$. This result demonstrates that tuning the balance between π-basicity and Lewis acidity of the unsaturated transition metal complexes can have a profound effect on the preferred reaction product.

Experimental Section

General Procedures. All reactions and manipulations were conducted using standard Schlenk and glovebox techniques. Solvents were dried and distilled under argon and stored in airtight solvent bulbs with Teflon closures. All NMR solvents were dried, vacuum-transferred, and stored in an argon-filled glovebox. ^{1}H, ^{31}P, and ^{13}C NMR spectra were recorded on a Varian Gem XL300 or a Unity I400 spectrometer. Chemical shifts are referenced to solvent peaks (^{1}H, ^{13}C) and external H$_3$PO$_4$ (^{31}P). Infrared spectra were recorded on a Nicolet 510P FT-IR spectrometer. $[RuH(CO)L_2]BAr'_4$ [18] is synthesized by a literature method. Other chemicals are available from commercial sources.

$[Ru(CH=C(Ph)(SiMe_3))(CO)(P^tBu_2Me)_2]BAr'_4$ (1). RuH(OTf)-(CO)(P^{t}Bu$_2$Me)$_2$ (300 mg, 0.50 mmol) and NaBAr$'_4$ (450 mg, 0.50 mmol) were placed in a test tube with a screw cap. Fluorobenzene (10 mL) was added to the test tube, and the mixture was stirred for 10 min. To the mixture was added PhCCSiMe$_3$ (100 μL, 0.51 mmol). The orange solution immediately turned dark brown. After 5 min, the mixture was centrifuged, and the solution was decanted to a Schlenk tube and layered with pentane. Dark orange crystals were obtained after 3 days. The solution was filtered, and the crystals were washed with pentane to give 350 mg (47%) of product. ^{1}H NMR (300 MHz, CD$_2$Cl$_2$, 20 °C): δ 8.35 (s, 1H, RuCH), 7.77 (m, overlapping with Ar$'$ ortho protons, meta H of Ph). 7.73 (s, 8H, ortho H of Ar$'$), 7.57 (s, 4H, para H of Ar$'$), 7.44 (m, 1H, para H of Ph), 6.0 (br, 2H, $w_{1/2}$ = 300 MHz, ortho H of Ph), 1.19 (vt, 18 H, N = 15 Hz, P^{t}Bu), 1.17 (vt, 18 H, N = 15 Hz, P^{t}Bu), 0.87 (vt, 6H, N = 5.7 Hz, PCH$_3$), 0.22 (s, 9H, Si(CH$_3$)$_3$). ^{31}P{^{1}H} NMR (121 MHz, CD$_2$Cl$_2$, 20 °C): δ 41.1 (s). IR (Nujol, cm^{-1}): 2691, 2730 (ν(C$-$H), agostic), 1968 (ν(CO)). ^{13}C{^{1}H} NMR (100 MHz, $-$60 °C, CD$_2$Cl$_2$): δ 202.4 (t, J_{PC} = 13.7 Hz, CO), 170.1 (t, J = 7.6 Hz, Ru$-$CH), 161.72 (m, B$-$C), 150.8 (s, CH=C(SiMe$_3$), 144.8 (s, ipso C of Ph),139.5 (s, meta C of Ph), 134.6 (s, ortho C of Ar$'$), 133.3 (s, meta C of Ph), 128.7 (q, J_{CF} = 31 Hz, meta C of Ar$'$), 128.0 (s, ortho C of Ph), 124.4 (q, J_{CF} = 270 Hz, CF$_3$), 117.5 (s, para C of Ar$'$), 109.6 (s, agostic ortho C of Ph, J_{CH} = 132 Hz, measured by J-resolved C,H correlation spectroscopy), 38.2 (vt, N = 19.8 Hz, PC(CH$_3$)$_3$), 36.6 (vt, N = 19.8 Hz, PC(CH$_3$)$_3$), 28.5 (s, PC(CH_3)$_3$), 28.1 (s, PC(CH_3)$_3$), 4.2 (br s, PCH$_3$), $-$0.70 (s, SiCH$_3$).

X-ray Crystal Structure of $[Ru(CH=C(Ph)(SiMe_3))(CO)(P^tBu_2Me)_2]$-BAr$'_4$. X-ray quality crystals were grown from the solvent mixture of pentane and fluorobenzene at room temperature. The air- and moisture-sensitive sample was handled in a nitrogen-filled glovebag. A small red prismatic crystal was selected and attached to a glass fiber using silicone grease. The crystal was then transferred to the goniostat, where it was cooled to $-$168 °C for characterization and data collection. A preliminary search for peaks and analysis using the programs DIRAX and TRACER revealed a monoclinic unit cell. Following complete data collection to 50° (2θ), the systematic extinctions of 0k0 for k = 2n + 1 and of h0l for l = 2n + 1 uniquely identified the space group as $P2_1/c$ (No. 14). The subsequent solution and refinement of the structure confirmed this choice. Details of the data collection are summarized in Table 1. During the initial data processing and averaging, 25 reflections severely affected by overlap due to the 40 Å axis were deleted. Attempts were made at locating the hydrogen atoms on C(7) and C(42), respectively, but none were located. All hydrogen atoms were then introduced in fixed idealized positions with isotropic thermal

parameters equal to 1.0 plus the isotropic equivalent of the parent atom. Atoms C(41), C(62), and C(176) failed to converge properly to anisotropic form, and they were refined with isotropic thermal parameters, while all other non-hydrogen atoms were refined with anisotropic thermal parameters. The final difference Fourier was essentially featureless. The largest peak was 1.08 e/Å^3, 0.71 Å from P(16), and the deepest hole was $-$0.90 e/Å^3.

$[Ru(C(O)CH=C(Ph)(SiMe_3))(CO)_2(P^tBu_2Me)_2]BAr'_4$ (4). In an NMR tube, $[Ru(CH=C(Ph)(SiMe_3))(CO)(P^tBu_2Me)_2]BAr'_4$ (70 mg, 0.05 mmol) was dissolved in CD$_2$Cl$_2$ (0.5 mL). The solution was degassed by freeze$-$pump$-$thaw cycles three times before CO was charged. Within the time of mixing, the dark orange color gave way to bright yellow. To ensure excess CO was added, the same NMR tube was exposed to CO (1 atm) again. NMR spectral analysis reveals clean formation of **4**. ^{1}H NMR (300 MHz, 20 °C): δ 7.73 (s, 8H, ortho H of Ar$'$), 7.57 (s, 4H, para H of Ar$'$), 7.28 (m, 3H, para and meta H of Ph), 6.85 (s, 1H, Ru(CO)CH), 6.65 (m, 2H, ortho H of Ph), 1.73 (vt, 6H, N = 5.4 Hz, PCH$_3$), 1.24 (vt, 36 H, N = 14.4 Hz, ^{t}Bu), 0.11 (s, 9H, Si(CH$_3$)$_3$). ^{31}P{^{1}H} NMR (121 MHz, 20 °C): δ 48.5 (s). IR (CD$_2$Cl$_2$): 2087 (ν(CO)), 1992 (ν(CO)), 1646 (ν(C=O). The volatiles were removed, and the yellow residue was dissolved in CD$_2$Cl$_2$ to give a pale yellow solution, which turned to colorless after 2 h. NMR spectra of the solution revealed clean formation of PhCCSiMe$_3$ and [RuH-(CO)$_3$(P^{t}Bu$_2$Me)$_2$]BAr$'_4$.

$[Ru[^{13}C(O)CH=C(Ph)(SiMe_3))(^{13}CO)_2(P^tBu_2Me)_2]BAr'_4$, $[Ru(^{13}C$-$(O)CH=C(Ph)(SiMe_3))(CO)_3(P^tBu_2Me)_2]BAr'_4$, and $[RuH(^{13}CO)_3$-$(P^tBu_2Me)_2]BAr'_4$. In an NMR tube, $[Ru(CH=C(Ph)(SiMe_3))(CO)$-(P^{t}Bu$_2$Me)$_2$]BAr$'_4$ (70 mg, 0.05 mmol) was dissolved in CD$_2$Cl$_2$ (0.5 mL). The solution was degassed by freeze$-$pump$-$thaw cycles three times before ^{13}CO was charged. Within the time of mixing, the dark orange color gave way to bright yellow. To ensure excess ^{13}CO was added, the same NMR tube was exposed to ^{13}CO (1 atm) again.

^{13}C{^{1}H} NMR of $[Ru(^{13}C(O)CH=C(Ph)(SiMe_3))(^{13}CO)_2(P^tBu_2Me)_2]$-BAr$'_4$ (100 MHz, CD$_2$Cl$_2$, $-$20 °C): δ 225.8 (m, C=O), 203.5 (br, CO), 197.5 (br, CO). The two CO resonances coalesce to one broad peak at room temperature at 20 °C at 200 ppm.

When the temperature was cooled to $-$50 °C, a significant amount of $[Ru(^{13}C(O)CH=C(Ph)(SiMe_3))(^{13}CO)_3(P^tBu_2Me)_2]BAr'_4$ was observed. ^{13}C{^{1}H} NMR (100 MHz, $-$50 °C): δ 242.9 (m, C=O), 200 (m, CO), 193.2 (m, CO). ^{31}P{^{1}H} NMR (162 MHz, $-$50 °C): δ 52.5 (q, J_{CP} = 10 Hz). ^{1}H NMR (400 MHz, $-$50 °C): δ 1.51 (vt, N = 7 Hz, PCH$_3$), 1.35 (vt, N = 14 Hz, ^{t}Bu). This complex was not observed at 20 °C by NMR spectra.

Removal of volatiles afforded a light yellow residue, which was dissolved in CD$_2$Cl$_2$ to give a colorless solution of [RuH(^{13}CO)$_3$-(P^{t}Bu$_2$Me)$_2$]BAr$'_4$. ^{13}C{^{1}H} NMR (75 MHz, 20 °C): δ 196.9 (m, 2C, CO), 194.2 (m, 1C, CO trans to hydride). ^{1}H NMR (300 MHz, 20 °C): δ 7.73 (s, 8H, ortho H of Ar$'$), 7.57 (s, 4H, para H of Ar$'$), 1.68 (vt, N = 5.6 Hz, PCH$_3$), 1.37 (vt, N = 15 Hz, ^{t}Bu), $-$7.57 (m, 1H, Ru$-$H). ^{31}P{^{1}H} NMR (121 MHz, 20 °C): δ 57.6 (m).

Procedure of Low-Temperature NMR Study for Intermediates. [RuH(CO)(P^{t}Bu$_2$Me)$_2$]BAr$'_4$ (20 mg, 0.017 mmol) was covered by C$_6$H$_5$F and toluene-d_8 (1:1) in an NMR tube. Onto the upper wall of the NMR tube was added PhCCSiMe$_3$ (3.3 μL, 0.017 mmol). The tube was transferred immediately to a dry ice acetone bath ($-$78 °C) and mixed thoroughly. The solution changed color from light orange to bright yellow. The tube was transferred to a precooled NMR probe for observation.

Supporting Information Available: Full crystallographic details, positional and thermal parameters, and distances and angles (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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