ORGANOMETALLICS
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Reactions of a Neutral Silylene Ruthenium Complex with Heterocumulenes: C=O Hydrosilylation of Isocyanates vs C=S Bond Cleavage of Isothiocyanate

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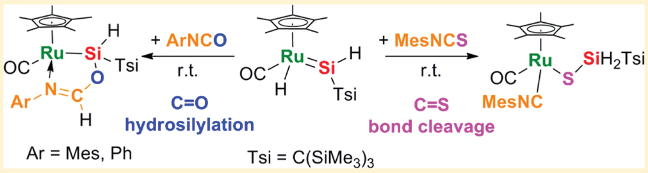
Supporting Information

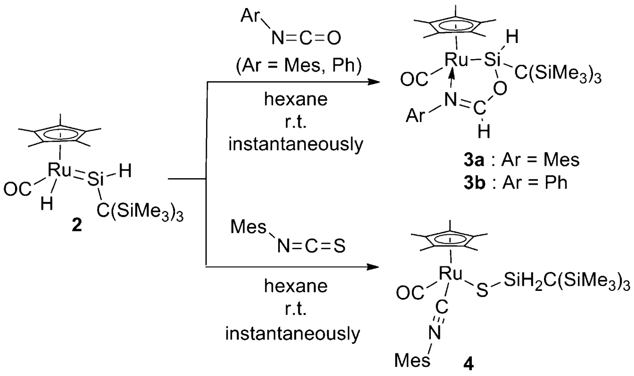


ABSTRACT: Reactions of the neutral silylene ruthenium complex $Cp^*(CO)(H)Ru{=}Si(H)\{C(SiMe_3)_3\}$ (**2**) with heterocumulenes were investigated. Treatment of **2** with ArNCO (Ar = Mes, Ph; Mes = 2,4,6-trimethylphenyl) resulted in hydrosilylation of ArNCO selectively at the C=O bond at room temperature to give the five-membered chelate complexes $Cp^*(CO)Ru[\kappa^2N,Si\text{-}N(Ar){=}C(H)OSi(H)\{C(SiMe_3)_3\}]$ (**3a**, Ar = Mes; **3b**, Ar = Ph). In contrast, the reaction of **2** with MesNCS led to cleavage of the C=S double bond to give the isocyanide complex $Cp^*(CO)Ru(CNMes)\{SSiH_2C(SiMe_3)_3\}$ (**4**). The structures of both types of products were unambiguously determined by X-ray crystallography.

In the chemistry of transition-metal carbene complexes, reactions with unsaturated organic substrates are particularly important and well investigated because they are extremely useful for the syntheses of various exotic organic compounds.[1] In contrast, although transition-metal silylene complexes have been postulated to play an important role in metal-mediated transformations of organosilicon substrates,[2] the fundamental reactivity of isolated silylene complexes, especially toward unsaturated organic substrates, have scarcely been reported until recently. This is mainly because the metal−silicon double bonds in most of the isolated silylene complexes are excessively protected by bulky groups and thus become nonreactive toward most regular-sized organic or inorganic substrates. One distinct exception is the cationic silylene complex $[Cp^*(PMe_3)_2Ru{=}SiMe_2]^+$, which has small methyl groups on the silicon atom and underwent [2 + 2] cycloaddition with RNCO (R = Me, Ph) to give Ru−Si−N−C four-membered-ring complexes.[3] Recently, another type of silylene complex in which the metal−silicon double bonds are less sterically protected, i.e. silylene complexes having hydrogen atoms on both silicon and metal centers, has been synthesized.[4−6] These silylene complexes have been demonstrated to show reactivity far higher than that of most of the previously reported silylene complexes. For example, our group reported that the neutral silylene complexes $Cp^*(CO)_2(H)W{=}Si(H)\{C(SiMe_3)_3\}$ (**1**)[4] and $Cp^*(CO)(H)Ru{=}Si(H)\{C(SiMe_3)_3\}$ (**2**)[5] reacted cleanly with nitriles, ketones, and α,β-unsaturated carbonyl compounds. This time, we examined the reactions of **2** with ArNCO and ArNCS. As a result, in contrast with the aforementioned cationic silylene complex, the reaction of **2** with ArNCO led to hydrosilylation of ArNCO at the C=O bond to give five-membered Ru−Si−O−C−N chelate complexes, while reaction with ArNCS led to the C=S double bond cleavage of ArNCS to give isocyanide complexes at room temperature. We report here these new reactions and structural characterization of two types of products and discuss possible mechanisms for formation of them.

Addition of 1 equiv of MesNCO (Mes = mesityl = 2,4,6-trimethylphenyl) to **2** in C_6D_6 at room temperature gave $Cp^*Ru(CO)[\kappa^2N,Si\text{-}N(Mes){=}C(H)OSi(H)\{C(SiMe_3)_3\}]$ (**3a**) instantaneously in 74% yield by NMR spectroscopy. Complex **3a** was isolated in 52% yield as yellow crystals by a preparative-scale reaction in hexane (Scheme 1). The formation of **3a** means that the C=O bond of MesNCO was hydrosilylated with **2**. The phenyl-substituted analogue $Cp^*Ru(CO)[\kappa^2N,Si\text{-}N(Ph){=}C(H)OSi(H)\{C(SiMe_3)_3\}]$ (**3b**) was also obtained in a similar procedure but in rather low yield (12%) because of its thermal instability. These products were

Scheme 1. Reactions of 2 with ArNCO and ArNCS

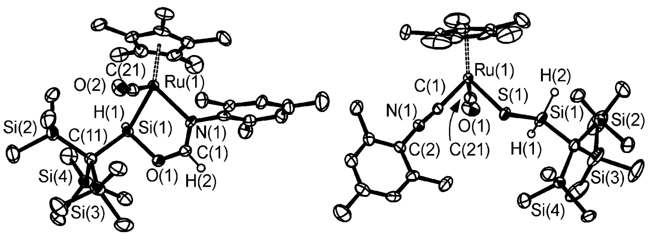


Received: November 5, 2011
Published: January 5, 2012

dx.doi.org/10.1021/om2010854 | *Organometallics* 2012, 31, 527−530

characterized by NMR, IR, and mass spectroscopy, and elemental analysis. The crystal structure of **3a** was determined by X-ray crystallography.

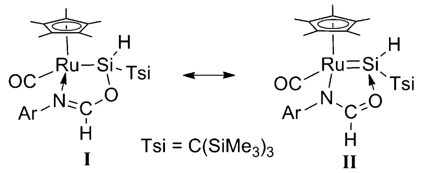
The ORTEP drawing of **3a** depicted in Figure 1 (left) shows that **3a** has a new five-membered Ru–Si–O–C–N ring.[7] The N(1)–C(1) bond length is 1.282(10) Å, which is in the range of N=C double-bond lengths (1.15–1.36 Å),[8] whereas the Si(1)–O(1) bond length (1.761(6) Å) is significantly longer than the usual Si–O single-bond length (1.63–1.65 Å) and rather close to the partially dative Si–O bond length of alkoxy-bridged bis(silylene) complexes (1.78–1.86 Å).[9] On the other hand, the Ru(1)–Si(1) bond length (2.365(2) Å) is relatively short as a typical Ru–Si single-bond length (2.35–2.55 Å) and is in the range of Ru=Si double-bond lengths (2.26–2.41 Å) of base-stabilized silylene ruthenium complexes.[9] The sum of the bond angles at Si(1), except for the Si(1)–O(1) bond, i.e. Ru(1)–Si(1)–C(11), Ru(1)–Si(1)–H(1), and C(11)–Si(1)–H(1), is 348°. This value is between the median of 328° for a typical sp^3-hybridized silicon atom and 360° for an sp^2-hybridized atom and is slightly closer to the latter value. Therefore, it is suggested that there is a significant contribution of canonical form **II** (silylene complex) in addition to form **I** (silyl complex) illustrated in Chart 1.



3a **4**

Figure 1. ORTEP drawings of **3a** (left) and **4** (right) showing thermal ellipsoids at the 50% probability level. Selected bond lengths (Å) and angles (deg) are as follows. **3a**: Ru(1)–Si(1) = 2.365(2), Ru(1)–N(1) = 2.164(6), Si(1)–O(1) = 1.761(6), O(1)–C(1) = 1.308(9), C(1)–N(1) = 1.282(10), Si(1)–C(11) = 1.928(7); Si(1)–Ru(1)–N(1) = 79.25(17), Ru(1)–N(1)–C(1) = 118.8(5), Ru(1)–Si(1)–O(1) = 99.87(18), Si(1)–O(1)–C(1) = 117.2(5), N(1)–Ru(1)–C(21) = 98.7(3). **4**: Ru(1)–S(1) = 2.442(2), Ru(1)–C(1) = 1.939(6), Ru(1)–C(21) = 1.893(7), Si(1)–S(1) = 2.092(2), C(1)–N(1) = 1.167(7), N(1)–C(2) = 1.394(7); S(1)–Ru(1)–C(1) = 84.6(2), S(1)–Ru(1)–C(21) = 95.7(2), Ru(1)–S(1)–Si(1) = 105.25(8), S(1)–Si(1)–C(11) = 115.6(2), Ru(1)–C(1)–N(1) = 174.4(6), C(1)–N(1)–C(2) = 170.9(6).

Chart 1



This resonance contribution of form **II** is also suggested on the basis of NMR data. For example, the $^{29}Si\{^1H\}$ NMR spectrum of **3a** shows a signal for SiH at 93.1 ppm. This downfield shift is comparable with those of base-stabilized silylene complexes.[10] The ^1H signal for SiH is observed at 6.47 ppm, which is shifted downfield compared with that for usual $Si(sp^3)$–H protons. Similarly, the ^{29}Si and ^1H signals for SiH of **3b** are observed at 95.9 and 6.12 ppm, respectively. In addition, the ^1H signal for N=CH appears at 7.18 ppm for **3a** and 7.65 ppm for **3b**, which is comparable with the chemical shifts of the corresponding protons of siloxyimines ($PhN=CHOSiR_1R_2R_3$).[11] In relation to the present results, we have reported very recently that the germylene analogue of tungsten silylene complex **1**, $Cp^*(CO)_2(H)W=Ge(H)\{C(SiMe_3)_3\}$, underwent hydrogermylation of PhNCO or RNCS to give a similar complex having a five-membered W–Ge–O–C–N or W–Ge–N–C–S ring kinetically, respectively.[12]

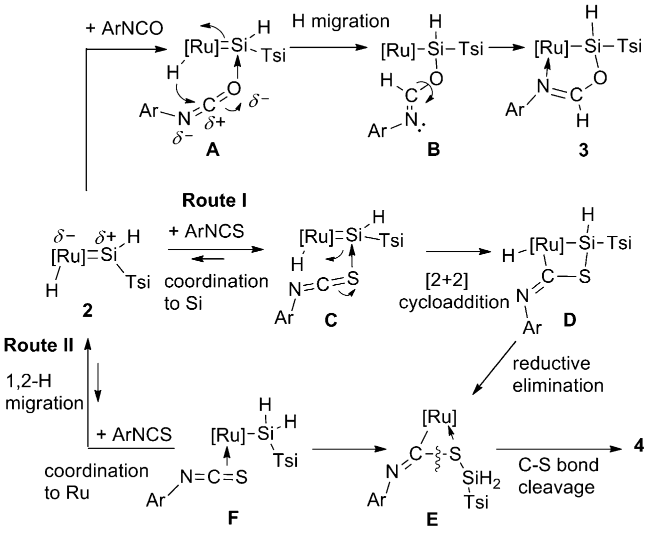
In contrast to the reactions of **2** with isocyanates, the reaction of **2** with an isothiocyanate led to the cleavage of the C=S double bond. Thus, the reaction of **2** with MesNCS in C_6D_6 proceeded at room temperature to afford $Cp^*Ru(CO)(CNMes)\{SSiH_2C(SiMe_3)_3\}$ (**4**) quantitatively, which was clearly observed by NMR spectroscopy. Complex **4** was isolated as yellow crystals in 78% yield by a preparative-scale reaction in hexane after recrystallization (Scheme 1). In this reaction, the C=S bond of the incoming MesNCS was cleaved and converted into an isocyanide ligand (CNMes) and a silanethiolato ligand $\{SSiH_2C(SiMe_3)_3\}$ in **4**. Although the C=S bond cleavage of isothiocyanates induced by $Cp^*Co(H_2C=CH_2)_2$,[13] $[RhIr(CO)_2(\mu\text{-}\eta^1{:}\eta^2\text{-}C_2Ph)(dppm)_2][X]$ (X = BF_4, SO_3CF_3; dppm = $Ph_2PCH_2PPh_2$),[14] and $[Mo(P_4)(dppm)]$ (P_4 = *meso-o*-$C_6H_4(PPhCH_2CH_2PPh_2)_2$)[15] has previously been reported, this is the first example of C=S bond cleavage induced by a silylene complex.

The X-ray crystal structure of **4** (Figure 1, right) clearly shows that **4** bears a CNMes and a $SSiH_2C(SiMe_3)_3$ ligand.[8] The Ru(1)–S(1) and S(1)–Si(1) bond lengths are 2.442(2) and 2.092(2) Å, respectively, and the Ru(1)–S(1)–Si(1) bond angle is 105.25(8)°. The Ru(1)–S(1) bond length is comparable with that reported for $CpRu(PPh_3)_2(SSi^iPr_3)$ (2.461 Å).[16] The S(1)–Si(1) bond length and the Ru(1)–S(1)–Si(1) bond angle are in the range of known silanethiolato complexes (S–Si, 2.05–2.18 Å; M–S–Si, 85.7–131.5°).[10] The Ru(1)–C(1)–N(1) linkage is almost linear (174.4(6)°). The Ru(1)–C(1) bond length is 1.939(6) Å, which is comparable with those of typical isocyanide ruthenium complexes (1.86–2.09 Å, average 1.98 Å).[10] The N(1)–C(1) bond length is 1.167(7) Å, which is also in the range of known isocyanide ruthenium complexes (1.07–1.27 Å).[10]

The NMR data also support this structure of **4**. For example, the signals of two diastereotopic hydrogen atoms on silicon are observed at 5.15 and 5.30 ppm in the ^1H NMR spectrum. The $^{13}C\{^1H\}$ NMR signal of the CN group appears at 165.9 ppm, which is a chemical shift characteristic of isocyanide ligands. The IR spectrum exhibits strong bands at 1950 and 2112 cm^{-1}, which are assigned to the stretching vibrations of CO and CN, respectively.[17]

Possible mechanisms for the reactions of **2** with ArNCO and ArNCS are illustrated in Scheme 2. In the reaction with ArNCO, coordination of the oxygen atom to the electron-deficient silylene silicon atom occurs as denoted by **A**. This coordination in turn enhances the electrophilicity of the isocyanate carbon and induces hydride migration from Ru to the carbon atom to form intermediate **B**. Subsequent rotation of the C–O bond in **B** and coordination of the nitrogen atom to Ru gives product **3**. In the reaction with ArNCS, there are at least two possible routes: I and II. Route I is started by coordination of the less sterically hindered sulfur atom of ArNCS to the silylene ligand. However, presumably this S-

Scheme 2. Possible Mechanisms for Reactions of 2 with ArNCO and ArNCS



[Ru] = Cp*Ru(CO), Tsi = $C(SiMe_3)_3$

coordination is so weak that the central carbon is not sufficiently polarized to accept hydride migration from Ru. Instead, [2 + 2] cycloaddition between the Ru═Si and C═S bonds leads to **D**, from which reductive elimination of the Si−H bond and coordination of sulfur to the metal center occur to generate **E**. The weak C−S bond of **E** cleaves easily to give **4**. The alternative route II involves coordination of ArNCS to the ruthenium atom of the unsaturated silyl complex produced by 1,2-H migration from Ru to Si in **2**. Subsequent silyl migration to the sulfur atom in **F** produces **E** and then **4**. At present, we do not have any concrete evidence to distinguish these two routes. It should be noted that the aforementioned reaction of $[Cp^*(Me_3P)_3Ru{=}SiMe_2]^+$ with RNCO gave the N-silylated product $[Cp^*(Me_3P)_2Ru(SiMe_2NRC{=}O)]^+$, having a Ru−Si−N−C four-membered ring instead of an O-silylated product. In this case, possibly the steric repulsion between the relatively bulky $Cp^*(Me_3P)_2Ru$ fragment and the R group on RNCO prevents [2 + 2] cycloaddition between the Ru═Si and C═O bonds accompanied by O-silylation.

In summary, we have found new reactions of neutral silylene complex **2** with isocyanates and an isothiocyanate. The former resulted in hydrosilylation of the C═O bond to form a novel Ru−Si−O−C−N five-membered ring, while the latter resulted in C═S double-bond cleavage. These reactions demonstrate the existence of new types of bond-forming and -breaking processes induced by a silylene complex. Further reactivity studies of **2** are underway.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Text giving experimental details and CIF files giving and X-ray crystallographic data of **3b** and **4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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■ ACKNOWLEDGMENTS

This work was supported by the Ministry of Education, Culture, Sports, Science and Technology of Japan (Grants-in-Aid for Scientific Research Nos. 18064003, 20038002, and 21550054).

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(7) Crystal data (150 K) for **3a**: $C_{31}H_{55}NO_2Si_4Ru$; fw 687.19; monoclinic; $P2_1/c$; a = 9.354(5) Å; b = 23.530(14) Å; c = 16.460(10) Å; β = 91.667(2)°, V = 3621(4) Å^3; calcd density 1.273 Mg/m^3; Z = 4. Final R indices: R_1 = 0.0783, wR_2 = 0.2191 for 5276 reflections with $I > 2\sigma(I)$. Crystal data (150 K) for **4**: $C_{31}H_{55}NOSSi_4Ru$; fw 703.25; triclinic; $P\bar{1}$; a = 11.7791(6) Å; b = 12.1471(5) Å; c = 14.9347(9) Å; α = 86.458(2)°; β = 74.9512(17)°; γ = 63.014(4)°; V = 1835.02(16) Å^3; calcd density 1.273 Mg/m^3; Z = 2. Final R indices: R_1 = 0.0703, wR_2 = 0.1717 for 6515 reflections with $I > 2\sigma(I)$. Crystallographic information has been deposited with the Cambridge Crystallographic Data Centre: CCDC 837728 (**3a**), CCDC 804700 (**4**).

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