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Synthesis and Structure of Ruthenium−Silylene Complexes: Activation of Si−Cl Bonds in N-Heterocyclic Silanes

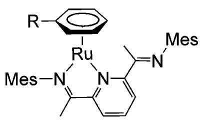
Hyojong Yoo, Patrick J. Carroll, and Donald H. Berry*

Department of Chemistry and Laboratory for Research on the Structure of Matter, University of Pennsylvania, Philadelphia, Pennsylvania 19104-6323

Received November 28, 2005; E-mail: berry@sas.upenn.edu

Transition metal silylene complexes—species with *formal* double bonds between metal and silicon atoms—have been the subject of considerable interest for many years.[1] Although several different synthetic approaches have been employed,[2,3] potentially the most general route to metal silylene complexes is the sequential addition of two groups from a tetravalent silane to a metal center. The first process, intermolecular oxidative addition, is well-known for silicon hydride bonds.[1b] The second step, intramolecular 1,2-migration or α-elimination of a second group from silicon to a metal, has been observed or implied for substituents, such as hydrides,[4] silyl,[5] or alkyl groups[6] in the formation of metal silylene complexes.

Our group has been interested in the activation of silicon chloride bonds as a route to reactive silyl and silylene complexes. There have been only a few previous reports of silicon chloride oxidative addition,[7] and α-halide elimination from a silyl ligand has not been previously described. Our initial studies have employed highly reactive zero-valent ruthenium complexes, $[\eta^2\text{-N}_3]\text{Ru}(\eta^6\text{-Ar})$ (**1**) and $\{[\text{N}_3]\text{Ru}\}_2(\mu\text{-N}_2)$ (**2**), where Ar = C_6H_6 or C_6H_5Me and $[\text{N}_3]$ = 2,6-(MesN=CMe)$_2$C$_5$H$_3$N.[8] Tetravalent heterocyclic silanes (X)(Cl)Si(NN) (X = H, Cl; Si(NN) = *N,N′*-bis(neopentyl)-1,2-phenylenedi(amino)silylene, Si[(NCH$_2$Bu^t)$_2$C$_6$H$_4$-1,2], were chosen as substrates because of the relative stability of the corresponding silylene[9] and expected weakening of the Si−Cl bonds in this system.



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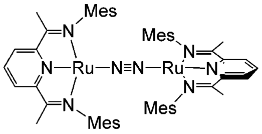

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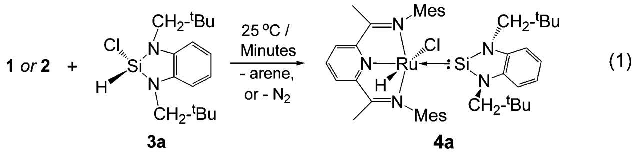
We now report the synthesis of ruthenium complexes with cyclic diaminosilylene ligands, [N$_3$]Ru(X)(Cl){Si(NN)}, formed by sequential and reversible activation of silicon hydride and chloride bonds of tetravalent silanes (X)(Cl)Si(NN). Furthermore, the silylene reversibly dissociates from the Ru(II) center and can be preferentially trapped with a more electron-rich metal complex, such as **2**, to generate a Ru(0) silylene complex, [N$_3$]Ru(N$_2$){Si(NN)}.

Treatment of either [N$_3$]Ru(0) complex **1** or **2** with cyclic diaminohydrochlorosilane **3a** in pentanes at 25 °C leads to rapid formation of ruthenium silylene complex, [N$_3$]Ru(H)(Cl){Si(NN)} (**4a**), which has been isolated as a red crystalline solid (77%, eq 1).[10]



3a **4a** (1)

The structure of **4a** in the solid state was determined by a single-crystal X-ray diffraction study. As illustrated in Figure 1, **4a** exhibits a six-coordinate, pseudo octahedral geometry with a trans arrangement of hydride and chloride ligands. The mesityl ligands are oriented approximately perpendicular to the [N$_3$] ligand plane and form a pocket surrounding the silylene ligand.

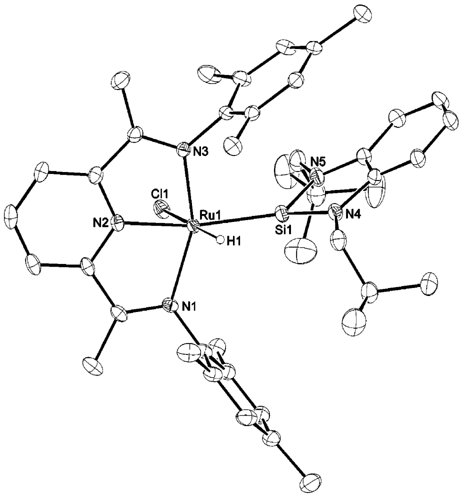


Figure 1. ORTEP drawing of complex **4a** (30% thermal ellipsoids). Hydrogen atoms other than Ru−H are omitted for clarity.

The silicon atom in **4a** is slightly pyramidal and lies 0.240 Å out of the plane defined by the three attached atoms (Ru, N, N). The metal silicon bond distance (2.304(1) Å) lies at the short end of the range of Ru−Si bonds located in the CSD[11] (ca. 2.20−2.50 Å, 2.39 Å average). For the most part, heterocyclic silylenes have been proposed to be excellent σ-donors and poor π-acids.[3c,d,12]

Complex **4a** is fluxional in solution on the ^{1}H NMR time scale. The ^{1}H NMR spectrum of **4a** at 285 K exhibits diastereotopic neopentyl CH$_2$ groups and no symmetry along either the H−Ru−Cl or N−Ru−N axes. This is comparable to the solid state structure and indicates hindered Ru−Si bond rotation and slow inversion at the slightly pyramidal silicon. The symmetrical spectrum observed at 350 K is consistent with both inversion and rotation of the silylene ligand. Coalescence of the various pairs of imine, methylene, and neopentyl ligand resonances is observed between 313 and 345 K. Similar conformational interconversions have been reported by Lappert and co-workers in palladium and platinum complexes of the silylene ligand.[3a]

Formation of silylene complex **4a** most likely proceeds by sequential Si−H oxidative addition and Si−Cl 1,2-migration to ruthenium. Various polar mechanisms are possible, but seem less likely for a reaction that is rapid in both pentane and THF. The putative five-coordinate Ru(II) silyl complex, [N$_3$]Ru(H)-Si(Cl)(NN) (**5a**), was not observed, but reaction of **4a** with excess PMe$_3$ at 25 °C results in the rapid formation of a phosphine complex tentatively identified as chlorosilyl complex [N$_3$]Ru(H)(PMe$_3$)(Si(NN)(Cl)) (**6**).[10] Complex **6** is not stable in solution at 25 °C and reacts with a second equivalent of PMe$_3$ to generate free silane (**3a**) and the bis(phosphine) complex, [N$_3$]Ru(PMe$_3$)$_2$.[8] This provides

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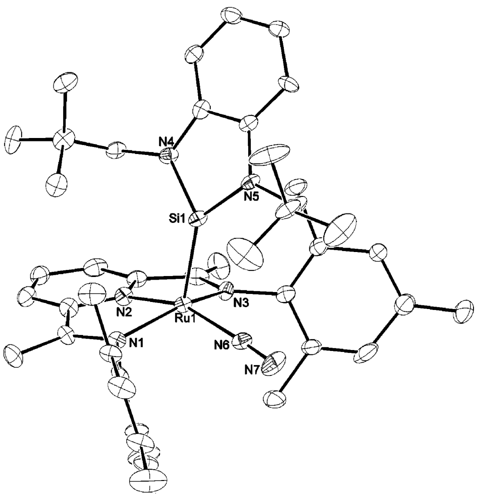
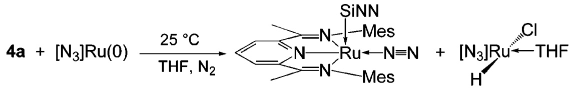


Figure 2. ORTEP drawing of complex **8** (30% thermal ellipsoids). Hydrogen atoms are omitted for clarity.

good evidence for reversible Si−H activation and the intermediacy of **5a**, as well as the reversibility of α-Cl migration.

Surprisingly, THF solutions of the Ru(II) silylene complex **4a** react slowly (days at 25 °C) with Ru(0) complexes, such as **1** or **2**, *under N_2* to yield $[N_3]Ru(H)(Cl)(THF)$ (**7a**) and the ruthenium(0) silylene dinitrogen complex $[N_3]Ru(N_2)\{Si(NN)\}$ (**8**, eq 2).[13] Presumably, this indicates that the silylene ligand can reversibly dissociate from **4a** and be trapped with a second metal center.



(2)

1 *or* **2** **8** **7a**

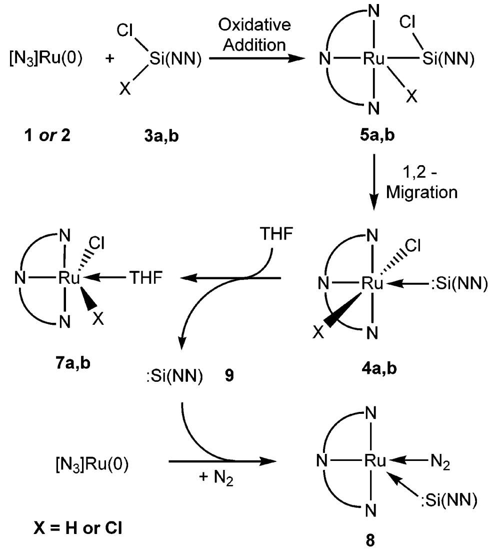
The geometry of **8** has been confirmed by a single-crystal X-ray diffraction study to be approximately square pyramidal (Figure 2),[10] with the Si(NN) ligand trans to the vacant site and the linear dinitrogen ligand trans to the pyridine. The Ru−Si bond distance (2.230(2) Å) is much shorter than in six-coordinate Ru(II) complex **4a** and is one of the shortest reported in the CSD.[11] However, it is difficult to attribute this shortening to any single factor, as both the reduced steric hindrance and increased electron density in the five-coordinate Ru(0) complex could favor closer Ru−Si contact.

The dichlorosilane **3b** ($Cl_2Si(NN)$) also reacts with Ru(0) complex **1**, but in the absence of N_2, the reaction stops after initial Si−Cl activation, and the 16 e^- silyl complex, $[N_3]Ru(Cl)$-$Si(Cl)$-(NN) (**5b**), can be isolated (50%) and characterized by multinuclear NMR spectroscopy.[10] Of particular note is the resonance in the ^{29}Si-$\{^1H\}$ NMR at δ −10.42 for the silyl ligand, which is more than 130 ppm upfield of silylene complexes **4a** (δ 126.9) and **8** (δ 133.69) and indicative of a four-coordinate silicon center. The silyl complex **5b** reacts with Ru(0) complexes under N_2 to form **8** and $[N_3]Ru(Cl)_2(THF)$ (**7b**), consistent with 1,2-migration of chloride from Si to Ru, and silylene dissociation, although the intermediate ruthenium silylene complex, $[N_3]Ru(Cl)_2\{Si(NN)\}$ (**4b**), is not observed under these reaction conditions. However, silylene complex **4b** has been prepared in 81% yield from the reaction of $[N_3]Ru(Cl)_2(C_2H_4)$ (**10**) with the free silylene, **9**.[10]

As in case of **4a**, treatment of the Ru(II) complex **4b** with **1** or **2** under N_2 leads to transfer of the silylene to the Ru(0) center and formation of **8** and **7b**. A likely mechanism for this series of transformations is shown in Scheme 1.

In conclusion, silyl complexes produced by Si−H or Si−Cl oxidative addition to ruthenium(0) centers can undergo 1,2-chloride migration to generate Ru(II) silylene complexes. This is the first example of the formation of metal silylene complexes from a silane via this type of α-chloride abstraction process. The activation of simple chlorosilanes, such as Me_2SiCl_2 with $[N_3]Ru(0)$, will be described in future reports.

Scheme 1. Proposed Mechanism



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Supporting Information Available: Details of synthetic procedures, spectroscopic details, and X-ray crystallographic data for **4a**, **4b**, **7b**, and **8** in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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(13) Compound **8** can be prepared more efficiently from the reaction of **9** with **1** or **2** under nitrogen.

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