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Stoichiometric Hydrosilylation of Nitriles and Catalytic Hydrosilylation of Imines and Ketones Using a μ-Silane Diruthenium Complex

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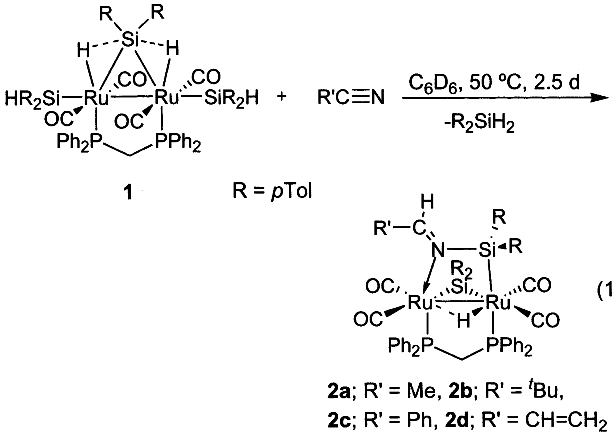
*Summary: The novel μ-iminosilyl complexes $Ru_2(CO)_4$-(μ-dppm)(μ-$SiTol_2$)(μ-R′CH=N$SiTol_2$) (**2**) were obtained in high yields during the stoichiometric reactions of a diruthenium complex having Ru−H−Si interactions, $\{Ru(CO)_2(SiTol_2H)\}_2(\mu\text{-dppm})(\mu\text{-}\eta^2\text{:}\eta^2\text{-}H_2SiTol_2)$ (**1**), with nitriles R′CN (R′ = Me, Ph, t-Bu, CH=CH_2). The catalytic hydrosilylation of various ketones and imines with dihydrosilanes were achieved using **1** as a catalyst. A novel reaction cycle involving the cooperative functions of the two Ru metals is proposed for the related hydrosilylation of various ketones and imines catalyzed by **1**.*

The hydrosilylation of unsaturated organic compounds catalyzed by transition-metal complexes has attracted much attention because of their great synthetic utility in laboratory and industry.[1] Experimental[2,3] and theoretical[4] studies for hydrosilylation of olefins have revealed the importance of the hydride silyl complexes on the Chalk−Harrods cycle[2] and the Seitz−Wrighton cycle.[3] Although nonclassical complexes having M−H−Si interactions are well characterized[5] and often assumed as one of the key intermediates in the hydrosilylation of unsaturated organic compounds,[1,6] such complexes have never been utilized as catalysts of the hydrosilylation. Recently, we have reported the synthesis and X-ray structure of a novel binuclear μ-silane complex with two Ru−H−Si interactions, $\{Ru(CO)_2(SiTol_2H)\}_2(\mu\text{-dppm})(\mu\text{-}\eta^2\text{:}\eta^2\text{-}H_2SiTol_2)$ (**1**; dppm = $Ph_2PCH_2PPh_2$, Tol = $p\text{-}C_6H_4CH_3$).[7] Here we report that the stoichiometric reactions of binuclear complex **1** with nitriles give interesting μ-iminosilyl-bridged diruthenium complexes. On the basis of the results, a unique reaction cycle involving the cooperative functions of the two Ru metals in complex **1** is proposed for the catalytic hydrosilylation of imines and ketones using dinuclear complex **1**.

When a mixture of **1** (0.093 mmol), acetonitrile (0.97 mmol), and benzene-d_6 (0.3 mL) in a sealed NMR tube was heated at 50 °C for 2.5 days, the novel iminosilyl-bridged complex **2a** was formed quantitatively and isolated in 90% yield (eq 1). Similar reactions using pivalonitrile, benzonitrile, and acrylonitrile gave the corresponding complexes **2b**−**d** almost quantitatively and were isolated in 71, 80, and 42% yields, respectively. Complexes **2a**−**d** were fully characterized by elemental analyses and NMR spectroscopy.[8] Attempted catalytic hydrosilylation of nitriles in the presence of excess (*p*-Tol)$_2$SiH$_2$ using a catalytic amount of complex **1** (5 mol %) failed even at 80 °C.



1 R = *p*Tol

(1)

2a; R′ = Me, **2b**; R′ = ^{t}Bu,
2c; R′ = Ph, **2d**; R′ = CH=CH_2

The structure of **2c** was confirmed by an X-ray crystal diffraction study.[9] As shown in an ORTEP drawing of **2c** in Figure 1, a nitrile was found to be hydrosilylated in a cis addition manner but bound to the two Ru metals by a covalent bond between an Si atom and a Ru metal and by a coordination bond of the imine N atom to another Ru metal.[10,11] On the basis of the similarities of the NMR spectral features among complexes **2a**−**d**, **2a**,**b**,**d** should have structural characteristics similar to those of **2c**.

While nitriles are not good substrates for the transition-metal-catalyzed hydrosilylations, the reported hydrosilylations of nitriles usually give the doubly hydrosilylated products, disilazanes or their derivatives;[12] the

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[8] For spectral details, see the Supporting Information.

[9] For experimental details, see the Supporting Information.

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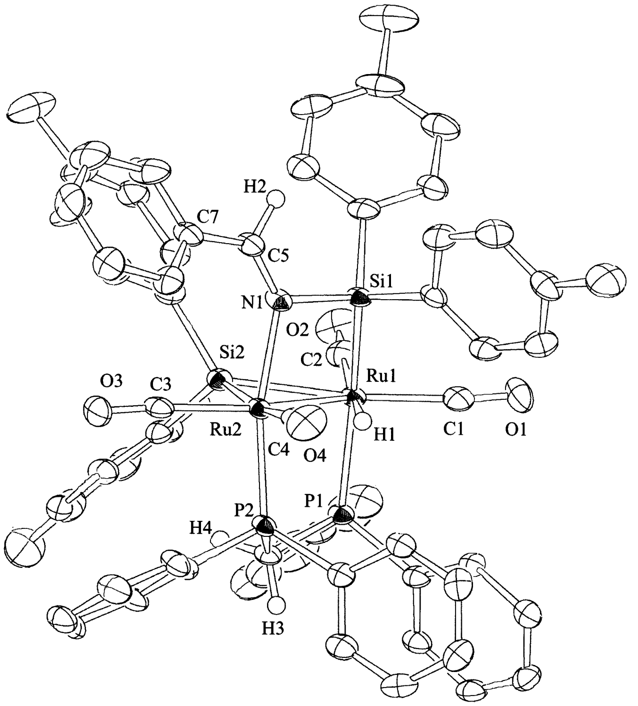
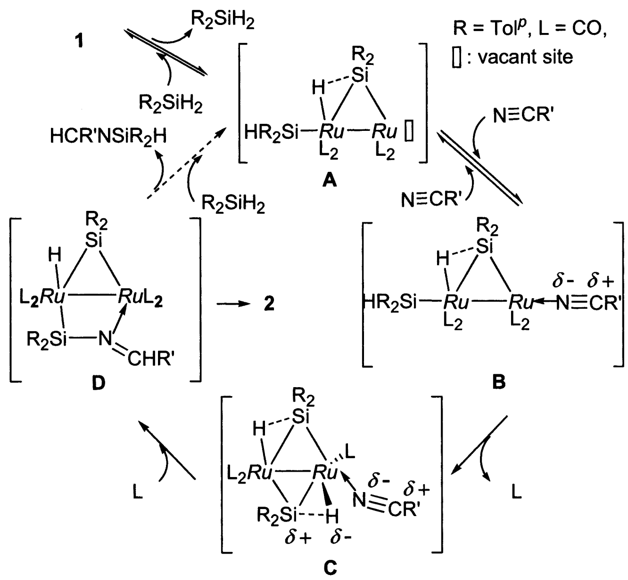


Figure 1. ORTEP drawing of $Ru_2(CO)_4(\mu\text{-dppm})(\mu\text{-SiTol}_2)(\mu\text{-PhCH=NSiTol}_2)$ (**2c**), showing 50% thermal ellipsoids. Hydrogen atoms, except for H1–H4, were omitted for clarity. Selected bond lengths (Å): Ru1–Ru2, 2.7913(5); Ru1–Si1, 2.177(1); Ru1–Si2, 2.610(1); Ru1–P1, 2.293(1); Ru2–Si2, 2.569(1); Ru2–N1, 2.153(4); Si1–N1, 1.761(4); N1–C5, 1.223(6). Selected bond angles (deg): Si1–Ru1–Ru2, 76.01(4); N1–Ru2–Ru1, 73.2(1); Ru1–Si1–N1, 98.4(1); Ru1–Si2–Ru2, 65.23(4).

corresponding iminosilanes have never been observed during the hydrosilylation, though they have been suggested as intermediates.[12a] The present results indicate that the hydrosilylation of acetonitriles using dinuclear complex **1** actually occurs but the strong binding of the μ-iminosilyl ligand to the Ru metals prevents the completion of the catalytic cycle.

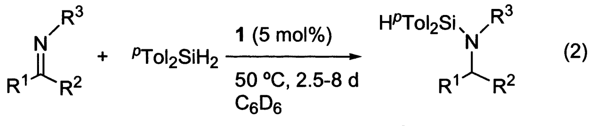
As shown in Scheme 1, a plausible reaction mechanism for the formation of **2a**–**d** during the reactions of eq 1 would involve the following key steps. (1) The reductive elimination of a dihydrosilane from **1** produces unsaturated complex **A**. (2) A nitrile coordinates to the vacant site in **A** to produce **B**. (3) The ligand L (CO) is released from **B** and an Si–H bond of a neighboring silyl group coordinates to the site to form intermediate **C** with an Si- - -H- - -Ru bond. (4) The activated Si–H bond

Scheme 1



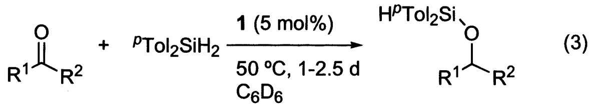
can react with the activated C≡N carbon in complex **C** to form complex **D** (a model for **2**); the formation of the cis-addition products **2a**–**d** is suggestive of the concerted feature of the addition of the Si–H bond to the C≡N bond at this step.

If the facile reductive elimination of a hydrosilane from complex **D** is achieved, the intermediate **A** is reproduced and the catalytic cycle in Scheme 1 is completed. Actually, various imines and ketones were found to be hydrosilylated with dihydrosilanes such as di-*p*-tolylsilane, diphenylsilane, and dihexylsilane in the presence of 5 mol % of **1** in C_6D_6 at 50 °C to afford the corresponding iminosilanes and alkoxysilanes in high yields (eqs 2 and 3; the yields were determined by ^1H NMR).[13] The hydrosilylation of imines and ketones did not proceed when a monohydrosilane was used instead of a dihydrosilane; the hydrosilylation of acetone with Et_3SiH in the presence of a catalytic amount of **1** did not occur even at 80 °C. The hydrosilylation is sensitive to the bulkiness of the substituent on the imine nitrogen



(2)

3a, $R^1 = R^2 = Ph$, $R^3 = H$, 74%
3b, $R^1 = {}^tBu$, $R^2 = Ph$, $R^3 = H$, 82%
3c, $R^1 = R^2 = Ph$, $R^3 = Me$, 82%



(3)

4a, $R^1 = R^2 = Me$, 96%
4b, $R^1 = Me$, $R^2 = CH{=}CMe_2$, 88%
4c, $R^1 = R^2 = (CH_2)_5$, 92%

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(10) Figure 1 shows the structure of one of two independent molecules in the unit cell for **2c**. The following are the structural characteristics of **2c**. (1) The Ru1–Si1 distance is one of the shortest distances (2.1766(12) Å) among those reported.[5b] Although the Ru1–Si1 distance in **2c** is even shorter than the Ru–Si distance in $[Cp^*(Me_3P)_2Ru{=}SiMe_2]^+$ (2.238(2) Å),[11] the ^{29}Si resonance of the iminosilyl silicon in **2c** was found at 28.6 ppm, which is reasonable for an iminosilyl silicon but further upfield than the reported resonances for the ^{29}Si nuclei in the reported silylene complexes. (2) The N1–Si1 bond distance (1.761(4) Å) and Ru2–N1 bond distance (2.153(4) Å) are normal for single bonds, respectively. (3) The hydride hydrogen (H1) bridges two Ru atoms unsymmetrically.

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(13) The reaction of **1** with 5 mol excess amounts of acetone afforded hydrosilylation product **4a** and a very unstable novel μ-silylene diruthenium complex, $Ru_2(CO)_4(\mu\text{-dppm})(\mu\text{-SiTol}^p{}_2)(\mu\text{-H})_2$, both in 80% yield. No hydrosilylated complex analogous to **2** was detected during the reaction by NMR. The μ-silylene diruthenium complex did not show catalytic activity in the hydrosilylation of ketones and imines.

atom;[14] no hydrosilylation occurred for an *N*-phenyl imine. The hydrosilylation of an α,*β*-unsaturated ketone occurred in a 1,2-addition mode. The hydrosilylation can be carried out similarly in THF and toluene and also without solvent. Although there have been many reports of transition-metal-catalyzed hydrosilylations of imines and ketones, the mechanisms have been hardly discussed.[14,15] The present catalytic hydrosilylation using a bimetallic complex is compatible with a novel catalytic cycle involving cooperative functions of the two Ru metals in complex **1**, analogous to the **A** → **B** → **C** → **D** → **A** cycle shown in Scheme 1, where R′CN should be substituted by $R'_2C{=}O$ or $R'_2C{=}NR''$. The unsuccessful hydrosilylation with a *mono*hydrosilane such as Et_3SiH is consistent with the proposed catalytic cycle, which requires the indispensable use of a *dihydro*silane.

Further studies on the electronic nature, reaction mechanisms, and synthetic applications of **1** are in progress.

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Supporting Information Available: Text giving experimental details for the isolation of **2a**−**c** and tables giving crystallographic data for **2c**. This material is available free of charge via the Internet at http://pubs.acs.org.

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