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Three- and Five-Membered W/C/N Metallacycles Formed by Incorporation of Acetonitrile Molecules into Silyltungsten Intermediates[†]

Eiji Suzuki,[‡] Takashi Komuro,[‡] Masaaki Okazaki,[§] and Hiromi Tobita*,[‡]

Department of Chemistry, Graduate School of Science, Tohoku University, Aoba-ku, Sendai 980-8578, Japan, and International Research Center for Elements Science, Institute for Chemical Research, Kyoto University, Uji, Kyoto 611-0011, Japan

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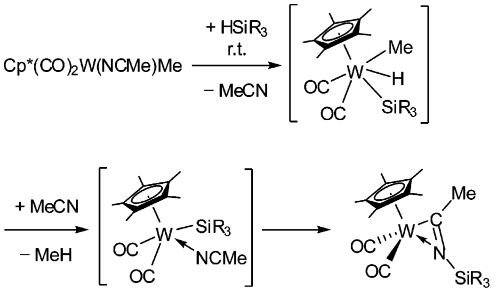
Summary: Treatment of $Cp^*(CO)_2W(NCMe)Me$ *(*$Cp^* = \eta^5\text{-}C_5Me_5$*) with* $HSiR_3$ *(R = Et, p-Tol) afforded N-silylated* η^2*-iminoacyl tungsten complexes* $Cp^*(CO)_2W\{\kappa^2(C,N)\text{-}C(Me){=}N(SiR_3)\}$ *(**1a**, R = Et; **1b**, R = p-Tol). Analogous reactions in the presence of excess acetonitrile for a prolonged reaction time led to the formation of five-membered metallacycles* $Cp^*(CO)_2W\{\kappa^2(C,N)\text{-}C(Me){=}N{-}C(Me){=}N(H)\}$ *(**2**) and* $Cp^*(CO)_2W\{\kappa^2(C,N)\text{-}C(CH_2SiR_3){=}N{-}C(Me){=}N(H)\}$ *(**3**, R = p-Tol) through a C−N coupling of nitrile molecules and migration of a silyl group.*

Transition-metal-mediated transformation of nitriles, e.g., insertion, coupling, C−N or C−C bond formation, and cycloaddition, is of considerable interest because of its potential application for the synthesis of nitrogen-containing organic compounds.[1] Recently, a new type of reaction between transition-metal silyl complexes and nitriles has been discovered, and its application to a catalytic reaction has been investigated.[2,3] In this reaction, importantly the C−C bond cleavage of nitriles resulted in the formation of silylisocyanide complexes having an alkyl or aryl ligand. A key intermediate of this reaction is a *N*-silylated η^2-iminoacyl complex derived from a silyl-nitrile complex through insertion of the nitrile into a metal−silicon bond. We recently reported the formation of a *N*-silylated η^2-iminoacyl complex by the reaction of a tungsten complex containing the hemilabile κ^3(*Si,Si,O*)-bis(silyl) ligand xantsil with *t*-BuCN.[4] As an extension of our study on nitrile activation chemistry mediated by metal silyl complexes, we focused on the tungsten methyl acetonitrile complex $Cp^*(CO)_2W(NCMe)Me$[5] as a useful precursor of tungsten silyl acetonitrile complexes, because the lability of the MeCN ligand facilitates oxidative addition of silanes.[6,7] In this communication, we describe the synthesis of *N*-silylated η^2-iminoacyl tungsten complexes, having a three-membered metallacycle structure, by treatment of $Cp^*(CO)_2W(NCMe)Me$ with tertiary silanes, and also their unexpected ring expansion to W−C−N−C−N five-membered metallacycles by treatment with an excess amount of acetonitrile.

Scheme 1



1a: R = Et
1b: R = *p*-Tol

Reaction of $Cp^*(CO)_2W(NCMe)Me$, prepared by irradiation of $Cp^*(CO)_3WMe$ in acetonitrile, with $HSiEt_3$ in acetonitrile or $HSi(p\text{-}Tol)_3$ in toluene at room temperature gave *N*-silylated η^2-iminoacyl complexes $Cp^*(CO)_2W\{\kappa^2(C,N)\text{-}C(Me){=}N(SiR_3)\}$ [**1a**, R = Et (74%); **1b**, R = *p*-Tol (59%)] (Scheme 1). The products were characterized by analytical and spectroscopic methods.[8,9] This transformation can be explained by the mech-

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[†] This paper is dedicated to the late Professor Yoshihiko Ito for his outstanding contribution to synthetic chemistry and organometallic chemistry.

* Author to whom correspondence should be addressed. Tel: +81-22-795-6539. Fax: +81-22-795-6543. E-mail: tobita@mail.tains.tohoku.ac.jp.

[‡] Tohoku University.

[§] Kyoto University.

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(8) Data for **1a**: ^{1}H NMR (300 MHz, C_6D_6, room temperature): δ 0.47−0.68 (m, 6 H, $SiCH_2CH_3$), 0.84 (t, J = 7.8 Hz, 9 H, $SiCH_2CH_3$), 1.83 (s, 15 H, Cp*), 2.42 (s, 3 H, N=C*Me*). $^{13}C\{^1H\}$ NMR (75.5 MHz, C_6D_6, room temperature): δ 4.8, 6.9 (SiEt), 11.3 (C_5Me_5), 22.4 (N=C*Me*), 104.1 (C_5Me_5), 228.7 (J_{W-C} = 53 Hz, N=*C*Me), 242.1, 246.0 (CO). $^{29}Si\{^1H\}$ NMR (59.6 MHz, C_6D_6, room temperature): δ 15.2. IR (C_6D_6): 1901 (s, ν_{CO}), 1801 (s, ν_{CO}), 1637 (w, ν_{CN}) cm^{-1}. EI-MS (70 eV): *m/z* 531 (M^+, 17), 503 (M^+ − CO, 15), 473 (100). Exact mass (EI) for $C_{20}H_{33}NO_2SiW$: calcd *m/z* 531.1784, found *m/z* 531.1779. Contamination with trace of impurities has prevented correct elemental analysis.

(9) Data for **1b**: ^{1}H NMR (300 MHz, C_6D_6, room temperature): δ 1.79 (s, 15 H, Cp*), 2.06 (s, 9 H, C_6H_4Me), 2.49 (s, 3 H, N=C*Me*), 7.04 (d, J = 7.7 Hz, 6 H, Ar−H), 7.63 (d, J = 7.7 Hz, 6 H, Ar−H). $^{13}C\{^1H\}$ NMR (75.5 MHz, C_6D_6, room temperature): δ 11.2 (C_5Me_5), 21.5 (C_6H_4Me), 23.9 (N=C*Me*), 104.3 (C_5Me_5), 129.3, 129.8, 136.3, 140.5 (aromatic carbons), 235.2 (J_{W-C} = 53 Hz, N=*C*Me), 242.4, 244.8 (br, CO). $^{29}Si\{^1H\}$ NMR (59.6 MHz, C_6D_6, room temperature): δ −17.9. IR (KBr-pellet): 1894 (s, ν_{CO}), 1792 (s, ν_{CO}), 1620 (m, ν_{CN}) cm^{-1}. EI-MS (70 eV): *m/z* 717 (M^+, 15), 659 (13), 645 (M^+ − 2 CO − MeH, 19), 620 (M^+ − 2 CO − MeCN, 100). Anal. Calcd for $C_{35}H_{39}NO_2SiW$: C, 58.58; H, 5.48; N, 1.95. Found: C, 59.16; H, 5.74; N, 1.77.

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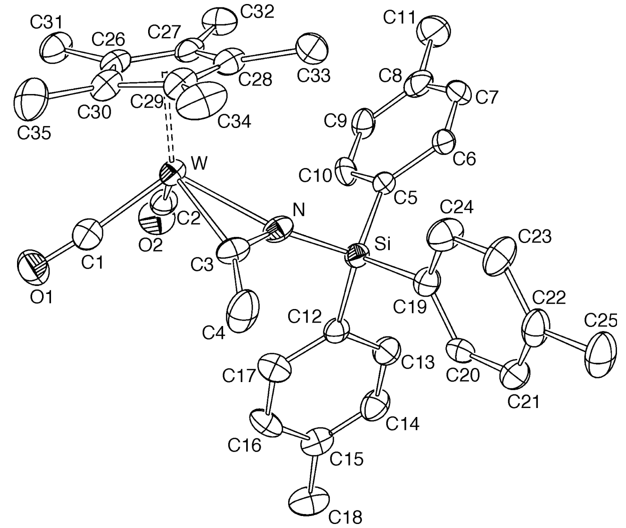
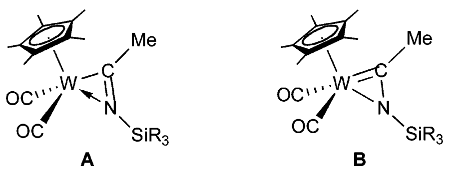


Figure 1. Molecular structure of **1b** (50% probability ellipsoids). Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): W−N = 2.215(7), W−C3 = 2.086(9), Si−N = 1.750(8), N−C3 = 1.266(12); W−N−Si = 149.4(4), W−N−C3 = 67.4(5), N−W−C3 = 34.1(3), Si−N−C3 = 140.4(7), W−C3−N = 78.5(6), W−C3−C4 = 152.6(7), N−C3−C4 = 128.8(9).

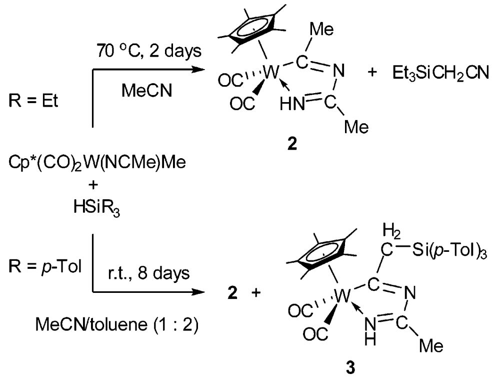
anism involving oxidative addition of $HSiR_3$, reductive elimination of MeH, coordination of acetonitrile, and final silyl migration to nitrogen (Scheme 1). Since the reaction of Cp*$(CO)_2$W(NCMe)Me with HSi(*p*-Tol)$_3$ in acetonitrile at room temperature afforded not only **1b** but also the five-membered-ring complex **2** that was derived by the reaction of **1b** with acetonitrile (*vide infra*), toluene was used as a solvent for the synthesis of **1b**. This higher reactivity of **1b** compared to that of **1a** toward acetonitrile can be rationalized by the decrease in the electron-releasing character of the group (*p*-Tol)$_3$Si compared to Et_3Si that facilitates the substitution of the coordinated iminoacyl nitrogen with an acetonitrile molecule. In contrast to *N*-silylated η^2-iminoacyl complexes of groups 8 and 9 metals, where C−C bond scission occurs rapidly at room temperature,[2] complexes **1** did not show any sign of decomposition in C_6D_6 at room temperature over 2 days, according to their ^1H NMR spectra.

The structure of η^2-iminoacyl complex **1b** was confirmed by X-ray crystal structure analysis (Figure 1), where **1b** adopts a four-legged piano-stool geometry: the tungsten center possesses one Cp*, two carbonyls, and one η^2-iminoacyl ligand having a silyl group on the nitrogen atom. The bond distances and angles in the W−C−N three-membered ring are comparable with those in the previously reported tungsten *N*-silylated η^2-iminoacyl complex Cp*(CO)(H)W{κ^3(*C,N,Si*)-C(*t*-Bu)=N(xantsil)}.[4] It is noteworthy that the crystal structure analysis of *N*-silylated η^2-iminoacyl complexes has been limited to only two examples: tungsten[4] and cationic rhodium[2b] complexes. The short W−C(iminoacyl) bond distance [2.086(9) Å] is similar to that of the carbene complex Cp*$(CO)_2$(Cl)W{=C(H)NEt_2} [2.141(3) Å].[10] Moreover, the $^{13}C\{^1H\}$ NMR spectra of **1a** and **1b** show the resonances of the iminoacyl carbons at 228.7 ppm for **1a** and 235.2 ppm for **1b** with ^{183}W satellites [$J_{W-C} = 53$ (**1a**), 53 (**1b**) Hz]. These resonances are even more downfield-shifted than those of *N*-alkylated η^2-iminoacyl tungsten complexes Cp*$(CO)_2$W{κ^2(*C,N*)-C(Me)=N(R)} [195.5 (R = *t*-Bu), 195.9 (R = *i*-Pr) ppm].[11] These observations imply that the contribution of the amido-carbene canonical structure **B** in the resonance hybrid of **1** (Chart 1) is fairly high. The W−N bond of **1b** [2.215(7) Å] is slightly longer than that of the *N*-alkylated η^2-iminoacyl complex (η^5-C_9H_7)$(CO)_2$W{κ^2(*C,N*)-C(Me)=N(*t*-Bu)} [2.144(5) Å].[12] This elongation of the W−N bond is probably due to the larger steric repulsion between the bulky silyl group on the N atom and the Cp*$(CO)_2$W{C(Me)=N} moiety in **1b**: the distances between the aryl carbon C5 on a *p*-Tol group and the methyl carbon C33 on Cp* [3.877(14) Å] and between the methyl carbon C4 bonded to the iminoacyl carbon and the aryl carbon C19 on a *p*-Tol group [3.632(14) Å] are comparable to the sum (3.7 Å) of the van der Waals radii of the methyl group (2.0 Å) and the half-thickness of the plane of the aromatic rings (1.7 Å).[13]

Chart 1



Scheme 2



The lability of η^2-iminoacyl complex **1b** in acetonitrile prompted us to investigate the thermal reactions of both **1a** and **1b** with excess acetonitrile. Heating of a mixture of isolated η^2-iminoacyl complex **1a** and a large excess of acetonitrile in C_6D_6 at 40−70 °C afforded five-membered-ring complex Cp*$(CO)_2$W{κ^2(*C,N*)-*C*(Me)=N−C(Me)=*N*(H)} (**2**) as a major product. A preparative-scale one-pot synthesis of **2** in 69% isolated yield was achieved by the thermal reaction of a mixture of Cp*$(CO)_2$W(NCMe)Me and $HSiEt_3$ in acetonitrile (ca. 300 equiv) at 70 °C for 2 days, where the η^2-iminoacyl complex **1a** should be generated transiently (Scheme 2). This reaction involves incorporation and coupling of two acetonitrile molecules. We observed silyl nitrile Et_3SiCH_2CN as a silicon-containing byproduct in the NMR and IR spectra of the reaction mixture.[14]

On the other hand, the thermal reaction of isolated η^2-iminoacyl complex **1b** with a large excess of acetonitrile in C_6D_6 at 40 °C for 3 days, which was monitored by ^1H NMR spectroscopy, mainly afforded a 1:1 mixture of complex **2** and

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(14) Et_3SiCH_2CN was identified on the basis of comparisons of its ^1H, $^{13}C\{^1H\}$, and $^{29}Si\{^1H\}$ NMR and IR spectra with those of the authentic sample that was prepared by a method analogous to that for the preparation of (*t*-Bu)Me_2SiCH_2CN: Furuta, K.; Ishiguro, M.; Haruta, R.; Ikeda, N.; Yamamoto, H. *Bull. Chem. Soc. Jpn.* **1984**, *57*, 2768.

silyl-containing five-membered-ring complex $Cp^*(CO)_2W[\kappa^2\text{-}(C,N)\text{-}C\{CH_2Si(p\text{-}Tol)_3\}{=}N{-}C(Me){=}N(H)]$ (**3**). The preparative-scale reaction of $Cp^*(CO)_2W(NCMe)Me$ with $HSi(p\text{-}Tol)_3$ in acetonitrile (ca. 300 equiv) at 60 °C for 20 h gave **2** as a major product, but the formation of **3** was considerably inhibited (**2**:**3** = 16:1). Isolation of **2** from the reaction mixture was unsuccessful owing to the difficulty of the separation from minor products, namely, complex **3** and unidentified byproducts. Taking into account the NMR-scale reaction in C_6D_6 that gave the 1:1 mixture of **2** and **3**, we also investigated the preparative-scale reaction under similar conditions in which acetonitrile was diluted in toluene, to improve the formation of complex **3**. Thus, the reaction of $Cp^*(CO)_2W(NCMe)Me$, $HSi(p\text{-}Tol)_3$, and a large excess (ca. 40 equiv) of acetonitrile in toluene (1:2 volume ratio of acetonitrile to toluene) at room temperature for 8 days gave a 1:1.3 ratio of **2** and **3** (Scheme 2). Only complex **3** was isolated in pure form in 34% yield by recrystallization from the mixture. The reason for the formation of the **3**-type complex only in the case of $(p\text{-}Tol)_3Si$ derivative **1b** and also the reason for the alteration in the ratio of products **2** and **3** depending on the concentrations of acetonitrile in solution are closely related to the reaction mechanism (*vide infra*), but are not clear so far.

The characterization of five-membered-ring complexes **2** and **3** was performed by analytical, spectroscopic, and crystallographic methods.[15−17] The X-ray crystal structure analysis established the molecular structure of **3** shown in Figure 2. Complex **3** adopts a four-legged piano-stool geometry: the tungsten center possesses one Cp*, two carbonyls, and a $\kappa^2(C,N)$-bidentate ligand. The sum of the interior angles of the chelate ring is 540(2)°, as expected for a planar five-membered metallacycle. A similar five-membered ring was structurally characterized for the iron complex $(\eta^5\text{-}C_5H_5)(CO)Fe\{\kappa^2(C,N)\text{-}C(CF_3){=}N{-}C(CF_3){=}N(H)\}$.[18] On the other hand, the bond lengths of W−C3 [2.164(6) Å] and W−N2 [2.112(5) Å] are comparable to those of the five-membered-ring carbene complex of tungsten $Cp^*(CO)_2W\{\kappa^2(C,N)\text{-}C(NHEt){-}C(H){=}C(H){-}N(Et)\}$ [W−C(ring) 2.179(6) Å; W−N 2.160(5) Å].[19] The downfield-shifted $^{13}C\{^1H\}$ NMR signals of W−C(ring) [273.6 (**2**), 276.1 (**3**) ppm] also indicate their strong carbene-ligand character. The C−N bond distances in the five-membered chelate ring of **3** are comparable with those in common π-conjugated heterocycles (1.35 Å),[20] and the difference among them is relatively small, implying the π-electron delocalization within the ring. Thus, we propose considerable contribution of the amido-carbene canonical structure **D** as well as the alkylimino canonical structure **C** (Chart 2).

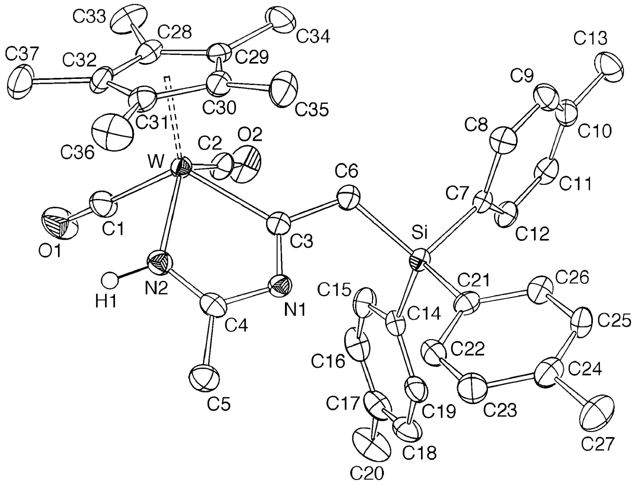
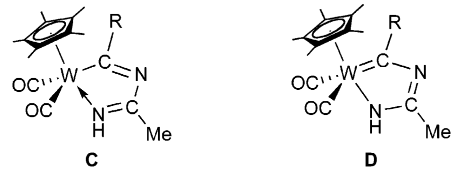


Figure 2. Molecular structure of **3** (50% probability ellipsoids). Hydrogen atoms bound to carbon atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): W−N2 = 2.112(5), W−C3 = 2.164(6), N1−C3 = 1.335(8), N1−C4 = 1.364(7), N2−C4 = 1.303(8); W−N2−C4 = 119.3(4), W−C3−N1 = 119.5(4), N2−W−C3 = 70.9(2), C3−N1−C4 = 112.0(5), N1−C4−N2 = 118.2(5).

Chart 2



In the ^1H NMR spectrum of **3** in toluene-d_8, one broad signal (4.06 ppm) assignable to the CH_2 moiety was observed at room temperature, while this signal changed to two inequivalent doublets (3.85, 4.32 ppm; J = 14.8 Hz) at 253 K. Furthermore, the CO signals of **3** in $^{13}C\{^1H\}$ NMR, which did not appear at room temperature, were observed as two signals (239.2, 244.3 ppm) at 253 K. These observations suggest the existence of a dynamic process involving the inversion of the chiral tungsten center on the NMR time scale. The $^{13}C\{^1H\}$ NMR spectrum of **2** at room temperature exhibits one broad signal assignable to CO, which suggests the existence of a dynamic behavior analogous to that of **3**.

A possible mechanism for the formation of **2** from **1** is illustrated in Scheme 3. The coordinated N atom of the η^2-iminoacyl ligand of **1** is substituted by MeCN to give an (η^1-iminoacyl)-nitrile complex **4**. The lability of the iminoacyl nitrogen atom of **1** is attributable to the ring strain. Nucleophilic attack of the iminoacyl nitrogen on the electrophilic CN carbon of the acetonitrile ligand results in the C−N bond formation to

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(15) Data for **2**: ^1H NMR (300 MHz, C_6D_6, room temperature): δ 1.62 (s, 15 H, Cp*), 2.29 (s, 3 H, N=CMe), 3.18 (s, 3 H, W−CMe), 7.98 (br, 1 H, NH). $^{13}C\{^1H\}$ NMR (75.5 MHz, C_6D_6, room temperature): δ 10.4 ($C_5\mathit{Me}_5$), 21.4 (N=C*Me*), 40.9 (W−C*Me*), 102.6 (C_5Me_5), 177.4 (N=C−N), 240.9 (br, CO), 273.6 (J_{W-C} = 75 Hz, W−*C*Me). IR (C_6D_6): 1940 (s, ν_{CO}), 1861 (s, ν_{CO}) cm^{-1}. ESI-MS: *m*/*z* 459 (M^+ + H). Anal. Calcd for $C_{16}H_{22}N_2O_2W$: C, 41.94; H, 4.84; N, 6.11. Found: C, 41.45; H, 4.97; N, 5.90.

(16) We could not get crystals of **2** suitable for a full X-ray analysis, but a tentative analysis using a poor-quality crystal of **2** revealed a piano-stool structure containing a five-membered metallacycle. Crystal data for **2**: formula $C_{16}H_{22}N_2O_2W$, $M = 458.21$, monoclinic, space group $P2_1/c$ (No. 14), $a = 19.3351(14)$ Å, $b = 10.2804(4)$ Å, $c = 18.4975(13)$ Å, $\beta = 110.6676(17)°$, $V = 3440.2(4)$ Å^3, $Z = 8$, R_1 (all data) = 0.158, wR_2 (all data) = 0.218.

(17) Data for **3**: ^1H NMR (300 MHz, C_6D_6, room temperature): δ 1.55 (s, 15 H, Cp*), 2.10 (s, 12 H, $C_6H_4\mathit{Me}$ + N=CMe), 4.12 (br, 2 H, CH_2Si), 7.10 (d, J = 8.1 Hz, 6 H, Ar−H), 7.42 (br, 1 H, NH), 7.92 (d, J = 8.1 Hz, 6 H, Ar−H). ^1H NMR (300 MHz, toluene-d_8, 253 K): δ 1.54 (s, 15 H, Cp*), 2.12 (s, 12 H, $C_6H_4\mathit{Me}$ + N=C*Me*), 3.85 (d, J = 14.8 Hz, 1 H, CH_2Si), 4.32 (d, J = 14.8 Hz, 1 H, CH_2Si), 7.10 (d, J = 7.8 Hz, 6 H, Ar−H), 7.39 (br, 1 H, NH), 7.93 (d, J = 7.8 Hz, 6 H, Ar−H). $^{13}C\{^1H\}$ NMR (75.5 MHz, C_6D_6, room temperature): δ 10.3 ($C_5\mathit{Me}_5$), 21.1 (N=C*Me*), 21.4 ($C_6H_4\mathit{Me}$), 45.1 (CH_2Si), 102.3 (C_5Me_5), 128.5, 134.7, 137.1, 138.4 (aromatic carbons), 176.9 (N=*C*Me), 276.1 (W−C=N), no signal assignable to CO was observed because of dynamic behavior. $^{13}C\{^1H\}$ NMR (75.5 MHz, toluene-d_8, 253 K): δ 10.3 ($C_5\mathit{Me}_5$), 21.3 (N=C*Me*), 21.6 ($C_6H_4\mathit{Me}$), 44.8 (CH_2Si), 102.2 (C_5Me_5), 134.5, 137.1, 138.4 (aromatic carbons, one of the signals is overlapped with those of toluene-d_8), 176.8 (N=*C*Me), 239.2, 244.3 (CO), 275.7 (W−C=N). $^{29}Si\{^1H\}$ NMR (59.6 MHz, C_6D_6, room temperature): δ −12.3. IR (C_6D_6): 1940 (s, ν_{CO}), 1861 (s, ν_{CO}) cm^{-1}. ESI-MS: *m*/*z* 759 (M^+ + H). Anal. Calcd for $C_{37}H_{42}N_2O_2SiW$: C, 58.58; H, 5.58; N, 3.69. Found: C, 58.87; H, 5.57; N, 3.62.

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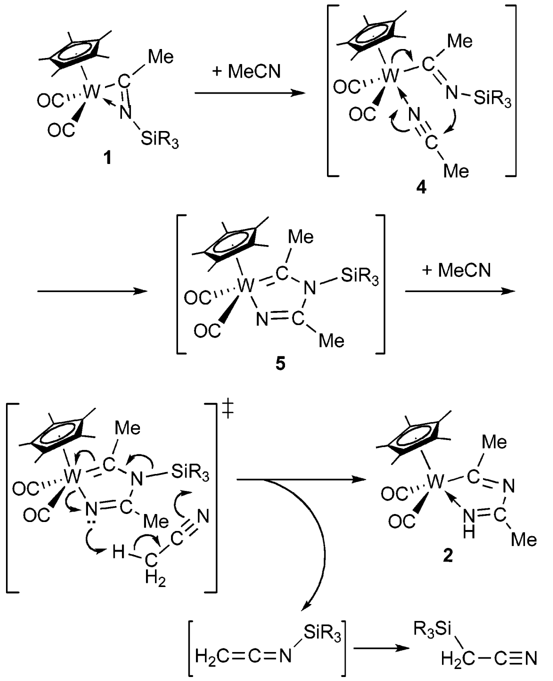
Scheme 3. Plausible Mechanism for the Formation of 2



give the five-membered-ring complex **5**. As an example of a similar reaction, Werner et al. have reported the [3+2]-cycloaddition of the cationic isocyanide-methyl cobalt complex [(η^5-C_5H_5)(PMe_3)Co(CNMe)Me]I with acetonitrile mediated by an (η^1-iminoacyl)-nitrile complex.[21] For the next step, we propose a concerted reaction between intermediate **5** and an external acetonitrile molecule via a cyclic transition state that leads to the formation of complex **2** and a *N*-silylated ketene imine molecule. This reaction involves deprotonation of the acetonitrile molecule by the basic imino nitrogen of the five-membered ring in **5** and nucleophilic attack of the nitrile nitrogen on the silicon atom of **5**. Legzdins et al. have proposed that the basic imino nitrogen in the intermediary generated W−C−C−C−N five-membered-ring complex can deprotonate cyclopentadiene.[22] However, an alternative pathway from **5** to **2** by a stepwise reaction, namely, desilylation followed by deprotonation or *vice versa*, cannot be ruled out. The resulting ketene imine can be rearranged to the silyl nitrile R_3SiCH_2CN, because the thermal 1,3-rearrangement of ketene imines to nitriles is known for *N*-(arylmethyl)diphenylketene imines.[23] The formation mechanism for **3** is not clear, but the first stage (formation of a five-membered-ring complex **5**) would be the same as that for **2**. In both cases, a possible driving force of the transformation is the formation of a resonance-stabilized, π-conjugated ring system.

In conclusion, we demonstrated a novel reaction sequence of the insertion and C−N coupling of acetonitrile molecules via tungsten silyl complexes. The reaction of Cp*$(CO)_2$W-(NCMe)Me with $HSiR_3$ (R = Et, *p*-Tol) gave η^2-iminoacyl complexes **1**, which are thermally stable in C_6D_6 at room temperature. A further reaction of **1** with acetonitrile afforded complexes **2** and **3**, both of them having a five-membered C,N-chelate ring. The formation of the five-membered metallacycles through incorporation of acetonitrile into the η^2-iminoacyl complexes is unprecedented. In contrast, the formation of similar M−C−N−C−N five-membered metallacycles via the reaction of low-valent iron and iridium complexes with electrophilic trifluoroacetonitrile has been explained by the completely different mechanism involving consecutive electrophilic attacks of two trifluoroacetonitrile molecules.[18] Further studies on formation mechanisms of the five-membered-ring complexes and reactivity of the isolated iminoacyl complexes **1** are in progress.

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Supporting Information Available: Text giving synthetic procedures and characterization data as a PDF file; X-ray crystallographic data as a CIF file. These materials are available free of charge via the Internet at http://pubs.acs.org.

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