

Synthesis and Characterization of $\kappa^2 C$, N-N-Silyliminoacyl Tungsten Complexes $Cp^*(CO)_2W{\kappa^2C, N-C(R)=NSiR'_3}$ [R = Me, Et, *i*-Pr, *t*-Bu; $R'_3 = (p-Tol)_2Me, (\tilde{p}-Tol)_3, Et_3; Cp^* = \eta^5 - C_5Me_5]$: Thermally Induced Carbon-Carbon Bond Cleavage of Their Iminoacyl Ligands

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DMAP-stabilized (p-tolyl)(silvlene) complexes $Cp^*(CO)_2W(p-Tol) = Si(p-Tol)R' \cdot DMAP$ [1a, R' = Me; 1b, R' = p-Tol; DMAP = 4-(dimethylamino)pyridine] reacted with excess nitrile RCN (R = Me, Et, *i*-Pr, *t*-Bu) in toluene to give $\kappa^2 C$, *N*-*N*-silyliminoacyl tungsten complexes Cp*(CO)₂W{ $\kappa^2 C$, *N*-C(R)=NSi- $(p-\text{Tol})_2 R'$ (2a, R = Me, R' = Me; 2b, R = Et, R' = Me; 2c, R = *i*-Pr, R' = Me; 2d, R = *t*-Bu, R' = Me; **3a**, R = Me, R' = p-Tol; **3b**, R = Et, R' = p-Tol; **3c**, R = i-Pr, R' = p-Tol; **3d**, R = t-Bu, R' = p-Tol). This reaction proceeds through 1,2-migration of a *p*-tolyl group from a tungsten center to a silylene ligand. Complexes **3a** and **3b** and similar complexes $Cp^*(CO)_2W\{\kappa^2C, N-C(R)=NSiEt_3\}$ (**4a**, R = Me; **4b**, R = Et) were also synthesized by reactions of methyl(nitrile) complexes $Cp^*(CO)_2W(NCR)Me(A, R = Me;$ **B**, $\mathbf{R} = \mathbf{E}t$) with hydrosilanes HSiR'₃ ($\mathbf{R}' = p$ -Tol, Et). A kinetic study on the dynamic process of 2c involving inversion of the chiral tungsten center reveals that the inversion can occur via dissociation of the iminoacyl nitrogen atom coordinating to the tungsten center. Thermal reaction of a toluene solution of *N*-silyliminoacyl complexes **3a** and **3b** at 120 °C in a sealed tube gave a cis/trans mixture of alkyl-(silvlisocyanide) complexes cis/trans-Cp*(CO)₂W(R){CNSi(p-Tol)₃} (5a, R = Me; 5b, R = Et) through cleavage of the C-C bond between the iminoacyl carbon and the alkyl substituent R in 3a or 3b. The molecular structures of **3b** and *cis*-**5b** were determined by X-ray crystallography.

Introduction

 $\kappa^2 C$, N-N-Silyliminoacyl complexes are attracting considerable attention recently as crucial intermediates in the C-C bond cleavage of nitriles by transition-metal silyl complexes.¹ This type of cleavage reaction can be applied to organic synthesis, where nitrile is used as a starting material. The C-C bond cleavage of an iminoacyl ligand in N-silyliminoacyl complexes easily occurs to give silvlisocyanide complexes having an alkyl or an aryl ligand. A pioneering study on the C-C bond cleavage of nitriles mediated by N-silvliminoacyl complexes was reported by Bergman, Brookhart, and co-workers: the reaction of a cationic silyl rhodium complex [Cp*(PMe₃)Rh(SiPh₃)(CH₂Cl₂)]BAr'₄ $[Ar' = 3,5-(CF_3)_2C_6H_3]$ with nitriles RCN $[R = Ph, 4-(CF_3)-$ C₆H₄, 4-(MeO)C₆H₄, Me, *i*-Pr, *t*-Bu] produced silylisocyanide complexes [Cp*(PMe₃)Rh(CNSiPh₃)(R)]BAr'₄ through $\kappa^2 C_{,N}$ -*N*-silyliminoacyl complexes [Cp*(PMe₃)Rh{ κ^2 C,N-C(R)=NSi-Ph₃]BAr'₄, which have only been observed and isolated at low temperature.² Nakazawa and co-workers independently proposed that an N-silvliminoacyl iron complex Cp(CO)Fe{ $\kappa^2 C$, $N-C(Me) = NSiMe_3$ works as an intermediate in the C-C bond

activation of acetonitrile by a silyl iron complex Cp(CO)₂FeSi-Me₃ under photoirradiation.³ Our group investigated related C-C bond cleavage reactions of nitriles induced by silvlene complexes, i.e., the reaction of a silvl(silvlene)iron complex Cp*(CO)- $Fe(=SiMes_2)SiMe_3$ with RCN (R = Me, Ph)^{4a} and the reaction of a hydrido(hydrosilylene)ruthenium complex Cp*(CO)(H)-Ru=Si(H){ $C(SiMe_3)_3$ } with RCN (R=Me, Ph).^{4b} In the former reaction, a possible mechanism involves the reaction sequence as follows: 1,2-migration of a silyl ligand from a metal center to a silylene silicon atom to generate 16-electron silyl complexes, coordination of nitrile, and insertion of the nitrile ligand into a M-Si bond to form N-silyliminoacyl complexes.^{4a} A few catalytic reactions involving C-C bond cleavage of nitriles via N-silyliminoacyl intermediates were also developed recently. Nakazawa and co-workers discovered the C-C bond cleavage reactions of nitriles RCN with Et₃SiH catalyzed by iron complexes to afford RH and Et₃SiCN.⁵ Chatani and co-workers reported rhodium-catalyzed silvlation of nitriles using disilanes via

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C-CN bond cleavage to form a C-Si bond.⁶ However, there are limited examples of the isolation and full-characterization of *N*-silyliminoacyl complexes because they are usually thermally unstable.

Known $\kappa^2 C_{,N}$ -N-silyliminoacyl complexes are mostly derived from a nitrile(silyl) complex through insertion of nitrile into a metal-silicon bond. For example, Bergman, Brookhart, and co-workers succeeded in the synthesis and the characterization of a $\kappa^2 C_{,N}$ -N-silyliminoacyl complex [Cp*(PMe₃)- $Rh{\kappa^2 C, N-C(4-(OMe)C_6H_4)=NSiPh_3}]BAr'_4$ by the thermal rearrangement of a nitrile(silyl) complex [Cp*(PMe₃)Rh(Si-Ph₃){NC(4-(OMe)C₆H₄)}]BAr'₄ below room temperature.^{2b} We also recently reported the synthesis of an *N*-silyliminoacyl complex Cp*(CO)(H)W{ $\kappa^{3}C,N,Si$ -C(t-Bu)=N(xantsil)} by the reaction of a tungsten complex containing a hemilabile $\kappa^3 Si, Si, O$ -bis(silyl) ligand (xantsil), namely, Cp*(CO)(H)W-($\kappa^3 Si, Si, O$ -xantsil), with *t*-BuCN.⁷ This reaction is presumed to proceed through formation of a nitrile(silyl) complex by dissociation of the labile oxygen in the $\kappa^3 Si_i Si_i O$ -xantsil ligand and coordination of nitrile. In this work, we applied the insertion reaction in nitrile(silyl) complexes to the synthesis of a new series of N-silyliminoacyl complexes.

We report here the synthesis of tungsten complexes composed of a Cp*(CO)₂W moiety and a $\kappa^2 C$,N-N-silyliminoacyl ligand by the reaction involving insertion of nitrile into a W-Si bond in a nitrile(silyl) complex. The N-silyliminoacyl complexes have sufficient stability to be isolated and characterized. To synthesize the N-silyliminoacyl complexes via a nitrile(silyl) complex, we employed two methods: (1) the reaction of base-stabilized aryl(silylene) complexes Cp*(CO)₂W-(p-Tol){=Si(p-Tol)R'·DMAP}[1a, R' = Me; 1b, R' = p-Tol; DMAP = 4-(dimethylamino)pyridine]⁸ with nitriles RCN (R = Me, Et, i-Pr, t-Bu) and (2) the reaction of methyl(nitrile) complexes $Cp^*(CO)_2W(NCR)Me(A, R = Me; {}^9B, R = Et)$ with tertiary silanes HSiEt₃ and HSi(p-Tol)₃. In method 1, we employed 1,2-migration of an aryl group from tungsten to silicon in complexes 1a and 1b to generate 16-electron silyl complexes $Cp^{*}(CO)_{2}W{Si(p-Tol)_{2}R'}(C)$,^{8,10} which can react with nitrile to form nitrile(silyl) complexes. In method 2, we used complex A or B as a precursor of nitrile(silyl) complexes, because the RCN ligand is known to be labile, which facilitates the Si-H oxidative addition of hydrosilanes.⁹ After this oxidative addition, reductive elimination of methane and coordination of nitrile are supposed to occur to generate nitrile(silyl) complexes. We also report here a thermal C-C bond cleavage reaction of some of the N-silyliminoacyl complexes to give the corresponding silylisocyanide complexes at

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Results and Discussion

Synthesis of $\kappa^2 C$, N-N-Silyliminoacyl Complexes. Method 1: Reactions of Silylene Complexes Cp*(CO)₂W(p-Tol)- $\{=$ Si(*p*-Tol)R' · DMAP $\}$ (1a, R' = Me; 1b, R' = *p*-Tol) with Nitriles. DMAP-stabilized (p-tolyl)(silylene)tungsten complexes $Cp^{*}(CO)_{2}W(p-Tol) = Si(p-Tol)R' \cdot DMAP$ (1a, R' = Me; **1b**, R' = p-Tol)⁸ reacted with excess nitrile RCN (R = Me, Et, *i*-Pr, *t*-Bu) in toluene to give $\kappa^2 C_i N$ -N-silyliminoacyl complexes $Cp^*(CO)_2W\{\kappa^2C, N-C(R)=NSi(p-Tol)_2R'\}$ (2a, R = Me, R' = Me; **2b**, R = Et, R' = Me; **2c**, R = i-Pr, R' = Me; **2d**, R = t-Bu, R' = Me; 3a, R = Me, R' = p-Tol; 3b, R = Et, R' = p-Tol; 3b, R = Et, R' = R' = R'*p*-Tol; **3c**, $\mathbf{R} = i$ -Pr, $\mathbf{R}' = p$ -Tol; **3d**, $\mathbf{R} = t$ -Bu, $\mathbf{R}' = p$ -Tol) (eq 1). To isolate complexes 2a-d and 3a-d from the reaction mixture, the Lewis acid BPh₃ was added to the mixture to form the adduct DMAP · BPh₃ with the byproduct DMAP. After filtration of DMAP·BPh3, which was sparingly soluble in hexane, 2a-d and 3a-d were isolated from the filtrate in 58–91% yields. A possible formation mechanism of 2a-d and 3a-d is depicted in Scheme 1. The mechanism involves (i) 1,2migration of a p-tolyl group in 1a and 1b from a tungsten center to a silvlene silicon atom to generate a 16-electron silvl complex $Cp^{*}(CO)_{2}W{Si(p-Tol)_{2}R'}(C)$,^{8,10} (ii) coordination of nitrile to tungsten in complex C to form a nitrile(silyl) complex D, and (iii) insertion of nitrile into a W-Si bond in complex D (Scheme 1).



Method 2: Reactions of Cp*(CO)₂W(NCR)Me (A, R = Me; B, R = Et) with HSiR'₃ (R' = *p*-Tol, Et). A methyl-(propiononitrile)tungsten complex Cp*(CO)₂W(NCEt)Me (B), a precursor of *N*-silyliminoacyl complexes in this research, was synthesized according to the method analogous to that for the synthesis of the acetonitrile(methyl) complex Cp*(CO)₂W(NCMe)Me (A).⁹ Thus, irradiation of Cp*-(CO)₃WMe in propiononitrile with a 450 W medium-pressure Hg lamp ($\lambda > 300$ nm) led to the dissociation of a CO ligand followed by coordination of EtCN to give complex B (eq 2). Complex B is thermally unstable in C₆D₆ at room temperature but has enough stability to be characterized by NMR and IR spectroscopy. The ¹³C{¹H} NMR spectrum of B shows a signal assignable to the methyl ligand at -11.7 ppm with ¹⁸³W satellites [$J_{WC} = 45$ Hz]. In the IR spectrum of B, a



Scheme 1. Possible Formation Mechanism of N-Silyliminoacyl Complexes 2a-d and 3a-d

band for the CN stretching is observed at 2262 cm⁻¹. Two CO ligands in **B** were located at mutually *cis* positions on the tungsten center on the basis of the observation of two inequivalent signals (244.1 and 257.3 ppm) assignable to the CO ligands in the ¹³C{¹H} NMR spectrum. This mutually *cis* arrangement is also supported by the observation in the IR spectrum that shows two bands for a symmetric (1911 cm⁻¹) and an asymmetric (1820 cm⁻¹) CO vibration, where the intensity of the former band is stronger than that of the latter one.



The methyl(nitrile) complexes Cp*(CO)₂W(NCR)Me (**A**, **R** = Me; **B**, **R** = Et) reacted with HSiR'₃ (**R**' = *p*-Tol, Et) at room temperature to give the corresponding $\kappa^2 C.N$ -N-silyliminoacyl complexes **3a**, **3b**, and Cp*(CO)₂W{ $\kappa^2 C.N$ -C-(**R**)=NSiEt₃} (**4a**, **R** = Me; **4b**, **R** = Et) (eq 3). In contrast to method 1 (eq 1), this method (method 2) for synthesizing $\kappa^2 C.N$ -N-silyliminoacyl complexes is applicable to a wider variety of hydrosilanes such as trialkylsilanes, which usually do not lead to stable silylene complexes.



Characterization of $\kappa^2 C$,*N*-*N*-Silyliminoacyl Complexes 2–4. *N*-Silyliminoacyl complexes 2a–d, 3a–d, and 4a,b were characterized on the basis of spectroscopy and elemental analysis. Their ¹H, ¹³C, and ²⁹Si NMR and IR spectra are summarized in Table 1. The ¹³C{¹H} NMR spectra of complexes 2–4 show a signal assignable to the iminoacyl carbon with ¹⁸³W satellites [J_{WC} =53–56 Hz] in the range 228.7–249.6 ppm. The chemical shifts of these resonances are comparable with those of carbone complexes Cp*(CO)₂W{=C(H)NEt₂}(X) [243.8 ppm]

 $(J_{WC} = 104 \text{ Hz})$ for X = Cl, 237.7 ppm $(J_{WC} = 92 \text{ Hz})$ for X = GeCl₃].¹² Moreover, these resonances are even more downfieldshifted than those of $\kappa^2 C_{,N-N-}$ alkyliminoacyl tungsten complexes Cp*(CO)₂W{ κ^2 C,N-C(Me)=N(R)} [195.5 (R = t-Bu), 195.9 (R = *i*-Pr) ppm].¹³ These comparisons imply that the $\kappa^2 C$, *N*-iminoacyl carbons of 2-4 have a strong carbone character due to the contribution of the amido(carbene) canonical structure F, as illustrated in Scheme 2, which is also supported by the crystal structure analysis of complexes 3a and 3b (vide infra). The ²⁹Si 1 H NMR spectra of **2**–**4** exhibit one resonance of the silicon in the range from -7.2 to -8.3 ppm for 2a-d, from -17.9 to -19.9 ppm for 3a-d, and from 15.1 to 15.2 ppm for 4a,b. The ²⁹Si NMR chemical shifts for 3a-d, where the $Si(p-Tol)_3$ group is bound to the iminoacyl nitrogen, are similar to that for the N-silyliminoacyl rhodium complex [Cp*(PMe₃)- $Rh{\kappa^2C, N-C(4-(OMe)C_6H_4)=NSiPh_3}]BAr'_4(-21.76 \text{ ppm}).^{2b}$ In the IR spectra of 2-4, a band for a C=N stretching of the iminoacyl ligand is observed in the range 1591-1637 cm⁻ These values are comparable with that for the N-silyliminoacyl tungsten complex Cp*(CO)(H)W{ $\kappa^{3}C,N,Si$ -C(t-Bu)=N(xantsil)} (1606 cm⁻¹)⁷ and shifted to lower wavenumbers compared to those of $\kappa^2 C$, N-N-alkyliminoacyl tungsten complexes $Cp^{*}(CO)_{2}W{\kappa^{2}C,N-C(Me)=N(R)}$ [1688 (R = t-Bu), 1678 (R = i-Pr) cm⁻¹].¹³ This reflects the large contribution of amido(carbene) resonance structure F in 2-4.

Dynamic Behavior of $\kappa^2 C, N$ -N-Silyliminoacyl Complexes 2a-d in Solution. Comparison of the ¹H NMR spectra of 2a-d in C₆D₆ at room temperature reveals that the signal of methyl substituents in the two p-tolyl groups changes the shape dramatically depending on the substituent R on the iminoacyl carbon: The methyl signal was observed as one sharp singlet for 2a (2.08 ppm), one broad singlet for 2b (2.07 ppm), and two slightly broadened singlets for 2c (2.06 and 2.09 ppm) and 2d (2.04 and 2.08 ppm). These observations suggest the existence of a dynamic process involving the inversion of the chiral tungsten center in 2a-d on the NMR time scale. This dynamic behavior becomes slower as the substituent R becomes bulkier and more electron-donating, because larger steric demand and electron-donating ability of the substituent R on the iminoacyl carbon disturb dissociation of the iminoacyl nitrogen atom coordinating to the tungsten center (Scheme 3, vide infra).

In order to clarify how the inversion of the chiral tungsten center occurs, variable-temperature ¹H NMR spectra of **2c** in C_6D_{12} were measured (Figure 1, left). The rate constants *k* of the dynamic process were determined by simulation of the spectra (Figure 1, right).¹⁴ The activation parameters of the inversion were estimated by the Eyring plot (Figure 2): $\Delta H^{\pm} = 98.6(7)$ kJ mol⁻¹, $\Delta S^{\pm} = 92(2)$ J K⁻¹ mol⁻¹, and $\Delta G^{\pm}_{298} = 71(1)$ kJ mol⁻¹. The large positive value of the activation entropy implies that the inversion proceeds by a dissociative mechanism as depicted in Scheme 3. The mechanism consists of dissociation and recoordination of the iminoacyl nitrogen atom in a $\kappa^2 C$,*N*-*N*-silyliminoacyl complex through a κ^1 -iminoacyl complex in the transition state.

X-ray Crystal Structure of $Cp^*(CO)_2W\{\kappa^2C, N-C(Et)=NSi(p-Tol)_3\}$ (3b). The X-ray crystal structure of 3a has

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Table 1. ¹ H, ¹³ C, and ²	²⁹ Si NMR and IR Data for	N-Silvliminoacyl Complex	xes 2a-d, 3a-d, and 4a,b

compound	1 H NMR (300 MHz, C ₆ D ₆) δ/ppm	$^{13}C{^{1}H} NMR$ (75.5 MHz, C ₆ D ₆) δ/ppm	²⁹ Si{ ¹ H} NMR (59.6 MHz, C ₆ D ₆) δ/ppm	$\mathrm{IR}^a \nu/\mathrm{cm}^{-1}$
$\frac{\text{Cp}^{*}(\text{CO})_{2}\text{W}[\kappa^{2}C,N\text{-C}(\text{Me})=}{\text{N}\{\text{SiMe}(p\text{-Tol})_{2}\}](2\mathbf{a})}$	0.64 (s, 3H, SiMe), 1.78 (s, 15H, Cp*), 2.08 (s, 6H, C ₆ H ₄ Me), 2.39 (s, 3H, NCMe), 6.96-7.09 (m, 4H, ArH), 7.39-7.57 (m, 4H, ArH)	$\begin{array}{l} -2.1 \text{ (SiMe), } 11.2 \text{ (} C_5Me_5\text{),} \\ 21.4 \text{ (} C_6H_4Me\text{), } 23.4 \text{ (} NCMe\text{),} \\ 104.5 \text{ (} C_5Me_5\text{), } 129.2, 130.7 \text{ (br),} \\ 131.5 \text{ (br), } 135.2, 140.4 \text{ (} ArC\text{),} \\ 233.9 \text{ [} J_{WC}\text{(satellite)} = 54 \text{ Hz,} \\ W-C=N\text{], } 242.9, 245.2 \text{ (br, CO)} \end{array}$	-8.3	1894 (s, ν _{COsym}), 1793 (s, ν _{COasym}), 1630 (m, ν _{CN})
$Cp^{*}(CO)_{2}W[\kappa^{2}C,N-C(Et)=N\{SiMe(p-Tol)_{2}\}] (2b)$	0.66 (s, 3H, SiMe), 1.28 (t, $J = 7.6$ Hz, 3H, CH ₂ Me), 1.79 (s, 15H, Cp*), 2.07 (br s, 6H, C ₆ H ₄ Me), 2.32–2.59 (m, 2H, CH ₂ Me), 6.99–7.06 (m, 4H, ArH), 7.47 (d, $J = 7.4$ Hz, 2H, ArH), 7.54 (d, $J = 7.3$ Hz, 2H, ArH)	-2.1 (SiMe), 11.3 (C_5Me_5), 11.6 (CH_2Me), 21.5 (C_6H_4Me), 30.3 (CH_2Me), 104.5 (C_5Me_5), 129.2, 130.7, 131.6, 135.2, 140.4 (ArC), 240.7 [J_{WC} (satellite) = 55 Hz, W-C=N], 243.6, 245.1 (CO)	-8.0	1882 (s, ν _{COsym}), 1786 (s, ν _{COasym}), 1630 (m, ν _{CN})
$Cp^{*}(CO)_{2}W[\kappa^{2}C,N-C(i-Pr)=N\{SiMe(p-Tol)_{2}\}] (2c)$	0.69 (s, 3H, SiMe), 1.03 (d, $J = 6.7$ Hz, 3H, CH Me_aMe_b), 1.04 (d, $J = 6.7$ Hz, 3H, CH Me_aMe_b), 1.80 (s, 15H, Cp*), 2.06 (s, 3H, C ₆ H ₄ Me), 2.09 (s, 3H, C ₆ H ₄ Me), 2.93 (sept, $J = 6.7$ Hz, 1H, C HMe_2), 7.00 (d, $J = 7.8$ Hz, 2H, ArH), 7.05 (d, $J = 7.8$ Hz, 2H, ArH), 7.49 (d, $J = 7.8$ Hz, 2H, ArH), 7.55 (d, $J = 7.8$ Hz, 2H, ArH)	$\begin{array}{l} -1.6 \text{ (SiMe), } 11.4 \text{ (} C_5 M e_5 \text{),} \\ 20.1, 20.4 \text{ (} CH M e_2 \text{),} \\ 21.5 \text{ (} C_6 H_4 M e), \\ 36.5 \text{ (} CH M e_2 \text{), } 104.7 \text{ (} C_5 M e_5 \text{),} \\ 129.17, 129.22, 130.9, \\ 131.8, 135.2, 135.3, \\ 140.3, 140.4 \text{ (} Ar C \text{),} \\ 243.7 \text{ [} J_{WC} \text{ (satellite)} = 55 \text{ Hz,} \\ W-C=N \text{],} \\ 244.5, 244.6 \text{ (} CO \text{)} \end{array}$	-7.7	1896 (s, <i>v</i> _{COsym}), 1793 (s, <i>v</i> _{COasym}), 1591 (m, <i>v</i> _{CN})
$Cp^{*}(CO)_{2}W[\kappa^{2}C,N-C(t-Bu) = N{SiMe(p-Tol)_{2}}] (2d)$	0.80 (s, 3H, SiMe), 1.10 (s, 9H, <i>t</i> -Bu), 1.81 (s, 15H, Cp*), 2.04 (s, 3H, C ₆ H ₄ Me), 2.08 (s, 3H, C ₆ H ₄ Me), 6.99 (d, $J = 7.8$ Hz, 2H, ArH), 7.04 (d, $J = 7.8$ Hz, 2H, ArH), 7.56 (d, $J = 7.8$ Hz, 2H, ArH), 7.61 (d, $J = 7.8$ Hz, 2H, ArH)	0.5 (SiMe), 11.4 (C_5Me_5), 21.4 (C_6H_4Me), 28.6 (CMe_3), 41.3 (CMe_3), 104.5 (C_5Me_5), 129.0, 129.1, 131.7, 132.1, 135.6, 135.7, 140.2, 140.3 (ArC), 243.9, 244.4 (CO), 247.9 [J_{WC} (satellite) = 54 Hz, W-C=N]	-7.2	1896 (s, <i>v</i> _{COsym}), 1793 (s, <i>v</i> _{COasym}), 1601 (m, <i>v</i> _{CN})
$Cp^{*}(CO)_{2}W[\kappa^{2}C,N-C(Me) = N{Si(p-Tol)_{3}}] (3a)$	1.79 (s, 15H, Cp*), 2.06 (s, 9H, C ₆ H ₄ Me), 2.49 (s, 3H, NCMe), 7.04 (d, $J = 7.7$ Hz, 6H, ArH), 7.63 (d, $J = 7.7$ Hz, 6H, ArH)	11.2 (C_5Me_5), 21.5 (C_6H_4Me), 23.9 (NCMe), 104.3 (C_5Me_5), 129.3, 129.8, 136.3, 140.5 (ArC), 235.2 [J_{WC} (satellite) = 53 Hz, W-C=N], 242.4, 244.8 (br, CO)	-17.9	1896 (s, ν _{COsym}), 1792 (s, ν _{COasym}), 1620 (m, ν _{CN})
$Cp^{*}(CO)_{2}W[\kappa^{2}C,N-C(Et)=N{Si(p-Tol)_{3}}] (3b)$	1.35 (t, $J = 7.6$ Hz, 3H, CH ₂ Me), 1.81 (s, 15H, Cp*), 2.06 (s, 9H, C ₆ H ₄ Me), 2.48–2.60 (m, 2H, CH ₂ Me), 7.04 (d, $J = 7.8$ Hz, 6H, ArH), 7.65 (d, $J = 7.8$ Hz, 6H, ArH)	11.3 (C_5Me_5), 11.8 (CH ₂ Me), 21.5 (C_6H_4Me), 30.6 (CH ₂ Me), 104.4 (C_5Me_5), 129.3, 129.8, 136.3, 140.5 (ArC), 242.2 [J_{WC} (satellite) = 55 Hz, W-C=N], 243.2, 244.7 (br, CO)	-18.9	1894 (s, ν _{COsym}), 1788 (s, ν _{COasym}), 1599 (m, ν _{CN})
$Cp^{*}(CO)_{2}W[\kappa^{2}C,N-C(i-Pr)=N{Si(p-Tol)_{3}}] (3c)$	1.01 (d, $J = 6.6$ Hz, 3H, CH Me_aMe_b), 1.17 (d, $J = 6.6$ Hz, 3H, CH Me_aMe_b), 1.83 (s, 15H, Cp*), 2.06 (s, 9H, C ₆ H ₄ Me), 3.04 (sept, $J = 6.6$ Hz, 1H, C HMe_2), 7.04 (d, $J = 7.8$ Hz, 6H, ArH), 7.69 (d, $J = 7.8$ Hz, 6H, ArH)	11.4 (C_5Me_5), 20.1, 20.8 (CH Me_2), 21.5 (C_6H_4Me), 37.0 (CHMe ₂), 104.7 (C_5Me_5), 129.2, 130.0, 136.4, 140.5 (ArC), 244.3 [J_{WC} (satellite) = 182 Hz, CO], 245.3 [J_{WC} (satellite) = 56 Hz, W-C=N]	-19.9	1894 (s, v _{COsym}), 1793 (s, v _{COasym}), 1606 (m, v _{CN})
$Cp^{*}(CO)_{2}W[\kappa^{2}C,N-C(t-Bu) = N{Si(p-Tol)_{3}}] (3d)$	1.15 (s, 9H, <i>t</i> -Bu), 1.79 (s, 15H, Cp*), 2.05 (s, 9H, C ₆ H ₄ Me), 7.04 (d, $J = 7.7$ Hz, 6H, ArH), 7.75 (d, $J = 7.7$ Hz, 6H, ArH)	11.3 (C_5Me_5), 21.4 (C_6H_4Me), 29.0 (CMe_3), 42.2 (CMe_3), 104.5 (C_5Me_5), 129.1, 130.7, 136.9, 140.3 (ArC), 243.7, 244.3 (CO), 249.6 [J_{WC} (satellite) = 54 Hz, W-C=N]	-19.0	1890 (s, <i>v</i> _{COsym}), 1784 (s, <i>v</i> _{COasym}), 1597 (m, <i>v</i> _{CN})
$Cp^{*}(CO)_{2}W\{\kappa^{2}C,N\text{-}C(Me)=NSiEt_{3}\} (4a)$	0.47-0.68 (m, 6H, SiC H_2 Me), 0.84 (t, $J = 7.8$ Hz, 9H, SiC H_2Me), 1.83 (s, 15H, Cp*), 2.42 (s, 3H, N=CMe)	4.8, 6.9 (SiEt), 11.3 (C_5Me_5), 22.4 (N=CMe), 104.1 (C_5Me_5), 228.7 [J_{WC} (satellite) = 53 Hz, W-C=N], 242.1, 246.0 (CO)	15.2	1901 (s, ν_{COsym}), 1801 (s, ν_{COasym}), 1637 (w, ν_{CN})

	Tabl	le 1. Continued		
$\frac{\operatorname{Cp}^{*}(\operatorname{CO})_{2}W\{\kappa^{2}C,N\text{-}C(\operatorname{Et})=}{\operatorname{NSiEt}_{3}\}(\mathbf{4b})}$	0.44-0.72 (m, 6H, SiC H_2 Me), 0.86 (t, $J = 7.8$ Hz, 3H, SiC H_2Me), 1.39 (t, $J = 7.7$ Hz, 3H, N=CC H_2Me), 1.85 (s, 15H, Cp*), 2.36-2.61 (m, 2H, N=CC H_2 Me)	4.9, 7.0 (SiEt), 11.4 (C_5Me_5), 11.9 (N=CCH ₂ Me), 29.3 (N=CCH ₂ Me), 104.1 (C_5Me_5), 235.8 [J_{WC} (satellite) = 55 Hz, W-C=N], 242.7 [J_{WC} (satellite) = 187 Hz, CO], 245.6 [J_{WC} (satellite) = 178 Hz, CO],	15.1	1901 (s, ν_{COsym}), 1801 (s, ν_{COasym}), 1620 (w, ν_{CN})

^aKBr pellet (for **2a-d** and **3a-d**) or C₆D₆ solution (for **4a,b**). Abbreviations: w, weak; m, medium; s, strong.









already been reported in a preliminary report.¹¹ This time, single-crystal X-ray analysis was performed for 3b (Figure 3, Table 2). Complex 3b adopts a four-legged piano-stool geometry: the tungsten center possesses a pentamethylcyclopentadienyl, a $\kappa^2 C_{,N}$ -N-silyliminoacyl, and two carbonyl ligands, in which the two carbonyl ligands are located at mutually cis positions. The bond distances and angles in the W-C-N threemembered ring are comparable with those in 3a and those in the *N*-silyliminoacyl tungsten complex Cp*(CO)(H)W{ $\kappa^{3}C$,*N*,*Si*-C(t-Bu)=N(xantsil)⁷ The short W-C(iminoacyl) bond distance in **3a** and **3b** [2.086(9) (**3a**), 2.088(6) (**3b**) Å] is similar to that of the carbene complex $Cp^{*}(CO)_{2}W{=C(H)NEt_{2}}$ -(Cl) [2.141(3) Å],¹² indicating the significant contribution of the amido(carbene) canonical structure F in the bonding modes of complexes 3a and 3b (Scheme 2). The W-N bond of **3b** [2.225(5) Å] is slightly longer than that of the *N*-alkyliminoacyl complex $(\eta^{5}-C_{9}H_{7})(CO)_{2}W{\kappa^{2}C,N-C(Me)=N(t-Bu)}$ [2.144(5) Å].¹⁵ 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 $Cp^{*}(CO)_{2}W{C(Et)=N}$ moiety in **3b**: the distances between aryl carbons C6 and C7 on a p-Tol group and a methyl carbon C32 on Cp* [C6 \cdots C32, 3.902(9) Å; $C7 \cdots C32$, 3.904(10) Å] and between the methylene carbon C2 bonded to the iminoacyl carbon and aryl carbons C20 and C25





Figure 1. Observed (left, in cyclohexane- d_{12}) and calculated (right) line shape of ¹H NMR signals for the methyl protons in the isopropyl group of **2c** at various temperatures. The rate constants *k* used for the spectral simulation are shown on the right side.



Figure 2. Eyring plot $[\ln(k/T) \text{ vs } 1000/T]$ for the inversion of the chiral tungsten center of 2c in C₆D₁₂ $[\ln(k/T) = 34.91 - 11.86(1000/T)$ (R = 0.9986)].

on a *p*-Tol group [C2···C20, 3.603(10) Å; C2···C25, 3.641(10) Å] are comparable with 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 aromatic rings (1.7 Å).¹⁶

⁽¹⁶⁾ Pauling L. *The Nature of the Chemical Bonds*, 3rd ed.; Cornell University Press: Ithaca, NY, 1960; pp 257–264.



Figure 3. ORTEP drawing of **3b**. Thermal ellipsoids are drawn at the 50% probability level, and all hydrogen atoms are omitted for clarity.

Table 2. Selected Bond Distances (Å) and Angles (deg) in $Cp^*(CO)_2W[\kappa^2C,N-C(Et)=N{Si(p-Tol)_3}]$ (3b)

W-N 2.225(5) $W-C1$ $W-C4$ 1.937(6) $W-C5$ $Si-N$ 1.742(5) $N-C1$ $N-W-C1$ 33.9(2) $N-W-C4$ $N-W-C5$ 92.0(2) $C1-W-C4$ $N-W-C5$ 92.0(2) $C1-W-C4$	2.088(6)
W-C4 1.937(6) W-C5 Si-N 1.742(5) N-C1 N-W-C1 33.9(2) N-W-C4 N-W-C5 92.0(2) C1-W-C4 Ol W C5 102.0(2) C1-W-C4	1.070(0)
Si-N 1.742(5) N-C1 N-W-C1 33.9(2) N-W-C4 N-W-C5 92.0(2) C1-W-C4 C1 UC5 UC4	1.9/2(6)
N-W-C1 33.9(2) N-W-C4 N-W-C5 92.0(2) C1-W-C4	1.264(8)
N-W-C5 92.0(2) C1-W-C4	113.3(2)
	92.3(3)
C1-W-C5 113.4(3) $C4-W-C5$	75.9(3)
W-N-Si 148.0(3) W-N-C1	67.1(3)
W-C1-N 79.0(4) W-C1-C2	152.3(5)
Si-N-C1 143.4(4) N-C1-C2	128.6(6)

Thermal Rearrangement of $Cp^{*}(CO)_{2}W{\kappa^{2}C, N-C(R)}$ = $NSi(p-Tol)_3$ (3a, R = Me; 3b, R = Et). The previously isolated $\kappa^2 C, N$ -N-silyliminoacyl complexes [Cp*(PMe₃)Rh-{ $\kappa^2 C, N$ -C(4-(OMe)C₆H₄)=NSiPh₃]]BAr'₄^{2b} and Cp*(CO)-(H)W{ $\kappa^{3}C,N,Si$ -C(t-Bu)=N(xantsil)}⁷ are thermally unstable even at room temperature. In contrast, complexes 2-4 did not show any sign of decomposition in C₆D₆ overnight at room temperature, according to their ¹H NMR spectra. To the best of our knowledge, there is only one example of a $\kappa^2 C$, N-N-silyliminoacyl complex that is stable at room temperature, namely, $[(\eta^5-C_5H_5)_2(\text{CNSiMe}_3)\text{Ti}\{\kappa^2C, N-C(\text{Me})=\text{NSiMe}_3\}]BPh_4$.¹⁷ In order to determine the thermal stability of $\kappa^2 C_{,N}$ -N-silvliminoacyl complexes **3a** and **3b**, thermolysis of these complexes was examined at high temperatures. Thus, heating a toluene- d_8 solution of complexes **3a**,**b** in a sealed NMR tube by raising the temperature in stages from 90 to 120 °C (for 3a) or from 100 to 120 °C (for 3b), which was monitored by ¹H NMR spectroscopy, led mainly to the formation of silylisocyanide complexes Cp*(CO)₂W(R)- $\{CNSi(p-Tol)_3\}$ (5a, R = Me; 5b, R = Et) as a mixture of cis/trans isomers. A large-scale experiment of the thermolysis was carried out for 3a in toluene at 120 °C for 54 h or for 3b in toluene- d_8 at 120 °C for 24 h to give **5a** or **5b** as a *cis/trans* mixture in 77% (5a) or 49% (5b) yield (eq 4). Thus, the C-Cbond cleavage in 3a,b requires a much higher temperature compared to those of the rhodium and iron *N*-silyliminoacyl complexes involving a Cp'(L)M moiety (M = Rh, Cp' = Cp*, L = PMe₃; M = Fe, Cp' = Cp or Cp*, L = CO).^{2,3,4a,5} This difference is attributable to the more sterically crowded tungsten center (four-legged piano-stool geometry) in the former complexes compared to the iron and rhodium centers (three-legged piano-stool geometry) in the latter complexes. According to the mechanism of the C–C bond cleavage of nitrile proposed by Nakazawa et al. on the basis of calculation,³ the R group on the nitrile carbon has to migrate to the metal center to form a silylisocyanide complex. This step must be retarded by the steric crowding around the metal center.



Characterization of Silylisocyanide Complexes 5a and 5b. Silvlisocyanide complexes 5a and 5b were characterized on the basis of NMR spectroscopy and elemental analysis for the mixtures of their *cis/trans* isomers. Each of the ¹H NMR spectra of 5a and 5b shows two sets of signals assignable to their cis and trans isomers, namely, cis-5a and trans-5a for 5a and *cis*-5b and *trans*-5b for 5b. In the ¹H NMR spectra of 5b, two signals assignable to the diastereotopic CH₂ protons in cis-5b are observed at 0.70 and 0.74 ppm, which are slightly upfield-shifted compared to that of *trans*-5b (0.79 ppm). The intensity of the ¹H signals for *cis*-5b is larger than that for trans-5b, and the molar ratio of cis-5b to trans-5b is 1.7 on the basis of the intensity ratio of their Cp* signals. Similarly, in the ¹H NMR spectra of **5a**, the upfield-shifted signal of the methyl ligand (-0.04 ppm) can be assigned to that of the *cis* isomer. The cis isomer is also the major component in 5a (cis-5a:trans-5a = 1.6:1, based on the intensity ratio of their Cp* signals). The same type of upfield shift for the cis isomer has also been observed in an alkylisocyanide complex: the signal of the methyl ligand in the *cis* isomer of $(\eta^5-C_9H_7)(CO)_2W_-$ (Me){CN(*t*-Bu)} (-0.09 ppm) is upfield-shifted compared to that of the *trans* isomer (0.33 ppm).¹⁵

In the ¹³C{¹H} NMR spectra of **5a** and **5b**, two sets of signals assignable to their *cis/trans* isomers are also observed. Since the *cis* isomer is the major component, we tentatively assigned a set of signals having larger intensity to the *cis* isomer (*cis*-**5a** and *cis*-**5b**). The signals of the carbon coordinated to the tungsten center in the methyl or ethyl ligand of the two isomers are observed at $-22.5 \text{ ppm} (J_{WC} = 36 \text{ Hz}, cis$ -**5a**) and $-24.6 (J_{WC} = 31 \text{ Hz}, trans-$ **5a**) for **5a** and $-5.2 \text{ ppm} (J_{WC} = 35 \text{ Hz}, cis-$ **5b**) and $-7.1 (J_{WC} = 32 \text{ Hz}, trans-$ **5b**) for**5b**. The chemical shifts for**5a** $are comparable with those for the (alkylisocyanide)(methyl) complex (<math>\eta^5$ -C₉H₇)-(CO)₂W(Me){CN(t-Bu)} [*cis* isomer, -20.4 ppm (W-Me);

⁽¹⁷⁾ Bochmann, M.; Wilson, L. M.; Hursthouse, M. B.; Motevalli, M. Organometallics 1988, 7, 1148.



Figure 4. ORTEP drawing of *cis*-5b. Thermal ellipsoids are drawn at the 50% probability level, and all hydrogen atoms are omitted for clarity.

trans isomer, -24.1 ppm (W-Me)].¹⁵ For **5a**, the signals of the isocyanide CN carbons are observed at 204.6 ppm for *cis*-**5a** and 211.1 ppm for *trans*-**5a**, and those of CO are observed at 230.8 and 242.7 ppm for *cis*-**5a** and 226.1 ppm for *trans*-**5a**. For **5b**, the signals of isocyanide CN carbons are observed at 207.4 ppm for *cis*-**5b** and 211.5 ppm for *trans*-**5b**, and those of CO are observed at 233.1 and 241.8 ppm for *cis*-**5b** and 228.9 ppm for *trans*-**5b**. These observations support the structures of **5a**, **b** having an alkyl ligand and a silylisocyanide ligand.

The ²⁹Si{¹H} NMR spectra of **5**a,**b** at room temperature did not show any signal. On the other hand, in the ²⁹Si{¹H} NMR spectrum of **5a** at 233 K, two signals assignable to the *cis/trans* isomers were observed at -25.3 and -25.4 ppm. These chemical shifts are similar to that for the silylisocyanide rhodium complex [Cp*(PMe₃)Rh(CNSiPh₃)(Me)]BAr'₄ (-17.95 ppm).^{2a} The broadening of the ²⁹Si signals of **5a,b** at room temperature may be attributed to the rapid isomerization between *cis*-**5a,b** and *trans*-**5a,b** on the NMR time scale.

X-ray Crystal Structure of cis-Cp*(CO)₂W(Et){CNSi(p-Tol)₃ (*cis*-5b). Recrystallization of a *cis/trans* mixture of 5b from toluene afforded a single crystal of cis isomer cis-5b suitable for X-ray crystallography. The molecular structure of cis-5b is illustrated in Figure 4, and selected bond distances and angles are listed in Table 3. Complex cis-5b adopts a four-legged piano-stool geometry where the tungsten center possesses an η^5 -pentamethylcyclopentadienyl ligand, two carbonyl ligands, an ethyl ligand, and a silylisocyanide ligand. The ethyl ligand and the silylisocyanide ligand are located mutually at *cis* positions on the tungsten center. The W-C(isocyanide) and W-C(alkyl) bond distances of cis-5b $[W-C1, 2.013(4) \text{ Å}; W-C2, 2.297(4) \text{ Å}, respectively}]$ are comparable with those of the alkylisocyanide complex (η^{5} - C_9H_7)(CO)₂W(Me){CN(*t*-Bu)} [W−C(isocyanide), 2.04(2) Å; W−C(alkyl), 2.26(2) Å].¹⁵ The C≡N and N−Si bond distances of cis-5b [C1-N, 1.183(5) Å; N-Si, 1.743(3) Å] are

Table 3. Selected Bond Distances (Å) and Angles (deg) in cis-Cp*(CO)₂W(Et){CNSi(p-Tol)₃} (cis-5b)

	1 ()= ()(u)6) (/
W-C1	2.013(4)	W-C2	2.297(4)
W-C4	1.941(5)	W-C5	1.959(5)
Si-N	1.743(3)	N-C1	1.183(5)
C1-W-C2	74.60(16)	C1-W-C4	80.22(17)
C1-W-C5	114.17(19)	C2-W-C4	129.37(18)
C2-W-C5	74.2(2)	C4-W-C5	77.4(2)
W-C1-N	175.1(3)	Si-N-C1	166.0(3)

similar to those of previously reported silylisocyanide complexes $[C-N = 1.13-1.23 \text{ Å}, N-Si = 1.70-1.79 \text{ Å}]^{2a,3,4a,18}$

Further Thermal Reaction of 5b. Prolonged heating of $\kappa^2 C$, *N*-iminoacyl complex **3b** at 120 °C for 2 weeks in toluene- d_8 afforded not only **5b** (24% NMR yield, *cis/trans* mixture) but also the η^3 -*N*-silyl-1-azaallyl complex Cp*(CO)₂W{ η^3 -HMeCCHNSi(*p*-Tol)₃} (**6**, 46% NMR yield) (eq 5).



In the ¹H NMR spectrum of the mixture of **5b** and **6**, the signals of the hydrogen atoms bound to the azaallyl carbons in 6 are observed at 2.30 ppm (dq, ${}^{3}J_{HH} = 6.0, 6.9$ Hz, *H*MeCCHN) and 5.20 ppm (d, ${}^{3}J_{HH} = 6.9$ Hz, HMeCCHN). The large coupling constant between the signals (${}^{3}J_{HH} = 6.9 \text{ Hz}$) indicates that these hydrogen atoms are located at mutually anti positions. In addition, the doublet signal of the methyl group bound to the azaallyl carbon is observed at 1.76 ppm (d, ${}^{3}J_{HH} = 6.0$ Hz). The chemical shifts of these signals are comparable with those of the η^3 -*N*-alkyl-1-azaallyl complex Cp*(CO)₂W(η^3 -HMeCCHNEt) $[1.54 \text{ ppm (dq, }^{3}J_{\text{HH}} = 6.1, 6.3 \text{ Hz}, HMeCCHNEt), 1.82 \text{ ppm}$ (d, ${}^{3}J_{\text{HH}} = 6.1 \text{ Hz}, \text{H}Me\text{CCHNEt}$), and 4.53 ppm (d, ${}^{3}J_{\text{HH}} = 6.3 \text{ Hz}, \text{HMeCCHNEt}$].¹⁹ The ${}^{13}\text{C}{}^{1}\text{H}$ NMR spectrum of the mixture of **5b** and **6** shows the signals of the azaallyl ligand in complex 6 at 59.7 ppm (HMeCCHN) and 113.5 ppm (HMeCCHN). The chemical shifts of these signals are also comparable with those of the η^3 -N-alkyl-1-azaallyl complex Cp*(CO)₂W(η^3 -HMeCCHNEt) [47.0 ppm (HMeCCHNEt) and 118.1 ppm (HMeCCHNEt)].¹⁹ These observations support the structure of complex 6, but the geometry (exo/endo and syn/ *anti* configurations) of the η^3 -1-azaallyl ligand in **6** is not clear.

Conclusion

In this work, we synthesized $\kappa^2 C$,*N*-*N*-silyliminoacyl tungsten complexes **2a**-**d**, **3a**-**d**, and **4a**,**b**. Two methods were utilized for the synthesis: (1) the reaction of DMAP-stabilized

^{(18) (}a) da Silva, M. F. C. G.; Lemos, M. A. N. D. A.; da Silva, J. J. R. F.; Pombeiro, A. J. L.; Pellinghelli, M. A.; Tiripicchio, A. J. Chem. Soc., Dalton Trans. 2000, 373. (b) Nakazawa, H.; Itazaki, M.; Owaribe, M. Acta Crystallogr., Sect. E 2005, 61, m1073. (c) Nakazawa, H.; Itazaki, M.; Owaribe, M. Acta Crystallogr., Sect. E 2005, 61, m1172.

⁽¹⁹⁾ Filippou, A. C.; Grünleitner, W.; Kiprof, P. J. Organomet. Chem. 1991, 410, 175.

(aryl)(silylene) complexes **1a,b** with excess nitrile, and (2) the reaction between methyl(nitrile) complexes **A** and **B** with hydrosilane. Complexes 2-4 are stable at room temperature. Upon raising the temperature, thermal rearrangements of complexes **3a,b** via C-C bond cleavage occurred at 120 °C to give silylisocyanide complexes **5a,b**.

NMR spectra of 2a-d showed that their chiral tungsten center undergoes inversion around room temperature. The kinetic study on the inversion process of 2c implies that this inversion proceeds through cleavage of the bond between tungsten and iminoacyl nitrogen. This means that the iminoacyl ligand in complexes 2-4 is hemilabile. The considerable thermal stability of complexes 2-4 is suitable for the investigation on their reactivity through the W–N bond cleavage. We are now trying to find reactions of complexes 2-4 with small molecules, which can be applied to new types of transformations of organic molecules. For instance, we already found that the reaction of complexes 3a and 4a in the presence of excess acetonitrile caused C–N coupling to give W–C–N–C–N five-membered-ring complexes.¹¹

Experimental Section

General Procedures. All manipulations were carried out under dry nitrogen in a glovebox or using a standard high-vacuum line. Benzene- d_6 , toluene, toluene- d_8 , hexane, cyclohexane- d_{12} , dichloromethane- d_2 , and nitriles RCN (R = Me, Et, *i*-Pr, *t*-Bu) were dried over calcium hydride and distilled before use. BPh₃ (Sigma Aldrich) was used as received. Cp*(CO)₃WMe²⁰ and Cp*(CO)₂W(*p*-Tol){=Si(*p*-Tol)R'·DMAP} (**1a**, R' = Me; **1b**, R' = *p*-Tol)^{8b} were prepared according to the literature methods.

Physical Measurements. ¹H, ¹³C{¹H}, and ²⁹Si{¹H} NMR spectra were recorded on a Bruker ARX-300 or AVANCE-300 spectrometer. ²⁹Si $\{^{1}H\}$ NMR experiments except for **3a** were performed using the DEPT pulse sequence. The residual proton (C₆D₅H, 7.15 ppm; C₆D₅CD₂H, 2.09 ppm; C₆D₁₁H, 1.38 ppm; CDHCl₂, 5.28 ppm) and the carbon resonances (C₆D₆, 128.0 ppm; $C_6D_5CD_3$, 20.4 ppm; CD_2Cl_2 , 53.7 ppm) of deuterated solvents were used as internal references for ¹H and ¹³C resonances, respectively. Aromatic proton or carbon is abbreviated as ArH or ArC. ²⁹Si{¹H} NMR chemical shifts were referenced to SiMe₄ as an external standard. The NMR data were collected at room temperature unless indicated otherwise. Infrared spectra were recorded with a C₆D₆ solution placed between KBr plates in a liquid cell or with a KBr pellet using a Horiba FT-730 spectrometer. Mass and high-resolution mass spectra were recorded on a Hitachi M-2500S spectrometer operating in the electron impact (EI) mode. Mass spectrometric analysis and elemental analysis were performed at the Research and Analytical Center for Giant Molecules, Tohoku University. NMR and IR data for N-silyliminoacyl complexes 2a-d, 3a-d, and 4a,b are listed in Table 1.

Synthesis of $Cp^*(CO)_2W(NCEt)Me(B)$. The title compound was prepared by modifying a literature method for the synthesis of $Cp^*(CO)_2W(NCMe)Me(A)$.⁹ A propiononitrile (2.5 mL) solution of $Cp^*(CO)_3WMe(57 \text{ mg}, 0.14 \text{ mmol})$ in a Pyrex sample tube with a Teflon vacuum valve was degassed by three freeze-pump-thaw cycles on a vacuum line. The mixture was irradiated for 40 min with a 450 W medium-pressure Hg lamp immersed in a water bath (ca. 5 °C). During the photoreaction, the reaction mixture was degassed at 10 min of irradiation by a freeze-pump-thaw cycle on a vacuum line. After irradiation was completed, the reaction mixture was evaporated to dryness. A brown powder of **B** was obtained as a crude product in 71% yield (44 mg, 0.099 mmol). ¹H NMR (300 MHz, C₆D₆): δ 0.26 (s, 3H, WMe), 0.33 (t, J = 7.6 Hz, 3H, CH₂Me), 1.45 (q, J = 7.6 Hz, 2H, CH₂Me), 1.79 (s, 15H, Cp*). ¹³C{¹H} NMR (75.5 MHz, C₆D₆): δ -11.7 [J_{WC}(satellite) = 45 Hz, WMe], 10.6 (C₅Me₅), 10.8, 12.4 (Et), 101.4 (C₅Me₅), 138.7 (NCEt), 244.1, 257.3 (CO). IR (C₆D₆, cm⁻¹): 2262 (w, ν_{CN}), 1911 (s, ν_{COsym}), 1820 (m, ν_{COasym}). The ¹H NMR spectrum of crude product **B** in C₆D₆ is depicted in Figure S1 in the Supporting Information.

Synthesis of Cp*(CO)₂W[k^2C ,*N*-C(Me)=N{SiMe(*p*-Tol)₂}] (2a). A toluene (2 mL) solution of 1a · 0.5toluene (54 mg, 0.070 mmol) and MeCN (207 mg, 5.04 mmol) in a round-bottomed flask was allowed to stand at room temperature for 1 day. The resulting deep red mixture was evaporated to dryness. BPh₃ (16 mg, 0.066 mmol) and hexane (2 mL) were added to the residue, and the mixture was stirred for 1 h. DMAP·BPh₃ was precipitated as a white powder. The mixture was filtered, and the residue was washed with hexane (1 mL). After the filtrate and the washing were combined, the mixture was evaporated under vacuum. Recrystallization of the residual oil from hexane at -35 °C afforded a red powder of 2a in 67% yield (30 mg, 0.047 mmol). Anal. Calcd for C₂₉H₃₅NO₂SiW: C, 54.29; H, 5.50; N, 2.18. Found: C, 54.01; H, 5.40; N, 2.32.

Synthesis of $Cp^*(CO)_2W[\kappa^2C,N-C(Et)=N{SiMe(p-Tol)_2}]$ (2b). The title compound was synthesized by a procedure similar to that for 2a using a toluene solution (2 mL) of 1a · 0.5toluene (73 mg, 0.095 mmol) and EtCN (239 mg, 4.34 mmol). After addition of BPh₃ (20 mg, 0.083 mmol) and hexane (2 mL) to the evaporated reaction mixture and stirring for 1 h, workup similar to that for 2a afforded a red powder of 2b in 58% yield (36 mg, 0.055 mmol). Anal. Calcd for C₃₀H₃₇NO₂SiW: C, 54.96; H, 5.69; N, 2.14. Found: C, 55.33; H, 5.73; N, 2.17.

Synthesis of $Cp^*(CO)_2W[\kappa^2C, N-C(i-Pr)=N{SiMe(p-Tol)_2}]$ (2c). The title compound was synthesized by a procedure similar to that for **2a** using a toluene solution (2 mL) of **1a** · 0.5toluene (75 mg, 0.098 mmol) and *i*-PrCN (324 mg, 4.69 mmol) (reaction period: 3 days). After addition of BPh₃ (22 mg, 0.091 mmol) and hexane (3 mL) to the evaporated reaction mixture and stirring for 1 h, workup similar to that for **2a** afforded a red powder of **2c** in 61% yield (40 mg, 0.060 mmol). Anal. Calcd for C₃₁H₃₉-NO₂SiW: C, 55.61; H, 5.87; N, 2.09. Found: C, 56.11; H, 5.86; N, 2.15.

Synthesis of $Cp^*(CO)_2W[\kappa^2 C, N-C(t-Bu)=N{SiMe(p-Tol)_2}]$ (2d). The title compound was synthesized by a procedure similar to that for 2a using a toluene solution (2 mL) of 1a · 0.5toluene (77 mg, 0.10 mmol) and *t*-BuCN (285 mg, 3.43 mmol) (reaction period: 3 days). After addition of BPh₃ (21 mg, 0.087 mmol) and hexane (3 mL) to the evaporated reaction mixture and stirring for 1 h, workup similar to that for 2a afforded a red powder of 2d in 91% yield (62 mg, 0.091 mmol). Anal. Calcd for C₃₂H₄₁NO₂-SiW: C, 56.22; H, 6.05; N, 2.05. Found: C, 56.68; H, 6.18; N, 2.04.

Synthesis of $Cp^*(CO)_2W[\kappa^2C,N-C(Me)=N{Si(p-Tol)_3}](3a)$. Method 1: Reaction of 1b with Acetonitrile. The title compound was synthesized by a procedure similar to that for 2a using a toluene solution (2.5 mL) of 1b.0.5toluene (83 mg, 0.098 mmol) and MeCN (208 mg, 5.07 mmol) (reaction period: 1 day). After addition of BPh₃ (22 mg, 0.091 mmol) and hexane (6 mL) to the evaporated reaction mixture and stirring for 1 h, workup similar to that for 2a afforded a red powder of 3a in 61% yield (43 mg, 0.060 mmol).

Method 2: Reaction of $Cp^*(CO)_2W(NCMe)Me$ (A) with HSi-(*p*-Tol)₃. An acetonitrile (6 mL) solution of $Cp^*(CO)_3WMe$ (152 mg, 0.364 mmol) in a Pyrex sample tube with a Teflon vacuum valve was degassed by three freeze-pump-thaw cycles on a vacuum line. The mixture was irradiated for 70 min with a 450 W medium-pressure Hg lamp immersed in a water bath (ca. 5 °C). After 15 and 40 min of irradiation, the reaction mixture was degassed by a freeze-pump-thaw cycle on a vacuum line. After irradiation was completed, the reaction mixture involving $Cp^*(CO)_2W(NCMe)Me$ (A) was evaporated to dryness.

⁽²⁰⁾ Mahmoud, K. A.; Rest, A. J.; Alt, H. G.; Eichner, M. E.; Jansen, B. M. J. Chem. Soc., Dalton Trans. **1984**, 175.

The residue was dissolved in toluene (1.5 mL), and the solution was added onto a solid of HSi(*p*-Tol)₃ (110 mg, 0.364 mmol) in a round-bottomed flask. The mixture was allowed to stand at room temperature for 15 min. After the resulting red solution was evaporated under vacuum, the residue was extracted with hexane (3 mL). The red extract was concentrated and cooled at -35 °C to give analytically pure **3a** as a red powder in 59% yield (153 mg, 0.213 mmol). Anal. Calcd for C₃₅H₃₉NO₂SiW: C, 58.58; H, 5.48; N, 1.95. Found: C, 58.18; H, 5.65; N, 1.97.

Synthesis of $Cp^*(CO)_2W[\kappa^2C,N-C(Et)=N{Si(p-Tol)_3}]$ (3b). Method 1: Reaction of 1b with Propiononitrile. The title compound was synthesized by a procedure similar to that for 2a using a toluene solution (2 mL) of 1b·0.5toluene (70 mg, 0.083 mmol) and EtCN (246 mg, 4.47 mmol) (reaction period: 1 day). After addition of BPh₃ (17 mg, 0.070 mmol) and hexane (6 mL) to the evaporated reaction mixture and stirring for 1 h, workup similar to that for 2a afforded a red powder of 3b in 76% yield (46 mg, 0.063 mmol).

Method 2: Reaction of Cp*(CO)₂W(NCEt)Me (B) with HSi(p-Tol)₃. $Cp^*(CO)_2W(NCEt)Me$ (B) was prepared by a procedure analogous to the synthesis of B (vide supra) using a propiononitrile (11 mL) solution of Cp*(CO)₃WMe (275 mg, 0.658 mmol) (period of irradiation: 2 h, degassed at 30 and 70 min of irradiation). After irradiation, the reaction mixture involving B was evaporated to dryness. The residue was dissolved in toluene (7 mL), and the solution was added onto a solid of HSi(p-Tol)₃ (216 mg, 0.714 mmol) in a round-bottomed flask. The mixture was allowed to stand at room temperature for 25 min. After the resulting red solution was evaporated under vacuum, the residue was extracted with hexane (4 mL). The red extract was cooled at -35 °C to give analytically pure **3b** as a red powder (359 mg, 0.491 mmol) in 75% yield. Anal. Calcd for C₃₆H₄₁NO₂SiW: C, 59.10; H, 5.65; N, 1.91. Found: C, 59.08; H, 5.65; N, 1.90.

Synthesis of $Cp^*(CO)_2W[\kappa^2C, N-C(i-Pr)=N{Si(p-Tol)_3}]$ (3c). The title compound was synthesized by a procedure similar to that for 2a using a toluene solution (3 mL) of 1b · 0.5toluene (90 mg, 0.11 mmol) and *i*-PrCN (341 mg, 4.93 mmol) (reaction period: 2 days). After addition of BPh₃ (22 mg, 0.091 mmol) and hexane (4 mL) to the evaporated reaction mixture and stirring for 1 h, workup similar to that for 2a afforded a red powder of 3c in 75% yield (61 mg, 0.082 mmol). Anal. Calcd for C₃₇H₄₃NO₂SiW: C, 59.60; H, 5.81; N, 1.88. Found: C, 59.69; H, 5.95; N, 2.10.

Synthesis of Cp*(CO)₂W[$\kappa^2 C$,*N*-C(*t*-Bu)=N{Si(*p*-Tol)₃}] (3d). The title compound was synthesized by a procedure similar to that for 2a using a toluene solution (1.5 mL) of 1b · 0.5toluene (51 mg, 0.060 mmol) and *t*-BuCN (224 mg, 2.69 mmol) (reaction period: 2 days). After addition of BPh₃ (13 mg, 0.054 mmol) and hexane (6 mL) to the evaporated reaction mixture and stirring for 1 h, workup similar to that for 2a afforded a red powder of 3d in 83% yield (38 mg, 0.050 mmol). Anal. Calcd for C₃₈H₄₅NO₂-SiW: C, 60.08; H, 5.97; N, 1.84. Found: C, 59.63; H, 6.36; N, 1.91.

Synthesis of $Cp^{*}(CO)_{2}W{\kappa^{2}C, N-C(Me)=NSiEt_{3}}$ (4a). Cp*-(CO)₂W(NCMe)Me (A) was prepared by a procedure analogous to the synthesis of 3a (method 2) using an acetonitrile (8 mL) solution of Cp*(CO)₃WMe (201 mg, 0.481 mmol) (period of irradiation: 90 min, degassed at 20, 50, and 90 min of irradiation). After the reaction mixture involving A was transferred into a round-bottomed flask, HSiEt₃ (67 mg, 0.58 mmol) was added to the flask by a syringe. After keeping the mixture at room temperature for 1 day, the resulting red solution was evaporated under vacuum. The residual oil was dissolved in hexane (1 mL). Concentration and cooling at -35 °C of the solution afforded a red oil. The supernatant liquid was separated from the red oil (unidentified products) by a syringe and was cooled at -35 °C to yield a red powder of 4a in 74% yield (188 mg, 0.354 mmol). EI-MS (70 eV): m/z 531 (M⁺, 17), 503 (M⁺ – CO, 15), 473 (100). Exact mass (EI) for $C_{20}H_{33}NO_2$ -SiW: calcd, m/z 531.1784; found, m/z 531.1779. Contamination with a trace of impurities has prevented correct elemental

Table 4. Crystallographic Data for 3b and cis-5b

	3b	cis-5b
formula	C ₃₆ H ₄₁ NO ₂ SiW	C ₃₆ H ₄₁ NO ₂ SiW
fw	731.64	731.64
cryst size/mm	$0.40 \times 0.35 \times 0.30$	0.28 imes 0.07 imes 0.02
cryst color	red	yellow
cryst syst	monoclinic	monoclinic
space group	$P2_1/c$ (No. 14)	$P2_1/c$ (No. 14)
a/Å	9.0675(3)	13.590(4)
\dot{b}/\dot{A}	14.7448(4)	14.312(4)
c/Å	24.3446(8)	17.018(5)
$\dot{\beta}/\text{deg}$	91.9946(10)	97.2518(11)
$V/Å^3$	3252.86(18)	3283.4(16)
Ź	4	4
$D_{\rm calcd}/{\rm g}~{\rm cm}^{-3}$	1.494	1.480
F(000)	1472	1472
$\mu(Mo K\alpha)/mm^{-1}$	3.62	3.59
reflns collected	26148	23 363
unique reflns (R_{int})	7063 (0.128)	7506 (0.061)
refined params	379	379
R_1, wR_2 (all data)	0.059, 0.158	0.055, 0.070
$R_1, wR_2 [I > 2\sigma(I)]$	0.051, 0.140	0.034, 0.062
GOF	1.13	0.99
largest residual peak, hole/e Å ⁻³	1.84, -3.16	1.06, -0.52

analysis. The ¹H NMR spectrum of isolated 4a in C_6D_6 is depicted in Figure S2 in the Supporting Information.

Synthesis of $Cp^{*}(CO)_{2}W{\kappa^{2}C, N-C(Et)=NSiEt_{3}}$ (4b). Cp*- $(CO)_2W(NCEt)Me$ (**B**) was prepared by a procedure analogous to the synthesis of **B** (vide supra) using a propion (10 mL)solution of Cp*(CO)₃WMe (257 mg, 0.615 mmol) (period of irradiation: 2 h, degassed after 30 and 70 min of irradiation). After irradiation, the reaction mixture involving **B** was evaporated to dryness. The residue was dissolved in toluene (6 mL), and the solution was added to a liquid of HSiEt₃ (82 mg, 0.71 mmol) by a syringe. The mixture was allowed to stand at room temperature for 30 min. After the resulting red solution was evaporated under vacuum, the residue was extracted with hexane (4 mL). The red extract was concentrated (ca. 1/3) and cooled at -35 °C to give 4b as a red powder in 61% yield (205 mg, 0.376 mmol). EI-MS (70 eV): m/z 545 (M⁺, 25), 517 $(M^+ - CO, 13), 487 (100)$. Exact mass (EI) for $C_{21}H_{35}NO_2SiW$: calcd, *m*/*z* 545.1941; found, *m*/*z* 545.1938. Contamination with a trace of impurities has prevented correct elemental analysis. The ¹H NMR spectrum of isolated **4b** in C_6D_6 is depicted in Figure S3 in the Supporting Information.

Measurement of Variable-Temperature ¹H NMR Spectroscopy of Cp*(CO)₂W[$\kappa^2 C$,*N*-C(*i*-Pr)=N{SiMe(*p*-Tol)₂}] (2c). A Pyrex NMR tube was charged with a solution of complex 2c (4 mg, 6 μ mol) in cyclohexane- d_{12} (0.5 mL). This NMR tube was attached to a vacuum line and flame-sealed under high vacuum. The ¹H NMR spectra of 2c were measured at various temperatures (283–343 K). ¹H NMR (300 MHz, C₆D₁₂, 283 K): δ 0.58 (s, 3H, SiMe), 0.91 (d, J = 6.7 Hz, 3H, CH Me_a Me_b), 1.10 (d, J = 6.7 Hz, 3H, CHMe_a Me_b), 1.84 (s, 15H, Cp*), 2.30 (s, 3H, C₆H₄Me), 2.31 (s, 3H, C₆H₄Me), 2.87 (sept, J = 6.7 Hz, 1H, CHMe₂), 7.09 (d, J = 7.7 Hz, 2H, ArH), 7.11 (d, J = 7.7 Hz, 2H, ArH), 7.34 (d, J = 7.7 Hz, 2H, ArH), 7.39 (d, J = 7.7 Hz, 2H, ArH).

Synthesis of cis/trans-Cp*(CO)₂W(Me){CNSi(p-Tol)₃} (5a). A toluene (4 mL) solution of 3a (102 mg, 0.142 mmol) in a Pyrex sample tube (12 mm o.d.) with a Teflon vacuum valve was attached to a vacuum line. This tube was flame-sealed under high vacuum. The toluene solution was heated at 120 °C for 54 h. The solution color changed from red to yellow. The reaction mixture was transferred into a round-bottomed flask and evaporated to dryness. After the residual brown oil was allowed to stand for 1 h, a solid was deposited. Washing the mixture to remove an oil with hexane afforded a pale yellow solid of 5a as a cis/trans mixture (cis-5a:trans-5a = 1.6:1 molar ratio in CD₂Cl₂,

based on the intensity ratio of the Cp* signals in their ¹H NMR spectra) in 77% yield (82 mg, 0.11 mmol). Data for the mixture of cis-5a and trans-5a: ¹H NMR data for cis-5a (300 MHz, CD_2Cl_2 : $\delta - 0.04$ [s, 3H, J_{WH} (satellite) = 3.7 Hz, WMe], 1.87 (s, 15H, Cp*), 2.36 (s, 9H, C₆H₄Me), 7.23 (br d, J = 8.0 Hz, 6H, ArH), 7.50 (d, J = 8.0 Hz, 6H, ArH). ¹H NMR data for *trans*-5a (300 MHz, CD₂Cl₂): δ 0.01 [s, 3H, J_{WH} (satellite) = 3.6 Hz, WMe], 1.82 (s, 15H, Cp*), 2.36 (s, 9H, C₆H₄Me), 7.24 (br d, J = 7.9 Hz, 6H, ArH), 7.55 (d, J = 7.9 Hz, 6H, ArH). ¹³C{¹H} NMR data for *cis*-**5a** (75.5 MHz, CD₂Cl₂): δ -22.5 $[J_{WC}(\text{satellite}) = 36 \text{ Hz}, \text{WMe}], 10.6 (C_5 Me_5), 21.7 (C_6 H_4 Me),$ 102.3 (C5Me5), 128.8, 129.4, 135.4, 141.5 (ArC), 204.6 (CN), 230.8, 242.7 (CO). ¹³C{¹H} NMR data for trans-5a (75.5 MHz, CD_2Cl_2): $\delta - 24.6 [J_{WC}(satellite) = 31 \text{ Hz}, WMe], 10.4 (C_5Me_5),$ 21.7 (C₆H₄Me), 101.6 (C₅Me₅), 129.0, 129.4, 135.5, 141.5 (ArC), 211.1 (CN), 226.1 (CO). ²⁹Si{¹H} NMR (59.6 MHz, CD₂Cl₂, 233 K): δ -25.3, -25.4. Anal. Calcd for C₃₅H₃₉NO₂SiW: C, 58.58; H, 5.48; N, 1.95. Found: C, 58.98; H, 5.39; N, 1.98.

Synthesis of cis/trans-Cp*(CO)₂W(Et){CNSi(p-Tol)₃} (5b). A toluene- d_8 solution (0.5 mL) of **3b** (51 mg, 0.070 mmol) in a Pyrex NMR sample tube with a Teflon vacuum valve was attached to a vacuum line. This NMR tube was flame-sealed under high vacuum. The toluene solution was heated at 120 °C for 24 h. The solution color changed from red to brown. The reaction mixture was transferred into a round-bottomed flask and evaporated to dryness. After the residual red oil was allowed to stand for 1 day, a solid was deposited. Washing the mixture to remove an oil with hexane afforded a pale yellow solid of 5b as a cis/trans mixture (cis-5b:trans-5b = 1.7:1 molar ratio in CD₂Cl₂, based on the intensity ratio of the Cp* signals in their ¹H NMR spectra) in 49% yield (25 mg, 0.034 mmol). Data for the mixture of cis-5b and trans-5b: ¹H NMR data for cis-5b (300 MHz, CD_2Cl_2): $\delta 0.70$ (q, J = 7.6 Hz, 1H, WCH_aH_bMe), 0.74 (q, J =7.6 Hz, 1H, WCH_a $H_{\rm b}$ Me), 1.41 (t, J = 7.6 Hz, 3H, WCH₂Me), 1.84 (s, 15H, Cp*), 2.36 (s, 9H, C_6H_4Me), 7.23 (br d, J = 7.9 Hz, 6H, ArH), 7.51 (d, J = 7.9 Hz, 6H, ArH). ¹H NMR data for *trans*-5b (300 MHz, CD_2Cl_2): δ 0.79 (q, J = 7.6 Hz, 2H, WCH_2 -Me), $1.56 (t, J = 7.6 \text{ Hz}, 3\text{H}, \text{WCH}_2Me)$, $1.80 (s, 15\text{H}, \text{Cp}^*)$, 2.36(s, 9H, C₆H₄Me), 7.24 (br d, J = 7.9 Hz, 6H, ArH), 7.54 (d, J = 7.9 Hz, 6H, ArH). ¹³C{¹H} NMR data for *cis*-5b (75.5 MHz, CD₂Cl₂): δ -5.2 [J_{WC}(satellite) = 35 Hz, WCH₂Me], 10.4 (C₅Me₅), 20.6 (WCH₂Me), 21.6 (C₆H₄Me), 102.1 (C₅Me₅), 128.9, 129.1, 135.3, 141.4 (ArC), 207.4 (CN), 233.1, 241.8 (CO). ¹³C{¹H} NMR data for *trans*-5b (75.5 MHz, CD₂Cl₂): δ -7.1 $[J_{WC}(satellite) = 32 \text{ Hz}, WCH_2Me], 10.2 (C_5Me_5), 20.7 (WCH_2-$ Me), 21.6 (C₆H₄Me), 101.5 (C₅Me₅), 129.0, 129.1, 135.4, 141.3 (ArC), 211.5 (CN), 228.9 (CO). Anal. Calcd for C₃₆H₄₁NO₂-SiW: C, 59.10; H, 5.65; N, 1.91. Found: C, 59.24; H, 5.60; N, 1.95.

Formation of η^3 -1-Azaallyl Complex Cp*(CO)₂W{ η^3 -HMeCC(H)/NSi(*p*-Tol)₃} (6) on the Thermal Reaction of 3b. A Pyrex NMR tube was charged with a solution of complex 3b (42 mg, 0.057 mmol) and Si(SiMe₃)₄ (less than 1 mg, internal standard) in toluene- d_8 (0.5 mL). This NMR tube was attached

to a vacuum line and flame-sealed under high vacuum. This sealed tube was heated at 120 °C, and the reaction was monitored by ¹H NMR spectroscopy. After 2 weeks, not only complex 5b (24% NMR yield, cis/trans mixture) but also complex 6 (46% NMR yield) were observed in the 1 H and ¹³C{¹H} NMR spectra. The NMR yields were determined by comparing the intensity of the Cp* signal of **5b** or **6** in the ¹H NMR spectrum of the reaction mixture to that of the internal standard. The molar ratio of the *cis/trans* isomers of **5b** is major: minor = 1.3:1 based on the intensity ratio of their Cp* signals, but we could not determine which isomer is the major component. NMR signals assignable to 6 in the reaction mixture: ¹H NMR (300 MHz, toluene- d_8): δ 1.54 (s, 15H, Cp*), 1.76 [d, J =6.0 Hz, 3H, HMeCC(H)N], 2.14 (s, 9H, C_6H_4Me), 2.30 [dq, J =6.0, 6.9 Hz, 1H, HMeCC(H)N], 5.20 [d, J = 6.9 Hz, 1H, HMe-CC(H)N], 7.07 (d, J = 7.8 Hz, 6H, ArH), 7.81 (d, J = 7.8 Hz, 6H, ArH). ¹³C{¹H} NMR (75.5 MHz, toluene- d_8): δ 10.5 (C₅M e_5), 16.8 [HMeCC(H)N], 21.4 (C₆H₄Me), 59.7 [HMeCC(H)N], 103.9 (C5Me5), 113.5 [HMeCC(H)N], 237.8, 240.1 (CO); aromatic carbons could not be assigned.

X-ray Crystal Structure Determination. Selected crystallographic data for 3b and cis-5b are summarized in Table 4. X-ray quality single crystals of **3b** were obtained from hexane at -35 °C as red blocks. Recrystallization of a cis/trans mixture of **5b** from toluene at room temperature gave an X-ray quality single crystal of *cis*-5b as a yellow plate. Intensity data for the analysis were collected on a Rigaku RAXIS-RAPID imaging plate or a Rigaku Saturn CCD diffractometer with graphitemonochromated Mo K α radiation ($\lambda = 0.71069$ Å) under a cold nitrogen stream [T = 150 K (for 3b) and 173 K (for cis-5b)].Numerical absorption corrections were applied to the data. The structures were solved by the Patterson method using the DIRDIF-99 program²¹ and refined by full matrix least-squares techniques on all F^2 data with SHELXL-97.²² Anisotropic refinement was applied to all non-hydrogen atoms, and all the hydrogen atoms were put at calculated positions. CCDC reference numbers: 765983 (3b) and 765984 (cis-5b). Crystallographic data are available as a CIF file.

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Supporting Information Available: ¹H NMR spectra of complexes **B**, **4a**, and **4b** 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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