η^2-Alkynyl and Vinylidene Transition Metal Complexes. 7.[1] Hydroamination of Neutral Tungsten−Vinylidene Complexes

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Primary and secondary amines **2a**−**d** have been found to react in THF at room temperature with the vinylidene complexes [W(=C=CHR)(η^5-C_5H_5)(CO)(NO)] (R = $C(CH_3)_3$ (**1**), R = $Si(CH_3)_2C(CH_3)_3$ (**4**)), affording the aminocarbene derivatives [W{=C(NR^1R^2)$CH_2C(CH_3)_3$}(η^5-C_5H_5)(CO)(NO)] and [W{=C(NR^1R^2)$CH_2Si(CH_3)_2C(CH_3)_3$}(η^5-C_5H_5)(CO)(NO)] (R^1 = H, R^2 = *n*-C_4H_9 (**3a**, **5a**); R^1 = H, R^2 = $CH(CH_3)_2$ (**3b**, **5b**); R^1 = H, R^2 = $C(CH_3)_3$ (**3c**, **5c**); R^1 = R^2 = $(CH_2)_4$ (**3d**, **5d**)). At short reaction time the nucleophilic addition of both primary and secondary amines to **1** occurs at the carbonyl carbon atom, leading stereoselectively to the thermodynamically less stable η^2-carbamoyl-(*Z*)-vinyl complexes [W{σ-(*Z*)-CH=CHC$(CH_3)_3$}-{η^2-C(O)NR^1R^2}(η^5-C_5H_5)(NO)] (R^1 = H, R^2 = *n*-C_4H_9 (**6a**); R^1 = H, R^2 = $CH(CH_3)_2$ (**6b**); R^1 = H, R^2 = $C(CH_3)_3$ (**6c**); R^1 = R^2 = $(CH_2)_4$ (**6d**)). At higher amine concentration and prolonged reaction time **6a**−**d** form the corresponding aminocarbene complexes **3a**−**d**. The structure of **6b** has been authenticated by a single-crystal X-ray diffraction analysis.

Introduction

Nucleophilic addition to unsaturated ligands such as alkynes, alkenes, and vinylidenes coordinated to a transition-metal center is involved as a key step in various stoichiometric and catalytic transformations mediated by organometallic species.[2] Several examples of addition of nucleophiles, including water,[3] alcohols,[3a,e,g,4] and thiols,[3e,5] as well as the addition of phosphines,[6] to vinylidene complexes have been reported. In general the chemical reactivity of the vinylidene moiety is oriented toward electrophilic attack at the β-carbon atom and nucleophilic attack at the α-carbon atom.[7] Theoretical studies also predict the electron deficiency at the α-carbon and the localization of electron density in the M=C double bond and at the β-carbon.[8,9]

The additions of primary amines to cationic vinylidene complexes have been found to give aminocarbene derivatives.[3e] It is believed that this hydroamination reaction proceeds via a nucleophilic attack at the vinylidene α-carbon atom by the amine, followed by proton transfer (two steps), or as an intermolecular-concerted process (Scheme 1).[10]

Recently for a monosubstituted ruthenium vinylidene complex a mechanism involving 2 equiv of amine was postulated. In the first step of the reaction one molecule of amine deprotonates the vinylidene β-carbon atom, while a second one coordinates the metal center prior to a transfer onto the α-carbon atom of a σ-alkynyl intermediate.[10]

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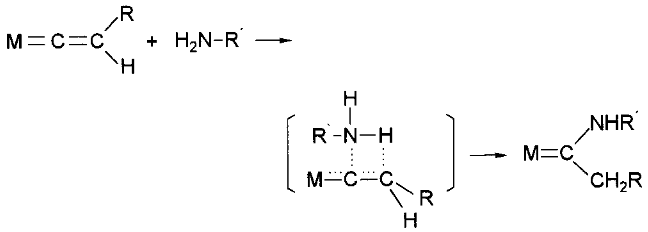
Scheme 1



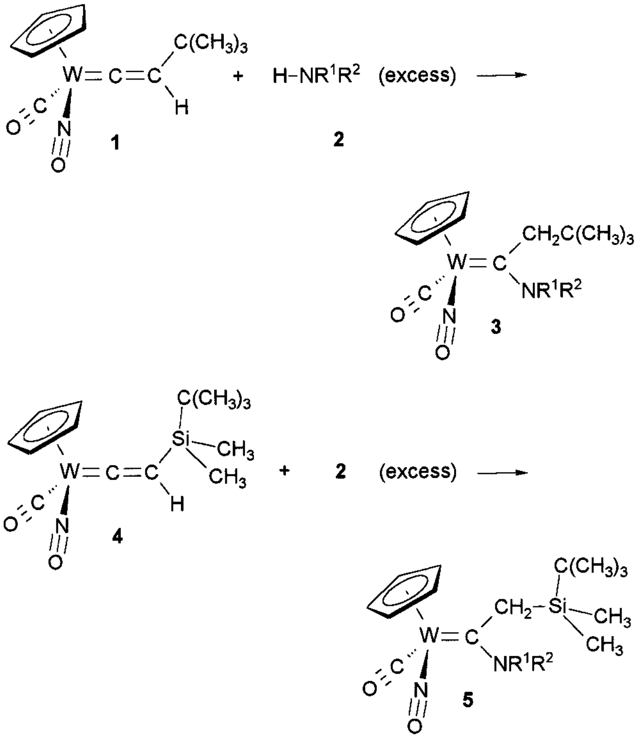
Intending to explore the reactivity of neutral tungsten vinylidene complexes, we investigated the reaction of monosubstituted vinylidene complexes **1** and **4** with a variety of amines. As a result, we have discovered an interesting pathway for the synthesis of complexes with a η^2-carbamoyl group[11] and a vinyl moiety.[12] This paper describes the hydroamination of **1** and **4** to the aminocarbene derivatives **3a**–**d** and **5a**–**d**, the synthesis of the η^2-carbamoyl-(*Z*)-vinyl complexes **6a**–**d**, and the X-ray diffraction analysis of **6b**.

Results and Discussion

Because of the presence of two electrophilic centers, CO and the vinylidene moiety, the tungsten vinylidene complex **1** shows a dichotomic behavior in reaction with amines. Treatment of **1** with a 20-fold excess of primary or secondary aliphatic amines **2a**–**d** in THF at room temperature leads to the aminocarbenes **3a**–**d** as a mixture of two rotamers by nucleophilic addition to the α-carbon atom of the vinylidene ligand (Scheme 2).[13] Similarly, addition of **2a**–**d** to a solution of **4** gives rise to the aminocarbenes **5a**–**d**. The rates of the formation of the aminocarbenes appear to be dependent upon the steric properties of the amines. While the addition of amine **2a** needs a few hours, the addition of **2c** requires 2 days to be completed.

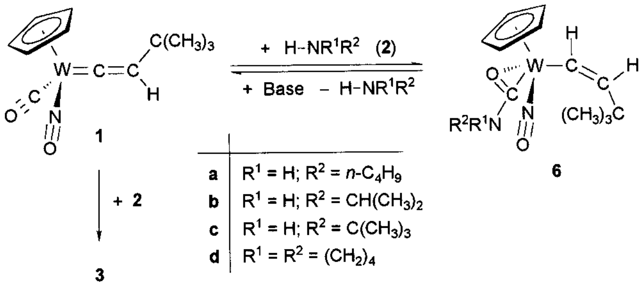
In contrast to the aminocarbenes **5a**,**b**,**d**, further purification was necessary for complexes **3a**–**d**. Because of the sensitivity of these compounds to silica gel, which was used for chromatography, the yields are very low (around 30%). Compounds **3a** and **5a**–**d** are dark red viscous oils, and the remaining aminocarbenes are rose-colored (**3b**,**d**) or dark orange crystalline solids (**3c**) with good solubility in polar organic solvents. All aminocarbenes can be stored under an argon atmosphere at −20 °C for a few days. Their unequivocal characterization was achieved by means of standard spectroscopic techniques, particularly the ^{13}C NMR signal at 252–262 ppm, characteristic for the α-carbon atom of the aminocarbenes, as well as elemental analyses, which were all consistent with the incorporation of one molecule of amine into the complex framework.

Scheme 2



a	$R^1 = H$; $R^2 = n\text{-}C_4H_9$
b	$R^1 = H$; $R^2 = CH(CH_3)_2$
c	$R^1 = H$; $R^2 = C(CH_3)_3$
d	$R^1 = R^2 = (CH_2)_4$

Scheme 3



Carbamoyl–Vinyl Complexes 6a–d. In a fast reaction, the nucleophilic addition of primary and secondary amines **2a**–**d** to vinylidene complex **1** occurs first at the carbonyl carbon atom. Immediately after the color of the solution brightened up, the solvent and the excessive amine were removed under reduced pressure. The solid residue was dissolved in CH_2Cl_2, and addition of *n*-pentane gave beige (**6a**–**c**) or brown crystals (**6d**) of the η^2-carbamoyl-(*Z*)-vinyl complexes of the general formula $[W\{\sigma\text{-}(Z)\text{-}CH{=}CHC(CH_3)_3\}\{\eta^2\text{-}C(O)NR^1R^2\}(\eta^5\text{-}C_5H_5)(NO)]$ (Scheme 3). The crystals of **6a**–**d** can be stored without decomposition under an argon atmosphere at −20 °C for several months. The structure of the products were fully characterized by spetroscopic

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(11) See, for example: (a) Anderson, S.; Cook, D. J.; Hill, A. F. *Organometallics* **1997**, *16*, 5595–5597. (b) Ishida, T.; Yasushi, M.; Tanase, T.; Hidai, M. *J. Organomet. Chem.* **1991**, *409*, 355–365. (c) Durfee, L. D.; Rothwell, I. P. *Chem. Rev.* **1988**, *88*, 1059–1079. (d) Fagan, P. J.; Manriquez, J. M.; Vollmer, S. H.; Day, C. S.; Day, V. W.; Marks, T. J. *J. Am. Chem. Soc.* **1981**, *103*, 2206–2220. (e) Müller, A.; Seyer, U.; Eltzner, W. *Inorg. Chim. Acta* **1979**, *32*, L65–66.

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(13) Aromatic amines such as aniline and tertiary amines such as dimethylethylamine do not react with **1** and **4**.

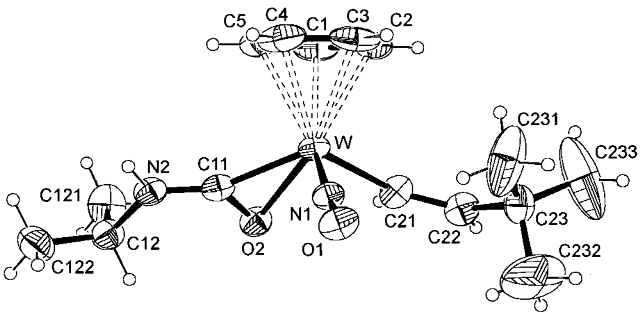

Figure 1. Molecular structure and atom-numbering scheme for [W{σ-(*Z*)-CH=CHC(CH_3)$_3$}{η^2-C(O)NCH(CH_3)$_2$}(η^5-C_5H_5)(NO)] (**6b**) with H atoms and thermal ellipsoids shown at the 30% probability level (ORTEP drawing).

methods, elemental analyses, and X-ray crystallographic studies of **6b**.

Spectroscopic Characterization. Significantly, the IR spectra of the carbamoyl−vinyl complexes exhibit a strong carbonyl band in the 1542−1551 cm^{-1} region. The substantially low C−O stretching frequency observed for **6a**−**d** is consistent with the η^2-coordination mode of the carbamoyl ligand.[11b,d] The nitrosyl group gives rise to a strong absorption in the range of 1626−1645 cm^{-1}, and the medium IR band at 3190−3197 cm^{-1} can be assigned to the N−H stretching vibration of **6a**−**c**.

The ^1H and ^{13}C NMR spectra show double sets of signals for **6a**,**b**,**d**, because these complexes exist in solution as a mixture of rotational isomers. No conclusion can be made whether the rotational barrier around the W−C(alkenyl)[12d] or W−C(carbamoyl) bond[11d,14] is responsible for the rotamers. The most notable feature in the ^{13}C NMR spectra of the carbamoyl−vinyl complexes is a signal in the region of 200 ppm, which is assigned to the carbamoyl carbon atom. Complexes **6a**−**d** show for the vinylic proton α to tungsten in the ^1H NMR spectra a signal at 6.45−7.07 ppm and for the proton β to tungsten a signal in the range of 7.10−7.27 ppm. These signals appear with the corresponding satellite signals caused by the coupling with the ^{183}W atom (14% ^{183}W abundance; $I = {}^1/_2$): $^2J_{H-W} \approx 12$ Hz for H_α and $^3J_{H-W} \approx 9.5$ Hz for H_β. Because of the interaction of the tungsten atom with the vinyl π-system the $^3J_{H-H}$ coupling constant for the vinyl protons of ∼13.5 Hz is comparatively large for a *Z*-configured vinyl group.

Table 1. Crystal Data and Conditions for Crystallographic Data Collection and Structure Refinement for 6b

formula	$C_{15}H_{24}N_2O_2W$
fw	448.22
cryst size	0.42 × 0.27 × 0.15 mm
color	beige, transparent
cryst syst	triclinic
space group	$P\bar{1}$ (No. 2)
lattice constants	$a = 7.5194(8)$ Å $b = 10.5859(13)$ Å $c = 11.4778(15)$ Å $\alpha = 91.200(15)°$ $\beta = 96.713(14)°$ $\gamma = 107.345(13)°$
vol	864.60(18) $Å^3$
formula units per unit cell	$Z = 2$
density (calcd)	1.718 g cm^{-3}
linear abs coeff	66.83 cm^{-1}
diffractometer	image plate diffractometer system (STOE)
radiation	Mo Kα ($\lambda = 0.710\ 73$ Å)
monochromator	graphite
temp	293 K
scan range	$5.2° \leq 2\theta \leq 56.1°$ $-9 \leq h \leq 9, -13 \leq k \leq 13, -14 \leq l \leq 15$
no. of rflns measd	7625
no. of indep rflns	3786
R_{int}	0.024
no. of indep rflns with $F_o > 4\sigma(F_o)$	3239
applied corrections	Lorentz and polarizan coeffs
structure determination and refinement	W positional parameters from direct methods (program SHELXS-97[a]); further atoms from ΔF synthesis (program SHELXL-97[b]), structure refinement by the anisotropic full-matrix least-squares procedure for all non-hydrogen atoms; hydrogen position refinement by “riding” model; atomic scattering factors from literature[c]
no. of params	181
wR2	0.0674
R1	0.0322
R1 ($F_o > 4\sigma(F_o)$)	0.0247
max and min in $\Delta\sigma$	1.079 and −1.154 e $Å^{-3}$

[a] Sheldrick, G. M. SHELXS-97, Program for the Solution of Crystal Structures; Universität Göttingen, 1997. [b] Sheldrick, G. M. SHELXL-97, Program for Crystal Structure Refinement; Universität Göttingen, 1997. [c] *International Tables for Crystallography*; Wilson, A. J. C., Ed.; Kluwer Academic: Dordrecht, The Netherlands, 1992; Vol. C.

Table 2. Selected Bond Distances (Å) and Angles (deg) for 6b

Distances			
W−C(11)	2.036(5)	C(21)−C(22)	1.332(8)
W−O(2)	2.202(4)	C(22)−C(23)	1.501(9)
C(11)−O(2)	1.273(6)	range W−C(Cp)	2.287(6)−2.402(5)
C(11)−N(2)	1.305(6)		
N(2)−C(12)	1.481(7)	W−N(1)	1.754(4)
W−C(21)	2.161(5)	N(1)−O(1)	1.232(5)
Angles			
N(1)−W−C(11)	96.12(18)	O(2)−C(11)−N(2)	126.6(5)
N(1)−W−C(21)	97.90(18)	O(2)−C(11)−W	79.9(3)
C(11)−W−C(21)	115.2(2)	N(2)−C(11)−W	153.5(4)
N(1)−W−O(2)	102.00(17)	C(11)−O(2)−W	65.5(3)
C(11)−W−O(2)	34.67(16)	C(11)−N(2)−C(12)	124.1(4)
C(21)−W−O(2)	80.52(19)	C(22)−C(21)−W	141.4(4)
O(1)−N(1)−W	171.8(4)	C(21)−C(22)−C(23)	133.1(5)

Molecular Structure of 6b. Suitable single crystals of [W{σ-(*Z*)-CH=CHC(CH_3)$_3$}{η^2-C(O)NHCH(CH_3)$_2$}(η^5-C_5H_5)(NO)] (**6b**) were obtained upon slow diffusion of *n*-pentane into a solution of **6b** in dichloromethane at −15 °C. The ORTEP drawing with atomic numbering scheme is provided in Figure 1, the crystallographic data are summarized in Table 1, and a list of selected bond distances and angles is given in Table 2. The geometry around the tungsten atom in **6b** is a pseudo four-legged piano-stool configuration. The vinyl ligand σ-bonded to the tungsten atom forms one of the four legs of the pianoo stool and has a *Z* stereochemistry. The W−C(vinyl) bond length of 2.161(5) Å implies some π contribution to W−vinyl bonding via interaction of filled orbitals on the metal and the π^* orbital of the vinyl ligand and is shorter than the bond length in the tungsten vinyl complex such as $[\{\overline{W{=}C(OEt)(CHPh)_2C}{=}C(Me)CH(OEt)(NEt_2)\}(CO)_4]$ (2.275(12) Å).[12c] The deviations of the W−C=C and C=C−C(CH_3)$_3$ angles (141.4(4) and 133.1-

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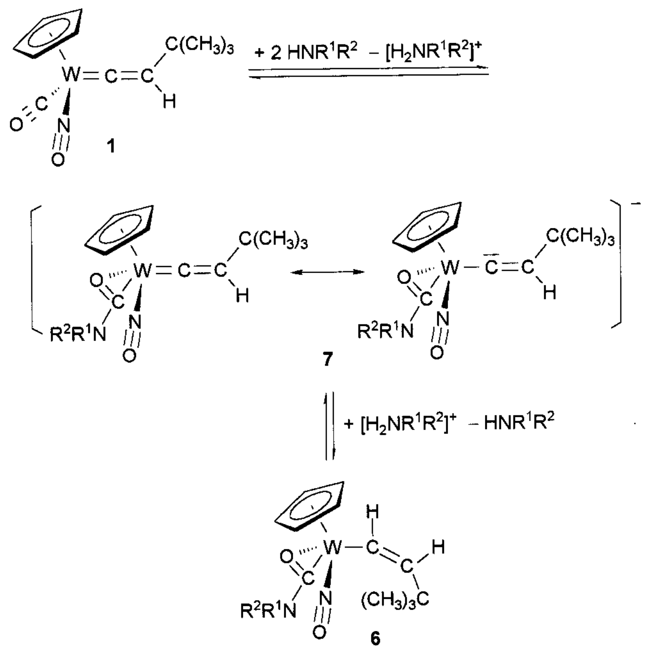
(14) Erker, G.; Rosenfeldt, F. *J. Organomet. Chem.* **1980**, *188*, C1−C4.

Scheme 4



(5)°) from the ideal value 120° of a C(sp^2) angle further reflects this interaction. The carbamoyl ligand is coordinated in η^2 fashion and is coplanar with atoms W, C11, O2, N2, and C12 (dihedral angle W−O2−C11−N2 = 178.9° and O2−C11−N2−C12 = −3.2°) (Figure 1), indicating a stabilization of the arrangement due to an interaction of the π system with the metal. This is confirmed by the short W−C(carbamoyl) bond length of 2.036(5) Å.

Mechanistic Considerations. Primarily, with a short reaction time, the nucleophilic attack of amines **2a**−**d** occurs on the complex **1** at the carbonyl carbon atom to afford the η^2-carbamoyl-(*Z*)-vinyl complexes **6a**−**d**. In the presence of an excess of the appropriate amine the complexes **6a**−**d** are not stable and undergo an elimination reaction to generate the starting materials. With a longer reaction time the amine attacks again the complex **1** and leads via addition to the C_α of the vinylidene moiety to the aminocarbenes **3a**−**d** (Scheme 3). Experimental evidence of this mechanism was provided by the following observation: in the presence of aniline or dimethylethylamine, which are unreactive toward vinylidene **1**, the complexes **6a**−**d** are not stable and create an equilibrium mixture of vinylidene **1** and the corresponding η^2-carbamoyl−vinyl complex as well as the aminocarbene derivative.[15] Treating **6a** with dimethylethylamine generates a mixture of **6a**, **1**, and aminocarbene **3a** in a ratio of 2:2:1 after 6 h. After longer reaction time the concentration of **6a** and **1** diminish and the amount of **3a** increases. We suggest that the initial formation of the thermodynamically less stable *Z* isomers of the η^2-carbamoyl−vinyl complexes **6a**−**d** proceeds in two steps (Scheme 4). First the addition of amines **2a**−**d** to the carbonyl group of **1** generates the anion **7**, which is protonated by an ammonium ion anti to the *tert*-butyl group due to the bulky size of this substituent. The outcome of the reaction is the formation of a vinyl moiety, which resembles formally an addition of hydride to the C_α atom of the vinylidene group.[12b,g]

Monitoring the reaction of vinylidene **4** and *n*-butylamine by ^{1}H NMR spectroscopy in THF-d_8 did not show any carbamoyl derivatives along with the formation of the aminocarbene **5a**. Obviously in the case of complex **4**, amine attack occurs only at the vinylidene C_α atom, because a negative charge at the position β to the tungsten atom can be stabilized by the α effect of the silyl group.[16]

Concluding Remarks. It is shown that the outcome of the additions depends on the vinylidene precursor leading stereoselectively to η^2-carbamoyl-(*Z*)-vinyl complexes in a short reaction time when a *tert*-butyl-substituted vinylidene complex is used as a precursor. These results show a novel reactivity pattern in the nucleophilic addition of amines to vinylidene complexes bearing carbonyl ligands as competitive electrophilic sites. We believe that the η^2-carbamoyl−vinyl complexes are not intermediates in the pathway to the appropriate aminocarbenes because the η^2-carbamoyl−vinyl complexes form an equilibrium mixture with the starting materials in the presence of an excess of amine.

Experimental Section

General Considerations. All reactions were carried out under an argon atmosphere (99.99%, by Messer-Griesheim) with the use of standard Schlenk techniques. Solvents were purified by standard methods and distilled under argon prior to use. Literature methods were used to prepare [W(η^5-C_5H_5)(CO)$_2$(NO)],[17] (*tert*-butyldimethylsilyl)acetylene,[18] and [W{=C=CHC(CH$_3$)$_2$}(η^5-C_5H_5)(CO)(NO)] (**4**).[19] Amines were purchased from Fluka, their purity was checked by ^{1}H NMR spectroscopy, and, when necessary, they were dried over KOH and distilled from CaH$_2$ under an argon atmosphere prior to use. All other compounds were commercially available. NMR spectra were obtained on Bruker AM 400 and AC 200 spectrometers. Proton and carbon chemical shifts are reported in ppm relative to the residual proton resonance (7.24 ppm) or the carbon multiplet (77.0 ppm) of the NMR solvent CDCl$_3$. ^{13}C-DEPT, ^{1}H,^{13}C-2D correlation, and ^{1}H,^{13}C-2D COLOC NMR experiments were run on the Bruker AM 400 spectrometer. MS measurements (70 eV) were performed on a Varian MAT 311-A. IR spectra were recorded on a Bruker FT-IR IFS 85. Microanalyses were done on a Carlo Erba 1104 elemental analyzer.

Preparation of Compounds. [W{=C=CHSi(CH$_3$)$_2$C(CH$_3$)$_3$}(η^5-C_5H_5)(CO)(NO)] (4). At −78 °C 3 mL (4.5 mmol) of *n*-BuLi (a solution of 1.5 mmol/mL in hexane) was added to a solution of 0.63 g (4.5 mmol) of (*tert*-butyldimethylsilyl)acetylene in 10 mL of THF. This soltution was added to 1.0 g (3.0 mmol) of [W(η^5-C_5H_5)(CO)$_2$(NO)] in 60 mL of THF, whereby the color changed from orange to deep green. Addition of 1 mL of concentrated HCl diluted with 20 mL of water led to a dark red solution. After the reaction mixture was allowed to reach room temperature, the THF was removed under reduced pressure. The residue was extracted with diethyl ether, washed with saturated aqueous sodium chloride, and

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[15] Also, ^{1}H NMR spectroscopy shows the presence of a small amount of vinylidene **1**, and some decomposed products which could not be identified, when a solution of the η^2-carbamoyl−vinyl complex **6a** in CDCl$_3$ was allowed to stand for several hours at room temperature.

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dried over magnesium sulfate. Chromatography of the dark red oil on silica gel with 3:1 *n*-pentane/diethyl ether yielded 0.85 g (63%) of **4** as orange crystals, mp 62 °C. Anal. Calcd for $C_{14}H_{21}NO_2SiW$: C, 37.60; H, 4,73, N, 3.13. Found: C, 37.49; H, 4.38; N, 3.29. Two rotamers were found in the NMR spectra. ^{1}H NMR (CDCl$_3$, 400.13 MHz): δ 5.75 (s, 5H, Cp), 5.70 and 5.66 (2 s, 2:3, 1H, C_βH), 0.92 and 0.89 [2 s, 3:2, 9H, Si(CH$_3$)$_2$C(C*H*$_3$)$_3$], 0.14 and 0.10 [2 s, 2:3, 6H, Si(C*H*$_3$)$_2$C(CH$_3$)$_3$]. ^{13}C NMR (CDCl$_3$, 100.61 MHz): δ 332.7 and 330.7 (2 C_α), 213.9 and 213.0 (2 CO), 118.7 and 117.7 (2 C_β), 95.4 and 95.3 (2 Cp), 26.2 [2 Si(CH$_3$)$_2$C(*C*H$_3$)$_3$], 17.6 and 17.2 [Si(CH$_3$)$_2$*C*(CH$_3$)$_3$], −4.5 and −4.7 [2 Si(*C*H$_3$)$_2$C(CH$_3$)$_3$]. IR (KBr; $\tilde{\nu}$ (cm^{-1})): 1992 (s, C═O), 1653 (s, N≡O), 1601 (s, C═C). MS (70 eV): *m/e* 447 (M$^+$, ^{184}W), 419 (M$^+$ − CO). High-resolution mass spectrum: *m/e* calcd for $C_{14}H_{21}NO_2Si^{182}W$ (M$^+$) 445.0825, found 445.0806.

Synthesis of the Aminocarbene Complexes [W{═C(NR^{1}R^2)CH$_2$C(CH$_3$)$_3$}(η^5-C$_5$H$_5$)(CO)(NO)] (R^1 = H, R^2 = *n*-C$_4$H$_9$ (3a); R^1 = H, R^2 = CH(CH$_3$)$_3$ (3b); R^1 = H, R^2 = C(CH$_3$)$_3$ (3c); R^1 = R^2 = (CH$_2$)$_4$ (3d)). General Procedure. A 20-fold excess of the appropriate primary amine (NH$_2$R; R = *n*-C$_4$H$_9$, CH(CH$_3$)$_3$, C(CH$_3$)$_3$) or secondary amine (pyrrolidine) was syringed at room temperature into a stirred red solution of the vinylidene complex **1** (0.50 g, 1.29 mmol) in 25 mL of THF. The color of the reaction mixture brightened and was dark red in the end. When the reaction was complete, the volatile components were removed under reduced pressure. After evaporation to dryness under vacuum the residue was chromatographed on silica gel with 1:1 *n*-pentane/diethyl ether. In the case of a solid residue the product was recrystallized additionally from CH$_2$Cl$_2$ and *n*-pentane.

[W{═C(NH-*n*-C$_4$H$_9$)CH$_2$C(CH$_3$)$_3$}(η^5-C$_5$H$_5$)(CO)(NO)] (3a): reaction time 7 h, dark red viscous oil (210 mg, 35%). Anal. Calcd for $C_{16}H_{26}N_2O_2W$: C, 41.57; H, 5.67, N, 6.06. Found: C, 41.44; H, 5.56; N, 5.83. Two rotamers were found in the NMR spectra. ^{1}H NMR (CDCl$_3$, 400.13 MHz): δ 7.31 (br s, 1H, N*H*), 5.54 ($^2J_{H-W}$ = 8.9 Hz) and 5.52 (2 s, 15:1, 5H, Cp), 3.52−3.40 and 3.23−3.18 (2 m, 15:1, 2H, C*H*$_2$CH$_2$CH$_2$CH$_3$), 2.92 ($^2J_{H-H}$ = 12.8 Hz), 2.86 (12.3 Hz), 2.61 (12.3 Hz) and 2.40 (12.8 Hz) (4 d, AB system, 1:15:1:15, 2H, C*H*$_2$C(CH$_3$)$_3$), 1.70−1.62 (m, 2H, CH$_2$C*H*$_2$CH$_2$CH$_3$), 1.47−1.37 (m, 2H, CH$_2$CH$_2$C*H*$_2$CH$_3$), 1.17 ($^3J_{H-H}$ = 7.1 Hz) and 0.94 (7.4 Hz) (2 t, 1:15, 3H, CH$_2$CH$_2$CH$_2$C*H*$_3$), 1.00 and 0.95 [2 s, 1:15, 9H, C(C*H*$_3$)$_3$]. ^{13}C NMR (CDCl$_3$, 100.61 MHz): δ 262.0 ($^1J_{C-W}$ = 159.5 Hz) (carbene C), 232.0 (CO), 93.9 and 93.8 (Cp), 66.5 [*C*H$_2$C(CH$_3$)$_3$], 52.5 (*C*H$_2$CH$_2$CH$_2$CH$_3$), 33.0 [*C*(CH$_3$)$_3$], 31.4 (CH$_2$*C*H$_2$CH$_2$CH$_3$), 31.0 and 29.8 [C(*C*H$_3$)$_3$], 20.4 (CH$_2$CH$_2$*C*H$_2$CH$_3$), 13.7 (CH$_2$CH$_2$CH$_2$*C*H$_3$). IR (KBr; $\tilde{\nu}$ (cm^{-1})): 3265 (w, N−H), 1905 (s, C═O), 1559 (s, N≡O). MS (70 eV): *m/e* 462 (M$^+$, ^{184}W), 434 (M$^+$ − CO). High-resolution mass spectrum: *m/e* calcd for $C_{16}H_{26}N_2O_2{}^{182}W$ (M$^+$) 460.1477, found 460.1453.

[W{═C(NHCH(CH$_3$)$_2$)CH$_2$C(CH$_3$)$_3$}(η^5-C$_5$H$_5$)(CO)(NO)] (3b): reaction time 15 h, rose-colored crystals (223 mg, 39%; mp 143 °C). Anal. Calcd for $C_{15}H_{24}N_2O_2W$: C, 40.20; H, 5.40, N, 6.25. Found: C, 40.61; H, 5.27; N, 6.24. Two rotamers were found in the NMR spectra. ^{1}H NMR (CDCl$_3$, 400.13 MHz): δ 7.23 (br s, 1H, NH), 5.55 and 5.51 (2 s, 22:1, 5H, Cp), 4.13−4.04 [m, 1H, C*H*(CH$_3$)$_2$], 2.75 ($^2J_{H-H}$ = 12.8 Hz) and 2.34 (12.8 Hz) [2 d, AB system 2H, C*H*$_2$C(CH$_3$)$_3$], 1.30 ($^3J_{H-H}$ = 2.0 Hz) and 1.28 ($^3J_{H-H}$ = 2.0 Hz) [2 d, diastereotopic methyl groups, 6H, CH(C*H*$_3$)$_2$], 1.01 and 0.95 [2 s, 1:22, 9H, C(CH$_3$)$_3$]. ^{13}C NMR (CDCl$_3$, 100.61 MHz): δ 258.7 ($^1J_{C-W}$ = 159.5 Hz) (carbene-C), 232.7 (CO), 93.8 (Cp), 66.4 [*C*H$_2$C(CH$_3$)$_3$], 53.4 [*C*H(CH$_3$)$_2$], 33.1 [*C*(CH$_3$)$_3$], 31.1 [C(*C*H$_3$)$_3$], 22.8 and 22.7 [CH(*C*H$_3$)$_2$]. IR (KBr; $\tilde{\nu}$ (cm^{-1})): 3267 (m, N−H), 1898 (s, C═O), 1570 (s, N≡O). MS (70 eV): *m/e* 448 (M$^+$, ^{184}W), 420 (M$^+$ − CO). High-resolution mass spectrum: *m/e* calcd for $C_{15}H_{24}N_2O_2{}^{182}W$ (M$^+$) 446.1321, found 446.1348.

[W{═C(NHC(CH$_3$)$_3$)CH$_2$C(CH$_3$)$_3$}(η^5-C$_5$H$_5$)(CO)(NO)] (3c): reaction time 43 h, dark orange crystals (169 mg, 28%; mp 108 °C). Anal. Calcd for $C_{16}H_{26}N_2O_2W$: C, 41.57; H, 5.67, N, 6.06. Found: C, 41.45; H, 5.68; N, 5.84. ^{1}H NMR (CDCl$_3$, 400.13 MHz): δ 7.70 (br s, 1H, NH), 5.59 ($^2J_{H-W}$ = 9.1 Hz) (s, 5H, Cp), 2.49 ($^2J_{H-H}$ = 13.3 Hz) and 2.23 (13.3) [2 d, AB system, 2H, C*H*$_2$C(CH$_3$)$_3$], 1.58 [s, 9H, NHC(C*H*$_3$)$_3$], 0.95 [s, 9H, C(CH$_3$)$_3$]. ^{13}C NMR (CDCl$_3$, 50.32 MHz): δ 258.9 (carbene C), 231.7 (CO), 94.4 (Cp), 67.5 (*C*H$_2$C(CH$_3$)$_3$), 56.2 [NH*C*(CH$_3$)$_3$], 33.5 [*C*(CH$_3$)$_3$], 31.3 [NHC(*C*H$_3$)$_3$], 28.9 [C(*C*H$_3$)$_3$]. IR (KBr; $\tilde{\nu}$ (cm^{-1})): 3278 (m, N−H), 1897 (s, C═O), 1559 (s, N≡O). MS (70 eV): *m/e* 462 (M$^+$, ^{184}W), 434 (M$^+$ − CO). High-resolution mass spectrum: *m/e* calcd for $C_{16}H_{26}N_2O_2{}^{182}W$ (M$^+$) 460.1477, found 460.1512.

[W{═C(cyclo-NC$_4$H$_8$)CH$_2$C(CH$_3$)$_3$}(η^5-C$_5$H$_5$)(CO)(NO)] (3d): reaction time 7 h, rose-colored crystals (184 mg, 31%; mp 177 °C). Anal. Calcd for $C_{16}H_{24}N_2O_2W$: C, 41.76; H, 5.26, N, 6.09. Found: C, 41.52; H, 4.97; N, 6.21. ^{1}H NMR (CDCl$_3$, 400.13 MHz): δ 5.50 ($^2J_{H-W}$ = 8.9 Hz) (s, 5H, Cp), 3.72−3.59 and 3.39 (m and br s, 4H, C*H*$_2$CH$_2$CH$_2$C*H*$_2$), 2.96 ($^2J_{H-H}$ = 10.1 Hz) [br d, 2H, C*H*$_2$C(CH$_3$)$_3$], 2.02−1.91 (m, 4H, CH$_2$C*H*$_2$C*H*$_2$CH$_2$), 1.01 [s, 9H, C(CH$_3$)$_3$]. ^{13}C NMR (CDCl$_3$, 100.61 MHz): δ 258.3 (carbene C), 236.1 (CO), 93.9 (Cp), 61.2 and 60.7 [*C*H$_2$C(CH$_3$)$_3$], 52.1 and 45.2 (*C*H$_2$CH$_2$CH$_2$*C*H$_2$), 33.5 [*C*(CH$_3$)$_3$], 31.3 [C(*C*H$_3$)$_3$], 25.6 and 25.0 (CH$_2$*C*H$_2$*C*H$_2$CH$_2$). IR (KBr; $\tilde{\nu}$ (cm^{-1})): 1878 (s, C═O), 1574 (s, N≡O). MS (70 eV): *m/e* 460 (M$^+$, ^{184}W), 430 (M$^+$ − NO). High-resolution mass spectrum: *m/e* calcd for $C_{16}H_{24}N_2O_2{}^{182}W$ (M$^+$) 458.1321, found 458.1354.

Synthesis of the Aminocarbene Complexes [W{═C(NR^{1}R^2)CH$_2$Si(CH$_3$)$_2$C(CH$_3$)$_3$}(η^5-C$_5$H$_5$)(CO)(NO)] (R^1 = H, R^2 = *n*-C$_4$H$_9$ (5a); R^1 = H, R^2 = CH(CH$_3$)$_2$ (5b); R^1 = H, R^2 = C(CH$_3$)$_3$ (5c); R^1 = R^2 = (CH$_2$)$_4$ (5d)). General Procedure. A 20-fold excess of the appropriate primary amine (NH$_2$R; R = *n*-C$_4$H$_9$, CH(CH$_3$)$_2$, C(CH$_3$)$_3$) or secondary amine (pyrrolidine) was syringed at room temperature into a stirred solution of the vinylidene complex **4** (0.50 g, 1.29 mmol) in 25 mL of THF. The color of the reaction mixture changed from orange to red. When the reaction was complete, the volatile components were removed under reduced pressure and dried under vacuum. The samples were spetroscopically pure, and no effort was made for any further purification.

[W{═C(NH-*n*-C$_4$H$_9$)CH$_2$Si(CH$_3$)$_2$C(CH$_3$)$_3$}(η^5-C$_5$H$_5$)(CO)(NO)] (5a): reaction time 1 h, dark red viscous oil (quantitative yield). Anal. Calcd for $C_{18}H_{32}N_2O_2SiW$: C, 41.54; H, 6.20, N, 5.38. Found: C, 41.64; H, 6.59; N, 5.70. Two rotamers were found in the NMR spectra. ^{1}H NMR (CDCl$_3$, 400.13 MHz): δ 7.81 and 6.98 (2 br s, 2:3, 1H, NH), 5.55 ($^2J_{H-W}$ = 8.9 Hz) and 5.51 (8.9 Hz) (2 s, 3:2, 5H, Cp), 3.58−3.42, 3.37−3.28, and 3.17−3.09 [4 m (partly overlapping), diastereotopic protons, 2H, C*H*$_2$CH$_2$CH$_2$CH$_3$], 2.85 ($^2J_{H-H}$ = 10.9 Hz), 2.59 (12.0 Hz), 2.46 (10.9 Hz), and 2.42 (12.1 Hz) [4 d, AB system, 2:3:2:3, 2H, C*H*$_2$Si(CH$_3$)$_2$C(CH$_3$)$_3$], 1.70−1.60 (m, 2H, CH$_2$C*H*$_2$CH$_2$CH$_3$), 1.48−1.36 (m, 2H, CH$_2$CH$_2$C*H*$_2$CH$_3$), 0.96 ($^3J_{H-H}$ = 7.3 Hz) and 0.95 (7.3 Hz) (2 t, 3:2, 3H, CH$_2$CH$_2$CH$_2$C*H*$_3$), 0.90 and 0.87 [2 s, 2:3, 9H, Si(CH$_3$)$_2$C(C*H*$_3$)$_3$], 0.11 ($^2J_{H-Si}$ = 5.9 Hz), 0.07, 0.06, and 0.01 ($^2J_{H-Si}$ = 5.9 Hz) [4 s, diastereotopic methyl groups, 2:3:2:3, 6H, Si(C*H*$_3$)$_2$C(CH$_3$)$_3$]. ^{13}C NMR (CDCl$_3$, 100.61 MHz): δ 259.7 and 259.3 (carbene C), 236.5 and 233.0 (CO), 93.7 and 93.6 (Cp), 52.3 and 46.8 (*C*H$_2$CH$_2$CH$_2$CH$_3$), 43.3 and 37.8 [*C*H$_2$Si(CH$_3$)$_2$C(CH$_3$)$_3$], 31.7 and 31.4 (CH$_2$*C*H$_2$CH$_2$CH$_3$), 26.3 [Si(CH$_3$)$_2$C(*C*H$_3$)$_3$], 20.4 and 20.1 (CH$_2$CH$_2$*C*H$_2$CH$_3$), 17.5 and 17.0 [Si(CH$_3$)$_2$*C*(CH$_3$)$_3$], 13.8 and 13.7 (CH$_2$CH$_2$CH$_2$*C*H$_3$), −4.1, −4.7, −5.5 and −6.1 [Si(*C*H$_3$)$_2$C(CH$_3$)$_3$]. IR (KBr; $\tilde{\nu}$ (cm^{-1})): 3260 (w, N−H), 1901 (s, C═O), 1559 (s, N≡O). MS (70 eV): *m/e* 520 (M$^+$, ^{184}W), 492 (M$^+$ − CO). High-resolution mass spectrum: *m/e* calcd for $C_{18}H_{32}N_2O_2Si^{182}W$ (M$^+$) 518.1716, found 518.1713.

[W{═C(NHCH(CH$_3$)$_2$)CH$_2$Si(CH$_3$)$_2$C(CH$_3$)$_3$}(η^5-C$_5$H$_5$)(CO)(NO)] (5b): reaction time 3 h, dark red viscous oil (quantitative yield). Anal. Calcd for $C_{17}H_{30}N_2O_2SiW$: C, 40.32; H, 5.97, N, 5.53. Found: C, 40.09; H, 5.89; N, 5.37. Two rotamers were found in the NMR spectra. ^{1}H NMR (CDCl$_3$, 400.13 MHz): δ 7.63 and 6.88 (2 br s, 1:3, 1H, NH), 5.54 ($^2J_{H-W}$ = 9.5 Hz) and 5.50 (8.8 Hz) (2 s, 3:1, 5H, Cp), 4.17−4.08 and 3.75−3.66 [2 m, 3:1, 1H, C*H*(CH$_3$)$_2$], 2.86 ($^2J_{H-H}$ = 11.0 Hz), 2.52 (11.0 Hz) and 2.46 (12.1 Hz), 2.42 (12.1 Hz) [4 d, AB system, 1:1:3:3, 2H, $C\mathit{H}_2Si(CH_3)_2C(CH_3)_3$], 1.29 ($^3J_{H-H}$ = 5.5 Hz), 1.28 (5.5 Hz) and 1.24 (6.6 Hz), 1.20 (6.3 Hz) [4 d, diastereotopic methyl groups, 3:3:1:1, 6H, $CH(C\mathit{H}_3)_2$], 0.89 and 0.86 [2 s, 1:3, 9H, $Si(CH_3)_2C(C\mathit{H}_3)_3$], 0.10, 0.08 ($^2J_{H-Si}$ = 6.6 Hz), 0.04 and 0.01 ($^2J_{H-Si}$ = 6.6 Hz) [4 s, diastereotopic methyl groups, 1:3:1:3, 6H, $Si(C\mathit{H}_3)_2C(CH_3)_3$]. ^{13}C NMR ($CDCl_3$, 100.61 MHz): δ 257.7 and 255.9 (carbene C), 236.7 and 233.8 (CO), 93.7 and 93.6 (Cp), 53.2 and 48.1 [$\mathit{C}H(CH_3)_2$], 43.1 and 37.1 [$\mathit{C}H_2Si(CH_3)_2C(CH_3)_3$], 26.3 and 26.3 [$Si(CH_3)_2C(\mathit{C}H_3)_3$], 23.4 and 23.1 [$CH(\mathit{C}H_3)_2$], 22.8 and 22.4 [$CH(\mathit{C}H_3)_2$], 17.3 and 16.9 [$Si(CH_3)_2\mathit{C}(CH_3)_3$], −4.2, −4.6, −5.5, and −6.4 [$Si(\mathit{C}H_3)_2C(CH_3)_3$]. IR (KBr; $\tilde{\nu}$ (cm^{-1})): 3252 (m, N−H), 1895 (s, C═O), 1558 (s, N≡O). MS (70 eV): *m*/*e* 506 (M^+, ^{184}W), 476 ($M^+ - NO$). High-resolution mass spectrum: *m*/*e* calcd for $C_{17}H_{30}N_2O_2Si^{182}W$ (M^+) 504.1559, found 504.1557.

[W{═C(NHC(CH$_3$)$_3$)CH$_2$Si(CH$_3$)$_2$C(CH$_3$)$_3$}(η^5-C$_5$H$_5$)(CO)(NO)] (5c): reaction time 43 h. Additional chromatography of the residue on silica gel with 3:1 *n*-pentane/diethyl ether was necessary to yield 138 mg (69%) of **5c** as a dark red viscous oil and 7% of vinylidene complex **4**. Anal. Calcd for $C_{18}H_{32}N_2O_2SiW$: C, 41.54; H, 6.20, N, 5.38. Found: C, 41.06; H, 6.22; N, 5.14. Two rotamers were found in the NMR spectra. ^1H NMR ($CDCl_3$, 400.13 MHz): δ 8.01 and 7.39 (2 br s, 1:8, 1H, NH), 5.57 ($^2J_{H-W}$ = 8.9 Hz) and 5.47 (8.9 Hz) (2 s, 8:1, 5H, Cp), 3.31 ($^2J_{H-H}$ = 11.3 Hz), 2.59 (10.8), 2.23 (12.8) and 2.18 (12.8) [4 d, AB system, 1:1:8:8, 2H, $C\mathit{H}_2Si(CH_3)_2C(CH_3)_3$], 1.50 and 1.43 [2 s, 8:1, 9H, $NHC(C\mathit{H}_3)_3$], 0.89 and 0.84 [2 s, 1:8, 9H, $Si(CH_3)_2C(C\mathit{H}_3)_3$], 0.12, 0.08 [$^2J_{H-Si}$ = 5.9 Hz] and 0.03 [3 s, diastereotopic methyl groups, 6H, $Si(C\mathit{H}_3)_2C(CH_3)_3$]. ^{13}C NMR ($CDCl_3$, 100.61 MHz): δ 256.3 [$^1J(^{183}W,^{13}C)$ = 152.2 Hz] (carbene C), 233.2 (CO), 94.2 and 93.7 (Cp), 57.7 and 56.0 [$NH\mathit{C}(CH_3)_3$], 44.4 and 38.8 [$\mathit{C}H_2Si(CH_3)_2C(CH_3)_3$], 31.2 and 29.1 [$NHC(\mathit{C}H_3)_3$], 26.9 and 26.2 [$Si(CH_3)_2C(\mathit{C}H_3)_3$], 16.9 [$Si(CH_3)_2\mathit{C}(CH_3)_3$], −3.3, −4.5, −5.2, and −5.6 [$Si(\mathit{C}H_3)_2C(CH_3)_3$]. IR (KBr; $\tilde{\nu}$ (cm^{-1})): 3326 (w, N−H), 1901 (s, C═O), 1570 (s, N≡O). MS (70 eV): *m*/*e* 520 (M^+, ^{184}W), 492 ($M^+ - CO$), 462 ($M^+ - CO - NO$). High-resolution mass spectrum: *m*/*e* calcd for $C_{18}H_{32}N_2O_2Si^{182}W$ (M^+) 518.1716, found 518.1683.

[W{═C(*cyclo*-NC$_4$H$_8$)CH$_2$Si(CH$_3$)$_2$C(CH$_3$)$_3$}(η^5-C$_5$H$_5$)(CO)(NO)] (5d): reaction time 1 h, dark red viscous oil (quantitative yield). Anal. Calcd for $C_{18}H_{30}N_2O_2SiW$: C, 41.71; H, 5.83, N, 5.40. Found: C, 41.21; H, 5.80; N, 5.22. ^1H NMR ($CDCl_3$, 400.13 MHz): δ 5.49 ($^2J_{H-W}$ = 8.9 Hz) (s, 5H, Cp), 3.77, 3.60−3.53, and 3.48−3.41 (br s and 2 m, 4H, $C\mathit{H}_2CH_2CH_2C\mathit{H}_2$), 2.78 ($^2J_{H-H}$ = 10.8 Hz) and 2.69 [br d and br s, AB system, 2H, $C\mathit{H}_2Si(CH_3)_2C(CH_3)_3$], 2.10−1.90 (m, 4H, $CH_2C\mathit{H}_2C\mathit{H}_2CH_2$), 0.89 [s, 9H, $Si(CH_3)_2C(C\mathit{H}_3)_3$], 0.12 and 0.04 [2 s, diastereotopic methyl groups, 6H, $Si(C\mathit{H}_3)_2C(CH_3)_3$]. ^{13}C NMR ($CDCl_3$, 100.61 MHz): δ 252.4 ($^1J_{C-W}$ = 158.1 Hz) (carbene C), 237.1 (CO), 93.7 (Cp), 60.3 and 51.8 ($\mathit{C}H_2CH_2CH_2\mathit{C}H_2$), 40.8 [$\mathit{C}H_2Si(CH_3)_2C(CH_3)_3$], 26.4 [$Si(CH_3)_2C(\mathit{C}H_3)_3$], 25.9 and 25.3 ($CH_2\mathit{C}H_2\mathit{C}H_2CH_2$), 17.6 [$Si(CH_3)_2\mathit{C}(CH_3)_3$], −3.9 and −6.2 [$Si(\mathit{C}H_3)_2C(CH_3)_3$]. IR (KBr; $\tilde{\nu}$ (cm^{-1})): 1889 (s, C═O), 1576 (s, N≡O). MS (70 eV) *m*/*e* 518 (M^+, ^{184}W), 488 ($M^+ - NO$). High-resolution mass spectrum: *m*/*e* calcd for $C_{18}H_{30}N_2O_2Si^{182}W$ (M^+) 516.1559, found 516.1554.

Synthesis of the η^2-Carbamoyl−(*Z*)-Vinyl Complexes [W{σ-(Z)-CH═CHC(CH$_3$)$_3$}{η^2-C(O)NR^{1}R^2}(η^5-C$_5$H$_5$)(NO)] (R^1 = H, R^2 = *n*-C$_4$H$_9$ (6a); R^1 = H, R^2 = CH(CH$_3$)$_2$ (6b); R^1 = H, R^2 = C(CH$_3$)$_3$ (6c); R^1 = R^2 = (CH$_2$)$_4$ (6d)). General Procedure. A 20-fold excess of the appropriate primary amine (NH_2R; R = *n*-C_4H_9, $CH(CH_3)_2$, $C(CH_3)_3$) or secondary amine (pyrrolidine) was syringed at room temperature into a stirred red solution of the vinylidene complex **1** (0.20 g, 0.51 mmol) in 10 mL of THF. The reaction was stopped immediately when the color of the reaction mixture changed to yellow (**6a**) or brightened up (**6b**−**d**) by rapid removal of the volatile components under reduced pressure. After evaporation to dryness under vacuum the solid residue was dissolved in 1−2 mL of CH_2Cl_2. The solution was cooled to −78 °C. Addition of ca. 10 mL of *n*-pentane gave beige crystals of the carbamoyl−vinyl complex, which were collected on sintered-glass frits and washed with *n*-pentane (2 × 5 mL) before being dried under vacuum.

[W{σ-(Z)-CH═CHC(CH$_3$)$_3$}{η^2-C(O)NH-*n*-C$_4$H$_9$}(η^5-C$_5$H$_5$)(NO)] (6a): reaction time about 1 min, beige crystals (186 mg, 78%; mp 95−97 °C dec). Anal. Calcd for $C_{16}H_{26}N_2O_2W$: C, 41.57; H, 5.67, N, 6.06. Found: C, 41.61; H, 5.79; N, 6.01. Two rotamers were found in the NMR spectra. ^1H NMR ($CDCl_3$, 400.13 MHz): δ 9.06 ($^3J_{H-H}$ = 4.8 Hz) (br t, 1H, NH), 7.27 ($^3J_{H-W}$ = 9.6 Hz, $^3J_{H-H}$ = 13.6 Hz) and 7.25 ($^3J_{H-H}$ = 13.2 Hz) [2 d, 11:1, 1H, $WCH{=}C\mathit{H}C(CH_3)_3$], 7.07 ($^2J_{H-W}$ = 12.1 Hz, $^3J_{H-H}$ = 13.6 Hz) and 7.03 ($^3J_{H-H}$ = 13.6 Hz) [2 d, 1:11, 1H, $WC\mathit{H}{=}CHC(CH_3)_3$], 5.84 and 5.82 ($^2J_{H-W}$ = 9.2 Hz) (2 s, 1:11, 5H, Cp), 3.58−3.56 and 3.52 ($^3J_{H-H}$ = 6.7 Hz) (m and dq, 1:11, 2H, $C\mathit{H}_2CH_2CH_2CH_3$), 1.70−1.63 and 1.60−1.52 (2 m, 1:11, 2H, $CH_2C\mathit{H}_2CH_2CH_3$), 1.47−1.39 and 1.39−1.30 (2 m, 1:11, 2H, $CH_2CH_2C\mathit{H}_2CH_3$), 1.19 and 1.17 [2 s, 11:1, 9H, $C(CH_3)_3$], 0.96 ($^3J_{H-H}$ = 7.5 Hz) and 0.91 (7.4 Hz) (2 t, 1:11, 3H, $CH_2CH_2CH_2C\mathit{H}_3$). ^{13}C NMR ($CDCl_3$, 100.61 MHz): δ 212.1 (CO), 158.4 [$WCH{=}\mathit{C}HC(CH_3)_3$], 148.6 ($^1J_{C-W}$ = 110.6 Hz) [$W\mathit{C}H{=}CHC(CH_3)_3$], 100.7 and 100.2 (Cp), 44.7 ($\mathit{C}H_2CH_2CH_2CH_3$), 35.3 [$\mathit{C}(CH_3)_3$], 31.5 ($CH_2\mathit{C}H_2CH_2CH_3$), 30.8 [$C(\mathit{C}H_3)_3$], 20.0 ($CH_2CH_2\mathit{C}H_2CH_3$), 13.8 ($CH_2CH_2CH_2\mathit{C}H_3$). IR (KBr; $\tilde{\nu}$ (cm^{-1})): 3190 (m, N−H), 1645 (s, N≡O), 1544 (m, C═O). MS (70 eV): *m*/*e* 434 ($M^+ - CO$, ^{184}W). High-resolution mass spectrum: *m*/*e* calcd for $C_{16}H_{26}N_2O_2{}^{182}W$ (M^+) 432.1528 (−CO), found 432.1541.

[W{σ-(Z)-CH═CHC(CH$_3$)$_3$}{η^2-C(O)NHCH(CH$_3$)$_2$}(η^5-C$_5$H$_5$)(NO)] (6b): reaction time about 5 min, beige crystals (193 mg, 84%; mp 110−112 °C dec). Anal. Calcd for $C_{15}H_{24}N_2O_2W$: C, 40.20; H, 5.40, N, 6.25. Found: C, 40.08; H, 5.18; N, 6.34. Two rotamers were found in the NMR spectra. ^1H NMR ($CDCl_3$, 400.13 MHz): δ 8.89 ($^3J_{H-H}$ = 7.4 Hz) (br d, 1H, NH), 7.27 ($^3J_{H-W}$ = 9.4 Hz, $^3J_{H-H}$ = 13.8 Hz) [d, 1H, $WCH{=}C\mathit{H}C(CH_3)_3$], 7.05 ($^2J_{H-W}$ = 11.8 Hz, $^3J_{H-H}$ = 13.3 Hz) [d, 1H, $WC\mathit{H}{=}CHC(CH_3)_3$], 5.84 and 5.82 ($^2J_{H-W}$ = 9.2 Hz) (2 s, 1:20, 5H, Cp), 4.25−4.17 ($^3J_{H-H}$ = 6.9 Hz) [sextet, 1H, $C\mathit{H}(CH_3)_2$], 1.40, 1.27, 1.26, and 1.23 [4 d, 1:1:20:20, 2H, $CH(C\mathit{H}_3)_2$], 1.20 and 1.16 [2 s, 20:1, 9H, $C(CH_3)_3$]. ^{13}C NMR ($CDCl_3$, 100.61 MHz): δ 212.4 (CO), 158.2 [$WCH{=}\mathit{C}HC(CH_3)_3$], 149.1 ($^1J_{C-W}$ = 114.4 Hz) [$W\mathit{C}H{=}CHC(CH_3)_3$], 100.8 and 100.1 (Cp), 47.8 [$\mathit{C}H(CH_3)_2$], 35.5 [$\mathit{C}(CH_3)_3$], 31.1 [$C(\mathit{C}H_3)_3$], 22.8 [$CH(\mathit{C}H_3)_2$]. IR (KBr; $\tilde{\nu}$ (cm^{-1})): 3197 (m, N−H), 1627 (s, N≡O), 1551 (s, C═O). MS (70 eV): *m*/*e* 420 ($M^+ - CO$, ^{184}W). High-resolution mass spectrum: *m*/*e* calcd for $C_{15}H_{24}N_2O_2{}^{182}W$ (M^+) 418.1371 (−CO), found 418.1380.

[W{σ-(Z)-CH═CHC(CH$_3$)$_3$}{η^2-C(O)NHC(CH$_3$)$_3$}(η^5-C$_5$H$_5$)(NO)] (6c): reaction time about 5 min, beige crystals (43 mg, 18%; mp 125−127 °C dec). Anal. Calcd for $C_{16}H_{26}N_2O_2W$: C, 41.57; H, 5.67, N, 6.06. Found: C, 41.45; H, 5.68; N, 5.84. ^1H NMR ($CDCl_3$, 400.13 MHz): δ 9.52 (br s, 1H, NH), 7.27 ($^3J_{H-W}$ = 10.3 Hz, $^3J_{H-H}$ = 13.6 Hz) [d, 1H, $WCH{=}C\mathit{H}C(CH_3)_3$], 7.06 ($^2J_{H-W}$ = 11.8 Hz, $^3J_{H-H}$ = 13.6 Hz) [d, 1H, $WC\mathit{H}{=}CHC(CH_3)_3$], 5.82 ($^2J_{H-W}$ = 9.2 Hz) (s, 5H, Cp), 1.44 [s, 9H, $NHC(C\mathit{H}_3)_3$], 1.19 [s, 9H, $WCH{=}CHC(C\mathit{H}_3)_3$]. ^{13}C NMR ($CDCl_3$, 100.61 MHz): δ 211.9 (CO), 158.6 [$WCH{=}\mathit{C}HC(CH_3)_3$], 147.8 [$W\mathit{C}H{=}CHC(CH_3)_3$], 100.7 (Cp), 56.2 [$NH\mathit{C}(CH_3)_3$], 35.6 [$WCH{=}CH\mathit{C}(CH_3)_3$], 30.8 [$NHC(\mathit{C}H_3)_3$], 28.8 [$WCH{=}CHC(\mathit{C}H_3)_3$]. IR (KBr; $\tilde{\nu}$ (cm^{-1})): 3190 (m, N−H), 1626 (s, N≡O), 1542 (s, C═O). MS (70 eV): *m*/*e* 434 ($M^+ - CO$, ^{184}W). High-resolution mass spectrum: *m*/*e* calcd for $C_{16}H_{26}N_2O_2{}^{182}W$ (M^+) 432.1528 (−CO), found 432.1503.

[W{σ-(Z)-CH═CHC(CH$_3$)$_3$}{η^2-C(O)-cyclo-NC$_4$H$_8$}(η^5-C$_5$H$_5$)(NO)] (6d): reaction time about 15 min, brown crystals (100 mg, 42%; mp 89−91 °C dec). Anal. Calcd for $C_{16}H_{24}N_2O_2W$: C, 41.76; H, 5.26, N, 6.09. Found: C, 41.20; H, 5.04; N, 6.15. Two rotamers were found in the NMR spectra. ^1H NMR ($CDCl_3$, 400.13 MHz): δ 7.25 ($^3J_{H-W}$ = 9.6 Hz, $^3J_{H-H}$ = 13.3 Hz) and 7.10 ($^3J_{H-H}$ = 12.8 Hz) [2 d, 6:1, 1H, $WCH{=}C\mathit{H}C(CH_3)_3$], 7.06 ($^2J_{H-W}$ = 12.3 Hz, $^3J_{H-H}$ = 13.3 Hz) and 6.45 ($^3J_{H-H}$ = 13.3 Hz) [2 d, 6:1, 1H, $WC\mathit{H}{=}CHC(CH_3)_3$], 5.90 and

5.81 ($^2J_{H-W}$ = 9.4 Hz) (2 s, 1:6, 5H, Cp), 4.37, 4.00−3.94, 3.79−3.72, 3.67−3.61, and 3.26 (5 m, 4H, $CH_2CH_2CH_2CH_2$), 2.12−1.98, 1.86, and 1.76−1.71 (3 m, 4H, $CH_2CH_2CH_2CH_2$), 1.15 and 1.07 [2 s, 6:1, 9H, $C(CH_3)_3$]. ^{13}C NMR ($CDCl_3$, 100.61 MHz): δ 213.0 and 184.2 (CO), 159.3 and 158.2 [$WCH{=}CHC(CH_3)_3$], 151.4 ($^1J_{C-W}$ = 150.0 Hz) and 148.8 (111.9 Hz) [$WCH{=}CHC(CH_3)_3$], 102.8 and 99.8 (Cp), 67.1, 64.5, 49.7, and 48.5 ($CH_2CH_2CH_2CH_2$), 35.5 and 35.2 [$C(CH_3)_3$], 31.1 and 30.8 [$C(CH_3)_3$], 26.7, 26.5, and 25.1 ($CH_2CH_2CH_2CH_2$). IR (KBr; $\tilde{\nu}$ (cm^{-1})): 1635 (s, N≡O), 1546 (s, C=O). MS (70 eV): *m*/*e* 432 (M^+ − CO, ^{184}W). High-resolution mass spectrum: *m*/*e* calcd for $C_{16}H_{24}N_2O_2{}^{182}W$ (M^+) 430.1371 (−CO), found 430.1359.

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Supporting Information Available: Listings giving data for the crystal structure determination and refinement, atomic coordinates, interatomic distances and angles, anisotropic thermal parameters, and hydrogen parameters of the compound **6b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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