Organometallics **2005,** *24,* 6239−6243

Reaction of Tungsten Vinylcarbene Complexes with Enamines

Junes Ipaktschi,* Parham Rooshenas, and Ansgar Dülmer

Institute of Organic Chemistry, Justus-Liebig University, Heinrich-Buff-Ring 58,
D-35392 Giessen, Germany

Received July 21, 2005

In this paper we describe the reaction of vinylcarbene complexes **4** and **7** with enamines **5** and **9** to form the η^1-acyl complexes **6**, **8**, and **10**. From a mechanistic point of view, the reaction starts with the nucleophilic addition of the β-carbon atom of the enamine to the α-carbon atom of the vinylcarbene complex, generating the zwitterionic structure **12**. Instead of the expected ring closure to a metallacyclobutane derivative and concomitant metathesis, intermediate **12** undergoes nucleophilic addition of a carbonyl carbon atom to the iminium carbon atom and rearrangement to the observed η^1-acyl complexes. Furthermore the reaction of the η^1-vinylidene complex [(CO)(NO)(Cp)W=C=CH$_2$)] (**1**) with the enamines **5** and **9** is described. While enamine **5** preferably reacts as a nucleophile and produces finally the alkene complex **11**, the reaction of enamine **9** with **1** begins by a proton transfer step and ends with the η^1-acyl complex **10**. Single-crystal X-ray diffraction data of **6** and **11** are reported.

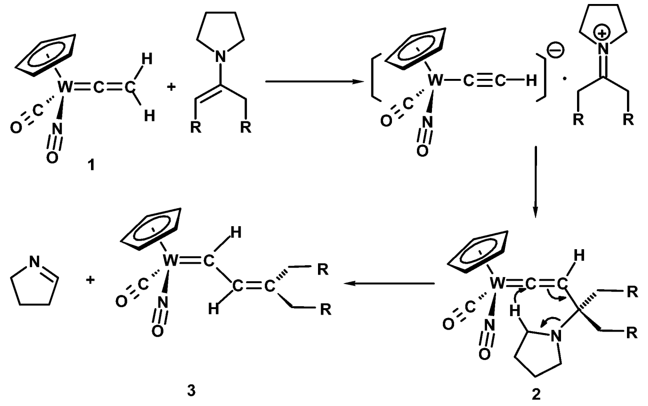
Introduction

Transition-metal carbene complexes have become valuable synthetic tools and have been applied toward a variety of reactions, including olefin isomerization, synthesis of small organic molecules, and metathesis reactions.[1] Among the large variety of carbene complexes containing different transition metals, low-valent pentacarbonyltungsten carbene complexes were the first carbene complexes launched by Katz et al. in metathesis reactions.[2] Very recently we have described an intramolecular metallo-retro-ene reaction of tungsten η^1-vinylidene complex **2**, formed as a reactive intermediate by the reaction of tungsten η^1-vinylidene complex **1** with enamines, giving rise to the low-valent vinylcarbene complexes **3** (Scheme 1).[3] With the aim to study the reactivity of these complexes toward metathesis reaction we investigated the reaction of vinylcarbenes **4** and **7** with enamines **5** and **9** as examples of electron-rich olefins. Herein, we present the results of this investigation.[4]

Results and Discussion

A solution of vinylcarbene complex **4** was treated at −20 °C with an excess of enamine **5**. After 4 h the color of the solution changed from red to yellowish and the carbonyl absorption of vinylcarbene complex **4** at 1980 cm^{-1} disappeared. After workup and recrystalization the η^1-acyl complex **6** was isolated as yellow crystals stable as solids under inert gas at −20 °C with 70% yield.

Scheme 1



The structure of compound **6** was confirmed by spectroscopic methods, elemental analysis, and X-ray crystallography.

The infrared spectrum of this complex showed a carbonyl absorption at 1648 cm^{-1}, indicating a η^1-acyl tungsten complex, and also one broad nitrosyl absorption at 1577 cm^{-1}.[5] The structure of **6** was further

---

* To whom correspondence should be addressed. E-mail: junes.ipaktschi@org.chemie.uni-giessen.de. Fax: (+)49 641-99 34 309.

[1] (a) Kremzow, D.; Seidel, G.; Lehmann, C. W.; Fürstner, A. *Chem. Eur. J.* **2005**, *11*, 1833−1853. (b) Barluenga, J.; Fañanás-Mastral, M.; Aznar, F. *Org. Lett.* **2005**, *7*, 1235−1237. (c) Diver, S. T.; Giessert, A. J. *Chem. Rev.* **2004**, *104*, 1317−1382. (d) Barluenga, J.; Santamaria, J.; Tomas, M. *Chem. Rev.* **2004**, *104*, 2259−2283. (e) Zhang, J.; Gunnoe, T. B. *Organometallics* **2003**, *22*, 2291−2297. (b) Aumann, R.; Fu, X.; Vogt, D.; Fröhlich, R.; Kataeva, *Organometallics* **2002**, *21*, 2736−2742. (f) deMeijere, A.; Schirmer, H.; Duetsch, M. *Angew. Chem.* **2000**, *112*, 4124−4162; *Angew. Chem., Int. Ed.* **2000**, *39*, 3964−4004.

[2] Katz, T. J. *Angew. Chem.* **2005**, *117*, 3070; *Angew. Chem., Int. Ed.* **2005**, *44*, 3010.

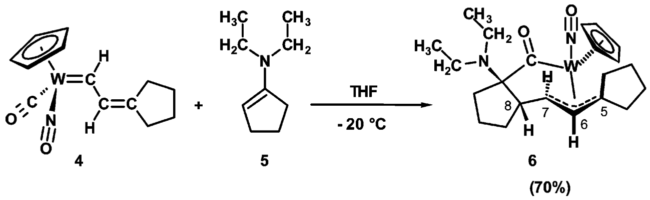
[3] Ipaktschi, J.; Mohsseni-Ala, J.; Dülmer, A.; Loschen, C.; Frenking, G. *Organometallics* **2005,** *24,* 977.

[4] For metathesis of enamines by tungsten carbene complexes see: (a) Aumann, R.; Roths, K.; Läge, M.; Krebs, B. *Synlett* **1993**, 667. (b) Aumann, R.; Roths, K.; Grehl, M. *Synlett* **1993**, 669. Further addition of enamines to carbene complexes see: (c) Aumann, R.; Fu, X.; Vogt, D.; Fröhlich, R.; Kataeva, O. *Organometallics* **2002**, *21*, 2736. (d) Barluenga, J.; Ballesteros, A.; Bernardo de la Rua, R.; Santamaria, J.; Rubio, E.; Tomas, M. *J. Am. Chem. Soc.* **2003**, *125*, 1834. (e) Barluenga, J.; Ballesteros, A.; Santamaria, J.; Bernardo de la Rua, R.; Rubio, E.; Tomas, M. *J. Am. Chem. Soc.* **2000,** *122,* 12874.

[5] Hermes, A. R.; Girolami, Gregory, S. *Organometallics* **1988**, *7*, 394.

10.1021/om050610d CCC: \$30.25

Scheme 2



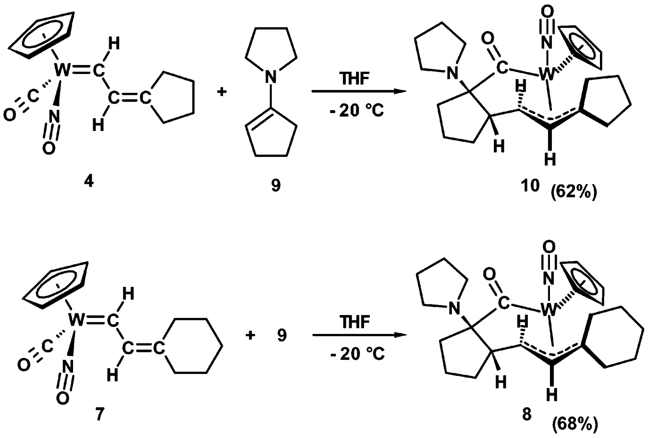
confirmed by the characteristic pattern for η^3-allyl complexes in the ^{1}H NMR spectra.[6] In accordance with the structure, the product showed a doublet at δ 5.50 ppm for the proton bonded to the central carbon atom of the η^3-allyl system (C6) and a doublet of doublets at δ 4.20 ppm for the proton on C7. The *anti* orientation of these two protons to each other is shown by the relatively large coupling constant $^3J_{\mathrm{H6-H7}}$ of 12.8 Hz.[7]

In agreement with the structure the ^{13}C NMR of **6** shows for C6 a signal at δ 111.3 ppm, and the signals for both carbon atoms at the terminus of the allyl system appear at δ 116.6 ppm (C5) and 91.7 ppm (C7). They resemble the characteristic low-field signals for sp^2 carbons bonded to a transition metal.[8] The difference in chemical shifts of both terminal carbon atoms could be attributed to a slight $\eta^3 \rightarrow \sigma, \eta^2$ distortion in the coordination of the allyl moiety to the metal center.[9] The carbon atom of the η^1-acyl group resonates at δ 256.1 ppm, which is comparable with other reported cases.[10]

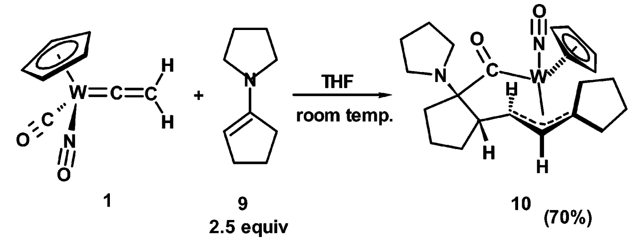
Very similarly to the above, the reaction of vinylcarbenes **4** and **7** with the enamine **9** gave rise to the η^1-acyl complexes **10** (62%) and **8** (68%), respectively (see Experimental Section).

Since the tungsten vinylcarbene complexes **4** and **7** are prepared by the reaction of η^1-vinylidene complex **1** with the enamine **9** and cyclopent-1-enyl-1-piperidine, respectively, as demonstrated mechanistically in Scheme 1,[3] it was reasonable to perform the reaction of complex **1** with excess enamine as a one-pot transformation in order to avoid the isolation of corresponding vinylcarbene complexes. We tested this mode of reaction by the addition of excess enamine **9** to a solution of complex **1**. It showed that the η^1-acyl complex **10** is more conveniently prepared directly by the addition of 2.5 equiv of enamine **9** to the solution of the η^1-vinylidene complex **1** without the isolation of the primarily formed vinylcarbene complexes (Scheme 4).

Scheme 3



Scheme 4



Remarkable differences in the reactivity between enamines containing a pyrrolidine as well as piperidine ring versus the one containing a diethyl amino group are observed by the reaction of enamines **5** and **9** with η^1-vinylidene complex **1**. Interestingly when a solution of enamine **5** in THF was added at room temperature to a solution of η^1-vinylidene complex **1**, after 40 min the expected η^1-acyl complex **6** was formed only as a minor component. The main reaction product is unambiguously identified as the η^2-alkene derivatives **11** by means of standard analytical and spectroscopic methods. Its molecular structure is also confirmed by the result of single-crystal structure analysis. The ratio of complexes **11**:**6** is dependent on the polarity of solvent applied. While in THF a ratio of 7:1 is observed; performing the reaction in diethyl ether as solvent produced quantitatively the η^2-alkene derivative **11**.

The infrared spectrum of **11** shows the carbonyl absorptions of the Cp(CO)(NO)W fragment at 1952 cm^{-1}, and the ^{1}H and ^{13}C NMR spectra revealed the presence of an η^2-olefine complex.[11] The methine proton on C2 showed a resonance in the ^{1}H NMR at δ 4.36 ppm as a doublet of doublets due to splitting of the protons on neighboring carbon atoms. The carbon atoms of the double bond coordinated at the metal were shifted to high field in the ^{13}C NMR, namely, at δ 39.9 (C1) and 30.1 ppm (C2). The last downfield signal at δ 223.7 ppm belongs to the carbonyl ligand.

Mechanistic Considerations. The formation of η^1-acyl complexes **6**, **8**, and **10** is rationally explained by the nucleophilic addition of the β-carbon atom of enamine **5** or **9** to the α-carbon atom of vinylcarbene complexes **4** and **7**, generating the zwitterionic structure **12**. Instead of ring closure to a metallacyclobutane deriva-

---

[6] (a) Ipaktschi, J.; Mirzaei, F.; Demuth-Eberle, G. J.; Beck, J.; Serafin, M. *Organometallics* **1997**, *16*, 3965. (b) Greenhough, J. T.; Legzdins; P.; Martin, D. T.; Trotter, J. *Inorg. Chem.* **1979**, *18*, 3268. (c) Kondo, H.; Yamaguchi, Y.; Nagashima, H. *Chem. Commun.* **2000**, 1075. (d) Liu, G.; Beetstra, D. J.; Meetsma, A.; Hessen, B. *Organometallics* **2004**, *23*, 3914. (e) Matsushima, Y.; Onitsuka, K.; Takahashi, S. *Organometallics* **2004**, *23*, 3763. (f) Yih, K. H.; Lee, G. H.; Huang, S. L.; Wang, Y. *Organometallics* **2002**, *21*, 5767. (g) van Staveren, D. R.; Weyhermüller, T.; Metzler-Nolte, N. *Organometallics* **2000**, *19*, 3730. (h) Ascenso, J. R.; Dias, R. A.; Fernandes, J. A.; Martins A. M.; Rodrigues S. S. *Inorg. Chim. Acta* **2003**, 356, 279.

[7] (a) Xue, P.; Bi, S.; Sung, H. H. Y.; Williams, I. D.; Lin, Z.; Jia, G. *Organometallics* **2004**, *23*, 4735. (b) Sasabe, H.; Nakanishi, S.; Takata, T.; *Inorg. Chem. Commun.* **2002**, *5*, 177. (c) Cadierno, V.; Crochet, P.; Diez, J.; Garcia-Garrido, S. E.; Gimeno, J. *Organometallics* **2003**, *22*, 5226.

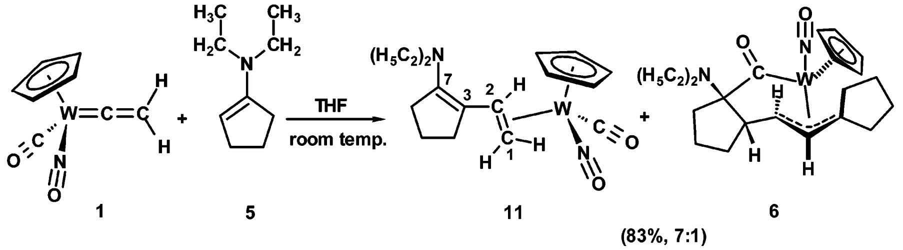
[8] (a) Collman, J. P., Hegedus, L. S.; Norton, J. R.; Finke, G. R. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987. (b) Mann, B. E. *Adv. Organomet. Chem.* **1974**, *12*, 135–213.

[9] Ward, D. Y.; Villanueva, L. A.; Allred, G. D.; Payne, S. C.; Semones, M. A.; Liebeskind, L. S. *Organometallics* **1995**, *14*, 4132.

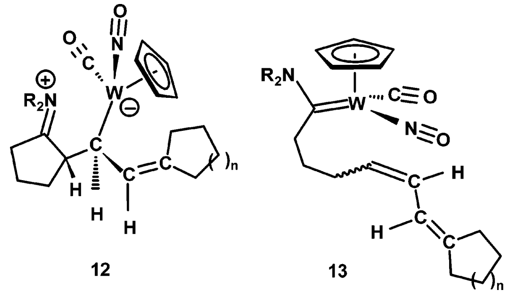
[10] Dryden, N. H.; Legzdins, P.; Lundmark, P. J.; Riesen, A.; Einstein, F. W. B. *Organometallics* **1993**, *12*, 2085.

[11] (a) Mayr, A.; Dorries, A. M.; Rheingold, A. L.; Geib, S. J. *Organometallics* **1990**, *9*, 964. (b) Alvarez, C.; Pacreau, A.; Parlier, A.; Rudler, H.; Daran, J. C. *Organometallics* **1987**, *6*, 1057.

Scheme 5



Scheme 6



tive and concomitant ring opening to the aminocarbene complexes **13**, intermediate **12** undergoes nucleophilic addition of the carbonyl carbon atom to the iminium carbon atom and the rearrangement to the observed η^1-acyl-η^3-allyl complexes.

Contrary to the reaction of η^1-vinylidene complex **1** with enamines containing a pyrrolidine or piperidine ring,[3] the enamine **5** shows two different modes of reactivity with **1**. In a minor reaction path it generates as a base the ion pair **14**, which undergoes Mannich type alkylation followed by the metallo-retro-ene reaction to the vinylcarbene **4** (path a Scheme 7). This mode of reaction with complex **1** is exclusively observed with enamines containing cyclic amines.[3] Reaction with an excess of enamine present in the reaction mixture gives rise to the η^1-acyl complex **6**. The major reaction mode of enamine **5** is the nucleophilic attack at the α-carbon atom of the η^1-vinylidene complex (path b) to generate the zwitterion **15**. Migration of hydrogen produces the metal hydride **16**, which undergoes reductive elimination to the observed alkene complex **11**.

Molecular Structure of 6 and 11. Crystals of complex **6** suitable for a single-crystal X-ray diffraction study were grown from a pentane solution of compound **6** at 4 °C. The molecular structure of **6** is shown in Figure 1, and relevant crystal data are included in Table 1. The crystal structure of the complex consists of a well-spaced array of molecular units, the intermolecular contacts corresponding to normal van der Waals distances. The C7−C6 and C5−C6 distances are nearly equally long at 1.421 and 1.427 Å, respectively, and are midway between typical carbon−carbon single- and double-bond values. The C−C−C angles within the allyl ligand imply sp^2 hybridization about those carbons [C8C7C6, 120.39(19)°; C5C6C7, 119.2°; C4C5C6, 118.7(2)°]. The torsion angles around the allyl group are C1−C5−C6−C7 173.1°; C4−C5−C6−C7−54.0°; C6−C7−C8−C9 114.1°; C5−C6−C7−C8 157.1°; and C6−C7−C8−C12 120.2° (calc with ORTEP). Furthermore, the W−C5 and W−C6 distances of 2.292(7) Å fall in the range expected for distances in η^3-allyl complexes,[12] whereas W−C7, at 2.337(4) Å, is only slightly longer. The cyclopentadienyl ligand is *endo* positioned to the allyl ligand.[13] The relatively long W−C(O) bond distances of 2.215(4) Å and the angle C12C13W (122.53°) are further indications of a η^1-acyl complex.

Suitable single crystals of complexes **11** were grown from an ether solution at −20 °C. The ORTEP plot is shown in Figure 2. For crystallographic data see Table 1. Compound **11** exhibits a pseudo-octahedral half-sandwich disposition around the W atom, with the cyclopentadienyl ligand occupying one face of the octahedron. The plane containing the coordinated double bond (C1 and C2) and tungsten atom is nearly perpendicular to the plane of W−C(O)−N(O). The olefin fragment is bound slightly asymmetrical to the metal center (W−C1 = 2.270(7) Å, W−C2 = 2.806(6) Å). Due to the weaker π-basic character of the [CpW(CO)(NO)]

Scheme 7

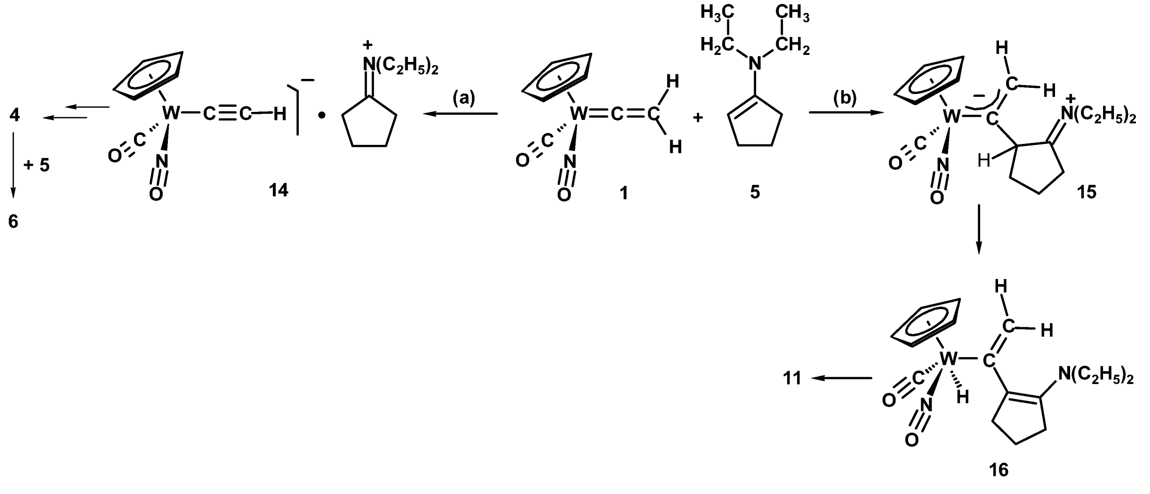


Table 1. Crystallographic Data for Complexes 6 and 11

	6	**11**
formula	$C_{22}H_{32}N_2O_2W$	$C_{17}H_{24}N_2O_2W$
fw	540.358	472.240
color and habit	yellow	orange
cryst syst	monoclinic	monoclinic
space group	$P2_1/c$ (No. 14)	$P2_1/c$ (No. 14)
lattice constants	$a = 11.330(2)$ Å $b = 13.6604(10)$ Å $c = 13.711(2)$ Å $\beta = 92.02(10)°$	$a = 16.0910(18)$ Å $b = 6.7543(5)$ Å $c = 16.8063(18)$ Å $\beta = 104.422(13)°$
volume	2120.8(5) Å^3	1769.0(3) Å^3
formula units per unit cell	$Z = 1$	$Z = 1$
density(calc)	1.591 g/cm^3	1.769 g/cm^3
linear absorp coeff	54.62 cm^{-1}	65.38 cm^{-1}
difractometer	Stoe IPDS	
radiation	Mo Kα ($\lambda = 0.71069$ Å)	Mo Kα ($\lambda = 0.71069$ Å)
monochromator	graphite	graphite
scan range	$2.73 \leq \theta \leq 28.05°$ $-14 \leq h \leq 14$, $-17 \leq k \leq 17$, $-16 \leq l \leq 18$	$3.40 \leq \theta \leq 28.04°$ $-21 \leq h \leq 21$, $-8 \leq k \leq 8$, $-22 \leq l \leq 22$
no. of reflns collected	18 720	15 178
R_{int}	0.0526	0.0286
no. of indep reflns	4961	4007
applied corrections	Lorentz and polarization coefficients	Lorentz and polarization coefficients
structure determination and refinement	*W* positional parameters from Patterson synthesis (program SHELXS-86)^a	*W* positional parameters from Patterson synthesis (program SHELXS-86)^a
no. of data/restraints/params	4961/0/190	4007/0/173
goodness-of-fit on F^2	0.971	1.146
final *R* indices [$F_o > 4\sigma(F_o)$]	R1 = 0.0489, wR2 = 0.1250	R1 = 0.0312, wR2 = 0.0802
R indices (all data)	R1 = 0.0652, wR2 = 0.1347	R1 = 0.0477, wR2 = 0.0831

[a] Sheldrick, G. M. *SHELXS-86*; Program for the Solution of Crystal Structures; Universität Göttingen, 1986. Further atoms from *F*-synthesis (Sheldrick, G. M. *SHELXL-93*; Program for Crystal Structure Refinement; Universität Göttingen, 1993); structure refinement by the anisotropic full-matrix least-squares procedure for all non-hydrogen atoms. Atomic scattering factors from *International Tables for Crystallography*, Volume C; Wilson, A. J. C., Ed.; Kluwer Academic Publishers: Dordrecht, 1992.

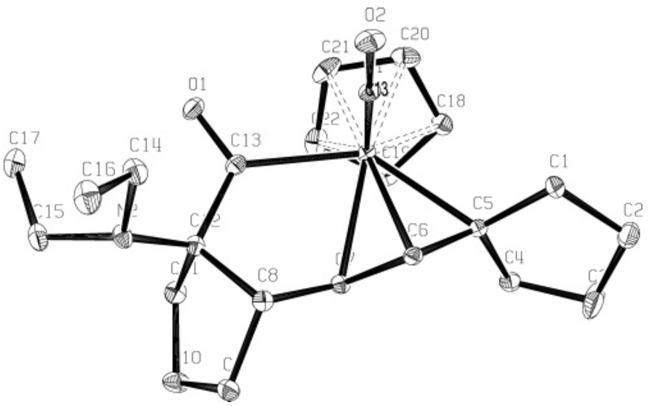


Figure 1. Molecular structure and atom-numbering scheme for complex **6** without H atoms. Thermal ellipsoids are shown at the 10% probability level. Selected bond lengths [Å] and angles [deg] (with standard deviations): W(1)−N(1) 1.758(6), W(1)−C(13) 2.215(4), W(1)−C(6) 2.292(4), W(1)−C(5) 2.293(4), W(1)−C(7) 2.337(4), N(2)−C(12) 1.478(9), O(1)−C(13) 1.200(7), C(7)−C(6) 1.421, C(7)−C(8) 1.484(5), C(6)−C(5) 1.427, C(13)−C(12) 1.562(8), N(1)−W(1)−C(13)− 85.7(2), C(6)−W(1)−C(5) 36.27(6), C(6)−C(7)−C(8) 120.39(19), C(7)−C(6)−C(5) 119.2, C(6)−C(5)−C(4) 120.6(2), C(6)−C(5)−C(1) 116.8(2), O(1)−C(13)−C(12) 118.2(5), O(1)−C(13)−W(1) 119.2(4).

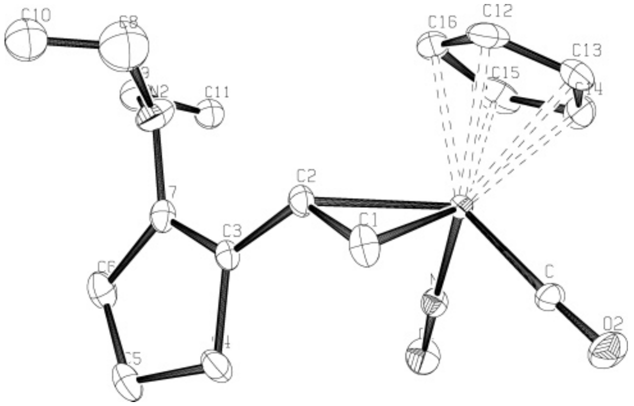


Figure 2. Molecular structure and atom-numbering scheme for complex **11** without H atoms. Thermal ellipsoids are shown at the 10% probability level. Selected bond lengths [Å] and angles [deg] (with standard deviations): W−N 1.786(7), W−C 1.972(6), W−C(1) 2.270(7), W−C(2) 2.286(6), W−C(14) 2.298(8), C(16)−C(12) 1.327(18), C(1)−C(2)1.393(11), C(2)−C(3) 1.467(10), C(3)−C(7) 1.309(10), C(7)−N(2) 1.449(11), C(7)−C(6) 1.515(12), C−W−C(1) 74.1(3), C(1)−W−C(2) 35.6(3), C(2)−C(1)−W 72.8(4), C(1)−C(2)−C(3) 124.5(7), C(1)−C(2)−W 71.6(4), C(3)−C(2)−W 117.1(4), C(7)−C(3)−C(2) 126.2(7), C(7)−C(3)−C(4) 111.1(7), C(2)−C(3)−C(4) 122.5(7), C(3)−C(7)−N(2) 124.3(8).

moiety, the C1−C2 bond length of 1.393 Å is somewhat shorter than other similar η^2-alkene complexes of tungsten.[14] The atoms N2−C7−C3−C2−C1 lie approximately in a plane (torsion angles: C7−C3−C2−C1 = 166.6° and N2−C7−C3−C2 = 4.1°), and the C2−C3 single-bond distance is 1.467(10) Å.

---

[12] (a) Frohnapfel, D. S.; White, P. S.; Templeton, J. L. *Organometallics* **1997**, 16, 3737. (b) Morales, D.; Navarro Clemente, M. E.; Pérez, J.; Riera, L.; Riera, V. *Organometallics* **2003**, *22*, 4124.

[13] Ariafard, A.; Lin, Z.; *Organometllics* **2005**, *24*, 2241−2244.

[14] (a) Berke, H.; Huttner, G.; Sontag, C.; Zsolnai, L. *Z. Naturforsch., Teil B* **1985**, *40B*, 799. (b) Grevels, F. W.; Lindemann, M.; Benn, R.; Goddard, R.; Krueger, C. *Z. Naturforsch., Teil B* **1980**, *35B*, 1298.

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 η^1-vinylidene complex **1** {[($\eta^5C_5H_5$)(CO)(NO)W=C=CH_2]},[15] carbene complexes **4** and **7**,[3] and enamines **5** and **9**,[16] and all other compounds were commercially available. NMR spectra were obtained on Bruker AM 400 and AC 200 spectrometers. Proton and carbon chemical shifts are referred to tetramethylsilane. Infrared spectra were recorded on a Bruker FT-IR IFS 85. Microanalyses were done on a Carlo Erba 1104 elemental analyzer.

Preparation of 6. To a solution of 200 mg (0.44 mmol) of carbene complex **4** in 5 mL of THF was added 139 mg (1.0 mmol) of cyclopent-1-enyldiethylamine (**5**) diluted with 1 mL of THF at −20 °C. The reaction was monitored by IR spectroscopy. After 4 h the educt disappeared. The solvent was evaporated to dryness, and the residue recrystallized from ether−pentane at −10 °C to give 166 mg of **6** as yellow crystals (70%). ^{1}H NMR (400 MHz, THF-d_8, −20 °C): δ 5.58 (s, 5H, Cp), 5.50 (d, $^3J_{H-H}$ = 12.79 Hz, 1H, C6), 4.20 (dd, $^3J_{H-H}$ = 12.8 Hz, $^3J_{H-H}$ = 3.9 Hz, 1H, C7), 2.67 (m, 1H, C8), 2.55−2.62 (m, 2H), 2.38−2.55 (m, 2H), 2.30−2.41 (m, 3H), 2.0−2.06 (m, 1H), 1.76−1.96 (m, 4H), 1.52−1.69 (m, 7H), 1.32−1.24 (m, 1H), 0.92 (t, CH_3). ^{13}C NMR (100 MHz, THF-d_8, −20 °C): δ 256.1 (CO), 116.6 (C5), 111.3 (C6), 101.5 (Cp), 91.7 (C7), 71.3 (C12), 44.2 (C8), 45.1 (N(CH_2)CH_3), 39.7, 37.7, 32.0, 29.2, 26.9, and 24.3 (−CH_2−), 15.7 (N(CH_2)CH_3). IR (KBr): $\tilde{\nu}$ (C=O) 1648 cm^{-1}, $\tilde{\nu}$ (N=O) 1577 cm^{-1}. Anal. Calcd for $C_{22}H_{32}N_2O_2W$: C 48.90, H 5.96, N 5.18. Found: C 49.04, H 5.94, N 5.21.

Preparation of 8 was as described for **6**; however, using 200 mg (0.43 mmol) of carbene complex **7** in 5.0 mL of THF and 137 mg (1.0 mmol) of cyclopent-1-enyl-1-pyrrolidine (**9**) in 1 mL of THF resulted in 167 g (68%) of **8**. The yellow crystals consist of two diasteromers in a ratio of 10:3 on the basis of ^{1}H NMR spectroscopy. ^{1}H NMR (400 MHz, THF-d_8, −20 °C): δ 5.56 and 5.53 (s, 5H, Cp), 5.31 and 5.19 (d, $^3J_{H-H}$ = 13.4 Hz C6), 4.67 and 4.41 (dd, $^3J_{H-H}$ = 13.4 Hz, $^3J_{H-H}$ = 3.2 Hz major component and dd, $^3J_{H-H}$ = 13.4 Hz,$^3J_{H-H}$ = 4.4 Hz minor component C7 1H), 2.69−2.11 (m, 6H), 2.08−1.53 (m, 17H), 1.4−1.15 (m, 4H). ^{13}C NMR (100 MHz, THF-d_8): δ 254.1 and 250.2 (CO), 116.5 and 113.5 (C5), 111.9 and 109.8 (C6), 101.1 and 100.3 (Cp), 93.1 and 88.8 (C7), 74.0 and 73.5 (C12), 45.8 and 42.8 (C8), 48.6, 47.9, 41.4, 41.5, 39.2, 39.0, 35.4, 35.1, 33.6, 33.1, 27.9, 27.8, 27.2, 24.6, 24.5, 24.2, 23.3, 22.8, and 21.8 (−CH_2−). IR (KBr): $\tilde{\nu}$ (C=O) 1641 cm^{-1}, $\tilde{\nu}$ (N=O) 1590 cm^{-1}. Anal. Calcd for $C_{23}H_{32}N_2O_2W$: C 50.01, H 5.83, N 5.07.Found: C 50.25, H 5.90, N 4.98.

Preparation of 10 was as described for **6**; however, using 200 mg (0.44 mmol) of carbene complex **4** in 1 mL of THF and 137 mg (1.0 mmol) of cyclopent-1-enyl-1-pyrrolidine (**9**) in 1 mL of ether resulted in 146 mg (62%) of **10**. The yellow crystals consist of two diasteromers in a ratio of 10:1 on the basis of ^{1}H NMR spectroscopy. ^{1}H NMR (400 MHz, THF-d_8, −20 °C): δ 5.59 and 5.56 (s, 5H, Cp), 5.34 and 5.21 (d, $^3J_{H-H}$ = 12.85 Hz, 1H, C6), 4.35 and 4.66 (dd, $^3J_{H-H}$ = 12.9 Hz, $^3J_{H-H}$ = 3.2 Hz major component and dd, $^3J_{H-H}$ = 13.9 Hz,$^3J_{H-H}$ = 4.2 Hz minor component C7 1H), 2.33−2.60 (m, 9H), 2.05−2.11 (m, 1H), 1.76−1.90 (m, 2H), 1.45−1.67 (m, 13H), 1.19−1.12 (m, 1H) δ 254 (CO), 112.9 (C5), 111.7 and 113.7 (C6), 101.5 and 100.7(Cp), 93.3 (C7), 71.4 (C12), 42.24 (C8), 48.6, 48, 39.5, 38.0, 33.2, 29.3, 26.7, 24.7, 24.4, 24.3, and 22.0 (−CH_2−). IR (KBr): $\tilde{\nu}$ (C=O) 1638 cm^{-1}, $\tilde{\nu}$ (N=O) 1600 cm^{-1}. Anal. Calcd for $C_{22}H_{30}N_2O_2W$: C 49.08, H 5.61, N 5.20. Found: C 48.94, H 5.29, N 5.32.

One-Pot Reaction of Enamine 9 and Complex 1. To a solution of 330 mg (1 mmol) of η^1-vinylidene complex **1** in 5 mL of THF was dropwise added at room temperature a solution of 345 mg (2.5 mmol) of enamine **9** in 2 mL of THF. The color of the solution changed slowly from red to yellow. The reaction was monitored by IR spectroscopy. After 4 h the CO signal of the intermediate carbene complex **4** disappeared. The solvent was evaporated and washed with 2 mL of pentane at −30 °C for 15 min and afterward was filtered immediately. This crude product was recrystallized from pentane at −20 °C overnight to give 375 mg of **10** (70% yield).

Preparation of 11. A solution of 306 mg (2.2 mmol) of dimethylamino-1-cyclopentene (**5**) in 1 mL of ether was added slowly to a stirred solution of 666 mg (2 mmol) of η^1-vinylidene complex **1** in 40 mL of ether at −30 °C drop by drop. After complete addition the mixture was allowed to warm to room temperature, whereby the color changed from orange to deep red. The reaction was monitored by TLC. After completion the ether was reduced and overlaid with pentane to crystallize overnight. The red crystals were collected to give 840 mg of **11** in 90% yield. ^{1}H NMR (400 MHz, THF-d_8, −20 °C): δ 5.72 (s, 5H, Cp), 4.36 (dd, $^3J_{H-H}$ = 12.3 Hz and d $^3J_{H-H}$ = 9.1 Hz, 1H, C2), 2.8 (2m, 4H, N(CH_2)CH3), 2.30−2.52 (m, 4H), 1.75−1.90 (m, 3H), 1.69−1.63 (m, 1H), 1.09 (t, 6H). ^{13}C NMR (100 MHz, THF-d_8, −20 °C): δ 223.7 (CO), 143.1 and 139.3 (C7 and C3), 95.6 (Cp), 48.5 (N(CH_2)CH_3), 39.9 (C2), 30.1 (C1), 29.8, 26.7, and 21.2 (CH_2), 14.2 (N(CH_2)CH_3). IR (KBr): $\tilde{\nu}$ (C=O) 1952 cm^{-1}, $\tilde{\nu}$ (N=O) 1571 cm^{-1}. Anal. Calcd for $C_{17}H_{24}N_2O_2W$: C 43.23, H 5.93, N 4.96. Found: C 43.54, H 5.92, N 5.12.

Reaction of the η^1-Vinylidene Complex 1 and Enamine 5 in THF. To a solution of 660 mg (2 mmol) of η^1-vinylidene complex **1** in 5 mL of THF was dropwise added at room temperature a solution of 417 mg (3 mmol) of enamine **5** in 2 mL of THF. The color of the solution changed from red to deep red. After 40 min the educt disappeared. The solvent was evaporated and washed with 2 mL of pentane at −30 °C for 15 min and afterward was filtered immediately, which resulted in 740 mg of a red powder. This crude product (83% yield) was subjected to ^{1}H NMR spectroscopy (400 MHz, $CDCl_3$). The comparison of Cp signals at δ 5.67 and 5.56 belonging to the complexes **11** and **6** showed the ratio of 7:1 for **11** to **6**.

Acknowledgment. This work was supported by the Deutsche Forschungsgemeinschaft (IP 7/5-2; IP 7/5-3.

Supporting Information Available: Data of crystal structure determination and refinement, tables of atomic coordinates, interatomic distances and angles, anisotropic thermal parameters, and hydrogen parameters of compounds **3** and **4a**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM050610D

---

(15) Ipaktschi, J.; Rooshenas, P.; Klotzbach, T.; Dülmer, A.; Hüseynova, E. *Organometallics* **2005**, *24,* 1351.

(16) White, A. W.; Weingarten, H. *J. Org. Chem.* **1967**, *32*, 213.