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Addition of Ynamines to the Tungsten η^1-Vinylidene Complexes (η^5-C_5H_5)(NO)(CO)W=C=C(H)R

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With the aim of synthesis of chiral-at-metal complexes with NLO properties, the reaction of ynamines **2a**,**b** with the η^1-vinylidene complexes (η^1-C_5H_5)(CO)(NO)W=C=(H)R (R = C_6H_5 (**1**), $C(CH_3)_3$ (**6**), H (**8**)) was investigated. It has been shown that the substituent R on the η^1-vinylidene complex determines the outcome of the reaction. Whereas the reaction of **2a**,**b** with complex **1** gave rise to the expected cyclobutenylidene complexes **4a**,**b** and **5a**,**b**, the reaction of ynamines with complexes **6** yielded the aminocarbene complexes **7a**,**b** and the reaction of η^1-vinylidene complexes **8** gave rise to a mixture of compounds **9** and **10**. The mechanism of formation of these complexes was investigated. Single-crystal X-ray diffraction data of **4a**, **7a**, and **9** are reported. Complex **4a** is composed of a strong electron-donating and -accepting group conjugated via double bonds of a cyclobutenylidene unit. Hence, the first hyperpolarizability β was determined by hyper-Rayleigh scattering measurements with a stimulating laser beam at $\lambda = 1500$ nm. A first hyperpolarizability of $\beta = 105 \times 10^{-30}$ esu was determined.

Introduction

The growing research activity in the synthesis of molecule-based materials with second-order nonlinear optical (NLO) properties has produced a wide range of new chromophores.[1] Among them are cyclobutenylidene complexes which are prepared by the reaction of pentacarbonyl vinylidene complexes ($(CO)_5M{=}C{=}CR_2$; M = Cr, W) with ynamines as well as 1-ethoxypropyne.[2] The resulting 3-amino-substituted cyclobutenylidene complexes exhibit in solution significant nonlinear optical properties.[2b,d] Intending to prepare cyclobutenylidene complexes containing a chiral metal atom, we investigated the reaction of tungsten η^1-vinylidene derivatives Cp(CO)(NO)W=C=C(H)R with ynamines. Surprisingly, the substituent R on the C_β atom of the vinylidene complex dramatically influenced the outcome of the reaction and gave rise to a wide range of different products. Herein we describe the reaction of η^1-vinylidene complexes Cp(CO)(NO)W=C=C(H)R (R = H, $C(CH_3)_3$, C_6H_5) with ynamines **2a**,**b** and the NLO properties of the chiral cyclobutenylidene complex **4a**.

Results and Discussion

Depending on the substituent R, three different types of reactions were observed when the η^1-vinylidene complexes Cp(CO)(NO)W=C=C(H)R (R = H, $C(CH_3)_3$, C_6H_5) were reacted with the ynamines **2a**,**b**: as expected, the addition of **2a**,**b** to the phenyl-substituted η^1-vinylidene complex **1** in THF at room temperature afforded in a fast reaction a mixture of the stereoisomeric cyclobutenylidene derivatives **4** and **5** (Scheme 1). These cyclobutenylidene complexes are dark red, air-stable crystalline solids and could be separated by column chromatography. Complexes **4** and **5** are very soluble and stable in polar organic solvents such as CH_2Cl_2 and DMF, but they decompose in acetonitrile.

A completely different path was observed in the reaction of the *tert*-butyl-substituted η^1-vinylidene complex **6** with ynamines **2a**,**b**. Addition of 3 equiv of ynamines **2a**,**b** to solutions of η^1-vinylidene complex **6** in THF at 55 °C gave the unsaturated (aminocarbene)-

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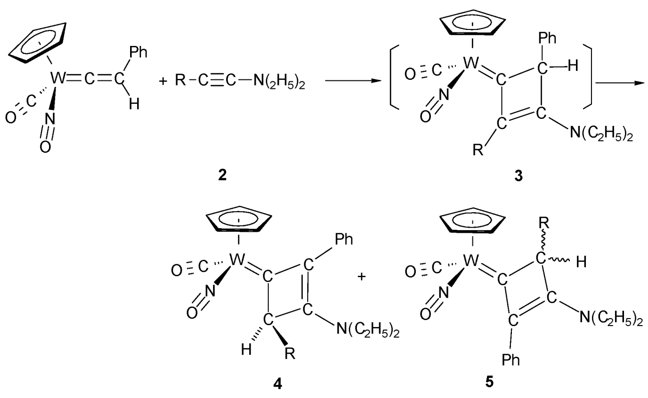
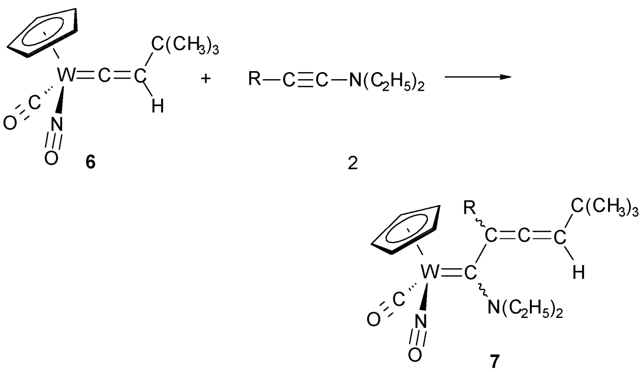
Scheme 1



1

	R
a	CH_3
b	C_2H_5

Scheme 2



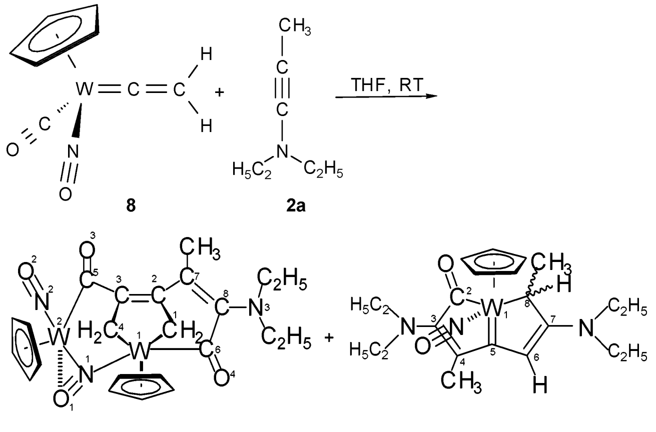
	R
a	CH_3
b	C_2H_5

tungsten complexes **7a**,**b** in 57% and 45% yields, respectively, as orange crystals (Scheme 2) after chromatography. The compounds **7a**,**b** can be stored under an argon atmosphere at −20 °C for a few months.

A third and astonishing reaction mode is observed in the addition of the ynamine **2a** to the parent vinylidene complex **8**. After addition of **2a** to a THF solution of **8** at room temperature, the solution immediately turned red. Chromatography of the reaction mixture at 0 °C on silica gel gave rise to the interesting binuclear complex **9** in 27% yield as a red crystal and the bicyclic carbene derivative **10** (32%) as a dark red oil (Scheme 3). Apparently the reaction of ynamines with η^1-vinylidene complexes is very sensitive to the substituent on C_β of the η^1-vinylidene complexes.

Characterization of Complexes 4a,b and 5a,b. In agreement with the structure, the IR spectra of complexes **4a**,**b** and **5a**,**b** exhibit a strong carbonyl band in the 1901−1905 cm^{-1} region. The nitrosyl group gives rise to a strong absorption in the range of 1623−1633 cm^{-1}. The ^{1}H and ^{13}C NMR spectra of compounds **4a**,**b** and **5a**,**b** consist of sharp and well-resolved resonance signals. The most informative features in the ^{13}C NMR spectra are the signals for the carbene carbon atoms located at low field between δ 268 and 271 ppm.[2b,f,g] Due to the partial double-bond character, the rotation around the C(3)−N(C_2H_5)$_2$ bond is hindered and the ^{1}H NMR spectra of **4a**,**b** and **5a**,**b** show two sets of signals for the ethyl protons. The C(2), C(3), and C(4) signals of **4a**,**b** and **5a**,**b** appear at δ 141−143, 161−166, and 55−61 ppm, respectively, in accordance with the related compounds described in the literature.[2f] In the ^{13}C NMR spectrum of **4b**, C(1) and the carbonyl carbon atom at δ 268.7 and 229.4 ppm show satellite signals caused by the coupling with the ^{183}W atom (14% ^{183}W abundance; $I = {}^{1}/_{2}$) with $^{1}J(^{183}W-^{13}C)$ = 76.3 and 102.7 Hz, respectively. The UV/vis spectrum of **4a** exhibits an intense absorption bond with a maximum at 418 nm without considerable solvatochromic behavior (solvents CH_2Cl_2, DMF, cyclohexane).

Scheme 3



Molecular Structure of 4a. The structure of **4a** was additionally determined by a single-crystal X-ray diffraction analysis. An ORTEP plot of **4a** is shown in Figure 1, crystallographic information are summarized in Table 1, and selected bond lengths and angles are presented in Table 2. The W−C(1) distance (2.045(4) Å) in **4a** is in the typical range of corresponding 3-aminocyclobutenylidene complexes.[2b,g] According to the crystallographic data the cyclobutenylidene ring is not planar but slightly puckered. The angle between the planes formed by the atoms C(1), C(2), C(4) and C(2), C(3), C(4) is 176°. Both C(sp^2)−C(sp^2) distances (C(1)−C(2) = 1.422(5) Å and C(2)−C(3) = 1.394(5) Å) are almost equal in length. The bond lengths are between

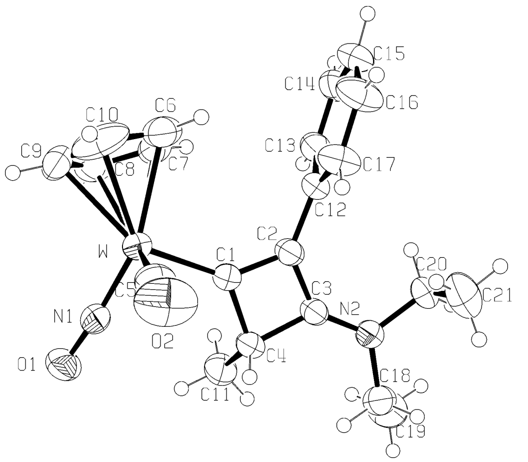


Figure 1. Molecular structure and atom-numbering scheme for **4a** with H atoms. Thermal ellipsoids are shown at the 40% probability level.

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

	4a	**7a**	**9**
formula	$C_{21}H_{24}N_2O_2W$	$C_{19}H_{28}N_2O_2W$	$C_{23}H_{27}N_3O_4W_2$
fw	520.27	500.28	777.18
color	red, transparent	orange, transparent	red, transparent
cryst syst	monoclinic	monoclinic	monoclinic
space group	$P2_1/n$	$P2_1/c$	$P2_1/n$
lattice constants			
a/Å	9.471(1)	7.838(1)	7.665(1)
b/Å	15.003(2)	14.031(2)	19.017(2)
c/Å	15.022(2)	18.567(1)	16.297(1)
α/deg	90	90	90
β/deg	107.82(1)	98.59(2)	98.941(7)
γ/deg	90	90	90
V/Å^3	2032.06	2019.09	2346.78
formula unit per unit cell	4	2	4
calcd density/g cm^{-3}	1.70	1.646	2.435
linear abs coeff/cm^{-1}	57	57.3	98.3
diffractometer	image plate diffractometer system (STOE)		
radiation	Mo Kα		
monochromator	graphite		
2θ range/deg	3.81−56.30	3.27−52.10	3.27−52.10
index ranges	$-12 \le h \le 12$ $-19 \le k \le 19$ $-19 \le l \le 19$	$-8 \le h \le 9$ $-17 \le k \le 17$ $-22 \le l \le 22$	$-9 \le h \le 9$ $-23 \le k \le 23$ $-19 \le l \le 20$
no. of rflns measd	18 300	14 726	17 444
no. of indep rflns	4788	3625	4317
R_{int}	0.0338	0.0283	0.0540
no. of indep rflns with $F_o > 4\sigma(F_o)$	3697	3103	3410
temp/K	295	293	293
applied corrections	Lorentz and polarization coefficients		
structure determination and refinment	W positional params from direct methods (SHELX-97)[a] and other atoms from ΔF synthesis (SHELX-97);[b] refinement by anisotropic full-matrix least-squares procedure for all non-hydrogen atoms and H(1A), H(1B), H(4A), and H(4B) in complex **9**, other H atom positions refined by “riding” model; atomic scattering factors from literature[c]		
no. of params	235	245	342
wR2	0.059	0.066	0.052
R1	0.045	0.032	0.038
R1 ($F_o > 4\sigma(F_o)$)	0.027	0.025	0.024
max, min in $\Delta\sigma$/e Å^{-3}	0.66, −0.60	0.74, −0.69	0.79, −0.54

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

Table 2. Selected Bond Distances (Å) and Bond Angles (deg) for 4a

Bond Distances			
W−C(5)	1.970(5)	C(2)−C(3)	1.394(5)
W−N(1)	1.793(3)	C(3)−C(4)	1.524(5)
W−C(1)	2.045(4)	C(4)−C(11)	1.516(6)
N(1)−O(1)	1.215(4)	C(2)−C(12)	1.484(5)
C(5)−O(2)	1.138(6)	C(3)−N(2)	1.316(5)
C(1)−C(2)	1.422(5)	N(2)−C(18)	1.462(5)
C(1)−C(4)	1.557(5)	N(2)−C(20)	1.461(5)
Bond Angles			
C(5)−W−N(1)	91.9(2)	C(2)−C(3)−C(4)	92.7(3)
C(2)−C(1)−W	139.5(3)	C(1)−C(2)−C(12)	131.1(3)
C(4)−C(1)−W	130.3(2)	C(3)−C(2)−C(12)	135.3(3)
O(2)−C(5)−W	178.0(5)	C(2)−C(3)−N(2)	136.4(3)
O(1)−N(1)−W	175.0(3)	C(4)−C(3)−N(2)	130.9(3)
C(1)−C(2)−C(3)	93.5(3)	C(3)−N(2)−C(18)	122.5(3)
C(1)−C(4)−C(3)	83.5(3)	C(3)−N(2)−C(20)	119.4(3)
C(2)−C(1)−C(4)	90.2(3)	C(18)−N(2)−C(20)	117.8(3)

a $C(sp^2)-C(sp^2)$ single bond (1.46 Å) and $C(sp^2)=C(sp^2)$ double bond (1.32 Å).[4] The amine substituent of the cyclobutenylidene ring is approximately coplanar with the ring, which allows optimal π-donation to the carbene ligand. The C(3)−N(2) distance is short (1.316(5) Å), shorter than expected for a $C(sp^2)-N(sp^2)$ single bond (1.355 Å).[3] This short C−N bond length as well as the bond length alternation between C(1), C(2), and C(3), which is between a complete localized and delocalized bonding mode, indicate considerable π-interaction between the donor in position 3 and the (Cp)(CO)(NO)W acceptor.

Characterization of 7a,b. The structure of complexes **7a**,**b** was fully determined by using ^{1}H NMR, ^{13}C NMR, and mass spectroscopic techniques and elemental analysis as well as a single-crystal X-ray diffraction analysis of **7a**. Typically, because of rotational barriers associated with the C(carbene)−N partial double bond,[4] these complexes show a fluxional behavior on the NMR time scale. This is demonstrated by variable-temperature ^{1}H NMR spectra of **7a** as well as **7b**. The ^{1}H NMR spectrum of **7a** at room temperature contains a broad singlet at 5.56 ppm for the cyclopentadienyl group (Cp) and also a broad singlet at 0.97 ppm for the *tert*-butyl protons. Below 5 °C the cyclopentadienyl and the *tert*-butyl signals split into two signals. At −30 °C, the two isomers have two signals for Cp protons at 5.59 and 5.57 ppm (ratio 2:3) and two signals for the *tert*-butyl group at 0.95 and 0.90 ppm (ratio 3:2).The free energy of activation of this process is estimated by line-shape analysis as $\Delta G^* = 14.7$ kcal/mol. Due to the fluxional

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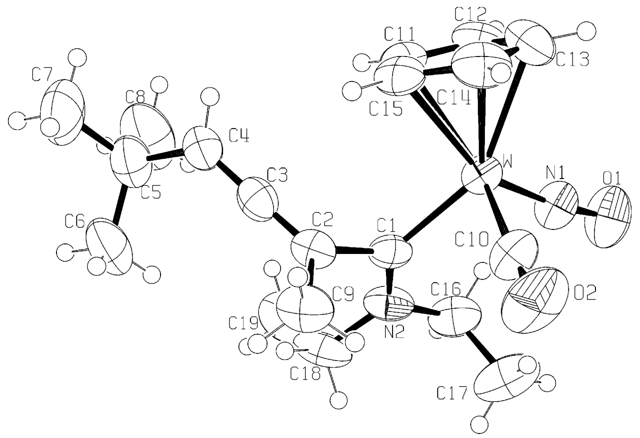

Figure 2. Molecular structure and atom-numbering scheme for **7a** with H atoms. Thermal ellipsoids are shown at the 40% probability level.

Table 3. Selected Bond Distances (Å) and Bond Angles (deg) for 7a

Bond Distances			
W−C(10)	1.958(6)	N(2)−C(16)	1.470(8)
W−N(1)	1.780(5)	N(2)−C(18)	1.476(8)
W−C(1)	2.118(5)	C(2)−C(9)	1.532(7)
N(1)−O(1)	1.227(6)	C(2)−C(3)	1.301(7)
C(10)−O(2)	1.154(7)	C(3)−C(4)	1.293(8)
C(1)−N(2)	1.345(7)	C(4)−C(5)	1.503(8)
C(1)−C(2)	1.509(8)	C(5)−C(6)	1.518(10)
Bond Angles			
C(10)−W−N(1)	93.7(2)	C(16)−N(2)−C(18)	114.1(5)
N(2)−C(1)−W	132.0(4)	C(1)−C(2)−C(9)	116.6(5)
C(2)−C(1)−W	114.5(4)	C(3)−C(2)−C(9)	122.0(5)
C(2)−C(1)−N(2)	113.5(4)	C(1)−C(2)−C(3)	121.4(4)
C(1)−N(2)−C(16)	121.4(5)	C(2)−C(3)−C(4)	175.1(7)
C(1)−N(2)−C(18)	124.4(5)	C(3)−C(4)−C(5)	127.9(6)

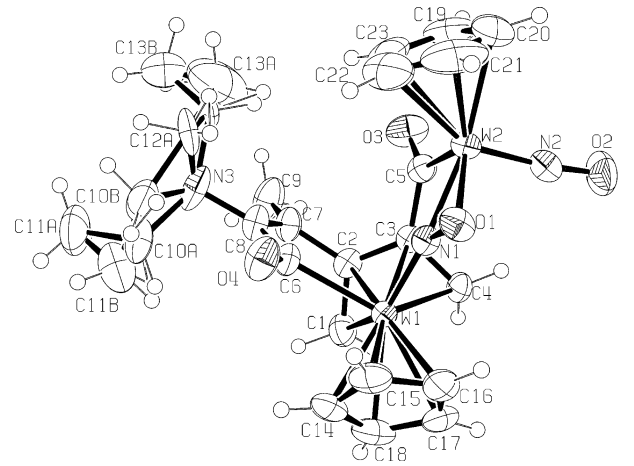

Figure 3. Molecular structure and atom-numbering scheme for **9** with H atoms. Thermal ellipsoids are shown at the 40% probability level.

behavior, the ^{13}C NMR spectra of **7a**,**b** show no signals for W═*C* and C═*C*═CHC(CH$_3$)$_3$ at room temperature. However, below −30 °C in the ^{13}C NMR spectrum the characteristic signal for the amino carbene C atom of both rotamers of **7a** appears at δ 251.6 and 250.9 ppm.[5] Also according to the allenic structure, the characteristic signals for C(3) appear at this temperature at δ 195.3 and 192.9 ppm, in the expected range for the allene group.[6] The characterization of **7b** is analogous to that for **7a**; $\Delta G^* = 14.2$ kcal/mol.

Molecular Structure of 7a. For the X-ray structural analysis suitable single crystals of diasteromerically pure **7a** were grown from a pentane/CH$_2$Cl$_2$ solution at −18 °C. The crystal parameters, data collection parameters, and conditions for structure refinement are summarized in Table 1. Selected bond lengths and angles are given in Table 3. A view of the molecule of **7a** is given in Figure 2. The most notable features of the structure are as follows. (a) The bond angles W−C(1)−N(2) (132.0(4)°), W−C(1)−C(2) (114.5(4)°), and N(2)−C(1)−C(2) (113.5(4)°) and the W−C(1) distance (2.118(5) Å) are typical for an (aminocarbene)tungsten complex.[4,7] (b) The sum of angles around the nitrogen atom (360.0°) and the C(1)−N(2) bond length of 1.345(7) Å demonstrate an sp^2 arrangement of the N(2) atom. (c) The C═C bond lengths of the almost linear propadienyl substituent (C(2)−C(3) = 1.301(7) Å and C(3)−C(4) = 1.293(8) Å) are comparable with the C═C═C bond length in allenes (1.32 Å).[3,8]

Characterization of 9. The structure of complex **9** was fully characterized by a combination of elemental analysis, ^{1}H, ^{13}C, DEPT, and HMQC NMR spectroscopy, and X-ray crystallographic data. The ^{1}H NMR spectrum of **9** shows for the diastereotopic protons on C(4) (for simplicity the numbering of the ORTEP plot is used) two doublets at δ 3.04 and 1.85 ppm ($J = 3.20$ Hz) and for the diastereotopic protons on C(1) two doublets at δ 1.43 and 0.84 ppm ($J = 1.20$ Hz). Due to the hindered rotation around the C(8)−N(3) bond, the methylene group of N(CH$_2$CH$_3$)$_2$ appears as a multiplet at δ 2.95−2.82 ppm. The ^{13}C NMR spectrum of **9** displays six quaternary signals: two signals at δ 258.6 and 248.0 ppm for two carbonyl carbons and four signals at δ 174.1, 168.8, 157.1, and 129.1 ppm for four olefinic carbon atoms, in the typical range for substituted olefins.[7] The signals for C(4) and C(1) appears at δ 47.5 and 45.9 ppm, respectively. The IR spectra of **9** exhibit two strong carbonyl bands in the 1609 and 1595 cm^{-1} regions.

Molecular Structure of 9. Suitable single crystals of complex **9** were grown from *n*-pentane/CH$_2$Cl$_2$. The X-ray diffraction study confirmed, in addition to the NMR spectroscopy and analytical data, the structure of **9**. An ORTEP view of molecule **9** is shown in Figure 3. The conditions for structure refinement are summarized in Table 1. Selected bond distances and angles are given in Table 4. In addition to the remarkable polycyclic structure, the most interesting feature of the structure of **9** is the bridging nitrosyl ligand. The W(1)−N(1) distance (1.908(5) Å) is slightly shorter than W(2)−N(1) (2.023(5) Å) but longer than W(2)−N(2) (1.768(5) Å). The N(1)−O(1) distance (1.338(6) Å) is longer than N(2)−O(2) (1.220(6) Å). The W(1)−C(1) (2.293(7) Å) and W(1)−C(4) (2.255(6) Å) distances are comparable with

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Table 4. Selected Bond Distances (Å) and Bond Angles (deg) for 9

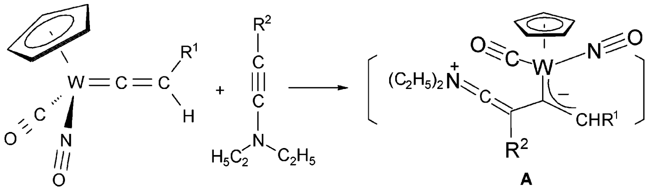
Bond Distances			
W(1)−N(1)	1.908(5)	C(7)−C(8)	1.319(9)
W(1)−C(1)	2.293(7)	C(7)−C(2)	1.490(8)
W(1)−C(4)	2.255(6)	C(7)−C(9)	1.501(9)
W(1)−C(3)	2.271(5)	C(8)−N(3)	1.415(8)
W(1)−C(2)	2.307(6)	C(3)−C(5)	1.511(8)
W(1)−C(6)	2.238(5)	C(5)−O(3)	1.217(7)
N(1)−O(1)	1.338(6)	W(2)−N(2)	1.768(5)
C(2)−C(1)	1.412(9)	W(2)−N(1)	2.023(5)
C(2)−C(3)	1.423(8)	W(2)−O(1)	2.077(4)
C(3)−C(4)	1.445(7)	W(2)−C(5)	2.183(6)
C(6)−O(4)	1.215(7)	N(2)−O(2)	1.220(6)
C(8)−C(6)	1.508(8)		

Bond Angles			
C(6)−W(1)−N(1)	84.4(2)	C(2)−C(3)−C(4)	114.1(5)
C(1)−W(1)−C(6)	85.9(3)	C(7)−C(8)−N(3)	122.6(6)
C(4)−W(1)−C(6)	127.7(2)	C(6)−C(8)−N(3)	122.1(6)
C(1)−W(1)−C(4)	71.3(3)	C(8)−C(6)−O(4)	121.1(5)
C(1)−W(1)−N(1)	137.8(2)	C(8)−N(3)−C(10A)	107.0(10)
C(4)−W(1)−N(1)	82.8(2)	C(8)−N(3)−C(10B)	127.5(10)
O(1)−N(1)−W(1)	140.9(3)	C(8)−N(3)−C(12A)	123.2(11)
O(4)−C(6)−W(1)	118.7(4)	C(8)−N(3)−C(12B)	109.1(8)
C(2)−C(1)−W(1)	72.7(4)	C(10A)−N(3)−C(12A)	107.9(14)
C(3)−C(4)−W(1)	72.0(3)	C(10B)−N(3)−C(12B)	105.4(15)
C(8)−C(6)−W(1)	120.1(4)	C(9)−C(7)−C(8)	127.7(6)
C(7)−C(8)−C(6)	115.3(5)	C(2)−C(7)−C(9)	115.8(6)
C(2)−C(7)−C(8)	116.1(5)	C(4)−C(3)−C(5)	122.0(5)
C(7)−C(2)−C(1)	118.7(5)	C(2)−C(3)−C(5)	123.6(5)
C(1)−C(2)−C(3)	116.8(5)	C(3)−C(5)−O(3)	115.9(6)
C(3)−C(5)−W(2)	116.9(4)	O(3)−C(5)−W(2)	127.2(5)
O(2)−N(2)−W(2)	173.6(5)	O(1)−W(2)−N(2)	99.8(2)
O(1)−N(1)−W(2)	73.2(3)	O(1)−W(2)−C(5)	115.4(2)
N(1)−O(1)−W(2)	68.8(3)	N(2)−W(2)−N(1)	101.3(2)
O(1)−W(2)−N(1)	38.1(2)	N(1)−W(2)−C(5)	77.3(2)
W(1)−N(1)−W(2)	145.2(3)	N(2)−W(2)−C(5)	89.3(2)

W−C(sp^3) single-bond lengths in tungsten complexes.[9] The butadiene moiety of the molecule has bond lengths of C(7)−C(8) = 1.319(9) Å, C(2)−C(7) = 1.490(8) Å, and C(2)−C(3) = 1.423(8) Å. The planar arrangement of N(3), the sum of angles at N(3) (360.0°), and the bond length of N(3)−C(8) (1.415(8) Å) demonstrate the C(sp^2)−N(sp^2) character of the N(3)−C(8) bond.[3]

Characterization of 10. ^{1}H NMR spectroscopic as well as mass spectroscopic data and elemental analysis confirm the constitution of **10** as a 1:2 adduct of the η^1-vinylidene complex **8** and ynamine **2a**. The IR spectra of **10** exhibit a strong carbonyl absorption in the 1541 cm^{-1} region. The structure of **10** was established by ^{1}H, ^{13}C, DEPT, HMQC (one-bond ^{13}C−^{1}H coupling),[10] and HMBC (long-range ^{13}C−^{1}H coupling)[11] NMR spectroscopy. The ^{1}H NMR spectrum of **10** shows the protons of the methyl group on C(8) as a doublet at 1.54 ppm (J = 4.4 Hz) and the protons of the methyl group on C(4) as a singlet at 2.03 ppm. Because of the interaction of the amine groups with a π system, two sets of multiplets are observed for the methylene protons of amine groups. The proton on C(6) appears at 7.16 ppm with the corresponding satellite signals caused by the coupling with the ^{183}W atom: $^3J(^{183}W-^1H) = 6$ Hz. The ^{13}C NMR spectrum displays resonances for the carbonyl carbon at δ 253.5 ppm with $^1J(^{183}W-^{13}C) = 49.6$ Hz, the carbene carbon atom appears at δ 224.9 ppm with $^1J(^{183}W-^{13}C) = 47.0$ Hz, C(6) at 117.0 ppm, C(4) at 143.7 ppm, C(7) at δ 185.7 ppm, C(3) at 165.4 ppm, and C(8) at 38.9 ppm. HMBC spectra proved to be particularly helpful for identifying resonances due to carbon atoms without protons bonded to them, as cross-peaks indicated the coupling of ^{13}C and ^{1}H nuclei separated by two and three bonds. For example, the HMBC spectrum shows a correlation of the ^{1}H signal at 7.16 ppm, H(6), to ^{13}C signals at 224.9 ppm (C(5)), 143.7 ppm (C(4)), 185.7 ppm (C(7)), and 38.9 ppm (C(8)). Selected one-bond ^{13}C−^{1}H couplings and long-range ^{13}C−^{1}H couplings found in the HMQC and HMBC spectra are listed in the Experimental Section. The features of CHN analysis, mass spectra, and ^{1}H, ^{13}C, DEPT, HMQC, and HMBC NMR spectra of complex **10** are completely compatible with the assigned structure.

Scheme 4. Proposed First Step for the Reaction of Ynamines with η^1-Vinylidene Complexes



Mechanistic Considerations. As a working hypothesis we expect that the common step for the formation of the products **4**, **5**, **7**, **9**, and **10** is the nucleophilic attack of ynamines **2a**,**b** at C$_\alpha$ of the η^1-vinylidene complexes to form the key intermediate **A** (Scheme 4). In the literature a similar reaction mode is described for the addition of ynamines to the allenylidene complexes of chromium.[2c] The electronic and steric properties of the substituent R^1 determine significantly the chemical reactivity of this zwitterionic species.

The sterically demanding *tert*-butyl group (R^1 = C(CH$_3$)$_3$) leads to the attack of the tungsten center at the C$_\alpha$ atom of the iminium group, generating the metallacyclobutene derivatives **B** (path a in Scheme 5). Subsequent ring opening gave rise to the observed aminocarbene moieties **7a**,**b**. On the other hand, a phenyl group as R^1 influences the electron density distribution of this intermediate and facilitates the addition of C$_\beta$ to C$_\alpha$ of the iminium group, forming the cyclobutenylidene complex **C** (path b in Scheme 5). Concomitant 1,3-migration of the hydrogen atom leads to the cyclobutenylidene derivatives **4a**,**b** and **5a**,**b**.

The intermediate **A** generated by the reaction of the parent η^1-vinylidene complex **8** with the ynamine **2a** (R^1 = H) shows a third reaction mode (path c). In this case the carbonyl carbon atom of the intermediate **A** attacks the C$_\alpha$ atom of the iminium group, producing the electronically unsaturated and therefore reactive cyclic acyl complex **D**. This intermediate is than trapped either by the η^1-vinylidene complex **8** or by the ynamine **2a** present in the reaction mixture (Scheme 6). Addition of the η^1-vinylidene complex **8** by its nucleophilic C$_\beta$ atom to the unsaturated metal center of **D** generates the carbyne intermediate **E**. A series of bond-forming and bond-breaking steps (**E**−**F**−**G**) produce the product **9**. An alternative to this process is trapping of the intermediate complex **D** by the nucleophilic ynamine **2a**, generating through the steps **D**−**H**−**I** the bicyclic carbene derivatives **10**.

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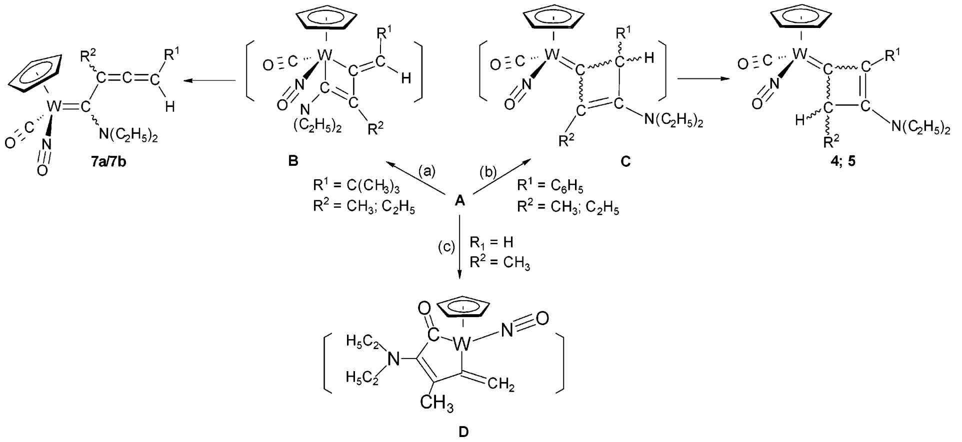
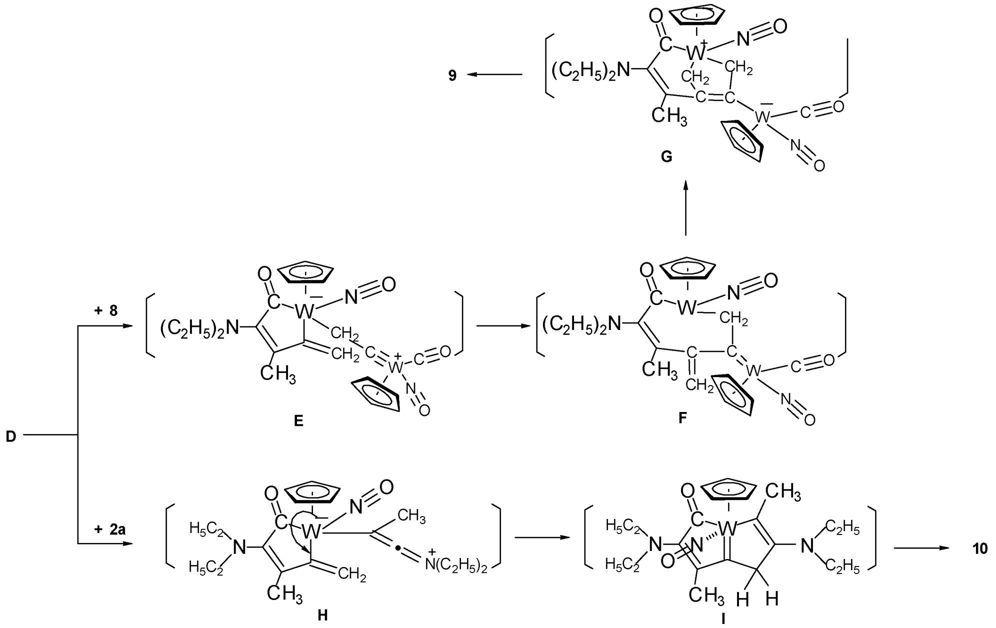
Scheme 5. Proposed Mechanisms for the Reaction of η^1-Vinylidene Complexes 1, 6, and 8 with Ynamines 2a,b



Scheme 6. Proposed Mechanisms for the Formation of Complexes 9 and 10



To support this hypothesis, we undertook the following experiment. Slow addition of ynamine **2a** over 4 h at room temperature to a solution of η^1-vinylidene complex **8** in THF afforded as the sole product of the reaction the complex **9** in 45% yield. According to the ^{1}H NMR spectra of the crude material, complex **10** was not formed. In contrast, the addition of complex **8** (0.33 equiv) to a solution of ynamine **2a** (1 equiv) in THF suppressed the formation of complex **9** and generated at room temperature the carbene derivative **10** in 41% yield.

NLO Properties of Complex 4a. The 3-amino-substituted cyclobutenylidene complexes **4** and **5** constitute organometallic push–pull systems, composed of a strong donor, $N(CH_2CH_3)_2$, and an acceptor moiety, Cp(CO)(NO)W, which are connected by a four-membered cyclic π system. Of particular interest is the first hyperpolarizability, β, of these compounds, which reflects the molecular capability to double the frequency of incoming laser light (second-harmonic generation, SHG). The first molecular hyperpolarizability β was determined by the hyper-Rayleigh scattering (HRS) method[12] with a Nd:YAG laser whose fundamental wavelength (λ 1064 nm) was shifted to λ 1500 nm by means of an optical parametric oscillator (OPO).[13]

Thus, the superposition of the strong low-energy absorption and the HRS signal was minimized, which makes the calculated static hyperpolarizability (β_0)[14] more reliable.[15,16] Another important reason for using the higher wavelength of the incident beam is an attempt to discriminate between a true SHG signal and a two photon absorption induced fluorescence (TPAF) enhanced signal.[16,17–19]

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(12) Clays, K.; Persoons, A. *Rev. Sci. Instrum.* **1992**, *63*, 3285.

(13) Paralite Optical Parametrical Oscillator, LAS GmbH.

(14) (a) Oudar, L. J.; Chemla, D. S. *Chem. Phys.* **1977**, *66*, 2664. (b) Hendrickx, E.; Clays, K.; Dehu, C.; Brédas, J. L. *J. Am. Chem. Soc.* **1995**, *117*, 3547.

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(19) (a) Wolff, J. J.; Wortmann, R. *J. Prakt. Chem.* **1998**, *340*, 99. (b) Stadler, S.; Dietrich, R.; Bourhill, G.; Bräuchle, C. *J. Phys. Chem.* **1996**, *100*, 6927.

The intensity of the scattered SHG at λ 750 nm was measured as a function of the **4a** concentrations in CH_2Cl_2 (0.1−0.6 mM). As an external reference Disperse Red 1 ($\beta(CH_2Cl_2) = 70 \times 10^{-30}$ esu) was used and $\beta = 105 \times 10^{-30}$ esu was obtained.[20] This value is resonance-enhanced, and therefore, the static first hyperpolarizability $\beta_0 = 34 \times 10^{-30}$ esu has been calculated using the two-level model (TLM),[14] which is quite good with regard to short dipole length and value compared to other β values obtained from organometallic push−pull complexes studied under similar conditions.[2d]

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^5-C_5H_5)(CO)(NO)W=C=C(H)R] (**1**, **6**, **8**)[21] and RC≡CN(C_2H_5)$_2$ (**2a**,**b**).[22] All other compounds were commercially available. NMR spectra were obtained on a Bruker AM 400 spectrometer (^{1}H NMR, 400.13 MHz; ^{13}C NMR, 100.61 MHz). 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 experiments were run on the Bruker AM 400 spectrometer. 2D gradient HMQC and HMBC spectra were recorded on a Bruker DRX 500 spectrometer. MS measurements (70 eV) were performed on a Varian MAT 311-A instrument. IR spectra were recorded on a Bruker FT-IR IFS 85. UV spectra were recorded on a Hewlett-Packard 8452 spectrometer. Microanalyses were performed on a Carlo Erba 1104 elemental analyzer.

Carbonyl(η^5-cyclopentadienyl)nitrosyl[3-(diethylamino)-2-phenyl-4-methyl-2-cyclobutenylidene]tungsten (4a and 5a). To 1 g (2.45 mmol) of the tungsten η^1-vinylidene species **1** in 20 mL of THF at room temperature was added 1 g (9 mmol) of 1-(diethylamino)-1-propyne (**2a**). The color immediately changed from orange to dark red. The reaction was complete within 4 h, as determined by IR spectroscopy. The solvent and excess 1-(diethylamino)-1-propyne was removed under vacuum at room temperature. Chromatography at 0 °C on silica gel with pentane−ether (ratio decreasing from 1:0 to 1:2) yielded 240 mg (18%) of **5a** and 433 mg (34%) of **4a** as red crystals.

4a: Anal. Calcd for $C_{21}H_{24}WN_2O_2$: C, 48.50; H, 4.61; N, 5.39. Found: C, 48.42; H, 4.36; N, 5.23. ^{1}H NMR ($CDCl_3$): δ 7.37−7.18 (m, 5H), 5.28 (s, 5H, Cp), 3.91 (q, J = 6.77 Hz, 1H), 3.29 (q, J = 7.42 Hz, 2H, NCH_2), 3.12−3.06 (m, 2H, NCH_2), 1.62 (d, J = 6.77 Hz, 3H, C(H)CH_3), 1.24 and 0.95 (2 t, J = 7.15 Hz, 6H, NCH_2CH_3). ^{13}C NMR ($CDCl_3$): δ 270.8 (C1), 228.7 (C=O), 163.7 (C3), 141.1 (C2), 137.5 (C_{ipso}), 129.6, 128.2, 128.12 (arom C), 93.6 (Cp), 55.7 (C4), 43.3, 41.9 (NCH_2), 18.7 (C(H)-CH_3), 14.1, 13.0 (NCH_2CH_3). IR (KBr; $\tilde{\nu}$, cm^{-1}): 1905 (C=O), 1633 (N=O). MS (70 eV): *m/e* 520 (M^+, ^{184}W), 492 (M^+ − CO), 462 (M^+ − CO − NO). High-resolution mass spectrum: calcd for $C_{21}H_{24}{}^{182}WN_2O_2$ (M^+) *m/e* 518.1301, found *m/e* 518.1301. UV/vis (λ, nm (log ϵ, solvent)): 418 (3.415, CH_2Cl_2).

5a: Anal. Calcd for $C_{21}H_{24}WN_2O_2$: C, 48.50; H, 4.61; N, 5.39. Found: C, 48.47; H, 4.42; N, 5.20. ^{1}H NMR ($CDCl_3$): δ 7.45−7.13 (m, 5H), 5.30 (s, 5H, Cp), 3.82 (q, J = 7.60 Hz, 1H), 3.26 (q, J = 7.20 Hz, 2H, NCH_2), 3.14−3.02 (m, 2H, NCH_2), 1.63 (d, J = 7.60 Hz, 3H, C(H)CH_3), 1,24 and 0.89 (2 t, J = 7.20 Hz, 6H, NCH_2CH_3). ^{13}C NMR ($CDCl_3$): δ 270.8 (C1), 229.2 (C=O), 163.6 (C3), 141.3 (C2), 137.5 (C_{ipso}), 129.6, 128.2, 127.1 (arom C), 93.6 (Cp), 56.8 (C4), 43.1, 41.9 (NCH_2), 19.4 (C(H)-CH_3), 14.1, 13.0 (NCH_2CH_3). IR (KBr; $\tilde{\nu}$, cm^{-1}): 1905 (C=O), 1633 (N=O). MS (70 eV): *m/e* 520 (M^+, ^{184}W), 492 (M^+ − CO), 462 (M^+ − CO − NO). High-resolution mass spectrum: calcd for $C_{21}H_{24}{}^{182}WN_2O_2$ (M^+) *m/e* 518.1301, found *m/e* 518.1302.

Carbonyl(η^5-cyclopentadienyl)nitrosyl[3-(diethylamino)-2-phenyl-4-ethyl-2-cyclobutenylidene]tungsten (4b and 5b). To 1 g (2.45 mmol) of the tungsten η^1-vinylidene **1** in 20 mL of THF at room temperature was added 1 g (8 mmol) of 1-(diethylamino)-1-butyne (**2b**). The color immediately changed from orange to dark red. The reaction was complete within 6 h, as determined by IR spectroscopy. The solvent and excess 1-(diethylamino)-1-butyne was removed under vacuum at room temperature. Chromatography at 0 °C on silica gel with pentane−ether (ratio decreasing from 1:0 to 1:2) yielded 221 mg (17%) of **5b** and 391 mg (30%) of **4b** as red crystals.

4b: Anal. Calcd for $C_{22}H_{26}WN_2O_2$: C, 49.45; H, 4.90; N, 5.24. Found: C, 49.25; H, 4.76; N, 5.23. ^{1}H NMR ($CDCl_3$): δ 7.44−7.11 (m, 5H), 5.28 (s, 5H, Cp), 4.01 (t, J = 3.76 Hz, 1H), 3.24 (q, J = 7.72 Hz, 2H, NCH_2), 3.08 (q, J = 6.62 Hz, 2H, NCH_2), 2.63−2.54 (m, 1H, CH_2CH_3), 1.89−1.78 (m, 1H, CH_2CH_3), 1.28 (t, J = 6.62 Hz, 3H, NCH_2CH_3), 0.94 (t, J = 6.62 Hz, 3H, CH_2CH_3), 0.89 (t, J = 7.72 Hz, 3H, NCH_2CH_3). ^{13}C NMR ($CDCl_3$): δ 268.7 (t, $^1J(^{183}W-^{13}C)$ = 76.3 Hz, C1), 229.4 (t, $^1J(^{183}W-^{13}C)$ = 102.7 Hz, C=O), 161.1 (C3), 143.0 (C2), 137.7 (C_{ipso}), 129.7, 128.2, 127.1 (arom C), 93.4 (Cp), 61.8 (C4), 43.3, 42.0 (NCH_2), 22.7 (CH_2CH_3), 13.9, 13.0 (NCH_2CH_3), 8.6 (CH_2CH_3). IR (KBr; $\tilde{\nu}$, cm^{-1}): 1901 (C=O), 1623 (N=O). MS (70 eV): *m/e* 534 (M^+, ^{184}W), 506 (M^+ − CO), 476 (M^+ − CO − NO). High-resolution mass spectrum: calcd for $C_{22}H_{26}{}^{182}WN_2O_2$ (M^+) *m/e* 532.1476, found *m/e* 532.1441. UV/vis (λ, nm (log ϵ; solvent)): 417 (4.350, CH_2Cl_2).

5b: Anal. Calcd for $C_{22}H_{26}WN_2O_2$: C, 49.45; H, 4.90; N, 5.24. Found: C, 49.31; H, 4.70; N, 5.28. ^{1}H NMR ($CDCl_3$): δ 7.42−7.13 (m, 5H), 5.27 (s, 5H, Cp), 4.05−3.99 (m, 1H), 3.34−3.01 (m, 4H, NCH_2), 2.49−2.39 (m, 1H, CH_2CH_3), 1.95−1.85 (m, 1H, CH_2CH_3), 1.24 (t, J = 8.37 Hz, 3H, NCH_2CH_3), 0.92 (t, J = 6.89 Hz, 3H, NCH_2CH_3), 0.92 (t, J = 7.38 Hz, 3H, CH_2CH_3). ^{13}C NMR ($CDCl_3$): δ 270.1 (C1), 229.6 (C=O), 165.6, 161.1 (C3), 143.0, 137.63 (C2), 133.2, 132.3 (C_{ipso}), 129.7, 128.7, 128.2, 128.1, 127.2, 126.3 (arom C), 93.5 (Cp), 60.2, 59.1 (C4), 43.6, 42.1, 41.6 (NCH_2), 22.9, 21.2 (CH_2CH_3), 13.9, 13.1 (NCH_2CH_3), 8.6, 8.2 (CH_2CH_3). IR (KBr; $\tilde{\nu}$, cm^{-1}): 1901 (C=O), 1628 (N=O). MS (70 eV): *m/e* 534 (M^+, ^{184}W), 506 (M^+ − CO), 476 (M^+ − CO − NO). High-resolution mass spectrum: calcd for $C_{22}H_{26}{}^{182}WN_2O_2$ (M^+) *m/e* 532.1476, found *m/e* 532.1471.

[(η^5-C_5H_5)(NO)(CO)]W=C[N(C_2H_5)$_2$]C(CH_3)=C=CH-[C(CH_3)$_3$] (7a). The preparation of **7a** is analogous to that for **4a**, except that 0.95 g (2.45 mmol) of **6** was used instead of **1** and the reaction mixture was heated at 55 °C for 6 h. Yield: 698 mg (57%) of **7a** as orange crystals. Anal. Calcd for $C_{19}H_{28}WN_2O_2$: C, 45.61; H, 5.64; N, 5.59. Found: C, 45.57; H, 5.59; N, 5.82. ^{1}H NMR ($CDCl_3$, −30 °C): δ 5.58 and 5.56 (two s, 2:3, 5H, Cp), 5.31 and 4.98 (two q, 3:2, J = 3.0 Hz and J = 2.9 Hz, 1H, H), 3.97−3.50 (m, 4H, NCH_2), 1.72 and 1.69 (two d, 3:2, J = 3.0 Hz and J = 2.9 Hz, 3H, CH_3), 1.28 (t, J = 7.08 Hz, 3H, NCH_2CH_3), 1.21 (m, 3H, NCH_2CH_3), 0.96 and 0.92 (two s, 9H, C(CH_3)$_3$). ^{13}C NMR ($CDCl_3$, −30 °C): δ 251.6 and 250.9 (W=C), 235.3 and 233.0 (C=O), 195.3 and 192.9 (C=*C*=C), 110.9 and 110.0 (*C*(CH_3)), 104.7 and 103.9 (CH), 94.8 and 94.7 (Cp), 52.0, 51.9, 48.1, and 47.8 (NCH_2), 33.2 and 33.0 (*C*(CH_3)$_3$), 30.0 and 29.8 (C(CH_3)$_3$), 23.2 and 19.9 (CCH_3), 15.8, 14.9, 12.6, and 12.4 (NCH_2CH_3). IR (KBr; $\tilde{\nu}$, cm^{-1}): 1907 (C=O), 1567 (N=O). MS (70 eV): *m/e* 500 (M^+, ^{184}W), 472 (M^+ − CO), 442 (M^+ − CO − NO). High-resolution mass spectrum: calcd for $C_{19}H_{28}{}^{182}WN_2O_2$ (M^+) *m/e* 498.163 29, found *m/e* 498.161 38.

[(η^5-C_5H_5)(NO)(CO)]W=C[N(C_2H_5)$_2$]C(C_2H_5)=C=CH-[C(CH_3)$_3$] (7b). The preparation of **7b** is analogous to that for **7a**, except that 1-(diethylamino)-1-butyne was used instead

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of 1-(diethylamino)-1-propyne. Yield: 566 mg (45%) of **7b** as orange crystals. Anal. Calcd for $C_{20}H_{30}WN_2O_2$: C, 46.70; H, 5.88; N, 5.44. Found: C, 46.67; H, 6.04; N, 5.42. ^{1}H NMR ($CDCl_3$, −23 °C): δ 5.61 and 5.60 (two s, 2:3, 5H, Cp), 5.52 and 5.19 (two t, 3:2, $J = 4$ Hz, 1H), 4.12−3.46 (m, 4H, NCH_2), 2.26−1.71 (m, CH_2), 1.26−1.35 (m, 6H, NCH_2CH_3), 1.04 and 0.99 (two s, 3:2, 9H, $C(CH_3)_3$), 0.93 (m, 3H, CH_2CH_3). ^{13}C NMR ($CDCl_3$, −23 °C): δ 252.7 and 252.4 (W═C), 234.3 and 235.0 (C═O), 194.6 and 191.0 (C═*C*═C), 118.9 and 117.5 (*C*(C_2H_5)), 107.6 and 106.7 (CH), 94.8 and 94.6 (Cp), 52.0, 51.3, and 47.9 (NCH_2), 33.2 and 33.1 (*C*($CH_3)_3$), 30.1 and 29.9 ($C(CH_3)_3$), 28.3 and 24.2 (CCH_2CH_3), 15.7 and 15.0 (CCH_2CH_3), 12.7, 12.4, 11.7, and 11.3 (NCH_2CH_3). IR (KBr; $\tilde{\nu}$, cm^{-1}): 1907 (C═O), 1570 (N═O). MS (70 eV): *m*/*e* 514 (M^+, ^{184}W), 486 ($M^+ - CO$), 456 ($M^+ - CO - NO$). High-resolution mass spectrum: calcd for $C_{20}H_{30}{}^{182}WN_2O_2$ (M^+) *m*/*e* 512.178 94, found *m*/*e* 512.180 76.

Synthesis of 9. To 1 g (3 mmol) of the tungsten η^1-vinylidene **8** in 10 mL of THF at room temperature was added a solution of 1 g (9 mmol) of 1-(diethylamino)-1-propyne (**2a**) in 15 mL THF over 4 h. The solvent and excess 1-(diethylamino)-1-propyne was removed under vacuum at room temperature. The residue was washed with pentane. Chromatography at 0 °C on silica gel with pentane−ether (ratio decreasing from 1:0 to 1:4) yielded 576 mg (45%) of **9** as dark red crystals. Anal. Calcd for $C_{23}H_{27}W_2N_3O_4$: C, 35.54; H, 3.50; N, 5.41. Found: C, 35.93; H, 3.32; N, 5.40. ^{1}H NMR ($CDCl_3$): δ 6.02 and 5.77 (two s, 10H, two Cp), 3.04 (d, $J = 3.20$ Hz, 1H, (C4)H), 2.95−2.82 (m, 4H, NCH_2), 2.48 (s, 3H, CH_3), 1.85 (d, $J = 3.20$ Hz, 1H, (C4)H), 1.43 (d, $J = 1.20$ Hz, 1H, (C1)H), 0.92 (t, $J = 7.20$ Hz, 6H, NCH_2CH_3), 0.84 (d, $J = 1.20$ Hz, 1H, (C1)H). ^{13}C NMR ($CDCl_3$): δ 258.6 (C6), 248.0 (C5), 174.1 (C8), 163.8 (C3), 157.1 (C7), 129.1(C2), 104.1 and 102.4 (Cp), 47.5 (C4), 46.9 (NCH_2), 45.9 (C1), 20.7 (CH_3), 14.5 (NCH_2CH_3). IR (KBr; $\tilde{\nu}$, cm^{-1}): 1609 and 1595 (C═O), 1563 (N═O).

Synthesis of 10. To 1 g (9 mmol) of 1-(diethylamino)-1-propyne (**2a**) in 10 mL of THF at room temperature was added a solution of 1 g (3 mmol) of the tungsten η^1-vinylidene **8** in 15 mL of THF over 4 h. The solvent and excess 1-(diethylamino)-1-propyne was removed under vacuum at room temperature. Chromatography at 0 °C on silica gel with pentane−ether (ratio decreasing from 1:0 to 0:1) and ether−methanol (ratio decreasing from 1:0 to 1:1) yielded 682 mg (41%) of **10** as a dark red oil. Anal. Calcd for $C_{22}H_{33}WN_3O_2$: C, 47.58; H, 5.99; N, 7.57. Found: C, 47.31; H, 5.59; N, 7.90. ^{1}H NMR ($CDCl_3$): δ 7.16 (t, $^3J(^{183}W-^1H) = 6$ Hz, 1H, C6H), 5.50 (s, 5H, Cp), 3.82−3.16 (m, 9H, NCH_2 and (C8)H), 2.03 (s, 3H, CH_3), 1.54 (d, $J = 4.43$ Hz, 3H, CH_3), 1.40−1.28 (m, 6H, NCH_2CH_3), 1.11 (t, $J = 8.86$ Hz, 6H, NCH_2CH_3). ^{13}C NMR ($CDCl_3$): δ 253.5 (t, $^1J(^{183}W-^{13}C) = 49.6$ Hz, C═O), 224.9 (t, $^1J(^{183}W-^{13}C) = 47.0$ Hz, C5), 185.7 (C7), 165.4 (C3), 143.7 (C4), 117.0 (C6), 99.7 (Cp), 47.3, 45.1, and 44.6 (NCH_2), 38.9 (C8), 24.7 ((C10)H_3), 14.6, 14.4, and 14.0 (NCH_2CH_3), 13.7 ((C9)H_3). IR (KBr; $\tilde{\nu}$, cm^{-1}): 1613 (N═O), 1541 (C═O). MS (70 eV): *m*/*e* 555 (M^+, ^{184}W). High-resolution mass spectrum: calcd for $C_{22}H_{33}{}^{182}WN_3O_2$ (M^+) *m*/*e* 553.2047, found *m*/*e* 553.2047.

Selected one-bond and long-range ^{1}H−^{13}C couplings of complex **10**:

H	one-bond ^{1}H−^{13}C coupling	long-range ^{1}H−^{13}C coupling
H(6)	C(6)	C(4), C(5), C(7), C(8)
H(8)	C(8)	C(6), C(7)
C*H*$_3$ at C(4)	*C*H$_3$ at C(4)	C(3), C(4), C(5)
C*H*$_3$ at C(8)	*C*H$_3$ at C(8)	C(7), C(8)

HRS Measurements of the First Hyperpolarizability of 4a. The measurements at 1500 nm wavelength were carried out similar to the setup described in ref 16. Instead of the third harmonic (355 nm) generated from a Nd:YAG laser with a wavelength of 1064 nm the optical parametric oscillator (OPO)[13] in use was pumped with the second harmonic (532 nm). The signal intensity at 824 nm and the fundamental at 532 nm were removed from the idler using dichroic mirrors (HR 650-850 and HR 532), a green light, and a silicon filter (transparent >1000 nm). An additional Glan−Taylor polarizer ensured the vertical polarization of the beam into the measurement cell. Measurements were performed with ~0.1−0.6 mM solutions of **4a** in CH_2Cl_2. The validity of Beer's law was proven by UV−vis measurements of samples with corresponding concentrations. Disperse Red 1 (DR1) was used as an external standard with a value of β_{1500}(DR1) = 70 × 10^{-30} esu. This value was obtained by comparing the slopes of the reference in CH_2Cl_2 and $CHCl_3$ to obtain the ratio of β_{solute}.[23] Using the value $\beta(CHCl_3) = 80 \times 10^{-30}$ esu[17] the hyperpolarizability of DR1 in CH_2Cl_2 is estimated to be 70 × 10^{-30} esu. The effect of the refractive indices of the solvents was corrected using the simple Lorentz local field.[24]

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Supporting Information Available: Tables giving crystal data and structure determination and refinement details, atomic coordinates, interatomic distances and angles, anisotropic thermal parameters, and hydrogen parameters of the compounds **4a**, **7a**, and **9**; these data are also available as CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.

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