η^2-Alkynyl and Vinylidene Transition Metal Complexes. 4.[1] Reaction of the Metal−Acetylide $[(\eta^5\text{-}C_5H_5)(NO)(CO)WC{\equiv}CR]^-$ with Allyl Halides To Give η^3-Allyl Complexes. (η^1-Alkynyl-η^3-allyl)tungsten Complexes: Preparation and Surface-Catalyzed Isomerization

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Treatment of anionic acetylide complexes $[(\eta^5\text{-}C_5H_5)(NO)(CO)WC{\equiv}CR]^-$ [R = $Si(CH_3)_3$ (**3**), $C(CH_3)_3$ (**11a**), or C_6H_5 (**11b**)] with allylic iodides **4b**, **14**, methallyl iodide, and 3-iodocyclohexene in THF at 0 °C afforded the corresponding η^1-alkynyl-η^3-allyl complexes **5**/**6**, **12**/**13**, and **15**−**19**. The formation of these η^3-allyl complexes is rationalized by the electrophilic attack on the metal center of acetylide complexes to create a η^1-allyl complex, which is further stabilized by elimination of a CO ligand. The η^3-allyl complexes **12a**/**13a**, **12b**/**13b**, **18a**, and **19a** undergo a surface-catalyzed isomerization on silica gel as well as neutral alumina to the (η^2-allene)tungsten complexes **20**−**23**. The crystal structures of complexes **17b** and **20** are reported.

Introduction

Transition metal complexes with η^1-acetylide ligands ($L_nMC{\equiv}CR$) continue to attract interest,[2] partially because of their strict relationship to the organometallic vinylidene chemistry[3,4] but also because of their role as precursors of molecules containing a linear array of delocalized π-systems.[5] In addition to the studies of basic chemical transformations,[6] the investigations in this area expand from nonlinear optical properties[7] to the preparation of liquid crystals[8] or polymeric materials.[9] A central question which remains to be answered is the bonding interaction of η^1-acetylide ligands ($C{\equiv}CR$) with the metal center. This is important for the understanding of the electronic interaction between the metal and the coordinated π-systems. The reactivity of metal acetylides with electrophiles gives some indirect indication of the metal/acetylide bonding interactions.

It is well recognized that the reactivity of transition metal acetylide complexes can be rationalized on the basis of resonance forms **A** and **B**, with form **B** becoming more prevalent with increasing electron density on the complex upon moving from cationic to anionic complexes.[3,4] The importance of resonance form **B** is

$$L_nM-\overset{\alpha}{C}\equiv\overset{\beta}{C}-R \longleftrightarrow L_n\overset{+}{M}=\overset{\alpha}{C}=\overset{\beta}{C}-R$$

A **B**

indicated by the general attack of electrophiles on the

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β-carbon atom to form vinylidene complexes **C** (eq 1).[10] In this way, a large number of vinylidene complexes were recently synthesized.[3,4] However, electrophilic

$$L_nM{-}C{\equiv}C{-}R + E^+ \longrightarrow \left[L_nM{=}C{=}C\begin{matrix}R\\E\end{matrix}\right]^+ \quad (1)$$

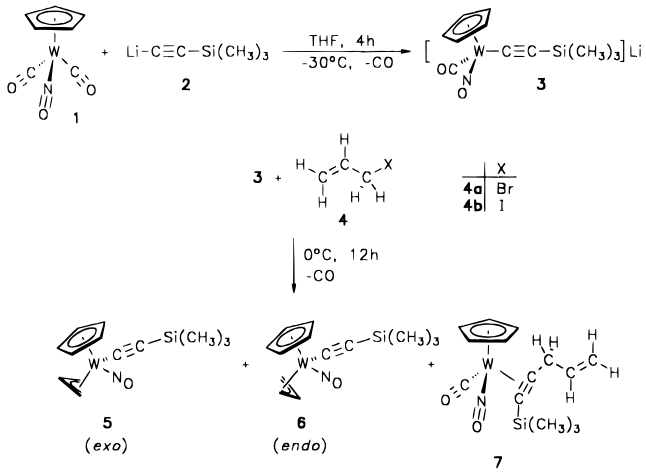
C

attacks on the metal centers were observed only very rarely.[4e] Addition at the metal center is more likely when electron-rich complexes or soft electrophiles are used. Spectroscopic evidence suggests that the protonation of the anionic acetylide complex *trans*-[RhCl(C≡CCO_2Et)(P^iPr_3)$_2$]$^-$[^{n}Bu_4N]$^+$ with nitromethane as a weak and soft acid occurs on rhodium and not on the alkynyl ligand.[11] There is no example so far where the product of an electrophilic addition on the metal center of an anionic acetylide complex has been isolated.[4e]

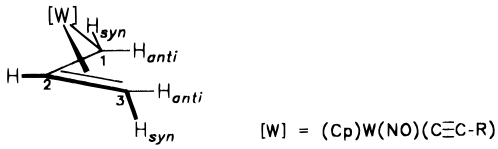
Intending to explore the possibility of electrophilic addition on the metal atom of metal acetylide anions, we investigated the reaction of tungsten complexes **3**, **11a**, and **11b** with a variety of allyl halides. Allylic electrophiles have the advantage that, after addition on the metal center as η^1-allyl ligands, they can undergo a $\sigma-\pi$-rearrangement to build stable η^3-allyl complexes. We found that, depending on the leaving group on the allyl halide, either exclusive attack on the metal atom to create a (η^3-allyl-η^1-alkynyl)tungsten complex occurs or a mixture of both metal allylation and C-allylation product is formed. Furthermore, we observed that the (η^3-allyl-η^1-alkynyl)tungsten complexes undergo an internal coupling reaction between allyl and alkynyl moieties on the surface of the silica gel or aluminum oxide leading to η^2-allene complexes.

Results and Discussion

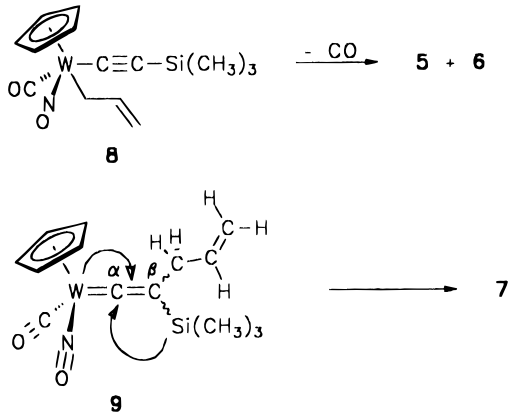
The emerald green solution of lithium metalate **3** is generated, as described before, by the reaction of lithium acetylide **2** with tungsten carbonyl complex **1** in THF at −30 °C for 4 h.[12] Addition of allyl iodide (**4b**) produces after 12 h at 0 °C a 1:3 mixture of *exo* and *endo* isomers of η^3-allyl -η^1-alkynyl complexes **5** and **6** in 62% yield.[13,14] In contrast to this result, addition of allyl bromide (**4a**) to **3** led with 53% yield to a 1:1 mixture of η^2-alkyne complex **7** and a mixture of η^3-allyl complexes **5** and **6**. Apparently the polarizability of the leaving group on the allyl halide plays a dominant role in this reaction.



The structures of **5** and **6** were confirmed by the characteristic pattern for η^3-allyl complexes in the ^{1}H NMR spectra.[15] In accordance with the structure, the *endo* product shows two signals for both H_{anti} at δ 1.1 and 3.0 and two signals for both H_{syn} at δ 2.3 and 4.2; the H2 appears at δ 5.1. The *anti* and *syn* protons, being closest to the metal, are shielded and appear at higher field.[16] The large chemical shift differences between both of the *anti* protons as well as between both of the *syn* protons is attributed to the asymmetric coordination of the allyl moiety and reveals a significant $\eta^3 \rightarrow \sigma,\eta^2$ distortion.



The formation of η^3-allyl complexes **5** and **6** can be rationalized by the electrophilic attack on the metal center of **3** to create the η^1-allyl complex **8**, which is further stabilized by the elimination of a CO ligand to produce the 18-electron (η^3-allyl)metal complexes as a mixture of *exo* and *endo* conformers **5** and **6**. As shown before, η^2-alkyne complex **7** is the result of allylation on the β-carbon atom of **3** to the vinylidene derivative **9**, followed by a shift of the trimethylsilyl group from the β-carbon to the α-carbon atom.[12a,17]



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(13) In idealized form the allyl group has been kept planar and parallel to the nitrosyl group. In the *exo* conformer, the central carbon atom of the allyl group is oriented toward the cyclopentadienyl ring, and in the *endo* isomer it is oriented away from to the Cp ring.[14]

(14) For *endo*, *exo* definition, see: Schilling, B. E. R.; Hoffmann, R.; Faller, J. W. *J. Am. Chem. Soc.* **1979**, *101*, 592−598.

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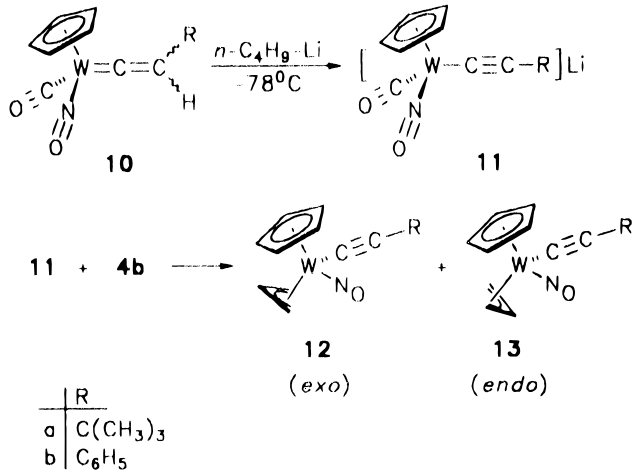
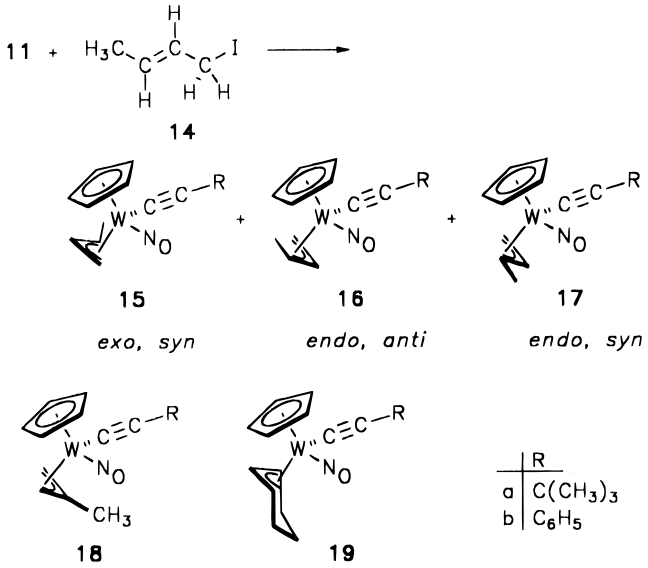
In order to extend these observations for the preparation of substituted η^3-allyl complexes, we studied the reaction of metalate anions **11a** and **11b** with **4b**, crotyl iodide (**14**) methallyl iodide, and 3-iodocyclohexene as electrophiles. For this purpose anions **11a** and **11b** were more conveniently generated by treatment of **10** with 1.0 equiv of *n*-BuLi in THF at −30 °C.[18] In all cases, allylic electrophiles interact with the metal atom of the metalate anions and exclusively produce the corresponding (η^3-allyl)metal complexes. It seems that the addition of a soft electrophile to the metal center of **3**, **11a**, and **11b** is a general behavior.

Similar to the reaction with **3**, the addition of allylic iodide **4b** to the anions **11a** and **11b** gave rise exclusively to the η^3-allyl complexes **12a/13a** and **12b/13b** as mixtures of *exo* and *endo* conformers in ratios of 5:2 and 10:3, respectively, the *endo* conformer being the major isomer in these cases. No vinylidene or η^2-alkyne complexes were formed. Faller et al. have shown that (η^3-allyl)dicarbonyl(η^5-cyclopentadienyl)molybdenum complexes exist in two conformers which are in dynamic equilibrium.[19] The preferred conformation of both the dicarbonyl and carbonyl nitrosyl η^3-allyl complexes largely depends upon steric factors.[20] For the unsubstituted (η^3-allyl)carbonylmolybdenum complexes the *endo* isomer is generally less stable and tends to convert in solution to the thermodynamically preferred *exo* orientation.[20,21] The *endo* conformers **6**, **13a**, and **13b** are, however, stable in solution at ambient temperature, and a conversion to the corresponding *exo* product could not be observed. The lack of isomerization is likely due to the high activation barrier in these systems.[22] It is noteworthy that the establishment of *endo*−*exo* equilibrium in cationic complexes (η^3-allyl)carbonylnitrosyl(η^5-cyclopentadienyl)molybdenum is over a million times slower than in the neutral (η^3-allyl)dicarbonyl(η^5-cyclopentadienyl)molybdenum complexes.[21]



From the eight potential stereoisomers, the addition of asymmetric crotyl iodide (**14**) to **11a** and **11b** gave rise to a mixture of three conformers, namely, *exo*, *syn* **15a**, *endo*, *anti* **16a**, and *endo*, *syn* **17a** (20:10:70), as well as *exo*, *syn* **15b**, *endo*, *anti* **16b**, and *endo*, *syn* **17b** (21:13:66). According to the NMR spectra the *endo*, *syn* conformers **17a** and **17b** were the predominant species in these mixtures.[23] Upon reaction of **11a** and **11b** with methallyl iodide, the *endo* isomers **18a** (50%) and **18b** (55%) are formed. Due to steric interaction between the methyl group and the cyclopentadienyl ring, the *endo* form is the more stable conformer in these cases. On the other hand, the addition of 3-iodocyclohexene also led exclusively to the *exo* conformers **19a** (62%) and **19b** (57%) largely for steric reasons. All of the η^3-allyl complexes form yellow solids and were fully characterized by their spectral and analytical data. In addition, the structure of **17b** was further confirmed by an X-ray crystal structure determination (Figure 1).



Spectroscopy. In the (η^3-allyl)(η^5-cyclopentadienyl)-nitrosylmolybdenum and -tungsten complexes the chemical shift of C2 in the ^{13}C NMR spectra and the proton chemical shift of the cyclopentadienyl resonance can be used diagnostically to distinguish between the *endo* and *exo* orientations of the π-allyl ligand.[20a] In general the resonances for C2 as well as for the protons of the cyclopentadienyl ring appear in the *exo* conformer at higher field than those of the *endo* conformer.[20a] On the basis of these empirical facts, the structures of complexes **5/6**, **12a/13a**, and **12b/13b** are characterized (see Table 1). Since complexes **18a**, **18b**, **19a**, and **19b** exist in only one conformer, the chemical shift of the

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(22) These compounds are heat sensitive. In an attempt to follow the isomerization by NMR, heating in C_6D_6 to 50 °C resulted in decomposition.

(23) In η^3-allyl complexes with a single terminal substituent, the conformer with the substituent on the same side as the hydrogen on the center carbon is described as *syn* and the one with the substituent *trans* to the hydrogen on the center as *anti*. The *syn* conformer is generally more stable than the *anti* conformer. In order to minimize allylic strain between substituents at the ends of the allyl, the sterically demanding substituent is located at a *syn* rather than an *anti* position. (Harrington, P. J. In *Comprehensive Organometallic Chemistry II*; Abel, E. W., Stone, F. G. A., Wilkinson, G., Eds.; Pergamon, Elsevier Science Ltd.: Oxford, 1995; Vol. 12, Chapter 8.2, pp 797−904.

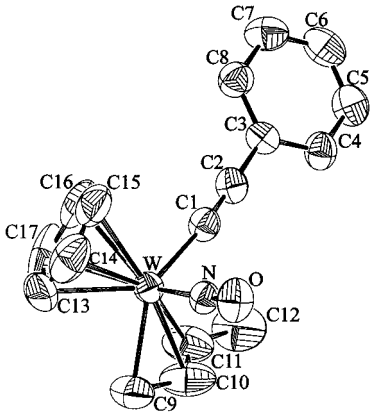


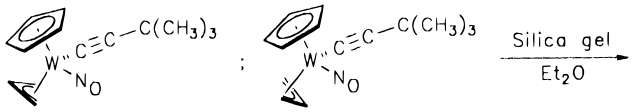
Figure 1. ORTEP drawing of compound **17b**.

cyclopentadienyl resonance is used for the assignment of geometry.

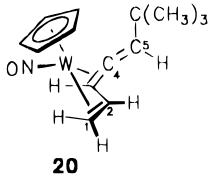
The *syn*- and *anti*-isomer assignments of **15**−**17** were made on the basis of ^{1}H NMR chemical shifts, coupling constants, and the X-ray crystallographic studies of the *endo, syn* complex **17b**. Relevant ^{1}H NMR data are listed in Table 2. Protons occupying the *anti* position exhibited significantly larger coupling constants (13.7−14.1 Hz) to the central proton H2 than the *syn* protons (7.1−7.2 Hz).[24]

Molecular Structure of Complex 17b. Crystallization of complex **17b** in ether resulted in single crystals. The X-ray diffraction study confirmed the structure of **17b** as an asymmetric π-allyl complex with an *endo, syn* arrangement and reveals a significant $\eta^3 \rightarrow \sigma,\eta^2$ distortion. The ORTEP plot and selected bond distances and angles are given in Figure 1 and Table 3. Crystallographic data are given in Table 6. The most notable features of the structure are carbon−carbon bond distances C9−C10 and C10−C11 and tungsten−carbon bond distances W−C9 and W−C11. Due to the good π-acceptance property of the NO group, the carbon−carbon bond opposite to the nitrosyl group [e.g., C10−C11 bond] is shorter and has more double-bond character than the carbon−carbon bond [C9−C10] *cis* to this group [1.30(2) Å vs 1.46(2) Å, respectively]. Concomitantly the W−C9, [2.261(8)] Å, is shorter than the W−C11 bond length of 2.527(9) Å. A similar phenomenon was recently observed in some (η^3-allyl)nitrosylmolybdenum and -tungsten complexes.[25]

Surface-Mediated Isomerization of the η^3-Allyl-η^1-alkynyl Complexes 12a/13a, 12b/13b, 18a, and 19a. To our surprise, we observed an isomerization to the (η^2-allene)tungsten complexes **20** during the column chromatography of a mixture of **12a**/**13a** on silica gel at room temperature. The structure assignment of **20** is based on NMR data and X-ray crystallographic studies.The NMR spectra do not show the π-allyl pattern and have the following characteristics: a large $^1J_{CH}$ value (160 Hz) for the methylenic group indicating sp^2 hybridization on this carbon; H1 appearing at lowest field and showing a $^3J(^{183}W,H)$ coupling of 13 Hz; and allenic carbon C2 revealing a chemical shift of 169.1 ppm and showing a $^1J(^{183}W,C)$ of 74.4 Hz. More conveniently, stirring a 10^{-2} molar solution of **12a**/**13a** in ether at room temperature with silica gel produces the complex **20** (47% after crystallization) after 12 h.



12a; 13a



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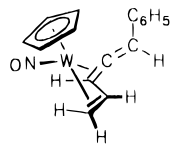
Similarly, the η^3-allyl-η^1-alkynyl complexes **12b/13b, 18a**, and **19a** isomerize in the presence of silica gel as well as neutral alumina to the corresponding η^2-allene compounds **21**−**23** in 31−57% yield. Representative NMR data of **20**−**22** are listed in Table 4.



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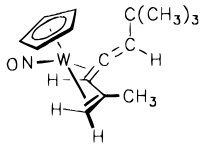

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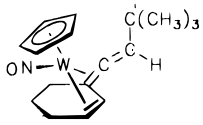
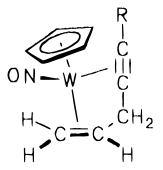


23

As a possible explanation for the formation of **20**−**23**, we propose that (η^3-allyl-η^1-alkynyl)metal complexes **12a/13a**, **12b/13b**, **18a**, and **19a** rearrange on the surface of silica gel or alumina via reductive elimination to η^2-alkene -η^2-alkyne complexes of type **D**. **D** undergoes an alkynyl−allene tautomerization, which is well-known in the chemistry of metal allene complexes,[26] to produce the observed products **20**−**23**.



D

Alternatively conceivable is also an acid-catalyzed isomerization of the (η^3-allyl-η^1-alkynyl)metal complexes to the observed products. Protonation at the basic β-carbon atom of the alkynyl ligand of **E** could produce the cationic vinylidene−allyl complex **F**. It is well documented that vinylidene ligands have a high propensity to undergo insertion reactions with other carbon ligands.[27,28] Deprotonation of the now doubly-allylic proton in intermediate **G** would complete the formation of the (η^2-allene)tungsten complexes **20**−**23**. Preliminary attempts to induce an acid-catalyzed rearrangement were not successful. Addition of catalytic amounts

(24) For NMR data, see also: Ward, Y. D.;.Villanueva, L. A.; Allred, G. D.; Payne, S. C.; Semones, M. A.; Liebeskind, L. S. *Organometallics* **1995**, *14*, 4132−4156.

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(28) We thank one of the referees for this suggestion.

Table 1. Selected ^{13}C NMR and ^{1}H NMR Resonances of [Cp(η³-Allyl)(NO)WC≡CR] and *Endo*:*Exo* Ratio of Products

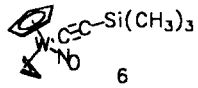
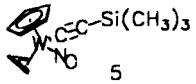
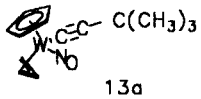
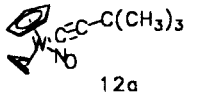
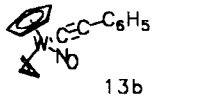
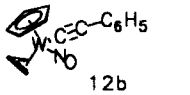
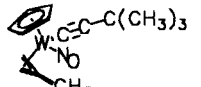
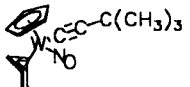
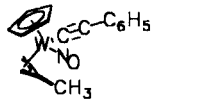
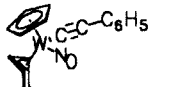
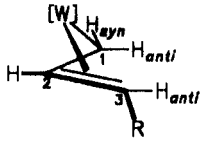
	δ_H Cp (ppm)	δ_c C2 (ppm)		δ_H Cp (ppm)	δ_c C2 (ppm)	*endo/exo* ratio
 6	5.06	109.5	 5	4.86	97.0	3:1
 13a	5.10	109.6	 12a	4.99	97.5	5:2
 13b	5.07	110.3	 12b	4.89	98.0	10:3
 18a	5.13	126.4	 19a	4.99		
 18b	5.17		 19b	4.99		

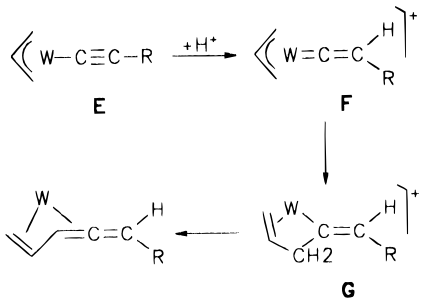
Table 2. Chemical Shifts of Allyl Protons of Crotyl-Derived Complexes 13a/13b and 17a/17b and Magnitude of Coupling Constants to the Central Proton H(2)



[W] = (Cp)W(NO)(C≡C-R)

		chemical shifts of allyl protons: δ (ppm)					coupling constants of terminal protons to central proton (Hz)	
complex	R	H_{1syn}	H_{1anti}	H_2	H_{3syn}	H_{3anti}	$^3J_{2-3anti}$	$^3J_{2-3syn}$
13a	H	2.26	1.04	5.08	4.05	3.08	14.0	7.2
13b	H	2.30	1.08	5.07	4.09	2.98	14.1	7.1
17a	CH_3	2.36	0.96	4.75		3.23	13.7	
17b	CH_3	2.40	1.12	4.78		3.28	13.8	

of HBF_4 solution in ether to a 10^{-2} M solution of **12a**/**13a** at 0 °C leads immediately to decomposition.



Molecular Structure of Complex 20. Crystallization of complex **20** in pentane resulted in single crystals. An X-ray diffraction study of complex **20** has confirmed the structure. The ORTEP plot of the structure is provided in Figure 2; selected bond distances and angles are provided in Table 5 and crystallographic data in Table 6. Figure 2 illustrates a twisted *trans*-η⁴-butadiene moiety with a dihedral angle C1−C2−C3−C4 of 114.8°. The C1−C2, C2−C3, and C3−C4 bonds were found to be of similar lengths [1.43(2), 1.44(2), and 1.42(2) Å, respectively], while the C4−C5 bond length, 1.35(2) Å, suggested a carbon−carbon double bond. Transoidal 1,3-butadiene coordination to a single metal is rare and scarcely reported.[29] The most striking property in the structure of **20** is the "allene" moiety C3−C4−C5 with a very acute angle of 132.2(8)°, which is probably due to a strong interaction with the tungsten atom. The C3−C4 bond length of the distorted allene ligand [1.42(2) Å] is longer than the C4−C5 bond [1.35(2) Å].

Table 3. Selected Bond Distances (Å) and Angles (deg) for 17b

W−C1	2.104(7)	W−C9	2.261(8)
W−C10	2.36(1)	W−C11	2.527(9)
C1−C2	1.21(1)	C9−C10	1.46(2)
C10−C11	1.30(2)	C11−C12	1.45(2)
W−C14	2.31(1)	W−N	1.77(5)
W−C1−C2	174.6(6)	C1−C2−C3	178.2(8)
W−C9−C10	75.3(6)	C9−C10−C11	125(2)
W−C10−C11	82.0(7)	W−C10−C9	68.1(6)
W−C11−C10	67.5(6)	W−C11−C12	130.9(8)
C10−C11−C12	130(2)	W−N−O	170.3(6)

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

Table 4. Selected ^{1}H NMR and ^{13}C NMR Chemical Shifts of (η^2-Allene)tungsten Complexes

	NMR chemical shifts: δ (ppm)									
	^{1}H					^{13}C				
complex	H5	H3	H2	H1a	H1b	C5	C4	C3	C2	C1
20	7.30	3.02	2.42	2.68	2.53	139.7	169.1	67.7	78.0	46.9
21	8.00	3.17	2.47	2.80	2.68	140.0	178.4	66.4	78.2	47.2
22	7.22	1.80	3.31	1.48	138.0	164.5	46.4	111.7	51.1	

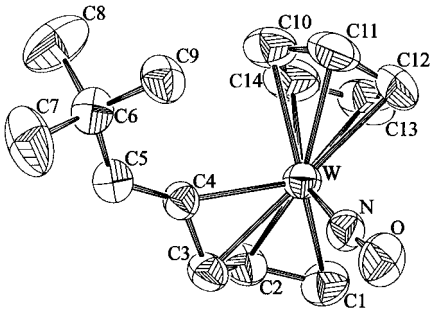


Figure 2. ORTEP drawing of compound **20**.

Table 5. Selected Bond Distances (Å) and Angles (deg) for 20

W−C1	2.30(1)	W−N	1.78(1)
W−C2	2.19(1)	W−C3	2.25(1)
W−C4	2.19(1)	C1−C2	1.43(2)
C2−C3	1.44(2)	C3−C4	1.42(2)
C4−C5	1.35(2)		
C1−C2−C3	118.3(9)	C1−W−C4	101.5(4)
C1−W−C3	65.4(4)	C1−W−C2	37.0(4)
C1−C2−W	75.8(5)	C2−C1−W	67.2(5)
C2−C3−W	68.9(5)	C2−C3−C4	115.9(8)
C2−W−C3	37.6(3)	C2−W−C4	67.3(3)
C3−C4−W	73.8(5)	C3−C2−W	73.5(5)
C3−W−C4	37.5(3)	C4−C3−W	68.7(4)
C5−C4−W	153.8(7)	C5−C4−C3	132.2(8)
W−N−O	173.5(7)		

purified by standard methods and distilled under argon prior to use. Literature methods were used to prepare (η^5-C_5H_5)W(CO)$_2$(NO) (**1**),[30] crotyl iodide,[31] cyclohexenyl iodide,[32] methallyl iodide,[33] and $(CH_3)_3SiC{\equiv}CH$.[34] 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. *J* values are given in hertz. 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 carried out on a Carlo Erba 1104 elemental analyzer.

[(η^5-C_5H_5)(η^3-C_3H_5)(NO)]WC≡CSi(CH$_3$)$_3$ (5/6). At −30 °C, a solution of 1.5 mmol of [(trimethylsilyl)ethynyl]lithium (**2**) in 5 mL of THF was added dropwise to an orange solution of **1** (335 mg, 1 mmol) in THF (20 mL). The progress of the reaction was monitored by TLC. After complete disappearance of **1** (ca. 4 h), 0.12 mL (221 mg, 1.3 mmol) of allyl iodide **4b** was added and temperature was raised to 0 °C. The progress of the reaction was monitored by TLC. After 12 h stirring at 0 °C, the reaction was complete. The solvent was removed under reduced pressure, the oily residue was dissolved in 100 mL of ether, and the resulting solution was washed with saturated aqueous sodium bicarbonate and saturated sodium chloride and dried over $MgSO_4$. After removal of two-thirds of the solvent under reduced pressure and storage overnight at −18 °C, yellow crystals precipitated, which were separated from the mother liquor, washed with pentane, and dried in vacuo: 188 mg (45%) mixture of **5** and **6** (1:3) as yellow crystals; mp 175−178 °C dec. Anal. Calcd for $C_{13}H_{19}NOSiW$: C, 37.42; H, 4.59; N, 3.36. Found: C, 37.41; H, 4.10; N, 3.49. Major isomer: ^{1}H NMR (400 MHz, C_6D_6) δ 5.06 (s, 5H, Cp), 4.99 (overlapping dddd, $^3J_{H2-H3anti}$ = 14.1, $^3J_{H2-H1anti}$ = 10.8, $^3J_{H2-H1syn}$ = 6.8, $^3J_{H2-H3syn}$ = 7.2, 1H, C2−H), 4.18 (dd, $^3J_{H2-H3syn}$ = 7.2, $^4J_{H1syn-H3syn}$ = 3.6 Hz, 1H, C3−H$_{syn}$), 3.02 (d, $^3J_{H2-H3anti}$ = 14.1, 1H, C3−H$_{anti}$), 2.25 (overlapping ddd, $^3J_{H2-H1syn}$ = 6.8, $^4J_{H1syn-H3syn}$ = 3.6, $^2J_{H1syn-H1anti}$ = 2.5 Hz, 1H, C1−H$_{syn}$), 1.13 (dd, $^3J_{H2-H1anti}$ = 10.8, $^2J_{H1syn-H1anti}$ = 2.5, 1H, C1−H$_{anti}$), 0.19 [s, 9H, Si(CH$_3$)$_3$]; ^{13}C NMR (100 MHz, C_6D_6) δ 132.4 (C≡C), 123.9 (C≡C), 109.5 (C2), 98.6 (Cp), 73.3 (C3), 36.8 (C1), 1.47 [Si(CH$_3$)$_3$]; IR (KBr) $\tilde{\nu}$ (cm^{-1}) 2036 (C≡C), 1595 (N═O); MS (70 eV) *m/e* 417 (M$^+$, ^{184}W), 402 (M$^+$ − CH$_3$). Minor isomer: ^{1}H NMR (400 MHz, C_6D_6) δ 4.89 (s, 5H, Cp), 4.04 (m, 1H, C3−H$_{syn}$), 3.92 (overlapping dddd, $^3J_{H2-H3anti}$ = 14.8, $^3J_{H2-H1anti}$ = 12.8, 1H, C2−H), 3.59 (d, $^3J_{H2-H3anti}$ = 14.8, 1H, C3−H$_{anti}$), 2.36 (m, 1H, C1−H$_{syn}$), 2.15 (d, $^3J_{H2-H1anti}$ = 12.8, 1H, C1−H$_{anti}$), 0.38 [s, 9H, Si(CH$_3$)$_3$]; ^{13}C NMR (100 MHz, C_6D_6) δ 133.5 (C≡C), 123.0 (C≡C), 97.4 (Cp), 97.0 (C2), 73.1 (C3), 41.7 (C1), 1.50 [Si(CH$_3$)$_3$].

[(η^5-C_5H_5)(η^3-C_3H_5)(NO)]WC≡CC(CH$_3$)$_3$ (12a/13a). At −78 °C, to a THF solution (20 mL) of tungsten vinylidene complex **10a** (389 mg, 1 mmol) was added 1 mmol of *n*-BuLi (a solution of 1.5 mmol/mL in hexane). The color changed immediately from orange to deep green. After the mixture was stirred for 0.5 h, 0.12 mL (221 mg, 1.3 mmol) of allyl iodide (**4b**) was added and the temperature was allowed to rise to 0 °C. The progress of the reaction was monitored by TLC. After 12 h of stirring at 0 °C the reaction was complete. The solvent was removed under reduced pressure, the oily residue was dissolved in 100 mL of ether, and the resulting solution was washed with saturated aqueous sodium bicarbonate and saturated sodium chloride and dried over $MgSO_4$. After removal of two-thirds of the solvent under reduced pressure and storage overnight at −18 °C, yellow crystals precipitated, which were separated from the mother liquor, washed with pentane, and dried under vacuum: 249 mg (62%) mixture of **12a** and **13a** (2:5); mp 150 °C dec. Anal. Calcd for $C_{14}H_{19}NOW$: C, 41.92; H, 4.77; N, 3.49. Found: C, 41.99; H, 4.44; N, 3.65. Major isomer: ^{1}H NMR (400 MHz, C_6D_6) δ 5.10 (s, 5H, Cp), 5.08 (overlapping dddd, $^3J_{H2-H3anti}$ = 14.0, $^3J_{H2-H1anti}$ = 10.3, $^3J_{H2-H1syn}$ = 6.5, $^3J_{H2-H3syn}$ = 7.2, 1H, C2−H), 4.05 (dd, $^3J_{H2-H3syn}$ = 7.2, $^4J_{H1syn-H3syn}$ = 3.5, 1H, C3−H$_{syn}$), 3.08 (d, $^3J_{H2-H3anti}$ = 14.0, 1H, C3−H$_{anti}$), 2.26 (overlapping ddd, $^3J_{H2-H1syn}$ = 6.5, $^4J_{H1syn-H3syn}$ = 3.5, $^2J_{H1syn-H1anti}$ = 2.0, 1H, C1−H$_{syn}$), 1.41 [s, 9H, C(CH$_3$)$_3$], 1.04 (dd, $^3J_{H2-H1anti}$ = 10.3, $^2J_{H1syn-H1anti}$ = 2.0 Hz, 1H, C1−H$_{anti}$); ^{13}C NMR (100 MHz, C_6D_6) δ 134.6 (C≡C), 109.6 (C2), 98.9 (Cp), 83.0 (C≡C), 74.6 (C3), 36.2 (C1), 32.7 [C(*C*H$_3$)$_3$], 29.9 [*C*(CH$_3$)$_3$]; IR (KBr) $\tilde{\nu}$ (cm^{-1}) 1592 (N═O); MS (70 eV) *m/e* 401 (M$^+$, ^{184}W). Minor isomer: ^{1}H NMR (400 MHz, C_6D_6) δ 4.92 (s, 5H, Cp), 4.05 (m, 1H, C2−

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Table 6. Crystal Data and Conditions for Crystallographic Data Collection and Structure Refinement for 17b and 20

	17b	20
formula	$C_{17}H_{17}NOW$	$C_{14}H_{19}NOW$
cryst size, mm	0.48 × 0.04 × 0.06	0.16 × 0.16 × 0.13
fw	435.178	401.161
color and habit	yellow, transparent	orange, transparent
cryst syst	triclinic	orthorhombic
space group	$P\bar{1}$ (No.2)	*Pbca* (No.61)
lattice constants	a = 9.372(4) Å, α = 63.49(3)°	a = 15.75(1) Å
	b = 9.498(4) Å, β = 83.40(4)°	b = 13.87(1) Å
	c = 9.619(5) Å, γ = 78.52(4)°	c = 12.82(1) Å
volume	750.50 Å^3	2798.9 Å^3
formula units per unit cell	Z = 2	Z = 8
density (calc)	1.85 g/cm^3	1.66 g/cm^3
linear abs coeff	76.9 cm^{-1}	82.3 cm^{-1}
diffractometer	four-circle diffractometer AEO2 (STOE)	Image Plate Diffractometer System (STOE)
radiation	Mo Kα (λ = 0.710 69 Å)	Mo Kα (λ = 0.710 69 Å)
monochromator	graphite	graphite
scan range	3° ≤ 2θ ≤ 56°	9.5 ≤ 2θ ≤ 56°
	−12 ≤ h ≤ 12, −12 ≤ k ≤ 12, −12 ≤ l ≤ 12	−20 ≤ h ≤ 20, −16 ≤ k ≤ 16, −16 ≤ l ≤ 16
rflns measd	7268	23 634
indep rflns	3634	3092
R_{int}	0.024	0.041
indep rflns with $F_o > 4\sigma(F_o)$	3015	2371
applied corrections	Lorentz and polarization coefficients, numerical absorption correction, description of the cryst shape by 9 faces (program HABITUS[a]); transmission factors 0.573−0.756	Lorentz and polarization coefficients, numerical absorption correction, description of the cryst shape by 20 faces (program HABITUS[a]); transmission factors 0.346−0.410
structure determination and refinement	W positional parameters from Patterson synthesis (program SHELXS-86[b]); further atoms from ΔF synthesis (program SHELXL-93[c]), 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 ref *d*	W positional parameters from Patterson synthesis (program SHELXS-86[b]); further atoms from ΔF synthesis (program SHELXL-93[c]), 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 ref *d*
no. of parameters	181	154
$R(F^2)$	0.0773	0.1145
$R(\|F\|)$	0.0443 for all 3634 rflns	0.0604 for all 3092 rflns
$R(\|F\|)$	0.0293 for 3015 rflns with $F_o > 4\sigma(F_o)$	0.0633 for 2371 rflns with $F_o > 4\sigma(F_o)$

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H), 4.07 (m, 1H, C3−H_{syn}), 3.76 (d, $^3J_{H2-H3anti}$ = 13.5, 1H, C3−H_{anti}), 2.30 (m, 1H, C1−H_{syn}), 2.16 (d, $^3J_{H2-H1anti}$ = 11 Hz, 1H, C1−H_{anti}), 1.42 [s, 9H, $C(CH_3)_3$]; ^{13}C NMR (100 MHz, C_6D_6) δ 134.6 (C≡C), 97.8 (Cp), 97.5 (C2), 83.0 (C≡C), 75.1 (C3), 40.7 (C1), 32.7 [$C(CH_3)_3$], 30.0 [$C(CH_3)_3$].

[(η⁵-C_5H_5)(η³-C_3H_5)(NO)]WC≡CPh (12b/13b). The preparation was carried out as described for **12a/13a**, but, instead of **10a**, tungsten vinylidene complex **10b** was used. Crystallization from ether yielded 210 mg (50%) of **12b/13b** (3:10) as yellow crystals, mp 145−147 °C dec. Anal. Calcd for $C_{16}H_{15}NOW$: C, 45.63; H, 3.59; N, 3.32. Found: C, 44.30; H, 3.15; N, 3.35. Major isomer: ^{1}H NMR (400 MHz, C_6D_6) δ 7.64−6.97 (m, 5H, C_6H_5), 5.07 (s, 5H, Cp), 5.07 (overlapping dddd, $^3J_{H2-H3anti}$ = 14.1, $^3J_{H2-H1anti}$ = 10.4, $^3J_{H2-H1syn}$ = 6.7, $^3J_{H2-H3syn}$ = 7.1, 1H, C2−H), 4.09 (dd, $^3J_{H2-H3syn}$ = 7.1, $^4J_{H1syn-H3syn}$ = 3.6, 1H, C3−H_{syn}), 2.98 (d, $^3J_{H2-H3anti}$ = 14.1, 1H, C3−H_{anti}), 2.30 (overlapping ddd, $^3J_{H2-H1syn}$ = 6.7, $^4J_{H1syn-H3syn}$ = 3.6, $^2J_{H1syn-H1anti}$ = 2.7, 1H, C1−H_{syn}), 1.08 (dd, $^3J_{H2-H1anti}$ = 10.4, $^2J_{H1syn-H1anti}$ = 2.7, 1H, C1−H_{anti}); ^{13}C NMR (100 MHz, $CDCl_3$) δ 130.8, 127.9, 125.8, 125.7 (arom C), 126.3 (C≡C), 110.3 (C2), 100.5 (C≡C), 99.2 (Cp), 74.4 (C3), 37.7 (C1); IR (KBr) $\tilde{\nu}$ (cm^{-1}) 2097 (C≡C), 1609 (N═O); MS (70 eV) *m/e* 421 (M^+, ^{184}W). Minor isomer: ^{1}H NMR (400 MHz, C_6D_6) δ 7.64−6.97 (m, 5H, C_6H_5), 4.89 (s, 5H, Cp), 4.00 (m, 1H, C2−H), 3.66 (d, $^3J_{H2-H3anti}$ = 14.6, 1H, C3−H_{anti}), 2.37 (m, 1H, C1−H_{syn}), 2.20 (d, $^3J_{H2-H1anti}$ = 12.2 Hz, 1H, C1−H_{anti}); ^{13}C NMR (100 MHz, $CDCl_3$) δ 130.7, 128.0, 126.2, 125.7 (arom C), 127.1 (C≡C), 99.8 (C≡C), 98.0 (C2), 98.0 (Cp), 74.5 (C3), 42.1 (C1).

[(η⁵-C_5H_5)(η³-crotyl)(NO)]WC≡CC(CH₃)₃ (15a−17a). The preparation was carried out as described for **12a/13a**, but, as electrophile, instead of allyl iodide (**4b**) 1.3 mmol of crotyl iodide (**14**) was used. Crystallization from ether yielded a 212 mg (51%) mixture of **15a**−**17a** (20:10:70 **15a**:**16a**:**17a**, respectively) as yellow crystals, mp 135−136 °C. Anal. Calcd for $C_{15}H_{21}NOW$: C, 43.39; H, 5.10; N, 3.37. Found: C, 43.45; H, 4.73; N, 3.54. Major isomer: ^{1}H NMR (400 MHz, C_6D_6) δ 5.12 (s, 5H, Cp), 4.75 (overlapping ddd, $^3J_{H2-H3anti}$ = 13.7, $^3J_{H2-H1syn}$ = 7.0, $^3J_{H2-H1anti}$ = 9.2, 1H, C2−H), 3.23 (overlapping dq, $^3J_{H2-H3anti}$ = 13.7, $^3J_{methyl-H3anti}$ = 6.0, 1H, C3−H_{anti}), 2.36 (overlapping dd, $^3J_{H2-H1syn}$ = 6.9, $^2J_{H1syn-H1anti}$ = 3.0, 1H, C1−H_{syn}), 1.95 (d, $^3J_{H3anti-methyl}$ = 6.0 Hz, 3H, CH_3), 1.40 [s, 9H, $C(CH_3)_3$], 0.96 (dd, $^3J_{H2-H1anti}$ = 9.2, $^2J_{H1syn-H1anti}$ = 3.0, 1H, C1−H_{anti}); ^{13}C NMR (50 MHz, C_6D_6) δ 134.8 (C≡C), 109.6 (C2), 98.9 (Cp), 83.0 (C≡C), 74.6 (C3), 36.2 (C1), 32.7 [$C(CH_3)_3$], 29.9 [$C(CH_3)_3$]; IR (KBr) $\tilde{\nu}$ (cm^{-1}) 2188 (C≡C), 1598, 1580 (N═O); MS (70 eV) *m/e* 415 (M^+, ^{184}W), 400 (M^+ − CH_3).

[(η⁵-C_5H_5)(η³-crotyl)(NO)]WC≡CPh (15b−17b). The preparation was carried out as described for **12a/13a**, but, instead of **10a**, 1 mmol of tungsten vinylidene complex **10b** was and, used as electrophile, instead of allyl iodide (**4b**) 1.3 mmol of crotyl iodide (**14**) was used. Crystallization from ether yielded a 196 mg (45%) mixture of **15b**−**17b** (21:13:66 **15b**:**16b**:**17b**, respectively) as yellow crystals, mp 118−120 °C. Anal. Calcd for $C_{17}H_{17}NOW$: C, 46.92; H, 3.94; N, 3.22. Found: C, 47.00; H, 3.92; N, 3.35. Major isomer: ^{1}H NMR (400 MHz, C_6D_6) δ 7.64−6.99 (m, 5H, C_6H_5), 5.11 (s, 5H, Cp),

4.78 (overlapping ddd, $^3J_{H2-H1anti}$ = 9.1, $^3J_{H2-H3anti}$ = 13.8, $^3J_{H2-H1syn}$ = 6.9, 1H, C2−H), 3.28 (dq, $^3J_{H2-H3anti}$ = 13.8, $^3J_{methyl-H3syn}$ = 5.9, 1H, C3−H_{anti}), 2.40 (dd, $^3J_{H2-H3anti}$ = 13.8, $^2J_{H1syn-H1anti}$ = 2.9, 1H, C1−H_{syn}), 1.96 (d, $^3J_{methyl-H3syn}$ = 5.9, 3H, CH_3) 1.12 (dd, $^3J_{H2-H1anti}$ = 9.1, $^2J_{H1syn-H1anti}$ = 2.9, 1H, C1−H_{anti}); IR (KBr) $\tilde{\nu}$ (cm^{-1}) 2099 (C≡C), 1600 (N═O); MS (70 eV) *m/e* 435 (M^+, ^{184}W).

[(η^5-C_5H_5)(η^3-methallyl)(NO)]WC≡CC(CH_3)$_3$ (18a). The preparation was carried out as described for **12a/13a**, but, as electrophile, instead of allyl iodide (**4b**) 1.3 mmol of methallyl iodide was used. Crystallization from ether yielded 208 mg (50%) of **18a** as yellow crystals, mp 138−141 °C. Anal. Calcd for $C_{15}H_{21}NOW$: C, 43.39; H, 5.10; N, 3.37. Found: C, 43.33; H, 4.68; N, 3.66. ^{1}H NMR (400 MHz, C_6D_6): δ 5.13 (s, 5H, Cp), 3.90 (d, $^4J_{H3syn-H1syn}$ = 4.4, 1H, C3−H_{syn}), 3.00 (s, 1H, C3−H_{anti}), 2.23 (dd, $^2J_{H1anti-H1syn}$ = 1.8, $^4J_{H1syn-H3syn}$ = 4.4, 1H, C1−H_{syn}), 2.21 [s, 9H, C(CH_3)$_3$], 1.40 (s, 3H, CH_3), 1.26 (d, $^2J_{H1syn-H1anti}$ = 1.8, 1H, C1−H_{anti}). ^{13}C NMR (100 MHz, C_6D_6): δ 133.9 (C≡C), 126.4 (C2), 99.0 (Cp), 83.2 (C≡C), 72.8 (C3), 39.0 (C1), 32.8 [C(*C*H_3)$_3$], 29.9 [*C*(CH_3)$_3$] 22.0 (CH_3). IR (KBr): $\tilde{\nu}$ (cm^{-1}) 1590 (N═O). MS (70 eV): *m/e* 415 (M^+, ^{184}W), 400 ($M^+ - CH_3$).

[(η^5-C_5H_5)(η^3-methallyl)(NO)]WC≡CPh (18b). The preparation was carried out as described for **18a** but, instead of **10a**, 1 mmol of tungsten vinylidene complex **10b** was used. Crystallization from ether yielded 239 mg (55%) of **18b** as yellow crystals, mp 135−137 °C. Anal. Calcd for $C_{17}H_{17}NOW$: C, 46.92; H, 3,94; N, 3.22. Found: C, 46.85 H, 3.62; N, 3.19. ^{1}H NMR (400 MHz, C_6D_6): δ 7.02−7.66 (m, 5H, C_6H_5), 5.17 (s, 5H, Cp), 4.04 (d, $^4J_{H3syn-H1syn}$ = 4.4, 1H, C3−H_{syn}), 2.97 (s, 1H, C3−H_{anti}), 2.32 (dd, $^2J_{H1anti-H1syn}$ = 2.4, $^4J_{H1syn-H3syn}$ = 4.4, 1H, C1−H_{syn}), 2.25 (s, CH_3, 3H), 1.36 (d, $^2J_{H1syn-H1anti}$ = 1.8, 1H, C1−H_{anti}). ^{13}C NMR (100 MHz, $CDCl_3$): δ 130.8, 127.9, 125.7, 125.4 (arom C), 127.4 (C≡C), 101.1 (C≡C), 99.3 (Cp), 72.1 (C3), 40.4 (C1), 21.9 (CH_3). IR (KBr): $\tilde{\nu}$ (cm^{-1}) 2101 (C≡C), 1606 (N═O). MS (70 eV): *m/e* 435 (M^+, ^{184}W).

[(η^5-C_5H_5)(η^3-cyclohexenyl)(NO)]WC≡CC(CH_3)$_3$ (19a). The preparation was carried out as described for **12a/13a**, but, as electrophile, instead of allyl iodide, 1.3 mmol of cyclohexenyl iodide was used. Crystallization from ether yielded 273 mg (62%) of **19a** as yellow crystals, mp 120−125 °C dec. Anal. Calcd for $C_{17}H_{23}NOW$: C, 46.28; H, 5.25; N, 3.17. Found: C, 45.77; H, 4.99; N, 3.45. ^{1}H NMR (400 MHz, C_6D_6): δ 5.98 (overlapping dd, $^3J_{H2-H3}$ = 7.1, $^3J_{H2-H1}$ = 6.7, 1H, C2−H), 4.99 (s, 5H, Cp), 4.34 (overlapping dd, $^3J_{H1-H2}$ = 7.1, ^3J = 7.1, 1H, C1−H), 3.33 (overlapping dd, $^3J_{H3-H2}$ = 7.1, ^3J = 6.6, 1H, C3−H), 3.06−3.14 (m, 1H), 2.75−2.83 (m, 1H), 2.61−2.68 (m, 1H), 2.54−2.59 (m, 1H), 1.43 [s, 9H, C(CH_3)$_3$], 1.08−1.21 (m, 2H). ^{13}C NMR (100 MHz, C_6D_6): δ 135.2 (C≡C), 109.0 (C2), 98.3 (Cp), 91.4 (C3), 87.0 (C≡C), 51.7 (C1), 32.7 [C(*C*H_3)$_3$], 31.1 [*C*(CH_3)$_3$], 27.3 (CH_2), 25.7 (CH_2), 22.4 (CH_2). IR (KBr): $\tilde{\nu}$ (cm^{-1}) 1575 (N═O). MS (70 eV): *m/e* 441 (M^+, ^{184}W).

[(η^5-C_5H_5)(η^3-cyclohexenyl)(NO)]WC≡CPh (19b). The preparation was carried out as described above, but, instead of **10a**, 1 mmol of tungsten vinylidene complex **10b** was used. Crystallization from ether yielded 263 mg (57%) of **19b** as yellow crystals, mp 148 °C dec. Anal. Calcd for $C_{19}H_{19}NOW$: C, 49.48; H, 4.15; N, 3.04. Found: C, 49.05; H, 3.66; N, 2.94. ^{1}H NMR (400 MHz, C_6D_6): δ 7,60−7.65 (m, 2H, C_6H_5), 6.97−7.18 (m, C_6H_5), 5.99 (overlapping dd, $^3J_{H2-H3}$ = 7.1, $^3J_{H2-H1}$ = 7.1, 1H, C2−H), 4.99 (s, 5H, Cp), 4.30 (overlapping dd, $^3J_{H1-H2}$ = 7.1, ^3J = 7.1, 1H, C1−H), 3.46 (overlapping dd, $^3J_{H3-H2}$ = 7.1, ^3J = 6.5, 1H, C3−H), 3.07−3.16 (m, 1H), 2.73−283 (m, 1H), 2.61−2.71 (m, 1H), 2.50−2.60 (m, 1H), 1.41−1.50 (m, 1H), 1.04−1.17 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 130.8, 128.0, 125.7 (arom C), 127.3 (C≡C or arom C), 126.7 (C≡C or arom C), 109.2 (C2), 104.9 (C≡C), 98.6 (Cp), 91.8 (C3), 53.9 (C1), 27.2 (CH_2), 25.1 (CH_2), 19.3 (CH_2). IR (KBr): $\tilde{\nu}$ (cm^{-1}) 2093 (C≡C), 1577 (N═O). MS (70 eV): *m/e* 461 (M^+, ^{184}W).

(η^5-C_5H_5)(NO)W[η^4-CH_2═CHCH═C═CHC(CH_3)$_3$] (20). **12a**/**13a** (401 mg, 1 mmol) and 2 g of silica gel were stirred in 20 mL of ether for 12 h. The solution was filtered and evaporated in vacuum, yielding 188 mg (47%) of **20** as orange crystals, mp 130 °C (pentane). Anal. Calcd for $C_{14}H_{19}NOW$: C, 41.92; H, 4.77; N, 3.49. Found: C, 42.26; H, 4.54; N, 3.46. ^{1}H NMR (400 MHz, C_6D_6): δ 7.30 (d/dd, $^4J_{H5-H3}$ = 2.6, $^3J_{W-H5}$ = 13, 1H, H5), 4.98 (s, 5H, Cp), 3.02 (dd, $^4J_{H5-H3}$ = 2.6, $^3J_{H3-H2}$ = 10.8, 1H, H3), 2.68 (dd/ddd, $^2J_{H1a-H1b}$ = 2.7, $^3J_{H1-H2}$ = 5.7, $^2J_{W-H1}$ = 5.4, 1H, H1a or H1b), 2.53 (dd/ddd, $^2J_{H1a-H1b}$ = 2.7, $^3J_{H1-H2}$ = 13.7, $^2J_{W-H1}$ = 6.1, 1H, H1a or H1b), 2.42 (ddd, $^3J_{H3-H2}$ = 10.8, $^3J_{H1-H2}$ = 13.7, $^3J_{H1-H2}$ = 5.7, 1H, H2), 0.99 [s, 9H, C(CH_3)$_3$]. ^{13}C NMR (100 MHz, C_6D_6): δ 169.12 (C4), 139.74 ($^1J_{CH}$ = 153, C5), 94.96 ($^1J_{CH}$ = 180, Cp), 77.99 ($^1J_{CH}$ = 163, C2), 67.74 ($^1J_{CH}$ = 166, C3), 46.87 ($^1J_{CH}$ = 160, C1), 33.92 [*C*(CH_3)$_3$], 30.89 [$^1J_{CH}$ = 127, C(*C*H_3)$_3$]. IR (KBr): $\tilde{\nu}$ (cm^{-1}) 1590 (N═O). MS (70 eV): *m/e* 401 (M^+, ^{184}W).

(η^5-C_5H_5)(NO)W(η^4-CH_2═CHCH═C═CHPh) (21). The preparation was carried out as described above: yield 42.5%, orange crystals, mp 111−112 °C (pentane). Anal. Calcd for $C_{16}H_{15}NOW$: C, 45.63; H, 3.59; N, 3.32. Found: C, 45.25; H, 3.09; N, 3.58. ^{1}H NMR (400 MHz, C_6D_6): δ 8.00 (d/dd, $^4J_{H5-H3}$ = 2.5 $^3J_{W-H5}$ = 11.8, 1H, H5), 7.59−7.65 (m, 2H, arom), 7.22−7.09 (m, arom), 4.81 (s, 5H, Cp), 3.17 (dd, $^4J_{H5-H3}$ = 2.5, $^3J_{H3-H2}$ = 10.8, 1H, H3), 2.80 (dd/ddd, $^2J_{H1a-H1b}$ = 3.0, $^3J_{H1-H2}$ = 5.9, $^2J_{W-H1}$ = 5.0, 1H, H1a or H1b), 2.68 (dd/ddd, $^2J_{H1a-H1b}$ = 3.0, $^3J_{H1-H2}$ = 13.7, $^2J_{W-H1}$ = 6.7, 1H, H1a or H1b), 2.47 (ddd, $^3J_{H3-H2}$ = 10.8, $^3J_{H1-H2}$ = 13.7, $^3J_{H1-H2}$ = 5.6, 1H, H2). ^{13}C NMR (50 MHz, C_6D_6): δ 178.42 (s/d $^1J_{W-C4}$ = 73, C4), 140.03 (C5), 128.38, 128.27, 127.72, 127.20 (arom C), 94.93 (Cp), 78.21 (C2), 66.35 (s/d $^1J_{W-C3}$ = 7.2, C3), 47.16 (s/d $^1J_{W-C1}$ = 14, C1). IR (KBr): $\tilde{\nu}$ (cm^{-1}) 1572 (N═O). MS (70 eV): *m/e* 421 (M^+, ^{184}W).

(η^5-C_5H_5)(NO)W[η^4-CH_2═C(CH_3)CH═C═CHC(CH_3)$_3$] (22). The preparation was carried out as described above: yield 57%, orange crystals, mp 98 °C (pentane). Anal. Calcd for $C_{15}H_{21}NOW$: C, 43.39; H, 5.10; N, 3.37. Found: C, 43.23; H, 4.71; N, 3.33. ^{1}H NMR (400 MHz, C_6D_6): δ 7.22 (d/dd, $^4J_{H5-H3}$ = 3.2, $^3J_{W-H5}$ = 13, 1H, H5), 5.02 (s, 5H, Cp), 3.31 (d/dd, $^4J_{H1a-H1b}$ = 3.6, $^2J_{W-H1}$ = 4.8, 1H, H1a or H1b), 1.98 (s, 3H, CH_3), 1.80 (dd, $^4J_{H3-H5}$ = 3.2, $^4J_{H3-H1}$ = 1.3, 1H, H3), 1.48 (dd/ddd, $^2J_{H1a-H1b}$ = 3.6, $^3J_{H1-H3}$ = 1.3, $^2J_{W-H1}$ = 3.4, 1H, H1a or H1b), 1.26 [s, 9H, C(CH_3)$_3$]. ^{13}C NMR (100 MHz, C_6D_6): δ 164.54 (s/d, $^1J_{W-C4}$ = 74.4, C4), 137.97 (C5), 111.68 (C2), 95.30 (Cp), 51.09 (s/d, $^1J_{W-C1}$= 29.4 Hz, C1), 46.43 (C3), 34.40 [*C*(CH_3)$_3$], 31.25 [C(*C*H_3)$_3$], 19.26 (CH_3). IR (KBr): $\tilde{\nu}$ (cm^{-1}) 1593, 1568 (N═O). MS (70 eV): *m/e* 415 (M^+, ^{184}W), 401 ($M^+ - CH_3$).

(η^5-C_5H_5)(NO)W−Cyclohexenyl Derivative 23. The preparation was carried out as described above: yield 31%, yellow crystals, mp 119 °C (pentane); ^{1}H NMR (400 MHz, C_6D_6) δ 7.27 (s/d, $^3J_{W-H5}$ = 13, 1H, H5), 4.99 (s, 5H, Cp), 4.31 (m, 1H, H1), 3.02 (m, 1H), 2.92 (d, $^3J_{H2-H1}$ = 5.5, 1H, H2), 2.42−2.63 (m, 3H), 1.56−1.66 (m, 2H), 1.21 [s, 9H, C(CH_3)$_3$]; ^{13}C NMR (100 MHz, C_6D_6) δ 166.57 (C4), 139.61 (C5), 95.48 (Cp), 87.77 (C2), 78.01 (C3), 65.67 (s/d $^1J_{W-C1}$ = 30, C1), 34.03 [*C*(CH_3)$_3$], 31.18 [C(*C*H_3)$_3$], 30.13 (CH_2), 26.66 (CH_2), 23.33 ($CH_2CH_2CH_2$); IR (KBr) $\tilde{\nu}$ (cm^{-1}) 1577 (N═O); MS (70 eV) *m/e* 441 (M^+, ^{184}W).

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Supporting Information Available: Data for the crystal structure determination and refinement and tables of atomic coordinates and bond lengths and angles for **17a** and **20** (9 pages). Ordering information is given on any current masthead page.

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