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Articles

Phosphorus-Substituted η^1-Vinylidene Tungsten Complexes: Synthesis and Cyclization

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Reaction of a dilute solution of $LiC\equiv CP(C_6H_5)_2$ (**5**) with the tungsten carbonyl complex (η^5-Cp)(CO)$_2$(NO)W (**1a**) afforded at −30 °C after protonation the bimetallic complexes [{(Ph$_2$P)HC=C}(NO)(η^5-Cp)W−W(η^5-Cp)(NO)(CO){C=CH(PPh$_2$)}] (**8a**,**b**). It could be shown that prior to the formation of **8a**,**b** the η^1-vinylidene complex (η^5-Cp)(CO)$_2$(NO)W=C=CH(PPh$_2$) (**7**) is formed as an intermediate, which reacts with an additional η^1-vinylidene complex **7** present in the solution to give the observed products by losing 1 mol of carbon monoxide. The η^1-vinylidene complex **7** and its analogous derivative (η^5-Cp)(CO)$_2$(NO)W=C=CH(PMes$_2$) (**10**; Mes = 2,4,6-trimethylbenzene) are stable in solution at −60 °C and could be identified by spectroscopic methods. The η^1-vinylidene complexes **7** and **10** are trapped with (η^5-Cp)(CO)$_2$(NO)W=C=CHR (R = H (**12a**), C$_6$H$_5$ (**12b**), CH$_3$C$_6$H$_4$ (**12c**)) to give the corresponding bimetallic complexes **13a**−**c** and **14a**−**c**. A different mode of reaction is observed, when the acetylide **5** is treated with a concentrated solution of tungsten carbonyl complex **1a**. Here after protonation the eight-membered bimetallic complex **15** is obtained. The crystal structures of bicyclic complexes **8a**, **11**, and **13a** as well as the monocyclic complex **15** are reported.

Introduction

The reactivity of transition-metal η^1-vinylidene complexes essentially is restricted to electrophilic attack at the M=C bond and the β-carbon atom and nucleophilic attack at the α-carbon atom,[1] predicted by theoretical studies.[2] Several examples of addition of nucleophiles, including amines,[3] water,[4] alcohols,[3c,4a,5] thiols,[3c,6] and phosphines,[7] to η^1-vinylidene complexes have been reported. To increase the electrophilic character of the α-carbon atom, we intended to prepare tungsten η^1-vinylidene complexes with an electron-withdrawing group such as a diarylphosphine oxide at the β-carbon atom. During the synthesis of these compounds we observed that η^1-vinylidene complexes containing a diarylphosphino group at the β-carbon atom are not stable at ambient temperature and undergo intermolecular cyclization, leading to binuclear complexes with a bicyclo[3.1.0]hexene skeleton. Here we describe the results of this investigation.

Results and Discussion

In a series of publications we have demonstrated that the tungsten and molybdenum η^1-vinylidene complexes **4** are accessible by the protonation of the acetylide complex **3**, which itself is generated via the reaction of carbonyl complex **1** with the lithium acetylide **2** (Scheme 1).[8]

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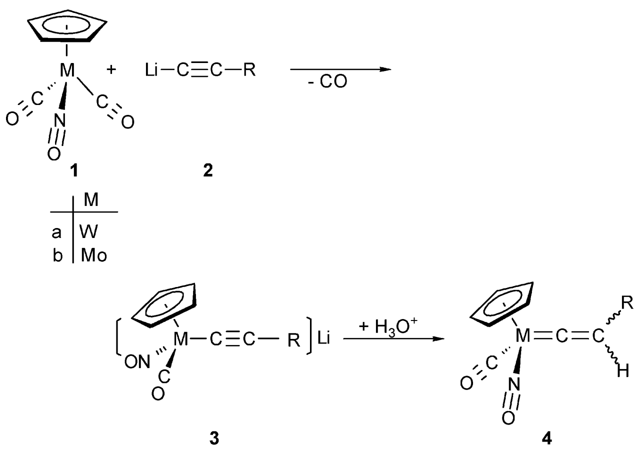
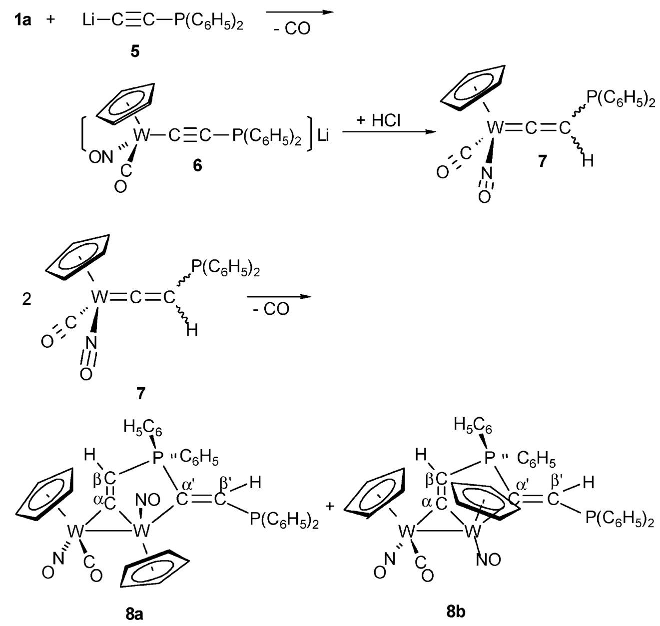
10.1021/om0493715 CCC: $30.25

Scheme 1



Scheme 2



For the preparation of η^1-vinylidene complexes with a diarylphosphino group on the β-carbon atom we investigated the reaction of the carbonyl complex (η^5-C_5H_5)W(CO)$_2$(NO) (**1a**) with the lithium acetylides **5**. In contrast to the generally observed formation of η^1-vinylidene derivatives, the reaction of a dilute solution of **1a** (0.034 M) with **5** (0.067 M) in THF at −30 °C afforded after protonation with HCl in diethyl ether a mixture of the binuclear complexes **8a**,**b** in a ratio of 1.2:1 and 22% yield (Scheme 2). The distinguishing features of **8a**,**b** are the different topological orientations of the η^5-cyclopentadienyl ligands relative to each other (*E* and *Z*) with respect to the orientation of the nitrosyl ligand on the same tungsten atom. The structures of these complexes are unambiguously confirmed by the spectroscopic data, elemental analysis, and single-crystal X-ray analysis of **8a**.

Inspection of the structures of (*E*)-/(*Z*)-[{(Ph$_2$P)HC=C}-(NO)(η^5-Cp)W−W(η^5-Cp)(NO)(CO){C=CH(PPh$_2$)}] (**8a**,**b**) suggests that these compounds are formed by the intermolecular reaction of two η^1-vinylidene complexes **7** containing a nucleophilc phosphine substituent attached on the β-carbon atom and simultaneous loss of 1 mol of carbon monoxide. To prevent the cyclization and to identify the expected η^1-vinylidene complex as an intermediate, we investigated the reaction of lithium acetylide **9** (Chart 1) containing the sterically bulky dimesitylphosphino group. Treatment of carbonyl complex **1a** with acetylide **9** at −30 °C in THF and protonation at −60 °C with HCl in Et$_2$O led indeed to the η^1-vinylidene complex **10** as a reactive species. By fast removal of the solvent at −30 °C and subsequent measuring of ^{1}H and ^{13}C NMR spectra at −60 °C in CD$_2$Cl$_2$ the structure of the η^1-vinylidene complex **10** was determined. Most informative for the structure are the signal at 331.9 ppm in the ^{13}C NMR spectra of **10**, which is characteristic for the α-carbon atom of a η^1-vinylidene complex, and the signals found at 211.5 (CO) and 95.4 (Cp), also verifying the structure.[8,9] Also, the ^{1}H NMR spectra show characteristic signals at 5.28 ppm (Cp) and a doublet at 6.42 ppm for C$_\beta$H with $^2J_{H-P}$ = 27 Hz. Stirring this solution at ambient temperature lead to the expected binuclear complex **11**: however, it exists only as the isomer with an *E* orientation of the cyclopentadienyl ligands.

Chart 1

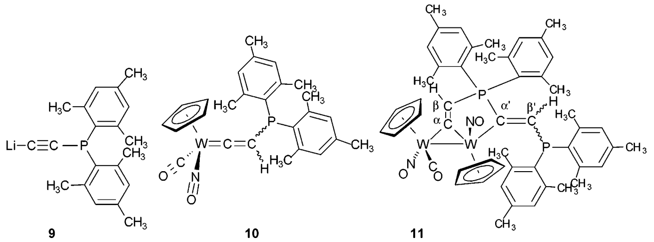
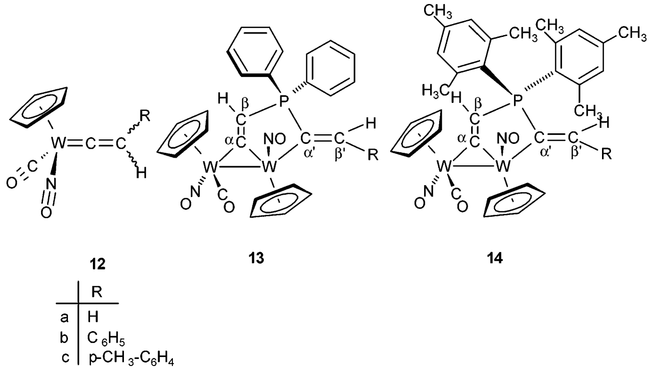


Chart 2



Furthermore, we succeeded in trapping the η^1-vinylidene complexes **7** and **10** by addition of a second differently substituted η^1-vinylidene complex to obtain the corresponding cross product. To suppress the intermolecular cyclization of **7** as well as **10**, the protonation step was carried out at −60 °C with HCl in Et$_2$O and the reaction product was trapped by addition of the η^1-vinylidene complexes **12a**−**c** (Chart 2). Stirring the

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(8) (a) Ipaktschi, J.; Demuth-Eberle, G. J.; Mirzaei, F.; Müller, B. G.; Beck, J.; Serafin, M. *Organometallics* **1995**, *14*, 3335. (b) Ipaktschi, J.; Müller, B. G.; Glaum, R. *Organometallics* **1994**, *13*, 1044.

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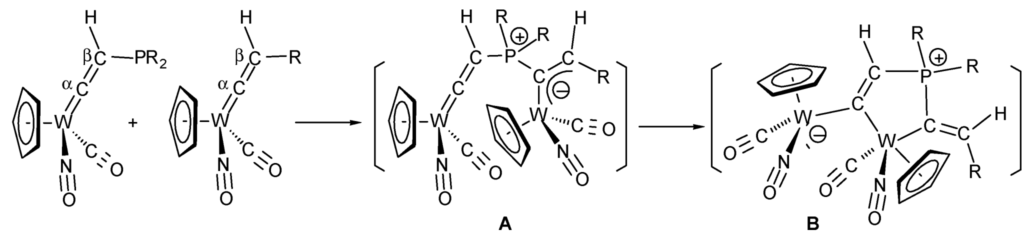
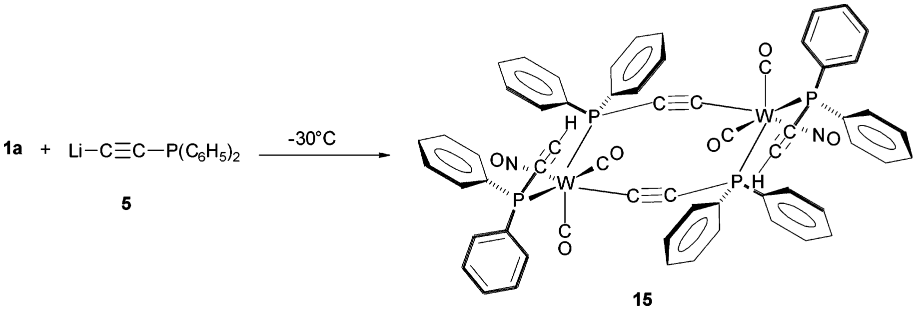
Scheme 3



Scheme 4



reaction mixture at ambient temperature gave rise to the bicyclic binuclear complexes **13a**–**c** and **14a**–**c**, respectively, in 15–36% yield. The solid compounds **8**, **11**, **13a**–**c**, and **14a**–**c** are stable under inert gas and can be stored at −20 °C.

The ^{1}H NMR spectra of the complexes **8** and **11** show characteristic chemical shifts as well as $^2J(^1\mathrm{H}{-}^{31}\mathrm{P})$ coupling constants for the proton at C_β (**8a**, δ 7.64 ppm ($^2J_{\mathrm{H-P}} = 60$ Hz); **11**, δ 7.84 ppm ($^2J_{\mathrm{H-P}} = 55$ Hz)) and for the proton at $C_{\beta'}$ (**8a**, δ 7.68 ppm ($^2J_{\mathrm{H-P}} = 36$ Hz); **11**, δ 8.53 ppm ($^2J_{\mathrm{H-P}} = 42$ Hz)). Similar signals are observed in ^{1}H NMR spectra of the complexes **13a**–**c** and **14a**–**c**.[10] The complexes **13a** and **14a** show $^3J(^1\mathrm{H}{-}^{31}\mathrm{P})$ coupling constants for the second proton at $C_{\beta'}$ (**13a**, δ 6.46 ppm (trans $^3J_{\mathrm{H-P}} = 62$ Hz); **14a**, δ 6.48 ppm (trans $^3J_{\mathrm{H-P}} = 64$ Hz)) which can be assigned to the trans position of the protons relative to the phosphorus atom. Compounds **11**, **13a**, and **14a**–**c** show additionally a $^3J_{\mathrm{H-W}}$ coupling (**11**, δ 8.53 ppm ($^3J_{\mathrm{H-W}} = 13$ Hz); **13a**, δ 6.45 ppm ($^3J_{\mathrm{H-W}} = 13$ Hz); **14a**, δ 6.66 ppm ($^3J_{\mathrm{H-W}} = 12$ Hz); **14b**, δ 7.86 ppm ($^3J_{\mathrm{H-W}} = 12$ Hz); **14c**, δ 7.81 ppm ($^3J_{\mathrm{H-W}} = 12$ Hz)). The ^{31}P NMR spectra of **8a**,**b** and **11** show long-range $^3J(^{31}\mathrm{P}{-}^{31}\mathrm{P})$ coupling constants confirming the trans orientation of phosphorus atoms (**8a**, δ 72.4 ppm ($^3J_{\mathrm{P-P}} = 63$ Hz); **8b**, δ 72.7 ppm ($^3J_{\mathrm{P-P}} = 64$ Hz); **11**, δ 79.8 ppm ($^3J_{\mathrm{P-P}} = 70$ Hz)). The assignment of the *E* orientation of the cyclopentadienyl rings is based on the crystal structure analysis of complexes **8a**, **11**, and **13a**. Although there are no crystallographic data available yet for the complexes **8b**, **13b**,**c** and **14b**,**c**, the ^{13}C and ^{1}H NMR spectra of these compounds imply a *Z* orientation of the cyclopentadienyl ligands in these complexes by shifting one of the Cp signals to higher field. Due to the steric overcrowding, the ^{1}H NMR spectra of complexes **14b**,**c** show at room temperature only broad shoulders for the protons of methyl groups. Also, the ^{13}C NMR has broad signals with low intensity at 24 ppm for the sp^3 carbon atoms and a broad signal at 132 ppm for the *C*−H carbon atoms of the mesityl ring. At −80 °C in CD_2Cl_2, however, the ^{1}H NMR spectrum of **14c** contains sharp signals at δ 2.69, 2.25, and 1.98 ppm as well as a multiplet at 2.34 ppm for the methyl protons.

Mechanistic Considerations. As a working hypothesis for the intermolecular cyclization of the η^1-vinylidene complexes **7** and **10** as well as their addition to the η^1-vinylidene complex **12**, we propose a multistep process, as presented in Scheme 3. In the first step the phosphorus atom on the β-carbon atom of the η^1-vinylidene complex nucleophilically attacks the α-carbon atom of the second η^1-vinylidene derivative, generating the intermediate **A**. The next step contains an intramolecular nucleophilic attack of the electron-rich tungsten atom at the α-carbon atom of the first η^1-vinylidene to give the intermediate **B**. This intermediate is then transformed to the observed product by elimination of a carbonyl group and formation of the tungsten–tungsten bond. Formation of stereoisomers is a consequence of the rotation of Cp around the tungsten−C_α single bond in **A**.

Synthesis of Complex 15. A different mode of reaction is observed when the acetylide $\mathrm{LiC{\equiv}CP(C_6H_5)_2}$ (**5**), a potential bifunctional ligand, is treated with a concentrated solution of tungsten carbonyl complex **1a**. Addition of a 0.36 M solution of the (diphenylphosphino)acetylide **5** in THF to a 0.15 M solution of **1a** in THF at −30 °C leads instead of the generally observed emerald green solution of the corresponding metalate anion to a red solution. Addition of aqueous HCl to this solution gave rise to a pale yellow, air-stable crystalline solid which is only sparingly soluble in organic solvents such as CH_2Cl_2, acetone, and THF (Scheme 4). Because of this low solubility our structure elucidation is based on the crystallographic data. Suitable single crystals for the X-ray diffraction analysis could be growing by recrystallization from large amounts of THF. X-ray analysis confirmed the structure of this compound as complex **15**, containing an eight-membered ring with two tungsten centers. The molecule consists of two units

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[10] For C_βH: **13a**, δ 7.73 ppm (54 Hz); **13b**, δ 7.77 ppm (54 Hz); **13c**, δ 7.77 ppm (54 Hz); **14a**, δ 7.53 ppm (54 Hz); **14b**, δ 7.70 ppm (56 Hz); **14c**, δ 7.69 ppm (56 Hz). For $C_{\beta'}$H: **13a**, δ 6.45 ppm (32 Hz); **13b**, δ 7.72 ppm (32 Hz); **13c**, δ 7.67 ppm (37 Hz); **14a**, δ 6.66 ppm (32 Hz); **14b**, δ 7.86 ppm (38 Hz); **14c**, δ 7.81 ppm (39 Hz).

Table 1. Crystal Data and Conditions for Crystallographic Data Collection and Structure Refinement for 8a, 11, 13a, and 15

	8a	**11**	**13a**	**15**
formula	$C_{39}H_{32}N_2O_3P_2W_2$	$C_{51}H_{56}N_2O_3P_2W_2$	$C_{27}H_{23}N_2O_3PW_2$	$C_{60}H_{42}N_2O_6P_2W_2$
cryst size, mm	0.15 × 0.23 × 0.50	0.19 × 0.31 × 0.19	0.31 × 0.15 × 0.39	0.039 × 0.12 × 0.19
fw	1006.3	1174.67	822.170	1378.61
color	red, transparent	red, transparent	red, transparent	yello, transparent
cryst syst	monoclinic	monoclinic	monoclinic	triclinic
space group	$P2_1/n$ (No. 14)	$P2_1/n$ (No. 14)	$P2_1/c$ (No. 14)	$P\bar{1}$ (No. 2)
cell params				
a, Å	12.795(1)	18.918(2)	12.023(1)	9.899(7)
b, Å	19.210(2)	12.582(1)	9.761(1)	11.551(11)
c, Å	14.483(1)	21.613(3)	21.661(2)	13.302(9)
α, deg				100.24(9)
β, deg	93.42(1)	115.63(1)	93.25(1)	105.11(7)
γ, deg				103.14(9)
V/A^3	3553.27	4638.46	2537.85	1383.77
Z	4	4	4	2
d_{calcd}, g cm^{-3}	1.881	1.682	2.152	1.654
μ, cm^{-1}	66.0	50.7	91.5	43.2
diffractometer	image plate diffractometer system (STOE)			
radiation	Mo Kα			
monochromator	graphite			
2θ, deg	$8.1 \leq 2\theta \leq 52.1$	$8.1 \leq 2\theta \leq 52.1$	$8.1 \leq 2\theta \leq 52.1$	$9.5 \leq 2\theta \leq 56.3$
h, k, l ranges	$-15 \leq h \leq 15$	$-21 \leq h \leq 23$	$-14 \leq h \leq 14$	$-13 \leq h \leq 13$
	$-23 \leq k \leq 23$	$-15 \leq k \leq 14$	$-11 \leq k \leq 11$	$-14 \leq k \leq 15$
	$-17 \leq l \leq 17$	$-26 \leq l \leq 26$	$-26 \leq l \leq 26$	$-17 \leq l \leq 17$
no. of rflns measd	25 486	9687	18 533	12 503
no. of indep rflns	6532	4279	4703	6130
R_{int}	0.0539	0.0719	0.0600	0.0525
no. of rflns with $F_o > 4\sigma(F_o)$	5456	3519	4103	4245
temp, K	293 K	293 K	293 K	293 K
applied corrections	Lorentz and polarizn coeff			
structure determin and refinement	W, Au, and P positional params from direct methods (SHELXS-97);[a] further atoms from ΔF synthesis (SHELXL-97);[b] refinement by anisotropic full-matrix least-squares procedures for all non-hydrogen; hydrogen position refinement by riding model			
no. of refined params	433	541	316	334
wR2	0.1129	0.1072	0.1268	0.0788
R1	0.0512	0.0502	0.0554	0.0657
R1 ($F_o > 4\sigma(F_o)$)	0.0440	0.0418	0.0503	0.0359
max, min in $\Delta\sigma$, e Å^{-3}	3.33, −4.18	1.47, −1.29	3.13, −4.83	1.35, −1.17

[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 Refinement; Universität Göttingen, Göttingen, Germany, 1997.

of σ-bonded tungsten (diphenylphosphino)acetylide, whereby each of the phosphorus atoms is simultaneously coordinated to the tungsten atom of the second unit, forming the eight-membered ring. Additionally, each tungsten atom is coordinated to the phosphorus atom of a further (diphenylphosphino)acetylene ligand and the 18-electron configuration of the tungsten atoms is reached by coordination with two carbonyl groups and one nitrosyl group. Consistent with the structure, the IR spectrum of **15** presents in the carbonyl region two strong absorptions at 2010 and 1947 cm^{-1}, and the absorptions for C≡C and N≡O groups appear at 2065 and 1620 cm^{-1}, respectively.

Interestingly during the reaction of **5** with **1a** the Cp ring is split off instead of the CO group, although CO is a better leaving group than the cyclopentadienyl ligand. This associative substitution of the cyclopentadienyl ligand is induced by a high concentration of lithium (diphenylphosphino)acetylide through a $\eta^5 \rightarrow \eta^3 \rightarrow \eta^1$ ring slippage process and subsequent elimination of cylopentadienyllithium. It is generally believed that the cyclopentadienyl−metal bonding slips from η^5 to η^3 by localizing Cp−M bonding electrons in the Cp ring.[11] This haptotropic shift facilitates the nucleophilic addition of the phosphorus atom and the further ring slippage from η^3 to η^1, and the coordination of the phosphorus with the second tungsten atom enables the formation of the eight-membered ring. The phosphorus atom of another molecule of LiC≡CP$(C_6H_5)_2$ induces the elimination of cyclopentadienyllithium and generates the observed complex **15**.

Related to the bifunctional lithium (diphenylphosphino)acetylene LiC≡CP$(C_6H_5)_2$ as ligand is the acetylenic bis(tertiary phosphine) bis(diphenylphosphino)acetylene, $(C_6H_5)_2$PC≡CP$(C_6H_5)_2$ (dppa), a potential trifunctional ligand. Recently 9- and 10-membered rings containing this ligand and tungsten as well as platinum have been reported.[12,13]

Molecular Structures. Crystal Structures of Complexes 8a, 11, and 13a. Suitable single crystals of **8a**, **11**, and **13a** were grown from dichloromethane solutions, layered with pentane by slow diffusion at ambient temperature. The crystal structure parameters are

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[11] (a) Mizuta, T.; Imamura, Y.; Miyoshi, K. *J. Am. Chem. Soc.* **2003**, *125*, 2068. (b) Ramachandran, B. M.; Trupia, S. M.; Geiger, W. E.; Carroll, P. J.; Sneddon, L. G. *Organometallics* **2002,** *21*, 5078. (c) Fan, H.-J.; Hall, M. B. *Organometallics* **2001**, *20*, 5724. (d) Veiros, L. F. *Organometallics* **2000**, *19*, 5549. (e) Veiros, L. F. *Organometallics* **2000**, *19*, 3127.

[12] Yeh, W.-Y.; Peng, S.-M.; Lee, G.-H. *J. Organomet. Chem.* **2003**, *671*, 145.

[13] Faivello, L. R.; Fourniés, J.; Gómez, J.; Lalinde, L.; Martín, A.; Martínez, F.; Moreno, M. T. *Dalton* **2001**, 2132.

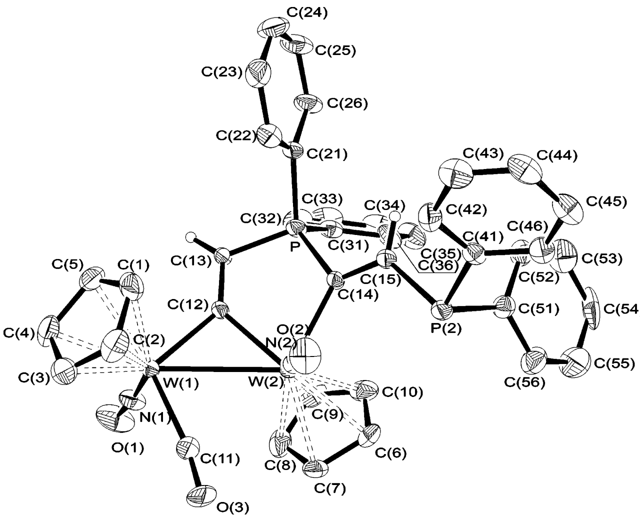

Figure 1. Molecular structure and atom-numbering scheme for [{(PPh$_2$)HC=C}(NO)(η^5-Cp)W–W(η^5-Cp)(NO)(CO){C=CH(PPh$_2$)}] (**8a**). Thermal ellipsoids are shown at the 30% probability level.

Table 2. Selected Distances (Å) and Bond Angles (deg) for 8a, 11, and 13a

	8a	**11**	**13a**
	Distances		
W(1)–W(2)	3.003(1)	2.995(1)	3.010(1)
W(1)–N(1)	1.795(7)	1.765(9)	1.783(8)
W(1)–C(11)	2.000(8)	2.005(11)	1.984(10)
W(1)–C(12)	2.098(7)	2.095(9)	2.100(8)
W(2)–N(2)	1.777(6)	1.783(8)	1.814(7)
W(2)–C(12)	2.068(6)	2.076(9)	2.102(8)
W(2)–C(14)	2.199(6)	2.230(9)	2.211(7)
P–C(13)	1.754(7)	1.778(9)	1.767(9)
P–C(14)	1.796(6)	1.819(9)	1.786(9)
P(2)–C(15)	1.826(7)	1.818(10)	
P(2)–C(41)	1.845(8)	1.854(9)	
C(12)–C(13)	1.337(9)	1.338(13)	1.313(11)
C(14)–C(15)	1.349(10)	1.364(13)	1.318(13)
	Angles		
W(1)–W(2)–C(12)	44.3(2)	44.4(3)	44.2(2)
W(1)–C(12)–W(2)	92.3(2)	91.8(4)	91.5(3)
W(2)–C(14)–P	112.2(3)	114.6(4)	111.1(4)
W(2)–C(14)–C(15)	130.5(5)	132.3(7)	128.5(6)
C(14)–W(2)–C(12)	76.9(3)	77.6(3)	75.7(3)
C(14)–P–C(13)	102.4(3)	101.5(4)	100.3(4)
C(41)–P(2)–C(51)	101.2(4)	108.1(5)	
C(21)–P–C(31)	107.9(3)	106.8(5)	105.4(4)

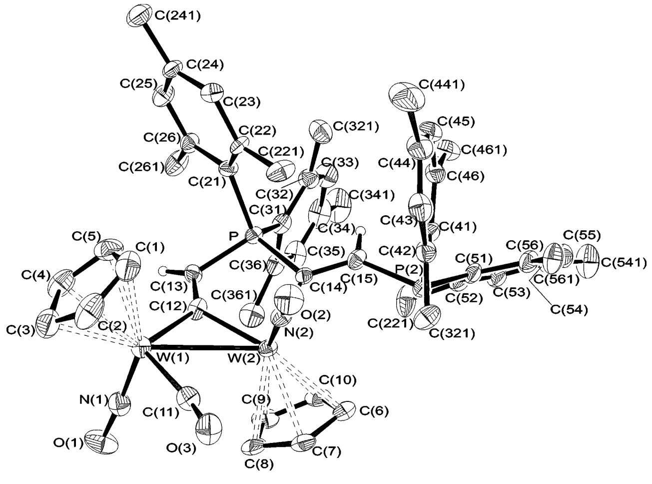

Figure 2. Molecular structure and atom-numbering scheme for [{((C$_9$H$_{11}$)$_2$P)CH=C}(NO)(η^5-Cp)W–W(η^5-Cp)(NO)(CO)-{C=CH(P(C$_9$H$_{11}$)$_2$)}] (**11**). Thermal ellipsoids are shown at the 30% probability level.

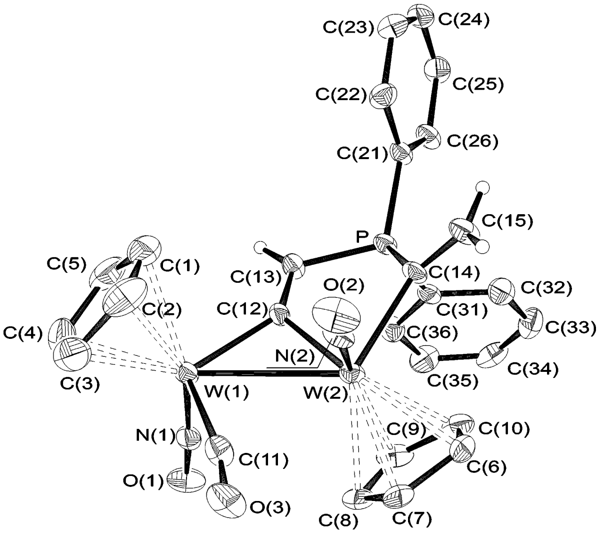

Figure 3. Molecular structure and atom-numbering scheme for [(H$_2$C=C)(NO)(η^5-Cp)W–W(η^5-Cp)(NO)(CO){C=CH-(PPh$_2$)}] (**13a**). Thermal ellipsoids are shown at the 30% probability level.

summarized in Table 1. Selected bond lengths and angles are given in Table 2. Figures 1–3 show the ORTEP plots of the complexes **8a**, **11**, and **13a.** The X-ray diffraction study confirms the 3-phospha-1,6-ditungstabicyclo[3.1.0]hex-4-ene skeleton for these complexes. The three-membered ring is built by a W–W single bond with bond distances of 2.995–3.010 Å (see Table 2), slightly shorter than the W–W bond found in [(OC)$_5$W]$_2$C=C=CPh$_2$ (3.15 Å).[14] As expected from the infrared absorptions at 1909–1893 cm^{-1}, the CO ligands are nonbridged. The cyclopentadienyl rings are in *E* positions with respect to each other. The distances of C$_\beta$–P in compounds **8a**, **11**, and **13a** are 1.754–1.778 Å,[15] but the C$_{\alpha'}$–P bond lengths at 1.819–1.786 Å are elongated. The bond distances of W1–C$_\alpha$ and W2–C$_\alpha$ are 2.068–2.102 Å, slightly shorter than the W2–C$_{\alpha'}$ bond lengths, which are from 2.199 to 2.230 Å.[14,15] In accordance with the ^{31}P NMR spectra ($^3J_{\text{P-P}}$ = 63–65 Hz) the tertiary phosphorus atoms in complexes **8a** and **11** are situated in trans positions with respect to the quaternary phosphorus atom.

Crystal Structure of Complex 15. The crystal structure parameters of the triclinic complex **15** are summarized in Table 1, and Figure 4 shows an ORTEP view of the molecular structure. The eight-membered ring is slightly distorted from planar geometry, confirmed by the small torsion angle of 8.79° for C(26)–P(1)–W–C(25). The angles C(25)–W–P(1) (84.37°) and W–P(1)–C(26) (113.03°) lead to a rhomboid-like structure for the eight-membered ring. With 1.219 Å the C(25)≡C(26′) bond is in the typical range (1.20 Å) for a triple bond. The WC≡CP units are not linear (P(1)–C(26)–C(25) = 168.85° and C(26′)-C(25)–W = 171.69°). The bond length W–C$_\alpha$ is 2.166(7) Å, comparable to the W–C$_{\text{sp}}$ bond length in complexes such as 1,1-W$_2$(CCMe)$_2$-

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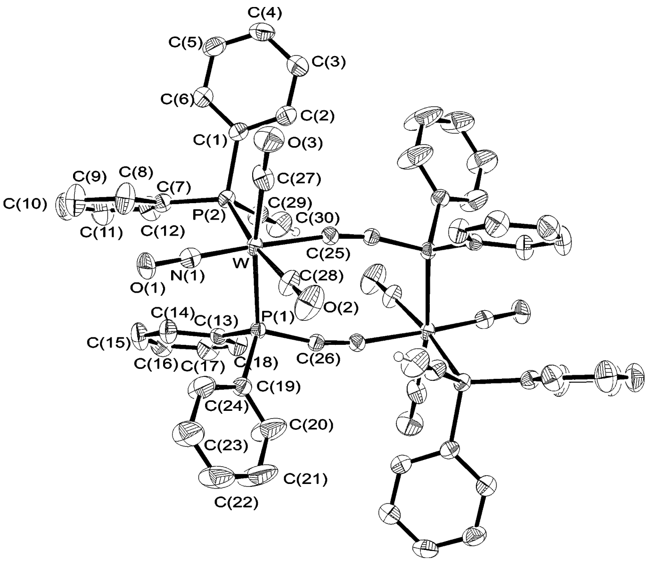

Figure 4. Molecular structure and atom-numbering scheme for complex **15**. Thermal ellipsoids are shown at the 30% probability level.

Table 3. Selected Distances (Å) and Bond Angles (deg) of Complex 15

Distances			
W–N(1)	1.808(7)	P(1)–C(19)	1.841(7)
W–P(1)	2.559(3)	P(1)–C(26)	1.739(7)
W–P(2)	2.552(3)	P(2)–C(1)	1.846(8)
W–C(25)	2.166(7)	P(2)–C(7)	1.821(7)
W–C(27)	2.015(9)	P(2)–C(29)	1.760(8)
W–C(28)	2.019(8)	C(25)–C(26′)	1.219(9)
P(1)–C(13)	1.838(6)	C(29)–C(30)	1.164(11)
Angles			
C(25)–W–C(27)	88.24(30)	W–P(1)–C(13)	118.47(24)
C(25)–W–C(28)	86.27(30)	W–P(1)–C(19)	113.44(25)
C(25)–W–N(1)	177.44(32)	W–P(1)–C(26)	113.03(23)
C(25)–W–P(1)	84.37(21)	W–P(2)–C(1)	113.74(23)
C(25)–W–P(2)	85.45(20)	W–P(2)–C(7)	118.48(23)
P(1)–C(26)–C(25)	168.85(68)	W–P(2)–C(29)	114.56(27)
P(2)–C(29)–C(30)	177.92(80)	W–C(25)–C(26)	171.69(65)

$Cl_2(PMe_3)_4$[16] and $[(\eta^5\text{-}C_5H_5)(\eta^3\text{-crotyl})(NO)]WC\equiv CPh$.[17] The W–P(1) and W–P(2) bonds (2.559 and 2.552 Å) are similar to those found in 1,1-$W_2(CCMe)_2Cl_2(PMe_3)_4$,[16] $(CO)_4W(dppb)$,[18] and $W_2(CO)_6(\mu\text{-}Ph_2PC\equiv CPPh_2)_3$.[12] The tungsten atom has a nearly ideal octahedral configuration, surrounded by two CO, one nonlinear NO, P(1), P(2), and C(25). Further information on the bond distances and angles is given in Table 3.

Experimental Section

General Procedures. All operations were carried out under argon. All solvents were purified by standard techniques. Literature methods were used to prepare **1a**,[19] **12a**–**c**,[8a] and $HC\equiv CPR_2$.[20,21] NMR spectra were obtained on a Bruker AM 400 spectrometer. ^1H NMR spectra were measured at 400 MHz, ^{13}C NMR spectra were measured at 100 MHz, and ^{31}P NMR spectra were measured at 162 MHz with H_3PO_4 as external standard. Proton and carbon chemical shifts are referred to TMS. IR spectra were recorded on a Bruker FT-IR IFS 85. Microanalyses were done with a Carlo-Erba 1104 elemental analyzer.

[{(PPh$_2$)HC=C}(NO)(η^5-Cp)W–W(η^5-Cp)(NO)(CO){C=CH(PPh$_2$)}] (8a,b). To 210 mg (1 mmol) of $HC\equiv CPPh_2$ in 15 mL of THF at −78 °C was added 0.69 mL (1 mmol) of n-BuLi in hexane. After it was stirred for a few minutes, the solution was added to a cooled (−30 °C) solution of 335 mg (1 mmol) of $(\eta^5\text{-}C_5H_5)W(CO)_2(NO)$ (**1a**) in 30 mL of THF. After it was stirred for 3.5 h at −30 °C, the green solution was protonated dropwise with a solution of HCl in Et_2O until the color changed from green to orange. After the mixture was stirred for 16 h at room temperature, the solvent was removed under reduced pressure. Purifying by column chromatography at SiO_2 with pentane/ether (1:1) yielded 59 mg (12%) of the *E* isomer **8a** and 50 mg (10%) of the *Z* isomer **8b** as orange crystals (mp 210–212 °C dec). Anal. Calcd for $C_{39}H_{32}N_2O_3P_2W_2$: C, 46.55; H, 3.20; N, 2.78. Found: C, 46.38; H, 2.90; N, 2.24. **8a**: ^1H NMR ($CDCl_3$, room temperature) δ 7.86–7.14 (m, 20 H, C_6H_5), 7.68 (d, 1H, $^2J_{H-P}$ = 36 Hz, $C_{\beta'}H$), 7.64 (d, 1H, $^2J_{H-P}$ = 60 Hz, $C_\beta H$), 5.67 and 5.18 (two s, 10H, Cp); ^{13}C NMR ($CDCl_3$, room temperature) δ 312.0 (d, $^2J_{C-P}$ = 22 Hz, C_α), 241.3 (CO), 159.2 (dd, $^1J_{C-P}$ = 14 Hz, $^2J_{C-P}$ = 4 Hz, $C_{\beta'}$), 158.4 (dd, $^1J_{C-P}$ = 52 Hz, $^2J_{C-P}$ = 18 Hz, $C_{\alpha'}$), 140.8 (two d, $^1J_{C-P}$ = 14 and 16 Hz, C_6H_5(ipso)), 133.2–132.2 (C_6H_5), 129.6–127.6 (C_6H_5), 126.5 (d, $^1J_{C-P}$ = 69 Hz, C_6H_5(ipso)), 123.7 (d, $^1J_{C-P}$ = 103 Hz, $^2J_{C-W}$ = 9.5 Hz, C_β), 98.4 (d, $^3J_{C-P}$ = 3 Hz, Cp), 95.6 (s, Cp); ^{31}P NMR ($CDCl_3$, room temperature) δ 72.4 (d, trans $^3J_{P-P}$ = 63 Hz, trans $^3J_{P-W}$ = 56 Hz, $^2J\ ^3J_{P-W}$ = 43 Hz), −15.2 (d, trans $^3J_{P-P}$ = 63 Hz, cis $^3J_{P-W}$ = 14 Hz); IR (KBr; $\tilde{\nu}$, cm^{-1}) 1909 (CO), 1603, 1575 and 1565 (NO). **8b**: ^1H NMR ($CDCl_3$, room temperature) δ 7.85–7.16 (m, 22 H, C_6H_5, $C_\beta H$, and $C_{\beta'}H$), 5.63 and 4.98 (two s, 10H, Cp); ^{13}C NMR ($CDCl_3$, room temperature) δ 309.2 (d, $^2J_{C-P}$ = 25 Hz, C_α), 238.5 (CO), 159.4 (dd, $^1J_{C-P}$ = 14 Hz, $_2J_{C-P}$ = 4 Hz, $C_{\beta'}$), 158.7 (d, $^2J_{C-P}$ = 16 Hz, $C_{\alpha'}$), 140.9 (two d, $^1J_{C-P}$ = 16 and 15 Hz, C_6H_5(ipso)), 133.5–132.0 (C_6H_5), 130.8–127 (C_6H_5), 127.5 (d, $^1J_{C-P}$ = 39 Hz, C_6H_5 (ipso)), 120.8 (d, $^1J_{C-P}$ = 104 Hz, $^2J_{C-W}$ = 10 Hz, C_β), 96.8 (d, $^3J_{C-P}$ = 3 Hz, Cp), 95.4 (s, Cp). ^{31}P NMR ($CDCl_3$, room temperature) δ 72.7 (d, trans $^3J_{P-P}$ = 64 Hz, trans $^3J_{P-W}$ = 56 Hz, $^2J\ ^3J_{P-W}$ = 44 Hz), −15.4 (d, trans $^3J_{P-P}$ = 64 Hz, cis $^3J_{P-W}$ = 13 Hz); IR (KBr; $\tilde{\nu}$, cm^{-1}) 1888 (CO), 1615 (NO).

[{(Mes$_2$P)CH=C}(NO)(η^5-Cp)W–W(η^5-Cp)(NO)(CO){C=CH(PMes$_2$)}] (11). A 588 mg amount (2 mmol) of $HC\equiv CP(Mes)_2$ in 30 mL of THF at −78 °C was deprotonated with 1.42 mL (2 mmol) of n-BuLi in *n*-hexane. This solution was added to a precooled (−30 °C) solution of 670 mg (2 mmol) of **1a** in 30 mL of THF and stirred for 3 h. The green solution was treated with HCl/Et_2O and stirred for 3 days at ambient temperature. The solution was added to saturated aqueous $NaHCO_3$, extracted with diethyl ether, washed with saturated aqueous NaCl, and dried over $MgSO_4$. Chromatography at SiO_2 with Et_2O yielded 270 mg (23%) of **11** as an orange-red solid (mp 180–182 °C dec). Anal. Calcd for $C_{51}H_{56}N_2O_3PW_2$: C, 52.15; H, 4.81; N, 2.38. Found: C, 52.25; H, 4.57; N, 2.30. ^1H NMR ($CDCl_3$, room temperature): δ 8.53 (d, $^2J_{H-P}$ = 42 Hz, $^3J_{H-W}$ = 13 Hz, $C_{\beta'}H$), 7.84 (dd, $^2J_{H-P}$ = 55 Hz, $C_\beta H$), 7.01, 6.87, 6.83, 6.71, and 6.66 (5s, 8 Mes H), 5.73 (s, 5H, Cp), 5.27 (s, 5H, Cp), 2.60, 2.34, 2.29, 2.17, 2.06, 1.91, 1.75, and 1.69 (8s, 36 H, Mes C*H*$_3$). ^{13}C NMR ($CDCl_3$, room temperature): δ 293.9 (d, $^2J_{C-P}$ = 25 Hz, C_α), 239.9 (CO), 161.3 (dd, $^1J_{C-P}$ = 14 Hz, $^2J_{C-P}$ = 5 Hz, $C_{\beta'}$), 153.3 (d, $^1J_{C-P}$ = 61 Hz, $C_{\alpha'}$), 134.6 (d, $^1J_{C-P}$ = 92 Hz, $^2J_{C-W}$ = 10 Hz, C_β), 99.6 (d, $^3J_{C-P}$ = 6.5 Hz, Cp), 95.9 (s, Cp), 24.9–20.9 (CH_3). ^{31}P NMR ($CDCl_3$, room temperature): δ 79.8 (d, trans $^3J_{P-P}$ = 70 Hz, trans $^3J_{P-W}$ = 64.5 Hz, $^2J^3J_{P-W}$ = 44.5 Hz), −29 (d, trans $^3J_{P-P}$ = 70 Hz). IR (KBr; $\tilde{\nu}$, cm^{-1}): 1898 (CO), 1603 and 1570 (NO).

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[($H_2C{=}C$)(NO)(η^5-Cp)W–W(η^5-Cp)(NO)(CO){C=CH(PPh$_2$)}] (13a). To 210 mg (1 mmol) of HC≡CPPh$_2$ in 15 mL of THF at −78 °C was added 0.69 mL (1 mmol) of n-BuLi in hexane. After it was stirred for a few minutes, the solution was added to a cooled (−30 °C) solution of 335 mg (1 mmol) of **1a** in 30 mL of THF. After it was stirred for 3.5 h at −30 °C, the green solution was cooled to −60 °C and protonated dropwise with a solution of HCl in Et$_2$O until the color changed from green to orange. This cooled (−60 °C) mixture was added dropwise to a solution of 333 mg (1 mmol) of **12a** in 15 mL of THF. After the mixture was stirred for 4 h at room temperature, the solvent was removed under reduced pressure. Purifying by column chromatography at SiO$_2$ with pentane/ether (1:1) yielded 120 mg (15%) of the product as orange crystals; mp 224−226 °C dec. Anal. Calcd for $C_{27}H_{23}N_2O_3PW_2$: C, 39.44; H, 2.82; N, 3.41. Found: C, 40.64; H, 2.82; N, 3.38. ^{1}H NMR (CDCl$_3$, room temperature): δ 7.92−7.40 (m, 10 H, C_6H_5), 7.73 (d, 1H, $^2J_{\mathrm{H-P}} = 54$ Hz, C_βH), 6.46 (dd, 1H, trans $^3J_{\mathrm{H-P}} = 62$ Hz, $^2J_{\mathrm{H-H}} = 1.5$ Hz, C=CH_2), 6.45 (dd, 1H, cis $^3J_{\mathrm{H-P}} = 32$ Hz, $^2J_{\mathrm{H-H}} = 1.5$ Hz, $^3J_{\mathrm{H-W}} = 13$ Hz, C=CH$_2$), 5.66 and 5.23 (two s, 10H, Cp). ^{13}C NMR (room temperature, CDCl$_3$): δ 310.8 (d, $^2J_{\mathrm{C-P}} = 22$ Hz, C_α), 243.1 (s, CO), 145.3 (d, $^1J_{\mathrm{C-P}} = 28$ Hz, $C_{\alpha'}$), 141.8 (d, $^2J_{\mathrm{C-P}} = 6$ Hz, $C_{\beta'}$), 132.8 and 132.5 (two d, $^4J_{\mathrm{C-P}} = 3$ Hz, C_6H_5 (para)), 132.8 and 132.6 (two d, $^3J_{\mathrm{C-P}} = 9$ and 8.5 Hz, C_6H_5 (meta)), 129.4 and 129.3 (two d, $^2J_{\mathrm{C-P}} = 11$ and 10 Hz, C_6H_5 (ortho)), 128.1 and 126.4 (two d, $^1J_{\mathrm{C-P}} = 55$ and 70 Hz, C_6H_5 (ipso)), 124.6 (d, $^1J_{\mathrm{C-P}} = 105$ Hz, $^2J_{\mathrm{C-W}} = 10$ Hz, C_β), 98.2 and 95.4 (two s, Cp). ^{31}P NMR (room temperature, CDCl$_3$): δ 71.5 (s, trans $^3J_{\mathrm{P-W}} = 56$ Hz, ^2J $^3J_{\mathrm{P-W}} = 41$ Hz). IR (KBr; $\tilde{\nu}$ (cm^{-1})): 1892 (CO), 1560 (NO).

[{(Ph)HC=C}(NO)(η^5-Cp)W–W(η^5-Cp)(NO)(CO){C=CH(PPh$_2$)}] (13b). The preparation was carried out as described before, except with 409 mg (1 mmol) of tungsten vinylidene complex **12b** instead of **12a**. The solution with both vinylidenes was stirred for 17 h. Chromatography on silica gel with pentane/diethyl ether (1:1) yielded 88 mg (10%) of the *E* isomer and 64 mg (7%) of the *Z* isomer as an orange solid (mp 221−223 °C dec). Anal. Calcd for $C_{33}H_{27}N_2O_3PW_2$: C, 44.13; H, 3.03; N, 3.12. Found: C, 45.45; H, 3.24; N, 3.05. *E* isomer: ^{1}H NMR (CDCl$_3$, room temperature) δ 7.97−7.27 (m, 15H, C_6H_5), 7.77 (d, 1H, $^2J_{\mathrm{H-P}} = 54$ Hz, C_βH), 7.72 (d, 1H, cis $^3J_{\mathrm{H-P}} = 36$ Hz, $C_{\beta'}$H), 5.71 (s, 5H, Cp), 5.06 (s, 5H, Cp); ^{13}C NMR (CDCl$_3$, room temperature) δ 309.8 (d, $^2J_{\mathrm{C-P}} = 22$ Hz, C_α), 240.3 (CO), 156.8 (d, $^2J_{\mathrm{C-P}} = 8$ Hz, $C_{\beta'}$), 140.1 (d, trans $^3J_{\mathrm{C-P}} = 32$ Hz, C_6H_5 (ipso to $C_{\beta'}$)), 139.0 (d, $^1J_{\mathrm{C-P}} = 26$ Hz, $C_{\alpha'}$), 129.3 and 127.7 (two d, $^1J_{\mathrm{C-P}} = 53$ and 75 Hz, C_6H_5 (ipso)), 125.4 (d, $^1J_{\mathrm{C-P}} = 105$ Hz, $^2J_{\mathrm{C-W}} = 8$ Hz, C_β), 98.4 and 95.7 (two s, Cp); ^{31}P NMR (CDCl$_3$, room temperature): δ 76.4 (s, trans $^3J_{\mathrm{P-W}} = 52$ Hz, ^2J $^3J_{\mathrm{P-W}} = 42$ Hz); IR (KBr; $\tilde{\nu}$ (cm^{-1})) 1897 (CO), 1597 and 1559 (NO). *Z* isomer: ^{1}H NMR (CDCl$_3$, room temperature) δ 7.97−7.21 (m, 17 H, C_6H_5, C_βH, $C_{\beta'}$H), 5.63 (s, 5 H, Cp), 4.81 (s, 5 H, Cp); ^{13}C NMR (CDCl$_3$, room temperature) δ 156.2 (d, $^1J_{\mathrm{C-P}} = 7$ Hz, $C_{\beta'}$), 139.6 (d, $^1J_{\mathrm{C-P}} = 32$ Hz, $C_{\alpha'}$), 121.4 (d, $^1J_{\mathrm{C-P}} = 107$ Hz, C_β), 95.6 and 94.5 (two s, Cp); ^{31}P NMR (CDCl$_3$, room temperature) δ 76.3 (broad); IR (KBr; $\tilde{\nu}$ (cm^{-1})) 1883 (CO), 1610 and 1543 (NO).

[{(*p*-Tol)HC=C}(NO)(η^5-Cp)W–W(η^5-Cp)(NO)(CO){C=CH(PPh$_2$)}] (13c). The preparation was carried out as described before, except with 423 mg (1 mmol) of tungsten vinylidene complex **12c** instead of **12a**. The solution with both vinylidenes was stirred for 17 h. Chromatography on silica gel with pentane/diethyl ether (1:1) yielded 97 mg (11%) of the *E* isomer as orange crystals and 79 mg (9%) of the *Z* isomer as an orange solid, mp 213-216 °C dec. Anal. Calcd for $C_{34}H_{29}N_2O_3PW_2$: C, 44.76; H, 3.20; N, 3.07. Found: C, 44.67; H, 2.77; N, 3.33. *E* isomer: ^{1}H NMR (CDCl$_3$, room temperature) δ 7.97−7.44 (m, 10H, C_6H_5), 7.77 (d, 1H, $^2J_{\mathrm{H-P}} = 54$ Hz, C_βH), 7.67 (d, 1H, cis $^3J_{\mathrm{H-P}} = 37$ Hz, $C_{\beta'}$H), 7.61 and 7.21 (two d, 4H, C_6H_4), 5.71 (s, 5H, Cp), 5.09 (s, 5H, Cp), 2.36 (s, 3H, CH$_3$); ^{13}C NMR (CDCl$_3$, room temperature) δ 309.7 (d, $^2J_{\mathrm{C-P}} = 23$ Hz, C_α), 240.5 (CO), 156.8 (d, $^2J_{\mathrm{C-P}} = 9$ Hz, $C_{\beta'}$), 138.1 (s, C_6H_4 (para to $C_{\beta'}$)), 137.5 (d, $^1J_{\mathrm{C-P}} = 27$ Hz, $C_{\alpha'}$), 137.2 (d, trans $^3J_{\mathrm{C-P}} = 33$ Hz, C_6H_4 (ipso to $C_{\beta'}$)), 127.9 (d, $^1J_{\mathrm{C-P}} = 70$ Hz, C_6H_5 (ipso)), 125.6 (d, $^1J_{\mathrm{C-P}} = 105$ Hz, $^2J_{\mathrm{C-W}} = 9$ Hz, C_β), 98.5 and 95.8 (two s, Cp), 21.3 (s, CH$_3$); ^{31}P NMR (CDCl$_3$, room temperature) δ 76.2 (s, trans $^3J_{\mathrm{P-W}} = 52$ Hz, ^2J $^3J_{\mathrm{P-W}} = 42$ Hz); IR (KBr; $\tilde{\nu}$, cm^{-1})) 1870 (CO), 1559 (NO). *Z* isomer: ^{1}H NMR (CDCl$_3$, room temperature) δ 7.94−7.40 (m, 14 H, C_{β}'H, C_βH, C_6H_4, C_6H_5), 7.21 (d, 2H, C_6H_4), 5.63 (s, 5 H, Cp), 4.83 (s, 5 H, Cp), 2.36 (s, 3 H, CH$_3$); ^{13}C NMR (CDCl$_3$, room temperature) δ 157.3 (d, $^2J_{\mathrm{C-P}} = 8$ Hz, $C_{\beta'}$), 138.4 (d, $^1J_{\mathrm{C-P}} = 26$ Hz, $C_{\alpha'}$), 137.8 (s, C_6H_4 (para to $C_{\beta'}$)), 137.7 (d, trans $^3J_{\mathrm{C-P}} = 32$ Hz, C_6H_4 (ipso to $C_{\beta'}$)), 122.5 (d, $^1J_{\mathrm{C-P}} = 107$ Hz, $^2J_{\mathrm{C-W}} = 9$ Hz, C_β), 96.7 and 95.5 (two s, Cp), 21.3 (s, CH$_3$); ^{31}P NMR (CDCl$_3$, room temperature) δ 76.1 (s, trans $^3J_{\mathrm{P-W}} = 55$ Hz, ^2J $^3J_{\mathrm{P-W}} = 44.5$ Hz); IR (KBr; $\tilde{\nu}$ (cm^{-1})) 1890 (CO), 1607 and 1550 (NO).

[($H_2C{=}C$)(NO)(η^5-Cp)W–W(η^5-Cp)(NO)(CO){C=CH(P(Mes)$_2$}] (14a). To 294 mg (1 mmol) of HC≡CP(Mes)$_2$ in 15 mL of THF at −78 °C was added 0.71 mL (1 mmol) of n-BuLi in hexane. After it was stirred for a few minutes, the solution was added to a cooled (−30 °C) solution of 335 mg (1 mmol) of **1a** in 15 mL of THF. After it was stirred for 5 h at −30 °C, the green solution was cooled to −60 °C and protonated dropwise with a solution of HCl in Et$_2$O until the color changed from green to orange. To the orange solution was added dropwise 333 mg (1 mmol) of **12a** in 15 mL of THF, and the mixture was warmed to room temperature. After 2.5 h at room temperature the solvent was removed under reduced pressure. Purifying by column chromatography at SiO$_2$ with pentane/ether (1:1) yielded 328 mg (36%) of the product as orange crystals (mp 190−192 °C dec). Anal. Calcd for $C_{33}H_{35}N_2O_3PW_2$: C, 43.73; H, 3.89; N, 3.09. Found: C, 44.61; H, 3.96; N, 3.07. ^{1}H NMR (CDCl$_3$, room temperature): δ 7.53 (d, 1H, $^2J_{\mathrm{H-P}} = 54$ Hz, C_βH), 6.96 (d, 2H, C_6H_2), 6.89 (d, 2H, C_6H_2), 6.66 (dd, 1H, cis $^3J_{\mathrm{H-P}} = 32$ Hz, $^2J_{\mathrm{H-H}} = 1$ Hz, $^3J_{\mathrm{H-W}} = 12$ Hz, C=CH$_2$), 6.48 (d, 1H, trans $^3J_{\mathrm{H-P}} = 64$ Hz, C=CH$_2$), 5.57 (s, 5H, Cp), 5.04 (s, 5H, Cp), 2.50, 2.31, 2.25, 2.17 (4 s, 18H, CH$_3$). ^{13}C NMR (CDCl$_3$, room temperature): δ 296.3 (C_α), 241.8 (CO), 146.1 (d, $^1J_{\mathrm{C-P}} = 20$ Hz, $C_{\alpha'}$), 143.0 (d, $^2J_{\mathrm{C-P}} = 9$ Hz, C_6H_2 (ortho)), 142.5 (d, $^2J_{\mathrm{C-P}} = 4$ Hz, $C_{\beta'}$), 141.9 (d, $^4J_{\mathrm{C-P}} = 2.5$ Hz, C_6H_2 (para)), 141.8 (d, $^2J_{\mathrm{C-P}} = 9$ Hz, C_6H_2 (ortho)), 131.8 and 131.6 (two d, $^3J_{\mathrm{C-P}} = 9.5$ Hz, C_6H_2 (meta)), 128.9 (d, $^1J_{\mathrm{C-P}} = 100$ Hz, $^2J_{\mathrm{C-W}} = 10$ Hz, C_β), 127.4 and 124.1 (d, $^1J_{\mathrm{C-P}} = 62$ and 48 Hz, C_6H_2 (ipso)), 96.7 and 94.7 (2 s, Cp), 25.5 to 20.98 (s, CH$_3$). ^{31}P NMR (CDCl$_3$, room temperature): δ 71.9 (s, broad). IR (KBr; $\tilde{\nu}$ (cm^{-1})): 1864 (CO), 1605 and 1560 (NO).

[(PhHC=C)(NO)(η^5-Cp)W–W(η^5-Cp)(NO)(CO){C=CH(P(Mes)$_2$}] (14b). The preparation was carried out as described before, except with 409 mg (1 mmol) of tungsten vinylidene complex **12b** instead of **12a**. The solution with both vinylidenes was stirred for 3 days. The solvent was removed under reduced pressure, and chromatography on silica gel with pentane/diethyl ether (1:1) yielded 137 mg (14%) of the *E* isomer as a light orange solid and 88 mg (9%) of the *Z* isomer as a yellow solid (mp 195−197 °C dec). Anal. Calcd for $C_{39}H_{39}N_2O_3PW_2$: C, 47.68; H, 4.00; N, 2.85. Found: C, 47.43; H, 3.76; N, 2.94. *E* isomer: ^{1}H NMR (CDCl$_3$, room temperature) δ 7.86 (d, 1H, cis $^3J_{\mathrm{H-P}} = 38$ Hz, $^3J_{\mathrm{H-W}} = 12$ Hz, $C_{\beta'}$H), 7.70 (d, 1H, $^2J_{\mathrm{H-P}} = 56$ Hz, C_βH), 7.59−7.25 (m, 5H, C_6H_5), 6.96 (s, 4H, C_6H_2), 5.52 (s, 5H, Cp), 5.06 (s, 5H, Cp), 2.80−2.0 (broad (2.31 and 2.30, 2 s), 18H, CH$_3$); ^{13}C NMR (CDCl$_3$, room temperature) δ 295.0 (d, $^2J_{\mathrm{C-P}} = 23$ Hz, C_α), 240.7 (CO), 156.1 (d, $^2J_{\mathrm{C-P}} = 8$ Hz, $C_{\beta'}$), 142.2 (d, $^4J_{\mathrm{C-P}} = 2$ Hz, C_6H_2 (para)), 141.8 (d, $^4J_{\mathrm{C-P}} = 3.5$ Hz, C_6H_2 (para)), 140.8 (d, trans $^3J_{\mathrm{C-P}} = 32$ Hz, C_6H_5 (ipso)), 139.8 (d, $^1J_{\mathrm{C-P}} = 19$ Hz, $C_{\alpha'}$), 132.8 (d, $^1J_{\mathrm{C-P}} = 95$ Hz, $^2J_{\mathrm{C-W}} = 9$ Hz, C_β), 129.1−127.6 (three s, C_6H_5, C_6H_2), 127.1 and 124.5 (two d, $^1J_{\mathrm{C-P}} = 60$ Hz and 49 Hz, C_6H_2 (ipso)), 98.6 and 95.6 (two s, Cp), 24.3−20.9 (s, CH$_3$); ^{31}P NMR (CDCl$_3$, room temperature) δ 77.7 (s, trans $^3J_{\mathrm{P-W}} = 60$ Hz, ^2J $^3J_{\mathrm{P-W}} = 44.5$ Hz); IR (KBr; $\tilde{\nu}$ (cm^{-1})) 1903 (CO), 1599 and 1559 (NO). *Z* isomer: ^{1}H NMR (CDCl$_3$, room temperature) δ 8.02 (d, 1 H, $^2J_{\mathrm{H-P}} = 38$ Hz, $^3J_{\mathrm{H-W}} = 13$ Hz, C_{β}'H), 7.66 (d, 1 H, $^2J_{\mathrm{H-P}} = 55$

Hz, $C_\beta H$), 7.58–7.26 (m, 5H, C_6H_5), 6.97 (d, 2 H, $^4J_{H-P} = 3$ Hz, C_6H_2), 6.86 (d, 2 H, $^4J_{H-P} = 3$ Hz, C_6H_2), 5.57 (s, 5 H, Cp), 4.93 (s, 5 H, Cp), 2.43, 2.33 and 2.23 (three s, 18 H, CH_3); ^{13}C NMR ($CDCl_3$, room temperature) 157.9 (d, $^1J_{C-P} = 8$ Hz, $C_{\beta'}$), 141.0–142.0 (m, C_6H_2), 131.8–127.3 (C_6H_5, C_6H_2), 129.9 (d, $^1J_{C-P} = 95$ Hz, $^2J_{C-W} = 11$ Hz, C_β), 97.2 and 95.2 (two s, Cp), 25.3, 24.9, and 21.0 (CH_3); ^{31}P NMR ($CDCl_3$, room temperature) δ 85.4 (s, broad); IR (KBr, $\tilde{\nu}$ (cm^{-1})) 1892 (CO), 1606 and 1549 (NO).

[{(CH_3Ph)HC=C}(NO)(η^5-Cp)W–W(η^5-Cp)(NO)(CO){C=CH(P(Mes)$_2$}] (14c). The preparation was carried out as described before, except with 423 mg (1 mmol) of tungsten vinylidene complex **12c** instead of **12a**. The solution with both vinylidenes was stirred for 4 days. Chromatography on silica gel with pentane/diethyl ether (1:1) yielded 101 mg (10%) of the *E* isomer as orange crystals and 82 mg (8%) of the *Z* isomer as an orange solid (mp 199–201 °C dec). Anal. Calcd for $C_{40}H_{41}N_2O_3PW_2$: C, 48.22; H, 4.15; N, 2.81. Found: C, 48.21; H, 3.59; N, 2.88. *E* isomer: ^1H NMR ($CDCl_3$, room temperature) δ 7.81 (d, 1H, cis $^3J_{H-P} = 39$ Hz, $^3J_{H-W} = 12$ Hz, $C_{\beta'}H$), 7.69 (d, 1H, $^2J_{H-P} = 56$ Hz, $C_\beta H$), 7.46 and 7.19 (two d, 4H, C_6H_4), 6.95 (s, 4H, C_6H_2), 5.52 (s, 5H, Cp), 5.08 (s, 5H, Cp), 2.80–1.88 (broad (2.35 s and 2.80 d), 21H, CH_3); ^{13}C NMR ($CDCl_3$, room temperature) δ 295.0 (d, $^2J_{C-P} = 23$ Hz, C_α), 240.8 (CO), 156.3 (d, $^2J_{C-P} = 8$ Hz, $C_{\beta'}$), 142.1 and 141.8 (two d, $^4J_{C-P} = 2.5$ and 2.5 Hz, C_6H_2 (para)), 138.5 (d, $^1J_{C-P} = 19$ Hz, $C_{\alpha'}$), 137.8 (d, trans $^3J_{C-P} = 32$ Hz, C_6H_4 (ipso to $C_{\beta'}$)), 137.6 (s, C_6H_4 (para to $C_{\beta'}$)), 132.9 (d,$^1J_{C-P} = 97$ Hz, $^2J_{C-W} = 9$ Hz, C_β), 129.2 and 128.7 (two s, C_6H_4), 127.3 and 124.7 (two d, $^1J_{C-P} = 60$ and 50 Hz, C_6H_2 (ipso)), 98.7 and 95.6 (two s, Cp), 21.3 (s, $C_6H_5\mathit{C}H_3$), 21.0 (d, $C_6H_2\mathit{C}H_3$); ^{31}P NMR ($CDCl_3$, room temperature) δ 77.6 (s, trans $^3J_{P-W} = 60$ Hz, $^2J\ ^3J_{P-W} = 44.5$ Hz); IR (KBr, $\tilde{\nu}$ (cm^{-1})) 1898 (CO), 1596 and 1554 (NO). *Z* isomer: ^1H NMR ($CDCl_3$, room temperature) δ 7.97 (d, 1 H, $^2J_{H-P} = 38$ Hz, $^3J_{H-W} = 12$ Hz, $C_\beta'H$), 7.65 (d, 1 H, $^2J_{H-P} = 55$ Hz, $C_\beta H$), 7.46 (d, 2H, 8 Hz, C_6H_4), 7.20 (d, 2H, 8 Hz, C_6H_4), 6.96 (d, 2 H, $^4J_{H-P} = 3$ Hz, C_6H_2), 6.85 (d, 2 H, $^4J_{H-P} = 3$ Hz, C_6H_2), 5.57 (s, 5 H, Cp), 4.95 (s, 5 H, Cp), 2.63–2.20 (21 H, CH_3); ^{13}C NMR ($CDCl_3$, room temperature) δ 158.0 (d, $^1J_{C-P} = 9$ Hz, $C_{\beta'}$), 141.0–142.0 (m, C_6H_2), 133–127 (C_6H_4, C_6H_2), 130.0 (d, $^1J_{C-P} = 97$ Hz, C_β), 97.2 and 95.1 (two s, Cp), 21.3 (s, $C_6H_5CH_3$), 20.9 ($C_6H_2(CH_3)_3$); ^{31}P NMR ($CDCl_3$, room temperature) δ 85.1 (s, broad); IR (KBr; $\tilde{\nu}$ (cm^{-1})) 1897 (CO), 1606 and 1555 (NO).

Preparation of Complex 15. To 2.27 g (10.8 mmol) of $HC{\equiv}CP(C_6H_5)_2$ in 30 mL of THF at −78 °C was added 6.25 mL (10 mmol) of n-BuLi in hexane. After it was stirred for 20 min, the solution was added dropwise to a cooled (−30 °C) solution of 2.0 g (5.97 mmol) of **1a** in 40 mL of THF and stirred for 2.5 h. During this time the color of the solution changed slowly from orange to red. Hydrolysis with saturated aqueous $NaHCO_3$, washing of the organic phases with saturated aqueous NaCl and H_2O, and drying over $MgSO_4$ led to 3.37 g of dark red crude product. After pentane was added, a drab-colored residue was obtained (2.19 g), which was dissolved in large amounts of CH_2Cl_2 and cooled to −20 °C for a few days to yield a brown precipitate which then was additionally dissolved in CH_2Cl_2 to give a pale orange residue. Recrystallization from THF yielded yellow transparent rhombic crystals suitable for X-ray diffraction analysis (mp 170–175 °C dec). Anal. Calcd for $C_{60}H_{42}N_2O_6P_4W_2$: C, 52.27; H, 3.07; N, 2.03 Found: C, 52.14; H, 2.79; N, 1.83. IR (KBr; $\tilde{\nu}$ (cm^{-1})) 3296 ($C{\equiv}CH$), 3057 (C_6H_5–H), 2065 ($C{\equiv}C$), 2010 (CO), 1947 (CO), 1620 (NO), 1587 and 1573 (C=C), 1436 (P–C_6H_5).

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Supporting Information Available: Data of crystal structure determination and refinement and tables of atomic coordinates, interatomic distances and angles, anisotropic thermal parameters, and hydrogen parameters of the compounds **8a, 11, 13a**, and **15**. This material is available free of charge via the Internet at http://pubs.acs.org.

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