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η^2-Alkynyl and Vinylidene Transition Metal Complexes. 6.[1] Reaction of Tungsten Vinylidene Complexes with Chlorophosphines as Nucleophile. Preparation and Crystal Structural Analysis of Neutral η^2-Phosphinovinyl Complexes

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The reaction of vinylidene complexes $[(\eta^5\text{-C}_5\text{H}_5)(\text{CO})(\text{NO})\text{W}{=}\text{C}{=}\text{CHR}]$ [R = H (**1a**), CH_3 (**1b**), C_6H_5 (**1c**)] with chlorodiphenylphosphine (**2**) leads to neutral $\{(\eta^5\text{-C}_5\text{H}_5)(\text{Cl})(\text{NO})\text{W}(\overline{\text{C}{=}\text{CHR})[\text{P}}(\text{C}_6\text{H}_5)_2]\}$ [R = H (**3a**), CH_3 (**3b**), C_6H_5 (**3c**)]. Analogously the reaction of chlorodi-*tert*-butylphosphine (**4**) with $[(\eta^5\text{-C}_5\text{H}_5)(\text{CO})(\text{NO})\text{W}{=}\text{C}{=}\text{CH}_2]$ (**1a**) gives rise to chloro(η^5-cyclopentadienyl)nitrosyl(η^2-di-*tert*-butylphosphinovinyl)tungsten (**5**). The formation of these metallacyclopropane rings is rationalized by the nucleophilic attack of chlorophosphine on the C_α carbon of the vinylidene, followed by substitution of the carbonyl ligand. Single-crystal X-ray diffraction data of **3a**−**c** and **5** are reported.

Introduction

The addition of nucleophiles to unsaturated ligands such as alkyne or alkene, activated by coordination to transition metals, has proven to be useful for the preparation of new organometallic complexes and is a versatile methodology in organic synthesis.[2] Although useful for synthetic purposes, so far the nucleophilic addition to the vinylidene moiety has hardly been studied.[3] Theoretical studies predict the electron deficiency at the α-carbon and the localization of electron density in the M=C double bond and at the β-carbon.[4,5] Chemical reactivity is oriented toward electrophilic attack at the β-carbon atom and nucleophilic attack at the α-carbon atom.[4,5] Several examples of addition of nucleophiles, including amines,[6] water,[7] alcohols,[7a,e,g,8] thiols,[7e,9] as well as the addition of *tert*-phosphines[10] to cationic vinylidene complexes have been reported.

Intending to explore the reactivity of neutral tungsten as well as molybdenum vinyliden complexes, we investigated the reaction of vinylidene complexes **1a**−**c** with chlorophosphines **2** and **4.** We observed a nucleophilic addition of phophines to the α-carbon atom, which gives rise to the mononuclear η^2-phosphinovinyl complexes **3a**−**c** and **5** with high yield.

Although three-membered metallacycles with the $\overline{\text{M}-\text{P}-\text{C}}$ unit were often the subject of investigation,[11] only a few examples of mononuclear complexes[12] with a $\overline{\text{M}-\text{P}-\text{C}}{=}\text{C}$ skeleton have been reported.

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Results and Discussion

The treatment of vinylidene complexes $[(\eta^5\text{-}C_5H_5)(CO)(NO)W{=}C{=}CHR]$ [R = H (**1a**), CH_3 (**1b**), C_6H_5 (**1c**)] with chlorodiphenylphosphine (**2**) and of **1a** with chlorodi-*tert*-butylphosphine (**4**) in THF at −30 °C to +15 °C yields after workup the neutral complexes $[(\eta^5\text{-}C_5H_5)(Cl)(NO)W(\overline{C{=}CHR)(P}R'_2)]$ **3a**−**c** [R = H, R′ = C_6H_5 (**3a**), R = CH_3, R′ = C_6H_5 (**3b**), R = R′ = C_6H_5 (**3c**)] and **5** [R = H, R′ = $C(CH_3)_3$ (**5**)] as orange crystals with 50−87% yield. Controlling the reaction by ^1H NMR experiments demonstrates the quantitative formation of **3a**−**c** and **5**.

The solid compounds **3a**−**c** and **5** can be stored under inert gas at −20 °C. The solutions of **3b** and **3c** decompose at room temperature.

The structures of **3a**−**c** and **5** are confirmed by spectroscopic as well as X-ray crystal structure analysis (see Experimental Section). According to the NMR spectra, **3b** and **3c** in solution undergo an *E*/*Z* isomerization, which can be pursued by ^{31}P NMR spectroscopy. At ambient temperature the E/Z isomer ratios of **3b** and **3c** are 3:1 and 1:1.2, respectively. The ^{31}P resonances are accompanied by ^{183}W satellites ($^1J_{P-W} = 118-133$ Hz). The $^1J(^{183}W-^{31}P)$ coupling constants of **3a**−**c** and **5** are comparable to those found in the complexes $\{(\eta^5\text{-}C_5H_5)(CO)_2W(\overline{C{=}CH_2)[P}(C_6H_5)_2]\}$[12] (135.5 Hz), $\{WMoCl_2\text{-}[\mu_2\text{-}(C_6H_5)_2PC{=}CH(C_6H_5)][\mu_2\text{-}P(C_6H_5)_2](\eta^5\text{-}C_5H_5)_2\}$[13a] (115 Hz), and $\{W_2Cl_2[\mu_2\text{-}(C_6H_5)_2PC{=}CH(C_6H_5)][\mu_2\text{-}P(C_6H_5)_2]\text{-}(\eta^5\text{-}C_5H_5)_2\}$[13b] (121.8 Hz).[14]

The ^1H NMR spectra of **3a** and **5** show characteristic signals of the magnetically nonequivalent methylene protons. Because of their different $^3J(^{31}P-^1H)$ coupling constants [**3a**, δ 7.65 ppm ($^3J_{H-P} = 15$ Hz) and 6.55 ppm ($^3J_{H-P} = 35$ Hz); **5**, δ 7.47 ppm ($^3J_{H-P} = 13$ Hz) and 6.49 ppm ($^3J_{H-P} = 32$ Hz)], they can be assigned to the *cis*- and *trans*-position relative to the phosphor atom.[12b,15] The $^3J(^{31}P-^{13}C)$ coupling constants[16] of the *E* and *Z* isomers of **3b** and **3c** also differ significantly: the carbon atoms of the *Z* isomers of **3b** and **3c** couple in both cases with $^3J_{C-P} = 17$ Hz, while the *E* isomers have a coupling constant of 9 and 6 Hz, respectively.

It is interesting to note that for **3a**−**c** and **5** the resonances of the Cp rings split into doublets with a coupling constant of 1.5 Hz due to a $^2J_{C-P}$ coupling.

The formation of metallacyclopropane rings **3a**−**c** and **5** can be explained by the initial nucleophilic attack of the phosphine on the vinylidene α-carbon atom, forming the intermediate **6**, followed by the substitution of chloride to **7** and the elimination of a carbonyl group.

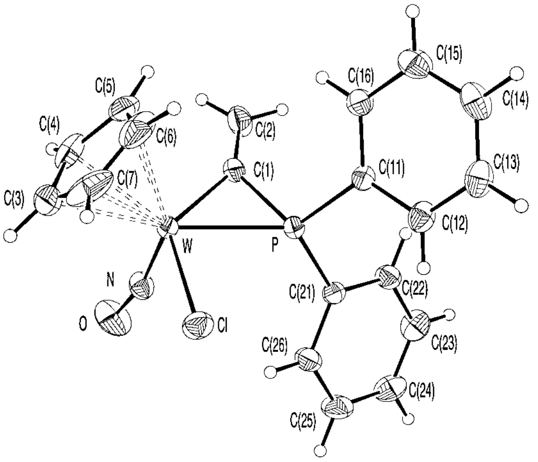

Figure 1. Molecular structure and atom-numbering scheme for $\{(\eta^5\text{-}C_5H_5)(Cl)(NO)W(\overline{C{=}CH_2)[P}(C_6H_5)_2]\}$ (**3a**) with H atoms. Thermal ellipsoids shown at the 30% probability level.

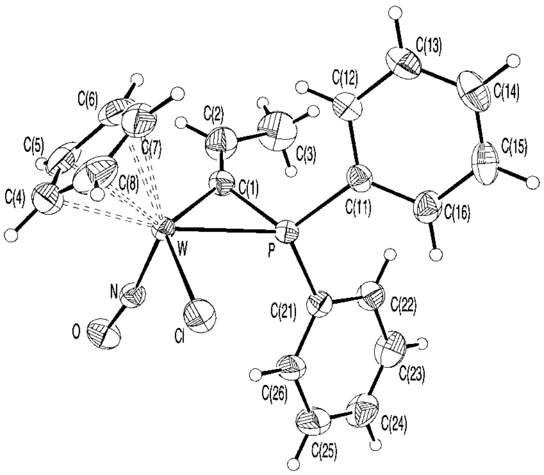

Figure 2. Molecular structure and atom-numbering scheme for $\{(\eta^5\text{-}C_5H_5)(Cl)(NO)W[\overline{C{=}CH(CH_3)][P}(C_6H_5)_2]\}$ (**3b**) with H atoms. Thermal ellipsoids shown at the 30% probability level.

Molecular Structures of 3a−c and 5. Suitable single crystals of **3a**−**c** and **5** were grown from a dichloromethane solution by slow diffusion of pentane at ambient temperature. The crystallization of **3b** and **3c** provides the *E* and *Z* isomer, respectively, which was confirmed by ^1H NMR spectra recorded shortly after the crystalline compounds have been dissolved and by their molecular structures.

The single crystal of compound **5** is an axis twin along [100]. The crystal parameters, data collection parameters, and conditions for structure refinement are summarized in Table 1. Selected bond distances and angles are given in Table 2. A view of the molecules **3a**−**c** and **5** is shown in Figures 1−4. The X-ray diffraction study confirmed the structures of the molecules as pseudo four-legged piano stool complexes with a W atom bonded to a η^5-Cp ring, to a terminal nitrosyl group and a terminal chlorine standing *cis* to each other, and to a phosphinovinyl ligand building a strained three-membered metallacycle.

The most notable features of the metallacyclic systems **3a**−**c** and **5** are the long W−P bonds on one hand

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

	3a	**3b**	**3c**	**5** (axis twin along [100])[a]
formula	$C_{19}H_{17}NOPClW$	$C_{20}H_{19}NOPClW$	$C_{25}H_{21}NOPClW$	$C_{15}H_{25}NOPClW$
cryst size, mm	0.31 × 0.15 × 0.27	0.35 × 0.27 × 0.34	0.35 × 0.46 × 0.42	0.08 × 0.08 × 0.23
fw	525.630	539.657	601.729	485.648
color	orange, transparent	orange, transparent	orange-red, transparent	yellow, transparent
cryst syst	orthorhombic	monoclinic	monoclinic	monoclinic
space group	*Pbca* (No. 61)	$P2_1/n$ (No. 14)	*Cc* (No. 15)	$P2_1/c$ (No. 14)
lattice constants	$a = 15.144(1)$ Å $b = 15.281(1)$ Å $c = 16.001(2)$ Å	$a = 15.157(1)$ Å $b = 7.850(1)$ Å, $\beta = 110.32\ (1)°$ $c = 17.645(1)$ Å	$a = 17.123(3)$ Å $b = 9.713(2)$ Å, $\beta = 116.84(3)°$ $c = 15.258(3)$ Å	$a = 13.138(1)$ Å $b = 12.995(2)$ Å, $\beta = 91.61(1)°$ $c = 10.420(1)$ Å
volume	3784.84 Å^3	1968.87 Å^3	2264.09 Å^3	1778.29 Å^3
formula units per unit cell	$Z = 8$	$Z = 4$	$Z = 4$	$Z = 4$
density calc	1.89 g/cm^3	1.82 g/cm^3	1.77 g/cm^3	1.81 g/cm^3
linear abs coeff	64.7 cm^{-1}	60.9 cm^{-1}	53.1 cm^{-1}	67.3 cm^{-1}
diffractometer	Image Plate Diffractometer System (STOE)			
radiation	Mo Kα	Mo Kα	Mo Kα	Mo Kα
monochromator	graphite	graphite	graphite	graphite
2θ range	$9.5° \le 2\theta \le 56.3°$ $-19 \le h \le 18$, $-19 \le k \le 20$, $-21 \le l \le 21$	$9.5° \le 2\theta \le 56.3°$ $-19 \le h \le 19$, $-10 \le k \le 10$, $-23 \le l \le 23$	$8.1° \le 2\theta \le 52.1°$ $-20 \le h \le 20$, $-11 \le k \le 11$, $-18 \le l \le 18$	$8.1° \le 2\theta \le 52.1°$ $-14 \le h \le 14$, $-14 \le k \le 14$, $-12 \le l \le 12$
no. of rflns measd	34 172	17 792	8294	5659
no. of indep rflns	4452	4715	3921	1817
R_{int}	0.102	0.0785	0.069	0.068
no. of indep rflns with $F_o > 4\sigma(F_o)$	3103	3988	3731	1448
temperature	293 K	293 K	293 K	293 K
applied corrections	Lorentz and polarization coefficients for **3a**−**c** and **5**			
structure determination and refinement	W, Cl, and P positional parameters from direct methods (program SHELXS-97[b]); further atoms from Δ*F* synthesis (program SHELXL-97[c]), structure refinement by the anisotropic full-matrix least-squares procedure for all non-hydrogen atoms; hydrogen position refinement by "riding" model			
no. of parameters	217	226	272	181
wR2	0.0686	0.0979	0.0897	0.0688
R1	0.0508	0.0468	0.0361	0.0383
R1[$F_o > 4\sigma(F_o)$]	0.0292	0.0387	0.0347	0.0274
max and min in Δσ (e Å^{-3})	1.59 −1.57	3.24 −1.98	2.34 −2.96	0.62 −0.73

[a] For integration the IPDS-software TWIN of the firm STOE was applied. [b] Sheldrick, G. M. *SHELXS-97*, Program for the Solution of Crystal Structures; Universität Göttingen, 1997. [c] Sheldrick, G. M. *SHELXL-97*, Program for Crystal Structure Refinement; Universität Göttingen, 1997.

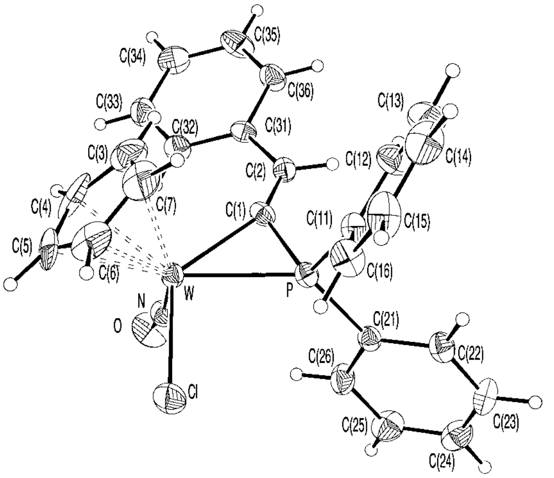


Figure 3. Molecular structure and atom-numbering scheme for {(η^5-C_5H_5)(Cl)(NO)W[C=CH(C_6H_5)][P(C_6H_5)$_2$]} (**3c**) with H atoms. Thermal ellipsoids shown at the 30% probability level.

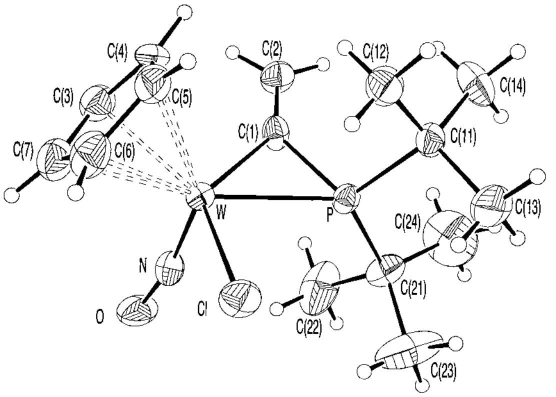


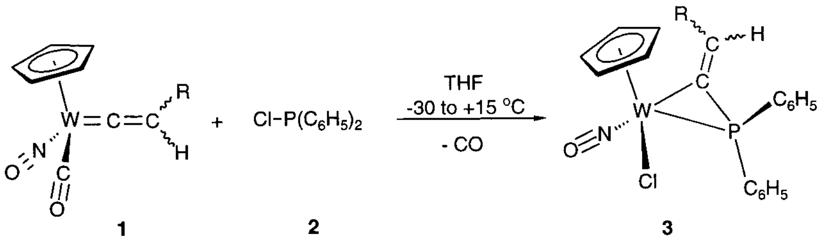
Figure 4. Molecular structure and atom-numbering scheme for {(η^5-C_5H_5)(Cl)(NO)W(C=CH_2)[P(CMe_3)$_2$]} (**5**) with H atoms. Thermal ellipsoids shown at the 30% probability level.

and the short W−C(1) and P−C(1) bonds on the other hand, indicating that complex **8** is the preferred structure in the solid state (Scheme 4). Similar bond lengths were found in binuclear complexes.[13a−d] The P−C(1) bond lengths of **3b**,**c** and **5**, ranging from 1.75 to 1.76 Å, indicate a bond order higher than unity and suggest an alternative view of the ligand as a Ph_2P=C=CHR unit.[11g,13c,d] The average W−P−C(1) angle of **3a**−**c** and **5** (59.0°), the P−W−C(1) angle (44.5°), and P−C(1)−W angle (76.5°) show a significant deformation of the

Table 2. Selected Bond Distances (Å) and Angles (deg) for 3a−c and 5

	3a	3b	3c	5
		Distances		
W−P	2.437(1)	2.448(1)	2.434(2)	2.467(2)
W−C(1)	2.171(5)	2.139(5)	2.178(7)	2.142(8)
P−C(1)	1.771(5)	1.755(6)	1.760(9)	1.760(7)
W−N	1.774(4)	1.778(5)	1.775(8)	1.766(7)
W−Cl	2.455(1)	2.444(2)	2.440 (2)	2.437(2)
C(1)−(C2)	1.312(8)	1.325(9)	1.328(11)	1.327(11)
P−C(11)	1.813(4)	1.809(6)	1.808(9)	1.907(8)
P−C(21)	1.807(4)	1.815(6)	1.820(8)	1.864(11)
C(2)−C(3)		1.487(12)		
C(2)−C (31)			1.448(13)	
range W−C(Cp)	2.298(6)−2.366(6)	2.282(6)−2.379(7)	2.289(11)−2.365(11)	2.307(10)−2.421(11)
		Angles		
P−W−C(1)	44.8(1)	44.4(2)	44.4(2)	44.2(2)
P−C(1)−W	75.6(2)	77.2 (2)	75.5(3)	77.07(3)
C(1)−P−W	59.6(2)	58.4(2)	60.0(3)	58.1(3)
N−W−Cl	95.7(2)	94.6(1)	94.0(3)	98.0(3)
C(1)−W−Cl	130.8(1)	131.6(2)	130.7(2)	129.6(2)
C(1)−W−N	91.8(2)	91.0(2)	87.2(3)	95.1(3)
W−P−C(11)	122.5(2)	124.7(2)	120.1(3)	119.3(3)
W−P−C(21)	124.7(2)	122.3(2)	127.2(3)	124.1(4)
W−N−O	168.2(4)	170.7(4)	170.5(8)	165.0(7)
W−C(1)−C(2)	148.7(4)	147.8(5)	149.1(7)	145.2(7)
P−C(1)−C(2)	135.2(4)	134.9(5)	134.8(7)	136.8(7)
C(1) −C(2) − C(3)		126.6(8)		
C(1)−C(2)−C(31)			128.8(9)	
C(1) − P − C(11)	111.7(2)	113.2(3)	113.1(4)	111.1(4)
C(1)−P−C(21)	118.2(2)	116.4(3)	116.8(4)	114.2(4)
C(11)−P−C(21)	109.4(2)	110.1(3)	109.2 (4)	114.5(5)

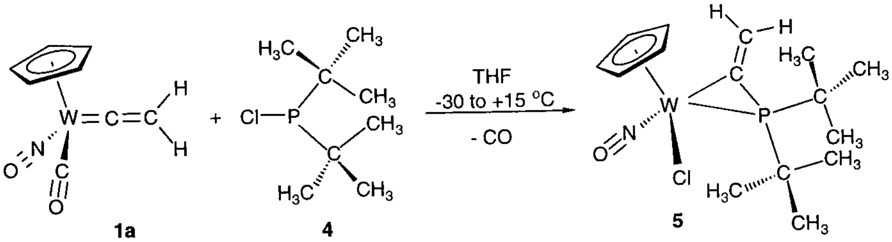
Scheme 1



1 2 3

	R
a	H
b	CH_3
c	C_6H_5

Scheme 2



1a 4 5

formal three-membered heterocyclic structure, also in favor of structure **8**. The small P−W−C(1) angle simultaneously expands the N−W−Cl angle to 95.6° on average.

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^5C$_5$H$_5$)(CO)(NO)W=C=CHR] **1a**,**c**,[17] [(η^5-C$_5$H$_5$)(CO)$_2$(NO)W],[18] and propynyllithium.[19] 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, phosphorus chemical shifts to

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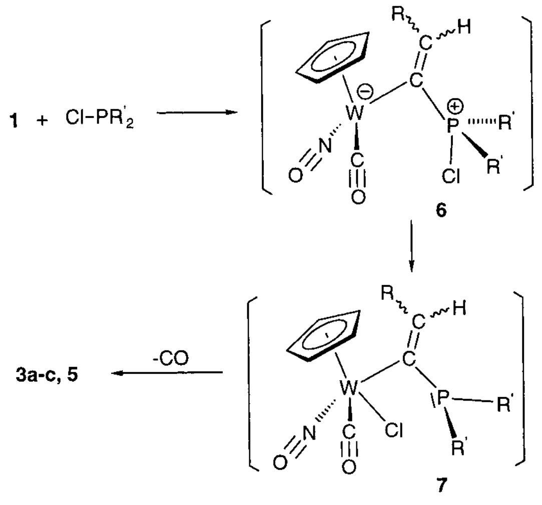
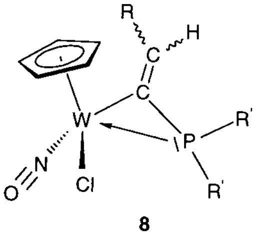
Scheme 3



Scheme 4



orthophosphoric acid as the external standard. MS measurements (70 eV) were performed on a Varian MAT 311-A. IR spectra were recorded on a Bruker FT-IR IFS 85. Microanalyses were done on a Carlo Erba 1104 elemental analyzer.

Preparation of Compounds. [(η^5-C_5H_5)(CO)(NO)W=C=CH(CH_3)] (1b). At −40 °C, a suspension of 23.1 mmol propynyllithium in 45 mL of THF was added dropwise to the orange solution of [(η^5-C_5H_5)$(CO)_2$(NO)W] (2.00 g, 6.0 mmol) in THF (60 mL). After stirring at −30 °C for 6 h, 20 mL of saturated aqueous sodium bicarbonate was added to the deep green reaction mixture, which immediately changed its color to wine red. The THF was removed under reduced pressure, the residue extracted with diethyl ether, and the organic phase dried over magnesium sulfate. Chromatography of the red-brown oil on silica gel with 5:1 pentane/ether yielded 1.24 g (60%) of **1b** as a red-brown oil. Anal. Calcd for $C_9H_9NO_2W$: C, 31.15; H, 2.61; N, 4.04. Found: C, 31.02; H, 2.24; N, 3.94. Two rotamers: ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.87 (s, 5H, Cp), 5.75 and 5.70 (two q, 4:3, 1H, C_βH), 1.70 and 1.65 (two d, 3:4, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 340.1 and 339.6 (two C_α), 210.7 and 210.4 (two CO), 123.5 and 123.2 (two C_β), 96.2 and 95.9 (two Cp), 11.5 and 10.8 (2 CH_3). IR (KBr): $\tilde{\nu}$ (cm^{-1}) 1993 (s, C═O), 1617 (s, N≡O); MS (70 eV) *m/e* 347 (M^+, ^{184}W), 319 (M^+ − CO), 289 (M^+ − CO − NO); high-resolution mass spectrum calcd for $C_9H_9NO_2$182W (M^+) *m/e* 345.0116, found *m/e* 345.0107.

{(η^5-C_5H_5)(Cl)(NO)W(C═CH_2)[P$(C_6H_5)_2$]} (3a). At −30 °C, a solution of 0.84 mL (4.5 mmol) of chlorodiphenylphosphine (**2**) in 20 mL of THF was added dropwise to the orange solution of **1a** (1.5 g, 4.5 mmol) in THF (40 mL). The progress of the reaction was monitored by TLC (silica gel, diethyl ether). The mixture was stirred at −30 °C for 1 h and then warmed to +15 °C and stirred for another 20 min. During this time the color changed from orange to wine red. The solvent was removed by vacuum evaporation, and crystallization of the residue from CH_2Cl_2 and pentane yielded 1.56 g (66%) of **3a** as orange crystals, mp 203−205 °C dec. Anal. Calcd for $C_{19}H_{17}NOPClW$: C, 43.42; H, 3.26; N, 2.67. Found: C, 43.39; H, 2.96; N, 2.95. ^{31}P NMR (162 MHz, $CDCl_3$, H_3PO_4 as external standard): δ −85.5 [s, $^1J_{P-W}$ = 131 Hz, P$(C_6H_5)_2$]. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.80−7.30 (m, 10H, C_6H_5), 7.65 (d, 1H, *cis*-$^3J_{H-P}$ = 15 Hz, C═CH_2), 6.55 (d, 1H, *trans*-$^3J_{H-P}$ = 35 Hz, C═CH_2), 5.85 (s, 5H, Cp). ^{13}C NMR (100 MHz, $CDCl_3$): δ 163.1 (d, $^1J_{C-P}$ = 51 Hz, $^1J_{C-W}$ = 51 Hz, W−C_α), 133.5 (d, $^2J_{C-P}$ = 9 Hz, C_β), 133.8 and 133.6 [two d, $^2J_{C-P}$ = 12 Hz, C_6H_5 (ortho)], 131.2 and 130.8 [two d, $^4J_{C-P}$ = 3 Hz, C_6H_5 (para)], 129.0 and 128.9 [two d, $^3J_{C-P}$ = 12 Hz, C_6H_5 (meta)], 128.5 and 127.0 [two d, $^1J_{C-P}$ = 50 Hz, C_6H_5(ipso)], 102.7 (d, $^2J_{C-P}$ = 1.5 Hz, Cp). IR (KBr): $\tilde{\nu}$ (cm^{-1}) 1610 (N≡O). MS (70 eV): *m/e* 525 (M^+, ^{184}W), 495 (M^+ − NO); high-resolution mass spectrum calcd for $C_{19}H_{17}NOPCl^{182}W$ (M^+) *m/e* 523.0219, found *m/e* 523.0248.

{(η^5-C_5H_5)(Cl)(NO)W[C═CH(CH_3)][P$(C_6H_5)_2$]} (3b). A 0.87 g (2.5 mmol) sample of tungsten vinylidene complex **1b** was dissolved in 15 mL of THF and cooled to −30 °C. To the orange solution was added dropwise 0.46 mL (2.5 mmol, 55 mg) of chlorodiphenylphosphine (**2**). After complete addition the cooling bath was removed immediately. When the formation of CO gas was complete, the THF was removed as fast as possible under vacuum to avoid decomposition. Chromatography on silica gel with 1:1 pentane/ether yielded 0.67 g (50%) of **3b** as a yellow solid. Crystallization from CH_2Cl_2 and pentane produced orange crystals of the *E* isomer, mp 180−182 °C dec. Anal. Calcd for $C_{20}H_{19}NOPClW$: C, 44.51; H, 3.55; N, 2.60. Found: C, 44.59; H, 3.32; N, 2.91. Two isomers, *E*:*Z* = 3:1 at room temperature: ^{31}P NMR (162 MHz, $CDCl_3$, H_3PO_4 as external standard): δ −80.5 and −87.0 [two s, $^1J_{P-W}$ = 124 and 126 Hz, P$(C_6H_5)_2$, *E* and *Z*]. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.18 [dq (overlapping), 1H, $^3J_{H-H}$ = 7 Hz, *cis*-$^3J_{H-P}$ = 14 Hz, $^3J_{H-W}$ = 7 Hz, C═CHR, *Z*], 7.80−7.33 (m, 10H, C_6H_5), δ 6.72 (dq, 1H, $^3J_{H-H}$ = 7 Hz, *trans*-$^3J_{H-P}$ = 34 Hz, C═CHR, *E*), 5.85 and 5.84 [two s (overlapping), 5H, Cp, *Z* and *E*], 2.11 and 1.96 (dd and d, 3H, $^3J_{H-H}$ = 7 Hz, $^4J_{H-P}$ = 1 Hz, CH_3, *E* and *Z*). ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.0 and 148.9 (two d, $^1J_{C-P}$ = 46 and 52 Hz, $^1J_{C-W}$ = 51 and 52 Hz, W−C_α, *Z* and *E*), 147.2 and 145.6 (two d, $^2J_{C-P}$ = 7 and 9 Hz, C_β, *Z* and *E*), 134.0−133.5 [m, C_6H_5 (ortho)], 131.1 and 130.8 [two d, $^4J_{C-P}$ = 3 Hz, C_6H_5 (para), *E*], 131.1 and 130.7 [two d, $^4J_{C-P}$ = 3 Hz, C_6H_5 (para), *Z*], 129.3−128.8 [m, C_6H_5 (meta)], 129.0 and 127.6 [two d, $^1J_{C-P}$ = 49 Hz, C_6H_5(ipso), *Z*], 128.1 and 126.5 [two d, $^1J_{C-P}$ = 51 and 50 Hz, C_6H_5(ipso), *E*], 102.7 and 101.6 (two d, $^2J_{C-P}$ = 1.5 Hz, Cp, *E* and *Z*), 26.0 and 20.6 (two d, $^3J_{C-P}$ = 9 and 17 Hz, CH_3, *E* and *Z*). IR (KBr): $\tilde{\nu}$ (cm^{-1}) 1611 (N≡O); MS (70 eV) *m/e* 539 (M^+, ^{184}W), 509 (M^+ − NO); high-resolution mass spectrum calcd for $C_{20}H_{19}NOPCl^{182}W$ (M^+) *m/e* 537.0375, found *m/e* 537.0338.

{(η^5-C_5H_5)(Cl)(NO)W[C═CH(C_6H_5)][P$(C_6H_5)_2$]} (3c). The preparation was carried out as described for **3a**, however using tungsten vinylidene complex **1c** instead of **1a**. Chromatography on silica gel with 1:1 pentane/ether at the beginning and pure diethyl ether at the end yielded 1.62 g (60%) of **3c** as a yellow solid. Crystallization from CH_2Cl_2 and pentane produced orange crystals of the *Z* isomer, mp 206−208 °C dec. Anal. Calcd for $C_{25}H_{21}NOPClW$: C, 49.90; H, 3.52; N, 2.33. Found: C, 49.92; H, 3.17; N, 2.66. Two isomers, *E*:*Z* = 1:1.2 at room temperature: ^{31}P NMR (162 MHz, $CDCl_3$, H_3PO_4 as external standard): δ −70.4 and −87.2 [two s, $^1J_{P-W}$ = 129 and 133 Hz, P$(C_6H_5)_2$, *E* and *Z*]. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.18 (d, 1H, *cis*-$^3J_{H-P}$ = 15 Hz, $^3J_{H-W}$ = 7 Hz, C═CHR, *Z*), 7.82 (m, 2H, C_6H_5, *Z*), 7.77−7.14 [m, 11H, C_6H_5 (10H) and C═CHR (*E*, 1H)], 5.88 and 5.71 (two s, 5H, Cp, *E* and *Z*). ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.0 and 150.0 (two d, $^1J_{C-P}$ = 50 Hz, $^1J_{C-W}$ = 55 Hz, W−C_α, *Z* and *E*), 150.3 and 147.6 (two d, $^2J_{C-P}$ = 6 and 11 Hz, C_β, *Z* and *E*), 139.1 and 138.6 [two d, $^3J_{C-P}$ = 17 and 6 Hz, C_β(C_6H_5), *Z* and *E*], 133.9−133.5 [m, C_6H_5 (ortho)], 131.4 and 131.1 [two d, $^4J_{C-P}$ = 3 Hz, C_6H_5 (para), *E*], 131.3 and 130.8 [two d, $^4J_{C-P}$ = 3 Hz, C_6H_5 (para), *Z*], 129.6−127.1 [m, C_6H_5 (meta)], 126.0 [d, $^1J_{C-P}$ = 50 Hz, C_6H_5-(ipso), *Z*], 103.0 and 102.8 [s(broad) and d, $^2J_{C-P}$ = 1.5 Hz, Cp, *E* and *Z*]. IR (KBr): $\tilde{\nu}$ (cm^{-1}) 1607 (N≡O); MS (70 eV) *m*/*e* 601 (M$^+$, ^{184}W), 571 (M$^+$ − NO); high-resolution mass spectrum calcd for $C_{25}H_{21}NOPCl^{182}W$ (M$^+$) *m*/*e* 599.0532, found *m*/*e* 599.0514.

$\{(\eta^5\text{-}C_5H_5)(Cl)(NO)W(\overline{C{=}CH_2)(P}[C(CH_3)_3]_2)\}$ (5). The preparation was carried out as described for **3a**; however chlorodi-*tert*-butylphosphine (**4**) was used instead of chlorodiphenylphosphine (**2**). Chromatography on silica gel with 3:1 pentane/ether yielded 1.91 g (87%) of **5** as a bright yellow solid. Crystallization from CH_2Cl_2 and pentane resulted in orange crystals, mp 157−158 °C dec. Anal. Calcd for $C_{15}H_{25}$-NOPClW: C, 37.10; H, 5.19; N, 2.88. Found: C, 37.19; H, 5.11; N, 3.11. ^{31}P NMR (162 MHz, $CDCl_3$, H_3PO_4 as external standard): δ −46.0 {s, $^1J_{P-W} = 118$ Hz, $P[C(CH_3)_3]_2$}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.47 (d, 1H, *cis*-$^3J_{H-P} = 13$ Hz, $^3J_{H-W} = 8.5$ Hz, $C{=}CH_2$), 6.49 (d, 1H, *trans*-$^3J_{H-P} = 32$ Hz, $C{=}CH_2$), 5.82 (s, 5H, Cp), 1.48 and 1.36 {two d, 18H, $P[C(CH_3)_3]_2$, $^3J_{H-P} = 16$ Hz }. ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.5 (d, $^1J_{C-P} = 58$ Hz, $^1J_{C-W} = 56$ Hz, W−C$_\alpha$), 132.8 (d, $^2J_{C-P} = 9$ Hz, C$_\beta$), 103.4 (d, $^2J_{C-P} = 1.5$ Hz, Cp), 40.1 and 33.7 [two d, $^1J_{C-P} = 10$ Hz, $C(CH_3)_3$], 31.0 (two d, $^2J_{C-P} = 3$ and 4 Hz, CH_3). IR (KBr): $\tilde{\nu}$ (cm^{-1}) 1620, 1528 (N≡O). MS (70 eV): *m*/*e* 485 (M$^+$, ^{184}W), 455 (M$^+$ − NO); high-resolution mass spectrum calcd for $C_{15}H_{25}$-NOPClW (M$^+$) *m*/*e* 483.0844, found *m*/*e* 483.0845.

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Supporting Information Available: Data of crystal structure determination and refinement, tables of atomic coordinates, interatomic distances and angles, anisotropic thermal parameters, and hydrogen parameters of the compounds **3a**−**c** and **5**. This material is available free of charge via the Internet at http://pubs.acs.org.

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