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Synthesis of Bridged Oxo-Tungsten Complexes

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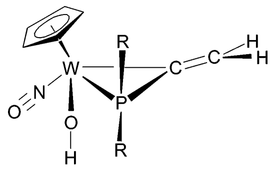
*Summary: The tungsten chlorophosphinovinyl complexes {(η^5-C_5H_5)(Cl)(NO)W(C=CH_2)[PR_2]} (R = C_6H_5, **3a**; R = $CH(CH_3)_2$, **3b**; R = $C(CH_3)_3$, **3c**) have been prepared, and their hydrolysis to μ-oxo complexes **4a**, **4b**, and **5** is described. The molecular structure of **4a**, **4b**, and **5** is determined by single-crystal X-ray diffraction studies.*

Introduction

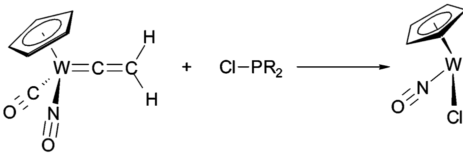
Transition metal complexes with terminal hydroxo and oxo ligands attract considerable interest due to their involvement in industrially relevant processes and enzyme-catalyzed reactions.[1] A variety of methods for the synthesis of early as well as late transition metal hydoxo and μ-oxo complexes are available, such as oxidation of metal–metal bonds by exposure to molecular oxygen or hydrolysis of metal–halogen bonds.[2–5] Intending to prepare the tungsten complex **A**, containing a terminal hydoxo group and a phosphane ligand, we investigated the hydrolysis of chlorophosphinovinyl complexes **3a**–**c**. Generally it is expected that phosphane groups stabilize the hydroxo complexes,[5] but the dehydratization to the μ-oxo complexes is a thermodynamically favored process and the hydroxo ligands have a strong propensity to bridge between two metal centers.[6] Here we report the results of our study.

Scheme 1



A

Scheme 2



1 **2** **3**

	R
a	C_6H_5
b	$CH(CH_3)_2$
c	$C(CH_3)_3$

Results and Discussion

The chlorophosphinovinyl complexes **3a**–**c** are prepared as previously described by nucleophilic addition of chlorophosphines **2a**–**c** to the tungsten η^1-vinylidene complex {(η^5-C_5H_5)(NO)(CO)W=C=CH_2)]} (**1**).[7] Hydrolysis of **3a**–**c** was carried out in THF by adding sodium hydroxide and a trace of H_2O. The progress of the reaction was followed by TLC. After the educt disappeared, the solid was filtered, the solvent was evaporated, and the product was extracted with pentane. While the reaction of chlorophosphinovinyl complex **3a** gave rise to a mixture of diastereomeric bridged μ-oxo complexes **4a** and **4b** (75% yield, 82:18 ratio), the reaction of diisopropylphosphinyl derivative **3b** yielded only the complex **5**, and the *tert*-butylphosphinyl derivative **3c** did not hydrolyze under the applied reaction conditions.

The two diasteromeric complexes **4a** and **4b** were separated by chromatography as air- and moisture-stable yellow-orange solids. The structures of products **4a**, **4b**, and **5** were unambiguously determined by elementary analysis, spectroscopic techniques, and single-crystal X-ray data. The significant differences in the structures of **4a** and **4b** are the relative orientation of the cylopentadienyl ligand (*E* or *Z*) and the nitrosyl groups, respectively, to each other. While in the major component **4a** the Cp ligands are oriented *E* relative to each other, the orientation of these ligands in complex **4b** is *Z*. The ^{1}H NMR and ^{13}C NMR spectra of compounds **4a**,**b** and **5** displayed sharp and well-resolved signals. The most characteristic features of the ^{1}H NMR and ^{13}C NMR spectra were the signals for the quater-

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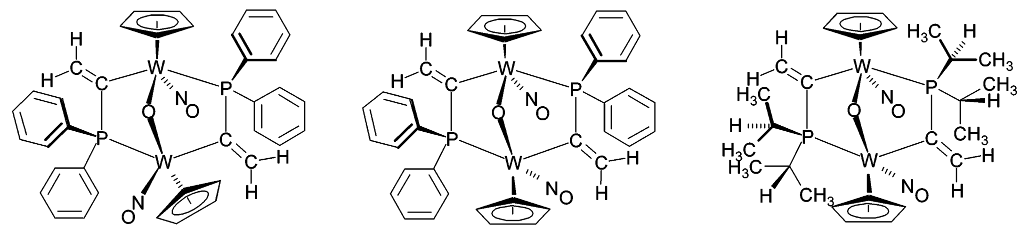
10.1021/om049079x CCC: $30.25

Scheme 3



4a **4b** **5**

nary carbon atom and the methylene group, respectively, with the corresponding satellite signals caused by the coupling with the ^{183}W atom (14% ^{183}W abundance). The protons of the methylene group in the ^{1}H NMR spectrum of **4a** appeared as two doublets at δ 7.21 and 6.39 ppm and two doublets centered at 6.60 ppm with $^3J_{\mathrm{P-H\,cis}} = 22$ Hz and $^3J_{\mathrm{P-Htrans}} = 47$ Hz as well as $^3J_{\mathrm{W-H\,cis}} = 7.5$ Hz and $^3J_{\mathrm{W-Htrans}} = 12.5$ Hz, respectively. Due to the C2 symmetry of the molecule, the ^{1}H NMR spectra of complexes **4b** and **5** show only two doublets for the methylene protons. The ^{13}C NMR spectrum of **4a** displays two doublets of doublets at δ 174.5 and 171.4 ppm ($^1J_{\mathrm{P-C}} = 43$ Hz, $^1J_{\mathrm{W-C}} = 21$ Hz) for the quaternary carbon atom. The methylene carbon atom appears as a doublet at δ 139.8 ppm and a singlet at 136.3 ppm, whereas complex **5** shows only one doublet of doublets at δ 173.11 ppm ($^1J_{\mathrm{P-C}} = 50.5$ Hz, $^1J_{\mathrm{W-C}} = 18.3$ Hz) for the quaternary carbon atom.

The ^{31}P NMR spectrum of **4a** shows an AMX spin system: two doublets at δ 35.4 ppm ($^1J_{\mathrm{P-W}} = 237$ Hz, $^3J_{\mathrm{P-P}} = 10.9$ Hz) and δ 14.8 ppm ($^1J_{\mathrm{P-W}} = 205$ Hz, $^3J_{\mathrm{P-P}} = 10.9$ Hz) for two different $P(C_6H_5)_2$ groups. Computer simulations with MestReC resulted in a $^2J_{\mathrm{P-W}}$ value of 11.4 Hz. The ^{31}P NMR spectrum of *cis* isomer **4b** shows a signal at δ 27.2 ppm (AA′X system, $^1J_{\mathrm{P-W}} = 233$ Hz, $^3J_{\mathrm{P-P}} = 17.7$ Hz). The chemical shift of the phosphorus atom in **4a** and **4b** as well as **5** allocates reduced electron density on the phosphorus atom compared to complex **3a** (^{31}P NMR signal at δ −85.5 ppm[7]). Remarkable also is $^1J_{\mathrm{P-W}} = 233$ Hz for **4a** compared to the related value for **3a** ($^1J_{\mathrm{P-W}} = 133$ Hz[7]), which can be attributed to the stronger involvement of the phosphorus s-orbital in the W−P bond of **4a**.[8]

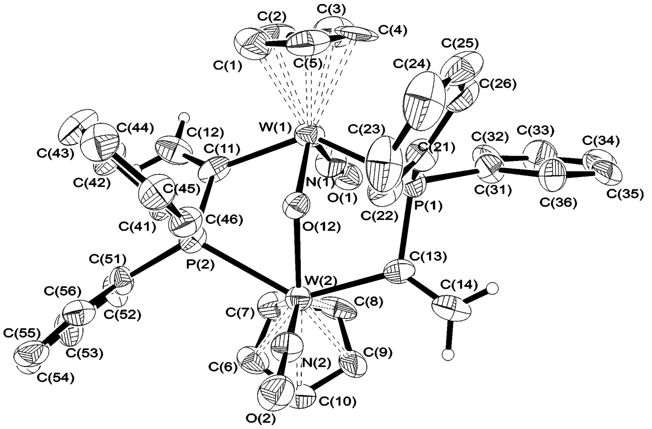


Figure 1. Molecular structure and atom-numbering scheme for complex **4a** without H atoms on Cp rings and phenyl groups. Thermal ellipsoids are shown at the 30% probability level. Selected bond lengths [Å] and angles [deg] (with standard deviations): W(1)−W(2) 3.446,[11] W(1)−N(1) 1.713(13), W(1)−O(12) 1.973(9), W(1)−C(11) 2.169(15), W(1)−P(1) 2.545(4), W(2)−N(2) 1.727(13), W(2)−O(12) 2.011(8), W(2)−C(13) 2.162(14), W(2)−P(2) 2.508(4), N(1)−W(1)−O(12) 113.(5), N(1)−W(1)−C(11) 90.1(5), O(12)−W(1)−C(11) 74.2(4), N(1)−W(1)−P(1) 91.8(4), W(2)−O(12)−W(1) 120.9(5), C(13)−P(1)−W(1) 106.0(5), C(11)−P(2)−W(2) 100.9(5).

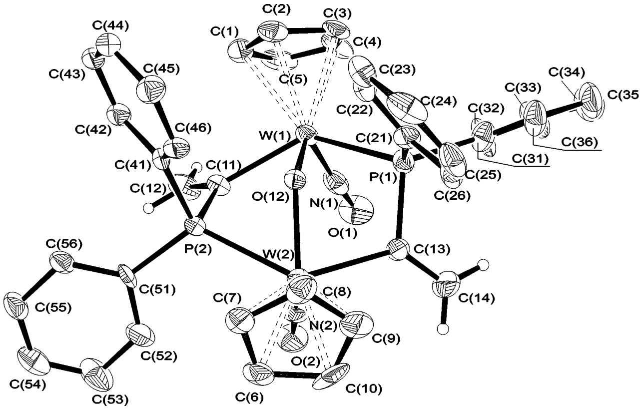


Figure 2. Molecular structure and atom-numbering scheme for complex **4b** without H atoms on Cp rings and phenyl groups. Thermal ellipsoids are shown at the 30% probability level. Selected bond lengths [Å] and angles [deg] (with standard deviations): W(1)−W(2) 3.560,[11] W(1)−N(1) 1.759(13), W(1)−O(12) 2.025(7), W(1)−C(11) 2.220(12), W(1)−P(1) 2.507(3), W(2)−N(2) 1.772(11), W(2)−O(12) 2.023(7), W(2)−C(13) 2.204(13), W(2)−P(2) 2.483(3) N(1)−W(1)−O(12) 113(6), N(1)−W(1)−C(11)88.1(5), O(12)−W(1)−C(11) 75.5(4), N(1)−W(1)−P(1) 88.1(4), W(2)−O(12)−W(1) 123.1(4), C(13)−P(1)−W(1) 101.0(5), C(11)−P(2)−W(2) 102.5(4).

The infrared spectrum shows a broad NO band for *trans* isomer **4a** at 1553 cm^{-1}, which is shifted slightly to lower frequency compared to the absorption of the nitrosyl group of complex **1** at 1635 cm^{-1}.

Suitable single crystals of complexes **4a**, **4b**, and **5** were grown from a dichloromethane solution by slow diffusion of pentane at −20 °C. The ORTEP plot is shown in Figures 1−3, and crystallographic data are given in Table 1. The molecules display a four-legged piano-stool geometry at tungsten atoms, which is a common structural motif for high-valent transition metal complexes of V, Cr, and W.[9] The μ-oxo bridge has an W−O−W angle of 123.1° and W−O bond length of 2.011 Å for **4b** (respectively W−O−W angle of 125.4° and W−O bond length of 1.995 Å for **5**). The W−P bond length of *trans* isomer **4a** is 2.545 Å, compared with 2.507 Å in *cis* isomer **4b**. Compared to the corresponding

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Table 1. Crystallographic Data for Complexes 4a, 4b, and 5

	4a	4b	5
formula	$C_{38}H_{34}N_2O_3P_2W_2$	$C_{38}H_{34}N_2O_3P_2W_2$	$C_{26}H_{42}N_2O_3P_2W_2$
fw	996.353	996.353	860.279
color and habit	yellow, transparent	orange, transparent	orange, transparent
cryst syst	monoclinic	monoclinic	monoclinic
space group	*C*2/*c* (No.15)	*P*21/*n* (No.14)	*P*21/*n* (No.14)
lattice constants	$a = 43.354(9)$ Å	$a = 11.235(1)$ Å	$a = 10.137(2)$ Å
	$b = 9.976(2)$ Å	$b = 23.2229(3)$ Å	$b = 14.412(2)$ Å
	$\beta = 98.02(3)°$	$\beta = 100.04(1)°$	$\beta = 109.26(2)°$
	$c = 34.402(7)$ Å	$c = 13.493(1)$ Å	$c = 21.374(3)$ Å
volume	15073.53 Å^3	3466.26 Å^3	2947.79 Å^3
formula units per unit cell	$Z = 16$	$Z = 4$	$Z = 1$
density(calc)	1.868 g/cm^3	1.909 g/cm^3	1.938 g/cm^3
linear absorp coeff	63.3 cm^{-1}	67.6 cm^{-1}	79.4 cm^{-1}
diffractometer	image plate diffractometer system (STOE)		
radiation	Mo Kα ($\lambda = 0.71069$ Å)	Mo Kα ($\lambda = 0.71069$ Å)	Mo Kα ($\lambda = 0.71073$ Å)
monochromator	graphite	graphite	graphite
scan range	$5.7 \le 2\theta \le 42.0°$	$8.1 \le 2\theta \le 52.0°$	$3.27 \le 2\theta \le 52.1°$
	$-44 \le h \le 43, -9 \le k \le 9,$	$-12 \le h \le 13, -28 \le k \le 28,$	$-12 \le h \le 13, -28 \le k \le 28,$
	$-16 \le l \le 16$	$-34 \le l \le 34$	$-34 \le l \le 34$
no. of reflns collected	28 377	24 389	21 419
R_{int}	0.0775	0.0611	0.0501
no. of indep reflns	7846	6632	5687
no. of indep reflns with $F_o > 4\sigma(F_o)$	4974	4448	5077
applied corr	Lorentz and polarization coefficients		
struct determination and refinement	W positional parameters from Patterson synthesis (program SHELXS-86)[a]		
number of params	893	424	316
R_w	0.0754	0.1668	0.0596
R_1	0.0785	0.0859	0.0274
R_1 [$F_o > 4\sigma(F_o)$]	0.0381	0.0565	0.0226

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

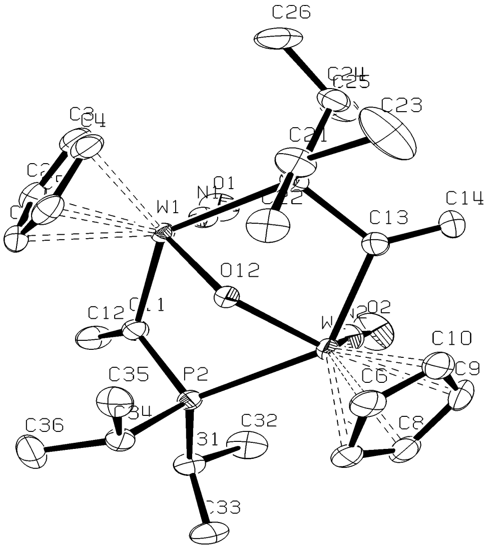

Figure 3. Molecular structure and atom-numbering scheme for complex **5** without H atoms on Cp rings and phenyl groups. Thermal ellipsoids are shown at the 30% probability level. Selected bond lengths [Å] and angles [deg] (with standard deviations): W(1)−W(2) 3.542,[11] W(1)−N(1) 1.772(4), W(1)−O(12) 1.989(2), W(1)−C(11) 2.209(4), W(1)−P(1) 2.528(12), W(2)−N(2) 1.755(4), W(2)−O(12) 1.995(2), W(2)−C(13) 2.217(5), W(2)−P(2) 2.5256(11), N(1)−W(1)−O(12) 117.71(13), N(1)−W(1)−C(11) 83.76(16), O(12)−W(1)−C(11) 76.52(13), N(1)−W(1)−P(1) 89.80(12), W(2)−O(12)−W(1) 125.48(13), C(13)−P(1)−W(1) 104.27(15).

W−P bond length of 2.437 Å in **3a**,[7] the bond lengths of **4a** and **4b** show a smaller participation of π-back-bonding.

Experimental Section

General Considerations. All reactions were carried out under an argon atmosphere (99.99%, by Messer-Griesheim) with the use of standard Schlenk techniques. Solvents were purified by standard methods and distilled under argon prior to use. Literature methods were used to prepare [(η^5-C_5H_5)-$(CO)_2$(NO)W],[10] {(η^5-C_5H_5)(Cl)(NO)W(C=CH_2)[P(C_6H_5)$_2$]} (**3a**),[7] and **3c**,[7] and all other compounds were commercially available. NMR spectra were obtained on Bruker AM 400 and AC 200 spectrometers. Proton and carbon chemical shifts are referenced to tetramethylsilane; phosphorus chemical shifts to 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 [(η^5-C_5H_5)(CO)(NO)W=C=CH_2] (1). A solution of 2.9 mL (1.96 g, 20 mmol) of trimethylsilylacetylene in 40 mL of freshly distilled THF was cooled with a dry ice/acetone bath at −78 °C. To this solution was dropped 11.3 mL (18 mmol) of *n*-buthyllithium (solution in hexane) via a syringe. After 45 min a cooled orange solution of 4 g of [(η^5-C_5H_5)$(CO)_2$-(NO)W] (12 mmol) in 50 mL of THF at −40 °C was added via cannula during 10 min to the reaction mixture. The temperature was kept under −30 °C. The reaction mixture was stirred for 3 h, and 40 mL of saturated aqueous sodium bicarbonate was added to the deep green reaction mixture, which immediately changed color to red. The THF was removed under reduced pressure, the residue extracted with diethyl ether, and the organic phase dried over magnesium sulfate. The product was crystallized from ether and can be used without further purification (87% yield according to tungsten complex). ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.87 (s, 5H, Cp), 5.28 and 5.21 (two

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[10] Chin, T. T.; Hoyano, J. K.; Legzdins, P.; Malito, J. T. *Inorg. Synth.* **1990**, *28*, 196.

[11] Calculated from ORTEP-3.

d, 2H). ^{13}C NMR (100 MHz, CDCl$_3$): δ 341.2 (C$_\alpha$), 209.9 (CO), 112.2 (C$_\beta$), 96.3 (two Cp). IR (KBr): $\tilde{\nu}$ (C=O) 1998, $\tilde{\nu}$ (N=O) 1635 cm^{-1}.[7]

Preparation of {(η^5-C$_5$H$_5$)(Cl)(NO)W(C=CH$_2$)[P(CH(CH$_3$)$_2$)$_2$]}, 3b. Diisopropylchlorophosphane (**2b**), 0.8 mL (5 mmol) in 10 mL of THF, was added to a stirred solution of η^1-vinylidene complex **1**, 1.6 g (4.82 mmol) in 60 mL of THF, at 0 °C drop by drop. After complete addition the mixture was allowed to warm to room temperature. The reaction was monitored by TLC. After completion the THF was removed under vacuum. Chromatography on silica gel from 1:1 pentane/ether to ether yielded 1.441 g (65%) of **3b** as a yellow solid. Crystallization from ether at −20 °C produced bright orange crystals, mp 145 °C dec. Anal. Calcd for $C_{13}H_{21}NOPClW$: C 34.24, H 4.62, N 3.06. Found: C 34.66, H 4.65, N 2.99. ^{31}P NMR (162 MHz, CDCl$_3$, H$_3$PO$_4$ as external standard): δ −57.63 (s, $^1J_{\text{P-W}} = 130.97$ Hz). ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.42 (d, 1H, $^3J_{\text{P-H cis}} = 12,6$ Hz, $^3J_{\text{W-Htrans}} = 8.95$ Hz, C$_\beta$H), 6.43 (d, 1H, $^3J_{\text{P-Htrans}} = 31.64$ Hz, $^3J_{\text{W-H cis}} = 5.12$ Hz C$_\beta$H), 5.83 (s, 5H, Cp), 2.8 and 2.6 (m, 4H, methine), from 1.1 to 1.5 (multiplet, 12H, methyl). ^{13}C NMR (100 MHz, CDCl$_3$): δ 161.9 (d, $^1J_{\text{P-C}} = 51.88$ Hz, C$_\alpha$), 132.7 (d, $^2J_{\text{P-C}} = 9.15$ Hz, C$_\beta$), 102.5 (d, Cp). IR (KBr): $\tilde{\nu}$ (N=O) 1611 and 1591 cm^{-1}. High-resolution mass spectrum calcd for $C_{13}H_{12}NOPClW$ (M$^+$) *m*/*e* 455.05315; found *m*/*e* 455.04924.

Preparation of 4a and 4b. To a cooled suspension of 1 g of NaOH in 30 mL of THF and 2 mL of distilled water at 0 °C was added a solution of 527 mg of **7** in 30 mL of THF via a syringe. The reaction mixture was warmed to room temperature. The course of the reaction was monitored by TLC. Removing the solvent and extraction of the organic compounds by CH$_2$Cl$_2$ yielded after drying over MgSO$_4$ 490 mg (75%) of a solid material, which consisted of two isomers, ***E*-4a** and ***Z*-4b**, in a ratio of 82:18. The diasteromers were separated with preparative TLC (silica gel, diethyl ether).

Complex 4a. Crystallization of **4a** from CH$_2$Cl$_2$ and pentane produced orange crystals, mp 142 °C dec. Anal. Calcd for $C_{38}H_{34}N_2O_3P_2W_2$ (996.35): C 45.81, H 3.44, N 2.81. Found: C 45.72, H 3.09, N 2.73. ^{31}P NMR (162 MHz, CDCl$_3$, H$_3$PO$_4$ as external standard): δ 35.4 (d, $^1J_{\text{P-W}} = 237$ Hz, $^3J_{\text{P-P}} = 10.9$ Hz), 14.8 (d, $^1J_{\text{P-W}} = 205$ Hz, $^3J_{\text{P-P}} = 10.9$ Hz). ^{1}H NMR (400 MHz, CDCl$_3$): δ 8.02 (m, 2H), 7.75 (m, 2H), 7.47−7.25 (m, 18H), 7.21 and 6.60 (two d, 2H,$^3J_{\text{P-H cis}} = 22$ and 24 Hz, $^3J_{\text{W-Htrans}} = 12.5$ Hz, C$_\beta$H), 6.60 and 6.39 (two d, 2H, $^3J_{\text{P-Htrans}} = 47$ and 46 Hz, $^3J_{\text{W-H cis}} = 7.5$ Hz, C$_\beta$H), 5.70 and 5.24 (two d, 10H, Cp). ^{13}C NMR (100 MHz, CDCl$_3$): δ 174.5 and 171.4 (two dd, $^1J_{\text{P-C}} = 43$ Hz, $^1J_{\text{W-C}} = 21$ Hz, C$_\alpha$), 141.1, 137.7, and 133.3 [d, s, d, $^1J_{\text{C-P}} = 35.5$, 36, and 2.5 Hz, C$_{\text{ipso}}$], 139.8 and 136.3 (d, s, $^2J_{\text{C-P}} = 4$ Hz, C$_\beta$), 134.9, 133.9, 133.0, and 132.4 [four d, $^2J_{\text{P-C}} = 9.5$, 11, 7, and 8.5 Hz, C$_{\text{ortho}}$], 130.6, 129.2, and 128.9, C$_{\text{para}}$], 128.9, 128.2, and 127.7, $^3J_{\text{P-C}} = 8.5$, 7, 12.5, and 8.5 Hz, C$_{\text{meta}}$], 103.2 and 101.9 (two s, Cp). IR (KBr): $\tilde{\nu}$ (N=O) 1550 and 1553 cm^{-1}. MS (70 eV): *m*/*e* 996 (M$^+$, ^{184}W), 966 (M$^+$ − NO).

Complex 4b. Crystallization of **4b** from CH$_2$Cl$_2$ and pentane produced light yellow orange crystals, mp 204 °C dec. Anal. Calcd for $C_{38}H_{34}N_2O_3P_2W_2$: C 45.81, H 3.44, N 2.81, Found: C 45.72, H 3.09, N 2.73. ^{31}P NMR (162 MHz, CDCl$_3$, H$_3$PO$_4$): δ 27.2 [s, $^1J_{\text{P-W}} = 233$ Hz, $^3J_{\text{P-P}} = 17.5$ Hz, two identical P(Ph)$_2$]. ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.62−7.30 (m, 20H, Ph), 6.70 [d, 2H, $^3J_{\text{P-H cis}} = 24$ Hz, $^3J_{\text{W-Htrans}} = 12$ Hz, (C$_\beta$H)], 6.24 [d, 2H, $^3J_{\text{P-Htrans}} = 50$ Hz, $^3J_{\text{W-H cis}} = 7$ Hz, (C$_\beta$H)], 5.29 (d, 10H, Cp). ^{13}C NMR (100 MHz, CDCl$_3$): δ 176.1 (dd, $^1J_{\text{P-C}} = 30.5$ Hz, $^1J_{\text{W-C}} = 30.5$ Hz, C$_\alpha$), 136.6 (two d, $^1J_{\text{P-C}} = 4$ and 4.5 Hz, C$_{\text{ipso}}$), 134.2 (s, $^2J_{\text{P-C}} = 4.5$ Hz, C$_{\text{ortho}}$ and two C$_\beta$), 133.4 (two d, $^2J_{\text{P-C}} = 4.5$ Hz, C$_{\text{ortho}}$), 132.9 (two d, $^1J_{\text{P-C}} = 60$ and 69 Hz, C$_{\text{ipso}}$), 129.4 and 129.15 (two s, C$_{\text{para}}$), 128.2 and 127.5 (two d, $^3J_{\text{P-C}} = 4$ and 5 Hz C$_{\text{meta}}$), 99.8 (s, two Cp). IR (KBr): $\tilde{\nu}$ (N=O) 1613 cm^{-1}. MS (70 eV): *m*/*e* 996 (M$^+$, ^{184}W).

Prepration of 5 was as described for **4a** and **4b** however using 2.02 g (4.82 mmol) of **3b** and 1.5 g of NaOH, resulting in **5** with 74% yield as crude material. Crystallization from chloroform and pentane gave rise to pure compound with 60% yield as red-orange crystals, mp 198 °C dec. Anal. Calcd for $(C_{26}H_{42}N_2O_3P_2W)_2\ CHCl_3$: C, 34.60; H, 4.65; N, 3.04. Found: C, 34.20; H, 4.48; N, 3.26. ^{31}P NMR (162 MHz, CDCl$_3$, H$_3$PO$_4$ as external standard): δ 31.34 (s, $^1J_{\text{P-W}} = 209.81$ Hz). ^{1}H NMR (400 MHz, CDCl$_3$): δ 6.53 [d, 2H, $^3J_{\text{P-H cis}} = 12.74$ Hz, $^3J_{\text{W-Htrans}} = 5.91$ Hz, (C$_\beta$H)], 6.15 [d, 2H, $^3J_{\text{P-H trans}} = 40.36$ Hz, $^3J_{\text{W-H cis}} =3.94$ Hz, (C$_\beta$H)], 5.73 (s, 10H, Cp), 2.62 and 2.11 (m, 8H, methine), from 1.25 to 0.93 (multiplet, 24H, methyl). ^{13}C NMR (100 MHz, CDCl$_3$): δ 173.1 (dd, $^1J_{\text{P-C}} = 59.9$ Hz, $^1J_{\text{W-C}} = 18.31$ Hz, C$_\alpha$), 134.2 (s, C$_\beta$), 99.8 (s, Cp), 25.26 to 25.5 (methine), 18 to 19.45 (methyl). IR (KBr): $\tilde{\nu}$ (N=O) 1585 cm^{-1}. High-resolution mass spectrum: calcd for $C_{26}H_{42}N_2O_3P_2W_2$ (M$^+$) *m*/*e* 856.1635, found *m*/*e* 856.16339.

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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 for compounds **4a**, **4b**, and **5**. This material is available free of charge via the Internet at http://pubs.acs.org.

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