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Synthesis and Oxidation of d⁶ Tungsten Pincer Complexes: A Complete Series of Tungsten(II) Hydridocarbonyl and Halocarbonyl Pincer Complexes[†]

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[†]Dedicated to Professor David Cole-Hamilton on the occasion of his retirement and for his outstanding contribution to transition metal catalysis.

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Abstract

Reaction of the neutral P^HNP ligand [HN(SiMe₂CH₂PPh₂)₂] with tungsten hexacarbonyl resulted in coordination of P^HNP through both phosphorus donor atoms to form the tungsten complex $[W(P^{HN}P)(CO)_4]$ (1). Reaction of $P^{H}NP$ with tris(acetonitrile)tricarbonyl tungsten gave both facial and meridional tridentate isomers $[W(P^{H}NP)(CO)_{3}]$ (2-fac and 3-mer). These three d⁶ tungsten complexes could be interconverted under appropriate conditions. The thermodynamically favored isomer **3** was protonated to form seven-coordinate $[W(P^{H}NP)(CO)_{3}H][BF_{4}]$ (4). A related series of cationic tungsten(II) halide complexes was synthesized, $[W(P^{H}NP)(CO)_{3}X]^{+}$ (6, X = I; 7. X = Br: 8. X = Cl: 9. X = F) by various routes. All of the tungsten(II) complexes underwent deprotonation at the amine site of the P^HNP ligand when triethylamine was added, resulting in neutral seven-coordinate complexes. Variable temperature ¹H, ${}^{31}P{}^{1}H$, and ${}^{13}C{}^{1}H$ NMR spectroscopy showed fluxional behavior for all the sevencoordinate complexes reported here. Analysis of IR and NMR spectroscopic data showed trends through the series of coordinated halides. Crystal structures of tetracarbonyl 1, meridional tricarbonyl 3, and cationic hydride 4 were determined to confirm the coordination mode of the P^HNP ligand.

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Introduction

Halocarbonyl complexes of tungsten(II) have been studied for over 50 years¹⁻⁵. Oxidation to tungsten(II) is most commonly achieved by addition of elemental halogens to zero-valent carbonyl complexes containing at least one non-carbonyl donor ligand^{6,7}. Halogenation by iodine⁸, bromine⁹, and chlorine¹⁰ are common in the literature. Oxidative decarboxylation with hydrofluoric acid¹¹ or addition of fluoride to a neutral tungsten (II) dicarbonyl complex¹² can provide access to the less common tungsten fluoride complexes. Despite decades of study, we are only aware of one literature report that includes the entire series of halocarbonyl tungsten complexes for a single ligand system¹¹, and the hydridocarbonyl analogs of the halide complexes are seldom mentioned. Halocarbonyl complexes can be used as catalysts for wide-ranging reactions in homogeneous catalysis^{13,14}, and they are also used as catalyst precursors for heterogeneous polymerization¹⁵. Chelating donor ligands anchor the coordination sphere of many seven-coordinate d⁴ complexes with halide ligands^{11,16-20}.

Phosphine-based pincer complexes have become popular due to their ability to sit at the pivot point of stability and reactivity in metal complexes²¹⁻²⁴. Chelating phosphines are known to increase the basicity of the metal center²⁵⁻²⁷, and for tridentate ligands this donor behavior can also be affected by the bonding geometry adopted by the chelate. Meridional pincer coordination typically increases basicity at the metal center compared to the facially coordinated isomer^{26,28-30}.

First synthesized in 1981 by Fryzuk, HN(SiMe₂CH₂PPh₂)₂ (P^HNP) is a neutral multidentate hybrid pincer ligand³¹. This silazane PNP ligand has two soft phosphine

donor sites linked to a hard amine donor nitrogen. The flexible silazane backbone can bind either as a tridentate meridional or tridentate facial ligand ($P^{H}NP$) or in a bidentate κ^2 -P₂ ($P^{HN}P$) chelation mode³¹⁻³⁴. The amine can be deprotonated to give an anionic tridentate amido ligand (PNP⁻). We report here coordination of $P^{H}NP$ to a d⁶ tungsten center and subsequent oxidation to form cationic and neutral d⁴ tungsten(II) hydride and halide complexes.



Results and Discussion

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Tungsten(0) Complexes. Upon refluxing a chlorobenzene solution of equimolar $W(CO)_6$ and neutral ligand (HN(SiMe_2CH_2PPh_2)_2, P^HNP) for 24 hours, complex 1 with a bidentate P^HNP ligand was synthesized (Scheme 1). An alternative method for the small scale preparation of 1 was the reaction of $W(CO)_6$ with HN(SiMe_2CH_2PPh_2)_2 in a methylene chloride solution in a photolysis chamber for one hour. Complex 1 slowly decomposed in air, but this tungsten (0) complex was stable under inert gas both in the solid state and in solution. The infrared spectrum showed three absorbances in the carbonyl region (2016, 1922, and 1885 cm⁻¹), typical for a sawhorse arrangement of the carbonyl ligands in a tungsten(0) tetracarbonyl complex³⁵.

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Scheme 1. Preparation of a bidentate tungsten(0) complex (1).

Yellow, needle-like crystals of **1** were obtained by slow evaporation at 0 °C. The molecular structure of **1** determined by single-crystal X-ray diffraction is depicted in Figure 1. The crystal structure showed a tetracarbonyl complex with a distorted octahedral geometry where the phosphine groups were *cis* to one another while the amine was not coordinated to tungsten (Figure 1). The *cis* phosphines were related by an obtuse bond angle of 104.2 °, while the carbonyl groups *trans* to the phosphines and *cis* to one another were squeezed to a decreased bond angle of 81.7 ° (C(3)-W(1)-C(7)). The carbonyls *trans* to one another were bent off axis as a result of the bulky bidentate ligand, with a *trans* angle of 173.3 ° (C(1)-W(1)-C(5)). Both W-P bonds were 2.54 Å long. The carbonyl groups *trans* to the phosphines had shorter W-C bonds, at 1.97 and 1.98 Å, than the carbonyls *trans* to one another, at 2.02 and 2.04 Å.

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Figure 1. ORTEP plot of 1.

 Table 1. Bond lengths and bond angles of 1.

Bond distances (Å)		Bond angles (deg)			
W(1)-C(7) W(1)-C(3) W(1)-C(1) W(1)-C(5) W(1)-P(1) W(1)-P(2)	$1.973(5) \\ 1.980(6) \\ 2.024(6) \\ 2.039(6) \\ 2.5351(14) \\ 2.5431(13)$	P(1)-W(1)-P(2) C(1)-W(1)-C(5) C(3)-W(1)-C(7) C(1)-W(1)-P(1)	104.20(4) 173.31(19) 81.7(2) 90.43(16)		

The ¹H NMR spectrum of **1** showed one sharp singlet for the four silazane methyl groups, indicating equivalence of the methyl groups on both sides of the eight-membered ligand metallocycle. A doublet with splitting of 10.4 Hz due to geminal phosphorus

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coupling was observed for the four methylene protons. The amine proton signal for the N-H was not observed. The ³¹P NMR spectrum showed a single peak at -0.37 ppm with one bond tungsten-phosphorus coupling of 233 Hz indicating that both phosphines experience the same magnetic environment. The tungsten-phosphorus coupling was observed as a doublet satellite due to ¹⁸³W, 14% abundant with I = ½ superimposed over the dominant singlet. Overall, the ¹H and ³¹P NMR data suggested an effective C_{2v} molecular symmetry on the NMR timescale as the eight-membered metallocycle rapidly flips through planarity, thus equilibrating both sides of the ring.

Use of facial tris(acetonitrile)tricarbonyl tungsten as a starting material resulted in clean metallation of the neutral P^HNP ligand. Reaction times of one hour or less resulted in formation of primarily facial $W(P^HNP)(CO)_3(2)$ while longer reaction times resulted in meridional $W(P^HNP)(CO)_3$ (3) (Scheme 2). In solution, facial isomer 2 converted to the more thermodynamically stable meridional isomer **3** over time. The isomerization could be catalyzed by addition of a trace of acid (Scheme 3). 3 could also be formed by photolysis of tetracarbonyl 1, and the reverse reaction to form 1 from 3 could be accomplished by bubbling carbon monoxide through a solution of 3. Since carbonyl stretching frequencies are exquisitely sensitive to metal-ligand bonding, coordination of the amine to tungsten resulted in an IR spectrum of 2 with lower carbonyl absorbance frequencies of 1923, 1831, and 1800 cm^{-1} relative to **1**. Isomerization to the meridionally coordinated P^HNP ligand resulted in carbonyl stretching frequencies of 1957, 1847, and 1798 cm⁻¹, with the highest frequency no doubt predominantly due to the trans carbonyls. The ³¹P NMR spectrum of **2** showed a singlet at 13.09 ppm with ${}^{1}J_{W-P} = 238$ Hz, which was comparable to the ${}^{1}J_{W-P}$ coupling constant for 1, which also had *cis*-

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phosphines. The trans-phosphines in 3 resulted in a downfield shift to 20.4 ppm and the one bond tungsten-phosphorus coupling increased significantly to 311 Hz.







Scheme 3. Interconversion of tungsten (0) complexes (1), (2), and (3).

Orange rod-like crystals of 3 were obtained by slow diffusion at -32 °C. The crystal structure of **3** showed coordination of the amine to tungsten in a distorted

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octahedral tricarbonyl complex (Figure 2). This locked the ligand in the tridentate meridional orientation, and the pyramidal amine forced puckering of the bicyclic ring system. Furthermore, the pyramidal amine group created distinctly different chemical environments on each side of the ring system, resulting in diastereotopic methyl groups on each silicon and diastereotopic methylene protons. The *trans* phosphines span an angle of 166°, as do the *trans* carbonyl ligands. The acute P-W-N bond angles averaged 83.3°. The W-P bond lengths had decreased slightly from those in the bidentate complex 1 to 2.46 and 2.47 Å. A weak *trans* influence from the coordinated amine was seen in the shortened W-C₁ bond length of 1.95 Å compared to the other W-C bonds of 2.04 Å. Another approach to examine the *trans* influence of the amine is to compare the W-O distances where O is the carbonyl oxygen since the carbon is not always reliably located and the C \equiv O distance varies only slightly, so the sum of W-C and C-O distances is a more reliable x-ray parameter than either distance alone. Here for the trans-carbonyl, the W-O₁ distance was 3.11 Å, compared with the *cis*-carbonyl W-O distances of 3.19 and 3.16 Å. This further reflected a weak *trans* influence by the nitrogen of the meridional P^HNP ligand.

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Figure 2. ORTEP diagram of meridional $W(P^HNP)(CO)_3$ (3).

Table 2.	Bond	lengths	and	bond	angles	of 3
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$\begin{array}{llllllllllllllllllllllllllllllllllll$	Bond distances (Å)		Bond angles (deg)			
P(2)-W(1)-C(1) 96.45(19)	W(1)-C(1) W(1)-C(3) W(1)-C(2) W(1)-N(1) W(1)-P(1) W(1)-P(2)	1.947(7) 2.009(6) 2.043(6) 2.443(5) 2.4606(16) 2.4731(17)	P(1)-W(1)-P(2) P(1)-W(1)-N(1) P(2)-W(1)-N(1) C(2)-W(1)-C(3) C(1)-W(1)-C(2) C(1)-W(1)-C(3) P(1)-W(1)-C(1) P(2)-W(1)-C(1)	$166.42(6) \\83.28(13) \\83.53(13) \\166.1(3) \\82.5(3) \\83.8(3) \\96.69(19) \\96.45(19)$		

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Tungsten(II) Hydride Complexes. Addition of tetrafluoroboric acid to a methylene chloride solution of **3** resulted in an immediate color change from orange to pale yellow consistent with protonation at the tungsten center to formally generate a tungsten(II) hydride complex (Scheme 4). The IR spectrum showed full conversion to **4** with absorbance frequencies of 2034, 1935, and 1914 cm⁻¹ for the cation, a shift of almost 100 cm⁻¹ to higher energy for the three carbonyl frequencies.



Scheme 4. Preparation of $[W(P^{HN}P)(CO)_3H][BF_4]$ (4).

Yellow rod-shaped crystals of **4** were obtained by slow evaporation of methylene chloride from a solution of **4** in an NMR tube at 0 °C. The crystal structure showed the tridentate $P^{H}NP$ ligand bound meridionally with three carbonyl ligands filling the remaining three sites. The carbonyl *trans* to nitrogen was pushed toward one of the phosphine ligands, presumably to accommodate the seventh ligand, a hydride not located by crystallography. The tetrafluoroborate counterion was crystallized in the cell. All three tungsten-carbon bonds were slightly lengthened relative to the neutral $W(P^{H}NP)(CO)_3$ tungsten-carbon distances (**3**). The two tungsten-phosphorus bonds were also lengthened (by ~0.05 Å from **3**), while the tungsten-nitrogen bond was shortened from 2.443 Å in **3** to 2.386 Å in **4**. The longer bond lengths around tungsten presumably reflected expansion of the six-coordinate geometry to seven-coordinate and the

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accompanying crowding from seven ligands. The P-W-P bond angle was decreased by 2° from **3** to 164.42° while one of the P-W-N bond angles stayed about the same at 83.7°. The other P(1)-W-N bond angle decreased to 81.4°, presumably due to placement of the hydride ligand near that phosphorus. The most noticeable change in the geometry of the coordination sphere is that the two P-W-C(1) angles, nearly identical at 96.5° in **3**, differ by twenty degrees in **4**. The C(1)-W-P(2) bond angle at 87.3° is much smaller than the C(1)-W-P(1) bond angle at 107.5°, surely opened to accommodate the hydride.



Figure 3. ORTEP diagram of $[W(P^HNP)(CO)_3H][BF_4]$ (4).

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Bond distances (Å)		Bond angles (deg)	Bond angles (deg)			
W(1)-C(1) W(1)-C(5) W(1)-C(7) W(1)-N(24) W(1)-P(2) W(1)-P(1)	1.965(13) 2.025(9) 2.044(9) 2.386(8) 2.505(2) 2.529(2)	P(1)-W(1)-P(2) P(1)-W(1)-N(24) P(2)-W(1)-N(24) C(5)-W(1)-C(7) C(1)-W(1)-C(5) C(1)-W(1)-C(5) N(24)-W(1)-C(1) P(1)-W(1)-C(1) P(2)-W(1)-C(1)	164.42(9) 81.4(2) 83.7(2) 176.8(4) 88.5(7) 88.3(7) 171.0(6) 107.5(6) 87.3(6)			

 Table 3 Bond lengths and bond angles of 4.

Both the crystal structure and the low temperature NMR data showed hydride complex **4** to be a C₁ symmetric molecule. The fluxional behavior of **4** was evident in variable temperature ¹H NMR spectra (Figure 4). At room temperature, the four P^HNP methyl groups appeared as singlets at 0.6 and 0.0 ppm, while the methylene protons appeared as a broad signal between 2.3 and 2.5 ppm. The hydride resonance appeared upfield at -5.03 ppm as a 76 Hz doublet with a broad central hump indicative of a dynamic process involving coupling to the *trans* phosphines. Each peak of the doublet also had tungsten satellites reflecting one bond W-H coupling of 16 Hz, a value comparable to reported one bond tungsten(II)-hydride couplings³⁶. The fluxional behavior of **4** at room temperature was further evident in the ³¹P{¹H} NMR spectrum, in which the inequivalent phosphines appeared as a broad doublet of doublets (Figure 5).

When cooled to 242K, the methylene protons resolved into four doublets of doublets in the region of 2.2 to 2.6 ppm with two-bond coupling to phosphorus of 10.5 Hz (Figure 4). The diastereotopic methylene protons had a geminal H-H coupling of 15

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Hz. The $P^{H}NP$ methyls between -0.1 and 0.6 ppm also resolved from two singlets to four singlets, indicating a distinct environment for each methyl group in the seven-coordinate tungsten coordination sphere. The hydride resonance resolved into a doublet of doublets while maintaining the same tungsten coupling of 16 Hz. The C₁ symmetry differentiated the two phosphorus atoms resulting in different geminal couplings between the hydride and the two phosphorus atoms of 53.0 Hz and 20.5 Hz. At 242K, the ³¹P{¹H} NMR resolved into two roofed doublets at 19.7 and 14.7 ppm (Figure 5). The geminal phosphorus coupling was 85.4 Hz while the one-bond tungsten-phosphorus couplings were 200.2 and 211.6 Hz. This general description of fluxionality on the NMR timescale applied to all of the cationic and neutral seven-coordinate tungsten(II) complexes reported here.

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Figure 4. Variable-temperature ¹H NMR spectra of 4, alkyl and hydride regions.

Figure 5. Variable-temperature ${}^{31}P{}^{1}H$ NMR spectrum of 4.

Addition of one equivalent of triethylamine to a methylene chloride solution of the cationic hydride complex **4** at 195 K resulted in selective kinetic deprotonation of the amine proton to form W(PNP)(CO)₃H (Scheme 5). The resulting lone pair on the

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nitrogen atom may have provided some electron density to the tungsten center, but all of the original ligands remained bound to the 18 electron tungsten in the neutral product. The carbonyl stretching frequencies dropped an average of 22 cm⁻¹ to 2008, 1923, and 1885 cm⁻¹. When warmed to room temperature, the metal hydride ¹H NMR signal disappeared as the proton was transferred to the amide nitrogen to reform the thermodynamically favored isomer of **5**, $W(P^HNP)(CO)_3$ (**3**), in a formal reduction to tungsten(0).



Scheme 5. Synthesis of W(PNP)(CO)₃H (5).

The low temperature NMR data for **5** showed a C₁ symmetric molecule much like **4**. The methylene protons shifted upfield and had a comparable geminal coupling to phosphorus of 14.5 Hz. The hydride resonance shifted slightly downfield about one half of a ppm from the hydride in **4** to -4.53 ppm in **5** as a doublet of doublets. The two geminal couplings between the hydride and phosphorus were slightly smaller than in **4**, at 51.0 Hz and 14.5 Hz. The low temperature ${}^{31}P{}^{1}H{}$ NMR showed a roofed doublet of doublets pattern as in **4**. The signals were shifter downfield to 21.7 ppm and 19.3 ppm with a larger geminal phosphorus-phosphorus coupling of 136 Hz. The one-bond tungsten-phosphorus couplings had increased as well to 213 Hz and 230 Hz in **5** from 200 Hz and 212 Hz in **4**. **Tungsten(II) Halide Complexes.** A complete series of cationic and neutral tungsten(II) halide complexes was established. All of the cationic seven-coordinate halide complexes were fluxional at room temperature on the NMR timescale and displayed C₁ symmetry when cooled. Given the differing reactivities of the halogens, different synthetic routes were required to access the full series of complexes. None of the tungsten(II) halide complexes could be isolated in the solid state or crystallized. They were thermally unstable and decomposed rapidly upon exposure to air.

To a methylene chloride solution of **3**, one equivalent of iodine was added, and the solution was stirred to dissolve the reagents (Scheme 6). The IR spectrum shows that the carbonyl frequencies shifted to 2031, 1950, and 1928 cm⁻¹ as the tungsten center was oxidized to W(II). The increase in CO stretching frequencies from **3** was comparable to that observed in forming **4** by protonation, as formal oxidation to a cationic tungsten(II) species occurred in both cases. Complex **6** decomposed over time, possibly passing through a dicarbonyl intermediate (Scheme 7). The nucleophilic iodide counterion may have participated in the decomposition reaction. By IR spectroscopy, CO stretches at 1931 and 1838 cm⁻¹ grew in as the carbonyl frequencies for **6** faded away. Perhaps the iodide counterion displaced a carbonyl ligand and formed a neutral W(P^HNP)(CO)₂(I)₂ intermediate. Further decomposition occurred rapidly, so identification of the intermediate was not possible. Addition of excess sodium tetraphenylborate to complex **6** resulted in precipitation of sodium iodide and a longer-lived tungsten(II) cationic complex [W(P^HNP)(CO)₃I][B(Ph)₄].

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Scheme 6. Preparation of $[W(P^HNP)(CO)_3I][I]$ (6).



Scheme 7. Proposed decomposition pathway of 6.

[W(P^HNP)(CO)₃Br][Br] could be synthesized by addition of bromine to **3**, analogous to the synthesis of **6**. However, elemental bromine could oxidize a phosphine ligand, and the nucleophilic bromide counterion may have promoted rapid decomposition. Surprisingly, a cleaner two-step synthetic method was available that began with a one-electron oxidation to tungsten(I) followed by addition of a bromine radical source to give the same cationic bromide complex **7**. To a methylene chloride solution of **3** cooled to 195K, excess silver triflate was added, and the solution was stirred for one hour (Scheme 8). The solution was cannula filtered, and one equivalent of Nbromosuccinimide was added to the filtrate and stirred for 30 minutes at 195K. The pink tungsten(I) intermediate, [W(P^HNP)(CO)₃][OTf], was characterized by IR spectroscopy, but this paramagnetic intermediate could not be analyzed by NMR. The carbonyl frequencies moved higher (2025, 1925, 1899 cm⁻¹) as the cationic tungsten(I) intermediate was formed, then they shifted even higher (2033, 1956, and 1928 cm⁻¹) when the bromine radical was added to form 7. The net increase in CO frequencies from 3 to 7 was comparable to those observed for the other cationic tungsten(II) complexes described above.



Scheme 8. Synthetic route to $[W(P^HNP)(CO)_3Br][OTf]$ (7).

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To form the chloride analogue, excess tris(4-bromophenyl)ammoniumyl hexachloroantimonate ($[N(PhBr)_3][SbCl_6]$) was added to a methylene chloride solution of **3** cooled to 195K and the reaction mixture was stirred for one hour. The solution was then cannula filtered. Since the tris(4-bromophenyl)ammoniumyl hexachloroantimonate is known to function as a radical one-electron oxidant^{37,38}, it would presumably initially oxidize the tungsten(0) complex **3** to a cationic tungsten(I) intermediate (Scheme 9). The hexachloroantimonate counterion could then provide a chlorine radical to convert the tungsten(I) to tungsten(II) and form **8**, similar to the reaction scheme outlined for the bromo analogue **7**.

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Scheme 9. Synthetic route to $[W(P^HNP)(CO)_3Cl][Cl]$ (8).

Addition of excess Selectfluor (1-chloromethyl-4-fluoro-1,4-

diazoniabicyclo[2.2.2]octane bis(tetrafluoroborate) to an acetonitrile solution of **3** resulted in fluorination of the tungsten center to produce **9** (Scheme 10). The reaction proceeded more slowly in methylene chloride, perhaps due to the lower solvent polarity. Selectfluor can serve as a net source of F^+ as a reagent, so in some ways this reaction is analogous to addition of a proton to **3** to form the cationic hydride complex **4**. The IR spectrum showed conversion of **3** to fluoride complex **9** over one hour with an increase in absorbance frequencies to 2024, 1939, and 1846 cm⁻¹. Although both protonation and fluorination occurred in this system, addition of methyl triflate to **3** did not lead to methylation.



Scheme 10. Synthetic route to $[WP^HNP)(CO)_3F][BF_4]$ (9).

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All four of the cationic tungsten(II) halide complexes described here (**6-9**) could be deprotonated at the pincer ligand amine nitrogen by addition of triethylamine (Scheme 11).



Scheme 11. Synthetic route to neutral W(PNP)(CO)₃X, where X = I (6a), Br(7a), Cl (8a), and F (9a).

The IR spectra were consistent throughout the series of halide and hydride tungsten complexes and provided a scheme for identifying the oxidation state and charge of the tungsten pincer complex in question (Table 4). The highest carbonyl frequencies were indicative of cationic tungsten(II) complexes, including **4**, **6**, **7**, **8**, and **9**. These cationic complexes had a weak but distinctive carbonyl stretch around 2030 cm⁻¹. When deprotonated to form the neutral tungsten(II) complex, that weak symmetric stretch shifted down about 25 cm⁻¹ to an average of 2005 cm⁻¹. The anomaly in the series was found with the fluoride complexes. While the highest frequency carbonyl stretches were comparable to the rest of the series, the two lower stretches came at much lower frequencies than those in the rest of the series.

Table 4. IR, ³¹P NMR, and ¹³C carbonyl NMR data for all complexes.

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Complex	<u>v_{CO} (cm⁻¹)</u>	<u>δ_P (ppm)</u>	¹ J _{W-P} (Hz)	² J _{P-P} (Hz)	<u>δ_{CO} (ppm)</u>
1	2016, 1922, 1885	-0.4	233		207, 204
2	1923, 1831, 1800	13.1	238		218, 215, 214
3	1957, 1847, 1798	20.4	311		220, 211, 208
4	2034, 1935, 1914	19.7, 14.7	200, 212	85	206, 204, 197
5	2008, 1923, 1885	21.7, 19.3	213, 230	136	209, 200
6	2031, 1956, 1928	14.4, -0.2	180, 136	141	231, 215
7	2033, 1956, 1928	22.8, 3.0	170, 142	160	220, 217, 206
8	2033, 1953, 1914	23.6, 4.3	152, 150	151	234, 218, 216
9	2024, 1939, 1846	37.9, 35.4	156, 160	32	222, 221
6a	2003, 1928, 1886	19.5, 17.9	189, 143	207	236, 217, 212
7a	2007, 1928, 1883	24.8, 21.3	192, 138	215	238, 219, 214
8 a	2009, 1927, 1880	27.2, 20.9	189, 141	223	239, 220, 215
9a	2008, 1915, 1807	43.1, 38.5	170, 162	34	228, 227

The phosphorus NMR data also showed a pattern for cationic versus neutral complexes (Table 4). The ³¹P signals were consistently downfield for the neutral complexes compared to the cationic complexes. Additionally, the neutral complexes all had larger geminal phosphorus-phosphorus coupling and larger one-bond tungsten-phosphorus couplings compared to their cationic analogues. An examination of the halide series revealed that as the halides became more electronegative, the chemical shift of the phosphorus atoms moved downfield while the tungsten-phosphorus couplings generally decreased. As seen in the IR data, the irregularity was with the tungsten-fluoride complexes, which had very small geminal coupling (32 Hz and 34 Hz). The ¹³C NMR data for the carbonyl carbons also showed the trend in which the neutral tungsten(II) complexes consistently had signals further downfield compared to their cationic counterparts.

In summary, we have reported the synthesis and characterization a series of PNP tungsten complexes. When coordinated to tungsten(0), the ligand could adopt three different coordination modes. Formal oxidation by protonation of the metal center occurred to form a cationic tungsten hydride species. Oxidation through different routes resulted in a series of cationic tungsten(II) halide complexes. The cationic species could all be deprotonated at the amine to form neutral tungsten(II) hydride or halide species. The structures of complexes **1**, **3**, and **4** were determined by X-ray single crystal analyses.

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Experimental

General Information. Reactions were performed under a dry nitrogen atmosphere using standard Schlenk techniques. Methylene chloride, hexanes, pentane, and diethyl ether were purified by passage through an activated alumina column under a dry argon atmosphere. Tetrahydrofuran (THF) was distilled from sodium benzophenone ketyl under argon atmosphere. Methylene chloride-d₂ was dried over CaH₂ and degassed using standard freeze-pump-thaw techniques. HN(SiMe₂CH₂PPh₂)₂ was synthesized according to a literature method³¹.

NMR spectra were recorded on Bruker DRX400, 500, or AVANCE400 spectrometers. Infrared spectra were recorded on an ASI Applied Systems ReactIR 1000 FT-IR spectrometer.

HN(SiMe₂CH₂PPh₂)₂W(CO)₄ (1). Thermal Synthesis. In a 200mL Schlenk flask, W(CO)₆ (0.50 g, 0.14 mmol) was added to chlorobenzene (40 mL). HN(SiMe₂CH₂PPh₂)₂ (0.75g , 0.14 mmol) was dissolved in a small amount of chlorobenzene (5 mL) and cannula transferred into the hexacarbonyl solution. The mixture was heated to 120 °C for 24 hours. The solvent was removed *in vacuo* and the orange-brown oil was washed several times with pentane. The product was extracted with ether, and was purified by dissolving in methylene chloride and layering with hexanes (1:10) in the freezer overnight (0.17 g, 14.5%). IR (diethyl ether): $v_{CO} = 2016$, 1922, 1885 cm⁻¹. ¹H NMR (CD₂Cl₂, δ): 7.56 (m, 8H, Ph C*H*), 7.40 (m, 12H, Ph C*H*), 1.92 (d, 4H, ²*J*_{PH} = 10.4 Hz, C*H*₂), -0.28 (s, 12H, C*H*₃). ³¹P NMR (CD₂Cl₂, δ): -0.38 (s, ¹J_{W-P} = 233.0 Hz). ¹³C{¹H} NMR (CD₂Cl₂, δ): 206.6 (t, CO, ²J_{P-C} = 10 Hz, ¹J_{W-C} = 70.4

25

Hz), δ): 203.8 (t, CO, ²J_{P-C} = 7.5 Hz, ¹J_{W-C} = 65.4 Hz), 141.2–128.4 (Ar C), 20.6 (-*C*H₂-), 2.7 (-*C*H₃).

HN(SiMe₂CH₂PPh₂)₂W(CO)₃ Facial (2). HN(SiMe₂CH₂PPh₂)₂ (1.5 g, 2.9

mmol) was combined with W(CH₃CN)₃(CO)₃ (1.1 g, 2.8 mmol) in THF (30 mL) and stirred at room temperature for 1 hour. Isolation was accomplished by precipitation of product with ether and subsequent pentane washes (740 mg, 33%). IR (THF): ν_{CO} = 1923, 1831, 1800 cm⁻¹. ¹H NMR (C₆D₆, δ): 8.02 (t, 4H, Ph C*H*), 7.23 (t, 4H, Ph C*H*), 7.11 (t, 4H, Ph C*H*), 6.94 (t, 2H, Ph C*H*), 6.66 (m, 6H, Ph C*H*), 1.83, 1.10 (each a dd, 2H, C*H*₂, ²J_{H-H} = 14.0 Hz, ²J_{P-H} = 9.2 Hz), 0.05, 0.01 (each a s, 6H, C*H*₃). ³¹P NMR (C₆D₆, δ): 13.09 (s, ¹J_{W-P} = 238.1 Hz). ¹³C{¹H} NMR (CD₂Cl₂, δ): 218.0 (t, CO, ²J_{P-C} = 5.7 Hz), 214.9, 214.7 (each a t, CO, ²J_{P-C} = 16.6Hz), 139.4, 139.0, 138.9, 138.8, 138.7, 130.4, 129.6, 129.0, 128.6, 128.5 (aryl C), 16.9 (s, -CH₂-), 3.9 (t, ¹J_{P-C} = 3.1Hz, -CH₂-), 1.8 (s, -CH₃). HRMS (m/z, ESI+, CHCl₃): found 798.1338, calcd for [M + H]⁺, 798.1375.

HN(SiMe₂CH₂PPh₂)₂W(CO)₃ Meridional (3). Synthesis from

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W(CH₃CN)₃(CO)₃. HN(SiMe₂CH₂PPh₂)₂ (7.0 g, 13.2 mmol) was combined with W(CH₃CN)₃(CO)₃ (4.9 g, 12.5 mmol) in THF (50 mL) and stirred at room temperature overnight. Isolation of **3** was accomplished by precipitation of product with ether and subsequent pentane washes (6.58 g, 65.7%). IR (THF): ν_{CO} = 1957, 1847, 1798 cm⁻¹. ¹H NMR (CD₂Cl₂, δ): 7.81 (m, 6H, Ph C*H*), 7.40 (m, 8H, Ph C*H*), 7.31 (m, 6H, Ph C*H*), 2.65, 1.61 (each a dt, 2H, ²J_{H-H} = 14.4 Hz, ²J_{P-H} = 8.8 Hz, C*H*₂), 0.36, 0.04 (each a s, 6H, C*H*₃). ³¹P NMR (CD₂Cl₂, δ): 20.40 (s, ¹J_{W-P} = 310.8 Hz). ¹³C {¹H} NMR (CD₂Cl₂, δ): 219.8 (t, CO, ²J_{P,C} = 9.3 Hz), 210.9, 208.0 (each a t, CO, ²J_{P,C} = 14.6 Hz),

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142.2, 139.7 (each a t, ipso Ar C, ${}^{1}J_{P-C} = 36.9$ Hz), 131.6, 131.4 (each a t, ortho Ar C, ${}^{2}J_{P-C} = 13.2$ Hz), 129.3, 129.3 (each a s, para Ar C), 128.5 (t, meta Ar C, ${}^{3}J_{P-C} = 9.2$ Hz), 21.4 (t, ${}^{1}J_{P-C} = 6.0$ Hz, -CH₂-), 2.7 (t, ${}^{1}J_{P-C} = 8.6$ Hz, -CH₂-), -0.3 (s, -CH₃). Analysis: Calculated for **3**: C, 49.69; H, 4.68; N, 1.76. Found: C, 49.72; H, 4.62; N, 1.71. HRMS (m/z, ESI+, MeOH): found 930.0397, calcd for [M + Cs]⁺, 930.0351.

[HN(SiMe₂CH₂PPh₂)₂W(CO)₃H][BF₄] (4). In an NMR tube, **3** (0.010 g, 0.013 mmol) was dissolved in CH₂Cl₂ (0.5 mL). Tetrafluoroboric acid (1.6 mg, 0.20 mmol) was added and immediately the orange solution faded to a pale yellow. IR and NMR indicated quantitative conversion to the seven-coordinate hydride. IR (CH₂Cl₂): ν CO = 2034, 1935, 1914 cm⁻¹. ¹H NMR (242K, CD₂Cl₂, δ): 7.89 (m, Ph C*H*), 7.62 (s, Ph C*H*), 7.54 (s, Ph C*H*), 7.34 (m, Ph C*H*), 2.58, 2.34 (each a dd, 1H, CH₂, ²J_{P-H} = 15Hz), 2.42, 2.23 (each a dd, 1H, CH₂, ²J_{H-H} = 14.5 Hz, ²J_{P-H} = 10.5 Hz), 0.61, 0.58, -0.05, -0.10 (each a s, 3H, CH₃), -5.02 (dd, 1H, W*H*, ¹J_{W-H} = 16.5 Hz, ²J_{P-H} = 53.0 Hz, ²J_{P-H} = 20.5 Hz). ³¹P {¹H} NMR (242K, CD₂Cl₂, δ): 19.7 (d, ¹J_{W-P} = 200.2 Hz, ²J_{P-P} = 85.4 Hz), δ): 14.7 (d, ¹J_{W-P} = 211.6 Hz, ²J_{P-P} = 85.4 Hz). ¹³C {¹H} NMR (230K, CD₂Cl₂, δ): 205.5, 203.9, 196.6 (each a dd, CO, ²J_{P-C} = 6.5 Hz), 137.3-124.6 (Ar *C*), 13.2, 12.7 (each a s, -CH₂-), 1.8, 1.7, 0.8, -0.7 (each a s, -CH₃). HRMS (m/z, ESI+, MeOH): found 820.1195, calcd for [M – H + Na]⁺, 820.1194.

$N(SiMe_2CH_2PPh_2)_2W(CO)_3H$ (5). [HN(SiMe_2CH_2PPh_2)_2W(CO)_3H][BF_4]

(0.013 mmol) was prepared in situ and cooled to 195K. Triethylamine (5.0 μ L, 0.036 mmol) was added and mixed. IR and NMR showed quantitative conversion to yellow product. IR (CH₂Cl₂): $v_{CO} = 2008$, 1923, 1885 cm⁻¹. ¹H NMR (185K, CD₂Cl₂,

δ): 7.51 (s, Ph C*H*), 7.37 (s, Ph C*H*), 1.94, 1.83 (each a d, 2H, C*H*₂, ²J_{P-H} = 10.5Hz), 0.006, -0.19 (each a s, 3H, C*H*₃), -4.53 (dd, 1H, W*H*, ²J_{P-H} = 51.0 Hz, ²J_{P-H} = 14.5 Hz). ³¹P {¹H} NMR (185K, CD₂Cl₂, δ): 21.7 (d, ¹J_{W-P} = 213 Hz, ²J_{P-P} = 136 Hz), δ): 19.3 (d, ¹J_{W-P} = 230 Hz, ²J_{P-P} = 136 Hz). ¹³C {¹H} NMR (185K, CD₂Cl₂, δ): 208.6, (dd, CO), 200.3 (t, CO, ¹J_{W-C} = 125Hz), 138.0, 135.6 (each a d, ipso Ar C, ¹J_{P-C} = 42Hz), 131.9 (dd, ortho Ar C, ²J_{P-C} = 10Hz, ²J_{P-C} = 16Hz), 129.6 (d, para Ar C, ⁴J_{P-C} = 13Hz), 127.9 (d, meta Ar C, ³J_{P-C} = 9Hz), 24.6, (d, ¹J_{P-C} = 14.2Hz, -CH₂-), 22.6 (d, ¹J_{P-C} = 11Hz, -CH₂-), 4.3, 4.2 (each a s, -CH₃).

[HN(SiMe₂CH₂PPh₂)₂W(CO)₃I][I] (6). In an NMR tube, **3** (30 mg, 0.038 mmol) was dissolved in CH₂Cl₂ (0.5 mL). Iodine (0.010 g, 0.038 mmol) was added and shaken to dissolve. IR and NMR showed quantitative conversion to yellow product. IR (CH₂Cl₂): $\nu_{CO} = 2031$, 1950, 1928 cm⁻¹. ¹H NMR (200K, CD₂Cl₂, δ): 7.68 (s, Ph C*H*), 7.47 (m, Ph C*H*), 2.78, 2.62, 2.58, 2.09 (each a t, 1H, C*H*₂, ²J_{H-H} = 16.5Hz), 0.76, 0.60, 0.38, 0.08 (each a s, 3H, C*H*₃). ³¹P{¹H} NMR (200K, CD₂Cl₂, δ): 14.4 (d, ¹J_{W-P} = 180 Hz, ²J_{P-P} = 140.5 Hz), δ): -0.24 (d, ¹J_{W-P} = 136Hz, ²J_{P-P} = 140.5 Hz). ¹³C{¹H} NMR (200K, CD₂Cl₂, δ): 230.8, 214.9 (CO), 133.5, 132.7, 131.9, 131.4, 129.4, 128.7, 127.9 (Ar C), 17.5, 14.7 (-CH₂-), 3.9, 3.6, 0.8, 0.12 (-CH₃). HRMS (m/z, ESI+, MeOH): found 930.0446, calcd for [M – I + Cs]⁺, 930.0351.

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N(SiMe₂CH₂PPh₂)₂W(CO)₃I (6a). [HN(SiMe₂CH₂PPh₂)₂W(CO)₃I][I] (0.038 mmol) was prepared in situ and cooled to 195K. Triethylamine (10 μ L, 0.076 mmol) was added and mixed. IR and NMR showed quantitative conversion to yellow product. IR (CH₂Cl₂): $v_{CO} = 2003$, 1928, 1886 cm⁻¹. ¹H NMR (195K, CD₂Cl₂, δ): 7.29–7.72 (Ph

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CH), 2.82, 2.56, 2.22, 1.89 (each a t, 1H,
$$CH_2$$
, ${}^{2}J_{P-H} = 12Hz$), 0.59, 0.30, 0.23, .0.01 (each a s, 3H, CH_3). ${}^{31}P\{{}^{1}H\}$ NMR (195K, CD_2Cl_2 , δ): 19.5 (d, ${}^{1}J_{W-P} = 189$ Hz, ${}^{2}J_{P-P} = 207$ Hz).
17.9 (d, ${}^{1}J_{W-P} = 143$ Hz, ${}^{2}J_{P-P} = 207$ Hz). ${}^{13}C\{{}^{1}H\}$ NMR (195K, CD_2Cl_2 , δ): 235.7 (dd, CO, ${}^{2}J_{P-C} = 25.8$ Hz, ${}^{2}J_{P-C} = 9.3$ Hz), 216.5 (dd, CO, ${}^{2}J_{P-C} = 23.4$ Hz, ${}^{2}J_{P-C} = 9.3$ Hz), 212.3 (dd, CO, ${}^{2}J_{P-C} = 15.2$ Hz, ${}^{2}J_{P-C} = 5.8$ Hz), 135.8-127.3 (aryl C), 23.7, 23.0 (each a d, -CH₂-), 7.8, 5.5, 5.4, 5.2 (each a s, -CH₃). HRMS (m/z, ESI+, MeOH): found 795.1451, calcd for [M – I – H]⁻, 795.1140.

[HN(SiMe₂CH₂PPh₂)₂W(CO)₃Br][OTf] (7). In a schlenk flask, 3 (30 mg, 0.038 mmol) was dissolved in CH₂Cl₂ (10 mL) and cooled to 195K. Excess silver triflate (0.10 g, 0.39 mmol) was added and stirred for one hour. The solution was cannula filtered into a cold Schlenk flask. N-bromosuccinimide (0.0070 g, 0.038 mmol) was added and stirred 30 minutes at 195K. IR (CH₂Cl₂): $v_{CO} = 2033$, 1956, 1928 cm⁻¹. ¹H NMR (230K, CD₂Cl₂, δ): 7.88–7.43 (Ph C*H*), 3.02, 2.74, 2.47, 2.16 (each a m, 1H, C*H*₂), 0.78, 0.59, 0.31, -0.19 (each a s, 3H, C*H*₃). ³¹P {¹H} NMR (230K, CD₂Cl₂, δ): 22.8 (d, ¹J_{W-P} = 170 Hz, ²J_{P-P} = 160 Hz), 3.0 (d, ¹J_{W-P} = 142Hz, ²J_{P-P} = 160 Hz). ¹³C {¹H} NMR (230K, CD₂Cl₂, δ): 219.5, 216.9, 205.7 (each a CO), 135.8-127.9 (aryl C), 20.5, 17.9 (each a d, - CH₂-), 6.2, 1.86, 0.5, -0.1 (each a s, -CH₃).

N(SiMe₂CH₂PPh₂)₂W(CO)₃Br (7a). [HN(SiMe₂CH₂PPh₂)₂W(CO)₃Br][OTf] (0.038 mmol) was prepared in situ and cooled to 195K. Triethylamine (10 μ L, 0.076 mmol) was added and mixed. IR and NMR showed quantitative conversion to yellow product. IR (CH₂Cl₂): ν CO = 2007, 1928, 1883 cm⁻¹. ¹H NMR (195K, CD₂Cl₂, δ): 7.68–7.26 (Ph C*H*), 2.56, 1.89, 1.20 (each a dd, C*H*₂), 0.56, 0.22, 0.20, 0.03 (each a s, 3H, CH₃). ³¹P{¹H} NMR (195K, CD₂Cl₂, δ): 24.8 (d, ¹J_{W-P} = 192 Hz, ²J_{P-P} = 215 Hz), δ): 21.3 (d, ¹J_{W-P} = 138 Hz, ²J_{P-P} = 215 Hz). ¹³C{¹H} NMR (195K, CD₂Cl₂, δ): 237.5 (dd, CO), 218.6 (dd, CO), 214.2 (dd, CO), 135.3-127.3 (aryl C), 22.6, 20.2 (each a d, -CH₂-), 8.5, 5.2, 5.1, 5.0 (each a s, -CH₃).

[HN(SiMe₂CH₂PPh₂)₂W(CO)₃Cl][Cl] (8). In a Schlenk flask, **3** (30 mg, 0.038 mmol) was dissolved in CH₂Cl₂ (10 mL). Tris(4-bromophenyl)ammoniumyl hexachloroantimonate (0.031 g, 0.038 mmol) was added and stirred for one hour. The solution was cannula filtered and the solvent was removed. IR and NMR showed quantitative conversion to yellow product. IR (CH₂Cl₂): $v_{co} = 2033$, 1953, 1914cm⁻¹. ¹H NMR (195K, CD₂Cl₂, δ): 7.67-7.38 (Ph C*H*), 2.68, 2.48, 1.84 (C*H*₂), 0.70, 0.59, 0.42, 0.22 (each a s, 3H, C*H*₃), -4.53 (dd, 1H, W*H*, ²J_{P-H} = 51.0 Hz, ¹J_{W-H} = 14.5 Hz). ³¹P{¹H} NMR (195K, CD₂Cl₂, δ): 23.6 (d, ¹J_{W-P} = 152 Hz, ²J_{P-P} = 151 Hz), 4.3 (d, ¹J_{W-P} = 150 Hz, ²J_{P-P} = 151 Hz). ¹³C{¹H} NMR (195K, CD₂Cl₂, d): 234.1, 218.4, 216.4 (each a dd, CO), 134.8-128.2 (Ar *C*), 16.6 (d, ¹J_{P-C} = 12.7 Hz, -CH₂-), 13.9 (d, ¹J_{P-C} = 10.5 Hz, -CH₂-), 3.5, 3.1 (each a d, ²J_{P-C} = 10.5 Hz, -CH₃), 0.6, 0.4 (each a s, -CH₃). HRMS (m/z, ESI+, CH₃CN): found 805.1155, calcd for [M + H - CO]²⁺, 805.1114.

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$N(SiMe_2CH_2PPh_2)_2W(CO)_3Cl(8a).$ [(HN(SiMe_2CH_2PPh_2)_2)W(CO)_3Cl][Cl]

(0.038 mmol) was prepared in situ and cooled to 195K. Triethylamine (10 μ L, 0.076 mmol) was added and mixed. IR and NMR showed quantitative conversion to yellow product. IR (CH₂Cl₂): $v_{CO} = 2009$, 1927, 1880 cm⁻¹. ¹H NMR (195K, CD₂Cl₂, δ): 7.73–7.60 (Ph C*H*), 2.47, 2.01, 1.71 (each a dd, C*H*₂), 0.49, 0.20, 0.19, 0.03 (each a s, 3H, C*H*₃). ³¹P{¹H} NMR (195K, CD₂Cl₂, δ): 27.2 (d, ¹J_{W-P} = 189 Hz, ²J_{P-P} = 223 Hz),

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20.9 (d,
$${}^{1}J_{W-P} = 141 \text{ Hz}$$
, ${}^{2}J_{P-P} = 223 \text{ Hz}$). ${}^{13}C\{{}^{1}H\}$ NMR (195K, CD₂Cl₂,
 δ): 239.1, 220.4, 215.3 (each a dd, CO), 134.2-127.3 (aryl C), 22.1 (d, ${}^{1}J_{P-C} = 15.5 \text{ Hz}$, -
 CH_{2} -), 18.3 (d, ${}^{1}J_{P-C} = 12.8 \text{ Hz}$, - CH_{2} -), 8.1, 5.1 (each a d, ${}^{3}J_{P-C} = 2.3 \text{ Hz}$, -
 CH_{3}), 5.0, 4.9 (each a s, - CH_{3}). HRMS (m/z, ESI+, CH₃CN): found 832.1003, calcd for
[M + H]⁺, 832.0985.

[HN(SiMe₂CH₂PPh₂)₂W(CO)₃F][BF₄] (9). In an NMR tube, **3** (30 mg, 0.038 mmol) was dissolved in CD₃CN (0.5 mL). 1-Chloromethyl-4-fluoro-1,4diazoniabicyclo[2.2.2]octane bis(tetrafluoroborate) (Selectfluor) (0.013 g, 0.038 mmol) was added and shaken to dissolve. IR and NMR showed conversion to yellow product. IR (NCCH₃): $\nu_{CO} = 2024$, 1939, 1846 cm⁻¹. ¹H NMR (230K, NCCD₃, ∂): 7.71-7.49 (Ph C*H*), 2.41 (d, 1H, C*H*₂), 2.18 (dd, 2H, C*H*₂), 2.02 (d, 1H, C*H*₂), 0.33, 0.32, 0.16, 0.15 (each a s, 3H, C*H*₃). ³¹P{¹H} NMR (230K, CD₂Cl₂, ∂): 37.9 (d, ¹J_{W-P} = 156 Hz, ²J_{P-P} = 32 Hz), 35.4 (d, ¹J_{W-P} = 160 Hz, ²J_{P-P} = 32 Hz). ¹³C{¹H} NMR (240K, NCCD₃, ∂): 221.9, 221.1 (each a s, CO), 133.7-129.2 (aryl *C*), 15.6 (d, ¹J_{P-C} = 74.2 Hz, -CH₂-), 11.7 (d, ¹J_{P-C} = 12.6 Hz, -CH₂-), 3.6, 2.0, -1.43, -1.58 (each a s, -CH₃). HRMS (m/z, ESI+, CH₃CN): found 797.1256, calcd for [M - F], 797.1297.

N(SiMe₂CH₂PPh₂)₂W(CO)₃F (9a). [HN(SiMe₂CH₂PPh₂)₂W(CO)₃F][OTf] (0.038 mmol) was prepared in situ and cooled to 195K. Triethylamine (10 μL, 0.076 mmol) was added and mixed. IR and NMR showed conversion to yellow product. IR (NCCH₃): $\nu_{CO} = 2008$, 1915, 1807 cm⁻¹. ¹H NMR (230K, NCCD₃, δ): 7.62-7.39 (Ph CH), 2.48 (dd, 2H, CH₂), 2.03 (dd, 2H, CH₂), 0.29, 0.11, 0.08, -0.16 (each a s, 3H, CH₃). ³¹P{¹H} NMR (215K, CD₂Cl₂, δ): 43.1 (d, ¹J_{W-P} = 170 Hz, ²J_{P-P} = 34 Hz), 38.5 (d, ¹J_{W-P} = 162 Hz, ²J_{P-P} = 34 Hz). ¹³C{¹H} NMR (215K, CD₂Cl₂, δ): 228.3, 227.3 (each a s, CO), 134.5-129.4 (aryl *C*), 16.6 (d, ${}^{1}J_{P-C} = 74.2 \text{ Hz}$, -*C*H₂-), 12.5 (d, ${}^{1}J_{P-C} = 12.6 \text{ Hz}$, -*C*H₂-),

4.3, 3.9, -0.9, -1.1 (each a s, -*C*H₃). HRMS (m/z, ESI+, CH₃CN): found 929.0010, calcd

for [M - F + Cs], 929.0273.

Table 7. Crystal and data collection parameters for $W(P^{HN}P)(CO)_4$ (1), meridional
$W(P^{H}NP)(CO)_{3}$ (3), and $[W(P^{H}NP)(CO)_{3}H][BF_{4}]$ (6).

Complex	<u>1</u>	<u>3</u>	<u>6</u>
Empirical Formula	$C_{37}H_{40}NO_4P_2Si_2W$	$C_{33}H_{36}NO_3P_2Si_2W$	$C_{34}H_{40}BCl_2F_4NO_3P_2Si_2W$
Formula Weight	864.67	796.60	970.35
Color	Yellow	Orange	Clear
Temperature	100(2) K	296(2) K	100(2) K
Wavelength	0.71073 Å	1.54178 Å	1.54178 Å
Crystal System	Monoclinic	Monoclinic	Monoclinic
Space Group	$P2_1/n$	$P2_1/n$	P 1 21/c 1
Unit Cell Dimensions	a = 8.9073(3) Å	a = 12.8236(8) Å	a = 13.1944(5) Å
	b = 24.0432(10) Å	b = 18.5277(13) Å	b = 18.9951(8) Å
	c = 17.5465(8) Å	c = 14.1186(8) Å	c = 15.4344(5) Å
	$\alpha = 90^{\circ}$	$\alpha = 90^{\circ}$	$\alpha = 90^{\circ}$
	$\beta = 94.894(3)^{\circ}$	$\beta = 97.327(5)^{\circ}$	$\beta = 90.665(2)^{\circ}$
	$\gamma = 90^{\circ}$	$\gamma = 90^{\circ}$	$\gamma = 90^{\circ}$
Volume	3744.1(3) Å ³	3327.1(4) Å ³	3868.0(3) Å ³
Ζ	4	4	4
Density (calculated)	1.534 Mg/m^3	1.590 Mg/m^3	1.666 Mg/m^3
Absorption Coefficient	3.273 mm ⁻¹	8.305 mm ⁻¹	8.654 mm ⁻¹
F(000)	1732	1588	1928
Crystal Size	$0.30 \ge 0.05 \ge 0.05 = $	$0.15 \ge 0.05 \ge 0.05 = 0.05 = 0.05$	$0.04 \ge 0.09 \ge 0.27 \text{ mm}^3$
Theta Range	2.06 to 25.71°	5.91 to 69.07°	3.35 to 67.96°
Index Ranges	-10,<=h<=10	-15<=h<=15	-14,<=h<=15
C	-23<=k<=29	-21<=k<=21	-22<=k<=21
	-21<=l<=21	-16<=l<=17	-12<=l<=18
Reflections Collected	25129	15353	31454
Data/Restraints/Parameters	7072/0/428	5881/0/384	6614/6/461
Goodness-of-fit on F ²	1.045	0.979	1.053
Final R indices	R1 = 0.0361,	R1 = 0.0501,	R1 = 0.0623,
[I>2sigma(I)]	wR2 = 0.0692	wR2 = 0.1144	wR2 = 0.1512
R Indices (all data)	R1 = 0.0634,	R1 = 0.0693,	R1 = 0.0910,
× *	wR2 = 0.0788	wR2 = 0.1245	wR2 = 0.1649
Largest diff. peak and hole	1.252 and -1.276e.Å ⁻³	2.382 and -1.630 e.Å ⁻³	2.416 and -2.251 $eÅ^{-3}$

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Oxidation of $d^6 W(P^HNP)(CO)_3$ gives a full series of cationic and neutral tungsten(II) hydridocarbonyls and halocarbonyls.

