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Electrophilic Aromatic Substitution Reactions of a Tungsten-Coordinated Phosphirenyl Triflate

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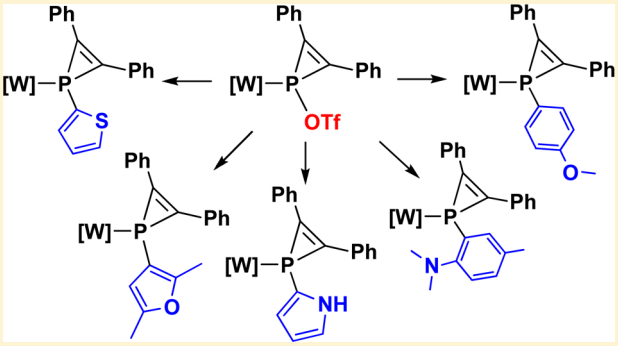
Supporting Information

ABSTRACT: The phosphirenyl cation complex $[W(CO)_5\{PC(Ph)C(Ph)\}]^+$ (**2**) is formed by chloride abstraction from the chlorophosphirene complex $[W(CO)_5\{P(Cl)C(Ph)C(Ph)\}]$ (**1**) with excess $AlCl_3$. The phosphirenyl triflate complex $[W(CO)_5\{P(OSO_2CF_3)C(Ph)C(Ph)\}]$ (**3**) is formed by reaction of the chlorophosphirene complex with $AgOSO_2CF_3$ and is in equilibrium with and typically reacts in the same fashion as the phosphirenyl cation. Reaction of **3** with diethylaniline or anisole leads to electrophilic aromatic substitution preferentially at the para position. Reaction with *N*,*N*-dimethyl-*p*-toluidine, in which the para position is blocked, leads to exclusive ortho substitution. The resulting 1,2-substituted arene can adopt a P,N bidentate coordination mode if a CO is removed from tungsten via photolysis. Compound **3** reacts with aromatic heterocycles thiophene, furan, and pyrrole, leading exclusively to substitution in the 2 position, with no evidence for P−S, P−O, or P−N bond formation. Reaction with indole led to substitution at the 3 position, also with no evidence for P−N bond formation. However, upon chromatographic purification, the substituted indole product decomposes into a disubstituted product, with W-coordinated phosphirenyl units at the 3 position and at N. Reaction with phenol and diphenyl amine led exclusively to P−O and P−N bond formation, with no evidence for aromatic substitution. Phosphine products can be removed via oxidation of W with I_2, followed by displacement with bipyridine. A computational study shows that coordination to $W(CO)_5$ greatly enhances electrophilicity at P in phosphenium ions, leading to the observed rapid electrophilic substitution reactions.



INTRODUCTION

Aromatic carbon−phosphorus bond formation is a key step in the synthesis of many organophosphorus compounds.[1] Aryl carbon−phosphorus bonds are commonly formed using nucleophilic substitution reactions, often involving organometallic reagents such as aryl lithium or Grignard reagents, and $ClPR_2$ electrophiles.[2] An alternative approach, which avoids the strongly basic conditions of the previous reactions, is a Friedel−Crafts-like electrophilic aromatic substitution using $ClPR_2$ and a Lewis acid such as $AlCl_3$.[3,4] Although these reactions were first recognized many years ago,[5] they have not gained as widespread applicability, possibly because they are relatively slow and low yielding.[1] These reactions involve in situ generation of a phosphenium ion (PR_2^+), and we were interested in the possibility of enhancing the electrophilicity of the phosphenium ions by generating them in the coordination sphere of a transition metal. Metal coordination provides several potential advantages. The metal complex can act as a protecting group for the phosphorus lone pair. Coordination to an electron poor metal complex may enhance electrophilicity as P-to-M σ donation reduces electron density at phosphorus. The metal complex can also enhance the stability of a phosphenium intermediate by providing steric protection and π-back-donation, and the metal complex may influence the steric environment and enhance regioselectivity. Depending on the nature of the metal complex, the bonding in planar metal coordinated PR_2 units can range between two extremes, four-electron phosphido, favored for electron-rich metals, or phosphenium, favored for electron-poor metals.[6] A four-electron phosphido complex has a formal P═M double bond and exhibits the reactivity expected for metal−element multiple bonds.[7] The phosphenium ion complex, on the other hand, is formally electron deficient and electrophilic at P.[8]

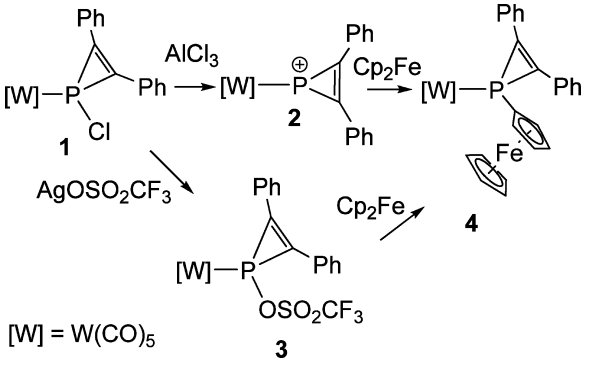
We initially chose to focus on metal complexes of the phosphirenyl cation because aromatic delocalization provides additional stability to the phosphenium ion.[9] The first metal complex of a phosphirenyl cation was a nickel complex containing an η^3-phosphirenyl cation, formed by condensation of vaporized atomic nickel with *tert*-butylphosphaalkyne.[10] An η^1-pentacarbonyltungsten complex, reported by Regitz et al., was prepared by abstraction of triflate from a phosphirenyl triflate complex using $B(OTf)_3$ in liquid SO_2 at −78 °C.[11] However, the reactivity of metal-coordinated phosphirenyl cations remained unexplored. In a recent communication,[12] we described the formation and characterization in solution of the

Received: October 29, 2013
Published: January 6, 2014

   dx.doi.org/10.1021/om401050w | *Organometallics* 2014, 33, 522−530

$W(CO)_5$-complexed phosphirenyl cation $[W(CO)_5\{PC(Ph)C(Ph)\}]^+$. We have shown that the phosphirenyl cation complex reacts as a metal-coordinated phosphenium ion. It is highly electrophilic and undergoes electrophilic substitution reactions, including an electrophilic aromatic substitution with ferrocene at ambient temperature (Scheme 1). We further showed that

Scheme 1



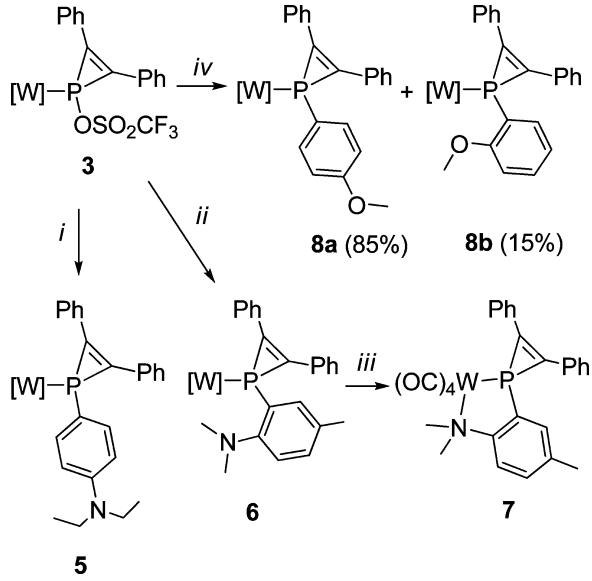
the phosphirenyl triflate $[W(CO)_5\{P(OSO_2CF_3)C(Ph)C(Ph)\}]$ acts as a surrogate for the phosphirenyl cation, showing the same electrophilic substitution reactions, but also showing much greater functional group tolerance. In this follow-up paper, we will further examine the electrophilic aromatic substitution reactions of the phosphirenyl triflate to detail the scope and functional group tolerance of this reaction and to probe its utility in P−C bond forming reactions.

RESULTS

The precursor to the phosphirenyl cation and phosphirenyl triflate complexes is the known chlorophosphirene complex $[W(CO)_5\{P(Cl)C(Ph)C(Ph)\}]$ (**1**).[13] It was formed via a simplified route.[12] Reaction of $W(CO)_5^{2-}$ with diisopropylamino-dichlorophosphine leads to a transient aminophosphinidene, which was trapped with diphenylacetylene, leading to the aminophosphirene complex. The aminophosphirene was converted to the chlorophosphirene by reaction with $HCl_{(g)}$. Compound **1** is converted to the metal-complexed phosphirenyl cation **2** via reaction with excess $AlCl_3$. Compound **2** can be observed in solution, but not isolated. The phosphirenyl triflate **3** is formed by reaction of **1** with $AgOSO_2CF_3$ and also formed in situ, but not isolated due to its extreme sensitivity.

Reaction of *N*,*N*-diethylaniline with the phosphirenyl cation **2** led to decomposition, likely as a result of the excess $AlCl_3$ needed to generate **2**. However, reaction with the phosphirenyl triflate **3** resulted in clean electrophilic aromatic substitution in the para position, leading to the 4-anilinyl phosphirene complex **5** as the sole product (Scheme 2). There was no evidence in the reaction solution for ortho-substituted product. The $^{31}P\{^1H\}$ NMR spectrum of **5** shows a peak at δ −157.9, with ^{183}W satellites and a $^1J_{WP}$ of 265 Hz. This peak falls in the typical low-field region for phosphirenes,[14] showing that the three-membered ring is maintained, while the tungsten coupling confirms that it is still metal coordinated. In the ^1H-coupled spectrum, this peak is split into a triplet by two equivalent ortho H atoms ($^3J_{PH}$ = 11.9 Hz), consistent with para substitution. The phenyl region of the ^1H NMR spectrum shows an AA′XX′ pattern as expected for a para-substituted phenyl ring, as well as peaks for N-bound ethyl groups and the phenyl groups on the phosphirene ring. The IR spectrum shows a pattern in the

Scheme 2[a]



[a]Reagents and conditions: (i) *N*,*N*-diethylaniline, 2 equiv, RT, CH_2Cl_2; (ii) *N*,*N*-dimethyl-*p*-toluidine, 2 equiv, RT, CH_2Cl_2; (iii) photolysis, THF, 2.5 h; (iv) anisole, 4 equiv, CH_2Cl_2, 45 °C, 12 h. [W] = $W(CO)_5$.

carbonyl region consistent with a $W(CO)_5$ fragment. The structure of **5** was confirmed by X-ray crystallography, and an ORTEP diagram is shown in Figure 1. The structure consists of a $W(CO)_5$ unit coordinated by the 4-aminophenyl phosphirene. All distances and angles are as expected.

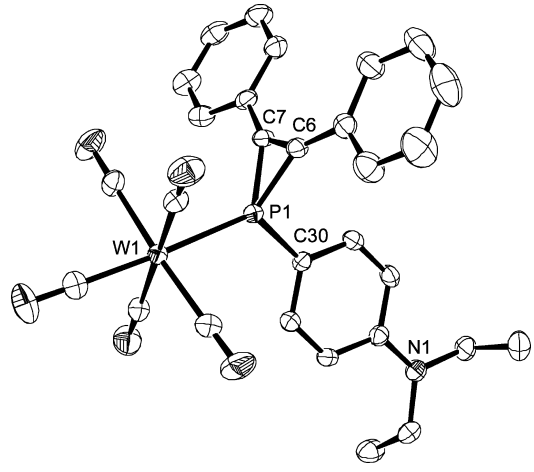


Figure 1. ORTEP diagram showing the X-ray crystal structure of **5**. Thermal ellipsoids are shown at the 50% level, and hydrogen atoms have been omitted. Selected distances and angles: W1−P1 = 2.5083(4), P1−C30 = 1.809(2), P1−C6 = 1.790(2), P1−C7 = 1.793(2), C6−C7 = 1.323(2). W1−P1−C6 = 125.63(5), W1−P1−C7 = 125.32(5), C7−P1−C6 = 43.34(8), P1−C6−C7 = 68.5(1), P1−C7−C6 = 68.2(1).

The reaction of **3** with *N*,*N*-diethylaniline led exclusively to para substitution. However, electrophilic substitution can also be easily directed to the ortho position by blocking the para position. Reaction of **3** with *N*,*N*-dimethyl-*p*-toluidine leads to the 2-anilinyl phosphirene complex **6** as the sole product (Scheme 2). The ^1H NMR spectrum of **6** shows peaks for three

dx.doi.org/10.1021/om401050w | *Organometallics* 2014, 33, 522−530

inequivalent phenyl hydrogen atoms, with couplings consistent with a 1, 2, 4 substitution. The coupled ^{31}P NMR spectrum of **6** shows a doublet of doublets at δ −155.2, with $^{3}J_{PH}$ = 13.4 Hz and $^{4}J_{PH}$ = 4.4 Hz, as expected for ortho substitution. Substitution at the position meta to N can be ruled out by the subsequent products. Other spectral features are similar to those of **5**.

The 1,2-disubstituted arene in **6** is a potential bidendate P,N ligand. Photolysis of **6** in THF resulted in a dissociation of a cis carbonyl and coordination of the amine to form the chelated complex **7** (Scheme 2). Upon chelation, the ^{31}P NMR resonance moves downfield to δ −118.2, while the IR spectrum now shows four peaks at 2015, 1893, 1889, and 1852 cm^{-1}, in a pattern consistent with *cis*-$L_2M(CO)_4$ substitution. The ^{13}C NMR spectrum shows three carbonyl environments at δ 203.7 ($^{2}J_{CP}$ = 10.0 Hz), 210.8 ($^{2}J_{CP}$ = 8.8 Hz), and 211.1 ($^{2}J_{CP}$ = 41.7 Hz), which correspond to two carbonyls cis to P and N ligands, one carbonyl trans to N, and one carbonyl trans to P, respectively, further confirming the cis bidentate coordination of the P,N ligand. Compound **7** has been structurally characterized, and an ORTEP diagram is shown in Figure 2.

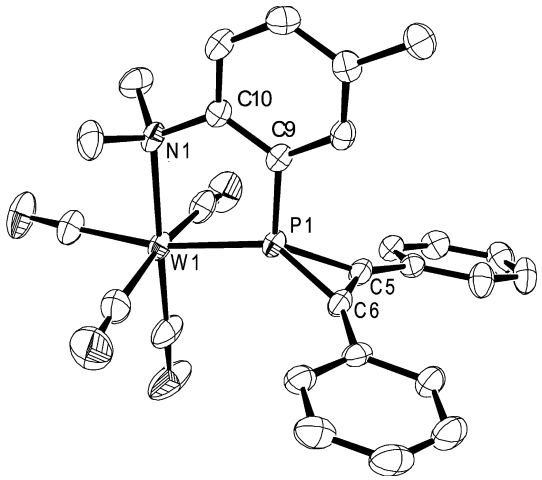


Figure 2. ORTEP diagram showing the X-ray crystal structure of **7**. One of two crystallographically inequivalent molecules is shown. Hydrogen atoms have been omitted for clarity. Thermal ellipsoids are shown at the 50% probability level. Selected distances and angles: W1−P1 = 2.4440(6), W1−N1 = 2.390(2), P1−C5 = 1.788(2), P1−C6 = 1.787(2), C5−C6 = 1.322(3), P1−C9 = 1.821(2), N1−C10 = 1.487(3), W1−P1−C9 = 105.37(8), P1−C9−C10 = 118.8(2), W1−N1−C10 = 117.0(1), N1−C10−C9 = 120.6(2), P1−C5−C6 = 68.2(1), P1−C6−C5 = 68.4(2), C5−P1−C6 = 43.4(1).

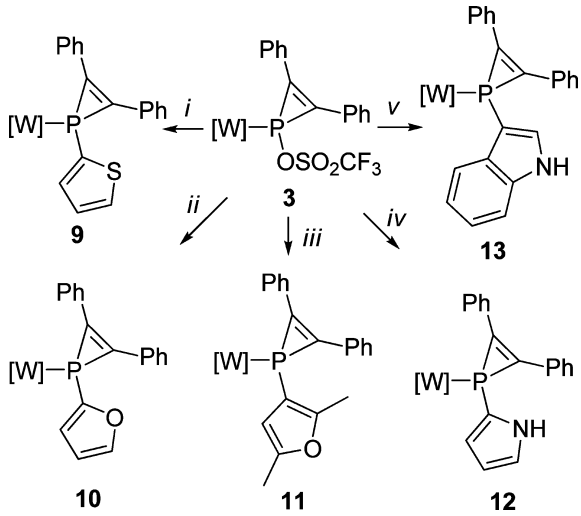
The structure consists of a $W(CO)_4$ unit with a cis bidentate P,N ligand and also confirms substitution ortho to N in the formation of **6**. All distances and angles are as expected.

Addition of anisole to **3** at room temperature resulted in no detectable reaction. However, at 45 °C, **3** reacts to form two products in an 85:15 ratio, which were shown to be products of para and ortho substitution, respectively (Scheme 2). The ^{31}P NMR spectrum of the reaction mixture shows peaks at δ −159.8 (85%) and δ −165.6 (15%). In the ^{1}H-coupled spectrum, the major signal is split into a triplet, with a $^{3}J_{PH}$ of 13.1 Hz, allowing us to assign it as the para-substituted product. The minor signal is split into a doublet of doublets, with $^{3}J_{PH}$ and $^{4}J_{PH}$ values of 11.9 and 4.7 Hz, respectively, and is assigned as the ortho-substituted product. Attempts to separate the regioisomers by flash chromatography were not successful, as both isomers have the same R_f value; therefore, only the major product **8a** was isolated in 58% yield by recrystallization from the mixture.

The reactivity of the phosphirenyl cation **2** and the phosphirenyl triflate **3** toward other aromatic compounds with nonactivating or deactivating substituents was also explored. The triflate **3** showed no reactivity toward naphthalene or chlorobenzene. Higher temperature (50 °C) led to decomposition, and no phosphorus-containing products could be isolated. Reaction with the phosphirenyl cation **2** led to decomposition even at RT. Neither **2** nor **3** reacted with toluene.

In addition to arenes, we have examined electrophilic substitution reactions with hereroaromatic substrates. Reaction of **3** with thiophene resulted in electrophilic substitution at the 2 position, leading to the 2-thienyl phosphirene complex **9**

Scheme 3[a]



[a]Reagents and conditions: CH_2Cl_2, RT, (i) thiophene, 3 equiv, (ii) furan, 3 equiv, (iii) 2,5-dimethylfuran, 2 equiv, NEt_3, 1 equiv, (iv) pyrrole, 4 equiv, (v) indole, 1 equiv. [W] = $W(CO)_5$.

(Scheme 3). The ^{31}P NMR spectrum of **9** gives a singlet with ^{183}W satellites at δ −171.7 ($^{1}J_{PW}$ = 279 Hz). In the ^{1}H-coupled spectrum, this peak is split into a doublet with a $^{3}J_{PH}$ of 7.4 Hz, consistent with substitution in the 2 position (substitution in the 3 position would lead to a doublet of doublets). The structure of **9** was also confirmed by X-ray crystallography, and an ORTEP diagram is shown in Figure 3. The structure consists of a $W(CO)_5$ unit coordinated by the 2-thienyl phosphirene ligand. All distances and angles are as expected.

Compound **3** reacts with furan in the same way as it reacts with thiophene, leading to the 2-furanyl phosphirene complex **10** (Scheme 3). The ^{31}P{^{1}H} NMR spectrum of **10** gives a singlet with ^{183}W satellites at δ −178.6 ($^{1}J_{PW}$ = 280 Hz), which, like that of **9**, splits into a doublet in the coupled spectrum, supporting substitution in the 2 position. The ^{1}H NMR shows two peaks at δ 6.40 and 6.79, which correspond to the H atoms in the 3 and 4 positions. The H atom in the 5 position is obscured by the phenyl resonances. Substitution can also be directed to the 3 position by blocking the 2 position. Reaction of **3** with 2,5-dimethylfuran led to the 3-furanyl phosphirene complex **11**. Compound **11** was characterized in solution, but decomposed upon attempted workup into the known

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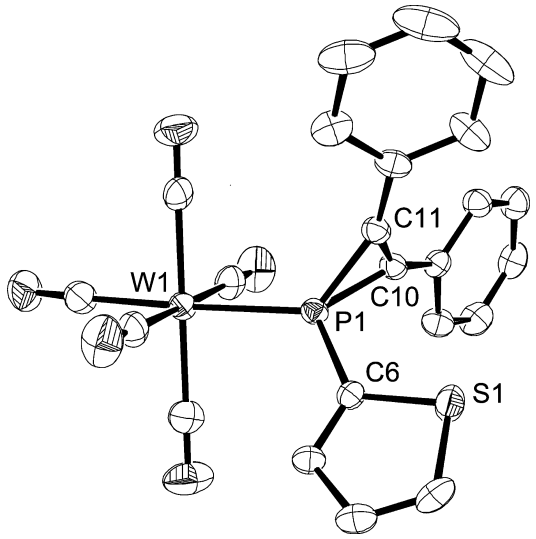


Figure 3. ORTEP diagram showing the crystal structure of **9**. One of two crystallographically inequivalent molecules is shown. Hydrogen atoms have been omitted for clarity. Thermal ellipsoids are shown at the 50% probability level. Selected distances and angles: W1−P1 = 2.4783(8), P1−C6 = 1.800(3), P1−C10 = 1.789(3), P1−C11= 1.791(3), C10−C11 = 1.327(4). W1−P1−C6 = 120.88(9), W1−P1−C10 = 126.3(1), C10−P1−C11 = 43.5(1), P1−C10−C11 = 68.3(2), P1−C11−C10 = 68.2(2).

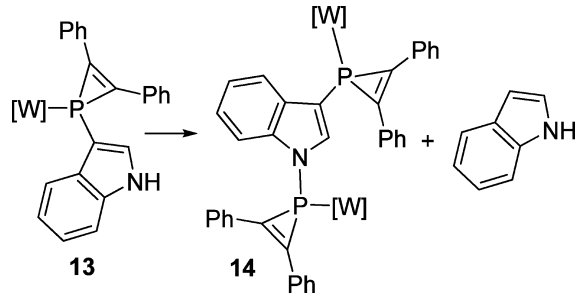
hydroxyphosphirene complex $[W(CO)_5\{P(OH)C(Ph)C(Ph)\}]$.[15] The ^{1}H NMR spectrum of **11** shows two inequivalent methyl groups at δ 2.16 and 2.25 and a peak for the H in the 4 position at δ 5.95 ($^3J_{PH}$ = 2.3 Hz), showing P substitution in the 3 position. It is not clear why **11** is significantly more sensitive to hydrolysis than the other products.

The reaction of **3** with nitrogen heterocycles containing N−H could potentially lead to electrophilic aromatic substitution or to P−N bond formation. In the reaction of **3** with pyrrole, however, the reaction mixture showed exclusively aromatic substitution at the 2 position, leading to the 2-pyrrolyl phosphirene complex **12** (Scheme 3). There was no evidence for N substitution. The ^{31}P NMR spectrum of **12** shows a peak at δ −174.6, consistent with the resonances of other C-substituted arylphosphirene compounds,[3] but distinctly different from N-substituted tungsten phosphirene complexes, which typically occur in the range δ −100 to −130.[16] Further, the ^{1}H NMR spectrum shows an NH resonance at δ 8.41, as well as three inequivalent pyrrole CH environments, confirming substitution at C rather than N.

Like pyrrole, indole reacts with **3** to give exclusively electrophilic aromatic substitution, in this case at the 3 position, leading to the 3-indolylphosphirene complex **13** (Scheme 3). The ^{31}P{^{1}H} NMR spectrum shows a singlet with W satellites at δ −172.5, very close to the shift observed for the pyrrole addition product, consistent with P−C bond formation. Substitution at the 3 position was confirmed by assignment of the ^{1}H and ^{13}C NMR spectra and the presence of H−P and C−P coupling in the expected resonances. Again, there was no evidence for a N-substituted product in the reaction solution. Unlike the other heterocycles, in indole the 3 position is activated, and this is the expected site for electrophilic substitution.

Compound **13** was purified using flash chromatography on alumina. However, earlier attempts to purify it using silica gel revealed an interesting transformation in which **13** disproportionates into indole and the disubstituted indole **14**, which has W-coordinated phosphirenyl units in both the 3 position and on N (Scheme 4). The ^{31}P NMR spectrum of **14** shows two

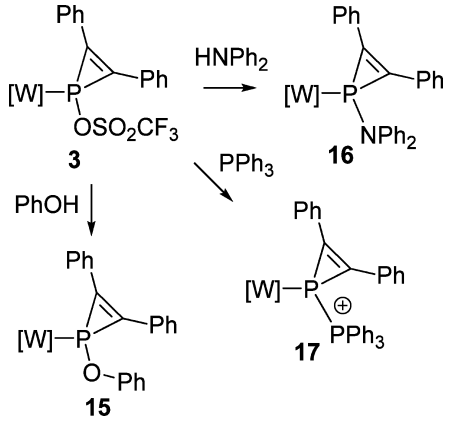
Scheme 4



peaks at δ −173.8 and −129.8. The first peak is very close to that of the precursor **13** and corresponds to the phosphirenyl unit in the 3 position. The second peak, at δ −129.8, falls in the typical range for N-substituted phosphirenyl tungsten complexes and is assigned as the N-bound phosphirenyl unit. Additional evidence for N substitution comes from the disappearance of the N−H peak from the ^{1}H NMR spectrum. The same product can also be made rationally by reaction of indole with two equivalents of **3**.

Reactions with phenol, diphenyl amine, and triphenyl phosphine demonstrate the functional group limits of the methodology. Reaction with phenol resulted in P−O bond formation, leading to the phenoxyphosphirene **15** in 87% isolated yield (Scheme 5). The resonance at δ −67.2 in the ^{31}P

Scheme 5



NMR spectrum of **15** is highly deshielded when compared with the other phosphirenes obtained in this study and is similar to the resonance (δ −72.9) of a known ethoxy phosphirene complex,[16] confirming P−O bond formation. Similarly, reaction with diphenylamine led to P−N bond formation and the aminophosphirene complex **16** (Scheme 5). As reported previously,[12] triphenylphosphine simply coordinates to the phosphirenyl phosphorus, leading to cationic adduct **17**.

The successful substitution of the phosphirenyl electrophile at an ortho position to the amino group of *N*,*N*-dimethyl-*p*-toluidine to form **6** and the subsequent chelation reaction by ligand displacement to form **7** prompted us to investigate the decomplexation of the chelating P,N ligand from **6**. Previous studies have shown that several monodentate phosphine

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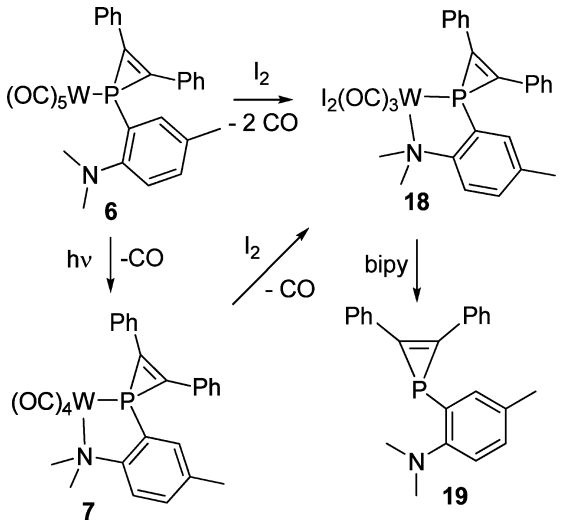
ligands, including phosphirenes, can be decomplexed by oxidation of the transition metal with iodine followed by the addition of a hard ligand.[17] This method was adopted to decomplex the chelating P,N ligand from **6**. Treatment of **6** with 1 equiv of iodine in CH_2Cl_2 resulted in oxidative addition of the I_2 to W. However, in this case oxidative addition was accompanied by loss of two carbonyls, and the observed product was the P,N-chelated 2-anilinyl phosphirene W(II) complex **18** (Scheme 6). The identity of **18** as a chelated

Scheme 6



complex was confirmed by reaction of the chelated W(0) complex **7** with iodine, which leads to the same product **18**. Addition of 1 equiv of 2,2′-bipyridine to **18** in CH_2Cl_2 then leads to the targeted free ligand **19** (Scheme 6).

Coordination of the phosphenium cation to the $W(CO)_5$ appears to significantly enhance its electrophilicity and to facilitate electrophilic aromatic substitution. In order to test this hypothesis and to understand the nature of the W–P bond, DFT computations were carried out at the B3LYP level of theory on the phosphirenyl complex **2** and on the free phosphirenyl cation. The optimized structure of **2** was already published and suggested that the phosphirenyl cation is stabilized by aromatic delocalization in the phosphirene ring, as well as by some tungsten to phosphorus π-back-donation. The interactions are apparent from the P–C and P–W bond shortening upon formation of the cation.[12] A comparison of the NBO charges for the phosphirenyl cation complex and the metal-free phosphirenyl cation shows that in both cases the positive charge is primarily localized on P (complexed: +1.234; free: +0.901). However, the P atom in the metal complex has a significantly larger positive charge (difference = +0.333). The charge increase on P is balanced by an overall negative charge of −0.223 on the $W(CO)_5$ fragment, which indicates that the increased charge on P in the complex can be primarily attributed to P-to-W σ-donation. The charge transfer that results from σ-donation to the metal will be counteracted by π-back-donation from the metal to phosphorus; however, back-donation from the $W(CO)_5$ unit is apparently not sufficient to alleviate the resulting positive charge buildup on P.

DISCUSSION

The reactions described here demonstrate that the phosphirenyl triflate complex **3** is a powerful reagent for P–C bond formation and undergoes electrophilic aromatic substitution reaction under very mild conditions without added Lewis acid. This facile reactivity strongly supports an equilibrium between **3** and **2**, as previously suggested for these compounds[12] and for other phosphine triflates.[11,18] Comparison to typical conditions for electrophilic addition by non-metal-coordinated phosphines suggests that metal coordination greatly enhances the electrophilicity, resulting in reactions that can be carried out under much milder conditions. For example, typical conditions for addition of $ClPPh_2$ to ferrocene using $AlCl_3$ are 107 °C for 24 h with 59% yield.[4] In contrast, the tungsten phosphirenyl complex **2** and the triflate complex **3** add to ferrocene instantaneously at RT. The enhanced electrophilicity upon metal coordination is supported by computational chemistry, which shows a substantial increase in the positive charge at P upon metal coordination.

Electrophilic addition reactions of the phosphirenyl triflate complex **3** require an activated aromatic system and thus far have a lower reactivity limit at anisole. Less activated substrates do not react. The phosphirenyl cation complex **2** is reactive toward a wider range of substrates, but the harsher conditions needed to form **2** typically lead to decomposition, except in the case of ferrocene. Raising the temperature to increase the reactivity of **3** also led to decomposition. The facile decomposition may be a function of the strained ring in the phosphirene product, and expansion of this methodology to other PR_2 phosphenium ion complexes, currently under way in our laboratory, will allow reactivity with a wider range of less activated substrates.

The methodology described here has good functional group tolerance. It is compatible with tertiary amines and ethers that lack N–H or O–H bonds, but not with secondary amine or alcohols. In contrast, aromatic heterocycles that contain N–H bonds are compatible, and additions to pyrrole and indole are selective for the C–H bonds. Here, the lower basicity that results from aromaticity prevents the N to P coordination that is the likely first step in P–N bond formation. In the case of indole, P–N bond formation does occur, but as the second reaction after electrophilic substitution in the 3 position. The regioselectivity of these reactions is also excellent. For all room-temperature reactions, single regioisomers are observed. However, at the higher temperature required in the anisole reaction, regioselectivity drops, and 15% of the minor ortho isomer is observed.

In conclusion, we have shown that the phosphirenyl cation complex and its surrogate, the phosphirenyl triflate complex, are versatile reagents for phosphorus–carbon bond formation via electrophilic aromatic substitution. We have also demonstrated the potential applicability of this chemistry by using it to synthesize a novel bidentate P,N ligand.

EXPERIMENTAL SECTION

General Comments. All procedures except flash chromatography were carried out using standard Schlenk techniques or in a glovebox under a nitrogen atmosphere. Diethyl ether, pentane, and THF were distilled from Na/benzophenone. Dichloromethane was purified using solvent purification columns containing alumina, followed by vacuum distillation from P_2O_5. $CDCl_3$ was vacuum distilled from P_2O_5. Solvents for flash chromatography were not purified. Photolysis reactions were carried out in Pyrex vessels using a Rayonet

dx.doi.org/10.1021/om401050w | Organometallics 2014, 33, 522–530

photochemical reactor equipped with nine lamps having a maximum output at 260 nm. The NMR spectra were recorded on a Varian Mercury 300 spectrometer at 300.177 MHz (^{1}H), 121.514 MHz (^{31}P), or 75.479 MHz (^{13}C{^{1}H}) in $CDCl_3$. IR spectra were recorded in CH_2Cl_2. Elemental analyses were not obtained for compounds **11**, **18**, and **19** due to low stability in the solid state. Their spectra are given in the Supporting Information. The compound [W(CO)$_5${P(Cl)C(Ph)-C(Ph)}] (**1**) was prepared according to the published procedure.[12]

*a. Generation of [W(CO)$_5${P(OSO$_2$CF$_3$)C(Ph)C(Ph)}] (**3**) in Solution.* The compound [W(CO)$_5${P(Cl)C(Ph)C(Ph)}] (**1**, 30.0 mg, 0.053 mmol) and $AgOSO_2CF_3$ (13.6 mg, 0.053 mmol) were dissolved in CH_2Cl_2 (4 mL). The solution was stirred for 15 min, resulting in a colorless solution and a white precipitate. The solution was filtered through Celite. Yield is quantitative by NMR spectroscopy. The dichloromethane solution was stable for days at −20 °C or hours at room temperature, but decomposed rapidly upon crystallization. This reaction was also carried out in $CDCl_3$ for NMR spectroscopy. IR (νCO, CH_2Cl_2, cm^{-1}): 2078(w), 1946(vs). ^{31}P{^{1}H} NMR ($CDCl_3$): δ −52.7 (s, $^1J_{PW}$ = 350.1 Hz). ^{19}F NMR ($CDCl_3$): δ −76.7 (s, OSO_2CF_3). ^{1}H NMR ($CDCl_3$): δ 7.62−8.03 (m, Ph). ^{13}C NMR ($CDCl_3$): δ 118.5 (q, $^1J_{CF}$ = 319.0 Hz, OSO_2CF_3), 125.8 (d, $^2J_{CP}$ = 3.5 Hz, *ipso*-Ph), 129.9 (s, Ph), 130.6 (s, Ph), 130.7 (s, Ph), 130.7 (s, Ph), 132.8 (s, Ph), 147.0 (d, $^1J_{CP}$ = 20.2 Hz, phosphirene ring C), 193.4 (d, $^2J_{CP}$ = 9.2 Hz, *cis*-CO), 196.3 (d, $^2J_{CP}$ = 51.2 Hz, *trans*-CO).

*b. Synthesis of [W(CO)$_5${P(p-C$_6$H$_4$N(CH$_2$CH$_3$)$_2$)C(Ph)C(Ph)}] (**5**).* A solution of [W(CO)$_5${P(OSO$_2$CF$_3$)C(Ph)C(Ph)}] (**3**) was prepared from [W(CO)$_5${P(Cl)C(Ph)C(Ph)}] (**1**, 70.0 mg, 0.123 mmol) and $AgOSO_2CF_3$ (31.6 mg, 0.123 mmol) in CH_2Cl_2 (6 mL) as described above. *N*,*N*-Diethylaniline (39 μL, 0.246 mmol) was then added, resulting in a color change to yellow. The solvent was removed under reduced pressure, and the residue was purified by flash chromatography (alumina, 25/75 v/v diethyl ether/petroleum ether). The yellow product was crystallized by cooling a saturated diethyl ether/pentane solution to −20 °C. Yield: 65 mg, 78%. IR (νCO, CH_2Cl_2, cm^{-1}): 2070(w), 1937(vs). ^{31}P NMR ($CDCl_3$): δ −157.9 (t, $^1J_{PW}$ = 265 Hz, $^3J_{PH}$ = 11.9 Hz). ^{1}H NMR ($CDCl_3$): δ 1.02 (t, 6H, $^3J_{HH}$ = 6.9 Hz, NCH_2CH_3), 3.22 (q, 4H, $^3J_{HH}$ = 6.9 Hz, NCH_2CH_3), 6.49 and 7.22 (AA′XX′, $^3J_{AX}$ = 9.0 Hz, $^3J_{XP}$ = 12.6 Hz, arene CH), 7.33−7.80 (m, 10H, Ph). ^{13}C NMR ($CDCl_3$): δ 12.67 (s, NCH_2CH_3), 44.56 (s, NCH_2CH_3), 111.20 (d, $^2J_{CP}$ = 11.5 Hz, arene C), 120.26 (d, $^1J_{CP}$ = 14.4 Hz, arene C), 128.01 (d, $^3J_{CP}$ = 6.9 Hz, arene C), 129.21 (d, $^2J_{CP}$ = 8.6 Hz, *ipso*-Ph), 129.41 (s, Ph), 130.48 (s, Ph), 130.49 (s, Ph), 130.57 (s, Ph), 133.29 (d, $^1J_{CP}$ = 17.3 Hz, phosphirene ring C), 149.56 (d, $^4J_{CP}$ = 1.7 Hz, *ipso*-C$_6$H$_4$N(CH$_2$CH$_3$)$_2$), 196.57 (d, $^2J_{CP}$ = 8.6 Hz, $^1J_{CW}$ = 125.5 Hz, *cis*-CO), 198.59 (d, $^2J_{CP}$ = 29.4 Hz, *trans*-CO). Anal. Calcd for $C_{29}H_{24}NO_5PW$: C, 51.12; H, 3.55; N, 2.06. Found: C, 51.27; H, 3.68; N, 2.13.

*c. Synthesis of [W(CO)$_5${P{C$_6$H$_3$(2-N(CH$_3$)$_2$)(5-CH$_3$)}C(Ph)C(Ph)}] (**6**).* A solution of [W(CO)$_5${P(OSO$_2$CF$_3$)C(Ph)C(Ph)}] (**3**) was prepared from [W(CO)$_5${P(Cl)C(Ph)C(Ph)}] (**1**, 90.0 mg, 0.158 mmol) and $AgOSO_2CF_3$ (40.7 mg, 0.158 mmol) in CH_2Cl_2 (6 mL) as described above. *N*,*N*-Dimethyl *p*-toluidene (46 μL, 0.318 mmol) was added, resulting in a color change to yellow. The solvent was removed under reduced pressure, and the residue was purified by flash chromatography (alumina, 30/70 v/v diethyl ether/petroleum ether) and crystallized as yellow crystals by cooling a saturated pentane solution to −20 °C. Yield: 86 mg, 82%. IR (νCO, CH_2Cl_2, cm^{-1}): 2070(w), 1937(vs). ^{31}P NMR ($CDCl_3$): δ −155.2 (dd, $^1J_{PW}$ = 270 Hz, $^3J_{PH}$ = 13.4 Hz, $^4J_{PH}$ = 4.4 Hz). ^{1}H NMR ($CDCl_3$): δ 2.25 (s, 3H, $C_6H_3CH_3$), 2.64 (s, 6H, $N(CH_3)_2$), 7.06 (dd, 1H, $^3J_{HH}$ = 8.3 Hz, $^4J_{HP}$ = 5.0 Hz, arene C*H*), 7.13 (dd, 1H, $^3J_{HH}$ = 8.3 Hz, $^4J_{HH}$ = 1.8 Hz, arene C*H*), 7.35 (dd, 1H, $^3J_{HP}$ = 13.4 Hz, $^4J_{HH}$ = 1.8 Hz, arene C*H*), 7.46−8.00 (m, 10H, phosphirene Ph). ^{13}C NMR ($CDCl_3$): δ 21.24 (s, $C_6H_3CH_3$), 46.82 (s, $N(CH_3)_2$), 120.90 (d, $^3J_{CP}$ = 5.0 Hz, arene C), 128.80 (d, $^2J_{CP}$ = 7.2 Hz, *ipso*-Ph), 129.34 (s, Ph), 129.75 (s, Ph), 129.81 (s, Ph), 130.43 (s, Ph), 131.98 (d, $^3J_{CP}$ = 9.4 Hz, arene C), 132.51 (d, $^4J_{CP}$ = 1.7 Hz, arene C), 133.29 (d, $^2J_{CP}$ = 9.4 Hz, arene C), 134.16 (d, $^3J_{CP}$ = 8.8 Hz, arene C), 137.06 (d, $^1J_{CP}$ = 10.0 Hz, phosphirene ring C), 154.14 (d, $^2J_{CP}$ = 8.8 Hz, arene C), 196.98 (d, $^2J_{CP}$ = 8.8 Hz, $^1J_{CW}$ = 126.1 Hz, *cis*-CO), 199.13 (d, $^2J_{CP}$ = 30.9 Hz, *trans*-CO). Anal. Calcd for $C_{28}H_{22}NO_5PW$: C, 50.40; H, 3.32; N, 2.10. Found: C, 50.49, H, 3.34; N, 2.18.

*d. Synthesis of [W(CO)$_4${P{C$_6$H$_3$(2-N(CH$_3$)$_2$)(5-CH$_3$)}C(Ph)C(Ph)-κ^2P,N}] (**7**).* Compound **6** (40.0 mg, 0.060 mmol) was dissolved in 3 mL of THF and irradiated with UV for 2.5 h. The solvent was then removed under reduced pressure, and the residue was extracted into CH_2Cl_2 (0.5 mL) and crystallized as yellow crystals by slow diffusion of pentane into a saturated CH_2Cl_2 solution. Yield: 37 mg, 96%. IR (νCO, CH_2Cl_2, cm^{-1}): 2015(w), 1893(s), 1889(s), 1852(s). ^{31}P NMR ($CDCl_3$): δ −118.2 (dd, $^1J_{PW}$ = 296 Hz, $^3J_{PH}$ = 9.6 Hz, $^4J_{PH}$ = 3.6 Hz). ^{1}H NMR ($CDCl_3$): δ 2.19 (s, 3H, $C_6H_3CH_3$), 3.62 (s, 6H, $N(CH_3)_2$), 6.75 (m, 1H, arene CH), 7.21 (m, 1H, arene CH), 7.47−7.96 (m, 11H, 10H of Ph and 1H of arene). ^{13}C NMR ($CDCl_3$): δ 20.78 (s, $C_6H_3CH_3$), 62.37 (s, $N(CH_3)_2$), 119.28 (d, $^2J_{CP}$ = 8.2 Hz, arene C), 124.87 (d, $^1J_{CP}$ = 11.7 Hz, arene C), 127.49 (d, $^3J_{CP}$ = 5.9 Hz, arene C), 129.05 (s, *ipso*-Ph), 129.52 (s, Ph), 130.80 (s, Ph), 130.86 (s, Ph), 132.57 (d, arene C), 137.45 (d, $^4J_{CP}$ = 1.1 Hz, arene C), 137.54 (d, $^2J_{CP}$ = 5.2 Hz, arene C), 159.79 (d, $^1J_{CP}$ = 23.5 Hz, phosphirene ring C), 203.74 (d, $^2J_{CP}$ = 10.0 Hz, *cis* CO), 210.79 (d, $^2J_{CP}$ = 8.8 Hz, CO *trans* to N), 211.05 (d, $^2J_{CP}$ = 41.7 Hz, CO *trans* to P). Anal. Calcd for $C_{27}H_{22}NO_4PW$: C, 50.73; H, 3.47; N, 2.19. Found: C, 50.41; H, 3.48; N, 2.27.

*e. Synthesis of [W(CO)$_5${P(p-C$_6$H$_4$OCH$_3$)C(Ph)C(Ph)}] (**8a**).* A solution of [W(CO)$_5${P(OSO$_2$CF$_3$)C(Ph)C(Ph)}] (**3**) prepared from [W(CO)$_5${P(Cl)C(Ph)C(Ph)}] (**1**, 50.0 mg, 0.088 mmol) and $AgOSO_2CF_3$ (22.6 mg, 0.088 mmol) in CH_2Cl_2 (2 mL) as described above was transferred to a Teflon-capped NMR tube. Anisole (38 μL, 0.352 mmol) was added, and the tube was sealed. The solution was then heated at 45 °C for 12 h, resulting in a color change to yellow. The solvent was removed under reduced pressure. The residue was purified by flash chromatography (alumina, 10/90 v/v diethyl ether/pet. ether), and the yellow fraction collected was shown to contain a mixture of para (85%, **8a**) and ortho (15%, **8b**) substituted product. Cooling a saturated pentane solution of the mixture to −20 °C led to yellow crystals of the major product **8a**. Yield: 33 mg, 58%. IR (νCO, CH_2Cl_2, cm^{-1}): 2074(w), 1941(vs). ^{31}P NMR ($CDCl_3$): δ −159.8 (t, $^1J_{PW}$ = 268 Hz, $^3J_{PH}$ = 13.0 Hz). ^{1}H NMR ($CDCl_3$): δ 3.78 (s, 3H, OCH_3), 6.88 (m, 2H, arene CH), 7.41−7.91 (m, 12H, 10H of Ph and 2H of arene). ^{13}C NMR ($CDCl_3$): δ 55.57 (s, $-OCH_3$), 114.39 (d, J_{CP} = 11.4 Hz, arene C), 127.56 (d, J_{CP} = 6.7 Hz, arene C), 128.40 (d, $^1J_{CP}$ = 9.9 Hz, arene C), 128.81 (d, $^2J_{CP}$ = 8.8 Hz, *ipso*-Ph), 129.55 (s, Ph), 130.53 (s, Ph), 130.61 (s, Ph), 130.79 (s, Ph), 133.21 (d, $^1J_{CP}$ = 17.1 Hz, phosphirene ring C), 161.93 (d, $^4J_{CP}$ = 2.1 Hz, arene C), 196.28 (d, $^2J_{CP}$ = 8.8 Hz, $^1J_{CW}$ = 125.6 Hz, *cis*-CO), 198.14 (d, $^2J_{CP}$ = 30.6 Hz, *trans*-CO). Anal. Calcd for $C_{26}H_{17}O_6PW$: C, 48.78; H, 2.68. Found: C, 49.03; H, 2.74.

*f. Synthesis of [W(CO)$_5${P(2-C$_4$H$_3$S)C(Ph)C(Ph)}] (**9**).* A solution of [W(CO)$_5${P(OSO$_2$CF$_3$)C(Ph)C(Ph)}] (**3**) was prepared from [W(CO)$_5${P(Cl)C(Ph)C(Ph)}] (**1**, 50.0 mg, 0.088 mmol) and $AgOSO_2CF_3$ (22.6 mg, 0.088 mmol) in CH_2Cl_2 (5 mL) as described above. Thiophene (21 μL, 0.264 mmol) was added, resulting in a color change to yellow. The solvent was removed under reduced pressure, and the residue was purified by flash chromatography (silica, 20/80 v/v diethyl ether/petroleum ether). The yellow product was crystallized by cooling a saturated CH_2Cl_2/pentane solution to −20 °C. Yield: 38 mg, 70%. IR (νCO, CH_2Cl_2, cm^{-1}): 2075(w), 1945(vs). ^{31}P NMR ($CDCl_3$): δ −171.7 (d, $^3J_{PH}$ = 7.4 Hz, $^1J_{PW}$ = 279 Hz). ^{1}H NMR ($CDCl_3$): δ 7.03 (m, 1H, C_4H_3S), 7.32 (m, 1H, C_4H_3S), 7.40−7.84 (m, 11H, 10H of Ph and 1H of C_4H_3S). ^{13}C NMR ($CDCl_3$): δ 126.98 (d, J_{CP} = 6.0 Hz, C_4H_3S), 128.77 (d, J_{CP} = 10.5 Hz, C_4H_3S), 129.45 (d, *ipso*-Ph), 129.56 (s, Ph), 130.52 (s, Ph), 130.60 (s, Ph), 130.96 (s, Ph), 132.24 (d, J_{CP} = 1.7 Hz, C_4H_3S), 135.86 (d, J_{CP} = 15.5 Hz, phosphirene ring C), 142.52 (d, J_{CP} = 4.4 Hz, C_4H_3S), 195.90 (d, $^2J_{CP}$ = 8.8 Hz, *cis*-CO), 197.71 (d, $^2J_{CP}$ = 32.6 Hz, *trans*-CO). Anal. Calcd for $C_{23}H_{13}O_5PSW$: C, 44.83; H, 2.13. Found: C, 45.42; H, 2.84.

*g. Synthesis of [W(CO)$_5${P(2-C$_4$H$_3$O)C(Ph)C(Ph)}] (**10**).* A solution of [W(CO)$_5${P(OSO$_2$CF$_3$)C(Ph)C(Ph)}] (**3**) was prepared from [W(CO)$_5${P(Cl)C(Ph)C(Ph)}] (**1**, 50.0 mg, 0.088 mmol) and $AgOSO_2CF_3$ (22.6 mg, 0.088 mmol) in CH_2Cl_2 (5 mL) as described above. Furan (20 μL, 0.275 mmol) was then added, resulting in an

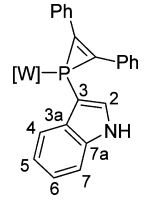
dx.doi.org/10.1021/om401050w | *Organometallics* 2014, 33, 522−530

immediate color change to yellow. The solvent was removed under reduced pressure, and the residue was purified by flash chromatography (silica, 20/80 v/v diethyl ether/petroleum ether). Yield: 33 mg, 63%. IR (νCO, CH_2Cl_2, cm^{-1}): 2076(w), 1944(vs). ^{31}P NMR ($CDCl_3$): δ −178.6 (s, $^1J_{PW}$ = 280 Hz). ^1H NMR ($CDCl_3$): δ 6.40 (m, 1H, PC_4H_3O), 6.79 (m, 1H, C_4H_3O), 7.50−7.91 (m, 11H, 10H of Ph and 1H of C_4H_3O). ^{13}C NMR ($CDCl_3$): δ 111.56 (d, J_{CP} = 6.5 Hz, C_4H_3O), 120.23 (d, J_{CP} = 17.8 Hz, C_4H_3O), 126.80 (d, J = 7.4 Hz, phosphirene ring C), 127.26 (d, $^2J_{CP}$ = 6.4 Hz, *ipso*-Ph), 129.52 (s, Ph), 130.53 (s, Ph), 130.61 (s, Ph), 130.90 (s, Ph),147.50 (d, $^1J_{CP}$ = 3.5 Hz, C_4H_3O), 152.83 (d, J_{CP} = 10.8 Hz, C_4H_3O), 195.73 (d, $^2J_{CP}$ = 8.9 Hz, *cis*-CO), 197.70 (d, $^2J_{CP}$ = 33.2 Hz, *trans*-CO). Anal. Calcd for $C_{23}H_{13}O_6PW$: C, 46.03; H, 2.18. Found: C, 46.27; H, 2.63.

*h. Synthesis of [W(CO)$_5${P{3-C$_4$H(2,5-CH$_3$)$_2$O}C(Ph)C(Ph)}] (**11**).* A solution of $[W(CO)_5\{P(OSO_2CF_3)C(Ph)C(Ph)\}]$ (**3**) was prepared from $[W(CO)_5\{P(Cl)C(Ph)C(Ph)\}]$ (**1**, 60.0 mg, 0.106 mmol) and $AgOSO_2CF_3$ (27.1 mg, 0.106 mmol) in CH_2Cl_2 (4 mL) as described above. 2,5-Dimethylfuran (23 μL, 0.213 mmol) was then added, and the solution was stirred for 15 min, resulting in a color change to red. Triethylamine (15 μL, 0.108 mmol) was then added, resulting in a color change to yellow. The solvent was removed under reduced pressure, and the residue was extracted into pentane (5 mL × 2). The extracts were combined and filtered, and the solvent was removed under reduced pressure. Yield: 25 mg, 74%. Attempts to purify **11** by chromatography or recrystallization led to its transformation into the known hydroxyphosphirene complex $[W(CO)_5\{P(OH)C(Ph)C(Ph)\}]$.[15] As a result, satisfactory elemental analysis could not be obtained. IR (νCO, CH_2Cl_2, cm^{-1}): 2073(w), 1940(vs). ^{31}P NMR ($CDCl_3$): δ −181.6 (d, $^1J_{PW}$ = 273 Hz, $^3J_{PH}$ = 2.3 Hz). ^1H NMR ($CDCl_3$): δ 2.16 (s, 3H, CH_3), 2.25 (s, 3H, CH_3), 5.95 (d, 1H, $^3J_{HP}$ = 1.8 Hz, $PC_4HO(CH_3)_2$), 7.48−7.93 (m, 10H, Ph). ^{13}C NMR ($CDCl_3$): δ 13.41 (s, CH_3), 13.97 (s, CH_3), 109.31 (d, $^2J_{CP}$ = 15.9 Hz, $C_4HO(CH_3)_2$), 117.31 (d, $^1J_{CP}$ = 14.3 Hz, $C_4HO(CH_3)_2$), 128.11 (d,^{2} J_{CP} = 6.9 Hz, *ipso*-Ph), 129.58 (s, Ph), 130.19 (d, $^1J_{CP}$ = 8.9 Hz, phosphirene ring C), 130.32 (s, Ph), 130.40 (s, Ph), 130.78 (s, Ph), 150.11 (d, $^3J_{CP}$ = 11.9 Hz, $C_4HO(CH_3)_2$), 153.94 (d, $^2J_{CP}$ = 13.4 Hz, $C_4HO(CH_3)_2$), 196.42 (d, $^2J_{CP}$ = 8.5 Hz, *cis*-CO), 198.34 (d, $^2J_{CP}$ = 30.7 Hz, *trans*-CO).

*i. Synthesis of [W(CO)$_5${P(2-C$_4$H$_3$NH)C(Ph)C(Ph)}] (**12**).* A solution of $[W(CO)_5\{P(OSO_2CF_3)C(Ph)C(Ph)\}]$ (**3**) was prepared from $[W(CO)_5\{P(Cl)C(Ph)C(Ph)\}]$ (**1**, 70.0 mg, 0.123 mmol) and $AgOSO_2CF_3$ (31.6 mg, 0.123 mmol) in CH_2Cl_2 (5 mL) as described above. Pyrrole (34 μL, 0.492 mmol) was then added, resulting in a color change to brown. The solvent was removed under reduced pressure, and the residue was purified by flash chromatography (silica, 50/50 v/v diethyl ether/petroleum ether). The yellow product was crystallized by cooling a saturated pentane solution to −20 °C. Yield: 52 mg, 81%. IR (νCO, CH_2Cl_2, cm^{-1}): 2072(w), 1939(vs). ^{31}P NMR ($CDCl_3$): δ −174.6 (s, $^1J_{PW}$ = 270 Hz). ^1H NMR ($CDCl_3$): δ 6.07 (m, 1H, C_4H_3NH), 6.75 (m, 1H, C_4H_3NH), 7.08 (m, 1H, C_4H_3NH), 7.44−7.91 (m, 10H, Ph), 8.41 (br s, 1H, N*H*). ^{13}C NMR ($CDCl_3$): δ 111.43 (d, $^3J_{CP}$ = 7.8 Hz, C_4H_3NH), 119.70 (d, $^2J_{CP}$ = 12.8 Hz, C_4H_3NH), 120.25 (d, $^1J_{CP}$ = 21.4 Hz, C_4H_3NH), 125.98 (d, $^1J_{CP}$ = 30.0 Hz, phosphirene ring C), 128.02 (d, $^4J_{CP}$ = 6.2 Hz, C_4H_3NH), 129.18 (d, $^2J_{CP}$ = 7.3 Hz, *ipso*-Ph), 129.41 (s, Ph), 130.41 (s, Ph), 130.46 (s, Ph), 130.48 (s, Ph), 196.58 (d, $^2J_{CP}$ = 9.0 Hz, $^1J_{CW}$ = 125.5 Hz, *cis*-CO), 198.54 (d, $^2J_{CP}$ = 30.0 Hz, *trans*-CO). Anal. Calcd for $C_{23}H_{14}NO_5PW$: C, 46.10; H, 2.36; N, 2.34. Found: C, 46.13; H, 2.32; N, 2.33.

*j. Synthesis of [W(CO)$_5${P(3-C$_8$H$_5$NH)C(Ph)C(Ph)}] (**13**).* A solution of $[W(CO)_5\{P(OSO_2CF_3)C(Ph)C(Ph)\}]$ (**3**) was prepared from $[W(CO)_5\{P(Cl)C(Ph)C(Ph)\}]$ (**1**, 70.0 mg, 0.123 mmol) and $AgOSO_2CF_3$ (31.6 mg, 0.123 mmol) in CH_2Cl_2 (5 mL) as described above and added dropwise to a solution of indole (14.4 mg, 0.123 mmol) in CH_2Cl_2 (2 mL), resulting in a color change to yellow. The solvent was removed under reduced pressure, and the residue was purified by flash chromatography (alumina, 50/45/5 v/v/v diethyl ether/petroleum ether/methanol). The yellow product was crystallized by cooling a saturated CH_2Cl_2/pentane solution to −20 °C. Yield: 58 mg, 73%. IR (νCO, CH_2Cl_2, cm^{-1}): 2072(w), 1938(vs). ^{31}P NMR ($CDCl_3$): δ −172.5 (d, $^1J_{PW}$ = 271 Hz, $^3J_{PH}$ = 4.4 Hz). ^1H NMR ($CDCl_3$): δ 6.90 (m, 1H, C_8H_5NH), 7.13 (m, 1H, C_8H_5NH), 7.35 (m, 2H, C_8H_5NH), 7.45−7.58 (m, 6H, Ph), 7.72 (m, 1H, C_8H_5NH), 7.91 − 7.96 (m, 4H, Ph), 8.46 (br s, 1H, C_8H_5NH). ^{13}C NMR ($CDCl_3$): δ 111.52 (d, $^1J_{CP}$ = 17.0 Hz, C^3), 111.86 (s, C^7), 120.66 (d, J_{CP} = 1.7 Hz, C^4), 121.48 (s, C^6), 123.24 (s, C^5), 127.89 (s, C^{3a}), 128.81 (d, $^2J_{CP}$ = 6.2 Hz, *ipso*-Ph), 129.51 (s, Ph), 130.33 (s, Ph), 130.41 (s, Ph), 130.53 (s, C^2), 130.64 (s, Ph), 135.65 (d, $^1J_{CP}$ = 39.0 Hz, phosphirene ring C), 137.29 (d, J_{CP} = 6.2 Hz, C^{7a}), 196.70 (d, $^2J_{CP}$ = 9.1 Hz, $^1J_{CW}$ = 125.4 Hz, *cis*-CO), 198.45 (d, $^2J_{CP}$ = 30.0 Hz, *trans*-CO). Anal. Calcd for $C_{27}H_{16}NO_5PW$: C, 49.95; H, 2.48; N, 2.16. Found: C, 49.45; H, 2.55; N, 2.21.



*k. Synthesis of [{W(CO)$_5$}$_2$-μ-{C$_8$H$_5$N-1,3-{PC(Ph)C(Ph)}$_2$}] (**14**).* A solution of $[W(CO)_5\{P(OSO_2CF_3)C(Ph)C(Ph)\}]$ (**3**) was prepared from $[W(CO)_5\{P(Cl)C(Ph)C(Ph)\}]$ (**1**, 60.0 mg, 0.106 mmol) and $AgOSO_2CF_3$ (27.2 mg, 0.106 mmol) in CH_2Cl_2 (4 mL) as described above. This solution was added rapidly to a solution of indole (6.2 mg, 0.053 mmol, 0.5 equivalent vs **1**) in CH_2Cl_2, resulting in a color change to yellow. To this solution was added triethylamine (15 μL, 0.108 mmol). ^{31}P NMR of the reaction mixture showed **14** to be the major product, while **13** is still present as a minor product. The solvent was removed in vacuo, and the residue was purified by flash chromatography with silica gel (20/80 v/v diethyl ether/petroleum ether). The yellow product was crystallized by cooling a saturated CH_2Cl_2/pentane solution to −20 °C. Yield: 31 mg, 25%. IR (νCO, CH_2Cl_2, cm^{-1}): 2076(w), 1944(vs). ^{31}P NMR ($CDCl_3$): δ −129.8 (s, $^1J_{PW}$ = 314 Hz, N-bound *P* nuclei), −173.8 (d, $^1J_{PW}$ = 274 Hz, $^3J_{PH}$ = 2.8 Hz, C bound *P* nuclei). ^1H NMR ($CDCl_3$): δ 6.88 (m, 1H, C_8H_5N), 7.12 (m, 1H, C_8H_5N), 7.25 (d, 1H, J_{HH} = 7.8 Hz, C_8H_5N), 7.42−7.54 (m, 6H, Ph), 7.58−7.68 (m, 6H, Ph), 7.73 (d, 1H, J_{HH} = 8.4 Hz, C_8H_5N), 7.78 (t, 1H, J_{HH} = 5.1 Hz, C_8H_5N), 7.84−7.87 (m, 4H, Ph), 8.03−8.06 (m, 4H, Ph). ^{13}C NMR ($CDCl_3$): δ 113.00 (d, J_{CP} = 3.8 Hz, C_8H_5N), 121.18 (s, C_8H_5N), 122.48 (s, C_8H_5N), 123.93 (s, C_8H_5N), 126.70 (d, $^2J_{CP}$ = 6.2 Hz, *ipso*-Ph), 128.45 (d, $^2J_{CP}$ = 6.3 Hz, *ipso*-Ph), 129.50 (s, Ph), 129.99 (s, Ph), 130.33 (s, Ph), 130.38 (s, Ph), 130.41 (s, Ph), 130.46 (s, Ph), 130.74 (s, Ph), 131.96 (s, Ph), 138.49 (s, C_8H_5N), 138.59 (d, J_{CP} = 1.5 Hz, C_8H_5N), 138.72 (d, J_{CP} = 5.6 Hz), 138.81 (s, C_8H_5N), 139.28 (d, J_{CP} = 5.5 Hz), 194.88 (d, $^2J_{CP}$ = 8.5 Hz, *cis*-CO), 196.29 (d, $^2J_{CP}$ = 9.1 Hz, *cis*-CO), 197.24 (d, $^2J_{CP}$ = 40.2 Hz, *trans*-CO), 198.16 (d, $^2J_{CP}$ = 31.1 Hz, *trans*-CO). Anal. Calcd for $C_{46}H_{25}NO_{10}P_2W_2$: C, 46.77; H, 2.13; N, 1.19. Found: C, 47.51; H, 2.26; N, 1.52.

*l. Synthesis of [W(CO)$_5${P(OPh)C(Ph)C(Ph)}] (**15**).* A solution of $[W(CO)_5\{P(OSO_2CF_3)C(Ph)C(Ph)\}]$ (**3**) was prepared from $[W(CO)_5\{P(Cl)C(Ph)C(Ph)\}]$ (**1**, 50.0 mg, 0.088 mmol) and $AgOSO_2CF_3$ (22.6 mg, 0.088 mmol) in CH_2Cl_2 (4 mL) as described above and added to a solution of phenol (8.3 mg, 0.088 mmol) in CH_2Cl_2 (2 mL), resulting in a color change to yellow. The solvent was removed under reduced pressure, and the residue was purified by flash chromatography (alumina, 10/90 v/v diethyl ether/petroleum ether). The pale yellow product was crystallized by cooling a saturated pentane solution to −20 °C. Yield: 48 mg, 87%. IR (νCO, CH_2Cl_2, cm^{-1}): 2078(w), 1947(vs). ^{31}P NMR ($CDCl_3$): δ −67.2 (s, $^1J_{PW}$ = 328 Hz). ^1H NMR ($CDCl_3$): δ 6.79 (m, 2H, OPh), 6.97 (m, 1H, OPh), 7.09 (m, 2H, OPh), 7.47−7.84 (m, 10H, Ph). ^{13}C NMR ($CDCl_3$): δ 122.27 (d, $^3J_{CP}$ = 4.6 Hz, OPh), 124.77 (d, $^4J_{CP}$ = 2.3 Hz, OPh), 128.07 (d, $^2J_{CP}$ = 4.0 Hz, *ipso*-Ph), 129.48 (s, Ph), 129.79 (d, $^5J_{CP}$ = 1.7 Hz, OPh), 129.87 (s, Ph), 129.94 (s, Ph), 131.22 (s, Ph), 145.73 (d, $^1J_{CP}$ = 17.3 Hz, phosphirene ring C), 151.85 (d, $^2J_{CP}$ = 13.2 Hz, *ipso*-OPh), 195.34 (d, $^2J_{CP}$ = 9.7 Hz, $^1J_{CW}$ = 125.5 Hz, *cis*-CO), 198.56 (d,

dx.doi.org/10.1021/om401050w | *Organometallics* 2014, 33, 522−530

$^2J_{CP}$ = 41.5 Hz, *trans*-CO). Anal. Calcd for $C_{25}H_{15}O_6PW$: C, 47.95; H, 2.41. Found: C, 48.39; H, 2.54.

*m. Synthesis of [W(CO)$_5${P(NPh$_2$)C(Ph)C(Ph)}] (**16**).* A solution of [W(CO)$_5${P(OSO$_2$CF$_3$)C(Ph)C(Ph)}] (**3**) was prepared from [W(CO)$_5${P(Cl)C(Ph)C(Ph)}] (**1**, 50.0 mg, 0.088 mmol) and $AgOSO_2CF_3$ (22.6 mg, 0.088 mmol) in CH_2Cl_2 (4 mL) as described above and added to a solution of diphenylamine (29.8 mg, 0.176 mmol) in CH_2Cl_2 (3 mL), resulting in a color change to yellow. The solvent was removed under reduced pressure, and the residue was purified by flash chromatography (alumina, 10/90 v/v diethyl ether/petroleum ether). The yellow product was crystallized by cooling the saturated pentane solution to −20 °C. Yield: 57 mg, 92%. IR (νCO, CH_2Cl_2, cm^{-1}): 2074(w), 1942(vs). ^{31}P NMR ($CDCl_3$): δ −108.3 (s, $^1J_{PW}$ = 310 Hz). ^{1}H NMR ($CDCl_3$): δ 6.96−7.06 (m, 6H, phosphirene ring Ph), 7.12−7.17 (m, 4H, N(Ph)$_2$), 7.34−7.44 (m, 6H, N(Ph)$_2$), 7.59−7.63 (m, 4H, phosphirene ring Ph). ^{13}C NMR ($CDCl_3$): δ 125.10 (s, NPh), 126.53 (s, NPh), 126.59 (s, NPh), 128.07 (d, $^2J_{CP}$ = 5.1 Hz, *ipso*-Ph), 129.28 (s, Ph), 129.34 (s, Ph), 129.69 (s, Ph), 130.56 (s, Ph), 140.46 (d, $^2J_{CP}$ = 14.6 Hz, phosphirene ring C), 144.04 (d, $^2J_{CP}$ = 2.8 Hz, *ipso*-NPh), 196.10 (d, $^2J_{CP}$ = 9.1 Hz, $^1J_{CW}$ = 125.6 Hz, *cis*-CO), 198.59 (d, $^2J_{CP}$ = 37.7 Hz, $^1J_{CW}$ = 149.8 Hz, *trans*-CO). Anal. Calcd for $C_{31}H_{20}NO_5PW$: C, 53.09; H, 2.87; N, 2.00. Found: C, 52.98; H, 2.94; N, 2.09.

*n. Synthesis of [W(CO)$_3$(I)$_2${P(2-C$_6$H$_3$(2-N(CH$_3$)$_2$)(5-CH$_3$))C(Ph)C(Ph)-κ^{2}P,N}] (**18**).* Compound **6** (60 mg, 0.090 mmol) was dissolved in CH_2Cl_2 (3 mL). A solution of iodine (22.8 mg, 0.090 mmol) in CH_2Cl_2 (5 mL) was added dropwise, resulting in a color change to dark yellow. The solvent was removed under reduced pressure, and the residue was washed with pentane. Compound **18** decomposes in solution, so further purification was not possible, and the crude product was used in the subsequent reaction. Yield: 72 mg, 93%. IR (νCO, CH_2Cl_2, cm^{-1}): 2034(m), 1958(s), 1917(m). ^{31}P NMR ($CDCl_3$): δ −100.7 (dd, $^1J_{PW}$ = 247 Hz, $^3J_{PH}$ = 13.4 Hz, $^4J_{PH}$ = 6.0 Hz). ^{1}H NMR ($CDCl_3$): δ 2.25 (s, 3H, C$_6$H$_3$C*H*$_3$), 3.74 (s, 6H, N(C*H*$_3$)$_2$), 6.90 (m, 1H, arene CH), 7.34 (m, 1H, arene CH), 7.50−8.01 (m, 11H, 10H of Ph and 1H of arene).

*o. Synthesis of P{2-C$_6$H$_3$(2-N(CH$_3$)$_2$)(5-CH$_3$)}C(Ph)C(Ph) (**19**).* Compound **18** (72 mg, 0.083 mmol) was dissolved in CH_2Cl_2 (5 mL). A solution of 2,2′-bipyridine (13.0 mg, 0.083 mmol) in CH_2Cl_2 (2 mL) was added, and the resulting solution was stirred for 16 h. The solution color changed from yellow to brown, and an orange precipitate was formed. The solvent was removed under reduced pressure, and the residue was purified by flash chromatography (alumina, 5/95 v/v ethylacetate/pentane). Yield: 21 mg, 73%. As a free ligand, **19** is thermally unstable and decomposes over time in the solid state or in solution. As a result, satisfactory elemental analysis could not be obtained. ^{31}P NMR ($CDCl_3$): δ −190.7 (s). ^{1}H NMR ($CDCl_3$): δ 1.97 (s, 3H, C$_6$H$_3$C*H*$_3$), 2.88 (s, 6H, N(C*H*$_3$)$_2$), 6.67 (m, 1H, arene CH), 6.89 (m, 2H, arene CH), 7.29−7.83 (m, 10H, Ph). ^{13}C NMR ($CDCl_3$): δ 21.06 (s, *C*H$_3$), 46.74 (s, N(*C*H$_3$)$_2$), 118.84 (s, Ar), 123.47 (d, $^2J_{CP}$ = 46 Hz, *ipso*-Ph), 127.0 (d, $^1J_{CP}$ = 32 Hz, *ipso*-Ar), 129.01 (s, Ph), 129.27 (s, Ph), 129.99 (s, Ar), 130.82 (s, Ph), 131.68 (d, $^1J_{CP}$ = 20 Hz, phosphirene ring C), 132.22 (s, Ar), 132.70 (s, *ipso*-Ar), 155.2 (s, *ipso*-Ar).

X-ray Crystallography. Suitable crystals of compounds **5**, **7**, and **9** were mounted on glass fibers. Programs for diffractometer operation, data collection, cell indexing, data reduction, and absorption correction were those supplied by Bruker AXS Inc., Madison, WI. Diffraction measurements were made on a PLATFORM diffractometer/SMART 1000 CCD using graphite-monochromated Mo Kα radiation at −80 °C. The unit cell was determined from randomly selected reflections obtained using the SMART CCD automatic search, center, index, and least-squares routines. Integration was carried out using the program SAINT, and an absorption correction was performed using SADABS. Structure solution was carried out using the SHELX97[19] suite of programs and the WinGX graphical interface.[20] Initial solutions were obtained by direct methods and refined by successive least-squares cycles. All non-hydrogen atoms were refined anisotropically.

Computational Details. The gas phase structures were optimized without any symmetry constraints using density functional theory (DFT), with the B3LYP exchange−correlation functional,[21] as implemented in the Gaussian 09 (revision C. 01) software package.[22] Basis set LANL2DZ was used for W, and 6-31G(d,p) was used for all other atoms (C, H, O, and P). The nature of the optimized structures was identified from the vibrational frequency analysis. Gaussion 09 was also used for computing the NBO charges.[23] The keywords used in the input files were *# opt freq=noraman rb3lyp pop=(npa) gen pseudo=read.*

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

NMR spectra for compounds **11**, **18**, and **19**. Optimized structures with NBO charges, numbers of imaginary frequencies, absolute energies, and Cartesian coordinates. CIF files containing crystallographic data for **5**, **7**, and **9**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We thank Bob McDonald and Mike Ferguson (University of Alberta) for X-ray data collection, Compute Canada (West-Grid) for computing resources, and the University of Regina for funding.

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