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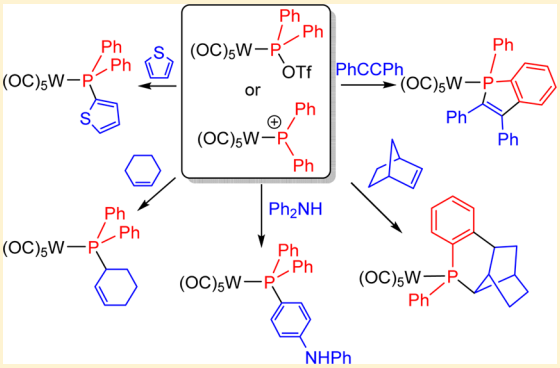
Phosphorus–Carbon Bond Forming Reactions of Diphenylphosphenium and Diphenylphosphine Triflate Complexes of Tungsten

Arumugam Jayaraman and Brian T. Sterenberg*

Department of Chemistry and Biochemistry, University of Regina, 3737 Wascana Parkway, Regina, Saskatchewan S4S 0A2, Canada

Supporting Information

ABSTRACT: The complex $[W(CO)_5\{PClPh_2\}]$ reacts with $AlCl_3$ to form a mixture of the phosphenium complex $[W(CO)_5\{PPh_2\}][AlCl_4]$ and an isocarbonyl, with $GaCl_3$ to form $[W(CO)_5\{PPh_2\}][GaCl_4]$, and with silver trifluoromethanesulfonate to form $[W(CO)_5\{P(OSO_2CF_3)Ph_2\}]$. All three complexes react as strong P electrophiles, undergoing electrophilic substitution reactions with aromatic and heteroaromatic compounds, alkenes, and alkynes, to form aromatic and heteroaromatic phosphines, allyl phosphines, and alkynyl phosphines, respectively. Alkenes lacking cleavable γ-H atoms and internal alkynes undergo tandem electrophilic addition/substitution reactions, adding between the P and one of the phenyl rings to form fused P heterocycles. The newly formed phosphines can be removed from the tungsten complex by photolysis in the presence of bis(diphenylphosphino)ethane.



INTRODUCTION

Organophosphorus compounds, which contain direct P–C bonds, have applications as ligands for catalysis, pesticides, and flame retardants.[1] Emerging applications include materials,[2] anticancer drugs,[3,4] and antibiotics.[3,5] Phosphorus–carbon bond formation is an important step in the synthesis of these compounds. Commonly used methods for making P–C bonds include addition of a P nucleophile such as diphenyl phosphide to an organic electrophile, addition of P–H across a multiple bond, and addition of an organic nucleophile to a P electrophile.[1] For the last method, the typical P electrophile is a chlorophosphine. However, chlorophosphines are not strong electrophiles and require strong organic nucleophiles, typically Grignard reagents, or aryl- and alkyllithium reagents. The electrophilicity of the phosphorus can be enhanced via chloride abstraction, leading to a reactive phosphenium intermediate. This approach has been applied to the Friedel–Crafts-like electrophilic addition of phosphine units to aromatic substrates.[6] However, although this methodology has been known for a long time, it has not gained widespread use, possibly because of the harsh conditions, long reaction times, and low yields.

One possible method for enhancing the electrophilicity of a phosphenium unit is via coordination to an electron-poor transition-metal complex. Although a number of phosphenium ion complexes have been described[7,8] and have been shown to be electrophilic at P,[9−11] the application of these complexes to P–C bond formation has received little attention.[8,10,11] We have previously shown that the electrophilicity of metal-coordinated phosphenium units can be exploited in P–C bond-forming reactions with a range of unsaturated organic fragments.[12,13] In this paper, we examine in detail the reactivity of the diphenyl phosphenium complex $[W(CO)_5\{PPh_2\}]^+$ toward unsaturated organic substrates. Because the PPh_2 unit is ubiquitous in the phosphine ligands used in homogeneous catalysis, new methods for adding this unit to organic substrates are potentially valuable.

RESULTS AND DISCUSSION

One of the most commonly used methods for the formation of phosphenium ions is abstraction of an anionic group with a Lewis acid.[10,14] We have also previously successfully used this route to form phosphenium ion complexes and have found $AlCl_3$ to be an effective reagent for chloride abstraction.[13,15] Here, we examined in detail the reaction of $[W(CO)_5\{PPh_2Cl\}]$ (**1**) with $AlCl_3$. Reaction with 1 equiv of $AlCl_3$ led to no observable change in the ^{31}P NMR spectrum. However, addition of 2 equiv or more led to the disappearance of the signal for **1** and no new signals at room temperature. At temperatures below 0 °C, two peaks appear at δ 429.2 and 85.7, in a 2:8 ratio. On the basis of the chemical shift, the peak at δ 429.2 is assigned as the phosphenium complex $[W(CO)_5\{PPh_2\}][AlCl_4]$ (**2a**). The large downfield shift in the former is also expected for the planar PR_2 ligands, which typically resonate downfield of precursor chlorophosphines by 150–300 ppm.[8] Further support for this assignment comes from a calculated ^{31}P chemical shift (see Experimental Section and Supporting Information for computational methods). The second component shows an upfield shift from the starting material, and is assigned as the isocarbonyl complex $[W(CO)_4\{COAlCl_3\}\{PPh_2Cl\}]$ (**3a**) (Scheme 1),

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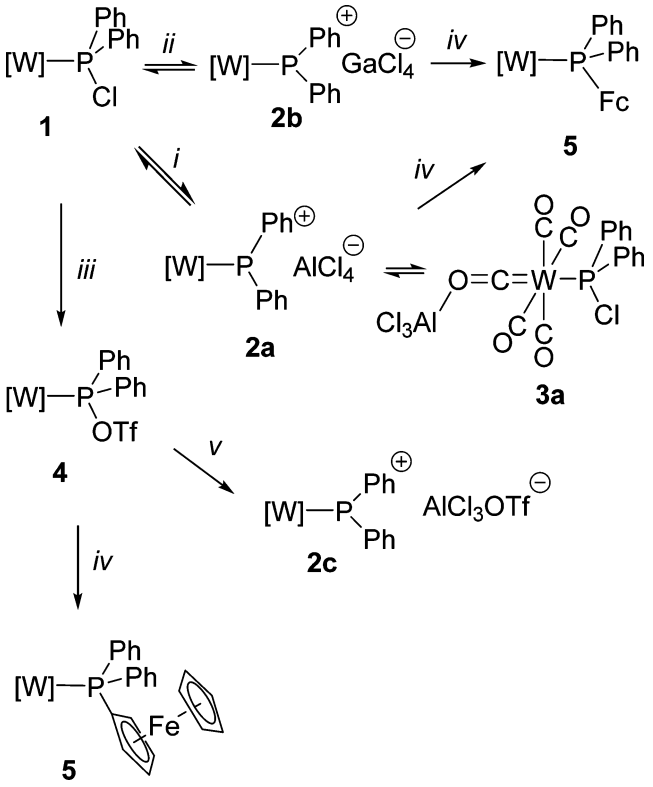
Scheme 1[a]



[a]Reagents and conditions: CH_2Cl_2, room temperature; (i) $AlCl_3$ 3 equiv; (ii) $GaCl_3$ 1 equiv; (iii) $AgOSO_2CF_3$ 1.2 equiv, 2 h. (iv) Cp_2Fe 2 equiv; (v) $AlCl_3$ 2 equiv. Abbreviations: [W] = $W(CO)_5$, OTf = OSO_2CF_3, Fc = ferrocenyl.

on the basis of a calculated chemical shift of δ 81.3. This complex results from a reversible interaction of a carbonyl of **1** with $AlCl_3$. Further support for the identification of **3a** as an isocarbonyl comes from reaction of $[W(CO)_5\{PPh_3\}]$ with 2 equiv of $AlCl_3$, which led to a similar upfield shift of the ^{31}P NMR resonance (δ 18.4 to δ 9.9). The coalescence of the ^{31}P resonances for **2a** and **3a** shows that they are in equilibrium. This equilibrium mixture is extremely reactive, and attempts to crystallize them and isolate them as solids were not successful. However, the solution prepared in situ readily reacts with a wide range of organic substrates. For example, it rapidly undergoes electrophilic addition to ferrocene, leading to the known ferrocenyl phosphine complex $[W(CO)_5\{P(C_{10}H_9Fe)Ph_2\}]$ (**5**),[16] as previously described.[13] The complete conversion of the mixture to **5** is further evidence that **2a** and **3a** are in equilibrium. The mixture of **1** with 1 equiv of $AlCl_3$, which shows no spectroscopic evidence of the phosphenium complex, also reacts with ferrocene, but much more slowly, requiring 48 h to go to completion. This indicates that this mixture contains some phosphenium complex, although the equilibrium lies far to the side of the starting chlorophosphine complex **1** or isocarbonyl **3a**.

In an attempt to avoid isocarbonyl formation, the softer Lewis acid $GaCl_3$ was also examined as a chloride abstracting reagent. Like $AlCl_3$, addition of 3 equiv of $GaCl_3$ changed the color of the solution from pale yellow to dark yellow. At room temperature, only a broad signal at δ 419.8 was observed by $^{31}P\{^1H\}$ NMR spectroscopy. At −40 °C, this signal moved to δ 429.3. Addition of 1 equiv of $GaCl_3$ to **1** resulted in a mixture of phosphenium ion **2b** and **1** in a 1:1 ratio. These observations clearly indicate that $GaCl_3$ does not interact with a carbonyl oxygen, driving the equilibrium further toward the phosphenium ion $[W(CO)_5\{PPh_2\}][GaCl_4]$ (**2b**). DFT free energies, calculated using B3LYP/LANL2TZ(f)/6-311G+(2d,p)//B3LYP/LANL2DZ/6-31G(d,p) model chemistry, show that with $AlCl_3$ formation of phosphenium **2a** and isocarbonyl **3a** are both exergonic, by 4.4 and 10.7 kcal/mol, respectively, and the isocarbonyl is only 6.3 kcal/mol higher in energy than the phosphenium complex **2a** (Figure 1). With $GaCl_3$ the formation

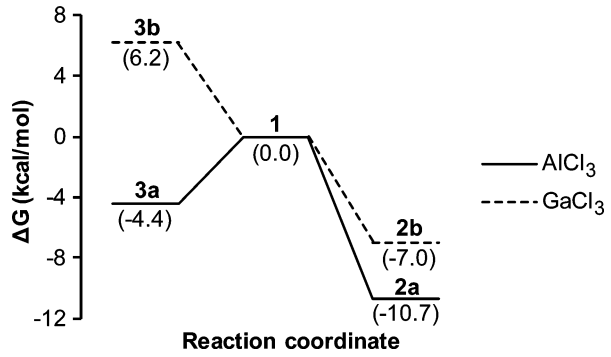


Figure 1. DFT computed free energy surface for the formation of phosphenium and isocarbonyl complexes using $AlCl_3$ and $GaCl_3$.

of isocarbonyl complex **3b** is endergonic by 6.2 kcal/mol and the formation of phosphenium ion **2b** is exergonic by 7.0 kcal/mol, and **3b** is 13.2 kcal/mol higher in energy than **2b**, supporting our experimental observations.

The **1**/$GaCl_3$ mixture is more reactive than the **1**/$AlCl_3$ mixture. Even with only 1 equiv of $GaCl_3$, it reacts immediately with ferrocene to form the ferrocenyl phosphine complex **5**. The greater reactivity reflects the higher concentration of phosphenium **2** in this mixture that results from the lack of isocarbonyl formation.

Silver triflate acts as an alternative reagent for chloride abstraction from **1**. Reaction of **1** with silver triflate leads to the phosphine triflate complex $[W(CO)_5\{PPh_2(OSO_2CF_3)\}]$ (**4**) (Scheme 1). Filtration to remove AgCl then leads to a chloride-free solution of **4**. The phosphine triflate **4** reacts rapidly with ferrocene to yield **5**,[13] showing the same reactivity as the **1**/$AlCl_3$ and **1**/$GaCl_3$ mixtures (hereafter referred to as **2a,b**). The phosphenium complex can also be made by first forming the triflate complex **4** and then abstracting triflate with $AlCl_3$, leading to $[W(CO)_5\{PPh_2\}][AlCl_3(OSO_2CF_3)]$ (**2c**). In this case, the equilibrium lies toward the phosphenium complex, and the ^{31}P NMR spectrum of the solution shows a peak at δ 426.2 at room temperature.

The rapid reaction of **2** or **4** with ferrocene suggests that the metal-coordinated diphenylphosphenium ion is more reactive than the metal-free phosphenium ion. To prove this, the reactivity of metal-free diphenylphosphenium ion toward ferrocene was examined under the same reaction conditions for comparison. Addition of ferrocene to the CH_2Cl_2 solution of a $PPh_2Cl/AlCl_3$ mixture resulted in slow formation of protonated diphenylferrocenylphosphine, through successive electrophilic substitution and protonation reactions (Scheme 2). This reaction comes to completion after 12 h at room temperature. The proton-coupled ^{31}P NMR spectrum shows a doublet at δ 8.0 with $^1J_{PH}$ = 511 Hz. The metal-free phosphine triflate $[PPh_2(OSO_2CF_3)]$ does not react cleanly with ferrocene under similar conditions.

Reaction of the phosphine triflate complex **4** with triphenylphosphine results in rapid displacement of triflate by the phosphine,

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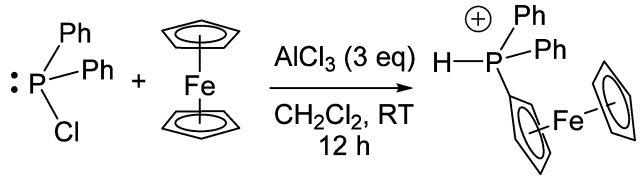
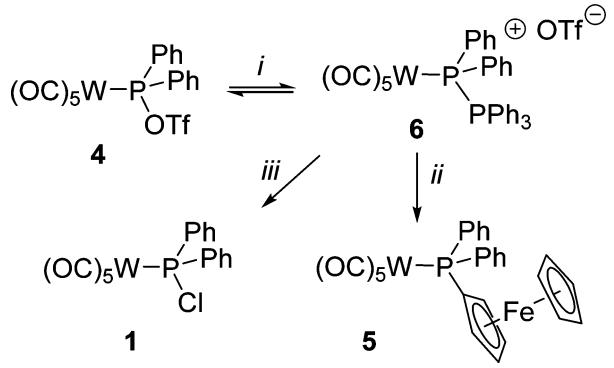
Scheme 2



leading to the phosphine-coordinated phosphenium complex **6** (Scheme 3). Reaction of **2a** with PPh_3 simply leads to re-formation

Scheme 3[a]



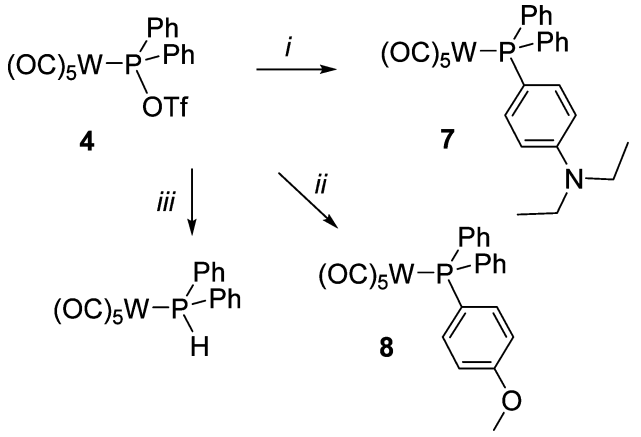
[a]Reagents and conditions: CH_2Cl_2, room temperature; (i) PPh_3 1 equiv; (ii) Cp_2Fe 2 equiv, 12 h; (iii) Bu_4NCl 1 equiv. Abbreviation: OTf = OSO_2CF_3.

of **1**, as PPh_3 consumes the $AlCl_3$. The metal-free triphenylphosphine coordinated diphenylphosphenium cation was described by Burford et al. and is a stable and isolable compound.[17] In contrast, compound **6** is relatively unstable. Addition of Bu_4NCl to **6** similarly leads to rapid displacement of the PPh_3 and re-formation of chlorophosphine complex **1**. With organic substrates, **6** reacts much like the triflate complex **4** or the phosphenium complex **2a**, although much more slowly, with the PPh_3 being displaced by the incoming organic nucleophile. For example, addition of ferrocene leads to the formation of **5** after 12 h at room temperature. The weakness of the P−P bond in **6** can likely be attributed to the increased steric crowding that results from the $W(CO)_5$ unit.

Addition of diethylaniline to **2a** or **4** leads exclusively to the *p*-anilinyl phosphine complex $[W(CO)_5\{PPh_2(p\text{-}C_6H_4N(CH_2CH_3)_2)\}]$ (**7**) (Scheme 4). With both reagents, the reaction is rapid, going to completion immediately at room temperature. The isolated yield is 88%. The $^{31}P\{^1H\}$ NMR spectrum of **7** shows a peak at δ 18.3, with ^{183}W satellites and $^1J_{PW}$ = 241 Hz. The phenyl region in the ^1H NMR spectrum shows the set of two doublets expected for a para-substituted phenyl ring, as well as the peaks for N-bound ethyl groups. Similarly, the reaction of **4** with anisole resulted in electrophilic aromatic substitution exclusively in the para position, leading to the anisolyl phosphine complex $[W(CO)_5\{P(p\text{-}C_6H_4OCH_3)Ph_2\}]$ (**8**) in 82% isolated yield, over 12 h at room temperature, as previously described.[13] The slower reaction rate with anisole reflects its weaker activation toward electrophilic aromatic substitution.

In an attempt to direct the reactivity to the ortho position, compound **4** was treated with *N,N*-dimethyl-*p*-toluidine. Previously, we showed that metal-coordinated phosphirenyl cations could be added to the position ortho to the amino group, leading to a potential P,N bidentate ligand.[12] However,

Scheme 4[a]

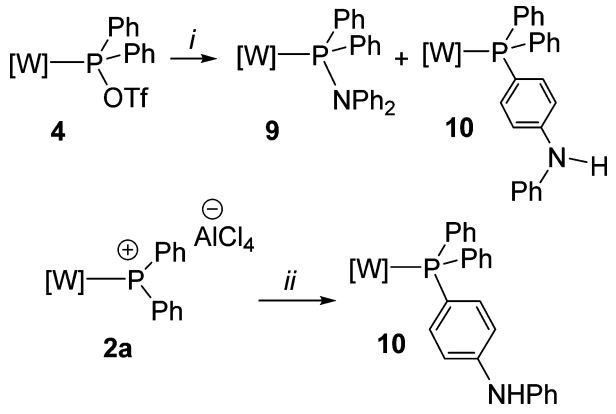


[a]Reagents and conditions: CH_2Cl_2, room temperature; (i) *N,N*-diethylaniline 2 equiv, 15 min; (ii) anisole 10 equiv, 12 h; (iii) *N,N*-dimethyl-*p*-toluidine 2 equiv, 30 min. Abbreviation: OTf = OSO_2CF_3.

in this case the reaction simply led to the known secondary phosphine complex $[W(CO)_5\{PHPh_2\}]$ (Scheme 4). This reactivity can be attributed to the greater steric congestion at P in the metal-coordinated diphenylphosphenium. Rather than adding to the crowded ortho position, it abstracts hydride from an *N*-methyl group. If the reaction is carried out in deuterated chloroform, the iminium ion formed via hydride abstraction from *N,N*-dimethyl-*p*-toluidine can be observed in solution. Hydride abstraction from tertiary alkyl amines by Lewis acids to form iminium ions is well documented.[18] This reaction shows that this methodology is very sensitive to sterics and may be limited to less crowded positions.

Reactions of **2a** or **4** with the secondary and primary amines diphenylamine and aniline were used to test the tolerance of this methodology for N−H bonds. Reaction of the triflate complex **4** with diphenylamine led to a mixture of two products, the diphenylaminophosphine complex $[W(CO)_5\{PPh_2(NPh_2)\}]$ (**9**) and the *p*-aminophenyl phosphine complex $[W(CO)_5\{PPh_2(p\text{-}C_6H_4NH(Ph)\}]$ (**10**), in a 6:4 ratio (Scheme 5). These two

Scheme 5[a]



[a]Reagents and conditions: CH_2Cl_2, room temperature, diphenylamine 1.1 equiv; (i) 15 min; (ii) 12 h. Abbreviations: OTf = OSO_2CF_3, [W] = $W(CO)_5$.

products result respectively from N−H and C−H activation by the phosphine triflate complex. This reactivity demonstrates that, even in the presence of N−H bonds, electrophilic aromatic

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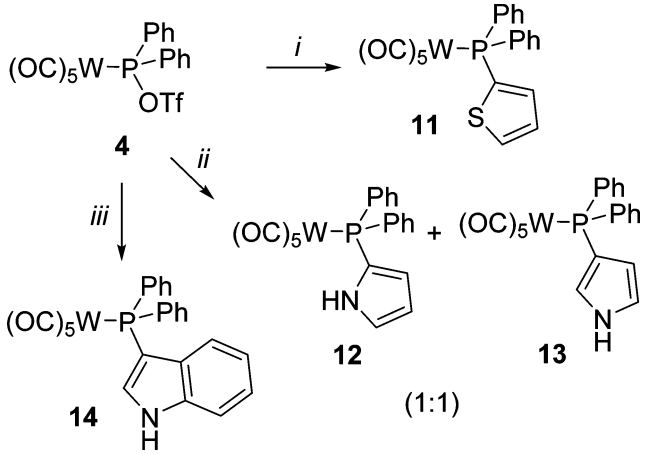
substitution still occurs. Reaction of **2a** with diphenylamine led exclusively to the C−H activated product **10**, in 78% isolated yield. The selectivity here is attributed to the generation of HCl under these reaction conditions, which cleaves the P−N bond. Formation of **9** may also occur in this case but is reversed by reaction with HCl, and **10** is the only observed product.

Reaction of **4** with the primary amine aniline led to $[W(CO)_5\{PPh_2(NHPh)\}]$ as the only product, with no evidence for P−C bond formation. Reaction of **2a** with aniline led to regeneration of **1** and again no evidence of P−C bond formation. In this case, the aniline is reacting with the $AlCl_4$ anion, regenerating chloride ion, which combines with **2a** to re-form **1**. The strong Lewis basicity of the primary amine appears to preclude electrophilic aromatic substitution. Interaction of $AlCl_3$ with aniline is well documented and is known to interfere with electrophilic aromatic substitution reactions on aniline.[19]

The heteroaromatic substrates thiophene, pyrrole, and indole can also be readily introduced onto the metal-coordinated phosphenium group. All three substrates react rapidly with **4** to give the expected substitution products (Scheme 6). In the case

Scheme 6[a]



[a]Reagents and conditions: CH_2Cl_2, room temperature, 15 min; (i) thiophene 3 equiv; (ii) pyrrole 4 equiv; (iii) indole 2 equiv. Abbreviation: OTf = OSO_2CF_3.

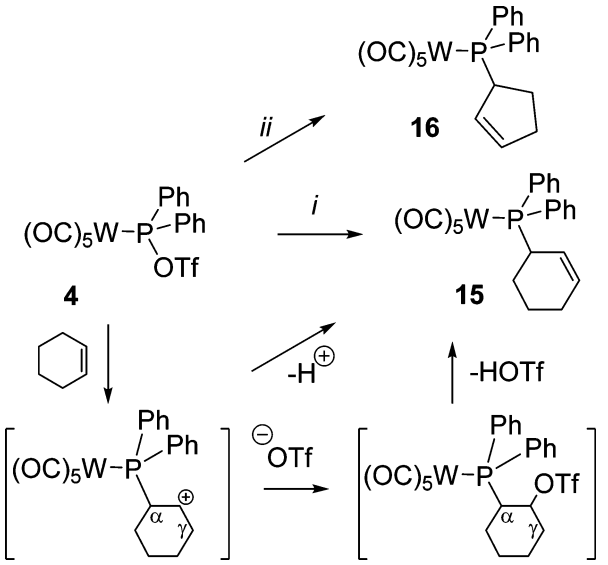
of thiophene, the only observed product, $[W(CO)_5\{PPh_2(2\text{-}C_4H_3S)\}]$ (**11**), results from substitution at the 2-position, which is expected to be the most reactive toward electrophilic substitution.[20] The $^{31}P\{^1H\}$ NMR spectrum of **11** gives a singlet with ^{183}W satellites at δ 7.7 ($^1J_{PW}$ = 247 Hz), while the ^1H NMR spectrum shows three thienyl peaks at δ 7.68, 7.36, and 7.21, in addition to phenyl peaks, and the isolated yield is 72%.

The reaction of **4** with pyrrole led to a 1:1 mixture of two isomers $[W(CO)_5\{PPh_2(2\text{-}C_4H_3NH)\}]$ (**12**) and $[W(CO)_5\{PPh_2(3\text{-}C_4H_3NH)\}]$ (**13**), in which the phosphenium unit added to the 2- or 3-position of pyrrole, respectively (Scheme 6). This reaction is very rapid, and carrying out the same reaction at −80 °C did not alter the regioselectivity. There is no evidence for P−N bond formation. The poor selectivity in pyrrole in comparison to thiophene is likely a consequence of the greater activation of pyrrole toward electrophilic substitution,[20] which results in rapid kinetics and no differentiation between two possible intermediates. Separation of the two isomers is straightforward, and both compounds have been isolated in 39% and 47% yields and fully characterized.

Reaction with indole led to regioselective substitution in the 3-position, the expected position for electrophilic substitution on indole (Scheme 6).[20] Again, no evidence was observed for P−N bond formation, and the 3-indolyl phosphine complex **14** is the only observed product (isolated yield 83%).

Addition of cyclohexene or cyclopentene to **4** led to the anticipated electrophilic substitution reaction; however, only the allyl products $[W(CO)_5\{PPh_2(C_6H_9)\}]$ (**15**) (84% isolated yield) and $[W(CO)_5\{PPh_2(C_5H_7)\}]$ (**16**) (93% isolated yield) are observed, with no evidence for vinyl products (Scheme 7).

Scheme 7[a]



[a]Reagents and conditions: CH_2Cl_2, room temperature, 8 h; (i) cyclohexene 10 equiv; (ii) cyclopentene 10 equiv. Abbreviation: OTf = OSO_2CF_3.

The phosphenium ion complex **2a** generated using $AlCl_3$ reacts with cyclohexene and cyclopentene to form the same allyl products. Similar γ proton eliminations are also commonly observed in Friedel−Crafts acylation of alkenes.[21] Mechanistically, this reaction likely occurs via a direct γ deprotonation of the carbocation intermediate or by addition−elimination (Scheme 7). In an attempt to explain the regioselectivities, DFT optimizations of the two possible intermediates were carried out. We were unable to optimize the carbocation, but the triflate was successfully optimized. Charges in this intermediate (NBO charges: C^α = −0.525, C^γ = −0.407; see the Supporting Information for the optimized structure) show that the $(OC)_5W\{PPh_2\}$ unit has a significant $+I$ effect, rendering the α-H atom less acidic than the γ-H atoms and favoring γ deprotonation and allyl formation.

Next, in an attempt to generate a vinyl phosphine, norbornene was added to compound **4**. Proton loss from the γ position in norbornene would lead to an unfavorable bridgehead double bond; thus we anticipated that, in this case, the α proton would be lost, leading to a vinyl phosphine. However, the observed product $[W(CO)_5\{PPh(C_6H_4C_7H_{10})\}]$ (**17**), isolated in 77% yield, is instead the result of tandem electrophilic addition reactions, in which the intermediate formed by electrophilic addition to the alkene carries out an electrophilic attack on the adjacent phenyl ring (Scheme 8), leading to a

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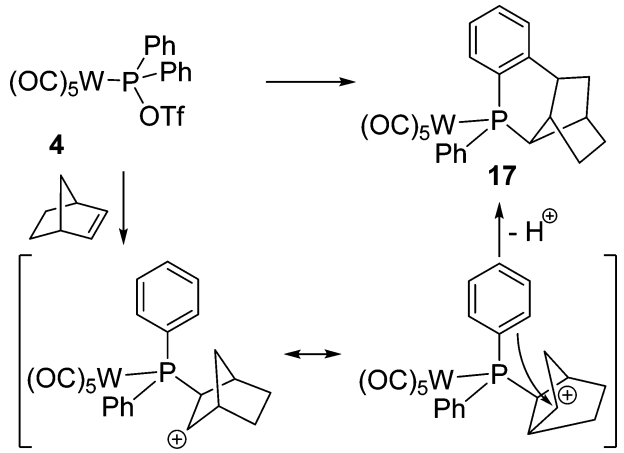
Scheme 8[a]



[a]Reagents and conditions: CH_2Cl_2, room temperature, norbornene 5 equiv, 1 h. Abbreviation: OTf = OSO_2CF_3.

novel six-membered P heterocycle, fused to both phenyl and norbornyl rings. The X-ray crystal structure of the product (Figure 2) shows that the P is bound to C7 of the norbornyl

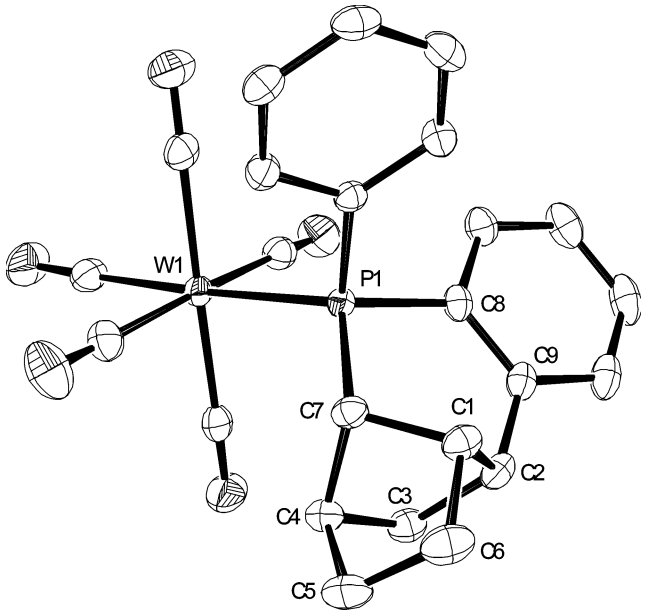
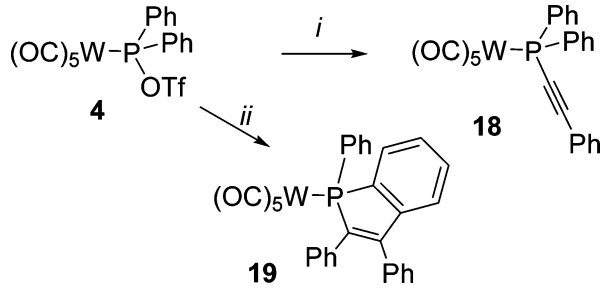


Figure 2. ORTEP diagram showing the molecular structure of **17**. Thermal ellipsoids are shown at the 50% level, and H atoms have been omitted. Selected distances (Å) and angles (deg): W(1)–P(1) = 2.5367(4), P(1)–C(7) = 1.844(2), P(1)–C(8) = 1.821(2), C(1)–C(2) = 1.542(2), C(2)–C(3) = 1.565(2), C(3)–C(4) = 1.540(2), C(4)–C(5) = 1.541(2), C(5)–C(6) = 1.550(3), C(6)–C(1) = 1.539(3), C(1)–C(7) = 1.548(2), C(7)–C(4) = 1.539(2), C(2)–C(9) = 1.507(3), C(8)–C(9) = 1.400(2); C(8)–P(1)–C(7) = 102.88(8), C(1)–C(7)–P(1) = 114.0(1), C(2)–C(1)–C(7) = 100.4(1), C(9)–C(2)–C(1) = 110.8(1), C(8)–C(9)–C(2) = 120.7(1), C(9)–C(8)–P(1) = 120.7(1).

group, while the phenyl ring is bound to C2. Assignment of the $^{13}C\{^1H\}$ NMR spectrum was used to confirm that the bulk sample was the same as the X-ray crystal. Simple addition across the alkene would lead to C2–C3 substitution for the P and aryl group. The observed regioselectivity can be rationalized by considering the nonclassical delocalization of the positive charge[22] in the P-substituted norbornyl cation intermediate (Scheme 8).

Addition of the terminal alkyne phenylacetylene to **2a** or **4** results in an electrophilic substitution reaction of the terminal H atom, leading to the known phenylalkynyl phosphine complex **18** in 79% isolated yield (Scheme 9).[23] In contrast to

Scheme 9[a]



[a]Reagents and conditions: CH_2Cl_2, room temperature; (i) phenylacetylene 2 equiv, 10 min; (ii) diphenylacetylene 2.5 equiv, 30 min. Abbreviation: OTf = OSO_2CF_3.

the reactions with alkenes, with phenylacetylene, elimination of the α proton is favored and rapid. Reaction of **2a** or **4** with diphenylacetylene results in an intermediate without an acidic proton and leads to a tandem electrophilic reaction, in which the intermediate attacks an adjacent phenyl ring, leading to the 1,2,3-triphenylbenzophosphole complex **19** in 58% isolated yield (Scheme 9). Compound **19** was completely characterized, including by X-ray crystallography (Figure 3). This reaction is

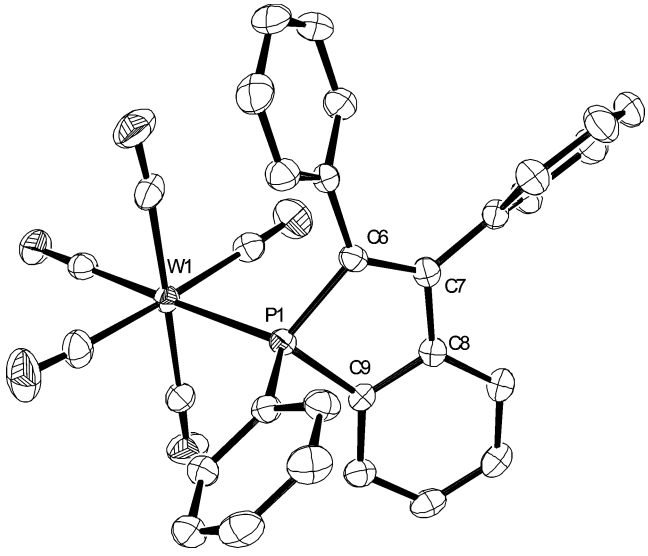


Figure 3. ORTEP diagram showing the molecular structure of **19**. Thermal ellipsoids are shown at the 50% level, and H atoms have been omitted for clarity. Selected distances (Å) and angles (deg): W(1)–P(1) = 2.5141(7), P(1)–C(9) = 1.817(3), C(9)–C(8) = 1.406(4), C(8)–C(7) = 1.474(4), C(6)–C(7) = 1.362(4), P(1)–C(6) = 1.823(3); C(9)–P(1)–C(6) = 91.3(1), C(9)–C(8)–C(7) = 113.9(2), C(6)–C(7)–C(8) = 114.1(2), C(7)–C(6)–P(1) = 110.8(2).

similar to that described above in the reaction with norbornene and is also reminiscent of the route to benzophospholes described by Mathey et al.[24] in which phosphinidene complexes are used to activate aryl C–H bonds, although here P–C and

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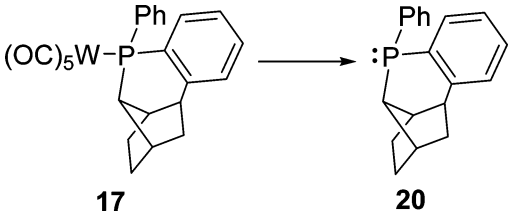
C−C bonds are formed sequentially in the same reaction, and the ring-closing reaction is a C−C bond formation. Metal-free 1,2,3-triphenylbenzophosphole was also previously prepared by oxidative cyclization of diphenylacetylene and diphenylenephosphine oxide, followed by reduction with $HSiCl_3$.[25] In contrast to the reactions described here, reactions of metal-free phosphenium ions with alkynes lead to phosphirenium rings.[26]

Application of the methodology described here to phosphine synthesis requires a means of removing the phosphine from the metal after the reaction. The novel fused-ring phosphine complex $[W(CO)_5\{PPh(C_6H_4C_7H_{10})\}]$ (**17**) was chosen to illustrate the methodology. Photolysis of a THF solution containing **17** and dppe readily afforded the targeted free phosphine **20** in 81% yield (Scheme 10). The $^{31}P\{^1H\}$ NMR

Scheme 10[a]



[a]Reagents and conditions: THF, room temperature, dppe 1.2 equiv, photolysis, 2.5 h.

spectrum of **20** shows a singlet with no W satellites at δ −29.9, and the ^1H NMR spectrum shows signals and splitting patterns similar to those of the metal complex. This methodology is a modification of the method described by Mathey et al., where tungsten phosphine complexes were heated with dppe to remove monodentate phosphines or phospholes.[24,27] The photolysis methodology has the advantages of being faster and cleaner than the method involving heat.

CONCLUSIONS

The phosphenium and phosphine triflate metal complexes **2** and **4** are versatile reagents for the formation of P−C bonds and undergo electrophilic addition reactions with a range of unsaturated organic substrates, including aromatics, heteroaromatics, alkenes, and alkynes. The reactions are much faster than those of metal-free phosphenium ions, and in some cases the reactivity is unique as a result of the protection of the P lone pair. The methodologies described here are useful for the formation of diphenylphosphines with aryl, heteroaryl, alkynyl, and allyl groups in the third position. They can also be used to form P heterocycles through tandem electrophilic addition reactions involving one of the phenyl substituents.

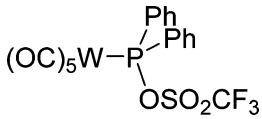
EXPERIMENTAL SECTION

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. CD_2Cl_2 and C_6D_6 were used as received. Solvents for flash chromatography were not purified. Aluminum chloride was purified by sublimation and stored under an inert atmosphere. Photolysis reactions were carried out in Pyrex vessels using a Rayonet 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 (^1H), 121.514 MHz (^{31}P), 75.479 MHz ($^{13}C\{^1H\}$), or 282.231 MHz (^{19}F) in $CDCl_3$, CD_2Cl_2 or C_6D_6. IR spectra were recorded on a Digilab FTIR instrument in CH_2Cl_2 solution. Elemental analyses were carried out by the Analytical and Instrumentation Laboratory in the Department of Chemistry at the University of Alberta. Compounds **1**, **5**, and **8** were synthesized as described previously.[13]

Reaction of $[W(CO)_5\{PPh_2Cl\}]$ (1) with $AlCl_3$. Compounds $[W(CO)_5\{PPh_2Cl\}]$ (**1**; 20 mg, 0.037 mmol) and $AlCl_3$ (14.7 mg, 0.110 mmol) were dissolved in CD_2Cl_2 (0.5 mL), resulting in the immediate formation of a dark yellow solution. $^{31}P\{^1H\}$ NMR (−40 °C): δ 429.2 (s, $^1J_{PW}$ = 353 Hz, **2a**) and 85.7 (s, $^1J_{PW}$ = 215 Hz, **3a**). Note: There was no apparent reaction when 1 equiv of $AlCl_3$ was added to **1**.

Reaction of $[W(CO)_5\{PPh_2Cl\}]$ (1) with $GaCl_3$. Compounds $[W(CO)_5\{PPh_2Cl\}]$ (**1**; 25 mg, 0.046 mmol) and $GaCl_3$ (8.1 mg, 0.046 mmol) were dissolved in CD_2Cl_2 (0.5 mL), resulting in the immediate formation of a dark yellow solution. $^{31}P\{^1H\}$ NMR (CD_2Cl_2, −80 °C): δ 431.1 (s, **2b**) and 96.6 (s, **1**) in a 1:1 ratio. Compounds **1** (25 mg, 0.046 mmol) and $GaCl_3$ (24.3 mg, 0.138 mmol) dissolved in CD_2Cl_2 (0.5 mL) showed only the signal for **2b** at room temperature and −40 °C (δ 429.3 (s, $^1J_{PW}$ = 353 Hz).

$[W(CO)_5\{PPh_2(OSO_2CF_3)\}]$ (4).



The compounds $[W(CO)_5\{PPh_2Cl\}]$ (**1**; 25 mg, 0.046 mmol) and $AgOSO_2CF_3$ (14.2 mg, 0.055 mmol) were dissolved in CH_2Cl_2 (2 mL). This solution was stirred for 2 h, resulting in a yellow solution and a white precipitate. The solution was filtered through Celite. Conversion is quantitative by NMR spectroscopy. This air- and moisture-sensitive solution is stable for days at −20 °C or hours at room temperature. This reaction was also carried out in $CDCl_3$ for NMR spectroscopy. IR (ν_{CO}, CH_2Cl_2, cm^{-1}): 2076 (w), 1941 (vs). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 167.4 (s, $^1J_{PW}$ = 308 Hz). ^{19}F NMR ($CDCl_3$): δ −76.4 (s, OSO_2CF_3). ^1H NMR ($CDCl_3$): δ 7.56−7.70 (m, Ph). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 118.4 (q, $^1J_{CF}$ = 319 Hz, OSO_2CF_3), 129.2 (d, $^3J_{CP}$ = 11 Hz, Ph), 131.6 (d, $^2J_{CP}$ = 15 Hz, Ph), 133.1 (d, $^4J_{CP}$ = 2 Hz, Ph), 137.0 (d, $^1J_{CP}$ = 39 Hz, *ipso*-Ph), 194.7 (d, $^2J_{CP}$ = 8 Hz, $^1J_{CW}$ = 126 Hz, *cis*-CO), 197.6 (d, $^2J_{CP}$ = 33 Hz, *trans*-CO).

$[W(CO)_5\{PPh_2(PPh_3)\}][OSO_2CF_3]$ (6). A solution of $[W(CO)_5\{PPh_2(OSO_2CF_3)\}]$ (**4**) was prepared from $[W(CO)_5\{PPh_2Cl\}]$ (**1**; 90.0 mg, 0.166 mmol) and $AgOSO_2CF_3$ (51 mg, 0.199 mmol) in CH_2Cl_2 (5 mL) as described above. PPh_3 (43.4 mg, 0.166 mmol) was then added, resulting in a color change to yellow. Crystals of $[W(CO)_5\{PPh_2(PPh_3)\}][OSO_2CF_3]\cdot CH_2Cl_2$ (**6**·CH_2Cl_2) were grown by cooling the saturated pentane/CH_2Cl_2 solution to −20 °C. Compound **6**·CH_2Cl_2 is crystalline; however, under reduced pressure it gradually reverts back to the triflate phosphine **4**. Yield: 143 mg, 86%. IR (ν_{CO}, CH_2Cl_2, cm^{-1}): 2074 (w), 1941 (vs). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 12.1 (d, $^1J_{PP}$ = 216 Hz, *P*Ph_3), 41.8 (d, $^1J_{PP}$ = 216 Hz, d, $^1J_{PW}$ = 262 Hz, *P*PPh_3). Anal. Calcd for $[W(CO)_5\{PPh_2(PPh_3)\}]$-$[OSO_2CF_3]\cdot CH_2Cl_2$: C, 44.20; H, 2.71; S, 3.19. Found: C, 44.20, H, 2.73; S, 3.14.

Reaction of $[W(CO)_5\{PPh_2(PPh_3)\}][OSO_2CF_3]$ (6) with NBu_4Cl. Compound **6** (20.0 mg, 0.022 mmol) was dissolved in CH_2Cl_2 (1 mL), and to this solution was added solid NBu_4Cl (6.7 mg, 0.024 mmol). After the addition of NBu_4Cl, the solution immediately turned pale yellow from yellow, and the spectra showed complete reversion to $[W(CO)_5\{PPh_2Cl\}]$ (**1**) and PPh_3. $^{31}P\{^1H\}$ NMR (CH_2Cl_2): δ 93.6 (s, $^1J_{PW}$ = 283 Hz), −6.6 (s, *P*Ph_3).

Reaction of $[W(CO)_5\{PPh_2(PPh_3)\}][OSO_2CF_3]$ (6) with Ferrocene. Compound **6** (35.0 mg, 0.038 mmol) was dissolved in CH_2Cl_2 (2 mL), and to the resulting solution was added solid ferrocene (14.1 mg, 0.076 mmol); this mixture was then stirred for 12 h at room temperature, resulting in a color change to brown. The spectrum showed complete conversion to $[W(CO)_5\{P(C_{10}H_9Fe)Ph_2\}]$ (**5**) and $[HPPh_3][OSO_2CF_3]$. $^{31}P\{^1H\}$ NMR (CH_2Cl_2): δ 9.4 (s, compound **5**), 1.5 (br s, $[HPPh_3][OSO_2CF_3]$).

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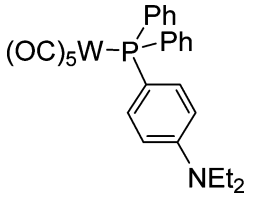
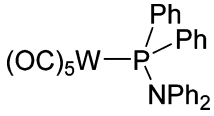
[W(CO)$_5${PPh$_2$(*p*-C$_6$H$_4$N(CH$_2$CH$_3$)$_2$)}] (7).



A solution of [W(CO)$_5${PPh$_2$(OSO$_2$CF$_3$)}] (**4**) was prepared from [W(CO)$_5${PPh$_2$Cl}] (**1**; 80.0 mg, 0.147 mmol) and AgOSO$_2$CF$_3$ (45.4 mg, 0.177 mmol) in CH$_2$Cl$_2$ (4 mL) as described above. *N*,*N*-Diethylaniline (47 μL, 0.294 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, 10/90 v/v diethyl ether/petroleum ether). The yellow product was crystallized by diffusion of pentane into a dichloromethane solution at −20 °C. Yield: 85 mg, 88%. IR (ν_{CO}, CH$_2$Cl$_2$, cm^{-1}): 2071 (w), 1937 (vs). ^{31}P{^{1}H} NMR (CDCl$_3$): δ 18.3 (s, $^1J_{PW}$ = 241 Hz). ^{1}H NMR (CDCl$_3$): δ 1.19 (t, 6H, $^3J_{HH}$ = 6.9 Hz, NCH$_2$C*H*$_3$), 3.39 (q, 4H, $^3J_{HH}$ = 7.2 Hz, NC*H*$_2$CH$_3$), 6.68 (d, 2H, $^3J_{HH}$ = 9.0 Hz, arene CH), 7.32 (dd, 2H, $^3J_{HH}$ = 9.0 Hz, $^3J_{HP}$ = 10.5 Hz, arene CH), 7.42 (m, 10H, Ph). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 12.8 (s, NCH$_2$CH$_3$), 44.5 (s, NCH$_2$CH$_3$), 111.2 (d, $^3J_{CP}$ = 11 Hz, arene C), 117.3 (d, $^1J_{CP}$ = 50. Hz, *ipso*-arene P-bound C), 128.6 (d, $^3J_{CP}$ = 10 Hz, Ph), 130.0 (d, $^4J_{CP}$ = 2 Hz, Ph), 132.8 (d, $^2J_{CP}$ = 12 Hz, Ph), 135.5 (d, $^2J_{CP}$ = 14 Hz, arene C), 137.2 (d, $^1J_{CP}$ = 42 Hz, *ipso*-Ph), 149.3 (s, *ipso*-arene N-bound C), 197.8 (d, $^2J_{CP}$ = 7 Hz, $^1J_{CW}$ = 126 Hz, *cis*-CO), 200.0 (d, $^2J_{CP}$ = 21 Hz, $^1J_{CW}$ = 145 Hz, *trans*-CO). Anal. Calcd for C$_{27}$H$_{24}$NO$_5$PW: C, 49.34; H, 3.68; N, 2.13. Found: C, 49.22, H, 3.69; N, 2.16.

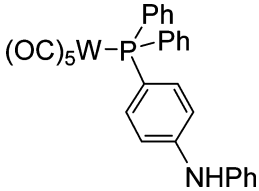
Reaction of [W(CO)$_5${PPh$_2$(OSO$_2$CF$_3$)}] (4) with Diphenylamine. A solution of [W(CO)$_5${PPh$_2$(OSO$_2$CF$_3$)}] (**4**) was prepared from [W(CO)$_5${PPh$_2$Cl}] (**1**; 150 mg, 0.276 mmol) and AgOSO$_2$CF$_3$ (85 mg, 0.331 mmol) in CH$_2$Cl$_2$ (8 mL) as described above. Diphenylamine (51.4 mg, 0.304 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, 10/90 v/v diethyl ether/petroleum ether). Two fractions were collected separately, and the solvent was evaporated under reduced pressure. The first fraction was obtained as yellow crystals and identified as the P−N-bound product **9**. The second fraction was obtained as pale yellow crystals and identified as the P−C bound product **10**.

*Characterization of [W(CO)$_5${PPh$_2$(NPh$_2$)}] (**9**).*



Yield: 93 mg, 50%. IR (ν_{CO}, CH$_2$Cl$_2$, cm^{-1}): 2072 (w), 1942 (vs). ^{31}P{^{1}H} NMR (CDCl$_3$): δ 77.3 (s, $^1J_{PW}$ = 274 Hz). ^{1}H NMR (CDCl$_3$): δ 7.02−7.07 (m, 6H, Ph), 7.12−7.18 (m, 4H, Ph), 7.36−7.44 (m, 6H, Ph), 7.67−7.73 (m, 4H, Ph). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 125.3 (s, N-bound Ph), 128.2 (d, $^3J_{CP}$ = 3 Hz, N-bound Ph), 128.5 (d, $^3J_{CP}$ = 10 Hz, P-bound Ph), 129.3 (s, N-bound Ph), 130.4 (d, $^4J_{CP}$ = 2 Hz, P-bound Ph), 132.4 (d, $^2J_{CP}$ = 13 Hz, P-bound Ph), 137.8 (d, $^1J_{CP}$ = 42 Hz, P-bound *ipso*-Ph), 146.3 (d, $^2J_{CP}$ = 5 Hz, N-bound *ipso*-Ph), 197.1 (d, $^2J_{CP}$ = 7 Hz, $^1J_{CW}$ = 127 Hz, *cis*-CO), 199.5 (d, $^2J_{CP}$ = 26 Hz, *trans*-CO). Anal. Calcd for C$_{29}$H$_{20}$NO$_5$PW: C, 51.43; H, 2.98; N, 2.07. Found: C, 51.47, H, 2.98; N, 2.12.

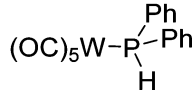
*Characterization of [W(CO)$_5${PPh$_2$(*p*-C$_6$H$_4$NH(Ph)}] (**10**).*



Yield: 62 mg, 33%. IR (ν_{CO}, CH$_2$Cl$_2$, cm^{-1}): 2071 (w), 1937 (vs). ^{31}P{^{1}H} NMR (CDCl$_3$): δ 19.7 (s, $^1J_{PW}$ = 243 Hz). ^{1}H NMR (CDCl$_3$): δ 5.92 (br s, 1H, N*H*), 7.03−7.06 (m, 3H, N-bound Ph), 7.16 (dd, 2H, $^3J_{HH}$ = 7.2 Hz, $^4J_{HH}$ = 0.9 Hz, -C$_6$*H*$_4$NH(Ph)), 7.30−7.51 (m, 14H, 2H of −C$_6$*H*$_4$NH(Ph), 2H of N-bound Ph, 10H of P-bound Ph). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 115.7 (d, $^3J_{CP}$ = 11 Hz, −C$_6$H$_4$NH(Ph)), 120.4 (s, N-bound Ph), 123.2 (s, N-bound Ph), 124.1 (d, $^1J_{CP}$ = 47 Hz, *ipso*-C$_6$H$_4$NH(Ph), 128.8 (d, $^3J_{CP}$ = 10 Hz, P-bound Ph), 129.7 (s, N-bound Ph), 130.3 (d, $^4J_{CP}$ = 2 Hz, P-bound Ph), 132.9 (d, $^2J_{CP}$ = 11 Hz, P-bound Ph), 135.2 (d, $^2J_{CP}$ = 14 Hz, −C$_6$H$_4$NH(Ph), 136.4 (d, $^1J_{CP}$ = 41 Hz, P-bound *ipso*-Ph), 141.2 (s, N-bound *ipso*-Ph), 146.1 (s, d, *ipso*−C$_6$H$_4$NH(Ph)), 197.7 (d, $^2J_{CP}$ = 7 Hz, $^1J_{CW}$ = 126 Hz, *cis*-CO), 199.7 (d, $^2J_{CP}$ = 21 Hz, *trans*-CO). Anal. Calcd for C$_{29}$H$_{20}$NO$_5$PW: C, 51.43; H, 2.98; N, 2.07. Found: C, 51.59, H, 2.99; N, 2.13.

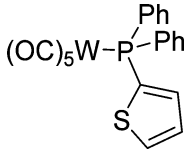
Reaction of [W(CO)$_5${PPh$_2$Cl}] (1) with Diphenylamine and AlCl$_3$. The compound [W(CO)$_5${PPh$_2$Cl}] (**1**; 80 mg, 0.147 mmol) and AlCl$_3$ (39.3 mg, 0.294 mmol) were dissolved in CH$_2$Cl$_2$ (4 mL). This solution was stirred for 5 min, resulting in a yellow solution. Diphenylamine (27.4 mg, 0.162 mmol) was added, and the solution was stirred for 12 h at room temperature, resulting in a color change to dark yellow. The ^{31}P NMR spectrum of the reaction solution shows that **10** is the major product and that **9** is not formed. The solvent was removed under reduced pressure, and compound **10** was purified by flash chromatography (alumina, 10/90 v/v diethyl ether/petroleum ether). Yield: 78 mg, 78%.

Reaction of [W(CO)$_5${PPh$_2$(OSO$_2$CF$_3$)}] (4) with *N*,*N*-Dimethyl-*p*-toluidine.



A solution of [W(CO)$_5${PPh$_2$(OSO$_2$CF$_3$)}] (**4**) was prepared from [W(CO)$_5${PPh$_2$Cl)}] (**1**; 80.0 mg, 0.147 mmol) and AgOSO$_2$CF$_3$ (48.7 mg, 0.191 mmol) in CH$_2$Cl$_2$ (4 mL) as described above. *N*,*N*-Dimethyl-*p*-toluidine (43 μL, 0.294 mmol) was added, and the solution was stirred for 30 min, 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) and crystallized as colorless crystals by cooling a saturated pentane/CH$_2$Cl$_2$ solution to −20 °C, yielding crystals of the known compound [W(CO)$_5${PHPh$_2$}]. Yield: 67 mg, 89%. ^{31}P NMR (CDCl$_3$): δ −12.5 (dm, $^1J_{PW}$ = 230 Hz, $^1J_{PH}$ = 346 Hz). ^{1}H NMR (CDCl$_3$): δ 6.84 (d, 1H, $^1J_{HP}$ = 345 Hz, P*H*), 7.41−7.60 (m, 10H, Ph). These spectroscopic data match previously published data.[28]

[W(CO)$_5${PPh$_2$(2-C$_4$H$_3$S)}] (11).



A solution of [W(CO)$_5${PPh$_2$(OSO$_2$CF$_3$)}] (**4**) was prepared from [W(CO)$_5${PPh$_2$Cl}] (**1**; 90.0 mg, 0.166 mmol) and AgOSO$_2$CF$_3$ (51.1 mg, 0.199 mmol) in CH$_2$Cl$_2$ (5 mL) as described above. Thiophene (40 μL, 0.497 mmol) was added, resulting in a color change to red. 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 slow diffusion of pentane into a saturated CH$_2$Cl$_2$ solution at −20 °C. Yield: 71 mg, 72%. IR (ν_{CO}, CH$_2$Cl$_2$, cm^{-1}): 2073 (w), 1946 (vs). ^{31}P{^{1}H} NMR (CDCl$_3$): δ 7.7 (s, $^1J_{PW}$ = 247 Hz). ^{1}H NMR (CDCl$_3$): δ 7.21 (m, 1H, C$_4$*H*$_3$S), 7.36 (m, 1H, C$_4$*H*$_3$S), 7.43−7.50 (m, 10H, Ph), 7.68 (m, 1H, C$_4$*H*$_3$S). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 128.6 (s, C$_4$H$_3$S), 128.8 (d, $^3J_{CP}$ = 10 Hz, Ph), 130.7 (d, $^4J_{CP}$ = 2 Hz, Ph), 132.4 (d, $^2J_{CP}$ = 13 Hz, Ph), 133.5 (d, $^3J_{CP}$ = 3 Hz, C$_4$H$_3$S), 136.5 (d, $^1J_{CP}$ = 44 Hz, *ipso*-Ph), 137.5 (d, $^2J_{CP}$ = 11 Hz, C$_4$H$_3$S), 137.8 (d, $^1J_{CP}$ = 39 Hz, *ipso*-C$_4$H$_3$S),197.3 (d, $^2J_{CP}$ = 7 Hz, $^1J_{CW}$ = 126 Hz, *cis*-CO), 199.2 (d, $^2J_{CP}$ = 22 Hz, *trans*-CO). Anal. Calcd for C$_{21}$H$_{13}$O$_5$PSW: C, 42.59; H, 2.21; S, 5.41. Found: C, 42.42; H, 2.31; S, 5.46.

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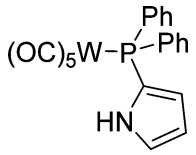
Organometallics XXXX, XXX, XXX−XXX

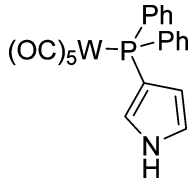
Reaction of $[W(CO)_5\{PPh_2(OSO_2CF_3)\}]$ (4) with Pyrrole. A solution of $[W(CO)_5\{PPh_2(OSO_2CF_3)\}]$ (**4**) was prepared from $[W(CO)_5\{PPh_2Cl\}]$ (**1**; 200 mg, 0.368 mmol) and $AgOSO_2CF_3$ (113 mg, 0.442 mmol) in CH_2Cl_2 (8 mL) as described above. Pyrrole (102 μL, 1.472 mmol) was then added, resulting in a color change to brown. The solvent was removed under reduced pressure, and the residue was purified by flash chromatography (silica, 10/90 v/v diethyl ether/petroleum ether). Two fractions were collected separately, and the solvent was evaporated under reduced pressure. Both fractions were obtained as pale yellow powders. The first fraction was identified as the C2-substituted isomer $[W(CO)_5\{PPh_2(2\text{-}C_4H_3NH)\}]$ (**12**) and the second fraction as the C3-substituted isomer $[W(CO)_5\{PPh_2(3\text{-}C_4H_3NH)\}]$ (**13**).

*Characterization of $[W(CO)_5\{PPh_2(2\text{-}C_4H_3NH)\}]$ (**12**).*



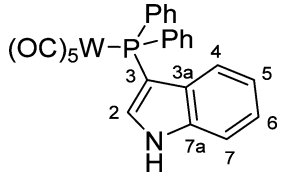
Yield: 83 mg, 39%. IR (ν_{CO}, CH_2Cl_2, cm^{-1}): 2072 (w), 1939 (vs). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 0.2 (s, $^1J_{PW}$ = 244 Hz). ^1H NMR ($CDCl_3$): δ 6.39 (m, 1H, C_4H_3NH), 6.81 (m, 1H, C_4H_3NH), 7.04 (m, 1H, C_4H_3NH), 7.35–7.48 (m, 10H, Ph), 7.98 (br s, 1H, N*H*). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 110.9 (d, $^3J_{CP}$ = 10 Hz, C_4H_3NH), 122.1 (d, $^2J_{CP}$ = 18 Hz, C_4H_3NH), 122.6 (d, $^1J_{CP}$ = 54 Hz, *ipso*-C_4H_3NH), 124.3 (d, $^3J_{CP}$ = 4 Hz, C_4H_3NH), 129.0 (d, $^3J_{CP}$ = 10 Hz, Ph), 130.6 (d, $^4J_{CP}$ = 2 Hz, Ph), 132.1 (d, $^2J_{CP}$ = 12 Hz, Ph), 135.8 (d, $^1J_{CP}$ = 44 Hz, *ipso*-Ph), 197.3 (d, $^2J_{CP}$ = 7 Hz, $^1J_{CW}$ = 126.1 Hz, *cis*-CO), 199.3 (d, $^2J_{CP}$ = 21 Hz, $^1J_{CW}$ = 143 Hz, *trans*-CO). Anal. Calcd for $C_{21}H_{14}NO_5PW$: C, 43.85; H, 2.45; N, 2.44. Found: C, 43.63, H, 2.51; N, 2.48.

*Characterization of $[W(CO)_5\{PPh_2(3\text{-}C_4H_3NH)\}]$ (**13**).*



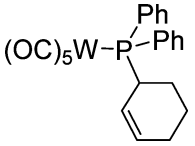
Yield: 99 mg, 47%. IR (ν_{CO}, CH_2Cl_2, cm^{-1}): 2070 (w), 1936 (vs). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ - 0.4 (s, $^1J_{PW}$ = 240 Hz). ^1H NMR ($CDCl_3$): δ 6.22 (m, 1H, C_4H_3NH), 6.94 (m, 2H, C_4H_3NH), 7.36–7.52 (m, 10H, Ph), 8.54 (br s, 1H, N*H*). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 113.5 (d, $^2J_{CP}$ = 9 Hz, C_4H_3NH), 115.7 (d, $^1J_{CP}$ = 59 Hz, *ipso*-C_4H_3NH), 120.5 (d, $^3J_{CP}$ = 10 Hz, C_4H_3NH), 126.4 (d, $^2J_{CP}$ = 24 Hz, C_4H_3NH), 128.6 (d, $^3J_{CP}$ = 10 Hz, Ph), 130.0 (d, $^4J_{CP}$ = 2 Hz, Ph), 132.4 (d, $^2J_{CP}$ = 12 Hz, Ph), 137.4 (d, $^1J_{CP}$ = 45 Hz, *ipso*-Ph), 197.8 (d, $^2J_{CP}$ = 7 Hz, $^1J_{CW}$ = 126 Hz, *cis*-CO), 200.0 (d, $^2J_{CP}$ = 20 Hz, $^1J_{CW}$ = 144 Hz, *trans*-CO). Anal. Calcd for $C_{21}H_{14}NO_5PW$: C, 43.85; H, 2.45; N, 2.44. Found: C, 43.76, H, 2.50; N, 2.45.

$[W(CO)_5\{P(3\text{-}C_8H_5NH)Ph_2\}]$ (14).



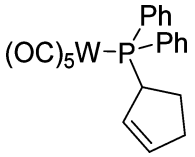
A solution of $[W(CO)_5\{PPh_2(OSO_2CF_3)\}]$ (**4**) was prepared from $[W(CO)_5\{PPh_2Cl\}]$ (**1**; 120.0 mg, 0.221 mmol) and $AgOSO_2CF_3$ (73.7 mg, 0.265 mmol) in CH_2Cl_2 (5 mL) as described above. A solution of indole (51.7 mg, 0.442 mmol) in CH_2Cl_2 (5 mL) was added, and the mixture was stirred at room temperature for 15 min, resulting in a color change to orange. The solvent was removed under reduced pressure, and the residue was purified by flash chromatography (alumina, 20/80 v/v diethyl ether/petroleum ether). The white product was crystallized by slow diffusion of pentane into a saturated CH_2Cl_2 solution at −20 °C. Yield: 115 mg, 83%. IR (ν_{CO}, CH_2Cl_2, cm^{-1}): 2071 (w), 1937 (vs). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ −2.4 (s, $^1J_{PW}$ = 240 Hz). ^1H NMR ($CDCl_3$): δ 6.95 (m, 2H, C_8H_5NH), 7.21 (m, 1H, C_8H_5NH), 7.37–7.46 (m, 7H, 1H of C_8H_5NH and 6H of Ph), 7.56–7.62 (m, 4H, Ph), 7.69 (m, 1H, C_8H_5NH), 8.60 (br s, 1H, C_8H_5NH). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 107.5 (d, $^1J_{CP}$ = 57 Hz, C^3), 112.1 (s, C^7), 121.1 (s, C^4), 122.1 (s, C^6), 123.4 (s, C^5), 127.8 (d, $^2J_{CP}$ = 3 Hz, C^{3a}), 128.7 (d, $^3J_{CP}$ = 10 Hz, Ph), 130.1 (d, $^4J_{CP}$ = 2 Hz, Ph), 132.3 (d, $^2J_{CP}$ = 12 Hz, Ph), 135.2 (d, $^2J_{CP}$ = 25 Hz, C^2), 135.7 (d, $^1J_{CP}$ = 39 Hz, *ipso*-Ph), 138.0 (d, J_{CP} = 7 Hz, C^{7a}), 197.9 (d, $^2J_{CP}$ = 7 Hz, $^1J_{CW}$ = 126 Hz, *cis*-CO), 199.8 (d, $^2J_{CP}$ = 21 Hz, *trans*-CO). Anal. Calcd for $C_{25}H_{16}NO_5PW$: C, 48.03; H, 2.58; N, 2.24. Found: C, 48.02, H, 2.21; N, 2.23.

$[W(CO)_5\{PPh_2(C_6H_9)\}]$ (15).



A solution of $[W(CO)_5\{PPh_2(OSO_2CF_3)\}]$ (**4**) was prepared from $[W(CO)_5\{PPh_2Cl\}]$ (**1**; 80.0 mg, 0.147 mmol) and $AgOSO_2CF_3$ (45.4 mg, 0.177 mmol) in CH_2Cl_2 (5 mL) as described above. Cyclohexene (149 μL, 1.472 mmol) was then added, and the solution was stirred at room temperature for 8 h, resulting in a color change to yellow from pale yellow. The solvent was removed under reduced pressure, and the residue was purified by flash chromatography (silica, 10/90 v/v diethyl ether/petroleum ether). The pale yellow crystals of $[W(CO)_5\{PPh_2(C_6H_9)\}]$ (**15**) were obtained by cooling a saturated pentane solution to −20 °C. Yield: 73 mg, 84%. IR (ν_{CO}, CH_2Cl_2, cm^{-1}): 2070 (w), 1936 (vs). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 24.1 (s, $^1J_{PW}$ = 241 Hz). ^1H NMR ($CDCl_3$): δ 1.27–1.78 (m, 4H, C_6H_9), 1.94–2.05 (m, 2H, C_6H_9), 3.42 (m, 1H, C_6H_9), 5.83 (m, 2H, C_6H_9), 7.35–7.47 (m, 8H, Ph), 7.61–7.70 (m, 2H, Ph). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 22.3 (d, $^2J_{CP}$ = 11 Hz, C_6H_9), 25.0 (d, $^4J_{CP}$ = 2 Hz, C_6H_9), 25.3 (d, $^3J_{CP}$ = 5 Hz, C_6H_9), 38.2 (d, $^1J_{CP}$ = 24 Hz, C_6H_9), 124.4 (d, $^3J_{CP}$ = 4 Hz, C_6H_9), 128.5 (d, $^3J_{CP}$ = 10 Hz, Ph), 128.9 (d, $^3J_{CP}$ = 9 Hz, Ph), 129.9 (d, $^4J_{CP}$ = 2 Hz, Ph), 130.8 (d, $^4J_{CP}$ = 2 Hz, Ph), 131.9 (d, $^2J_{CP}$ = 10 Hz, Ph), 132.5 (d, $^1J_{CP}$ = 47 Hz, *ipso*-Ph), 132.7 (d, $^2J_{CP}$ = 8 Hz, C_6H_9), 134.5 (d, $^2J_{CP}$ = 11 Hz, Ph), 136.5 (d, $^1J_{CP}$ = 38 Hz, *ipso*-Ph), 197.4 (d, $^2J_{CP}$ = 7 Hz, $^1J_{CW}$ = 126 Hz, *cis*-CO), 199.5 (d, $^2J_{CP}$ = 22.0 Hz, *trans*-CO). Anal. Calcd. for $C_{23}H_{19}O_5PW$: C, 46.81; H, 3.24. Found: C, 46.68; H, 3.27.

$[W(CO)_5\{PPh_2(C_5H_7)\}]$ (16).



A solution of $[W(CO)_5\{PPh_2(OSO_2CF_3)\}]$ (**4**) was prepared from $[W(CO)_5\{PPh_2Cl\}]$ (**1**; 95.0 mg, 0.175 mmol) and $AgOSO_2CF_3$ (53.9 mg, 0.210 mmol) in CH_2Cl_2 (5 mL) as described above. Cyclopentene (160 μL, 1.758 mmol) was then added, and the solution was stirred at room temperature for 8 h, resulting in a color change to yellow from pale yellow. The solvent was removed under reduced pressure, and the residue was purified by flash chromatography (silica, 10/90 v/v diethyl ether/petroleum ether). Pale yellow crystals of $[W(CO)_5\{PPh_2(C_5H_7)\}]$ (**16**) were obtained by cooling a saturated pentane solution to −20 °C. Yield: 94 mg, 93%. IR (ν_{CO}, CH_2Cl_2, cm^{-1}): 2070 (w), 1935 (vs). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 22.0 (s, $^1J_{PW}$ = 240 Hz). ^1H NMR ($CDCl_3$): δ 1.54 (m, 1H, C_5H_7), 1.95 (m, 1H, C_5H_7), 2.16 (m, 1H, C_5H_7), 2.32 (m, 1H, C_5H_7), 3.96 (m, 1H, C_5H_7), 5.80 (m, 2H, C_5H_7), 7.38–7.52 (m, 8H, Ph), 7.56–7.65 (m, 2H, Ph). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 26.5 (d, $^2J_{CP}$ = 3 Hz, C_5H_7), 32.3 (d, $^3J_{CP}$ = 1 Hz, C_5H_7), 48.8 (d, $^1J_{CP}$ = 23 Hz, C_5H_7), 128.2 (d, $^3J_{CP}$ = 4 Hz, C_5H_7), 128.5 (d, $^3J_{CP}$ = 10 Hz, Ph), 128.7 (d, $^3J_{CP}$ = 9 Hz, Ph), 130.0 (d, $^4J_{CP}$ = 2 Hz, Ph), 130.6 (d, $^4J_{CP}$ = 2 Hz, Ph), 132.1 (d, $^2J_{CP}$ = 10 Hz, Ph), 133.5 (d, $^1J_{CP}$ = 38 Hz, *ipso*-Ph), 134.1 (d, $^2J_{CP}$ = 11 Hz, Ph), 136.0 (d, $^2J_{CP}$ = 10 Hz, C_5H_7), 136.3 (d, $^1J_{CP}$ = 39 Hz, *ipso*-Ph), 197.5 (d, $^2J_{CP}$ = 7 Hz, $^1J_{CW}$ = 126 Hz,

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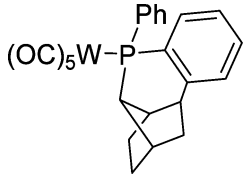
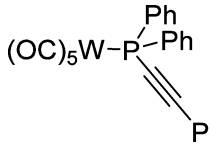
cis-CO), 199.6 (d, $^2J_{CP}$ = 22 Hz, $^1J_{CW}$ = 143 Hz, *trans*-CO). Anal. Calcd. for $C_{22}H_{17}O_5PW$: C, 45.86; H, 2.97. Found: C, 46.02; H, 3.03.

[W(CO)$_5${PPh(C$_6$H$_4$C$_7$H$_{10}$)}] (17).



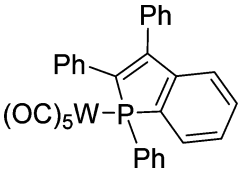
A solution of [W(CO)$_5${PPh$_2$(OSO$_2$CF$_3$)}] (**4**) was prepared from [W(CO)$_5${PPh$_2$Cl}] (**1**; 140.0 mg, 0.258 mmol) and AgOSO$_2$CF$_3$ (79.4 mg, 0.309 mmol) in CH_2Cl_2 (5 mL) as described above. Norbornene (122 mg, 1.288 mmol) was then added, and the solution was stirred at room temperature for 1 h, resulting in a color change to brown. The solvent was removed under reduced pressure, and the residue was purified by flash chromatography (silica, 10/90 v/v diethyl ether/petroleum ether). Pale yellow crystals of [W(CO)$_5${PPh-(C$_6$H$_4$C$_7$H$_{10}$)}] (**17**) were obtained by cooling a saturated pentane/CH_2Cl_2 solution to −20 °C. Yield: 119 mg, 77%. IR (ν_{CO}, CH_2Cl_2, cm^{-1}): 2071 (w), 1937 (vs). ^{31}P{^{1}H} NMR ($CDCl_3$): δ − 4.5 (s, $^1J_{PW}$ = 239 Hz). ^{1}H NMR ($CDCl_3$): δ 1.38−1.91 (m, 6H, C$_6$H$_4$C$_7$*H*$_{10}$), 2.07−2.13 (m, 2H, C$_6$H$_4$C$_7$*H*$_{10}$), 2.77 (d, *J* = 8 Hz, 1H, C$_6$H$_4$C$_7$*H*$_{10}$), 2.88 (m, 1H, C$_6$H$_4$C$_7$*H*$_{10}$), 7.15 (m, 1H, C$_6$*H*$_4$C$_7$H$_{10}$), 7.26−7.41 (m, 7H, 2H of C$_6$*H*$_4$C$_7$H$_{10}$ and 5H of Ph), 7.52−7.59 (m, 1H, C$_6$*H*$_4$C$_7$H$_{10}$). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 28.7 (d, $^4J_{CP}$ = 9 Hz, *C*H$_2$ of C$_6$H$_4$C$_7$H$_{10}$), 31.2 (d, $^3J_{CP}$ = 13 Hz, *C*H$_2$ of C$_6$H$_4$C$_7$H$_{10}$), 40.7 (s, *C*H$_2$ of C$_6$H$_4$C$_7$H$_{10}$), 41.2 (d, $^3J_{CP}$ = 5 Hz, *C*H of C$_6$H$_4$C$_7$H$_{10}$), 41.6 (d, $^2J_{CP}$ = 7 Hz, *C*H of C$_6$H$_4$C$_7$H$_{10}$), 45.9 (d, $^2J_{CP}$ = 3 Hz, *C*H of C$_6$H$_4$C$_7$H$_{10}$), 53.0 (d, $^1J_{CP}$ = 23 Hz, *C*H of C$_6$H$_4$C$_7$H$_{10}$), 126.7 (d, $^3J_{CP}$ = 11 Hz, C$_6$H$_4$C$_7$H$_{10}$), 127.5 (d, $^3J_{CP}$ = 6 Hz, C$_6$H$_4$C$_7$H$_{10}$), 127.6 (d, $^1J_{CP}$ = 37 Hz, *ipso*-C$_6$H$_4$C$_7$H$_{10}$), 128.6 (d, $^3J_{CP}$ = 10 Hz, Ph), 129.8 (d, $^4J_{CP}$ = 2 Hz, C$_6$H$_4$C$_7$H$_{10}$), 130.4 (d, $^4J_{CP}$ = 2 Hz, Ph), 131.6 (d, $^2J_{CP}$ = 11 Hz, Ph), 135.4 (d, $^2J_{CP}$ = 15 Hz, C$_6$H$_4$C$_7$H$_{10}$), 139.3 (d, $^1J_{CP}$ = 37 Hz, *ipso*-Ph), 151.4 (d, $^2J_{CP}$ = 3 Hz, *ipso*-C$_6$H$_4$C$_7$H$_{10}$), 197.5 (d, $^2J_{CP}$ = 7 Hz, $^1J_{CW}$ = 126 Hz, *cis*-CO), 198.9 (d, $^2J_{CP}$ = 21 Hz, *trans*-CO). Anal. Calcd for $C_{24}H_{19}O_5PW$: C, 47.87; H, 3.18. Found: C, 47.97; H, 3.20.

[W(CO)$_5${PPh$_2$(C$_2$Ph)}] (18).



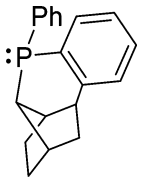
A solution of [W(CO)$_5${PPh$_2$(OSO$_2$CF$_3$)}] (**4**) was prepared from [W(CO)$_5${PPh$_2$Cl}] (**1**; 100.0 mg, 0.184 mmol) and AgOSO$_2$CF$_3$ (56.7 mg, 0.221 mmol) in CH_2Cl_2 (5 mL) as described above. Phenylacetylene (40.4 μL, 0.368 mmol) was added, and the mixture was stirred for 10 min at room temperature, resulting in a color change to brown. The solvent was removed in vacuo, and the residue was purified by flash chromatography (silica gel, 5/95 v/v diethyl ether/petroleum ether). Yellow crystals of [W(CO)$_5${PPh$_2$(C$_2$Ph)}] (**18**) were obtained by cooling a saturated pentane solution to −20 °C. Yield: 89 mg, 79%. IR (ν_{CO}, CH_2Cl_2, cm^{-1}): 2074 (w), 1942 (vs). ^{31}P{^{1}H} NMR ($CDCl_3$): δ −7.0 (s, $^1J_{PW}$ = 244 Hz). ^{1}H NMR ($CDCl_3$): δ 7.37−7.52 (m, 9H), 7.61−7.65 (m, 2H), 7.73−7.80 (m, 4H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 83.2 (d, $^1J_{CP}$ = 84 Hz, CCPh), 110.5 (d, $^2J_{CP}$ = 14 Hz, CCPh), 121.2 (d, $^3J_{CP}$ = 2 Hz, *ipso*-Ph of alkyne substituent), 128.9 (d, $^3J_{CP}$ = 14 Hz, Ph), 129.1 (s, alkyne-Ph), 130.5 (s, alkyne-Ph), 130.8 (d, $^4J_{CP}$ = 2 Hz, Ph), 131.5 (d, $^2J_{CP}$ = 14 Hz, Ph), 132.7 (s, alkyne-Ph), 135.2 (d, $^1J_{CP}$ = 49 Hz, *ipso*-Ph), 197.0 (d, $^2J_{CP}$ = 7 Hz, $^1J_{CW}$ = 126 Hz, *cis*-CO), 199.7 (d, $^2J_{CP}$ = 22 Hz, *trans*-CO). Compound **18** is a known compound, having been previously prepared by an alternate route. These spectroscopic data match previously published data.[23]

[W(CO)$_5${PPh(C$_6$H$_4$C(Ph)C(Ph)}] (19).



A solution of [W(CO)$_5${PPh$_2$(OSO$_2$CF$_3$)}] (**4**) was prepared from [W(CO)$_5${PPh$_2$Cl}] (**1**; 160 mg, 0.294 mmol) and AgOSO$_2$CF$_3$ (91 mg, 0.353 mmol) in CH_2Cl_2 (8 mL) as described above. Diphenylacetylene (131 mg, 0.736 mmol) was then added, and the mixture was stirred for 30 min at room temperature, resulting in a color change to brown. The solvent was removed under reduced pressure, and the residue was purified by flash chromatography (silica gel, 10/90 v/v diethyl ether/petroleum ether). Yellow crystals of [W(CO)$_5${PPh(C$_6$H$_4$C(Ph)C(Ph)}] (**19**) were obtained by cooling a saturated CH_2Cl_2/pentane solution to −20 °C. Yield: 117 mg. 58%. IR (ν_{CO}, CH_2Cl_2, cm^{-1}): 2073 (w), 1940 (vs). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 25.8 (s, $^1J_{PW}$ = 234 Hz). ^{1}H NMR ($CDCl_3$): δ 6.74−7.73 (m, 19H, 4H of arene, 15H of Ph). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 125.0 (d, J_{CP} = 6 Hz), 128.1 (d, J_{CP} = 2 Hz), 128.2 (d, J_{CP} = 10 Hz), 128.4 (s), 128.5 (s), 129.0 (s), 129.4 (d, J_{CP} = 14 Hz), 129.4 (s), 129.6 (s), 130.0 (s), 130.0 (s), 130.7 (d, J_{CP} = 2 Hz), 131.2 (s), 131.6 (d, J_{CP} = 2 Hz), 133.0 (d, J_{CP} = 14 Hz), 134.6 (d, J_{CP} = 14 Hz), 135.2 (d, J_{CP} = 9 Hz), 142.1 (d, $^1J_{CP}$ = 48 Hz), 143.3 (d, $^1J_{CP}$ = 38 Hz), 145.0 (d, J_{CP} = 12 Hz), 147.1 (d, J_{CP} = 10 Hz), 196.2 (d, $^2J_{CP}$ = 7 Hz, $^1J_{CW}$ = 125 Hz, *cis*-CO), 198.3 (d, $^2J_{CP}$ = 21 Hz, *trans*-CO). Anal. Calcd. for $C_{31}H_{19}O_5PW$: C, 54.25; H, 2.79. Found: C, 53.91; H, 2.82.

{PPh(C$_6$H$_4$C$_7$H$_{10}$)} (20).



Compounds **17** (80 mg, 0.133 mmol) and dppe (63.5 mg, 0.159 mmol) were dissolved in THF (3 mL) and irradiated with UV for 2.5 h, resulting in a color change from colorless to yellow. The solvent was removed under reduced pressure, and the residue was purified by flash chromatography (alumina, 20/80 v/v diethyl ether/petroleum ether). After purification, the free phosphine {PPh(C$_6$H$_4$C$_7$H$_{10}$)} (**20**) was obtained as a yellow oil. Yield: 30 mg, 81%. ^{31}P{^{1}H} NMR (C_6D_6): δ − 29.9 (s). ^{1}H NMR (C_6D_6): δ 0.97−1.28 (m, 5H, C$_6$H$_4$C$_7$*H*$_{10}$), 1.43−1.60 (m, 3H, C$_6$H$_4$C$_7$*H*$_{10}$), 2.01 (m, 1H, C$_6$H$_4$C$_7$*H*$_{10}$), 2.41−2.47 (m, 1H, C$_6$H$_4$C$_7$*H*$_{10}$), 6.88−7.48 (m, 9H, 4H of C$_6$*H*$_4$C$_7$H$_{10}$ and 5H of Ph). ^{13}C{^{1}H} NMR (C_6D_6): δ 27.7 (d, J_{CP} = 3 Hz, *C*H$_2$ of C$_6$H$_4$C$_7$H$_{10}$), 30.6 (d, J_{CP} = 13 Hz, *C*H$_2$ of C$_6$H$_4$C$_7$H$_{10}$), 38.0 (d, J_{CP} = 3.9 Hz, *C*H of C$_6$H$_4$C$_7$H$_{10}$), 40.5 (d, J_{CP} = 2 Hz, *C*H$_2$ of C$_6$H$_4$C$_7$H$_{10}$), 41.6 (d, J_{CP} = 24 Hz, *C*H of C$_6$H$_4$C$_7$H$_{10}$), 46.3 (s, *C*H of C$_6$H$_4$C$_7$H$_{10}$), 46.87 (d, J_{CP} = 14 Hz, *C*H of C$_6$H$_4$C$_7$H$_{10}$), 126.3 (d, J_{CP} = 7 Hz, C$_6$H$_4$C$_7$H$_{10}$), 126.7 (s, C$_6$H$_4$C$_7$H$_{10}$), 127.2 (s, C$_6$H$_4$C$_7$H$_{10}$), 128.5 (s, Ph), 128.6 (s, C$_6$H$_4$C$_7$H$_{10}$), 128.8 (d, J_{CP} = 1 Hz, Ph), 133.1 (d, J_{CP} = 14 Hz, Ph), 133.8 (d, J_{CP} = 23 Hz, C$_6$H$_4$C$_7$H$_{10}$), 133.83 (s, Ph), 134.10 (s, C$_6$H$_4$C$_7$H$_{10}$). Note: Because compound **20** is an oil, complete removal of trace solvent was not possible, and satifactory elemental analysis could not be obtained. Spectra are provided in the Supporting Information.

X-ray Crystallography. X-ray quality crystals of **17** were grown by evaporation of the diethyl ether solution at room temperature. Crystals of **19** were grown by slow diffusion of pentane into a saturated CH_2Cl_2 solution at −20 °C. 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. Unit cells were 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,

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and an absorption correction was performed using SADABS. Structure solution was carried out using the SHELX[29] suite of programs and the WinGX graphical interface.[30] Initial solutions were obtained by direct methods and refined by successive least-squares cycles. All non-hydrogen atoms were refined anisotropically.

Computational Details. All calculations were performed with the hybrid DFT functional B3LYP,[31] as implemented in the Gaussian 09 (revision C.01 or D.01) software program.[32] Basis sets used for geometry optimizations and frequency calculations were LANL2DZ for W and 6-31G(d,p) for other atoms (H, C, O, F, P, Al, Ga, and Cl). The keywords used in the input files for optimization and frequency calculations were *# opt freq rb3lyp gen (pseudo = read was included when a transition metal is present)*. Single-point energies were computed at the B3LYP/LANL2TZ(F)/6-311g+(2d,p) level of theory with an added polarizable continuum model (SCRF = IEFPCM) to account for the dichloromethane solvent effect.[33] The LANL2TZ(f)[34] basis set information was obtained from the EMSL basis set library.[35] Phosphorus-31 NMR shielding constants, σ, were calculated on the optimized structures using the gauge-independent atomic orbital method (GIAO)[36] with basis sets LANL2TZ(f) on W and 6-311g +(2d,p) on other atoms. The keywords used in the input files for NMR calculations were *# NMR = giao rb3lyp gen (pseudo = read was included when a transition metal is present)*. Phosphorus-31 chemical shift values, δ, of the studied phosphorus compounds were obtained by substituting the computed isotropic shielding constant values into eq 1. Since calculating σ for aqueous H_3PO_4 is not practical, we used one of our complexes (compound **1**, δ_{exptl} 95.7 ppm) as a standard. A similar approach has also been used previously to calculate δ on a variety of organophosphorus compounds.[37]

$$\delta(\text{studied compound}) = \sigma(\text{standard}) - \sigma(\text{studied compound}) + \delta(\text{standard}) \quad (1)$$

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.6b00348.

NMR spectra for all new compounds and optimized structures, numbers of imaginary frequencies, absolute energies, ^{31}P NMR shielding constants, NBO charges, and Cartesian coordinates (PDF)

Crystallographic data for compounds **17** and **19** (CIF)

Coordinates of calculated structures (XYZ)

■ AUTHOR INFORMATION

Corresponding Author

*E-mail for B.T.S.: brian.sterenberg@uregina.ca.

Notes

The authors declare no competing financial interest.

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