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Reactivity of 2-Silyl- and 2-Stannyl-Substituted Phosphirenes

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Summary: Two methodologies have been tested for the functionalization of phosphirenes. In the first one, the C−Si bond of a 2-silylphosphirene is activated by a substoichiometric quantity of fluoride ion (TBAF) in THF at −78 °C. Using this technique, it is possible to perform a protodesilylation or a functionalization by benzaldehyde. However, at room temperature with a stoichiometry of fluoride, a nucleophilic attack takes place at P, leading to a ring-opened fluorophosphine. Stille cross-coupling with a 2-stannylphosphirene in the presence of [PdL_2] as a catalyst leads to an alkynylphosphine by [1,3] migration of tin from C to P.

Introduction

Since their discovery in 1982,[1] the chemistry of phosphirenes has been actively developed, and its foundations are now well established.[2] One problem has not been satisfactorily solved, however. All of the described C-functional phosphirenes have been made by condensation of functional alkynes with phosphinidene units, and today, no method allows the installation of a functional group on a preformed phosphirene. In an attempt to solve this problem, we have decided to study the reactivity of 2-silyl- and 2-stannyl-substituted phosphirenes. We describe our results in this report.

Results and Discussion

As usual for this kind of strained phosphorus−carbon heterocycle, we decided to work in the coordination sphere of tungsten for convenience. The products are easier to synthesize and more stable. The reaction of [PhP-$W(CO)_5$] as generated from the appropriate 7-phosphanorbornadiene precursor[3] with PhC≡C-$SiMe_3$ affords the expected 2-silylphosphirene (**1**) in good yield (eq 1).

The X-ray crystal structure of **1** shows a lot of disorder, but the key parameters of the ring remain reliable. The most significant finding is that the P−C(Si) bond is elongated by comparison with the other P−C ring bond (1.812 and 1.843(1) vs 1.791 and 1.763(1) Å). This elongation could have a steric origin since both P and C are substituted by bulky groups, but we favor an electronic origin because this elongation is reproduced by the computed structure of the 2-silyl-1,3-dimethylphosphirene $W(CO)_5$ complex at the B3LYP/6-31G(d)-Lanl2dz (W) level. The most interesting result of the computation concerns the shape of the LUMO (Figure 1). It shows a significant presence at phosphorus but no presence at silicon. We were planning to activate the ring-C−Si bond of **1** by fluoride ion, and thus, this finding casts some doubt on the feasibility of this approach. Our initial experiments were carried out with nonstoichiometric amounts of TBAF in the presence of water or benzaldehyde, and we were delighted to find that the expected protonation and functionalization do take place (eq 2). Obviously, these reactions are not under the control of the LUMO. The high affinity of silicon for F^- plays the leading role.

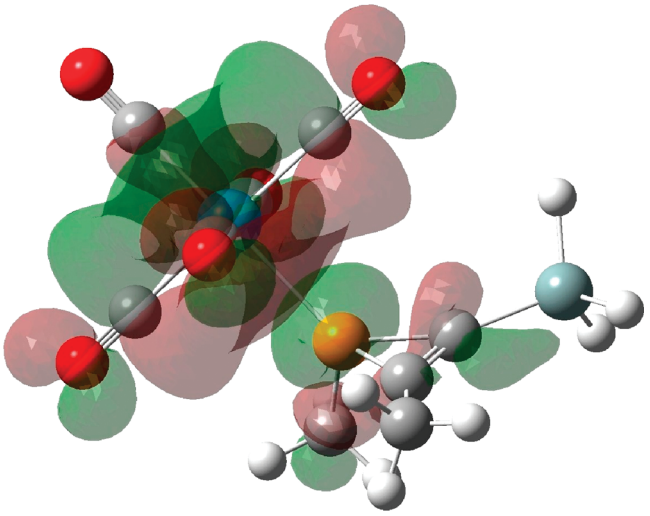
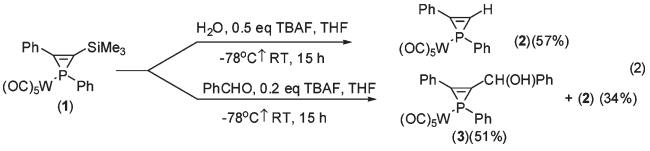


Figure 1. LUMO of 2-silyl-1,2-dimethylphosphirene pentacarbonyltungsten complex as computed by DFT at the B3LYP/6-31G(d)-Lanl2dz (W) level.



Phosphirene **2** is characterized by the expected high-field shift of its ^{31}P resonance ($\delta^{31}P$ −156.6 ppm in CD_2Cl_2) and its highly deshielded vinylic proton at 8.48 ppm with a $^2J_{H-P}$ coupling of 21 Hz. Phosphirene **3** exists as a 1:1 mixture of two nonseparable diastereomers with their phosphorus

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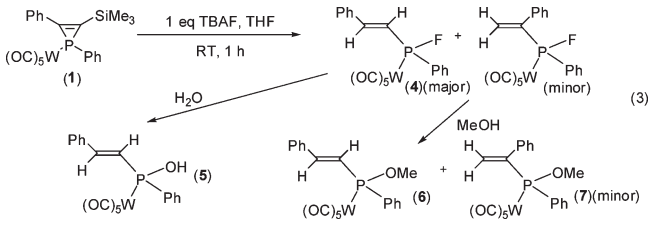
resonances at high fields (δ^{31}P −149.5 and −149.3 ppm in CD_2Cl_2). The ^{13}C spectrum shows the two sp^3 C−O resonances at 72.45 and 72.77 ppm.

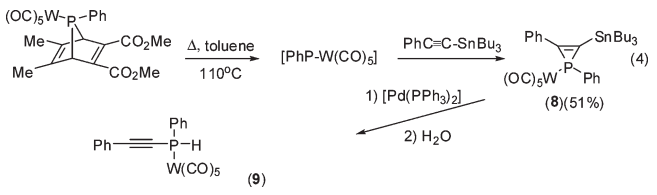
The result was entirely different when operating at room temperature with a stoichiometric equivalent of TBAF. We also observed a desilylation, but it was followed by an attack of the fluoride ion at phosphorus with formation of the ring-opened vinylic phosphinous fluoride **4** (eq 3). The resulting phosphinous fluoride **4** was characterized by its ^{31}P resonance at very low fields (δ^{31}P 197.2 ppm in $CDCl_3$), its huge $^1J_{F-P}$ coupling of 850 Hz, and its ^{19}F resonance at −132.8 ppm ($PhCF_3$). It was accompanied by a minor isomer (δ^{31}P 201.8 ppm) whose formula was established by methanolysis (see later). The major product **4** results from the preferential cleavage of the P−C(Ph) ring bond of **2** favored by the stabilizing effect of the phenyl substituent on the resulting carbanion, whereas the minor product comes from the cleavage of the P−CH bond. The formula of **4** was further ascertained by hydrolysis and methanolysis.



(3)

The hydrolysis product **5** shows the two expected vinylic carbons at 142.90 (=CHPh, $^2J_{C-P}$ = 9.6 Hz) and 129.00 ppm (=CHP, $^1J_{C-P}$ = 34.5 Hz). The CHPh proton shows a $^3J_{H-P}$ coupling of 18 Hz, in agreement with an *E* geometry.[4] The structural assignment of **6** is straightforward. More interesting is the structure of the minor product **7** that we were able to get in the pure state. The key finding is that it contains a vinylic CH_2 carbon at 129.54 ppm ($^2J_{C-P}$ = 14.4 Hz). The interpretation of these results is as follows. At low temperature, the fluoride ion induces the desilylation of phosphirene **1** to give phosphirene **2**. Then, at room temperature, F^- attacks the phosphorus of **2** with preferential cleavage of the P−C(Ph) ring bond. This means that this technique can be used for the functionalization of phosphirenes only at low temperature and with highly reactive coreagents such as water and aldehydes.

Looking for other potential methods of functionalization of phosphirenes, we prepared the 2-stannyl-substituted phosphirene **8** as shown in eq 4.



(4)

We expected to use **8** as a partner in a Stille cross-coupling reaction. In fact we observed that **8** readily rearranges to the secondary alkynylphosphine **9** in the presence of the [PdL_2] catalyst. Secondary phosphine **9** displays a ^{31}P resonance at −59.9 ppm ($CDCl_3$) with a $^1J_{H-P}$ coupling of 372.5 Hz. Its ^{13}C spectrum shows the two sp carbons at 109.20 ($^2J_{C-P}$ = 13.4 Hz) and 78.52 ppm ($^1J_{C-P}$ = 82.4 Hz). It appears that [PdL_2] readily catalyzes the [1,3] shift of tin from carbon to phosphorus. This is not a real surprise since it is known that Pd(0) readily inserts into the P−C ring bonds of phosphirenes.[5]

From these series of experiments, it clearly appears that the functionalization of preformed phosphirenes is a very tricky problem. Even mild nucleophilic functionalization methodologies are limited by the competing nucleophilic ring-opening promoted by the significant localization of the LUMO at P. On the other hand, electrophilic methodologies have not produced any useful results until now, and catalytic methodologies are limited by the easy activation of the P−C ring bonds. More work is obviously needed to solve this problem.

Experimental Section

General Procedures. NMR spectra were obtained on a JEOL ECA400 or JEOL ECA400SL spectrometer. All spectra were recorded at 298 K unless otherwise specified. Elemental analyses were performed in the Division of Chemistry and Biological Chemistry, Nanyang Technological University. HRMS spectra were obtained in ESI mode on a Finnigan MAT95XP HRMS system (Thermo Electron Corp.). X-ray crystallographic analyses were performed on a Bruker X8 APEX diffractometer. All reactions were performed under argon. Silica gel (230−400 mesh) was used for the chromatographic separations. All commercially available reagents were used as received from the suppliers.

Preparation of Phosphirene 1. The 7-phosphanorbornadiene complex (0.30 g, 0.458 mmol) and trimethyl(phenylethynyl)-silane (0.241 g, 1.37 mmol) in 5 mL of toluene was heated at 110 °C for 15 h. After evaporation, the residue was chromatographed on silica gel with 100% hexane as eluent to give crystals of **1** (0.242 g, 87% yield). ^{31}P NMR (162 MHz, $CDCl_3$): δ −177.5 (d, J_{PW} = 273.6 Hz, 1P). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.75 (d, J = 6.9 Hz, 2H, Ar*H*), 7.55−7.48 (m, 3H, Ar*H*), 7.40−7.32 (m, 5H, Ar*H*), 0.38 (s, 9H, 3 × C*H*$_3$). ^{13}C NMR (100 MHz, $CDCl_3$): δ 198.0 (d, J = 31.6 Hz, *trans* CO), 196.3 (d, J = 8.6 Hz, *cis* CO), 145.7 (d, J = 16.3 Hz, =C(Ph)), 139.1 (d, J = 11.5 Hz, *ipso* C PhP), 131.7 (d, J = 35.5 Hz, =C-SiMe$_3$)), 131.2 (CH (PhP)), 131.2 (CH (PhP)), 131.1 (CH (PhP)), 130.6 (CH (PhP)), 130.6 (CH), 130.1 (CH), 129.4 (2 × CH (PhP)), 128.5 (CH), 128.4 (CH), 127.6 (d, J = 7.7 Hz, *ipso* C (PhC)), −0.70 (3 × CH$_3$). The ^{13}C assignments were made by comparison with previous data.[6] Anal. Calcd for $C_{22}H_{19}O_5PSiW$: C, 43.58; H, 3.16. Found: C, 43.69; H, 3.61.

General Procedure for the Preparation of Compounds 2 and 3. 2-Phenylmethanol-1,3-diphenylphosphirene (3). 2-Trimethylsilyl-1,3-diphenylphosphirene tungsten complex (**1**) (0.235 g, 0.387 mmol) was dissolved in 5 mL of THF, and benzaldehyde (0.041 g, 0.387 mmol) was then added. Tetra-*n*-butylammonium fluoride (TBAF) (0.08 mL, 0.08 mmol) was added dropwise to the mixture at −78 °C and stirred overnight at room temperature. After evaporation, the residue was chromatographed on silica gel with 100% hexane as eluent and later 90:10 hexane/ethyl acetate to give **3** as a pale yellow solid (0.126 g, 51% yield) and **2** as a brown solid (71 mg, 34% yield). **3**: ^{31}P NMR (162 MHz, CD_2Cl_2): δ −149.5 and −149.3 (d, J_{PW} = 269 and 282 Hz). ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.78−7.76 (m, 1H, Ar*H*), 7.73−7.70 (m, 1H, Ar*H*), 7.52−7.47 (m, 9H, Ar*H*), 7.42−7.35 (m, 4H, Ar*H*), 7.33−7.23 (m, 5H, Ar*H*), 6.25 (d, J = 2.8 Hz, 0.5 H, C*H*-Ph), 6.18 (d, J = 5.0 Hz, 0.5H, C*H*-Ph), 2.68 (br s, 1H, O*H*). ^{13}C NMR

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(100 MHz, CD_2Cl_2): δ 198.64 and 198.52 (2d, J = 29.6 and 30.5, *trans* CO), 196.66 and 196.58 (2d, J = 18.1 Hz, *cis* CO), 140.50 (d, J = 8.6 Hz, =C(Ph)), 138.85 and 138.35 (2d, J = 5.7 and 8.6 Hz, =*C*(CH)), 133.85 and 133.45 (2d, J = 13.4 Hz, *ipso* C (PhP)), 131.8 (CH), 131.7 (CH), 131.5 (CH), 131.3 (CH), 131.1 (CH), 130.9 (CH), 129.7 (CH), 129.5 (CH), 129.4 (CH), 129.2 (CH), 129.1 (CH), 129.0 (CH), 128.9 (CH), 128.8 (CH), 127.1 (d, J = 28.6 Hz, CH (Ph)), 126.3 (d, J = 5.7 Hz, *ipso* C (Ph-C=C)), 72.7 (br, CH-OH), 72.4 (br, CH-OH). Exact mass: calcd for $C_{26}H_{17}O_6PW$ 640.0272, found: 640.0264

1,3-Diphenylphosphirene (2). 2-Trimethylsilyl-1,3-phenylphosphirene (**1**) (0.020 g, 0.0330 mmol) was dissolved in 2 mL of THF, and TBAF (0.02 mL, 0.0165 mmol) was added into the reaction flask. Three drops of water were added to the mixture at −78 °C and stirred overnight at room temperature. After evaporation, the residue was chromatographed on silica gel with 100% hexane as eluent to give **2** as a brown solid (10 mg, 57% yield). ^{31}P NMR (162 MHz, $CDCl_3$): δ −156.6 (d, J_{PW} = 273.6 Hz). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.47 (d, J = 21.0 Hz, 1H, C*H*), 7.84−7.80 (m, 2H, Ar*H*), 7.58−7.50 (m, 5H, Ar*H*), 7.47−7.40 (m, 3H, Ar*H*). ^{13}C NMR (100 MHz, $CDCl_3$): δ 198.2 (d, J = 31.5 Hz, *trans* CO), 196.2 (td, J = 62.0, 8.6 Hz, *cis* CO), 138.29 and 138.27 (d, J = 9.6 Hz, =C(Ph)+ *ipso* PhP), 131.6 (CH), 131.4 (CH), 130.8 (CH), 130.5 (d, J = 3.8 Hz, CH), 129.3 (CH), 129.0 (CH), 128.6 (d, J = 10.5 Hz, CH), 127.4 (CH), 126.0 (*ipso* C), 125.93 (d, J = 6.7 Hz, *ipso* C), 117.6 (d, J = 6.7 Hz, CH). Anal. Calcd for $C_{19}H_{11}O_5PW$: C, 42.73; H, 2.08. Found: C, 43.11; H, 1.74.

General Procedure for the Preparation of Compounds 4 and 5. Alkenylfluorophosphine (4). 2-Trimethylsilyl-1,3-diphenylphosphirene (**1**) (15.2 mg, 0.025 mmol) was dissolved in 2 mL of THF, and TBAF (0.025 mL, 0.025 mmol) was added dropwise at −78 °C and stirred for 1 h at room temperature. After evaporation, the crude product was obtained as a dark brown oil. ^{31}P NMR (162 MHz, $CDCl_3$): δ 197.2 (dd, $^1J_{PF}$ = 850 Hz, $^1J_{PW}$ = 328.7, 319.9 Hz). ^{19}F NMR (376 MHz, $CDCl_3$, $PhCF_3$): δ −132.8.

Alkenylphosphinous acid (5). 2-Trimethylsilyl-1,3-diphenylphosphirene (**1**) (0.103 g, 0.17 mmol) was dissolved in 5 mL of THF, and TBAF (0.17 mL, 0.17 mmol) was added dropwise at −78 °C and stirred for 1 h at room temperature. After evaporation, the residue was chromatographed on silica gel with 90:10 hexane/ethyl acetate to give **5** as a white solid (26 mg, 28% yield). ^{31}P NMR (162 MHz, CD_2Cl_2): δ 101.6 (d, J_{PW} = 280.5 Hz). ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.67−7.62 (m, 2H, Ar*H*), 7.52−7.45 (m, 5H, Ar*H*), 7.38−7.34 (m, 3H, Ar*H*), 7.14 (dd, J = 18.8 and 17.4 Hz, 1H, =C*H*Ph), 6.84 (dd, J = 22.9, 17.4 Hz, 1H, =C*H*P), 4.00 (br s, 1H, O*H*). ^{13}C NMR (100 MHz, CD_2Cl_2): δ 199.7 (d, J = 24.0 Hz, *trans* CO), 196.5 (d, J = 8.6 Hz, *cis* CO), 142.9 (d, J = 9.6 Hz, =CHPh), 140.5 (d, J = 46.9 Hz, *ipso* C (PhP)), 135.1 (d, J = 15.3 Hz, *ipso* C (Ph)), 130.7 (CH), 129.9 (CH), 129.1 (d, J = 34.5 Hz, =CHP), 128.9 (2 × CH), 128.9 (CH), 128.8 (CH), 128.7 (CH), 128.7 (CH), 127.6 (2 × CH). Anal. Calcd for $C_{19}H_{13}O_6PW$: C, 41.33; H, 2.37. Found: C, 40.91; H, 2.77.

General Procedure for the Preparation of Compounds 6 and 7. 2-Trimethylsilyl-1,3-diphenylphosphirene (**1**) (0.121 g, 0.2 mmol) was dissolved in 5 mL of THF, and 2 mL of MeOH was added to the reaction. TBAF (0.2 mL, 0.2 mmol) was added dropwise at −78 °C and stirred for 1 h at room temperature. After evaporation, the residue was chromatographed on silica gel with 80:20 hexane/ethyl acetate to give **6** as a white solid (37 mg, 33% yield) and **7** (13 mg, 11% yield).

Alkenylphosphinite 6. ^{31}P NMR (162 MHz, $CDCl_3$): δ 117.56 (d, J_{PW} = 284.8 Hz). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.62−7.39 (m, 10H, Ar*H*), 7.29 (t, J = 17.9 Hz, 1H, C*H*), 6.80 (t, J = 17.4 Hz, 1H, C*H*), 3.55 (d, J = 12.8 Hz, 3H, OCH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 199.9 (d, J = 25.9 Hz, *trans*-CO), 196.6 (d, J = 8.6 Hz, *cis*-CO), 146.9 (d, J = 13.4 Hz, CH), 138.5 (d, J = 46.0 Hz, C), 135.2 (d, J = 16.3 Hz, C), 130.9 (CH), 130.3 (CH), 129.7 (CH), 129.6 (CH), 129.2 (2 × CH), 129.0 (CH), 128.9 (CH), 127.9 (2 × CH), 125.7 (d, J = 38.3 Hz, CH), 54.3 (d, J = 6.7 Hz, OCH_3). Exact mass: calcd for $C_{20}H_{15}O_6PW$ 566.0116, found 566.0106.

Alkenylphosphinite 7. ^{31}P NMR (162 MHz, $CDCl_3$): δ 125.9 (d, J_{PW} = 284.8 Hz, 1P). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.66−7.61 (m, 2H, Ar*H*), 7.50−7.44 (m, 3H, Ar*H*), 7.24−7.17 (m, 3H, Ar*H*), 7.08−7.06 (m, 2H, Ar*H*), 6.18 (d, J = 32 Hz, 1H, =C*H trans* P), 6.14 (d, J = 16 Hz, 1H, =C*H cis* P), 3.50 (d, J = 13.7 Hz, 3H, OCH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 198.8 (d, J = 27.8 Hz, *trans*-CO), 196.9 (d, J = 7.7 Hz, *cis*-CO), 148.6 (d, J = 32.6 Hz, C), 137.9 (d, 13.4 Hz, C), 137.1 (d, J = 42.2 Hz, C), 131.1 (CH), 130.8 (CH), 130.7 (CH), 129.5 (d, J = 14.4 Hz, CH_2), 128.8 (CH), 128.6 (CH), 128.3 (2 × CH), 128.26 (CH), 128.15 (CH), 128.12 (CH), 53.9 (OCH_3). Exact mass: calcd for $C_{20}H_{15}O_6PW$ 566.0116, found 566.0109

Preparation of 2-Tributylstannyl-1,3-diphenylphosphirene (8). The 7-phosphanorbornadiene complex (1.96 g, 3 mmol) and tributyl(phenylethynyl)stannane (2.35 g, 6 mmol) in 10 mL of toluene were heated at 110 °C for 15 h. After evaporation, the residue was chromatographed on silica gel with 100% hexane as eluent to give **8** as a brown solid (1.26 g, 51% yield). ^{31}P NMR (162 MHz, $CDCl_3$): δ −179.7 (d, J_{PW} = 273.5 Hz). ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.93 (d, J = 6.9 Hz, 2H, Ar*H*), 7.65−7.54 (m, 5H, Ar*H*), 7.43 (br s, 3H, Ar*H*), 1.76−1.70 (m, 2H, 3 × CH_2), 1.50−1.41 (m, 12H, 3 × CH_2CH_2), 0.98 (t, J = 3.0 Hz, 9H, 3 × CH_3). ^{13}C NMR (100 MHz, CD_2Cl_2): δ 199.2 (d, J = 30.6 Hz, *trans*-CO), 197.4 (d, J = 8.6 Hz, *cis*-CO), 148.6 (d, J = 14.4 Hz, C), 141.0 (d, J = 7.7 Hz, C), 133.1 (C), 132.7 (C), 132.2 (CH), 132,1 (CH), 131.6 (CH), 130.7 (CH), 130.5 (2 × CH), 130.0 (2 × CH), 129.0 (CH), 128.9 (CH), 29.9 (t, J = 22.0 Hz, 3 × CH_2), 28.1 (t, J = 59.4 Hz, 3 × CH_2), 14.2 (3 × CH_3), 12.4 (3 × CH_2). Anal. Calcd for $C_{31}H_{37}O_5PSnW$: C, 45.23; H, 4.53. Found: C, 45.62; H, 4.02.

Preparation of Alkynylphosphine 9. The catalyst was prepared from $Pd(dba)_2$ (16.4 mg, 0.03 mmol) and PPh_3 (15.8 mg, 0.06 mmol) in toluene (10 mL). After 10 min of stirring at room temperature, phosphirene **8** (0.56 g, 0.66 mmol) was added. The mixture was then heated at 120 °C for 3 h. After evaporation of the solvent, purification on silica gel with 80:20 hexane/ethyl acetate gave **9** as a yellow solid (0.114 g, 32% yield). ^{31}P NMR (162 MHz, $CDCl_3$): δ −59.9 (dd, J_{PH} = 372.5 Hz, J_{PW} = 236.7 Hz). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.76−7.71 (m, 3H, Ar*H*), 7.57−7.49 (m, 5H, Ar*H*), 7.42−7.38 (m, 3H, Ar*H*), 6.48 (d, J_{PH} = 372.0 Hz, 1H, P*H*). ^{13}C NMR (100 MHz, $CDCl_3$): δ 199.0 (d, J = 23.0 Hz, *trans*-CO), 195.9 (d, J = 6.7 Hz, *cis*-CO), 132.6 (2 × CH), 131.2 (CH), 131.1 (CH), 131.0 (CH), 130.9 (CH), 130.4 (CH), 129.7 (C), 129.3 (CH), 129.2 (CH), 128.7 (2 × CH), 128.0 (d, J = 4.8 Hz, C), 109.2 (d, J = 13.4 Hz, ≡C), 78.5 (d, J = 82.4 Hz, ≡C). Exact mass: calcd for $C_{19}H_{11}O_5PW$ 533.9853, found 533.9865

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Supporting Information Available: X-ray crystal structure analysis of compound **1**. This material is available free of charge via the Internet at http://pubs.acs.org.