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A Phospha-Wittig Route to 5-Phosphaphenanthrene

Huaiqiu Wang,[a] Weining Zhao,[a] Yang Zhou,[a] Zheng Duan,*[a] and François Mathey*[a,b]

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The reaction of tributylphosphane with a 7-(2′-formyl-2-biphenylyl)phosphanorbornadiene P-$W(CO)_5$ complex leads to the 5-phosphaphenanthrene P-$W(CO)_5$ complex via an intramolecular phospha-Wittig condensation. This complex is stable enough for detection by ^{31}P NMR spectroscopy but cannot be isolated due to its high reactivity. It is trapped by addition of MeOH or cycloaddition with 2,3-dimethylbutadiene or a nitrileimine. The adducts were characterized by X-ray crystal structure analysis.

Introduction

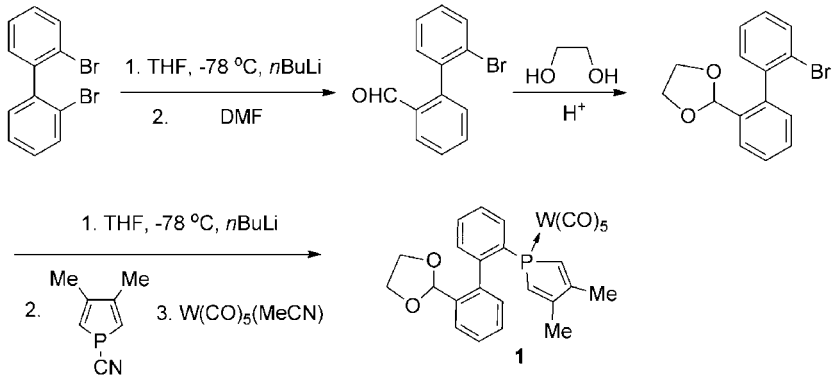
5-Phosphaphenanthrenes (phosphanthridines) are still a very poorly studied class of compounds in spite of their interesting structure. Indeed, they can be viewed as stabilized all-carbon-substituted phosphaalkenes with a planar core. The parent 5-phosphaphenanthrene was briefly mentioned as early as 1968 by Bickelhaupt[1] as an unstable species, only characterized by UV spectroscopy and mass spectrometry. Sometime later, some of us synthesized the stable 6-phenyl derivative.[2] The chemistry of these species remains essentially unknown at the moment.[3] In view of this state of affairs, we decided to investigate a new approach to 5-phosphaphenanthrene based on the phospha-Wittig reaction.[4] In so doing, we highlight the phosphaalkene character of these species.

Results and Discussion

Our starting point was the functional phosphole complex **1** with a protected aldehyde functionality. It was prepared from 2,2′-dibromobiphenyl[5] in three steps and 81% overall yield as shown in Equation (1).

In spite of the steric bulk of the phosphorus substituent, it proved possible to react complex **1** with neat dimethyl acetylenedicarboxylate to obtain the corresponding 7-phosphanorbornadiene complex **2** [Equation (2)].

In the normal case, when the substituent at P is not bulky, dimethyl acetylenedicarboxylate (DMAD) reacts on the phosphole face opposite to tungsten. The ^{13}C spectrum of the product displays a Me-*C* resonance at ca. 138 ppm with a strong J_{CP} coupling of ca. 17 Hz and a MeO_2C-*C* resonance at ca. 147 ppm with a weak J_{CP} coupling of ca. 4–5 Hz.[6] In the present case, it is possible to detect the MeO_2C-*C* resonance at δ = 147.65 ppm with a strong J_{CP} coupling of 19.2 Hz. Thus, we suspect that the cycloaddition has taken place on the same side as tungsten. An interesting side product (compound **3**) is also formed during this synthesis. Its formula was established by a combination of NMR spectroscopy and mass spectrometry. The ^{13}C



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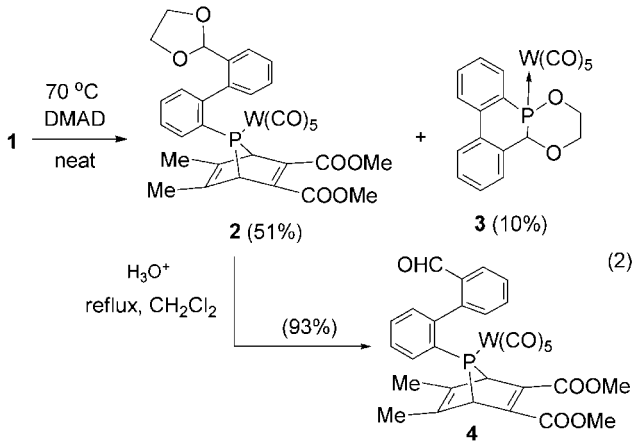
[a] Chemistry Department, International Phosphorus Laboratory, Zhengzhou University,
Zhengzhou 450052, P. R. China
[b] Division of Chemistry & Biological Chemistry, School of Physical & Mathematical Sciences, Nanyang Technological University,
21 Nanyang Link, Singapore 637371
E-mail: duanzheng@zzu.edu.cn
fmathey@ntu.edu.sg



spectrum shows an O-CH resonance at δ = 84.50 ppm (J_{CP} = 37.2 Hz) and two OCH_2 at 64.58 (J_{CP} = 3.2 Hz) and 69.83 ppm (J_{CP} = 3.6 Hz). The calculated exact mass is 602.9806 [M + Na^+] vs. 602.9844 (found). The product results from the intramolecular insertion of the electrophilic phosphanylidene formed via the collapse of the bridge of **2** into one of the O–C bonds of the dioxolane ring. This type of reaction has never been reported before.[7] In spite of the sensitivity of **2**, we were then able to perform the unmasking of the aldehyde under mild acidic conditions to obtain **4** in very good yield. Following a protocol that we had already used for the synthesis of other cyclic phosphaalkenes,[8] we then reacted **4** with tributylphosphane in dichloromethane at room temperature. We detected the formation of the 5-phosphaphenanthrene complex **5** (δ^{31}P = 164.9 ppm, $^1J_{PW}$ = 267.3 Hz) but its reactivity precluded its isolation. We trapped it by reaction with methanol, 2,3-dimethylbutadiene, and a nitrileimine as shown in Equation (3).

All three adducts were obtained in good yields and characterized by X-ray crystal structure analysis (see Figures 1, 2, and 3). The structure of the central six-membered phosphorus ring is remarkably insensitive to the type of reaction performed with **5**. The C–C bridge bond of the biphenyl unit varies between 1.482 and 1.485 Å, the C–P–C intracyclic angle varies between 96.9 and 97.8° and the phenyl interplane angle within the biphenyl unit stays within the range 26.44(**7**) to 28.58° (compound **8**).

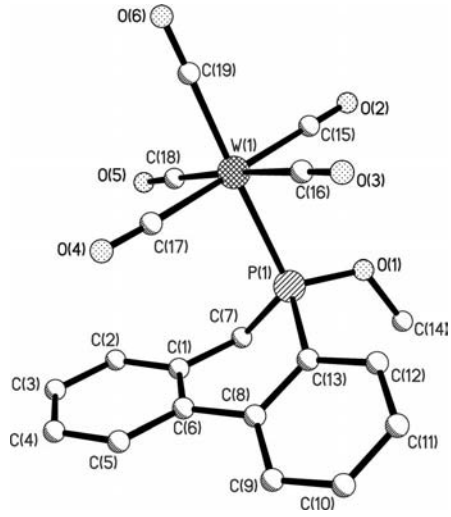
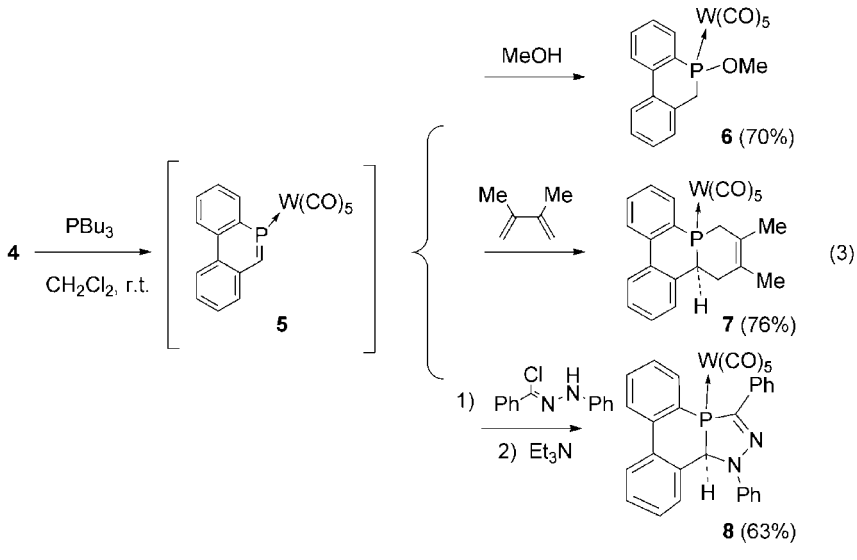


Figure 1. X-ray crystal structure of MeOH adduct **6**. Significant distances [Å] and angles (°): O1–P1 1.607(4), P1–W1 2.4660(14), P1–C7 1.819(5), P1–C13 1.822(5), C1–C7 1.510(8), C1–C6 1.396(7), C6–C8 1.484(8), C8–C13 1.404(7); C7–P1–C13 96.9(2).

Finally, this work highlights the high versatility of both phosphanylidene and phospha-Wittig chemistries. Besides, the tungstenpentacarbonyl complexation of 5-phosphaphenanthrene stabilizes it to a sufficient extent to allow its use in a variety of high yield addition and cycloaddition reactions. More chemistry can be envisaged.



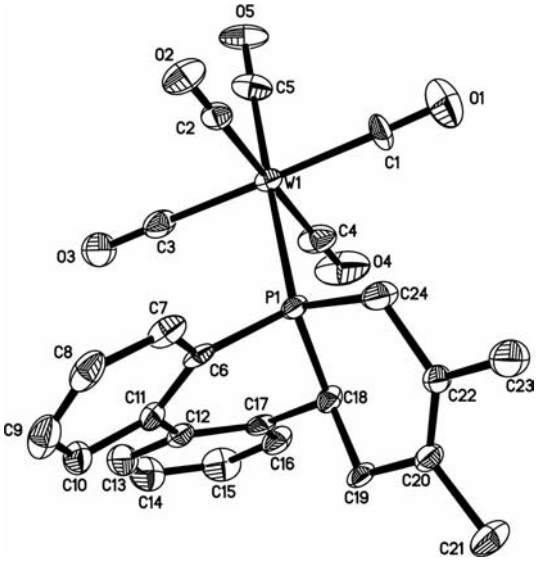


Figure 2. X-ray crystal structure of dimethylbutadiene adduct **7**. Significant distances [Å] and angles (°): P1–W1 2.519(3), P1–C6 1.820(12), P1–C18 1.824(10), P1–C24 1.836(11), C6–C11 1.425(16), C11–C12 1.485(16), C12–C17 1.404(16), C17–C18 1.517(14); C6–P1–C18 97.7(5).

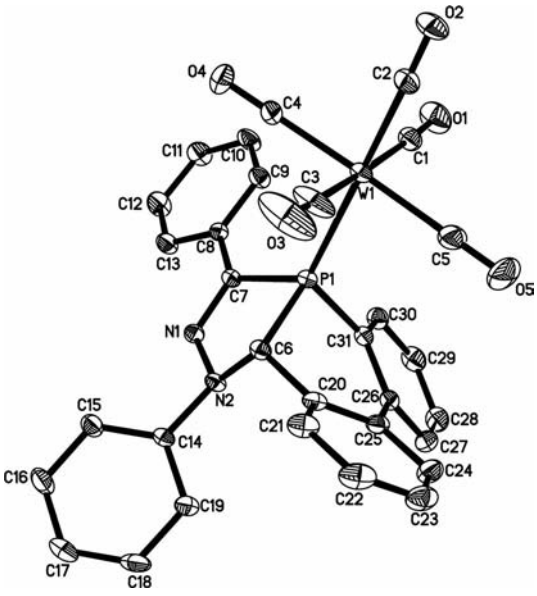


Figure 3. X-ray crystal structure of nitrileimine adduct **8**. Significant distances [Å] and angles (°): P1–W1 2.4853(10), P1–C6 1.841(30), P1–C7 1.846(3), P1–C31 1.825(30), C6–C20 1.497(5), C20–C25 1.410(5), C25–C26 1.482(5), C26–C31 1.402(5); C6–P1–C31 97.78(15).

Experimental Section

General: All reactions were routinely performed under an inert atmosphere of nitrogen using standard Schlenk techniques and dry deoxygenated solvents.

Dry CH_2Cl_2 was obtained by distillation from P_2O_5. THF was obtained by distillation from Na/benzophenone. Silica gel (200–300 mesh) purchased from Qing Dao Hai Yang Chemical Industry Co. Ltd. was used for chromatographic separations. PBu_3 was purchased from Aladdin Chemistry Co. Ltd., DMAD and *n*-butyllithium (2.2 M in hexane) were purchased from Alfa Aesar. Nuclear magnetic resonance spectra were recorded with a Bruker 300 MHz spectrometer operating at 300.13 MHz for ^1H, 75.47 MHz for ^{13}C, and 121.495 MHz for ^{31}P. Chemical shifts are expressed from internal TMS (^1H and ^{13}C) or external 85% H_3PO_4 (^{31}P). All coupling constants (*J* values) are reported in Hertz [Hz]. HRMS were obtained with a Micromass Q-TOF mass spectrometer. Mass spectra were recorded with a Bruker Esquire 3000 (Bruker Dalton, Germany) ion trap mass spectrometer that interfaced an ESI source. 1-Phenyl-3,4-dimethylphosphole was prepared according to a published procedure.[9]

2-Bromobiphenyl-2′-carbaldehyde: *n*-BuLi (5 mL, 2.2 M, 11 mmol) in hexane was added to a solution of 2,2′-dibromobiphenyl (3.43 g, 11 mmol) in THF (70 mL) over a period of 10 min at –78 °C. Then, a solution of *N*,*N*-dimethylformamide (2 mL, 25.8 mmol) in THF (10 mL) was added over 10 min at –78 °C. The reaction mixture was warmed to room temperature and stirred overnight. Then, it was quenched with saturated aqueous NH_4Cl solution and the separated organic layer was dried with $MgSO_4$. After removal of the solvent, the residue was chromatographed on silica gel. Elution with a mixture of petroleum ether and ethyl acetate (95:5) afforded the formyl derivative (colorless oil, 2.77 g, yield 97%). ^1H NMR ($CDCl_3$): δ = 7.24–7.31 (m, 3 H), 7.35–7.38 (m, 1 H), 7.51–7.53 (m, 1 H), 7.59–7.67 (m, 2 H), 8.01–8.04 (m, 1 H), 9.79 (s, 1 H, CHO) ppm. ^{13}C NMR ($CDCl_3$): δ = 123.83, 127.36, 127.47, 128.58, 129.86, 130.87, 131.61, 132.74, 133.61, 133.74, 138.85, 144.44, 191.44 ppm.

Dioxolane Derivative of 2-Bromobiphenyl-2′-carbaldehyde: A solution of 2-bromobiphenyl-2′-carbaldehyde (5.2 g, 20 mmol), ethylene glycol (11 mL, 200 mmol), and *p*-toluenesulfonic acid monohydrate (380 mg, 2 mmol) in toluene was refluxed with water separation until total consumption of the starting aldehyde as monitored by GC. After removal of toluene, the reaction mixture was extracted with diethyl ether and the organic layer was dried with $MgSO_4$. After evaporation of the solvent, the crude product was chromatographed on silica gel. Elution with hexane/CH_2Cl_2 (3:1) afforded the pure dioxolane derivative (5.78 g, yield 95%). ^1H NMR ($CDCl_3$): δ = 3.74–3.88 (m, 2 H), 3.92–3.98 (m, 1 H), 4.03–4.09 (m, 1 H), 5.51 (s, 1 H), 7.14–7.22 (m, 2 H), 7.29–7.32 (m, 2 H), 7.36–7.46 (m, 2 H), 7.62–7.70 (m, 2 H) ppm. ^{13}C NMR ($CDCl_3$): δ = 65.27, 65.57, 101.59, 123.74, 126.54, 126.86, 128.29, 128.87, 129.08, 130.06, 131.86, 132.47, 135.41, 140.79, 140.82 ppm.

Phosphole Complex 1: To a THF (30 mL) solution of dioxolane (608 mg, 2.2 mmol), *n*BuLi (1 mL, 2.2 M, 2.2 mmol) was added at –78 °C. The reaction mixture was stirred at –78 °C for 10 min and then a THF (5 mL) solution of 1-cyano-3,4-dimethylphosphole[10] (301 mg, 2.2 mmol) was added. The mixture was warmed to room temperature and stirred for 2 h. After removal of the solvent, the residue was quickly chromatographed with CH_2Cl_2. After evaporation of the solvent, the crude product (yellow viscous oil, ^{31}P NMR: δ = –4.8 ppm in CH_2Cl_2) was obtained and used without further purification.

To a stirred solution of crude phosphole (672 mg, 2 mmol) in dry THF (30 mL), a freshly prepared THF (20 mL) solution of $W(CO)_5$-(CH_3CN) (803 mg, 2.2 mmol) was added. The reaction mixture was stirred at 50 °C for 2 h. After evaporation of the solvent, the residue was chromatographed on silica gel with petroleum ether/CH_2Cl_2 (1:1) as eluent to give pure **1** (yellow crystal, 1.27 g, yield 88% from the dioxolane). ^{31}P NMR ($CDCl_3$): δ = 9.1 ($^1J_{PW}$ = 207.1 Hz) ppm. ^1H NMR ($CDCl_3$): δ = 1.78 (s, 3 H, Me), 1.85 (s, 3 H, Me), 3.62–3.97 (m, 4 H, 2OCH$_2$), 4.97 (d, $^2J_{HP}$ = 36.9 Hz, 1 H, =CH), 5.07 (s, 1 H, CH), 6.17 (d, $^2J_{HP}$ = 35.7 Hz, 1 H, =CH),

7.10–7.15 (m, 2 H), 7.21–7.39 (m, 4 H), 7.58–7.69 (m, 2 H) ppm. ^{13}C NMR ($CDCl_3$): δ = 16.79 (d, J_{CP} = 11.5 Hz, CH_3), 16.95 (d, J_{CP} = 11.3 Hz, CH_3), 65.11 (s, OCH_2), 65.42 (s, OCH_2), 101.42 (s, CH), 126.40 (s, C_{sp^2}), 127.46 (d, J_{CP} = 14.7 Hz, C_{sp^2}), 127.62 (d, J_{CP} = 40 Hz, C_{sp^2}), 128.53–128.60 ($3C_{sp^2}$), 129.31 (d, J_{CP} = 41.8 Hz, C_{sp^2}), 129.62 (s, C_{sp^2}), 131.91 (d, J_{CP} = 5.9 Hz, C_{sp^2}), 132.20 (d, J_{CP} = 37.5 Hz, C_{sp^2}), 133.33 (d, J_{CP} = 18.3 Hz, C_{sp^2}), 136.42 (s, C_{sp^2}), 140.33 (d, J_{CP} = 3.2 Hz, C_{sp^2}), 141.37 (d, J_{CP} = 2.6 Hz, C_{sp^2}), 148.46 (d, J_{CP} = 10.4 Hz, C_{sp^2}), 148.66 (d, J_{CP} = 9.8 Hz, C_{sp^2}), 196.65 (d, J_{CP} = 6.5 Hz, *cis*-CO), 199.52 (d, J_{CP} = 17.7 Hz, *trans*-CO) ppm. The inequivalency of the two sides of the phosphole ring indicates a blocked rotation of the substituent at phosphorus. MS (ESI): *m*/*z* (%) = 683.0 ([M + Na]$^+$). HRMS (ESI) calcd. for $C_{26}H_{21}O_7PW$: [M + Na]$^+$, 683.0432; found *m*/*z* 683.0452.

Phosphanorbornadiene Complex 2: A mixture of **1** (1.32 g, 2 mmol) and DMAD (2.4 mL, 20 mmol) was heated and stirred at 70 °C for 15 h in a sealed tube (the reaction cannot proceed completely). The crude mixture was first chromatographed on silica gel with petroleum ether as eluent to get a mixture of **1**, DMAD, and compound **3**, and then the column was washed with CH_2Cl_2 to give the crude product **2**. After evaporation of the solvent, the mixture of **1**, DMAD, and compound **3** can be directly used for [4+2] cycloaddition and the same procedure was repeated until complete consumption of **1**. The crude product **2** was collected and chromatographed on silica gel with petroleum ether/CH_2Cl_2 (1:3) to give pure **2** (yellow crystal, 816 mg, yield 51%). ^{31}P NMR ($CDCl_3$): δ = 219.7 ($^1J_{PW}$ = 233.1 Hz) ppm. ^1H NMR ($CDCl_3$): δ = 1.28 (s, 3 H, Me), 1.51 (s, 3 H, Me), 2.71–2.73 (m, 1 H, CH), 3.81 (s, 6 H, 2OMe), 3.96–3.99 (m, 2 H), 4.12–4.13 (m, 1 H), 4.14–4.26 (m, 2 H), 5.42 (s, 1 H, 1CH), 7.34–7.54 (m, 5 H), 7.58–7.62 (m, 1 H), 7.68–7.71 (m, 1 H), 7.83–7.86 (m, 1 H) ppm. ^{13}C NMR ($CDCl_3$): δ = 15.04 (d, J_{CP} = 2.1 Hz, Me), 15.61 (d, J_{CP} = 2.0 Hz, Me), 52.46 (s, 2OMe), 60.61 (d, J_{CP} = 22.3 Hz, CH), 61.62 (d, J_{CP} = 19.4 Hz, CH), 65.23 (s, OCH_2), 65.84 (s, OCH_2), 100.94 (s, CH), 127.50 (d, J_{CP} = 9.1 Hz, C_{sp^2}), 127.72 (s, C_{sp^2}), 128.41 (d, J_{CP} = 1.4 Hz, C_{sp^2}), 128.80 (s, C_{sp^2}), 128.97 (d, J_{CP} = 14.4 Hz, C_{sp^2}), 129.01 (s, C_{sp^2}), 129.57 (d, J_{CP} = 0.9 Hz, C_{sp^2}), 133.13 (d, J_{CP} = 4.1 Hz, C_{sp^2}), 136.22 (s, C_{sp^2}), 136.84 (d, J_{CP} = 3.9 Hz, C_{sp^2}), 138.22 (d, J_{CP} = 2.7 Hz, C_{sp^2}), 139.55 (d, J_{CP} = 1.4 HZ, C_{sp^2}), 140.01 (d, J_{CP} = 3.5 Hz, C_{sp^2}), 140.95 (d, J_{CP} = 16.0 Hz, C_{sp^2}), 142.52 (d, J_{CP} = 21.1 Hz, C_{sp^2}), 147.65 (d, J_{CP} = 19.2 Hz, C_{sp^2}), 164.07 (d, J_{CP} = 2.2 Hz, COO), 165.46 (d, J_{CP} = 3.3 Hz, COO), 196.77 (m, J_{CP} = 6.3 Hz, *cis*-CO), 198.68 (d, J_{CP} = 25.5 Hz, *trans*-CO) ppm.

As in the case of **1**, the two sides of **2** are inequivalent due to a blocked rotation of the *P*-substituent. MS (ESI): *m*/*z* (%) = 825.1 ([M + Na]$^+$). HRMS (ESI) calcd. for $C_{32}H_{27}O_{11}PW$: [M + Na]$^+$, 825.0698; found *m*/*z* 825.0696. $C_{32}H_{27}O_{11}PW$ (802.38): calcd. C 47.90, H 3.39; found C 47.07, H 3.38.

Complex 3: After complete consumption of **1**, the reaction mixture was chromatographed on silica gel with petroleum ether/CH_2Cl_2 (2:1) to give the pure product **3**: white crystals, 115 mg, yield 10%. ^{31}P NMR ($CDCl_3$): δ = 113.2 ($^1J_{PW}$ = 283.2 Hz) ppm. ^1H NMR ($CDCl_3$): δ = 4.08–4.28 (m, 3 H), 4.56–4.68 (m, 1 H), 5.38 (d, $^2J_{HP}$ = 11.1 Hz, 1 H), 7.39–7.44 (m, 2 H), 7.45–7.53 (m, 3 H), 7.55–7.63 (m, 2 H), 7.69–7.73 (m, 1 H) ppm. ^{13}C NMR ($CDCl_3$): δ = 64.58 (d, J_{CP} = 3.2 Hz, OCH_2), 69.83 (d, J_{CP} = 3.6 Hz, OCH_2), 84.50 (d, J_{CP} = 37.2 Hz, CH), 122.62 (d, J_{CP} = 5.5 Hz, C_{sp^2}), 126.95 (d, J_{CP} = 3.3 Hz, C_{sp^2}), 126.96 (d, J_{CP} = 7.1 Hz, C_{sp^2}), 127.10 (d, J_{CP} = 5.8 Hz, C_{sp^2}), 128.35 (d, J_{CP} = 7.6 Hz, C_{sp^2}), 128.50 (d, J_{CP} = 3.2 Hz, C_{sp^2}), 129.30 (d, J_{CP} = 2.3 Hz, C_{sp^2}), 131.45 (d, J_{CP} = 1.3 Hz, C_{sp^2}), 131.97 (d, J_{CP} = 6.6 Hz, C_{sp^2}), 132.03 (d, J_{CP} = 4.4 Hz, C_{sp^2}), 134.80 (d, J_{CP} = 9.7 Hz, C_{sp^2}), 135.27 (d, J_{CP} = 43.2 Hz, C_{sp^2}), 196.69 (d, J_{CP} = 7.6 Hz, *cis*-CO), 197.90 (d, J_{CP} = 28.0 Hz, *trans*-CO) ppm. MS (ESI): *m*/*z* (%) = 546.8 ([M + Na-2CO]$^+$). HRMS (ESI) calcd. for $C_{20}H_{13}O_7PW$: [M + Na]$^+$ 602.9806; found *m*/*z* 602.9844.

Phosphanorbornadiene Complex 4: A solution of **2** (802 mg, 1 mmol), *p*-toluenesulfonic acid monohydrate (380 mg, 2 mmol), and water (90 mg, 5 mmol) in CH_2Cl_2 (10 mL) was refluxed and monitored by ^{31}P NMR until the disappearance of **2**. The solution was extracted with CH_2Cl_2 (25 mL)/ H_2O (20 mL × 3) and the organic layer was dried with $MgSO_4$. After evaporation of the solvent, pure **4** (green crystals, 705 mg, yield 93%) was obtained after recrystallization. ^{31}P NMR ($CDCl_3$): δ = 217.3 ($^1J_{PW}$ = 235.7 Hz) ppm. ^1H NMR ($CDCl_3$): δ = 0.98 (s, 3 H, Me), 1.33 (s, 3 H, Me), 2.57 (d, $^2J_{CP}$ = 0.9 Hz, 1 H, CH), 3.62 (d, 6 H, 2OMe), 3.98 (d, $^2J_{CP}$ = 1.5 Hz, 1 H, CH), 6.97–7.00 (m, 1 H), 7.20–7.62 (m, 6 H), 7.93–7.96 (m, 1 H), 9.60 (s, 1 H, CHO) ppm. ^{13}C NMR ($CDCl_3$): δ = 15.24 (d, J_{CP} = 1.7 Hz, Me), 15.60 (d, J_{CP} = 2.0 Hz, Me), 52.53 (s, 2OMe), 60.50 (d, J_{CP} = 22.0 Hz, CH), 61.65 (d, J_{CP} = 19.2 Hz, CH), 128.42 (d, J_{CP} = 8.8 Hz, C_{sp^2}), 128.54 (s, C_{sp^2}), 128.89 (s, C_{sp^2}), 129.261 (d, J_{CP} = 14.3 Hz, C_{sp^2}), 129.26 (s, C_{sp^2}), 130.02 (s, C_{sp^2}), 133.64 (s, $2C_{sp^2}$), 134.36 (s, C_{sp^2}), 135.80 (d, J_{CP} = 4.2 Hz, C_{sp^2}), 136.18 (d, J_{CP} = 2.8 Hz, C_{sp^2}), 141.28 (d, J_{CP} = 3.5 Hz, C_{sp^2}), 141.29 (d, J_{CP} = 15.1 Hz, C_{sp^2}), 142.56 (d, J_{CP} = 20.4 Hz, C_{sp^2}), 143.65 (d, J_{CP} = 1.2 Hz, C_{sp^2}), 147.29 (d, J_{CP} = 19.5 Hz, C_{sp^2}), 163.89 (d, J_{CP} = 2.1 Hz, COO), 165.19 (d, J_{CP} = 3.2 Hz, COO), 191.42 (s, CHO), 196.58 (d, J_{CP} = 6.3 Hz, *cis*-CO), 198.31 (d, J_{CP} = 25.7 Hz, *trans*-CO) ppm. Same inequivalency as in **2**. MS (ESI): *m*/*z* (%) = 780.9 ([M + Na]$^+$). HRMS (ESI) calcd. for $C_{30}H_{23}O_{10}PW$: [M + Na]$^+$, 781.0436; found *m*/*z* 781.0435.

Methanol Adduct 6: To a well-stirred solution of **4** (379 mg, 0.5 mmol), PBu_3 (122 mg, 0.6 mmol) was added quickly and the solution was stirred for 3 h at room temperature. After the disappearance of **4** (monitored by ^{31}P NMR), MeOH (64 mg, 2 mmol) was added and the mixture was stirred for another 2 h. The crude mixture was chromatographed on silica gel with petroleum ether/CH_2Cl_2 (4:1) as eluent to give **6** (colorless crystal, 194 mg, yield 70%). ^{31}P NMR ($CDCl_3$): δ = 108.0 ($^1J_{PW}$ = 235.7 Hz) ppm. ^1H NMR ($CDCl_3$): δ = 3.21 (d, $^2J_{HH}$ = 14.4 Hz, 1 H), 3.44 (d, $^2J_{HP}$ = 12.3 Hz, 3 H, OMe), 4.04 (dd, $^2J_{HP}$ = $^2J_{HH}$ = 14.4 Hz, 1 H), 7.19–7.34 (m, 3 H), 7.38–7.50 (m, 2 H), 7.57–7.63 (m, 2 H), 7.70–7.74 (m, 1 H) ppm. ^{13}C NMR ($CDCl_3$): δ = 37.59 (d, J_{CP} = 24.3 Hz, CH_2), 54.33 (d, J_{CP} = 9.4 Hz, OMe), 126.30 (d, J_{CP} = 5.8 Hz, C_{sp^2}), 126.74 (d, J_{CP} = 1.8 Hz, C_{sp^2}), 127.98 (d, J_{CP} = 9.6 Hz, C_{sp^2}), 128.64 (d, J_{CP} = 1.3 Hz, C_{sp^2}), 128.91 (s, C_{sp^2}), 129.29 (d, J_{CP} = 1.7 Hz, C_{sp^2}), 129.93 (d, J_{CP} = 13.2 Hz, C_{sp^2}), 131.55 (d, J_{CP} = 7.8 Hz, C_{sp^2}), 131.90 (d, J_{CP} = 1.4 Hz, C_{sp^2}), 132.58 (d, J_{CP} = 37.7 Hz, C_{sp^2}), 134.43 (d, J_{CP} = 7.8 Hz, C_{sp^2}), 137.14 (d, J_{CP} = 5.5 Hz, C_{sp^2}), 195.76 (d, J_{CP} = 8.1 Hz, *cis*-CO), 199.05 (d, J_{CP} = 25.8 Hz, *trans*-CO) ppm. MS (ESI): *m*/*z* (%) = 536.8 ([M – Me]).

Dimethylbutadiene Adduct 7: To a solution of **4** (379 mg, 0.5 mmol), PBu_3 (122 mg, 0.6 mmol) was added quickly and the solution was stirred for 3 h at room temperature. After the disappearance of **4** (monitored by ^{31}P NMR), 2,3-dimethyl-1,3-butadiene (164 mg, 2 mmol) was added and the mixture was stirred for another 2 h. The crude mixture was chromatographed on silica gel with petroleum ether/CH_2Cl_2 (8:1) as eluent to give **7** (colorless crystal, 227 mg, yield 76%). ^{31}P NMR ($CDCl_3$): δ = –25.1 ($^1J_{PW}$ = 235.5 Hz) ppm. ^1H NMR ($CDCl_3$): δ = 1.44 (s, 3 H, Me), 1.73 (s, 3 H, Me), 1.94–2.03 (m, 1 H), 2.18–2.33 (m, 1 H), 3.00 (s, 2 H), 3.07–3.13 (m, 1 H), 7.26–7.41 (m, 6 H), 7.65–7.73 (m, 2 H) ppm. ^{13}C NMR ($CDCl_3$): δ = 20.56 (s, CH_3), 21.17 (d, J_{CP} = 7.5 Hz, CH_3), 33.71 (d, J_{CP} = 22.1 Hz, CH_2), 36.29 (d, J_{CP} = 5.1 Hz, CH_2),

36.51 (d, J_{CP} = 28.0 Hz, CH), 120.39 (d, J_{CP} = 8.2 Hz, C_{sp^2}), 126.20 (d, J_{CP} = 6.2 Hz, C_{sp^2}), 127.43 (d, J_{CP} = 1.5 Hz, C_{sp^2}), 127.82 (d, J_{CP} = 7.2 Hz, C_{sp^2}), 128.26 (d, J_{CP} = 7.2 Hz, C_{sp^2}), 128.46 (d, J_{CP} = 8.2 Hz, C_{sp^2}), 128.73 (d, J_{CP} = 1.4 Hz, C_{sp^2}), 129.02 (s, C_{sp^2}), 130.17 (d, J_{CP} = 36.2 Hz, C_{sp^2}), 130.23 (d, J_{CP} = 1.5 Hz, C_{sp^2}), 130.47 (d, J_{CP} = 8.2 Hz, C_{sp^2}), 133.79 (d, J_{CP} = 9.9 Hz, C_{sp^2}), 136.25 (d, J_{CP} = 2.8 Hz, C_{sp^2}), 137.18 (d, J_{CP} = 5.7 Hz, C_{sp^2}), 196.22 (d, J_{CP} = 7.1 Hz, *cis*-CO), 199.38 (d, J_{CP} = 20.8 Hz, *trans*-CO) ppm. MS (ESI): *m*/*z* = 568.9 ([M + Na – 2CO]$^+$). $C_{24}H_{19}O_5PW$ (602.23): calcd. C 47.87, H 3.18; found C 48.33, H 3.20.

Nitrileimine Adduct 8: To a well-stirred solution of **4** (379 mg, 0.5 mmol), PBu_3 (122 mg, 0.6 mmol) was added quickly and the solution was stirred for 3 h at room temperature. After the disappearance of **4** (monitored by ^{31}P NMR), *N*-phenylbenzohydrazonoyl chloride[11] (126 mg, 0.55 mmol) was added and then a solution of Et_3N (61 mg, 0.6 mmol) in CH_2Cl_2 (2 mL) was added dropwise to the mixture. The solution was stirred for another 2 h. After removal of the solvent, the residue was chromatographed on silica gel with petroleum ether/CH_2Cl_2 (3:1) as eluent to give **8** (light-yellow crystals, 223 mg, yield 63%). ^{31}P NMR ($CDCl_3$): δ = 0.9 ($^1J_{PW}$ = 247.2 Hz) ppm. ^1H NMR ($CDCl_3$): δ = 5.04 (d, $^2J_{HP}$ = 6.9 Hz, 1 H, CH), 6.91–7.00 (m, 2 H), 7.01–7.05 (m, 1 H), 7.11–7.16 (m, 2 H), 7.23–7.31 (m, 3 H), 7.33–7.53 (m, 6 H), 7.74–7.76 (d, 1 H), 7.79–7.83 (m, 1 H), 8.16–8.19 (d, 2 H) ppm. ^{13}C NMR (CDCl3): δ = 75.75 (d, J_{CP} = 36.2 Hz, CH), 122.12 (s, 2C_{sp^2}), 125.09 (d, J_{CP} = 5.2 Hz, C_{sp^2}), 125.28 (s, C_{sp^2}), 126.21 (d, J_{CP} = 2.3 Hz, C_{sp^2}), 127.06 (d, J_{CP} = 30.1 Hz, C_{sp^2}), 127.85 (d, J_{CP} = 4.6 Hz, 2C_{sp^2}), 127.92 (s, C_{sp^2}), 128.53 (s, C_{sp^2}), 128.70 (s, 2C_{sp^2}), 128.93 (s, 2C_{sp^2}), 129.14 (d, J_{CP} = 5.0 Hz, C_{sp^2}), 129.17 (d, J_{CP} = 4.6 Hz, C_{sp^2}), 129.81 (d, J_{CP} = 11.8 Hz, C_{sp^2}), 130.83 (s, C_{sp^2}), 130.97 (d, J_{CP} = 1.4 Hz, C_{sp^2}), 133.52 (d, J_{CP} = 19.6 Hz, C_{sp^2}), 134.48 (d, J_{CP} = 7.7 Hz, C_{sp^2}), 134.84 (d, J_{CP} = 7.2 Hz, C_{sp^2}), 136.83 (d, J_{CP} = 2.2 Hz, C_{sp^2}), 141.91 (d, J_{CP} = 6.5 Hz, C_{sp^2}), 145.54 (d, J_{CP} = 3.3 Hz, C_{sp^2}), 195.50 (d, J_{CP} = 6.7 Hz, *cis*-CO), 197.67 (d, J_{CP} = 25.2 Hz, *trans*-CO) ppm. MS (ESI): *m*/*z* (%) = 737.0 ([M + Na]$^+$).

CCDC-821260 (for **6**), -821259 (for **7**), and -821258 (for **8**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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