Electronic Supplementary Material (ESI) for Dalton Transactions.

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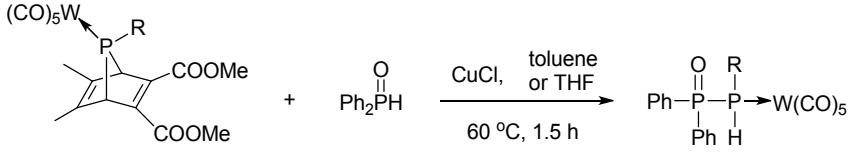
General Experimental Details

All reactions were performed under nitrogen using solvents dried by standard methods. NMR spectra were obtained using Bruker AV300 spectrometer. All spectra were recorded at 298 K in $CDCl_3$. All coupling constants (*J* values) are reported in Hertz (Hz). Chemical shifts are expressed in parts per million (ppm) downfield from internal TMS. HRMS spectra were obtained on an Agilent 1290-6540 UHPLC Q-Tof HR-MS spectrometer. Element analyses were performed on a Thermo Flash EA 1112 automatic element analyzer. IR spectra were obtained on a Thermo Nicolet is50 FT-IR spectrometer. X‑ray crystallographic analyses were performed on an Oxford diffraction Gemini E diffractometer. Silica gel (200-300 mesh) was used for the chromatographic separations. 7-phosphanorbornadiene complexes 1a, 1b, 1c, 1d, 1e were prepared according to literature methods. Commercially available reagents were used without further purification.

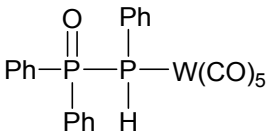
General procedure and characterization data for 2a-2e:



1a-1e **2a-2e**

	R	isolated yield of **2a-2e** (%)
a:	Ph	77
b:	Me	76
c:	CH2CH2COOEt	51
d:	CH_2CH_2Cl	52
e:	2-Th	45

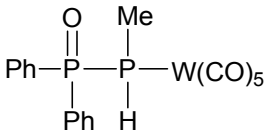
A solution of 7-R-7-phosphanorbornadiene complex **1a-1e**, diphenylphosphine oxide (1 eq) and CuCl (0.4 eq) in toluene or THF was stirred at 60 °C for 1.5 h. The solvents were removed *in vacuo*, and the residue was chromatographed at -15°C on silica gel using a 50:1 dichloromethane:THF mixture, to give a yellowish solid.

2a: 

7-phenyl-7-phosphanorbornadiene complex **1a** (2.57 g, 3.9 mmol). Yield: 1.91 g, 77 %. Single crystal for X-ray analysis was grown from a solution of the compound **2a** in dichloromethane

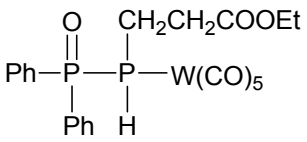
$^{31}P\{^{1}H\}$ NMR ($CDCl_3$): δ 34.0 (J_{PP} = 72.0 Hz, P^{V}), -33.2 (J_{PP} = 71.7 Hz, $^{1}J_{PW}$ = 226.4 Hz, $^{1}J_{PH}$ = 327.8 Hz, P^{III}). ^{1}H NMR ($CDCl_3$): δ 6.24 (dd, 1H, PH, J_{PH} = 326.7 Hz), 7.29-7.39 (m, 7H, Ph), 7.46-7.66 (m, 6H, Ph), 7.80-7.87 (m, 2H, Ph). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ 126.31 (d, J_{CP} = 35.6 Hz, C, Ph), 128.72 (d, J_{CP} = 12.3 Hz, CH, Ph), 128.99 (d, J_{CP} = 10.9 Hz, CH, Ph), 129.17 (d, J_{CP} = 12.2 Hz, CH, Ph), 129.92 (dd, $^{1}J_{CP}$ = 87.1 Hz, $^{2}J_{CP}$ = 14.9 Hz, C, Ph), 130.67 (dd, $^{1}J_{CP}$ = 87.1 Hz, $^{2}J_{CP}$ = 11.1 Hz, C, Ph), 131.02 (d, J_{CP} = 10.0 Hz, CH, Ph), 131.44 (d, J_{CP} = 9.7 Hz, CH, Ph), 132.64 (d, J_{CP} = 2.9 Hz, CH, Ph), 133.11 (d, J_{CP} = 2.6 Hz, CH, Ph), 133.64 (d, J_{CP} = 3.1 Hz, CH, Ph), 133.78 (d, J_{CP} = 3.1 Hz, CH, Ph), 194.88 (dd, J_{CP} = 6.4 Hz, J_{CP} = 1.4 Hz, J_{CW} = 126.8 Hz, CO *cis*), 197.48 (d, $^{2}J_{CP}$

= 25.3 Hz, CO *trans*). HRMS: m/z 635.0020 (calcd for $C_{23}H_{17}O_6P_2W$: $[M+H]^+$, 635.0010). IR (KBr) ν(CO) 2076 s, 1991s, 1909 vs cm^{-1}. Anal. Calcd for $C_{23}H_{16}O_6P_2W$: C, 43.56; H, 2.54. Found: C, 43.55; H, 2.41.

2b: 

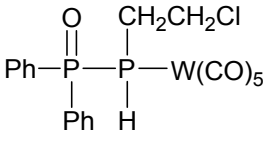
7-methyl-7-phosphanorbornadiene complex **1b** (1.20 g, 2.0 mmol). Yield: 0.93 g, 76 %.

^{31}P NMR ($CDCl_3$): δ 34.2 (J_{PP} = 62.7 Hz, P^V), -68.3 (J_{PP} = 63.0 Hz, $^1J_{PW}$ = 223.6 Hz, $^1J_{PH}$ = 320.4 Hz, P^{III}). ^1H NMR ($CDCl_3$): δ 1.74-1.82 (m, 3H, CH_3), 5.42 (dm, $^1J_{PH}$ = 320.6 Hz, 1H, PH), 7.58-7.65 (m, 6H, Ph), 7.83-7.92 (m, 4H, Ph). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 7.39 (d, J_{CP} = 22.8 Hz, CH_3), 129.32 (d, J_{CP} = 12.3 Hz, CH, Ph), 129.97 (d, J_{CP} = 10.9 Hz, C, Ph), 130.52 (d, J_{CP} = 16.7 Hz, C, Ph), 131.06 (d, J_{CP} = 10.1 Hz, CH, Ph), 131.25 (d, J_{CP} = 9.7 Hz, CH, Ph), 133.06 (d, J_{CP} = 2.7 Hz, CH, Ph), 133.21 (d, J_{CP} = 2.3 Hz, CH, Ph), 194.89 (dd, $^2J_{CP}$ = 6.4 Hz, $^3J_{CP}$ = 1.2 Hz, $^1J_{CW}$ = 126.5 Hz, CO *cis*), 197.49 (d, $^2J_{CP}$ = 24.5 Hz, CO *trans*). HRMS: m/z 572.9852 (calcd for $C_{18}H_{15}O_6P_2W$: $[M+H]^+$, 572.9853). IR (KBr) ν(CO) 2075 s, 1992 w, 1912 vs cm^{-1}. Anal. Calcd for $C_{18}H_{14}O_6P_2W$: C, 37.79; H, 2.47. Found: C, 37.79; H, 2.47.

Diphosphine monoxide **2c**: 

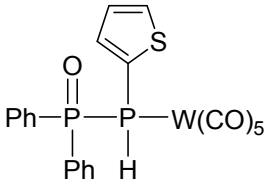
1c (3.9 g, 5.75 mmol). Yield: 1.39 g, 51 %.

$^{31}P\{^{1}H\}$ NMR ($CDCl_3$): δ 34.7 (J_{PP} = 65.8 Hz, P^{V}), -53.7 ppm (J_{PP} = 64.9 Hz, $^{1}J_{PW}$ = 223.9 Hz, $^{1}J_{PH}$ = 330.1 Hz, P^{III}). ^{1}H NMR ($CDCl_3$): δ 1.24 (t, J_{HH} = 7.2 Hz, 3H, CH_3), 2.12-2.55 (dm, 2H, PCH_2), 2.57-2.72 (m, 2H, $CH_2C{=}O$), 4.12 (q, J_{HH} = 7.2 Hz, 2H, OCH_2), 5.60 (dm, $^{1}J_{PH}$ = 325.5 Hz, 1H, PH), 7.58-7.64 (m, 6H, Ph), 7.86-7.93 (m, 4H, Ph). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ 14.10 (s, CH_3), 18.24 (d, J_{CP} = 21.0 Hz, PCH_2), 31.07 (d, J_{CP} = 5.5 Hz, $\underline{C}H_2C{=}O$), 61.21 (s, OCH_2), 129.38 (d, J_{CP} = 12.2 Hz, CH, Ph), 129.43 (d, J_{CP} = 12.2 Hz, CH, Ph), 130.35 (d, J_{CP} = 9.7 Hz, C, Ph), 130.69 (d, J_{CP} = 16.7 Hz, C, Ph), 131.01 (d, J_{CP} = 10.1 Hz, CH, Ph), 131.21 (d, J_{CP} = 10.2 Hz, CH, Ph), 133.09 (d, J_{CP} = 2.9 Hz, CH, Ph), 133.27 (d, J_{CP} = 2.7 Hz, CH, Ph), 171.55 (d, J_{CP} = 8.4 Hz, C=O), 194.68 (dd, $^{2}J_{CP}$ = 6.4 Hz, $^{3}J_{CP}$ = 1.7 Hz, $^{1}J_{CW}$ = 124.7 Hz, CO *cis*), 196.82 (d, $^{2}J_{CP}$ = 24.8 Hz, CO *trans*). HRMS: m/z 659.0225 (calcd for $C_{22}H_{21}O_8P_2W$: $[M+H]^+$, 659.0221). IR (KBr) ν(CO) 2077 s , 1939 vs cm^{-1}.

Diphosphine monoxide **2d**: 

1d (580 mg, 0.9 mmol). Yield: 582 mg, 52 %.

$^{31}P\{^{1}H\}$ NMR ($CDCl_3$): δ 34.1 (J_{PP} = 64.3 Hz, P^V), -61.5 (J_{PP} = 64.3 Hz, $^{1}J_{PW}$ = 226.7 Hz, $^{1}J_{PH}$ = 323.2 Hz, P^{III}). ^{1}H NMR ($CDCl_3$): δ 2.34-2.78 (dm, 2H, PCH_2), 3.69-3.79 (m, 2H, CH_2Cl), 5.63 (dm, $^{1}J_{PH}$ = 322.8 Hz, 1H, PH), 7.59-7.66 (m, 6H, Ph), 7.85-7.94 (m, 4H, Ph). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ 27.05 (dd, $^{1}J_{CP}$ = 19.2 Hz, $^{2}J_{CP}$ = 2.2 Hz, PCH_2), 41.29 (d, $^{2}J_{CP}$ = 6.3 Hz, CH_2Cl), 129.47 (d, J_{CP} = 12.2 Hz, CH, Ph), 129.52 (d, J_{CP} = 12.3 Hz, CH, Ph), 130.20 (d, $^{2}J_{CP}$ = 10.0 Hz, C, Ph), 130.48 (d, $^{2}J_{CP}$ = 17.4 Hz, C, Ph), 130.98 (d, J_{CP} = 10.1 Hz, CH, Ph), 131.23 (d, J_{CP} = 9.1 Hz, CH, Ph), 133.27 (d, J_{CP} = 3.0 Hz, CH, Ph), 133.42 (d, J_{CP} = 2.5 Hz, CH, Ph), 194.54 (dd, $^{2}J_{CP}$ = 6.4 Hz, $^{3}J_{CP}$ = 1.7 Hz, $^{1}J_{CW}$ = 126.3 Hz, CO *cis*), 196.55 (d, $^{2}J_{CP}$ = 25.4 Hz, CO *trans*). HRMS: m/z 620.9609 (calcd for $C_{19}H_{16}ClO_6P_2W$: $[M+H]^+$, 620.9620).

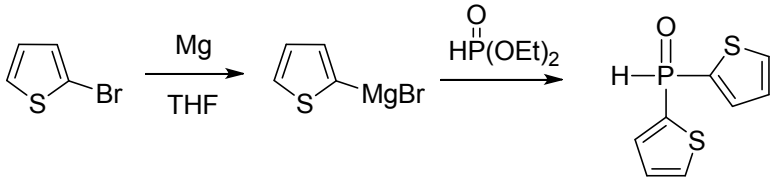
Diphosphine monoxide **2e**: 

1e(528 mg, 0.8 mmol). Yield: 210 mg, 45 %.

$^{31}P\{^{1}H\}$ NMR ($CDCl_3$): δ 34.4 (J_{PP} = 66.1 Hz, P^V), -53.7 (J_{PP} = 66.2 Hz, $^{1}J_{PW}$ = 231.6 Hz, $^{1}J_{PH}$ = 336.3 Hz, P^{III}). ^{1}H NMR ($CDCl_3$): δ 6.56 (dd, J_{PH} = 332.7 Hz, 1H, PH), 7.11-7.78 (m, 13H, Ph, Th). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ 124.04 (d, $^{1}J_{CP}$ = 33.6 Hz, C, Th), 128.97 (d, J_{CP} = 12.5 Hz, CH, Ph), 129.15 (d, J_{CP} = 12.8 Hz, CH, Ph), 129.98 (d, $^{2}J_{CP}$ = 11.4 Hz, C, Ph), 130.15 (d, $^{2}J_{CP}$ = 14.3 Hz, C, Ph), 131.45 (d, J_{CP} = 9.8 Hz, CH, Ph), 131.65 (d, J_{CP} = 9.7 Hz, CH, Ph), 133.07 (d,

J_{CP} = 2.7 Hz, CH, Ph), 133.22 (d, J_{CP} = 2.8 Hz, CH, Ph), 133.93 (s, CH, Th), 138.25 (d, J_{CP} = 3.9 Hz, CH, Th), 138.37 (d, J_{CP} = 3.9 Hz, CH, Th), 194.78 (dd, $^2J_{CP}$ = 6.3 Hz, $^3J_{CP}$ = 1.3 Hz, $^1J_{CW}$ = 124.5 Hz, CO *cis*), 197.12 (d, $^2J_{CP}$ = 26.1 Hz, CO *trans*). HRMS: m/z 640.9575 (calcd for $C_{21}H_{15}O_6P_2SW$: $[M+H]^+$, 640.9574). IR (KBr) ν(CO) 2076 s, 1982 s, 1915 vs cm^{-1}. Anal. Calcd for $C_{21}H_{14}O_6P_2SW$: C, 39.40; H, 2.20; S, 5.01. Found: C, 39.14; H, 2.29; S, 4.90.

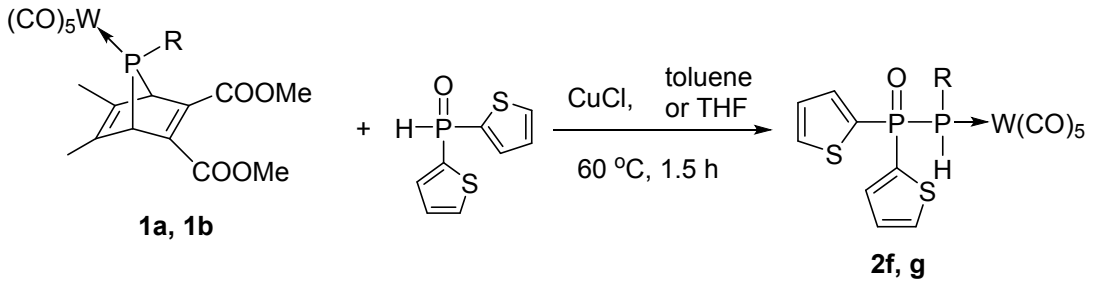
Procedure and characterization data for dithienylphosphine oxide:



A 100 mL Schlenk flask with 360 mg (15 mmol, 3.0 eq) Mg was evacuated/N_2 filled 3 times, then 10 mL dried THF and 0.2 mL 2-bromothiophene were added. After the initiation, 5 mL dried THF and 1.25 mL(15 mmol in total, 3.0 eq) 2-bromothiophene were added to the mixture. The mixture was stirred at ambient temperature for two hours and then cooled to -30 °C. A solution of diethylphosphite (0.64 mL, 5 mmol, 1.0 eq.) in 5 mL THF was then added dropwise over 15 minutes to the mixture. The mixture was kept 15 minutes at 0 °C, then the cold bath was removed, and the mixture stirred for two hours at ambient

temperature. 30 mL 0.3N HCl was added dropwise over 10 minutes at 0 ^{o}C, then 20 mL ethyl acetate was added to the mixture. The mixture was extracted with EtOAc and the organic phase was dried with $MgSO_4$, and then filtered through a Celite pad. Solvents were removed *in vacuo* to give 843 mg (79% yield) of dithienylphosphine oxide as a yellow oil. $^{31}P\{^{1}H\}$ NMR ($CDCl_3$): δ -1.2 (J_{PH} = 515.4 Hz). ^{1}H NMR ($CDCl_3$): δ 7.22-7.25 (m, 2H, Th), 7.64-7.81 (m, 4H, Th), 8.46 (d, $^{1}J_{PH}$ = 515.4 Hz, 1H, PH). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ 128.48 (d, J_{CP} = 15.2 Hz, CH, Th), 131.78 (d, J_{CP} = 116.6 Hz, C, Th), 124.55 (d, J_{CP} = 5.6 Hz, CH, Th), 136.04 (d, J_{CP} = 12.4 Hz, CH, Th). HRMS: m/z 646.9139 (calcd for $C_{19}H_{13}O_6P_2S_2W$: $[M+H]^+$, 646.9138).

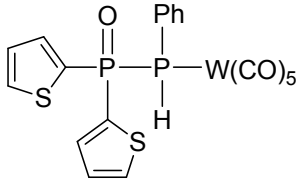
General procedure and characterization data for 2f, 2g:



	R	isolated yield of **3a, 3b** (%)
2f:	Ph	71
2g:	Me	40

A solution of 7-R-7-phosphanorbornadiene complex **1a-1b** (0.8 mmol, 1eq), dithienylphosphine oxide (0.8 mmol, 1eq) and CuCl (0.3 mmol) in toluene or THF (10 mL) was stirred at 60 °C for 1.5 h. The solvents were

removed *in vacuo*, and the residue was chromatographed at -15°C on silica gel using a 50:1 dichloromethane:THF mixture, to give a yellowish solid.

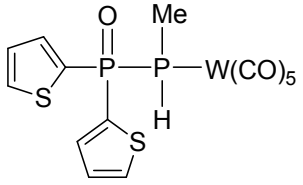


2f:

463 mg, 71 %.

$^{31}P\{^{1}H\}$ NMR ($CDCl_3$): δ 21.0 (J_{PP} = 46.9 Hz, P^{V}), -19.9 (J_{PP} = 46.9 Hz, $^{1}J_{PW}$ = 228.3 Hz, $^{1}J_{PH}$ = 330.6 Hz, P^{III}). ^{1}H NMR ($CDCl_3$): δ 6.19 (dd, $^{1}J_{PH}$ = 330.3 Hz, $^{2}J_{PH}$ = 2.7 Hz, 1H, PH), 7.10 (s, 1H, Ph), 7.26-7.43 (m, 7H, Ph, Th), 7.67-7.74 (m, 2H, Ph), 7.84-7.86 (m, 1H, Th). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ 126.48 (d, $^{1}J_{CP}$ = 35.2 Hz, C, Ph), 128.64 (d, J_{CP} = 14.5 Hz, CH, Ph), 128.99 (d, J_{CP} = 14.6 Hz, CH, Ph), 129.02(d, J_{CP} = 1.7 Hz, CH, Th), 129.15 (d, J_{CP} = 1.6 Hz, CH, Th), 130.27 (dd, $^{1}J_{CP}$ = 99.6 Hz, $^{2}J_{CP}$ = 17.1 Hz, C, Th), 130.62 (dd, $^{1}J_{CP}$ = 100.9 Hz, $^{2}J_{CP}$ = 15.7 Hz, C, Th), 131.42 (t, CH, Ph), 133.62 (d, J_{CP} = 3.6 Hz, CH, Ph), 133.76 (d, J_{CP} = 3.5 Hz, CH, Ph), 135.16 (d, J_{CP} = 4.7 Hz, CH, Th), 135.36 (d, J_{CP} = 4.6 Hz, CH, Th), 137.15 (d, J_{CP} = 10.0 Hz, CH, Th), 137.47 (d, J_{CP} = 9.9 Hz, CH, Th), 194.70 (dd, $^{2}J_{CP}$ = 6.6 Hz, $^{3}J_{CP}$ = 2.0 Hz, $^{1}J_{CW}$ = 127.5 Hz, CO *cis*), 197.42 (d, $^{2}J_{CP}$ = 25.5 Hz, CO *trans*). HRMS: m/z 646.9139 (calcd for $C_{19}H_{13}O_6P_2S_2W$: $[M+H]^+$, 646.9138). IR (KBr) ν(CO) 2077 s, 1991 s, 1940 vs, 1913 vs cm^{-1}. Anal. Calcd for $C_{19}H_{12}O_6P_2S_2W$: C, 35.31; H, 1.87; S, 9.92.

Found: C, 35.38; H, 1.90; S, 9.71.

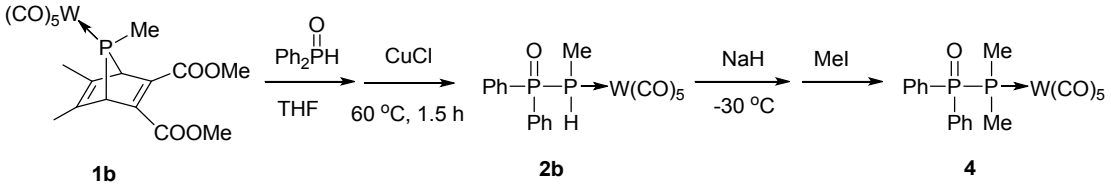


2g:

182 mg, 40 %.

$^{31}P\{^{1}H\}$ NMR ($CDCl_3$): δ 20.7 (J_{PP} = 38.2 Hz, P^{V}), -54.2 (J_{PP} = 38.0 Hz, $^{1}J_{PW}$ = 226.0 Hz, $^{1}J_{PH}$ = 322.9 Hz, P^{III}). ^{1}H NMR ($CDCl_3$): δ 1.81-1.89 (m, 3H, CH_3), 5.40 (dm, $^{1}J_{PH}$ = 323.1 Hz, 1H, PH), 7.32 (s, 2H, Th), 7.79-7.90 (m, 4H, Th). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ 8.19 (d, J_{CP} = 22.0 Hz, CH_3), 129.13 (d, J_{CP} = 14.5 Hz, CH, Th), 129.84 (dd, $^{1}J_{CP}$ = 102.5 Hz, $^{2}J_{CP}$ = 18.9 Hz, C, Th), 130.37 (dd, $^{1}J_{CP}$ = 100.5 Hz, $^{2}J_{CP}$ = 15.3 Hz, C, Th), 135.50 (d, J_{CP} = 4.8 Hz, CH, Th), 135.67 (d, J_{CP} = 4.5 Hz, C, Th), 137.41 (d, J_{CP} = 10.0 Hz, CH, Th), 137.71 (d, J_{CP} = 10.0 Hz, CH, Th), 194.74 (dd, $^{2}J_{CP}$ = 6.6 Hz, $^{3}J_{CP}$ = 2.0 Hz, $^{1}J_{CW}$ = 125.1 Hz, CO *cis*), 197.40 (d, $^{2}J_{CP}$ = 25.0 Hz, CO *trans*). HRMS: m/z 584.8974 (calcd for $C_{14}H_{11}O_6P_2S_2W$: $[M+H]^+$, 584.8982). IR (KBr) ν(CO) 2077 s, 1991 s, 1910 vs cm^{-1}. Anal. Calcd for $C_{14}H_{10}O_6P_2S_2W$: C, 28.79; H, 1.73; S, 10.98. Found: C, 28.75; H, 1.71; S, 10.83.

Procedure and characterization data for compound 4:

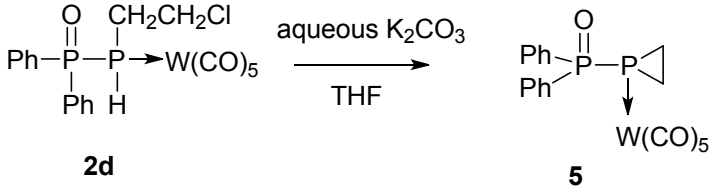


A solution of 7-Me-7-phosphanorbornadiene complex **1b** (300 mg, 0.5 mmol), diphenylphosphine oxide (105 mg, 0.5 mmol) and CuCl (25mg, 0.25 mmol) in THF (10 mL) was stirred at 60 °C for 1.5 h. Then NaH (60%, 20 mg, 0.5 mmol) was added at -30°C, the mixture was stirred at ambient temperature for 30 min. MeI (40 μL, 0.6 mmol) was added to the mixture at ambient temperature and stirred for 20 min. The solvents were removed *in vacuo*. A light yellow solid (140 mg, 60 %) was recovered by TLC using DCM as the eluent.

$^{31}P\{^{1}H\}$ NMR ($CDCl_3$): δ 35.3 (J_{PP} = 78.7 Hz, P^{V}), -33.6 (J_{PP} = 78.6 Hz, $^{1}J_{PW}$ = 228.2 Hz, P^{III}),. ^{1}H NMR ($CDCl_3$): 1.83 (dd, J_{PH} = 2.5Hz, J_{PH} = 1.6Hz, CH_3), 7.57-7.67 (m, 6H, Ph), 7.83-7.90 (m, 4H, Ph). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ 15.75 (dd, $^{1}J_{CP}$ = 22.2 Hz, $^{2}J_{CP}$ = 1.6 Hz, CH_3), 129.16 (d, J_{CP} = 12.0 Hz, CH, Ph), 129.37 (dd, $^{1}J_{CP}$ = 86.6 Hz, $^{2}J_{CP}$ = 14.0 Hz, C, Ph), 131.75 (dd, J_{CP} = 9.6 Hz, J_{CP} = 1.0 Hz, CH, Ph), 133.09 (d, J_{CP} = 2.6 Hz, CH, Ph), 195.96 (d, $^{2}J_{CP}$ = 6.6 Hz, $^{1}J_{CW}$ = 124.9 Hz, CO *cis*), 198.15 (d, $^{2}J_{CP}$ = 23.1 Hz, CO *trans*). HRMS: m/z 587.0005 (calcd for $C_{19}H_{16}O_6P_2W$: $[M+H]^+$, 587.0004). IR (KBr) ν(CO) 2074 w, 1983 w, 1933 vs, 1912 cm^{-1}. Anal. Calcd for $C_{19}H_{16}O_6P_2W$: C,

38.93; H, 2.75. Found: C, 38.91; H, 2.71.

Procedure and characterization data for compound 5:



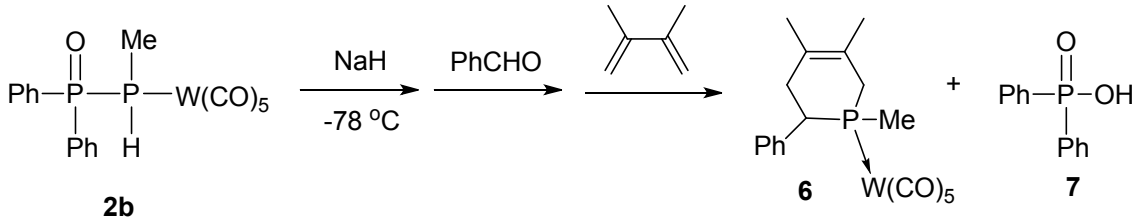
2d **5**

Aqueous K_2CO_3 (4 mL, 0.2 mol/L) was added dropwise to a solution of **2d** (139 mg, 0.22 mmol) in THF (3 mL) at r. t. and stirred for 10 min. The mixture was extracted with Et_2O and the solvents were removed *in vacuo.* The residue was chromatographed at -15°C on silica gel using a 50:1 dichloromethane:THF mixture, to give a yellowish solid (114 mg, 89 %).

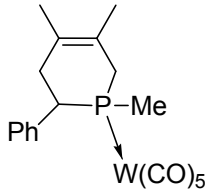
$^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 34.8 (J_{PP} = 129.4 Hz, P^V), -226.0 (J_{PP} = 129.2 Hz, $^1J_{PW}$ = 240.1 Hz, P^{III}),. ^1H NMR ($CDCl_3$): 1.54-1.61 (m, 2H, CH_2), 2.15-2.24 (m, 2H, CH_2), 7.57-7.68 (m, 6H, Ph), 7.80-7.86 (m, 4H, Ph). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 10.79 (d, $^1J_{CP}$ = 18.8 Hz, CH_2), 129.29 (d, J_{CP} = 12.5 Hz, CH, Ph), 129.74 (dd, $^1J_{CP}$ = 92.5 Hz, $^2J_{CP}$ = 16.8 Hz, C, Ph), 131.95 (dd, J_{CP} = 10.4 Hz, J_{CP} = 2.3 Hz, CH, Ph), 133.26 (d, J_{CP} = 2.6 Hz, CH, Ph), 194.70 (d, $^2J_{CP}$ = 7.2 Hz, $^1J_{CW}$ = 125.8 Hz, CO *cis*), 196.03 (dd, $^2J_{CP}$ = 33.0 Hz, $^3J_{CP}$ = 2.9 Hz, CO *trans*). HRMS: m/z 584.9850 (calcd for $C_{19}H_{15}O_6P_2W$: $[M+H]^+$, 584.9853).

IR (KBr) ν(CO) 2076 s, 1917 vs cm^{-1}. Anal. Calcd for $C_{19}H_{14}O_6P_2W$: C, 39.07; H, 2.42. Found: C, 39.17; H, 2.31.

Procedure and characterization data for compound 6:



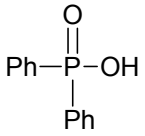
PhCHO (55 μL, 0.5 mmol), and excess of 2,3-dimethyl-1,3-butadiene (565 μL, 5 mmol) was added to a solution of **2b** (286 mg, 0.5 mmol) in THF (8 mL) successively. Then NaH (20 mg, 0.5 mmol) was added to the solution at − 78 °C and stirred at room temprature for 10 min. The solvents were removed in *vacuo.* The residue was washed with THF to give **7** (78 mg, 72 %) as a white solid. Then the residue was chromatographed on silica gel using petroleum ether to give **6** as a yellowish oil (81mg, 30 %).



6

$^{31}P\{^{1}H\}$ NMR ($CDCl_3$): δ -17.9 (J_{PW} = 239.6 Hz). ^{1}H NMR ($CDCl_3$): 1.61 (d, $^{2}J_{PH}$ = 6.6 Hz, 3H, CH_3P), 1.74 (s, 3H, CH_3), 1.82 (s, 3H, CH_3), 2.44-2.58 (m, 2H, CH_2), 2.65-2.81 (m, 2H, CH_2), 3.09-3.18 (m, 1H, CH), 7.25-7.33 (m, 5H, Ph). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ 18.57 (d, $^{1}J_{CP}$ = 25.0 Hz, CH_3P), 20.14 (d, J_{CP} = 1.5 Hz, CH_3), 21.57 (d, J_{CP} = 8.1 Hz, CH_3), 36.51 (s, CH_2), 37.71 (d, $^{1}J_{CP}$ =

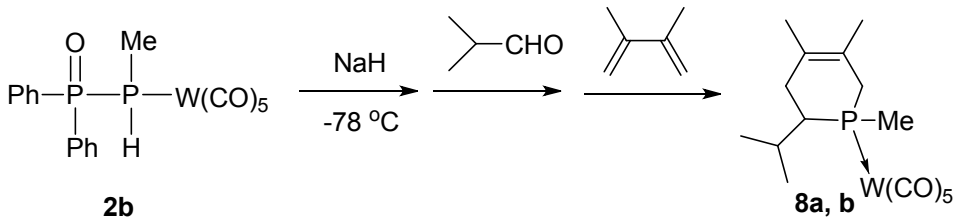
25.1 Hz, CH_2P), 44.0 (d, $^1J_{CP}$ = 21.7 Hz, CHP), 121.33 (d, J_{CP} = 4.1 Hz, =C-), 127.52 (d, J_{CP} = 3.0 Hz, CH, Ph), 128.08 (d, J_{CP} = 9.4 Hz, =C-), 128.31 (d, J_{CP} = 4.8 Hz, CH, Ph), 128.83 (d, J_{CP} = 2.4 Hz, CH, Ph), 138.86 (d, J_{CP} = 0.7 Hz, C, Ph), 196.70 (d, J_{CP} = 7.2 Hz, CO *cis*), 198.98 (d, J_{CP} = 21.5 Hz, CO *trans*).



7

$^{31}P\{^1H\}$ NMR (CD_3OD): δ 20.63. ^1H NMR (CD_3OD): δ 5.07 (s, 1H), 7.35-7.38 (m, 6H, Ph), 7.77-7.84 (m, 4H, Ph). $^{13}C\{^1H\}$ NMR (CD_3OD): δ 127.49 (d, J_{CP} = 12.1 Hz, CH, Ph), 129.65 (d, J_{CP} = 2.2 Hz, CH, Ph *para*), 130.91 (d, J_{CP} = 9.4 Hz, CH, Ph), 139.41 (d, J_{CP} = 131.7 Hz, C, Ph *ipso*).

Procedure and characterization data for compound 8a,b:



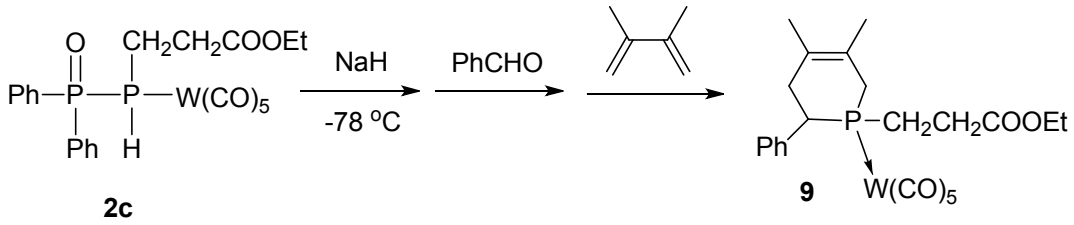
2b **8a, b**

Isobutyraldehyde (46 µL, 0.5 mmol), and excess of 2,3-dimethyl-1,3-butadiene (565 µL, 5 mmol) was added to a solution of **2b** (286 mg, 0.5 mmol) in THF (8 mL) successively. Then NaH (20 mg, 0.5 mmol) was added to the solution at − 78 °C and stirred at room temperature for 10 min. The solvents were removed in *vacuo.* The residue was chromatographed on silica gel using petroleum ether to give a mixture of **8a, b** as a yellowish solid (53 mg, 21 %, **8a**:**8b** = 1:0.8).

8a: $^{31}P\{^{1}H\}$ NMR ($CDCl_3$): δ -22.4 (J_{PW} = 230.8 Hz). ^{1}H NMR ($CDCl_3$): 0.90 (d, *J* = 6.9 Hz, 3H, CH_3), 1.10 (d, *J* = 2.7 Hz, 3H, CH_3), 1.53 (d, *J* = 6.9 Hz, 3H, CH_3), 1.66-1.72 (m, 6H,CH_3), 1.77-1.79 (m, 1H, CH), 2.03-2.20 (m, 2H, CH_2), 2.28-2.50 (m, 3H, CH + CH_2). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ 12.55 (d, $^{1}J_{CP}$ = 23.0 Hz, CH_3P), 17.50 (d, J_{CP} = 1.7 Hz, CH_3), 20.43 (s, CH_3), 21.11 (d, J_{CP} = 8.2 Hz, CH_3), 22.56 (d, J_{CP} = 14.6 Hz, CH_3), 29.76 (d, J_{CP} = 4.4 Hz, CH), 35.14 (s, CH_2), 38.83 (d, $^{1}J_{CP}$ = 29.2 Hz, CH_2P), 40.14 (d, $^{1}J_{CP}$ = 24.2 Hz, CHP), 121.13 (d, J_{CP} = 8.0 Hz, =C-), 126.91 (d, J_{CP} = 7.0 Hz, =C-), 197.11 (d, J_{CP} = 7.2 Hz, CO *cis*), 199.55 (d, J_{CP} = 19.8 Hz, CO *trans*).

8b: $^{31}P\{^{1}H\}$ NMR ($CDCl_3$): δ-23.4 (J_{PW} = 230.1 Hz). ^{1}H NMR ($CDCl_3$): 1.04 (d, *J* = 6.6 Hz, 3H, CH_3), 1.07 (d, *J* = 2.7 Hz, 3H, CH_3), 1.61 (d, *J* = 6.6 Hz, 1H, CH), 1.66-1.72 (m, 9H,CH_3), 1.87-1.94 (m, 1H, CH), 2.03-2.20 (m, 2H, CH_2), 2.63-2.79 (m, 2H, CH_2). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ 19.83 (d, J_{CP} = 1.7 Hz, CH_3), 20.03 (s, CH_3), 20.89 (d, $^{1}J_{CP}$ = 24.7 Hz, CH_3P), 21.29 (d, J_{CP} = 1.8 Hz, CH_3), 23.82 (d, J_{CP} = 6.6 Hz, CH_3), 27.62 (d, J_{CP} = 6.4 Hz, CH_2), 31.52 (d, J_{CP} = 3.5 Hz, CH), 38.56 (d, $^{1}J_{CP}$ = 29.0 Hz, CH_2P), 40.41 (d, $^{1}J_{CP}$ = 22.2 Hz, CHP), 120.87 (d, J_{CP} = 3.8 Hz, =C-), 128.08 (d, J_{CP} = 10.9 Hz, =C-), 196.95 (d, J_{CP} = 7.1 Hz, CO *cis*), 198.97 (d, J_{CP} = 20.1 Hz, CO *trans*).

Procedure and characterization data for compound 9:



2c **9**

PhCHO (100 μL, 1.0 mmol), and excess of 2,3-dimethyl-1,3-butadiene (1.13 mL, 10 mmol) was added to a solution of **2c** (658 mg, 1 mmol) in THF (10 mL) successively. Then NaH (40 mg, 1 mmol) was added to the solution at − 78 °C and stirred at room temperature for 10 min. The solvents were removed in *vacuo.* The residue was chromatographed on silica gel using petroleum ether/ ethyl acetate 10:1 to give a yellowish oil (152mg, 24%).

$^{31}P\{^{1}H\}$ NMR ($CDCl_3$): δ -7.4 (J_{PW} = 243.4 Hz). ^{1}H NMR ($CDCl_3$): 1.25 (t, J_{HH} = 7.2 Hz, 3H, CH_3 Et), 1.73 (s, 3H, CH_3), 1.83 (s, 3H, CH_3), 2.10-2.74 (m, 8H, CH_2), 3.14-3.23 (m, 1H, CH), 4.14 (q, J_{HH} = 6.9 Hz, 2H, CH_2 Et), 7.24-7.32 (m, 5H, Ph). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ 14.16 (s, CH_3), 20.09 (d, J_{CP} = 1.1 Hz, CH_3), 21.65 (d, J_{CP} = 7.6 Hz, CH_3), 26.58 (d, J_{CP} = 23.2 Hz, CH_2), 29.36 (d, J_{CP} = 2.5 Hz, CH_2), 34.95 (d, J_{CP} = 24.1 Hz, CH_2), 36.91 (s, CH_2), 42.11 (d, J_{CP} = 20.4 Hz, CHP), 61.06 (s, CH_2), 121.40 (d, J_{CP} = 4.8 Hz, =C-), 127.73 (d, J_{CP} = 2.8 Hz, CH, Ph), 128.11 (d, J_{CP} = 9.2 Hz, =C-), 128.37 (d, J_{CP} = 4.8 Hz, CH, Ph), 129.04 (d, J_{CP} = 2.1 Hz, CH, Ph), 139.52 (s, C, Ph), 172.10 (d, J_{CP} = 14.8 Hz, C=O), 196.43 (d, J_{CP} = 7.0 Hz, CO *cis*), 198.14 (d, J_{CP} = 22.2 Hz, CO *trans*).