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Simple Access to Tungsten-Stabilized Disecondary Diphosphines

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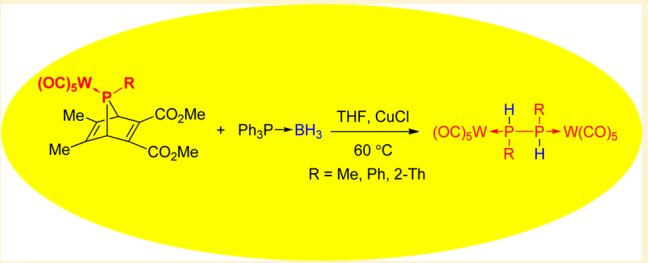
Supporting Information

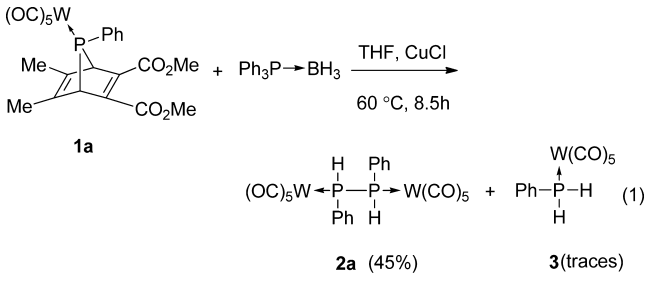
ABSTRACT: Transient terminal phosphinidene complexes [RP-W(CO)$_5$] dimerize in the presence of copper chloride, and the dimers react in situ with triphenylphosphine–borane to give the disecondary diphosphine complexes [RPH–PHR][W(CO)$_5$]$_2$. When R = CH_2CH_2Cl, a cyclization takes place to give the diphosphirane complex. A 1,2-diphospholane is obtained for R = Ph by further reaction with 1,3-dibromopropane in the presence of aqueous K_2CO_3.



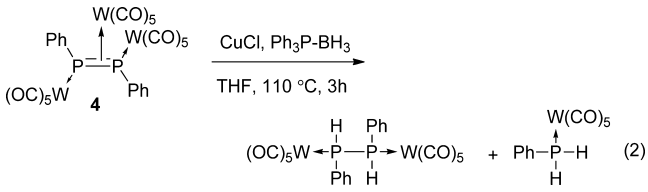
Disecondary diphosphines have been known for a long time[1] but have not attracted a great deal of interest, probably as a result of their high reactivity and difficult handling. The most recent contribution to their synthesis relies on the dehydrocoupling of primary phosphines by transition-metal catalysts.[2] In a recent paper, we prepared some decacarbonyl ditungsten complexes of disecondary diphosphines and noticed their good stability and the possibility of obtaining crystals for X-ray analysis.[3] It was thus desirable to devise a simple access to such species in order to fully develop their synthetic potential. This is the subject of this report.

RESULTS AND DISCUSSION

In a preceding study,[4] we described the insertion of terminal phosphinidene complexes [RP–W(CO)$_5$] into the B–H bonds of H_3B–L (L = NEt_3, PPh_3). The reaction was performed in boiling toluene with the appropriate 7-phosphanorbornadiene precursors. It is known that the generation of phosphinidenes from such species is catalyzed by CuCl.[5] Thus, we reinvestigated this reaction in the presence of the copper catalyst. The outcome proved to be entirely different, as shown in eq 1.



Both THF and CuCl are necessary to obtain a satisfactory yield of the diphosphine complex **2a**, which is obtained as a 1:1 mixture of the *meso* and *rac* diastereomers that have been described in our previous paper.[3] Since copper chloride favors the formation of diphosphene complexes[6] and since bulky diphosphenes are known to be reducible to the corresponding diphosphines,[7] it was tempting to suspect that the phosphinidene species only sluggishly inserts into the B–H bond at 60 °C (the insertion is normally performed at 110 °C) and prefers to dimerize to give the diphosphene, which is then cleanly reduced by the borane adduct. THF is absolutely necessary to perform the reaction depicted in eq 1. The mechanism of the reduction of P═P by BH_3L probably involves a nucleophilic attack of the negative boron onto the double bond, which is favored by THF. The probable intermediacy of the phosphinidene dimer has been proven by replacing **1a** by the preformed diphosphene complex **4**[6] (eq 2).



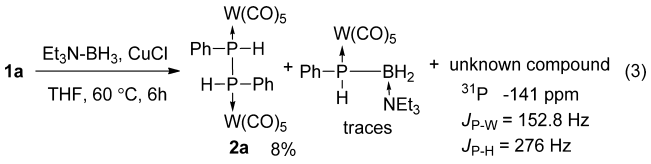
The higher temperature (110 vs 60 °C) needed to carry out the reduction is probably due to the initial decomplexation step of the π bond.

Quite unexpectedly, the replacement of the triphenylphosphine by the triethylamine–borane adduct led to a much lower yield of **2a** together with an unstable product (eq 3).

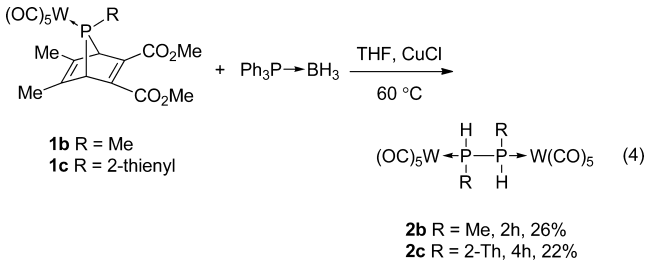
We separately observed that both Et_3N–BH_3 + CuCl and Et_3N catalyze the decomposition of **2a**. The triphenylphosphine adduct was, thus, the reagent of choice for the synthesis of the

Received: July 2, 2013
Published: September 12, 2013

   dx.doi.org/10.1021/om400637j | *Organometallics* 2013, 32, 5615–5618



disecondary diphosphine complexes. We checked that the reaction is general (eq 4).



The *rac* diastereomer of **2c** was obtained in the crystalline state and characterized by X-ray crystal structure analysis (Figure 1). The main difference with the crystal structure of

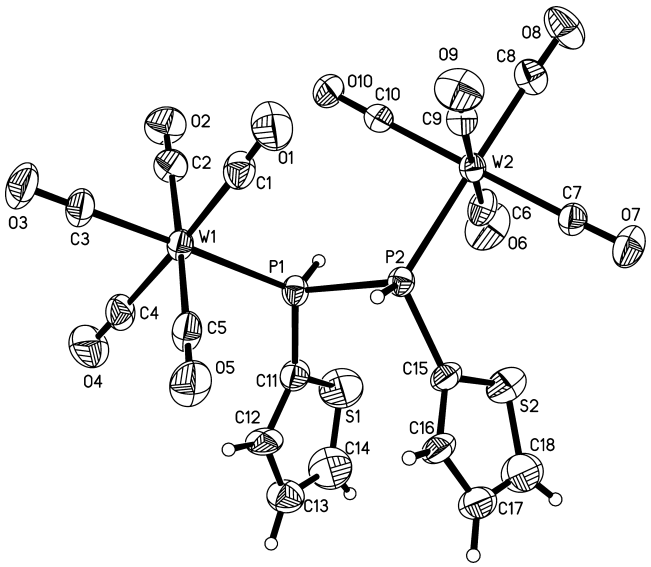
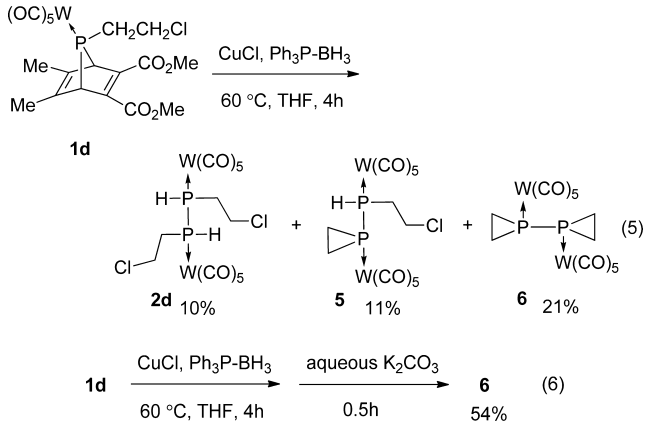


Figure 1. X-ray crystal structure of *rac*-diphosphine complex **2c**. Main distances (Å) and angles (deg): W1–P1 = 2.4846(17), W2–P2 = 2.4847(18), P1–C11 = 1.817(7), P2–C15 = 1.820(9), P1–P2 = 2.248(2); P2–P1–W1 = 113.59(8), P2–P1–C11 = 104.6(5), W1–P1–P2–W2 = 96.15, C11–P1–P2–C15 = 0.45.

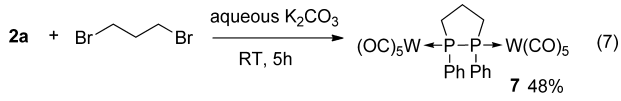
rac-**2a**[3] lies in the value of the R–P–P–R dihedral angle which varies from 78.3° for R = Ph to 2.16° for R = 2-Th. The two thiophene planes make an angle of 23.3°. The C11···C15 distance is 3.305 Å, suggesting a possible π–π interaction between the two aromatic rings.

The next step was to perform a preliminary evaluation of the synthetic potential of these diphosphine complexes. We started with R = CH_2CH_2Cl in order to verify the possibility of obtaining phosphirane derivatives (eq 5).

In addition to the normal diphosphine **2d**, which is unstable and difficult to purify, we also obtained the monocyclized product **5** and the diphosphirane complex **6**. It is possible to perform a complete cyclization using potassium carbonate as the base and to obtain **6** in good yield (eq 6).



It must be noted that **6** has already been obtained from **1d** using the naked fluoride ion as the base, although in lower yield.[8] In another series of experiments, we prepared a diphospholane from **2a** (eq 7).



The diphospholane **7** was obtained as a mixture of two diastereomers. One of these was obtained in the crystalline state and submitted to a X-ray crystal structure analysis (Figure 2). The P–P bond length is in the normal range at 2.235 Å in spite of the ring strain (intracyclic C–P–P angles ca. 90°), the phenyl substituents are in a quasi-*trans* disposition (Ph–P–P–Ph torsion angle 173.9°), and the complexing groups are in a staggered conformation (W–P–P–W = 78.0°). 1,2-Diphenyl-1,2-diphospholane has already been described in the literature.[2c,9] At this stage, it is clear that it is possible to develop easily a

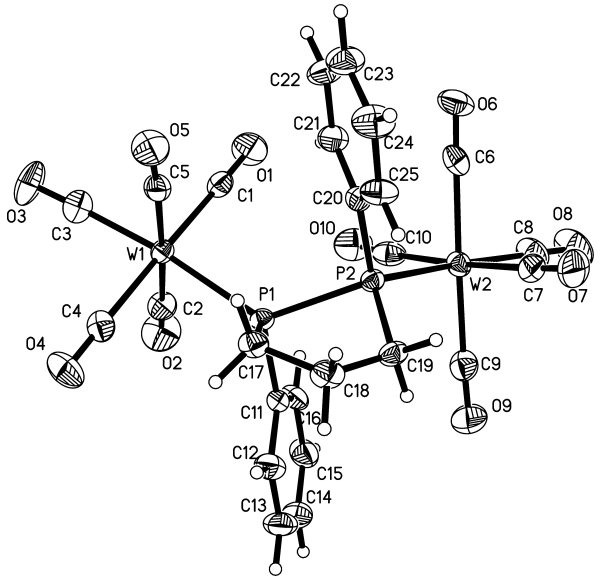


Figure 2. X-ray crystal structure of one diastereomer of the 1,2-diphospholane complex **7**. Main distances (Å) and angles (deg): W1–P1 = 2.5118(14), W2–P2 = 2.5062(14), P1–P2 = 2.235(2), P1–C11 = 1.827(5), P2–C20 = 1.820(5), P1–C17 = 1.832(5), P2–C19 = 1.836(5), C17–C18 = 1.539(8), C18–C19 = 1.538(8); C11–P1–P2 = 101.32(18), C17–P1–P2 = 91.1(2), C11–P1–C17 = 104.8(2), C19–P2–P1 = 90.5(2).

dx.doi.org/10.1021/om400637j | *Organometallics* 2013, 32, 5615–5618

sizable synthetic chemistry from these disecondary diphosphine complexes.

EXPERIMENTAL SECTION

All reactions were performed under nitrogen using solvents dried by standard methods. NMR spectra were obtained using a 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. X-ray crystallographic analyses were performed on an Oxford diffraction Gemini E diffractometer. Silica gel (200−300 mesh) was used for the chromatographic separations. The 7-phosphanorbornadiene complexes **1a**−**d** were prepared according to literature methods.[6,10,11] Commercially available reagents were used without further purification.

Diphosphine 2a. A solution of 7-phenyl-7-phosphanorbornadiene complex **1a** (328 mg, 0.5 mmol), borane−triphenylphosphine complex (276 mg, 1 mmol), and CuCl (20 mg, 0.2 mmol) in THF (10 mL) was stirred at 60 °C for 8.5 h. After evaporation, the residue was chromatographed on silica gel using a 10/1 petroleum ether/dichloromethane mixture, to give a yellowish solid (96.3 mg, 45%).

Isomer A. ^{31}P NMR (CH_2Cl_2): δ −20.4 ($^1J_{PW}$ = 157.8 Hz, $^2J_{PW}$ = 70.2 Hz). ^{1}H NMR ($CDCl_3$): δ 6.38 (d, $^1J_{HP}$ = 342.9 Hz, 2H, PH), 7.34−7.56 (m, 10H, Ph). ^{13}C NMR ($CDCl_3$): δ 129.72 (pseudo-t, J_{CP} = 4.1 Hz, C *meta*), 130.07 (pseudo-t, J_{CP} = 18.0 Hz, C *ipso*), 131.94 (s, C *para*), 133.07 (pseudo-t, J_{CP} = 6.8 Hz, C *ortho*), 194.91 (pseudo-t, J_{CP} = 2.3 Hz, CO *cis*), 197.24 (pseudo-t, J_{CP} = 12.8 Hz, CO *trans*).

Isomer B. ^{31}P NMR (CH_2Cl_2): δ −23.5 ($^1J_{PW}$ = 161.2 Hz, $^2J_{PW}$ = 64.2 Hz). ^{1}H NMR ($CDCl_3$): δ 6.39 (d, $^1J_{HP}$ = 350.1 Hz, 2H, PH), 7.34−7.56 (m, 10H, Ph). ^{13}C NMR ($CDCl_3$): δ 128.16 (pseudo-t, J_{CP} = 17.8 Hz, C *ipso*), 129.35 (pseudo-t, J_{CP} = 4.1 Hz, C *meta*), 131.68 (s, C *para*), 133.76 (pseudo-t, J_{CP} = 6.6 Hz, C *ortho*), 195.16 (pseudo-t, J_{CP} = 2.3 Hz, CO *cis*), 197.43 (pseudo-t, J_{CP} = 12.8 Hz, CO *trans*).

Diphosphine 2b. A solution of 7-methyl-7-phosphanorbornadiene complex **1b** (824 mg, 1.5 mmol), borane−triphenylphosphine complex (825 mg, 3 mmol), and CuCl (58 mg, 0.6 mmol) in THF was stirred at 60 °C for 2 h. After evaporation, the residue was chromatographed on silica gel using a 6/1 petroleum ether/dichloromethane mixture, to give a yellowish solid (144 mg, 26%).

Isomer A. ^{31}P NMR ($CDCl_3$): δ −61.5 ($^1J_{PW}$ = 159.4 Hz, $^2J_{PW}$ = 65.1 Hz). ^{1}H NMR ($CDCl_3$): δ 1.89−2.06 (m, 6H, Me), 5.57 (dm, $^1J_{HP}$ = 336.6 Hz, 2H, PH). ^{13}C NMR ($CDCl_3$): δ 12.73 (pseudo-t, J_{CP} = 13.1 Hz, Me), 195.03 (q, J_{CP} = 2.3 Hz, CO *cis*), 197.06 (pseudo-t, J_{CP} = 13.1 Hz, CO *trans*).

Isomer B. ^{31}P NMR ($CDCl_3$): δ −66.3 ($^1J_{PW}$ = 165.0 Hz, $^2J_{PW}$ = 59.8 Hz). ^{1}H NMR: δ 1.89−2.06 (m, 6H, Me), 5.59 (dm, $^1J_{HP}$ = 336.6 Hz, 2H, PH). ^{13}C NMR ($CDCl_3$): δ 10.21 (pseudo-t, J_{CP} = 14.3 Hz, Me), 195.03 (q, J_{CP} = 2.3 Hz, CO *cis*), 197.06 (pseudo-t, J_{CP} = 13.1 Hz, CO *trans*).

Diphosphine 2c. A solution of 7-thiophenyl-7-phosphanorbornadiene complex **1c** (657 mg, 1 mmol), borane−triphenylphosphine complex (552 mg, 2 mmol), and CuCl (40 mg, 0.4 mmol) in THF was stirred at 60 °C for 4 h. After evaporation, the residue was chromatographed on silica gel using a 10/1 petroleum ether/dichloromethane mixture, to give a yellowish solid (96 mg, 22%).

Isomer A. ^{31}P NMR ($CDCl_3$): δ −35.6 (J_{PH} = 355.0 Hz, $^1J_{PW}$ = 162.0 Hz, $^2J_{PW}$ = 75.0 Hz). ^{1}H NMR ($CDCl_3$): δ 6.83 (d, $^1J_{HP}$ = 360.6 Hz, 2H, PH), 7.27 (t, J = 3.9 Hz, 2H, Th), 7.36−7.41 (m, 2H, Th), 7.78 (d, J = 4.8 Hz, 2H, Th). ^{13}C NMR ($CDCl_3$): δ 128.48 (pseudo-t, J_{CP} = 16.1 Hz, C), 129.41 (q, J_{CP} = 4.5 Hz, CH), 134.74(s, CH), 138.65 (pseudo-t, J_{CP} = 7.0 Hz, CH), 194.66 (pseudo-t, J_{CP} = 2.0 Hz, CO *cis*), 196.83 (pseudo-t, J_{CP} = 13.4 Hz, CO *trans*).

Isomer B. ^{31}P NMR ($CDCl_3$): δ −44.5 (J_{PH} = 354.9 Hz, $^1J_{PW}$ = 168.4 Hz, $^2J_{PW}$ = 68.3 Hz). ^{1}H NMR ($CDCl_3$): δ 6.83 (d, $^1J_{HP}$ = 360.6 Hz, 2H, PH), 7.18 (t, J = 4.2 Hz, 2H, Th), 7.36−7.41 (m, 2H, Th), 7.72 (d, J = 4.8 Hz, 2H, Th). ^{13}C NMR ($CDCl_3$): δ 126.68 (pseudo-t, J_{CP} = 17.9 Hz, C), 129.41 (q, J_{CP} = 4.5 Hz, CH), 134.74(s, CH), 138.85 (pseudo-t, J_{CP} = 6.8 Hz, CH), 194.84 (pseudo-t, J_{CP} = 2.3 Hz, CO *cis*), 196.83 (pseudo-t, J_{CP} = 13.4 Hz, CO *trans*).

HRMS: calcd for $C_{18}H_7O_{10}P_2S_2W_2$ $[M - H]^-$ 876.7975, found 876.7979.

Diphosphine 2d. A solution of 7-phosphanorbornadiene complex **1d** (2.56 g, 4 mmol), borane−triphenylphosphine complex (2.2 g, 8 mmol), and CuCl (156 mg, 1.6 mmol) in THF was stirred at 60 °C for 4 h. After evaporation, the residue was purified by chromatography with petroleum ether/dichloromethane (10/1) as the eluent. Yield: compound **2d**, 172 mg, 10%; compound **5**, 176 mg, 11%; compound **6**, 320 mg, 21%. Compound **6** has already been described.[8]

Compound 2d (Two Isomers). ^{31}P NMR ($CDCl_3$): δ −59.2 ($^1J_{PW}$ = 156.4 Hz, $^2J_{PW}$ = 72.7 Hz, J_{PH} = 325.4 Hz), −66.1 ($^1J_{PW}$ = 159.2 Hz, $^2J_{PW}$ = 72.6 Hz, J_{PH} = 341.1 Hz). ^{1}H NMR ($CDCl_3$): δ 2.48−2.91 (dm, 4H, PCH_2), 3.79−3.98 (m, 4H, CH_2Cl), 4.98−6.86 (dm, $^1J_{HP}$ = 327.6 Hz, $^1J_{HP}$ = 344.0 Hz, 2H, PH). ^{13}C NMR ($CDCl_3$): δ 32.09 (pseudo-t, J_{CP} = 22.4 Hz, PCH_2), 30.15 (pseudo-t, J_{CP} = 28.6 Hz, PCH_2), 41.10 (s, CH_2), 40.91 (s, CH_2,), 194.60 (pseudo-t, J_{CP} = 4.3 Hz, CO *cis*,), 194.45 (pseudo-t, J_{CP} = 4.5 Hz, CO *cis*,), 195.5−196.1 (m, CO *trans*).

Compound 5. ^{31}P NMR ($CDCl_3$): δ −33.0 (J_{PP} = 193.8 Hz, J_{PW} = 230.7 Hz), −212.4 (J_{PP} = 194.0 Hz, J_{PW} = 249.2 Hz). ^{1}H NMR ($CDCl_3$): δ 1.59−2.04 (m, 4H, CH_2), 2.62 (dm, J_{HP} = 60.0 Hz, 2H, PCH_2), 3.87−3.97 (m, 2H, CH_2Cl), 5.26 (dm, $^1J_{HP}$ = 330.0 Hz, 2H, PH). ^{13}C NMR ($CDCl_3$): δ 10.86 (dd, J_{CP} = 15.4 Hz, J = 3.9 Hz CH_2), 17.46 (dd, J_{CP} = 17.6 Hz, J = 2.2 Hz CH_2), 31.50 (dd, J_{CP} = 12.1 Hz, J = 6.6 Hz CH_2P), 41.53 (pseudo-t, J_{CP} = 5.5 Hz, CH_2Cl), 194.41−194.63 (m, CO *cis*), 196.54 (d, J_{CP} = 25.6, CO *trans*).

Diphosphirane 6. A solution of 7-phosphanorbornadiene complex **1d** (1.29 g, 2 mmol), borane−triphenylphosphine complex (1.11 g, 4 mmol) and CuCl (79 mg, 0.8 mmol) in THF was stirred at 60 °C for 4 h. Then, an excess of aqueous K_2CO_3 (0.24 mol/L) was added to the reaction mixture at room temperature. The reaction mixture was stirred at room temperature for 30 min. THF was removed by rotary evaporator. The aqueous phase was extracted with CH_2Cl_2 three times. The organic layer was dried with magnesium sulfate, filtered, and concentrated by rotary evaporator. The residue was chromatographed on silica gel using a 10/1 petroleum ether/dichloromethane mixture, to give **6** as a yellowish solid (417 mg, 54%). For the NMR data, see ref 8.

Diphospholane 7. Aqueous K_2CO_3 (2 mL, 0.4 mol/L) was added dropwise to a solution of secondary diphosphine complex **2a** (112 mg, 0.13 mmol) and $BrCH_2CH_2CH_2Br$ (18 μL, 0.17 mmol) in THF (3 mL). The mixture was stirred at room temperature for 5 h. THF was removed by a rotary evaporator. The aqueous phase was extracted three times with CH_2Cl_2. The organic layer was dried with magnesium sulfate, filtered, and concentrated. The residue was chromatographed on silica gel using a 5/1 petroleum ether/dichloromethane mixture, to give a yellowish solid (57 mg, 48%).

Compound 7. ^{31}P NMR (CH_2Cl_2): δ 14.5 ($^1J_{PW}$ = 156.5 Hz, $^2J_{PW}$ = 89.7 Hz), 22.9 ($^1J_{PW}$ = 155.6 Hz, $^2J_{PW}$ = 84.7 Hz).

One of the two isomers was purified by recrystallization (hexane and dichloromethane).

^{31}P NMR ($CDCl_3$): δ 22.6 ($^1J_{PW}$ = 155.6 Hz, $^2J_{PW}$ = 84.7 Hz). ^{1}H NMR ($CDCl_3$): δ 2.42−2.59 (m, 4H), 3.01−3.08 (m, 2H), 7.46−7.57 (m, 6H, Ph), 7.63−7.68 (m, 4H, Ph). ^{13}C NMR ($CDCl_3$): δ 25.98 (pseudo-t, J_{CP} = 3.8 Hz, CH_2), 32.82 (pseudo-t, J_{CP} = 12.1 Hz, CH_2P), 129.35 (pseudo-t, J_{CP} = 4.5 Hz, C *meta*), 131.03 (s, C *para*), 131.45 (pseudo-t, J_{CP} = 6.8 Hz, C *ortho*), 133.80 (pseudo-t, J_{CP} = 15.8 Hz, C *ipso*), 195.76 (pseudo-t, J_{CP} = 3.0 Hz, CO *cis*), 197.94 (pseudo-t, J_{CP} = 12.8 Hz, CO *trans*).

HRMS: calcd for $C_{25}H_{16}O_{10}P_2W_2$ $[M]^+$ 905.9237, found 905.9235.

ASSOCIATED CONTENT

Supporting Information

CIF files giving X-ray data for **2c** and **7** and figures giving NMR spectra of all the compounds described. This material is available free of charge via the Internet at http://pubs.acs.org.

dx.doi.org/10.1021/om400637j | *Organometallics* 2013, 32, 5615−5618

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

We thank the National Natural Science Foundation of China (Nos. 21072179, 21272218), the Scientific Research Foundation for the returned overseas Chinese, Zhengzhou University, and Nanyang Technological University in Singapore for financial support of this work.

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