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Reaction of Terminal Phosphinidene Complexes with Dihydrogen

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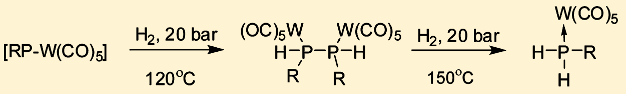
Ⓢ *Supporting Information*

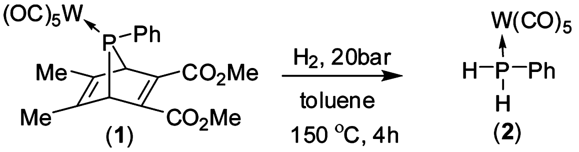
ABSTRACT: The reaction of H_2 with $[RP\text{-}W(CO)_5]$ (R = Ph, Me) above 120 °C leads, first, to the secondary diphosphine complex $(RPH\text{-}PHR)(W(CO)_5)_2$ and then to the primary phosphine complex $(RPH_2)(W(CO)_5)$. On the basis of DFT calculations, the mechanism most likely involves the addition of H_2 to the P−W bond, followed by the formation of the radical $[RPH\text{-}W(CO)_5]^\bullet$ by homolysis of the W−H bond. In the case of $[PhNHP\text{-}W(CO)_5]$, the hydrogenolysis takes place at the P−N bond and ultimately produces the secondary diaminophosphine complex $((PhNH)_2PH)(W(CO)_5)$.



The carbene-like chemistry of terminal phosphinidene complexes $[RP\text{-}M(CO)_5]$ (M = Cr, Mo, W) is now well established,[1] but their reaction with dihydrogen has not been investigated up to now. Two recent reports led us to get a closer look at it. The first paper by Bertrand and co-workers[2] described the insertion of reactive singlet carbenes into the H−H bond of dihydrogen. It must be stressed that $[RP\text{-}M(CO)_5]$ is strictly isolobal with a singlet carbene. The second paper by Ruiz and co-workers[3] described the reaction of H_2 with a bridging η^2-phosphinidene complex leading to a primary phosphine η^1 complex with the breaking of one P−M bond. We were thus curious to see whether it would be possible to duplicate these reactions with $[RP\text{-}M(CO)_5]$. To some extent, the answer is positive, although the reaction conditions are harsher and the mechanism of the reaction is quite different.

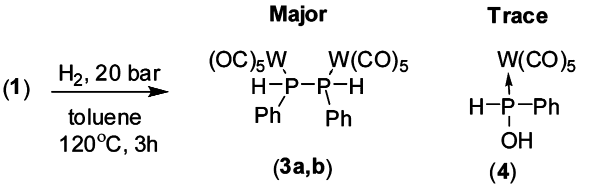
■ RESULTS AND DISCUSSION

Our initial experiments were performed with $[PhP\text{-}W(CO)_5]$. Accordingly, the 7-phosphanorbornadiene precursor **1**[4] was heated in an autoclave with hydrogen at variable temperature and pressure. A complete conversion into the expected phenylphosphine complex **2** was observed at 150 °C under 20 bar of H_2 (eq 1).



(1)

As can be noticed, these conditions are significantly harsher than those used with carbenes[2] and bridging phosphinidenes,[3] where the reactions take place around room temperature. However, it must be stressed that the precursor yields the phosphinidene only above 100−110 °C. In order to have an insight into the possible mechanism, we repeated the experiment at 120 °C, with unexpected results (eq 2).



(2)

The trace product **4** has already been described[5] and comes from the addition of traces of water, present in the solvent, to the phosphinidene. The major product **3a**,**b** is formed as a mixture of two diastereomers. The structure of the *rac* isomer was fully established by X-ray crystal structure analysis (Figure 1). When **3a**,**b** is heated at 150 °C under 20 bar of H_2, it is completely transformed into **2** and, thus, appears as the initial

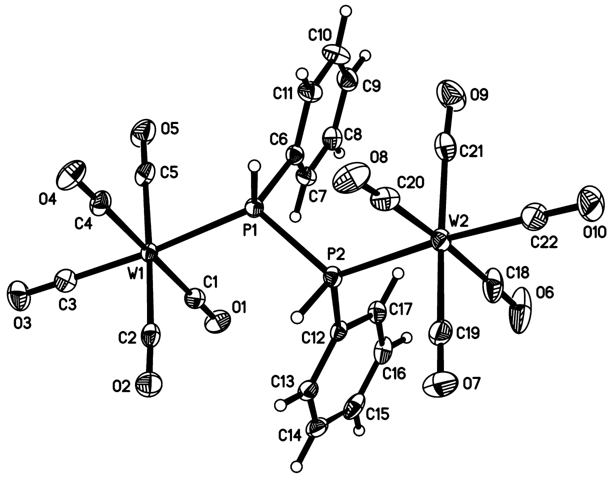


Figure 1. X-ray crystal structure of *rac*-diphosphine complex **3**. Main distances (Å) and angles (deg): W1−P1 = 2.4931(9), W2−P2 = 2.4961(9), P1−C6 = 1.820(4), P2−C12 = 1.817(4), P1−P2 = 2.2352(13); P2−P1−W1 = 119.04(4), P2−P1−H = 97(2), P2−P1−C6 = 105.38(12), W1−P1−P2−W2 = 166.77, C6−P1−P2−C12 = 78.23, H−P1−P2−H = 82.3.

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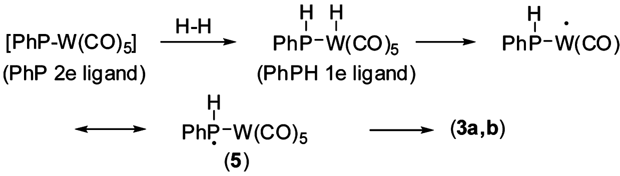
product of the reaction of hydrogen with [PhP-W(CO)$_5$]. An obvious explanation for the formation of **3** would be the addition of H_2 onto the diphosphene [(PhP=PPh)(W-(CO)$_5$)$_3$] resulting from the dimerization of [PhP-W(CO)$_5$].[6] We have indeed demonstrated that this reaction cleanly proceeds at 90 °C under 20 bar of H_2 (reaction time 16 h, yield of **3a,b** 32%). However, this pathway appears to be unlikely, because the thermolysis of **1** does not produce the diphosphene in the absence of copper chloride. Another possibility (as suggested by one of the reviewers) would be the insertion of [PhP-W(CO)$_5$] into the P−H bonds of **2**. In order to check this possibility, we allowed **2** to react with **1** at 120 °C in toluene and in the absence of H_2. Only traces of **3a,b** were observed. These observations lead us to propose the



$$\underset{\text{(PhP 2e ligand)}}{[\mathrm{PhP\text{-}W(CO)_5}]} \xrightarrow{\text{H-H}} \underset{\text{(PhPH 1e ligand)}}{\mathrm{Ph}\overset{\mathrm{H}}{\mathrm{P}}\text{-}\overset{\mathrm{H}}{\mathrm{W}}\mathrm{(CO)_5}} \longrightarrow \mathrm{Ph}\overset{\mathrm{H}}{\mathrm{P}}\text{-}\overset{\bullet}{\mathrm{W}}\mathrm{(CO)_5} \longleftrightarrow \underset{(\mathbf{5})}{\mathrm{Ph}\overset{\mathrm{H}}{\underset{\bullet}{\mathrm{P}}}\text{-}\mathrm{W(CO)_5}} \longrightarrow (\mathbf{3a,b}) \qquad (3)$$

mechanism given in eq 3 for the reaction of H_2 with [PhP-W(CO)$_5$].

This mechanism is closely related to the well-known conversion of [H−Co(CO)$_4$] into [$Co_2(CO)_8$] via the intermediate radical [Co(CO)$_4$]$^\bullet$ formed by homolysis of the metal−hydrogen bond.[7] In order to check if this mechanism is likely, we decided to perform a DFT analysis of **5**. The calculations were performed at the uB3PW91/6-31G(d)-Lanl2dz(W) level.[8] The structure is shown in Figure 2. It corresponds to a local minimum on the energy hypersurface (no negative frequency). At 2.468 Å, the P−W bond is relatively short (compare with the structure of **3**) and has probably some multiple-bond character. However, the P atom retains some pyramidality ($\sum$(C−P−C) = 354°). The SOMO (Figure 3) shows a high localization at phosphorus. According to the calculations, 75% of the spin is localized at P and only 5% at W. This explains why the dimerization takes place at P and supports the proposed mechanism. Another interesting observation was also made. The side product **4** is completely converted into **2** at 150 °C under 20 bar of H_2 (see the Experimental Section). Many phosphites are used as ligands in catalytic reactions where hydrogen is present, such as the hydroformylation reaction. Their industrial use has been hampered by their sensitivity to hydrolysis. It is interesting to know that hydrogenation of the P−O bond is another possible pathway for their decomposition.

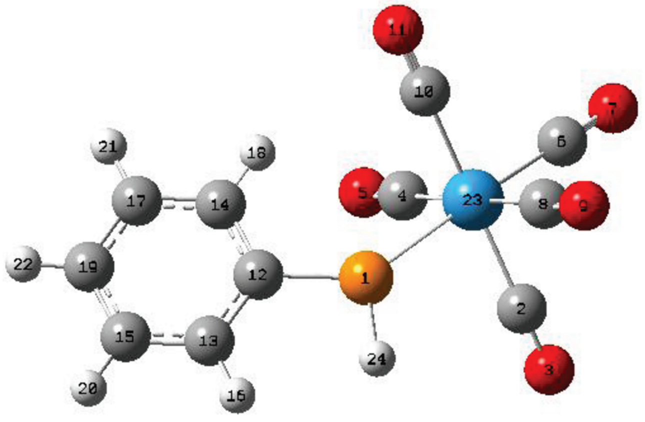


Figure 2. Structure of radical **5** as computed by DFT. Main distances (Å) and angles (deg): P1−W23 = 2.4682, P1−C12 = 1.7891, P1−H24 = 1.4138; C12−P1−W23 = 130.14, C12−P1−H24 = 100.84, H24−P1−W23 = 122.95.

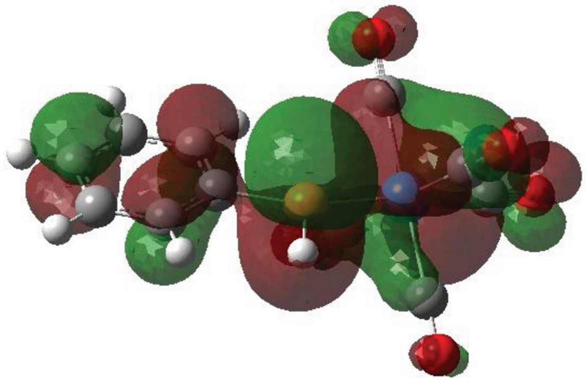
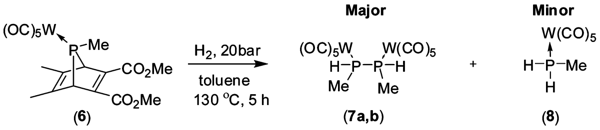


Figure 3. SOMO (Kohn−Sham) of radical **5**.

Then, we repeated similar experiments with [MeP-W(CO)$_5$]. The conditions were slightly different, but the products were similar. Just above the decomposition temperature of the 7-phosphanorbornadiene precursor, we obtained mainly the diphosphine complex (eq 4).



(4)

The primary phosphine complex **8** is the sole product at 150 °C for 6.5 h. We have been able to crystallize the *meso* isomer of **7**. Its X-ray crystal structure is shown in Figure 4. It displays an all-trans conformation. The most striking difference with the structure of *rac*-**3** is the much shorter P−P bond at 2.2061(11) Å vs 2.2352(13) Å for **3**. This probably reflects the steric repulsion that exists between the two P subunits in *rac*-**3**.

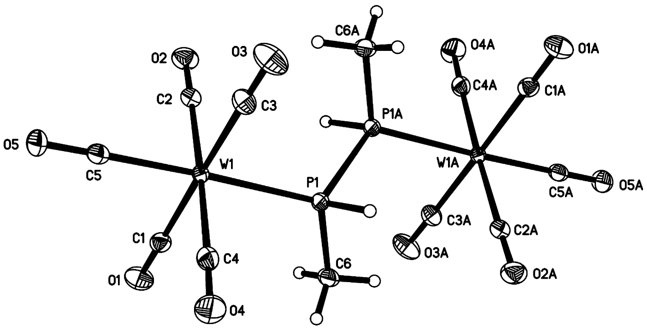
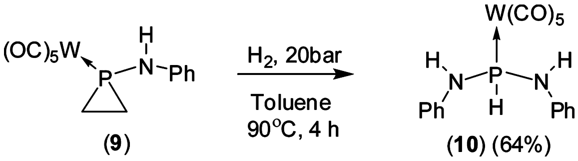


Figure 4. X-ray crystal structure of *meso*-diphosphine complex **7**. Main distances (Å) and angles (deg): W1−P1 = 2.4940(6), P1−C6 = 1.823(3), P1−P1A = 2.2061(11); P1A−P1−W1 = 119.83(4), P1A−P1−H = 97.9(15), P1A−P1−C6 = 102.06(9), W1−P1−P1A−W1A = C6−P1−P1A−C6A = H−P1−P1A−H = 180.00.

Bertrand[2] has stressed the fact that the reactivity of carbenes toward hydrogen is heavily dependent on their substitution pattern. We, therefore, decided to check whether the use of an aminophosphinidene such as [PhNHP-W(CO)$_5$] would change the course of the reaction with hydrogen. In this case, the precursor is the phosphirane complex[9] **9** and the phosphinidene is generated at lower temperature than in the preceding cases. The outcome of the reaction was unexpected. The sole product is the secondary diaminophosphine complex **10** (eq 5).



(5)

Complex **10** has been fully characterized by X-ray crystal structure analysis (see the Supporting Information). The mechanism of its formation is quite obvious. The hydrogenolysis of the P−N bond produces aniline, which reacts with the aminophosphinidene complex to yield **10**. On the basis of this result, we can expect a number of different outcomes with functional phosphinidene complexes and, in some cases, we might get interesting products for further synthetic applications.

■ EXPERIMENTAL SECTION

All reactions were carried out with distilled dry solvents. Silica gel (230−400 mesh) was used for the chromatographic separations. NMR spectra were recorded on either a JEOL ECA 400 or JEOL ECA 400SL spectrometer. All spectra were recorded at 298 K. Proton decoupling was applied for ^{13}C and ^{31}P spectra. HRMS were obtained on a Water Q-Tof Premier MS. X-ray crystallographic analyses were performed on a Bruker X8 APEX CCD diffractometer or a Bruker Kappa CCD diffractometer. Purified hydrogen (99.9995%) was used for all reactions. All reactions were performed inside a glass line in a Parr Instrument Co. 4560 mini bench top reactor, using a Parr Instrument Co. 4848 reactor controller.

Reaction of Dihydrogen with [PhP-W(CO)$_5$] at 120 °C. In the Parr reactor were added 7-phenylphosphanorbornadiene tungsten pentacarbonyl complex (0.1075 g, 0.16 mmol) and toluene (6 mL). Next the reactor was filled with hydrogen gas (20.0 bar) and heated for 3 h at 120 °C. The reactor was cooled to room temperature, the pressure was released, and the reaction mixture was transferred to another flask where the solvent was removed by vacuum. The product was purified by column chromatography (0 °C) with 90/10 hexane/methylene chloride solution as the eluent, to give a colorless film containing two inseparable isomers (0.0223 g, 31.3% yield). Crystals were grown from a 50/50 hexane/methylene chloride solution at −25 °C.

Isomer A. ^{31}P NMR (CD$_2$Cl$_2$): δ −19.7, $^1J_{PH}$ = 345 Hz, $\sum J_{PW}$ = 152 Hz. ^{1}H NMR (CD$_2$Cl$_2$): δ 6.40 (d, $^1J_{PH}$ = 345 Hz, H−P), 7.33−7.58 (m, Ph). ^{13}C NMR (CD$_2$Cl$_2$): δ 130.24 (pseudo-t, $\sum J_{CP}$ = 3.8 Hz, meta C), 130.60 (pseudo-t, $\sum J_{CP}$ = 18.1 Hz, ipso C), 132.44 (s, para C), 133.71 (pseudo-t, $\sum J_{CP}$ = 6.7 Hz, ortho C), 195.64 (s, cis CO), 198.12 (pseudo-t, $\sum J_{CP}$ = 12.4 Hz, trans CO). HRMS: *m/z* 866.8997 (calcd for $C_{22}H_{13}O_{10}P_2{}^{184}W_2$ 866.9003).

Isomer B. ^{31}P NMR (CD$_2$Cl$_2$): δ −22.8, $^1J_{PH}$ = 352 Hz, $\sum J_{PW}$ = 161 Hz. ^{1}H NMR (CD$_2$Cl$_2$): δ 6.41 (d, $^1J_{PH}$= 352 Hz, H−P), 7.33−7.58 (m, Ph). ^{13}C NMR (CD$_2$Cl$_2$): δ 128.78 (pseudo-t, $\sum J_{CP}$ = 18.1 Hz, ipso C), 129.90 (pseudo-t, $\sum J_{CP}$ = 3.8 Hz, meta C), 132.19 (s, para C), 134.38 (pseudo-t, $\sum J_{CP}$ = 6.7 Hz, ortho C), 195.89 (s, cis CO), 198.33 (pseudo-t, $\sum J_{CP}$ = 12.4 Hz, trans CO). HRMS: *m/z* 866.8997 (calcd for $C_{22}H_{13}O_{10}P_2{}^{184}W_2$ 866.9003).

Reaction of Dihydrogen with [PhP-W(CO)$_5$] at 150 °C. In the Parr reactor were added 7-phenylphosphanorbornadiene tungsten pentacarbonyl complex (0.2006 g, 0.31 mmol) and toluene (6 mL). Next the reactor was filled with hydrogen gas (20.0 bar) and heated for 4 h at 150 °C. The reactor was cooled to room temperature, the pressure was released, and the reaction mixture was transferred to another flask, where the solvent was removed by vacuum. The product was purified by column chromatography (0 °C) with 90/10 hexane/methylene chloride solution as the eluent, to give a white film of **2** (0.0383 g, 28.8% yield).

^{31}P NMR (CD$_2$Cl$_2$): δ −86.2, $^1J_{PW}$ = 220 Hz, $^1J_{PH}$ = 343 Hz (t). ^{1}H NMR (CD$_2$Cl$_2$): δ 5.80 (d, $^1J_{PH}$ = 343 Hz, H−P), 7.47−7.64 (m, Ph). HRMS: *m/z* 433.9539 (calcd for $C_{11}H_7O_5P^{184}W$ 433.9541).

Complex **2** has been previously described.[10]

Reaction of Dihydrogen with 3 at 150 °C. In the Parr reactor were added the two inseparable isomers of **3** (0.0418 g, 0.048 mmol) and toluene (6 mL). Next the reactor was filled with hydrogen gas (20.0 bar) and heated for 3 h at 150 °C. The reactor was cooled to room temperature, the pressure was released, and the reaction mixture was transferred to another flask, where the solvent was removed by vacuum. The product was purified by column chromatography (0 °C) with 90/10 hexane/methylene chloride solution as the eluent, to give a white film of **2** (0.0227 g, 54.2% yield).

Reaction of Dihydrogen with 4 at 150 °C. In the Parr reactor were added compound **4** (0.1116 g, 0.25 mmol) and toluene (6 mL). Next the reactor was filled with hydrogen gas (20.0 bar) and heated for 10 h at 150 °C. The reactor was cooled to room temperature, the pressure was released, and the reaction mixture was transferred to another flask where the solvent was removed by vacuum. The product was purified by column chromatography (−5 °C) with 90/10 hexane/methylene chloride solution as the eluent, to give a white film of **2** (0.0484 g, 45.0% yield).

Reaction of Dihydrogen with [MeP-W(CO)$_5$] at 120 °C. In the Parr reactor were added 7-methylphosphanorbornadiene tungsten pentacarbonyl complex (0.1994 g, 0.34 mmol) and toluene (7 mL). Next the reactor was filled with hydrogen gas (20.0 bar) and heated for 7 h at 120 °C. The reactor was cooled to room temperature, the pressure was released, and the reaction mixture was transferred to another flask where the solvent was removed by vacuum. The product was purified by column chromatography (−15 °C) with 80/20 hexane/methylene chloride solution as the eluent, to give a light yellow solid containing two inseparable isomers of **7** (0.0273 g, 21.9% yield). Crystals were grown from a 50/50 hexane/methylene chloride solution at −25 °C.

Isomer A. ^{31}P NMR (C$_6$D$_6$): δ −62.6, $^1J_{PH}$ = 342 Hz, $\sum J_{PW}$ = 156 Hz. ^{1}H NMR (C$_6$D$_6$): δ 1.01 (m, CH$_3$), 4.12 (dm, H−P) ^{13}C NMR (C$_6$D$_6$): δ 12.21 (pseudo-t, $\sum J_{CP}$ = 12.5 Hz, CH$_3$), 195.76 (pseudo-t, $\sum J_{CP}$ = 2.9 Hz, cis CO), 197.75 (pseudo-t, $\sum J_{CP}$ = 12.4 Hz, trans CO). HRMS: *m/z* 742.8691 (calcd for $C_{12}H_9O_{10}P_2{}^{184}W_2$ 742.8690).

Isomer B. ^{31}P NMR (C$_6$D$_6$): δ −67.0, $^1J_{PH}$ = 341 Hz, $\sum J_{PW}$ = 156 Hz. ^{1}H NMR (C$_6$D$_6$): δ 1.01 (m, CH$_3$), 4.42 (dm, H−P). ^{13}C NMR (C$_6$D$_6$): δ 10.28 (pseudo-t, $\sum J_{CP}$ = 14.4 Hz, CH$_3$), 195.76 (pseudo-t, $\sum J_{CP}$ = 2.9 Hz, cis CO), 197.72 (pseudo-t, $\sum J_{CP}$ = 12.4 Hz, trans CO). HRMS: *m/z* 742..8691 (calcd for $C_{12}H_9O_{10}P_2{}^{184}W_2$ 742.8690).

Reaction of Dihydrogen with [MeP-W(CO)$_5$] at 150 °C. In the Parr reactor were added the 7-methylphosphanorbornadiene tungsten pentacarbonyl complex (0.2286 g, 0.39 mmol) and toluene (7 mL). Next the reactor was filled with hydrogen gas (20.0 bar) and heated for 5 h at 150 °C. The reactor was cooled to room temperature, the pressure was released, and the reaction mixture was transferred to another flask where the solvent was removed by vacuum. The product was purified by column chromatography (−15 °C) with 90/10 hexane/methylene chloride solution as the eluent, to give a white film of **8** (0.0519 g, 36.1% yield).

^{31}P NMR (C$_6$D$_6$): δ −122.1, $^1J_{PW}$ = 221 Hz. ^{1}H NMR (C$_6$D$_6$): δ 0.57 (m, CH$_3$), 3.37 (dq, $^1J_{PH}$ = 340 Hz, H−P). ^{13}C NMR (C$_6$D$_6$): δ 4.40 (d, $^1J_{CP}$ = 31.6 Hz, CH$_3$), 196.33 (d, J_{CP} = 6.7 Hz, cis CO), 199.00 (d, J_{CP} = 21.1 Hz, trans CO). HRMS: *m/z* 371.9386 (calcd for $C_6H_5O_5P^{184}W$ 371.9384).

Complex **8** has been previously described.[11]

Reaction of Dihydrogen with [PhNHP-W(CO)$_5$]. In the Parr reactor were added the 1-phenylaminophosphirane tungsten pentacarbonyl complex[12] (0.1152 g, 0.24 mmol) and toluene (6 mL). Next the reactor was filled with hydrogen gas (20.0 bar) and heated for 4 h at 90 °C. The reactor was cooled to room temperature, the pressure was released, and the reaction mixture was transferred to another flask, where the solvent was removed by vacuum. The product was purified by column chromatography (−10 °C) with 70/30 hexane/methylene chloride solution as the eluent, to give **10** as a faint yellow solid (0.0424 g, 64.7% yield). Colorless crystals were grown from a 50/50 hexane/methylene chloride solution at −25 °C.

^{31}P NMR (CD_2Cl_2): δ 29.8, $^1J_{PW}$ = 289 Hz. ^{1}H NMR (CD_2Cl_2): δ 5.05 (dd, $^2J_{HP}$ = 14.2 Hz, $^3J_{HH}$ = 6.4 Hz, H−N), 6.98−7.27 (m, H−Ph), 8.02 (dt, $^1J_{HP}$ = 401 Hz, ^3J = 6.4 Hz, H−P). ^{13}C NMR (CD_2Cl_2): δ 119.52 (d, $^3J_{CP}$ = 5.7 Hz, ortho C), 123.19 (s, para C), 129.93 (s, meta C), 143.30 (d, $^2J_{CP}$ = 5.8 Hz, ipso C), 196.24 (d, $^2J_{CP}$ = 7.7 Hz, cis CO), 198.77 (d, $^2J_{CP}$ = 26.9 Hz, trans CO). HRMS: *m/z* 540.0070 (calcd for $C_{17}H_{13}N_2O_5P^{184}W$, 540.0072)

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

CIF files and figures giving X-ray crystal structure analysis and NMR spectra of compounds **3**, **7**, and **10**. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

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■ REFERENCES

(1) Recent reviews: Slootweg, J. C.; Lammertsma, K. *Sci. Synth.* **2009**, *42*, 15. Waterman, R. *Dalton Trans.* **2009**, 18. Rani, M. *Synlett* **2008**, 2078. Mathey, F. *Dalton Trans.* **2007**, 1861. Lammertsma, K. *Top. Curr. Chem.* **2003**, *229*, 95. Lammertsma, K.; Vlaar, M. J. M. *Eur. J. Org. Chem.* **2002**, 1127. Mathey, F.; Tran Huy, N. H.; Marinetti, A. *Helv. Chim. Acta* **2001**, *84*, 2938.

(2) Frey, G. D.; Lavallo, V.; Donnadieu, B.; Schoeller, W. W.; Bertrand, G. *Science* **2007**, *316*, 439.

(3) Alvarez, M. A.; Garcia, M. E.; Gonzalez, R.; Ramos, A.; Ruiz, M. A. *Organometallics* **2010**, *29*, 1875.

(4) Marinetti, A.; Mathey, F.; Fischer, J.; Mitschler, A. *Chem. Commun.* **1982**, 667.

(5) Marinetti, A.; Mathey, F. *Organometallics* **1982**, *1*, 1488.

(6) Marinetti, A.; Charrier, C.; Mathey, F.; Fischer, J. *Organometallics* **1985**, *4*, 2134.

(7) Wegman, R. W.; Brown, T. L. *J. Am. Chem. Soc.* **1980**, *102*, 2494.

(8) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A.; , Jr., Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; M. A. Al-Laham., Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian 03, Revision B.05*; Gaussian, Inc., Pittsburgh, PA, 2003.

(9) Mercier, F.; Deschamps, B.; Mathey, F. *J. Am. Chem. Soc.* **1989**, *111*, 9098.

(10) McFarlane, H. C. E.; McFarlane, W.; Rycroft, D. S. *J. Chem. Soc., Dalton Trans.* **1976**, 1616.

(11) De, R. L.; Vahrenkamp, H. *Z. Naturforsch., B* **1985**, *40*, 1250.

(12) Deschamps, B.; Ricard, L.; Mathey, F. *Polyhedron* **1989**, *8*, 2671.