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Activation of a 1-Chlorophosphirane Complex by Aluminum Trichloride: Generation and Trapping of [Fc-P-W(CO)$_5$] (Fc = Ferrocenyl)

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Keywords: Lewis acids / Sandwich complexes / Phosphiranes / Phosphorus / Tungsten

Aluminum trichloride catalyzes the ring opening of a 1-chlorophosphirane W(CO)$_5$ complex and its reaction with thiophene and ferrocene to give the corresponding 1-(2-thienyl)- and 1-ferrocenylphosphirane derivatives. The W(CO)$_5$ complex of the 1-ferrocenylphosphirane is an efficient precursor of the phosphinidene complex [FcP-W(CO)$_5$], which is trapped by tolan, *trans*-stilbene, and water.

Introduction

Several methods have been described in the literature for the synthesis of 1-chlorophosphiranes either as free species or as P-W(CO)$_5$ complexes.[1–7] These species have been allowed to react with a variety of nucleophiles (Nu$^-$) to give the corresponding P–Nu phosphiranes. However, their reactions with strong Lewis acids have been left untouched except for one case in which a Cl-to-Me intramolecular exchange between phosphorus and silicon in a 1-chloro-2-trimethylsilylphosphirane was promoted by AlCl$_3$.[2] The recent availability of a transient chlorophosphinidene complex [ClP-W(CO)$_5$][7] has given us ready access to 1-chlorophosphirane complexes by reaction with alkenes. This has prompted us to investigate more closely their reactions with strong Lewis acids such as AlCl$_3$.

Results and Discussion

To have an idea of what could be expected, we first decided to investigate the interaction of 1-chlorophosphirane-pentacarbonyltungsten complex **1** with AlCl$_3$ by DFT at the B3LYP/6-31G(d)-Lanl2dz(W) level.[8] The computed structure of **1** is shown in Figure 1. Good agreement with the X-ray crystal structure[4] is observed. Optimization of the **1**-AlCl$_3$ system leads to loose complex **2** in which AlCl$_3$ interacts with the chlorine atom of **1** (Figure 2). Comparison of the structures of **1** and **2** leads to some interesting conclusions. The P–Cl bond is weakened by interaction with AlCl$_3$, and its length increases from 2.092 to 2.216 Å. On the contrary, the structure of the phosphirane ring itself is practically not affected. Notably, the Al···Cl interaction is loose (2.479 vs. 2.107–2.123 Å for normal Al–Cl bonds). The difference between the energies of **2** and its two components **1** + AlCl$_3$ indeed indicates a dissociation energy of only 0.3 kcal mol^{-1} for this interaction. This means that, under practical experimental conditions, there will be an equilibrium between **2** and **1** + AlCl$_3$ that will be shifted toward **2** by an excess amount of aluminum chloride. Also significant is the fact that the fully ionized system P$^+$ + AlCl$_4^-$ is 82 kcal mol^{-1} higher in energy than **2**. The full ionization of the P–Cl bond is thus excluded.

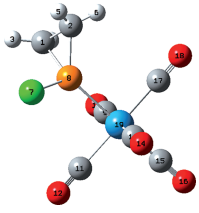

Figure 1. Computed structure of 1-chlorophosphirane complex **1**. Main distances [Å] and angles [°]: P8–W19 2.512, P8–Cl7 2.092, P8–C1 1.838; C1–P8–C2 48.96, Cl7–P8–C1 103.62, C1–P8–W19 129.56, Cl7–P8–W19 120.59.

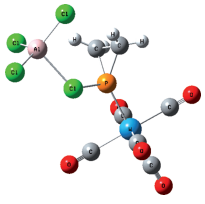

Figure 2. Computed structure of AlCl$_3$–phosphirane loose complex **2**. Main distances [Å] and angles [°]: P–W 2.469, P–Cl 2.216, P–C 1.831, Cl···Al 2.479, Al–Cl 2.107–2.120–2.123; C–P–C 49.21, Cl–P–C 103.79, W–P–C 133.96, W–P–Cl 115.71; P–Cl–Al 121.88; Cl–Al–Cl 115.07–118.24–117.68.

We selected 7-chloro-7-phosphabicyclo[4.1.0]heptane complex **3** for our experiments because it is obtained as an

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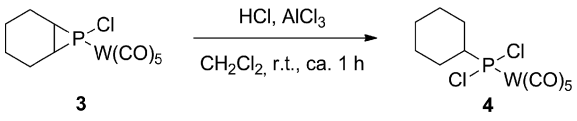
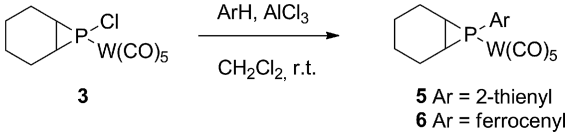
almost pure diastereomer by reaction of cyclohexene with [ClP-W(CO)$_5$].[7] We immediately noticed that **3** slowly decomposes in the presence of $AlCl_3$ contaminated by HCl [Equation (1)].



3 **4** (1)

We were unable to get good crystals of **4**, but its identity was established as follows. The ^{31}P NMR spectrum [**4**: $\delta(^{31}P)$ = 162.9 ppm, $^1J_{PW}$ = 320.8 Hz] shows that the phosphirane ring has been opened. The ^{13}C NMR spectrum shows one CH at δ = 57.19 ppm (J_{CP} = 5 Hz) and three different CH_2 groups at δ = 25.75 (s), 26.18 (J_{CP} = 15 Hz), and 26.97 ppm (J_{CP} = 2.5 Hz). HRMS indicates that the formula is $C_{11}H_{11}O_5PCl_2W$ (calcd. 507.9230; found 507.9223). Finally, the identity of **4** was confirmed by comparison with another sample made by reaction of [Cl_3P-W(CO)$_5$] with cyclohexylmagnesium bromide. It is known that chlorophosphirane complexes are stable in the presence of HCl (see the synthesis of the parent chlorophosphirane tungsten complex[9]), but it appears that $AlCl_3$ catalyzes their ring opening. From a practical standpoint, consequently, the reaction of **3** with electron-rich arenes in the presence of $AlCl_3$ must be faster than ring opening by HCl, the presence of which cannot be avoided completely. Anisole and furan were not reactive enough, but we were successful with thiophene and ferrocene [Equation (2)]. We think that the failures with furan and anisole are due to complexation of $AlCl_3$ with the oxygen atoms. This complexation is quite strong with furan (14.7 kcal mol^{-1})[10] and probably prevents the formation of the complex with the chlorophosphirane. The complexation of $AlCl_3$ with thiophene (8.5 kcal mol^{-1})[10] is much weaker and does not interfere with the reaction at P–Cl.



3 **5** Ar = 2-thienyl **6** Ar = ferrocenyl (2)

The X-ray crystal structure of **5** is shown in Figure 3. The key observation is that the stereochemistry of phosphorus has been kept during the substitution of chlorine by thienyl. In both **3**[7] and **5**, the tungsten complexing group faces the cyclohexane ring. Owing to steric congestion resulting from interaction between the W(CO)$_5$ complexing group and the six-membered ring, we could expect that **5** and **6** are potential precursors of [ArP-W(CO)$_5$]. In the case of **6**, this possibility was quite exciting, as it is impossible to use the classical 7-phosphanorbornadiene route to obtain [FcP-W(CO)$_5$] because the bulkiness of the ferrocenyl group prevents cycloaddition between the 1-ferrocenylphosphole complex and dimethyl acetylenedicarboxylate.[11] We tested our hypothesis by using diphenylacetylene, *trans*-stilbene, and water as the trapping reagents [Equation (3)].

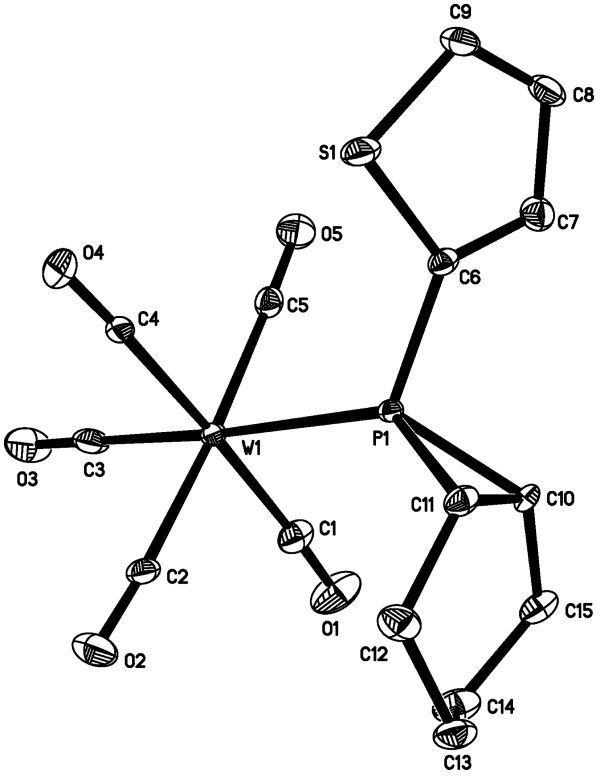
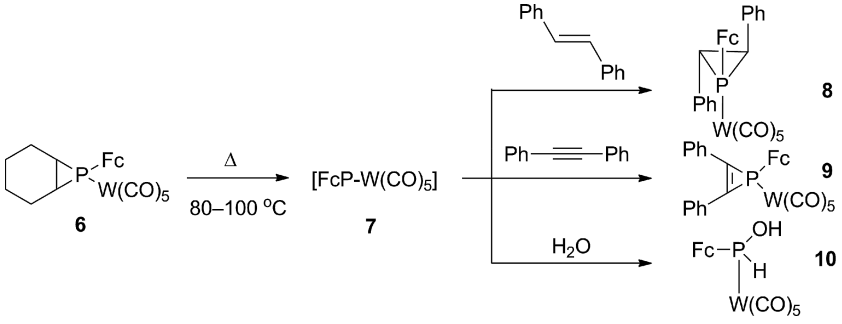


Figure 3. X-ray crystal structure of **5**. Main distances [Å] and angles [°]: P1–W1 2.5078(9), P1–C6 1.803(4), P1–C10 1.841(4), P1–C11 1.849(4), C6–S1 1.724(4), C9–S1 1.718(4), C6–C7 1.370(5), C7–C8 1.418(6), C8–C9 1.348(6), C10–C11 1.520(5); C10–P1–C11 48.64(17), C10–P1–C6 102.75(17), C11–P1–C6 105.43(17), C6P1–W1 116.83(12).

Phosphirene **9** has already been described in the literature.[12] The molecular structure of new phosphirane **8** was confirmed by X-ray crystal structure analysis (Figure 4).



(3)

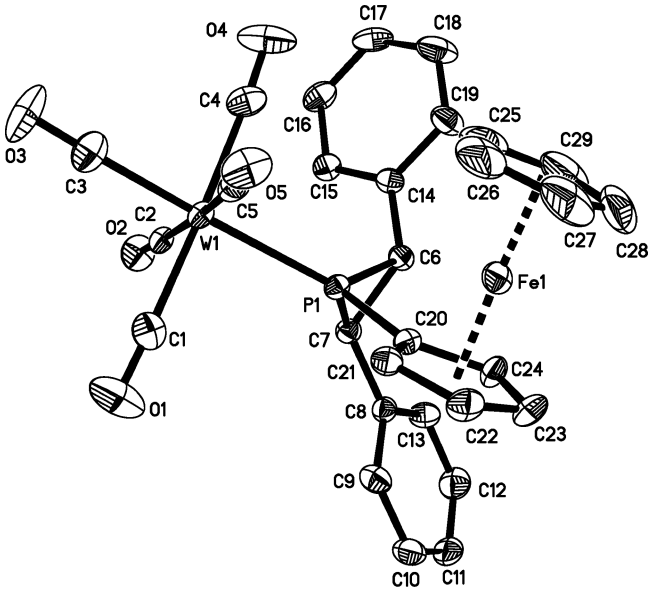


Figure 4. X-ray crystal structure of **8**. Main distances [Å] and angles [°]: P1–W1 2.5012(9), P1–C6 1.849(3), P1–C7 1.835(3), P1–C20 1.797(3), C6–C7 1.523(5), Fe1–C20–24 2.038–2.046(4), Fe1–C25–29 2.030–2.044(4); C6–P1–C7 48.84(15), C6–P1–W1 125.80(11), C7–P1–W1 121.34(11), C6–P1–C20 105.87(15), C7–P1–C20 109.64(15), C20–P1–W1123.07(11).

Phosphirane **6** appears to be an efficient precursor of ferrocenylphosphinidene complex **7** working between 80 and 100 °C with a very easily eliminated byproduct (cyclohexene). In view of the numerous applications of ferrocenylphosphines as ligands for transition metals in homogeneous catalysis,[13] it is quite interesting to have a new powerful tool[14] to synthesize additional members of this family of ligands. Given that the ferrocenyl substituent is known to stabilize electron-deficient centers, it was interesting to have a look at the structure of **7**. The computed geometrical structure of **7** is shown in Figure 5. It is immediately clear that there is an attractive interaction between P and Fe. This interaction leads to displacement of phosphorus from the cyclopentadienyl plane toward the iron atom. The out-of-plane angle is 18.4°. The HOMO–LUMO gap at 2.51 eV is larger than that for [MeP-W(CO)$_5$] at 2.34 eV. From this standpoint, **7** lies between the C-substituted phosphinidene complex and the less-electrophilic N-substituted phosphinidene complex.[15] From another standpoint, it is quite interesting to compare the reactions of the 1-chlorophosphirane and 1-chlorophosphirene complexes with $AlCl_3$. In the second case, full ionization of the P–Cl bond takes place, which leads to the aromatic phosphirenylium ion, as shown by Sterenberg.[12]

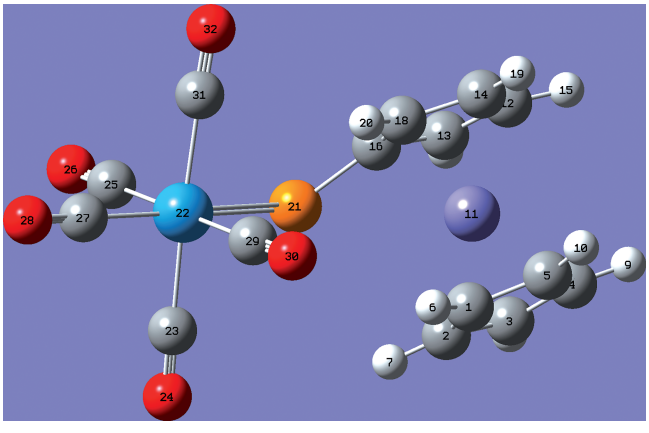


Figure 5. Computed structure of ferrocenylphosphinidene complex **7**. Main distances [Å] and angles [°]: P21–C16 1.781, P21–W22 2.481. P21–Fe11 3.198; C16–P21–W22 115.51.

Conclusions

The most useful result of this work is that complex **3**, due to its congested structure, is a potential source of new terminal phosphinidene complexes [RP-W(CO)$_5$] of wide synthetic interest.

Experimental Section

General Methods: All reactions were performed with distilled dry solvents. Silica gel (230–400 mesh) was used for chromatographic separations. NMR spectra were recorded with a Bruker BBFO 400 MHz, AV 400 MHz, or AV 500 MHz spectrometer. All spectra were recorded at 298 K. Proton decoupling was applied for ^{13}C and ^{31}P spectra. HRMS was recorded with a Water Q-TOF Premier MS. X-ray crystallographic analyses were performed with a Bruker X8 APEX CCD diffractometer or a Bruker Kappa CCD diffractometer.

Ring Opening of 3 by HCl: Phosphirane **3** (33 mg, 0.07 mmol) was stirred with aluminum trichloride contaminated with HCl (28 mg, 0.21 mmol) in CH_2Cl_2 (2 mL) for 45 min at room temperature. Adding a drop of wet toluene into the mixture favored the reaction. The crude product was purified by chromatography (hexane) on a jacketed column at –10 °C to prevent partial hydrolysis of **4**,which afforded pure complex **4** (12 mg, 33.7%). ^1H NMR ($CDCl_3$): δ = 1.28 (m, 1 H, CH_2), 1.42 (m, 4 H, CH_2), 1.79 (d, $^3J_{HP}$ = 12 Hz, 1 H, CH_2), 2.02 (s, 2 H, CH_2), 2.30 (m, 2 H, CH_2), 2.42 (m, 1 H, C*H*P) ppm. ^{13}C NMR ($CDCl_3$): δ = 25.75 (s, CH_2), 26.18 (d, $^2J_{CP}$ = 15 Hz, CH_2), 26.97 (d, $^3J_{CP}$ = 2.5 Hz, CH_2), 57.19 (d, $^1J_{CP}$ = 5 Hz, *C*HP), 195.08 (d, $^2J_{CP}$ = 7.5 Hz, *cis*-CO), 198.01 (d, $^2J_{CP}$ = 42.8 Hz, *trans*-CO) ppm. ^{31}P NMR ($CDCl_3$): δ = 162.9 ($^1J_{PW}$ = 320.8 Hz) ppm. MS: *m*/*z* = 507.9223 (calcd. for $C_{11}H_{11}O_5Cl_2PW$ *m*/*z* = 507.9230).

1-(2-Thienyl)phosphirane Complex 5: A mixture of phosphirane **3** (90 mg, 0.19 mmol), aluminum trichloride (151 mg, 1.14 mmol), and thiophene (0.09 mL, 1.14 mmol) was stirred in CH_2Cl_2 (3 mL) for 1 h at room temperature. Purification by cold column chromatography (–10 °C, hexane) yielded phosphirane **5** (26 mg, 26.3%). ^1H NMR (CD_2Cl_2): δ = 1.47 (m, 4 H, CH_2), 1.90 (m, 2 H, CH_2), 2.28 (m, 2 H, *C*HP), 2.31 (m, 2 H, CH_2), 7.08 (m, 1 H, C_4H_3S), 7.30 (m, 1 H, C_4H_3S), 7.48 (m, 1 H, C_4H_3S) ppm. ^{13}C NMR (CD_2Cl_2): δ = 21.06 (d, J_{CP} = 4 Hz, CH_2), 22.06 (d, J_{CP} = 3 Hz, CH_2), 26.05 (d, $^1J_{CP}$ = 14 Hz, *C*HP), 127.70 (d, J_{CP} = 11 Hz, C_4H_3S), 129.76 (d, J_{CP} = 2 Hz, C_4H_3S), 133.98 (d, J_{CP} = 2 Hz, C_4H_3S), 139.20 (d, $^1J_{CP}$ = 24 Hz, C_4H_3S), 195.66 (d, $^2J_{CP}$ = 8 Hz, *cis*-CO), 197.18 (d, $^2J_{CP}$ = 31.2 Hz, *trans*-CO) ppm. ^{31}P NMR (CD_2Cl_2): δ = –171.5 ($^1J_{PW}$ = 269 Hz) ppm. HRMS: calcd. for $C_{15}H_{13}O_5PSW$ 519.9731; found 519.9709.

1-Ferrocenylphosphirane Complex 6: A mixture of phosphirane **3** (33 mg, 0.07 mmol), aluminum trichloride (55 mg, 0.42 mmol), and ferrocene (78 mg, 0.42 mmol) was stirred in CH_2Cl_2 (2 mL) for 1 h at room temperature to give phosphirane **6**. Purification by cold column chromatography (–10 °C; hexane/dichloromethane, 9:1) yielded **6** (20 mg, 46%). ^{1}H NMR ($CDCl_3$): δ = 1.48 (m, 4 H, CH_2), 1.86 (m, 2 H, CH_2), 2.05 (m, 2 H, C*H*P), 2.26 (m, 2 H, CH_2), 4.18 (d, J_{HH} = 2 Hz, 2 H, C_5H_4P), 4.23 (s, 5 H, C_5H_5), 4.33 (s, 2 H, C_5H_4P) ppm. ^{13}C NMR ($CDCl_3$): δ = 21.57 (d, $^2J_{CP}$ = 3.8 Hz, CH_2), 22.66 (d, $^3J_{CP}$ = 2.7 Hz, CH_2), 26.67 (d, $^1J_{CP}$ = 12.3 Hz, *C*HP), 69.65 (s, C_5H_5), 70.72 (d, $^3J_{CP}$ = 7.5 Hz, C_5H_4P), 71.92 (d, $^2J_{CP}$ = 13.4 Hz, C_5H_4P), 79.60 (d, $^1J_{CP}$ = 30.4 Hz, C_5H_4P), 196.34 (d, $^2J_{CP}$ = 8 Hz, *cis*-CO), 197.05 (d, $^2J_{CP}$ = 29.2 Hz, *trans*-CO) ppm. ^{31}P NMR ($CDCl_3$): δ = –166.6 ($^1J_{PW}$ = 264 Hz) ppm. HRMS: calcd. for $C_{21}H_{19}O_5PWFe$ 621.9829; found 621.9814.

1-Ferrocenylphosphirane Complex 8: Phosphirane **6** (40 mg, 0.06 mmol) was stirred with *trans*-stilbene (65 mg, 0.36 mmol) in toluene (2 mL) at 100 °C for 7.5 h. Purification by cold column chromatography (–10 °C; hexane/dichloromethane, 8:2) gave phosphirane **8** (15 mg, 34.9%). ^{1}H NMR (CD_2Cl_2): δ = 3.70 (s, 2 H, C*H*P), 3.70 (s, 1 H, $C_{10}H_9Fe$), 4.22–4.31 (m, 8 H, $C_{10}H_9Fe$), 7.23–7.47 (m, 10 H, aromatic CH) ppm. ^{13}C NMR (CD_2Cl_2): δ = 35.40 (d, $^1J_{CP}$ = 9.7 Hz, *C*HP), 39.81 (d, $^1J_{CP}$ = 14.6 Hz, *C*HP), 70.29 (s, C_5H_5), 71.52 (s, C_5H_4), 71.85 (s, C_5H_4), 71.95 (s, C_5H_4), 76.38 (s, C_5H_4), 76.61 (s, C_5H_4), 127.66 (s, aromatic CH), 128.0 (s, aromatic CH), 129.19 (s, aromatic CH), 129.26 (s, aromatic CH), 129.32 (s, aromatic CH), 129.62 (s, aromatic CH), 130.49 (s, aromatic CH), 135.91 (s, *ipso*-C), 137.56 (s, *ipso*-C), 196.36 (d, $^2J_{CP}$ = 8.0 Hz, *cis*-CO), 197.81 (d, $^2J_{CP}$ = 32.3 Hz, *trans*-CO) ppm. ^{31}P NMR (CD_2Cl_2): δ = –130.9 ($^1J_{PW}$ = 268.9 Hz) ppm. HRMS: calcd. for $C_{29}H_{21}O_5PWFe$ 719.9986; found: 720.0004.

1-Ferrocenylphosphirene Complex 9: Phosphirane **6** (17 mg, 0.03 mmol) was stirred with diphenylacetylene (32 mg, 0.18 mmol) in toluene (1.5 mL) at 100 °C for 7.5 h. Purification by cold column chromatography (–10 °C; hexane/dichloromethane, 8:2) yielded phosphirene **9** (10 mg, 46.7%). ^{1}H NMR (CD_2Cl_2): δ = 4.16 (s, 5 H, C_5H_5), 4.21 (m, 2 H, C_5H_4P), 4.36 (m, 2 H, C_5H_4P), 7.50–7.93 (m, 10 H, aromatic CH) ppm. ^{13}C NMR (CD_2Cl_2): δ = 70.13 (s, C_5H_5), 71.83 (d, J_{CP} = 7.3 Hz, C_5H_4P), 72.74 (d, J_{CP} = 14.8 Hz, C_5H_4P), 80.85 (d, J_{CP} = 7.8 Hz, C_5H_4P), 128.30 (d, $^2J_{CP}$ = 6.2 Hz, *ipso*-Ph), 129.32 (d, $^1J_{CP}$ = 7.8 Hz, *C*P), 129.81 (s, aromatic CH), 130.56 (d, J_{CP} = 4.8 Hz, aromatic CH), 130.98 (s, aromatic CH), 196.97 (d, J_{CP} = 8.6 Hz, *cis*-CO), 198.64 (d, J_{CP} = 32.6 Hz, *trans*-CO) ppm. ^{31}P NMR (CD_2Cl_2): δ = –161.5 ($^1J_{PW}$ = 272.2 Hz) ppm. HRMS: calcd. for $C_{29}H_{19}O_5PWFe$ 717.9858; found 717.9829.

Ferrocenylhydroxyphosphine Complex 10: Phosphirane **6** (12 mg, 0.019 mmol) was stirred with a drop of deionized water in toluene (1.5 mL) at 100 °C for 7.5 h. Purification by cold column chromatography (–10 °C, ethyl acetate) gave **10** (4 mg, 37.7%). ^{1}H NMR ($CDCl_3$): δ = 4.30 (s, 5 H, C_5H_5), 4.50 (m, 2 H, C_5H_4P), 4.55 (s, 1 H, C_5H_4P), 4.58 (s, 1 H, C_5H_4P), 8.01 (d, $^1J_{HP}$ = 365.2 Hz, 1 H, *H*P) ppm. ^{13}C NMR ($CDCl_3$): δ = 69.60 (s, C_5H_5), 72.11 (d, J_{CP} = 9.4 Hz, C_5H_4P), 72.57 (d, J_{CP} = 8.6 Hz, C_5H_4P), 72.89 (d, J_{CP} = 6.9 Hz, C_5H_4P), 73.33 (d, $^2J_{CP}$ = 20.1 Hz, C_5H_4P), 78.85 (d, $^1J_{CP}$ = 50.2 Hz, C_5H_4P), 196.14 (d, $^2J_{CP}$ = 7.9 Hz, *cis*-CO), 198.84 (d, $^2J_{CP}$ = 23.7 Hz, *trans*-CO) ppm. ^{31}P NMR (CH_2Cl_2): δ = 71.0 ($^1J_{PW}$ = 268.7 Hz, $^1J_{PH}$ = 364.9 Hz) ppm. HRMS: calcd. for $C_{15}H_{11}O_6PWFe$ 557.9152; found 557.9137.

CCDC-1014059 (for **5**) and -1014060 (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.

Supporting Information (see footnote on the first page of this article): X-ray crystal structure analyses of **5** and **8** and NMR spectra of compounds **4**–**6** and **8**–**10**.

Acknowledgments

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