

Supporting Information for Reviewers Only

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**Redox-active Phosphines: Synthesis and Crystal Structures of Palladium(II) Complexes
that contain Metallaphosphines in Two different Oxidation States.**

Including:

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1. Synthesis of Pd(II) Complexes with Fe(II) Metallo-Phosphanes

General. All reactions and workup procedures were carried out under dry, high purity argon using standard Schlenk techniques. All solvents were freshly distilled and purged with argon before use. Infrared spectra were obtained using a Bruker IFS28 FT-IR spectrometer (400-4000 cm^{-1}). NMR spectra were acquired at 298 K on a Bruker DPX200, a Bruker Ascend 400 MHz NMR or a Bruker AVANCE 500, with a 5 mm broadband observe probe equipped with a z-gradient coil. Chemical shifts are given in ppm and referenced to the residual non-deuterated solvent signal for ^1H and ^{13}C and external H_3PO_4 (0.0 ppm) for ^{31}P NMR spectra. Cyclic voltammograms were recorded in dry CH_2Cl_2 solutions (containing 0.10 M $[\text{nBu}_4\text{N}][\text{PF}_6]$, purged with argon and maintained under argon atmosphere) using a Versastat 3 potentiostat in a home-made three-electrode Teflon cell. The working electrode was a Pt disk, the counter electrode a Pt wire and the reference electrode a saturated calomel electrode (SCE). The $\text{FeCp}_2^{0/1+}$ couple ($E_{1/2}$: 0.46 V, $\Delta E_p = 0.09$ V; $I_{pa}/I_{pc} = 1$) was used as an internal calibrant for the potential measurements. UV-visible spectra were recorded as CH_2Cl_2 solutions, using a 1 cm long quartz cell on a Cary 5000 spectrometer. EPR spectra were recorded on a Bruker EMX-8/2.7 (X-band) spectrometer, at 77K. High-resolution mass spectra were performed at the “Centre Regional de Mesures Physiques de l’Ouest” (CRMPO), Université de Rennes 1.

{[Fe(κ^2 -dppe)(η^5 -C₅Me₅)(C \equiv CPPh₂)]Pd(μ -Cl)Cl₂} (3). In a Schlenk tube, Fe(κ^2 -dppe)(η^5 -C₅Me₅)(C \equiv CPPh₂) (**1**; 79.9 mg, 0.1 mmol) and [Pd(1,5-cod)Cl₂] (28.5 mg, 0.1 mmol) were dissolved in dichloromethane (5 mL) and stirred overnight at room temperature. Addition of *n*-pentane and filtration gave the title complex as a blue solid (90 mg, 92%). X-ray quality crystals were grown from slow diffusion of pentane in a dichloromethane solution of the

complex. HRMS: calc: 1948.1611 [M^+], found: 1948.1645. IR (KBr, ν in cm^{-1}): 1930 (s, $\text{C}\equiv\text{C}$). CV (CH_2Cl_2 , vs. SCE, 0.1 M [$n\text{-Bu}_4\text{N}$][PF_6]): $E^1_{1/2} = 0.16$ V ($\Delta E_p = 85$ mV), $E^2_{1/2} = 0.25$ V ($\Delta E_p = 85$ mV). ^1H NMR (300 MHz, C_6D_6 , ppm): $\delta = 8.06\text{--}8.01$ (m, 8H, $H_{\text{aromatics}}$), 7.91–7.84 (m, 8H, $H_{\text{aromatics}}$), 7.43–7.38 (m, 8H, $H_{\text{aromatics}}$), 7.19–6.97 (m, 38H, $H_{\text{aromatics}}$), 3.18 (m, 4H, CH_2 dppe), 1.99 (m, 4H, CH_2 dppe), 1.41 (s, 30H, $\text{C}_5(\text{CH}_3)_5$). ^{31}P NMR (121 MHz, C_6D_6 , ppm): $\delta = 97.8$ (s, 4P, dppe), -16.8 (s, 2P, PPh_2).

***trans*-{Fe(κ^2 -dppe)(η^5 - C_5Me_5)($\text{C}\equiv\text{CPh}_2$)} $_2$ PdCl $_2$ (5).** In a Schlenk tube, Fe(κ^2 -dppe)(η^5 - C_5Me_5)($\text{C}\equiv\text{CPh}_2$) (**1**; 159.8 mg, 0.2 mmol) and [Pd(1,5-cod)Cl $_2$] (28.5 mg, 0.1 mmol) were dissolved in dichloromethane (5 mL) and stirred overnight at room temperature. Addition of *n*-pentane and filtration gave the title complex as a purple solid (170 mg, 96%). X-ray quality crystals were grown from slow diffusion of pentane vapours in a benzene solution of the complex. HRMS: calc: 1772.3229 [M^+], found: 1772.3235. IR (KBr, ν in cm^{-1}): 1948 (s, $\text{C}\equiv\text{C}$). CV (CH_2Cl_2 , vs. SCE, 0.1 M [$n\text{-Bu}_4\text{N}$][PF_6]): $E^1_{1/2} = -0.02$ V ($\Delta E_p = 77$ mV), $E^2_{1/2} = 0.11$ V ($\Delta E_p = 73$ mV). ^1H NMR (300 MHz, C_6D_6 , ppm): $\delta = 8.09\text{--}7.97$ (m, 16H, $H_{\text{aromatics}}$), 7.28–6.96 (m, 46H, $H_{\text{aromatics}}$), 2.95 (m, 4H, CH_2 dppe), 1.78 (m, 4H, CH_2 dppe), 1.45 (s, 30H, $\text{C}_5(\text{CH}_3)_5$). ^{31}P NMR (121 MHz, C_6D_6 , ppm): $\delta = 99.6$ (s, 4P, dppe), -10.3 (s, 2P, PPh_2).

2. Synthesis of Pd(II) Complexes with Fe(III) Metallo-Phosphanes

[{Fe(κ^2 -dppe)(η^5 - C_5Me_5)($\text{C}\equiv\text{CPh}_2$)]Pd(μ -Cl)Cl} $_2$][PF_6] $_2$ (4) by Chemical Oxidation of

3. In a Schlenk tube, {[Fe(κ^2 -dppe)(η^5 - C_5Me_5)($\text{C}\equiv\text{CPh}_2$)]Pd(μ -Cl)Cl} $_2$ (**3**; 195.2 mg, 0.1 mmol) and [FcH][PF_6] (66.2 mg, 0.2 mmol) were dissolved in dichloromethane (5 mL) and

stirred for 1 h at room temperature. Addition of *n*-pentane and filtration gave the title complex as black solid (220 mg, 98%).

[{Fe(κ^2 -dppe)(η^5 -C₅Me₅)(C≡CPh₂)Pd(μ -Cl)Cl₂][PF₆]₂ (4) from Diphosphane Dimer 1[PF₆]₂ and a Pd(II) Precursor. In a Schlenk tube, [{Fe(κ^2 -dppe)(η^5 -C₅Me₅)(C≡C)PPh₂}]₂[PF₆]₂ (**2**; 95 mg, 0.05 mmol) and [Pd(1,5-cod)Cl₂] (28.5 mg, 0.1 mmol) were dissolved in dichloromethane (5 mL) and stirred for 1 h at room temperature. Removal of the solvent after vacuum gave the title complex as a unique product in nearly quantitative yield (*ca.* 100 %). X-ray quality crystals were grown from slow diffusion of pentane in a dichloromethane solution of the complex. IR (KBr, ν in cm⁻¹): 1975 (s, C≡C), 838 (s, PF₆). CV (CH₂Cl₂, vs. SCE, 0.1 M [*n*-Bu₄N][PF₆]): E¹_{1/2} = 0.16 V, E²_{1/2} = 0.25 V. ¹H NMR (300 MHz, CD₂Cl₂, ppm): δ = 12.5, 8.7, 7.7, 7.4, 6.7, 6.0, 3.1, 2.5, 0.1, -1.0, -3.6, -8.5.

[*trans*-{Fe(κ^2 -dppe)(η^5 -C₅Me₅)(C≡CPh₂)₂PdCl₂][PF₆]₂ (6) by Chemical Oxidation of 5. In a Schlenk tube, *trans*-{Fe(κ^2 -dppe)(η^5 -C₅Me₅)(C≡CPh₂)₂PdCl₂ (**5**; 177.5 mg, 0.1 mmol) and [FcH][PF₆] (66.2 mg, 0.2 mmol) were dissolved in dichloromethane (5 mL) and stirred for 1 h at room temperature. Addition of *n*-pentane and filtration gave the title complex as black solid (200 mg, 97%).

[*trans*-{Fe(κ^2 -dppe)(η^5 -C₅Me₅)(C≡CPh₂)₂PdCl₂][PF₆]₂ (6) from Diphosphane Dimer 3[PF₆]₂ and a Pd(II) Precursor. In a Schlenk tube, [{Fe(κ^2 -dppe)(η^5 -C₅Me₅)(C≡CPh₂)}]₂[PF₆]₂ (**2**; 95 mg, 0.05 mmol) and [Pd(1,5-cod)Cl₂] (14.2 mg, 0.05 mmol) were dissolved in dichloromethane (5 mL) and stirred for 1 h at room temperature. Removal of the solvent after vacuum gave *the title complex* as a unique product in nearly quantitative yield (*ca.* 100 %). IR (KBr, ν in cm⁻¹): 1971/1916 (w, C≡C), 838 (s, PF₆). CV

(CH₂Cl₂, vs. SCE, 0.1 M [*n*-Bu₄N][PF₆]): E¹_{1/2} = -0.02 V, E²_{1/2} = 0.11 V. ¹H NMR (300 MHz, CD₂Cl₂, ppm): δ = 12.3, 9.5, 7.8, 7.6, 7.4, 6.9, 5.5, 3.3, 3.0, 0.1, -1.8, -8.7.

3. Evans¹ Measurements on 4 and 6

The difference in frequency between the TMS signals of the paramagnetic solution and of the reference solution, gives access to the magnetic susceptibility (χ_M) and, subsequently, the effective magnetic moment (μ_{eff}), according to eqs 1 – 3²:

$$\chi_s = \frac{3 \cdot \Delta f}{4 \cdot \pi \cdot m} + \chi_0 \quad (1)$$

Δf : frequency difference (Hz)

m : concentration of the complex studied (g/mL)

χ_0 : magnetic susceptibility of the solvent (emu/g).

$$\chi_M = \chi_s \cdot M \quad (2)$$

M : molecular weight of the compound studied (g)

$$\mu_{\text{eff}} = (8 \cdot \chi_M \cdot T)^{1/2} \quad (3)$$

T : temperature (K)

Thus, taking *ca.* 20 mg/mL of the complexes, we find at 295 K μ_{eff} values of $2.2 \pm 0.1 \mu_B$ and of $2.4 \pm 0.1 \mu_B$ for **4** and for **6**, respectively, when using a classical value of $\chi_0 = -0.549 \times 10^{-6} \text{ cm}^3 \cdot \text{g}^{-1}$ for CD₂Cl₂.³ Within experimental uncertainty, the two values are the same, and have values that are approximately 75 % of those that would be expected for a $S = 1$ compound ($3.04 \mu_B$) when using a quite classical value of 2.15 for the isotropic g factor of **4** and **6** in

¹ Evans, D. F.; *J. Chem. Soc.*, **1959**, 2003 – 2005.

² Sur, S. K.; *J. Magn. Res.*, **1988**, 82, 169 – 173.

³ *CRC Handbook of Chemistry and Physics*, 52nd Ed.; The CRC Publishing Company: Cleaveland, 1971.

solution.⁴ This means that they correspond well to the value expected for two uncoupled spins at room temperature.

4. Reaction of **4** with **2**

In an NMR tube, [$\{\text{Fe}(\kappa^2\text{-dppe})(\eta^5\text{-C}_5\text{Me}_5)(\text{C}\equiv\text{CPh}_2)\}_2$][PF₆]₂ (**2**; 18.9 mg, 10 μmol) and [$\{\text{Fe}(\kappa^2\text{-dppe})(\eta^5\text{-C}_5\text{Me}_5)(\text{C}\equiv\text{CPh}_2)\}\text{Pd}(\mu\text{-Cl})\text{Cl}\}_2$][PF₆]₂ (**4**; 11.3 mg, 5 μmol) were dissolved in CD₂Cl₂ (1 mL). The mixture was left to react for 15 min at room temperature then checked by NMR spectroscopy. The complex [*trans*- $\{\text{Fe}(\kappa^2\text{-dppe})(\eta^5\text{-C}_5\text{Me}_5)(\text{C}\equiv\text{CPh}_2)\}_2\text{PdCl}_2$][PF₆]₂ (**6**) was the largely dominant (> 95 %) species in solution, along with traces of decomposition products.

The above reaction was repeated with a twofold excess of **2** (37.8 mg) to give the same outcome at the end. Of course, one equivalent of starting dimer **2** was also identified in the medium alongside to the product **6**.

⁴ Paul, F.; Toupet, L.; Thépot, J.-Y.; Costuas, K.; Halet, J.-F.; Lapinte, C. *Organometallics* **2005**, *24*, 5464-5478.

5. Cyclic Voltammograms of **3** and **5**

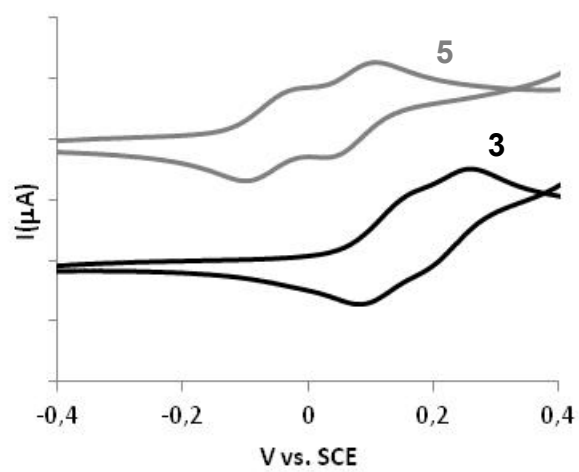


Figure S1. Cyclic Voltammograms of **3** and **5** in CH_2Cl_2 at 25 °C, $[\text{NBu}_4][\text{PF}_6]$ (0.1 M) at 0.1 V/s.