Reactivity of mononuclear Pd(II) and Pt(II) complexes containing the primary phosphane (ferrocenylmethyl)phosphane towards metal chlorides and PPh₃.

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Figure S1: (a) $^{31}$P{¹H} and (b) $^{31}$P NMR spectra of 2 (CD₂Cl₂, 273 K, 162 MHz). The starred peaks are due to impurities.
Figure S2: $^1$H-COSY spectrum of 2 (CD$_2$Cl$_2$, 273 K, 400 MHz).
Figure S3: $^1$H-$^{31}$P-COSY spectrum of 2 (CD$_2$Cl$_2$, 273 K, 400 MHz).
**Figure S4:** portion of the $^1$H-NOESY spectrum of 2 (CD$_2$Cl$_2$, 273 K, 400 MHz): the red cross peaks indicate *noesy* interaction.
Figure S5: $^{13}$C-$^1$H APT NMR spectrum of 2 (CD$_2$Cl$_2$, 273 K, 100 MHz, C and CH$_2$ point upward, CH and CH$_3$ point downward).
Figure S6: portion of the $^1$H-$^{13}$C HMQC spectrum of complex 2 in the methylenic region (CD$_2$Cl$_2$, 273 K).

Figure S7: Portion of the $^1$H-$^{13}$C HMQC spectrum of 2 in the vinylic region (CD$_2$Cl$_2$, 273 K). In the $^{13}$C{$^1$H} APT NMR spectrum of F1 the signals of primary and tertiary carbons point downward. The starred cross peak is due to the [Pt(cod)Cl$_2$] impurity.

$^{13}$C{$^1$H}-APT and $^1$H-$^{13}$C HMQC spectra of 2 (Figure S5-7) show the magnetic inequivalence of the four vinylic carbon nuclei.
Figure S8: $^{31}$P-$^1$H HETCOR spectrum of 2 (CD$_2$Cl$_2$, 273 K). The projection on F1 is the $^1$H-$^{31}$P NMR spectrum.
The $^1$H-$^{195}$Pt HMQC spectrum of 2 in Figure S9 shows that the four different vinylic protons of the coordinated diene couple only with Pt$^1$ ($H_d$ and $H_d'$, $\delta_{H_d} = \delta_{H_d'} = 5.86$, $^2J_{H_d$-Pt$^1} = ^2J_{H_d'$-Pt$^1} = 40$ Hz; $H_c'$, $\delta_{H_c'} = 5.33$, $^2J_{H_c'$-Pt$^1} = 72$ Hz; $H_c$, $\delta_{H_c} = 4.06$, $^2J_{H_c$-Pt$^1} = 77$ Hz). The chemical shifts of the diastereotopic vinylic protons cis to the phosphido bridging ligand ($H_c$ and $H_c'$) are significantly different; on the contrary, the chemical shifts of the diastereotopic vinylic protons trans to the phosphido bridging ligand ($H_d$ and $H_d'$) are coincident.

Figure S10: Portion of the $^1$H-$^{195}$Pt HMQC spectrum of 2 (CD$_2$Cl$_2$, 273 K, Pt$^1$ region).
Figure S11: Experimental (solid line) and simulated (dashed line) HRMS(+) spectrum of 2 (exact mass = 1065.9425 da) in THF diluted with CH₃CN. The error between simulated and observed isotopic patterns is –0.9 ppm.
Figure S12: portion of the $^1$H-$^{31}$P HMQC spectrum of 3 (CD$_2$Cl$_2$, 265 K) in the terminal phosphane region.
Figure S13: portion of the $^1$H-$^{31}$P HMQC spectrum of 3 (CD$_2$Cl$_2$, 265 K) in the phosphido-bridged region.
Figure S14: $^{1}$H-$^{31}$P HMBC spectrum of 3 (CD$_2$Cl$_2$, 265 K).
Figure S15. $^1$H-COSY spectrum of 3 (CD$_2$Cl$_2$, 265 K, 400 MHz).
Figure S16: $^1$H-$^{31}$P-COSY spectrum of 3 (CD$_2$Cl$_2$, 265 K, 400 MHz).
Figure S17: $^{13}$C{$^{1}$H}APT NMR spectrum of 3 (CD$_2$Cl$_2$, 265 K, 100 MHz, C and CH$_2$ point upward, CH and CH$_3$ point downward).
**Figure S18:** Portion of the $^1$H-$^{13}$C HMQC spectrum of complex 3 in the vinylic region (CD$_2$Cl$_2$, 265 K). In the reported $^{13}$C{$^1$H} APT NMR spectrum (F1) the signals of primary and tertiary carbons point downward. The cross-peaks marked with the star and with the rhomb are due to the vinylic protons of [Pd(cod)Cl$_2$] and of free COD impurities, respectively.
Figure S19: $^{31}$P-$^1$H HETCOR spectrum of 4a and 4b (CD$_2$Cl$_2$, 295 K). The projection on F1 is the $^1$H-$^{31}$P NMR spectrum.
Figure S20: $^1$H-$^{31}$P HMBC spectrum of 4a and 4b (CD$_2$Cl$_2$, 295 K)
Figure S21: Methyleneic region of the $^1$H-$^{13}$C-HMQC spectrum of 4a and 4b (CD$_2$Cl$_2$, 295 K)
Figure S22: Experimental (black line) and simulated (red line) HRMS(+) spectrum of 4a and 4b (exact mass = 1901.8977 da) in THF diluted with CH₃CN. The error between simulated and observed isotopic patterns is 6.8 ppm.
Figure S23: $^{31}$P–1H-COSY spectrum (CD$_2$Cl$_2$, 295 K) of 5.
**Figure S24**: Portion of $^1$H-COSY spectrum of 5 (CD$_2$Cl$_2$, 295 K).
Figure S25: Portion of $^1\text{H}$$^{[31\text{P}]}$-COSY spectrum of 5 (CD$_2$Cl$_2$, 295 K).
Figure S26: $^{31}$P–$^1$H HETCOR spectrum of 5 (CD$_2$Cl$_2$, 295 K). The projection in F1 is the $^1$H$_{^{31}$P}^{}$ NMR spectrum.
Figure S27: $^1$H-$^{31}$P HMBC spectrum of 5 (CD$_2$Cl$_2$, 295 K)
Figure S28: portion of $^1$H-$^{13}$C HMQC spectrum of 5 (CD$_2$Cl$_2$, 295 K): methylene region.
Figure S29: Experimental (black line) and simulated (red line) HRMS(+) spectrum of 5 (exact mass = 1871.8175 da) in THF diluted with CH$_3$CN. The error between simulated and observed isotopic patterns is 3.5 ppm.
Table S1. $^{31}$P and $^1$H NMR parameters for complexes A (top), B (middle), and C (bottom), deriving from PPh$_3$ addition to 2. (C$_6$D$_6$, 295 K, 162 MHz); chemical shifts (bold) are in ppm; coupling constants (normal) are in Hz.
Table S2. $^{31}$P and $^1$H NMR parameters for complex D (CD$_2$Cl$_2$, 295 K, 162 MHz); chemical shifts (bold) are in ppm; coupling constants (normal) are in Hz.