Supplementary Information

Platinum complexes having redox-active PPh$_2$C≡CFc and/or C≡CFc as terminal or bridging ligands.

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Figure S1. a) View of the π⋯π interactions between the C$_6$F$_5$ and Cp rings of adjacent molecules of complex 2 (left), which give rise to a bidimensional network along the $b$ and $c$ axes (right). The layers are additionally connected by the CH$_2$Cl$_2$ crystallization
solvent molecules, giving rise to a three-dimensional network. Two different types of contacts are observed involving one (F⋯H 2.455(4) Å; b), or three (Cl⋯H 2.495(8) Å and C(Ph)⋯H(CH₂Cl₂) 2.589(7) Å; c) molecules of solvent.
Figure S2. The molecular structure of complex 3 shows weak intermolecular contacts with distances F⋯H(Ph) (2.525(5), 2.552(4) Å), F⋯H-C(tht) (2.615(5), 2.656(4) Å), F⋯H-C(Fc) (2.622(5) Å), F⋯C(Fc) (3.14(2) Å), C(Fc)-H⋯C(Ph) (2.893(6) Å), C(Fc)-H⋯C(Fc) (2.89 Å), C(Ph)-H⋯C(Fc) (2.882(9), 2.81(2) Å), C(tht)-H⋯C(\text{C}_6\text{F}_5) (2.815(8) Å), C(Fc)-H⋯H-C(Fc) (2.32 Å).
Thermal behavior of complex 9:

Prolongated heating in solid state (\( \sim 140 ^\circ C \)) or in solution of complex 9 (CHCl\(_3\) or Toluene) evolves with considerable decomposition and the only stable phosphorous containing species observed by \(^{31}\)P\{\(^1\)H\} NMR spectroscopy was the precursor. However, by heating at 70\(^\circ\)C a toluene solution of 9 for a short time (3 min), the expected signals (\(^{31}\)P\{\(^1\)H\} and \(^{19}\)F NMR, see Experimental Section) due to the double inserted product 9\(^{'}\) (Scheme S1, ii) are observed in the final reaction mixture, together with other decomposition products, including the precursor 9. The most characteristic signals in the \(^{19}\)F NMR spectrum corresponds to the inserted C\(_6\)F\(_5\) group (C-C\(_6\)F\(_5\), A), for which the separation between the two F-ortho resonances and the F-para is reduced to \( \sim 16 \) ppm (-136.6, -137.4 o-F\(^A\), -153.8 p-F\(^A\)) and in the \(^{31}\)P\{\(^1\)H\} NMR spectrum the expected low-field signals (\( \delta \) 21.11, 33.71 ppm) with platinum satellites, in accordance with previous results.\(^{S1, S2}\) All attempts to isolate 9\(^{'}\) as pure solid from the mixture have been unsuccessful.

![Scheme S1](image)


Experimental Section:

Heating of \([\{\text{Pt(C}_6\text{F}_5\}_2(\mu-1\kappa^2\eta^2-\text{PPh}_2\text{C}≡\text{CFc})\}_2]\text{Pt(C}_6\text{F}_5\}_2]\) \(\textbf{9}\). Formation of \([\text{Pt(C}_6\text{F}_5)(S)\mu-\{\text{C}(\text{Fc})=\text{C(PPH}_2\text{)}\text{C(PPH}_2\text{)}=\text{C(Fc)}(\text{C}_6\text{F}_5\}_3]\text{Pt}(\text{C}_6\text{F}_5\}_2]\) \(\textbf{9}'\). Monitoring by multinuclear NMR spectra of a solution of \(\textbf{9}\) heating in toluene for 3 min reveals the presence of signals corresponding to \(\textbf{9}'\), together with other decomposition products including \(\textbf{9}\). Data for \(\textbf{9}'\) extracted from the NMR spectra of the mixture: \(\delta_P\) (121.5 MHz; CDCl\(_3\); 20ºC) 21.11 (s, \(\text{J}_{\text{Pt-P}}\) 2336 Hz), 33.71 (s, \(\text{J}_{\text{Pt-P}}\) 2324 Hz); \(\delta_F\) (282.4 MHz; CDCl\(_3\); 20ºC) -113.5 (m, 1F, o-F), -114.1 (m, 1F, o-F), -115.2 (m, 1F, o-F), -115.8 (m, 1F, o-F) -117.2 (m, 2F, o-F), -136.6 (s, 1F, o-F\(^A\)), -137.4 (s, 1F, o-F\(^A\)), -153.8 (t, 1F, p-F\(^A\)), -158.2 (t, 1F), -160.8 (m, 1F), -161.7 (m, 2F, p-F), -162.3 (m, 1F, -136.1 (m, 2F), -163.6 (m, 4F, m-F).
Figure S3. (a) CVs of complex 4 in CH₂Cl₂ solution at different sweep rates. (b) Quasireversible peak current variation with the square root of the scan rate, which shows a linear trend.
**Figure S4.** CV and DPV of complex 5a (a) in CH₂Cl₂ showing four unresolved waves and CV of complex 5c (b), which shows additional waves due to by-products (*) at 100 mv s⁻¹.
Figure S5. CV (and DPV) of complex 10a in CH$_2$Cl$_2$ at a scan rate of 100 mV s$^{-1}$. 