Supplementary Information

Platinum complexes having redox-active $PPh_2C{\equiv}CFc$ and/or $C{\equiv}CFc$ as terminal or bridging ligands.

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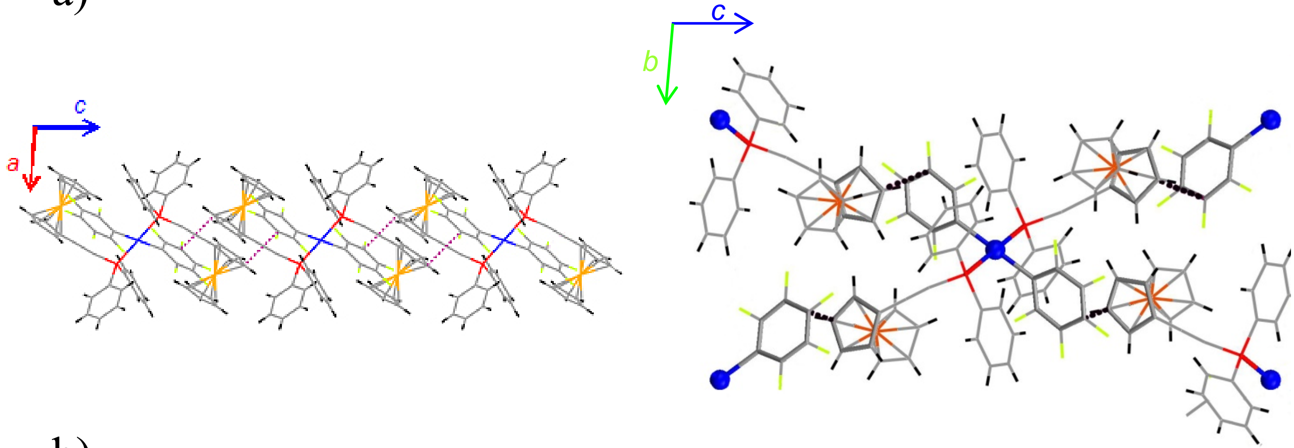
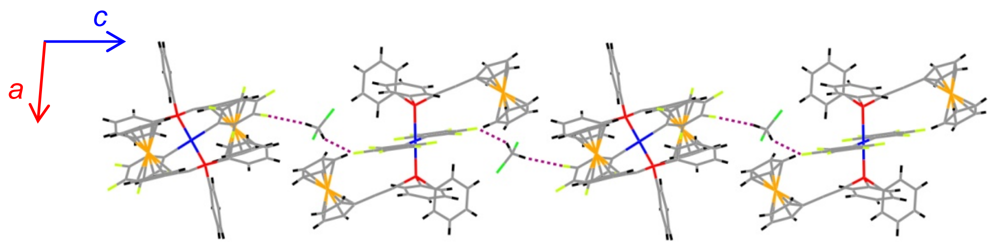
a)



b)



c)

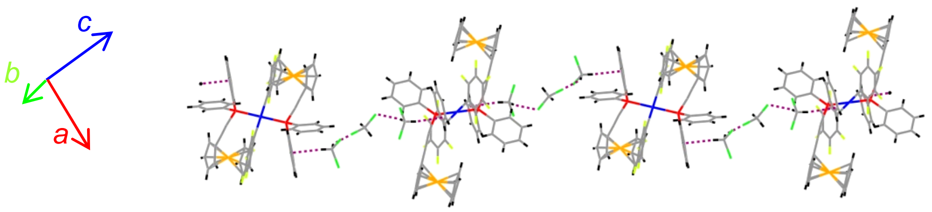


Figure S1. a) View of the π···π interactions between the C_6F_5 and Cp rings of adjacent molecules of complex **2** (left), which give rise to a bidimensional network along the *b* and *c* axes (right). The layers are additionally connected by the CH_2Cl_2 crystallization solvent molecules, giving rise 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(CH_2Cl_2) 2.589(7) Å; c) molecules of solvent.

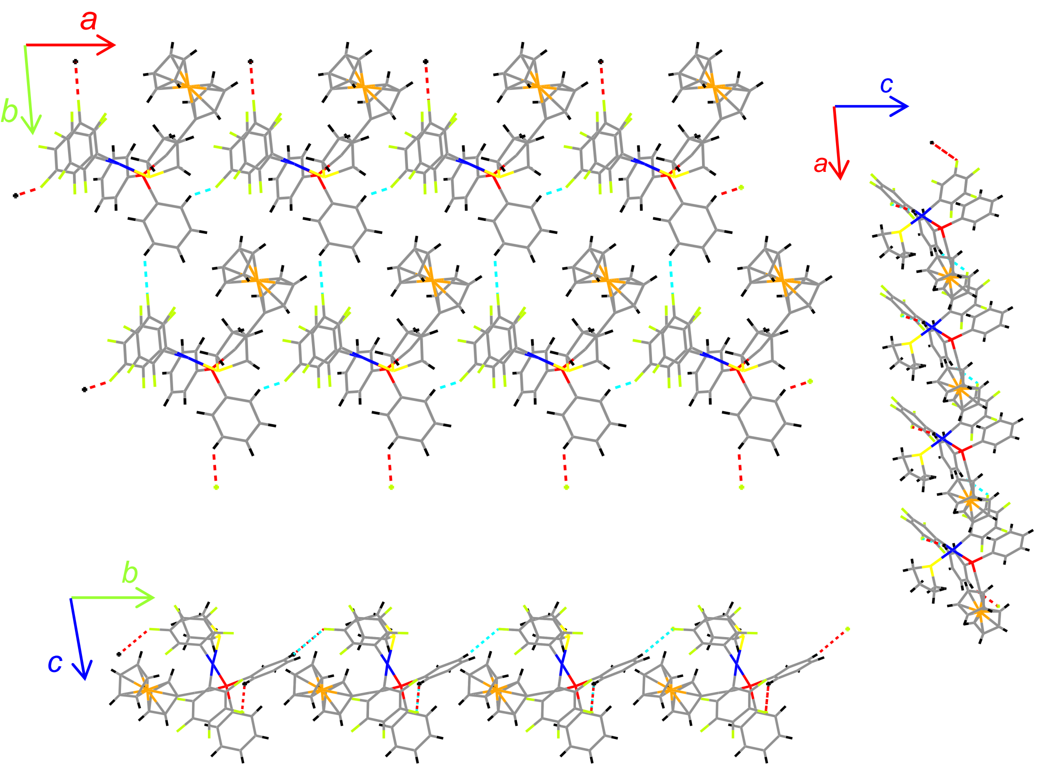
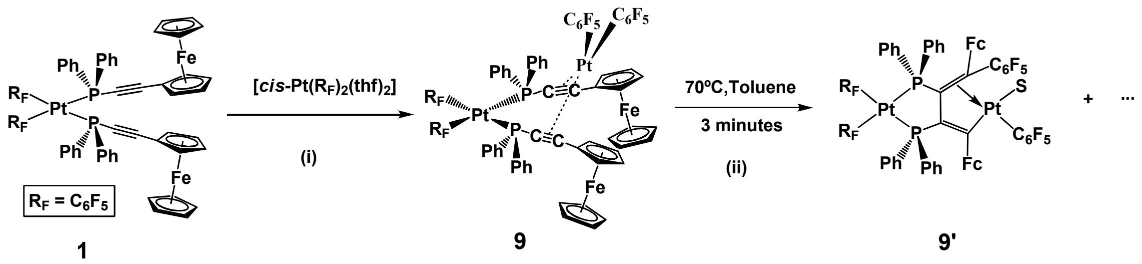


Figure S2. The molecular structure of complex **3** shows weak intermolecular contacts with distances F···H(Ph) (2.525(5), 2.552(4) Å), F···H-C(tht) (2.615(5), 2.656(4) Å), F···H-C(Fc) (2.622(5) Å), F···C(Fc) (3.14(2) Å), C(Fc)-H···C(Ph) (2.893(6) Å), C(Fc)-H···C(Fc) (2.89 Å), C(Ph)-H···C(Fc) (2.882(9), 2.81(2) Å), C(tht)-H···C(C_6F_5) (2.815(8) Å), C(Fc)-H···H-C(Fc) (2.32 Å).

Thermal behavior of complex 9:

Prolongated heating in solid state (~ 140 ºC) or in solution of complex **9** ($CHCl_3$ or Toluene) evolves with considerable decomposition and the only stable phosphorous containing species observed by $^{31}P\{^1H\}$ NMR spectroscopy was the precursor. However, by heating at 70ºC a toluene solution of **9** for a short time (3 min), the expected signals ($^{31}P\{^1H\}$ 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_6F_5 group (C-C_6F_5, A), for which the separation between the two F-*ortho* resonances and the F-*para* is reduced to ~ 16 ppm (-136.6, -137.4 *o*-F^A, -153.8 *p*-F^A) and in the $^{31}P\{^1H\}$ NMR spectrum the expected low-field signals (δ 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

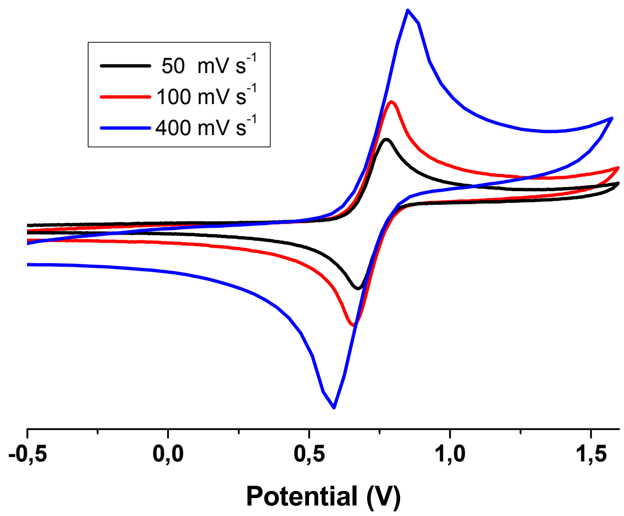
S1 J. P. H. Charmant, J. Forniés, J. Gómez, E. Lalinde, M. T. Moreno, A. G. Orpen and S. Solano, *Angew. Chem., Int. Ed. Engl.*, 1999, **38**, 3058.

S2 I. Ara, J. Forniés, A. García, J. Gómez, E. Lalinde and M. T. Moreno, *Chem. Eur. J.*, 2002, **8**, 3698.

Experimental Section:

Heating of [{Pt(C_6F_5)$_2$(μ-1κP:2η^2-PPh$_2$C≡CFc)$_2$}Pt(C_6F_5)$_2$] 9. Formation of [Pt(C_6F_5)(S)μ-{C(Fc)=C(PPh$_2$)C(PPh$_2$)=C(Fc)(C_6F_5)}Pt(C_6F_5)$_2$] 9′. Monitoring by multinuclear NMR spectra of a solution of **9** heating in toluene for 3 min reveals the presence of signals corresponding to **9′**, together with other decomposition products including **9**. Data for **9′** extracted from the NMR spectra of the mixture: δ_P (121.5 MHz; $CDCl_3$; 20ºC) 21.11 (s, $^1J_{Pt-P}$ 2336 Hz), 33.71 (s, $^1J_{Pt-P}$ 2324 Hz); δ_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).

a)



b)

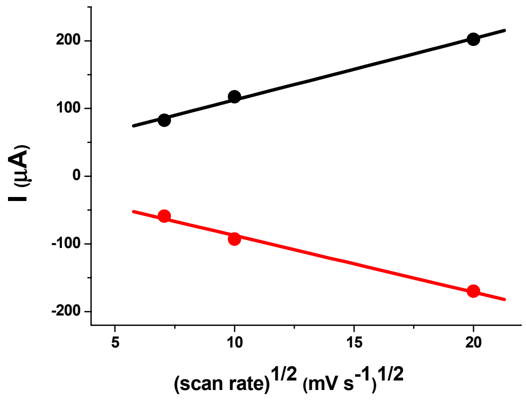


Figure S3. (a) CVs of complex **4** in CH_2Cl_2 solution at different sweep rates. (b) Quasireversible peak current variation with the square root of the scan rate, which shows a linear trend.

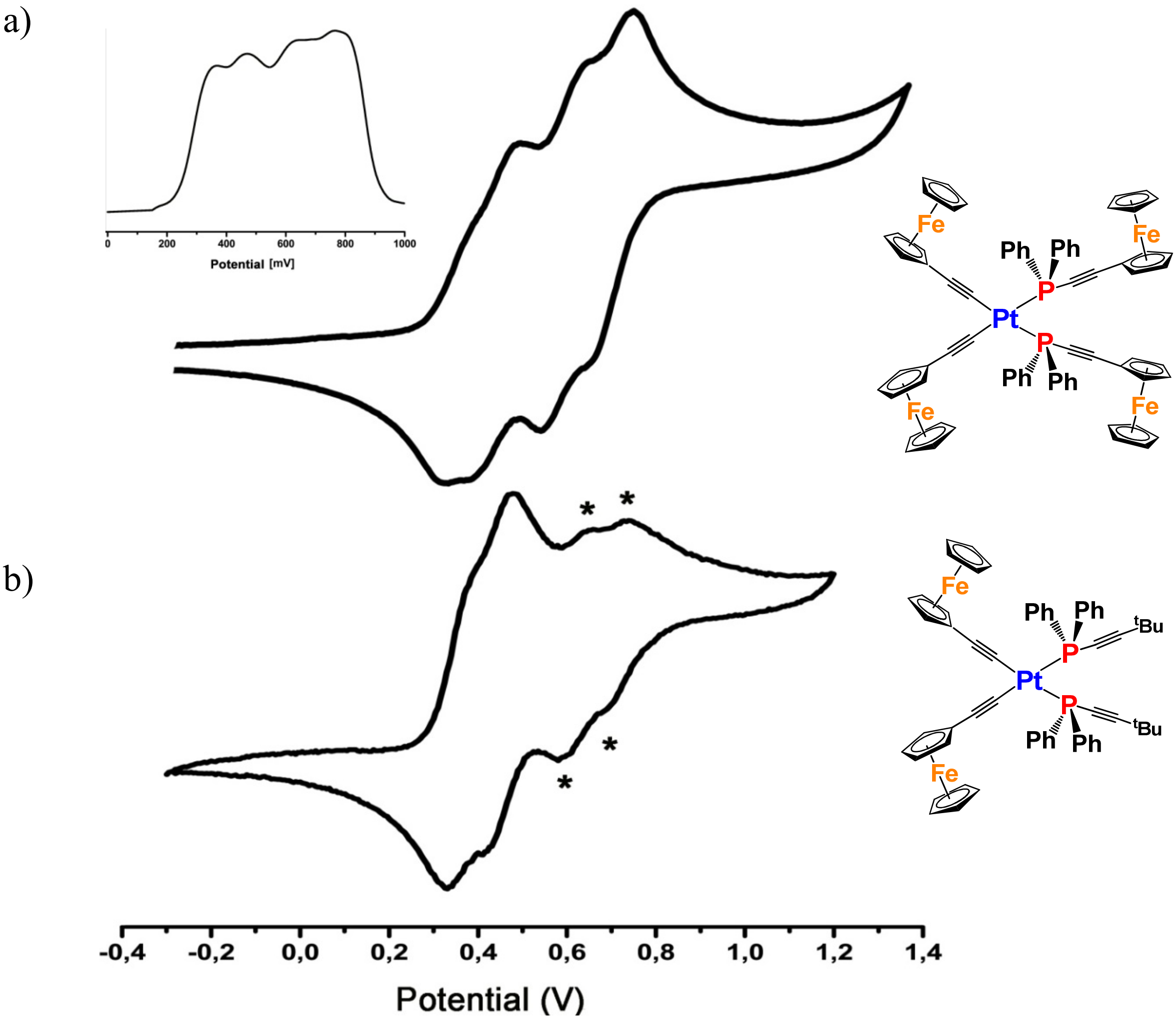


Figure S4. CV and DPV of complex **5a** (a) in CH_2Cl_2 showing four unresolved waves and CV of complex **5c** (b), which shows additional waves due to by-products (*) at 100 mv s^{-1}.

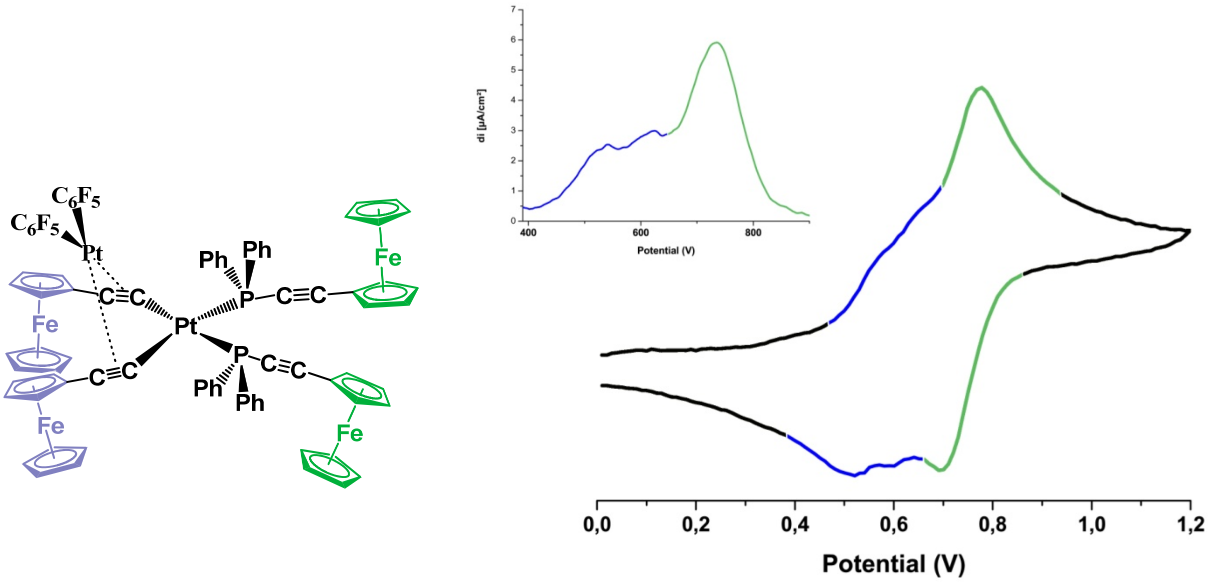


Figure S5. CV (and DPV) of complex **10a** in CH_2Cl_2 at a scan rate of 100 mv s^{-1}