

Supporting Information for

Cyclopalladated Complexes Containing 2-C₆R₄PPh₂ Ligands (R = H, F): One-Electron Electrochemical Reduction Leading to Metal–Carbon σ -Bond Cleavage via Palladium(I)

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All potentials are referenced to the DmFc^{0/+} redox couple.

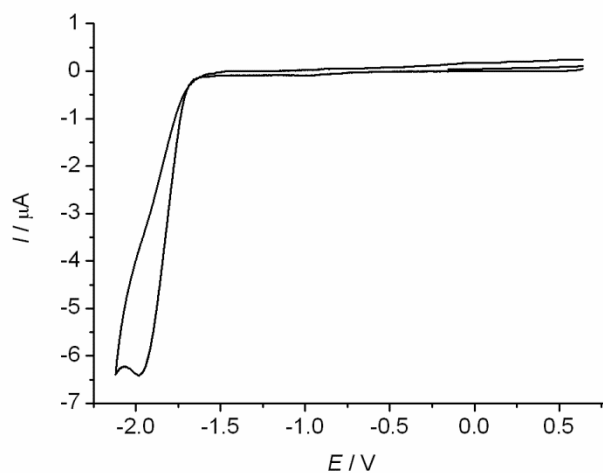


Figure S1. Cyclic voltammogram of a 1 mM solution of [PdBr(PPh₃)(κ²-2-C₆H₄PPh₂)] (**1**) in CH₃CN containing 0.1 M [Bu₄N][PF₆] at a 1 mm diameter glassy carbon electrode. Scan rate: 100 mV s⁻¹.

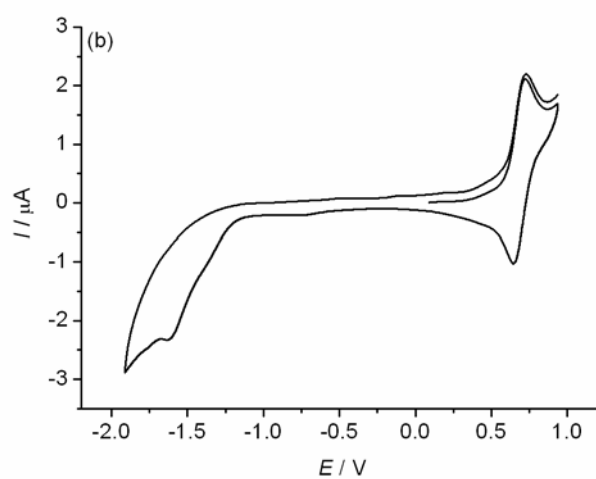
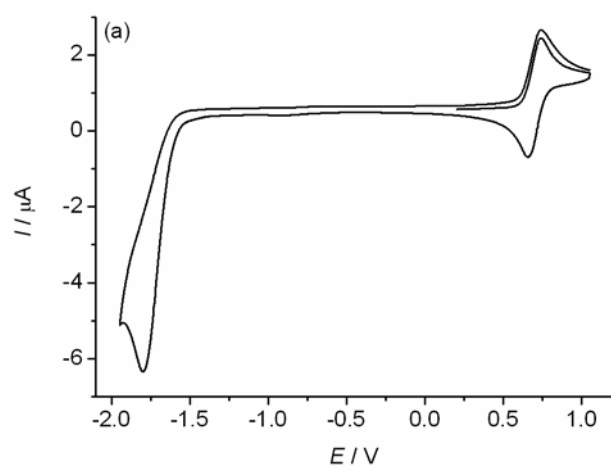


Figure S2. Cyclic voltammogram of a 1 mM solution of [PdBr(PPh₂Fc)(κ²-2-C₆H₄PPh₂)] (**2**) containing 0.1 M [Bu₄N][PF₆] at a 1 mm diameter glassy carbon electrode in (a) CH₂Cl₂ and (b) CH₃CN. Scan rate: 100 mV s⁻¹.

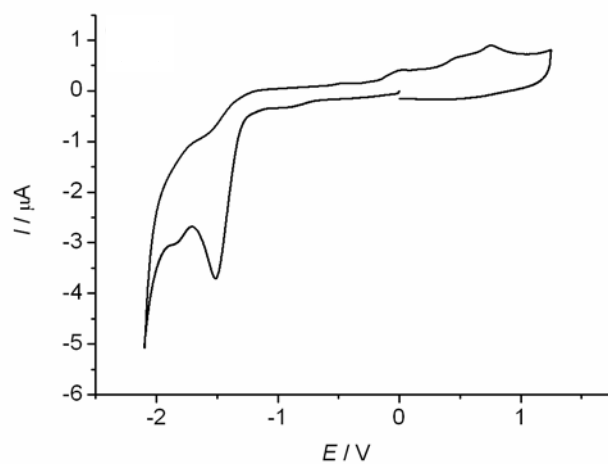


Figure S3. Cyclic voltammogram of 1 mM $[\text{PdBr}(\text{PPh}_3)(\kappa^2\text{-2-C}_6\text{F}_4\text{PPh}_2)]$ (**4**) in CH_2Cl_2 containing 0.1 M $[\text{Bu}_4\text{N}][\text{PF}_6]$ at a 1 mm glassy carbon electrode. Scan rate: 200 mV s^{-1} .

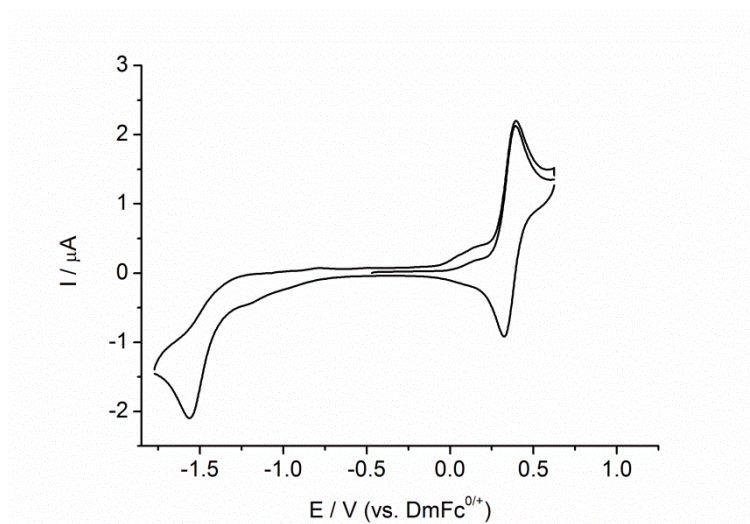


Figure S4. Cyclic voltammogram of a 1 mM solution of $[\text{PdBr}(\text{PPh}_2\text{Fc})(\kappa^2\text{-2-C}_6\text{F}_4\text{PPh}_2)]$ (**5**) in CH_2Cl_2 containing 0.1 M $[\text{Bu}_4\text{N}][\text{PF}_6]$. Scan rate: 100 mV s^{-1} .

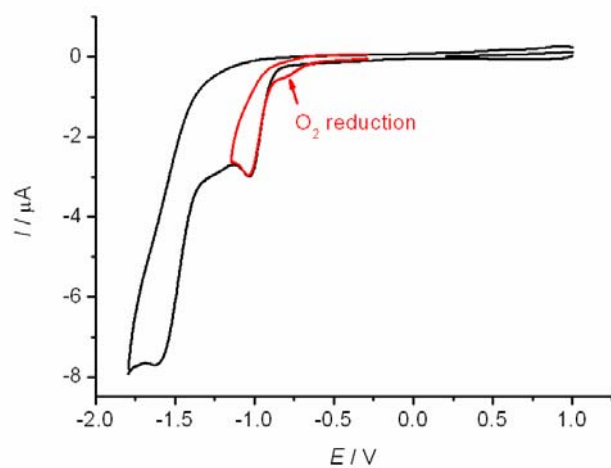


Figure S5. Cyclic voltammogram of a 1 mM solution of $[\text{Pd}_2(\mu\text{-Br})_2(\kappa^2\text{-}2\text{-C}_6\text{F}_4\text{PPh}_2)_2]$ (**7**) in CH_2Cl_2 containing 0.1 M $[\text{Bu}_4\text{N}][\text{PF}_6]$. Scan rate: 100 mV s^{-1} . Black trace: without the presence of oxygen, red trace: with the presence of oxygen.

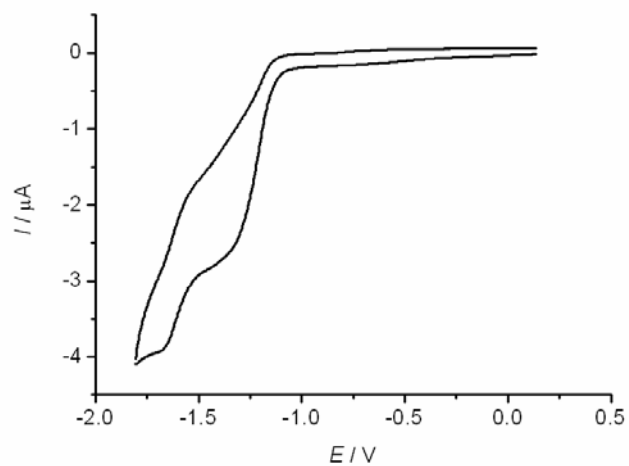


Figure S6. Cyclic voltammogram of a 0.7 mM solution of $[\text{Pd}_2\text{Br}_2(\text{NCMe})_2(\mu\text{-}2\text{-C}_6\text{F}_4\text{PPh}_2)_2]$ (**9**) in CH_2Cl_2 containing 0.1 M $[\text{Bu}_4\text{N}][\text{PF}_6]$. Scan rate: 100 mV s^{-1} .