

Figure S1. (A): ESI-MS spectrum of **Me₂phen** displaced from complex $[PtCl(\eta^1-CH_2CH_2OMe)(Me_2phen)]$, **1a**, synthesized in *d*₄-methanol (0 °C, ≈ 3h), by treatment with triphenylphosphine. Extensive H/D exchange at the Me groups (>70%) is observed. (B): ESI-MS spectrum of undeuterated **Me₂phen** reported for comparison.

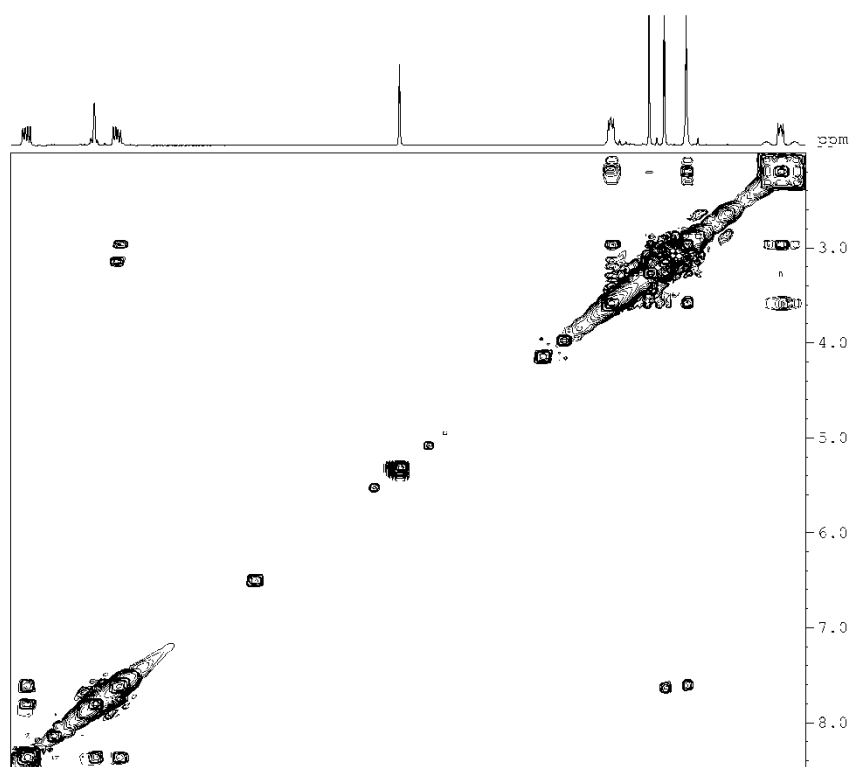


Figure S2. NOESY spectrum of complex [PtCl(η^1 -CH₂CH₂OMe)(Me₂phen)], **1a**, in CDCl₃

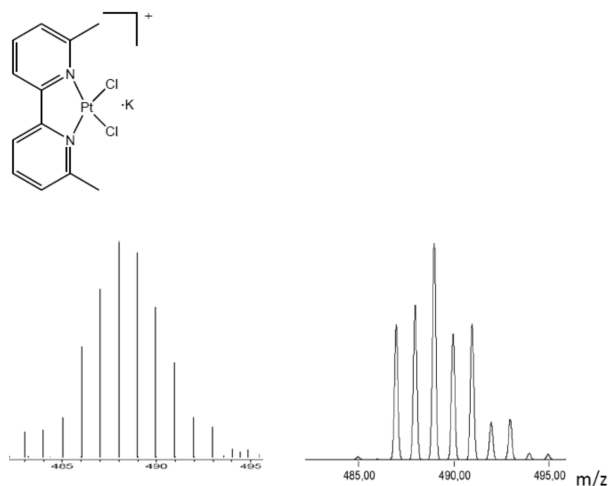


Figure S3. ESI-MS analysis (positive mode) of [Pt(**Me₂bpy**)Cl₂], **2b**, dissolved in CD₃OD, in the presence of 0.25 M [KOD] and incubated for 1h at 25 °C. No H/D exchange at **Me₂bpy** Me's is observed. The simulated isotopic distribution is reported on the right (the differences between observed and simulated isotopic distributions could be attributed to partial hydrogen loss induced during formation of the molecular ion C₁₂H₁₂Cl₂KN₂Pt⁺, producing the species C₁₂H₁₁Cl₂KN₂Pt⁺, characterized by an highest abundant ion at m/z = 488).

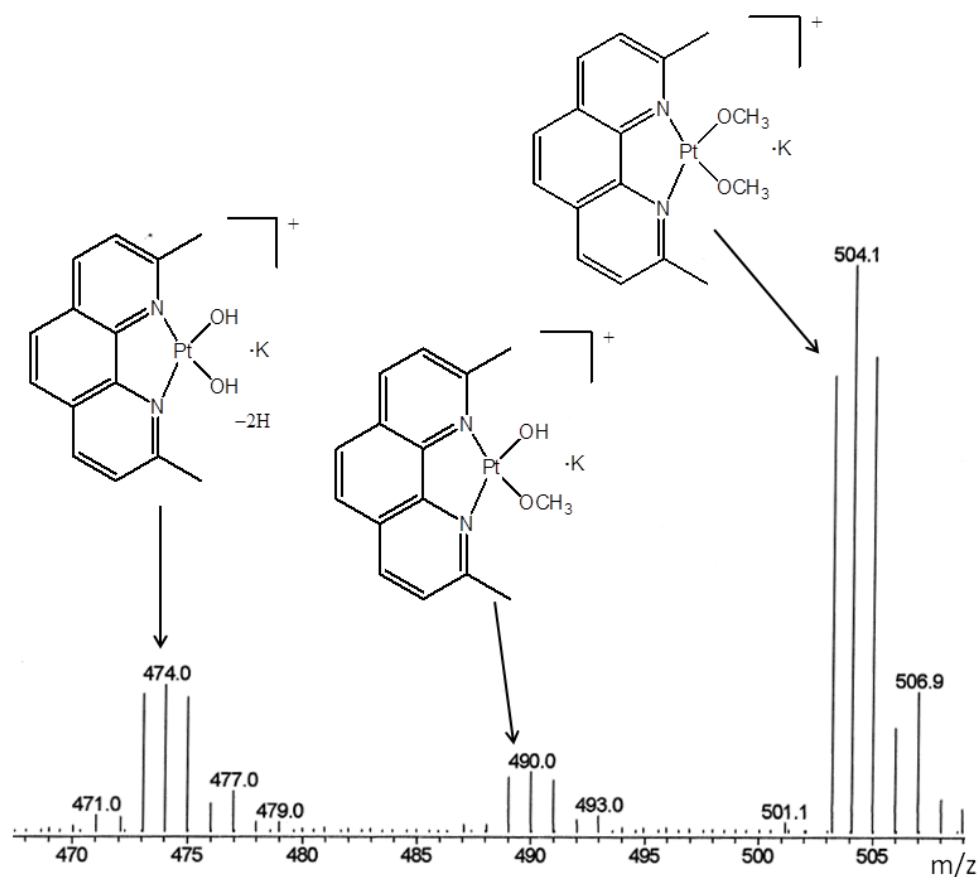


Figure S4. ESI-MS analysis (positive mode) of $[\text{Pt}(\text{Me}_2\text{phen})\text{Cl}_2]$, **2a**, pre-treated with AgNO_3 to displace chlorides and then dissolved in basic CH_3OH (0.25 M KOH) and incubated for 24h at room temperature. Detected ions correspond to $\{[\text{Pt}(\text{Me}_2\text{phen})(\text{OH})_2]\cdot\text{K}(-2\text{H})\}^+$, $\{[\text{Pt}(\text{Me}_2\text{phen})(\text{OH})(\text{OMe})]\cdot\text{K}\}^+$, and $\{[\text{Pt}(\text{Me}_2\text{phen})(\text{OMe})_2]\cdot\text{K}\}^+$.

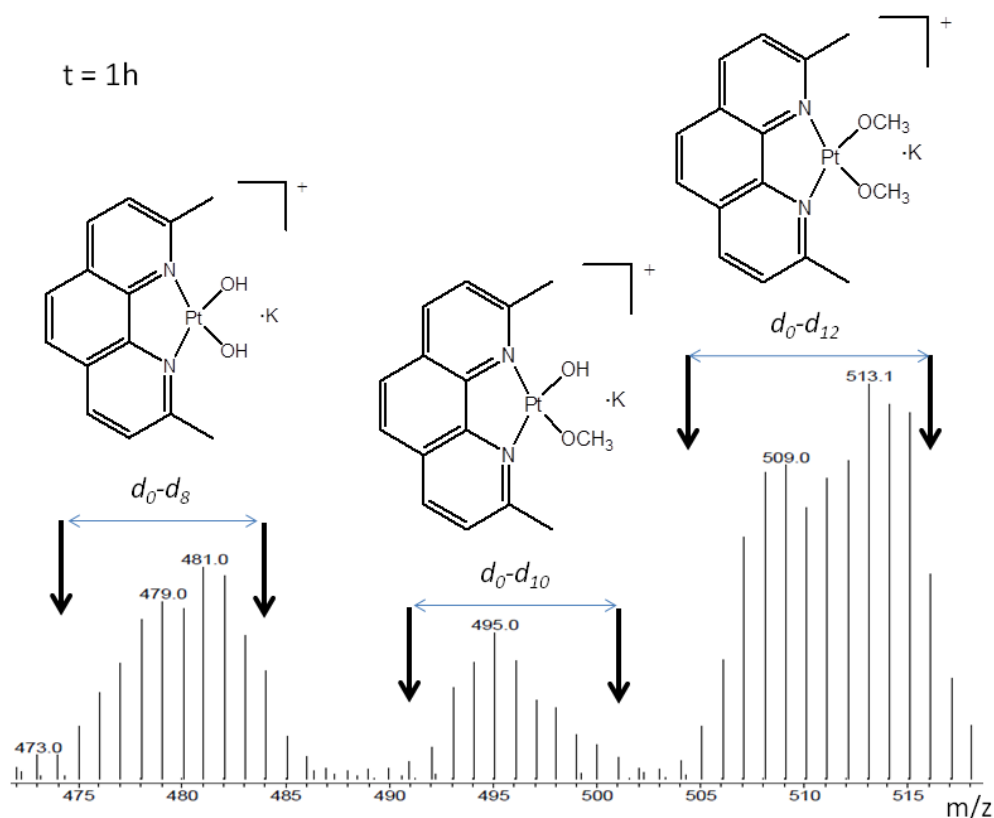


Figure S5. ESI-MS SPECTRA (positive mode) of $[\text{Pt}(\text{Me}_2\text{phen})(\text{OR})_2]$, **3a**, (the same solution of Figure S3) diluted in a ten fold excess of basic CD_3OD (0.25 M KOD) and incubated for 1 h at 25°C . Only partial deuteration of ions $\{[\text{Pt}(\text{Me}_2\text{phen})(\text{OH})_2]\cdot\text{K}\}^+$, $\{[\text{Pt}(\text{Me}_2\text{phen})(\text{OMe})_2]\cdot\text{K}\}^+$, and $\{[\text{Pt}(\text{Me}_2\text{phen})(\text{OH})(\text{OMe})]\cdot\text{K}\}^+$ is observed, indicating that the H/D exchange is very slow if compared to the case of $[\text{Pt}(\text{Me}_2\text{phen})\text{Cl}_2]$ complex.