SUPPORTING INFORMATION FOR

Reversible Redox Chemistry and Catalytic C(sp^3)-H Amination Reactivity of a Paramagnetic Pd Complex bearing a Redox-Active *o*-Aminophenol-derived NNO Pincer Ligand

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1. Experimental details

Theoretical ratio of NNO^{ISQ}PdCl + CoCp$_2$: [CoCp$_2$][NNO^{AP}PdCl]

By using equation 1, 2 and 3 and the standard reduction and oxidation potentials ($E^{o'}$) of NNO^{ISQ}PdCl (-0.96 V vs. Fc/Fc$^+$,) and CoCp$_2$ (-1.33 V vs Fc/Fc$^+$), it can be calculated that one-electron reduction of NNO^{ISQ}PdCl with and equimolar amount of CoCp$_2$ at 298 K affords a 1.36*10^3 : 1 ratio of [CoCp$_2$][NNO^{AP}PdCl] and NNO^{ISQ}PdCl, which corresponds to an equilibrium constant (K_{eq}) of 1.85*10^6. Thus, reduction of NNO^{ISQ}PdCl with CoCp$_2$ provides an almost quantitative conversion to [CoCp$_2$][NNO^{AP}PdCl].

$$CoCp_2 + NNO^{ISQ}PdCl \xrightleftharpoons{K_{eq}} CoCp_2^+ + NNO^{AP}PdCl^-$$

Scheme S1   Reduction of NNO^{ISQ}PdCl by CoCp$_2$ as clarification with equation 1, 2 and 3.

(1) $\quad \Delta E^{o'} = E^{o'}(NNO^{ISQ}PdCl/NNO^{AP}PdCl^-) - E^{o'}(CoCp_2/CoCp_2^+)$

(2) $\quad \log\dfrac{CoCp_2^+}{CoCp_2} = \log\dfrac{NNO^{AP}PdCl^-}{NNO^{ISQ}PdCl} = 8.47\Delta E^{o'}$ (at 298 K)

(3) $\quad K_{eq} = \dfrac{[CoCp_2^+][NNO^{AP}PdCl^-]}{[CoCp_2][NNO^{ISQ}PdCl]}$

¹H NMR spectra of 5
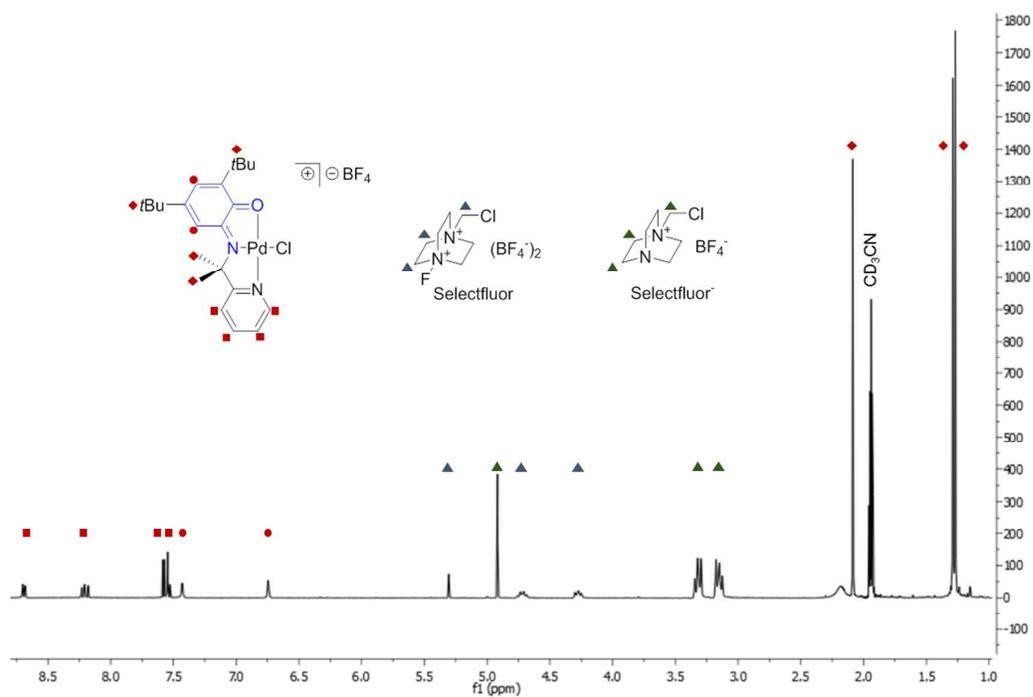

Figure S1. ¹H-NMR spectrum of the *in situ* reduction of **1** with SelectFluor.
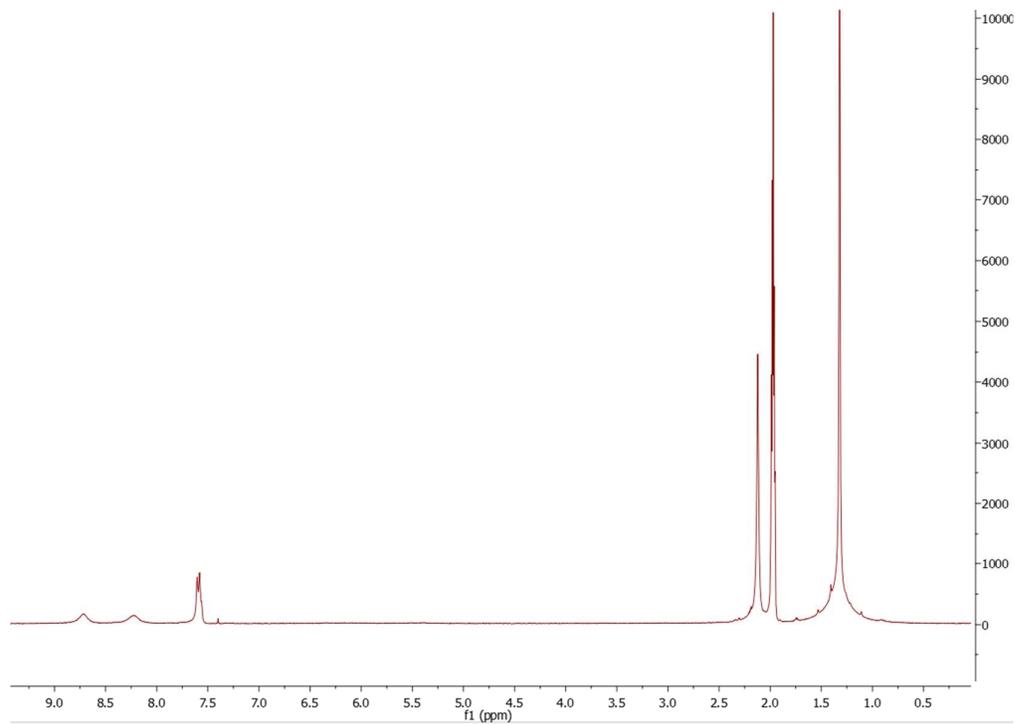
Figure S2 ¹H-NMR spectrum of **5** showing the broadened resonances.

DFT calculations (gas phase)

Chloride dissociation from $\textbf{NNO}^{\textbf{AP}}\text{PdCl}^-$ is a highly endergonic step, which is likely due to the poor description of ionic processes in the gas phase by DFT. Subsequent coordination of CH_2Cl_2 to a naked neutral $Pd(\textbf{NNO}^{\textbf{AP}})$ fragment (**A**) is exergonic by -2.0 kcal mol^{-1}.[S1] Both a closed-shell singlet (CSS) and triplet solution were found for $Pd(CH_2Cl_2)(\textbf{NNO}^{\textbf{AP}})$ (**C**), with the CSS being lower in energy by 5.7 kcal mol^{-1}. The barrier ($\Delta G^{\text{o}}_{298}$) on the open-shell singlet (OSS) surface for homolytic cleavage of the $Cl-CH_2Cl$ bond relative to species **C** was found to be only $+12.4$ kcal mol^{-1} (**TS**).[S2] The reaction to form $PdCl(\textbf{NNO}^{\textbf{ISQ}})$ and a chloromethyl radical ($\bullet CH_2Cl$) is exergonic ($\Delta G^{\text{o}}_{298} = -7.5$ kcal mol^{-1}) (**D**). Chloromethyl radicals are known to be short-lived due to follow-up dimerization to form dichloroethane,[S3] which was calculated to be exergonic by -32.7 kcal mol^{-1} (**E**), making the overall reaction endergonic by $+4.0$ kcal mol^{-1}.
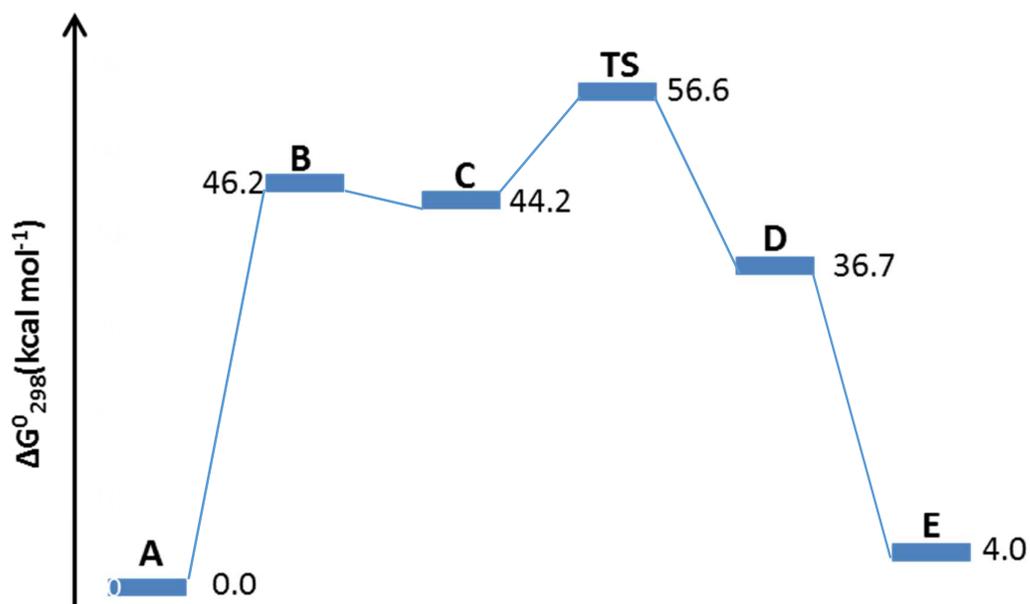
Figure S3. DFT (gas phase) calculated energy profile (ΔG°_{298} in kcal mol^{-1}) for the homolytic cleavage of the $Cl-CH_2Cl$ bond on $Pd(\textbf{NNO}^{\textbf{AP}})$ (b3-lyp, def2-TZVP).

2. References

S1   Using the pure GGA BP86 functional provided similar results.

S2   The applied broken-symmetry approach is an approximation of the multideterminant problem of bond-splitting reactions, hence introducing some (unavoidable) additional error to the computed barrier.

S3   Emmi, S. S.; Beggiato, G.; Casalbore-Miceli, G. *Int. J. Radiat. Appl. Instrum. C Radiat. Phys. Chem.* **1989**, *33*, 29-37.