

Supporting Information

A Two-Step Catalytic Cycle for the Acceptorless Dehydrogenation of Ethane by Group 10 Metal Complexes: Role of the Metal in Reactivity and Selectivity.

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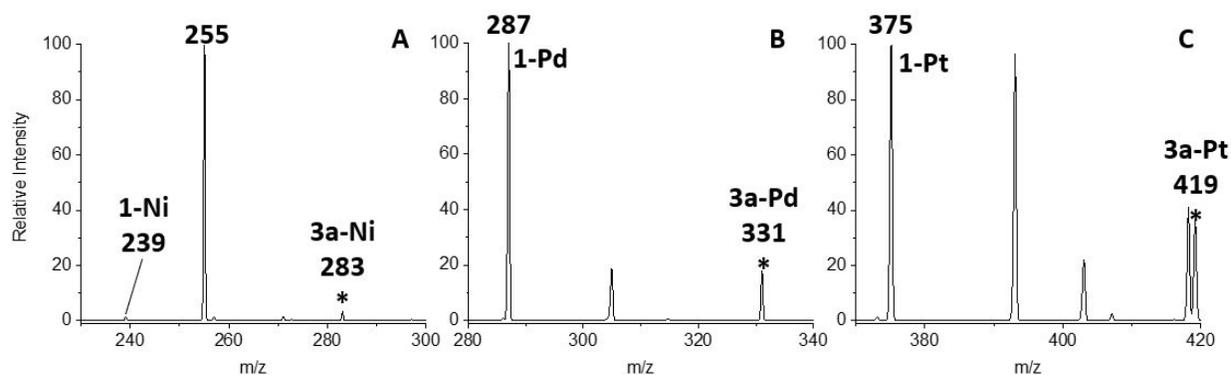


Figure S1. CID of [(phen)M(O₂CH)]⁺ for M= Ni (a), Pd (b), and Pt (c).

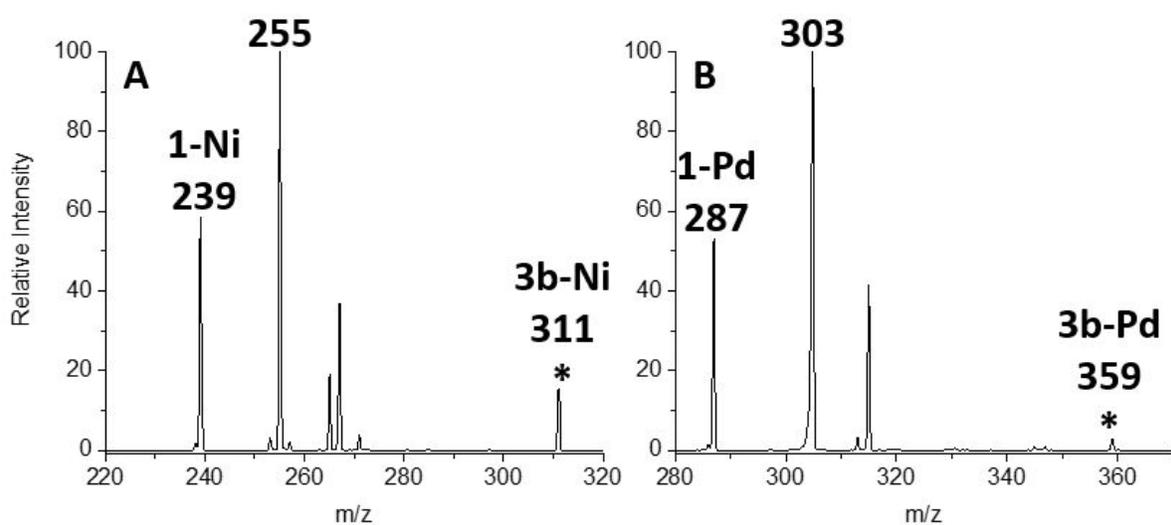


Figure S2. CID of [(phen)M(O₂CC₂H₅)]⁺ **3b** for M= Ni (a), Pd (b), and Pt (c).

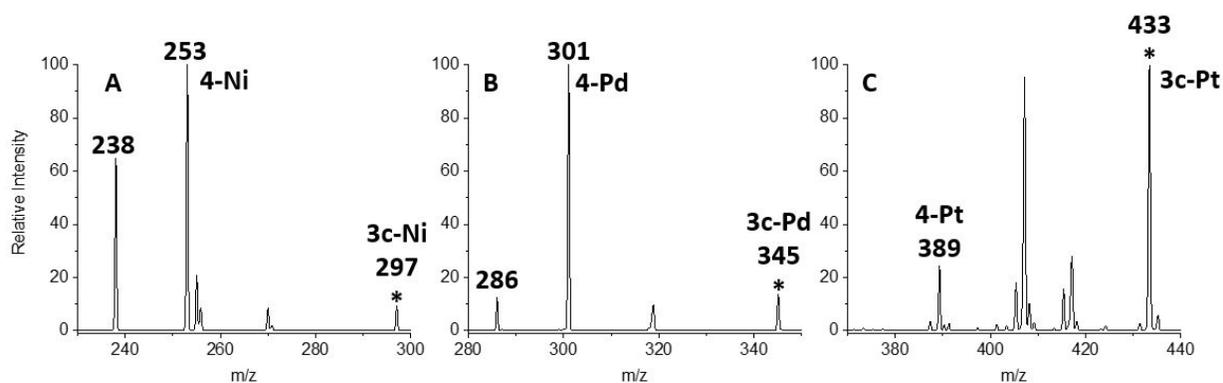


Figure S3. CID of [(phen)M(O₂CCH₃)]⁺ **3c** for M= Ni (a), Pd (b), and Pt (c).

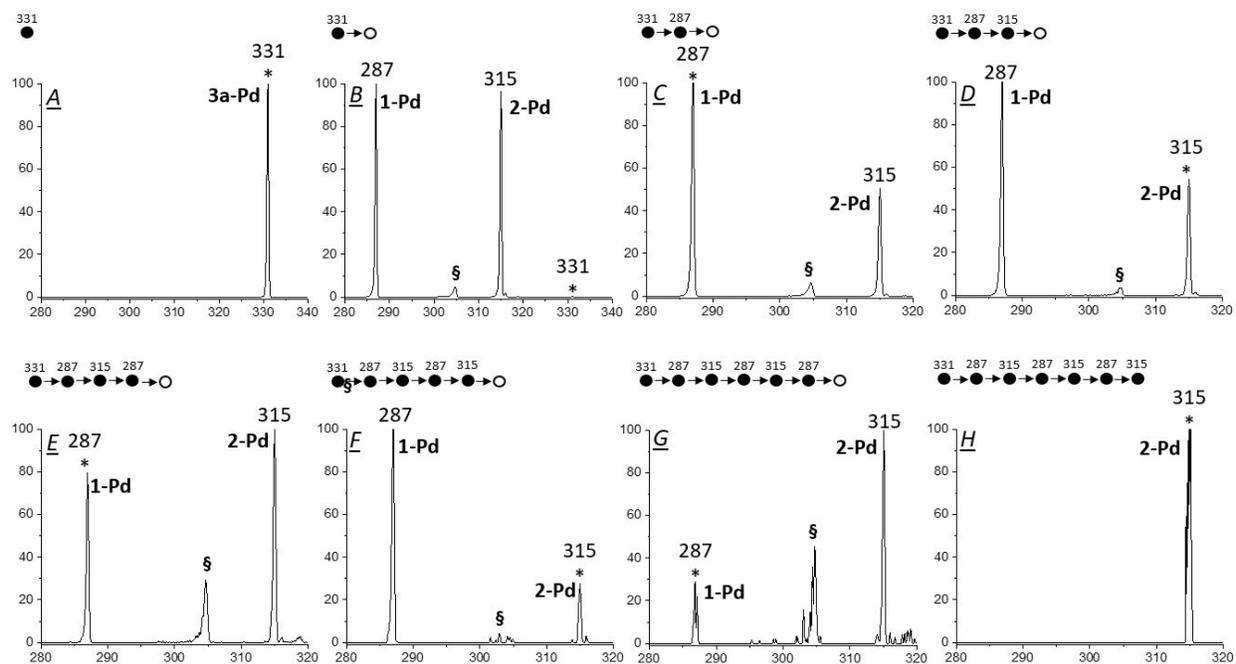


Figure S4. Traversing through the catalytic cycle using multistage mass spectrometry experiments. (A) Isolation of **3a-Pd** (B) CID of **3a-Pd** (C) IMR of **1-Pd** with ethane (D) CID of **2-Pd** (E) IMR of **1-Pd** with ethane (F) CID of **2-Pd** (G) IMR of **1-Pd** with ethane (H) Isolation of **2-Pd**. The symbol “§” designates the water adduct of **1-Pd** at m/z 305.

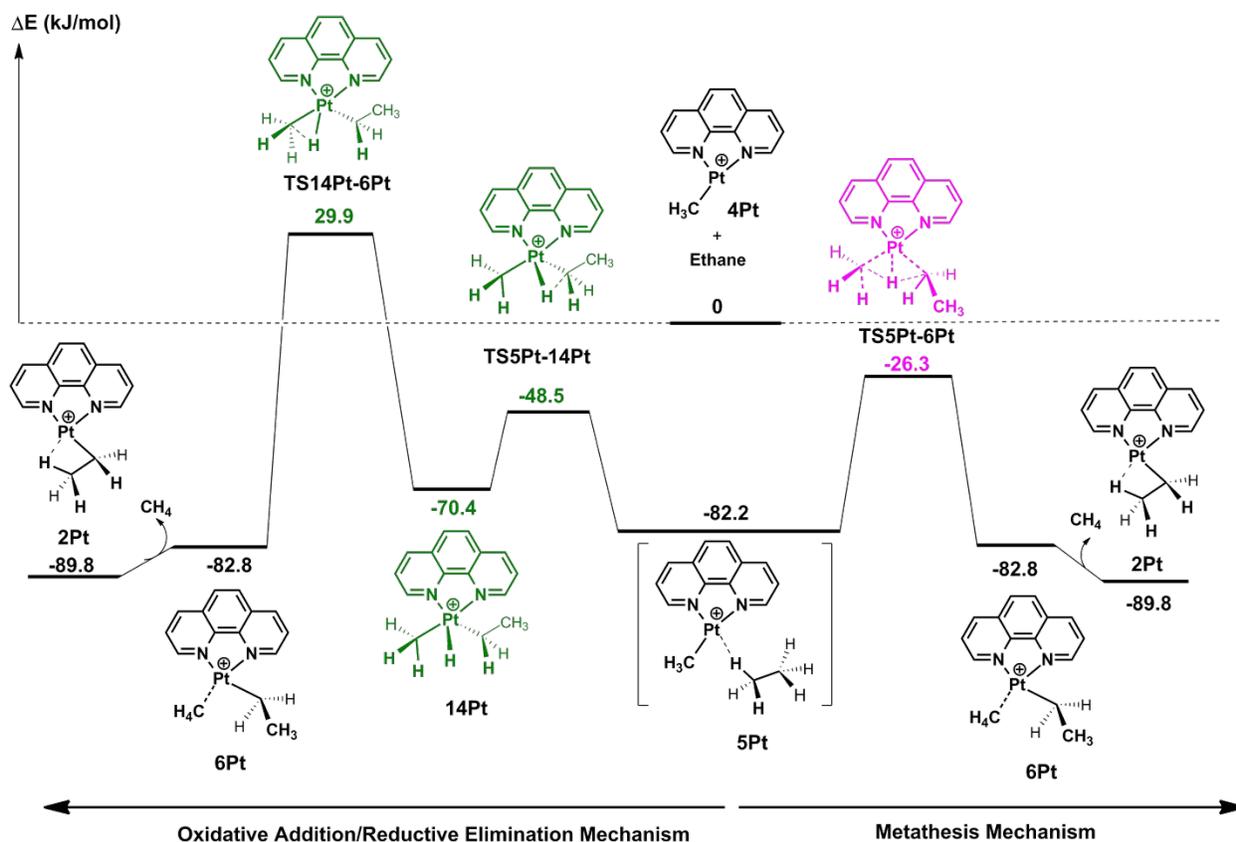


Figure S5. DFT calculated potential energy profiles allowing comparison of the σ -complex-assisted metathesis and oxidative addition/reductive elimination mechanisms for $[(\text{phen})\text{Pt}(\text{CH}_3)]^+$ reacting with ethane. The relative energies are given in kJ/mol and are the B3LYP-D3BJ/BS2 single point energies corrected for the M06/BS1 zero-point vibrational energies.

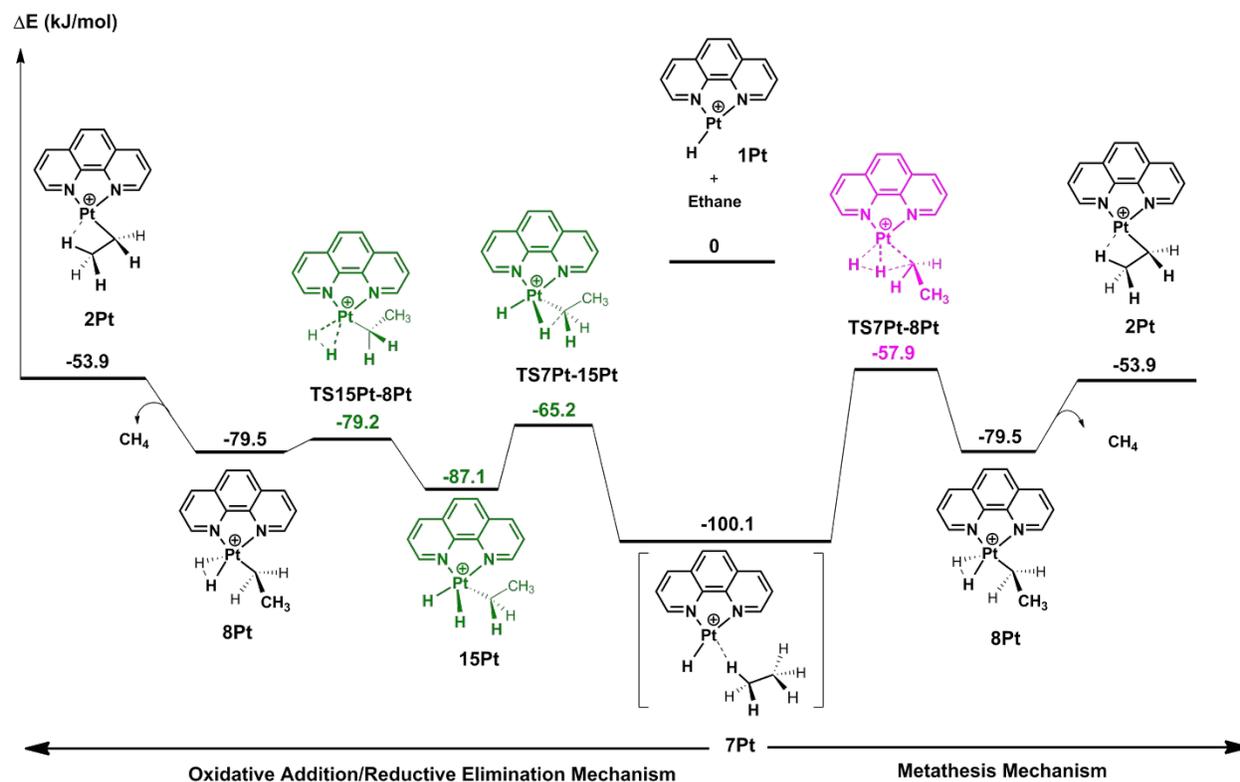


Figure S6. DFT calculated potential energy profiles allowing comparison of the σ -complex-assisted metathesis and oxidative addition/reductive elimination mechanisms for $[(\text{phen})\text{Pt}(\text{H})]^+$ reacting with ethane. The relative energies are given in kJ/mol and are the B3LYP-D3BJ/BS2 single point energies corrected for the M06/BS1 zero-point vibrational energies.

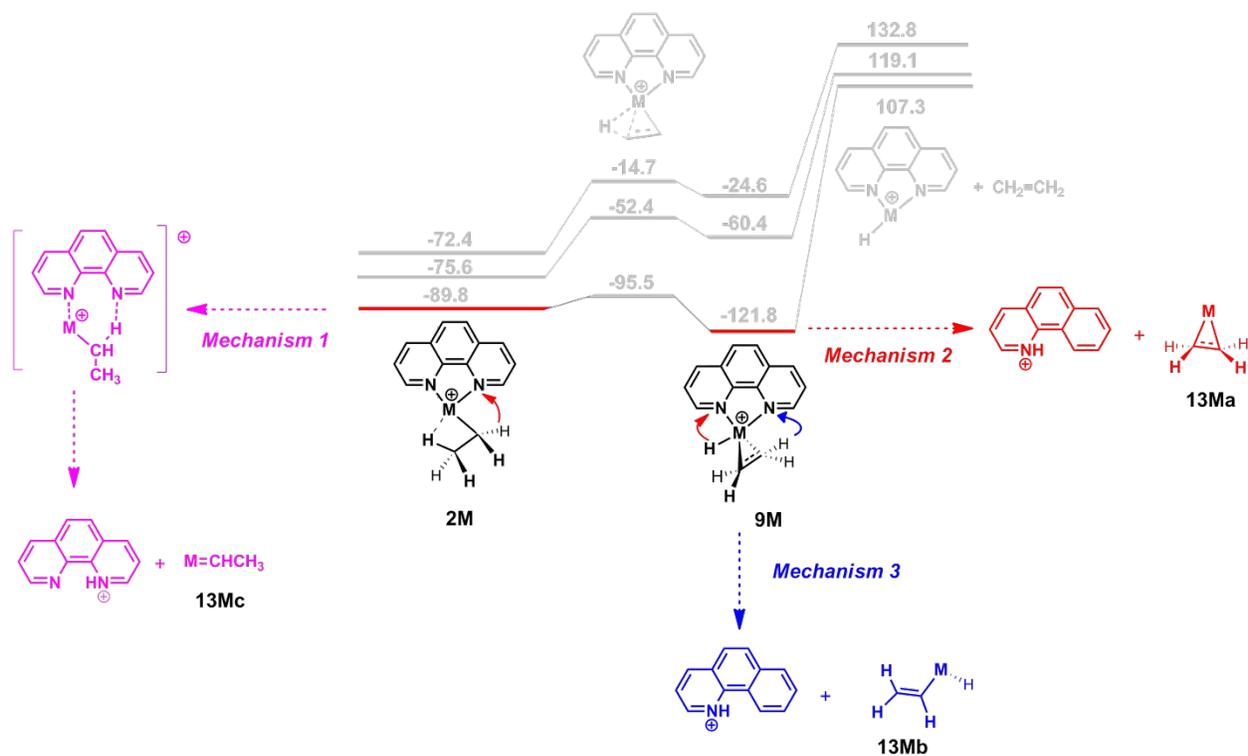
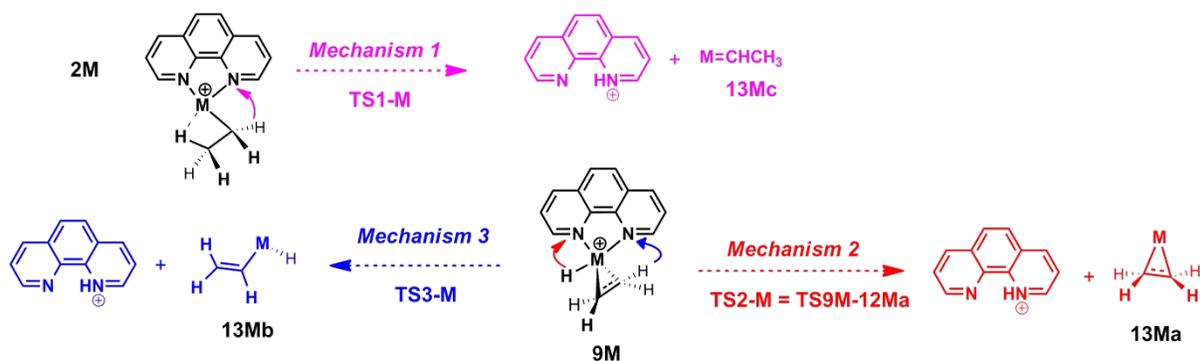


Figure S7. DFT calculated potential energy profiles allowing comparison of the various pathways for protonated ligand loss that gave rise to isomers of $[M,C_2,H_4]$, **13-M**. The relative energies are given in kJ/mol and are the B3LYP-D3BJ/BS2 single point energies corrected for the M06/BS1 zero-point vibrational energies.



	E (kJ/mol) wrt. IMR reactants B3LYP-D3BJ/def2-TZVP//M06/SDD 6-311(G)d								
	2M	TS1-M	13Mc + PhenH ⁺	9M	TS2-M	13Ma + PhenH ⁺	9M	TS3-M	13Mb + PhenH ⁺
Pd	-75.6	303.2	272.9	-60.4	38.5	114.5	-60.4	240.5	226.8
Ni	-72.4	307.3	343.1	-24.6	89.9	219.9	-24.6	243.7	304.1
Pt	-89.8	267.8	221.9	-121.8	3.5	150.2	-121.9	189.4	184.9

Mechanism 1
 Mechanism 2: Plausible Pathway (Figure 7)
 Mechanism 3

Table S1. DFT calculated potential energy profiles allowing comparison of the various pathways for protonated ligand loss that gave rise to isomers of $[M, C_2, H_4]$, **13-M**. The relative energies are given in kJ/mol and are the B3LYP-D3BJ/BS2 single point energies corrected for the M06/BS1 zero-point vibrational energies.