CYCLOMETALLATION ON PLATINUM(II) COMPLEXES; THE ROLE OF THE SOLVENT AND ADDED BASE DONOR CAPABILITY ON THE REACTION MECHANISMS

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TABLE S1.– Selected bond lengths (Å) and angles (deg.) for compound **2** with estimated standard deviations.

TABLE S2.– Values of the observed rate constants for the cyclometallation reaction of compound **1**, according to Scheme 2, as a function of solvent, temperature, pressure and base added. Stated values correspond to the average of 3–4 runs at different concentrations where no differences are found.

FIGURE S1.– Molecular structure of compound **2**.

FIGURE S2.– Values of the observed rate constants corresponding to the first reaction step determined when proton sponge or neat solvent were used.

FIGURE S3.– 1D-NOESY spectra on irradiating imine signal of complex **1** for a) Z-isomer; b) E-isomer

Table S1.-

Pt-N(1)	1.936(14)	C(1)-C(6)	1.37(2)
Pt-C(1)	2.008(14)	C(1)-C(2)	1.41(2)
Pt-N(2)	2.176(11)	C(2)-C(3)	1.41(2)
Pt-Cl	2.295(5)	C(3)-C(4)	1.39(2)
N(1)-C(7)	1.333(18)	C(4)-C(5)	1.42(3)
N(1)-C(8)	1.449(16)	C(5)-C(6)	1.444(18)
N(2)-C(11)	1.422(15)	C(6)-C(7)	1.45(2)
N(2)-C(9)	1.494(19)	C(8)-C(9)	1.54(2)
N(2)-C(10)	1.533(18)		
N(1)-Pt-C(1)	82.2(6)	N(1)-Pt-Cl	177.0(3)
N(1)-Pt-N(2)	82.0(5)	C(1)-Pt-Cl	97.9(5)
C(1)-Pt-N(2)	164.2(6)	N(2)-Pt-Cl	97.8(3)

Table S2.‒

Solvent	Base added	Temperature /°C	Pressure /atm	$^{fast}k_{obs}$ /s^{-1}	$^{slow}k_{obs}$ /s^{-1}
Methanol	NaCH$_3$CO$_2$	25	1	1.5×10^{-5}	–
		35	1	3.6×10^{-5}	
		40	1	6.1×10^{-5}	
		44	1	–	1.2×10^{-5}
		49	1	9.5×10^{-5}	2.1×10^{-5}
		55	1	1.8×10^{-4}	3.3×0^{-5}
		57	1	2.0×10^{-4}	4.3×10^{-5}
		59	1	–	4.0×10^{-5}
			400	3.1×10^{-4}	7.6×10^{-5}
			800	3.8×10^{-4}	9.5×10^{-5}
			1200	5.0×10^{-4}	9.6×10^{-5}
			1600	5.5×10^{-4}	1.2×10^{-4}
			1800	–	1.3×10^{-4}
	NEt$_3$	25	1	3.2×10^{-6}	–
		30	1	4.5×10^{-6}	–
		35	1	1.2×10^{-5}	–
		44	1	4.5×10^{-5}	–
		49	1	5.5×10^{-5}	–
		50	1	–	3.0×10^{-6}
		55	1	1.5×10^{-4}	–
		57	1	–	5.8×10^{-6}
		59	1	2.5×10^{-4}	–
		65	1	–	9.1×10^{-6}
			400	–	1.0×10^{-5}
			800	–	9.9×10^{-6}
			1200	–	1.2×10^{-5}
			1600	–	1.2×10^{-5}
	Proton sponge	44	1	2.8×10^{-5}	–
		55	1	1.8×10^{-4}	–
	None	57	1	4.5×10^{-4}	
Ethanol	NaCH$_3$CO$_2$	51	1	1.6×10^{-4}	1.0×10^{-5}
		57	1	2.2×10^{-4}	–

	61	1	2.6×10^{-4}	2.3×10^{-5}
	68	1	4.1×10^{-4}	4.3×10^{-5}
	69	1	–	4.2×10^{-5}
		400	5.7×10^{-4}	6.3×10^{-5}
		800	6.3×10^{-4}	6.7×10^{-5}
		1200	7.0×10^{-4}	9.5×10^{-5}
		1600	9.3×10^{-4}	9.8×10^{-5}
	73	1	6.5×10^{-4}	8.4×10^{-5}
NEt$_3$	51	1	1.1×10^{-4}	
	55	1	–	9.0×10^{-6}
	61	1	3.0×10^{-4}	–
	63	400	4.6×10^{-4}	–
		800	3.4×10^{-4}	–
		1200	2.5×10^{-4}	–
		1600	2.0×10^{-4}	–
	65	1	–	2.7×10^{-5}
	68	1	8.9×10^{-4}	–
	71	1	–	5.0×10^{-5}
		400	4.5×10^{-5}	–
		800	3.6×10^{-5}	–
		1200	2.9×10^{-5}	–
		1600	2.6×10^{-5}	–
	73	1	1.7×10^{-3}	–
	75	1	–	6.9×10^{-5}
None	57	1	3.1×10^{-4}	–

FIGURE S1
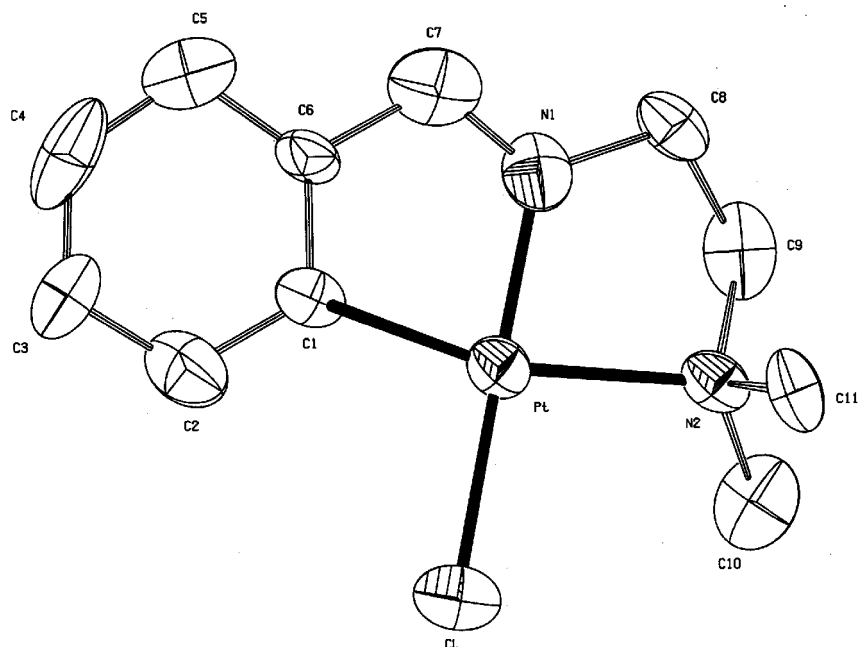
A fused [5,5,6] tricyclic system results from terdentate [C,N,N'] coordination of the ligand, containing a five membered metallacycle and a chelate ring with two nitrogen atoms. A chloro ligand completes the coordination around the platinum center. The metallacycle is approximately planar, the largest deviation from the mean plane defined by the five atoms is 0.0394 for N(1), and is nearly coplanar with the coordination plane, the dihedral angle between the mean planes being 4.21 °. Bond lengths and angles are well within the range of values obtained for analogous cyclometallated compounds. The Pt-NMe$_2$ bond distance increases (2.176(11) Å) and the Pt-NCH decreases (1.936(14) Å) upon cyclometallation due to replacement of a chloro ligand for a phenyl group. The sum of bond angles at platinum is nearly 360 ° as expected for a square planar coordination although higher distorsions from the ideal value of 90 ° are observed for **2** than for **1**. The smallest angles (82.0(5) ° and 82.2(6) °) correspond to the terdentate ligand.
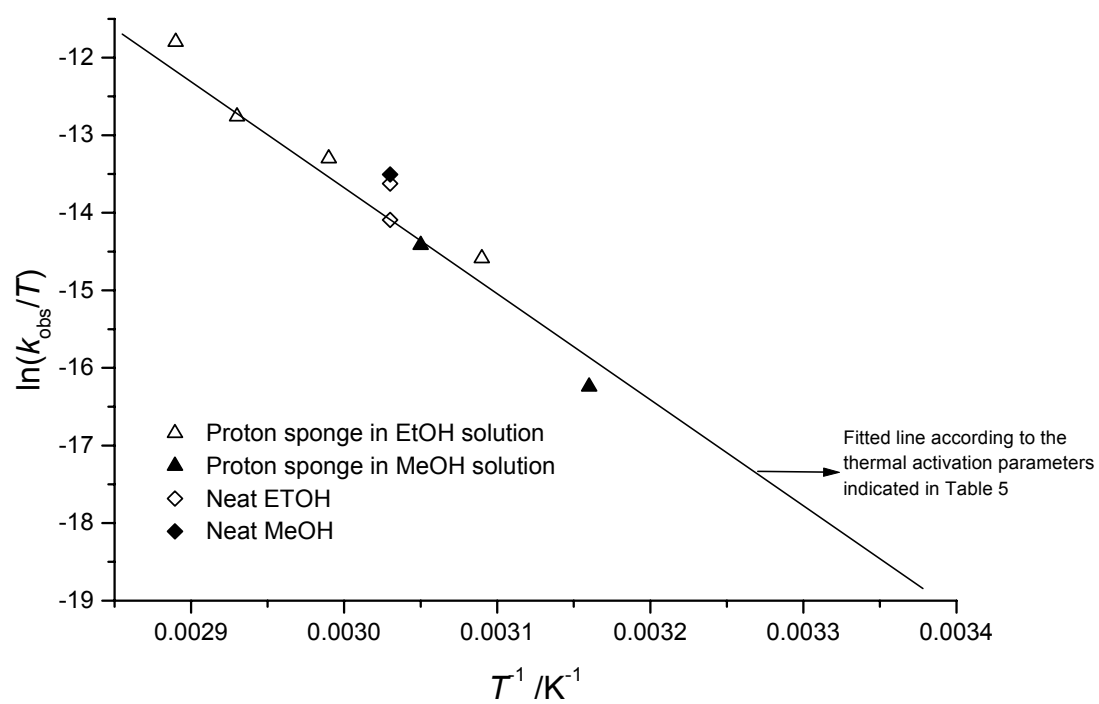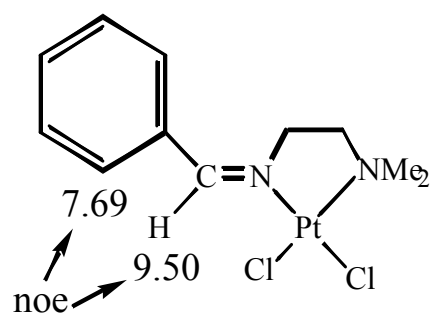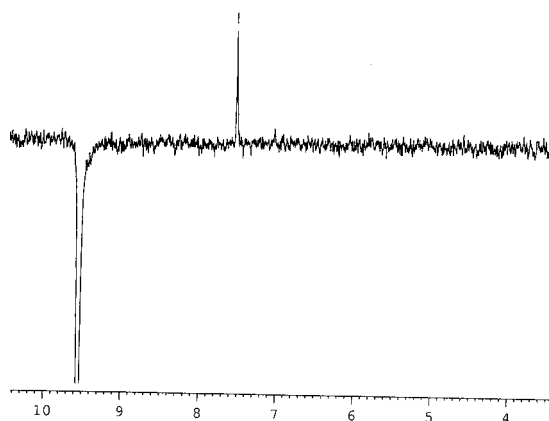
FIGURE S2

FIGURE S3

a)

b)