

CYCLOMETALLATION OF AMINO-IMINES ON PALLADIUM COMPLEXES. THE EFFECT OF THE SOLVENT ON THE EXPERIMENTAL AND CALCULATED MECHANISM.

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Supplementary material

Figure S1.– UV–Vis spectral changes of the $Z \rightleftharpoons E$ isomerization reaction of complex $Z\text{-}2\text{AcO}$, in methanol solution at 25 °C and $[\text{Pd}] \approx 5 \times 10^{-5} \text{ M}$.

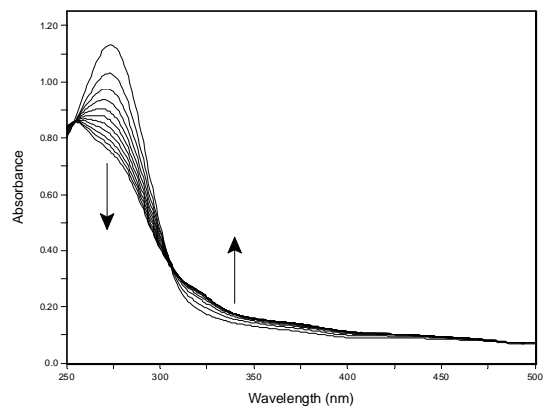
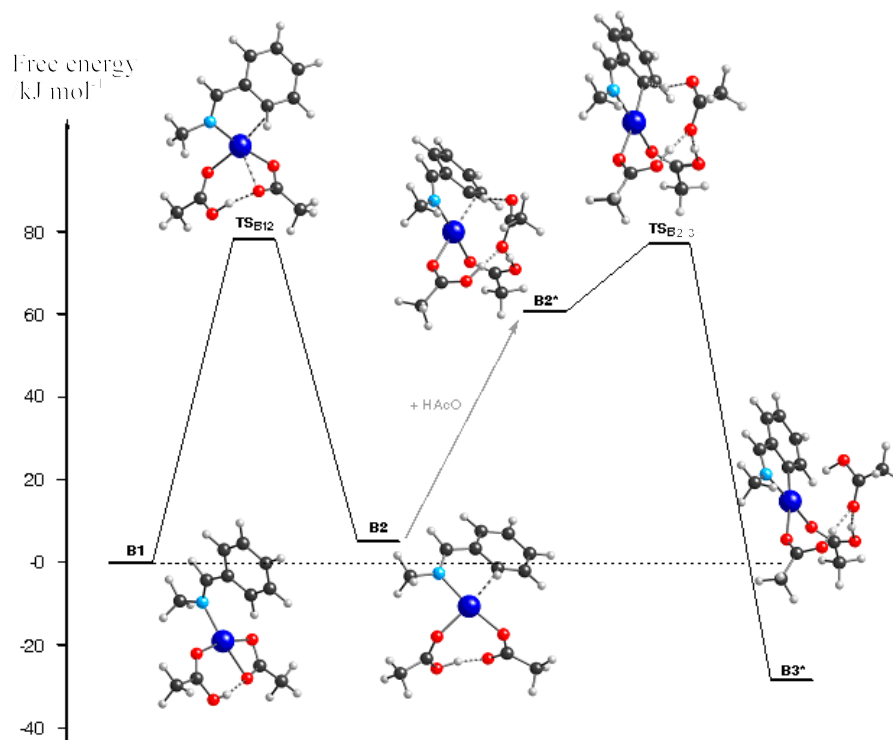
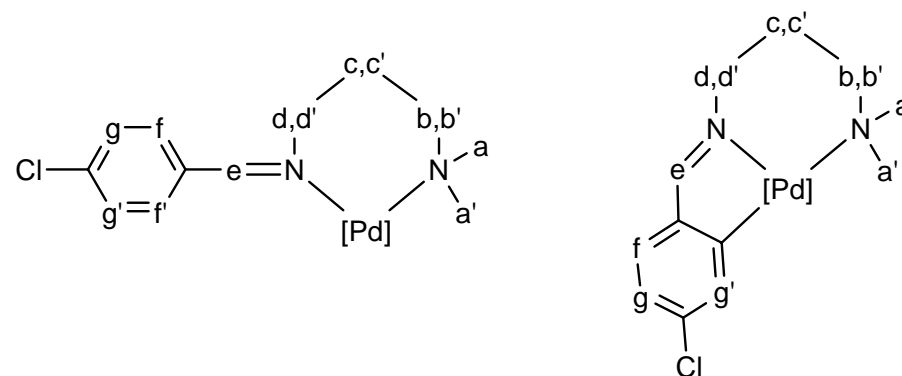


Figure S2.– Energy profile (data from Table 2) for the proposed mechanism from $[\text{Pd}(\eta^2\text{-AcO})(\text{HAcO})(\kappa^1\text{-N}_{\text{imino}})]^+$ (**B1**) having an external acetic molecule assisting the transition state in methanol.



The individual values of the relative energies for this assisted mechanism have been estimated by comparison with those having an acetic acid molecule obtained from a half dimer, $\text{H}_2(\text{AcO})_2$, and are probably overstabilized by two intermolecular hydrogen bonds.

Table S1.– Numbering scheme and ^1H NMR (CD_3OD solution, 400 MHz, 298 K) data (δ (J) /ppm(Hz), reference TMS) for all the complexes studied; n.e. stands for non-existent nucleus in the compound.



Compound	a; a'	b; b'	c; c'	d; d'	e	f; f'	g; g'
<i>E</i> -1AcO	2.64	2.52 (m)	n.e.	4.04 (m)	8.22 (b)	8.21 (d, 8.4)	7.42 (d,8.4)
<i>Z</i> -1AcO	2.59	2.61 (m)	n.e.	3.89 (td, 6.0, 2.0)	7.81 (b)	7.54 (d, 8.8)	7.49 (d, 8.8)
<i>E</i> -1Cl	2.61; 2.49	1.94 (m); 2.38 (m)	n.e.	3.3 (m); 4.55 (m)	8.22 (b)	9.15 (d, 8.4)	7.58 (d, 8.4)
<i>E</i> -2AcO	2.22; 2.41	3.50–3.56–4.70 (m)			8.07 (b)	9.42 (d, 8.4)	7.62 (d, 8.4)
<i>E</i> -2Cl	2.53; 2.71	3.82 (m)	2.05 (m)	4.65 (m)	8.32	9.21 (d, 8.8)	7.67 (d, 8.8)
<i>CM</i> -1AcO	2.54	2.85 (t, 6.1)	n.e.	3.82 (td, 6.1, 2.6)	8.00 (t, 8.0)	7.15 (d, 8.2); n.e.	6.94 (dd, 8.2, 2.2); 6.75 (d, 2.2)
<i>CM</i> -1Cl	2.52	2.55 (t, 5.2)	n.e.	3.62 (td, 5.4, 1.6)	8.13 (b)	7.15 (d 8.0);n.e.	6.93(dd, 8.0, 2.0); 7.64 (d, 2.0)
<i>CM</i> -2AcO	2.4	2.55 (m)	2.03 (b)	3.55 (m)	8.05	7.17 (d, 8.0); n.e.	6.94 (dd, 8.0, 2.0); 6.74 (d, 2.0)
<i>CM</i> -2Cl	2.62	2.64 (m)	1.94 (m)	3.71 (m)	8.22 (t, 1.8)	7.25 (d, 8.0); n.e.	7.02 (dd, 8.0, 2.0); 7.74 (d, 2.0)

m = multiplet; d = doublet; t = triplet; dd = doublet of doublets; b = broad

Table S2. – Calculated relative energies (in kJ/mol) for the stationary points in the cyclopalladation process in gas phase, toluene, methanol and water solutions (**A1 = B1** and **A3 = B4**).

	Gas phase	Toluene	Methanol	Water
<i>6-membered transition state mechanism</i>				
A1	0.0	0.0	0.0	0.0
TS_{A1-2}	45.0	43.1	40.1	38.6
A2	31.2	20.5	8.6	6.7
TS_{A2-3}	57.4	50.4	46.2	46.6
A3	-31.9	-36.9	-39.2	-39.1
<i>4-membered transition state mechanism</i>				
B1 = A1	0.0	0.0	0.0	0.0
TS_{B1-2}	67.8	58.1	72.3	72.0
B2	32.2	20.2	9.7	8.3
B2*	43.4	39.3	35.1	8.3
TS_{B2-3}	160.2	154.3	146.2	145.7
TS_{B2-3}*	49.0	47.6	49.5	50.6
B3	14.4	4.3	-4.2	-5.8
B3*	-44.8	40.2	-31.7	-15.2
B4 = A3	-31.9	-36.9	-39.2	-39.1
<i>Acid-assisted mechanism</i>				
C1	0.0	0.0	0.0	0.0
TS_{C1-2}	38.1	38.0	31.0	26.7
C2	20.4	19.0	14.0	15.0
TS_{C2-3}	41.2	41.2	40.7	43.5
C3	-155.4	-74.5	-18.9	-6.7

Table S3.– Absolute energies, and free energies for calculated stationary points. Data are in atomic units (Hartrees) (**A1 = B1** and **A3 = B4**).

	$E_{\text{ELECTRONIC}}$	ΔG°
<i>6-membered cycle</i>		
A1	-949.7575134	-949.544722
TS_{A12}	-949.7403813	-949.522199
A2	-949.7456401	-949.530644
TS_{A23}	-949.7356411	-949.522476
A3	-949.7696494	-949.553018
<i>4-membered cycle (including assisted pathway)</i>		
B1	-949.7575134	-949.516309
TS_{B12}	-949.7316896	-949.532067
B2	-949.7452629	-949.485946
TS_{B23}	-949.6964862	-949.536522
B3	-949.7520097	-949.529584
B4	-949.7696494	-949.553018
B1+HAcO	-1178.6920952	-1178.434926
B2*	-1178.6755488	-1178.408799
TS_{B23}*	-1178.6734296	-1178.405647
B3*	-1178.7091604	-1178.440987
<i>Acid-catalyzed mechanism</i>		
C1	-1178.9442668	-1178.663295
TS_{C12}	-1178.9297607	-1178.654821
C2	-1178.9364890	-1178.661302
TS_{C23}	-1178.9285663	-1178.653466
C3	-1179.0034479	-1178.736704
Only Complex	-949.7695653	-949.551170
<i>Acetic derivatives</i>		
H₂(AcO)₂	-457.8691636	-457.780408
AcO⁻	-228.3323232	-228.310590
H₂AcO⁺	-229.2338826	-229.185534

Table S4. – Values of k_{obs} for the systems studied in methanol solution, as a function of the starting coordination compound, temperature and pressure; $[\text{Pd}] = (5-10) \times 10^{-4}$ M. All the values are the average of 2 to 4 runs.

Palladium complex	T /°C	P /atm	$10^4 \times k_{\text{obs}} / \text{s}^{-1}$
<i>E</i> - 1AcO fast step	20	1	2
	25	1	3.8
	31.7	1	8
	35	1	13
	40.7	1	24
	45	1	35
	48.6	1	48
<i>E</i> - 1AcO slow step	20	1	0.08
	25	1	0.017
	31.7	1	0.5
	35	1	0.9
	40.7	1	1.8
	45	1	4.1
	46.5	300	5.2
		600	5.5
		900	6.5
		1200	6.8
	1500	7.3	
	48.6	1	7.8
<i>Z</i> - 1AcO fast step	54.4	1	16
	23	300	3.5
		600	5
		900	4.5
		1200	4
		1500	3.3
	25	1	1.6
	26.9	1	2
	39.4	1	8
	48	1	16
54	1	38	
<i>Z</i> - 1AcO slow step	25	1	0.19
	26.9	1	0.26

	39.4	1	1.8
	43	300	3.2
	43	600	3.4
	43	900	3.6
	43	1500	4.3
	48	1	6.9
	54	1	13
<i>E-1Cl</i>	13	600	2.4
		900	2.9
		1200	3
		1500	3.8
	13.1	1	2.1
	19	300	5.2
		600	5.3
		900	7
		1200	7
		1500	8
	21.5	1	6.8
	25	1	13
	29.6	1	19
	40	1	48
	44.6	1	61
<i>E-2AcO</i>	14.4	1	0.39
	22.2	1	1.3
	29.3	1	3.6
	30	300	4.1
		600	4.4
		900	5.2
		1200	5.3
		1500	6.1
	34.5	1	11
	39.4	1	29
	45	1	62
<i>E-2Cl</i>	17	300	5.1
		600	5.6
		900	6.5
		1200	7.4

	1500	7.6
18.1	1	4.6
25	1	11
31.8	1	18
37.4	1	37
44.9	1	60

^{fast step} Corresponds to the establishment of the $Z \rightleftharpoons E$ equilibrium

^{slow step} Correspond to formation of the **1AcO**-*CM*