SUPPORTING INFORMATION

New Light on an Old Debate: Does the RCN-$PtCl_2$ Bond include any Back-Donation? RCN←$PtCl_2$ Backbonding vs the IR $\nu_{C\equiv N}$ Blue-shift Dichotomy in organonitriles-platinum(II) complexes. A Thorough Density Functional Theory – Energy Decomposition Analysis study.§

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§ We wish to dedicate this work to the memory of Prof. Rino A. Michelin and his enduring human and scientific legacy.

List of abbreviations

ACN	acetonitrile
PhCN	benzonitrile
CF_3CN	trifluoroacetonitrile
p-TOL	p-tolunitrile; (4-methylbenzonitrile)
p-TFM	(trifluoromethyl)benzonitrile
cis-1	cis-$PtCl_2(ACN)_2$
trans-1	trans-$PtCl_2(ACN)_2$
cis-2	cis-$PtCl_2(CF_3CN)_2$
trans-2	trans-$PtCl_2(CF_3CN)_2$
cis-3	cis-$PtCl_2(PhCN)_2$
trans-3	trans-$PtCl_2(PhCN)_2$
cis-4	cis-$PtCl_2(TOL)_2$
trans-4	trans-$PtCl_2(TOL)_2$
cis-5	cis-$PtCl_2(TFM)_2$
trans-5	trans-$PtCl_2(TFM)_2$

Table S1 Overlap ⟨L|Pt⟩[a] (L=ACN,CF_3CN,PhCN,p-TFM,p-TOL; Pt= cis/trans $PtCl_2$) and relevant orbitals population of the (cis/trans)-$PtCl_2L$ complexes investigated. Virtual orbitals are indicated with an asterisk. Ligand orbitals number in the overlap integrals are given on the left.

FMO overlap, *S*					**STEP1**					
	cis-1	**trans-1**	**cis-2**	**trans-2**	**cis-3**	**trans-3**	**cis-4**	**trans-4**	**cis-5**	**trans-5**
A'	0.02 ⟨6a'|34*a'⟩σ	0.04 ⟨6a'|37a'⟩σ	0.03 ⟨14a'|34a'⟩σ	0.06 ⟨14a'|37a'⟩σ	0.02 ⟨15a'|34a'⟩σ	0.06 ⟨15a'|37a'⟩σ	0.02 ⟨18a'|34a'⟩σ	0.05 ⟨18a'|37a'⟩σ	0.02 ⟨25a'|34a'⟩σ	0.04 ⟨25a'|37a'⟩σ
	0.03 ⟨6a'|35*a'⟩σ	0.06 ⟨6a'|38*a'⟩σ	0.05 ⟨14a'|35*a'⟩σ	0.10 ⟨14a'|38*a'⟩σ	0.05 ⟨15a'|35a'⟩σ	0.10 ⟨15a'|38*a'⟩σ	0.04 ⟨18a'|35a'⟩σ	0.09 ⟨18a'|38*a'⟩σ	0.04 ⟨25a'|35a'⟩σ	0.08 ⟨25a'|38a'⟩σ
	0.04 ⟨6a'|40*a'⟩σ		0.06 ⟨14a'|40*a'⟩σ		0.06 ⟨15a'|40*a'⟩σ		0.06 ⟨18a'|40*a'⟩σ		0.05 ⟨25a'|40*a'⟩σ	
	0.07 ⟨6a'|41*a'⟩σ		0.12 ⟨14a'|41*a'⟩σ		0.12 ⟨15a'|41*a'⟩σ		0.12 ⟨18a'|41*a'⟩σ		0.09 ⟨25a'|41*a'⟩σ	
	0.08 ⟨8a'|34*a'⟩σ		0.08 ⟨15a'|34a'⟩σ		0.08 ⟨17a'|34a'⟩σ		0.07 ⟨19a'|34a'⟩σ		0.08 ⟨27a'|34a'⟩σ	
	0.15 ⟨8a'|35*a'⟩σ		0.15 ⟨15a'|35*a'⟩σ		0.15 ⟨17a'|35a'⟩σ		0.15 ⟨19a'|35a'⟩σ		0.15 ⟨27a'|35a'⟩σ	
	0.21 ⟨8a'|40*a'⟩σ	0.18 ⟨8a'|37a'⟩σ	0.20 ⟨15a'|40*a'⟩σ	0.18 ⟨15a'|37a'⟩σ	0.20 ⟨17a'|40*a'⟩σ	0.17 ⟨17a'|37a'⟩σ	0.20 ⟨19a'|40*a'⟩σ	0.17 ⟨19a'|37a'⟩σ	0.20 ⟨27a'|40*a'⟩σ	0.18 ⟨27a'|37a'⟩σ
	0.39 ⟨8a'|41*a'⟩σ	0.32 ⟨8a'|38*a'⟩σ	0.37 ⟨15a'|41*a'⟩σ	0.31 ⟨15a'|38*a'⟩σ	0.38 ⟨17a'|41*a'⟩σ	0.31 ⟨17a'|38*a'⟩σ	0.37 ⟨19a'|41*a'⟩σ	0.31 ⟨19a'|38*a'⟩σ	0.38 ⟨27a'|41*a'⟩σ	0.31 ⟨27a'|38*a'⟩σ
	0.03 ⟨10*a'|38a'⟩π	0.12 ⟨10*a'|35a'⟩π	0.08 ⟨17*a'|38a'⟩π	0.12 ⟨17*a'|35a'⟩π	0.04 ⟨19*a'|38a'⟩π	0.12 ⟨19*a'|35a'⟩π	0.04 ⟨22*a'|38a'⟩π	0.07 ⟨22*a'|35a'⟩π	0.04 ⟨29*a'|38a'⟩π	0.07 ⟨29*a'|35a'⟩π
		0.02 ⟨10*a'|40a'⟩π								
A''	0.01 ⟨3*a''|16a''⟩π	0.12 ⟨3*a''|15a''⟩π	0.09 ⟨8*a''|16a''⟩π	0.12 ⟨8*a''|15a''⟩π	0.09 ⟨11*a''|16a''⟩π	0.12 ⟨11*a''|15a''⟩π	0.09 ⟨12*a''|16a''⟩π	0.12 ⟨12*a''|15a''⟩π	0.09 ⟨17*a''|16a''⟩π	0.12 ⟨17*a''|15a''⟩π
	0.06 ⟨3*a''|17a''⟩π		0.06 ⟨8*a''|17a''⟩π		0.06 ⟨11*a''|17a''⟩π		0.07 ⟨12*a''|17a''⟩π		0.06 ⟨17*a''|17a''⟩π	
					STEP2					
A'	0.01 ⟨6a'|39*a'⟩σ	0.09 ⟨6a'|39*a'⟩σ	0.02 ⟨14a'|45a'⟩σ	0.03 ⟨14a'|45a'⟩σ	0.01 ⟨15a'|45a'⟩σ	0.03 ⟨15a'|45a'⟩σ	0.02 ⟨18a'|47a'⟩σ	0.03 ⟨18a'|47*a'⟩σ	0.01 ⟨25a'|53a'⟩σ	0.01 ⟨25a'|50a'⟩σ
	0.01 ⟨6a'|40*a'⟩σ	0.06 ⟨6a'|40*a'⟩σ	0.05 ⟨14a'|50a'⟩σ	0.01 ⟨14a'|50a'⟩σ	0.05 ⟨15a'|50a'⟩σ	0.01 ⟨15a'|50a'⟩σ	0.04 ⟨18a'|52a'⟩σ	0.01 ⟨18a'|52a'⟩σ	0.04 ⟨25a'|60a'⟩σ	0.02 ⟨25a'|53a'⟩σ
	0.03 ⟨6a'|43*a'⟩σ	0.17 ⟨6a'|46*a'⟩σ	0.02 ⟨14a'|52a'⟩σ	0.05 ⟨14a'|53a'⟩σ	0.02 ⟨15a'|53a'⟩σ	0.05 ⟨15a'|55a'⟩σ	0.02 ⟨18a'|56a'⟩σ	0.05 ⟨18a'|58a'⟩σ	0.01 ⟨25a'|63a'⟩σ	0.04 ⟨25a'|65a'⟩σ
	0.07 ⟨6a'|49*a'⟩σ	0.38 ⟨6a'|49*a'⟩σ	0.11 ⟨14a'|56*a'⟩σ	0.12 ⟨14a'|56*a'⟩σ	0.11 ⟨15a'|58*a'⟩σ	0.12 ⟨15a'|58*a'⟩σ	0.11 ⟨18a'|61*a'⟩σ	0.11 ⟨18a'|61*a'⟩σ	0.08 ⟨25a'|68*a'⟩σ	0.09 ⟨25a'|68*a'⟩σ
	0.04 ⟨8a'|39*a'⟩σ	0.09 ⟨8a'|39*a'⟩σ	0.05 ⟨15a'|45a'⟩σ	0.10 ⟨15a'|45a'⟩σ	0.05 ⟨17a'|45a'⟩σ	0.08 ⟨17a'|45a'⟩σ	0.05 ⟨19a'|47a'⟩σ	0.09 ⟨19a'|47*a'⟩σ	0.05 ⟨27a'|53a'⟩σ	0.06 ⟨27a'|50a'⟩σ
	0.03 ⟨8a'|40*a'⟩σ	0.06 ⟨8a'|40*a'⟩σ	0.17 ⟨15a'|50a'⟩σ	0.04 ⟨15a'|50a'⟩σ	0.15 ⟨17a'|50a'⟩σ	0.05 ⟨17a'|50a'⟩σ	0.13 ⟨19a'|52a'⟩σ	0.05 ⟨19a'|52a'⟩σ	0.16 ⟨27a'|60a'⟩σ	0.08 ⟨27a'|53a'⟩σ
	0.17 ⟨8a'|43*a'⟩σ	0.17 ⟨8a'|46*a'⟩σ	0.08 ⟨15a'|52a'⟩σ	0.17 ⟨15a'|53a'⟩σ	0.05 ⟨17a'|53a'⟩σ	0.17 ⟨17a'|55a'⟩σ	0.07 ⟨19a'|56a'⟩σ	0.017 ⟨19a'|58a'⟩σ	0.04 ⟨25a'|63a'⟩σ	0.17 ⟨27a'|65a'⟩σ
	0.35 ⟨8a'|49*a'⟩σ	0.38 ⟨8a'|49*a'⟩σ	0.34 ⟨15a'|56*a'⟩σ	0.36 ⟨15a'|56*a'⟩σ	0.34 ⟨17a'|58*a'⟩σ	0.36 ⟨17a'|58*a'⟩σ	0.34 ⟨19a'|61*a'⟩σ	0.36 ⟨19a'|61*a'⟩σ	0.34 ⟨27a'|68*a'⟩σ	0.36 ⟨27a'|68*a'⟩σ
	0.10 ⟨10*a'|45a'⟩π	0.12 ⟨10*a'|44a'⟩π	0.12 ⟨17*a'|52a'⟩π	0.12 ⟨17*a'|51a'⟩π	0.02 ⟨19*a'|57a'⟩π	0.06 ⟨19*a'|52a'⟩π	0.02 ⟨22*a'|60a'⟩π	0.06 ⟨22*a'|55a'⟩π	0.02 ⟨29*a'|67a'⟩π	0.05 ⟨29*a'|62a'⟩π
	0.01 ⟨11*a'|45a'⟩π		0.07 ⟨17*a'|55a'⟩π		0.03 ⟨21*a'|57a'⟩π		0.05 ⟨25*a'|60a'⟩π		0.03 ⟨31*a'|67a'⟩π	0.05 ⟨29*a'|63a'⟩π
	0.02 ⟨10*a'|48a'⟩π									
	0.07 ⟨11a'|48*a'⟩π									

A''	0.1 ⟨3*a''|18a''⟩π	0.12 ⟨3*a''|17a''⟩π	0.09 ⟨8*a''|23a''⟩π	0.11 ⟨8*a''|22a''⟩π	0.10 ⟨11*a''|25a''⟩π	0.10 ⟨11*a''|4a''⟩π	0.10 ⟨12*a''|26a''⟩π	0.13 ⟨12*a''|25a''⟩π	0.10 ⟨17*a''|31a''⟩π	0.12 ⟨17*a''|30a''⟩π
	0.02 ⟨3*a''|19a''⟩π		0.04 ⟨8*a''|24a''⟩π		0.02 ⟨11*a''|26a''⟩π		0.02 ⟨12*a''|27a''⟩π		0.02 ⟨17*a''|32a''⟩π	
FMO population, P[e]										
A'					**STEP1**					
L	6a' (2.01) 8a' (1.66) 10*a' (0.07)	8a' (2.00) 8a' (1.52) 10*a' (0.08)	14a' (1.98) 15a' (1.70) 17*a' (0.12)	14a' (1.98) 15a' (1.55) 17*a' (0.11)	15a' (1.98) 17a' (1.68) 19*a' (0.07)	17a' (1.97) 17a' (1.54) 19*a' (0.06)	18a' (1.98) 19a' (1.68) 22*a' (0.06)	18a' (1.98) 19a' (1.54) 22*a' (0.05)	25a' (1.99) 27a' (1.68) 29*a' (0.07)	25a' (1.98) 27a' (1.54) 29*a' (0.06)
Pt	34a' (1.98) 35a' (1.96) 38a' (1.90) 40*a' (0.25) 41*a' (0.16)	35a' (1.95) 37a' (1.63) 38*a' (0.87)	34a' (1.98) 35a' (1.96) 38a' (1.88) 40*a' (0.24) 41*a' (0.15)	35a' (1.93) 37a' (1.64) 38*a' (0.85)	34a' (1.98) 35a' (1.96) 38a' (1.88) 38a' (1.89) 40*a' (0.26) 41*a' (0.16)	35a' (1.94) 37a' (1.62) 38*a' (0.88)	34a' (1.98) 35a' (1.96) 38a' (1.90) 40*a' (0.26) 41*a' (0.16)	35a' (1.95) 37a' (1.62) 38*a' (0.88)	34a' (1.98) 35a' (1.96) 38a' (1.89) 40*a' (0.25) 41*a' (0.16)	35a' (1.94) 37a' (1.63) 38*a' (0.84)
A''										
L	3*a''(0.11)	3*a''(0.10)	8*a''(0.16)	8*a''(0.14)	11*a''(0.12)	11a''(0.11)	12*a''(0.12)	12*a''(0.11)	17*a''(0.12)	17*a''(0.11)
Pt	16a''(1.94) 17a''(1.96)	15a'' (1.90)	16a''(1.91) 17a''(1.94)	15a'' (1.86)	16a''(1.94) 17a''(1.95)	15a'' (1.89)	16a'' (1.99) 17a'' (1.91)	15a'' (1.89)	16a'' (1.94) 17a'' (1.95)	15a'' (1.89)
A'					**STEP2**					
L	6a' (2.01) 8a' (1.69) 10*a' (0.06) 11*a' (0.02)	6a' (2.01) 8a' (1.69) 10*a' (0.08)	14a' (1.98) 15a' (1.71) 17*a' (0.10)	14a' (1.99) 15a' (1.70) 17*a' (0.10)	15a' (1.98) 17a' (1.69) 19*a' (0.06) 21*a' (0.03)	15a' (1.99) 17a' (1.70) 19*a' (0.05)	18a' (1.99) 19a' (1.68) 22*a' (0.06) 25*a' (0.02)	18a' (1.99) 19a' (1.70) 22*a' (0.05)	25a' (1.99) 27a' (1.69) 29*a' (0.06) 31*a' (0.03)	25a' (1.99) 27a' (1.71) 29*a' (0.05)
Pt	39a' (2.00) 40a' (2.00) 43a' (1.95) 45a' (1.96) 48a' (1.92) 49*a' (0.41)	39a' (1.97) 40a' (1.99) 44a' (1.95) 46a' (1.89) 49*a' (0.40)	45a' (2.00) 50a' (1.95) 52a' (1.95) 55a' (1.91) 56*a' (0.39)	45a' (1.98) 50a' (2.00) 51a' (1.93) 53a' (1.88) 56*a' (0.41)	45a' (2.00) 50a' (1.95) 53a' (1.97) 57a' (1.91) 58*a' (0.41)	45a' (1.98) 50a' (2.00) 52a' (1.96) 55a' (1.89) 58*a' (0.40)	47a' (2.00) 52a' (1.96) 56a' (1.97) 60a' (1.92) 61*a' (0.41)	47a' (1.96) 52a' (2.00) 55a' (1.96) 58a' (1.89) 61*a' (0.40	53a' (1.91) 60a' (1.95) 63a' (1.97) 67a' (1.91) 68*a' (0.40)	50a' (1.97) 53a' (1.97) 60a' (2.00) 62a' (1.97) 63a' (1.97) 65a' (1.89) 68*a' (0.39)
A''										
L	3*a''(0.11)	3*a''(0.09)	8*a''(0.15)	8*a''(0.12)	11*a''(0.12)	11*a''(0.10)	12*a''(0.12)	12*a''(0.10)	17*a''(0.12)	17*a''(0.10)
Pt	18a'' (1.91) 19a'' (1.99)	17a'' (1.90)	23a'' (1.90) 24a'' (1.96)	22a'' (1.88)	25a'' (1.91) 26a'' (1.99)	24a'' (1.90)	26a'' (1.91) 27a'' (1.99)	25a'' (1.90)	31a'' (1.91) 32a'' (1.99)	30a'' (1.90)

[a] ⟨L|Pt⟩: L=orbital number of the ligand (STEP1 and STEP2); Pt=orbital number of the $PtCl_2$ fragment (STEP1) or mono-coordinated $LPtCl_2$ fragment (STEP2). L=ACN;CF_3CN,PhCN;TOL;TFM.

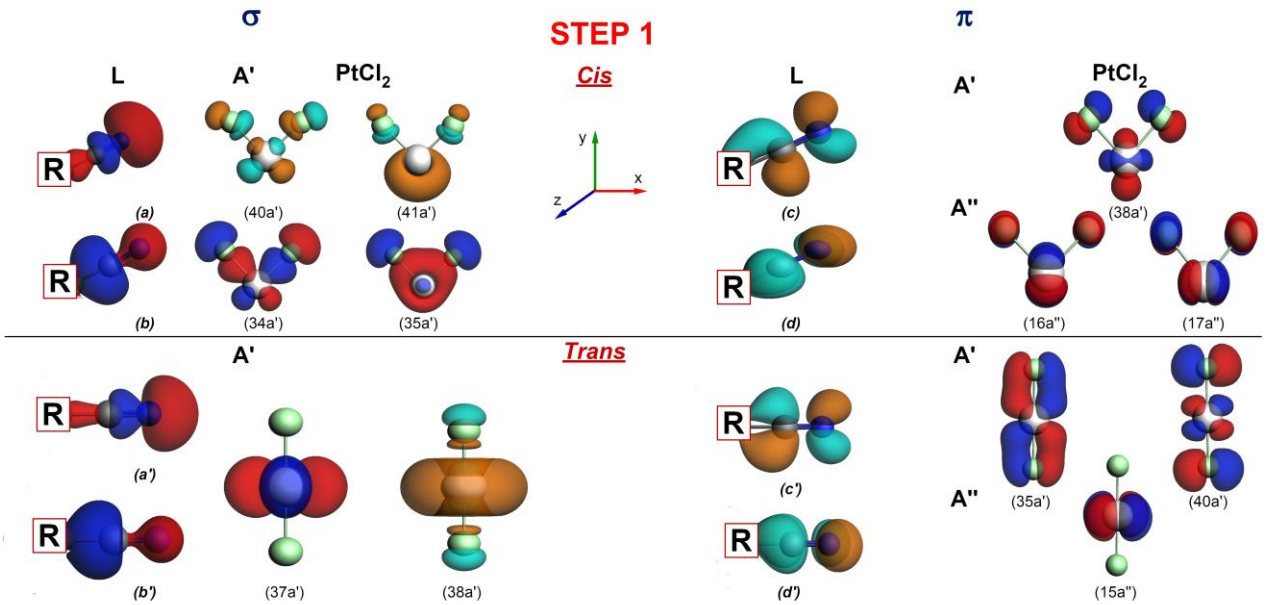

Figure S1. General shape of the RC≡N and $PtCl_2$ σ and π orbitals involved in STEP1 in the symmetry irreducible representations obtained for the Cs symmetry. R= CH_3, CF_3, Ph, CH_3Ph, CF_3Ph.
The letters in parentheses correspond to the orbitals numbering of Table S4 for each ligand. Isosurface value: 0.5 e1/2/Å 3/2.
LIGANDS (R=) *(a)*: CH_3 (8a′); CF_3 (15a′); Ph (17a′); CH_3Ph (19a′); CF_3Ph (27a′). *(b)*: CH_3 (6a′); CF_3 (14a′); Ph (15a′); CH_3Ph (18a′); CF_3Ph (25a′). *(c)*: CH_3 (10*a′); CF_3 (17*a′); Ph (19*a′); CH_3Ph (22*a′); CF_3Ph (29*a′). *(d)*: CH_3 (3*a″); CF_3 (8*a″); Ph (11*a″); CH_3Ph (12*a″); CF_3Ph (17*a″). *(a′)*: CH_3 (8a′); CF_3 (15a′); Ph (17a′); CH_3Ph (19a′); CF_3Ph (27a′).
***(b′)*: CH_3 (6a′); CF_3 (14a′); Ph (15a′); CH_3Ph (18a′); CF_3Ph (25a′). *(c′)*: CH_3 (10*a′); CF_3 (15*a′); Ph (19*a′); CH_3Ph (22*a′); CF_3Ph (29*a′). *(d′)*: CH_3 (3*a″); CF_3 (8*a″); Ph (11*a″); CH_3Ph (12*a″); CF_3Ph (17*a″).**

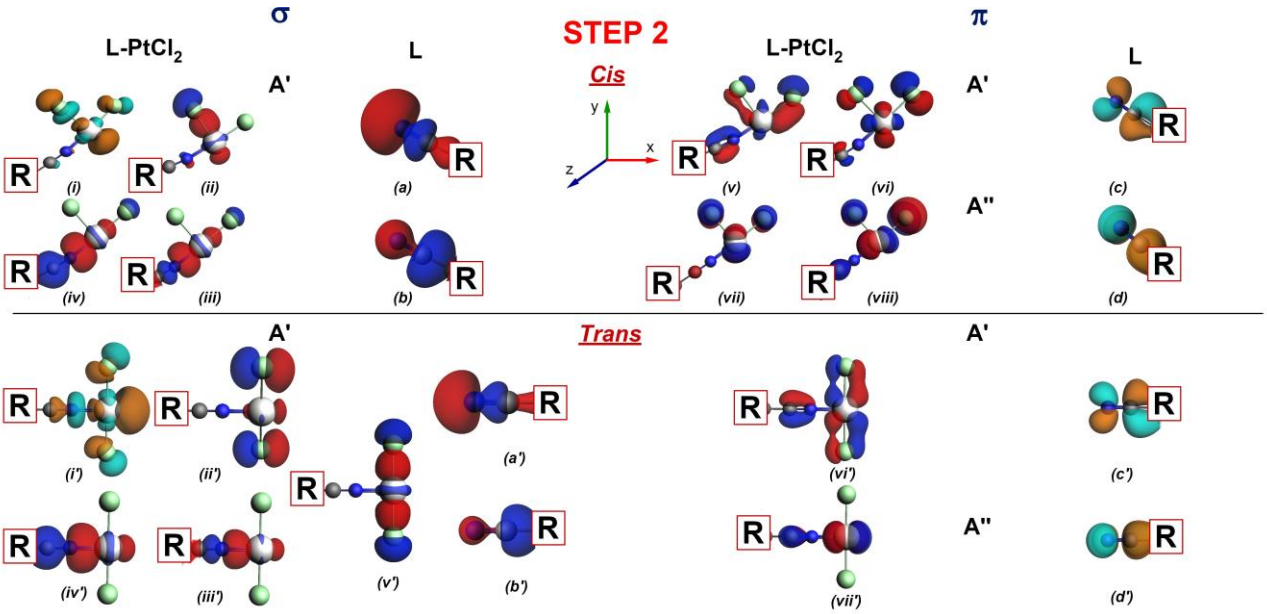

Figure S2. General shape of the RC≡N and $PtCl_2$ σ and π orbitals involved in STEP2 in the symmetry irreducible representations obtained for the Cs symmetry. R= CH_3, CF_3, Ph, CH_3Ph, CF_3Ph.
The letters in parentheses correspond to the orbitals numbering of Table S4 for each ligand. Isosurface value: 0.5 e1/2/Å 3/2.
LIGANDS (R=) *(a)*: CH_3 (8a′); CF_3 (15a′); Ph (17a′); CH_3Ph (19a′); CF_3Ph (27a′). *(b)*: CH_3 (6a′); CF_3 (14a′); Ph (15a′); CH_3Ph (18a′); CF_3Ph (25a′). *(c)*: CH_3 (10*a′); CF_3 (17*a′); Ph (19*a′); CH_3Ph (22*a′); CF_3Ph (29*a′). *(d)*: CH_3 (3*a″); CF_3 (8*a″); Ph (11*a″); CH_3Ph (12*a″); CF_3Ph (17*a″). *(a′)*: CH_3 (8a′); CF_3 (15a′); Ph (17a′); CH_3Ph (19a′); CF_3Ph (27a′).
***(b′)*: CH_3 (6a′); CF_3 (14a′); Ph (15a′); CH_3Ph (18a′); CF_3Ph (25a′). *(c′)*: CH_3 (10*a′); CF_3 (15*a′); Ph (19*a′); CH_3Ph (22*a′); CF_3Ph (29*a′). *(d′)*: CH_3 (3*a″); CF_3 (8*a″); Ph (11*a″); CH_3Ph (12*a″); CF_3Ph (17*a″).**
LPtCl2 (L=) *(i)*: ACN (49*a′); CF_3CN (56*a′); PhCN (58*a′); p-TOL (61*a′); p-TFM (68*a′). *(ii)*: ACN (43a′); CF_3CN (50a′); PhCN (58a′); p-TOL (52a′); p-TFM (60a′). *(iii)*: ACN (40a′); CF_3CN (45a′); PhCN (45a′); p-TOL (47a′); p-TFM (53a′). *(iv)*: ACN (39a′); CF_3CN (n.u.); PhCN (n.u.); p-TOL (n.u.); p-TFM (n.u). *(v)*: ACN (45a′); CF_3CN (52a′); PhCN (53a′); p-TOL (56a′); p-TFM (63a′). *(vi)*: ACN (48a′); CF_3CN (55a′); PhCN (57a′); p-TOL (60a′); p-TFM (67a′). *(vii)*: ACN (18a″); CF_3CN (23a″); PhCN (25a″); p-TOL (26a″); p-TFM (31a″). *(viii)*: ACN (19a″); CF_3CN (24a″); PhCN (26a″); p-TOL (27a″); p-TFM (32a″). *(i′)*: ACN (49*a′); CF_3CN (56*a′); PhCN (58*a′); p-TOL (61*a′); p-TFM (68*a′). *(ii′)*: ACN (46a′); CF_3CN (53a′); PhCN (55a′); p-TOL (58a′); p-TFM (65a′). *(iii′)*: ACN (40a′); CF_3CN (45a′); PhCN (45a′); p-TOL (47a′); p-TFM (53a′). *(iv′)*: ACN (39a′); CF_3CN (n.u.); PhCN (n.u.); p-TOL (n.u.); p-TFM (60a′). *(v′)*: ACN (n.u); CF_3CN (50a′); PhCN (50a′); p-TOL (52a′); p-TFM (60a′). *(vi′)*: ACN (44a′); CF_3CN (51a′); PhCN (52a′); p-TOL (55a′); p-TFM (62a′). *(vii′)*: ACN (17a″); CF_3CN (22a″); PhCN (24a″); p-TOL (25a″); p-TFM (30a″).**

NOTES:
****(n.u.) not used.**
For *cis* complexes, the set of orbitals labeled (v)-*(vi)* represent also the main contributions to the σ/π mixed interaction in the A′ irreducible representation. These interactions were not reported in Figure 6 of the manuscript. For the benzonitrile derivatives, orbitals labelled *(iv)* were not involved in the bonding interaction.
For *trans-benzonitrile derivatives* complexes, the set of orbitals labeled *(v′) were used, instead of the (iv′) as in the analogous acetonitrile derivative.*

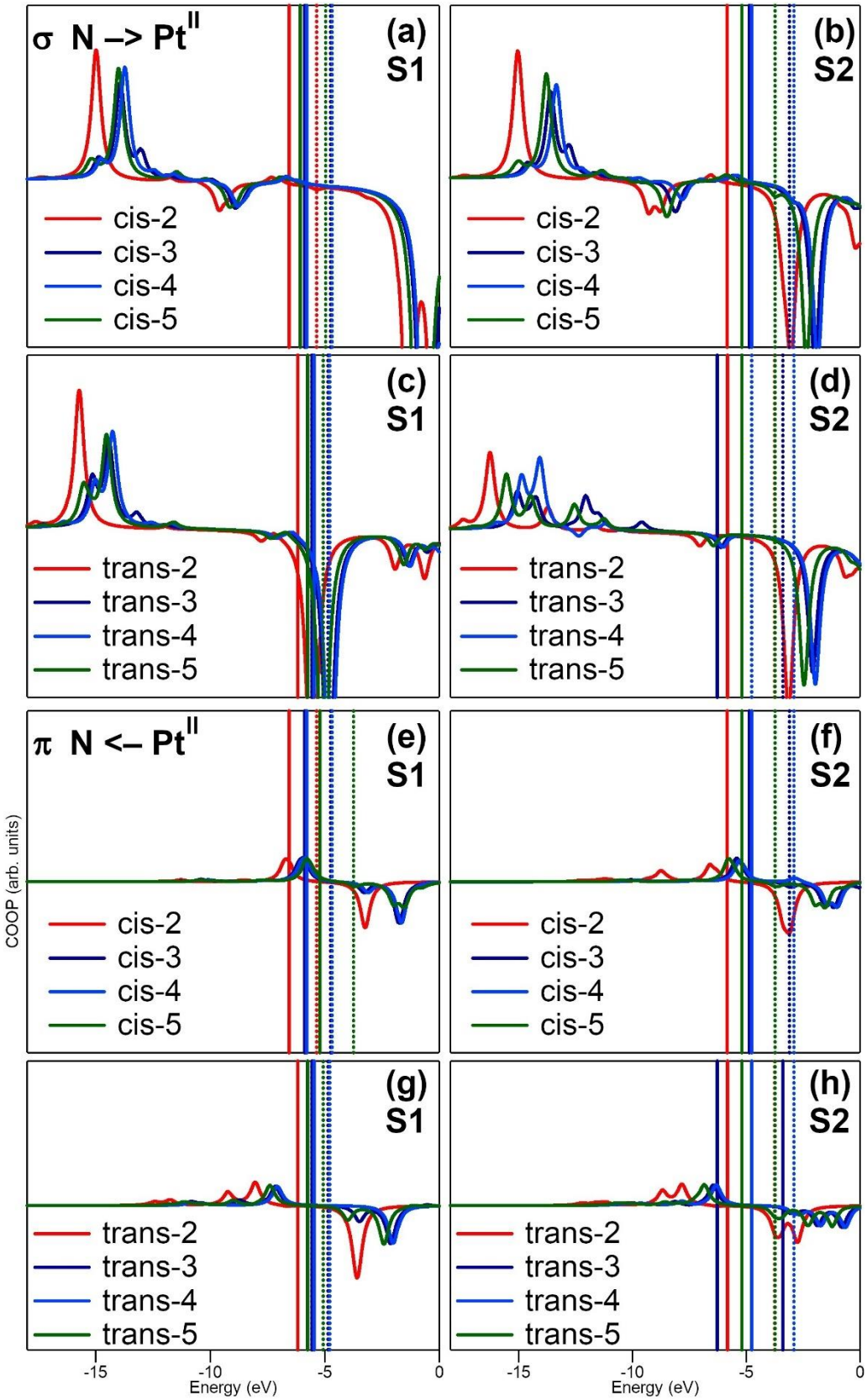

Figure S3. Plot of the COOP for cis-/trans-(2,3,4,5) complexes. Panels (a),(b): N→Pt σ donation in cis-(2,3,4,5) complexes in S1 and S2; Panels (c),(d): N→Pt σ donation in trans-(2,3,4,5) complexes in S1 and S2; Panels (e),(f): N←Pt π back-donation in cis-(2,3,4,5) complexes in S1 and S2; Panels (g),(h): N←Pt π back-donation in trans-(2,3,4,5) complexes in S1 and S2.

Table S2 Voronoi ΔQ and ΔQ^{Γ} contributions, for Pt-L bond formation in cis-/trans-2 complexes. For ΔQ^{Γ}, Pauli ($\Delta Q^{\Gamma}_{Pauli}$) and orbitals ($\Delta Q^{\Gamma}_{Orb}$) contributions are given in parentheses, respectively.[a,b]

	Cis-2						Trans-2		
	S1			S2			S2		
	ΔQ	ΔQ^{Γ} ($\Delta Q^{\Gamma}_{Pauli}$; ΔQ^{Γ}_{Orb})		ΔQ	ΔQ^{Γ} ($\Delta Q^{\Gamma}_{Pauli}$; ΔQ^{Γ}_{Orb})		ΔQ	ΔQ^{Γ}	
	TOT	A'	A''	TOT	A'	A''	TOT	A'	A''
Pt	0.155	0.046 (0.049;-0.003)	0.109 (-0.008;0.127)	0.145	0.055 (0.050;0.005)	0.090 (-0.008;0.078)	0.101	0.036 (0.060;-0.024)	0.065 (-0.005;0.070)
Cl	-0.023^{C} -0.096^{T}	-0.028 (-0.031;0.003) -0.131 (-0.045;-0.086)	0.005 (0.000;0.005) 0.035 (-0.001;0.036)	-0.119^{T} -0.049^{C}	-0.162 (-0.043;-0.076 -0.061 (-0.042;-0.007)	0.043 (-0.001;0.044) 0.012 (-0.001;0.013)	-0.045	-0.052 (0.031;-0.83)	0.007 (-0.001;0.008)
N	-0.082	0.045 (0.044;0.001)	-0.127 (0.018;-0.145)	0.019 -0.056	0.015 (0.003;0.012) 0.070 (0.052;0.018)	0.004 (0.000;0.004) -0.126 (0.017;-0.143)	-0.021^{S1} -0.072^{S2}	-0.046 (0.017;-0.063) 0.053 (0.039;0.014)	0.025 (-0.001;0.026) -0.125 (0.016;-0.141)
C_N	0.030	0.046 (-0.015;0.061)	-0.016 (-0.008;-0.008)	0.005 0.035	0.005 (-0.001;0.006) 0.052 (-0.016; 0.068)	0.000 (0.000;0.000) -0.017 (0.017;-0.034)	-0.006^{S1} 0.063^{S2}	-0.012 (-0.002;-0.010) 0.051 (-0.016;0.067)	0.006 (-0.001;0.007) 0.012 (-0.007;-0.019)
$C(F_3)$	0.002	0.010 (-0.001;0.011)	-0.008 (0.000;-0.008)	0.000 0.002	0.000 (0.000;0.000) 0.011 (-0.001;0.012)	0.000 (0.000;0.000) -0.009 (0.000;-0.009)	-0.001^{S1} 0.005^{S2}	-0.003 (0.000;-0.003) 0.011 (-0.001;0.010)	0.002 (0.000;0.002) -0.006 (0.000;-0.006)

[a] The C,T superscripts are referred to the cis/trans position of the incoming ligand, respectively.
[b] S1, S2 superscripts are referred to the atoms bonded in S1 and S2, respectively.

Table S3 Voronoi ΔQ and ΔQ^{Γ} contributions, for Pt-L bond formation in cis-/trans-3 complexes. For ΔQ^{Γ}, Pauli ($\Delta Q^{\Gamma}_{Pauli}$) and orbitals ($\Delta Q^{\Gamma}_{Orb}$) contributions are given in parentheses, respectively.[a,b]

	Cis-3						Trans-3		
	S1			S2			S2		
	ΔQ	ΔQ^{Γ} ($\Delta Q^{\Gamma}_{Pauli}$; ΔQ^{Γ}_{Orb})		ΔQ	ΔQ^{Γ} ($\Delta Q^{\Gamma}_{Pauli}$; ΔQ^{Γ}_{Orb})		ΔQ	ΔQ^{Γ}	
	TOT	A'	A''	TOT	A'	A''	TOT	A'	A''
Pt	0.136	0.052 (0.051;0.001)	0.084 (-0.008;0.092)	0.142	0.061 (0.053;0.008)	0.081 (-0.008;0.089)	0.107	0.040 (0.062;-0.022)	0.067 (-0.006;0.073)
Cl	-0.045^{C} -0.127^{T}	-0.047 (-0.031;-0.016) -0.154 (-0.045;-0.109)	-0.002 (0.000;-0.002) 0.027 (-0.001;0.028)	-0.137^{T} -0.058^{C}	-0.170 (-0.043;-0.127) -0.068 (-0.041;-0.027)	0.033 (-0.001;0.034) 0.010 (-0.001;0.011)	-0.051	-0.055 (-0.028;-0.027)	0.004 (0.000;-0.004)
N	-0.055	0.061 (0.041;0.020)	-0.116 (0.018;-0.134)	0.022^{S1} -0.026^{S2}	0.014 (0.003;0.048) 0.085 (0.048;0.035)	0.084 (0.000;0.084) -0.111 (0.018;-0.129)	-0.027^{S1} -0.047^{S2}	-0.053 (-0.018;-0.045) 0.066 (0.034;0.032)	0.026 (-0.001;0.027) -0.113 (0.017;-0.130)
C_N	0.048	0.051 (-0.015;0.066)	-0.003 (-0.007;0.004)	-0.004^{S1} 0.045^{S2}	0.000 (-0.001;0.001) 0.052 (-0.016;0.068)	-0.004 (0.000;-0.004) -0.007 (-0.007;0.000)	-0.016^{S1} 0.065^{S2}	-0.014 (-0.002;-0.012) 0.053 (-0.017;0.070)	-0.002 (-0.001;-0.001) 0.012 (-0.001;0.013)
$C(F_3)$	0.000	0.018 (-0.001;0.019)	-0.018 (0.000;-0.018)	0.000^{S1} 0.001^{S2}	-0.002 (0.000;-0.002) 0.016 (-0.002;0.018)	0.002 (0.000;0.002) -0.015 (0.000;-0.015)	0.001^{S1} 0.003^{S2}	-0.007 (0.000;-0.007) 0.017 (0.001;0.016)	0.008 (0.000;0.008) -0.014 (0.000;-0.014)

[a] The C,T superscripts are referred to the cis/trans position of the incoming ligand, respectively.
[b] S1, S2 superscripts are referred to the atoms bonded in S1 and S2, respectively.

Table S4 Voronoi ΔQ and ΔQ^{Γ} contributions, for Pt-L bond formation in cis-/trans-4complexes. For ΔQ^{Γ}, Pauli ($\Delta Q^{\Gamma}{}_{Pauli}$) and orbitals ($\Delta Q^{\Gamma}{}_{Orb}$)) contributions are given in parentheses, respectively.[a,b]

	Cis-4						Trans-4		
	STEP1			STEP2			STEP2		
	ΔQ	ΔQ^{Γ}		ΔQ	ΔQ^{Γ}		ΔQ	ΔQ^{Γ}	
	TOT	A'	A''	TOT	A'	A''	TOT	A'	A''
Pt	0.133	0.057 (0.052;0.007)	0.076 (-0.009;0.085)	0.141	0.072 (0.055;0.017)	0.069 (-0.008;0.077)	0.109	0.049 (0.064;-0.015)	0.060 (-0.006;0.066)
Cl	-0.043^{C} -0.136^{T}	-0.045 (-0.030;-0.015) -0.159 (-0.045;-0.114)	0.002 (0.000;0.002) 0.023 (-0.001;0.024)	-0.143^{T} 0.054^{C}	-0.172 (-0.044;-0.128) -0.062 (-0.040;-0.022)	0.029 (-0.001;0.030) 0.008 (-0.001;0.009)	-0.050	-0.054 (-0.028;-0.026)	0.004 (0.000;0.004)
N	-0.058	0.050 (0.042;0.008)	-0.108 (0.019;-0.127)	0.023^{S1} -0.027^{S2}	0.017 (0.003;0.014) 0.076 (0.048;0.028)	0.006 (0.000;0.085) -0.103 (0.018;-0.121)	-0.027^{S1} -0.046^{S2}	-0.049 (-0.019;-0.030) 0.059 (0.033;0.026)	0.022 (-0.001;0.023) -0.105 (0.018;-0.123)
C_N	0.047	0.046 (-0.014;0.050)	0.001 (-0.008;0.009)	-0.004^{S1} 0.026^{S2}	0.000 (-0.001;0.001) 0.048 (-0.015;0.063)	-0.005 (0.000;-0.005) -0.005 (-0.008;0.003)	0.018^{S1} 0.063^{S2}	-0.014 (-0.003;-0.011) 0.048 (-0.017;0.065)	-0.004 (-0.001;-0.003) 0.015 (-0.007;0.022)
C_{ipso}	-0.001	0.003 (-0.001;0.004)	-0.004 (0.000;-0.004)	0.001^{S1} 0.000^{S2}	0.001 (-0.001;0.002) 0.004 (-0.002;0.006)	0.000 (0.000;0.000) -0.004 (0.000;-0.004)	0.003^{S1} 0.002^{S2}	0.001 (0.000;0.001) 0.005 (0.000;0.005)	-0.002 (0.000;-0.002) -0.003 (0.000;-0.003)

[a] The C,T superscripts are referred to the cis/trans position of the incoming ligand, respectively.
[b] S1, S2 superscripts are referred to the atoms bonded in S1 and S2, respectively.

Table S5 Voronoi ΔQ and ΔQ^{Γ} contributions, for Pt-L bond formation in cis-/trans-5 complexes. For ΔQ^{Γ}, Pauli ($\Delta Q^{\Gamma}{}_{Pauli}$) and orbitals ($\Delta Q^{\Gamma}{}_{Orb}$)) contributions are given in parentheses, respectively.[a,b]

	Cis-5						Trans-5		
	STEP1			STEP2			STEP2		
	ΔQ	ΔQ^{Γ}		ΔQ	ΔQ^{Γ}		ΔQ	ΔQ^{Γ}	
	TOT	A'	A''	TOT	A'	A''	TOT	A'	A''
Pt	0.138	0.059 (0.051;0.008)	0.079 (-0.008;0.087)	0.140	0.070 (0.053;0.017)	0.070 (-0.008;0.072)	0.104	0.046 (0.063;-0.017)	0.058 (-0.005;0.066)
Cl	-0.037^{C} -0.122^{T}	-0.040 (-0.032;-0.008) -0.147 (-0.045;-0.102)	0.003 (0.000;0.003) 0.025 (-0.001;0.026)	-0.135^{T} -0.054^{C}	-0.166 (-0.043;-0.123) -0.063 (-0.043;0.020)	0.031 (-0.001;0.032) 0.009 (-0.001;0.010)	-0.048	-0.053 (-0.029;-0.024)	0.005 (-0.001;0.006)
N	-0.066	0.044 (0.043;0.001)	-0.110 (0.019;0.129)	0.021^{S1} -0.037^{S2}	0.015 (0.003;0.012) 0.069 (0.049;0.020)	0.006 (0.000;0.006) -0.106 (0.018;-0.124)	-0.026^{S1} -0.055^{S2}	-0.048 (-0.018;-0.030) 0.054 (0.035;0.019)	0.026 (-0.001;0.025) -0.109 (0.017;-0.126)
C_N	0.043	0.045 (-0.016;0.061)	-0.002 (-0.007;0.005)	-0.002^{S1} 0.042^{S2}	0.002 (-0.001;0.003) 0.047 (-0.017;0.064)	-0.004 (0.000;0.004) -0.005 (-0.007;0.002)	-0.014^{S1} 0.064^{S2}	-0.013 (-0.002;-0.011) 0.048 (-0.017;0.065)	-0.001 (-0.001;0.000) 0.016 (-0.007;0.023)
C_{ipso}	-0.002	0.002 (-0.001;0.003)	0.004 (-0.000;0.004)	0.001^{S1} -0.001^{S2}	0.000 (-0.001;0.001) 0.002 (0.002;0.000)	0.001 (0.000;0.001) -0.003 (0.000;-0.003)	0.002^{S1} 0.001^{S2}	0.001 (0.001;0.001) 0.004 (-0.001;0.005)	0.001 (0.008;-0.001) -0.003 (0.000;-0.003)

[a] The C,T superscripts are referred to the cis/trans position of the incoming ligand, respectively.
[b] S1, S2 superscripts are referred to the atoms bonded in S1 and S2, respectively.

EDA-NOCV analysis

EDA results will be discussed by considering two main issues: i) comparison of **S1** and **S2** outcomes for all *cis* complexes, and ii) comparison of **S2** data for *cis* and *trans* complexes.

Concerning point i), **S1** results for all *cis* complexes, showed very similar trends. Pauli repulsion contributions resulted almost identical, differing only by *ca.* 2 kcal/mol. Moreover, also the electrostatic contributions differ no more than 3 kcal/mol except for the **cis-2** complex. For **cis-2**, this behavior could be due to the electron-withdrawing properties of the close fluorine atoms to the CN group, which contribute to a further depletion of electron density and the ensuing decreasing of the attractive electrostatic interaction. Finally, the orbital contributions differ no more than 3 kcal/mol, and even in this case except for **cis-2**. Nonetheless, the comparison between **S1** and **S2** indicates very similar dissociation energies ΔEs. These results are ascribable to the balancing of two contributions, i.e., ΔE_{prep} and ΔE_{Pauli}. Concerning ΔE_{prep}, the higher value in **S1** for all mono-coordinated *cis* species, is rooted almost entirely to the distortion of $^{C}PtCl_2$. In particular: it corresponds to the energy needed to shrink the ClPtCl angle from *ca.* 129° to 90°, going from the free to the mono-coordinated $^{C}PtCl_2$. The ΔE_{Pauli} in **S2**, about 10 kcal/mol higher than in **S1**; this should be ascribable to the bonding mechanisms proposed where the main bonding interactions involve more filled orbitals (see Figures 4 and 6 in the manuscript), making this contribution responsible for the less negative value of the corresponding bonding energy (BE) in **S2**. Concerning point ii) **S2** data allow to report a comparison of the energies contributions between *cis* and *trans* species. The repulsive ΔE_{Pauli} terms, are almost the same both for *cis* and *trans* series. Thus, remarkable differences, which cause the trans species being more stable with respect to the homologous cis ones, resides in the attractive terms, ΔE_{Elec}, and ΔE_{Orb} which resulted more negative for trans species. The outcomes so far discussed agree with the thermodynamic results. In particular, by considering the calculated ΔH° values as corrections to the electronic energies (which resulted very similar for all the complexes), DE values for *cis* complexes well match the trend of ΔH° values. For *trans* species, the lack of data for **S1**, allows only to observe the agreement of data in **S2** which definitively confirm the higher stability of the bond in the *trans* species with respect to the analogous *cis* ones.

ETS-NOCV results for N→Pt σ interaction and N←Pt π back-donation are given in Table S6. Data show that the total N←Pt π back-donation represent about the 30%-40% of the total ΔE_{orb} term and range from 30% to 45% with respect to the N→Pt σ interaction

Table S6 EDA-NOCV contributions for all the complexes. The coordination STEP1 for trans- complexes is not reported due to the non-Aufbau configuration used for the trans-$PtCl_2$ fragment (See Computational Methods section).

Complex	1			2			3			4			5		
	cis		trans	cis		trans	cis		trans	cis		trans	cis		trans
	S1	S2	S2	S1	S2	S2	S1	S2	S2	S1	S2	S2	S1	S2	S2
ΔE_{Pauli}	141.63	152.33	155.54	142.68	155.83	155.74	143.88	154.80	154.74	143.82	154.68	155.56	142.92	154.11	152.36
ΔE_{Elec}	-112.34	-113.91	-120.76	-104.25	-108.79	-114.08	-113.45	-114.79	-120.46	-114.06	-114.98	-121.26	-111.07	-113.38	-118.12
ΔE_{Orb}	-72.83	-73.44	-82.25	-78.53	-78.93	-84.85	-75.04	-75.37	-80.71	-74.85	-75.16	-80.68	-75.33	-75.76	-80.87
$\Delta E^{\sigma A'}_{Orb}$	-41.08	-43.14	-48.16	-38.90	-41.99	-48.23	-41.16	-43.39	-48.34	-41.38	-43.52	-48.37	-40.34	-42.87	-48.05
$\Delta E^{\pi A'}_{Orb}$	-11.34	-9.69	-10.55	-14.92	-12.19	-13.04	-12.83	-10.63	-11.38	-12.56	-10.41	-11.20	-13.63	-11.19	-11.76
$\Delta E^{\pi A''}_{Orb}$	-12.34	-11.81	-11.60	-16.42	-15.44	-14.37	-12.82	-12.25	-11.91	-12.68	-12.12	-11.81	-13.20	-12.58	-12.13
ΔE_{Disp}	-3.78	-4.55	-5.26	-3.79	-4.65	-4.74	-4.25	-5.11	-5.16	-4.25	-5.12	-5.17	-4.29	-5.14	-5.16
BE	-47.32	-39.56	-52.73	-43.89	-36.54	-47.93	-48.86	-40.47	-51.60	-49.35	-40.58	-51.54	-47.78	-40.17	-51.78
ΔE_{Strain}	9.00	3.01	5.10	8.00	2.72	6.35	8.96	3.09	5.48	9.01	3.16	5.24	8.85	3.28	5.94
ΔE (-DE)[a]	38.32	36.55	47.63	35.89	33.82	41.58	39.90	37.38	46.12	40.34	37.42	46.30	38.93	36.89	45.84

[a] $DE = BE + \Delta E_{strain}$

Table S7 EDA contributions (kcal/mol) to the RC≡NY bond (R=CH_3, Ph; Y=H^+, BF_3, BCl_3, $PtCl_2ACN$, $PtCl_2CNPh$) for free and coordinated ACN and PhCN ligands.

	ACN	**ACNH$^+$**	**ACN-BF_3**	**ACN-BCl_3**	**cis-1**	**trans-1**	**PhCN**	**PhCNH$^+$**	**cis-3**	**trans-3**
Vacuum										
ΔE_{Pauli}	1184.09	1048.02	1162.09	1181.25	1107.79	1140.79	1192.88	1016.35	1107.79	1126.06
ΔE_{Elec}	-224.89	-145.75	-221.23	-254.10	-247.30	-289.72	-240.50	-143.74	-261.78	-269.43
ΔE_{Steric}	**959.20**	**902.27**	**940.86**	**927.15**	**860.48**	**851.07**	**952.38**	**872.62**	**846.00**	**856.63**
ΔE_{Orb}	**-1349.44**	**-1422.22**	**-1337.31**	**-1297.03**	**-1210.59**	**-1207.98**	**-1323.72**	**-1382.70**	**-1176.69**	**-1196.92**
ΔE_{Disp}	**-0.88**	**-1.09**	**-1.75**	**-2.88**	**-3.07**	**-3.12**	**-1.08**	**-1.34**	**-3.80**	**-3.82**
BE	**-391.12**	**-521.04**	**-398.20**	**-372.76**	**-353.18**	**-360.03**	**-372.41**	**-511.42**	**-334.49**	**-344.11**
CH_2Cl_2										
ΔE_{Pauli}	1199.11	1055.04	-	-	1140.36	1161.00	1203.39	1054.13	1120.95	1172.00
ΔE_{Elec}	-232.94	-146.39	-	-	-266.11	-273.01	-248.69	-165.99	-268.67	-303.77
ΔE_{Steric}	**966.17**	**908.66**	**-**	**-**	**874.25**	**887.99**	**954.69**	**888.14**	**852.28**	**868.24**
ΔE_{Orb}	**-1357.16**	**-1429.20**	**-**	**-**	**-1228.07**	**-1253.05**	**-1327.04**	**-1399.16**	**-1210.53**	**-1234.84**
ΔE_{Disp}	**-0.88**	**-1.10**	**-**	**-**	**-3.07**	**-3.12**	**-1.08**	**-1.34**	**-3.80**	**-3.82**
BE	**-391.87**	**-521.64**	**-**	**-**	**-356.89**	**-368.18**	**-373.43**	**-512.36**	**-362.05**	**-370.42**

Coordinates orientation

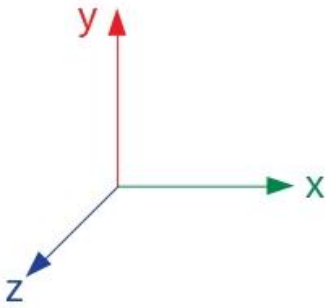

Table S8 Optimized Coordinates

Cis-1 (N Imag freqs= 0;)

1.Pt	0.000000	-0.003349	0.000000
2.Cl	-1.625446	1.600186	0.000000
3.Cl	1.625446	1.600186	0.000000
4.N	-1.445063	-1.321670	0.000000
5.C	-2.396717	-1.982479	0.000000
6.C	-3.612840	-2.770710	0.000000
7.H	-3.376858	-3.842551	0.000000
8.H	-4.208571	-2.537283	-0.892577
9.H	-4.208571	-2.537283	0.892577
10.N	1.445063	-1.321670	0.000000
11.C	2.396717	-1.982479	0.000000
12.C	3.612840	-2.770710	0.000000
13.H	3.376858	-3.842551	0.000000
14.H	4.208571	-2.537283	0.892577
15.H	4.208571	-2.537283	-0.892577

Trans-1 (N Imag freqs= 0)

1.Pt	0.000000	0.044238	0.000000
2.Cl	-0.000012	2.375167	0.000000
3.Cl	0.000012	-2.285893	0.000000
4.N	1.923059	0.045006	0.000000
5.C	3.078313	0.045738	0.000000
6.C	4.526936	0.048928	0.000000
7.H	4.897806	1.082105	0.000000
8.H	4.903116	-0.466905	0.893154
9.H	4.903116	-0.466905	-0.893154
10.N	-1.923059	0.044997	0.000000
11.C	-3.078313	0.045739	0.000000
12.C	-4.526936	0.048957	0.000000
13.H	-4.897785	1.082150	0.000000
14.H	-4.903125	-0.466872	-0.893152
15.H	-4.903125	-0.466872	0.893152

Cis-2 (N Imag freqs= 0)

1.Pt	0.000000	0.094956	0.000000
2.Cl	-1.612789	1.691764	0.000000
3.Cl	1.612789	1.691764	0.000000
4.N	-1.420101	-1.227695	0.000000
5.C	-2.314161	-1.964875	0.000000
6.C	-3.460573	-2.899262	0.000000
7.F	-3.010466	-4.171567	0.000000
8.F	-4.220204	-2.708855	-1.093975
9.F	-4.220204	-2.708855	1.093975
10.N	1.420101	-1.227695	0.000000
11.C	2.314161	-1.964875	0.000000
12.C	3.460573	-2.899262	0.000000
13.F	3.010466	-4.171567	0.000000
14.F	4.220204	-2.708855	1.093975
15.F	4.220204	-2.708855	-1.093975

Trans-2 (N Imag freqs= 0)

1.Pt	0.000000	-0.041749	0.000000
2.Cl	0.000000	-2.368619	0.000000
3.Cl	0.000000	2.284788	0.000000
4.N	-1.907776	-0.043709	0.000000
5.C	-3.062050	-0.046934	0.000000
6.C	-4.546198	-0.052504	0.000000
7.F	-4.998904	-1.317801	0.000000
8.F	-5.006457	0.578246	1.094668
9.F	-5.006457	0.578246	-1.094668
10.N	1.907776	-0.043709	0.000000
11.C	3.062050	-0.046934	0.000000
12.C	4.546198	-0.052504	0.000000
13.F	4.998904	-1.317801	0.000000
14.F	5.006457	0.578246	-1.094668
15.F	5.006457	0.578246	1.094668

Cis-3 (N Imag freqs= 0)

1.Pt	-0.000021	-0.042982	0.000000
2.Cl	-1.620620	1.563709	0.000000
3.Cl	1.620569	1.563841	0.000000
4.N	-1.443105	-1.355201	0.000000
5.C	-2.415612	-1.991524	0.000000
6.C	-3.619302	-2.740763	0.000000
7.C	-4.221897	-3.098145	-1.220927
8.C	-5.417500	-3.808848	-1.212067
9.C	-6.015685	-4.164775	0.000000
10.C	-5.417500	-3.808848	1.212067
11.C	-4.221897	-3.098145	1.220927
12.H	-3.750598	-2.805649	-2.156461
13.H	-5.887618	-4.081926	-2.154956
14.H	-6.953781	-4.717913	0.000000
15.H	-5.887618	-4.081926	2.154956
16.H	-3.750598	-2.805649	2.156461
17.N	1.443188	-1.355214	0.000000
18.C	2.415447	-1.991895	0.000000
19.C	3.619052	-2.741283	0.000000
20.C	4.221789	-3.098415	1.220926
21.C	5.417748	-3.808526	1.212066
22.C	6.016117	-4.164142	0.000000
23.C	5.417748	-3.808526	-1.212066
24.C	4.221789	-3.098415	-1.220926
25.H	3.750435	-2.805991	2.156450
26.H	5.888028	-4.081333	2.154963
27.H	6.954400	-4.716966	0.000000
28.H	5.888028	-4.081333	-2.154963
29.H	3.750435	-2.805991	-2.156450

Trans-3 (N Imag freqs= 0)

1.Pt	0.000000	0.000000	0.000000
2.Cl	0.000000	2.330680	0.000000
3.Cl	0.000000	-2.330680	0.000000
4.N	-1.919530	0.000000	0.000000
5.C	-3.078590	0.000000	0.000000
6.C	-4.497120	0.000000	0.000000
7.C	-5.195640	0.000000	1.221600
8.C	-6.586670	0.000000	1.212150
9.C	-7.282290	0.000000	0.000000
10.C	-6.586670	0.000000	-1.212150
11.C	-5.195640	0.000000	-1.221600
12.H	-4.640700	0.000000	2.157010
13.H	-7.130550	0.000000	2.155040
14.H	-8.371430	0.000000	0.000000
15.H	-7.130550	0.000000	-2.155040
16.H	-4.640700	0.000000	-2.157010
17.N	1.919530	0.000000	0.000000
18.C	3.078590	0.000000	0.000000
19.C	4.497120	0.000000	0.000000
20.C	5.195640	0.000000	1.221600
21.C	6.586670	0.000000	1.212150
22.C	7.282290	0.000000	0.000000
23.C	6.586670	0.000000	-1.212150
24.C	5.195640	0.000000	-1.221600
25.H	4.640700	0.000000	2.157010
26.H	7.130550	0.000000	2.155040
27.H	8.371430	0.000000	0.000000
28.H	7.130550	0.000000	-2.155040
29.H	4.640700	0.000000	-2.157010

Cis-4 (N Imag freqs= 0)

1.Pt	0.000000	0.002429	0.000000
2.Cl	-1.621301	1.609652	0.000000
3.Cl	1.621301	1.609652	0.000000
4.N	-1.441798	-1.312576	0.000000
5.C	-2.416500	-1.946035	0.000000
6.C	-3.620415	-2.691587	0.000000
7.C	-4.227560	-3.052763	1.216844
8.C	-5.421270	-3.762578	1.205413
9.C	-6.041189	-4.126581	0.000000
10.C	-5.421270	-3.762578	-1.205413
11.C	-4.227560	-3.052763	-1.216844
12.C	-7.356234	-4.858811	0.000000
13.H	-3.758721	-2.766722	2.155333
14.H	-5.886206	-4.038025	2.151895
15.H	-5.886206	-4.038025	-2.151895
16.H	-3.758721	-2.766722	-2.155333
17.H	-8.192426	-4.143394	0.000000
18.H	-7.464227	-5.489417	0.890401
19.H	-7.464227	-5.489417	-0.890401
20.N	1.441798	-1.312576	0.000000
21.C	2.416500	-1.946035	0.000000
22.C	3.620415	-2.691587	0.000000
23.C	4.227560	-3.052763	1.216844
24.C	5.421270	-3.762578	1.205413
25.C	6.041189	-4.126581	0.000000
26.C	5.421270	-3.762578	-1.205413
27.C	4.227560	-3.052763	-1.216844
28.H	3.758721	-2.766722	2.155333
29.H	5.886206	-4.038025	2.151895
30.H	5.886206	-4.038025	-2.151895
31.H	3.758721	-2.766722	-2.155333
32.H	8.192426	-4.143394	0.000000
33.C	7.356234	-4.858811	0.000000
34.H	7.464227	-5.489417	-0.890401
35.H	7.464227	-5.489417	0.890401

Trans-4 (N Imag freqs= 0)

1.Pt	0.000000	0.000000	0.057758
2.Cl	0.000000	0.000000	2.387481
3.Cl	0.000000	0.000000	-2.273169
4.N	-1.919956	0.000000	0.052877
5.C	-3.078953	0.000000	0.036597
6.C	-4.495196	0.000000	0.012896
7.C	-5.199775	-1.217357	-0.003612
8.C	-6.588095	-1.205439	-0.035906
9.C	-7.306587	0.000000	-0.050858
10.C	-6.588095	1.205439	-0.035906
11.C	-5.199775	1.217357	-0.003612
12.H	-4.650462	2.155780	0.004943
13.H	-7.128280	2.151842	-0.053704
14.C	-8.811893	0.000000	-0.056186
15.H	-7.128280	-2.151842	-0.053704
16.H	-4.650462	-2.155780	0.004943
17.H	-9.199519	0.000000	0.973726
18.H	-9.210673	0.890181	-0.556913
19.H	-9.210673	-0.890181	-0.556913
20.N	1.919956	0.000000	0.052877
21.C	3.078953	0.000000	0.036597
22.C	4.495196	0.000000	0.012896
23.C	5.199775	1.217357	-0.003612
24.C	6.588095	1.205439	-0.035906
25.C	7.306587	0.000000	-0.050858
26.C	6.588095	-1.205439	-0.035906
27.C	5.199775	-1.217357	-0.003612
28.H	4.650462	-2.155780	0.004943
29.H	7.128280	-2.151842	-0.053704
30.C	8.811893	0.000000	-0.056186
31.H	7.128280	2.151842	-0.053704
32.H	4.650462	2.155780	0.004943
33.H	9.199519	0.000000	0.973726
34.H	9.210673	-0.890181	-0.556913
35.H	9.210673	0.890181	-0.556913

Cis-5 (N Imag freqs= 0)

1.Pt	0.007827	-0.080601	0.000000
2.Cl	1.471639	1.666830	0.000000
3.Cl	-1.747768	1.373430	0.000000
4.N	1.569671	-1.248283	0.000000
5.C	2.612192	-1.762062	0.000000
6.C	3.901155	-2.351645	0.000000
7.C	4.544773	-2.628716	1.220185
8.C	5.820332	-3.178223	1.214463
9.C	6.456327	-3.454030	0.000000
10.C	5.820332	-3.178223	-1.214463
11.C	4.544773	-2.628716	-1.220185
12.H	4.041696	-2.403719	2.157286
13.H	6.323168	-3.395891	2.153545
14.H	6.323168	-3.395891	-2.153545
15.H	4.041696	-2.403719	-2.157286
16.C	7.862540	-4.008137	0.000000
17.F	8.787855	-3.009702	0.000000
18.F	8.107055	-4.773617	1.094699
19.F	8.107055	-4.773617	-1.094699
20.N	-1.317298	-1.511294	0.000000
21.C	-2.249835	-2.204895	0.000000
22.C	-3.411026	-3.017659	0.000000
23.C	-3.993717	-3.406841	-1.220197
24.C	-5.148561	-4.178412	-1.214472
25.C	-5.723835	-4.565194	0.000000
26.C	-5.148561	-4.178412	1.214472
27.C	-3.993717	-3.406841	1.220197
28.H	-3.539778	-3.094347	-2.157298
29.H	-5.603671	-4.483555	-2.153544
30.H	-5.603671	-4.483555	2.153544
31.H	-3.539778	-3.094347	2.157298
32.C	-7.005918	-5.365620	0.000000
33.F	-7.107316	-6.162786	-1.094700
34.F	-8.097172	-4.551860	0.000000
35.F	-7.107316	-6.162786	1.094700

Trans-5 (N Imag freqs= 0)

1.Pt	0.000000	0.000000	-0.019318
2.Cl	0.000000	0.000000	2.314263
3.Cl	0.000000	0.000000	-2.352661
4.N	1.921413	0.000000	-0.018323
5.C	3.081045	0.000000	-0.016238
6.C	4.501799	0.000000	-0.011648
7.C	5.202532	1.220452	-0.010367
8.C	6.592248	1.214327	-0.007549
9.C	7.286848	0.000000	-0.007589
10.C	6.592248	-1.214327	-0.007549
11.C	5.202532	-1.220452	-0.010367
12.H	4.653327	-2.158990	-0.014266
13.H	7.138571	-2.154794	-0.012477
14.C	8.799601	0.000000	0.035443
15.H	7.138571	2.154794	-0.012477
16.H	4.653327	2.158990	-0.014266
17.N	-1.921413	0.000000	-0.018323
18.C	-3.081045	0.000000	-0.016238
19.C	-4.501799	0.000000	-0.011648
20.C	-5.202532	-1.220452	-0.010367
21.C	-6.592248	-1.214327	-0.007549
22.C	-7.286848	0.000000	-0.007589
23.C	-6.592248	1.214327	-0.007549
24.C	-5.202532	1.220452	-0.010367
25.H	-4.653327	2.158990	-0.014266
26.H	-7.138571	2.154794	-0.012477
27.C	-8.799601	0.000000	0.035443
28.H	-7.138571	-2.154794	-0.012477
29.H	-4.653327	-2.158990	-0.014266
30.F	9.260348	0.000000	1.317700
31.F	9.325326	-1.094757	-0.571973
32.F	9.325326	1.094757	-0.571973
33.F	-9.260348	0.000000	1.317700
34.F	-9.325326	1.094757	-0.571973
35.F	-9.325326	-1.094757	-0.571973

Table S9 optimized coordinates for CN vibrational frequencies analysis of $ACNH^+$, $PhCN^+$, $ACN\text{-}Cl_3$, $ACN\text{-}BF_3$.

$ACNH^+$ (N Imag freqs= 0)

1.C	-3.591940	-2.798827	0.000000
2.C	-2.437108	-1.958669	0.000000
3.N	-1.511114	-1.284080	0.000000
4.H	-3.267741	-3.846526	0.000000
5.H	-4.183857	-2.587124	-0.899042
6.H	-4.183857	-2.587124	0.899042
7.H	-0.695179	-0.686326	0.000000

$PhCNH^+$ (N Imag freqs= 0)

1.N	-1.426697	-1.259503	-0.000837
2.C	-2.329162	-1.973795	-0.000923
3.C	-3.419562	-2.852648	-0.000200
4.C	-3.954066	-3.281694	-1.233795
5.C	-5.036172	-4.150470	-1.218286
6.C	-5.573926	-4.581565	0.000143
7.C	-5.035736	-4.150283	1.218367
8.C	-3.953605	-3.281549	1.233746
9.H	-3.519419	-2.933108	-2.166290
10.H	-5.462981	-4.492336	-2.157907
11.H	-6.423152	-5.261868	0.000389
12.H	-5.462643	-4.491956	2.157966
13.H	-3.518805	-2.932652	2.166188
14.H	-0.664425	-0.596479	0.000132

$ACN\text{-}Cl_3$ (N Imag freqs= 0)

1.C	2.669203	-0.179093	0.000000
2.C	1.233534	-0.014548	0.000000
3.N	0.089065	0.115064	0.000000
4.H	3.154131	0.805729	0.000000
5.H	2.976979	-0.734792	-0.895306
6.H	2.976979	-0.734792	0.895306
7.B	-1.474763	0.292289	0.000000
8.Cl	-2.158144	-1.413144	0.000000
9.Cl	-1.856382	1.229113	1.536036
10.Cl	-1.856382	1.229113	-1.536036

$ACN\text{-}F_3$ (N Imag freqs= 0)

1.C	2.693356	-0.122074	0.000000
2.C	1.251323	0.016499	0.000000
3.N	0.104334	0.126221	0.000000
4.H	3.160402	0.870744	0.000000
5.H	3.012302	-0.671635	-0.894454
6.H	3.012302	-0.671635	0.894454
7.B	-1.679534	0.301619	0.000000
8.F	-2.088923	-0.998294	0.000000
9.F	-1.890439	0.992817	1.155171
10.F	-1.890439	0.992817	-1.155171

Table S10 Comparison between selected experimental and calculated geometrical parameters for cis-1, cis-2, trans-1, and trans-2.

	Cis-1[a]		**Trans-1**[b]		**Cis-2**[a]		**Trans-2**[a]	
	Exp.	Calc.	Exp.	Calc.	Exp.	Calc.	Exp.	Calc.
Pt – N1	1.976(4)	1.957	1.944(10)	1.923	1.968(3)	1.951	1.949(3)	1.919
Pt – N2	1.980(4)	1.957			1.972(3)	1.951	-	
Pt – Cl1	2.270(1)	2.283	2.296(4)	2.331	2.2727(9)	2.282	2.295(7)	2.331
Pt – Cl2	2.273(1)	2.283			2.2806(9)	2.282	-	
N1 – C1	1.123(6)	1.158	1.152(6)	1.155	1.142(5)	1.162	1.141(4)	1.159
N2 – C2	1.132(6)	1.158			1.138(5)	1.162	-	
C1 – C11	1.464(6)	1.449	1.434(19)	1.449	1.434(5)	1.418	1.432(4)	1.418
C2 – C21	1.443(6)	1.449			1.427(6)	1.418	-	
N1 – Pt – N2	90.8(2)	95.3	180.0	180.0	88.8(1)	95.3	180	180.0
Cl1 – Pt – Cl2	90.67(4)	90.8	180.0	180.0	91.10(3)	90.5	180	180.0
N1 – Pt – Cl2	89.6(1)	87.0	90.4(3)	90.0	91.7(1)	87.1	90.52(8)	90.0
N2 – Pt – Cl1	89.0(1)	87.0	89.6(3)	90.0	88.5(1)	87.1	89.48(8)	90.0
N1 – Pt – Cl1	178.2(1)	177.8	-		177.2(1)	177.6	-	
N2 – Pt – Cl2	177.2(1)	177.8	-		178.06	177.6	-	
N1 – C1 – C11	179.8(6)	178.2	180.0(24)	179.9	176.7(4)	178.7	178.0(3)	179.9
N2 – C2 – C21	177.6(5)	178.2			176.3(4)	178.7	-	
Pt – N1 – C1	178.0(4)	172.5	177.8(10)	180.0	170.1(3)	171.2	179.0(3)	179.8
Pt – N2 – C2	174.5(4)	172.5			177.0(3)	171.2	-	

[a] R. Bertani, M. Mozzon, P. Sgarbossa, S. Tamburini, M. Casarin, G. Mangione, G. Casella, A. Venzo, S. Rizzato and A. Albinati, *Inorganica Chim. Acta*, 2017, 489–504.

[b] J. Kritzenberger, H. Yersin, K.-J. Range and M. Zabel, *Z. Für Naturforschung B*, 1994, **49**, 297–300.

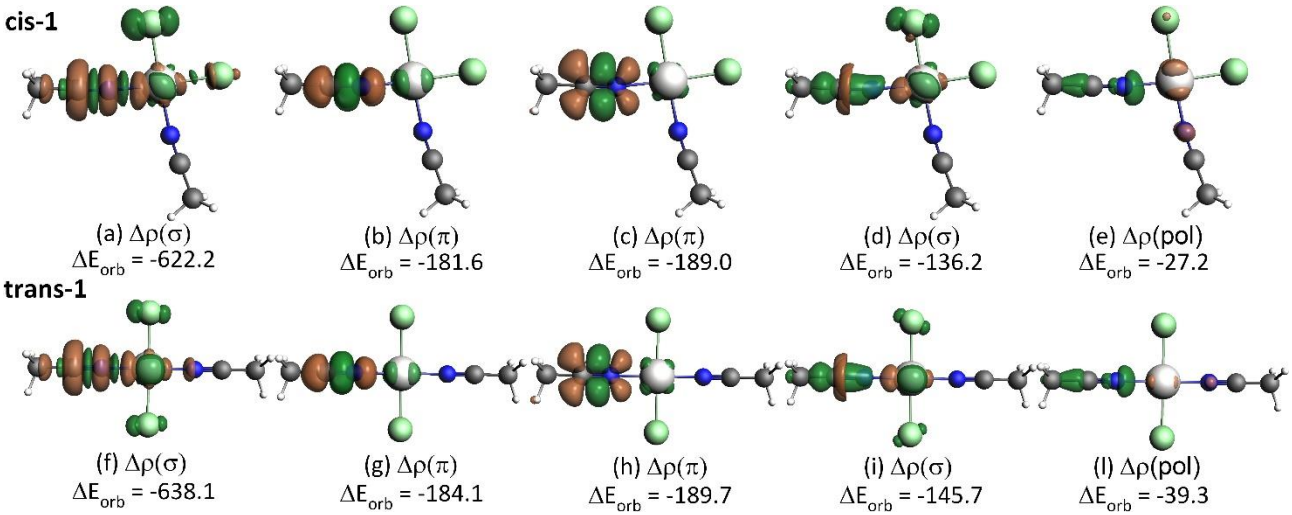

Figure S4. Plot of deformation densities Δρ of the pairwise orbital interactions and relevant ΔEorb (kcal/mol) for the benzonitrile derivatives.