Supplementary Information (SI) for Physical Chemistry Chemical Physics.

Support Information for

Exploring the trans effect of NH_3 ligand in platinum halide complexes $Pt(NH_3)ClX_2^-$ (X=Cl, Br, I) using cryogenic photoelectron spectroscopy and quantum chemical calculations

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This file contains 16 pages , 9 figures and 6 tables.

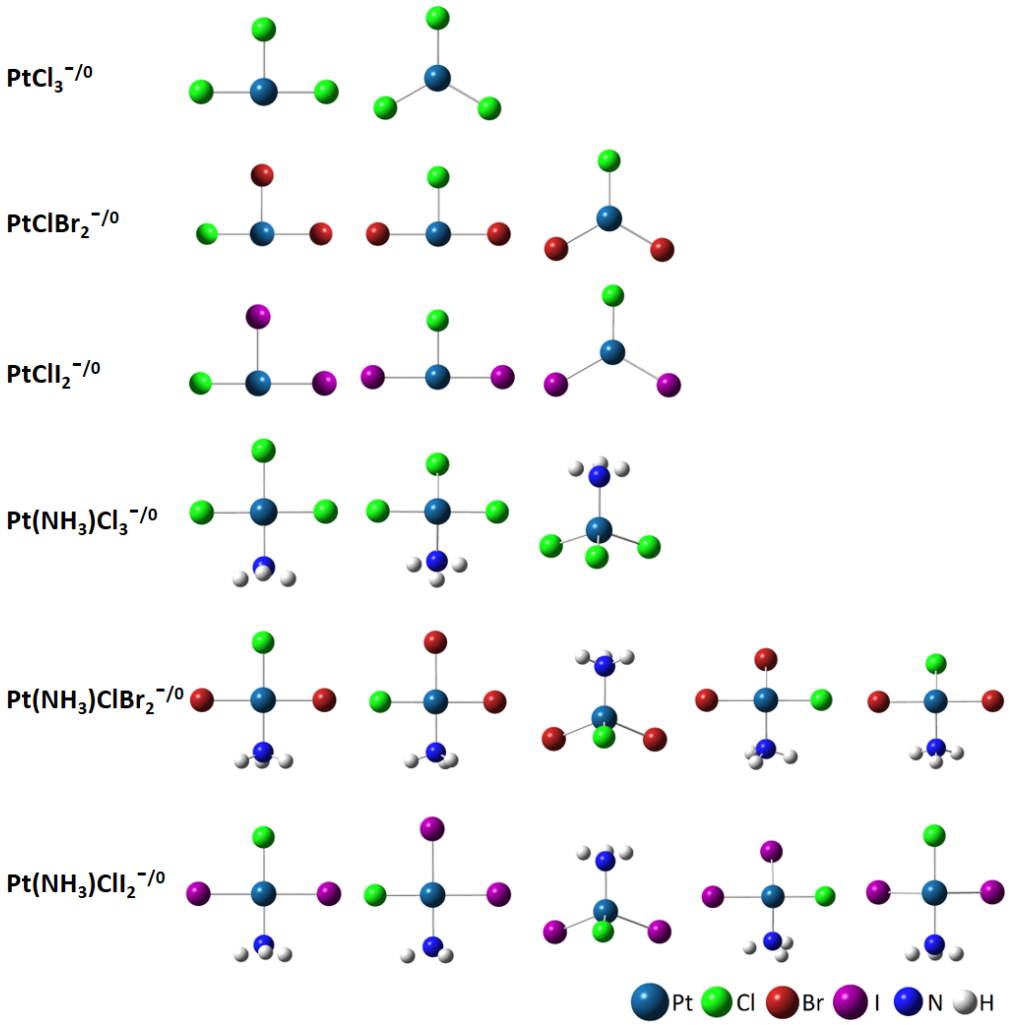


Figure S1. Initial geometries of $PtClX_2^-$, $Pt(NH_3)ClX_2^-$ (X = Cl, Br, I) anions and the corresponding neutrals.

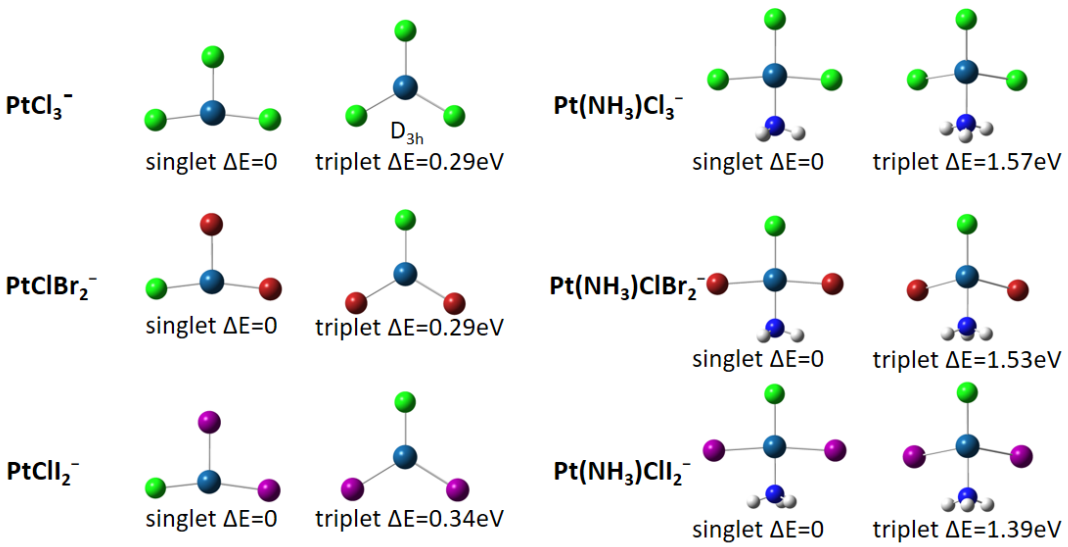


Figure S2. Optimized geometries of $PtClX_2^-$ and $Pt(NH_3)ClX_2^-$ (X = Cl, Br, I) anions at different spin multiplicities, optimized at the B3LYP-D3(BJ)/aug-cc-pVTZ(-pp) level.

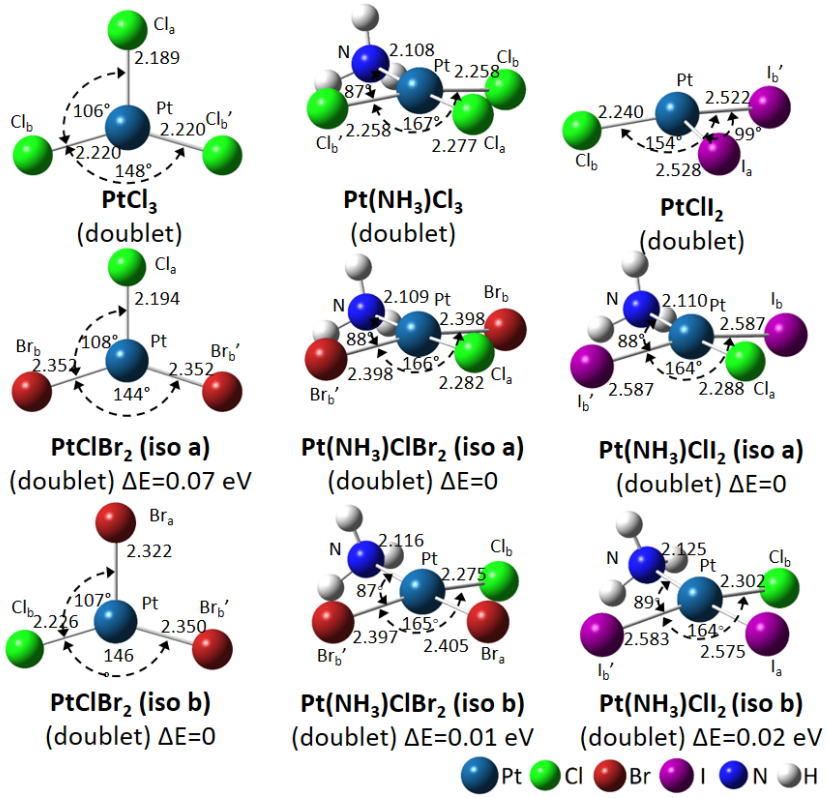


Figure S3. Lowest energy structures of $PtClX_2$, $Pt(NH_3)ClX_2$ (X = Cl, Br, I) neutrals, and their isomers optimized at the B3LYP-D3(BJ)/aug-cc-pVTZ(-pp) level. Selected bond lengths (Å) and bond angles (deg) are provided. A variety of different initial structures were calculated for $PtClI_2$, and no isomer structures appeared.

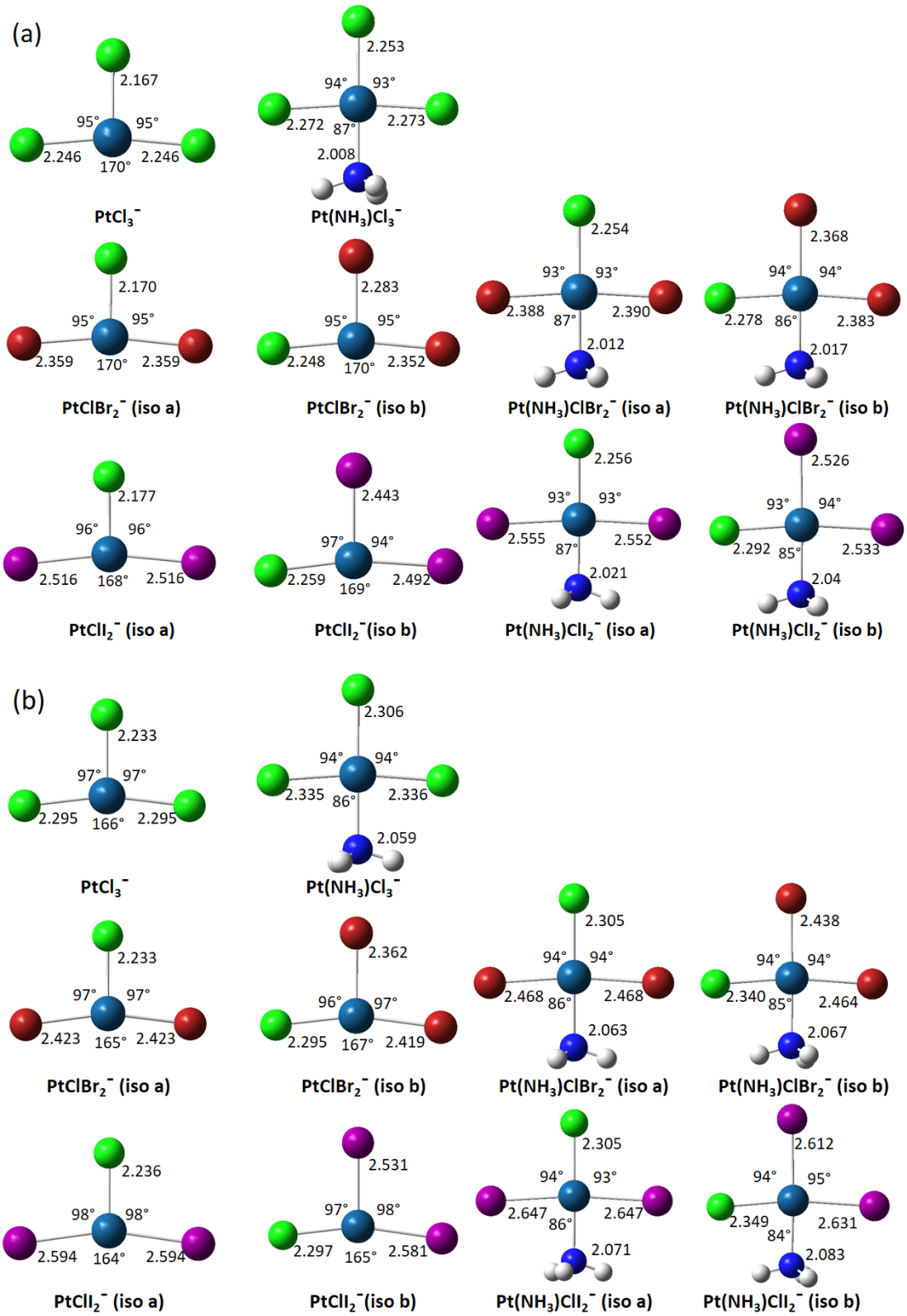


Figure S4. Optimized structures of $PtClX_2^-$ and $Pt(NH_3)ClX_2^-$ (X = Cl, Br, I) anions at different computational methods, MP2/aug-cc-pVTZ(-pp) (a) and CAMB3LYP/aug-cc-pVTZ(-pp) (b).

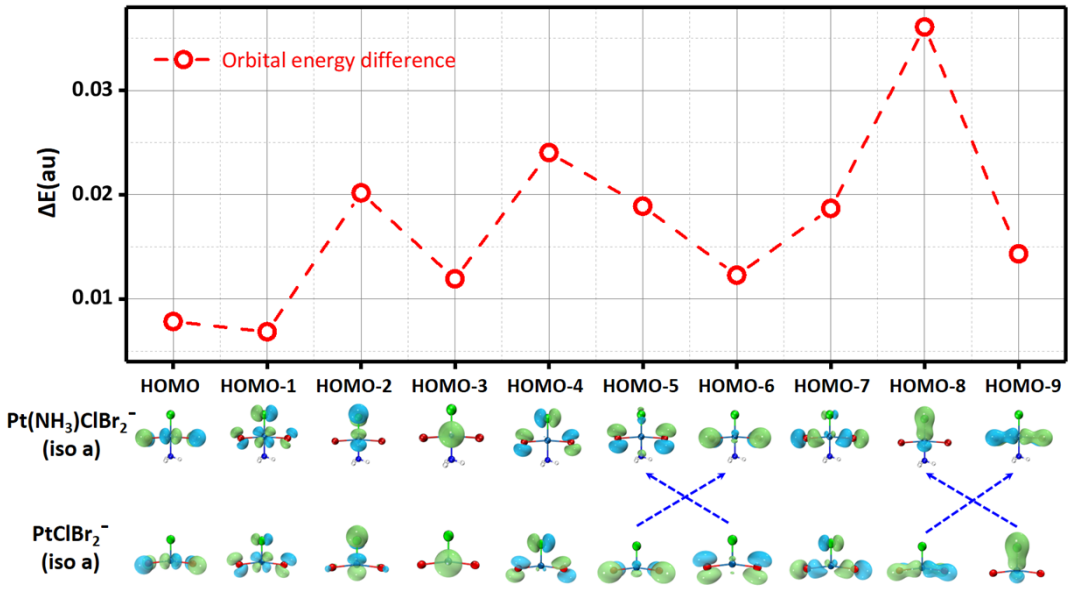


Figure S5. The HOMOs energy difference upon NH3 coordination and orbital rearrangement between (iso a)$PtClBr_2^-$ and (iso a)$Pt(NH3)ClBr_2^-$ with the pictures of the corresponding MOs illustrated. Δ E = ε (FMO)((iso a)$Pt(NH_3)ClBr_2^-$) - ε (FMO)((iso a)$PtClBr_2^-$) for FMO = HOMO, HOMO-1,-2,-3,-4,-7; and the correlated orbital energy differences (lined by blue lines) for deeper FMOs (HOMO-5,-6,-8,-9)

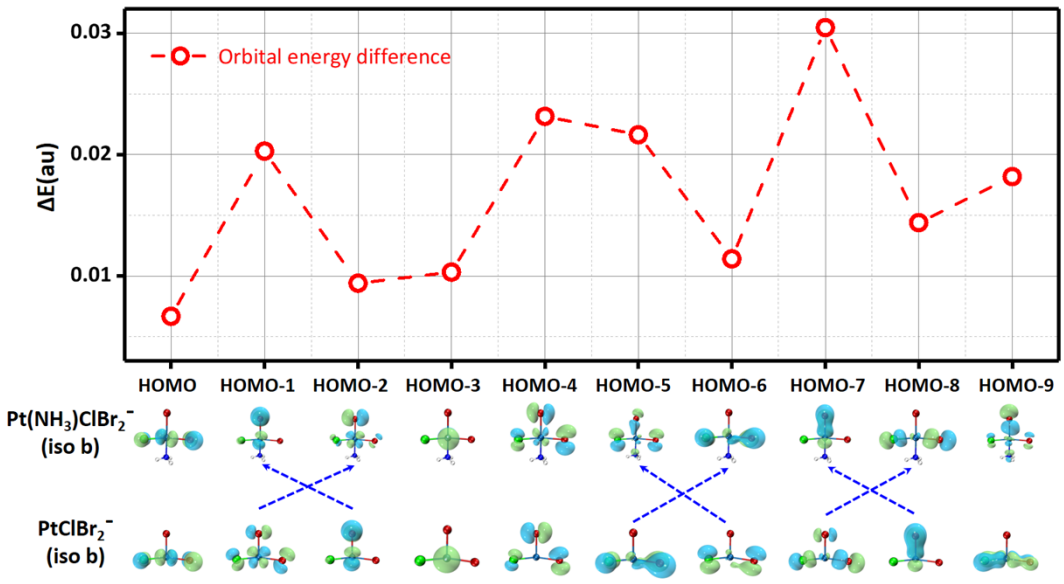


Figure S6. The HOMOs energy difference upon NH3 coordination and orbital rearrangement between (iso b)$PtClBr_2^-$ and (iso b)$Pt(NH_3)ClBr_2^-$ with the pictures of the corresponding MOs illustrated. Δ E = ε (FMO)((iso b)$Pt(NH_3)ClBr_2^-$) - ε (FMO)((iso b)$PtClBr_2^-$) for FMO = HOMO, HOMO-3,-4,-9; and the correlated orbital energy differences (lined by blue lines) for FMOs (HOMO-1,-2,-5,-6,-7,-8)

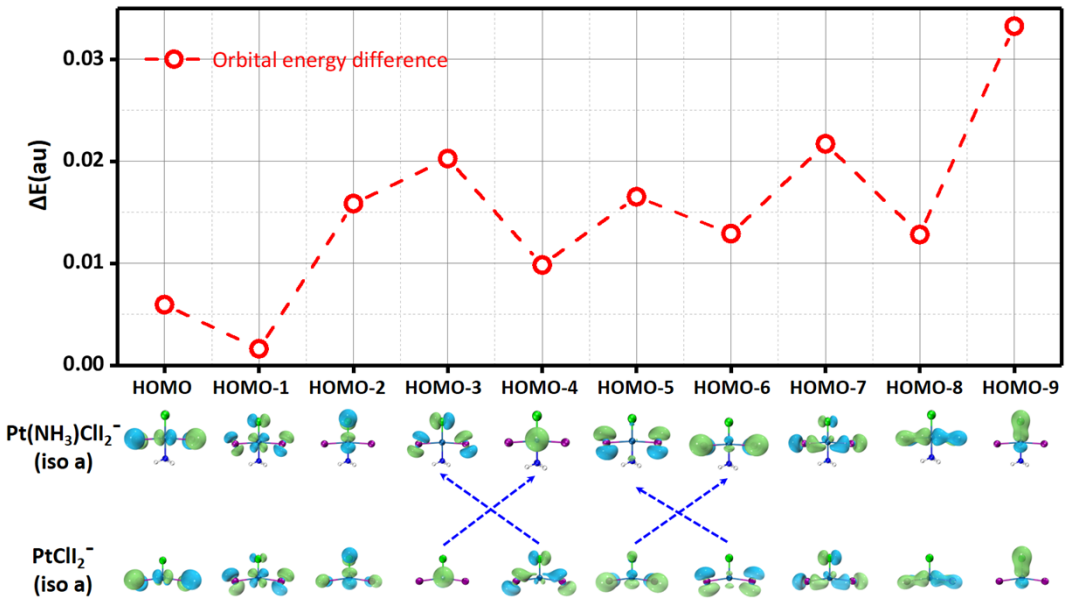


Figure S7. The HOMOs energy difference upon NH3 coordination and orbital rearrangement between (iso a)$PtCl_2^-$ and (iso a)$Pt(NH_3)Cl_2^-$ with the pictures of the corresponding MOs illustrated. Δ E = ε (FMO)((iso a)$Pt(NH_3)Cl_2^-$) - ε (FMO)((iso a)$PtCl_2^-$) for FMO = HOMO, HOMO-1,-2,-7,-8,-9; and the correlated orbital energy differences (lined by blue lines) for FMOs (HOMO-3,-4,-5,-6)

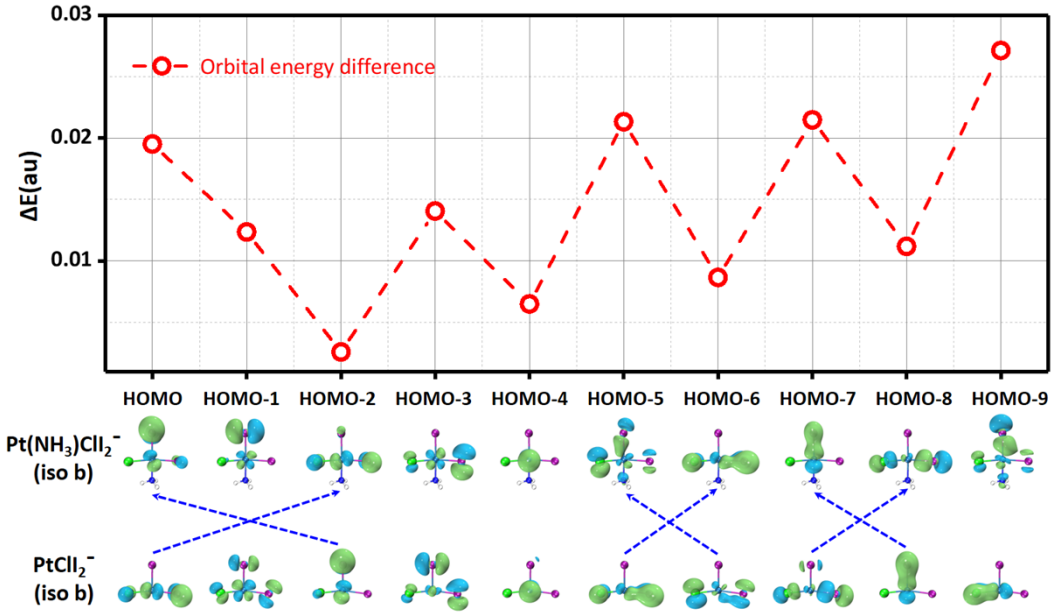


Figure S8. The HOMOs energy difference upon NH3 coordination and orbital rearrangement between (iso b)$PtCll_2^-$ and (iso b)$Pt(NH_3)Cll_2^-$ with the pictures of the corresponding MOs illustrated. Δ E = ε (FMO)((iso b)$Pt(NH_3)Cll_2^-$) - ε (FMO)((iso b)$PtCll_2^-$) for FMO = HOMO-3,-4,-9; and the correlated orbital energy differences (lined by blue lines) for FMOs (HOMO, HOMO-1,-2,-5,-6,-7,-8)

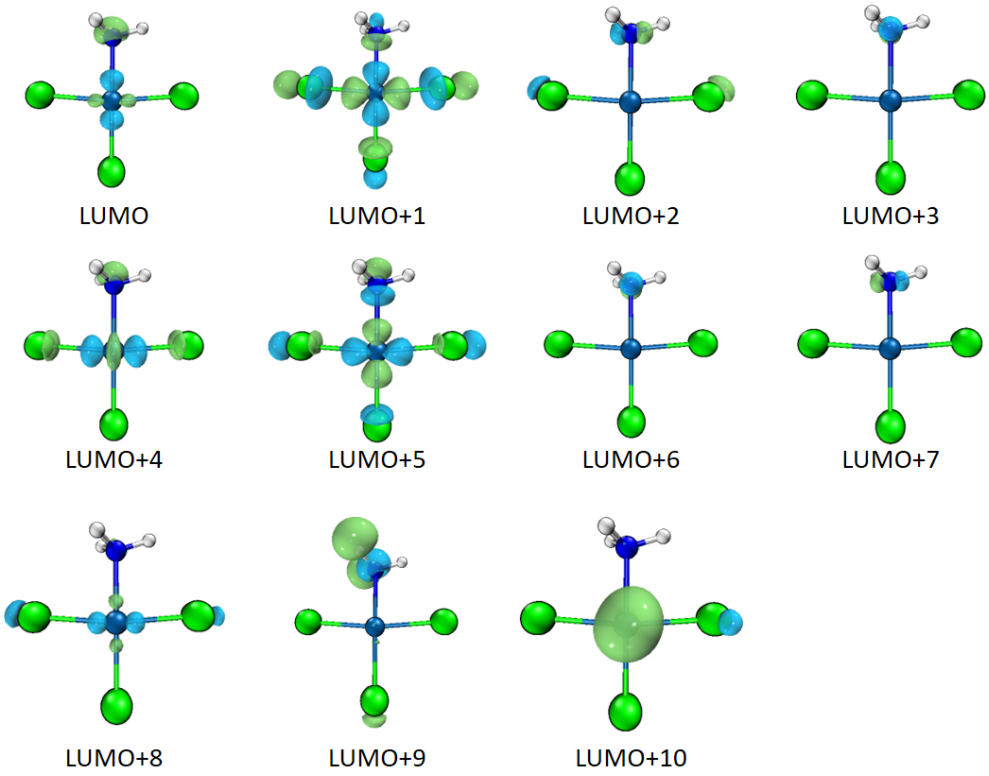


Figure S9. The LUMOs of $Pt(NH_3)Cl_3^-$, isovalue = 0.04.

Table S1. The experimental and calculated ADEs and VDEs of $PtClX_2^-$ and $Pt(NH_3)ClX_2^-$ (X = Cl, Br, I) anions. The calculations were performed at the B3LYP-D3(BJ)/aug-cc-pVTZ-(pp), MP2/aug-cc-pVTZ(-pp) and CAMB3LYP/aug-cc-pVTZ(-pp) level of theory, respectively.

Anions	ADE (eV)				VDE (eV)			
	Exp.	B3LYP	MP2	CAMB3LYP	Exp.	B3LYP	MP2	CAMB3LYP
$PtCl_3^-$	4.26	4.18	4.31	4.37	4.46	4.35	4.63	5.09
$Pt(NH_3)Cl_3^-$	3.85	3.83	4.15	4.08	4.06	4.00	4.43	4.18
$PtClBr_2^-$ (iso a)	4.23	4.13	4.07	4.15	4.37	4.28	5.39	5.07
$PtClBr_2^-$ (iso b)		4.12	4.44	4.33		4.26	4.64	4.47
$Pt(NH_3)ClBr_2^-$ (iso a)	3.79	3.86	4.48	4.33	4.01	4.00	4.82	4.45
$Pt(NH_3)ClBr_2^-$ (iso b)		3.84	4.12	4.04		3.98	4.47	4.21
$PtClI_2^-$ (iso a)	4.08	3.79	3.73	4.00	4.23	4.12	4.24	4.98
$PtClI_2^-$ (iso b)		3.99	4.08	4.19		4.10	4.67	4.31
$Pt(NH_3)ClI_2^-$ (iso a)	3.96	3.80	3.58	4.03	4.09	3.90	4.16	4.17
$Pt(NH_3)ClI_2^-$ (iso b)		3.77	4.04	4.02		3.86	4.48	4.15

Table S2. The ionic proportion of chemical bond Pt-Cl, Pt-Br, and Pt-I of $PtClX_2^-$, $Pt(NH_3)ClX_2^-$ (X = Cl, Br, I) anions and their isomers.

Bond / Anions	Pt-Cl_b/Br_b/I_b	Pt-Cl_a/Br_a/I_a	Pt-Cl_b'/Br_b'/I_b'
$PtCl_3^-$	47.3%	28.6%	47.3%
$Pt(NH_3)Cl_3^-$	48.6%	45.1%	48%
$PtClBr_2^-$ (iso a)	44%	28.1%	44%
$Pt(NH_3)ClBr_2^-$ (iso a)	45.3%	44.6%	44.7%
$PtClBr_2^-$ (iso b)	47.6%	22.7%	43.6%
$Pt(NH_3)ClBr_2^-$ (iso b)	48.7%	41.3%	43.8%
$PtClI_2^-$ (iso a)	40.7%	28.3%	40.7%
$Pt(NH_3)ClI_2^-$ (iso a)	41%	44.5%	40.8%
$PtClI_2^-$ (iso b)	49.1%	14.4%	37.5%
$Pt(NH_3)ClI_2^-$ (iso b)	50.5%	34.3%	37.2%

Table S3. The dissociation energies of different dissociation channels of $PtClX_2^-$, $Pt(NH_3)ClX_2^-$(X= Br, I) and corresponding isomers. All calculations were carried out at the B3LYP-D3(BJ)/aug-cc-pVTZ-(pp) level of theory.

Dissociation channels	E(ev)	Dissociation channels	E(ev)
$PtClBr_2^-$ (iso a) → $PtBr_2+Cl_a^-$	3.48	$Pt(NH_3)ClBr_2^-$ (iso a) → $Pt(NH_3)Br_2+Cl_a^-$	2.99
$PtClBr_2^-$ (iso a) → $PtClBr+Br_b^-$	3.05	$Pt(NH_3)ClBr_2^-$ (iso a) → $Pt(NH_3)ClBr+Br_b^-$	2.73
$PtClBr_2^-$ (iso a) → $PtClBr+Br_b'^-$	3.05	$Pt(NH_3)ClBr_2^-$ (iso a) → $Pt(NH_3)ClBr+Br_b'^-$	2.73
$PtClBr_2^-$ (iso b) → $PtBr_2+Cl_b^-$	3.19	$Pt(NH_3)ClBr_2^-$ (iso b) → $Pt(NH_3)Br_2+Cl_b^-$	2.91
$PtClBr_2^-$ (iso b) → $PtClBr+Br_a^-$	3.42	$Pt(NH_3)ClBr_2^-$ (iso b) → $Pt(NH_3)ClBr+Br_a^-$	2.79
$PtClBr_2^-$ (iso b) → $PtClBr+Br_b'^-$	3.13	$Pt(NH_3)ClBr_2^-$ (iso b) → $Pt(NH_3)ClBr+Br_b'^-$	2.81
$PtClI_2^-$(iso a) → $PtI_2+Cl_a^-$	3.32	$Pt(NH_3)ClI_2^-$ (iso a) → $Pt(NH_3)I_2+Cl_a^-$	3.09
$PtClI_2^-$ (iso a) → $PtClI+I_b^-$	2.84	$Pt(NH_3)ClI_2^-$(iso a) → $Pt(NH_3)ClI+I_b^-$	2.50
$PtClI_2^-$ (iso a) → $PtClI+I_b'^-$	2.84	$Pt(NH_3)ClI_2^-$ (iso a) → $Pt(NH_3)ClI+I_b'^-$	2.50
$PtClI_2^-$ (iso b) → $PtI_2+Cl_b^-$	3.00	$Pt(NH_3)ClI_2^-$ (iso b) → $Pt(NH_3)I_2+Cl_b^-$	2.77
$PtClI_2^-$ (iso b) → $PtClI+I_a^-$	3.32	$Pt(NH_3)ClI_2^-$(iso b) → $Pt(NH_3)ClI+I_a^-$	2.74
$PtClI_2^-$ (iso b) → $PtClI+I_b'^-$	3.01	$Pt(NH_3)ClI_2^-$ (iso b) → $Pt(NH_3)ClI+I_b'^-$	2.73

Table S4. Optimized structures of $Pt(C_2H_4)ClX_2^-$ (X = Cl, Br, I) anions at the B3LYP-D3(BJ)/aug-cc-pVTZ-(pp) level of theory.

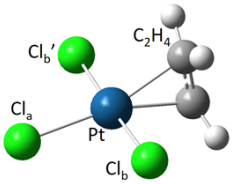
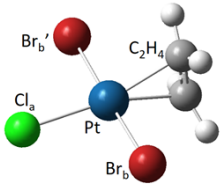
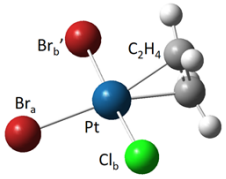
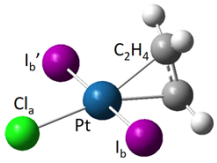
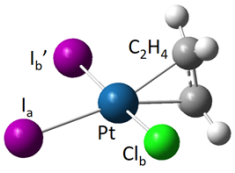
Anions	**$Pt(C_2H_4)Cl_3^-$ (singlet)**	
		
$Pt–Cl_a$	**2.338**	
$Pt–Cl_b$	**2.348**	
$Pt–Cl_b'$	**2.348**	
	$Pt(C_2H_4)ClBr_2^-$ (iso a, singlet)	**$Pt(C_2H_4)ClBr_2^-$ (iso b, singlet)**
		
$Pt–Cl_{a/b}$	**2.336**	**2.354**
$Pt–Br_{a/b}$	**2.489**	**2.476**
$Pt–Br_b'$	**2.490**	**2.483**
	$Pt(C_2H_4)ClI_2^-$ (iso a, singlet)	**$Pt(C_2H_4)ClI_2^-$ (iso b, singlet)**
		
$Pt–Cl_{a/b}$	**2.335**	**2.367**
$Pt–I_{a/b}$	**2.680**	**2.659**
$Pt–I_b'$	**2.680**	**2.661**

Table S5. The dissociation energies of different dissociation channels of $Pt(C_2H_4)ClX_2^-$(X=Cl, Br, I) and corresponding isomers. All calculations were carried out at the B3LYP-D3(BJ)/aug-cc-pVTZ-(pp) level of theory.

Dissociation channels	E(ev)
$Pt(C_2H_4)Cl_3^- \rightarrow Pt(C_2H_4)Cl_2 + Cl_a^-$	2.82
$Pt(C_2H_4)Cl_3^- \rightarrow Pt(C_2H_4)Cl_2 + Cl_b^-$	3.20
$Pt(C_2H_4)Cl_3^- \rightarrow Pt(C_2H_4)Cl_2 + Cl_b'^-$	3.20
$Pt(C_2H_4)ClBr_2^-$ (iso a) $\rightarrow Pt(C_2H_4)Br_2+Cl_a^-$	2.87
$Pt(C_2H_4)ClBr_2^-$ (iso a) $\rightarrow Pt(C_2H_4)ClBr+Br_b^-$	2.93
$Pt(C_2H_4)ClBr_2^-$ (iso a) $\rightarrow Pt(C_2H_4)ClBr+Br_b'^-$	2.93
$Pt(C_2H_4)ClBr_2^-$ (iso b) $\rightarrow Pt(C_2H_4)Br_2+Cl_b^-$	3.09
$Pt(C_2H_4)ClBr_2^-$ (iso b) $\rightarrow Pt(C_2H_4)ClBr+Br_a^-$	2.66
$Pt(C_2H_4)ClBr_2^-$ (iso b) $\rightarrow Pt(C_2H_4)ClBr+Br_b'^-$	3.04
$Pt(C_2H_4)ClI_2^-$ (iso a) $\rightarrow Pt(C_2H_4)I_2+Cl_a^-$	2.93
$Pt(C_2H_4)ClI_2^-$(iso a) $\rightarrow Pt(C_2H_4)ClI+I_b^-$	2.62
$Pt(C_2H_4)ClI_2^-$ (iso a) $\rightarrow Pt(C_2H_4)ClI+I_b'^-$	2.62
$Pt(C_2H_4)ClI_2^-$ (iso b) $\rightarrow Pt(C_2H_4)I_2+Cl_b^-$	2.86
$Pt(C_2H_4)ClI_2^-$(iso b) $\rightarrow Pt(C_2H_4)ClI+I_a^-$	2.55
$Pt(C_2H_4)ClI_2^-$ (iso b) $\rightarrow Pt(C_2H_4)ClI+I_b'^-$	2.93

Table S6. The binding energies (BEs) of NH_3 and C_2H_4 within the $PtClX_2^-$ (X=Cl, Br, I), calculated at the B3LYP-D3(BJ)/aug-cc-pVTZ(-pp) level of theory. The BEs were corrected for BSSE and ZPE.

different channels	BEs (ev)	different channels	BEs (ev)
$Pt(NH_3)Cl_3^- \rightarrow PtCl_3^- + NH_3$	1.48	$Pt(C_2H_4)Cl_3^- \rightarrow PtCl_3^- + C_2H_4$	1.98
$Pt(NH_3)ClBr_2^-$ (iso a)$\rightarrow PtClBr_2^- + NH_3$	1.49	$Pt(C_2H_4)ClBr_2^-$ (iso a)$\rightarrow PtClBr_2^- + C_2H_4$	2.26
$Pt(NH_3)ClBr_2^-$ (iso b)$\rightarrow PtClBr_2^- + NH_3$	1.39	$Pt(C_2H_4)ClBr_2^-$ (iso b)$\rightarrow PtClBr_2^- + C_2H_4$	2.14
$Pt(NH_3)ClI_2^-$(iso a)$\rightarrow PtClI_2^- + NH_3$	1.47	$Pt(C_2H_4)ClI_2^-$ (iso a)$\rightarrow PtClI_2^- + C_2H_4$	2.27
$Pt(NH_3)ClI_2^-$ (iso b)$\rightarrow PtClI_2^- + NH_3$	1.22	$Pt(C_2H_4)ClI_2^-$(iso b)$\rightarrow PtClI_2^- + C_2H_4$	1.93