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Supporting Information

Internal charge-transfer in metal-catalyzed oxidative addition reaction turns an inhibitive electric field stimulus to catalytic.

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Computational Details

The geometry optimizations and energy calculations for the Pt^{II}-catalyzed C-H activation reaction were conducted using Gaussian 16 programs.[1] The optimization of the transition states (**TS**s) and reaction complexes (**RC**s) geometries was performed using the B3LYP (DFT) level of theory[2] with the Def2SVP[3,4] basis set (B1). SMD solvation model with water as a solvent was used for geometrical optimization.[5] The true minima and the first-order saddle points of the **RC**s and **TS**s respectively were validated via frequency calculations. No imaginary vibrations were detected for the **RC**s while optimized **TS**s displayed one imaginary frequency along the reaction axis. Further verification of the **TS**s were conducted using the intrinsic reaction coordinate (IRC) calculations.[6,7] Oriented external electric field (EEF) calculations were performed by a single point calculations on the B1 optimized geometries at the ωB97xD/Def2TZVP level of theory and basis sets (B2) along with SMD solvation. Grimme's D3 dispersion correction was included during the geometry optimization.[8]

The B1 optimized geometries of the **RC**s and **TS**s of $PtCl_2(L)(CH_4)$ model systems with Ph and CH_3 groups as *trans*-ligands were re-evaluated for EEF analysis using single point with the MP2 level of theory and Def2TZVP basis set.[9] Only marginal variation in the Electrostatic Resistance Point (ERP) values (from **100.2** mV/Å to **90.15** mV/Å for Ph_{trans}-Pt^{II}-CH_4 and from **0.6** mV/Å to **0.13** mV/Å for Me_{trans}-Pt^{II}-CH_4 were detected when compared to the results from ωB97xD functional (Table S1, S2 and S7). EEF analysis for the Me_{trans}-Pt^{II}-CH_4 system using B3LYP as well as M06-L functional[10] with Def2TZVP basis set (Table S7) also provided negligible deviation in the ERP values. SMD solvation model with water was used for the geometrical optimization and energy calculations. The solvation model under water as the solvent was applied due to the popular usage of water as a solvent for Shilov type C-H activation reactions.[11,12] EEF correlation with the gas-phase optimized geometries under B1 level of theory (Table S8) for the CH_3-$PtCl_2$-(CH_4) system were undertaken with ωB97xD/Def2TZVP and MP2/Def2TZVP level of theories and basis sets. The variations were negligible as in the absence of solvation model the ERP of Me_{trans}-Pt^{II}-CH_4 was found to change from **0.6** mV/Å to **-1.24** mV/Å for the ωB97xD functional and from **0.13** mV/Å to **1.59** mV/Å for the MP2 functional. Similar negligible variations were also observed in the solvation analysis of cyclopentadiene-ethylene Diels-Alder reaction.[13]

The energy decomposition analysis of the Me_{trans}-Pt^{II}-CH_4 model was conducted using Multiwfn program.[14,15] The decomposed energies are provided in Table S9. The relative change in Electrostatic energy ($\Delta E_{Electrostatic}$) with EEF provided a direct corelation with the relative change in **TS** energy (ΔTS_{EEF}). Both $\Delta E_{Electrostatic}$ and ΔTS_{EEF} displayed similar characteristics of having a highest energy point with variable EEF. The highest energy point of $\Delta E_{Electrostatic}$ was found to be **-3.02** mV/Å which is close to the ERP value of **0.6** mV/Å. The similarity between the $E_{Electrostatic}$ and the TS_{EEF} shows that the mechanistic swapping of charge-transfer in Pt^{II}-catalyzed C-H activation reaction is a product of the electrostatic interference from the EEF.

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Table S1. Energies in Hartree for **TS**s of all $PtCl_2(L)(CH_4)$ model systems with variable *trans*-ligands under applied EEF (mV/Å). (0.001 a.u. = 51.4 mV/Å)

	Field	0	154.2	308.4	462.6	616.8	771	925.2	1079.4	1233.6
Br-$PtCl_2$-CH_4	$+F_z$	-3654.819	-3654.812	-3654.806	-3654.802	-3654.799	-3654.798	-3654.798	-3654.800	-3654.805
	$-F_z$		-3654.828	-3654.839	-3654.851	-3654.864	-3654.879	-3654.895	-3654.913	-3654.932
CO-$PtCl_2$-CH_4	$+F_z$	-1193.734	-1193.735	-1193.737	-1193.741	-1193.745	-1193.751	-1193.759	-1193.767	-1193.777
	$-F_z$		-1193.735	-1193.737	-1193.740	-1193.745	-1193.752	-1193.759	-1193.769	-1193.780
C_2H_4-$PtCl_2$-CH_4	$+F_z$	-1159.005	-1159.007	-1159.011	-1159.017	-1159.024	-1159.032	-1159.043	-1159.055	-1159.068
	$-F_z$		-1159.004	-1159.004	-1159.006	-1159.010	-1159.015	-1159.022	-1159.030	-1159.041
CH_3-$PtCl_2$-CH_4	$+F_z$	-1120.441	-1120.442	-1120.444	-1120.449	-1120.455	-1120.462	-1120.472	-1120.483	-1120.497
	$-F_z$		-1120.442	-1120.444	-1120.449	-1120.455	-1120.462	-1120.472	-1120.483	-1120.497
Cl-$PtCl_2$-CH_4	$+F_z$	-1540.814	-1540.806	-1540.800	-1540.795	-1540.791	-1540.789	-1540.788	-1540.789	-1540.791
	$-F_z$		-1540.823	-1540.834	-1540.846	-1540.859	-1540.873	-1540.889	-1540.906	-1540.924
CN-$PtCl_2$-CH_4	$+F_z$	-1173.411	-1173.401	-1173.393	-1173.386	-1173.381	-1173.377	-1173.375	-1173.375	-1173.376
	$-F_z$		-1173.422	-1173.434	-1173.449	-1173.464	-1173.481	-1173.500	-1173.520	-1173.542
Ph-$PtCl_2$-CH_4	$+F_z$	-1312.181	-1312.180	-1312.182	-1312.187	-1312.195	-1312.206	-1312.221	-1312.239	-1312.263
	$-F_z$		-1312.184	-1312.191	-1312.200	-1312.212	-1312.227	-1312.245	-1312.266	-1312.290
OH-$PtCl_2$-CH_4	$+F_z$	-1156.405	-1156.400	-1156.395	-1156.392	-1156.390	-1156.389	-1156.390	-1156.392	-1156.395
	$-F_z$		-1156.412	-1156.420	-1156.429	-1156.440	-1156.451	-1156.464	-1156.477	-1156.492
NO_2-$PtCl_2$-CH_4	$+F_z$	-1285.708	-1285.698	-1285.689	-1285.681	-1285.675	-1285.671	-1285.668	-1285.667	-1285.669
	$-F_z$		-1285.720	-1285.733	-1285.748	-1285.764	-1285.781	-1285.800	-1285.820	-1285.841
NH_3-$PtCl_2$-CH_4	$+F_z$	-1137.011	-1137.016	-1137.023	-1137.030	-1137.039	-1137.049	-1137.060	-1137.073	-1137.086
	$-F_z$		-1137.007	-1137.004	-1137.002	-1137.001	-1137.002	-1137.003	-1137.006	-1137.010

Table S2. Energies in Hartree for the **RC**s of all $PtCl_2(L)(CH_4)$ model systems with variable *trans*-ligands under applied EEF (mV/Å). (0.001 a.u. = 51.4 mV/Å)

	Field	0	154.2	308.4	462.6	616.8	771	925.2	1079.4	1233.6
Br-$PtCl_2$-CH_4	$+F_z$	-3654.838	-3654.831	-3654.826	-3654.822	-3654.819	-3654.818	-3654.819	-3654.821	-3654.825
	$-F_z$		-3654.847	-3654.856	-3654.868	-3654.880	-3654.894	-3654.910	-3654.927	-3654.945
CO-$PtCl_2$-CH4	$+F_z$	-1193.778	-1193.776	-1193.775	-1193.776	-1193.777	-1193.780	-1193.784	-1193.789	-1193.795
	$-F_z$		-1193.782	-1193.786	-1193.792	-1193.799	-1193.808	-1193.818	-1193.829	-1193.841
C_2H_4-$PtCl_2$-CH4	$+F_z$	-1159.044	-1159.046	-1159.048	-1159.052	-1159.057	-1159.064	-1159.072	-1159.082	-1159.093
	$-F_z$		-1159.045	-1159.046	-1159.049	-1159.053	-1159.059	-1159.067	-1159.076	-1159.086
CH_3-$PtCl_2$-CH4	$+F_z$	-1120.502	-1120.501	-1120.502	-1120.503	-1120.507	-1120.511	-1120.517	-1120.524	-1120.533
	$-F_z$		-1120.504	-1120.507	-1120.512	-1120.518	-1120.525	-1120.534	-1120.543	-1120.555
Cl-$PtCl_2$-CH4	$+F_z$	-1540.831	-1540.823	-1540.816	-1540.811	-1540.807	-1540.804	-1540.803	-1540.803	-1540.805
	$-F_z$		-1540.840	-1540.850	-1540.862	-1540.875	-1540.889	-1540.904	-1540.921	-1540.939
CN-$PtCl_2$-CH4	$+F_z$	-1173.455	-1173.444	-1173.434	-1173.425	-1173.418	-1173.413	-1173.408	-1173.406	-1173.404
	$-F_z$		-1173.467	-1173.481	-1173.496	-1173.513	-1173.531	-1173.550	-1173.571	-1173.594
Ph-$PtCl_2$-CH4	$+F_z$	-1312.241	-1312.240	-1312.241	-1312.244	-1312.250	-1312.259	-1312.270	-1312.284	-1312.309
	$-F_z$		-1312.246	-1312.252	-1312.261	-1312.273	-1312.287	-1312.304	-1312.323	-1312.346
OH-$PtCl_2$-CH4	$+F_z$	-1156.421	-1156.414	-1156.408	-1156.404	-1156.401	-1156.399	-1156.398	-1156.398	-1156.400
	$-F_z$		-1156.428	-1156.437	-1156.447	-1156.458	-1156.470	-1156.484	-1156.498	-1156.514
NO_2-$PtCl_2$-CH4	$+F_z$	-1285.738	-1285.728	-1285.719	-1285.712	-1285.707	-1285.703	-1285.700	-1285.699	-1285.701
	$-F_z$		-1285.749	-1285.761	-1285.775	-1285.791	-1285.807	-1285.825	-1285.845	-1285.866
NH_3-$PtCl_2$-CH4	$+F_z$	-1137.034	-1137.039	-1137.045	-1137.052	-1137.059	-1137.068	-1137.078	-1137.090	-1137.102
	$-F_z$		-1137.031	-1137.028	-1137.027	-1137.027	-1137.027	-1137.029	-1137.032	-1137.036

Table S3. Dipole moment along F_z (μ_z) in Debye for the **TS**s of all $PtCl_2(L)(CH_4)$ model systems with variable *trans*-ligands under applied EEF (mV/Å). (0.001 a.u. = 51.4 mV/Å)

	Field	0	154.2	308.4	462.6	616.8	771	925.2	1079.4	1233.6
Br-$PtCl_2$-CH_4	+F_z	6.95	5.67	4.37	3.05	1.68	0.28	-1.16	-2.67	-4.24
	-F_z		8.21	9.45	10.68	11.90	13.12	14.33	15.55	16.77
CO-$PtCl_2$-CH_4	+F_z	-0.05	-1.19	-2.32	-3.44	-4.56	-5.68	-6.81	-7.94	-9.10
	-F_z		1.10	2.28	3.48	4.71	5.97	7.27	8.61	10.00
C_2H_4-$PtCl_2$-CH_4	+F_z	-1.49	-2.77	-4.06	-5.37	-6.69	-8.04	-9.43	-10.87	-12.38
	-F_z		-0.20	1.10	2.41	3.75	5.12	6.53	8.00	9.53
CH_3-$PtCl_2$-CH_4	+F_z	0.00	-1.44	-2.89	-4.35	-5.82	-7.32	-8.86	-10.46	-12.12
	-F_z		1.45	2.89	4.35	5.83	7.34	8.88	10.48	12.15
Cl-$PtCl_2$-CH_4	+F_z	7.24	6.11	4.96	3.78	2.58	1.34	0.06	-1.27	-2.65
	-F_z		8.36	9.46	10.55	11.64	12.72	13.80	14.88	15.96
CN-$PtCl_2$-CH_4	+F_z	8.84	7.59	6.34	5.06	3.77	2.44	1.08	-0.33	-1.81
	-F_z		10.09	11.33	12.58	13.84	15.11	16.41	17.73	19.08
Ph-$PtCl_2$-CH_4	+F_z	1.97	-0.44	-2.91	-5.46	-8.12	-10.96	-14.07	-17.67	-22.24
	-F_z		4.34	6.70	9.05	11.42	13.83	16.31	18.91	21.71
OH-$PtCl_2$-CH_4	+F_z	5.27	4.27	3.25	2.21	1.15	0.06	-1.06	-2.22	-3.44
	-F_z		6.27	7.25	8.23	9.20	10.18	11.16	12.15	13.15
NO_2-$PtCl_2$-CH_4	+F_z	9.48	8.28	7.05	5.77	4.42	3.00	1.48	-0.16	-1.97
	-F_z		10.65	11.79	12.93	14.05	15.18	16.32	17.46	18.63
NH_3-$PtCl_2$-CH_4	+F_z	-4.00	-4.97	-5.95	-6.94	-7.93	-8.95	-9.98	-11.04	-12.13
	-F_z		-3.03	-2.06	-1.09	-0.11	0.89	1.89	2.92	3.98

Table S4. Dipole moment along F_z (μ_z) in Debye for the **RC**s of all $PtCl_2(L)(CH_4)$ model systems with variable *trans*-ligands under applied EEF (mV/Å). (0.001 a.u. = 51.4 mV/Å)

	Field	0	154.2	308.4	462.6	616.8	771	925.2	1079.4	1233.6
Br-$PtCl_2$-CH_4	+F_z	6.49	5.26	4.02	2.76	1.48	0.17	-1.17	-2.56	-4.00
	-F_z		7.71	8.92	10.13	11.33	12.55	13.77	15.01	16.27
CO-$PtCl_2$-CH_4	+F_z	2.32	1.28	0.26	-0.76	-1.77	-2.78	-3.80	-4.83	-5.87
	-F_z		3.36	4.42	5.50	6.60	7.72	8.87	10.06	11.29
C_2H_4-$PtCl_2$-CH_4	+F_z	-0.44	-1.60	-2.76	-3.93	-5.09	-6.27	-7.46	-8.68	-9.92
	-F_z		0.73	1.92	3.12	4.35	5.61	6.91	8.25	9.65
CH_3-$PtCl_2$-CH_4	+F_z	1.20	0.10	-1.00	-2.11	-3.24	-4.40	-5.59	-6.83	-8.13
	-F_z		2.28	3.37	4.47	5.57	6.69	7.84	9.02	10.25
Cl-$PtCl_2$-CH_4	+F_z	7.24	6.15	5.05	3.93	2.79	1.61	0.41	-0.84	-2.14
	-F_z		8.31	9.38	10.44	11.50	12.56	13.63	14.71	15.80
CN-$PtCl_2$-CH_4	+F_z	9.99	8.85	7.70	6.56	5.40	4.23	3.03	1.80	0.53
	-F_z		11.14	12.30	13.47	14.65	15.87	17.11	18.38	19.69
Ph-$PtCl_2$-CH_4	+F_z	2.39	0.30	-1.81	-3.94	-6.11	-8.34	-10.66	-13.11	-77.15
	-F_z		4.48	6.58	8.71	10.88	13.12	15.45	17.91	20.55
OH-$PtCl_2$-CH_4	+F_z	6.13	5.18	4.22	3.24	2.24	1.21	0.15	-0.96	-2.12
	-F_z		7.06	7.99	8.92	9.85	10.78	11.72	12.67	13.64
NO_2-$PtCl_2$-CH_4	+F_z	8.96	7.78	6.58	5.34	4.06	2.73	1.33	-0.15	-1.73
	-F_z		10.11	11.26	12.40	13.54	14.69	15.86	17.06	18.30
NH_3-$PtCl_2$-CH_4	+F_z	-3.49	-4.39	-5.29	-6.20	-7.12	-8.05	-9.00	-9.98	-10.98
	-F_z		-2.59	-1.69	-0.79	0.13	1.07	2.02	3.00	4.02

Table S5. HOMO-LUMO energies in eV for the catalyst ($PtCl_2(L)$) and substrate (CH_4) systems with variable *trans*-ligands under applied EEF (mV/Å). (0.001 a.u. = 51.4 mV/Å)

			Field	0	154.2	308.4	462.6	616.8	771	925.2	1079.4	1233.6
Br-$PtCl_2$-CH_4	**Br-$PtCl_2$**	**HOMO**	+F_z	-0.3001	-0.2990	-0.2980	-0.2502	-0.2498	-0.2500	-0.2507	-0.2519	-0.2537
			-F_z		-0.3013	-0.3025	-0.3038	-0.3051	-0.3065	-0.3079	-0.2737	-0.3108
		LUMO	+F_z	-0.0499	-0.0487	-0.0477	-0.1077	-0.1075	-0.1077	-0.1083	-0.1092	-0.1106
			-F_z		-0.0514	-0.0532	-0.0552	-0.0574	-0.0598	-0.0625	-0.1185	-0.0685
	CH_4	**HOMO**	+F_z	-0.4456	-0.4595	-0.4734	-0.4873	-0.5013	-0.5153	-0.5293	-0.5434	-0.5576
			-F_z		-0.4318	-0.4180	-0.4043	-0.3906	-0.3769	-0.3633	-0.3497	-0.3361
		LUMO	+F_z	0.1342	0.1197	0.1045	0.0886	0.0720	0.0550	0.0374	0.0195	0.0012
			-F_z		0.1479	0.1609	0.1731	0.1845	0.1953	0.2055	0.2151	0.2242
CO-$PtCl_2$-CH_4	**CO-$PtCl_2$**	**HOMO**	+F_z	-0.3451	-0.3438	-0.3427	-0.3416	-0.3407	-0.3399	-0.3392	-0.3386	-0.3381
			-F_z		-0.3464	-0.3478	-0.3493	-0.3509	-0.3526	-0.3544	-0.3563	-0.3582
		LUMO	+F_z	-0.0635	-0.0622	-0.0612	-0.0605	-0.0601	-0.0600	-0.0604	-0.0614	-0.0629
			-F_z		-0.0650	-0.0667	-0.0687	-0.0708	-0.0731	-0.0756	-0.0783	-0.0812
	CH_4	**HOMO**	+F_z	-0.4449	-0.4589	-0.4728	-0.4868	-0.5009	-0.5150	-0.5292	-0.5434	-0.5577
			-F_z		-0.4311	-0.4172	-0.4035	-0.3897	-0.3761	-0.3624	-0.3488	-0.3353
		LUMO	+F_z	0.1348	0.1203	0.1052	0.0894	0.0731	0.0561	0.0388	0.0209	0.0028
			-F_z		0.1485	0.1616	0.1740	0.1858	0.1972	0.2081	0.2186	0.2288
C_2H_4-$PtCl_2$-CH_4	**C_2H_4-$PtCl_2$**	**HOMO**	+F_z	-0.3297	-0.3278	-0.3260	-0.3242	-0.3226	-0.3210	-0.3194	-0.3179	-0.3166
			-F_z		-0.3316	-0.3336	-0.3356	-0.3378	-0.3400	-0.3422	-0.3446	-0.3471
		LUMO	+F_z	-0.0517	-0.0497	-0.0480	-0.0466	-0.0457	-0.0453	-0.0456	-0.0466	-0.0485
			-F_z		-0.0541	-0.0567	-0.0595	-0.0626	-0.0659	-0.0696	-0.0735	-0.0777
	CH_4	**HOMO**	+F_z	-0.4476	-0.4618	-0.4759	-0.4901	-0.5044	-0.5187	-0.5331	-0.5475	-0.5620
			-F_z		-0.4336	-0.4195	-0.4056	-0.3916	-0.3778	-0.3639	-0.3502	-0.3364
		LUMO	+F_z	0.1347	0.1201	0.1047	0.0887	0.0721	0.0549	0.0372	0.0191	0.0007
			-F_z		0.1486	0.1618	0.1744	0.1863	0.1978	0.2088	0.2193	0.2296
CH_3-$PtCl_2$-CH_4	**CH_3-$PtCl_2$**	**HOMO**	+F_z	-0.2830	-0.2820	-0.2811	-0.2805	-0.2800	-0.2798	-0.2798	-0.2801	-0.2807
			-F_z		-0.2841	-0.2854	-0.2868	-0.2883	-0.2900	-0.2917	-0.2936	-0.2956
		LUMO	+F_z	0.0193	0.0199	0.0197	0.0184	0.0160	0.0123	0.0074	0.0016	-0.0050
			-F_z		0.0180	0.0161	0.0136	0.0106	0.0069	0.0025	-0.0029	-0.0097
	CH_4	**HOMO**	+F_z	-0.4620	-0.4783	-0.4946	-0.5109	-0.5272	-0.5435	-0.5598	-0.5760	-0.5923
			-F_z		-0.4458	-0.4296	-0.4134	-0.3972	-0.3811	-0.3650	-0.3490	-0.3330
		LUMO	+F_z	0.1350	0.1182	0.1006	0.0822	0.0631	0.0433	0.0231	0.0024	-0.0187
			-F_z		0.1510	0.1661	0.1804	0.1940	0.2069	0.2193	0.2311	0.2426
Cl-$PtCl_2$-CH_4	**Cl-$PtCl_2$**	**HOMO**	+F_z	-0.3048	-0.3039	-0.3030	-0.3022	-0.2579	-0.2578	-0.2583	-0.2592	-0.2606
			-F_z		-0.3058	-0.3069	-0.3080	-0.3091	-0.3102	-0.3114	-0.3126	-0.3139
		LUMO	+F_z	-0.0521	-0.0513	-0.0507	-0.0504	-0.1103	-0.1104	-0.1108	-0.1116	-0.1126
			-F_z		-0.0532	-0.0544	-0.0558	-0.0574	-0.0592	-0.0611	-0.0631	-0.0653
	CH_4	**HOMO**	+F_z	-0.4418	-0.4553	-0.4689	-0.4825	-0.4961	-0.5098	-0.5235	-0.5373	-0.5511
			-F_z		-0.4283	-0.4149	-0.4015	-0.3882	-0.3748	-0.3616	-0.3483	-0.3351
		LUMO	+F_z	0.1339	0.1197	0.1048	0.0893	0.0731	0.0564	0.0393	0.0217	0.0038
			-F_z		0.14725	0.15989	0.17177	0.18292	0.19339	0.20324	0.21252	0.22132
CN-$PtCl_2$-CH_4	**CN-$PtCl_2$**	**HOMO**	+F_z	-0.3140	-0.3127	-0.3115	-0.3104	-0.3095	-0.3087	-0.3080	-0.3075	-0.3042
			-F_z		-0.3154	-0.3169	-0.3185	-0.3202	-0.3221	-0.3240	-0.3261	-0.3283
		LUMO	+F_z	-0.0217	-0.0208	-0.0203	-0.0202	-0.0208	-0.0220	-0.0241	-0.0271	-0.0312
			-F_z		-0.0230	-0.0246	-0.0265	-0.0286	-0.0310	-0.0337	-0.0367	-0.0399
	CH_4	**HOMO**	+F_z	0.1349	0.1199	0.1042	0.0877	0.0706	0.0529	0.0347	0.0161	-0.0029
			-F_z		0.1491	0.1626	0.1754	0.1876	0.1992	0.2104	0.2211	0.2315
		LUMO	+F_z	-0.4527	-0.4672	-0.4818	-0.4965	-0.5111	-0.5259	-0.5407	-0.5555	-0.5704
			-F_z		-0.4382	-0.4238	-0.4094	-0.3950	-0.3807	-0.3665	-0.3523	-0.3381
Ph-$PtCl_2$-CH_4	**Ph-$PtCl_2$-CH_4**	**HOMO**	+F_z	-0.2901	-0.2817	-0.2690	-0.2553	-0.2408	-0.2259	-0.2106	-0.1953	-0.1918
			-F_z		-0.2923	-0.2947	-0.2973	-0.3001	-0.3032	-0.3065	-0.3102	-0.3143
		LUMO	+F_z	0.0143	0.0161	0.0171	0.0170	0.0156	0.0126	0.0082	0.0025	-0.0026
			-F_z		0.0116	0.0079	0.0014	-0.0134	-0.0311	-0.0545	-0.0914	-0.1290
	CH_4	**HOMO**	+F_z	-0.4614	-0.4777	-0.4940	-0.5103	-0.5267	-0.5430	-0.5594	-0.5757	-0.5921
			-F_z		-0.4452	-0.4290	-0.4128	-0.3967	-0.3806	-0.3646	-0.3486	-0.3327
		LUMO	+F_z	0.1351	0.1183	0.1007	0.0823	0.0633	0.0436	0.0234	0.0028	-0.0182
			-F_z		0.1510	0.1661	0.1804	0.1940	0.2069	0.2194	0.2313	0.2429

OH-$PtCl_2$-CH_4	**OH-$PtCl_2$**	**HOMO**	+F_z	-0.3013	-0.3005	-0.2997	-0.2991	-0.2985	-0.2980	-0.2955	-0.2931	-0.2910
			-F_z		-0.3023	-0.3033	-0.3044	-0.3055	-0.3068	-0.3081	-0.3094	-0.3109
		LUMO	+F_z	-0.0265	-0.0265	-0.0269	-0.0277	-0.0291	-0.0310	-0.0336	-0.0368	-0.0407
			-F_z		-0.0268	-0.0275	-0.0284	-0.0295	-0.0310	-0.0326	-0.0346	-0.0369
	CH_4	**HOMO**	+F_z	-0.4429	-0.4565	-0.4702	-0.4839	-0.4976	-0.5114	-0.5252	-0.5390	-0.5529
			-F_z		-0.4294	-0.4159	-0.4024	-0.3889	-0.3755	-0.3621	-0.3488	-0.3355
		LUMO	+F_z	0.1338	0.1195	0.1045	0.0888	0.0725	0.0556	0.0383	0.0205	0.0025
			-F_z		0.1473	0.1601	0.1720	0.1831	0.1936	0.2034	0.2126	0.2212
NO_2-$PtCl_2$-CH_4	**NO_2-$PtCl_2$**	**HOMO**	+F_z	-0.3121	-0.3106	-0.3090	-0.3074	-0.3060	-0.3047	-0.3035	-0.3025	-0.3017
			-F_z		-0.3139	-0.3156	-0.3174	-0.3192	-0.3211	-0.3230	-0.3252	-0.3274
		LUMO	+F_z	-0.0371	-0.0360	-0.0352	-0.0347	-0.0347	-0.0352	-0.0362	-0.0378	-0.0400
			-F_z		-0.0385	-0.0401	-0.0420	-0.0440	-0.0462	-0.0527	-0.0627	-0.0727
	CH_4	**HOMO**	+F_z	-0.4480	-0.4622	-0.4764	-0.4906	-0.5049	-0.5192	-0.5336	-0.5480	-0.5624
			-F_z		-0.4339	-0.4198	-0.4057	-0.3917	-0.3777	-0.3638	-0.3499	-0.3360
		LUMO	+F_z	0.1346	0.1198	0.1042	0.0880	0.0712	0.0538	0.0359	0.0176	-0.0010
			-F_z		0.1486	0.1618	0.1743	0.1861	0.1972	0.2077	0.2177	0.2272
NH_3-$PtCl_2$-CH_4	**NH_3-$PtCl_2$**	**HOMO**	+F_z	-0.3142	-0.3133	-0.3125	-0.3119	-0.3113	-0.3108	-0.3105	-0.3103	-0.3103
			-F_z		-0.3151	-0.3162	-0.3173	-0.3185	-0.3198	-0.3212	-0.3227	-0.3243
		LUMO	+F_z	-0.0434	-0.0431	-0.0431	-0.0435	-0.0443	-0.0455	-0.0473	-0.0497	-0.0528
			-F_z		-0.0440	-0.0449	-0.0460	-0.0475	-0.0492	-0.0514	-0.0540	-0.0573
	CH_4	**HOMO**	+F_z	-0.4411	-0.4545	-0.4680	-0.4815	-0.4951	-0.5087	-0.5224	-0.5361	-0.5498
			-F_z		-0.4277	-0.4143	-0.4010	-0.3877	-0.3745	-0.3613	-0.3482	-0.3351
		LUMO	+F_z	0.1339	0.1199	0.1051	0.0896	0.0736	0.0570	0.0399	0.0225	0.0047
			-F_z		0.1473	0.1599	0.1717	0.1829	0.1934	0.2033	0.2126	0.2215

Table S6. The values of ERP, maximum barrier under EEF, and μ_z for pristine reaction for $PtCl_2(L)(CH_4)$ systems with variable *trans*-ligands. (0.001 a.u. = 51.4 mV/Å)

***trans*-ligand (L)**	**∆E for $PtCl_2(L)(CH_4)$**	**Charge-transfer at Pristine conditions**	**ERP** (mV/Å)	**Maximum inhibition on ∆E w.r.t EEF**	**μ_z for pristine reaction**
Br	10.59	LMCT	799.1	944.92	6.9503
CO	25.97	LMCT	7.9	-*a*-	-0.0519
C_2H_4	22.88	LMCT	-171.5	-*a*-	-1.4856
CH_3	35.50	MLCT	0.6	-498.22	0.0035
Cl	8.96	LMCT	938.1	0	7.2402
CN	25.73	MLCT	1058.8	-*a*-	8.8426
Ph	35.62	MLCT	100.2	-242.5	1.9682
OH	9.51	LMCT	776.6	-*a*-	5.2732
NO_2	17.06	LMCT	1101.7	1144.55	9.4777
NH_3	12.87	LMCT	-627.6	-*a*-	-3.9995

-*a*- The maximum inhibition on barrier energy (∆E) under applied EEF were found to be beyond 1400 mV/Å, which is the experimentally tested limit. Experimental simulation of EEF on organocatalytic reactions were tested at electric field strength of +/- 260 mV/Å (0.005 a.u.) whereas the highest strength of electric field strength measured in enzymes was 1400 mV/Å (0.027 a.u.).[16-19]

Table S7. Single point energies in Hartree for the **RC**s and **TS**s of $PtCl_2(L)(CH_4)$ model systems with Ph and CH_3 groups as *trans*-ligands under MP2, M06-L and B3LYP level of theories with Def2TZVP basis set along with their corresponding ERP values under applied EEF (mV/Å). Geometries optimized at the B1 level of theory is used for single point calculations. (0.001 a.u. = 51.4 mV/Å).

	MP2/Def2TZVP		**MP2/Def2TZVP**		**M06-L/Def2TZVP**		**B3LYP/Def2TZVP**	
Field	**Ph-$PtCl_2$-CH_4**		**CH_3-$PtCl_2$-CH_4**		**CH_3-$PtCl_2$-CH_4**		**CH_3-$PtCl_2$-CH_4**	
	TS	RC	TS	RC	TS	RC	TS	RC
-1233.6	-1310.124	-1310.154	-1118.734	-1118.765	-1120.522	-1120.581	-1120.582	-1120.612
-1079.4	-1310.100	-1310.133	-1118.720	-1118.755	-1120.507	-1120.569	-1120.568	-1120.600
-925.2	-1310.080	-1310.114	-1118.708	-1118.746	-1120.495	-1120.559	-1120.556	-1120.590
-771	-1310.062	-1310.098	-1118.699	-1118.738	-1120.485	-1120.550	-1120.546	-1120.581
-616.8	-1310.047	-1310.085	-1118.691	-1118.732	-1120.477	-1120.543	-1120.538	-1120.574
-462.6	-1310.035	-1310.074	-1118.684	-1118.726	-1120.471	-1120.537	-1120.532	-1120.568
-308.4	-1310.026	-1310.066	-1118.680	-1118.723	-1120.467	-1120.533	-1120.527	-1120.563
-154.2	-1310.019	-1310.061	-1118.677	-1118.720	-1120.464	-1120.529	-1120.525	-1120.560
0	-1310.016	-1310.057	-1118.676	-1118.719	-1120.463	-1120.527	-1120.524	-1120.558
154.2	-1310.015	-1310.057	-1118.677	-1118.719	-1120.464	-1120.527	-1120.525	-1120.558
308.4	-1310.017	-1310.059	-1118.680	-1118.720	-1120.467	-1120.527	-1120.527	-1120.558
462.6	-1310.022	-1310.063	-1118.684	-1118.723	-1120.471	-1120.529	-1120.532	-1120.560
616.8	-1310.030	-1310.070	-1118.691	-1118.727	-1120.477	-1120.533	-1120.538	-1120.564
771	-1310.042	-1310.079	-1118.699	-1118.732	-1120.485	-1120.537	-1120.546	-1120.569
925.2	-1310.057	-1310.092	-1118.708	-1118.739	-1120.495	-1120.544	-1120.556	-1120.575
1079.4	-1310.077	-1310.107	-1118.720	-1118.747	-1120.507	-1120.551	-1120.568	-1120.583
1233.6	-1310.101	-1310.072	-1118.734	-1118.757	-1120.521	-1120.560	-1120.581	-1120.593
ERP values	**90.15** mV/Å		**0.13** mV/Å		**0.76** mV/Å		**0.52** mV/Å	

Table S8. Energies in Hartree for the gas-phase optimized **RC**s and **TS**s of Me_{trans}-Pt^{II}-CH_4 under ωB97xd and MP2 level of theories with Def2TZVP basis set along with their corresponding ERP values under applied EEF (mV/Å). Geometries optimized at the B1 level of theory is used for single point calculations. (0.001 a.u. = 51.4 mV/Å)

Field	ωB97xD/Def2TZVP		MP2/Def2TZVP	
	TS	RC	TS	RC
-1233.6	-1120.408	-1120.468	-1118.649	-1118.686
-1079.4	-1120.399	-1120.460	-1118.640	-1118.679
-925.2	-1120.392	-1120.452	-1118.632	-1118.672
-771	-1120.386	-1120.446	-1118.626	-1118.666
-616.8	-1120.381	-1120.441	-1118.621	-1118.661
-462.6	-1120.377	-1120.436	-1118.617	-1118.658
-308.4	-1120.374	-1120.433	-1118.614	-1118.655
-154.2	-1120.373	-1120.430	-1118.612	-1118.653
0	-1120.372	-1120.429	-1118.612	-1118.652
154.2	-1120.373	-1120.428	-1118.612	-1118.652
308.4	-1120.374	-1120.428	-1118.614	-1118.652
462.6	-1120.377	-1120.430	-1118.617	-1118.654
616.8	-1120.381	-1120.432	-1118.621	-1118.657
771	-1120.386	-1120.435	-1118.626	-1118.661
925.2	-1120.392	-1120.439	-1118.632	-1118.665
1079.4	-1120.399	-1120.444	-1118.640	-1118.671
1233.6	-1120.408	-1120.451	-1118.648	-1118.678
	-1.24 mV/Å		**1.59 mV/Å**	

Table S9. Energies in Hartree for the **TS** of Me_{trans}-Pt^{II}-CH_4 using energy decomposition analysis under applied EEF (mV/Å). (0.001 a.u. = 51.4 mV/Å)

Field	E_{Steric}	$E_{Electrostatic}$	$E_{Quantum}$
-1233.6	14556.324	-2077.984	-13598.792
-925.2	14556.296	-2077.937	-13598.799
-616.8	14556.277	-2077.903	-13598.806
-308.4	14556.267	-2077.882	-13598.812
0	14556.263	-2077.875	-13598.813
308.4	14556.266	-2077.882	-13598.811
616.8	14556.276	-2077.904	-13598.804
925.2	14556.293	-2077.938	-13598.796
1233.6	14556.320	-2077.985	-13598.788

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Fig. S1. Effect of EEF on the relative energies of **TS**s and **RC**s of $PtCl_2(L)(CH_4)$ C-H activation reaction, where L corresponds to the *trans*-ligands. a) Plot between relative change in **TS** energies for each system to pristine **TS** (ΔTS_{EEF}) to the applied EEF. b) Plot between relative change in **RC** energies for each system to pristine **RC** (ΔRC_{EEF}) to the applied EEF. (0.001 a.u. = 51.4 mV/Å)

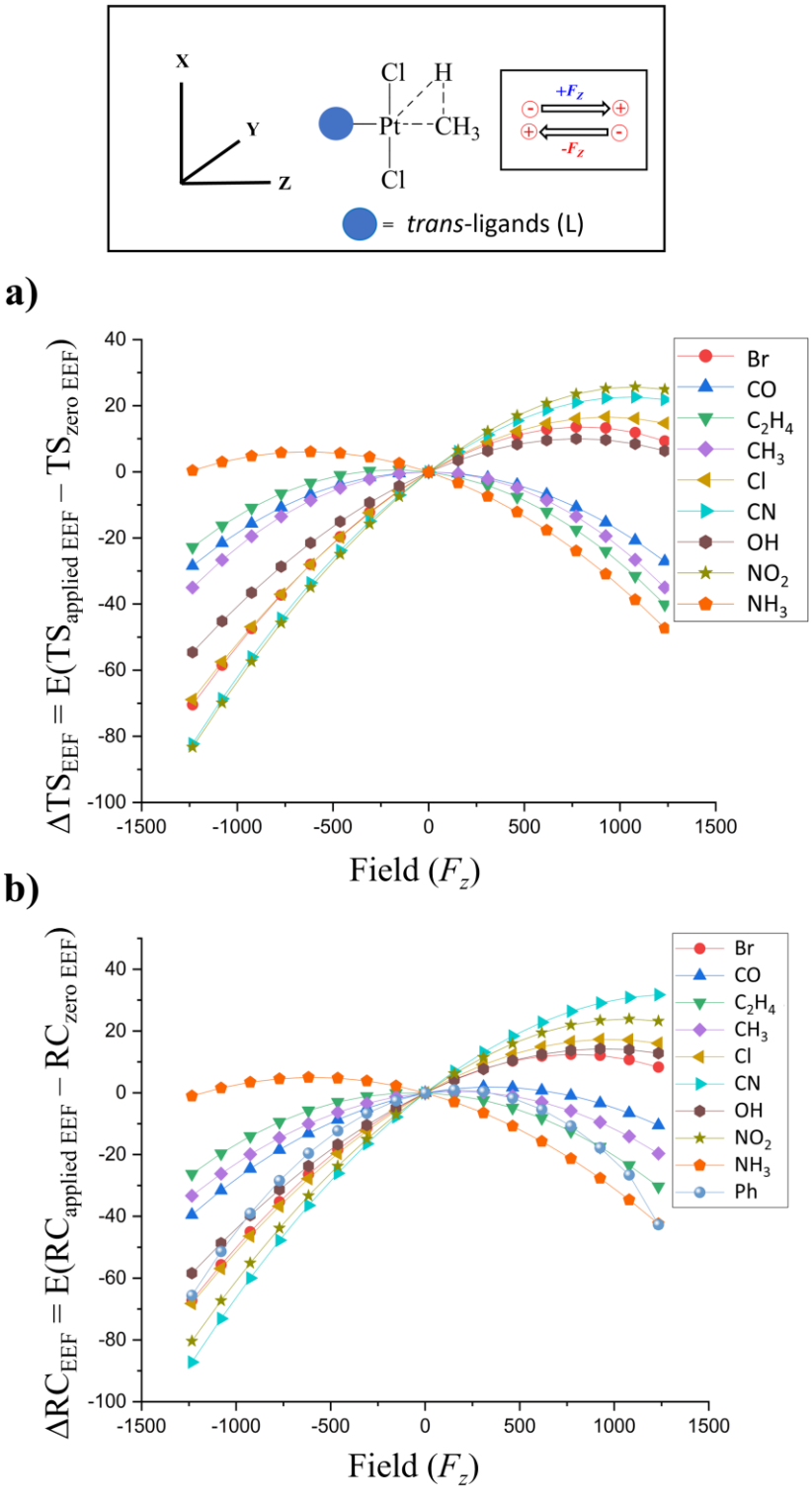
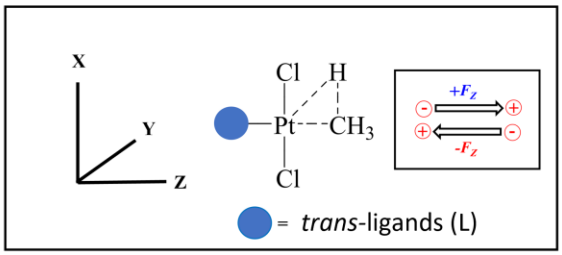
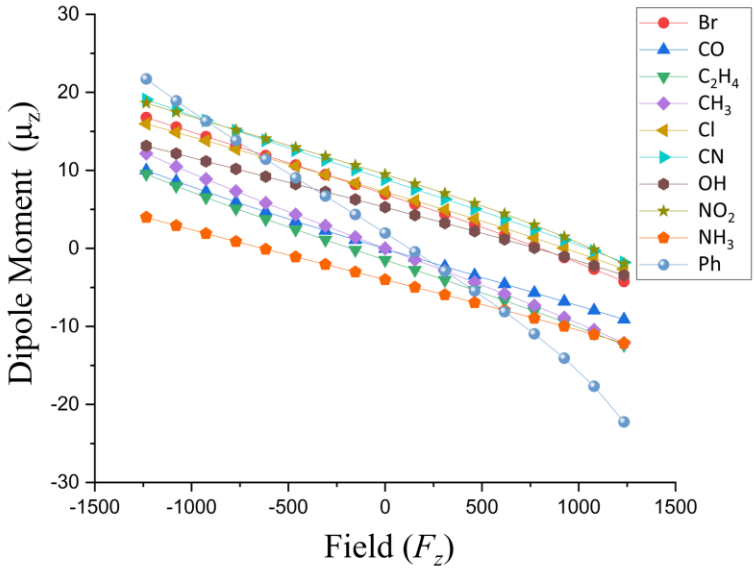


Fig. S2. Effect of EEF on the dipole moment of **TS**s and **RC**s of $PtCl_2(L)(CH_4)$ C-H activation reaction, where L corresponds to the *trans*-ligands. a) Plot between relative change in **TS** dipole moment for each system to the applied EEF. b) Plot between relative change in **RC** dipole moment for each system to the applied EEF. (0.001 a.u. = 51.4 mV/Å)



a)



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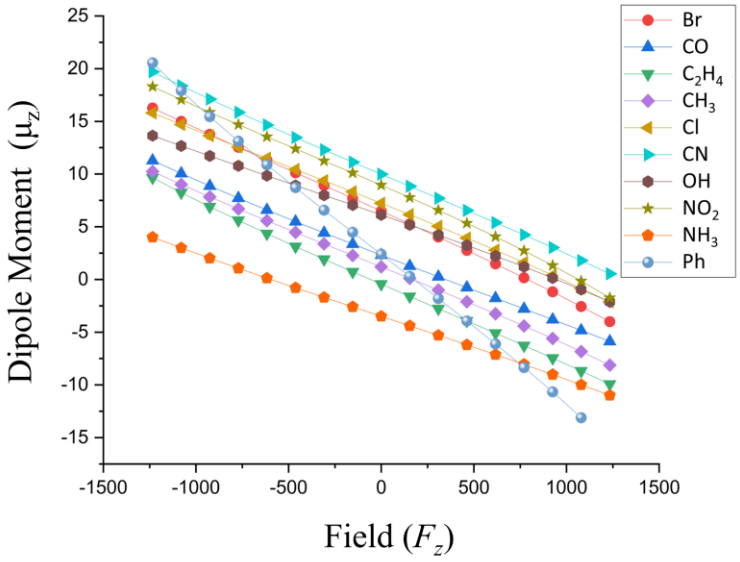


Fig. S3. Mechanistic crossover between the charge-transfer process in the oxidative addition reaction of CO_{trans}-Pt^{II}-CH_4 complex in the presence of variable EEF. (0.001 a.u. = 51.4 mV/Å)

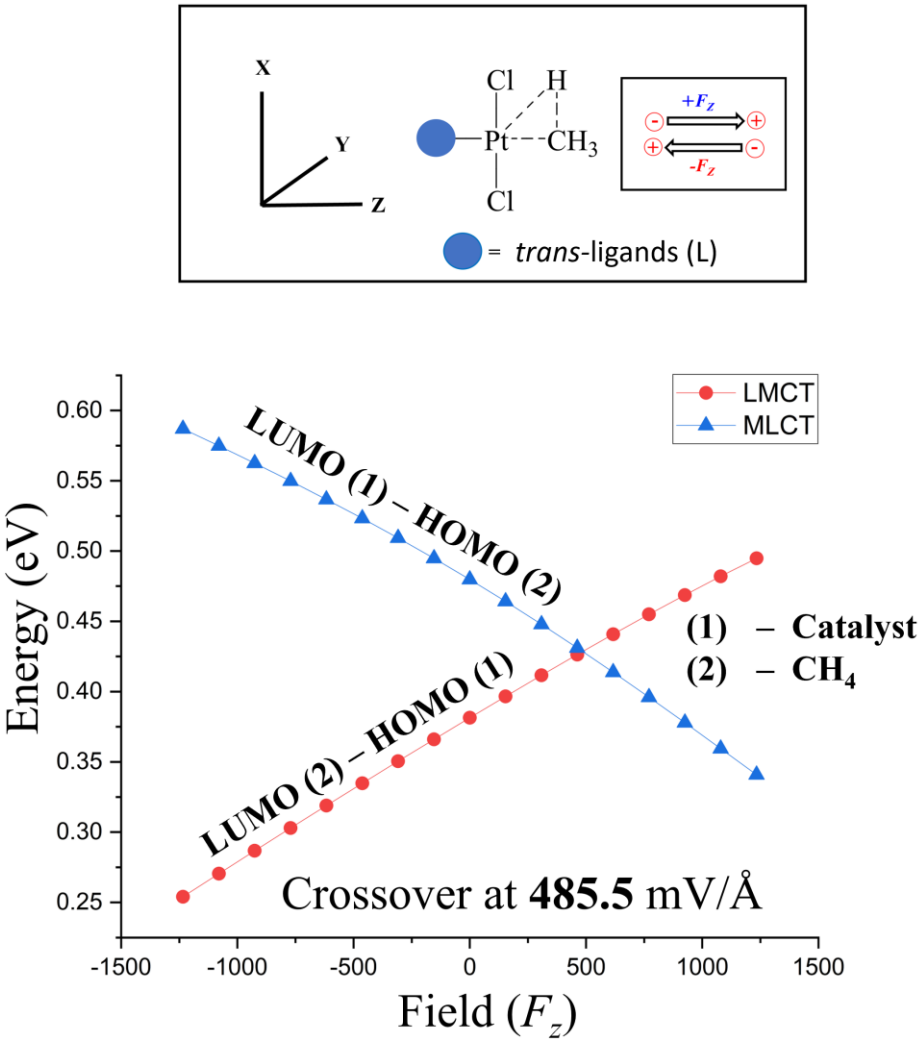


Fig. S4. Effect of EEF on the barrier energy (ΔE) of $PtCl_2(L)(CH_4)$ catalyzed C-H activation reaction, where L corresponds to the *trans*-ligands. a) Plot between ΔE to the applied EEF for $PtCl_2(Ph)(CH_4)$ C-H activation. b) Plot between ΔE for each system to the applied EEF for $PtCl_2(Ph)(CH_4)$ catalyzed C-H activation reaction. (0.001 a.u. = 51.4 mV/Å)

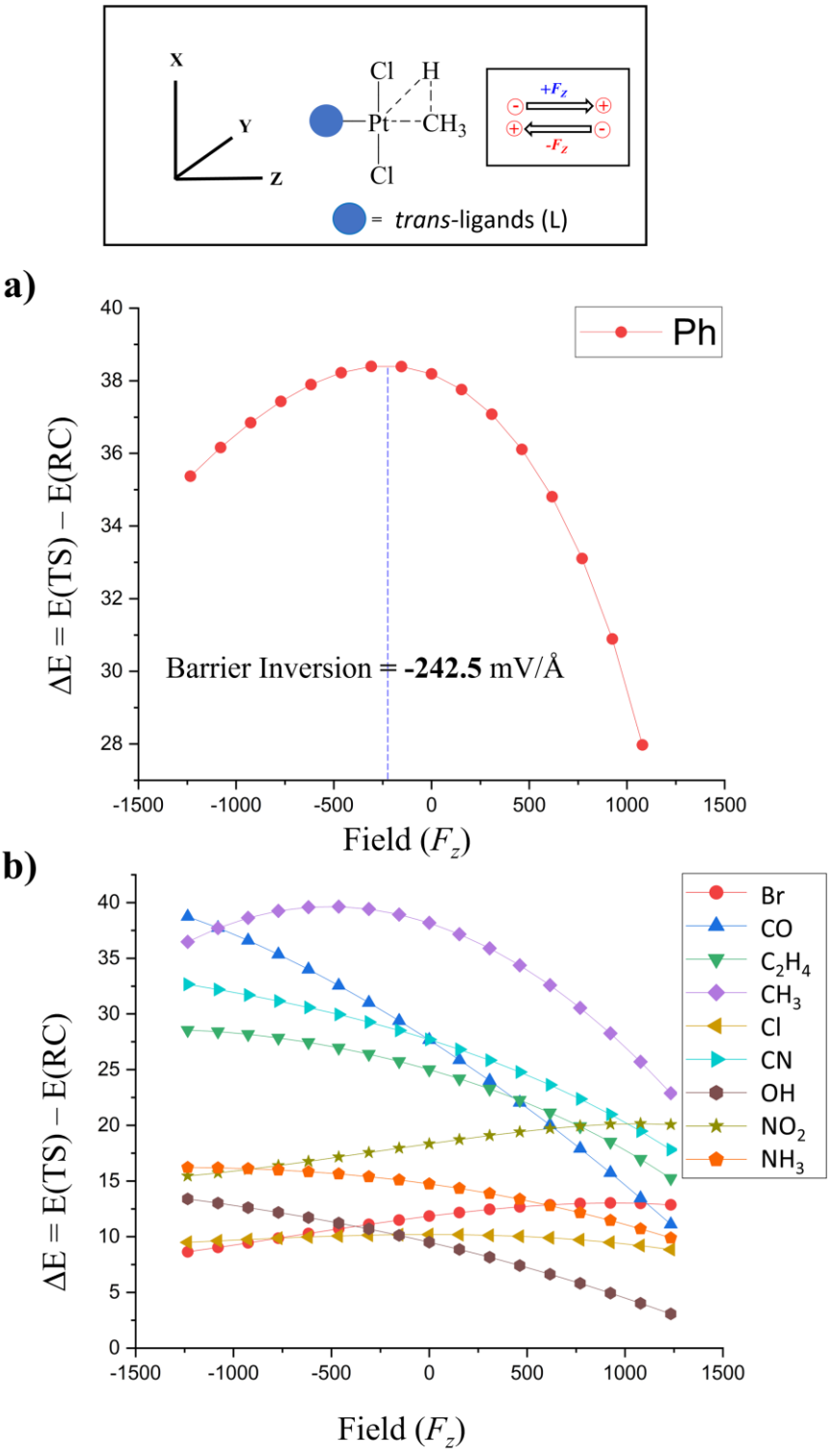
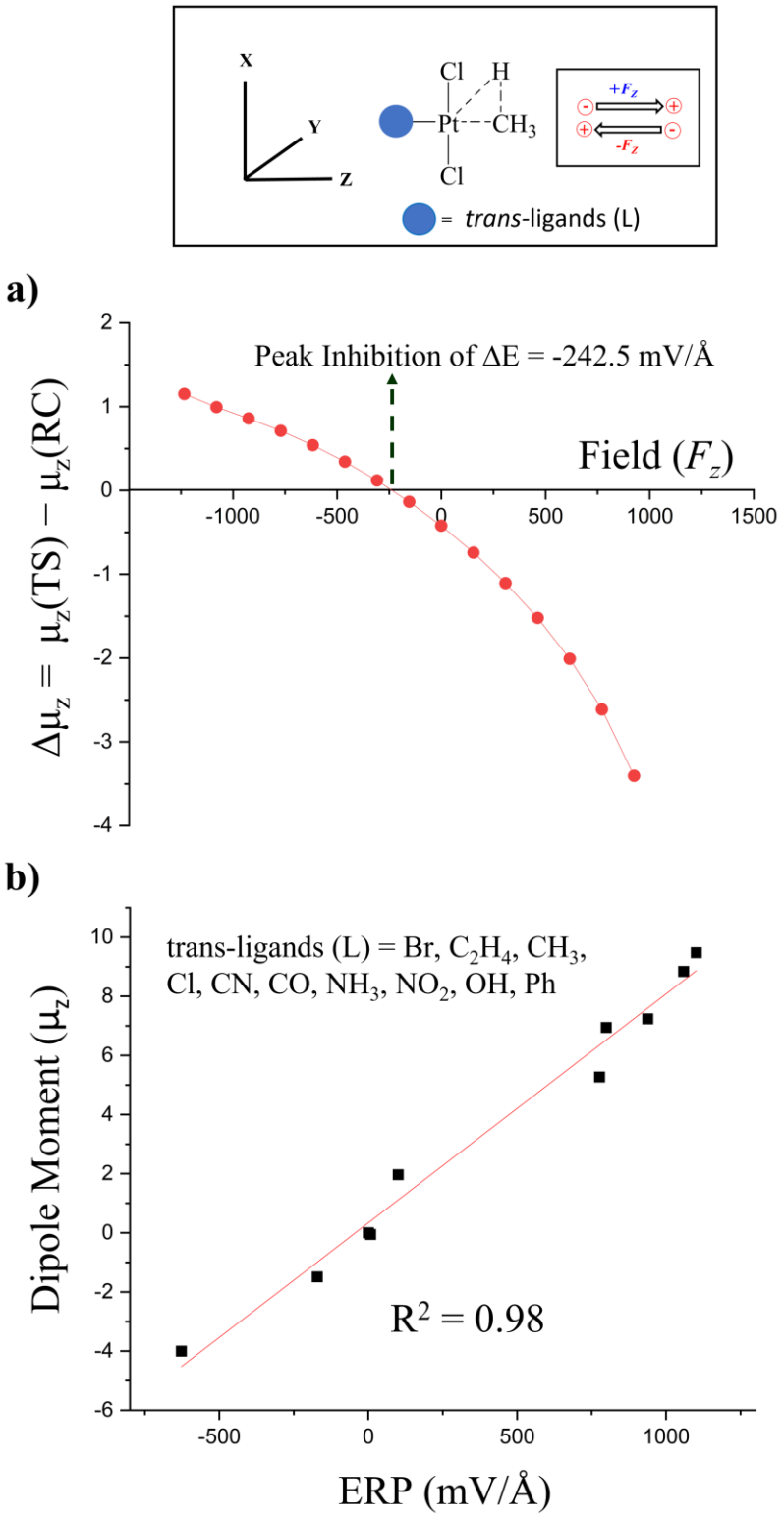


Fig. S5. Correlation between the change in dipole moment along the reaction axis ($\Delta\mu_z$) with EEF and in dipole moment along the reaction axis (μ_z) for the pristine reaction with their ERP values. a) Plot between the change in dipole moment along the reaction axis ($\Delta\mu_z$) and the applied EEF for Ph_{trans}-Pt^{II}-catalyzed C-H activation. b) Correlation between the dipole moment along the reaction axis (μ_z) of the pristine $PtCl_2(L)$-catalyzed C-H activation reaction, where L corresponds to the *trans*-ligands, to their corresponding ERP (mV/Å) values.



Full citation of Gaussian 16.

Gaussian 16, Revision C.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2016.

Cartesian Coordinates of the Optimized Geometries $PtCl_2(L)(CH_4)$ systems with variable *trans*-ligands.

The Cartesian coordinates of the **RC**s optimized at the B3LYP/Def2SVP with Grimme's D3 dispersion correction and their corresponding energies re-calculated at ωB97xD/Def2TZVP using SMD model with water as solvent are given in Hartree.

Br_{trans}-$PtCl_2$-CH_4

Energy = -3654.838 Hartree

Pt	0.00000000	0.00000000	0.00000000
C	0.00000000	0.00000000	2.50718800
Cl	2.36091700	0.00000000	0.08949700
Cl	-2.36089500	-0.01569800	0.08940800
H	0.00250700	-0.81077200	1.70677600
H	-0.91400400	-0.20241600	3.08039100
H	0.91490800	-0.19701100	3.08082800
H	-0.00303300	1.04919500	2.18145800
Br	-0.00083600	0.26798100	-2.41405600

$(C_2H_4)_{trans}$-$PtCl_2$-CH_4

Energy = - 1159.044 Hartree

Pt	0.00000000	0.00000000	0.00000000
C	0.00000000	0.00000000	2.49439000
Cl	2.34667400	0.00000000	0.04112000
H	-0.91602000	0.00087400	3.09841300
H	0.00017500	-0.95894400	1.92584300
H	-0.00017500	0.95751900	1.92313700
Cl	-2.34667400	-0.00070900	0.04112000
H	0.91601900	0.00121100	3.09841300

C	-0.00013200	0.71003600	-1.99536600
C	0.00013100	-0.70190600	-1.99823400
H	0.92920100	1.25966900	-2.16847800
H	-0.92967500	1.25931800	-2.16847600
H	-0.92921400	-1.25074400	-2.17377600
H	0.92968300	-1.25039400	-2.17377500

$(CH_3)_{trans}$-$PtCl_2$-CH_4

Energy = -1120.502 Hartree

Pt	0.00000000	0.00000000	0.00000000
C	0.00000000	0.00000000	2.89065900
Cl	2.35564300	0.00000000	0.07275400
H	-0.90543200	0.09717900	3.50613400
H	-0.00466400	-0.98407200	2.39801000
H	0.00465800	0.82834500	2.15551400
Cl	-2.35551300	0.02382800	0.07313500
H	0.90563800	0.08802500	3.50721700
C	-0.00056400	-0.07807900	-2.01190000
H	-0.90125000	0.41417900	-2.40973000
H	0.90503600	0.40495800	-2.40987600
H	-0.00600700	-1.13966600	-2.31691900

Cl $_{trans}$-$PtCl_2$-CH_4

Energy = -1540.831 Hartree

Pt	0.00000000	0.00000000	0.00000000
C	0.00000000	0.00000000	2.45483000
Cl	2.36152300	0.00000000	0.06285400
Cl	-2.36116500	0.04110100	0.06251600
H	0.00736000	0.81749200	1.64811200
H	0.91660200	0.20976500	3.02066200
H	-0.91278900	0.22606700	3.02056400
H	-0.00940500	-1.05753400	2.15994300
Cl	-0.00284700	-0.34466800	-2.28222000

CN $_{trans}$-$PtCl_2$-CH_4

Energy = -1173.455 Hartree

Pt	0.00000000	0.00000000	0.00000000
C	0.00000000	0.00000000	2.56753600
Cl	2.35313700	0.00000000	0.05724000
Cl	-2.35313700	0.00000000	0.05724000
H	0.00000000	-0.94112800	1.97840400
H	-0.91392900	-0.00001400	3.17516500
H	0.91392800	-0.00001400	3.17516500
H	0.00000000	0.94114700	1.97843700
C	0.00000000	0.00001500	-1.89856600
N	0.00000000	0.00002400	-3.06975300

CO $_{trans}$-$PtCl_2$-CH_4

Energy = -1193.778 Hartree

Pt	0.00000000	0.00000000	0.00000000
C	0.00000000	0.00000000	2.45860100
Cl	2.35121800	0.00000000	0.05841800
Cl	-2.35120800	-0.00015700	0.05871600
H	0.00005400	-0.96413500	1.89814000
H	-0.91895400	-0.00000600	3.05759100
H	0.91873700	-0.00007800	3.05792100
H	0.00012300	0.96418100	1.89823700
C	-0.00012500	0.00000900	-1.83290000
O	-0.00000600	0.00000800	-2.96967200

Ph $_{trans}$-$PtCl_2$-CH_4

Energy = -1312.241 Hartree

Pt	0.00000000	0.00000000	0.00000000
C	0.00000000	0.00000000	2.88108500
Cl	2.35298800	0.00000000	0.10552600
H	-0.89759200	0.12659700	3.50247100
H	-0.06015600	-0.96991800	2.36341700
H	0.04765700	0.84924400	2.17318800
Cl	-2.35200400	-0.00265300	0.11339800
H	0.91138400	0.02004000	3.49485300

C	-0.00416100	-0.04536400	-1.96805700
C	0.73904900	-1.01629500	-2.66504300
C	-0.75141700	0.89170000	-2.70585100
C	0.72750700	-1.04983000	-4.06444200
H	1.34057700	-1.74080500	-2.11452000
C	-0.74884700	0.85837100	-4.10527100
H	-1.34940400	1.64187900	-2.18677100
C	-0.01303900	-0.11270400	-4.79221100
H	1.30927800	-1.81398500	-4.58771000
H	-1.33400500	1.59681000	-4.66068300
H	-0.01666500	-0.13886700	-5.88471200

OH $_{trans}$-$PtCl_2$-CH_4

Energy = -1156.421 Hartree

Pt	0.00000000	0.00000000	0.00000000
C	0.00000000	0.00000000	2.47845500
Cl	2.36612700	0.00000000	0.00948100
H	-0.92090200	0.24624800	3.02217700
H	-0.00307900	-1.06380300	2.21402000
H	0.03085900	0.79123000	1.64597200
Cl	-2.35930200	-0.00982100	-0.06598100
H	0.90094600	0.23001400	3.06194900
O	-0.02815000	-0.29212200	-1.95292400
H	-0.98046800	-0.31654900	-2.14905000

(NO_2) $_{trans}$-$PtCl_2$-CH_4

Energy = -1285.738 Hartree

Pt	0.00000000	0.00000000	0.00000000
C	0.00000000	0.00000000	2.54946900
Cl	2.36133500	0.00000000	0.02985900
H	-0.91896400	-0.17237300	3.12424700
H	-0.00051900	-0.81563500	1.76726700
H	0.01278200	1.03948200	2.19447600
Cl	-2.36105700	-0.00151000	0.03375500
H	0.90808300	-0.19067500	3.13603800
N	-0.00215100	0.21251200	-1.95472500

O	0.26840000	-0.75371400	-2.65766800
O	-0.27432700	1.31145100	-2.42442400

$(NH_3)_{trans}$-$PtCl_2$-CH_4

Energy = -1137.034 Hartree

Pt	0.00000000	0.00000000	0.00000000
C	0.00000000	0.00000000	2.43279800
Cl	2.35453700	0.00000000	-0.03849800
H	-0.91259800	0.21537700	3.00235200
H	-0.00812100	-1.05545300	2.12666300
H	0.00638600	0.83417300	1.64644000
Cl	-2.35425700	0.03630800	-0.03858700
H	0.91584900	0.20132400	3.00227300
N	-0.00208700	-0.27435200	-2.00558600
H	-0.00973800	-1.27488300	-2.23417400
H	-0.83122400	0.14551500	-2.43856400
H	0.83338100	0.13278500	-2.43855400

The Cartesian coordinates of the **TS**s optimized at the B3LYP/Def2SVP with Grimme's D3 dispersion correction and their corresponding energies re-calculated at ωB97xD/Def2TZVP using SMD model with water as solvent are given in Hartree.

Br_{trans}-$PtCl_2$-CH_4

Energy = -3654.819 Hartree

Pt	0.00000000	0.00000000	0.00000000
C	0.00000000	0.00000000	2.12694700
Cl	2.36550100	0.00000000	0.03826200
H	-0.89968100	0.43409200	2.58078200
H	-0.01578700	-1.09494300	2.24238100
H	0.01722200	1.19553000	0.99422000
Cl	-2.36451900	0.06814500	0.03826200
H	0.91182500	0.40797500	2.58077600
Br	-0.01369000	-0.95028900	-2.34447600

$(C_2H_4)_{trans}$-$PtCl_2$-CH_4

Energy = -1159.005 Hartree

Pt	0.00000000	0.00000000	0.00000000
C	0.00000000	0.00000000	2.10377200
Cl	2.35176000	0.00000000	-0.01256200
H	-0.91253500	0.40770000	2.55393100
H	0.01054500	-1.09969400	2.19712600
H	-0.01158700	1.24783200	0.92951400
Cl	-2.35135900	-0.04349300	-0.01255200
H	0.90450300	0.42509400	2.55405600
C	-0.00539600	0.60566300	-2.33013400
C	0.00678700	-0.75776100	-2.24782400
H	0.92282700	1.17446700	-2.42895800
H	-0.94361900	1.15781200	-2.42900700
H	-0.92386900	-1.32978600	-2.29874400
H	0.94751500	-1.31307300	-2.29871100

$(CH_3)_{trans}$-$PtCl_2$-CH_4

Energy = -1120.441 Hartree

Pt	0.00000000	0.00000000	0.00000000
C	0.00000000	0.00000000	2.14802500
Cl	2.36294800	0.00000000	0.00155300
H	-0.90895400	0.45676000	2.57659400
H	0.02813100	-1.05420300	2.49106100
H	-0.04243600	1.50901700	-0.03741500
Cl	-2.35921600	-0.13274800	0.00174200
H	0.88332700	0.50459900	2.57651600
C	0.00294200	-0.10712200	-2.14535600
H	-0.90626400	0.32604300	-2.59724800
H	0.88593100	0.37709300	-2.59742300
H	0.03338200	-1.17706400	-2.43537100

Cl $_{trans}$-$PtCl_2$-CH_4

Energy = -1540.814 Hartree

Pt	0.00000000	0.00000000	0.00000000
C	0.00000000	0.00000000	2.12184100

Cl	2.36431500	0.00000000	0.02552900
H	-0.89995800	0.43104900	2.57813600
H	-0.01391700	-1.09528200	2.23417900
H	0.01505800	1.18714300	1.00130700
Cl	-2.36355300	0.05997100	0.02553400
H	0.91062400	0.40804500	2.57812600
Cl	-0.01147200	-0.90411400	-2.21859900

CN $_{trans}$-$PtCl_2$-CH_4

Energy = -1173.411 Hartree

Pt	0.00000000	0.00000000	0.00000000
C	0.00000000	0.00000000	2.09864900
Cl	2.36267400	0.00000000	0.01096500
H	-0.90553500	0.44383700	2.53388700
H	0.00884800	-1.08598900	2.29538400
H	-0.01130000	1.38025200	0.66162600
Cl	-2.36236100	-0.03872000	0.01097400
H	0.89819200	0.45853100	2.53386900
C	0.00309700	-0.37863200	-2.06486900
N	0.00487200	-0.59550400	-3.21451700

CO $_{trans}$-$PtCl_2$-CH_4

Energy = -1193.734 Hartree

Pt	0.00000000	0.00000000	0.00000000
C	0.00000000	0.00000000	2.10152200
Cl	2.35914400	0.00000000	0.01051100
H	-0.91445700	0.41368300	2.54276300
H	0.01811300	-1.09725900	2.21876000
H	-0.01889000	1.28387600	0.86715500
Cl	-2.35806000	-0.06941400	0.01053200
H	0.90004100	0.44349300	2.54348200
C	0.00017500	0.00055400	-2.04969000
O	-0.00154500	0.13243000	-3.17111700

Ph $_{trans}$-$PtCl_2$-CH_4

Energy = -1312.181 Hartree

Pt	0.00000000	0.00000000	0.00000000
C	0.00000000	0.00000000	2.13458200
Cl	2.36248400	0.00000000	0.03317900
H	-0.90769500	0.44888000	2.56946800
H	0.02762000	-1.06571300	2.43325400
H	-0.03712800	1.48879500	0.27229900
Cl	-2.35616900	-0.11828100	0.02571700
H	0.88579800	0.49441100	2.56527600
C	-0.00535100	-0.15429100	-2.13420500
C	0.96623500	-0.91130900	-2.82301100
C	-0.99494300	0.46276100	-2.92938600
C	0.94773900	-1.05760800	-4.21671900
H	1.77276600	-1.38746500	-2.25808000
C	-1.01257100	0.34206000	-4.32444400
H	-1.78620200	1.04118300	-2.44409700
C	-0.04145300	-0.42581300	-4.97725300
H	1.71419800	-1.66207200	-4.71189500
H	-1.79172700	0.84489600	-4.90591600
H	-0.05541800	-0.52924600	-6.06570700

OH $_{trans}$-$PtCl_2$-CH_4

Energy = -1156.405 Hartree

Pt	0.00000000	0.00000000	0.00000000
C	0.00000000	0.00000000	2.11907900
Cl	2.36618300	0.00000000	-0.02525800
H	-0.90809200	0.41580300	2.57588900
H	0.00823100	-1.09339500	2.25775000
H	0.01717900	1.21104600	0.97048000
Cl	-2.35982600	-0.01894000	-0.09041300
H	0.89236700	0.43071500	2.59281300
O	-0.01989800	-0.81926400	-1.84653400
H	-0.96465100	-0.89456600	-2.05795300

$(NO_2)_{trans}$-$PtCl_2$-CH_4

Energy = -1285.708 Hartree

Pt	0.00000000	0.00000000	0.00000000
C	0.00000000	0.00000000	2.09900100
Cl	2.35871300	0.00000000	-0.04688300
H	-0.90596400	0.43774600	2.53746000
H	0.00527300	-1.09077300	2.25726100
H	-0.00391100	1.30800800	0.80112500
Cl	-2.35797400	-0.01868300	-0.04602700
H	0.90088400	0.44693000	2.53864100
N	-0.00024800	-0.63361500	-2.05229600
O	0.00209700	-1.85367000	-2.25261600
O	-0.00312000	0.15571600	-2.99620300

$(NH_3)_{trans}$-$PtCl_2$-CH_4

Energy = -1137.011 Hartree

Pt	0.00000000	0.00000000	0.00000000
C	0.00000000	0.00000000	2.09044200
Cl	2.35303100	0.00000000	-0.06238500
H	-0.90234600	0.44406500	2.52917600
H	-0.00107700	-1.09087500	2.24645800
H	0.00125900	1.29568800	0.82246000
Cl	-2.35302500	0.00488900	-0.06255300
H	0.90322200	0.44228300	2.52917400
N	-0.00079300	-0.73488700	-2.04558800
H	-0.00151700	-1.76038600	-2.05535800
H	-0.83020700	-0.43361400	-2.56375300
H	0.82888600	-0.43480000	-2.56401500

The Cartesian coordinates of the **RC** and **TS** of $(CH_3)_{trans}$-$PtCl_2$-CH_4 optimized under gas phase at the B3LYP/Def2SVP with Grimme's D3 dispersion correction and their corresponding energies re-calculated at ωB97xD/Def2TZVP and MP2/Def2TZVP are given in Hartree.

RC

Energy (ωB97xD/Def2TZVP) = -1120.372 Hartree

Energy (MP2/Def2TZVP) = -1118.612 Hartree

Pt	0.00000000	0.00000000	0.00000000

C	0.00000000	0.00000000	2.78027188
Cl	2.31784198	0.00000000	0.04910855
H	-0.90910455	0.01234708	3.39373945
H	-0.00467549	-0.90959029	2.15885411
H	0.00467280	0.89585132	2.13820216
Cl	-2.31770753	0.02556292	0.04895309
H	0.90910513	0.00292573	3.39385283
C	-0.00003894	-0.02089604	-1.97306721
H	-0.90625480	0.48189786	-2.33903855
H	0.91162625	0.47199811	-2.33897312
H	-0.00578377	-1.07808676	-2.28773838

TS

Energy (ωB97xD/Def2TZVP) = -1120.372 Hartree

Energy (MP2/Def2TZVP) = -1118.612 Hartree

Pt	0.00000000	0.00000000	0.00000000
C	0.00000000	0.00000000	2.11939136
Cl	2.32174878	0.00000000	0.00275637
H	-0.91768251	0.44228558	2.54079219
H	0.03780073	-1.05679414	2.45106006
H	-0.05261934	1.49227123	-0.04947295
Cl	-2.31597732	-0.16363437	0.00266968
H	0.88376104	0.50668244	2.54079489
C	0.00500452	-0.14019570	-2.11474232
H	-0.91155107	0.27335593	-2.56667121
H	0.88991767	0.33735094	-2.56664617
H	0.04325934	-1.21663004	-2.37565711

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