Supporting Information for the Paper Entitled "Trans Effect and Trans Influence: Importance of Metal Transferred Ligand-Ligand Repulsion"

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Table S1. Comparison of reference systems. Results of energy decomposition analysis between $TPtCl_2$ and NH_3 fragments in the reactant (**R**) state of $TPtCl_2NH_3$ (1: T=NH_3, 2: T=PH_3, 3: T=CO, 4: C_2H_4) systems, and between $TPtCl_2$ and $(NH_3)_2$ fragments in the prereactive complex state (**C**). Δ gives the difference between the two reference systems. These Δ values indicate that changing the reference (**R** or **C**) system results only in a constant shift in the values and, thus, does not effect the conclusions one can draw for the differences between systems **1-4**.

	ΔE_{Pauli}	ΔV_{elstat}	ΔE_{oi}	ΔE_{int}
1-R	128.2	-122.6	-60.9	-55.3
2-R	119.8	-109.1	-52.7	-41.9
3-R	126.2	-116.4	-59.3	-49.5
4-R	126.0	-113.4	-55.6	-42.9
1-C	141.9	-139.0	-67.6	-64.7
2-C	135.4	-126.4	-60.3	-51.3
3-C	141.4	-134.6	-66.7	-59.8
4-C	140.8	-129.8	-62.2	-51.2
Δ(**1**)	13.7	-16.4	-6.7	-9.4
Δ(**2**)	15.6	-17.3	-7.7	-9.3
Δ(**3**)	15.2	-18.2	-7.4	-10.4
Δ(**4**)	14.7	-16.4	-6.7	-8.3

Table S2. Interaction energy and its components calculated between fragments T and $PtCl_2NH_3$ for reactants (R) and fragments T and $PtCl_2(NH_3)_2$ for transition states (TS). $\Delta\Delta E_{int}$ represents the interaction energy difference between transition state and reactant. Values are in kcal mol^{-1}. The interaction energies (ΔE_{int}) calculated between fragments T and $PtCl_2NH_3$ differ as much as 32.7 kcal mol^{-1} between structures exaggerating the effect of T on the barrier and indicating that important details remain hidden in the deformation of the fragments (i.e. ΔE_{strain} is in not negligible). Nevertheless, the most critical drawback of using fragments T + $PtCl_2(NH_3)_2$ is that the compared interactions are between different contact atoms, e.g. between Pt and N (NH_3) in **1-TS**, Pt and P (PH_3) in **2-TS** whereas Pt and C (CO) in **3-TS**. In these cases the components of the interaction energy differ so much that no clear, chemically meaningful trends can be anticipated: for example going from N (NH_3 in **1-TS**) to P (PH_3 in **2-TS**) the Pauli repulsion increases by 77.5 kcal mol^{-1}, which is compensated by more attractive orbital (-33.1 kcal mol^{-1}) and electrostatic interactions (-65.1 kcal mol^{-1}). Very recently we introduced and successfully applied a protocol (Pinter, B.; Nagels, N.; Herrebout, W. A.; De Proft, F.; *Chem. Eur. J.* **2013**, *19*, 519) to conceptually scrutinize interactions with different contact atoms by using the *relative* contributions of the components, however, this method can only be applied when ΔE_{strain} is negligible.

	ΔE_{Pauli}	ΔV_{elstat}	ΔE_{oi}	ΔE_{int}	$\Delta\Delta E_{int}$
1-R	128.2	-122.6	-60.9	-55.3	
1-TS	148.2	-128.9	-65.3	**-46.1**	9.3
2-R	182.1	-158.0	-90.8	-66.8	
2-TS	225.7	-194.0	-98.4	**-66.7**	0.1
3-R	212.3	-165.5	-117.7	-70.9	
3-TS	281.6	-213.9	-142.9	**-75.2**	-4.3
4-R	184.1	-142.7	-103.1	-61.7	
4-INT	258.6	-201.3	-136.1	**-78.8**	-17.1

Table S3. Energy barriers $\Delta E^{\ddagger}$ and interaction energy difference between the transition state (intermediate for 4) and the reactant, $\Delta\Delta E^{\ddagger}_{int}$, for the investigated systems with three different basis sets, DZP, TZ2P and QZ4P (small core in all cases) using PBE functional and ZORA for relativistic effects. Values are in kcal mol^{-1}.

		$\Delta E^{\ddagger}$	$\Delta\Delta E^{\ddagger}_{int}$
	DZP	22.1	16.1
1	TZ2P	21.7	16.7
	QZ4P	22.3	17.1
	DZP	8.2	4.7
2	TZ2P	7.6	4.9
	QZ4P	8.6	5.3
	DZP	4.4	0.1
3	TZ2P	3.4	0.4
	QZ4P	4.7	0.8
	DZP	-4.3	-7.3
4	TZ2P	-4.2	-6.9
	QZ4P	-3.9	-6.4

Table S4. Interaction energy, ΔE_{int}, and its components between fragments $TPCl_2$ and NH_3 for the investigated reactants with three different basis sets, DZP, TZ2P and QZ4P (small core in all cases) using PBE functional and ZORA for relativistic effects. Values are in kcal mol^{-1}.

		ΔE_{Pauli}	ΔV_{elstat}	ΔE_{oi}	ΔE_{int}
	DZP	127.8	-121.1	-61.2	-54.5
1-R	TZ2P	128.2	-122.6	-60.9	-55.3
	QZ4P	127.4	-121.9	-61.1	-55.6
	DZP	118.3	-107.4	-51.9	-41.1
2-R	TZ2P	119.8	-109.1	-52.7	-41.9
	QZ4P	119.4	-108.7	-53.0	-42.3
	DZP	124.9	-114.9	-59.0	-49.0
3-R	TZ2P	126.2	-116.4	-59.3	-49.5
	QZ4P	125.5	-116.1	-59.1	-49.7
	DZP	125.5	-112.3	-55.2	-42.0
4-R	TZ2P	126.0	-113.4	-55.6	-42.9
	QZ4P	125.4	-113.0	-55.8	-43.4

Table S5. Interaction energy, ΔE_{int}, and its components between fragments $TPCl_2$ and $(NH_3)_2$ for the investigated transition states with three different basis sets, DZP, TZ2P and QZ4P (small core in all cases) using PBE functional and ZORA for relativistic effects. Values are in kcal mol^{-1}.

		ΔE_{Pauli}	ΔV_{elstat}	ΔE_{oi}	ΔE_{int}
	DZP	88.8	-84.2	-43.1	-38.4
1-TS	TZ2P	89.1	-83.9	-43.9	-38.6
	QZ4P	89.2	-82.9	-44.9	-38.6
	DZP	98.9	-90.0	-45.3	-36.3
2-TS	TZ2P	100.1	-90.4	-46.8	-37.1
	QZ4P	99.1	-88.4	-47.8	-37.1
	DZP	117.2	-108.1	-58.1	-48.9
3-TS	TZ2P	118.1	-107.6	-59.6	-49.1
	QZ4P	116.8	-105.6	-60.1	-48.9
	DZP	128.7	-117.4	-60.6	-49.3
4-TS	TZ2P	129.1	-117.4	-61.5	-49.8
	QZ4P	127.8	-115.0	-62.6	-49.8

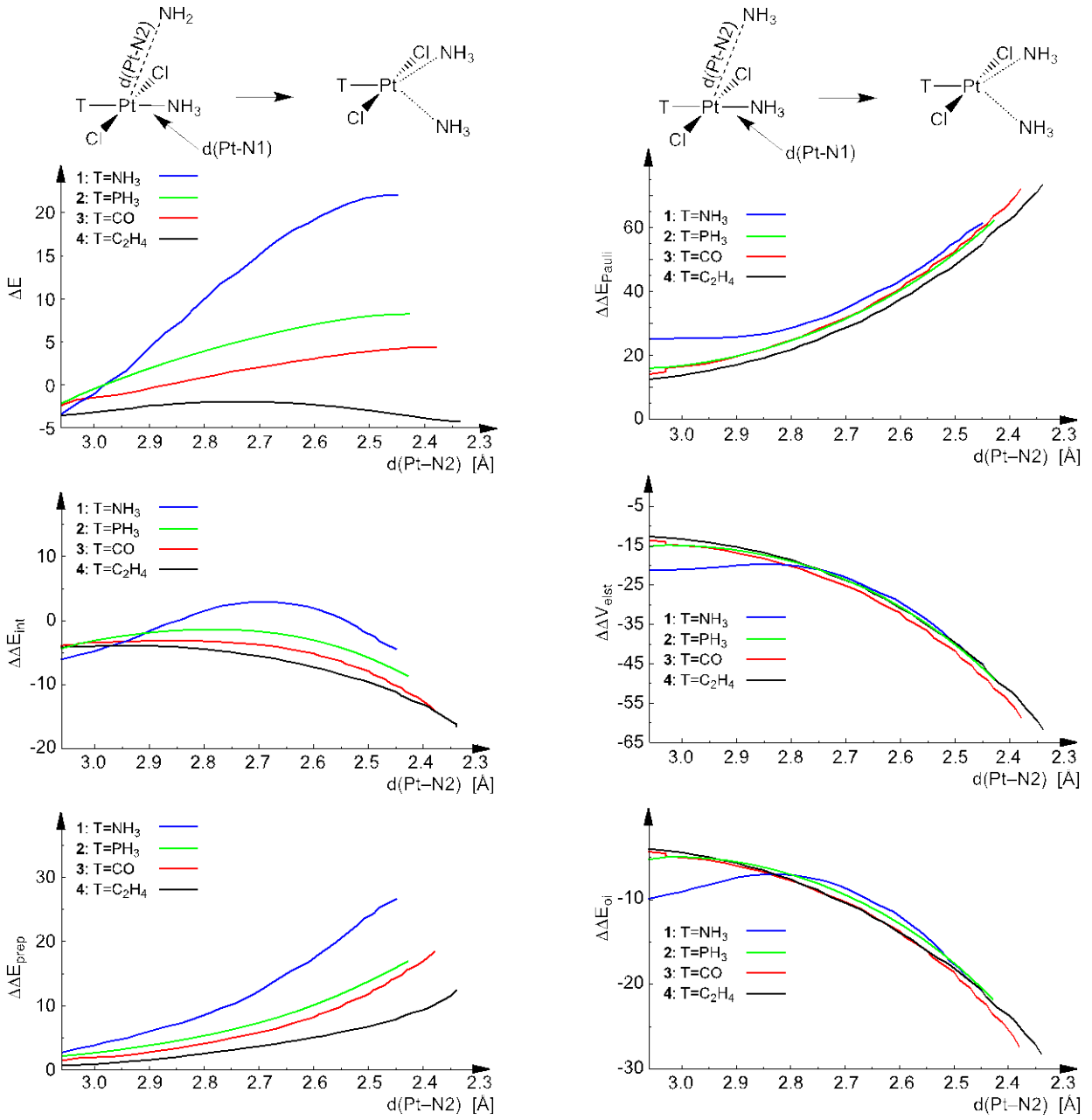

Figure S1. Critical energy (ΔE) and its contributions, such as preparation ($\Delta\Delta E_{strain}$) and interaction energy ($\Delta\Delta E_{int}$) for fragments $TPtCl_2NH_3$ and NH_3 along the reaction coordinate projected onto the Pt-N2 distance. Energy values are given in kcal mol^{-1}.

Figure S1 clearly shows that using fragments $TPtCl_2NH_3$ and NH_3 does not result in a strain-free situation and $\Delta\Delta E_{int}$ accounts for only part of the critical energy differences. Thus, the differences between systems can not be explained on pure electronic origins between fragments $TPtCl_2NH_3$ and NH_3.

Figure S2. Components of interaction energy ($\Delta\Delta E_{int}$) for fragments $TPtCl_2NH_3$ and NH_3: Pauli repulsion ($\Delta\Delta E_{Pauli}$), electrostatic interaction ($\Delta\Delta V_{elst}$) and orbital interaction ($\Delta\Delta E_{oi}$) along the reaction coordinate projected onto the Pt-N2 distance. Energy values are given in kcal mol^{-1}.

Figure S2 indicates how the components of $\Delta\Delta E_{int}$ (Figure S1) vary along the reaction coordinate. As expected, the Pauli repulsion between fragments increases, which is compensated with more attractive orbital and electrostatic interactions as the reaction proceeds. Then again, there are only small differences between the four systems.

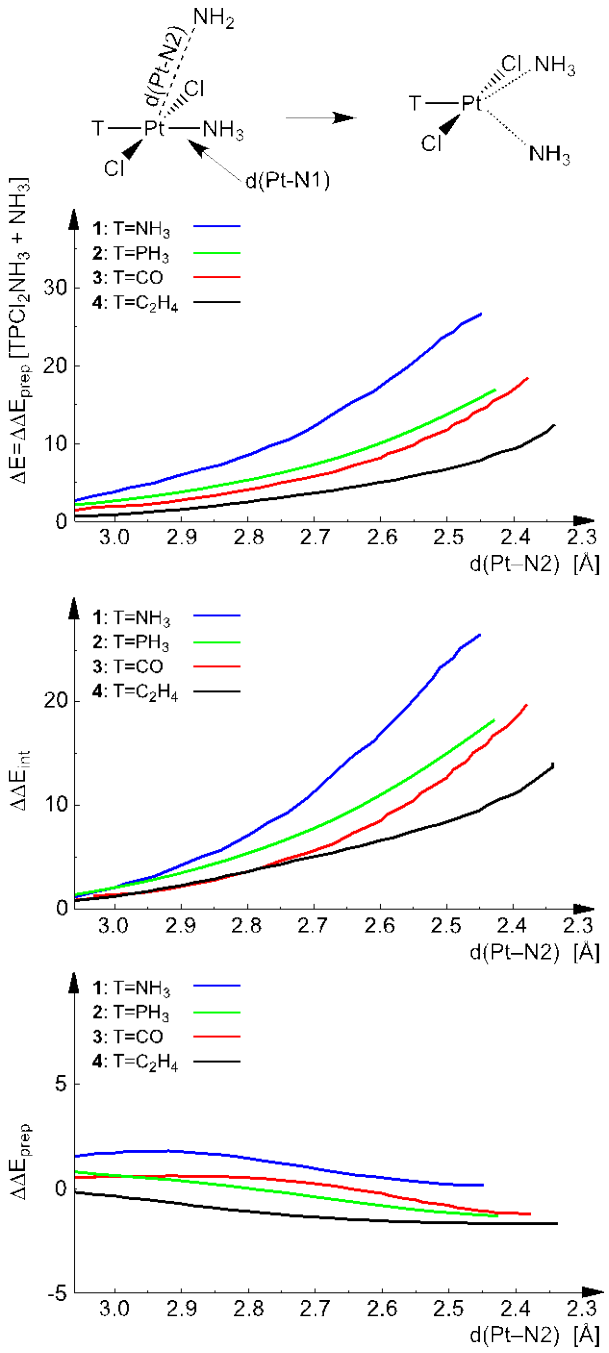

Figure S3. Critical energy (ΔE) for fragment $TPtCl_2NH_3$ and its contributions, such as preparation ($\Delta\Delta E_{strain}$) and interaction energy ($\Delta\Delta E_{int}$) between fragments $TPtCl_2$ and NH_3 along the reaction coordinate projected onto the Pt-N2 distance. Energy values are given in kcal mol^{-1}.

According to Figure S3 the strain emerging in the $TPtCl_2NH_3$ fragments can be originated form the interaction fragments $TPtCl_2$ and NH_3.

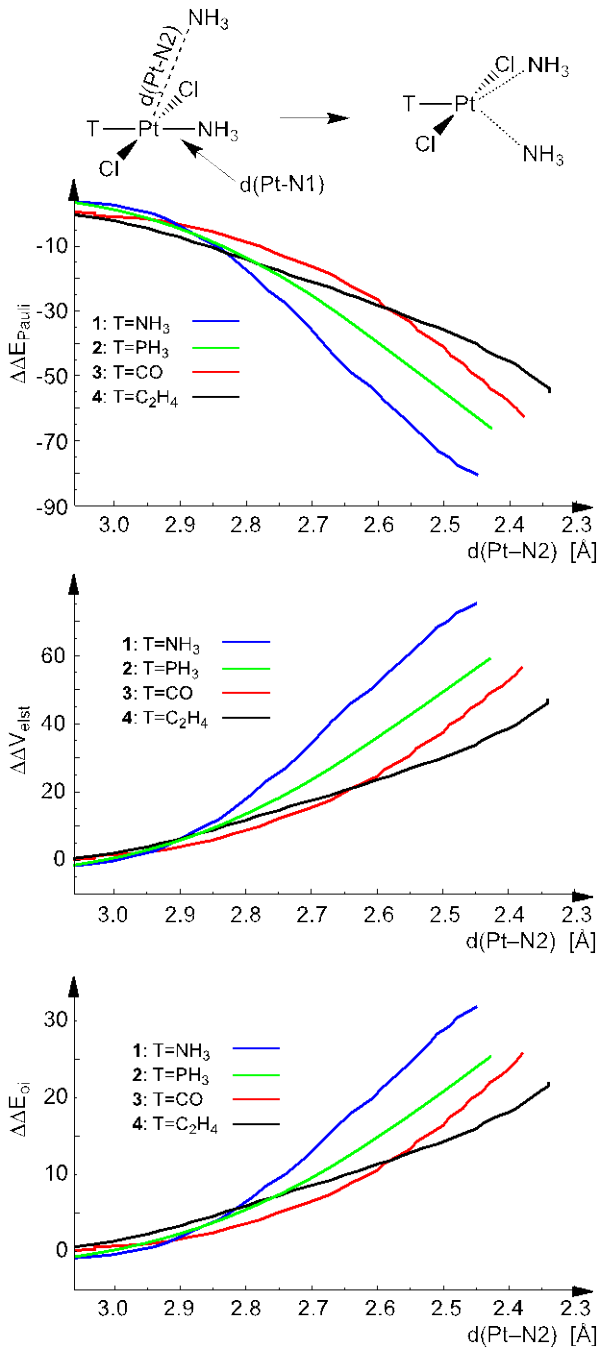

Figure S4. Components of interaction energy (Eint) for fragments TPtCl2NH3 and NH3: Pauli repulsion (EPauli), electrostatic interaction (Velst) and orbital interaction (Eoi) along the reaction coordinate projected onto the Pt-N2 distance. Energy values are given in kcal mol–1.

Due to the departure of the NH_3 fragment, the Pauli repulsion fragments $TPtCl_2NH_3$ and NH_3 drops significantly, whereas electrostatic and orbital interactions become less attractive.

Table S2. **Cartesian coordinates of the optimized structures. (Values are in Å)**

1-R

Pt	-0.00000400	0.00000000	0.00866800
H	0.14521000	2.42458600	0.95005800
H	0.74256700	2.42541400	-0.58742700
H	-0.90880600	2.41343400	-0.32637400
N	-0.00659500	2.05983900	0.00632100
H	0.90894900	-2.41333700	-0.32613500
H	-0.14543100	-2.42457100	0.95002100
H	-0.74236000	-2.42542700	-0.58764400
N	0.00661500	-2.05983300	0.00632300
Cl	-2.34106900	-0.00341100	-0.02462100
Cl	2.34107300	0.00340200	-0.02462100

1-C

Pt	0.23069300	0.10703500	-0.07963100
H	-2.76537600	-1.66923400	1.90736000
H	-3.02407400	-0.53585100	0.76955000
H	-3.96429400	-1.87668400	0.82750300
H	-0.98126800	-1.42229700	-1.80017400
H	-0.04014700	-2.35755300	-0.80898000
H	-1.54052300	-1.78694900	-0.26414300
H	1.58406900	1.60340600	1.59508100
H	1.94241000	2.07457600	0.05952800
H	0.51326500	2.56415000	0.75317600
Cl	-1.73515200	1.37959900	-0.32317100
Cl	2.19882200	-1.12204400	0.19519500
N	-0.69060300	-1.56734900	-0.83074300
N	-3.00084300	-1.55189100	0.91996400
N	1.17708300	1.78770800	0.67477300

1-TS

Pt	0.00607300	-0.12458100	0.00261600
H	-0.93459500	2.36629400	1.38041300
H	-0.06988600	1.47303000	2.44629300
H	0.72072100	2.46173300	1.40728700
H	0.70595300	1.67824500	-2.12811500
H	-0.93453900	1.74324300	-1.98739500
H	0.01022600	2.79089500	-1.14670100
H	-0.37817600	-2.56300200	0.85783000
H	-0.41780300	-2.57558400	-0.78918400
H	1.04827000	-2.48390800	0.00017500
Cl	2.35436200	-0.10531600	-0.01260600
Cl	-2.34091800	-0.21458000	-0.01919600
N	-0.05879800	1.82371100	-1.46722600
N	-0.07443500	1.82619800	1.48939100
N	0.06859800	-2.18353900	0.02012300

2-R

Pt	-0.01691000	-0.12642900	0.00318700
H	-0.04830300	-2.60567500	0.94732400
H	-1.10960100	-2.52506900	-0.31970000
H	0.53648800	-2.66180300	-0.59243800
N	-0.18053000	-2.23872900	0.00202000
H	-0.98841500	2.88587800	0.00763200
H	0.91565500	2.68398500	1.08637100
H	0.90212000	2.68136500	-1.09191000
P	0.20043600	2.10666100	0.00231200
Cl	2.31748000	-0.35529600	-0.00983900
Cl	-2.35464400	-0.02858700	-0.00984600

2-C

Pt	0.14239300	-0.03587700	-0.13586900
H	-2.89232100	-0.90468600	2.19321800
H	-3.06131600	0.17086900	0.98455300
H	-4.25563000	-0.90381500	1.30393100
H	-1.60988800	-1.28167800	-1.68270900
H	-0.81998100	-2.41388700	-0.75920600
H	-2.05894400	-1.47355200	-0.08175800
H	2.42433100	1.15869300	1.70045800
H	2.72957400	1.77244700	-0.36498100
H	1.22025700	2.78907100	0.84733400
Cl	-1.49839100	1.61819500	-0.46611500
Cl	1.71122600	-1.74711200	0.16971200
N	-1.25302200	-1.48698500	-0.74731800
N	-3.24155100	-0.80820000	1.23759500
P	1.67074000	1.47618600	0.53758800

2-TS

Pt	-0.00478200	0.00201600	0.00033500
H	0.32528000	-2.53730800	1.50003000
H	-0.49873900	-1.47856900	2.44340300
H	-1.31567000	-2.35576100	1.32982600
H	-1.50308300	-1.87898900	-1.65049600
H	-0.04848000	-1.64240500	-2.38049800
H	-0.18883200	-2.79211800	-1.22672800

H	1.17936700	2.67025900	1.16894700
H	1.51236600	2.56826800	-0.96533300
H	-0.47986800	3.07543500	-0.19250800
Cl	-2.30294600	0.49119000	0.00697500
Cl	2.27188600	-0.59260300	-0.01658300
N	-0.49440100	-1.85294900	-1.48703600
N	-0.43911000	-1.85929000	1.49883800
P	0.56354800	2.12824200	0.00186400

3-R

Pt	-0.00015700	-0.06130000	0.00273700
H	-0.06911400	-2.51911100	0.96175400
H	-0.80363300	-2.53367400	-0.51496200
H	0.87063300	-2.52839800	-0.39791800
N	-0.00010400	-2.16693400	0.00316800
C	0.00087800	1.80074500	0.00372700
O	0.00173100	2.93909600	0.00284900
Cl	2.33396000	-0.20037600	-0.00971000
Cl	-2.33419800	-0.19880600	-0.00968500

3-C

Pt	-0.18913100	0.01567600	-0.12578600
H	3.09945200	0.10717800	1.09115600
H	2.63193700	-0.98892400	2.19191600
H	4.07836500	-1.14970400	1.46769500
H	0.75584600	-2.32088200	-0.88232900
H	1.58571000	-1.13517700	-1.70677000
H	1.98038800	-1.43367800	-0.10642400
Cl	-1.68330600	-1.76057800	0.15172800
Cl	1.48513100	1.63138900	-0.46047900
N	1.19457700	-1.39975600	-0.80003200
N	3.10475300	-0.89932300	1.29015700
C	-1.42947000	1.27495100	0.47870500
O	-2.19112600	2.04231600	0.83771100

3-TS

Pt	0.00000200	0.05884900	-0.00000800
H	0.85542700	-2.37555400	1.41258800
H	-0.03416400	-1.42588000	2.40565600
H	-0.80542300	-2.43176800	1.37126900
H	0.03434200	-1.42591500	-2.40561700
H	0.80519100	-2.43199000	-1.37111500
H	-0.85564200	-2.37537100	-1.41268600
Cl	-2.34522200	-0.06620900	0.00137900
Cl	2.34522000	-0.06628400	-0.00136600
N	-0.00323800	-1.81315800	-1.46158700
N	0.00317200	-1.81313400	1.46162000
C	0.00003500	1.88109000	0.00000400
O	0.00005200	3.02826200	0.00001000

4-R

Pt	0.00020100	-0.05818500	0.00247900
C	0.00231600	1.96970400	-0.69582200
H	-0.93181800	2.11244100	-1.24873000
H	0.93543000	2.11052000	-1.25088900
C	0.00374400	1.97081300	0.69545600
H	-0.92953500	2.11586300	1.24924100
H	0.93836500	2.11392500	1.24745400
H	-0.08928400	-2.51633900	0.95608600
H	-0.80500900	-2.53532600	-0.52817100
H	0.86724600	-2.54223700	-0.39118800
N	-0.00502800	-2.17185500	-0.00346900
Cl	-2.33484500	-0.13710500	-0.00578300
Cl	2.33471500	-0.14292600	-0.00602300

4-C

Pt	-0.00010800	-0.16639800	-0.14630800
C	-0.00144100	-2.26586400	0.30420500
H	-0.93536900	-2.67263800	-0.09741800
H	0.93186300	-2.67390300	-0.09760200
C	-0.00083800	-1.55264000	1.49785100
H	0.93358200	-1.39810700	2.04719600
H	-0.93494300	-1.39687100	2.04738500
Cl	-2.33688500	-0.07497000	-0.14944100
Cl	2.33678500	-0.07772100	-0.14951500
H	0.81317200	2.45413200	1.71782600
H	0.00316200	3.87260200	1.73685400
H	-0.81071300	2.45635700	1.71796700
H	-0.83642300	1.73678500	-1.80143000
H	0.00134100	2.37018000	-0.48412600
H	0.83850400	1.73579800	-1.80132900
N	0.00185600	2.93884700	1.32426000
N	0.00094400	1.63279300	-1.22474100

4-TS

Pt	0.00000000	-0.06501800	-0.08642800
C	0.00000000	-2.14939300	-0.30875300
H	-0.93005100	-2.45602500	-0.79986700
H	0.92976300	-2.45603300	-0.80018000
C	0.00017000	-1.81598000	1.06541200

H	0.93193100	-1.88950100	1.63721500
H	-0.93140300	-1.88949400	1.63752300
Cl	-2.34489800	0.00125700	-0.09218900
Cl	2.34486700	0.00124000	-0.09296400
H	0.81844900	1.61201700	2.21882500
H	0.00034500	2.92890700	1.71276600
H	-0.81766700	1.61206700	2.21911400
H	-0.00066200	1.47797700	-2.35632000
H	-0.83371000	2.27313500	-1.17444400
H	0.83356100	2.27288200	-1.17509800
N	0.00030700	1.90720700	1.68143700
N	-0.00023400	1.71211400	-1.36293500

4-INT

Pt	-0.00037800	0.05205000	-0.00029500
C	-0.00332600	1.99583100	0.71656300
H	-0.93146500	2.22202500	1.25449700
H	0.92463300	2.22560900	1.25328600
C	-0.00437900	1.99660400	-0.71522800
H	0.92278900	2.22688100	-1.25311100
H	-0.93328700	2.22325300	-1.25163100
Cl	-2.34675700	-0.03129900	0.00091500
Cl	2.34669800	-0.02417400	-0.00099900
H	-0.00738900	-1.32691400	-2.44655800
H	0.83950200	-2.30275800	-1.44198800
H	-0.82344800	-2.31813300	-1.43225000
H	-0.04075800	-1.32634500	2.44663600
H	-0.79701300	-2.34453100	1.41371900
H	0.86373700	-2.27456500	1.46501100
N	0.00215800	-1.71994500	-1.50461400
N	0.00632700	-1.71948000	1.50587000