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Electronic Supplementary Information

Interaction of electron with cisplatin and the subsequent effect on DNA damage: a density functional theory study

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Content

M06 results of 17 explicit H_2O plus SMD bulk hydration

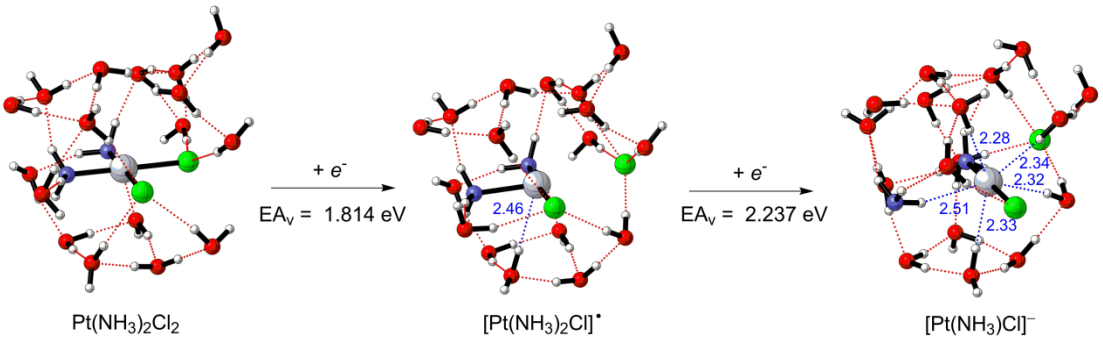


Fig. S1 SMD/B3LYP/BS-1 optimized structures of cisplatin and its one- and two-electron adducts.

Table S1 Bond distances (Å) of cisplatin and its one- and two-electron adducts optimized in the presence of 17 explicit water molecules plus SMD bulk hydration environment

	$Pt(NH_3)_2Cl_2$	$[Pt(NH_3)_2Cl]^\bullet$	$[Pt(NH_3)Cl]^-$
$Pt–Cl_L$ [a]	2.39 (2.39)[b]	3.60	4.58
Pt–Cl	2.39 (2.37)[b]	2.42	2.37
$Pt–N_L$ [a]	2.05 (2.04)[b]	2.26	3.48
Pt–N	2.05 (2.05)[b]	2.10	2.07

[a] The subscript L denotes the leaving groups. [b] The values in parentheses are gas-phase optimized distances in the presence of 15 explicit water molecules (ref. 19).

B3LYP results of dissociative electron attachment on cisplatin

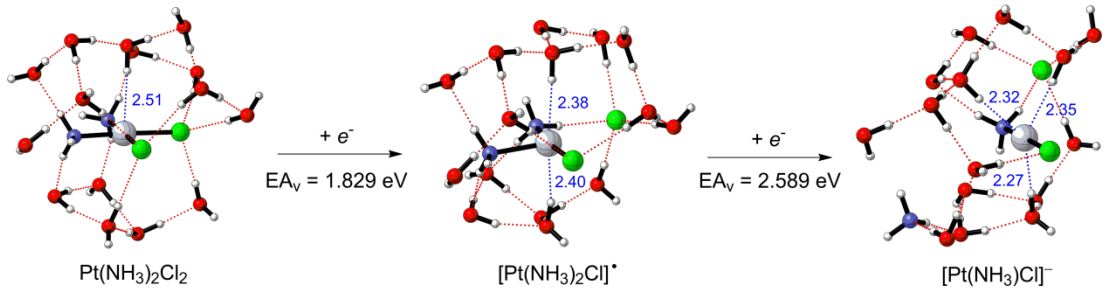


Fig. S2 SMD/B3LYP/BS-1 optimized structures of cisplatin and its one- and two-electron adducts.

Table S2 Bond distances (Å) of cisplatin and its one- and two-electron adducts optimized in the presence of 15 explicit water molecules plus SMD bulk hydration environment

	$Pt(NH_3)_2Cl_2$	$[Pt(NH_3)_2Cl]^\bullet$	$[Pt(NH_3)Cl]^-$
$Pt–Cl_L$[a]	2.40 (2.39)[b]	4.43	4.93
Pt–Cl	2.39 (2.37)[b]	2.40	2.36
$Pt–N_L$[a]	2.05 (2.04)[b]	2.24	5.21
Pt–N	2.05 (2.05)[b]	2.09	2.06

[a] The subscript L denotes the leaving groups. [b] The values in parentheses are gas-phase optimized distances in the presence of 15 explicit water molecules (ref. 19).

Relative energies of sugar radicals

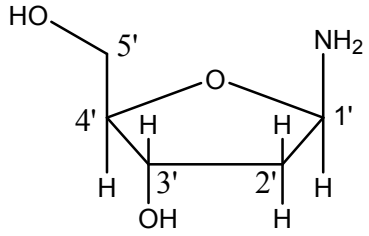


Table S3. SMD/M06/6-31++G** total electronic energies and relative electronic energies of sugar radicals derived from hydrogen abstraction.

	total energy (hartree)	relative energy (kcal/mol)
C1'-based sugar radical	–476.674486	3.88
C2'-based sugar radical	–476.669761	6.85
C3'-based sugar radical	–476.675469	3.27
C4'-based sugar radical	–476.680676	0.00
C5'-based sugar radical	–476.676132	2.85

Temperature effect on the free energies

To examine the temperature effect, we also carried out free energy corrections at 310 K (i.e., human body temperature). It turns out that the small temperature change from 298 to 310K has minor influences on the computed free energies; the differences between free energies evaluated at 298 and 310K do not exceed 0.6 kcal mol^{-1} (Fig. S2).

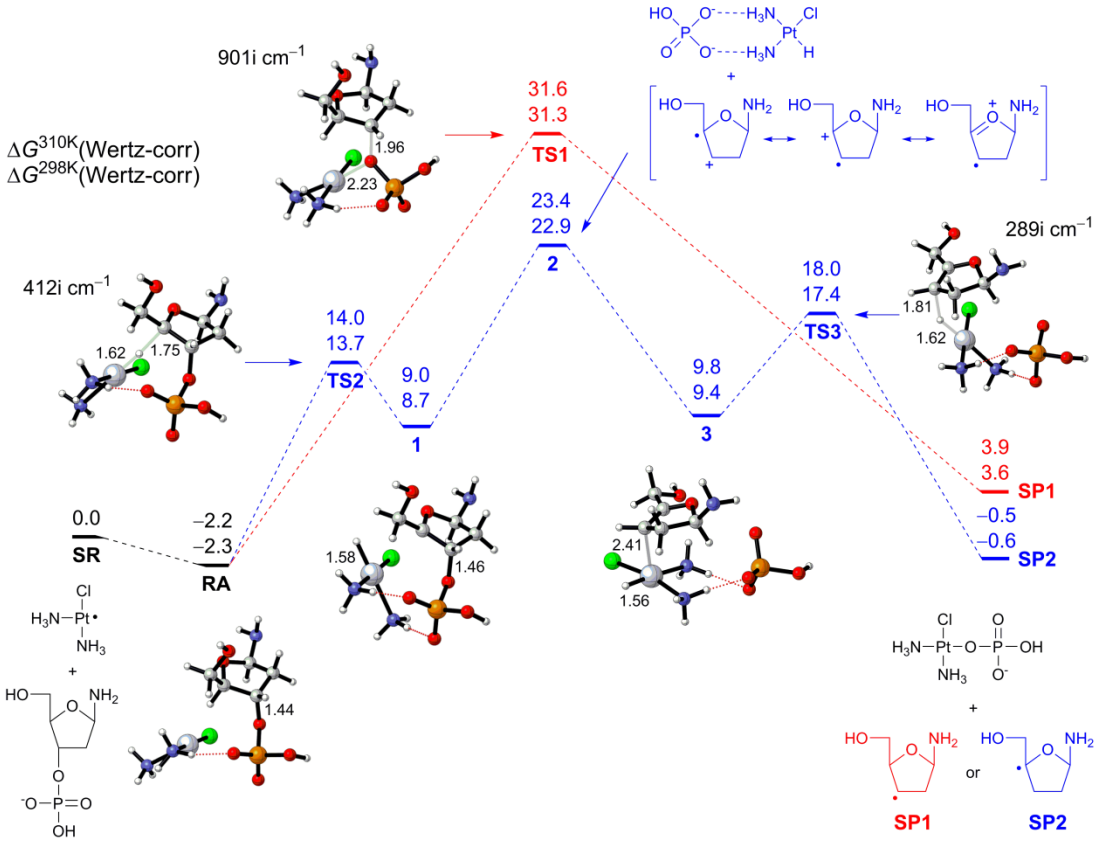


Fig. S3 SMD/M06/BS-2 free energy profile (in kcal mol^{-1}) for C3'–O bond cleavage induced by [Pt(NH$_3$)$_2$Cl]•. Free energies with Wertz corrections are reported.

Cavity effect on PCM calculations

The solute cavity is a crucial parameter in the continuum solvation models. Recently, Burda and co-workers demonstrated that the experimental pK_a and pK of the hydration reactions of cisplatin and transplatin complexes can be nicely reproduced by carefully adjusting the cavity parameters.[1,2] We performed a preliminary test for the cavity effect on the H4'-abstraction reaction as this is a critical step in the proposed mechanism.

To examine the effect of solute cavity, single point calculations of IEF-PCM using Pauling, Bondi, and UFF radii with scaling factor of 1.2 were performed on the SMD optimized geometries. Thermal corrections were based on the vibrational frequency calculations using the SMD model. It has been suggested that the cavity of ionic compounds should be reduced with respect to neutral species.[3] To consider the effect of charge on cavity size, we defined a modified UFF cavity (mUFF) by scaling the atomic radii of the phosphate group, the Cl, the moving H in **TS2,** and the H bonded to Pt in **1** by a factor of 1.1 while keeping the scaling factor of other atoms at 1.2. The non-electrostatic energies, including dispersion, repulsion, and cavitation terms, were incorporated in the IEF-PCM calculations. The computed results are summarized in Fig. S3 and Table S3.

The activation and reaction energies computed by different cavity models fall in the range of 14–17 kcal mol^{-1} and 5.1–11.8 kcal mol^{-1}, respectively (Fig. S3 and Table S3 in ESI). Although the influence of cavity models is non-negligible, all calculations predict a moderately high reaction barrier, suggesting that the $[Pt(NH_3)_2Cl]^{\bullet}$ exhibits substantial reactivity toward hydrogen abstraction. The performance of different cavity models cannot be assessed in the present study due to the lack of relevant experimental data. Under this situation, we are inclined to select the SMD solvation model. After all, the SMD model was parametrized with a large training set (2821 solvation data) and is one of the most reliable continuum solvation models so far.[4]

References

1. T. Zimmermann and J. V. Burda, *J. Chem. Phys.*, 2009, **131**, 135101.
2. T. Zimmermann, J. Leszczynski and J. V. Burda, *J. Mol. Model.*, 2011, **17**, 2385.
3. J. Tomasi, B. Mennucci and R. Cammi, *Chem. Rev.*, 2005, **105**, 2999.
4. A. V. Marenich, C. J. Cramer and D. G. Truhlar, *J. Phys. Chem. B*, 2009, **113**, 6378.

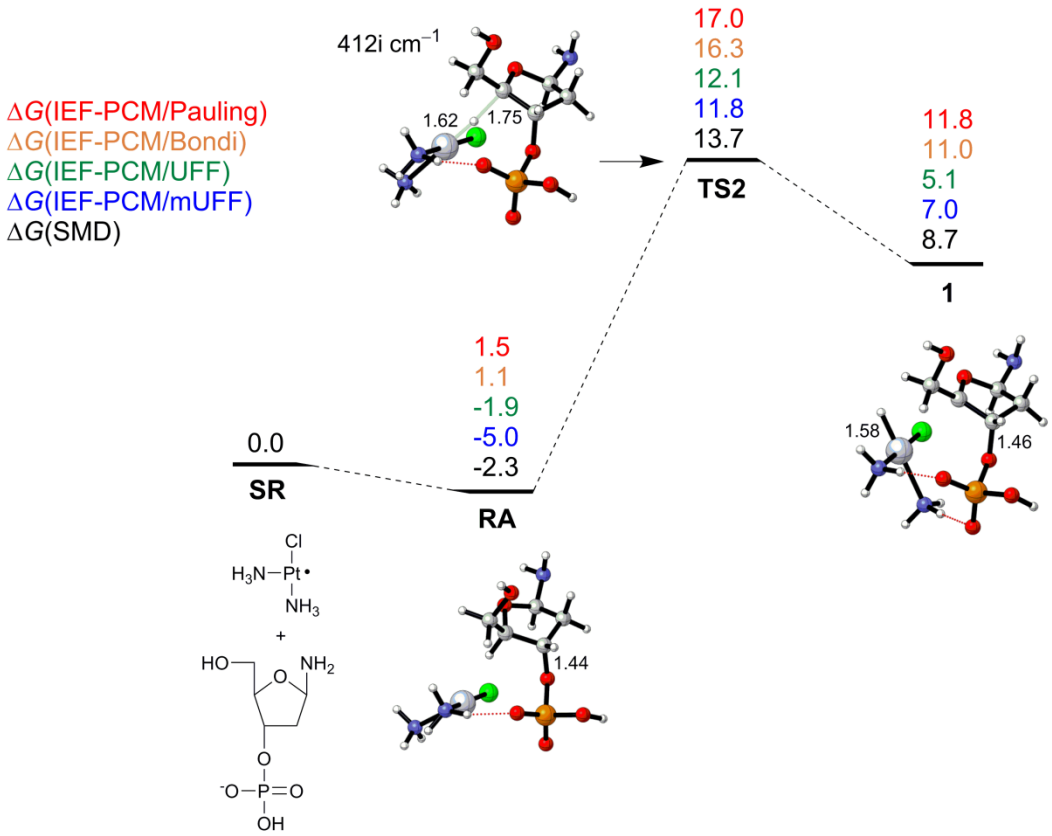
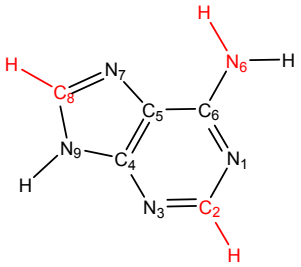


Fig. S4 M06/BS-2 free energy profile (in kcal mol^{-1}) for the H4'-abstraction reaction. The values in parentheses are results without Wertz corrections.

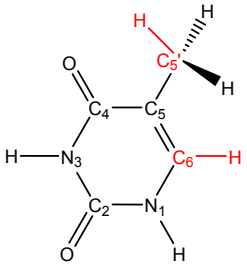
Table S4. Activation and reaction free energies (in kcal mol^{-1}) for the H4'-abstraction reaction.

	ΔG*	ΔG_{rxn}
Pauling	17.0	11.8
Bondi	16.3	11.0
UFF	14.0	5.1
mUFF	16.8	7.0
SMD	16.0	8.7

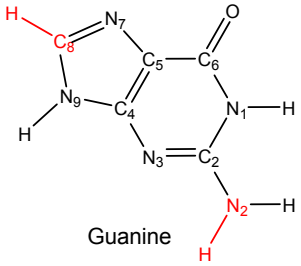
C–H and N–H bond energies of nucleobases



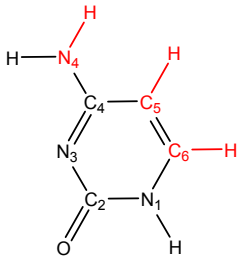
Adenine



Thymine



Guanine



Cytosine

Table S5. SMD/M06/6-31++G** bond energies (in kcal/mol).

Adenine C2–H	117.2
Adenine N6–H	107.0
Adenine C8–H	126.1
Guanine N2–H	102.7
Guanine C8–H	126.3
Thymine C5'–H	96.9
Thymine C6–H	122.3
Cytosine N4–H	116.4
Cytosine C5–H	122.9
Cytosine C6–H	121.6

Coordinates of optimized structures

Cisplatin in Fig.1

0 1

Pt	0.35730800	0.23534900	0.08877500
Cl	0.52969000	-2.14791800	0.09034500
Cl	0.12929000	0.28913900	-2.27905700
N	0.22469000	2.27510600	0.16471700
H	1.13181200	2.64076300	0.49756900
H	0.02253600	2.70560500	-0.74129000
N	0.65322100	0.25404200	2.12253100
H	1.61532600	-0.06612000	2.30199700
H	0.57369600	1.19348900	2.52085800
H	-0.00446900	-0.34788100	2.64399400
H	-0.51181600	2.56498100	0.82308900
O	-2.03746200	2.49106200	2.06675400
H	-2.41538400	2.86049100	2.87948300
H	-2.77698500	2.00247600	1.62676300
O	-3.86516800	1.17565600	0.48256000
H	-3.54400400	0.27084600	0.69660500
H	-3.40702500	1.41960500	-0.35188600
O	-2.63533900	-1.19664600	1.28703500
H	-2.99849200	-1.99034600	0.82346100
O	-2.51924900	2.12017300	-1.80469700
H	-1.73914200	1.58718600	-2.06027200
H	-1.81919900	-0.98369300	0.79426900
H	-3.13033800	2.04355500	-2.55459900
O	-2.42100900	4.38569200	-0.06553500
H	-2.31037800	3.88701200	0.77004600
H	-2.42858000	3.68362600	-0.74724000
O	-1.20166900	-1.52507500	3.68141800
H	-0.47941700	-2.17681600	3.55205100
H	-1.76642400	-1.58983500	2.88138000
O	3.08086100	2.60113000	0.90757400
H	3.19344900	2.45416400	-0.05243300
O	3.51820000	-0.10182700	1.78568600
H	3.72181100	-0.30105800	0.83759300

H	3.21914600	1.71366000	1.30490000
H	4.36574100	-0.18552200	2.24887400
O	4.08740800	-0.32412000	-0.90089100
H	3.70784100	0.50400700	-1.26788800
O	2.90043900	2.04771100	-1.91223100
H	2.06256800	1.63691500	-2.20418600
H	3.36604700	2.28100600	-2.73090700
H	3.64755200	-1.04372300	-1.40637300
O	2.74682400	-2.35923700	-2.32958800
H	2.04004400	-2.45171300	-1.66210000
H	2.31655000	-1.89431900	-3.06534900
H	-2.70034100	-0.53744200	-1.44721200
O	-3.08356500	-1.16229700	-2.08566800
H	-2.31030500	-1.66567000	-2.43325100
O	-3.62708200	-3.23554800	-0.31466600
H	-4.56541800	-3.35890800	-0.10463300
H	-3.60954900	-2.55487200	-1.02795200
O	-1.00074700	-2.88571600	-2.80735400
H	-1.40795600	-3.72092600	-2.52631300
H	-0.42628800	-2.63722100	-2.05864800
O	1.20541400	-2.95105700	3.22188500
H	1.18388000	-2.79890500	2.25803400
H	1.78258200	-2.24559300	3.55621900

Cisplatin + 1e- in Fig.1

-1 2

Pt	0.46066600	0.35029100	-0.22018700
Cl	-1.13535200	-3.12373200	-0.10288500
Cl	0.92490800	0.23091900	-2.57851300
N	1.16852800	2.49262300	-0.04478400
H	2.06633900	2.45464700	0.45149000
H	1.31189300	2.95057200	-0.94590100
N	0.09370300	0.34397100	1.84329300
H	0.90836500	-0.03945700	2.33375100
H	-0.06535200	1.29762200	2.18874000
H	-0.72227400	-0.21004800	2.11227800
H	0.52249500	3.05778200	0.51171400
O	-0.88829400	3.23942500	2.15448300

H	-1.12572400	3.69873100	2.97476300
H	-1.69448600	2.72580800	1.89694300
O	-2.93830800	1.82620300	0.99978200
H	-2.75565400	0.87062400	1.13963100
H	-2.60734700	2.02181500	0.09655100
O	-2.75407600	-0.95604100	1.55926500
H	-3.65125200	-1.04133700	1.16083000
O	-1.82848600	2.43183600	-1.59719800
H	-1.00344900	1.97350300	-1.32735800
H	-2.19826000	-1.51739300	0.97190200
H	-2.34644900	1.70345500	-1.99874300
O	-1.54041200	4.88020200	-0.10100300
H	-1.29163200	4.44888800	0.74343400
H	-1.74411200	4.12985100	-0.69155400
O	-1.53822500	-2.04681500	3.90193300
H	-0.71904300	-2.33952000	3.44360900
H	-2.10848700	-1.70865800	3.18167100
O	3.70052500	1.59061200	1.37317800
H	3.89710300	1.31240300	0.45626600
O	2.76564700	-0.94839700	2.35981700
H	3.13673300	-1.28943100	1.50295100
H	3.32409100	0.78795800	1.79212700
H	3.40343700	-1.21628900	3.03994300
O	3.71901500	-1.71033700	-0.08106000
H	3.83038400	-0.84750500	-0.53840100
O	3.89356700	0.81141600	-1.38120200
H	3.03150000	0.74075100	-1.84376800
H	4.56346100	0.78184000	-2.08243300
H	2.97582200	-2.14261700	-0.56209000
O	1.65108000	-2.80905100	-1.64119000
H	0.84902600	-2.94592200	-1.09095100
H	1.47082200	-1.95387300	-2.08297100
H	-1.97478400	-0.23706100	-1.13577200
O	-2.73005000	-0.22473200	-1.76055500
H	-2.51716800	-0.95601300	-2.38677100
O	-4.91661800	-0.97427000	-0.19424300
H	-5.41078700	-0.16004000	-0.01277600
H	-4.20394500	-0.69766000	-0.81809500

O	-1.82846100	-2.48617200	-3.15080400
H	-2.57528400	-3.02146300	-3.46113200
H	-1.61184900	-2.85396500	-2.26607300
O	0.74473200	-2.94938400	2.47924700
H	0.30998100	-2.91600300	1.60139300
H	1.44277200	-2.25895700	2.44998300

Cisplatin + 2e- in Fig.1

-2 1

Pt	0.47277800	-0.17369800	-0.45496400
Cl	-3.50835300	-1.02361100	0.11149800
Cl	0.51450100	-0.31100000	-2.82367700
N	3.88076100	0.93620200	-0.66674900
H	4.37944500	0.45343800	0.08196900
H	3.84657600	1.92002800	-0.38970000
N	0.46444400	-0.12297200	1.62084400
H	0.54837400	-1.06527700	2.01473700
H	1.23659600	0.43992400	1.99598300
H	-0.39979200	0.28495900	1.98823400
H	2.90918500	0.59992300	-0.61289400
O	2.30553300	2.20386300	2.30195400
H	2.50425400	2.44693200	3.21919100
H	1.41577300	2.59531400	2.12020200
O	-0.06654100	3.27065200	1.35377400
H	-0.74422800	2.56312000	1.41236500
H	0.26641500	3.22481500	0.43097100
O	-2.24295700	1.44280600	1.75824100
H	-2.83108700	2.17236500	1.45178800
O	1.10542500	2.96879700	-1.26159600
H	1.07111200	1.99173900	-1.09151700
H	-2.47244700	0.70244800	1.15270800
H	0.29186900	3.13653700	-1.77047400
O	3.19750900	4.07497600	0.34168700
H	3.02841400	3.46883400	1.09410900
H	2.49464500	3.83995600	-0.29590500
O	-2.19851700	-0.21376300	4.06111500
H	-2.07360900	-1.04284400	3.54603300
H	-2.29442700	0.47471800	3.37130400

O	3.36744900	-1.96751500	1.81470800
H	3.42521900	-2.02486600	0.83932300
O	0.76883600	-3.14111800	2.05140200
H	0.70441800	-3.51288400	1.13369500
H	2.49059600	-2.36669000	2.00010800
H	0.87469800	-3.91175500	2.63107500
O	0.61778400	-4.06100000	-0.54730700
H	1.40530800	-3.57625400	-0.87370800
O	2.85629900	-2.35925800	-0.95655600
H	2.19775300	-1.61756000	-0.89828100
H	3.38173100	-2.15596900	-1.74793200
H	-0.15018400	-3.59431300	-0.95022800
O	-1.52342300	-2.71087500	-1.84027700
H	-2.10323500	-2.28706600	-1.17141800
H	-0.93319900	-1.97783300	-2.11818900
H	-1.21582800	1.54553400	-1.07186400
O	-1.79418300	2.20466700	-1.52237300
H	-2.39143800	1.63812400	-2.06568200
O	-3.53480200	3.40445800	0.28377500
H	-3.13799900	4.24388300	0.56293400
H	-2.91378600	3.04801500	-0.39728400
O	-3.41776900	0.30447600	-2.77619700
H	-4.29644400	0.68601400	-2.92673300
H	-3.50028600	-0.16957900	-1.91795800
O	-1.95386800	-2.52094100	2.46712700
H	-2.29746000	-2.10907600	1.64636600
H	-1.00874500	-2.72220700	2.28645800

1 in Fig. 2

-1 2

O	2.50675700	1.83570100	2.75826100
C	1.44324700	1.02092000	2.22469500
H	1.62335700	-0.03582300	2.46474200
H	0.48391200	1.32483900	2.67022700
C	1.39584800	1.18830200	0.76231200
H	-1.84024300	0.82486100	1.50115500
O	0.88503100	2.37733100	0.30816500
C	1.22417800	2.50359600	-1.11811200

H	0.42267600	1.98367300	-1.66376800
N	1.28501600	3.85303300	-1.53348900
C	2.34005800	0.60034100	-0.23849500
H	3.27238000	0.24678500	0.22210800
C	2.54048000	1.75836000	-1.19799100
H	3.33745100	2.41493300	-0.82123300
H	2.79194900	1.43596800	-2.21186100
O	1.73934900	-0.49635000	-0.98385300
P	1.99389700	-2.03060000	-0.50066400
O	1.17044600	-2.87652400	-1.43973000
O	1.81652700	-2.15261600	0.99323100
O	3.58663300	-2.26075200	-0.75807700
H	0.38352800	4.31140400	-1.43471000
H	1.97980000	4.36507800	-0.99366400
Pt	-1.73838500	-0.20872100	0.31427100
H	2.53509200	1.69879600	3.71522500
N	-1.02139100	-1.62568200	1.65042400
H	-0.02839700	-1.83127000	1.45962400
H	-1.08843000	-1.32499900	2.62067500
N	-1.60736700	-1.66588100	-1.34497200
H	-0.69022900	-2.12263600	-1.41249600
H	-2.30827400	-2.40055700	-1.26738900
H	-1.53577300	-2.50288200	1.57199200
H	-1.77823400	-1.18506000	-2.22666700
Cl	-2.56327700	1.41601600	-1.20698600
H	3.80609300	-2.30988300	-1.70055100

3 in Fig.2

-1 2

O	0.42496400	1.59603300	2.82488300
C	1.33694100	2.09193600	1.86185300
H	1.54379800	3.16226100	2.02669900
H	2.29265200	1.55215500	1.88129100
C	0.73969200	1.96218300	0.51043700
H	2.18433700	-0.62019300	-1.72706400
O	-0.53342100	2.26290200	0.37946200
C	-0.91801400	2.09542700	-1.08570300
H	-1.42764500	1.12569800	-1.09120900

N	-1.80122900	3.09304500	-1.50839600
C	1.36960700	1.62282900	-0.68907800
H	2.45024600	1.68496300	-0.78170200
C	0.43357900	2.07008100	-1.77592000
H	0.70882700	3.08780100	-2.09723100
H	0.42462400	1.43718500	-2.66802500
O	-3.02728300	0.47136000	1.26192100
P	-3.30980500	-0.73010800	0.35013500
O	-2.66196400	-2.03387000	0.85299600
O	-3.04296400	-0.46965100	-1.14228900
O	-4.96104800	-0.97532400	0.37802300
H	-2.69671000	3.04101400	-1.03161700
H	-1.40433800	4.02586700	-1.43069200
Pt	1.31413400	-0.76678100	-0.44099200
H	0.83993900	1.66379700	3.69492800
N	-0.28800600	-1.22323500	-1.69755000
H	-1.23129400	-0.95675500	-1.35918500
H	-0.17559300	-0.80867700	-2.62184900
N	0.10636100	-1.13894300	1.39694100
H	-0.84412500	-1.49390100	1.21165100
H	0.59024600	-1.83631200	1.96045200
H	-0.29797600	-2.23448600	-1.83679400
H	0.01291200	-0.30816000	1.98647900
Cl	3.29282600	-0.68715800	0.88446900
H	-5.28031700	-1.06248300	1.28681000

RA in Fig.2

-1 2

O	-3.74099300	-0.66308400	2.30773300
C	-2.33226500	-0.47577700	2.27576900
H	-2.06444900	0.53952200	2.60617800
H	-1.82986600	-1.19489600	2.94014600
C	-1.82657300	-0.66702000	0.87132100
H	-0.74282700	-0.44414400	0.86676100
O	-2.02863800	-2.02187200	0.46334200
C	-2.40903700	-2.03582200	-0.93387600
H	-1.48736600	-1.96951300	-1.53498900
N	-3.10427100	-3.22572500	-1.28371700

C	-2.49543400	0.21745300	-0.20029300
H	-3.15112700	0.97851300	0.24157900
C	-3.24112700	-0.77676300	-1.06381100
H	-4.23580600	-0.97198400	-0.63913600
H	-3.35560100	-0.43088300	-2.09510200
O	-1.49388200	0.85644300	-1.01083300
P	-0.99765100	2.36495100	-0.63010400
O	0.14235300	2.66103900	-1.56815800
O	-0.84550100	2.51229100	0.86407700
O	-2.29809500	3.27942500	-1.00796700
H	-2.51567300	-4.04186200	-1.14037300
H	-3.93362200	-3.32306700	-0.70006700
Pt	1.75264300	-0.20301200	0.18949700
H	-4.04884100	-0.49021400	3.20608300
N	1.37221900	0.88442300	1.95843000
H	0.66844300	1.60457000	1.75031600
H	0.98885500	0.28807800	2.69130200
N	3.92950500	-0.57020400	0.72346300
H	4.32046400	0.18084700	1.28825200
H	4.04284700	-1.43930700	1.24062200
H	2.19919900	1.33792300	2.34360800
H	4.48081500	-0.64428500	-0.12871700
Cl	1.87732000	-1.36176200	-1.89219800
H	-2.42880400	3.34550900	-1.96571600

TS1 in Fig.2

-1 2

O	-4.49301300	-0.30373200	1.56538400
C	-3.20525200	-0.49237200	2.13447300
H	-2.96159100	0.31882700	2.83715000
H	-3.15713100	-1.44608400	2.68012900
C	-2.15872000	-0.50237900	1.04010200
H	-1.17480700	-0.59080300	1.53644400
O	-2.35669000	-1.62127000	0.17214400
C	-2.44998300	-1.19205100	-1.21470500
H	-1.45937800	-1.34236900	-1.66942000
N	-3.40938700	-1.95360500	-1.94281900
C	-2.19889400	0.70201800	0.15614900

H	-2.38594700	1.67859400	0.59690600
C	-2.79672700	0.28562300	-1.13379000
H	-3.89452700	0.40227300	-1.09352300
H	-2.43735900	0.85145600	-2.00010100
O	-0.29818100	0.84930500	-0.28950500
P	0.19029100	2.38065800	-0.47481900
O	1.37897100	2.44983000	-1.41672600
O	0.30354200	3.06558400	0.87824800
O	-1.08208500	3.12245500	-1.20221000
H	-3.14796200	-2.93574600	-1.95734400
H	-4.32105400	-1.87435800	-1.49388100
Pt	1.43916900	-0.44456600	0.24632800
H	-5.14986700	-0.37548200	2.26946500
N	1.46898500	0.58951100	2.12193900
H	1.15598700	1.55656300	1.97436200
H	0.82797300	0.15454200	2.78396400
N	2.99261600	-1.82655800	0.87890700
H	3.60927300	-1.43013500	1.58624300
H	2.59771200	-2.68297000	1.26479600
H	2.38814700	0.61124900	2.56039000
H	3.56624400	-2.09148900	0.07987600
Cl	1.40432700	-1.50912900	-1.93398600
H	-1.16722100	2.84958700	-2.12727300

TS2 in Fig.2

-1 2

O	-2.74602700	-0.96327800	2.87599300
C	-1.48433000	-0.61475700	2.28852600
H	-1.24728500	0.43883200	2.49350500
H	-0.68236800	-1.24114500	2.70864700
C	-1.56214300	-0.81961600	0.82369500
H	0.09233900	-0.41500700	0.43892600
O	-1.64130800	-2.14392600	0.44465700
C	-2.20150600	-2.19134500	-0.91054400
H	-1.36120900	-2.00752000	-1.59772100
N	-2.78746700	-3.44597600	-1.19884100
C	-2.43391600	0.02259000	-0.07989700
H	-3.10528800	0.67242700	0.49839400

C	-3.17438700	-1.03140800	-0.88325200
H	-4.07457300	-1.34697200	-0.33641300
H	-3.46331200	-0.68194800	-1.87817700
O	-1.66476100	0.83432200	-0.99475500
P	-1.38053500	2.40123600	-0.64501300
O	-0.42536600	2.88190600	-1.70545800
O	-1.06653100	2.57406300	0.82113300
O	-2.84778400	3.09570600	-0.83866700
H	-2.09402100	-4.18812000	-1.17510300
H	-3.52314800	-3.65889200	-0.52796100
Pt	1.66075200	-0.13299900	0.17274600
H	-2.71155500	-0.74255000	3.81666900
N	1.52392000	1.39669400	1.58267500
H	0.68324200	1.95985500	1.39197700
H	1.43390500	1.02714500	2.52853000
N	3.86331500	0.29785300	-0.20412100
H	4.10281300	1.28333600	-0.11337600
H	4.46407100	-0.21622600	0.43694000
H	2.33464100	2.01424700	1.57658000
H	4.11560500	0.00803100	-1.14703900
Cl	1.72865900	-1.87391100	-1.45029300
H	-3.10818100	3.14321100	-1.77076200

TS3 in Fig.2

-1 2

O	-4.19941500	1.31294900	-1.53255300
C	-3.93310400	0.84438400	-0.23336300
H	-4.71582400	1.13655900	0.48445200
H	-3.85594700	-0.25728100	-0.19554300
C	-2.64250600	1.37097300	0.25602100
H	-1.37158200	-0.49225000	1.22203100
O	-1.89399300	2.10193700	-0.51586600
C	-0.55362000	2.37703600	0.22017700
H	0.10284400	1.61812800	-0.22877100
N	-0.08431800	3.65988100	-0.01899400
C	-2.08480200	1.14032600	1.52136000
H	-2.64568400	0.70954300	2.34434800
C	-0.91725100	2.05210400	1.65478500

H	-1.22760600	2.96724600	2.18544700
H	-0.06916300	1.62855400	2.20125600
O	2.13198100	1.14361500	-1.63016200
P	3.09383700	0.84200800	-0.47183300
O	3.61466100	-0.60802500	-0.48585100
O	2.59575400	1.29551900	0.91061900
O	4.42723000	1.82455900	-0.69922800
H	0.19418500	3.81787500	-0.98158100
H	-0.70014300	4.39111400	0.32470300
Pt	-0.24967200	-1.26654400	0.34741700
H	-5.03895000	0.93072100	-1.82016600
N	1.09964000	-0.96709300	1.89213400
H	1.68874200	-0.14443400	1.65867100
H	0.65277200	-0.80016400	2.79182200
N	1.29047100	-2.35695400	-0.73109800
H	2.15545400	-1.79097100	-0.75514700
H	1.50595000	-3.24815100	-0.28796400
H	1.71819000	-1.76996000	2.00703000
H	0.99537300	-2.55308300	-1.68589400
Cl	-1.75898300	-1.60487300	-1.44697300
H	4.81834600	1.67553400	-1.57101700

PA in Fig.3

-1 2

O	-1.43269300	-2.90091600	1.37506600
C	-1.04171600	-2.65280700	0.08561800
H	1.68711600	-1.59309700	1.07335900
H	-0.55592000	-3.45854600	-0.45895200
C	-1.71239900	-1.52704800	-0.58688800
H	-1.18983800	-1.33656400	-1.53469800
O	-3.10373000	-1.84268300	-0.87459000
C	-3.96239900	-0.76704100	-0.41996300
H	-4.07341200	-0.04657000	-1.24534600
N	-5.25547900	-1.23611000	-0.05199900
C	-1.75336000	-0.22603300	0.23459400
H	-1.00834300	-0.23246800	1.03958200
C	-3.18287800	-0.16330800	0.72731500
H	-3.29190300	-0.81205800	1.60821200

H	-3.51215700	0.84519300	0.99427700
O	-1.44304500	0.84166000	-0.67605400
P	-1.24638800	2.37536500	-0.15463400
O	-0.35806600	3.03521000	-1.18027900
O	-0.87775400	2.38472500	1.30775300
O	-2.74546600	3.01012400	-0.23920200
H	-5.72648800	-1.65091900	-0.85154400
H	-5.17148600	-1.94849600	0.67178800
Pt	1.95146500	-0.26646500	0.26128300
H	-0.99696400	-3.70136100	1.69952100
N	1.55898700	0.85261400	1.96241100
H	0.72178300	1.43427100	1.80495200
H	1.39314900	0.28805100	2.79272700
N	2.31100600	1.60941100	-0.85273900
H	2.93779500	2.24115500	-0.35728800
H	2.73854100	1.40789400	-1.75480200
H	2.33624000	1.47747500	2.17557700
H	1.43955200	2.12329100	-1.03084600
Cl	2.41538100	-1.52219700	-1.69909300
H	-3.00667600	3.20495600	-1.15177600

RA in Fig.3

-1 2

O	-1.81133000	-2.54418700	1.68458400
C	-1.16297100	-2.45937100	0.42418700
H	-0.09265400	-2.19834000	0.54410300
H	-1.21998600	-3.41895200	-0.11027800
C	-1.80988100	-1.38755000	-0.41379500
H	-1.20200400	-1.26525200	-1.32524000
O	-3.13707800	-1.78280900	-0.76487700
C	-3.99415200	-0.61576400	-0.73193900
H	-3.86901700	-0.07601400	-1.68377900
N	-5.36296900	-0.96857100	-0.57909000
C	-1.93058300	-0.01356400	0.27315600
H	-1.39781900	0.01645300	1.22979900
C	-3.42709400	0.17875400	0.42537000
H	-3.76816000	-0.28120400	1.36374400
H	-3.72366000	1.23196200	0.42162000

O	-1.35188500	0.96020700	-0.61077000
P	-0.88565700	2.42798700	-0.06892000
O	0.12932500	2.92034000	-1.07060600
O	-0.55641300	2.36654100	1.40175300
O	-2.24101800	3.32912800	-0.17361900
H	-5.67821000	-1.52749000	-1.36727300
H	-5.48254500	-1.51867300	0.26992800
Pt	1.86628100	-0.43770400	0.17647500
H	-1.40897100	-3.26495900	2.18529800
N	1.24636700	0.10389600	2.12235700
H	0.63149700	0.92417900	2.04252000
H	0.72274800	-0.62876100	2.59916400
N	2.73531500	1.63700200	-0.11085800
H	3.09695600	2.04541100	0.74837900
H	3.48189500	1.63527200	-0.80183300
H	2.02812800	0.35521500	2.72530100
H	1.97137000	2.22590800	-0.45743700
Cl	2.43810500	-1.27649300	-1.97908800
H	-2.45808500	3.55164500	-1.09122200

TS in Fig.3

-1 2

O	-1.37628200	-2.46991100	1.68145900
C	-1.00044100	-2.35577400	0.36203800
H	0.58114300	-1.51770500	0.32233400
H	-0.68575300	-3.27806100	-0.12758700
C	-1.79050100	-1.36880000	-0.40919700
H	-1.30099900	-1.22275600	-1.38505300
O	-3.13261800	-1.85336200	-0.61859600
C	-4.02200000	-0.70983800	-0.62390600
H	-3.94011200	-0.22096600	-1.60796400
N	-5.37451200	-1.08783700	-0.40620400
C	-1.94141400	0.01160900	0.27000400
H	-1.38701800	0.06436400	1.21228900
C	-3.43785600	0.16072600	0.46727500
H	-3.72652800	-0.26540600	1.43918200
H	-3.77003600	1.20276000	0.42636600
O	-1.41106900	0.99075600	-0.63372000

P	-0.89993100	2.44964400	-0.10443300
O	0.09684700	2.92538200	-1.12953500
O	-0.54980900	2.38619800	1.36179800
O	-2.24505400	3.37304900	-0.18160000
H	-5.70252500	-1.69528700	-1.15220000
H	-5.45409700	-1.59165200	0.47559400
Pt	1.76120500	-0.42852100	0.16832700
H	-0.92812600	-3.22873000	2.07984700
N	1.34873400	0.24343600	2.09839300
H	0.68081100	1.02265700	2.01976500
H	0.93352400	-0.46640500	2.69899000
N	3.34052600	1.19412200	-0.06313100
H	3.90432800	1.35327500	0.76958900
H	3.97455200	0.97002000	-0.82730800
H	2.18265200	0.58965400	2.57116400
H	2.89055900	2.07794600	-0.29508800
Cl	2.19036500	-1.20071000	-2.04278500
H	-2.46964800	3.60585100	-1.09470100

RA in Fig.4

0 2

N	-2.59290900	1.39862100	-0.67955600
C	-2.21978600	1.39538400	0.63968100
H	-2.10813900	2.37707200	1.09031700
C	-1.99477100	0.25166200	1.32897100
C	-1.54563000	0.22787100	2.74960800
H	-1.42799200	1.24685900	3.13227900
H	-2.26050700	-0.30267200	3.39049700
H	-0.58011500	-0.28784400	2.84354500
C	-2.14808300	-0.99995700	0.62228900
O	-1.93978300	-2.11937000	1.10925400
N	-2.56516900	-0.89938600	-0.70064200
H	-2.67008100	-1.76937900	-1.21870700
C	-2.76862300	0.25814300	-1.41342100
O	-3.09025200	0.26121600	-2.60137000
H	-2.73411400	2.27804200	-1.16671100
Pt	1.13685100	-0.13397900	-0.04893400
N	0.85255800	-2.21828100	-0.21756800

H	1.65290600	-2.73913100	0.13894800
H	0.02753500	-2.53593700	0.29678200
N	3.28534800	-0.30463900	-0.76162100
H	3.33337600	-0.53894900	-1.75083500
H	3.75992600	0.58599900	-0.62898300
H	0.72541300	-2.50193000	-1.18834900
H	3.80214100	-1.01641300	-0.24937500
Cl	1.24988900	2.22864800	0.23631400

TS in Fig.4

0 2

N	-3.61243100	1.37749100	-0.00888900
C	-2.64744300	1.21717900	0.95242100
H	-2.40513100	2.10586200	1.52711400
C	-2.03790700	0.00634400	1.17872400
C	-0.99488700	-0.18053100	2.12720300
H	-0.78455600	0.62494200	2.82814000
H	-0.75202700	-1.19059900	2.44816600
H	0.43011400	-0.01445400	1.24855600
C	-2.40874900	-1.10283500	0.30526200
O	-1.89459800	-2.22474700	0.33417400
N	-3.40920100	-0.83287500	-0.61350900
H	-3.69145300	-1.59674700	-1.22430500
C	-4.04132300	0.37332000	-0.82742100
O	-4.91166900	0.52065600	-1.68569000
H	-4.05290900	2.28316100	-0.13846900
Pt	1.49245100	-0.09701700	0.02921500
N	1.19948400	-2.16201800	0.07283800
H	1.65027500	-2.58600800	0.88311300
H	0.19994500	-2.37767700	0.13784700
N	2.91925000	-0.24436700	-1.71990200
H	2.42838000	-0.08626300	-2.59783300
H	3.64331700	0.46816900	-1.65178000
H	1.56786200	-2.63318200	-0.75278900
H	3.38315900	-1.14790600	-1.79413300
Cl	1.73671300	2.26484100	0.06404700

a in Fig.5

1 1

N	1.34513700	3.31973200	-0.14119900
C	2.27953000	2.33595700	-0.14972700
H	3.34259700	2.53400800	-0.16357000
N	1.72284900	1.14274200	-0.14366500
C	0.34890700	1.36067400	-0.12995500
C	-0.76381400	0.47896900	-0.08646400
O	-0.75980700	-0.76553100	-0.08170600
N	-1.96810000	1.17081700	-0.05055000
H	-2.82284400	0.57996200	-0.00698600
C	-2.10307500	2.53696300	-0.04931200
N	-3.34963700	3.01496400	0.00447800
H	-4.17018800	2.39899500	-0.03641500
H	-3.47116800	4.01778300	-0.03053600
N	-1.06761100	3.36647200	-0.08963500
C	0.10944500	2.72962400	-0.12147300
N	-6.74858600	-0.65496700	0.09834400
C	-6.72545200	-2.00325900	0.26686800
C	-5.59014800	0.10233800	0.01965500
H	-7.68906500	-2.49893500	0.32040800
C	-5.54212400	-2.65473500	0.36058500
N	-4.39978100	-0.52970700	0.10086300
O	-5.69421300	1.33841900	-0.12273300
H	-5.48717300	-3.72918800	0.49583200
C	-4.35849200	-1.86115700	0.26252100
N	-3.15744300	-2.43989800	0.33407100
H	-2.31094400	-1.87654900	0.22846200
H	-3.08784500	-3.44175100	0.44866300
H	1.54117800	4.31605600	-0.13969300
H	-7.63228200	-0.16063500	0.02630200
Pt	2.77374300	-0.61426500	-0.14133400
N	3.84890400	-2.37406800	-0.15452600
H	4.34746600	-2.50775600	0.72618600
H	3.26013900	-3.19584100	-0.29802100
N	1.60712000	-1.30116700	-1.70613400
H	1.88929900	-2.21602000	-2.05798600
H	0.63752800	-1.36893000	-1.37489100
H	1.62389100	-0.65587000	-2.49619100

H	4.54888900	-2.37405400	-0.89792100
Cl	4.11776800	0.13833100	1.64208100

b in Fig.5

0 2

N	1.28345500	3.32818000	-0.18387800
C	2.21930100	2.33739600	-0.13120600
H	3.28241000	2.53739100	-0.12884000
N	1.66934600	1.14387500	-0.08619900
C	0.29773000	1.36843200	-0.10672500
C	-0.81289600	0.48820800	-0.01129200
O	-0.81043800	-0.75114000	0.09567400
N	-2.02284500	1.17796400	-0.04155400
H	-2.87623100	0.59008100	0.02636500
C	-2.16191600	2.54004400	-0.13293400
N	-3.41294400	3.01432800	-0.15231800
H	-4.23167600	2.39600800	-0.13780200
H	-3.53694900	4.01372900	-0.23518200
N	-1.13025400	3.37100500	-0.19238200
C	0.05144500	2.73620700	-0.16629800
N	-6.81059700	-0.65597200	0.15228900
C	-6.78113300	-2.00052000	0.34856500
C	-5.65549600	0.10520700	0.05928800
H	-7.74238000	-2.49989900	0.41009500
C	-5.59473000	-2.64368400	0.45841600
N	-4.46225400	-0.51814400	0.15952000
O	-5.76609200	1.33699000	-0.11285400
H	-5.53479900	-3.71478800	0.61637600
C	-4.41456600	-1.84576000	0.35001500
N	-3.21105500	-2.41640700	0.43988600
H	-2.36523700	-1.84836300	0.34456300
H	-3.13771700	-3.41383600	0.58656500
H	1.47630400	4.32376700	-0.22015000
H	-7.69644700	-0.16773400	0.06757000
Pt	2.77809100	-0.63253600	-0.17464600
N	3.96810100	-2.39193500	-0.21180400
H	4.46597700	-2.49706600	0.67103600
H	3.42757100	-3.24193400	-0.36552100

N	1.38214700	-1.54563300	-1.91816200
H	1.59119100	-2.52388900	-2.10250900
H	0.42591300	-1.48206800	-1.57203100
H	1.43900800	-1.04421500	-2.80099900
H	4.67471300	-2.35472800	-0.94528400
Cl	4.62360800	0.32438600	1.75181300

c in Fig.5

1 1

N	-1.71326300	3.40725300	0.15717500
C	-2.56936900	2.36121300	0.11562600
H	-3.64400600	2.47054000	0.18042800
N	-1.92746700	1.21599300	-0.01626200
C	-0.57650300	1.53178200	-0.05567800
C	0.61176300	0.77231100	-0.13230200
N	0.65993300	-0.56084700	-0.20329500
H	1.56823800	-1.03189500	-0.17277100
H	-0.19670900	-1.10312200	-0.15914000
N	1.77421300	1.46123800	-0.12707400
C	1.75836000	2.79535300	-0.03165200
H	2.73796900	3.27265400	-0.03227700
N	0.70692400	3.60240500	0.06646300
C	-0.43874700	2.91055100	0.05223700
N	6.67264000	0.30667600	0.07386100
C	6.77315900	-1.05714400	0.17687700
C	5.47645100	0.95998900	-0.05294700
H	7.78506400	-1.43992000	0.27440900
C	5.68948400	-1.86889100	0.15788600
N	4.38285900	0.13488700	-0.07256500
O	5.38548800	2.18593200	-0.14290100
C	5.77342100	-3.35287500	0.27030500
C	4.39095700	-1.24550200	0.02689100
H	3.45676700	0.60257300	-0.13751800
H	5.22511200	-3.71499700	1.14862800
H	5.33443200	-3.84397800	-0.60678400
H	6.81530500	-3.67486000	0.35899900
O	3.31587000	-1.86578300	0.00075700
H	-1.97771200	4.38346800	0.24906400

H	7.50840300	0.88276100	0.09409000
Pt	-2.83281600	-0.60867500	-0.15887800
N	-3.75991600	-2.44243200	-0.32754800
H	-4.06163300	-2.79026200	0.58379500
H	-4.58830200	-2.39155700	-0.92213200
N	-2.46090500	-0.59450300	-2.19844200
H	-1.48875600	-0.34722500	-2.39281800
H	-2.63733300	-1.49337800	-2.64844200
Cl	-3.29283000	-0.61010200	2.14596700
H	-3.04670000	0.09830300	-2.66652300
H	-3.14223200	-3.14733300	-0.73247500

d in Fig.5

0 2

N	-1.68119700	3.46656400	-0.03085200
C	-2.53283900	2.40635000	-0.02076600
H	-3.60797700	2.52275900	0.01692800
N	-1.89165100	1.25563400	-0.06644500
C	-0.54626200	1.58726900	-0.10473400
C	0.63798600	0.82159600	-0.10188900
N	0.66076300	-0.51342600	-0.06699700
H	1.55552300	-1.00606500	-0.01811600
H	-0.22204400	-1.02139400	-0.03600500
N	1.80736400	1.50039100	-0.12491300
C	1.79420700	2.83958000	-0.12504800
H	2.77589900	3.31224300	-0.14621800
N	0.74575600	3.65610400	-0.09758000
C	-0.40577700	2.96915400	-0.08386900
N	6.67254000	0.29834800	0.17970700
C	6.76870400	-1.06487700	0.29442800
C	5.47846200	0.95373600	0.04401100
H	7.77938400	-1.45021800	0.39461000
C	5.68226200	-1.87288900	0.28365000
N	4.38171200	0.13298100	0.03505400
O	5.39217700	2.17890400	-0.06201200
C	5.76125200	-3.35613100	0.40884900
C	4.38536000	-1.24637200	0.14834800
H	3.45833600	0.60604900	-0.04805500

H	5.21436100	-3.70877800	1.29191400
H	5.31758400	-3.85319400	-0.46252200
H	6.80223500	-3.68118800	0.49708700
O	3.30860900	-1.86368700	0.12957200
H	-1.95111700	4.44446800	-0.00229700
H	7.51013200	0.87193600	0.19230400
Pt	-2.76421800	-0.64218900	-0.19400000
N	-3.67232200	-2.55873900	-0.28359900
H	-4.16659300	-2.75020900	0.58714900
H	-4.35557700	-2.62325400	-1.03684500
N	-1.76154800	-1.05056000	-2.37513500
H	-1.11168400	-0.31342400	-2.64017300
H	-1.24725100	-1.92864200	-2.36973300
Cl	-4.19089300	-0.29196200	2.19165900
H	-2.47183200	-1.11276000	-3.10045500
H	-3.00152400	-3.31151600	-0.42883900

Product in Fig.6

-1 1

Pt	0.77770000	-0.62177000	-0.27823200
Cl	2.93080000	-0.17955500	0.54306600
N	-1.12525000	-1.02210000	-0.97138700
H	-1.63120700	-1.58642700	-0.28171600
H	-1.67193100	-0.15721700	-1.09656800
H	-1.12151400	-1.52867100	-1.85575600
O	-0.44613000	2.99496400	-0.97386900
H	0.65683400	0.75985400	-0.88721800
H	0.83957300	2.83851400	0.34576000
H	-0.02532900	2.75596800	-1.80851400
H	-1.23398200	2.38447800	-0.88833800
O	-2.62702900	1.44809600	-0.67552600
H	-3.24572500	2.17191000	-0.82486700
O	1.54233500	2.82591500	1.02886200
H	1.95096500	1.94879800	0.94294300
O	-1.49507100	1.02429500	1.72044400
H	-0.60977100	0.75175100	1.42303400
H	-1.96617200	1.25121100	0.86875200
H	-3.75861900	0.22913300	-0.39807500

O	-4.36763300	-0.54718600	-0.22729700
H	-3.34641800	-1.35681800	1.09667300
H	-5.16944200	-0.16819600	0.15107200
O	-2.61966300	-1.60152000	1.70586300
H	-2.16915600	-0.74556300	1.85468400

Reactant in Fig.6

-1 1

Pt	0.77353500	-0.64317300	-0.23872000
Cl	2.92366200	-0.10148700	0.55111300
N	-1.12819700	-1.14588800	-0.92333800
H	-1.71498900	-1.49707100	-0.16115700
H	-1.62307600	-0.34530200	-1.32000500
H	-1.11343700	-1.86479000	-1.64575900
O	-0.25131300	2.27968900	-1.24849900
H	0.08321700	1.36721600	-1.04723000
H	1.07237400	2.90687800	0.03335800
H	-0.02623300	2.43192900	-2.17618700
H	-1.98635400	2.13090600	-0.77153400
O	-2.80560300	1.92546700	-0.26974000
H	-3.27034700	2.76532800	-0.16834700
O	1.78351400	2.96188900	0.69719100
H	2.14178700	2.05518200	0.72059700
O	-1.26812200	0.88606600	1.88866100
H	-0.55269100	0.48727400	1.33960100
H	-1.82733700	1.35294200	1.23582200
H	-3.87371000	0.46331500	-0.52770300
O	-4.32284500	-0.40715100	-0.54184800
H	-3.52536300	-1.12221400	0.99009800
H	-5.26062100	-0.21110000	-0.42888700
O	-2.92455400	-1.43827400	1.69397700
H	-2.35245200	-0.66796700	1.88401800

TS in Fig.6

-1 1

Pt	0.75013500	-0.63910900	-0.24869700
Cl	2.90258500	-0.14853900	0.54757000
N	-1.15088400	-1.11259300	-0.92881300

H	-1.72271700	-1.49388500	-0.16699600
H	-1.64489300	-0.28901300	-1.27737900
H	-1.13789900	-1.79900200	-1.68243000
O	-0.25037000	2.43593700	-1.08623800
H	0.41508700	0.80610600	-0.67127300
H	1.00982100	2.80047300	0.03755000
H	-0.08459000	2.41307100	-2.03537000
H	-1.51430300	2.10541800	-0.78984700
O	-2.51187300	1.80051700	-0.43748800
H	-3.02147300	2.61127300	-0.32487900
O	1.71077100	2.94142900	0.72200100
H	2.14650800	2.07601100	0.78741400
O	-1.34729700	0.88396100	1.91506700
H	-0.53772300	0.51270900	1.51351200
H	-1.81681500	1.27952400	1.14369100
H	-3.72755000	0.49967600	-0.52332900
O	-4.34068900	-0.26984100	-0.47964800
H	-3.53036900	-1.13037900	0.96434300
H	-5.19705700	0.10082500	-0.23543100
O	-2.89590700	-1.49331000	1.61509400
H	-2.35139100	-0.71853200	1.86148900