Supporting Information for:

Combined DFT and experimental studies of C–C and C–X elimination reactions promoted by a chelating phosphine–alkene ligand: the key role of *penta*-coordinate Pd^{II}

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Contents

Fig. S1 AIMALL plots for *cis*-[$PdMe_2(\kappa^2$-P,C-**L1**)] (**1**) and *cis*-[$PdMe_2(\kappa^1$-P-**L1**)] (**1'**) and corresponding transition states (**$TS_{1\rightarrow 2}$** and **$TS_{1'\rightarrow 2}$**); significant bond critical points (BCP) in green and ring critical points (RCP) in red are shown.

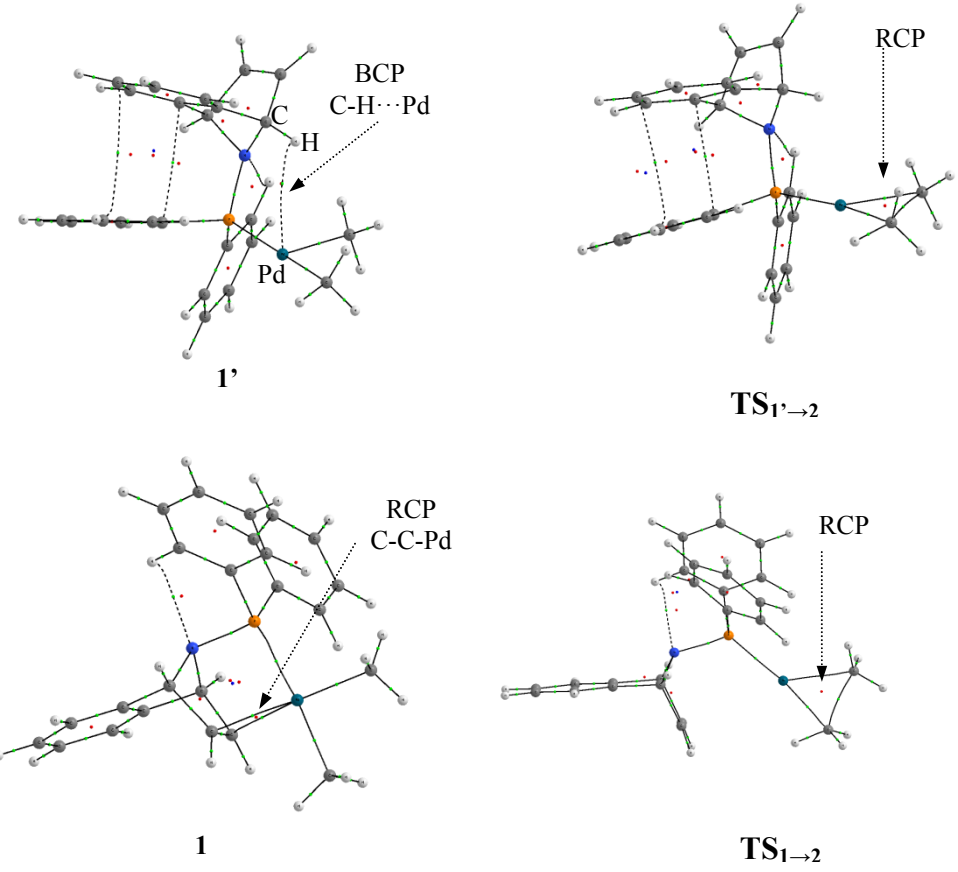
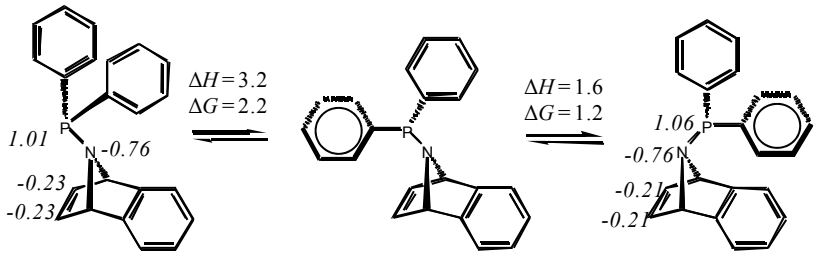
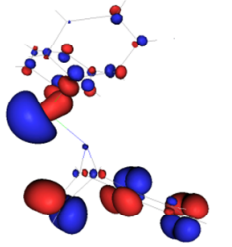


Fig. S2 Molecular structures for different geometries of phosphine-alkene ligand **L1**. Relative energies (in kcal mol^{-1}) for the different geometries. NPA atomic charges (in au) computed with NBO5 program for the main atoms in the chelating geometry and the most stable one. Plot and energetic positions of the main MO (HOMO, HOMO-1, LUMO and LUMO+1) for each structure.

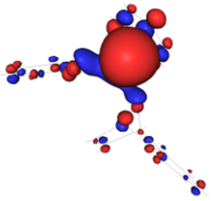


Chelating geometry

Most stable geometry



HOMO-1: -0.1896



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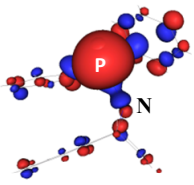

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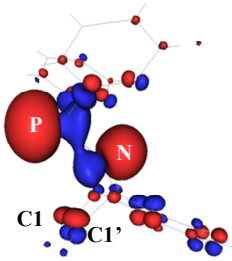

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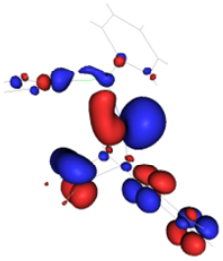

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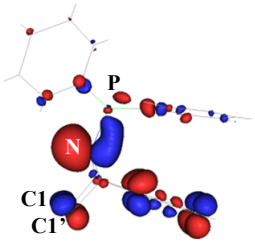

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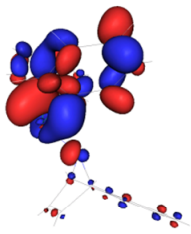

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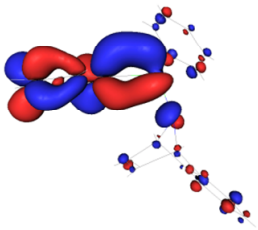

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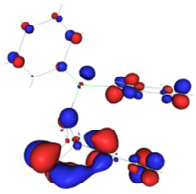
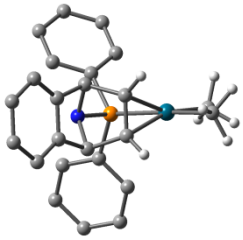


LUMO:-0.043

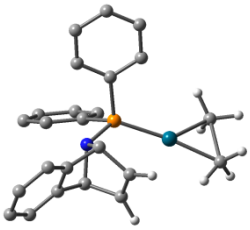
Fig. S3 NPA charges (in au) computed from NBO analysis of complexes **1**, **3**, **3'** and **4** and their corresponding TS (**$TS_{1\rightarrow2}$**, **$TS_{3\rightarrow2}$**, **$TS_{3'\rightarrow2}$** and **$TS_{4\rightarrow2}$**).

1



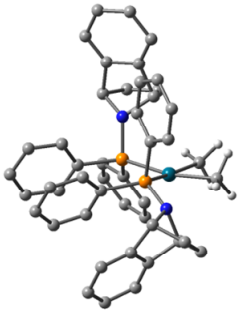
$q(P) = 1.18$; $q(Pd) = 0.33$; $q(Me^{Ptrans}) = -0.29$;
$q(Me^{CCtrans}) = -0.27$; $q(C^{olefinic}) = -0.28$

$TS_{1\rightarrow2}$



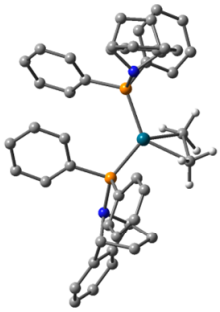
$q(P) = 1.14$; $q(Pd) = -0.03$; $q(Me^{Ptrans}) = -0.09$;
$q(Me^{CCtrans}) = -0.05$.

3'



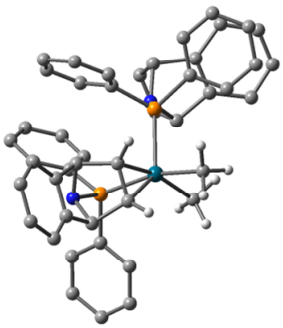
$q(P) = 1.21$; $q(P) = 1.22$; $q(Pd) = 0.16$;
$q(Me) = -0.31$; $q(Me) = -0.27$

$TS_{3'\rightarrow2}$



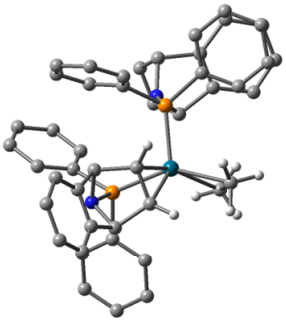
$q(P) = 1.07$; $q(P) = 1.11$; $q(Pd) = 0.08$;
$q(Me) = -0.08$; $q(Me) = -0.10$

3



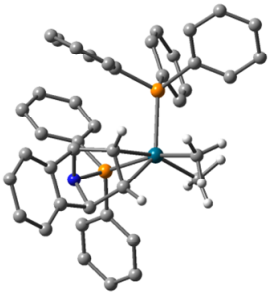
$q(P)^{apical} = 1.16$; $q(P) = 1.20$; $q(Pd) = 0.40$;
$q(Me^{Ptrans}) = -0.23$; $q(Me^{CCtrans}) = -0.32$;
$q(C^{olefinic}) = -0.33$

$TS_{3\rightarrow2}$



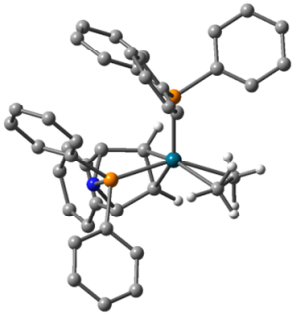
$q(P)^{apical} = 1.12$; $q(P) = 1.06$; $q(Pd) = 0.29$;
$q(Me^{Ptrans}) = -0.06$; $q(Me^{CCtrans}) = -0.09$;
$q(C^{olefinic}) = -0.37$

4



$q(P)^{apical} = 0.98$; $q(P) = 1.19$; $q(Pd) = 0.40$;
$q(Me^{Ptrans}) = -0.20$; $q(Me^{CCtrans}) = -0.32$;
$q(C^{olefin}) = -0.33$

$TS_{4\rightarrow2}$



$q(P)^{apical} = 0.95$; $q(P) = 1.06$; $q(Pd) = 0.29$;
$q(Me^{Ptrans}) = -0.06$; $q(Me^{CCtrans}) = -0.09$;
$q(C^{olefin}) = -0.37$

Electronic properties of phosphine-alkene ligand L1

NLMO analysis of complex 1

Natural Localized Molecular Orbital (NLMO) analysis indicates that there is a significant degree of electron density transferred from the Pd d orbitals to the bound olefin moiety of **L1**. Indeed, for complex **1**, the NLMO associated with the d_{xz} orbital of the Pd centre (88.7%) exhibits an interaction with the olefin $\pi^*_{C1=C1}$ molecular orbital [5% C1, 5% C1'], consistent with the olefin's π-acceptor character. This interaction is confirmed by the more positive charge at palladium, *q*(Pd), for **1** than for **1'**. A degree of back-donation from palladium {d_{xz}(Pd)} to the olefin $\pi^*_{C=C}$ molecular orbital is also evidenced by the NPA charges of the carbons of this double bond, with C1 and C1' being more negatively charged (–0.28 au each carbon atom with NBO; –0.07 au computed with AIM) relative to the equivalent carbons in free **L1** (–0.23 au on each carbon atom with NBO analysis, –0.03 au computed with AIM).

NLMO analysis of complex 3

The palladium centre of the *penta*-coordinate *bis*(phosphine) complex **3** is only very slightly more positive ($q(Pd)^{NBO}$ = 0.40 au; $q(Pd)^{AIM}$ = 0.28 au) than the Pd atom in **1**. The similarity in the degree of positive charge associated with the palladium centres in complexes **1** and **3** is explained by the fact that in **3**, significant negative charge is associated with the olefinic carbons of the chelating ligand **L1** ($q(C_{olefin})^{NBO}$ = –0.33 au; $q(C_{olefin})^{AIM}$ = –0.08), which essentially neutralises the electronic impact of the additional σ-donating phosphine moiety. This effect is reflected in a slightly greater degree of back-donation from the palladium centre to the $\pi^*_{C1=C1'}$ orbital in **3** compared to that determined for **1**. Indeed, the NLMO orbital associated with the d_{xz} orbital of the palladium centre is slightly more

delocalized into the $\pi^*_{C1=C1'}$ orbital (84 %, d_{xz}: 7.4% C1 (C=C), 5.7% C1' (C=C) *versus* 89% in **1**, d_{xz}: 5 % C1 (C=C), 5.0% C1' (C=C)).

Influence of addition of auxiliary ligands (PPh_3, propene) on reductive elimination from 1

- **Add of PPh_3**

$TS_{4\rightarrow 2}$, leading to the reductive elimination from the *penta*-coordinate complex [$PdMe_2(\kappa^1$-P–**PPh_3**$)(\kappa^2$-P,C-**L1**$)$] (**4**) is found at 22.5 kcal mol^{-1}, an energy difference very similar to that computed for the difference between **3** and its corresponding TS ($\Delta G^{\ddagger}$ = 22.2 kcal mol^{-1}). Notably, the barriers to reductive elimination from both *penta*-coordinate complexes **3** and **4** are identical, which is consistent with the similarity in the experimentally-determined rates of reductive elimination, which are comparable for the two reactions, *cf.* 5h for **1**+**L1** and 7 h for **1**+PPh_3. To an extent this suggests that both PPh_3 and the P-donor component of **L1** possess similar electronic character, something consistent with the similar energies computed for the phosphorus lone pairs of PPh_3 (–0.18 au) and **L1** (–0.18 au), see ESI, Fig. S2 for MO of ligand **L1**.

No significant differences in molecular geometry are found between *penta*-coordinate complexes **3** and **4** (P–Pd, Pd–Me and P–$C_{olefinic}$ bond distances differ by only ~0.01 Å) or between their transition states **$TS_{3\rightarrow 2}$** and **$TS_{4\rightarrow 2}$** (Fig. 2). These results are in agreement with the observations of Bo and co-workers, who have shown that the energy barriers to reductive elimination from palladium(II) complexes depend largely on the electronic nature of substrates, with steric factors (and hence geometric differences) playing only a marginal role.

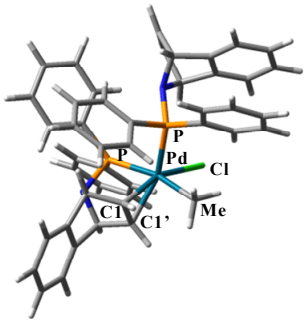
E. Zuidema, P. W. N. N. van Leeuwen and C. Bo, *Organometallics*, 2005, **24**, 3703

On considering the thermodynamics of the reductive elimination reaction, the process is about 2 kcal mol^{-1} more exergonic with ligand **L1** (**1**→**2** : –47.5 kcal mol^{-1}) than with PPh_3 (**1**→**4** : –45.1 kcal mol^{-1}). Moreover, the direct formation of the extremely stable complex [Pd(κ^2-P,C-**L1**)$_2$] (**2**) from **3** after reductive elimination has occurred, will also favour the reaction from **3** over that from **4**. In contrast, for the sequence that involves reaction of complex **1** with PPh_3, extra steps (Scheme 4, Path B) are required (reaction first goes *via* **2''**) to form the experimentally-observed palladium-containing product from this reaction, namely complex **2**.

- **Additional propene**

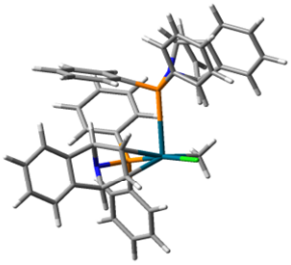
  In the presence of propene the reductive elimination becomes significantly more exergonic ($\Delta G_{1\rightarrow 2''}$ = –27.0 kcal mol^{-1}) compared to the reaction without addition of this auxiliary ligand (Fig. 1, Path A, $\Delta G_{1\rightarrow 2'}$ = –7.1 kcal mol^{-1}). It is found that on addition of propene to the *penta*-coordinate complex **3** the formation of the stable complex **2**, is slightly less favorable than the analogous reaction of **3** with **L1** ($\Delta G_{1\rightarrow 2}$ = –32.3 kcal mol^{-1}, L : propene; $\Delta G_{1\rightarrow 2}$ = –47.5 kcal mol^{-1}, L : **L1**), in agreement with the greater rate of reaction with **L1** (5 h) than with propene (30 h).

Fig. S4 Representation of the optimized structures for the four relevant structures of the *penta*-coordinate *cis*-[PdMeCl(κ^2-P,C-**L1**)(κ^1-P-**L1**)] palladium complex **7** (**7a**, **7b**, **7c** and **7d**). Relative stability (in kcal mol^{-1}) of the four isomers are also shown. Main bond distances (in Å) and bond angles (°), involved in the RE process.



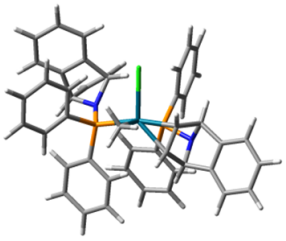
0.0

7a: PdMe: 2.13 Å; PdCl: 2.56 Å; MePdCl: 87.9°



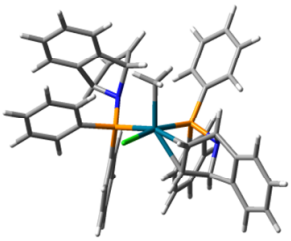
6.0

7b: PdMe: 2.10 Å; PdCl: 2.41 Å; MePdCl: 89.1°



1.4

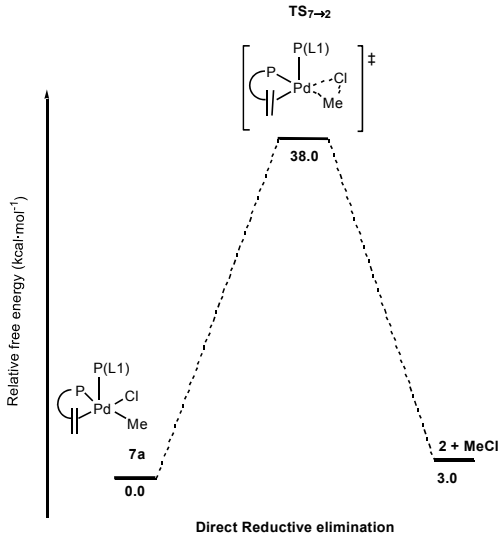
7c: PdMe: 2.12 Å; PdCl: 2.64 Å; MePdCl: 86.4 °

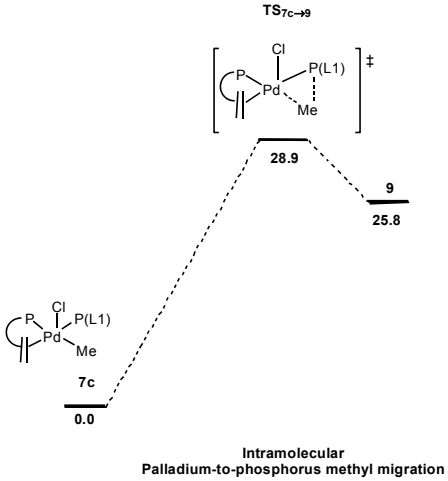


23.6

7d:PdMe: 2.20 Å; PdCl: 2.44 Å; MePdCl: 89.4°

Fig. S5 Gibbs energy profile for direct reductive elimination (left) and the palladium-to-phosphorus methyl migration (right) pathway computed from the *penta*-coordinate [PdMeCl(κ^1-P-L1)(κ^2-P,C-L1)] complex **7**. Main geometrical parameters (bond lengths in Å and bond angles in °).





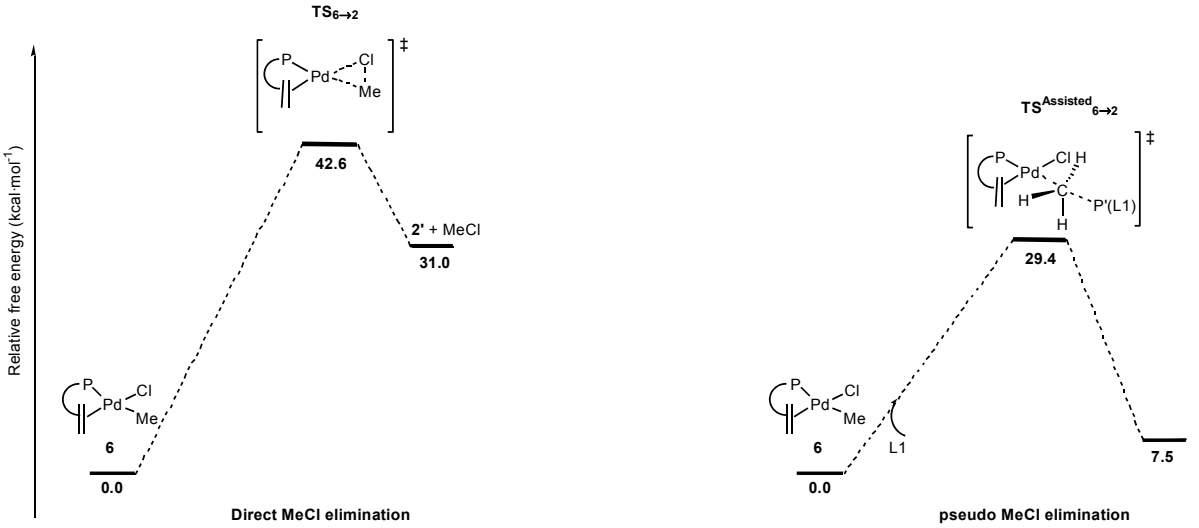
7a: Pd-Me: 2.13 Å; Pd-Cl:2.56 Å; Me···Cl: 3.27Å; MePdCl: 87.9°

TS$_{7\rightarrow2}$: Pd···Me: 2.72 Å; Pd···Cl: 2.62 Å; Me···Cl: 2.26 Å; MePdCl: 50.1°

7c: Pd-Me: 2.12 Å; Pd-Cl:2.64 Å; P(L1)-Pd: 2.34 Å; MePdCl: 86.4°; PPdMe: 88.6°

TS$_{7c\rightarrow9}$: Pd···Me: 2.56 Å; P(L1)-Me: 2.32 Å; P(L1)-Pd: 2.30 Å; MePdP(L1): 56.0°

Fig. S6 Energy profile for direct reductive elimination (left) and the assisted pathway (right) computed from *tetra*-coordinate *cis*-[PdMeCl(κ^2-P,C-L1)] complex **6**. Main geometrical parameters are also shown (bond lengths in Å and bond angles in °). MO description of $\mathbf{TS}^{\mathbf{Assisted}}_{\mathbf{6\rightarrow 2}}$ (bottom) similar to that explained in the text for complex **7**. Plot of the HOMO and LUMO for $\mathbf{TS}^{\mathbf{Assisted}}_{\mathbf{6\rightarrow 2}}$ and LUMO +2 for complex **6** (σ^*_{PdC} orbital involved in the assisted transition state).



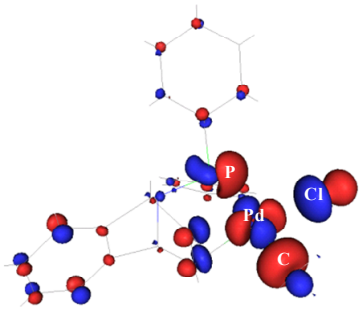
6: Pd-Me: 2.10 Å; Pd-Cl:2.37 Å; P-Pd: 2.35 Å; C_{olef}-Pd:2.16 Å MePdCl: 90.2°

$\mathbf{TS_{6\rightarrow 2}}$: Pd···Me: 2.68 Å; Pd···Cl: 2.49 Å; MePdCl: 49.3°

$\mathbf{TS_{6\rightarrow 2}}$: Pd···Me:2.60 Å; Me···P': 2.30Å; PdMeP':162.4°

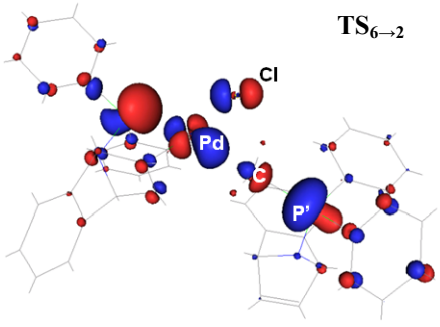
Molecular Orbitals :

Complex 6

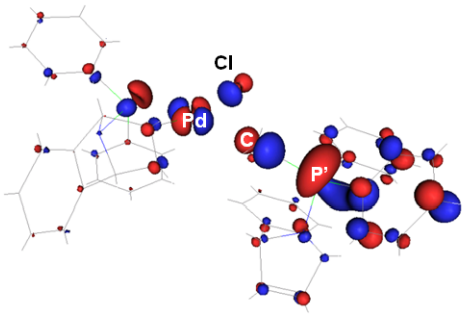


LUMO+1 σ^*_{PdC}

$\mathbf{TS_{6\rightarrow 2}}$



HOMO



LUMO

Fig. S7 Plot of the $\sigma^*_{Pd\text{-}C}$ (LUMO) orbital in the *penta*-coordinate [PdMeCl(κ^1-P–**L1**)(κ^2-P,C-**L1**)] complex **7a**, orbital involved in the assisted transition state (path C, scheme 5).

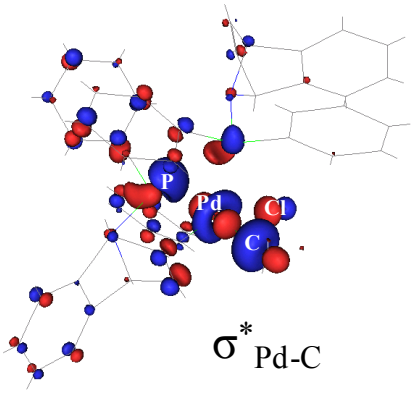


Table S1. Thermodynamic data ($\Delta G^{\ddagger}$ in kcal mol^{-1}, relative to complex **1**) for the reductive elimination of Me-Me starting from the *cis*-[$PdMe_2(\kappa^2$-P,C-L1)] complex **1**, the *tetra*-coordinate *cis*-[$PdMe_2(\kappa^1$-P-**L1**$)_2$] complex **3'** and the *penta*-coordinate intermediate [$PdMe_2(\kappa^1$-P -**L**$)(\kappa^2$-P,C-**L1**)] (L = L1 (**3**), L = PPh_3 (**4**))

L	$\Delta G_{1\rightarrow X}$ (X : 3', 3 or 4)	$\Delta G^{\ddagger}_{1\rightarrow 2}$	$\Delta G_{1\rightarrow 2}$	Reaction time
Empty (1)	/	28.1	–1.9	120 h
L1 (3')	–5.1	20.5	–48.5	/
L1 (3)	–4.0	18.2	–48.5	5 h
Ph_3P (4)	–0.2	22.3	–32.7	7 h

Table S2. Stabilization free energies (in kcal mol^{-1}) of elemental Pd(0) [Pd(0) + L → Pd-L] and **L1**Pd-L complexes [**L1**Pd + L → **L1**Pd-L] for L : **L1**, PPh_3 and propene, computed at the B97D level of theory.

		ΔG	
L	**L1**	**PPh_3**	**propene**
Pd-L (**2'**)	–45.4	–42.9	–30.3
L1Pd-L (**2''**)	–27.2	–25.7	–20.0

Cartesian Coordinates

1

Pd	-0.29524400	2.09264400	0.56273600
P	-0.83828000	-0.11666600	0.02537800
N	0.80008100	-0.73916400	-0.13683000
C	0.39339300	4.00338200	0.94896100
H	0.14448700	4.65160100	0.10101900
H	-0.08625800	4.40900100	1.84535100
H	1.48135100	4.01278900	1.09205600
C	-2.17462700	2.92261000	0.82647000
H	-2.38444100	2.87530600	1.90290600
H	-2.20475700	3.97151700	0.51965400
H	-2.95691800	2.37051000	0.29533500
C	1.60130500	0.10661500	-1.07313500
H	1.22609800	0.11033000	-2.09638400
C	1.66144400	1.46912800	-0.33405300
H	2.05181600	2.37004800	-0.79228000
C	1.67875200	1.15180800	1.00958900
H	2.08891800	1.75226300	1.81292400
C	1.62605400	-0.39461100	1.06390600
H	1.27226900	-0.84797800	1.99006500
C	2.98072800	-0.85639600	0.53321500
C	4.08566700	-1.43960100	1.11884800
H	4.10390400	-1.69308000	2.17547800
C	5.19743400	-1.70631800	0.30098400
H	6.07979400	-2.17003800	0.73300700
C	5.18198200	-1.38682500	-1.05247200
H	6.05230600	-1.60409000	-1.66526600
C	4.05425100	-0.78815100	-1.64041300
H	4.04772100	-0.54314000	-2.69916100
C	2.96516800	-0.53425200	-0.83223600
C	-1.54218800	-0.49644000	-1.62101500
C	-1.62960900	-1.80063900	-2.12589300
H	-1.28982200	-2.63915700	-1.52583400
C	-2.15476400	-2.02328900	-3.39494400
H	-2.21949100	-3.03614400	-3.78269700
C	-2.60124200	-0.94937800	-4.16727100
H	-3.01464400	-1.12824500	-5.15608000
C	-2.51986400	0.34929800	-3.67060700
H	-2.86825800	1.18658300	-4.26861600
C	-1.99099200	0.57686100	-2.40047200
H	-1.91964100	1.58665700	-2.00329400
C	-1.56821500	-1.35056500	1.15963000
C	-1.04517400	-2.64275900	1.30426300
H	-0.16157000	-2.92629100	0.73922600
C	-1.64583900	-3.54367200	2.18101000
H	-1.23408000	-4.54302600	2.29290100
C	-2.77097200	-3.16565300	2.91306200
H	-3.23740600	-3.87103100	3.59517900
C	-3.29094600	-1.87919200	2.77733800
H	-4.16067300	-1.57848800	3.35453900
C	-2.68804200	-0.97080100	1.91042100
H	-3.07805500	0.03964800	1.82014400

Sum of electronic and thermal Enthalpies= -1452.224701
Sum of electronic and thermal Free Energies= -1452.307083

$TS_{1\rightarrow2}$

P	0.88754800	-0.12540400	0.02720700
N	-0.80672200	-0.64660200	0.02650600
C	-1.59977100	-0.00588400	-1.06231100
H	-1.24104700	-0.23514400	-2.06549800
C	-1.62206900	1.48201600	-0.63960600
H	-1.97611300	2.27813700	-1.28424400
C	-1.63578500	1.47194700	0.73641200
H	-2.02232900	2.24530500	1.39092600
C	-1.60562100	-0.02447100	1.12987800
H	-1.24762000	-0.26863600	2.13057000
C	-2.97505600	-0.56940000	0.72901400
C	-2.97214700	-0.55573000	-0.67450100
C	-4.07449300	-0.96538700	-1.39545900
H	-4.07800400	-0.96134300	-2.48234900
C	-5.20388900	-1.40123300	-0.67935300
H	-6.08484700	-1.73410400	-1.22125300
C	-5.20669800	-1.41457100	0.71082700
H	-6.08954000	-1.75778000	1.24306800
C	-4.07984400	-0.99210300	1.43879100
H	-4.08718200	-1.00783900	2.52562400
C	1.42695300	-0.88770900	-1.55899700
C	1.23229300	-2.24421600	-1.85257800
H	0.74974100	-2.88910200	-1.12439200
C	1.65311300	-2.76430400	-3.07296000
H	1.49879400	-3.81704600	-3.29403700
C	2.27523600	-1.93762600	-4.01043700
H	2.60562800	-2.34786400	-4.96091700
C	2.47265300	-0.58840300	-3.72668700
H	2.95552600	0.05806800	-4.45436900
C	2.04887200	-0.06561300	-2.50489800
H	2.19324300	0.98789300	-2.27464600
C	1.54376800	-1.28750200	1.29455300
C	2.79612200	-0.99997100	1.85310700
H	3.33499300	-0.11086700	1.53274200
C	3.35214800	-1.84156600	2.81377600
H	4.32690900	-1.61159800	3.23520800
C	2.65280800	-2.96922100	3.24209900
H	3.08152300	-3.62083200	3.99857900
C	1.39888700	-3.25418900	2.70305400
H	0.84965200	-4.13044200	3.03760800
C	0.84637500	-2.42170000	1.73152700
H	-0.12938000	-2.63803900	1.30575200
Pd	0.44546100	2.19757700	0.19895900
C	1.81804900	3.58033500	1.15398900
H	1.65653800	4.47306200	1.75794300
H	1.83069500	2.72704300	1.85779200
H	2.77427100	3.64215100	0.63447100
C	0.45762200	4.34488300	-0.08639000
H	-0.32373900	4.81149600	0.51532900
H	1.22248400	5.08290500	-0.32800600
H	0.04529500	4.01301700	-1.05876200

Sum of electronic and thermal Enthalpies= -1452.175695
Sum of electronic and thermal Free Energies= -1452.258281

1'

P	-0.67859100	0.07359800	0.08299600
N	0.00145100	0.08474200	-1.50949800
C	0.89049200	-1.04288900	-1.95433500
H	0.49404300	-2.03149700	-1.70328200
C	2.22582900	-0.63343900	-1.29409300
C	2.23889300	0.77850200	-1.33110900
C	0.90689300	1.17463700	-2.01441500
H	0.53182400	2.18667100	-1.83122500
C	1.01509100	0.69827100	-3.48102900
C	1.00887400	-0.64587500	-3.44337400
C	-2.05167400	1.27798400	-0.13164300
C	-2.68591700	1.80189800	1.01577000
H	-2.31107600	1.54582200	2.00799000
C	-3.78591400	2.65975600	0.88657400
H	-4.26582300	3.06201800	1.77993800
C	-4.26887500	3.00052700	-0.38822200
H	-5.12601400	3.66800300	-0.48750600
C	-3.64793900	2.47556900	-1.53159500
H	-4.02090000	2.73427200	-2.52391800
C	-2.54621400	1.61469900	-1.40749200
H	-2.06217800	1.19714000	-2.29016100
C	0.47684100	0.94625600	1.23026100
C	1.39931100	0.14684600	1.93656400
H	1.37694900	-0.93829700	1.81020900
C	2.36614300	0.73691000	2.76086200
H	3.08241500	0.10909200	3.29188700
C	2.41446300	2.13329600	2.89485400
H	3.16583700	2.59432700	3.53760200
C	1.49562400	2.93681100	2.20027700
H	1.53156900	4.02256400	2.30401800
C	0.53218500	2.34742400	1.36954900
H	-0.18276600	2.97150700	0.83290900
Pd	-1.06936800	-2.11685200	0.76303900

C	-2.17459900	-2.68454300	-0.88447600
H	-1.98904000	-3.73783300	-1.13032200
H	-3.22674700	-2.53385000	-0.60015900
H	-1.89370300	-2.02242800	-1.71576800
C	-1.25633300	-4.07435000	1.41055000
H	-0.83669500	-4.08097200	2.43761200
H	-2.30539100	-4.40745100	1.44668300
H	-0.67878000	-4.76732300	0.77757300
H	1.15075900	1.35725200	-4.33541700
H	1.14056700	-1.35120700	-4.26025900
C	3.26610700	-1.34970200	-0.71987400
H	3.25340700	-2.44043200	-0.68230700
C	3.29410800	1.50205600	-0.79679600
H	3.30000300	2.59278300	-0.80280000
C	4.34339900	-0.61869000	-0.16167500
H	5.16861800	-1.15331800	0.31104800
C	4.35569700	0.78075200	-0.19884900
H	5.18787100	1.32495500	0.24966900

Sum of electronic and thermal Enthalpies= -1452.100236
Sum of electronic and thermal Free Energies= -1452.186153

$TS_{1'\rightarrow 2}$

P	-0.63658500	-0.13979700	-0.02400500
N	0.11720600	-0.19002900	1.54300500
C	0.87988100	1.00930600	2.02747500
H	0.34470300	1.95202600	1.86710500
C	2.21757800	0.82534400	1.27454100
C	2.41332200	-0.57236500	1.21105500
C	1.18152700	-1.18291800	1.92407900
H	0.93109600	-2.22142700	1.68612400
C	1.31103100	-0.79545100	3.41468600
C	1.13402400	0.53612100	3.47588400
C	-1.88932500	-1.47913100	0.17077400
C	-2.52009700	-1.99005500	-0.98366500
H	-2.22115000	-1.62772500	-1.96866600
C	-3.51943000	-2.96522200	-0.87118900
H	-3.99829200	-3.35557700	-1.77058100
C	-3.90366300	-3.43901800	0.39504900
H	-4.68274400	-4.19783400	0.48180700
C	-3.28358200	-2.92999000	1.54607700
H	-3.57870500	-3.29318500	2.53204500
C	-2.28203700	-1.95191300	1.43798500
H	-1.79849200	-1.54547500	2.32630200
C	0.54778200	-0.89022300	-1.23221500
C	1.32874400	-0.01383300	-2.01018800
H	1.15933000	1.06136400	-1.92345900
C	2.31748800	-0.51502600	-2.86719600
H	2.92460800	0.17325100	-3.45666900
C	2.52569300	-1.89981700	-2.96454600
H	3.29270400	-2.29158200	-3.63450300
C	1.74223700	-2.78155900	-2.20218300
H	1.89712400	-3.85905800	-2.28147900
C	0.75937500	-2.27960100	-1.33750000
H	0.14662300	-2.96474700	-0.75060300
Pd	-1.34231700	1.93892700	-0.55147700
C	-2.77788000	3.33785500	0.35886800
H	-2.75060700	4.40553700	0.58969200
H	-3.76635700	3.04338400	-0.00890700
H	-2.51156400	2.77979700	1.27326900
C	-1.76131100	3.86355400	-1.34948800
H	-1.19486200	3.30804300	-2.14484000
H	-2.69613300	4.21900100	-1.79041900
H	-1.15330200	4.68934300	-0.96683800
H	1.57753100	-1.48644100	4.21123300
H	1.22427600	1.19660600	4.33500000
C	3.11878500	1.70610600	0.69390000
H	2.96410800	2.78600100	0.73100400
C	3.51803400	-1.11585400	0.57377000
H	3.66103700	-2.19446100	0.50031000
C	4.24330900	1.15933900	0.02800600
H	4.96044500	1.82622300	-0.45312200
C	4.43860200	-0.22559000	-0.02998900
H	5.30299800	-0.62690100	-0.56077600

Sum of electronic and thermal Enthalpies= -1452.076072
Sum of electronic and thermal Free Energies= -1452.160948

3

Pd	-0.61051800	-0.59844900	-1.58748600
P	-1.42695300	1.16964300	-0.27668900
N	-2.81589600	0.33622500	0.44849100
C	-0.47308400	-2.16756300	-3.01817800
H	-1.43795400	-2.24331500	-3.53832600
H	0.30799000	-1.95968500	-3.75899000
H	-0.25571200	-3.10698600	-2.48861800
C	0.17270300	0.59188000	-3.21096300
H	1.16559000	0.20861400	-3.49083300
H	-0.49255000	0.50286100	-4.08294200
H	0.24901600	1.65097000	-2.92312900
C	-3.69358300	-0.23694800	-0.63329900
H	-4.15841400	0.52360900	-1.26768200
C	-2.74881600	-1.26864200	-1.32622100
H	-3.07609400	-1.83063400	-2.19801000
C	-1.94374000	-1.78642200	-0.27730300
H	-1.60005300	-2.81644000	-0.21542300
C	-2.40537900	-1.02041100	0.99918800
H	-1.69417300	-0.96056100	1.82663100
C	-3.80352700	-1.55261200	1.30317300
C	-4.31133200	-2.38683000	2.29041900
H	-3.67607800	-2.76239200	3.09459000
C	-5.68248300	-2.73002800	2.22468100
H	-6.11309100	-3.37656100	2.99104000
C	-6.49612500	-2.24795000	1.18977900
H	-7.55149600	-2.52321100	1.16132600
C	-5.96785700	-1.40580600	0.18238500
H	-6.60541800	-1.03282000	-0.62127500
C	-4.62348100	-1.06613500	0.25914900
C	-2.23847400	2.54938100	-1.17622900
C	-2.56750700	3.76650900	-0.54682200
H	-2.31226500	3.91928800	0.50191000
C	-3.22090200	4.77442100	-1.27007500
H	-3.47353100	5.71603700	-0.78013100
C	-3.55298100	4.57174700	-2.61981100
H	-4.05985200	5.35901100	-3.18007300
C	-3.22707000	3.35974100	-3.24948900
H	-3.47847500	3.20232100	-4.29940800
C	-2.56435900	2.35251600	-2.53361100
H	-2.28564300	1.41168200	-3.00840700
C	-0.67562100	1.96607700	1.18952300
C	-1.27811200	1.93321500	2.46191500
H	-2.24990900	1.45553100	2.57891300
C	-0.61896300	2.50931900	3.55807500
H	-1.08397600	2.47808300	4.54492800
C	0.63366800	3.12143100	3.38817100
H	1.14717300	3.56015200	4.24543800
C	1.22705300	3.17220900	2.11545600
H	2.20095300	3.63736900	1.97354600
C	0.57242400	2.59405500	1.02126700
H	1.04467900	2.60922300	0.04160400
P	1.39011700	-1.16086400	-0.28281600
C	0.93366100	-1.57618300	1.45151100
C	0.96940000	-0.61230300	2.47924100
C	0.37220600	-2.84441800	1.72288100
C	0.44376700	-0.91022000	3.74633300
H	1.38481700	0.37263600	2.27775100
C	-0.15544300	-3.13591400	2.98650800
H	0.34877100	-3.60143500	0.93886000
C	-0.12609900	-2.16589200	4.00400600
H	0.46952500	-0.14653600	4.52393800
H	-0.58955700	-4.11869200	3.17685900
H	-0.54232000	-2.38998100	4.98724800
C	2.44325300	-2.61236400	-0.76474300
C	2.67474300	-2.82005300	-2.13927600
C	3.12869600	-3.41470200	0.17053300
C	3.56667000	-3.81077600	-2.57165500
H	2.16491800	-2.19183500	-2.86613800
C	4.02256100	-4.40570000	-0.26137400
H	2.96421700	-3.26234300	1.23706100
C	4.24310500	-4.60651800	-1.63349100
H	3.73376800	-3.96075600	-3.63941000

H	4.54730400	-5.01942900	0.47302400
H	4.93713300	-5.37886500	-1.96865400
N	2.48300100	0.16028200	0.01458900
C	3.82042600	-0.02485000	0.67798200
H	3.79318300	-0.66892500	1.56194600
C	3.01007200	1.00007800	-1.11182000
H	2.25264900	1.27856300	-1.84837800
C	4.13008600	1.46813400	0.89829900
C	4.70840600	-0.46664000	-0.51624900
H	5.58783400	-1.09997200	-0.43407900
C	4.21937800	0.15560200	-1.60069000
H	4.61166000	0.16250900	-2.61466200
C	3.62429900	2.12094000	-0.24940000
C	4.76921400	2.17541500	1.90642900
H	5.15518000	1.67678600	2.79711600
C	4.90935300	3.57614200	1.74675900
H	5.40890100	4.15835400	2.52237200
C	4.41320100	4.22250300	0.60704800
H	4.52955600	5.30231300	0.50528200
C	3.75580700	3.49221500	-0.41421600
H	3.36306500	4.00097900	-1.29621100

Sum of electronic and thermal Enthalpies= -2696.356331
Sum of electronic and thermal Free Energies= -2696.479258

$TS_{3\rightarrow2}$

Pd	-0.40157800	-0.80574000	-1.47960000
P	-1.41513100	1.13595200	-0.33293000
N	-2.78833200	0.19582100	0.32239000
C	-0.25888200	-2.00521900	-3.46044900
H	-1.23644200	-1.92979400	-3.94387700
H	0.51732200	-2.20522700	-4.20605600
H	-0.24375200	-2.83898700	-2.74384600
C	0.38982400	-0.09087300	-3.54654000
H	1.46833200	-0.24368500	-3.63897800
H	-0.08344500	-0.04571400	-4.53242500
H	0.17989400	0.86157800	-3.04070600
C	-3.57755400	-0.50477000	-0.74871400
H	-4.03427600	0.17736500	-1.47223500
C	-2.56158800	-1.55790500	-1.29654000
H	-2.78387900	-2.18834500	-2.15617600
C	-1.80726300	-1.94570800	-0.17504400
H	-1.37651300	-2.92830100	0.00418300
C	-2.34958800	-1.08672600	1.00366400
H	-1.67791400	-0.93251300	1.85222500
C	-3.74429000	-1.64339700	1.29356400
C	-4.27341400	-2.39540000	2.33344500
H	-3.66595200	-2.67470100	3.19636100
C	-5.63205300	-2.78359900	2.24392900
H	-6.07949000	-3.36835400	3.04938300
C	-6.41065100	-2.42294700	1.13603100
H	-7.45671000	-2.73015200	1.08966100
C	-5.85991100	-1.66124000	0.07674800
H	-6.47215900	-1.38100400	-0.78257800
C	-4.52874300	-1.27955100	0.17456500
C	-2.32599200	2.38605400	-1.33611400
C	-2.80006500	3.60655900	-0.81331100
H	-2.65296600	3.83137100	0.24330400
C	-3.45819100	4.52193300	-1.64706300
H	-3.82311100	5.46449000	-1.23523700
C	-3.65710100	4.22534600	-3.00597500
H	-4.17045600	4.93998100	-3.65126400
C	-3.18970700	3.01060200	-3.53353600
H	-3.34029800	2.77771900	-4.58910800
C	-2.51675200	2.10003600	-2.70570300
H	-2.13587900	1.15785100	-3.10547400
C	-0.93339200	2.05856100	1.18730200
C	-1.66342500	2.01159600	2.39180100
H	-2.61027700	1.47261000	2.41758000
C	-1.16265100	2.64562500	3.53933400
H	-1.72911200	2.60058700	4.47154200
C	0.06035800	3.33573100	3.49347600
H	0.44889400	3.81868000	4.39191800
C	0.78359100	3.40107500	2.28973200
H	1.73953200	3.92267700	2.23777800
C	0.28802700	2.76047700	1.14717800
H	0.87484400	2.77690400	0.23113700
P	1.49733500	-1.14759100	-0.16572300
C	1.05385800	-1.47874500	1.59050300
C	0.96294200	-0.43485000	2.53320500
C	0.60805700	-2.76914700	1.95260300
C	0.42631400	-0.67671500	3.80748100
H	1.28783700	0.56645200	2.25921600
C	0.06962000	-3.00613300	3.22390100
H	0.67976000	-3.58643700	1.23370600
C	-0.02808800	-1.95764500	4.15559800
H	0.35022500	0.14824100	4.51612400
H	-0.27454600	-4.00771500	3.48705000
H	-0.45461300	-2.14063800	5.14302500
C	2.65616600	-2.54357400	-0.54918000
C	2.78230500	-2.92190300	-1.90054000
C	3.47096500	-3.16999800	0.41595700
C	3.71131300	-3.89912900	-2.28492100
H	2.14957600	-2.43816700	-2.64357600
C	4.39902000	-4.14942600	0.03324500
H	3.36970000	-2.89475000	1.46622700
C	4.52341900	-4.51335200	-1.31801900
H	3.79984800	-4.18375800	-3.33478700
H	5.02462200	-4.62963600	0.78787000
H	5.24525100	-5.27622300	-1.61382700
N	2.47159100	0.27536000	0.04823400
C	3.84174100	0.26115700	0.65948100
H	3.91839000	-0.34889400	1.56457900
C	2.85497700	1.12206600	-1.12511300
H	2.03695600	1.28667800	-1.83203800
C	3.98921200	1.78705900	0.81938400
C	4.72443700	-0.12981500	-0.55719600
H	5.67495900	-0.65321000	-0.49190200
C	4.12681200	0.39320000	-1.64040300
H	4.48212600	0.41019100	-2.66819800
C	3.37066000	2.33706000	-0.32728500
C	4.55906300	2.59858700	1.78964400
H	5.02873400	2.17899700	2.68087200
C	4.50833300	4.00081000	1.59356400
H	4.94739800	4.66411500	2.34019100
C	3.89921700	4.54593600	0.45587900
H	3.86794900	5.62861700	0.32668200
C	3.31795800	3.70882900	-0.52862900
H	2.83301600	4.13826300	-1.40699500

Sum of electronic and thermal Enthalpies= -2696.316321
Sum of electronic and thermal Free Energies= -2696.443792

3'

P	1.91459900	-0.61665000	-0.35192000
P	-1.73752000	-0.48902000	0.08768300
N	2.91533700	0.80102800	-0.03643900
N	-2.92549700	0.75617500	-0.03336100
C	2.42560400	1.82061500	0.95903600
H	2.18615100	1.40119400	1.94065000
C	1.28516200	2.52639400	0.17944300
H	0.41556900	2.98921300	0.63510400
C	1.64299100	2.49775000	-1.11647700
H	1.13862900	2.93323000	-1.97402800
C	3.02461900	1.78870800	-1.16847500
H	3.32342800	1.34460600	-2.12154500
C	4.02530200	2.73895100	-0.48475300
C	3.64512700	2.75600300	0.87605000
C	4.32954300	3.52299900	1.80791400
H	4.04060200	3.53679600	2.86046800
C	5.42905100	4.29031600	1.35109300
H	5.99039200	4.90028100	2.06035900
C	5.80659200	4.27310700	0.00256400
H	6.65871100	4.86988900	-0.32586400
C	5.09953600	3.48867200	-0.94156800
H	5.39984100	3.47546800	-1.99063000
C	-2.69656000	2.06667300	-0.71359800
H	-2.05724600	1.99610000	-1.59685900
C	-2.21217100	2.95156100	0.46610000
H	-1.60964700	3.85044000	0.35613800
C	-2.82256500	2.48770500	1.56991400
H	-2.81908300	2.90240500	2.57511400

C	-3.72355300	1.31219300	1.10063400
H	-4.01866000	0.57467900	1.85295300
C	-4.83870000	1.95228500	0.24557400
C	-4.18329900	2.43240700	-0.91347600
C	-4.88589000	3.07446800	-1.92200000
H	-4.38685300	3.43848500	-2.82154600
C	-6.28451800	3.23262600	-1.75718700
H	-6.86402100	3.72840000	-2.53725200
C	-6.93258700	2.75657300	-0.61123000
H	-8.01075800	2.88711100	-0.50755200
C	-6.20708000	2.10304900	0.41585400
H	-6.71738400	1.73020100	1.30594000
C	2.03229600	-1.43850100	1.30066900
C	1.08654100	-2.42961300	1.61875600
H	0.28447500	-2.65525000	0.91712900
C	1.15357200	-3.10919900	2.84209600
H	0.40463300	-3.86415200	3.08153000
C	2.16327700	-2.79600200	3.76410700
H	2.20757800	-3.31407000	4.72329700
C	3.11662100	-1.81448000	3.44967800
H	3.90978200	-1.57455600	4.15988700
C	3.06103700	-1.14576000	2.21878100
H	3.81078600	-0.39787000	1.96312000
C	3.12973500	-1.62772600	-1.30918200
C	2.62458800	-2.59659700	-2.19635900
H	1.54601600	-2.65502400	-2.35589500
C	3.50318400	-3.43548300	-2.89638000
H	3.10688500	-4.18246000	-3.58586900
C	4.89036400	-3.29690900	-2.72736900
H	5.57492900	-3.94187400	-3.28059800
C	5.39672600	-2.32007100	-1.85415500
H	6.47475900	-2.20578300	-1.72824200
C	4.52021400	-1.49141800	-1.13848000
H	4.90042800	-0.72886700	-0.45876700
C	-2.72830800	-2.00419700	-0.26184600
C	-2.04190100	-3.14882300	-0.71201600
H	-0.96625100	-3.08715100	-0.89135100
C	-2.74102500	-4.33465100	-0.97879700
H	-2.20278300	-5.21470000	-1.33427500
C	-4.13479800	-4.37971500	-0.81222700
H	-4.68148200	-5.29875700	-1.02859300
C	-4.82712400	-3.23281500	-0.39074800
H	-5.91277500	-3.25851400	-0.28374400
C	-4.12742200	-2.04763900	-0.11725500
H	-4.66495600	-1.14580800	0.17522300
C	-1.44434800	-0.61087400	1.90994000
C	-0.54181900	0.30378800	2.48874600
H	-0.05405000	1.04045100	1.85375400
C	-0.26308100	0.25959400	3.85894100
H	0.45058200	0.96225300	4.29179500
C	-0.88742400	-0.70103200	4.67188100
H	-0.66069100	-0.74551500	5.73797800
C	-1.79848000	-1.60558700	4.10743900
H	-2.28878800	-2.35143800	4.73532100
C	-2.07822400	-1.56166000	2.73255200
H	-2.77918300	-2.27327500	2.29666100
Pd	-0.07946900	-0.29734000	-1.51608700
C	-1.67772900	-0.16073000	-2.93344500
H	-1.52820900	0.72532000	-3.56883200
H	-1.58933600	-1.06441100	-3.55481000
H	-2.68306300	-0.12877300	-2.49353000
C	1.03936900	-0.00872600	-3.30873000
H	2.12585900	-0.09960000	-3.18736200
H	0.70791700	-0.75877000	-4.04165200
H	0.79308700	0.99298400	-3.69353300

Sum of electronic and thermal Enthalpies= -2696.353060
Sum of electronic and thermal Free Energies= -2696.480904

$TS_{3'\rightarrow 2}$

P	2.00131300	-0.63903800	-0.54061500
P	-1.91625700	-0.53517400	0.25353200
N	3.06052900	0.66684800	0.04332000
N	-3.04407200	0.74823200	-0.06145700
C	2.65077900	1.43750000	1.26519000
H	2.44413600	0.80847700	2.13611200
C	1.50262300	2.33731400	0.72895300
H	0.67201800	2.70774300	1.32370600
C	1.81301300	2.61037800	-0.54954800
H	1.30157500	3.27211600	-1.24466600
C	3.15734900	1.88319300	-0.83582600
H	3.40090300	1.65819600	-1.87940700
C	4.22402300	2.62371600	-0.00620900
C	3.89919300	2.33785000	1.33927700
C	4.65014800	2.84961800	2.38730800
H	4.40475700	2.62878600	3.42770200
C	5.76019800	3.66927100	2.06569200
H	6.37315700	4.08273800	2.86791500
C	6.08196300	3.95281900	0.73267100
H	6.94270700	4.58460800	0.50869400
C	5.30678200	3.42792400	-0.33084300
H	5.56410200	3.64863800	-1.36824100
C	-2.53767300	2.10714600	-0.43958900
H	-1.69672700	2.07251600	-1.14069200
C	-2.29242700	2.75179400	0.95166000
H	-1.58030400	3.54944000	1.15128300
C	-3.21305100	2.22725400	1.77790900
H	-3.41757300	2.47892800	2.81567400
C	-4.06201700	1.25101200	0.91892900
H	-4.61113700	0.46058900	1.43895500
C	-4.85389200	2.12946000	-0.07063500
C	-3.87897000	2.67855900	-0.93727400
C	-4.23456000	3.53423500	-1.96995400
H	-3.48682800	3.95662200	-2.64386000
C	-5.60822400	3.83907300	-2.13436300
H	-5.91807300	4.50567800	-2.94054200
C	-6.57315800	3.29227300	-1.27924800
H	-7.62580500	3.53829600	-1.42673700
C	-6.20164600	2.42089000	-0.22600700
H	-6.95819700	1.99334600	0.43446400
C	2.22596100	-1.81824100	0.86737300
C	1.19469100	-2.75002200	1.09141900
H	0.32131300	-2.73473000	0.43529900
C	1.27860200	-3.65817200	2.15567900
H	0.47494800	-4.37781700	2.32097900
C	2.38486000	-3.62522300	3.01961000
H	2.44358500	-4.31878700	3.85993800
C	3.41510600	-2.69484400	2.80313800
H	4.27699600	-2.66949800	3.47243100
C	3.34430700	-1.80150000	1.72376600
H	4.14183200	-1.07948700	1.54567400
C	3.14336300	-1.30467500	-1.84196900
C	2.55302400	-1.98166100	-2.92723200
H	1.46423000	-2.06761800	-2.96272900
C	3.35273600	-2.51756400	-3.94799900
H	2.88800300	-3.04533200	-4.78252200
C	4.74701200	-2.35894500	-3.90241500
H	5.36978800	-2.76371400	-4.70188000
C	5.33934500	-1.67108400	-2.82960800
H	6.42290700	-1.54366100	-2.79515000
C	4.54381100	-1.15190200	-1.79797400
H	4.99327100	-0.61371200	-0.96323500
C	-3.02723300	-1.98850500	0.06178800
C	-2.69261400	-3.21069400	0.68690300
H	-1.85871300	-3.24551100	1.38939100
C	-3.43767200	-4.36884900	0.42813800
H	-3.17272000	-5.30455500	0.92362400
C	-4.52530300	-4.32541700	-0.46046900
H	-5.10529700	-5.22747000	-0.66082100
C	-4.86195500	-3.11507600	-1.08706100
H	-5.70859500	-3.07281000	-1.77454500
C	-4.11683400	-1.95343300	-0.83371800
H	-4.37642200	-1.00925500	-1.31238100
C	-1.59892900	-0.54775300	2.08157900
C	-0.34514100	-0.08916400	2.51988800
H	0.38979100	0.18323100	1.76637500
C	-0.04900800	-0.00077700	3.88606300
H	0.93288700	0.34826800	4.21104500
C	-1.01316400	-0.37791800	4.83424000
H	-0.78701400	-0.31711100	5.89999300
C	-2.26737100	-0.84742200	4.40799000
H	-3.01502600	-1.15061300	5.14317600

C	-2.55859600	-0.93467000	3.03866600
H	-3.52488700	-1.31926000	2.71000700
Pd	-0.17218100	-0.36892900	-1.27064800
C	-1.34545900	-0.82112100	-3.12608600
H	-1.02751000	-1.07628400	-4.14167000
H	-1.45693500	-1.77032100	-2.56819800
H	-2.28826400	-0.26629300	-3.13772700
C	0.08752600	0.63280700	-3.26019800
H	0.47637700	1.41105800	-2.57662700
H	0.90226500	0.16633200	-3.82248100
H	-0.62532200	1.11986700	-3.93293700

Sum of electronic and thermal Enthalpies= -2696.308392
Sum of electronic and thermal Free Energies= -2696.440230

4

Pd	0.01996400	-0.14002100	-1.57707900
P	-1.35701800	1.04641900	-0.07465800
N	-2.50077400	-0.26015700	0.29645000
C	0.71990900	-1.33506700	-3.18200400
H	-0.03153100	-1.30788200	-3.98313600
H	1.67379400	-0.95420600	-3.55811500
H	0.84198100	-2.36341000	-2.80929600
C	0.46427500	1.45799700	-2.96742300
H	1.53841200	1.45967800	-3.20640000
H	-0.09663000	1.28631300	-3.89881000
H	0.17640200	2.43401700	-2.55007900
C	-3.09425600	-0.80850500	-0.97628100
H	-3.70844100	-0.08354600	-1.51915400
C	-1.84507900	-1.38735400	-1.71396900
H	-1.92938700	-1.82410800	-2.70682900
C	-1.00892800	-1.87678500	-0.67456200
H	-0.38033500	-2.76066000	-0.74623900
C	-1.76246700	-1.54528600	0.64394400
H	-1.15757300	-1.47507700	1.55169200
C	-2.97048100	-2.47819600	0.66461300
C	-3.28946300	-3.60592800	1.40958300
H	-2.63450200	-3.95947200	2.20792200
C	-4.49396200	-4.28187000	1.10231300
H	-4.77653600	-5.16660600	1.67506900
C	-5.33064700	-3.82848200	0.07294200
H	-6.25611000	-4.36392000	-0.14438400
C	-4.99302600	-2.68336600	-0.68729500
H	-5.64776800	-2.33482700	-1.48811100
C	-3.81390400	-2.02018200	-0.37355300
C	-2.45829700	2.33270000	-0.78244900
C	-3.12677800	3.28033100	0.01827600
H	-2.98003700	3.27665700	1.09837500
C	-3.97815700	4.22308300	-0.57521100
H	-4.49258500	4.95624100	0.04793000
C	-4.17281200	4.22065300	-1.96626100
H	-4.83533600	4.95633300	-2.42488400
C	-3.51065800	3.27592400	-2.76667400
H	-3.65546200	3.27554500	-3.84797700
C	-2.64806100	2.33902100	-2.17991300
H	-2.10873600	1.61215200	-2.78740100
C	-0.96961100	1.65774200	1.61369700
C	-1.58439900	1.12439600	2.76375600
H	-2.36554100	0.37414200	2.65077400
C	-1.18480100	1.55862900	4.03648100
H	-1.66136500	1.13798800	4.92347900
C	-0.17604300	2.52593000	4.17175900
H	0.14050000	2.85076600	5.16410200
C	0.41867100	3.08096600	3.02600900
H	1.20148000	3.83419500	3.11738100
C	0.01963500	2.65161000	1.75388300
H	0.49504300	3.07539000	0.87206400
P	2.01319700	-0.35610000	-0.18920400
C	1.61282500	-1.32975400	1.32081900
C	1.23298500	-0.70018000	2.52557100
C	1.45660500	-2.73143300	1.21314100
C	0.71992100	-1.45378500	3.59221400
H	1.31399700	0.37982400	2.62744400
C	0.94636300	-3.48047900	2.28043700
H	1.72700500	-3.23391500	0.28451600
C	0.57354400	-2.84404900	3.47695200
H	0.42221800	-0.94049700	4.50676200
H	0.83477900	-4.56067500	2.17515500
H	0.17063400	-3.42661300	4.30650700
C	2.79868900	1.19624200	0.44491700
C	3.61692500	1.22031800	1.59166900
C	2.61721700	2.37786200	-0.29901500
C	4.21158800	2.41801000	2.01079800
H	3.77550800	0.30433100	2.16060900
C	3.22916500	3.57293400	0.11144000
H	1.97821700	2.36000600	-1.18046800
C	4.01758400	3.59775300	1.27212700
H	4.83226300	2.42993500	2.90818600
H	3.08030200	4.48399500	-0.47027600
H	4.48565500	4.52840800	1.59667800
C	3.50609800	-1.17599100	-0.91531700
C	3.92276100	-0.70330900	-2.17809800
C	4.26715000	-2.17175700	-0.27222500
C	5.06947500	-1.22551600	-2.79054600
H	3.34814800	0.07802600	-2.67562600
C	5.40906400	-2.70107400	-0.89315700
H	3.97516200	-2.52905100	0.71420700
C	5.81198100	-2.23243500	-2.15299100
H	5.37861500	-0.85025200	-3.76715000
H	5.98825600	-3.47429200	-0.38559500
H	6.70028600	-2.64558200	-2.63287900

Sum of electronic and thermal Enthalpies= -2487.639195
Sum of electronic and thermal Free Energies= -2487.756458

$TS_{4\rightarrow2}$

P	1.38451800	1.01640900	-0.17542000
N	2.43914700	-0.36501200	0.25555200
C	2.93553900	-1.12268400	-0.94596100
H	3.54805200	-0.51832000	-1.62159500
C	1.62740400	-1.74939000	-1.52889800
H	1.62678000	-2.31523400	-2.45982500
C	0.83666700	-2.03975800	-0.39877900
H	0.14071800	-2.87006900	-0.29151000
C	1.66132200	-1.54154800	0.82044100
H	1.10401000	-1.31139500	1.73221200
C	2.83312600	-2.51737300	0.93504700
C	3.64434200	-2.25684100	-0.19315100
C	4.78949500	-3.00147600	-0.44131900
H	5.42140000	-2.80450000	-1.30950800
C	5.12389600	-4.02813500	0.47494500
H	6.02241300	-4.62475400	0.30917400
C	4.31848700	-4.28622200	1.59231900
H	4.59759700	-5.08155400	2.28544500
C	3.14885900	-3.52624000	1.83503300
H	2.51966700	-3.72722700	2.70424000
C	2.55448600	2.05959400	-1.13998100
C	3.33021200	3.09297400	-0.57518300
H	3.28201700	3.27812200	0.49803800
C	4.16210500	3.87549300	-1.38900700
H	4.75938800	4.67297400	-0.94354100
C	4.23811200	3.62866600	-2.76988800
H	4.88817200	4.23863400	-3.39898300
C	3.47186300	2.59845700	-3.33937500
H	3.52609900	2.40374900	-4.41186500
C	2.62405300	1.82703400	-2.53207700
H	2.01046300	1.03333800	-2.96393200
C	1.29115300	1.85257200	1.46794100
C	0.37304200	2.91625700	1.60692900
H	-0.19191400	3.26355000	0.74168600
C	0.14943900	3.50367000	2.85899900
H	-0.57274500	4.31597600	2.95143500
C	0.83327900	3.02812800	3.99119500
H	0.64720400	3.47252500	4.97024400
C	1.75662600	1.97797800	3.85747200
H	2.29876600	1.61355600	4.73217500
C	1.99069400	1.39442600	2.60312100
H	2.70537300	0.57977500	2.48934900
Pd	-0.18702500	-0.38723100	-1.48350000
C	-0.79769700	-1.21585800	-3.54758700
H	0.08136800	-1.34502800	-4.18480100
H	-1.70458300	-1.10186500	-4.14806000

H	-0.93528800	-2.10929500	-2.92219600
C	-0.81639500	0.79192400	-3.38206600
H	-1.88759500	1.00210600	-3.33401500
H	-0.24181700	1.55783400	-2.84111400
H	-0.46482500	0.80480100	-4.41827600
P	-2.10037300	-0.23827100	-0.12235300
C	-2.69082300	1.45569400	0.32087100
C	-3.41778800	1.73685700	1.49606600
C	-2.37694800	2.51022800	-0.55925100
C	-3.81072300	3.05040800	1.79104400
H	-3.65294000	0.92886700	2.18864900
C	-2.78205600	3.82257300	-0.27094200
H	-1.79409000	2.30053600	-1.45505000
C	-3.49309500	4.09588800	0.90806400
H	-4.36207800	3.25783200	2.70947700
H	-2.52942600	4.63099900	-0.95876600
H	-3.79744700	5.11782100	1.13926600
C	-3.62347400	-1.10045200	-0.71864600
C	-3.44829200	-2.34303100	-1.36654100
C	-4.92343100	-0.56626400	-0.60907900
C	-4.55035400	-3.05124200	-1.86529700
H	-2.44104500	-2.74494900	-1.48442600
C	-6.02306900	-1.26699800	-1.12741000
H	-5.07366000	0.39730400	-0.12307300
C	-5.84174500	-2.51194500	-1.75024800
H	-4.39898800	-4.01381300	-2.35631600
H	-7.02369500	-0.84024600	-1.04055800
H	-6.69944800	-3.05426300	-2.15062400
C	-1.77206100	-1.01353700	1.52614400
C	-1.94896400	-2.39944400	1.71931400
C	-1.15254100	-0.25928600	2.54621500
C	-1.50516600	-3.01703400	2.89718600
H	-2.43645500	-2.99680600	0.94893200
C	-0.71716600	-0.87892100	3.72682300
H	-0.99434400	0.80857300	2.41571000
C	-0.88390900	-2.26089000	3.90515700
H	-1.65034600	-4.09059500	3.02887100
H	-0.23290000	-0.27440200	4.49415400
H	-0.53792500	-2.74441200	4.81986500

Sum of electronic and thermal Enthalpies= -2487.598946
Sum of electronic and thermal Free Energies= -2487.720650

5

P	0.76519500	-0.46613900	0.00649000
N	-0.93043100	-0.90033000	0.26199000
C	-1.72981400	-0.64488700	-0.99477200
H	-1.41622300	-1.26428600	-1.84126800
C	-1.61524100	0.90393000	-1.16414000
H	-2.09907600	1.40058600	-2.00357100
C	-1.56347100	1.41200700	0.16770800
H	-1.98446900	2.36607600	0.47959700
C	-1.65177400	0.15164000	1.07790900
H	-1.26864800	0.24199000	2.10022200
C	-3.07307500	-0.38952200	0.90568000
C	-3.12404300	-0.89177300	-0.41557600
C	-4.29621000	-1.41916000	-0.94145900
H	-4.33985800	-1.80519900	-1.96144100
C	-5.43973700	-1.45105100	-0.10868900
H	-6.37186100	-1.86946300	-0.49100400
C	-5.38931900	-0.95461800	1.20115600
H	-6.28300500	-0.99161500	1.82582600
C	-4.19408400	-0.40891800	1.72588900
H	-4.16049600	-0.02205200	2.74604600
C	1.33131900	-1.89702300	-0.99791800
C	0.67570000	-3.14466600	-0.94713000
H	-0.19984200	-3.26137700	-0.30873700
C	1.14535000	-4.21191200	-1.72482500
H	0.63320700	-5.17474400	-1.68877300
C	2.27460400	-4.04586100	-2.54453900
H	2.63802700	-4.87954500	-3.14719300
C	2.93127300	-2.80647800	-2.59253500
H	3.80320400	-2.67208000	-3.23404400
C	2.45797500	-1.73081000	-1.82636800
H	2.94599200	-0.75889700	-1.88314800
C	1.44805100	-0.79670100	1.68646500
C	2.63735700	-0.15194100	2.07955500
H	3.13139600	0.53998600	1.39733200
C	3.18418700	-0.38912000	3.34962300
H	4.10549900	0.11430200	3.64556700
C	2.54099300	-1.26459300	4.23806200
H	2.96233000	-1.44432500	5.22809100
C	1.35295700	-1.90761700	3.85199000
H	0.85206100	-2.58934900	4.54112800
C	0.80900600	-1.68140200	2.57999100
H	-0.11161500	-2.17582700	2.27035400
Pd	0.39286900	1.70891600	-0.86802800
C	-0.32016800	3.45172600	-1.81428600
H	-0.74207500	3.18870600	-2.79286600
H	-1.09488300	3.89291500	-1.16946500
H	0.51440400	4.15170400	-1.95086400
C	2.14649800	2.89773200	0.05017000
H	2.26781400	3.76997800	-0.59351800
C	1.19785800	2.89688300	1.05900300
H	1.23039500	2.09979500	1.80436400
H	2.95647900	2.16989000	0.02567300
C	1.52447100	1.43741600	-2.69148500
H	2.59459000	1.33707700	-2.45487300
H	1.17018300	0.52520400	-3.19267000
H	1.38311800	2.30250000	-3.35293300
C	0.32695100	4.08650600	1.38489700
H	-0.68803100	3.77902800	1.67670900
H	0.75721900	4.64949600	2.23184300
H	0.25159200	4.76507600	0.52537600

Sum of electronic and thermal Enthalpies= -1569.868058
Sum of electronic and thermal Free Energies= -1569.959089

6

Pd	-0.44011100	1.97170200	-0.00011000
P	-0.73630100	-0.36075200	0.00000600
N	0.98430000	-0.79211600	0.00001500
C	1.70138200	-0.06150700	1.10877200
H	1.36674900	-0.34803900	2.11011000
C	1.53738100	1.44572600	0.70555200
H	1.91059900	2.24835100	1.33968400
C	1.53740500	1.44568500	-0.70566000
H	1.91064600	2.24826800	-1.33983000
C	1.70139700	-0.06157600	-1.10878300
H	1.36677600	-0.34816800	-2.11010900
C	4.30279300	-0.63540700	-1.42829600
H	4.30774500	-0.63348300	-2.51936000
C	5.49002600	-0.88528700	-0.70087700
H	6.41832800	-1.08039400	-1.23908800
C	5.49001800	-0.88523900	0.70096100
H	6.41831400	-1.08030900	1.23919700
C	4.30277600	-0.63530900	1.42835000
H	4.30771700	-0.63331400	2.51941400
C	3.13923600	-0.40313100	0.70645300
C	3.13924500	-0.40317900	-0.70642700
C	-1.34691800	-1.23613300	1.48187000
C	-2.37786700	-0.62457300	2.22390600
H	-2.77641700	0.33950500	1.90120100
C	-2.87286100	-1.26010100	3.37309800
H	-3.67220100	-0.79098800	3.94787900
C	-2.33389300	-2.48846800	3.78708000
H	-2.71635500	-2.97601400	4.68498700
C	-1.29746100	-3.09030500	3.05229200
H	-0.87578600	-4.04168100	3.38007100
C	-0.80423900	-2.47007700	1.89661900
H	0.00716900	-2.92045100	1.32471400
C	-1.34693800	-1.23627800	-1.48176200
C	-2.37793300	-0.62481600	-2.22381400
H	-2.77649900	0.33928200	-1.90118400
C	-2.87295200	-1.26046300	-3.37292900
H	-3.67232800	-0.79142600	-3.94772200
C	-2.33396600	-2.48885400	-3.78681800
H	-2.71644900	-2.97649400	-4.68466400
C	-1.29748800	-3.09059300	-3.05201500
H	-0.87579900	-4.04198800	-3.37972100
C	-0.80423900	-2.47024400	-1.89641800
H	0.00720400	-2.92054100	-1.32450100

Cl	-2.72352700	2.59928300	-0.00019500
C	0.10085900	3.99855100	0.00001500
H	-0.34454400	4.44436600	-0.90034700
H	-0.34468500	4.44430800	0.90033600
H	1.19472000	4.11867000	0.00010300

Sum of electronic and thermal Enthalpies= -1872.531707
Sum of electronic and thermal Free Energies= -1872.614871

TS Direct MeCl RE from 6 ($TS_{6\rightarrow2}$)

P	0.54736200	0.81494700	-0.23875900
N	-1.13013000	0.22258600	0.04600900
C	-1.23347000	-0.91669400	1.02230700
H	-0.86293100	-0.67266300	2.02203300
C	-0.53025100	-2.09692700	0.26927900
H	-0.38369300	-3.07032400	0.73941300
C	-0.79923300	-1.86888300	-1.09068800
H	-0.89133300	-2.63742000	-1.85940000
C	-1.66499700	-0.56650100	-1.12082500
H	-1.68657700	-0.00354200	-2.06017100
C	-3.01159000	-0.96361200	-0.50235200
C	-2.73445200	-1.18839900	0.86550700
C	-3.72745600	-1.60158300	1.74339600
H	-3.51824500	-1.77498900	2.80044900
C	-5.03332500	-1.78139500	1.22731900
H	-5.83636000	-2.09693900	1.89496900
C	-5.30853900	-1.55623100	-0.12799100
H	-6.32316500	-1.69871700	-0.50269700
C	-4.28799500	-1.14374400	-1.01833900
H	-4.50738100	-0.96834600	-2.07301800
C	0.95405800	1.29843200	1.49549700
C	0.29815800	2.35545500	2.15783000
H	-0.44782300	2.94405800	1.62342200
C	0.60774900	2.64704200	3.49366100
H	0.09824700	3.46689600	4.00266500
C	1.57185200	1.88609200	4.17681900
H	1.81185800	2.11668700	5.21595100
C	2.22952000	0.83325500	3.52113500
H	2.98186300	0.24378800	4.04745500
C	1.92423100	0.54114300	2.18282600
H	2.43090600	-0.27618700	1.66454600
C	0.11520000	2.43214800	-1.04056900
C	1.15568300	3.12834400	-1.69090200
H	2.16259700	2.70436700	-1.70608300
C	0.90406000	4.35682200	-2.31771700
H	1.71725500	4.89094400	-2.81160400
C	-0.39475900	4.89178400	-2.32040900
H	-0.59283000	5.84299300	-2.81687000
C	-1.43870500	4.19570500	-1.68988200
H	-2.44932900	4.60830400	-1.69199400
C	-1.18813400	2.97292900	-1.04858800
H	-1.98827200	2.42681700	-0.54905900
Pd	1.32533900	-1.46012300	-0.70817000
C	2.55780700	-3.82938500	-0.93398200
H	1.94310800	-3.82545500	-1.83646600
H	3.46361700	-4.42501500	-1.04295000
H	2.01848200	-4.02629500	-0.00682100
Cl	3.75308300	-2.03178700	-0.74933000

Sum of electronic and thermal Enthalpies= -1872.454033
Sum of electronic and thermal Free Energies= -1872.539874

$TS^{assist}{}_{6\rightarrow2}$: ligand assisted mechanism from 6

Pd	-1.00584200	-0.11125000	-1.07303600
P	-3.41843700	-0.59136600	-0.61052800
N	-3.63971800	1.05146100	0.07601800
C	1.48632200	0.58338100	-1.02141200
H	1.20707600	1.60370700	-0.77338100
H	1.33194000	-0.20355400	-0.28684700
H	1.51046600	0.30185300	-2.07178100
C	-2.64272000	1.41697600	1.13579400
H	-2.67817900	0.76626600	2.01443200
C	-1.29225700	1.48344200	0.34773700
H	-0.36927300	1.73185900	0.86857900
C	-1.64379600	1.93721700	-0.94324400
H	-1.02984200	2.57329300	-1.58242300
C	-3.19878900	2.12410200	-0.88699800
H	-3.73861400	2.10846500	-1.83998500
C	-3.41049600	3.33391800	0.02949200
C	-3.80525300	4.64693200	-0.19093400
H	-4.08258800	4.99973200	-1.18584400
C	-3.84788300	5.52051700	0.92191300
H	-4.16359100	6.55527800	0.78112100
C	-3.49225100	5.07349200	2.20158900
H	-3.53522400	5.76448300	3.04480100
C	-3.08187200	3.73588200	2.41580100
H	-2.80834900	3.39113600	3.41478700
C	-3.05318300	2.88217500	1.32099200
C	-3.51214800	-1.57045100	0.94988500
C	-4.62614100	-1.50165800	1.81052400
H	-5.48868500	-0.89868800	1.52559300
C	-4.61810800	-2.20239600	3.02463500
H	-5.48033600	-2.14610500	3.69131900
C	-3.50096600	-2.97712000	3.38304200
H	-3.49645500	-3.52043200	4.32942800
C	-2.39549300	-3.05765100	2.52192300
H	-1.52980600	-3.66067200	2.79905400
C	-2.39867400	-2.35840700	1.30433000
H	-1.54895500	-2.41685000	0.62116100
C	-5.10160500	-0.80679900	-1.35733600
C	-6.18699700	0.05421400	-1.09060700
H	-6.04508800	0.88425000	-0.39831800
C	-7.42487800	-0.16216900	-1.71480000
H	-8.26133600	0.50696300	-1.50401200
C	-7.59201900	-1.23723400	-2.60274800
H	-8.55631900	-1.40261700	-3.08587300
C	-6.51244200	-2.09385800	-2.87526100
H	-6.63532500	-2.92556700	-3.57077000
C	-5.26964700	-1.87438600	-2.26490500
H	-4.42444300	-2.52720200	-2.49467600
Cl	-0.21364000	-2.21858100	-1.92595400
P	3.69310500	0.65160300	-0.54149200
N	3.65383900	0.86856300	1.17570100
C	4.44008600	-0.04827700	2.09425000
H	5.48077400	-0.19458800	1.79034900
C	2.37084600	0.73978300	1.96500700
H	1.53753300	1.31840100	1.56195900
C	3.52725600	-1.29758600	2.09079000
C	4.17333900	0.69329500	3.41831000
H	4.86750700	0.72986900	4.25421700
C	2.20996900	-0.79459600	2.00119000
C	2.91903900	1.16949300	3.34067200
H	2.33605000	1.68851000	4.09747100
C	3.77480300	-2.66168500	2.09752600
H	4.79032300	-3.05666200	2.13787500
C	1.11443200	-1.63978500	1.88908000
H	0.10043200	-1.25604600	1.77422100
C	2.66554500	-3.53396300	1.97910400
H	2.83332000	-4.61101300	1.94488400
C	1.36295900	-3.03347800	1.86759900
H	0.52876700	-3.72150800	1.73109200
C	4.27733100	-1.04105300	-0.93949100
C	5.64659500	-1.37111800	-0.81540100
C	3.34933500	-2.04878600	-1.27052300
C	6.07431100	-2.69016500	-1.00987200
H	6.37206300	-0.59366100	-0.57561400
C	3.78595100	-3.36600800	-1.46906500
H	2.28603500	-1.84087600	-1.37027100
C	5.14290500	-3.69179100	-1.33489300
H	7.13281800	-2.93582300	-0.91053200
H	3.05086500	-4.12968800	-1.72339100
H	5.47826200	-4.71917400	-1.48525900
C	5.08243100	1.74084000	-1.01599100
C	5.44300000	2.85079100	-0.21771000
C	5.70554400	1.56062600	-2.27460900
C	6.42563100	3.74485200	-0.66311700
H	4.96007600	2.98277100	0.75028700
C	6.68512800	2.46041400	-2.71048300
H	5.43589300	0.70608800	-2.89665200
C	7.04917300	3.55576100	-1.90788500
H	6.70861000	4.59024300	-0.03384800

H	7.16779000	2.30508900	-3.67643800
H	7.81168800	4.25601800	-2.25098800

Sum of electronic and thermal Enthalpies= -3116.707721
Sum of electronic and thermal Free Energies= -3116.837803

7a

Pd	-0.29935900	-0.19742700	-1.36432100
P	-1.67366900	1.08762500	0.13954600
N	-3.08001900	0.01285600	0.05902300
C	0.47627600	-1.55536700	-2.80687400
H	-0.35115400	-1.87193100	-3.45401400
H	1.22093000	-0.98696500	-3.36943300
H	0.92600900	-2.42122200	-2.30488600
C	-3.53098300	-0.13912900	-1.37026500
H	-3.88936400	0.79388400	-1.81465400
C	-2.30703300	-0.83033800	-2.04766600
H	-2.32066200	-1.06515100	-3.11000800
C	-1.76924500	-1.68418400	-1.02896300
H	-1.36215600	-2.67949000	-1.20246800
C	-2.67099300	-1.43700400	0.21787800
H	-2.23522100	-1.67249400	1.19296300
C	-4.00877600	-2.07944400	-0.14243400
C	-4.65464400	-3.23441200	0.27959800
H	-4.23093500	-3.86893300	1.06013500
C	-5.88869100	-3.56054900	-0.33004300
H	-6.42606500	-4.45533100	-0.01270000
C	-6.43083600	-2.74749800	-1.33558400
H	-7.38494900	-3.01793900	-1.79018200
C	-5.75959800	-1.57982000	-1.76851400
H	-6.18517000	-0.95215700	-2.55323300
C	-4.55416500	-1.25955100	-1.15702800
C	-2.40436400	2.67642200	-0.40771900
C	-3.21594800	3.43515300	0.46208000
H	-3.36295100	3.10863400	1.49163800
C	-3.83219400	4.60410800	-0.00251200
H	-4.45996300	5.19007300	0.67048000
C	-3.64289500	5.01911400	-1.33200000
H	-4.12197800	5.93199600	-1.68967800
C	-2.83441000	4.26514600	-2.19629700
H	-2.67746100	4.59030600	-3.22551900
C	-2.21039600	3.09367800	-1.73984600
H	-1.55459500	2.52008800	-2.39491900
C	-1.49039800	1.27359900	1.95545800
C	-2.35952700	0.64492800	2.86897700
H	-3.20118400	0.06342900	2.49704800
C	-2.14484300	0.78382100	4.24811700
H	-2.81959800	0.29190100	4.95041400
C	-1.07022100	1.55189100	4.72360100
H	-0.90228500	1.65206600	5.79705300
C	-0.21776900	2.19908700	3.81390500
H	0.62394300	2.79390000	4.16844500
C	-0.42938500	2.06218900	2.43694000
H	0.24049400	2.55574100	1.73809300
P	1.50464100	-0.67302600	0.10202500
C	0.80863800	-1.79737900	1.37477300
C	0.46579600	-1.33941900	2.66107700
C	0.43725200	-3.10358500	0.98490600
C	-0.24062700	-2.17491900	3.54071800
H	0.72538700	-0.32396000	2.95310600
C	-0.26746100	-3.93317100	1.86545200
H	0.69559200	-3.46401500	-0.01103200
C	-0.61336400	-3.46861900	3.14696200
H	-0.51097800	-1.79989600	4.52803000
H	-0.54870000	-4.93972900	1.55194000
H	-1.16825900	-4.11257600	3.83081300
C	2.93633000	-1.59195600	-0.60042800
C	3.48731200	-1.08886500	-1.79723700
C	3.54313500	-2.69077600	0.03838900
C	4.63500100	-1.67697700	-2.34068000
H	3.02349900	-0.23040000	-2.28244100
C	4.68606600	-3.28455700	-0.51785000
H	3.12451100	-3.07974400	0.96666100
C	5.23337100	-2.77766300	-1.70646700
H	5.06385900	-1.27180800	-3.25745200
H	5.15019200	-4.13783000	-0.02028100
H	6.12569000	-3.23667400	-2.13509700
N	2.11068200	0.61933700	1.07342600
C	3.37185800	0.48616400	1.89099600
H	3.42485700	-0.43541900	2.47976900
C	2.48591300	1.95008500	0.47148100
H	1.75111400	2.34069600	-0.23838800
C	3.26861900	1.82644300	2.65483700
C	4.45365300	0.70530400	0.80767200
C	3.88739800	1.63408700	-0.09193000
C	2.74430700	2.71405900	1.79189400
H	3.65122700	1.99304400	3.65911100
H	2.59720800	3.78375900	1.92172500
C	4.57563900	2.06596600	-1.21583700
H	4.11982700	2.75667700	-1.92531000
C	5.72554900	0.19115100	0.60579800
H	6.15985300	-0.54393200	1.28481300
C	5.87250800	1.54177600	-1.43301100
H	6.43447000	1.84856500	-2.31643100
C	6.43619000	0.62177600	-0.54007400
H	7.43057200	0.21860700	-0.73662700
Cl	0.84843500	1.68864500	-2.66370300

Sum of electronic and thermal Enthalpies= -3116.780715
Sum of electronic and thermal Free Energies= -3116.904172

TS for Direct MeCl RE from 7a ($TS_{7\rightarrow 2}$)

Pd	-0.15671900	0.00984900	-1.31089100
P	-1.68967200	1.08561800	0.28421900
N	-2.99547900	-0.08733900	-0.04555900
C	0.97863500	-0.49752500	-3.72556400
H	-0.04885400	-0.69225500	-4.02446700
H	1.62409700	-0.15485700	-4.53147100
H	1.44148200	-1.24190600	-3.07998700
C	-3.39002500	-0.12295500	-1.49530100
H	-3.78208600	0.82928000	-1.86470900
C	-2.10972900	-0.68836000	-2.19126400
H	-2.06874900	-0.80354400	-3.27401100
C	-1.57205500	-1.60967200	-1.25606000
H	-1.07750100	-2.55075800	-1.49748500
C	-2.51243400	-1.52431900	-0.01372300
H	-2.08685400	-1.82885500	0.94633600
C	-3.81447600	-2.18578100	-0.46183400
C	-4.42523700	-3.39393700	-0.15355400
H	-3.99193300	-4.07680400	0.57969600
C	-5.63631600	-3.71004300	-0.81441700
H	-6.14566700	-4.64778200	-0.58668200
C	-6.19093500	-2.83173900	-1.75533400
H	-7.12685600	-3.09465100	-2.25091600
C	-5.55645400	-1.60568100	-2.06939300
H	-5.99454500	-0.92524700	-2.80194800
C	-4.37306700	-1.29850000	-1.41097500
C	-2.50242700	2.64731800	-0.24470800
C	-3.40304700	3.36159100	0.57134100
H	-3.63834400	2.98897700	1.56864800
C	-3.99169900	4.54262400	0.09776800
H	-4.68904900	5.09307500	0.73163200
C	-3.69095600	5.01397500	-1.19157800
H	-4.15167100	5.93347000	-1.55629800
C	-2.79454400	4.30519800	-2.00777400
H	-2.55545100	4.67118100	-3.00746900
C	-2.19389900	3.12871300	-1.53524300
H	-1.48570600	2.57632300	-2.15591500
C	-1.78005700	1.13135900	2.12403500
C	-2.75017800	0.42769700	2.86591000
H	-3.53452700	-0.11129200	2.33558800
C	-2.69589900	0.42511200	4.26814700
H	-3.44839500	-0.12460100	4.83654000
C	-1.68203300	1.12686000	4.94056800
H	-1.64000100	1.11732100	6.03099500
C	-0.72060100	1.84020600	4.20382300
H	0.07709400	2.38108100	4.71517900
C	-0.76774100	1.83813500	2.80470700
H	0.00670400	2.35498500	2.24027400
P	1.51751500	-0.71460400	0.12317600
C	0.76547400	-1.91337900	1.29700800
C	0.30120700	-1.50325500	2.56141600

C	0.45973200	-3.21531600	0.84208400
C	-0.46229700	-2.37606400	3.35258700
H	0.51020100	-0.49206400	2.90327900
C	-0.30007600	-4.08481000	1.63478600
H	0.81119400	-3.54298000	-0.13722800
C	-0.76948100	-3.66500600	2.89226800
H	-0.83018000	-2.03228300	4.31935900
H	-0.53018400	-5.08727000	1.27022100
H	-1.37089600	-4.33876900	3.50435500
C	3.02173500	-1.59242800	-0.50067100
C	3.64550700	-1.05401500	-1.64627800
C	3.60813700	-2.70246500	0.14158200
C	4.83264100	-1.61165800	-2.13675800
H	3.21890500	-0.17380500	-2.12519900
C	4.79113700	-3.26637700	-0.35870200
H	3.13871100	-3.12311100	1.03102300
C	5.40562400	-2.72263600	-1.49803400
H	5.31472900	-1.17081500	-3.00995800
H	5.23613000	-4.12632200	0.14511600
H	6.32886800	-3.15942700	-1.88187700
N	2.04543100	0.53079400	1.21030300
C	3.28958500	0.44764400	2.05046500
H	3.39380900	-0.49228300	2.60208800
C	2.33593000	1.90402500	0.67573200
H	1.57447700	2.26755000	-0.02149800
C	3.08173900	1.74525300	2.86594400
C	4.37529400	0.77960700	0.99928300
C	3.76641200	1.70593500	0.12315100
C	2.51428900	2.63156300	2.02830800
H	3.42839700	1.89534500	3.88583000
H	2.29122700	3.68229700	2.19823300
C	5.67860700	0.35044400	0.80026000
H	6.14642500	-0.38126300	1.46044200
C	4.44640400	2.21809100	-0.97197600
H	3.96738400	2.91317800	-1.66240200
C	6.37852900	0.86037800	-0.31962200
H	7.39723200	0.52234600	-0.51456800
C	5.77450700	1.77678200	-1.18893600
H	6.32969500	2.14829300	-2.05167100
Cl	1.07115600	1.62825100	-2.96430100

Sum of electronic and thermal Enthalpies= -3116.716133
Sum of electronic and thermal Free Energies= -3116.843592

$TS^{assist}_{7\rightarrow 2}$: ligand assisted mechanism from 7a

Pd	-0.95544000	-0.40550300	-0.23148200
P	-3.32263500	-0.61289100	-0.93477500
N	-3.58498100	-2.04214000	0.10015800
C	1.36946400	-0.80501800	0.57210600
H	1.17478200	-1.83575200	0.85357800
H	1.48595600	-0.53268800	-0.47309200
H	1.30539200	-0.04082700	1.33609100
C	-2.63948600	-3.16104600	-0.24228300
H	-2.75378700	-3.52883900	-1.26663800
C	-1.24588300	-2.57882400	0.15732700
H	-0.34210800	-3.17081500	0.01413200
C	-1.51361200	-1.76603600	1.29928800
H	-0.86509900	-1.67412600	2.17111300
C	-3.05834300	-1.85905900	1.50676500
H	-3.52935700	-1.03837600	2.05599600
C	-3.29621300	-3.28283400	2.00564200
C	-3.63674700	-3.81472000	3.24228100
H	-3.84366800	-3.17019600	4.09884900
C	-3.71743400	-5.22297100	3.35748800
H	-3.99377900	-5.67077500	4.31345600
C	-3.45018500	-6.04929600	2.25728900
H	-3.52170200	-7.13257500	2.36772600
C	-3.09297000	-5.49866100	1.00308100
H	-2.88665600	-6.14789800	0.15006300
C	-3.02494500	-4.11555300	0.89454600
C	-3.79795700	-1.34999300	-2.55569900
C	-5.12780900	-1.73085500	-2.82995600
H	-5.90405400	-1.55086900	-2.08576600
C	-5.44406600	-2.33711300	-4.05287000
H	-6.47384200	-2.63090400	-4.26387200
C	-4.43588500	-2.56749500	-5.00546700
H	-4.68515000	-3.03828000	-5.95815900
C	-3.11227000	-2.18860200	-4.73373000
H	-2.32922700	-2.36200900	-5.47367700
C	-2.78772800	-1.57720100	-3.51158200
H	-1.76240100	-1.26994400	-3.29777200
C	-4.80801100	0.37415100	-0.46430300
C	-5.80038700	-0.09602400	0.41898000
H	-5.73257100	-1.11368600	0.80182400
C	-6.86108000	0.74235300	0.79515300
H	-7.62375500	0.37242600	1.48293000
C	-6.94485100	2.05027600	0.29078100
H	-7.76863500	2.70081800	0.58950400
C	-5.96379400	2.51784500	-0.60042500
H	-6.01182200	3.53498500	-0.99209300
C	-4.90105200	1.68531300	-0.97183200
H	-4.12344400	2.06854300	-1.62966500
P	-1.03095300	1.69567600	0.77452000
C	-2.14628700	1.56893900	2.23112000
C	-3.48449800	2.00173200	2.17831400
C	-1.69900900	0.85162900	3.36276500
C	-4.36200100	1.71410100	3.23566400
H	-3.83975200	2.53016200	1.29654800
C	-2.57577700	0.56842500	4.41710500
H	-0.66390000	0.51174200	3.41223700
C	-3.91453400	0.99457400	4.35353300
H	-5.40005300	2.03969100	3.16795900
H	-2.21731400	0.01237600	5.28499800
H	-4.60084800	0.76490200	5.17005900
C	0.51206100	2.44459300	1.47510100
C	1.66772700	2.39069600	0.66822700
C	0.57619900	3.10084900	2.72099600
C	2.86120600	2.98953700	1.09008600
H	1.61982700	1.89570700	-0.29981300
C	1.77616900	3.68734300	3.15107700
H	-0.31031200	3.15141600	3.35318900
C	2.91887600	3.63433400	2.33650400
H	3.73614800	2.95093400	0.44353300
H	1.81553700	4.19118800	4.11864400
H	3.84867300	4.10029500	2.66793500
N	-1.82627200	2.91270400	-0.16488000
C	-1.74247100	4.38740900	0.12551600
H	-1.92824000	4.64801800	1.17271000
C	-1.50745500	3.04538600	-1.62962700
H	-1.46439500	2.08973900	-2.15920900
C	-2.76277200	4.86889000	-0.93175600
C	-0.34598400	4.72080500	-0.45330500
C	-0.19595700	3.86022200	-1.56321900
C	-2.60908700	4.06414500	-1.99852700
H	-3.39117100	5.75030300	-0.82514400
H	-3.08227900	4.13240100	-2.97538300
C	0.97209700	3.84032300	-2.31146900
H	1.09721600	3.13500800	-3.13318300
C	0.66234200	5.59701300	-0.08099400
H	0.56232400	6.24877500	0.78833000
C	2.01147400	4.72307100	-1.92995100
H	2.95273500	4.71595700	-2.48158500
C	1.85871600	5.58630600	-0.83789900
H	2.68012900	6.24468700	-0.55141700
Cl	0.31980100	0.09912600	-2.52125800
P	3.69768500	-1.02424200	0.74980600
N	3.95276500	-2.56716400	0.04615200
C	5.26932400	-2.97380100	-0.58240100
H	6.14095500	-2.75132600	0.04188000
C	3.11220600	-3.04002100	-1.12079400
H	2.03688000	-2.88078100	-1.00446400
C	5.16970300	-2.25805000	-1.94680600
C	4.92642400	-4.45806000	-0.83692000
H	5.65122500	-5.26832900	-0.82148600
C	3.80069600	-2.30200900	-2.28944700
C	3.62299700	-4.49679600	-1.16354600
H	3.02433600	-5.34597500	-1.48346200
C	6.09556900	-1.62577700	-2.76361200
H	7.15150700	-1.56935800	-2.49432600
C	3.32125500	-1.71229900	-3.45002000
H	2.25611000	-1.69046400	-3.67917300
C	5.61941300	-1.01685200	-3.94943300

H	6.32014600	-0.49306200	-4.60117200
C	4.26016100	-1.05872400	-4.28409000
H	3.91234000	-0.56340600	-5.19152900
C	4.52275200	0.31666700	-0.19846600
C	5.78104300	0.84171600	0.16568200
C	3.86202400	0.83140300	-1.33544100
C	6.35876000	1.87548700	-0.58404100
H	6.30224900	0.44899100	1.03778600
C	4.44944200	1.85708700	-2.08502000
H	2.89441900	0.44789900	-1.65490200
C	5.69352400	2.38763400	-1.71010100
H	7.33026200	2.27704200	-0.29117700
H	3.92439300	2.23883100	-2.95998500
H	6.14490700	3.19250100	-2.29224900
C	4.58162700	-1.13283700	2.33565500
C	5.00215900	-2.37067500	2.87160900
C	4.70965100	0.04212200	3.11680500
C	5.57693100	-2.42259000	4.14932500
H	4.86869100	-3.27859800	2.28394000
C	5.28448200	-0.02202000	4.39148600
H	4.36045900	0.99900200	2.72495700
C	5.72493500	-1.25201400	4.91068500
H	5.90899800	-3.38110400	4.55123700
H	5.38444100	0.88948600	4.98264900
H	6.17065500	-1.29814500	5.90510300

Sum of electronic and thermal Enthalpies= -4360.978077
Sum of electronic and thermal Free Energies= -4361.151217

7c

Pd	0.36802900	-0.31695400	-1.27778100
P	1.55861800	-0.34354000	0.81510000
N	3.18243300	-0.32529300	0.09283800
C	-0.29012500	0.01670700	-3.27038000
H	0.50095100	-0.34541700	-3.93968400
H	-1.20500300	-0.56664900	-3.39798100
H	-0.46839000	1.09068700	-3.42040400
C	3.32381800	-1.39805600	-0.95904600
H	3.21423300	-2.41350800	-0.56775100
C	2.30643800	-0.95059900	-2.05575100
H	2.11704500	-1.56416400	-2.93358600
C	2.31148100	0.46474600	-2.00633300
H	2.14194400	1.12647500	-2.85331000
C	3.33240200	0.81903200	-0.88584900
H	3.24324700	1.80651900	-0.42370000
C	4.70063100	0.42961700	-1.45420400
C	5.78772400	1.16346400	-1.91051500
H	5.79502100	2.25441400	-1.87702600
C	6.89953500	0.44952100	-2.41661800
H	7.77278800	0.99721500	-2.77356000
C	6.89406200	-0.95130800	-2.46340200
H	7.76334700	-1.48009500	-2.85665300
C	5.77780200	-1.69065100	-2.00555300
H	5.77746800	-2.78102400	-2.04485700
C	4.69529000	-0.98308600	-1.50024000
C	1.60755500	-1.78709200	1.94689800
C	1.93523500	-1.64968600	3.31225100
H	2.19558700	-0.67104200	3.71376300
C	1.91718600	-2.77150500	4.15236100
H	2.16865800	-2.65996100	5.20818700
C	1.57567000	-4.03341300	3.63756100
H	1.55749700	-4.90351600	4.29578900
C	1.24987000	-4.17160800	2.27905600
H	0.97278000	-5.14656300	1.87596000
C	1.25846800	-3.05372400	1.43174400
H	0.94885500	-3.15387800	0.38921600
C	1.67977400	1.11647100	1.93271800
C	2.92278700	1.72367700	2.21288500
H	3.83478500	1.30450800	1.78988300
C	2.98118400	2.85369300	3.04222800
H	3.94519700	3.32208000	3.24710500
C	1.80869900	3.37230300	3.61388500
H	1.85698100	4.25438900	4.25444400
C	0.57765500	2.74609600	3.36661600
H	-0.33742900	3.13885500	3.81140200
C	0.50907700	1.62322700	2.53166500
H	-0.44732000	1.14497200	2.32700700
P	-1.53684800	0.80752400	-0.51955100
C	-1.18994100	2.57218100	-0.10797200
C	-2.11967700	3.42290000	0.52729200
C	0.10510300	3.05986700	-0.37196000
C	-1.75005400	4.71853100	0.91495800
H	-3.13972400	3.08616700	0.70253800
C	0.47349600	4.35709500	0.01048800
H	0.82236800	2.39795700	-0.85725400
C	-0.44965800	5.18539600	0.66427700
H	-2.47821100	5.36361600	1.40895700
H	1.48542600	4.71294800	-0.18672100
H	-0.16169100	6.19106700	0.97360200
C	-3.01643300	0.82045600	-1.60813900
C	-3.44463100	-0.43413500	-2.09620900
C	-3.72476400	1.98361100	-1.97036400
C	-4.59199600	-0.52286700	-2.89150200
H	-2.87565200	-1.33142000	-1.85545900
C	-4.86883000	1.88795700	-2.77850500
H	-3.38406500	2.96176300	-1.63479000
C	-5.31070400	0.63554700	-3.22995500
H	-4.92109400	-1.49963900	-3.24640800
H	-5.41100200	2.79374700	-3.05498300
H	-6.20414400	0.56361300	-3.85227000
N	-1.95738800	0.16156900	1.03052400
C	-3.24005900	0.38665300	1.79320800
H	-3.59041500	1.42118000	1.80968800
C	-1.90808100	-1.32260000	1.30770600
H	-1.06547600	-1.83539600	0.84491000
C	-2.78178700	-0.21534800	3.14535700
C	-4.15814900	-0.66056500	1.13124000
C	-3.31241700	-1.74957200	0.83380800
C	-1.97727000	-1.25009100	2.84667400
H	-3.13289200	0.12443000	4.11700300
H	-1.49698800	-1.96368700	3.51116500
C	-3.79384600	-2.89102300	0.20910900
H	-3.12382300	-3.70717400	-0.05868000
C	-5.50710400	-0.68377800	0.80704600
H	-6.16250900	0.16329400	1.01760600
C	-5.16746900	-2.92146200	-0.13094000
H	-5.57410000	-3.79564700	-0.64181900
C	-6.00770000	-1.83854200	0.15970000
H	-7.05978900	-1.87960900	-0.12619300
Cl	-0.57806800	-2.76608900	-1.55280800

Sum of electronic and thermal Enthalpies= -3116.776900
Sum of electronic and thermal Free Energies= -3116.901934

$TS^{migration}$ from 7c : migration pathway ($TS_{7c\rightarrow 9}$)

Pd	0.42832600	-0.70364900	-1.08827500
P	1.56936400	0.02433100	0.73462200
N	3.23373100	-0.22358800	0.15130000
C	-0.93633400	0.55054500	-3.02111200
H	0.10875700	0.76336200	-3.27718600
H	-1.26366600	-0.40591500	-3.43986900
H	-1.56346900	1.38080900	-3.37200700
C	3.48462000	-1.62937000	-0.34053200
H	3.37762800	-2.39246500	0.43427700
C	2.54511400	-1.73208300	-1.57966900
H	2.23446400	-2.65963800	-2.05189800
C	2.50671600	-0.45991000	-2.11692600
H	2.23471800	-0.19515200	-3.13723300
C	3.43479200	0.40677000	-1.20834700
H	3.27315000	1.48942400	-1.21934000
C	4.85976500	-0.09874500	-1.46349300
C	5.96699200	0.44365400	-2.10072100
H	5.94708600	1.44839500	-2.52636900
C	7.13592200	-0.35094100	-2.17854900
H	8.02477400	0.04811100	-2.66890700
C	7.16627800	-1.64166300	-1.63429400
H	8.07887200	-2.23471800	-1.70590200
C	6.02964500	-2.18766500	-0.99091500
H	6.05823000	-3.19271200	-0.56729700
C	4.89035500	-1.39897700	-0.91340100
C	1.48107800	-1.13622100	2.15272800
C	1.69201400	-0.71812900	3.48068000

H	1.92660700	0.32472700	3.68962900
C	1.58283700	-1.64093800	4.53131900
H	1.74018200	-1.31048900	5.55895500
C	1.26743300	-2.98245900	4.26294300
H	1.17667600	-3.69625400	5.08290800
C	1.06092000	-3.40388300	2.93813100
H	0.80539700	-4.44236300	2.72441500
C	1.16100300	-2.48472500	1.88586400
H	0.95058600	-2.79619700	0.85959900
C	1.70146800	1.68910200	1.48563800
C	2.91818900	2.40157700	1.50512900
H	3.82138000	1.93881400	1.11001100
C	2.96385200	3.68851800	2.06195800
H	3.90731300	4.23658400	2.07505000
C	1.80737800	4.26159900	2.61233600
H	1.84650500	5.26270700	3.04461600
C	0.60106200	3.54275900	2.60804900
H	-0.30143500	3.98493900	3.03086100
C	0.54053100	2.26352200	2.04384100
H	-0.39446700	1.70547400	2.01193200
P	-1.51107700	0.58838600	-0.98592600
C	-1.08176400	2.37660600	-0.76798000
C	-1.92200900	3.32703600	-0.15392400
C	0.19839400	2.79497500	-1.18537400
C	-1.49745600	4.65100600	0.03138100
H	-2.92143600	3.05001400	0.16771300
C	0.63071800	4.11175300	-0.98958100
H	0.86919500	2.06519400	-1.63603700
C	-0.21680000	5.04689900	-0.37863400
H	-2.16948300	5.36922700	0.50351500
H	1.63502100	4.40229700	-1.29961400
H	0.11892000	6.07234700	-0.22018400
C	-3.25257000	0.43226600	-1.61664900
C	-3.72104000	-0.86417400	-1.91196200
C	-4.08573000	1.53788000	-1.87216400
C	-5.01836300	-1.04866700	-2.40439500
H	-3.07263500	-1.72383800	-1.75616300
C	-5.38745800	1.34528200	-2.36340800
H	-3.72498100	2.55261000	-1.71925400
C	-5.86132800	0.05204600	-2.62171300
H	-5.36937500	-2.06003200	-2.60983000
H	-6.02345900	2.21223400	-2.55166400
H	-6.87442000	-0.09635400	-2.99882400
N	-1.80110600	0.25116100	0.83415300
C	-3.03249800	0.64136500	1.63300500
H	-3.35849400	1.67680000	1.51636200
C	-1.81039000	-1.17060000	1.34249400
H	-1.03584000	-1.80334200	0.91297500
C	-2.48215200	0.25474900	3.03021800
C	-4.04105300	-0.45576100	1.25165200
C	-3.25921800	-1.61435200	1.07465000
C	-1.74244900	-0.85412800	2.85106000
H	-2.72957300	0.77490900	3.95354100
H	-1.22953500	-1.46949000	3.58556400
C	-3.83444500	-2.83125800	0.73746900
H	-3.22302300	-3.71887100	0.57141100
C	-5.41862600	-0.48280800	1.09051100
H	-6.02708000	0.41565100	1.20649500
C	-5.23819000	-2.86852100	0.56271200
H	-5.72003500	-3.80469300	0.27603600
C	-6.01515000	-1.71508700	0.73289300
H	-7.09378500	-1.76344700	0.57607200
Cl	-0.66336700	-2.86574400	-1.75057900

Sum of electronic and thermal Enthalpies= -3116.734139
Sum of electronic and thermal Free Energies= -3116.855254

L1

P	-0.82279200	-0.15661500	-1.31501800
N	-0.17929400	-1.52164900	-0.43508700
C	1.01860900	-2.26523900	-0.94614100
H	0.98526500	-2.48195200	-2.01935200
C	0.96830800	-3.46337400	0.03063100
H	1.30666000	-4.46927800	-0.20624400
C	0.53125300	-2.97493300	1.20453200
H	0.42195700	-3.48660200	2.15801700
C	0.30444900	-1.46152400	0.98828000
H	-0.37932400	-0.94459400	1.66845200
C	1.70868400	-0.84267400	0.79017400
C	2.16533400	-1.35539500	-0.44463000
C	3.40105600	-0.99317000	-0.96165400
H	3.75579000	-1.38181500	-1.91819000
C	4.19079400	-0.08335900	-0.21638400
H	5.15960800	0.23286300	-0.60621400
C	3.73725400	0.42332000	1.00701100
H	4.35349800	1.13504000	1.55809400
C	2.48023700	0.03820800	1.53216000
H	2.12194600	0.45550700	2.47376400
C	-0.00949800	1.35412500	-0.57511200
C	-0.39133800	1.93409200	0.65278100
H	-1.26492700	1.55035600	1.17980500
C	0.33753100	3.00196800	1.19471700
H	0.02994500	3.44219300	2.14514000
C	1.46328000	3.50136000	0.52013100
H	2.03308800	4.32949700	0.94465300
C	1.85246100	2.93250000	-0.70192800
H	2.72869700	3.31251800	-1.22901500
C	1.11637500	1.87170000	-1.24766400
H	1.42947000	1.42704900	-2.19379400
C	-2.49189100	-0.07102800	-0.50664900
C	-3.25716200	1.10939100	-0.63448900
H	-2.82954800	1.98096600	-1.13336000
C	-4.55337700	1.18138000	-0.10649600
H	-5.12820900	2.10342300	-0.20834700
C	-5.10908500	0.07337500	0.55455400
H	-6.11764300	0.12977300	0.96686500
C	-4.35940300	-1.10609200	0.67854600
H	-4.78401400	-1.97208800	1.18969800
C	-3.06170100	-1.18189900	0.14828600
H	-2.47832800	-2.09847300	0.23696300

Sum of electronic and thermal Enthalpies= -1244.201632
Sum of electronic and thermal Free Energies= -1244.269723