

Supporting Information

Application of the ONIOM-Molecular Dynamics (MD) Method to the Organometallic Reaction $\text{Cis-(H)}_2\text{Pt(PR}_3)_2 \rightarrow \text{H}_2 + \text{Pt(PR}_3)_2$ (R = H, Me, Ph, and t-Bu). An Insight into the Dynamical Environmental Effects.

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TABLE S-1: Selected Optimized Geometric Parameters (Å and degree) of the Reactants, Transition States, and Products of the Reaction, $\text{Cis-(H)}_2\text{Pt(PR}_3)_2 \rightarrow \text{H}_2 + \text{Pt(PR}_3)_2$ (R = H, Me, Ph, and t-Bu), by the QM(HF/BSI) and ONIOM(HF/BSI:MM3)-MD Methods^a

geometric parameters	reactant	transition state	product
R = H			
Pt-P	2.407	2.345	2.334
Pt-H	1.582	1.912	
H-H	2.114	0.801	0.735
∠P-Pt-P	102.0	133.9	180.0
∠H-Pt-H	83.8	24.2	
∠H-H-Pt-P	0.0	0.0	
R = Me			
Pt-P	2.394	2.358	2.327
Pt-H	1.591	1.746	
H-H	2.163	0.850	0.735
∠P-Pt-P	107.1	118.9	180.0
∠H-Pt-H	85.6	28.2	
∠H-H-Pt-P	0.0	0.0	
R = Ph			
Pt-P	2.404	2.361	2.326
Pt-H	1.589	1.769	
H-H	2.141	0.850	0.735
∠P-Pt-P	107.0	124.3	180.0
∠H-Pt-H	84.7	27.8	
∠H-H-Pt-P	2.5	5.6	
R = t-Bu			
Pt-P	2.474	2.416	2.332
Pt-H	1.571	1.660	
H-H	1.989	1.030	0.735
∠P-Pt-P	124.6	135.3	180.0
∠H-Pt-H	78.6	36.2	
∠H-H-Pt-P	6.7	8.9	

^aThe geometry optimizations were performed by the QM method for R = H and by the ONIOM-MD method for R = Me, Ph, and t-Bu.

TABLE S-2: Relative Energies (kcal/mol) of the Reactants, Transition States, and Products of the Reaction, $\text{Cis-(H)}_2\text{Pt(PR}_3)_2 \rightarrow \text{H}_2 + \text{Pt(PR}_3)_2$ (R = H, Me, Ph, and t-Bu), calculated by the QM(HF/BSI) and ONIOM(HF/BSI:MM3) Methods^a

components of the energy	reactant	transition state	product
R = H			
E(QM)	0.0	25.6	9.3
R = Me			
E(ONIOM)	0.0	28.6	10.7
E(QM,inner)	0.0	28.3	10.3
E(MM,outer)	0.0	0.3	0.4
R = Ph			
E(ONIOM)	0.0	28.1	12.6
E(QM,inner)	0.0	28.5	10.8
E(MM,outer)	0.0	-0.4	1.8
R = t-Bu			
E(ONIOM)	0.0	15.2	-13.5
E(QM,inner)	0.0	24.4	6.1
E(MM,outer)	0.0	-9.2	-19.6

^aThe energies were calculated by the QM method for R = H and by the ONIOM method for R = Me, Ph, and t-Bu.

TABLE S-3: Minimum Value and Number of Values Less than 1.5 Å for the H4-H5 distance of Cis-(H)₂Pt(PR₃)₂ (R = H, Me, Ph, and t-Bu) in the QM-MD and ONIOM-MD Simulations at 900 K^a

R	run 1		run 2		run 3	
	minimum	< 1.5 Å	minimum	< 1.5 Å	minimum	< 1.5 Å
H	1.737	0	1.775	0	1.748	0
Me	1.438	15	1.563	10	1.441	24
Ph	1.447	17	1.438	31	1.419	24
t-Bu	1.068	220				

^aThe simulations were performed by the QM-MD method for R = H and by the ONIOM-MD method for R = Me, Ph, and t-Bu.

TABLE S-4: Average Energy $\langle E \rangle$ (kcal/mol) of $\text{Cis-(H)}_2\text{Pt(PR}_3)_2$ (R = H, Me, Ph, and t-Bu) Calculated by the Eq. (12) at the Various Temperature

R	$\langle E \rangle$ (inner)	$\langle E \rangle$ (outer)	$\langle E \rangle$ (entire)
300 K			
H	8.0		
Me		16.1	24.1
Ph		53.7	61.7
t-Bu		64.4	72.4
600 K			
H	16.1		
Me		32.2	48.3
Ph		107.3	123.4
t-Bu		128.8	144.9
900 K			
H	24.1		
Me		48.3	72.4
Ph		161.0	185.1
t-Bu		193.2	217.3

TABLE S-5: Increase in the Temperature of the Inner Part (ΔT^{QM}) by the Dynamical Effects of the Environment (Outer Part) in the ONIOM-MD Simulation of Cis-(H)₂Pt(PR₃)₂ (R = H, Me, Ph, and t-Bu) at the Various Temperature ^a

R	ΔT^{QM} (K)		
	300 K	600 K	900 K
H	+0.0	+0.0	+0.0
Me	+109.6	+191.7	+301.3
Ph	+232.8	+383.5	+534.1
<i>t</i> -Bu	+410.9	+547.8	+753.3

^a ΔT^{QM} was calculated by the following equation, $\Delta T^{QM} = \sqrt{\frac{2}{f^{QM}} \frac{\sigma_{E,R}^{QM}}{k_B}} - \sqrt{\frac{2}{f^{QM}} \frac{\sigma_{E,H}^{QM}}{k_B}}$ (R=Me, Ph, and t-Bu; $f^{QM}=27$).

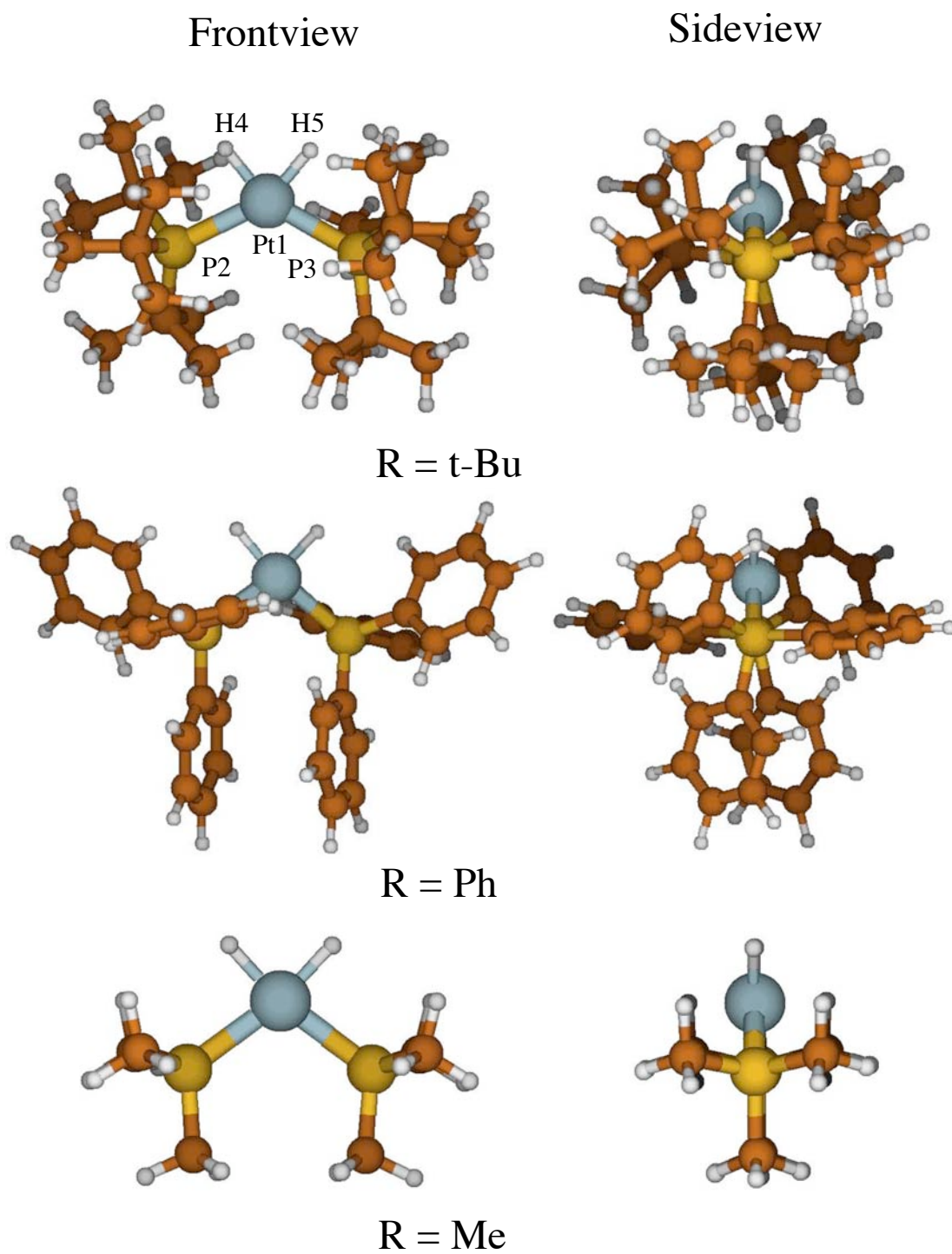


Figure S-1. Optimized structures of $\text{cis}-(\text{H})_2\text{Pt}(\text{PR}_3)_2$ ($R = \text{Me}$, Ph , and $t\text{-Bu}$) by the ONIOM-MD method.

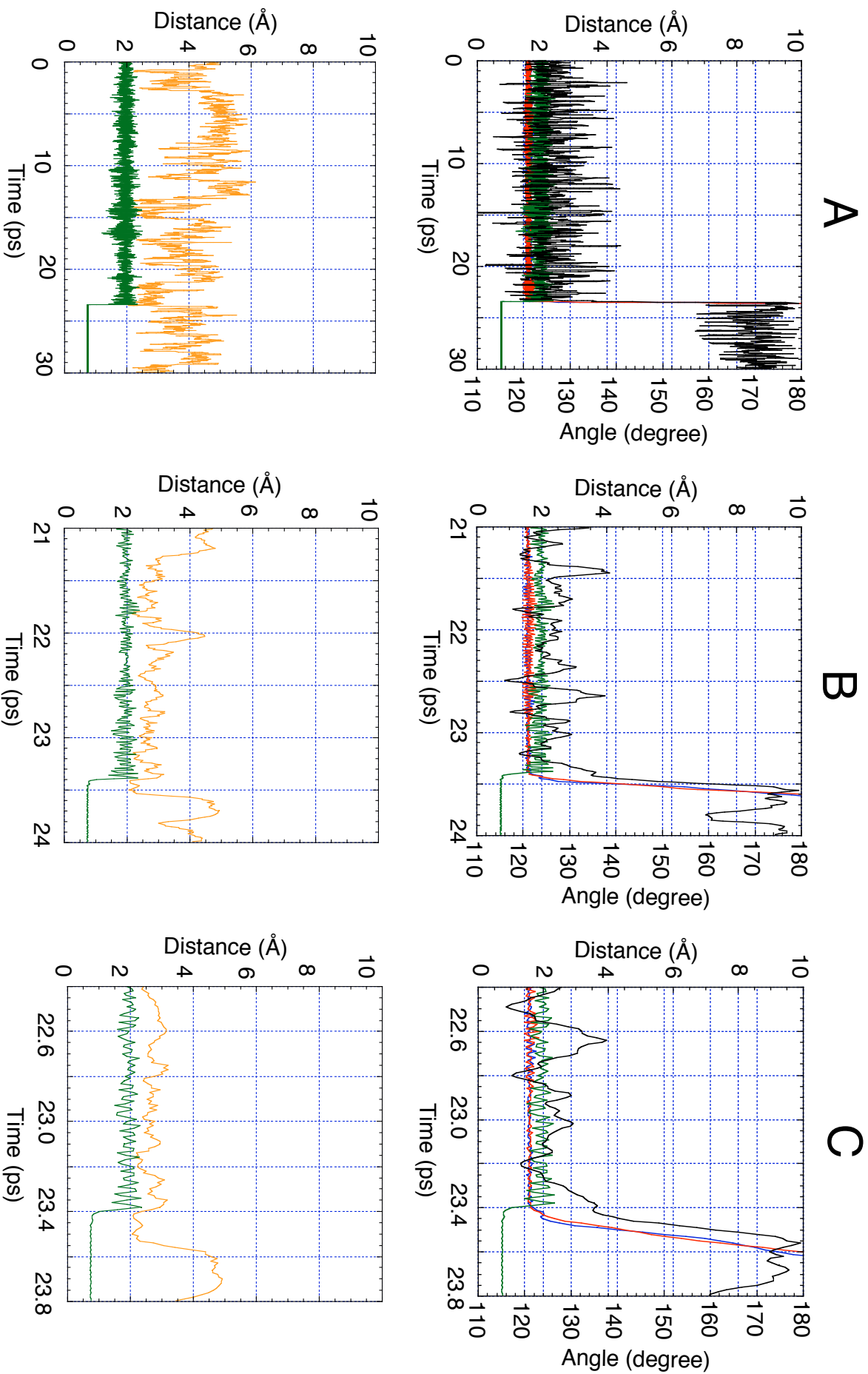


Figure S-2. Changes in the geometric parameters in the reaction $\text{cis-(H)}_2\text{Pt[P(t-Bu)}_3)_2] \rightarrow \text{H}_2 + \text{Pt[P(t-Bu)}_3)_2]$ during the ONIOM-MD simulation (run 2) at 900 K. The color of the lines represents the geometric parameters as follows: red: d(Pt1-H4), blue: d(Pt1-H5), green: d(H4-H5), orange: d(Pt1-H33), and black: $\angle$ P2-Pt1-P3. A, B, and C have the different time scale.

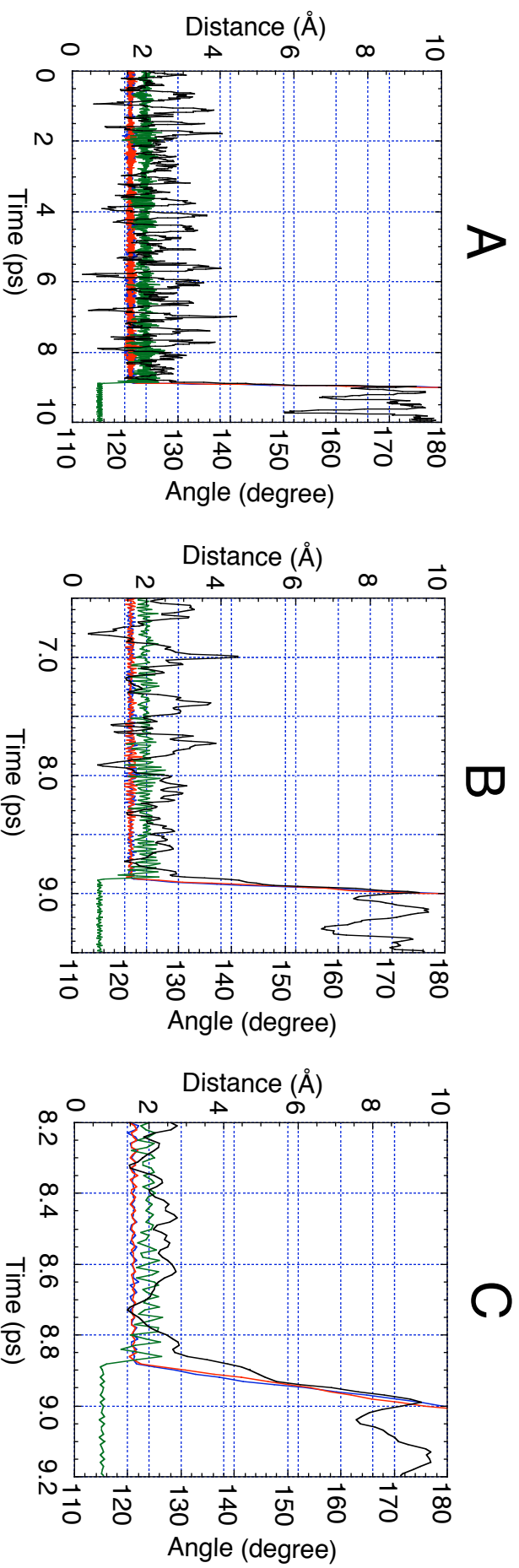


Figure S-3. Changes in the geometric parameters in the reaction $\text{cis-(H)}_2\text{Pt[P(t-Bu)}_3)_2] \rightarrow \text{H}_2 + \text{Pt[P(t-Bu)}_3)_2]$ during the ONIOM-MD simulation (run 3) at 900 K. The color of the lines represents the geometric parameters as follows; red: $d(\text{Pt1-H4})$, blue: $d(\text{Pt1-H5})$, green: $d(\text{H4-H5})$, orange: $d(\text{Pt1-H55})$, and black: $\angle \text{P2-Pt1-P3}$. A, B, and C have the different time scale.

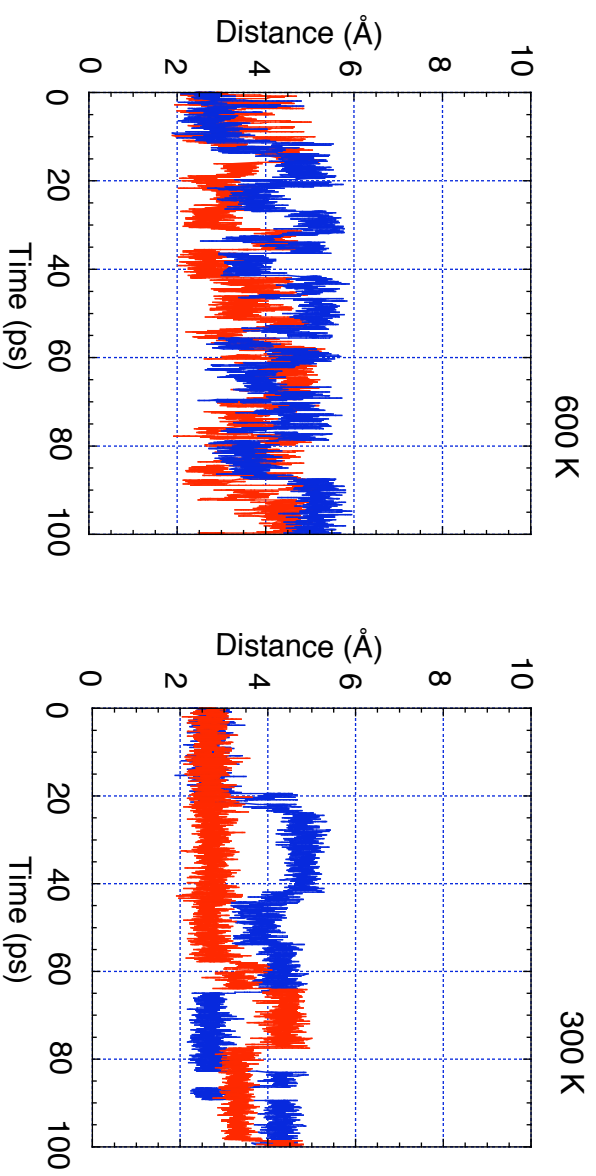


Figure S-4. Changes in two selected Pt-H(tBu) distances in the ONIOM-MD simulation at 600 and 300 K for $\text{cis-(H)}_2\text{Pt[P(t-Bu)}_3)_2]$.

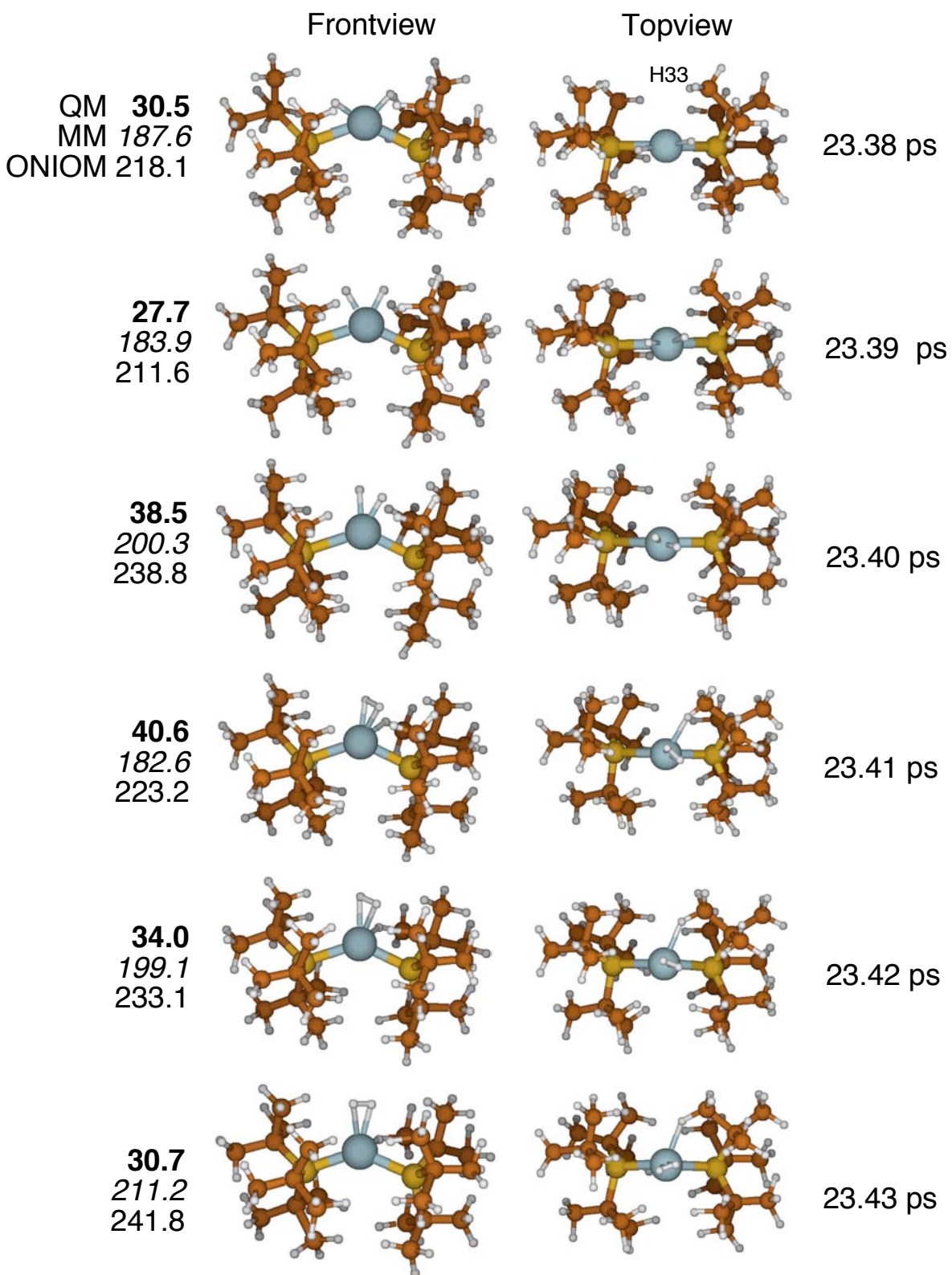


Figure S-5. Snapshots of the reaction $\text{cis}-(\text{H})_2\text{Pt}[\text{P}(\text{t-Bu}_3)_2] \rightarrow \text{H}_2 + \text{Pt}[\text{P}(\text{t-Bu}_3)_2]$ in the ONIOM-MD simulation (run 2) at 900 K. The values (kcal/mol) in the bold, italic, and normal type on the left hand side are the QM energy of the inner part, the MM energy of the outer part, and the ONIOM energy of the entire system, respectively.

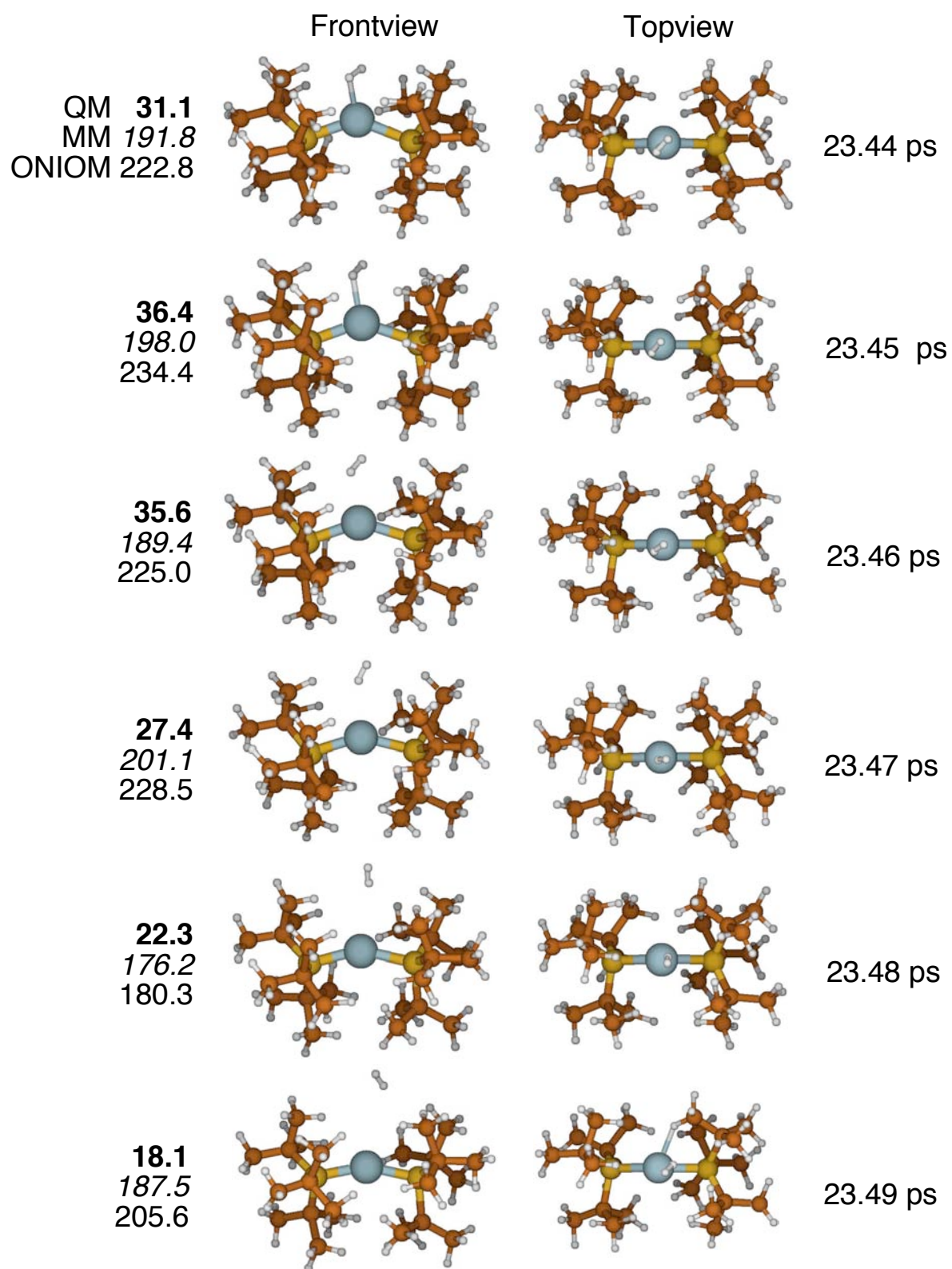


Figure S-5. To be continued.

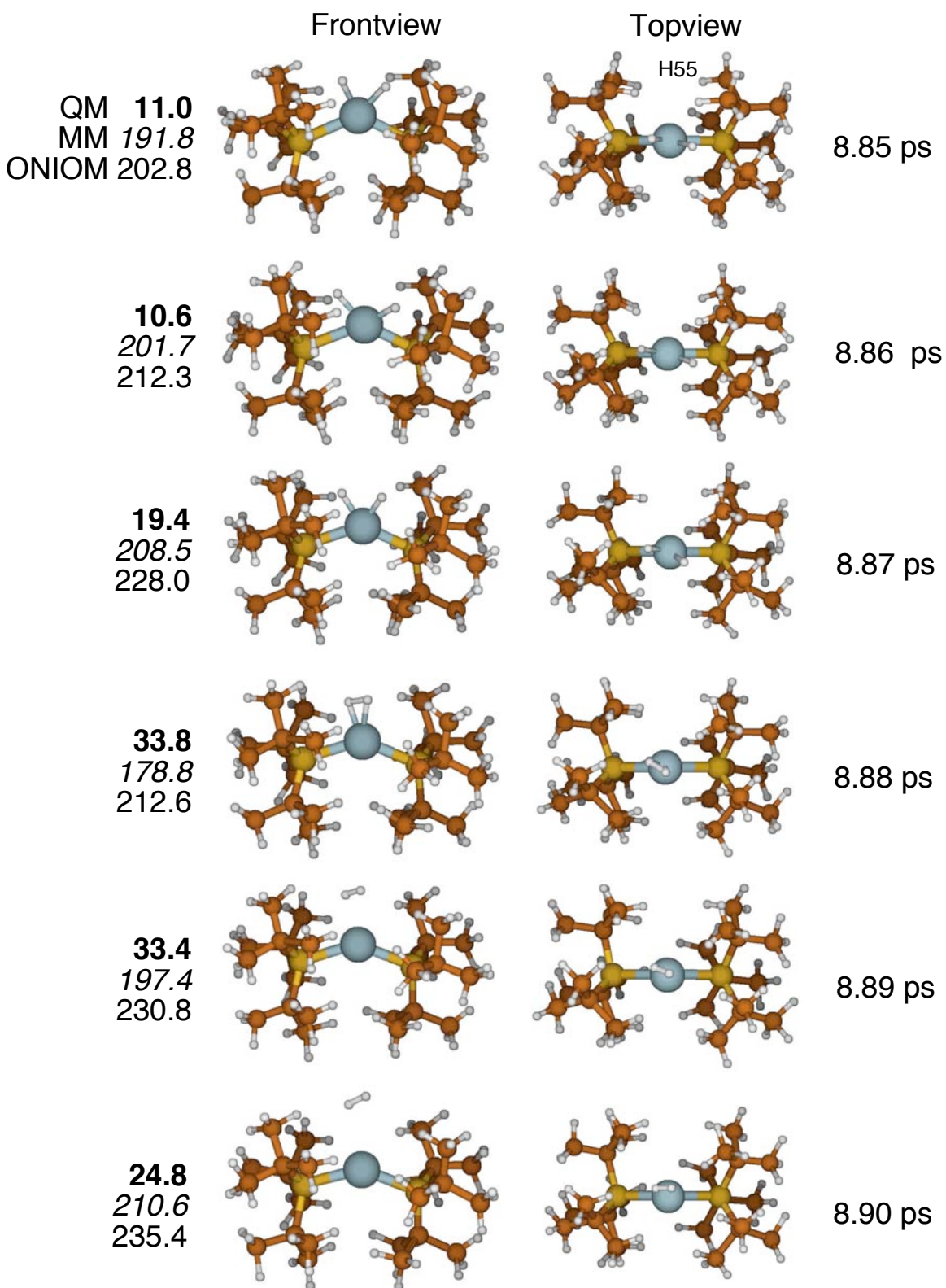


Figure S-6. Snapshots of the reaction $\text{cis}-(\text{H})_2\text{Pt}[\text{P}(\text{t-Bu}_3)_2] \rightarrow \text{H}_2 + \text{Pt}[\text{P}(\text{t-Bu}_3)_2]$ in the ONIOM-MD simulation (run 3) at 900 K. The values (kcal/mol) in the bold, italic, and normal type on the left hand side are the QM energy of the inner part, the MM energy of the outer part, and the ONIOM energy of the entire system, respectively.

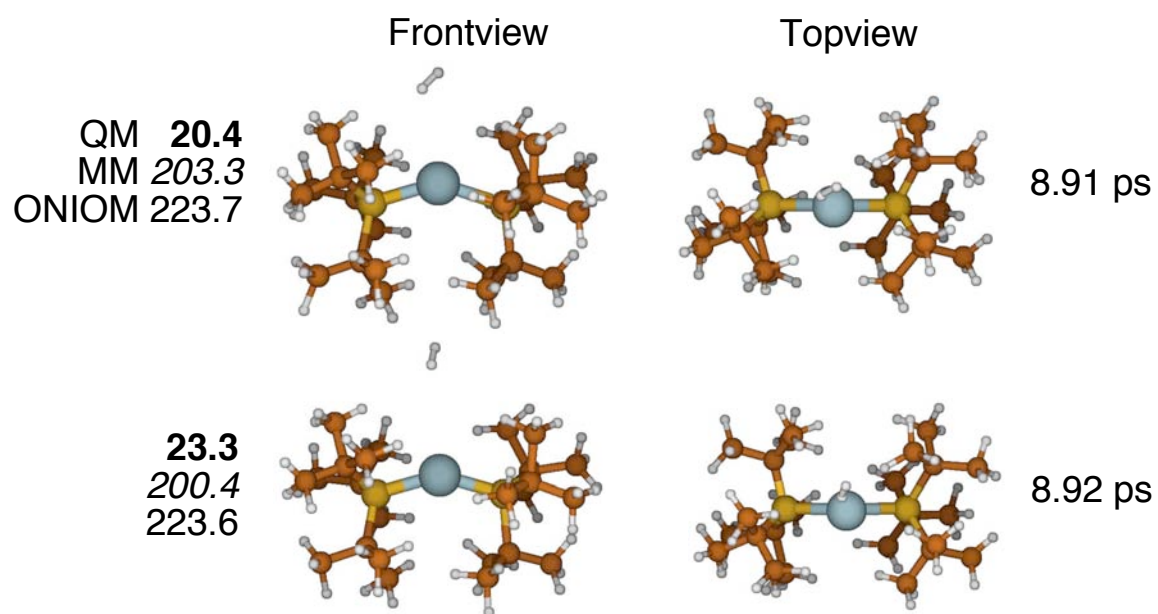


Figure S-6. To be continued.