Supporting Information:

Mo-Mo Quintuple Bond is Highly Reactive in H-H, C-H, and O-H σ-Bond Cleavages Because of Polarized Electronic Structure in Transition State

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Analysis of Electron Population of MO of Fragment:

We investigated first NBO changes in the reaction (Figures S5 and S6), but we could not find good explanation based on them becasue the CT from Mo-Mo bond to H_2 and that from H_2 to Mo-Mo bond compensate the NBO change.

Here, we explored the change transfer interactions in transition states to clarify the how phosphorus oxidation state changes during the reaction by using the electron populations of several important MOs of fragments. Generally, MOs of a total system AB can be represented by a linear combination of MOs of fragments A and B; see Eq S1.[S1-S3]

$$\varphi_{\mathrm{i}}(\mathrm{AB}) = \sum_{\mathrm{m}} \mathrm{C}^{\mathrm{A}}_{\mathrm{im}} \varphi_{\mathrm{m}}(\mathrm{A}) + \sum_{\mathrm{n}} \mathrm{C}^{\mathrm{B}}_{\mathrm{in}} \varphi_{\mathrm{n}}(\mathrm{B}) \qquad \text{(S1)}$$

where $\varphi_i(AB)$ represents the i-th MO of the complex AB, $\varphi_m(A)$ and $\varphi_n(B)$ are the m-th MO and n-th MO of fragments A and B, respectively, and C^A_{im} and C^B_{in} are the expansion coefficients of $\varphi_m(A)$ and $\varphi_n(B)$, respectively. The Mulliken populations of $\varphi_m(A)$ and $\varphi_n(B)$ can be obtained from these coefficients C^A_{im} and C^B_{in}.

(S1) Baba, H.; Suzuki, S.; Takemura, T. Configuration Analysis in the LCAO Molecular Orbital Theory. *J. Chem. Phys.* **1969**, *50*, 2078.

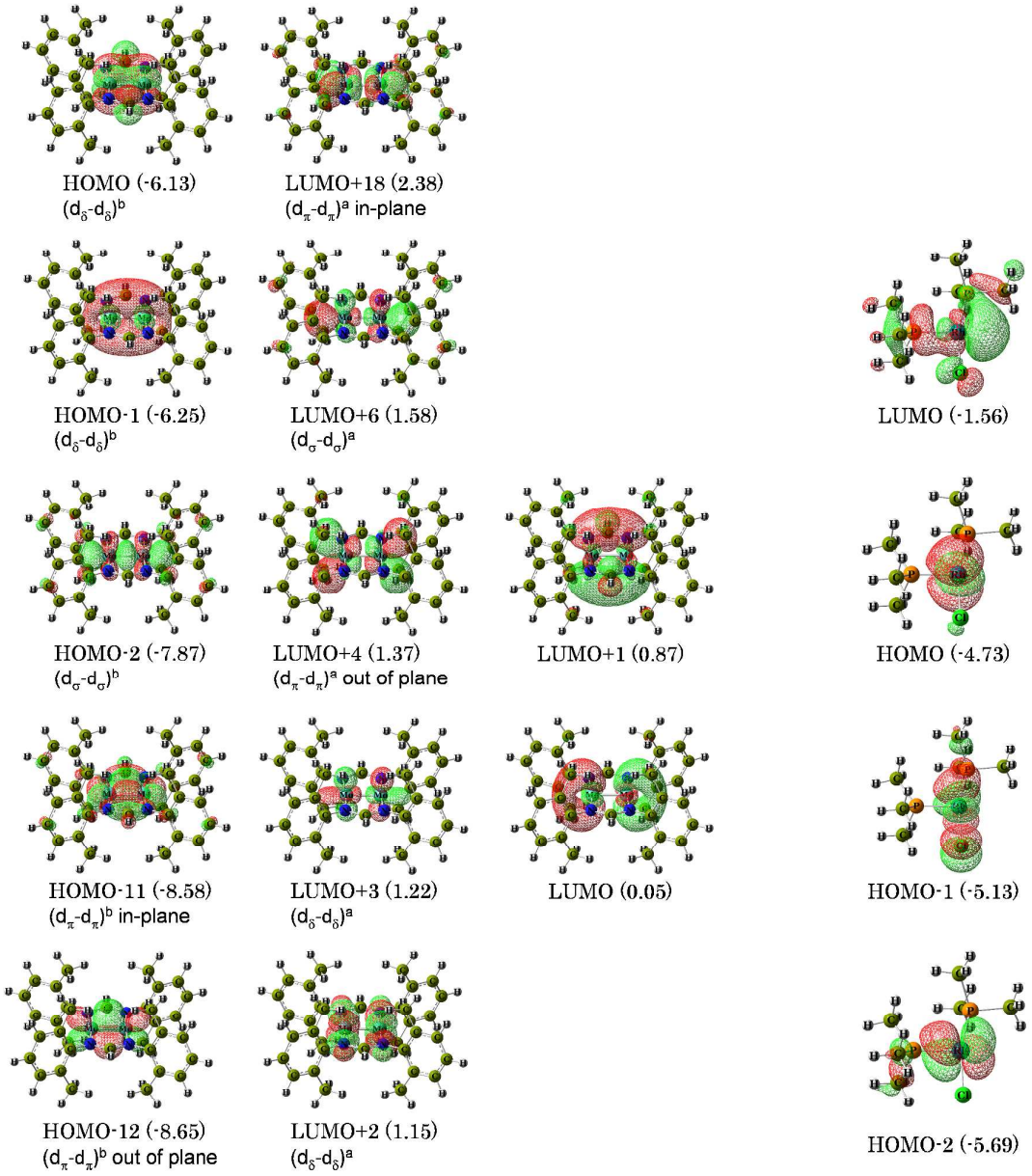
(S2) Kato, S.; Yamabe, S.; Fukui, K. Molecular orbital calculations of the electronic structure of borazane. *J. Chem. Phys.* **1974**, *60*, 572.

(S3) Dapprich, S.; Frenking, G. Investigation of Donor-Acceptor Interactions: A Charge Decomposition Analysis Using Fragment Molecular Orbitals. *J. Phys. Chem.* **1995**, *99*, 9352.

Table S1. The electron populations of important MOs of fragments[a] (unit, e).

	INT8	**TS8**	**TS9**	**TS1'$_{C-H}$**	**TS1$_{C-H}$**	**TS1'$_{O-H}$**	**TS1$_{O-H}$**
σ^*(H-H)	0.189	0.218	0.786	0.626	0.408	0.656	0.606
σ(H-H)	1.848	1.839	1.588	1.715	1.821	1.892	1.869
$\delta^*_{d_{xz}}$	0.119	0.074	0.116	0.160	0.039	0.177	0.024
$\delta^*_{d_{z^2}}$	0.472	0.539	0.626	0.808	0.553	0.193	0.347
$\delta_{d_{z^2}}$	1.536	1.376	1.319	1.406	1.076	1.484	1.102
$\delta_{d_{xz}}$	1.669	1.843	1.186	0.990	1.947	1.367	1.947
$\pi_{d_{yz}}$	1.999	1.916	1.951	2.019	1.759	2.002	1.902

a) Total system is separated into to moieties, **1** and H_2 (or CH_4 and MeOH).



Complex **1** $RhCl(PMe_3)_2$

Figure S1. Several important MOs of $Mo_2(N\text{^}N)_2$ **1** and $RhCl(PMe_3)_2$. In parentheses are Kohn-Sham orbital energies (in eV).

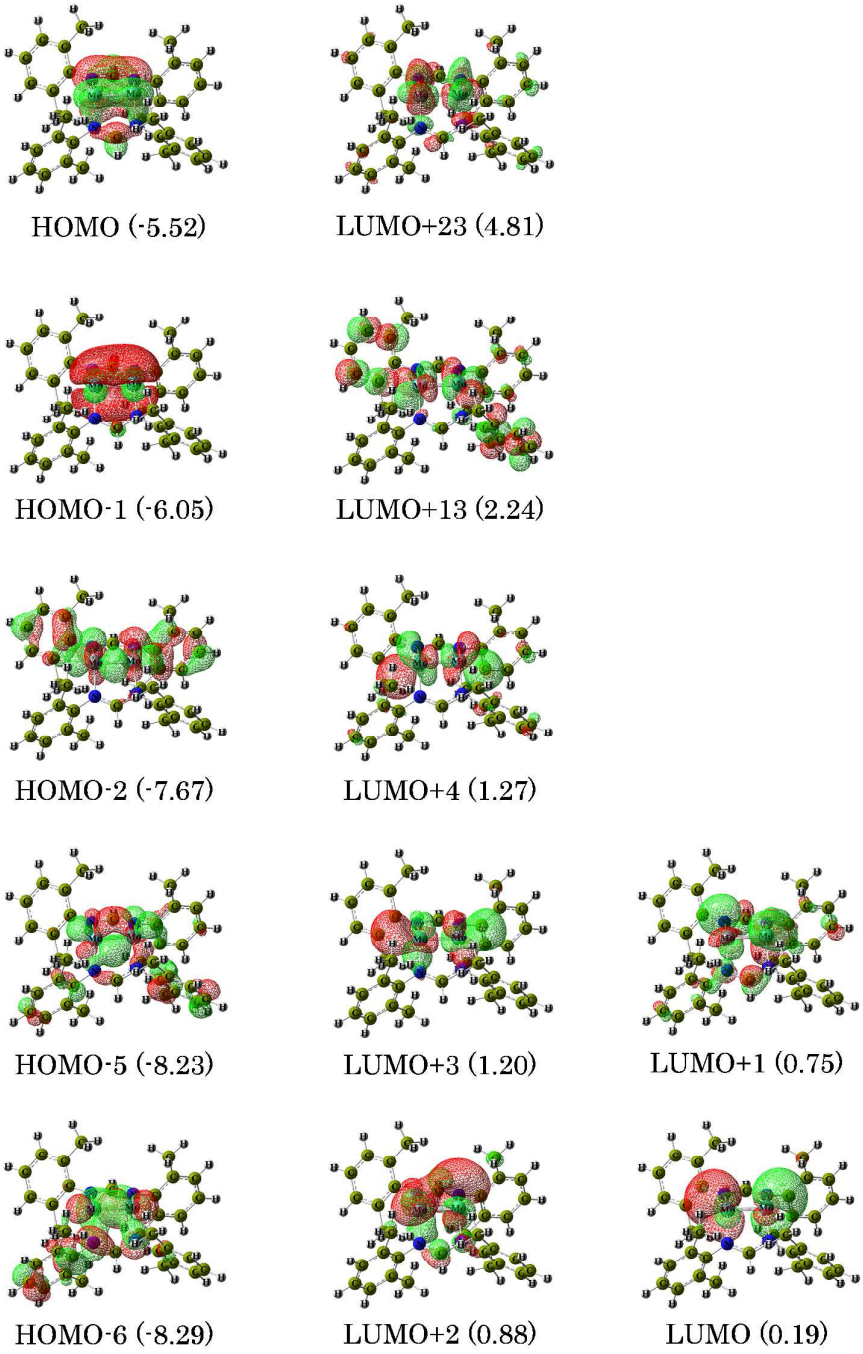


Figure S2. Several important MOs of $Mo_2(N^N)_2$ **1** bearing the distorted geometry in **TS1**.

In parentheses are orbital energies (in eV).

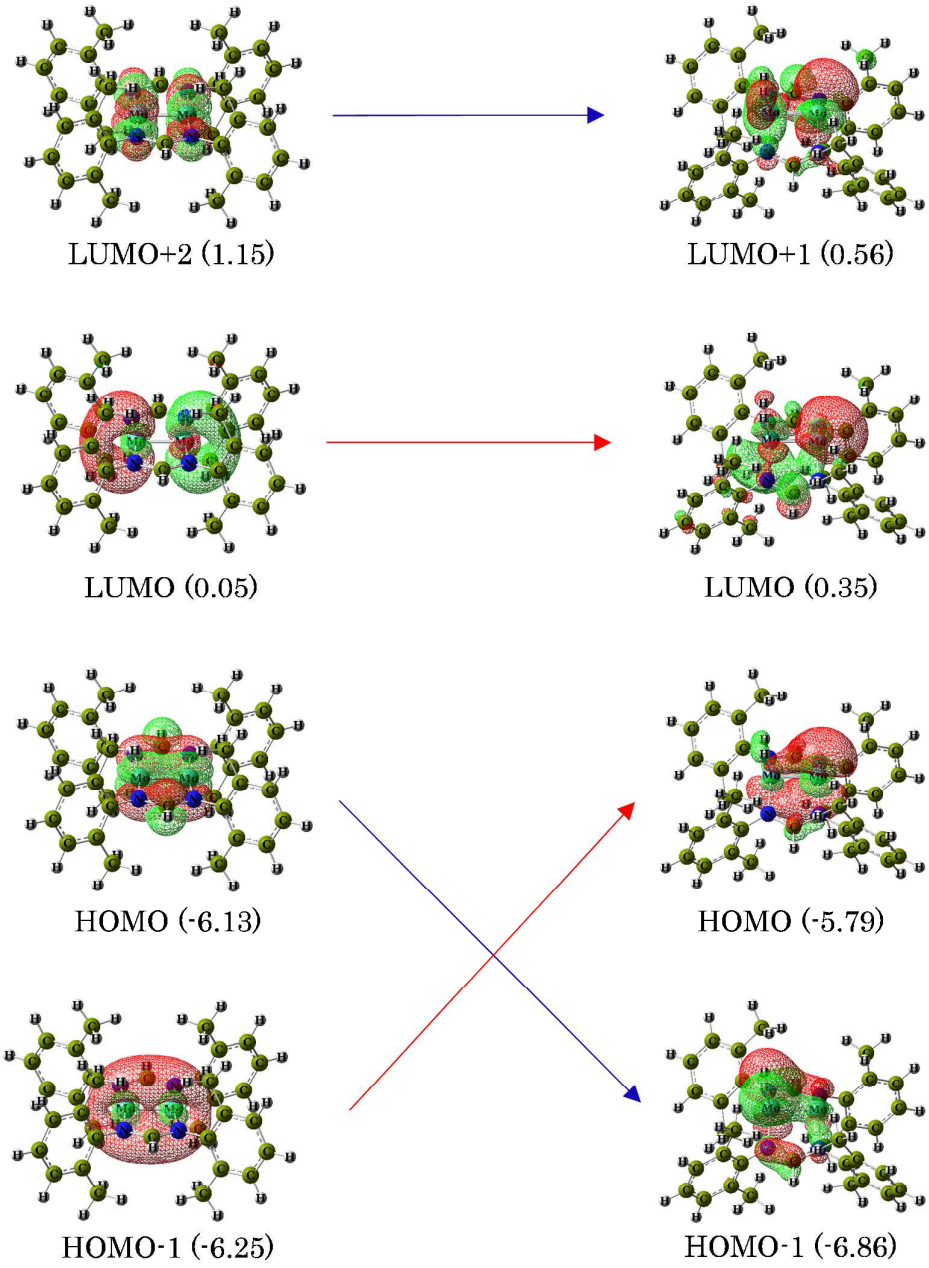


Figure S3. Changes of important MOs as going from $Mo_2(N^{\wedge}N)_2$ **1** to **TS1**.

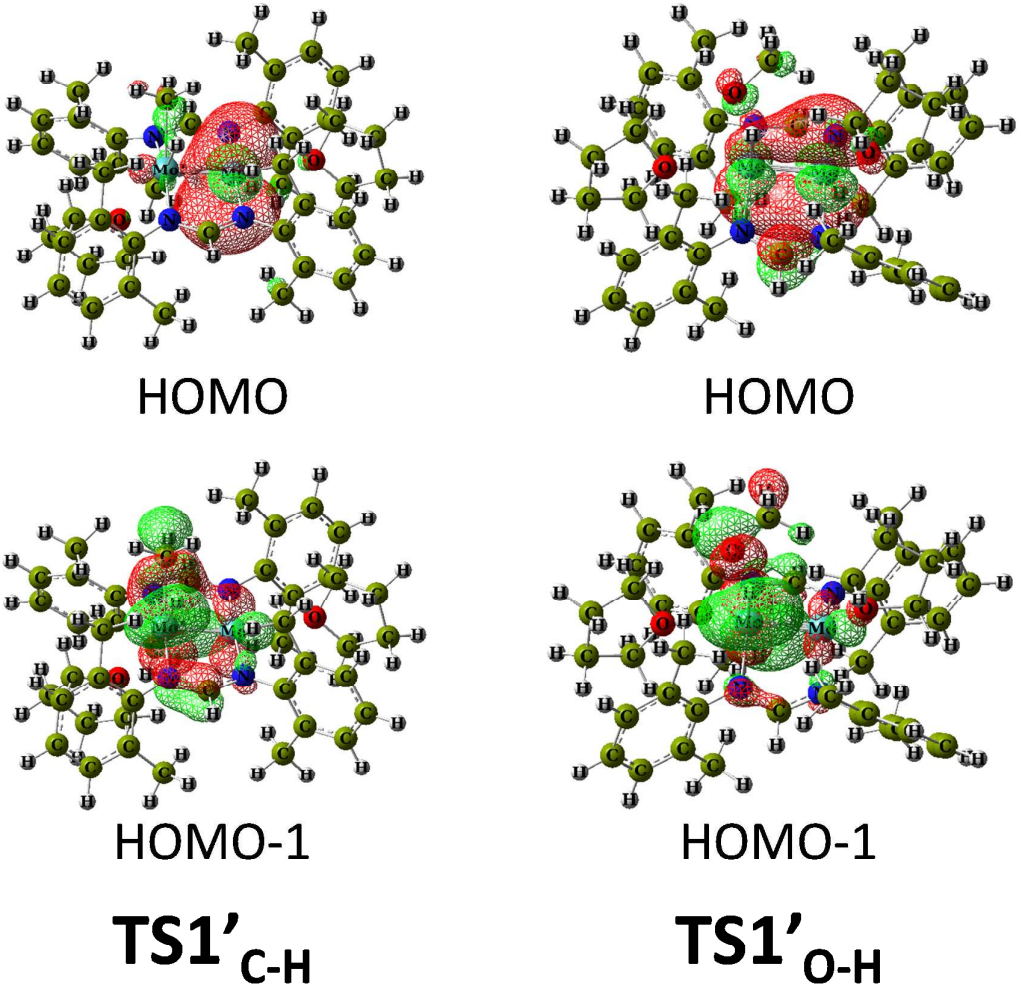
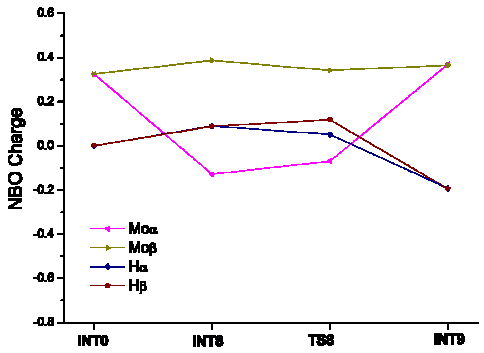
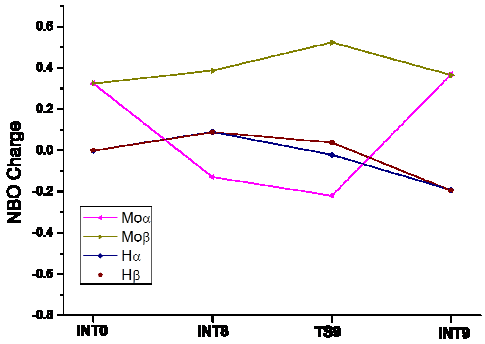


Figure S4. HOMO and HOMO-1 in **TS1'$_{C-H}$** and **TS1'$_{O-H}$**.

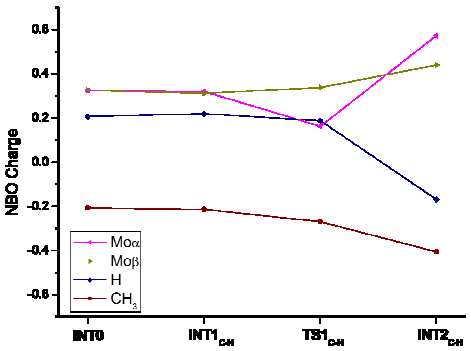


(A) H-H Cleavage via TS8

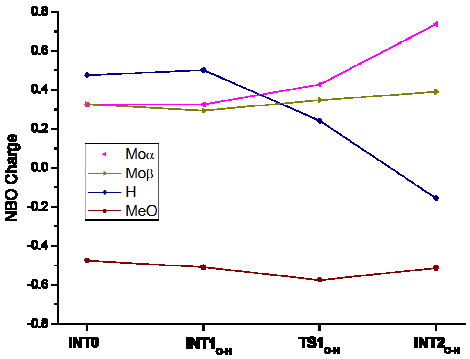


(B) H-H Cleavage via TS9

Figure S5. (A) Changes in NBO atomic charge in the H-H σ-bond cleavage via **TS8** and (B) those via **TS9**.



(A) C-H Cleavage via $TS1_{C-H}$



(B) O-H Cleavage via $TS1_{O-H}$

Figure S6. (A) Changes in NBO atomic charge in the C-H σ-bond cleavage and (B) those in the O-H σ-bond cleavage

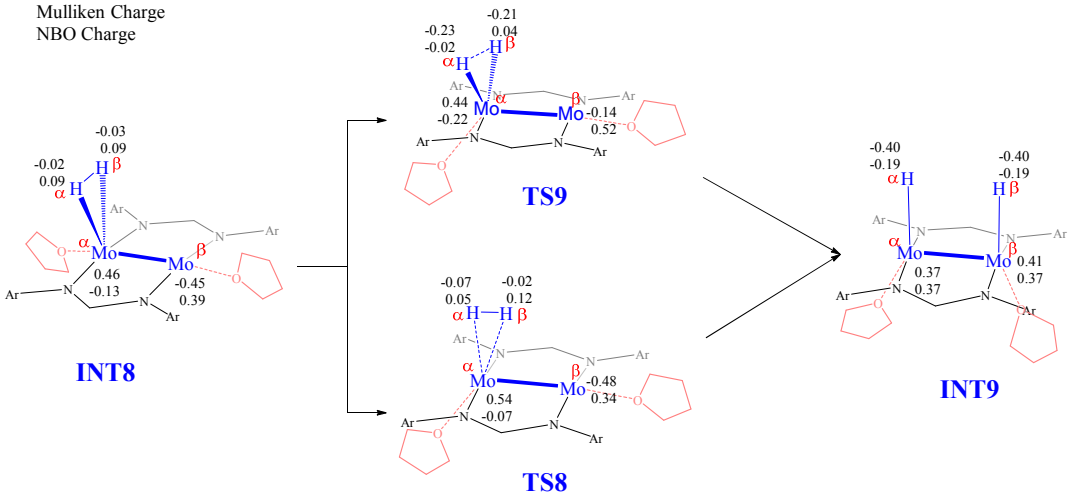


Figure S7. Changes in Mulliken and NBO atomic charge in the H-H cleavage in the presence of THF.