

铂钉团簇活化甲醇 C—H 和 O—H 键的理论研究

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Theoretical Study of Methanol C—H and O—H Bond Activation by PtRu Clusters

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表 S1 B3LYP 水平下 Pt_3 ($S=0, 1$) 与 CH_3OH 反应的 ΔH , $\Delta H_{(g)}$, $\Delta H_{(\epsilon)}$, $\Delta H_{(a)}$, $\Delta H_{(w)}$ 分别表示气相、介电常数 $\epsilon=4$ 、乙腈溶剂($\epsilon=36.6$)、和水($\epsilon=78.4$)条件下的相对焓变(单位: $\text{kJ}\cdot\text{mol}^{-1}$)

Table S1 Enthalpies involved in the methanol dehydrogenation reaction over Pt_3 ($S=0, 1$) cluster. Calculated energies using SR (${}^1\text{Pt}_3+\text{CH}_3\text{OH}$) as the reference species (Unit, $\text{kJ}\cdot\text{mol}^{-1}$)

Species	$\Delta H_{(g)}$	$\Delta H_{(\epsilon)}$	$\Delta H_{(a)}$	$\Delta H_{(w)}$	Species	$\Delta H_{(g)}$	$\Delta H_{(\epsilon)}$	$\Delta H_{(a)}$	$\Delta H_{(w)}$
${}^1\text{SR}$	0.0	0.0	0.0	0.0	${}^3\text{SR}$	67.0	27.2	33.5	33.9
${}^1\text{RC}_\text{O}$	-70.3	-57.4	-61.1	-56.9	${}^3\text{RC}_\text{O}$	-62.0	-41.0	-41.9	-35.6
${}^1\text{TSOa}$	20.5	42.7	40.2	45.2	${}^3\text{TSOa}$	25.1	51.9	51.1	56.9
${}^1\text{I1}$	-55.7	-35.2	-40.6	-36.4	${}^3\text{I1}$	-50.7	-29.7	-5.9	-2.5
${}^1\text{TSOaHd}$	-49.4	-27.2	-31.8	-28.1	${}^3\text{TSOaHd}$	-45.2	-22.2	-26.8	-23.4
${}^1\text{TSOb}$	55.3	78.7	74.9	80.8	${}^3\text{TSOb}$	27.6	55.3	56.5	62.4
${}^1\text{I2}$	-81.2	-61.1	-69.5	-62.0	${}^3\text{I2}$	-81.6	-51.5	-54.8	-46.1
${}^1\text{TSOaHCa}$	-70.8	-46.1	-60.3	-49.8	${}^3\text{TSOaHCa}$	-25.1	8.0	0.0	10.9
${}^1\text{I3}$	-81.2	-51.9	-66.2	-52.3	${}^3\text{I3}$	-44.0	-4.6	-13.0	1.3
${}^1\text{RC}_\text{C}$	-27.2	-8.8	-16.3	-14.2	${}^3\text{RC}_\text{C}$	-32.7	-7.5	-11.7	-11.7
${}^1\text{TSCa}$	-18.8	3.3	-4.2	1.3	${}^3\text{TSCa}$	-17.6	10.0	5.9	11.7
${}^1\text{I4}$	-56.9	-32.7	-40.2	-31.4	${}^3\text{I4}$	-67.4	-15.9	-19.7	-36.8
${}^1\text{TSCaHd}$	15.9	42.7	33.9	43.1	${}^3\text{TSCaHd}$	-15.1	13.0	7.5	14.7
${}^1\text{I5}$	-63.2	-44.8	-48.6	-44.0	${}^3\text{I5}$	-82.1	-50.7	-46.1	-38.9
${}^1\text{TSCaHOa}$	-14.7	18.0	11.3	23.4	${}^3\text{TSCaHOa}$	28.1	69.5	67.4	78.7
${}^1\text{I6}$	-113.0	-83.3	-95.0	-82.5	${}^3\text{I6}$	-72.0	-36.0	-44.8	-33.5
${}^1\text{TSCaOb}$	-31.4	-5.9	-18.0	-8.4	${}^3\text{TSCaOb}$	24.3	68.2	43.1	51.9
${}^1\text{I7}$	-144.4	-105.9	-121.0	-103.8	${}^3\text{I7}$	-4.2	33.1	45.2	59.9

表 S2 B3LYP 水平下 Pt_2Ru ($S=1, 2$) 与 CH_3OH 反应的 ΔH , $\Delta H_{(g)}$, $\Delta H_{(\epsilon)}$, $\Delta H_{(a)}$, $\Delta H_{(w)}$ 分别表示气相、介电常数 $\epsilon=4$ 、乙腈溶剂($\epsilon=36.6$)、和水($\epsilon=78.4$)条件下的相对焓变(单位: $\text{kJ}\cdot\text{mol}^{-1}$)

Table S2 Enthalpies involved in the methanol dehydrogenation reaction over Pt_2Ru ($S=1, 2$) cluster. Calculated energies using SR (${}^5\text{Pt}_2\text{Ru}+\text{CH}_3\text{OH}$) as the reference species (unit, $\text{kJ}\cdot\text{mol}^{-1}$)

Species	$\Delta H_{(g)}$	$\Delta H_{(\epsilon)}$	$\Delta H_{(a)}$	$\Delta H_{(w)}$	Species	$\Delta H_{(g)}$	$\Delta H_{(\epsilon)}$	$\Delta H_{(a)}$	$\Delta H_{(w)}$
${}^3\text{SR}$	32.7	44.8	35.2	33.5	${}^5\text{SR}$	0.0	0.0	0.0	0.0
${}^3\text{RC}_\text{O}$	-26.4	-2.1	-1.3	8.0	${}^5\text{RC}_\text{O}$	-56.9	-41.0	-46.9	-37.3
${}^3\text{TSOa}$	50.2	69.9	67.8	82.9	${}^5\text{TSOa}$	18.0	25.5	13.8	18.0
${}^3\text{I1}$	-13.0	0.4	2.9	-5.4	${}^5\text{I1}$	-42.3	-40.6	-52.8	-61.1
${}^3\text{TSOaHd}$	-12.1	-0.4	-7.5	-5.4	${}^5\text{TSOaHd}$	-13.0	-25.1	-68.7	-71.2
${}^3\text{TSOb}$	128.5	165.8	85.0	91.3	${}^5\text{TSOb}$	72.0	101.3	95.9	94.6
${}^3\text{I2}$	-40.6	-30.6	-41.0	-38.1	${}^5\text{I2}$	-65.7	-67.4	-87.9	-86.7
${}^3\text{TSOaHCa}$	17.6	50.2	48.1	58.2	${}^5\text{TSOaHCa}$	8.4	35.6	21.8	34.8
${}^3\text{I3}$	-0.8	32.2	18.8	27.2	${}^5\text{I3}$	-104.7	-111.8	-123.5	-114.7
${}^3\text{RC}_\text{C}$	0.8	27.2	25.1	61.5	${}^5\text{RC}_\text{C}$	-30.6	-15.5	-24.3	-20.5
${}^3\text{TSCa}$	12.6	44.4	41.4	46.5	${}^5\text{TSCa}$	-21.8	-8.4	-18.0	-14.2
${}^3\text{I4}$	-37.3	-12.6	-18.4	-7.5	${}^5\text{I4}$	-78.3	-64.9	-78.3	-71.2
${}^3\text{TSCaOb}$	-6.7	24.3	34.8	36.4	${}^5\text{TSCaOb}$	-29.7	-13.4	-9.6	-13.0

³ I5	-94.2	-59.5	-38.9	-49.4	⁵ I5	-126.9	-98.4	-76.2	-92.9
³ TSCaOa	80.8	103.8	96.7	102.2	⁵ TSCaOa	78.3	110.1	97.6	101.3
³ I6	-59.9	-44.4	-64.9	-59.9	⁵ I6	-103.4	-93.8	-116.0	-105.9

表 S3 B3LYP 水平下 PtRu₂ (S=2, 3)与 CH₃OH 反应的 ΔH , $\Delta H_{(g)}$, $\Delta H_{(\epsilon)}$, $\Delta H_{(a)}$, $\Delta H_{(w)}$ 分别表示气相、介电常数 $\epsilon=4$ 、乙腈溶剂($\epsilon=36.6$)、和水($\epsilon=78.4$)条件下的相对焓变(单位: $\text{kJ}\cdot\text{mol}^{-1}$)

Table S3 Enthalpies involved in the methanol dehydrogenation reaction over PtRu₂ (S=2, 3) cluster. Calculated energies using SR (⁷PtRu₂+CH₃OH) as the reference species (unit, $\text{kJ}\cdot\text{mol}^{-1}$)

Species	$\Delta H_{(g)}$	$\Delta H_{(\epsilon)}$	$\Delta H_{(a)}$	$\Delta H_{(w)}$	Species	$\Delta H_{(g)}$	$\Delta H_{(\epsilon)}$	$\Delta H_{(a)}$	$\Delta H_{(w)}$
⁵ SR	-6.3	35.2	58.2	56.9	⁷ SR	0.0	0.0	0.0	0.0
⁵ RC_O	-51.1	-8.0	-13.0	-2.1	⁷ RC_O	-51.5	-14.2	-17.6	-7.1
⁵ TSOa	27.6	70.8	62.4	63.2	⁷ TSOa	32.7	57.8	45.6	45.2
⁵ I1	-78.3	-84.6	-116.4	-117.6	⁷ I1	-65.3	-72.9	-104.3	-106.3
⁵ TSOaHd	-56.5	-63.6	-103.8	-88.3	⁷ TSOaHd	-41.9	-64.1	-112.2	-116.4
⁵ TSOb	105.9	131.5	117.6	118.1	⁷ TSOb	77.9	104.3	84.2	81.2
⁵ I2	-64.1	-76.6	-120.6	-121.8	⁷ I2	-49.4	-69.5	-117.2	-110.5
⁵ TSOaHCa	-9.6	-26.8	-75.8	-75.8	⁷ TSOaHCa	36.0	35.2	-14.7	-12.1
⁵ I3	-78.7	-62.0	-96.3	-88.8	⁷ I3	-90.4	-77.0	-103.8	-95.9
⁵ RC_C	-10.0	38.1	36.0	-10.9	⁷ RC_C	-10.9	25.5	20.1	22.6
⁵ TSCa	6.3	72.9	46.1	51.5	⁷ TSCa	15.5	51.5	36.8	42.7
⁵ I4	-14.2	-8.4	-20.1	-9.6	⁷ I4	-35.2	-6.7	-25.1	-19.7
⁵ TSCaOb	16.7	31.0	12.1	34.3	⁷ TSCaOb	26.8	37.7	20.5	14.2
⁵ I5	-120.6	-108.4	-126.9	-130.6	⁷ I5	-76.2	-65.7	-90.4	-99.2
⁵ TSCaOa	45.2	105.5	46.9	33.9	⁷ TSCaOa	80.0	108.4	81.2	87.9
⁵ I6	-41.4	-28.1	-66.2	-60.3	⁷ I6	-21.8	-9.6	-29.7	-23.4

表 S4 B3LYP 水平下 Pt₃ (S=0, 1)与 CH₃OH 反应的 $\Delta H_{(g)}$ 和 $\Delta G_{(g)}$ (单位: $\text{kJ}\cdot\text{mol}^{-1}$)

Table S1 Enthalpies and Free energy involved in the methanol dehydrogenation reaction over Pt₃ (S=0, 1) cluster (Unit, $\text{kJ}\cdot\text{mol}^{-1}$)

Species	$\Delta H_{(g)}$	$\Delta G_{(g)}$	Species	$\Delta H_{(g)}$	$\Delta G_{(g)}$
¹ SR	0.0	0.0	³ SR	67.0	63.6
¹ RC_O	-70.3	-26.4	³ RC_O	-62.0	-20.1
¹ TSOa	20.5	65.7	³ TSOa	25.1	66.6
¹ I1	-55.7	-11.3	³ I1	-50.7	-11.3
¹ TSOaHd	-49.4	-4.2	³ TSOaHd	-45.2	-4.6
¹ TSOb	55.3	102.2	³ TSOb	27.6	75.4
¹ I2	-81.2	-36.0	³ I2	-81.6	-44.8
¹ TSOaHCa	-70.8	-22.6	³ TSOaHCa	-25.1	18.8
¹ I3	-81.2	-36.0	³ I3	-44.0	-2.9
¹ RC_C	-27.2	15.5	³ RC_C	-32.7	5.4
¹ TSCa	-18.8	28.1	³ TSCa	-17.6	25.5

¹ I4	-56.9	-7.5	³ I4	-67.4	-23.4
¹ TSCaHd	15.9	64.9	³ TSCaHd	-15.1	26.8
¹ I5	-63.2	-17.6	³ I5	-82.1	-32.7
¹ TSCaHOa	-14.7	33.1	³ TSCaHOa	28.1	74.5
¹ I6	-113	-68.7	³ I6	-72	-29.9
¹ TSCaOb	-31.4	19.7	³ TSCaOb	24.3	71.2
¹ I7	-144.4	-101.3	³ I7	-4.2	23.0

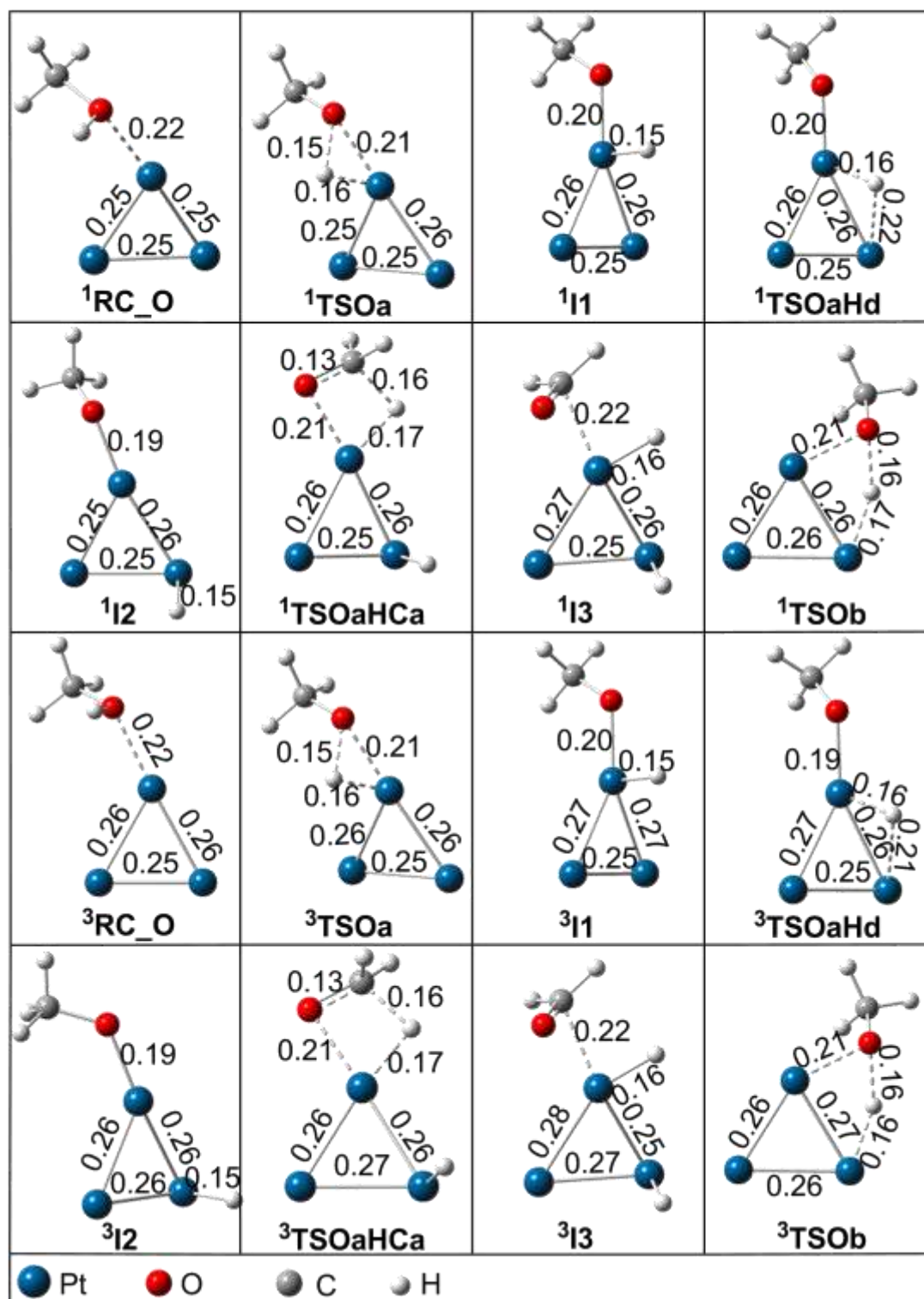


图 S1 在 B3LYP 水平下优化得到 Pt₃ (S=0, 1) 与 CH₃OH 反应(M1)的反应复合物、过渡态、中间体的几何构型

Fig.S1 Optimized geometries of the reactant complex, transition state, intermediate in the reaction of Pt₃ (S=0, 1) with CH₃OH starting from O—H bond activation at B3LYP level of theory
bond length in nm

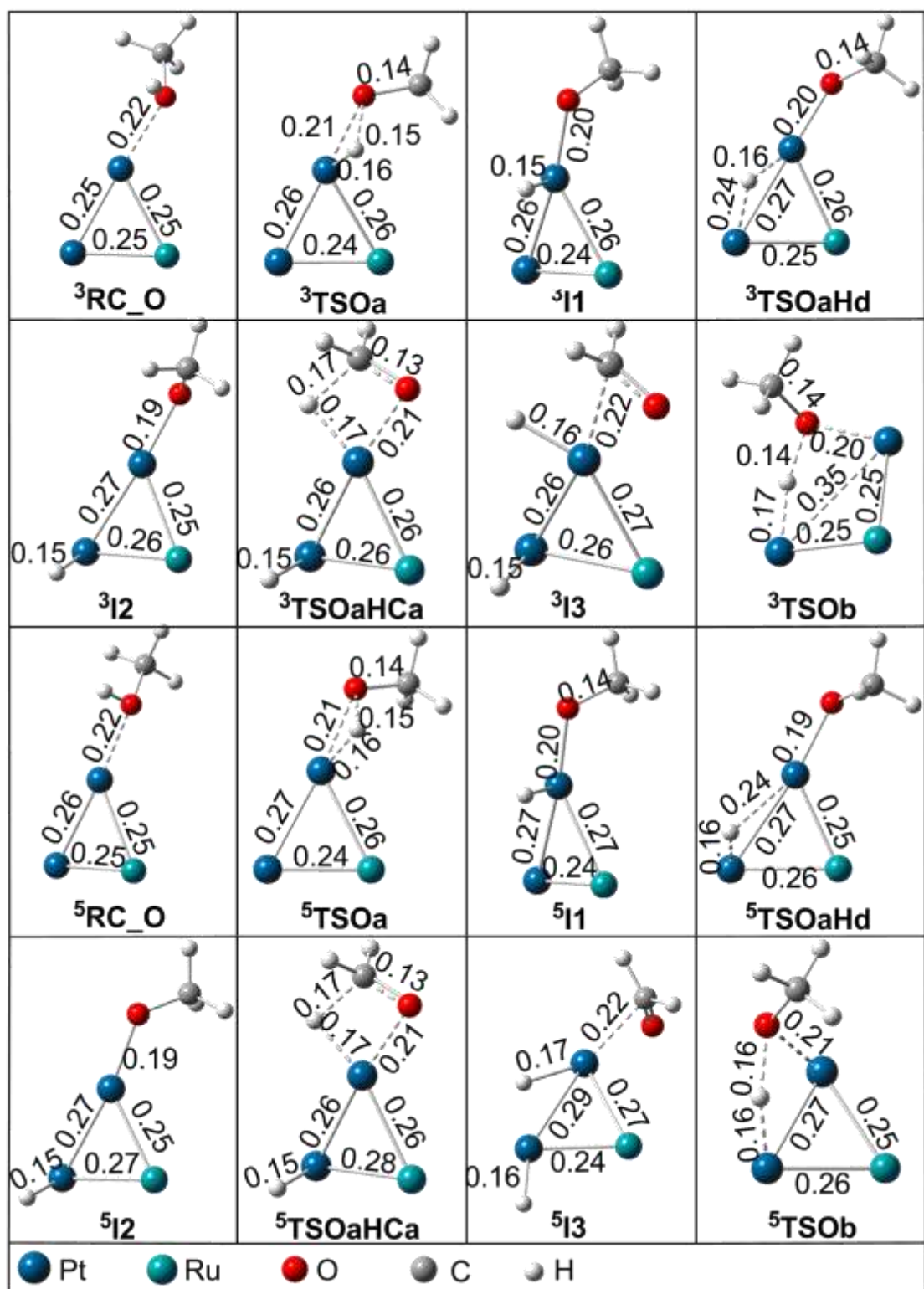


图 S2 在 B3LYP 水平下优化得到 Pt_2Ru ($S=1, 2$) 与 CH_3OH 反应(M1)的络合物、过渡态、中间体的几何构型

Fig.S2 Optimized geometries of the reactant complex, transition state, intermediate in the reaction of Pt_2Ru ($S=1, 2$) with CH_3OH starting from O—H bond activation at B3LYP level of theory
bond length in nm

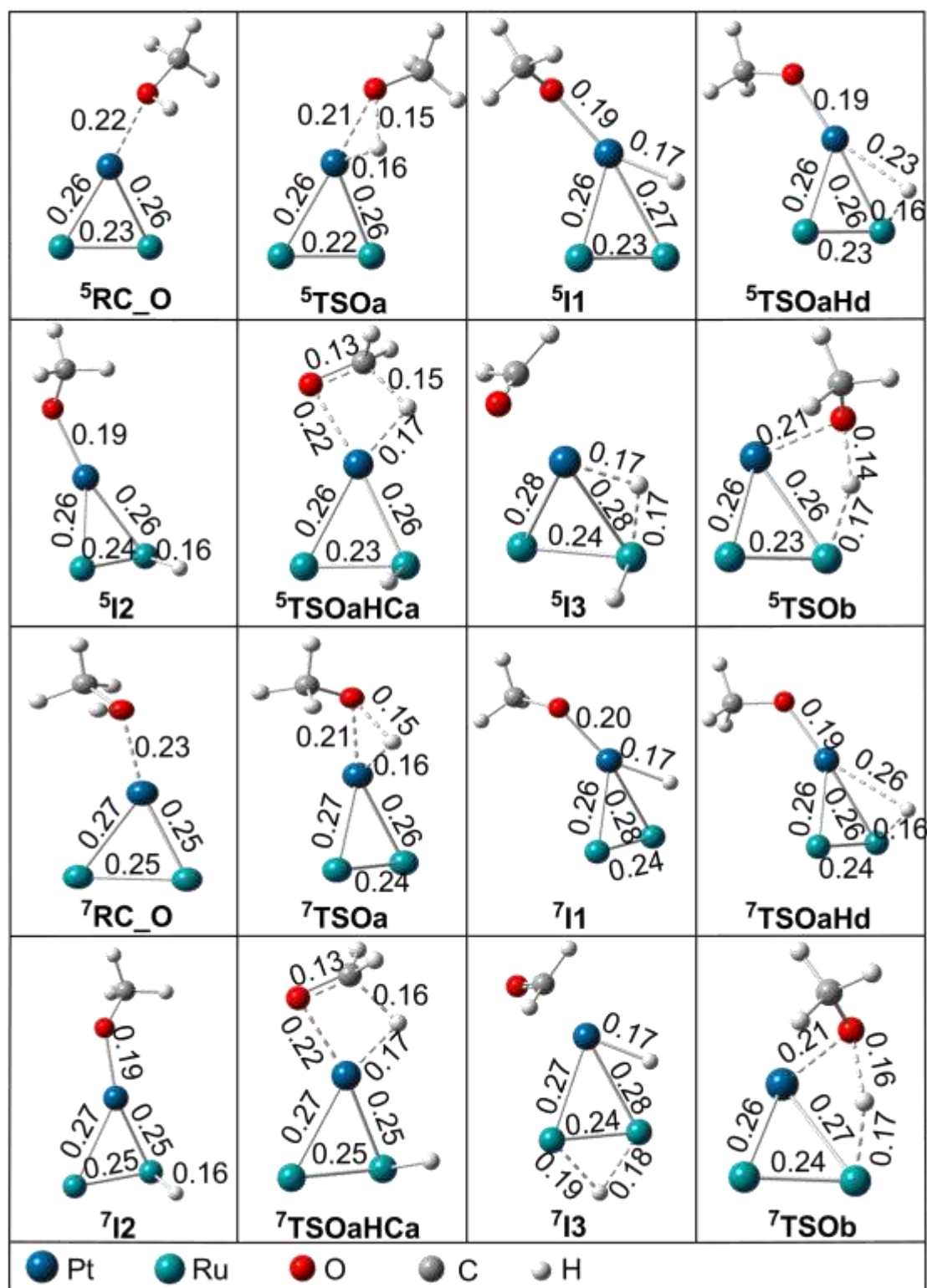


图 S3 在 B3LYP 水平下优化得到 PtRu₂ (S=2, 3)与 CH₃OH 反应(M1)的络合物、过渡态、中间体的几何构型

Fig.S3 Optimized geometries of the reactant complex, transition state, intermediate in the reaction of PtRu₂ (S=2, 3) with CH₃OH starting from O—H bond activation at B3LYP level of theory
bond length in nm

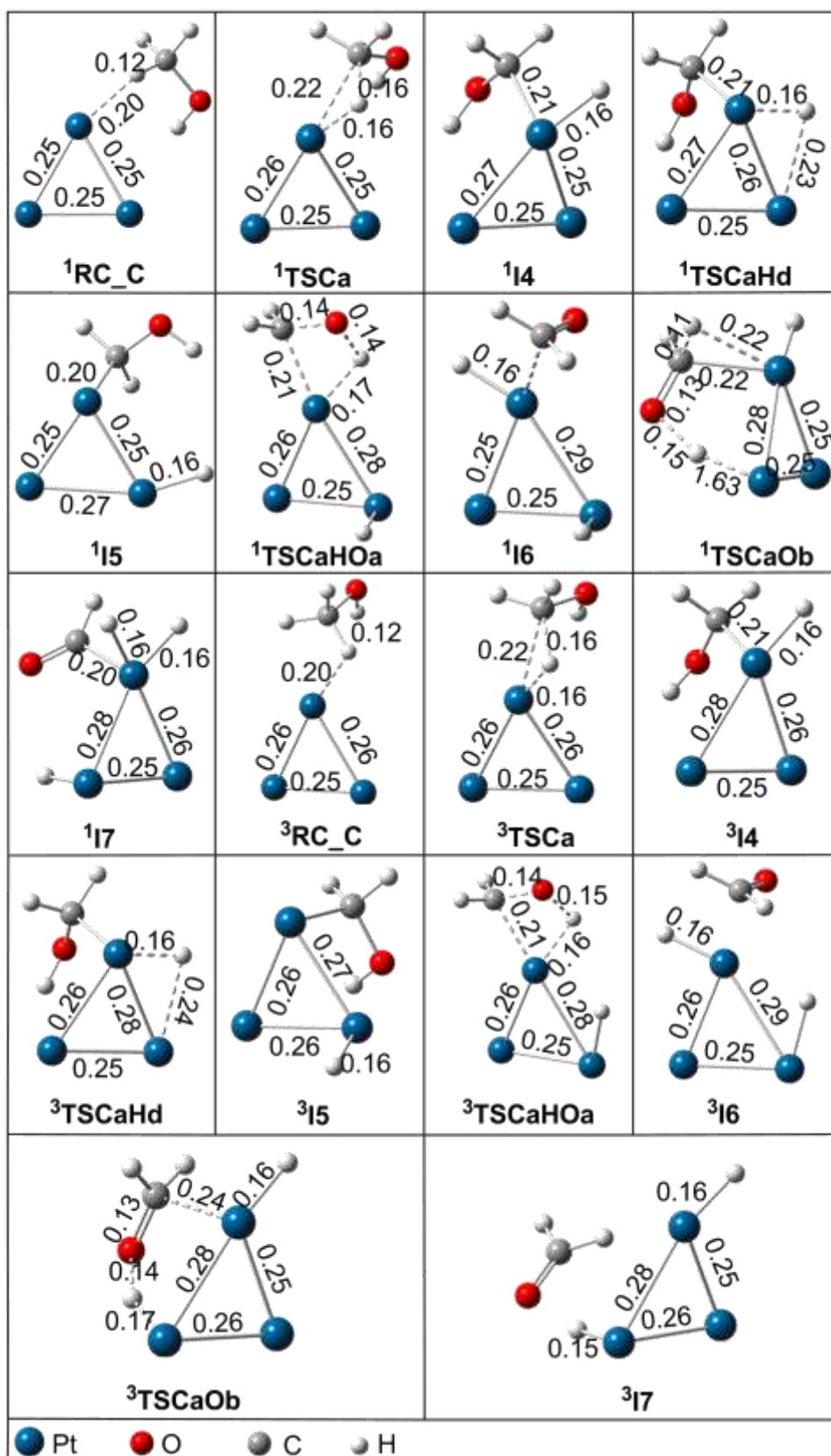


图 S4 在 B3LYP 水平下优化得到 Pt_3 ($S=0, 1$) 与 CH_3OH 反应(M2)的络合物、过渡态、中间体的几何构型

Fig.S4 Optimized geometries of the reactant complex, transition state, intermediate in the

reaction of Pt_3 ($S=0, 1$) with CH_3OH starting from C—H bond activation
 at B3LYP level of theory
 bond length in nm

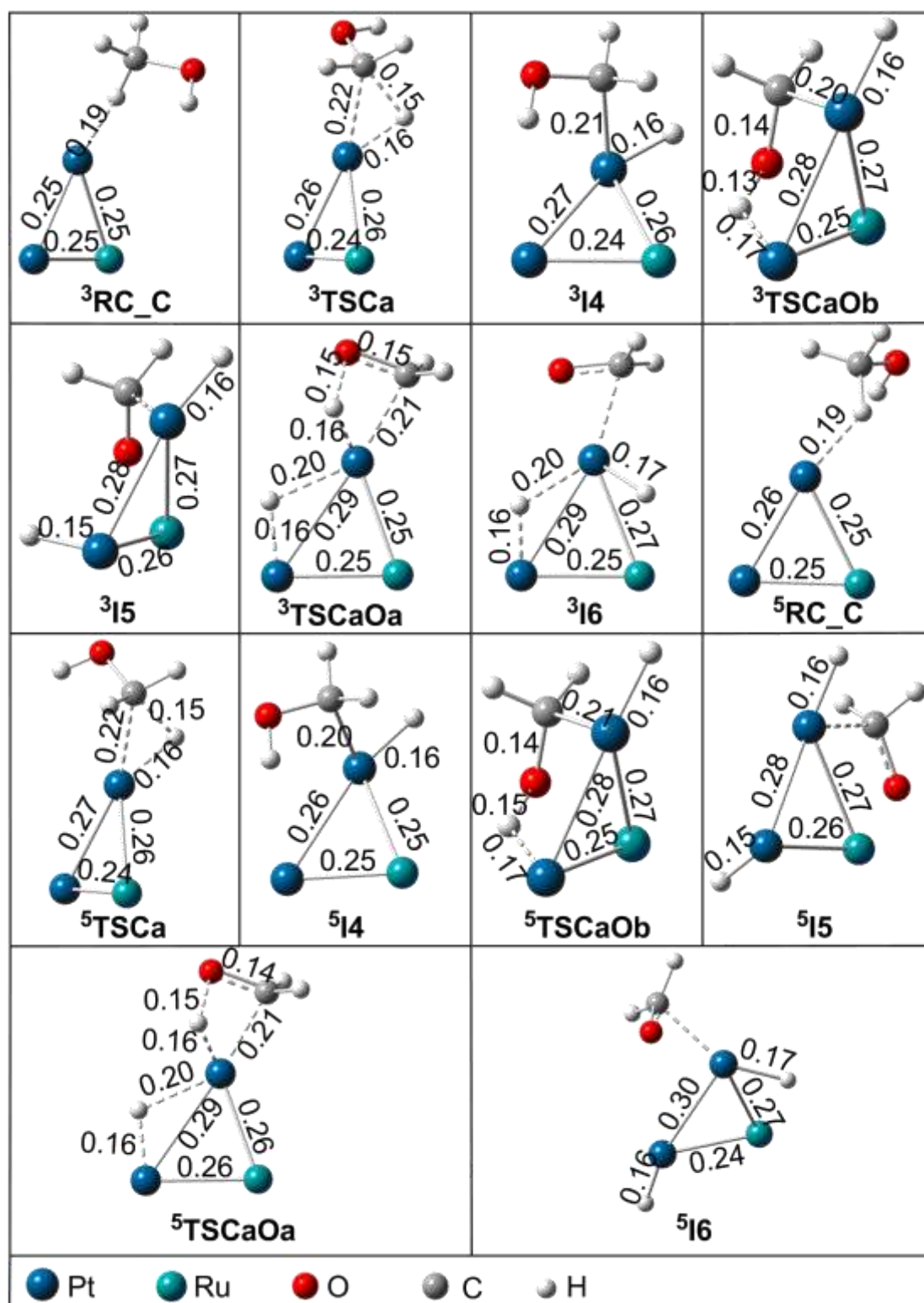


图 S5 在 B3LYP 水平下优化得到 Pt_2Ru ($S=1, 2$)与 CH_3OH 反应(M2)的反应复合物、过渡

态、中间体的几何构型

Fig.S5 Optimized geometries of the reactant complex, transition state, intermediate in the reaction of Pt₂Ru (S=1, 2) with CH₃OH starting from C—H bond activation at B3LYP level of theory
bond length in nm

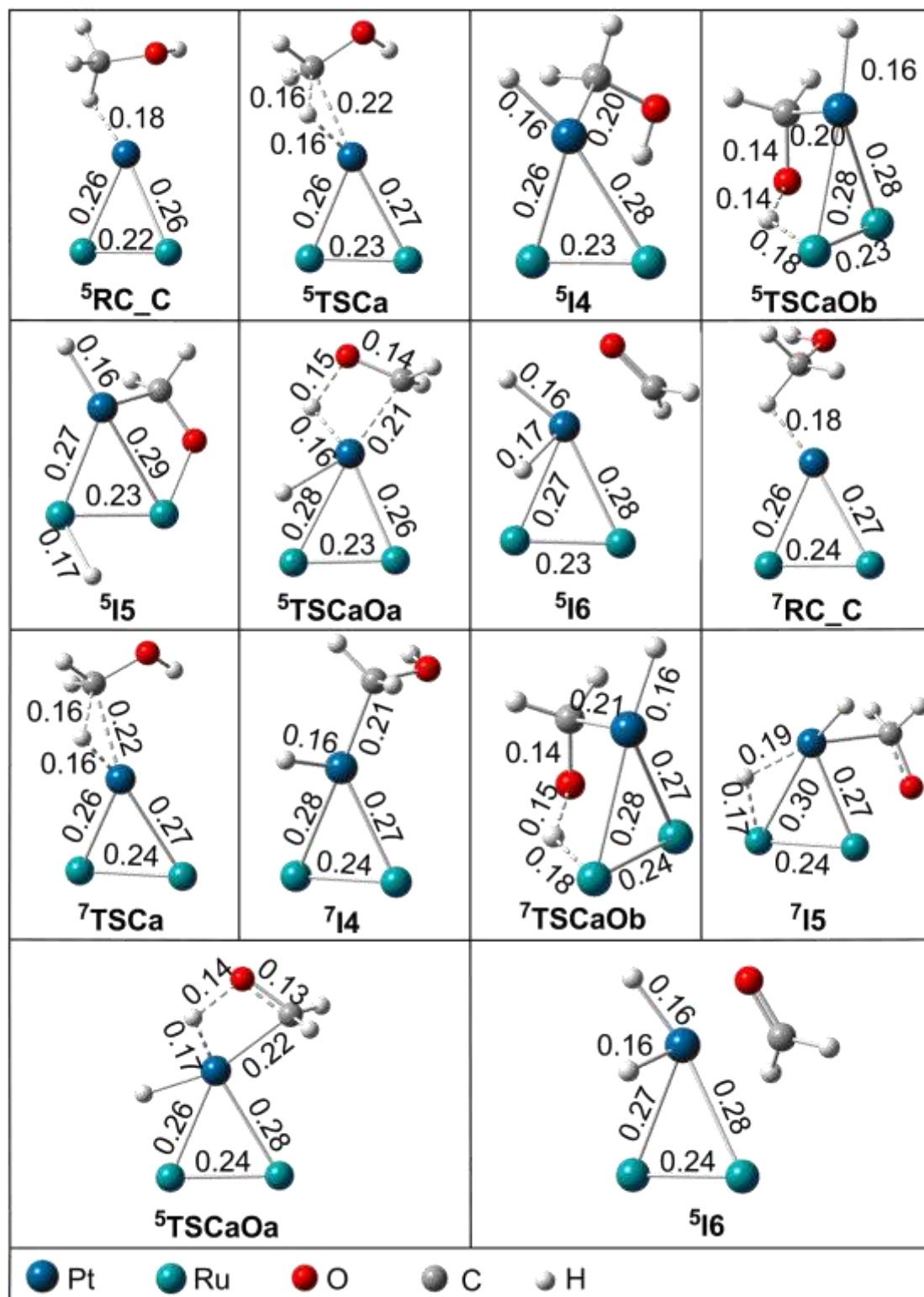


图 S6 在 B3LYP 水平下优化得到 PtRu₂ (S=2, 3)与 CH₃OH 反应(M2)的反应复合物、过渡态、中间体的几何构型

Fig.S6 Optimized geometries of the reactant complex, transition state, intermediate in the reaction of PtRu₂ (S=2, 3) with CH₃OH starting from C—H bond activation at B3LYP level of theory
bond length in nm



图 S7 Pt₃ (S=0, 1) 活化甲醇中 O—H 键过程的电子结构图。

Fig.S7 Electronic structure diagrams of reactant complex, transition state and intermediate in the progress of O—H bond activation by Pt₃ (S=0, 1).

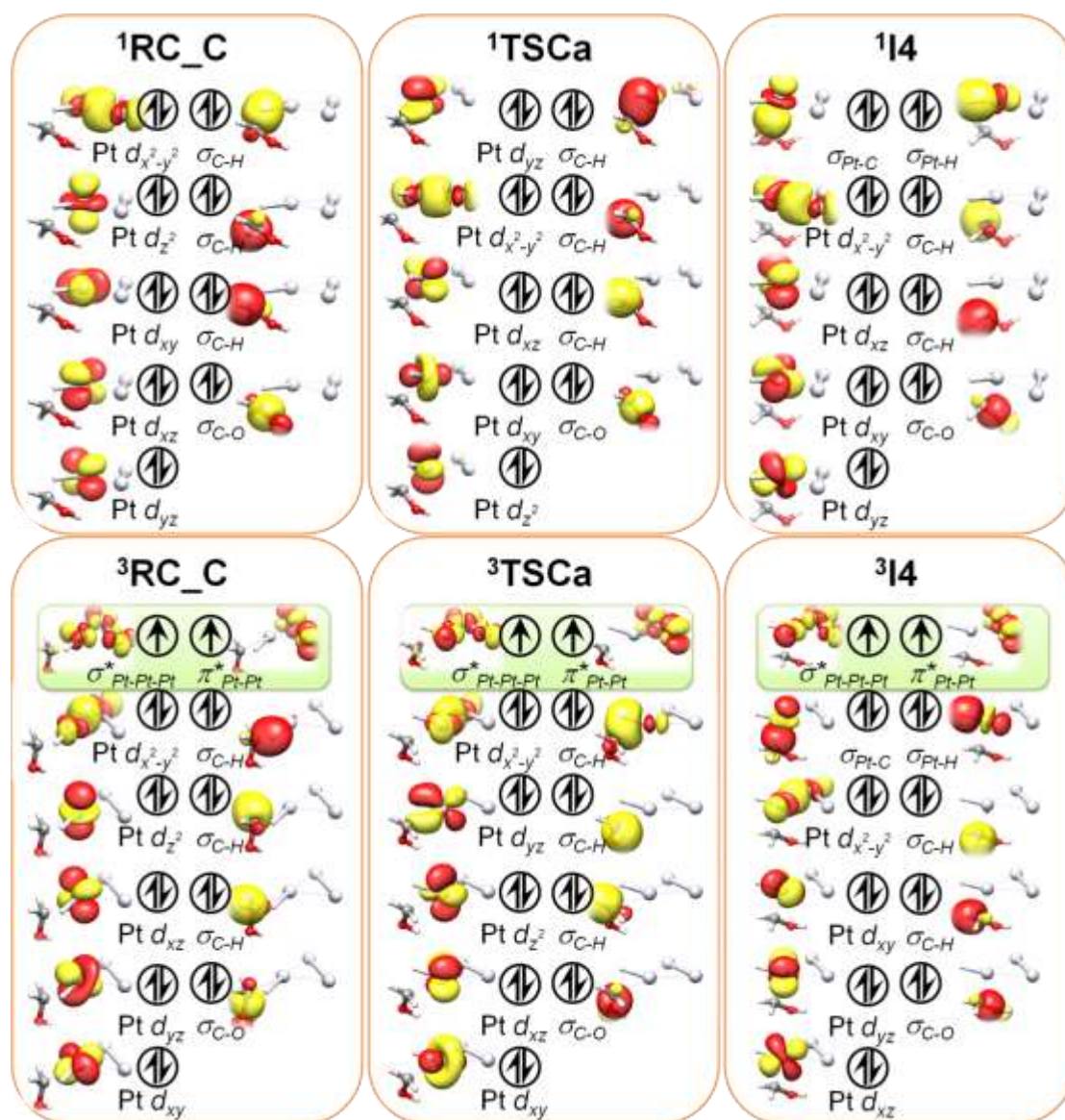


图 S8 Pt_3 ($S=0, 1$) 活化甲醇中 C—H 键过程的电子结构图

Fig.S8 Electronic structure diagrams of reactant complex, transition state and intermediate in the progress of C—H bond activation by Pt_3 ($S=0, 1$)

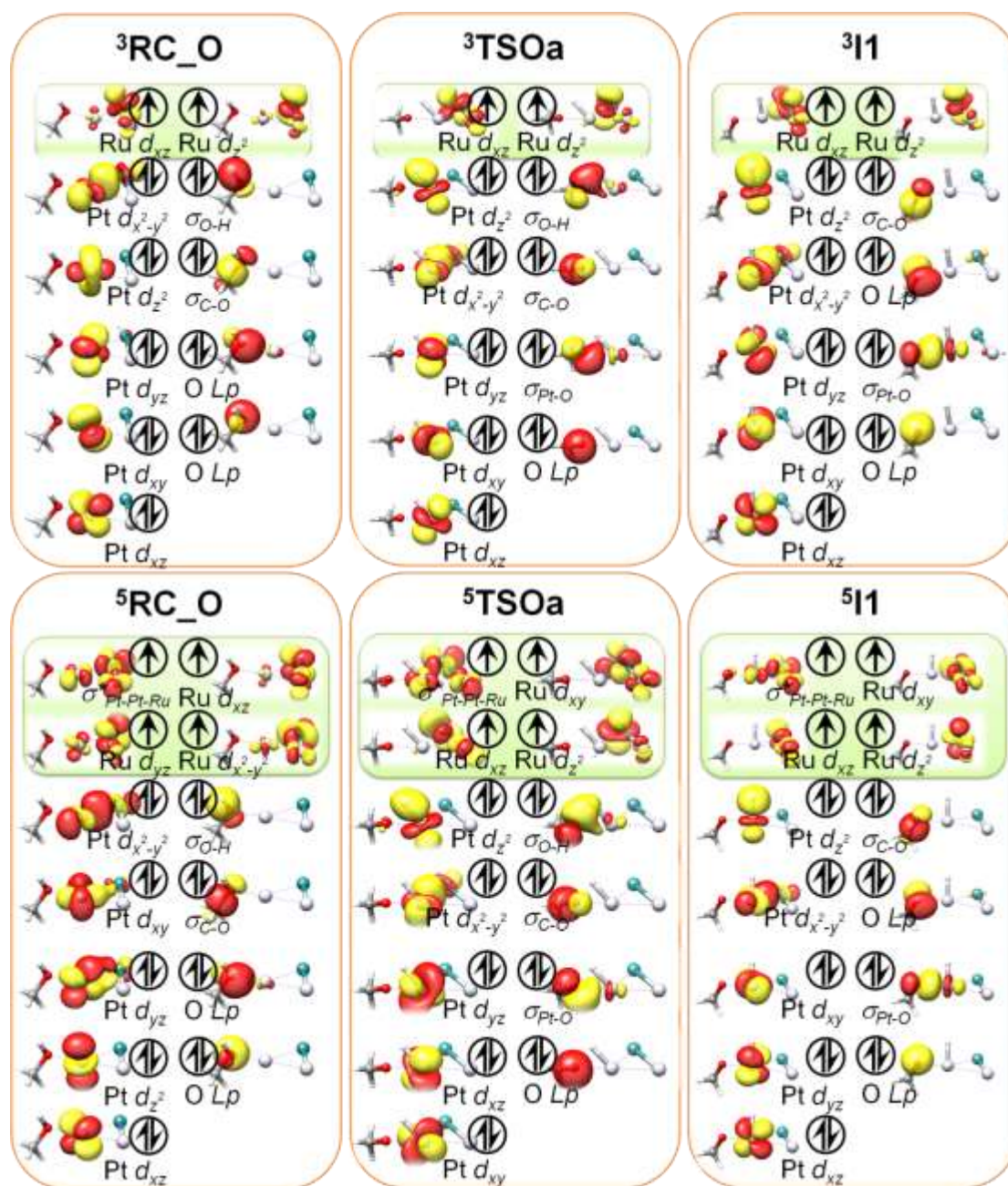


图 S9 Pt_2Ru ($S=1, 2$) 活化甲醇中 O—H 键过程的电子结构图

Fig.S9 Electronic structure diagrams of reactant complex, transition state and intermediate in the progress of O—H bond activation by Pt_2Ru ($S=1, 2$)

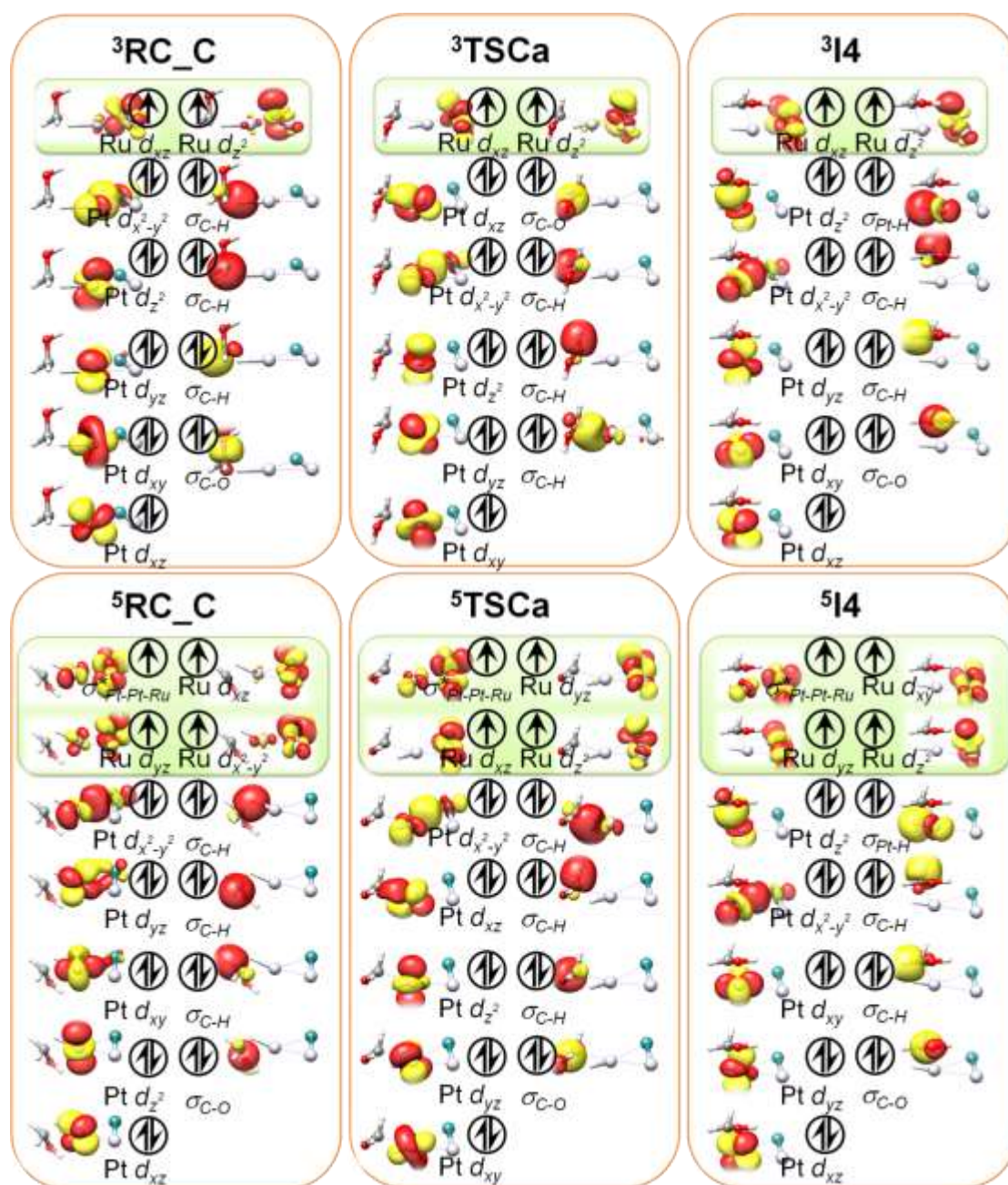


图 S10 Pt_2Ru ($S=1, 2$) 活化甲醇中 C—H 键过程的电子结构图

Fig.S10 Electronic structure diagrams of reactant complex, transition state and intermediate in the progress of C—H bond activation by Pt_2Ru ($S=1, 2$)

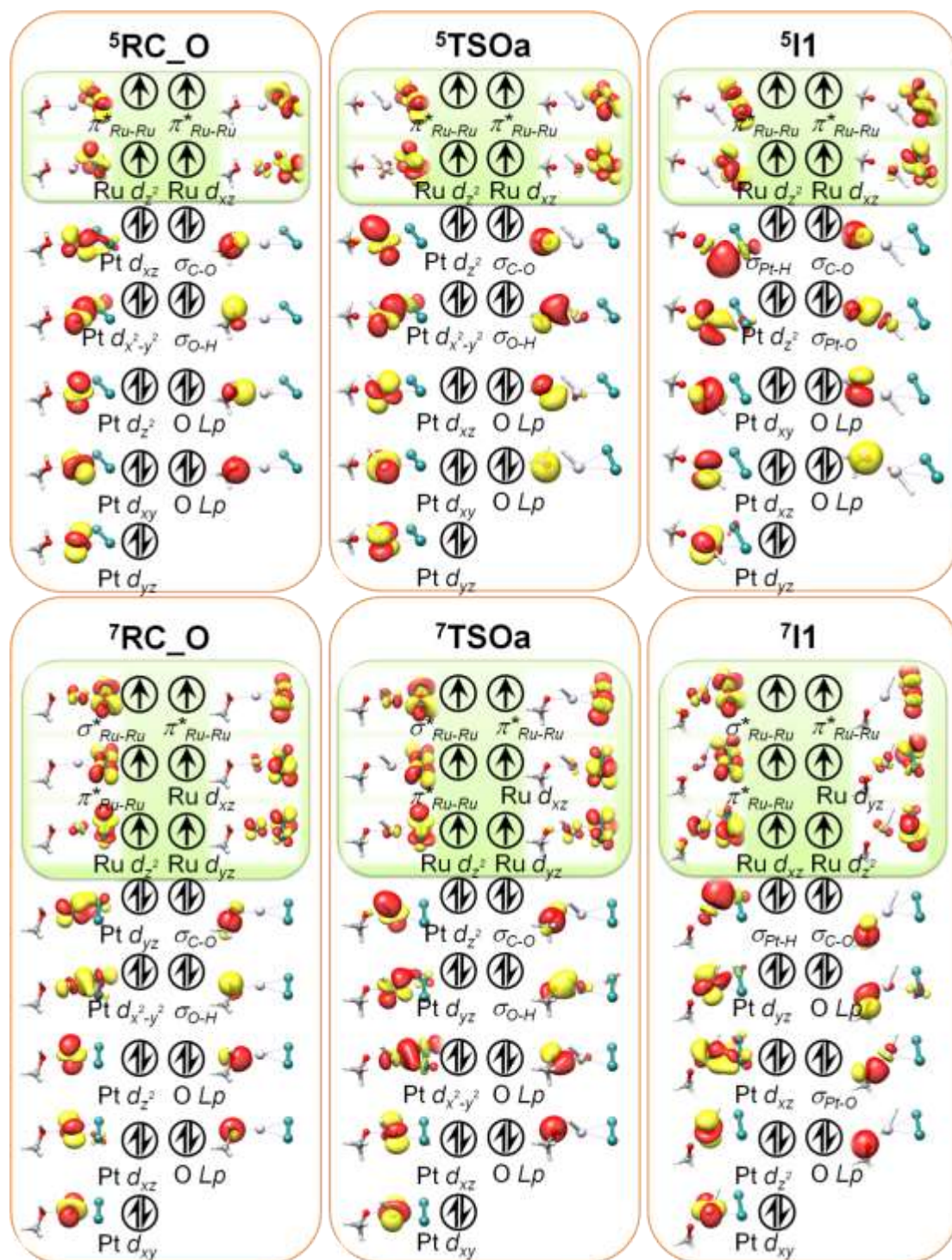


图 S11 PtRu₂ (S=2, 3) 活化甲醇中 O—H 键过程的电子结构图

Fig.S11 Electronic structure diagrams of reactant complex, transition state and intermediate in the progress of O—H bond activation by PtRu₂ (S=2, 3)

