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铂钌团簇及电荷对甲醇活性的理论研究

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A Theoretical Study on the Reactivity and Charge Effect of PtRu Clusters toward Methanol Activation

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表 S1　$[Pt_nRu_m]^+$($m + n = 3, n \geq 1$)不同自旋态下的相对能量

Table S1　Energies of different spin state of $[Pt_nRu_m]^+$($m + n = 3, n \geq 1$)

Species	$S = 1/2$	$S = 3/2$	$S = 5/2$	$S = 7/2$
$[Pt_3]^+$	0.0	8.0	167.5	380.161
$[Pt_2Ru]^+$	111.4	2.5	0.0	129.8
$[PtRu_2]^+$	167.1	135.7	33.9	0.0

Units: $kJ \cdot mol^{-1}$

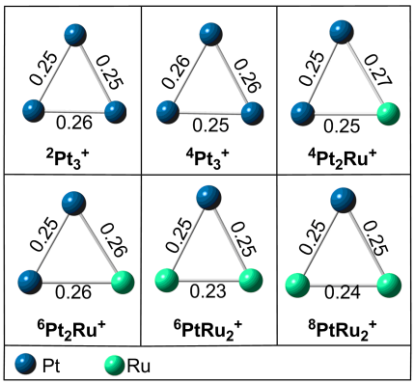

图 S1　在 B3LYP 水平下优化得到$[Pt_nRu_m]^+$($m + n = 3, n \geq 1$)几何构型

Fig.S1　Optimized geometries of the $[Pt_nRu_m]^+$($m + n = 3, n \geq 1$) clusters at the B3LYP level of theory

Bond length: nm. The superscripts 2, 4, 6 and 8 represent the spin multiplicities.

表S2　$[Pt_nRu_m]^{+/0}$团簇和反应络合物的键长参数

表S2　Important distances of $[Pt_nRu_m]^{+/0}$ and reactant complexes

		Pt–Pt	Pt–Pt	Pt–Pt	Pt–O	Pt–H		Pt–Pt	Pt–Ru	Pt–Ru	Pt–O	Pt–H		Pt–Ru	Pt–Ru	Ru–Ru	Pt–O	Pt–H
$[Pt_nRu_m]$	$^{1}Pt_3$	0.252	0.252	0.252	-	-	$^{3}Pt_2Ru$	0.253	0.251	0.251	-	-	$^{5}PtRu_2$	0.258	0.255	0.228	-	-
	$^{3}Pt_3$	0.258	0.258	0.250	-	-	$^{5}Pt_2Ru$	0.262	0.250	0.250	-	-	$^{7}PtRu_2$	0.265	0.252	0.237	-	-
	^{1}RC_O	0.254	0.253	0.251	0.221	-	^{3}RC_O	0.254	0.254	0.247	0.224	-	^{5}RC_O	0.257	0.261	0.226	0.221	-
	^{3}RC_O	0.260	0.259	0.249	0.220	-	^{5}RC_O	0.263	0.254	0.246	0.223	-	^{7}RC_O	0.270	0.252	0.252	0.231	-
	^{1}RC_C	0.252	0.252	0.253	-	0.197	^{3}RC_C	0.253	0.254	0.248	-	0.193	^{5}RC_C	0.258	0.258	0.224	-	0.176
	^{3}RC_C	0.259	0.260	0.248	-	0.195	^{5}RC_C	0.261	0.252	0.246	-	0.193	^{7}RC_C	0.257	0.271	0.237	-	0.175
$[Pt_nRu_m]^+$	$^{2}Pt_3^+$	0.251	0.251	0.257	-	-	$^{4}Pt_2Ru^+$	0.254	0.269	0.245	-	-	$^{6}PtRu_2^+$	0.251	0.251	0.227	-	-
	$^{4}Pt_3^+$	0.257	0.257	0.253	-	-	$^{6}Pt_2Ru^+$	0.251	0.257	0.257	-	-	$^{8}PtRu_2^+$	0.254	0.254	0.240	-	-
	^{2}RC_O	0.256	0.257	0.244	0.211	-	^{4}RC_O	0.265	0.256	0.241	0.215	-	^{6}RC_O	0.261	0.247	0.231	0.218	-
	^{4}RC_O	0.252	0.253	0.248	0.218	-	^{6}RC_O	0.245	0.267	0.243	0.217	-	^{8}RC_O	0.244	0.263	0.259	0.220	-
	^{2}RC_C	0.251	0.249	0.257	-	0.184	^{4}RC_C	0.265	0.256	0.242	-	0.182	^{6}RC_C	-	-	-	-	-
	^{4}RC_C	0.261	0.251	0.258	-	0.181	^{6}RC_C	0.247	0.267	0.244	-	0.184	^{8}RC_C	0.246	0.257	0.262	-	0.199

bond length: nm

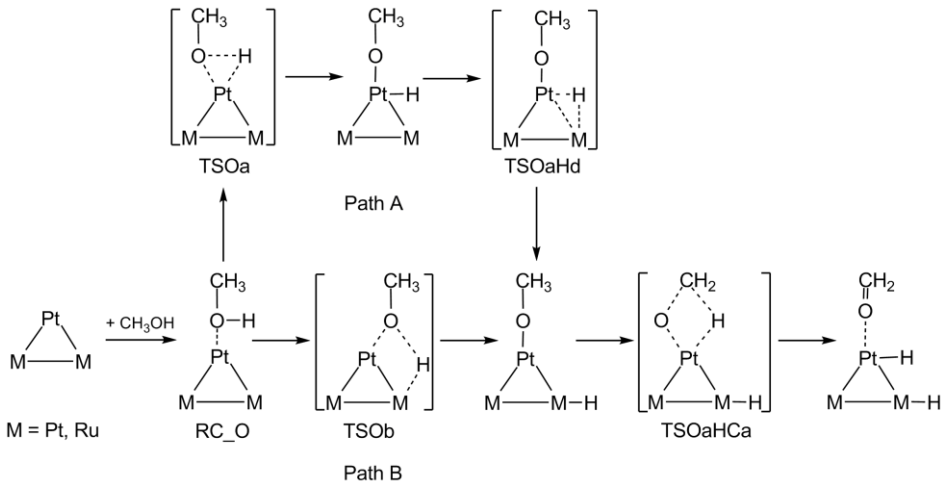

示意图 S1　$[Pt_nRu_m]^+$与 CH_3OH 以 O—H 键活化为初始步骤(M1)的反应

Scheme S1　Reaction of $[Pt_nRu_m]^+$ with CH_3OH starting from O—H bond activation (M1)

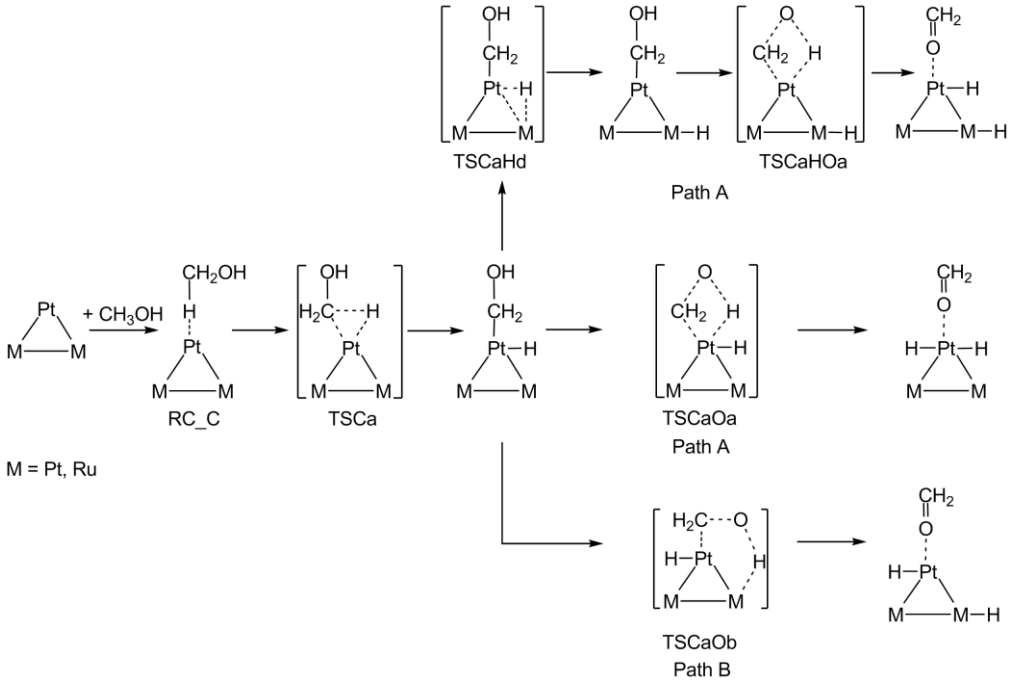

示意图 S2　$[Pt_nRu_m]^+$与 CH_3OH 以 C—H 键活化为初始步骤(M2)的反应

Scheme S2　Reaction of $[Pt_nRu_m]^+$ with CH_3OH starting from C—H bond activation (M2)

表 S3　$[Pt_2Ru]^+$ (S = 3/2, 5/2)与 CH_3OH 反应的主要过渡态的能量

Table S3　Energies (kJ·mol^{-1}) of main transition states involved in the methanol dehydrogenation reaction over $[Pt_2Ru]^+$ (S = 3/2, 5/2)cluster.

Species	ΔE	Species	ΔE
$^4TSCa_{Pt}$	-48.1	$^4TSCa_{Ru}$	25.0
$^6TSCa_{Pt}$	-35.2	$^6TSCa_{Ru}$	37.2
$^4TSOa_{Pt}$	33.9	$^4TSOa_{Ru}$	47.1
$^6TSOa_{Pt}$	24.8	$^6TSOa_{Ru}$	33.4
$^4TSOb_{Pt}$	19.4	$^4TSOb_{Ru}$	54.7
$^6TSOb_{Pt}$	21.4	$^6TSOb_{Ru}$	86.7

Pt: the reaction is occurring on Pt active center; Ru: the reaction is occurring on Ru active center.

表 S4　B3LYP 水平下$[Pt_3]^+$ (S = 1/2, 3/2)与 CH_3OH 反应的ΔH, Δ$H_{(g)}$, Δ$H_{(ε)}$, Δ$H_{(a)}$, Δ$H_{(w)}$分别表示气相、介电常数 $ε$ = 4、乙腈溶剂($ε$ = 36.6)、和水($ε$ = 78.4)条件下的相对焓变

Table S4　Energies (kJ·mol^{-1}) involved in the methanol dehydrogenation reaction over $[Pt_3]^+$ (S = 1/2, 3/2) cluster

Species	Δ$H_{(g)}$	Δ$H_{(ε)}$	Δ$H_{(a)}$	Δ$H_{(w)}$	Species	Δ$H_{(g)}$	Δ$H_{(ε)}$	Δ$H_{(a)}$	Δ$H_{(w)}$
^{2}SR	0.0	0.0	0.0	0.0	^{4}SR	-15.5	32.7	4.2	-24.7
^{2}RC_O	-174.2	-113.5	-102.6	-100.9	^{4}RC_O	-163.7	-97.6	-83.3	-82.5
^{2}TSOa	-6.7	40.6	33.9	38.5	^{4}TSOa	-7.5	48.1	45.2	51.1
^{2}I1	-110.1	-58.6	-64.1	-58.6	^{4}I1	-98.4	-42.3	-46.5	-39.8
^{2}TSOaHd	-93.4	-33.5	-41.9	-35.6	^{4}TSOaHd	-85.4	-19.3	-36.8	-27.6
^{2}TSOb	-33.9	18.0	18.4	23.9	^{4}TSOb	-8.8	37.3	33.9	39.4
^{2}I2	-145.3	-88.3	-93.4	-85.4	^{4}I2	-108.9	-46.1	-49.0	-41.0
^{2}TSOaHCa	-95.0	-47.7	-65.3	-54.8	^{4}TSOaHCa	-34.8	32.2	24.3	37.3
^{2}I3	-202.6	-120.6	-119.3	-106.8	^{4}I3	-106.3	-25.1	-24.7	10.9
^{2}RC_C	-81.6	-27.2	-23.9	-19.7	^{4}RC_C	-80.4	-23.4	-27.6	4.2
^{2}TSCa	-81.2	-35.2	-23.9	-34.3	^{4}TSCa	-49.8	10.5	7.1	13.8
^{2}I4	-143.6	-84.6	-68.7	-65.7	^{4}I4	-120.2	-59.0	-55.7	-51.9
^{2}TSCaHd	-131.0	-67.0	-58.2	-57.8	^{4}TSCaHd	-94.2	-34.8	-33.9	-29.3
^{2}I5	-200.5	-139.0	-132.3	-130.2	^{4}I5	-118.1	-60.3	-62.4	-56.1
^{2}TSCaHOa	-70.3	-0.8	-5.0	7.1	^{4}TSCaHOa	27.6	86.7	96.3	94.6
^{2}I6	-202.6	-120.6	-144.9	-106.8	^{4}I6	-129.0	-48.6	-48.1	-34.8
^{2}TSCaOb	29.3	24.3	17.2	25.1	^{4}TSCaOb	14.2	124.8	87.9	99.6
^{2}I7	-92.1	-50.2	-65.3	-59.0	^{4}I7	-113.9	-13.8	-17.6	-23.0

calculated energies using SR ($[^2Pt_3]^+$ + CH_3OH) as the reference species

表 S5　B3LYP 水平下$[Pt_2Ru]^+$ (*S* = 3/2, 5/2)与 CH_3OH 反应的ΔH, $\Delta H_{(g)}$, $\Delta H_{(\varepsilon)}$, $\Delta H_{(a)}$, $\Delta H_{(w)}$ 分别表示气相、介电常数 ε = 4、乙腈溶剂(ε = 36.6)、和水(ε = 78.4)条件下的相对焓变

Table S5　Energies (kJ·mol^{-1}) involved in the methanol dehydrogenation reaction over $[Pt_2Ru]^+$ (*S* = 3/2, 5/2) cluster

Species	$\Delta H_{(g)}$	$\Delta H_{(\varepsilon)}$	$\Delta H_{(a)}$	$\Delta H_{(w)}$	Species	$\Delta H_{(g)}$	$\Delta H_{(\varepsilon)}$	$\Delta H_{(a)}$	$\Delta H_{(w)}$
^{4}SR	20.5	25.1	46.9	49.0	^{6}SR	0.0	0.0	0.0	0.0
^{4}RC_O	-121.0	-49.4	-16.7	-7.1	^{6}RC_O	-141.5	-82.1	-59.5	-50.7
^{4}TSOa	28.9	61.1	75.8	84.6	^{6}TSOa	20.5	38.9	33.5	40.2
^{4}I1	-61.5	-8.8	5.0	10.9	^{6}I1	-48.1	-7.5	-32.7	-33.9
^{4}TSOaHd	-52.8	-16.7	-19.3	-8.0	^{6}TSOaHd	-48.1	-1.3	-31.8	-32.2
^{4}TSOb	45.6	111.0	137.3	148.2	^{6}TSOb	41.9	88.8	109.7	132.7
^{4}I2	-64.1	-16.3	-15.5	-9.2	^{6}I2	-73.3	-28.5	-49.4	-48.1
^{4}TSOaHCa	-38.5	10.0	26.0	40.6	^{6}TSOaHCa	22.6	69.1	67.0	76.6
^{4}I3	-115.1	21.8	58.6	79.1	^{6}I3	-102.2	-17.2	13.8	34.3
^{4}RC_C	-43.1	14.7	33.5	43.1	^{6}RC_C	-67.8	-25.1	-18.8	-13.4
^{4}TSCa	-38.9	45.6	89.6	98.8	^{6}TSCa	-37.7	40.6	35.6	41.4
^{4}I4	-105.1	-35.2	-1.3	5.9	^{6}I4	-79.1	-9.2	16.7	21.8
^{4}TSCaOb	-21.4	35.2	79.5	71.6	^{6}TSCaOb	-13.0	20.5	49.4	34.8
^{4}I5	-121.0	-46.9	20.1	3.3	^{6}I5	-87.1	-50.7	-8.8	-42.7
^{4}TSCaOa	22.2	103.0	131.0	148.2	^{6}TSCaOa	65.3	136.5	154.1	169.1
^{4}I6	-95.5	54.8	58.6	79.1	^{6}I6	-77.9	16.3	48.1	64.9

Calculated energies using SR ($[^6Pt_2Ru]^+$ + CH_3OH) as the reference species

表 S6 B3LYP 水平下$[PtRu_2]^+$ (*S* = 5/2, 7/2)与 CH_3OH 反应的ΔH, $\Delta H_{(g)}$, $\Delta H_{(\varepsilon)}$, $\Delta H_{(a)}$, $\Delta H_{(w)}$分别表示气相、介电常数 ε = 4、乙腈溶剂(ε = 36.6)、和水(ε = 78.4)条件下的相对焓变

Table S6 Energies (kJ·mol^{-1}) involved in the methanol dehydrogenation reaction over $[PtRu_2]^+$ (*S* = 5/2, 7/2)cluster

Species	$\Delta H_{(g)}$	$\Delta H_{(\varepsilon)}$	$\Delta H_{(a)}$	$\Delta H_{(w)}$	Species	$\Delta H_{(g)}$	$\Delta H_{(\varepsilon)}$	$\Delta H_{(a)}$	$\Delta H_{(w)}$
^{6}SR	21.4	-10.0	-5.0	25.1	^{8}SR	0.0	0.0	0.0	0.0
^{6}RC_O	-97.1	-40.2	78.3	77.9	^{8}RC_O	-100.5	-30.6	-23.4	77.5
^{6}TSOa	74.1	87.5	78.3	111.4	^{8}TSOa	65.7	72.9	60.7	91.3
^{6}I1	-7.1	6.3	-0.8	31.4	^{8}I1	-25.5	-53.6	-93.8	-64.9
^{6}TSOaHd	-6.7	-2.9	-25.5	6.7	^{8}TSOaHd	-6.7	-37.3	-81.2	-52.3
^{6}TSOb	98.8	137.7	180.9	218.6	^{8}TSOb	103.0	100.5	85.0	114.3
^{6}I2	-16.7	-31.4	-68.7	-34.8	^{8}I2	-15.1	-51.1	-91.3	-61.1
^{6}TSOaHCa	84.2	72.0	34.8	84.2	^{8}TSOaHCa	94.6	87.1	54.4	85.0
^{6}I3	-51.1	25.1	37.3	87.5	^{8}I3	-59.5	-21.4	-9.2	18.0
					^{8}RC_C	-33.9	-13.4	-13.8	20.1
^{6}TSCa	-5.0	52.3	80.0	123.9	^{8}TSCa	8.0	42.3	46.5	83.7
^{6}I4	-58.2	6.7	24.3	62.0	^{8}I4	-33.9	3.8	10.0	47.3
^{6}TSCaOa	71.2	104.3	88.3	127.7	^{8}TSCaOa	119.7	136.5	108.4	149.1
^{6}I5	-62.4	39.8	51.1	97.1	^{8}I5	-32.2	13.4	-1.7	51.5
^{6}TSCaOb	77.5	86.2	83.3	93.8	^{8}TSCaOb	93.8	82.1	65.3	82.9

^{6}I6	-35.2	-38.9	-51.1	-38.5	^{8}I6	-37.3	-18.8	72.4	-30.1

calculated energies using SR ($[^{8}PtRu_2]^+$ + CH_3OH) as the reference species

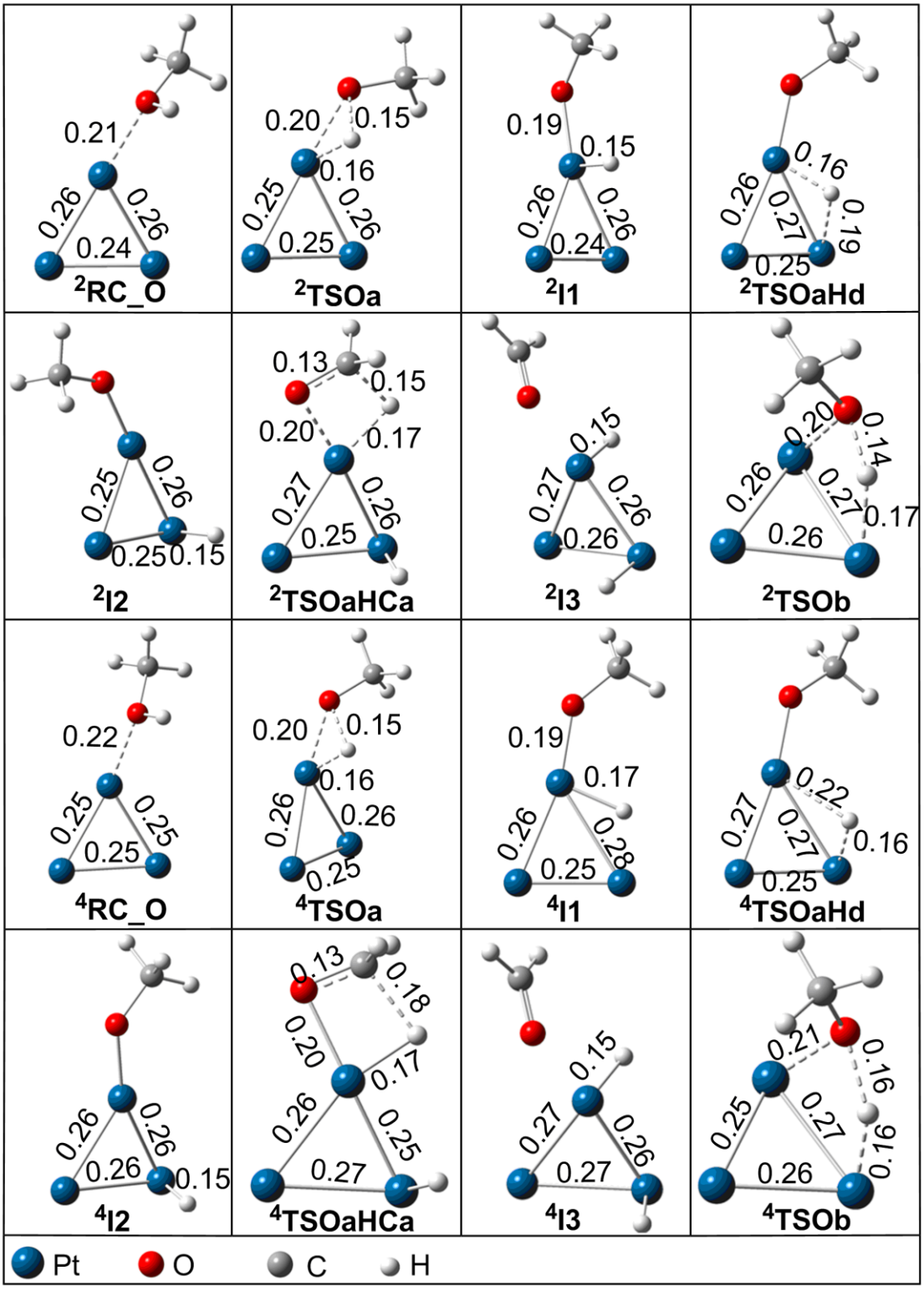

图 S2　在 B3LYP 水平下$[Pt_3]^+$与 CH_3OH 反应的以 O—H 键活化为反应初始步骤(M1)的反应复合物、过渡态、中间体的几何构型

Fig.S2　Optimized geometries of the reactant complex, transition state, intermediate in the reaction of $[Pt_3]^+$ with CH_3OH starting from O—H bond activation at B3LYP level of theory

Bond length: nm. The superscripts 2 and 4 represent the spin multiplicities.

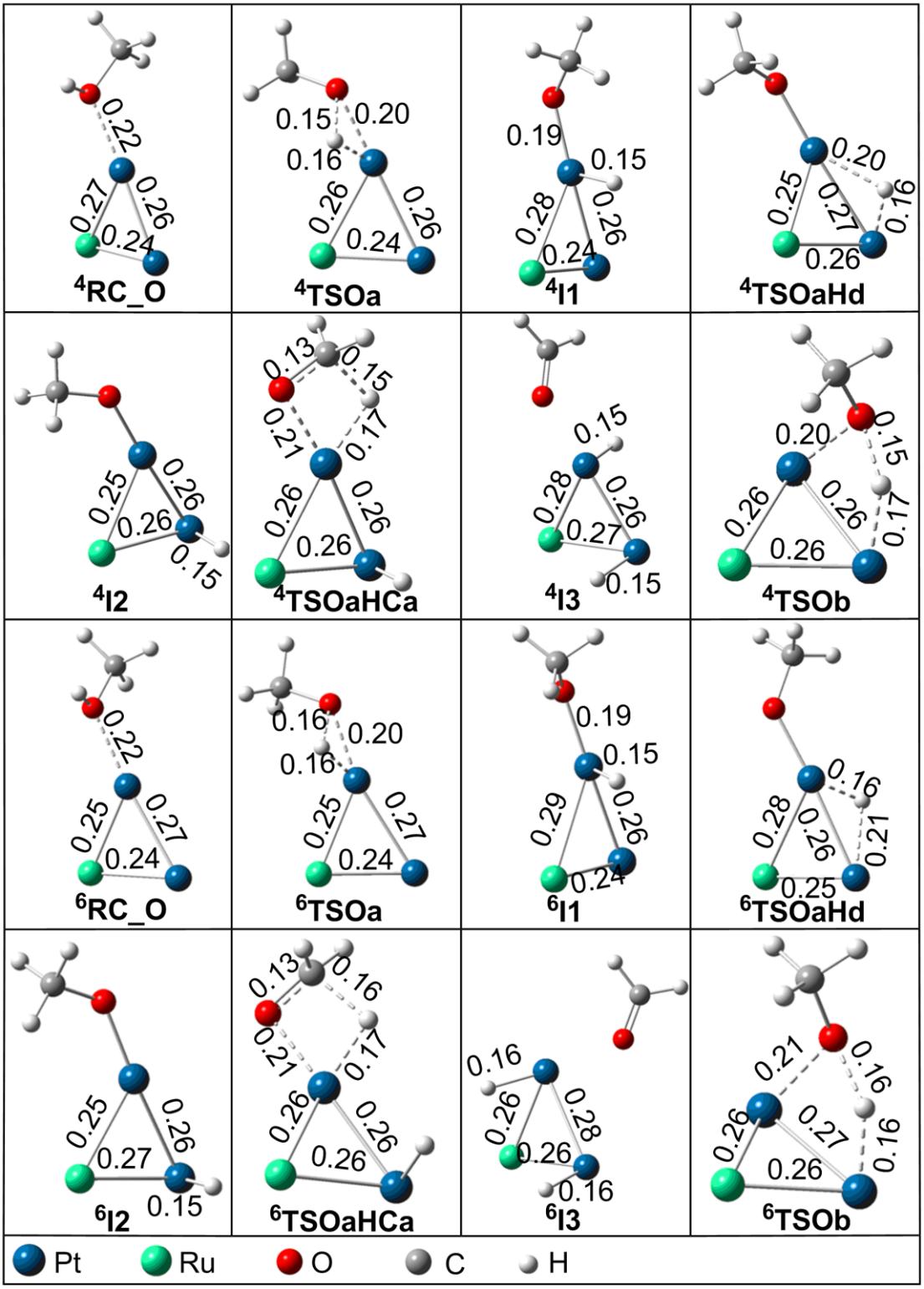

图 S3　在 B3LYP 水平下$[Pt_2Ru]^+$与 CH_3OH 反应的以 O—H 键活化为反应初始步骤(M1)的反应复合物、过渡态、中间体的几何构型

Fig.S3　Optimized geometries of the reactant complex, transition state, intermediate in the reaction of $[Pt_2Ru]^+$ with CH_3OH starting from O—H bond activation at B3LYP level of theory

Bond length: nm. The superscripts 4 and 6 represent the spin multiplicities.

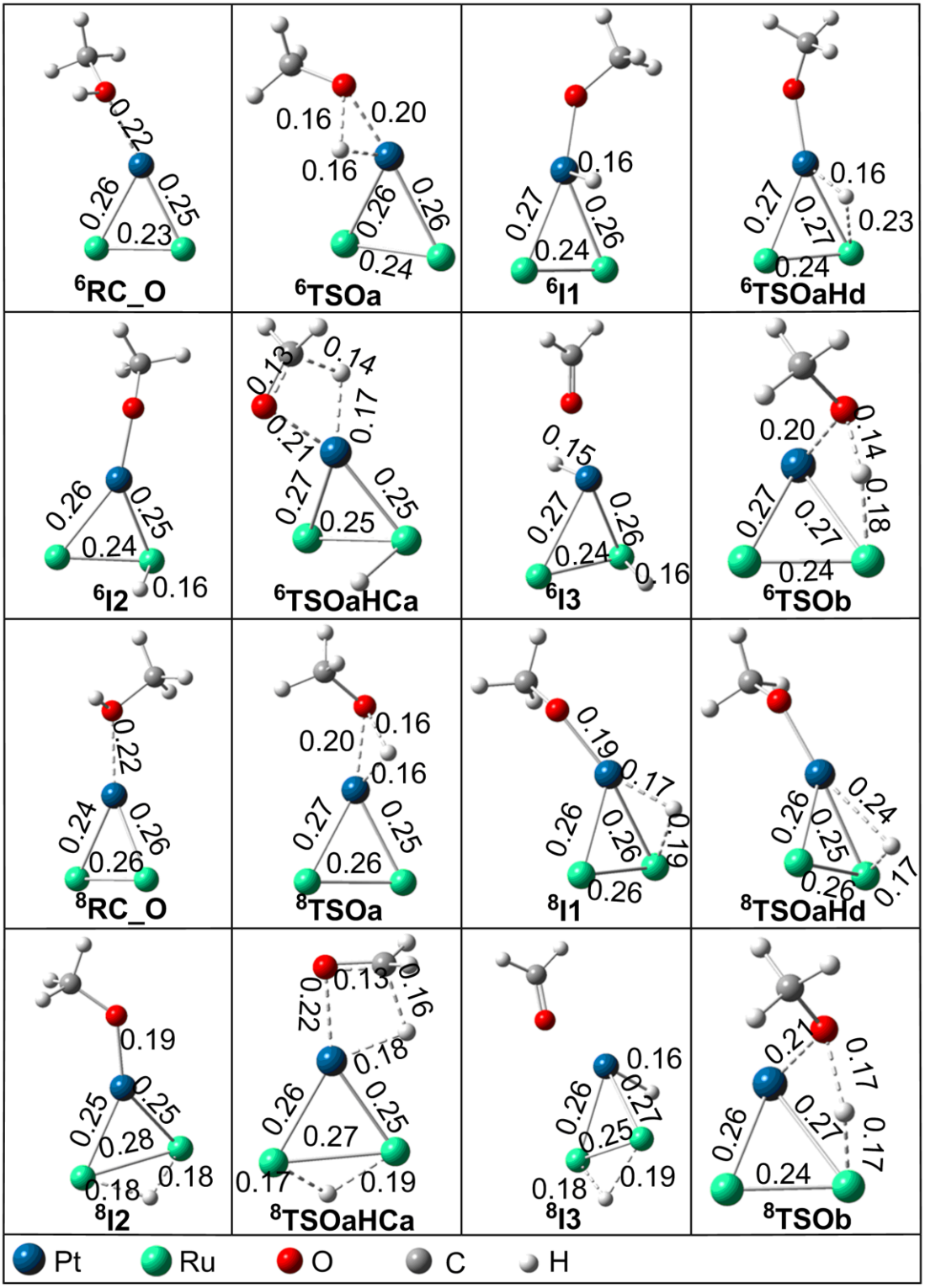

图 S4　在 B3LYP 水平下$[PtRu_2]^+$与 CH_3OH 反应的以 O—H 键活化为反应初始步骤(M1)的反应复合物、过渡态、中间体的几何构型

Fig.S4　Optimized geometries of the reactant complex, transition state, intermediate in the reaction of $[PtRu_2]^+$ with CH_3OH starting from O—H bond activation at B3LYP　level of theory

Bond length: nm. The superscripts 6 and 8 represent the spin multiplicities.

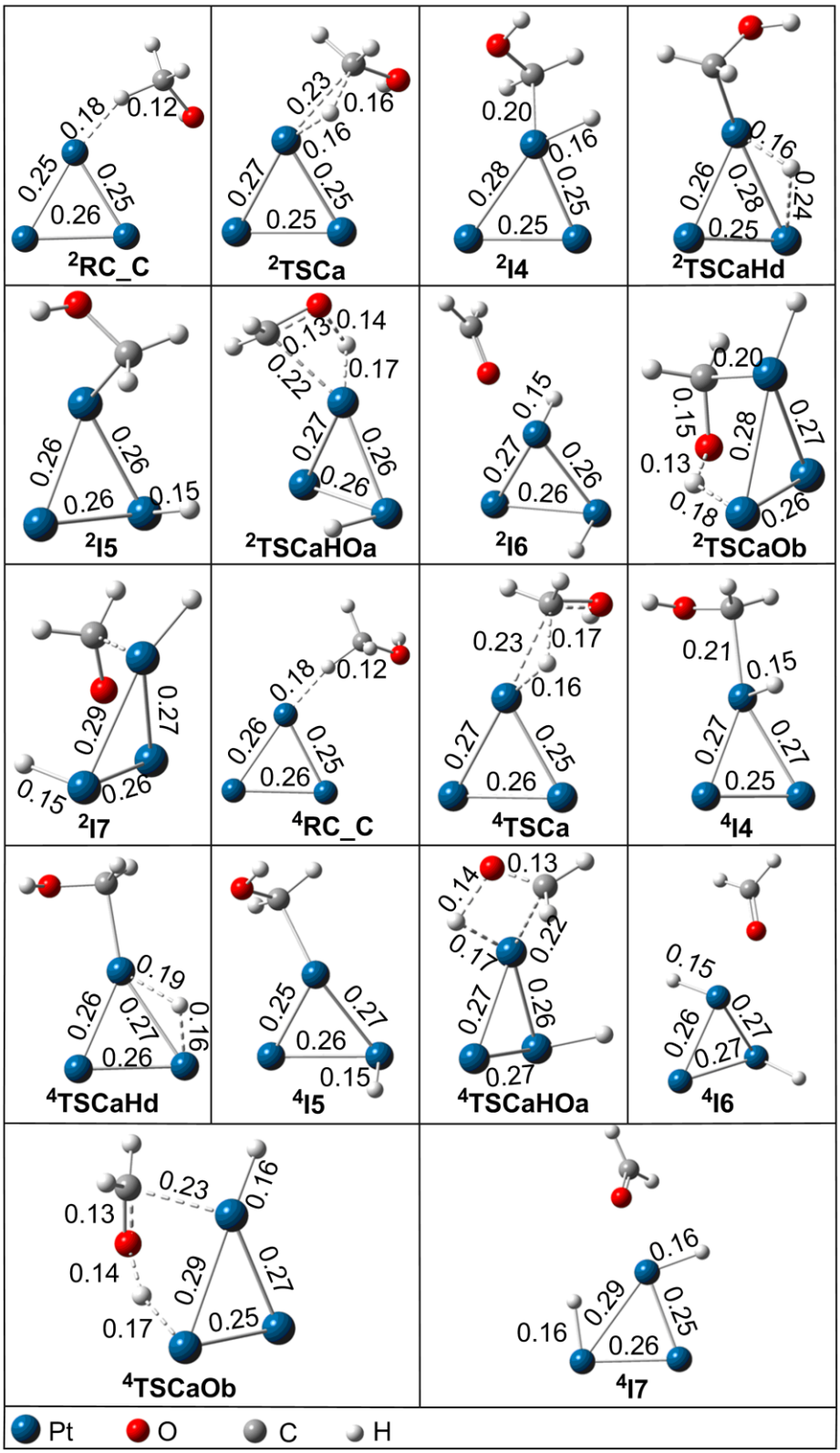

图 S5　在 B3LYP 水平下$[Pt_3]^+$与 CH_3OH 反应的以 C—H 键活化为反应初始步骤(M1)的反应复合物、过渡态、中间体的几何构型

Fig.S5　Optimized geometries of the reactant complex, transition state, intermediate in the reaction of $[Pt_3]^+$ with CH_3OH starting from C—H bond activation at B3LYP level of theory

Bond length: nm. The superscripts 2 and 4 represent the spin multiplicities.

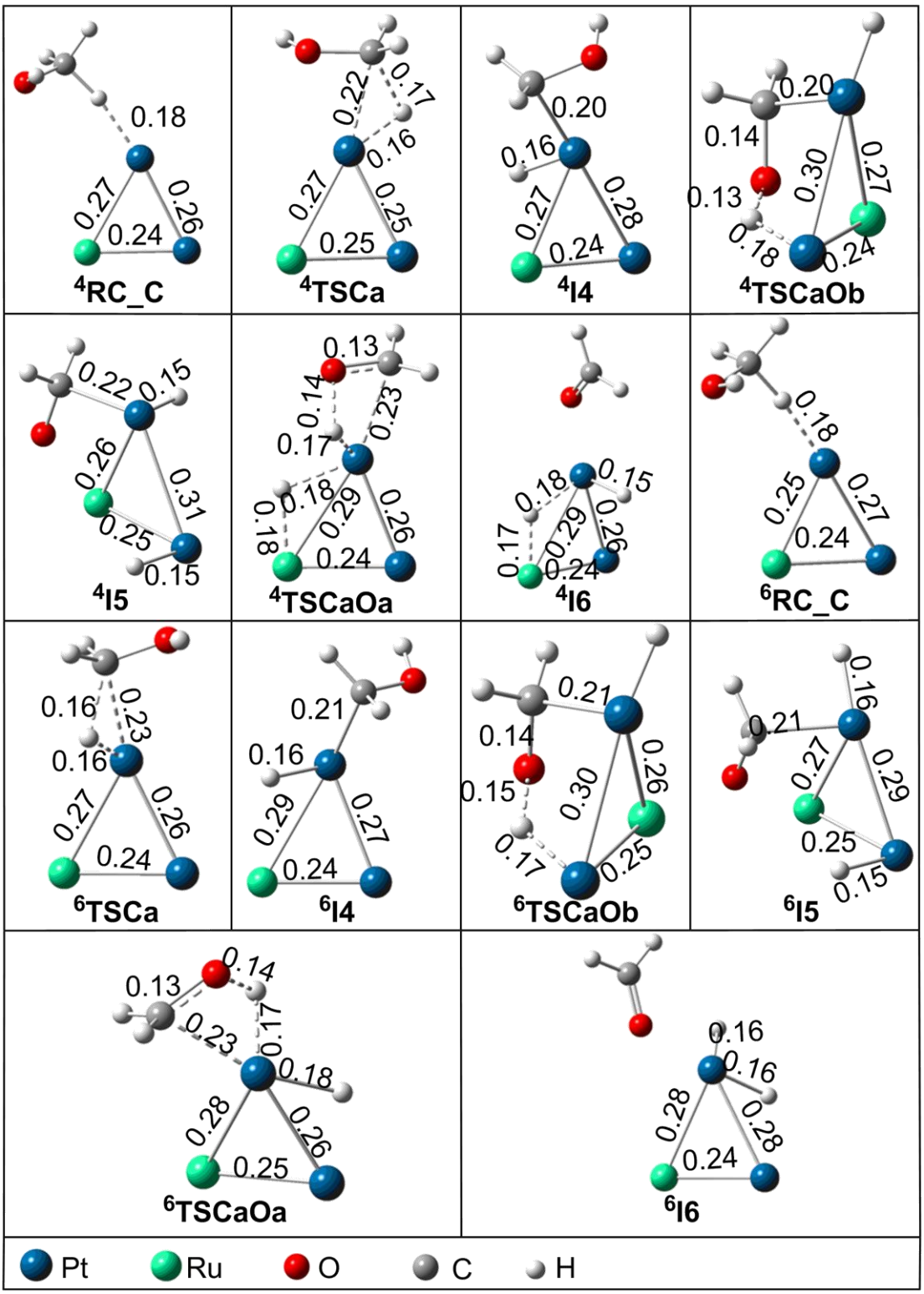

图 S6　在 B3LYP 水平下$[Pt_2Ru]^+$与 CH_3OH 反应的以 C—H 键活化为反应初始步骤(M1)的反应复合物、过渡态、中间体的几何构型

Fig.S6　Optimized geometries of the reactant complex, transition state, intermediate in the reaction of $[Pt_2Ru]^+$ with CH_3OH starting from C—H bond activation at B3LYP level of theory

Bond length: nm. The superscripts 4 and 6 represent the spin multiplicities.

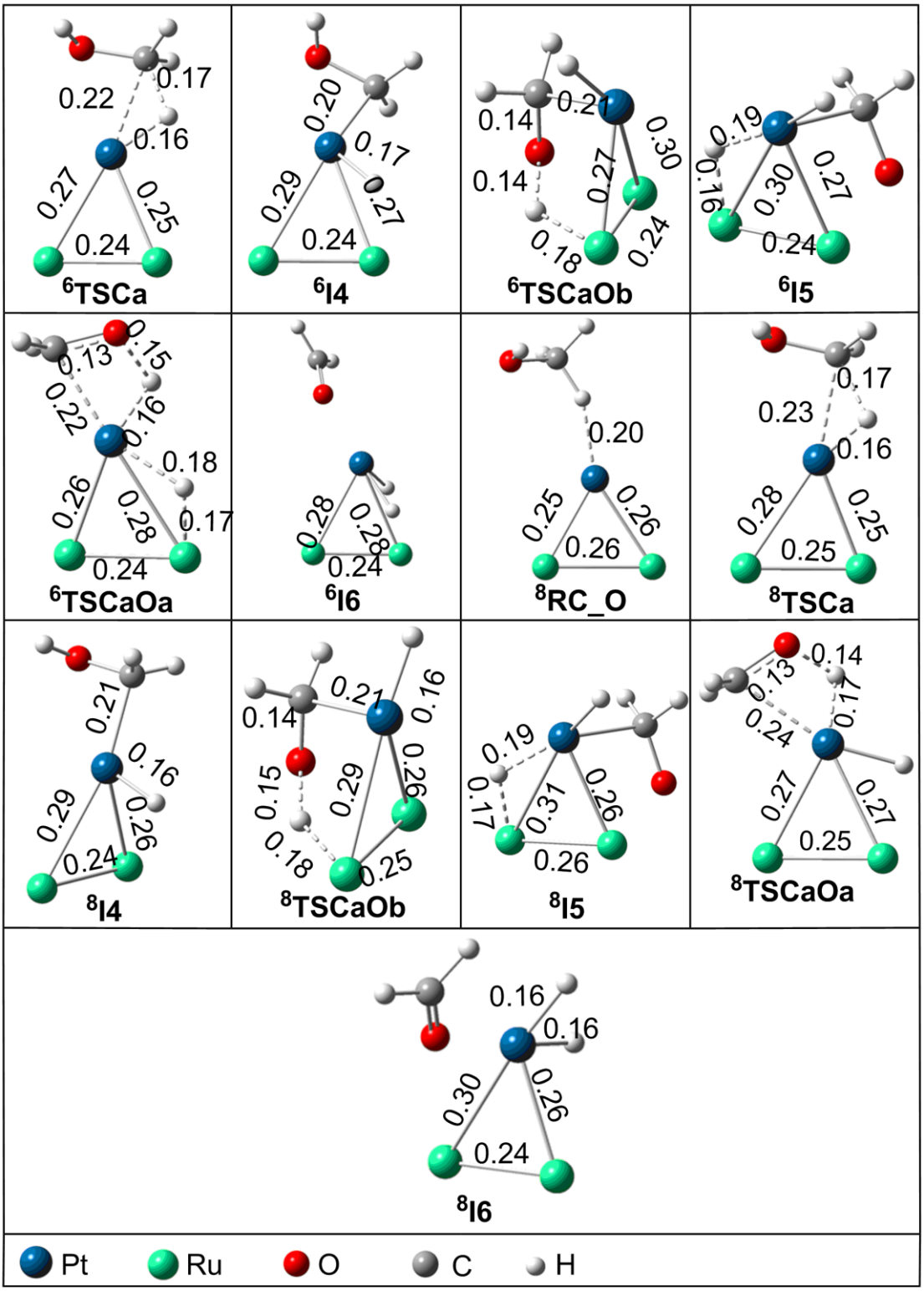

图 S4 在 B3LYP 水平下$[PtRu_2]^+$与 CH_3OH 反应的以 C—H 键活化为反应初始步骤(M1)的反应复合物、过渡态、中间体的几何构型

Fig.S4 Optimized geometries of the reactant complex, transition state, intermediate in the reaction of $[PtRu_2]^+$ with CH_3OH starting from C—H bond activation at B3LYP level of theory

Bond length: nm. The superscripts 6 and 8 represent the spin multiplicities.

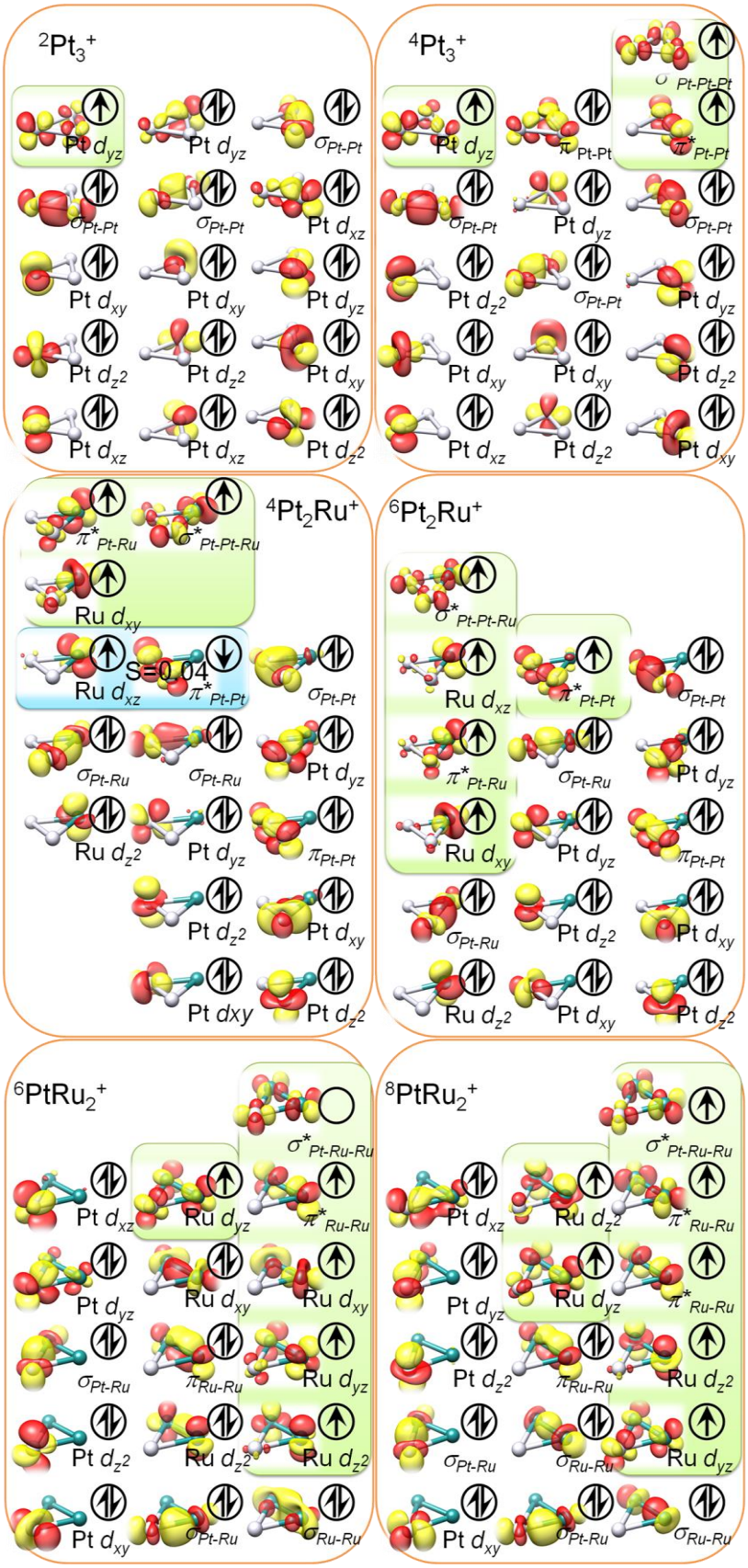

图 S8　$[Pt_3]^+$、$[Pt_2Ru]^+$、$[PtRu_{2]}]^+$的前线分子轨道图.

Fig.S8　Schematic FMO diagram of $[Pt_3]^+$, $[Pt_2Ru]^+$ and $[PtRu_{2]}]^+$.

The superscripts 2, 4, 6 and 8 represent the spin multiplicities.

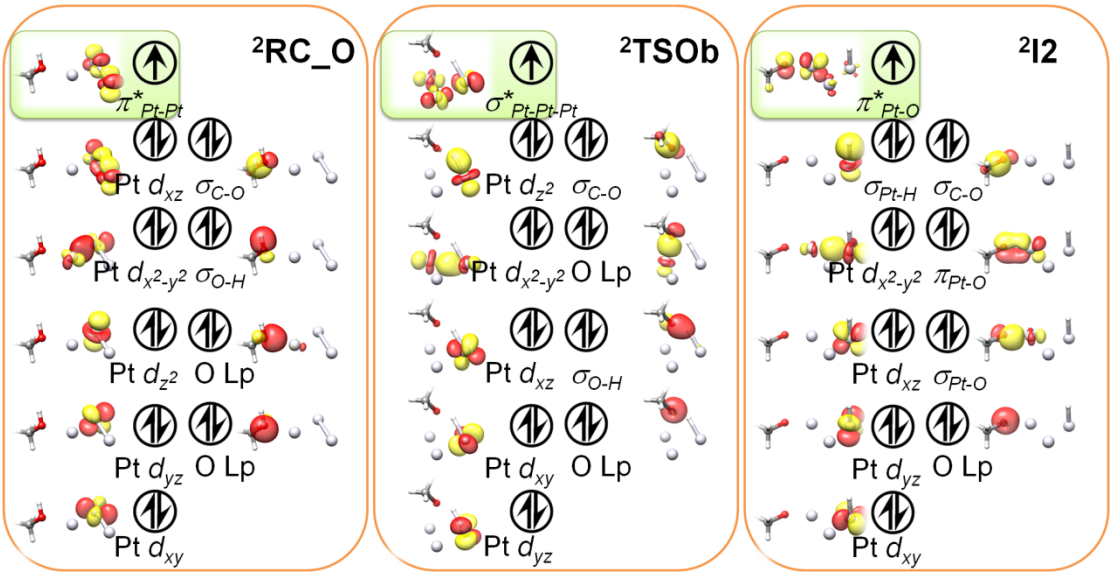

图 S9　$[Pt_3]^+$ (*S* = 1/2)活化甲醇中 O—H 键过程的电子结构图.

Fig.S9　Electronic structure diagrams of reactant complex, transition state and intermediate in the progress of O—H bond activation by $[Pt_3]^+$ (*S* = 1/2).

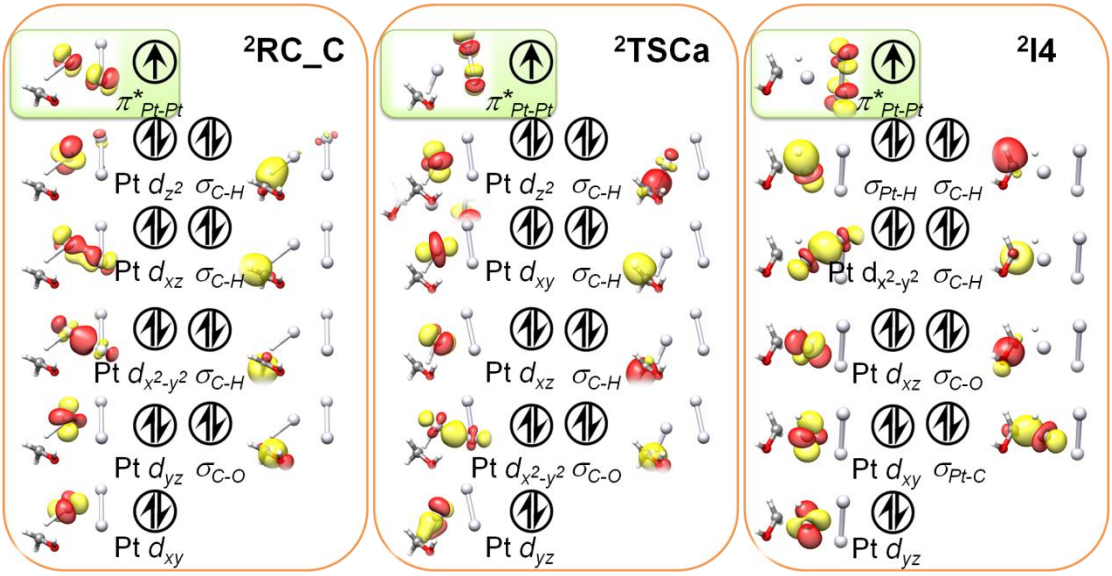

图 S10　$[Pt_3]$ (*S* = 1/2) 活化甲醇中 C—H 键过程的电子结构图

Fig.S10　Electronic structure diagrams of reactant complex, transition state and intermediate in the progress of C—H bond activation by $[Pt_3]^+$ (*S* = 1/2)

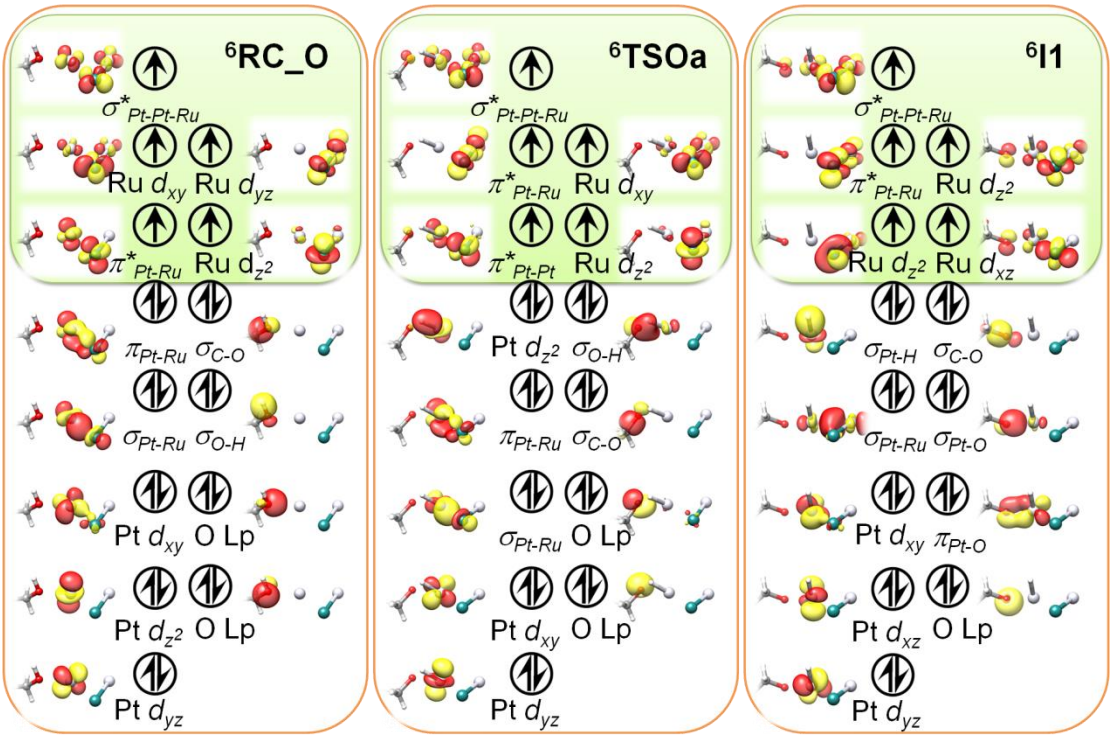

图 S11　[Pt_2Ru]$^+$ (*S* = 5/2) 活化甲醇中 O—H 键过程的电子结构图

Fig.S11　Electronic structure diagrams of reactant complex, transition state and intermediate in the progress of O—H bond activation by [Pt_2Ru]$^+$ (*S* = 5/2)

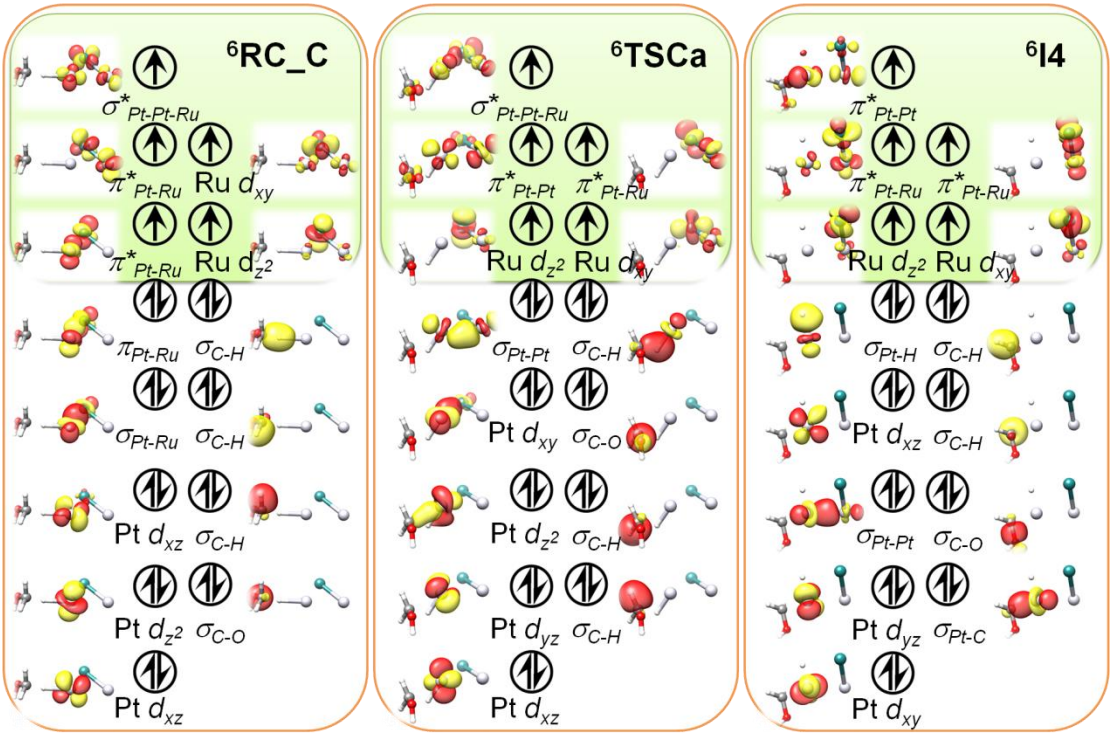

图 S12　[Pt_2Ru]$^+$ (*S* = 5/2) 活化甲醇中 C—H 键过程的电子结构图

Fig.S12　Electronic structure diagrams of reactant complex, transition state and intermediate in the progress of C—H bond activation by [Pt_2Ru]$^+$ (*S* = 5/2)

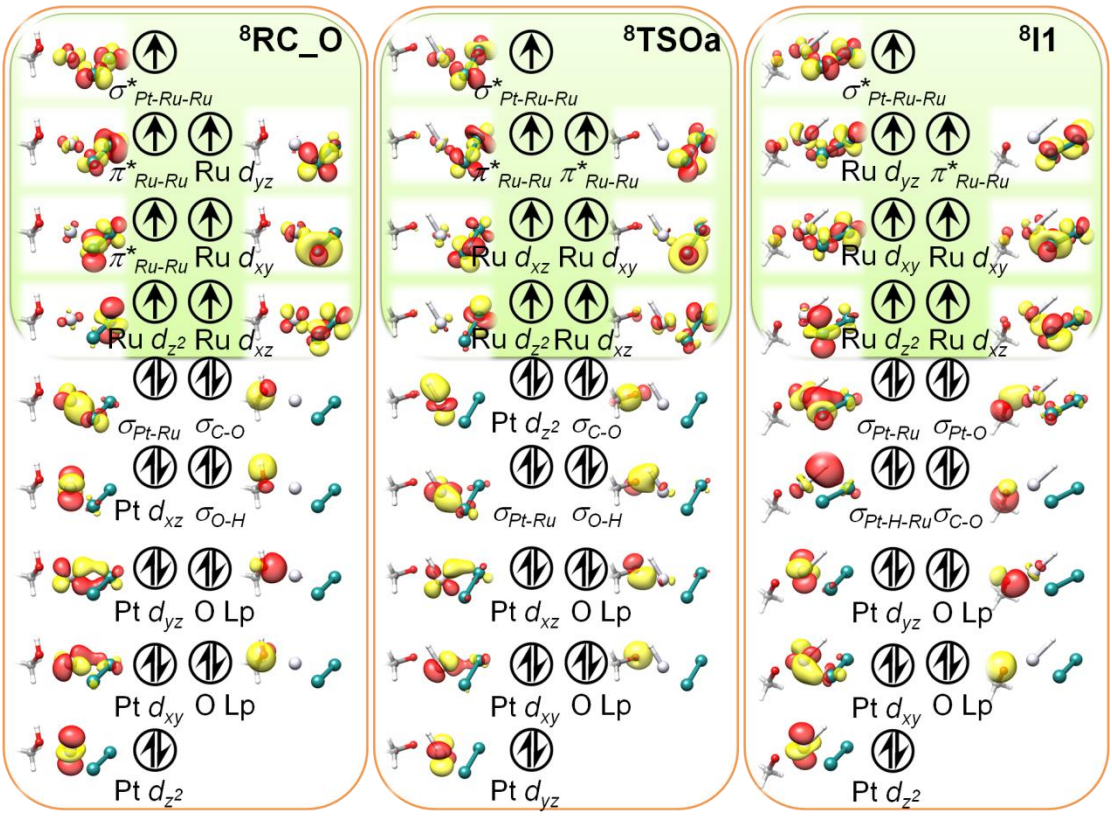

图 S13　$[PtRu_2]^+$ (S = 7/2) 活化甲醇中 O—H 键过程的电子结构图

Fig.S13　Electronic structure diagrams of reactant complex, transition state and intermediate in the progress of O—H bond activation by $[PtRu_2]^+$ (S = 7/2)

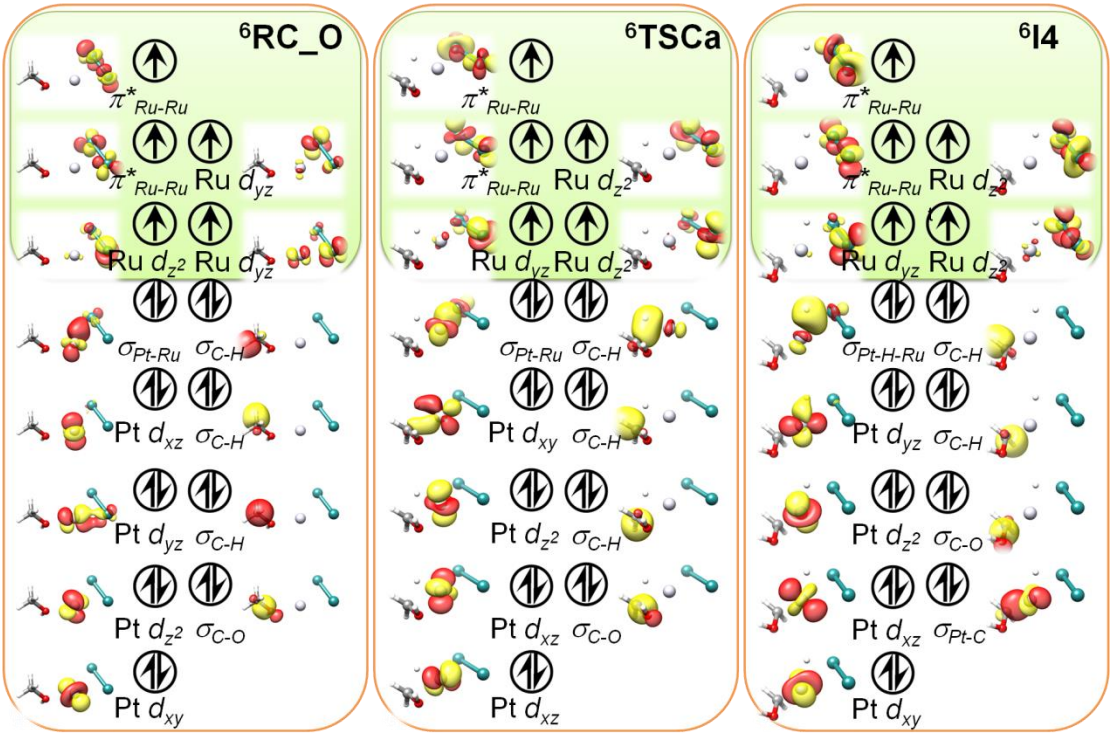

图 S14　$[PtRu_2]^+$ (S = 5/2) 活化甲醇中 C—H 键过程的电子结构图.

Fig.S14　Electronic structure diagrams of reactant complex, transition state and intermediate in the progress of C—H bond activation by $[PtRu_2]^+$ (S = 5/2)