Supporting Information

for

Sulfur monoxide complex of platinum fluoride with a positively charged ligand

Deji Leng,[a,b] Zhixin Xiong,[a,b] Jingwen Hu,[a,b] Tiejian Zhu,[a] Xiuting Chen,[a] Yu Gong[*a]

[a] Department of Radiochemistry, Shanghai Institute of Applied Physics, Chinese Academy of

Sciences, Shanghai 201800, China

[b] School of Nuclear Science and Technology, University of Chinese Academy of Sciences,

Beijing 100049, China

*E-mail: gongyu@sinap.ac.cn.
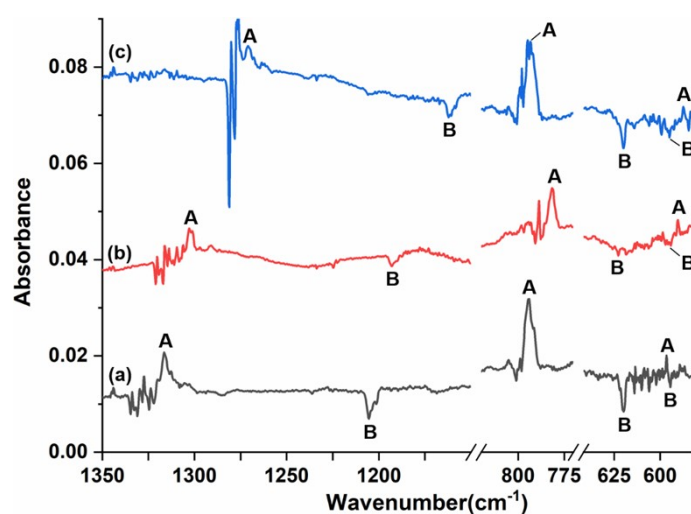
Additional Experimental and Theoretical Results

Figure S1. Infrared difference spectra in the 1350-1150, 820-770 and 640-585 cm^{-1} regions from codeposition of laser-ablated platinum atoms and isotopically labeled SOF$_2$ in solid argon at 4 K (spectra taken after 25 K annealing minus spectra taken after $\lambda > 220$ nm irradiation): (a) 0.5% SOF$_2$, (b) 0.5% ^{34}SOF$_2$, (c) 0.5% S^{18}OF$_2$. Labels A and B denote the Pt(SOF$_2$) and PtF$_2$(η^1-SO) products, respectively.
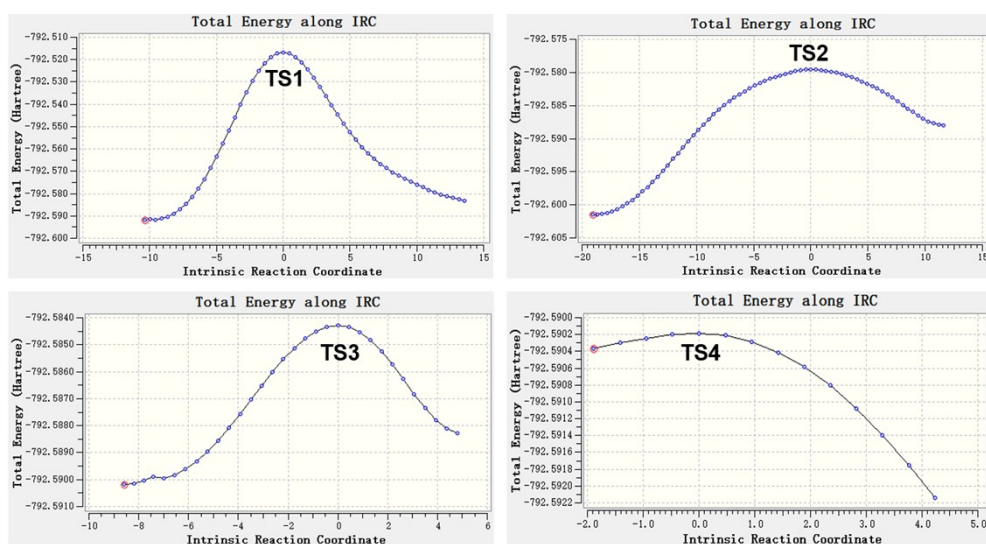

Figure S2. IRC plots of **TS1-4** associated with the structural transformation as shown in the potential energy profile.

Table S1. Experimental infrared absorptions (cm^{-1}) of Pt(SOF$_2$) and PtF$_2$(η^1-SO) in solid argon.

	mode	SOF$_2$	^{34}SOF$_2$	S^{18}OF$_2$
	S-O str.	1316.4 [a]	1302.8 [a]	1270.8 [a]
Pt(SOF$_2$)	sym.F-S-F str.	794.3 [a]	781.5 [a]	793.4 [a]
	wagging	596.6	590.6	587.5
	S-O str.	1205.4	1193.0	1162.0
PtF$_2$(η^1-SO)	antisym.F-Pt-F str.	619.8	622.1	619.6
	sym.F-Pt-F str.	594.9	594.7	594.8

[a] Determined from the infrared difference spectrum as they are partially covered by the SOF$_2$ precursor bands.

Table S2. Orbital composition of the S–O and Pt–S bonds in $PtF_2(\eta^1\text{-SO})$ from NBO calculations at the B3LYP/6-311+G(3df)/SDD level.

	bond type	% of NBO on each atom	% of each hybrid in the NBO from each atom			
			s	p	d	f
S-O	π	O (68.54)	0.00	99.25	0.74	0.01
		S (31.46)	0.00	98.05	1.86	0.09
S-O	σ	O (68.63)	25.92	72.51	1.55	0.02
		S (31.37)	16.87	80.95	2.04	0.14
Pt-S	σ	S (47.90)	6.23	91.88	1.84	0.06
		Pt (52.10)	21.51	0.21	78.28	-
S-O	π*	O (31.46)	0.00	99.25	0.74	0.01
		S (68.54)	0.00	98.05	1.86	0.09
Pt-S	σ*	S (52.10)	6.23	91.88	1.84	0.06
		Pt (47.90)	21.51	0.21	78.28	-

Table S3. NPA charges of SO and Pt in the $PtF_2(\eta^1\text{-SO})$ complex calculated at different level of theory.

functional	SO	Pt
B3LYP	0.37	0.82
M06	0.39	0.84
M06-L	0.30	0.84
PBE0	0.38	0.82
TPSSh	0.33	0.81

Table S4. Vibrational frequencies and bond lengths of free SO and the SO ligand in

PtF$_2$(η^1-SO) calculated at different level of theory.

functional	SO in PtF$_2$(η^1-SO)		free SO	
	frequency (cm^{-1})	bond length (Å)	frequency (cm^{-1})	bond length (Å)
B3LYP	1245.7	1.449	1157.3	1.488
M06	1309.3	1.438	1198.7	1.479
M06-L	1250.5	1.453	1167.5	1.487
PBE0	1286.6	1.441	1200.7	1.478
TPSSh	1224.3	1.457	1153.8	1.491

Cartesian coordinates for PtF$_2$(η^1-SO), Pt(SOF$_2$) as well as the transition states and intermediates involved in the isomerization process obtained at the B3LYP/6-311+G(3df)/SDD level of theory. All of these species possess singlet ground states.

PtF$_2$(η^1-SO)

F	0.05974800	0.85788800	1.87175700
O	-1.21955600	-2.36141200	0.00000000
F	0.05974800	0.85788800	-1.87175700
S	0.05974800	-1.68038900	0.00000000
Pt	0.09903900	0.38891700	0.00000000

Pt(SOF$_2$)

O	-1.83055800	-1.49863500	0.00000000
F	0.22970800	-1.97387700	1.15088100
F	0.22970800	-1.97387700	-1.15088100
S	-0.46296900	-1.11177300	0.00000000
Pt	0.22970800	0.83727200	0.00000000

TS1 **(−371.30 cm^{-1})**

O	2.04892700	-1.36713100	-0.44702700
F	1.98916600	0.43737700	1.09510100
F	0.76315500	1.75206600	-0.60024100
S	1.33087100	-0.13122500	-0.25971200

| Pt | -0.80072100 | -0.08549200 | 0.04202400 |

IM1

O	-1.41087700	-1.20191500	-0.24929500
F	-2.29375800	1.12967000	-0.45153600
F	2.12868600	0.84452200	0.14756700
S	-1.56792000	0.07511800	0.52532000
Pt	0.48537700	-0.11992700	-0.04711600

TS2 (−80.26 cm⁻¹)

O	2.11617800	0.87071000	-0.90142500
F	2.02451400	-1.02074200	0.66588600
F	-1.64364700	1.14689900	0.72603300
S	1.46568000	0.50170500	0.33548600
Pt	-0.56164300	-0.20677400	-0.13697000

IM2

O	2.24033700	1.14508600	-0.54553400
F	1.38664500	-1.35864800	-0.09149500
F	-1.90785200	1.10677800	0.07933600
S	1.54305500	0.37222500	0.44526000
Pt	-0.48616300	-0.16473700	-0.03398000

TS3   (−128.38 cm⁻¹)

O	-2.21540700	-1.27977400	-0.43672200
F	-0.88049100	1.72255100	-0.13520000
F	1.76653900	-1.25997100	0.06303500
S	-1.58659900	-0.25355700	0.35836300
Pt	0.45044100	0.12989600	-0.02039200

IM3

O	2.49809300	-0.76561200	-0.00053800
F	-0.46868300	1.98213200	-0.00006800
F	-0.80987100	-1.90626200	0.00026600
S	1.60691700	0.37136400	0.00041300
Pt	-0.43831300	-0.00640700	-0.00005200

TS4   (−61.87 cm⁻¹)

F	-0.64264200	1.95503100	-0.07262500
O	2.54928600	0.56778600	0.19670400
F	-0.69826500	-1.93134300	0.04050700
S	1.58168800	-0.44898200	-0.14689800
Pt	-0.43119400	0.03113100	0.01366400