Electronic Supplementary Material (ESI) for Dalton Transactions.

Vanadium, niobium and tantalum complexes with terminal sulfur radical ligands

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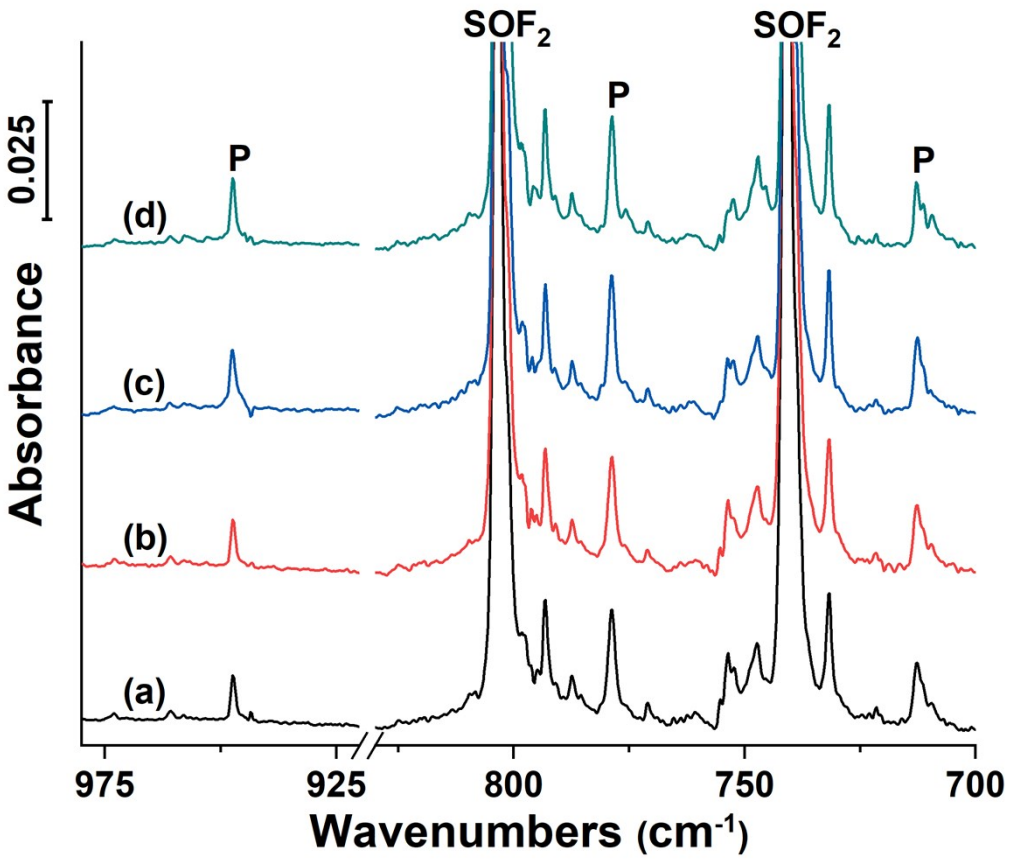

Fig. S1. Infrared spectra in the product regions from the reactions of laser-ablated vanadium atoms and 0.5% SOF_2 in neon matrixes at 4 K. (a) after codeposition for 30 min; (b) after annealing to 6 K; (c) after $\lambda > 220$ nm UV-vis irradiation for 15 min; (d) after annealing to 8 K. P denotes the $V(O)(S)F_2$ bands at 1004.2, 778.7 and 712.8 cm^{-1}.

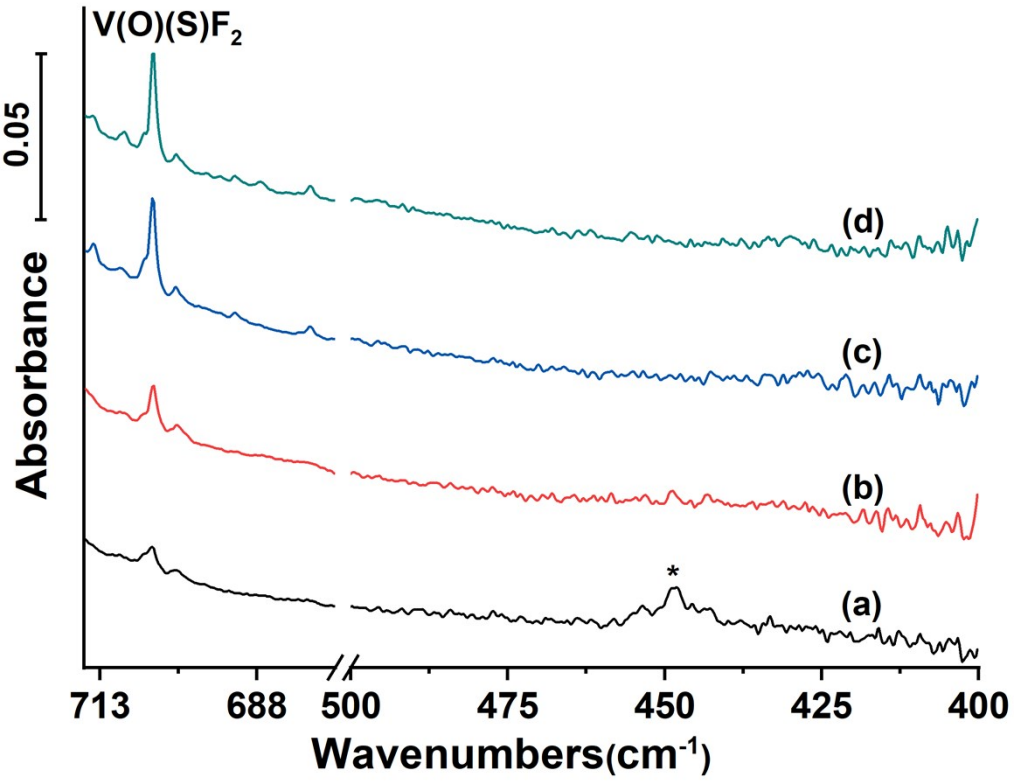

Fig. S2. Infrared spectra showing the region down to 400 cm^{-1} from the reactions of laser-ablated vanadium atoms and 0.5% SOF_2 in argon matrixes at 4 K. (a) after codeposition for 60 min; (b) after annealing to 25 K; (c) after $\lambda > 220$ nm UV-vis irradiation for 20 min; (d) after annealing to 30 K. The asterisk denotes a metal independent band.

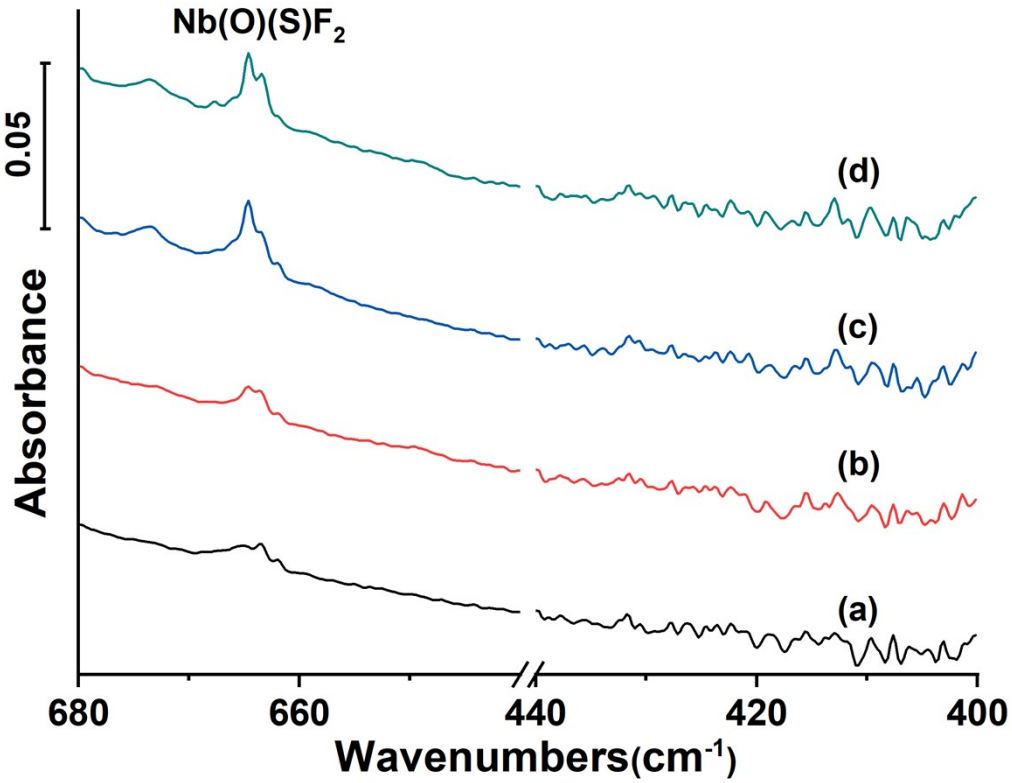

Fig. S3. Infrared spectra showing the region down to 400 cm^{-1} from the reactions of laser-ablated niobium atoms and 0.5% SOF_2 in argon matrixes at 4 K. (a) after codeposition for 60 min; (b) after annealing to 25 K; (c) after $\lambda > 220$ nm UV-vis irradiation for 20 min; (d) after annealing to 30 K.

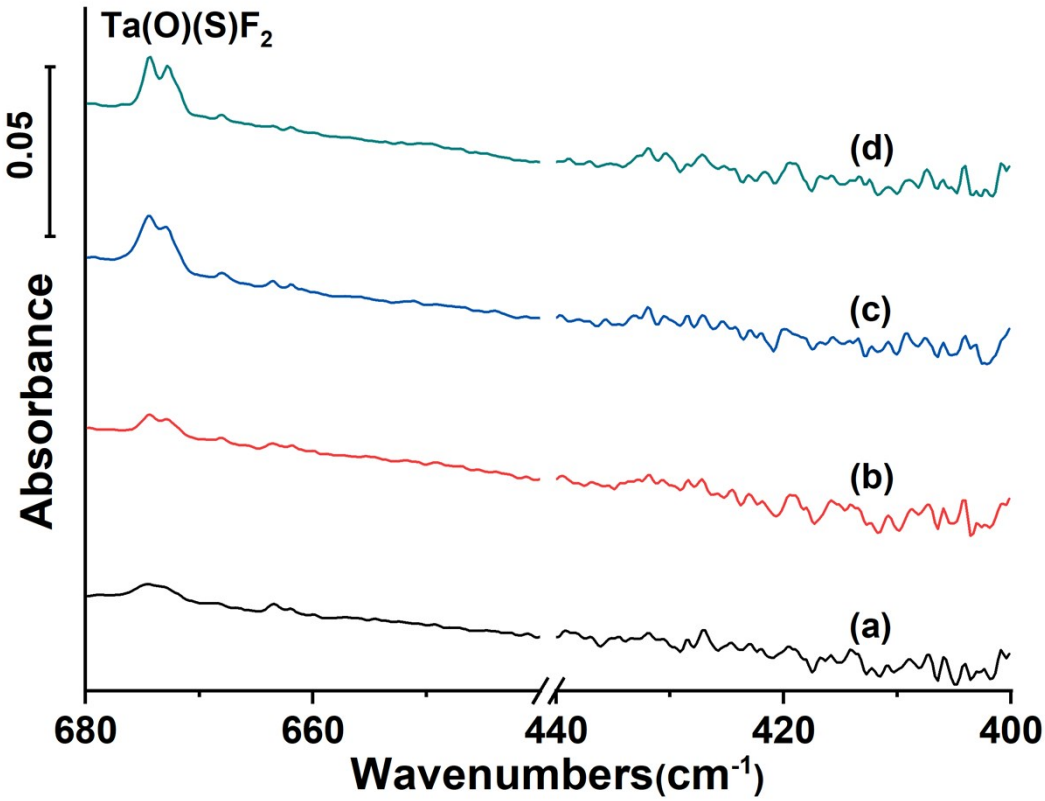

Fig. S4. Infrared spectra showing the region down to 400 cm^{-1} from the reactions of laser-ablated tantalum atoms and 0.5% SOF_2 in argon matrixes at 4 K. (a) after codeposition for 60 min; (b) after annealing to 25 K; (c) after $\lambda > 220$ nm UV-vis irradiation for 20 min; (d) after annealing to 30 K.

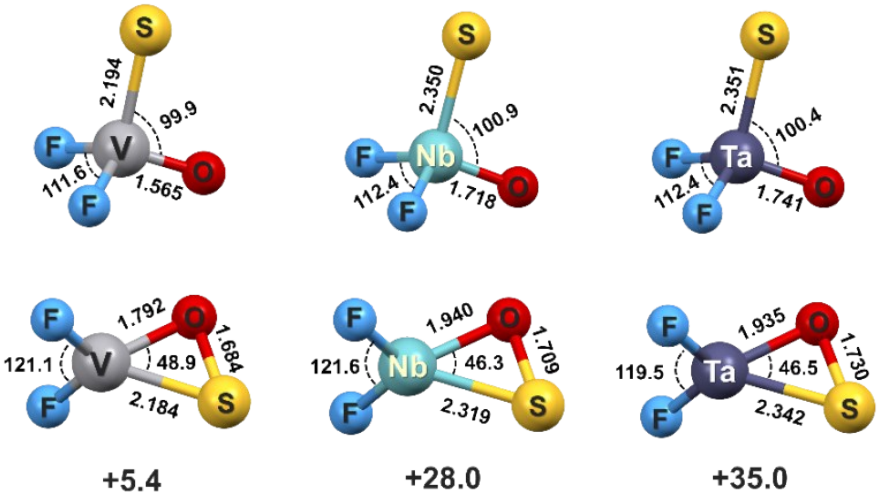

Fig. S5. Optimized structures of $M(O)(S)F_2$ and $MF_2(\eta^2\text{-}SO)$ (M = V, Nb and Ta) (bond lengths in angstroms and bond angles in degrees) with C_s symmetry and $^2A'$ ground state at the B3LYP/6-311+G(3df)/SDD level of theory. The energies (kcal/mol) are relative to the most stable $M(O)(S)F_2$ isomers.

Table S1. Experimental vibrational frequencies (cm^{-1}) of the $M(O)(S)F_2$ (M = V, Nb and Ta) complexes in argon matrixes.

	mode	SOF_2	$S^{18}OF_2$	$^{34}SOF_2$
$V(O)(S)F_2$	V-O str.	999.4	959.3	
	antisym. F-V-F str.	770.1	770.0	
	sym. F-V-F str.	704.0	702.5	
$Nb(O)(S)F_2$	Nb-O str.	961.4	914.5	961.4
	antisym. F-Nb-F str.	689.1	689.0	689.1
	sym. F-Nb-F str.	664.6	664.5	664.6
$Ta(O)(S)F_2$	Ta-O str.	955.2	905.7	
	antisym. F-Ta-F str.	674.4	674.3	
	sym. F-Ta-F str.	672.8	672.8	

Table S2. Calculated vibrational frequencies (cm^{-1}) and intensities (km/mol, in parenthesis) of $M(O)(S)F_2$ (M = V, Nb and Ta) with different functionals and the 6-311+G(3df)/SDD basis sets.

mode	B3LYP	M06	BP86
$V(O)(S)F_2$			
V–O str.	1079.4(133)	1102.9(153)	1015.8(101)
antisym. F–V–F str.	782.8(174)	794.3(185)	762.2(148)
sym. F–V–F str.	723.6(167)	735.0(178)	702.4(135)
V–S str.	455.6(32)	474.0(32)	444.1(19)
$Nb(O)(S)F_2$			
Nb–O str.	979.6(114)	1000.8(134)	923.3(81)
antisym. F–Nb–F str.	696.9(164)	705.6(178)	683.2(145)
sym. F–Nb–F str.	669.8(140)	675.1(147)	654.7(123)
Nb–S str.	405.2(35)	413.7(40)	400.0(21)
$Ta(O)(S)F_2$			
Ta–O str.	946.8(81)	965.8(97)	891.3(56)
antisym. F–Ta–F str.	671.3(129)	678.4(141)	658.5(116)
sym. F–Ta–F str.	664.9(112)	670.6(116)	650.6(101)
Ta-S str.	381.9(22)	390.4(26)	381.0(12)

Table S3. Orbital composition of the M–S bond in $M(O)(S)F_2$ (M = V, Nb and Ta) from NBO calculations at the B3LYP/6-311+G(d)/SDD level.

	bond type		% of NBO on each atom	% of each hybrid in the NBO from each atom		
				s	p	d
$V(O)(S)F_2$	σ(V-S)	α	V (27.83)	33.45	1.33	65.14
			S (72.17)	9.99	89.76	0.25
		β	V (31.50)	33.64	1.39	64.88
			S (68.50)	9.92	89.77	0.31
	$n_1(S)$	α	S	0.03	99.92	0.05
	$n_2(S)$	α	S	0.00	99.90	0.10
		β	S	0.00	99.87	0.13
$Nb(O)(S)F_2$	σ(Nb-S)	α	Nb (25.02)	33.45	1.10	65.45
			S (74.98)	11.55	88.17	0.28
		β	Nb (27.37)	33.88	1.15	64.97
			S (72.63)	12.04	87.62	0.34
	$n_1(S)$	α	S	0.02	99.91	0.07
	$n_2(S)$	α	S	0.00	99.89	0.11
		β	S	0.00	99.88	0.12
$Ta(O)(S)F_2$	σ(Ta-S)	α	Ta (23.82)	33.91	1.17	64.92
			S (76.18)	12.39	87.34	0.27
		β	Ta (25.88)	34.49	1.19	64.32
			S (74.12)	13.18	86.49	0.33
	$n_1(S)$	α	S	0.01	99.90	0.09
	$n_2(S)$	α	S	0.00	99.87	0.13
		β	S	0.00	99.86	0.14

Table S4. Calculated vibrational frequencies (cm^{-1}) and intensities (km/mol) of $MF_2(\eta^2\text{-SO})$ (M = V, Nb and Ta).

	frequency (intensity) [a]
$VF_2(\eta^2\text{-SO})$	822.6 (131), 773.7 (227), 717.7 (143), 542.0 (15), 423.8 (13)
$NbF_2(\eta^2\text{-SO})$	770.7 (88), 698.6 (189), 666.0 (138), 547.4 (5), 398.1 (16)
$TaF_2(\eta^2\text{-SO})$	752.0 (64), 678.2 (140), 667.7 (110), 525.3 (11), 369.9 (16)

[a] only frequencies above 350 cm^{-1} are listed.

Cartesian coordinates of all the optimized geometries (doublet states) obtained at the B3LYP/6-311+G(3df)/SDD level of theory.

$VF_2(\eta^2$-SO)

Atom	X	Y	Z
V	-0.032542	0.467204	0.000000
F	-0.257744	1.293902	1.518074
F	-0.257744	1.293902	-1.518074
S	-0.257744	-1.705190	0.000000
O	1.188972	-0.844112	0.000000

TS (V)

Atom	X	Y	Z
V	0.011279	0.426031	0.000000
F	-0.323860	1.259764	1.490646
F	-0.323860	1.259764	-1.490646
S	-0.323860	-1.772999	0.000000
O	1.343981	-0.513312	0.000000

$V(O)(S)F_2$

Atom	X	Y	Z
V	-0.334259	-0.031877	0.000000
F	-0.833212	-0.871740	1.438723
F	-0.833212	-0.871740	-1.438723
S	1.834467	0.300770	0.000000
O	-0.833212	1.451522	0.000000

$NbF_2(\eta^2\text{-SO})$

Atom	X	Y	Z
F	-0.247930	1.289059	1.648795
F	-0.247930	1.289059	-1.648795
S	-0.247930	-1.917428	0.000000
O	1.236961	-1.072387	0.000000
Nb	-0.035757	0.391583	0.000000

TS (Nb)

Atom	X	Y	Z
Nb	-0.449075	-0.269164	-0.001287
F	-1.035278	-1.022367	1.631428
F	-1.012318	-1.026896	-1.640125
S	1.682954	0.781899	0.011893
O	-0.185724	1.513462	-0.001910

$Nb(O)(S)F_2$

Atom	X	Y	Z
F	-0.839484	-0.916703	1.572557
F	-0.839484	-0.916703	-1.572557
S	2.054824	0.315922	0.000000
O	-0.839484	1.589739	0.000000
Nb	-0.269527	-0.031025	0.000000

$TaF_2(\eta^2\text{-SO})$

Atom	X	Y	Z
F	-0.243889	1.207357	1.631700
F	-0.243889	1.207357	-1.631700
S	-0.243889	-2.050733	0.000000
O	1.249569	-1.177235	0.000000

Ta	-0.023347	0.280783	0.000000

TS (Ta)

Atom	**X**	**Y**	**Z**
Ta	-0.457410	-0.271580	0.000000
F	-1.000352	-1.064140	1.630343
F	-1.000352	-1.064140	-1.630343
S	1.655370	0.841689	0.000000
O	-0.196684	1.535107	0.000000

Ta(O)(S)F_2

Atom	**X**	**Y**	**Z**
F	-0.765002	-0.913453	1.575766
F	-0.765002	-0.913453	-1.575766
S	2.129493	0.333170	0.000000
O	-0.765002	1.619956	0.000000
Ta	-0.194272	-0.0253	