Supporting Information

Chalcogen atom abstraction from NCE^- (E = O, S, Se) and *i*-Pr_2S by the excited state of a luminescent tricyano osmium(VI) nitride

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Table of Contents

Experimental and Instrumentation

Materials: $(PPh_4)[Os^{VI}(N)(L)(CN)_3]$ (**OsN**) was synthesized according to our recent literature method (HL = 2-(2-hydroxy-5-nitrophenyl)-benzoxazole). Iodosobenzene (PhIO) was synthesized from hydrolysis of iodosylbenzene diacetate. $[^{n}Bu_4N]PF_6$ (Aldrich) for electrochemistry was recrystallized three times from boiling ethanol and dried under vacuum at 120 °C for 24 h. Acetonitrile (Aldrich) for electrochemistry was distilled over calcium hydride. HPLC grade CH_2Cl_2 obtained from RCI Labscan with <0.01% water was used for photochemical experiments. All other chemicals were of reagent grade and used without further purification. All manipulations were performed without precaution to exclude air or moisture unless otherwise stated.

Physical measurements: IR spectra were obtained as KBr discs using a Nicolet 360 FTIR spectrophotometer. UV/vis spectra were recorded using a Perkin–Elmer Lamda 19 spectrophotometer in 1 cm quartz cuvettes. Elemental analysis was performed using an Elementar Vario EL Analyzer. Electrospray ionization mass spectrometry (ESI/MS) was performed using a PE-SCIEX API 365 triple quadruple mass spectrometer. Cyclic voltammogram (CV) was performed using a PAR model 273 potentiostat using a glassy carbon working electrode, a saturated calomel electrode (SCE) reference electrode, and a Pt-wire counter electrode with ferrocene (Cp_2Fe) as the internal standard. ^1H NMR spectra were recorded on a Bruker AV400 (400 MHz) FT-NMR spectrometer. Chemical shifts (δ, ppm) are reported relative to tetramethylsilane (Me_4Si).

X-ray crystallography: Measurements were collected on an Oxford CCD diffractometer using graphite-monochromated MoK_a radiation ($\lambda = 0.71073$ Å) for **OsNO**, **OsNS** and **OsNSe**. Details of the intensity data collection and crystal data are given in Supplementary Table S1. Absorption corrections were done by the multi-scan method. The structures were resolved by the heavy-atom Patterson method or direct methods and refined by full-matrix least-squares using SHELX-97 and expanded using Fourier techniques. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were generated by the program SHELXL-97.[1] The positions of hydrogen atoms were calculated on the basis of riding mode with thermal parameters equal to 1.2 times that of the associated C atoms and participated in the calculation of final R indices. All calculations were performed using the teXsan crystallographic software. CCDC 2267408-2267410 for **OsNO**, **OsNS**, and **OsNSe** respectively.

Computational methods: Density functional theory (DFT) calculations were performed with the Gaussian 16 quantum chemistry software package.[2] All molecular geometries were optimized at the B3LYP-D3(BJ)/def2-SVPD level in dichloromethane as solvent.[3] The solvent effects were taken account by polarization continuum model (PCM).[4] All optimized geometries were verified by vibrational frequency computations as minima (no imaginary frequency) or transition state (single imaginary frequency) at the same level of theory.[5] The transition states (TSs) were also confirmed by viewing normal mode vibrational vector and by intrinsic reaction coordinate calculation.

Table S1. Crystal data and structure refinement details for compounds **OsNE** (E = O, S, Se).

	OsNO	**OsNS**	**OsNSe**
Empirical formula	$C_{40}H_{27}N_6O_5OsP$	$C_{40}H_{27}N_6O_4OsPS$	$C_{40}H_{27}N_6O_4OsPSe$
Formula weight	892.84	908.90	955.80
Temperature [K]	150.00(10)	100.00(10)	293(2)
Crystal system	triclinic	monoclinic	monoclinic
Space group (number)	$P\bar{1}$ (2)	$P2_1/c$ (14)	$P2_1/c$ (14)
a [Å]	10.34220(10)	14.4747(11)	17.352(4)
b [Å]	10.6164(2)	22.6180(11)	15.775(3)
c [Å]	17.8604(3)	12.9846(8)	13.259(3)
α [°]	80.2750(10)	90	90
β [°]	78.3850(10)	103.070(7)	92.82(3)
γ [°]	73.6360(10)	90	90
Volume [Å^3]	1829.87(5)	4140.9(5)	3625.0(13)
Z	2	4	4
ρ_{calc} [gcm^{-3}]	1.620	1.458	1.751
μ [mm^{-1}]	7.438	3.213	4.617
F(000)	880	1792	1864
2θ range [°]	8.74 to 148.44 (0.80 Å)	4.21 to 59.23 (0.72 Å)	2.35 to 53.85 (0.78 Å)
Index ranges	$-12 \le h \le 12$ $-13 \le k \le 13$ $-21 \le l \le 11$	$-19 \le h \le 15$ $-29 \le k \le 31$ $-12 \le l \le 18$	$-22 \le h \le 21$ $-19 \le k \le 19$ $-16 \le l \le 16$
Reflections collected	19840	19595	81985
Independent reflections	7180 R_{int} = 0.0441 R_{sigma} = 0.0440	9378 R_{int} = 0.0677 R_{sigma} = 0.1300	7692 R_{int} = 0.0774 R_{sigma} = 0.0376
Completeness to θ = 67.679°	99.6 %	96.8 %	100.0 %
Data / Restraints / Parameters	7180/3/478	9378/6/466	7692/0/478
Goodness-of-fit on F^2	1.054	0.998	1.048
Final R indexes [$I \geq 2\sigma(I)$]	R_1 = 0.0396 wR_2 = 0.0977	R_1 = 0.0554 wR_2 = 0.0991	R_1 = 0.0263 wR_2 = 0.0485
Final R indexes [all data]	R_1 = 0.0451 wR_2 = 0.1000	R_1 = 0.0902 wR_2 = 0.1151	R_1 = 0.0418 wR_2 = 0.0527

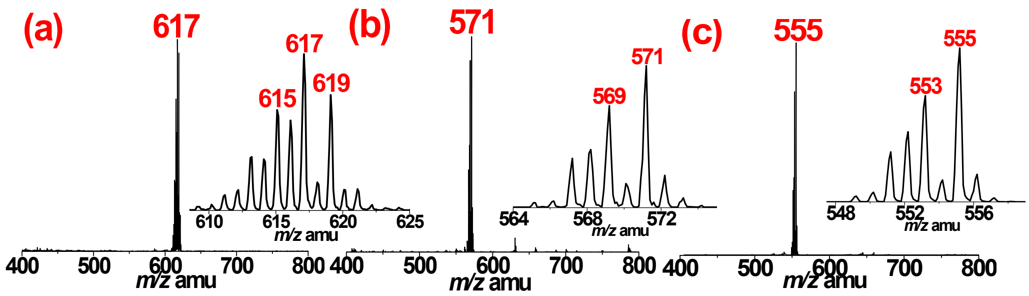

Figure S1. ESI/MS of **OsNSe**(a), **OsNS**(b) and **OsNO**(c) in MeOH (-ve mode) (Insets show the expanded isotopic distribution patterns of *m/z* 617, 571, 555).

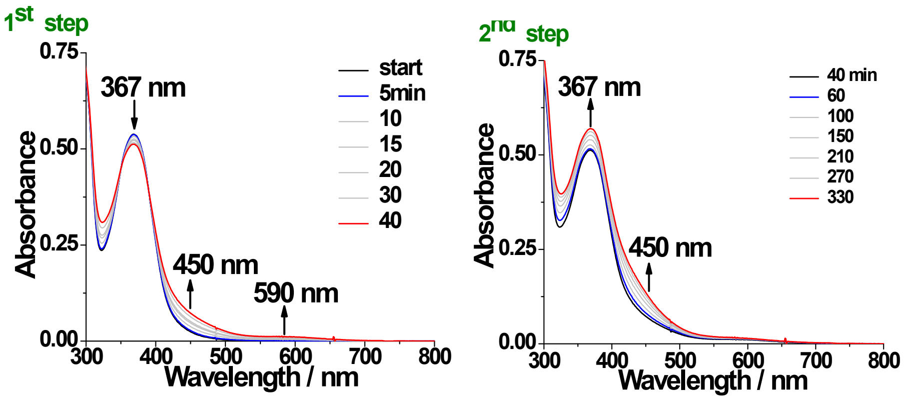

Figure S2. UV/vis spectra changes of **OsN** (3.5×10^{-5} M) with 10 equiv. of PPh_4NCS in $C_2H_4Cl_2$ by blue LED (λ > 460 nm).

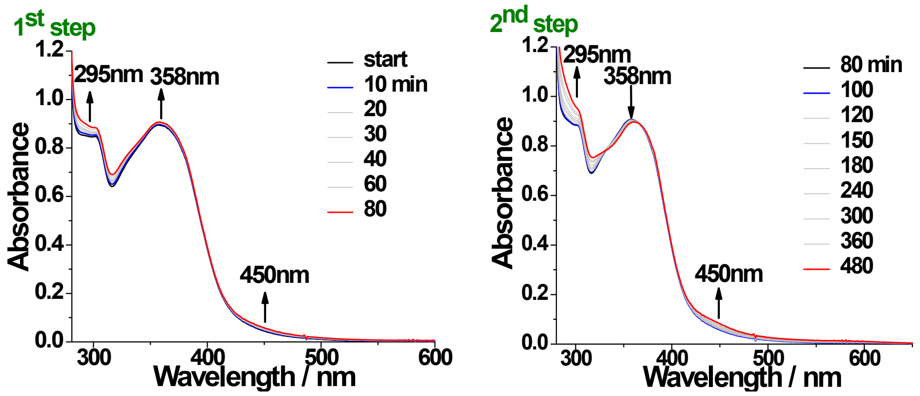

Figure S3. UV/vis spectra changes of **OsN** (3.5×10^{-5} M) with 10 equiv. of PPh_4NCSe in $C_2H_4Cl_2$ by blue LED (λ > 460 nm).

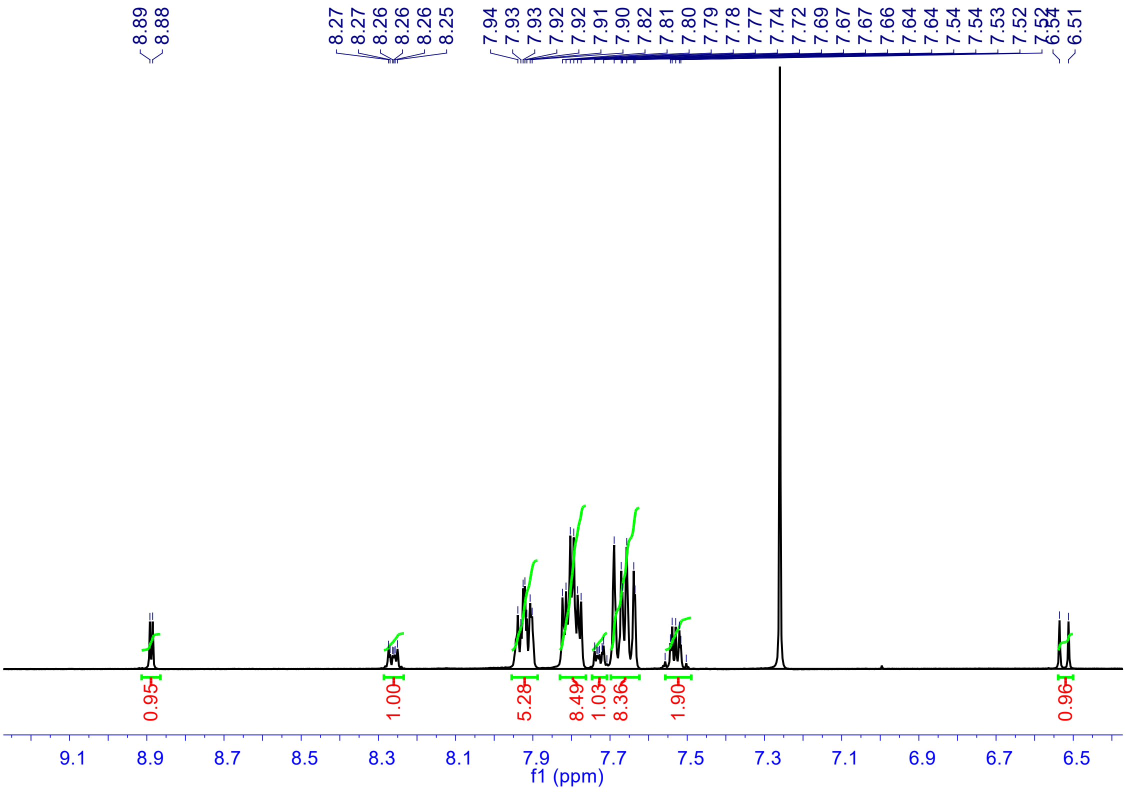
Figure S4. ^{1}H NMR spectrum of **OsNSe** in $CDCl_3$.

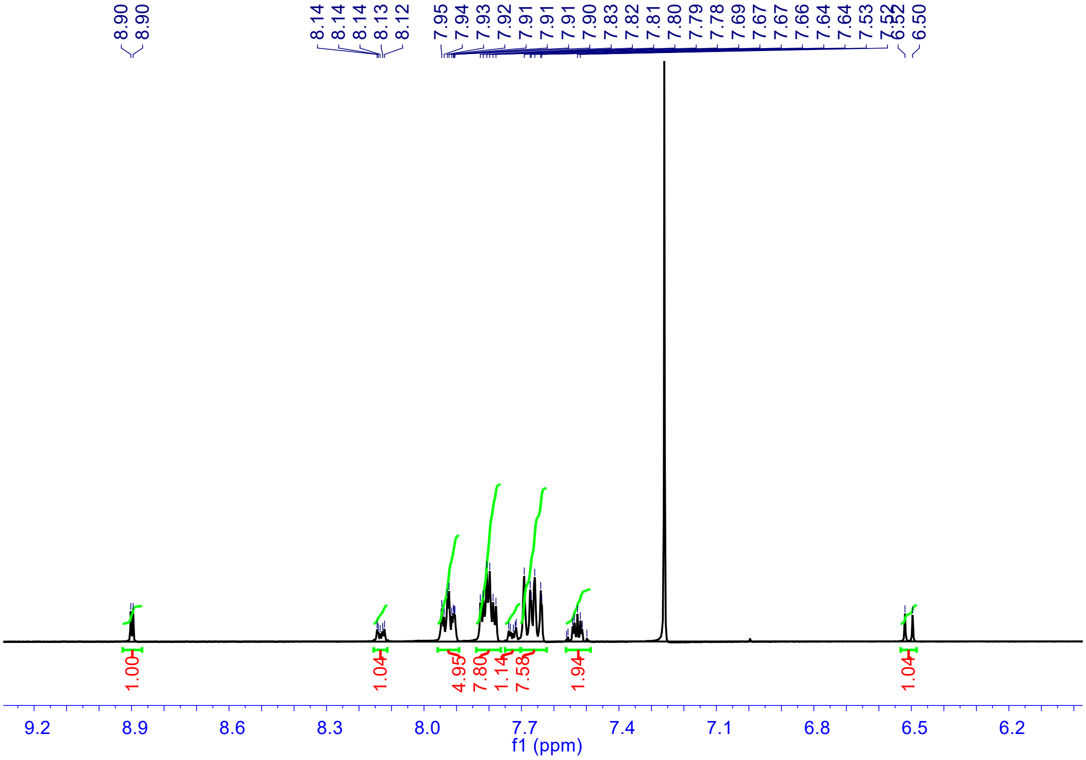
Figure S5. ^{1}H NMR spectrum of **OsNS** in $CDCl_3$.

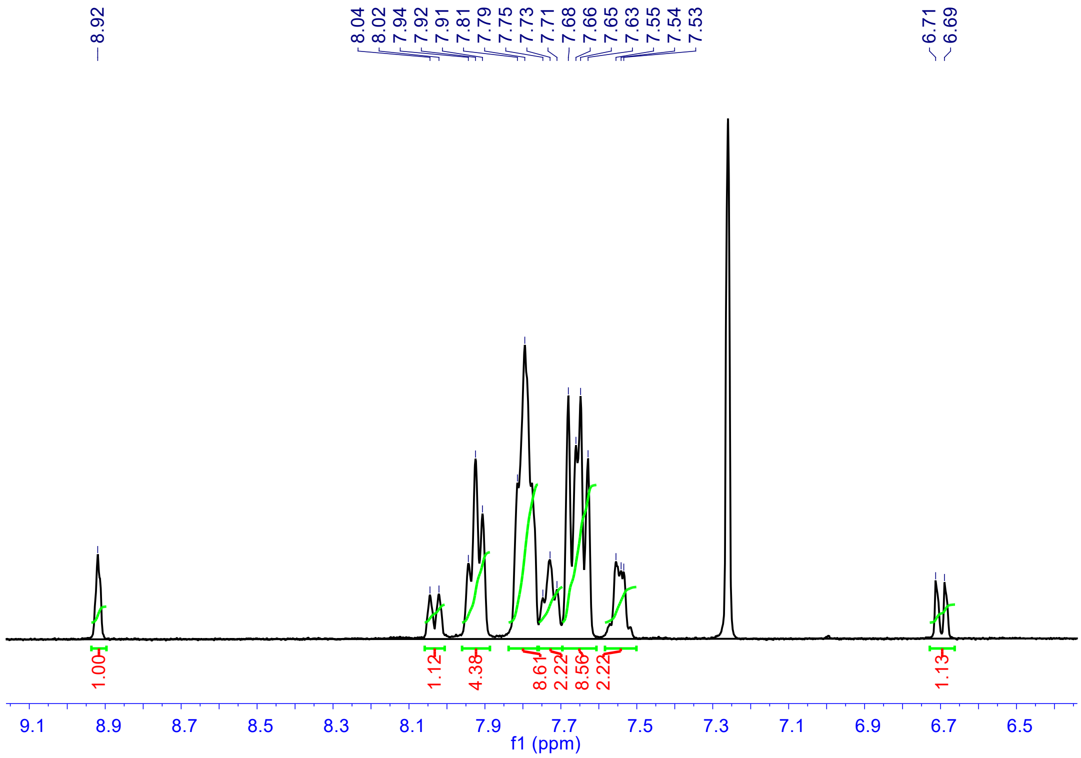

Figure S6. ^{1}H NMR spectrum of **OsNO** in $CDCl_3$.

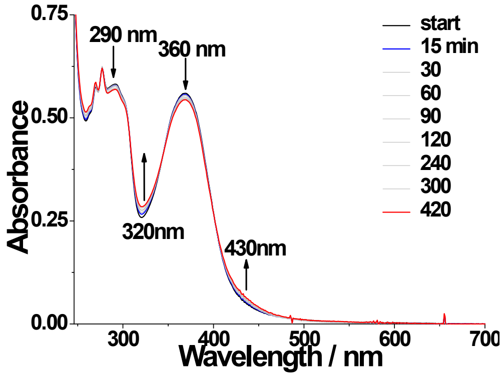

Figure S7. UV/vis spectra changes of **OsN** (3.5×10^{-5} M) with 1000 equiv. of *i*-Pr_2S in $C_2H_4Cl_2$ by blue LED (λ > 460 nm).

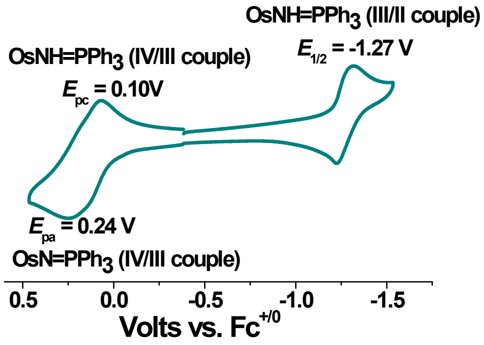

Figure S8. CV of **Os^{III}NH=PPh$_3$** in CH_3CN containing 0.1 M [^{n}Bu$_4$N](PF$_6$) with scan rate 100 mV/s.

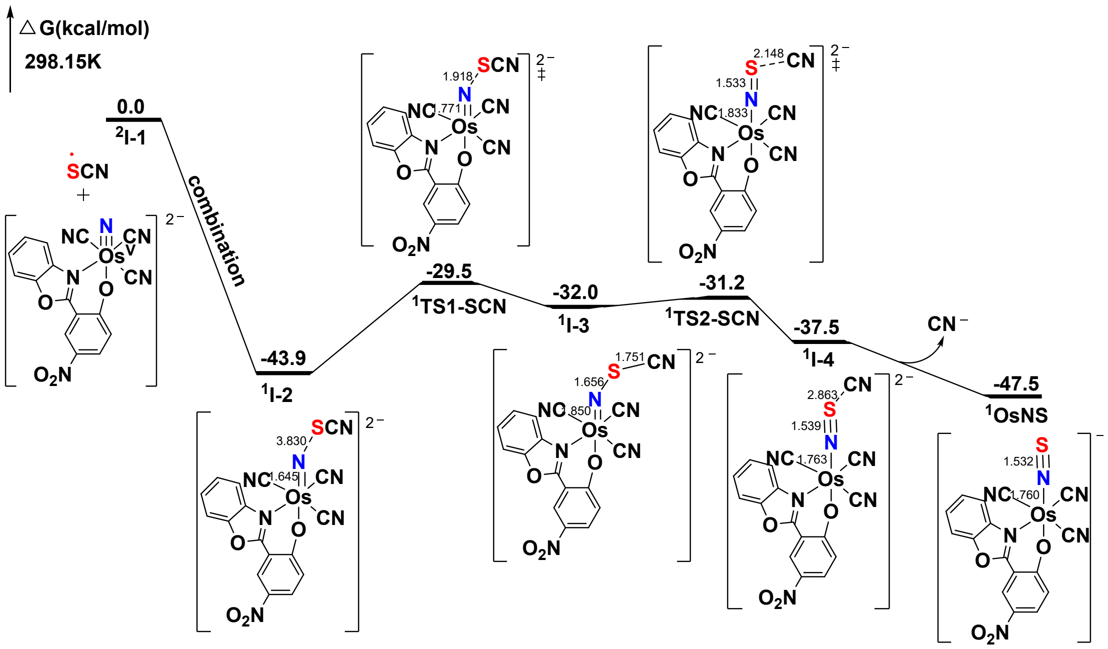

Figure S9. Gibbs free energy profile for reaction of **Os^{V}N** and the •SCN radical. The reaction is downhill in energy after the initial recombination of **Os^{V}N** and •SCN species to afford the intermediate [Os^{IV}(L)(CN)$_3$(N-SCN)]$^{2-}$, which then undergoes spontaneous S-CN bond cleavage to produce **OsNS** and CN^{-}.

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