

## RESEARCH ARTICLE

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Cite this: *Inorg. Chem. Front.*, 2023, **10**, 5678Chalcogen atom abstraction from  $\text{NCE}^-$  (E = O, S, Se) and  $i\text{-Pr}_2\text{S}$  by the excited state of a luminescent tricyano osmium(vi) nitride<sup>†</sup>Li-Xin Wang,<sup>‡a</sup> Miaomiao Zhou,<sup>‡b</sup> Lu-Lu Liu,<sup>a</sup> Jing Xiang,<sup>id</sup>\*<sup>a</sup> Ji-Yan Liu,<sup>a</sup> Kai-Chung Lau<sup>id</sup>\*<sup>b</sup> and Tai-Chu Lau<sup>id</sup>\*<sup>b</sup>

Upon irradiation by blue LED ( $\lambda > 460$  nm), the tricyano osmium nitrido complex  $[\text{Os}^{\text{VI}}(\text{N})(\text{L})(\text{CN})_3]^-$  (**OsN**) in its excited state readily abstracts chalcogen atoms from the anions  $\text{NCE}^-$  (E = O, S, Se) to give the corresponding metal chalcogenonitrosyls  $[\text{Os}^{\text{II}}(\text{N}=\text{E})(\text{L})(\text{CN})_3]^-$  (**OsNE**) and  $\text{CN}^-$ . A similar S atom abstraction also occurs in the photoreaction of **OsN** with organic sulfide, such as diisopropyl sulfide, to give **OsNS** and **Os-N=C(CH<sub>3</sub>)<sub>2</sub>**. The molecular structures of  $(\text{PPh}_4)[\text{Os}^{\text{II}}(\text{N}=\text{E})(\text{L})(\text{CN})_3]$  have been determined by X-ray crystallography, which show N–O, N–S and N–Se bond distances of 1.206, 1.507 and 1.675 Å, respectively.

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## Introduction

Metal nitrido complexes ( $\text{M}=\text{N}$ ) have been proposed as key intermediates in  $\text{N}_2$  fixation; they are also potentially useful reagents for the nitrogenation of various organic substrates.<sup>1–5</sup> A number of electrophilic nitrido complexes have been reported recently. For instance, *cis*- and *trans*- $[\text{Os}^{\text{VI}}(\text{N})(\text{tpy})\text{Cl}_2]^+$  (tpy = 2,2':6',2''-terpyridine) have been shown to exhibit novel electrophilic properties. A variety of reagents such as phosphines, amines, cyanide, azide, arylboranes, amine *N*-oxides, alkenes, and benzenethiols have been reported to react with the osmium nitrido complexes.<sup>6</sup> Higher reactivity is found for  $\text{Ru}=\text{N}$  and  $\text{Fe}=\text{N}$ , such as  $[\text{Ru}(\text{N})(\text{salchda})(\text{MeOH})]^+$  (salchda = *N,N'*-bis(salicylidene)-*o*-cyclohexyldiamine dianion)<sup>7</sup> and  $[\text{PhB}(\text{RIm})_3\text{Fe}=\text{N}]$  (Im = imidazol, R = <sup>t</sup>Bu, Mes, and <sup>i</sup>Pr<sub>2</sub>).<sup>8</sup> Although these nitrido complexes exhibit novel electrophilic properties and react readily with a variety of nucleophiles, their reactivity is still relatively limited compared to analogous metal-oxo ( $\text{M}=\text{O}$ ) species.<sup>9</sup>

In search of more reactive  $\text{M}=\text{N}$  species that are comparable to  $\text{M}=\text{O}$ , we recently started to investigate the reactivity of

$\text{M}=\text{N}$  in their excited states. Accordingly, a highly luminescent  $\text{Os}(\text{vi})$  nitrido complex,  $[\text{Os}^{\text{VI}}(\text{N})(\text{L})(\text{CN})_3]^-$  (**OsN**, HL = 2-(2-hydroxy-5-nitrophenyl)benzoxazole) with long-lived LMCT excited state has been prepared.<sup>10</sup> This species is highly reactive in the excited state (**OsN\***) due to its nitridyl [ $\text{Os}=\text{N}^*$ ] character. Indeed, upon irradiation with visible light ( $\lambda > 460$  nm), **OsN\*** readily activates the strong C–H bonds of alkanes and arenes,<sup>11</sup> undergoes oxidative *N*-dealkylation of various tertiary amines<sup>12</sup> and C–O bond cleavage of dihydroxybenzene,<sup>13</sup> exhibits formal N atom transfer to aliphatic secondary amines<sup>14</sup> and ring-nitrogenation of aromatic amines.<sup>15</sup> Recently, we have also found that **OsN\*** could activate both  $\alpha$ - and  $\delta$ -C–H bonds of alcohols in the presence of PhIO, due to the formation of the highly potent oxidant  $\text{PhIO}^+$ <sup>16</sup> (Fig. 1).

We report herein that **OsN\*** readily undergoes unprecedented chalcogen atom abstraction from the stable inorganic anions  $\text{NCE}^-$  (N = O, S, Se), as well as from organic sulfide such as  $i\text{-Pr}_2\text{S}$ .

## Results and discussion

Upon irradiation of a solution of **OsN** in  $\text{CH}_2\text{Cl}_2$  containing 10 equiv. of  $(\text{PPh}_4)\text{NCSe}$  with blue LED ( $\lambda > 460$  nm) for 24 h, the bright yellow solution turned pale-yellow. Electrospray ionization mass spectrometry (ESI/MS, –ve mode) of the resulting solution exhibits a new peak at  $m/z$  617, which is assigned to  $[\text{Os}(\text{N}=\text{Se})(\text{L})(\text{CN})_3]^-$  (**OsNSE**). Similarly, ESI/MS for the photoreaction of **OsN** with 10 equiv. of  $(\text{PPh}_4)\text{NCS}$  for 48 h shows a major peak at  $m/z$  571, which is assigned to  $[\text{Os}(\text{N}=\text{S})(\text{L})(\text{CN})_3]^-$  (**OsNS**) (Fig. 2 and S1<sup>†</sup>). When the reactions were

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<sup>†</sup>Electronic supplementary information (ESI) available: Experimental section, crystal data, ESI/MS, and <sup>1</sup>H NMR. CCDC 2267408–2267410. For ESI and crystallographic data in CIF or other electronic format see DOI: <https://doi.org/10.1039/d3qi01081c>

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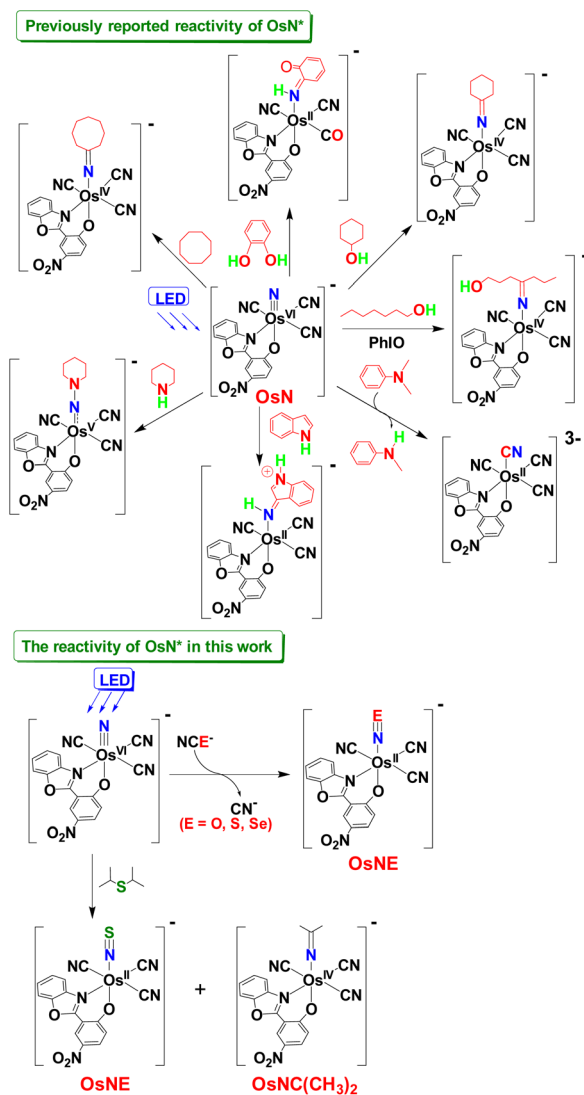


Fig. 1 (a) Reported reactivity of  $\text{OsN}^*$  towards various substrates; (b) reaction of  $\text{OsN}^*$  with  $\text{NCE}^-$  and *i*-Pr<sub>2</sub>S in this work.

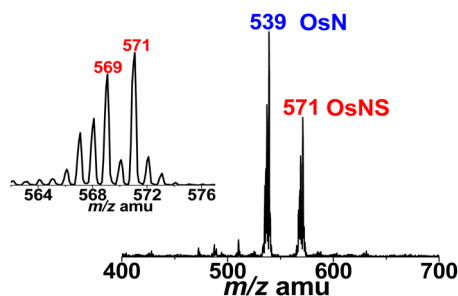


Fig. 2 ESI/MS of the photoreaction of  $\text{OsN}$  with 10 equiv. of  $(\text{PPh}_4)\text{NCS}$  for 24 h showing a new product peak at  $m/z$  571 ( $\text{OsNS}$ ).

carried out on a preparative scale,  $(\text{PPh}_4)[\text{Os}(\text{N}\equiv\text{E})(\text{L})(\text{CN})_3]$  ( $\text{OsNE}$ , E = Se and S) were isolated as light yellow crystalline solids with 45% and 52% yields, respectively. ESI/MS ( $-ve$

mode) of these photoreaction solutions also show a small peak at  $m/z = 26$  due to the formation of  $\text{CN}^-$ .  $\text{M-NE}$  complexes have been prepared from the reaction of metal nitrides with  $\text{S}_8$  or elemental Se.<sup>17–19</sup> However, to the best of our knowledge, S/Se atom transfer from  $\text{NCE}^-$  anions, which involves cleavage of strong  $\text{C}=\text{E}$  bonds, has not been reported. The photoreaction of  $\text{OsN}$  with  $(\text{PPh}_4)\text{NCO}$  has also been investigated; however, its reaction rate is much slower, and the yield of  $(\text{PPh}_4)[\text{Os}(\text{N}\equiv\text{O})(\text{L})(\text{CN})_3]$  ( $\text{OsNO}$ )<sup>20,21</sup> is only  $\sim 10\%$ , which is probably due to the stronger  $\text{C}=\text{O}$  bond than  $\text{C}=\text{S}$  and  $\text{C}=\text{Se}$  bonds in  $\text{NCE}^-$ . O atom transfer to metal nitride usually occurs with oxidants such as  $\text{Me}_3\text{NO}$ .<sup>17a</sup> When  $^{15}\text{N}$ -labelled  $\text{Os}^{15}\text{N}$  was used, ESI/MS shows that the parent  $\text{OsNE}$  ions all increase by one mass unit, indicating that the N atoms in  $\text{OsNE}$  are from the nitrido ligand rather than from  $\text{NCE}^-$ .

Both  $\text{OsNS}$  and  $\text{OsNSE}$  are stable for  $>2$  weeks in the solid state or in various solvents at room temperature. However, upon exposure to air for more than two months, these complexes were partially converted into  $\text{OsNO}$  ( $m/z$  555). Attempts were also made to synthesize the tellurium analog ( $\text{OsNTe}$ ) from the photoreaction of  $\text{OsN}$  and  $\text{NCTe}^-$ . However, no products could be isolated, presumably due to the instability of the  $[\text{Os}(\text{N}\equiv\text{Te})(\text{L})(\text{CN})_3]^-$  species. Also, no reaction of  $\text{OsN}^*$  with elemental tellurium in various solvents was observed, presumably due to the poor solubility of Te.

The IR spectrum of  $\text{OsNSE}$  shows strong  $\nu(\text{C}\equiv\text{N})$  stretches at 2148, 2133  $\text{cm}^{-1}$  and  $\nu(\text{N}\equiv\text{Se})$  stretch at 1136  $\text{cm}^{-1}$ . Similar  $\nu(\text{C}\equiv\text{N})$  stretches in  $\text{OsNS}$  and  $\text{OsNO}$  are also found at 2149, 2133  $\text{cm}^{-1}$  and 2150, 2139  $\text{cm}^{-1}$ , respectively; while the  $\nu(\text{N}\equiv\text{S})$  and  $\nu(\text{N}\equiv\text{O})$  stretches occur at 1291  $\text{cm}^{-1}$  and 1849  $\text{cm}^{-1}$ , respectively. The ratio of  $\nu(\text{N}\equiv\text{O})$  to  $\nu(\text{N}\equiv\text{S})$  stretching frequencies in  $\text{OsNO}$  and  $\text{OsNS}$  is 1.432, a typical value for structurally similar NO and NS compounds.<sup>22</sup> The UV/vis spectra of these compounds show strong absorption bands due to ligand centered  $\pi\text{-}\pi^*$  transitions below 400 nm, with molar extinction coefficients ( $\epsilon$ ) on the order of  $10^4 \text{ M}^{-1} \text{ cm}^{-1}$  (Fig. 3a).  $\text{OsNO}$  also shows a weak absorption band tailing down to the visible region, while for  $\text{OsNS}$  and  $\text{OsNSE}$  there is a well-defined absorption band in the visible region; these are tentatively assigned to the  $\text{O}^-\text{N}$  ligand to metal (Os) charge transfer (LMCT) (Fig. S2 and S3<sup>†</sup>). All compounds are diamagnetic, as evidenced by their sharp proton signals in the normal range in their  $^1\text{H}$  NMR spectra (Fig. S4–S6<sup>†</sup>).

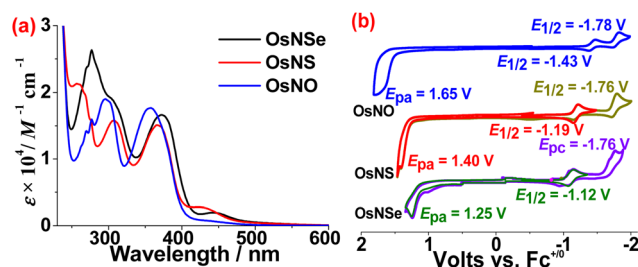


Fig. 3 (a) UV/vis spectra of  $\text{OsNE}$  in  $\text{CH}_3\text{CN}$ ; (b) CV of  $\text{OsNE}$  in  $\text{CH}_3\text{CN}$  containing 0.1 M  $[\text{tBu}_4\text{N}](\text{PF}_6)$  with a scan rate of  $0.1 \text{ V s}^{-1}$ .



Cyclic voltammetry (CV) of **OsNE** was conducted in 0.1 M [<sup>t</sup>Bu<sub>4</sub>N](PF<sub>6</sub>) CH<sub>3</sub>CN solution. As shown in Fig. 3b, these compounds all show two reduction waves. The first reduction potentials  $E_{1/2}$  are in the range of  $-1.12$  to  $-1.43$  V (*vs.* Fc<sup>+0</sup>), which are dependent on the coordinated NE<sup>+</sup> ligand with the order of NSe ( $-1.12$  V) > NS ( $-1.19$  V) > NO ( $-1.43$  V). Thus, the first reduction waves are tentatively assigned to the ligand-centered NE<sup>+0</sup> reduction. On the other hand, the second reduction waves have very similar potentials for these complexes, hence they are assigned to the reduction of the O<sup>^N</sup> ligand. **OsNE** also exhibits an irreversible wave with  $E_{pa}$  of **OsNO** (1.65 V) > **OsNS** (1.40 V) > **OsNSe** (1.25 V), in line with the decreasing  $\pi$ -accepting ability of these chalcogenonitrosyl ligands on going from O to Se. Thus, these oxidation waves should be metal centered, since the Os<sup>II</sup> center is more stabilized by the stronger  $\pi$ -accepting NO ligand.

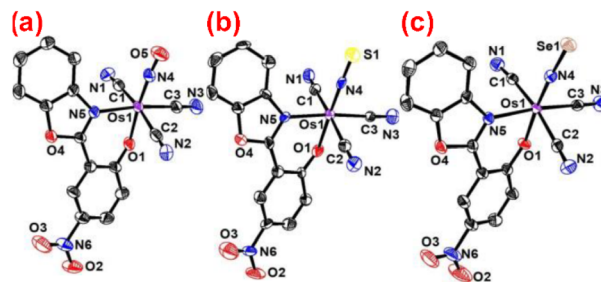
### Molecular structures

The molecular structures of **OsNE** have been determined by X-ray crystallography and selected bond parameters are listed in Table 1. As shown in Fig. 4, the coordination geometries of the metal centers are similar to that of **OsN**. The Os centers are all 6-coordinated by three CN<sup>-</sup> in a meridional configuration, a bidentate O<sup>^N</sup> ligand and a chalcogenonitrosyl ligand. The Os–N4 bond length in the complexes are similar; 1.727(5) Å in **OsNO**, 1.767(5) Å in **OsNS** and 1.749(3) Å in **OsNSe**, indicating that they have double bond character. These bond lengths follow the order: Os–NO < Os–NSe < Os–NS. This trend is also found in the iridium chalcogenonitrosyl series [Ir(NE){N(CHCHP<sup>t</sup>Bu<sub>2</sub>)<sub>2</sub>}] [PF<sub>6</sub>].<sup>23</sup> The Os1–N4–E bonds are close to linear; 174.1(4)°, 177.8(4)°, 175.4(2)°, respectively, for E = O, S, Se. The N–E bond lengths are 1.206(6) Å, 1.507(5) Å, and 1.675(3) Å, respectively, for E = O, S, Se, which are very close to the sum of the covalent radii of the double bonds; N–O = 1.17 Å; N–S = 1.54 Å; N–Se = 1.67 Å. The Os–O1<sub>(phenoxy)</sub> bond lengths are comparable to the value of 2.024(2) Å in (PPh<sub>4</sub>)[Os(NH<sub>3</sub>)(L)(CN)<sub>3</sub>],<sup>13</sup> indicating the absence of the strong *trans* influence for these chalcogenonitrosyl ligands.

In our previous work, we showed that **OsN\*** readily undergoes an initial one-electron oxidation of various substrates,<sup>12–16</sup> hence it is reasonable to propose that the present photoreactions proceed *via* an initial 1e<sup>-</sup> transfer (ET) from NCE<sup>-</sup> to **OsN\*** to generate **Os<sup>V</sup>N** and the NCE<sup>•</sup> radical;

**Table 1** Selected bond parameters (Å, °) for **OsNE**

	<b>OsNO</b>	<b>OsNS</b>	<b>OsNSe</b>
Os1–N4	1.727(5)	1.767(5)	1.749(3)
Os1–C2	2.082(7)	2.084(8)	2.069(4)
Os1–C3	2.041(5)	2.037(6)	2.020(4)
Os1–C1	2.091(7)	2.083(8)	2.066(4)
Os1–N5	2.129(4)	2.117(5)	2.127(3)
Os1–O1	2.022(3)	2.034(4)	2.037(2)
N4–E	1.206(6)	1.507(5)	1.675(3)
Os1–N4–E	174.1(4)	177.8(4)	175.4(2)
O1–Os1–N4	174.4(2)	177.1(2)	175.3(1)



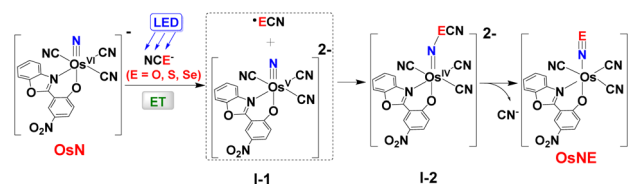
**Fig. 4** The structures of the anions **OsNO** (a), **OsNS** (b), and **OsNSe** (c).

this is followed by rapid recombination of the two species to afford the unstable intermediate [Os<sup>IV</sup>(L)(CN)<sub>3</sub>(N–ECN)]<sup>2-</sup>, which then undergoes spontaneous E–CN bond cleavage to produce **OsNE** and CN<sup>-</sup> (Fig. 5). The estimated reduction potentials ( $E^\circ$ ) for NCE<sup>•</sup>/NCE<sup>-</sup> are 1.27 V, 1.63 V, and 2.15 V for E = Se, S, and O, respectively.<sup>24</sup> The observed reaction rates are inversely dependent on the  $E^\circ$  values, consistent with ET being involved in the rate-determining step.

### Reaction of **OsN\*** with diisopropyl sulfide

The above results indicate that **OsN\*** readily abstracts various chalcogen atoms from NCE<sup>-</sup>. A similar reaction occurs between **OsN\*** and organic sulphide such as diisopropyl sulfide (i-Pr<sub>2</sub>S). Upon irradiation of a solution of **OsN** with 300 equiv. of i-Pr<sub>2</sub>S in CH<sub>2</sub>Cl<sub>2</sub> for 4 h, ESI/MS shows two new product peaks at *m/z* 571 and 581 (Fig. 6), which are assigned to **OsNS** and [Os<sup>IV</sup>(L)(CN)<sub>3</sub>(N=C(CH<sub>3</sub>)<sub>2</sub>)]<sup>-</sup> (**Os–N=C(CH<sub>3</sub>)<sub>2</sub>**),<sup>12</sup> respectively (Fig. 7). The reaction was also followed by UV/vis spectroscopy, which shows that the absorption band due to **OsN** gradually decreases, while those of the products gradually increase with time (Fig. S7†). When the reaction was carried out on a preparative scale, the two species were isolated with a molar ratio of ~1 : 2.

Oxidative desulfurization is an important process for the removal of sulfur from liquid fuels. In this process, sulfur-containing compounds are converted to their corresponding sulfones/sulfoxides using various oxidants.<sup>25</sup> To the best of our knowledge, direct S atom abstraction from S-containing substrates has yet to be reported. The proposed mechanism for the reaction of **OsN\*** with i-Pr<sub>2</sub>S is shown in Fig. 8. The first step is ET from i-Pr<sub>2</sub>S to **OsN\*** to produce **Os<sup>V</sup>N** and the radical cation i-Pr<sub>2</sub>S<sup>•+</sup>, this is followed by their combination to give the Os(IV) species (**I**). **I** then undergoes an internal 2e<sup>-</sup> transfer to give an Os(II) species (**II**). This is followed by rapid oxidation of



**Fig. 5** Proposed mechanism for the reaction of **OsN\*** with NCE<sup>-</sup>.



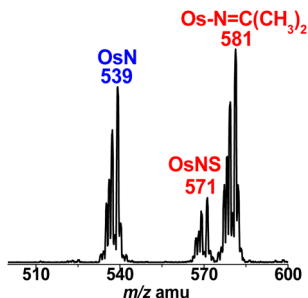


Fig. 6 ESI/MS of the photoreaction of OsN with excess *i*-Pr<sub>2</sub>S for 24 h.

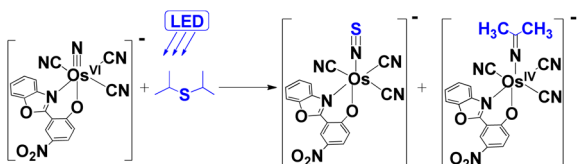


Fig. 7 The photoreaction of OsN with *i*-Pr<sub>2</sub>S.

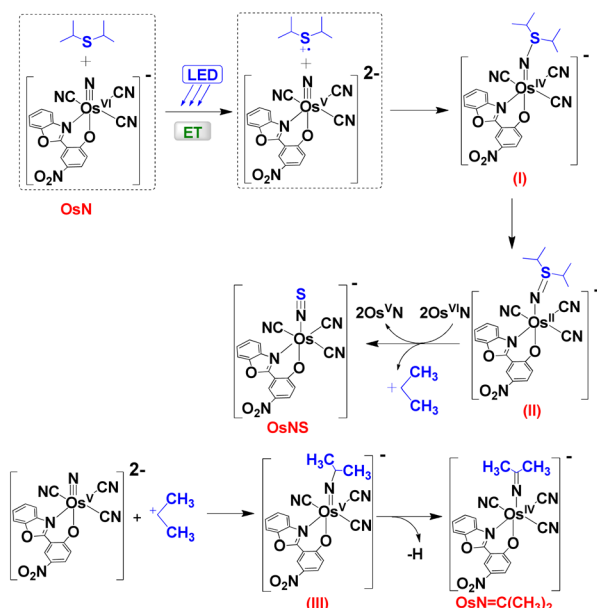


Fig. 8 Proposed mechanism for the reaction of OsN\* with *i*-Pr<sub>2</sub>S.

II by two 2OsN\*, resulting C–S bond cleavage and the formation of Os<sup>V</sup>N, OsNS, and CH<sub>3</sub>CH<sup>+</sup>CH<sub>3</sub>. CH<sub>3</sub>CH<sup>+</sup>CH<sub>3</sub> then adds to the nitrido ligand of Os<sup>V</sup>N to form the Os(v) species III, which further undergoes an internal 1e<sup>−</sup> oxidative dehydrogenation to afford Os–N=C(CH<sub>3</sub>)<sub>2</sub>.<sup>12</sup>

We have carried out DFT calculations on the reaction of OsN\* + NCS<sup>−</sup> and OsN\* + *i*-Pr<sub>2</sub>S (Fig. S9† and Fig. 9), which support our proposed mechanisms. As shown in Fig. 9, the reaction is downhill in energy after the initial combination of Os<sup>V</sup>N and the radical cation *i*-Pr<sub>2</sub>S<sup>•+</sup> to give the Os(IV) species. The Os(IV) species then undergoes an internal 2e<sup>−</sup> transfer to

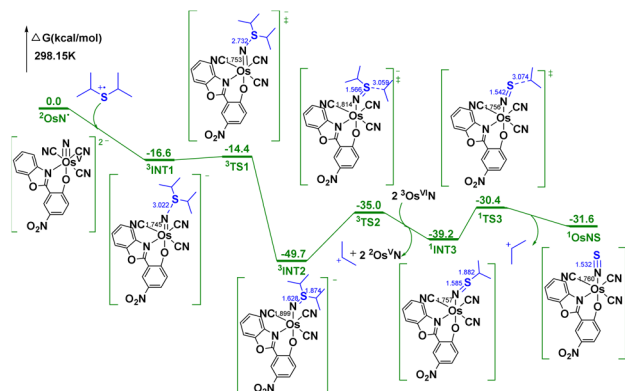


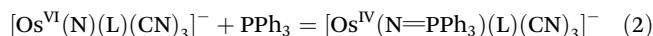
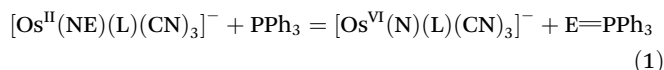
Fig. 9 Gibbs free energy profile for reaction of OsN\* with *i*-Pr<sub>2</sub>S at the B3LYP-D3(BJ)/def2-TZVPD level.

give an Os(II) species (<sup>3</sup>INT2) and this is followed by rapid oxidation of <sup>3</sup>INT2 by two 2Os<sup>V</sup>N, resulting in C–S bond cleavage and the formation of Os<sup>V</sup>N, OsNS, and CH<sub>3</sub>CH<sup>+</sup>CH<sub>3</sub>.

### Dechlorination of OsNE

Dechlorination of OsNS and OsNSE occur readily by using PPh<sub>3</sub>. As shown in Fig. 10a, ESI/MS of OsNS with 100 equiv. of PPh<sub>3</sub> for 6 h at 313 K shows a new product peak at *m/z* 801, which is tentatively assigned to [Os<sup>IV</sup>(L)(CN)<sub>3</sub>(N=PPh<sub>3</sub>)]<sup>−</sup> (Os<sup>IV</sup>N=PPh<sub>3</sub>).<sup>26</sup> A minor peak also occurs at *m/z* 539, which is due to OsN, suggesting that OsN may be an intermediate that further reacts with excess PPh<sub>3</sub> to give Os<sup>IV</sup>N=PPh<sub>3</sub>. The reaction rate of OsNSE with PPh<sub>3</sub> is much faster; as shown in Fig. 10b, the ESI/MS for the reaction of OsNSE with 5 equiv. of PPh<sub>3</sub> for 0.5 h at 298 K shows two major product peaks at *m/z* 539 and 801, while the parent peak at *m/z* 617 disappears completely.

The reaction of OsNE (E = S, Se) with PPh<sub>3</sub> can be represented by the following equation.



When the reactions were carried out on a preparative scale, SPPPh<sub>3</sub> and SePPh<sub>3</sub> were formed and could be extracted with

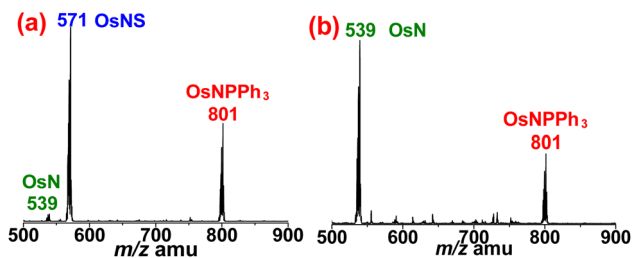


Fig. 10 (a) ESI/MS for OsNS with 100 equiv. of PPh<sub>3</sub> in CH<sub>2</sub>Cl<sub>2</sub> at 313 K for 6 h; (b) ESI/MS for OsNSE with 5 equiv. of PPh<sub>3</sub> in CH<sub>2</sub>Cl<sub>2</sub> at 298 K for 0.5 h.



Et<sub>2</sub>O with >80% yield (Fig. 11). Although for both **OsNS** and **OsNSe**, the Os(IV) phosphineiminato complex [Os<sup>IV</sup>(L)(CN)<sub>3</sub>(N=PPh<sub>3</sub>)]<sup>-</sup> (**Os<sup>IV</sup>N=PPh<sub>3</sub>**, *m/z* 801) could be observed by ESI/MS, the osmium product that was actually isolated (after chromatography) is the osmium(III) complex [Os<sup>III</sup>(L)(CN)<sub>3</sub>(NH=PPh<sub>3</sub>)]<sup>-</sup> with PPh<sub>4</sub><sup>+</sup> counter ion in ~70% yield (**Os<sup>III</sup>NH=PPh<sub>3</sub>**). ESI/MS (–ve mode) of **Os<sup>III</sup>NH=PPh<sub>3</sub>** in MeOH shows a predominant parent anion peak at *m/z* 802, which is one mass unit higher than **Os<sup>IV</sup>N=PPh<sub>3</sub>**. Presumably **Os<sup>IV</sup>N=PPh<sub>3</sub>** is reduced to **Os<sup>III</sup>NH=PPh<sub>3</sub>** during the work-up. The IR spectrum of **Os<sup>III</sup>NH=PPh<sub>3</sub>** shows  $\nu(\text{C}\equiv\text{N})$  stretches at 2113 and 2084 cm<sup>-1</sup>, and  $\nu(\text{N-H})$  stretches at 3276 cm<sup>-1</sup>. It has a room-temperature magnetic moment of 1.91 $\mu_{\text{B}}$  (Gouy method, solid sample), consistent with its formulation as a low-spin d<sup>5</sup> Os<sup>III</sup> compound. The CV of **Os<sup>III</sup>NH=PPh<sub>3</sub>** in CH<sub>3</sub>CN containing 0.1 M [t<sup>+</sup>Bu<sub>4</sub>N](PF<sub>6</sub>) shows a quasi-reversible Os(III/II) couple at  $E_{1/2} = -1.27$  V (vs. Fc<sup>+0</sup>) (Fig. S8†). There is also a broad wave at ~0.17 V, which is tentatively assigned to **Os<sup>IV</sup>N=PPh<sub>3</sub>**/**Os<sup>III</sup>NH=PPh<sub>3</sub>**.

Oxidative dechalcogenation of **OsNSe** and **OsNS** also occurs by using PhIO (Fig. 12), which is much more rapid than with PPh<sub>3</sub>. Upon mixing **OsNS** or **OsNSe** with 5 equiv. of PhIO for 0.5 h in CH<sub>3</sub>CN, ESI/MS (–ve mode) for both solutions show a predominant peak at *m/z* 539. When the reactions were carried out on a preparative scale, **OsN** could be isolated with >90% yield, indicating that **OsNSe** and **OsNS** were almost quantitatively converted to **OsN** by PhIO. Moreover, ESI/MS (–ve mode) for the **OsNS** + PhIO solution also shows a minor peak at *m/z* 81, possibly due to HSO<sub>3</sub><sup>-</sup>. On the other hand, for the reaction of **OsNSe** with PhIO, a grey precipitate was observed, which is presumably SeO<sub>2</sub>. However, no reaction of **OsNO** with PhIO was observed, probably due to its much stronger N–O bond.

## Conclusions

We have demonstrated that **OsN\*** readily undergoes unprecedented chalcogen atom abstraction from NCE<sup>-</sup> and i-Pr<sub>2</sub>S; such reaction has not been observed even by metal oxo species. We propose that these reactions occur by initial one-electron oxidation of the substrates by **OsN\***. The resulting **OsNE** products readily undergoes dechalcogenation by using PPh<sub>3</sub> or PhIO. Notably PhIO regenerates **OsN\*** from **OsNE**, which suggests that it is possible to construct a catalytic cycle for dechalcogenation of substrates based on OsN/PhIO/visible light.

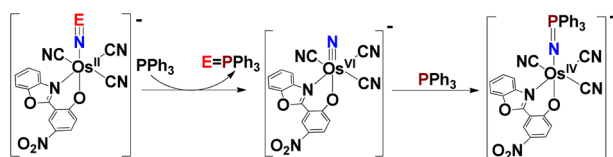


Fig. 11 Chalcogen abstraction by PPh<sub>3</sub> from **OsNE** (E = S, Se).

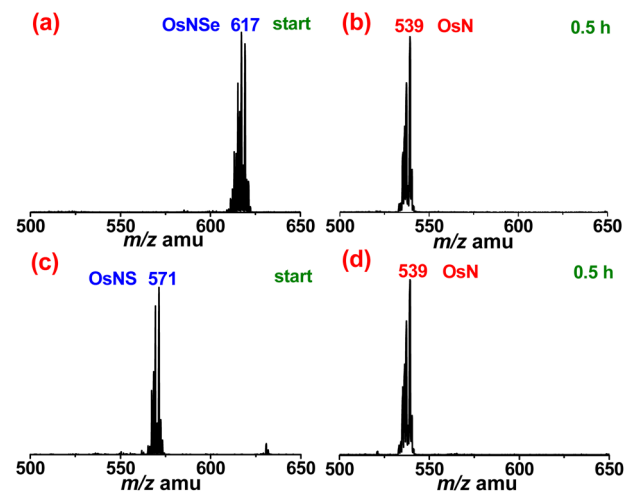


Fig. 12 (a) ESI/MS of **OsNSe** and (b) after addition of 5 equiv. PhIO for 0.5 h in CH<sub>3</sub>CN; (c) ESI/MS of **OsNS** and (d) after addition of 5 equiv. PhIO for 0.5 h in CH<sub>3</sub>CN.

## Experimental

### (PPh<sub>4</sub>)[Os(NSe)(L)(CN)<sub>3</sub>] (**OsNSe**)

Ten Pyrex tubes (15 × 2 cm) each containing **OsN** (5 mg, 5.7  $\mu\text{mol}$ ) and (PPh<sub>4</sub>)NCSe (12 mg, 27  $\mu\text{mol}$ ) in CH<sub>2</sub>Cl<sub>2</sub> were irradiated with blue LED light ( $\lambda > 460$  nm) for 96 h, whereby the light-yellow solutions became pale yellow. The solvent was removed by a rotary evaporator and the residue was dissolved in a minimum amount of CH<sub>2</sub>Cl<sub>2</sub> and then loaded onto a silica gel column. The pale yellow band was eluted by CH<sub>2</sub>Cl<sub>2</sub>/acetone (v : v, 5 : 1). (PPh<sub>4</sub>)[Os(NSe)(L)(CN)<sub>3</sub>] was obtained as a yellow microcrystalline solid. Yield: 25 mg, 45%. Light yellow crystals were obtained from the slow diffusion of diethyl ether into a CH<sub>2</sub>Cl<sub>2</sub> solution of **OsNSe**. Selected IR (KBr disc, cm<sup>-1</sup>):  $\nu(\text{C}\equiv\text{N})$  2148 and 2133;  $\nu(\text{N}=\text{Se})$  1136; ESI/MS (–ve mode): *m/z* 617 ([M]<sup>-</sup>); UV/vis (CH<sub>3</sub>CN):  $\lambda_{\text{max}}$  [nm] ( $\epsilon$  [mol<sup>-1</sup> dm<sup>3</sup> cm<sup>-1</sup>]): 256 (21 320), 277sh (15 950), 307 (15 770), 367 (15 080), 427sh (2750). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  8.89 (d, *J* = 2.9 Hz, 1H, Ar-H), 8.29–8.23 (m, 1H, Ar-H), 7.95–7.89 (m, 5H, Ar-H and PPh<sub>4</sub>-H), 7.80 (td, *J* = 7.8, 3.6 Hz, 8H, PPh<sub>4</sub>-H), 7.75–7.71 (m, 1H, Ar-H), 7.70–7.62 (m, 8H, PPh<sub>4</sub>-H), 7.53 (dt, *J* = 10.9, 3.7 Hz, 2H, Ar-H), 6.52 (d, *J* = 9.3 Hz, 1H, Ar-H). Calcd (%) for C<sub>40</sub>H<sub>27</sub>N<sub>6</sub>O<sub>4</sub>OsPSe: C, 50.26; H, 2.85; N, 8.79; found: C, 50.28; H, 2.81; N, 8.76.

### (PPh<sub>4</sub>)[Os(NS)(L)(CN)<sub>3</sub>] (**OsNS**)

The synthesis of **OsNS** is similar to that of **OsNSe** except (PPh<sub>4</sub>)NCS (23 mg, 58  $\mu\text{mol}$ ) was used instead. Yield for **OsNS**: 27 mg, 52%. Selected IR Selected IR (KBr disc, cm<sup>-1</sup>):  $\nu(\text{C}\equiv\text{N})$  2149 and 2133;  $\nu(\text{N}=\text{S})$  1291; ESI/MS (–ve mode): *m/z* 571 ([M]<sup>-</sup>); UV/vis (CH<sub>3</sub>CN):  $\lambda_{\text{max}}$  [nm] ( $\epsilon$  [mol<sup>-1</sup> dm<sup>3</sup> cm<sup>-1</sup>]): 270sh (23 710), 277 (26 320), 302sh (19 240), 374 (16 600), 447 (1940). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  8.90 (d, *J* = 2.9 Hz, 1H, Ar-H), 8.15–8.11 (m, 1H, Ar-H), 7.95–7.89 (m, 5H, Ar-H and PPh<sub>4</sub>-H), 7.80 (td, *J* = 7.8, 3.6 Hz, 8H, PPh<sub>4</sub>-H), 7.75–7.70 (m, 1H, Ar-H),



7.70–7.62 (m, 8H, PPh<sub>4</sub>-H), 7.56–7.49 (m, 2H, Ar-H), 6.51 (d, *J* = 9.3 Hz, 1H, Ar-H). Calcd (%) for C<sub>40</sub>H<sub>27</sub>N<sub>6</sub>O<sub>4</sub>OsP<sub>3</sub>: C, 52.86; H, 2.99; N, 9.25; found: C, 52.82; H, 3.02; N, 9.27.

### (PPh<sub>4</sub>)[Os(NO)(L)(CN)<sub>3</sub>](OsNO)

The synthesis of OsNO is similar to that of OsNSe except (PPh<sub>4</sub>)NCO (22 mg, 58 μmol) was used instead. Yield for OsNO: 5 mg, 10%. The OsNO also could be obtained from oxidation of the guanidine precursor (OsG) by excess *m*-chloroperbenzoic acid (*m*-cpba) in CH<sub>3</sub>CN with about 60% yield.<sup>20,21</sup> Selected IR (KBr disc, cm<sup>-1</sup>): ν(C≡N) 2150 and 2139; ν(N≡O) 1849; ESI/MS (–ve mode): *m/z* 555 ([M]<sup>–</sup>); UV/vis (CH<sub>3</sub>CN): λ<sub>max</sub> [nm] (ε [mol<sup>-1</sup> dm<sup>3</sup> cm<sup>-1</sup>]): 270 (14 210), 277 (15 950), 295 (18 980), 357 (17 660), 435sh (760). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 8.92 (s, 1H, Ar-H), 8.03 (d, *J* = 9.5 Hz, 1H, Ar-H), 7.92 (t, *J* = 7.4 Hz, 4H, PPh<sub>4</sub>-H), 7.80 (d, *J* = 7.8 Hz, 8H, PPh<sub>4</sub>-H), 7.73 (t, *J* = 7.4 Hz, 2H, Ar-H), 7.65 (dd, *J* = 12.8, 7.9 Hz, 8H, PPh<sub>4</sub>-H), 7.58–7.50 (m, 2H, Ar-H), 6.70 (d, *J* = 9.3 Hz, 1H, Ar-H). Calcd (%) for C<sub>40</sub>H<sub>27</sub>N<sub>6</sub>O<sub>5</sub>OsP: C, 53.81; H, 3.05; N, 9.41; found: C, 53.76; H, 3.02; N, 9.44.

### Dechalcogenation of OsNE

(PPh<sub>4</sub>)[Os<sup>III</sup>(L)(CN)<sub>3</sub>(NH=PPh<sub>3</sub>)] (OsNH=PPh<sub>3</sub>). OsNSe (20 mg, 20.8 μmol) and PPh<sub>3</sub> (55 mg, 0.2 mmol) were dissolved in CH<sub>2</sub>Cl<sub>2</sub> and stirred at room temperature for 6 h to give a dark red solution. The solvent was removed by a rotary evaporator and the residue was dissolved in a minimum amount of CH<sub>2</sub>Cl<sub>2</sub> and then loaded onto a silica gel column. The red band was eluted by CH<sub>2</sub>Cl<sub>2</sub>/MeOH (v : v, 10 : 1). OsNH=PPh<sub>3</sub> was isolated as a red microcrystalline solid. Yield: 16.7 mg, 70%. Selected IR (KBr disc, cm<sup>-1</sup>): ν(C≡N) 2113 and 2084; ν(N-H) 3276; ESI/MS (–ve mode): *m/z* 802 ([M]<sup>–</sup>); μ<sub>eff</sub> = 1.91μ<sub>B</sub>; UV/vis (CH<sub>3</sub>CN): λ<sub>max</sub> [nm] (ε [mol<sup>-1</sup> dm<sup>3</sup> cm<sup>-1</sup>]): 263sh (15 180), 268(15 790), 275(15 760), 290sh (14 800), 311(14 790), 392 (12 810), 440sh (10 580), 550sh (970). Calcd (%) for C<sub>58</sub>H<sub>43</sub>N<sub>6</sub>O<sub>4</sub>OsP<sub>2</sub>: C, 61.10; H, 3.80; N, 7.37; found: C, 61.13; H, 3.78; N, 7.39.

## Author contributions

The manuscript was written through the contributions of all authors. All authors have given approval to the final version of the manuscript.

## Conflicts of interest

There are no conflicts to declare.

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