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Visible light-induced oxidative *N*-dealkylation of alkylamines by a luminescent osmium(vi) nitrido complex†Jing Xiang,<sup>a\*</sup> Min Peng,<sup>a</sup> Yi Pan,<sup>b</sup> Li-Juan Luo,<sup>a</sup> Shun-Cheung Cheng,<sup>b</sup> Xin-Xin Jin,<sup>a</sup> Shek-Man Yiu,<sup>b</sup> Wai-Lun Man,<sup>c</sup> Chi-Chiu Ko,<sup>b</sup> Kai-Chung Lau<sup>b\*</sup> and Tai-Chu Lau<sup>b\*</sup>

*N*-Dealkylation of amines by metal oxo intermediates (M=O) is related to drug detoxification and DNA repair in biological systems. In this study, we report the first example of *N*-dealkylation of various alkylamines by a luminescent osmium(vi) nitrido complex induced by visible light.

High-valent metal oxo (M=O) species play key roles in many chemical and biological oxidation processes.<sup>1</sup> They are versatile oxidants that can perform oxidation of substrates *via* a variety of pathways, including electron transfer, H-atom transfer, hydride transfer and O-atom transfer. In principle, high-valent metal nitrido (M≡N) complexes should also function as versatile oxidants similar to M=O. Although there have been significant advances in M≡N oxidation chemistry in recent years, the reactivity of M≡N is still rather limited in scope compared to M=O.<sup>2</sup> M≡N is intrinsically less oxidizing than M=O due to the stronger electron donating property of the N<sup>3-</sup> ligand than the O<sup>2-</sup> ligand. Attempts to increase the oxidizing power of M≡N by increasing the oxidation state or by using less electron-donating ancillary ligands often led to decomposition of the complexes, mainly due to facile coupling of the nitrido ligands to yield N<sub>2</sub> (2M≡N → 2M + N<sub>2</sub>).<sup>3</sup> One appealing strategy to enhance the reactivity of M≡N is photochemical excitation. We have recently designed an osmium(vi) nitrido complex [Os<sup>VI</sup>(N)(L)(CN)<sub>3</sub>]<sup>-</sup> (NO<sub>2</sub>-OsN, HL = 2-(2-hydroxy-5-nitrophenyl) benzoxazole) that is strongly luminescent in the solid state and in fluid solutions.<sup>4</sup> It readily absorbs visible light to generate a long-lived and highly oxidizing excited state with a redox potential of *ca.* 1.4 V. The excited state of this complex also possesses [Os=N<sup>•</sup>] nitridyl characteristics that enable it to readily abstract H-atoms from inert organic substrates.<sup>5</sup>

We report herein the visible-light induced *N*-dealkylation of various alkylamines by NO<sub>2</sub>-OsN. Iron oxo species have been used by heme and nonheme enzymes to carry out *N*-dealkylation reactions of tertiary amines, which are important processes involved in detoxification and DNA repair.<sup>6</sup> A number of synthetic iron(IV) oxo complexes are also able to carry out such *N*-dealkylation reactions.<sup>7</sup> Mechanistic studies using cytochrome P<sub>450</sub> and synthetic iron oxo complexes indicate that there are two possible mechanisms for *N*-dealkylation of amines, namely hydrogen-atom transfer (HAT) and electron transfer–proton transfer (ET-PT) (Fig. 1).<sup>8</sup> In this work we report the first example of *N*-dealkylation of various aromatic as well as aliphatic tertiary amines by a nitrido complex upon visible light excitation. We also provide unambiguous evidence that these reactions occur *via* an ET/PT mechanism.

*N*-Dealkylation of amines

The reactions of NO<sub>2</sub>-OsN with various amines are summarized in Fig. 2. The reaction with *N,N*-dimethylaniline (DMA) is described in detail. Upon irradiation with blue light ( $\lambda > 460$  nm), the light-yellow solution containing NO<sub>2</sub>-OsN and 10

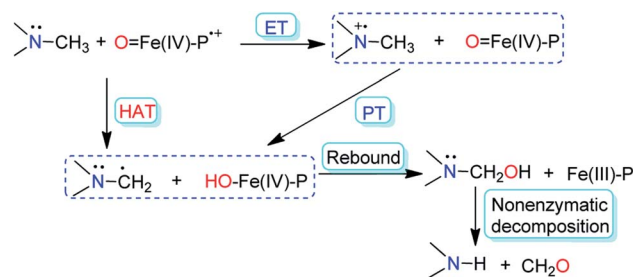


Fig. 1 Two possible mechanisms for *N*-demethylation of tertiary amines by cytochrome P<sub>450</sub> and synthetic Fe(IV) oxo complexes (P = porphyrin).

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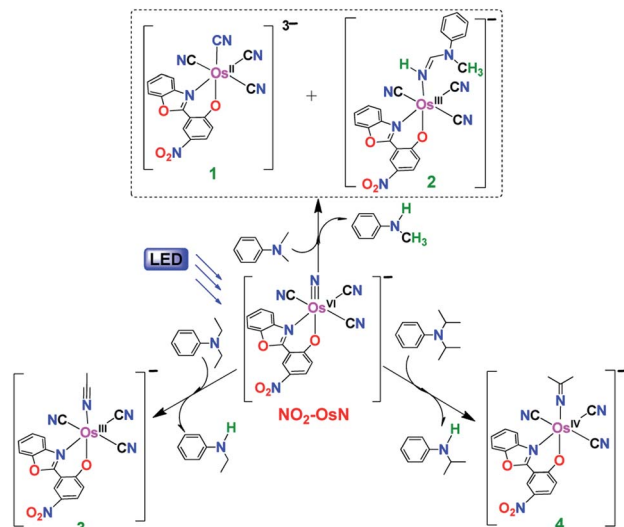


Fig. 2 The photoreactions of  $\text{NO}_2\text{-OsN}^*$  with various amines.

equiv. of DMA in  $\text{CH}_2\text{Cl}_2$  gradually turned red. Analysis of the product solution by GC/MS and GC/FID reviewed the formation of *N*-methylaniline in 71% yield (based on  $\text{NO}_2\text{-OsN}$  consumed) (Table S1†), indicating that *N*-demethylation of DMA has occurred. The fate of the fragmented methyl group and the nature of the osmium product(s) were investigated by ESI/MS (Fig. S1†). The ESI/MS of the product solution exhibits a predominant peak at  $m/z$  275.6, which can be assigned to  $[\text{Os}(\text{L})(\text{CN})_4]^{2-}$ , and this peak shifted to  $m/z$  276.1 when the  $^{15}\text{N}$ -labeled nitrido complex ( $\text{NO}_2\text{-Os}^{15}\text{N}$ ) was used, indicating that the extra  $\text{CN}^-$  is derived from the addition of the fragmented  $\text{CH}_3$  group to the nitrido ligand, followed by internal redox (see the Proposed mechanism section below). The ESI/MS also shows a major peak at  $m/z$  659, which is assigned to the amidine product  $[\text{Os}(\text{L})(\text{CN})_3(\text{NH}=\text{DMA}_{(-2\text{H})})]^-$  (2), see Fig. S1†.

An attempt to isolate complex 1 by extracting the product residue with  $\text{H}_2\text{O}$  followed by the addition of  $\text{PPh}_4\text{Cl}$  resulted in a  $\text{PPh}_4^+$  salt of  $[\text{Os}^{\text{II}}(\text{L})(\text{CN})_4]^{3-}$  (1) mixed with a small amount of  $[\text{Os}^{\text{III}}(\text{L})(\text{CN})_4]^{2-}$  (1'). However, pure  $(\text{PPh}_4)_2\text{1}$  could be isolated as a dark red microcrystalline solid in ca. 68% yield by slow evaporation of a  $\text{MeOH}/\text{H}_2\text{O}$  solution of the mixture under air. Both 1 and 1' show the same peak at  $m/z$  275.6 in ESI/MS. On the other hand, complex 2 could be readily separated from the reaction mixture by column chromatography and isolated as the  $\text{PPh}_4^+$  or  $^n\text{Bu}_4\text{N}^+$  salt in ca. 16% yield.  $(\text{PPh}_4)_2\text{1}$  and  $(\text{PPh}_4)_2\text{2}$  were characterized by IR, UV/vis, cyclic voltammetry (CV) and ESI/MS (Fig. S2–S6†). The IR spectrum of 1' shows three  $\nu(\text{C}\equiv\text{N})$  stretches at 2085, 2038 and 1995  $\text{cm}^{-1}$ , while that of 2 shows two  $\nu(\text{C}\equiv\text{N})$  stretches at 2113 and 2088  $\text{cm}^{-1}$ .

*N*-Dealkylation also occurs in the reactions of  $\text{NO}_2\text{-OsN}^*$  with *N,N*-diethylaniline (DEA) and *N,N*-diisopropylaniline (DPA), resulting in 87% of *N*-ethylaniline and 91% of *N*-isopropylaniline, respectively. Similar to the case of DMA, the fragmented alkyl groups in DEA and DPA are attached to the nitrido ligand, followed by internal redox to give  $[\text{Os}^{\text{III}}(\text{L})(\text{CN})_3(\text{N}\equiv\text{CCH}_3)]^-$  (3) and  $[\text{Os}^{\text{IV}}(\text{L})(\text{CN})_3(\text{N}=\text{C}(\text{CH}_3)_2)]^-$  (4), respectively. 3 and 4 were

isolated as the  $\text{PPh}_4^+$  salts in 80% and 82% yields, respectively, and they were characterized by IR, UV/vis, ESI/MS and  $^1\text{H}$  NMR (Fig. S7–S9†). Besides the aromatic tertiary amines, dealkylation of the aliphatic tertiary amine  $\text{Et}_3\text{N}$  by  $\text{NO}_2\text{-OsN}^*$  was also found, with diethylamine formed in 72% yield. In contrast to the case of DMA, <2% of amidine products were found for DEA and  $\text{Et}_3\text{N}$  reactions, while no amidine product was found for DPA reaction. The UV/vis and ESI/MS collected at various time intervals for these photochemical reactions are summarized in Fig. S10 and S11.†

The molecular structures of  $(^n\text{Bu}_4\text{N})_2$ ,  $(\text{PPh}_4)_3$  and  $(\text{PPh}_4)_4$  were determined by X-ray crystallography. As shown in Fig. 3a, the Os center in 2 is 6-coordinated by three  $\text{CN}^-$  ligands, a bidentate  $\text{O}^-\text{N}$  ligand and a neutral amidine ligand in a distorted octahedral geometry. The Os–N6 bond length is 2.048(4) Å and the Os–N6–C17 bond angle is 126.3(3)°, consistent with a neutral amidine ligand. The C17–N6 (1.276(6) Å) and C17–N7 (1.338(6) Å) bond distances, and the N6–C17–N7 bond angle (127.8(5)°) are similar to those of reported amidine complexes.<sup>9</sup> In 3, the Os–N5 and N5–C17 bond lengths of 2.017(4) and 1.135(7) Å, respectively, and the close to linear Os1–N5–C17 bond angle of 172.0(4)° are consistent with a neutral  $\text{CH}_3\text{CN}$  ligand. Complex 4 features an anionic iminato ligand; the Os–N5 bond length is 1.849(9) Å, indicating a double bond character. The C5–N17 bond is 1.187(13) Å, typical of the  $\text{C}=\text{N}$  double bond.

Quenching of the excited state of  $\text{NO}_2\text{-OsN}$  by *N,N*-dimethylaniline (DMA) and *N,N*-diethylaniline (DEA) in  $\text{CH}_2\text{Cl}_2$  was investigated. The bimolecular quenching rate constants ( $k_q$ ) obtained from Stern–Volmer plots are  $(8.5 \pm 0.1) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$  and  $(9.2 \pm 0.3) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ , respectively for DMA and DEA (Fig. 4a).  $k_q$  for  $\text{d}^6\text{-DMA}$  is  $(9.0 \pm 0.1) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ , indicating that there is no deuterium isotope effect. The observed near diffusion-controlled rate constants are consistent with the high excited state redox potential of  $\text{NO}_2\text{-OsN}$  (ca. 1.4 V vs. NHE).<sup>4a</sup> Upon excitation of a mixture of  $\text{NO}_2\text{-OsN}$  and DMA in  $\text{CH}_2\text{Cl}_2$ , a band at ca. 460 nm was observed in the nanosecond transient absorption (ns-TA) spectrum (Fig. 4b), which is similar to that of the  $\text{DMA}^{+\bullet}$  cation radical,<sup>10</sup> indicating one-electron oxidation of DMA by  $\text{NO}_2\text{-OsN}^*$ .

The electronic effects of various *para*-substituents on the aromatic ring of DMA have been investigated by the method of initial rates ( $R_x$ ), which were obtained from the UV/vis spectral changes of the photoreactions of  $\text{NO}_2\text{-OsN}$  with various DMAs (Fig. S12†). The rates were found to be accelerated by electron

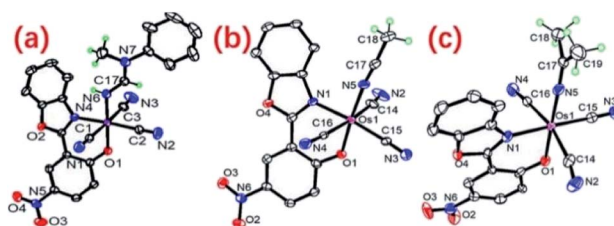


Fig. 3 Molecular structures of 2 (a), 3 (b) and 4 (c). Cations were omitted for simplicity.



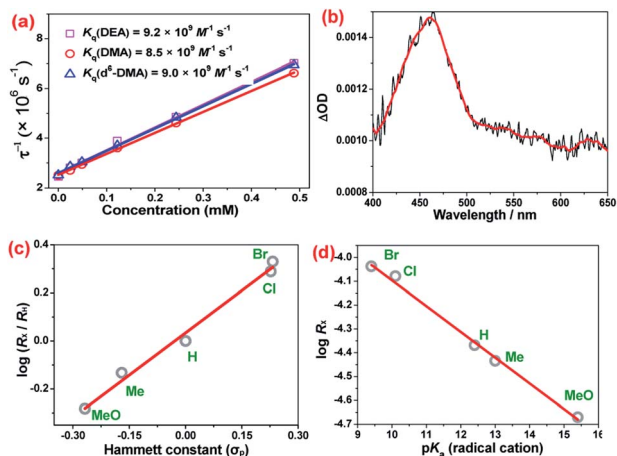


Fig. 4 (a) Stern–Volmer plots for the quenching of  $\text{NO}_2\text{-OsN}^*$  ( $2.46 \times 10^{-5} \text{ M}$ ) by DEA, DMA and  $\text{d}^6\text{-DMA}$ . (b) ns-Transient absorption spectrum of DMA taken immediately after 355 nm laser excitation. (c) Hammett plot of  $\sigma_p$  versus the relative initial rates  $\log(R_x/R_H)$  ( $y$ -intercept =  $0.03 \pm 0.01$ ; slope =  $1.17 \pm 0.06$ ;  $r^2 = 0.989$ ). (d) Plot of  $\log(R_x)$  vs.  $\text{p}K_a$  for the radical cation of  $\text{para}$ -substituted DMAs ( $y$ -intercept =  $-3.01 \pm 0.08$ ; slope =  $-(1.08 \pm 0.06) \times 10^{-1}$ ;  $r^2 = 0.992$ ).

withdrawing groups, and the Hammett plot of  $\log(R_x/R_H)$  versus  $\sigma_p$  is linear with a positive  $\rho$  value of 1.17 (Fig. 4c). A linear relationship supports a common transition state (TS)/mechanism for the series of reactants, and a positive  $\rho$  value indicates that the TS is stabilized by electron-withdrawing substituents. A linear plot was also found for  $\log(R_x)$  vs.  $\text{p}K_a$  of the radical cations of the DMAs (Fig. 4d and Table S2†).<sup>11</sup> These results are consistent with proton transfer from  $\text{DMA}^{+\cdot}$  to  $\text{NO}_2\text{-Os}^{\text{V}}\text{N}$  in the rate-limiting step, since the acidity of  $\text{DMA}^{+\cdot}$  is enhanced by electron-withdrawing substituents.<sup>12</sup> The photoreaction of  $\text{NO}_2\text{-OsN}^*$  with  $N$ -ethyl- $N$ -methylaniline was also studied. The result shows that the  $N$ -demethylation product (72%) is greatly favored over that of  $N$ -deethylation (4%) (Fig. S13†), which further supports proton transfer as the rate-limiting step, since the acidity of the methyl proton in the radical cation is higher than that of the ethyl protons.<sup>13</sup>

The kinetic isotope effects (KIE) for the  $N$ -dealkylation reaction of DMA by  $\text{NO}_2\text{-OsN}^*$  were determined. Inter-molecular KIE was obtained by competition experiments using equimolar  $\text{C}_6\text{H}_5\text{N}(\text{CH}_3)_2$  and  $\text{C}_6\text{H}_5\text{N}(\text{CD}_3)_2$  as the substrate (Fig. S14†). A KIE value of  $4.0 \pm 0.5$  was obtained from analysis of the products  $\text{C}_6\text{H}_5\text{NHCH}_3$  and  $\text{C}_6\text{H}_5\text{NHCD}_3$  by GC/FID and GC/MS. The inter-molecular KIE for amidine formation was also investigated by analysis of the products by ESI/MS, and a KIE of  $\sim 4.5$  was estimated from the ratio of the most intense peaks at  $m/z$  659 and  $m/z$  664 for the protio- and deuterio-osmium(IV) amidine species, respectively, assuming that the spraying and ionization efficiencies of the two ions are similar (Fig. S15†). Intra-molecular KIE was also determined by using 4- $\text{BrC}_6\text{H}_4\text{-N}(\text{CH}_3)(\text{CD}_3)$  as the substrate and a KIE value of  $4.9 \pm 0.5$  was obtained from analysis of the products 4- $\text{BrC}_6\text{H}_5\text{NHCH}_3$  and 4- $\text{BrC}_6\text{H}_5\text{NHCD}_3$  (Fig. S16†). Similar KIE values for the  $N$ -dealkylation and amidine formation suggest that these two pathways occur *via* a common intermediate.

## Proposed mechanism

The experimental results are consistent with an ET/PT mechanism in the  $N$ -dealkylation of various tertiary amines with  $\text{NO}_2\text{-OsN}^*$ , as shown in Fig. 5 using DMA as an example. The first step is electron transfer from DMA to  $\text{NO}_2\text{-OsN}^*$  to generate  $\text{DMA}^{+\cdot}$  and  $\text{NO}_2\text{-Os}^{\text{V}}\text{N}$ , which occurs at the near diffusion-controlled rate. This step is supported by the observation of the transient  $\text{DMA}^{+\cdot}$  species. Rate-limiting proton transfer then occurs from  $\text{DMA}^{+\cdot}$  to  $\text{NO}_2\text{-Os}^{\text{V}}\text{N}$ , followed by rapid  $N$ -rebound to give an osmium(IV) amido intermediate, a species that is analogous to the carbinolamine species proposed in cytochrome  $\text{P}_{450}$  catalyzed  $N$ -dealkylation of amines,<sup>6</sup> except that in this case the intermediate amide remains bound to the metal center. The rate-limiting proton transfer step is supported by a large KIE of 4.5, a +ve Hammett  $\rho$  value of 1.17, a linear dependence of  $\log(R_x)$  on  $\text{p}K_a$  and a high preference for  $N$ -demethylation over  $N$ -deethylation in the photoreaction of  $N$ -ethyl- $N$ -methylaniline. The osmium(IV) amido species further decomposes *via* two parallel pathways. In pathway A, spontaneous C–N cleavage occurs to give the dealkylated product  $N$ -methylaniline and an Os(IV) iminato complex, the latter species then undergoes internal redox to afford **1**. In pathway B, the osmium(IV) amido intermediate undergoes H-atom abstraction by another  $\text{NO}_2\text{-OsN}^*$  followed by internal redox to give the osmium(III) amidine product. This proposed step is supported by the observed formation of around 1/3 equiv. of  $\text{NO}_2\text{-Os}^{\text{III}}\text{NH}_3$ :  $\text{NO}_2\text{-Os}^{\text{V}}\text{N} + 3\text{H} \rightarrow \text{NO}_2\text{-Os}^{\text{III}}\text{NH}_3$ , by UV-vis spectrophotometry. We and others have previously shown that  $\text{Os} \equiv \text{N}$  readily abstracts H-atoms from various substrates to give the ammine complex  $\text{Os}^{\text{III}}\text{-NH}_3$ .<sup>4a,14</sup> Similar mechanisms are proposed for

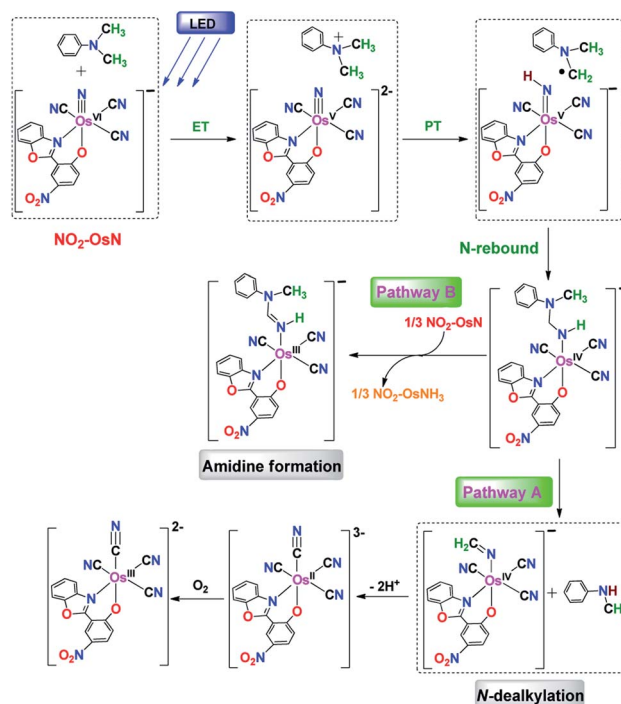


Fig. 5 Proposed mechanism for the reaction of  $\text{NO}_2\text{-OsN}^*$  with DMA.



the other substrates (Fig. S17–S19†). Pathway B is much less significant for the other substrates as it does not result in a stable, conjugated amidine ligand as 2.

## DFT calculations

Our proposed mechanism for the oxidative dealkylation of tertiary amines by  $\text{NO}_2\text{-OsN}$  is also supported by DFT calculations (see ESI, Computational details†). The potential energy surface for the reaction of  $\text{NO}_2\text{-Os}^{\text{V}}\text{N}$  with  $\text{DMA}^+$ , that is generated from electron transfer between  $\text{DMA}$  and  $\text{NO}_2\text{-OsN}^*$ , is shown in Fig. 6; and insets are the structures of the intermediates and transition states.  $^3\text{INT1}$  is formed by binding  $\text{NO}_2\text{-Os}^{\text{V}}\text{N}$  with  $\text{DMA}^+$  via a weak hydrogen bond. A rapid proton transfer from  $\text{DMA}^+$  to  $\text{NO}_2\text{-Os}^{\text{V}}\text{N}$  occurs via  $^3\text{TS1}$  with a barrier height ( $\Delta G_{298}^\ddagger$ ) of  $9.8 \text{ kcal mol}^{-1}$ , with a simultaneous N-rebound step to generate a stable Os(IV) amido intermediate ( $^3\text{INT2}$ ). The Os–N bond is elongated from  $1.739 \text{ \AA}$  in  $^3\text{INT1}$  to  $1.766 \text{ \AA}$  in  $^3\text{TS1}$  to  $1.923 \text{ \AA}$  in  $^3\text{INT2}$ . This is followed by a second proton transfer step from Os(IV) amido to the nitrogen of aniline via  $^3\text{TS2}$  ( $\Delta G_{298}^\ddagger = -1.8 \text{ kcal mol}^{-1}$ ) to give an osmium(IV) species ( $^3\text{INT3}$ ) via  $^3\text{TS2}$  with a four-member-ring structure. The weak  $\text{HN}\dots\text{CH}_2$  bond ( $\sim 1.581 \text{ \AA}$ ) in  $^3\text{INT3}$  is then broken to afford the products *N*-methylaniline and osmium(IV) iminato species ( $^3\text{INT4}$ ) via  $^3\text{TS3}$ ; this step is almost barrierless ( $0.1 \text{ kcal mol}^{-1}$  relative to  $^3\text{INT3}$ ). Based on our calculations, the rate-determining step is the simultaneous proton transfer and N-rebound step via  $\text{TS1}$ .

In conclusion, we have shown that the strongly luminescent osmium(VI) nitrido complex  $[\text{Os}^{\text{VI}}(\text{N})(\text{L})(\text{CN})_3]^-$  undergoes facile *N*-dealkylation of aromatic and aliphatic tertiary amines upon irradiation with visible light. We have provided definitive evidence that these reactions occur via an ET/PT mechanism. Our results should contribute to a significant advance in metal nitrido chemistry.

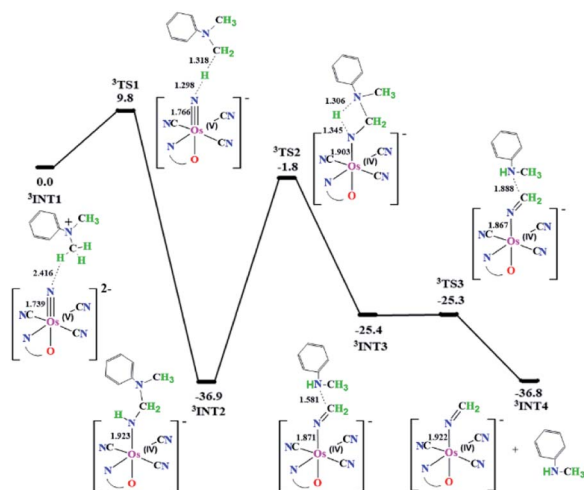


Fig. 6 The potential energy surface for *N*-dealkylation of  $\text{DMA}^+$  by  $[\text{Os}^{\text{V}}(\text{N})(\text{CN})_3(\text{L})]^{2-}$  in  $\text{CH}_3\text{CN}$  at the B3LYP–D3(BJ)/def2-TZVP level with the PCM solvent effect. Relative 298 K Gibbs free energies in acetonitrile are given in  $\text{kcal mol}^{-1}$ . Bond lengths are in angstrom ( $\text{\AA}$ ).

## Data availability

The datasets supporting this article have been uploaded as part of the ESI.†

## Author contributions

J. X. and T.-C. L. designed the experiments, analysed the data and wrote the manuscript. S. M. Y. and W.-L. M. solved the X-ray structures. S.-C. C. and C.-C. K investigated the photophysical properties. M. P., L. J. L. and X. X. J. carried out experiments and analysed the data. Y. P. and K. C. L. did the DFT calculations.

## Conflicts of interest

There are no conflicts to declare.

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