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Oxidation of phenols by the excited state of an osmium(vi) nitrido complex†

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The photoreaction of an osmium(vi) nitrido complex, $[\text{Os}^{\text{VI}}(\text{N})(\text{L})(\text{CN})_3]^-$ (**OsN**), with various phenols has been investigated. Upon irradiation of **OsN** with visible light, the excited state (**OsN***) is generated which reacts readily with a variety of phenols. **OsN*** reacts with mono- and di-substituted phenols, including 2,6-dimethylphenol, 2,6-dichlorophenol and 4-methylphenol to afford the corresponding osmium(II) benzoquinone monoimine and osmium(IV) benzoquinone monoiminato complexes. On the other hand, in the reactions of **OsN*** with bulky tri-substituted phenol such as 2,4,6-tri-*tert*-butylphenol, C–C bond cleavage occurred and $[\text{Os}^{\text{IV}}(\text{L})(\text{CN})_3(\text{N}=\text{fBu}_2\text{Ph}_{(-2\text{H})}\text{O})]^-$ was formed as the major product. The electronic effects of various *para*-substituents (X) on the oxidation of phenols were investigated by the method of initial rates (R_x). A Hammett plot of $\log(R_x/R_{\text{H}})$ versus σ_p is linear with a ρ value of -0.54 . A linear correlation of $\log(R_x)$ with the oxidation potentials (E) of phenols was also found with a slope of -0.80 . On the other hand, no correlations were found between $\log(R_x)$ and O–H bond dissociation energy (BDE), as well as the $\text{p}K_{\text{a}}$ of phenols. The oxidation of phenols by **OsN*** exhibits a negligible kinetic isotope effect (KIE), $k(\text{C}_6\text{H}_5\text{OH})/k(\text{C}_6\text{D}_5\text{OD}) \sim 1$. These results are consistent with a mechanism that involves an initial 1e^- oxidation of the phenol followed by rapid proton transfer (ET-PT) to generate a phenoxy radical, this is followed by a N-rebound step to give the osmium products.

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Introduction

Transition metal nitrido ($\text{M}\equiv\text{N}$) complexes are intermediates in N_2 fixation and potentially useful reagents for the nitrogenation of organic substrates.^{1,2} Compared to metal oxo ($\text{M}=\text{O}$) species, there are relatively few nitrido complexes that are reactive towards common organic substrates. Examples include osmium(vi) nitrido complexes containing various N-based ligands such as 2,2'-bipyridine (bpy), 2,2':6',2''-terpyridine (tpy), and tris(1-pyrazolyl)methane (tpm); they are highly electrophilic and readily undergo N-atom transfer to a variety of organic substrates.³ Moreover, Ru(vi) nitrido complexes bearing salen type ligands, such as $[\text{Ru}^{\text{VI}}(\text{N})(\text{salchda})(\text{CH}_3\text{OH})]^+$ (**RuN**, salchda = *N,N'*-bis(salicylidene)-*o*-cyclohexyldiamine dianion),⁴ and several iron(v/iv)⁵ and Mn(v/vi)⁶ nitrido

complexes are also highly reactive species that are capable of oxidizing various organic substrates.

The oxidation of phenols to quinones by various oxidants has been extensively studied, mainly because such reactions are relevant to many biological processes.^{7–13} Phenols can be oxidized by various pathways (Fig. 1), the most common one is initial 1e^- oxidation resulting in the formation phenoxy radicals, which is followed by rapid loss of the phenolic proton (consecutive electron transfer-proton transfer, ET-PT). Further rapid loss of $1\text{e}^- + 1\text{H}^+$ results in the formation of quinones.^{14,15} On the other hand, oxidation of phenols by some metal oxo species may involve an H-atom transfer mechanism (or concerted ET-PT).^{16–22} Oxidation *via* an initial electrophilic attack on the aromatic ring of phenol has also been reported for a ruthenium(IV) species.^{23,24}

Prior to this work, there was only one example on oxidation of phenols by a metal nitrido species. **RuN** readily reacts with phenols in the presence of pyridine to afford (salchda)ruthenium(II) *p*-benzoquinone imine complexes.²⁵ The reactions were proposed to proceed *via* an initial electrophilic attack by **RuN** at the aromatic ring of phenols.

In an attempt to design a highly active metal nitrido complex, we turned our attention to the excited state chemistry of $\text{M}\equiv\text{N}$. We reported recently the synthesis of a highly luminescent Os(vi) nitrido complex, $[\text{Os}^{\text{VI}}(\text{N})(\text{L})(\text{CN})_3]^-$

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(a) Possible reaction pathways for phenol oxidation

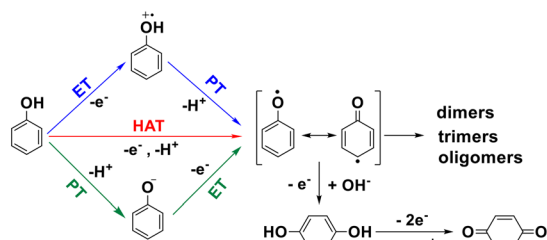
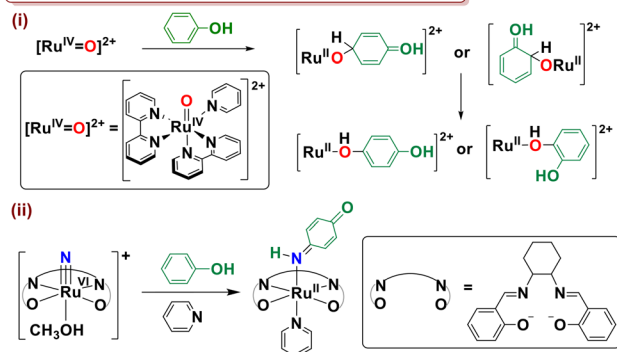
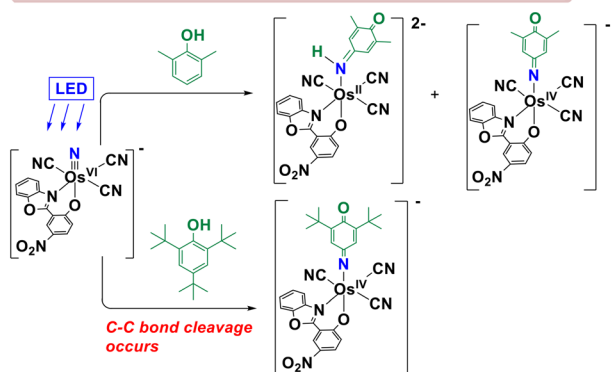
(b) Electrophilic attack by (i) Ru^{IV}O and (ii) Ru^{VI}N(c) This work: phenol oxidation by the excited state of Os^{VI}N

Fig. 1 Oxidation pathways of phenols by oxidants.

(OsN, HL = 2-(2-hydroxy-5-nitrophenyl)benzoxazole);^{26–33} OsN is highly luminescent in both solid state and fluid solution (solid state: $\lambda_{em} = 591$ nm, $\phi = 11.7\%$, $\tau = 1.90$ μ s; in degassed CH₂Cl₂: $\lambda_{em} = 594$ nm, $\phi = 3.0\%$, $\tau = 0.48$ μ s). The CV of OsN shows an irreversible oxidation wave at $E_{pa} = 1.88$ V and an irreversible reduction wave at $E_{pa} = -0.99$ V vs. Saturated Calomel Electrode (SCE), which are tentatively assigned as the metal-centered Os^{VII/VI} and Os^{VI/V} process, respectively. The excited state (OsN*) of this complex is readily generated by visible light irradiation ($\lambda > 460$ nm). OsN* was found to be highly oxidizing and it reacts readily with various organic substrates, including alkanes, arenes, amines, alcohols, and dihydroxybenzenes.^{26–33}

Herein, we reported the oxidation of phenols by OsN*. These reactions have a number of unusual/novel features. In contrast to the oxidation of phenols by RuN, which occurs *via*

an electrophilic ring attack mechanism, oxidation by OsN* occurs by an ET-PT followed by an N-rebound mechanism. Similar to oxidation by RuN, oxidation of various mono- and di-substituted phenols by OsN* produced the corresponding osmium(II) benzoquinone imine complexes. However, because OsN* is a powerful oxidant, further oxidation of the osmium(II) products by OsN* occur to afford novel osmium(IV) iminato complexes as a second product. Moreover, oxidation of tri-substituted phenol such as 2,4,6-*t*-Bu₃C₆H₂OH results in C–C bond cleavage of the substrate.

Results and discussion

Upon irradiation with blue LED ($\lambda > 460$ nm) for 24 h, the light-yellow CH₂Cl₂ solution of OsN and 10 equiv. of 2,4,6-Me₃C₆H₂OH rapidly turned dark red (Fig. 2). A mixture of the osmium(II) *p*-benzoquinone monoimine complex [Os^{II}(L)(CN)₃(NH=Me₂Ph_(-2H)=O)]²⁻ (**1a**) and osmium(IV) *p*-benzoquinone monoiminato complex [Os^{IV}(L)(CN)₃(N=Me₂Ph_(-2H)=O)]⁻ (**1b**), were isolated as PPh₄⁺ salts with 20% and 26% yields, respectively. Similarly, the photo-reaction of OsN with 2,6-Cl₂C₆H₃OH afforded a mixture of (PPh₄)₂[Os^{II}(L)(CN)₃(NH=Cl₂Ph_(-2H)=O)] [(PPh₄)₂**2a**] and (PPh₄)₂[Os^{IV}(L)(CN)₃(N=Cl₂Ph_(-2H)=O)] [(PPh₄)₂**2b**] with 32% and 25% yields, respectively. In addition, (PPh₄)₂[Os^{II}(L)(CN)₃(NH₃)] (OsNH₃)²⁸ was isolated with ~10% yield in reactions with these phenols. Controlled experiments showed that

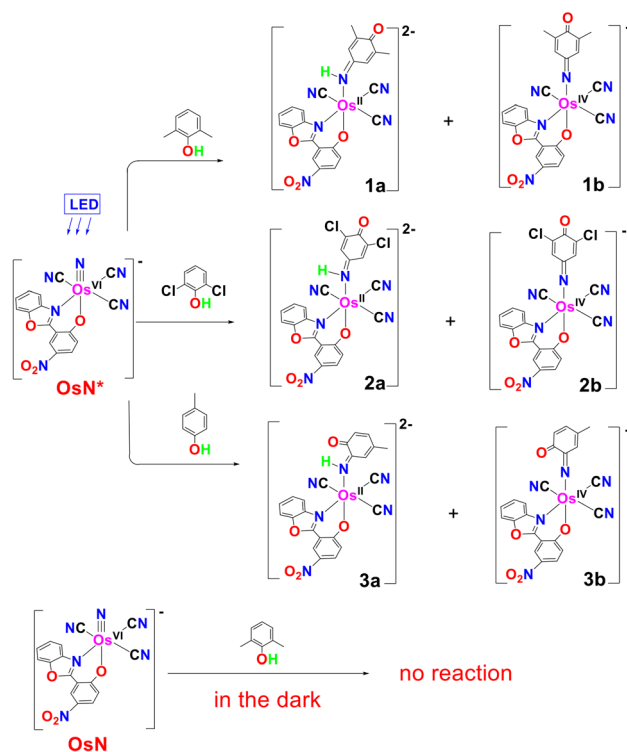


Fig. 2 Reactions of OsN with various phenols in the excited state and ground state.



no reaction between **OsN** and phenols was observed in the dark.

On the other hand, in the photoreaction with 4-methylphenol, **OsN** undergoes electrophilic attack at the *ortho* position to afford an $[\text{PPh}_4]_2[\text{Os}^{\text{II}}(\text{L})(\text{CN})_3(o\text{-NH}=\text{MePh}_{(-2\text{H})}=\text{O})]$ [**(PPh₄)₂3a**] and $[\text{PPh}_4][\text{Os}^{\text{IV}}(\text{L})(\text{CN})_3(o\text{-N}=\text{MePh}_{(-2\text{H})}=\text{O})]$ [**(PPh₄)₃b**], with yields of 37% and 32%, respectively.

The photoreactions of **OsN** with 2,4,6-tri-*tert*-butylphenol and 2,4,6-tri-methylphenol were also investigated (Fig. 3); for these substrates with three alkyl substituents, direct electrophilic attack on the aromatic ring by **OsN*** may be inhibited. Reaction of **OsN*** with 2,4,6-*t*-Bu₃C₆H₂OH afforded $[\text{Os}^{\text{IV}}(\text{L})(\text{CN})_3(p\text{-N}=\text{tBu}_2\text{Ph}_{(-2\text{H})}=\text{O})]^-$ (**4a**), isolated as PPh_4^+ salt with ~52% yield. The structure of **4a** (see characterization below) reveals formal C–C bond cleavage of 2,4,6-*t*-Bu₃C₆H₂OH; GC/MS and GC show that the 2-methylpropene was formed with ~50% yield. ¹H NMR spectrum of **(PPh₄)₄a** shows that the remaining two *t*Bu groups are symmetry-related, consistent with the *para* attack of 2,4,6-*t*-Bu₃C₆H₂OH by **OsN***. ESI/MS (–ve mode) of the photoreaction solution of **OsN** and 2,4,6-*t*-Bu₃C₆H₂OH shows a predominant peak at *m/z* 743 (Fig. 4), attributed to $[\text{Os}^{\text{IV}}(\text{L})(\text{CN})_3(p\text{-N}=\text{tBu}_2\text{Ph}_{(-2\text{H})}=\text{O})]^-$ (**4a**). There is also a very minor peak at *m/z* 801, (estimated to be 5%), which is tentatively assigned to $[\text{Os}^{\text{IV}}(\text{L})(\text{CN})_3(\text{NH}=\text{tBu}_3\text{Ph}_{(-2\text{H})}=\text{O})]^-$ (**4b**), arising from an electrophilic attack of **OsN** at the *para* position of the phenol.

In the case of 2,4,6-Me₃C₆H₂OH with less bulky methyl substituents, electrophilic ring attack by **OsN*** occurred predominantly at the *para* position, and the amido complex, $[\text{Os}^{\text{IV}}(\text{L})(\text{CN})_3(\text{NH}(\text{Me}_3\text{Ph}_{(-2\text{H})}=\text{O}))]^-$ (**5**), was isolated as PPh_4^+ salt with ~75% yield. The ESI/MS (–ve mode) of the product solution shows a predominant peak at *m/z* = 675 due to complex **5**. In addition, there are two minor peaks at *m/z* 659.1 and 275.6, which are tentatively assigned to **1b** and $[\text{Os}^{\text{II}}(\text{L})(\text{CN})_4]^{3-}$, respectively. These two species should arise from C–C bond cleavage of 2,4,6-Me₃C₆H₂OH; however, the total yields of these two products are estimated to be <5%.

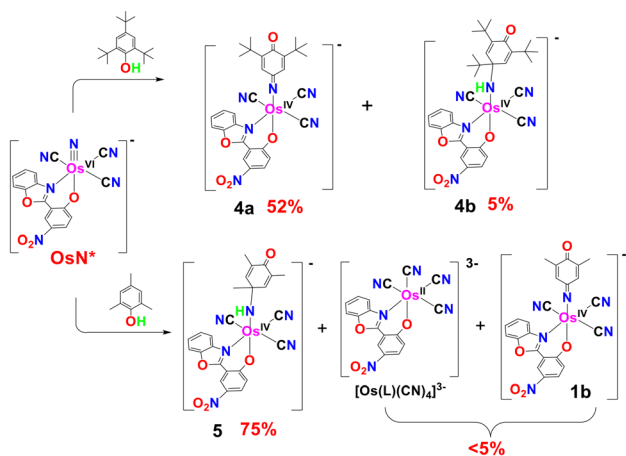


Fig. 3 Photoreaction of **OsN** with 2,4,6-*t*-Bu₃C₆H₂OH and 2,4,6-Me₃C₆H₂OH.

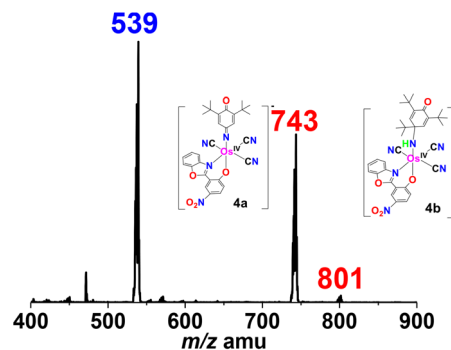


Fig. 4 ESI/MS of photoreaction of **OsN** with 10 equiv. 2,4,6-*t*-Bu₃C₆H₂OH for 4 h showing a predominant peak at *m/z* 743 and a small peak at *m/z* 801.

All products have been characterized by IR, UV/vis, CV, ESI/MS, and ¹H NMR (Fig. S1–S12†). All the Os(II) and Os(IV) compounds are diamagnetic, as evidenced by the sharp resonances found in the normal range in their ¹H NMR spectra. The diamagnetism of these compounds is consistent with the low spin d⁶ and d⁴ electronic configurations for Os(II) and Os(IV), respectively. The IR spectra of **(PPh₄)₂1a** and **(PPh₄)₂2a** show $\nu(\text{C}\equiv\text{N})$ stretches at 2096, 2070 cm⁻¹ and 2108, 2082 cm⁻¹, and $\nu(\text{C}=\text{O})$ stretches at 1609 cm⁻¹ and 1610 cm⁻¹, respectively. The IR spectra of **(PPh₄)₁b** and **(PPh₄)₂b** show $\nu(\text{C}\equiv\text{N})$ stretches at 2145, 2134 cm⁻¹ and 2153, 2142 cm⁻¹, and $\nu(\text{C}=\text{O})$ stretches at 1629 cm⁻¹ and 1639 cm⁻¹, respectively which are at higher wavenumbers as compared with **(PPh₄)₂1a** and **(PPh₄)₂2a**. Similar $\nu(\text{C}\equiv\text{N})$ and $\nu(\text{C}=\text{O})$ stretches are also found in **(PPh₄)₂3a** and **(PPh₄)₃b**.

As shown in Fig. S6,† the UV/vis spectra of these compounds show ligand-centered $\pi\text{-}\pi^*$ transitions in the UV regions. In the osmium(II) products **(PPh₄)₂1a**, **(PPh₄)₂2a**, and **(PPh₄)₂3a**, there are strong absorption bands at 500–650 nm with molar extinction coefficients (ϵ) of the order of 10⁴ M⁻¹ cm⁻¹, which are assigned to Os(II) to *p*-benzoquinone monoimine charge transfer (MLCT) transitions. Notably, there is an intense absorption band with $\epsilon > 6 \times 10^4$ M⁻¹ cm⁻¹ in **(PPh₄)₂2a**. In the osmium(IV) products **(PPh₄)₁b**, **(PPh₄)₂b** and **(PPh₄)₃b**, the broad absorption bands at ~450 nm are probably due to LMCT transitions.

The cyclic voltammograms (CVs) of the osmium complexes **(PPh₄)₂1a**, **(PPh₄)₂2a**, and **(PPh₄)₂3a** in CH₃CN exhibit a reversible/quasi-reversible Os^{III/II} couples at –0.67 V, –0.38 V and –0.78 V vs. Fc⁺⁰, respectively (Fig. 5). There is also an irreversible wave at $E_{\text{pc}} = -1.46$ V, –1.35 V and –1.72 V, respectively which are tentatively assigned to the reduction of the benzoquinone imine ligands. The oxidation waves at $E_{1/2} = 1.25$ V, $E_{\text{pc}} = 1.46$ V and 1.23 V, respectively, are assigned to Os^{IV/III}. The CVs of the osmium(IV) products **1b**, **2b** and **3b** exhibit irreversible Os^{IV/III} waves at $E_{\text{p}} = -0.65$ V, –0.39 V and –0.66 V, respectively (Fig. 6); while the waves at $E_{\text{p}} = -1.61$ V, –1.35 V and –1.49 V, respectively are tentatively assigned to the reduction of benzoquinone imine ligands.



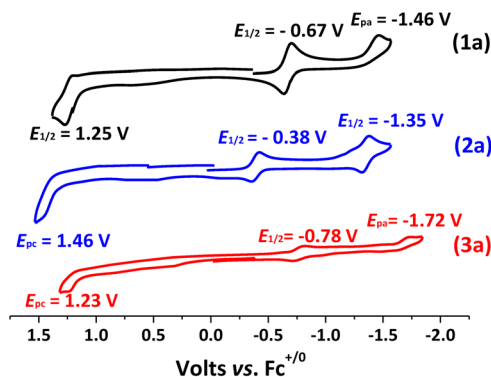


Fig. 5 CVs for 1a, 2a, and 3a in MeCN solutions containing 0.1 M $[t\text{Bu}_4\text{N}](\text{PF}_6)$ with a scan rate = 0.1 V s^{-1} .

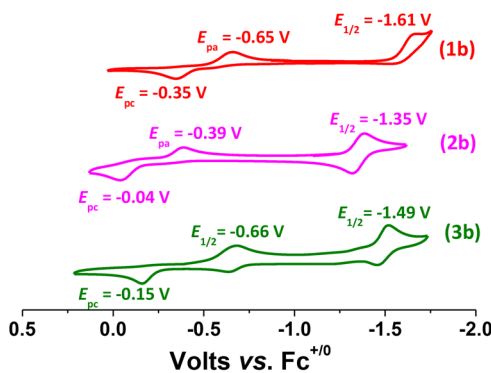


Fig. 6 CVs for 1b, 2b, and 3b in MeCN solutions containing 0.1 M $[t\text{Bu}_4\text{N}](\text{PF}_6)$ with a scan rate = 0.1 V s^{-1} .

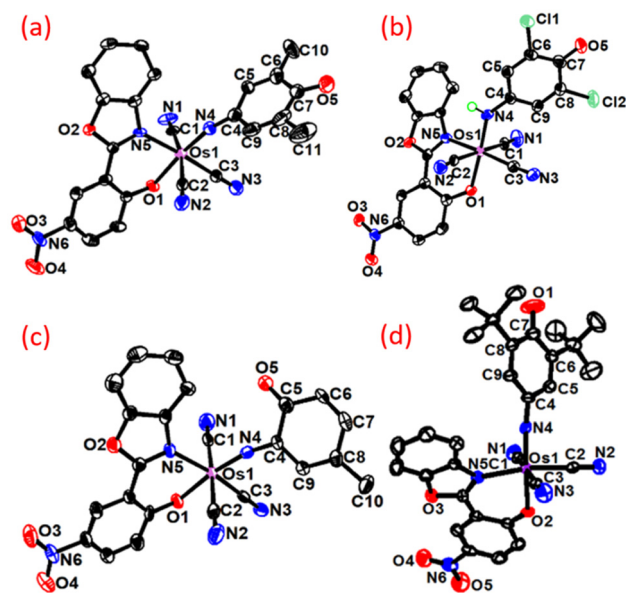


Fig. 7 The structures of (a) 1b, (b) 2a, (c) 3b and (d) 4a.

Table 1 Selected bond parameters (\AA , $^\circ$) for 1b, 2a, 3b and 4a

	1b	2a	3b	4a
Os1–C1	2.074 (5)	2.053 (4)	2.082 (5)	2.081(5)
Os1–C2	2.077 (5)	2.070 (4)	2.081 (5)	2.029(4)
Os1–C3	2.025 (5)	2.009 (4)	2.034 (6)	2.066(5)
Os1–N4	1.781 (4)	1.927 (3)	1.768 (4)	1.779(4)
Os1–N5	2.117 (4)	2.129 (3)	2.118 (4)	2.115(3)
Os1–O1	2.010 (3)	2.066 (3)	2.028 (3)	—
Os1–O2	—	—	—	2.022(3)
Os1–N4–C4	167.2 (4)	136.6 (3)	167.9 (5)	163.8(3)

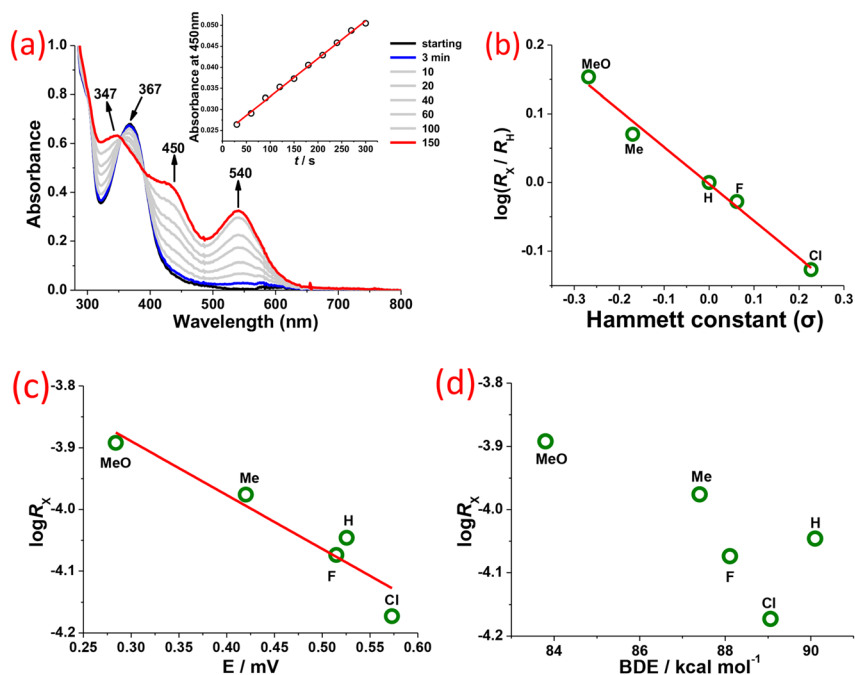


Fig. 8 (a) UV/vis spectral changes for the photoreaction of OsN ($2.5 \times 10^{-5} \text{ M}$) with phenol ($1.8 \times 10^{-3} \text{ M}$) in $\text{C}_2\text{H}_4\text{Cl}_2$. Inset shows the time-trace absorbance at 450 nm. (b) Hammett plot for the photoreaction of OsN with 4-substituted phenols in $\text{C}_2\text{H}_4\text{Cl}_2$. Slope = -0.54 . Intercept = -0.00217 . (c) Plot of $\log(R_x)$ vs. E^{ox} . (d) Plot of $\log(R_x)$ vs. BDE.



The molecular structures of **(PPh₄)1b**, **(PPh₄)₂2a**, **(PPh₄)3b**, and **(PPh₄)4a** have been determined by X-ray crystallography (Fig. 7). Selected bond parameters are summarized in Table 1. The *mer*-configuration of OsN is retained in these complexes. There are two PPh₄⁺ in **2a** and only one PPh₄⁺ in **1b** and **3b**. The Os–N4 bond length in **2a** is 1.927(3) Å, which is significantly shorter than related Os–N bond lengths in [Os^{III}{N(H)C(NH₂)}(L¹)(CN)₃][−] and [Os^{III}{N(H)CN}(L¹)(CN)₃]^{2−} (HL¹ = 2-(2-hydroxyphenyl)benzoxazole),^{32,33} indicating the presence of strong π back-bonding interaction between Os^{II} and the benzoquinone monoimine ligand. On the other hand, the Os–N4 bond lengths are 1.781(4) and 1.768(4) Å, respectively for **1b** and **3b**, which are much shorter than that in **2a**, indicating Os–N double bond character in these Os(IV) complexes. This is also evidenced by the more linear Os1–N4–C4 bond angles of 167.2(4)° and 167.9(5)° than that in **2a** (136.6(3)°). The bond parameters of **3b** and **4a** are essentially identical to those in **1b**, as the metal centers have the same oxidation state.

Substituent effects

The photoreactions of OsN with various 4-substituted phenols (4-X-C₆H₄OH; X = MeO, Me, H, F, Cl) were also investigated by UV/vis spectroscopy (Fig. S10†). The initial rates (R_x) of these reactions were obtained at 450 nm (Fig. 8a). R_x was found to increase with increasing electron donating properties of the substituents: MeO > Me > H > F > Cl. A linear correlation was obtained in the Hammett plot of $\log(R_x/R_H)$ versus the substituent constant (σ), with a ρ value of -0.54 ± 0.01 (Fig. 8b), indicating that the phenol center is more positive in the transition state. $\log(R_x)$ also correlates well with the oxidation potentials (E^{ox}) of these phenols with a slope of -0.80 (Fig. 8c).³⁴ The results indicate that the reaction may proceed *via* an initial rate-limiting $1e^-$ transfer (ET) from phenols to OsN*. No clear correlation between $\log(R_x)$ and pK_a of phenols, suggesting that proton transfer (PT) is not involved in the rate-limiting step. There is also no clear relationship between $\log(R_x)$ and the O–H bond dissociation energies (BDEs) of the phenols (Fig. 8d),³⁵ which does not support a hydrogen atom transfer (HAT) mechanism for the oxidation of phenols by OsN*.

Kinetic isotope effects (KIE)

The KIE for the reaction of OsN* with phenol was determined by ESI/MS, using an equimolar mixture of phenol (C₆H₅OH) and d⁶-phenol (C₆D₅OD) as substrate. As shown in Fig. 9a, the KIE value was estimated to be $\sim(1 \pm 0.05)$ from the ratios of the most intense peaks for two Os(IV) benzoquinone monoiminato products, ($m/z = 631$ and 635 for [Os^{IV}(L)(CN)₃(N=C₆H₄=O)][−] and [Os^{IV}(L)(CN)₃(N=C₆D₄=O)][−] respectively), assuming that the spraying and ionization efficiencies of the two ions are similar. The isotopic distribution pattern obtained is also in agreement with the simulated one. The KIE is also determined by UV/vis spectroscopy. As shown in Fig. S11,† the UV/vis spectral changes were obtained from the photoreaction of OsN with phenol (C₆H₅OH) and d⁶-phenol (C₆D₅OD) under the same conditions. The reactions were followed by the change in absorbance at 367 nm, which gives a KIE of $R_H/R_D = 0.97 \pm$

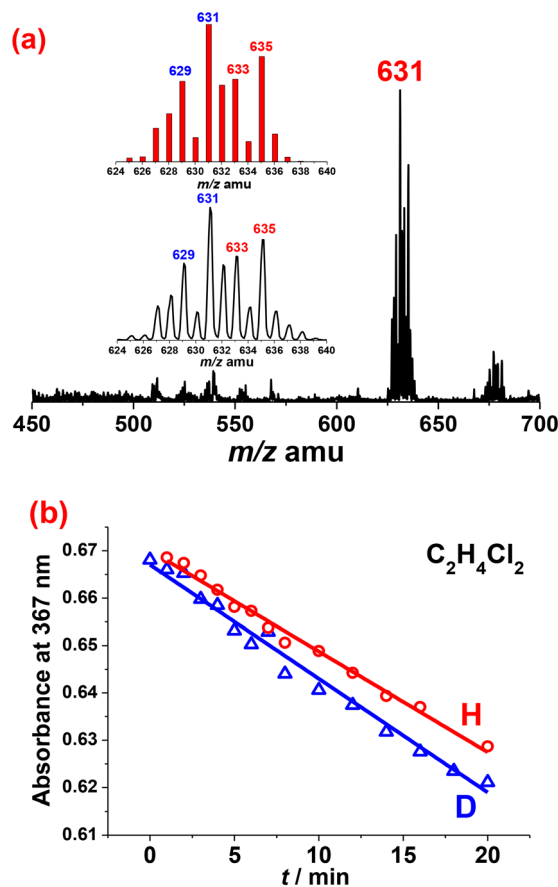


Fig. 9 (a) ESI/MS for the photoreaction of OsN with equimolar of phenol and d⁶-phenol showing a predominant peak around m/z 631. Inserts show the expanded isotopic distribution of peak m/z 631, which agrees with the simulated isotopic distribution of m/z 631 and 635 with a mole ratio of 0.505 : 0.495 (KIE ~ 1). (b) Time trace for absorbance at 367 nm of OsN (2.5×10^{-5} M) with 100 equiv. of phenol (red line) and d⁶-phenol (blue line) in C₂H₄Cl₂. The linear fitting gives initial rates of $R_H = (-2.13 \pm 0.06) \times 10^{-3}$, $r^2 = 0.98$ and $R_D = (-2.40 \pm 0.10) \times 10^{-3}$, $r^2 = 0.99$; $R_H : R_D = 0.97$.

0.01 (Fig. 9b). Based on the above results, the photoreaction of OsN with phenol exhibits negligible KIE, indicating that C–H bond cleavage is not involved in the rate-limiting step, in line with the conclusion obtained from investigation of substituent effects.

Proposed mechanism

Based on the above experiments, the proposed mechanism for the photoreaction of OsN with phenols is illustrated in Fig. 10 (using 2,6-Me₂C₆H₃OH as an example). The initial step is rate-limiting $1e^-$ oxidation of 2,6-Me₂C₆H₃OH (ET), followed by rapid proton transfer (PT) to give the Os^VNH and phenoxy radical, which is supported by a linear correlation between $\log(R_x)$ and E of the phenols with a slope of -0.80 . The proposed mechanism is also supported by the linear Hammett correlation with ρ value of -0.54 and a negligible KIE effect ($k(\text{C}_6\text{H}_5\text{OH})/k(\text{C}_6\text{D}_5\text{OD}) \sim 1.03$). Moreover, the initial rate (R) for phenolate is 60 times faster than that of phenol, further vali-



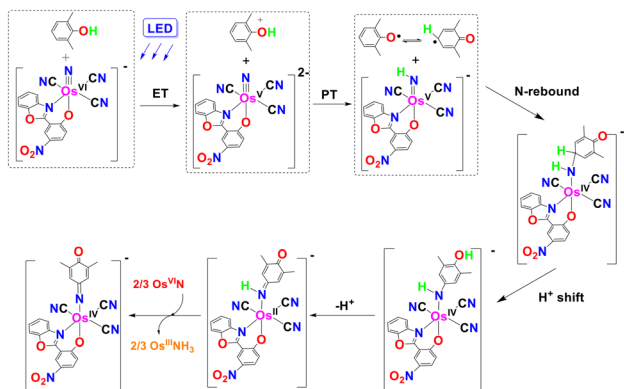


Fig. 10 The proposed reaction mechanism for the reaction of OsN^* with 2,6- $\text{Me}_2\text{C}_6\text{H}_3\text{OH}$.

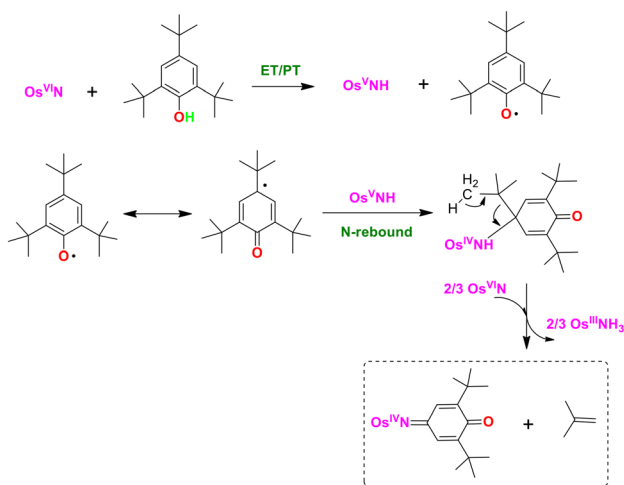


Fig. 11 The proposed mechanism for the C–C bond cleavage of 2,4,6- $\text{tBu}_3\text{C}_6\text{H}_2\text{OH}$ by OsN^* .

dating the initial ET mechanism (Fig. S12†). This is followed by tautomerism and N-rebound to give an Os^{IV} amido species. An internal $2e^-$ redox results in the Os^{II} hydroquinone monoimine product. The other product, Os^{IV} hydroquinone monoiminato complex, was formed by further $2e^-$ oxidation by OsN^* ($2/3\text{OsN}^* + \mathbf{1a} \rightarrow \mathbf{1b} + 2/3\text{OsNH}_3$). This last step is supported by the isolation of OsNH_3 in 10% yield.

For the photoreaction of OsN and 2,4,6- $\text{tBu}_3\text{C}_6\text{H}_2\text{OH}$, the first four steps are similar (Fig. 11), *i.e.* $1e^-$ oxidation of 2,4,6- $\text{tBu}_3\text{C}_6\text{H}_2\text{OH}$ (ET), followed by rapid proton transfer (PT) to give the $\text{Os}^{\text{V}}\text{NH}$ and phenoxyl radical; followed by tautomerism and N-rebound to give an Os^{IV} amido species. Further $2e^-$ oxidation of this Os^{IV} amido species by OsN^* leads to C–C bond cleavage with the formation of **4a**, 2-methylpropene, and OsNH_3 .

Conclusion

In conclusion, we have demonstrated novel reactivity of the excited state of an osmium(vi) nitrido complex towards

phenols. The photoreactions of OsN with the parent phenol, as well as mono- and di-substituted phenols afforded Os^{II} *p*-benzoquinone monoimine and osmium(IV) *p*-benzoquinone monoiminato complexes. On the other hand, oxidation of bulky tri-substituted phenol such as 2,4,6- $\text{tBu}_3\text{C}_6\text{H}_2\text{OH}$ resulted in C–C bond cleavage of the substrate. Mechanistic studies indicate that the photoreactions proceed *via* an initial $1e^-$ oxidation followed by a rapid proton transfer (ET-PT) to generate phenoxyl radicals, this is followed by a N-rebound step to give the osmium products. We believe that our work is a significant contribution to $\text{M}\equiv\text{N}$ excited state as well as phenol oxidation chemistry.

Experimental

$(\text{PPh}_4)_2[\text{Os}^{\text{II}}(\text{L})(\text{CN})_3(\text{NH}=\text{Me}_2\text{PhOH}_{(-2\text{H})})]$ [(PPh_4)₂**1a**] and $(\text{PPh}_4)[\text{Os}^{\text{IV}}(\text{L})(\text{CN})_3(\text{N}=\text{Me}_2\text{PhOH}_{(-2\text{H})})]$ [(PPh_4)**1b**]

10 tubes each containing OsN (5 mg, 5.7 μmol) and 2,6- $\text{Me}_2\text{C}_6\text{H}_3\text{OH}$ (73 mg, 0.6 mmol) in CH_2Cl_2 under argon were irradiated with blue LED light for 24 h, whereby the light-yellow solutions turned dark red. The solutions were combined, and the solvent was removed under reduced pressure. The residue was washed with diethyl ether (100 ml) to remove the unreacted 2,6- $\text{Me}_2\text{C}_6\text{H}_3\text{OH}$. The residue was dissolved in a minimum amount of CH_2Cl_2 and then loaded onto a silica gel column. The first yellow band ($(\text{PPh}_4)[\text{Os}^{\text{IV}}(\text{L})(\text{CN})_3(\text{N}=\text{Me}_2\text{Ph}_{(-2\text{H})}=\text{O})]$ [(PPh_4)**1b**]) was eluted by $\text{CH}_2\text{Cl}_2/\text{acetone}$ (v:v, 4:1). Yellow needle crystals were obtained from slow diffusion of diethyl ether into a MeCN solution of (PPh_4)**1b**. The second blue band was eluted by $\text{CH}_2\text{Cl}_2/\text{acetone}/\text{MeOH}$ (v:v:v, 8:2:1). The solvent was removed under reduced pressure. The solid obtained was dissolved in H_2O (10 ml) and excess PPh_4Cl (30 mg) was added to give the blue precipitate. The crude product was further purified by slow diffusion of diethyl ether into a CH_2Cl_2 solution of (PPh_4)₂**1a**. Yield for (PPh_4)₂**1a**: 15 mg, 20% (based on the OsN consumed). Selected IR (KBr disc, cm^{-1}): $\nu(\text{N-H})$ 3248; $\nu(\text{C}\equiv\text{N})$ 2096 and 2070; $\nu(\text{C}=\text{O})$ 1645; $\nu(\text{C}=\text{N})$ 1609; $\nu(\text{N}=\text{O})$ 1303. ^1H NMR (400 MHz, CDCl_3): δ 8.92 (s, 1H, Ar-H), 7.92–7.78 (m, 8H, Ar-H), 7.77–7.64 (m, 18H, Ar-H), 7.62–7.48 (m, 18H, Ar-H), 7.38 (d, $J = 8.0$ Hz, 1H, Ar-H), 7.29 (m, 1H, Ar-H), 7.19 (t, $J = 8.0$ Hz, 1H, Ar-H), 6.67 (s, 1H, Ar-H), 1.69 (s, 6H). ESI/MS (–ve mode) in MeOH: at m/z 329.7 ($[\text{M}]^{2-}$); Anal. Calcd for $\text{C}_{72}\text{H}_{56}\text{N}_6\text{O}_5\text{P}_2\text{Os}$: C, 64.66; H, 4.22; N, 6.28. Found: C, 64.80; H, 4.25; N, 6.32%. UV/Vis (CH_2Cl_2): λ_{max} [nm] (ϵ [$\text{mol}^{-1}\text{dm}^3\text{cm}^{-1}$]): 269 (22 472), 276 (21 630), 287 (16 020), 344 (14 050), 377sh (11 870), 432 (11 270), 541 (17 340), 586 (17 670). Yield for (PPh_4)**1b**: 15 mg, 26% (based on the OsN consumed). Selected IR (KBr disc, cm^{-1}): $\nu(\text{C}\equiv\text{N})$ 2145 and 2135; $\nu(\text{C}=\text{O})$ 1630; $\nu(\text{C}=\text{N})$ 1611. ^1H NMR (400 MHz, CDCl_3): δ 9.04 (s, 1H, Ar-H), 8.19 (s, 2H, Ar-H), 8.07 (d, $J = 9.5$ Hz, 1H, Ar-H), 7.96–7.88 (m, 4H, Ar-H), 7.84–7.74 (m, 9H, Ar-H), 7.72 (d, $J = 7.4$ Hz, 1H, Ar-H), 7.69–7.61 (m, 8H, Ar-H), 7.53 (t, $J = 8.3$ Hz, 2H, Ar-H), 6.92 (d, $J = 9.2$ Hz, 1H, Ar-H), 3.15 (s, 6H, $-\text{CH}_3$). ESI-MS (–ve mode) in MeOH: m/z 659 (M^-); Anal. Calcd for $\text{C}_{48}\text{H}_{35}\text{N}_6\text{O}_5\text{OsP}$: C, 57.82; H, 3.54; N, 8.43. Found: C, 57.93; H, 3.60; N, 8.31%. UV/Vis (CH_2Cl_2): λ_{max} [nm] (ϵ [mol^{-1}



$\text{dm}^3 \text{cm}^{-1}$): 269 (23 710), 277 (25 070), 288 (23 480), 330 (22 610), 432 (33 300).

(PPh₄)₂[Os^{II}(L)(CN)₃(NH=Cl₂PhOH_(-2H))] [(PPh₄)₂2a] and (PPh₄)₂[Os^{IV}(L)(CN)₃(N=Cl₂PhOH_(-2H))] [(PPh₄)₂2b]

The synthesis and isolation of (PPh₄)₂2a and (PPh₄)₂2b are similar to that of (PPh₄)₂1a and (PPh₄)₂1b except that 2,6-Cl₂C₆H₃OH was used instead of 2,6-dimethylphenol. Yield for (PPh₄)₂2a: (25 mg, 32%, based on the OsN consumed). Selected IR (KBr disc, cm^{-1}): $\nu(\text{N-H})$ 3235; $\nu(\text{C}\equiv\text{N})$ 2108 and 2082; $\nu(\text{C}=\text{O})$ 1638; $\nu(\text{C}=\text{N})$ 1609; $\nu(\text{N}=\text{O})$ 1307; ¹H NMR (400 MHz, CDCl₃): δ 8.96 (d, $J = 2.9$ Hz, 1H), 7.90–7.82 (m, 8H), 7.80 (d, $J = 2.9$ Hz, 1H), 7.77–7.68 (m, 16 H), 7.65–7.56 (m, 16H), 7.55–7.48 (m, 2H), 7.37–7.29 (m, 3H), 7.23 (s, 1H); 6.78 (d, $J = 9.4$ Hz, 1H). ESI-MS (–ve mode) in MeOH: m/z 350.2 [M]²⁻. Anal. Calcd for C₇₀H₅₀Cl₂N₆O₅OsP₂: C, 61.00; H, 3.66; N, 6.10. Found: C, 61.10; H, 3.71; N, 6.18%. UV/Vis (CH₂Cl₂): λ_{max} [nm] (ϵ [mol⁻¹ dm³ cm⁻¹]): 262sh (18 090), 269 (19 810), 276 (18 740), 285sh (12 760), 338 (12 110), 363sh (9360), 417sh (7070), 593 (60 850). Yield for (PPh₄)₂2b: 15 mg, 25% (based on the OsN consumed). Selected IR (KBr disc, cm^{-1}): $\nu(\text{C}\equiv\text{N})$ 2153 and 2141; $\nu(\text{C}=\text{O})$ 1639; $\nu(\text{C}=\text{N})$ 1614. ¹H NMR (400 MHz, CDCl₃): δ 9.08 (s, 1H, Ar-H), 8.50 (s, 2H, Ar-H), 8.21 (d, $J = 8.9$ Hz, 1H, Ar-H), 7.97–7.89 (m, 4H, Ar-H), 7.84–7.75 (m, 9H, Ar-H), 7.72–7.58 (m, 11H, Ar-H), 7.13 (d, $J = 9.2$ Hz, 1H, Ar-H). ESI-MS (–ve mode) in MeOH: m/z 699 [M]⁻; Anal. Calcd for C₄₆H₂₉Cl₂N₆O₅OsP₂: C, 53.23; H, 2.82; N, 8.10. Found: C, 53.29; H, 2.76; N, 8.21%. UV/Vis (CH₂Cl₂): λ_{max} [nm] (ϵ [mol⁻¹ dm³ cm⁻¹]): 270 (40 050), 277 (44 140), 288sh (42 330), 331sh (37 880), 447 (60 490).

(PPh₄)₂[Os^{II}(L)(CN)₃(NH=MePhOH_(-2H))] [(PPh₄)₂3a] and (PPh₄)₂[Os^{IV}(L)(CN)₃(N=MePhOH_(-2H))] [(PPh₄)₂3b]

The synthesis and isolation of (PPh₄)₂3a and (PPh₄)₂3b are similar to that of (PPh₄)₂1a and (PPh₄)₂1b except that 4-MeC₆H₄OH was used instead of 2,6-Me₂C₆H₃OH. Yield for (PPh₄)₂3a, 28 mg, 37%. Selected IR (KBr disc, cm^{-1}) for (PPh₄)₂3a: $\nu(\text{N-H})$ 3253; $\nu(\text{C}\equiv\text{N})$ 2125 and 2086; $\nu(\text{C}=\text{O})$ 1645; $\nu(\text{C}=\text{N})$ 1612. ¹H NMR (400 MHz, CDCl₃): δ 9.03 (d, $J = 2.9$ Hz, 1H, Ar-H), 8.01 (s, 1H), 7.99 (s, 1H), 7.80–7.86 (m, 8H), 7.77–7.68 (m, 16 H), 7.65–7.56 (m, 16H), 7.18–7.10 (t, $J = 8.0$ Hz, 1H), 7.08 (d, $J = 10.2$ Hz, 1H), 6.72 (m, 2H), 6.38 (m, 2H), 5.32 (s, 1H) 1.27 (s, 3H), 3.50 (s, 3H, Me). ESI-MS (–ve mode) in MeOH: m/z 323.3 [M]²⁻. Anal. Calcd for C₇₁H₅₄N₆O₅OsP₂: C, 64.44; H, 4.11; N, 6.35. Found: C, 64.10; H, 4.21; N, 6.18%. UV/Vis (CH₂Cl₂): λ_{max} [nm] (ϵ [mol⁻¹ dm³ cm⁻¹]): 262sh (18 090), 269 (19 810), 276 (18 740), 285sh (12 760), 338 (12 110), 363sh (9360), 417sh (7070), 593 (60 850). Yield for (PPh₄)₂3b, 18 mg, 32%. Selected IR (KBr disc, cm^{-1}): $\nu(\text{C}\equiv\text{N})$ 2139 and 2130; $\nu(\text{C}=\text{O})$ 1649; $\nu(\text{C}=\text{N})$ 1614. ¹H NMR (400 MHz, CDCl₃): δ 9.07 (d, $J = 2.8$ Hz, 1H), 8.65 (dd, $J = 6.3, 2.8$ Hz, 1H) 8.13 (dd, $J = 9.3, 2.9$ Hz, 1H), 7.90–7.82 (m, 4H), 7.77–7.84 (m, 8H), 7.65–7.73 (m, 10H), 7.60–7.53 (m, 2H), 7.21 (dd, $J = 9.8, 2.2$ Hz, 1H), 6.99 (d, $J = 9.3$ Hz, 1H); 5.77 (d, $J = 9.8$ Hz, 1H) 3.58 (s, 3H). ESI-MS (–ve mode) in MeOH: m/z 645 [M]⁻. Anal. Calcd for C₄₇H₃₃N₆O₅OsP₂: C, 57.43; H, 3.38; N, 8.55. Found: C, 57.10;

H, 3.71; N, 8.18%. UV/Vis (CH₂Cl₂): λ_{max} [nm] (ϵ [mol⁻¹ dm³ cm⁻¹]): 262sh (18 090), 269 (19 810), 276 (18 740), 285sh (12 760), 338 (12 110), 363sh (9360), 417sh (7070), 593 (60 850).

(PPh₄)₂[Os^{IV}(L)(CN)₃(N=^tBu₂Ph_(-2H)=O)] [(PPh₄)₂4a] and (PPh₄)₂[Os^{IV}(L)(CN)₃(NH=^tBu₃PhOH_(-2H))] [(PPh₄)₂4b]

The synthetic route of (PPh₄)₂4a and (PPh₄)₂4b is similar to that of (PPh₄)₂1a and (PPh₄)₂1b, except that the 2,4,6-^tBu₃C₆H₂OH is used instead of 2,6-Me₂C₆H₃OH. The first yellow band (PPh₄)₂4a was eluted by CH₂Cl₂/acetone (v : v, 10 : 1). Yellow needle crystals were obtained from the slow diffusion of diethyl ether into an acetone solution of (PPh₄)₂4a. The solvent was removed under reduced pressure.

Yield for (PPh₄)₂4a: 32 mg, 52%. Selected IR (KBr disc, cm^{-1}): $\nu(\text{C}\equiv\text{N})$ 2142 and 2128, $\nu(\text{C}=\text{O})$ 1638; $\nu(\text{C}=\text{N})$ 1615; $\nu(\text{N}=\text{O})$ 1307. ¹H NMR (400 MHz, CDCl₃): δ 9.03 (d, $J = 2.8$ Hz, 1H, Ar-H), 8.12 (s, 2H, Ph-H), 8.05 (dd, $J = 9.3, 2.9$ Hz, 1H, Ar-H), 7.92 (dd, $J = 8.0, 6.0$ Hz, 4H, PPh₄-H), 7.83–7.76 (m, 9H, Ar-H and PPh₄-H), 7.73 (d, $J = 7.2$ Hz, 1H, Ar-H), 7.68–7.62 (m, 8H, PPh₄-H), 7.54 (dtd, $J = 13.9, 7.8, 6.2$ Hz, 2H, Ar-H), 6.89 (d, $J = 9.4$ Hz, 1H, Ar-H), 1.28 (s, 18H, CH₃). ESI-MS (–ve mode) in MeOH: m/z 743 [M]²⁻. Anal. Calcd for C₅₄H₄₇N₆O₅OsP₂: C, 59.99; H, 4.38; N, 7.77. Found: C, 60.10; H, 4.31; N, 7.78%. UV/Vis (CH₂Cl₂): λ_{max} [nm] (ϵ [mol⁻¹ dm³ cm⁻¹]): 230 (27 380), 277 (15 620), 288 (14 640), 330 (13 030), 428 (20 930).

(PPh₄)₂[Os^{IV}(L)(CN)₃(NH-Me₃PhOH_(-H))] [(PPh₄)₂5]

The synthetic route of (PPh₄)₂5 is similar to that of (PPh₄)₂1a and (PPh₄)₂1b, except that the 2,4,6-Me₃C₆H₂OH is used instead of 2,6-Me₂C₆H₃OH. (PPh₄)₂5 was purified by silica gel CH₂Cl₂/acetone (5 : 3) as the eluent. Yield: 43 mg, 75% (based on the OsN consumed). UV/Vis (CH₂Cl₂) for (PPh₄)₂5: λ_{max} [nm] ($\epsilon/\text{M}^{-1} \text{cm}^{-1}$): 233 (42 430), 270 (18 030), 277 (19 430), 293 (20 360), 353 (20 460), 457 (6420). Selected IR (KBr disc, cm^{-1}) for 5: $\nu(\text{C}\equiv\text{N})$ 2135 and 2127; $\nu(\text{N-H})$ 3247; $\nu(\text{C}=\text{N})$ 1610. ESI-MS (–ve mode) in MeOH: m/z 675 [M]⁻. Anal. Calcd for C₄₉H₃₉N₆O₅OsP₂: C, 58.09; H, 3.88; N, 8.30. Found: C, 58.10; H, 3.81; N, 8.28%. ¹H NMR (400 MHz, CDCl₃): δ 8.93 (d, $J = 2.8$ Hz, 1H, Ar-H), 7.96 (d, $J = 6.6$ Hz, 1H, Ar-H), 7.89 (t, $J = 7.2$ Hz, 4H), 7.75 (td, $J = 7.6, 3.7$ Hz, 8H), 7.65–7.57 (m, 10H, Ar-H and PPh₄-H), 7.43 (t, $J = 7.1$ Hz, 1H, Ar-H), 7.20 (t, $J = 8.4$ Hz, 1H, Ar-H), 6.78 (s, 2H, Ph-H), 6.57 (d, $J = 9.4$ Hz, 1H, Ar-H), 2.23 (s, 3H, CH₃), 1.27 (s, 6H, CH₃).

Author contributions

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

Data availability

The authors will supply the relevant data in response to reasonable requests.



Conflicts of interest

There are no conflicts to declare.

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