

Photochemistry

International Edition: DOI: 10.1002/anie.201604959
German Edition: DOI: 10.1002/ange.201604959Labilizing the Photoinert: Extraordinarily Facile Photochemical Ligand Ejection in an $[\text{Os}(\text{N}^{\wedge}\text{N})_3]^{2+}$ Complex

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Abstract: Whilst $[\text{Os}(\text{N}^{\wedge}\text{N})_3]^{2+}$ complexes are supposed to be photochemically inert to ligand loss, the complex $[\text{Os}(\text{btz})_3]^{2+}$ ($\text{btz} = 1,1'$ -dibenzyl-4,4'-bi-1,2,3-triazolyl) undergoes unprecedented photolytic reactivity to liberate free btz ($\Phi_{363} \approx 1.2\%$). Further, both *cis* and *trans* isomers of the photodechelated ligand-loss solvento intermediate $[\text{Os}(\kappa^2\text{-btz})_2(\kappa^1\text{-btz})(\text{NCMe})]^{2+}$ are unambiguously observed and characterized by NMR spectroscopy and mass spectrometry.

Kinetically inert d^6 complexes of second- and third-row transition-metal elements (e.g. Re^{I} , Ru^{II} , Os^{II} , and Ir^{III}) have attracted enormous interest due to their attractive photo-physical properties that make them potentially amenable to application in light-emitting technologies,^[1] dye-sensitized photovoltaics,^[2] phosphorescent biological imaging microscopy^[3] and solar catalysis.^[4] The utility in phosphorescent and electron/energy-transfer applications stems from the relatively long-lived triplet metal-to-ligand charge-transfer ($^3\text{MLCT}$) states that complexes of these metals exhibit. These can however be deactivated by triplet metal-centered (^3MC) states if these are sufficiently close in energy to photoexcited $^3\text{MLCT}$ states^[5] and can induce photochemical reactivity such as ligand-loss or isomerization.^[6] For example, photochemical reactivity can be designed into ruthenium(II) complexes; inclusion of steric bulk in the ligand set in order to weaken metal–ligand bonds lowers the ^3MC state making thermal population from $^3\text{MLCT}$ states after photoexcitation achievable. This methodology has been exploited in the design of photoinitiated DNA binding complexes with anti-cancer activity.^[7]

We have recently reported results on the non-sterically promoted photochemical reactivity of the complexes $[\text{Ru}(\text{bpy})_2(\text{btz})]^{2+}$ and $[\text{Ru}(\text{bpy})(\text{btz})_2]^{2+}$ ($\text{bpy} = 2,2'$ -bipyridyl).^[8] Here, presence of the btz ligand appears to induce a destabilization of the $^3\text{MLCT}$ state, bringing it into closer energetic proximity to the ^3MC state thereby enabling thermal population of the ^3MC state with consequential photochemical btz ligand ejection in acetonitrile solutions. In the case of the latter of these complexes, this is accompanied by the unprecedented observation of a metastable ligand-loss intermediate, *trans*- $[\text{Ru}(\text{bpy})(\kappa^2\text{-btz})(\kappa^1\text{-btz})(\text{NCCH}_3)]^{2+}$, which can be formed quantitatively by photolysis in an NMR tube

within minutes and has been crystallographically characterized.^[9] The btz ligand has also been observed to induce photochemical decomposition in the iridium(III) complex $[\text{Ir}(\text{dfptz})_2(\text{btz})]^+$ ($\text{dfptzH} = 4$ -(2,4-difluorophenyl)-1,2,3-triazole)^[10] which one would expect to be far more inert due to the typically higher lying ^3MC states associated with the 5d metal center.

These intriguing results led us to explore osmium(II) triazole-based complexes. $[\text{Os}(\text{N}^{\wedge}\text{N})_3]^{2+}$ -type complexes are typically highly kinetically inert and require harsh conditions in their synthesis in order to effect ligand exchange. This is due to a large ligand-field splitting yielding high-energy ^3MC states regarded as thermally inaccessible. Consequently these complexes are photochemically stable, avoiding the ligand ejection photochemistry that sometimes afflicts, or can be designed into, Ru^{II} analogues. Indeed, for such osmium complexes Meyer noted that “ligand-loss photochemistry is either extremely inefficient or nonexistent”,^[11] a view that has prevailed for some time.

We present in this contribution, however, the unprecedentedly facile photochemical conversion of the homoleptic btz complex $[\text{Os}(\text{btz})_3]^{2+}$ (**1**) in which ^3MC states are evidently efficiently populated. In pyridine and acetonitrile solutions the complex is observed to undergo formal loss of a btz ligand and formation of bis(solvent) species upon irradiation. We further show that as photolysis proceeds in acetonitrile, as followed by ^1H NMR spectroscopy, that two ligand-loss intermediate complexes, *cis*- and *trans*- $[\text{Os}(\kappa^2\text{-btz})_2(\kappa^1\text{-btz})(\text{NCCH}_3)]^{2+}$ are observed which subsequently undergo formal loss of a btz ligand to yield the bis(solvent) complexes *cis*- and *trans*- $[\text{Os}(\text{btz})_2(\text{NCCH}_3)_2]^{2+}$ respectively. We therefore present firm evidence for the existence of experimentally elusive ligand-loss intermediates long suspected of involvement in ligand-loss mechanisms in $[\text{M}(\text{N}^{\wedge}\text{N})_3]^{2+}$ -type ($\text{M} = \text{Ru}, \text{Os}$) complexes.

We have previously reported the synthesis and characterization of complex **1** as its hexafluorophosphate salt.^[12] We noted that on being left to stand in ambient daylight that NMR samples in donor solvents appeared to darken, presumably due to some photochemical decomposition process. This appeared to be accelerated by irradiation with the 363, 403 and 433 nm mercury emission lines of a 23 W fluorescent lamp or a 1 mW 405 nm LED. Under identical conditions only small changes are evident in spectra of $[\text{Ru}(\text{bpy})_3]^{2+}$ whilst there is no evidence of any photolysis for $[\text{Os}(\text{bpy})_3]^{2+}$ (see Supplementary Information). When **1** is dissolved in d_5 -pyridine in an NMR tube and subsequently irradiated for an hour, resonances for an equivalent of free btz are observed to grow-in alongside new resonances for a *bis*-bitriazolyl ligand-loss product (Figure 1a and Scheme 1);

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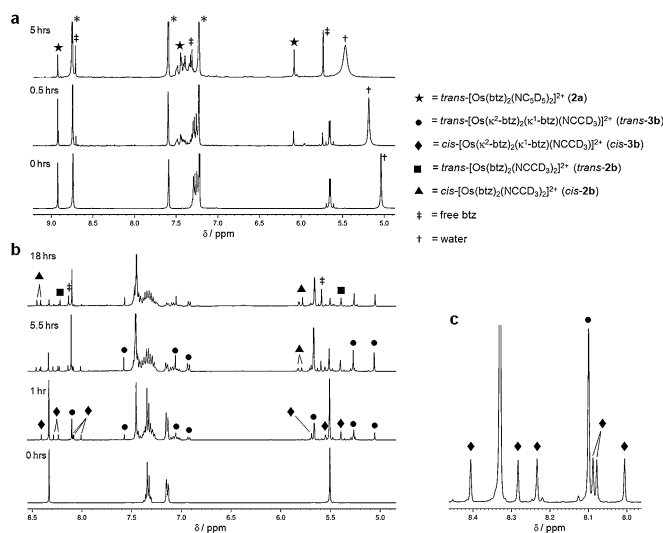
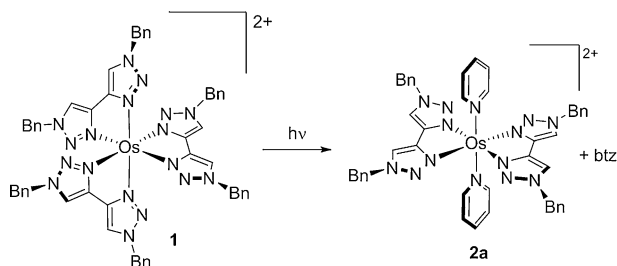


Figure 1. a) ^1H NMR spectra recorded during photolysis of **1** in d_5 -pyridine (* residual proteo-solvent signals. ‡ As the photolysis proceeds the resonance for the adventitious water signal is observed to broaden and become deshielded); b) ^1H NMR spectra recorded during the photolysis of **1** in d_3 -acetonitrile; c) expansion of the spectrum at 1 hour in (b) showing the region for triazole ring resonances of *cis*-**3b**.



Scheme 1. Photochemical reactivity of **1** in pyridine (Bn = benzyl).

singlet resonances are observed at δ 8.91 and 6.08 which are assigned to the triazole ring and methylene protons, respectively of the ligated btz ligands of the product. Due to the apparent equivalence of the four triazole rings of the two btz ligands in this product the conversion of **1** must proceed with a concomitant rearrangement of the remaining btz ligands such that they become coplanar as was previously observed in the novel photochemical conversion of [Ru(bpy)(btz)₂]²⁺.^[8b,9] We thus assign this complex as *trans*-[Os(btz)₂(NC₅D₅)₂]²⁺ (**2a**). A comparable sample in proteo-pyridine was subject to photolysis, the solvent subsequently removed in vacuo and the residue taken up in d_2 -dichloromethane. In addition to the characteristic coordinated btz ligand resonances (δ 8.25 (T_z) and 5.81 (CH_2)) signals are also visible at δ 8.35, 7.44 and 6.81 for the pyridine ligands (see Figures S8 and S9 in the Supporting Information).

Crystals of X-ray diffraction quality of the photoproduct **2a** as its hexafluorophosphate salt were grown from a post-photolysis sample of **1** in H_5 -pyridine. The complex crystallizes in the space group $P\bar{1}$ and exhibits a single cation per unit cell with four co-crystallized solvent molecules. The asym-

metric unit contains the osmium center and just one of each of the btz and pyridine ligands. The molecular structure of the cation is shown in Figure 2, clearly demonstrating the loss of one of the btz ligands from **1**, coordination of two pyridine ligands and the rearrangement of the remaining coordinated btz ligands such that they are coplanar.

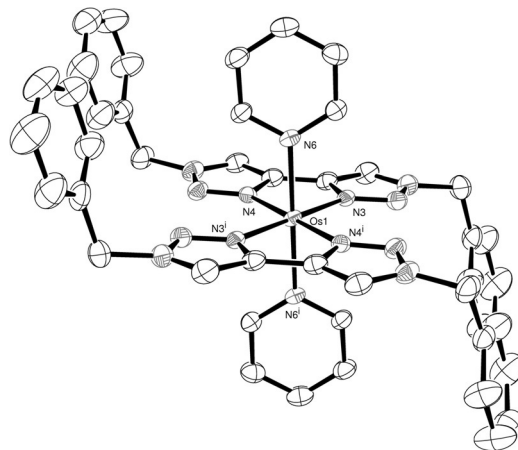


Figure 2. Molecular structure of the cation *trans*-[Os(btz)₂(NC₅H₅)₂]²⁺ (hydrogen atoms, co-crystallized solvent molecules and counterions removed for clarity. Thermal ellipsoids at 50% probability. Selected bond lengths [Å] and angles [°]: Os1–N3 2.046(3); Os1–N4 2.049(3); Os1–N6 2.081(3); N3–Os1–N4 76.74(13); N3–Os1–N6 89.22(12); N4–Os1–N6 92.29(12); N4–Os1–N4i 180.00(18); N6–Os1–N6i 180.00(15)).

When the photolysis of **1** is monitored by UV/Vis absorption spectroscopy in pyridine in a 1 cm path-length quartz cuvette the absorption band for **1** at 320 nm is observed to undergo bleaching whilst new bands are observed to grow in intensity between 370 and 500 nm (Figure 3a). The spectrum evolves within 2 minutes to match that obtained from solutions derived from dissolving the crystals grown of **2a** (Figure S4). A quantum yield for photochemical ligand ejection from **1** of $\Phi_{363} = 1.17\%$ was determined. This value shows that the conversion of **1** to **2a** through full photochemical ligand ejection occurs with comparable efficiency to known photoreactive Ru^{II} complexes in the literature where mono-dechelation of triazole-based ligands has been observed.^[13] In direct contradiction to the prevailing view that ³MC state population and ligand photosubstitution in osmium(II) complexes is extremely inefficient or non-existent, the observed reactivity of **1** clearly demonstrates more than efficient ³MC state population and unprecedentedly facile ligand photoejection.

Photolysis of **1** was also investigated in acetonitrile as an alternative donor solvent. When an NMR sample of **1** in d_3 -acetonitrile is subject to photolysis new resonances are observed in ^1H NMR spectra as irradiation time progresses (Figure 1b) which can be assigned to a total of four new osmium btz complexes (Scheme 2); two of these are identified as formal ligand ejection photoproducts (*trans*-**2b** & *cis*-**2b**) with the remaining two species identified as ligand-loss intermediates (*trans*-**3b** & *cis*-**3b**). A number of other

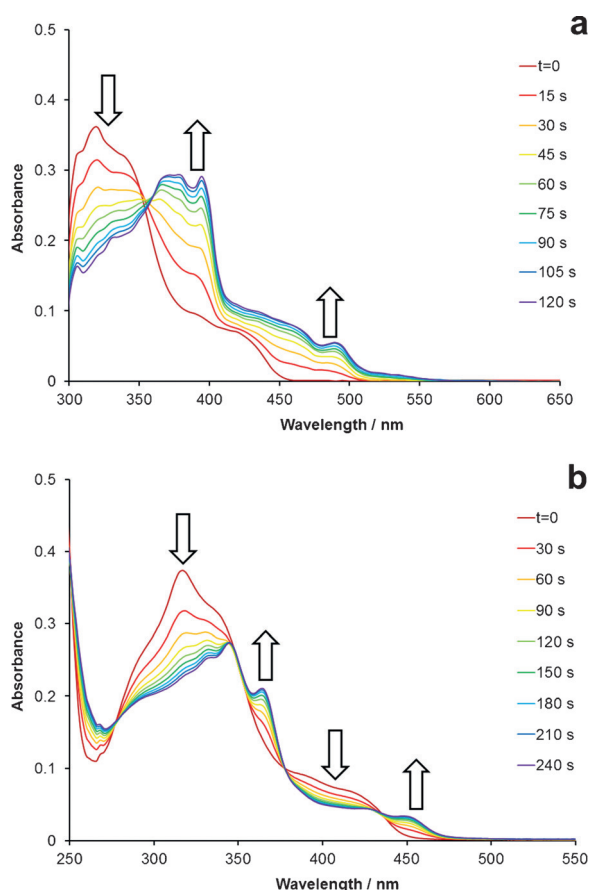
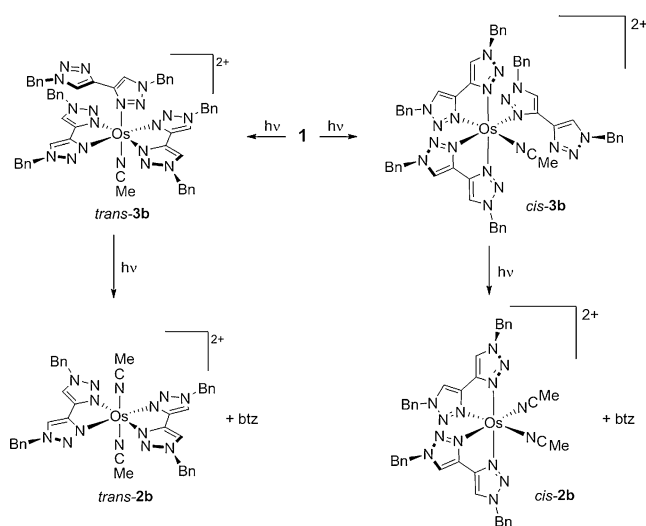


Figure 3. UV/Vis absorption spectra recorded during the photolysis of **1** in a) pyridine and b) acetonitrile.



Scheme 2. Mechanism of photolysis reactivity of **1** in acetonitrile solutions.

resonances at much lesser intensity are observed after long irradiation times indicating formation of further, as yet unidentified, photoproducts. Again $[\text{Os}(\text{bpy})_3]^{2+}$ is unreactive under identical conditions.

The proposed routes of photochemical reactivity are depicted in Scheme 2. Early in the photolysis, resonances for two of these new species are observed. The first of these is characterized by two singlet benzylic methylene resonances at δ 5.26 and 5.05 which display nOe correlations with two further singlet resonances for triazole ring protons at δ 7.05 and 7.57 respectively. Based on results from our earlier work on the photochemistry of $[\text{Ru}(\text{bpy})(\text{btz})_2]^{2+}$, involving the formation of $\text{trans}-[\text{Ru}(\text{bpy})(\kappa^2\text{-btz})(\kappa^1\text{-btz})(\text{NCMe})]^{2+}$, these two sets of resonances are highly characteristic of a $\kappa^1\text{-btz}$ ligand in a $\text{trans}-[\text{M}(\kappa^2\text{-N}^{\wedge}\text{N})_2(\kappa^1\text{-btz})(\text{solvent})]^{2+}$ coordination environment.^[8b,9] The emergence of these signals is accompanied by the observation of a singlet resonance of a relative integration consistent with two btz ligands at δ 8.10 (Tz). Data from nOe spectra allow assignment of a geminal pair of doublets ($J_{\text{HH}} = 15.3$ Hz) centered at δ 5.66 to the benzylic methylene protons of the same ligands. Taken together, and with the striking similarity of these resonances to those previously observed in the formation of $\text{trans}-[\text{Ru}(\text{bpy})(\kappa^2\text{-btz})(\kappa^1\text{-btz})(\text{NCMe})]^{2+}$, this confidently enables the assignment of this species as the ligand-loss intermediate $\text{trans}-[\text{Os}(\kappa^2\text{-btz})_2(\kappa^1\text{-btz})(\text{NCMe})]^{2+}$ (**trans-3b**, Scheme 2).

Unlike in the case of the photolysis of $[\text{Ru}(\text{bpy})(\text{btz})_2]^{2+}$, signals for a second apparent ligand loss intermediate appear to grow in the spectrum early in photolysis; a set of six new singlet resonances of equal integration corresponding to triazole ring protons grow-in together at δ 8.40, 8.28, 8.23, 8.09, 8.08 & 8.01, each of which display nOe connections to resonances for benzylic methylene protons (Figure 1c). We therefore assign these resonances as arising from an osmium(II) *trans*-btz complex but in which the D_3 symmetry has been lost. Due to the magnetically unique nature of each triazole ring environment we propose the identity of this second species to be the solvento complex $\text{cis}-[\text{Os}(\kappa^2\text{-btz})_2(\kappa^1\text{-btz})(\text{NCMe})]^{2+}$ (**cis-3b**) which is isomeric with **trans-3b**. An intermediate of this type is implicated in the previously reported photolysis of $[\text{Ru}(\text{bpy})_2(\text{btz})]^{2+}$ to yield *cis*- $[\text{Ru}(\text{bpy})_2(\text{NCCH}_3)_2]^{2+}$, and many other similar conversions, but where no such species is observed.^[6,7b,8a] NMR resonances assigned to a similar intermediate have been observed, albeit at trace levels, during the photolysis of the complex $[\text{Ru}(\text{bpy})_2(\text{dmbpy})]^{2+}$ ($\text{dmbpy} = 3,3'$ -dimethyl-2,2'-bipyridyl)^[14] where the photodechelation of the dmbpy ligand is sterically "spring-loaded" to occur and rechelation is presumably hindered for the same reason. Whilst **1** undeniably undergoes photolysis readily, the striking stability that enables NMR characterization of **cis-3b** likely arises from osmium(II) being a far less kinetically labile metal center compared to ruthenium(II), thus retarding loss of the solvent ligand and btz rechelation.

Later during the photolysis, resonances for *trans*- and *cis*-**3b** are still visible but new resonances are observed for ligand ejection photoproduct complexes **trans-2b**, the acetonitrile analogue of **2a**, and also **cis-2b** along with signals for free btz (Figure 1b). Firstly, singlet resonances are observed at δ 8.22 and 5.39 for the triazole ring and methylene protons, respectively of what is assigned as $\text{trans}-[\text{Os}(\text{btz})_2(\text{NCMe})_2]^{2+}$ (**trans-2b**). For the second product, two triazole ring proton resonances appear at δ 8.45 & 8.42 with resonances for

benzylic methylene protons appearing as a singlet at δ 5.78 and a geminal pair of doublets centered at δ 5.82. These signals are indicative of the formation of the C_2 symmetric bis(solvent) ligand ejection product cis -[Os(bt z) $_2$ (NCMe) $_2$] $^{2+}$ (*cis*-**2b**). Despite the steric impediment of the pendant triazole of the κ^1 -btz ligand, photochemical exchange of the solvent ligand in **3b** might be expected to dominate. It is therefore possible that bifurcating pathways exist with formal btz loss as the minor route which would account for the second step being comparatively slow. Conversely, as pyridine will be more strongly bound this may also explain the lack of an observed intermediate during formation of **2a** as bifurcation is shifted to loss of btz.

UV/Vis absorption spectra for a dilute solution of **1** in acetonitrile were recorded after successive irradiation periods of 30 s and are presented in Figure 3b. Over the course of 4 minutes the absorption maximum at 317 nm and shoulders at 390 and 417 nm are observed to undergo bleaching whilst new features are observed to grow at 365 and 450 nm. 1H NMR analysis of the solution after the evolution of these spectral features revealed the composition of the sample to be predominantly a mixture of ligand loss intermediates *trans*- and *cis*-**3b** (see the Supporting Information).

Using a potassium ferrioxalate chemical actinometer the quantum yield for the photochemical conversion of **1** into *trans*- and *cis*-**3b** in acetonitrile at room temperature was estimated at $\Phi_{365} \approx 1.25\%$. Since the reaction coordinate from the 3MLCT state of **1** must bifurcate in leading to the two κ^1 -btz intermediates, this represents the estimated yield for global consumption of **1** rather than for formation of *trans*-**3b** and/or *cis*-**3b**.

When a sample seen to exhibit 1H NMR signals for *trans* and *cis* isomers of **2b** and **3b** in d_3 -acetonitrile was analyzed by electrospray mass spectrometry, ions corresponding to these osmium-containing species are observed (Figure 4);

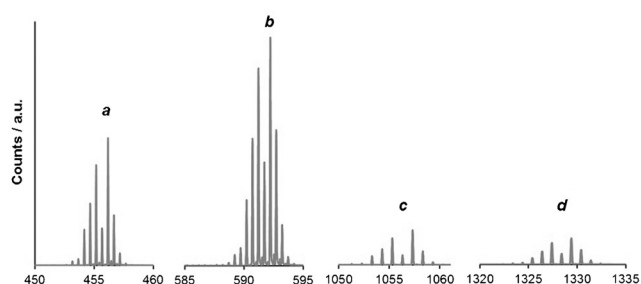


Figure 4. Positive ion ESI-MS data for a sample of **1** in CD_3CN having undergone photolysis: a) [Os(bt z) $_2$ (NCCD $_3$) $_2$] $^{2+}$, b) [Os(κ^2 -bt z) $_2$ (κ^1 -bt z)-(NCCD $_3$)] $^{2+}$, c) {[Os(bt z) $_2$ (NCCD $_3$) $_2$][PF $_6$]} $^+$, d) {[Os(κ^2 -bt z) $_2$ (κ^1 -bt z)-(NCCD $_3$)][PF $_6$]} $^+$.

indications are observed with $m/z = 456.17$ and 592.22 consistent with the formulae [Os(bt z) $_2$ (NCCD $_3$) $_2$] $^{2+}$ and [Os(bt z) $_3$ -(NCCD $_3$)] $^{2+}$ respectively as well as signals for the monocationic ion-pairs {[Os(bt z) $_2$ (NCCD $_3$) $_2$][PF $_6$]} $^+$ and {[Os(bt z) $_3$ -(NCCD $_3$)][PF $_6$]} $^+$ ($m/z = 1057.30$ and 1329.40 respectively). None of these ions are observable for a fresh sample of **1** dissolved in acetonitrile.

As far as we are aware from surveying the literature this represents the first example of reported facile photochemical ligand dechelation and substitution in an [Os(N $\wedge$ N) $_3$] $^{2+}$ -type complex. Since the LUMO of the btz ligand is calculated to be approximately 1 eV higher in energy than that of bpy, the 3MLCT state of **1** is predicted to be significantly destabilized with respect to that of [Os(bpy) $_3$] $^{2+}$ and other osmium(II) complexes that do not exhibit this behaviour. Hence, the 3MC state of **1** clearly undergoes unprecedentedly efficient thermal population from the photoexcited 3MLCT states, which must lie in close energetic proximity, thus resulting in the observed reactivity.

In conclusion, we have demonstrated the first known example of facile photochemical ligand substitution reactivity in a [Os(N $\wedge$ N) $_3$] $^{2+}$ -type complex. Further, during the progress of this photolytic ligand ejection reaction we have observed and characterized in acetonitrile solutions the isomeric ligand-loss intermediate complexes *cis*- and *trans*-[Os(κ^2 -bt z) $_2$ (κ^1 -bt z)(NCMe) $_2$] $^{2+}$ by 1H NMR spectroscopy and mass spectrometry, each containing a κ^1 -btz ligand. The *trans* isomer of this intermediate is in agreement with previously reported data on photoreactive ruthenium(II) btz complexes. The detection of the *cis* isomer, on the other hand, provides firm evidence for repeatedly proposed yet largely elusive ligand-loss intermediates implicated in many ligand ejection reactions from [M(N $\wedge$ N) $_3$] $^{2+}$ complexes reported in the literature. In acetonitrile **1** forms both *cis*- and *trans*-**2b** whereas in pyridine only *trans*-**2a** is observed. We would expect the *trans* isomers to be the more thermodynamically stable based on previous reports.^[8a,9] Product formation will depend on the kinetically controlled evolution of the geometry on the excited state potential energy surface but also on the steric demands and therefore accessibility to coordination of the incoming solvent ligand. The smaller steric demands of acetonitrile may therefore enable the trapping of the more congested *cis* isomer as well as the *trans* whereas for the larger pyridine ligand only the *trans* isomer is accessible. Further computational work to address this is ongoing. The work presented here offers opportunities for further investigation and exploitation. Given the current interest in light-initiated DNA coordinating agents operating by photochemical ligand ejection mechanisms, this discovery opens up new avenues for the development of novel targeted osmium(II)-based anti-cancer agents. The facile photoejection chemistry combined with the synthetically versatile nature of the “click” chemistry approach to ligand construction has the potential to yield potent DNA coordination agents that will form highly stable DNA-adducts. Our current ongoing work on this fascinating photochemical system is continuing with time-resolved spectroscopic and computational studies of the excited state properties of this and related systems. Results from these ongoing investigations will be reported elsewhere.

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