Exploration of uncharted ^{3}PES territory for [Ru(bpy)$_3$]$^{2+}$: a new ^{3}MC minimum prone to ligand loss photochemistry

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Abstract

We have identified a new ^{3}MC state bearing two elongated Ru-N bonds to the same ligand in [Ru(bpy)$_3$]$^{2+}$. This DFT-optimized structure is a local minimum on the ^{3}PES. This distal MC state (^{3}MC$_{cis}$) is destabilized by less than 2 kcal/mol with respect to the classical MC state (^{3}MC$_{trans}$), and energy barriers to populate ^{3}MC$_{cis}$ and ^{3}MC$_{trans}$ from the ^{3}MLCT state are similar according to nudged elastic band minimum energy path calculations. Distortions in the classical ^{3}MC$_{trans}$, i.e. elongation of two Ru-N bonds towards two different bpy ligands, are not expected to favour the formation of ligand-loss photoproducts. On the contrary, the new ^{3}MC$_{cis}$ could be particularly relevant in the photodegradation of Ru(II) polypyridine complexes.

For the last four decades, [Ru(bpy)$_3$]$^{2+}$ has been at the heart of inorganic photochemistry and has been thoroughly studied for its intrinsic photophysical properties, which arise from the interplay of two excited states of different electronic nature.[1] Irradiation in the visible region populates a singlet metal-to-ligand charge transfer state (^{1}MLCT), which populates a ^{3}MLCT state following quantitative intersystem crossing. This charge transfer state can deactivate radiatively (the complex is phosphorescent at room temperature), non radiatively,[2] or via the population of a metal-centred state (^{3}MC). This ^{3}MC state is by nature highly distorted with respect to the ground state geometry, which is thought to be related to its capacity to quench the ^{3}MLCT luminescence through direct crossing with the reactant's ground state surface or through photoreactivity.[1] But this photoreactivity, resulting in the loss of bpy, seems unlikely to be due to classical axially-elongated ^{3}MC states repelling two pyridines from two distinct bpy ligands.

The recent computational identification of several ^{3}MC minima displaying various modes of elongations in heteroleptic tris(bidentate) Ru(II) complexes evidenced the existence of novel ^{3}MC states, in which bond elongations are focused towards a single bidentate ligand (hence involving elongation of two Ru-N bonds *cis* to one another. This class of MC state is called ^{3}MC$_{cis}$ hereafter). This type of ^{3}MC minimum, only once previously reported in a photochromic Ru sulfoxide complex,[3] has been shown to be particularly prone to eject a bidentate ligand.[4] Very recently this type of geometry has also been reported to be involved in Δ/Λ isomerism, and its involvement in ligand loss was suggested.[5] In relation with the reported (relative) photoinstability of the archetypical [Ru(bpy)$_3$]$^{2+}$,[6,7,8,9,10] we were interested in testing the hypothesis that such MC states had a more general existence and could also be found in homoleptic tris(bidentate) complexes. The aim of this work was therefore to search for such a ^{3}MC$_{cis}$ minimum on

the triplet excited potential energy surface of $[Ru(bpy)_3]^{2+}$ and we report its successful characterization here. We show that this new $^3MC_{cis}$ state is only marginally higher in energy than the classical axially-elongated ^3MC state, and that both ^3MC states have a similar barrier to their population from the ^3MLCT state. Thus, these novel $^3MC_{cis}$ states are likely to have significant involvement in the photophysics and photochemistry of $[Ru(bpy)_3]^{2+}$-type complexes. We may therefore need to fundamentally reassess our presumptions of how photorelease of bpy and other ligands occurs in this class of complexes, in search for a better photoreactive ^3MC candidate.

Experimental background. In the 1970s, $[Ru(bpy)_3]^{2+}$ was reported to undergo photolysis in the presence of coordinating solvents (e.g. water or acetonitrile)[6] or ions (e.g. chloride[7,10] or thiocyanato[8]). This photodegradation phenomenon was specifically studied in particularly unfavourable conditions (0.1 M HCl at 95°C) in order to allow the complete characterization and quantification of photoproducts.[6,11] In terms of mechanism, to our knowledge, no structural data is available on ^3MC states of Ru(II) complexes, which are short-lived species. The population of such ^3MC states has been recently evidenced through characteristic signatures obtained in transient absorption spectroscopy[12,13] and time-resolved infrared spectroscopy.[14,15,16] But the fact that κ^1-bpy intermediates bearing a monodentate bpy ligand are obtained[10,11,17] leads us to think that a specific ^3MC state is distorted in such a way as to allow for this, in line with the postulated dissociative mechanism.[17,18]

Methodology. In order to rationalize the photoreactivity of ruthenium complexes, one needs to map the topology of their lowest triplet potential energy surface (^3PES). Once the minima are localized and identified, the quantification of the energy barrier that is encountered by the system along the minimum energy path (MEP) is highly informative as it is related to the ease with which one triplet state populates another. In addition, the localization of singlet/triplet minimum energy crossing points (MECPs) is crucial because these points lead the system to closed-shell species that will either repopulate reactant GS or, according to Wigner rules, react with solvent and form the photoproduct (the latter being out of the scope of this work).[18] This work therefore reports minima, MEPs and MECPs for $[Ru(bpy)_3]^{2+}$ in MeCN solution, following the same computational procedure as the one recently used to establish the ^3MLCT-^3MC energy barrier.[19] Only a limited number of mechanistic theoretical studies have highlighted the crucial role of distorted ^3MC states in photoreactive Ru(II) complexes,[3,4,5,20,21,22,23,24,25,26,27,28,29,30,31] but only three of these describe ^3MC states displaying elongations towards both bonds to the same bidentate ligand.[3,4,5]

Computational methods. This study was performed in solvent (MeCN, as modelled by SMD)[32] since solvent significantly stabilizes ^3MLCT states.[19] Geometry optimizations were performed with Orca 3[33] using the B3LYP functional,[34,35] a relativistic small-core pseudopotential on Ru (SD28),[36] the def2-TZVP(-f) basis set,[37] and the empirical D3 dispersion correction.[38,39] The restricted Kohn-Sham formalism was used for ground states, while its unrestricted analogue was used for triplet states. SCF convergence was achieved using the DIIS algorithm followed by a semi-quadratic SOSCF converger. Geometries of the minima in solvent were optimized starting from the gas phase ones. Geometries of the MECPs were optimized starting from the geometries of the corresponding ^3MC states in MeCN. Frequency calculations were run at the same level of theory and the absence of imaginary frequencies ascertained the nature of these points as minima. Mulliken spin densities on Ru were used as a straightforward descriptor of the electronic nature of the triplet excited state (~1 for a ^3MLCT state, ~1.8 for a ^3MC state) and a full orbital analysis was conducted using Gabedit[40] to confirm the localization of the unpaired electrons. MEPs were optimized in SMD-MeCN with the nudged elastic band (NEB) method[41,42] using a python module developed in the Clancy group that is interfaced with Orca.[43] A 10-frame initial path was prepared by interpolating start and end geometries using the IDPP method.[44]

Minima. Up to now, the lowest triplet excited potential energy surface of $[Ru(bpy)_3]^{2+}$ was known to display two minima: a minimum of MLCT nature in the region of the GS equilibrium geometry, and a minimum of MC nature obtained after manual elongation of two *trans* Ru–N bonds (hereafter called $^3MC_{trans}$ to highlight the elongation of two *trans* Ru–N bonds).[45,46] The rationale behind this strategy of manual distortion was guided by the ground state molecular orbitals, which indicated that the lowest of the two e_g-type orbitals was of the d_{z2}-type (the terminology d_{z2}-like and d_{x2-y2}-like is employed for the sake of clarity, although it is not related to the actual axis systems of the states). The population of this d_{z2}-like orbital in the triplet excited state would thus result in the aforementioned bond elongations. The resulting *trans*-elongated minimum is considered to be the classical ^3MC state. Initially optimized under C_2 symmetry constraints in vacuum to reduce the computational cost,[45] this MC minimum is here more distorted but the characteristic elongation of two *trans* Ru–N bonds is maintained (2.42 and 2.53 Å, Figure 1 & Table S1). In MeCN solvent (SMD), the GS-$^3MC_{trans}$ gap is 2.21 eV (51.0 kcal/mol) while the ^3MLCT-$^3MC_{trans}$ gap is 0.18 eV (4.2 kcal/mol).[19] These gaps are in good agreement with previous reports.[12]

Figure 1: Structures of optimized $^3MC_{trans}$ and $^3MC_{cis}$ (B3LYP-D3, SMD-MeCN; Ru label not shown). Ru-N distances in angstroms.

$^3MC_{trans}$ $\quad\quad$ $^3MC_{cis}$ side view $\quad\quad$ $^3MC_{cis}$ top view
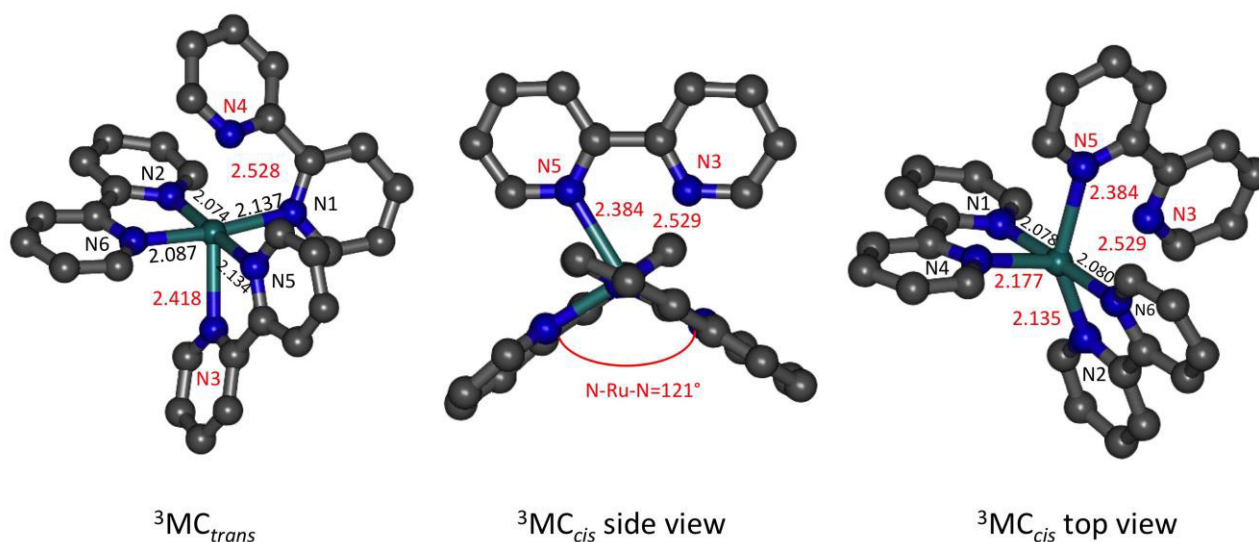
A possible distal *cis*-elongated ^3MC state was searched for by building a starting geometry with two elongated Ru–N distances of ca. 2.5 Å involving a single bpy ligand, while keeping the other two bpy ligands at more classical Ru–N distances (2.08-2.18 Å). The angle between the mean planes of these two ligands was also increased to ca. 130° to mimic the flattened geometry observed in a related series of bi(triazolyl) (btz) complexes.[4] This geometry gently optimized to a minimum, as testified by the absence of imaginary frequencies in the calculation. Due to the steric clash between α-hydrogen atoms in bpy ligands, the equilibrium geometry of the $[Ru(bpy)_3]^{2+}$ distal ^3MC ($^3MC_{cis}$) is not as flat as with btz (which does not induce such a steric clash), and a final interligand angle of 121° is observed in the opposite quadrant with respect to the distal ligand (Figure 1). The distal bpy displays final Ru–N distances of 2.38 and 2.53 Å. The other two bpy ligands display final Ru–N distances of 2.09 and 2.17 Å. Note that Ru-N1 and Ru-N5 are necessarily elongated in $^3MC_{trans}$ as a consequence of the major elongations observed on the two attached pyridines (Ru-N4 and Ru-N3). On the other hand, Ru-N4 (and to a lesser extent Ru-N2) are elongated in $^3MC_{cis}$ as a result of direct antibonding interactions with two lobes of the d_{x2-y2}-like dσ* orbital. Remarkably, the distal $^3MC_{cis}$ state is only 0.08 eV destabilized (1.9 kcal/mol) with respect to the classical $^3MC_{trans}$ state. Overall the $^3MC_{cis}$ state displays four

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elongated Ru–N bonds (two elongations of which are more pronounced) with respect to the GS geometry, and results from the occupation of a d_{x2-y2}-like antibonding orbital (Figure 2).

As shown on Figure 3, the singly occupied natural orbitals of these two ^{3}MC minima, ^{3}MC$_{trans}$ and ^{3}MC$_{cis}$, display clear d_{z2}-like and d_{x2-y2}-like features that are responsible for the observed geometric distortions in these excited states. These d-orbital contributions match those for singly occupied natural orbitals for ^{3}MC states for [Ru(N^N)(btz)$_2$]$^{2+}$ complexes reported recently (N^N = bpy, 4-(pyrid-2-yl)-1,2,3-triazole).[4]

Figure 2. Schematic antibonding interactions in the classical ^{3}MC$_{trans}$ (d_{z2}-like, left) and in the new ^{3}MC$_{cis}$ (d_{x2-y2}-like, right) minima (Ru atom not shown). The dashed lines signify the approximate planes of the two other bpy ligands for ^{3}MC$_{cis}$. Remarkable Ru–N distances and N-Ru-N angles with B3LYP-D3 in SMD-MeCN.
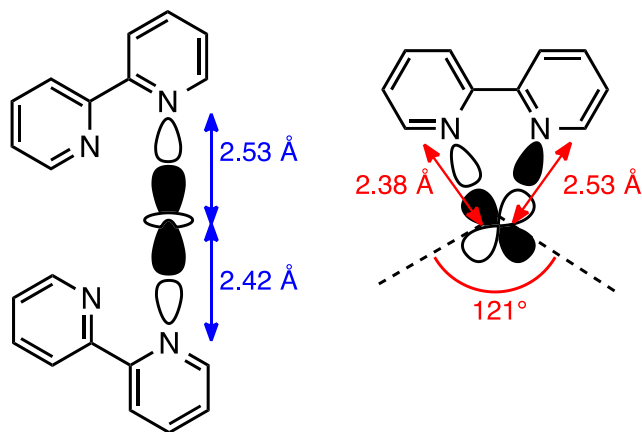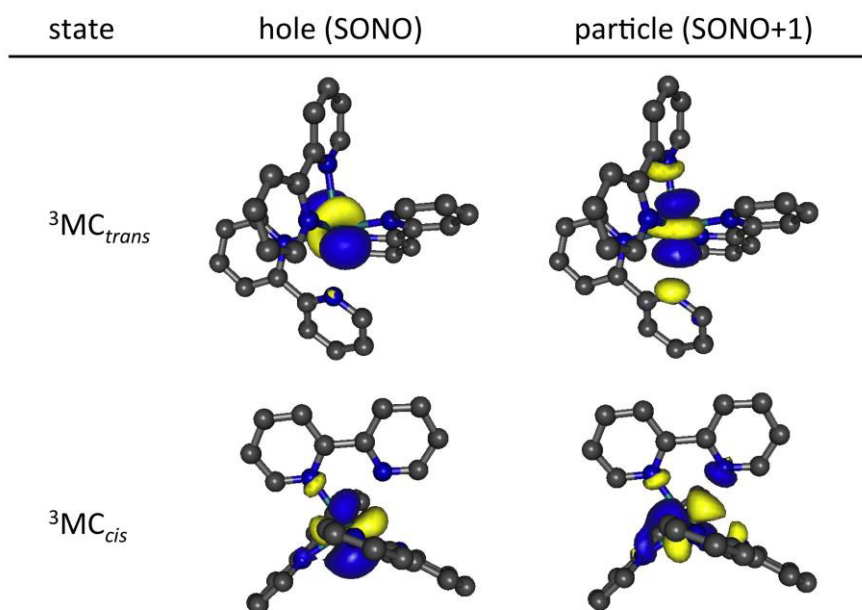

Figure 3. ^{3}MC singly occupied natural orbitals.

state	hole (SONO)	particle (SONO+1)
^{3}MC$_{trans}$		
^{3}MC$_{cis}$		

Minimum energy paths (MEPs). We have previously shown that the nudged elastic band (NEB) method,[41,42] which derives from a chain-of-states approach,[47,48] is a powerful method to probe the topology of the ^{3}PES.[19,21] This type of method determines the minimum energy path and provides the

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activation barrier encountered along this MEP, with no apriorism regarding the geometry of a transition state (explicit searching for which is not required). Further confirmation of the quality of the ^{3}MEP computed using the NEB method came from transition state optimization starting from the NEB crests, which converged smoothly at similar energies and geometries.[19] In this work, MEPs have been computed in solvent between the three triplet excited state minima (Table S2). As schematized in Figure 4, the ^{3}MLCT-^{3}MC$_{trans}$ and ^{3}MLCT-^{3}MC$_{cis}$ barriers are similar at 9 and 10 kcal/mol respectively, whilst the ^{3}MC$_{trans}$-^{3}MC$_{cis}$ barrier only amounts to 2 kcal/mol.

Figure 4. Energy profiles for the ^{3}MLCT-^{3}MC$_{trans}$ (blue) and ^{3}MLCT-^{3}MC$_{cis}$ (red) conversions following two distinct reaction coordinates. The green dashed line schematizes the direct ^{3}MC$_{trans}$-^{3}MC$_{cis}$ conversion with a 2 kcal/mol barrier.
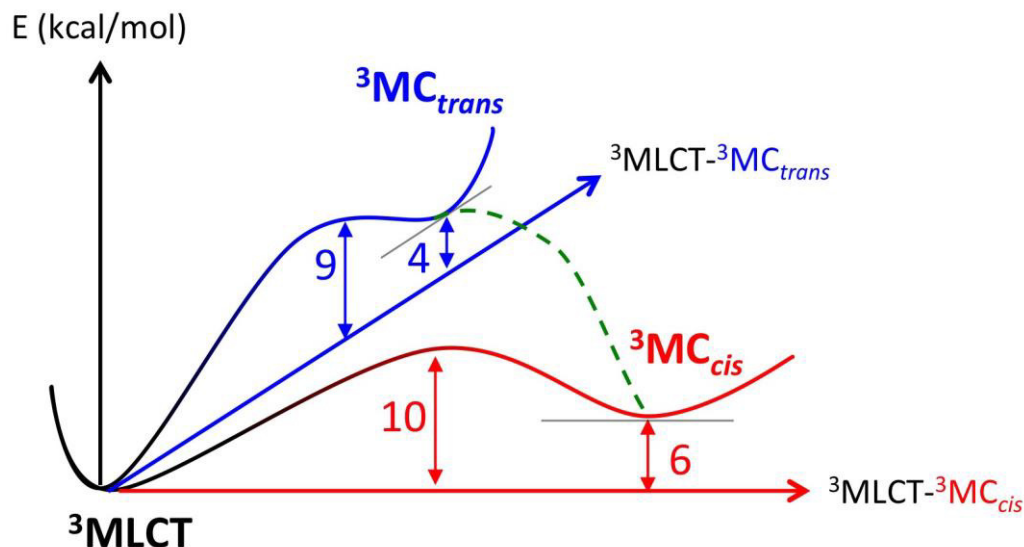
Minimum energy crossing points (MECPs). The existence of singlet/triplet MECPs in the vicinity of a ^{3}MC minimum is well established and provides an efficient nonradiative deactivation funnel. In [Ru(bpy)$_3$]$^{2+}$, the MECP between the classical ^{3}MC$_{trans}$ state and the ground state PES was described in 2009 in vacuum,[46] lying 7 kcal/mol (0.3 eV) above the ^{3}MC minimum after further geometrical distortions along the GS $\rightarrow$ ^{3}MC reaction coordinate. This MECP is called MECP$_{trans}$ hereafter. At the current level of theory, MECP$_{trans}$ is found 6.2 kcal/mol above the ^{3}MC$_{trans}$ minimum. Having now characterized another ^{3}MC state, we also searched for the MECP between this ^{3}MC$_{cis}$ state and the ground state PES. This crossing point, called MECP$_{cis}$, was found to lie only 1.3 kcal/mol above ^{3}MC$_{cis}$. The two MECPs are distinct and MECP$_{cis}$ is lower in energy than MECP$_{trans}$ by 3 kcal/mol. Table S1 displays selected geometrical parameters and Table S3 displays the singly occupied natural orbitals (SONOs) of the *cis* and *trans* ^{3}MECPs, showing the orbital parentage between each ^{3}MC minimum and its corresponding MECP. These two MECPs connect the ^{3}PES to the reactant GS PES, but others would bring the system further towards photoreactivity, once the system has entered the region where pentacoordinate species are accessible. This was hypothesized in ref. [21] and further developed in ref. [4]

Impact on the photoreactivity of [Ru(bpy)$_3$]$^{2+}$. The formation of bis(bipyridine) ligand-loss photoproducts from the reaction of [Ru(bpy)$_3$]$^{2+}$ in the presence of coordinating solvents or anions indicates that the complex is able to lose one bpy ligand after photoexcitation, albeit in very low yield under normal experimental conditions. Photoinduced ligand loss is triggered by the population of dissociative excited states. As shown in Figure 1, the classical ^{3}MC$_{trans}$ state displays two elongated *trans* Ru–N bonds. As such, it does not seem to be prone to lose one bpy ligand, although we may not completely exclude it from all possible photoreactivity mechanisms. On the other hand, the newly

identified distal $^3MC_{cis}$ excited state displaying major bond elongations towards a *single* bpy ligand may be expected to evolve towards photoproducts involving loss of bpy. Mechanistically, the new $^3MC_{cis}$ is equivalent to previously described flattened ^3MC states,[4] in that it could be the last step before ligand decoordination and diffusion. In any case, the comparative ease with which both $^3MC_{trans}$ and $^3MC_{cis}$ states will be populated from the ^3MLCT state, and the highly accessible MECP for the latter, mean that hitherto unrecognised $^3MC_{cis}$ states will undoubtedly play a major role in the photophysics and excited state deactivation dynamics of $[Ru(bpy)_3]^{2+}$ and related complexes.

Conclusion. A ^3MC state displaying one distal bpy ligand was identified and optimized to a minimum for $[Ru(bpy)_3]^{2+}$. This distal MC state ($^3MC_{cis}$) is destabilized by less than 2 kcal/mol with respect to the classical MC state ($^3MC_{trans}$). The ^3MLCT-$^3MC_{trans}$ and ^3MLCT-$^3MC_{cis}$ barriers are both ~10 kcal/mol in acetonitrile solution, and the $^3MC_{trans}$-$^3MC_{cis}$ barrier is as low as 2 kcal/mol. These figures are larger than those recently reported for photoreactive Ru bi(triazolyl) derivatives,[4] in line with the much greater photostability of $[Ru(bpy)_3]^{2+}$. Nevertheless the very existence of the distal $^3MC_{cis}$ state as a local minimum, and its accessibility, may have broad implications in our understanding of the photochemistry and photophysics of $[Ru(bpy)_3]^{2+}$ and related complexes. The lowest ^3PES is clearly far more complex than previously appreciated and previous presumptions regarding excited state processes involved in photoreactivity may therefore require some reassessment. At this moment the existence of other ^3MC minima cannot be excluded, and we are currently exploring photoreactivity mechanisms in relation with the observed photochemistry of $[Ru(bpy)_3]^{2+}$.

Supporting Information. Computational details regarding NEB calculations; selected geometrical parameters and total energies; NEB minimum energy paths (MEPs) and Mulliken spin population on Ru along the MEPs; singly occupied natural orbitals for ^3MC states and associated MECPs (PDF). Cartesian coordinates (xyz).

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Author Contributions

The manuscript was written through contributions of all authors.

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TOC graphic
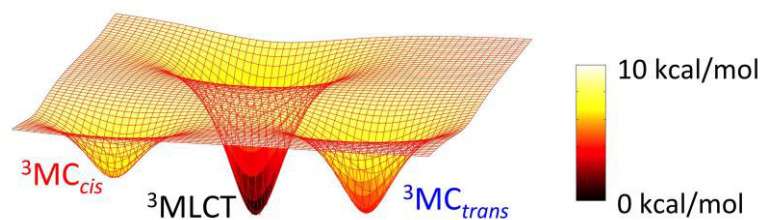
A new ³MC minimum displaying bond elongations towards a single ligand is described (³MC*cis*). According to NEB calculations of the minimum energy paths, this new state is equally accessible from the ³MLCT state than the well-known dz²-like ³MC state (³MC*trans*). This new electronic excited state should be relevant in the photodecomposition of $Ru(bpy)_3^{2+}$.