Mechanism and substituent effects on reactivity of the photochemical ligand substitution of *fac*-[Re^I(bpy)(CO)$_3$(PR$_3$)]$^+$ complex

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Rhenium(I) diimine tricarbonyl complexes of type *fac*-[Re^I(bpy)(CO)$_3$L]$^{n+}$ (bpy = 2,2′-bipyridine, L = various monodentate ligands, *n* = 0, 1) have been extensively studied since they show emissions at ambient temperature even in solution[1] and can play a role as a photocatalyst for CO$_2$ reduction.[2,3] The electronic states of these complexes are characterised by 5d orbitals of the rhenium atom (d^6 metal ion) and low-lying π and π* orbitals localised on the diimine ligand. Triplet metal-to-ligand charge-transfer (^{3}MLCT) states have been mostly studied over the last three decades, since their emissions or photocatalytic activities are related to the lowest ^{3}MLCT state.[4] The triplet metal-centred (^{3}MC) states also play an important role in the photochemical ligand substitution (PLS; Scheme 1),[5] which is an useful reaction to build supramolecules such as photoactive molecular-scale wires.[6]
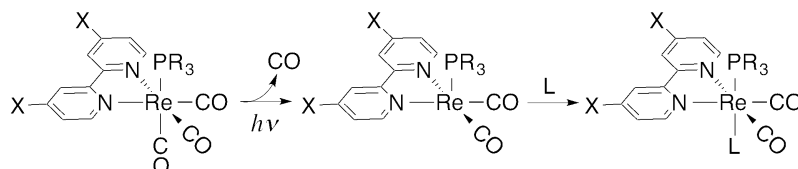
Scheme 1. Photochemical ligand substitution (PLS) reaction.

The complex with a phosphorus ligand, *fac*-[Re^I(bpy)(CO)$_3$PR$_3$]$^+$, is more reactive in PLS than that without a phosphorus ligand, *e.g.* *fac*-[Re^I(bpy)(CO)$_3$Cl]. The origin of difference in PLS reactivity has recently been investigated by *ab initio* calculations.[7] In both cases, the ultrafast decay process to the lowest triplet (T$_1$) state after photo-excitation was very similar, and the character of the T$_1$ state changed from ^{3}MLCT to ^{3}MC according as the Re-CO distance increased (Scheme 2). Dissociation barriers of the Re-CO were found in the ^{3}MC state along the reaction coordinate even in *fac*-[Re^I(bpy)(CO)$_3$P(OMe)$_3$]$^+$ case. Equatorial CO ligands had a much higher energy barrier to dissociate than that of the axial CO, so that the axial CO ligand selectively dissociated. The single component artificial force induced reaction (SC-AFIR) search[8] revealed that the minimum-energy seams of crossing between the T$_1$ and S$_0$ (ground) states (S$_0$/T$_1$-MESXs) were located before the barrier. The MESX is the minimum energy point of the crossing seam of two potential energy surfaces (different spin states), and the non-radiative decay of the intersystem crossing (ISC) could efficiently occur at the MESX. While the less PLS reactive complex *fac*-[Re^I(bpy)(CO)$_3$Cl] had lower energy S$_0$/T$_1$-MESXs than the dissociation barrier (Scheme 2a), no S$_0$/T$_1$-MESXs below the barrier were found in *fac*-[Re^I(bpy)(CO)$_3$P(OMe)$_3$]$^+$ (Scheme 2b). Therefore *fac*-[Re^I(bpy)(CO)$_3$Cl] can decay into the S$_0$ state and it shows no PLS reactions.
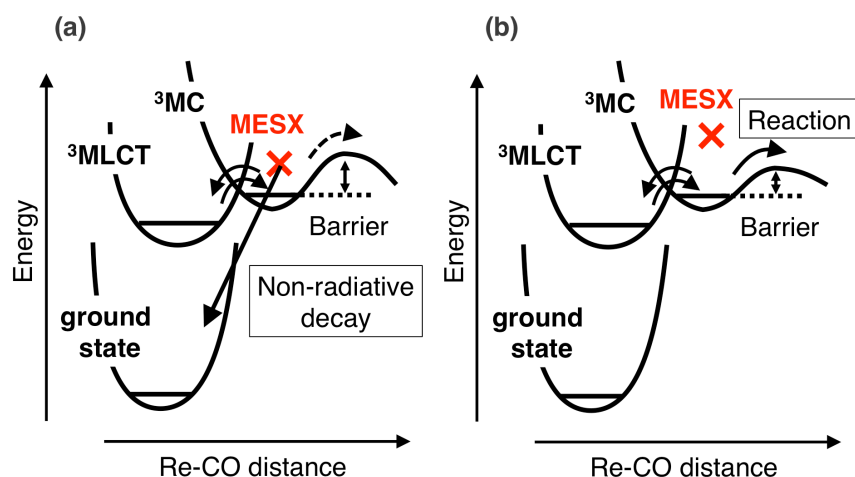
Scheme 2. Mechanisms of PLS reaction of (a) fac-[Re^I(bpy)(CO)$_3$Cl] and (b) fac-[Re^I(bpy)(CO)$_3$P(OMe)$_3$]$^+$.

Substituent effects on the PLS reactivity of fac-[Re^I(X$_2$bpy)(CO)$_3$P(OMe)$_3$]$^+$ (X$_2$bpy = 4,4$'$-X$_2$-2,2$'$-bipyridine, X = Me, OMe, CF$_3$) have also been studied.[9] An electron-withdrawing group stabilised the ^{3}MLCT. On the other hand, an electron-donating group raised the energy of the ^{3}MLCT. But the substitution on bpy did not affect the ^{3}MC. Therefore, it was suggested that the PLS reactivity decreases as OMe > Me > H > CF$_3$. This series of results confirms our proposed mechanism.

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