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ARTICLE

## Properties and Prospects for Rhenium(I) Tricarbonyl *N*-Heterocyclic Carbene Complexes

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Re(I) complexes bound to  $\pi$ -conjugated bidentate *N*-heterocyclic carbene ligands with formulation  $\text{Re}(\text{CO})_3(\text{N}^{\wedge}\text{NHC})\text{L}$  (where  $\text{N}^{\wedge}\text{NHC}$  represents an imidazole or benzimidazole carbene ligand conjugated to a *N*-based heterocycle such as pyridine, pyrimidine, quinoline or quinoxaline) are a relatively new class of complexes belonging to the archetypal family of well known luminescent  $\text{Re}(\text{CO})_3(\text{diim})\text{X}$  species (where diim is a conjugated diimine ligand and X is a halogen anion). The complexes  $\text{Re}(\text{CO})_3(\text{N}^{\wedge}\text{NHC})\text{L}$  are characterised by blue-shifted emission compared to  $\text{Re}(\text{CO})_3(\text{diim})\text{X}$ , but with shorter excited state lifetime decays and lower quantum yields, in contrast to trends expected by the energy gap law. Detailed investigations elucidated that these complexes are photochemically active and undergo ligand exchange reactions when excited to their lowest metal-to-ligand charge transfer excited states. This mechanism is entirely different from previously known mechanisms of photoactivated ligand substitution reactions in Re(I) tricarbonyl complexes. Therefore, the species  $\text{Re}(\text{CO})_3(\text{N}^{\wedge}\text{NHC})\text{L}$  represent a new and unique class of photoactive Re(I) complexes. This feature article illustrates the research effort dedicated to the design and synthesis of  $\text{Re}(\text{CO})_3(\text{N}^{\wedge}\text{NHC})\text{L}$  complexes and the elucidation of their photophysical and photochemical behaviour by means of a variety of spectroscopic techniques. Furthermore, for their unique characteristics, these new complexes have demonstrated potential value in several applications including catalysis, diagnosis and therapy. These studies will also be illustrated herein.

### Introduction

#### The luminescence of Re(I) complexes

Luminescent transition metal complexes have continued to be at the centre of an intense research effort worldwide since the very early studies on the emissive  $[\text{Ru}(\text{bpy})_3]^{2+}$  (bpy = 2,2'-bipyridine).<sup>1-3</sup> The potential applications of this class of heavy metal based compounds are numerous and include advanced optical displays, sensors, diagnostic agents and photocatalysis. Amongst the various transition metal cations, typical luminescent complexes include those of Cu(I),<sup>4</sup> Ru(II),<sup>2</sup> Re(I),<sup>5</sup> Ir(III),<sup>6</sup>

Au(I),<sup>7</sup> and Pt(II).<sup>8</sup> However, advances in this rapidly expanding field also include very recent examples of luminescent metal complexes of Ni(0),<sup>9</sup> Pd(0),<sup>10</sup> and Rh(III).<sup>11</sup> The luminescent species including the above mentioned transition metal elements are not limited to mononuclear complexes, but include aggregated architectures with dominating metal-metal interactions as well as coordination polymers and clusters. On a broader overview, the area of metal-based luminescence indeed expands into quantum dots, nanoparticles and rare

earths-containing species.<sup>12-14</sup>

Amongst the commonly investigated transition metal cations for the preparation of luminescent complexes, those containing Re(I) have certainly unique chemical features.<sup>5</sup> The element Re forms complexes in a variety of oxidation states, as typical of the elements belonging to group VII of the periodic table. However, Re(I)-containing species are those dominating the field of metal-based luminescence. The archetypal luminescent Re(I) complex has a generic formulation  $[\text{Re}(\text{CO})_3(\text{diim})\text{L}]^{0/+}$ , where diim is a diimine ligand such as phen (phen = 1,10-phenanthroline) or bpy (bpy = 2,2'-bipyridine). On the other hand, the L ancillary ligand can be either anionic (such as Cl<sup>-</sup> or Br<sup>-</sup>) or neutral (such as pyridine), thus determining the overall neutral or cationic charge of the complex, respectively. Rarer examples of luminescent Re(I) complexes display isonitrile ligands.<sup>15</sup> A small number of luminescent Re(II) complexes have also been reported, and these are generally coordinated to Cp-type ligands (Cp = cyclopentadienyl anion).<sup>5</sup>

#### Excited states in $[\text{Re}(\text{CO})_3(\text{diim})\text{L}]^{0/+}$ complexes

The origin of the luminescent properties and the nature of the emissive excited state in  $[\text{Re}(\text{CO})_3(\text{diim})\text{L}]^{0/+}$  complexes has been studied since the early investigation by Wrighton and Morse.<sup>16</sup> The ground state has a singlet multiplicity, given the fact that these complexes have a low spin  $5d^6$  valence electronic configuration. Therefore, electronic excitation leads to the singlet manifold of excited states having ligand centred

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$\pi\pi^*$  character (LC) or metal-to-ligand charge transfer character (MLCT), with the Re $\rightarrow$ diim MLCT states being generally lower in energy than LC states. These transitions can be easily identified in the UV-Vis absorption spectra of  $[\text{Re}(\text{CO})_3(\text{diim})\text{L}]^{0/+}$  complexes, with MLCT transitions appearing as bands of lower intensity or shoulders around 350-410 nm. On the other hand, LC transitions typically exhibit more intense bands in the 250-350 nm region. After population of the singlet manifold, the strong spin-orbit coupling of Re causes mixing of states with singlet and triplet spin multiplicity, therefore relaxing the spin selection rule and favouring intersystem crossing processes typical of heavy metal-containing species.<sup>17</sup> The fast population of the triplet excited state lying the lowest in energy, generally  $^3\text{MLCT}$ , is at the origin of the luminescent properties of  $[\text{Re}(\text{CO})_3(\text{diim})\text{L}]^{0/+}$  complexes. The spin-forbidden nature of the phosphorescent decay from the populated  $^3\text{MLCT}$  to the singlet ground state means that excited state lifetime decays are in a range going from hundreds of nanoseconds to few microseconds. Furthermore, the singlet-to-triplet stabilisation contributes to the typically longer Stokes shift of Re(I) complexes, and more generally in phosphorescent metal complexes, when compared to classical organic fluorophores. The origin and nature of the phosphorescence of  $[\text{Re}(\text{CO})_3(\text{diim})\text{L}]^{0/+}$  complexes, which strongly depends on the relative energy and interplay of LC and MLCT excited states, has been further refined with more advanced models over the years.<sup>18-20</sup>

#### Energy modulation of the excited states

The detailed elucidation of the origin of the emissive properties of  $[\text{Re}(\text{CO})_3(\text{diim})\text{L}]^{0/+}$  complexes has facilitated the design and preparation of species with targeted luminescent features for specific applications.<sup>21</sup> Chemical modification of the diim system through the addition of electron withdrawing or donating functional groups, and/or the extension of the  $\pi$  conjugation on the diim ligand, have important implications in modulating the energy of the emitted photons. As the excited state is of MLCT character, it can be represented by a simplified electronic configuration where one electron from the  $5d$  orbitals of the Re(I) centre is promoted to the empty antibonding  $\pi^*$  orbitals of the diim coordinated ligand. Therefore, an increase of electron density of the diim system (e.g. with the inclusion of the electron-donating functional groups) generally results in a rise in energy of the MLCT states, whereas a decrease of electron density (e.g. with the inclusion of the electron-withdrawing functional groups) results in a lowering of the energy of the MLCT states. On the other hand, the  $5d$  orbitals can be energetically stabilised or destabilised by the electron-poor or electron-rich character of the ancillary ligand, respectively. A destabilisation of the  $5d$  orbitals causes a lowering of the MLCT energy, and a stabilisation  $5d$  orbitals causes a raise of the MLCT energy. Families of  $[\text{Re}(\text{CO})_3(\text{diim})\text{L}]^{0/+}$  with tuneable emission can therefore be prepared by exploiting chemical variations at the diim and L ligands independently or in conjugation.

Modulating the energy of the excited emissive states has not only a direct consequence on the photons emitted, but also on the luminescent quantum yield and excited state lifetime decay. In fact, it has been established that phosphorescent  $[\text{Re}(\text{CO})_3(\text{diim})\text{L}]^{0/+}$  complexes are largely influenced by the energy gap law,<sup>22</sup> and therefore the non-radiative decay constant  $k_{\text{nr}}$  exponentially grows as the energy gap between the emissive  $^3\text{MLCT}$  state and the ground state becomes smaller. Typically, orange-to-red emitting Re(I) complexes have shorter excited state lifetime decays and smaller quantum yields compared to green emitting Re(I) complexes.  $[\text{Re}(\text{CO})_3(\text{diim})\text{L}]^{0/+}$  complexes are generally considered to be photochemically stable and excited state of ligand field nature (LF) are not often considered as playing a dominant role in the luminescent properties.<sup>23-25</sup> The lack of involvement of excited states of  $^3\text{LF}$  nature is ascribed to the fact that Re is a heavy element of the fifth period and to the fact that CO is a strong field ligand. Both of these features cause a raise in energy of the LF states compared to LC and MLCT states. However, the involvement of LF states has been implicated for the photochemical CO substitution of Re(I) complexes when bound to ligands exerting a strong *trans* effect.<sup>26</sup>

#### Photochemistry of $[\text{Re}(\text{CO})_3(\text{diim})\text{L}]^{0/+}$ complexes (Type I and II)

Photochemical ligand substitution reactions on  $[\text{Re}(\text{CO})_3(\text{diim})\text{L}]^{0/+}$  complexes are known, and generally these reactions have been originally exploited to access dicarbonyl complexes by substitution of one CO ligand.<sup>18, 23, 24, 26-29</sup> The combined studies on these photoreactions by means of ultrafast spectroscopies have led to the rationalisation of two general types of mechanisms.

In Type I complexes, photoexcitation to the MLCT manifold with values of wavelength generally longer than 350 nm leads to photodissociation of a CO ligand. Complexes that follow this mechanism are usually bound to ligands such as phosphines or isocyanates that are efficient in the labilisation of the ligand in the *trans* position. The proposed mechanism by Koike, Ishitani and co-workers involves the thermal population of  $^3\text{LF}$  states accessible from the emissive  $^3\text{MLCT}$  state.<sup>26</sup> The mechanism is supported by the fact that the quantum yield of the photochemical ligand substitution reaction rapidly decreases by lowering the temperature, whereas both the excited state lifetime decay and quantum yield increase. The population of antibonding  $\sigma^*$  orbitals in the  $^3\text{LF}$  state elongates metal-ligand bonds. This effect, coupled with the strong *trans* effect, promotes the dissociation of the CO ligand. Type I complexes like  $[\text{Re}(\text{CO})_3(\text{bpy})(\text{PR}_3)]^+$  yield one product upon photoexcitation of formulation  $[\text{Re}(\text{CO})_2(\text{bpy})\text{S}(\text{PR}_3)]^+$  (S = solvent molecule such as acetonitrile) with the new ligand S in *trans* to  $\text{PR}_3$  and inserted *via* dissociative substitution of the bound CO ligand.

Type II complexes are those of formulation  $\text{Re}(\text{CO})_3(\text{bpy})\text{Cl}$ , whose photoinduced CO dissociation usually occurs at values of wavelengths shorter than 315 nm.<sup>23</sup> This mechanism is more complex than that typical of Type I complexes, and involves ultrafast reactions and isomerisations originating from

higher energy excited states, with ligand substitution pathways being both dissociative and associative (the latter therefore solvent dependent). Photochemical ligand substitution reactions in  $\text{Re}(\text{CO})_3(\text{bpy})\text{Cl}$  with higher energy photons therefore yield multiple products, compared to a unique product obtained from  $[\text{Re}(\text{CO})_3(\text{bpy})(\text{PR}_3)]^+$  after photoexcitation to the lowest MLCT manifold.

### From diim to NHC ligands

About a decade ago, our research group started investigating  $\text{Re}(\text{I})$  complexes bound to *N*-heterocyclic carbene (NHC) ligands. The rationale that prompted this study was to elucidate the effect on the photophysical properties of  $\text{Re}(\text{I})$  complexes upon complexation by *N*-heterocyclic carbene ligands.  $\text{Re}(\text{I})$  complexes bound to this class of ligands were known,<sup>30, 31</sup> but detailed photophysical studies on this class of compounds were lacking. On the other hand, only a small library of luminescent  $\text{Re}(\text{I})$  complexes bound to an NHC ligand as an ancillary was known, with formulation  $[\text{Re}(\text{CO})_3(\text{diim})(\text{NHC})]^+$  (Figure 1).<sup>32</sup> The study did report the luminescent properties of the complexes, which were all emitting via the expected  $\text{Re} \rightarrow \text{diim}^3\text{MLCT}$  excited states. The study also investigated in details the rigidochromism causing a blue shift the  $^3\text{MLCT}$  excited state upon freezing of solvent and consequent mixing with higher lying  $^3\text{LC}$  excited states. However, no report was available on  $\text{Re}(\text{I})$ -NHC complexes where the NHC ligand contributed to a direct participation into the excited state, e.g. where the  $\pi^*$  orbitals of the NHC ligand could directly modulate the nature of the emissive MLCT state.

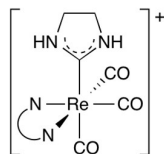


Figure 1.  $\text{Re}(\text{I})$ -NHC complex whose luminescent properties were studied by Che and co-workers. The NHC ligand represents a variously functionalised diimine ligand.

The targeted complexes for this study were of formulation  $\text{Re}(\text{CO})_3(\text{N}^{\wedge}\text{NHC})\text{X}$  (where N represents a N-donor ligand conjugated to an NHC functional group, and X is Cl or Br), so that a direct comparison between their luminescent properties and those of the well established  $\text{Re}(\text{CO})_3(\text{phen})\text{X}$  (X = Cl, Br) could be made to elucidate the role of the NHC.

## Properties of $\text{Re}(\text{I})$ -NHC Complexes

### Early photophysical studies on $\text{Re}(\text{I})$ -NHC complexes

The first set of complexes synthesised by our group is reported in Figure 2.<sup>33</sup> The two complexes **1Cl** and **1Br** were obtained *via* simple substitution of two CO ligands in  $\text{Re}(\text{CO})_5\text{X}$  (X = Cl, Br) by the corresponding benzimidazolium salt.

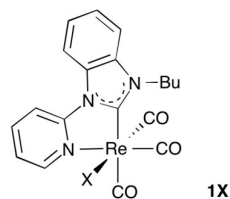


Figure 2. Initial  $\text{Re}(\text{I})$  complexes investigated to assess the effect of the NHC ligand on the photophysical properties (Bu = *n*-butyl; X = Cl, Br).

The absorption spectra of the two complexes from diluted dichloromethane solutions revealed the expected bands associated to LC (250-300 nm) and MLCT (320-400 nm) transitions (for simplicity, we will use the term MLCT; a more accurate description of this transition would be metal-ligand-to-ligand charge transfer as an admixture of metal-to-ligand charge transfer and ligand-to-ligand charge transfer, typically occurring when the ancillary ligand is electron rich). The emission profiles were structureless with maxima around 500-510 nm. Rigidochromism was observed upon freezing the solvent down to 77 K, with consequent blue-shift of the emission maxima and the appearance of vibronic progression. The emissive state was ascribed to a  $^3\text{MLCT}$ . The blue-shift observed from the complexes **1X** compared to  $\text{Re}(\text{CO})_3(\text{phen})\text{Cl}$  was rationalised by lowering of the  $\pi$  conjugation on passing from phen to the NHC ligand. However, contrary to a trend expected from the energy gap law, **1X** displayed significantly shortened excited lifetime decays and smaller quantum yields with respect to  $\text{Re}(\text{CO})_3(\text{phen})\text{Cl}$ , despite the former having a larger energy gap between the emissive  $^3\text{MLCT}$  state and the ground state. Furthermore, measuring the absorption and emission spectra from diluted acetonitrile solutions to assess the solvatochromic behaviour of the complexes revealed a progressive change of the profile, with the disappearance of the original MLCT bands and the appearance of a new red-shifted MLCT transition. The transformation was caused by excitation of the complexes to the MLCT manifold at 365 nm, as the complexes were otherwise stable with no change observed from acetonitrile solutions kept in the dark for the same timeframe ( $\approx 60$  min).

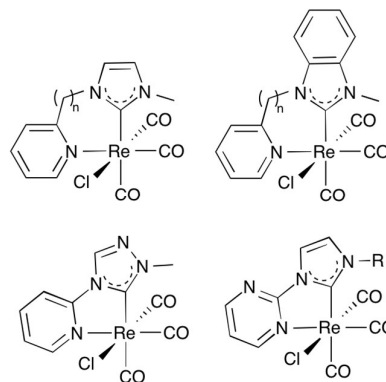


Figure 3. Library of  $\text{Re}(\text{I})$ -NHC complexes investigated by Zheng and co-workers ( $n = 0, 1$ ; R = methyl, *n*-butyl, benzyl, mesityl).

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Shortly after the publication of the **1X** complexes, Zheng and co-workers synthesised the family of Re(I)-NHC complexes shown in Figure 3.<sup>34</sup> The complexes were prepared *via* silver transfer reactions using Ag<sub>2</sub>O. The complexes present variations on the NHC ligand where the pyridyl substituent is exchanged for pyrimidyl, the imidazole ring is exchanged for benzimidazole, and the conjugation between the two heterocycles forming the bidentate NHC ligand is interrupted by the insertion of a methylene spacer. The investigation of the photophysical properties of the complexes bound to the pyridyl-functionalised NHC ligand, without the methylene spacer, from diluted dichloromethane solutions revealed data in line with those obtained for complexes **1X**. The shorter excited state lifetime decay and lower quantum yields compared to Re(CO)<sub>3</sub>(phen)Cl were tentatively ascribed to the thermal population of lower lying <sup>3</sup>LF excited states, although other possible non-radiative pathways were not excluded. On the other hand, those complexes bearing a methylene spacer were found to be non-emissive, a feature explained by lowering the rigidity of the NHC ligand. Interestingly, the exchange of a pyridyl for a pyrimidyl substituent, as shown in Figure 2, resulted in a significant red-shift of the MLCT manifold and emission maxima ( $\Delta\lambda_{\text{max}} \approx 60$  nm) measured from diluted dichloromethane solutions. The excited state lifetime decays ranged around 1.5–1.7  $\mu\text{s}$ , with values significantly elongated with respect to the analogous complexes bearing a pyridyl-functionalised NHC ligand. The quantum yield values were also found to be higher. The study of Zheng and co-workers, coupled with our investigation of complexes **1X** provided intriguing features of this type of luminescent Re(I)-NHC complexes, as their behaviour indicated opposite trends with respect to the energy gap law. However, the family of complexes reported by Zheng and co-workers (Figure 3) did not report any data in diluted acetonitrile solutions, where complexes **1X** were found to be photochemically active upon excitation to the MLCT manifold.

#### Early photochemical studies on Re(I)-NHC complexes

In order to elucidate the origin of the anomalous behaviour upon photoexcitation of the Re(I)-NHC complexes shown in Figures 2 and 3, our group investigated in more details the variation of the photophysical and associated photochemical trends in a family of targeted Re(I)-NHC complexes (Figure 4).<sup>35, 36</sup> The aim of this study was to relate variations in the chemical structures with photophysical/photochemical properties.

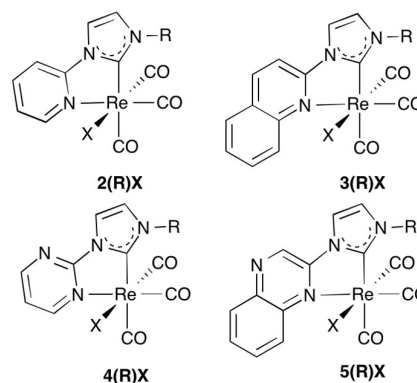


Figure 4. Re(I)-NHC complexes investigated to establish the link between chemical structure and photophysical/photochemical properties, including pyridyl-functionalised series **2(R)X** (R = *n*-butyl, phenyl, mesityl; X = Cl, Br), quinolinyl-functionalised series **3(R)X** (R = phenyl; X = Cl, Br), pyrimidyl-functionalised series **4(R)X** (R = phenyl, mesityl; X = Cl, Br), and quinoxyl-functionalised series **5(R)X** (R = phenyl, mesityl; X = Cl, Br).

The overall photophysical trend from diluted dichloromethane solutions followed the previously observed trend, with the complexes belonging to the **2(R)X** series displaying blue-shifted emission maxima around 520 nm, relatively short excited state lifetime decays and low values of quantum yield. The trend suggest that the chemical nature of the R group has no profound effect on the relative energy of the <sup>3</sup>MLCT emissive state, nor the presence of a fused benzene ring on passing from benzimidazole to imidazole on the NHC ligand. This conclusion was also supported by time dependent density functional theory (TD-DFT) calculations, highlighting the contour of the LUMO predominantly localised on the pyridine ring and partially on the NCN region of the NHC ring. Furthermore, all these complexes were found to be photochemically active in diluted acetonitrile solutions, displaying the same changes previously observed for the **1X** complexes. On the other hand, the complexes **3(R)X** and **4(R)X**, displayed red-shifted emission maxima around 570–590 nm, with longer excited state lifetime decays and higher quantum yield values. None of these complexes displayed photochemically activated changes upon excitation to the MLCT manifold. The complexes **5(R)X** were found to be essentially quenched in fluid solution at room temperature, but <sup>3</sup>MLCT emission could be revived on freezing the solution to 77 K. These complexes were also found to be stable when irradiated to the MLCT manifold.



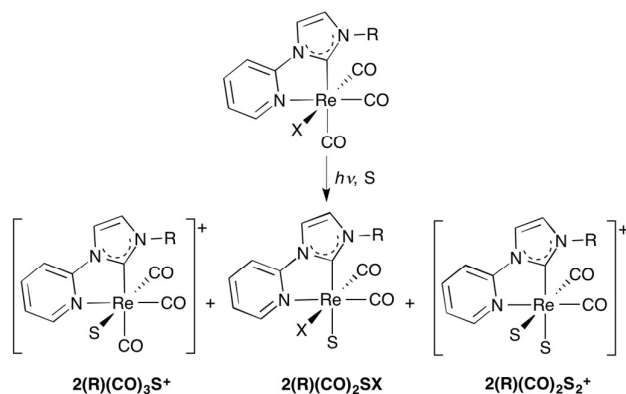


Figure 5. Structures of the three products formed during the photolysis of  $2(R)X$ . While the stereochemistry of  $2(R)(CO)_2SX$  was confirmed by single crystal X-ray diffraction, the stereochemistry of  $2(R)(CO)_2S_2^+$  is only assumed on the basis of its chemical formulation.

The photochemical transformation of the complexes  $2(R)X$  was monitored by sequentially recording  $^1H$ -NMR and IR spectra during the photolysis in deuterated acetonitrile solutions. Contrary to the unique dicarbonyl product formed by photolysis of  $[Re(CO)_3(bpy)(PR_3)]^+$  upon irradiation to the MLCT manifold, the photolysis of the  $2(R)X$  complexes under similar conditions displayed the formation of three distinct products. The variation of the IR spectra at the carbonyl region ( $2050$ – $1800\text{ cm}^{-1}$ ) also highlighted the disappearance of the typical three peaks of  $2(R)X$  and the appearance of a peak at higher wavenumbers ( $2036\text{ cm}^{-1}$ ) and two sets of two peaks each between  $1940$  and  $1830\text{ cm}^{-1}$ . Three products formed during the photolysis were identified as shown in Figure 5, with the first product formed being the tricarbonyl solvatocomplex  $2(R)(CO)_3S^+$ , which is itself photochemically active and might originate the remaining two products during the photochemical reaction. The data were also independently confirmed by comparing the  $^1H$ -NMR and IR spectra of  $2(\text{phenyl})(CO)_3S^+$  synthesised by exchange of the chloro ligand in  $2(\text{phenyl})Cl$  with a molecule of acetonitrile by reaction with  $Ag(I)$  salts. On the other hand, the product  $2(\text{phenyl})(CO)_2(NCCH_3)Cl$  could be identified by growing single crystals suitable for X-ray diffraction upon purification of the mixture of three products after photolysis. The red-shifted MLCT bands in the absorption spectra are associated to this neutral dicarbonyl complex, as the exchange of a strong  $\pi$ -acidic ligand such as CO with a weakly  $\sigma$ -donating acetonitrile molecule causes the destabilisation of the  $5d$  orbitals of the Re(I) centre and hence lowering of the energy gap between the  $^3MLCT$  and ground state. The exact stereochemistry of the second cationic dicarbonyl complex  $2(R)(CO)_2S_2^+$  could only be inferred from the spectroscopic data. The photolysis of the  $2(R)X$  complexes in acetonitrile solution also occurred at temperatures as low as  $233\text{ K}$ , which is close to the freezing point of the acetonitrile. Furthermore, the photochemical reaction occurred in acetonitrile or pyridine, but the complexes were photostable in non-coordinating solvents such as dichloromethane as well as coordinating solvents such as acetone or dimethylsulfoxide.

The investigation evidenced that the photochemistry of Re(I)-NHC complexes such as  $2(R)X$  are not associated to Type II, since the photoactivated reactions occur upon irradiation to the lowest MLCT manifold and with wavelengths longer than  $350\text{ nm}$ . Furthermore, the  $2(R)X$  complexes are also not associated to Type I, as multiple products are formed and the reaction proceeds at temperatures as low as  $233\text{ K}$ .

### Photochemistry of Re(I)-NHC complexes (Type III)

The mechanism of photolysis of Re(I) was indeed a new type of photoactivated reaction, and therefore these species were associated to a new Type III. The overall mechanism was elucidated by means of temperature dependent measurements of the excited state lifetime decays as well as by time-resolved infrared spectroscopy (TR-IR).<sup>37</sup> The measurements for both techniques were obtained in non-reactive conditions (dichloromethane) and reactive conditions (acetonitrile). The complex  $2(\text{phenyl})Br$  was chosen for this investigation.

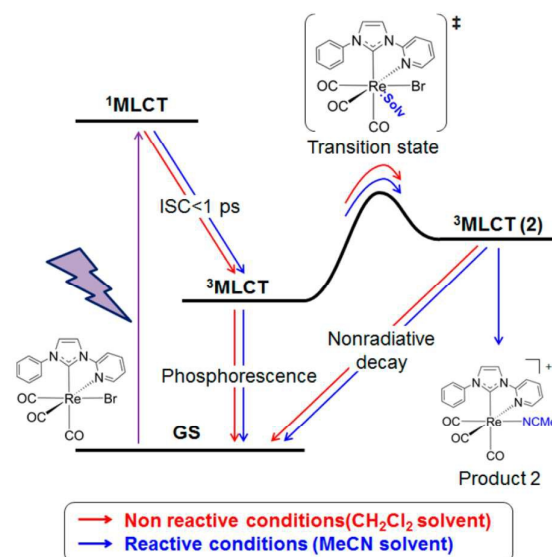


Figure 6. Jablonski diagram illustrating the proposed Type III mechanism of photophysics occurring in Re(I)-NHC complexes, where the complex  $2(\text{phenyl})Br$  in acetonitrile is chosen as exemplar. Reprinted (adapted) with permission from T. Mukuta, P. V. Simpson, J. G. Vaughan, B. W. Skelton, S. Stagni, M. Massi, K. Koike, O. Ishitani and K. Onda, *Inorg. Chem.*, 2017, **56**, 3404–3413. Copyright 2017 American Chemical Society.

The overall mechanism is schematised by the Jablonski diagram in Figure 6. The analysis of the Arrhenius plots from the measurements of the temperature dependent excited state lifetime decays displayed virtually identical behaviour in dichloromethane and acetonitrile solution. The data indicated the presence of a thermally populated excited state, which was ascribed to a higher lying MLCT state,  $^3MLCT(2)$  (Figure 6). The Gibbs free energy of activation  $\Delta G_{298}^\ddagger$  at  $298\text{ K}$  was estimated from the obtained values of  $\Delta H^\ddagger$  and  $\Delta S^\ddagger$  and found at  $2460$  and  $2100\text{ cm}^{-1}$  for non-reactive and reactive conditions, respectively. These values are significantly lower than those obtained from the thermal population of  $^3LF$  states in Type I complexes such as  $[Re(CO)_3(bpy)(PR_3)]^+$ , for which

typical activation energies are around  $4000\text{ cm}^{-1}$ .<sup>26</sup> Therefore, the nature of the thermally populated state was associated to a higher lying MLCT rather than LF. TD-DFT calculations highlighted significant distortion occurring upon population of the  $^3\text{MLCT}(2)$  excited state. In reactive conditions, the distortion allows the coordination of a solvent molecule, followed by the exchange of the Br ligand by acetonitrile with formation of  $2(\text{phenyl})(\text{CO})_3\text{S}^+$ . This mechanism is supported by the positive value of  $\Delta\text{S}^\ddagger$ , suggesting that the structures of the transition state and the packaging of the surrounding solvents are more ordered for  $^3\text{MLCT}(2)$  than  $^3\text{MLCT}$ . In non-reactive conditions, the population of  $^3\text{MLCT}(2)$  leads to rapid non-radiative decay to the ground state, explaining the relative short excited state lifetime decays and low values of quantum yield originally reported in the early photophysical studies of Re(I)-NHC complexes from dichloromethane solutions. The formation of  $2(\text{phenyl})(\text{CO})_3\text{S}^+$  can also be observed by analysis the sequence of TR-IR spectra at the nanosecond time scale. No other product is visible from the TR-IR measurements, in agreement with the fact that the first compound appearing in the  $^1\text{H-NMR}$  spectra during the photolysis of  $2(\text{R})\text{X}$  is always  $2(\text{R})(\text{CO})_3\text{S}^+$ . As  $2(\text{R})(\text{CO})_3\text{S}^+$  is photochemically active, it is likely that the other two products  $2(\text{R})(\text{CO})_2\text{SX}$  and  $2(\text{R})(\text{CO})_2\text{S}_2^+$  are obtained directly from  $2(\text{R})(\text{CO})_3\text{S}^+$ .

While the investigation demonstrated the facile photochemical substitution of the halogen ancillary ligand in  $2(\text{R})\text{X}$  complexes, later studies by Barnard and co-workers highlighted an increase of the lability of the Re-X bond in Re(I)-NHC complexes.<sup>38</sup> In fact, spectroscopic data highlighted the slow exchange of the halogen ligand for an acetonitrile molecule coordinated to the Re centre over several hours. This feature seems of pivotal importance for the properties of Re(I)-NHC complexes in catalysis and as anticancer therapeutic agents.

## Prospects for Re(I)-NHC Complexes

### Electrocatalytic reduction of CO<sub>2</sub>

The ever-growing CO<sub>2</sub> in Earth's atmosphere, the consequence of increasing industrialisation over the last several centuries, is an under utilised waste product. The ability to harness this waste product and convert it to fuel or fuel precursors using the power of the sun and a catalyst would be of massive economic and environmental import.

There is a growing interest in finding new catalytic systems for the efficient conversion of CO<sub>2</sub> to its reduced products, including CO, HCO<sub>2</sub>H, CH<sub>3</sub>OH, and CH<sub>4</sub>, that could have applications as potential fuels. While the one electron reduction of CO<sub>2</sub> to CO<sub>2</sub><sup>•-</sup> is an energetically demanding process, multi-electron reduction processes to form the products listed above are less demanding but suffer from slow rates. The use of catalysts can increase this rate and promote multi-electron reduction while at the same time afford some product selectivity. Re(I) complexes of the type Re(CO)<sub>3</sub>(bpy)Cl have long been known to act as effective catalysts in the electro- and photocatalytic reduction of CO<sub>2</sub>,<sup>39</sup> but only very recently have isoelectronic Re(CO)<sub>3</sub>(NHC)X complexes, where NHC is a bidentate carbene ligand that binds the metal

through the carbenic carbon and an imine type N-donor, been explored in this context. Advantageously, more facile modification of the steric and electronic parameters of the NHC ligand compared to the bipyridine-based system can lead to more selective and efficient catalysts in the former case. The group of Agarwal, spurred on their first use of an analogous Mn(I)-NHC complex as a CO reduction catalyst in 2014,<sup>40</sup> recently studied the utility of Re(I)-NHC complexes **6** and **7** in this context (Figure 7).<sup>41</sup>

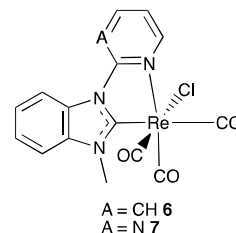


Figure 7. Re(I) complexes bound to NHC ligands trialled for the electrocatalytic reduction of CO<sub>2</sub> investigated by Agarwal and co-workers.

The authors show that one electron reduction of Re(CO)<sub>3</sub>(NHC)Cl occurs at the metal centre, which leads to dissociation of the halide ligand and formation of the five-coordinate neutral radical [Re(CO)<sub>3</sub>(NHC)]<sup>•</sup> as the catalytically active species. This is in contrast to Re(CO)<sub>3</sub>(bpy)Cl, where the catalytically active species is formed only after the second reduction wave. Infrared spectroelectrochemistry was used to show that further reduction of the five-coordinate radical formed upon one electron reduction gives rise to the [Re(CO)<sub>3</sub>(NHC)]<sup>-</sup> anion. Addition of a proton source can increase CO<sub>2</sub> reduction rates, but often at the expense of reaction selectivity. This is a problem for many electrocatalysts. Controlled electrolysis at a potential just negative of the first reduction of an acetonitrile solution of **6** and **7** containing a Brønsted acid (0.5 M PhOH) under CO<sub>2</sub> saturated argon, leads to the catalytic production of CO and minor amounts of H<sub>2</sub> as well as HCO<sub>2</sub>H. The formation of small amounts of H<sub>2</sub> and HCO<sub>2</sub>H suggest that protons can interact with the reduced metal centre. Importantly, for both cases CO was produced with a Faradaic efficiency (FE<sub>CO</sub>) of ca 60%, albeit lower than for Re(CO)<sub>3</sub>(bpy)Cl. A general proposed scheme for the electrocatalytic conversion of CO<sub>2</sub> to CO after the first reduction of the catalyst is shown in Figure 8.

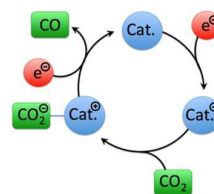


Figure 8. Proposed scheme for electrocatalytic conversion of CO<sub>2</sub> to CO by a Re(CO)<sub>3</sub>(NHC)X type catalyst. Two proton transfers are understood with an added proton source but are not explicitly denoted when they occur. Reprinted (adapted) with permission from N. P. Liyange, H. A. Dulaney, A. J. Huckaba, J. W. Jurs and J. H. Delcamp, *Inorg. Chem.*, 2016, **55**, 6085-6094. Copyright 2016 American Chemical Society.

In a similar study, the groups of Jurss and Delcamp reported the synthesis of a series of Re(I)-NHC complexes **8** – **11** as catalysts for the electrocatalytic reduction of CO<sub>2</sub> to CO (Figure 9).<sup>42</sup> The complexes possessed electron withdrawing substituents on the aryl ring that serve to lower the overpotentials required for catalysis. Initial studies showed that complex **8** displayed the highest catalytic rate of CO<sub>2</sub> reduction, even higher than that of Re(CO)<sub>3</sub>(bpy)Cl, while complex **9** was unstable in solution and started to decompose before a single scan could be obtained. In an attempt to optimise the reaction, the effect of three proton sources (phenol, trifluoroethanol, and water) on the efficiency of CO generation catalysed by **8** was investigated. Addition of 0.5 M phenol caused little change in the peak FE but 1.5 M phenol led to a lower FE<sub>CO</sub> for CO production and a large increase (35% FE<sub>H<sub>2</sub></sub>) in H<sub>2</sub> generation. Addition of 1.1 M trifluoroethanol led to only trace formation of H<sub>2</sub> and a significantly improved efficiency of CO production (77% FE<sub>CO</sub>). Remarkably, addition of 2 M water gave peak FE<sub>CO</sub> values close to 100% with only trace amounts of H<sub>2</sub>, a significant improvement over Re(CO)<sub>3</sub>(bpy)Cl under the same conditions.

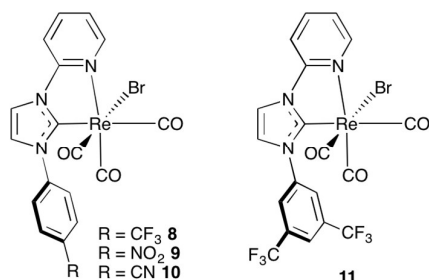


Figure 9. Re(I) complexes bound to NHC ligands trialled for the electrocatalytic reduction of CO<sub>2</sub> investigated by Jurss, Delcamp co-workers.

### Photocatalytic reduction of CO<sub>2</sub>

Although there are many electrocatalysts based on Re, Ru,<sup>43</sup> Co,<sup>44</sup> Fe,<sup>45</sup> and Ni<sup>46</sup> that can reduce CO<sub>2</sub> in the presence of a visible light photosensitizer, only three catalyst series – Re(CO)<sub>3</sub>(bpy)Cl, Ir(tpy)(ppy)Cl, and Ir(thiazole)<sub>2</sub>(bpy) – are capable of absorbing solar spectrum radiation and reducing CO<sub>2</sub>. Indeed, the parent complex Re(CO)<sub>3</sub>(bpy)Cl is now taken as the standard when evaluating the photocatalytic properties of new catalysts for CO<sub>2</sub> reduction. Generalised schemes for the non-sensitised and sensitised photocatalytic reduction of CO<sub>2</sub> are shown in Figure 10.

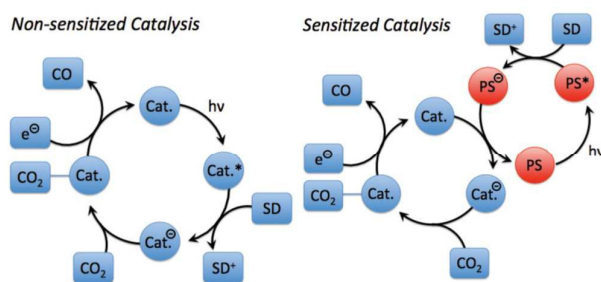


Figure 10. Non-sensitised (left) and sensitised (right) CO<sub>2</sub> reduction cycles (PS = photosensitizer, SD = sacrificial donor). Reprinted (adapted) with permission from A. J. Huckaba, E. A. Sharp and J. H. Delcamp, *Inorg. Chem.*, 2016, **55**. Copyright 2016 American Chemical Society.

Delcamp and co-workers recently reported the synthesis and photocatalytic studies of a series of Re(I)-NHC complexes where the aryl imidazolyl groups are functionalised with electron donating, electron neutral, and electron withdrawing groups.<sup>47</sup> Both bromido and chlorido versions of each analogue were prepared. As expected, those complexes with electron withdrawing substituents performed better in the photocatalytic reduction of CO<sub>2</sub> compared to those with electron neutral or donating substituents. Complex **8** outperformed the standard Re(CO)<sub>3</sub>(bpy)Cl in the presence of photosensitizer *fac*-Ir(ppy)<sub>3</sub> and sacrificial donor 1,3-dimethyl-2-phenyl-2,3-dihydro-1H-benzo[d]imidazole (BIH). More importantly, catalyst **8** is capable of non-photosensitised CO<sub>2</sub> reduction with visible light, making it just the fourth such class of compounds. In an elegant extension of their previous work, Jin and co-workers adsorbed Re(I)-NHC complexes **6** and **7** onto the surface of silicon nanowire (SiNW) photoelectrodes and examined the photocatalytic reduction of CO<sub>2</sub>.<sup>39</sup> Importantly, the use of a photoelectrode surface eliminates the need for a sacrificial donor, and in this way **6** and **7** displayed FE<sub>CO</sub> values of 57 and 53%, respectively. The efficiency of this process could be enhanced for **7** by the addition of 5% H<sub>2</sub>O, which increased the FE<sub>CO</sub> to 68%, with minor H<sub>2</sub> production (FE<sub>H<sub>2</sub></sub> = 9%).

### Anticancer activity

In addition to studying the photophysical and photochemical properties of Re(I)-NHC complexes, as described above, we have recently started an investigation into the biological properties of these complexes as anticancer agents. Indeed, we were prompted to do so by several recent reports that showed that coordination compounds of rhenium (of non carbenic ligands) that contained the Re(CO)<sub>3</sub> fragment were highly cytotoxic against various cancer strains.<sup>48-50</sup> We decided to prepare a series of rhenium and ruthenium complexes (Figure 11), and compare their activity against various pancreatic cancer cell lines.<sup>51</sup> It was anticipated that those compounds conjugated to the non-steroidal anti-inflammatory (NSAID) indomethacin might exhibit some dual effect properties due to the metal fragment and the indomethacin with concurrent enhanced activity. Knowing that compounds based on ruthenium had, in many cases, shown good anticancer activity,<sup>52</sup> we were expecting the ruthenium containing compounds to be superior to that of the rhenium analogues. To our surprise, we observed the complete opposite, with the Re(I)-NHC complexes clearly superior against the cell lines tested. Almost all the complexes were more active than the platinum based anticancer drug carboplatin with IC<sub>50</sub> values below 10 μM, but most importantly, we learned that the Re(I)-NHC tricarbonyl fragment alone is responsible for the high activity. In previous examinations of the biological properties of rhenium complexes, no substantial mechanistic studies were performed, and thus we embarked on a study to understand



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the mechanism of action of our rhenium compounds, which would help us to design new and more active rhenium-based drugs. Most of the complexes do not induce apoptosis, but instead act as cytostatic drugs. Further mechanistic studies demonstrated that the complexes induced cell cycle arrest at the G2/M phase by inhibiting the phosphorylation of Aurora-A kinase. Indeed, Aurora-A is overexpressed in different tumours, including pancreatic cancer, and is an attractive target. A larger series of complexes were then prepared in order to conduct a detailed structure activity relationship (SAR); we found that while the structure of the N-donor ring and R substituent on the imidazolyl group had some effect, the activity of the Re(I)-NHC complexes was strongly linked to the lability of the ancillary ligand, with those containing bromo and chloro ligands generally the most active. Indeed, we believe, and are in the process of validating, that the rhenium complexes lose their halido ancillary ligand inside cells, it being replaced by water, and then form a covalent interaction with a target protein/receptor. Continued work in this area is ongoing within our group.

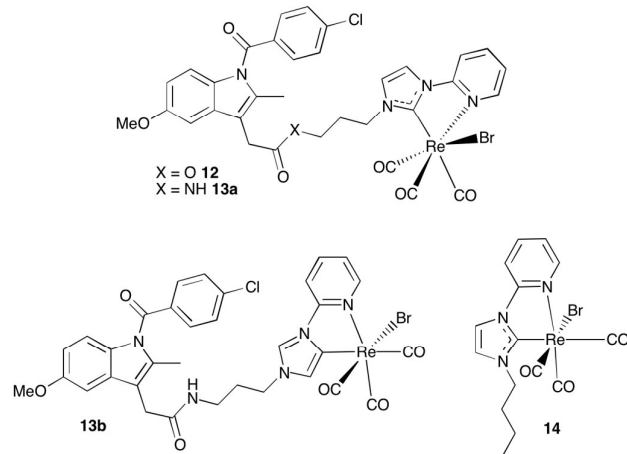


Figure 11. Re(I)-NHC complexes investigated as anticancer agents against pancreatic cancer.

In the last several years, it has become well established that complexes of rhenium, particularly those bearing a facial tricarbonyl ligand arrangement, possess interesting anticancer properties, and should not be solely relegated to the toolbox of luminescent compounds.<sup>53</sup> Although this article focuses on those rhenium complexes containing NHC ligands, it would be remiss of us when extolling the virtues of this class of compounds, if we did not mention other significant contributions to the field of bioactive rhenium complexes in general. The group of Wilson recently reported the *in vitro* anticancer activity and *in vivo* biodistribution studies of a series of rhenium(I) tricarbonyl aqua complexes bearing functionalised bipyridine or phenanthroline ligands (Figure 12).<sup>54</sup> Three of the compounds, **15** – **17**, which showed comparable activity to cisplatin against HeLa cells, were tested in a panel of wild type and cisplatin resistant cell lines. While cisplatin showed poor activity against cisplatin resistant cells, the rhenium complexes were almost equally effective in both.

Confocal microscopy studies of **17** in HeLa cells showed that the complex does not accumulate in the nucleus, mitochondria, or endoplasmic reticulum, but rather in the cytosol and large cytosolic vacuoles that could be a broad population of endosomes and lysosomes. Cell cycle analysis in HeLa cells treated with complex **17** showed arrest of the cells in the G2/M phase, the same as we observed for our rhenium(I)-NHC complexes mentioned above. Consistent with the confocal studies showing no mitochondrial accumulation, no increase in intracellular ROS levels or mitochondrial membrane depolarisation was observed. Given that these complexes possess a labile aqua ligand and our Re(I)-NHC complexes possess halido ligand that dissociate in aqueous media, it seems entirely possible that both classes of complexes have similar mechanisms by which they exert biological activity. This could be the formation of a covalent interaction between the rhenium centre and N-donor ligands found in proteins or other intracellular components. It is also possible that the structure of the bidentate ligand changes the nature of the target but not ability of the compounds to form covalent interactions.

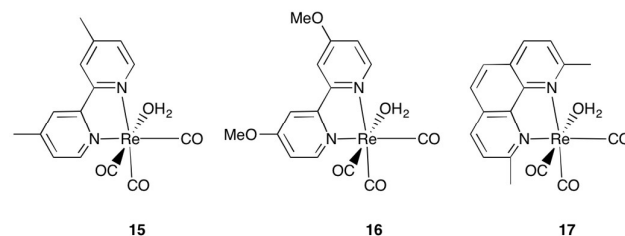


Figure 12. Re(I) aqua complexes investigated as anticancer agents.

### Diagnosis and treatment of Alzheimer's disease

Rhenium complexes, in particular those containing carbene ligands, have also been studied in a biological context for the treatment and diagnosis of Alzheimer's disease (AD). The luminescent properties of these complexes does not originate from <sup>3</sup>MLCT states of the Re(I) complex. Nevertheless, this class of Re(I)-NHC complexes is worth mentioning to emphasise even further the potential application of these species in areas of biology other than the treatment of cancers. The group of Barnard recently reported a series of Re(I)-bis(NHC) complexes that were coupled to stilbene or benzothiazole based amyloid binding groups, for potential use against Alzheimer's disease (Figure 13).<sup>55</sup> The ability of the rhenium complexes to bind to fibrils formed from synthetic amyloid beta peptide A $\beta_{1-42}$  was evaluated using the ThT (thioflavin T) fluorescence assay. Addition of ThT to a freshly prepared solution of amyloid beta peptide A $\beta_{1-42}$  caused an increase in the emission intensity of ThT at 485 nm, associated with ThT-fibril binding. In contrast, addition of the Re(I)-NHC complexes **18a,b** and **19a,b** in the presence of ThT led to little to no increase in emission intensity at 485 nm. The authors postulate that this either means that the rhenium complexes competitively bind to A $\beta_{1-42}$  fibrils or that the complexes inhibit fibril formation. Two of the complexes, **18b** and **19a**, were then selected to study their binding to A $\beta$  plaques in human

AD brain tissue. While **18b** showed no A $\beta$  binding, complex **19a** showed high levels on co-localisation with the immunostaining (Figure 13). The authors are further developing the use of these NHC ligands for incorporation into AD diagnostic agents and are investigating the feasibility of labelling the ligands with radioactive Tc-99m.

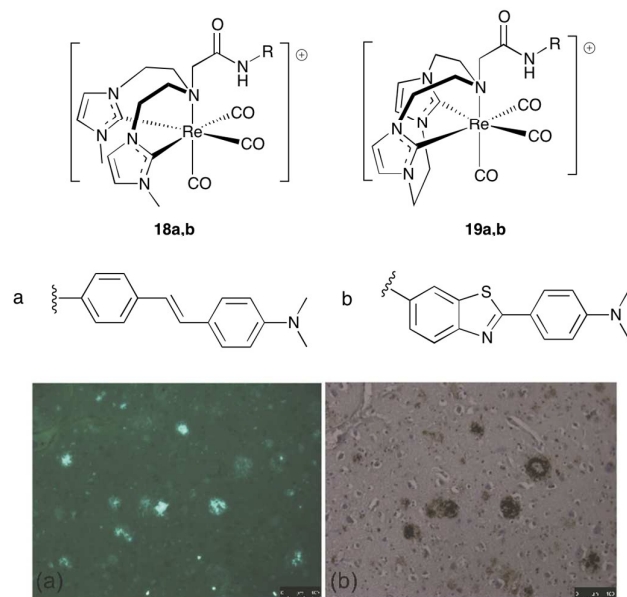


Figure 13. Complexes **18a,b**, and **19a,b** and epi-fluorescence microscopy image of AD affected frontal cortex brain tissue treated with the Re(I) complex **19a** ( $\lambda_{\text{exc}} = 359$  nm,  $\lambda_{\text{em}} = 461$  nm) and (b) microscopy image of the contiguous section immune-stained with an anti-amyloid  $\beta$  peptide antibody 1E8 showing the positions of the amyloid plaques. Adapted from Ref. 55 with permission from The Royal Society of Chemistry.

### Antimicrobial activity

In addition to their early study in cancer and Alzheimer's disease research, Re-NHC complexes have also recently been found by the Metzler-Nolte group to exhibit potent antimicrobial activity on Gram-positive bacterial strains.<sup>56</sup> By utilising an elegant template-based approach, cationic complexes of the type shown in Figure 14 were prepared. The complexes were generally found to exhibit moderate to low micromolar activity against three Gram-positive bacterial strains: *B. subtilis* 168 DSM 402, *S. aureus* DSM 20231, and *S. aureus* ATCC43300. The minimal inhibitory activity (MIC) of the complexes varied significantly depending on the nature of the diim ligand and the carbene nitrogen substituent, with some indications that the more lipophilic benzyl substituted complexes were more active than those substituted with H. Nevertheless, complex **20** was the active of the complexes tested, exhibiting MIC values around 0.7  $\mu\text{M}$ .

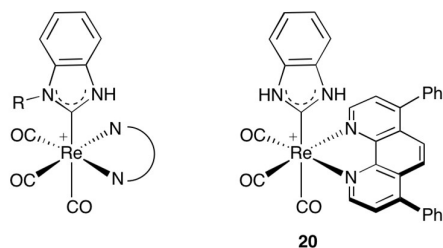


Figure 14. New class of Re(I)-NHC investigated as antibacterial agents.

### Conclusions and Outlooks

Compared to the well know family of  $[\text{Re}(\text{CO})_3(\text{diim})\text{L}]^{0/+}$  complexes, whose luminescent properties and potential application have been extensively studied for more that forty years, the analogous Re(I) complexes bound to conjugated NHC ligands are relatively unexplored. Early investigations into the synthesis and photophysical properties of these new species highlighted in general blue-shifted emission, shorter excited state lifetime decays and lower quantum yields due to enhanced non-radiative decay pathways from  $^3\text{MLCT}$  excited states. Shortly later, these pathways were identified as photochemical ligand substitution reactions. Photosubstitution of CO ligands from  $[\text{Re}(\text{CO})_3(\text{diim})\text{L}]^{0/+}$  are known, and can be divided into two mechanisms depending on the chemical nature of the Re(I) complex and the energy of the photons used during the photolysis. However, through a systematic study involving synthetic chemistry, spectroscopy techniques ( $^1\text{H-NMR}$ , IR, UV-Vis absorption and emission), as well as time resolved IR spectroscopy, it was highlighted that these Re(I)-NHC species undergo a unique photochemical ligand dissociation, establishing themselves as a third type of photoactive Re(I) complexes.

These Re(I)-NHC species have also recently found wide investigations in areas such as electrocatalytic and photocatalytic reduction of carbon dioxide, as well as biology. Re(I)-NHC complexes have allowed the elucidation of the anticancer properties of Re(I) tricarbonyl species via inhibition of phosphorylation of Aurora kinases. In particular, these complexes have been trialed with promising outcomes against pancreatic cancer cell lines. Furthermore, Re(I)-NHC complexes have been used for the diagnosis of Alzheimer plaques and represent a favourable model study for radioactive Tc complexes. Very recent investigations also demonstrated promising antibacterial properties.

Given their novelty, Re(I)-NHC complexes represent a fertile research ground for future fundamental and applied studies.

### Conflicts of interest

There are no conflicts to declare.

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