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Matthew Stout, Brian Skelton, Alexandre N. Sobolev, **Paolo Raiteri**, **Massimiliano Massi**, Peter Simpson

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Synthesis and Photochemical Properties of Re(I) Tricarbonyl Complexes Bound to Thione and Thiazole-2-ylidene Ligands

Matthew J. Stout,^[a] Brian W. Skelton,^[b] Alexandre N. Sobolev,^[b] Paolo Raiteri,^[a] Massimiliano Massi,^{*[a]} Peter V. Simpson^{*[a]}

[a] Curtin Institute for Functional Molecules and Interfaces, School of Molecular and Life Sciences, Curtin University, Kent Street, Bentley 6102, Perth, Australia

[b] School of Molecular Sciences and CMCA, the University of Western Australia, 35 Stirling Highway, 6009, Perth, Western Australia

Abstract

Three Re(I) tricarbonyl complexes, with general formulation $\text{Re}(\text{N}^{\wedge}\text{L})(\text{CO})_3\text{X}$ (where $\text{N}^{\wedge}\text{L}$ is a bidentate ligand containing a pyridine functionalized in the position 2 with a thione or a thiazol-2-ylidene group and X is either chloro or bromo) were synthesized and their reactivity explored in terms of solvent-dependent ligand substitution, both in the ground and excited states. When dissolved in acetonitrile, the complexes bound to the thione ligand underwent ligand exchange with the solvent resulting in the formation of $\text{Re}(\text{NCMe})_2(\text{CO})_3\text{X}$. The exchange was found to be reversible, and the starting complex was reformed upon removal of the solvent. On the other hand, the complexes appeared inert in dichloromethane or acetone. Conversely, the complex bound to the thiazole-2-ylidene ligand did not display any ligand exchange reaction in the dark, but underwent photoactivated ligand substitution when excited to its lowest metal-to-ligand charge transfer manifold. Photolysis of this complex in acetonitrile generated multiple products, including Re(I) tricarbonyl and dicarbonyl solvato-complexes as well as free thiazole-2-ylidene ligand.

Introduction

The photophysical properties of Re(I) tricarbonyl complexes consisting of the general formula $\text{fac}[\text{Re}(\text{diim})(\text{CO})_3\text{L}]^{0/+}$, where diim is a π -conjugated diimine ligand, such as 1,10-phenanthroline, and L is a monodentate neutral or anionic ancillary ligand, have been studied extensively.^[1-2] These complexes are generally phosphorescent due to radiative decay from their lowest triplet metal-to-ligand charge transfer excited states ($^3\text{MLCT}$),^[3-4] with potential

admixture with ligand-to-ligand charge transfer excited states ($^3\text{LLCT}$), depending on the chemical identity of the ancillary ligand.^[5-7] The photophysical properties of this class of complexes, which can be fine-tuned by chemically altering the diim and ancillary ligands, have been extensively explored in the past decades for fundamental studies^[8-12] as well as for a range of applications such as light emitting devices,^[13-16] biological labels^[17-20] and photocatalysis.^[21]

Although Re(I) tricarbonyl diim based complexes have been explored extensively, the analogous carbene complexes *fac*-[Re(NHC)(CO)₃L]^{0/+}, where NHC is a bidentate *N*-heterocyclic carbene that binds to rhenium through a pyridine N atom and a carbene C atom, have started to be investigated only more recently. These ligands are found to confer rich photophysical properties when bound to metal complexes of Au(I), Ir(III), Pt(II) and Ru(II).^[22-28] Xue *et al.*,^[29-30] Barnard *et al.*,^[28, 31] Delcamp *et al.*,^[32-34] and our research group^[28, 35-39] have investigated the effect of exchanging a diim for a NHC ligand had on the reactivity and luminescent properties of Re(I) tricarbonyl complexes. The explored NHC ligands were based on pyridyl, pyrimidyl, quinolyl, and quinoxyl substituted imidazole or benzimidazole systems. These NHC ligands were found to activate tuneable metal-to-ligand charge transfer (MLCT) transitions through their π^* system, followed by phosphorescent decay from the $^3\text{MLCT}$ manifold. The complexes exhibited blue-shifted emission due to a decrease in conjugation within the NHC ligands when compared to diim ligands. Furthermore, it was reported that when the NHC ligand contained a pyridyl group as the N donor, the complexes underwent photochemical ligand substitution reactions when irradiated in acetonitrile at $\lambda = 375 \text{ nm}$.^[36-37] This photochemical process led to the formation of multiple products, by substitution of the halogen and CO ligands with acetonitrile molecules. The mechanism of this photochemical transformation was later established by time-resolved IR (TR-IR) studies and computer modelling.^[35] The pyridyl-imidazole Re(I) complex was found to react via thermal population of higher lying $^3\text{MLCT}$ states, resulting in substitution of the halogen with a molecule of acetonitrile. The formed solvato complex then underwent exchange of one CO ligand for a molecule of acetonitrile.

Studies conducted by Strassner *et al.*^[40-41] outlined a synthetic pathway to prepare a broad range of *N*-arylthiazole-2-thiones, which were further reacted to form the corresponding *N*-arylthiazolium salts. Upon deprotonation, these ligands were bound to Pt(II) in a bidentate fashion, with an acetylacetonato ligand filling the Pt(II) coordination sphere. These complexes were found to be highly emissive at room temperature. We believed that this synthetic pathway could be modified to provide access to 3-(pyrid-2-yl)-4,5-dimethylthiazole-2-thione (**1**) and 3-(pyrid-2-yl)-4,5-dimethylthiazolium hexafluorophosphate (**2H**[PF₆]) (Scheme 1). In addition, the *N*-arylthiazole-2-thione precursors were not explored as bidentate ligands for the Pt(II) complexes. We therefore sought to investigate Re(I) tricarbonyl NHC complexes where the NHC ligand was characterized by a N⁺C⁻S motif, as comparative study to our previous Re(I) NHC complexes. Furthermore, we endeavoured to prepare the analogous complexes by binding the precursor ligand containing the thiazolethione functional group to the Re(I) centre, given Re(I) complexes coordinated to thiazole-2-thione ligands are not currently common in the literature.^[42-47] The work presented herein describes the synthesis and structural determination of these complexes, along with the investigation of their ligand substitution reactions from the ground and excited states through a combination of UV-Vis, IR and NMR spectroscopies.

Results and Discussions

Synthesis and spectroscopic characterization

The syntheses of **1** and **2H**[PF₆] were adapted from previously published works (Scheme 1, see Figures S1-4 for ¹H-NMR and ¹³C-NMR spectra).^[40-41] The thione complexes Re(**1**)(CO)₃X (X = Cl, Br) were synthesized by reacting the ligand **1** with Re(CO)₅X in tetrahydrofuran at reflux under nitrogen and in the dark for 24 h (Scheme 1). The target complexes were isolated by precipitation from dichloromethane solutions with the addition diethyl ether, and obtained in good yields of 76% and 77%, respectively. The preparation of the carbene complex Re(**2**)(CO)₃Br was based on our previously published procedure.^[36] Complex Re(**2**)(CO)₃Br was formed by reacting Re(CO)₅Br with **2H**[PF₆] and triethylamine in toluene at reflux and in the dark for 24 h (Scheme 1). The complex was purified via column chromatography and obtained in 30% yield.

The synthesized rhenium complexes are soluble in common organic solvents, including acetone, dichloromethane, methanol, acetonitrile, and dimethylsulfoxide.

Scheme 1. Synthesis of **1** and **2H[PF₆]** and subsequent formation of **Re(1)(CO)₃Cl**, **Re(1)(CO)₃Br** and **Re(2)(CO)₃Br**. Reagents and conditions: (I) NaOH, DMSO, CS₂, 0 °C to rt, 3-chlorobutan-2-one; (II) HCl, EtOH, reflux; (III) H₂O₂, AcOH, rt; (IV) KPF₆, MeOH/H₂O, rt. (V) Re(CO)₅Br or Re(CO)₅Cl, reflux, THF. (VI) Re(CO)₅Br, **2[PF₆]**, Et₃N, reflux, toluene.

The complexes were analyzed via ¹H and ¹³C-NMR spectroscopy in deuterated acetone (Figures S5-10). The ¹H-NMR spectra for **Re(1)(CO)₃Cl** and **Re(1)(CO)₃Br** suggest the presence of two rhenium complexes with identical formula, in a ~3:1 ratio. The peaks in the ¹³C-NMR spectra are also split, consistently with the presence of two isomers. Conversely, the ¹H-NMR and ¹³C-NMR spectra of **Re(2)(CO)₃Br** contain the expected signals for a unique complex. The IR spectra of the complexes exhibit three bands characteristic of *facially* arranged CO ligands, with frequency analogous to previously reported Re-NHC complexes (Figures S11-13).^[36-37]

X-ray structural determination

Single crystals suitable for X-ray diffraction were grown via vapor diffusion of petroleum spirits into dichloromethane solutions containing the complexes. The structures of the complexes are shown in Figure 1. Both **Re(1)(CO)₃Cl** and

and X ligands for both diastereomers is shown for $\text{Re}(\mathbf{1})(\text{CO})_3\text{Cl}$ and $\text{Re}(\mathbf{1})(\text{CO})_3\text{Br}$ (top).

Computational studies

Time-dependent density functional theory (TD-DFT) was used to determine the relative energy of the two diastereomers for both $\text{Re}(\mathbf{1})(\text{CO})_3\text{Cl}$ and $\text{Re}(\mathbf{1})(\text{CO})_3\text{Br}$. The structure of both isomers was relaxed in acetone for a direct comparison with the recorded ^1H -NMR spectra (Figure 2; see S14 for $\text{Re}(\mathbf{1})(\text{CO})_3\text{Br}$ structures). For both $\text{Re}(\mathbf{1})(\text{CO})_3\text{Cl}$ and $\text{Re}(\mathbf{1})(\text{CO})_3\text{Br}$, the energy of one of the isomers is predicted to be higher by 3 and 4 kJmol^{-1} respectively. This result is in agreement with the integration ratios observed in the ^1H -NMR spectra. According to the TD-DFT results, the most stable diastereomer is the complex where the thiazole-2-thione ligand is twisted pointing towards the halogen ligand (right structure in Figure 2).

Figure 2: TD-DFT relaxed structures of the two diastereomers of the $\text{Re}(\mathbf{1})(\text{CO})_3\text{Cl}$ in acetone. The most stable structure is the one on the right hand side.

Photophysical Studies

A summary of the photophysical properties is provided in Table 1. The absorption spectra for all three complexes were recorded from diluted dichloromethane solutions (Figure 3). Each complex displays high energy bands below 300 nm. The complexes $\text{Re}(\mathbf{1})(\text{CO})_3\text{Cl}$ and $\text{Re}(\mathbf{1})(\text{CO})_3\text{Br}$ also exhibit a band with relatively high molar absorptivity ϵ centered around 310 nm, which is also observed in the spectra of the free ligands **1** and **2** $\text{H}[\text{PF}_6]$ (Figures

S15-16). These bands are therefore attributed to intra-ligand (IL) $\pi\text{-}\pi^*$ transitions. The three complexes also exhibit lower energy broad bands above 350 nm that are ascribed to metal-to-ligand charge transfer transitions (MLCT) with potential admixture of ligand-to-ligand charge transfer transitions (LLCT).^[36]

Table 1. Photophysical properties of the complexes from diluted dichloromethane solutions (ca. 10^{-5} M)

	Re(1)(CO) ₃ Cl	Re(1)(CO) ₃ Br	Re(2)(CO) ₃ Br
λ_{abs} (nm)	260 [10.8]	260 [14.6]	264 [7.7]
$[\epsilon]$ ($10^3\text{M}^{-1}\text{cm}^{-1}$)	311 [7.0] 400 [2.6]	310 [10.0] 400 [3.8]	398 [3.0]
$\lambda_{\text{em}}^{\text{a}}$ (nm)	-	-	540
$\lambda_{\text{em}}^{\text{c}}$ (nm)	-	-	498
τ^{a} (ns)	-	-	111
τ^{b} (ns)	-	-	399
$\phi^{\text{a, d}}$ (%)	-	-	1.8
$\phi^{\text{b, d}}$ (%)	-	-	4.0

^a air-equilibrated solutions; ^b degassed solutions; ^c 77 K; ^d [Ru(bpy)₃]Cl₂ in air-equilibrated water used as reference.

Figure 3. Absorption profiles of Re(1)(CO)₃Cl (blue), Re(1)(CO)₃Br (black) and Re(2)(CO)₃Br (red) in diluted dichloromethane solutions.

Both $\text{Re(1)(CO)}_3\text{Cl}$ and $\text{Re(1)(CO)}_3\text{Br}$ were found to be non-emissive in fluid solution at room temperature and barely emissive at 77 K. Therefore, these complexes were not investigated any further. Comparatively, the room temperature emission profile of $\text{Re(2)(CO)}_3\text{Br}$ in diluted dichloromethane solution displays a featureless broad band centred at 540 nm with excitation at 400 nm (Figure 4). This profile is typical of emission from $^3\text{MLCT}$ excited states, as previously observed in the analogous Re-NHC complexes.^[36] In degassed solution, the excited state lifetime decay τ at room temperature was fitted with a monoexponential function and calculated to be 399 ns, with a photoluminescence quantum yield Φ of 4.0%. The values of τ and Φ are reduced to 111 ns and 1.8% in air-equilibrated solution, respectively, as a result of the quenching of the $^3\text{MLCT}$ excited state caused by $^3\text{O}_2$. At 77 K, the emission profile appears blue-shifted with a maximum at 498 nm (Figure 4). This blue shift is typical of $^3\text{MLCT}$ bands and is ascribed to rigidochromism.^[48] Overall, the photophysical properties of $\text{Re(2)(CO)}_3\text{Br}$ are analogous to those of the previously reported Re-NHC complexes,^[36-37] indicating that effect of the carbene ligand is similar for imidazol-2-ylidene or thiazol-2-ylidene.

Figure 4. Normalised emission spectra of dichloromethane solutions containing $\text{Re(2)(CO)}_3\text{Br}$ at room temperature (red trace) and 77 K (black trace). The spectra were recorded with excitation at 400 nm.

Ground State Ligand Exchange Reactions

Ligand exchange reactions for the $\text{Re(1)(CO)}_3\text{Cl}$ and $\text{Re(1)(CO)}_3\text{Br}$ complexes were monitored by sequentially recording ^1H -NMR spectra over time, while the

solutions were kept in the dark. The reactions were followed focusing on the downfield signal belonging pyridyl H₆ atom. Figures 5 and 6 display the spectral sequence for Re(**1**)(CO)₃Cl and Re(**1**)(CO)₃Br, respectively. The peaks highlighted a and b belong to the two diastereomers. A new peak, c, appears very rapidly after dissolution in deuterated acetonitrile. The peak c increases in intensity over time, while the peaks a and b progressively become smaller, almost disappearing after 4 h. The peak c is identical to one of the peaks present in the ¹H-NMR spectrum of **1** in deuterated acetonitrile. The data suggest dissociation of the ligand **1**. The complex Re(**1**)(CO)₃Cl reacts faster, with the reaction completed after 3 h (completion assessed by the relative integration values of a, b, and c) compared to ~13 h for Re(**1**)(CO)₃Br (Figure 6). Mole fractions were calculated for the conversion of the major and minor diastereomers of Re(**1**)(CO)₃Cl and Re(**1**)(CO)₃Br using the relative integral values of H₆ protons (Figures 7 and 8).

Figure 5. Stacked ¹H-NMR spectra taken at different time intervals during the reaction of Re(**1**)(CO)₃Cl in deuterated acetonitrile, kept in the dark. The peaks a and b belong to the starting diastereomers, whereas the peak c belong to the dissociated ligand **1**.

Figure 6. Stacked ^1H -NMR spectra taken at different time intervals during the reaction of $\text{Re}(\mathbf{1})(\text{CO})_3\text{Br}$ in deuterated acetonitrile, kept in the dark. The peaks a and b belong to the starting diastereomers, whereas the peak c belong to the dissociated ligand **1**.

Figure 7. Mole fractions of the $\text{Re}(\mathbf{1})(\text{CO})_3\text{Cl}$ reaction in acetonitrile- d_6 as determined by relative integration of the H_6 signals a, b, and c.

Figure 8. Mole fractions of the $\text{Re}(\mathbf{1})(\text{CO})_3\text{Br}$ reaction in acetonitrile- d_6 as determined by relative integration of the H_6 signals a, b, and c.

The exchange of the ligand **1** for two molecules of acetonitrile also was investigated by IR spectroscopy, monitoring changes in the CO bands over time. Both the chloro and bromo complexes behaved identically, with the initial tricarbonyl bands (red scan) collapsing over time upon dissolution in acetonitrile (Figure 9; see Figure S17 for $\text{Re}(\mathbf{1})(\text{CO})_3\text{Br}$). A new tricarbonyl species formed in solution (blue trace) indicates that the CO ligands were not substituted by solvent during the reaction. In order to confirm the identity of the formed rhenium complex, $\text{Re}(\text{NCMe})_2(\text{CO})_3\text{Cl}$ and $\text{Re}(\text{MeCN})_2(\text{CO})_3\text{Br}$ were synthesised using a previously published procedure by heating $\text{Re}(\text{CO})_5\text{X}$ ($\text{X} = \text{Cl}, \text{Br}$) in acetonitrile at reflux for 24 h.^[49] The IR spectra of these complexes matched identically to that of the final species observed in the ligand exchange of both $\text{Re}(\mathbf{1})(\text{CO})_3\text{Cl}$ and $\text{Re}(\mathbf{1})(\text{CO})_3\text{Br}$ (see Figures S18-19).

Figure 9. FT-IR spectra monitoring the carbonyl collapse of $\text{Re}(\mathbf{1})(\text{CO})_3\text{Cl}$ and the simultaneous carbonyl formation of $\text{Re}(\text{NCMe})_2(\text{CO})_3\text{Cl}$ in acetonitrile.

The ligand exchange reactions were also monitored by UV-Vis spectroscopy using diluted acetonitrile solutions of $\text{Re}(\mathbf{1})(\text{CO})_3\text{Cl}$ and $\text{Re}(\mathbf{1})(\text{CO})_3\text{Br}$. The sequential UV-Vis spectra of $\text{Re}(\mathbf{1})(\text{CO})_3\text{Cl}$ (Figure 10; see Figure S20 for $\text{Re}(\mathbf{1})(\text{CO})_3\text{Br}$) display a blue-shift of the LC maximum and an isosbestic point at 345 nm. Comparatively, the UV-Vis spectrum of the ligand **1** in diluted acetonitrile (see Figure S21) displays a broad band centered at 333 nm that overlaps with the broad band observed for the product of the ligand exchange reactions of $\text{Re}(\mathbf{1})(\text{CO})_3\text{Cl}$ and $\text{Re}(\mathbf{1})(\text{CO})_3\text{Br}$. Furthermore, the UV-Vis spectra of $\text{Re}(\text{NCMe})_2(\text{CO})_3\text{Cl}$ and $\text{Re}(\text{NCMe})_2(\text{CO})_3\text{Br}$ in acetonitrile displayed high energy bands above 300 nm, confirming the formation of the solvatocomplex (Figures S22-23).

Figure 10. UV-Vis spectra of $\text{Re}(\mathbf{1})(\text{CO})_3\text{Cl}$ complex dissolved in acetonitrile kept in the dark at time 0 (red trace) and subsequent scans over time during the formation of free ligand ($\mathbf{1}$) (blue trace). No change was observed beyond 24 h scan. Legend time intervals in hours.

Photochemical studies were conducted on both $\text{Re}(\mathbf{1})(\text{CO})_3\text{Cl}$ and $\text{Re}(\mathbf{1})(\text{CO})_3\text{Br}$ using the same conditions as previously reported for Re-NHC complexes.^[35-37] Both $\text{Re}(\mathbf{1})(\text{CO})_3\text{Cl}$ and $\text{Re}(\mathbf{1})(\text{CO})_3\text{Br}$ remain stable in acetone when kept in the dark and when irradiated at 365 nm (see Figures S24-27).

Using previously reported photochemical conditions, $\text{Re}(\mathbf{2})(\text{CO})_3\text{Br}$ was found to be stable in deuterated acetone, analogously to reported Re-NHC complexes (see Figures S28-29).^[35-38] $\text{Re}(\mathbf{2})(\text{CO})_3\text{Br}$ was then dissolved in deuterated acetonitrile with no changes observed when kept under darkness for 6 hours (see Figure S30). However, upon irradiation at 365 nm, the complex reacts and forms four new species. The clearest region of the ^1H -NMR spectra taken during photolysis is between 9.9 and 8.5 ppm, showing the downfield signals belonging to the pyridyl- H_6 protons of the reacting and forming complexes. Over the 7 hour photolysis period, the initial pyridyl- H_6 doublet at 9.00 (a) ppm, belonging to $\text{Re}(\mathbf{2})(\text{CO})_3\text{Br}$, decreases significantly in intensity. Four new signals appear and increase in intensity at 8.96 (b), 8.82 (c), 8.80 (d) and 8.70 (e) ppm. The singlet at 8.68 ppm indicated that one of the species is the free ligand. This conclusion is further confirmed with the doublet at 8.70 (e) ppm matching identically to the pyridyl- H_6 proton of the overlaid free ligand spectrum (Figure 11; see Figure S31 for the full spectra).

Figure 11. Stacked ^1H -NMR spectra of $\text{Re}(\mathbf{2})(\text{CO})_3\text{Br}$ irradiated with 365 nm light in acetonitrile- d_3 . The top spectrum (purple trace) belongs to the ligand $\mathbf{2H}[\text{PF}_6]$.

FT-IR spectroscopy was used to identify the other three species (b, c and d) formed during the reaction. A solution of acetonitrile- d_3 containing $\text{Re}(\mathbf{2})(\text{CO})_3\text{Br}$ was photolysed for 7 hours at 365 nm (Figure 12, black trace) and compared to the spectrum of the sample before photolysis (Figure 12, red trace). The carbonyl peaks at 2018, 1927 and 1899 cm^{-1} collapse, and new peaks form at 2042, 2026, 1946, 1931, 1877 and 1854 cm^{-1} . The peaks at 2042 and 2026 cm^{-1} are associated to the cationic solvatocomplexes.^[50] On the other hand, the pairs of signals at 1946, 1931, 1877 and 1854 are assigned to two separate dicarbonyl Re complexes. These results, in conjunction with those observed in ^1H -NMR studies, match what was observed for the analogous compounds published by our group.^[35-37]

Figure 12. Overlaid solution IR spectra in DCM of $\text{Re}(\mathbf{2})(\text{CO})_3\text{Br}$ before photolysis (red trace) and after 7 h photolysis (black trace).

Conclusion

Thione ligand **1** and thiazole ligand $\mathbf{2H}[\text{PF}_6]$ were successfully synthesized using the modified procedures outlined by Leopald *et al.* These bidentate ligands were bound to rhenium (I) to form tricarbonyl complexes $\text{Re}(\mathbf{1})(\text{CO})_3\text{Br}$, $\text{Re}(\mathbf{1})(\text{CO})_3\text{Cl}$ and $\text{Re}(\mathbf{2})(\text{CO})_3\text{Br}$. $\text{Re}(\mathbf{1})(\text{CO})_3\text{Br}$ and $\text{Re}(\mathbf{1})(\text{CO})_3\text{Cl}$ reacted instantly in acetonitrile- d_3 and dimethylsulfoxide- d_6 with $\text{Re}(\mathbf{1})(\text{CO})_3\text{Cl}$ reacting faster. Photolysis at 365 nm had no effect on the rate of the reactions which was identified as solvent exchange with ligand **1** confirmed with UV-Vis and FT-IR studies. In comparison, $\text{Re}(\mathbf{2})(\text{CO})_3\text{Br}$ exhibited similar photochemical and photophysical properties previously reported by Vaughan *et al.*, forming two photo unstable dicarbonyl complexes, one photo unstable tricarbonyl complex and free ligand $\mathbf{2[X]}$ upon photolysis with 365 nm light.

Experimental Section

General considerations

All reagents were purchased from Sigma Aldrich, Alfa Aesar or Strem Chemicals and used as received without further purification. All were performed in the dark by wrapping glassware in aluminium foil. Nuclear magnetic resonance spectra were recorded using a Bruker Avance 400 spectrometer (400.1 MHz for ^1H ; 100 MHz for ^{13}C) at 300 K. All the NMR spectra were calibrated to residual solvent signals. Infrared spectra were recorded using an attenuated total reflectance Perkin Elmer Spectrum 100 FT-IR with a sodium chloride cell. IR spectra were recorded from 4000 to 650 cm^{-1} . Elemental analyses were obtained at Curtin University using a Thermo Finnigan EA 1112 Series Flash. Absorption spectra were recorded at room temperature using a Cary 4000 UV-Vis spectrometer. Lamp photolysis experiments were carried out using a UVP Blak-Rays B-100AP High Intensity UV lamp with a 100 W bulb at a single wavelength output of 365 nm. The experiments were performed under darkness, the complexes dissolved in dichloromethane and stored in a quartz cuvette. Distance between quartz and lamp source was kept constant at a distance of 3 cm. The lamp was switched off at set intervals and the solutions analysed in a NaCl (5 mm) disc on a Perkin-Elmer Spectrum 2000 FT-IR

spectrometer. Uncorrected steady state emission and excitation spectra were recorded using an Edinburgh FLSP920 spectrometer equipped with a 450 W xenon arc lamp, double excitation and single emission monochromators and a peltier cooled Hamamatsu R928P photomultiplier tube (185–850 nm). Emission and excitation spectra were corrected for source intensity (lamp and grating) and emission spectral response (detector and grating) by a calibration curve supplied with the instrument. According to the approach described by Demas and Crosby,^[51] luminescence quantum yields (Φ_{em}) were measured in optically dilute solutions (O.D. < 0.1 at excitation wavelength) obtained from absorption spectra on a wavelength scale [nm] and compared to the reference emitter by the following equation:

$$\Phi_x = \Phi_r \left[\frac{A_r(\lambda_r)}{A_x(\lambda_x)} \right] \left[\frac{I_r(\lambda_r)}{I_x(\lambda_x)} \right] \left[\frac{n_x^2}{n_r^2} \right] \left[\frac{D_x}{D_r} \right]$$

where A is the absorbance at the excitation wavelength (λ), I is the intensity of the excitation light at the excitation wavelength (λ), n is the refractive index of the solvent, D is the integrated intensity of the luminescence and Φ is the quantum yield. The subscripts r and x refer to the reference and the sample, respectively. The quantum yield determinations were performed at identical excitation wavelength for the sample and the reference, therefore cancelling the $I(\lambda_r)/I(\lambda_x)$ term in the equation. All the Re complexes were measured against an air-equilibrated water solution of $[\text{Ru}(\text{bipy})_3]\text{Cl}_2$ used as a reference ($\Phi_r = 0.028$).^[52] Emission lifetimes (τ) were determined with the single photon counting technique (TCSPC) with the same Edinburgh FLSP920 spectrometer using pulsed picosecond LEDs as the excitation source and the above-mentioned R928P PMT as the detector. The goodness of fit was assessed by minimizing the reduced χ^2 function and by visual inspection of the weighted residuals. To record the 77 K luminescence spectra, the samples were put in glass tubes (2 mm diameter) and inserted in a special quartz Dewar filled with liquid nitrogen. All the solvents used in the preparation of the solutions for the photophysical investigations were of spectrometric grade. All the prepared solutions were filtered through a 0.2 μm syringe filter before measurement. Deaerated samples were prepared by the freeze–pump–thaw technique.

Experimental uncertainties are estimated to be $\pm 8\%$ for lifetime determinations, $\pm 20\%$ for quantum yields, and ± 2 nm and ± 5 nm for absorption and emission peaks, respectively.

Synthetic Details

1: Ligand **1** was synthesised by a modification of a previously reported procedure Leopold *et al.*^[40-41] 2-Aminopyridine (5.0 g, 53.0 mmol) was added to dimethylsulfoxide (20 mL) and the resulting yellow/brown solution stirred for 15 min. Crushed sodium hydroxide (2.0 g, 50.0 mmol) was added, followed by water (5 mL) and the mixture stirred at 50°C for 1 h. The mixture was cooled to 0°C, and carbon disulfide (3.0 mL, 50.0 mmol) was added, forming a blood red solution which was stirred at room temperature for 1 h. The solution was cooled to 0°C and 3-chloro-2-butanone (5.0 mL, 50.0 mmol) was added, the solution turning yellow upon the addition. The solution was stirred at room temperature for 1 h then diluted with water (200 mL). Diethyl ether (30 mL) was added and the mixture stirred vigorously overnight. The solution was decanted and the remaining orange solid/oil was dissolved in ethanol (60 mL). Hydrochloric acid (32%, 1.5 mL) was added and the solution was refluxed for 1 h. The solution was reduced *in vacuo* until ~20 mL of ethanol remained, then diethyl ether (20 mL) was added and the solution cooled to 0°C for 1 h. The resulting precipitate was filtered, washed with minimal cold ethanol/diethyl ether (1:1, 1 $\times$ 5 mL) and dried to afford the product as a pink solid. Yield 2.3 g (62%). Elemental analysis for C₁₀H₁₀N₂S₂: calculated C 54.02, H 4.53, N 12.60; found C 53.74, H 4.24, N 12.38. ν_{max} (ATR)/cm⁻¹: 1590 m, 1470 m, 1433 s, 1317 s, 1252 s, 992 m, 774 m: ¹H-NMR (δ , ppm, Acetone-d₆): 8.66 (1H, ddd, ³J_{H-H} = 5.6 Hz, ⁴J_{H-H} = 1.6 Hz, ⁵J_{H-H} = 0.8 Hz, H₆), 8.06 (1H, ddd, ³J_{H-H} = 8.0 Hz, ³J_{H-H} = 7.6 Hz, ⁴J_{H-H} = 1.6 Hz, H₄), 7.59-7.53 (2H, m, H_{3,5}), 2.20 (3H, d, ⁵J_{H-H} = 1.2 Hz, H₇), 1.89 (3H, d, ⁵J_{H-H} = 1.2 Hz, H₈). ¹³C-NMR (δ , ppm, Dimethylsulfoxide-d₆): 186.46, 150.48, 149.83, 139.20, 134.92, 124.91, 124.40, 117.33, 12.75, 11.06.

Re(**1**)(CO)₃X (X = Cl, Br): A suspension of thione ligand **1** (100 mg, 0.45 mmol) and rhenium(I)pentacarbonylchloride (163 mg, 0.45 mmol) or rhenium(I)pentacarbonylbromide (183 mg, 0.45 mmol) in tetrahydrofuran (10 mL) was heated at reflux for 24 h. The solvent was removed *in vacuo*, dissolved in a minimal amount of dichloromethane and dropped into rapidly stirring diethyl ether. The

resulting precipitate was collected, washed with diethyl ether (3 × 5 mL) and dried to afford the products as yellow solids.

Characterization data for Re(1)(CO)₃Cl: Yield 179 mg (76%). Elemental analysis for C₁₃ClH₁₀N₂O₃ReS₂: calculated C 29.56, H 1.91, N 5.31; found: C 29.81, H 1.75, N 5.20. ν_{max} (ATR)/cm⁻¹: 2024 (CO), 1921 (CO), 1892 (CO): ¹H-NMR (δ , ppm, Acetone-d₆): 9.42 (0.3H, dd, ³J_{H-H} = 5.6 Hz, ⁴J_{H-H} = 1.8 Hz, H_{6min}), 9.36 (1H, dd, ³J_{H-H} = 5.8 Hz, ⁴J_{H-H} = 1.8 Hz, H_{6maj}), 8.51 (0.3H, ddd, ³J_{H-H} = 8.0 Hz, ³J_{H-H} = 7.5 Hz, ⁴J_{H-H} = 1.8 Hz, H_{4min}), 8.44 (1H, ddd, ³J_{H-H} = 8.0 Hz, ³J_{H-H} = 7.5 Hz, ⁴J_{H-H} = 1.8 Hz, H_{4maj}), 7.96-7.83 (3H, m, H_{3maj}, H_{3min}, H_{5maj}, H_{5min}), 2.47 (3H, d, ⁵J_{H-H} = 0.8 Hz, H_{7maj}), 2.40 (3H, d, ⁵J_{H-H} = 0.8 Hz, H_{7min}), 2.39 (3H, d, ⁵J_{H-H} = 0.8 Hz, H_{8maj}), 2.20 (3H, d, ⁵J_{H-H} = 0.8 Hz, H_{8min}). ¹³C-NMR (δ , ppm, Acetone-d₆): 191.2_{maj}, 190.0_{min}, 157.5_{maj}, 157.3_{min}, 148.5_{min}, 148.0_{maj}, 144.2_{min}, 143.5_{maj}, 139.7_{min}, 139.1_{maj}, 127.2_{maj}, 127.1_{min}, 125.7_{min}, 125.4_{maj}, 125.0_{min}, 122.9_{maj}, 14.6_{min}, 14.5_{maj}, 12.0_{min}, 11.9_{3maj}. Crystals suitable for X-ray analysis were grown via vapour diffusion of petroleum spirits into dichloromethane solution containing the complex.

Characterization data for Re(1)(CO)₃Br: Yield 200 mg (77%). Elemental analysis for BrC₁₃H₁₀N₂O₃ReS₂: calculated C 27.27, H 1.76, N 4.90; found C 27.29, H 1.63, N 5.04. ν_{max} (ATR)/cm⁻¹: 2025 (CO), 1923 (CO), 1893 (CO): ¹H-NMR (δ , ppm, Acetone-d₆): 9.49 (1H, ddd, ³J_{H-H} = 5.6 Hz, ⁴J_{H-H} = 1.6 Hz, ⁵J_{H-H} = 0.8 Hz, H_{6maj}), 9.45 (0.3H, dd, ³J_{H-H} = 5.6 Hz, ⁴J_{H-H} = 1.6 Hz, H_{6min}), 8.50 (0.3H, ddd, ³J_{H-H} = 8.8 Hz, ³J_{H-H} = 7.6 Hz, ⁴J_{H-H} = 1.6 Hz, H_{4min}), 8.43 (1H, ddd, ³J_{H-H} = 8.8 Hz, ³J_{H-H} = 7.6 Hz, ⁴J_{H-H} = 1.6 Hz, H_{4maj}), 7.96-7.80 (2.8H, m, H_{3maj}, H_{3min}, H_{5maj}, H_{5min}), 2.47 (3H, d, ⁵J_{H-H} = 0.8 Hz, H_{7maj}), 2.40 (3H, d, ⁵J_{H-H} = 1.2 Hz, H_{7min}), 2.38 (3H, d, ⁵J_{H-H} = 0.8 Hz, H_{8maj}), 2.20 (3H, d, ⁵J_{H-H} = 1.2 Hz, H_{8min}). ¹³C-NMR (δ , ppm, Acetone-d₆): 192.00_{maj}, 191.13_{min}, 158.65_{maj}, 157.66_{min}, 148.58_{min}, 148.08_{maj}, 144.15_{min}, 143.49_{maj}, 139.93_{min}, 139.22_{maj}, 127.16_{maj}, 127.09_{min}, 125.70_{maj}, 125.45_{min}, 125.00_{min}, 123.02_{maj}, 14.62_{min}, 14.54_{maj}, 12.11_{min}, 11.97_{maj}. Crystals suitable for X-ray analysis were grown via vapour diffusion of petroleum spirits into dichloromethane solution containing the complex.

2[PF₆]: 1 (150 mg, 0.68 mmol) was dissolved in acetic acid (5 mL) and cooled to 0°C. Hydrogen peroxide was added dropwise and the yellow solution stirred at room temperature for 1 hour. The solvent was removed *in vacuo* and the remaining yellow oil dissolved in methanol (1 mL). The solution was added to a solution of methanol/water (5 mL, 1:1) containing ammonium hexafluorophosphate (0.54 mg,

3.40 mmol). A cream powder precipitated and the mixture was stirred vigorously for 1 hour. The mixture was filtered, and the solid dissolved in minimal dichloromethane and dropped into rapidly stirring diethyl ether. The resulting precipitate was collected, washed with diethyl ether (3 × 5 mL) and dried to afford a cream solid. Yield 45 mg (35%). Elemental analysis for C₁₀F₆H₁₁N₂PS: calculated C 35.71, H 3.30, N 8.33; found C 35.76, H 3.00, N 8.39 $\nu_{\max}$ (ATR)/cm⁻¹: 1610 m, 1511 m, 1422 s, 1353 s, 1251s: ¹H NMR (δ , ppm, Acetone-d₆): 10.36 (1H, s, H₉), 8.81 (1H, dd, ³J_{H-H} = 4.8 Hz, ⁴J_{H-H} = 1.8, H₆), 8.30 (1H, ddd, ³J_{H-H} = 8.0 Hz, ³J_{H-H} = 7.6 Hz, ⁴J_{H-H} = 1.8 Hz, H₄), 8.02 (1H, app. d, ³J_{H-H} = 8.0 Hz, H₃), 7.87 (1H, dd, ³J_{H-H} = 7.6 Hz, ³J_{H-H} = 4.8 Hz, ⁴J_{H-H} = 1.2 Hz, H₅), 2.76 (3H, d, ⁵J_{H-H} = 0.8 Hz, H₇), 2.33 (3H, d, ⁵J_{H-H} = 0.8 Hz, H₈). ¹³C-NMR (δ , ppm, dimethylsulfoxide-d₆): 157.67, 149.75, 149.00, 141.41, 140.59, 133.45, 126.90, 121.26, 12.06, 11.94.

Re(2)(CO)₃Br: 2H[PF₆] (60 mg, 0.12 mmol), rhenium(I)pentacarbonylbromide (48 mg, 0.12 mmol) and triethylamine (170 μ L, 1.2 mmol) were combined in toluene. The mixture was refluxed for 24 hours under nitrogen forming a yellow solution with black precipitate. The solvent was removed *in vacuo* and the resulting yellow residue dissolved in minimal dichloromethane. The compound was purified via acid alumina (Brockmann II 3% H₂O) chromatography using dichloromethane as the eluent. The second fraction was combined, the solvent reduced *in vacuo* then dropped into rapidly stirring diethyl ether. The resulting precipitate was collected, washed with diethyl ether (3 × 5 mL) and dried to afford a yellow solid. Yield 20 mg (30%). Elemental analysis for BrC₁₃H₁₀N₂O₃ReS: calculated C 28.88, H 1.87, N 5.18; found C 28.78, H 1.80, N 5.05. $\nu_{\max}$ (ATR)/cm⁻¹ 2020 (CO), 1923 (CO), 1900 (CO): ¹H-NMR (δ , ppm, Acetone-d₆): 9.09 (1H, ddd, ³J_{H-H} = 5.6 Hz, ⁴J_{H-H} = 1.6 Hz, ⁵J_{H-H} = 0.8 Hz, H₆), 8.59 (1H, app. d, ³J_{H-H} = 8.8 Hz, H₃), 8.36 (1H, ddd, ³J_{H-H} = 8.8 Hz, ³J_{H-H} = 7.6 Hz, ⁴J_{H-H} = 1.6 Hz, H₄), 7.66 (1H, ddd, ³J_{H-H} = 7.6 Hz, ³J_{H-H} = 5.6 Hz, ⁴J_{H-H} = 1.2 Hz, H₅), 2.96 (3H, d, ⁵J_{H-H} = 0.8 Hz, H₇), 2.50 (3H, d, ⁵J_{H-H} = 0.8 Hz, H₈). ¹³C-NMR (δ , ppm, Acetone-d₆): 189.13, 156.34, 155.84, 142.40, 140.87, 132.65, 125.69, 117.09, 15.55, 12.18. Crystals suitable for X-ray analysis were grown via vapour diffusion of petroleum spirits into dichloromethane solution containing the complex.

X-ray diffraction analysis

All crystals were grown via the diffusion of petroleum spirits into dichloromethane. Crystallographic data for the structures were collected at

100(2) K on either an Oxford Diffraction Xcalibur or Gemini diffractometer. Following Lp, and absorption corrections, and solution by direct methods, the structures were refined against F^2 with full-matrix least squares using the program SHELXL-2014.^[53] Anisotropic displacement parameters were employed for the non-hydrogen atoms. All hydrogen atoms were added at calculated positions and refined by use of a riding model with isotropic displacement parameters based on those of the parent atom. Crystallographic data for the structures reported in this paper can be found in the Supporting Information and have been deposited at the Cambridge Crystallographic Data Centre. CCDC numbers are given below. Copies of the data can be obtained free of charge via <https://www.ccdc.cam.ac.uk/structures/>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, U.KCB21EZ, UK (fax +441223336033; email deposit@ccdc.cam.ac.uk).

Re(1)(CO)₃Cl: C₁₃ClH₁₀N₂O₃ReS₂, $M = 528.00$, colourless prism, 0.194 x 0.091 x 0.080 mm³, triclinic, space group $P\bar{1}$, $a = 7.4256(2)$, $b = 8.4558(2)$, $c = 13.0002(3)$ Å, $\alpha = 86.419(2)$, $\beta = 78.536(2)$, $\gamma = 85.231(2)^\circ$, $V = 796.34(3)$ Å³, $Z = 2$, $D_c = 2.202$ g/cm³, $\mu = 8.071$ mm⁻¹. $\lambda = 0.71073$ Å, $T = 100(2)$ K, $2\theta_{\max} = 65.1^\circ$, 16676 reflections collected, 5351 unique ($R_{\text{int}} = 0.0308$). Final $\text{Goof} = 1.002$, $R1 = 0.0214$, $wR2 = 0.0426$, R indices based on 4926 reflections with $I > 2\sigma(I)$ (refinement on F^2), $|\Delta\rho|_{\max} = 0.9(1)$ e Å⁻³, 229 parameters, 0 restraints. CCDC: 2004622

Re(1)(CO)₃Br: BrC₁₃H₁₀N₂O₃ReS₂, $M = 572.46$, yellow prism, 0.124 x 0.062 x 0.043 mm³, triclinic, space group $P\bar{1}$, $a = 7.4496(5)$, $b = 8.5515(4)$, $c = 13.0436(7)$ Å, $\alpha = 87.518(4)$, $\beta = 78.646(5)$, $\gamma = 86.087(4)^\circ$, $V = 812.41(8)$ Å³, $Z = 2$, $D_c = 2.340$ g/cm³, $\mu = 10.206$ mm⁻¹. $\lambda = 0.71073$ Å, $T = 100(2)$ K, $2\theta_{\max} = 64.7^\circ$, 16493 reflections collected, 5331 unique ($R_{\text{int}} = 0.0383$). Final $\text{Goof} = 1.000$, $R1 = 0.0327$, $wR2 = 0.0823$, R indices based on 4828 reflections with $I > 2\sigma(I)$ (refinement on F^2), $|\Delta\rho|_{\max} = 1.9(2)$ e Å⁻³, 228 parameters, 24 restraints. CCDC: 2004623

Re(2)(CO)₃Br: BrC₁₃H₁₀N₂O₃ReS, *M* = 540.40, orange needle, 0.391 x 0.091 x 0.051 mm³, monoclinic, space group *P*2₁/*c*, *a* = 6.58960(10), *b* = 23.5450(4), *c* = 9.6408(2) Å, β = 96.502(2)°, *V* = 1486.17(5) Å³, *Z* = 4, *D*_c = 2.415 g/cm³, μ = 11.015 mm⁻¹. λ = 0.71073 Å, *T* = 100(2)K, 2θ_{max} = 33.3°, 19256 reflections collected, 5381 unique (*R*_{int} = 0.0314). Final *GooF* = 1.163, *R*1 = 0.0317, *wR*2 = 0.0581, *R* indices based on 5381 reflections with *I* > 2σ(*I*) (refinement on *F*²), |Δρ|_{max} = 2.162 e Å⁻³, 192 parameters, 0 restraints. CCDC: 1961065.

TD-DFT Calculations

Time-dependent density functional theory (TD-DFT) calculations were performed with GAUSSIAN 16^[54] in order to calculate the absorption spectra for the synthesized complexes. Prior to these calculations, the structures were optimised in vacuum using the CAM-B3LYP exchange and correlation functional. The Re atoms were treated with the Stuttgart–Dresden (SDD) effective core potential^[55] and the Pople 6-311G** basis set was used for C, H, N, and O atoms. The effect of the solvent was mimicked with the PCM implicit solvation model^[56] with parameters adequate for DMSO, acetonitrile and dichloromethane. The low-lying singlet–singlet excitation energies were calculated at the same level of theory, and the spectra were reproduced as the superposition of Gaussian functions with heights proportional to calculated intensities and a variance of 11 nm.

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Synthesis and Photochemical Properties of Re(I) Tricarbonyl Complexes Bound to Thione and Thiazole-2-ylidene Ligands

Matthew J. Stout,^[a] Brian W. Skelton,^[b] Alexandre N. Sobolev,^[b] Paolo Raiteri,^[a] Massimiliano Massi,^{*[a]} Peter V. Simpson^{*[a]}

[a] Curtin Institute for Functional Molecules and Interfaces, School of Molecular and Life Sciences, Curtin University, Kent Street, Bentley 6102, Perth, Australia

[b] School of Molecular Sciences and CMCA, the University of Western Australia, 35 Stirling Highway, 6009, Perth, Western Australia

E-mail: m.massi@curtin.edu.au; peter.v.simpson@gmail.com

Supporting Information

Figure S1 and S2: ¹H and ¹³C-NMR of **1** in acetone-d₆ dimethylsulfoxide-d₆, respectively.

Figure S3 and S4: ^1H and ^{13}C -NMR of $2\text{H}[\text{PF}_6]$ in acetone- d_6 dimethylsulfoxide- d_6 , respectively.

Figures S5 and S6: ¹H and ¹³C-NMR of Re(1)(CO)₃Cl in acetone-*d*₆.

Figures S7 and S8: ¹H and ¹³C-NMR of Re(1)(CO)₃Br in acetone-d₆.

Figures S9 and S10: ¹H and ¹³C-NMR of Re(2)(CO)₃Br in acetone-d₆.

Figure S11: FT-IR spectrum of $\text{Re(1)(CO)}_3\text{Cl}$ in dichloromethane.

Figure S12: FT-IR spectrum of $\text{Re(1)(CO)}_3\text{Br}$ in dichloromethane.

Figure S13: FT-IR spectrum of $\text{Re}(\mathbf{2})(\text{CO})_3\text{Br}$ in dichloromethane.

Figure S14: TD-DFT relaxed structures of the two diastereomers of the $\text{Re}(\mathbf{1})(\text{CO})_3\text{Br}$ in acetone.

Figure S15. UV-Vis absorption spectra of $\text{Re}(\mathbf{1})(\text{CO})_3\text{Cl}$, $\text{Re}(\mathbf{1})(\text{CO})_3\text{Br}$ and free ligand $\mathbf{1}$ from diluted dichloromethane solutions.

Figure S16. UV-Vis absorption spectra of $\text{Re}(\mathbf{2})(\text{CO})_3\text{Br}$ and free ligand $\mathbf{2}[\text{PF}_6]$ from diluted dichloromethane solutions.

Figure S17: FT-IR spectra monitoring the carbonyl collapse of $\text{Re(1)(CO)}_3\text{Br}$ and the simultaneous carbonyl formation of $\text{Re(NCMe)}_2(\text{CO})_3\text{Br}$ in acetonitrile.

Figure S18: FT-IR spectra of synthesised $\text{Re(NCMe)}_2(\text{CO})_3\text{Cl}$ in acetonitrile.

Figure S19: FT-IR spectra of synthesised $\text{Re}(\text{NCMe})_2(\text{CO})_3\text{Br}$ in acetonitrile.

Figure S20: UV-Vis spectra of $\text{Re}(\mathbf{1})(\text{CO})_3\text{Br}$ complex dissolved in acetonitrile kept in the dark at time 0 (red trace) and subsequent scans over time during the formation of free ligand (**1**) (blue trace). No change was observed beyond 24 h scan. Legend time intervals in hours.

Figure 21: Free Ligand **1** UV-VIS spectrum in diluted acetonitrile.

Figure 22: $\text{Re}(\text{NCMe})_2(\text{CO})_3\text{Cl}$ UV-VIS spectrum in diluted acetonitrile.

Figure 23: $\text{Re}(\text{NCMe})_2(\text{CO})_3\text{Br}$ UV-VIS spectrum in diluted acetonitrile.

Figure S24: ^1H -NMR spectra of $\text{Re}(\mathbf{1})(\text{CO})_3\text{Cl}$ in acetone- d_6 kept in the dark.

Figure S25: ^1H -NMR spectra of $\text{Re}(\mathbf{1})(\text{CO})_3\text{Cl}$ in acetone- d_6 exposed to radiation at 365 nm.

Figure S26: ^1H -NMR spectra of $\text{Re}(\mathbf{1})(\text{CO})_3\text{Br}$ in acetone-d_6 kept in the dark.

Figure S27: ^1H -NMR spectra of $\text{Re}(\mathbf{1})(\text{CO})_3\text{Br}$ in acetone-d_6 exposed to radiation at 365 nm.

Figure S28: ^1H -NMR spectra of $\text{Re}(\mathbf{2})(\text{CO})_3\text{Br}$ in acetone-d_6 kept in the dark.

Figure S29: ^1H -NMR spectra of $\text{Re}(\mathbf{2})(\text{CO})_3\text{Br}$ in acetone-d_6 exposed to radiation at 365 nm.

Figure S30: ^1H -NMR spectra of $\text{Re}(\mathbf{2})(\text{CO})_3\text{Br}$ in acetonitrile-d_3 kept in the dark.

Figure S31: ^1H -NMR spectra of $\text{Re}(\mathbf{2})(\text{CO})_3\text{Br}$ in acetonitrile-d_3 exposed to radiation at 365 nm.

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