Note

Reaction of 2,3-bis(methylthio)pyrrolo[1,2-a]benzimidazol-1-one with BrRe(CO)₃(THF)₂: X-ray diffraction structure, redox chemistry, and luminescence behavior of *fac*-BrRe(CO)₃{*N,S*-2,3-bis(methylthio)pyrrolo[1,2-a]benzimidazol-1-one}

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Abstract

The reaction of the heterocyclic ligand 2,3-bis(methylthio)pyrrolo[1,2-a]benzimidazol-1-one with the rhenium(I) compound BrRe(CO)₃(THF)₂ has been explored and found to give the new complex *fac*-BrRe(CO)₃(*N,S*-heterocycle) (**1**) upon stirring at room temperature. The same product has also been isolated in lower yield by heating BrRe(CO)₅ and the starting heterocycle. Compound **1** has been isolated and characterized in solution by IR and NMR spectroscopies, and the *N,S*-chelation mode exhibited by the ancillary heterocyclic ligand has been confirmed by X-ray diffraction analysis. The redox properties of **1** have been investigated by cyclic voltammetry, where an irreversible reduction is observed at $E_p^c = -0.63$ V. The nature of the LUMO in **1** has been evaluated through the means of extended Hückel MO calculations, and the electrochemical and MO data are discussed relative to the parent heterocyclic ligand that possesses a low-lying, ligand-based π^* LUMO. The photophysical behavior of the starting heterocycle and compound **1** has been analyzed in CH_2Cl_2 and MeCN solvents; emission quantum yields at room temperature are on the order of 10^{-5} in CH_2Cl_2 and one order of magnitude higher in MeCN. The lowest excited state arises from an intraligand (IL) transition resulting from a $\pi \to \pi^*$ excitation that is confined to the heterocycle.
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1. Introduction

The synthesis and study of the rhenium(I) complexes XRe(CO)₃(α-diimine) have attracted considerable attention over the last few decades given their prominence as integral components in the construction of redox-active and luminescent sensing devices [1]. Moreover, this genre of compounds has also been extensively investigated as catalyst precursors in thermal and electrocatalytic CO_2 reduction schemes [2] and in electron-transfer reactions given their propensity to stabilize electron counts in excess of 18 electrons [3].

We have previously published our results on the structural consequences associated with electron transfer in the related complex *fac*-BrRe(CO)₃(bma) [where bma = 2,3-bis(diphenylphosphino)maleic anhydride] [4], which is a closely related mimic of the rhenium compounds

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XRe(CO)$_3$(α-diimine) insomuch that the ancillary bma ligand possesses a low-lying π^* orbital that is able to serve as an electron reservoir during chemical and electrochemical reductions. For the most part, the electron-accepting α-diimine ligands 2,2'-bipyridine (bpy) and 1,10-phenanthroline (phen) and the diphosphine bma ligand display analogous chemical and reactivity patterns. As part of our program directed towards the synthesis of new redox-active ligands for electrochemical and photophysical studies, we have synthesized the new heterocyclic ligand 2,3-bis(methylthio)pyrrolo[1,2-a]benzimidazol-1-one, whose synthesis and structure are shown below [5]. This particular ligand contains structural elements common to both the α-diimine and bma ligands. For example, our new ligand has the potential to serve as a bidentate ligand through coordination of the *N,S*, *S,S*, and *S,O* functionalities, in addition to possessing a low-lying π^* LUMO that is confined to the exterior pyrrol-1-one ring in a fashion identical to that exhibited by the bma ligand. In order to establish the coordination chemistry of this new heterocyclic ligand, we have examined its reaction with the labile compound *fac*-BrRe(CO)$_3$(THF)$_2$, which affords the new compound *fac*-BrRe(CO)$_3$(*N,S*-heterocycle) (**1**). The solid-state structure, electrochemical properties, and photophysics of **1** are presented within.
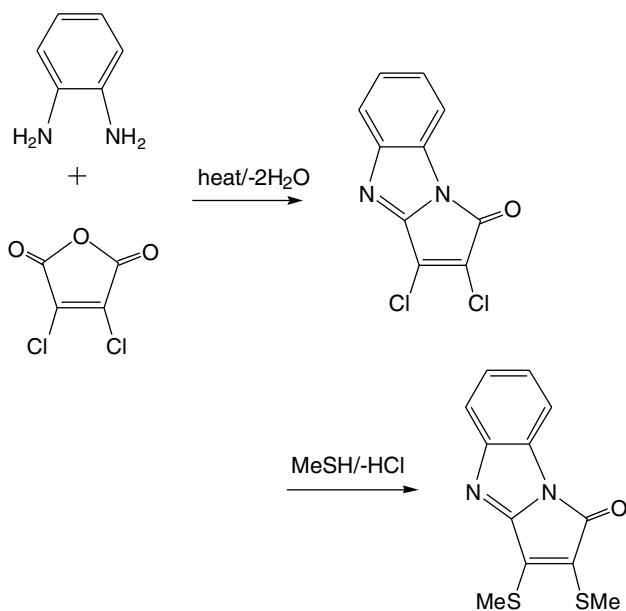
2. Experimental

2.1. General

The BrRe(CO)$_5$ employed in our study was prepared from Re$_2$(CO)$_{10}$ and Br$_2$ [6], with *fac*-BrRe(CO)$_3$(THF)$_2$ synthesized according to the known procedure [7]. The *o*-phenylenediamine and 2,3-dichloromaleic anhydride used in the synthesis of the title heterocycle were pur-

chased from Aldrich Chemical Co. and used as received. All reaction, IR, and NMR solvents were of reagent grade and were either degassed with argon prior to their use or distilled from a suitable drying agent and stored in Schlenk vessels equipped with Teflon stopcocks [8]. The combustion analysis was performed by Atlantic Microlab, Norcross, GA.

Routine infrared spectra were recorded on a Nicolet 20 SXB FT-IR spectrometer in a 0.1 mm NaCl cell, using PC control and OMNIC software, while the ^{1}H NMR spectrum was recorded at 200 MHz on a Varian Gemini-200 spectrometer. For the UV–Vis absorption and emission measurements standard 10 mm pathlength fluorescence cuvettes (Starna) were employed. The organic solvents used in the photophysical studies were spectrophotometric grade CH$_2$Cl$_2$ and MeCN (which were degassed with N$_2$ for 30 min prior to storage in a Vacuum-Atmospheres Dribox). Solutions of Ru(bpy)$_3$-(PF$_6$)$_2$ (CH$_2$Cl$_2$) and fluorescein (0.1 M NaOH$_{(aq)}$, nondegassed) were used as reference standards. The absorption spectra were collected on a HP 8453 Chem-Station, while the emission data were recorded on a Jobin Yvon Fluorolog FL3-22 spectrometer equipped with DataMax software.

2.2. Synthesis of fac-BrRe(CO)$_3$\{N,S-2,3-bis(methylthio)-pyrrolo[1,2-a]benzimidazol-1-one\}

To 44 mg (0.09 mmol) of *fac*-BrRe(CO)$_3$(THF)$_2$ in 20 mL of toluene under argon was added 25 mg (0.10 mmol) of the parent heterocycle. The reaction solution was stirred at room temperature overnight, with precipitation of a red solid observed slowly over the course of the reaction. The solid was isolated by filtration and was verified as the desired product based on IR and NMR analyses. The product was subsequently recrystallized from CH$_2$Cl$_2$/hexane to afford 28 mg (63% yield) of compound **1**. IR (CH$_2$Cl$_2$): ν(CO) 2035 (vs), 1938 (s), 1910 (s), 1796 (w), 1780 (w) cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 2.92 (s, SMe), 3.05 (s, SMe), 7.37–7.76 (m, 4 H, aryl). Anal. Calc. (found) for C$_{15}$H$_{10}$BrN$_2$O$_4$ReS$_2$: C, 29.39 (29.24); H, 1.63 (1.51).

2.3. X-ray diffraction structure for fac-BrRe(CO)$_3$\{N,S-2,3-bis(methylthio)pyrrolo[1,2-a]benzimidazol-1-one\} (1)

Single crystals of the title compound suitable for X-ray crystallography were grown from an ethyl acetate solution containing compound **1** that had been layered with nitromethane. X-ray data were collected on a Bruker SMART™ 1000 CCD-based diffractometer at 213 K. The frames were integrated with the available SAINT software package using a narrow-frame algorithm [9], and the structure was solved and refined using the SHELXTL program package [10]. The molecular structure

was checked by using PLATON [11], and all nonhydrogen atoms were refined anisotropically. All hydrogen atoms were assigned calculated positions and allowed to ride on the attached heavy atom, unless otherwise noted. Compound **1**: $C_{15}H_{10}BrN_2O_4ReS_2$, FW = 612.46, monoclinic, $P2_1/c$, $a = 9.766(3)$ Å, $b = 14.521(4)$ Å, $c = 12.972(3)$ Å, $\beta = 98.868(5)°$, $V = 1817.7(8)$ Å^3, $Z = 4$, $D_{calc} = 2.238$ Mg/m^3, $\theta = 2.11–22.50°$, $\mu = 9.135$ mm^{-1}, $F(000) = 1152$, 2357 reflections, 229 parameters, $R = 0.0365$, $R_w = 0.0843$, GOF on $F^2 = 0.966$.

2.4. Cyclic voltammetry

The cyclic voltammogram was recorded on a PAR Model 273 potentiostat/galvanostat, equipped with positive feedback circuitry to compensate for iR drop. An airtight, three-electrode design CV cell was used, with a platinum disk (0.3 mm diameter) serving as the working and auxiliary electrodes. The reference electrode utilized a silver wire as a quasi-reference electrode, and the reported potential data are referenced to the formal potential of the Cp_2Fe/Cp_2Fe^+ (internally added) redox couple, taken to have $E_{1/2} = 0.307$ V [12].

2.5. Extended Hückel MO calculations

The extended Hückel calculations on compound **1** were carried out using the original program developed by Hoffmann [13], as modified by Mealli and Proserpio [14]. The weighted H_{ij}'s contained in the program were employed in the calculations. The input Z-matrix for model complex fac-BrRe(CO)$_3${N,S-2,3-bis(thio)pyrrolo[1,2-a]benzimidazol-1-one} was constructed from the X-ray fractional coordinates of **1** with the two methyl groups belonging to the methylthio ligands replaced by hydrogen atoms. Here the S–H bond distances were set at 1.42 Å [15].

2.6. Fluorescence measurements and quantum yields

Reference standardization: First, suitable standards [fluorescein and Ru(bpy)$_3$(PF$_6$)$_2$] were selected for the quantum yield studies, with the emission intensity vs. concentration of each standard measured and compared with each other. Measurements of the two standards were taken at analyte concentrations yielding absorptions of 0.02, 0.04, 0.06, 0.08, and 0.10 using an excitation wavelength of 454 nm [16], which represented the optimum excitation wavelength for the standards, the parent heterocycle and the title rhenium compound. Plots of the integrated emission vs. the absorption value at λ_{ex} were found to be linear and whose gradients, in conjunction with the refractive index (η), were used to compute the reported lifetime quantum yields (Φ) as follows:

$$\Phi_x = \Phi_{ST}[\text{Grad}_x/\text{Grad}_{ST}]/[(\eta_x^2)/(\eta_{ST}^2)]. \tag{1}$$

The experimentally determined Φ values found for each standard were compared to the published literature values, with our results being within ±2.5% of the published Φ values for fluorescein and Ru(bpy)$_3$(PF$_6$)$_2$ and well within the limits of reliability stated in the procedural guidelines [17].

Compound quantum yield measurements: Using the same methodology and experimental conditions, the photophysical characteristics of the parent heterocycle and compound **1** were studied in CH_2Cl_2 and MeCN. All samples were prepared in a Vacuum-Atmospheres Dribox in quartz fluorescence cuvettes equipped with Teflon stopcocks. A total of four runs were performed and the data averaged to give the reported quantum yields.

3. Results and discussion

3.1. Synthesis, spectroscopic data, and X-ray diffraction structure

Treatment of fac-BrRe(CO)$_3$(THF)$_2$ with one mole equivalent of 2,3-bis(methylthio)pyrrolo[1,2-a]benzimidazol-1-one in toluene leads to THF displacement and formation of compound **1**, which is readily isolated by filtration due to its low solubility in toluene. The thermolysis reaction between BrRe(CO)$_5$ and an added measure of the parent heterocycle also furnishes **1** albeit in slightly lower yields. Compound **1** is relatively soluble in such solvents as CH_2Cl_2 and THF and is essentially insoluble in saturated hydrocarbons. **1** appears to be indefinitely stable in the solid state and is relatively stable in oxygen-containing solutions, with slight decomposition observed over a period of several days. Eq. (1) illustrates the course of this reaction employing fac-BrRe(CO)$_3$(THF)$_2$ as the starting rhenium complex.

compound **1**
with N,S chelation

(1)
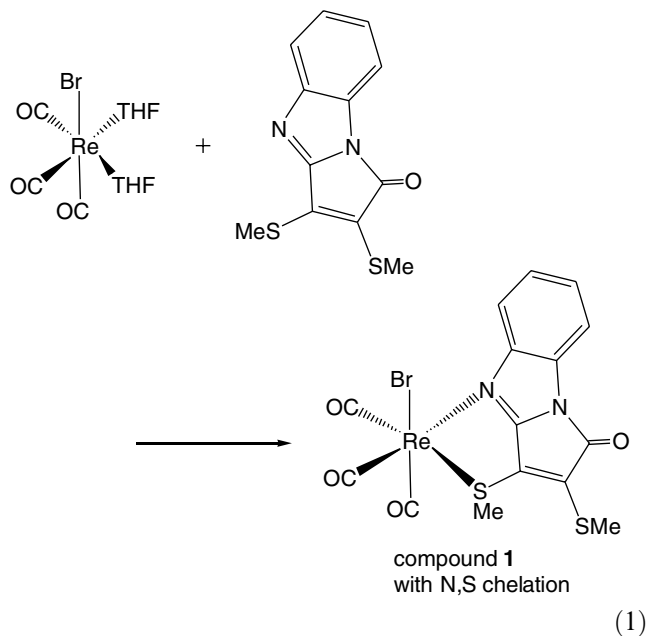
Compound **1** was characterized in solution by IR and ^{1}H NMR spectroscopies. The IR spectrum of **1** exhibits three $v(CO)$ stretching bands at 2035 (vs), 1938 (s), and 1910 (s) cm^{-1} that belong to the facially bound, terminal rhenium CO ligands [4], along with two very weak stretches at 1796 and 1780 cm^{-1} ascribed to the C=O and C=N moieties associated with the heterocyclic ligand [18]. The ^{1}H NMR spectrum of compound **1** is straightforward and consistent with the proposed structure insomuch as it exhibits two methyl singlets at δ 2.92 and 3.05 and a classical ABCD spin system from δ 7.37–7.76 for the four aromatic hydrogens belonging to the six-membered ring of the heterocyclic ligand.

The thermal ellipsoid plot of *fac*-BrRe(CO)$_3$(*N,S*-heterocycle) shown in Fig. 1 confirms the chelation of the ancillary heterocycle through coordination of the N(2) and S(2) atoms to the rhenium center. The rhenium center is six-coordinate and displays an idealized octahedral geometry. The three facial CO ligands are situated *trans* to the N(2), S(2), Br(1) groups. The Re(1)–N(2) and Re(1)–S(2) bond distances of 2.191(7) and 2.559(3) Å, respectively, are in good agreement with the Re–N and Re–S distances found in related rhenium(I) compounds containing heterocyclic ligands [19]. The three rings comprising the heterocyclic ligand are essentially planar with $\sigma_p = 0.02$ Å, with the bond distances and angles associated with the heterocyclic portion of **1** being unexceptional with respect to the parent ligand [5b]. The
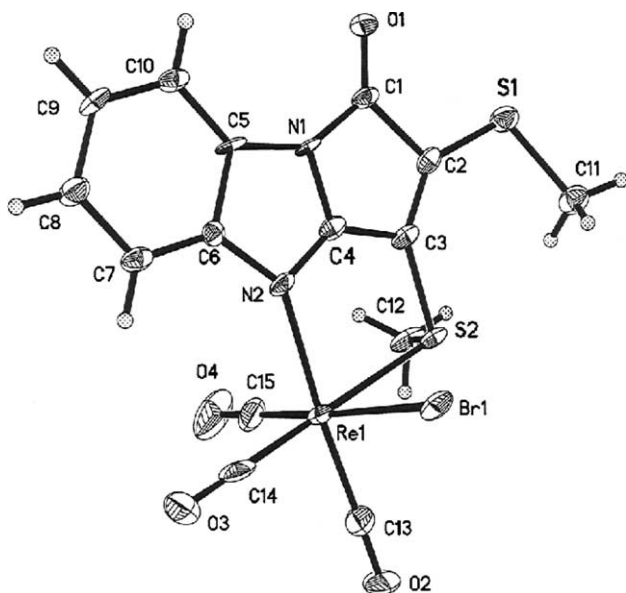
remaining bond distances and angles exhibit acceptable values and do not require comment.

3.2. Photophysical studies

The absorption and emission spectra of **1** and the free heterocycle were examined in oxygen-free CH$_2$Cl$_2$ and MeCN solvents at room temperature, with only very minor differences observed in these solvents. Fig. 2 shows representative spectra of **1** and the free heterocycle in CH$_2$Cl$_2$ and Table 1 summarizes the absorption and emission data. Unlike the myriad examples of MLCT emission in XRe(CO)$_3$(α-diimine) complexes [1,20], the emissive behavior from the lowest excited state of **1** is attributed to an intraligand (IL) transition resulting from a $\pi \rightarrow \pi^*$ excitation that is localized on the heterocycle. We attribute the lowest energy visible band to a $\pi \rightarrow \pi^*$ transition due to the magnitudes of the molar absorptivities and to the relative insensitivity to solvent polarity [for the ligand: λ_{max} = 464 (EtOH), 460 (MeCN), 466 (CH$_2$Cl$_2$), 465 (cyclohexane)]. The fluorescence emission that is observed at room temperature for **1** is also relatively solvent insensitive, supporting an IL transition involving a redistribution of electron density within a common π-platform [21]. The negative
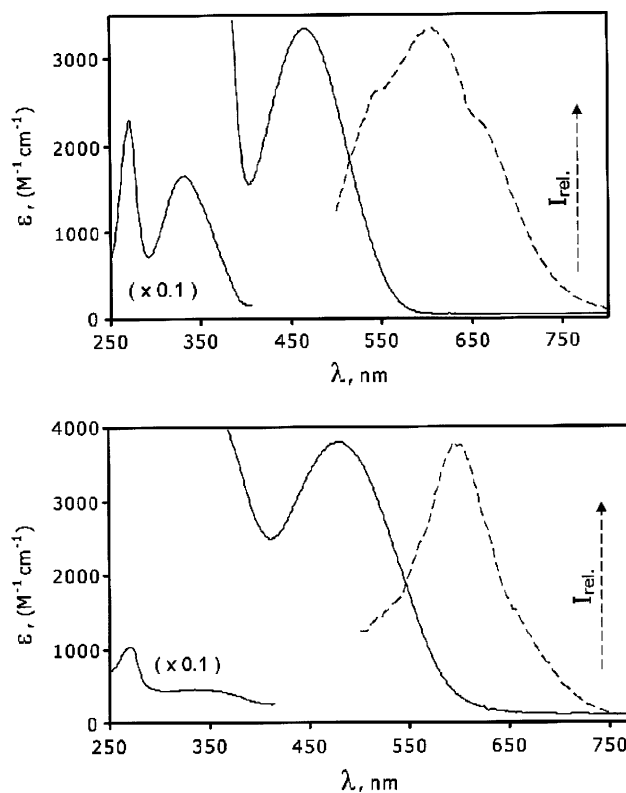
Fig. 1. Thermal ellipsoid plot of *fac*-BrRe(CO)$_3${*N,S*-2,3-bis(methylthio)pyrrolo[1,2-*a*]benzimidazol-1-one} showing the thermal ellipsoids at the 50% probability level. Selected bond distances (Å) and angles (°): Re(1)–N(2) = 2.191(7), Re(1)–S(2) = 2.559(3), Re(1)–Br(1) = 2.608(1), C(2)–C(3) = 1.35(1), C(14)–Re(1)-N(2) = 96.0(4), C(13)–Re(1)–S(2) = 93.1(3), N(2)–Re(1)–S(2) = 81.6(2), N(2)–Re(1)–Br(1) = 87.7(2), S(2)–Re(1)–Br(1) = 79.34(6), N(2)–C(4)–N(1) = 115.83(8).

Fig. 2. UV–Vis absorption and emission spectra of the parent heterocycle (top) and *fac*-BrRe(CO)$_3${*N,S*-2,3-bis(methylthio)pyrrolo[1,2-*a*]benzimidazol-1-one} (bottom) in CH$_2$Cl$_2$ at room temperature. The excitation wavelengths for the emission spectra were 466 nm for the parent ligand and 477 nm for compound **1**.

Table 1
Photophysical data for compound **1** and the free ligand 2,3-bis(methylthio)pyrrolo[1,2-*a*]benzimidazol-1-one in CH$_2$Cl$_2$ and MeCN solvents

Compound	λ_{abs}^{max} (ε M^{-1} cm^{-1})	λ_{em}^{max} (nm)	$\Phi(10^6)$[a]
1 (CH$_2$Cl$_2$)	338 (4500), 477 (3800)	600	30
Free heterocycle (CH$_2$Cl$_2$)	331 (17000), 466 (3300)	610	41
1 (MeCN)	328 (11000), 460 (1800)	610	110
Free heterocycle (MeCN)	329 (15000), 460 (3000)	602	150

[a] The error in each number is less than the significant figures reported.
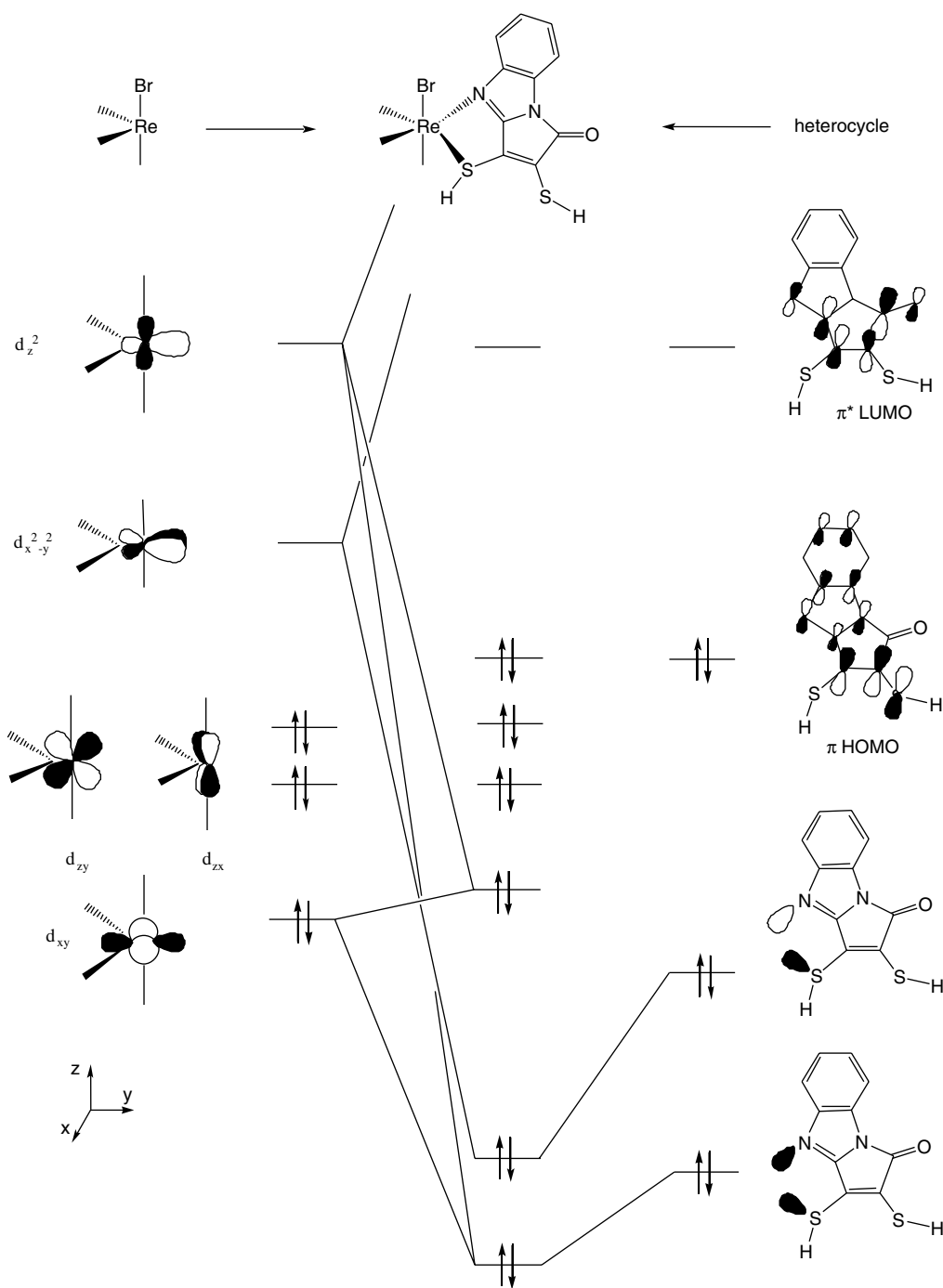
Fig. 3. Qualitative MO diagram for *fac*-BrRe(CO)$_3$(*N*,*S*-2,3-dimercaptopyrrolo[1,2-*a*]benzimidazol-1-one) showing the important frontier orbital interactions.

solvatochromism for **1**, the fact that both the free heterocyclic ligand and compound **1** display similar absorption data in the low-energy portion of the UV–Vis spectrum, and the common emissive features for the two compounds provide further support for the proposed nature of the emission. The photophysical behavior exhibited by **1** is reminiscent of the cyclophane-substituted complex $ClRe(CO)_3(phanephos)$ where the transannular π-system favors an IL over a MLCT transition [22].

3.3. Electrochemical and MO data

The cyclic voltammetric properties of **1** were next examined at a platinum disk electrode in CH_2Cl_2 solvent containing 0.25 M tetra-*n*-butylammonium perchlorate (TBAP) as the supporting electrolyte. A single, irreversible reduction wave was found at $E_p^c = -0.63$ V at a scan rate of 250 mV/s when the sample was scanned over the potential region of 1.00 to -1.50 V at room temperature. The one-electron stoichiometry associated with the forward reduction wave in **1** was verified by current calibration against the one-electron standard ferrocene, taking into account differences in the diffusion coefficients between the two compounds according to Walden's rule [12]. Given that the parent heterocycle exhibits a reversible $0/1^-$ reduction wave at $E_{1/2} = -1.15$ V under identical CV conditions [5b], the irreversible reduction found in **1** must arise from an ECE process that is triggered upon electron accession. Recording the CV at $-20\,°C$ and at scan rates up to 1.0 V/s did not improve the reversibility of the reduction.

The qualitative molecular orbital diagram for the model compound *fac*-$BrRe(CO)_3(N,S$-2,3-dimercaptopyrrolo[1,2-*a*]benzimidazol-1-one) depicted in Fig. 3 was constructed from the results obtained from extended Hückel MO calculations. Here, we examined the formation of the model compound from the union of the d^6-ML_4 species $BrRe(CO)_3$ with the heterocyclic ligand. The frontier orbitals of the $BrRe(CO)_3$ fragment consist of a filled "t_{2g}" set of orbitals and two higher-lying, empty orbitals that are ideally hybridized for bonding with the lone-electron pairs on the nitrogen and sulfur donor atoms of the heterocycle. The orbital composition and approximate energies of the rhenium frontier molecular orbitals are consistent with the trends reported for other ML_4 fragments [23], while the HOMO and LUMO belonging to the free heterocyclic ligand have already been described by us [5b]. A salient feature that emerges from our MO study is that the π HOMO and the π* LUMO associated with the heterocycle find no appropriate metal orbitals with which to interact with and translate unchanged upon formation of *fac*-$BrRe(CO)_3(N,S$-2,3-dimercaptopyrrolo[1,2-*a*]benzimidazol-1-one) and become the HOMO and LUMO in the rhenium(I) complex. The energies of these two orbitals are found at -11.84 and -9.95 eV, respectively. Optical excitation within the HOMO/LUMO manifold accounts nicely for our proposed IL transition and emissive behavior (vide supra). The major difference between compound **1** and the $XRe(CO)_3(bpy)$ systems that exhibit MLCT absorption and emission chemistry stems from the HOMO energy level in 2,3-bis(methylthio)pyrrolo[1,2-*a*]benzimidazol-1-one vs. the corresponding π HOMO in the free bpy ligand (ψ_6), the latter which is found at an energy slightly below the t_{2g} nest of rhenium orbitals ensuring that an IL transition is not observed with this particular class of diimine-substituted complexes [24]. This orbital stabilization renders one of the metal-based t_{2g} orbitals as the HOMO in the $XRe(CO)_3(bpy)$ compound and guarantees a low-energy MLCT upon near-UV excitation.

4. Conclusions

The reaction of $BrRe(CO)_3(THF)_2$ and $BrRe(CO)_5$ with the heterocyclic ligand 2,3-bis(methylthio)pyrrolo[1,2-*a*]benzimidazol-1-one affords the new compound *fac*-$BrRe(CO)_3(N,S$-heterocycle) as the sole observable product. The redox and photophysical properties of *fac*-$BrRe(CO)_3(N,S$-heterocycle) have been examined and contrasted with related $BrRe(CO)_3$(α-diimine) compounds. The observed IL emissive behavior in **1** is attributed to a π → π* transition localized on the heterocyclic ligand. Future research will concentrate on the synthetic modification of the heterocyclic ligand with the goal of engineering a lower-lying, ligand π HOMO whose energy lies below the metal-based t_{2g} orbitals on the rhenium fragment, leading to promotion of MLCT over IL emission chemistry.

5. Supporting information available

X-ray crystallographic files, in CIF format, for the structure determination of **1** have been deposited with the Cambridge Crystallographic Data Center, CCDC: 260091. Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ (fax: +44 1223 336033; email: deposit@ccdc.cam.uk or at www: http://www.ccdc.cam. ac.uk).

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