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Using Hydrazine to Link Ferrocene with $\text{Re}(\text{CO})_3$: A Modular Approach

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Abstract

Acetyl ferrocene and diacetyl ferrocene both readily react with an excess of hydrazine to afford the corresponding hydrazone compounds. These compounds can then be linked to $\text{Re}(\text{CO})_3$ via a metal-mediated Schiff base reaction, resulting in a series of ferrocene- $\text{Re}(\text{CO})_3$ conjugates with different stoichiometries. Conjugates with 1:1, 1:2, and 2:1 ferrocene: $\text{Re}(\text{CO})_3$ ratios can be produced via this “modular” type synthesis approach. Several examples of these conjugates were structurally characterized, and their spectroscopic, electrochemical, and spectroelectrochemical behaviors were investigated. The electronic structures of these compounds were also probed using DFT and TDDFT calculations.

Graphical Abstract

Acetyl ferrocene and diacetyl ferrocene both readily react with an excess of hydrazine to afford the corresponding hydrazone compounds, which can be coupled to $\text{Re}(\text{CO})_3$ groups via Schiff base formation reactions.

Keywords

Ferrocene; tricarbonyl rhenium(I); Schiff base conjugate; electrochemistry; density functional theory

1.0 Introduction

Organometallic compounds have employed in a wide variety of applications, ranging from catalysis to materials science [1–4]. Accordingly, much work has focused on the covalent attachment of organometallic fragments to other molecules to produce conjugate compounds, which continues in the recent literature [5–8]. For example, over the past few decades there has been increasing interest in the linking of organometallic compounds to molecules of biological interest [9–11]. Organometallic compounds are of interest in biochemistry and medicine as both therapeutic and diagnostic agents [12–14], and as a probe to understand structure and function in biological macromolecules [15,16]. As a result of this interest, there is a need for the development of new synthetic methodologies to produce these biologically relevant conjugates.

Two commonly used examples of organometallic moieties used as components of conjugate molecules are ferrocene [17–20] and the $\text{Re}(\text{CO})_3$ unit [21,22]. Both of these groups are stable to water and dioxygen, and are robust enough to handle a variety of chemical manipulations. For example, both moieties are stable enough to append to biological or pharmacologically active compounds. Additionally, ferrocene and $\text{Re}(\text{CO})_3$ compounds can be readily incorporated into molecules for potential materials applications. In work from our laboratories, we have functionalized proteins and peptides with the $\text{Re}(\text{CO})_3$ unit [23,24], and have appended the ferrocene unit to chromophores like porphyrin, phthalocyanine, BODIPY, azaBODIPY and the recent BOPHY fluorophore [25–29].

In this report, we present a series of ferrocene- $\text{Re}(\text{CO})_3$ conjugate compounds synthesized via a modular approach. These compounds are shown in Figure 1. In all cases, we can use hydrazine-derived Schiff base formation to produce 1:1 $\text{Fc}:\text{Re}(\text{CO})_3$ adducts as well as 2:1 and 1:2 $\text{Fc}:\text{Re}(\text{CO})_3$ systems. Both 1-acetylferrocene and 1,1'-diacetylferrocene react with hydrazine to afford the corresponding hydrazones. These hydrazones can then form a second C-N double bond via a $\text{Re}(\text{CO})_3$ mediated reaction involving a chelating aldehyde. In addition to the synthesis of these modular constructs, we have probed their spectroscopy and electrochemistry, and have investigated their electronic structures via DFT and TDDFT methods.

2.0 Experimental

2.1 Materials and methods

All reagents were purchased from Strem, Acros Organics, TCI AMERICA or Sigma-Aldrich and used as received without further purification. Diacetylferrocene (**2**) was synthesized by using a previously reported procedure [30]. All solvents were purified by alumina and copper columns in the Pure Solve solvent system (Innovative Technologies, Inc.) and were stored over molecular sieves. Syntheses were performed under nitrogen atmosphere with a

Schlenk line apparatus equipped to a pre-drying column to minimize exposure to air and water. NMR spectra were recorded on a Varian Mercury 300 MHz. Chemical shifts were reported with respect to residual solvent peaks as internal standard (^1H : CDCl_3 , $\delta = 7.26$ ppm; ^{13}C : CDCl_3 , $\delta = 77.2$ ppm). Infrared spectra were collected on Thermo Scientific Nicolet iS5 which was equipped with iD5 ATR. Electronic absorption spectra were recorded on Hitachi U-2000 UV-vis spectrophotometer. Electrospray MS (ES-MS; positive mode) spectra were recorded using a Bruker HCT-ultra ETD II Ion Trap mass spectrometer at the University of Minnesota Duluth using THF as the solvent.

2.2 X-ray data collection and structure determination

X-ray crystallographic analysis: Single crystal data for **4** were collected on a Bruker SMART APEX I diffractometer. Samples were coated in Paratone-N (Exxon) oil, mounted on a pin and placed on a goniometer head under a stream of nitrogen cooled to 100 K. The detector was placed at a distance of 5.009 cm from the crystal. The data of compound **4** was collected on Mo-target X-ray tube (Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$) operated at 2000 W power. The data for compound **5** were collected on a Bruker APEX II DUO system using a Cu source with ImuS microfocus optics (Cu $K\alpha$ radiation, $\lambda = 1.54178 \text{ \AA}$). The frames for both crystals were integrated with the Bruker SAINT software package using a narrow-frame algorithm. Data were corrected for absorption effects using the multiscan method (SADABS) and the structure was solved and refined using the Bruker SHELXTL Software Package until the final anisotropic full-matrix, least-squares refinement of F^2 converged [31].

2.3 Synthetic procedures

Synthesis of 1—An ethanolic solution of acetylferrocene (1.00 g, 4.38 mmol) was slowly added into a reaction flask containing 2.56 mL (a 12-fold excess, ~53 mmol) of hydrazine hydrate. A catalytic amount (0.42 g, 2.19 mmol) of *p*-toluenesulfonic acid was then added. The reaction was stirred at room temperature for three days. Reaction completeness was monitored by thin layer chromatography (silica, 100% dichloromethane). Upon completion, an excess of ice-cold DI water was added to the reaction flask and a golden crystalline solid started to form. The crystals were filtered and air-dried. **1**: Yield 0.72 g (68%). ^1H NMR (300 MHz, CDCl_3) δ 5.07 (s, 2H, NH_2), 4.50 (br s, 2H, C_5H_4), 4.26 (br s, 2H, C_5H_4), 4.15 (s, 5H, C_5H_5), 2.05 (s, 3H, CH_3); HRMS (ESI): m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{12}\text{H}_{14}\text{FeN}$: 243.0579, found 243.0724; UV-Vis spectrum in THF λ_{max} 436 nm ($\epsilon = 6.7 \times 10^2 \text{ M}^{-1} \text{ cm}^{-1}$).

Synthesis of 3—The synthesis and crystal structure of **3** was reported previously [32,33] and we used a slightly modified synthetic method in this work. Compound **2** (1.0 g, 3.7 mmol) was dissolved in ethanol and which was then added to a large excess amount (3.6 mL, 74 mmol) of hydrazine hydrate. The reaction was stirred at room temperature for 48 hours. The resultant orange precipitate was filtered and air-dried. Yield 0.2 g (18%). ^1H NMR (300 MHz, CDCl_3) δ 5.07 (s, 4H, NH_2), 4.50 (m, 4H, C_5H_4), 4.24 (m, 4H, C_5H_4), 1.96 (s, 6H, CH_3); HRMS (ESI): m/z $[\text{M}+\text{H}]^+$ calcd for calc. for $\text{C}_{14}\text{H}_{18}\text{FeN}_4$: 299.0954, found 299.1123; UV-Vis spectrum in THF λ_{max} 449 nm ($\epsilon = 4.4 \times 10 \text{ M}^{-1} \text{ cm}^{-1}$).

Synthesis of $\text{Re}(\text{CO})_3$ -pyca-ferrocene complexes

Synthesis of 4 and 5: The procedure for **4** is representative of both compounds. **4:** $\text{Re}(\text{CO})_5\text{Cl}$ (50 mg, 0.14 mmol) and pyridine-2-carboxaldehyde (15 μL , 0.14 mmol) were refluxed in 15 mL of toluene for 30 minutes. The mixture turned purple as the reaction proceeded. Compound **1** (36 mg, 0.14 mmol) in toluene (20 mL) was then added to the purple reaction mixture and the combined solution was refluxed. The reaction was monitored by TLC (silica, 2% MeOH/DCM). The reaction was complete in 4 hours according to the total consumption of compound **1** in TLC. The reaction was cooled and a red precipitate appeared. The solid was filtered, washed with ether, and dried under vacuum. Crystals suitable for X-ray diffraction were prepared by slow evaporation from DCM. Yield 61 mg (68%). ^1H NMR (300 MHz, CDCl_3) δ 9.02 (s, 1H, N=CH), 8.23 (m, 1H, H on py), 8.04 (m, 1H, H on py), 7.83 (m, 1H, H on py), 7.54 (m, 1H, H on py), 4.74–4.79 (m, 2H, C_5H_4), 4.51 (m, 2H, C_5H_4) 4.31 (s, 5H, C_5H_5) 2.42 (s, 3H, CH_3); ^{13}C NMR (125 MHz CDCl_3) δ 196.6, 195.6, 186.8, 165.9, 154.8, 157.4, 153.1, 139.1, 127.5, 126.8, 80.1, 71.4, 71.4, 69.9, 17.7; IR (CO stretch, cm^{-1}): 2016 (m), 1916 (s), 1883 (s); HRMS (ESI): m/z $[\text{M}]^+$ calcd for $\text{C}_{21}\text{H}_{17}\text{FeN}_3\text{O}_3\text{ReClC}_4\text{H}_8\text{O}$: 709.0427, found 709.0540; UV-Vis spectrum in THF λ_{max} 417 nm ($\epsilon = 4.3 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$).

5: Yield 71 mg (80%). ^1H NMR (300 MHz, CDCl_3) δ 9.05 (s, 1H, N=CH), 8.20 (m, 1H, H on py), 8.03 (m, 1H, H on py), 7.83 (m, 1H, H on py), 7.53 (m, 1H, H on py), 4.81–4.76 (m, 2H, C_5H_4), 4.52 (m, 2H, C_5H_4) 4.31 (s, 5H, C_5H_5) 2.43 (s, 3H, CH_3); ^{13}C NMR (125 MHz CDCl_3) 196.6, 195.6, 186.7, 166.0, 154.7, 154.4, 153.1, 138.9, 127.4, 126.7, 80.2, 71.4, 71.3, 69.9, 17.7; IR (CO stretch, cm^{-1}): 2017 (m), 1918 (s), 1885 (s); HRMS (ESI): m/z $[\text{M}]^+$ calcd for $\text{C}_{21}\text{H}_{17}\text{FeN}_3\text{O}_3\text{ReBr}$: 680.9339, found 680.9350; UV-Vis spectrum in THF λ_{max} 427 nm ($\epsilon = 3.6 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$).

Synthesis of 6 and 7—The procedure for **6** is representative of both compounds. **6:** $\text{Re}(\text{CO})_5\text{Cl}$ (50 mg, 0.14 mmol) and pyridine-2-carboxaldehyde (15 μL , 0.14 mmol) were refluxed in 15 mL of toluene for 30 minutes. The mixture turned purple as the reaction proceeded. Compound **3** (21 mg, 0.07 mmol) in toluene was then added to the purple reaction mixture and the combined solution was refluxed. The reaction was monitored by TLC (silica, 2% MeOH/DCM). The reaction was complete in 1.5 hours according to the total consumption of compound **3**. The reaction was cooled down and an orange precipitate appeared. The resultant solid was filtered, washed with ether, and dried under vacuum. Yield 61 mg (80%). ^1H NMR (300 MHz, d_6 -DMSO) δ 9.01 (s, 2H, N=CH), 8.84–8.81 (m, 2H, H on py), 8.31 (m, 2H, H on py), 8.19–8.17 (m, 2H, H on py), 7.76 (m, 2H, H on py), 4.98 (m, 4H, C_5H_4), 4.69 (m, 4H, C_5H_4) 2.38 (s, 6H, CH_3); ^{13}C NMR data could not be obtained due to decomposition of the compound; IR (CO stretch, cm^{-1}): 2020 (s), 1909 (m), 1870 (s); HRMS (ESI): m/z $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{32}\text{H}_{24}\text{Cl}_2\text{FeN}_6\text{O}_6\text{Re}_2\text{C}_4\text{H}_8\text{O}(\text{CH}_3\text{CN})_2$: 1265.0597, found 1265.0500; UV-Vis spectrum in THFNEt_3 λ_{max} 410 nm ($\epsilon = 7.9 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$).

7: Yield 57 mg (74%). ^1H NMR (300 MHz, d_6 -DMSO) δ 9.02 (s, 1H, N=CH), 8.82–8.80 (m, 1H, H on py), 8.30 (m, 1H, H on py), 8.19 (m, 2H, H on py), 7.75 (m, 2H, H on py), 4.99 (m, 4H, C_5H_4), 4.70 (m, 4H, C_5H_4) 2.38 (s, 6H, CH_3); ^{13}C NMR data could not be obtained due to decomposition of the compound; IR (CO stretch, cm^{-1}): 2021 (s), 1909 (m),

1876 (s); HRMS (ESI): m/z $[M]^+$ calcd for $C_{32}H_{24}Br_2FeN_6O_6Re_2N_2$: 1203.8644, found 1203.9744; UV-Vis spectrum in THF/ NEt_3 λ_{max} 418 nm ($\epsilon = 8.2 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$).

Synthesis of 8 and 9—The procedure for **8** is representative of both compounds. **8**: $Re(CO)_5Cl$ (50 mg, 0.14 mmol) and glyoxal (7 μ L, 0.14 mmol) were refluxed in 10 mL of methanol for 1 hour. Compound **1** (71 mg, 0.28 mmol) in methanol was added to the reaction mixture and it was refluxed. The reaction was monitored by TLC (silica, 2% MeOH/DCM). The reaction was complete in 3 hours based on the consumption of compound **1**. The reaction was cooled down and reddish-brown precipitate appeared. The resulting solid was purified by column chromatography (silica, 2% MeOH/DCM). A red band was collected yielding a red solid that was filtered, washed with ether, and dried under vacuum. Yield 45 mg (40%). 1H NMR (300 MHz, d_6 -DMSO) δ 8.43 (s, 2H, glyoxal $N=CH$), 4.91 (br s, 4H, C_5H_4), 4.66 (br s, 4H, C_5H_4), 4.38 (br s, 10H, C_5H_5), 2.43 (br s, 6H, CH_3); ^{13}C NMR data cannot be obtained due to decomposition of the compound; IR (CO stretch, cm^{-1}): 2018 (m), 1888 (s); HRMS (ESI): m/z $[M]^+$ calcd for $C_{29}H_{26}Fe_2N_4O_3ReCH_3CN$: 818.0521, found 818.0501; UV-Vis spectrum in THF λ_{max} 442 nm ($\epsilon = 5.1 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$).

9: Yield 42 mg (38%). 1H NMR (300 MHz, d_6 -DMSO) δ 8.32 (s, 2H, glyoxal $N=CH$), 4.83 (m, 4H, C_5H_4), 4.57 (m, 4H, C_5H_4), 4.30 (s, 10H, C_5H_5), 2.34 (s, 6H, CH_3); ^{13}C NMR data cannot be obtained due to decomposition of the compound; IR (CO stretch, cm^{-1}): 2010 (m), 1884 (s); HRMS (ESI): m/z $[M]^+$ calcd for $C_{29}H_{26}Fe_2N_4O_3ReBr$: 855.9439 found 855.9236; UV-Vis spectrum in THF λ_{max} 454 nm ($\epsilon = 4.4 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$).

Spectroscopy—All UV-vis spectra were recorded using Hitachi U-2000 UV-vis spectrophotometer and JASCO-720 instruments. The UV-visible absorption maxima, extinction coefficients, and infrared carbonyl stretching vibrations are listed in Table 2.

Electrochemistry—Electrochemical measurements were conducted using a CHI- 620C electrochemical analyzer utilizing the three-electrode scheme. Unless stated otherwise, platinum working, platinum auxiliary, and Ag/ AgCl pseudo-reference electrodes were employed in a 0.1 M solution of TBAP in DMF for electrochemical experiments. In all cases, the redox potentials are referenced to the FcH/FcH^+ couple using decamethylferrocene as an internal standard.

Spectroelectrochemistry—Spectroelectrochemical data were collected on a JASCO-720 spectrophotometer at room temperature. The experiments were conducted using a CHI-620C electrochemical analyzer using a custom-made 1 mm cell with a platinum mesh-working electrode. In order to suppress overtones in the NIR region of the optical spectra, measurements were conducted in 0.3 M TBAP in DMF and in 0.05 M TFAB in DCM.

Computational—The starting geometries of all compounds were adopted from X-ray structures. All were optimized using the TPSSh exchange–correlation functional [34,35] coupled with the Wachter’s full-electron basis set [36] for the Fe atom and the 6–311G(d) basis set [37] for the remaining atoms. Energy minima in optimized geometries were confirmed by frequency calculations. DMF was used as a solvent in all of the single point

DFT-PCM and TDDFT-PCM calculations; solvent effects were calculation using the polarized continuum model (PCM) [38]. The first 50 states of each compound were calculated in all TDDFT-PCM calculations. All DFT calculations were conducted using the Gaussian 09 software package [39], For full citation, see Supporting Information, and the QMForge program [40] was used for the molecular orbital analysis.

3.0 Results and discussion

Previously, we have used hydrazine to synthesize dimeric compounds via Schiff base formation with aldehydes. For example, we have used hydrazine with pyridine-2-carboxaldehyde to afford dimeric $\text{Re}(\text{CO})_3$ compounds that exhibit strong coupling between the metal-diimine units [41]. In a separate system, we also used hydrazine to produce the precursor to the dimeric BF_2 chromophore BOPHY, where the hydrazine unit links two pyrrole-2-carboxyaldehyde units to form the boron-chelating ligand [42,43]. Although aldehydes work well making symmetric dimeric ligands with hydrazine, we have found that using this bridge to link different aldehydes does not result in the formation of asymmetric diimines; rather, mixtures of the symmetric products result from the reaction of hydrazine and different aldehydes. We hypothesized that using the differential reactivity of aldehydes and ketones towards hydrazine might be useful for producing asymmetric systems.

Acetyl ferrocene and diacetyl ferrocene both readily react with an excess of hydrazine to afford the corresponding hydrazone compounds, as shown in Scheme 1. The bis-hydrazone compound **3** has been previously synthesized [32,33]. Although we did not structurally elucidate either the mono or bis hydrazone modified ferrocenes, all of the spectroscopy on compound **1** is in good agreement with the proposed structures, and our characterization of compound **3** is in agreement with literature values. For both **1** and **3**, half of the hydrazine reacts to form Schiff bases with the ketones, leaving the remaining NH_2 group to form a second Schiff base which can coordinate to a $\text{Re}(\text{CO})_3$ center. Thus, we can readily generate a connection to a $\text{Re}(\text{CO})_3$ center using metal-mediated Schiff base formation, as shown in Figure 1. We and others have used this reaction to append a wide variety of molecules to the $\text{Re}(\text{CO})_3$, including aryl rings, fluorescent compounds, peptides and isomerizable groups like azobenzene [44]. These reactions can be carried out using one-pot conditions, and thus for the synthesis of conjugate systems is an attractive way to obtain a variety of structures.

All of the 1:1, 2:1, and 1:2 ferrocene: $\text{Re}(\text{CO})_3$ conjugate complexes have been fully characterized; we were able to structurally elucidate the 1:1 conjugates (compounds **4** and **5**), which are shown in Figure 2. For both **4** and **5**, there are two molecules per asymmetric unit. With regard to connectivity and overall bond length patterns, the structures of **4** and **5** are identical with the exception of the identity of the halide. The C-N bonds of the hydrazone unit have double bond character (1.289(9) and 1.285(9) Å for **4** and 1.258(17) and 1.253(18) Å for **5**). The N-N bonds, however, are single in character, with lengths of 1.402(8) and 1.434(8) Å for **4** and 1.422(15) and 1.374(17) Å for **5**. The ferrocene units and the Re-diimine planes are neither co-planar nor orthogonal; the complexes in the structures of **4** and **5** exhibit angles between these planes ranging from $\sim 71^\circ$ to $\sim 78^\circ$. The remaining 2:1 and 1:2 conjugates were not structurally elucidated, however NMR and mass spectrometric characterization was in complete agreement with the expected structures. We did obtain

crystals of **9**, but the quality was poor and we were not able to get a converged solution to the structure. However, a partial solution did provide confirmation of connectivity that is in agreement with the proposed structure; this partial structure can be found in Figure S38 in the supplemental information.

Since both ferrocene and $\text{Re}(\text{CO})_3$ complexes have been investigated for their uses as optical and electronic materials, we probed the electronic structures of the six new conjugates presented in this report using spectroscopy, electrochemistry, and theoretical methods. The UV-visible maxima and extinction coefficients are listed in Table 2, and the UV-visible spectra of the conjugate compounds are shown in Figure 3. All of the compounds presented in this report are colored, resulting from both ferrocene and $\text{Re}(\text{CO})_3$ diimine based transitions. For compounds **1** and **3**, ferrocene hydrazones exhibit low molar absorptivities in the range of hundreds. $\text{Re}(\text{CO})_3$ diimine complexes exhibit metal-to-ligand charge-transfer (MLCT) transitions that show much higher molar absorptivity (>5 times higher for **4** and **5**, and ~20 times higher for **6** and **7**). The molar absorptivities of **4** and **5** were comparable to those observed in mono-rhenium tricarbonyl Schiff's base compounds with absorptivities around $3,000\text{--}4,000\text{ M}^{-1}\text{cm}^{-1}$ [44,45]. Complexes (**6** and **7**) show stronger absorptivities in the range of $7,000\text{--}8,000\text{ M}^{-1}\text{cm}^{-1}$, about twice as much as those of monomeric $\text{Re}(\text{CO})_3$ Schiff's base complexes, which is consistent with their dimeric structures [41,46]. All of the transitions occur between 400 and 500 nm, which is typical for this class of compounds. Compounds **7** and **8** exhibit a significant amount of bathochromic shifting; we observed similar trends in other dimeric $\text{Re}(\text{CO})_3$ complexes [41,46]. All of the conjugates display diagnostic CO stretching frequencies in their IR spectra; these correspond to the a_1 and e type modes that result from the facial $\text{Re}(\text{CO})_3$ unit.

The electrochemistry of both ferrocene and $\text{Re}(\text{CO})_3$ diimine complexes have been extensively investigated; the two metal complexes can exhibit reversible oxidations and reductions respectively. In conjugates with either two ferrocenes or two $\text{Re}(\text{CO})_3$ diimine centers, we have previously observed coupling and the formation of mixed valence behavior [41,46]. We probed the precursor molecules **1** and **3** as well as the 1:1 conjugate compounds **4** and **5** using cyclic voltammetry. Both ferrocenes and the chloride analog data **4** are shown in Figure 4. The voltammograms for the bromide analog are found in the supplementary information. Unlike unmodified ferrocene, these substituted variants do not show reversible oxidations, clearly due to the oxidative reactivity of the hydrazone functional groups. The 1:1 complexes **4** and **5** show slightly more reversible oxidations of the ferrocenes, as well as exhibit quasi-reversible reduction waves attributable to the $\text{Re}(\text{CO})_3$ diimine units. In these complexes, reduction of the $\text{Re}(\text{CO})_3$ diimine unit is a ligand based processes; we have reported this phenomenon previously and this conclusion is supported by our DFT-PCM calculations.

For the conjugates with either two ferrocenes or two rhenium centers, we were interested in possibly observing coupling between the peripheral units on these compounds. The cyclic voltammograms of the 1:2 ferrocene:rhenium compound **6** as well as the 2:1 ferrocene:rhenium compound **8** are also shown in Figure 4. The bromide analog voltammograms can be found in the supplementary information. Compounds **6** and **7** with 1:2 ferrocene:rhenium ratio exhibit irreversible oxidation waves, and quasi-reversible

reduction processes. Unlike our previously reported $\text{Re}(\text{CO})_3$ dimer compounds, we do not observe any separation of the reduction wave into two peaks, and thus do not identify any electronic coupling across the ferrocene unit. In compounds **8** and **9**, with 2:1 ferrocene:rhenium ratio we observe the opposite trend from **6** and **7**: quasi reversible oxidations of ferrocene fragments and irreversible reductions of the Schiff-based ligand. In these cases as well, we do not observe any evidence for electronic coupling between the ferrocene units in the cyclic voltammetry experiments.

In addition to using cyclic voltammetric behavior, the presence of a mixed valence system also can be detected via the presence of intervalence charge transfer bands upon either one electron oxidation or reduction. Previously, we have used this approach to confirm the presence of mixed-valence systems in both ferrocene and $\text{Re}(\text{CO})_3$ systems [41,46]. Figure 5 shows the oxidative and reductive spectroelectrochemistry of compound **4** and **5**, with the 1:1 ferrocene:rhenium ratio. We observe, upon oxidation, the formation of a new band at ~580 nm, which corresponds to the expected charge transfer transition seen for the ferricenium cation. Unfortunately, compounds **6–9** are unstable in solution during the time course of the spectroelectrochemistry experiment, so we were not able to observe any intervalence charge transfer bands.

We also probed the electronic structures of all target compounds using DFT methods. The energy levels of the frontier orbitals for compounds **4–9** are shown in Figure 6. Graphs of molecular composition and a diagram showing the energy levels of the frontier orbitals of **1** and **3** compared to the other compounds presented in this report can be found in the supplementary information. The structures of the HOMOs and LUMOs for ferrocenes **1** and **3** and conjugates **4–9** can be seen in Figure 7. For compounds **1** and **3**, we observe that the HOMO orbital is primarily composed of iron and cyclopentadienyl orbital contributions, while the LUMO has a significant contribution from the hydrazone orbitals. Compound **3**, with two hydrazone functional groups, has approximately twice as much of this contribution to the LUMO. With regard to the conjugate complexes, they exhibit similar patterns in their frontier orbital energies. For the 1:1 conjugates **4** and **5**, the HOMO and HOMO-1 are ferrocene based, and the LUMO is localized on the ligand. The same trends are also observed for the conjugate compounds **6–9**. The rhenium d-orbital contributions are lower in energy than the occupied ferrocene frontier orbitals, starting at HOMO-3 for compounds **4–7**, and HOMO-5 for **8** and **9**. For all of the conjugate complexes, replacement of chloride with bromide results in slight destabilization of the frontier orbitals.

We also used TDDFT-PCM method to predict the optical spectra of the compounds presented in this report, as can be seen in Figure 8. We observe good agreement between calculated and observed spectra for the ferrocene compounds **1** and **3**. For the conjugates **4–9** (the chloride analogs are shown in the figure) we see a red shift to our calculated spectra versus the observed. The UV-visible transitions between 400 and 460 in these conjugates can be characterized as MLCT bands (metal d-orbital to diamine ligand). For the bis-rhenium conjugate systems, we observe a red shifting and expansion of the primary visible absorption band to lower wavelengths; this may result from long range coupling interactions between the rhenium centers, and we have observed this phenomenon previously.

4.0 Conclusions

In conclusion, hydrazine can be used a linking reagent to connect the two well studied organometallic fragments ferrocene and $\text{Re}(\text{CO})_3$. A modular approach to producing conjugates was developed, resulting in 1:1 as well as 2:1 and 1:2 ferrocene: $\text{Re}(\text{CO})_3$. By first reacting hydrazine with acyl ferrocenes, we can produce hydrazones that can be subsequently used in $\text{Re}(\text{CO})_3$ mediated Schiff base formation reactions. The resultant conjugates have been fully characterized, but the 1:2 and 2:1 complexes exhibit stability problems in solution. We investigated their electrochemistry and spectroscopy of the compounds presented in this report; we do not observe fully reversible oxidations or reductions in these conjugates, most likely due to the redox sensitivity of the Schiff base bridge. Finally, DFT and TDDFT calculations provided insight into the electronic structures of the ferrocene precursor compounds as well as the conjugate systems. We are continuing our investigations into the covalent coupling of organometallic moieties to both biologically relevant compounds as well as chromophore systems.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

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Research highlights

- A series of ferrocene-Re(CO)₃ conjugates was synthesized and characterized.
- Compounds with various ferrocene: Re(CO)₃ ratios were made via a modular approach.
- The spectroscopic, redox, and spectroelectrochemical behaviors were studied.
- The electronic structures were also probed using DFT and TDDFT calculations.

Fig. 1.
Structures of compounds 1-9.

Fig. 2. Crystal structures of compounds **4** and **5** with 35% thermal ellipsoids. Hydrogen atoms have been omitted for clarity. Crystal data and structure refinement parameters can be found in Table 1. Selected bond lengths and angles are reported in Table S17 (supplementary information).

Fig. 3.
UV-visible spectra of compounds **4-9** in THF.

Fig. 4.
Cyclic voltammograms of compounds **1**, **3**, **4**, **6**, and **8**.

Fig. 5. Spectroelectrochemistry of compounds **4** (top) and **5** (bottom) upon oxidation (left) and reduction (right).

Fig. 6.
DFT predicted energy diagram of rhenium complexes **4–9**. HOMOs and LUMOs are connected by a dotted line.

Fig. 7.
The DFT-PCM predicted isosurfaces of the HOMOs and LUMOs for ferrocene compounds **1** and **3** and conjugates **4–9**.

Fig. 8.
Experimental and TDDFT predicted UV-visible spectra for compounds **1**, **3**, **4**, **6** and **8**.

Scheme 1.
Syntheses of new compounds reported in this paper.

Table 1

Crystal data and structure refinement parameters.

Compound	4	5
Emp. form	C ₂₁ H ₁₇ ClFeN ₃ O ₃ Re	C ₂₁ H ₁₇ BrFeN ₃ O ₃ Re
Form. weight	636.88	681.34
Crystal system	Triclinic	Triclinic
Space group	P-1	P-1
a/ Å	11.5372(9)	11.5739(9)
b/ Å	13.4291(10)	13.3692(10)
c/ Å	14.4988(11)	14.7085(11)
α(°)	85.604(3)	84.731(5)
β(°)	88.865(3)	88.560(5)
γ(°)	67.679(3)	68.617(4)
Volume (Å ³)	2071.8(3)	2110.2(3)
Z	4	4
D _c (Mg/m ³)	2.042	2.145
μ (mm ⁻¹)	6.695	19.018
F(000)	1224	1296
Reflections collected	8377	6728
Data/Restraints/Parameters	8377 / 7 / 489	6728 / 66 / 534
GOF on F ²	1.100	1.002
R1 (on F _o ² , I > 2σ(I))	0.0530	0.0783
wR2 (on F _o ² , I > 2σ(I))	0.1447	0.2495
R1 (all data)	0.0654	0.0955
wR2 (all data)	0.1544	0.2615

Table 2

UV-visible absorption and FTIR data for all compounds.

Compound	λ_{max} (nm)	ϵ ($\times 10^3 \text{ M}^{-1}\text{cm}^{-1}$)	$\nu \text{ C}\equiv\text{O}$ (cm^{-1})
1	436	0.67	n/a
3	449	0.44	n/a
4	417	4.3	2016 (m) 1916 (s) 1883 (s)
5	424	3.6	2017 (m) 1918 (s) 1885 (s)
6 *	410	7.9	2020 (s) 1909 (m) 1870 (s)
7 *	418	8.2	2021 (s) 1909 (m) 1876 (s)
8	446	4.3	2018 (m) 1888 (s)
9	454	4.4	2010 (m) 1884 (s)

* For UV-vis experiments, a few drops of triethylamine (NEt₃) were added to this solution prior to the experiment to prevent oxidation.