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Using hydrazine to link ferrocene with $Re(CO)_3$: 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 $Re(CO)_3$ via a metal-mediated Schiff base reaction, resulting in a series of ferrocene-$Re(CO)_3$ conjugates with different stoichiometries. Conjugates with 1:1, 1:2, and 2:1 ferrocene: $Re(CO)_3$ 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.

1. 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 $Re(CO)_3$ 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 $Re(CO)_3$ compounds can be readily incorporated into molecules for potential materials applications. In work from our laboratories, we have functionalized proteins and peptides with the $Re(CO)_3$ 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-$Re(CO)_3$ conjugate compounds synthesized via a modular approach. These compounds are shown in Fig. 1. In all cases, we can use hydrazine-derived Schiff base formation to produce 1:1 Fc:$Re(CO)_3$ adducts as well as 2:1 and 1:2 Fc:$Re(CO)_3$ 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 $Re(CO)_3$ 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. Experimental

2.1. Materials and methods

All reagents were purchased from Strem, Acros Organics, TCI

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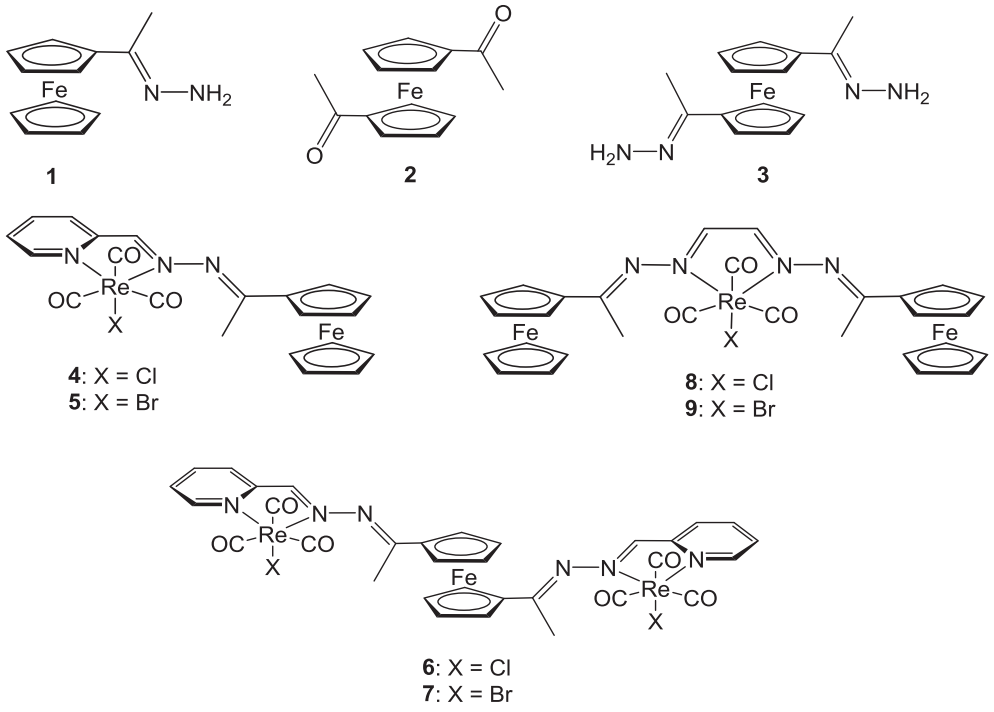

Fig. 1. Structures of compounds **1**–**9**.

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 (^{1}H: $CDCl_3$, $\delta = 7.26$ 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 Kα radiation, $\lambda = 0.71073$ Å) 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 Kα radiation, $\lambda = 1.54178$ Å). 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 multi-scan 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%). ^{1}H 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* $[M+H]^+$ calcd for $C_{12}H_{14}FeN$: 243.0579, found 243.0724; UV–Vis spectrum in THF λ_{max} 436 nm ($\varepsilon = 6.7 \times 10^2$ M^{-1} 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 h. The resultant orange precipitate was filtered and air-dried. Yield 0.2 g (18%). ^{1}H 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* $[M+H]^+$ calcd for calc. for $C_{14}H_{18}FeN_4$: 299.0954, found 299.1123; UV–Vis spectrum in THF λ_{max} 449 nm ($\varepsilon = 4.4 \times 10^2$ M^{-1} cm^{-1}).

2.3.1. Synthesis of $Re(CO)_3$-pyca-ferrocene complexes

Synthesis of 4 and 5. The procedure for **4** is representative of both compounds. **4**: $Re(CO)_5Cl$ (50 mg, 0.14 mmol) and pyridine-2-carboxaldehyde (15 μL, 0.14 mmol) were refluxed in 15 mL of toluene for 30 min. 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%