

New emissive *fac*-tricarbonylchlorobis(ligand)rhenium(I) complexes prepared from pyridine/thiophene hybrid ligands [☆]

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Abstract

Stille coupling between tributyl-(2,3-dihydro-thieno[3,4-b][1,4]dioxin-5-yl)-stannane and 4-bromopyridine resulted in the preparation of the new pyridine/thiophene hybrid ligand 4-(2,3-dihydro-thieno[3,4-b][1,4]dioxin-5-yl)-pyridine [4-py-EDOT] (**1**). Reaction of **1**, 4-thiophen-2-yl-pyridine (**2**), or 4-[2,2']bithiophenyl-5-yl-pyridine (**3**) with ClRe(CO)₅ resulted in the isolation of complexes **4–6**, ClRe(L)₂(CO)₃, where L = **1**, **2**, or **3** respectively. The solid-state structure of **4** was determined by X-ray crystallography, which clearly shows the *fac* arrangement of the three CO ligands and the two 4-py-EDOT ligands arranged *cis* to one another. The metal complexes **4–6** have been characterized by ¹H and ¹³C NMR, ESI or FAB MS, FTIR, UV–Vis, fluorescence, and elemental analysis.

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1. Introduction

fac-Tricarbonylchlorobis(ligand)rhenium(I) complexes have long been studied because they are emissive in solutions [1,2]. More recently, researchers have taken advantage of the fact that the non-carbonyl, non-chloride ligands in these rhenium complexes are *cis* (and therefore separated by 90°) to prepare a variety of organometallic macrocycles [3–5]. Thiophene and its derivatives are of current interest due to their potential uses in molecular electronics including nonlinear optics, energy storage, electrochromic devices and electrochemical sensors [6]. An array of thiophene/pyridine hybrid compounds have been prepared [7–15] for uses as optical switches [8], non-linear optics [9], fluorophores [12], and several have been bound to metals such as

copper [14], rhenium [8], ruthenium [11], and tungsten [8]. One derivative of thiophene that is of particular interest is 3,4-ethylenedioxythiophene (EDOT), which exhibits increased solubility and lower oxidation potentials than thiophene. Additionally, by blocking the β positions of the thiophene ring, a higher regiochemically defined polymer can be obtained with EDOT because α–β linkages are prevented [16–18]. We report herein the preparation and characterization of a new EDOT-pyridine hybrid ligand (**1**, Chart 1) along with preparation of a series of *fac*-tricarbonylchlorobis(ligand)rhenium(I)

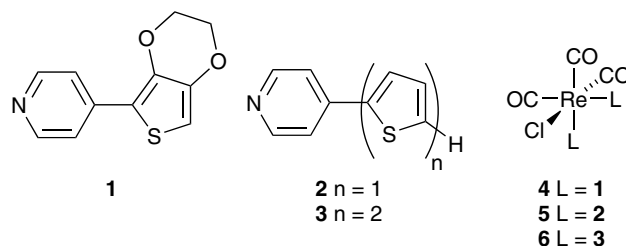


Chart 1. Compounds **1–6**.

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complexes where the ligands are different pyridine–thiophene derivative hybrids. All of these compounds could be used in the future as starting materials to incorporate fluorescent metal centers into conducting polymers.

2. Experimental

2.1. Materials and general procedures

Compounds tributyl-(2,3-dihydro-thieno[3,4-b][1,4]-dioxin-5-yl)-stannane [19], 4-thiophen-2-yl-pyridine [10], 4-[2,2']bithiophenyl-5-yl-pyridine [10], and 4-bromopyridine [9] were prepared using procedures reported in the literature. All other compounds were purchased from commercial sources and used as received. Air sensitive compounds were either handled using standard Schlenk techniques or in a MBraun glovebox under nitrogen. Solvents used were dried and purified using standard methods [20]. NMR spectra were recorded on an Oxford AS400 spectrometer and referenced to residual peaks in the deuterated solvents. MS data were collected either on a Bruker Daltonics-LC Ion trap mass spectrometer (ESI) or a JEOL MStation JMS 700 (FAB) both located at the UMass Amherst Mass Spectrometry Center. GCMS data were collected on a Hewlett Packard 6890 series GC System interfaced with the HP 5973 Mass Selective Detector. IR data were collected on a Nicolet Series II Magna-IR 750 Spectrometer. UV–Vis data were collected on a Hewlett Packard 8452A Diode Array Spectrophotometer. Fluorescence data were collected on a Jobin Yvon Fluorolog-3 (FL3-22) instrument equipped with a 450 W Xenon lamp as the source. Data were processed with the DataMax for Windows software program. Degassed THF (Fisher OPTIMA grade with no inhibitors) solutions of **1** and **4–6** were made so that they absorbed 0.10 AU at their respective λ_{\max} values. The samples were then excited at their λ_{\max} values and emission maxima recorded.

2.2. X-ray crystallography

Crystallographic data for **4**·CH₂Cl₂: C₂₆H₂₀Cl₃–N₂O₇ReS₂, $M = 829.21$, orthorhombic, $a = 21.973(4)$ Å, $b = 7.3397(13)$ Å, $c = 18.403(3)$ Å, $V = 2968.0(9)$ Å³, $T = 100(2)$ K, space group $Pna2(1)$ (No. 33), $Z = 4$, μ (Mo K α) = 4.368 mm⁻¹, 22,632 reflections measured, 7021 independent reflections ($R_{\text{int}} = 0.0450$), Final R_1 [$I > 2\sigma(I)$] = 0.0624, $wR_2 = 0.1531$. X-ray intensity data were measured at 100 K (Bruker KRYO-FLEX) on a Bruker SMART APEX CCD-based X-ray diffractometer system equipped with a Mo-target X-ray tube ($\lambda = 0.71073$ Å) operated at 2000 watts power. The crystal was mounted on a cryoloop using Paratone N-Exxon oil and placed under a stream of nitrogen. The detector was

placed at a distance of 5.009 cm from the crystal. Analysis of the data set showed negligible decay during data collection. The data were corrected for absorption using the SADABS program. The structure was refined using the Bruker SHELXTL Software Package (Version 6.1), and was solved using direct methods until the final anisotropic full-matrix, least squares refinement of F^2 converged [21]. The solvent disorder (one dichloromethane per asymmetric unit) was refined as a diffuse contribution without specific atom positions using the SQUEEZE program, but the density, absorption coefficient and other parameters reflect the full formula. The chloride and its *trans* carbonyl were disordered in the structure, and both components of the disorder were refined using 50% occupancy for each part. The carbon of the disordered carbonyl was refined isotropically in a fashion similar to that presented by Bélanger et al. [22] on the structurally analogous compound Re(py)₂(CO)₄Cl.

2.3. Synthesis of 4-(2,3-dihydro-thieno[3,4-b][1,4]dioxin-5-yl)-pyridine [4-py-EDOT] (**1**)

In a 200 mL Schlenk flask equipped with a condenser and magnetic stir bar, PdCl₂(PPh₃)₂ (0.361 g, 0.515 mmol), 4-bromopyridine (1.63 g, 10.3 mmol), and tributyl-(2,3-dihydro-thieno[3,4-b][1,4]dioxin-5-yl)-stannane (4.70 g, 12.1 mmol) were combined with 100 mL of DMF. The reaction mixture was heated to 85 °C for 18 h. The solvent was removed in vacuo and the resulting black oil was purified by column chromatography (silica gel) using 1.5 L of pentane to wash away the tin byproducts, and then 2% MeOH in CHCl₃. Four bands were collected, the first and fourth are unidentified, the second was a mixture of EDOT and bi-EDOT, and the third band was product. After recrystallization from CH₂Cl₂/hexanes, 0.792 g of analytically pure product was obtained, yield = 35%. ¹H NMR (CDCl₃) δ 8.54–8.55 (m, 2H, PyH α); 7.59–7.60 (m, 2H, PyH β); 6.45 (s, 1H, CH); 4.36–4.38 (m, 2H, CH₂); 4.27–4.29 (m, 2H, CH₂). ¹³C NMR (CDCl₃) δ 150.2, 142.6, 141.2, 140.6, 119.8, 114.7, 100.7, 65.2, 64.6. MS (EI) m/z 219 (calculated m/z 219 for M⁻). Anal. Calc. for C₁₁H₉NO₂S: C, 60.26; H, 4.14; N, 6.39. Found: C, 60.18; H, 4.34; N, 6.74%. Melting point: 129.7–130.4 °C.

2.4. General procedure for synthesis of rhenium complexes, [ClRe(CO)₃(L)₂] (**4–6**)

To a 200 mL Schlenk flask equipped with a condenser and magnetic stir bar, ClRe(CO)₅ (0.100 g, 0.276 mmol), ligand (two equivalents, 0.552 mmol) and 100 mL of 1:1 THF:toluene were combined. The reaction was heated to 70 °C for 4 h. The solvent was removed by rotary evaporation and the reaction mixture was redissolved in 5 mL of 1:1 THF:toluene. The product was filtered,

washed with 5 mL of hexanes. A second portion of product was collected repeating this procedure using 1 mL of THF:toluene. A final portion of product could be reclaimed through recrystallization of the remaining reaction mixture from CH₂Cl₂:ether. After drying the precipitates in vacuo the resulting mixture was analytically pure and yields were as high as 96%.

2.4.1. [ClRe(CO)₃(4-py-EDOT)₂] (**4**)

IR (CDCl₃, ν_{CO} , cm⁻¹) 2026, 1923, 1885. ¹H NMR (CDCl₃) δ 8.62–8.63 (m, 2H, PyH α); 7.57–7.59 (m, 2H, PyH β); 6.55 (s, 1H, CH); 4.37–4.39 (m, 2H, CH₂); 4.27–4.29 (m, 2H, CH₂). ¹³C NMR (CDCl₃) δ 195.9, 153.4, 143.0, 142.8, 142.8, 120.9, 113.1, 103.2, 65.4, 64.4. MS (ESI) m/z 709.0 (calculated m/z 709.0 for M–Cl⁻). Anal. Calc. for C₂₅H₁₈ClN₂O₇S₂Re: C, 40.35; H, 2.44; N, 3.76. Found: C, 40.10; H, 2.51; N, 3.73%.

2.4.2. [ClRe(CO)₃(4-py-thiophene)₂] (**5**)

IR (CDCl₃, ν_{CO} , cm⁻¹) 2028, 1927, 1889. ¹H NMR (CDCl₃) δ 8.72–8.74 (m, 2H, PyH α); 7.59 (dd, 1H, $J = 1.2, 4.8$ Hz, BithiH β_1); 7.53 (dd, 1H, $J = 1.2, 6.0$ Hz, BithiH α); 7.49–7.50 (m, 2H, PyH β); 7.17–7.20 (m, 1H, BithiH β_2). ¹³C NMR (CDCl₃) δ 195.7, 153.9, 143.8, 139.2, 129.9, 129.3, 127.6, 121.4. MS (ESI) m/z 593.0 (calculated m/z 593.0 for M–Cl⁻). Anal. Calc. for C₂₅H₁₈ClN₂O₇S₂Re: C, 40.16; H, 2.25; N, 4.46. Found: C, 40.28; H, 2.52; N, 4.42%.

2.4.3. [ClRe(CO)₃(4-py-bithiophene)₂] (**6**)

IR (CDCl₃, ν_{CO} , cm⁻¹) 2027, 1927, 1888. ¹H NMR (Acetone-d₆) δ 8.76–8.78 (m, 2H, PyH α); 7.86 (d, 1H, $J = 4.0$ Hz, BithiH β_1); 7.77–7.79 (m, 2H, PyH β); 7.53 (dd, 1H, $J = 1.2, 5.2$ Hz, BithiH α); 7.43 (dd, 1H, $J = 1.2, 4.2$ Hz, BithiH β_3); 7.40 (d, 1H, $J = 4.0$ Hz, BithiH β_2); 7.12 (dd, 1H, $J = 3.8, 5.2$ Hz, BithiH β_4). ¹³C NMR (Acetone-d₆) δ 154.9, 144.2, 142.2, 138.2, 136.9, 130.4, 129.4, 127.4, 126.4, 126.2, 121.8. The solubility of this compound in organic solvent was too low to pick out the peaks for the CO attached to the Re. MS (FAB) m/z 756.66 (calculated m/z 756.98 for M–Cl⁻). Anal. Calc. for C₂₉H₁₈ClN₂O₃S₄Re: C, 43.96; H, 2.29; N, 3.54. Found: C, 43.90; H, 2.25; N, 3.44%.

3. Results and discussion

The new compound 4-(2,3-dihydro-thieno[3,4-b][1,4]-dioxin-5-yl)-pyridine (4-py-EDOT, **1**) was prepared via a Stille coupling between 4-bromopyridine [9] and tributyl-(2,3-dihydro-thieno[3,4-b][1,4]dioxin-5-yl)-stannane [19] in DMF. Compound **1** has been fully characterized by ¹H and ¹³C NMR, EIMS, mp, and elemental analysis and all data are consistent with its formulation. The previously known compounds 4-thiophen-2-yl-pyridine (4-py-thiophene, **2**), [10] and 4-[2,2']bithiophenyl-5-

yl-pyridine (4-py-bithiophene, **3**) [10] (Chart 1) were prepared using the same methodology.

The new *fac*-tricarbonylchlorobis(ligand)rhenium(I) complexes **4–6** where the ligands are **1**, **2**, and **3**, respectively (Chart 1) were prepared by combining two equivalents of the appropriate ligand with one equivalent of ClRe(CO)₃ in a 1:1 mixture of THF:toluene and heating to 70 °C for 4 h. The solvent was then removed from the reaction mixture by rotary evaporation, 1–5 mL of 1:1 THF:toluene was added to the crude reaction mixture. Filtration followed by a hexane wash (5 mL) yielded analytically pure product in >90% yield.

Compounds **4–6** have been completely characterized by ¹H and ¹³C NMR, ESI or FAB MS, FTIR, UV–Vis, elemental analysis, and, in the case of **4**, a single crystal X-ray diffraction study. All data are consistent with their formulation. FTIR for all three compounds shows a characteristic three band spectrum for the carbonyl region indicative of the *fac*-tricarbonyl geometry (Table 1) [2]. The positions of the IR bands in the carbonyl region are similar to the previously characterized complexes **7** and **8** where the nitrogen ligands on the rhenium(I) center are pyridine and 4-phenylpyridine, respectively [2].

The UV–Vis spectra of compound **1** in THF exhibits a λ_{max} of 302 nm ($\epsilon = 1.97 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$). This band is lower in energy than that of **2** ($\lambda_{\text{max}} = 295 \text{ nm}$, $\epsilon = 1.60 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$), but higher in energy than that of **3** ($\lambda_{\text{max}} = 381 \text{ nm}$, $\epsilon = 3.95 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$) measured in 40% aq. MeOH [12]. Re complex **4**, which contains two equivalents of **1**, has two bands in its UV–Vis spectra with maxima at 338 and 242 nm, respectively (Table 2). The lower energy band has previously been ascribed to a Re → L CT band and the higher energy

Table 1
IR absorption maxima for ClRe(CO)₃(L)₂ in CO stretching region

Compound	L	Bands (cm ⁻¹)		
4 ^a	1	2026	1923	1885
5 ^a	2	2028	1927	1889
6 ^a	3	2027	1927	1888
7 ^b	Pyridine	2027	1922	1886
8 ^b	4-Phenylpyridine	2025	1922	1888

^a CDCl₃ solution.

^b CH₂Cl₂ solution [2].

Table 2
Electronic absorption maxima for ClRe(CO)₃(L)₂ complexes

Compound	L	Bands, nm ($\epsilon, \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$)
4 ^a	1	338 (4.63), 242 (0.83)
5 ^a	2	326 (3.16), 272 (1.37)
6 ^a	3	380 (5.51), 262 (2.1)
7 ^b	Pyridine	292 (0.68), 262 (0.87)
8 ^b	4-Phenylpyridine	303 (2.26), 268 (3.65)

^a THF solution.

^b CH₂Cl₂ solution [2].

band is associated with an intraligand $\pi-\pi^*$ transition [2]. Comparing the CT transitions between **4** and **6** one can see that addition of the electron donating ethylenedioxy-unit to the thiophene portion of the ligand results in a lower energy band. A similar result occurs when the monothiophene ligand in complex **5** is changed to a bithiophene unit in complex **6**. The new ligand **1** and the three metal compounds **4–6** are all emissive in solution. Degassed THF solutions of **1** and **4–6** were prepared so that they absorb 0.10 AU at their λ_{\max} values. Excitation at the λ_{\max} of each compound results in excitation maxima at 368 nm for **1** and 378 nm, 398 nm, and 428 nm for **4–6**, respectively. In addition compounds **4–6** all exhibited broad luminescent peaks centered at 530, 549, and 533 nm, respectively.

X-ray quality crystals of **4**·CH₂Cl₂ were grown by vapor diffusion of pentane into a CH₂Cl₂ solution of **4** and a 0.40 × 0.20 × 0.03 yellow block was subjected to a single crystal X-ray diffraction study. An ORTEP diagram of **4**·CH₂Cl₂ is pictured in Fig. 1 and selected bond distances and angles are presented in Table 3. The

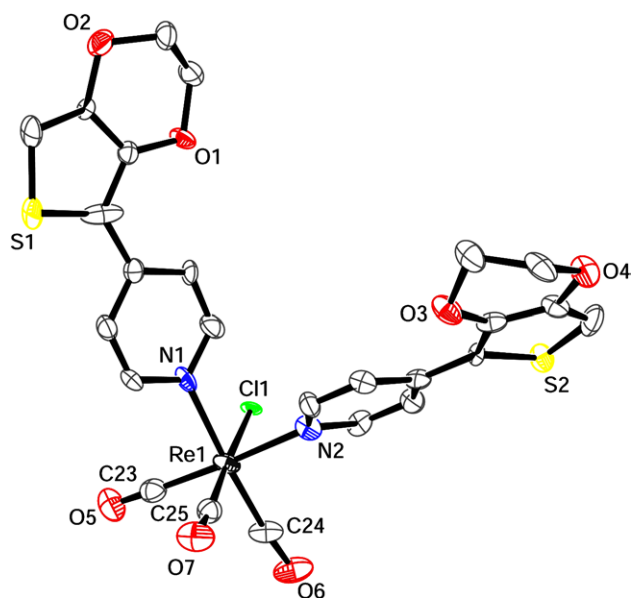


Fig. 1. ORTEP drawing of **4**·CH₂Cl₂ with solvent and hydrogen atoms omitted for clarity. See paper for discussion of CO/Cl disorder.

Table 3
Selected bond distances (Å) and angles (°) for **4**·CH₂Cl₂

C(23)–O(5)	1.137(16)	N(1)–Re(1)	2.220(10)
C(23)–Re(1)	1.931(14)	N(2)–Re(1)	2.199(10)
C(24)–O(6)	1.190(15)		
C(24)–Re(1)	1.914(12)	N(2)–Re(1)–N(1)	83.0(3)
Cl(1)–Re(1)	2.505(5)	N(2)–Re(1)–Cl(2)	87.9(3)
O(7)–C(25)	1.180(9)	N(1)–Re(1)–Cl(2)	87.1(3)
C(25)–Re(1)	1.900(9)	N(2)–Re(1)–Cl(1)	89.1(3)
Cl(2)–Re(1)	2.491(7)	N(1)–Re(1)–Cl(1)	87.8(3)
O(8)–C(26)	1.177(9)	Cl(2)–Re(1)–Cl(1)	174.3(2)
C(26)–Re(1)	1.937(9)		

solid state structure of **4**·CH₂Cl₂ possesses a slightly distorted octahedral geometry about the Re(I) metal center. The *fac* arrangement of the three carbonyl ligands and the *cis* arrangement of the two 4-Py-EDOT ligands are clearly shown in Fig. 1. The metal-ligand bond lengths and angles are generally similar to other known *fac*-tricarbonylchlorobis(ligand)rhenium(I) complexes [22]. The N(1)–Re(1)–N(2) angle for **4** is slightly compressed compared to **7** [17] (83.0(3)° versus 84.8(2)°). Axial disorder between the chloride and the carbonyl ligands *trans* to the chloride, a common problem with this family of complexes, complicated the refinement [22]. The disordered ligands were split into two parts (C11/Cl2 and C25/C26) and assigned occupancy factors of 0.5. All non-H atoms were then refined anisotropically except for the C atoms of the disordered carbonyls (see Supplementary Information).

4. Conclusion

In conclusion we have prepared the new ligand **1**, a pyridine/EDOT hybrid which could be used to incorporate metal centers into polythiophene conducting polymers. Compound **1** is emissive in solution and maintains that emission upon binding to Re(I). A family of *fac*-tricarbonylchlorobis(ligand)rhenium(I) complexes, where the ligands are pyridine/thiophene hybrid ligands, have been prepared and characterized. Current work is aimed at incorporating these metal complexes into polythiophene polymers and organometallic macrocycles.

5. Supporting information available

Crystallographic data for **4** has been deposited with the Cambridge Crystallographic Data Center as supplemental publication number CCDC 219742. Copies of the data can be obtained, free of charge, on application to The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: 44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>).

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