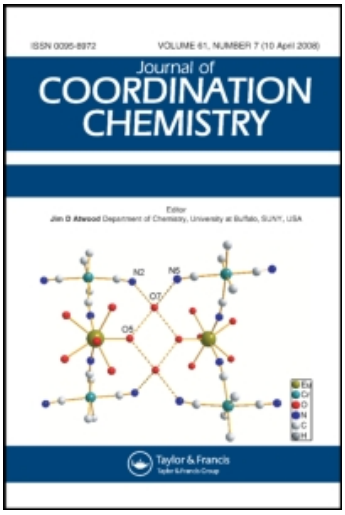

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Synthesis of chiral salen Mn(III) complexes covalently linked to Re(I)-based photosensitizers

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Synthesis of chiral salen Mn(III) complexes covalently linked to Re(I)-based photosensitizers

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Two Mn(III)Re(I) binuclear complexes were prepared as catalyst-photosensitizer models, in which the chiral pyrrolidine salen Mn(III) unit was covalently bonded to an Re(I) bipyridyl carbonyl moiety via a carboxamide linkage. The spectral and electrochemical properties of the Mn(III)Re(I) complexes were studied.

Keywords: Manganese complex; Rhenium complex; Heterobinuclear complex; Chiral salen ligand; Pyrrolidine; Light-driven catalyst

1. Introduction

In recent years, a variety of bi- or trinuclear organometallic electron donor- and acceptor-photosensitizer (D-S and A-S) arrays have been prepared [1] for potential application in photoelectric molecular devices [2], catalysts [3] and biomimetic chemistry [4]. Only a few were reported as photoactive catalysts for light-driven redox reactions [5]. Our interest is the preparation of catalyst-photosensitizer (C-S) binuclear complexes as catalyst candidates for photoinduced asymmetric oxidation of organic substrates. The advantages of C-S binuclear complexes over mononuclear photocatalysts are: (1) the central metal and the ligands of both parts, catalyst and photosensitizer, can be optimized independently in terms of the individual reaction, and (2) the lifetime of the excited state of the photosensitizer and the rate of intramolecular electron transfer can be tuned by adjusting the length and the structure of the binding chain between catalyst and photosensitizer moieties to improve quantum yields of light-driven catalytic reactions.

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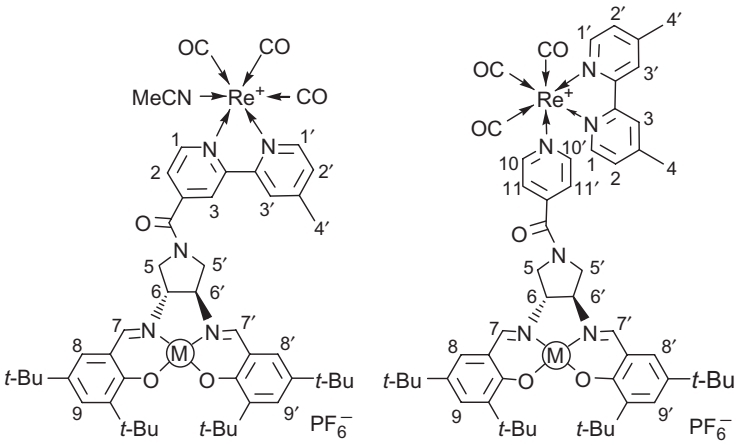
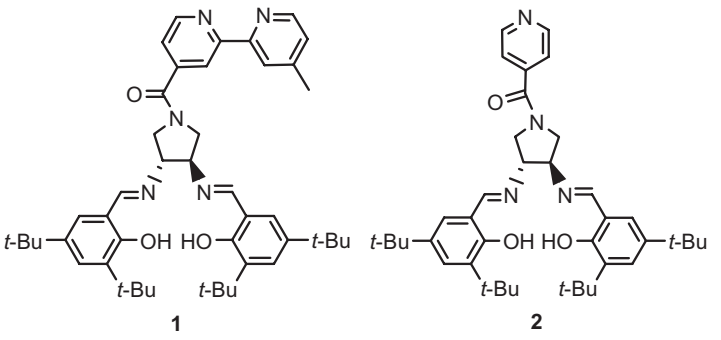


Chart 1.

A strategy for construction of stereoselective photocatalysts is to covalently link a photosensitizer, with absorption in the desired range, to a chiral catalyst precursor. For our target reactions, photoinduced asymmetric epoxidation and oxidation, the best candidates for catalyst precursors are chiral salen transition metal complexes, especially Mn(III) salen complexes. The proper photosensitizers are multi-pyridyl complexes of d^6 transition metal ions, such as Ru(II), Re(I) and Os(II), in light of their favorable photochemical and synthetic properties. Here we report the preparation, characterization and electrochemical properties of covalently linked Mn(III)Re(I) heterobinuclear complexes **3b** and **4b** (see chart 1), where the catalyst is a Mn(III) unit with a chiral pyrrolidine salen ligand and the photosensitizer is a Re(I) bipyridyl (bpy) carbonyl fragment. The two moieties are connected by a carboxamide linkage between the secondary amine of the chiral pyrrolidine salen ligand and the carbonyl group on a pyridyl or a 2,2′-bipyridyl ligand.

2. Results and discussion

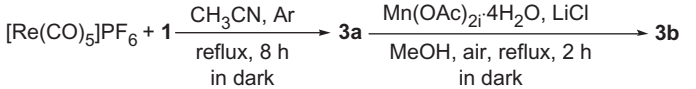
The chiral pyrrolidine salen ligands **1** and **2** with potentially binuclear-binding sites (see chart 2) were prepared readily by the reaction of a pyridyl- or a 2,2′-bipyridyl acyl chloride and (3*R*,4*R*)-*N*,*N*′-bis(3,5-di-*tert*-butylsalicylidene)-3,4-diaminopyrrolidine, which was synthesized according to literature procedures [6]. Complex **3a** was prepared by the reaction of ligand **1** and pentacarbonylrhenium hexafluorophosphate in CH_3CN in low yield (26%, equation (1)). The reaction of (4,4′-dimethyl-2,2′-bipyridine)tricarbonylrhenium chloride and ligand **2** in EtOH afforded a good yield (62%) of pyridine-coordinated Re(I) complex **4a** (equation (2)). The corresponding Mn(III)Re(I) binuclear complexes **3b** and **4b** were obtained by treatment of **3a** and **4a** with $Mn(OAc)_2 \cdot 4H_2O$, respectively, followed by addition of methanol solution of LiCl, similar to the previously reported protocol for



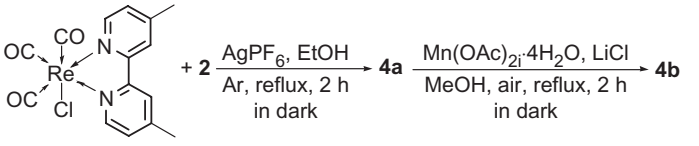
1 **2**

Chart 2.

preparation of mononuclear Mn(III) salen complexes [7]. All reactions for preparation of **3a**, **3b**, and **4a**, **4b** were made in the dark to avoid decomposition of rhenium carbonyl complexes.



(1)



(2)

Complexes **3a** and **4a** were characterized by HRMS, IR, UV-Vis and ^{1}H and ^{13}C NMR spectra, and the binuclear complexes **3b** and **4b** were identified by HRMS, IR and UV-Vis spectra. Complexes **3b** and **4b** did not give readily interpretable ^{1}H NMR spectra, in which all signals were greatly broadened due to the paramagnetic Mn(III) salen unit in their molecules [7a, 8].

The peaks of the singly charged species, $[M-PF_6]^+$, are observed as primary peaks in the HRMS spectra of rhenium complexes **3a** and **4a**. Complex **3b** exhibits a singly charged species $[M-PF_6-CH_3CN]^+$ at m/z 1088.2939 and complex **4b** shows the primary peak of $[M-PF_6]^+$ at m/z 1181.3743. The HRMS spectra of **3b** and **4b** give clear evidence for the incorporation of manganese in the chiral pyrrolidine salen ligand.

In addition to the strong bands of ν(C=O) and ν(C=N) at 1620–1624 cm^{-1} in the IR spectra of **3**(**a**,**b**) and **4**(**a**,**b**), two characteristic strong bands of CO ligands, at 2025, 1919 cm^{-1} for **3a** and **3b** and at 2033, 1921 cm^{-1} for **4a** and **4b**, are in good agreement with those of previously reported rhenium complexes [*fac*-$Re(CO)_3(bpy)L]^+$ (L = CH_3CN, 4-Xpy) [9]. The UV-Vis spectra of **3a** and **4a** are similar. Both show absorption bands of pyridyl ligands at 264–267 nm and the MLCT absorption maxima at 335–340 nm, which are in the absorption region reported for [*fac*-$Re(CO)_3(bpy)L]^+$ [10]. When Mn ion was introduced into the salen ligand cavity, the absorption maxima of pyridyl ligands appear at 293 nm for **3b** and 289 nm for **4b**, and their MLCT bands were considerably broadened to the bandwidth

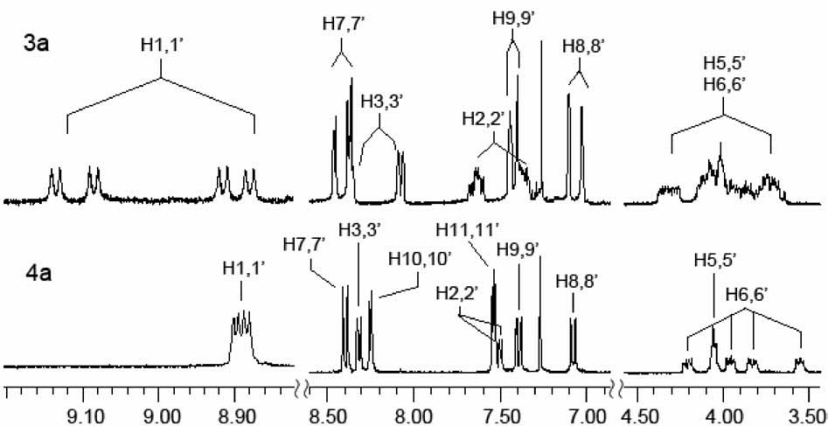


Figure 1. ^{1}H NMR spectra of **3a** (top) and **4a** (bottom) in the selected regions. The protons of **3a** and **4a** are labeled as in chart 1.

of 350–450 nm and red shifted by ca. 30 nm as compared with the corresponding bands of **3a** and **4a**.

The selected region (δ 3.5–9.5) of the ^{1}H NMR spectra of **3a** and **4a** is shown in figure 1 for comparison. The assignment of signals is based on gCOSY (^{1}H–^{1}H), gHSQC (^{1}H–^{13}C) and gHMBC (^{1}H–^{13}C) NMR spectra. The signals of principal interest in the ^{1}H NMR spectrum of **3a** (figure 1(top)) are in two regions: δ 8.8–9.2 for H1 and H1′ (chart 1) of bpy and 3.5–4.5 for H5,5′ and H6,6′ of the pyrrolidine ring. The H1 and H1′ protons of bpy of **3a** exhibit four doublets at δ 9.13, 9.07, 8.85 and 8.81 ($^{3}J_{HH} = 5.6$ Hz) with approximately equal integrations. In contrast, the ^{1}H NMR spectrum of **4a** (figure 1(bottom)) shows two doublets at δ 8.87 and 8.86 ($^{3}J_{HH} = 5.7$ Hz) for H1 and H1′ protons of bpy. Signals of the protons on the chiral pyrrolidine ring of **3a** are more intricate than **4a** (figure 1). The CH_3 group of bpy displays a singlet at δ 2.63 and the CH_3 of acetonitrile ligand shows a singlet at δ 2.17. The imino protons of **3a** appear as four singlets in the region of δ 8.36–8.46, while **4a** displays two singlets at δ 8.38 and 8.35, each for one imino proton. The noteworthy character in the ^{13}C NMR spectrum of **3a** is that both methine and methylene carbon atoms of the pyrrolidine ring display four discrete signals with quite similar chemical shifts. The ^{1}H and ^{13}C NMR spectra of **3a** suggest that complex **3a** may exist as a mixture of two isomers, even though **3a** gives only one spot in TLC analysis. With a *fac*-configuration, the Re atom of **3a** should be a chiral center. As the chiral salen substituted bipyridine **1** coordinates to the Re atom, two diastereomers can be formed in approximately equal amounts, labeled as *fac*-*S*-*R*,*R* and *fac*-*R*-*R*,*R* (chart 3(a) and (b)) depending on the configuration at Re and at the methine-carbon atoms of pyrrolidine ring [11]. The known Re(I) analogues $[Re(bpy)(CO)_3L]^{+}$ (L = Py, R_3P, $NCCH_3$) are mostly with bipyridine or symmetrically bisubstituted bipyridine ligands, leading to a non-chiral Re center in *fac*-configuration [9, 10, 12]. To the best of our knowledge, only a limited number of rhenium(I) complexes with the central Re atom in the chiral *fac*-configuration are found in literature [11b, 13]. Although the ^{1}H NMR spectrum of **3a** shows evidence of the presence of two diastereomers in solution, the complete assignment of the chemical shifts to each diastereomer is difficult since the signals of the two diastereomers are not well resolved

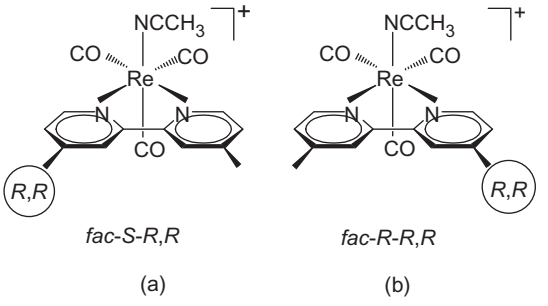


Chart 3.

Table 1. Electrochemical data of complexes **3(a,b)** and **4(a,b)**[a].

Compound	E_{pa} (V), Re(I/II)	E_{pc} (V), bpy(0/−1)	E_{pc}, E_{pa} (V), bpy(−1/−2)
3a	+1.39	−1.38	−1.62, −1.48
3b	+1.15	−1.43	−1.65, −1.53
4a	+1.42	−1.63	−1.87, −1.73
4b	+1.03	−1.62	−1.86, −1.73

[a]All potentials in this table are *vs.* Ag/Ag^+ (0.01 M $AgNO_3$ in CH_3CN).

in the ^1H NMR spectrum. The plain ^1H and ^{13}C NMR spectra of **4a** indicate that it is a pure "chiral-at-ligand" complex. According to the IR, ^1H and ^{13}C NMR spectra and the *fac*-configuration of previously reported analogue $[Re(bpy)(CO)_3(4\text{-}Xpy)]^+$ (X = H, Me, Et, *tert*-Bu, CH_3CO, CN) [12a], a *fac*-configuration is assumed for complex **4a**. If the large chiral salen group on the pyridyl ligand is disregarded, the Re of **4a** in a *fac*-configuration is symmetric about a mirror plane.

The electrochemical data of **3(a,b)** and **4(a,b)**, with 0.1 M nBu_4NPF_6/CH_3CN as electrolyte, are listed in table 1. Complex **3a** displays a typical cyclic voltammogram (CV) of $[Re(CO)_3(bpy)L]^+$ and $[Re(CO)_3(bpy)X]$ complexes [14], with an irreversible and a quasi-reversible reduction peak at −1.38 and −1.62 V *versus* Ag/Ag^+ for the bipyridyl ligand and an irreversible peak at +1.39 V for the oxidation process of Re(I) to Re(II). The CV of **4a** shows more cathodic reduction peaks for pyridyl ligands and a somewhat higher oxidation potential of Re(I) to Re(II) compared with that of **3a**. The irreversible oxidation peaks of the Re(I)/Re(II) process for complexes **3b** and **4b** exhibit cathodic shifts, by 240 mV for **3b** and by 390 mV for **4b**, as compared with their corresponding precursors **3a** and **4a**, while the two reduction peaks of pyridyl ligands are nearly unvarying as **3a** is converted to **3b** and **4a** to **4b**. The CVs show that the Re(I) ions of **3b** and **4b** are more readily oxidized than **3a** and **4a**, which is also indicated by the red-shifts of MLCT absorption maxima in UV-Vis spectra. Moreover, the oxidation potential of the Re(I)/Re(II) process for **4b** is 120 mV lower than that for **3b**, probably caused by the better electron-donating property of a pyridine relative to an acetonitrile ligand.

Further studies on the photophysical properties and the catalytic capability of Mn(III)Re(I) binuclear complex **3b** and **4b** in photoinduced asymmetric aerobic oxidation reactions are in progress.

3. Experimental

3.1. *General procedures*

Commercially available chemicals of reagent grade 4,4′-dimethyl-2,2′-bipyridine (Aldrich), isonicotinoyl chloride hydrochloride (Avocado), $Mn(OAc)_2 \cdot 4H_2O$ (Bejing chemical factory), $Re(CO)_5Cl$, NH_4PF_6 and $AgPF_6$ (Acros) were all used as received. Chiral ligand (3*R*,4*R*)-*N*,*N*′-bis(3,5-di-*tert*-butylsalicylidene)-3,4-diaminopyrrolidine was prepared with modified literature procedures from natural L-(+)-tartaric acid [6]. Starting complex $Re(4,4'\text{-}Me_2\text{-}2,2'\text{-bpy})(CO)_3Cl$ was synthesized according to the literature protocol [15].

Infrared spectra were recorded from KBr pellets on a JASCO FTIR 430 spectrophotometer and UV-Vis spectra on an HP 8453 diode-array spectrophotometer. NMR spectra were measured on a Varian INOVA 400 MHz apparatus. Mass spectra were performed by electro-spray ionization (ESI) on an HP1100 MSD instrument and TOF-ESI-MS on an HPLC-Q-TOF MS (Micromass) mass spectrometer. Elemental analyses were performed on a THERMOQUEST-FLASH EA 1112 elemental analyzer. Observed rotations for ligands **1** and **2** at 589 nm were measured by a JASCO P-1010 digital polarimeter.

3.2. *Syntheses*

3.2.1. Preparation of ligands 1 and 2

(3*R*,4*R*)-*N*-(4′-Methyl-2,2′-bipyridyl-4-oyl)pyrrolidine salen ligand 1. A solution of 4-carboxy-4′-methyl-2,2′-bipyridine (0.21 g, 1.0 mmol) in $SOCl_2$ (5 mL) was refluxed under dinitrogen for 3 h. The excess of $SOCl_2$ was thoroughly removed in vacuo. The residue was redissolved in CH_3CN (4 mL), to which a solution of (3*R*,4*R*)-*N*,*N*′-bis(3,5-di-*tert*-butylsalicylidene)-3,4-diaminopyrrolidine (0.51 g, 0.95 mmol) and triethylamine (0.5 mL, 3.6 mmol) in CH_3CN (10 mL) was added dropwise. The mixture was stirred under dinitrogen at 0°C for 2 h. After the solvent was evaporated in vacuo, the crude product was purified by flash chromatography on a column of silica gel using CH_3CN/CH_2Cl_2 (1 : 4) as eluent. The chiral ligand **1** was obtained as a yellow solid from the yellow band. Yield 85% (0.59 g); $[\alpha]_{589}^{27} = -221.9$ (c = 0.01 g/mL, MeOH). ^{1}H NMR ($CDCl_3$): δ 13.01 (s, 1H, O*H*), 12.89 (s, 1H, O*H*), 8.78 (d, J = 4.8 Hz, 1H, bpy), 8.57 (s, 1H, bpy), 8.55 (d, J = 4.8 Hz, 1H, bpy), 8.44 (s, 1H, N=C*H*), 8.34 (s, 1H, N=C*H*), 8.25 (s, 1H, bpy), 7.49 (d, J = 4.8 Hz, 1H, bpy), 7.41 (d, J = 2.4 Hz, 1H, Ph), 7.38 (d, J = 2.4 Hz, 1H, Ph), 7.17 (d, J = 4.8 Hz, 1H, bpy), 7.08 (d, J = 2.4 Hz, 1H, Ph), 6.99 (d, J = 2.4 Hz, 1H, Ph), 4.30 (dd, J = 12.39, 7.19 Hz, 1H, CH_2), 4.12 (dd, J = 7.19, 7.19 Hz, 1H, C*H*), 4.09–3.99 (m, 2H, C*H* and 1H of CH_2), 3.94 (dd, J = 7.19, 7.19 Hz, 1H, C*H*), 3.83 (dd, J = 12.39, 7.19 Hz, 1H, CH_2), 2.45 (s, 3H, CH_3-bpy), 1.46, 1.43, 1.29, 1.24 (all s, each for 9H of *t*-Bu). ^{13}C NMR ($CDCl_3$): δ 168.53, 168.47 (each for a N=*C*H), 167.79 (*C*=O), 158.01, 157.90 (each for an *ipso*-*C* of Ph-OH), 157.05 (*ipso*-*C* of bpy), 155.15 (*ipso*-*C* of bpy), 149.90, 149.24 (each for a *C*H of bpy), 148.31, 144.54 (each for an *ipso*-*C* of bpy), 140.66 (2*ipso*-*C* of Ph-3-*t*-Bu), 136.89, 136.86 (each for an *ipso*-*C* of Ph-5-*t*-Bu), 128.02, 126.68 (each for 2*C*H of Ph), 125.22, 122.13, 121.42, 118.78 (each for a *C*H of bpy), 117.51, 117.39 (each for an *ipso*-*C* of Ph-CH=N), 73.77, 72.37 (each for a *C*H of pyrrolidine), 54.00, 51.34 (each for a *C*H_2 of pyrrolidine), 35.14, 35.11, 34.22, 34.18

(each for an *ipso-C* of *t*-Bu), 31.51, 31.47, 29.52, 29.48 (each for 3*C*H$_3$ of *t*-Bu), 21.28 (*C*H$_3$-bpy). IR (KBr): ν 3438, 2956, 2870, 1625, 1440 cm^{-1}; MS: *m*/*z* 730.3 [MH$^+$]. Anal. Calcd for $C_{46}H_{59}N_5O_3 \cdot H_2O$ (747): C, 73.86; H, 8.22; N, 9.36; found: C, 74.03; H, 8.16; N, 9.16%.

(3*R*,4*R*)-*N*-(Isonicotinoyl)pyrrolidine salen ligand 2. (3*R*,4*R*)-*N*,*N*′-bis(3,5-di-*tert*-butylsalicylidene)-3,4-diaminopyrrolidine (0.51 g, 0.95 mmol) and triethylamine (0.5 mL, 3.6 mmol) were dissolved in CH_3CN (10 mL) and the resulting solution was added dropwise to a solution of isonicotinoyl chloride hydrochloride (0.18 g, 1.0 mmol) in CH_3CN (5 mL) under dinitrogen. The mixture was stirred at 0°C for 1 h. The solution was concentrated in vacuo and chromatographed on a column of silica gel with CH_3CN/CH_2Cl_2 (1 : 3) as eluent. Product **2** was obtained as a yellow crystalline solid by complete evaporation of solvent. Yield 87% (0.53 g); $[\alpha]_{589}^{23} = -261.4$ ($c = 0.01$ g mL^{-1}, MeOH); ^{1}H NMR ($CDCl_3$): δ 13.00 (s, 1H, O*H*), 12.88 (s, 1H, O*H*), 8.74 (d, $J = 6.0$ Hz, 2H, Py), 8.44 (s, 1H, N=C*H*), 8.36 (s, 1H, N=C*H*), 7.46 (d, $J = 6.0$ Hz, 2H, Py), 7.43 (d, $J = 2.4$ Hz, 1H, Ph), 7.40 (d, $J = 2.4$ Hz, 1H, Ph), 7.09 (d, $J = 2.4$ Hz, 1H, Ph), 7.02 (d, $J = 2.4$ Hz, 1H, Ph), 4.29 (dd, $J = 11.5$, 6.4 Hz, 1H, CH_2), 4.10, (dd, $J = 6.4$, 6.4 Hz, 1H, C*H*), 4.03 (dd, $J = 6.4$, 6.4 Hz, 1H, C*H*), 3.98–3.90 (m, 2H, each from a CH_2), 3.74 (dd, $J = 11.5$, 6.4 Hz, 1H, CH_2), 1.45, 1.44, 1.29, 1.26 (all s, each for 9H of *t*-Bu). ^{13}C NMR ($CDCl_3$): δ 168.55, 168.45 (each for a N=*C*H), 167.62 (*C*=O), 158.03, 157.94 (each for an *ipso-C* of Ph-OH), 150.55 (2*C*H of Py), 143.51 (*ipso-C* of Py), 140.83, 140.78 (each for an *ipso-C* of Ph-3-*t*-Bu), 136.98 (2*ipso-C* of Ph-5-*t*-Bu), 128.21, 128.13 (each for a *C*H of Py), 126.72, 121.47 (each for 2*C*H of Ph), 117.51, 117.39 (each for an *ipso-C* of Ph-CH=N), 73.90, 72.47 (each for a *C*H of pyrrolidine), 54.22, 51.56 (each for a *C*H$_2$ of pyrrolidine), 35.20, 35.19, 34.29, 34.26 (each for an *ipso-C* of *t*-Bu), 31.57, 31.53, 29.55, 29.53 (each for 3*C*H$_3$ of *t*-Bu). IR (KBr): ν 3446, 2956, 2869, 1626, 1439 cm^{-1}. ESI-MS: *m*/*z* 639.5 [MH$^+$]. Anal. Calcd for $C_{40}H_{54}N_4O_3 \cdot H_2O$ (656): C, 73.14; H, 8.59; N, 8.53. Found: C, 72.76; H, 8.39; N, 8.45%.

3.3. *Preparation of 3a*

$AgPF_6$ (200 mg, 0.79 mmol) was added to a suspension of $Re(CO)_5Cl$ (264 mg, 0.73 mmol) in CH_2Cl_2/MeOH (40/6 mL) under argon atmosphere. The suspension was stirred in the dark at room temperature for 20 h. The resulting purple precipitate was filtered off and the filtrate was evaporated to dryness. Chiral pyrrolidine salen ligand **1** (490 mg, 0.67 mmol) was added to the solution of the residue in CH_3CN (15 mL). The mixture was refluxed under argon in the dark for 8 h. The product was purified by flash chromatography on a column of silica gel using hexane/acetone/CH_2Cl_2 (8 : 3 : 1) as eluent. Complex **3a** was obtained as yellow solid after thorough removal of solvent. Yield 26% (210 mg). IR (KBr): ν 3421, 2958, 2150, 2025, 1919, 1624, 1439 cm^{-1}. UV-Vis (CH_3CN): λ_{max} 264 (34 900), 309 (14 500), 320 (16 600), 340 (11 100 M^{-1} cm^{-1}) nm. TOF-ESI-MS: *m*/*z* 1041.4298 $[M - PF_6]^+$ (Calcd for $C_{51}H_{65}N_6O_6Re$: 1041.4288), 1000.3917 $[M - PF_6 - CH_3CN]^+$ (Calcd for $C_{49}H_{62}N_5O_6Re$: 1000.4023). ^{1}H NMR ($CDCl_3$): δ 12.91, 12.76 (2br, 4H, O*H*), 9.13, 9.07, 8.85, 8.81 (4d, 4H, H1 and H1′ of bpy), 8.46, 8.44, 8.38, 8.36 (4s, 4H, N=C*H*), 8.35 (shoulder, 2H, bpy), 8.09, 8.06 (2s, 2H, bpy), 7.63, 7.35 (2m, 4H, bpy), 7.44, 7.40 (2s, 4H, Ph), 7.10, 7.02 (2s, 4H, Ph), 4.36–3.65 (m, 12H, CH_2 and C*H* of pyrrolidine rings for two stereoisomers), 2.63 (s, 6H, CH_3-bpy), 2.17 (s, 6H, CH_3CN),

1.46, 1.43, 1.29, 1.25 (4s, 72H, CH_3 of *t*-Bu).^{13}C NMR ($CDCl_3$): δ 197.22 (*C*O), 168.82, 168.52 (N=*C*H), 166.30 (*C*=O), 158.00, 157.94 (*ipso-C* of Ph–OH), 157.00, 154.76 (*ipso-C* of bpy), 154.52, 153.67, 153.59, 152.74 (*C*H of bpy), 151.88, 148.65 (*ipso-C* of bpy), 141.03, 136.99 (*ipso-C* of Ph-*t*-Bu), 128.67, 124.73, 124.46, 121.73 (*C*H of bpy), 128.38, 126.87 (*C*H of Ph), 118.94 (CH_3CN), 117.56, 117.44 (*ipso-C* of Ph-CH=N), 74.02, 73.85, 72.52, 72.37 (*C*H of pyrrolidine), 54.41, 54.36, 52.11, 51.99 (CH_2 of pyrrolidine), 35.22, 34.29 (*ipso-C* of *t*-Bu), 31.59, 31.55, 29.62, 29.58 (CH_3 of *t*-Bu), 21.81 (CH_3-bpy), 14.27 (CH_3CN).

3.4. *Preparation of 4a*

Chiral pyrrolidine salen ligand **1** (403 mg, 0.63 mmol) and $AgPF_6$ (160 mg, 0.63 mmol) were added to a solution of Re(4,4′-Me_2-2,2′-bpy)$(CO)_3Cl$ (345 mg, 0.70 mmol) in EtOH (20 mL). The mixture was refluxed under argon in the dark for 2 h and then cooled to room temperature. The precipitated AgCl was filtered off and the filtrate was concentrated to about 5 mL. The crude product was purified by flash chromatography on a column of neutral alumina gel using acetone/hexane (1 : 2) as eluent. The solvent was completely removed by rotary evaporation to give **4a** as bright yellow solid. Yield 62% (482 mg). IR (KBr): ν 3446, 2958, 2870, 2033, 1921, 1622, 1439, 845, 557 cm^{-1}. UV-Vis (CH_3CN): λ_{max} 267 (37 500), 304 (14 800), 317 (16 200), 335 (10 900 $M^{-1}cm^{-1}$) nm. TOF-ESI-MS: m/z 1093.4612 $[M-PF_6]^+$ (Calcd for $C_{55}H_{66}N_6O_6Re$: 1093.401). ^{1}H NMR ($CDCl_3$): δ 12.94 (br, 2H, O*H*), 8.87, 8.86 (2d, $^3J = 5.7$ Hz, each for 1H, H1 and H1′ of bpy), 8.38, 8.35 (2s, each for 1H, N=C*H*), 8.30, 8.28 (2s, each for 1H, bpy), 8.22, 7.52 (2d, $^3J = 6.8$ Hz, 4H, Py), 7.51, 7.47 (2d, $^3J = 5.7$ Hz, each for 1H, bpy), 7.38, 7.35 (2d, $^4J = 2.4$ Hz, each for 1H, Ph), 7.06, 7.04 (2d, $^4J = 2.4$ Hz, each for 1H, Ph), 4.17, 3.93, 3.80, 3.52 (all dd, $^2J = 10.4$ Hz, $^3J = 5.6$ Hz, each for 1H, CH_2 of pyrrolidine), 4.03 (m, 2H, C*H* of pyrroliine), 2.60, 2.55 (2s, each for 3H, CH_3-bpy), 1.41, 1.40, 1.26, 1.24 (4s, each for 9H, *t*-Bu). ^{13}C NMR ($CDCl_3$): δ 195.78 (*C*O), 169.99, 168.66 (N=*C*H), 165.07 (*C*=O), 158.05, 157.84 (*ipso-C* of Ph-OH), 155.54 (*ipso-C* of bpy), 152.35 (*C*H of Py), 152.02 (*C*H of bpy), 146.64 (*ipso-C* of Py), 140.64, 140.50 (*ipso-C* of Ph-*t*-Bu), 136.97, 136.85 (*ipso-C* of Ph-*t*-Bu), 129.78 (*ipso-C* of bpy), 129.71 (*C*H of bpy), 127.99, 127.88, 127.25, 126.74 (*C*H of Ph), 126.53, 126.41 (*C*H of bpy), 125.21 (*C*H of Py), 117.75, 117.56 (*ipso-C* of Ph-CH=N), 73.10, 72.32 (*C*H of pyrrolidine), 53.64, 51.71 (CH_2 of pyrrolidine), 35.19, 34.28 (*ipso-C* of *t*-Bu), 31.57, 29.60 (CH_3 of *t*-Bu), 21.88 (CH_3-bpy).

3.5. *Preparation of 3b and 4b*

A solution of **3a** (180 mg, 0.15 mmol) in MeOH (8 mL) was added dropwise to a solution of $Mn(OAc)_2 \cdot 4H_2O$ (367 mg, 1.5 mmol) in MeOH (10 mL). The mixture was stirred at reflux for 2 h in the dark, and afterwards air was bubbled through the refluxing mixture for another 2 h. After heating and air flow were stopped, a saturated solution of LiCl in MeOH (8 mL) was added. The solvent was removed in vacuo and the residue was dissolved in CH_2Cl_2 (10 mL). The organic phase was washed with water (3×10 mL) and dried with anhydrous Na_2SO_4 overnight. The concentrated filtrate was purified by flash chromatography on a column of neutral alumina gel using hexane/acetone/CH_2Cl_2 (10 : 6 : 1) as eluent. The brown fraction was collected

and the organic solvent was removed by rotary evaporation. To the resulting suspension was added 10 mL of CH_2Cl_2 and the organic layer was washed sequentially with water (2×10 mL) and 5 mL of concentrated ammonium hexafluorophosphate aqueous solution. After being dried over anhydrous Na_2SO_4 and filtered, the organic phase was evaporated to dryness to give **3b** as dark brown solid. **3b**: yield 57% (110 mg). IR (KBr): ν 3446, 2956, 2160, 2025, 1919, 1624, 1435, 843, 559 cm^{-1}. UV-Vis (CH_3CN): λ_{max} 293 (23 900), 322 (14 600), 372 (8400) nm. TOF-ESI-MS: m/z 1088.2939 $[M - PF_6 - CH_3CN]^+$ (Calcd for $C_{49}H_{57}N_5O_6ClMnRe$: 1088.2935), 547.1760 $[M - Cl - PF_6]^{2+}$ (Calcd for $C_{51}H_{60}N_6O_6MnRe/2$: 547.1756).

Complex **4b** was prepared in a similar procedure as **3b**. Product **4b** was purified by flash chromatography using CH_2Cl_2/acetone (4 : 1) as eluent. **4b**: yield 33% (66 mg). IR(KBr): ν 3444, 2957, 2033, 1921, 1620, 1434, 845, 558 cm^{-1}. UV-Vis (CH_3CN): λ_{max} 289 (28 500), 319 (18 400), 367 (9400) nm. TOF-ESI-MS: m/z 1181.3743 $[M - PF_6]^+$ (Calcd for $C_{55}H_{64}N_6O_6ClMnRe$: 1181.3541).

4. Electrochemistry

Acetonitrile (Merck, spectroscopy grade) used for electrochemistry was dried with molecular sieves (4 Å) and then freshly distilled from CaH_2 under N_2. A solution of 0.05 M *n*-Bu_4NPF_6 (Fluka, electrochemical grade) in CH_3CN was used as electrolyte. Electrochemical measurements were recorded using a BAS-100W electrochemical potentiostat. The electrolyte solution was degassed by bubbling with dry argon for 10 min before measurement. Cyclic voltammograms were obtained in a three-electrode cell under argon. The working electrode was a glassy carbon disc (diameter 3 mm) successively polished with 3 and 1 μm diamond pastes and sonicated in ion-free water for 10 min. The reference electrode was a non-aqueous Ag/Ag^+ electrode (0.01 M $AgNO_3$ in CH_3CN) and the auxiliary electrode was a platinum wire.

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