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Cobaltocene Reductions of Multiply Bonded Dirhenium Complexes. II.* The Isolation of the Paramagnetic Species $[(\eta^5\text{-}C_5H_5)_2Co][Re_2(hp)_4X_2]$ (hp = Anion of 2-Hydroxypyridine; X = Cl, Br, or I)

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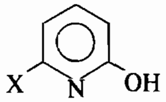
Abstract

Reaction of the quadruply bonded dirhenium(III) complexes $(n\text{-}Bu_4N)_2Re_2X_8$ (X = Cl, Br, or I) with 2-hydroxypyridine (Hhp) in refluxing n-pentanol gives $Re_2(hp)_4X_2$ in high yield (>90%). These complexes are reduced by cobaltocene to yield the paramagnetic salts $[(\eta^5\text{-}C_5H_5)_2Co][Re_2(hp)_4X_2]$. The spectroscopic (electronic absorption and infrared) and electrochemical properties of these sets of complexes are in accord with them possessing $\sigma^2\pi^4\delta^2$ (Re_2^{6+}) or $\sigma^2\pi^4\delta^2\delta^{*1}$ (Re_2^{5+}) ground state electronic configurations.

Introduction

A number of important compounds have been prepared recently in which a ligand of the general structure shown below has been used to stabilize a metal–metal multiply bonded unit [1]. For the Cr, Mo and W family, 6-methyl-2-hydroxypyridine (Hmhp) leads to stable dinuclear complexes of the type $M_2(mhp)_4$ [2]. On the other hand, while Tc and Re have not yet been found to form complexes with Hmhp, they do so with the 2-hydroxypyridine ligand (Hhp). In 1979, Cotton and Gage [3] described the preparation and structural characterization of dichlorotetrakis(o-oxypyridine)dirhenium(III), $Re_2(hp)_4Cl_2$, and the analogous ditechnetium(II,III) complex $Tc_2(hp)_4Cl$ one year later [4]. Surprisingly, the chemistry of the complex $Re_2(hp)_4Cl_2$ has not been examined further.



X = H or CH_3

In this paper, an alternate synthesis of $Re_2(hp)_4Cl_2$ is described, as well as the preparation and characterization of the analogous species $Re_2(hp)_4Br_2$ and $Re_2(hp)_4I_2$. In addition, the reaction of these materials with the one-electron reducing agent cobaltocene, and the isolation and characterization of the series $[(\eta^5\text{-}C_5H_5)_2Co][Re_2(hp)_4X_2]$ (X = Cl, Br, or I), are reported.

Experimental

Starting Materials

The complexes $(n\text{-}Bu_4N)_2Re_2X_8$ (X = Cl, Br, or I) were prepared by standard literature methods [5–7]. The 2-hydroxypyridine (Hhp) ligand was obtained from Aldrich Chemical Co. and was purified by sublimation in static vacuum prior to use. Cobaltocene was purchased from Strem Chemicals Inc. All other reagents were used as received from commercial sources.

Reaction Procedures

All reactions were performed under a dry nitrogen atmosphere and all reagents were thoroughly deoxygenated prior to use. Standard Schlenk techniques were used in the preparation of the cobaltocenium salts and in the handling of cobaltocene.

A. Preparation of the Dirhenium(III) Complexes $Re_2(hp)_4X_2$

(i) $Re_2(hp)_4Cl_2$

A mixture of $(n\text{-}Bu_4N)_2Re_2Cl_8$ (0.71 g, 0.62 mmol) and Hhp (0.30 g, 3.1 mmol) in 20 ml of deoxygenated n-pentanol was refluxed for 22 h. The dark red solid which resulted was filtered off, washed with fresh n-pentanol, then with diethyl ether, and finally dried *in vacuo*; yield 0.45 g (91%). *Anal.* Calcd. for $C_{20}H_{16}Cl_2N_4O_4Re_2$: C, 29.31; H, 1.97. Found: C, 29.08; H, 2.29.

(ii) $Re_2(hp)_4Br_2$

A solution of $(n\text{-}Bu_4N)_2Re_2Br_8$ (0.54 g, 0.36 mmol) and Hhp (0.23 g, 2.4 mmol) in 20 ml of deoxygenated n-pentanol was refluxed for 15 h to

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yield a dark red-orange solid which was filtered off, washed with fresh n-pentanol followed by diethyl ether, and dried *in vacuo*; yield 0.32 g (97%). *Anal.* Calcd. for $C_{20}H_{16}Br_2N_4O_4Re_2$: C, 26.44; H, 1.78. Found: C, 26.35; H, 1.99.

(iii) $Re_2(hp)_4I_2$

The reaction between $(n\text{-}Bu_4N)_2Re_2I_8$ (1.29 g, 0.69 mmol) and Hhp (0.46 g, 4.92 mmol) in 30 ml of deoxygenated n-pentanol for 24 h, followed by the usual work-up procedure, gave the title complex: yield 0.63 g (91%). *Anal.* Calcd. for $C_{20}H_{16}I_2N_4O_4Re_2$: C, 23.96; H, 1.61. Found: C, 24.66; H, 2.48.

An alternative method for preparing the iodide complex involved a halide-exchange reaction between $Re_2(hp)_4Cl_2$ and liquid HI. A sample of $Re_2(hp)_4Cl_2$ (0.15 g, 0.18 mmol) was placed in a test tube which was cooled in a cyclohexanone-liquid nitrogen slush bath. The sample was flushed with dry nitrogen gas for 15 min, then HI(g) was condensed onto the solid until about 5 ml of liquid had collected (~10 min). The test tube was removed from the slush bath and again flushed with dry nitrogen until all the liquid had evaporated and the tube and its contents were at room temperature. The resulting red-brown oil was dissolved in dry dichloromethane, filtered and diethyl ether added to the filtrate. The precipitate which resulted was filtered off, washed with diethyl ether, and dried *in vacuo*; yield 0.074 g (39%). The identity of the material as $Re_2(hp)_4I_2$ was confirmed by measurement of its cyclic voltammetric and spectroscopic properties.

B. Cobaltocene Reduction of $Re_2(hp)_4Cl_2$

(i) $[(\eta^5\text{-}C_5H_5)_2Co][Re_2(hp)_4Cl_2]$

A small amount of cobaltocene (0.058 g, 0.304 mmol) was dissolved in 20 ml of deoxygenated acetone which had been dried over molecular sieves. This solution was filtered under nitrogen onto $Re_2(hp)_4Cl_2$ (0.09 g, 0.11 mmol), and the mixture stirred for 15 h. The black solid which separated was filtered off, washed with fresh, dry, deoxygenated acetone, and dried *in vacuo*; yield 0.06 g (54%). Microanalytical data were consistent with its formulation as the dihydrate. *Anal.* Calcd. for $C_{30}H_{30}Cl_2CoN_4O_6Re_2$: C, 34.49; H, 2.90. Found: C, 34.29; H, 2.81.

(ii) $[(\eta^5\text{-}C_5H_5)_2Co][Re_2(hp)_4Br_2]$

Cobaltocene (0.12 g, 0.63 mmol) was dissolved in 20 ml of dry, deoxygenated acetone, then filtered onto $Re_2(hp)_4Br_2$ (0.32 g, 0.35 mmol). The mixture was stirred for 15 h, and the green-black powder worked-up as described in B(i); yield 0.32 g (83%). *Anal.* Calcd. for $C_{30}H_{26}Br_2CoN_4O_4Re_2$: C, 32.83; H, 2.39. Found: C, 32.70; H, 2.37.

(iii) $[(\eta^5\text{-}C_5H_5)_2Co][Re_2(hp)_4I_2]$

A solution of cobaltocene (0.28 g, 1.5 mmol) in 20 ml of dry, deoxygenated acetone was filtered onto a sample of $Re_2(hp)_4I_2$ (0.60 g, 0.60 mmol). The resulting slurry was stirred for 18 h, then filtered, and the solid washed with deoxygenated acetone. The product was then vacuum dried; yield 0.50 g (70%). Although the identity of this compound was confirmed by its spectroscopic and electrochemical properties, satisfactory carbon and hydrogen microanalytical data were not obtained.

Physical Measurements

Far infrared spectra were recorded as Nujol mulls using a Digilab FTS-20B Fourier transform spectrometer. Electronic absorption spectra were recorded on IBM Instruments 9420 (900–300 nm) and Cary 17 (1800–900 nm) UV-visible spectrophotometers. Electrochemical measurements were carried out on dichloromethane solutions that contained 0.2 M tetra-n-butylammonium hexafluorophosphate (TBAH) as supporting electrolyte. $E_{1/2}$ values, determined as $(E_{p,a} + E_{p,c})/2$, were referenced to the Ag/AgCl electrode at room temperature and are uncorrected for junction potentials. Voltammetric experiments were performed using a Bioanalytical Systems Inc. Model CV-1A instrument in conjunction with a Hewlett-Packard Model 7035B x–y recorder. X-band ESR spectra of frozen dichloromethane solutions were recorded at −160 °C with the use of a Varian E-109 spectrometer. Conductivity measurements were performed on 1×10^{-3} M acetonitrile solutions using an Industrial Instruments Inc. Model RC-16B2 conductivity bridge.

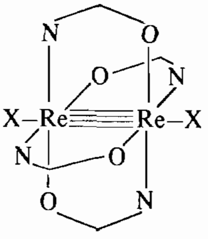
Analytical Procedures

Elemental microanalyses were performed by Dr. H. D. Lee of the Purdue University microanalytical laboratory.

Results and Discussion

Synthetic Details and Spectroscopic Characterization of $Re_2(hp)_4X_2$

The procedure that was used previously to prepare the quadruply-bonded dirhenium(III) complex $Re_2(hp)_4Cl_2$ (hp is the anion of 2-hydroxypyridine) (see structure I) involved the reaction between $(n\text{-}Bu_4N)_2$-



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X = Cl, Br, or I

TABLE I. Spectroscopic Data for Oxypyridinato Complexes of Dirhenium(III,III) and Dirhenium(II,III).

Complex	Elect. Abs. Spectra (nm)[a]	Far IR Spectra (cm^{-1})[d]
$Re_2(hp)_4Cl_2$	558(330), 390(9200) 565, ~400[b]	457m, 445sh, 332s, 278m, *201vs*
$Re_2(hp)_4Br_2$	554(340), 393(9800) ~560sh, 395[b]	456m, 330s, 277m, ~220m, *135s*
$Re_2(hp)_4I_2$	556(430), 389(14,000)	455m, 442sh, 331s, 271m, ~215m-w, *108s*
[(η^5-C_5H_5)$_2$Co] [$Re_2(hp)_4Cl_2$]	783(370), 546(790), 392[c] 790, ~550, ~400[b]	460s, 320s, 270w, 215sh, 170s
[(η^5-C_5H_5)$_2$Co] [$Re_2(hp)_4Br_2$]	~900sh, 750(~200), 550(530) 750, ~560sh, ~380sh[b]	460s, 320s, 265w, 106m-w
[(η^5-C_5H_5)$_2$Co] [$Re_2(hp)_4I_2$]		460s, 325s, 260w, ~75m-w

[a] Spectra recorded on CH_2Cl_2 solutions from 1600 to 300 nm unless otherwise stated; λ_{max} values given with molar extinction coefficients (ϵ) in parentheses. [b] Solid state Nujol mull spectra. [c] Molar extinction coefficient (>10^3) not accurately measured because of solution instability. [d] Recorded as Nujol mulls; bands in italics are assigned to ν(Re–X) modes of $Re_2(hp)_4X_2$.

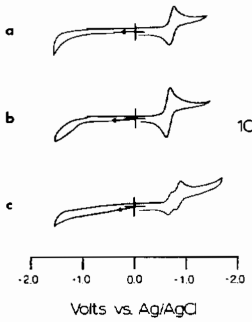

Fig. 1. Cyclic voltammograms (scan rate 200 mV/s at a Pt-bead electrode) in 0.2 M n-Bu_4NPF_6–CH_2Cl_2 showing the $Re_2(hp)_4X_2$/[$Re_2(hp)_4X_2$]$^-$ couple: (a) $Re_2(hp)_4Cl_2$; (b) $Re_2(hp)_4Br_2$; (c) [(η^5-C_5H_5)$_2$Co] [$Re_2(hp)_4Cl_2$].

Re_2Cl_8 and molten 2-hydroxypyridine. In the present study, we have modified this procedure so that it is easily adaptable to the synthesis of the analogous bromide and iodide complexes. The reaction between (n-$Bu_4N)_2Re_2X_8$ (X = Cl, Br, or I) and Hhp in refluxing n-pentanol was complete in less than 24 h to give $Re_2(hp)_4X_2$ in close to quantitative yield (>90%). The conversion of $Re_2(hp)_4Cl_2$ to $Re_2(hp)_4I_2$ upon treatment with HI(*l*) indicates that this type of halide exchange reaction is also a suitable synthetic procedure, as has been demonstrated previously [8] in the conversion of the dirhenium(III) carboxylates $Re_2(O_2CR)_4Cl_2$ to their analogous bromides and iodides upon reaction with HX (X = Br or I).

All available evidence supports a close structural relationship between these complexes. Their far-IR and electronic absorption spectra are very similar (Table I). The ν(Re–X) modes at 201 cm^{-1} (X = Cl), 135 cm^{-1} (X = Br) and 108 cm^{-1} (X = I) resemble closely the data for the alkyl carboxylates $Re_2(O_2CR)_4X_2$ (245–220 cm^{-1}, 150–134 cm^{-1}, and 118 ± 5 cm^{-1}, respectively) [8]. In addition, we find that there are close similarities between the electronic absorption spectra of these two groups of complexes with prominent absorption bands at ~555 and ~390 nm for $Re_2(hp)_4X_2$ and at ~500 and ~400 nm for $Re_2(O_2CR)_4X_2$ [8]. The lowest energy one of each pair is assigned [8, 9] to the electric dipole allowed $\delta \rightarrow \delta^*$ transition.

Redox Characteristics of $Re_2(hp)_4X_2$

Cyclic voltammetric measurements on solutions of $Re_2(hp)_4X_2$ (X = Cl or Br) in 0.2 M n-Bu_4NPF_6–CH_2Cl_2 show that these complexes possess a one-electron (by coulometry) reduction process characterized by an $E_{1/2}$ value of −0.73 V and −0.67 V *vs.* Ag/AgCl for X = Cl and Br, respectively (Fig. 1). This reduction corresponds to the process, $Re_2(hp)_4X_2 + e^- \rightarrow [Re_2(hp)_4X_2]^-$, and gives rise to a species which should possess the paramagnetic $\sigma^2\pi^4\delta^2\delta^{*1}$ ground state electronic configuration [1]. For sweep rates (ν) in the range 50 to 500 mV/s, the ratio $i_p/\nu^{1/2}$ was found to be constant and $i_{p,c}/i_{p,a} \approx 1$, in accord with diffusion control. The potential separation between the coupled anodic and cathodic peaks, ΔE_p, was equal to 100–110 mV at ν = 200 mV/s, and increased slightly with an increase in scan rate. These properties accord with an electron transfer process which is reversible, or approaches reversibility. We define reversibility here in terms of a comparison with the behavior of the known reversible couples ferrocenium/ferrocene and $Ru(bpy)_3^{3+}/Ru(bpy)_3^{2+}$. The characteristics of these systems, as measured using our experimental set-up and the 0.2 M n-Bu_4NPF_6–CH_2Cl_2 solvent system, are described elsewhere [10]. We note that $Re_2(hp)_4I_2$ exhibits similar redox activity to its chloride and bromide analogues ($E_{1/2}$(red) ≈ −0.55 V *vs.* Ag/AgCl), with the exception that its electrochemical behavior is complicated by the occurrence of adsorption at the Pt bead electrode.

For the series $Re_2(hp)_4X_2$, the reductions shift progressively to more negative potentials in the order I < Br < Cl. This trend, which is the same as that observed for the related carboxylates $Re_2(O_2CR)_4X_2$ [8], is the one expected based upon the normal redox characteristics of transition metal halides [11].

While these electrochemical reductions occur at potentials which are more negative than those for the reduction of $Re_2(O_2CR)_4X_2$ to $[Re_2(O_2CR)_4X_2]^-$, they are, nonetheless, within the reducing capability of the one-electron reducing agent cobaltocene. Recently, we have developed cobaltocene as a reducing agent for other multiply bonded dimetal complexes, including the reductions of $Re_2(O_2CR)_4Cl_2$ to $[(\eta^5\text{-}C_5H_5)_2Co][Re_2(O_2CR)_4Cl_2]$ [12], $Os_2(O_2CR)_4Cl_2$ to $[(\eta^5\text{-}C_5H_5)_2Co][Os_2(O_2CR)_4Cl_2]$ [13], $Re_2(\mu\text{-}Cl)_2(\mu\text{-dppm})_2Cl_4$ to $[(\eta^5\text{-}C_5H_5)_2Co]\text{-}[Re_2(\mu\text{-}Cl)_2(\mu\text{-dppm})_2Cl_4]$ [14] and $[Re_2(\mu\text{-}Cl)(\mu\text{-}CO)(\mu\text{-dppm})_2Cl_2(CO)L]^+$ to $Re_2(\mu\text{-}Cl)(\mu\text{-}CO)(\mu\text{-dppm})_2Cl_2(CO)L$ (L = RCN or RNC; dppm = $Ph_2PCH_2PPh_2$) [15]. Cobaltocene proved to be an ideal reductant for the conversion of $Re_2(hp)_4X_2$ to $[Re_2(hp)_4X_2]^-$. The reactions between $Re_2(hp)_4X_2$ and cobaltocene in acetone gave precipitates of $[(\eta^5\text{-}C_5H_5)_2Co][Re_2(hp)_4X_2]$ in quite high yield (>50%). In all instances, these complexes proved to be rather unstable and they decomposed very rapidly upon exposure to the atmosphere. Indeed, we have been unable to isolate an analytically pure sample of the iodide derivative, although its properties clearly accord with this formulation.

Cyclic voltammetry on solutions of these complexes in 0.2 M $n\text{-}Bu_4NPF_6\text{–}CH_2Cl_2$ show that the redox process at *ca.* −0.7 V *vs.* Ag/AgCl now corresponds to a one-electron oxidation. A couple at −0.90 V *vs.* SCE is due to cobaltocenium/cobaltocene**; the close similarity of the magnitudes of the currents associated with the two couples at −0.7 V and −0.9 V confirms the stoichiometry of these complexes (see Fig. 1).

Solutions of $[(\eta^5\text{-}C_5H_5)_2Co][Re_2(hp)_4X_2]$ (X = Cl or Br) in acetonitrile (*ca.* 1×10^{-3} M) had conductivities in the range expected for 1:1 electrolytes (Λ_m = 140–150 ohm^{-1} cm^2 mol^{-1}). In spite of the instability of solutions of these complexes, we were able to record their electronic absorption spectra (Table I). Especially noteworthy is the appearance of a band at ~775 nm which we assign to the $\delta \rightarrow \delta^*$ transition. This is the lowest energy absorption in the spectral region 1600–300 nm. This feature exhibits the expected shift to lower energy relative to the $\delta \rightarrow \delta^*$ transition (λ_{max} ~555 nm) in the spectra of the neutral complexes $Re_2(hp)_4X_2$, and therefore mirrors closely the spectral changes observed upon reducing $Re_2(O_2CR)_4X_2$ to $[Re_2(O_2CR)_4X_2]^-$, *viz.*, a red shift from ~500 nm to ~700 nm [8]. The low frequency IR spectra are rather similar to those of the neutral species, although there is evidence (Table I) that the ν(Re–X) modes shift to lower energies upon formation of the monoanions.

In all instances, solutions of $[(\eta^5\text{-}C_5H_5)_2Co]\text{-}[Re_2(hp)_4X_2]$ (X = Cl, Br, or I) in dichloromethane at −160 °C exhibit complex X-band ESR spectra. All three spectra are rather similar and have complex splitting patterns of a type that is commonly encountered for species which contain the paramagnetic Re_2^{5+} core [8, 12]. The complex broad signals, which are centered at g ~2.15–2.25, occur over the range 500 to ~6000 Gauss and display hyperfine coupling to two equivalent rhenium nuclei (I = 5/2) as well as ligand hyperfine. Accordingly, they are consistent with a bonding model in which the unpaired electron resides in the metal–metal δ^* antibonding orbital.

Acknowledgements

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**The Cp_2Co^+/Cp_2Co couple has been reported to have a value of −0.94 V *vs.* SCE in acetonitrile (see ref. 16).