Coordination Compounds of Pentaaminerhenium(III/II)

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Reduction of $[ReO_2(en)_2]^+$, $[ReO_2(NH_3)_4]^+$, or $[ReO_2(ampy)_2]^+$ (en = ethylenediamine; ampy = 2-(aminomethyl)-pyridine) in HCl (aq) produces $[ReCl_2(en)_2]^+$, $[ReCl_2(NH_3)_4]^+$, and $[ReCl_2(ampy)_2]^+$ respectively. Chloride substitution on *trans*-$[ReCl_2(en)_2]^+$ by pyridine, isonicotinamide, nicotinamide, 4-picoline, 4-(dimethylamino)-pyridine, and *n*-propylamine is accomplished with accompanying isomerization to a cis geometry. The crystal structures of $[ReCl_2(en)_2](PF_6)$ (triclinic; $P\bar{1}$ (No. 2); a = 8.717(1) Å, b = 12.618(2) Å, c = 6.523(1) Å, α = 98.44(2)°, β = 102.66(1)°, γ = 78.50(1)°; D_{calcd} = 2.543 g/cm^3; Z = 2), $[ReCl_2(ampy)_2](BPh_4)$,(triclinic; $P\bar{1}$ (No. 2); a = 12.334(1) Å, b = 17.345(2) Å, c = 8.918(1) Å, α = 91.30(3)°, β = 94.75(3)°, γ = 73.29(2)°; D_{calcd} = 1.551 g/cm^3; Z = 2), and $[ReCl(picoline)(en)_2](PF_6)_2$, (monoclinic; $P2_1/c$ (No. 14); a = 9.233(3) Å, b = 17.824(5) Å, c = 13.979(5) Å, β = 108.15(3)°; D_{calcd} = 2.202 g/cm^3; Z = 4) are reported, and various equilibrium constants are determined which pertain to the relative affinity of Re(II) and of Re(III) for π-acid ligands. Parallels are drawn to the established π-bases $[Ru(NH_3)_5]^{2+}$ and $[Os(NH_3)_5]^{2+}$.

Introduction

Amines, halides, alkoxides, and other "saturated" ligands are common in classical coordination compounds, where the metal center is highly electropositive. The metallofragments $[Ru(NH_3)_5]^{2+}$,[2] $[Tc(NH_3)_4(H_2O)]^{2+}$,[3] and $[Os(NH_3)_5]^{2+}$ [4] are exceptions to this trend, as the metal centers in these compounds are uncharacteristically electron-rich. Such an arrangement of electron-rich metal with σ-donating ligands can render the transition metal a tenacious back-bonding agent and, in the case of Os(II) in particular, has led to a wide variety of stable complexes with unsaturated organic ligands including η^2-arenes,[5] η^2-pyridines,[6] and η^2-pyrroles.[7]

As with other early transition-metals, the chemistry of rhenium with amine ligands has been confined, for the most part, to high oxidation states as in the complexes $[ReL_4O_2]^+$ (L = py, NH_3, $^1/_2$(en)). As part of our continuing program on the activation of aromatic molecules,[8] we have embarked on a detailed study of low-valent rhenium in classical coordination environments. In this paper we describe some of the first examples of mononuclear, octahedral Re(III) and Re(II) species with predominantly amine ligands.

Abbreviations. OTf = $CF_3SO_3^-$; DME = 1,2-dimethoxyethane; DMAc = *N*,*N*-dimethylacetamide; TBAH = tetrabutylammonium hexafluorophosphate; DMAP = 4-(dimethylamino)pyridine; nic = nicotinamide; isn = isonicotinamide; en = ethylenediamine; ampy = 2-(aminomethyl)pyridine; py = pyridine; pic = 4-picoline. (PPN)Cl = bis(triphenylphosphoranylidene)ammonium chloride.

Experimental Section

Infrared spectra were recorded on a Mattson Cygnus 100 FTIR spectrometer. Electronic spectra were recorded on an HP 8452A diode array spectrophotometer. Routine ^{1}H and ^{13}C NMR spectra were recorded on a General Electric QE-300 or GN-300 spectrometer and are reported in ppm shift from tetramethylsilane. Electrochemical experiments were performed under nitrogen using a PAR Model 362 potentiostat driven by a PAR Model 175 universal programmer. Cyclic voltammograms were recorded (Kipp & Zonen BD90 XY recorder) in a standard three-electrode cell from +1.50 to −2.3 V with a glassy-carbon working electrode. All potentials are reported vs NHE and, unless otherwise noted, were determined in DMAc (~0.5 M TBAH) using ferrocene ($E_{1/2}$ = 0.55 V), decamethylferrocene ($E_{1/2}$ = 0.04 V), or cobaltocenium hexafluorophosphate ($E_{1/2}$ = −0.78 V) in situ as a calibration standard. The peak-to-peak separation ($E_{p,a} - E_{p,c}$) was between 70 and 100 mV for all reversible couples reported unless otherwise noted. This work was carried out under nitrogen atmosphere in a Vacuum Atmospheres Co. glovebox, separate boxes being used for aqueous and nonaqueous operations, unless otherwise noted.

Solvents. All distillations were performed under nitrogen, and all solvents were deoxygenated by purging with nitrogen for at least 20 min; deuterated solvents were deoxygenated by repeated freeze–pump–thaw cycles. Methylene chloride was refluxed for at least 8 h over P_2O_5 and distilled. Diethyl ether was refluxed for at least 8 h over Na/benzophenone and distilled. Methanol was refluxed over $Mg(OMe)_2$, prepared in situ from Mg^0 activated by I_2, and distilled. DME was refluxed over Na^0 and distilled. Acetonitrile was refluxed over CaH_2 and distilled. DMAc was dried over CaH_2 and then refluxed 24 h and distilled under reduced pressure. Acetone (Burdick and Jackson) was deoxygenated prior to use.

Reagents. $[ReO_2(en)_2]Cl$,[9] $[ReO_2(NH_3)_4]Cl$,[10] and $Re(O)Cl_3(PPh_3)_2$,[11] were prepared by literature methods. Magnesium powder (Aldrich, 50 mesh) was activated by treating with iodine in DME under nitrogen, stirring for several hours, and washing with DMAc, acetone, and ether. Granular Zn^0/Hg^0 amalgam was prepared from 30-mesh granular Zn^0 that was washed with 3 M HCl(aq) and then treated with a saturated $HgCl_2$(aq) solution for 20 min.

***trans*-$[ReCl_2(en)_2]PF_6$ (1).** $[ReO_2(en)_2]Cl$ (1.9 g, 5.16 mmol) was dissolved in 65 mL of 1 M HCl giving a rust-colored solution. Zinc amalgam (3 g) was added and the reaction stirred for 3 h. The resulting yellow solution was filtered through Celite, and the filtrate was diluted to 3 times its original volume and loaded on a Sephadex SP C-25 ion exchange column. A yellow band was eluted with 0.25 M HCl and collected. A saturated solution of NH_4PF_6(aq) was added to the fraction, and the resulting yellow microcrystals were filtered and washed with H_2O (2 × 3 mL) and OEt_2 (3 × 3 mL) then dried in vacuo. Yield: 2.132 g, 4.09 mmol (79%). ^{1}H NMR (acetone-d_6): 169.06 (s, 8H, NH_2);

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10.54 (s, 8H, CH_2). Anal. Calcd for $C_4H_{16}N_4Cl_2F_6PRe$: C, 9.20; H, 3.07; N, 10.74. Found; C, 9.52; H, 3.19; N, 10.73.

***cis*-[ReCl(py)(en)$_2$](PF$_6$)$_2$ (2).** To **1** (490.8 mg, 0.94 mmol) were added pyridine (258.5 mg, 3.3 mmol) and DMAc (4.5 mL) giving a dark yellow solution. $TlPF_6$ (358.3 mg, 1.0 mmol) was added resulting in a white precipitate. The mixture was stirred 24 h and filtered. Addition of OEt_2 to the brown filtrate gave an oil. The OEt_2 layer was decanted, the oil dissolved in a minimum amount of acetone, and this solution added dropwise to 100 mL of stirring CH_2Cl_2. The resulting brown precipitate was filtered, washed with CH_2Cl_2 (3 × 2 mL), and dried in vacuo. Yield: 503.8 mg, 0.709 mmol (83%). ^{1}H NMR (acetone-d_6): 200.79, 200.12, 175.87, 168.46, 161.27, 155.12, 149.38, 126.35 (m, 1H each, NH*H*); 6.66, 5.29, 3.57, –0.37, –4.86, –5.77, –12.31, –18.20 (m, 1H each, CH*H*); 16.66 (t, 2H), 14.66 (t, 1H), 13.41 (d, 2H, NC_5H_5). Anal. Calcd for $C_9H_{21}N_5ClF_{12}P_2Re$: C, 15.21; H, 2.96; N, 9.86; Cl, 4.99. Found: C, 15.32; H, 3.12; N, 9.57; Cl, 4.97.

***cis*-[ReCl(isn)(en)$_2$](PF$_6$)$_2$ (3).** To **1** (121.7 mg, 0.233 mmol) were added 1.5 mL of DMAc and $TlPF_6$ (89.0 mg, 0.255 mmol) resulting in a yellow solution. Isonicotinamide (44.2 mg, 0.362 mmol) was then added giving a red solution. After being stirred for 2 days, the mixture was filtered and the dark red filtrate treated with OEt_2 until an oil formed. The OEt_2 layer was decanted and the oil taken up in a minimum amount of acetone and then added dropwise to 80 mL of stirring CH_2Cl_2. The resulting precipitate was filtered, washed with CH_2Cl_2 (3 × 1 mL), and dried in vacuo. Yield: 113.5 mg, 0.151 mmol (65%). ^{1}H NMR (acetone-d_6): 210.84, 205.12, 181.44, 169.43, 155.97, 148.84, 125.82 (m, 1H each, NH*H*); 15.89, 7.35, 5.88, –1.24, –7.23, –7.73, –14.50, –20.85 (m, 1H each, CH*H*); 17.88 (d, 2H), 16.90 (d, 2H, $NC_5H_4CONH_2$); 9.68 (d, 1H), 8.41 (d, 1 H, $NC_5H_4CONH_2$). Anal. Calcd for $C_{10}H_{22}N_6ClF_{12}P_2Re$: C, 15.93; H, 2.92; N, 11.15; Cl, 4.71. Found: C, 15.40; H, 3.02; N, 10.56; Cl, 4.79.

***cis*-[ReCl(nic)(en)$_2$](PF$_6$)$_2$ (4).** The procedure for the synthesis of this complex is similar to that for the isonicotinamide complex (**3**) above. Yield: 89%. ^{1}H NMR (acetone-d_6): 205.70, 202.32, 178.12, 168.57, 163.55, 155.42, 151.12, 125.49 (m, 1H each, NH*H*); 15.35, 6.93, 5.81, –0.65, –6.03, –6.36, –12.95, –19.35 (m, 1H each, CH*H*); 17.40 (s, 1H), 16.08 (d-d, 1H), 14.59 (d, 1H), 5.43 (t, 1H, ($NC_5H_4CONH_2$); 9.90 (s, 1H), 8.70 (s, 1H; $NC_5H_4CONH_2$). Anal. Calcd for $C_{10}H_{22}N_6ClF_{12}P_2Re$: C, 15.93; H, 2.92; N, 11.15; Cl, 4.71. Found: C, 15.93; H, 3.06; N, 10.59; Cl, 5.23.

***cis*-[ReCl(pic)(en)$_2$](PF$_6$)$_2$ (5).** The procedure for the synthesis of this complex is similar to that for the pyridine complex (**2**) above. Yield: 76%. ^{1}H NMR (acetone-d_6): 198.61, 195.12, 172.31, 169.28, 160.01, 156.04, 150.35, 127.01 (m 1H each, NH*H*); 13.56, 6.57, 4.90, 0.22, –3.57, –4.54, –10.81, –16.72 (m, 1H each, CH*H*); 16.16 (d, 2H), 11.27 (d, 2H) $NC_5H_4CH_3$; 15.58 (s, 3H) $NC_5H_4CH_3$. Anal. Calcd for $C_{10}H_{23}N_5ClF_{12}P_2Re$: C, 16.57; H, 3.18; N, 9.67; Cl, 4.90. Found: C, 16.90; H, 3.42; N, 9.44; Cl, 5.59.

***cis*-[ReCl(DMAP)(en)$_2$](PF$_6$)$_2$ (6).** The procedure for the synthesis of this complex is similar to that for the pyridine complex (**2**) above. Yield: 39%. All attempts to isolate this complex free of **1** were unsuccessful. Longer reaction times led to significant decomposition. ^{1}H NMR (acetone-d_6): 193.04, 176.13, 171.47, 168.84, 161.68, 155.62, 152.45, 134.22 (m, 1H each, NH*H*); 8.42, 4.71, 3.50, 3.21, 2.38, 1.23, –3.40, –8.67 (m, 1H each, CH*H*); 14.53, 10.52 (s, 2H each, $NC_5H_4NMe_2$); 11.48 (s, 6H, $NC_5H_4NMe_2$).

***cis*-[ReCl(*n*-prNH$_2$)(en)$_2$](PF$_6$)$_2$ (7).** The procedure for the synthesis of this complex is similar to that for the pyridine complex (**2**) above. All attempts to isolate this complex free of **1** were unsuccessful. Longer reaction times led to significant decomposition. ^{1}H NMR (DMSO-d_6): 201.17, 183.17, 162.20, 161.16, 160.53, 159.55, 156.08, 135.01 (m, 1H each, NH*H* of en); 10.32, 4.58, –0.26, –2.98, –9.72, –13.91 (m, 1H each), –2.87 (m, 2H, CH*H* of en); 174.38, 179.45 (m, 1H each, NH*H* of *n*-PrNH$_2$); 0.86 (t, 3H); 1.50 (m, 2H); α-CH_2 hidden under solvent peaks. Peaks were assigned from decoupling experiments.

***trans*-[ReCl(py)(en)$_2$](PF$_6$)$_2$ (8).** To **2** (62.4 mg, 0.0879 mmol) was added 2 mL of MeOH and the solution stirred 4 days. The resulting yellow precipitate was filtered, washed with MeOH (2 × 1 mL), and dried in vacuo. Yield: 13.3 mg, 0.0187 mmol (21%). ^{1}H NMR (acetone-d_6): 152.54, 162.30 (s, 4H each, NH_2); 2.67, 1.55 (m, 4H each, CH_2); 11.71 (t, 2H, meta); –6.66 (d, 2H, ortho); –12.86 (t, 1H, para).

***trans*-[ReCl(DMAP)(en)$_2$](PF$_6$)$_2$ (9).** To **6** (79.4 mg, 0.105 mmol) was added 2 mL of MeOH and the solution stirred 2 days. The resulting green precipitate was filtered, washed with MeOH (2 × 1 mL), and dried in vacuo. Yield: 21.5 mg, 0.0285 mmol (27%). ^{1}H NMR (acetone-d_6): 176.21, 168.84 (m, 4H each, NH_2); 12.18, 11.21 (m, 4H each, CH_2); 3.67 (d, 2H), 2.81 (broad m, 2H) $NC_5H_4NMe_2$; 12.92 (s, 6H, $NC_5H_4NMe_2$).

***trans*-[ReCl$_2$(NH$_3$)$_4$]PF$_6$ (10).** [$ReO_2(NH_3)_4$]Cl (544.0 mg, 1.69 mmol) was placed in 5 mL concentrated HCl and stirred for 30 min resulting in a milky gray mixture. The reaction flask was placed in a 20 °C water bath, and excess zinc amalgam was added. The exothermic reaction bubbled vigorously, was swirled every 10 min, and was removed from the water bath after 30 min. After another 30 min, the reaction was filtered and the yellow solid (**10**-Cl), was collected with the zinc. The solid was dissolved in a minimum amount of H_2O and filtered. The filtrate was treated with a saturated solution of NH_4PF_6 and allowed to sit overnight. The resulting yellow precipitate was collected, washed with H_2O (3 × 2 mL) and OEt_2 (2 × 1 mL), and dried in vacuo. Yield: 242.0 mg, 0.517 mmol (31%). ^{1}H NMR (CD_3CN): 134.22. Anal. Calcd for $H_{12}N_4Cl_2F_6PRe$: H, 2.56; N, 11.97; Cl, 15.15. Found: H, 2.62; N, 12.18; Cl, 16.56.

***trans*-[ReO$_2$(ampy)$_2$]Cl (11).** In a fume hood $Re(O)Cl_3(PPh_3)_2$ (1.1 g, 1.32 mmol) was suspended in acetone (25 mL), 2-(aminomethyl)-pyridine (2 mL), and H_2O (1 mL) and the reaction mixture refluxed for 90 min. The resulting yellow solid was collected, washed with acetone (3 × 3 mL) and OEt_2 (4 mL), and dried in vacuo. Yield = 0.52 g, 1.11 mmol (84%). ^{1}H NMR (D_2O): 9.07 (d, 1H), 8.23 (t, 1H), 7.98 (d, 1H), 7.65 (t, 1H); 4.93 (s, 2H, CH_2). Anal. Calcd for **11**·3H_2O: $C_{12}H_{22}N_4ClO_5Re$: C, 27.51; H, 4.23; N, 10.69. Found: C, 27.70; H, 4.15; N, 10.70.

***trans*-[ReCl$_2$(ampy)$_2$]PF$_6$ (12).** Compound **11** (0.455 g, 0.97 mmol) was dissolved in 6 mL of H_2O, and then treated with 5 mL of 1 M HCl(aq). The solution stirred for 10 min, and upon the addition of Zn/Hg (2.4 g), the reaction immediately darkened. The reaction was stirred for 10 min, and the resulting orange solid and Zn/Hg were collected on a medium frit. The orange solid was extracted with a minimum of H_2O and filtered. Addition of NH_4PF_6 to the filtrate resulted in an orange precipitate. This solid was collected on a fine frit, washed with H_2O (3 × 2 mL), and dried in vacuo. Yield: 0.216 g, 0.349 mmol (36%). ^{1}H NMR (acetone-d_6): 182.36 (s, 4H, NH_2); 26.17 (s, 4H, CH_2); 21.67 (s, 1H), 18.87 (s, 1H), –2.24 (s, 1H), –6.40 (s, 1H). Anal. Calcd for $C_{12}H_{16}N_4Cl_2F_6PRe$: C, 23.30; H, 2.59; N, 9.06. Found: C, 22.90; H, 2.66; N, 9.15.

Crystal Structure Determinations. All X-ray experiments were carried out on a Rigaku AFC6S diffractometer at –120 °C using Mo Kα radiation (λ = 0.710 69 Å). Pertinent details of the data collections and structure determinations are listed in Table I. Crystals of the compounds were mounted on glass fibers and quickly transferred to the cold N_2 stream of the diffractometer. Unit cells were determined using the setting angles of 25 high-angle reflections. The intensities of three standard reflections were monitored during each data collection, showing neither significant decay nor instrument instability. Empirical absorption corrections were applied based on the ψ scans of several reflections. All calculations were performed on a VAXstation 3520 computer using the TEXAN 5.0 crystallographic software package.[12] The structures were solved by direct methods (SIR88).[13] The rhenium atoms were located on two independent inversion centers 0,0,0; 0,$^1/_2$,0 and 0,0,0; 0,$^1/_2$,$^1/_2$, in compounds **1** and **12**, respectively. Full-matrix least-squares refinement was carried out with anisotropic thermal displacement parameters for all non-hydrogen atoms except for the carbon atoms of the ethylenediamine rings in **5**. These carbon atoms were found to be disordered between two equally populated conformations and were refined with isotropic temperature factors. The hydrogen atoms were found in difference Fourier map and included in the calculations without further refinement. The final difference maps showed a peak 2.1 e/Å^3 high located close to the Re(1) atom in the structure of **1**. Otherwise, the difference maps were essentially featureless.

Equilibrium Measurements. A solution of the pyridine complex **2** (1.18 × 10^{-2} M) and 2.2 equiv of isonicotinamide (2.58 × 10^{-2} M) were dissolved in DMAc and allowed to stand. Over a period of several days, aliquots were removed and cyclic voltammograms were recorded to determine the ratio of [**2**]:[**3**]. Once equilibrium was established, K_1 was calculated as (5.6 ± 0.8) × 10^{-1} (eq 1) using the known initial concentrations and equilibrium ratio.[14] This equilibrium constant was also calculated by

(12) TEXAN: Single Crystal Structure Analysis Software, Version 5.0 (1989). Molecular Structure Corp., The Woodlands, TX 77381.
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(14) This error was estimated by taking two limiting interpretations of the ratio of peak currents for **2** and **3**.

Table I. Crystallographic Experimental Details

compound	1	5	12
empirical formula	$ReCl_2PF_6N_4C_4H_{16}$	$ReClP_2F_{12}N_5C_{10}H_{23}\cdot(CH_3)_2CO$	$ReCl_2ON_4C_{39}BH_{42}$
color, habit	yellow, prism	olive-green, prism	yellow, prism
space group	$P\bar{1}$ (No. 2)	$P2_1/c$ (No. 14)	$P\bar{1}$ (No. 2)
cryst syst	triclinic	monoclinic	triclinic
cell dimens			
a (Å)	8.717(1)	9.233(3)	12.334(4)
b (Å)	12.618(2)	17.824(5)	17.345(5)
c (Å)	6.523(1)	13.979(5)	8.918(2)
α (deg)	98.44(2)	90	91.30(3)
β (deg)	102.66(1)	108.15(3)	94.75(3)
γ (deg)	78.50(1)	90	73.29(2)
Z	2	4	2
V, Å^3	682.0(4)	2186(2)	1821(2)
calcd density, g/cm^3	2.543	2.202	1.551
mol wt	522.27	724.91	850.71
2θ max	50.0	50.0	50.0
no. observns ($I > 3\sigma(I)$)	1971	2817	4532
reflcn/param ratio	11.80	10.17	10.37
R	0.033	0.027	0.022
R_w	0.044	0.034	0.035
abs cor	yes	yes	yes
μ(Mo Kα), cm^{-1}	95.98	60.08	35.64

making use of the differing visible absorption spectra for **2** and **3**. A DMAc solution of the isonicotinamide complex **3** (1.71×10^{-2} M) and free pyridine (1.62×10^{-1} M) was prepared, and over a period of 24 h, aliquots were removed, and their absorption spectrum recorded. After 14 h, equilibrium was established, and an equilibrium constant of $K_1 = (6.3 \pm 0.1) \times 10^{-1}$ was calculated using the known molar absorptivities for **2** and **3** at 378 and 502 nm.[15]

Results

The reaction of $[ReO_2(en)_2]Cl$ with excess zinc amalgam in 1 M HCl leads to the formation of the rhenium(III) species *trans*-$[ReCl_2(en)_2]Cl$ which can be precipitated from aqueous solution as the PF_6^- salt (**1**). This bright yellow material is air-stable as a solid but decomposes in air as an acetone solution. The analogous reduction of *trans*-$[ReO_2(ampy)_2]Cl$ (**11**) to *trans*-$[ReCl_2(ampy)_2]Cl$ (**12**) is accomplished in highest yield when 0.4 M acid is used. With greater concentrations of acid, significant decomposition occurs. In similar fashion, *trans*-$[ReO_2(NH_3)_4]Cl$ is reduced with Zn^0/Hg^0 amalgam in HCl(aq) to form *trans*-$[ReCl_2(NH_3)_4]Cl$ (**10**-Cl), which precipitates from the reaction at high concentrations of chloride. In contrast to the ethylenediamine analog, concentrated HCl is required; in 1 or 3 M acid this reaction generates intractable products. The stated reaction conditions evolve a great deal of gas and heat, presumably as a result of the reduction of H^+ to hydrogen,[16] and a water bath is necessary to moderate the reaction. Without the bath, an uncharacterized gray precipitate is formed. *trans*-$[ReCl_2(NH_3)_4]Cl$ (**10**-Cl) has a limited solubility in pure H_2O but can be washed with this solvent to remove traces of acid. Crystalline material is isolated by precipitation from water with NH_4PF_6 in 17% yield. The amine complexes **1**, **10**, and **12** are all moderately water sensitive as solutions of these materials decompose over a period of hours.

When *trans*-$[ReCl_2(en)_2]PF_6$ (**1**) is treated with $TlPF_6$ in the presence of pyridine or a pyridine derivative (L), substitution of one of the chloride ligands occurs, giving *cis*-$[Re(Cl)L(en)_2](PF_6)_2$ and TlCl. In the absence of an appropriate ligand, no chloride abstraction is observed. Limited chloride loss was observed when $NaPF_6$ was used in place of $TlPF_6$ for the same period of time. With L = pyridine, picoline or DMAP, high yields (70–80%) of the dicationic complexes *cis*-$[Re(Cl)L(en)_2]^{2+}$ were obtained after 20–24 h. With the poorer nucleophiles L = isonicotinamide or nicotinamide, a longer reaction time (2 days) was necessary for high yield (65–75%) of the product for a given set of reaction conditions. If more than 1 equiv of $TlPF_6$ is used, some monochloride substitution product is isolated; however, the yield is somewhat reduced. All attempts to cleanly extract both chloride ligands on Re(III) failed. All of the complexes of the form *cis*-$[Re(Cl)L(en)_2](PF_6)_2$ (**2**–**7**) react with acetonitrile to give intractable products, as does their precursor, **1**.

Under concentrations similar to those used for synthesis of the bis(ethylenediamine)–pyridine complex (**2**), substitution of chloride with *n*-propylamine requires at least 48 h for a 34% NMR yield of product. If left to react longer (5 days), significant decomposition occurs and the major product recovered is the starting material *trans*-$[ReCl_2(en)_2]PF_6$ (**1**). Attempted substitution reactions with trimethylphosphine, pyrazine, or *tert*-butyl isonitrile each gave crude products with preliminary evidence of chloride substitution; however, attempts to further purify and characterize these products have been unsuccessful. Attempted substitution reactions with cyclohexylphosphine or carbon monoxide at 25 °C gave only starting materials after 5 days.

Substitution of pyridine for another ligand was observed when $[Re(Cl)py(en)_2](PF_6)_2$ (**2**) was allowed to react in DMAc with either *tert*-butylisonitrile, 4-picoline, DMAP, *n*-propylamine, or isonicotinamide. In each case, though beginning with pure **2**, a significant amount (up to 50%) of *trans*-$[ReCl_2(en)_2]PF_6$ (**1**) was isolated along with the substitution product. All attempts to isolate or characterize other products, (e.g. $[Re(en)_2L_2]^{2+}$ species) from these reactions have been unsuccessful.

Attempted substitution of a chloride on $[ReCl_2(ampy)_2]PF_6$ (**12**) with $TlPF_6$ and pyridine or cyclohexene in DMAc, acetone, or acetonitrile (20 °C) or in refluxing acetonitrile (82 °C) gave decomposition of the starting material along with traces of substitution product.

^{1}H NMR. $[ReCl_2(en)_2]PF_6$ (**1**) exhibits a sharp, paramagnetically shifted ^{1}H NMR spectrum such as has been observed for other Re(III) compounds.[17] Resonances at 169.5 and 10.5 ppm are assigned to the amine protons and the methylene protons respectively, based upon the observation that the intensity of the downfield peak decreases upon addition of D_2O to the NMR sample. Each of the complexes $[Re(Cl)L(en)_2](PF_6)_2$ (**2**–**7**) exhibit a paramagnetically shifted ^{1}H NMR spectrum in which a distinct resonance for each of the amine (207–134 ppm) and ethylene (+12 to −15 ppm) protons is observed, and the implied asymmetry of these complexes indicates a cis-coordination geometry.

(15) Isonicotinamide and pyridine are transparent at 378 and 502 nm.
(16) The reduction of hydrogen appears to be catalyzed by a rhenium species. For a detailed analysis of a related system, see ref 25.

(17) Conry, R. R.; Mayer, J. M. *Inorg. Chem.* **1990**, *29*, 4862.

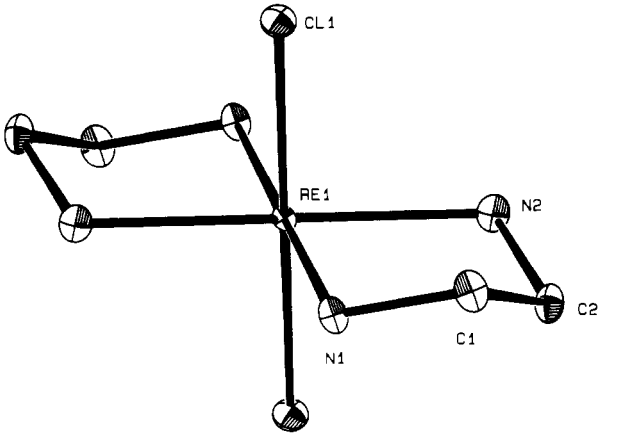

Figure 1. ORTEP drawing of *trans*-$[ReCl_2(en)_2]^+$ shown with 50% thermal elipsoids.

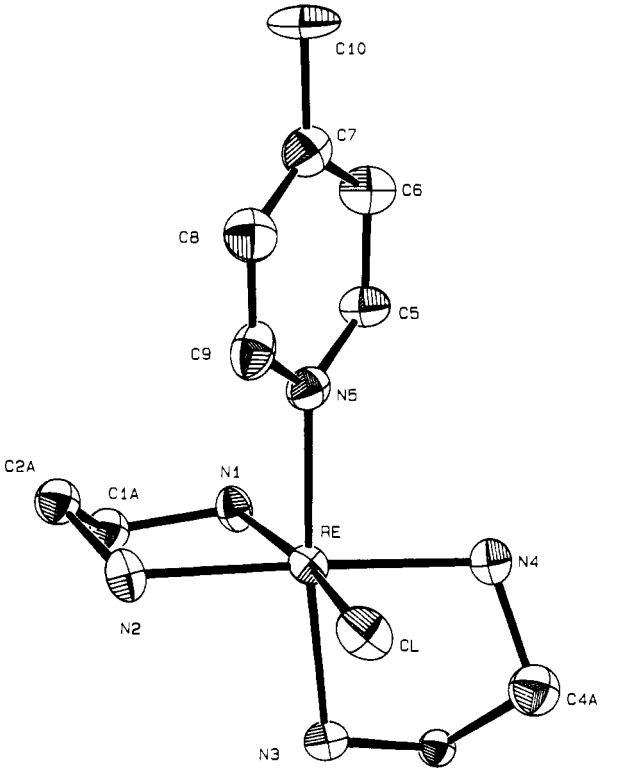

Figure 2. ORTEP drawing for *cis*-$[ReCl(picoline)(en)_2]^{2+}$ shown with 50% thermal elipsoids.

Similar to **1**, the compound $[ReCl_2(NH_3)_4]PF_6$ (**10**) shows a single resonance in acetonitrile-d_3 at 134.2 ppm for the ammine protons while $[ReCl_2(ampy)_2]PF_6$ (**12**) has a corresponding resonance in the Re(III)–amine region at 182.4 ppm. Thus, in solution a trans configuration is observed for each of the dichloride compounds reported.

Structural Features. ORTEP drawings for the cations $[ReCl_2(en)_2]^+$ (**1**), $[ReCl(pic)(en)_2]^{2+}$ (**5**), and $[ReCl_2(ampy)_2]^+$ (**12**) are presented in Figures 1–3 respectively, and the corresponding geometrical data are listed in Tables III and IV. In all cases, the ligands form an octahedral geometry about the Re metal center with metal–ligand bond distances which are typical of other Re(III) complexes.[18] The rhenium atoms in the structures of the bis(chloride) species **1** and **12** each occupy an inversion center which confers a Cl–Re–Cl angle of 180° for each complex. For the picoline compound **5**, a cis stereochemistry between the halide and heterocycle is observed. For all three structures, rhenium-chloride bonds are consistantly 2.35 ± 0.01 Å, and rhenium–nitrogen distances range from 2.11 to 2.18 Å where the heterocyclic nitrogens are held on average 0.04 Å closer to the metal than those of the saturated amine ligands.

(18) Orpen, A. G.; Brammer, L.; Allen, F. H.; Kennard, O.; Watson, D. G.; Taylor, R. *J. Chem. Soc., Dalton Trans.* **1989**, S1–S83.

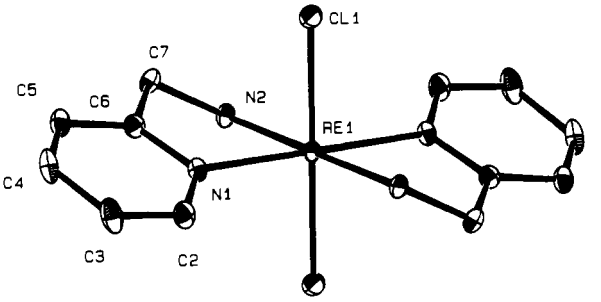

Figure 3. ORTEP drawing for *trans*-$[ReCl_2(ampy)_2]^+$ shown with 50% thermal elipsoids.

Table II. Selected Positional Parameters for the Structural Determinations of **1**, **5**, and **12**

atom	*x*	*y*	*z*	*B*, Å^2
		$[ReCl_2(en)_2]PF_6$ (**1**)		
Re(1)	0	0	0	0.71(2)
Cl(1)	–0.0527(2)	0.1294(1)	–0.2455(3)	1.36(7)
N(1)	0.2517(7)	0.0020(4)	0.0366(8)	1.1(2)
N(2)	0.0630(7)	–0.1309(4)	–0.2372(8)	1.3(2)
C(1)	0.3125(8)	–0.0616(5)	–0.150(1)	1.3(3)
C(2)	0.2406(9)	–0.1641(5)	–0.205(1)	1.4(3)
		$[ReCl(pic)(en)_2](PF_6)_2$ (**5**)		
Re	0.12778(3)	0.02041(2)	0.21840(2)	1.79(1)
Cl	0.2066(2)	0.0380(1)	0.0751(1)	3.04(8)
N(1)	0.0740(6)	0.0172(3)	0.3580(4)	1.8(2)
N(2)	0.2258(7)	0.1246(3)	0.2854(4)	2.5(2)
N(3)	0.3272(6)	–0.0494(4)	0.2851(4)	2.5(2)
N(4)	0.0379(6)	–0.0877(3)	0.1594(4)	2.4(2)
N(5)	–0.0823(6)	0.0760(3)	0.1526(4)	2.1(2)
C(1a)	0.159(2)	0.0756(9)	0.428(1)	2.3(3)
C(2a)	0.158(2)	0.1465(8)	0.367(1)	2.3(3)
C(3a)	0.280(1)	–0.1315(7)	0.281(1)	1.4(2)
C(4a)	0.173(2)	–0.142(1)	0.168(1)	2.6(3)
C(5)	–0.2152(8)	0.0441(4)	0.1535(5)	2.3(3)
C(6)	–0.3552(8)	0.0769(4)	0.1148(5)	2.7(3)
C(7)	–0.3668(8)	0.1483(4)	0.0705(5)	2.6(3)
C(8)	–0.2319(9)	0.1807(4)	0.0683(5)	3.0(3)
C(9)	–0.0952(9)	0.1443(4)	0.1061(5)	2.8(3)
C(10)	–0.5191(9)	0.1869(5)	0.0321(7)	3.9(4)
		$[ReCl_2(ampy)_2]BPh_4$ (**12**)		
Re(1)	0	0	0	1.23(1)
Cl(1)	0.0095(1)	0.09199(8)	0.1945(1)	2.13(6)
N(1)	0.0242(3)	0.0841(2)	–0.1528(4)	1.5(2)
N(2)	0.1819(3)	–0.0295(2)	–0.0056(4)	1.6(2)
C(2)	–0.0562(4)	0.1274(3)	–0.2531(6)	2.3(3)
C(3)	–0.0410(4)	0.01885(4)	–0.3342(6)	2.8(3)
C(4)	0.0604(4)	0.2087(3)	–0.3100(6)	2.6(3)
C(5)	0.1457(4)	0.1618(3)	–0.2144(5)	2.0(3)
C(6)	0.1264(4)	0.0994(3)	–0.1380(5)	1.8(2)
C(7)	0.2164(4)	0.0447(3)	–0.0346(5)	1.7(2)

Table III. Selected Bond Lengths (Å) for Compounds **1**, **5**, and **12**

	$[ReCl_2(en)_2]PF_6$ (**1**)		
Re(1)–Cl(1)	2.364(2)	Re(1)–N(2)	2.164(5)
Re(1)–N(1)	2.159(5)		
	$[ReCl(pic)(en)_2](PF_5)_2$ (**5**)		
Re–Cl	2.352(3)	Re–N(3)	2.186(7)
Re–N(1)	2.167(7)	Re–N(4)	2.173(7)
Re–N(2)	2.163(7)	Re–N(5)	2.123(7)
	$[ReCl_2(ampy)_2]BPh_4$ (**12**)		
Re(1)–Cl(1)	2.349(1)	Re(1)–N(2)	2.157(4)
Re(1)–N(1)	2.118(4)		

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

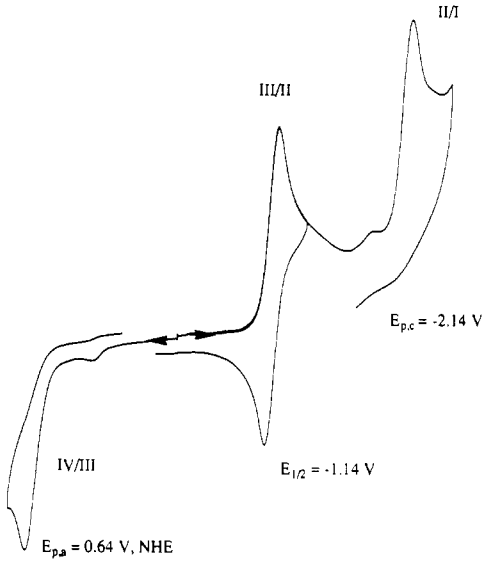

Figure 4. Cyclic voltammogram for the complex $[ReCl(py)(en)_2]^{2+}$ recorded in DMAc (TBAH; 100 mV/s).

Table IV. Selected Bond Angles (deg) for Compounds **1**, **5**, and **12**

$[ReCl_2(en)_2]PF_6$ (**1**)	
Cl(1)–Re(1)–N(1)	88.8(1)
Cl(1)–Re(1)–N(2)	91.4(1)
$[ReCl(pic)(en)_2](PF_6)_2$ (**5**)	
Cl–Re–N(1)	172.5(5)
Cl–Re–N(2)	92.7(2)
Cl–Re–N(3)	89.6(2)
Cl–Re–N(4)	88.5(2)
Cl–Re–N(5)	93.1(2)
N(3)–Re–N(5)	173.1(3)
N(4)–Re–N(5)	93.4(3)
$[ReCl_2(ampy)_2]BPh_4$ (**12**)	
Cl(1)–Re(1)–N(1)	88.3(1)
Cl(1)–Re(1)–N(2)	89.2(1)
N(1)–Re(1)–N(2)	75.7(1)

Electrochemistry. A cyclic voltammogram of $[ReCl_2(en)_2]^+$ (**1**) recorded in DMAc at 100 mV s^{-1} shows a chemically irreversible 1 e^- oxidation wave at 0.18 V (NHE) and an irreversible two-electron reduction wave at −1.88 V.[19] When recorded in CH_3CN at the same scan rate, the oxidation wave becomes reversible with $E_{1/2}$ = 0.42 V, NHE. Similar behavior is observed for *cis*-$[ReCl(n\text{-}prNH_2)(en)_2](PF_6)_2$ (**7**), which in DMAc at 100 mV s^{-1} has an irreversible one-electron oxidation wave at 0.44 V and a two-electron reduction wave at −1.73 V. A cylic voltammogram for the pyridine complex **2** is shown in Figure 4 and features three one-electron waves: an irreversible III/IV oxidation, a reversible III/II couple, and an irreversible II/I reduction. Values for $E_{1/2}$ and E_p are summarized in Table V. The reversible nature of the III/II couple for the complexes **2**–**7** is diminished upon decreasing the scan rate or upon holding at a potential more negative than the reduction potential. These observations are consistent with the notion that the Re(II) species is unstable for extended periods. Attempts to reduce **2** or **3** chemically (Na^0/Hg^0 or Mg^0; 20 min) fail to produce detectable amounts of their Re(II) analogs, as determined from rotating-disk-electrode voltammetry, and aside from $[ReCl_2(en)_2]^+$, the nature of the decomposition products has not been identified.

trans-$[ReCl_2(NH_3)_4]PF_6$ (**10**) exhibits an irreversible 2 e^- reduction wave at −1.84 V and a reversible III/IV couple at 0.34 V in DMAc at 100 mV s^{-1}, similar to the bis(ethylenediamine) complex **1**. In contrast, *trans*-$[ReCl_2(ampy)_2]PF_6$ (**12**) exhibits a reversible III/II couple at −1.15 V, and an irreversible II/I wave at −2.01 V, potentials which are similar to the pyridine complex $[Re(Cl)py(en)_2](PF_6)_2$ (**2**).

(19) The number of electrons corresponding to the redox process was determined by preparing a sample with a weighed amount of ferrocene and a weighed amount of the compound and comparing the ratio of the unknown wave to the ferrocene wave.

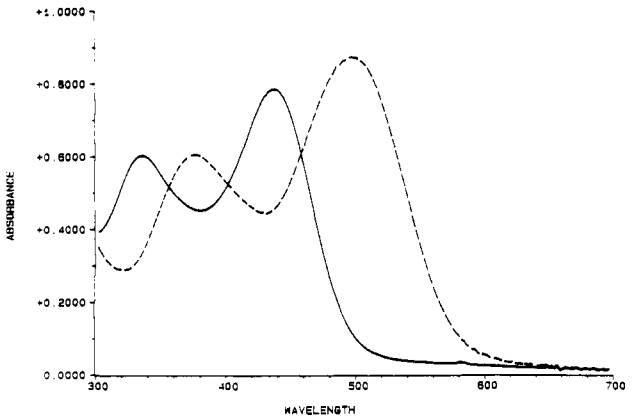

Figure 5. Absorption spectra for $[Re(en)_2(py)Cl](PF_6)_2$ (solid line) and $[Re(en)_2(isn)Cl](PF_6)_2$ (dashed line).

Table V. Cyclic Voltammetric Data for Re(III) Cations[d]

complex	Re(IV/III) $E_{p,a}$ (V)	Re(III/II) $E_{1/2}$ (V)	Re(II/I) $E_{p,c}$ (V)
$[ReCl(isn)(en)_2]^{2+}$	0.76	−0.93[a]	−2.11
$[ReCl(nic)(en)_2]^{2+}$	0.65	−1.10[a]	−1.98
$[ReCl(py)(en)_2]^{2+}$	0.64	−1.14[a]	−2.14
$[ReCl(pic)(en)_2]^{2+}$	0.60	−1.24[a]	−2.24
$[ReCl(DMAP)(en)_2]^{2+}$	0.42	−1.44[a]	*c*
$[ReCl(n\text{-}prNH_2)(en)_2]^{2+}$	0.44	−1.73[b]	
$[ReCl_2(en)_2]^+$	0.18	−1.88[b]	
$[ReCl_2(ampy)_2]^+$	0.53	−1.15[a]	−2.01
$[ReCl_2(NH_3)_4]^+$	0.34[a]	−1.84	

[a] Reversible couple; ($E_{1/2}$). [b] A 2-electron wave. [c] Not observed; $E_{p,c}$ < −2.3 V. [d] Note: All scans recorded in DMAc; values reported vs NHE.

Table VI. Electronic Absorption Features for the Compounds $[ReCl(L)(en)_2]^{2+}$

compound	wavelength (nm)	ϵ (M^{-1} cm^{-1})
cis-$[ReCl(isn)(en)_2]^{2+}$ (**3**)	378	2.9×10^3
	502	4.4×10^3
cis-$[ReCl(nic)(en)_2]^{2+}$ (**4**)	352	2.1×10^3
	462	2.8×10^3
cis-$[ReCl(py)(en)_2]^{2+}$ (**2**)	336	2.4×10^3
	438	3.1×10^3
trans-$[ReCl(py)(en)_2]^{2+}$ (**8**)	330	
	434	
cis-$[ReCl(pic)(en)_2]^{2+}$ (**5**)	328	3.4×10^3
	428	2.7×10^3
cis-$[ReCl(DMAP)(en)_2]^{2+}$ (**6**)	324	1.7×10^4
	368	4.3×10^3
trans-$[ReCl_2(ampy)_2]^+$ (**12**)	372	2.8×10^3
	478	3.8×10^3
$[Os(NH_3)_5(py)]^{2+}$ (H_2O/HCO_3^-)[a]	430	1.1×10^4
	553	3.5×10^3
$[Os(NH_3)_5(isn)]^{2+}$ (H_2O/HCO_3^-)[a]	508	1.5×10^4

[a] See reference 26.

Electronic Spectra. In Table VI, relevant absorption data are presented for these Re(III) compounds. The parent ethylenediamine complex, $[ReCl_2(en)_2]PF_6$ (**1**) shows no absorbance maximum between 270 and 800 nm, but the spectra of the pyridine analogs (**2**–**6**) show two broad bands with molar absorptivities on the order of 10^3 M^{-1} cm^{-1} (Figure 5). As noted in Table VII, both absorption bands of the pyridine complex **2** show λ_{max} values which are solvent dependent. For the ampy complex **12**, absorption maxima occur at 478 and 372 nm, absorptions which are similar, both in energy and in intensity, to those of the monosubstituted pyridine analogs.

Isomerization. When *cis*-$[ReCl(py)(en)_2](PF_6)_2$ (**2**) is stirred in MeOH over a 4-day period, a precipitate, **8**, forms. The ^1H NMR is paramagnetically shifted and shows only two amine resonances and two methylene resonances for the new material. A cyclic voltammogram of **8** reveals virtually no change in the reduction potential from its precursor **2**. A UV/Vis absorption spectrum of **8** shows absorption maxima at 434 and 388 nm, values which also are virtually identical to those for **2**. When **8** is stirred in DMAc for 24 h, the ^1H NMR spectrum of the resulting product shows complete conversion back to the original material (**2**).[20] Taken together, these observations indicate that a cis-to-trans isomerization occurs in methanol which appears to be thermodynamically driven by the insolubility of **8** in this solvent. Virtually identical behavior is witnessed for the DMAP analog **6**, which converts to its insoluble trans isomer (**9**) in methanol.

The rate of the conversion of **8** to **2** was measured by recording the ^1H NMR spectra of the mixture in acetone-d_6 over a 24-h period and observing the appearance of the peaks corresponding to the cis form. From these data we estimate the half-life for isomerization in acetone to be on the order of 28 h for *trans*-$[ReCl(py)(en)_2](PF_6)_2$ (**8**).

Substitution. In order to gain insight into the relative affinities of Re(III) and Re(II) for various ligands in the ethylenediamine ligand environment, the equilibrium constant for the substitution of pyridine by isonicotinamide was established on Re(III) by two separate methods. For the equilibrium constant for eq 1, a value of $K_1 = (6.3 \pm 0.1) \times 10^{-1}$ was calculated, as determined from absorption spectra recorded at equilibrium. This value was verified by cyclic voltammetric data, which yielded on equilibrium ratio of $(5.6 \pm 0.8) \times 10^{-1}$.

$$cis\text{-}[ReCl(py)(en)_2]^{2+} + isn = cis\text{-}[ReCl(isn)(en)_2]^{2+} + py \quad (1)$$

Now taking the reduction potentials for the Re(III) isonicotinamide (**3**) and pyridine (**2**) complexes, and combining these equations, an equilibrium constant (K_2) can be calculated for the redox reaction shown in eq 2. When eqs 1 and 2 are combined (eq 3), an equilibrium constant, $K_3 = 2.2 \times 10^3$, is obtained corresponding to substitution of isn for pyridine on Re(II).[21] This relates to a free energy of substitution of –4.5 kcal/mol. at 25 °C, where Re(II) favors the electron-deficient isonicotinamide ligand over its parent pyridine.

$$[ReCl(isn)(en)_2]^{2+} + [ReCl(py)(en)_2]^{+} = [ReCl(py)(en)_2]^{2+} + [ReCl(isn)(en)_2]^{+}$$

$$K_2 = 3.5 \times 10^3 \quad (2)$$

$$[ReCl(isn)(en)_2]^{2+} + [ReCl(py)(en)_2]^{+} = [ReCl(py)(en)_2]^{2+} + [ReCl(isn)(en)_2]^{+}$$

$$isn + [ReCl(py)(en)_2]^{2+} = py + [ReCl(isn)(en)_2]^{2+}$$

$$\text{net: } isn + [ReCl(py)(en)_2]^{+} = py + [ReCl(isn)(en)_2]^{+}$$

$$K_3 = 2.2 \times 10^3 \quad (3)$$

(20) A small amount of $[ReCl_2(en)_2]PF_6$ (**1**) is isolated along with the substituted products, even when beginning with pure pyridine complex **2**.

(21) Where $\log K_{eq} = n(E^\circ_1 - E^\circ_2)/(0.0592\ V)$. The stereochemistry of Re(II) could not be defined.

Table VII. Selected Electronic Absorption Features for $[ReCl(py)(en)_2](PF_6)_2$ (**2**) in Various Solvents

solvent	λ_1 (nm)	λ_2 (nm)
DMAc	336	438
DMSO	334	438
Acetone	336	418
MeOH	330	426
H_2O	338	424

In a related experiment, a DMAc solution of the pyridine complex **2** and 1 equiv of PPNCl, a soluble chloride ion source, was allowed to stand for 20 h. After precipitation of the rhenium, ^1H NMR and cyclic voltammograms revealed the complete transformation to $[ReCl_2(en)_2]PF_6$. Thus, for the equilibrium defined in eq 4, the equilibrium constant (K_4) is estimated to be >20. However, when a DMAc solution of **1** was stirred with 1 M pyridine, cyclic voltammograms taken over a period of 24 h revealed ~50% conversion to the pyridine complex **2**. Taking the known initial concentrations of **1** and pyridine together with the equilibrium quotient of [**1**]/[**2**] = 1.0, an equilibrium constant may be calculated for eq 4 of $K_{eq} = 140$ in DMAc.

$$cis\text{-}[ReCl(py)(en)_2]^{2+} + Cl^- = trans\text{-}[ReCl_2(en)_2]^{+} + py$$

$$K_4 = 140 \text{ (in DMAc)} \quad (4)$$

Discussion

It was once believed that the tendency of Re(III) to form metal–metal bonds virtually precluded the existence of mononuclear rhenium(III). Though reports of mononuclear, octahedral rhenium(III) are now commonplace, virtually all of these structures include moderate to strong π-acid ligands such as phosphines, arsines, CO, or isonitriles in the coordination sphere.[22] Only in the last few years have the first Re(III) complexes been described which contain predominantly saturated ligand environments. Mayer et al. have reported several complexes of the form $[Re(Me_3tacn)Cl_2L]^+$ (Me_3tacn = 1,4,7-trimethyltriazacyclononane; L = OPR_3, CH_3CN, py), prepared from phosphine reduction of the corresponding Re(V)–oxo species,[17] and Wieghardt et al. have described a procedure similar to that of the present study in which $[Re^V(tacn)(O)(OCH_2CH_2O)]^+$ was reduced with Zn^0 dust in excess HX to form $[Re(tacn)X_3]^+$ (X = Br, Cl).[23]

Given the abundance of Re(III) complexes containing π-acid ligands, and the reported ability of certain Re(III) species to catalyze the reduction of protons (pH = 1) at modest reduction potential (–0.52 V, SSCE),[24] it is noteworthy that the affinity of $[Re(en)_2Cl]^{2+}$ for chloride is greater than that for pyridine in DMAc where $K_4 = 140$. When one considers that this equilibrium constant also reflects an isomerization, then for the case where the trans configuration is mantained, $[Re(en)_2Cl]^{2+}$ prefers the halide by $>10^3$. Though a comparison is not readily available for Os(III), the moiety $[Ru(NH_3)_5]^{3+}$ has a clear preference for pyridine over chloride ion in aqueous solution ($K_{eq} = 0.035$). Note in Table VIII that the analogous equilibrium constant for the reputed π-base $[Ru(NH_3)_5]^{2+}$ is 6×10^{-8}. The greater ability of water to solvate chloride ion and to stabilize more highly charged cations accounts for part of this deficiency, but one can safely conclude that pyridine ligands essentially function as pure σ donors for Re(III), even when the metal is in a saturated ligand field (i.e. $[Re(en)_2Cl]$). Re(III) complexes have been reported which

(22) (a) Rouschias, G. *Chem Rev*, **1974**, *74*, 531. (b) Lever, A. P. B., *Inorg. Chem.* **1991**, *30*, 1980 and references within.

(23) Böhm, G.; Wieghardt, K.; Nuber, B.; Weiss, J. *Inorg. Chem.* **1991**, *30*, 3464.

(24) Pipes, D. W.; Meyer, T. J.; *Inorg. Chem.* **1986**, *25*, 3256.

Table VIII. Equilibrium Data for the Generalized Reaction

$$L_nM\text{-}L_A + L_B = L_nM\text{-}L_B + L_A$$

L_nM	L_A	L_B	K_{eq}	ref
$[Ru(NH_3)_5]^{2+}$	H_2O	Cl^-	1.6^a	31
$[Ru(NH_3)_5]^{2+}$	H_2O	py	$2.5 \times 10^{7\,a}$	32
$[Ru(NH_3)_5]^{2+}$	H_2O	isn	$3.0 \times 10^{8\,a}$	32
$[Ru(NH_3)_5]^{2+}$	py	isn	1.2×10^{1}	*c*
$[Ru(NH_3)_5]^{2+}$	py	Cl^-	6.4×10^{-8}	*c*
$[Ru(NH_3)_5]^{3+}$	H_2O	Cl^-	$1.0 \times 10^{2\,a}$	31
$[Ru(NH_3)_5]^{3+}$	H_2O	py	$3 \times 10^{3\,a}$	32
$[Ru(NH_3)_5]^{3+}$	H_2O	isn	$1.8 \times 10^{3\,a}$	32
$[Ru(NH_3)_5]^{3+}$	py	isn	6.0×10^{-1}	*c*
$[Ru(NH_3)_5]^{3+}$	py	Cl^-	3.5×10^{-2}	*c*
$[Os(NH_3)_5]^{3+}$	py	isn	~ 1	33
$[Os(NH_3)_5]^{2+}$	py	isn	$\sim 2.5 \times 10^{2}$	34
$[Re(en)_2Cl]^{2+}$	py	isn	$6.3 \times 10^{-1\,b}$	*d*
$[Re(en)_2Cl]^{2+}$	nic	isn	~ 1	*d*
$[Re(en)_2Cl]^{2+}$	py	Cl^-	$1.4 \times 10^{2\,b}$	*d*
$[Re(en)_2Cl]^{+}$	py	isn	$2.2 \times 10^{3\,b}$	*d*
$[Re(en)_2Cl]^{+}$	nic	isn	$7.5 \times 10^{2\,b}$	*d*
$[Re(en)_2Cl]^{+}$	py	Cl^-	$<4 \times 10^{-11\,b}$	*d*

[a] Reported for aqueous solution where the activity of water is unity. [b] Value reported for DMAc solution. [c] See Discussion. [d] This work.

function as π-bases with stronger π-acids such as CO.[25] This point is further illustrated when the equilibrium between the pyridine (**2**) and isonicotinamide (**3**) complexes is considered. In DMAc solvent, the moiety $[Re(en)_2Cl]^{2+}$ slightly favors pyridine to the better π-acid isonicotinamide ($K_1 = 0.63$). For comparison, $[Ru(NH_3)_5]^{3+}$ has a corresponding $K_{eq} = 0.6$ for substitution of pyridine by isonicotinamide (Table VIII).

In contrast to Re(III), the more electron-rich moiety $[Re^{II}(en)_2Cl]^+$ is shown to have a pronounced preference for the more electron-deficient π-acid isonicotinamide compared to pyridine (recall $K_3 = 2.2 \times 10^3$). For $[Ru(NH_3)_5]^{2+}$ $K_{eq} = 12$ for substitution of pyridine by isonicotinamide. Though no experimental information is available for the π-base $[Os(NH_3)_5]^{2+}$, if one assumes that the affinity for $[Os(NH_3)_5]^{3+}$ is comparable ($K_{eq} \sim 1$) for these two heterocycles, as is the case for $[Re(en)_2Cl]^{2+}$ and $[Ru(NH_3)_5]^{3+}$, the reported reduction potentials for $[Os(NH_3)_5(isn)]^{3+}$ (0.395 V, NHE) and $[Os(NH_3)_5(isn)]^{3+}$ (0.240 V)[26] indicate an equilibrium constant for Os(II) of about $K_{eq} \sim 250$ (Table VIII), an order of magnitude less than for Re(II).

Given that the Re(III) affinities for py and isonicotinamide are nearly identical, the 170-mV difference between the III/II couples for isonicotinamide and nicotinamide is likely to be entirely a consequence of differences in binding affinities on Re(II). This interpretation leads to an estimate of $K_5 = 750$ for the equilibrium quotient $[[ReCl(isn)(en)_2]^+][nic]/[[ReCl(nic)(en)_2]^+][isn]$. The magnitude of this ratio is most likely a direct result of the lower energy and greater coefficient on N for the LUMO of the C4-substituted pyridine (isn), relative to its 3-substituted isomer (nic).[27]

The irreversible nature of the reduction of $[ReCl_2(en)_2]^+$ prevents an accurate assignment of the corresponding III/II reduction potential from our cyclic voltammetric data. Given that the cathodic peak of −1.88 V corresponds to a 2 e^- reduction, the process occurring at the electrode surface is most likely described by an E_rC_iE type reaction where the hypothetical transient reduction product $[ReCl_2(en)_2]^0$ is chemically unstable and converts to a second electroactive product. As the scan rate is varied from 20 to 100 mV/s, the ratio of i_p to $v^{1/2}$ decreases by less than 5% (where i_p and v are peak current and scan rate, respectively) an observation which supports the notion that the first electrochemical step is reversible.[28] $E_{p,c}$ shifts negative by about 40 mV over this range, and at scan rates as high as 2 V/s, no return wave is detected. Taken together, these observations suggest that $E° < -1.88$ V, the value for $E_{p,c}$ reported at 100 mV/s. With a limiting value for the reduction potential of **1**, the reduction potential of **2**, and the equilibrium constant K_4 in hand, an upper limit of $K_7 < 4 \times 10^{-11}$ may be established for the equilibrium constant which governs the substitution of a chloride for a pyridine on $[Re^{II}Cl_2(en)_2]^+$ in DMAc. This value, which corresponds to a free energy of ≥14 kcal/mol, is not available from experiment for $[Os(NH_3)_5]^{2+}$, but can be compared with $K_{eq} = 6.4 \times 10^{-8}$ for the π-base $[Ru(NH_3)_5]^{2+}$ (Table VIII). For the pentaammineosmium system, it is tempting to assign a value for the equilibrium constant governing the substitution of Cl^- by pyridine on $[Os(NH_3)_5]^{3+}$ as equal to that for its congener. Making this approximation allows one to estimate the corresponding value for Os(II) from the reported electrochemical data.[29] Thus, an estimate of $K_{eq} \sim 10^{-9}$ can be made for the affinity of chloride ion compared to pyridine for Os(II). In comparing the relative affinities for Cl and py ligands for $[Ru^{II}(NH_3)_5]^{2+}$, $[Os^{II}(NH_3)_5]^{2+}$, and $[Re^{II}Cl(en)_2]^+$, Re(II) clearly shows the greatest preference for the π-acid over the halide when one considers that the value established for K_7 is an upper limit and is valid only for DMAc, a solvent which is less effective than water at solvating chloride ion.[30]

$$[ReCl_2(en)_2]^+ + e^- = [ReCl_2(en)_2]^0$$

$$[ReCl(py)(en)_2]^+ = [ReCl(py)(en)_2]^{2+} + e^- \qquad K_6 < 3 \times 10^{-13}$$

$$[ReCl(py)(en)_2]^{2+} + Cl^- = [ReCl_2(en)_2]^+ + py \qquad K_4 = 140$$

$$\text{net:} \quad [ReCl(py)(en)_2]^+ + Cl^- = [ReCl_2(en)_2]^0 + py \qquad K_7 < 4 \times 10^{-11} \quad (5)$$

In contrast to the parent complex $[ReCl_2(en)_2]^+$ (**1**), which has no absorption maxima over the range 270–800 nm, two absorptions are observed for the monopyridine derivatives, each with extinction coefficients well over 10^3 M^{-1} cm^{-1} (Table VI). As the bis(chloride) complex **1** fails to show any low-energy absorptions, the possibility of a chloride-to-rhenium charge transfer in the visible region for the monpyridine complexes seems unlikely. As the pyridine-derived ligand ranges from electron-deficient (e.g. isn) to electron-rich (e.g. DMAP), the energies of the absorption maxima steadily increase, consistent with the behavior of a rhenium-to-pyridine charge transfer. The moderate solvent dependence of the λ_{max} values (Table VII) and the intensities of these absorptions further support this interpretation.

(25) As an example, the complex $ReCl_3(CO)(PMe_2Ph)_3$ may be obtained by passing CO through $ReCl_3(PMe_2Ph)_3$ in boiling ethanol solution. (See ref 22a and references within).
(26) Sen, J.; Taube, H. *Acta Chem. Scand.* **1979**, *33*, 125.
(27) Extended Hückel Calculations: isonicotinamide: E(LUMO) = −9.874 eV; coefficient on pyridine N: 0.46. nicotinamide: E(LUMO) = −9.452 eV; coefficient on pyridine N: 0.33.
(28) Bard, A. J.; Faulkner, L. R. In *Electrochemical Methods*; John Wiley & Sons, Inc.: New York, 1980; pp 452–461.
(29) $[Os(NH_3)_5(py)]^{3+/2+}$: $E° = -0.395$ V, NHE). See ref 26. $[Os(NH_3)_5Cl]^{2+/+}$: ($E° = -0.85$ V, NHE): Gulens, J. Page, J. A. *J. Electroanal. Chem. Interfacial Electrochem.* **1976**, *67*, 215.
(30) The stereochemistry of the Re(II) complexes could not be defined. In water, K_4 is expected to be lower. For instance, taking K_4 as equal to that reported for Ru(III), ($K = 0.035$) leads to a value for K_7 of $<1 \times 10^{-14}$.
(31) Lim, H. S.; Barclay, D. J.; Anson, F. C. *Inorg. Chem.* **1972**, *11*, 1460.
(32) Wishart, J. F.; Taube, H.; Breslauer, K. J.; Isied, S. S. *Inorg. Chem.* 23, 2997.
(33) Estimated value. Compare to Re(III) and Ru(III) data in Table 8.
(34) Value calculated from reduction potentials (see ref 25) and $K_{eq} \sim 1$ for Os(III) analog.

Notably, the energies corresponding to these charge transfer events are closer to those observed for the $[Os(NH_3)_5(py)]^{2+}$ derivatives, than to the Os(III) analogs which are featureless above 300 nm.[26] This observation is consistent with the notion that the energy of the metal orbitals is somewhat higher for the earlier transition metal.

The conversion of *cis*-$[ReCl(L)(en)_2](PF_6)_2$ to *trans*-$[ReCl(L)(en)_2](PF_6)_2$ (L = pyridine or DMAP) in methanol also deserves comment. Only the cis product is isolated from the reaction of *trans*-$[ReCl_2(en)_2]^+$ with the pyridine derivative. Prolonged stirring (1 week) of the product **2** at room temperature or refluxing in a DMAc/pyridine mixture produces no conversion to the trans isomer. However, stirring in methanol produces this isomer exclusively. As the yield for this isomerization reaction is low and some *trans*-$[ReCl_2(en)_2]PF_6$ is isolated along with the product, we are unable to determine whether this isomerization is driven by the insolubility of the products or by some sort of chemical mediation by methanol. When the trans isomers **8** or **9** are returned to DMAc or to acetone solvent, complete conversion to **2** and **6** occurs, respectively, which confirms that the cis products are thermodynamically preferred.

It was our hope that these Re(III) complexes would serve as useful precursors to Re(II) and Re(I) amine species and that these reduction products could be effective dearomatization agents for organic synthesis such as has been demonstrated for pentammineosmium(II).[7] Reductions of both $[Re(Cl)isn(en)_2](PF_6)_2$ and $[ReCl_2(ampy)_2](PF_6)$ were carried out under a variety of conditions. With either Na^0 or Mg^0 in the presence of benzene, anisole or pyridine, the reductions failed to produce detectable amounts of any diamagnetic Re(I) complex. Electrochemical experiments also were conducted to probe for transient η^2-arene complexes. In a typical experiment, the rhenium complex was placed in the electrochemical cell along with the solvent, electrolyte, and an arene (benzene or anisole). The potential was scanned negatively through the III/II couple and the II/I couple, held momentarily, then reversed. For compounds **1–3**, **6**, **9**, and **12**, no new electrochemical features were observed which differed from the control where the arene was omitted.

Summary

Several mononuclear octahedral Re(III) and Re(II) species are reported containing only amine and halide ligands, complexes which represent a significant departure from those previously reported in that the ligand environment is predominantly saturated. The rhenium fragment $[ReCl(en)_2]^{2+}$ shows preference for σ and π donors much the same as for osmium(III) amine complexes or other platinum metals. In contrast, the corresponding Re(II) fragment, $[ReCl(en)_2]^+$, is a tenacious backbonding moiety which shows a relative affinity for pyridine π-acids which surpasses even that of $[Os(NH_3)_5]^{2+}$. The stabilities of the Re(II) complexes reported herein are limited owing, at least in part, to the highly reducing nature of the metal in the saturated ligand environment. Efforts are currently underway in our laboratory to increase the number of pyridine-based ligands in order to stabilize the Re(II) and Re(I) oxidation states through π interactions.

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Supplementary Material Available: Tables of experimental details, atomic position parameters, thermal parameters, and bond distances and angles and ORTEP drawings and packing diagrams for compounds **1**, **2**, and **12**. (30 pages). Ordering information is given on any current masthead page.