Synthesis and Characterization of Rhodium(III) Dichloro Complexes with Unsymmetrically Bound Salen-Type Ligands

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We have synthesized a series of novel octahedral Rh(III) salen-type complexes where the salen ligand is unsymmetrically bound to the Rh(III) dichloride center. This mode of bonding left one intact phenol group coordinating to the rhodium center and has never before been observed in salen−metal chemistry. These remarkably stable complexes possess unique coordination geometry and represent the first time that Rh(III) salen complexes have been successfully isolated from the direct combination of $RhCl_3 \cdot 3H_2O$ and the salen ligand in the absence of a nucleophilic base. The (salen)Rh(III) dichloride complex can be converted to the analogous monochloride complex by reaction with metal carbonate salts.

Introduction

The synthesis of metal−salen complexes has been widely investigated in inorganic chemistry. Symmetrical metal−salen compounds have been found to be catalytically active for the asymmetric Diels−Alder reaction, the ring opening of epoxides, the oxidation of sulfides, aziridination, cyclopropanation, and most notably the epoxidation of olefins.[1] The diversity in chemical reactivity shown by these complexes illustrates the ability of the salen ligand environment to accommodate many metals with diverse oxidation states as well as the versatility of the salen ligand in homogeneous catalysis. The salen ligand has been successfully metalated by many transition metals as well as main group elements.[2−4] Many of these complexes have been successfully characterized by X-ray crystallography. In all of these complexes the dianionic N,N,O^-,O^--tetradentate binding mode is observed. Some of these complexes contain axial ligands, both neutral and anionic, that bind to the metal center.

Rhodium salen complexes are of interest to our group because of the versatile nature of the salen ligand. By modifying the phenolic group of the salicylaldehyde, we hope to be able to use the salen ligand framework to access multiple oxidation states of the rhodium metal center. This is particularly interesting in our continuing study of the effect of metal oxidation state in homogeneous catalysis.

Organometallic rhodium complexes with tetradentate Schiff base ligands coordinating to the Rh metal center in the N, N, O^-, O^- mode are known. In the early 1970s West et al. reported the synthesis of octahedral Rh(III) salen complexes that contain pyridine as a neutral axially bound ligand.[5−7] In 1994, Eisenberg reported the synthesis of square pyramidal Rh(III)salen alkyl complexes from Rh(I) precursors.[8,9] Bunn has reported the synthesis of (R)Rh(III)salen where R = CH_2CH_3, CH_3, H, or I from Rh(II) starting materials and has observed that the direct synthesis of Rh(III) salen complexes from $RhCl_3 \cdot 3H_2O$ was not successful.[10] However, with the hope of obtaining a coordinatively unsaturated salen-type Rh(III) center containing a labile anionic axial ligand, we have set out to reinvestigate the synthesis of Rh(III) salen-type complexes directly from $RhCl_3 \cdot 3H_2O$.

Experimental Section

General Information and Materials. High-resolution mass spectra were obtained using a VG 70-250SE high-resolution mass spectrometer and the fast-atom bombardment (FAB) technique. ^1H and ^{13}C NMR spectra were recorded on a Varian Gemini FT-NMR spectrometer (300.075 MHz for ^1H NMR, 75.462 MHz for ^{13}C NMR). ^1H NMR data are reported as follows: chemical shift (multiplicity (b = broad, s = singlet, d = doublet, t = triplet, q = quartet, and m = multiplet) and integration). ^1H and ^{13}C chemical shifts are reported in ppm downfield from tetramethylsilane (TMS, δ scale) with the solvent resonances as internal standards. IR data were collected either on a Nicolet 520 FT-IR spectrometer with OMNIR software or on a Nicolet 5PC FT-IR spectrometer with PC-IR software. Elemental analyses were provided by Desert Analytics, Inc. (Tucson, AZ) and Atlantic Microlab, Inc. (Norcross, GA)

$RhCl_3 \cdot 3H_2O$ was purchased from Pressure Chemical and used as received. Dehydrated 200 °C ethyl alcohol was purchased from Pharmco and degassed with a stream of nitrogen prior to use. Schiff base ligands

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were synthesized by combining the substituted salicylaldehyde (2 equiv) with the diamine (1 equiv) in refluxing absolute ethanol. $RhCl_3(CH_3CN)_3$ was synthesized according to published procedures.[11] Acetonitrile and dichloromethane were distilled over calcium hydride. Tetrahydrofuran (THF), benzene, and diethyl ether were distilled over sodium/benzophenone. All solvents were distilled under nitrogen and saturated with nitrogen prior to use. Deuterated solvents were purchased from Cambridge Isotope Laboratories and used without further purification. All other reagents were purchased from the Aldrich Chemical Co. and used without further purification unless otherwise noted. All reactions were carried out under a dry nitrogen atmosphere using standard Schlenk techniques unless otherwise noted.

General Procedure for the Synthesis of 1a−e. $RhCl_3 \cdot 3H_2O$ (100.0 mg, 0.38 mmol) and the Schiff base ligand (1 equiv) were added to a 50 mL Schlenk flask equipped with a magnetic stirrer bar using standard Schlenk technique. Degassed ethanol (25 mL) was transferred into the reaction flask via a cannula. The flask was then fitted with a reflux condenser attached to a gas flow adapter and N_2 bubbler. The mixture was heated to reflux under N_2 for 6 h and was then allowed to cool to room temperature. If the product precipitated out from the reaction mixture, it was isolated by filtration. If the product was soluble in ethanol, the solvent was removed in vacuo. The remaining solid was washed with ether (3 × 10 mL). The ether-insoluble material was dissolved in methylene chloride and passed through a short column of Celite. The CH_2Cl_2 solution was then evaporated, and the solid product was dried under vacuum overnight at 70−80 °C.

Dichloro-1,2-cyclohexanediamino-*N*-(3,5-di-*tert*-butylsalicylidene)-*N*′-(3,5-di-*tert*-butyl-2-hydroxysalicylidene) Rhodium(III) (1a). Yield = 48.5%. ^{1}H NMR ($CDCl_3$): δ 7.99 (s, 2H, C*H*═N), 7.54 (d, 2H, aromatic), 7.20 (d, 2H, aromatic), 4.48 (b, 2H, O*H*), 3.9 (d, 2H, cyclohexyl), 2.83 (d, 2H, cyclohexyl), 2.06 (d, 2H, cyclohexyl) 1.85 (m, 2H, cyclohexyl), 1.60 (s, 9H, ^{t}Bu), 1.4−1.6 (m, 2H, cyclohexyl), 1.32 (s, 9H ^{t}Bu). ^{13}C NMR ($CDCl_3$): δ 154.87 (Ar*C*$_o$−OH), 146.73 (Ar*C*$_m$−^{t}Bu), 141.07 (Ar*C*$_m$−^{t}Bu), 120.86 (Ar*C*−C═N), 130.85 (Ar*C*$_o$−H), 130.51 (Ar*C*$_p$−H), 160.25 (*C*═N), 71.60 (cyclohexyl, N−*C*H$_2$*C*H$_2$−N), 35.52 (*C*(CH$_3$)$_3$), 34.41 (*C*(CH$_3$)$_3$), 31.52 (C(*C*H$_3$)$_3$), 30.52 (C(*C*H$_3$)$_3$), 29.05 (cyclohexyl −*C*H$_2$CH$_2$CH$_2$*C*H$_2$−), 24.37 (cyclohexyl −CH$_2$*C*H$_2$-*C*H$_2$CH$_2$−). IR (Nujol): ν_{OH} = 3627.51 cm^{-1} (br). IR (CH_2Cl_2): ν_{OH} = 3682.49 cm^{-1}. Anal. Calcd for $C_{36}H_{53}O_2N_2RhCl_2$: C, 60.09; H, 7.42; N, 3.89; Rh, 14.3; Cl, 9.85. Found: C, 59.90; H, 7.71; N, 3.67; Rh, 14.13; Cl, 9.56. FAB$^+$/MS: M^+ = 719, (M^+ − H_2Cl) = 682, (M^+ − H_2Cl_2) = 647.

Dichloro-1,2-cyclohexanediamino-*N*-(3-*tert*-butyl-5-methylsalicylidene)-*N*′-(3-*tert*-butyl-2-hydroxy-5-methylsalicylidene) Rhodium(III) (1b). Yield = 39.0%. ^{1}H NMR ($CDCl_3$): δ 7.86 (s, 2H, C*H*═N), 7.25 (d, 2H, aromatic), 7.03, (d, 2H, aromatic), 3.73 (d, 2H, cyclohexyl), 2.69 (d, 2H, cyclohexyl), 2.55 (s, 2H, O*H*), 2.24 (s, 3H, C*H*$_3$), 1.95 (d, 2H cyclohexyl, J = 1.5 Hz), 1.85 (m, 2H, cyclohexyl), 1.45 (s, 9H, ^{t}Bu). ^{13}C NMR ($CDCl_3$): 155.38 (Ar*C*$_o$−OH)), 142.57 (Ar*C*$_m$−^{t}Bu), 134.25 (Ar*C*$_o$−H), 129.28 (Ar*C*$_p$−H), 160.41 (*C*═N), 71.91 (cyclohexyl, N−*C*H$_2$*C*H$_2$−N), 35.82 (*C*(CH$_3$)$_3$), 30.55 (C(*C*H$_3$)$_3$), 29.05 (cyclohexyl −*C*H$_2$CH$_2$CH$_2$*C*H$_2$−), 24.72 (cyclohexyl −CH$_2$*C*H$_2$*C*H$_2$-CH$_2$−), 20.84 (*m*-*C*H$_3$). IR (Nujol): ν_{OH} = 3744.07 cm^{-1} (br). Anal. Calcd for $C_{30.5}H_{42}O_2N_2RhCl_3$ (0.5 molecules CH_2Cl_2/Rh): C, 54.13; H, 6.26; N, 4.14. Found: C, 54.88; H, 6.37; N, 4.15. FAB$^+$/MS: M^+ = 633, (M^+ − Cl) = 598, (M^+ − 2Cl) = 563.

Dichloro-1,2-ethanediamino-*N*-(3-*tert*-butyl-5-methylsalicylidene)-*N*′-(3-*tert*-butyl-2-hydroxy-5-methylsalicylidene) Rhodium(III) (1c). Yield = 42.6%. ^{1}H NMR ($CDCl_3$): δ 8.04 (s, 2H, C*H*═N), 7.33 (s, 2H, aromatic), 7.05 (s, 2H, aromatic), 4.40 (b, 2H, O*H*), 4.11 (s, 4H, NC*H*$_2$C*H*$_2$N), 2.32 (s, 3H, C*H*$_3$), 1.60 (s, 9H, ^{t}Bu CH$_3$). ^{13}C NMR ($CDCl_3$): δ 154.80 (Ar C_o−OH)), 128.55 (Ar*C*$_m$−^{t}Bu), 133.99 (Ar*C*$_o$−H), 133.52 (Ar*C*$_p$−H), 163.42 (*C*═N), 59.81 (N*C*H$_2$*C*H$_2$N), 35.24 (*C*(CH$_3$)$_3$), 30.23 (C(*C*H$_3$)$_3$), 20.56 (*m*-*C*H$_3$). IR (Nujol): ν_{OH} = 3853.73 cm^{-1} (br). FAB$^+$/MS: M^+ = 580, (M^+−HCl) = 544, (M^+−HCl$_2$) = 509.

Dichloro-1,2-ethanediamino-*N*-(3,5-di-*tert*-butylsalicylidene)-*N*′-(3,5-di-*tert*-butyl-2-hydroxysalicylidene) Rhodium(III) (1d). Yield = 21.4%. ^{1}H NMR ($CDCl_3$): δ 8.12 (s, 2H, C*H*═N), 7.57 (s, 2H, aromatic), 7.20 (s, 2H, aromatic), 4.13 (s, 4H, NC*H*$_2$C*H*$_2$N), 3.57 (b, 2H, O*H*), 1.61 (s, 9H, ^{t}Bu), 1.32 (s, 9H, ^{t}Bu). ^{13}C NMR ($CDCl_3$): 154.78 (Ar*C*$_o$−OH)), 141.34 (Ar*C*$_m$−^{t}Bu), 141.71 (Ar*C*$_m$−^{t}Bu), 120.70 (Ar*C*−C═N), 130.63 (Ar*C*$_o$−H), 130.25 (Ar*C*$_p$−H), 163.82 (*C*═N), 59.84 (N*C*H$_2$*C*H$_2$N), 35.62 (*C*(CH$_3$)$_3$), 34.25 (*C*(CH$_3$)$_3$), 31.34 (C(*C*H$_3$)$_3$), 30.37 (C(*C*H$_3$)$_3$). IR (Nujol): ν_{OH} = 3682.63 cm^{-1} (br). Anal. Calcd for $C_{32.2.5}H_{47.5}O_2N_2RhCl_{2.5}$ (0.25 molecules CH_2Cl_2/Rh): C, 56.48; H, 6.99; N, 4.09. Found: C, 56.67; H, 7.08 N, 4.15. FAB$^+$/MS: M^+ = 664, (M^+ − Cl) = 628, (M^+ − Cl$_2$) = 593.

Dichloro-1,2-propanediamino-*N*-(3,5-di-*tert*-butylsalicylidene)-*N*′-(3,5-di-*tert*-butyl-2-hydroxysalicylidene) Rhodium(III) (1e). Yield = 34.1%. ^{1}H NMR ($CDCl_3$): 7.85 (s, 2H, C*H* = N), 7.52 (d, 2H, aromatic), 7.12 (d, 2H, aromatic), 4.16 (m, 4H, NC*H*$_2$CH$_2$C*H*$_2$N), 3.37 (b, 2H, O*H*), 2.40 (s, 2H, NCH$_2$C*H*$_2$CH$_2$N), 1.60 (s, 9H, ^{t}Bu), 1.31 (s, 9H, ^{t}Bu). ^{13}C NMR ($CDCl_3$): δ 153.69 (Ar*C*$_o$−OH)), 139.23 (Ar*C*$_m$−^{t}Bu), 141.57 (Ar*C*$_m$−^{t}Bu), 119.68 (Ar*C*−C═N), 130.76 (Ar*C*$_o$−H), 130.57 (Ar*C*$_p$−H), 165.87 (*C*═N), 62.51 (N*C*H$_2$CH$_2$*C*H$_2$N), 35.40 (*C*(CH$_3$)$_3$), 34.17 (*C*(CH$_3$)$_3$), 31.31 (C(*C*H$_3$)$_3$), 30.75 (C(*C*H$_3$)$_3$), 27.61 (NCH$_2$*C*H$_2$CH$_2$N). IR (Nujol): ν_{OH} = 3583.23 cm^{-1} (br). Anal. Calcd for $C_{33.5}H_{50}O_2N_2RhCl_3$ (0.5 molecules CH_2Cl_2/Rh): C, 55.82; H, 7.00; N, 3.89. Found: C, 55.80; H, 7.15; N, 4.02. FAB$^+$/MS: M^+ = 677, (M^+ − Cl) = 642, (M^+ − Cl$_2$) = 607.

Synthesis of Chloro-*trans*-1,2-cyclohexanediamino-*N*,*N*′-bis(3,5-di-*tert*-butylsalicylidene) Rhodium(III) (2a). Complex **1a** (300 mg, 0.42 mmol) and silver carbonate (58.1 mg, 0.21 mmol, 0.5 equiv) were added to a 50 mL Schlenk flask equipped with a magnetic stirrer bar, in the presence of air. THF (25 mL) was added to the flask via a cannula. The flask was next covered with aluminum foil to exclude light. The mixture was then stirred at room temperature for 24 h. The mixture appeared dark-brown in color. The mixture was filtered through Celite to remove any insoluble solids, and the solvent was evaporated to isolate the solid product (264 mg, 92.4%). ^{1}H NMR (THF-d_8): δ 8.19 (s, 1H, C*H*═N), 8.06 (s, 1H, C*H*═N), 7.35 (t, 2H, aromatic), 7.07 (t, 2H, aromatic), 3.70 (b, 1H, cyclohexyl), 3.00 (d, 1H, cyclohexyl), 2.90 (d, 1H, cyclohexyl), 1.95 (m, 2H, cyclohexyl), 1.53 (d, 9H, ^{t}Bu), 1.25 (s, 9H ^{t}Bu). ^{13}C NMR (THF-d_8): δ 120.56, 160.86 (Ar*C*$_o$−OH), 143.02, 142.71 (Ar*C*$_m$−^{t}Bu), 135.12 (Ar*C*$_m$−^{t}Bu), 134.88, 134.82 (Ar*C*−C═N), 130.77, 130.41 (Ar*C*$_o$−H), 129.65, 129.48 (Ar*C*$_p$−H), 161.57 (*C*═N), 74.01, 71.02 (cyclohexyl, N−*C*H$_2$*C*H$_2$−N), 37.01, 36.94 (*C*(CH$_3$)$_3$), 34.59 (*C*(CH$_3$)$_3$), 32.12 (C(*C*H$_3$)$_3$), 30.91, 30.75 (C(*C*H$_3$)$_3$), 29.89, 29.64 (cyclohexyl −*C*H$_2$CH$_2$CH$_2$*C*H$_2$−), 24.99 (cyclohexyl −CH$_2$*C*H$_2$*C*H$_2$CH$_2$−). FAB$^+$/MS: M^+ = 682, (M^+ − Cl) = 647.

Reaction of 1a with Ammonium Chloride. In a 25 mL round-bottom flask **1a** (50 mg, 0.07 mmol) dissolved in CH_2Cl_2 (10 mL) was combined with an aqueous solution of ammonium chloride (394 mg in 5 mL of H_2O, 0.7 mmol, 10 equiv). The two-phase mixture was stirred vigorously at room temperature overnight. The reaction mixture was evaporated to dryness in vacuo, and a sample was taken for NMR analysis. ^{1}H NMR ($CDCl_3$): δ 7.90 (s, 1H, C*H*═N), 7.53 (s, 1H, C*H*═N), 7.39, 7.38 (s, 2H, aromatic), 7.03, 6.98 (s, 2H, aromatic), 3.50 (b, 1H, cyclohexyl), 3.10 (d, 1H, cyclohexyl), 2.90 (d, 1H, cyclohexyl), 2.0 (b, 2H, cyclohexyl and 4H, ammonium), 1.40 (d, 9H, ^{t}Bu), 1.30 (s, 9H ^{t}Bu).

Reaction of 1a with Tetrabutylammonium Chloride. In a 25 mL round-bottom flask **1a** (50 mg, 0.07 mmol) and tetrabutylammonium chloride (20.1 mg, 0.07 mmol, 1equiv) were dissolved in CH_2Cl_2 (15 mL). The homogeneous mixture was stirred at room temperature for 24 h. The mixture was then washed with water to remove any unreacted tetrabutylammonium chloride. The organic phase was collected and dried over Na_2SO_4, and the solvent was evaporated to isolate a solid product. ^{1}H NMR (CD_2Cl_2): δ 7.91 (s, 2H, C*H*═N), 7.5 (b, 2H, aromatic), 7.2 (b, 2H, aromatic), 2.91 (t, NC*H*$_2$CH$_2$CH$_2$CH$_3$), 2.76 (d, 2H, cyclohexyl), 1.97 (d, 2H, cyclohexyl), 1.60 (b, 2H, cyclohexyl), 1.55 (s, 9H, ^{t}Bu), 1.42 (m, NCH$_2$*C*H$_2$CH$_2$CH$_3$), 1.34 (t, NCH$_2$CH$_2$-CH$_2$*C*H$_3$), 1.26 (m), 0.90 (s, 9H ^{t}Bu).

Results and Discussion

We report here the observance of a novel salen−metal binding mode discovered during attempts to directly synthesize a

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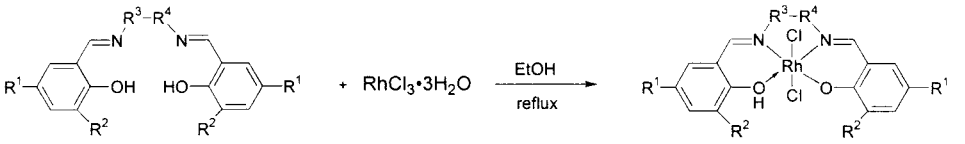
Scheme 1



1a: R^1= ^{t}Bu, R^2= ^{t}Bu, R^3-R^4 = 1,2-Cyclohexanediyl
1b: R^1= CH_3, R^2= ^{t}Bu, R^3-R^4 = 1,2-Cyclohexanediyl
1c: R^1= CH_3, R^2= ^{t}Bu, R^3-R^4 = 1,2-Ethanediyl
1d: R^1= ^{t}Bu, R^2= ^{t}Bu, R^3-R^4 = 1,2-Ethanediyl
1e: R^1= ^{t}Bu, R^2= ^{t}Bu, R^3-R^4 = 1,3-Propanediyl

Table 1. Crystal Data and Structure Refinement for (salen)$RhCl_2$·$2CH_2Cl_2$ (**1a**)

empirical formula	$C_{38}H_{57}N_2O_2Cl_6Rh$
fw	888.46
temp (K)	198(2)
wavelength (Å)	0.710 73
cryst syst	monoclinic
space group	$P2_1/c$
a (Å)	12.5463(3)
b (Å)	12.4447(3)
c (Å)	28.2073(3)
α (deg)	90
β (deg)	96.4862
γ (deg)	90
V (Å^3)	4376.0(3)
Z	4
ρ (calcd) (g/cm^3)	1.349
μ (mm^{-1})	0.789
goodness-of-fit on F^2	1.301
final R^a indices [$I > 2\sigma(I)$]	R1 = 0.0595, wR2 = 0.1226
R^a indices (all data)	R1 = 0.0959, wR2 = 0.1394

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$.

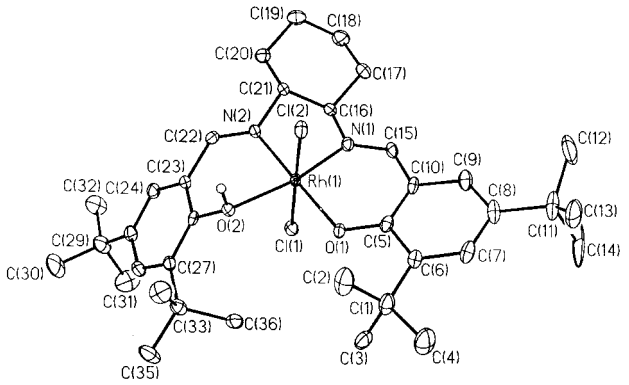


Figure 1. ORTEP diagram of **1a**·$2CH_2Cl_2$ showing atom labeling scheme. Thermal ellipsoids are shown at 30% probability. Solvent molecules and hydrogen atoms, except for O(2)H, are omitted for clarity.

coordinatively unsaturated Rh(III) Schiff base monohalide complex from Rh(III) starting materials. We have successfully synthesized a series of novel octahedral Rh(III) salen-type complexes where the ligand is unsymmetrically bound to the Rh(III) dichlo center. *This mode of bonding left one intact phenol group coordinating to the rhodium center and has never before been observed in salen−metal chemistry.* These remarkably stable complexes possess unique coordination chemistry and represent the first time that Rh(III) Schiff base complexes have been successfully isolated from the direct combination of $RhCl_3$·$3H_2O$ and the salen-type ligand.[10] The only other examples of a tetradentate monoanionic Schiff base ligand framework come from unsymmetrical salen ligands that have an N, N, N, O^- binding mode.[12,13] Ours is the first example of an N, N, O, O^-

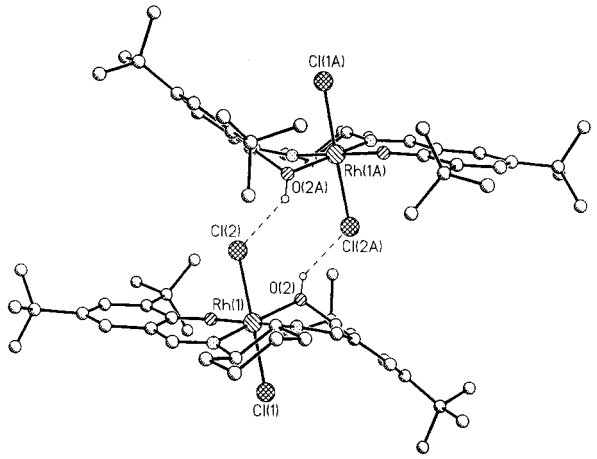


Figure 2. ORTEP drawing of one-half of a unit cell of **1a**·$2CH_2Cl_2$ showing hydrogen bonds (O−H···Cl = 3.01(2) Å) between two neighboring molecules.

monoanionic ligand, similar to what might be expected if the proton of one phenol group was replaced by an alkyl group (Scheme 1).[14] The (salcen)Rh(III) dichloride complex (salcen = *trans*-1,2-diaminocyclohexane-*N*,*N*′-bis(3,5-di-*tert*-butylsalicylidene) was synthesized by combining the free imine ligand with rhodium trichloride trihydrate in refluxing ethanol (Scheme 1). Some decomposition of the starting imine ligand is always observed with product formation. This decomposition was not impeded by the addition of various bases to the reaction mixture. In some cases, the desired product precipitates out of the reaction mixture. In other cases, the solid product can be obtained in pure form by washing the solid residue obtained after removal of the solvent with ether. The ^{1}H NMR resonance for the imine protons of **1a** shifts to 8.0 ppm from 8.3 ppm for the free ligand. Furthermore, the O*H* proton resonates in the range between 2 and 6 ppm as a broad peak depending on the concentration and solvent. The IR spectrum of **1a** in Nujol exhibits an OH stretch at 3627.5 cm^{-1} as a low-intensity broad peak, and the IR spectrum of **1a** in CH_2Cl_2 shows a high-intensity broad peak at 3741.5 cm^{-1}. These data are consistent with the presence of a hydrogen-bonding network in the solid state. An X-ray crystal structure of **1a**·$2CH_2Cl_2$ further confirmed the indicated structure (Figure 1 and Table 1). The Rh(III) center lies slightly above the salcen ligand plane in an octahedral geometry with axial chloride ligands. The Rh−O(2) bond is 2.143(3) Å, quite a bit

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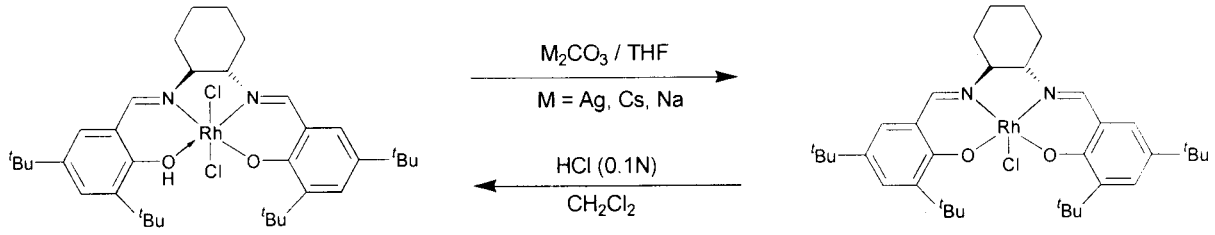
(14) Lopez, J.; Liang, S.; Bu, X. R. *Tetrahedron Lett.* **1998**, *39*, 4199−4202.

Scheme 2



longer than the Rh−O(1) bond (1.996(3) Å), and is consistent with a dative OH ligation mode. The O*H* proton (O(2)−H bond length = 0.81 Å) can be located unequivocally in the X-ray structure, and there is no hydrogen bonding between O(1) and H−O(2). Instead, there is hydrogen bonding between the OH of one molecule and the Cl of another (Figure 2). In solution, however, ^{1}H NMR experiments indicate a room-temperature equivalency between the two salicylaldimine halves of the molecule, suggesting that this proton may exchange rapidly between the two O sites.

Complex **1a** is a potential intermediate in the synthesis of the monochloride complex **2a** and is the result of the first loss of HCl from the $RhCl_3$ starting material and the salcen ligand. As such, it is remarkably stable toward the thermal elimination of the second equivalent of HCl. It is air- and moisture-stable and can be made in gram quantities. Complex **1a** is the first example of a Rh(III) Schiff base complex in which both of the axial ligands are anionic, which dictates that one of the phenol groups of the salen ligand must exist as a neutral ligand to the rhodium metal center.

By variation of the aldehyde and diamine substituents, different Schiff base ligands have been synthesized and metalated using $RhCl_3 \cdot 3H_2O$ as the rhodium precursor (**1a**−**e**). The synthesis of **1a** has also been achieved in other solvents including THF and acetonitrile, as well as from a different rhodium precursor, $RhCl_3(CH_3CN)_3$.[11] Less ligand decomposition occurs when the $RhCl_3(CH_3CN)_3$ precursor is used in THF. Schiff base ligands made from the condensation of 1,2-phenylenediamine, 1,3-phenylenediamine, 3,4-diaminotoluene, 3,4-diaminomethoxybenzene, and 1,2-diphenylethylenediamine with 3,5-di-*tert*-butyl-2-hydroxybenzaldehyde could not be metalated under the conditions listed in Scheme 1.

The (salcen)Rh(III) dichloro complex **1a** can be converted to the corresponding monochloro complex **2a** by reaction with silver carbonate (Scheme 2). NMR experiments in THF-d_8 revealed that Cs_2CO_3 and Na_2CO_3 are also effective reagents for the production of the monochloride species. The reaction with Ag_2CO_3 has been successfully scaled up, and the product was isolated in 92% yield. The FAB-MS spectrum of **2a** exhibits a molecular ion peak at 682 and an $(M - 35)^+$ peak at 647 (Rh(salcen) − Cl), corresponding to the monochloride product. The ^{1}H NMR spectrum of **2a** in THF-d_8 shows two imine peaks at 8.24 and 8.11 ppm. These protons are inequivalent in the ^{1}H NMR spectrum because the C_2 axis through the ligand present in **1** (assuming that the proton in **1** is exchanging rapidly) is lost in **2**. The two halves of the ligand are no longer equivalent, giving rise to a unique signal for each proton environment, including the cyclohexylmethine protons. The infrared spectrum of **2a** shows no OH stretch, consistent with the proposed structure. The synthesis of **2a** is an important step in the rational synthesis of a coordinatively unsaturated Rh(III) salen-type complex.

The reaction in Scheme 2 was found to be reversible. At room temperature over several days, the conversion of **2a** back to **1a** in the presence of excess aqueous hydrochloric acid was confirmed by ^{1}H NMR and IR analyses. The two imine peaks converged to one peak in the ^{1}H NMR, and a broad OH stretch was evident in the IR spectrum, indicating the re-formation of **1a**.

Complex **1a** can also be considered as a $[Rh(salcenCl_2)]^-$ anion with a H^+ counterion. Thus, cation-exchange experiments were conducted in an effort to replace the phenolic proton of **1a** with a different cation. The biphasic reaction between a CH_2Cl_2 solution of **1a** and an aqueous solution of ammonium chloride yields a new brown product. The ^{1}H NMR spectrum of this compound in CD_2Cl_2 contains a broad resonance at 2 ppm for the NH_4^+ protons and an unsymmetric imine region that is characteristic of the loss of the C_2 axis in **1a** due to hydrogen bonding of the ammonium protons to one of the phenoxide oxygens. In a homogeneous reaction between **1a** and tetrabutylammonium chloride in CH_2Cl_2, a chloroform-insoluble product was obtained after workup. The ^{1}H NMR spectrum of this compound in CD_2Cl_2 clearly shows the presence of 1 equiv of NBu_4^+ cation. The aromatic resonances are broadened and symmetric. The imine and aromatic regions remain symmetric because hydrogen bonding is not possible between the NBu_4^+ cation and the phenoxide oxygen. Taken together, these data indicate that the hydroxyl protons are exchangeable with other cations, consistent with the reversibility indicated in Scheme 2.

In conclusion, we have reported the synthesis and complete structural characterization of a novel salen-type Rh(III) dichloride complex. This discovery has demonstrated an unprecedented binding mode of the salen ligand outside the normal N, N, O^-, O^- binding mode. The (salen)Rh(III) dichloride complex can be converted to the monochloride derivative using simple carbonate salts. We are currently investigating further coordination and catalytic chemistry of the complexes described herein.

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Supporting Information Available: An X-ray crystallographic file (IC990548A) in CIF format for the structure determination of **1a**·$2CH_2Cl_2$. This material is available free of charge via the Internet at http://pubs.acs.org.

IC990548A