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Binuclear Ruthenium Macrocycles Formed via the Weak-Link Approach

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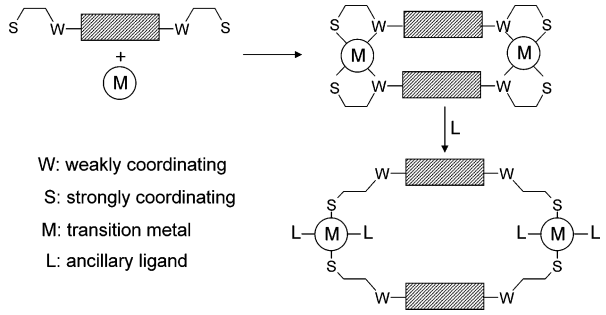
The "weak-link approach" for the synthesis of metallomacrocycles has been used to synthesize a series of novel Ru(II) macrocycles in high yield. $RuCl_2(PPh_3)_3$ has been reacted with two different phosphino-alkyl-ether hemilabile ligands, 1,4-$(PPh_2(CH_2)_2O)_2C_6H_4$ and 1,4-$(PPh_2(CH_2)_2OCH_2)_2C_6H_4$. The hemilabile bidentate ligand coordinates to Ru(II) centers through both the P and O atoms to form bimetallic "condensed intermediates". The weak Ru–O bonds have been selectively cleaved with CO, 1,2-diaminopropane, and pyridine to yield large open macrocycles. This is the first example of the weak-link approach employed to synthesize macrocycles with Ru, and metal centers in general that have more than four coordination sites.

Introduction

Over the past decade, major advances have been made in the field of supramolecular chemistry. A significant component of the field is coalescing around the challenge of developing synthetic routes for rationally synthesizing structures with well-defined shape, chirality, and function, and then using such control for preparing molecules with unusual and potentially useful catalytic and molecular sensing properties.[1] Most recently, a novel type of allosteric catalyst was reported that behaves like a synthetic metalloenzyme, which demonstrates the type of sophisticated molecular function possible via the supramolecular coordination chemistry approach.[2]

Our group has developed the "weak-link approach" to supramolecular structures, Scheme 1.[2,3] With this methodology, metallomacrocycles are prepared in high yield from transition metal precursors and flexible organic ligands containing strong and weak metal bonding groups capable of chelating to a metal center of interest to template the formation of a condensed intermediate.[3,4] The condensed intermediate can be subsequently opened into a targeted macrocyclic structure through ligand substitution reactions involving small molecules that can break the weak metal–ligand interactions while keeping the strong ones intact. This approach has predominantly focused on the preparation of complexes with four-coordinate, square-planar transition metals, namely rhodium(I), palladium(II), and iridium(I), and more recently tetrahedral copper(I) complexes.[3a,g,k,p]

Scheme 1. Weak Link Approach



By including higher-coordinate metal centers into this approach, one could, in principle, take advantage of the additional coordination sites in stoichiometric and catalytic reactions. Herein, we introduce the use of ruthenium(II), a metal that often prefers an octahedral coordination sphere,

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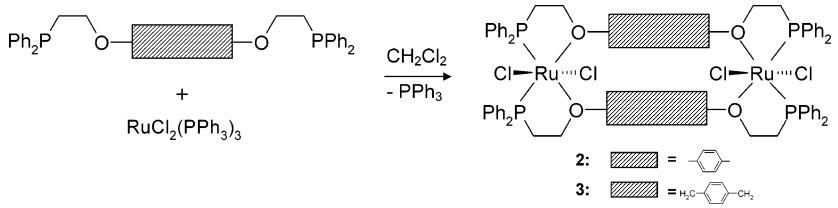
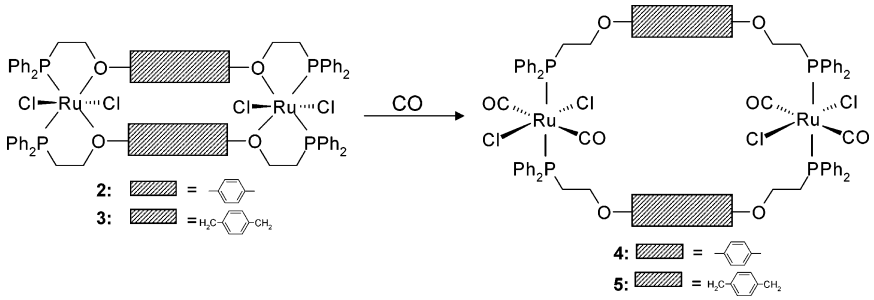
Scheme 2. Synthetic Outline for Closed Ru(II) Macrocycles **2** and **3**



Scheme 3. Synthetic Outline for Open Ru(II) Macrocycles **4** and **5**



into the weak-link approach, and a variety of ancillary ligands that can be used to tailor the electronic and steric properties of the metal centers within the resulting macrocyclic structures (Scheme 2). Mononuclear ruthenium(II) systems with hemilabile phosphine−ether ligands have been extensively studied.[5−10] It has been shown that the weak Ru−O bond can be easily cleaved by a variety of small molecules,[7a,h,i,8] including CO[5,6,7c−g,10c] and nitrogen-based ligands.[7j] This knowledge has been used to synthesize two new bimetallic condensed macrocycles via the weak link approach (Schemes 3 and 4).

Experimental Section

General Procedures. Unless otherwise noted, all reactions were carried out under a nitrogen atmosphere in reagent grade solvents, using standard Schlenk techniques or an inert atmosphere glovebox at room temperature.[11] All other solvents were purified by published methods.[12] Deuterated solvents were purchased from Cambridge Isotope Laboratories Inc. and used as received. 1,4-(2-Diphenylphosphinoethoxy) benzene[3c] and α,α′-dichloroethoxy-*p*-xylene[13] were prepared according to literature methods. $RuCl_2(PPh_3)_3$ was purchased from Strem Chemicals and used as received. All other chemicals were used as received from Aldrich Chemical Co.

Physical Measurements. ^1H NMR spectra were recorded on a Varian Gemini 300 MHz FT-NMR spectrometer and referenced relative to residual proton resonances in $CDCl_3$ or CD_2Cl_2. $^{31}P\{^1H\}$ NMR spectra were recorded on a Varian Gemini 300 MHz FT-NMR spectrometer at 121.53 MHz and referenced relative to an external 85% H_3PO_4 standard. All chemical shifts are reported in ppm. FT-IR spectra were obtained in solution with a Thermo Nicolet Nexus 670 FT-IR with NaCl cells with 0.1-mm spacers or CsI cells with 0.5-mm spacers for far IR work. They were collected in the

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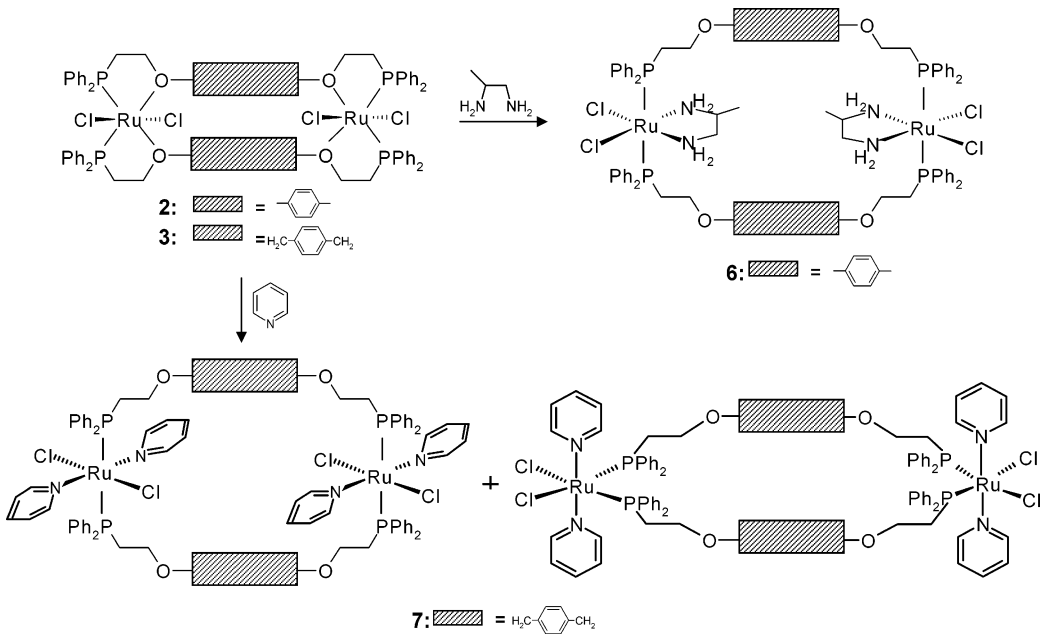
Scheme 4. Synthetic Outline for Open Ru(II) Macrocycles **6** and **7**



solid state with the same instrument using a KBr pellet or a CsI pellet for far IR work. Electrospray mass spectra (ESMS) were recorded on a Micromas Quatro II triple quadrapole mass spectrometer. Fast atom bombardment (FAB) and electron ionization mass spectra (EIMS) were recorded on a Fisions VG 70-250 SE mass spectrometer. Elemental analyses were performed by Quantitative Technologies, Inc., Whitehouse, NJ.

Synthesis of α,α′-Bis(2-diphenylphosphinoexthoxy)-*p*-xylene (1). A solution of $KPPh_2$ in THF (0.5 M, 25.5 mL, 12.7 mmol) was added dropwise to a stirring solution of α,α′-dichloroethoxy-*p*-xylene (1.68 g, 6.4 mmol) in THF (50 mL). The orange solution was passed through a column of alumina to remove the KCl, and the solvent was removed in vacuo. The crude product was washed with EtOH (20 mL) and then recrystallized from CH_2Cl_2 and hexanes. The product was dried, yielding 1.78 g (49% yield) of analytically pure white powder. ^{1}H NMR: ($CDCl_3$) δ 2.43 (t, 4H, CH_2P, J_{H-H} = 7.8 Hz), 3.60 (q, 8H, CH_2CH_2O, J_{H-H} = 7.2 Hz), 4.46 (s, 4H, CH_2O), 7.22−7.45 (complex m, 24H, Ph-*H*). ^{31}P{^{1}H} NMR: ($CDCl_3$) δ −21.07 (s). $C_{36}H_{36}O_2P_2$: calcd 76.85% C, 6.45% H; found 76.91% C, 6.34% H. EI-MS: [M] calcd: 562.2, expt: 562.2 *m*/*z*.

Synthesis of [1,4-Bis(2-diphenylphosphinoethoxy)benzene]$_2$-Ru_2Cl_4 (2). A solution of 1,4-(2-di-phenylphosphinoethoxy)-benzene (28 mg, 0.052 mmol) in CH_2Cl_2 (25 mL) was added dropwise over 30 min to a solution of $RuCl_2(PPh_3)_3$ (50 mg, 0.052 mmol) in CH_2Cl_2 (25 mL). The solution was stirred for an additional 2 h. The deep red solution was concentrated to approximately 2 mL under reduced pressure. Addition of Et_2O (80 mL) caused the precipitation of solid **2**, which was collected by filtration and washed with additional Et_2O (5 mL). This process was repeated twice to completely remove excess PPh_3. Yield: 60.2 mg, 0.043 mmol; 82%. ^{1}H NMR: (CD_2Cl_2) δ 2.85−2.98 (br m, 8H, CH_2P), 4.52−4.59 (br m, 8H, CH_2O), 6.99 (s, 8H, C_6H_4), 7.07−7.13 (m, 24H, P(C_6H_5)$_2$), 7.30−7.38 (m, 16H, P(C_6H_5)$_2$). ^{31}P{^{1}H} NMR: (CD_2Cl_2) δ 64.1 (s). $C_{68}H_{64}Cl_4O_4P_4Ru_2$: calcd 57.79% C, 4.57% H, 9.91% Cl, 8.77% P; found 58.30% C, 4.54% H, 10.04% Cl, 9.32% P. ESMS: [M − 2 Cl$^-$]$^{2+}$ calcd = 671.1, expt = 671.0 *m*/*z*. Crystals of **2** were grown by slow diffusion of Et_2O vapor into a dilute solution of **2** in CH_2Cl_2 at room temperature.

Synthesis of [α,α′-Bis(2-diphenylphosphinoexthoxy)-*p*-xylene]$_2$-Ru_2Cl_4 (3). A solution of **1** (29 mg, 0.052 mmol) in CH_2Cl_2 (25 mL) was added dropwise over 30 min to a solution of $RuCl_2(PPh_3)_3$ (50 mg, 0.052 mmol) in CH_2Cl_2 (25 mL). The solution was stirred for an additional 2 h. The deep red solution was concentrated to approximately 2 mL under reduced pressure. Addition of Et_2O (80 mL) caused the precipitation of solid **3**, which was collected by filtration and washed with additional Et_2O (5 mL). This process was repeated once to completely remove excess PPh_3. Yield: 60.4 mg, 0.041 mmol, 79%. ^{1}H NMR: (CD_2Cl_2) δ 2.98 (br m, 8H, CH_2P), 4.05−4.12 (br m, 8H, CH_2CH_2O), 5.13 (s, 8H, CH_2O), 7.08−7.30 (complex m, 48H, Ph-*H*). ^{31}P{^{1}H} NMR: (CD_2Cl_2) δ 64.2 (s). $C_{72}H_{72}Cl_4O_4P_4Ru_2$: calcd 58.86% C, 4.94% H; found 58.53% C, 4.62% H. ESMS: [M − 2 Cl$^-$]$^{2+}$ calcd = 700.1, expt = 700.3 *m*/*z*.

Synthesis of [1,4-Bis(2-diphenylphosphinoethoxy)benzene]$_2$$Ru_2$-$Cl_4(CO)_4$ (4). A solution of complex **2** (10.0 mg, 0.007 mmol) in CD_2Cl_2 (0.7 mL) was bubbled with CO (1 atm) until a color change from bright pink to bright yellow occurred. Compound **4** precipitated from solution as a pale yellow powder. Yield: 9.6 mg, 0.006 mmol, 90%. ^{1}H NMR: ($CDCl_3$) δ 3.13 (br m, 8H, CH_2P), 4.14 (br m, 8H, CH_2O), 6.58 (s, 8H, C_6H_4), 7.19−7.26 (m, 24H, P(C_6H_5)$_2$), 7.60−7.78 (m, 16H, P(C_6H_5)$_2$). ^{31}P{^{1}H} NMR: (CD_2Cl_2) δ 15.2 (s). FTIR: (KBr pellet used for CO stretches; CsI pellet used for Ru−Cl stretch) ν(CO) 2002 cm^{-1} (s), ν(CO) 1944 cm^{-1} (m), ν(Ru−Cl) 333 cm^{-1}. $C_{72}H_{64}Cl_4O_8P_4Ru_2$: calcd 56.69% C, 4.23% H; found 56.17% C, 4.15% H. FAB-MS: [M − CO − Cl]$^+$ calcd = 1463.1, expt = 1463.6 *m*/*z*; [M − 2CO − Cl]$^+$ calcd = 1435.0, expt = 1434.5 *m*/*z*.

Synthesis of [α,α′-Bis(2-diphenylphosphinoexthoxy)-*p*-xylene]$_2$-$Ru_2Cl_4(CO)_4$ (5). A solution of complex **3** (10 mg, 0.007 mmol) in CD_2Cl_2 (0.7 mL) was bubbled with CO (1 atm) until a color change from bright pink to bright yellow occurred. The solvent was removed in vacuo to yield a pale yellow powder. Yield: 10.2 mg, 0.006 mmol, 92%. ^{1}H NMR: (CD_2Cl_2) δ 3.05 (br m, 8H, CH_2P), 3.60 (br m, 8H, CH_2CH_2O), 4.31 (s, 8H, CH_2O), 7.05 (br s, 8H, Ph-*H*), 7.41−7.72 (complex m, 40H, Ph-*H*). ^{31}P{^{1}H} NMR: (CD_2Cl_2) δ 14.6 (s). FTIR: (NaCl solution cell used for CO stretches; CsI solution cell used for Ru−Cl stretch; CH_2Cl_2)

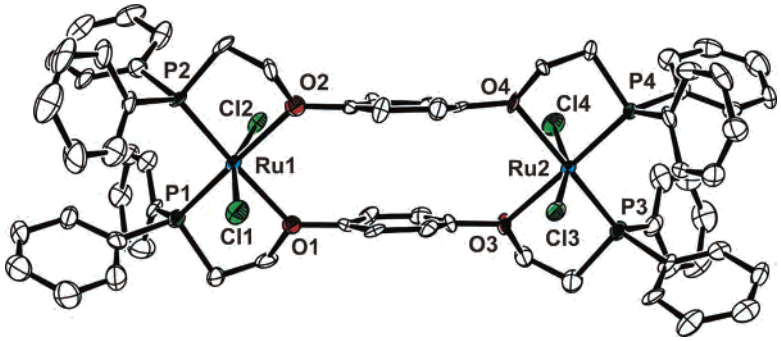


Figure 1. ORTEP diagram of **2**, [1,4-bis(diphenylphosphinoethoxy)benzene]$_2$Ru$_2$Cl$_4$, showing the labeling scheme of selected atoms and thermal ellipsoids at 50% probability. Hydrogen atoms and solvent molecules are omitted for clarity.

ν(CO) 2006 cm^{-1}(s), ν(CO) 1948 cm^{-1}(m), ν(Ru−Cl) 333 cm^{-1}. $C_{76}H_{72}Cl_4O_8P_4Ru_2$: calcd 57.73% C, 4.59% H; found 57.73% C, 3.97% H. FAB-MS: [M − CO − Cl]$^+$ calcd: 1520.1, expt: 1520.6 *m*/*z*; [M − 2CO − Cl]$^+$ calcd: 1491.1, expt: 1490.6 *m*/*z*.

Synthesis of [1,4-Bis(2-diphenylphosphinoethoxy)benzene]$_2$Ru$_2$Cl$_4$(1,2-diaminopropane)$_2$ (6). A solution of 1,2-diaminopropane (3 μL, 0.036 mmol) in CH_2Cl_2 (20 mL) was added dropwise over 30 min to a solution of **2** (20 mg, 0.014 mmol) in CH_2Cl_2 (20 mL). The mixture was stirred for an additional hour to give a clear yellow solution. The solvent was removed in vacuo to give a yellow powder. Yield: 19.2 mg, 0.012 mmol, 88%. ^{1}H NMR: (CD_2Cl_2) δ 0.90 (d, 6H, J_{H-H} = 6.3 Hz, CHC*H*$_3$), 2.47−2.85 (m, 20H, N*H*$_2$, C*H*$_2$P, NH$_2$C*H*$_2$), 3.00−3.10 (br m, 2H, C*H*CH$_3$), 3.67 (br m, 8H, C*H*$_2$O), 6.33 (s, 8H, C$_6$*H*$_4$), 7.16−7.58 (complex m, 40H, P(C$_6$*H*$_5$)$_2$). ^{31}P{^{1}H} NMR: (CD_2Cl_2) 36.8 (s). $C_{74}H_{84}Cl_4O_4N_4P_4Ru_2$: calcd 56.93% C, 5.42% H, 3.59% N; found 57.45% C, 5.51% H, 3.51% N. FAB-MS: [M] calcd = 1560.2, expt = 1560.8 *m*/*z*; [M − Cl$^-$]$^+$ calcd = 1525.3, expt = 1525.8 *m*/*z*.

Synthesis of [α,α′-Bis(2-diphenylphosphinoexthoxy)-*p*-xylene]$_2$Ru$_2$Cl$_4$(pyridine)$_4$ (7). Pyridine-*d5* (15 μL, 0.199 mmol) was added to a solution of **3** (70 mg, 0.048 mmol) in CH_2Cl_2. Upon addition of the pyridine-*d5*, a color change from red to yellow/green occurred. The solvent was removed in vacuo to give a yellow/green powder, as a mixture of *cis*-chloro-*cis*-phosphine-*trans*-pyridine and all trans isomers. Yield: 74.6 mg, 0.041 mmol, 87%. ^{1}H NMR: (CD_2Cl_2) δ 2.41 (br m, 8H, C*H*$_2$P), 2.90 (br m, 8H, CH$_2$C*H*$_2$O), 4.02 (br s, 8H, C*H*$_2$O), 7.03−7.78 (complex m, 48H, Ph-*H*). ^{31}P{^{1}H} NMR: (CD_2Cl_2) δ 35.07 (s), 35.80 (s). $C_{92}H_{92}Cl_4O_4N_4P_4Ru_2$: calcd 61.88% C, 5.19% H, 3.14% N, 7.94% Cl; found 61.84% C, 4.98% H, 3.33% N, 7.91% Cl. FAB-MS: [M] calcd = 1618.2, expt = 1617.6 *m*/*z*.

Results and Discussion

Ligand Synthesis. Ligand **1** was synthesized via a substitution reaction between α,α′-dichloroethoxy-*p*-xylene and KPPh$_2$ in THF. The ligand is a mildly air-sensitive white solid, which has been characterized by ^{1}H and ^{31}P{^{1}H} NMR spectroscopies, mass spectrometry, and elemental analysis. All data are consistent with the assigned structure.

Condensed Macrocycles 2 and 3. The ruthenium condensed intermediates, **2** and **3**, were synthesized via a route analogous to those previously published for rhodium and palladium macrocycles, Scheme 2.[3b,g] The ligand 1,4-bis(2-diphenylphosphino-ethoxy)benzene and ligand **1**, dissolved in CH_2Cl_2, were added dropwise to solutions of $RuCl_2(PPh_3)_3$ in CH_2Cl_2 to form condensed intermediates **2** and **3**, respectively. In this reaction, PPh_3 is replaced by the chelating phosphine-ether ligand to form the bimetallic complexes. Due to the affinity of PPh_3 for Ru(II), all precautions must be taken to remove even trace amounts of this ligand to avoid any subsequent reactions with it. Indeed, when a CH_2Cl_2 solution of complex **2** was charged with CO in the presence of trace quantities of PPh_3, ligand substitution occurred, resulting in the formation of trace quantities of the mononuclear complex, $Ru(CO)_2Cl_2(PPh_3)_2$. This known compound[14] readily crystallizes, and its identity was confirmed by X-ray crystallography. To completely remove the PPh_3, successive recrystallizations of **2** and **3** from CH_2Cl_2 and Et_2O were carried out, leaving pure condensed intermediates, **2** and **3**. Compounds **2** and **3** have been fully characterized in solution (see Experimental Section), and **2** has been characterized in the solid state by a single-crystal X-ray diffraction study, Figure 1.

The ^{31}P{^{1}H} NMR spectra of these complexes are analogous to the spectra for similar mononuclear Ru(II) complexes with phosphine-ether ligands.[7f,h,8,10c] Unlike condensed intermediates incorporating four-coordinate rhodium(I) and palladium(II), closed macrocycles with octahedral ruthenium(II) centers can form as two geometric isomers. However, the ^{31}P{^{1}H} NMR spectra of **2** and **3** exhibit singlets at 64.1 and 64.2 ppm, respectively, indicative of the formation of only a single isomer of the condensed intermediate, with the phosphines in identical magnetic environments. Solid-state characterization of **2** suggests that the isomer formed is the *trans*-chloro, *cis*-phosphine, *cis*-ether isomer, Figure 1. NMR spectroscopy of the crystals after they have been redissolved in CD_2Cl_2 show that no additional isomerization has taken place.

Solid State Characterization of 2·4(CH_2Cl_2)·4(Et_2O). Pink needle single crystals of **2** were grown by slow diffusion of Et_2O into a dilute solution of **2**·4(CH_2Cl_2)·4(Et_2O) in CH_2Cl_2. The structure of **2**·4(CH_2Cl_2)·4(Et_2O) was determined by single-crystal X-ray diffraction methods. Diffraction intensity data were collected with a Bruker Smart Apex CCD diffractometer at 150 K. Crystal, data collection, and refinement parameters are given in Table 1. The structures were solved using the Patterson function, completed by subsequent difference Fourier syntheses, and refined by full matrix least-squares procedures on F^2. SADABS[15] absorption

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Table 1. Crystallographic Data for **2**

formula	$(C_{68}H_{64}O_4P_4Cl_4Ru_2)\cdot 4(CH_2Cl_2)\cdot 4(C_4H_{10}O)$
formula weight	2049.20
space group	$I\bar{4}$
a, Å	42.5605(18)
b, Å	42.5605(18)
c, Å	9.7061(8)
V, Å^3	17582(2)
Z	8
crystal color, habit	red, block
crystal sizes (mm)	0.15 × 0.10 × 0.05
D(calc), g cm^{-3}	1.548
μ(Mo Kα), cm^{-1}	8.37
temp, K	150(2)
diffractometer	Bruker Smart Apex CCD
radiation	Mo Kα (0.71073) Å
reflections measured	53897
reflections ind.	20119 [R_{int}=0.0584]
R(F), %[a]	6.05
R(wF^2),%[b]	13.38

corrections were applied to all data (T_{min}/T_{max} = 0.801). In the crystal structure, there are four CH_2Cl_2 and four Et_2O solvate molecules. They are highly disordered and were treated by SQUEEZE.[16] Corrections of the X-ray data by SQUEEZE (350 electrons per symmetrically independent part) were close to the required values (328 electrons). Non-hydrogen atoms were refined with anisotropic displacement coefficients. The anisotropic thermal parameters of the O(1), O(2), and C(33) atoms were negative and these atoms were refined with isotropic thermal parameters. Hydrogen atoms were treated as idealized contributions. The found Flack parameter was 0.48(4), and the structure was refined finally as a racemic twin structure. All software and sources of scattering factors are contained in the SHELXTL (5.10) program package (G. Sheldrick, Bruker XRD, Madison, WI).

The coordination environments around the Ru atoms are distorted octahedral, with the chlorine atoms pointed inward toward the cavity, with the Cl−Ru−Cl angles of 162.49(6)° and 162.83(6)°, respectively, at the Ru(1) and Ru(2) atoms. The same distortion was found in mononuclear Ru(II) complexes with hemilabile phosphine-ether ligands, where the chlorine atoms shift toward a square planar arrangement. Such slight distortion of the Cl−Ru−Cl angles from an ideal octahedral environment serves to compensate for the weakly coordinating oxygen atoms and minimizes their steric interactions with the phenyl groups on the phosphines.[5,6a−b,9] The average Ru−O bond distance of 2.31(2) Å compares well with mononuclear complexes with analogous phosphine-alkoxy ligands.[5,6a] The Ru−O distances in **2** are significantly longer than the sum of the covalent radii of these two atoms (1.99 Å),[17] suggesting the weak coordination of the O atoms. The average of the cis Ru−P bond lengths, 2.228(1) Å, is considerably shorter than those observed in a number of six-coordinate Ru(II) complexes with mutually trans phosphines, where values commonly range from 2.41 to 2.44 Å.[18] This effect is presumably due to the low trans influence of O atom compared with that of phosphorus.[5] The Ru(1)···Ru(2) distance, 8.5503(6) Å, and the arene−arene distance, 4.02 Å, as well, are slightly longer than those in rhodium and palladium based analogues.[3c,g]

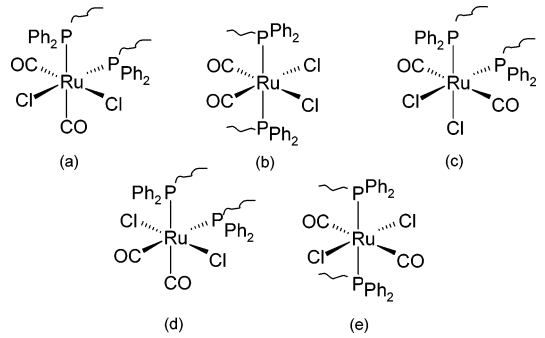

Figure 2. Possible geometric isomers about Ru(II) center for macrocycles **4** and **5**.

Neutral Macrocycles 4 and 5. Macrocycle complexes **4** and **5** were synthesized by bubbling a CH_2Cl_2 solution of **2** or **3** with CO, Scheme 3. Based on $^{31}P\{^1H\}$ NMR and FTIR data, only single isomers of open complexes **4** and **5** are formed. These new binuclear macrocycles have been characterized by ^1H, $^{31}P\{^1H\}$ NMR, and FTIR spectroscopies, mass spectrometry, and elemental analysis. Complexes **4** and **5** each yield two bands indicative of CO stretches in the IR, 1944, 2002, and 1948 cm^{-1}, 2006 cm^{-1}, respectively. Although the frequencies of these stretches fall in the range of similar mononuclear compounds,[5,6a,7c,e,f,h,10c,19] the relative intensities of the bands do not match theory to dictate a cis or trans arrangement of COs.[19] To determine which of the five possible isomers formed (Figure 2), further FTIR and NMR experiments were conducted. The far-FTIR spectra of complexes **4** and **5** each display a band at 333 cm^{-1}, associated with a Ru−Cl stretch, and indicative of *trans*-Cl groups.[20,21] The following ranges have been quoted for ν(Ru−Cl) in octahedral Ru(II) complexes: Cl trans to Cl, 347−299 cm^{-1}, Cl trans to CO, 311−266 cm^{-1}, and Cl trans to PR_3, 262−229 cm^{-1}.[20,21] These data rule out all geometric isomers with mutually *cis*-chlorides, Figure 2a−c. To distinguish between the final two possible geometric isomers, ^{13}CO was used to open the closed macrocycles. The $^{31}P\{^1H\}$ NMR spectrum displayed one triplet with J_{P-C} = 12.5 Hz, indicative of magnetically equivalent phosphines cis to the ^{13}C nuclei.[22] Taken together, these data lead to the conclusion that the geometric isomer formed is the all trans isomer, Figure 2e. The arrangement of the ligands about the Ru center in these complexes is similar to that in analogous mononuclear ruthenium complexes.[5,7c,e,f,h,10c] In many of these mononuclear examples, reaction with CO results in uptake of only one equivalent of CO, yielding a monocarbonyl species.[5,6a,7c,e,f,h] After prolonged exposure to CO, the kinetically stable all trans $RuCl_2(CO)_2(P\sim O)_2$ product is obtained

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for all mononuclear complexes studied thus far. Over time, through heating, or upon removal of the CO atmosphere, an isomerization to the thermodynamically stable *cis*-CO, *cis*-chloride, *trans*-phosphine isomer occurs.[5,7c,e,10c] Interestingly, complexes **4** and **5** form immediately as the all trans isomers but do not isomerize over time. Any attempts at heating these complexes to drive this isomerization resulted in the formation of a variety of decomposition products.

Neutral Macrocycles 6 and 7. In contrast to the rhodium and palladium based macrocycles previously synthesized,[3b,g] the weak ruthenium−oxygen bonds in **2** and **3** can be cleaved with certain types of amines. For example, addition of a stoichiometric or excess amount of 1,2-diaminopropane or pyridine to CH_2Cl_2 solutions of condensed macrocycles **2** and **3** results in the clean formation of complexes **6** and **7**, respectively (Scheme 4). The ruthenium−oxygen bonds are displaced by one equivalent per metal of the incoming bidentate 1,2-diaminopropane (complex **6**) or by two equivalents of pyridine per metal center (complex **7**). These macrocycles have been characterized by ^{1}H and ^{31}P{^{1}H} NMR spectroscopies, mass spectrometry, and elemental analysis.

Due to the octahedral coordination environment of ruthenium(II), the formation of different geometric isomers of the open complex is possible. Initially, the condensed macrocycle was combined with a variety of symmetric diamines, to yield a mixture of two products, as evidenced by the ^{31}P{^{1}H} NMR. To establish these products as geometric isomers, an asymmetric diamine, 1,2-diaminopropane, was chosen to open the condensed intermediates. Unlike the macrocycles formed from symmetric diamines, the ^{31}P{^{1}H} NMR for the different geometric isomers should display coupling of the inequivalent phosphorus atoms, establishing the different products as isomers of one another. Macrocycle **2** reacted with 1,2-diaminopropane to form complex **6** with *trans*-phosphines. This is in contrast to similar mononuclear examples, where the *trans*-chloro isomer is the most favored geometry in solution.[7j] Addition of 1,2-diaminopropane also introduces an element of chirality into the macrocycle. Though experiments in this study were conducted with a racemic mixture of the diamine, enantiomerically pure diamine can be used to cleave the ruthenium−oxygen bond to create a chiral macrocycle. Phosphorus NMR is consistent with the formation of a single isomer, but a mixture of diastereomers cannot be completely ruled out.

Addition of pyridine to macrocycle **3** yields a mixture of two geometric isomers: the all trans isomer, as well as the *cis*-chloro, *cis*-phospine, *trans*-pyridine isomer (as evidenced by ^{31}P{^{1}H} NMR spectroscopy), Scheme 4. To eliminate the possibility of the formation of isomers with cis pyridines, 2,2′-bipyridine was used as the amine and the reaction was monitored by ^{31}P{^{1}H} NMR spectroscopy. The open complexes formed and displayed ^{31}P{^{1}H} NMR chemical shifts significantly different from the shifts associated with the pyridine opened complex, **7**, indicating pyridines in a cis arrangement would have ^{31}P{^{1}H} NMR chemical shifts different from those in a trans arrangement about the ruthenium metal center. The reaction between **2** and pyridine gave a mixture of many products, including the expected open macrocycle. The side products are most likely due to the more constrained geometry and smaller cavity size of macrocycle **2** making it difficult to incorporate the bulky pyridine groups.

Conclusion

Herein, we have reported that the weak-link approach has been successfully applied to the synthesis of ruthenium containing macrocycles. This approach has now been made more general with the inclusion of a d^6 transition metal with an octahedral coordination environment, allowing for more reactive sites at the metal center. The chemistry of ruthenium(II) is different from previous four-coordinate metal centers used in this approach, allowing for new molecules, such as 1,2-diaminopropane, to be used to open the condensed intermediates. Although the additional coordination sites provided by the octahedral coordination geometry of ruthenium(II) are beneficial for conducting further chemistry, they also introduce the possibility of mixtures of geometric isomers. Characterizing and separating these mixtures adds a degree of difficulty not encountered with four-coordinate metal centers.

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Supporting Information Available: Detailed X-ray structural data including a summary of crystallographic parameters, atomic coordinates, bond distances and angles, anisotropic thermal parameters, and H atom coordinates for **2** (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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