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Isomerization of *trans*-[Ru(PTA)$_4$Cl$_2$] to *cis*-[Ru(PTA)$_4$Cl$_2$] in Water and Organic Solvent: Revisiting the Chemistry of [Ru(PTA)$_4$Cl$_2$]

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trans-[Ru(PTA)$_4$Cl$_2$] (*trans*-**1**), (PTA = 1,3,5-triaza-7-phosphatricyclo[3.3.1.1^{3,7}]decane) has been isolated and structurally characterized by X-ray crystallography. The structure reveals ruthenium in a slightly distorted-octahedral environment bound to two axial chlorides and four equatorial PTA ligands. In organic solvents, *trans*-**1** undergoes a relatively clean isomerization to *cis*-**1**. In aqueous environments, *trans*-**1** undergoes a more complicated transformation involving isomerization, protonation, and ligand substitution affording *cis*-**1** and a series of structurally related molecules. From these results, we conclude that the synthesis of [Ru(PTA)$_4$Cl$_2$] (**1**) affords *trans*-**1**, not *cis*-**1**, as earlier reports suggest. The water-soluble hydride *cis*-[Ru(PTA)$_4$H$_2$] (**2**) has also been synthesized from the reaction of *trans*-[Ru(PTA)$_4$Cl$_2$] with excess sodium formate. Compound **2** is stable in deoxygenated water and undergoes H/D exchange with D$_2$O ($t_{1/2} \approx 120$ min, at 25 °C). The solid-state structures of both *trans*-**1** and **2** are described.

Introduction

Over the past few years, there has been a resurgence of attention given to the design and synthesis of water-soluble metal complexes of 1,3,5-triaza-7-phosphaadamantane (PTA).[1] Inorganic and organometallic complexes of PTA have found applications in coordination chemistry,[2] medicine,[3] and aqueous/biphasic catalysis.[4] The earliest reports on the synthesis and catalytic activity of PTA complexes involved the ruthenium compound [Ru(PTA)$_4$Cl$_2$] (**1**), synthesized in essentially quantitative yield by the reaction of PTA with RuCl$_3$·3H$_2$O in ethanol (Scheme 1).[5] Compound **1** has been employed as a catalyst for the hydrogenation of aldehydes,[5] olefins,[5] and CO$_2$[6] in aqueous or biphasic media. In the previous report on the synthesis of **1**, crystals obtained from an aqueous solution of [Ru(PTA)$_4$Cl$_2$] were analyzed by X-ray crystallography and determined to be *cis*-[Ru(PTA)$_4$Cl$_2$], which led to the conclusion that the synthesis of **1** affords the cis isomer even though the ^{31}P NMR

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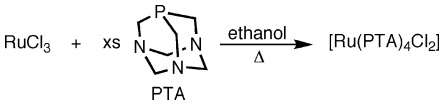
Scheme 1



spectrum contained only a single resonance.[5] Though *cis*-[Ru(PTA)$_4$Cl$_2$] has been isolated and characterized by X-ray crystallography, the trans isomer has remained unidentified.

The hydride species *cis*-[Ru(PTA)$_4$H$_2$] (**2**), and [RuCl(PTA)$_4$H] have been implicated as the catalytically active species in hydrogenation.[5,6] An understanding of the aqueous chemistry of **1** and derivatives such as **2** are important in the understanding and elucidation of reaction mechanisms involving metal hyrides. [Ru(PTA)$_4$H$_2$] and [Ru(PTA)$_4$ClH] have been generated in situ by the reaction of **1** with 60 bar H_2 or by the reaction of $Ru(OH_2)_6^{2+}$ with PTA and H_2.[6a] The decomposition of (η^6-arene)RuPTACl$_2$ in aqueous solutions, at 60 °C and 100 bar H_2, has also been shown to result in the formation of [Ru(PTA)$_4$H$_2$] and [Ru(PTA)$_4$ClH] in addition to other products.[7]

Herein, we report the solution and solid-state characterization of *trans*-[Ru(PTA)$_4$Cl$_2$] as well as evidence that *trans*-**1** isomerizes in solution, yielding *cis*-**1**. The synthesis, reactivity, and solid-state structure of the water-soluble ruthenium dihydride *cis*-[Ru(PTA)$_4$H$_2$] are also reported.

Experimental Section

Materials and Methods. All reagents were obtained from commercial sources, checked by NMR and GC/MS, and used as received. PTA[8] and [Ru(PTA)$_4$Cl$_2$][5] were prepared according to the literature procedures. The NMR spectra were recorded on a Varian NMR System 400 spectrometer. ^{1}H NMR spectra were referenced to residual solvent relative to TMS. Phosphorus chemical shifts are relative to an external reference of 85% H_3PO_4 in D_2O with positive values downfield of the reference. UV−vis spectra were recorded on a Hewlett−Packard 8453 diode-array spectrometer. The IR spectra were recorded on Perkin-Elmer 2000 FT-IR spectrometer, in a 0.1 mm CaF_2 cell for solutions or as a KBr pellet for solid samples.

Synthesis of *trans*-[Ru(PTA)$_4$Cl$_2$] (*trans*-1). *trans*-**1** was synthesized following the same procedure reported for the preparation of *cis*-[Ru(PTA)$_4$Cl$_2$] (Scheme 1).[5] An ethanol solution of $RuCl_3 \cdot 3H_2O$ (1.00 g, 3.8 mmol) and excess PTA (3.60 g, 23.0 mmol) were refluxed under nitrogen for 4 h affording 3.0 g of *trans*-[Ru(PTA)$_4$Cl$_2$] as a yellow precipitate (98% yield). The ^{31}P{^{1}H} and ^{1}H NMR spectra of a D_2O solution of *trans*-**1** are consistent with those reported by Darensbourg and co-workers.[5] ^{1}H NMR (500 MHz, D_2O): δ 4.52 (s, 24H NCH_2N); 4.24 (s, 24H PCH_2N). ^{31}P{^{1}H} NMR (162 MHz): δ −51.6 (s, 4P) in D_2O; −49.29 (s, 4P) in $CDCl_3$. Isomerization occurred upon standing in solution and was evident by the appearance of new peaks in the ^{31}P NMR spectrum assigned to *cis*-**1**. ^{31}P{^{1}H}: δ −23.40, (t, *cis*-PTA, $^2J_{PP}$ = 21.7 Hz); and −57.64 (t, *trans*-PTA, $^2J_{PP}$ = 21.7 Hz). Orange crystals of *trans*-**1** were obtained by the slow diffusion of diethyl ether into a CH_2Cl_2 solution of **1**.

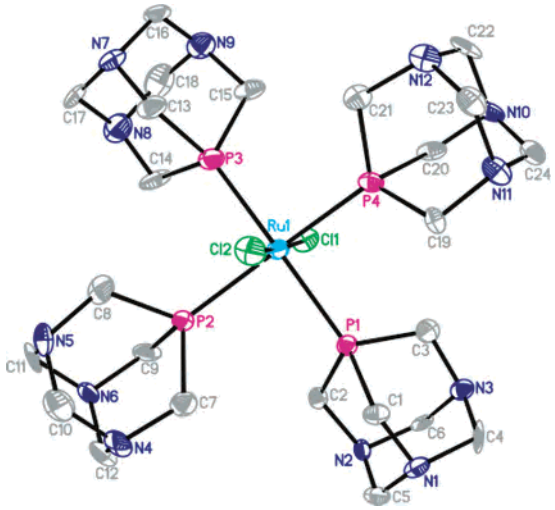


Figure 1. Thermal ellipsoid representation of *trans*-**1** (50% probability) including the atomic numbering scheme. Hydrogen atoms have been omitted for clarity.

Synthesis of *cis*-[Ru(PTA)$_4$H$_2$] (2). A suspension of **1** (0.80 g, 1.0 mmol) and HCOONa (0.68 g, 10 mmol) was refluxed for 12 h under nitrogen in 50 mL methanol, yielding a pale yellow precipitate. The solvent was removed by cannula, and the precipitate was washed three times with freshly distilled methanol. The resulting solid was dried under vacuum, affording 0.46 g of **2** (62% yield) as a white crystalline powder. ^{1}H NMR (400 MHz, D_2O): δ 4.34 and 4.26 (AB spin system, $^2J_{HAHB}$ = 14.5 Hz, 24H NCH_2N), 3.63 (s, 12H PCH_2N), 3.59 (s, 12H PCH_2N), −11.50 (m, 2H, Ru−H). ^{31}P{^{1}H} NMR (162 MHz, D_2O): δ −26.60 (t, *cis*-PTA, $^2J_{PP}$ = 25.0 Hz), −32.19 (t, *trans*-PTA, $^2J_{PP}$ = 25.0 Hz). IR (KBr): ν(Ru−H) = 1800 (br) cm^{-1}. Colorless block crystals of **2** suitable for X-ray diffraction were obtained by the slow diffusion of acetone into an aqueous solution of **2**.

X-ray Crystallography. Crystals of *trans*-**1** and **2** suitable for X-ray diffraction were obtained as described above. The data were collected at 123(±2) K for *trans*-**1** and 100(±2) K for **2** on a Bruker APEX CCD diffractometer with Mo Kα radiation (λ = 0.71073 Å) and a detector-to-crystal distance of 4.94 cm. A full sphere of data was collected utilizing four sets of frames, 600 frames per set, with 0.5° rotation about ω between frames, and an exposure time of 10 s per frame. Data integration, correction for Lorentz and polarization effects, and final cell refinement were performed using *SAINTPLUS* and corrected for absorption using *SADABS*. The structures of *trans*-**1** and **2** were solved using direct methods followed by successive least-squares refinement on F^2 using the *SHELXTL 5.12* software package.[9] All non-hydrogen atoms were refined anisotropically, and hydrogen atoms were placed in calculated positions. Crystallographic data and data collection parameters are listed in Table 1.

Results and Discussion

The synthesis of **1** has been previously described by Darensbourg and co-workers and may exist as two geometric isomers, *trans*-**1** and *cis*-**1**.[5] The cis isomer was isolated from an aqueous solution of **1**, leading to the reasonable conclusion

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(9) *XRD Single-Crystal Software*; Bruker Analytical X-ray Systems: Madison, WI, 1999.

Table 1. Crystal Data and Structure Refinement for *trans*-**1** and **2**

	trans-Ru(PTA)$_4$Cl$_2$	*cis*-Ru(PTA)$_4$H$_2$
empirical formula	$C_{25.5}H_{48}Cl_2N_{12}O_2P_4Ru$	$C_{24}H_{62}N_{12}O_{6.25}P_4Ru$
fw	850.61	843.81
T (K)	123(2)	100(2)
λ (Å)	0.71073	0.71073
cryst syst	orthorhombic	monoclinic
space group	$Pca2_1$	$P2_1/n$
a (Å)	19.0404(18)	10.8018(2)
b (Å)	13.3413(12)	15.7700(2)
c (Å)	13.7702(13)	21.6830(3)
α (deg)	90	90
β (deg)	90	97.66
γ (deg)	90	90
V (Å^3)	3498.0(6)	3660.59(10)
Z	4	4
D_{calc} (Mg/m^3)	1.657	1.531
abs coeff (mm^{-1})	0.835	0.659
cryst size (mm^3)	0.26 × 0.06 × 0.02	0.21 × 0.12 × 0.10
θ range for data collection (deg)	1.53−24.99	1.60−29.58
index ranges	$-22 \le h \le 10$ $-15 \le k \le 15$ $-15 \le l \le 16$	$-14 \le h \le 14$ $-21 \le k \le 21$ $-30 \le l \le 27$
reflns collected	17 867	46 098
indep reflns	6045 [R_{int} = 0.1302]	10 199 [R_{int} =0.0497]
abs correction	*SADABS*	*SADABS*
data/rest/param	6045/15/433	10199/0/489
GOF F^2	0.819	1.021
final R indices	R_1 = 0.0536	R_1 = 0.0345
[$I > 2\sigma(I)$]	R_2 = 0.0902	R_2 = 0.0683
R indices	R_1 = 0.0897	R_1 = 0.0573
(all data)	R_2 = 0.0999	R_2 = 0.0770
CCDC no.	642802	642803

that the cis isomer is formed in the reaction. The cis geometry is, however, inconsistent with the observation of a single resonance at −47.3 ppm in the $^{31}P\{^1H\}$ NMR spectrum of **1** in D_2O.[5,10]

During a reinvestigation of some of the chemistry previously reported for **1**, we isolated orange crystals of *trans*-**1** from a dichloromethane solution (Figure 1). *trans*-[Ru(PTA)$_4$Cl$_2$] crystallized in the orthorhombic space group $Pca2_1$. The solid-state structure shows ruthenium in a distorted-octahedral environment bound to two mutually trans chloride ligands and four PTA ligands occupying equatorial positions of the octahedron cis to the chloride ligands (Figure 2). Relevant structural parameters of *trans*-[Ru(PTA)$_4$Cl$_2$] are presented in Table 2. The two Ru−Cl bond lengths of *trans*-**1** are identical, 2.437(2) Å, and slightly shorter than those reported for the cis isomer, 2.488(2) and 2.503(2) Å.[5] The Ru−P bond distances in *trans*-**1** range from 2.316 to 2.353 Å, slightly longer than the Ru−P bond lengths trans to Cl in *cis*-**1** (2.260(2) Å), and shorter than the Ru−P bond lengths trans to phosphorus in *cis*-**1** (2.370(2) Å).[5] The (N)C−N distances of the PTA ligands are found to be in the range of 1.41 to 1.50 Å, consistent with those of nonprotonated PTA ligands.[11] The bond angles of the *trans*-PTA ligands, P(1)−Ru−P(3) = 161.538° and P(2)−Ru−P(4) = 164.248° for *trans*-**1**, significantly deviate from linearity much more so than that of Cl(1)−Ru−Cl(2), 175.568°. This deviation from linearity of the P−Ru−P angles may be attributed to steric encumbrance of the phosphine ligands at the equatorial plane, Figure 2.

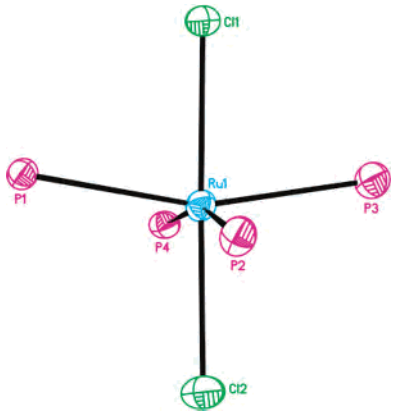
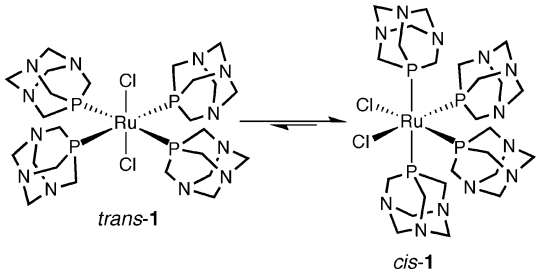


Figure 2. Thermal ellipsoid representation (50% probability) of *trans*-**1** showing the distorted-octahedral environment. For clarity, only the P, Cl, and Ru atoms are shown.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for *trans*-**1**, *cis*-**1**, and **2**

	trans-**1**	*cis*-**1**[5]	**2**
Ru−P1	2.353(2)	2.267(2)	2.2999(5)
Ru−P2	2.349(2)	2.351(2)	2.2990(5)
Ru−P3	2.333(2)	2.252(2)	2.2904(6)
Ru−P4	2.317(2)	2.388 (2)	2.2904(6)
Ru−Cl/H1	2.437(2)	2.488(2)	1.60(2)
Ru−Cl/H2	2.438(2)	2.503(2)	1.62(2)
P1−Ru−P2	88.73(8)	94.2(1)	100.402(19)
P1−Ru−P3	161.53(8)	96.5(1)	100.002(19)
P1−Ru−P4	91.37(8)	100.1(1)	99.780(19)
P2−Ru−P3	90.21(8)	92.2(1)	98.89(2)
P2−Ru−P4	164.24(8)	164.8(1)	99.38(2)
P3−Ru−P4	94.58(9)	91.3(1)	150.05(2)
Cl/H1−Ru−P1	81.76(8)	169.7(1)	84.6(9)
Cl/H1−Ru−P2	102.58(8)	82.1(1)	174.9(9)
Cl/H1−Ru−P3	80.48(8)	93.3(1)	78.9(8)
Cl/H1−Ru−P4	91.37(8)	83.0(1)	80.9(8)
Cl/H2−Ru−P1	100.46(8)	86.2(1)	174.6(8)
Cl/H2−Ru−P2	81.38(8)	90.0(1)	85.0(8)
Cl/H2−Ru−P3	97.60(8)	176.3(1)	78.8(8)
Cl/H2−Ru−P4	83.11(8)	85.7(1)	79.3(8)
Cl/H1−Ru−Cl/H2	175.56(8)	84.2(1)	90.0(12)

Scheme 2



Isomerization of *trans*-1 in Chloroform. After the isolation of *trans*-**1** in the solid form, we examined the reactivity of *trans*-**1** in solution. Specifically, we looked for evidence of isomerization to the previously isolated *cis*-**1** (Scheme 2). Freshly prepared solutions of *trans*-**1** provide ^1H and ^{31}P NMR spectra similar to that previously reported for **1**. The $^{31}P\{^1H\}$ NMR spectrum of [Ru(PTA)$_4$Cl$_2$] in $CDCl_3$ contains a single resonance at −49.29 ppm. Over the

(10) A single $^{31}P\{^1H\}$ resonance would, of course, be expected for *cis*-[Ru(PTA)$_4$Cl$_2$] if the molecule was fluxional.

(11) Darensbourg, D. J.; Decuir, T. J.; Reibenspies, J. H. *Aqueous Organometallic Chemistry and Catalysis*; Horvath, I. T., Joó, F., Eds.; High Technology; Kluwer: Dordrecht, The Netherlands, 1995; pp 61−80.

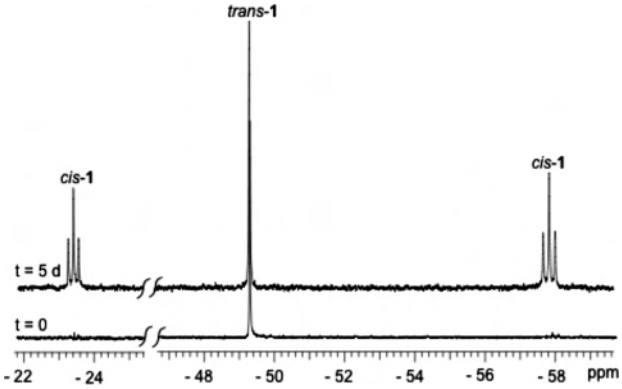


Figure 3. $^{31}P\{^1H\}$ NMR spectra of $[Ru(PTA)_4Cl_2]$ in $CDCl_3$ showing the isomerization of *trans*-**1** to *cis*-**1**; a small singlet at −11.83 ppm has been omitted for clarity.

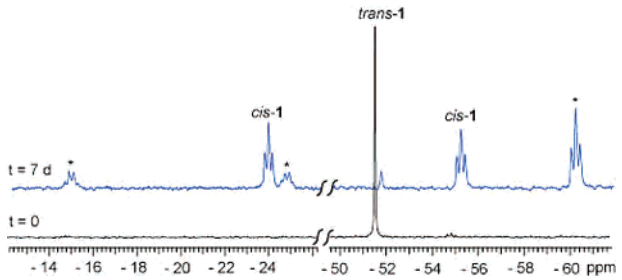


Figure 4. $^{31}P\{^1H\}$ NMR spectra over time of *trans*-**1** in D_2O (* denotes unidentified product(s)). The top spectrum is shifted slightly to show the remaining *trans*-**1** signal.

course of days, this singlet decreases in intensity, concomitant with the appearance of two triplets at −23.40 (t, *cis*-PTA, $^2J_{PP} = 21.7$ Hz) and −57.64 ppm (t, *trans* PTA, $^2J_{PP} = 21.7$ Hz) (Figure 3). The isomerization process is relatively clean, with a small impurity at −11.83 ppm appearing and some decomposition evident as a small amount of precipitate is observed over time. The cis/trans ratio appears to reach equilibrium in $CDCl_3$ over the course of a week ($K_{eq} \approx 1.84$).

Isomerization of *trans*-1 in Water. The dissolution of **1** in D_2O was monitored by $^{31}P\{H\}$ NMR spectroscopy. Freshly prepared samples of **1** in D_2O contain a single phosphorus resonance at −51.62 ppm attributed to *trans*-**1**. Over a period of 1 week, *trans*-**1** is observed to essentially completely isomerize to *cis*-**1** along with the formation of at least one other species (Figure 4). This is consistent with reports of Joó and co-workers, who observed a series of substitutional isomers $[Ru(PTA)_n(OH_2)_{6-n}]^{2+}$ from the reaction of $[Ru(OH_2)_6]^{2+}$ with PTA.[12] The resonances for *cis*-**1** are observed at −24.0 ppm (t, $^2J_{PP} = 22.7$ Hz, *cis*-PTA) and −54.9 ppm (t, $^2J_{PP} = 22.7$ Hz, *trans*-PTA). This agrees well with the $^{31}P\{^1H\}$ NMR data reported by Joó for *cis*-$[Ru(PTA)_4(OH)_2]$, which exhibited peaks at −17.1 (t) and −51.8 (t) ppm in D_2O with $^2J_{PP} = 27.6$ Hz.[12] Other resonances observed include quartets at −15.1 ppm ($^2J_{PP} = 26.2$ Hz) and −25.2 ppm ($^2J_{PP} = 24.6$ Hz) and a triplet at −59.7 ppm ($^2J_{PP} = 21.7$ Hz). The dynamic behavior of *trans*-**1** in an aqueous medium was further confirmed by UV−vis absorption spectroscopy. The UV−vis absorption spectrum of an aqueous solution of *trans*-**1** contains two major absorbance features at 320 and 459 nm. The absorbance at 320 nm increases and shows a slight bathochromic (red) shift over time, attributed to ligand-exchange processes of $[Ru(PTA)_4Cl_2]$.

Isomerization of *trans*-1 in Acidic Solution. The speciation of **1** in 2 mM HCl solution was also investigated by $^{31}P\{^1H\}$ NMR spectroscopy. The $^{31}P\{^1H\}$ NMR spectrum of **1** in acidic solution contains resonances assigned to *trans*-**1** (−49.41 ppm), $[Ru(PTAH)(PTA)_2Cl_3]$, and free $[PTAH]^+$ (−90 ppm). The resulting acidic solution of **1** was monitored for 2 weeks, revealing the consumption of *trans*-**1** and the formation of *cis*-**1**. The $^{31}P\{^1H\}$ NMR resonances for *cis*-**1** appear at δ −24.45 ppm (t, $^2J_{PP} = 22.7$ Hz, *cis*-PTA) and −55.19 ppm (t, $^2J_{PP} = 22.7$ Hz, *trans*-PTA). The ^{31}P NMR spectrum also contains a triplet at −4.54 ppm ($^2J_{PP} = 28.2$ Hz, $[PTAH]^+$) and a doublet at −43.88 ppm ($^2J_{PP} = 28.2$ Hz, PTA) tentatively assigned as $[Ru(PTAH)(PTA)_2Cl_3]$. Darensbourg et al. have observed the formation of $[Ru(PTAD)(PTA)_2Cl_3]$ in a DCl solution and isolated $[Ru(PTAH)_2(PTA)_2Cl_2](Cl)_2$ from a 0.1 M HCl solution.[5b] An analogous rhodium complex, $[RhCl(PTAH)(PTA)_2]Cl_3$, has been synthesized and spectroscopically characterized.[13] Other potential products include the previously reported $[Ru(PTAH)_2Cl_4]$,[14] the Ru(III) complex $RuCl_3(PTA)_2 \cdot 2HCl$,[5a] or any of the varieties of Ru(II) aquo/hydroxide/PTA species such as $[Ru(PTA)_4(H_2O)(OH)]^+$ or $[Ru(PTA)_4(H_2O)_2]^{2+}$ reported by Joó and co-workers.[12]

The aforementioned results confirmed that $[Ru(PTA)_4Cl_2]$ is synthesized as the trans isomer. $[Ru(PTA)_4Cl_2]$ undergoes trans−cis isomerization in water and chloroform at room temperature and explains the isolation of *cis*-**1** from an aqueous solution of **1**.[5] Similarly, the analogous complex $[Ru(PMe_3)_4Cl_2]$ is reported to afford the trans isomer confirmed by a single resonance at −47.0 ppm in CD_2Cl_2.[15] Cis−trans isomerization of the related metal−phosphine complexes $[MCl_2(DPPM)_2]$ (M = Ru, Os; DPPM = bis-(diphenylphosphino)methane), has been reported to occur by photochemical or electrochemical processes.[16,17] The reverse process, trans−cis isomerization of $[MCl_2(DPPM)_2]$, was shown to occur by employing heat or copper(I) halides as catalysts.[17]

Synthesis and Reactivity of *cis*-$[Ru(PTA)_4(H)_2]$. The reaction of *trans*-**1** with 10-fold excess of sodium formate afforded the water-soluble ruthenium hydride, *cis*-$[Ru(PTA)_4H_2]$ (**2**); $S_{25^\circ C} = 106$ mg/mL (0.15 M), as a yellow precipitate in 62% yield after workup (Scheme 3). Compound **2** has been partially generated (<5%) in solution[6a] by the reaction of an aqueous solution of **1** under H_2 pressure at pH 12.[6a] Compound **2** is insoluble in methanol, acetone, and chlorinated solvents such as chloroform and methylene

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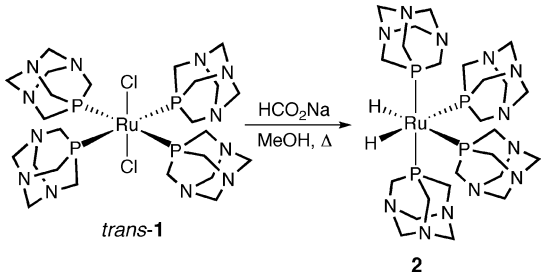
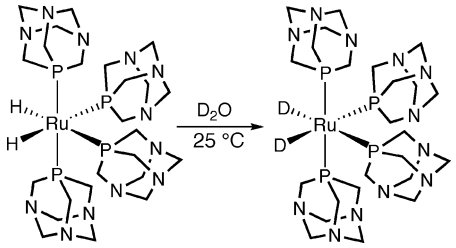
Scheme 3



Scheme 4



chloride. The proton NMR spectrum of **2** in D_2O contains an AB quartet centered at δ 4.34 and 4.26 ppm ($^2J_{HAHB}$ = 14.5 Hz) for NCH_2N protons and two singlets at 3.63 and 3.58 ppm for the PCH_2N protons of PTA. The Ru−H signal was recorded at high field, −11.50 ppm, as a multiplet in agreement with the value earlier reported.[6] ^{31}P{^{1}H} NMR spectrum of **2** is also consistent with that reported in the literature.[6] The IR spectrum of **2** contains a broad absorbance at 1800 cm^{-1} assigned to the ν(Ru−H) stretch.

Compound **2** is stable in air both in the solid state and in aqueous solution. Unlike **1**, an aqueous solution of **2** monitored by ^{31}P{^{1}H} NMR spectroscopy over a week showed no evidence of decomposition, ligand protonation, or exchange.

The ruthenium hydride, **2**, does undergo H/D exchange with D_2O, affording *cis*-[Ru(PTA)$_4$D$_2$], Scheme 4. This is confirmed by the disappearance of the hydride resonance in the ^{1}H NMR spectrum of **2**.[18] Upon the addition of D_2O, the absorption at 1800 cm^{-1}, ν(Ru−H), is no longer visible in the IR spectrum and a new absorbance at 1303 cm^{-1} is observed corresponding to ν(Ru−D). The isotopic shift ($\Delta\nu$ = 497 cm^{-1}) is close to the value expected from Hooke's law for a pure Ru−H stretching mode (calculated shift 554 cm^{-1}).[19] The rate of H/D exchange for **2** in D_2O ($t_{1/2} \approx$ 120 min, at 25 °C) is comparable to that observed for the related organometallic analogue CpRu(PTA)$_2$H ($t_{1/2}$ = 127 min, at 25 °C).[4e] Joó and co-workers have reported that **1** catalyzes the H/D exchange between D_2O and H_2 under acidic conditions (pH 5.5 TOF = 8.5 h^{-1} at 25 °C, TOF = mol HDO formed/mol cat/h).[20] Presumably occurring through a Ru−H complex, either Ru(PTA)$_4$HCl or Ru(PTA)$_4$H$_2$.

Colorless block crystals of the tetrakis-phosphino ruthenium(II) dihydride, *cis*-[Ru(PTA)$_4$H$_2$], were obtained by the slow diffusion of acetone into an aqueous solution of **2**. *cis*-

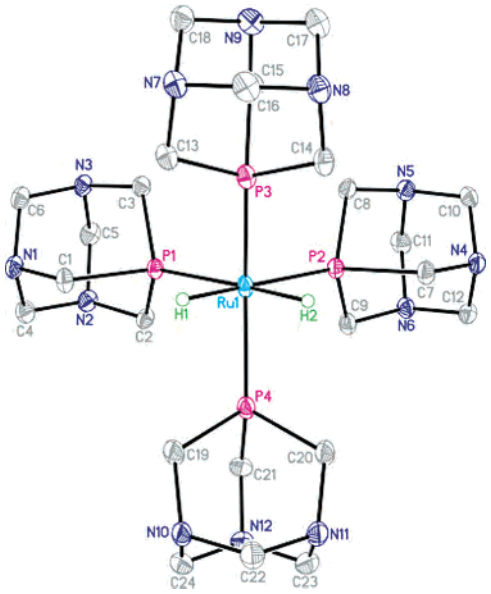


Figure 5. Thermal ellipsoid representation of **2** (50% probability) including the atomic numbering scheme. Hydrogen atoms have been omitted for clarity.

[Ru(PTA)$_4$H$_2$] crystallized in the monoclinic space group $P2_1/c$. Presented in Figure 5 is the thermal ellipsoid representation of *cis*-[Ru(PTA)$_4$H$_2$]. Selected bond lengths and angles of *cis*-[Ru(PTA)$_4$H$_2$] are contained in Table 2. The Ru−P bond lengths for **2** are 2.2904(5) Å for the cis PTA ligands and 2.2999(5) Å for the trans phosphorus ligands. These values are within the range recorded for the chloride analogue (2.252−2.388 Å).[5] The most significant structural difference between **2** and *cis*-[Ru(PTA)$_4$Cl$_2$] is the P−Ru−P bond angle of the trans PTA ligands. The P−Ru−P bond angle for *cis*-[Ru(PTA)$_4$Cl$_2$] (164.81 Å) is 14.8° greater than that for *cis*-[Ru(PTA)$_4$H$_2$] (150.05 Å) and can be ascribed to both the smaller steric requirement of H$^-$ versus Cl$^-$ and an electronic effect. On the basis of electronic effects, the PTA ligands would be expected to move toward the hydride, as H$^-$ is a better σ donor than Cl$^-$.[21] The (N)C−N distances of the PTA ligands are found to be in the range of 1.45−1.49 Å, consistent with that of nonprotonated PTA ligands.[11] Six equiv of water co-crystallize with **2** and are hydrogen bound to the nitrogen atoms of the PTA ligands. The N···O separations are found to be between 2.8301 and 2.908 Å, well within standard hydrogen-bonding distances.[18]

Conclusions

We have presented here the isolation and solid-state characterization of *trans*-[Ru(PTA)$_4$Cl$_2$] and *cis*-[Ru(PTA)$_4$H$_2$]. The air-stable ruthenium hydride *cis*-[Ru(PTA)$_4$H$_2$] has been synthesized, isolated, and characterized by X-ray crystallography. *cis*-[Ru(PTA)$_4$H$_2$] undergoes H/D exchange with D_2O at room temperature ($t_{1/2} \approx$ 120 min, 25 °C). From the spectroscopic and crystallographic data presented, we conclude that the isolation of *cis*-[Ru(PTA)$_4$Cl$_2$] from an aqueous solution of **1** results from the isomerization of the trans

(18) See the Supporting Information.
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*i*somer. This study and others[5−7,12,20] show that the ligand-exchange chemistry of **1** and related compounds in water is complicated and affords a wide variety of species.

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Supporting Information Available: Full tables of bond lengths and angles for *trans*-**1** and **2**, IR spectra of **2** and **2**-D, UV−vis spectra of *trans*-**1** in water, ^{31}P and ^{1}H NMR spectra of **1** and **2**, ^{1}H NMR spectra of **2** in D_2O over time; crystallographic files in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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