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# New Rhodium(III) and Ruthenium(II) Water-Soluble Complexes with 3,5-Diaza-1-methyl-1-azonia-7-phosphatricyclo[3.3.1.1<sup>3,7</sup>]decane

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New Rhodium(III) and Ruthenium(II) Water-Soluble Complexes with 3,5-Diaza-1-methyl-1-azonia-7-phosphatricyclo[3.3.1.1<sup>3,7</sup>]decane

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The new water-soluble phosphine complexes of rhodium(III),  $[\text{RhI}_4(\text{mtpa})_2]\text{I}$  (**1**), and ruthenium(II),  $[\text{RuI}_4(\text{mtpa})_2] \cdot 2\text{H}_2\text{O}$  (**2**) and  $[\text{RuI}_2(\text{mtpa})_3(\text{H}_2\text{O})]\text{I}_3 \cdot 2\text{H}_2\text{O}$  (**3**) (mtpa = 3,5-diaza-1-methyl-1-azonia-7-phosphatricyclo[3.3.1.1<sup>3,7</sup>]decane cation), have been prepared in the reactions of  $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$  and  $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$  in water in the presence of phosphine and potassium iodide. Properties and reactivity of the complexes have been investigated using  $^1\text{H}$  and  $^{31}\text{P}$  NMR and IR spectroscopies. The complexes have also been structurally characterized by single crystal X-ray diffraction studies. The compounds  $[\text{RhI}_4(\text{mtpa})_2]\text{I}$  and  $[\text{RuI}_4(\text{mtpa})_2] \cdot 2\text{H}_2\text{O}$  are zwitterionic octahedral complexes. The compounds were tested as catalysts for two-phase hydroformylation of 1-hexene and hydrogenation of cinnamaldehyde. Complex **1** is a selective catalyst for reduction of the C=C bond while complexes **2** and **3** selectively hydrogenate the C=O bond.

## Introduction

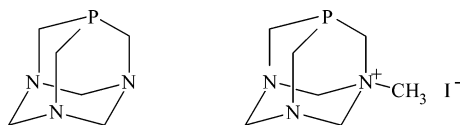
Water-soluble organometallic chemistry has received significant interest in the past few years. The basic problem of homogeneously catalyzed processes is the separation of the product from the solvent and the catalyst, which is soluble in it. Water-soluble catalysts combine the advantages of homogeneous and heterogeneous catalysis: simple separation of the product from the catalyst and high activity and selectivity.<sup>1–5</sup> Water solubilization of known coordination and organometallic catalysts is performed by incorporating highly polar functional groups such as  $\text{SO}_3\text{H}$ ,  $\text{COOH}$ ,  $\text{NH}_2$ ,  $\text{NR}_3^+$ ,  $\text{PR}_3^+$ , or  $\text{OH}$  into phosphine ligands.<sup>1–11</sup> Most

investigations of metal phosphine complexes involve the sulfonated arylphosphine ligands. Comparatively little work has been carried out on hydrophilic trialkylphosphines. Interesting properties are exhibited by 1,3,5-triaza-7-phosphatricyclo[3.3.1.1<sup>3,7</sup>]decane (tpa) (Chart 1).<sup>12</sup> It has a very small cone angle ( $103^\circ$ ).<sup>13</sup> The preparation and characterization of rhodium<sup>14–16</sup> and ruthenium<sup>13,17–18</sup> complexes; ruthenium and iridium clusters;<sup>19</sup> and platinum,<sup>20,21</sup> nickel,<sup>21</sup> palladium,<sup>21</sup> gold,<sup>22,23</sup> chromium,<sup>24</sup> molybdenum,<sup>24,25</sup> iron,<sup>24</sup>

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Chart 1



and tungsten<sup>24</sup> coordination compounds with tpa have already been reported, and their catalytic activity and spectroscopic properties have been investigated. 3,5-Diaza-1-methyl-1-azonia-7-phosphatricyclo[3.3.1.1<sup>3,7</sup>]decane iodide (mtpaI) (Chart 1) is more readily soluble in polar solvents than tpa. Complexes with this ligand show stronger hydrophilic properties, and therefore, their concentration in organic phases is lower in comparison with complexes containing the tpa ligand.<sup>26</sup> Catalytic properties of rhodium(I) complexes with mtpaI have been described.<sup>27</sup> In this paper, we report on the structure and properties of three new rhodium(III) and ruthenium(II) complexes with mtpaI and their catalytic properties.

## Experimental Section

All manipulations were done under inert atmosphere using standard Schlenk technique.

**Reagents.** Preparation of the phosphine mtpaI<sup>28</sup> was carried out as reported in the literature. RhCl<sub>3</sub>·3H<sub>2</sub>O and RuCl<sub>3</sub>·3H<sub>2</sub>O (Aldrich) were used as received.

**Instrumentation.** Infrared spectra (KBr pellets and Nujol mulls) were recorded on a Bruker IFS113v, and <sup>1</sup>H and <sup>31</sup>P NMR, on a Bruker 300 AMX. Chromatographic measurements were carried out on a HP5990 chromatograph using FID, TCD, and MS detectors. Elemental analyses were performed on a Perkin-Elmer 2400 CHN analyzer.

**Catalytic Reactions.** Hydrogenation and hydroformylation reactions under high pressure were carried out in autoclaves (Berghof) and at atmospheric pressure in glass vessels at constant volume. The autoclaves and glass vessels were first filled with nitrogen and then with solvent, reactants, and catalyst. The reactors were subsequently filled with H<sub>2</sub> with several evacuation/refill cycles. Catalytic reactions with sodium formate were performed in nitrogen atmosphere. After reaction, the organic layer and water solution containing catalyst were separated under nitrogen, and the catalyst was used in the next catalytic reaction performed analogously as previous one. Each catalyst was recycled three times.

**X-ray Structural Determinations.** X-ray quality crystals of complexes **1**, **2**, and **3** were grown from aqueous solutions, and those of complex **2a**, from DMSO–methanol solution under nitrogen atmosphere. X-ray data were collected on a Kuma diffraction KM-4 CCD diffractometer. The intensities were corrected for Lorentz and polarization effects for analytical (**1**) and

empirical absorption (**2**, **2a**, and **3**) using the XEMP program.<sup>29</sup> Computing of molecular graphics was done using the XP program from the SHELXTL/PC.<sup>29</sup> Structures were solved by the heavy atom method using the SHELXS program<sup>30</sup> and refined on *F*<sup>2</sup> values by full-matrix least-squares using the SHELXL program<sup>31</sup> with anisotropic displacement parameters for non-hydrogen atoms.

**Synthesis of Complexes. [RhI<sub>4</sub>(mtpa)<sub>2</sub>]**1**.** A mixture of 1.2 mmol (0.3588 g) of mtpaI, 0.60 mmol of RhCl<sub>3</sub>·3H<sub>2</sub>O (0.1580 g), and 1.8 mmol of potassium iodide (0.2988 g) in water (30 cm<sup>3</sup>) was stirred at room temperature for ca. 2 h. The dark-red product was filtered off, washed with water, and dried in vacuo. Yield: 0.5582 g (86%). Anal. Calcd for C<sub>14</sub>H<sub>30</sub>I<sub>5</sub>N<sub>6</sub>P<sub>2</sub>Rh: C, 15.54; H, 2.80; N, 7.77. Found: C, 15.26; H, 2.82; N, 7.42.

**[RuI<sub>4</sub>(mtpa)<sub>2</sub>]**2**, and [RuI<sub>4</sub>(mtpa)<sub>2</sub>]**2a**.** To 0.0787 g (0.301 mmol) of RuCl<sub>3</sub>·3H<sub>2</sub>O and 0.7495 g (4.515 mmol) of potassium iodide dissolved in 10 cm<sup>3</sup> water was added 0.2115 g (0.707 mmol) of mtpaI. A mixture was stirred at ca. 40 °C for 1 h. The solution changed to deep-green, and precipitated product was separated and recrystallized from DMSO–water giving yellow-brown crystals. The product was washed with cold water and dried in vacuo. Yield: 0.1340 g, (45%). Anal. Calcd for [RuI<sub>4</sub>(mtpa)<sub>2</sub>]**2**·2H<sub>2</sub>O, C<sub>14</sub>H<sub>34</sub>I<sub>4</sub>N<sub>6</sub>O<sub>2</sub>P<sub>2</sub>Ru: C, 17.00; H, 3.46; N, 8.50. Found: C, 17.07; H, 3.36; N, 8.54. Complex **2a**, [RuI<sub>4</sub>(mtpa)<sub>2</sub>], was obtained after recrystallization of compound **2** from a DMSO–methanol mixture. Anal. Calcd for [RuI<sub>4</sub>(mtpa)<sub>2</sub>]**2a**, C<sub>14</sub>H<sub>30</sub>I<sub>4</sub>N<sub>6</sub>P<sub>2</sub>Ru: C, 17.63; H, 3.15; N, 8.81. Found: C, 17.94; H, 3.20; N, 8.74.

**[RuI<sub>2</sub>(mtpa)<sub>3</sub>(H<sub>2</sub>O)]I<sub>3</sub>·2H<sub>2</sub>O, **3**.** To 0.2149 g (0.822 mmol) of RuCl<sub>3</sub>·3H<sub>2</sub>O and 2.047 g (12.33 mmol) of potassium iodide dissolved in 35 cm<sup>3</sup> water was added 1.475 g (4.93 mmol) of mtpaI, and the mixture was stirred at 80 °C for 2 h. The color of the solution changed from brown to dark-red. The solution was left overnight at 5 °C, and a dark-red crystalline precipitate was filtered off, washed with cold water, and dried in vacuo. Yield: 0.7301 g, 68%. Anal. Calcd for [RuI<sub>2</sub>(mtpa)<sub>3</sub>(H<sub>2</sub>O)]I<sub>3</sub>·2H<sub>2</sub>O, C<sub>21</sub>H<sub>51</sub>I<sub>5</sub>N<sub>9</sub>O<sub>3</sub>P<sub>3</sub>-Ru: C, 19.31; H, 3.94; N, 9.65. Found: C, 19.22; H, 3.80; N, 9.43.

## Results and Discussion

The reaction of stoichiometric quantities of mtpaI and RhCl<sub>3</sub> (Rh/mtpa = 1:2) in the presence of potassium iodide in water at room temperature leads to formation of a dark-red, crystalline complex of rhodium(III), **1**. The analogous reaction of RuCl<sub>3</sub> with excess mtpaI in the presence of KI in water gives ruthenium(II) complexes. It means that Ru(III) undergoes reduction with this phosphine easier than the Rh(III) compound. The complexes **1**, **2**, **2a**, and **3** are air-stable in the solid state. They are soluble in polar solvents such as dimethyl sulfoxide, acetonitrile, dimethylformamide, and water, slightly soluble in alcohols, and insoluble in nonpolar solvents. All complexes have been characterized by elemental analysis and spectroscopic methods: IR and <sup>1</sup>H and <sup>31</sup>P NMR. The <sup>1</sup>H and <sup>31</sup>P[<sup>1</sup>H] NMR spectra are given in Tables 1 and 2. The <sup>1</sup>H NMR spectra of **1** and **2** are very similar to those of the other complexes containing RtpaI ligands.<sup>26,27</sup> <sup>1</sup>H NMR spectra of methylene groups NCH<sub>2</sub>N,

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**Table 1.**  $^1\text{H}$  NMR Spectra of Complexes with mtpaI

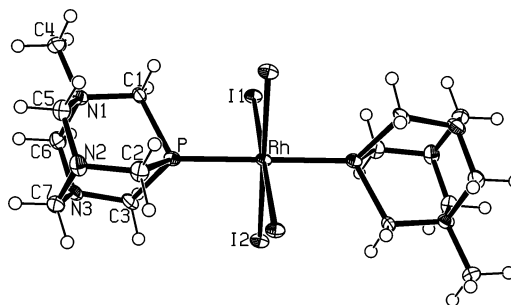
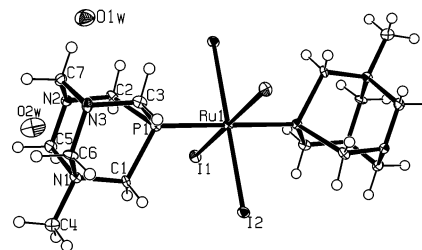
compd (solvent)	$\text{H}_3\text{CN}^+ \delta$ [ppm]	$\text{PCH}^{\text{A}}\text{H}^{\text{B}}\text{N} \delta\text{H}^{\text{A}}, \delta\text{H}^{\text{B}}$ [ppm] ( $J(\text{AB})$ [Hz])	$\text{PCH}_2\text{N}^+ \delta$ [ppm]	$\text{NCH}^{\text{A}}\text{H}^{\text{B}}\text{N} \delta\text{H}^{\text{A}}, \delta\text{H}^{\text{B}}$ [ppm] ( $J(\text{AB})$ [Hz])	$\text{NCH}^{\text{A}}\text{H}^{\text{B}}\text{N}^+ \delta\text{H}^{\text{A}}, \delta\text{H}^{\text{B}}$ [ppm] ( $J(\text{AB})$ , [Hz])
<b>1</b> ( $\text{CD}_3\text{CN}$ )	2.80, s, 6H	4.22, 4.31 (8.3); 8H	4.77, s; 4H	4.16, 4.49 (9.7); 4H	4.65, 4.74 (7.0); 8H
<b>2</b> ( $\text{DMSO}-d_6$ )	2.81, s; 6H	4.32, 4.41 (16.7); 8H	4.76, s; 4H	4.39, 4.46 (15.6); 4H	4.88, 5.15 (11.9); 8H
<b>3</b> ( $\text{DMSO}-d_6$ )	2.85, s; 6H 2.89, s; 3H	4.0–5.1, m; 36H			

**Table 2.**  $^{31}\text{P}\{^1\text{H}\}$  NMR Spectra of Complexes with mtpaI

compd (solvent)	$\delta^{31}\text{P}\{^1\text{H}\}$ NMR [ppm]	$\Delta\delta^{31}\text{P}\{^1\text{H}\}^a$ [ppm]
<b>1</b> ( $\text{CD}_3\text{CN}$ )	−77.4, d, $J(\text{P-Rh}) = 96.8$ Hz	18.6
<b>2</b> ( $\text{DMSO}-d_6$ )	−60.8, s,	35.2
<b>3</b> ( $\text{DMSO}-d_6$ )	−8.3, t, −52.1 d, $J(\text{P-P}) = 31.6$ Hz	87.7, 43.9

$$^a \Delta\delta^{31}\text{P}\{^1\text{H}\} = \delta^{31}\text{P}\{^1\text{H}\}_{\text{complex}} - \delta^{31}\text{P}\{^1\text{H}\}_{\text{ligand}}.$$

$\text{NCH}_2\text{N}^+$ , and  $\text{PCH}_2\text{N}$  are all of AB type. In the case of  $\text{PCH}_2\text{N}^+$ , the singlet has been observed. The  $^{31}\text{P}$  NMR spectrum of **1** exhibits a doublet at −77.4 ppm. The value of the  $^1J_{\text{PRh}}$  coupling constant is relatively small (96.8 Hz) which indicates the six-coordinated rhodium atom. In the  $^{31}\text{P}$  NMR spectrum of complex **2**, a singlet at −60.8 ppm is observed. This shows that the ruthenium compound is an octahedral complex with phosphine ligands in the axial positions. The  $^1\text{H}$  NMR spectrum of **3** exhibits a multiplet in the range 4.0–5.1 ppm for methylene groups and two singlets for  $\text{NCH}_3$  groups with intensity ratio 1:2. The  $^{31}\text{P}$  NMR spectrum of complex **3** consists of two signals: a triplet at −8.3 ppm and a doublet at −52.1 ppm ( $^2J_{\text{PP}} = 31.6$  Hz). This indicates that cation in compound **3** is a meridional octahedral complex,  $(\text{OC-6-13})\text{-[RuI}_2(\text{H}_2\text{O})\text{-(mtpa)}_3]^{3+}$ . Structures of all presented compounds have been confirmed by X-ray diffraction measurement. Crystallographic data for complexes **1**, **2**, **2a**, and **3** with a listing of important bond distances and bond angles are given in Tables 3 and 4, and the ORTEP views are in Figures 1–4. Complexes **1** and **2a** crystallize in the monoclinic crystal

**Figure 1.** ORTEP representation of the  $[\text{RhI}_4(\text{mtpa})_2]^+$  cation of complex **1**.**Figure 2.** ORTEP representation of complex **2**.

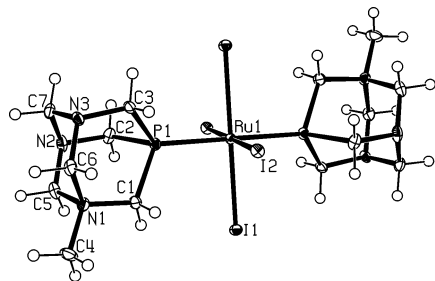
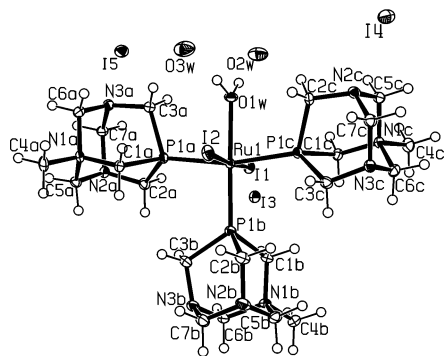
system,  $P2_1/c$  and  $P2_1/n$  space groups, respectively, and complex **2** crystallizes in the triclinic crystal system (space group  $P\bar{1}$ ). The  $\text{Rh-P}$  distance for **1** is 2.318(2) Å. The ruthenium(III) compound with tpa,  $\text{RuCl}_3(\text{tpa})_2 \cdot 2\text{HCl}$ ,<sup>13</sup> exhibits a similar structure to that of **1**, **2**, and **2a**. The  $\text{Ru-P}$  distances in **2** (2.298(2) Å) and in **2a** (2.299(2) Å) are shorter than those for  $\text{RuCl}_3(\text{tpa})_2 \cdot 2\text{HCl}$  (2.342(2) Å). The molecular

**Table 3.** Crystallographic Data for Complexes **1**, **2**, **2a** and **3**

	<b>1</b>	<b>2</b>	<b>2a</b>	<b>3</b>
formula	$\text{C}_{14}\text{H}_{30}\text{I}_5\text{N}_6\text{P}_2\text{Rh}$	$\text{C}_{14}\text{H}_{34}\text{I}_4\text{N}_6\text{O}_2\text{P}_2\text{Ru}$	$\text{C}_{14}\text{H}_{30}\text{I}_4\text{N}_6\text{P}_2\text{Ru}$	$\text{C}_{21}\text{H}_{51}\text{I}_5\text{N}_9\text{O}_3\text{P}_3\text{Ru}$
fw [ $\text{g}\cdot\text{mol}^{-1}$ ]	1081.79	989.08	953.05	1306.19
$T$ [K]	100(2)	293(2)	100(2)	100(2)
wavelength [Å]	0.71073	0.71073	0.71073	0.71073
cryst syst	monoclinic	triclinic	monoclinic	monoclinic
space group	$P2_1/c$	$P\bar{1}$	$P2_1/n$	$P2_1/n$
$a$ [Å]	10.803(3)	8.0410(16)	9.7954(9)	13.6234(11)
$b$ [Å]	9.295(3)	8.4240(17)	12.8494(10)	15.3353(9)
$c$ [Å]	13.786(3)	10.870(2)	10.6979(9)	18.1723(12)
$\alpha$ [deg]		106.77(3)		
$\beta$ [deg]	96.27(3)	94.71(3)	109.740(8)	92.824(6)
$\gamma$ [deg]		94.55(3)		
$V$ [Å <sup>3</sup> ]	1376.03(7)	698.5(2)	1267.36(19)	3791.9(5)
$Z$	2	1	2	4
calcd $d$ [ $\text{g}\cdot\text{cm}^{-3}$ ]	2.611	2.351	2.497	2.288
$\mu$ [ $\text{mm}^{-1}$ ]	6.360	5.117	5.630	4.649
cryst size [ $\text{mm}^3$ ]	$0.03 \times 0.25 \times 0.35$	$0.05 \times 0.07 \times 0.12$	$0.14 \times 0.14 \times 0.08$	$0.18 \times 0.14 \times 0.10$
$\theta$ range [deg]	3.69–28.73	3.40–28.59	3.46–28.42	3.28–28.41
$h, k, l$ ranges	−14 → 14, 0 → 12, 0 → 18	−10 → 8, −11 → 11, −14 → 13	−7 → 13, −16 → 16, −14 → 13	−17 → 13, −20 → 20, −24 → 23
reflns collected	7535	5024	8614	25592
indep reflns ( $R_{\text{int}}$ )	3182(0.0323)	3157 (0.0699)	2976 (0.0352)	8911 (0.0320)
GOF on $F^2$	1.140	1.093	1.030	1.043
final $R1/wR2$ indices	0.0287/0.0703	0.0384/0.0942	0.0341/0.0458	0.0315/0.0627
$[I > 2\sigma(I)]^a$				

$$^a R1 = \sum(|F_o| - |F_c|)/\sum|F_o|; wR2 = [\sum w(|F_o| - |F_c|)^2]^{0.5}.$$



Figure 3. ORTEP representation of **2a**.Figure 4. ORTEP representation of **3**.Table 4. Selected Bond Lengths and Angles for Complexes **1**, **2**, **2a**, and **3**

compd	bond distances (Å)		bond angles (deg)	
<b>1</b>	Rh–I1	2.701(1)	I1–Rh–I2	90.71(2)
	Rh–I2	2.684(2)	I1–Rh–P	89.44(4)
	Rh–P	2.318(2)	I2–Rh–P	92.70(3)
	P–C2	1.842(5)		
	P–C3	1.854(5)		
<b>2</b>	Ru1–P1	2.298(2)	P1–Ru1–I1	87.75(4)
	Ru1–I1	2.725(1)	P1–Ru1–I2	91.30(4)
	Ru1–I2	2.736(2)	I1–Ru1–I2	89.25(3)
	P1–C3	1.846(6)		
	P1–C1	1.849(5)		
	P1–C2	1.849(6)		
<b>2a</b>	Ru1–I1	2.745(1)	P1–Ru1–I2	86.91(3)
	Ru1–I2	2.743(1)	P1–Ru1–I1	92.29(3)
	Ru1–P1	2.299(2)	I2–Ru1–I1	91.29(2)
	P1–C2	1.840(5)		
	P1–C3	1.843(5)		
	P1–C1	1.859(5)		
<b>3</b>	Ru1–O1W	2.202(3)	O1W–Ru1–P1B	178.61(8)
	Ru1–P1B	2.228(2)	O1W–Ru1–P1C	82.56(8)
	Ru1–P1C	2.335(2)	P1B–Ru1–P1C	96.08(4)
	Ru1–P1A	2.348(2)	O1W–Ru1–P1A	84.48(8)
	Ru1–I1	2.710(1)	P1B–Ru1–P1A	96.87(4)
	Ru1–I2	2.717(1)	P1C–Ru1–P1A	166.98(4)
	P1A–C1A	1.851(4)	O1W–Ru1–I1	87.12(7)
	P1A–C3A	1.854(4)	P1B–Ru1–I1	93.29(3)
	P1A–C2A	1.861(4)	P1C–Ru1–I1	94.26(3)
	P1B–C2B	1.849(4)	P1A–Ru1–I1	86.30(3)
	P1B–C3B	1.851(4)	O1W–Ru1–I2	88.97(7)
	P1B–C1B	1.852(4)	P1B–Ru1–I2	90.63(3)
	P1C–C1C	1.854(4)	P1C–Ru1–I2	85.71(3)
	P1C–C2C	1.861(4)	P1A–Ru1–I2	92.85(3)
	P1C–C3C	1.863(4)	I1–Ru1–I2	176.06(2)

structures of **1**, **2**, and **2a** consist of octahedral arrangements. Four iodide atoms occupy equatorial coordination sites while the two phosphine ligands are in *trans* positions. Complex **3** crystallizes in the monoclinic space group  $P2_1/n$ . It exhibits distorted octahedral coordination with three phosphorus atoms and an aqua ligand in the equatorial plane and two iodide ligands in axial positions. The angles P1a–Ru1–P1c

Table 5. Two-Phase Hydroformylation of 1-Hexene and Hydrogenation of Cinnamaldehyde by Complexes with mtpal

catalyst	TOF <sup>a</sup>	yield, %	products, %
<b>1<sup>b</sup></b>	138	93	Hydroformylation of 1-Hexene
			<i>n</i> -C <sub>6</sub> H <sub>13</sub> CHO 59; C <sub>4</sub> H <sub>9</sub> CH(CH <sub>3</sub> )CHO 34
<b>1<sup>c</sup></b>	190	95	Hydrogenation of PhCH=CHCHO
			PhCH <sub>2</sub> CH <sub>2</sub> CHO 84; Ph(CH <sub>2</sub> ) <sub>3</sub> OH 8; PhCH=CHCH <sub>2</sub> OH 2.5
<b>1<sup>d</sup></b>	25	13	PhCH <sub>2</sub> CH <sub>2</sub> CHO 13
<b>2<sup>c</sup></b>	40	89	PhCH=CHCH <sub>2</sub> OH 84; Ph(CH <sub>2</sub> ) <sub>3</sub> OH 5
<b>2<sup>d</sup></b>	8	4	PhCH=CHCH <sub>2</sub> OH 2.5; PhCH <sub>2</sub> CH <sub>2</sub> CHO 1
<b>3<sup>c</sup></b>	183	45	PhCH=CHCH <sub>2</sub> OH 36; PhCH <sub>2</sub> CH <sub>2</sub> CHO 5; Ph(CH <sub>2</sub> ) <sub>3</sub> OH 4
<b>3<sup>d</sup></b>	4	2	PhCH=CHCH <sub>2</sub> OH 2
<b>3<sup>e</sup></b>	4	17	PhCH=CHCH <sub>2</sub> OH 17

<sup>a</sup> Average TOF [mol substr·(mol catalyst h)<sup>−1</sup>]. The rates of the reactions in the second and third cycles were the same. <sup>b</sup>  $p(\text{CO}) = p(\text{H}_2) = 3.5$  MPa; 333 K; catalyst 0.01 mmol; H<sub>2</sub>O 15 cm<sup>3</sup>; 1-hexene 30 mmol. <sup>c</sup>  $p(\text{H}_2) = 3.0$  MPa; 333 K; catalyst 0.01 mmol; H<sub>2</sub>O 15 cm<sup>3</sup>; substrate 20 mmol in toluene 15 cm<sup>3</sup>. <sup>d</sup> 348 K; 5 M NaO<sub>2</sub>CH 5 cm<sup>3</sup>; catalyst 0.01 mmol; substrate 3.8 mmol in 5 cm<sup>3</sup> chlorobenzene. <sup>e</sup>  $p(\text{H}_2) = 0.1$  MPa; 293 K; catalyst 0.01 mmol; H<sub>2</sub>O 15 cm<sup>3</sup>; substrate 20 mmol in toluene 15 cm<sup>3</sup>.

(ca. 167°) and P1a–Ru1–P1b or P1c–Ru1–P1b (ca. 97°) indicate that distortion from octahedral coordination is relatively strong. The Ru1–P1a and Ru1–P1c distances are slightly longer than the Ru1–P1b bond because the *trans* effect of phosphine ligands is stronger than that of an aqua ligand. The complexes **1**, **2**, and **2a** in the solid state exhibit “zwitterionic” properties. In complexes **2** and **2a**, all iodide anions are coordinated to the central atom while in the case of compound **1** there is one I<sup>−</sup> counteranion. They are tripolar compounds with positive charge located in axial positions and negative charge in the equatorial plane. Cationic compound **3** is polypolar with positive charges in axial and one equatorial positions.

Complex **1** is an active catalyst for biphasic hydroformylation of 1-hexene (see Table 5). Average turnover frequency for this reaction is 138 [mol substrate·(mol catalyst·hour)<sup>−1</sup>], and the ratio of linear to branched aldehyde is 1.7:1. Compound **1** is also an effective catalyst for hydrogenation of cinnamaldehyde as the rhodium complex RhCl(tppms)<sub>3</sub>·4H<sub>2</sub>O (tppms = P(*m*-C<sub>6</sub>H<sub>4</sub>SO<sub>3</sub>Na)Ph<sub>2</sub>) and much more active than ruthenium complexes with tppms at similar experimental conditions.<sup>32</sup> Complexes **2** and **3** are more effective catalysts for hydrogenation of cinnamaldehyde (pressure of H<sub>2</sub> 3.0–0.1 MPa) than the analogous ruthenium complex with tpa, but they are less active in the reduction of this aldehyde by means of HCO<sub>2</sub>Na/H<sub>2</sub>O. Compound **3** is a much more active catalyst for hydrogenation of cinnamaldehyde than ruthenium complexes with tppms and tpa.<sup>32</sup> The average TOF at 3.0 MPa of hydrogen is 183 [mol substrate·(mol catalyst·hour)<sup>−1</sup>]. Complexes **1**, **2**, and **3** show high selectivity in hydrogenation of cinnamaldehyde. Rhodium complex **1** catalyzes mainly the reduction of the C=C bond, and ruthenium compounds **2** and **3** selectively hydrogenate the C=O bond, giving saturated aldehyde and cinnamyl alcohol, respectively. It was found that the rate of catalytic reaction did not decrease after three cycles. The complexes with mtpal show strong hydrophilic properties, and therefore, their concentration in the

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organic phase is lower in comparison with complexes containing tpa ligands. That is why they are better catalysts for two-phase reactions in comparison with tpa complexes.

### Conclusions

The new water-soluble phosphine complexes of rhodium(III),  $[\text{RhI}_4(\text{mtpa})_2]\text{I}$  (**1**), and ruthenium(II),  $[\text{RuI}_4(\text{mtpa})_2]$  (**2**) and  $[\text{RuI}_2(\text{mtpa})_3(\text{H}_2\text{O})]\text{I}_3 \cdot 2\text{H}_2\text{O}$  (**3**), show relatively high activity in two-phase hydroformylation of 1-hexene and hydrogenation of cinnamic aldehyde in comparison with rhodium and ruthenium complexes with tppms and tpa ligands. Because of their strong hydrophilic properties, they are better catalysts for two-phase catalytic reactions than tpa complexes. Activity of the catalysts did not diminish after

three cycles. The compounds have been structurally characterized using NMR and IR spectroscopies and also by single crystal X-ray diffraction studies. In octahedral complexes **1**, **2**, and **2a**, the phosphine ligands occupy the *trans*-position. In complex **3**, the aqua ligand is coordinated in the *trans* position with respect to phosphine molecule. The complexes belong to the interesting polypolar (zwitterionic) coordination compounds.

**Supporting Information Available:** X-ray crystallographic file in CIF format. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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