

Two in one: Charged tertiary phosphines held together by ionic or covalent interactions as bidentate phosphorus ligands for synthesis of half-sandwich Ru(II)-complexes.

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Abstract

Ion pairs containing N-substituted derivatives of 1,3,5-triaza-7-phosphaadamantane (pta-R; R= benzyl, butyl, hexyl) as cations and monosulfonated triphenylphosphine (*mtpms*) as anion were synthesized and characterized (including X-ray diffraction, too). These ion pairs act as bidentate phosphorus ligands in reactions with $[(\eta^6\text{-C}_{10}\text{H}_{14})\text{RuCl}_2]_2$, yielding mononuclear or dinuclear half sandwich Ru(II) complexes. A bisphosphine **3** of good water-solubility was synthesized in reaction of pta with 1,4-bis(chloromethyl)benzene and used for the synthesis of the water-soluble dinuclear complex $[\{(\eta^6\text{-C}_{10}\text{H}_{14})\text{RuCl}_2\}_2(\mu\text{-3})]\text{Cl}_2$.

Keywords: ion pairs, 1,3,5-triaza-7-phosphaadamantane, sulfonated, phosphines, bidentate ligand

1. Introduction

Bi- or multidentate ligands play important role in coordination chemistry and homogeneous catalysis. In several cases, however, their synthesis requires time-consuming, multistep reactions as donor atoms are held together in the ligand molecule by covalent bonds of appropriate connectivity.

The essence of homogeneous catalysis is the tuning of electronic, steric and coordination properties of the central metal ion to make it possible to roll along the path of the catalytic cycle and perform the required electron and/or atom transfer between the substrate molecules, mostly within the coordination sphere of the metal. Multidentate ligands provide the necessary versatility in terms of coordination mode and steric requirements to assist the catalysis. However, chelating donor atoms connected *via* secondary interactions represent the supramolecular approach for the delicate tuning of the catalytic metal complex which opens new horizons in both aqueous and non aqueous chemistry. Moreover, basically this is one of the working principles of enzyme catalysis where secondary interactions are crucial to held

together the active site where electron and atom transfer to the pretreated substrate molecule(s) occurs.

So, instead of the traditional synthetic procedures, it has been conceived that bidentate ligands may also be obtained by self-assembly of monodentate ones. Construction of complex structures from simple building units capable of association by secondary interaction can be faster and more economic than synthesis of ligands of similar size and complexity based on covalent bonding.

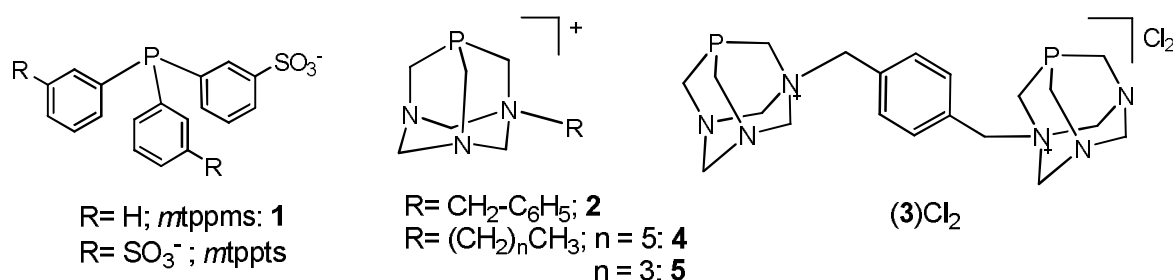
Some important steps are already taken on this novel field as several groups are active in research on formation of supramolecular complexes including studies of transition metal complexes with supramolecular bidentate ligands produced by self-organization [1]. For example, wheel-and-axle-type organometallic complexes were synthesized having two half-sandwich Ru(II)-units as wheels, while the axle was formed by H-bridge dimerization of the non-coordinated carboxylic acid groups in the two $[(\eta^6\text{-C}_{10}\text{H}_{14})\text{RuCl}_2(4\text{-aminobenzoic acid})]$ complexes [2]. Similar phenomena were described with $[(\eta^6\text{-C}_{10}\text{H}_{14})\text{RuCl}_2(\text{L})]$ complexes having iso-nicotinic acid or 4-aminocinnamic acid [3] as well as $\text{Ph}_2\text{CH}_2\text{NHC}_6\text{H}_4\text{COOH}$ [4] ligands.

Association of ligands may lead not only to bridging units but to chelating ligands, too. In the presence of transition metal ions 6-diphenylphosphinopyridone forms an H-bridged associate with its own tautomer. Bidentate character of this self-organized molecule was established both in solution (NMR) and in solid phase (X-ray) [5].

Gulyás et al obtained bidentate phosphorus ligands held together by ionic interactions. Triphenylphosphine derivatives with oppositely charged substituents ($-\text{SO}_3^-$ and $-\text{NH}_3^+$, respectively) formed ion pairs even in polar media. In the investigated Rh- and Pd-complexes, both phosphorus donor atoms of such strongly held ion pairs coordinated to the same metal ion [6].

We have also reported on formation of stable ion pairs formed by oppositely charged water-soluble tertiary phosphines [7]. As anions we used mono-sulfonated triphenylphosphine (*m*tpmps, **1**; well known from aqueous organometallic catalysis [8]) while the cation was N-benzyl-1,3,5-triaza-7-phosphaadamantane, **2** (Scheme 1.).

Scheme 1.



Scheme 1. Water-soluble phosphines used in this study

1,3,5-triaza-7-phosphaadamantane (pta) is often used in aqueous organometallic catalysis [9]. $[\text{RuCl}_2(\text{pta})_4]$ has been studied in hydrogenation of aldehydes [10] but this complex was found active also in hydrogenation of bicarbonate [11] and in hydration of nitriles [12]. These reactions are also catalyzed by the half-sandwich complexes formed in reactions of $[(\text{arene})\text{RuCl}_2]_2$ and pta [13-15]. Half-sandwich Ru(II)-pta complexes with the general name RAPTA are subject to scrutiny not only because of their catalytic effect but also of their anticancer activity [16].

N-Alkyl derivatives of pta can also be used as ligands in half-sandwich Ru-complexes [15, 17]. Already at the time of the first synthesis of pta it was established that it can be methylated on one of the *N*-atoms by MeI [18]. In addition, several cationic pta-R derivatives were obtained by longer chain alkyl iodides (EtI [19], *n*PrI [20], *n*BuI [21], $\text{I}(\text{CH}_2)_4\text{I}$ [22]) as well as with various bromomethyl compounds (BrCH_2Y , where $\text{Y} = \text{C}_6\text{H}_4\text{N}$ [23], C_6H_5 , COOMe [24-25]). With benzyl chloride 1-benzyl-1-azonia-3,5-diaza-7-phosphaadamantyl cation, pta-Bn (**2**) is formed [26] while 1,4-bis(chloromethyl)benzene [7] and bis(bromomethyl)benzene are able to alkylate two pta molecules. Attempts to use the bisphosphine ligand, 1,1'-[1,4-phenylenebis(methylene)]bis-3,5-diaza-1-azonia-7-phosphatricyclo[3.3.1.1]decane, **3** (as its bromide salt) for synthesis of a binuclear complex in reaction with *cis*- $[\text{PtBr}_2(\text{cod})]$ did not yield well defined products [27].

In this paper we report successful syntheses of dinuclear and chelate complexes obtained from Ru(II) precursors and ionic phosphine ligands. We show that reaction of $(\mathbf{3})\text{Cl}_2$ and $[(\eta^6\text{-C}_{10}\text{H}_{14})\text{RuCl}_2]_2$ yields a binuclear complex in which **3** serves as bridging ligand between the two half-sandwich Ru(II)-arene units. Synthesis of (pta-R)(mtppps) ion pairs ($R = \text{benzyl}$, hexyl or butyl) is described for the first time as well as their use for synthesis of binuclear wheel and axle complexes. It is also demonstrated, that (pta-Bn)(mtppps) is able to coordinate to the same Ru(II) center, and this way half-sandwich Ru(II)-complexes with two different phosphine ligands can be synthesised in a single step.

2. Experimental

2.1. Materials and methods

All reactions and manipulations were carried out under argon or nitrogen atmosphere with use of standard Schlenk techniques. ^1H , ^{31}P and ^{13}C NMR spectra were recorded on a Bruker Avance 360 MHz spectrometer and referenced to 3-(trimethylsilyl)propanesulfonic acid Na-salt (DSS). ESI mass data were collected on a BRUKER BioTOF II ESI-TOF spectrometer. Elemental analysis were carried out using Elementar Vario Micro instrument.

All reagents and solvents were commercially available and used as received with the exception of Na(*mtp*pms) [28], Na₃(*mtp*ppts) [29], pta [30], (pta-Me)I [18], (pta-Me)CF₃SO₃ [17], (pta-R)Br (R = Et, *n*Pr, *n*Bu [21]), (pta-Bn)Cl [26], [(η^6 -C₁₀H₁₄)RuCl₂]₂ [31], Na[(η^6 -C₁₀H₁₄)RuCl₂(*mtp*pms)] [32] and [(η^6 -C₁₀H₁₄)RuCl₂(pta-Bn)]Cl, **6** [15] which were prepared according to the literature.

2.2. Synthesis of ligands

2.2.1. 1,1'-[1,2-phenylenebis(methylene)]bis-3,5-diaza-1-azonia-7-phosphatricyclo[3.3.1.1]decane dichloride, (**3**)Cl₂

A suspension of 100.0 mg (0.637 mmol) pta and 55.7 mg (0.318 mmol) of 1,4-bis(chloromethyl)benzene in acetone (3 mL) was refluxed for 3 h. The mixture was cooled to room temperature and the precipitate was collected on a frit. The solid was washed with a small amount of cold acetone and vacuum-dried. The white compound is well soluble in water. Yield 115 mg (74 %). *Anal.* (%) calc. for P₂Cl₂N₆C₂₀H₃₂ (M=489.36): C, 49.08; H, 6.59; N, 17.17; found: C, 48.54; H, 6.21; N, 16.95. Electrospray MS (in H₂O): observed *m/z* 209.107, calcd. 209.100 for P₂N₆C₂₀H₃₂ = M²⁺. ^1H NMR (360 MHz, D₂O, 25°C): δ /ppm 3.85 (m, 8H, PCH₂N), 4.20 (s, 4H, PCH₂N⁺), 4.54 (m, 8H, PCH₂N⁺, NCH₂N), 4.98 (m, 8H, NCH₂N⁺), 7.64 (s, 4H, H_{Ph}). ^{13}C { ^1H } NMR (90 MHz, D₂O, 25°C): δ /ppm 45.56 (d, $^1J_{\text{PC}}$ = 22 Hz, PCH₂N), 52.89 (d, $^1J_{\text{PC}}$ = 33 Hz, PCH₂N⁺), 65.83 (s, PhCH₂N⁺), 69.38 (s, NCH₂N), 78.90 (s, NCH₂N⁺), 127.38 (s, CH_{Ph}), 133.68 (s, C_{Ph}). ^{31}P { ^1H } NMR (145 MHz, D₂O, 25°C): δ = -82.03 ppm (s). ^{31}P { ^1H } NMR (145 MHz, MeOD, 25°C): δ = -79.5 ppm (s).

2.2.2. 1-hexyl-1-azonia-3,5-diaza-7-phosphaadamantyl bromide, (**4**)Br

A solution of pta (150 mg, 0.95 mmol) and 1-bromo-hexane (0.33 mL, 2.34 mmol) in 10 mL acetone was refluxed for 1 hour. The mixture was cooled to room temperature and the precipitate was separated by filtration. The white solid was washed with acetone (2x5mL) and Et₂O (3x5mL) and dried. Yield 202 mg (60%). *Anal.* (%) calc. for C₁₂H₂₄N₃PBr (M=320.31): C, 44.92; H, 7.55; N, 13.11; found: C, 44.72; H, 7.69; N, 13.04. Electrospray MS (in MeOH): observed *m/z* 241.310, calcd. 241.316 for PN₃C₁₂H₂₅ = M⁺. ^1H NMR (360 MHz, MeOD, 25°C): δ /ppm 0.93 (t, 3H, $^1J_{\text{HH}}$ =7 Hz, CH₃), 1.01-1.30 (m, 6H, N⁺-CH₂CH₂CH₂CH₂CH₂CH₃), 1.65-1.74 (m, 2H, N⁺-CH₂CH₂), 2.84 (m, 2H, N⁺-CH₂CH₂), 3.76-4.04 (m, 4H, PCH₂N), 4.32

(d, 2H, $J_{\text{PH}}=6$ Hz, PCH_2N^+), 4.37-4.64 (m, 2H, NCH_2N), 4.71-5.09 (m, 4H, $\text{N}^+\text{CH}_2\text{N}$).

$^{13}\text{C}\{^1\text{H}\}$ NMR (90 MHz, MeOD, 25°C): δ/ppm 13.00 (s, CH_3), 19.31 (s, CH_2CH_3), 19.34 (s, $\text{CH}_2\text{CH}_2\text{CH}_3$), 21.30 (s, $\text{N}^+-\text{CH}_2\text{CH}_2\text{CH}_3$), 24.60 (s, $\text{N}^+-\text{CH}_2\text{CH}_2$), 45.77 (d, $J_{\text{PC}}=22$ Hz, PCH_2N), 53.11 (d, $J_{\text{PC}}=33$ Hz, PCH_2N^+), 62.99 (s, $\text{N}^+\text{CH}_2\text{CH}_2$), 70.01 (s, NCH_2N), 78.12 (s, $\text{N}^+\text{CH}_2\text{N}$). $^{31}\text{P}\{^1\text{H}\}$ NMR (145 MHz, D_2O , 25°C): $\delta = -83.7$ ppm (s).

2.2.3. General procedure for the preparation of salts containing N-alkylated pta as a cation and monosulfonated triphenylphosphine as an anion

0.075 mmol of (pta-R)X {21.3 mg for (pta-Bn)Cl, 22.0 mg for (pta-butyl)Br, and 24.0 mg for (pta-hexyl)Br} was dissolved in 0.5 mL of water and it was added to a solution of 0.075 mmol (30 mg) of Na-mtppms in 3.0 mL water. White precipitate was formed almost immediately what was filtered out and washed with small amount of water and Et_2O (3x6 mL). The salt dissolves well in CHCl_3 and CH_2Cl_2 but poorly in water, hexane, acetone and Et_2O .

2.2.3.1. (pta-Bn)(mtppms), (2)(1)

Yield: 31.1 mg (70 %). *Anal.* (%) calc. for $\text{C}_{31}\text{H}_{33}\text{N}_3\text{O}_3\text{P}_2\text{S}$ (M=589.62): C, 63.14; H, 5.60; N, 7.12; found: C, 63.48; H, 5.92; N, 7.07. ^1H NMR (360 MHz, MeOD, 25°C): δ/ppm 3.54-3.87 (m, 4H, PCH_2N), 4.18-4.63 (m, 2H, PCH_2N^+ and d, 2H NCH_2N , s, 2H, $\text{N}^+\text{CH}_2\text{Ph}$), 5.03-5.30 (m, 4H, $\text{N}^+\text{CH}_2\text{N}$), 7.57-7.46 (m, 5H_{Ph of 2} and 14H_{mtppms}). $^{13}\text{C}\{^1\text{H}\}$ NMR (90 MHz, CDCl_3 , 25°C): δ/ppm 46.87 (d, $J_{\text{PC}}=21$ Hz NCH_2P), 52.41 (d, $J_{\text{PC}}=33$ Hz, $\text{N}^+\text{CH}_2\text{P}$), 65.22 (s, $\text{N}^+\text{CH}_2\text{Ph}$), 70.47 (s, NCH_2N), 79.12 (s, $\text{N}^+\text{CH}_2\text{N}$), 125.39-146.69 (m, 4 C_{Ph of 2} and 10 C_{mtppms}). $^{31}\text{P}\{^1\text{H}\}$ NMR (145 MHz, CDCl_3 , 25°C): $\delta = -84.0$ ppm (s), -4.3 ppm (s).

2.2.3.2. (pta-hexyl)(mtppms), (4)(1)

Yield: 22.3 mg (51 %). *Anal.* (%) calc. for $\text{C}_{30}\text{H}_{39}\text{N}_3\text{O}_3\text{P}_2\text{S}$ (M=583.66): C, 61.73; H, 6.73; N, 7.19; S, 5.49; found: C, 60.85; H, 6.89; N, 7.16; S, 5.46. ^1H NMR (360 MHz, MeOD, 25°C): δ/ppm 0.82 (m, 3H, CH_3), 1.13-1.35 (m, 6H, $\text{N}^+-\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 1.52-1.70 (m, 2H, $\text{N}^+-\text{CH}_2\text{CH}_2$), 2.63-2.82 (m, 2H, $\text{N}^+-\text{CH}_2\text{CH}_2$), 3.67-3.94 (m, 4H, PCH_2N), 4.13-4.55 (m, 2H, PCH_2N^+ and 2H, NCH_2N), 4.60-4.99 (m, 4H, $\text{N}^+\text{CH}_2\text{N}$), 6.93-7.78 (m, 14 H, aromatic). $^{13}\text{C}\{^1\text{H}\}$ NMR (90 MHz, MeOD, 25°C): δ/ppm 14.29 (s, CH_3), 20.68 (s, CH_2CH_3), 23.49 (s, $\text{CH}_2\text{CH}_2\text{CH}_3$), 27.38 (s, $\text{N}^+\text{CH}_2\text{CH}_2\text{CH}_2$), 32.34 (s, $\text{N}^+\text{CH}_2\text{CH}_2$), 47.38 (d, $J_{\text{PC}}=21$ Hz, NCH_2P), 54.01 (d, $J_{\text{PC}}=33$ Hz, $\text{N}^+\text{CH}_2\text{P}$), 63.68 (s, $\text{N}^+-\text{CH}_2\text{CH}_2$), 71.38 (s, NCH_2N), 80.93 (s, $\text{N}^+\text{CH}_2\text{N}$). $^{31}\text{P}\{^1\text{H}\}$ NMR (145 MHz, MeOD, 25°C) $\delta = -82.9$ (s), $\delta = -4.4$ ppm (s). $^{31}\text{P}\{^1\text{H}\}$ NMR (145 MHz, CDCl_3 , 25°C) $\delta = -85.0$ ppm (s), $\delta = -4.3$ ppm (s).

2.2.3.3. (pta-Bu)(mtppms), (5)(1)

Yield: 27.1 mg (64 %). *Anal.* (%) calc. for $\text{C}_{28}\text{H}_{35}\text{N}_3\text{O}_3\text{P}_2\text{S}$ (M=555.66): C, 60.53; H, 6.34; N, 7.56; S, 5.77; found: C, 59.92; H, 6.48; N, 7.56; S, 5.82. ^1H NMR (360 MHz, MeOD, 25°C): δ/ppm 0.89 (t, $J_{\text{HH}}=7$ Hz, 3H, CH_3), 1.26 (sextet, $J_{\text{HH}}=7$ Hz, 2H, CH_2CH_3), 1.50-1.74 and 2.62-2.91 (m, 4H, $\text{N}^+-\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 3.67-4.02 (m, 4H, PCH_2N), 4.15-4.57 (m, 2H, PCH_2N^+ , 2H, NCH_2N), 4.61-5.03 (m, 4H, $\text{N}^+\text{CH}_2\text{N}$), 7.07-7.82 (m, 14 H, aromatic). $^{13}\text{C}\{^1\text{H}\}$ NMR (90 MHz, MeOD, 25°C): δ/ppm 13.94 (s, CH_3), 21.04 (s, CH_2CH_3), 22.70 (s,

$\text{CH}_2\text{CH}_2\text{CH}_3$), 46.85 (d, $J_{\text{PC}}=21$ Hz, PCH_2N), 54.00 (d, $J_{\text{PC}}=33$ Hz, PCH_2N^+), 63.44 (s, $\text{N}^+-\text{CH}_2\text{CH}_2$), 71.36 (s, NCH_2N), 80.91 (s, $\text{N}^+\text{CH}_2\text{N}$), 127.45-146.87 (m, aromatic). $^{31}\text{P}\{^1\text{H}\}$ NMR (145 MHz, MeOD, 25°C): $\delta = -82.9$ ppm (s) $\delta = -4.4$ ppm (s). $^{31}\text{P}\{^1\text{H}\}$ NMR (145 MHz, CDCl_3 , 25°C): $\delta = -85.2$ ppm (s), $\delta = -4.3$ ppm (s).

2.3. Synthesis of half sandwich Ru-complexes

2.3.1. $[(\eta^6\text{-C}_{10}\text{H}_{14})\text{RuCl}_2]_2(\mu\text{-}\mathbf{3})\text{Cl}_2$

A solution of the dimeric precursor $[(\eta^6\text{-C}_{10}\text{H}_{14})\text{RuCl}_2]_2$ (100.0 mg, 0.163 mmol) and an equimolar amount of $(\mathbf{3})\text{Cl}_2$ (80.0 mg, 0.163 mmol) in methanol (10 mL) was refluxed for 20 minutes. After cooling to room temperature, the volume was reduced to approximately 5 mL by vacuum-evaporation what led to the precipitation of an orange solid. The product was washed with EtOH (3x3 mL) and Et₂O (3x10 mL) and vacuum-dried. The complex dissolves well in water, methanol and ethanol but poorly in chloroform. Yield: 91.0 mg (51 %). *Anal.* (%) calc. for $\text{Ru}_2\text{C}_{40}\text{H}_{60}\text{Cl}_6\text{N}_6\text{P}_2 \cdot 2\text{H}_2\text{O}$ (M=1138.01): C, 42.22; H, 5.67; N, 7.38; found: C, 41.95; H, 5.29; N, 7.00. Electrospray MS (in H₂O): observed m/z 515.051; calcd 515.059 for $[\text{C}_{40}\text{H}_{60}\text{N}_6\text{P}_2\text{Cl}_4\text{Ru}_2]^{2+} = \text{M}^{2+}$. ^1H NMR (360 MHz, MeOD, 25°C): δ/ppm 1.07 (d, 12H, $J = 7.0$ Hz, $\text{CH}(\text{CH}_3)_2$), 1.89 (m, 6H, C- CH_3), 2.46 (m, 2H, $\text{CH}(\text{CH}_3)_2$), 3.92 (m, 8H, PCH_2N , 4H PCH_2N^+ , 4H, N^+CH_2), 4.54 (m, 4H, NCH_2N), 4.97 (m, 8H, NCH_2N^+), 5.76 (m, 8H, CH_{Ph} of *p*-cymene), 7.57 (s, 4H, H_{Ph} of $\mathbf{3}$). $^{13}\text{C}\{^1\text{H}\}$ NMR (90 MHz, D₂O, 25°C): δ/ppm 17.95 (s, CH_3), 21.18 (s, $\text{CH}(\text{CH}_3)_2$), 30.61 (s, $\text{CH}(\text{CH}_3)_2$), 48.45 (d, $J = 22$ Hz, PCH_2N), 51.08 (d, $J = 33$ Hz, PCH_2N^+), 65.12 (s, $\text{N}^+\text{CH}_2\text{Ph}$), 69.31 (s, NCH_2N), 79.46 (s, NCH_2N^+), 86.24 and 88.78 (s, CH_{Ph} of *p*-cymene), 99.00 and 108.07 (s, C_{Ph} of *p*-cymene), 127.10 (s, CH of C_{Ph}), 133.62 (s, C of C_{Ph}). $^{31}\text{P}\{^1\text{H}\}$ NMR (145 MHz, D₂O, 25°C): δ/ppm -17.9 ppm (s).

2.3.2. $[(\eta^6\text{-C}_{10}\text{H}_{14})\text{RuCl}_2(\text{pta-Bn})(\text{mtppms})]\text{Cl}$

A solution of $[(\eta^6\text{-C}_{10}\text{H}_{14})\text{RuCl}_2(\text{pta-Bn})]\text{Cl}$, **6** (100.0 mg, 0.169 mmol) and Na(*mtppms*) (67.8 mg, 0.169 mmol) in methanol (15 mL) was refluxed for 10 h. After cooling to room temperature the solution was filtered through a pad of Hyflo Supercel and the filtrate was evaporated to dryness. The oily residue was cooled in ice and triturated with Et₂O several times. The resulting yellow powder was washed at room temperature with Et₂O (3x10 mL) and dried. The complex dissolves well in water, methanol and ethanol but poorly in chloroform. Yield: 112 mg (76 %). *Anal.* (%) calc. for $\text{C}_{41}\text{H}_{47}\text{N}_3\text{O}_3\text{P}_2\text{SCl}_2\text{Ru} \cdot \text{H}_2\text{O}$ (M=913.81): C, 53.89; H, 5.40; N, 4.59; S, 3.50; found: C, 53.29; H, 5.35; N, 4.44; S, 3.06. Electrospray MS (in H₂O): observed m/z : 860.154; calcd. 860.154 for $[\text{C}_{41}\text{H}_{47}\text{N}_3\text{O}_3\text{P}_2\text{SClRu}]^+ = (\text{M})^+$. ^1H NMR (360 MHz, MeOD, 25°C): δ/ppm 1.23 (m, 6H, $\text{CH}(\text{CH}_3)_2$), 2.04 (m, 3H, - CH_3), 2.64 (m, 1H, $\text{CH}(\text{CH}_3)_2$), 4.01-5.02 (m, 14H, PCH_2N , PCH_2N^+ , $\text{N}^+\text{CH}_2\text{Ph}$, NCH_2N , NCH_2N^+), 5.73 (m, 4H_{Ph} for *p*-cymene), 6.83-8.90 (m, 5H, H_{Ph} of **2**, 14H, H_{mtppms}). $^{13}\text{C}\{^1\text{H}\}$ NMR (90 MHz, D₂O, 25°C): δ/ppm 16.99 (s, CH_3), 20.35 (d, $J = 22$ Hz, $\text{CH}(\text{CH}_3)_2$), 30.63 (s, $\text{CH}(\text{CH}_3)_2$), 48.43 (d, $J = 17$ Hz, PCH_2N), 50.71 (d, $J = 19$ Hz, PCH_2N^+), 64.91 (s, $\text{N}^+\text{CH}_2\text{Ph}$), 68.60 (s, NCH_2N), 79.88 NCH_2N^+ , 89.04 and 92.52 (s, CH_{Ph} of *p*-cymene), 94.25 and 103.71 (s, C of *p*-cymene), 127.25-144 (m, C_{Ph} of **2** and C_{mtppms}). $^{31}\text{P}\{^1\text{H}\}$ NMR (145 MHz, D₂O, 25°C) $\delta = 28.1$ ppm (d, $J_{\text{PP}} = 46$ Hz) and $\delta = -24.1$ ppm (d, J_{PP}

= 53 Hz). $^{31}\text{P}\{^1\text{H}\}$ NMR (145 MHz, MeOD, 25°C) δ = 27.6 ppm (d, J_{PP} = 46 Hz) and δ = -24.7 ppm (d, J_{PP} = 53 Hz).

2.3.3. $[(\eta^6\text{-C}_{10}\text{H}_{14})\text{RuCl}_2(\text{pta-Bn})][(\eta^6\text{-C}_{10}\text{H}_{14})\text{RuCl}_2(\text{mtppms})]$

A solution of the dimeric precursor $[(\eta^6\text{-C}_{10}\text{H}_{14})\text{RuCl}_2]_2$ (100.0 mg, 0.163 mmol) and an equimolar amount of $(\text{pta-Bn})(\text{mtppms})$ (96.2 mg, 0.163 mmol) in methanol (8 mL) was stirred at room temperature for 1 h. The solvent was evaporated under vacuum and the residue was washed with 2 mL of water. The orange solid was washed with Et_2O (3x10 mL) and dried under vacuum. The compound dissolves well in methanol, ethanol and chloroform but poorly in water. Yield: 139 mg (70 %). *Anal.* (%) calc. for $\text{C}_{51}\text{Cl}_4\text{H}_{61}\text{N}_3\text{O}_3\text{P}_2\text{Ru}_2\text{S}$ (M=1201.99): C, 50.96; H, 5.11; N, 3.49; found: C, 50.77; H, 4.95; N, 3.38. Spectral parameters for $[(\eta^6\text{-C}_{10}\text{H}_{14})\text{RuCl}_2(\text{pta-Bn})]^+$ 1.23 (d, J = 7 Hz, 6 H, $\text{CH}(\text{CH}_3)_2$), 2.05 (s, 3H, CH_3), 2.69 (m, 2H, $\text{CH}(\text{CH}_3)_2$), 4.30 (m, 4H, PCH_2N and 2H, PCH_2N^+), 4.35 (s, 2H, $\text{N}^+\text{CH}_2\text{Ph}$), 4.60 (m, 2H NCH_2N), 5.12 (m, 4H, NCH_2N^+), 5.87 (m, 4H CH_{Ph} of *p*-cymene), 7.30-8.54 (m, 5 H_{Ph} of 2 and 14 H_{mtppms}).

$^{31}\text{P}\{^1\text{H}\}$ NMR (145 MHz, in MeOD, 25°C) δ = -18.6 (s)

Spectral parameters for $[(\eta^6\text{-C}_{10}\text{H}_{14})\text{RuCl}_2(\text{mtppms})]^-$: ^1H NMR (360 MHz, MeOD, 25°C): δ /ppm 1.13 (d, J = 7 Hz, 6H, $\text{CH}(\text{CH}_3)_2$), 1.94 (s, 3 H, CH_3), 2.69 (m, 2H, $\text{CH}(\text{CH}_3)_2$), 5.33 (d, J = 6.0 Hz, 4H, CH_{Ph} of *p*-cymene), 7.30-8.54 (m, 5 H_{Ph} of 2 and 14 H_{mtppms}).

$^{31}\text{P}\{^1\text{H}\}$ NMR (145 MHz, in MeOD, 25°C) δ = 26.1 ppm (s).

van vele baj, mivel két jelcsoport a 2.69-nél a mindkettő komplexre vonatkozik, illetve az aromás tartományban is lefedik egymást a jelek.

2.4. X-ray crystallographic studies

A summary of crystallographic data for **(2)**Cl·H₂O, **(2)**Cl·MeOH, **(2)**(**1**), **(4)**(**1**), **(5)**(**1**) and **6**·2H₂O are collected in Table 1. X-ray quality crystals of **(2)**Cl were obtained both from aqueous and methanolic solutions by slow evaporation of solvents. Crystals of **(2)**(**1**), **(4)**(**1**), and **(5)**(**1**) were also obtained by slow evaporation of MeOH from methanolic solutions of the corresponding salts. A suitable crystal of **6** was prepared by layering a CH_2Cl_2 solution with Et_2O (Table 1).

Data were collected using Enraf Nonius MACH3 diffractometer for **(2)**(**1**), **(4)**(**1**), **(5)**(**1**) and **6**·2H₂O, Bruker GADDS diffractometer for **(2)**Cl·H₂O and Bruker SMART diffractometer for **(2)**Cl·MeOH using Mo K_α radiation (λ = 0.71073 Å) or Cu K_α radiation (λ = 1.541847 Å) in case of **(2)**Cl·H₂O. The structures were routinely solved using the SIR-92 software[33] and refined on F^2 using SHELX-97 program[34], publication material was prepared with the WINGX-97 suite[35]. Hydrogen atoms were placed into geometric position except O-H protons which could be found at the difference electron density map and the oxygen-hydrogen distances were constrained. Additional crystallographic information is provided in the deposited CIF file.

Table 1

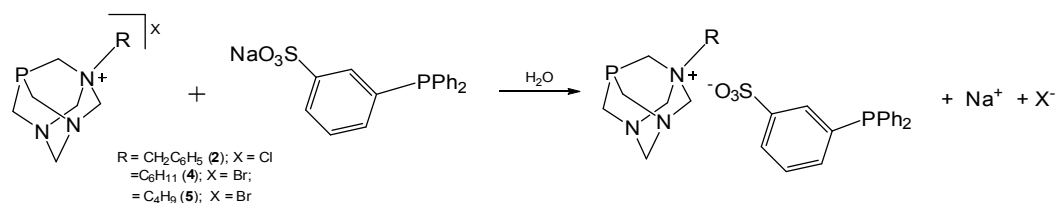
Crystallographic data and structure refinement results for (pta-Bn)Cl·H₂O, **(2)**Cl H₂O; (pta-Bn)Cl·MeOH, **(2)**Cl MeOH; (pta-Bn)(mtppps), **(2)**(1); (pta-hexyl)(mtppps), **(4)**(1); (pta-butyl)(mtppps), **(5)**(1) and [(η⁶-C₁₀H₁₄)RuCl₂(pta-Bn)]Cl·2 H₂O, **6**·2 H₂O

Structure	(2)Cl H ₂ O	(2)Cl MeOH	(2)(1)	(4)(1)	(5)(1)	6
Formula	C₁₃H₂₁ClN₃OP	C₁₄H₂₃ClN₃OP	C₃₁H₃₃N₃O₃P₂S	C₂₈H₃₅N₃O₃P₂S	C₃₀H₃₉N₃O₃P₂S	C₂₃H₃₇Cl₃N₃O₂PRu
Formula weight	301.75	315.77	589.6	555.59	583.64	625.95
Crystal system	Triclinic	Monoclinic	Monoclinic	Triclinic	Triclinic	Monoclinic
Space-group	P-1 (No. 2)	P21/n (No. 14)	P21/n (No. 14)	P-1 (No.2)	P-1 (No.2)	P21/c (No. 14)
<i>a</i> / Å	6.854(4)	8.2864(17)	11.1885(10)	8.827(1)	8.812(11)	10.6944(10)
<i>b</i> / Å	10.294(6)	11.283(2)	8.9866(10)	10.891(1)	10.865(5)	10.0645(10)
<i>c</i> / Å	11.030(6)	16.762(3)	29.5232(10)	15.466(1)	16.399(5)	25.50488(10)
<i>α</i> / °	68.65(2)	90	90	74.97(1)	100.82(2)	90
<i>β</i> / °	78.73(2)	97.08(1)	97.71(1)	84.12(1)	100.20(4)	97.66(1)
<i>γ</i> / °	89.00(3)	90	90	85.28(1)	93.44(7)	90
<i>V</i> / Å ³	709.7(7)	1555.2(5)	2941.7(4)	1426.0(2)	1511(2)	2720.7(4)
<i>Z</i>	2	4	4	2	2	4
<i>D_c</i> / g cm ⁻³	1.412	1.349	1.331	1.294	1.283	1.528
<i>F</i> (000)	320	672	1240	588	620	1288
<i>μ</i> / mm ⁻¹	0.378	0.35	0.26	0.26	0.25	0.96
Temperature of measurement (K)	110	110	293	293	293	293
Reflections collected	4867	17488	5396	5737	6135	5343
Unique reflections with <i>I</i> > 2σ(<i>I</i>)	379	3273	3938	2186	2660	2531
Parameters refined	179	186	361	335	355	313
GOF on <i>F</i> ²	0.80	0.82	1.05	0.96	1.49	0.98
<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)]	0.092	0.029	0.076	0.088	0.157	0.069
<i>R_{int}</i>	0.366	0.030	0.019	0.026	0.05	0.00
<i>wR</i> (<i>F</i> ²)	0.238	0.084	0.247	0.231	0.211	0.158
δρ _{max} , δρ _{min} / e Å ⁻³	0.28, -0.39	0.53, -0.28	0.63, -0.81	0.38, -0.31	0.37, -0.37	0.97, -0.62

3. Results and discussion

3.1. Synthesis and crystallographic analysis of (pta-*R*)(mtppps) salts

1-benzyl-1-azonia-3,5-diaza-7-phosphaadamantyl chloride, (2)Cl was obtained by known methods in reaction of pta and benzyl chloride [26]. Since the solid state structure of this compound, (2)Cl was hitherto not determined single crystals of them were isolated from both methanolic and aqueous solutions and subjected to X-ray analysis. On addition of an equivalent amount of Na(*m*tpms) to an aqueous solution of (2)Cl a white precipitate separated (Scheme 2).



Scheme 2. Formation of salts containing water-soluble phosphines both as cation and anion

The precipitate dissolves well in methanol; slow evaporation of such solutions yielded single crystals of (2)(1) suitable for X-ray structure determination (Fig. 1).

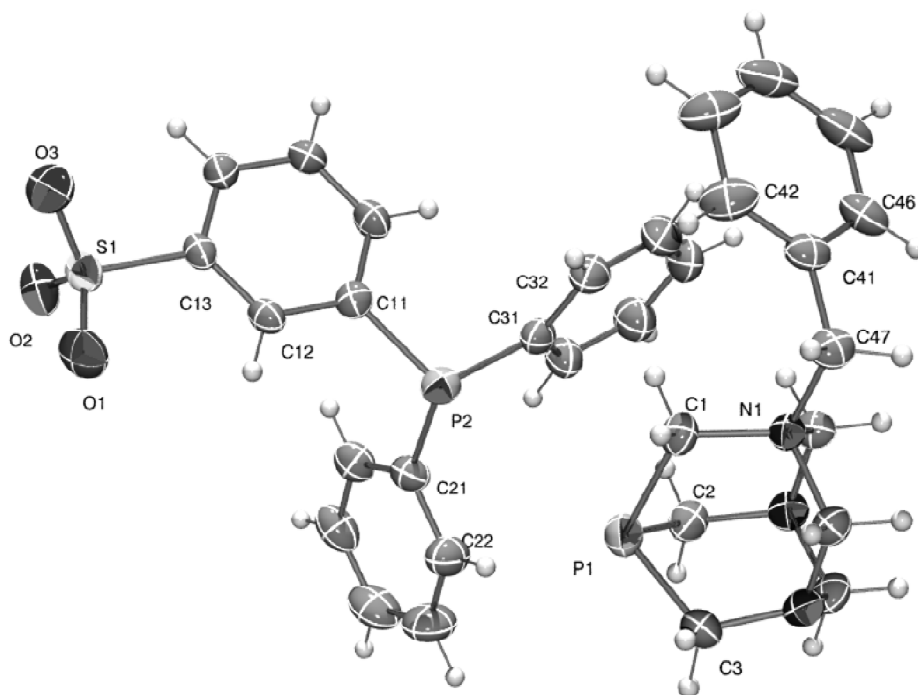


Fig. 1. ORTEP view of compound (2)(1) at 50% probability level with partial numbering scheme. Selected bond lengths (Å), angles (°) and torsion angles (°) with estimated standard deviations: P1 - C1: 1.844(5); P1 - C2: 1.836(5); P1 - C3: 1.852(5); P2 - C11: 1.846(4); P2 - C21: 1.838(5); P2 - C31: 1.835(5); P1 - C1 - N1: 114.6(3); C1 - N1 - C47: 111.9(3); C1 - N1 - C47 - C41: -67.0(1); N1 - C47 - C41 - C42: 91.9(1); N1 - C47 - C41 - C46: -89.9(1).

The most important structural parameters of (2)Cl·H₂O, (2)Cl·MeOH and (2)(1) are shown in the footnotes of Fig. 1. and in the Supplementary Fig. S1. and Fig. S2., respectively. The covalent structure of the studied ligands is rather rigid as it is evidenced by the P-C and C-N bond length data shown. CSD search gave an average P-C distance for free pta derivative ligands (15 hits) and their metal complexes (267 hits) as 1.845(17) and 1.84(2) Å, respectively which also shows the conformational rigidity of the pta ligand. However, versatility was expected and found in the supramolecular architecture of the studied ion pairs.

Similarly to a recently disclosed structure, (2)Br·MeOH [25], (2)Cl·MeOH is also monoclinic they are isostructural and belong to the space group P2₁/n (No.14). However, having a water molecule as solvent in the lattice results a different conformation of the (pta-Bn) unit and (2)Cl·H₂O crystallizes in the triclinic P-1 space group. The rotation around the N1-C47 bond occurs and is shown in the solid state structure depending on the solvate molecule of water or methanol. Fig. S3. shows the overlaid structures with significant difference in the position of the phenyl ring. Rigidity of the pta backbone is also mirrored by the small deviation of its carbon and nitrogen atoms. Examining the π - π interactions it can be concluded, that the distance between the centroids of the phenyl rings in (2)Cl·H₂O and in (2)Cl·MeOH is 3.73 and 5.03 Å, respectively and this also the result of the observed conformation change of the molecule.

For the synthesis of further (pta-R)(mtpmps) salts we have prepared several (pta-R)X derivatives, among them the known ones with R = {CH₂}_n-CH₃, n=0, X= I or MeOTf; n=1-3, X= Br}. The new 1-hexyl-1-azonia-3,5-diaza-7-phosphaadamantyl cation, (4), was obtained by refluxing pta and 1-Br-hexane in acetone.

Mixing equivalent quantities of alkyl-pta salts and mtpmps in aqueous solutions led to the formation of precipitates in the case of pta-hexyl (4) and pta-butyl (5). Cations obtained by N-alkylation of pta with shorter chain alkyl halides or triflates did not yield precipitates with mtpmps. It is noteworthy that with trisulfonated triphenylphosphine (mtppts) none of the alkyl-pta cations gave water-insoluble products.

Though salts (2)(1), (4)(1) and (5)(1) were found insoluble in water they dissolve well in chlorinated solvents or alcohols. The ³¹P NMR spectra of these solutions display only singlets of cation, pta-R (R = Bn: δ = -84.0 ppm and R = butyl or hexyl: δ = -82.9 ppm) and anion, mtpmps (δ = -4.4 ppm) with equal intensity (Fig. S5-7.). Similarly to (2)(1) single crystals of (4)(1) and (5)(1) for X-ray analysis could be obtained from methanolic solutions by slow evaporation (Fig. 2. and Fig. 3.).

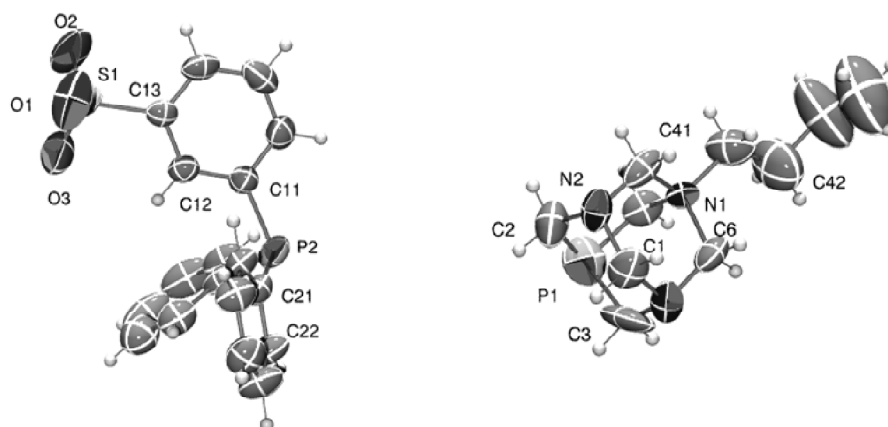


Fig. 2. ORTEP view of compound **(4)(1)** at 50% probability level with partial numbering scheme. Selected bond lengths (Å), angles (°) and torsion angles (°) with estimated standard deviations: P1 - C1: 1.761(7); P1 - C2: 1.807(7); P1 - C3: 1.807(9); P2 - C11: 1.827(6); P2 - C21: 1.819(6); P2 - C31: 1.830(7); P1 - C1 - N1: 115.2(4); C1 - N1 - C41: 113.0(5); C1 - N1 - C41 - C42: -68.4(1).

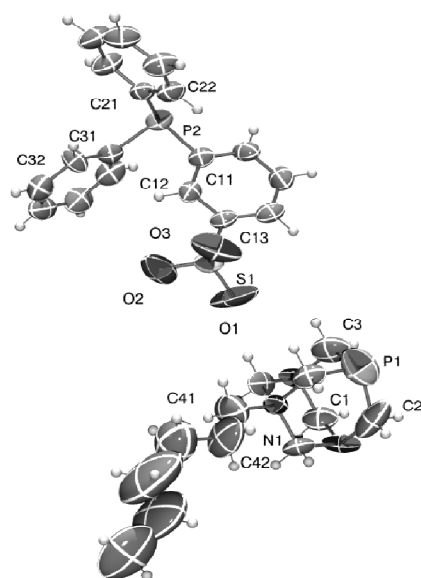


Fig. 3. ORTEP view of compound **(5)(1)** at 50% probability level with partial numbering scheme. Selected bond lengths (Å), angles (°) and torsion angles (°) with estimated standard deviations: P1 - C1: 1.730(9); P1 - C2: 1.761(13); P1 - C3: 1.793(10); P2 - C11: 1.827(7); P2 - C21: 1.815(8); P2 - C31: 1.828(8); P1 - C1 - N1: 114.2(6); C1 - N1 - C41: 112.7(8); C1 - N1 - C41 - C42: -160.8(1).

Sodium salt of *m*tppps was prepared already in 1958 [36], however, due to its poor crystallization properties its X-ray structure was not determined until 2010 [37]. In addition, structure of *m*tppps was determined with benzyltriethylammonium [38], guanidinium [39] and imidazolium [40] cations, however, **(2)(1)**, **(4)(1)** and **(5)(1)** are the first structurally characterized *m*tppps salts containing water-soluble phosphines both as cation and anion.

Secondary interactions can be tuned to use them as fixing and chelate forming tools to prepare bidentate phosphorous ligands. Note even small difference in the lattice interactions such as changing a side chain (butyl to hexyl) causes significant change in conformation and P-P distance (see Fig. S4.), hence coordination properties of the mixed tertiary phosphorous ligand.

3.2. Half sandwich Ru-complexes with homo- and heterobidentate ligands

3.2.1. Synthesis of $[(\eta^6\text{-C}_{10}\text{H}_{14})\text{RuCl}(\text{pta-Bn})(\text{mtppps})]\text{Cl}$

To our knowledge there are only two half sandwich Ru-complexes known which contain both anionic (*mtppps*) and cationic (*pta-Me*) phosphine ligands. Both $[\text{CpRu}(\text{pta-Me})(\text{mtppps})_2]$ and $[\text{CpRu}(\text{pta-Me})(\text{PPh}_3)(\text{mtppps})]^+$ were obtained in two-step procedures by stepwise replacement of PPh_3 in $[\text{CpRuCl}(\text{PPh}_3)_2]$ with *pta-Me* and *mtppps* [17].

Similarly, $[(\eta^6\text{-C}_{10}\text{H}_{14})\text{RuCl}(\text{pta-Bn})(\text{mtppps})]\text{Cl}$ was synthesized by stepwise complex formation. First, $[(\eta^6\text{-C}_{10}\text{H}_{14})\text{RuCl}_2(\text{pta-Bn})]\text{Cl}$, **6** was prepared in reaction of (*pta-Bn*)Cl with $[(\eta^6\text{-C}_{10}\text{H}_{14})\text{RuCl}_2]_2$. The resulting complex has already been described in the literature [15], however, its solid state molecular structure was not determined. By layering hexane on top of a dichloromethane solution of **6** we obtained good quality crystals which were subjected to single crystal X-ray diffraction analysis.

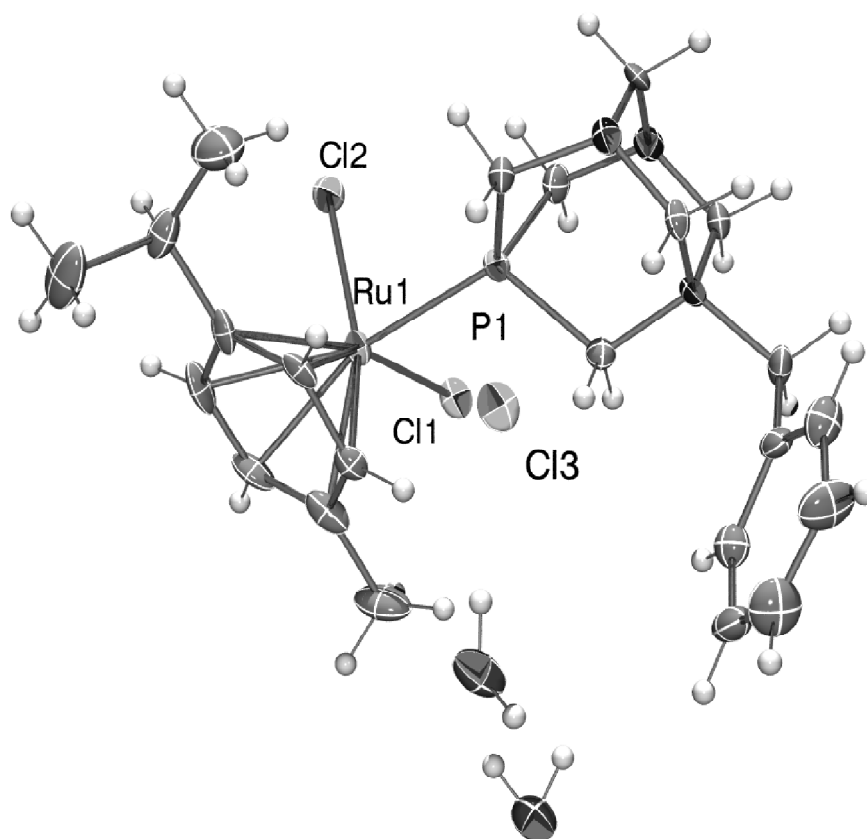
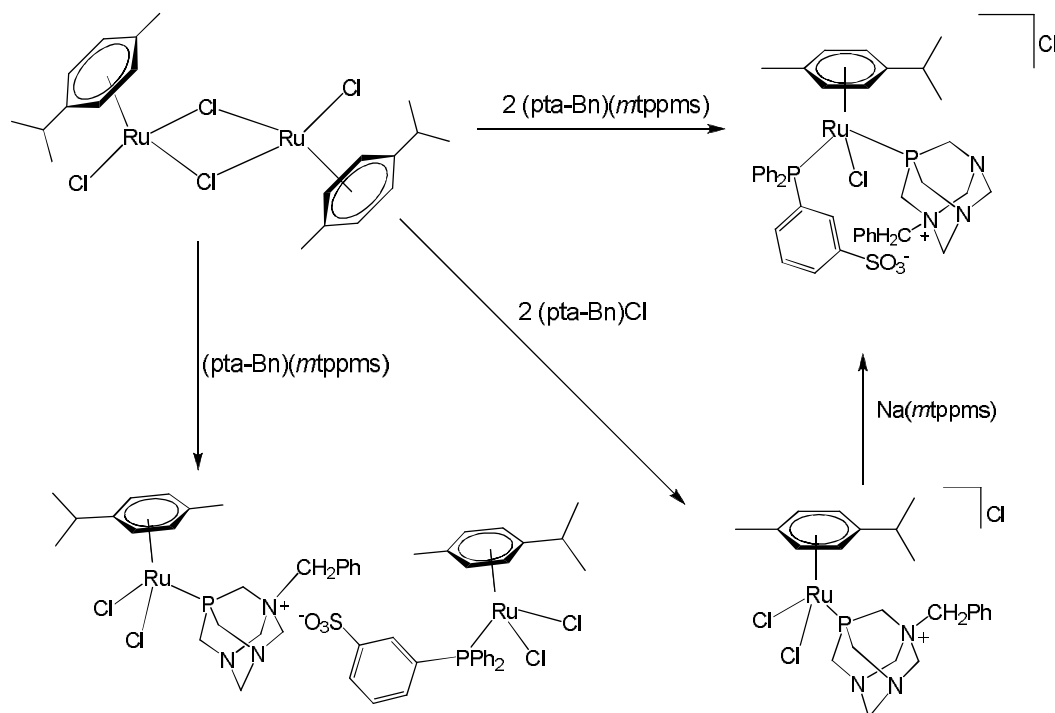


Fig. 4. ORTEP view of $[(\eta^6\text{-C}_{10}\text{H}_{14})\text{RuCl}_2(\text{pta-Bn})]\text{Cl}\cdot 2\text{H}_2\text{O}$ with partial numbering scheme. Selected bond lengths (Å) and angles (°) with estimated standard deviations: P1 - C1: 1.873(10); P1 - C2: 1.825(11); P1 - C3: 1.822(11); P1 - Ru1: 2.295(3); Cl1 - Ru1: 2.419(3); Cl2 - Ru1: 2.408(3); P1 - Ru1 - Cl1: 83.2(1); P1 - Ru1 - Cl2: 83.9(1); Cl1-Ru1-Cl2: 88.4(1)°.

Search of CSD (Version 5.33 Update May, 2012) gave 268 hits for aryl-RuCl₂P complexes. Average values for Ru-Cl: 2.41(2) Å, Ru-P: 2.33(3) Å, Cl-Ru-Cl angle 88(4)°, Cl-Ru-P angle 86(4)°. It can be seen from data at Fig. 4. that our observation is completely agrees with these data.

In water, reaction of $[(\eta^6\text{-C}_{10}\text{H}_{14})\text{RuCl}_2(\text{pta-Bn})]\text{Cl}$ and Na(*m*tppps) immediately gives a white precipitate what can be formulated as $[(\eta^6\text{-C}_{10}\text{H}_{14})\text{RuCl}_2(\text{pta-Bn})](\text{m}(\text{tppps}))$ according to its ³¹P NMR spectrum (Fig. S8.). Therefore the synthesis was performed in methanol at reflux temperature. In the ³¹P NMR spectrum the singlets characteristic for *m*tppps ($\delta = -4.4$ ppm) and for **6** ($\delta = -18.6$ ppm) were gradually replaced by two doublets of the same intensity at $\delta = 27.6$ ppm (d, $J_{\text{pp}} = 46$ Hz) and at $\delta = -24.7$ ppm (d, $J_{\text{pp}} = 53$ Hz). After ten hours reflux these latter were the only signals in the spectrum, characteristic for $[(\eta^6\text{-C}_{10}\text{H}_{14})\text{RuCl}(\text{pta-Bn})(\text{m}(\text{tppps}))]\text{Cl}$.

The complex was isolated as yellow powder and was characterized also by ¹H and ¹³C NMR spectroscopy, elemental analysis and mass spectroscopy. The strongest signal in the ESI MS spectrum belongs to $[(\eta^6\text{-C}_{10}\text{H}_{14})\text{RuCl}(\text{pta-Bn})(\text{m}(\text{tppps}))]^+ = (\text{M})^+$ (observed *m/z*: 860.154; calcd. 860.154 with correct isotope distribution; Fig. S9.). All these data agree well with the suggested composition of $[(\eta^6\text{-C}_{10}\text{H}_{14})\text{RuCl}(\text{pta-Bn})(\text{m}(\text{tppps}))]\text{Cl}$ (Scheme 3).



Scheme 3. Synthesis of half-sandwich Ru(II)-complexes using (pta-Bn)(mtppps) as a ligand

The desired mixed-phosphine complex could also be prepared in an one-step procedure. In this case, a methanolic solution of $[(\eta^6\text{-C}_{10}\text{H}_{14})\text{RuCl}_2]_2$ was added to a solution of (pta-Bn)(mtppps) in MeOH to obtain a reaction mixture with $[\text{Ru}^{2+}] = [\mathbf{2}] = [\mathbf{1}]$. Two strong doublet signals of $[(\eta^6\text{-C}_{10}\text{H}_{14})\text{RuCl}(\text{pta-Bn})(\text{mtppps})]\text{Cl}$ was observed already after two hours reflux. Nevertheless, at this reaction time singlet signals of the free phosphines **2** and **1** as well as those of **6** ($\delta = -18.6$ ppm) and $[(\eta^6\text{-C}_{10}\text{H}_{14})\text{RuCl}_2(\text{mtppps})]^-$ ($\delta = 26.1$ ppm) were still seen. In four hours the signals of the free phosphines disappeared, however, only ten hours reflux produced solutions with clean ^{31}P NMR spectrum of $[(\eta^6\text{-C}_{10}\text{H}_{14})\text{RuCl}(\text{pta-Bn})(\text{mtppps})]\text{Cl}$ (Fig. S10.). During the reaction the colour of the solution gradually changed from orange to lemon yellow. The product was isolated as yellow powder and analysed by the same techniques used for identification of the product of the stepwise synthetic procedure; all parameters were found identical.

3.2.2. (pta-R)(mtppps) as bridging ligand

In contrast to the above synthesis of the mononuclear $[(\eta^6\text{-C}_{10}\text{H}_{14})\text{RuCl}(\text{pta-Bn})(\text{mtppps})]\text{Cl}$, when equimolar amounts of $[(\eta^6\text{-C}_{10}\text{H}_{14})\text{RuCl}_2]_2$ and (pta-Bn)(Na-mtppps), (**2**)(**1**) were reacted in MeOH (concentration ratio $[\text{Ru}^{2+}]:[\mathbf{2}]:[\mathbf{1}] = 2:1:1$) a different product was obtained (Scheme 3). In addition to signals of **2** and **1**, the ^{31}P NMR spectrum of the solution displayed only singlets of $[(\eta^6\text{-C}_{10}\text{H}_{14})\text{RuCl}_2(\text{pta-Bn})]^+$ ($\delta = -18.6$ ppm) and $[(\eta^6\text{-C}_{10}\text{H}_{14})\text{RuCl}_2(\text{mtppps})]^-$ ($\delta = 26.1$ ppm) with equal intensity (Fig. S11.). After two hours reaction time only these two signals could be observed, and not other species could be detected by ^{31}P NMR spectroscopy even upon prolonged reflux of the solution.

According to elemental analysis the isolated orange solid has the formula of $[(\eta^6\text{-C}_{10}\text{H}_{14})\text{RuCl}_2(\text{pta-Bn})][(\eta^6\text{-C}_{10}\text{H}_{14})\text{RuCl}_2(\text{mtppms})]$. Containing a big monovalent cation and anion, the compound has poor solubility in water, however, it dissolves well in alcohols, benzene and in chlorinated solvents. Ionic interaction between $(\text{pta-Bn})^+$ and $(\text{mtppms})^-$, each coordinated to a different Ru(II) center, makes **(2)(1)** a bridging ligand between the two half sandwich Ru(II) moieties.

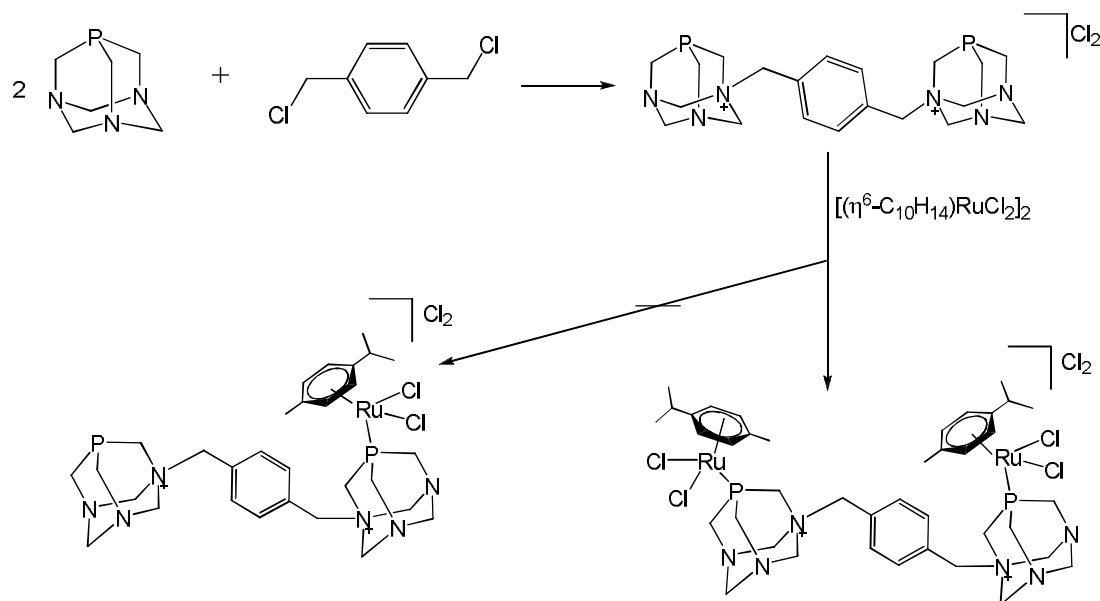
Similar observations were made when equimolar amounts of $[(\eta^6\text{-C}_{10}\text{H}_{14})\text{RuCl}_2]_2$ were added to methanolic solutions of **(4)(1)** or **(5)(1)**. After ≥ 2 hours reaction time, the ^{31}P NMR spectra of the solutions displayed only the singlet characteristic for $[(\eta^6\text{-C}_{10}\text{H}_{14})\text{RuCl}_2(\text{mtppms})]^-$ ($\delta = 26.0$ ppm) and an other singlet of equal intensity at $\delta = -20.4$ ppm; the latter refers to the presence of $[(\eta^6\text{-C}_{10}\text{H}_{14})\text{RuCl}_2(\text{pta-R})]^+$ ions (R = butyl, hexyl) (Fig. S12-13.).

The $[(\eta^6\text{-C}_{10}\text{H}_{14})\text{RuCl}_2(\text{Ph}_2\text{PCH}_2\text{NHC}_6\text{H}_4\text{COOH})]$ complex **[4]** mentioned in the introduction was found to dimerize through intermolecular H-bonds between the carboxylic acid groups. Therefore the dimer necessarily consists of two monomeric half sandwich Ru-complexes having the same phosphine substituents and consequently has a symmetric structure. In our case, the ionic interaction between various phosphine cations and anions allows formation of self-organized dimers containing different phosphine units in the bridge. By this way, this modular approach makes possible the synthesis of non-symmetric wheel and axle half sandwich Ru-dimers, too.

3.3 Synthesis of 1,1'-[1,4-phenylenebis(methylene)]bis-3,5-diaza-1-azonia-7-phosphatricyclo[3.3.1.1]decane, **(3)**, and its half sandwich Ru(II)-complex

The water-soluble bisphosphine 1,1'-[1,4-phenylenebis(methylene)]bis-3,5-diaza-1-azonia-7-phosphatricyclo[3.3.1.1]decane, **3** (as its chloride salt) was obtained by refluxing a suspension of pta and 1,4-bis(chloromethyl)benzene in acetone (Scheme 4). Spectral parameters of the compound agree well with those disclosed for the related **(3)Br₂** [27].

Upon refluxing equimolar amounts of **(3)Cl₂** and $[(\eta^6\text{-C}_{10}\text{H}_{14})\text{RuCl}_2]_2$ in methanol an orange precipitate separated. In aqueous solution of the isolated complex a singlet ^{31}P NMR signal was observed ($\delta = -17.9$ ppm) referring to identical environments of the two phosphorus atoms (Fig. S14.). In the ESI MS spectrum (aqueous solution) the highest intensity peaks were observed with correct isotope distribution at $m/z = 515.051$ (calcd: 515.059 $[\text{C}_{40}\text{H}_{60}\text{N}_6\text{P}_2\text{Cl}_4\text{Ru}_2]^{2+} = \text{M}^{2+}$), showing the presence of $[\{(\eta^6\text{-C}_{10}\text{H}_{14})\text{RuCl}_2\}_2(\mu\text{-3})]^{2+}$ (Fig. S15.). This finding is in accordance with data of elemental analysis what shows the formation of a dinuclear $[\{(\eta^6\text{-C}_{10}\text{H}_{14})\text{RuCl}_2\}_2(\mu\text{-3})]\text{Cl}_2$ in which the pta-derived bisphosphine acts as bridging ligand between two Ru(II)-centers. It is of interest that exclusive formation of the dinuclear complex was observed on those cases, too, when higher than equimolar amounts of the bisphosphine was used. Note, that in contrast to reactions of **(3)Br₂** with *cis*-[PtBr₂(cod)] where no pure dinuclear complexes could be obtained [27], interaction of **(3)Cl₂** and $[(\eta^6\text{-C}_{10}\text{H}_{14})\text{RuCl}_2]_2$ afforded cleanly the desired dinuclear complex having **3** as bridging ligand.



Scheme 4. Synthesis of $[\{(\eta^6\text{-C}_{10}\text{H}_{14})\text{RuCl}_2\}_2(\mu\text{-}\mathbf{3})]\text{Cl}_2$ containing a bisphosphine (**3**) obtained from pta and 1,4-bis(chloromethyl)benzene

4. Conclusion

Up till now only ion pairs of cationic and anionic derivatives of triphenylphosphine were used as bidentate ligands in various transition metal complexes. In this work we demonstrated that Coulombic interaction between monosulfonated triphenylphosphine anion (*mtpms*) and various cationic alkyl and benzyl derivatives of 1,3,5-triaza-7-phosphaadamantane (pta-R; R= benzyl, butyl, hexyl) is also strong enough to make the ion pairs suitable to act as bidentate phosphorus ligands. The ion pairs, (pta-R)(*mtpms*) were crystallized and the solid state structures determined by X-ray diffraction for the first time. Interestingly, the (pta-Bn)(*mtpms*) ion pair is able to coordinate to the same Ru(II) in $[(\eta^6\text{-C}_{10}\text{H}_{14})\text{RuCl}(\text{pta-Bn})(\text{mtpms})]\text{Cl}$ while all the (pta-R)(*mtpms*) ion pairs can act as bridging ligands between two $[(\eta^6\text{-C}_{10}\text{H}_{14})\text{RuCl}_2]$ units. These neutral dinuclear complexes are poorly soluble in water, while the one containing the well soluble cationic bisphosphine obtained from pta and 1,4-bis(chloromethyl)benzene is itself cationic and shows good solubility in water. The results show that an efficient modular approach for synthesis of complexes containing two different phosphine ligands can be based on use of such ion pairs.

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Appendix

CCDC 929756 - 929761 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at ...

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