Polyhedron 60 (2013) 1–9

Contents lists available at SciVerse ScienceDirect

Polyhedron

journal homepage: www.elsevier.com/locate/poly

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

Antal Udvardy [a], Attila Csaba Bényei [a,b], Péter Juhász [a], Ferenc Joó [a,c], Ágnes Kathó [a,*]

[a] Department of Physical Chemistry, University of Debrecen, P.O. Box 7, Debrecen H-4010, Hungary
[b] Department of Pharmaceutical Chemistry, Medical and Health Science Centre, University of Debrecen, P.O. Box 70, Debrecen H-4010, Hungary
[c] MTA-DE Research Group of Homogeneous Catalysis and Reaction Mechanisms, P.O. Box 7, Debrecen H-4010, Hungary

ARTICLE INFO

Article history:
Received 28 March 2013
Accepted 4 May 2013
Available online 13 May 2013

Keywords:
1,3,5-Triaza-7-phosphaadamantane
Sulfonated
Phosphines
Ion pairs
Bidentate ligand

ABSTRACT

Ion pairs consisting of N-substituted derivatives of 1,3,5-triaza-7-phosphaadamantane (pta-R; R = benzyl, butyl, hexyl) as cations and monosulfonated triphenylphosphine (*m*tppms) as anion were synthesized and characterized (including X-ray diffraction, too). These ion pairs act as bidentate phosphorus ligands in reactions with $[(\eta^6\text{-}C_{10}H_{14})RuCl_2]_2$, yielding mononuclear or dinuclear half sandwich Ru(II) complexes. 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 $[\{(\eta^6\text{-}C_{10}H_{14})RuCl_2\}_2(\mu\text{-}\mathbf{3})]Cl_2$.

1. Introduction

Bi- or multidentate ligands play important role in coordination chemistry and homogeneous catalysis. Since the two or more donor atoms are held together by covalent bonds of appropriate connectivity in several cases synthesis of such ligand molecules requires time-consuming, multistep reactions.

The essence of homogeneous catalysis is in the tuning of electronic, steric and coordination properties of the catalytically active metal complex species 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 catalysis. Capitalizing on secondary interactions instead of covalent bonding to connect the appropriate donor atoms represent a supramolecular approach for the delicate tuning of the catalytic metal complex. Moreover, 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 substrate molecule(s) occur. This is why it has been conceived that instead of the traditional synthetic procedures bidentate ligands may also be obtained by self-assembly of monodentate ones. Construction of a number of complex structures from simple building units via association by secondary interactions can be faster, more versatile and economic than synthesis of ligands of similar size and complexity based on covalent bonding.

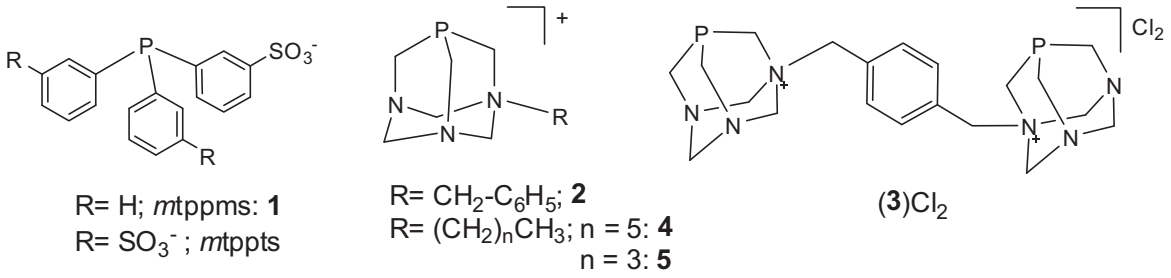
Some important steps are already taken on this novel field including studies of transition metal complexes with supramolecular bidentate ligands produced by self-organization [1]. For example, wheel-and-axle-type organometallic complexes were synthesized having two half-sandwich Ru(II)-units as wheels, while the axle was formed by H-bonding between the non-coordinated carboxylic acid groups in the two $[(\eta^6\text{-}C_{10}H_{14})RuCl_2$(4-aminobenzoic acid)] complexes [2]. Similar phenomena were described with $[(\eta^6\text{-}C_{10}H_{14})RuCl_2(L)]$ complexes having iso-nicotinic acid or 4-aminocinnamic acid [2] as well as $Ph_2CH_2NHC_6H_4COOH$ [3] 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 the solid phase (X-ray) [4].

Gulyás et al obtained bidentate phosphorus ligands held together by ionic interactions. Triphenylphosphine derivatives with oppositely charged substituents ($-SO_3^-$ and $-NH_3^+$, 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 [5].

* Corresponding author. Tel.: +36 52 512900; fax: +36 52 512915.
E-mail address: katho.agnes@science.unideb.hu (Á. Kathó).

0277-5387/$ - see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.poly.2013.05.008



Scheme 1. Water-soluble phosphines used in this study.

We have also reported on formation of stable ion pairs formed by oppositely charged water-soluble tertiary phosphines [6]. As anions we used mono-sulfonated triphenylphosphine (*m*tppms, **1**; well known from aqueous organometallic catalysis [7]) while the cation was N-benzyl-1,3,5-triaza-7-phosphaadamantane, **2** (Scheme 1).

1,3,5-Triaza-7-phosphaadamantane (pta) is often used in aqueous organometallic catalysis [8]. $[RuCl_2(pta)_4]$ has been studied in hydrogenation of aldehydes [9] and this complex was found active also in hydrogenation of bicarbonate [10] and in hydration of nitriles [11]. These reactions are also catalyzed by the half-sandwich complexes formed in reactions of $[(arene)RuCl_2]_2$ and pta [12–14]. 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 [15].

N-Alkyl derivatives of pta can also be used as ligands in half-sandwich Ru-complexes [14,16]. Already at the time of the first synthesis of pta it was established that it could be methylated on one of the *N*-atoms by MeI [17]. In addition, several cationic pta-R derivatives were obtained by longer chain alkyl iodides (EtI [18], *n*PrI [19], *n*BuI [20], $I(CH_2)_4I$ [21]) as well as with various bromomethyl compounds ($BrCH_2Y$, where $Y = C_6H_4N$ [22], C_6H_5, COOMe, CN [23,24]). With benzyl chloride 1-benzyl-1-azonia-3,5-diaza-7-phosphaadamantyl cation, pta-Bn (**2**) is formed [25] while 1,4-bis(chloromethyl)benzene [6] and bis(bromomethyl)benzene are able to alkylate and connect 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*-$[PtBr_2(cod)]$ did not yield well defined products [26].

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 $(\mathbf{3})Cl_2$ and $[(\eta^6\text{-}C_{10}H_{14})RuCl_2]_2$ yields a binuclear complex in which **3** serves as bridging ligand between the two half-sandwich Ru(II)-arene units. Synthesis of (pta-R)(*m*tppms) ion pairs (R = 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)(*m*tppms) 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 synthesized in a single step.

2. Experimental

2.1. Materials and methods

All reactions and manipulations were carried out under an 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). Mass data were collected on a BRUKER BioTOF II ESI-TOF spectrometer. Elemental analyses were carried out using Elementar Vario Micro instrument.

All reagents and solvents were commercially available and used as received with the exception of Na(*m*tppms) [27], Na_3(*m*tppts) [28], pta [29], (pta-Me)I [17], (pta-Me)CF_3SO_3 [16], (pta-R)Br (R = Et, *n*Pr, *n*Bu [20]), (pta-Bn)Cl [25], $[(\eta^6\text{-}C_{10}H_{14})RuCl_2]_2$ [30], $Na[(\eta^6\text{-}C_{10}H_{14})RuCl_2(mtppms)]$ [31] and $[(\eta^6\text{-}C_{10}H_{14})RuCl_2$(pta-Bn)]Cl, **6** [14] which were prepared according to the literature.

2.2. Synthesis of ligands

2.2.1. 1,1′-[1,4-phenylenebis(methylene)]bis-3,5-diaza-1-azonia-7-phosphatricyclo[3.3.1.1]decane dichloride

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 soluble in water. Yield 115 mg (74%). *Anal.* Calc. for $P_2Cl_2N_6C_{20}H_{32}$ (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 H_2O): observed *m*/*z* 209.107, calcd. 209.100 for $P_2N_6C_{20}H_{32} = M^{2+}$. ^1H NMR (360 MHz, D_2O, 25 °C): δ/ppm 3.85 (m, 8H, PCH_2N), 4.20 (s, 4H, PCH_2N^+), 4.54 (m, 8H, PCH_2N^+, NCH_2N), 4.98 (m, 8H, NCH_2N^+), 7.64 (s, 4H, H_{Ph}). $^{13}C\{^1H\}$ NMR (90 MHz, D_2O, 25 °C): δ/ppm 45.56 (d, $^1J_{PC}$ = 22 Hz, PCH_2N), 52.89 (d, $^1J_{PC}$ = 33 Hz, PCH_2N^+), 65.83 (s, $PhCH_2N^+$), 69.38 (s, NCH_2N), 78.90 (s, NCH_2N^+), 127.38 (s, CH_{Ph}), 133.68 (s, C_{Ph}). $^{31}P\{^1H\}$ NMR (145 MHz, D_2O, 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 h. The mixture was cooled to room temperature and the precipitate was separated by filtration. The white solid was washed with acetone (2 × 5 mL) and Et_2O (3 × 5 mL) and dried. Yield 202 mg (60%). *Anal.* Calc. for $C_{12}H_{24}N_3PBr$ (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, Calc. 241.316 for $PN_3C_{12}H_{25} = M^+$. ^1H NMR (360 MHz, MeOD, 25 °C): δ/ppm 0.93 (t, 3H, $^1J_{HH}$ = 7 Hz, CH_3), 1.01–1.30 (m, 6H, $N^+–CH_2CH_2CH_2CH_2CH_2CH_3$), 1.65–1.74 (m, 2H, $N^+–CH_2CH_2$), 2.84 (m, 2H, $N^+–CH_2CH_2$), 3.76–4.04 (m, 4H, PCH_2N), 4.32 (d, 2H, J_{PH} = 6 Hz, PCH_2N^+), 4.37–4.64 (m, 2H, NCH_2N), 4.71-5.09 (m, 4H, N^+CH_2N). $^{13}C\{^1H\}$ NMR (90 MHz, MeOD, 25 °C): δ/*ppm* 13.00 (s, CH_3), 19.31 (s, CH_2CH_3), 19.34 (s, $CH_2CH_2CH_3$), 21.30 (s, $N^+–CH_2CH_2CH_3$), 24.60 (s, $N^+–CH_2CH_2$), 45.77 (d, J_{PC} = 22 - Hz, PCH_2N), 53.11 (d, J_{PC} = 33 Hz, PCH_2N^+), 62.99 (s, $N^+CH_2CH_2$), 70.01 (s, NCH_2N), 78.12 (s, N^+CH_2N). $^{31}P\{^1H\}$ NMR (145 MHz, D_2O, 25 °C): δ = −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-*m*tppms 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 (3 × 6 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 $C_{31}H_{33}N_3O_3P_2S$ (M = 589.62): C, 63.14; H, 5.60; N, 7.12. Found: C, 63.48; H, 5.92; N, 7.07%. ^{1}H NMR (360 MHz, MeOD, 25 °C): δ/ppm 3.54–3.87 (m, 4H, PC*H*$_2$N), 4.18–4.63 (m, 2H, PC*H*$_2$N$^+$ and d, 2H NC*H*$_2$N, s, 2H, N$^+$C*H*$_2$Ph), 5.03–5.30 (m, 4H, N$^+$C*H*$_2$N), 7.57–7.46 (m, 5H$_{Ph\ of\ 2}$ and 14H$_{mtppms}$). ^{13}C{^{1}H} NMR (90 MHz, $CDCl_3$, 25 °C): δ/ppm 46.87 (d, J_{PC} = 21 Hz NCH$_2$P), 52.41 (d, J_{PC} = 33 Hz, N$^+$*C*H$_2$P), 65.22 (s, N$^+$CH$_2$Ph), 70.47 (s, NCH$_2$N), 79.12 (s, N$^+$*C*H$_2$N), 125.39-146.69 (m, 4 C$_{Ph\ of\ 2}$ and 10 C$_{mtppms}$). ^{31}P{^{1}H} NMR (145 MHz, $CDCl_3$, 25 °C): δ = −84.0 ppm (s), −4.3 δ = ppm (s).

*2.2.3.2. (pta-hexyl)(mtppms), (**4**)(**1**).* Yield: 22.3 mg (51%). *Anal.* Calc. for $C_{30}H_{39}N_3O_3P_2S$ (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%. ^{1}H NMR (360 MHz, MeOD, 25 °C): δ/ppm 0.82 (m, 3H, C*H*$_3$), 1.13–1.35 (m, 6H, N$^+$–CH$_2$CH$_2$*CH*$_2$*CH*$_2$*CH*$_2$CH$_3$), 1.52–1.70 (m, 2H, N$^+$–CH$_2$*CH*$_2$), 2.63–2.82 (m, 2H, N$^+$–*C*H$_2$CH$_2$), 3.67–3.94 (m, 4H, PC*H*$_2$N), 4.13–4.55 (m, 2H, PC*H*$_2$N$^+$ and 2H, NC*H*$_2$N), 4.60–4.99 (m, 4H, N$^+$C*H*$_2$N), 6.93–7.78 (m, 14 H, aromatic). ^{13}C{^{1}H} NMR (90 MHz, MeOD, 25 °C): δ/ppm 14.29 (s, *C*H$_3$), 20.68 (s, *C*H$_2$CH$_3$), 23.49 (s, *C*H$_2$CH$_2$-CH$_3$), 27.38 (s, N$^+$CH$_2$CH$_2$*C*H$_2$), 32.34 (s, N$^+$CH$_2$*C*H$_2$), 47.38 (d, J_{PC} = 21 Hz, NCH$_2$P), 54.01 (d, J_{PC} = 33 Hz, N$^+$*C*H$_2$P), 63.68 (s, N$^+$–*C*H$_2$CH$_2$), 71.38 (s, NCH$_2$N), 80.93 (s, N$^+$*C*H$_2$N). ^{31}P{^{1}H} NMR (145 MHz, MeOD, 25 °C) δ = −82.9 (s), δ = −4.4 ppm (s). ^{31}P{^{1}H} NMR (145 MHz, $CDCl_3$, 25 °C) δ = −85.0 ppm (s), δ = −4.3 ppm (s).

*2.2.3.3. (pta-Bu)(mtppms), (**5**)(**1**).* Yield: 27.1 mg (64%). *Anal.* Calc. for $C_{28}H_{35}N_3O_3P_2S$ (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%. ^{1}H NMR (360 MHz, MeOD, 25 °C): δ/ppm 0.89 (t, J_{HH} = 7 Hz, 3H, C*H*$_3$), 1.26 (sextet, J_{HH} = 7 Hz, 2H, C*H*$_2$CH$_3$), 1.50–1.74 and 2.62–2.91 (m, 4H, N$^+$–C*H*$_2$*CH*$_2$CH$_2$CH$_3$), 3.67–4.02 (m, 4H, PC*H*$_2$N), 4.15–4.57 (m, 2H, PC*H*$_2$N$^+$, 2H, NC*H*$_2$N), 4.61–5.03 (m, 4H, N$^+$C*H*$_2$N), 7.07–7.82 (m, 14 H, aromatic). ^{13}C{^{1}H} NMR (90 MHz, MeOD, 25 °C): δ/ppm 13.94 (s, *C*H$_3$), 21.04 (s, *C*H$_2$CH$_3$), 22.70 (s, *C*H$_2$CH$_2$CH$_3$), 46.85 (d, J_{PC} = 21 Hz, PCH$_2$N), 54.00 (d, J_{PC} = 33 Hz, PCH$_2$N$^+$), 63.44 (s, N$^+$–*C*H$_2$CH$_2$), 71.36 (s, NCH$_2$N), 80.91 (s, N$^+$CH$_2$N), 127.45–146.87 (m, aromatic). ^{31}P{^{1}H} NMR (145 MHz, MeOD, 25 °C): δ = −82,9 ppm (s) δ = −4.4 ppm (s). ^{31}P{^{1}H} NMR (145 MHz, $CDCl_3$, 25 °C): δ = −85.2 ppm (s), δ = −4.3 ppm (s).

2.3. Synthesis of half sandwich Ru-complexes

*2.3.1. [{(η^6-$C_{10}H_{14}$)$RuCl_2$}$_2$(μ-**3**)] Cl_2*

A solution of the dimeric precursor [(η^6-$C_{10}H_{14}$)$RuCl_2$]$_2$ (100.0 mg, 0.163 mmol) and an equimolar amount of (**3**)Cl_2 (80.0 mg, 0.163 mmol) in methanol (10 mL) was refluxed for 20 min. 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 (3 × 3 mL) and Et_2O (3 × 10 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 Ru_2C_{40}-$H_{60}Cl_6N_6P_2 \cdot 2H_2O$ (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 H_2O): observed *m*/*z* 515.051; Calc. 515.059 for $[C_{40}H_{60}N_6P_2Cl_4Ru_2]^{2+}$ = M^{2+}. ^{1}H NMR (360 MHz, MeOD, 25 °C): δ/ppm 1.07 (d, 12H, J = 7.0 Hz, CH(C*H*$_3$)$_2$), 1.89 (m, 6H, C–C*H*$_3$), 2.46 (m, 2H, C*H*(CH$_3$)$_2$), 3.92 (m, 8H, PC*H*$_2$N, 4H PC*H*$_2$N$^+$, 4H, N$^+$C*H*$_2$), 4.54 (m, 4H, NC*H*$_2$N), 4.97 (m, 8H, NC*H*$_2$N$^+$), 5.76 (m, 8H, CH$_{Ph}$ of *p*-cymene), 7.57 (s, 4H, H$_{Ph}$ of **3**). ^{13}C{^{1}H} NMR (90 MHz, D_2O, 25 °C): δ/ppm 17.95 (s, *C*H$_3$), 21.18 (s, CH(*C*H$_3$)$_2$), 30.61 (s, *C*H(CH$_3$)$_2$), 48.45 (d, J = 22 Hz, PCH$_2$N), 51.08 (d, J = 33 Hz, PCH$_2$N$^+$), 65.12 (s, N$^+$*C*H$_2$Ph, 69.31 (s, NCH$_2$N), 79.46 (s, NCH$_2$N$^+$), 86.24 and 88.78 (s, *C*H$_{Ph}$ of *p*-cymene), 99.00 and 108.07 (s, C$_{Ph}$ of *p*-cymene), 127.10 (s, *C*H of C$_{Ph}$), 133.62 (s, C of C$_{Ph}$). ^{31}P{^{1}H} NMR (145 MHz, D_2O, 25 °C): δ/ppm −17.9 ppm (s).

2.3.2. [(η^6-$C_{10}H_{14}$)$RuCl_2$(pta-Bn)(mtppms)]Cl

A solution of [(η^6-$C_{10}H_{14}$)$RuCl_2$(pta-Bn)]Cl, **6** (100.0 mg, 0.169 mmol) and Na(*m*tppms) (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 Et_2O several times. The resulting yellow powder was washed at room temperature with Et_2O (3x10 mL) and dried. The complex dissolves well in water, methanol and ethanol but poorly in chloroform. Yield: 112 mg (76%). *Anal.* Calc. for $C_{41}H_{47}N_3O_3P_2SCl_2Ru \cdot H_2O$ (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 H_2O): observed *m*/*z*: 860.154; Calc. 860.154 for $[C_{41}H_{47}N_3O_3P_2$-$SClRu]^+$ = M^+. ^{1}H NMR (360 MHz, MeOD, 25 °C): δ/ppm 1.23 (m, 6H, CH(C*H*$_3$)$_2$), 2.04 (m, 3H, –C*H*$_3$), 2.64 (m, 1H, C*H*(CH$_3$)$_2$), 4.01–5.02 (m, 14H, PC*H*$_2$N, PC*H*$_2$N$^+$, N$^+$C*H*$_2$Ph, NC*H*$_2$N, NC*H*$_2$N$^+$), 5.73 (m, 4H$_{Ph}$ for *p*-cymene), 6.83–8.90 (m, 5H, H$_{Ph\ of\ 2}$, 14H, H$_{mtppms}$). ^{13}C{^{1}H} NMR (90 MHz, D_2O, 25 °C): δ/ppm 16.99 (s, *C*H$_3$), 20,35 (d, J = 22 Hz CH(*C*H$_3$)$_2$), 30,63 (s, *C*H(CH$_3$)$_2$), 48.43 (d, J = 17 Hz, PCH$_2$N), 50.71 (d, J = 19 Hz, PCH$_2$N$^+$), 64.91 (s, N$^+$CH$_2$Ph), 68.60 (s, NCH$_2$N), 79.88 NCH$_2$N$^+$), 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$_{m}$-$_{tppms}$). ^{31}P{^{1}H} NMR (145 MHz, D_2O, 25 °C) δ = 28.1 ppm (d, J_{PP} = 46 Hz) and δ = −24.1 ppm (d, J_{PP} = 53 Hz). ^{31}P{^{1}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. [(η^6-$C_{10}H_{14}$)$RuCl_2$(pta-Bn)][(η^6-$C_{10}H_{14}$)$RuCl_2$(mtppms)]

A solution of the dimeric precursor [(η^6-$C_{10}H_{14}$)$RuCl_2$]$_2$ (100.0 mg, 0.163 mmol) and an equimolar amount of (pta-Bn)(*m*tppms) (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 (3 × 10 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 $C_{51}Cl_4H_{61}N_3O_3P_2Ru_2S$ (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 [(η^6-$C_{10}H_{14}$)$RuCl_2$(pta-Bn)]$^+$ 1.23 (d, J = 7 Hz, 6 H, CH(C*H*$_3$)$_2$), 2.05 (s, 3H, C*H*$_3$), 2.69 (m, C*H*(CH$_3$)$_2$), 4.30 (m, 4H, PC*H*$_2$N and 2H, PC*H*$_2$-N$^+$), 4.35 (s, 2H, N$^+$C*H*$_2$Ph), 4.60 (m, 2H NC*H*$_2$N), 5.12 (m, 4H, NC*H*$_2$-N$^+$), 5.87 (m, 4H CH$_{Ph}$ of *p*-cymene), 7.30–8.54 (m, aromatic).

^{31}P{^{1}H} NMR (145 MHz, in MeOD, 25 °C) δ = −18.6 (s).

Spectral parameters for [(η^6-$C_{10}H_{14}$)$RuCl_2$(*m*tppms)]$^-$: ^{1}H NMR (360 MHz, MeOD, 25 °C): δ/ppm 1.13 (d, J = 7 Hz, 6H, CH(C*H*$_3$)$_2$), 1.94 (s, 3 H, C*H*$_3$), 2.69 (m, 2H, C*H*(CH$_3$)$_2$), 5.33 (d, J = 6.0 Hz, 4H, CH$_{Ph}$ of *p*-cymene), 7.30–8.54 (m, aromatic).

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

2.4. X-ray crystallographic studies

A summary of crystallographic data for (**2**)(**1**), (**4**)(**1**), (**5**)(**1**) and **6**·2H_2O are collected in Table 1. Crystals of (**2**)(**1**), (**4**)(**1**), and (**5**)(**1**)

Table 1
Crystallographic data and structure refinement results for (pta-Bn)(*m*tppms), (**2**)(**1**); (pta-hexyl)(*m*tppms), (**4**)(**1**); (pta-butyl)(*m*tppms), (**5**)(**1**) and [(η^6-$C_{10}H_{14}$)$RuCl_2$(pta-Bn)]Cl·2 H_2O, **6**·2 H_2O.

Structure	(**2**)(**1**)	(**4**)(**1**)	(**5**)(**1**)	**6**
Formula	$C_{31}H_{33}N_3O_3P_2S$	$C_{28}H_{35}N_3O_3P_2S$	$C_{30}H_{39}N_3O_3P_2S$	$C_{23}H_{37}Cl_3N_3O_2PRu$
Formula weight	589.6	555.59	583.64	625.95
Crystal system	monoclinic	triclinic	triclinic	monoclinic
Space group	*P*21/*n* (No. 14)	*P*$\bar{1}$ (No. 2)	*P*$\bar{1}$ (No. 2)	*P*21/*c* (No. 14)
a (Å)	11.1885(10)	8.827(1)	8.812(11)	10.6944(10)
b (Å)	8.9866(10)	10.891(1)	10.865(5)	10.0645(10)
c (Å)	29.5232(10)	15.466(1)	16.399(5)	25.5048810)
α (°)	90	74.97(1)	100.82(2)	90
β (°)	97.71(1)	84.12(1)	100.20(4)	97.66(1)
γ (°)	90	85.28(1)	93.44(7)	90
V (Å^3)	2941.7(4)	1426.0(2)	1511(2)	2720.7(4)
Z	4	2	2	4
D_{calc} (g cm^{-3})	1.331	1.294	1.283	1.528
F(000)	1240	588	620	1288
μ (mm^{-1})	0.26	0.26	0.25	0.96
T (K)	293	293	293	293
Reflections collected	5396	5737	6135	5355
Unique reflections with $I > 2\sigma(I)$	3938	2186	2660	2253
Parameters refined	361	335	355	313
Goodness-of-fit (GOF) on F^2	1.05	0.96	1.49	1.00
$R[F^2 > 2\sigma(F^2)]$	0.076	0.088	0.157	0.086
R_{int}	0.019	0.026	0.05	0.027
$wR(F^2)$	0.247	0.231	0.211	0.245
$\delta\rho_{max}$, $\delta\rho_{min}$ (e Å^{-3})	0.63, −0.81	0.38, −0.31	0.37, −0.37	0.95, −0.74

were obtained by slow evaporation of MeOH from methanolic solutions of the corresponding salts. A suitable crystal of **6** was prepared by layering its CH_2Cl_2 solution with Et_2O. X-ray quality crystals of (**2**)Cl were obtained both from aqueous and methanolic solutions by slow evaporation of solvents (a summary of crystallographic data for (**2**)Cl·H_2O, (**2**)Cl·MeOH are collected in the Supplementary Table S1).

Data were collected using Enraf Nonius MACH3 diffractometer for (**2**)(**1**), (**4**)(**1**), (**5**)(**1**) and **6**·2H_2O, Bruker GADDS diffractometer for **(2)**Cl.H_2O and Bruker SMART diffractometer for **(2)**Cl.MeOH using Mo Kα radiation (λ = 0.71073 Å) or Cu Kα radiation (λ = 1.541847 Å) in case of **(2)**Cl.H_2O. Crystals of (**2)**Cl·H_2O and (**4**)(**1**) had very low quality. The structures were routinely solved using the SIR-92 software [32a] and refined on F^2 using SHELX-97 program [32b], publication material was prepared with the WINGX-97 suite [32c]. Hydrogen atoms were placed into geometric positions except O–H protons which could be found at the difference electron density map and the oxygen-hydrogen distances as well as 1,3 H distances were constrained. The hexyl side chain in (pta-hexyl)(*m*tppms) structure shows high anisotropic motion because of positional disorder. The occupancy of the other position was approximately 6% so according to literature recommandation [33] the carbon atoms have been refined in a single position. Additional crystallographic information is provided in the deposited CIF file and in Supplementary material.

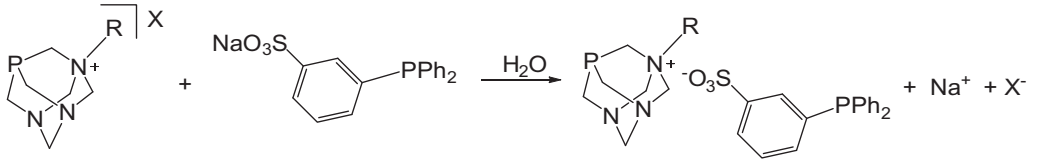
3. Results and discussion

3.1. Synthesis and crystallographic analysis of (pta-R)(mtppms) 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 [25]. 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*tppms) to an aqueous solution of (**2**)Cl a white precipitate separated (Scheme 2).

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).

The most important structural parameters of (**2**)(**1**) are shown in the legend to Fig. 1, whereas structures of (**2**)Cl·H_2O and (**2**)Cl·MeOH are presented in the Supplementary as Figs. S1 and 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 [34] search (Cambridge Structural Database Ver. 5.33 May, 2012) 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



R = $CH_2C_6H_5$ (**2**); X = Cl
=C_6H_{11} (**4**); X = Br
= C_4H_9 (**5**); X = Br

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

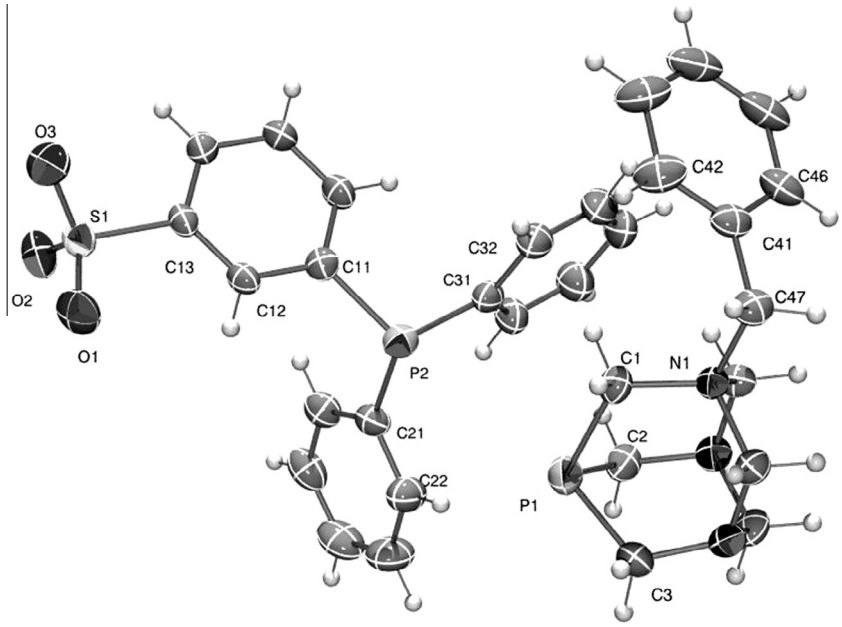


Fig. 1. ORTEP view of compound (**2**)(**1**) at 50% probability level with partial numbering scheme. Selected bond lengths (Å), angles (°) and torsion angles (°) with estimated standard deviations: P1–C1: 1.844(5); P1–C2: 1.836(5); P1–C3: 1.852(5); P2–C11: 1.846(4); P2–C21: 1.838(5); P2–C31: 1.835(5); 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).

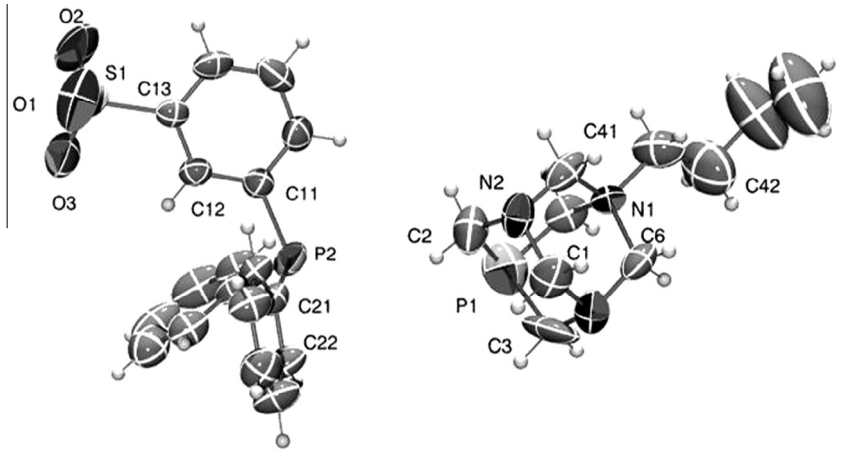


Fig. 2. ORTEP view of compound (**4**)(**1**) at 50% probability level with partial numbering scheme. Selected bond lengths (Å), angles (°) and torsion angles (°) with estimated standard deviations: P1–C1: 1.761(7); P1–C2: 1.807(7); P1–C3: 1.807(9); P2–C11: 1.827(6); P2–C21: 1.819(6); P2–C31: 1.830(7);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

and found in the supramolecular architecture of the studied ion pairs.

For further studies on (pta-R)(*m*tppms) salts we have prepared several (pta-R)X derivatives, among them the known ones with R = $\{CH_2\}_n$-CH_3, 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 *m*tppms in aqueous solutions led to the formation of precipitates in the case of pta-hexyl (**4**) and pta-butyl (**5**). 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 (Figs. 2 and 3).

Cations obtained by N-alkylation of pta with shorter chain alkyl halides or triflates did not yield precipitates with *m*tppms. It is noteworthy that with trisulfonated triphenylphosphine (*m*tppts) none of the alkyl-pta cations gave water-insoluble products.

Monosulfonated triphenylphosphine was prepared already in 1958 [35], however, due to the poor crystallization properties of Na(*m*tppms) X-ray structure determinations of the *m*tppms anion were made on benzyltriethylammonium [36], guanidinium [37], imidazolium [38], and potassium [39] salts. In contrast, (**2**)(**1**), (**4**)(**1**) and (**5**)(**1**) are the first structurally characterized *m*tppms salts containing water-soluble phosphines both as cation and anion.

Secondary interactions can be tuned to prepare bidentate phosphorous ligands by fixing phosphorus atoms in appropriate positions for coordination to the same metal center. Note that even a small difference in the lattice interactions such as changing a side chain (butyl to hexyl) causes significant changes in conformation and P–P distances (see Fig. S4), hence in the coordination properties of the mixed tertiary phosphorous ligand.

Though salts (**2**)(**1**), (**4**)(**1**) and (**5**)(**1**) were found insoluble in water they dissolve well in chlorinated solvents or alcohols. The

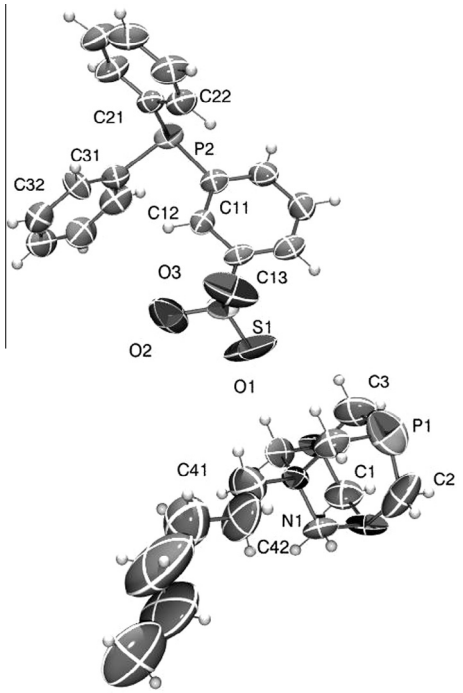


Fig. 3. ORTEP view of compound (**5**)(**1**) at 50% probability level with partial numbering scheme. Selected bond lengths (Å), angles (°) and torsion angles (°) with estimated standard deviations: P1–C1: 1.730(9); P1–C2: 1.761(13); P1–C3: 1.793(10); P2–C11: 1.827(7); P2–C21: 1.815(8); P2–C31: 1.828(8);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

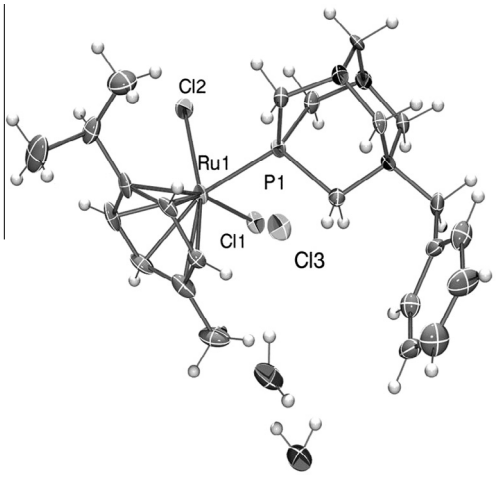


Fig. 4. ORTEP view of $[(\eta^6\text{-}C_{10}H_{14})RuCl_2(pta\text{-}Bn)]Cl{\cdot}2\ H_2O$ with partial numbering scheme. Selected bond lengths (Å) and angles (°) with estimated standard deviations: P1–C1: 1.886(13); P1–C2: 1.813(14); P1–C3: 1.822(11); P1–Ru1: 2.295(3); Cl1–Ru1: 2.418(4); Cl2–Ru1: 2.406(4); P1–Ru1–Cl1: 83.3(1); P1–Ru1–Cl2: 83.9(1); Cl1–Ru1–Cl2: 88.4(1)°.

^{31}P NMR spectra of these solutions display only singlets of cation, pta-R (R = Bn: $\delta = -84.0$ ppm and R = butyl or hexyl: $\delta = -82.9$ ppm) and anion, *m*tppms ($\delta = -4.4$ ppm) with equal intensity (Figs. S5–7).

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

3.2.1. Synthesis of $[(\eta^6\text{-}C_{10}H_{14})RuCl(pta\text{-}Bn)(mtppms)]Cl$

To our knowledge there are only two half sandwich Ru-complexes known which contain both anionic (*m*tppms) and cationic (pta-Me) phosphine ligands. Both $[CpRu(pta\text{-}Me)(mtppms)_2]$ and $[CpRu(pta\text{-}Me)(PPh_3)(mtppms)]^+$ were obtained in two-step procedures by stepwise replacement of PPh_3 in $[CpRuCl(PPh_3)_2]$ with pta-Me and *m*tppms [16].

Similarly, $[(\eta^6\text{-}C_{10}H_{14})RuCl(pta\text{-}Bn)(mtppms)]Cl$ was synthesized by stepwise complex formation. First, $[(\eta^6\text{-}C_{10}H_{14})RuCl_2(pta\text{-}Bn)]Cl$, **6** was prepared in reaction of (pta-Bn)Cl with $[(\eta^6\text{-}C_{10}H_{14})RuCl_2]_2$. The resulting complex has already been described in the literature [14], 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.

Search of CSD (Version 5.33 May, 2012) gave 268 hits for aryl-$RuCl_2P$ 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 completely agrees with these data.

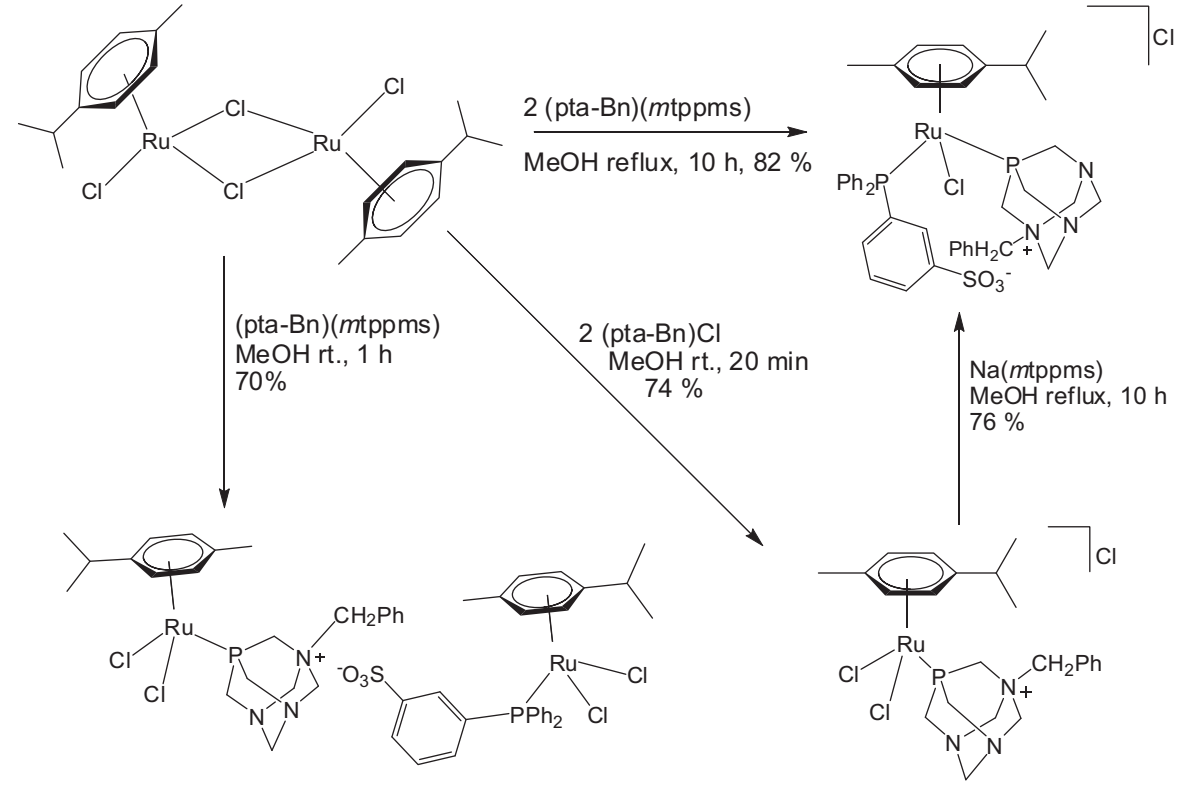
In water, reaction of $[(\eta^6\text{-}C_{10}H_{14})RuCl_2(pta\text{-}Bn)]Cl$ and Na(*m*tppms) immediately gives a white precipitate what can be formulated as $[(\eta^6\text{-}C_{10}H_{14})RuCl_2(pta\text{-}Bn)](mtppms)$ according to its ^{31}P NMR spectrum (Fig. S8). This precipitate could be transformed to $[\eta^6\text{-}C_{10}H_{14})RuCl(pta\text{-}Bn)(mtppms)]Cl$ via reflux in methanol. Nevertheless, synthesis of the latter complex was more cleanly performed directly from $[(\eta^6\text{-}C_{10}H_{14})RuCl_2(pta\text{-}Bn)]Cl$ and Na(*m*tppms) in methanol at reflux temperature when no intermediate precipitate formed. In the ^{31}P NMR spectrum the singlets characteristic for *m*tppms ($\delta = -4.4$ ppm) and for **6** ($\delta = -18.6$ ppm) were gradually replaced by two doublets of the same intensity at $\delta = 27.6$ ppm (d, $J_{pp} = 46$ Hz) and at $\delta = -24.7$ ppm (d, $J_{pp} = 53$ Hz). After 10 h reflux these latter were the only signals in the spectrum, characteristic for $[\eta^6\text{-}C_{10}H_{14})RuCl(pta\text{-}Bn)(mtppms)]Cl$.

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

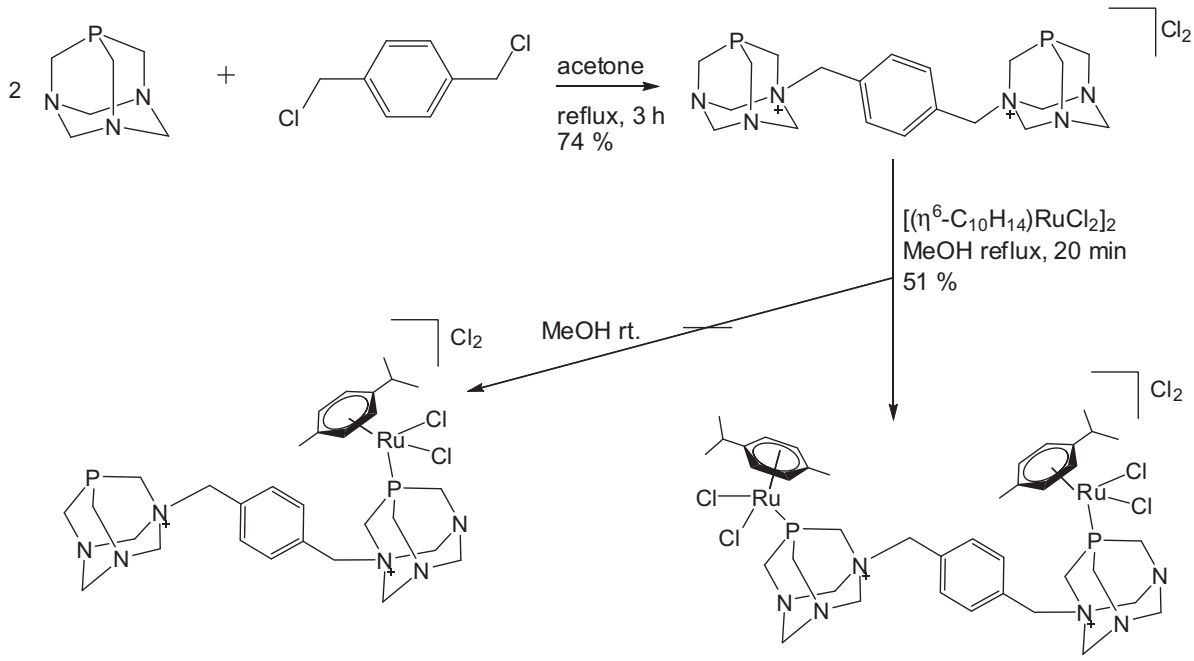
The desired mixed-phosphine complex could also be prepared in a one-step procedure. In this case, a methanolic solution of $[(\eta^6\text{-}C_{10}H_{14})RuCl_2]_2$ was added to a solution of (pta-Bn)(*m*tppms) in MeOH to obtain a reaction mixture with $[Ru^{2+}] = [\mathbf{2}] = [\mathbf{1}]$. Two strong doublet signals of $[\eta^6\text{-}C_{10}H_{14})RuCl(pta\text{-}Bn)(mtppms)]Cl$ was observed already after 2 h 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 $[(\eta^6\text{-}C_{10}H_{14})RuCl_2(mtppms)]^-$ ($\delta = 26.1$ ppm) were still seen. In 4 h the signals of the free phosphines disappeared, however, only 10 h reflux produced solutions with clean ^{31}P NMR spectrum of $[(\eta^6\text{-}C_{10}H_{14})RuCl(pta\text{-}Bn)(mtppms)]Cl$ (Fig. S10). During the reaction the color of the solution gradually changed from orange to lemon yellow. The product was isolated as yellow powder and analyzed 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)(mtppms) as bridging ligand

In contrast to the above synthesis of the mononuclear $[(\eta^6\text{-}C_{10}H_{14})RuCl(pta\text{-}Bn)(mtppms)]Cl$, when equimolar amounts of $[(\eta^6\text{-}C_{10}H_{14})RuCl_2]_2$ and (pta-Bn)(Na-*m*tppms), (**2**)(**1**) were reacted in MeOH (concentration ratio $[Ru^{2+}]$:[**2**]:[**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 $[(\eta^6\text{-}C_{10}H_{14})RuCl_2(pta\text{-}Bn)]^+$ ($\delta = -18.6$ ppm) and $[(\eta^6\text{-}C_{10}H_{14})RuCl_2(mtppms)]^-$ ($\delta = 26.1$ ppm) with equal intensity (Fig. S11). After



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



Scheme 4. Synthesis of $[\{(\eta^6\text{-}C_{10}H_{14})RuCl_2\}_2(\mu\text{-}\mathbf{3})]Cl_2$ containing a bisphosphine (**3**) obtained from pta and 1,4-bis(chloromethyl)benzene.

2 h reaction time only these two signals could be observed, and no 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 $[(\eta^6\text{-}C_{10}H_{14})RuCl_2(pta\text{-}Bn)][(\eta^6\text{-}C_{10}H_{14})RuCl_2(\text{-}m\text{tppms})]$. Containing a big monovalent cation and a big monovalent anion, the compound has poor solubility in water, however, it dissolves well in alcohols, benzene and in chlorinated solvents. Ionic interaction between $(pta\text{-}Bn)^+$ and $(m\text{tppms})^-$, 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 $[(\eta^6\text{-}C_{10}H_{14})RuCl_2]_2$ were added to methanolic solutions of (**4**)(**1**) or (**5**)(**1**). After $\geqslant$2 h reaction time, the ^{31}P NMR spectra of the solu-

tions displayed only the singlet characteristic for $[(\eta^6\text{-}C_{10}H_{14})RuCl_2(m\text{tppms})]^-$ ($\delta = 26.0$ ppm) and another singlet of equal intensity at $\delta = -20.4$ ppm; the latter refers to the presence of $[(\eta^6\text{-}C_{10}H_{14})RuCl_2(\text{pta-R})]^+$ ions (R = butyl, hexyl) (Figs. S12–13).

The $[(\eta^6\text{-}C_{10}H_{14})RuCl_2(Ph_2PCH_2NHC_6H_4COOH)]$ complex [3] mentioned in the Introduction was found to dimerize through intermolecular H-bonds between the carboxylic acid groups. Therefore the dimer necessarily consisted of two monomeric half-sandwich Ru-complexes having the same phosphine substitutents and consequently had 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-type 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**)Br_2 [26].

Upon refluxing equimolar amounts of (**3**)Cl_2 and $[(\eta^6\text{-}C_{10}H_{14})RuCl_2]_2$ 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 $[C_{40}H_{60}N_6P_2Cl_4Ru_2]^{2+} = M^{2+}$), showing the presence of $[\{(\eta^6\text{-}C_{10}H_{14})RuCl_2\}_2(\mu\text{-}\mathbf{3})]^{2+}$ (Fig. S15). This finding is in accordance with data of elemental analysis what shows the formation of a dinuclear $[\{(\eta^6\text{-}C_{10}H_{14})RuCl_2\}_2(\mu\text{-}\mathbf{3})]Cl_2$ 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 in those cases, too, when higher than equimolar amounts of the bisphosphine was used. Note, that in contrast to reactions of (**3**)Br_2 with *cis*-$[PtBr_2(cod)]$ where no pure dinuclear complexes could be obtained [26], interaction of (**3**)Cl_2 and $[(\eta^6\text{-}C_{10}H_{14})RuCl_2]_2$ afforded cleanly the desired dinuclear complex having **3** as bridging ligand.

4. Conclusion

Until 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 interactions between monosulfonated triphenylphosphine anion (*m*tppms) and various cationic alkyl and benzyl derivatives of 1,3,5-triaza-7-phosphaadamantane (pta-R; R = benzyl, butyl, hexyl) are also strong enough to make the ion pairs suitable to act as bidentate phosphorus ligands. The ion pairs, (pta-R)(*m*tppms) were crystallized and their solid state structures determined by X-ray diffraction for the first time. Interestingly, the (pta-Bn)(*m*tppms) ion pair is able to coordinate to the same Ru(II) in $[(\eta^6\text{-}C_{10}H_{14})RuCl(\text{pta-Bn})(m\text{tppms})]Cl$ while all the (pta-R)(*m*tppms) ion pairs can act as bridging ligands between two $[(\eta^6\text{-}C_{10}H_{14})RuCl_2]$ 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 demonstrate that an efficient modular approach for synthesis of complexes containing two different phosphine ligands can be based on use of such ion pairs.

Acknowledgements

The authors are indebted for the support of the Hungarian Science Fund (OTKA K101372). The research was supported by the EU and co-financed by the European Social Fund under the projects ENVIKUT (TÁMOP-4.2.2.A-11/1/KONV-2012-0043) and TÁMOP-4.2.2/B-10/1/KONV-2010-0024.

Thanks are due to Dr. Attila Kiss-Szikszay for the elementary analyzes and to Dr. Lajos Nagy for the ESI-MS measurements. The assistance of Ms. Evelin Nagy in some experiments is gratefully acknowledged.

Appendix A. Supplementary data

CCDC 929756–929761 contains the supplementary crystallographic data for (pta-Bn)Cl·H_2O, (**2**)Cl·H_2O; (pta-Bn)Cl·MeOH, (**2**)Cl·MeOH; (pta-Bn)(*m*tppms), (**2**)(**1**); (pta-hexyl)(*m*tppms), (**4**)(**1**); (pta-butyl)(*m*tppms), (**5**)(**1**) and $[(\eta^6\text{-}C_{10}H_{14})RuCl_2(\text{pta-Bn})]Cl\cdot 2\ H_2O$, **6**·2 H_2O. 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 http://dx.doi.org/10.1016/j.poly.2013.05.008.

References

[1] (a) M.J. Wilkinson, P.W.N.M. van Leeuwen, J.N.H. Reek, Org. Biomol. Chem. 3 (2005) 2371;
(b) B. Breit, Angew. Chem., Int. Ed. 44 (2005) 6816;
(c) A.J. Sandee, J.N.H. Reek, Dalton Trans. (2006) 3385;
(d) B. Breit, Pure Appl. Chem. 80 (2008) 855;
(e) J. Wieland, B. Breit, Nat. Chem. 2 (2010) 832;
(f) P.W.N.M. van Leeuwen, D. Rivillo, M. Raynal, Z. Freixa, J. Am. Chem. Soc. 133 (2011) 18562;
(g) K. Ohmatsu, M. Ito, T. Kunieda, T. Ooi, Nat. Chem. 4 (2012) 473.
[2] A. Bacchi, G. Cantoni, M. Granelli, S. Mazza, P. Pelagatti, G. Rispoli, Cryst. Growth Des. 11 (2011) 5039.
[3] S.E. Dann, S.E. Durran, M.R.J. Elsegood, M.B. Smith, P.M. Staniland, S. Talib, S.H. Dale, J. Organomet. Chem. 691 (2006) 4829.
[4] B. Breit, W. Seiche, J. Am. Chem. Soc. 125 (2003) 6608.
[5] H. Gulyás, J. Benet-Buchholz, E.C. Escudero-Adan, Z. Freixa, P.W.N.M. van Leeuwen, Chem. A: Eur. J. 13 (2007) 3424.
[6] Á. Kathó, A. Udvardy, P. Juhász, 16th Int. Symp. Hom. Catal., Florence, Italy, 2008 Book of Abstracts, P296.
[7] (a) F. Joó, M.T. Beck, React. Kinet. Catal. Lett. 2 (1975) 257;
(b) F. Joó, Aqueous Organometallic Catalysis (Catalysis by Metal Complexes) Kluwer, Academic Publishers, Dordrecht, The Netherlands, 2001.
[8] (a) A.D. Phillips, L. Gonsalvi, A. Romerosa, F. Vizza, M. Peruzzini, Coord. Chem. Rev. 248 (2004) 955;
(b) J. Bravo, S. Bolano, L. Gonsalvi, M. Peruzzini, Coord. Chem. Rev. 254 (2010) 555.
[9] (a) D.J. Darensbourg, F. Joó, M. Kannisto, Á. Kathó, J.H. Reibenspies, Organometallics 11 (1992) 1990;
(b) D.J. Darensbourg, F. Joó, M. Kannisto, Á. Kathó, J.H. Reibenspies, D.J. Daigle, Inorg. Chem. 33 (1994) 200.
[10] G. Laurenczy, F. Joó, L. Nádasdi, Inorg. Chem. 39 (2000) 5083.
[11] W.-C. Lee, B.J. Frost, Green Chem. 14 (2012) 62.
[12] P.J. Dyson, D.J. Ellis, G. Laurenczy, Adv. Synth. Catal. 345 (2003) 211.
[13] H. Horváth, G. Laurenczy, Á. Kathó, J. Organomet. Chem. 689 (2004) 1036.
[14] V. Cadierno, J. Francos, J. Gimeno, Chem. Eur. J. 14 (2008) 6601.
[15] W.H. Ang, A. Casini, G. Sava, P.J. Dyson, J. Organomet. Chem. 696 (2011) 989.
[16] (a) B. González, P. Lorenzo-Luis, P. Gili, A. Romerosa, M. Serrano-Ruiz, J. Organomet. Chem. 694 (2009) 2029;
(b) A. Romerosa, M. Saoud, T. Campos-Malpartida, C. Lidrissi, M. Serrano-Ruiz, M. Peruzzini, J.A. Garrido, F. García-Maroto, Eur. J. Inorg. Chem. 2007 (2007) 2803.
[17] (a) D.J. Daigle, A.B. Pepperman Jr., J. Vail, J. Heterocycl. Chem. 11 (1974) 407;
(b) D.J. Daigle, A.B. Pepperman, J. Heterocycl. Chem. 12 (1975) 579.
[18] J.M. Forward, R.J. Staples, C.W. Liu, J.P. Fackler Jr., Acta Crystallogr., Sect. C 53 (1997) 195.

[19] F.P. Pruchnik, P. Smolenski, Appl. Organomet. Chem. 13 (1999) 829.
[20] A.M. Kirillov, P. Smolenski, M. Haukka, M.F.C. Guedes da Silva, A.J.L. Pombeiro, Organometallics 28 (2009) 1683.
[21] J.M. Forward, R.J. Staples, J.P. Fackler Jr., Z. Kristallogr. 211 (1996) 129.
[22] D.A. Krogstad, G.S. Ellis, A.K. Gunderson, A.J. Hammrich, J.W. Rudolf, J.A. Halfen, Polyhedron 26 (2007) 4093.
[23] S. Schafer, W. Frey, A.S.K. Hashmi, V. Cmrecki, A. Luquin, M. Laguna, Polyhedron 29 (2010) 1925.
[24] E. García-Moreno, E. Cerrada, M.J. Bolsa, A. Luquin, M. Laguna, Eur. J. Inorg. Chem. 2013 (2013) 2020.
[25] (a) K.J. Fisher, E.C. Alyea, N. Shahnazarian, Phosphorus Sulfur 48 (1990) 37; (b) F.-X. Legrand, F. Hapiot, S. Tilloy, A. Guerriero, M. Peruzzini, L. Gonsalvi, E. Monflier, Appl. Catal. A: Gen. 362 (2009) 62.
[26] D.A. Krogstad, K.E. Gohmann, T.L. Sunderland, A.L. Geis, P. Bergamini, L. Marvelli, V.G. Young Jr., Inorg. Chim. Acta 362 (2009) 3049.
[27] F. Joó, J. Kovács, Á. Kathó, A.C.s. Bényei, T. Decuir, D.J. Darensbourg, Inorg. Synth. 32 (1998) 1.
[28] W.A. Herrmann, C.W. Kohlpaintner, Inorg. Synth. 32 (1998) 8.
[29] D.J. Daigle, Inorg. Synth. 32 (1998) 40.
[30] M.A. Benett, J. Chem. Soc., Dalton Trans. (1974) 233.
[31] J. Díez, M.P. Gamasa, E. Lastra, A. García-Fernández, M.P. Tarazone, Eur. J. Inorg. Chem. 2006 (2006) 2855.
[32] (a) A. Altomare, G. Cascarano, C. Giacovazzo, A. Guagliardi, J. Appl. Crystallogr. 26 (1993) 343; (b) G.M. Sheldrick, Acta Crystallogr., Sect. A 64 (2008) 112; (c) L.J.J. Farrugia, Appl. Crystallogr. 32 (1999) 837.
[33] Peter Müller (Ed.), Crystal Structure Refinement. A Crystallographer's Guide to SHELX, Oxford University Press, 2006, p. 61.
[34] F.R. Allen, Acta Crystallogr., Sect. B 58 (2002) 380.
[35] S. Ahrland, J. Chatt, N.R. Davies, A.A. Williams, J. Chem. Soc. (1958) 276.
[36] P.J. Roman, D.P. Paterniti Jr., R.F. See, M.R. Churchill, J.D. Atwood, Organometallics 16 (1997) 1484.
[37] (a) Á. Kathó, A. Cs. Bényei, F. Joó, M. Sági, Adv. Synth. Catal. 344 (2002) 278.; (b) A.D. Burrows, R.W. Harrington, M.F. Mahon, S.J. Teat, Eur. J. Inorg. Chem. 2003 (2003) 1433.
[38] P.B. Webb, M.F. Sellin, T.E. Kunene, S. Williamson, A.M.Z. Slawin, D.J. Cole-Hamilton, J. Am. Chem. Soc. 125 (2003) 15577.
[39] W. Karschin, W. Klaui, B. Peters, Eur. J. Inorg. Chem. 2010 (2010) 942.