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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 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 $[\{(\eta^6\text{-}C_{10}H_{14})\text{-}RuCl_2\}_2(\mu\text{-}\mathbf{3})]Cl_2$.

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].

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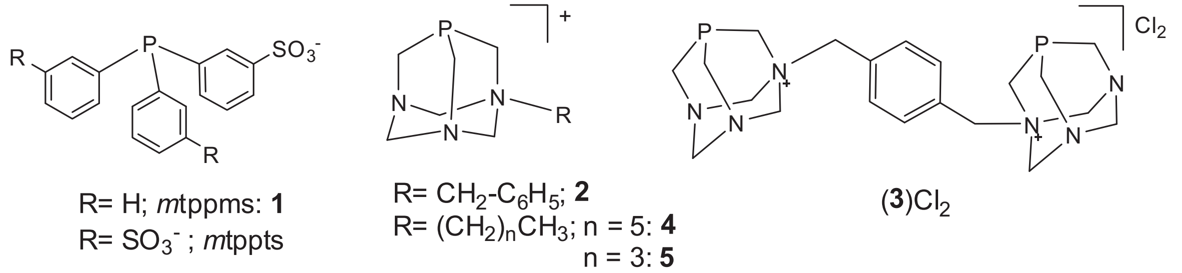

Scheme 1. Water-soluble phosphines used in this study.

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$_2$)$_4$I [21]) as well as with various bromomethyl compounds (BrCH$_2$Y, where Y = C$_6$H$_4$N [22], C$_6$H$_5$, 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 (**3**)Cl$_2$ and [(η^6-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. ^{1}H, ^{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$_3$SO$_3$ [16], (pta-R)Br (R = Et, *n*Pr, *n*Bu [20]), (pta-Bn)Cl [25], [(η^6-C$_{10}$H$_{14}$)RuCl$_2$]$_2$ [30], Na[(η^6-C$_{10}$H$_{14}$)RuCl$_2$(*m*tppms)] [31] and [(η^6-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$_2$Cl$_2$N$_6$C$_{20}$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$_2$O): observed *m*/*z* 209.107, calcd. 209.100 for P$_2$N$_6$C$_{20}$H$_{32}$ = M^{2+}. ^{1}H NMR (360 MHz, D$_2$O, 25 °C): δ/ppm 3.85 (m, 8H, PC*H*$_2$N), 4.20 (s, 4H, PC*H*$_2$N$^+$), 4.54 (m, 8H, PC*H*$_2$N$^+$, NC*H*$_2$N), 4.98 (m, 8H, NC*H*$_2$N$^+$), 7.64 (s, 4H, H$_{Ph}$). ^{13}C{^{1}H} NMR (90 MHz, D$_2$O, 25 °C): δ/ppm 45.56 (d, $^{1}J_{PC}$ = 22 Hz, *P*CH$_2$N), 52.89 (d, $^{1}J_{PC}$ = 33 Hz, P*C*H$_2$N$^+$), 65.83 (s, Ph*C*H$_2$N$^+$), 69.38 (s, N*C*H$_2$N), 78.90 (s, N*C*H$_2$N$^+$), 127.38 (s, *C*H$_{Ph}$), 133.68 (s, *C*$_{Ph}$). ^{31}P{^{1}H} NMR (145 MHz, D$_2$O, 25 °C): δ = −82.03 ppm (s). ^{31}P{^{1}H} 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$_2$O (3 × 5 mL) and dried. Yield 202 mg (60%). *Anal.* Calc. for C$_{12}$H$_{24}$N$_3$PBr (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$_3$C$_{12}$H$_{25}$ = M$^+$. ^{1}H NMR (360 MHz, MeOD, 25 °C): δ/ppm 0.93 (t, 3H, $^{1}J_{HH}$ = 7 Hz, C*H*$_3$), 1.01–1.30 (m, 6H, N$^+$–CH$_2$CH$_2$C*H*$_2$C*H*$_2$C*H*$_2$CH$_3$), 1.65–1.74 (m, 2H, N$^+$–CH$_2$C*H*$_2$), 2.84 (m, 2H, N$^+$–C*H*$_2$CH$_2$), 3.76–4.04 (m, 4H, PC*H*$_2$N), 4.32 (d, 2H, J_{PH} = 6 Hz, PC*H*$_2$N$^+$), 4.37–4.64 (m, 2H, NC*H*$_2$N), 4.71-5.09 (m, 4H, N$^+$C*H*$_2$N). ^{13}C{^{1}H} NMR (90 MHz, MeOD, 25 °C): δ/*ppm* 13.00 (s, *C*H$_3$), 19.31 (s, *C*H$_2$CH$_3$), 19.34 (s, *C*H$_2$CH$_2$CH$_3$), 21.30 (s, N$^+$–CH$_2$CH$_2$*C*H$_3$), 24.60 (s, N$^+$–CH$_2$*C*H$_2$), 45.77 (d, J_{PC} = 22 - Hz, PCH$_2$N), 53.11 (d, J_{PC} = 33 Hz, PCH$_2$N$^+$), 62.99 (s, N$^+$*C*H$_2$CH$_2$), 70.01 (s, N*C*H$_2$N), 78.12 (s, N$^+$*C*H$_2$N). ^{31}P{^{1}H} NMR (145 MHz, D$_2$O, 25 °C): δ = −83.7 ppm (s).