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Reactions of $[Ru(H_2O)_6]^{2+}$ with water-soluble tertiary phosphines†

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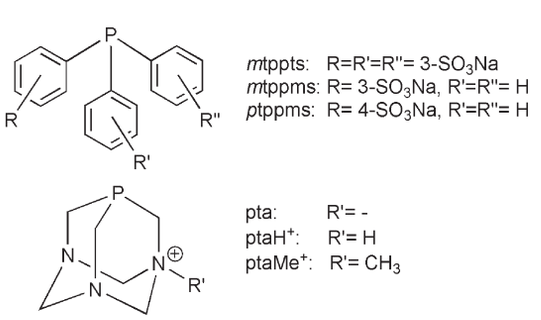
In aqueous solutions under mild conditions, $[Ru(H_2O)_6]^{2+}$ was reacted with various water-soluble tertiary phosphines. As determined by multinuclear NMR spectroscopy, reactions with the sulfonated arylphosphines L = *m*tppms, *p*tppms and *m*tppts yielded only the mono- and bisphosphine complexes, $[Ru(H_2O)_5L]^{2+}$, *cis*-$[Ru(H_2O)_4L_2]^{2+}$, and *trans*-$[Ru(H_2O)_4L_2]^{2+}$ even in a high ligand excess. With the small aliphatic phosphine L = 1,3,5-triaza-7-phosphatricyclo-[3.3.1.1^{3,7}]decane (pta) at [L] : [Ru] = 12 : 1, the tris- and tetrakisphosphino species, $[Ru(H_2O)_3(pta)_3]^{2+}$, $[Ru(H_2O)_2(pta)_4]^{2+}$, $[Ru(H_2O)(OH)(pta)_4]^{+}$, and $[Ru(OH)_2(pta)_4]$ were also detected, albeit in minor quantities. These results have significance for the *in situ* preparation of Ru(II)-tertiary phosphine catalysts. The structures of the complexes *trans*-$[Ru(H_2O)_4(ptaMe)_2](tos)_4\cdot 2H_2O$, *trans*-$[Ru(H_2O)_4(ptaH)_2](tos)_4\cdot 2H_2O$, and *trans-mer*-$[RuI_2(H_2O)(ptaMe)_3]I_3\cdot 2H_2O$, containing protonated or methylated pta ligands (ptaH and ptaMe, respectively) were determined by single crystal X-ray diffraction.

Introduction

Liquid–liquid biphasic catalysis allows the separation of the catalyst-containing phase and the product-containing phase by simple decantation. The mild conditions of catalyst recovery mostly eliminate the degradation of the soluble catalyst that is often observed during the evaporation of the liquid constituents of the reaction mixture.[1–5] The efficiency of such a technology is convincingly shown by the Ruhrchemie-Rhône Poulenc process of propene hydroformylation applying a water-soluble Rh-based catalyst.[5–7] In this process, the catalyst is pre-formed from suitable precursors (hydrated rhodium(III) acetate and *m*tppts under synthesis gas pressure, (*m*tppts = 3,3′,3″-phosphinetriylbenzene-sulfonic acid, *meta*-trisulfonated triphenylphosphine) and used without isolation. *In situ* formation of the catalyst can provide a convenient and efficient use of the precious metal and the ligands. However, the reactions may lead to a mixture of several metal complexes and the study of the reactions both from equilibrium and kinetic aspects is clearly needed. Aqua complexes are particularly suited to serve as catalyst precursors in aqueous organometallic catalysis,[8–10] since the coordinated water molecules can be easily replaced by other ligands (*e.g.* phosphines) and halide-free catalysts can also be obtained. $[Ru(H_2O)_6]^{2+}$ can be isolated as a *p*-toluenesulfonate (tosylate) salt;[11] an X-ray structure determination showed the complex cation to be octahedral.[12] Its aqueous solutions are sensitive to oxygen and the complex is hydrolysed above pH 6. $[Ru(H_2O)_6]^{2+}$ has already been used as catalyst in the isomerization of hexene-1[13] and in the dimerization of ethene,[14] moreover, it served as a catalyst precursor in the hydrogenation of aldehydes[15] and hydrodehalogenation of organic halides.[16] In the latter two cases water-soluble tertiary phosphines such as *m*tppts, *m*tppms ((3-diphenylphosphino)-benzensulfonic acid, *meta*-monosulfonated triphenylphosphine) and 1,3,5-triaza-7-phosphatricyclo-[3.3.1.1^{3,7}]decane (1,3,5-triaza-7-phosphaadamantane, pta) have been used as ligands (Scheme 1) in the *in situ* formed catalyst. It is of interest that both $[Ru(H_2O)_5(N_2)]^{2+}$ and $[Ru(H_2O)_5(H_2)]^{2+}$ were obtained[17,18] under relatively mild conditions (room temperature and 50 bar (N_2) or 40 bar (H_2) pressure). Other catalytically important ligands in $[Ru(H_2O)_5L]$ complexes also included L = CO[19] and C_2H_4.[14,20] Stunningly, only a few phosphines are found among the ligands hitherto studied in substitution reactions with $[Ru(H_2O)_6]^{2+}$, despite the critically important role some water-soluble tertiary phosphines had played during the development of coordination chemistry[21] and aqueous organometallic catalysis.[5,22] One recent study[23] describes the synthesis of a Ru(II)-complex containing both aqua and phosphine ligands $[RuI_2(H_2O)(ptaMe)_3]I_3\cdot 2H_2O$ (together with the preparation of $[RuI_4(ptaMe)_2]$ and $[RuI_4(ptaMe)_2]\cdot 2H_2O$; $ptaMe^+$ = 3,5-diaza-1-azonia-7-phosphatricyclo[3.3.1.1^{3,7}]decane cation, *N*-methylated pta, Scheme 1), however the source of Ru in that case was $RuCl_3\cdot 3H_2O$. Furthermore, $[Ru(H_2O)_6](tos)_2$ was used as starting material for the preparation of several *water-insoluble* Ru(II)-tertiary phosphine complexes such as $[Ru(H_2O)_2(PPh_3)_2(tos)_2]$ (tos = *p*-toluenesulfonate anion) and $[Ru(dppe)_2(tos)_2]$[24] (as well as for the synthesis of complexes with *N*-heterocyclic nitrogen donor ligands[25]). However, no equilibrium or kinetic studies have been carried out in *aqueous* solutions. Therefore we investigated the reaction of $[Ru(H_2O)_6]^{2+}$ with *m*tppts, *m*tppms, *p*tppms, pta and ptaMe (Scheme 1) in order to establish the composition of the species formed in solution. The solid state structures of *trans*-$[Ru(H_2O)_4(ptaMe)_2](tos)_4\cdot 2H_2O$, *trans*-$[Ru(H_2O)_4(ptaH)_2](tos)_4\cdot 2H_2O$, and *trans-mer*-$[RuI_2(H_2O)(ptaMe)_3]I_3\cdot 2H_2O$ have also been determined by single crystal X-ray diffraction.



Scheme 1 Structures of the water-soluble tertiary phosphines used in this study.

† Electronic supplementary information (ESI) available: X-Ray structural information for **8**, **9** and **10**. See http://www.rsc.org/suppdata/dt/b4/b405878j/

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Table 1 ^{31}P-NMR chemical shifts (δ/ppm) of $[Ru(H_2O)_5L]^{2+}$ (**A**), *cis*-$[Ru(H_2O)_4L_2]^{2+}$ (**B**) and *trans*-$[Ru(H_2O)_4L_2]^{2+}$ (**C**) obtained in the reaction of $[Ru(H_2O)_6](tos)_2$ and L in aqueous solution[a]

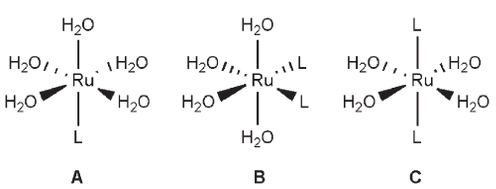
L	A	B	C
*m*tppts	73.3 (s)	31.7 (s)	54.0 (s)
*m*tppms	71.0 (s)	30.3 (s)	54.3 (s)
*p*tppms	70.4 (s)	29.3 (s)	53.6 (s)

[a] Conditions: [Ru] = 7.26×10^{-3} M, [*m*tppts] = 4.50×10^{-2} M; [Ru] = 3.63×10^{-3} M, [*m*tppms] or [*p*tppms] = 4.50×10^{-2} M; D_2O, rt, pH = 2.5.

Results and discussion

Reaction of $[Ru(H_2O)_6]^{2+}$ with the sulfonated triphenylphosphines *m*tppts, *m*tppms and *p*tppms

In aqueous solutions at room temperature $[Ru(H_2O)_6]^{2+}$ reacts with the sulfonated triphenylphosphines L = *m*tppts, *m*tppms and *p*tppms to yield complex ions of the general formulae $[Ru(H_2O)_5L]^{2+}$ (**A**), *cis*-$[Ru(H_2O)_4L_2]^{2+}$ (**B**), and *trans*-$[Ru(H_2O)_4L_2]^{2+}$ (**C**). The structures of these complexes in solution (Scheme 2) were inferred from ^{31}P-NMR data which are collected in Table 1. The ^{17}O-NMR spectrum of $[Ru(H_2O)_5(mtppts)]^{2+}$ showed broad singlets at $\delta = -48.0$ ppm (H_2O_{ax}) and at $\delta = -171.0$ ppm (H_2O_{eq}), while that of the *trans*-$[Ru(H_2O)_4(mtppts)_2]^{2+}$ contained one broad singlet resonance at $\delta = -169.2$ ppm (H_2O_{eq}). For comparison, the ^{17}O-NMR spectrum of $[Ru(H_2O)_6]^{2+}$ consists of a broad singlet at −192.0 ppm. These data are consistent with the structures **A** and **C** for $[Ru(H_2O)_5(mtppts)]^{2+}$ and *trans*-$[Ru(H_2O)_4(mtppts)_2]^{2+}$, respectively, and allowed the assignment of the relevant ^{31}P-NMR chemical shifts also for *cis*-$[Ru(H_2O)_4(mtppts)_2]^{2+}$. The ^{17}O-NMR spectrum of this latter compound showed very broad signals at room temperature and was unsuitable for structure determination, while at higher temperatures the complex was rapidly converted to *trans*-$[Ru(H_2O)_4(mtppts)_2]^{2+}$. The structures of the complexes with *m*tppms and *p*tppms ligands also could not be obtained from direct ^{17}O-NMR measurements due to their insufficient solubility, nevertheless they could be established by analogy to the *m*tppts-containing species. The relative amounts of **A**, **B** and **C** depended on the [L] : [Ru] ratio and on the temperature. When [L] : [Ru] was set 1 : 1, at room temperature the main product was **A**, and only traces of **B** could be detected. At high excess of L over Ru ([L] : [Ru] = 12 : 1) *m*tppms and *p*tppms gave the *trans*-bisphosphine species, **C**, already at room temperature. Conversely, with *m*tppts the major species at room temperature was **B** (approximately 77% of all Ru), and **A** prevailed for several days. However, in the same solution but at 40 °C, substitution of another H_2O in **A** and isomerization of **B** rapidly converted all ruthenium species to the stable *trans*-bisphosphine complex, **C**. In solution these complexes did not decompose for several weeks under an inert atmosphere. No signs of the formation of the trisphosphine $[Ru(H_2O)_3L_3]^{2+}$, or higher substituted species could be seen in the ^{31}P-NMR spectra at [L] : [Ru] = 12 : 1. The exclusive formation of bisphosphine complexes at [L] : [Ru] ≥ 2 : 1 is in accord with the solid state composition of $[\{RuCl_2(mtppms)_2\}_2]$[26] in contrast to $[RuCl_2(PPh_3)_3]$, and with its stability towards further *m*tppms coordination in aqueous solution.[27] It should be mentioned, however, that with hydride co-ligand(s) Ru(II)-complexes with three and four sulfonated phosphine ligands, such as $[RuHCl(mtppms)_3]$[27] and $[RuH_2(mtppts)_4]$[28] are also known.



Scheme 2 Structures of $[Ru(H_2O)_5L]^{2+}$ (**A**), *cis*-$[Ru(H_2O)_4L_2]^{2+}$ (**B**) and *trans*-$[Ru(H_2O)_4L_2]^{2+}$ (**C**); L = *m*tppts, *m*tppms, *p*tppms.

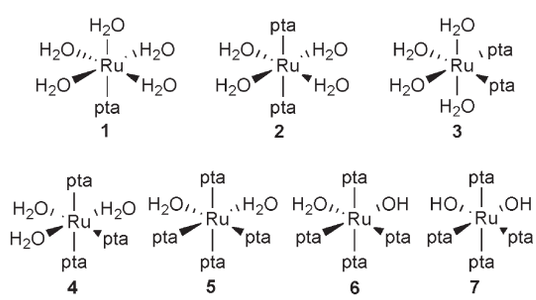
Table 2 ^{31}P-NMR spectral data of the species formed in the reaction of $[Ru(H_2O)_6]^{2+}$ and pta[a]

	Chemical shift(s) (δ/ppm) and coupling constant(s) {$^2J_{P-P}$/Hz}
$[Ru(H_2O)_5(pta)]^{2+}$ (**1**)	−41.3 (s)
$[Ru(H_2O)_4(pta)_2]^{2+}$ (**2,3**)[b]	−49.7 (s)[b]; −50.1 (s)[b]
$[Ru(H_2O)_3(pta)_3]^{2+}$ (**4**)	−7.4 (t) {30.1}, −48.3 (d) {30.1}
$[Ru(H_2O)_2(pta)_4]^{2+}$ (**5**)[c]	−16.5 (t) {27.0}, −46.4 (t) {27.0}
$[Ru(H_2O)(OH)(pta)_4]^{+}$ (**6**)[c]	−13.3 (dt) {30.6, 34.0}, −23.4 (dt) {26.0, 34.0} −53.1 (dd) {26.0, 30.6}
$[Ru(OH)_2(pta)_4]$ (**7**)[c]	−17.1 (t) {27.6}, −51.8 (t) {27.6}

[a] Conditions: [Ru] = 8.31×10^{-2} M, [pta] = 1.25 M, D_2O, T = 44 °C, pH = 6.29. [b] *cis*- and *trans*-$[Ru(H_2O)_4(pta)_2]^{2+}$ could not be distinguished. [c] The $[RuX_2(pta)_4]^{2+}$ (X = H_2O or OH^-) species give rise to closely similar ^{31}P-NMR spectra; assignments are based on the changes of signal intensities upon variation of pH.

Reaction of $[Ru(H_2O)_6]^{2+}$ with pta and ptaMe

These studies required a careful control of pH in order to keep a delicate balance between the hydrolysis of $[Ru(H_2O)_6]^{2+}$ (above pH 6) and the notable protonation of pta (below pH 6.5). For this reason we made most of our measurements around pH 6. Earlier data on the protonation of pta show some disagreement (pK_a = 6.0,[29] 5.70,[30] 6.07[31]); we have determined a $pK_a = 5.89 \pm 0.01$ at 25 °C in 0.01 M KCl solution (see Experimental). Depending on the [L] : [Ru] ratio, the reaction of $[Ru(H_2O)_6]^{2+}$ and pta gave mixtures of several compounds (**1–7**, Scheme 3). Extensive ^{31}P-NMR studies were made of samples with various [L] : [Ru] ratios including homonuclear $^{31}P\{^{31}P\}$ decoupling measurements at several temperatures. These led to the determination of the ^{31}P-NMR spectral features of the various Ru(II)-pta complexes as shown in Table 2. At [L] : [Ru] = 2 : 1 ratios the main species in the solutions at room temperature was $[Ru(H_2O)_5(pta)]^{2+}$ and the bis- and trisphosphine species could be detected only in traces. Conversely, at [L] : [Ru] ratios as high as 15 : 1, $[Ru(H_2O)_5(pta)]^{2+}$ (**1**) was gradually replaced by $[Ru(H_2O)_4(pta)_2]^{2+}$ (**2, 3**); however, **4** was still present only in low concentration together with negligible amounts of **5** and with even smaller quantities of **6** and **7** (Fig. 1).



Scheme 3 Ru(II)-pta species formed in the reaction of $[Ru(H_2O)_6]^{2+}$ and pta.

X-Ray structural determination of *trans*-$[Ru(H_2O)_4(ptaMe)_2](tos)_4 \cdot 2H_2O$, 8, *trans*-$[Ru(H_2O)_4(ptaH)_2](tos)_4 \cdot 2H_2O$, 9, and *trans-mer*-$[RuI_2(H_2O)(ptaMe)_3]I_3 \cdot 2H_2O$, 10. As mentioned earlier, the reactions of $[Ru(H_2O)_6]^{2+}$ and pta had to be studied at pH ≥ 6 in order to avoid protonation of pta. In order to avoid protonation *N*-methylated pta, ptaMe$^+$ was used in some of the experiments. The iodide salt, ptaMe$^+$I$^-$ can be easily synthesized in the reaction of pta with methyl iodide, and indeed ptaMe$^+$I$^-$ (as well as the ethyl derivative, ptaEt$^+$I$^-$) have already been used as ligands in catalytically active phosphine complexes.[23] However, due to the fast and stable coordination of I$^-$, ptaMe$^+$I$^-$ could not be used for complex formation studies with $[Ru(H_2O)_6]^{2+}$. Therefore we have prepared the iodide-free *p*-toluenesulfonate salt, ptaMe$^+$tos$^-$ using ion-exchange chromatography and this was successfully used for the isolation of *trans*-$[Ru(H_2O)_4(ptaMe)_2](tos)_4 \cdot 2H_2O$, **8**, from *p*-toluenesulfonic acid solutions (pH 5.5). The analogous iodide-free protonated complex *trans*-$[Ru(H_2O)_4(ptaH)_2](tos)_4 \cdot 2H_2O$, **9** was

Table 3 Summary of data collection, structure solution and refinement for compounds **8** and **9**

Compound	**8**	**9**
Empirical formula	$C_{42}H_{70}N_6O_{18}P_2RuS_4$	$C_{40}H_{66}N_6O_{18}P_2RuS_4$
Formula weight	1238.29	1210.24
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/n$ (No. 14)	$P2_1/a$ (No. 14)
Lattice parameters		
a/Å	9.1426(1)	9.978(3)
b/Å	10.653(1)	16.255(2)
c/Å	28.2278(1)	16.374(2)
($\alpha/\beta/\gamma$)/°	90/91.9(1)/90	90/100.9(1)/90
V/Å^3	2747.9(4)	2607.8(9)
Z	2	2
μ(Mo-Kα)/cm^{-1}	0.569	0.598
Θ_{max}/°	25.3	25.3
Decay (%)	5	1
No. observed reflections [$I > 2.00\sigma(I)$]	3301	3030
No. variables	350	386
Reflection/parameter ratio	14.21	11.68
Residuals: R, R_w (%)	6.31 19.53	4.81 13.08
Goodness of fit	1.139	1.014
Max./Min. peak in final difference map/e Å^{-3}	1.171–0.476	0.505–0.876

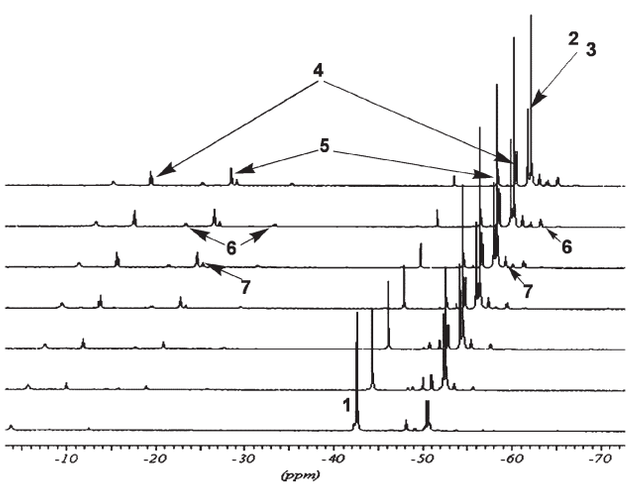


Fig. 1 ^{31}P-NMR spectra of the solutions of $[Ru(H_2O)_6](tos)_2$ + pta. Conditions: [Ru] = 8.31 × 10^{-2} M, [pta] = 1.25 M, T = 27 °C, pH = 6.29, spectra taken at every 30 min.

obtained in the reaction of $[Ru(H_2O)_6]^{2+}$ and ptaH$^+$ in slightly more acidic solutions (pH 4, acidified with *p*-toluenesulfonic acid). In the presence of KI the reaction of $[Ru(H_2O)_6]^{2+}$ and ptaMe$^+$tos$^-$ led to the formation of the mixed ligand aqua-iodo-phosphine complex, *trans-mer*-$[RuI_2(H_2O)(ptaMe)_3]I_3\cdot 2H_2O$, **10**. X-ray quality crystals of these complexes could be easily obtained by recrystallization from aqueous *p*-toluenesulfonic acid (**8** and **9**) or KI (**10**) solutions. The parameters of the X-ray structural determination are given in Table 3. In all structures the coordination sphere of ruthenium is distorted octahedral. Selected bond length and bond angle data for complexes **8** and **9** are shown in Table 4. In both **8** and **9** the two phosphine ligands are in *trans* positions and the plane of the four water ligands dissects the molecules (see Fig. 2 and 3). The ruthenium atoms are in special positions (inversion centre). There are polar tosylate and metal complex layers separated by apolar tosylate phenyl layers in the crystal structure of complexes **8** and **9**. Complex **10** was also analyzed by single crystal X-ray diffraction in order to compare its structure to those of **8** and **9**. The molecular structure of **10** is given as ESI.† In this complex, the three ptaMe$^+$ ligands are coordinated in a meridional arrangement which leads to the weakest electrostatic repulsion between the three charged phosphines and similarly, between the five iodide anions. Due to the coulombic repulsion and the steric requirements of the ptaMe$^+$ ligands, the P1–Ru–P3 angle is only 166.9°. This distortion of

Table 4 Selected bond length (Å) and bond angle (°) data of complexes **8** and **9**

	Compound[a]	**8**	**9**
	Ru–P	2.325(1)	2.322(1)
	Ru–O	2.112(5)	2.102(5)
		2.129(5)	2.110(5)
	N_s–C_{Me}	1.518(8)	—
	C–N_s–C	110.0(5)	109.7(4)
		109.8(5)	110.8(4)
		108.1(5)	111.2(4)
	P–Ru–P	180.0	180.0
	O–Ru–O	88.5(2)	87.6(2)
		91.5(2)	92.4(2)
		180.0	180.0
	O–Ru–P	86.2(1)	87.1(1)
		93.8(1)	92.9(2)
		91.1(1)	92.6(3)

[a] N_s = methyl-substituted (quaternary) nitrogen.

the octahedral coordination sphere (and the *trans* effect of P2) is also manifested in the elongation of the Ru–O distance relative to the Ru–O distances in **8** and **9**. During the preparation of this manuscript the structure of **10** has been published;[23] the data of the two determinations are in good agreement.

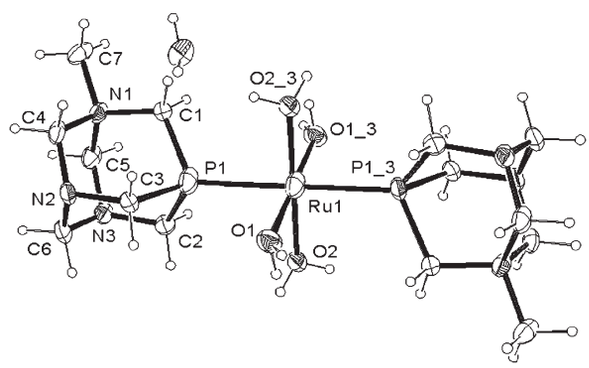


Fig. 2 ORTEP view of **8** with partial numbering scheme, the tosylate counter ions were omitted for clarity. (symmetry operation: $-x$, $-y$, $-z$).

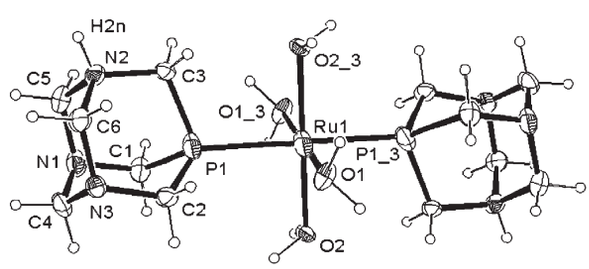
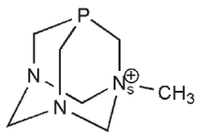


Fig. 3 ORTEP view of **9** with partial numbering scheme. (symmetry operation: $-x$, $-y$, $-z$).

Effect of *N*-alkylation or protonation on the structure of coordinated pta

The structural features of the coordinated pta and ptaH$^+$ have been analyzed earlier on the basis of 37 individual structure determinations.[32] Presently the Cambridge Structural Database contains data for 75 pta, 24 ptaH$^+$ and 13 ptaMe$^+$ ligands bound to various metal ions, not including those in **8, 9** and **10** (our determination). The CSD set of structural data of the pta-ligated complexes yielded an average (P)C–N distance of 1.473 Å, while the average (N)C–N bond length was found to be 1.465 Å. In **8, 9** and **10**, the (N)C–N distances (Scheme 4) remain unchanged (1.466 Å) while the (N_s)C–N distances (1.473 Å) in ptaMe$^+$ were found somewhat shorter relative to pta. The bonds involving the quaternary nitrogen atom, (N)C–N_s, are elongated (average of **8** and **10**: 1.510 Å) and close in the length of the N_s–C_{Me} bond (1.504 Å; the CSD-average is 1.529 Å). Similarly, the (P)C–N_s bonds in

the protonated or alkylated pta ligands are stretched compared to the unsubstituted pta (average 1.495 Å in **8, 9** and **10** as opposed to 1.473 Å), while the other two (P)C–N distances are not affected by the protonation or alkylation (1.472 Å *vs.* 1.473 Å). Based on these data it can be concluded that protonation or alkylation of one of the nitrogen atoms in pta led to the same slight distortion of the phosphatriazaadamantane skeleton.



Scheme 4 Structure of ptaMe$^+$.

Relevance to catalysis. *In situ* formation of homogeneous catalysts from suitable metal-containing precursors and ligands (often phosphines) is a widely used practice in catalysis. For example, in a study on the hydrogenation of benzaldehyde the catalyst was prepared by mixing solutions of $[Ru(H_2O)_6]^{2+}$ and pta in several molar ratios and mechanistic conclusions were drawn from the dependence of the reaction rate on the [pta] : [Ru] ratios.[15] Similarly, hydrodehalogenation reactions were catalysed with mixtures of $[Ru(H_2O)_6]^{2+}$ and pta or *m*tppms.[16] In the present study we have shown that in the case of the sulfonated triphenylphosphine complexes the catalytically important $[Ru(H_2O)_5L]^{2+}$ and $[Ru(H_2O)_4L_2]^{2+}$ complexes are formed instantaneously from $[Ru(H_2O)_6]^{2+}$ and an excess of L. Conversely, the reaction of $[Ru(H_2O)_6]^{2+}$ and pta first leads mainly to $[Ru(H_2O)_5(pta)]^{2+}$ which is only slowly replaced by *cis*- and *trans*-$[Ru(H_2O)_4(pta)_2]^{2+}$ and those remain by far the major species even in a large excess of pta. Although under the catalytic conditions applied in refs.15 and 16 the complex formation equilibria may be shifted relative to the conditions of this study, the formation of higher coordinated species must be dealt with care. *In situ* preparation of the catalysts starting with $[Ru(H_2O)_6]^{2+}$ and water-soluble phosphines can be practical but the actual composition of the catalytic species may not be directly related to the [metal] : [ligand] ratio employed in their synthesis.

Experimental

$[Ru(H_2O)_6](tos)_2$,[11] pta,[33] (ptaMe$^+$I$^-$),[33] *m*tppms-Na,[26] *p*tppms-K[34] and *m*tppts-Na_3[35] have been prepared according to the literature. All reagents were high purity products of Aldrich and used as received. Manipulations with the air-sensitive Ru-complexes were done in an inert atmosphere using Schlenk-techniques. NMR measurements were run on Bruker AC 200 MHz, Bruker AM 360 MHz and Bruker DRX 400 MHz spectrometers. The spectra were referenced to 2,2-dimethyl-2-silapentane-5-sulfonate (dss) sodium salt (^{1}H) and to 85% H_3PO_4 (^{31}P) and were analyzed by the WINNMR software. ^{17}O spectra were obtained using 10% ^{17}O-enriched water (Cambridge Isotope Laboratories). Microanalyses were carried out by Analytische Laboratorien (Lindau, Germany) and Analytical Services, ICMB, EPFL (Lausanne).

Preparation of ligand and Ru(II) complexes

ptaMe-*p*-toluenesulfonate (ptaMe$^+$tos$^-$). This was obtained by ion exchange of ptaMe$^+$I$^-$ on a Molselect DEAE-25 (Reanal, Hungary) column in tosylate form. 1 g of ptaMe$^+$I$^-$ was dissolved in 10 mL H_2O and passed very slowly through a column of 2.5 g Molselect DEAE-25 tosylate. The column was eluted with a further 50 mL of H_2O. The pH of the combined eluates was adjusted to neutral with a few drops of aqueous Htos. This solution was concentrated to 2–5 mL on a rotary evaporator and added drop by drop to 50 mL of rapidly stirred acetone; stirring was continued for 2 h. The resulting white precipitate was filtered, washed with acetone and dried. Yield 980 mg (85%). This compound still contains 0.93% w/w I$^-$ as shown by ICP-AAS determinations (Perkin Elmer OPTIMA 3300 DV, λ = 182.976 nm and 206.163 nm, calibrated to KI standard solutions). Purification included precipitation of ptaMe$^+$tos$^-$ by addition of 15 mL ethyl acetate to a solution of 2.2 g of the raw product in 3 mL of methanol with stirring (97% recovery) followed by another ion exchange as above. The product of the second ion exchange procedure contained no iodide above the ICP detection limit (0.05 ppm). ^{1}H-NMR (D_2O, rt): δ/ppm 2.35 (s, 3H, CH_3, tos); 2.68 (s, 3H, CH_3, ptaMe); 3.73–3.94 (m, 4H, P–CH_2–N); 4.25 (d, 2H, P–CH_2–N$^+$), $^2J_{P-H}$ = 5.4 Hz; 4.36–4.55 (m, 2H, N–CH_2–N); 4.74–4.88 (m, 4H, N–CH_2–N$^+$); 7.35 (d, 2H,–CH–C(−)–CH_3), $^3J_{H-H}$ = 7.2 Hz; 7.6 Hz (d, 2H,–CH–C(−)–SO_3^-), $^3J_{H-H}$ = 7.2 Hz. ^{31}P-NMR (D_2O, r.t.): δ/ppm −83.30 (s).

***trans*-[Ru(H$_2$O)$_4$(ptaMe)$_2$](tos)$_4$·2H$_2$O, 8.** This was obtained by slow crystallization at room temperature from a solution of 400 mg (1.91 mmol) ptaMe$^+$tos$^-$ and 180 mg (0.33.mmol) $[Ru(H_2O)_6](tos)_2$ in 3 mL H_2O; the pH was adjusted to 5.5 by addition of Htos. The solution was stirred for 3 min and then left to stand for one day. The yellow-brown crystals (307 mg, 75.9%) were isolated by filtration and submitted for X-ray structure determination. ^{31}P-NMR (H_2O, rt): δ/ppm −23.3 (s). Analysis for $RuC_{42}H_{70}P_2N_6S_4O_{18}$, M = 1238.30 (found/required): C 40.81/40.74, H 5.84/5.70, N 6.61/6.79.

***trans*-[Ru(H$_2$O)$_4$(ptaH)$_2$](tos)$_4$·2H$_2$O, 9.** This was obtained by reacting 300 mg (1.91 mmol) pta in 3 mL H_2O acidified to pH 4 (Htos) with 180 mg (0.33 mmol) $[Ru(H_2O)_6](tos)_2$. The reaction mixture was stirred for 3 min then left to stand for one day, after which 347 mg (88%) of the yellow-brown crystals were collected. X-ray quality yellow crystals were deposited during long standing of a strongly acidic (Htos) solution of the complex. ^{31}P-NMR (D_2O, rt): δ/ppm −31.4 (s). Analysis for $RuC_{40}H_{66}P_2N_6S_4O_{18}$, M = 1210.25, (found/required): C 39.96/39.70, H 5.46/5.50, N 7.04/6.94.

***trans-mer*-[RuI$_2$(H$_2$O)(ptaMe)$_3$]I$_3$·2H$_2$O, 10.** The following procedure is faster and yields a cleaner product than the previously published[23] method. 488 mg (1.63 mmol) ptaMe$^+$I$^-$ and 108 mg (0.65 mmol) KI in 6 mL water was reacted with 180 mg (0.33 mmol) $[Ru(H_2O)_6]^{2+}(tos)_2$ at room temperature. The solution was stirred for 3 min then left to stand for one day yielding 351 mg (82%) of the product as strongly pink crystals. ^{31}P-NMR (D_2O, rt): δ/ppm 10.6 (t), $^2J_{P-P}$ = 33.8 Hz; −37.1 (d), $^2J_{P-P}$ = 34.5 Hz. Analysis for $RuC_{21}H_{51}P_3N_9I_5O_3$, M = 1306.29 (found/required): C 19.31/18.11, H 3.94/3.56, N 9.65/9.07.

pH-potentiometric studies. The acid dissociation constant of ptaH$^+$ was determined by titration with 0.2113 M HCl of solutions of approximately 30 mg pta in 10 mL 0.01 M KCl under inert atmosphere at 25.0 °C using an ABU 91 autoburette (Radiometer). The data were analyzed with the SUPERQUAD[36] program resulting in a pK_a = 5.89 ± 0.01.

X-ray structural determinations. Data collection was performed using an Enraf Nonius MACH3 diffractometer at room temperature with Mo-Kα radiation (λ = 0.71069 Å). Structures were determined using direct methods with the SIR-92 package[37] and refined using the SHELX97[38] program. Hydrogen atoms were placed into geometric positions in the case of C–H atoms or found at the difference electron density map in the case of O–H and N–H atoms. Remaining electron densities are close to heavy atoms *i.e.* iodine or ruthenium. All structures are stabilized by extensive hydrogen bond networks. In structure **2** the phenyl rings in symmetry related tosylates are disordered perpendicular to each other and the coordinated water molecules are also disordered over two positions with an occupancy of 60/40. These disorders resulted in remaining errors *i.e.* acceptor contacts in the final refinement. The publication material was prepared using the WINGX suite,[39] and analysis of H-bond network and other crystallographic calculations were performed using the PLATON program.[40]

CCDC reference numbers 236511–236513.

See http://www.rsc.org/suppdata/dt/b4/b405878j/ for crystallographic data in CIF or other electronic format.

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