New water-soluble rhodium(I) complexes containing 1-methyl-1-azonia-3,5-diaza-7-phosphaadamantane iodide

Florian P. Pruchnik,[*,a] **Piotr Smoleński,**[a] **Ewa Gałdecka,**[b] **Zdzisław Gałdecki**[c]

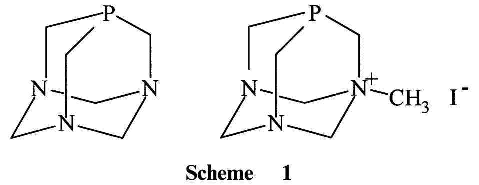
[a] *Faculty of Chemistry, University of Wrocław, Joliot-Curie 14, 50-383 Wrocław, Poland*
[b] *Institute of Low Temperature and Structure Research, Polish Academy of Sciences, Okólna 2, 50-950 Wrocław, Poland*
[c] *Institute of General and Ecological Chemistry, Technical University of Łódź, Żwirki 36, 90-924 Łódź, Poland*

Reaction of [$Rh_2Cl_2(CO)_4$] with stoichiometric quantities of 1-methyl-1-azonia-3,5-diaza-7-phosphaadamantane iodide (mtpa$^+$I$^-$) in MeOH and H_2O yields square-planar [RhI(CO)(mtpa$^+$I$^-$)$_2$] **1** and trigonal-bipyramidal [RhI(CO)(mtpa$^+$I$^-$)$_3$] · 4H_2O **2**, respectively. The complexes are stable in aqueous solution under inert atmosphere and catalyse the hydroformylation and the hydrocarboxylation of alkenes and the hydrogenation of aldehydes and alkenes. An X-ray crystallography study revealed that **2** has a TBPY-5 structure. The coordination around the Rh atom forms a nearly ideal trigonal bipyramid [$a = 15.705(3)$ Å, $b = 13.219(3)$ Å, $c = 20.894(4)$ Å, monoclinic, space group $P2_1/c$, $Z = 4$, $\beta = 110.72(3)°$].

Classical organometallic chemistry and homogeneous organometallic catalysis are typically considered as chemistry in organic solutions. The basic problem of homogeneously catalysed processes is the separation of the product from the solvent and the catalyst. Water-soluble catalysts combine the advantages of homogeneous and heterogeneous catalysis: simple separation of the product from the catalyst with high activity and selectivity.[1,2] Water solubilization of known coordination and organometallic catalysts is performed by incorporating highly polar functional groups such as $-SO_3H$, $-COOH$, $-NH_2$, $-NR_3^+$, $-PR_3^+$ or OH groups into phosphine ligands.[1-8] Most investigations of metal phosphine complexes involve the sulfonated arylphosphine ligands. Comparatively little work has been carried out on hydrophilic trialkylphosphines. Interesting properties are exhibited by 1,3,5-triaza-7-phosphatricyclo[3.3.1.1^{3,7}]decane (tpa)[9-15] and 1-methyl-1-azonia-3,5-diaza-7-phosphatricyclo[3.3.1.1^{3,7}]decane iodide (mtpa$^+$I$^-$)[12] (Scheme 1). The cone angle for the first phosphine is 102° [10,11,14,15] and for mtpa$^+$I$^-$ it is approximately the same.[16,17] Thus the properties of complexes with these ligands should depend mainly on their electronic properties. We describe herein new rhodium(I) complexes with mtpa$^+$I$^-$.

Results and Discussion

Reaction of [$Rh_2Cl_2(CO)_4$] with mtpa$^+$I$^-$ in methanol in a molar ratio of 1 : 4 gives the square-planar complex **1**; however, in water with a molar ratio of 1 : 6 the five-coordinate complex **2** is formed. The iodo complexes only were obtained because the solubility of compounds containing the chloro ligand or Cl$^-$ counter ion is higher. The yields are considerably higher in the case of reactions performed in the presence of stoichiometric amounts of sodium iodide:



Scheme 1

$$[Rh_2Cl_2(CO)_4] + 6\ mtpa^+I^- + 2NaI + 8H_2O \rightarrow 2[RhI(CO)(mtpa^+I^-)_3]\cdot 4H_2O + 2CO + 2NaCl \quad (1)$$

The complexes **1** and **2** are air-stable in the solid state; however, in solutions they are oxidized in air with loss of the carbonyl ligand and formation of mtpaO$^+$I$^-$ and water-insoluble brown iodo complexes with mtpaO$^+$I$^-$. They are soluble in water, moderately soluble in methanol, sparingly soluble in ethanol and insoluble in higher alcohols and in nonpolar solvents. Relatively high values of ν(CO) stretching vibrations for **1** and **2**, 1990 and 2001 cm^{-1}, respectively, indicate that the mtpa$^+$I$^-$ ligand possesses stronger π-acceptor properties than most alkyl- and arylphosphines.

An X-ray crystallographic study revealed that compound **2** has a TBPY-5 structure with equatorial phosphine ligands. Crystallographic data for **2** are given in Table 1 and the ORTEP view of **2** is depicted in Fig. 1, along with a listing of important bond distances and bond angles. The coordination around the Rh atom forms a nearly ideal trigonal bipyramid. The rhodium atom lies only 0.067 Å below the phosphorus plane toward the carbonyl ligand. The C—Rh—I axis is perpendicular to the latter plane. The Rh—P distances are a little shorter than those in *trans*-[RhI(CO)(PPh$_3$)$_2$][18] and *trans*-[RhCl(CO)(PPh$_3$)$_2$],[19] the Rh—I distance is somewhat longer and the Rh—C1 distance is, within experimental error, the same as in square planar *trans*-[RhX(CO)(PR$_3$)$_2$] complexes.[19]

The $^{31}P\{^1H\}$ NMR spectrum of **1** consists of a doublet at -50.2 ppm with $^1J_{RhP} = 123.6$ Hz. The ^{31}P coordination chemical shift, $\Delta\delta(^{31}P) = \delta_{complex} - \delta_{ligand}$, amounts to 44.8 ppm. The complex **2** shows dynamic properties. In the $^{31}P\{^1H\}$ NMR spectrum in D_2O at 20 °C only one signal at -58.4 ppm is observed. It is very broad at 5 °C and as the temperature is increased the resonance narrows; however, even at 85 °C spin coupling between ^{103}Rh and ^{31}P was not observed. This indicates that the fluxional process is intermolecular. Thus, the five-coordinate complex **2** in solution gives a mixture of several complexes with different structures, such as isomers of trigonal bipyramid, square pyramid and four-coordinate square planar complexes of formulae [RhI(CO)(mtpa$^+$I$^-$)$_3$], [RhI-(CO)

Table 1 Crystallographic data for $[RhI(CO)(mtpa^+I^-)_3] \cdot 4H_2O$, **2**

Formula	$C_{22}H_{53}I_4N_9O_5P_3Rh$
Formula weight	1227.16
Crystal system	Monoclinic
Space group	$P2_1/c$
a/Å	15.705(3)
b/Å	13.219(3)
c/Å	20.894(4)
β/°	110.72(3)
U/Å^3	4057.2(16)
Z	4
T/K	293
ρ_{calcd}/g cm^{-3}	2.01
μ/cm^{-1}	35.85
Wavelength of X-ray	MoK$_\alpha$(λ = 0.71073 Å)
2θ range/deg	0.2–44
Scan range/deg	0.8 + 0.345 tgθ
Scan type	ω/2θ
Reflect. collected	6196
Indep. reflect.	5992
Obsd reflect.	3572[$\lvert F \rvert > 4\ \sigma(F)$]
No of parameters refined	397
R	0.0353
R_w	0.0398
GOF	1.123

$R = \Sigma(\lVert F_o\rvert - \lvert F_c\rVert)/\Sigma\lvert F_o\rvert$; $R_w = [\Sigma w^{1/2}(\lvert F_o\rvert - \lvert F_c\rvert)/\Sigma w^{1/2}\lvert F_o\rvert]$; GOF = $\{\Sigma[w(F_o - F_c)^2]/(n - p)\}^{1/2}$

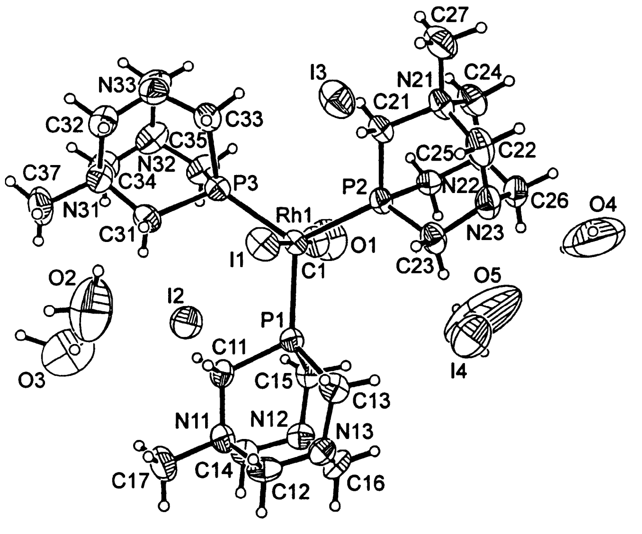


Fig. 1 Ortep representation of complex $[RhI(CO)(mtpa^+I^-)_3] \cdot 4H_2O$, **2**. Selected bond lengths (Å) and angles (°): Rh1—I1, 2.713(1); Rh1—P1, 2.309(2); Rh1—P2, 2.313(3); Rh1—P3, 2.302(2); Rh1—C1, 1.817(12); I1—Rh1—C1, 179.6(3); I1—Rh1—P1, 88.4(1); I1—Rh1—P2, 88.2(1); I1—Rh1—P3, 87.7(1); P1—Rh1 – P2, 116.4(1); P1—Rh1—P3, 122.3(1); P2—Rh1—P3, 120.9(1); P1—Rh1—C1, 91.3(3); P2—Rh1—C1, 92.2(3); P3—Rh1—C1, 92.2(3)

$(mtpa^+I^-)_2]$, $[RhI(mtpa^+I^-)_3]$, $[RhI(L)(mtpa^+I^-)_2]$ and $[RhI(L)(mtpa^+I^-)_3]$ (L = solvent, $mtpaO^+I^-$). The CO ligand can be partially removed from the coordination sphere because complexes **1** and **2** are catalysts for the water gas-shift reaction. In aqueous solution complexes **1** and **2** are relatively stable under inert atmosphere, in contrast to $RhCl(tpa)_3$ which is oxidized with formation of tpaO owing to the oxidative addition of water.[20,21] However in methanol–water and wet acetonitrile solutions even traces of oxygen oxidize $mtpa^+I^-$ to $mtpaO^+I^-$. The formation of different complexes and oxidation of $mtpa^+I^-$ was confirmed by the $^{31}P\{^1H\}$ NMR spectra of **2** in CD_3OD–D_2O (1 : 1) and wet CD_3CN. In CD_3OD–D_2O at 20 °C there appear only two singlets at −11.4 ppm, assigned to $OP(CH_2)_6NMeI$, and at 1.4 ppm, which most likely should be assigned to the coordinated phosphine oxide. However, at −30 °C, in addition to two singlets (−11.0 and 2.2 ppm), three doublets emerge at −48.4 ($^1J_{RhP}$ = 125.7 Hz), −62.7 ($^1J_{RhP}$ = 129.2 Hz) and −65.2 ppm ($^1J_{RhP}$ = 111.3 Hz) in an approximate intensity ratio 5 : 2 : 1. The $^{31}P\{^1H\}$ NMR of **2** in CD_3CN consists of a singlet at −10.8 ppm, indicating the presence of phosphine oxide and four doublets at −40.1 ($^1J_{RhP}$ = 101.7 Hz), −41.7 ($^1J_{RhP}$ = 120.0 Hz), −43.0 ($^1J_{RhP}$ = 124.1 Hz) and −59.9 ppm ($^1J_{RhP}$ = 91.6 Hz) in an approximate intensity ratio of 1 : 3 : 2 : 6. The phosphine ligand at low temperatures was not split off; only resonances of several rigid rhodium complexes were observed and the signal of free phosphine was not found.

Table 2 Catalytic properties of complexes **1** and **2**

			Hydroformylation of 1-hexene[a]	
Catalyst	Ave TOF	Yield/%	Products (%)	
1	117	70	n-$C_6H_{13}CHO$ (29); $C_4H_9CH(CH_3)CHO$ (25); $CH_3CH{=}CHC_3H_7$ (10); $CH_3CH_2CH{=}CHC_2H_5$ (6)	
2–$mtpa^+I^-$ (1 : 6)	150	91	n-$C_6H_{13}CHO$ (39); $C_4H_9CH(CH_3)CHO$ (25); n-$C_6H_{13}COOH$ (14); $C_4H_9CH(CH_3)COOH$ (13)	
			Hydrogenation of aldehydes[b]	
2	Ave TOF	Yield/%	Substrate	Products (%)
	109	98	n-C_3H_7CHO	Bu^nOH (6); $PrCH{=}CEtCHO$ (6); $BuEtCHCH_2OH$ (2); $EtC(Pr^nCHOH)_2CHO$ (77); Pr^nCOOBu^n (1)
	108	97	n-C_4H_9CHO	n-$C_5H_{11}OH$ (80); $Bu^nCH{=}C(Pr^n)CHO$ (3); other (14)
	108	97	n-$C_5H_{11}CHO$	n-$C_6H_{13}OH$ (84); n-$C_5H_{11}CH{=}C(Bu^n)CHO$ (6); n-$C_6H_{13}CH(Bu^n)CH_2OH$ (2); other (8)
	106	95	n-$C_6H_{13}CHO$	n-$C_7H_{15}OH$ (78); n-$C_6H_{13}CH{=}C(n\text{-}C_5H_{11})CHO$ (12); n-$C_7H_{15}CH(n\text{-}C_5H_{11})CHO$ (2); other (3)
			One-phase hydrogenation[c]	
2	Initial TOF/ mol substr. (mol Rh)$^{-1}$ h^{-1}		Substrate	Products
	110		*cis*-$HOOCCH{=}CHCOOH$	$HOOC(CH_2)_2COOH$
	210		*trans*-$HOOCCH{=}CHCOOH$	$HOOC(CH_2)_2COOH$
	160		$CH_2{=}CHCH_2OH$	C_3H_7OH

[a] $p(CO) = p(H_2)$ = 3.0 MPa; 353 K; **1**, **2**: 0.01 mmol; 15 cm^3 H_2O; 1-hexene: 30 mmol.
[b] $p(H_2)$ = 8.0 MPa; 353 K; **1**, **2**: 0.01 mmol; 15 cm^3 H_2O; substrate: 20 mmol.
[c] $p(H_2)$ = 0.1 MPa; 293 K; **1**, **2**: 0.01 mmol; 15 cm^3 H_2O; substrate: 10 mmol.

Compounds **1** and **2** are active catalysts for the water gas-shift reaction. In the case of complex **2** the turnover frequency TOF = 140 mol CO_2 (mol Rh)$^{-1}$ h^{-1} at 80 °C and *p*(CO) = 8 MPa. Complexes **1** and **2** catalyse the hydroformylation and carboxylation of alkenes as well as the hydrogenation of aldehydes and compounds containing a C=C bond (Table 2). The biphasic reaction of 1-hexene with CO and H_2 in H_2O in the presence of **1** gives 1-heptanal, 2-methylhexanal and 2- and 3-hexene. The reaction products consisted of 29% *n*-aldehyde, 25% *iso*-aldehyde and 45% hexenes. Compound **2** in the presence of an excess of phosphine catalyses hydroformylation and carboxylation of alkenes. Reaction of 1-hexene with CO and H_2 in the presence of **2** and mtpa$^+$I$^-$ in water gives *n*-heptanal, 2-methylhexanal, 1-heptanoic acid and 2-methylhexanoic, acid as well as traces of hexane. Thus, in the presence of an excess of mtpa$^+$I$^-$, 1-hexene is slowly hydrogenated with H_2–CO. The hydrocarboxylation of alkenes probably proceeds *via* the migratory insertion of CO into the Rh—alkyl bond, followed by nucleophilic attack of water molecule or hydroxo ligand on the coordinated acyl ligand. The formation of heptanoic acids does not occur owing to the migratory insertion of carbon dioxide (formed in the water gas-shift reaction) into the Rh—alkyl bond. This is shown by the fact that the same products were obtained in the reaction of 1-hexene with H_2–CO_2 (1 : 1), however, the rate of reaction was five times slower and the yield of acids was lower in comparison with the aldehydes. This indicates that hydroformylation of 1-hexene in an H_2–CO_2 atmosphere proceeds owing to the reduction of CO_2 with H_2. The rate of hydroformylation of 1-hexene in the presence of complexes with mtpa$^+$I$^-$ is relatively fast; the activity of these complexes is about two times lower than that of rhodium coordination compounds with $P(C_6H_4SO_3Na\text{-}3)_3$ (tppts) under analogous conditions. Compounds **1** and **2** catalyse the hydrogenation of aldehydes, in contrast to rhodium compounds with tpa,[10,11,20,22] and C=C bonds. It is interesting that the rate of hydrogenation of fumaric acid is much higher than that of maleic acid. Complexes with mtpa$^+$I$^-$ show very strong hydrophilic properties and therefore their concentration in the organic phase is very low in comparison with complexes containing tpa ligands. Thus they are better catalysts for two-phase catalytic reactions than tpa complexes.

Experimental

Syntheses and catalytic reactions

All manipulations were carried out under inert atmosphere using standard Schlenk techniques. Catalytic reactions under high pressure were carried out in autoclaves (Berghof) and at atmospheric pressure in glass vessels at constant volume. The autoclaves and glass vessels were first filled with nitrogen and then with solvent, reactants and catalyst. The reactors were subsequently filled with $H_2 + CO$, $H_2 + CO_2$ or H_2 with several evacuation/refill cycles. The products of the catalytic reactions were analysed on an HP 6890 chromatograph with high temperature capillary columns using FID and MS detectors. ^1H and ^{31}P NMR spectra were measured with a Bruker AMX 300 and IR spectra on a Bruker IFS113v spectrometer. $RhCl_3 \cdot 3H_2O$ (Aldrich) was used as received. 1-Methyl-1-azonia-3,5-diaza-7-phosphatricyclo[3.3.1.1^{3,7}]decane iodide (mtpa$^+$I$^-$)[12] and $[Rh_2Cl_2(CO)_4]$[23] were prepared according to literature.

[RhI(CO)(mtpa$^+$I$^-$)$_2$], 1. Method *(a)* A mixture of mtpa$^+$I$^-$ (0.0849 g, 0.284 mmol) and $[Rh_2Cl_2(CO)_4]$ (0.0276 g, 0.071 mmol) in methanol (20 cm^3) was stirred at room temperature for *ca.* 1 h and then at 0 °C for 0.25 h. The yellow complex **1** was filtered off, washed with cold methanol and dried *in vacuo* (yield 0.0646 g, 53.1%). Anal. calcd for $C_{15}H_{30}I_3N_6OP_2Rh$ (fw 856.01): C, 21.05; H, 3.53; N, 9.82; I, 44.48. Found: C, 21.42; H, 3.70; N, 9.64; I, 44.22. ^1H NMR (D_2O, r.t.): δ 2.76 (s, 6H, N^+CH_3); 4.16 H^A, 4.31 H^B (d, J_{AB} = 15.4 Hz, 8H; PCH^AH^BN); 4.33 H^A, 4.49 H^B (d, J_{AB} = 13.8 Hz, 4H NCH^AH^BN); 4.62 (s, 4H, PCH_2N^+); 4.83 H^A, 4.95 H^B (d, J_{AB} = 12.1 Hz, 8H, $NCH^AH^BN^+$), $^{31}P\{^1H\}$ NMR: δ −50.5 (d, J_{PRh} = 123.6 Hz); for mtpa$^+$I$^-$ δ −95, IR: ν(CO) = 1990 cm^{-1}.

Method (*b*) The method of preparation was the same as above, however two equivalents of NaI were added and the volume of the solvent was reduced to 75%. A mixture of mtpa$^+$I$^-$ (0.0928 g, 0.310 mmol) and $[Rh_2Cl_2(CO)_4]$ (0.0302 g, 0.0776 mmol) in methanol (15 cm^3) and NaI (0.025 g, 0.155 mmol) was stirred at room temperature for *ca.* 1 h The yellow complex **1** was filtered off, washed with cold methanol and dried *in vacuo* (yield: 0.103 g, 85%)

[RhI(CO)(mtpa$^+$I$^-$)$_3$] · 4H$_2$O, 2. A mixture of mtpa$^+$I$^-$ (0.1302 g, 0.435 mmol), $[Rh_2Cl_2(CO)_4]$ (0.0282 g, 0.0726 mmol) and NaI (0.0218 g, 0.1452 mmol) in H_2O (5 cm^3) was stirred under a nitrogen atmosphere for 1 h at room temperature. The brown-red compound **2** was filtered off, washed with methanol and dried *in vacuo* (yield 0.169 g, 95 %). The yield of product in analogous reaction carried out in the absence of NaI is equal to 72 %. Anal. Calcd. for $C_{22}H_{53}I_4N_9O_5P_3Rh$ (fw 1227.16): C, 21.53; H, 4.35; N, 10.27; I, 41.37. Found: C, 21.93; H, 4.03; N, 10.45; I, 40.96. ^1H NMR (D_2O, 278 K): δ 2.71 (s, 9H, N^+CH_3); 4.13 H^A, 4.22 H^B (d, J_{AB} = 15.5 Hz, 12H, PCH^AH^BN); 4.32 H^A, 4.48 H^B (d, J_{AB} = 13.9 Hz, 6H, NCH^AH^BN); 4.57 (s, 6H, PCH_2N^+); 4.81 H^A, 4.93 H^B (d, J_{AB} = 12.2 Hz, 12H, $NCH^AH^BN^+$), $^{31}P\{^1H\}$ NMR: δ − 58.4 (br s), IR: ν(CO) = 2001 cm^{-1}.

X-Ray structural determinations

Dark red, X-ray quality crystals of complex **2** were grown from aqueous solution under nitrogen atmosphere. Data collection was performed on a Kuma-Diffraction KM-4 diffractometer. The data were collected to a maximum θ of 44^0 in an ω/2θ scan mode at room temperature. Intensities were corrected by use of the DECAY program.[24] An empirical absorption correction was applied (ψ-scan method), using the EAC program.[24,25] The data were also corrected for Lorentz and polarization effects. The structure was solved by direct methods and refined by full-matrix least-squares on *F* with anisotropic temperature factors for non-hydrogen atoms. H atoms were located from *F* maps and their parameters were not refined. All calculations were performed with the SHELXTL system[26] and CSU program.[27] CCDC reference number 440/078.

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