APPLIED ORGANOMETALLIC CHEMISTRY
Appl. Organometal. Chem. **13**, 829–836 (1999)

New Rhodium(I) Water-soluble Complexes with 1-Alkyl-1-azonia-3,5-diaza-7-phospha-adamantane Iodides and their Catalytic Activity

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The water-soluble phosphine ligands, 1,3,5-triaza-7-phosphatricyclo[3.3.1.1^{3,7}]decane (tpa) and 1-alkyl-1-azonia-3,5-diaza-7-phosphatricyclo[3.3.1.1^{3,7}]decane iodides (Rtpa$^+$I$^-$), with alkyl=methyl(mtpa$^+$I$^-$), ethyl (etpa$^+$I$^-$) and n-propyl, (ptpa$^+$I$^-$), and mtpa$^+$Cl$^-$ react with [Rh$_2$Cl$_2$(CO)$_4$] giving the rhodium(I) complexes [RhCl(CO)(tpa)$_2$], [RhI(CO)(Rtpa$^+$I$^-$)$_2$], [RhCl(CO)(mtpa$^+$Cl$^-$)$_3$] and [RhI(CO)(Rtpa$^+$I$^-$)$_3$]. The properties and reactivities of the complexes have been investigated using ^{1}H and ^{31}PNMR and IR spectroscopies. The five-coordinate complexes in solutions show dynamic properties. The complexes are catalysts of the water-gas shift reaction, the hydrogenation of C=C and C=O bonds, the hydroformylation of alkenes and the isomerization of unsaturated compounds.

Keywords: rhodium(I) complexes; water-soluble phosphines; homogeneous catalysis; hydrogenation; hydroformylation

Received 14 September 1998; accepted 15 March 1999

INTRODUCTION

Water-soluble organometallic chemistry has received significant interest in the last few years. The basic problem of homogeneously catalyzed processes is the separation of the product from the solvent and the catalyst, which is soluble in it. Water-soluble catalysts combine the advantages of homogeneous and heterogeneous catalysis: simple separation of the product from the catalyst and high activity and selectivity.[1–5] 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.[1–11] Most investigations of metal–phosphine complexes involve 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)[10,12–18] and 1-methyl-1-azonia-3,5-diaza-7-phosphatricyclo-[3.3.1.1^{3,7}]decane iodide (mtpa$^+$I$^-$) (Fig. 1). The cone angle for the first phosphine is 102 °[12,13,16,18] and for mtpa$^+$I$^-$ it is approximately the same.[18–20] Thus properties of complexes with these ligands should depend mainly on their electronic properties. We describe here rhodium(I) complexes with 1,3,5-triaza-7-phosphatricyclo-[3.3.1.1^{3,7}]decane (tpa) and its alkylazonia derivatives: 1-methyl- (mtpa$^+$I$^-$ and mtpa$^+$Cl$^-$), 1-ethyl-(etpa$^+$I$^-$) and 1-propyl-1-azonia-3,5-diaza-7-phosphatricyclo[3.3.1.1^{3,7}]decane iodide (ptpa$^+$I$^-$)

EXPERIMENTAL

Synthesis and catalytic reactions

All manipulation were carried out under an 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 $H_2 + CO$ or H_2 with several evacuation/refill cycles. $RhCl_3 \cdot 3H_2O$ (Aldrich) was used as re-

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Contract/grant sponsor: Committee of Scientific Research, KBN; Contract/grant number: 3 T09 092 10.

 CCC 0268–2605/99/110829–08 $17.50

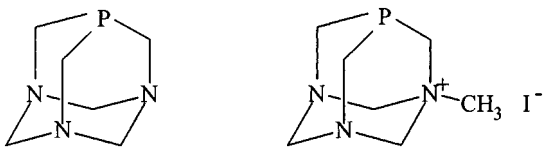

Figure 1 Structure of tpa and $mtpa^+I^-$.

ceived. Tpa and $mtpa^+I^-$,[14] $[Rh_2Cl_2(CO)_4]$,[21] $[RhCl(CO)(tpa)_2]$ (**1**),[10] $[RhI(CO)(mtpa^+I^-)_2]$ (**2**),[20] and $[RhI(CO)(mtpa^+I^-)_3]\cdot 4H_2O$ (**5**)[20] were prepared as reported in the literature.

Physical measurements

Infrared (IR) spectra (KBr pellets and Nujol mulls) were recorded on a Bruker IFS113v instrument and ^1H NMR and ^{31}P NMR on a Bruker 300 AMX. Chromatographic measurements were carried out on an HP5990 chromatograph using FID, TCD and MS detectors. Elemental analyses were performed on a Perkin-Elmer 2400 CHN analyzer.

Synthesis of ligands: $mtpa^+I^-$, $etpa^+I^-$ and $ptpa^+I^-$

A mixture of tpa (1.000 g, 6.37 mmol) and RI (6.37 mmol; MeI 0.904 g, EtI 0.994 g, crnPrI 1.083 g) was refluxed in 30 cm^3 of acetone for 1 h. The white product was filtered off and washed with THF. Yields: $mtpa^+I^-$ 1.733 g (91%), $etpa^+I^-$ 1.695 g (85%) and $ptpa^+I^-$ 1.480 g (71%). $^{31}P\{^1H\}$ NMR in D_2O (δ): −95.0 ppm ($mtpa^+I^-$); −81.3 ppm ($etpa^+I^-$); −82.7 ppm ($ptpa^+I^-$).

Synthesis of $mtpa^+ Cl^-$

A solution of $mtpa^+I^-$ (0.388 g) in water (4 cm^3) was poured into a column containing anion exchanger (Dowex 1). After elution, the solution containing product was evaporated to dryness under vacuum and then recrystallized from ethanol. Yield: 0.190 g (71%). $^{31}P\{^1H\}$ NMR in D_2O (δ) −95.0 ppm.

Synthesis of $[RhI(CO)(Rtpa^+I^-)_2]2EtOH$ (R = C_2H_5, 3; R = C_3H_7, 4

A mixture of $Rtpa^+I^-$ (1.2 mmol; $etpa^+I^-$ 0.3756 g on $ptpa^+I^-$ 0.3924 g) and $Rh_2Cl_2(CO)_2$ (0.3 mmol, 0.1167 g) in ethanol (20 cm^3) was stirred at room temperature for *ca* 1 h. The yellow–orange product was filtered off, washed with cold ethanol and dried *in vacuo*. Yield: **3**, 0.3806 g, 65%, **4**, 0.3675 g, 61%. Analysis: calcd for **3**, $C_{21}H_{46}I_3N_6O_3P_2Rh$: C, 25.84; H, 4.75; N, 8.61; for **4**, $C_{23}H_{50}I_3N_6O_3P_2Rh$: C, 27.51; H, 5.02; N, 8.37. Found for **3**, C, 25.76; H, 4.70; N, 9.57%, for **4**, C, 27.06; H, 4.92; N, 9.0%.

Synthesis of $[RhCl(CO)(mtpa^+Cl^-)_3]$, 6

A mixture of $mtpa^+Cl^-$ (0.1158 g, 0.558 mmol) and $Rh_2Cl_2(CO)_2$ (0.0362 g, 0.093 mmol) in water (5 cm^3) was stirred at room temperature for *ca* 30 min. The solvent was removed under reduced pressure. The orange product was washed with diethyl ether and a small amount of cold THF and dried *in vacuo* (yields 0.1241 g, 85%). Analysis calcd for $C_{22}H_{45}Cl_4N_9OP_3Rh$: C, 33.48; H, 5.75; N, 15.97; Cl, 17.77. Found: C, 33.81; H, 5.76; N, 15.10; Cl, 16.38%.

synthesis of $[RhI(CO)(Rtpa^+I^-)_3]\cdot 4H_2O$ (R = C_2H_5, 7; R = C_3H_7, 8)

A mixture of $Rtpa^+I^-$ (0.5 mmol; $etpa^+I^-$ 0.1565 g or $ptpa^+I^-$ 0.1635 g) and $Rh_2Cl_2(CO)_2$ (0.083 mmol, 0.0324 g) in water (5 cm^3) was stirred at room temperature for *ca* 1 h. The orange product was filtered off, washed with cold ethanol and dried *in vacuo*. Yield: **7**, 0.1590 g, 74%; **8**, 0.1511 g, 69%. Analysis: calcd for **7**, $C_{25}H_{59}I_4N_9O_5P_3Rh$: C, 23.31; H, 4.58; N, 9.79; **8**, $C_{28}H_{65}I_4N_9O_5P_3Rh$: C, 25.63; H, 4.96; N, 9.96. Found for: **7**, C, 23.91; H, 4.40; N, 10.01% do for; **8**, C, 25.87; H, 4.90; N, 9.98%.

RESULTS AND DISCUSSION

Synthesis

Treatment of $[Rh_2Cl_2(CO)_4]$ with 1,3,5-triaza-7-phosphatricyclo[3.3.1.1^{3,7}]decane (tpa) and its 1-alkyl-1-azonia-3,5-diaza-7-phosphatricyclo-[3.3.1.1^{3,7}]decane iodide derivatives in methanol, ethanol and water at stoichiometric ratios afforded the complexes $[RhCl(CO)(tpa)_2]$ **(1)**, $[RhI(CO)(mtpa^+I^-)_2]$ **(2)**, $[RhI(CO)(etpa^+I^-)_2]\cdot 2EtOH$ **(3)**, $[RhI(CO)(ptpa^+I^-)_2]\cdot 2EtOH$ **(4)**, $[RhI(CO)(mtpa^+I^-)_3]\cdot 4H_2O$ **(5)**, $[RhCl(CO)(etpa^+Cl^-)_3]$ **(6)**, $[RhI(CO)(etpa^+I^-)_3]\cdot 4H_2O$ **(7)**, and $[RhI(CO)(ptpa^+I^-)_3\cdot 4H_2O$ **(8)**. In reactions of $[Rh_2Cl_2(CO)_4]$

Table 1 ^{1}H NMR spectra of rhodium(I) complexes with phospha-adamantanes

Compound	RN^+ δ(ppm); [J (Hz)]	PCH^AH^BN δH^A, δH^B (ppm); [J(AB) (Hz)]	PCH^AH^BN J(AX), J(BX) (Hz)	PCH_2N^+ δ(ppm) m($J(PCH_2)$, (Hz)	NCH^AH^BN δH^A, δH^B (ppm); [J(AB) (Hz)]	$^+NCH^AH^BN$ δH^A, δH^B [ppm]; [J(AB) (Hz)]
tpa ($CDCl_3$)		4.03, d (PCH_2N) [9.5]; 6H			4.58, s (NCH_2N); 6H	
tpa (D_2O)		3.94, d (PCH_2N) [9.6]; 6H			4.46, 4.39 (12.62); 6H	
$mtpa^+I^-$	CH_3: 2.62, s; 3H	3.84, 3.72 [14.06]; 4H	13.54, 9.55	4.22, d [6.72]; 2H	4.47, 4.31 [14.05]; 2H	4.82, 4.70 [11.39]; 4H
$etpa^+I^-$	CH_3: 1.30, t [6.92]; 3H CH_2: 2.98, q [7.54]; 2H	3.97, 3.89 [9.19]; 4H	14.97, 14.50	4.34, d [6.39]; 2H	4.58, 4.45 [13.67]; 2H	5.01, 4.83 [11.36]; 4H
$ptpa^+I^-$	CH_3: 1.02, t [7.25]; 3H CH_2: 2.86, 1.79, 2 m; 4H	4.00, 3.92 [10.80]; 4H	15.69, 15.16	4.39, d [6.33]; 2H	4.62, 4.48 [15.72]; 2H	5.04, 4.86 [11.32]; 4H
$mtpa^+Cl^-$	CH_3: 2.61, s; 3H	3.83, 3.70 [14.76]; 4H	15.03, 9.70	4.21, d [6.60]; 2H	4.54, 4.30 [13.78]; 2H	4.86, 4.70 [12.87]; 4H
1 (D_2O)		4.12, s; (PCH_2N) 12H			4.42, 4.38 [13.06]; 12H	
1 ($CDCl_3$)		4.27, s; (PCH_2N) 12H			4.53, s; (NCH_2N) 12H	
3 (213 K)	CH_3: 1.17, t [7.04]; 6H CH_2: 3.10, q [7.37]; 4H	4.27, 4.22 [15.52]; 8H		4.63, s; 4H	4.63, 4.44 [13.58]; 4H	5.05, 4.88 [11.07]; 8H
4 (223 K)	CH_3: 1.04, br m; 6H CH_2:, 3.06, 1.82, 2 br m; 8H	3.97, 3.85 [10.39]; 8H		4.76, s, 4H	4.55, 4.45 [12.00]; 4H	5.00, 4.92 [9.01]; 8H
6	CH_3: 2.74, s; 9H	4.21, 4.07 [15.45]; 12H		4.54, s; 6H	4.49, 4.33 [14.09]; 6H	4.94, 4.82 [12.02]; 12H
7	CH_3; 1.18, t[7.50]; 9H CH_2: 3.00, q [7.50]; 6H	4.15, 4.03 [15.64]; 12H		4.41, s; 6H	4.49, 4.32 [13.57]; 6H	4.92, 4.70 [11.89]; 12H
8	CH_3: 1.02, t [7.30]; 9H CH_2: 2.84, 1.80, 2 m; 12H	4.02, 3.93 [15.39]; 12H		4.38, d (4.53); 6H	4.55, 4.45 [13.66]; 6H	5.03, 4.83 [10.94]; 12H

with the alkylazoniaphosphine iodides, complexes with coordinated iodo ligands are always formed. The complexes are soluble in water and methanol, slightly soluble in higher alcohols and other polar solvents, and insoluble in nonpolar solvents. The complexes are air-stable in the solid state, but in solution they are oxidized in air with loss of carbonyl ligand and formation of the appropriate phosphine oxide. All complexes have been characterized by a combination of elemental analysis, IR, and ^{1}H and ^{31}P NMR spectra.

The ^{1}H and $^{31}P\{^1H\}$ NMR and IR spectra are given in Table 1 and 2. The spectra indicate that, in solution, complexes **1–4** exhibit *trans* structure; both chemical shifts and ^1J(RhP) are typical of *trans*-[$RhX(CO)(PR_3)_2$].

Table 2 $^{31}P\{^{1}H\}$ NMR and IR spectra of rhodium(I) complexes with phospha-adamantanes

Compound	$\delta^{31}P\{^{1}H\}$ NMR (ppm) [J(P—Rh) (Hz)]	$\Delta\delta^{31}P\{^{1}H\}$ NMR[a] (ppm)	IR ν(CO) (cm^{-1})
tpa	−98.3		
$mtpa^{+}I^{-}$	−95.0		
$etpa^{+}I^{-}$	−81.3		
$ptpa^{+}I^{-}$	−82.7		
$mtpa^{+}Cl^{-}$	−95.0		
1[10]	−60.1 d [127.0]	38.2	1963
2[20]	−50.2 d [123.6]	44.8	1990
3[b]	−49.1 d [131.4]	32.2	1982
4[c]	−46.8 [125.7]	35.9	1987
5[20]	−58.4, s br	36.6	2001
6	−47.8, s br	47.2	1996
7	−43.5, s br	37.8	1999
8	−42.0, s br	40.7	2000

[a] $\Delta\delta^{31}P\{H\} = \delta^{31}P\{^{1}H\}_{complex} - \delta^{31}P\{H\}_{ligand}$.
[b] Recorded at 213 K in CD_3OD.
[c] Recorded at 223 K in CD_3OD.

The ^{31}P coordination chemical shift ($\Delta\delta^{31}P$) = $\delta_{complex} - \delta_{ligand}$ for these complexes changes in the range 32.2–44.8 ppm. The complexes **5–8** show dynamic properties. In the $^{31}P\{^{1}H\}$ NMR spectra of these compounds in D_2O at 20 °C only one signal, in the range −42.0 to −58.4 ppm, is observed. It is very broad at 5 °C and as the temperature is increased the resonance narrows, but even at 85 °C spin coupling between ^{103}Rh and ^{31}P was not observed. This indicates that the fluxional process is intermolecular. Thus five-coordinate complexes in solution give a mixture of several complexes with different geometries, e.g. isomers of trigonal-bipyramidal and square-pyramidal complexes.

In aqueous solution all complexes are relatively stable in an inert atmosphere, in contrast to $RhCl(tpa)_3$, which is oxidized with formation of tpaO owing to the oxidative addition of water.[23,24] However, complexes **2–8** in methanol/water and wet acetonitrile solutions are oxidized, even with only traces of oxygen, giving $RtpaO^{+}I^{-}$.

The $mtpa^{+}I^{-}$, $etpa^{+}I^{-}$ and $ptpa^{+}I^{-}$ ligands and complexes **2–8** give ^{1}H NMR spectra typical of nonequivalent protons of NCH_2N, NCH_2N^{+} and PCH_2N methylene groups, apart from the PCH_2N^{+} group, for which only coupling with ^{31}P is observed (Table 1). Thus, in these compounds equivalence of the methylene protons is removed owing to the leakage of the alkyl group to one of the nitrogen atoms. The ^{1}H NMR spectra of tpa and complex **1** in $CDCl_3$ are simple, since axial and equatorial differences of methylene protons were not observed (Table 1).

Complexes $RhCl(CO)(tpa)_2$ **(1)** and $RhI(CO)(Rtpa^{+}I^{-})_3$ are efficient catalysts for the watergas shift reaction. The rates of reaction in the presence of **1** and **5** at 80 °C are 6 mol CO_2 (mol RH)$^{-1}$ h^{-1} ($p$co = 0.1 MPa),[10] and 140 mol CO_2 (mol Rh) h^{-1} ($p$co = 8 MPa), respectively. The compounds **2** and **5** catalyse the hydrogenation of aldehydes, in contrast to rhodium compounds with tpa.[10,12,13,23] They are also catalysts for the aldol condensation (Table 3). In the case of 1-butanal, the yields of $EtC(nPrCHOH)_2CHO$ are 89% and 77% for condensations catalyzed by complexes **2** and **5**, respectively. However, during the reduction of 1-pentanal, 1-hexanal and 1-heptanal, the appropriate alcohols are mainly formed (*ca* 80–85%). A much higher yield from the condensation for n-butanal, in comparison with that for higher aldehydes, indicates that an important role is played by the bulkiness of the coordinated RCHO molecule. This conclusion is confirmed also by the higher yield of $EtC(nPrCHOH)_2CHO$ obtained in the presence of complex **2** than in the reaction catalyzed by trigonal-bipyramidal compound **5**. The average turnover frequency (TOF) for the reduction of aldehydes is *ca* 100 mol RCHO (mol Rh)$^{-1}h^{-1}$ at $p(H_2)$ = 8 MPa. The C=C bonds are reduced more easily than C=O. Acrolein (CH_2 =CHCHO), crotonaldehyde (MeCH=CHCHO) and cinnamaldehyde (PhCH=CHCHO) at $p(H_2)$ = 0.1 MPa are reduced to aldehydes (Table 4).

These complexes are also active catalysts for the hydrogenation of unsaturated acids and alcohols, which are relatively quickly reduced under mild conditions (Table 4). The rates of hydrogenation of unsaturated compounds strongly depend on their

Table 3 Two-phase hydroformylation of hexlene and hydrogenation of aldehydes by rhodium complexes **1**, **2** and **5**

Catalyst	TOF[a]	Yield (%),	Products (%)
(a) Hydroformylation of hexlene[b]			
1	162	98	n-$C_6H_{13}CHO$ 53; $C_4H_9CH(CH_3)CHO$ 41; n-$C_6H_{13}COOH$ 2.5; $C_4H_9CH(CH_3)COOH$ 1.5
2	117	70	n-$C_6H_{13}CHO$ 29; $C_4H_9CH(CH_3)CHO$ 25; $CH_3CH = x\ CHC_3H_7$ 10; $CH_3CH_2CH = CHC_2H_5$ 6
2/mtpa = 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
5	167	~100	n-$C_6H_{13}CHO$ 3.1; $C_4H_9CH(CH_3)CHO$ 2.2; n-C_6H_{14} 94; n-$C_6H_{13}COOH$ 0.1; n-$C_7H_{15}OH$ 0.5
5/Co = 1:6	163	98	n-$C_6H_{13}CHO$ 54; $C_4H_9CH(CH_3)CHO$ 36; n-C_6H_{14} 7.6

Catalyst	TOF[a]	Yield (%),	Substrate	Products (%)
(b) Hydrogenation of aldehydes[c]				
2	106	95	nPrCHO	nBuOH 6; $EtC(nPr\ CHOH)_2CHO$ 89
2	88	79	n-$C_5H_{11}CHO$	n-$C_6H_{13}OH$ 79
5	109	98	nPrCHO	nBuOH 6; PrCH=CEtCHO 6; $BuEtCHCH_2OH$ 2 $EtC(nPrCHOH)_2CHO$ 77; nPrCOOnBu 1
5	108	97	n-C_4H_9CHO	n-$C_5H_{11}OH$ 80; nBuCH—C(nPr)CHO 3; others 14
5	108	97	n-$C_5H_{11}CHO$	n-$C_6H_{13}OH$ 84; n-$C_5H_{11}CH$—C(nBu)CHO 6; n-$C_6H_{13}CH(nBu)CH_2OH$ 2; others 8
5	106	95	n-$C_6H_{13}CHO$	n-$C_7H_{15}OH$ 78; n-$C_6H_{13}CH$—C(n-C_5H_{11})CHO 12; n-$C_7H_{15}CH$(n-C_5H_{11})CHO 2; others 2

[a] Average TOF [mol substrate (mol Rh h)$^{-1}$].
[b] $p(CO) = p(H_2) = 3.0$ MPa; $T = 333$ K; **1**,**2** and **3**, 0.01 mmol; H_2O, 15 cm^3; hexlene, 30 mmol.
[c] $p(H_2) = 8.0$ MPa; $T = 353$ K; **2** and **5** 0.01 mmol; H_2O, 15 cm^3; substrate, 20 mmol.

structure. This indicates that the stabilities of complexes formed in reactions between the investigated complexes and unsaturated substrates [$RhX(CO)(Rtpa^+I^-)_n(R^1R^2C{=}CR^3R^4)$] depend on the nature of these latter. It is interesting that the initial rate of hydrogenation of fumaric acid is much higher than that of maleic acid. However, during the reaction, the rate of hydrogenation of fumaric acid diminishes and becomes comparable with that observed for maleic acid. This follows from the rather strong dependence of the hydrogenation rate on the concentration of fumaric acid. Complexes **2** and **5** also catalyze migration of the double bond. During hydroformylation of hex-1-ene in the presence of complex **2**, apart from hexane, the isomerization products hex-2-ene and hex-3-ene are also formed (Table 3). Many complexes present in equilibrium in solution are responsible for catalytic activity. This conclusion is confirmed by the dependence of the rate of allyl alcohol hydrogenation on the concentration of complex **5** and pH (Figs 2 and 3). The maximum rate of hydrogenation was observed at a concentration of compound **5** equal to 0.3 mM. The rate of hydrogenation also depends strongly on the pH of the solution. Hydrogenation of allyl alcohol does not proceed below pH 3 and increases to *ca* 350 mol H_2 (mol Rh)$^{-1}$ h^{-1} at pH 7, and then slowly decreases. The dependence of the rate of reduction of allyl alcohol on its concentration (Fig 4) indicates that stabilities of rhodium complexes with C=C bonds of unsaturated substrates are considerable. Usually, activation of dihydrogen by alkene complexes of transition elements formed in catalytic systems is difficult. Therefore, at higher concentrations of allyl alcohol, the concentration of species capable of activating dihydrogen diminishes and the rate of hydrogenation strongly decreases. During the catalytic hydrogenation of C=C bonds, the carbonyl ligand undergoes a water-gas shift reaction. Complexes obtained after hydrogenation of allyl alcohol do not contain CO ligands. Thus, the hydrogenation reaction is most probably catalyzed by iodo complexes $RhI(Rtpa^+I^-)_n$. The catalytic activity of rhodium(I) complexes with $mtpa^+I^-$ is comparable with that of $[RhCl(tpa)_3]$.[23] Very interesting is the influence of different cations and anions, including 3*d* metal compounds, on the rate of hydrogenation (Table 4 and Fig. 5). It is likely that these compounds are in

Table 4 Hydrogenation of unsaturated substrates by rhodium complexes **5**, **6**, **7** and **8**[a]

Catalyst	Substrate	Product	Number of phases	Init. rate [mol (*h* mol Rh)$^{-1}$]
5	*cis*-HOOCCH=CHCOOH	$HOOCCH_2CH_2COOH$	1	110
5	*trans*-HOOCCH=CHCOOH	$HOOCCH_2CH_2COOH$	1	210
5	CH_2=C(COOH)CH_2COOH	$CH_3CH(COOH)CH_2COOH$	1	40
5	CH_2=CHCOOH	CH_3CH_2COOH	1	65
5	CH_2=CHCH_2OH	$CH_3CH_2CH_2OH$	1	167
5/Mn^{2+b}	CH_2=CHCH_2OH	$CH_3CH_2CH_2OH$	1	130
5/Fe^{2+b}	CH_2=CHCH_2OH	$CH_3CH_2CH_2OH$	1	110
5/Co^{2+b}	CH_2=CHCH_2OH	$CH_3CH_2CH_2OH$	1	213
5/Ni^{2+b}	CH_2=CHCH_2OH	$CH_3CH_2CH_2OH$	1	170
5/Zn^{2+b}	CH_2=CHCH_2OH	$CH_3CH_2CH_2OH$	1	123
5/NaOAc = 1:2	CH_2=CHCH_2OH	$CH_3CH_2CH_2OH$	1	221
5/NaOAc/$Co(OAc)_2$ = 1:2:2	CH_2=CHCH_2OH	$CH_3CH_2CH_2OH$	1	203
5/NaOAc = 1:20	CH_2=CHCH_2OH	$CH_3CH_2CH_2OH$	1	191
5/NaOAc/$Co(OAc)_2$ = 1:20:2	CH_2=CHCH_2OH	$CH_3CH_2CH_2OH$	1	180
5/NaOAc/$Co(OAc)_2$ = 1:60:2	CH_2=CHCH_2OH	$CH_3CH_2CH_2OH$	1	66
6	CH_2=CHCH_2OH	$CH_3CH_2CH_2OH$	1	28
7	CH_2=CHCH_2OH	$CH_3CH_2CH_2OH$	1	58
8	CH_2=CHCH_2OH	$CH_3CH_2CH_2OH$	1	49
5	CH_2=CHCHO	CH_3CH_2CHO	1	158
5	CH_2=CHCONH$_2$	$CH_3CH_2CONH_2$	1	81
5	*trans*-PhCH=CHCHO	$PhCH_2CH_2CHO$	2	68

[a] $p(H_2)$ = 0.1 MPa; 305 K; **5**–**8**, 0.005 mmol; H_2O, 15 cm^3; substrate, 10 mmol.
[b] **5**/MSO_4 = 1:1.

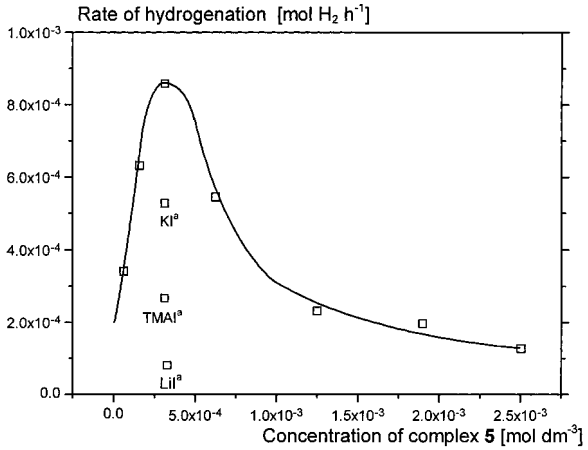

Figure 2 Dependence of the rate of hydrogenation of allyl alcohol on the concentration of complex **5**. Conditions: CH_2=CHCH_2OH, 10 mmol; H_2O, 15 cm^3; $p(H_2)$ = 0.1 MPa; T = 305 K. [a]KI/**5**, $[N(CH_3)]_4$I/**5** and LiI/**5** = 3:1.

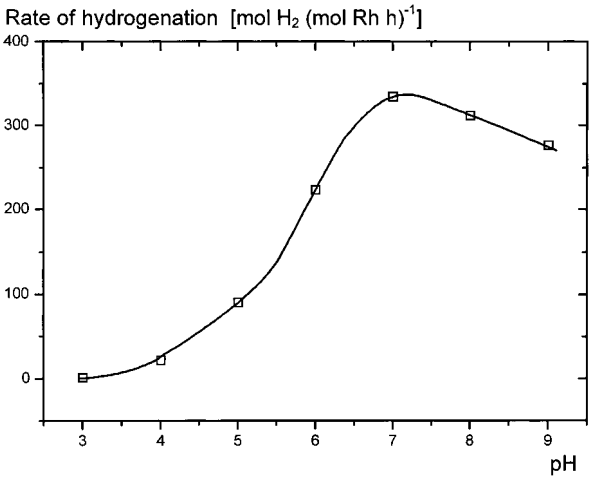

Figure 3 Dependence on pH of the rate of hydrogenation of allyl alcohol catalyzed by **5**. Conditions: **5** 0.005 mmol; H_2O, 15 cm^3; CH_2=CHCH_2OH, 10 mmol; $p(H_2)$ = 0.1 MPa; T = 305 K. Catalyst/substrate = 0.0005:1 (0.05%).

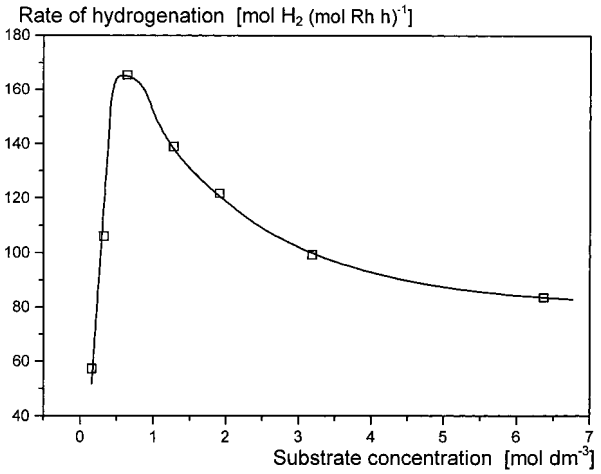

Figure 4 Dependence of the rate of hydrogenation of allyl alcohol catalyzed by **5** on substrate concentration. Conditions: **5**, 0.005 mmol; H_2O, 15 cm^3; substrate $CH_2{=}CHCH_2OH$ 10 mmol; $p(H_2)$ = 0.1 MPa; T = 305 K.

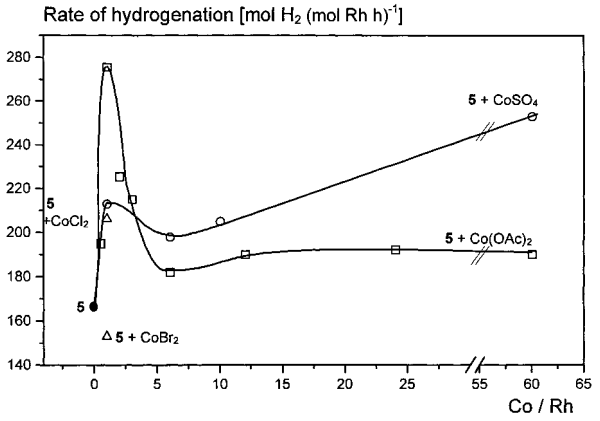

Figure 5 Dependence of the rate of hydrogenation of allyl alcohol on the Co^{2+}/**5** ratio. Conditions: **5**, 0.005 mmol; H_2O, 15 cm^3; $CH_2{=}CHCH_2OH$, 10 mmol; $p(H_2)$ = 0.1 MPa; T = 305 K.

the second coordination sphere or even coordinated with rhodium complexes containing tpa or $Rtpa^+I^-$ ligands (R = Me, Et, Pr) via the nitrogen atom. Considerable enhancement of the hydrogenation rate was observed after addition of cobalt(II) compounds. Activities of rhodium/cobalt catalytic systems increase in the series: $[Co(H_2O)_6]Cl_2 < [Co(H_2O)_6]SO_4 < Co(CH_3COO)_2{\cdot}4H_2O$. Unfortunately, we are not as yet able to obtain a binuclear complex with rhodium and cobalt central atoms. However, formation of N···H—O(H)—Co, N···H—O—C(Me)—O—Co or similar hydrogen bonds is also possible. Both coordination of cobalt(II) with the N atom of the $mtpa^+$ ligand and formation of hydrogen bonds can change the activity of the catalytic systems because these interactions influence (σ)-donor and π-acceptor properties of the phosphine ligand and the pK_a of the $Co(H_2O)_5(N)^{2+}$ moiety. The addition of salts can lead to the stabilization of phosphine complexes because of formation of an organized network of phosphine–cation–anion interactions. The most active catalytic system was obtained in the presence of cobalt(II) acetate at a Rh : Co ratio of 1:1 (TOF = 276; Fig. 5). Very important is the influence of CH_3COO^- ions on the catalytic activity of complex **5**. Addition of 2 mol of NaOAc per mol of **5** enhances the TOF for hydrogenation of allyl alcohol from 167 to 221. This suggests that in the case of $Co(OAc)_2$, both the Co^{2+} cation and the OAc^- anion play crucial roles in the increase in catalytic activity. Complexes **2** and **5** containing iodo ligands are better catalysts for hydrogenation of C=C bonds than chloro complexes since the rate of hydrogenation of allyl alcohol in the presence of $[RhCl(CO)(mtpa^+Cl^-)_2]$ or $[RhCl(CO)(mtpa^+Cl^-)_3]$ is lower in comparison with the iodo complexes (Table 4). However, excess of iodide, ions diminishes the catalytic activity of **5**. After addition of LiI, NaI, KI and $[NMe_4]I$, the catalytic activity of **5** strongly decreased. In this case, the influence of the nature of the cation is also strong (Fig. 2). An increase in the number of carbon atoms in the alkyl substituent in $Rtpa^+I^-$ also leads to a decrease in catalytic activity (Table 4). Previously an effect of salts on activity and selectivity of $RhH(CO)(tppts)_3$[9,25,26] in the hydroformylation of alkenes, and $RuCl_2(tppts)_3$ in the hydrogenation of aldehydes, had been found.[27] The TOF values for hydroformylation of hex-1-ene in the presence of complexes **2** and **5** are higher (*ca* 20%) than those for $RhH(CO)(tppts)_3$[9,25,26] and the activities of **2**, **5** and $RuCl_2(tppts)_3$ in the hydrogenation of aldehydes are comparable.[27]

Complexes **1**, **2** and **5** catalyze hydroformylation and carboxylation of alkenes (Table 3). The biphasic reaction of hex-1-ene with CO and H_2 in H_2O in the presence of **2** gives heptan-1-al, 2-methylhexanal and hex-2-ene and hex-3-ene. The product of the reaction contained 29% n-aldehyde, 25% isoaldehyde and 45% hexenes. Compound **2** in the presence of excess of the phosphine catalyzes hydroformylation and carboxylation of alkenes. Reaction of hex-1-ene 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 excess of $mtpa^+I^-$, hex-1-ene is slowly hydrogenated with H_2/CO. Hydrocarboxylation of alkenes probably proceeds via migratory insertion of CO into the Rh–alkyl bond followed by nucleophilic attack of a 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 because the same products were obtained in reaction of hex-1-ene with H_2/CO_2 (1:1); however, the rate of reaction was five times slower and the yield of the acids was lower in comparison with the aldehydes. This indicates that hydroformylation of hex-1-ene in an H_2/CO_2 atmosphere proceeds owing to the reduction of CO_2 with H_2.

Complexes with $mtpa^+I^-$ show very strong hydrophilic properties and therefore their concentration in organic phases is very low in comparison with complexes containing the tpa ligand. Thus they are better catalysts for two-phase catalytic reactions than tpa complexes.

Acknowledgements The authors are grateful to the Committee of Scientific Research, KBN, for support of this work (Grant No. 3 T09A 092 10).

REFERENCES

1. F. Joó and A. Katho, *J. Mol. Catal. A: Chemical*, **116**, 3 (1997).
2. W. A. Herrmann and C. W. Kohlpaintner, *Angew. Chem., Int. Ed. Engl.* **32**, 1524 (1993); B. Cornils, and W. A. Herrmann (eds), *Applied Homogeneous Catalysis by Organometallic Complexes*, VCH, Weinheim, 1996; W. A. Herrmann, G. P. Albanese, R. B. Manetsberger, P. Lappe and H. Bahrmann, *Angew. Chem., Int. Ed. Engl.* **34**, 811 (1995); B. Cornils, in: *New Syntheses with Carbon Monoxide*, Falbe J. (ed), Springer Verlag, Berlin, 1980.
3. G. Süss-Fink, A. Meister and G. Meister, *Coord. Chem, Rev.* **143**, 97 (1995).
4. P. Kalck and F. Monteil, *Adv. Organometal. Chem.* **34**, 219 (1992).
5. W. Koelle, *Coord. Chem. Rev.* **135/136**, 623 (1994).
6. J. W. Ellis, K. N. Harrison, P. A. T. Hoye, A. G. Orpen, P. G. Pringle and M. B. Smith, *Inorg. Chem.* **31**, 3026 (1992); P. A. T. Hoye, P. G. Pringle, M. B. Smith and K. Worboys, *J. Chem. Soc., Dalton Trans.* 269 (1993).
7. T. L. Schull, J. C. Fettinger and A. D. Knight, *J. Chem. Soc., Chem. Commun.* 1487 (1995).
8. T. Bartik, H. Ding, B. Bartik and B. E. Hanson, *J. Mol. Catal. A: Chemical* **98**, 117 (1995).
9. H. Ding and B. E. Hanson, *J. Mol. Catal. A: Chemical* **99**, 131 (1995).
10. P. Pruchnik, P. Smoleński and I. Raksa, *Polish J. Chem.* **69**, 5 (1995).
11. K. Wajda-Hermanowicz, F. P. Pruchnik, M. Zuber, G. Rusek, E. Galdecka and Z. Galdecki, *Inorg. Chim. Acta* **232**, 207 (1995); E. Galdecka, Z. Galdecki, K. Wajda-Hermanowicz and F. P. Pruchnik, *J. Chem. Crystallogr.* **25**, 717 (1995).
12. D. J. Darensbourg, F. Joó, M. Kannisto, A. Katho and J. H. Reibenspies, *Organometallics* **11**, 1990 (1992).
13. D. J. Darensbourg, F. Joó, N. Kannisto, A. Katho, J. H. Reibenspies and D. J. Daigle, *Inorg. Chem.* **33**, 200 (1994).
14. D. J. Daigle, A. B. Pepperman Jr and S. L. Vail, *J. Heterocycl. Chem.* **11**, 407 (1974) 14. **12**, 579 (1975).
15. M. Y. Darensbourg and D. Daigle, *Inorg. Chem.* **14**, 1217 (1975).
16. J. R. DeLerno, L. M. Trefonas, M. Y. Darensbourg and R. J. Majeste, *Inorg. Chem.* **15**, 816 (1976).
17. J. P. Fackler Jr, R. J. Staples and Z. Assefa, *J. Chem. Soc., Chem. Commun.* 431 (1994).
18. Z. Assefa, B. G. McBurnett, R. J. Staples, J. P. Fackler Jr, B. Assmann, K. Angermeier and H. Schmidbaur, *Inorg. Chem.* **34**, 75 (1995).
19. J. M. Forward, J. P. Fackler Jr and R. J. Staples, *Organometallics* **14**, 4194 (1995).
20. F. P. Pruchnik, P. Smoleński, E. Galdecka and Z. Galdecki, *New J. Chem.* 1395 (1998).
21. F. P. Pruchnik, *Syntheses of Organometallic Compounds*, PWN, Warsaw, 1993.
22. J. M. Brown and A. G. Kent, *J. Chem. Soc., Perkin Trans. II* 1597 (1987).
23. D. J. Darensbourg, N. W. Stafford, F. Joó and J. H. Reibenspies, *J. Organometal. Chem.* **488**, 99 (1995); F. Joó, A. Cs. Benyei and D. J. Darensbourg, *J. Organometal. Chem.* **512**, 45 (1996).
24. V. V. Grushin and H. Alper, *Organometallics* **12**, 1890 (1993).
25. D. J. Darensbourg and C. J. Bischoff, *Inorg. Chem.* **32**, 47 (1993); R. M. Deshpande, Purwanto, H. Delmas and R. V. Chaudhari, *J. Mol. Catal. A: Chemical* **126**, 133 (1997).
26. H. Ding and B. E. Hanson, *Inorg. Chim. Acta* **229**, 329 (1995); *J. Chem. Soc., Chem. Commun.* 2747 (1994).
27. E. Fache, F. Senocq, C. Santini and J. M. Basset, *J. Chem. Soc., Chem. Commun.* 1776 (1990).

