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Rhodium(I) acetylacetonato complexes with functionalized phosphines

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Abstract

Rhodium(I) complexes [Rh(acac)(CO)(PR_3)] with 1,3,5-triaza-7-phosphatricyclo[3.3.1.1^{3,7}]decane (tpa), tris(2-cyanoethyl)phosphine (cyep), tris(3-sodium sulfonatophenyl)phosphine (tppts), tris(*o*-methoxyphenyl)phosphine (ompp), tris(*p*-methoxyphenyl)phosphine (pmpp), tris(2,4,6-trimethoxyphenyl)phosphine (tmpp), PPh_2(pyl), PPh$(pyl)_2$ and P$(pyl)_3$ (pyl = 2-pyridyl) have been synthesized and characterized with ^1H- and ^{31}P-NMR and IR spectra. The measured ^{31}P coordination chemical shifts, $\Delta\delta\,^{31}P\{^1H\}$, correlate well with ν(CO). Differences in ^1H chemical shifts of methyl groups of acac ligand, $\Delta\delta_{Me}$, depend both on steric and electronic properties of phosphine ligand. Thus $\Delta\delta_{Me}$ increases with decrease of $\Delta\delta\,^{31}P\{^1H\}$ and increases with increase of the cone angle of phosphine. Catalytic activity of complexes with tpa, cyep and tppts has been investigated. They are efficient catalysts for hydrogenation of C=C and C=O bonds, isomerization of alkenes and hydroformylation of alkenes. The mechanism of isomerization of allyl alcohol to propanal has been elucidated. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Rhodium(I) complexes; Acetylacetonate complexes; Water soluble phosphines; Homogeneous catalysis; Hydrogenation; Hydroformylation

1. Introduction

Complexes of transition metals with functionalized phosphines are thoroughly investigated because of their interesting catalytic activity. Complexes with water soluble phosphines are especially intensely studied. The basic problem of homogeneously catalyzed 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 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 the sulfonated arylphosphine ligands. Comparatively little work has been carried out on hydrophilic trialkylphosphines. Interesting ligands are 1,3,5-triaza-7-phosphatricyclo[3.3.1.1^{3,7}]decane (tpa) [10,12–18] (Fig. 1), tris(2-cyanoethyl)phosphine (cyep). The cone angle is 102° for the first phosphine [12,13,17,18] and 132° for the second [10]. Thus structure and reactivity of complexes with these ligands should depend mainly on their electronic properties. We describe herein rhodium(I) complexes with 1,3,5-triaza-7-phosphatricyclo[3.3.1.1^{3,7}]decane (tpa), tris(2-cyanoethyl)phosphine (cyep) and tris(3-sodium sulfonatophenyl)phosphine (tppts) as well as with methoxyphenylphosphines and 2-pyridylphosphines. Catalytic properties of complexes with tpa, cyep and tppts in one and two-phase systems are also described.

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2. Experimental details

2.1. Synthesis and catalytic reactions

All manipulation were carried out under inert atmosphere using standard Schlenk technique. 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), cyep (Strem), ompp (ABCR), pmpp (ABCR) and tmpp (Aldrich) were used as received. Tpa [14], tppts [15], $Rh(acac)(CO)_2$ [19], [Rh(acac)(CO)(PPh_2pyl)] [22], [Rh(acac)(CO)(PPhpyl$_2$)] [22], [Rh(acac)(CO)(Ppyl$_3$)] [22], were prepared as reported in the literature.

2.2. Physical measurement

IR spectra (KBr pellets and nujol mulls) were recorded on a Bruker IFS113v, NMR on a Bruker 300 AMX. Chromatographic measurements were carried out on a HP5990 chromatograph using FID, TCD and MS detectors. Elemental analyses were performed on a Perkin Elmer 2400 CHN analyzer.

2.3. Synthesis of [Rh(acac)(CO)(tpa)] (1)

A mixture of tpa (0.0561 g, 0.357 mmol) and $Rh(acac)(CO)_2$ (0.0922 g, 0.357 mmol) in ethanol (5 cm^3) was refluxed for ca. 3 h. The yellow product was filtered off, washed with cold ethanol and dried in vacuo (yield 0.089 g, 65%). Anal. Calc. for $C_{12}H_{19}N_3PO_3Rh$: C, 37.23; H, 4.95; N, 10.85.. Found: C, 36.70; H, 4.57; N, 10.65. ^{1}H-NMR (CD_3OD, r.t.): δ(ppm) CH, 5.60 (s, 1H); NCH_2N, 4.60 (s, 6H); PCH_2N, 4.27 (s, 6H); CH_3, 1.97 (s, 6H); $^{31}P\{^1H\}$-NMR: δ −25,5 d, J(RhP) = 172.4 Hz. IR: ν(CO) = 1958 cm^{-1}.

2.4. Synthesis of [Rh(acac)(CO)(tppts)] · 4H$_2$O (2)

A mixture of tppts (0.2201 g, 0.388 mmol) and $Rh(acac)(CO)_2$ (0.1000 g, 0.388 mmol) in methanol (8 cm^3) was stirred at room temperature (r.t.) for ca. 1 h and then concentrated to ca. 4 cm^3. After addition of diethyl ether (2 cm^3), the yellow product was filtered off, washed with cold methanol and diethyl ether and dried in vacuo (yield 0.234 g, 76%). Anal. Calc. for $C_{24}H_{27}Na_3PO_{16}RhS_3$: C, 33.10; H, 3.10. Found: C, 32.97; H, 2.96.^{1}H-NMR (CD_3OD, r.t.); δ(ppm): $C_6H_4SO_3^-$–H^2, 8.365 (d, 3H, $^3J(PH^2) = 11.5$ Hz); H^4, 7.944 (dq, 3H, $^4J(H^2H^4) = {}^4J(H^4H^6 = {}^5J(PH^4) = 1.5$ Hz); H^6, 7.631 (t, 3H, $^3J(PH^6 = 10.4$ Hz); H^5, 7.508 (dt, 3H, $^3J(H^5H^6) = {}^3J(H^4H^5) = 7.7$ Hz); CH, 5.60 (s, 1H); CH_3, 2.03 (s, 3H); CH_3, 1.67 (s, 3H); $^{31}P\{^1H\}$-NMR in CD_3OD: δ 51.5 ppm, d, ^1J(RhP) = 178.0 Hz. IR: ν(CO) = 1980 cm^{-1}

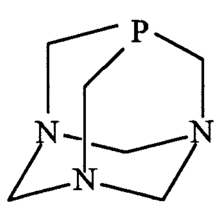


Fig. 1. Tpa.

2.5. Synthesis of [Rh(acac)(CO)(cyep)] (3)

A mixture of cyep (0.0606 g, 0.314 mmol) and $Rh(acac)(CO)_2$ (0.0810 g, 0.314 mmol) in acetone (5 cm^3) was stirred at r.t. for 0.5 h. The yellow solution was evaporated to dryness and the yellow compound was recrystallized from methanol. The product was washed with cold methanol and dried in vacuo (yield 0.1011 g, 76%). Anal. Calc. for $C_{15}H_{19}N_3PO_3Rh$: C, 42.55; H, 4.49; N, 9.92; P, 7.32. Found: C, 42.09; H, 4.32; N, 9.71; P, 7.26. ^{1}H-NMR (CD_3OD, r.t.): δ (ppm): CH, 5.60 (s, 1H); PCH_2 2.89(m, 6H), CH_2CN 2.37 (m, 6H); CH_3, 2.06 (s, 3H); CH_3, 1.97 (s, 3H); $^{31}P\{^1H\}$-NMR: δ 37.5 ppm, d, ^1J(PRh) = 171.2 Hz. IR: ν(CO) = 1968 cm^{-1}, ν(CN) = 2244 cm^{-1}.

2.6. Synthesis of [Rh(acac)(CO)P(2-MeOC$_6$H$_4$)$_3$] (4)

To a hot $Rh(acac)(CO)_2$ (0.0750 g, 0.291 mmol) solution in hexane (5 cm^3) P(2-MeOC$_6$H$_4$)$_3$ (0.103 g, 0291 mmol) in hexane (5 cm^3) was added. The mixture was refluxed for ca. 3 h. The yellow product was filtered off, washed with hexane and dried in vacuo. (yield 0.1130 g, 66%). Anal. Calc. for $C_{27}H_{28}O_6PRh$: C, 55.11; H, 5.82;. Found: C, 55.61; H, 5.77. ^{1}H-NMR ($CDCl_3$, r.t.): δ (ppm): $C_6H_4OCH_3$–H^6, 7.66 (dd, 3H, $^3J(H^6H^5) = 7.7$Hz, $^3J(PH^6) = 12.8$ Hz); H^4, 7.35 (t, 3H, $^3J(H^5H^{6,4}) = 7.7$ Hz); H^5, 6.89 (t, 3H, $^3J(H^4H^{5,3}) = 7.7$ Hz); H^3, 6.79 (dd, 3H, $^3J(H^3H^4) = 8.1$ Hz, $^4J(PH^3) =$ 4.5 Hz); CH, 5.28 (s, 1H), OCH_3, 3.51 (s, 9H); CH_3, 2.03 (s, 3H), CH_3, 1.43 (s, 3H); $^{31}P\{^1H\}$-NMR ($CDCl_3$): δ 33.9 ppm, d, ^1J(PRh) = 181.3 Hz. IR: ν(CO) = 1963 cm^{-1}.

2.7. Synthesis of [Rh(acac)(CO)P(4-MeOC$_6$H$_4$)$_3$] (5)

To a hot $Rh(acac)(CO)_2$ (0.0750 g, 0.291 mmol) solution in hexane (5 cm^3) P(4-MeOC$_6$H$_4$)$_3$ (0.103 g, 0291 mmol) in hexane (5 cm^3) was added. The mixture was refluxed for ca. 3 h. The yellow product was filtered off, washed with hexane and dried in vacuo. (yield 0.1260 g, 74%). Anal. Calc. for $C_{27}H_{28}O_6PRh$: C, 55.11;

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

Compound	$^{31}P\{^{1}H\}$-NMR δ (ppm) ($^{1}J_{RhP}$ (Hz))	$\Delta\delta\,^{31}P\{^{1}H\}$ -NMR (ppm)	$\Delta\delta$ CH_3(acac) ^{1}H-NMR (ppm)	Phosphine cone angle Θ (°)	IR ν(CO), (cm^{-1})	Reference
1	−25.5 d (172.4)[b]	72.8	0		1958	
2	50.8 d (178.0)[b]	54.3	0.36		1980	
3	37.5 d (171.2)[b]	67.8	0.09		1968 2244[a]	
4	33.9 d (181.3)[c]	73.2	0.60		1963	
5	43.5 d (175.6)[c]	64.3	0.44		1976	
6	−5.03 d (186.9)[d]	61.3	0.50		1944	
7	49.1 d (179.7)[c]	54,6	0.49		1981	[21]
8	52.7 d (180.2)[c]	55.9	0.57		1981	
9	56.6 d (177.0)[c]	58.5	0.46		1975	
10	61.1 d (174.7)[c]	61.5	0.43		1975	
11	58.9 d (182.1)[c]	47.6			1946	[23]
12	69.2 d (166)[c]	49.2	0.18		1962	[24]
13			0.46		1976	[27]
14			0.42		1976	[27]
15			0.52		1986	[27]
16			0.46		1980	[27]
tpa	−98.3[b]			102		[10]
tppts	−3.5[b]			145		[20]
cyep	−30.3[b]			132		[10]
ompp	−39.3[c]			200		[25]
pmpp	−10.8[c]			145		[25]
tmpp	−66.3[e]			184		[26]
PPh_3	−5.5[c]			145		
PPh_2pyl	−3.2[c]			145		
Pphpyl$_2$	−1.9[c]			145		
Ppyl$_3$	−0.4[c]			145		
PCy_3	11.3[c]			170		([23]b)
$P(Pr^{i})_3$	19.3			160		([23]b)
PPh_2(2-tol)				161		
P(3-tol)$_3$	−5.3[f]			165		[29]
$P(4\text{-}CF_3C_6H_4)_3$				145		
$P(4\text{-}FC_6H_4)_3$				145		

7, Rh(acac)(CO)(PPh_3); **8**, Rh(acac)(CO)(PPh_2pyl); **9**, Rh(acac)(CO)(PPhpyl$_2$); **10**, Rh(acac)(CO)(Ppyl$_3$); pyl, 2-pyridyl; **11**, Rh(acac)(CO)(PCy_3); **12**, Rh(acac)(CO)(PPr^{i}_3); **13**, Rh(acac)(CO)(PPh_2(2-tol)); **14**, Rh(acac)(CO)(P(3-tol)$_3$); **15**, Rh(acac)(CO)($P(4\text{-}CF_3C_6H_4)_3$); **16**, Rh(acac)(CO)($P(4\text{-}FC_6H_4)_3$).
[a] ν(CN), [b] Recorded as a CD_3OD solution. [c] Recorded as a $CDCl_3$ solution. [d] Recorded as a toluene-d_8 solution. [e] Recorded as a CD_3CN solution. [f] Recorded as a CD_2Cl_2 solution.

H, 5.82;. Found: C, 54.78; H, 5.06; ^{1}H-NMR ($CDCl_3$, r.t.): δ (ppm), $C_6H_4OCH_3$–$H^{2,6}$, 7.54 (dd, 6H, $^{3}J(H^{2,6}H^{3,5}) = 8,5$ Hz, $^{3}J(PH^{2,6}) = 10.6$ Hz); $H^{3,5}$, 6.87 (dd, 6H, $^{4}J(PH^{3,5}) = 2.1$ Hz); CH, 5.40(s, 1H), OCH_3, 3.82 (s, 9H); CH_3, 2.06 (s, 3H), CH_3, 1.62 (s, 3H); $^{31}P\{^{1}H\}$-NMR ($CDCl_3$): δ 43.5 ppm, d, $^{1}J(PRh) = 175.6$ Hz. IR: $\nu(CO) = 1976$ cm^{-1}.

2.8. *Synthesis of [Rh(acac)(CO)P(2,4,6-MeOC$_6$H$_4$)$_3$] (6)*

A hot solution of Rh(acac)$(CO)_2$ (0.0750 g, 0.291 mmol) in hexane (5 cm^3) was added dropwise to a suspension of P(2,4,6-MeOC$_6$H$_4$)$_3$ (0.1548 g, 0291 mmol) in hexane (10 cm^3). The mixture was refluxed for ca. 3 h. The orange product was filtered off, washed with hexane and dried in vacuo (yield 0.1770 g, 80%). Anal. Calc. for $C_{33}H_{40}O_{12}PRh$: C, 51.98; H, 5.29;. Found: C, 51.09; H, 5.17; ^{1}H-NMR (benzene d_6, r.t.): δ (ppm), $C_6H_2(OCH_3)_3$–$H^{3,5}$, 6.15 (d, 2H, $^{4}J(PH^{3,5}) = 3.5$ Hz); $H^{3,5}$, 6.02 (d, 4H, $^{4}J(PH^{3,5}) = 2.5$ Hz); CH, 5.18(s, 1H), OCH_3, 3.40, 3.34, 3.29 (s, 27H); CH_3, 2.90 (s, br, 3H); CH_3, 1.59 (s, br, 3H); $^{31}P\{^{1}H\}$-NMR (toluene d_8): δ −5.03 ppm, d, $^{1}J(PRh) = 186.9$ Hz. IR: $\nu(CO) =$ 1944 cm^{-1}.

3. Results and discussion

3.1. *Syntheses*

Treatment of Rh(acac)$(CO)_2$ with stoichiometric amounts of 1,3,5-triaza-7-phosphatricyclo[3.3.1.1^{3,7}]-

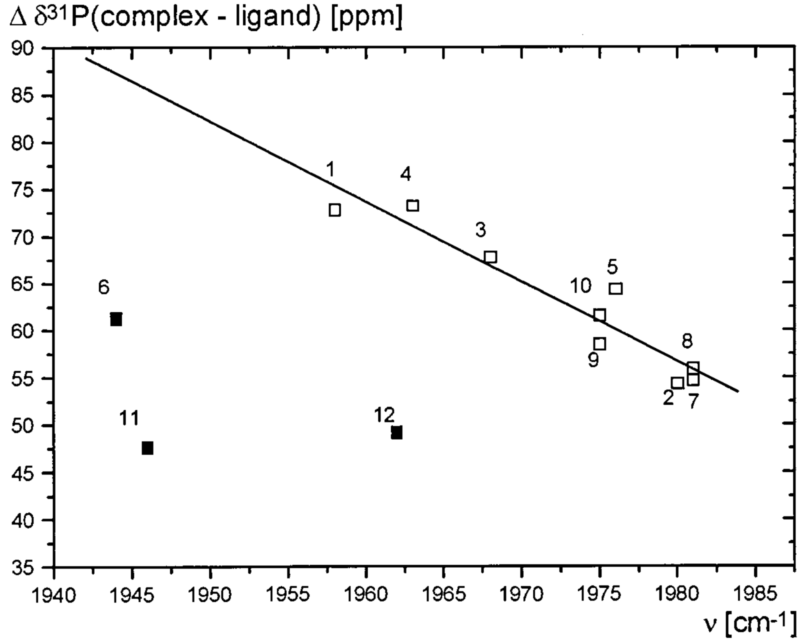


Fig. 2. The dependence of the coordination chemical shift $\Delta\delta(^{31}P)$ on the ν_{CO} stretching frequency for [Rh(acac)(CO)(PR_3)] complexes. $R = 0.95$; S.D. $= 2.48$. Points for **6**, **11** and **12** are not included in the regression line.

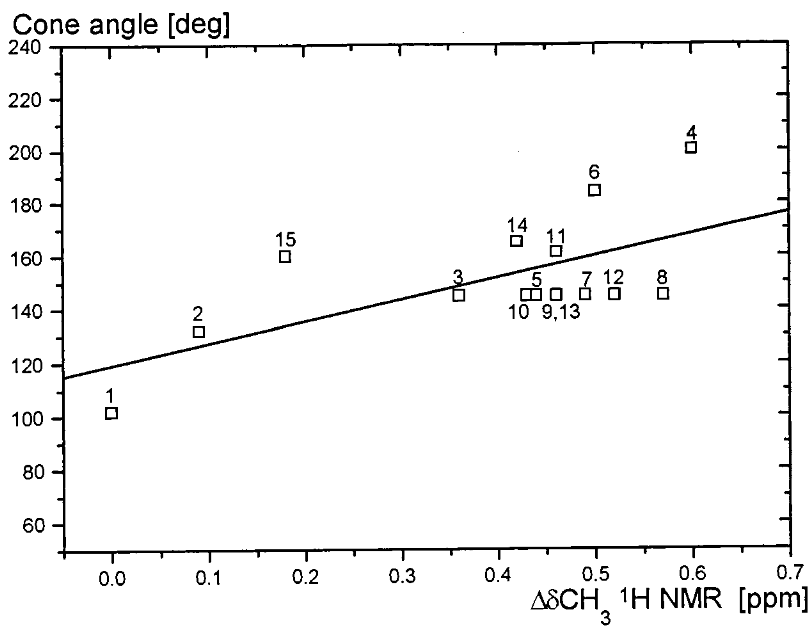


Fig. 3. The dependence of the cone angle on the $\Delta\delta CH_3$ ^{1}H-NMR for [Rh(acac)(CO)(PR_3)] complexes. $R = 0.64$; S.D. $= 17.81$.

decane (tpa), tris(2-cyanoethyl)phosphine (cyep) and tris(3-sodium sulfonatophenyl)phosphine (tppts) in methanol, ethanol or acetone at stoichiometric ratios afforded the complexes [Rh(acac)(CO)(tpa)] **1**, [Rh(acac)(CO)(tppts)]·4H_2O **2**, and [Rh(acac)(CO)-(cyep)] **3**. Coordination compounds with ompp, pmpp and tmpp can be prepared in nonpolar solvents. Complexes **1**, **2**, **3** are soluble in water, methanol, dichloromethane and other polar solvents, slightly soluble in chloroform and higher alcohols and insoluble in nonpolar solvents and complexes **4**–**10** are soluble in dichloromethane, chloroform, acetone, arenes, sparingly soluble in alkanes and insoluble in water. However, complexes with pyridylphosphine are soluble in water in the presence of strong acids owing to protonation of nitrogen atoms of 2-pyridyl rings. The complexes are air stable in solid state, however in solutions they are oxidized in air with the loss of a carbonyl ligand and formation of appropriate phosphine oxide. All complexes have been characterized by means of elemental analysis, IR and ^{1}H- and ^{31}P-NMR spectra.

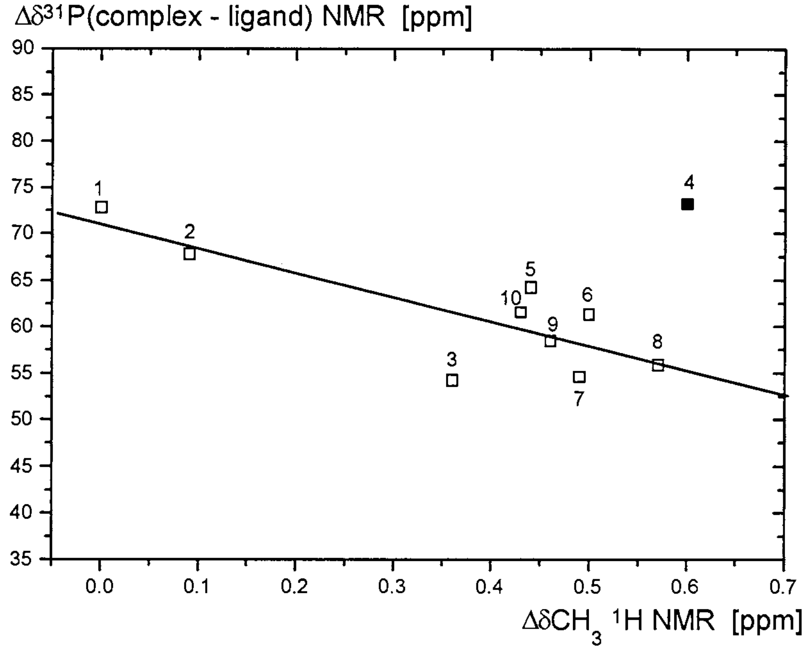


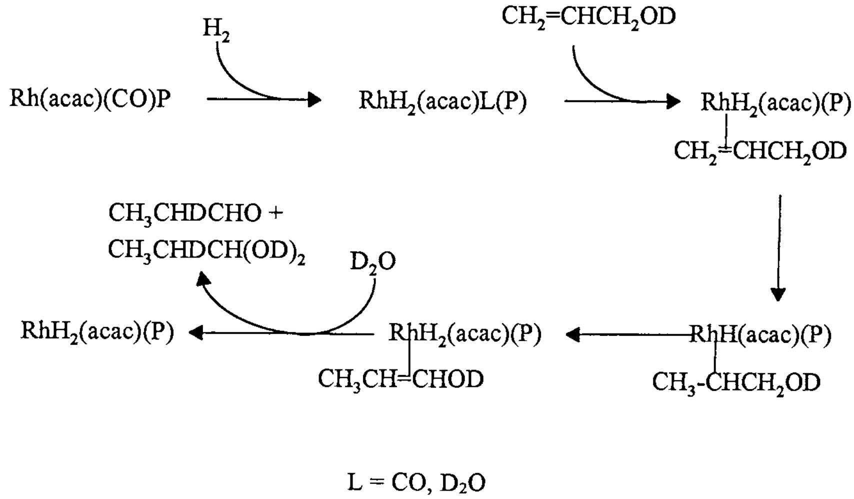
Fig. 4. The dependence of the coordination chemical shift $\Delta\delta(^{31}P)$ on the $\Delta\delta CH_3$ ^1H-NMR for $[Rh(acac)(CO)(PR_3)]$ complexes. $R = 0.81$; S.D. = 3.97. The point for **4** is not included in the regression line.

The $^{31}P\{^1H\}$-NMR and $\nu(CO)$ stretching vibration for $Rh(acac)(CO)(PR_3)$ complexes are given in Table 1. The ^{31}P coordination chemical shift $\Delta\delta(^{31}P)$ as well as $^1J(RhP)$ are typical for $Rh(acac)(CO)(PR_3)$ complexes.

The $\nu(CO)$ frequencies for investigated complexes change in the range 1944–1981 cm^{-1} and depend on σ-donor and π-acceptor properties of phosphines because PR_3 and CO interact with the same rhodium d_π orbital. Electron density donated by phosphines is then back-donated from the central atom into the π^* orbital of the CO ligand and this leads to the decrease of the $\nu(CO)$ frequency. Low $\nu(CO)$ frequencies for complexes **1** and **6** are indicative of relatively strong σ-donor and rather weak π-acceptor properties of tpa and ompp, while σ-donor and π-acceptor abilities of tppts, pmpp and pyridylphsphines are similar to those of PPh_3, cyep shows intermediate properties. On the other hand the more strength of the metal–phosphine bond the larger $\Delta\delta^{31}P\{^1H\} = \delta_{complex} - \delta_{phosphine}$. Thus a relationship between $\Delta\delta^{31}P$ and the carbonyl stretching frequency should be observed. Data given in Table 1 and presented in Fig. 2 confirm this conclusion. It is interesting that this dependence is fulfilled both for alkyl- and arylphosphines, except of phosphines with cone angle considerably greater than that for PPh_3 (145°).

In the ^1H-NMR spectra of $Rh(acac)(CO)(PR_3)$ complexes, two signals of CH_3 groups of 2,4-pentanodionato ligand are observed since one oxygen atom occupies trans coordination site to the phosphine molecule and other *trans* position to the carbonyl ligand. The differences between chemical shifts of the methyl groups, $\Delta\delta_{Me}$, should chiefly depend on *trans* influence, thus, on electronic properties of PR_3 and CO ligands. The $\Delta\delta_{Me}$ values should depend to a lesser extent on bulkiness of phosphine ligands because their steric interaction with the CH_3 group of acac is rather weak. Therefore the correlation between $\Delta\delta_{Me}$ and $\Delta\delta^{31}P$ is better than the dependence of $\Delta\delta_{Me}$ on Θ cone angle (Fig. 3 and Fig. 4). Similar dependeces of reactivity of phosphine complexes on the electronic and steric properties of PR_3 ligands have also been found [27,28,30], e.g. enthalpies of carbonyl ligand substitution by PR_3 in $Rh(acac)(CO)_2$ show a proportional dependence on the carbonyl stretching frequencies of $Rh(acac)(CO)(PR_3)$ complexes [27]. In the case of complex **1**, there is only one signal of methyl groups. This suggests that *trans* influences for tpa and CO are comparable and steric influences of the compact tpa ligand is negligible and therefore acetylacetonato ligand is symmetrically coordinated with rhodium. The ^1H-NMR spectrum of **1** is simple, PCH_2N and NCH_2N methylene groups give singlets showing that axial and equatorial protons in this complex, like in free tpa, are equivalent. In all complexes deshielding effect of the central atom was observed. In complex **2**, H^2 is the most effectively deshielded; its chemical shift (8.365 ppm) is higher than that in $OP(C_6H_4SO_3Na\text{-}3)_3$ (8.25 ppm).

Complexes **1**–**3** in aqueous solutions are effective catalysts for hydrogenation of alkenes and allyl alcohol under mild conditions. The initial TOF values are much higher for alkenes than for $CH_2{=}CHCH_2OH$. This suggests that C=C bond of allyl alcohol is relatively strongly coordinated with the rhodium atom and therefore transfer of the hydrido ligand to the substrate is



Scheme 1. Mechanism of isomerisation of allyl alcohol.

Table 2
Hydrogenation and hydroformylation of alkenes and allyl alcohol in the presence of [Rh(acac)(CO)(PR_3)] complexes **1**–**3**

Catalyst	Substrate	Products (%)	Initial rate of reaction (mol·(h·mol Rh)$^{-1}$)
1	1-Hexene, H_2^{a}	*n*-Hexane	143
1	1-Cyclohexene, H_2^{a}	Cyclohexane	92
1	Allyl alcohol, $H_2^{a,c}$	*n*-Propanol(90), propanal(10)	26
1	1-Hexene, H_2, CO[b]	*n*-Heptanal(34.1), *i*-heptanal(13.6), 2-hexene (11.0), 3-hexene (6.2)	61[d]
2	1-Hexene, H_2^{a}	*n*-Hexane	260
2	1-Cyclohexene, H_2^{a}	Cyclohexane	257
2	Allyl alcohol, $H_2^{a,c}$	*n*-Propanol(99), propanal(1)	23.4
2	1-Hexene, H_2, CO[b]	*n*-Heptanal(53), *i*-heptanal(47)	111[d]
3	1-Hexene, H_2^{a}	*n*-Hexane	96
3	Allyl alcohol, $H_2^{a,c}$	*n*-Propanol(95), propanal(5)	21.2
3	1-Hexene, H_2, CO [b]	*n*-Heptanal(53), *i*-heptanal(43), isomers of hexene(1.9), *n*-heptanoic acid(1.2), *i*-heptanoic acid(0.9)	109[d]

[a] Substrate 0.02 mol; catalyst 10^{-5} mol; 15 cm^3 H_2O; $p(H_2) = 0.1$ MPa; temperature 30°C. [b] Substrate 0.02 mol; catalyst 10^{-5} mol; 15 cm^3 H_2O; $p(H_2) = p(CO) = 3.0$ MPa; temperature 60°C; 18 h. [c] One-phase system. [d] Average TOF.

slower than that in the case of 1-hexene. In the presence of all complexes, allyl alcohol is partly isomerized to propanal. Hydrogenation of CH_2=$CHCH_2OH$ in D_2O solution gives *n*-propanol, $CH_3CHDCHO$ and $CH_3CHDCH(OD)_2$. The ^{1}H-NMR spectrum of the reaction products shows a doublet of triplets at 0.88 ppm with $^3J(HH) = 7.2$ and $^3J(HD) = 1.1$ Hz for the methyl group of propanal and a quartet of doublets at 2.39 ppm with $^3J(HH) = 7.2$ and $^2J(HD) = 1.3$ Hz for the CHD group apart from signals of *n*-propanol. Thus isomerization is most likely catalyzed by hydrido rhodium complexes, according to the mechanism given in Scheme 1. Most probably homolytic splitting of H_2 molecule occurs because propanal containing deuterium atoms in methyl group $CDH_2CDHCHO$ is not formed. In the case of heterolytic splitting of dihydrogen, easy isotopic exchange between H_2 and deuterated solvent should take place and propanal with deuterated methyl group should be formed.

The yield of isomerization decreases in the order: **1** > **3** > **2**, thus, the lower ν(CO) the higher yield of isomerization. This indicates also that the decrease of stability of hydrido complexes is: tpa > cyep > tppts, it confirms also the proposed mechanism of isomerization. However, even for complex with tpa, hydrido complexes have not been detected with ^{1}H-NMR.

The investigated complexes catalyze also hydroformylation of alkenes in aqueous solutions. The average values of TOF are relatively high (60–110), however, selectivity of complexes without excess of phosphine ligand is low. It is interesting that among the products of hydroformylation of 1-hexene in the presence of complex **3**, *n*-heptanoic and 2-methylhexanoic acids were found. They are most likely formed owing to the nucleophilic attack of water molecule on RC(O)–Rh bond. Complexes **1**, **2** and **3** are also catalysts for isomerization of alkenes in dihydrogen atmosphere. This indicates that isomerization, analogously as in the case of isomerization of allyl alcohol, is catalyzed by hydrido rhodium(III) complexes $[RhH_2(acac)L(PR_3)]$. During hydrogenation of 1-hexene substantial amounts of 2-hexene and 3-hexene are formed (Table 2). Thus rate of isomerization is comparable with the rate of hydrogenation. The carbonyl ligand in all catalytic reactions is transformed into formic acid which in the case of complex **1**, most likely, forms formates with tpa owing to protonation of nitrogen atoms of phosphine.

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