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Rhodium complexes $HRh[P(NC_4H_4)_3]_4$ and $HRh(CO)[P(NC_4H_4)_3]_3$ as active catalysts of olefins and arenes hydrogenation X-ray structure of $HRh(CO)[P(NC_4H_4)_3]_3$

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Abstract

The rhodium hydrido complexes $HRh[PPh_x(NC_4H_4)_{3-x}]_4$ ($x = 0–2$) and $HRh(CO)[PPh_x(NC_4H_4)_{3-x}]_3$ have been obtained in reactions of $Rh(acac)(CO)_2 + PPh_x(NC_4H_4)_{3-x}$ with H_2 or H_2/CO (0.1 MPa, room temperature) respectively. The crystal structure of $HRh(CO)[P(NC_4H_4)_3]_3$ has been determined. The complex is slightly distorted trigonal bipyramidal with H and CO ligands occupying the axial positions. The Rh atom is located 0.336 Å out of plane of the three equatorial P atoms. The Rh–H distance in two crystallographically independent molecules is 1.51(5) and 1.69(6) Å respectively. The complexes $HRh[P(NC_4H_4)_3]_4$ and $HRh(CO)[P(NC_4H_4)_3]_3$ are active catalysts of hydrogenation reaction of olefins and arenes (cyclohexene, 1,3-cyclohexadiene, 1,4-cyclohexadiene, propenylbenzene, styrene, toluene) at 353 K and 0.5 MPa H_2. The TOF up to 836 mol/mol Rh per h have been obtained. © 1998 Elsevier Science S.A.

Keywords: $HRh[P(NC_4H_4)_3]_4$; $HRh(CO)[P(NC_4H_4)_3]_3$; Olefins and arenes hydrogenation

1. Introduction

Rhodium complexes with strong basic ligands, like phosphines represent the largest group of homogeneous hydrogenation catalysts of unsaturated compounds. Wilkinson's complex $RhCl(PPh_3)_3$ [1] and its catalytically active form—$[H_2RhCl(PPh_3)_3]$—demonstrate an excellent example. Rhodium complexes with bi- and terdentate amino-phosphines and amino-arsines were successfully applied to hydrogenation of cyclohexene and other olefins [2–4]. Application of chiral amino-phosphines as ligands allow asymmetric hydrogenation of activated ketones [5]. Rhodium complexes with diphosphines of $Rh(P–P)_2Cl$ type ($P–P = Ph_2P(CH_2)_nPPh_2$, $n = 1–4$) are active in hydrogenation of methylenesuccinic acid and chiral products can be obtained when (+) DIOP is applied as diphosphine ligand [6].

Dimeric rhodium complexes with bisdiphenylphosphinomethane (dppm) of $Rh_2H_2(CO)_2(dppm)_2$ type can be considered as model hydrogenation catalysts [7]. Recently, cationic complex $[Rh(nbd)(PPh_3)_2]PF_6$ [8] (nbd = norbornadiene) was applied for pent-1-ene hydrogenation in two-phase systems [9].

Rhodium phosphite compared with phosphine complexes were used much less frequently but $\{HRh[P(OR)_3]_2\}_3$, $\{HRh[P(OR)_3]_2\}_2$ and $\{H_2Rh[P(OR)_3]_2\}_2$ were found as quite active in catalytic hydrogenation [10,11]. Linear olefins as well as aromatic hydrocarbons are hydrogenated with $Rh(acac)[P(OPh)_3]_2$ [12].

$HRh[P(OPh)_3]_4$ catalyses hydrogenation of methylacrylate (at 0.1 MPa H_2) [13], hex-1-ene and propenylbenzene [14].

The elevated pressure applied in typical hydrogenation reaction facilitates H_2 activation in coordination sphere of metal complex catalyst. From that point of view, rhodium complexes with strong π-acceptor ligands (like $P(OPh)_3$) are specially interesting since they form monohydride species in reaction with H_2 at 0.1 MPa and room temperature. This allows to synthesise $HRh[P(OPh)_3]_4$ [15] and $HRh(CO)[P(OPh)_3]_3$ [16], which are active catalysts of olefin hydrogenation and hydroformylation [17].

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According to our earlier studies, rhodium(I) complexes with *N*-pyrrolyl phosphines ($P(NC_4H_4)_3$, $PPh(NC_4H_4)_2$, $PPh_2(NC_4H_4)$) as well as rhodium(I) phosphite complexes are similar in H_2 splitting via oxydative addition to metal center at mild conditions (0.1 MPa, room temperature). Moreover it was found that $HRh(CO)[PPh_x(NC_4H_4)_{3-x}]_3$-type complexes are active catalysts for hex-1-ene hydroformylation [18].

In this paper we present the studies of catalytic activity of two hydrido complexes—$HRh[P(NC_4H_4)_3]_4$ and $HRh(CO)[P(NC_4H_4)_3]_3$ synthesised under 0.1 MPa of H_2 in hydrogenation of aromatics and cyclic olefins. The investigations of H_2 activation mechanism by rhodium(I) *N*-pyrrolyl phosphino complexes leading to the formation of $HRh(CO)(PPh_3)_3$ are also reported.

2. Results and discussion

The passing of a mixture of H_2/CO (0.1 MPa) through a solution containing $Rh(acac)(CO)_2$ and a *N*-pyrrolyl phosphine ($PPh_x(NC_4H_4)_{3-x}$) proceeds with formation of the rhodium hydrido complexes of formula $HRh(CO)[PPh_x(NC_4H_4)_{3-x}]_3$ [18]. The corresponding reaction with only H_2 leads to the formation of two complexes: $HRh(CO)[PPh_x(NC_4H_4)_{3-x}]_3$ and $HRh[PPh_x(NC_4H_4)_{3-x}]_4$ in the ratio dependent on the initial concentration of *N*-pyrrolyl phosphine. Higher *N*-pyrrolyl phosphine concentrations favour formation of the corresponding hydrido complex without CO in coordination sphere, so that at the concentration ratio $[Rh(acac)(CO)_2]:[P(NC_4H_4)_3] = 1:5$, $HRh[P(NC_4H_4)_3]_4$ is the only reaction product. Its structure was confirmed by quintet of doublets observed in ^1H NMR spectrum at $\delta = -10.2$ ppm. The spectrum was recorded directly for the reaction mixture because of very low solubility of the complex in organic solvents. Stirring the suspension of $HRh[P(NC_4H_4)_3]_4$ in toluene in CO atmosphere (0.1 MPa pressure applied) causes in 5 min formation of totally transparent solution from which $HRh(CO)[P(NC_4H_4)_3]_3$ was isolated as the only product according to the reaction:

$$HRh[P(NC_4H_4)_3]_4 + CO \rightarrow HRh(CO)[P(NC_4H_4)_3]_3 + P(NC_4H_4)_3$$

The formation of hydride complexes of $HRh[PPh_x(NC_4H_4)_{3-x}]_4$ type have the similar course (reaction below) for all *N*-pyrrolyl phosphines and in each case the compound of low solubility was obtained.

$$Rh(acac)(CO)_2 + 4PPh_x(NC_4H_4)_{3-x} + H_2 \rightarrow HRh[PPh_x(NC_4H_4)_{3-x}]_4 + Hacac + 2CO$$

This reaction is analogues to the earlier described synthesis of phosphite complex $HRh[P(OPh)_3]_4$ [15]. It was found convenient to use $Rh(acac)(C_2H_4)_2$ instead of $Rh(acac)(CO)_2$ as starting rhodium complex to prevent formation even traces of carbonyl containing species, like $HRh(CO)[P(NC_4H_4)_3]_3$, in reaction products.

2.1. Hydrogen activation by the system: $Rh(acac)(CO)(PPh_3) + H_2 + PPh_3 + PPh_x(NC_4H_4)_{3-x}$

In contrast to the rhodium(I) complexes with $P(OPh)_3$ or *N*-pyrrolyl phosphines, similar complexes with PPh_3 (weaker π-acceptor) form only traces of $HRh(CO)(PPh_3)_3$ in reaction with H_2 under 0.1 MPa. To split dihydrogen molecule effectively the application of higher pressure is required. We have found as quite interesting that even small amounts of *N*-pyrrolyl phosphines added to the system containing $Rh(acac)(CO)(PPh_3)$ and PPh_3 facilitate this reaction and ca. 80% of $HRh(CO)(PPh_3)_3$ could be obtained.

In order to elucidate the most important steps of $HRh(CO)(PPh_3)_3$ complex formation at the presence of *N*-pyrrolyl phosphines the spectroscopic studies have been done. In ^{31}P NMR spectrum of the solution containing equimolar concentration of $Rh(acac)(CO)(PPh_3) + P(NC_4H_4)_3$ briefly after mixing two above components, the doublet, typical for $Rh(acac)[P(NC_4H_4)_3]_2$ was observed. Other complexes present in solution were in dynamic exchange with phosphine ligands. This was indicated by the presence of the ^1H NMR signal at 1.84 ppm (next to 1.71 ppm derived from $Rh(acac)[P(NC_4H_4)_3]_2$) which is an average signal of $CH_3(acac)$ in $Rh(acac)(CO)(PPh_3)$ and $Rh(acac)(CO)[P(NC_4H_4)_3]$ complexes. At the same time, in ^{31}P NMR spectra two broad lines at ca. 40 ppm and ca. 85 ppm assigned for complexes with PPh_3 and $P(NC_4H_4)_3$ respectively, were observed. The spectra are changing in time and after several hours the mixed ligand complex of formula $Rh(acac)(PPh_3)(P(NC_4H_4)_3)$ was identified in reaction mixture by the characteristic ^{31}P NMR spectrum (Table 1).

It can be concluded, that *N*-pyrrolyl phosphine labilises the coordination sphere of $Rh(acac)(CO)(PPh_3)$ and partially substitutes PPh_3 and CO leading to the formation of the mixture of complexes according to the reaction:

$$nRh(acac)(CO)(PPh_3) \xrightarrow{P(NC_4H_4)_3} Rh(acac) \times [P(NC_4H_4)_3]_2 + Rh(acac)(CO)[P(NC_4H_4)_3] + Rh(acac)(PPh_3)[P(NC_4H_4)_3]$$

The presence of *N*-pyrrolyl phosphine, $PPh_2(NC_4H_4)$, facilitates the reaction of $Rh(acac)(CO)(PPh_3)$ complex with dihydrogen and $HRh(CO)[PPh_2(NC_4H_4)]_2(PPh_3)$ is formed within 1 h of the reaction:

$$Rh(acac)(CO)(PPh_3) + 2PPh_2(NC_4H_4) + H_2 \rightarrow HRh(CO)[PPh_2(NC_4H_4)]_2(PPh_3) + Hacac$$

Table 1
Spectroscopic (^{1}H and ^{31}P NMR) data of Rh(I) complexes with PPh_3 and $P(NC_4H_4)_3$ in C_6D_6

Compound	^{31}P NMR			^{1}H NMR (hydride)		
	δ (ppm)	J(Rh–P)	J(P–P)	δ (ppm)	J(P–H)	J(Rh–H)
$Rh(acac)(PPh_3)[P(NC_4H_4)_3]$	52.6	179.4	72			
	107	281				
$HRh(CO)(PPh_3)_2[P(NC_4H_4)_3]$	37.7	145.4	168	−9.04	11.7	
	110.4	237				
$HRh(CO)(PPh_3)[P(NC_4H_4)_3]_2$	35.3	137.4	137	−9.05	10.5	
	110.2	222				
$HRh(CO)[P(NC_4H_4)_3]_3$	109	211		−9.1	7.8	2.7
$HRh[P(NC_4H_4)_3]_4$	[a]			−10.2	30.0	4.0
$HRh(CO)(PPh_3)_3$	47.4	132.5		−9.1		

[a] Not determined because of low complex solubility.

In a similar experiment with $P(NC_4H_4)_3$ the main reaction product was $HRh(CO)–[P(NC_4H_4)_3]_3$. In both reactions (when $[Rh(acac)(CO)(PPh_3)]$: $[PPh_x(NC_4H_4)_{3-x}] = 1{:}1$) rhodium hydride complexes with coordinated *N*-pyrrolyl phosphine were obtained. These results confirm that hydrogen activation occur in rhodium complex with coordinated *N*-pyrrolyl phosphine. In the reaction performed with an excess of PPh_3 the $HRh(CO)(PPh_3)_3$ complex was obtained as the main product. The small amounts of mixed ligand species of formula $HRh(CO)(PPh_3)_x[PPh_2(NC_4H_4)]_{3-x}$ were also found (Table 1, reaction below).

$$Rh(acac)(CO)(PPh_3) + 4PPh_3 + 0.5\ PPh_2(NC_4H_4) + H_2 \rightarrow HRh(CO)(PPh_3)_3 + HRh(CO)(PPh_3)_2[PPh_2(NC_4H_4)] + HRh(CO)(PPh_3)[PPh_2(NC_4H_4)]_2$$

It was independently confirmed that free PPh_3 substitutes coordinated $P(NC_4H_4)_3$ and in ca. 1 h after addition of PPh_3 to the solution of $HRh(CO)[P(NC_4H_4)_3]_3$ complex the two mixed ligand complexes were found in solution: $HRh(CO)(PPh_3)_2[P(NC_4H_4)_3]$ and $HRh(CO)–(PPh_3)[P(NC_4H_4)_3]_2$. It is worthy to note that the reverse substitution reaction of PPh_3 by *N*-pyrrolyl phosphines is much faster and ca. 30 min after addition of $PPh_2(NC_4H_4)$ the $HRh(CO)(PPh_3)_3$ was totally converted to $HRh(CO)[PPh_2(NC_4H_4)]_3$. As expected, the stronger π-acceptor ligand ($P(NC_4H_4)_3$) substitutes easily the σ-donor ligand like PPh_3.

The synthesis of $HRh(CO)(PPh_3)_3$ complex from $Rh(acac)(CO)(PPh_3)$ at 0.1 MPa H_2 is much less effective at the presence of amines ($N(CH_2Ph)_3$, NEt_3, NPr_3) than at the presence of *N*-pyrrolyl phosphines. With application of $N(CH_2Ph)_3$ only ca. 15% yield was achieved after 24 h.

2.2. Hydrogenation of cyclic olefins with $HRh[P(NC_4H_4)_3]_4$ and $HRh(CO)[P(NC_4H_4)_3]_3$

Rhodium(I) hydride complexes containing the $P(NC_4H_4)_3$ ligand are active hydrogenation reaction

Table 2
Hydrogenation of arenes and cyclic olefins catalyzed by $HRh[P(NC_4H_4)_3]_4$ and $HRh(CO)[P(NC_4H_4)_3]_3$ complexes

Hydrocarbon	Catalyst			
	$HRh[P(NC_4H_4)_3]_4$		$HRh(CO)[P(NC_4H_4)_3]_3$	
	Products (yield % mol)	TOF mol/mol Rh × h	Products (yield % mol)	TOF mol/mol Rh × h
cyclohexene	cyclohexane (64)	756	cyclohexane (75)	889
1,3-cyclohexadiene	cyclohexene (37)	466	cyclohexane (63)	836
	cyclohexene (28)	353	cyclohexane (37)	491
1,4-cyclohexadiene	cyclohexene (31)	391	cyclohexene (28)	371
	cyclohexane (20)	252	cyclohexane (21)	278
1-propenylbenzene	propylbenzene (74)	677	propylbenzene (76)	684
	2-propylbenzene (13)	112	2-propenylbenzene (17)	146
styrene	ethylbenzene (75)	788	ethylbenzene (93)	977
	ethylcyclohexane (0.8)	8	ethylcyclohexane (0.8)	8
o-xylene[a]	dimethylcyclohexane (3)	11		
toluene[a]	methylcyclohexane (1.3)	7	methylcyclohexane (3)	14

Reaction conditions: $[Rh] = 1 \times 10^{-5}$ mol, 2 cm^3 of substrate, 353 K, 0.5 MPa H_2, time: 100 min.
[a] Time: 250 min.

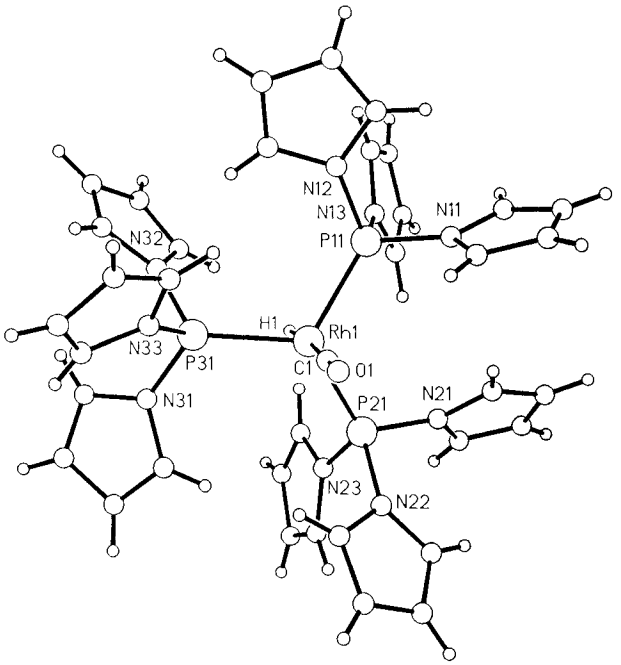

Fig. 1. Molecular structure of $HRh(CO)[P(NC_4H_4)_3]_3$.

catalysts for cyclic olefins. The reactions were conducted in neat substrates, without addition of solvent. It is worthy to note that the low solubility of $HRh[P(NC_4H_4)_3]_4$ is not disturbing its application because under hydrogenation reaction conditions it dissolves and acts as a homogeneous catalyst.

The catalytic activity of $HRh[P(NC_4H_4)_3]_4$ and $HRh(CO)[P(NC_4H_4)_3]_3$ in hydrogenation of 1,4-cyclohexadiene and propenylbenzene is very similar (Table 2). In hydrogenation of 1,4-cyclohexadiene ca. 50% conversion was obtained with formation of cyclohexene (ca. 30%) as well as cyclohexane (ca. 20%). The main product of 1-propenylbenzene was propylbenzene (74–76%), but also some amounts of isomerisation product 2-propenylbenzene were found. $HRh(CO)[P(NC_4H_4)_3]_3$, however, is a better catalyst for the hydrogenation of cyclohexene, 1,3-cyclohexadiene and styrene giving conversion 75%, 100% and 93.8% respectively. It is remarkable difference in activity of $HRh(CO)[P(NC_4H_4)_3]_3$ in hydrogenation of 1,3-cyclohexadiene and 1,4-cyclohexadiene represented by ca. twice higher yield of hydrogenated products in the first case. When $HRh[P(NC_4H_4)_3]_4$ was used the difference in hydrogenation reaction yield was only ca. 15%. Both catalysts show insignificant but measurable activity in hydrogenation of aromatic hydrocarbons (Table 2).

The analysis of post-reaction mixtures shown unchanged hydride-complexes in both cases. The complex $HRh[P(NC_4H_4)_3]_4$ was separated by filtration directly from the reaction mixture, $HRh(CO)[P(NC_4H_4)_3]_3$ was recovered after vacuum distillation of liquid products.

2.3. Molecular structure of $HRh(CO)[P(NC_4H_4)_3]_3$

The molecular structure of $HRh(CO)[P(NC_4H_4)_3]_3$, an active intermediate in catalytic system, is shown on Fig. 1. Important bond length and angles are listed in Table 3.

$HRh(CO)[P(NC_4H_4)_3]_3$ complex is distorted trigonal bipyramid and is structurally analogous to $HRh(CO)(PPh_3)_3$ [19]. The rhodium atoms are placed 0.339 Å (molecule 1) and 0.334 Å (molecule 2), out of plane of three equatorial phosphorus atoms of $P(NC_4H_4)_3$ ligands. The corresponding out of plane displacements of rhodium in $HRh(CO)(PPh_3)_3$ [19] and $HRh(PF_3)(PPh_3)_3$ [20] are 0.36 Å and 0.38 Å respectively. Distortion of regular bipyramidal structure of $HRhP_3X$ type complexes can be also characterised by the value of C–Rh–P or P_{ax}–Rh–P_{eq} angles. The average C–Rh–P angle in $HRh(CO)[P(NC_4H_4)_3]_3$ complex is equal 98.6° (for molecule 1) and 98.5° (for molecule 2). These angles are close to that determined for $HRh(CO)(PPh_3)_3$ (98.9°) [19] and $HRh(PF_3)(PPh_3)_3$ (99°) [20]. Higher values of P_{ax}–Rh–P_{eq} angle (ca. 109°) are characteristic for tetrahedral complexes, like $HRh(PPh_3)_4$ [21] and $HRh(AsPh_3)(PPh_3)_3$ [22]. The rhodium–hydrogen distances determined for two crystallographically independent molecules are equal 1.51(5) Å and 1.69(6) Å respectively. Comparable values have been obtained for $HRh(CO)(Pcy_3)_3$ 1.72(2) Å [23], $HRh(PF_3)(PPh_3)_3$ 1.6 ± 0.1 Å [20] and

Table 3
Selected bond lengths [Å] and bond angles [°] in $HRh(CO)[P(NC_4H_4)_3]_3$

Molecule 1		Molecule 2	
Rh(1) C(1)	1.914(6)	Rh(2) C(2)	1.919(6)
Rh(1) H(1)	1.53(5)	Rh(2) H(2)	1.68(6)
Rh(1) P(11)	2.271(1)	Rh(2) P(41)	2.261(1)
Rh(1) P(21)	2.251(2)	Rh(2) P(51)	2.265(2)
Rh(1) P(31)	2.256(1)	Rh(2) P(61)	2.258(1)
P(11) N(11)	1.713(4)	P(41) N(41)	1.705(4)
P(11) N(12)	1.709(4)	P(41) N(42)	1.697(4)
P(11) N(13)	1.696(4)	P(41) N(43)	1.708(4)
P(21) N(21)	1.706(4)	P(51) N(51)	1.706(4)
P(21) N(22)	1.709(4)	P(51) N(52)	1.712(4)
P(21) N(23)	1.717(4)	P(51) N(53)	1.709(4)
P(31) N(31)	1.703(4)	P(61) N(61)	1.705(4)
P(31) N(32)	1.716(4)	P(61) N(62)	1.713(4)
P(31) N(33)	1.701(4)	P(61) N(63)	1.700(4)
C(1) Rh(1) P(21)	98.6(2)	C(2) Rh(2) P(61)	100.5(2)
C(1) Rh(1) P(31)	98.4(2)	C(2) Rh(2) P(41)	97.4(2)
C(1) Rh(1) P(11)	98.9(2)	C(2) Rh(2) P(51)	97.7(2)
P(21) Rh(1) P(31)	121.57(5)	P(61) Rh(2) P(41)	115.03(5)
P(21) Rh(1) P(11)	114.62(5)	P(61) Rh(2) P(51)	116.64(5)
P(31) Rh(1) P(11)	117.16(5)	P(41) Rh(2) P(51)	121.90(5)
C(1) Rh(1) H(1)	175(2)	C(2) Rh(2) H(2)	178(2)
P(21) Rh(1) H(1)	81(2)	P(61) Rh(2) H(2)	78(2)
P(31) Rh(1) H(1)	78(2)	P(41) Rh(2) H(2)	83(2)
P(11) Rh(1) H(1)	86(2)	P(51) Rh(2) H(2)	84(2)

$HRh(CO)(PPh_3)_3$ 1.6 Å [19]. Relatively short Rh–H distance, 1.31(8) Å, has been found for $HRh(PPh_3)_4$ via neutron diffraction analysis [20].

The average Rh–P distance in $HRh(CO)[P(NC_4H_4)_3]_3$ is 2.26 Å, similar to that obtained for $RhCl(CO)[P(NC_4H_4)_3]_2$ equal 2.288(4)–2.275(3) Å [24]. Slightly shorter Rh–P bonds, 2.161(2)–2.176(2) Å, were found in $Rh(acac)(CO)[P(NC_4H_4)_3]$ and $Rh(acac)[P(NC_4H_4)_3]_2$ respectively [18].

The bond lengths and angles in $P(NC_4H_4)$ ligands coordinated to rhodium in $HRh(CO)[P(NC_4H_4)_3]_3$ complex are similar to corresponding values in other rhodium complexes [18,24] and in free *N*-pyrrolyl phosphine molecule [25].

3. Experimental

Rhodium complexes were prepared according to the literature methods: $Rh(acac)(CO)_2$ [26], $HRh(CO)[P(NC_4H_4)_3]_3$ [18], $HRh(CO)(PPh_3)_3$ [27].

$Rh(acac)(CO)(PPh_3)$ complex was obtained by the modified method [28] using stoichiometric amount of PPh_3 ($[Rh(acac)(CO)_2]$: $[PPh_3] = 1$) in acetone.

3.1. HRh $[P(NC_4H_4)_3]_4$

The mixture containing 0.1 g of $Rh(acac)(CO)_2$ and 0.5 g $P(NC_4H_4)_3$ in 3 cm^3 of toluene was stirred under H_2 atmosphere in room temperature. After 3 h the white complex started to precipitate. The stirring was continued next 5 h, the product was filtrated and dried in vacuo. Yield 0.27 g (70%). Anal. Calc. for $C_{48}H_{49}N_{12}P_4Rh$: C 56.5; H 4.8; N 16.5. Found: C 55.9; H 4.8; N 16.0.

3.2. $HRh(CO)(PPh_3)_3$

In typical experiment the solution containing 0.06 g $Rh(acac)(CO)(PPh_3)$, 0.14 g PPh_3 and 0.014 g $PPh_2(NC_4H_4)$ in 1 cm^3 of toluene (or C_6D_6) was stirred in H_2 atmosphere 1–24 h. During that time samples were IR and/or NMR analysed.

3.3. Hydrogenation reaction

Hydrogenation reaction was carried out in thermostated steel autoclave (150 cm^3) with magnetic stirrer. The catalyst (0.0085 g $HRh(CO)[P(NC_4H_4)_3]_3$ or 0.0105 g $HRh[P(NC_4H_4)_3]_4$) was introduced to the autoclave in nitrogen atmosphere in small teflon vessel. Next, 2 cm^3 of substrate was added. The autoclave was filled with 0.5 MPa of H_2 and heated to 353 K. After 100 min (or 250 min for aromatic hydrocarbons) autoclave was cooled down, opened and reaction products were separated from the catalyst by distillation. The reaction products were analysed by GC-MS (Hewlett-Packard).

3.4. X-ray crystal structure determination

All measurements were made on a Kuma KM-4 computer controlled κ-axis diffractometer with graphite-monochromated MoKα radiation. Experimental details are given in Table 4. The structures were solved by the direct methods with SHELXL-86 [29] and refined by full-matrix least-square methods using SHELXL-93 [30].

Carbon bonded H-atoms in all pyrrolyl rings were included in geometrically calculated positions with C–H distance 0.93 Å. After refinement positions of H(1) and H(2) have been found by difference Fourier synthesis. Refinement with anisotropic thermal parameters for Rh, P, C, O and N gave final $R = 0.0301$ and $R_w = 0.0726$.

3.5. Instruments

The following instruments were used: Bruker 300 MHz (121.5 MHz for ^{31}P), GC-MS Hewlett-Packard 5890 II, FT IT Nicolet Impact.

Table 4
Crystal data and structure refinement parameters for $HRh(CO)[P(NC_4H_4)_3]_3$

Empirical formula	$C_{37}H_{37}N_9O_1P_3Rh$
Formula weight	1092.77
Temperature	293(2) K
Wavelength	0.71069 Å
Crystal system	monoclinic
Space group	$P2_1/n$
a (Å)	23.339(5)
b (Å)	15.775(3)
c (Å)	23.435(5)
β (°)	116.54(3)
Volume (Å^3)	7719(3)
Z	8
Density (calculated)	1.410 g/cm^3
Crystal size (mm)	$0.30 \times 0.35 \times 0.35$
Cell measurement 2θ range (°)	23.2–38.7
Absorption coefficient (cm^{-1})	6.09
$F(000)$	3360
Data collection method	ω-2θ scan
2θ range (°)	4.10–46.10
Number of standard reflections	3 (100 reflections)
Range of h, k, l	$0 \rightarrow 25$, $0 \rightarrow 17$, $-25 \rightarrow 23$
Reflections collected	10 796
Independent reflections	10 796
Goodness-of-fit on F^2	1.010
Data $[I > 2\sigma(I)]$, parameters	5803, 927
Final R indices $[I > 2\sigma(I)]$	$R_1 = 0.0301$
	$wR_2 = 0.0726$
Largest difference peak and hole (e/Å^3)	0.662–0.769

Weighing scheme: calc. $w = 1/[\sigma^2(F_o^2) + (0.0379P)^2 + 6.2814P]$, where $P = (F_o^2 + 2F_c^2)/3$.

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