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Substitution of CO by picolines and amines in $RhCl(CO)(PR_3)_2$. Synthesis and crystal structure of *cis*-$RhCl(3\text{-pic})\{P(OPh)_3\}_2$

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Abstract

The title complex, cis-$RhCl(3\text{-pic})\{P(OPh)_3\}_2$ (3-pic = 3-picoline), has been prepared with two other isostructural rhodium complexes, respectively with 4-picoline and $CH_2{=}CH{-}CH_2NH_2$. The $RhCl(3\text{-pic})\{P(OPh)_3\}_2$ compound crystallizes in space group $P\bar{1}$ with $a = 10.531(6)$, $b = 12.025(9)$, $c = 15.943(8)$ Å, $\alpha = 83.01(5)$, $\beta = 79.46(4)$, $\gamma = 86.33(5)^\circ$; $Z = 2$. The $RhCl(amine)\{P(OPh)_3\}_2$ complexes were obtained in the reactions of $[Rh(\mu\text{-OMe})(cod)]_2$, $[Rh(\mu\text{-Cl})(cod)]_2$ (cod = cycloocta-1,5-diene) or $RhCl(CO)\{P(OPh)_3\}_2$ with amines. CO substitution by amines in $RhCl(CO)(PR_3)_2$ complexes [PR_3 = $P(OMe)_3$, $P(OPh)_3$, $P(O\text{-}o\text{-}MeC_6H_4)_3$, $P(O\text{-}m\text{-}MeC_6H_4)_3$, PEt_2Ph, $PEtPh_2$, PMe_2Ph, $PMePh_2$ or PPh_3] is limited by steric properties of amine and PR_3 ligands. 3-Picoline substitutes CO only in complexes with PR_3 ligands with cone angle $\theta \leqslant 140^\circ$ [16]. The rate of CO substitution by 2-picoline is less than half that by 3-picoline.

Introduction

The extensively studied reaction between $[Rh(\mu\text{-Cl})(cod)]_2$ (cod = cycloocta-1,5-diene) and N-donor ligands (amines) usually gives the $RhCl(cod)(amine)$ or $[Rh(cod)(amine)_2]^+$ complexes, depending on the solvent used [1–6]. Cationic complexes $[Rh(cod)(amine)_2]^+$ were also obtained in reaction of $[Rh(cod)_2]^+$ with amines [7,8]. In $[Rh(\mu\text{-Cl})(CO)_2]_2$ and $[Rh(\mu\text{-Cl})(CO)(C_2H_4)]_2$ dimers CO is not substituted by pyridine and the reaction yields the monomeric $RhCl(CO)_2py$, $RhCl(CO)_2py_2$ [9] and $RhCl(CO)py_2$ [10] complexes. The only known reaction in which pyridine substitutes CO is synthesis of $[Rh(CO)py\{P(o\text{-}MeC_6H_4)_3\}_2]ClO_4$ by the treatment of $[Rh(CO)_2\{P(o\text{-}MeC_6H_4)_3\}_3]ClO_4$ with pyridine [11]. In some cases, however, pyridine could be substituted by phosphine; in this way such complexes as $[Rh(cod)(PPh_3)py]^+$ [1,7] and $[Rh(CO)(PPh_3)(py)_2]^+$ [7] were obtained.

In this paper synthesis and structural investigations of the new rhodium(I) complex, of the formula $RhCl(3\text{-pic})\{P(OPh)_3\}_2$ are reported. This compound was synthesized by three different routes described in this paper (Scheme 1), one of which CO substitution by 3-picoline in the $RhCl(CO)\{P(OPh)_3\}_2$ complex, was the subject of further detailed studies.

Results and discussion

The $RhCl(3\text{-pic})\{P(OPh)_3\}_2$ complex was first obtained by reaction of $[Rh(\mu\text{-}OMe)(cod)]_2$ with $P(OPh)_3$ and 3-picoline (Scheme 1). NMR studies of the reaction of $[Rh(\mu\text{-}OMe)(cod)]_2$ dimer with $P(OPh)_3$ revealed that $P(OPh)_3$ not only substitutes the coordinated cyclooctadiene but also changes the dimeric structure of the starting complex. In the ^1H NMR spectrum the signal at $\delta = 2.7$ ppm, deriving from the OMe bridging group declined and the new signal, corresponding to the free CH_3OH appeared at $\delta = 3.45$ ppm. With $P(OPh)_3$ in 1.5–2 fold excess with respect to rhodium the reaction was completed and after introduction of 3-picoline transparent, yellow crystals of $RhCl(CO)\{P(OPh)_3\}_2$ were formed.

The compound was synthesized only in $CHCl_3$ and CH_2Cl_2 solvents (route 1) which supply the chloride ions (a similar reaction with CH_2Cl_2 and $CHCl_3$ was reported recently for $RhCl(PMe_3)_3$ [12]). However, the reaction with a chloride-donor solvent was not effective with a yield of $RhCl(3\text{-pic})\{P(OPh)_3\}_2$ of only ca. 20%. The yield of 70–80% was achieved by application of complexes $[Rh(\mu\text{-}Cl)(cod)]_2$ (route 2) and $RhCl(CO)\{P(OPh)_3\}_2$ (route 3) as substrates. The X-ray and ^{31}P NMR investigations revealed that the $RhCl(3\text{-pic})\{P(OPh)_3\}_2$ complex exists both in the solid state and after solution in $CDCl_3$ as the *cis* isomer (Fig. 1).

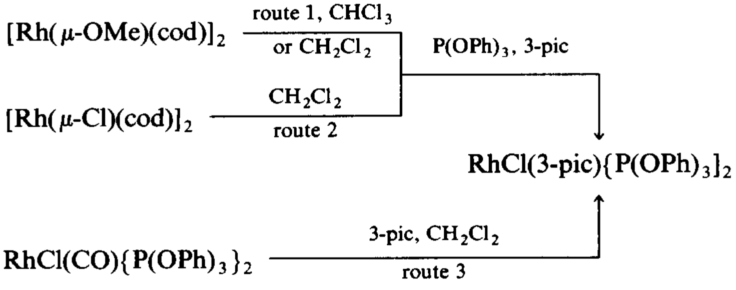
The relevant bond distances and angles and fractional coordinates are presented in tables 1 and 2 respectively.

The same *cis* configuration, indicated by the ^{31}P NMR spectra (table 3) is a feature of the analogous complexes with 4-picoline and $CH_2{=}CH{-}CH_2NH_2$. This is the first example to be announced of a Rh^I tetracoordinated complex of the formula $RhCl(X)\{P(OPh)_3\}_2$ ($X \neq P(OPh)_3$) in which phosphorous ligands are coordinated in the *cis* position.

A similar configuration was found earlier in dimeric complexes, e.g. $(cod)RhCl_2Rh\{P(OPh)_3\}_2$ [13] and in the complexes with chelate ligands, e.g. $Rh(acac)\{P(OPh)_3\}_2$ [14]. All monomeric complexes of the formula $Rh(X)(CO)(PR_3)_2$ (PR_3≡phosphines, phosphites, $X = Cl^-$) are found as the *trans* isomers [15]. It is noteworthy that the substitution reaction of CO by amine (eq. 1) is accompanied by *trans* to *cis* rearrangement of phosphorous ligands:

$$trans\text{-}RhCl(CO)\{P(OPh)_3\}_2 + \text{amine} \longrightarrow cis\text{-}RhCl(\text{amine})\{P(OPh)_3\}_2 + CO \qquad (1)$$

(amine = 3-pic, 4-pic, $CH_2{=}CH{-}CH_2NH_2$)



Scheme 1

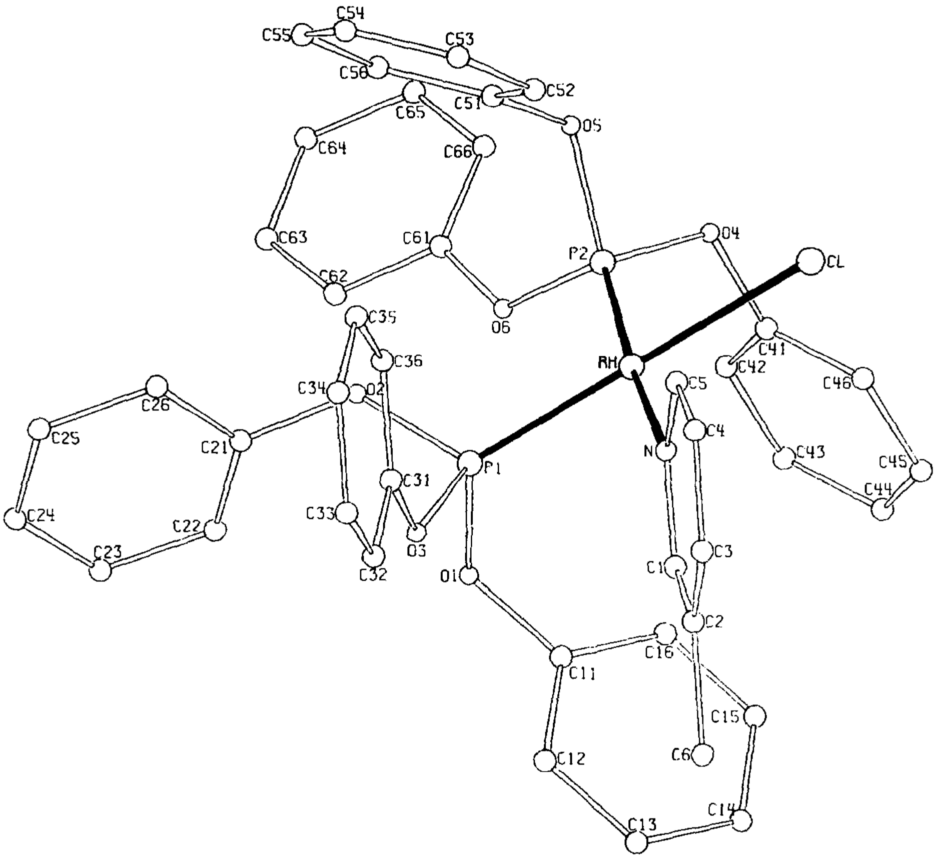


Fig. 1. View of the *cis*-RhCl(3-pic){P(OPh)$_3$}$_2$ molecule.

Table 1

Important interatomic distances (Å) and angles (deg) of RhCl(3-pic){P(OPh)$_3$}$_2$

Bond distances			
Rh–P(1)	2.150(2)	Rh–P(2)	2.167(2)
Rh–Cl	2.398(2)	Rh–N	2.132(3)
P(1)–O(1)	1.616(3)	P(1)–O(2)	1.602(3)
P(1)–O(3)	1.627(3)	P(2)–O(4)	1.612(3)
P(2)–O(5)	1.611(3)	P(2)–O(6)	1.605(3)
Bond angles			
Cl–Rh–P(1)	177.6(1)	Cl–Rh–P(2)	89.3(1)
Cl–Rh–N	85.8(1)	P(1)–Rh–P(2)	93.0(1)
P(1)–Rh–N	91.9(1)	P(2)–Rh–N	173.3(2)
Rh–P(1)–O(1)	118.9(2)	Rh–P(1)–O(2)	118.1(2)
Rh–P(1)–O(3)	118.1(2)	Rh–P(2)–O(4)	120.7(2)
Rh–P(2)–O(5)	115.9(2)	Rh–P(2)–O(6)	116.5(2)

The IR studies of reaction 1 permitted detection the intermediates involved. At the ratio of 3-pic/Rh < 8, the IR spectrum exhibits only one ν(CO) band at 2010 cm^{-1}, with intensity declining in time. At the higher 3-picoline concentration two equally intense bands appeared at 2028 and 2002 cm^{-1}, and declined with comparable rate. Attempts at ^{31}P NMR determination of intermediates failed because of the presence of broad inseparable signals. Better results were achieved for the system derived from $RhCl(CO)\{P(OPh)_3\}_2$ and 2-picoline, which substitutes CO much slower than 3-picoline does. In the ^{31}P NMR spectrum of a solution containing $RhCl(CO)\{P(OPh)_3\}_2$ and approximately threefold excess of 2-picoline a broad signal probably derived from unreacted $RhCl(CO)\{P(OPh)_3\}_2$ and from the final product, $RhCl(2\text{-pic})\{P(OPh)_3\}_2$ is observed in the region $\delta = 112$ ppm. Dynamics of the system are indicated by the line broadening caused by the fast exchange between the coordinated and free CO. The spectrum exhibits also two double doublets at $\delta = 121.8$ ppm (J(Rh–P) = 269.1, J(P–P) = 69.5 Hz) and at $\delta = 110.6$ ppm (J(Rh–P) = 319.3, J(P–P) = 69.5 Hz), both indicating the presence of rhodium complex containing two $P(OPh)_3$ ligands in *cis* position.

The ν(CO) band at 2002 cm^{-1} suggests that the carbonyl ligand is still in the coordination sphere of rhodium. This allows us to state, that the first stage of the reaction between $RhCl(CO)\{P(OPh)_3\}_2$ and 2-picoline produced the intermediate pentacoordinated $RhCl(CO)(2\text{-pic})\{P(OPh)_3\}_2$ complex of square pyramidal symmetry, with $P(OPh)_3$ ligands in *cis* position (Scheme 2)

Displacement of ligands in the coordination sphere of rhodium can be observed in the electronic spectrum. The band at 361 nm, characteristic for $RhCl(CO)\{P(OPh)_3\}_2$, disappeared, whereas new bands are formed at 373 and 325 nm. The situation of new bands is typical for complexes with two $P(OPh)_3$ ligands in *cis* position, (e.g. for $Rh(acac)\{P(OPh)_3\}_2$ and $RhCl(3\text{-pic})\{P(OPh)_3\}_2$). Rearrangement of $P(OPh)_3$ ligands from *trans* to *cis* positions proceeds also in the presence of amines, like 2,4,6-Me_3py (2,4,6-trimethylpyridine), NPr_3 (tripropylamine) and NEt_3(triethylamine) which do not substitute CO in $RhCl(CO)\{P(OPh)_3\}_2$.

Further investigations of the CO substitution reaction of amines revealed it to be limited first of all by the steric properties of substrates. The results supporting this conclusion are presented in Table 4.

Substitution of CO by 3-picoline in the $RhCl(CO)(PR_3)_2$ complex proceeds only when cone angle (θ) of PR_3-ligand [16] is smaller than 140°. However the reaction course does not depend on σ/π donor–acceptor properties of PR_3 ligands since among the complexes which do not react with 3-picoline are complexes with strong σ-donor phosphine like $PEtPh_2$ and complexes with a π-acceptor phosphite like $P(O\text{-}o\text{-}MeC_6H_4)_3$.

The reaction course depends not only on the structure of the ligand PR_3, but also on the structure of amine applied. The rate of substitution of CO by 2-picoline is less than half that by 3-picoline (Table 5). The reaction 1 does not proceed with amines of greater steric hindrance, such as $N(CH_2Ph)_3$, NPh_3, NEt_3, NPr_3.

The CO substitution by amine in $RhCl(CO)(PR_3)_2$ is reversible. For that reason it is slower in a closed vessel, where removal of CO is restricted. The very fast reaction of $RhCl(3\text{-pic})\{P(OPh)_3\}_2$ with CO is indicated by the appearance of a band at 2016 cm^{-1} in the IR spectrum of CO saturated rhodium complex solution. The product of that reaction was isolated and identified as *trans*-$RhCl(CO)\{P(OPh)_3\}_2$ (^{31}P NMR: $\delta = 113.3$ ppm, J(Rh–P) = 214.9 Hz). Substitu-

Table 2

Fractional coordinates of the non-hydrogen atoms of RhCl(3-pic){P(OPh)$_3$}$_2$ and equivalent thermal parameters (esd's in parentheses)

Atom	x	y	z	B_{eq} (Å^2)
Rh	0.06528(2)	0.24017(2)	0.33413(2)	2.93(1)
Cl	−0.08647(9)	0.19736(8)	0.46415(6)	4.64(5)
P(1)	0.20761(8)	0.27468(7)	0.22012(5)	3.14(4)
P(2)	−0.09434(9)	0.27128(8)	0.26461(6)	3.50(5)
N	0.21073(26)	0.19267(23)	0.41023(16)	3.35(15)
O(1)	0.24122(24)	0.40343(18)	0.18620(14)	3.93(14)
O(2)	0.18275(23)	0.23335(20)	0.13291(14)	3.99(14)
O(3)	0.35608(21)	0.22962(19)	0.22259(14)	3.71(13)
O(4)	−0.22424(22)	0.33888(20)	0.30423(16)	4.35(15)
O(5)	−0.17037(23)	0.16264(21)	0.25519(16)	4.56(16)
O(6)	−0.06157(23)	0.33391(22)	0.16887(15)	4.42(15)
C(11)	0.25964(34)	0.47631(27)	0.24477(20)	3.55(19)
C(21)	0.27381(36)	0.23768(35)	0.05521(22)	4.47(22)
C(31)	0.39324(32)	0.11781(29)	0.24521(21)	3.58(19)
C(41)	−0.21368(34)	0.45090(32)	0.31961(27)	4.81(23)
C(51)	−0.09798(38)	0.06242(33)	0.23771(27)	4.82(24)
C(61)	−0.13032(36)	0.33685(31)	0.10058(23)	4.18(21)
C(12)	0.38355(36)	0.49700(33)	0.25240(25)	4.66(23)
C(13)	0.40177(42)	0.57033(35)	0.30955(29)	5.60(28)
C(14)	0.29643(45)	0.62263(34)	0.35739(27)	5.42(27)
C(15)	0.17386(42)	0.60009(33)	0.34893(26)	5.08(25)
C(16)	0.15346(36)	0.52810(30)	0.29138(24)	4.15(21)
C(22)	0.31058(40)	0.33806(37)	0.01030(24)	5.19(25)
C(23)	0.39578(47)	0.33857(45)	−0.06766(27)	6.61(32)
C(24)	0.43969(54)	0.24056(54)	−0.09833(30)	8.41(40)
C(25)	0.40297(63)	0.13980(51)	−0.05455(33)	9.11(44)
C(26)	0.31544(57)	0.13712(43)	0.02593(29)	7.53(36)
C(32)	0.51587(37)	0.10015(35)	0.26355(25)	4.85(24)
C(33)	0.56187(39)	−0.00737(37)	0.28493(27)	5.38(26)
C(34)	0.48384(42)	−0.09716(35)	0.28878(26)	5.23(26)
C(35)	0.36143(41)	−0.07858(33)	0.27058(27)	5.11(26)
C(36)	0.31479(35)	0.03026(31)	0.24764(25)	4.26(22)
C(42)	−0.22866(41)	0.53650(37)	0.25510(32)	6.15(30)
C(43)	−0.21987(49)	0.64589(39)	0.27133(38)	7.77(37)
C(44)	−0.20044(50)	0.66905(39)	0.35031(41)	8.34(39)
C(45)	−0.18475(53)	0.58299(43)	0.41297(36)	7.92(39)
C(46)	−0.19131(45)	0.47098(37)	0.39834(29)	6.05(29)
C(52)	−0.05661(38)	−0.00526(33)	0.30293(28)	4.96(25)
C(53)	0.01021(47)	−0.10516(36)	0.28604(35)	6.63(33)
C(54)	0.03324(57)	−0.13530(43)	0.20588(42)	8.68(44)
C(55)	−0.00931(68)	−0.06844(51)	0.13979(37)	9.76(49)
C(56)	−0.07917(58)	0.03439(42)	0.15487(31)	7.62(38)
C(62)	−0.05895(40)	0.36060(34)	0.02087(25)	4.86(24)
C(63)	−0.11836(49)	0.36631(40)	−0.05083(27)	6.32(31)
C(64)	−0.24757(52)	0.34772(40)	−0.04129(30)	6.75(34)
C(65)	−0.31857(48)	0.32510(44)	0.03987(33)	7.10(35)
C(66)	−0.26081(42)	0.32056(42)	0.11261(28)	6.13(30)
C(1)	0.30196(34)	0.26085(29)	0.41718(21)	3.67(19)
C(2)	0.39962(34)	0.22846(33)	0.46436(22)	4.18(21)
C(3)	0.39904(38)	0.12139(36)	0.50573(24)	4.91(24)
C(4)	0.30338(37)	0.05055(32)	0.50024(24)	4.66(23)
C(5)	0.20947(35)	0.08966(29)	0.45162(22)	4.00(20)
C(6)	0.50069(45)	0.30981(45)	0.46897(32)	6.76(34)

Table 3

The ^{31}P NMR data for $RhCl(amine)\{P(OPh)_3\}_2$ complexes

Amine	δ (ppm) (*J*(Rh–P) (Hz))	δ (ppm) (*J*(Rh–P) (Hz)	*J*(P–P) (Hz)
3-picoline	126.3 (267.4)	114.8 (317.3)	67.7
4-picoline	125.9 (267.2)	115.0 (317.2)	67.4
CH_2=CH-CH_2NH_2	121.0 (271.1)	114.4 (317.0)	68.8

$$\begin{tikzcd} RhCl(CO)\{P(OPh)_3\}_2 \arrow[r, "\text{2-picoline}"] & RhCl(CO)(2\text{-pic})\{P(OPh)_3\}_2 \arrow[d, "-CO"] \\ & RhCl(2\text{-pic})\{P(OPh)_3\}_2 \end{tikzcd}$$

Scheme 2

Table 4

Data for substitution of CO by 3-picoline in $RhCl(CO)(PR_3)_2$ complexes ([3-pic]/[Rh] = 50)

PR_3	(θ) [a] (deg)	$\%_{10}$ [b]	$\%_{20}$ [b]	$\%_{30}$ [b]	ν(CO) [c] (cm^{-1})	$\nu(CO)_{Ni}$ [d] (cm^{-1})
$P(OMe)_3$	107	37	72	76	2006	2079.5
PMe_2Ph	122	4	27	51	1968	2065.3
$P(OPh)_3$	130	68	76	78	2016	2085.3
$P(O\text{-}m\text{-}MeC_6H_4)_3$	130	56	68	75	2014	
PEt_2Ph	136	0	2	3	1964	2063.7
$PMePh_2$	136	conversion ⩽ 3% after 120 min			1974	2067.0
$PEtPh_2$	140				1970	2066.7
$P(O\text{-}o\text{-}MeC_6H_4)_3$	141				2012	2084.1
PPh_3	145				1968	2068.9

[a] Cone angle of PR_3 ligand [16]. [b] Conversion (in %) of $RhCl(CO)(PR_3)_2$ complex after 10, 20, 30 min calculated from the IR ν(CO) band intensity. [c] ν(CO) stretching frequency in $RhCl(CO)(PR_3)_2$. [d] ν(CO) stretching frequency in $Ni(CO)_3(PR_3)$ [16].

Table 5

Data for substitution of CO by 2-picoline and 3-picoline in $RhCl(CO)\{P(OMe)_3\}_2$ and $RhCl(CO)\{P(OPh)_3\}_2$ complexes

Complex	Amine	[amine]/[Rh]	$\%_{10}$ [a]	$\%_{20}$ [a]	$\%_{30}$ [a]
$RhCl(CO)\{P(OPh)_3\}_2$	2-pic	50	36	42	46
$RhCl(CO)\{P(OPh)_3\}_2$	3-pic	2	60	72	77
$RhCl(CO)\{P(OPh)_3\}_2$	3-pic	4	74	82	85
$RhCl(CO)\{P(OPh)_3\}_2$	3-pic	6	74	82	85
$RhCl(CO)\{P(OPh)_3\}_2$	3-pic	8	82	87	90
$RhCl(CO)\{P(OMe)_3\}_2$	2-pic	50	16	24	30

[a] See Table 4.

tion of 3-picoline by CO proceeds with the change of configuration of a complex from *cis* to *trans*.

Crystal structure of RhCl(3-pic){P(OPh)$_3$)$_2$

The overall structure of the RhCl(3-pic){P(OPh)$_3$}$_2$ molecule is shown in Fig. 1, and selected bond distances and bond angles are listed in Table 1. The rhodium atom has an almost square planar coordination. The Rh–P distances 2.150(2) and 2.167(2) Å are very closely comparable with those observed in other rhodium(I) triphenylphosphite complexes, e.g. 2.161(2), 2.150(2) Å in Rh(TFBA){P(OPh)$_3$}$_2$ [17]; 2.147(2), 2.156(2) Å in Rh(acac){P(OPh)$_3$}$_2$ [14] and 2.142 Å in (cod)RhCl$_2$Rh{P(OPh)$_3$}$_2$ [13]. The Rh–N distance of 2.132(3) Å is the same as in [Rh(cod)(μ-mhp)]$_2$ 2.132(3) Å [18] and comparable with that noted in [({C$_5$Me$_5$) Rh(py)}$_2$(μ-OH)$_2$](ClO$_4$)$_2$ 2.141(4) Å [19], [Rh(μ-S$_2$NC$_3$H$_4$)(cod)]$_2$ 2.103(3), 2.079(3) Å [20] and in Rh(pic)(CO)(PPh$_3$) 2.088(6) Å [21]. The bond distances and angles in all phosphite ligands are similar to those observed in other rhodium-triphenylphosphite complexes.

Experimental

The rhodium(I) complexes were synthesized according to literature methods: [Rh(μ-Cl)(cod)]$_2$ [21], [Rh(μ-OMe)(cod)]$_2$ [22], [Rh(μ-Cl)(CO)$_2$]$_2$ [23]. The complexes RhCl(CO)(PR$_3$)$_2$ (PR$_3$ = P(OMe)$_3$, P(OPh)$_3$, P(O-*o*-MeC$_6$H$_4$)$_3$, P(O-*m*-MeC$_6$H$_4$)$_3$, PEt$_2$Ph, PEtPh$_2$, PMe$_2$Ph, PMePh$_2$, PPh$_3$) were obtained by the treatment of [Rh(μ-Cl)(CO)$_2$]$_2$ with stoichiometric amounts of phosphine in hexane. The IR, ^{1}H and ^{31}P NMR spectra of the obtained compounds were as expected and consistent with literature data [24].

Synthesis of RhCl(3-pic){P(OPh)$_3$}$_2$

Route 1. To the [Rh(μ-OMe)(cod)]$_2$ (0.057 g) solution in CH$_2$Cl$_2$ (0.4 cm^3) P(OPh)$_3$ (0.13 g) in CH$_2$Cl$_2$ (0.4 cm^3) and 3-picoline (0.1 cm^3) were added. After 10 min hexane (0.5 cm^3) was added slowly and the solution was left for crystallization. Yield: 0.04 g (20%). A good quality crystal was selected for X-ray examination.

Route 2. To the [Rh(μ-Cl)(cod)]$_2$ (0.068 g) solution in CH$_2$Cl$_2$ (0.5 cm^3) P(OPh)$_3$ (0.19 g) in CH$_2$Cl$_2$ (0.5 cm^3) and 3-picoline (0.18 cm^3) were added, then ca. 0.5 cm^3 hexane was added slowly. The compound crystallized after a few minutes. Yield: 0.17 g (71%).

Route 3. The procedure for route 2 was followed. The amounts of reagents were: RhCl(CO){P(OPh)$_3$}$_2$ (0.076 g) in CH$_2$Cl$_2$ (0.6 cm^3), 3-picoline (0.2 cm^3), ca. 1 cm^3 hexane. Yield: 0.067 g (82%).

Analyses. Found: C, 58.8; H, 4.3; Cl, 5.2. C$_{42}$H$_{31}$ClNO$_6$P$_2$Rh (846.2) calc.: C, 59.2; H, 4.3; Cl, 4.2%. ^{1}H NMR (CDCl$_3$): $\delta = 1.85$ (3H, s); 7.25 (28H, m) ppm. UV–Vis (CHCl$_3$): 373 (1000), 324 (4300) nm.

The RhCl(amine){P(OPh)$_3$}$_2$ complexes (amine = 4-picoline, CH$_2$=CH–CH$_2$NH$_2$) were synthesized as described above (route 3).

Synthesis of RhCl(CO){P(OPh)$_3$}$_2$ from RhCl(3-pic){P(OPh)$_3$}$_2$

RhCl(3-pic){P(OPh)$_3$}$_2$ (0.108 g) in CH$_2$Cl$_2$ (1 cm^3) was saturated with CO for 3 min. The solvent was removed *in vacuo*, the residue was dissolved in CH$_2$Cl$_2$ and saturated again with CO. Removal of solvent yielded 0.088 g (88%) of $RhCl(CO)\{P(OPh)_3\}_2$.

The IR spectra were recorded on a Specord M-80 spectrometer; ^1H NMR spectra on Tesla 100MHz spectrometer; ^{31}P NMR spectra on a Varian 300 and Bruker MSL 300 spectrometers using 85% H_3PO_4 as an external standard and $CDCl_3$ as solvent.

Crystal structure determination of $RhCl(3\text{-}pic)\{P(OPh)_3\}_2$

Transparent yellow crystals of $C_{42}H_{37}ClNO_6P_2Rh$ are triclinic, space group $P\bar{1}$, with two molecules in a unit cell of dimensions: $a = 10.531(6)$, $b = 12.025(9)$, $c = 15.943(8)$ Å, $\alpha = 83.01(5)$, $\beta = 79.46(4)$, $\gamma = 86.33(5)°$, and $D_m = 1.436$ g cm^{-3}, $D_c = 1.438$ g cm^{-3}. 7716 Intensities ($2\theta < 50°$) were measured (for crystal 0.8 × 0.5 × 0.4 mm) on Syntex $P2_1$ diffractometer, at 300(1) K, using graphite monochromatized Mo-K_α radiation [λ(Mo-K_α) = 0.71069 Å]. 6656 Reflections were above the $3\sigma(I)$ level; $R_{merg} = 0.024$.

The Rh positions were located on a Patterson map. The positions of all other non-H atoms were obtained by standard difference Fourier techniques. The methyl H atoms were found from the difference map and other H atoms were kept at their idealized positions. The block-diagonal least-squares refinement [26] converged of $R = 0.034$ and $R_w = 0.041$ for 6035 unique reflections. Since the calculated absorption coefficient is 6.22 cm^{-1}, absorption corrections were not applied. The scattering factors were taken from set [27] and were corrected for anomalous dispersion.

Supplementary material available. Tables of observed and calculated structure factors and anisotropic thermal parameters are available from the authors.

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