Available online at www.sciencedirect.com
ScienceDirect
Journal of Organometallic Chemistry 692 (2007) 4297–4302
Journal of Organometallic Chemistry
www.elsevier.com/locate/jorganchem

A novel reaction producing the rhodium(I) complexes with π-coordinated tetraphenylborate anion, $(\pi\text{-}PhBPh_3)^-$. X-ray study of $[Rh(PPh_3)_2(\pi\text{-}PhBPh_3)]$

Elizaveta P. Shestakova [a], Yuri S. Varshavsky [a,*], Viktor N. Khrustalev [b], Ivan S. Podkorytov [a]

[a] *Institute of Chemistry, St. Petersburg State University, Petrodvorets, Universitetskii Pr., 26, 198504 St. Petersburg, Russia*
[b] *Nesmeyanov Institute of Organoelement Compounds, Vavilova Str., 28, 117813 Moscow, Russia*

Received 2 May 2007; received in revised form 21 June 2007; accepted 28 June 2007
Available online 4 July 2007

Abstract

Treating the complexes $[Rh(TFA)(PPh_3)_2]$, $[Rh(HFA)(PPh_3)_2]$, and $[Rh(TFA)(Cod)]$ (TFA – trifluoroacetylacetonate, HFA – hexafluoroacetylacetonate, Cod – 1,5 cyclooctadiene) with an excess of $NaBPh_4$ in acetonitrile yields the rhodium(I) complexes with coordinated $[BPh_4]^-$ anion, $[Rh(PPh_3)_2(\pi\text{-}PhBPh_3)]\cdot 2MeCN$ (**I**) and $[Rh(Cod)(\pi\text{-}PhBPh_3)]$ (**II**). The reactions present a new example of β-diketonate ligand replacement. The ^1H, ^{31}P, and ^{11}B NMR spectra of **I** and **II** are discussed. $[Rh(PPh_3)_2(\pi\text{-}PhBPh_3)]$ has been characterized by single crystal X-ray analysis.

Keywords: Rhodium; Tetraphenylborate coordination; ^1H, ^{31}P, ^{11}B NMR; X-ray

1. Introduction

Tetraphenylborate anion has been widely used as a counterion for the isolation of cationic species from solution. Recently, we succeeded in the isolation and characterization of the cationic complexes *cis*-$[Rh(\beta\text{-diket})(PPh_3)_2(CH_3)(MeCN)][BPh_4]$ (β-diket is acetylacetonate or benzoylacetonate) [1], which were obtained by CH_3I oxidative addition to the rhodium(I) complexes $[Rh(\beta\text{-diket})(PPh_3)_2]$ in acetonitrile in the presence of $NaBPh_4$. However, in attempting to prepare according to the same procedure the cationic complexes containing β-diketonate ligand with at least one CF_3 group, we recognized, that, immediately after mixing of the rhodium(I) complexes $[Rh(TFA)(PPh_3)_2]$, $[Rh(HFA)(PPh_3)_2]$, or $[Rh(TFA)(Cod)]$, (TFA – trifluoroacetylacetonate, HFA – hexafluoroacetylacetonate, Cod – 1,5 cyclooctadiene) with an excess of $NaBPh_4$ in acetonitrile, the known complexes with coordinated phenyl ring of anion $[BPh_4]^-$, $[Rh(PPh_3)_2(\pi\text{-}PhBPh_3)]$ and $[Rh(Cod)(\pi\text{-}PhBPh_3)]$ [2], were formed. Although rhodium complexes of this type are well documented [2–9] and widely studied in organic catalysis [9–14], an uncommon way of their formation arrested our attention. In the chemistry of $[Rh(\beta\text{-diket})(L)_2]$ complexes, a plethora of ligand L (CO, phosphines, arsines, olefins) mutual substitutions is known, whereas the examples of β-diketonate ligand replacement are limited with several reactions of bidentate σ-donors, such as other β-diketonate ligands, *o*-phenantroline, 2,2′-bipyridyl and their derivatives, or bis(diphenylphosphino)ethane [15–18]. Thus, the ability of the phenyl group of the $[BPh_4]^-$ anion to replace β-diketonate ligand forming complexes of the π-arene type seems to be fairly unexpected.

In this paper, we report a new reaction of β-diketonate ligand replacement in rhodium(I) complexes with tetraphe-

* Corresponding author. Tel.: +7 812 428 4710; fax: +7 812 2743445.
E-mail address: yurel@peterlink.ru (Y.S. Varshavsky).

0022-328X/$ - see front matter © 2007 Elsevier B.V. All rights reserved.
doi:10.1016/j.jorganchem.2007.06.057

nylborate anion in acetonitrile, ^{1}H, ^{31}P{^{1}H}, and ^{11}B{^{1}H} NMR spectra of [Rh(PPh$_3$)$_2$(π-*Ph*BPh$_3$)] · 2MeCN (**I**) and [Rh(Cod)(π-*Ph*BPh$_3$)] (**II**), and the X-ray structure of [Rh(PPh$_3$)$_2$(π-*Ph*BPh$_3$)].

2. Results and discussion

Stirring of the [Rh(TFA)(PPh$_3$)$_2$] or [Rh(HFA)(PPh$_3$)$_2$] suspension with an excess of NaBPh$_4$ in acetonitrile at room temperature results in fast formation of yellow microcrystalline solid. The product was isolated by filtration and characterized by elemental analysis and ^{1}H and ^{31}P{^{1}H} NMR spectra as [Rh(PPh$_3$)$_2$(π-*Ph*BPh$_3$)] · 2MeCN (**I**). The ^{1}H NMR spectrum of **I** (in CDCl$_3$) contains the well resolved signals from coordinated phenyl group at δ 5.62 ppm (*ortho*-, doublet, $^3J \sim 6$ Hz, 2H) and 4.68 ppm (*meta*-, triplet, $^3J \sim 6$ Hz, 2H); a triplet from *para*-proton is masked by the assemblage of signals from PPh$_3$ and non-coordinated phenyl groups (BPh$_3$) in the region δ 6.9–7.5 ppm. A sharp singlet at δ 2.02 ppm (6H) belongs to free acetonitrile, 2MeCN per Rh, which passes into solution upon dissolving the solvated complex. The ^{31}P{^{1}H} NMR spectrum of **I** (in CDCl$_3$) shows one sharp doublet from 2 equivalent triphenylphosphine ligands (δ 44.2 ppm, ^1J(PRh) 207.1 Hz). The related complexes, [Rh(diphos)(π-*Ph*BPh$_3$)] [11] and [Rh{Fe(η^5-C$_5$H$_4$PPh$_2$)$_2$}(π-*Ph*BPh$_3$)] [7], have close values of the ^{1}H and ^{31}P NMR parameters. The unsolvated complex [Rh(PPh$_3$)$_2$(π-*Ph*BPh$_3$)] described previously [2] was prepared as red-brown crystals whose low solubility prevented recording of NMR spectra. We succeeded in recording NMR spectra of the chloroform solution of the red-brown form of [Rh(PPh$_3$)$_2$(π-*Ph*BPh$_3$)] obtained by recrystallization of **I** from methylene chloride/diethyl ether solution. Its ^{1}H spectrum coincided with the spectrum of **I** except the signal at δ 2.02 ppm (free MeCN) was absent.

As already noted, formation of **I** proceeds fast. In 20 min, at room temperature, its yield amounts to about 98%. Additional stirring of the suspension results in decrease of the yield (~50% after 50 min). We believe that coordinating solvent MeCN gradually displaces the coordinated tetraphenylborate anion, and this reaction is responsible for the yield decreasing. Examples of coordinated [BPh$_4$]$^-$ replacement by coordinating solvents, such as MeCN, DMF, THF, were described in literature [8,11,12]. In the solid state, **I** is stable for a long time even in the presence of air.

Stirring of [Rh(TFA)(Cod)] with an excess of NaBPh$_4$ in acetonitrile at room temperature results in the formation of pale yellow [Rh(Cod)(π-*Ph*BPh$_3$)] (**II**). The complex was characterized by elemental analysis and, despite its low solubility, we recorded its ^{1}H NMR spectrum in CDCl$_3$. In this spectrum, signals from coordinated and three uncoordinated phenyl groups of tetraphenylborate ion are separated rather well. The signals from uncoordinated phenyl groups (BPh$_3$) appear at δ (ppm) 7.42 (*ortho*-, doublet, $^3J = 7.3$ Hz, 6H); 7.20 (*meta*-, triplet, $^3J = 7.3$ Hz, 6H), 7.08 (*para*-, triplet, $^3J = 7.3$ Hz, 3H). Resonances of coordinated phenyl group are clearly resolved and located at δ (ppm) 6.76 (*para*-, triplet, $^3J \sim 6$ Hz, 1H), 6.63 (*ortho*-, doublet, $^3J \sim 6$ Hz, 2H), 6.08 ppm (*meta*-, triplet, $^3J \sim 6$ Hz, 2H). Signals at δ 4.23, 2.32, 1.99, and 1.96 ppm (poorly resolved multiplets) belong to Cod ligand. Similar Cod ^{1}H NMR patterns were observed in the spectra of initial [Rh(TFA)(Cod)] (δ 4.19, 2.51–2.47, 1.88, and 1.85 ppm) and other complexes with Cod ligand [15,19,20]. We failed to find in the literature the ^{1}H NMR spectrum of [Rh(Cod)(π-*Ph*BPh$_3$)], but the related complex [Rh(NBD)(π-*Ph*BPh$_3$)] [2] has close values of the spectral parameters.

The reported reactions run fast and with high yield when β-diketonate ligand contains at least one CF$_3$ group. In the case of the acetylacetonate complex the reaction proceeds to only a small extent. In our experiments, only ~30% of starting [Rh(Acac)(PPh$_3$)$_2$] was converted after 3.5 h stirring.

It is worth noting that we observed weak signals corresponding to [Rh(PPh$_3$)$_2$(π-*Ph*BPh$_3$)] in the ^{1}H and ^{31}P NMR spectra of *cis*-[Rh(β-diket)(PPh$_3$)$_2$(CH$_3$)(MeCN)][BPh$_4$] and *trans*-[Rh(β-diket)(PPh$_3$)$_2$(COCH$_3$)][BPh$_4$] reported previously [21] when their solutions (in CH$_2$Cl$_2$ or CHCl$_3$) were kept under an inert atmosphere for days.

Along with a few known complexes [Rh(L)$_2$(π-*Ph*BPh$_3$)] with one coordinated phenyl ring of anion [BPh$_4$]$^-$, examples of a tetraphenylborate anion bridging two and three rhodium metal centers are documented in the literature, namely the cationic complexes {[(C$_2$H$_4$)$_2$Rh(π-*Ph*)]$_2$BPh$_2$}(O$_3$SCF$_3$) and {[(C$_2$H$_4$)$_2$Rh(π-*Ph*)]$_3$BPh)}(O$_3$SCF$_3$)$_2$ [8]. In order to examine whether **I** and **II** are able to form related dirhodium cationic derivatives, we stirred the mixtures {[Rh(PPh$_3$)$_2$(π-*Ph*BPh$_3$)] · 2MeCN + [Rh(TFA)(PPh$_3$)$_2$]} and {[Rh(Cod)(π-*Ph*BPh$_3$)] + [Rh(TFA)(Cod)]} at room temperature in the mixed methanol/toluene solvent. The ^{1}H and ^{31}P{^{1}H} NMR spectra of the reaction mixtures showed that in both cases the starting compounds remained unchanged, and any indication of the presence of dirhodium complexes with bridging tetraphenylborate anion was absent. However, after stirring the mixture {[Rh(PPh$_3$)$_2$(π-*Ph*BPh$_3$)] · 2MeCN + [Rh(TFA)(Cod)]} under the same conditions, the complexes [Rh(TFA)(PPh$_3$)$_2$] and [Rh(Cod)(π-*Ph*BPh$_3$)] were distinctively detected in the reaction mixture by ^{1}H and ^{31}P{^{1}H} NMR. We believe that formation of these complexes in this case proceeded *via* a dirhodium intermediate contained [Rh(PPh$_3$)$_2$Rh(Cod)((π-*Ph*)$_2$BPh$_2$)]$^+$ cationic unit with TFA$^-$ as a counterion. Our assumption is based on the results of authors [8,12] who reported the first example of coordinated tetraphenylborate ion transfer between two metal centers.

The ^{11}B{^{1}H} NMR spectra of **I** and **II** (in THF) show singlets at δ −7.50 and −7.60 ppm, respectively. The signals of the complexes are up-field shifted (Δδ ≅ −1 ppm) with respect to the ^{11}B resonance of NaBPh$_4$ (−6.50 ppm in THF), and are significantly broadened ($w_{1/2} = 22$ Hz

(**I**), 15 Hz (**II**) *vs.* 1 Hz for $NaBPh_4$). These findings are consistent with the results published earlier [11]. The appearance of a very week singlet at −6.50 ppm in the ^{11}B spectrum of **I** points to the partial detachment of $[BPh_4]^-$ anion under our experimental conditions.

Crystal of the complex $[Rh(PPh_3)_2(\pi\text{-}PhBPh_3)]$ for the X-ray investigation was obtained by recrystallization of the solvated complex, $[Rh(PPh_3)_2(\pi\text{-}PhBPh_3)]\cdot 2MeCN$ (**I**), from methylene chloride/diethyl ether solution. The molecular structure of the complex is shown in Fig. 1.

Selected bond lengths and angles are listed in Table 1. As shown in Fig. 1, the rhodium atom is coordinated to the phosphorus atoms of two PPh_3 ligands and to one of the phenyl rings of a tetraphenylborate anion. In its substantial structural patterns, $[Rh(PPh_3)_2(\pi\text{-}PhBPh_3)]$ is closely similar to other rhodium complexes containing $(\pi\text{-}PhBPh_3)^-$ ligand [3,4,6–8,22]. As in other studied structures, the coordinated phenyl ring markedly deviates from planarity, resulting in a boat conformation. Four carbon atoms, C(38), C(39), C(41), C(42), form a quasi planar (within 0.01 Å) rectangle **R**, whereas, *ipso*-C(37) and *para*-C(40), are displaced from this plane pointing from the metal. The dihedral angles between the **R** plane and two planes deflected from the metal atom are 8.6° (*ipso*-carbon) and 5.5° (*para*-carbon). The Rh distance to the geometrical centroid of the rectangle **R** is 1.842 Å.

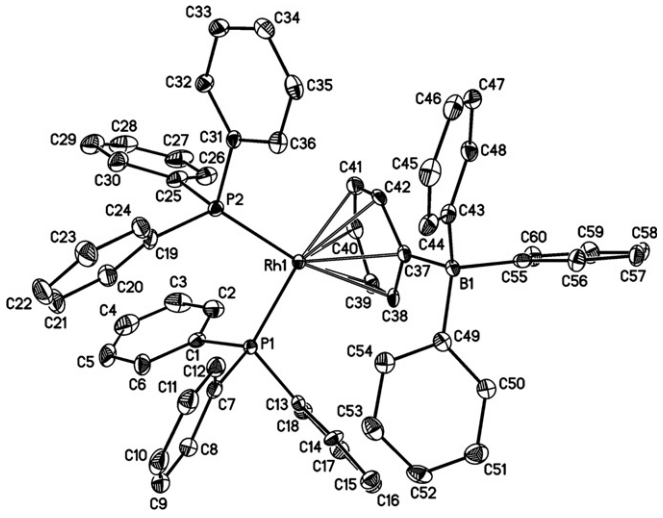

Fig. 1. The structure of $[Rh(PPh_3)_2(\pi\text{-}PhBPh_3)]$ (50% probability ellipsoids).

Table 1
Selected bond lengths (Å) and angles (°) for the complex $[Rh(PPh_3)_2(\pi\text{-}PhBPh_3)]$ with estimated standard deviations in parentheses

Bond lengths (Å)		Bond angles (°)	
Rh–P(1)	2.2458(10)	P(1) Rh(1) P(2)	95.15(4)
Rh–P(2)	2.2731(10)		
Rh–C(37)	2.499(4)		
Rh–C(38)	2.294(4)	P(1) Rh(1) C(38)	98.36(10)
Rh–C(39)	2.267(4)	P(1) Rh(1) C(39)	95.27(10)
Rh–C(40)	2.340(4)		
Rh–C(41)	2.300(4)	P(2) Rh(1) C(41)	98.18(10)
Rh–C(42)	2.364(4)	P(2) Rh(1) C(42)	103.25(10)

The structural features of the first described complex with coordinated tetraphenylborate anion, $[Rh(P(OCH_3)_3)_2(\pi\text{-}PhBPh_3)]$, prompted authors [3,22] to consider them as a quasi tetracoordinate rhodium(I) complex with midpoints ***X*** and ***Y*** of two C–C bonds at the opposite edges of ***R*** as "olefin like" ligands. This interpretation has then been applied to the cationic toluene complex $[Rh(P(OPh)_3)_2(\pi\text{-}PhCH_3)][ClO_4]$ [23] which turned out very close in its geometry to the complexes of rhodium(I) with $(\pi\text{-}PhBPh_3)^-$ ligand. We believe that the structure of $[Rh(PPh_3)_2(\pi\text{-}PhBPh_3)]$ can be analogously treated from this viewpoint. Some geometrical parameters of these three structures are collected in Table 2.

The similarity between complexes containing isoelectronic ligands $(\pi\text{-}PhBPh_3)^-$ and $(\pi\text{-}PhCH_3)$ suggests that the boat like, partially "de-aromatized", conformation of the coordinated phenyl ring is caused by intramolecular bonding effects, primarily by electronic demand of metal center which tends to achieve 16e configuration, the most typical one for rhodium(I) complexes. However, it should be emphasized, that coordination of rhodium atom in these complexes is far from the ideal tetragonal planar mode. For instance, in the complex reported here, the triangles P(1)Rh(P(2) and ***X***Rh***Y*** are tilted at an angle of 7.2° to each other (***X*** and ***Y*** are midpoints of C(38)–C(39) and C(41)–C(42) bonds, respectively, Fig. 1). The "coordination quadrangle" P(1)P(2)***XY*** in these complexes is rather a trapezium due to low value of ***X***Rh***Y*** angle (Table 2).

The ^1H NMR data reported above may be considered in terms of the preceding discussion on the ligand L electronic effects in $[Rh(L)_2(\pi\text{-}PhBPh_3)]$ complexes [8,9,11]. The data collected in Table 3 show that proton chemical shifts of the

Table 2
Some geometrical parameters of the complexes $[Rh(PPh_3)_2(\pi\text{-}PhBPh_3)]$, $[Rh(P(OCH_3)_3)_2(\pi\text{-}PhBPh_3)]$ [22], and $[Rh(\pi\text{-}PhCH_3)(P(OPh)_3)_2][ClO_4]$ [23]

Compound	Distances (Å)				Angles (°)	
	Rh-***X***	Rh-***Y***	Rh-P(1)	Rh-P(2)	***X***Rh***Y***	P(1)RhP(2)
$[Rh(PPh_3)_2(\pi\text{-}PhBPh_3)]$	2.169	2.222	2.246	2.273	65.9	95.15
$[Rh(P(OCH_3)_3)_2(\pi\text{-}PhBPh_3)]$	2.19	2.20	2.19	2.18	66.6	90.4
$[Rh(P(OPh)_3)_2(\pi\text{-}PhCH_3)]^+$	2.194	2.202	2.180	2.188	64.1	90.07

X and ***Y*** are midpoints of two C–C bonds at the opposite edges of a quasi planar rectangle ***R***; in the case of $[Rh(PPh_3)_2(\pi\text{-}PhBPh_3)]$, ***R*** is the rectangle, formed by four carbon atoms, C(38), C(39), C(41), C(42) (Fig. 1).

Table 3
^{1}H NMR chemical shifts (δ, ppm) for coordinated (π-*Ph*) and non-coordinated (BPh_3) phenyl rings of tetraphenylborate anion in the complexes $[Rh(L)_2(\pi\text{-}PhBPh_3)]$ and free anion $[BPh_4]^-$ in $NaBPh_4$

Compound	Solvent	*ortho*-H	*meta*-H	*para*-H	Ref.
Coordinated phenyl ring					
[Rh(dppf)(π-*Ph*BPh_3)][a]	$CDCl_3$	5.76	4.43	Masked	[7]
$[Rh(PPh_3)_2(\pi\text{-}PhBPh_3)]$	$CDCl_3$	5.62	4.68	Masked	This work
[Rh(dppb)(π-*Ph*BPh_3)][b]	CD_2Cl_2	5.63	4.95	6.81	[9]
[Rh(diphos)(π-*Ph*BPh_3)]	$CDCl_3$	6.34	5.42	6.22	[11]
	CD_2Cl_2	6.23	5.47	6.32	[11]
[Rh(bpy)(π-*Ph*BPh_3)]	CD_2Cl_2	5.96	5.59	Masked	[8]
$[Rh[P(OCH_3)_3]_2(\pi\text{-}PhBPh_3)]$	$CDCl_3$	6.48	5.84	6.82	[4]
$[Rh(C_2H_4)_2(\pi\text{-}PhBPh_3)]$	CD_2Cl_2	6.44	6.07	6.98	[8]
[Rh(NBD)(π-*Ph*BPh_3)]	1,2-Dichloroethane	6.47	6.07	6.62	[2]
[Rh(Cod)(π-*Ph*BPh_3)]	$CDCl_3$	6.63	6.08	6.76	This work
[Rh(1,3-butadien)(π-*Ph*BPh_3)]	1,2-Dichloroethane	6.70	6.31	6.60	[2]
Non-coordinated phenyl rings					
[Rh(diphos)(π-*Ph*BPh_3)]	$CDCl_3$	7.15	6.95	6.92	[11]
$[Rh(C_2H_4)_2(\pi\text{-}PhBPh_3)]$	CD_2Cl_2	7.32	7.14	7.02	[8]
[Rh(Cod)(π-*Ph*BPh_3)]	$CDCl_3$	7.42	7.20	7.08	This work
$Na^+[BPh_4]^-$	CD_3CN	7.30	7.02	6.87	This work

[a] dppf = $Fe(\eta^5\text{-}C_5H_4PPh_2)_2$.
[b] dppb = 1,4-bis(diphenylphosphino)butan.

coordinated phenyl in the spectra of both complexes, **I** and **II**, fall into the ranges of values for their close analogs.

It may be seen that the up-field shifts of proton resonances of the coordinated phenyl group are much more significant in $[Rh(L)_2(\pi\text{-}PhBPh_3)]$ complexes with the strongest σ-donor ligands L, phosphines and bipyridyl, whereas the lesser up-field shifts are associated with higher π-acceptor and poorer σ-donor abilities of L, olefins and phosphite. Notice that the electron donating groups, for instance in substituted aromatics, affect δ^1H values in a similar manner. The presented data are consistent with the previous idea [8,9] that the up-field shift of proton resonances upon phenyl coordination is due to the electron density transfer from ligands L to the coordinated phenyl ring through the metal center. The proton chemical shifts of non-coordinated phenyls (BPh_3) may imply some redistribution of electron density between coordinated and non-coordinated phenyl rings. It should be remarked that the chemical shifts of *meta*-protons (in the case of **I**, protons at C(39) and C(41)) are particularly sensitive to the σ-donor ability of ligands L, whereas the chemical shifts of *para*-protons (at C(40)) are poorly influenced by it. This difference may reflect the unequal role of corresponding carbon atoms in phenyl to rhodium coordination.

3. Experimental

All operations were performed under an atmosphere of dry argon. The rhodium complexes $[Rh(Acac)(PPh_3)_2]$, [Rh(TFA)(Cod)], $[Rh(TFA)(PPh_3)_2]$, and [Rh(HFA)-$(PPh_3)_2$] were synthesized by published procedures [24,25]. Elemental analyses were performed with a Hewlett–Packard 185 microanalyzer. NMR spectra (300.1 MHz ^{1}H, 96.3 MHz ^{11}B {^{1}H}, and 121.5 MHz ^{31}P {^{1}H}) were measured on a Bruker DPX-300 spectrometer. The ^{1}H chemical shifts were measured with solvent ($CDCl_3$) residual proton as internal standard, $\delta^1H = 7.28$ ppm. The ^{31}P chemical shifts were measured with 85% phosphoric acid as external standard, $\delta^{31}P = 0.0$ ppm. The ^{11}B chemical shifts were measured with $BF_3 \cdot (C_2H_5)_2O$ as external standard, $\delta^{11}B = 0.0$ ppm.

3.1. Preparation of $[Rh(PPh_3)_2(\pi\text{-}PhBPh_3)] \cdot 2MeCN$ (**I**)

Mixture of $[Rh(TFA)(PPh_3)_2]$ (0.10 g, 0.13 mmol) and $NaBPh_4$ (0.13 g, 0.38 mmol) suspended in acetonitrile (1 ml) was stirred for 20 min at 20 °C. A yellow solid was isolated by filtration, washed with acetonitrile and dried in vacuo. Yield: 0.13 g (97.8%). Anal. Calc. for $C_{64}H_{56}BN_2P_2Rh$: C, 74.72; H 5.49; N, 2.72. Found: C, 74.86; H, 5.49; N, 2.90%. The reaction with starting $[Rh(HFA)(PPh_3)_2]$ under the same conditions gave the identical product. Anal. Found: C, 74.94; H, 5.63; N, 2.32%.

3.2. Preparation of $[Rh(Cod)(\pi\text{-}PhBPh_3)]$ (**II**)

Mixture of [Rh(TFA)(Cod)] (0.089 g, 0.24 mmol) and $NaBPh_4$ (0.26 g, 0.76 mmol) suspended in acetonitrile (1 ml) was stirred for 1 h at 20 °C. A pale yellow solid was isolated by filtration, washed with acetonitrile and hexane, and dried in vacuo. Yield: 0.096 g (74.1%). Anal. Calc. for $C_{32}H_{32}BRh$: C, 72.46; H 6.09. Found: C, 72.11; H, 5.96%.

3.3. The reaction between $[Rh(Cod)(\pi\text{-}PhBPh_3)]$(**II**) and $[Rh(TFA)(Cod)]$

Methanol (3 ml) and toluene (1 ml) were added to a mixture of [Rh(Cod)(π-*Ph*BPh_3)] (0.13 g, 0.24 mmol) and

[Rh(TFA)(Cod)] (0.089 g, 0.24 mmol). The mixture was stirred for 2 h at 20 °C. A yellow solid was removed by filtration, dried in vacuo (weight 0.13 g). ^{1}H NMR ($CDCl_3$): δ 7.8–7.0 (m, C_6H_5), 6.76 (t, *p*-H, $^3J \sim 6$ Hz), 6.63 (d, *o*-H, $^3J \sim 6$ Hz), 6.08 (t, *m*-H, $^3J \sim 6$ Hz), 4.23 (s), 2.32, 1.99, 1.96 (poorly resolved multiplets) (starting **II**). The solvents were removed from filtrate under reduced pressure. ^{1}H NMR ($CDCl_3$): δ 5.75 (s, CH), 4.19 (s), 2.5, 1.88–1.85 (poorly resolved multiplets) (Cod), 2.09 (s, C–CH_3) (starting [Rh(TFA)(Cod)]).

3.4. The reaction between [Rh(PPh$_3$)$_2$(π-PhBPh$_3$)] · 2MeCN (**I**) and [Rh(TFA)(Cod)]

Methanol (1 ml) and toluene (1 ml) were added to a mixture of [Rh(PPh$_3$)$_2$(π-PhBPh$_3$)] · 2MeCN (**I**) (0.08 g, 0.08 mmol) and [Rh(TFA)(Cod)] (0.03 g, 0.08 mmol). The mixture was stirred for 2 h at 20 °C. Yellow-orange solid was isolated by filtration, dried in vacuo (weight 0.047 g). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 57.9 (dd, ^1J(PRh) 198.1 Hz, ^2J(PP) 56.5 Hz), δ 54.0 (dd, ^1J(PRh) 193.3 Hz, ^2J(PP) 56.5 Hz) ([Rh(TFA)(PPh$_3$)$_2$]); 44.2 (d, ^1J(PRh) 207.1 Hz) (starting **I**), 30.3(s) Ph_3PO. ^{1}H NMR ($CDCl_3$): δ 7.8–7.0 (group of signals, C_6H_5), 6.76 (t, *p*-H, $^3J \sim 6$ Hz), 6.63 (d, *o*-H, $^3J \sim 6$ Hz), 6.08 (t, *m*-H, $^3J \sim 6$ Hz), 4.23 (s), 2.32, 1.99, 1.96 (poorly resolved multiplets) (**II**), 5.66 (s, CH), 1.47 (s, C–CH_3) ([Rh(TFA)(PPh$_3$)$_2$]), 5.62 (d, *o*-H, $^3J \sim 6$ Hz), 4.68 (t, *m*-H, $^3J \sim 6$ Hz) (starting **I**). The solvents were removed from dark-orange filtrate under reduced pressure. NMR spectra of the residue ($CDCl_3$): ^{31}P{^{1}H}: δ 30.3 (s) (Ph_3PO); ^{1}H: δ 7.8–7.0 (m, C_6H_5, Ph_3PO), 5.75 (s, CH), 4.19 (s), 2.5, 1.88–1.85 (poorly resolved multiplets) (Cod), 2.09 (s, C–CH_3) (starting [Rh(TFA)(Cod)]).

Table 4
Crystallographic data for [Rh(PPh$_3$)$_2$(π-*Ph*BPh$_3$)]

Compound	[Rh(PPh$_3$)$_2$(π-*Ph*BPh$_3$)]
Empirical formula	$C_{60}H_{50}BP_2Rh$
Fw	946.66
Temperature (K)	100.0(2)
Crystal size (mm)	0.30 × 0.25 × 0.20
Crystal system	Triclinic
Space group	$P\bar{1}$
a (Å)	9.9184(7)
b (Å)	13.7097(10)
c (Å)	18.3991(13)
α (°)	85.437(5)
β (°)	75.271(5)
γ (°)	70.971(5)
V (Å^3)	2287.4(3)
Z	2
d_c (g cm^{-3})	1.374
F(000)	980
μ (mm^{-1})	0.484
θ Range (°)	1.94–27.03
Index range	$-12 \leqslant h \leqslant 12$ $-17 \leqslant k \leqslant 17$ $-23 \leqslant l \leqslant 23$
Number of reflections collected	23625
Number of unique reflections (R_{int})	9811 (0.0440)
Number of reflections with $I > 2\sigma(I)$	8221
R_1; wR_2 ($I > 2\sigma(I)$)	0.0515; 0.1174
R_1; wR_2 (all data)	0.0640; 0.1227
Data/restraints/parameters	9811/0/577
GOF on F^2	1.038
Largest difference in peak/hole (e Å^{-3})	0.717/−0.778
Absolute correlations T_{max}; T_{min}	0.909; 0.868

3.5. X-ray structure determinations

Data were collected on a Bruker three-circle diffractometer equipped with an X8-APEX-II CCD detector and corrected for absorption [26]. For details see Table 4.

The structure was solved by direct methods and refined by full-matrix least-squares technique on F^2 with anisotropic thermal parameters for non-hydrogen atoms. The hydrogen atoms were placed in calculated positions and refined in the riding model with fixed thermal parameters. All calculations were carried out by use of the SHELXTL program (PC Version 6.12) [27].

Acknowledgement

Financial support from the Russian Foundation for Basic Research (Project No. 05-03-32463) is gratefully acknowledged.

Appendix A. Supplementary material

CCDC 638558 contains the supplementary crystallographic data for [Rh(PPh$_3$)$_2$(π-PhBPh$_3$)]. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2007.06.057.

References

[1] E.P. Shestakova, Yu.S. Varshavsky, K.A. Lyssenko, A.A. Korlyukov, V.N. Khrustalev, M.V. Andreeva, J. Organomet. Chem. 689 (2004) 1930.
[2] R.R. Schrock, J.A. Osborn, Inorg. Chem. 9 (1970) 2339.
[3] M.J. Nolte, G. Gafner, L.M. Haines, Chem. Commun. (1969) 1406.
[4] L.M. Haines, Inorg. Chem. 10 (1971) 1685.
[5] R. Uson, P. Lahuerta, J. Reyes, L.A. Oro, Trans. Met. Chem. 4 (1979) 333.
[6] P. Albano, M. Aresta, M. Manassero, Inorg. Chem. 19 (1980) 1069.
[7] B. Longato, G. Pilloni, R. Graziani, U. Casellato, J. Organomet. Chem. 407 (1991) 369.
[8] M. Aresta, E. Quaranta, A. Albinati, Organometallics 12 (1993) 2032.
[9] Z. Zhou, G. Facey, B.R. James, H. Alper, Organometallics 15 (1996) 2496.
[10] H. Alper, J.Q. Zhou, J. Chem. Soc., Chem. Commun. (1993) 316.
[11] M. Aresta, E. Quaranta, I. Tommasi, Gaz. Chim. Ital. 123 (1993) 271.

[12] M. Aresta, E. Quaranta, I. Tommasi, S. Dérien, E. Duňach, Organometallics 14 (1995) 3349.
[13] Y.S. Lin, B. El Ali, H. Alper, Tetrahedron Lett. 42 (2001) 2423, and refs. therein.
[14] Y.S. Lin, B. El Ali, H. Alper, J. Am. Chem. Soc. 123 (2001) 7719, and refs. therein.
[15] C. Pettinari, F. Marchetti, A. Cingolani, G. Bianchini, A. Drozdov, V. Vertlib, S. Troyanov, J. Organomet. Chem. 651 (2002) 5.
[16] (a) J. Potgieter, J. Organomet. Chem. 366 (1989) 369;
(b) B.T. Heaton, C. Jacob, J. Markopoulos, O. Markopoulou, J. Nähring, C.-K. Skylaris, A.K. Smith, J. Chem. Soc., Dalton Trans. (1996) 1701.
[17] (a) J.G. Leipoldt, E.C. Grobler, Trans. Met. Chem. 11 (1986) 110;
(b) J.G. Leipoldt, G.J. Lamprecht, E.C. Steynberg, J. Organomet. Chem. 402 (1991) 259.
[18] (a) K. Angermund, W. Baumann, E. Dinjus, R. Fornika, H. Görls, M. Kessler, C. Krüger, W. Leitner, F. Lutz, Chem. Eur. J. 3 (1997) 755;
(b) R. Fornika, C. Six, H. Görls, M. Kessler, C. Krüger, W. Leitner, Can. J. Chem. 79 (2001) 642.
[19] Yu.S. Varshavsky, T.G. Cherkasova, L.S. Bresler, Russ. J. Coord. Chem. 12 (1987) 452.
[20] P.G.A. Kumar, P.S. Pregosin, T.M. Schmid, G. Consiglio, Magn. Reson. Chem. 42 (2004) 795.
[21] E.P. Shestakova, Yu.S. Varshavsky, A.B. Nikolskii, J. Organomet. Chem. 690 (2005) 3397.
[22] M.J. Nolte, G. Gafner, Acta Cryst. B 30 (1974) 738.
[23] R. Uson, P. Lahuerta, J. Reyes, L.A. Oro, Inorg. Chim. Acta 42 (1980) 75.
[24] F. Bonati, G. Wilkinson, J. Chem. Soc. (1964) 3156.
[25] E.P. Shestakova, T.G. Cherkasova, I.S. Podkorytov, Yu.S. Varshavsky, Rhodium Express 7–8 (1993) 17.
[26] G.M. Sheldrick, SADABS, v. 2.03, Bruker/Siemens Area Detector Absorption Correction Program, Bruker AXS, Madison, Wisconsin, USA, 2003.
[27] G.M. Sheldrick, SHELXTL, v. 6.12. Structure Determination Software Suite, Bruker AXS, Madison, Wisconsin, USA, 2001.