Coordination Behavior of $^t\mathrm{Bu_2PH}$ towards $[\{\mathrm{Rh}(\mu\text{-Cl})(\mathrm{coe})_2\}_2]$ (coe = *cis*-cyclooctene): Crystal and Molecular Structure of $[\{\mathrm{Rh}(\mu\text{-Cl})(^t\mathrm{Bu_2PH})_2\}_2]$

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Z. Naturforsch. **2008**, *63b,* 1035 – 1039; received May 15, 2008

Dedicated to Professor Wolfgang A. Herrmann on the occasion of his 60th birthday

The reaction of $[\{\mathrm{Rh}(\mu\text{-Cl})(\mathrm{coe})_2\}_2]$ (coe = *cis*-cyclooctene) with $^t\mathrm{Bu_2PH}$ in different solvents in various molar ratios was investigated. Working with a molar ratio of Rh to P = 1 : 2 in heptane overnight afforded $[\{\mathrm{Rh}(\mu\text{-Cl})(^t\mathrm{Bu_2PH})_2\}_2]$ (**1**) in nearly quantitative yield. Upon tuning the molar ratio (Rh/P) in the range from 1 : 2 to 1 : 0.5, $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR spectroscopy indicated the formation of $[(^t\mathrm{Bu_2PH})_2\mathrm{Rh}(\mu\text{-Cl})_2\mathrm{Rh}(\mathrm{coe})_2]$ (**3**) besides the complexes $[\{\mathrm{Rh}(\mu\text{-Cl})(\mathrm{coe})(^t\mathrm{Bu_2PH})\}_2]$ (*cis*, **2a**; *trans*, **2b**). The constitution of **3** was established by an independent synthesis mixing **1** with $[\{\mathrm{Rh}(\mu\text{-Cl})(\mathrm{coe})_2\}_2]$ or $[\{\mathrm{Rh}(\mu\text{-Cl})(\mathrm{cod})\}_2]$ (cod = 1.4-cyclooctadiene), respectively, which also yielded $[(^t\mathrm{Bu_2PH})_2\mathrm{Rh}(\mu\text{-Cl})_2\mathrm{Rh}(\mathrm{cod})]$ (**4**). Single crystals of **1** have been analyzed by X-ray crystallography (monoclinic, *Cc*, $Z = 8$, $a = 32.7375(3)$, $b = 11.1294(1)$, $c = 24.5134(3)$ Å; $\beta = 106.7228(4)°$; $V = 8553.70(15)$ Å^3; $T = 200$ (2) K).

Key words: Rhodium, Olefin Complex, Secondary Phosphane, Crystal Structure

Introduction

We are currently interested in the reaction behavior of complexes $[\{\mathrm{M}(\mu\text{-Cl})(\mathrm{coe})_2\}_2]$ (M = Rh, Ir; coe = *cis*-cyclooctene) towards sterically demanding phosphanes such as $^t\mathrm{Bu_2PH}$ [1]. Recently we found that $[\{\mathrm{Ir}(\mu\text{-Cl})(\mathrm{coe})_2\}_2]$ reacts with this phosphane under optimized conditions to give the complex *trans*-$[\mathrm{IrCl}(\mathrm{coe})(^t\mathrm{Bu_2PH})_2]$ as crystals [1a]. In this light we tested similar reaction conditions to prepare the closely related species *trans*-$[\mathrm{IrCl}(\mathrm{coe})(\mathrm{P}^i\mathrm{Pr_3})_2]$. In the course of the latter investigations using a dinitrogen atmosphere, we obtained as the only isolable compound *trans*-$[\mathrm{IrCl}(\mathrm{N_2})(\mathrm{P}^i\mathrm{Pr_3})_2]$ and confirmed its molecular structure by X-ray crystallography [1c]. The title complex $[\{\mathrm{Rh}(\mu\text{-Cl})(^t\mathrm{Bu_2PH})_2\}_2]$ (**1**) was synthesized by us during thermolytic studies of *trans*-$[\mathrm{RhCl}(\mathrm{C_2H_4})(^t\mathrm{Bu_2PH})_2]$ in refluxing octane [2]. To date no crystal structure data of **1** have been reported to confirm its dinuclear framework. Now we found a convenient synthesis for this compound, in nearly quantitative yield, by the reaction of $[\{\mathrm{Rh}(\mu\text{-Cl})(\mathrm{coe})_2\}_2]$ with $^t\mathrm{Bu_2PH}$ and obtained single crystals suitable for an X-ray diffraction study. Moreover, equilibria in the system $[\{\mathrm{Rh}(\mu\text{-Cl})(\mathrm{coe})_2\}_2]/^t\mathrm{Bu_2PH}$ with molar ratios of Rh to P from 1 : 2 to 1 : 0.5 were detected by $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR spectroscopy. Several reports in the literature have described similar reactions with tertiary phosphanes: see *e. g.* refs. [3 – 5].

Results and Discussion

Synthesis and spectroscopy

The reaction of $[\{\mathrm{Rh}(\mu\text{-Cl})(\mathrm{coe})_2\}_2]$ with $^t\mathrm{Bu_2PH}$ (molar ratio of Rh to P = 1 : 2) in heptane at ambient temperature yielded compound **1** in nearly quantitative yield. This process represents a more convenient synthesis of **1** as compared to the pathway starting from *trans*-$[\mathrm{RhCl}(\mathrm{C_2H_4})(^t\mathrm{Bu_2PH})_2]$ [2]. It reflects moreover the greater stability of the ethene-containing precursor towards olefin loss in comparison with analogous complexes bearing the coe ligand. Other authors made similar observations in view of the synthesis of $[\{\mathrm{Rh}(\mu\text{-Cl})(\mathrm{PR_3})_2\}_2]$ (R = ^{i}Pr, Cy) [6]. Com-

0932–0776 / 08 / 0900–1035 $ 06.00 © 2008 Verlag der Zeitschrift für Naturforschung, Tübingen · http://znaturforsch.com

pound **1** was identified by its known spectroscopic data [2], and single crystals for an X-ray structure analysis were obtained from hot heptane solutions by cooling to r. t. In this study the assumed dinuclear structure of **1** was confirmed (see below). Monitoring the reaction by ^{31}P{^{1}H} NMR spectroscopy afforded no hints to an intermediate *trans*-[RhCl(coe)(^{t}Bu$_2$PH)$_2$]. This is in contrast to the existence of several ethene-containing compounds representing this type of complex. Generally, no species *trans*-[RhCl(coe)(PR$_3$)$_2$] has ever been isolated, although many reactions of olefin-containing rhodium complexes (ethene, coe, cod) with phosphanes were carried out [7]. The only isolated related coe-containing compound is represented by *trans*-[IrCl(coe)(^{t}Bu$_2$PH)$_2$] [1c].

In a detailed investigation of the title reaction the following complexes were detected by ^{31}P{^{1}H} NMR spectroscopy: [{Rh(μ-Cl)(^{t}Bu$_2$PH)$_2$}$_2$] (**1**), [RhCl(^{t}Bu$_2$PH)$_2$(C$_6$H$_6$)] (**1a**), *cis*-[{Rh(μ-Cl)(coe)(^{t}Bu$_2$PH)}$_2$] (**2a**), *trans*-[{Rh(μ-Cl)(coe)(^{t}Bu$_2$PH)}$_2$] (**2b**), [RhCl(coe)(^{t}Bu$_2$PH)(C$_6$H$_6$)] (**2c**), [(^{t}Bu$_2$PH)$_2$Rh(μ-Cl)$_2$Rh(coe)$_2$] (**3**), [(^{t}Bu$_2$PH)$_2$Rh(μ-Cl)$_2$Rh(cod)] (**4**), and [RhCl(^{t}Bu$_2$PH)$_3$] (**5**). In the early stage of the reaction (10 – 30 min, heptane, molar ratio of Rh to P = 1 : 2) the following phosphorus-containing species were detected by ^{31}P{^{1}H} NMR spectroscopy (C$_6$D$_6$): **2b** (δ = 106.1, d, $J_{\text{Rh-P}}$ = 186 Hz, minor) **3** (δ = 89.5, d, $J_{\text{Rh-P}}$ = 191 Hz, minor), **1** (δ = 88.9, d, $J_{\text{Rh-P}}$ = 191 Hz, major), **5** (δ = 81.7, dt; 76.7, dd; 40.8, dd; major), and the free ligand ^{t}Bu$_2$PH (δ = 20.2, s, minor). Among these four complexes, only **1** and **5** could be identified with certainty. The latter was easily detected by its characteristic ^{31}P{^{1}H} NMR spectrum reflecting special stereodynamic effects of the ^{t}Bu$_2$P group [1d]. Similarly, in the reaction of [{Rh(μ-Cl)(coe)$_2$}$_2$] with PEt$_3$ (Rh to P = 1 : 2, few minutes, r. t.), formation of [RhCl(PEt$_3$)$_3$] as the major complex was reported by other authors [3]. We made this observation only in heptane as the solvent after short reaction times (1 – 2 h). In the later stage of the reaction compound **1** was detected exclusively. Therefore, some of the initially formed rhodium complexes must show rapid ligand-exchange kinetics under these conditions. In other solvents, like CH$_2$Cl$_2$ or benzene, the reaction was too fast to detect the Wilkinson-type complex **5** in the early stage of the reaction. In all these cases only compound **1** was detected after short reaction times. Interestingly, in contrast to this observation, we registered the formation of [IrCl(^{t}Bu$_2$PH)$_3$] to some extent using the ratio of Ir to P = 1 : 2 at the early – and even the later – stage of the analogous reaction starting from [{Ir(μ-Cl)(coe)$_2$}$_2$] [1d]. Moreover, till now we have no evidence for the formation of [{Ir(μ-Cl)(^{t}Bu$_2$PH)$_2$}$_2$] using similar reaction conditions.

Furthermore, the distribution of products in the title reaction varied with the stoichiometry of the reactants. If the ratio of Rh to P was changed stepwise from 1 : 2 to 1 : 0.5, the following scenario could be monitored by ^{31}P {^{1}H} NMR spectroscopy. Starting with a ratio of Rh to P = 1 : 2, the only detectable product was compound **1**. This is in agreement with the observations of other authors in analogous reactions with PEt$_3$ or Ph$_2$PMe [3, 5]. A change to the molar ratio of Rh to P = 1 : 1.5 afforded further signals corresponding to two new species: **2a** (δ = 105.3, d, $J_{\text{Rh-P}}$ = 185 Hz), and **3** (δ = 89.5, d, $J_{\text{Rh-P}}$ = 191 Hz). However, at this stage, these products were formed only in traces (< 10 %). Finally, a change to the ratio of Rh to P = 1 : 1 yielded signals for a total of six species: **2b** (δ = 106.1, d, $J_{\text{Rh-P}}$ = 186 Hz, ~ 50 %), **2a** (δ = 105.3, d, $J_{\text{Rh-P}}$ = 185 Hz, ~ 20 %), **2c** (δ = 104.9, d, $J_{\text{Rh-P}}$ = 186 Hz, traces), **3** (δ = 89.5, d, $J_{\text{Rh-P}}$ = 191 Hz, ~ 20 %), **1** (δ = 88.9, $J_{\text{Rh-P}}$ = 191 Hz, ~ 10 %), and **1a** (δ = 88.1, $J_{\text{Rh-P}}$ = 191 Hz, traces). We could assign the signal corresponding to **3** with some certainty. Thus, by mixing equimolar amounts of **1** and [{Rh(μ-Cl)(coe)$_2$}$_2$] in dichloromethane (or benzene), only two doublets at δ = 89.5 and 88.1 ppm were detected (with nearly equal intensity). In the past, the formation of this type of complex [L$_2$Rh(μ-Cl)$_2$Rh(coe)$_2$] (L = phosphane) was not taken into account in similar investigations in this field, *e. g.* [3, 5]. However, reports on related mixing experiments exist in the literature [8], and these results confirm the occurrence of mononuclear species in solution (stabilized by solvent molecules).

Because of the strong similarities in the chemical environment of Rh in **1** and **3**, the ^{31}P NMR shift values of these two species should be located closely together, and this was confirmed in the present study. We corroborated our assumption by an additional ^{31}P{^{1}H} NMR crossing experiment: Mixing of **1** and [{Rh(μ-Cl)(cod)}$_2$] (cod = 1.4-cyclooctadiene) in dichloromethane (or benzene, molar ratio 1 : 1) afforded, after short reaction times, two signals at δ = 88.1 (d, $J_{\text{Rh-P}}$ = 195 Hz) and δ = 87.6 (d, $J_{\text{Rh-P}}$ = 192 Hz) with nearly equal intensity (CH$_2$Cl$_2$). We assign the doublet at 88.1 ppm to [(^{t}Bu$_2$PH)$_2$Rh(μ-Cl)$_2$Rh(cod)] (**4**), and take this as evidence that in the former case the doublet at δ = 89.5 belongs to compound **3** (neither to **2a** nor to **2b**). For the ^{31}P NMR data of **3** and **4**, the question of a coupling $^3J_{\text{Rh-P}}$ arises. We were not able, however, to detect such a coupling. This is in accordance with observations of other authors on similarly constituted complexes bearing phosphorus donor ligands [9]. The small signals detected at δ = 104.9 (d) and 88.1 (d) we assign to measurable concentrations of **2c** and **1a**, respectively. For the related complex [{Rh(μ-Cl)(PCy$_3$)$_2$}$_2$] a monomer–dimer equilibrium was assumed, whereas in the case of [{Rh(μ-Cl)(P^{i}Pr$_3$)$_2$}$_2$] such a scenario was excluded, based also on calculations of bond-dissociation enthalpies [10]. Furthermore, we assume that [RhCl(coe)$_2$(benzene)] could be also present in the solution, however it is difficult to detect such a species in the mixtures *e. g.* by ^{1}H NMR spectroscopy. Unfortunately, despite many efforts, we obtained no crystals of compounds **3** and **4** for X-ray diffraction studies to confirm their molecular structures. By changing the molar ratio of Rh to P = 1 : 0.5 in the title reaction, the signals indicating the species **1**, **1a**, **2c**, and **3** were detected only as traces (together $< 10\,\%$ of total). Compound **2b** was identified as the main product at δ = 106.1 ($\sim 60\,\%$ of total). Because of the lowest steric congestion, this product is likely to be the dominant one.

*The crystal and molecular structure of **1***

The X-ray diffraction analysis has shown that crystals of **1** belong to the monoclinic space group *Cc* with *Z* = 8 dimers in the unit cell. Thus, two independent dinuclear species of **1** are found in each asymmetric unit. The coordination sphere at the Rh centers can be considered planar, whereas the central Rh(μ-Cl)$_2$Rh moieties are folded with an angle between the two planes defined by the atoms Cl(1), Rh(1), Cl(2) and Cl(1), Rh(2), Cl(2)] of 144.3° (molecule A). A view of one molecule is shown in Fig. 1, selected bond lengths and angles are given in Table 1.

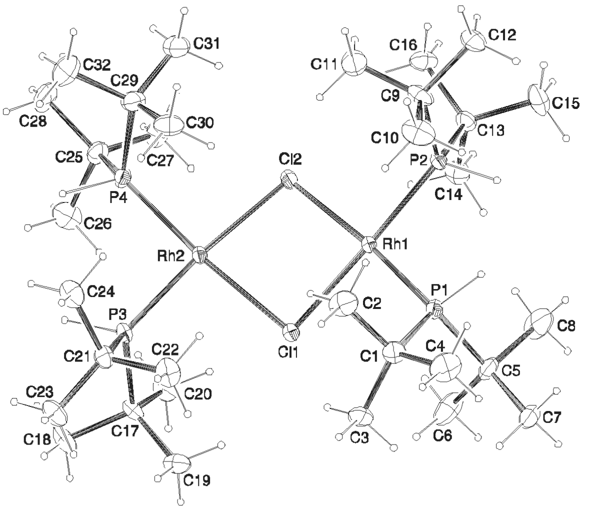

Fig. 1. View of one of the two independent molecules of [{Rh(μ-Cl)(^{t}Bu$_2$PH)$_2$}$_2$] (**1**) in the crystal. Displacement ellipsoids are at the 50 % probability level.

Table 1. Selected bond lengths (Å) and bond angles (deg) of **1** (the corresponding values of the two crystallographic independent molecules are separated by a slash.

Rh(1)-Cl(1)	2.420(1)/2.420(1)	Cl(1)-Rh(1)-Cl(2)	81.2(5)/81.2(5)
Rh(1)-Cl(2)	2.429(1)/2.430(1)	Cl(1)-Rh(1)-P(1)	94.4(5)/93.4(5)
Rh(2)-Cl(1)	2.422(1)/2.418(1)	Cl(2)-Rh(1)-P(2)	93.5(5)/94.1(5)
Rh(2)-Cl(2)	2.427(1)/2.427(1)	P(1)-Rh(1)-P(2)	91.2(5)/91.4(5)
Rh(1)-P(1)	2.207(1)/2.205(1)	Cl(1)-Rh(2)-P(3)	93.5(5)/92.7(4)
Rh(1)-P(2)	2.000(1)/2.205(1)	P(3)-Rh(2)-P(4)	91.1(6)/91.5(5)
Rh(2)-P(3)	2.205(1)/2.205(1)	Cl(1)-Rh(1)-P(2)	172.3(6)/173.7(5)
Rh(2)-P(4)	2.204(1)/2.208(1)	Rh(1)-Cl(1)-Rh(2)	92.7(5)/93.9(4)
Rh$\cdots$Rh	3.505/3.536	Rh(1)-Cl(2)-Rh(2)	92.4(4)/93.4(4)

The molecular structure of **1** is related to those of other compounds bearing phosphane ligands as in [{Rh(μ-Cl)(P^{i}Pr$_3$)$_2$}$_2$] [6], [{Rh(μ-Cl)(PPh$_3$)$_2$}$_2$] [11], [{Rh(μ-Cl)(L)$_2$}$_2$] (L = P^{i}Pr$_2$C$_2$H$_4$Ph) [4b], [{Rh(μ-Cl)(L)$_2$}$_2$] (L = Cy-1,2-CH$_2$CH$_2${OPPh$_2$}) [12], [{Rh(μ-Cl)(dtbpm)}$_2$] (dtbpm = ^{t}Bu$_2$PCH$_2$-P^{t}Bu$_2$) [13], [{Rh(μ-Cl)(PF$_3$)$_2$}$_2$] [14], [{Rh(μ-Cl)-(PMe$_3$)$_2$}$_2$] [15], [{Rh(μ-Cl)(PR$_3$)$_2$}$_2$] (R = C$_6$H$_4$-*p*-SiMe$_3$) [16], and [{Rh(μ-Cl)(L)$_2$}$_2$] (L = biphen-{OPCy$_2$}) [12]. The four first-mentioned complexes exhibit exactly planar Rh(μ-Cl)$_2$Rh cores, whereas in all the other compounds this framework is more or less folded. The corresponding folding angles reach from 148° (which is the largest observed value for non-planar structures of this type: molecule B in this work) to 113° in [{Rh(μ-Cl)(PF$_3$)$_2$}$_2$] [14]. As a consequence, for the latter species the smallest intramolecular Rh$\cdots$Rh distance of 2.9709(5) Å was observed for this series of compounds. The reasons for the folding in these structures were controversially discussed [11, 13, 15, 16]. Some authors propose steric (cone angle, interligand repulsion) rather than electronic factors of the phosphane ligands as the origin of the folding effect. Furthermore, Extended Hückel calculations revealed that it only costs about 10 kJ mol^{-1} in energy to fold these structures from 180 to 140° [13]. Therefore, packing effects and/or intramolecular steric interactions could be responsible for the folding angles in the solid-state structures rather than electronic features of the phosphane ligands. This is clearly indicated by the following arguments: The ligands P^{i}Pr$_3$, ^{t}Bu$_2$PH, and ^{t}Bu$_2$PCH$_2$P^{t}Bu$_2$ should exhibit no significant differences in basicity. However, whereas the compound bearing P^{i}Pr$_3$ ligands is exactly planar in the central Rh(μ-Cl)$_2$Rh core, the other two compounds containing ^{t}Bu$_2$ groups exhibit a folding (134 – 148°). Finally, the bonding characteristics of the central Rh(μ-Cl)$_2$Rh core in molecules of **1** agree well with those of the above-mentioned, closely related compounds (see *e. g.* [6, 11, 14, 15]).

Experimental Section

All manipulations were carried out under a dry nitrogen atmosphere using standard Schlenk techniques. Solvents were dried according to standard procedures and stored under nitrogen. The complexes [{Rh(μ-Cl)(coe)$_2$}$_2$] and [{Rh(μ-Cl)(cod)}$_2$] were prepared according to literature procedures [17, 18]. ^{1}H and ^{31}P{^{1}H} NMR spectra were recorded using Jeol Eclipse 270 and 400 instruments operating at 270 and 400 (^{1}H) and at 109 MHz (^{31}P), respectively. Elemental analyses (C, H, Cl) were performed by the Microanalytical Laboratory of the Department of Chemistry and Biochemistry, LMU Munich, using a Heraeus Elementar Vario El instrument.

Synthesis of [{Rh(μ-Cl)(^{t}Bu$_2$PH)$_2$}$_2$] (1) in heptane

To a slurry of [{Rh(μ-Cl)(coe)$_2$}$_2$] (360 mg, 0.5 mmol) in 25 mL of heptane ^{t}Bu$_2$PH (290 mg, 2 mmol) was added at r. t. The solution became clear immediately. After stirring for 2 h, **1** precipitated from the cloudy solution. The mixture was stirred at r. t. over night. During this time the product precipitated from the solution in nearly quantitative yield. The red-orange crystals were filtered off, washed three times with 10 mL portions of cold pentane and dried *in vacuo*. Yield 420 mg (97 %). – ^{31}P{^{1}H} NMR (109 MHz, C$_6$D$_6$): δ = 88.9 (d, $J_{\text{Rh–P}}$ = 191 Hz). – ^{1}H NMR (400 MHz, C$_6$D$_6$): δ = 3.69 (dd, 1H, J_{PH} = 341 Hz, P*H*), 1.50 (d, 18H, $^3J_{\text{PH}}$ = 12.9 Hz, t-C$_4$*H*$_9$). – C$_{32}$H$_{76}$Cl$_2$P$_4$Rh$_2$ (861.57): calcd. C 44.61, H 8.89, Cl 8.23; found C 44.47, H 8.80, Cl 8.56.

Synthesis of [{Rh(μ-Cl)(^{t}Bu$_2$PH)$_2$}$_2$] (1) in CH$_2$Cl$_2$

[{Rh(μ-Cl)(coe)$_2$}$_2$] (360 mg, 0.5 mmol) was dissolved in 20 mL of CH$_2$Cl$_2$ at r. t., and ^{t}Bu$_2$PH (290 mg, 2 mmol) was added by a syringe. The resulting orange solution was stirred for 2 h. Then the solvent was evaporated to about 1 mL under reduced pressure, and the product was precipitated by adding 15 mL of heptane. The resulting orange powder was filtered off, washed twice with 10 mL portions of cold pentane, and dried *in vacuo*. Yield 310 mg (72 %).

Reactions of [{Rh(μ-Cl)(coe)$_2$}$_2$] with ^{t}Bu$_2$PH (general description)

In a typical experiment, a solution of [{Rh(μ-Cl)(coe)$_2$}$_2$] (0.5 mmol) in 20 mL of dichloromethane was stirred at r. t. To this solution the corresponding amount of ^{t}Bu$_2$PH (ratio of Rh to P in the range from 1 : 2 to 1 : 0.5), dissolved in 20 mL of dichloromethane, was added over a period of 15 min using a dropping funnel. The resulting solution was evaporated to dryness *in vacuo*, the remaining residue was dissolved in 2 mL of C$_6$D$_6$ and investigated by ^{31}P{^{1}H} NMR spectroscopy without delay.

Table 2. Details of the X-ray data collection and refinement for **1**.

Formula	C$_{32}$H$_{76}$Cl$_2$P$_4$Rh$_2$
M_r	861.557
Temperature, K	200(2)
Crystal system	monoclinic
Space group	*Cc*
a, Å	32.7375(3)
b, Å	11.1294(1)
c, Å	24.5134(3)
β, deg.	106.7228(4)
V, Å^3	8553.70(15)
Z	8
D_{calcd}, g cm^{-3}	1.338
μ (MoK_α), mm^{-1}	1.065
θ range for data collection, deg	3.34 – 27.46
hkl range	$-42 \le h \le 41$, $-14 \le k \le 14$, $-31 \le l \le 31$
Reflections collected/ independent	58768/19104
Parameters/restraints	745/10
R_1 [$I \ge 2\sigma(I)$]	0.044
wR_2 (all data)	0.111
Flack parameter x	0.04(3)
S	1.130
Largest diff. peak/hole, e Å^{-3}	2.87/−0.82

Mixing experiment of [{Rh(μ-Cl)(^{t}Bu$_2$PH)$_2$}$_2$] with [{Rh(μ-Cl)(coe)$_2$}$_2$]

A solution of **1** (215 mg, 0.25 mmol) in 10 mL of dichloromethane was combined with a solution of [{Rh(μ-Cl)(coe)$_2$}$_2$] (180 mg, 0.25 mmol) in 10 mL of the same solvent at r. t. After stirring for 1 h, the solution was evaporated to dryness *in vacuo*, and the remaining residue was dissolved in 2 mL of C$_6$D$_6$ and immeditately investigated by ^{31}P{^{1}H} NMR spectroscopy. The spectrum indicated the presence of two phosphorus-containing components: δ = 88.5, d, $J_{\text{Rh–P}}$ = 191 Hz (**1**), and δ = 89.3, d, $J_{\text{Rh–P}}$ = 191 Hz (**3**).

Mixing experiment of [{Rh(μ-Cl)(^{t}Bu$_2$PH)$_2$}$_2$] with [{Rh(μ-Cl)(cod)}$_2$]

A solution of **1** (215 mg, 0.25 mmol) in 10 mL of dichloromethane was combined with a solution of [{Rh(μ-Cl)-(cod)}$_2$] (124 mg, 0.25 mmol) in 10 mL of the same solvent at r. t. After stirring for 1 h, the solution was evaporated to dryness *in vacuo*, and the remaining residue was dissolved in 2 mL of C_6D_6 and immeditately investigated by $^{31}P\{^1H\}$ NMR spectroscopy. The spectrum indicated the presence of two phosphorus-containing components: δ = 88.8, d, J_{Rh-P} = 192 Hz (**1**), and δ = 89.5, d, J_{Rh-P} = 194 Hz (**4**).

X-Ray crystal structure determination

Single crystals of **1** suitable for an X-ray diffraction analysis were obtained by slowly cooling a hot heptane solution. A crystal was selected by means of a polarization microscope, mounted on the tip of a glass fiber, and investigated on a Nonius Kappa CCD diffractometer using MoK_α radiation (λ = 0.71073 Å). The structure was solved by Direct Methods (SIR 97) [19] and refined by full-matrix least-squares methods on F^2 (SHELXL-97) [20]. Anisotropic displacement parameters were refined for all non-hydrogen atoms. Details of crystal data, data collection, structure solution, and refinement parameters of **1** are summarized in Table 2.

CCDC 680203 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgement

The authors are grateful to the Department of Chemistry and Biochemistry, Ludwig Maximilian University Munich, for support of this work.

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