Complex Catalysis, XLIX[◇]

On the Coordination of Olefins and Secondary Amines at the Cationic [2,6-Bis(diphenylphosphanylmethyl)pyridine]rhodium(I) Fragment $[Rh(PNP)]^+$ – Synthesis and Characterization of [Rh(PNP)(L)]X (L = Ethylene, Styrene, HNR_2; X = BF_4, PF_6, CF_3SO_3)☆

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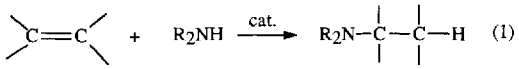
The cationic rhodium(I) complexes $[Rh(PNP)(C_2H_4)]X$; X = BF_4 (**1a**), PF_6 (**1b**), CF_3SO_3 (**1c**) were prepared by addition of the tridentate ligand 2,6-bis(diphenylphosphanylmethyl)pyridine (PNP) to a solution of $[Rh(C_2H_4)_2(solv)_2]X$ (solv = acetone or THF) under ethylene. The complexes were characterized by IR and ^1H-, ^{13}C-, and ^{31}P-NMR spectroscopy. The coordination of two ethylene molecules at the $[Rh(PNP)]^+$ fragment could be detected by dynamic proton resonance of a solution of **1a** under free ethylene. The styrene complex $[Rh(PNP)(styrene)]BF_4$ (**4**) was obtained by substitution of the ethylene from **1a** with an excess of styrene. The π coordination of C_2H_4 and styrene in **1a** and **4** respectively was confirmed by X-ray crystal structure analysis. The olefin complexes react with an excess of the secondary amine to give the corresponding amine complexes $[Rh(PNP)(HNR_2)]X$; HNR_2 = piperidine (**5**), $HNMe_2$ (**6**), $HNEt_2$ (**7**). Conversly, the amine could be released from the amine complexes with an excess of ethylene at low temperature by the formation of the ethylene complex **1**.

The catalytic amination of olefins by N–H addition at the C–C double bond is of considerable interest in organic chemistry. By this method amines can be obtained directly without any by-product. The reaction (eq. 1) is thermodynamically allowed but kinetically strongly inhibited as a result of an insufficient interaction between the reactants at normal conditions. Since the reaction is also entropically unfavoured, catalysis is indispensible to realize the hydroamination of unactivated olefins. But up to now an effective catalyst for this reaction could not be developed[1–3].

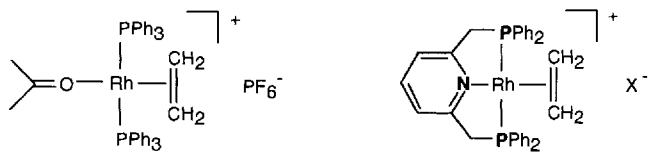


(1)

With the cationic ethylene Rh^I complex $[Rh(C_2H_4)(PPh_3)_2(Me_2CO)]PF_6$ the addition of secondary amines, such as piperidine, at the ethylene succeeded for the first time at room temperature and under normal pressure. Because of a fast deactivation reaction by the formation of catalytically inactive complexes a maximum TON of only 8 mol amine per 1 mol rhodium could be realized[4,5].

In order to learn more details about the possible reaction mechanism of the rhodium complex catalyzed hydroamination of ethylene, we are trying to trace those reaction steps considered crucial for the catalytic cycle with suitable model complexes. The ligand sphere of the catalyst complex is simulated in the model complex by using the tridentate ligand 2,6-bis(diphenylphosphanylmethyl)pyridine (PNP)[6] which forms with the rhodium(I) the chloride complex described by Vasapollo and co-workers[7]. The *trans* position of the phosphane ligand is stabilized in the complex by the chelate structure of the PNP ligand, cf. Scheme 1.

Scheme 1. The catalyst complex[4,5] and the model complex **1**



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The synthesis and spectroscopic characterization of the model complex **1** and its reactivity toward ethylene will be discussed, as well as the synthesis and NMR investigations

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of the analogous cationic Rh^I–styrene complex. The X-ray crystal structure analyses of both cationic olefin complexes, and the reactivity toward secondary amines is reported.

Results and Discussion

Synthesis and Characterization of $[Rh(PNP)(C_2H_4)]X$ (X = BF_4, PF_6, CF_3SO_3)

Attempts were made to prepare the cationic ethylene complexes $[Rh(PNP)(C_2H_4)X$ (**1**) by the treatment of $[Rh(PNP)Cl]$[7] with $AgBF_4$ and $TlBF_4$ under ethylene[8]. The reaction with the silver salt led to the deposition of silver. The reaction with the thallium salt progressed incompletely, yielding chloride-containing products. However, the synthesis succeeded when using the silver salt method of Schrock and Osborn[9] in the first step (cf. eq. 2), and by addition of the PNP ligand to the solution of the $[Rh(C_2H_4)_2(solv)_2]X$ complex in the second step according to eq. 3.

$$1/2\,[\{Rh(C_2H_4)_2Cl\}]_2 + AgX \xrightarrow{solv.} [Rh(C_2H_4)_2(solv)_2]X + AgCl \quad (2)$$

X = BF_4, solv = acetone
X = PF_6, CF_3SO_3, solv. = THF

$$[Rh(C_2H_4)_2(solv)_2]X + PNP \xrightarrow[-2\ solv.]{-C_2H_4} [Rh(PNP)(C_2H_4)]X \quad (3)$$

X = BF_4 **1a**; PF_6 **1b**; CF_3SO_3 **1c**

After the addition of the PNP ligand, the reaction mixture was stirred for 3 h under ethylene. During this time some yellow solid precipitated which was analyzed as the dinuclear ethylene free complex $[Rh_2(PNP)_3]X_2$ (X = BF_4 **2a**, PF_6 **2b**, CF_3SO_3 **2c**), cf. eq. 4. The same feature occurs in the case of the synthesis of the chloride complex[7].

$$2\,[Rh(C_2H_4)_2(solv)_2]X + 3\,PNP \xrightarrow[-2\ solv.]{-C_2H_4} [Rh_2(PNP)_3]X_2 \quad (4)$$

X = BF_4 **2a**; PF_6 **2b**; CF_3SO_3 **2c**

Since the dinuclear complexes are poorly soluble in acetone and THF, they could be separated easily by filtration. The cationic ethylene complexes were precipitated from the solution by dropping diethyl ether saturated with ethylene into the solution. The complexes were isolated as orange coloured air-stable solids in relatively good yields after recrystallization in acetone/diethyl ether, except the hexafluorophosphate complex which was obtainable only in a smaller yield since the formation of the dinuclear complex **2b** is pronounced here (cf. Table 1).

The characteristic IR bands (KBr pellet) of the complexes **1a–c** are listed in Table 2. The bands at $\tilde{\nu}$ = 1600 cm^{-1} and $\tilde{\nu}$ = 1560 cm^{-1} indicate the coordination of the pyridine[6]. The band of the tetrafluoroborate anion in **1a** at $\tilde{\nu}$ = 1084 cm^{-1} lies in the region of the absorption of the free ion[10]. In the spectrum of **1b** the asymmetric stretching band at $\tilde{\nu}$ = 838 cm^{-1} and the band of the deformation vibration at $\tilde{\nu}$ = 538 cm^{-1} are characteristic of the non-coordination of the hexafluorophosphate[11]. Also the different absorption bands for the triflate found in the spectrum of **1c** suggest that the $CF_3SO_3^-$ anion is not coordinated to the rhodium[12].

Table 1. Yield, temperature of decomposition of **1a–c** and the proportion of the by-products **2a–c**

Complex		Yield [%]	m.p.(dec.) [°C]	By-product [%] $[Rh_2(PNP)_3]X_2$ **2**	
$[Rh(PNP)(C_2H_4)]BF_4$	**1a**	70	180–190	**2a**	7
$[Rh(PNP)(C_2H_4)]PF_6$	**1b**	45	190–200	**2b**	23
$[Rh(PNP)(C_2H_4)]SO_3CF_3$	**1c**	62	130–140	**2c**	6

Table 2. Infrared absorption bands for the pyridine ring and the anions of **1a–c**

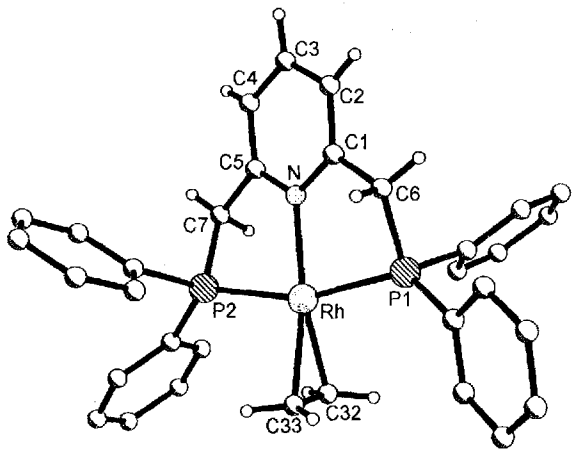
Complex		$\tilde{\nu}$ (pyridine ring)	$\tilde{\nu}$ (anion)
$[Rh(PNP)(C_2H_4)]BF_4$	**1a**	1602, 1560	1084
$[Rh(PNP)(C_2H_4)]PF_6$	**1b**	1600, 1560	838, 558
$[Rh(PNP)(C_2H_4)]SO_3CF_3$	**1c**	1600, 1560	1276, 1224, 1150, 1030, 638, 572

The NMR spectra were recorded in $[D_6]$acetone at room temperature. In the ^{31}P-NMR spectra of **1a–c** a doublet at δ = 38.2 appears with a coupling constant of J_{P-Ph} = 130 Hz and is shifted downfield in comparison to the chlororhodium(I) complex $[Rh(PNP)Cl]$ (δ = 21.4, J_{P-Ph} = 152 Hz, in $[D_8]$toluene). The signal of the CH_2P group in **1a–c** exhibits a virtual triplet in the ^1H-NMR spectra at δ = 4.60 and in the ^{13}C-NMR spectra at δ = 43.8. The identical chemical shifts of the complexes **1a–c** in all NMR spectra confirm that the anions (BF_4^-, PF_6^-, $CF_3SO_3^-$) must be non-coordinating in all cases. The relatively sharp singlet of the ethylene protons at δ = 3.52 indicates fast rotation of the coordinated ethylene molecule at room temperature. The ^{13}C-signal of the coordinated ethylene in **1a–c** at δ = 59.5 is less upfield shifted in comparison to the chemical shift of free ethylene as in the catalyst complex $[Rh(C_2H_4)(Me_2CO)(PPh_3)_2]PF_6$($\delta$ = 46.7)[4].

Orange-coloured single crystals of **1a** suitable for X-ray structural analysis were obtained by warming up a solution of the complex saturated at −78°C in acetone under ethylene to room temperature.

In Figure 1 the molecular structure of the cation of **1a** is shown. The coordination of PNP and the ethylene generates a nearly square planar geometry. The complex exhibits C_2-symmetry. The phosphanes are in a *trans* arrangement with a P(2)–Rh–P(1) angle of 161.39(5)°. This angle is remarkably small compared to that of the catalyst complex $[Rh(C_2H_4)(PPh_3)_2(Me_2CO)]PF_6$ [173.95(3)°][13] due to the geometric strain of the two five-membered rings formed by the coordination of the chelate PNP ligand at the rhodium atom. The carbon–carbon distance in the coordinated ethylene molecule of the model complex **1a** is 1.351(11) Å and the rhodium–carbon distances are Rh–C(32) [2.142(6) Å] and Rh–C(33) [2.157(6) Å], both are practically the

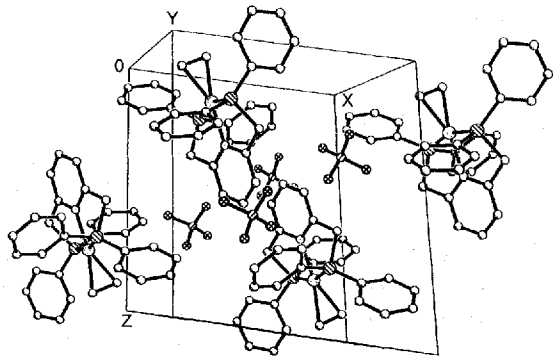
Figure 1. Schakal drawing structure of the cation of **1a** without the phenyl protons[a]



[a] Selected bond lengths [Å] and angles [°]: Rh–N 2.092(4), Rh–C(32) 2.142(6), Rh–C(33) 2.157(6), Rh–P(2) 2.2690(13), Rh–P(1) 2.3001(13), C(32)–C(33) 1.351(11), P(1)–C(6) 1.837(5), P(2)–C(7) 1.833(7); P(1)–Rh–P(2) 161.39(5), N–Rh–P(1) 80.73(12), N–Rh–P(2) 80.72(12), C(32)–Rh–C(33) 36.6(3), N–Rh–C(32) 156.3(3), N–Rh–C(33) 166.8(2).

same as in the catalyst complex (C–C [1.382(6) Å] and Rh–C [2.120(4) Å, 2.124(4) Å]). In agreement with the spectroscopic data the BF_4^- ion is arranged in the elemental cell without the close interaction to the rhodium atom visible in Figure 2.

Figure 2. Arrangement of the ions of **1a** in the elemental cell



Reactivity of [Rh(PNP)(C_2H_4)]BF_4 (1a) toward Ethylene and Styrene

When a solution of the complex **1** was cooled down in acetone saturated with ethylene, its colour changed from orange at room temperature to pale yellow at −78°C. This behaviour of the ethylene complex was monitored by a dynamic proton NMR experiment for the case of **1a** in [D_6]-acetone under ethylene. The chemical shifts of the spectra from room temperature to −85°C are summarized in Table 3.

At room temperature an average sharp signal at δ = 4.68 appears indicating a fast exchange of free and coordinated ethylene relative to the NMR time scale. By cooling the sample this signal became very broad. The coalescence temperature lies between −45 and −50°C.

Table 3. Dynamic ^{1}H-NMR experiment of [Rh(PNP)(C_2H_4)]BF_4 **1a** in [D_6]acetone under ethylene (500 MHz)

ϑ °C	py-4 (t)	py-3,5(d)	Ph (m)	CH_2 (vt)	C_2H_4 free	C_2H_4 coord.
23	8.02	–	7.76–7.72, 7.59–7.52	4.65	4.68 s	
−20	8.24	8.01	7.57–7.50	4.88	4.09 br	
−30	8.28	8.06	7.57–7.43	4.93	4.16 br	
−40	8.30	8.09	7.56–7.43	4.97	3.94 br	
−45	8.31	8.09	7.56–7.43	4.97	4.11 br	
−50	8.32	8.10	7.57–7.43	4.98	4.7 br	3.5 br
−60	8.33	8.10	7.57–7.46	4.99	5.30 br	2.79 br
−70	8.35	8.12	7.58–7.49	5.03	5.40 br	3.25 br, 2.20 br
−80	8.36	8.13	7.57–7.50	5.05	5.41 br	3.39 br, 2.02 br
−85	8.37	8.14	7.57–7.51	5.06	5.42 s	3.40 br, 2.01 br

In the spectrum at −70°C two broad signals of the coordinated ethylene were visible. While on cooling to −85°C the signal of the free ethylene became sharp the signals of the coordinated ethylene remained relatively broad. That means the rotation of the coordinated ethylene is faster than the intermolecular exchange. Obviously at low temperature a five-coordinate bisethylene rhodium(I) complex **3** was formed, cf. eq. 5, established by integration of the signal at δ = 3.40 in the spectrum at −85°C.

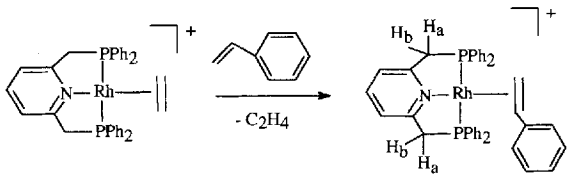
$$[Rh(PNP)(C_2H_4)]BF_4 \underset{-C_2H_4}{\overset{+C_2H_4}{\rightleftharpoons}} [Rh(PNP)(C_2H_4)_2]BF_4 \quad (5)$$

3

orange, room temp. pale yellow, −78°C

Similar intermolecular exchange of ethylene was described by Bennett for the case of the analogous cationic bis(ethylene){2,2′-bis(diphenylphosphanyl)-*trans*-stilbene}-rhodium(I) complex[14].

By the treatment of a solution of **1a** in acetone with an excess of styrene, the precipitation of a reddish orange solid was observed after 3–5 h. The volume of the reaction mixture was reduced to one half under reduced pressure. On addition of diethyl ether a further amount of the product was precipitated. The solid was filtered off and recrystallized in acetone/diethyl ether. The product was identified as the cationic styrene complex [Rh(PNP)(styrene)]BF_4 (**4**) by ^{31}P-, ^{1}H-, and ^{13}C-NMR spectroscopy, formed by substitution of the ethylene according to eq. 6.



(6)

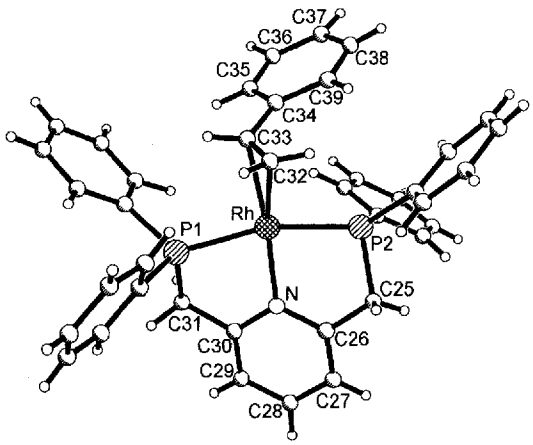
1a **4**

The expected displacement of the ethylene by the styrene was possible since the styrene is an olefin with the stronger acceptor strength, as the studies about the relative stabilities of rhodium(I)–olefin complexes show[15,16]. In the ^{31}P-NMR spectrum of doublet at δ = 41.7 with a coupling

constant of J_{P-Ph} = 126 Hz is slightly downfield shifted compared to the appropriate signal of the ethylene complexes **1a–c** also indicating the stronger back donation in the styrene–Rh bond. The chemical shifts of the coordinated styrene are upfield shifted compared to the free styrene. In the ^{1}H-NMR spectrum the signals of the olefinic protons lie at δ = 4.96, 3.87, and 3.72 and in the ^{13}C-NMR spectrum the signals of the olefinic carbons appear as doublets at δ = 51.5 (J_{C-Rh} = 12.2 Hz) and δ = 75.8 (J_{C-Rh} = 11.4 Hz). Upon coordination of the styrene, the [Rh(PNP)]$^+$ fragment loses its C_2 symmetry. Therefore the methylene protons become chemically inequivalent. In the ^{1}H-NMR spectrum a signal pattern of an AA'BB'XX' spin system appears for these protons consisting of two doublets of virtual triplets at δ = 4.85 and δ = 4.47 with a geminal coupling constant of J_{Ha-Hb} = 16.7 Hz, whereas in the ^{13}C-NMR spectrum the signal of the methylene group is one virtual triplet at δ = 43.5.

Single crystals for X-ray crystal structure analysis were obtained from a saturated solution of **4** in acetone at room temperature. The molecular structure of the cation of **4**, [Rh(PNP)(styrene)]$^+$, is shown in Figure 3.

Figure 3. SCHAKAL drawing of the cation of [Rh(PNP)(styrene)]$^+$ (**4**)[a]



[a] Selected bond lengths [Å] and angles [°]: Rh–N 2.102(3), Rh–C(32) 2.144(5), Rh–C(33) 2.201(4), Rh–P(2) 2.2916(10), Rh–P(1) 2.3004(11), C(32)–C(33) 1.383(7), P(1)–C(31) 1.843(5), P(2)–C(25) 1.836(5); P(1)–Rh–P(2) 161.96(4), N–Rh–P(1) 81.67(9), N–Rh–P(2) 80.44(9), C(32)–Rh–C(33) 37.1(2), N–Rh–C(32) 157.0(2), N–Rh–C(33) 165.8(2).

The carbon–carbon distance in the olefinic double bond of the η^2-coordinated styrene is 1.383(7) Å. The rhodium–carbon distances are slightly different {Rh–C(32) [2.144(5) Å], Rh–C(33) [2.201(4) Å]}. The bond lengths and angles of the coordinated PNP ligand are almost identical to those found in the ethylene complex **1a**.

Reactivity toward Secondary Amines

The ethylene complexes **1a–c** react with secondary amines such as piperidine, dimethylamine, and diethylamine in THF by substitution of the ethylene at room temperature within a few hours to give the corresponding amine complexes **5a–c**, **6**, and **7** according to eq. 7, except to isopropylamine which did not show any reaction even after refluxing for several hours. Also the reaction of the styrene complex **4** with dimethylamine led to the liberation of the styrene and the formation of **6** in the same manner at room temperature as well as at −20°C.

Conversely, the amine could be released from the amine complex with an excess of ethylene at low temperature by the formation of the starting ethylene complex **1**. Obviously the ethylene and the amine complexes are in thermodynamic equilibrium. No indication of a nucleophilic attack of the amine at the C–C double bond was observed.

$$[Rh(PNP)(olefin)]X + HNR_2 \rightleftharpoons [Rh(PNP)(HNR_2)]X + olefin \quad (7)$$

olefin = C_2H_4 **1a–c**; PhC_2H_3 **4**

HNR_2 = piperidine; X = BF_4, PF_6, CF_3SO_3 **5a–c**; R = Me X = BF_4 **6**; R = Et, X = BF_4 **7**

The cationic amine complexes **5a–c**, **6**, and **7**, isolated from the reaction solution, are crystalline reddish orange-coloured solids and stable in air. The IR spectroscopic investigations of the piperidine complexes [Rh(PNP)(pip)]X, (X = BF_4: **5a**; PF_6: **5b**; CF_3SO_3: **5c**) show that the anions are also non-coordinated in each case as discussed for the corresponding cationic ethylene complexes (see above), cf. Table 4.

Table 4. Infrared absorption bands for the pyridine ring and the anions of **5a–c**

Complex		ν̃ (pyridine ring)	ν̃ (anion)
[Rh(PNP)(pip)]BF_4	**5a**	1602, 1558	1056
[Rh(PNP)(pip)]PF_6	**5b**	1604, 1566	840, 558
[Rh(PNP)(pip)]SO_3CF_3	**5c**	1604, 1568	1274, 1224, 1154, 1030, 638, 572

The amine complexes **5a–c**, **6**, and **7** were characterized by ^{31}P-, ^{1}H-, and ^{13}C-NMR spectroscopy. As expected, the chemical shifts of the piperidine complexes **5a–c** are identical. In the ^{31}P-NMR spectrum the doublet is observed at δ = 34.9 [$J_{P\ Rh}$ = 152.7 Hz (**5a**), 164.9 Hz (**5b**), 149.3 Hz (**5c**)], δ = 34.3 [J_{P-Rh} = 157.0 Hz] (**6**), and δ = 38.9 [J_{P-Rh} = 156.6 Hz] (**7**). The characteristic virtual triplet of the CH_2P group found in the ^{1}H NMR at δ = 4.23 (**5a–c**), 4.22 (**6**), and 4.30 (**7**) is slightly upfield shifted compared to the corresponding signal of **1a–c**. In the ^{13}C-NMR spectrum the virtual triplet of the CH_2P group of the amine complexes appears in the same region as the ethylene complexes **1a–c** (δ = 44.3: **5a–c**; 44.5: **6**; 43.9: **7**). The hindered mobility of the coordinated secondary amines is indicated by ^{1}H NMR. Instead of the quadruplet for the NCH_2 group in the case of the free diethylamine, the ^{1}H-NMR spectrum of **7** exhibits two multiplets (δ = 2.22, 2.45) for each proton of this methylene group, whereas the triplet for the terminal methyl group is maintained (δ = 1.20) which is downfield shifted. The ^{1}H-NMR spectrum of **5a–c** in the region of the CH_2 groups of the coordinated piperidine is more complicated (δ = 0.87 m, 1.14–0.98 m, 1.38 d, 2.27 dq, 3.15 d). All respective geminal protons are no longer chemically equivalent.

Conclusions

As was shown, the cationic fragment $[Rh(PNP)]^+$ is capable of coordinating olefins, such as ethylene and styrene, by the formation of the cationic olefin rhodium(I) complexes [Rh(PNP)(olefin)]X (X = BF_4, PF_6, CF_3SO_3) which have been extensively characterized by ^1H-, ^{13}C-, and ^{31}P-NMR and X-ray crystal structure analysis. In their structure the ethylene complexes $[Rh(PNP)(C_2H_4)]X$ can be considered as model complexes for $[Rh(C_2H_4)(PPh_3)_2(Me_2CO)]PF_6$ which catalyzed the hydroamination of ethylene. However, in the case of the PNP complexes no indication of a nucleophilic attack of secondary amines to the C–C double bond could be found either with ethylene or with styrene. Only a reversible substitution of the olefin takes place by the amine, and the corresponding amine complexes $[Rh(PNP)(HNR_2)]X$ (R_2NH = piperidine, Me_2NH, Et_2NH) formed could be isolated and have been fully characterized.

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Experimental Section

All reactions were carried out under dry argon or ethylene. All solvents were dried, degassed and distilled before use. Acetone, CD_2Cl_2, $CDCl_3$, and [D_6]acetone were refluxed over 4-Å molecular sieves and degassed by bubbling argon through. THF and diethyl ether were refluxed over Na/benzophenone. Piperidine, diethylamine, and styrene were dried over 4-Å molecular sieve and distilled before use. Dimethylamine was obtained from H_2NMe_2Cl and KOH and condensed. – Infrared spectra were recorded on KBr pellets with a Perkin-Elmer FT-IR 16 spectrometer. – The ^1H-, $^{13}C\{^1H\}$-, and $^{31}P\{^1H\}$-NMR spectra were recorded at 300, 75, and 121 MHz respectively, with a Varian Gemini 300 NMR spectrometer. For the dynamic proton NMR experiment a Varian Unity 500 NMR spectrometer was used with a frequency of 500 MHz. The ^1H- and ^{13}C-NMR shifts were referenced to the resonance of the residual protons of the solvents. The ^{31}P-NMR shifts were referenced to external 85% H_3PO_4. – The Chrompack gas chromatograph CP 9000 was used for the identification of liquid organic compounds. – Elemental analyses of C, H, and N were carried out on LECO CHN 932 analyzer and Rh by using of a photometric method[17]. – $[\{RhCl(C_2H_4)_2\}_2]$ was prepared according to the literature procedure[18].

Synthesis of 2,6-Bis(diphenylphosphanylmethyl)pyridine PNP: The PNP ligand was pepared from 2,6-bis(chloromethyl)pyridine and two equivalents of $NaPPh_2$ in dioxane/THF using the procedure of Dahlhoff et al.[6]. The 2,6-bis(chloromethyl)pyridine was obtained by reaction of 2,6-bis(hydroxymethyl)pyridine with thionylchloride[19]. $NaPPh_2$ was prepared by using the published procedure of Kagan et al.[20].

[Rh(PNP)(C$_2$H$_4$)]X (X = BF_4: **1a**; PF_6: **1b**; CF_3SO_3: **1c**): To a suspension of 389 mg (2 mmol) of $[\{RhCl(C_2H_4)_2\}_2]$ in 40 ml of solvent (for **1a** acetone, for **1b** and **1c** THF) 2 mmol of the silver salt AgX was added. The mixture was stirred for 10 min under ethylene. After filtration of AgCl, 950 mg (2 mmol) of the PNP ligand was added slowly to the solution as solid (**1a**) or as a solution in 7 ml of THF (**1b**, **1c**). The reaction mixture changed its colour from orange to red and the evolution of gas was observed. The reaction mixture was stirred for 3 h under ethylene. The yellow solid precipitated and was filtered off, washed with acetone or THF and with diethl ether, and dried under vacuum. These by-products were analyzed as $[Rh_2(PNP)_3]X_2$ (X = BF_4: **2a**; PF_6: **2b**, CF_3SO_3: **2c**).

2a: Yield 130 mg (7%). – $C_{93}H_{81}B_2F_8N_3P_6Rh_2$: calcd. Rh 11.41; found Rh 11.69. – ^{31}P NMR ($CDCl_3$): δ = 34.6 (d br., 2 P $J_{P\text{-}Rh}$ = 168 Hz), 44.4 (dd, 4 P, $J_{P\text{-}Rh}$ = 141, $J_{P\text{-}P}$ = 37 Hz).

2b: Yield 481 mg (23%). – $C_{93}H_{81}F_{12}N_3P_8Rh_2$: calcd. Rh 10.71; found Rh 10.72. – ^{31}P NMR (CD_2Cl_2): δ = 37.4 (dt, 2 P $J_{P\text{-}Rh}$ = 160, $J_{P\text{-}P}$ = 37 Hz), 41.4 (dd, 4 P, $J_{P\text{-}Rh}$ = 144, $J_{P\text{-}P}$ = 37 Hz).

2c: Yield 108 mg (6%). – $C_{95}H_{81}F_6N_3O_6P_6Rh_2S_2$: calcd. Rh 10.66; found Rh 10.73. – ^{31}P NMR ([D_6]acetone): δ = 36.2 (dt, 2 P $J_{P\text{-}Rh}$ = 161, $J_{P\text{-}P}$ = 37 Hz), 40.9 (dd, 4 P, $J_{P\text{-}Rh}$ = 145, $J_{P\text{-}P}$ = 37 Hz).

To the filtrate diethyl ether, saturated with ethylene, was dropped. An orange-coloured solid precipitated was filtered off, washed with diethyl ether, and dried in vacuum. For recrystallization the crude products was dissolved in a minimum amount of acetone under ethylene, and diethyl ether saturated with ethylene was dropped slowly to the solution. The products precipitated as orange-coloured crystalline solids which were filtered off, washed with diethyl ether and dried under vacuum.

1a: Yield 970 mg (70%). – Temp. of decompn. 180–190°C. – $C_{33}H_{31}BF_4NP_2Rh$: calcd. C 56.94, H 4.27, N 2.64, Rh 14.82; found C 57.13, H 4.50, N 2.02, Rh 14.85. – ^{31}P NMR ([D_6]acetone): δ = 38.2 (d, $J_{P\text{-}Rh}$ = 129.9 Hz). – ^1H NMR ([D_6]acetone): δ = 3.54 (s, 4H, C_2H_4), 4.60 (vt, N = 4.4 Hz, 4H, CH_2P), 7.54 (m, 12H, Ph), 7.69 (d, $J_{H\text{-}H}$ = 7.7 Hz, 2H, 3,5-py), 7.78 (m, 8H, Ph), 7.96 (t, $J_{H\text{-}H}$ = 7.7 Hz, 1H, 4-py). – ^{13}C NMR ([D_6]acetone): δ = 43.9 (vt, N = 10.9 Hz, CH_2P), 59.5 (s, C_2H_4), 123.4 (vt, N = 6.2 Hz, $C_{3,5\text{-py}}$), 130.3 (vt, N = 5.1 Hz, PC_{meta}), 130.7 (vt, N = 21.3 Hz, PC_{ipso}), 132.3 (s, PC_{para}), 133.9 (vt, N = 6.8 Hz, PC_{ortho}), 141.9 (s, $C_{4\text{-py}}$), 163.0 (vt, N = 3.2 Hz, $C_{2,6\text{-py}}$).

1b: Yield 670 mg (45%). – Temp. of decompn. 190–200°C. – $C_{33}H_{31}F_6NP_3Rh$: calcd. C 52.20, H 4.44, N 2.19, Rh 13.51; found C 52.74, H 4.16, N 1.86, Rh 13.69. – ^{31}P NMR ([D_6]acetone): δ = 38.4 (d, $J_{P\text{-}Rh}$ = 129.9 Hz). – ^1H NMR ([D_6]acetone): δ = 3.52 (s, 4H, C_2H_4), 4.60 (vt, N = 4.4 Hz, 4H, CH_2P), 7.55 (m, 12H, Ph), 7.69 (d, $J_{H\text{-}H}$ = 7.7 Hz, 2H, 3,5-py), 7.78 (m, 8H, Ph), 7.96 (t, $J_{H\text{-}H}$ = 7.7 Hz, 1H, 4-py). – ^{13}C NMR ([D_6]acetone): δ = 43.9 (vt, N = 11.8 Hz, CH_2P), 59.6 (s, C_2H_4), 123.3 (vt, N = 5.6 Hz, $C_{3,5\text{-py}}$), 130.2 (vt, N = 5.0 Hz, PC_{meta}), 130.7 (vt, N = 20.9 Hz, PC_{ipso}), 132.3 (s, PC_{para}), 133.8 (vt, N = 6.8 Hz, PC_{ortho}), 141.8 (s, $C_{4\text{-py}}$), 163.0 (vt, N = 2.9 Hz, $C_{2,6\text{-py}}$).

1c: Yield 900 mg (62%). – Temp. of decompn. 130–140°C. – $C_{34}H_{31}F_3NO_3P_2RhS_2$: calcd. C 54.74, H 4.37, N 2.11, Rh 13.53; found C 54.05, H 4.13, N 1.85, Rh 13.62. – ^{31}P NMR ([D_6]acetone): δ = 38.2 (d, $J_{P\text{-}Rh}$ = 130.8 Hz). – ^1H NMR ([D_6]acetone): δ = 3.50 (s, 4H, C_2H_4), 4.60 (vt, N = 4.4 Hz, 4H, CH_2P), 7.55 (m, 12H, Ph), 7.69 (d, $J_{H\text{-}H}$ = 7.7 Hz, 2H, 3,5-py), 7.78 (m, 8H, Ph), 7.95 (t, $J_{H\text{-}H}$ = 7.7 Hz, 1H, 4-py). – ^{13}C NMR ([D_6]acetone): δ = 43.8 (vt, N = 12.3 Hz, CH_2P), 58.6 (s, C_2H_4), 123.3 (vt, N = 5.3 Hz, $C_{3,5\text{-py}}$), 130.2 (vt, N = 5.0 Hz, PC_{meta}), 130.7 (vt, N = 21.1 Hz, PC_{ipso}), 132.2 (s, PC_{para}), 133.8 (vt, N = 6.8 Hz, PC_{ortho}), 141.8 (s, $C_{4\text{-py}}$), 163.0 (vt, N = 2.8 Hz, $C_{2,6\text{-py}}$).

Preparation of [Rh(PNP)(styrene)]BF$_4$ (**4**): To a solution of 1.3 g of $[Rh(PNP)(C_2H_4)]BF_4$ in 8 ml of acetone 1 ml of fresh distilled styrene was added. The mixture was stirred for 5 h. A reddish-orange coloured solid precipitated. The reaction mixture was reduced to 4 ml under vacuum and further product was precipitated by dropping of diethyl ether. The crude product was filtered off

washed three times with diethyl ether and dried under vacuum. For recrystallization the solid was dissolved in a minimum amount of acetone. The product crystallized by slow dropping of diethyl ether. Yield 1.2 g (83%). – Temp. of decompn. 221–225°C. – $C_{39}H_{35}BF_4NP_2Rh$: calcd. C 60.89, H 4.58, N 1.82, Rh 13.38; found C 59.70, H 4.62, N 1.38, Rh 13.62. – ^{31}P NMR ([D$_6$]acetone): δ = 41.7 (d, $J_{P\text{-}Rh}$ = 126.3 Hz). – ^1H NMR ([D$_6$]acetone): δ = 3.72 (m, 1H, styrene), 3.87 (d, J = 7.7 Hz, 1H, styrene), 4.47 (dvt, N = 4.6 Hz, $J_{H\text{-}H}$ = 16 Hz, 2H, CH_2P), 4.85 (dvt, N = 3.6 Hz, $J_{H\text{-}H}$ = 16 Hz, 2H, CH_2P), 4.96 (br, 1H, styrene), 6.77 (m, 2H, styrene), 7.02 (m, 3H, styrene), 7.85–7.28 (m, 27H, Ph, py). – ^{13}C NMR ([D$_6$]acetone): δ = 43.5 (vt, N = 12.1 Hz, CH_2P), 51.5 (d, $J_{C\text{-}Rh}$ = 12.2 Hz, styrene), 75.8 (d, $J_{C\text{-}Rh}$ = 11.4 Hz, styrene), 122.8 (vt, N = 4.6 Hz, $C_{3,5\text{-}py}$), 126.4 (s, styrene), 128.2 (s, styrene), 129.4 (s, styrene), 129.5 (vt, N = 5.2 Hz, PC_{meta}), 129.9 (vt, N = 4.7 Hz, PC_{meta}), 131.8 (s, PC_{para}), 132.0 (s, PC_{para}), 132.9 (vt, N = 5.8 Hz, PC_{ortho}), 135.0 (vt, N = 7.1 Hz, PC_{ortho}), 141.3 (s, $C_{4\text{-}py}$), 162.0 (vt, N < 3 Hz, $C_{2,6\text{-}py}$).

Reaction of [Rh(PNP)(C$_2$H$_4$)]BF$_4$ (**1a**) *with Piperidine:* To a suspension of 1.53 g (2.2 mmol) of [Rh(C$_2$H$_4$)(PNP)]BF$_4$ **1a** in 15 ml of THF 4 ml (40 mmol) of piperidine was added at room temperature. An evolution of gas was observed, the solution changed its colour to red and in a short time an orange-coloured solid precipitated. The suspension was stirred for a further 2 h and filtered off. The crude product was washed with THF and diethyl ether and dried under vacuum. The product was recrystallized after extraction with 10 ml of refluxed THF.

[Rh(PNP)(pip)]BF$_4$ (**5a**): Yield 1.53 g (93.2%). – Temp. of decompn. 165–169°C. – $C_{36}H_{38}BF_4N_2P_2Rh$: calcd. C 57.73, H 5.33, N 3.68, Rh 13.22; found C 57.76, H 5.10, N 3.73, Rh 13.71. – ^{31}P NMR ([D$_6$]acetone): δ = 34.8 (d, $J_{P\text{-}Rh}$ = 152.7 Hz). – ^1H NMR ([D$_6$]acetone): δ = 0.87 (m, 1H, piperidine), 1.14–0.98 (m, 4H, piperidine), 1.38 (d br., $J_{H\text{-}H}$ = 11.0 Hz, 1H, piperidine), 2.27 (m, $J_{H\text{-}H}$ = 11.5 Hz, 2H, piperidine), 3.15 (d br., $J_{H\text{-}H}$ = 12.3 Hz, 2H, piperidine), 4.23 (vt, N = 4.4 Hz, 4H, CH_2P), 7.29 (d, $J_{H\text{-}H}$ = 7.7 Hz, 2H, 3,5-py), 7.54 (m, 12H, Ph), 7.61 (t, $J_{H\text{-}H}$ = 7.7 Hz, 1H, 4-py), 7.97 (m, 8H, Ph). – ^{13}C NMR ([D$_6$]acetone): δ = 24.3 (s, C_γ, piperidine), 28.2 (s, C_β, piperidine), 44.3 (vt, N = 12.0 Hz, CH_2P), 56.7 (s, C_α, piperidine), 122.4 (vt, N = 5.7 Hz, $C_{3,5\text{-}py}$), 130.0 (vt, N = 4.8 Hz, PC_{meta}), 131.6 (s, PC_{para}), 134.0 (vt, N = 7.0 Hz, PC_{ortho}), 136.8 (s, $C_{4\text{-}py}$), 162.9 (vt, N < 3 Hz, $C_{2,6\text{-}py}$).

5b and **5c** were obtained from **1b** and **1c**, respectively, in the same manner.

5b: Yield 59%. – Temp. of decompn. 157–160°C. – $C_{36}H_{38}F_6N_2P_3Rh$ calcd.C 53.48, H 4.74, N 3.46, Rh 12.73; found C 53.65, H 4.40, N 3.43 Rh 12.62. – ^{31}P NMR ([D$_6$]acetone): δ = 34.9 (d, $J_{P\text{-}Rh}$ = 164.9 Hz). – ^1H NMR ([D$_6$]acetone): δ = 0.87 (m, 1H, piperidine), 1.15–0.98 (m, 4H, piperidine), 1.38 (d br., $J_{H\text{-}H}$ = 11.3 Hz, 1H, piperidine), 2.27 (m, $J_{H\text{-}H}$ = 11.8 Hz, 2H, piperidine), 3.15 (d br., $J_{H\text{-}H}$ = 12.6 Hz, 2H, piperidine), 4.23 (vt, N = 4.4 Hz, 4H, CH_2P), 7.29 (d, $J_{H\text{-}H}$ = 7.6 Hz, 2H, 3,5-py), 7.54 (m, 12H, Ph), 7.61 (t, $J_{H\text{-}H}$ = 7.6 Hz, 1H, 4-py), 7.97 (m, 8H, Ph). – ^{13}C NMR ([D$_6$]acetone): δ = 24.3 (s, C_γ, piperidine), 28.2 (s, C_β, piperidine), 44.3 (vt, N = 12.1 Hz, CH_2P), 56.7 (s, C_α, piperidine), 122.4 (vt, N = 5.3 Hz, $C_{3,5\text{-}py}$), 130.0 (vt, N = 4.8 Hz, PC_{meta}), 131.6 (s, PC_{para}), 134.0 (vt, N = 7.0 Hz, PC_{ortho}), 136.8 (s, $C_{4\text{-}py}$), 162.9 (vt, N = < 3 Hz, $C_{2,6\text{-}py}$).

5c: Yield 60%. – Temp. of decompn. 177–179°C. – $C_{37}H_{38}F_3N_2O_3P_2Rh$: calcd. C 54.69, H 4.71, N 3.45, Rh 12.66; found C 54.69, H 4.31, N 3.30, Rh 12.63. – ^{31}P NMR ([D$_6$]acetone): δ = 34.9 (d, $J_{P\text{-}Rh}$ = 149.3 Hz). – ^1H NMR ([D$_6$]acetone): δ = 0.87 (m, 1H, piperidine), 1.14–0.98 (m, 4H, piperidine), 1.38 (d br., $J_{H\text{-}H}$ = 12.4 Hz, 1H, piperidine), 2.27 (m, $J_{H\text{-}H}$ = 11.6 Hz, 2H, piperidine), 3.15 (d br., $J_{H\text{-}H}$ = 12.9 Hz, 2H, piperidine), 4.23 (vt, N = 4.2 Hz, 4H, CH_2P), 7.29 (d, $J_{H\text{-}H}$ = 7.7 Hz, 2H, 3,5-py), 7.54 (m, 12H, Ph), 7.61 (t, $J_{H\text{-}H}$ = 7.7 Hz, 1H, 4-py), 7.98 (m, 8H, Ph). – ^{13}C NMR ([D$_6$]acetone): δ = 24.2 (s, C_γ, piperidine), 28.1 (s, C_β, piperidine), 44.2 (vt, N = 10.4 Hz, CH_2P), 56.7 (s, C_α, piperidine), 122.3 (vt, N = 5.7 Hz, $C_{3,5\text{-}py}$), 129.9 (vt, N = 4.8 Hz, PC_{meta}), 131.5 (s, PC_{para}), 133.9 (vt, N = 7.0 Hz, PC_{ortho}), 136.7 (s, $C_{4\text{-}py}$), 162.8 (vt, N = < 3 Hz, $C_{2,6\text{-}py}$).

Reaction of **1a** *with HNMe$_2$:* To a suspension of 2.7 g of **1a** (3.89 mmol) in 50 ml of THF 2.5 ml of HNMe$_2$ was added at –78°C. The mixture was warmed up slowly to room temperature and stirred for 1 h. The orange-coloured solid precipitate was filtered off washed with THF and diethyl ether and dried under vacuum. For recrystallization the crude product was dissolved in acetone and diethyl ether was dropped slowly. The product crystallized as a reddish-orange coloured solid and was filtered off, washed with diethyl ether, and dried under vacuum.

[Rh(PNP)(HNMe$_2$)]BF$_4$ (**6**): Yield 2.2 g (80%). – Temp. of decompn. 197°C. – $C_{33}H_{34}BF_4N_2P_2Rh$: calcd. C 55.80, H 4.82, N 3.94, Rh 14.65; found C 54.70, H 3.51, N 3.91, Rh 14.49. – ^{31}P NMR ([D$_6$]acetone): δ = 34.3 (d, $J_{P\text{-}Rh}$ = 157.0 Hz). – ^1H NMR ([D$_6$]acetone): δ = 2.33 (d, J = 5.4 Hz, 6H, CH_3), 4.24 (vt, N = 4.1 Hz, 4H, CH_2P), 7.33 (d, $J_{H\text{-}H}$ = 7.6 Hz, 2H, 3,5-py), 7.56 (m, 12H, Ph), 7.63 (t, $J_{H\text{-}H}$ = 7.7 Hz, 1H, 4-py), 8.00 (m, 8H, Ph). – ^{13}C NMR ([D$_6$]acetone): δ = 44.5 (vt, N = 11.4 Hz, CH_2P), 46.4 (s, CH_3), 122.3 (vt, $^3J_{C\text{-}P}$ = 5.4 Hz, $C_{3,5\text{-}py}$), 130.0 (vt, N = 4.5 Hz, PC_{meta}), 131.6 (s, PC_{para}), 134.0 (vt, N = 6.8 Hz, PC_{ortho}), 136.8 (s, $C_{4\text{-}py}$), 163.0 (vt, N < 3 Hz, $C_{2,6\text{-}py}$).

Reaction of **1a** *with HNEt$_2$:* The reaction was carried out in the similar manner to that described for the reaction of **1a** with piperidine. [Rh(PNP)(HNEt$_2$)]BF$_4$ (**7**) was obtained as a reddish-orange coloured crystalline solid. Yield: 82%. – Temp. of decompn. 176–183°C. – $C_{35}H_{38}BF_4N_2P_2Rh$: calcd. C 56.94, H 5.19, N 3.79, Rh 13.94; found C 56.78, H 5.16, N 3.65, Rh 14.24. – ^{31}P NMR ([D$_6$]acetone): δ = 38.9 (d, $J_{P\text{-}Rh}$ = 156.6 Hz). – ^1H NMR ([D$_6$]acetone): δ = 1.20 (t, J = 7.1 Hz, 6H, CH_3), 2.22 (m, 4H, CH_2), 2.45 (m, 4H, CH_2), 4.30 (vt, N = 4.0 Hz, 4H, CH_2P), 7.29 (d, $J_{H\text{-}H}$ = 7.7 Hz, 2H, 3,5-py), 7.53 (m, 12H, Ph), 7.61 (t, $J_{H\text{-}H}$ = 7.7 Hz, 1H, 4-py), 7.94 (m, 8H, Ph). – ^{13}C NMR ([D$_6$]acetone): δ = 16.3 (s, CH_3), 43.9 (vt, N = 11.2 Hz, CH_2P), 52.2 (m, CH_2), 122.6 (vt, N = 5.8 Hz, $C_{3,5\text{-}py}$), 130.0 (vt, N = 4.8 Hz, PC_{meta}), 131.7 (s, PC_{para}), 134.0 (vt, N = 6.9 Hz, PC_{ortho}), 137.0 (s, $C_{4\text{-}py}$), 162.7 (vt, N < 3 Hz, $C_{2,6\text{-}py}$).

Reaction of **4** *with HNMe$_2$:* The reaction was carried out in a similar manner to that described for the reaction of **1a** with HNMe$_2$. The solid obtained was identified as **6** by ^1H-NMR spectroscopy. In a second experiment the mixture was stored at –20°C for three weeks. The solution contained free styrene, found by gas chromatography, and the isolated solid was identified as **6** by ^1H-NMR spectroscopy.

Reaction of [Rh(PNP)(HNR$_2$)]X (**5a–c**, **6**, **7**) *with C$_2$H$_4$:* A suspension of the respective amine complex in THF was stirred for 3 h at –78°C under ethylene. The orange coloured solid was filtered off, washed with diethyl ether, and dried under vacuum. In each case the product was identified as the respesentative pure ethylene complex **1a**, **1b**, or **1c** by ^1H-NMR spectroscopy.

X-ray Structural Analyses: Selected crystals were covered with perfluoroether oil and mounted on a glass fibre. The data collection was performed at 200 K. An empirical absorption correction for **1a** (φ-scan, 10 reflections) and for **4** (SADABS[21]) was applied.

Table 5. Summary of data related to crystallography, data collection, and refinement

	1a	**4**
Empirical formula	$C_{33}H_{31}BF_4NP_2Rh$	$C_{39}H_{35}BF_4NP_2Rh$
Formula mass	693.25	769.34
Crystal size [mm]	0.32 × 0.26 × 0.20	0.32 × 0.15 × 0.15
Crystal system	Triclinic	Monoclinic
Diffractometer	STADI4 (Fa. Stoe)	CCD (Fa. Siemens)
Space group	*P*-1 (2)	$P2_1/c$ (14)
a [Å]	10.953(1)	11.7452(7)
b [Å]	11.563(1)	12.8761(8)
c [Å]	13.387(1)	22.603(1)
α [°]	72.293(4)	90
β [°]	80.496(6)	95.724(1)
γ [°]	71.931(5)	90
V [Å^3]	1530.8(2)	3401.3(4)
Z	2	4
ρ (calcd.) [Mg/m^3]	1.504	1.502
μ [mm^{-1}]	0.711	0.648
F(000)	704	1502
2Θ (max.)	52	52
T [K]	200	200
Refl. collected	6152	24813
Refl. unique	6029	6336
R(int)	0.1056	0.0461
No. of variables	486	573
GOOF	1.018	1.092
Final $R(4\sigma)$ *R*1; *wR*2	0.0543; 0.151	0.0485; 0.1090
Final *R*1; *wR*2	0.07995; 0.1694	0.0635; 0.1178
Larg. res. peak [e/Å^3]	2.826	1.531

SHELXS-86[22] and SHELXS-93[23] programs were used for structural solution by Patterson method and refined by a full-matrix least-squares method. Hydrogen atom positions were obtained from difference Fourier map and included in the refinement with individual isotopic displacement parameters. Anisotropic displacement parameters for all non-hydrogen atoms were used. All experimental data for the X-ray structure analyses are given in Table 5.

Further details of the crystal structure determination are deposited at Fachinformationszentrum Karlsruhe, D-76344 Leopoldshafen-Eggenstein, and may be obtained by quoting the depository numbers CSD-406244 (**1a**) and CSD-406245 (**4**).

[☆] Dedicated to Prof. Dr. *Wolfgang Beck* on the occasion of his 65th birthday.

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