Complex Catalysis, LIV[◇]

Synthesis and Characterization of Organorhodium(I) Complexes with the Tridentate Ligand 2,6-Bis(diphenylphosphanylmethyl)pyridine [Rh(PNP)R] (R = CH_3, C_6H_5) and Their Reactivity toward Ethylene and Protic Acids

Christine Hahn[a], Michael Spiegler[b], Eberhardt Herdtweck[b], and Rudolf Taube*[b]

Institut für Anorganische Chemie, Universität Würzburg[a],
Am Hubland, D-97074 Würzburg, Germany
E-mail: christine.hahn@mail.uni-wuerzburg.de

Anorganisch-Chemisches Institut, Technische Universität München[b],
Lichtenbergstraße 4, D-85747 Garching, Germany
Fax: (internat.) + 49(0)89/289-13473

Received April 27, 1998

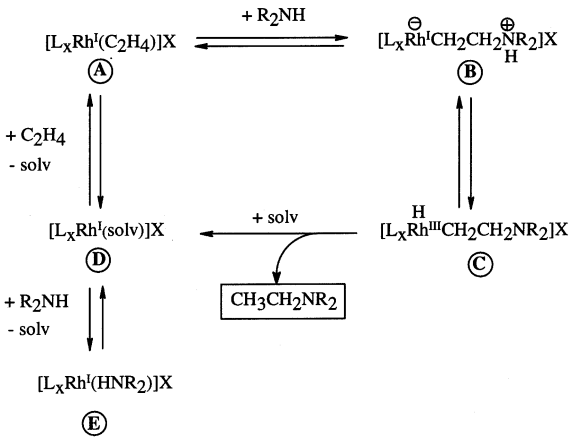
Keywords: Organorhodium(I) complexes / Tridentate ligand / Protolysis / Reductive elimination / C–H coupling

The organorhodium(I) complexes [Rh(PNP)R] [PNP = 2,6-bis(diphenylphosphanylmethyl)pyridine, R = CH_3 (**3a**), C_6H_5 (**3b**)] were synthesized from [Rh(PNP)(C_2H_4)]BF_4 (**1a**) and LiR and characterized by ^{31}P-, ^{1}H-, and ^{13}C-NMR spectroscopy and EI mass spectrometry. In a THF solution saturated with ethylene **3a** and **3b** form the five-coordinate ethylene organorhodium(I) complexes [Rh(PNP)R(C_2H_4)] (**5a**, **b**). The stable monohydridorhodium(III) complex [Rh(PNP)ClH-(CH_3CN)]SO_3CF_3 (**7**) was obtained by the reaction of [Rh(PNP)Cl] with HSO_3CF_3 in a solution of THF/acetonitrile and characterized by X-ray crystallography. In a THF solution the organorhodium(I) complexes **3a**, **b** react upon the addition of either HSO_3CF_3 or $HNMe_3Cl$ with the immediate release of the respective hydrocarbon HR.

The hydroamination of ethylene was first achieved at room temp. and normal pressure by a cationic ethylenerhodium(I) complex [Rh(PPh_3)$_2$(Me_2CO)(C_2H_4)]PF_6[1]. However, the low productivity of this rhodium complex catalyst could not be improved by variation of the ligand sphere[2]. Therefore we started upon a series of model studies to investigate the reaction mechanism of the rhodium complex catalyzed hydroamination of olefins, trying to trace systematically those reaction steps considered crucial for the catalytic cycle by the use of the [2,6-bis(diphenylphosphanylmethyl)pyridine]rhodium(I) complex fragment $[Rh(PNP)]^+$ as a stable structural moiety for the respective model compounds. The hypothetical reaction mechanism of the catalyses is formulated in Scheme 1.

It was recently found that model complexes of the type **A** [Rh(PNP)(olefin)]X (olefin = ethylene, styrene; X = BF_4, PF_6, SO_3CF_3) are only in a thermodynamic equilibrium with the corresponding amine complex **E**. In this case no indication of a nucleophilic attack of the secondary amine at the C−C double bond could be detected[3]. On the other hand the nucleophilic attack of secondary amines (HNR_2) was succesful with related dicationic olefin palladium(II) complexes [Pd(PNP)(olefin)]BF_4 (olefin = ethylene, styrene), however the Pd−C σ-bond in the formed (β-aminoethyl)palladium(II) complexes [Pd(PNP)($CHR'CH_2NR_2$)]-

Scheme 1



BF_4 (R′ = H, Ph) is so stable that it can not be cleaved protolytically under the reaction conditions[4].

It is known from other rhodium-catalyzed reactions, such as the hydrogenation of olefins[5][6], that the cleavage of the Rh−C σ-bond and the formation of the C−H bond can be realized by intramolecular reductive elimination, which is proposed as the product-forming step, cf. the formation of the ethylamine, shown as the step **C**→**D** in Scheme 1.

In this paper we report on the synthesis of related organorhodium(I) model complexes [Rh(PNP)R] (R = CH_3, C_6H_5) which were used to characterize the stability of the

[◇] Part LIII: R. Taube, H. Windisch, H. Hemling, H. Schumann, *J. Organomet. Chem.* **1998**, *555*, 201−210.

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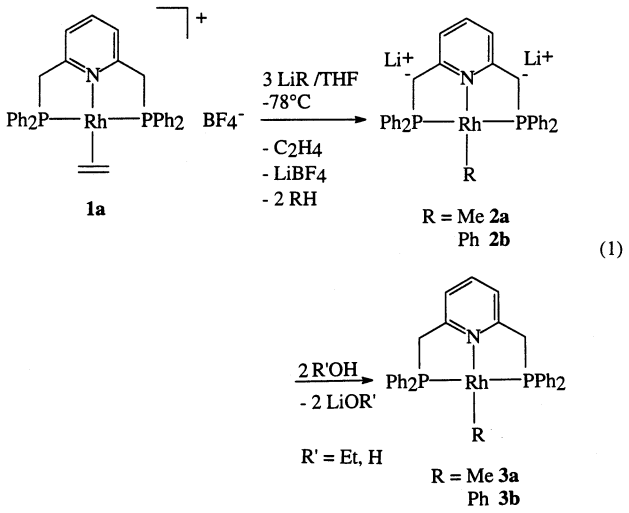
Rh−C σ-bond. For this purpose their reactivities toward ethylene and protic acids were investigated, and these results are presented here.

Results and Discussion

Synthesis and Characterization of [Rh(PNP)R]

The organorhodium(I) complexes [Rh(PNP)R] [R = CH_3 (**3a**), C_6H_5 (**3b**)] were synthesized from the cationic ethylenerhodium(I) complex [Rh(PNP)(C_2H_4)]BF_4 (**1a**)[3] with slightly more than three equiv. of the corresponding organyllithium compound, cf. Eq. 1.



(1)

The intermediates **2a**, **b** formed were characterized in situ by NMR spectroscopy. The ^{31}P-NMR spectrum of the reaction solution of **1a** with 3.1 equiv. of $LiCH_3$ in [D_8]THF shows one doublet at δ = 17.2 (J_{P-Rh} = 148 Hz) which is shifted upfield by about 11 ppm compared to the starting complex **1a**. In the ^{1}H-NMR spectrum of this solution a signal is found at δ = 0.30 (td, J_{H-P} = 4.9 Hz, $J_{H-Rh} \approx 1$ Hz, CH_3) for the methyl group coordinated at the rhodium centre. The corresponding ^{13}C signal for the methyl group appears at δ = −15.4 (dt, J_{C-P} = 10.3 Hz, J_{C-Rh} = 27.5 Hz).

A virtual triplet in the ^{1}H-NMR spectrum at δ = 3.34 has an intensity of 2 H, consistent with deprotonated methylene groups of the PNP ligand in **2a**, while the corresponding ^{13}C signal is observed at δ = 58.0 (vt, N = 24.6 Hz), which is shifted downfield in comparison to that of **1a** (δ = 43.9, vt, N = 10.9 Hz). Thus, the NMR data suggests the formation of **2a**.

The formation of the analogous phenyl compound **2b** is suggested by the ^{31}P-NMR-spectroscopic investigation of a reaction solution of **1a** and 3.2 equiv. of LiC_6H_5 in THF, where again one doublet is observed, at δ = 16.7, showing the same phosphorus-rhodium coupling constant (J_{P-Rh} = 148 Hz) as that found for **2a**.

Upon reprotonation with ethanol or water these intermediates **2a**, **b** are converted into the neutral organorhodium(I) complexes **3a**, **b**. The methyl and the phenyl complexes which are obtained in good yields are reddish/brown air-sensitive solids which are soluble in THF and toluene, moderately soluble in ethanol, and insoluble in diethyl ether. In contrast to the structurally analogous organorhodium(I) complexes [Rh(PPh_3)$_3$R], which form spontaneously the *ortho*-metallated product [Rh(*o*-$C_6H_4PPh_2$)(PPh_3)$_2$] by release of the respective hydrocarbon HR[7], the complexes **3a**, **b** are quite stable as solid compounds under an inert gas, as well as in solution at room temp.

However, only a few stable square-planar alkyl- and arylrhodium(I) complexes of the type [Rh{R′P(CH_2CH_2-CH_2PPh_2)$_2$}R] (R′ = *t*Bu, Ph) are known[8]. The *ortho*-metallation of a PPh group in these complexes as well as in **3a**, **b** is obviously prevented by the chelating structure of the tridentate ligand.

The complexes **3a**, **b** were characterized by ^{31}P-, ^{1}H-, and ^{13}C-NMR spectroscopy and by EI mass spectrometry. In the ^{31}P-NMR spectra a doublet was found at δ = 28.9 (J_{P-Rh} = 177 Hz) for **3a**, and at δ = 20.6 (J_{P-Rh} = 180 Hz) for **3b**. These signals are shifted upfield and have a larger phosphorus-rhodium coupling constant compared to those of the related cationic (PNP)rhodium(I) complexes [Rh(PNP)L]X (L = HNR_2, py, CH_3CN, DMSO, olefin; X = BF_4, PF_6, SO_3CF_3) which are found in the region of δ = 31−41 with coupling constants of 126−157 Hz[3][9].

The ^{1}H-NMR signal for the methyl group of **3a** at δ = 0.19 (J_{H-P} = 6.2 Hz; J_{H-Rh} = 1.7 Hz), as well as the corresponding ^{13}C-NMR signal at δ = −20.8 (J_{C-P} = 11.7 Hz; J_{C-Rh} = 24.6 Hz), is shifted upfield in comparison to that found for the intermediate **2a**. The characteristic virtual triplet for the methylene group of the PNP ligand appears at δ = 3.88 in the ^{1}H-NMR spectrum, and at δ = 46.8 in the ^{13}C-NMR spectrum.

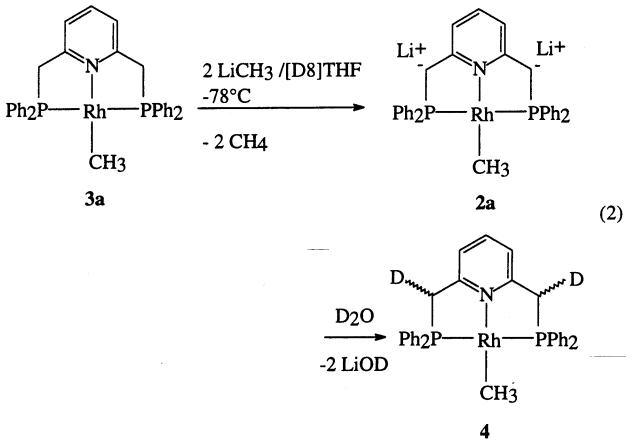
The ^{1}H-NMR signals for the phenyl moiety of **3b** are found at δ = 6.45, 6.57, and 7.36, and in the ^{13}C-NMR spectrum the corresponding signals are observed at δ = 119.0, 125.2, 140.9. While in the ^{1}H-NMR spectrum of **3b** the characteristic virtual triplet for the methylene group at δ = 4.02 is shifted slightly downfield compared to that of **3a**, the corresponding ^{13}C-NMR signal appears at the same chemical shift (δ = 46.8) as is found for **3a**.

In the EI mass spectra of **3a** and **3b** the respective peaks $[M]^+$ and $[M - R]^+$ could be observed.

A further piece of evidence for the formation of the twofold deprotonated intermediate **2a** is given by the reaction of **3a** with two equiv. of CH_3Li, cf. Eq. 2.

By the reaction of **2a** with D_2O the corresponding twofold deuterated methyl complex **4** is obtained and characterized by ^{1}H-NMR spectroscopy, where the signal for the methylene group is observed at δ = 3.87 with half the intensity found in the spectrum of **3a**. Accordingly, in the mass spectrum of **4**, the peaks for $[M]^+$ and $[M - CH_3]^+$ appear at the corresponding *m/z* values which are higher by two units than those found for **3a**.

This deprotonation reaction was also described for the structurally related [2,6-bis(diphenylphosphanylmethyl)-phenyl](methyl)platinum(II) complex, where an analogous

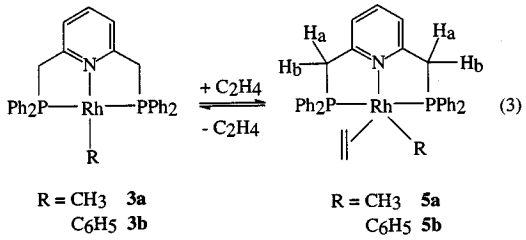


twofold deprotonated complex is obtained by the reaction with two equiv. of CH_3Li[10].

Reactivity of [Rh(PNP)R] toward Ethylene

Since the possibility of an insertion of an ethylene molecule into the Rh−C bond (cf. Scheme 1: e.g. in **B**) has to be taken into consideration as a side reaction during the hydroamination of ethylene, the investigation of the reactivity of the organorhodium(I) complexes **3a**, **b** toward ethylene was included in the model studies.

When a solution of **3a** or **3b** in THF saturated with ethylene was cooled down its colour changed reversibly from red (at room temp.) to orange-red (at −78°C). The formation of the corresponding five-coordinate ethylene organorhodium(I) complexes **5a**, **b** (cf. Eq. 3) is suggested by ^{1}H-NMR spectroscopy at room temp.: In addition to the slightly shifted signals for the coordinated PNP ligand and the organo moiety (see Experimental Section), relatively broad average signals at δ = 5.08 and δ = 4.36 are found for the methyl and phenyl complexes respectively, indicating an exchange between free and coordinated ethylene (the chemical shift of the average signal depends on the concentration of free ethylene).



In the ^{31}P-NMR spectra of these solutions the doublets at δ = 39.0 (J_{P-Rh} = 152 Hz) and 27.5 (J_{P-Rh} = 171 Hz) are observed at room temp. for the methyl and phenyl complexes **5a**, **b** respectively; these are show a remarkable downfield shift compared to those found for **3a**, **b**. These features are in agreement with the coordination of an ethylene molecule. As a consequence of the increased coordination number the phosphorus−rhodium bond becomes weaker, as reflected by the decreased phosphorus-rhodium coupling constants.

The behaviour of the solution of **3b** (under ethylene in [D_8]THF and during the cooling) was monitored by a dynamic proton-NMR experiment. The chemical shifts of the spectra run in the temperature range room temp. to −80°C are summarized in Table 1.

By cooling the sample the average signal for the ethylene becomes very broad. The coalescence temp. lies between −20°C and −40°C. At −60°C a broad signal at δ = 5.36 for the free ethylene, and two broad signals at δ = 2.48 and 1.85 for the coordinated ethylene, are visible and the signal for the methylene protons of the PNP ligand at δ ≈ 4.1 begins to split into two signals. By cooling to −80°C the signals for free and coordinated ethylene become sharper, which indicates a slow exchange relative to the NMR time scale. At this temperature the five-coordinate complex **5b** has a relatively stable coordination geometry which is no longer of C_{2v} symmetry, consequently the signals for the methylene protons become inequivalent and there is a split into two doublets at δ = 4.16 and 4.06 (J_{H-H} = 14.8 Hz).

When the solvent was removed under vacuum from a solution of **5a** or **5b** a red solid remained, identified as **3a** or **3b**, respectively. This indicates a weak coordination of the ethylene at the organorhodium(I) complexes. No indication of an insertion of the ethylene into the Rh−C σ-bond could be observed, under these conditions, for either **3a** or **3b**.

Synthesis and Structure of [Rh(PNP)ClH(CH_3CN)]SO_3CF_3

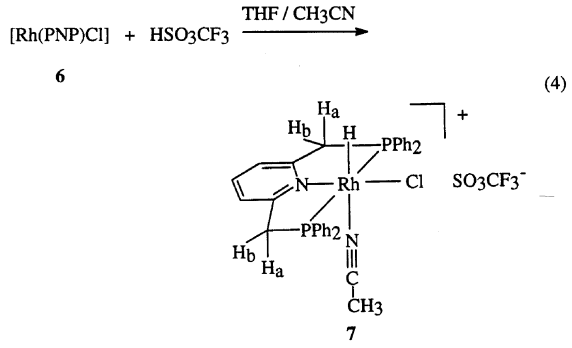
In the proposed catalytic cycle of the hydroamination of ethylene (cf. Scheme 1) the liberation of the ethylamine from the (β-ammonioethyl)rhodium(I) complex **B** is assumed to be achieved by oxidative addition of the proton of the β-ammonio group at the rhodium centre, forming the (β-aminoethyl)(hydrido)rhodium(III) complex **C** from which the product is reductively eliminated in an irreversible reaction step.

As is known (monohydrido)rhodium(III) complexes can be obtained by the oxidative addition of protic acids to rhodium(I) complexes[11][12], which is demonstrated here by the reaction of [Rh(PNP)Cl] (**6**)[13] with HSO_3CF_3, cf. Eq. 4.

The (chloro)(hydrido)rhodium(III) complex [Rh(PNP)-ClH(CH_3CN)]SO_3CF_3 (**7**) obtained was isolated as an air-stable pale yellow solid and characterized by IR and ^{1}H-NMR spectroscopy. In the IR spectrum the band at 2138 cm^{-1} is assigned to the Rh−H vibration, the two bands at 2293 and 2366 cm^{-1} are observed for the end-on coordinated acetonitrile[14], and the corresponding bands for the triflate anion (see Experimental Section) suggest its non-coordination[15]. The ^{1}H-NMR signal of the hydrido ligand appears at δ = −15.99 as a broad triplet, while for the coordinated acetonitrile a singlet is observed at δ = 1.48. For the inequivalent methylene protons of the PNP ligand the corresponding two doublets of virtual triplets appear at δ = 4.22 and 4.83.

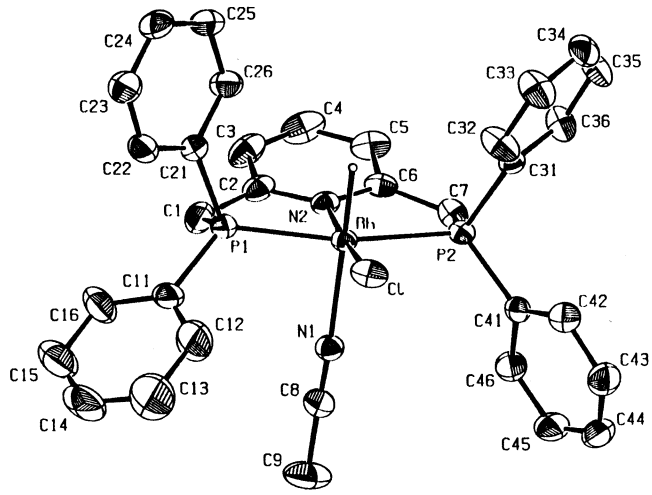
Table 1. Dynamic ^{1}H-NMR experiment of the solution of [Rh(PNP)(C_6H_5)] (**3a**) in [D_8]THF under ethylene (500 MHz)

T [°C]	py-4 (t)	PPh, Ph (m)	Ph (m)	CH_2	C_2H_4 free	coord.
23	7.52	7.08−7.34	6.48−6.57	4.05 vt	4.20 br.	
0	7.52	7.02−7.26	6.50−6.57	4.07 br.	3.96 br.	
−20	7.52	7.00−7.28	6.50−6.58	4.09 br.	3.9 br.	
−40	7.54	6.99−7.30	6.51−6.58	4.10 br.	5.3 br.	2.5 br.
−60	7.56	6.99−7.31	6.54−6.59	4.12 br. 4.09 br.	5.36 br.	2.50 br., 1.86 br.
−70	7.57	6.99−7.36	6.52−6.59	4.15 d 4.07 d J_{H-H} = 14.8 Hz	5.40 br.	2.48 br., 1.85 br.
−80	7.58	6.99−7.36	6.52−6.60	4.16 d 4.06 d J_{H-H} = 14.8 Hz	5.41 br.	2.48 d, 1.84 d J_{H-H} = 14.8 Hz



Single crystals of complex **7** were obtained from the mother liquor (THF/CH_3CN/diethyl ether) which stood three days at room temp. The molecular structure of the complex cation $[Rh(PNP)ClH(CH_3CN)]^+$ is shown in Figure 1. The Rh−Cl distance [2.3480(7) Å] is identical with that found for the chlororhodium(I) complex [Rh(PNP)Cl] [2.344(2) Å], while the Rh−N(1) distance [2.1451(19) Å] is significantly longer than the corresponding Rh−N bond length [1.984(3) Å] found in the (acetonitrile)rhodium(I) complex $[Rh(PNP)(CH_3CN)]BF_4$[9] due to the strong *trans* influence of the hydrido ligand. The Rh^{III}(PNP) fragment in **7** exhibits practically the same features of the bonding parameters as found in the Rh^{I}(PNP) fragment in **6** and in other Rh^{I}(PNP) complexes[3][9].

Figure 1. Platon[16] drawing of the complex cation $[Rh(PNP)ClH(CH_3CN)]^+$ of **7**



Reactivity of [Rh(PNP)R] toward Protic Acids

Analogous to the formation of the hydridorhodium(III) complex **7**, the reaction of the organorhodium(I) complexes **3a**, **b** with protic acids can be used as a simplified reaction model for the product-forming steps (**B** → **C** → **D** in Scheme 1). It is of interest to investigate the protolysis of [Rh(PNP)R], in one case in the presence of a weak coordinating anion X^- such as $CF_3SO_3^-$, and in another case with a stronger coordinating anion such as Cl^-. Thus, the proposed hydrido organorhodium(III) intermediates, either five-coordinate **I** or six-coordinate **II** (cf. Scheme 2), might show different reactivities concerning the reductive elimination of the hydrocarbon HR (discussed in detail by Milstein[6]).

First HSO_3CF_3 was added to a solution of **3a** or **3b** in THF. In the case of the methyl complex **3a** the release of the methane was observed immediately, visible as an evolution of gas, whereas from the phenyl complex **3b** the corresponding benzene was detected by gas chromatography of the reaction solution. However, no defined Rh^{I} complex could be isolated from the reaction solution. Obviously, the remaining $[Rh(PNP)]^+$ fragment (analogous to **D**, Scheme 1) cannot be stabilized either by the solvent (THF) or by the triflate anion. Decomposition of the reaction solution occurred and the formation of the dinuclear complex $[Rh_2(PNP)_3](SO_3CF_3)_2$ (**8**)[3] was detected by ^{31}P NMR.

However, when some acetonitrile was added to the reaction solution after the protolysis the corresponding cationic acetonitrile complex **9**[9] could be isolated, cf. Eq. 5.

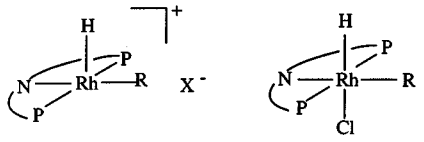
According to the last step of the catalytic cycle (**D** → **A**, Scheme 1) the remaining $[Rh(PNP)]^+$ fragment can also be trapped with ethylene by formation of the cationic ethylene complex **1b**[3], cf. Eq. 6.

When cyclooctadiene was added after the protolyses of **3b** a dinuclear COD complex **10** was obtained, cf. Eq. 7, which was fully characterized by ^{31}P-, ^{1}H-, and ^{13}C-NMR

Table 2. Selected bond lengths [Å] and angles [°] for $[Rh(PNP)ClH(CH_3CN)]SO_3CF_3$ (**7**)

Rh−Cl(1)	2.3480(7)	Rh−P(1)	2.3013(7)	Rh−P(2)	2.2863(6)
Rh−N(1)	2.1451(19)	Rh−N(2)	2.0656(17)	P(1)−C(1)	1.841(3)
P(2)−C(7)	1.828(2)				
P(1)−Rh−P(2)	166.90(2)	Cl−Rh−P(1)	96.77(2)	Cl−Rh−P(2)	93.42(2)
Cl−Rh−N(1)	91.95(5)	Cl−Rh−N(2)	175.06(5)	P(1)−Rh−N(1)	91.02(5)
P(1)−Rh−N(2)	84.53(6)	P(2)−Rh−N(1)	96.85(5)	P(2)−Rh−N(2)	84.82(5)
N(1)−Rh−N(2)	92.83(7)				

Scheme 2



$$[Rh(PNP)R] + HSO_3CF_3 \xrightarrow{THF\,/\,CH_3CN} [Rh(PNP)(CH_3CN)]SO_3CF_3 + HR \quad (5)$$

R = Me **3a**, Ph **3b** — **9**

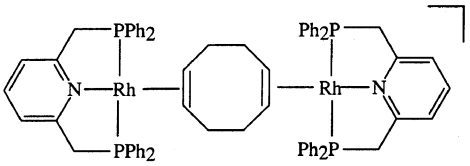
$$[Rh(PNP)R] + HSO_3CF_3 \xrightarrow{THF\,/\,C_2H_4} [Rh(PNP)(C_2H_4)]SO_3CF_3 + HR \quad (6)$$

R = Me **3a**, Ph **3b** — **1b**

spectroscopy (see Experimental Section). Thus, it is shown that the regeneration of the cationic olefin complex is possible after the elimination of the hydrocarbon, which is of great importance for the catalysis.

$$2\,[Rh(PNP)(C_6H_5)] + 2\,HSO_3CF_3 \xrightarrow{THF\,/\,COD} 2\,C_6H_6 +$$

3b



$$2\,SO_3CF_3^- \quad (7)$$

10

In another experiment trimethylammonium chloride was added to a solution of **3a** or **3b**. In both cases the respective hydrocarbon was also released immediately while the chlororhodium(I) complex **6** formed, which is poorly soluble in THF, began to precipitate and was filtered off after 4 h with a yield of 80−90%, cf. Eq. 8.

$$[Rh(PNP)R] + [HNMe_3]Cl \xrightarrow{THF} [Rh(PNP)Cl] + HR + NMe_3 \quad (8)$$

R = Me **3a**, Ph **3b** — **6**

Since a (hydrido)(phenyl)rhodium(III) complex $[Rh(PMe_3)_2(CO)(C_6H_5)HCl]$ could be detected upon the reaction of $[Rh(PMe_3)_2(CO)(C_6H_5)]$ with HCl, although only in solution at −40°C by NMR spectroscopy[17], the formation of a hydrido organo-PNP−rhodium(III) intermediate during the protolysis reaction described above might be postulated. Furthermore, the reductive elimination step from this complex seems to proceed without any kinetic inhibition, independent of the coordinating ability of the anion in the Brönsted acid used for protolysis.

Conclusions

The synthesis of the new organorhodium(I) complexes [Rh(PNP)R] (R = CH_3, C_6H_5) succeeded by the reaction of the cationic ethylene complex $[Rh(PNP)(C_2H_4)]BF_4$ with three equiv. of LiR. Organorhodium complexes containing deprotonated methylene groups of the PNP ligand occur as intermediates, which can be reprotonated with ethanol or water.

The square-planar coordination geometry of the organorhodium complexes is stabilized by the chelating structure of the tridentate PNP ligand, which avoids the release of the hydrocarbon HR by *ortho*-metallation of a PPh moiety.

The organorhodium(I) complexes [Rh(PNP)R] react with ethylene by the formation of five-coordinate complexes $[Rh(PNP)R(C_2H_4)]$ in which the ethylene is weakly coordinated and can be removed under vacuum. No indication of an insertion of the ethylene in the Rh−C σ-bond could be observed, which may be important to exclude the oligomerization of ethylene as a side reaction of the hydroamination.

As was shown a stable (monohydrido)rhodium(III) complex $[Rh(PNP)ClH(CH_3CN)]SO_3CF_3$ can be obtained by oxidative addition of HSO_3CF_3 to the chlororhodium(I) complex [Rh(PNP)Cl]. Upon protolysis with HSO_3CF_3 of the organorhodium(I) complexes [Rh(PNP)R] the hydrocarbons RH are liberated, and it is possible to trap the remaining Rh^I complex fragment with olefins, so the cationic olefin complex can be regenerated, which is as expected for the starting complex in the catalytic cycle of the hydroamination of olefins.

Independently, if a protic acid with a weakly coordinating (HSO_3CF_3) or a stronger coordinating anion ($HNMe_3Cl$) is used, the protolytic reaction of the organorhodium(I) complexes [RhPNP)R] [proceeding by intermediate formation of corresponding hydrido-organorhodium(III) complex] leads immediately in each case to the reductive elimination of the hydrocarbon HR. These results also suggest that the reductive elimination of the ethylamine (cf. Scheme 1) may proceed irreversibly and without kinetic inhibition, which is essential for a product-forming step closing the catalytic cycle. The proposed reaction mechanism for the hydroamination of olefins finds strong chemical support from these model reactions.

We thank Dr. *A. Porzel* of the *Institut für Pflanzenbiochemie* of the University of Halle for the measurement of the dynamic proton-resonance experiment and the *Deutsche Forschungsgemeinschaft* (*Sonderforschungsbereich 347* of the University of Würzburg) for financial support.

Experimental Section

General: All reactions were carried out under dry and oxygen-free argon or ethylene. Ethanol, acetone, $CDCl_3$ and [D_6]acetone were refluxed over 4-Å molecular sieves and made oxygen-free by bubbling argon through the liquid. THF and diethyl ether were refluxed in the presence of Na/benzophenone and [D_8]THF in the presence of K/Na alloy. Acetonitrile and DMSO were dried over 4-Å molecular sieves and distilled before use. HSO_3CF_3, $LiCH_3$ and LiC_6H_5 were obtained from Fluka. – IR: KBr pellets with a Perkin-Elmer FT-IR 16 spectrometer. – ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR: Varian Gemini 300 NMR spectrometer (300, 75, and 121 MHz respectively), ^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. – Dynamic proton NMR: Varian Unity 500 NMR spectrometer (500 MHz). – EI MS: AMD 402 spectrometer (AMD Intectra) at 70 eV. – (C, H, and N): LECO CHN 932 analyzer. Rh elemental analysis was determined using a photometric method[18]. The Chrompack gas-chromatograph CP 9000 was used for the identification of liquid organic compounds.

Syntheses: [Rh(PNP)(C_2H_4)]BF_4 (**1a**) was prepared according to the procedure described in ref.[3].

[Rh(PNP)(CH_3)] (**3a**): 10.5 ml of a 1.6 M $LiCH_3$ solution in diethyl ether (3.2 equiv.) was added slowly at −78°C to a suspension of 3.6 g (5.2 mmol) of [Rh(PNP)(C_2H_4)]BF_4 (**1a**) in 20 ml of THF. The mixture was warmed up to room temp. and stirred for a further 10 min to give a red solution. The solvent was removed under reduced pressure. 20 ml of ethanol was added dropwise slowly at −78°C to the remaining red crystalline solid with rigorous stirring. After stirring for another 20 min at room temp., the reddish/brown solid was filtered off, washed with ethanol (2 ×), then with diethyl ether and dried under vacuum. After recrystallization of the crude product in hot THF, 2.2 g of **3a** (3.7 mmol, 71%), reddish/brown solid was isolated, temp. of decomposition 220−230°C. – ^{31}P NMR ([D_8]THF): δ = 28.89 (d, J_{P-Rh} = 177 Hz). – ^1H NMR([D_8]THF): δ = 0.19 (td, $^3J_{H-P}$ = 6.2 Hz, J_{H-Rh} = 1.7 Hz, 3 H, CH_3), 3.88 (vt, N_{H-P} = 3.9 Hz, 4 H, CH_2), 7.07 (d, J_{H-H} = 7.6 Hz, 2 H, *3,5*-py), 7.30 (m, 12 H, PPh), 7.49 (t, J_{H-H} = 7.6 Hz, 1 H, *4*-py), 7.78 (m, 8 H, PPh). – ^{13}C NMR([D_8]THF): δ = −20.8 (dt, $^2J_{C-P}$ = 11.7 Hz, J_{C-Rh} = 24.6 Hz, *C*H_3), 46.8 (vt, N_{C-P} = 9.7 Hz, *C*H_2), 120.8 (vt, N_{C-P} = 5.1 Hz, $C_{3,5\text{-py}}$), 128.6 (vt, N_{C-P} = 4.4 Hz, PC_{meta}), 129.3 (s, PC_{para}), 131.4 (s, $C_{4\text{-py}}$), 133.6 (vt, N_{C-P} = 7.5 Hz, PC_{ortho}), 138.3 (vt, N_{C-P} = 14.9 Hz, PC_{ipso}), 159.9 (vt, N_{C-P} < 3 Hz, $C_{2,6\text{-py}}$). – EI MS; *m/z* (%): 593 (100) $[M]^+$, 578 (62) $[M - CH_3]^+$. – $C_{32}H_{30}NP_2Rh$ (593.45): calcd. C 64.77, H 5.10, N 2.36, Rh 17.34; found C 64.26, H 5.04, N 2.63, Rh 17.88.

[Rh(PNP)(C_6H_5)] (**3b**): The complex **3b** was prepared in the same manner as described for **3a** from 3 g (4.3 mmol) of **1a** in 20 ml of THF and 7.5 ml of a ca. 1.8 M Et_2O/cyclohexane solution of LiC_6H_5 (13.4 mmol, 3.1 equiv.). When the solvent was removed from the red solution, a red oil remained which was treated with 20 ml of ethanol at −78°C by rigorously stirring, giving a reddish/brown suspension. After stirring for another 20 min, the solid was filtered off washed with ethanol (3 ×)and then with diethyl ether and dried under vacuum. The crude product was recrystallized in hot THF giving 2.1 g of **3b** (3.2 mmol, 75%), reddish/brown solid, temp. of decomposition 215−220°C. – ^{31}P NMR ([D_8]THF): δ = 20.6 (d, J_{P-Rh} = 180 Hz). – ^1H NMR ([D_8]THF): δ = 4.02 (vt, N_{H-P} = 3.8 Hz, 4 H, CH_2), 6.45 (t, J_{H-H} = 7.0 Hz, 1 H, H_{para}), 6.57 (t, J_{H-H} = 7.2 Hz, 2 H, H_{meta}), 7.21 (m, 14 H, PPh, *3,5*-py), 7.36 (d, J_{H-H} = 7.3 Hz, 2 H, H_{ortho}), 7.50 (m, 8 H, PPh), 7.60 (t, J_{H-H} = 7.6 Hz, 1 H, *4*-py). – ^{13}C NMR ([D_8]THF): δ = 46.8 (vt, N_{C-P} = 9.9 Hz, *C*H_2), 119.0 (s, C_{para}), 120.9 (vt, N_{C-P} = 5.2 Hz, $C_{3,5\text{-py}}$), 125.24 (s, C_{meta}), 128.5 (vt, N_{C-P} = 4.6 Hz, PC_{meta}), 129.3 (s, PC_{para}), 133.5 (s, $C_{4\text{-py}}$), 133.6 (vt, N_{C-P} = 6.9 Hz, PC_{ortho}), 137.9 (vt, N_{C-P} = 16.1 Hz, PC_{ipso}), 140.9 (vt, N_{C-P} = 3.8 Hz, C_{ortho}), 160.9 (vt, N_{C-P} < 3 Hz, $C_{2,6\text{-py}}$). – EI MS; *m/z* (100): 655 (6.7) $[M]^+$, 578 (0.1) $[M - C_6H_5]^+$. – $C_{37}H_{32}NP_2Rh$ (655.52): calcd. C 67.79, H 4.92, N 2.14, Rh 15.70; found C 63.92 (premature decomposition of the sample), H 5.03, N 1.91, Rh 15.58.

Alternatively the complexes could be obtained by reprotonation with 5 equiv. of H_2O which were added directly to the red reaction solution (**2a** or **2b**). The crude products **3a**, **b** precipitated after a few minutes from the THF solution and were isolated in yields of about 65%.

*NMR-Spectroscopic Characterization of [Rh{2,6-($Ph_2PCHLi)_2$-(NC_5H_3)}(R)] [R = CH_3 (**2a**), C_6H_5 (**2b**)]*

2a: (a) [Rh(PNP)(C_2H_4)]BF_4 (148 mg, 0.21 mmol, **1a**) was dissolved in 1 ml of [D_8]THF and 3.1 equiv. of solid $LiCH_3$ (0.66 mmol, obtained from 0.41 ml of a 1.6 M Et_2O solution by removing the solvent) were added at −78°C and warmed up to room temp. The NMR spectra, which were measured instantly from the red solution obtained are consistent with **2a**. – ^{31}P NMR ([D_8]THF): δ = 17.2 (d, J_{P-Rh} = 148 Hz). – ^1H NMR ([D_8]THF): δ = 0.30 (td, $^3J_{H-P}$ = 4.9 Hz, $J_{H-Rh} \approx$ 1 Hz, 3 H, CH_3), 3.34 (vt, N_{H-P} = 3.8 Hz, 2 H, C*H*), 5.10 (d, J_{H-H} = 7.6 Hz, 2 H, *3,5*-py), 6.06 (t, J_{H-H} = 7.6 Hz, 1 H, *4*-py), 6.92−7.05 (m, 12 H, PPh), 7.72 (m, 8 H, PPh). – ^{13}C NMR ([D_8]THF): δ = −15.4 (dt, $^2J_{C-P}$ = 10.3 Hz, J_{C-Rh} = 27.5 Hz, *C*H_3), 58.0 (vt, N_{C-P} = 24.6 Hz, *C*H), 92.3 (vt, N_{C-P} = 8.0 Hz, $C_{3,5\text{-py}}$), 126.1 (s, PC_{para}), 127.2 (vt, N_{C-P} = 4.2 Hz, PC_{meta}), 131.0 (s, $C_{4\text{-py}}$), 132.5 (vt, N_{C-P} = 6.6 Hz, PC_{ortho}), 148.6 (vt, N_{C-P} = 14.4 Hz, PC_{ipso}), 171.6 (vt, N_{C-P} < 3 Hz, $C_{2,6\text{-py}}$).

(b) [Rh(PNP)(CH_3)] (197 mg, 0.33 mmol, **3a**) was dissolved in 1 ml of [D_8]THF and 2.2 equiv. of solid CH_3Li (0.73 mmol, obtained from 0.46 ml of a 1.6 M Et_2O solution by removing the solvent) were added at −78°C and warmed up to room temp. The obtained red solution was instantly characterized by NMR spectroscopy. The ^{31}P-, ^1H-, and ^{13}C-NMR spectra are identical with those found for the reaction solution of **1a** and 3.1 equiv. of CH_3Li described in (a).

2b: The reaction solution of **1a** and 3.2 equiv. of C_6H_5Li (1.8 M solution in Et_2O/cyclohexane) in THF prepared in the same manner as described for **2a** was characterized by ^{31}P NMR (with external ref. C_6D_6): δ = 16.7 (d, J_{P-Rh} = 148 Hz).

Reaction of **2a** *with* D_2O: 5 equiv. of D_2O were added to a solution of **2a** in THF, which was prepared from **3a** and 2.2 equiv. of CH_3Li as described above. The reddish/brown crystalline solid which was precipitated was filtered off washed with ethanol and diethyl ether and dried under vacuum. The ^1H-NMR spectrum of the solid is consistent with [Rh{2,6-($Ph_2PCHD)_2$(NC_5H_3)}(CH_3)] (**4**). For the deuterated methylene group a multiplet at δ = 3.87 was found with an intensity of 2 H. All other signals of **4** agree with those of **3a**. – EI MS of **4**; *m/z* (%): 595 $[M]^+$ (81), 580 $[M - CH_3]^+$ (53).

Reaction of **3a**, **b** *with Ethylene:* The complexes **3a**, **b** were dissolved in [D_8]THF. The solutions were saturated with ethylene at −78°C. The five-coordinate complexes [Rh(PNP)R(C_2H_4)] [R = CH_3 (**5a**), C_6H_5 (**5b**)] were identified by ^{31}P- and ^{1}H-NMR spectroscopy.

5a: ^{31}P NMR ([D_8]THF): δ = 39.0 (d, J_{P-Rh} = 152 Hz). − ^{1}H NMR ([D_8]THF): δ = −0.54 (td, $^3J_{H-P}$ = 7.3 Hz, J_{H-Rh} = 1.5 Hz, 3 H, CH_3), 4.04 (vt, N_{H-P} = 3.0 Hz, 4 H, CH_2), 5.08 (br., average signal for free and coord. C_2H_4), 7.12−7.62 (m, 23 H, PPh, py).

5b: ^{31}P NMR ([D_8]THF): δ = 27.5 (d, J_{P-Rh} = 171 Hz). − ^{1}H NMR ([D_8]THF): δ = 4.05 (vt, N_{H-P} = 3.0 Hz, 4 H, CH_2), 4.36 (br., average signal for free and coord. C_2H_4), 6.45 (t, J_{H-H} = 7.3 Hz, 1 H, H_{para}), 6.55 (t, J_{H-H} = 7.3 Hz, 2 H, H_{meta}), 7.07−7.40 (m, 23 H, PPh, *3,5*-py, H_{ortho}), 7.54 (t, J_{H-H} = 7.9 Hz, 1 H, *4*-py).

[Rh(PNP)ClH(CH$_3$CN)]SO$_3$CF$_3$ (**7**): 0.2 ml of HSO_3CF_3 was added to a suspension of 345 mg (0.56 mmol) of [Rh(PNP)Cl][9][13] in 5 ml of THF and 1 ml of acetonitrile. The mixture changed its colour to pale yellow. After filtration of the solution, diethyl ether was added dropwise and a yellow/brown oil precipitated which crystallized to a pale yellow solid. The crude product was filtered off, washed with diethyl ether (2 ×), and recrystallized in acetone/diethyl ether to give 290 mg of **7** (0.38 mmol, 67%), temp. of decomposition 160−170°C. − IR (KBr): $\tilde{\nu}$ = 2366 cm^{-1}, 2293 (CH_3CN); 2138 (Rh−H); 1602, 1568 (py); 1261, 1223, 1159, 1030, 638, 572 (SO_3CF_3). − ^{1}H NMR ($CDCl_3$): δ = −15.9 (t, $^2J_{H-P}$ = 9.5 Hz, 1 H, Rh*H*), 1.49 (s, 3 H, NCH_3) 4.22 (dvt, J_{Ha-Hb} = 17.8 Hz, N_{H-P} = 4.6 Hz, 2 H, CH_a), 4.83 (dvt, J_{Ha-Hb} = 17.8 Hz, N_{H-P} = 4.6 Hz, 2 H, CH_b), 7.41−7.94 (m, 23 H, PPh, py).

Reactivity of **3a**, **b** *toward HSO$_3$CF$_3$:* (a) 1 equiv. of HSO_3CF_3 was added to a solution of 1 mmol of **3a** or **3b** in 8 ml of THF. In the case of the reaction with **3a** the evolution of methane was immediately visible. In the reaction solution of **3b** benzene was correspondingly detected by gas chromatography. By addition of diethyl ether to the respective reaction solutions dark red oil precipitated giving reddish/brown solids upon removal of the solvent in vacuum. The solids obtained from both reaction solutions contain the dinuclear complex [$Rh_2(PNP)_3$](SO_3CF_3)$_2$ (**8**) among decomposition products; detected by ^{31}P-NMR spectroscopy (δ = 43.9 dd, $J_{P(a)-Rh}$ = 139 Hz, $J_{P(a)-P(b)}$ = 39 Hz; δ = 26.4, dt $J_{P(b)-Rh}$ = 169 Hz)[3].

(b) In presence of CH_3CN: After the protolysis of **3a** or **3b** with HSO_3CF_3 (see above), 1 ml of acetonitrile was added to the reaction solution and stirred for 20 min at room temp. Upon dropwise addition of diethyl ether an orange/brown oil precipitated which crystallized after 1 d to give a brown/yellow solid which was filtered off washed with diethyl ether and dried under vacuum. In each case the solid was analyzed by ^{1}H-NMR spectroscopy as the pure acetonitrile complex [Rh(PNP)(CH_3CN)]SO_3CF_3 (**9**) when compared to the spectrum of an authentic sample prepared according to the procedure in the literature[9] (yield: 50−60%).

(c) In presence of ethylene: After the protolysis of **3a** or **3b** with HSO_3CF_3 (see above), the reaction solution was stirred for 20 min under ethylene at −78°C. The mixture was warmed up to room temp. Upon addition of diethyl ether to the solution an orange yellow crystalline solid precipitated which was filtered off, washed with diethyl ether and dried under vacuum. The solid was identified as the pure ethylene complex [Rh(PNP)(C_2H_4)]SO_3CF_3 (**1b**) by ^{1}H-NMR spectroscopy when compared to an authentic sample[3] (yield: 60−80%).

(d) In the presence of COD: 114 μl of HSO_3CF_3 was added to a solution of 830 mg (1.26 mmol) of [Rh(PNP)(C_6H_5)] (**3b**) in 8 ml of THF. After 5 min, 1.6 ml (12.6 mmol) of cyclooctadiene (COD) was added and stirred for 30 min while an orange yellow solid crystallized slowly from the solution. The solid was filtered off the next day. For recrystallization the solid was dissolved in acetone and precipitated after addition of diethyl ether to the solution. The crystalline solid was filtered off, washed with diethyl ether and dried under vacuum. The solid was characterized as [$Rh_2(PNP)_2$(COD)](SO_3CF_3)$_2$ (**10**) which was isolated in a yield of 520 mg (0.66 mmol, 53%), temp. of decomposition 232°C. − ^{31}P NMR ([D_6]acetone): δ = 41.2 (d, J_{P-Rh} = 142 Hz). − ^{1}H NMR ([D_6]acetone): δ = 1.18 (m, 4 H, COD), 2.25 (m, 4 H, COD), 4.09 (m, 4 H, COD), 4.36 (vt, N_{H-P} = 3.6 Hz, 4 H, CH_2), 7.37−7.81 (m, 23 H, PPh, py). − ^{13}C NMR ([D_6]acetone): δ = 44.7 (vt, N_{C-P} = 11.5 Hz, *C*H$_2$), 77.8 (d, J_{C-Rh} = 12 Hz), 122.7 (vt, N_{C-P} < 3 Hz, $C_{3,5\text{-py}}$), 129.9 (vt, N_{C-P} = 4.2 Hz, PC_{meta}), 131.0 (vt, N_{C-P} = 15.8 Hz, PC_{ipso}), 132.2 (s, PC_{para}), 134.5 (vt, N_{C-P} = 6.6 Hz, PC_{ortho}), 141.7 (s, $C_{4\text{-py}}$), 161.9 (vt, N_{C-P} < 3 Hz, $C_{2,6\text{-py}}$). − $C_{72}H_{66}F_6N_2O_6P_4Rh_2S_2$ (1563.15): calcd. C 55.31, H 4.26, N 1.79, Rh 13.17; found C 54.91, H 4.26, N 1.65, Rh 13.07.

Reactivity of **3a**, **b** *toward HNMe$_3$Cl:* 48 mg (0.5 mmol) of $HNMe_3Cl$, dissolved in 2 ml of THF, was added to a solution of 0.5 mmol of **3a** or **3b**, dissolved in 8 ml of THF. A red crystalline solid precipitated and, in the case of the methyl complex **3a**, an evolution of gas was observed immediately. In the reaction solution of **3b** benzene was detected by gas chromatography. After 4 h, the red solid was filtered off, washed with THF and diethyl ether and dried under vacuum. The solid was identified in each case as [Rh(PNP)Cl][9][13] (**6**) by ^{31}P-NMR and IR spectroscopy (yield: 80−90%).

Crystal-Structure Determination of **7**: A single crystal of approximate dimensions 0.64 × 0.28 × 0.08 mm was mounted inside a Lindemann glass capillary. Crystal data and structure refinement details are given in Table 3.

Table 3. Crystal data and structure refinement for **7**

Formula	$C_{34}H_{31}ClF_3N_2O_3P_2RhS$
Molecular mass	805.00
Crystal system	triclinic
Space group	*P*1 (I. T. No. 2)
a [Å]	9.2052(5)
b [Å]	12.6582(8)
c [Å]	15.7936(10)
α [°]	79.231(7)
β [°]	74.202(6)
γ [°]	77.905(6)
V [Å^3]	1714.9(2)
Z	2
D(calcd.) [g cm^{-3}]	1.559
μ (Mo-K_α) [cm^{-1}]	7.8
F(000)	816
Θ range [°]	2.28−25.60
T [K]	193
Reflections, collected	10392
Independent reflections	5972
Data/restraints/parameters	5972/0/548
Goodness-of-fit on F^2	0.948
Final *R* indices [$I > 2\sigma(I)$]	$R1$ = 0.0249, $wR2$ = 0.0571
R indices (all data)	$R1$ = 0.0337, $wR2$ = 0.0588
Largest diff peak and hole [e Å^{-3}]	+0.53; −0.62

The data were measured with a STOE IPDS[18] using graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å). A decay correction using the program DECAY[19] was applied. The structure was solved by direct methods[20], completed by subsequent difference Fourier syntheses, and refined by full-matrix least-squares procedures[21]. Final cycles of refinement converged at $R1 = \Sigma(||F_o| -$

$||F_c||)/\Sigma|F_o| = 0.0249$ and $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2} = 0.0571$ for 4931 observed reflections [$I > 2\sigma(I)$]. All non-hydrogen atoms were refined with anisotropic displacement coefficients. All hydrogen atom positions were found in the difference map calculated from the model containing all non-hydrogen atoms. The hydrogen positions were refined with individual isotropic temperature parameters. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre (CCDC-101416). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033, E-mail: deposit@ccdc.cam.ac.uk].

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