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N-phosphanylamidine ligands and their catalytic activity in the hydroformylation of 1-octene and styrene

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ABSTRACT

Pyridine-based *N*-phosphanylamidine ligands *i*-Pr_2N–C(pyr)=N–PR_2 (R = Ph (**3**), *i*-Pr (**4**)) were synthesized and fully characterized by NMR spectroscopy and X-ray crystallography. Mononuclear rhodium complexes **7** and **8** were obtained in one step from the $[RhCl(COD)]_2$ dimer and the monodentate ligands **1** and **2**. Their single-crystal X-ray diffraction studies revealed the structural adaptive behavior of the monodentate *N*-phosphanylamidine ligands **1** and **2** upon k^1-*P* coordination mode in rhodium(I) complexes with the imino nitrogen atom of the amidine function which behaves as a "universal joint". Compounds **1**–**4** were evaluated as ligands in the 1-octene and styrene hydroformylation reactions. The results obtained are encouraging and represent the first report on the use of *N*-phosphanylamidine ligands of the type R''_2N–C(R′)=N–PR_2 in catalytic reactions.

1. Introduction

Hydroformylation is a straightforward synthetic methodology affording aldehydes by creating a C–C bond in only one step from quite inexpensive feedstock. It represents one of the most important homogeneous catalytic processes applied on an industrial scale [1,2]. A large number of ligands have been developed and applied to this reaction [3–8] and there is continued interest in the development of new mono- and heteroditopic bidentate phosphane ligands to increase the efficiency and selectivity of this chemical transformation. The straightforward formation of P–N bonds from halophosphanes is a method of choice to prepare easily a large scope of phosphane ligands. This synthetic methodology allows a fine tuning of the steric and electronic properties of the phosphane moiety [9,10]. This high versatility is one of the reasons why, for example, aminophosphane R_2P–NR'_2 [10] and phosphoramidite $(RO)_2P$–NR'_2 [11] ligands are extensively studied for their applications in catalysis. It is noteworthy that very few examples of methylenaminophosphine-type ligands of the general formula R^1R^2C=N–PR_2 have been tested in catalytic chemical transformations [12,13].

"Hybrid" ligands, such as bifunctional *P,N*-ligands bearing two chemically different donor atoms, are of particular interest in catalytic reactions since they can reversibly adopt either a κ^1-*P* or a κ^2-*P,N* coordination mode along the catalytic cycle and therefore modify the catalytic properties of the metallic center. Even though the κ^1-*P* and κ^2-*P,N* coordination modes to Rh(I) have been identified with *P,N* hybrid ligands, very few experimental data have evidenced the κ^2-*P,N* chelating mode under hydroformylation conditions [14]. Nevertheless, the results recorded up to now with these *P,N* hybrid ligands highlight the beneficial effect of the presence of the non-coordinated nitrogen function in the catalytic activity [14,15].

On the basis of these considerations, we were interested in developing a class of hybrid *P,N*-ligands incorporating P–N bonds. We have a strong experience in the ligand design of monodentate *N*-phosphanylamidine of the general formula R''_2N–C(R′)=N–PR_2 (R′ = H, Ph). We have previously reported their reactivity towards Brönsted acids [16], phospheniums [17] and initiated their coordination chemistry with ruthenium metal fragment [18]. Complexes with *N*-phosphanylamidines as ligands have been reported in the literature before our studies [19,20] but as far as we know, this class of ligands has never been tested in catalysis. In this paper, we report the coordination behavior of monodentate *N*-phosphanylamidine

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ligands *i*-Pr_2N–C(Ph)=N–PR_2 (R = Ph, *i*-Pr) towards rhodium precursors and the synthesis of their corresponding bidentate pyridine-based ligands *i*-Pr_2N–C(pyr)=N–PR_2 (R = Ph, *i*-Pr). Both monodentate and bidentate ligands were applied to the catalytic hydroformylation reaction of 1-octene and styrene.

2. Results and discussion

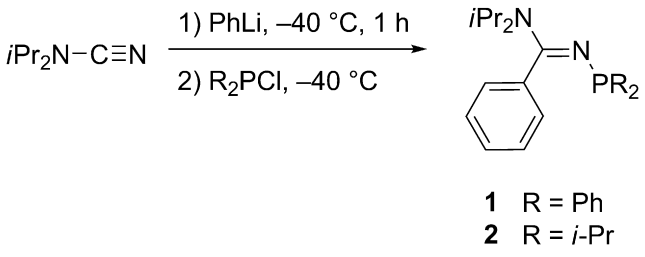
2.1. Synthesis of the N-phosphanylamidine ligands 1–4

As previously described [18], the monodentate *N*-phosphanylamidine ligands **1** and **2** were isolated in good yields (82% and 85%, respectively) by successive addition of phenyllithium and the corresponding chlorophosphane R_2PCl onto the *N*,*N*-diisopropylcyanamide (Scheme 1).

By introducing a pyridine fragment into the amidine organic framework, we prepared the bidentate *N*-phosphanylamidine ligand **3** by successive addition of the *N*,*N*-diisopropylcyanamide onto the lithiated pyridine, obtained by lithiation of 2-bromopyridine using butyllithium, and Ph_2PCl. The ^{31}P NMR analysis of the crude reaction mixture revealed the presence of the expected product at 43.4 ppm along with two side products at 112.5 and −14.6 ppm. In order to facilitate the purification of **3**, addition of the BH_3·THF adduct was performed and afforded the phosphorus borane-protected compound **5** in 20% yield after purification by column chromatography (Scheme 2, pathway A). Compound **6** resulting from the coordination of the BH_3 moiety onto the phosphorus and the nitrogen atom of the pyridyl group was also isolated in 7% yield (Scheme 2, pathway A). In order to improve the reaction yield, we investigated another way of synthesizing ligand **3** starting from 2-cyanopyridine. Successive addition of lithiumdiisopropylamide (LDA) freshly prepared and Ph_2PCl onto 2-cyanopyridine afforded the bidentate ligand **3** in good yield (82%). Following the same reaction sequence, ligand **4** was isolated in 60% yield (Scheme 2, pathway B). Compounds **3**–**6** were fully characterized by mass spectrometry and ^1H, ^{31}P and ^{13}C NMR spectroscopy. The ^1H NMR spectra of compounds **3**–**6** showed the characteristic proton chemical shifts of the isopropyl groups. In ^{31}P NMR, **3** and **4** exhibited signals at 43.4 and 69.4 ppm, respectively; the spectra of **5** and **6** showed the presence of a broad doublet at 45.9 (J_{PB} = 74.8 Hz) and 45.2 (J_{PB} = 85.4 Hz) ppm, respectively, characteristic of a phosphorus atom bearing a BH_3 moiety. In ^{13}C NMR spectra, the $^2J_{CP}$ imino carbon >C=N–P coupling constants [30.9 Hz (**3**), 29.0 Hz (**4**), 7.2 Hz (**5**) and 4.1 Hz (**6**)] confirmed the presence of the phosphanyl group attached to the amidine pattern. The low $^2J_{CP}$ imino carbon coupling constant values observed for **5** and **6** are consistent with a tetracoordinated σ^4-*P* phosphorus fragment [16–18].

2.2. Synthesis of the rhodium complexes 7 and 8

In order to get a better insight into the coordination mode of the *N*-phosphanylamidine ligands with the catalytic rhodium precursor [Rh(acac)$(CO)_2$], we reacted this latter with one or two equivalents of ligand **1** and **3**. Unfortunately, the reactions did not lead to a single compound but to a mixture of complexes as evidenced by the ^{31}P NMR spectra. After treatment of the different crude reaction mixtures, we could not obtain X-ray quality crystals which could have allowed us to state on the coordination mode of ligands **1** and **3** with [Rh(acac)$(CO)_2$]. Nevertheless, we ascertained the compatibility of ligands **1** and **2** with rhodium(I) by reacting two equivalents of **1** and **2** with the rhodium dimer [Rh(COD)Cl]$_2$ affording the corresponding complexes **7** and **8** in 79% and 83% yield, respectively, as outlined in Scheme 3. The ^{31}P NMR spectra exhibit a doublet at 58.3 ppm for compound **7** (J_{RhP} = 154.2 Hz) and at 74.0 ppm for compound **8** (J_{RhP} = 147.0 Hz) which clearly indicates the *P*-coordination of the *N*-phosphanylamidine ligands. In ^{13}C NMR, complexes **7** and **8** exhibit a resonance at 164.1 and 161.8 ppm, respectively, assigned to the carbon of the imino C=N moiety. For **7**, the low $^2J_{CP}$ coupling constant value ($^2J_{CP}$ = 8.6 Hz) is consistent with the *P*-coordination mode of the ligand. In complex **8**, the corresponding $^2J_{CP}$ coupling constant value was too low to be observed. As expected, proton NMR spectra show two sets of signals for the CH protons of the cyclooctadiene resulting from the two different *trans* substituents at the metallic center [21,22]: signals at 5.26 (**7**) and 5.70 (**8**) ppm are assigned to the *trans* P-CH protons and signals at 3.18 (**7**) and 3.62 (**8**) ppm to the *trans* Cl–CH protons which fall in the range of chemical shifts observed for these protons in [RhCl(COD)(PR_3)] type complexes [23].



Scheme 1. Synthesis of the *N*-phosphanylamidines **1** and **2**.

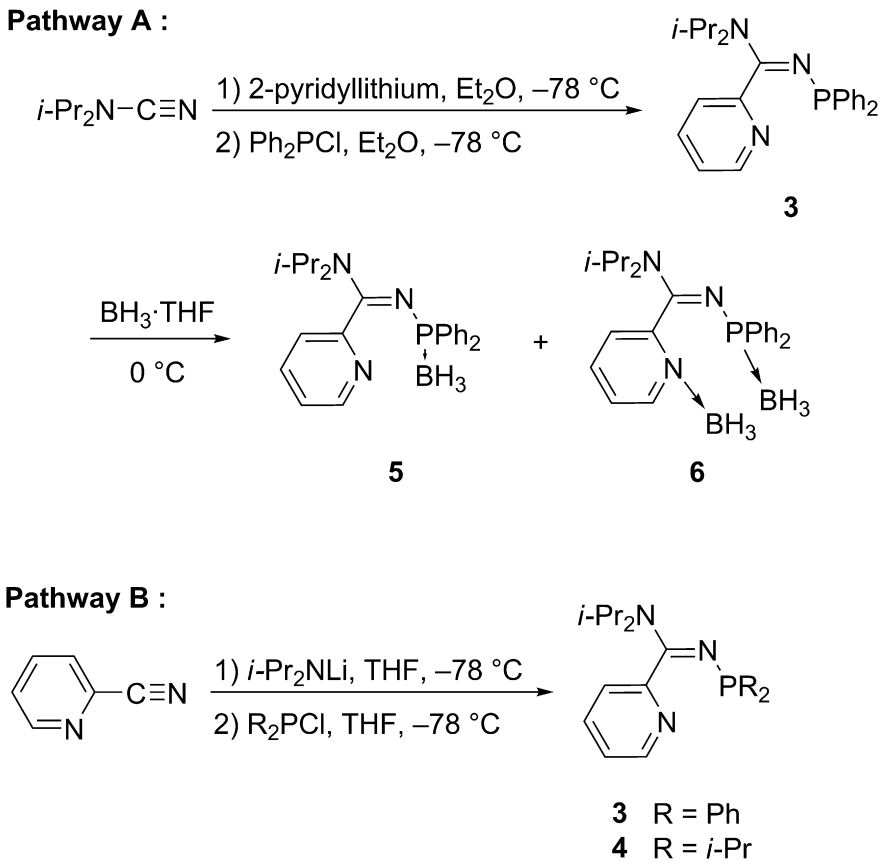
2.3. Single-crystal X-ray studies of compounds 3 and 5–8

X-ray quality crystals were obtained from a saturated solution of **3** in diethylether at −20 °C and by slow evaporation of a saturated Et_2O/pentane solution at room temperature of each compound **5** and **6**. Monocrystals of rhodium complexes **7** and **8** were grown by slow evaporation of a saturated diethylether solution of each complex at room temperature. Selected geometric data for all structures are reported in Table 1.

The structures of **3**, **5** and **6** revealed an *E*-stereoisomer which is consistent with the other three structurally characterized *N*-phosphanylamidines *i*-Pr_2N–C(Ph)=N–PR_2 (R = Ph, *i*-Pr) [18], $(Me_3Si)_2N$–C(Ph)=N–PPh_2 [24] and *i*-Pr_2N–C(H)=N–PPh_2 [16]. As expected, the amino nitrogen atom *i*-Pr_2N– is planar and the phosphorus atom exhibits a pyramidal geometry in all compounds (Figs. 1–3). The difference of 0.06 Å between the C1–N1 and C1–N2 bond lengths in the ligand **3** is more significant than in compounds **5** (0.035 Å) and **6** (0.045 Å), which may be due to a stronger localisation of the >C1=N1– double bond in **3**. The coordination of the BH_3 moiety is *trans* to the electronic lone pair of the imino nitrogen atom in both *N*-phosphanylamidines **5** and **6**. Moreover the P1–B1 bond lengths, 1.908(2) Å in (**5**) and 1.922(2) Å in (**6**), and the N3–B2 bond length of 1.596(3) Å in compound **6**, are in the range of those reported in literature for aminophosphine borane [25–28] and pyridine-borane [29] complexes, respectively.

The molecular structures of complexes **7** and **8** depicted in Figs. 4 and 5 assessed the *P*-coordination of ligands **1** and **2** and confirm the conclusions deduced from the spectroscopic data recorded in solution.

The metallic center displays a slightly distorted square-planar geometry with the four coordination positions being defined by the chloride ligand, the phosphorus atom of the κ^1-*PN*-phosphanylamidine ligand and the centroids of the two cyclooctadiene (COD) olefin bonds. The COD ligand adopts a "tub" conformation with both C–C double bonds being approximately normal to the coordination plane. In complexes **7** and **8**, the P-*trans* Rh–CH(COD) distances are ca 0.1 Å longer than the Cl-*trans* Rh–CH(COD) distances due to a strong *trans* influence of the phosphane ligand. As it was already observed for *N*-phosphanylamidine ligands **1** and **2** upon *P*-coordination to ruthenium metal fragment [18], in

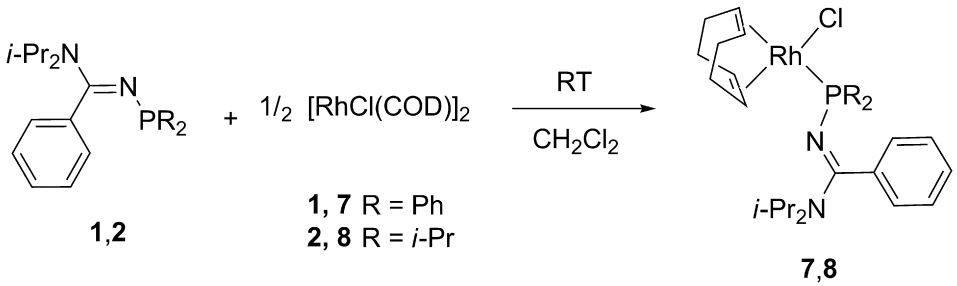


Scheme 2. Synthesis of the *N*-phosphanylamidines **3** and **4**.

complexes **7** and **8**, the N2–C1–N1 bond angle value does not change to any great extent compared to the corresponding free ligands and a shortening of the N1–P1 bond length is observed. The C1–N1–P1 bond angle value of 143.1(3) Å in **8** is the largest recorded to date for *N*-phosphanylamidine ligands. This dramatic opening of the C1–N1–P1 bond angle reflects the ability of these ligands to adapt their geometry to minimize the steric constraints. In marked contrast to what was expected, the C1–N1–P1 bond angle of ligand **1** remains almost unchanged in complex **7** with a value of 123.9(3) Å. The *N*-phosphanylamidine ligand **1** in the κ^1-*P* rhodium complex **7** adopts a π–π stacking arrangement between the phenyl ring linked to the carbon atom of the methylene >C(Ph)═N– fragment and one of the two phenyl substituents on the phosphorus atom defined by the C8–C13 and C14–C19 carbon atoms, respectively. This interaction is characterized by a centroid–centroid distance of 3.849 Å and an offset angle α of 32°. This intramolecular π–π interaction in complex **7** induces some rigidity into the structure of ligand **1** which results in a higher steric constraint around the metal fragment compared to ligand **2**. It is then not surprising to observe that the distortion from the square planar geometry is more pronounced in complex **7** than in complex **8**. This is reflected by the position of the centers of the C–C double bonds of COD which are displaced by 0.118 and 0.408 Å with respect to the plane defined by the P1, Rh1 and Cl1 atoms.

*2.4. Catalytic activity of {[Rh(acac)(CO)$_2$/**1**–**4**} systems in hydroformylation reactions*

It is known [3a,30] that the [Rh(H)(CO)$_2$L$_2$] catalyst precursor, which usually provides the active species by dissociation of a CO ligand [31], is instantaneously and selectively produced by addition of the L phosphine ligand to [Rh(acac)(CO)$_2$] under typical hydroformylation conditions. Thus, *N*-phosphanylamidine ligands **1**–**4** have been introduced in the coordination sphere of [Rh(acac)(CO)$_2$]



Scheme 3. Synthesis of the *N*-phosphanylamidines rhodium complexes **7** and **8**.

Table 1
Selected bond lengths (Å) and angles (°) for compounds **3**, **5**, **6**–**8**.

	3	5	6	7	8
C1–N1	1.301(2)	1.309(2)	1.297(2)	1.301(5)	1.284(4)
C1–N2	1.360(2)	1.343(2)	1.341(2)	1.357(5)	1.369(5)
N1–P1	1.7098(16)	1.6427(15)	1.6681(14)	1.674(3)	1.653(3)
B1–P1	/	1.908(2)	1.922(2)	/	/
Rh1–P1	/	/	/	2.3030(10)	2.3077(9)
Rh1–Cl1	/	/	/	2.3777(10)	2.3676(9)
N2–C1–N1	121.59(16)	120.93(16)	121.07(14)	120.1(4)	119.8(3)
C1–N1–P1	118.98(13)	130.51(13)	128.32(12)	123.9(3)	143.1(3)
N1–P1–B1	/	113.63(10)	124.11(8)	/	/

in order to evaluate their catalytic activity in the hydroformylation reaction of 1-octene (Scheme 4) and styrene (Scheme 5). The hydroformylation reactions were carried out at 60 °C and 30 bar of syngas CO/H_2 (1:1) using a stock solution of the rhodium pre-catalyst (1.0 mM in toluene) prepared in situ from $[Rh(acac)(CO)_2]$ and the corresponding ligands **1**–**4**. The production of all derivatives generated during the reaction (products and side products) was monitored by gas chromatography.

2.4.1. Hydroformylation of 1-octene

The hydroformylation results with the *N*-phosphanylamidine ligands **1**–**4** are displayed in Table 2.

In a first approach, the catalytic experiments were conducted under mild conditions of temperature (60 °C) and pressure (30 bar) with a molar ratio ligand/Rh of 5:1 and a molar ratio 1-octene/Rh of 510:1. Conversions and selectivities were determined after 6 h of reaction by GC. High conversions near to 99% were reached, either for **1** and **3** which compare quite well with that obtained with PPh_3 (entries 1, 3 and 7). The reaction rate is somewhat lower with ligand **2** since in 6 h the conversion is 84% (entry 6). Increasing the substrate to catalyst ratio from 510 to 832 does not significantly affect the conversion (entries 4, 5, 7, 9 and 10). However, this conversion is dramatically reduced to 49% (entry 12) when this ratio is increased to 1020. A comparison of results of entries 3, 6, 7 and 13 performed with the four ligands **1**–**4** reveal that ligand **3** displays a better chemoselectivity towards aldehydes (>99%) and a better regioselectivity for the linear aldehyde with a linear to branched ratio of 2.22 (entry 7). Under the same catalytic conditions, ligands **1** (entry 3) and **4** (entry 13) induce a significant isomerization reaction, respectively, 15% and 9% of formation of internal octenes, than ligands **2**, **3** and PPh_3 (entries 1, 6 and 7) which suggests a higher β-H elimination reaction rate. This isomerization process increases also in varying the catalytic conditions (entries 7–12), especially when the ligand to rhodium ratio is only equal to 1 (entry 11), when the temperature is reduced to 45 °C (entry 8), or when the substrate to rhodium ratio reaches the 1020 value (entry 12). We can note that high conversion rates can be reached with however lower *l*/br ratios than for PPh_3.

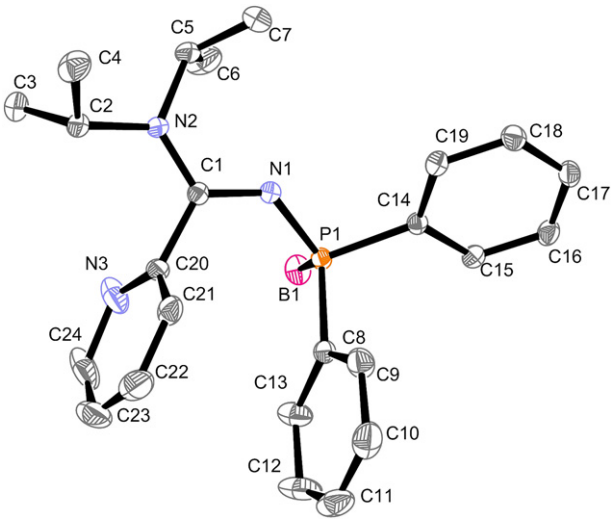


Fig. 2. Molecular structure of *N*-phosphanylamidine **5**. Hydrogen atoms have been omitted for clarity.

2.4.2. Hydroformylation of styrene

Similarly, we compared the activities and selectivities of the *N*-phosphanylamidine ligands **1** and **3**. The hydroformylation results are displayed in Table 3. The corresponding complexes formed in situ are good precursors to catalyze the hydroformylation of styrene, under the same experimental conditions of 30 bar of CO/H_2 syngas (CO/H_2:1/1) at 60 °C. We choose to keep a ligand to rhodium ratio of 3.3 and a substrate to rhodium ratio of 832. After 6 h, conversions up to 85–94% are reached (entries 3, 4), **1** and **3**

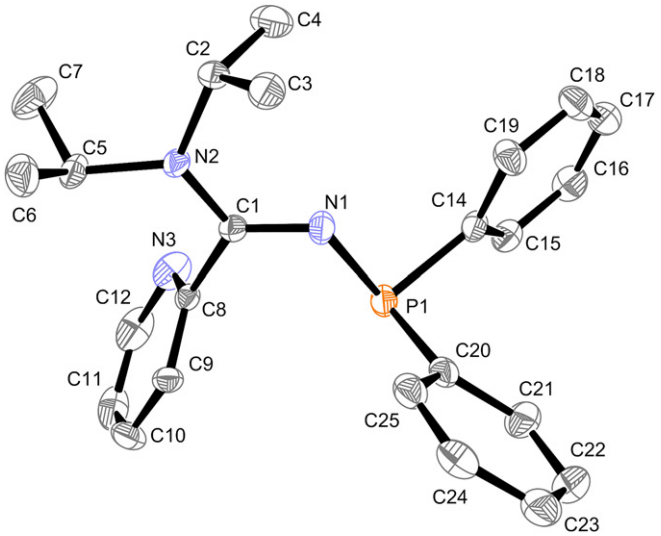


Fig. 1. Molecular structure of *N*-phosphanylamidine **3**. Hydrogen atoms have been omitted for clarity.

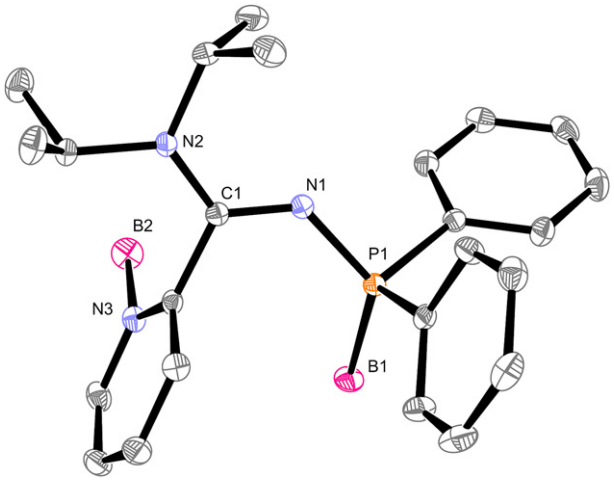


Fig. 3. Molecular structure of *N*-phosphanylamidine **6**. Hydrogen atoms have been omitted for clarity.

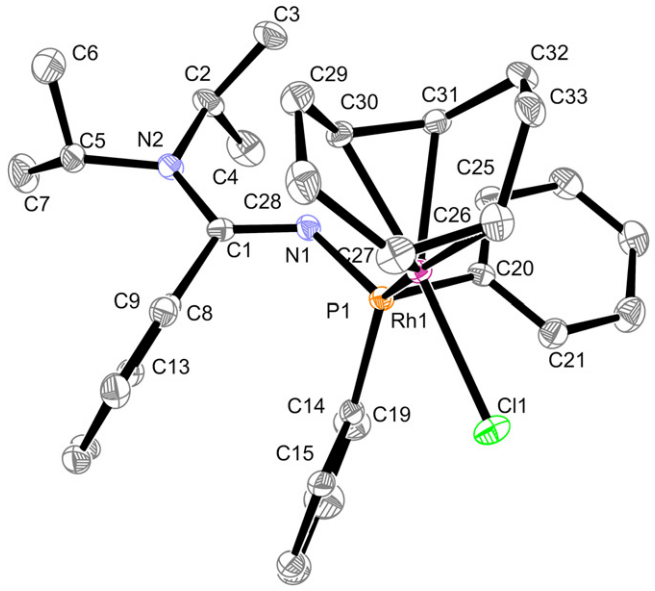


Fig. 4. Molecular structure of η^1-*P N*-phosphanylamidine rhodium complex **7**. Hydrogen atoms have been omitted for clarity.

comparing well to PPh_3 ligand. Satisfactory turnovers (TON) are gained to around 750. No loss of chemioselectivity was observed when using ligands **1** and **3** in place of Ph_3P (no ethylbenzene as styrene hydrogenation product was detected by GC analysis). Moreover, regarding the regioselectivity, a comparison of the *b*/*l* ratio obtained with the ligands **1** and **3** (*b*/*l* = 15.7) with the one obtained with Ph_3P (entry 2) (*b*/*l* = 5.7) evidences the beneficial effect of the amidine moiety in the hydroformylation reaction of styrene. At this stage of the study, it is difficult to attribute this encouraging result to the electronic and/or steric properties of the *N*-phosphanylamidine ligands.

3. Conclusions

The new bidentate pyridine-based *N*-phosphanylamidine ligands *i*-Pr_2N–C(pyr)=N–PR_2 **3** (R = Ph) and **4** (R = *i*-Pr) were synthesized and fully characterized. The coordination chemistry of the monodentate ligands **1** and **2** with rhodium was studied. The X-ray diffraction analyses of the resulting complexes [RhCl(COD)(**1**)] **7** and [RhCl(COD)(**2**)] **8** revealed that the monodentate *N*-phosphanylamidine ligands **1** and **2** are able to adapt to a large extent their molecular structure with a significant amplitude of 20° for the C1–N1–P1 bond angle value depending on the steric hindrance around the metal center or the formation of an intramolecular π–π interaction in the amidine organic function. To conclude on this preliminary approach in hydroformylation of 1-octene and styrene, the reactivity induced by the present new ligands **1**–**4** is consistent with the coordination of two phosphorus atoms on the rhodium metal center, since we did not detect sufficient differences to state the bidentate coordination of pyridine-based *N*-phosphanylamidine ligands **3** and **4**. The better regioselectivity observed in the hydroformylation reaction of styrene with ligands **1** and **3** prompt us to study further the influence of the electronic and steric properties of the *N*-amidine moiety on the catalytic activity and regioselectivity of carbonylation reactions. Moreover, the synthesis of this class of *N*-phosphanylamidine ligands enables a large variation of the alkyl/aryl groups on the phosphorus atom which is essential for further catalytic investigations. Particularly, we are currently exploring the introduction of a chiral backbone on the phosphorus atom for applications in asymmetric hydroformylation reactions.

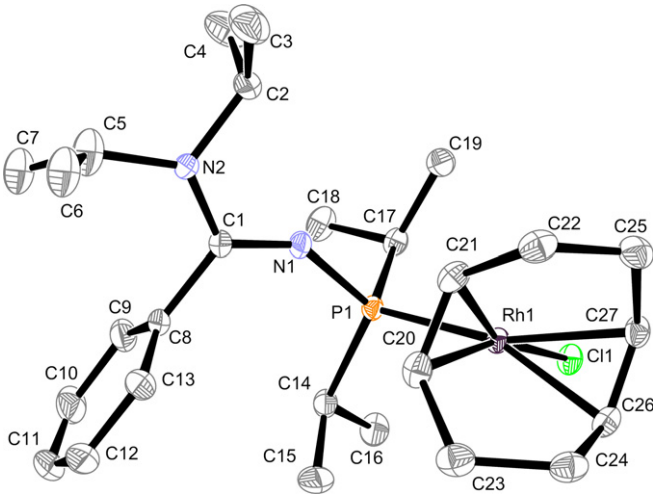


Fig. 5. Molecular structure of η^1-*P N*-phosphanylamidine rhodium complex **8**. Hydrogen atoms have been omitted for clarity.

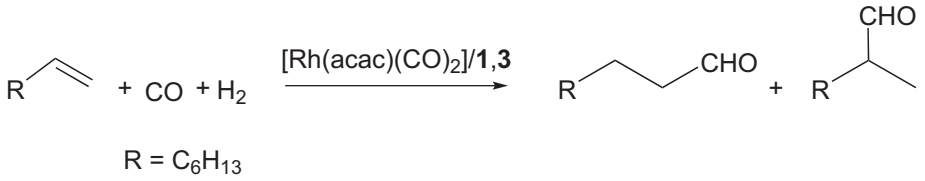
4. Experimental

4.1. General

All reactions were conducted under an inert atmosphere of dry argon using standard Schlenk-line techniques. Solvents were dried and degassed by standard methods before use. NMR spectra were recorded on a Bruker AV 500, AV 300, DPX 300 or AC200 spectrometer. Chemicals shifts for ^1H and ^{13}C are referenced to residual solvent resonances used as an internal standard and reported relative to $SiMe_4$. ^{31}P NMR chemical shifts are reported relative to external aqueous 85% H_3PO_4. Mass spectra were recorded on a TSQ 7000 Thermo Electron mass spectrometer. Melting points were obtained using an Electrothermal Digital Melting Point apparatus and are uncorrected. The synthesis of ligands **1** and **2** has previously been described [18]. GC chromatograms were recorded on a Perkin–Elmer Clarus 500 apparatus equipped with a flame ionization detector and a 30 m DB-5GC capillary column (0.25 mm i.d., 0,25 μm film thickness).

4.2. Preparation of *N*-phosphanylamidines *3* and *4*

Six millilitres of *n*-BuLi (1.6 mol L^{-1}, 9.60 mmol) were added to a solution of *N*,*N*-diisopropylamine (1.35 mL, 9.6 mmol) in 8 mL of THF at 0 °C. The solution was stirred for 10 min and then cooled down to −78 °C. A solution of 2-cyanopyridine (1.0 g, 9.60 mmol) in 6 mL of THF was added dropwise and the mixture was stirred for 1 h before the addition of the corresponding chlorophosphane R_2PCl (9.6 mmol). After 1 h stirring at room temperature the solution was concentrated down to 5 mL before the addition of 10 mL of degassed Et_2O, LiCl was removed by filtration. The solvent was removed and the reaction product was extracted with Et_2O (3 × 10 mL) to give **3** in 82% (3.06 g, 7.87 mmol) yield and **4** in 60% yield (1.85 g, 5.76 mmol). Compound **3**: $^{31}P\{^1H\}$ NMR (121.5 MHz, C_6D_6): [δ/ppm] 43.4 (s). ^1H NMR (300.1 MHz, C_6D_6): [δ/ppm] 8.48–8.45 (m, 1H, Ar), 7.95–7.90 (m, 4H, Ar), 7.32–7.27 (m, 5H, Ar), 7.19–7.05 (m, 2H, Ar), 6.96–6.94 (m, 1H, Ar), 6.67–6.64 (m, 1H, Ar), 3.52 (h, $^3J_{HH}$ = 6.7 Hz, 2H, NC*H*(CH_3)$_2$), 1.41 (br s, 12H, NCH(CH_3)$_2$). $^{13}C\{^1H\}$ NMR (62.9 MHz, $CDCl_3$): [δ/ppm] 164.6 (d, $^2J_{CP}$ = 30.9 Hz, C=N), 156.1 (d, J_{CP} = 7.0 Hz, Ar), 149.5 (s, Ar), 145.2 (d, J_{CP} = 12.0 Hz, Ar), 136.0 (s, Ar), 131.2 (d, J_{CP} = 19.7 Hz, Ar), 127.7 (d, J_{CP} = 7.9 Hz, Ar), 122.9 (s, Ar), 122.0 (d, J_{CP} = 5.7 Hz, Ar), 48.8 (br s, NCH(CH_3)$_2$), 20.8 (s, NCH(CH_3)$_2$). DCI



Scheme 4. The hydroformylation of 1-octene.

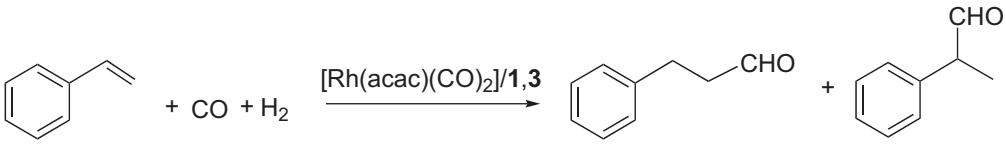
[NH_3] MS *m/z*: 390 $[M+H]^+$. Compound **4**: $^{31}P\{^1H\}$ NMR (121.5 MHz, C_6D_6): [δ/ppm] 69.4 (s). ^1H NMR (300.1 MHz, C_6D_6): [δ/ppm] 8.58 (br d, $J_{HH}=4.8$ Hz, 1H, Ar), 7.21 (ddd, $J_{HH}=7.8$ Hz, $J_{HH}=7.8$ Hz, $J_{HH}=1.8$ Hz, 1H, Ar), 7.01 (br d, $J_{HH}=7.8$ Hz, 1H, Ar), 6.70 (ddd, $J_{HH}=7.5$ Hz, $J_{HH}=4.8$ Hz, $J_{HH}=0.9$ Hz, 1H, Ar), 3.49 (h, $^3J_{HH}=6.9$ Hz, 2H, NC*H*$(CH_3)_2$), 1.94 (h, $^3J_{HH}=6.9$ Hz, 2H, PC*H*$(CH_3)_2$), 1.40 (dd, $^3J_{HH}=6.9$ Hz, $^3J_{HP}=10.0$ Hz, 6H, PCH(C*H*$_3)_2$), 1.22 (dd, $^3J_{HH}=7.2$ Hz, $^3J_{HP}=14.5$ Hz, 6H, PCH(C*H*$_3)_2$), 1.43–1.21 (m, 12H, NCH(C*H*$_3)_2$). RMN $^{13}C\{^1H\}$ (75.5 MHz, C_6D_6): [δ/ppm] 165.6 (d, $^2J_{CP}=29.0$ Hz, C=N), 157.1 (d, $J_{CP}=6.6$ Hz, Ar), 149.1 (d, $J_{CP}=0.6$ Hz, Ar), 135.0 (d, $J_{CP}=1.4$ Hz, Ar), 122.6 (d, $J_{CP}=5.7$ Hz, Ar), 121.9 (s, Ar), 48.0 (br s, NCH$(CH_3)_2$), 27.4 (d, $^1J_{CP}=12.7$ Hz, PCH$(CH_3)_2$), 20.6 (s, NCH(C*H*$_3)_2$), 18.9 (d, $^2J_{CP}=19.5$ Hz, PCH(C*H*$_3)_2$), 18.2 (d, $^2J_{CP}=8.9$ Hz, PCH(C*H*$_3)_2$). DCI[NH_3] MS *m/z*: 322 $[M+H]^+$.

4.3. Preparation of N-phosphanylamidines **5** and **6**

The 8.30 mL of *n*-BuLi (1.6 mol L^{-1}, 13.30 mmol) were added slowly at −78 °C to a solution of 2-bromopyridine (2.10 g, 13.30 mmol) in 20 mL of Et_2O. The mixture was stirred for 1 h and a solution of *i*Pr_2CN (2.02 mL, 13.30 mmol) in 8 mL of Et_2O was added. After 1 h at −40 °C, Ph_2PCl (2.40 mL, 13.30 mmol) was added. The reaction mixture was stirred for 1 h at −40 °C and then allowed to reach 0 °C before the addition of $BH_3\cdot THF$ (1.0 mol L^{-1}, 13.30 mL, 13.30 mmol). The reaction mixture was stirred overnight at room temperature. LiCl formed during the reaction was removed by filtration and the crude product was then purified by column chromatography (eluent Et_2O/pentane: 20/80). Compound **5** was obtained in 20% yield as a white powder. The side product **6** was isolated in 7% yield. Compound **5**: $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$): [δ/ppm] 45.9 (br d, $^1J_{PB}=74.8$ Hz). ^1H NMR (200.1 MHz, $CDCl_3$): [δ/ppm] 8.21 (d, $J_{HH}=5.1$ Hz, 1H, Ar), 7.81–7.04 (m, 13H, Ar), 3.75 (m, 1H, NC*H*$(CH_3)_2$), 3.43 (m, 1H, NC*H*$(CH_3)_2$), 1.73 (d, $^3J_{HH}=6.6$ Hz, 6H, NCH(C*H*$_3)_2$), 1.13 (br s, 6H, NCH(C*H*$_3)_2$). $^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$): [δ/ppm] 163.6 (d, $^2J_{CP}=7.2$ Hz, C=N), 153.3 (d, $J_{CP}=7.6$ Hz, Ar), 149.2 (s, Ar), 136.2 (s, Ar), 131.8 (br s, Ar), 129.7 (s, Ar), 127.8 (d, $J_{CP}=10.1$ Hz, Ar), 123.5 (s, Ar), 122.6 (s, Ar), 51.6 (s, NCH$(CH_3)_2$), 47.0 (s, NCH$(CH_3)_2$), 20.4 (s, NCH(C*H*$_3)_2$). DCI[NH_3] MS *m/z*: 404 $[M+H]^+$. Mp: 154–156 °C (dec.). Compound **6**: $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$): [δ/ppm] 45.2 (br d, $^1J_{PB}=85.4$ Hz). ^1H NMR (300.1 MHz, $CDCl_3$): [δ/ppm] 8.18 (d, $J_{HH}=5.8$ Hz, 1H, Ar), 7.84–7.78 (m, 3H, Ar), 7.57–7.52 (m, 2H, Ar), 7.44–7.39 (m, 4H, Ar), 7.21–7.15 (m, 4H, Ar), 3.78 (h, $^3J_{HH}=6.8$ Hz, 1H, NC*H*$(CH_3)_2$), 3.22 (h, $^3J_{HH}=6.5$ Hz, 1H, NC*H*$(CH_3)_2$), 2.4 (br s, 3H, BH_3), 1.75 (d, $^3J_{HH}=6.8$ Hz, 3H, NCH(C*H*$_3)_2$), 1.68 (d, $^3J_{HH}=6.8$ Hz, 3H, NCH(C*H*$_3)_2$), 1.41 (d, $^3J_{HH}=6.5$ Hz, 3H, NCH(C*H*$_3)_2$), 1.02 (d, $^3J_{HH}=6.5$ Hz, 3H, NCH(C*H*$_3)_2$), 0.50 (br s, 3H, BH_3). $^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$): [δ/ppm] 156.9 (d, $^2J_{CP}=4.1$ Hz, C=N), 150.3 (d, $J_{CP}=7.5$ Hz, Ar), 148.5 (s, Ar), 139.5 (s, Ar), 135.9 (d, $J_{CP}=78.9$ Hz, Ar), 133.6 (d, $J_{CP}=52.1$ Hz, Ar), 132.6 (d, $J_{CP}=10.5$ Hz, Ar), 131.4 (d, $J_{CP}=10.6$ Hz, Ar), 130.1 (d, $J_{CP}=2.4$ Hz, Ar), 129.9 (d, $J_{CP}=2.3$ Hz, Ar), 128.1 (d, $J_{CP}=10.8$ Hz, Ar), 127.7 (d, $J_{CP}=9.7$ Hz, Ar), 125.3 (s, Ar), 124.9 (s, Ar), 123.5 (s, Ar), 122.7 (s, Ar), 52.1 (d, $^4J_{CP}=1.0$ Hz, NCH$(CH_3)_2$), 47.4 (s, NCH$(CH_3)_2$), 20.7 (s, NCH(C*H*$_3)_2$), 20.6 (s, NCH(C*H*$_3)_2$), 20.5 (s, NCH(C*H*$_3)_2$), 20.0 (s, NCH(C*H*$_3)_2$). DCI [NH_3] MS *m/z*: 418 $[M+H]^+$. Mp: 160–164 °C (dec.).

4.4. Preparation of N-phosphino amidines rhodium complexes **7** and **8**

To a solution of $[Rh(COD)Cl]_2$ (0.10 g, 0.20 mmol) in CH_2Cl_2 (4 mL) was added a solution of 0.40 mmol of ligand (**1**, 155 mg; **2**, 128 mg) in CH_2Cl_2 (4 mL). The reaction mixture was stirred at room temperature for 2 h. The solvent was removed and the resulting yellow powder was washed with *n*-pentane (3 × 3 mL) to give **7** in 79% (200 mg, 0.32 mmol) yield and **8** in 83% yield (188 mg, 0.33 mmol). Compound **7**: $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$): [δ/ppm] 58.3 (d, $^1J_{PRh}=154.2$ Hz). ^1H NMR (200.1 MHz, $CDCl_3$): [δ/ppm] 7.64–7.53 (m, 5H, Ar), 7.34–7.14 (m, 10H, Ar), 5.26 (br s, 2H, olefinic H_{COD}), 3.69 (m, 1H, NC*H*$(CH_3)_2$), 3.40 (h, $^3J_{HH}=6.7$ Hz, 1H, NC*H*$(CH_3)_2$), 3.18 (br s, 2H, olefinic H_{COD}), 2.35–2.06 (m, 4H, aliphatic H_{COD}), 1.94–1.76 (m, 4H, aliphatic H_{COD}), 1.61 (d, $^3J_{HH}=6.9$ Hz, 6H, NCH(C*H*$_3)_2$), 0.99 (d, $^3J_{HH}=6.7$ Hz, 6H, NCH(C*H*$_3)_2$). $^{13}C\{^1H\}$ NMR (50.3 MHz, $CDCl_3$): [δ/ppm] 164.1 (d, $^2J_{CP}=8.6$ Hz, C=N), 138.5 (d, $J=46.0$ Hz, Ar), 132.9 (d, $J=11.9$ Hz, Ar), 128.5 (d, $J=2.0$ Hz, Ar), 128.4 (s, Ar), 127.2 (d, $J=10.0$ Hz, Ar), 126.8 (s, Ar), 103.9 (dd, $^1J_{CRh}=6.2$ Hz, $^2J_{CP}=12.9$ Hz, CH_{COD}), 69.4 (d, $^1J_{CRh}=14.5$ Hz, CH_{COD}), 51.3 (s, NCH$(CH_3)_2$), 46.6 (s, NCH$(CH_3)_2$), 32.7 (s, CH_{2COD}), 28.4 (s, CH_{2COD}), 20.6 (s, NCH(C*H*$_3)_2$), 20.1 (s, NCH(C*H*$_3)_2$). DCI[CH_4] MS *m/z*: 635 $[M+H]^+$, 634 $[M]^+$. Compound **8**: $^{31}P\{^1H\}$ NMR (121.5 MHz, C_6D_6): [δ/ppm] 74.0 (d, $^1J_{PRh}=147.0$ Hz). ^1H NMR (300.1 MHz, C_6D_6): [δ/ppm] 7.62–7.60 (m, 2H, Ar), 7.29–7.18 (m, 3H, Ar), 5.70 (br s, 2H, olefinic H_{COD}), 3.62 (br s and m, 3H, olefinic H_{COD} and NC*H*$(CH_3)_2$), 3.38–3.36 (m, 1H, NC*H*$(CH_3)_2$), 2.42 (hd, $^3J_{HH}=7.2$ Hz, $^2J_{PH}=7.2$ Hz, 2H, PC*H*$(CH_3)_2$), 2.31–2.24 (m, 4H, aliphatic H_{COD}), 1.88–1.82 (m, 4H, aliphatic H_{COD}), 1.66–1.56 (m, 6H, NCH(C*H*$_3)_2$), 1.52 (dd, $^3J_{HH}=7.2$ Hz, $^3J_{PH}=12.9$ Hz, 6H, PCH(C*H*$_3)_2$), 1.36 (dd, $^3J_{HH}=7.2$ Hz, $^3J_{PH}=14.7$ Hz, 6H, PCH(C*H*$_3)_2$), 0.79–0.77 (m, 6H, NCH(C*H*$_3)_2$). $^{13}C\{^1H\}$ NMR (75.5 MHz, C_6D_6): [δ/ppm] 161.8 (s, C=N), 139.6 (d, $J_{CP}=6.7$ Hz, Ar), 128.4 (s, Ar), 128.1 (s, Ar), 127.8 (s, Ar), 101.4 (dd, $^1J_{CRh}=6.8$ Hz, $^2J_{CP}=12.8$ Hz, CH_{COD}), 66.1 (d, $^1J_{CRh}=14.2$ Hz, CH_{COD}), 50.4 (br s, NCH$(CH_3)_2$), 46.3 (s, NCH$(CH_3)_2$), 33.3 (d, $^3J_{CP}=2.6$ Hz, CH_{2COD}), 29.7 (d, $^1J_{CP}=25.2$ Hz, PCH



Scheme 5. The hydroformylation of styrene.

Table 2
Rh-catalyzed hydroformylation of 1-octene.

Entry	Ligand	Ligand/Rh ratio	Substrate/Rh ratio	Conversion [%]	l/br ratio	Isomerization [%]	Selectivity [%]	TON[a]
1	PPh_3	5	510	>99	3.00	<1	>99	505
2	PPh_3	3.3	510	>99	2.12	<1	>99	505
3	**1**	5	510	99	1.67	15	85	429
4	**1**	3.3	510	96	1.83	14	82	401
5	**1**	3.3	832	99	1.67	12	88	725
6	**2**	5	510	84	1.32	1	99	424
7	**3**	5	510	>99	2.22	<1	>99	505
8	**3**	5	510	20[b]	2.12	15	85	88
9	**3**	5	832	99	2.22	12	88	725
10	**3**	3.3	832	99	2.13	27	73	601
11	**3**	1	510	83	2.03	39	61	258
12	**3**	5	1020	49	2.12	23	51	255
13	**4**	5	510	98	1.70	9	91	455

[a] Defined as mol of aldehydes (l + br)/mol of Rh.
[b] 45 °C.

$(CH_3)_2$), 28.3 (d, $^3J_{CP} = 1.3$ Hz, CH_{2COD}), 20.5 (br s, NCH(CH_3)$_2$), 20.1 (s, NCH(CH_3)$_2$), 19.6 (d, $^2J_{CP} = 2.9$ Hz, PCH(CH_3)$_2$). DCI[CH_4] MS *m/z*: 567 $[M + H]^+$, 566 $[M]^+$. Mp: 129–131 °C.

4.5. Structure determination and refinement for compounds 3, 5–8

Data of the structures **5**, **6**, and **7** were collected at low temperature (180 K) on an Xcalibur Oxford Diffraction diffractometer using a graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å) and equipped with an Oxford Instrument Cooler Device. Data of the structures **3** and **8** were collected at low temperature (180 k) on an IPDS STOE diffractometer using a graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å) and equipped with an Oxford Cryosystems Cryostream Cooler Device. The final unit cell parameters have been obtained by means of a least-squares refinement. The structures have been solved by Direct Methods using SIR92 [32], and refined by means of least-squares procedures on a F^2 with the aid of the program SHELXL97 [33] included in the software package WinGX version 1.63 [34]. The Atomic Scattering Factors were taken from International Tables for X-Ray Crystallography [35]. All hydrogen atoms were geometrically placed and refined by using a riding model. All non-hydrogen atoms were anisotropically refined, and in the last cycles of refinement a weighting scheme was used, where weights are calculated from the following formula: $w = 1/[\sigma^2(Fo^2) + (aP)^2 + bP]$ where $P = (Fo^2 + 2Fc^2)/3$. Drawing of molecule is performed with the program ORTEP32 [36] with 30% probability displacement ellipsoids for non-hydrogen atoms.

4.6. General procedure for the catalytic hydroformylation reactions

The catalyst precursor [Rh(acac)$(CO)_2$] and the ligand were dissolved in 15 mL of toluene under argon. The substrate and the internal standard (decane) were added to the solution. The reaction mixture was transferred into the evacuated autoclave by aspiration. It was pressurized to an initial 10 bar pressure of syngas ($CO:H_2 = 1:1$) and heated at the required temperature. Then, the autoclave was pressurized at 30 bar, and the reaction mixture was stirred at 1200 rpm for the desired time. The autoclave was then cooled and slowly depressurized. A sample was analysed by GC.

Table 3
Rh-catalyzed hydroformylation of styrene.

Entry	Ligand[a, b]	Time (h)	Conv. (%)	br/*l* ratio	TON[c]
1	PPh_3	3	95[d]	4.0	790
2	PPh_3	6	94	5.7	782
3	**1**	6	94	15.7	782
4	**3**	6	85	15.7	707

[a] Ligand/Rh ratio = 3.3.
[b] Substrate/Rh ratio = 832.
[c] defined as mol of aldehydes (l + br)/mol of Rh.
[d] 80 °C.

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Appendix A. Supplementary data

CCDC-786352–786356 contains the supplementary crystallographic data for compounds **3**, **5**–**8**. These data can be obtained free of charge from the Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif.

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