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Synthesis of neutral rhodium(I) complexes containing a rigid P–O ligand and their use as catalyst precursors for the hydroformylation of 1-hexene

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ABSTRACT

The first rhodium complexes with the anionic 2-(bis(2-methoxyphenyl)phosphino)benzenesulfonate (**L**) ligand have been synthesized and characterized. Selected complexes have been used as catalyst precursors for the homogeneous hydroformylation of 1-hexene, which has been carried out in preparative autoclaves and studied under *operando* conditions by means of both high-pressure NMR (HPNMR) and high-pressure IR (HPIR) spectroscopy. *Operando* spectroscopic hydroformylation experiments have shown that the catalyst precursors bearing either 1,5-cyclooctadiene or triethylamine as ancillary ligand are rapidly converted into di-carbonyl complexes. Rhodium(I) mono-and di-carbonyl complexes have been shown to be resting states of the catalytic cycle, most likely in equilibrium with other species containing either the zwitterionic ligand **HL** coordinated in the κ^1-*O* bonding mode or exclusively carbonyl ligands.

1. Introduction

The study of transition metal complexes supported by mixed-donor chelate ligands is still an active and fruitful area of chemical research, especially as regards homogeneous catalysis [1]. Of particular interest are dissymmetric chelate ligands bearing different donor atoms, as they have the potential of regioselectively creating a free coordination site at the metal centre, thus affecting substrate recognition and activation as well as reaction rates [1,2].

A class of mixed-donor ligands that is attracting increasing attention in catalytic polymerization reactions in conjunction with late transition metals is constituted by anionic P–O ligands [3]. Nickel P–O catalysts are effective for the polymerization and oligomerization of α-olefins [3a,4], while some palladium systems are active for the non-alternating CO-ethylene copolymerization [3d,j,k] as well as the copolymerization of ethylene with functionalized olefins (Scheme 1a and b) [3e–i]. Accomplishing these reactions requires the coordination of Pd^{II} ions by anionic P–O ligands generated by the deprotonation of 2-(bis(2-methoxyphenyl)phosphino)benzenesulfonic acid (**HL**) and its derivatives (Scheme 1c). Other C–C bond forming processes that are successfully catalyzed by Pd**L**$^+$ fragments are the Suzuki and Heck reactions [3k,l].

In this paper, we report the synthesis and characterization of the first rhodium complexes with the anionic **L** ligand, which include [Rh(κ^2-*O*,*P*-**L**)(η^4-COD)] (COD = 1,5-cyclooctadiene) (**1**) [Rh(κ^2-*O*,*P*-**L**)(CO)$_2$] (**2**) and [Rh(κ^2-*O*,*P*-**L**)(CO)(Y)] (Y = PPh_3 (**3**) $PAr_2(OMe)$ (Ar = 2-methoxyphenyl) (**4**) 1-phospha-3,5,7-triazaadamantane (PTA, **5**) $PHAr_2$ (Ar = 2-methoxyphenyl) (**6**) NEt_3 (**7**) Py (**8**) (Scheme 2).

Some of these complexes have been used as catalyst precursors for the homogeneous hydroformylation of 1-hexene, which has been carried out in preparative autoclaves and studied under *operando* conditions by means of both high-pressure NMR (HPNMR) and high-pressure IR (HPIR) spectroscopy. The results of the batch reactions and of the *operando* spectroscopic experiments are reported in this paper.

2. Results and discussion

2.1. Synthesis of rhodium(I) complexes

The reaction of the binuclear rhodium(I) complex [RhCl(η^4-COD)]$_2$ with $AgPF_6$ in a solvent mixture of dichloromethane and acetone is a well known method to generate the adduct [Rh(η^4-COD)(acetone)$_2$]PF_6 [5]. The reaction of the latter complex with the zwitterionic P–O ligand **HL** [3d] gave the neutral micro-crystalline compound **1** in almost quantitative yield, which was characterized in solution by multinuclear NMR spectroscopy and in the solid state by both elemen-

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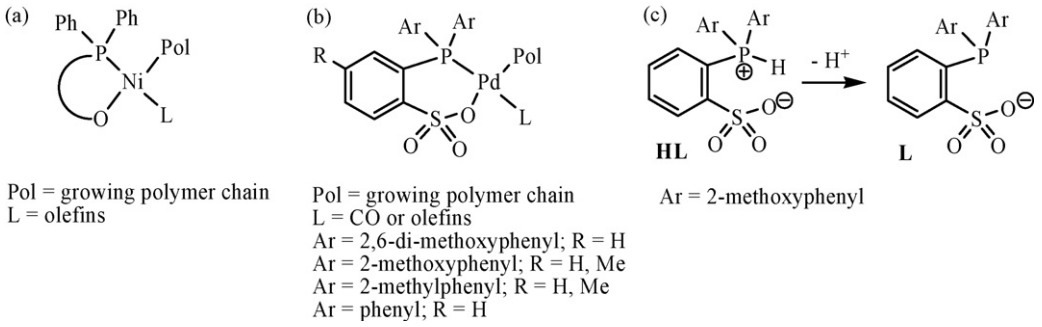
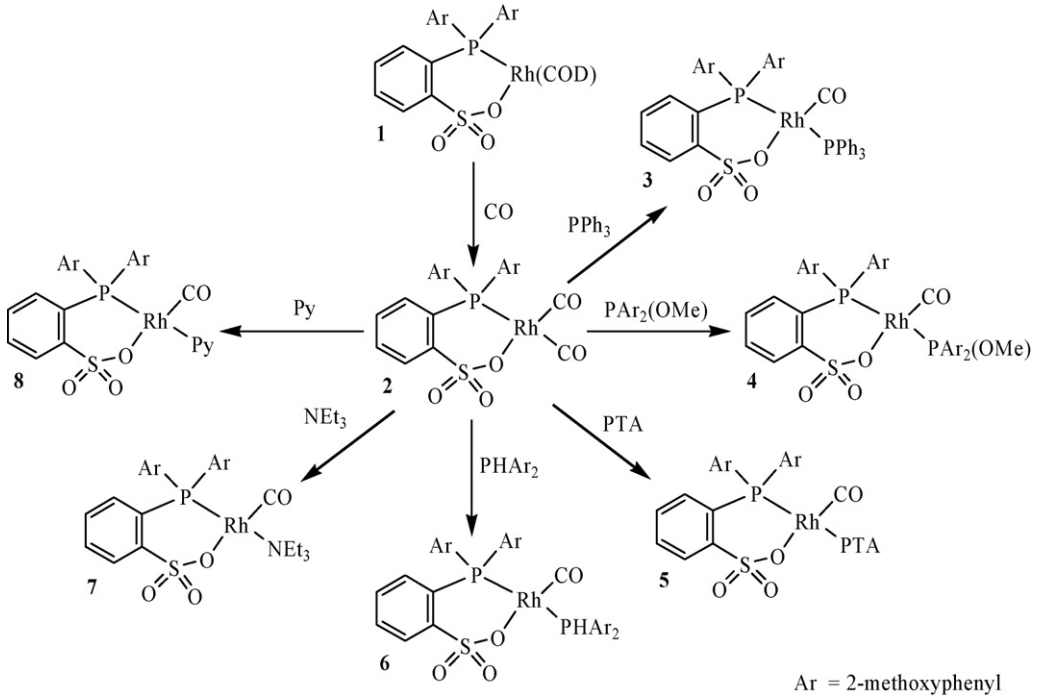


Scheme 1.



Scheme 2. Synthesis of the rhodium–carbonyl complexes **2**–**8**.

tal analysis and a single crystal X-ray structure determination (Scheme 2).

The asymmetric coordination of COD to the metal centre in **1** was proved by the presence of two $^{13}C\{^1H\}$ NMR signals, at 69.98 ppm ($^2J_{P,C}$ = 14.8 Hz) and 104.30 ppm attributable to the sp^2-hybridized carbon atoms *trans* to the oxygen and phosphorus atom of the P–O ligand, respectively. Accordingly, the ^1H NMR spectrum showed a high-field shifted broad singlet at 2.81 ppm for the olefin protons located *trans* to the oxygen atom, while the olefin protons *cis* to the latter atom gave a singlet at 5.36 ppm, which is in line with the different *trans* influence of oxygen and phosphorus atoms.

The overall stereochemistry of **1** in the solid state is shown in the ORTEP drawing of Fig. 1, while selected bond distances and angles as well as crystallographic data are reported in Tables 1 and 3, respectively.

The crystal structure of **1** shows the ligand **L** coordinated to the metal center in the κ^2-*O,P* mode. The rhodium coordination sphere is completed by two C=C bonds from COD. The metal is part of a twisted six-membered ring system, which is characterized by a torsion angle of 37.39(24)°, defined by the atoms Rh(1) P(1) C(1) and C(2). The value of the P(1)–Rh(1)–O(1) coordination angle (92.20(2)°) is in the range of six membered metallarings [6].

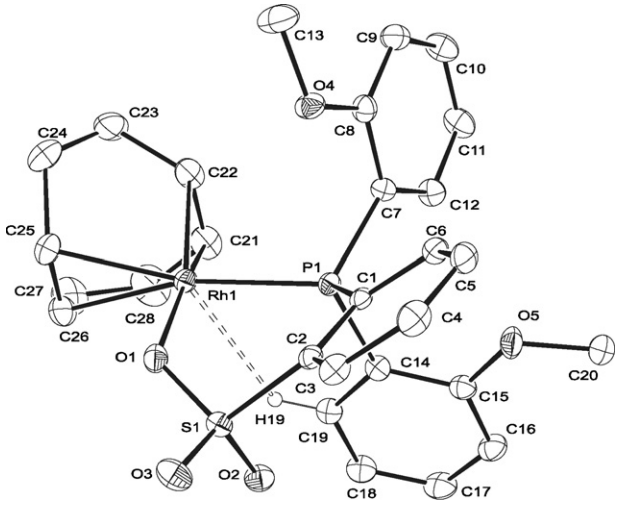


Fig. 1. ORTEP plot of **1**. Thermal ellipsoids are shown at the 30% probability level. Hydrogen atoms are omitted, except the one showing an intra-molecular short distance to the metal atom.

Table 1
Selected bond lengths (Å) and angles (°) for **1**

Rh(1)–P(1)	2.3127(9)
Rh(1)–O(1)	2.103(2)
Rh(1)–C(21)	2.116(4)
Rh(1)–C(22)	2.114(4)
Rh(1)–C(25)	2.232(3)
Rh(1)–C(26)	2.241(3)
C(21)–C(22)	1.406(6)
C(25)–C(26)	1.357(5)
P(1)–Rh(1)–O(1)	92.20(6)
S(1)–O(1)–Rh(1)	125.26(11)
C(21)–Rh(1)–C(26)	80.99(15)
C(22)–Rh(1)–C(25)	81.69(14)
Intramolecular distances (Å)	
Rh(1)···O(4)	3.597(3)
Rh(1)···O(5)	5.254(2)
Rh(1)···H(19)	2.876
O(3)···H(3)	2.415

The COD ligand coordinates asymmetrically to the rhodium atom, due to the different *trans* influence of the P(1) and O(1) donor atoms [7]. The Rh–C bonds *trans* to both donor atoms are thus significantly different (2.116(4) and 2.114(4) (*trans* oxygen) vs. 2.232(3) and 2.241(3) (*trans* phosphorus). Consequently, the C(25)–C(26) bond located *trans* to the P atom is significantly shorter (1.357(5) Å) as compared to the C(21)–C(22) bond located *cis* to the same P atom (1.406(6) Å).

The sp^2-hybridized carbon atoms of COD are not equidistant from the coordination plane defined by the atoms P(1) Rh(1) and O(1), showing the following deviations in Å from the latter plane: C(21) 0.5863(47); C(22) −0.8099(48); C(25) −0.6281(40) and C(26) 0.7082(41). The spatial disposition of the two 2-methoxyphenyl groups is such to originate two different rhodium methoxy–oxygen distances of 3.597(3) and of 5.254(2) Å and one intra-molecular rhodium *ortho*-hydrogen interaction (i.e. Rh(1)···H(19)) of 2.876 Å (Fig. 1). Similar metal–hydrogen interactions have been encountered in other 2-methoxyphenyl modified phosphine complexes [8].

Complex **1** was transformed into the corresponding di-carbonyl complex **2** by bubbling CO into a $CHCl_3$ solution of the former complex (Scheme 2). All our attempts to isolate a pure specimen of **2**, even at low temperature, were unsuccessful, which may be due to a rapid intermolecular CO-exchange process. The presence of two *cis* coordinating CO groups in **2** was unambiguously demonstrated by IR spectroscopy, showing two bands at 2097 and 2019 cm^{-1} (CH_2Cl_2 solution). Consistently, the $^{13}C\{^1H\}$ NMR spectrum of **2** at room temperature contained two broad signals at 184.58 (CO *trans* to O) and 180.43 ppm (CO *trans* to P), that resolved at −60 °C into a doublet at 184.72 ppm ($^1J_{Rh,C}$ = 55.3 Hz) and a doublet of doublets at 179.60 ppm ($^2J_{P,C}$ = 115.9 Hz, $^1J_{Rh,C}$ = 65.4 Hz) respectively.

Compound **2**, synthesized *in situ*, was transformed into the mono-carbonyl derivatives **3**–**8** by reaction with various nucleophiles (Scheme 2).

The synthesis of compounds **3**–**8** is straightforward and allowed for the isolation of micro-crystalline, yellow products in quite satisfactory yields (ca. 70%).

The phosphine or phosphinite complexes **3**–**6** are characterized by a $^{31}P\{^1H\}$ NMR pattern consisting of a doublet of doublets with a large $^2J_{P,P}$ value, which is typical for two mutually *trans* phosphorus donor atoms. The *trans* $^2J_{P,P}$ values are in the range from 319.1 to 373.1 Hz, with **4** and **5** showing the largest and the smallest value, respectively. The $^1J_{Rh,P}$ values of these complexes are, as expected, in the range from 123.1 to 155.1 Hz [9]. The presence of a unique CO ligand in **3**–**6** was proved by IR and $^{13}C\{^1H\}$ NMR measurements. A single CO stretching band was invariably observed at ca. 1983 cm^{-1}, while the $^{13}C\{^1H\}$ NMR spectra of the ^{13}CO enriched complexes acquired in $CDCl_3$ at room temperature showed a singlet centered at ca. 189 ppm. At −60 °C, **3** exhibited a $^{13}C\{^1H\}$ NMR doublet of triplets at 189.36 ppm ($^1J_{Rh,C}$ = 77.2 Hz, $^2J_{P,C}$ = 16.9 Hz) while the spectra of **4** and **5** contained doublets at 189.13 ($^1J_{Rh,C}$ = 50.3 Hz) and at 188.35 ppm ($^1J_{Rh,C}$ = 72.4 Hz), respectively. Only **6** showed, even at lower temperature, a broad hump centered at 189.19 ppm, consistent with a very fast Rh–CO exchange rate.

The reaction of **2** with either a stoichiometric amount or an excess of triethylamine or pyridine gave the neutral mono-carbonyl complexes **7** and **8**, respectively (Scheme 2). Both complexes are featured by a similar stereochemistry, where the N atom is located *trans* to the P atom, as indicated by a $^{13}C\{^1H\}$ NMR study in $CDCl_3$ at room temperature with the ^{13}CO-enriched derivatives. Compound **7** showed a $^{13}C\{^1H\}$ NMR doublet of doublets at 187.72 ppm ($^1J_{Rh,C}$ = 85.2 Hz and $^2J_{P,C}$ = 21.4 Hz) for the coordinated CO, while **8** was featured by a doublet at 188.07 ppm ($^1J_{Rh,C}$ = 79.1 Hz). The rapid CO-exchange reaction for the latter complex was frozen out at −60 °C. At this temperature, a multiplet at 188.28 ppm was clearly visible with the expected multiplicity (dd, $^1J_{Rh,P}$ = 83.6 Hz and $^2J_{P,C}$ = 19.8 Hz). The corresponding IR spectra of **7** and **8** in CH_2Cl_2

Table 2
Hydroformylation of 1-hexene catalyzed by rhodium catalysts[a]

Entry	Precursor	Time [h]	Conversion (%)	*n*-Heptanal (%)	2-Methyl-hexanal (%)	2-Ethyl-pentanal (%)	2-Hexenes (%)	TOF aldehydes (h^{-1})	l/b Ratio
1	**1**	1	64.5	43.2	19.1		2.2	125	2.26
2[b]	**1**	1	90.4	53.1	26.9	0.2	10.2	160	1.96
3	**1**	2	94.5	59.2	27.2		8.1	86	2.18
4[c]	**1**	1	63.3	42.4	19.0		1.9	123	2.23
5	**3**	1	50.6	35.7	14.9		0	101	2.40
6[b]	**3**	1	70.9	45.7	21.6		3.6	135	2.12
7	**3**	2	67.1	45.9	20.3		0.9	66	2.26
8	**4**	1	60.8	41.5	19.3		0	122	2.15
9	**5**	1	60.3	40.4	18.7		1.2	118	2.16
10	**5**	2	81.0	47.1	22.6		11.3	70	2.08
11	**6**	1	80.1	50.0	22.7		7.4	145	2.20
12	**7**	1	54.1	35.7	15.9		2.5	103	2.25
13[d]	**7**	1	49.4	30.7	15.2		3.5	92	2.02
14	Rh[e]	1	99.8	51.9	34.5	6.3	7.1	185	1.27
15[b]	Rh[e]	1	78.0	47.1	23.5	0.3	7.0	142	1.98

[a] *Reaction conditions*: 0.01 mmol Rh, 30 ml THF, 250 μl (2.0 mmol) 1-hexene, 60 °C, 42 bar 1:2 CO/H_2 at 60 °C.
[b] 1:1 CO/H_2.
[c] Reaction in 30 ml of cyclohexane.
[d] Reaction in the presence of NEt_3 (0.04 mmol).
[e] $[RhCl(\eta^4\text{-COD})]_2$.

contained a broad CO stretching band at 1970 and 1979 cm^{-1}, respectively.

2.2. Catalytic study

The rhodium complexes **1** and **3**–**7** were employed to catalyze the hydroformylation of 1-hexene in THF at 60 °C. The results of the catalytic reactions and the experimental conditions are summarized in Table 2.

The catalytic reactions were performed for 1 h in the presence of a 1:2 CO/H_2 mixture at 42 bar and gave mixtures of *n*-heptanal and 2-methylhexanal with modest regioselectivity in all cases and small amounts of *cis*/*trans* 2-hexene. Performing the experiments in the presence of a 1:1 CO/H_2 gas mixture gave also 2-ethylpentanal and an increased amount of 1-hexene isomerization products with an overall product composition and l/b ratio similar to those obtained with the unmodified rhodium catalyst precursor $[RhCl(\eta^4\text{-COD})]_2$ (entries 2 and 6 vs. 15). The hydroformylation reaction performed with the precursor **1** in cyclohexane gave a result comparable to that obtained in THF (entry 4 vs. 1), ruling out any potential role of THF in the catalytic cycle such as that of promoting the heterolytic splitting of H_2 with formation of mono-hydride species [9a,10].

Although we did not have direct spectroscopic evidence of catalyst degradation with time, it is very likely that some decomposition occurs. Indeed, we observed a decrease in the aldehyde regioselectivity as well as a concomitant increase in the 1-hexene isomerization on increasing the reaction time from 1 to 2 h for the reactions catalyzed by **1** and **5** (entries 1 and 9 vs. 3 and 10, respectively).

Unlike **1** and **5**, the catalyst derived from **3**, containing the strongly coordinating co-ligand PPh_3, showed comparable aldehyde regioselectivity and isomerization rate in the reactions lasting either 1 h or 2 h (entries 5 and 7) which corroborates the hypothesis of significant decomposition of the catalysts containing a less coordinating co-ligand than PPh_3.

Using **7**, that contains a nitrogen coligand such as NEt_3 (entry 12) which, in principle, might favor the heterolytic splitting of H_2 [11], increased neither the catalytic activity nor the regioselectivity for *n*-heptanal formation. Interestingly, the addition of an excess of NEt_3 to the reaction mixture containing **7** showed a decrease of the l/b-ratio of the aldehydes (entry 13 vs. 14), indicating a transformation of the initially active catalytic species (*vide infra*).

2.3. Operando spectroscopic studies

In an attempt of intercepting rhodium species, which might be relevant to rationalize the hydroformylation of 1-hexene, catalyzed by **1**–**7**, HPIR and HPNMR spectroscopic studies were carried out. The HPIR studies were performed in THF with an approximately twelve-fold concentration of the precursor. The HPIR cell was incorporated into a titanium autoclave, equipped with an effective mechanical stirring and all the other necessary control devices [12]. The IR spectra were acquired at room temperature and at 60 °C. The reactions were monitored at this temperature for 1 h. A representative absorption IR spectrum of each catalytic system studied is shown in Fig. 2.

Typically, a THF solution of the rhodium precursors (**1** or **3**–**7**) containing the desired amount of 1-hexene was pressurized with a 1:2 CO/H_2 gas mixture to a total pressure of 36 bar at room temperature. The autoclave was then heated to 60 °C, reaching an internal pressure of 42 bar. The IR spectra clearly showed the conversion of **1** into the di-carbonyl **2** (trace a), whereas the mono-carbonyl complexes **3**–**6** remained unchanged (traces b–e). At variance with all the other precursors investigated, **7**, bearing the very weakly coordinating ligand NEt_3, was rapidly transformed into **2** together with a small amount of an unidentified rhodium carbonyl species, whose concentration, however, increased by adding extra NEt_3 (trace f vs. g). Intrigued by this fact, the hydroformylation of 1-hexene by **7** was studied by $^{31}P\{^1H\}$ HPNMR spectroscopy by means of a 10 mm OD sapphire tube equipped with a titanium valve in a 1:1 (v:v) mixture of THF and CD_2Cl_2. A sequence of variable-temperature $^{31}P\{^1H\}$ NMR spectra is reported in Fig. 3.

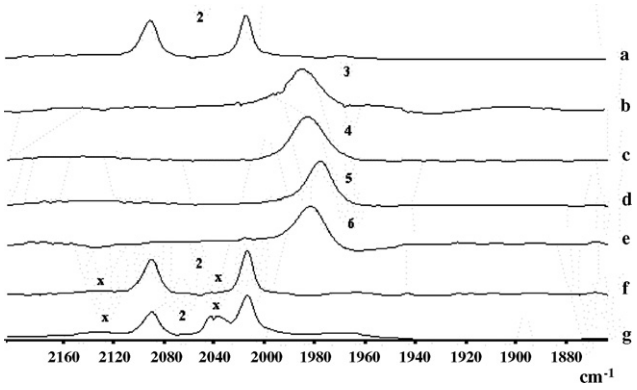


Fig. 2. HPIR study of 1-hexene hydroformylation with precursors **1**, **3**, **4**, **5**, **6** and **7** (precursor (0.063 mmol), 1-hexene (12.6 mmol), THF (25 ml), 60 °C, CO/H_2 (1:2) (42.0 bar), 1 h, 60 °C): (a) precursor **1**, (b) precursor **3**, (c) precursor **4**, (d) precursor **5**, (e) precursor **6**, (f) precursor **7** and (g) precursor **7** and NEt_3 (4 equiv.); × (unidentified rhodium species).

The $^{31}P\{^1H\}$ NMR spectrum of **7** at room temperature showed a doublet centered at 21.50 ppm ($^1J_{Rh,P}$ = 155.1 Hz) (trace a). On addition of 1-hexene (200 equiv.), no spectral change occurred (trace b). Upon pressurizing the NMR tube with CO (14 bar), NEt_3 was replaced by CO to yield the di-carbonyl **2** (trace c). At this point, the tube was pressurized with H_2 (28 bar) at room temperature.

As a result, a $^{31}P\{^1H\}$ NMR singlet at −29.30 ppm appeared which we safely assign to the ammonium salt of the P–O ligand $[HNEt_3(\mathbf{L})]$ (**9**) (*vide infra*). On heating the NMR probe at 60 °C for 1 h (trace e) the concentration of **9** increased at the expense of that of **2**. A **2**/**9** ratio of ca. 1 was estimated by signal integration in the $^{31}P\{^1H\}$ NMR spectrum acquired at room temperature (trace f) while an analogous HPNMR study performed in the presence of

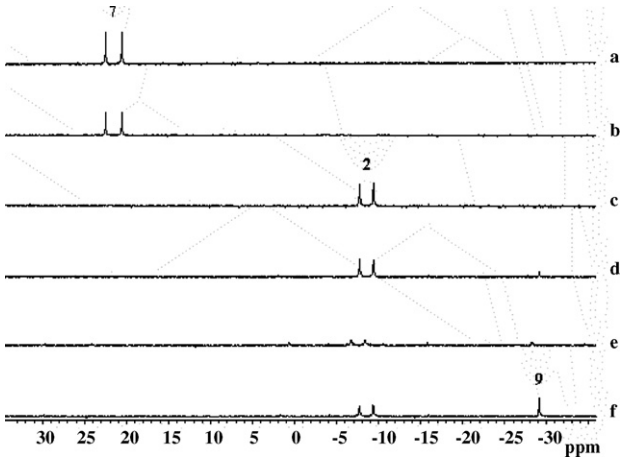


Fig. 3. Variable-temperature $^{31}P\{^1H\}$ HPNMR study of the hydroformylation of 1-hexene with **7** (sapphire tube, THF/CD_2Cl_2 (1:1, v:v) (2 ml), 1-hexene (200 equiv.), 81.01 MHz): (a) **7** at room temperature; (b) addition of 1-hexene, (c) immediately after pressurizing the tube with CO (14 bar), (d) immediately after pressurizing the tube with H_2 (28 bar) at room temperature, (e) after 1 h at 60 °C and (f) after cooling to room temperature.

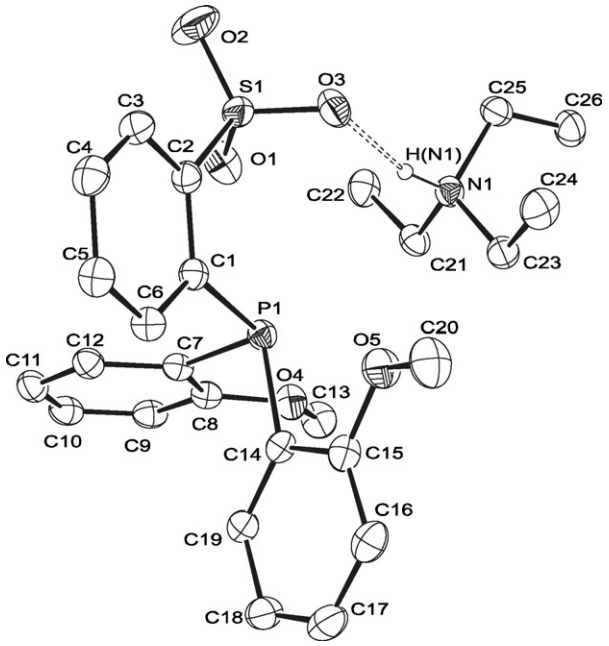


Fig. 4. ORTEP plot of **9**. Thermal ellipsoids are shown at the 30% probability level. Hydrogen atoms are omitted, except the one attached to N(1) showing a short intermolecular contact to O(3) of 1.914(21) Å. Selected bond distances in [Å]: P(1)–C(1) = 1.8536(14); P(1)–C(7) = 1.8414(15); P(1)–C(14) = 1.8488(15).

an excess of NEt_3 (4 equiv.) showed the complete conversion of **2** into **9** just after 1.5 h.

The authentication of **9** was achieved by its independent synthesis and characterization by means of both NMR spectroscopy and a single crystal X-ray structure determination. An ORTEP drawing of **9** is presented in Fig. 4 together with selected bond distances.

In conclusion, on the basis of *operando* spectroscopic studies, there is little doubt that the hydroformylation of 1-hexene with **7** is largely biased by the instability of the catalyst, due to the presence of the strong base NEt_3 which sequestrates the **HL** ligand, thus generating an unmodified rhodium carbonyl catalyst (Fig. 2, trace f) [13].

Operando HPNMR experiments were carried out also for the other catalyst precursors investigated in this work. In all cases, the spectra were poorly informative, as only mono-carbonyl or di-carbonyl complexes were seen for all reactions lasting 1 h at 60 °C. Even HPNMR experiments carried out in the absence of substrate showed no additional species.

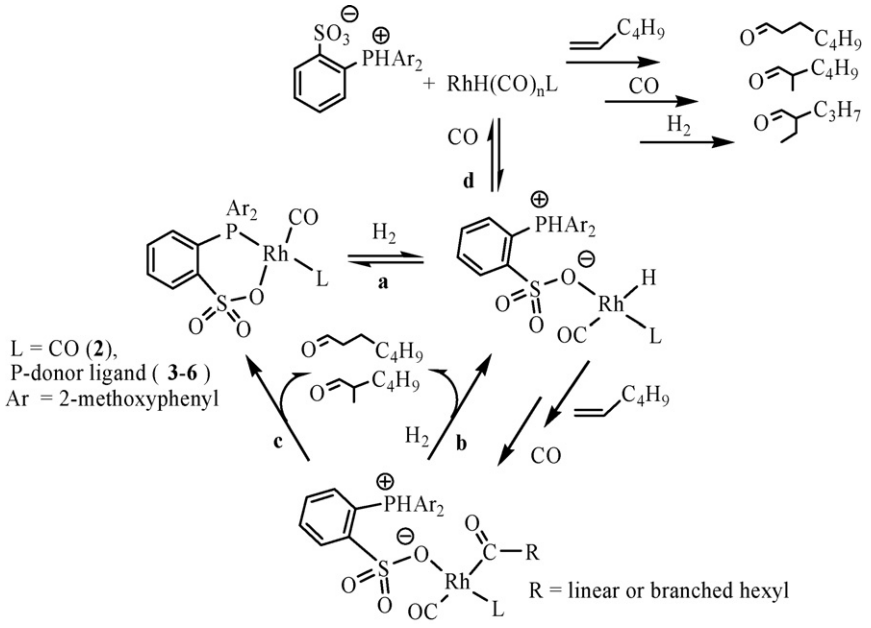
2.4. Mechanistic considerations

On the basis of the results obtained from the catalytic and *operando* experiments, we feel that the hydroformylation of 1-hexene catalyzed by the neutral rhodium complexes **2**–**6** is a complicated process, probably involving different catalytically active species depending on the CO pressure, reaction time and nature of the co-ligands.

Unlike many examples of hydroformylation reactions catalyzed by rhodium diphosphine complexes [14], no evidence of the formation of rhodium hydride species was obtained, even under *operando* conditions on the short timescale of IR spectroscopy (10^{-13} s).

Furthermore, the catalytic activity does not depend on the Lewis basicity of the solvent (Table 2, entry 1 vs. 4), which rules out the participation of the latter in the activation of hydrogen. The scarce regioselectivity observed for the hydroformylation reactions is consistent with the loss of the P–O chelating structure, especially on increasing the CO-partial pressure (Table 2, entry 2 vs. 1), as catalysts supported by firmly chelating ligands generally exhibit a higher selectivity in the linear product [14]. In this regard, it is worth recalling that a similarly scarce regioselectivity in the linear aldehyde has been recently obtained with a κ^2-*P,O*-1′-(diphenylphosphino)ferrocenecarboxylate rhodium precursor that would form a κ^1-*P* species under hydroformylation conditions [15].

A possible, yet highly speculative, catalytic cycle as shown in Scheme 3 might comprise a ligand assisted H_2-activation, generating the κ^1-*O* mono-hydride species (Scheme 3, a) and a closure of the catalytic cycle either by intramolecular protonation of the acyl complexes to re-generate the κ^2-*P,O* mono- or di-carbonyl precursors (c) or by reaction of the acyl complexes with H_2 in order to



Scheme 3. Proposed catalytic cycle operative in the hydroformylation of 1-hexene with the neutral rhodium complexes **2**–**6**.

re-generate the κ^1-*O* mono-hydride species (b), that, in turn, may originate a P–O free catalyst (d).

3. Conclusion

In this work are reported the synthesis and characterization of a series of neutral rhodium(I) complexes containing the κ^2-*O*,*P* 2-(bis(2-methoxyphenyl)phosphino)benzenesulfonate ligand. Some of these complexes have been employed as precursors to catalyze the hydroformylation reaction of 1-hexene in THF in the presence of a 1:2 CO/H_2 mixture. The regioselectivity in *n*-heptanal were quite modest, ranging from 68 to 70%. Lower regioselectivity was found for catalytic reactions either lasting 2 h instead of 1 h or performing the catalytic reactions in the presence of a 1:1 CO/H_2 mixture. *Operando* spectroscopic studies by means of HPIR and HPNMR techniques proved the absence of Rh-H species in the catalytic cycle of sufficient lifetime to be detected on the fast timescale of IR spectroscopy. *Operando* HPIR and HPNMR spectroscopic experiments have shown that either rhodium(I)-mono or di-carbonyl complexes are resting state of the catalytic cycle, most likely in equilibrium with other species containing, besides the eventual extra phosphine ligand, either the zwitterionic ligand **HL** in the κ^1-*O* bonding mode or carbonyl ligands. A rhodium catalyst containing CO ligands, together with the ammonium salt of the **HL** ligand, is actually formed by adding NEt_3 to the catalytic mixture.

4. Experimental

4.1. General

All reactions and manipulations were carried out under a nitrogen atmosphere by using standard Schlenk-type techniques. The solvents were distilled from suitable dehydrating reagents and were deoxygenated before use. The reagents were used as purchased from Aldrich or Fluka, unless stated otherwise. Compounds $[RhCl(\eta^4\text{-COD})]_2$ [16], bis(2-methoxyphenyl)methoxyphosphine [3d], 2-(bis(2-methoxyphenyl)phosphino)benzenesulfonic acid [3d], and bis(2-methoxyphenyl)phosphine [17] were prepared according to the literature methods. Hydroformylation reactions were performed in a 320 ml stainless steel autoclave, constructed at ICCOM-CNR (Florence, Italy), equipped with a magnetic drive stirrer and a Parr 4842 temperature and pressure controller. GC analyses were performed with a Shimadzu GC 2010 apparatus, equipped with a SPB-5 Supelco fused silica capillary column (60 m × 0.25 mm, 0.25 μm film thickness) employing toluene as internal standard, while GC–MS analyses were performed with a Shimadzu QP2100S apparatus, equipped with a SPB-1 Supelco fused silica capillary column (30 m × 0.25 mm, 0.25 μ(m film thickness). Deuterated solvents for routine NMR measurements were dried over activated molecular sieves. ^1H, $^{13}C\{^1H\}$, $^{31}P\{^1H\}$ NMR spectra were obtained on either a Bruker Avance II DRX 300 spectrometer (300.13, 75.49, 121.49 MHz, respectively) or a Bruker Avance DRX-400 spectrometer (400.13, 100.62 and 161.98 MHz, respectively). Chemical shifts (δ) are reported in ppm relative to TMS, referenced to the chemical shifts of residual solvents resonances (^1H and ^{13}C NMR) or 85% H_3PO_4. $^{13}C\{^1H\}$ NMR spectra of the rhodium carbonyl complexes **2**–**8** were acquired after an *in situ* preparation of each complex with enriched ^{13}CO (i.e. ^{13}C content >99%). HPNMR experiments were carried out on a Bruker ACP 200 spectrometer, operating at 200.13 and 81.01 MHz for ^1H and $^{31}P\{^1H\}$, respectively, using a 10-mm sapphire NMR tube (Saphikon, Milford, NH), equipped with a titanium high-pressure charging head constructed at the ICCOM-CNR (Florence, Italy) [18]. Elemental analyses were performed using a Carlo Erba Model 1106 elemental analyzer. Infrared spectra were recorded on a FT-IR PerkinElmer BX spectrometer. The HPIR cell, constructed at ICCOM-CNR, is constituted by a 75 ml autoclave, equipped with ZnS windows (4 mm thickness, 8 mm diameter, optical path length 0.2 mm) [10c,12].

4.2. Preparation of complexes

1. $[Rh(\eta^4\text{-COD})Cl]_2$ (91.9 mg, 0.19 mmol) was dissolved in a deareated (3:1, v:v) solvent mixture of CH_2Cl_2 and acetone (10 ml). $AgPF_6$ (98.9 mg, 0.39 mmol) was added to this solution and the resulting suspension was allowed to stir for 20 min. Afterwards, the suspension was filtered through a small plug of Celite which was washed with CH_2Cl_2 (2 ml). Then ligand **HL** (150.0 mg, 0.37 mmol) was added to the solution, which was allowed to stir for 1 h, followed by evaporation under vacuum. The yellow–orange residue was suspended in diethyl ether (10 ml) stirred for 10 min, then filtered under nitrogen and dried in a stream of nitrogen. Yield: 215.2 mg (95%). Anal. calcd. for $C_{28}H_{30}O_5PRhS$ (612.2): C, 54.93; H, 4.90. Found: C, 54.88; H, 4.82. ^1H NMR (300.13 MHz, $CDCl_3$, 25 °C): δ 1.90 (m, 2H, CH*H*′), 2.01 (m, 2H, C′H*H*′), 2.43 (m, 4H, C*H*H′ + C′*H*H′), 2.81 (br. s, 2H, CH(*trans* O)), 3.61 (s, 6H, OCH_3), 5.36 (br. s, 2H, CH(*trans* P)), 6.96–7.56 (m, 10H, Ar), 8.02 (br. s 1H, *o*-H-Ar), 8.09 (ddd, $^3J_{H,H}$ = 7.8 Hz, $^4J_{P,H}$ = 4.1 Hz, $^4J_{H,H}$ = 0.9 Hz, 1H, *m*-H-Ar). $^{13}C\{^1H\}$ NMR (75.49 MHz, $CDCl_3$, 25 °C): δ 28.80 (d, $^4J_{P,H}$ = 12.5 Hz, C′HH′), 32.67 (s, *C*HH′), 55.06 (s, OCH_3), 69.98 (d, $^2J_{P,C}$ = 14.8 Hz, CH(*trans* O)), 104,30 (s, CH(*trans* P)), 110.45–160.39 (Ar). $^{31}P\{^1H\}$ NMR (121.49 MHz, $CDCl_3$, 25 °C): δ 8.09 (d, $^1J_{Rh,P}$ = 151.8 Hz).

2. CO was bubbled through a deareated CD_2Cl_2 (1.5 ml) solution of **1** (25.0 mg, 0.04 mmol) for 5 min. Then the solution was transferred into a 5 mm NMR tube, followed by the acquisition of the NMR data. ^1H NMR (300.13 MHz, $CDCl_3$, 25 °C): δ 3.84 (s, 6H, OCH_3), 6.94–7.62 (m, 11H, Ar), 8.15 (ddd, $^3J_{H,H}$ = 7.7 Hz, $^4J_{P,H}$ = 4.9 Hz, $^4J_{H,H}$ = 1.2 Hz, 1H, *m*-H–Ar). $^{13}C\{^1H\}$ NMR (75.49 MHz, $CDCl_3$, 25 °C): δ 55.09 (s, OCH_3), 111.10–160.70 (Ar), 180.43 (br. s, CO), 184.58 (br. s, CO). $^{13}C\{^1H\}$ NMR (75.49 MHz, $CDCl_3$, −60 °C): δ 55.20 (s, OCH_3), 56.20 (s, OCH_3), 111.10–160.90 (Ar), 179.74 (dd, $^2J_{P,C}$ = 115.9 Hz, $^1J_{Rh,C}$ = 65.4 Hz, CO(*trans* P)), 184.72 (d, $^1J_{Rh,C}$ = 55.3 Hz, CO(*trans* O)). $^{31}P\{^1H\}$ NMR (121.49 MHz, $CDCl_3$, 25 °C): δ −8.39 (d, $^1J_{Rh,P}$ = 131.3 Hz). IR (CH_2Cl_2): ν(C=O) 2019 and 2097 cm^{-1}.

3–**8**. Compound **1** (200.0 mg, 0.33 mmol) was dissolved in deareated CH_2Cl_2 (10 ml). Through this solution was successively bubbled CO for 5 min and nitrogen for 5 min at room temperature, followed by the addition of the appropriate ligand (0.33 mmol). The obtained solution was then allowed to stir for 30 min at room temperature, followed by its concentration to a small volume (4 ml) and on addition of diethyl ether (10 ml) a yellow, micro-crystalline compound precipitated, which was filtered off, washed with diethyl ether (5 ml) and dried in a stream of nitrogen. **3**: Yield 196.6 mg (75%). Anal. calcd. for $C_{39}H_{33}O_6P_2RhS$ (794.3): C, 58.97; H, 4.15. Found: C, 58.82; H, 4.08. ^1H NMR (300.13 MHz, $CDCl_3$, 25 °C): δ 3.70 (s, 6H, OCH_3), 6.95–7.68 (m, 26H, Ar), 8.13 (ddd, $^3J_{H,H}$ = 7.5 Hz, $^4J_{P,H}$ = 4.9 Hz, $^4J_{H,H}$ = 1.1 Hz, 1H, *m*-H–Ar). $^{13}C\{^1H\}$ NMR (75.49 MHz, $CDCl_3$, 25 °C): δ 55.09 (s, OCH_3), 111.12–160.70 (Ar), 189.37 (s, CO). $^{13}C\{^1H\}$ NMR (75.49 MHz, $CDCl_3$, −60 °C): δ 55.13 (s, OCH_3), 111.15–160.90 (Ar), 189.36 (dt, $^1J_{Rh,C}$ = 77.2 Hz, $^2J_{P,C}$ = 16.9 Hz, CO). $^{31}P\{^1H\}$ NMR (121.49 MHz, $CDCl_3$, 25 °C): δ −0.27 (dd, $^1J_{Rh,P}$ = 130.1 Hz, $^2J_{P,P}$ = 327.3 Hz, L), 28.87 (dd, $^1J_{Rh,P}$ = 135.4 Hz, $^2J_{P,P}$ = 327.3 Hz, P). IR (CH_2Cl_2): ν(C=O) 1983 cm^{-1}; IR (KBr): ν(C=O) 1975 cm^{-1}. **4**: Yield 197.4 mg (74%). Anal. calcd. for $C_{36}H_{35}O_9P_2RhS$ (808.3): C, 53.49; H, 4.33. Found: C, 53.35; H, 4.27. ^1H NMR

(300.13 MHz, $CDCl_3$, 25 °C): δ 3.63 (s, 6H, OCH_3), 3.64 (s, 6H, OCH_3), 4.06 (d, $^3J_{P,H}$ = 13.9 Hz, 3H, $POCH_3$), 6.85–7.73 (m, 19H, Ar), 8.11 (ddd, $^3J_{H,H}$ = 7.6 Hz, $^4J_{P,H}$ = 4.9 Hz, $^4J_{H,H}$ = 1.1 Hz, 1H, *m*-H–Ar). $^{13}C\{^1H\}$ NMR (75.49 MHz, $CDCl_3$, 25 °C): δ 55.09 (s, OCH_3), 55.48 (s, OCH_3), 57.89 (s, $POCH_3$), 110.93–160.76 (Ar), 188.97 (s, CO). $^{13}C\{^1H\}$ NMR (75.49 MHz, $CDCl_3$, −60 °C): δ 55.26 (s, OCH_3), 55.80 (s, OCH_3), 58.20 (s, $POCH_3$), 110.88–160.28 (Ar), 189.13 (br d, $^1J_{Rh,C}$ = 50.3 Hz, CO). $^{31}P\{^1H\}$ NMR (121.49 MHz, $CDCl_3$, 25 °C): δ 0.32 (dd, $^1J_{Rh,P}$ = 123.1 Hz, $^2J_{P,P}$ = 373.1 Hz, L$^-$), 116.20 (dd, $^1J_{Rh,P}$ = 156.7 Hz, $^2J_{P,P}$ = 373.1 Hz, P). IR (CH_2Cl_2): ν(C=O) 1983 cm^{-1}; IR (KBr): ν(C=O) 1984 cm^{-1}. **5**: Yield 159.2 mg (70%). Anal. calcd. for $C_{27}H_{30}N_3O_6P_2RhS$ (689.2): C, 47.05; H, 4.35. Found: C, 47.12; H, 4.40. ^1H NMR (400.13 MHz, $CDCl_3$, 25 °C): δ 3.73 (s, 6H, OCH_3), 4.35 (s, 6H, NCH_2P), 4.59 (s, 6H, NCH_2N), 6.99–7.52 (m, 11H, Ar), 8.21 (dd, $^3J_{H,H}$ = 5.4 Hz, $^4J_{P,H}$ = 3.0 Hz, 1H, *m*-H-Ar). $^{13}C\{^1H\}$ NMR (100.62 MHz, $CDCl_3$, 25 °C): δ 51.50 (d, $^1J_{P,C}$ = 13.2 Hz, NCH_2P), 55.28 (s, OCH_3), 73.30 (d, $^3J_{P,C}$ = 5.7 Hz, NCH_2N), 111.19–160.57 (Ar), 188.25 (s, CO). $^{13}C\{^1H\}$ NMR (100.62 MHz, $CDCl_3$, −60 °C): δ 51.10 (d, $^1J_{P,C}$ = 12.7 Hz, NCH_2P), 55.05 (s, OCH_3), 56.05 (s. OCH_3), 73.30 (br. s, NCH_2N), 111.10–160.16 (Ar), 188.35 (d, $^1J_{Rh,C}$ = 72.4 Hz, CO). $^{31}P\{^1H\}$ NMR (161.98 MHz, $CDCl_3$, 25 °C): δ −46.47 (dd, $^1J_{Rh,P}$ = 127.9 Hz, $^2J_{P,P}$ = 319.1 Hz, P), −3.95 (dd, $^1J_{Rh,P}$ = 129.9 Hz, $^2J_{P,P}$ = 319.1 Hz, L). IR (CH_2Cl_2): ν(C=O) 1983 cm^{-1}; IR (KBr): ν(C=O) 1983 cm^{-1}. **6**: Yield 187.5 mg (73%). Anal. calcd. for $C_{35}H_{33}O_8P_2RhS$ (778.3): C, 54.01; H, 4.24. Found: C, 53.94; H, 4.17. ^1H NMR (400.13 MHz, $CDCl_3$, 25 °C): δ 3.68 (s, 6H, OCH_3), 3.76 (s, 6H, OCH_3), 6.77 (dd, $^1J_{P,H}$ = 381.3 Hz, $^2J_{Rh,H}$ = 3.4 Hz, 1H, pH), 6.85–7.49 (m, 17H, Ar), 7.79 (ddd, $^3J_{P,H}$ = 13.6 Hz, $^3J_{H,H}$ = 7.2 Hz, $^4J_{H,H}$ = 1.6 Hz, 2H, *o*-H-Ar(P)), 8.16 (ddd, $^3J_{H,H}$ = 7.6 Hz, $^4J_{P,H}$ = 8.0 Hz, $^4J_{H,H}$ = 1.2 Hz, 1H, *m*-H-Ar(L)). $^{13}C\{^1H\}$ NMR (100.62 MHz, $CDCl_3$, 25 °C): δ 55.18 (s, OCH_3), 55.61 (s, OCH_3), 110.46–160.77 (Ar), 188.86 (s, CO). $^{13}C\{^1H\}$ NMR (100.62 MHz, $CDCl_3$, −60 °C): δ 55.16 (s, OCH_3), 55.74 (s, OCH_3), 110.20–160.11 (Ar), 189.19 (br. s, CO). $^{31}P\{^1H\}$ NMR (161.98 MHz, $CDCl_3$, 25 °C): δ −26.14 (dd, $^1J_{Rh,P}$ = 133.3 Hz, $^2J_{P,P}$ = 340.9 Hz, P), 1.10 (dd, $^1J_{Rh,P}$ = 133.8 Hz, $^2J_{P,P}$ = 340.9 Hz, L). IR (CH_2Cl_2): ν(C=O) 1984 cm^{-1}; IR (KBr): ν(C=O) 1969 cm^{-1}. **7**: Yield 135.8 mg (65%). Anal. calcd. for $C_{27}H_{33}NO_6PRhS$ (633.2): C, 51.21; H, 5.21. Found: C, 51.15; H, 5.12. ^1H NMR (300.13 MHz, $CDCl_3$, 25 °C): δ 1.39 (t, $^3J_{H,H}$ = 7.2 Hz, 9H, CH_3), 2.99 (dq, $^4J_{P,H}$ = 2.4 Hz, $^3J_{H,H}$ = 7.2 Hz, 6H, CH_2), 3.67 (s, 6H, OCH_3), 6.94–7.48 (m, 11H, Ar), 8.14 (ddd, $^3J_{H,H}$ = 7.8 Hz, $^4J_{P,H}$ = 4.6 Hz, $^4J_{H,H}$ = 1.4 Hz, 1H, *m*-H-Ar). $^{13}C\{^1H\}$ NMR (75.49 MHz, $CDCl_3$, 25 °C): δ 10.60 (s, CH_3), 49.22 (s, CH_2), 54.88 (s, OCH_3), 110.93–160.31 (Ar), 187.72 (dd, $^1J_{Rh,C}$ = 85.2 Hz, $^2J_{P,C}$ = 21.4 Hz, CO). $^{31}P\{^1H\}$ NMR (121.49 MHz, $CDCl_3$, 25 °C): δ 21.87 (d, $^1J_{Rh,P}$ = 155.1 Hz). IR (CH_2Cl_2): ν(C=O) 1970 cm^{-1}; IR (KBr): ν(C=O) 1963 cm^{-1}. **8**: Yield 135.8 mg (70%). Anal. calcd. for $C_{26}H_{23}NO_6PRhS$ (611.2): C, 51.09; H, 3.76. Found: C, 50.93; H, 3.65. ^1H NMR (400.13 MHz, $CDCl_3$, 25 °C): δ 3.75 (s, 6H, OCH_3), 6.97 + 7.12 + 7.34 (m, 8H, Ar(L)), 7.41 (pseudo t, $^3J_{H,H}$ = 8.0 Hz, 2H, *m*-H-Ar(Py)), 7.51 (m, 3H, Ar(L)), 7.85 (tt, $^3J_{H,H}$ = 7.7 Hz, $^4J_{H,H}$ = 1.5 Hz, 1H, *p*-H-Ar(Py)), 8.24 (ddd, $^3J_{H,H}$ = 7.8 Hz, $^4J_{P,H}$ = 4.6 Hz, $^4J_{H,H}$ = 1.0 Hz, 1H, *m*-H-Ar(L)), 8.87 (m, 2H, *o*-H-Ar(Py)). $^{13}C\{^1H\}$ NMR (100.62 MHz, $CDCl_3$, 25 °C): δ 55.17 (s, OCH_3), 111.39–160.53 (Ar), 188.07 (d, $^1J_{Rh,C}$ = 79.1 Hz, CO). $^{13}C\{^1H\}$ NMR (100.62 MHz, $CDCl_3$, −60 °C): δ 55.17 (s, OCH_3), 55.78 (s, OCH_3), 111.38–160.41 (Ar), 188.28 (dd, $^1J_{Rh,C}$ = 83.6 Hz, $^2J_{P,C}$ = 19.8 Hz, CO). $^{31}P\{^1H\}$ NMR (161.98 MHz, $CDCl_3$, 25 °C): δ 19.69 (d $^1J_{Rh,P}$ = 155.0 Hz). IR (CH_2Cl_2): ν(C=O) 1979 cm^{-1}; IR (KBr): ν(C=O) 1981 cm^{-1}.

4.3. Preparation of **9**

To a solution of ligand **HL** (89.8 mg, 0.22 mmol) in CH_2Cl_2 (3 ml) was added triethylamine (62.2 μl, 0.45 mmol) and the solution obtained was allowed to stir for 20 min, followed by its concentration to dryness by means of a vacuum pump. Then diethyl ether (5 ml) was added to the solid residue and the suspension was stirred for half an hour. Afterwards the solid was filtered off, washed with diethyl ether (5 ml) and dried in a stream of nitrogen. Yield: 97.0 mg (88%). Anal. calcd. for $C_{26}H_{34}NO_5PS$ (503.3): C, 62.04; H, 6.75. Found: C, 62.12; H, 6.85. ^1H NMR (300.13 MHz, $CDCl_3$, 25 °C): δ 1.26 (t, $^3J_{H,H}$ = 7.2 Hz, 9H, CH_3), 3.15 (q, $^3J_{H,H}$ = 7.2 Hz, 6H, CH_2), 3.63 (s, 6H, OCH_3), 6.67–7.35 (m, 11H, Ar), 8.24 (ddd, $^3J_{H,H}$ = 7.8 Hz, $^4J_{P,H}$ = 4.6 Hz, $^4J_{H,H}$ = 1.4 Hz, 1H, *m*-H-Ar), 10.20 (br. s, 1H, NH). $^{13}C\{^1H\}$ NMR (75.49 MHz, $CDCl_3$, 25 °C): δ 8.43 (s, CH_3), 45.99 (s, CH_2), 55.34 (s, OCH_3), 109.96–160.82 (Ar). $^{31}P\{^1H\}$ NMR (121.49 MHz, $CDCl_3$, 25 °C): δ −28.01 (s).

4.4. Crystal structure determinations

Crystals of **1** and **9**, suitable for a single crystal X-ray diffraction analysis were obtained by diffusion of toluene into a layered CH_2Cl_2 solution of either compound at room temperature. X-ray diffraction intensity data were collected at 173 K on Oxford Diffraction CCD diffractometers with graphite monochromated Mo Kα radiation (λ = 0.71073 Å) and Cu Kα radiation (λ = 1.54184 Å) using ω-scans for compound **1** and **9**, respectively. Cell refinement, data reduction and empirical absorption correction were carried out with the Oxford diffraction software and SADABS [19a]. All structure determination calculations were performed with the WINGX package [19b] with SIR-97 [19c], SHELXL-97 [19d], and ORTEP-3 programs [19e]. Final refinements based on F^2 were carried out with anisotropic thermal parameters for all non-hydrogen atoms while the hydrogen atoms were included in calculated positions and refined using a riding model with isotropic U_{iso}(H) values depending on the U_{eq}(C) of the adjacent carbon atoms. Relevant crystallographic data and structure refinement details are summarized in Table 3. CCDC-675841 and CCDC-675840 contain the supplementary crystallographic data for compound **1** and **9**, respectively. Copies of the data can be obtained free of charge from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223/336033; e-mail: deposit@ccdc.cam.ac.uk).

Table 3
Crystallographic data and structure refinement details for **1** and **9**

	1	**9**
Formula	$C_{28}H_{30}O_5PRhS$	$C_{26}H_{34}NO_5PS$
Molecular weight	612.46	503.57
Crystal habit	Yellow prism	White prism
Crystal size (mm)	0.4 × 0.2 × 0.2	0.2 × 0.2 × 0.2
Temperature (K)	173(2)	173(2)
Wavelength (Å)	0.71069	1.54184
Crystal system	Orthorhombic	Monoclinic
Space group	*Pbca*	*P*2(1)/*n*
a (Å)	17.475(5)	14.6465(2)
b (Å)	15.873(5)	11.4819(1)
c (Å)	18.568(5)	16.7465(3)
α (°)	90.000	90.000
β (°)	90.000	112.982(2)
γ (°)	90.000	90.000
Volume (Å^3)	5150(3)	2592.72(6)
Z	8	4
ρ_{calc} (g cm^{-3})	1.580	1.290
μ (mm^{-1})	0.844	1.991
F(000)	2512	1072
θ range (°)	3.72–28.61	4.80–72.72
Reflections collected	5685	5045
Independent reflections	5685	5045
Refined parameters	329	316
*R*1 (2σ(*I*)]	0.0362	0.0390
*R*1 (all data)	0.0575	0.0411
Goodness-of-fit on F^2	1.043	1.019
Largest diff. peak and hole (Å^{-3})	0.762/−0.541	0.320/−0.274

4.5. Batch hydroformylation tests

In a typical experiment, deareated THF (30 ml) and 1-hexene (250 μl, 2.0 mmol) were introduced into an autoclave (320 ml), which had been previously evacuated by means of a vacuum pump and charged with the catalyst precursor (0.01 mmol). In those cases where the catalytic reactions were carried out in the presence of an excess of NEt_3 (0.04 mmol), the reagent was added to the THF solution. Then the autoclave was charged with a (1:2) CO/H_2 gas mixture to a total pressure of 20 bar at room temperature, followed by heating it by means of an electric heater to 60 °C. Once the desired reaction temperature was reached, the total pressure of the appropriate gas mixture was adjusted to 42 bar and stirring was started (600 rpm). After the desired reaction time, the autoclave was cooled to 0 °C by means of an ice-acetone bath and unreacted gases were vented off and the reaction solution was analyzed by GC–MS as well as by GC after toluene (100 μl) had been added to the catalysis solution.

4.6. Operando spectroscopic studies

4.6.1. HPIR experiments

Typically, the catalyst precursor (**1**, **3**, **4**, **5**, **6** or **7**, 0.063 mmol) was dissolved in deareated THF (25 ml) containing 1-hexene (1.6 ml, 12.6 mmol). In those cases where the IR study was carried out in the presence of an excess of NEt_3 (0.252 mmol) this latter reagent was added to the THF solution of the catalyst precursor. The resulting solution was introduced into the HPIR cell by means of a syringe under a stream of nitrogen, followed by pressurization with a 1:2 CO/H_2 gas mixture to a total pressure of 36 bar at room temperature. The HPIR cell was placed into the IR spectrometer and stirring was started (1500 rpm), followed by the acquisition of IR spectra in the region 1800–2300 cm^{-1} at room temperature. Afterwards the HPIR cell was heated to 60 °C (total gas pressure of 42 bar) and IR spectra were acquired every 20 min for 1 h. At the end of the experiment, the HPIR cell was cooled to room temperature, the gases were vented off and the solution was analyzed by GC, showing the same regioselectivity of the aldehydes formed as observed in parallel batch catalytic reactions.

4.6.2. HPNMR experiments

A solution of compound **7** (12.7 mg, 0.02 mmol) in a deareated (1:1, v:v) solvent mixture of THF/CD_2Cl_2 (2 ml) was transferred under nitrogen into a 10 mm sapphire tube, which was placed into a NMR probe head at room temperature followed by the acquisition of a $^{31}P\{^1H\}$ NMR spectrum at this temperature. Then, the NMR tube was removed from probe and 1-hexene (500 μl, 4.0 mmol) was added under nitrogen. Afterwards, a $^{31}P\{^1H\}$ NMR spectrum was acquired at room temperature, followed by charging the sapphire tube with CO (14 bar) outside the NMR probe at room temperature and acquiring a $^{31}P\{^1H\}$ NMR spectrum at room temperature. The NMR tube was then again removed from NMR probe head and charged with hydrogen (28 bar), in order to have a CO/H_2 ratio of 1:2 inside the NMR tube, followed by the acquisition of a $^{31}P\{^1H\}$ NMR spectrum at room temperature. Afterwards, the sapphire tube was heated to 60 °C in a temperature-interval of 10 °C, lasting the catalytic reaction at 60 °C for 1 h. At each reaction temperature a $^{31}P\{^1H\}$ NMR spectrum was acquired and at 60 °C, NMR spectra were acquired at a time-interval of 20 min, before the probe head had been cooled to room temperature. Once the probe head reached room temperature, the last $^{31}P\{^1H\}$ NMR spectrum was acquired, followed by the depressurization of the sapphire tube and the analysis of the NMR solution by GC–MS. An analogous NMR experiment in the presence of an excess of NEt_3 (11.1 μl, 0.08 mmol) has been carried out, adding NEt_3 to the initial (1:1, v:v) THF/CD_2Cl_2. solution mixture of **7**. HPNMR experiments with compounds **1** and **3**–**6** were carried out analogously to that described above for **7**.

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