

# 1-Hexene Hydroformylation with the Rhodium(I) Triphosphane Complex $[\text{Rh}(\text{CO})\{\text{PhP}(\text{CH}_2\text{CH}_2\text{PPh}_2)_2\}]\text{PF}_6$ : An In Situ Study Using High-Pressure NMR Spectroscopy

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The rhodium-catalyzed hydroformylation of 1-hexene in THF with the linear triphosphane  $\text{PhP}(\text{CH}_2\text{CH}_2\text{PPh}_2)_2$  [ $\text{PP}_2$ ] has been studied both in situ and in high-pressure autoclaves. Sapphire NMR tubes with titanium valves have proved useful for studying the in situ reactions under conditions of relatively high syngas pressure (30–90 atm  $\text{H}_2/\text{CO}$ ) and temperature (60–100 °C). Under conditions conducive to effective hydroformylation, the catalyst precursor  $[(\text{PP}_2)\text{Rh}(\text{CO})]^+$  is quantitatively converted to the dicarbonyl  $[(\text{PP}_2)\text{Rh}(\text{CO})_2]^+$ , which is also the termination product of the catalysis. Irrespective of the syngas composition and of the total pressure, the dicarbonyl complex is the only phosphorus-containing species detectable on the NMR time-scale during the course of the isomerization and hydroformylation of the alkene. The  $\text{PP}_2$ -Rh catalytic system exhibits some peculiar features that may be summarized as follows. (i) Very high partial pressures of CO (120 atm) neither inhibit the hydroformylation nor af-

fect the *n/i* selectivity; (ii) alkene hydrogenation occurs neither at very high partial pressures of  $\text{H}_2$  (120 atm) nor in the absence of added CO; (iii) the isomerization rate is slightly faster than that of hydroformylation; (iv) terminal and internal alkenes (2-, 3-hexenes) are hydroformylated with comparable rates. Various control experiments have been carried out using in-situ NMR, as well as batch experiments under different reaction conditions or with different catalyst precursors. Despite these extensive studies, unambiguous conclusions about the catalysis mechanism have not been reached. In particular, the possibility that different catalysts may be operative depending on the reaction conditions cannot be ruled out. The hydroformylation results rule out the involvement of phosphane-free "Rh-CO" catalysts, even under conditions of very high partial pressure of CO, and point to " $(\text{PP}_2)\text{Rh}(\text{CO})_x$ " catalysts with small steric hindrance over the whole range of syngas pressures investigated.

## Introduction

Hydroformylation – the metal-catalyzed transformation of alkenes to aldehydes with CO and  $\text{H}_2$  – represents one of the largest industrial applications of homogeneous catalysis. The reaction, discovered by Roelen in 1938, was launched in the chemical industry about thirty years later<sup>[1]</sup>. Since then, a lot of progress has been made through the development of more efficient metal catalysts, particularly those comprising phosphane–rhodium complexes<sup>[2]</sup>. Nonetheless, hydroformylation is still the subject of innumerable studies motivated by the need to increase the selectivity in either linear or branched aldehydes, to reduce by-product formation and to apply milder and more environmentally friendly reaction conditions<sup>[2][3]</sup>.

In the light of successful reactions with bidentate phosphane ligands<sup>[2a]</sup>, the use of rhodium catalysts stabilized by phosphanes with higher hapticity, i.e. tri- and tetradentate ligands, has also been considered<sup>[4][5][6][7]</sup>. The underlying motivations were based on the assumption that a polydentate ligand, controlling the stereochemistry of the metal complex, would have better controlled the regiochemistry of hydroformylation while maintaining or even improving

the stability and efficiency of the catalysts<sup>[8]</sup>. However, with the exception of the binuclear catalyst precursor  $\text{rac}[\text{Rh}_2(\text{nbd})\text{L}]^{2+}$  [ $\text{nbd}$  = norbornadiene;  $\text{L} = (\text{Et}_2\text{PCH}_2\text{CH}_2)\text{-PhPCH}_2\text{PPh}(\text{CH}_2\text{CH}_2\text{PEt}_2)$ ]<sup>[3e][5]</sup>, all the other polyphosphane–rhodium complexes investigated have failed to combine high catalytic activity with high regioselectivity<sup>[6][7]</sup>. The poor regioselectivity exhibited by catalyst precursors such as  $[(\text{triphos})\text{RhH}(\text{C}_2\text{H}_4)]$  or  $[(\text{triphos})\text{RhH}(\text{CO})]$  [ $\text{triphos} = \text{MeC}(\text{CH}_2\text{PPh}_2)_3$ ]<sup>[7]</sup>, was later rationalized in terms of an "arm-off" dissociation process occurring under the actual hydroformylation conditions<sup>[8]</sup>.

The limited number of rhodium compounds studied, essentially a few examples with the tripodal ligand triphos, does not allow one to state that "arm-off" processes invariably occur in hydroformylation reactions catalyzed by triphosphane complexes. This is because a  $d^8$ -metal complex of a tridentate phosphane containing participative ligands (e.g. hydride, CO, alkene) in the fourth and/or fifth position(s) would not need, in principle, to unfasten a phosphane arm to accommodate the three components of a hydroformylation reaction<sup>[4]</sup>. With the aim of providing more information on this matter, we decided to study the hydroformylation of 1-hexene in the presence of the  $\text{Rh}^I$

catalyst precursor  $[(PP_2)Rh(CO)]PF_6$ , where  $PP_2$  is the linear triphosphane  $PhP(CH_2CH_2PPh_2)_2$ . Unlike triphos, this ligand can adopt either meridional or facial coordination geometries<sup>[9]</sup>.

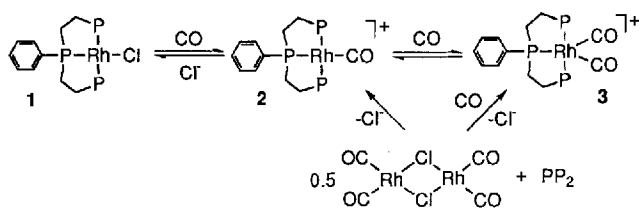
The results of various studies ranging from batch to in situ reactions are reported herein, together with a qualitative mechanistic interpretation.

## Results

### Synthesis and Characterization of the Catalyst Precursor $[(PP_2)Rh(CO)]PF_6$

Reaction of the square-planar  $Rh^I$  chloride complex  $[(PP_2)RhCl]^{[9][10]}$  (**1**) with  $TiPF_6$  in THF, followed by treatment with CO (1 atm), provides an excellent method for the synthesis of the carbonyl derivative  $[(PP_2)Rh(CO)]PF_6$  (**2**). A one-pot procedure for obtaining **2** is also available using the dimer  $[Rh(\mu-Cl)(CO)_2]_2$  as the source of the  $Rh-CO$  moiety. Irrespective of the synthetic route, however, the selective formation of **2** only occurs when the product is isolated by adding *n*-hexane to the reaction mixture after purging with  $N_2$  (yellow crystals), or by removing the solvent in vacuo (yellow powder). Any attempt to precipitate **2** under a CO atmosphere actually resulted in the isolation of the five-coordinate dicarbonyl complex  $[(PP_2)Rh(CO)_2]PF_6$  (**3**) (Scheme 1). At ambient temperature, the latter compound dissolves in THF under nitrogen, slowly converting to **2** via CO decoordination. This process is completely reversible and **3** is regenerated by bubbling CO through the solution. The tetraphenylborate salts  $[(PP_2)Rh(CO)]BPh_4$  (**2'**) and  $[(PP_2)Rh(CO)_2]BPh_4$  (**3'**) can be prepared by trivial metathesis reactions in THF between **2** (or **3**) and  $NaBPh_4$ .

Scheme 1



Overall, the reactivity pattern exhibited by **1** and illustrated in Scheme 1 is comparable to that of the complex  $[RhLCl]$ , where  $L$  is the triphosphane ligand  $PhP(CH_2CH_2CH_2PPh_2)_2$ , differing from  $PP_2$  in that it contains trimethylene linkages between the phosphorus atoms<sup>[11]</sup>.

NMR and IR characterization of **2** is unambiguously consistent with a square-planar  $Rh^I$  complex containing a terminal carbonyl ligand *trans* to the central phosphorus atom. In particular, the temperature-invariant  $^{31}P\{^1H\}$ -NMR spectrum shows a canonical  $AM_2X$  system with chemical shifts and coupling constants typical of four-coordinate  $Rh^I$  complexes stabilized by tridentate phosphanes<sup>[11][12]</sup>. The presence of a CO ligand in a square-planar  $d^8$ -metal complex is unequivocally shown by a band at  $2016\text{ cm}^{-1}$  in the IR spectrum and by a carbon resonance at  $\delta = 193.2$  in the  $^{13}C\{^1H\}$ -NMR spectrum. This reso-

nance appears as a doublet of doublets of triplets, with the largest coupling being that to the central phosphorus atom ( $J_{C,P} = 89.8\text{ Hz}$ ).

In the early 1970s, Taqui Khan and Martell reported that a beige-colored product, formulated as  $[(PP_2)Rh(CO)]Cl$ , was obtained by the reaction of  $PP_2$  with  $[RhCl(CO)(PPh_3)_2]$  in benzene<sup>[13]</sup>. This compound was assigned a cationic square-planar structure, almost exclusively on the basis of IR data [ $\nu(CO)$   $1935\text{ cm}^{-1}$ ]. However, these data are at variance with our data for **2**, as well as those for other similar  $Rh^I$  complexes<sup>[11]</sup>. Indeed, a  $\nu(CO)$  value significantly below  $2000\text{ cm}^{-1}$  is much more consistent with a five-coordinate  $Rh^I$  monocarbonyl species<sup>[11]</sup>. On the other hand, the existence of  $[(PP_2)Rh(CO)]Cl$  in solutions free from dissolved CO is highly questionable as we have found that the addition of LiCl to a solution of **2** under nitrogen yields the chloride complex **1** and CO.

The dicarbonyl derivative **3** is assigned a five-coordinate coordination geometry both in the solid state [two  $\nu(CO)$  bands at  $2045$  and  $2000\text{ cm}^{-1}$ ] and in solution, where no free phosphane atom is seen by variable-temperature NMR spectroscopy. In the absence of an X-ray analysis, unambiguous discrimination between trigonal-bipyramidal and square-pyramidal structures cannot be made. However, on the basis of theoretical arguments<sup>[14]</sup> as well as the NMR characterization, **3** may be assigned a trigonal-bipyramidal geometry with the two CO ligands and the bridgehead phosphorus of  $PP_2$  in the equatorial positions. Indeed, the  $^{31}P\{^1H\}$ -NMR spectrum (temperature invariant  $AM_2X$  spin system) is quite similar to that of the precursor **2**, indicating that the triphosphane ligand has not changed its meridional bonding mode<sup>[15]</sup>. Consistently, in the  $^{13}C\{^1H\}$ -NMR spectrum, the two carbonyl ligands appear as a single resonance at  $\delta = 194.1$  with no resolvable coupling over the temperature window investigated ( $-50/80\text{ }^\circ\text{C}$ ).

### 1-Hexene Hydroformylation. Autoclave Experiments

Complex **2** has been used as a catalyst precursor for the hydroformylation of 1-hexene in THF under different reaction conditions. Selected results are presented in Tables 1 and 2 for a 1-hexene to **2** ratio of 100, a reaction temperature of  $60\text{ }^\circ\text{C}$  and a reaction time of 3 h.

Appreciable catalytic activity is apparent using just 6 atm of a 1:1  $CO/H_2$  mixture. Most 1-hexene (ca. 80%), however, is isomerized, aldehydes (*n/i* ratio = 2.5) accounting for only ca. 8% of the converted substrate (entry 1). Among the internal alkenes produced, 2-hexenes, particularly the *trans* isomer, are formed to a much greater extent than 3-hexenes (75:7 ratio). Increasing the  $H_2$  pressure to 27, 60, and 120 atm at a constant CO pressure of 3 atm (entries 2, 3, 4, respectively) steadily increases the conversion to aldehydes and concomitantly lowers the *n/i* ratio due to hydroformylation of the internal alkenes, which proceeds at a slower rate than that of 1-hexene (vide infra). At the highest  $H_2$  pressure investigated, 86% of the substrate is converted to a ca. 1:1 mixture of linear and branched aldehydes. A similar trend is observed using a fixed CO pressure of 15 atm and varying the  $H_2$  pressure from 15 to 45 atm (entries

Table 1. Hydroformylation of 1-hexene catalyzed by  $[(PP_2)Rh(CO)]PF_6$  (**2**): dependence on the partial pressure of  $H_2$ <sup>[a]</sup>

entry	P(CO) [atm]	P( $H_2$ ) [atm]	ald. conv. [%]	<i>n/i</i>	reaction mixture composition (%)								
					heptanal	2-methyl-hexanal	2-ethyl-pentanal	hexane	<i>cis</i> -2-hexene	<i>trans</i> -2-hexene	<i>cis</i> -3-hexene	<i>trans</i> -3-hexene	1-hexene
1	3	3	7.3	2.5	5.2	2.0	0.1	0.5	19.0	55.9	0.4	6.3	10.6
2	3	27	38.5	2.6	27.7	10.0	0.8	0.8	14.1	36.9	0.4	4.2	5.1
3	3	60	55.0	2.0	36.9	15.4	2.7	0.8	9.1	26.4	0.8	5.5	2.4
4	3	120	86.1	1.3	49.0	28.1	9.0	1.0	1.9	7.3	0.2	2.0	1.5
5	15	15	54.7	2.0	36.7	16.8	1.2	0.4	10.9	28.4	0.3	3.5	1.8
6 <sup>[b]</sup>	15	15	35.4	2.0	23.5	11.9	—	0.3	1.8	4.1	—	0.1	58.3
7	15	45	91.8	1.0	46.0	34.3	11.5	0.1	1.4	4.3	0.1	1.4	0.9

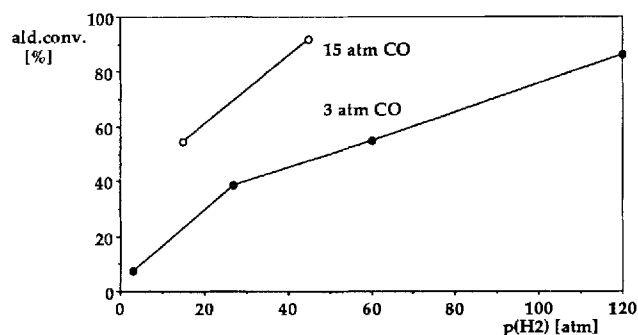
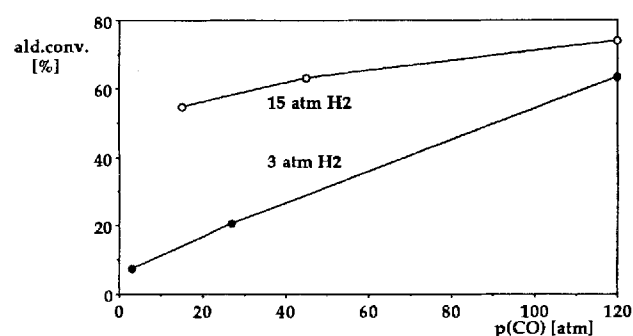
<sup>[a]</sup> Conditions: catalyst (16 mg, 0.02 mmol), 1-hexene (168 mg, 2 mmol), THF (25 ml), 60 °C, 3 h. — <sup>[b]</sup> Reaction carried out in the presence of  $NEt_3$  (0.1 ml, 0.72 mmol).

5, 7). At the latter pressure, almost all of the 1-hexene is consumed to give aldehydes (*n/i* ratio = 1).

When, on the other hand, the  $H_2$  pressure is maintained constant at 3 atm (or 15 atm) and the CO pressure is increased from 3 to 120 atm (or from 15 to 120 atm) (Table 2), it is apparent that the overall conversion to aldehydes still increases with the total pressure. The rate, however, is significantly slower than that of comparable runs in which  $H_2$  prevails over CO. In contrast, at comparable total pressure, neither the isomerization rate nor the *n/i* selectivity are significantly affected by the composition of the syngas (see for example entries 2/8; 4/9), which suggests either a unique catalytically active species or different catalysts with a similar structure over the whole range of  $H_2$  and CO pressures investigated. Irrespective of the reaction conditions, no Rh precipitation was seen at the end of any of the runs and the dicarbonyl complex **3** was recovered almost quantitatively.

The dependence of the conversion of 1-hexene to aldehydes on the partial pressure of either  $H_2$  or CO is presented schematically in Figures 1 and 2.

Notably, irrespective of the hydroformylation conditions, the amount of hydrogenated substrate, hexane, is negligible, even at elevated temperatures and with a syngas disproportionately rich in  $H_2$  (entry 4). This result prompted us to investigate the hydrogenation of 1-hexene in the presence of **2** in THF (60 °C, alkene-to-**2** ratio: 100, 15 atm  $H_2$ ). Almost no hydrogenation occurred within 3 h (< 2% hexane), which is unexpected behavior for a rhodium catalyst exhibiting good efficiency for the hydroformylation of the same substrate<sup>[2]</sup>. Instead, isomerization of 1-hexene to a

Figure 1. Hydroformylation of 1-hexene catalyzed by  $[(PP_2)Rh(CO)]PF_6$  (**2**). Effect of the partial pressure of  $H_2$  on the formation of aldehydesFigure 2. Hydroformylation of 1-hexene catalyzed by  $[(PP_2)Rh(CO)]PF_6$  (**2**). Effect of the partial pressure of CO on the formation of aldehydesTable 2. Hydroformylation of 1-hexene catalyzed by  $[(PP_2)Rh(CO)]PF_6$  (**2**): dependence on the partial pressure of CO<sup>[a]</sup>

entry	P(CO) [atm]	P( $H_2$ ) [atm]	ald. conv. [%]	<i>n/i</i>	reaction mixture composition (%)								
					heptanal	2-methyl-hexanal	2-ethyl-pentanal	hexane	<i>cis</i> -2-hexene	<i>trans</i> -2-hexene	<i>cis</i> -3-hexene	<i>trans</i> -3-hexene	1-hexene
1	3	3	7.3	2.5	5.2	2.0	0.1	0.5	19.0	55.9	0.4	6.3	10.6
8	27	3	20.4	2.6	14.8	5.6	—	1.0	17.0	46.2	0.5	3.3	11.6
9	120	3	63.3	1.9	41.4	21.9	—	1.2	7.4	21.1	0.4	1.3	5.3
5	15	15	54.7	2.0	36.7	16.8	1.2	0.4	10.9	28.4	0.3	3.5	1.8
10	45	15	63.2	1.9	41.3	21.9	—	0.4	6.7	19.1	0.4	1.1	9.1
11	120	15	74.0	1.5	44.4	29.6	—	1.0	3.2	7.8	0.5	0.3	13.2

<sup>[a]</sup> Conditions: catalyst (16 mg, 0.02 mmol), 1-hexene (168 mg, 2 mmol), THF (25 ml), 60 °C, 3 h.

Table 3. Hydroformylation of 1-, *trans*-2- and *trans*-3-hexene catalyzed by [(PP<sub>2</sub>)Rh(CO)]PF<sub>6</sub> (**2**)<sup>[a]</sup>

entry	substrate	time [h]	ald. conv [%]	<i>n/i</i>	reaction mixture composition (%)								1-hexene
					heptanal	2-methyl- hexanal	2-ethyl- pentanal	hexane	<i>cis</i> -2- hexene	<i>trans</i> -2- hexene	<i>cis</i> -3- hexene	<i>trans</i> -3- hexene	
5	1-hexene	3	54.7	2.0	36.7	16.8	1.2	0.4	10.9	28.4	0.3	3.5	1.8
12	1-hexene	24	98.5	0.7	42.1	40.5	15.9	0.2	0.2	0.8	—	0.2	0.1
13	<i>trans</i> -2-hex.	3	40.0	0.1	5.3	23.5	11.2	0.6	11.9	35.7	—	9.7	2.1
14	<i>trans</i> -2-hex.	24	97.1	0.1	11.2	53.7	32.2	0.3	0.4	1.6	—	0.4	0.2
15	<i>trans</i> -3-hex.	3	40.0	0.1	4.3	17.1	18.6	0.5	9.3	29.4	—	18.0	2.8
16	<i>trans</i> -3-hex.	24	98.1	0.1	11.3	47.5	39.3	0.2	0.2	0.9	—	0.5	0.1

<sup>[a]</sup> Conditions: catalyst (16 mg, 0.02 mmol), hexene (168 mg, 2 mmol), THF (25 ml), 60 °C, 3 h, 15 atm of CO, 15 atm of H<sub>2</sub>.

ca. 10:10:2:0.5 mixture of *cis*-2-hexene, *trans*-2-hexene, *trans*-3-hexene, and *cis*-3-hexene took place. Under these conditions, the total conversion to internal alkenes, however, did not exceed 22.5% of the starting terminal alkene, a percentage that is remarkably lower than that observed using 3 atm of H<sub>2</sub> and 3 atm of CO (ca. 82%, entry 1), and in general when CO is present in the reaction mixture (Table 1). This finding thus indicates that the reaction of the monocarbonyl complex **2** with CO is a necessary step for the formation of an active isomerization catalyst.

In order to acquire further information on the hydroformylation of 1-hexene catalyzed by **2** at 60 °C and with a fixed substrate to **2** ratio of 100, several experiments with **2** as catalyst precursor were carried out under different reaction conditions.

In a series of runs at a fixed total pressure, but with varied partial pressures of H<sub>2</sub> and CO, the product composition was determined every 30 min, showing the absence of an induction period in all cases.

Randomly, some reactions were performed using the tetraphenylborate salt **2'** as the catalyst precursor to explore a possible counterion effect on either the hydroformylation rate or on the product composition. From this study, it was concluded that the substitution of BPh<sub>4</sub><sup>−</sup> for PF<sub>6</sub><sup>−</sup> has no effect on the catalysis. In contrast, the presence of a strong base such as NEt<sub>3</sub> was found to significantly affect the hydroformylation of 1-hexene (entry 6). In comparison to the analogous run 5, the reaction with NEt<sub>3</sub> yields less of the aldehydes (35 vs. 55%) with a similar *n/i* selectivity, while isomerized alkenes are produced in a much smaller amount (6 vs. 43%). Hence, a different catalyst is most probably at work in the base-assisted reactions. This is indirectly but substantially demonstrated by a hydrogenation reaction of 1-hexene (60 °C, 15 atm H<sub>2</sub>) carried out in the

presence of an excess of NEt<sub>3</sub>. In contrast to the analogous "neutral" reaction, the hydrogenation to hexane does occur (23% conversion in 3 h), together with isomerization (17%) almost exclusively to *trans*-2- and *cis*-2-hexenes in a 1:1 ratio.

Finally, the hydroformylation reactions of the internal isomers *trans*-2-hexene and *trans*-3-hexene were studied and the results compared to analogous reactions of 1-hexene (Table 3). As one might have inferred from analysis of the data in Tables 1 and 2, the hydroformylation rates of these internal alkenes are slower than that of the terminal alkene. The difference, however, is fairly small (40 vs. 55% conversion in 3 h), which is a good indication of a non-sterically congested catalytically active species. Consistently, 2- and 3-hexenes show identical hydroformylation rates.

Reactions at 30 atm of a 1:1 H<sub>2</sub>/CO mixture were also performed using either higher temperature (80 °C) or higher catalyst concentrations (0.02 vs. 0.04 and 0.06 mmol). In either case, increased conversions to aldehydes were observed, which is in line with the vast majority of phosphane-modified rhodium hydroformylation catalysts<sup>[2]</sup>.

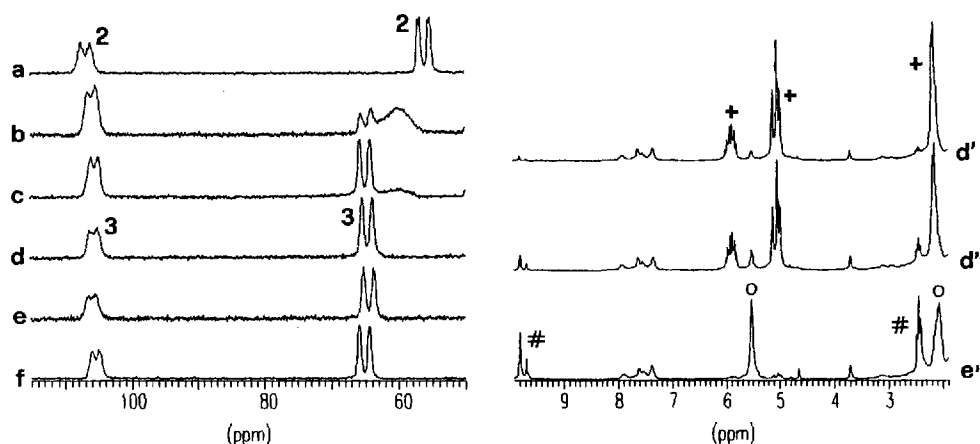
Independent hydroformylation control experiments were carried out using either Rh<sub>4</sub>(CO)<sub>12</sub> or a 1:4 mixture of Rh<sub>4</sub>(CO)<sub>12</sub>/PP<sub>2</sub> as catalyst precursors under comparable conditions (30 atm 1:1 CO/H<sub>2</sub>, 60 °C, 1-hexene to rhodium ratio of 100). The results obtained are reported in Table 4 and clearly show that the presence of PP<sub>2</sub> leads to a product distribution that is similar to that of the analogous reaction catalyzed by **2** (see entries 5 and 18). In particular, 2-ethylpentanal is not formed and heptanal prevails over 2-methylhexanal (*n/i* ratio of 2.4). In contrast, the reaction with Rh<sub>4</sub>(CO)<sub>12</sub> yields an appreciable amount of 2-ethylpentanal and a linear to branched ratio of 0.6, which is consistent with a phosphane-free rhodium catalyst<sup>[2]</sup>.

Table 4. Hydroformylation of 1-hexene catalyzed by Rh<sub>4</sub>(CO)<sub>12</sub><sup>[a]</sup>

entry	ald. conv [%]	<i>n/i</i>	reaction mixture composition (%)								1-hexene
			heptanal	2-methyl- hexanal	2-ethyl- pentanal	hexane	<i>cis</i> -2- hexene	<i>trans</i> -2- hexene	<i>cis</i> -3- hexene	<i>trans</i> -3- hexene	
17	69.8	0.6	27.2	31.4	11.2	1.5	5.6	15.3	0.2	5.3	2.3
18 <sup>[b]</sup>	73.2	2.4	51.9	21.3	—	0.5	3.8	10.3	0.6	1.8	9.7

<sup>[a]</sup> Conditions: catalyst (4 mg, 0.005 mmol), hexene (168 mg, 2 mmol), THF (25 ml), 60 °C, 3 h, 15 atm of CO, 15 atm of H<sub>2</sub>. — <sup>[b]</sup> Reaction carried out in the presence of PP<sub>2</sub> (11 mg, 0.02 mmol).

Figure 3.  $^{31}\text{P}\{^1\text{H}\}$  (81.01 MHz) and  $^1\text{H}$  (200.13 MHz) HPNMR study of the hydroformylation of 1-hexene catalyzed by  $[(\text{PP}_2)\text{Rh}(\text{CO})]\text{PF}_6$  (**2**) (sapphire tube,  $[\text{D}_8]\text{THF}$ , 30 atm of a 1:1 mixture of  $\text{CO}/\text{H}_2$ , 1-hexene/**2** = 50:1)<sup>[a]</sup>



[a]  $^{31}\text{P}\{^1\text{H}\}$ -NMR spectra: at 20 °C under nitrogen (a); after 45 min (b) and 110 min (c) under  $\text{CO}/\text{H}_2$  at room temperature; after 60 min under  $\text{CO}/\text{H}_2$  at 60 °C (d); after 60 min under  $\text{CO}/\text{H}_2$  at 80 °C (e); after the NMR probe was cooled to room temperature (f).  $^1\text{H}$ -NMR spectra: after 20 min (d') and 55 min (d'') under  $\text{CO}/\text{H}_2$  at 60 °C; after 70 min under  $\text{CO}/\text{H}_2$  at 80 °C (e'). (3)  $[(\text{PP}_2)\text{Rh}(\text{CO})_2]\text{PF}_6$ ; (+) 1-hexene; (o) 2- and 3-hexenes; (#) aldehydes.

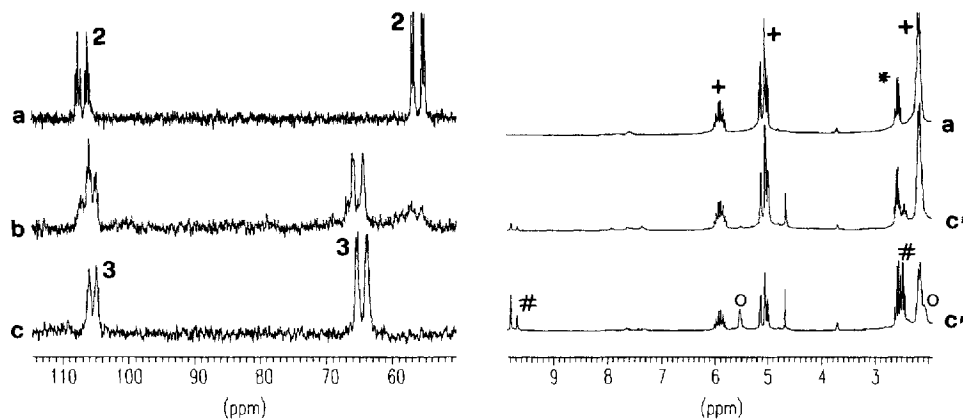
#### In-Situ NMR Spectroscopy

Figure 3 shows the  $^{31}\text{P}\{^1\text{H}\}$ - and  $^1\text{H}$ -NMR spectra obtained during a typical catalysis in the high-pressure NMR tube. The conditions employed in the in-situ study were as similar as possible to those of the autoclave reactions (15 atm  $\text{CO}$ , 15 atm  $\text{H}_2$ , 1-hexene/**2** = 50,  $[\text{D}_8]\text{THF}$ ), the most diverging parameter being a higher concentration of the catalyst precursor. This modification was made simply to reduce the time of acquisition of reliable NMR spectra.

Prior to the introduction of  $\text{CO}/\text{H}_2$ , all rhodium is present as **2** (trace a). Upon addition of syngas,  $^{31}\text{P}\{^1\text{H}\}$ -NMR shows that **2** starts converting to the dicarbonyl complex **3** even at room temperature (trace b). After ca. 2 h at room temperature, the latter complex largely prevails over the monocarbonyl precursor **2** (trace c). During this time no

reaction involving 1-hexene occurs. Increasing the temperature to 60 °C converts all **2** to **3** after 1 h (trace d) and also promotes both the isomerization and the hydroformylation of 1-hexene, to afford a mixture of internal alkenes and aldehydes, respectively (trace d' after 20 min; trace d'' after 55 min). Heating the tube to 80 °C transforms most of the 1-hexene (> 94%) after ca. 1 h (trace e'), while **3** remains as the only phosphorus-containing species detectable by  $^{31}\text{P}$ -NMR spectroscopy (trace e). The dicarbonyl complex is again the only complex detectable after the reaction is quenched by cooling the probe-head to room temperature (trace f). Only when the tube is depressurized and the syngas is flushed out with  $\text{N}_2$ , **3** is consumed to give the monocarbonyl precursor **2**. GC/MS analysis showed the reaction mixture to contain 54% of isomerization products

Figure 4.  $^{31}\text{P}\{^1\text{H}\}$  (81.01 MHz) and  $^1\text{H}$  (200.13 MHz) HPNMR study of the hydroformylation of 1-hexene catalyzed by  $[(\text{PP}_2)\text{Rh}(\text{CO})]\text{PF}_6$  (**2**) in the presence of  $\text{NEt}_3$  (sapphire tube,  $[\text{D}_8]\text{THF}$ , 30 atm of a 1:1 mixture of  $\text{CO}/\text{H}_2$ , 1-hexene/ $\text{NEt}_3$ /**2** = 50:4:1)<sup>[a]</sup>



[a]  $^{31}\text{P}\{^1\text{H}\}$ -NMR spectra: at 20 °C under nitrogen (a); after 60 min under  $\text{CO}/\text{H}_2$  at room temperature (b); after 60 min under  $\text{CO}/\text{H}_2$  at 60 °C (c).  $^1\text{H}$ -NMR spectra: at 20 °C under nitrogen (a'); after 70 min (c') and 180 min (c'') under  $\text{CO}/\text{H}_2$  at 60 °C. (3)  $[(\text{PP}_2)\text{Rh}(\text{CO})_2]\text{PF}_6$ ; (+) 1-hexene; (o) 2-hexenes; (+)  $\text{NEt}_3$ ; (#) aldehydes.

(*cis*- and *trans*-2-hexene, *trans*-3-hexene) and 40% of aldehydes (heptanal, 2-methylhexanal, and 2-ethylpentanal in a ratio of 70:28:2).

At first glance, the overall HPNMR picture of the hydroformylation of 1-hexene in the presence of an excess of  $\text{NEt}_3$  (Figure 4) is not too dissimilar from that just described. On more detailed inspection, however, one may readily infer that, analogously to the autoclave reaction, the addition of the base leads to the formation of different catalytically active species.

The dicarbonyl complex **3** remains as the only metal complex that is formed when the tube is subjected to a 1:1 mixture of  $\text{H}_2/\text{CO}$  (30 atm) in the temperature range from 20 to 60 °C. At the latter temperature, however, aldehydes are already produced after the acquisition of the first spectrum (ca. 10 min) and their concentration steadily increases with time. Only after 70 min (trace c') do signals due to the internal alkenes become apparent in the  $^1\text{H}$ -NMR spectrum, consistent with a slow isomerization reaction. Appreciable isomerization to *cis*- and *trans*-2-hexenes (GC) occurs only after 3 h at 60 °C (trace c''). At this stage, the hydroformylation products, heptanal and 2-methylhexanal, are formed in a ratio of 72:28.

Qualitatively, these HPNMR experiments are in good accord with the corresponding autoclave reaction. Some minor differences in the product distribution (i.e. a greater proportion of isomerization products) may be due to mass transfer limitations<sup>[16]</sup>. Indeed, mass transfer of reactive gases from the head-space of the NMR tube might not be efficient enough to replenish the solution, which is being depleted of CO and  $\text{H}_2$  by the catalyst. This may explain why isomerization is generally favored in the HPNMR reactions.

In separate HPNMR experiments,  $[\text{D}_8]\text{THF}$  solutions of **2**, either alone or together with 1-hexene, were subjected to 15–30 atm of  $\text{H}_2$  at 60–80 °C. The thermal reaction of **2** with 1-hexene under a nitrogen atmosphere was also investigated. In no case was a change in the  $^{31}\text{P}$ -NMR spectrum seen within 4 h. Only when the tube containing the  $[\text{D}_8]\text{THF}$  solution of **2** was pressurized with 30 atm of CO was the selective formation of the dicarbonyl **3** observed.

In line with the autoclave experiments, a hydrogenation reaction of 1-hexene catalyzed by **2** carried out in the HPNMR tube yielded isomerization products, whilst neither *n*-hexane nor aldehydes were apparently formed. The lack of aldehyde products (obviously, we expected to detect only traces of aldehydes as the amount of **2** that is converted to the catalytically active species is not detected by  $^{31}\text{P}$ -NMR spectroscopy) may be taken as an indication that the original CO ligand in **2** does not insert into the Rh-alkyl bond that necessarily forms during isomerization.

## Discussion

In the course of the hydroformylation and isomerization of 1-hexene, NMR spectroscopy shows the quantitative conversion of the precursor **2** to the dicarbonyl complex **3**. The latter is the only Rh-phosphane species to be detected by  $^{31}\text{P}\{^1\text{H}\}$ -NMR spectroscopy during the catalysis over the

wide range of partial pressures of  $\text{CO}/\text{H}_2$  investigated, and is also the species that is recovered at the end of the catalysis. As it is, **3** cannot be a hydroformylation catalyst, however. Any step to initiate the catalytic process (e.g. the coordination of the alkene or the oxidative addition of  $\text{H}_2$ ) would necessarily involve the decoordination of either the CO or phosphane arm(s) of  $\text{PP}_2$  from **3** (metal complexes containing  $\text{PP}_2$  acting as either a bidentate ( $\text{P}_{\text{central}}-\text{P}_{\text{terminal}}$ ) or a monodentate ( $\text{P}_{\text{central}}$ ) ligand are known)<sup>[12b][17]</sup>. On the basis of the in situ NMR evidence and of the batch hydroformylation reactions, we cannot exclude either mechanism for the generation of the catalytically active species. Moreover, it cannot be ruled out that different catalysts might be operative depending on the reaction conditions. In contrast, the involvement of phosphane-free “Rh-CO” catalysts can be ruled out in the light of the hydroformylation results obtained with  $\text{Rh}_4(\text{CO})_{12}$ , as well as the HPNMR spectra, which do not show phosphane-arm dissociation even during catalysis<sup>[8]</sup>. Moreover, we are not aware of hydroformylation reactions with phosphane-Rh precursors in which the effective catalyst does not contain phosphane ligands. Alkene hydroformylation by “Rh-CO” has been demonstrated in some cases in which the catalyst precursors contain non-carbonyl ligands. These, however, are invariably groups with much weaker coordinating properties than phosphanes (e.g. cycloocta-1,5-diene)<sup>[18]</sup>.

From a qualitative viewpoint, the fact that the present  $\text{PP}_2$ -Rh system catalyzes isomerization concurrently with hydroformylation at any partial pressure of either CO or  $\text{H}_2$  is a good indication that the formation of the acyl intermediate is not as fast as alkyl formation<sup>[12]</sup>. In turn, the fact that hydrogenation to hexane does not occur, even under very high partial pressures of  $\text{H}_2$ , indicates that the reductive coupling between alkyl and hydride to form alkane is very much disfavored compared to both alkyl migration (or CO insertion) and  $\beta$ -H elimination. In general, this occurs when the hydride and alkyl ligands are *trans* to each other in the metal coordination sphere. Finally, the low *n/i* selectivity indicates the  $\pi$ -alkene intermediate to be a non-sterically congested species and thus suggests that  $\text{PP}_2$  does not use all its phosphorus donor atoms for coordination in the catalytically active species.

The addition of  $\text{NEt}_3$  to the catalytic mixture generates a different catalyst, most likely a monohydride species formed by heterolytic splitting of  $\text{H}_2$  as generally occurs in base-assisted hydroformylations catalyzed by phosphane-modified rhodium complexes<sup>[2][19]</sup>. This catalytic system exhibits its own activity and selectivity, which differ from those of the  $\text{PP}_2$  system in the absence of base. Nonetheless, in situ  $^{31}\text{P}$ -NMR experiments under actual hydroformylation conditions do not show any  $\text{PP}_2$  complexes other than the dicarbonyl **3** generated by CO addition to **2**. This means that, irrespective of the presence of the base, the step that influences the hydroformylation rate by  $\text{PP}_2$ -Rh catalysis is the generation of the catalytically active species from the dicarbonyl **3**.

## Conclusions

In a hypothetical classification of phosphane-modified rhodium catalysts for the hydroformylation of terminal alkenes, the present  $\text{PP}_2\text{-Rh}$  systems would be inserted among those exhibiting moderate activity and poor selectivity.<sup>[2]</sup> On the other hand, this  $\text{PP}_2$  system shows some interesting characteristics in the hydroformylation of 1-hexene, which may be summarized as follows. (i) Very high partial pressures of CO neither inhibit the hydroformylation nor affect the *n/i* selectivity; (ii) alkene hydrogenation does not occur even at very high partial pressures of  $\text{H}_2$ ; (iii) the hydroformylation of the isomerized alkenes (2-, 3-hexenes) proceeds at a rate that is only slightly slower than that of the terminal alkene. The most notable features of the present system, however, are the adaptability to a great variety of reaction conditions (a variety of syngases can efficiently be employed) and the remarkable robustness as all the rhodium is recovered at the end of the reactions as the dicarbonyl complex **3**.

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## Experimental Section

Unless otherwise stated, all reactions and manipulations were routinely performed under a nitrogen atmosphere by using standard Schlenk techniques. High-pressure reactions under controlled pressures of  $\text{H}_2$  and CO were performed in a stainless steel Parr 4561 reactor (160 ml) equipped with a magnetic drive stirrer rotating at 300 rpm and a Parr 4842 temperature and pressure controller. Tetrahydrofuran (THF) was purified by distillation under nitrogen from  $\text{LiAlH}_4$  prior to use. Commercial 1-hexene (Aldrich) was passed through an activated  $\text{Al}_2\text{O}_3$  column, distilled under nitrogen and stored at 0 °C. The ligand  $\text{PhP}(\text{CH}_2\text{CH}_2\text{PPh}_2)_2$  [ $\text{PP}_2$ ] and the cluster  $\text{Rh}_4(\text{CO})_{12}$  were purchased from Aldrich and Strem, respectively. All the other reagents and chemicals were reagent grade and were used as received from commercial suppliers. The rhodium complexes  $[\text{Rh}(\mu\text{-Cl})(\text{CO})_2]_2$ <sup>[20]</sup> and  $[(\text{PP}_2)\text{RhCl}]$ <sup>[10]</sup> (**1**) were prepared as described previously. Deuterated solvents for NMR measurements (Merck) were dried over activated molecular sieves (4 Å). —  $^1\text{H}$ -,  $^{13}\text{C}\{^1\text{H}\}$ - and  $^{31}\text{P}\{^1\text{H}\}$ -NMR spectra were obtained on either a Bruker ACP 200 (200.13, 50.32, and 81.01 MHz, respectively) or a Varian VXR 300 (299.94, 75.43, and 121.42 MHz, respectively) spectrometer. All chemical shifts are reported in ppm ( $\delta$ ) relative to tetramethylsilane, referenced to the chemical shifts of residual solvent resonances ( $^1\text{H}$ ,  $^{13}\text{C}$ ) or 85%  $\text{H}_3\text{PO}_4$  ( $^{31}\text{P}$ ). The 10-mm sapphire NMR tube was purchased from Saphikon, Milford (NH, USA), while the titanium high-pressure valve was constructed at ISSECC-CNR (Firenze, Italy)<sup>[21]</sup>. — GC analyses were performed on a Shimadzu GC-14 A gas chromatograph equipped with a flame-ionization detector. A UCON-oil LB 550-X packed column (PPG, 2 m, 1/8" i.d.) was employed for the determination of hydrocarbons, 2-ethylpentanal, 2-methylhexanal, and heptanal. An  $\text{Al}_2\text{O}_3$ -PLOT capillary column (50 m, 0.32 mm i.d.) was employed for the determination of hexane, 1-hexene, *cis*- and *trans*-2-hexene, and *cis*- and *trans*-3-hexene. The identification of the products was confirmed by GC/MS analyses performed on a Shimadzu QP 5000 apparatus equipped with a 30 m (0.25 mm i.d., 0.25  $\mu\text{m}$  film-thickness) SPB-1 Supelco fused silica capillary column. — Infrared spectra were recorded on a Perkin-Elmer 1600 Series FT-IR spectrophotometer using samples mullied in Nujol between KBr plates. — Conductivities were measured with an Orion Model 990101 conductance cell connected to a Model 101 conductivity meter. The

conductivity data were obtained at sample concentrations of ca.  $10^{-3}$  M in nitroethane solutions at room temperature.

**Preparation of  $[(\text{PP}_2)\text{Rh}(\text{CO})]\text{PF}_6$  (**2**):** A solution of  $\text{TIPF}_6$  (0.35 g, 1 mmol) in THF (10 ml) was slowly added to a stirred suspension of **1** (0.67 g, 1 mmol) in THF (15 ml). Within a few minutes, the starting material dissolved to give a bright-red solution, which turned yellow upon bubbling CO through it for 5 min. After CO was replaced by nitrogen, the solution was stirred for a further 30 min, and then filtered to remove the precipitated  $\text{TiCl}_4$ . Concentration in vacuo to a volume of ca. 10 ml followed by portionwise addition of *n*-hexane (15 ml) led to the precipitation of **2** as yellow crystals, which were collected by filtration and washed with *n*-pentane; yield 85%. —  $\text{C}_{35}\text{H}_{33}\text{F}_6\text{OP}_4\text{Rh}$  (810.44): calcd. C 51.87, H 4.10, Rh 12.70; found C 51.21, H 4.01, Rh 12.35. —  $\Lambda_{\text{M}}$ :  $79 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$ . — IR:  $\tilde{\nu} = 2016$  (vs)  $\text{cm}^{-1}$  ( $\text{C}=\text{O}$ ). —  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 20 °C):  $\text{AM}_2\text{X}$  spin system,  $\delta = 104.7$  [dt,  $J(\text{P}_A, \text{P}_M) = 28.6$  Hz,  $J(\text{P}_A, \text{Rh}) = 115.8$  Hz;  $\text{P}_A$ ], 55.5 [dd,  $J(\text{P}_M, \text{Rh}) = 128.5$  Hz;  $\text{P}_M$ ]. —  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 20 °C):  $\delta = 27.3$  [dt,  $J(\text{C}, \text{P}) = 30.3$ , 7.4 Hz;  $\text{CH}_2$ ], 32.1 [q,  $J(\text{C}, \text{P}) = 15.2$  Hz;  $\text{CH}_2$ ], 193.2 [ddt,  $J(\text{C}, \text{P}_{\text{trans}}) = 89.8$  Hz,  $J(\text{C}, \text{Rh}) = 63.5$  Hz,  $J(\text{C}, \text{P}_{\text{cis}}) = 11.6$  Hz; CO].

**Preparation of  $[(\text{PP}_2)\text{Rh}(\text{CO})]\text{BPh}_4$  (**2'**):** Metathetical reaction of **2** with  $\text{NaBPh}_4$  in  $\text{CH}_2\text{Cl}_2$ /ethanol followed by partial evaporation of the solvents gave **2'** as yellow crystals in 95% yield. —  $\text{C}_{59}\text{H}_{53}\text{BOP}_3\text{Rh}$  (984.71): calcd. C 71.97, H 5.43, Rh 10.45; found C 71.77, H 5.41, Rh 10.00. —  $\Lambda_{\text{M}}$ :  $55 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$ .

**Preparation of  $[(\text{PP}_2)\text{Rh}(\text{CO})_2]\text{Y}$  ( $\text{Y} = \text{PF}_6$ , **3**;  $\text{BPh}_4$ , **3'**):** Compound **2** (or **2'**, 1 mmol) was dissolved in THF (15 ml) saturated with CO at room temperature. After 1 h, ethanol (20 ml) was added and the resulting solution was maintained under CO atmosphere (1 atm). Yellow crystals of **3** (or **3'**) precipitated on standing overnight. They were collected by filtration and washed with *n*-pentane; yield 75–85%. Alternatively, compounds **3** and **3'** were synthesized by reacting the  $\text{PP}_2$  ligand (1 mmol) with  $[\text{Rh}(\mu\text{-Cl})(\text{CO})_2]_2$  (0.5 mmol) in THF under CO atmosphere (1 atm) at room temperature in the presence of  $\text{TIPF}_6$  or  $\text{NaBPh}_4$ , respectively. Compounds **3** and **3'**, which are fairly stable in the solid state under inert atmosphere, convert to the corresponding monocarbonyls **2** and **2'** in ambient temperature solutions unless a positive pressure of CO is provided.

**3:**  $\text{C}_{36}\text{H}_{33}\text{F}_6\text{O}_2\text{P}_4\text{Rh}$  (838.45): calcd. C 51.57, H 3.97, Rh 12.27; found C 51.43, H 3.90, Rh 12.07. —  $\Lambda_{\text{M}}$ :  $82 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$ . — IR:  $\tilde{\nu} = 2045$  (s), 2000 (vs)  $\text{cm}^{-1}$  ( $\text{C}=\text{O}$ ). —  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 20 °C):  $\text{AM}_2\text{X}$  spin system,  $\delta = 104.1$  [dt,  $J(\text{P}_A, \text{P}_M) = 23.5$  Hz,  $J(\text{P}_A, \text{Rh}) = 91.5$  Hz;  $\text{P}_A$ ], 63.6 [dd,  $J(\text{P}_M, \text{Rh}) = 124.3$  Hz;  $\text{P}_M$ ]. —  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 1 atm CO, 20 °C):  $\delta = 29.5$  [dt,  $J(\text{C}, \text{P}) = 32.3$ , 12.2 Hz;  $\text{CH}_2$ ], 31.1 [q,  $J(\text{C}, \text{P}) = 13.2$  Hz;  $\text{CH}_2$ ], 194.1 [br m; CO].

**3':**  $\text{C}_{60}\text{H}_{53}\text{BO}_2\text{P}_3\text{Rh}$  (1012.72): calcd. C 71.16, H 5.28, Rh 10.16; found C 71.01, H 5.21, Rh 10.02. —  $\Lambda_{\text{M}}$ :  $54 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$ .

**Reaction of **2** with LiCl:** A solid sample of LiCl (32 mg, 0.75 mmol) was added to a stirred solution of **2** (200 mg, 0.25 mmol) in THF (20 ml) at room temperature. After 2 h, the solution was concentrated to dryness in vacuo to give **1**.

**Catalytic Hydroformylation Experiments with  $[(\text{PP}_2)\text{Rh}(\text{CO})]^+$ :** The reaction conditions and the results of these experiments are collected in Tables 1–3. In a typical experiment, a solution of **2** (or **2'**, 0.02 mmol) in THF (25 ml) and a 100-fold excess of the substrate (168 mg, 2 mmol) were introduced by suction into a Parr reactor previously evacuated with a vacuum pump. The reac-

tor was then pressurized with  $H_2$  and CO to the desired pressures at room temperature, heated to the appropriate temperature and the contents were stirred. After the chosen time, the reactor was rapidly cooled to room temperature by means of an ice-water bath. After being depressurized and vented under a nitrogen stream, samples of the contents were collected and analyzed by GC and GC/MS.

In selected experiments (3:27 atm  $H_2$ /CO; 27:3 atm  $H_2$ /CO; 15:15 atm  $H_2$ /CO) the course of the reaction was followed with time by GC.

**Catalytic Hydrogenation Experiments with  $[(PP_2)Rh(CO)]^+$ :** In a typical experiment, a solution of **2** (or **2'**, 0.02 mmol) in THF (25 ml) and a 100-fold excess of 1-hexene (168 mg, 2 mmol) were introduced by suction into a Parr reactor previously evacuated with a vacuum pump. The reactor was then pressurized with  $H_2$  to 15 atm at room temperature, heated to 60 °C and the contents were stirred. After 3 h, the reactor was rapidly cooled to room temperature by means of an ice-water bath. After being depressurized and vented under a nitrogen stream, samples of the contents were collected and analyzed by GC and GC/MS.

**Control Hydroformylation Experiments with Other Catalyst Precursors**

(A) **With  $Rh_4(CO)_{12}$ :** A solution of  $Rh_4(CO)_{12}$  (4 mg, 0.005 mmol) in THF (25 ml) and a 100-fold excess of 1-hexene (168 mg, 2 mmol) were introduced by suction into a Parr reactor previously evacuated with a vacuum pump. The reactor was then pressurized with a 1:1 mixture of  $H_2$ /CO to 30 atm at room temperature, heated to 60 °C and the contents were stirred. After 3 h, the reaction was quenched by rapid cooling with an ice-water bath.

(B) **With  $Rh_4(CO)_{12}/PP_2$ :** To a solution of  $Rh_4(CO)_{12}$  (4 mg, 0.005 mmol) and 1-hexene (168 mg, 2 mmol) in THF (25 ml) was added solid  $PP_2$  (11 mg, 0.02 mmol). The Parr reactor was pressurized with a 1:1 mixture of  $H_2$ /CO to 30 atm at room temperature, heated to 60 °C and the contents were stirred. After 3 h, the reaction was quenched by rapid cooling with an ice-water bath.

The results of these experiments are collected in Table 4.

**Hydroformylation of 1-Hexene Catalyzed by **2**. – HPNMR Experiment:** A 10-mm sapphire HPNMR tube was charged with a solution of **2** (50 mg, 0.06 mmol) in  $[D_8]THF$  (2 ml) and a 50-fold excess of 1-hexene (370  $\mu$ l, 3 mmol) under nitrogen, pressurized with a 1:1 mixture of CO and  $H_2$  to 30 atm at room temperature and then placed in an NMR probe at room temperature. The reaction was followed by variable-temperature  $^{31}P\{^1H\}$ - and  $^1H$ -NMR spectroscopy. Sequences of selected  $^{31}P\{^1H\}$ - and  $^1H$ -NMR spectra are presented in Figure 3. The starting monocarbonyl complex **2** (trace a, under nitrogen at 20 °C) reacted with CO at room temperature, yielding the dicarbonyl complex **3** ( $^{31}P$   $AM_2X$  pattern) (traces b–c). During the course of the transformation of **2** into **3**, no reaction involving 1-hexene was observed by  $^1H$ -NMR spectroscopy. Increasing the temperature to 60 °C converted all **2** to **3** (trace d) and concomitantly led to the formation of 1-hexene isomers ( $^1H$  NMR, traces d'–d'') along with aldehydes. At 80 °C, 1-hexene was rapidly consumed ( $^1H$  NMR, trace e') with **3** being the only rhodium species detected by  $^{31}P$ -NMR spectroscopy (trace e). Complex **3** was also the only metal-containing product observable by  $^{31}P$ -NMR spectroscopy when the catalytic reaction was quenched by cooling the NMR probe to room temperature (trace f). The tube was then removed from the probe of the spectrometer and depressurized. GC and GC/MS analyses showed the reaction mixture to contain 54% of isomerization products (*cis*- and *trans*-

2-hexene, *trans*-3-hexene) and 40% of aldehydes (heptanal/2-methylhexanal/2-ethylpentanal = 70:28:2).

Analogous HPNMR experiments were carried out using syngas disproportionately rich in either CO (90 atm CO/3 atm  $H_2$ ) or  $H_2$  (3 atm CO/90 atm  $H_2$ ). In all cases,  $^{31}P$ -NMR spectra showed the exclusive presence of **3** in the reaction mixture.

**Hydroformylation of 1-Hexene Catalyzed by **2** in the Presence of  $NEt_3$ . – HPNMR Experiment:** A 10-mm sapphire HPNMR tube was charged with a solution of **2** (40 mg, 0.05 mmol), 1-hexene (310  $\mu$ l, 2.5 mmol) and  $NEt_3$  (30  $\mu$ l, 0.2 mmol) in  $[D_8]THF$  (2 ml) under nitrogen, pressurized with a 1:1 mixture of CO and  $H_2$  to 30 atm at room temperature and then placed in an NMR probe at room temperature. The reaction was followed by variable-temperature  $^{31}P\{^1H\}$ - and  $^1H$ -NMR spectroscopy. Sequences of selected  $^{31}P\{^1H\}$ - and  $^1H$ -NMR spectra are presented in Figure 4. As in the absence of  $NEt_3$ , the starting monocarbonyl complex **2** (trace a, under nitrogen at 20 °C) reacted with CO at room temperature yielding **3** (trace b). At this temperature, no reaction involving 1-hexene occurred. Increasing the temperature to 60 °C converted all **2** to **3** (trace c), while 1-hexene started to undergo conversion to aldehydes and, to a lesser extent, to its isomers ( $^1H$  NMR, traces c'–c''). After 3 h, the catalytic reaction was quenched by cooling the NMR probe to room temperature. A  $^{31}P\{^1H\}$ -NMR spectrum showed **3** to be the only phosphorus-containing product. The tube was then removed from the spectrometer and depressurized. A sample of the contents, withdrawn and analyzed by GC and GC/MS, was found to contain heptanal, 2-methylhexanal, 1-hexene, and *cis*- and *trans*-2-hexene (aldehydes conversion ca. 35%, heptanal/2-methylhexanal = 72:28; 1-hexene 45%).

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