In Situ High-Pressure $^{31}P\{^{1}H\}$ NMR Studies of the Hydroformylation of 1-Hexene by $RhH(CO)(PPh_3)_3$

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The hydroformylation of 1-hexene with syngas (40 bar of 1:1 CO/H_2) in the presence of the catalyst precursor $RhH(CO)(PPh_3)_3$ has been studied by high-pressure NMR spectroscopy in a 10 mm sapphire tube equipped with a Ti-alloy valve. Except for $RhH(CO)_2(PPh_3)_2$, no direct observation of labile intermediates involved in the catalytic cycle has been detected; however as many as four rhodium resting states have been seen, and some factors controlling their formation/interconversion/inhibition have been identified. The information gathered from this in situ investigation is particularly relevant to a better understanding of the inhibiting action of the CO pressure as well as the positive action of PPh_3 addition.

Introduction

Hydridocarbonyltris(triphenylphosphine)rhodium-(I), $RhH(CO)(PPh_3)_3$ (**1**),[1,2] is one of the most commercially important catalysts for the homogeneous hydroformylation of alkenes, particularly for the low-pressure conversion of propylene to *n*-butyraldehyde.[3] The first mechanistic studies of the hydroformylation of alkenes catalyzed by **1** were reported by Wilkinson and co-workers over thirty years ago.[4] Since then, innumerable studies of the oxo activity of **1** have been carried out applying a variety of experimental and theoretical approaches.[5−8] The general mechanistic concepts proposed by Wilkinson and co-workers are still accepted as being essentially correct; however, new insights, largely concerning the structure, relative stability, and exchange processes of either active intermediates or resting states, continue to be discovered as new spectroscopic or computational techniques become available.

A relatively new spectroscopic technique for in situ studies of catalytic reactions at elevated gas pressure is high-pressure NMR (HPNMR) spectroscopy.[7,9] With the advent of 10 mm-o.d. sapphire tubes equipped with Ti-alloy valves, the HPNMR technique has further developed as any commercial spectrometer may be employed with standard operation; moreover, the headspace of the tubes is large enough to maintain a constant concentration of gases into the solution if fast diffusion takes place. Indeed, mass transfer of reactive gases from the headspace of 10 mm-o.d. NMR tubes has generally been found to be efficient enough to replenish the solution which is being depleted of gaseous reactants by the catalyst.[7,10]

Notwithstanding that NMR spectroscopy is featured by slower time scale and lower sensitivity as compared to infrared spectroscopy,[11] the HPNMR technique is preferable when the catalytic process under investigation contains many magnetically active nuclei as well as many closely related species. No doubt, a reaction with these characteristics is the hydroformylation of alkenes promoted by phosphine-modified rhodium cata-

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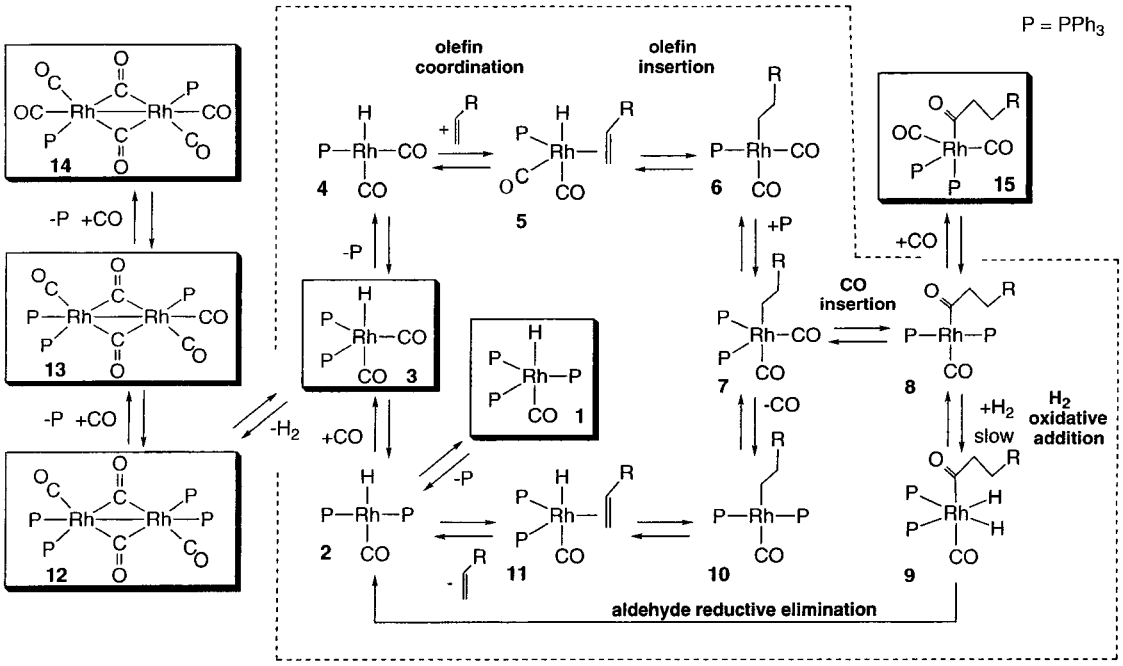
Scheme 1



lysts, as shown by the proposed *dissociative* mechanism of the catalytic hydroformylation of alkenes mediated by **1** illustrated in Scheme 1 (dashed box).[4,5]

Of the various transient intermediates in the catalytic cycle only the five-coordinate complex $RhH(CO)_2(PPh_3)_2$ (**3**) has been characterized spectroscopically as a very fluxional species due to fast exchange of a phosphine ligand from equatorial to axial position.[5c,8b] Some related derivatives and analogues of the species in the catalytic cycle have been either isolated or detected in situ, however. The structure of the square-planar Rh(I) hydride $RhH(CO)(PCy_3)_2$ (PCy_3 = tricyclohexylphosphine),[12] similar to $RhH(CO)(PPh_3)_2$ (**2**), has been determined by X-ray methods, while acyl complexes of the formula $Rh(COR)(CO)_2(PPh_3)_2$ have been observed by NMR upon carbonylation of **1** in the presence of alkenes (R = alkyl).[4e,5b,c] An HPNMR study in toluene-d_8 at room temperature of the reaction of **1** with 30 bar of CO/H_2 in the presence of 3 molar excess of PPh_3 has also been carried out.[7c] Complex **3** was reported to be the only species detectable by NMR.

In this work is reported a $^{31}P\{^1H\}$ HPNMR study of the hydroformylation of 1-hexene catalyzed by **1** in either the absence or presence of added PPh_3. The combination of experiments in both actual catalytic conditions and at low temperature has provided for the first time a complete picture of the equilibria involving all the species that are visible on the NMR time scale.

Experimental Section

General Procedures. All manipulations were carried out under an atmosphere of nitrogen by using Schlenk-type techniques. The catalyst precursor $RhH(CO)(PPh_3)_3$ (**1**)[4b] and the dimeric complexes $Rh_2(CO)_{4+x}(PPh_3)_{4-x}$ ($x = 0$, **12**; $x = 1$, **13**; $x = 2$, **14**) were prepared according to literature methods.[13,14] 1-Hexene was percolated through neutral silica prior to use. All the other reagents and solvents were used as purchased from Aldrich. Toluene-d_8 for NMR measurements was dried over molecular sieves. ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra were obtained on a Bruker ACP 200 spectrometer (200.13, 50.32, and 81.01 MHz, respectively). All chemical shifts are reported in ppm (δ) relative to tetramethylsilane, referenced to the chemical shifts of residual solvent resonances (^1H, ^{13}C) or 85% H_3PO_4 (^{31}P). The 10 mm sapphire NMR tube was purchased from Saphikon, Milford, NH, while the titanium high-pressure charging-head was constructed at the ISSECC−CNR (Firenze, Italy).[15] *Note*: *Since high gas pressures are involved, safety precautions must be taken at all stages of studies involving high-pressure NMR tubes.* GC analyses of the solutions were performed on a Shimadzu GC-14 A gas chromatograph equipped with a flame ionization detector and a 30 m (0.25 mm i.d., 0.25 μm film thickness) SPB-1 Supelco fused silica capillary column. A UCON-oil LB 550-X packed column (PPG, 2 m, 1/8 in. i.d.) was employed for the determination of hydrocarbons, 2-ethylpentanal, 2-methylhexanal, and heptanal. An Al_2O_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. GC/MS analyses were performed on a Shimadzu QP 5000 apparatus equipped with a SPB-1 Supelco fused silica capillary column.

HPNMR Study of the Hydroformylation of 1-Hexene Catalyzed by 1. General Procedure. A 10 mm sapphire HPNMR tube was charged with a solution of **1** (18.4 mg, 0.02 mmol) in toluene-d_8 (2.5 mL) and a 30-fold excess of 1-hexene (75 μL, 0.6 mmol) under nitrogen. After $^{31}P\{^1H\}$ and ^1H NMR spectra were recorded, the tube was pressurized with a 1:1 mixture of CO/H_2 to 40 bar at room temperature. The reaction was followed by variable-temperature $^{31}P\{^1H\}$ and ^1H NMR spectroscopy. After the desired time, the tube was removed from the probe of the spectrometer and depressurized. NMR spectra were acquired, and the product composition was determined by GC and GC/MS analyses.

In some experiments, to avoid initial olefin isomerization,[2,4b] 1-hexene was added into the toluene-d_8 solution of **1** under a stream of 1:1 CO/H_2.

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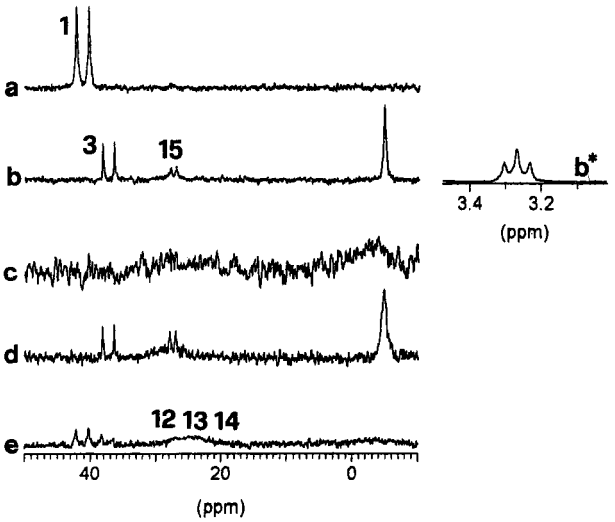


Figure 1. $^{31}P\{^1H\}$ and ^1H HPNMR study of the hydroformylation of 1-hexene catalyzed by $RhH(CO)(PPh_3)_3$ (**1**) (sapphire tube, toluene-d_8, 40 bar of a 1:1 mixture of CO/H_2, 1-hexene/**1** = 30:1). $^{31}P\{^1H\}$ NMR spectra: under nitrogen, before pressurizing with CO/H_2, at room temperature (a); under CO/H_2 at room temperature (b); after 1 h under CO/H_2 at 60 °C (c); after the NMR probe was cooled to room temperature (d); after the tube was depressurized (e). ^1H NMR spectrum in the 3.5−3.0 ppm region under CO/H_2 at room temperature (b*).

HPNMR experiments were carried out adding 20 equiv of PPh_3 (105 mg, 0.4 mmol) or using syngas disproportionately rich in H_2 (H_2, 35 bar; CO, 5 bar). HPNMR experiments were also performed in the absence of H_2 using a CO pressure of 20 bar.

Reaction of $Rh_4(CO)_{12}$ with PPh_3. A 10 mm NMR tube was charged with a solution of $Rh_4(CO)_{12}$ (4 mg, 0.005 mmol) in toluene-d_8 (2.5 mL) and an 8-fold excess of PPh_3 (11 mg, 0.04 mmol) under nitrogen. The reaction was followed by variable-temperature $^{31}P\{^1H\}$ NMR spectroscopy.

Reaction of $Rh_4(CO)_{12}$ with PPh_3/CO. A 10 mm NMR tube was charged with a solution of $Rh_4(CO)_{12}$ (4 mg, 0.005 mmol) in toluene-d_8 (2.5 mL) and an 8-fold excess of PPh_3 (11 mg, 0.04 mmol) under nitrogen, pressurized with CO to 20 bar at room temperature, and then placed in an NMR probe. The reaction was followed by variable-temperature $^{31}P\{^1H\}$NMR spectroscopy.

Results and Discussion

The hydroformylation of 1-hexene in the presence of **1** has been studied in a 10 mm HPNMR tube with 40 bar of 1:1 CO/H_2. The concentration of **1** was ca. 8 mM in all experiments in order to have a satisfactory signal-to-noise ratio as well as maintain the system in the conditions of the dissociative mechanism and first-order rate in catalyst concentration.[4d]

A sequence of selected $^{31}P\{^1H\}$ NMR spectra is shown in Figure 1.

In the absence of syngas, no appreciable transformation of **1** was observed (trace a, doublet at δ 41.3, J(PRh) = 153.9 Hz). Only in the presence of CO/H_2 did **1** immediately transform into several products at room temperature (trace b). The carbonylation of the precursor was revealed by the formation of **3** (doublet at δ 37.3, J(PRh) = 138.7 Hz) and free PPh_3 (singlet at δ −4.8), while the occurrence of alkene coordination/hydride migration was indirectly shown by the formation of the acyl complex $Rh(CO(CH_2)_5CH_3)(CO)_2(PPh_3)_2$ (**15**) (*anti-Markovnikov* hydride migration) characterized by a doublet at δ 27.5 with J(PRh) = 78.0 Hz.[4e,5b,c] A triplet at δ 3.28 (J(HH) = 7.2 Hz) in the ^1H NMR spectrum (trace b*) appeared contemporaneously to the ^{31}P NMR doublet at δ 27.5 and was safely assigned to the CH_2 group proximal to the CO group in **15** by comparison with the spectra of related $Rh(COR)(CO)_2(PPh_3)_2$ complexes.[4c,f,5b] In terms of the mechanism shown in Scheme 1, the formation of **15** is consistent with the occurrence of the reaction sequence **1** → **2** → **3** → **4** → **5** → **6** → **7** → **8**. Consistently, no trace of aldehydes was seen by ^1H NMR at this stage. From a perusal of trace b, however, we noted that the baseline rose forming a broad hump just below the signal of **15**. As will be shown later in this work, the broad hump is originated by at least three fluxional and exchanging dimeric Rh(0) complexes of the formula $Rh_2(CO)_{4+x}(PPh_3)_{4-x}$ (x = 0, **12**; x = 1, **13**; x = 2, **14**), which at this stage of the reaction are in very low concentration.

Increasing the temperature of the NMR probe to 60 °C resulted in extensive broadening of all resonances, indicating a fast exchange and interaction of ligands around the rhodium centers (trace c). After 1 h at 60 °C, heptanal and 2-methylhexanal were formed in a ca. 1:1 ratio (NMR evidence) together with traces of isomerized alkenes. GC/MS analysis, carried out on a sample of the solution recovered at the end of the HPNMR experiment, confirmed the formation of aldehydes in a normal/iso ratio of 1. The $^{31}P\{^1H\}$ NMR spectrum at room temperature (trace d) was similar to that prior to aldehyde formation (trace b), the only relevant differences being a major intensity of the acyl signal and of the hump below. The HPNMR tube was then removed from the probe and depressurized. The respective ^{31}P NMR spectrum gave trace e, showing the reappearance of the precursor **1** and the complete disappearance of the signal at δ 27.5, in line with the fact that the acyl derivatives are stable under a CO atmosphere only.[4f,5c] Also, appreciable increase in the concentration of the dimeric species occurred, which is consistent with the mechanism of their formation (vide infra). Sweeping the NMR tube with N_2 led to the complete disappearance of the signal due to **3**, while the concentration of the dimeric complexes was apparently unaffected.

The products that give rise to the broad hump centered at δ 25 were identified by several experiments, including their independent synthesis. First of all, a low-temperature spectrum of the catalytic mixture was acquired. As is shown in trace a of Figure 2, the broad hump resolved at −20 °C into several signals spanning from 30 to 22 ppm, none of which was found to contain hydride ligands (^1H NMR evidence).

A ^{31}P NMR spectrum of a mixture of **1**, CO (20 bar), and 1-hexene (30 equiv) was then acquired in the absence of H_2 (trace b). Three defined resonances at identical chemical shifts with those of trace a but with increased intensity were clearly visible at −20 °C (again only a broad hump was observed at room temperature). In these conditions, only a very small amount of the acyl complex **15** was detected due to the competing formation of the dimeric Rh(0) complexes. In other words, in the absence of H_2, the acyl complex **15** cannot accumulate during the carbonylation reaction.[4f,5c,6] In a third experiment (trace c), **1** was reacted with 20 bar CO in the

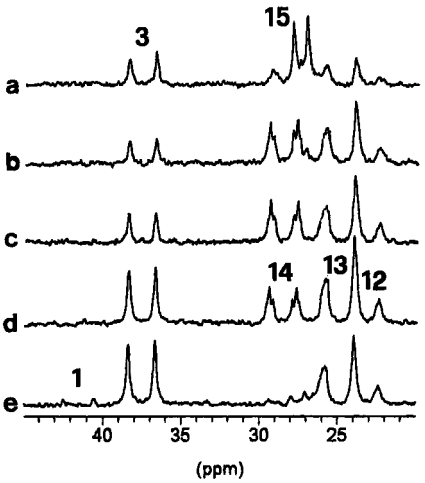
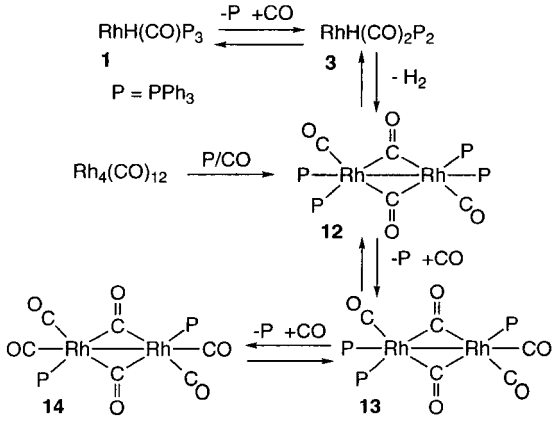


Figure 2. $^{31}P\{^1H\}$ HPNMR spectra (sapphire tube, toluene-d_8, 20 bar of CO, −20 °C): $RhH(CO)(PPh_3)_3$ (**1**) and 30 equiv of 1-hexene (b); **1** and 30 equiv of 2-hexene (c); **1** (d); **1**, 20 equiv of PPh_3, and 30 equiv of 1-hexene (e). Trace a, reported for comparative purposes, shows the spectrum, acquired at −20 °C, of the final solution of the HPNMR study of the hydroformylation of 1-hexene catalyzed by **1** (sapphire tube, toluene-d_8, 40 bar of a 1:1 mixture of CO/H_2, 1-hexene/**1** = 30).

presence of 2-hexene: the ^{31}P NMR spectrum was substantially similar to that with 1-hexene, but no trace of acyl complex was observed in agreement with a much higher energy barrier to 2-alkene insertion into the Rh−H bond as compared to 1-alkenes.[4d] Consistently, the carbonylation of **1** in the absence of alkene gave an identical ^{31}P NMR spectrum (trace d). Finally, **1** was reacted with CO (20 bar) and 1-hexene in the presence of a 20-fold excess of PPh_3. The ^{31}P NMR spectrum (trace e) showed the formation of the acyl complex **15** and of the dimers $Rh_2(CO)_{4+x}(PPh_3)_{4-x}$ (x = 0, **12**; x = 1, **13**), therefore indicating that the excess PPh_3 inhibits the formation of the dimer with the highest content of CO, i.e., $Rh_2(CO)_6(PPh_3)_2$ (**14**).

The first evidence of the formation of dimeric Rh(0) complexes upon carbonylation of **1** was reported in 1968 by Wilkinson et al., who discovered that the action of CO on toluene solutions of **1** involved rapid conversion into **3** and the yellow complex $Rh_2(CO)_4(PPh_3)_4$ (**12**).[4a,f] The formation of the latter dimer has been reported to proceed by reversible thermal elimination of H_2 from **3**, as shown in Scheme 2. Once formed, **12** is in equilibrium with **13** and **14** via phosphine displacement by CO,[13] and with **3** via H_2 uptake.[4a,f] Obviously, the equilibrium concentration of the various species depends on the CO and H_2 pressures as well as the PPh_3 concentration. X-ray structural analyses are available for **13**[14] and for the model compound, analogous to **12**, $Rh_2(CO)_2[P(O\text{-}i\text{-}C_3H_7)_3]_4$.[16] A detailed ^{31}P NMR analysis has been reported for $Rh_2(CO)_6[P(OPh)_3]_2$, which exhibits a second-order AA′XX′ ^{31}P NMR spectrum.[7a] A similar second-order NMR pattern is shown by the PPh_3 derivative **14** (doublet of multiplets centered at δ 28.5) that indeed was found to disappear by addition of PPh_3 to the reaction mixture (trace e in Figure 2).

Scheme 2



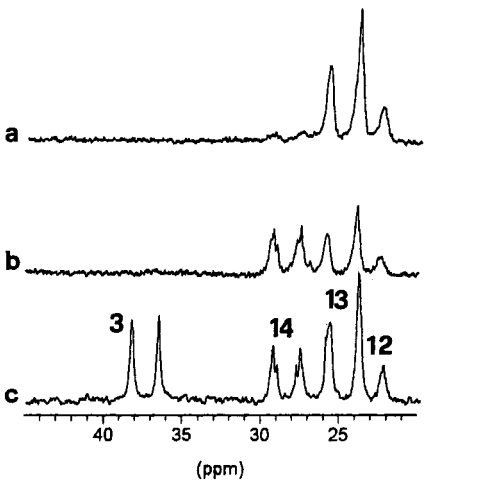


Figure 3. $^{31}P\{^1H\}$ HPNMR spectra (sapphire tube, toluene-d_8, −20 °C): $Rh_4(CO)_{12}$ and 8 equiv of PPh_3 under nitrogen (a); $Rh_4(CO)_{12}$ and 8 equiv of PPh_3 under 20 bar of CO (b); $RhH(CO)(PPh_3)_3$ under 20 bar of CO (c).

To unambiguously establish the nature of the products formed upon carbonylation of **1**, the Rh(0) dimers were generated following a known procedure.[13,14] To a solution of $Rh_4(CO)_{12}$ in toluene-d_8 in an HPNMR tube was added an excess of PPh_3 (8 equiv) under nitrogen. The respective ^{31}P NMR spectrum at −20 °C is reported as trace a in Figure 3. Under these conditions, **12** (doublet at ca. δ 23) and **13** (doublet at ca. δ 25) were largely predominant over **14**. Pressurizing the HPNMR tube with 20 bar of CO increased the concentration of **14** at the expense of those of **12** and **13** (trace b).

A comparison with the spectrum of **1** under 20 bar of CO at −20 °C (trace c) confirms that a high pressure of CO is needed to form an appreciable amount of **14**.

From this study it is reasonable to conclude that the formation of the Rh(0) dimers largely depends on the CO pressure, although a certain influence is exerted also by the concentration of free PPh_3.[4d] A quite similar situation takes place in actual hydroformylation conditions: almost no trace of dimers was spectroscopically detected by treatment of a toluene solution of **1** and 1-hexene with syngas disproportionately rich in H_2 (H_2, 35 bar; CO, 5 bar). Similarly, scarce production of dimers was observed by NMR when the hydroformylation of 1-hexene with **1** was carried out in the presence of an excess of free phosphine as actually occurs in industrial conditions.[3]

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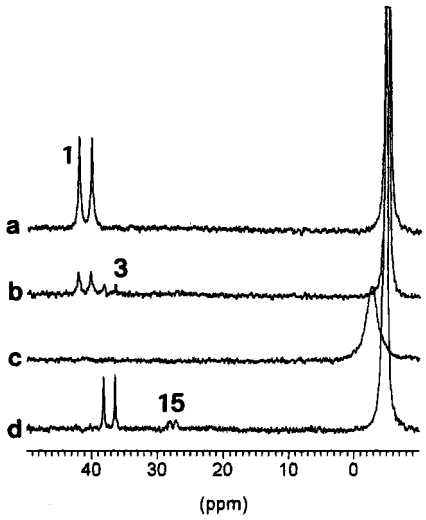

Figure 4. $^{31}P\{^1H\}$ HPNMR study of the hydroformylation of 1-hexene catalyzed by $RhH(CO)(PPh_3)_3$ (**1**) in the presence of PPh_3 (sapphire tube, toluene-d_8, 40 bar of a 1:1 mixture of CO/H_2, 1-hexene/**1** = 30, PPh_3/**1** = 20). $^{31}P\{^1H\}$ NMR spectra: under nitrogen, before pressurizing with CO/H_2, at room temperature (a); under CO/H_2 at room temperature (b); after 1 h under CO/H_2 at 60 °C (c); after the NMR probe was cooled to room temperature (d).

In Figure 4 are displayed selected $^{31}P\{^1H\}$ HPNMR spectra of the hydroformylation of 1-hexene in toluene-d_8 in the presence of a 20-fold excess of PPh_3.

Before pressurizing with 40 bar of 1:1 CO/H_2 syngas, **1** and free phosphine were the only species visible on the NMR time scale (trace a). Intermediate **3** started to form upon addition of syngas. At room temperature the conversion of **1** to **3** was much slower than observed with no added phosphine, however (trace b was actually taken after the same reaction time of trace b in Figure 1). With time, the concentration of **3** increased and the acyl complex **15** slowly accumulated. No trace of aldehyde products was seen by ^1H NMR at room temperature. Heating the NMR probe to 60 °C resulted in a rapid equilibration of all Rh species (trace c) as well as hydroformylation of 1-hexene to give a normal/iso ratio of ca. 2, consistent with the presence of an excess of phosphine.[4d] After cooling to room temperature, the first spectrum showed the presence of **3** and of traces of **15** (trace d). A ^{31}P NMR spectrum at −20 °C showed a very low concentration of dimers.

The overall picture of the hydroformylation of 1-hexene with **1** provided by the present HPNMR studies is in nice agreement with all previous mechanistic studies of the oxo chemistry of **1**. In particular, the information gathered from this in situ investigation is indeed relevant to a better understanding of the inhibiting action of the CO pressure as well as the positive action of PPh_3 addition. Experimental evidence has been obtained for the effect of the CO pressure that increasing the concentration of inactive species such as the five-coordinate acyl complex **15** and the Rh(0) dimers **12**, **13**, and **14**, actually reduces the rate of reaction. Analogously, the addition of PPh_3 to the reaction mixture has been shown to have the desirable effect of inhibiting dimerization reactions.

An increased normal/iso ratio of aldehydes in the presence of excess PPh_3 has been found to occur also in the HPNMR reactions. Although neither **2** nor **4** has been detected spectroscopically, it has been found that the presence of PPh_3 reduces the rate of formation of **3** and consequently that of **4**. In other words, the presence of PPh_3 increases the equilibrium concentration of the more sterically demanding square-planar intermediate **2** which favors the occurrence of the *anti-Markovnikov* addition and hence the production of the linear aldehyde. Indeed, previous mechanistic studies and HPNMR experiments in water using $RhH(CO)[P(m\text{-}C_6H_4SO_3Na)_3]_3$ have shown that the normal/iso ratio of the aldehydes is largely controlled by the competitive reactions of the alkene with intermediates **2** and **4**, resulting in high or low normal/iso ratio, respectively.[7c]

Conclusions

The hydroformylation of 1-hexene in the presence of $RhH(CO)(PPh_3)_3$ has been studied in actual hydroformylation conditions using high-pressure NMR spectroscopy. Scheme 1 reports a simplified hydroformylation mechanism promoted by the catalyst precursor $RhH(CO)(PPh_3)_3$ and highlights all the species that have been characterized by HPNMR spectroscopy.

Although no direct observation of labile intermediates involved in the catalytic cycle has been detected [except for $RhH(CO)_2(PPh_3)_2$], as many as four rhodium resting states have been seen and some factors controlling their formation/inhibition have been identified.

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