Intramolecular Hydroformylation of Allyldiphenylphosphine Using a Monodentate Phosphorus Diamide Based Rhodium Catalyst: An NMR Study

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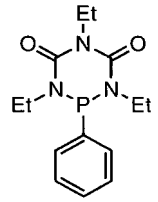
The stepwise intramolecular hydroformylation reaction of allyldiphenylphosphine using a monodentate phosphorus diamide based rhodium catalyst has been studied using NMR spectroscopy. Reaction of the rhodium−hydride complex $HRhL_3CO$ (L = triethylbiuretphenylphosphorus diamide) with allyldiphenylphosphine results in the formation of $HRhL_2$(allylPPh_2)CO. This compound undergoes hydride migration to form a cyclic rhodium−alkyl complex. When carbon monoxide is added to this complex, ligand exchange and CO insertion occur, leading to the formation of the cyclic rhodium−acyl complex $Rh(CO)CH_2CH_2CH_2PPh_2L(CO)_2$. Addition of hydrogen completes the cycle forming the coordinated hydroformylated allyldiphenylphosphine ligand. The aldehyde-functionalized phosphine ligand is hydrogenated to the corresponding alcohol.

Introduction

The rhodium-catalyzed hydroformylation using phosphorus ligands is one of the most extensively studied catalytic processes.[1−6] Not only has the catalyst performance been an important aspect of the studies during the past decades but also the reaction mechanism and the solution structure of the catalyst have been investigated in great detail.[7,8] Although several intermediates of the unmodified rhodium catalyst have been characterized,[9−11] only a small number of intermediates proposed for the phosphorus-modified catalyst have been identified,[12−14] and very little is known about the reactivity of the reaction intermediates and the reversibility of the reaction steps proposed.[15,16]

Scheme 1



(1)

Recently we presented a new group of phosphorus diamide ligands for the rhodium-catalyzed hydroformylation reaction[17] that is based on a biuret structure. Although the ligands are very bulky, moderate selectivity for the linear aldehyde was found in the hydroformylation reaction of 1-octene;[17] bulky diphosphite ligands for instance often lead to high linear-to-branched ratios.[18] Here we report on a detailed study of the stoichiometric hydroformylation reaction of allyldiphenylphosphine using the monodentate phosphorus diamide based rhodium catalyst $HRh(\mathbf{1})_3CO$. The allyldiphenylphosphine rhodium complex **2** (Scheme 2) is used as a model compound to investigate the hydroformylation reaction in a stepwise manner. The structures of the hydroformylation reaction intermediates as proposed in Scheme 2 are investigated using NMR spectroscopy. Not only is this type of intramolecular

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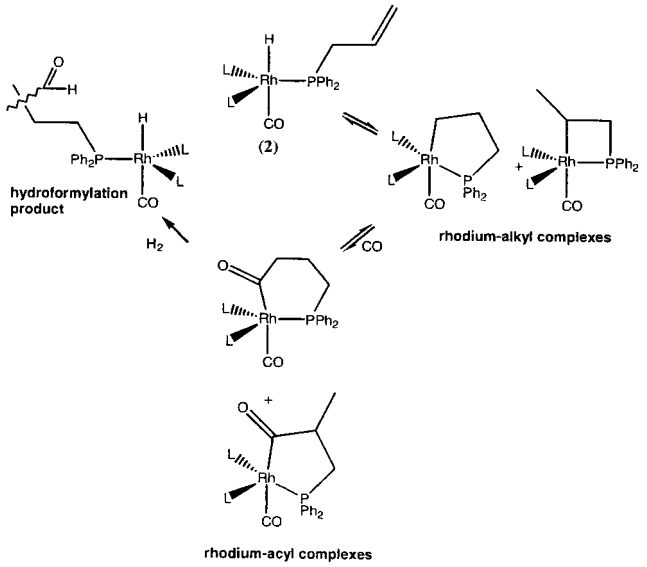
Scheme 2. Possible Reaction Intermediates of the Intramolecular Hydroformylation of Allyldiphenylphosphine



hydroformylation of interest from a mechanistic point of view, but coupling of the substrate and ligand function can lead to increased selectivity for either the linear or branched product, as has been shown by Jackson[19] and Breit.[20]

Since this biuret-based rhodium catalyst shows moderate selectivity for the linear aldehyde in the hydroformylation of 1-octene,[17] special attention will be paid to the regioselectivity of the hydride migration and isomerization reaction. Van Leeuwen and co-workers[21] investigated the hydride migration of several alkenylphosphine−platinum complexes. They observed for vinyldiphenylphosphine both the linear and branched alkyl−platinum complex. The branched alkyl complex, a three-membered ring system, is the initial product formed by kinetic control; the linear alkyl complex, a four-membered ring system, is the thermodynamically more stable product formed after longer reaction times. They observed only the linear (five-membered ring system) product for allyldiphenylphosphine. Recently van Leeuwen et al.[22] studied the stepwise hydroformylation reaction of allyldiphenylphosphine using a rhodium catalyst containing a bidentate bulky phosphite ligand. Similar to the platinum complexes, the linear rhodium−alkyl complex was observed exclusively after hydride migration, but after CO insertion both the linear and branched rhodium−acyl complexes were observed, indicating that the branched rhodium−alkyl complex must have been formed as a transient intermediate. Thus kinetically the formation of small rings seems to be favored both in the rhodium and in the platinum systems. In this study we will focus on the reversibility of the hydride migration step and the effect of using monodentate instead of chelating phosphorus ligands in this reaction step. Using the bidentate phosphite-based rhodium complex, all subsequent steps of the hydroformylation mechanism except the hydrogenolysis were observed. The use of a monodentate ligand instead of a bidentate ligand could enhance ligand dissociation and thereby the hydrogenolysis, leading to the hydroformylated allyldiphenylphosphine.

Results and Discussion

The rhodium−hydride complex HRh(**1**)$_3$CO was used as starting material for this mechanistic study.[17] This complex has a trigonal bipyramidal structure with the hydride ligand coordinated at an apical position. The ^{1}H, ^{13}C, and ^{31}P NMR data for this complex are summarized in Table 1 to facilitate comparison with the data of the intermediates formed in this study. The $^2J_{PH}$ coupling constant of 13 Hz is relatively large for a pure *cis*-orientation of the phosphorus and hydride ligands, indicating a small distortion of the trigonal bipyramidal structure. The crystal structure confirmed that the hydride and carbonyl ligands are coordinated at an apical position.[17] The rhodium atom is located slightly below the equatorial plane defined by the phosphorus atoms, displaced toward the carbonyl ligand. The ^{13}C-{^{1}H} NMR spectrum showed a doublet of quartets in the terminal CO region when the complex synthesis was performed using ^{13}CO. The large $^2J_{CH}$ coupling constant of 36 Hz for *trans* CO-hydride coordination in a trigonal bipyrimidal rhodium complex has also been reported by Brown[15] and van Leeuwen.[23] The P−Rh−CO angle is larger than 90°, leading to a relatively large $^2J_{PC}$ coupling constant of 13 Hz.

Reaction of HRh(1)$_3$CO and Allyldiphenylphosphine. One equivalent of allyldiphenylphosphine was made to react with HRh(**1**)$_3$CO at 233 K. The difference in electronic ligand properties favors the exchange of a π-acidic phosphorus ligand with an electron-donating phosphine ligand. Free allyldiphenylphosphine was not observed in the ^{31}P NMR spectra ($\delta(^{31}P) = -13.6$ ppm). The major compound formed is the rhodium−hydride complex **2** (Scheme 2), but in all cases approximately 10% of the disubstituted complex (HRh(**1**)(allylPPh$_2$)$_2$-CO) and HRh(**1**)$_3$CO were obtained in the ^{31}P NMR spectra (Figure 1, spectrum 1). When the reaction mixture was warmed to room temperature, complete conversion to complex **2** was obtained, but at this temperature hydride migration occurs. To characterize complex **2** completely, the solution was kept at 253 K after addition of allyldiphenylphosphine to the rhodium−hydride complex.

The structure of **2** (Scheme 2) was elucidated using various NMR techniques (Table 1). The ^{1}H NMR spectrum showed that the alkene moiety was still present. All allyl protons were shifted upfield compared to the resonances of noncoordinated allyldiphenylphosphine. The hydride resonance was shifted downfield. The magnitude of the phosphorus−hydride coupling constant is approximately the same for both the phosphine and the phosphorus diamide ligands and shows that the trigonal bipyramidal structure is still slightly distorted. The $^2J_{CH}$ coupling constant of **2** (48 Hz) is slightly larger than the $^2J_{CH}$ coupling constant of HRh(**1**)$_3$CO (36 Hz).

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Table 1. Spectroscopic Data of the Different Intermediates Observed

complex	$\delta(^{31}P)^a$ (ppm)	$J_{RhP}{}^a$ (Hz)	$J_{P1P2}{}^a$ (Hz)	$\delta(^{13}C)$ (ppm)	J_{RhC} (Hz)	J_{PC} (Hz)	$\delta(^1H)$ (Hz)	J_{PH} (Hz)	J_{CH} (Hz)	J_{RhH} (Hz)
$HRh(\mathbf{1})_3CO$	116 (P1)[b]	180 (P1)		200[c]	52	13	−11.1[b]	13	36	≤3
2	116 (P1)[b]	188 (P1)	131	202[c]	52	13	−10.8[b]	11	48	≤3
	23 (P2)	143 (P2)								
3b	119 (P1)[d]	195 (P1)	112	197[d]	47	16				
	60 (P2)	147 (P2)								
5a	106 (P1)[c]	205 (P1)	117	195 (broad)[d]	n.d.	n.d.				
	16 (P2)	147 (P2)		243 (broad)[d]						
5b	106 (P1)[c]	205 (P1)	117	n.d.	n.d.	n.d.				
	56 (P2)	156 (P2)								
6	109 (P1)	185	77	197	63	24 (P1)	−10.3	10 (P1)	8	5
	27 (P2)	122				<3 (P2)		33 (P2)		
7	117 (P1)[e]	188	130	202	51	13	−10.7	12	n.d.	≤3
	25 (P2)	141								

[a] P1 belongs to the phosphorus diamide ligand resonance, P2 belongs to the allyldiphenylphosphine resonance. [b] Determined at 253 K. [c] Determined at 233 K. [d] Determined at 203 K. [e] Determined at 268 K.

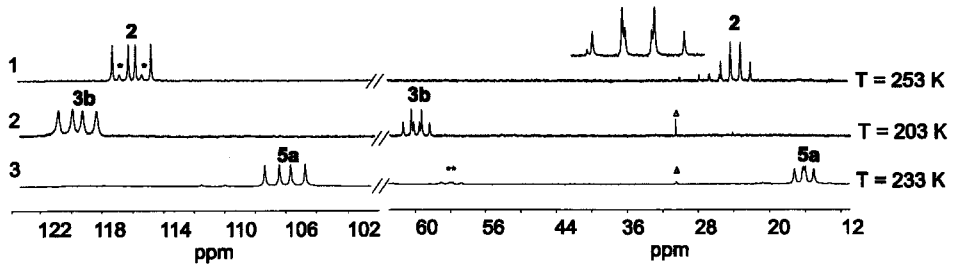

Figure 1. $^{31}P\{^1H\}$ NMR spectra of Complexes **2**, **3b**, and **5a**: (1) $^{31}P\{^1H\}$ NMR of complex **2** obtained at 253 K, (2) $^{31}P\{^1H\}$ NMR of complex **3b** obtained at 203 K, (3) $^{31}P\{^1H\}$ NMR of complex **5a** obtained at 233 K, (*) $HRh(\mathbf{1})_3CO$, (**) **5b**, (Δ) allyldiphenylphosphineoxide.

The phosphorus NMR spectrum (Figure 1, spectrum 1) showed a doublet of doublets in the rhodium−phosphorus diamide region and a doublet of triplets in the rhodium−phosphine region in a ratio of 2:1. The large $^2J_{PP}$ coupling constant of 131 Hz is consistent with the coordination of all three phosphorus atoms in the equatorial plane. The $^{13}C\{^1H\}$ NMR spectrum showed a doublet of quartets at 202 ppm for **2** prepared with ^{13}CO. The $^1J_{RhC}$ coupling constant (52 Hz) and $^2J_{PC}$ coupling constant (13 Hz) are in the same range as the data found for $HRh(\mathbf{1})_3CO$, indicating that similar to this complex, the phosphorus ligands are coordinated in the equatorial plane and the carbonyl ligand and hydride ligands are coordinated at an apical position of the distorted trigonal bipyramid.

Hydride Migration. When a solution of **2** in CD_2-CL_2 was warmed to room temperature, additional (broad) resonances in the phosphorus spectrum appeared. The intensity of the hydride and allyl resonances in the ^1H NMR spectrum decreased in intensity and new resonances in the alkyl region appeared, indicating that the hydride migration reaction has started. When the solution of **2** was warmed for 10 min at 313 K, complete conversion of the rhodium−hydride complex was reached. At room temperature, the ^{31}P NMR spectrum showed a very broad resonance at the position of the free phosphorus diamide ligand (64 ppm) and a broad doublet around 60 ppm. The broad resonances in the phosphorus NMR spectrum indicate that fluxional processes occur at room temperature (vide infra). When the temperature was decreased to 203 K, these processes became slow on the NMR time scale, and a doublet of doublets in the rhodium−phosphorus diamide region (119 ppm) and a doublet of triplets at 60 ppm in a ratio 2:1 appeared (Figure 1, spectrum 2). The downfield shift of the phosphine chemical shift of approximately 40 ppm compared to the phosphine chemical shift of complex **2** is characteristic of the formation of a five-membered ring.[21,24] The formation of a four-membered ring will lead to an upfield shift of approximately 40 ppm, as reported by Garrou.[24] We conclude from the downfield shift of the allyldiphenylphosphine resonance that the linear rhodium−alkyl complex **3b** has been formed (Scheme 3). The spectroscopic data of complex **3b** are presented in Table 1. The $^2J_{PP}$ coupling constant found for **3b** (112 Hz) is much smaller than the $^2J_{PP}$ found for **2** (131 Hz). The formation of the five-membered chelate ring will lead to a more distorted trigonal bipyramidal structure, resulting in a smaller P−Rh−P angle. The $^{13}C\{^1H\}$ NMR spectrum showed a doublet of quartets at 197 ppm for the ^{13}CO complex. Both $^1J_{RhC}$ (47 Hz) and $^2J_{PC}$ (16 Hz) coupling constants are slightly different from **2**, which indicates a change in the structure of the complex. The branched alkyl **3d** (Scheme 3) was not observed in the ^{31}P NMR spectra.

Two different mechanisms have been proposed for the hydroformylation reaction.[2] These mechanisms differ in the mode of attack of the alkene on the catalyst. In the associative pathway the alkene coordinates to the five-coordinated rhodium center; the six-coordinated 20-electron complex undergoes hydride migration to form a rhodium−alkyl complex. Immediately after coordination of the phosphine ligand, a very fast insertion would be expected according to this mechanism, which does not appear to be the case. In the dissociative pathway, the commonly accepted mechanism,[25] the five-coordi-

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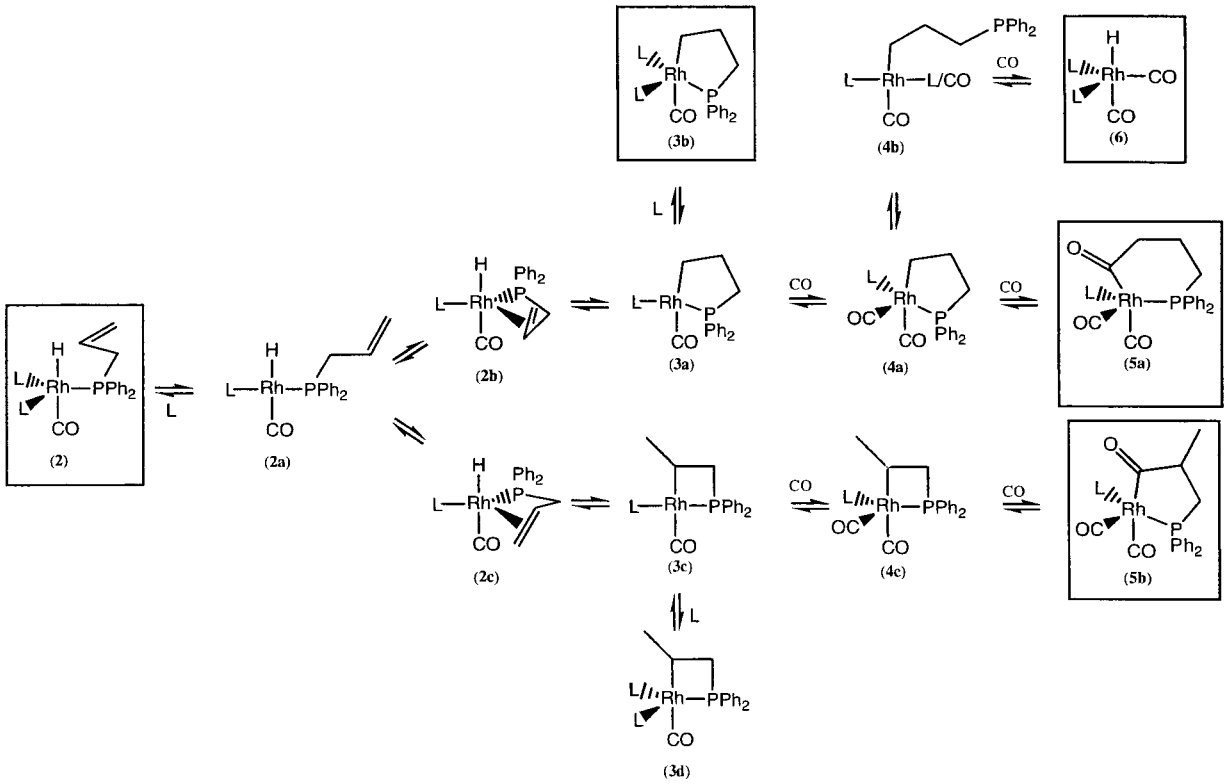
Scheme 3. Overview of the Intermediates Formed in the Intramolecular Hydroformylation of Allyldiphenylphosphine

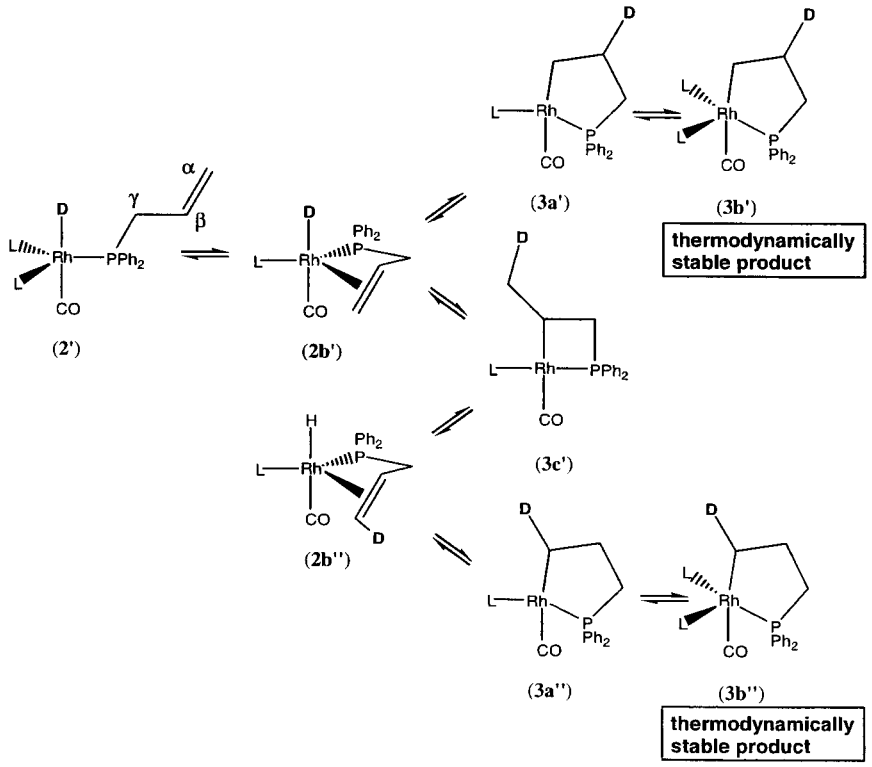


nated rhodium−hydride complex first splits off one ligand to form a 16-electron rhodium center. The alkene coordinates to this four-coordinate rhodium center followed by hydride migration.[2] At room temperature, the ^{31}P NMR spectrum of the rhodium−alkyl complex showed very broad resonances, indicating that fluxional processes occur at room temperature. The ^{31}P NMR spectrum showed a very broad resonance at the position of the free ligand (64 ppm) and a broad doublet around 60 ppm. Similar to the phosphorus diamide ligands in HRh(**1**)$_3$CO, the phosphorus diamide ligands in complex **2** are in fast exchange with the free ligand.[17] When we consider the dissociative pathway for the hydride migration, this ligand coordination/dissociation process creates a free coordination site for the alkene moiety at the rhodium center (complex **2a**, Scheme 3). After alkene coordination (complex **2b/2c**, Scheme 3), hydride migration can occur to form the four-coordinate (cyclic) alkyl complexes **3a** and **3c** (Scheme 3). Probably, these coordinatively unsaturated complexes will coordinate a phosphorus ligand to form the five-coordinate alkyl complexes **3b** and **3d**. Comparison of the reaction times to complete the hydride migration reaction using the monodentate biuret-based rhodium complex (10 min at 313 K) with the bidentate phosphite-based rhodium complex (3 h at 313 K)[22] indicates that the hydride migration in the former case is much faster. The use of monodentate ligands instead of a bidentate ligand causes the faster hydride migration observed in this study. The monodentate phosphorusdiamide ligands are in fast exchange on the NMR time scale with free ligand in solution. Ligand dissociation creates a free coordination site for the alkene moiety at the rhodium center. Formation of a free coordination site in case of the bidentate phosphite ligand is hindered by the formation of the rhodium−phosphite chelate ring. Since the observed hydride migration is still orders of magnitude slower than ligand exchange (NMR line broadening at 293 K), the alkene coordination/hydride migration may involve dissociation of a ligand and hence a 16-electron species.

In the hydroformylation reaction of 1-octene using ligand **1**, high isomerization rates and low selectivity toward the linear product are observed,[17] but using the allyldiphenylphosphine as substrate the branched alkyl complex was not observed in the NMR spectra. This in combination with the observation of the branched rhodium−acyl complex using the bidentate bulky phosphite system suggests that the branched rhodium−alkyl complex is formed in the reaction mixture. Fast equilibrium between the alkene complex **2b/2c** and both alkyl complexes **3a** and **3c** may occur at temperatures higher than 203 K and the branched rhodium−alkyl complex could be formed in the reaction mixture. Similar to the vinyldiphenylphosphine platinum complexes,[21] the linear rhodium−alkyl complex (**3b**) could be thermodynamically more stable than the branched rhodium−alkyl complex (**3d**) as a result of the larger ring strain in the four-membered ring of complex **3d**. Therefore complex **3b** is the only rhodium−alkyl complex observed in the reaction mixture.

To visualize the formation of the branched alkyl complex, we performed the hydride migration reaction using the deuteriorhodium complex instead of the hydridorhodium complex. When deuteride migration leads exclusively to the linear alkyl complex, only a deuterium label at the β-carbon atom will be observed (complex **3b′**, Scheme 4). When the branched alkyl complex is formed but rearranges to the linear alkyl complex, a complex with a deuterium label at the

Scheme 4. Position of the Deuterium Label after Deuterium Migration[a]



[a] Complex **2c′** has been omitted for brevity.

Table 2. Proton and Deuterium Chemical Shifts of the Allyl− and Alkyl−Rhodium Complexes

rhodium−allyl complexes	hydride/deuteride (ppm)	$\delta(H_\gamma/D_\gamma)$ (ppm)	$\delta(H_\beta/D_\beta)$ (ppm)	$\delta(H_\alpha/D_\alpha)$ (ppm)
$HRh(\mathbf{1})_2(allylPPh_2)CO$ (**2**)	−10.8 (^{1}H)	2.5 (m) (^{1}H)	5.2 (m) (^{1}H)	4.7 (m) (^{1}H)
$DRh(\mathbf{1})_2(allylPPh_2)CO$ (**2′**)	−10.6 (broad)			
$HRh(\mathbf{1})_2(CH_2CD_bCH_2PPh_2)CO$			5.0 (m)	
$HRh(\mathbf{1})_2(CHD_cCHCH_2PPh_2)CO$				4.6 (m)
rhodium−alkyl complexes				
$RhCH_2CHDCH_2PPh_2(1)_2CO$ (**3b′**)			1.7 (broad, m)	
$RhCH_2CHDCH_2PPh_2(1)_2CO$ (**3b″**)				1.2 (broad)

α-position will be observed (complex **3b″**, Scheme 4). For the deuteride migration using $DRh(\mathbf{1})_2(allylPPh_2)CO$ (**2′**) the same procedure was followed as for the hydride complex. The complexes formed were investigated using deuterium and phosphorus NMR spectroscopy. After coordination of allyldiphenylphosphine to $DRh(\mathbf{1})_3(CO)$, the solution was warmed to room temperature. The ^{31}P NMR spectra observed for the deuterated complexes are identical to those of the hydride complexes. The deuterium resonances observed and the corresponding proton chemical shifts are displayed in Table 2. The alkyl resonances of the rhodium−alkyl complex are not resolved in the ^{1}H NMR spectrum because of overlapping with the ethyl resonances of ligand **1**. Directly after warming to room temperature, the ^{2}H NMR spectrum clearly shows the (broad) deuteride resonance at −10.6 ppm, together with additional resonances at 5.0 and 4.6 ppm. These chemical shifts correspond to those observed for the protons of the coordinated allyldiphenylphosphine (5.2 and 4.7 ppm) and belong to the deuterium labels at the β- and α-carbon atoms. Appearance of deuterium labels at these positions of the allyl moiety shows that there is a fast equilibrium between the rhodium−hydride/deuteride and the rhodium−alkyl complexes (hydride migration followed by β-hydride elimination). The scrambling of the deuterium label between the α- and β-position indicates that both the four- and five-membered alkyl rings were formed. Together with the allyl resonances, several broad resonances in the alkyl region appeared. Similar to the hydride migration experiments the reaction mixture was warmed for 10 min at 313 K. Completion of the deuteride migration was checked using ^{31}P NMR spectroscopy. After cooling to room temperature, the two allyl resonances had disappeared and two broad resonances at 1.7 and 1.2 ppm were the only resonances remaining in the ^{2}H NMR spectrum. The position of these two resonances is strongly indicative of a deuterium label at the α- or β-carbon atom of the linear rhodium−alkyl complex, indicating that the four-membered rhodium−alkyl complex was formed.

Summarizing the results of the deuterium migration, we conclude that initially both the linear and branched rhodium−alkyl complexes are formed in the reaction mixture. Similar to the vinyldiphenylphosphine platinum complexes, the larger ring system is the thermodynamically more stable product. Probably, the four-membered ring system is more sensitive toward β-hydride elimination (as a result of the ring strain) than the five-membered ring system. When the hydride migration is complete, all complexes present are converted to the stable linear alkyl complex.

CO Insertion. The ^{31}P NMR spectrum changed tremendously when the solution of **3b** was pressurized with 5 bar CO at 253 K (Figure 1, spectrum 3). A sharp doublet of doublets appeared in the rhodium−phosphorus diamide region, and a sharp doublet of doublets appeared in the rhodium−phosphine region in a ratio of 1:1. One of the phosphorus diamide ligands is replaced by a CO ligand. The upfield shift of the phosphine resonance compared to complex **3b** indicated that the phosphine ligand is now part of a six-membered ring. The $^{13}C\{^1H\}$ NMR spectrum showed a very broad singlet ($W_{1/2} \approx 60$ Hz) at 243 ppm and two very broad resonances around 195 ppm when ^{13}CO was used. The ^{13}C NMR resonance at 243 ppm is strongly indicative of a rhodium−acyl carbon atom, proving that CO insertion has occurred. The broad carbonyl resonances in the ^{13}C NMR spectrum indicate that the equatorial and apical CO ligands are in slow exchange. A broad multiplet appeared in the carbonyl ligand region when the solution was cooled to 193 K, but the acyl carbon resonance remained broad upon cooling to this temperature. The J_{PC}, J_{RhC}, and J_{CC} coupling constants remained unresolved. On the basis of the upfield shift of the phosphine resonance of approximately 40 ppm compared to complex **3b**, we conclude that the linear rhodium−acyl complex **5a** (Scheme 3) is the major complex formed after CO insertion.

When CO was added to the solution of **3b** at room temperature, approximately 10% of the rhodium−hydride complex $HRh(\mathbf{1})_2(CO)_2$ was formed next to the rhodium−acyl complex **5a**. Reformation of the rhodium−hydride complex ($HRh(\mathbf{1})_3CO$) followed by exchange of the phosphine ligand with CO can occur, since all reaction steps are reversible. An additional pathway to form the hydride complex $HRh(\mathbf{1})_2(CO)_2$ is β-hydride elimination, one of the main side reactions in the hydroformylation cycle. Dissociation of the phosphine ligand induced by the ring strain will create a vacant site for the coordination of the hydride (see Scheme 3). After β-hydride elimination a carbonyl ligand coordinates at the remaining vacant site. β-Hydride elimination is not unlikely in this system, as was shown in the previous section.

For the hydride migration reaction, we proposed that initially both the linear and branched rhodium−alkyl complexes were formed in the reaction mixture. As a result of ring strain, the four-membered ring system was converted to the thermodynamically stable linear rhodium−alkyl complex. To detect the branched product indirectly, we performed the hydride migration reaction in the presence of CO. When the branched alkyl complex is formed, it can immediately give CO insertion, and the more stable five-membered acyl ring will be trapped. This five-membered ring, if formed, will have the characteristic downfield shift in the ^{31}P NMR spectrum as reported by Garrou.[24] After the coordination of allyldiphenylphosphine to $HRh(\mathbf{1})_3CO$, the (high-pressure) NMR tube was pressurized to 6 bar of CO at 253 K. The tube was warmed to room temperature, and the reaction was monitored using NMR spectroscopy. Initially, the ^{31}P NMR spectrum showed two complexes: the hydride complex **2** and a small amount of the linear alkyl complex **3b**. Different from the hydride migration experiments, the tube was not warmed to 313 K, but it was kept at room temperature. Slowly, the CO insertion started and the resonances of the linear acyl complex **5a** appeared. An additional doublet of doublets appeared at 56 ppm ($^1J_{RhP} = 156$ Hz, $^2J_{PP} = 117$ Hz). An additional resonance in the phosphorus diamide region was not observed, but a ^{31}P COSY spectrum showed cross-peaks for the resonance at 56 ppm and the phosphorus diamide resonance 106 ppm. The resonance at 106 ppm also showed cross-peaks with the phosphine resonance at 16 ppm, which belongs to the linear rhodium−acyl complex. On the basis of the downfield shift of this resonance, the correlation with the phosphorus diamide resonances that belong to a rhodium−acyl complex, and the deuterium labeling experiments, we conclude that the phosphorus resonance at 56 ppm belongs to the branched rhodium−acyl complex **5b** (Scheme 3). Additional proof for the formation of the branched alkyl/acyl complex is the presence of both the resonances of the linear and branched aldehyde proton in the ^1H NMR spectra after addition of hydrogen. The deuterium experiments showed that the branched alkyl complex is formed in the reaction mixture, although this complex was not observed in the ^{31}P NMR spectra. The presence of CO in the reaction mixture traps this branched product by the formation of a five-membered ring system after CO insertion.

Hydrogenolysis After the CO insertion we bubbled H_2 through the solution of **5a** at room temperature. Under atmospheric hydrogen pressure, hydrogenolysis did not occur. Deinsertion of CO is observed, probably because the insertion−deinsertion equilibrium is driven to the rhodium−alkyl complex since CO is removed by the H_2 flow. A flow of ^{13}CO through a solution of the ^{12}CO rhodium−acyl complex **5a** resulted in the appearance of the rhodium−acyl resonance of complex **5a** in the $^{13}C\{^1H\}$ NMR spectrum showing the reversibility of the CO insertion. The rhodium−acyl complex **5a** and the hydride complex $HRh(\mathbf{1})_2(CO)_2$ were the only complexes observed when a 1:1 mixture of CO and H_2 was bubbled through the solution. These results indicate that the hydrogenolysis does not occur at atmospheric hydrogen pressure. This is not unlikely since kinetic experiments with this ligand system showed that hydrogenolysis, depending on the conditions used, is one of the rate-determining steps.[14]

When the solution of the rhodium−acyl complex **5a** was pressurized to 15 bar of $CO/H_2 = 1:2$, the hydrogenolysis occurred slowly overnight at room temperature. Directly after pressurizing with hydrogen, a weak hydride resonance appeared in the hydride region of the ^1H NMR spectrum and aldehyde resonances appeared at approximately 10 ppm, proving that the hydrogenolysis had started. After complete conversion of the rhodium−acyl complex has been reached, the aldehyde resonance is present only in low concentration in the proton NMR spectrum. The IR spectrum of this solution showed a weak aldehyde absorption at 1751 cm^{-1} and a medium absorption at 3340 cm^{-1} that probably belongs to the hydroxyl group. Jackson and co-workers[13] performed the hydroformylation of a range of alkenylphosphines. Their results showed complete conversion of the allyldiphenylphosphine to the alcohol instead of the aldehyde. The presence of the aldehyde moiety in close proximity of the rhodium center probably leads to

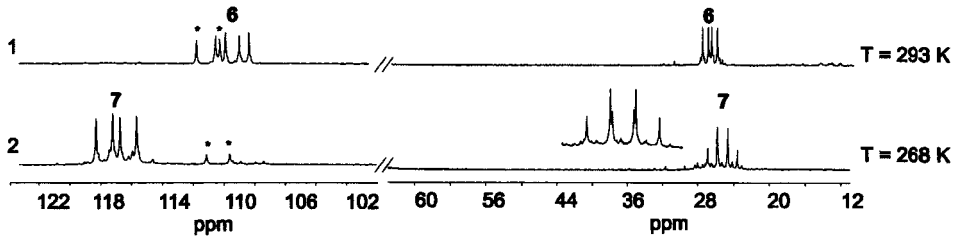


Figure 2. $^{31}P\{^1H\}$ NMR spectra of complexes **6** and **7**: (1) $^{31}P\{^1H\}$ NMR of complex **6** obtained at 293 K, (2) $^{31}P\{^1H\}$ NMR of complex **7** obtained at 268 K, (*) $HRh(\mathbf{1})_2(CO)_2$.

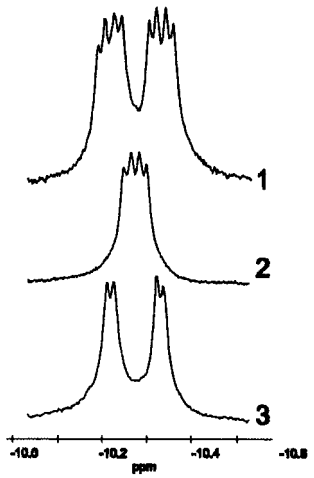


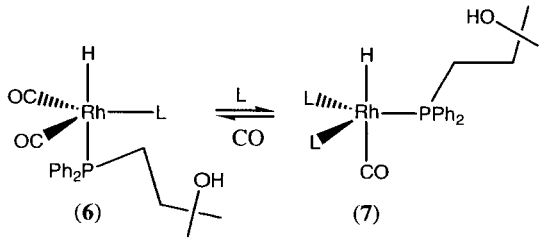
Figure 3. Hydride resonance after selectively decoupling of the phosphine or phosphorus diamide resonance: (1) Hydride resonance of complex **6**, (2) hydride resonance of complex **6** after selective decoupling of the rhodium−phosphine resonance, (3) hydride resonance of complex **6** after selective decoupling of the rhodium−phosphorus diamide resonance.

further hydrogenation of the aldehyde to the corresponding alcohol. (The hydrogenation of the aldehyde is one of the side reactions observed in the hydroformylation reaction.)

After complete conversion of the rhodium−acyl complex **5a**, the ^{31}P NMR spectrum showed a doublet of doublets in both the phosphorus diamide (109 ppm) and phosphine region (27 ppm) (Figure 2, spectrum 1). Different from the previously described hydride complex (**2**), the $^2J_{PH}$ coupling constants for the phosphine and the phosphorus diamide ligand are not equal (33 and 10 Hz). Selectively decoupling of the phosphorus resonance at 27 ppm or at 109 ppm showed that the large $^2J_{PH}$ coupling constant of 33 Hz results from the phosphine atom, whereas the small coupling of 10 Hz results from the phosphorus diamide atom (Figure 3). The $^2J_{PH}$ coupling constant of 10 Hz is similar to the previously obtained data, whereas the $^2J_{PH}$ coupling constant of 33 Hz is too large for a *cis* coordination of the hydride and phosphorus ligand. Two explanations can be brought forward: an equilibrium mixture of ee−ea coordination giving averaged signals in the NMR spectra, provided that there is a fast exchange of the ligand between the equatorial and apical positions;[26] second, coordination of the phosphorus ligand in the equatorial plane of a slightly distorted trigonal bipyramid would lead to an increase of the $^2J_{PH}$ coupling

(26) van der Veen, L. A.; Boele, M. D. K.; Bregman, F. R.; Kamer, P. C. J.; van Leeuwen, P. W. N. M.; Goubitz, K.; Fraanje, J.; Schenk, H.; Bo, C. *J. Am. Chem. Soc.* **1998**, *120*, 11616.

Scheme 5. Complexes Formed after Intramolecular Hydroformylation and Hydrogenation of Complex 2



constant. The large J_{PH} coupling constant suggests that the phosphine ligand is now coordinated to some extent at an apical position of the trigonal bipyramid (complex **6**, Scheme 5). The phosphorus diamide ligand is still coordinated at an equatorial position. The ^{13}C NMR spectrum confirms this hypothesis, showing only one resonance for both carbonyl ligands having one large $^2J_{CP}$ coupling (24 Hz) and one small $^2J_{CP}$ coupling constant (<3 Hz).

We depressurized the NMR tube after the hydrogenolysis and hydrogenation reaction and removed the hydrogen and CO gases by bubbling argon through the solution. After removing the CO from the solution the phosphorus NMR spectrum showed a doublet of doublets in the phosphorus diamide region (117 ppm) and a double triplet appears in the phosphine region (25 ppm) (spectrum 2, Figure 2). The multiplicity of the rhodium−phosphine resonance shows that complex **6** exchanged a carbonyl ligand with a phosphorus diamide ligand. The $^2J_{PH}$ coupling constant (12 Hz) is again similar for both the rhodium−phosphorus diamide and the phosphine, indicating that the phosphine ligand has moved to the equatorial plane (complex **7**, Scheme 5).

The hydrogenolysis reaction is much slower than the insertion reactions under the conditions studied. At higher temperatures these differences are less pronounced, and thus we conclude that the activation enthalpy for the hydrogenolysis step is relatively high.

Conclusion

The stepwise hydroformylation of allyldiphenylphosphine has been investigated using a monodentate biuret-based rhodium catalyst. Coupling of the ligand and substrate functions stabilized the intermediates of the hydroformylation reaction and enabled the characterization of the complexes using NMR spectroscopy.

Hydride migration in the absence of CO led to complete conversion of the rhodium−hydride complex to the linear rhodium−alkyl complex (**3b**). The deuterium complex showed scrambling of deuterium at the

α- and β-positions of the allyl/alkyl moiety in the hydride migration reaction, indicating that both the linear and the branched rhodium−alkyl complex had been formed. The linear rhodium−alkyl complex was shown as the thermodynamically stable product formed after longer reaction times, similar to the results observed for comparable platinum−alkyl complexes.[21] Deuterium scrambling at the α- and β-position of the allyl moiety shows that the hydride migration is a reversible process in the absence of carbon monoxide. Recently we studied the reversibility of the hydride migration reaction in the hydroformylation reaction of 1-octene using this biuret-based rhodium catalyst.[14] These experiments showed that under hydroformylation conditions the hydride migration is virtually irreversible. The results obtained using allyldiphenylphosphine are in agreement with the results observed for 1-octene. In the presence of CO the hydride migration was directly followed by CO insertion, and both the linear and branched rhodium−acyl complexes were observed in the ^{31}P NMR spectra, showing that in the presence of CO the hydride migration is irreversible. On the basis of these observations we conclude that the selectivity in this system for either the linear or branched aldehyde is determined by the ratios of the rates of reaction that can take place immediately after the hydride migration.

Experimental Section

General Information. All preparations were carried out under an atmosphere of argon using standard Schlenk techniques. Dichloromethane-d_2 was distilled from calcium hydride. Other solvents were distilled from sodium/benzophenone. All glassware was dried by heating under vacuum. The NMR spectra were recorded on a Bruker DRX-300 spectrometer. Chemical shifts are given in ppm referenced to TMS or H_3PO_4 (external). Ligand **1** and HRh(**1**)$_3$CO were synthesized according literature procedures.[17] Because of the low yield of HRh(**1**)$_3$CO described in the literature,[17] an optimized procedure is described below.

In a typical 5 mm tube NMR experiment 20 mg (0.020 mmol) of **2** was dissolved in 0.5 mL of CD_2Cl_2. A 0.2 mL (0.020 mmol) portion of a 0.1 M stock solution of allyldiphenylphosphine in CD_2Cl_2 was added dropwise to this solution at −40 °C. The yellow solution was stirred for 15 min at this temperature before the NMR spectra were recorded. For the 10 mm high-pressure NMR tube, 80 mg (0.08 mmol) of HRh(**1**)$_3$CO in 1.5 mL of CD_2Cl_2 was used.

HRh(1)$_3$CO. A 20 mg (0.078 mmol) sample of Rh(acac)$(CO)_2$ and 114 mg (0.39 mmol) of ligand **1** were dissolved in 20 mL of cyclohexane. The solution was brought to an autoclave. The autoclave was put under a pressure of 15 bar CO/H_2 (1:1) and stirred at 40 °C for 2 h. The solution was transferred to a Schlenk flask. (The solution was saturated with ^{13}CO in the case of the ^{13}CO-labeled complex.) The white complex precipitated when the solution was concentrated to a volume of 5 mL. The complex was washed three times with 10 mL of pentane and dried under vacuum. Yield: 56 mg (72%), mp 106 °C (dec). The precise NMR data of this compound are displayed in Table 1: IR (CH_2Cl_2) ν_{NCO} 1695 cm^{-1} (vs), 1660 cm^{-1} (vs), ν_{Rh-CO} 2019 cm^{-1}.

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