NMR study of intermediates in the bulky diphosphite modified rhodium catalysed hydroformylation

Annemiek van Rooy, Paul C.J. Kamer, Piet W.N.M. van Leeuwen *

Van 't Hoff Institute, University of Amsterdam, Nieuwe Achtergracht 166, 1018 WV Amsterdam, Netherlands

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Abstract

The stoichiometric hydroformylation reaction of allyldiphenylphosphine with $RhH(CO)_2(2)$ (2 is a bulky diphosphite) was studied using ^1H and ^{31}P NMR spectroscopy. Reaction of equimolar amounts in benzene resulted in the formation of $RhH(CO)(CH_2=CHCH_2PPh_2)(2)$ in which all three phosphorus ligands are coordinated equatorially (4). When 4 was heated, hydride migration occurred leading to two products. Migration to the terminal carbon gave 5, $Rh(CO)(PPh_2CH_2CH_2CH_2)(2)$. Migration of the hydride to the internal carbon atom was rapidly followed by CO insertion, resulting in the acyl compound 6, containing a five-membered rhodacycle. Complex 6 did not undergo reaction with H_2. Reaction of 5 with CO reversibly yielded acyl complex 7, containing a six-membered rhodacycle. Hydrogenation of 5 yielded 8, the diphenylpropylphosphine analogue of 4. © 1997 Elsevier Science S.A.

1. Introduction

Recently it has been shown that 1-alkenes are hydroformylated very selectively to linear aldehydes when certain bulky diphosphites are used as modifying ligands [1–4]. We found that the catalyst present during the reaction is $RhH(CO)_2$(diphosphite) containing a bisequatorially coordinated diphosphite. The X-ray structure of $RhH(CO)_2(1)$ (1 = $P[O(2,2'-(4,6(C(CH_3)_3)_2-C_6H_2)_2)O][O(2,2'(4,6(C(CH_3)_3)_2-C_6H_2)_2)OP][O(4-Cl-C_6H_4)]_2)$ was solved, being the first crystal structure of a hydridorhodium complex containing two CO molecules and a bidentate phosphorus ligand [5].

Very few intermediates of rhodium catalysed hydroformylation reactions have been characterised. The putative rhodium intermediates are often unstable and hence in-situ techniques must be used. HP-IR spectroscopy is the most attractive technique to identify reaction intermediates under reaction conditions [6]. In 1990 Garland [7] identified $RhC(O)C_2H_4-t-Bu(CO)_4$ as intermediate in the hydroformylation of 3,3-dimethyl-1-butene. Very recently we characterised $RhC(O)C_nH_{2n+1}(CO)_3L$ (L = tris(2-tert-butyl-4-methyl-phenyl)phosphite) as the predominant species in

the bulky monophosphite modified hydroformylation of various 1-alkenes [8]. Upon addition of styrene to $RhH(CO)_2(PPh_3)_2$, the acyl product $RhC(O)C_2H_4Ph(CO)_2(PPh_3)_2$ was characterised with HP-NMR spectroscopy [9]. Previously [10] we studied the stoichiometric, stepwise reaction of platinum diphenylphosphinito catalysts with allyl phosphites and phosphines. Jackson et al. [11] reported that the catalytic hydroformylation of allyldiphenylphosphine with rhodium triphenylphosphine catalysts yielded mainly terminal products.

In an attempt to gain more insight into the different reaction steps, we studied the stoichiometric reaction of a rhodium–diphosphite complex $RhH(CO)_2(2)$, 3, with an alkenylphosphine. Because of the decomposition of the complexes upon isolation, studies were mostly performed in a HP-NMR tube. We studied the reaction of 3 with allyldiphenylphosphine and subsequently with CO and H_2. The obtained products have been characterised by their ^{31}P and ^1H NMR spectra. Although cyclometallation reactions have not been widely studied for rhodium – the majority of these type of reactions have been performed using Ni, Pd and Pt – general rules for spectroscopic behaviour can be extracted [12]. The change in the ^{31}P chemical shift from free ligand to cyclic complex is indicative of the ring size of the phosphametallacycle.

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* Corresponding author.

(2)   (3)   (5)   (6)   (6')

(7)
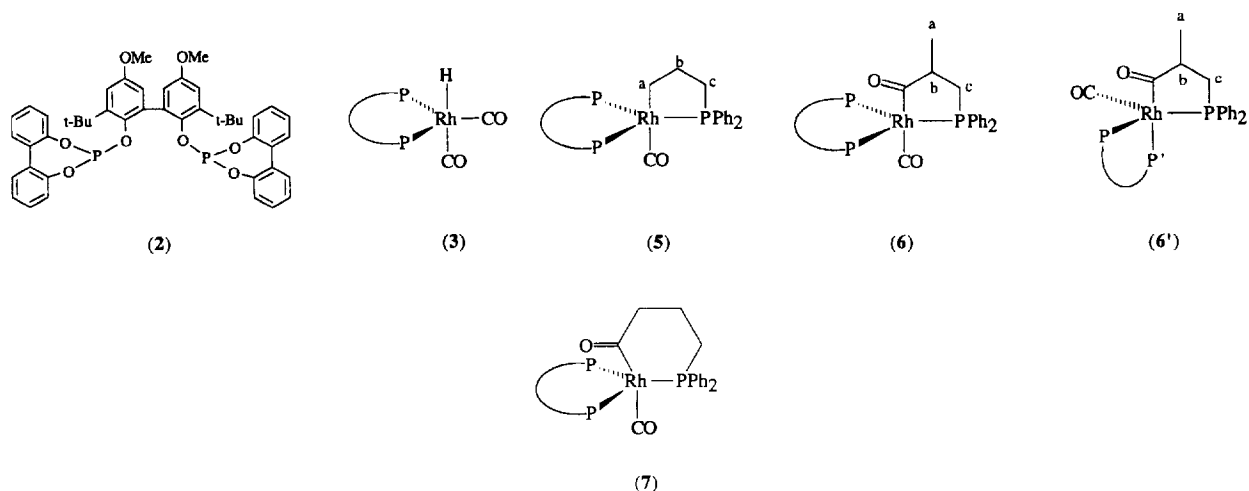
2. Results

2.1. Reaction of 3 with $CH_2CHCH_2PPh_2$

First, the reaction of equimolar amounts of $CH_2=CHCH_2PPh_2$ and **3** was followed by means of IR spectroscopy. After stirring for 3 h at 40 °C the two absorptions (for compound **3** three absorptions are expected, but due to overlap in solution only two are detected; an IR spectrum of **3** as Nujol mull yields the three absorption bands, see Ref. [4]) of the starting compound **3** at 2072 and 2013 cm^{-1} were replaced by two new bands due to a carbonyl and a hydride at 2045 and 1950 cm^{-1}, which is in concert with substitution of a CO molecule with an electron-donating phosphine ligand. The two observed absorptions are combination bands of a CO stretch and an Rh–H vibration, as in $RhH(CO)(PPh_3)_3$ [13].

The ^{31}P NMR spectrum of the reaction product shows a strongly coupled multiplet in the phosphite region and a multiplet in the phosphine region (see Fig. 1). In the hydride region of the ^1H NMR spectrum, the sharp signal of **3** changes into a somewhat broader multiplet. The olefinic absorptions of the allyl group (at 5 and 6.5 ppm) are still present. Data obtained by simulation are listed in Table 1. Due to the complexity of the phosphite region of the ^{31}P NMR spectra all data have been carefully simulated. Only the values for P1 in compound **7** remain somewhat uncertain; the chemical shift was estimated and J_{Rh-P3} and J_{P1-P3} might be exchanged. These results point towards formation of $RhH(CO)(2)P(allyl)Ph_2$, **4**. The two phosphorus atoms of the diphosphite are now magnetically inequivalent as is shown by the ^{31}P NMR spectrum and also by the occurrence of two ^tBu and two MeO signals in the ^1H NMR spectrum. Atropisomerism in **3** also predicts two
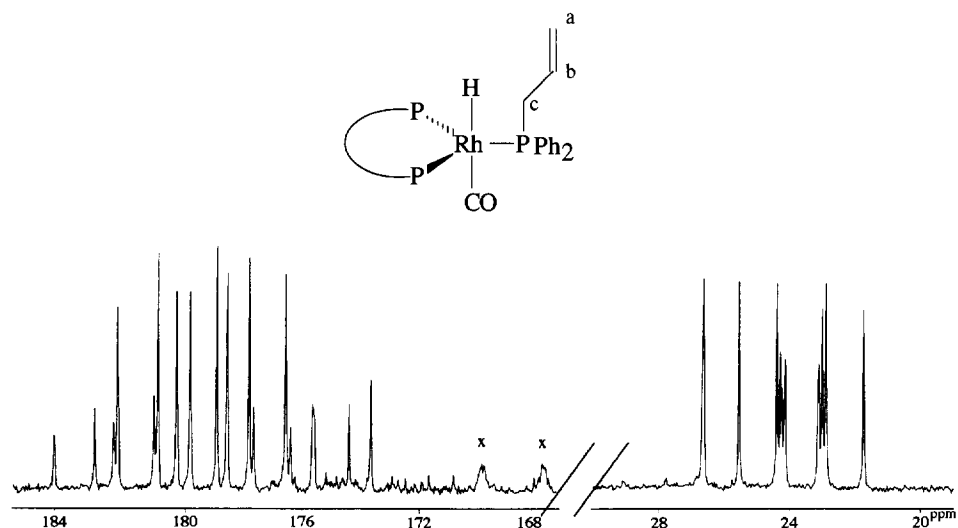

Fig. 1. Phosphite and phosphine region of ^{31}P NMR spectrum of **4**. x = small amount of **3**; the additional peak at 26 ppm originates from phosphine oxide.

Table 1
^{31}P data of the characterised complexes measured in C_6D_6

Complex	$\delta\,^{31}$P (ppm)	J_{RhP} (Hz)	J_{PP} (Hz)	$\delta\,^1$H (hydrido)	ν_{CO} (cm^{-1})
3	165	240	—	−10.80	2072, 2013
4	177.4 (P1)	248 (P1)	266 (P1–P2)	−11.02 (m)	2045, 1950
	181.4 (P2)	248 (P2)	153 (P1–P3)		
	23.6 (P3)	139 (P3)	169 (P2–P3)		
5	173.5 (P1)	257 (P1)	253 (P1–P2)		2010
	165.5 (P2)	228 (P2)	204 (P1–P3)		
	66.3 (P3)	151 (P3)	149 (P2–P3)		
6	172.6 (P1)	237 (P1)	133 (P1–P2)		1970
	167.0 (P2)	266 (P2)	105 (P1–P3)		
	59.7 (P3)	160 (P3)	179 (P2–P3)		
7	≈ 165 (P1)	n.d.	180 (P1–P2)		2020
	158.6 (P2)	266 (P2)	133 (P1–P3)		
	12.6 (P3)	152 (P3)	180 (P2–P3)		
8	25.6 (P3)	155 (P3)	260 (P1–P2)	−11.04 (m,b)	2034(s)
			190 (P1–P3)		1947(w)
			−150 (P2–P3)		

inequivalent phosphorus atoms in this complex, but as a result of a rapid exchange only one averaged signal is observed in most complexes studied so far [4,14]. Two hydrido rhodium complexes containing a diphosphite and a PPh$_3$ ligand are known in the literature [4]. It was found that the phosphine–phosphorus to phosphite–phosphorus coupling constant is small ($J_{P-P} = 38$ and 56 Hz) when the two ligands are cis to one another, i.e. equatorial–axial coordination. The coupling constant is larger ($J_{P-P} \approx 170$ Hz) when they both occupy equatorial positions. In compound 4 the coupling constants J_{P-P} amount to 170 and 190 Hz. Furthermore, we [4,14] and Takaya and coworkers [15] found that the coupling constant of a trans hydride-to-phosphorus (phosphite) is very large (up to 220 Hz). From the two almost equal phosphorus (phosphite) rhodium coupling constants ($\approx$ 245 and 250 Hz), the three very small hydride-to-phosphorus coupling constants and the large phosphorus-to-phosphorus coupling constants, we conclude that in 4 all the phosphorus ligands are equatorially coordinated to the rhodium centre as in RhH(CO)(PPh$_3$)$_3$ [16].

2.2. Reactions of 4

Heating of 4 ($T = 60\,^{\circ}$C, 1/2 h) results in the disappearance of the hydride and the olefinic signals in the ^{1}H NMR spectrum and new absorptions in the aliphatic region appear. The phosphine region of the ^{31}P NMR indicates the presence of two new compounds: 5, showing a doublet of triplets, and 6, showing a doublet of a double doublet (Fig. 2). In the phosphite region the signals of the two new compounds strongly overlap (not shown in the figures). When the experiment was repeated while purging with N$_2$, only 5 was irreversibly formed. The largest change in the ^{31}P NMR spectrum is the downfield shift of the phosphine absorption (43 ppm for 5 and 36.1 ppm for 6), which indicates [10,12,17,18] that the phosphorus atom becomes part of a ring. From the downfield shift ($\approx$ 40 ppm) of the ^{31}P phosphine absorption in compounds 5 and 6 we conclude that in both compounds the phosphine phosphorus atoms are part of a five-membered ring as was previously observed for phosphines [19] and phosphites [20] coordi-
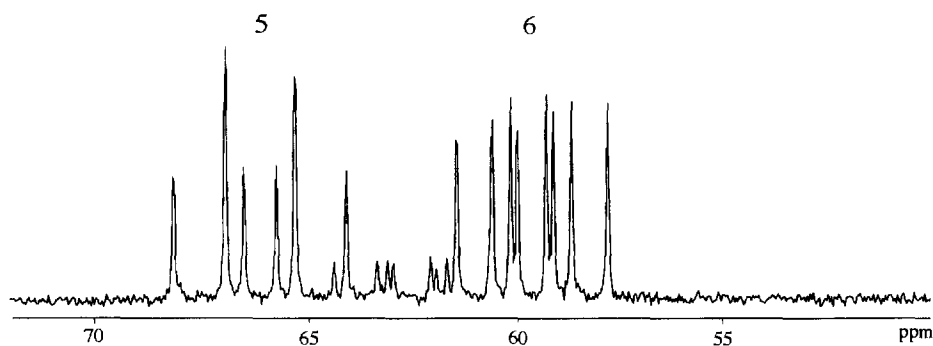

Fig. 2. Phosphine region of ^{31}P NMR spectrum of products after heating of 4.

Table 2
Relevant ^{1}H data of characterised complexes. Chemical shifts in ppm

Complex	δ (H$_a$)	δ (H$_b$)	δ (H$_c$)	δ (hydrido)
3				− 10.80 (dt)
4	4.4 (m)	5.5 (m)	2.54 (d, J = 8.1 Hz)	− 11.02 (m)
5	0.50 (m)	0.86 (m)	1.5 ^{a}	
6	1.70 (d, J = 6.3 Hz)	2.00 (m)	3.18 (dd)	

^{a} Signal largely overlapped by ^{t}Bu signals.

nated to rhodium. From the absence of the hydrido signal, we conclude that hydride migration has occurred. The assignment of the ^{1}H absorptions are given in Table 2. Hydride migration can lead to two species: the branched and the linear alkyl rhodium complexes. The linear insertion compound leads indeed to a compound, 5, containing a five-membered ring, but the branched alkylphosphine complex contains a four-membered ring. This strained ring leads to an unstable complex that will be prone to CO insertion. More importantly, its ^{31}P absorption is expected upfield (30–50 ppm) compared to the absorption of the monodentate ligand in 4 [10]. Therefore, it is more likely that insertion of CO has taken place in the carbon rhodium bond of the putative intermediate 9, giving rise to an acylphosphine rhodium complex containing a five-membered ring, 6 [18]. This explains the presence of two products, 5 and 6. Further evidence was obtained when CO was removed by purging with N$_2$. Under these conditions formation of 6 was not observed and only 5 was obtained.

The infrared spectrum shows one CO stretch vibration both for 5 and 6. In the acyl region (around 1700 cm^{-1}) no absorption could be detected, because of the large solvent peaks and the weakness of metal–acyl carbonyl stretching bands. ^{13}C (natural abundance) NMR spectroscopy did not clarify this problem either, since decomposition had occurred (10 h, 298 K) before an acceptable spectrum could be obtained. Comparison of the ^{31}P NMR spectra reveal that the coupling constants J_{P1-P3} and J_{P2-P3} of 6 differ more in magnitude than those of 5. Also, the constant J_{P1-P2} of 6 is much smaller. The structure of 6 seems to deviate considerably from the structures 4 and 5 that both have the expected values for the coupling constants of a complex in which the three phosphorus ligands are equatorially coordinated. A distorted structure between 6 and 6′ would be in accord with the ^{31}P NMR data as would be the lower CO vibration in 6 (1970 vs. 2010 cm^{-1} in 5). The X-ray structure of the rhodium diphosphite complex RhH(CO)$_2$(1) revealed a distorted TBP geometry as well [4]. Alternatively, this complex could be described as a strongly distorted tetrahedron with a hydride on one of its faces.

2.3. Reactions of 5

Bubbling of CO through a solution of 5 at room temperature did not result in the formation of an insertion compound. However, at 225 K a new product was observed, 7, showing a phosphine signal at 13 ppm (Fig. 3, spectrum 2). The compound disappeared when the solution was warmed to room temperature. An almost complete conversion to 7 was reached when the reaction was performed at elevated CO pressure (10 bar), using a high-pressure NMR tube (Fig. 3, spectrum 3). Immedi-
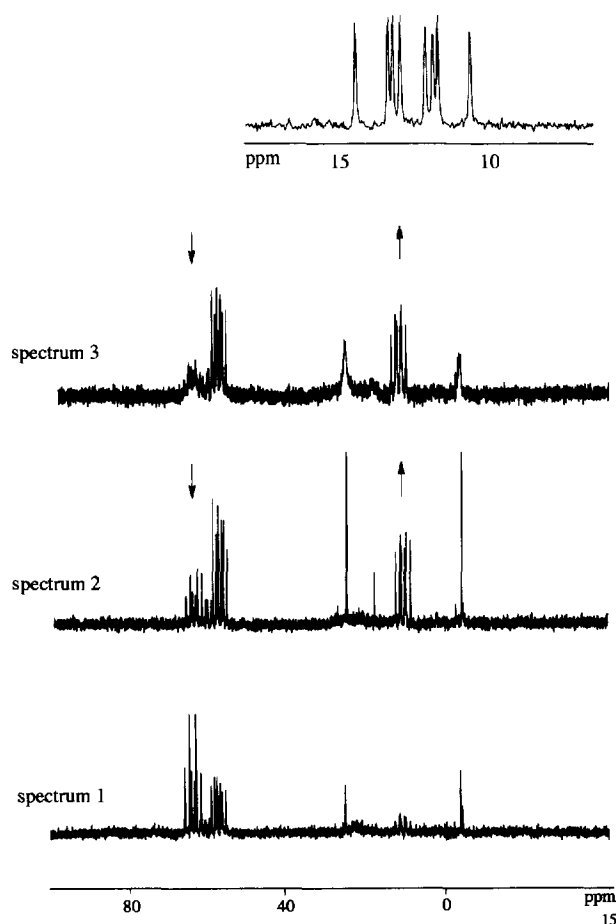

Fig. 3. Reaction of 5 with CO. Spectrum 1: starting spectrum; spectrum 2: after leading through CO for 1 h at T = 225 K; spectrum 3: after one night under 10 bar CO, T = 298 K.

ately after the release of the CO pressure an IR spectrum was measured and a decrease in the intensity of the band at 2010 was observed while a new absorption at $2020 \, cm^{-1}$ appeared. After several minutes, the reverse reaction was already complete and no further change was observed. When this experiment was carried out with a mixture of 5 and 6, the signals of 6 did not undergo any change. The larger stability of compound 7 at low temperatures and increased CO pressures implies the formation of an insertion (CO) product. The phosphine is now part of a six-membered ring as is invoked by the upfield shift of the phosphine signal compared to the signal of allylphosphine in 4. Because of the overlap of the ^{31}P NMR signals in the phosphite region we only determined the phosphine data (Table 1). Simultaneous heating of 4 and bubbling through of CO resulted in primary formation of 5 (of which a small amount readily reacted to 7) and only after some time was the formation of 6 observed.

When H_2 was led through a mixture of 5 and 6, no change in the absorptions belonging to 6 was observed. Eventually, after the signal belonging to 5 had disappeared, two new products were obtained: 4 and a new hydride species 8. The ^1H NMR and ^{31}P NMR spectra of 8 closely resemble those of 4 and therefore they are assigned to an analogous hydride species. The conversion of 5 into these two products is almost complete. The reappearance of 4 points toward β-H elimination of the alkyl group. The β-H elimination reaction is an important side reaction in the rhodium catalysed hydroformylation [21,22], especially at higher temperatures and low CO pressures. Although the branched alkyl rhodium compound is in general much more susceptible towards β-H elimination, this reaction is not observed for the branched analogue in this instance; de-insertion of CO from 6 to the unstable complex 9 does not occur. A complex containing the isomerisation product 2-propenylphosphine was not observed and it can be ruled
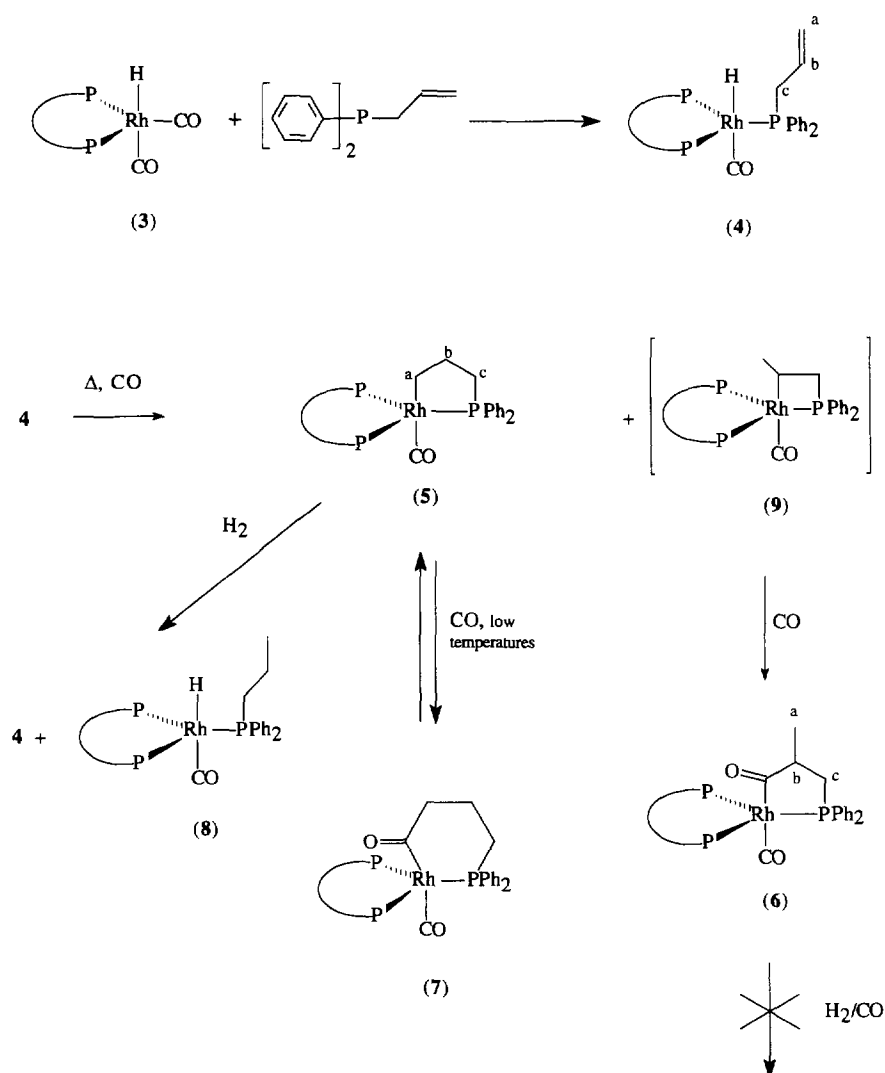
Scheme 1. Overview of the reactions.

out as a structure for **8**. On the basis of the spectra we propose that the hydride product **8** is the hydrogenation product of **5**, i.e. a complex of propyldiphenylphosphine.

2.4. Reaction of 7

Hydroformylation of allyldiphenylphosphine was attempted by the reaction of **5** with a mixture of CO and H$_2$. However, no aldehyde containing product was obtained under these conditions. As in the former experiment, only an amount of **4** resulting from β-H elimination was eventually observed.

3. Discussion

An overview of the observed reactions is depicted in Scheme 1. Reaction of allyldiphenylphosphine with **3** yields the phosphine substituted rhodium complex **4** with all phosphorus ligands in equatorial positions. Hydride migration occurs on heating of **4**, resulting in the linear alkyl complex **5** containing a five-membered ring. Compared to catalytic hydroformylation reactions, for which in most instances the complexation of the alkene substrate is rate-determining [3,4,23], the reaction of **4** is surprisingly slow. An associative reaction of rhodium hydride and alkene implying a 20-electron intermediate is therefore highly unlikely. Our results support the generally accepted dissociative reaction mechanism of Wilkinson and coworkers [24]. We propose that a phosphorus atom of the diphosphite dissociates from the rhodium centre before alkene coordination occurs. Because of the stability of the chelated diphosphite complex, dissociation of the phosphorus ligand is slow and as a result the intermediacy of **4** could be observed. Alternatively, dissociation of allyldiphenylphosphine may occur, but the present experiments cannot distinguish between these possibilities.

The branched alkyl cyclometallated complex contains a four-membered ring and is too unstable to be observed. The reaction towards the branched migration product is evidenced indirectly when CO is present in the reaction medium. The species containing the four-membered ring undergoes rapid insertion of a CO molecule and an acyl complex is obtained in which the phosphine is part of a five-membered, stable ring structure. Insertion of CO into the alkylrhodium bond of **5** does occur, but the acyl product can only be 'trapped' at low temperatures or high CO pressure. The equilibrium between **5** and **7** is mainly determined by entropy since **7** is stable at low temperatures only. Formation of the acyl species does not require the creation of an open site. Yet the reaction is relatively slow. This may be due to the fact that the ground-state *trans*-disposition of the

carbonyl moiety and the alkyl moiety is far from ideal for an insertion reaction.

Hydrogenolysis of the acyl compounds is not observed. Acyl complex **6** is too stable to undergo any subsequent reaction. Complex **5** undergoes hydrogenation and β-H elimination, yielding the propyldiphenylphosphine coordinated hydrido complex and the starting compound **4**.

In conclusion, the use of a rhodium hydrido species containing a chelating diphosphite ligand and allyldiphenylphosphine as the substrate has allowed the characterisation of several compounds that are intermediates in the hydroformylation reaction. Complexes with a five-membered ring structure are highly favoured. This is advantageous for the characterisation of these complexes, but on the other hand, it has prevented us, as yet, from completing the reaction cycle; the acyl intermediates are too stable (**5**) or not stable enough (**6**) under our reaction conditions to form the aldehyde product.

4. Experimental section

All operations were performed under argon using standard Schlenk techniques. Solvents were distilled from sodium/benzophenone before use. Diphenylallylphosphine was obtained from Aldrich. NMR spectra were recorded on a Bruker AMX 300 MHz spectrometer and chemical shifts were reported referenced to tetramethylsilane and H$_3$PO$_4$ respectively. Infrared spectra were recorded on a Nicolet 510 FT-IR spectrophotometer. Compounds **2** and **3** were prepared according to an earlier published method [4]. Reactions were performed in an NMR tube kept under argon with C$_6$D$_6$ as the solvent. Standard quantities were 3.9×10^{-5} mol RhH(CO)$_2$(diphosphite), one equivalent of allyldiphenylphosphine in 1 ml of C$_6$D$_6$. In solution at ambient conditions, the diphosphite complexes are stable for several hours, but after longer reaction times, some decomposition cannot be prevented. High-pressure NMR was performed in a sapphire tube ($\emptyset = 10$ mm).

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