Structural Characterisation in Solution of Intermediates in Rhodium-catalysed Hydroformylation and their Interconversion Pathways

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The reaction of $HRh(CO)(PPh_3)_3$ (**1**) with CO has been studied by ^1H, ^{13}C, and ^{31}P n.m.r. The main species present under ambient conditions is $HRh(CO)_2(PPh_3)_2$ (**2**) which exists as two rapidly equilibrating trigonal bipyramidal isomers. Complexes (**1**) and (**2**) are in rapid equilibrium *via* CO and PPh_3 dissociation steps and the square-planar complexes $HRh(CO)(PPh_3)_2$ (**3**) and $HRh(CO)_2PPh_3$ (**4**) are likely transient intermediates. The chemistry of these PPh_3 complexes is compared with that of closely related 5-phenyl-5*H*-dibenzophosphole and 1,3-bis(diphenylphosphino)propane analogues. Complex (**1**) catalyses the isomerisation of (*Z*)-[1,2-$^2H_2$]styrene, effectively suppressed by CO or PPh_3. $HRh(CO)_2P_2$ complexes trap methylenecyclopropane. In the presence of styrene and CO, complex (**1**) is converted into a branched acyl derivative which readily equilibrates with its linear isomer; the stereochemistry of these acyl derivatives $(CO)_2(PPh_3)_2RhCOR$ is determined by low-temperature n.m.r.; at higher temperatures rapid inter- and intra-molecular exchange processes occur. The relevance of these observations to rhodium-catalysed hydroformylation is discussed and it is proposed that the regiochemistry of reaction is largely controlled by competitive olefin trapping involving complexes (**3**) and (**4**).

Since its feasibility was demonstrated by Wilkinson and his co-workers in the late 1960s,[1] hydroformylation catalysed by rhodium triphenylphosphine complexes has become an industrial reaction of considerable economic importance.[2] The early work was based on the readily prepared complex $HRhCO(PPh_3)_3$[3] and under the reaction conditions this was known to be in equilibrium with $HRh(CO)_2(PPh_3)_2$ by CO–PPh_3 ligand exchange,[1] presumed to involve dissociation to a square-planar four-co-ordinate intermediate. At room temperature, more deep-seated equilibria take place slowly with the formation of at least two dimeric species, one of which has been structurally characterised.[4]

Current practice does not differ greatly from the catalysts and procedures introduced in the original work. Much effort has been directed towards the synthesis of new catalytic species, with some recent focus on heteroatom-bridged dimeric complexes[5] and water-soluble catalysts.[6] Typical commerical processes are based on triphenylphosphinerhodium complexes and operate at moderate temperature and pressure.[2]

Much of the extensive mechanistic work on the rhodium hydroformylation reaction has been carried out in industrial laboratories and is not published in the open literature.[7] For terminal olefins it is known that the generally more desirable pathway to straight-chain aldehyde is enhanced by higher than stoicheiometric concentrations of PPh_3 and lowered pressures of CO.[8] The rate-determining stage of reaction is thought to be hydrogen addition to a rhodium acyl formed in a multi-step sequence[9] and many workers have adopted Wilkinson's early suggestion[1] that there are two pathways in competition. These differ only in the extent of CO ligation, so that A is favoured at high [CO] and B is favoured at low [CO]. A particular problem is that path A (Figure 1), leading to low regioselectivity, involves an intrinsically unlikely 20-electron intermediate as normally written, although this could be circumvented by reversible hydride migration to CO giving a formylrhodium species[10] or by a four-centre addition mechanism akin to hydroboration[11] which bypasses the bound olefinic complex. In one case[12] where the kinetics of hydroformylation of propene was studied, it was noted that the ratio of n- to iso-butyraldehyde could be fitted quite well by competition between associative and dissociative pathways but equally well by competition between two dissociative pathways in which the olefin is trapped by $HRhCO(PPh_3)_2$ or by $HRh(CO)_2PPh_3$. The former was assumed to react with higher regioselectivity than the latter.

There is a distinct lack of information on the structure, stereochemistry, and dynamics of interconversion of intermediates in rhodium hydroformylation. The present work[13] offers new results on observable species early and late in the catalytic cycle which may provide some clarification.

Results and Discussion

Equilibria involving Phosphinerhodium Hydrides.—$HRhCO(PPh_3)_3$ (**1**) is unstable in benzene or toluene solution, giving rise to dimeric rhodium species over protracted periods.[1] We examined first the phosphine dissociation step in the presence of excess of PPh_3, using the DANTE technique of Morris and Freeman[14] to monitor spin-excitation transfer in the ^{31}P n.m.r. spectrum at 280 K (Figure 2). Dynamic interchange is evident by inspection of the spectra, and a very satisfactory simulation was obtained employing programs written for a Hewlett–Packard HP85 computer. The rate constant k_1 4 s^{-1} is that for dissociation of PPh_3 from (**1**) and in addition T_1 values of 16.7 and 1.2 s for free PPh_3 and complex (**1**) respectively can be derived. This implies that the dissociation rate constant at room temperature is $\geqslant 10$ s^{-1}, much faster than catalytic turnover in hydroformylation under ambient conditions. A similar conclusion may be reached by extrapolation of data derived by ^{31}P dynamic n.m.r. exchange between complex (**1**) and PPh_3 at higher temperatures.[15]

Whilst complex (**1**) has a normal *cis*-P–H coupling of 14 Hz, manifested in the ^1H n.m.r. spectrum and a small Rh–H coupling ($\leqslant 2$ Hz), the spectrum of the major species produced under a CO atmosphere is rather anomalous, with very small apparent coupling constants to both Rh and P. The new complex is clearly the dicarbonyl $HRh(CO)_2(PPh_3)_2$[1,16] since an additional triplet splitting is observed in both the ^1H and ^{31}P n.m.r. spectra with reaction is conducted under a ^{13}CO atmosphere, and free PPh_3 is apparent when the ^{31}P n.m.r. spectrum is monitored. The iridium analogue is known[17] and exhibits a complex n.m.r. spectrum whose temperature dependence reflects rapid equilibration between two trigonal-pyramidal

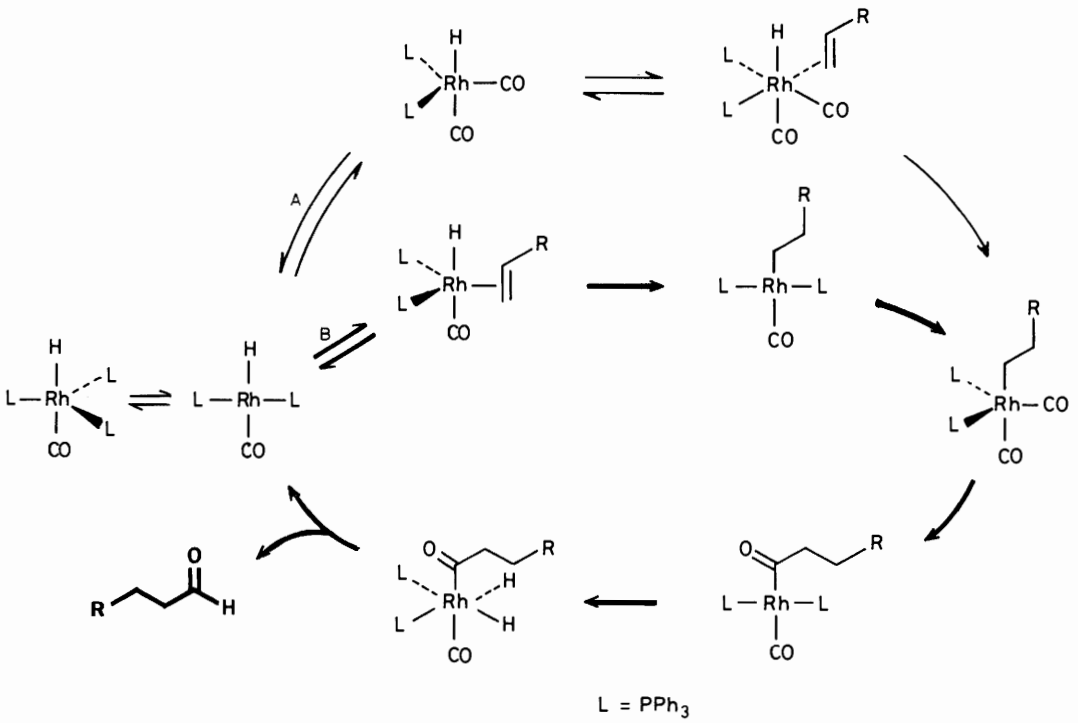
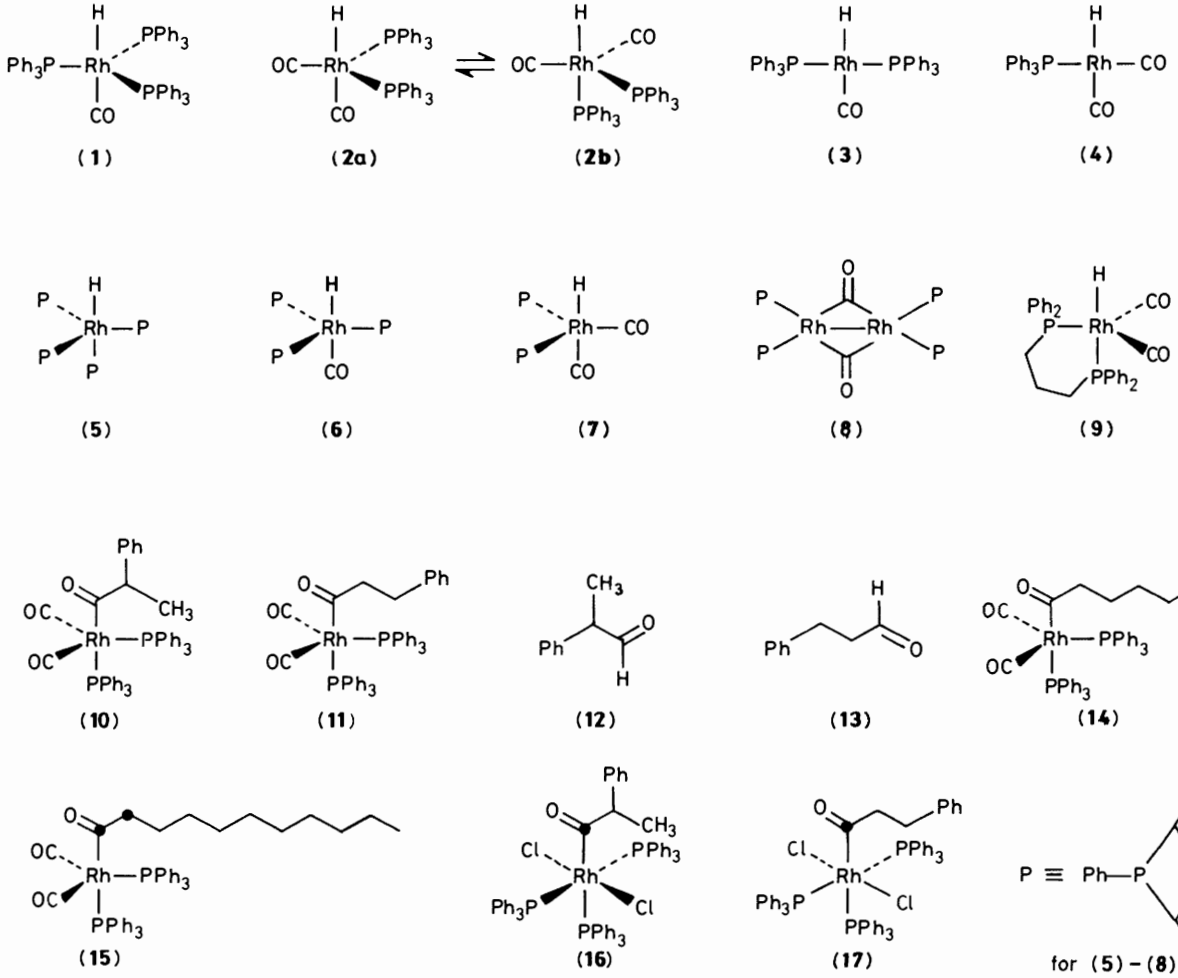


Figure 1. The established[1] mechanism for rhodium hydroformylation involving regioselectivity set at the olefin addition step and competition between saturated and unsaturated rhodium hydrides



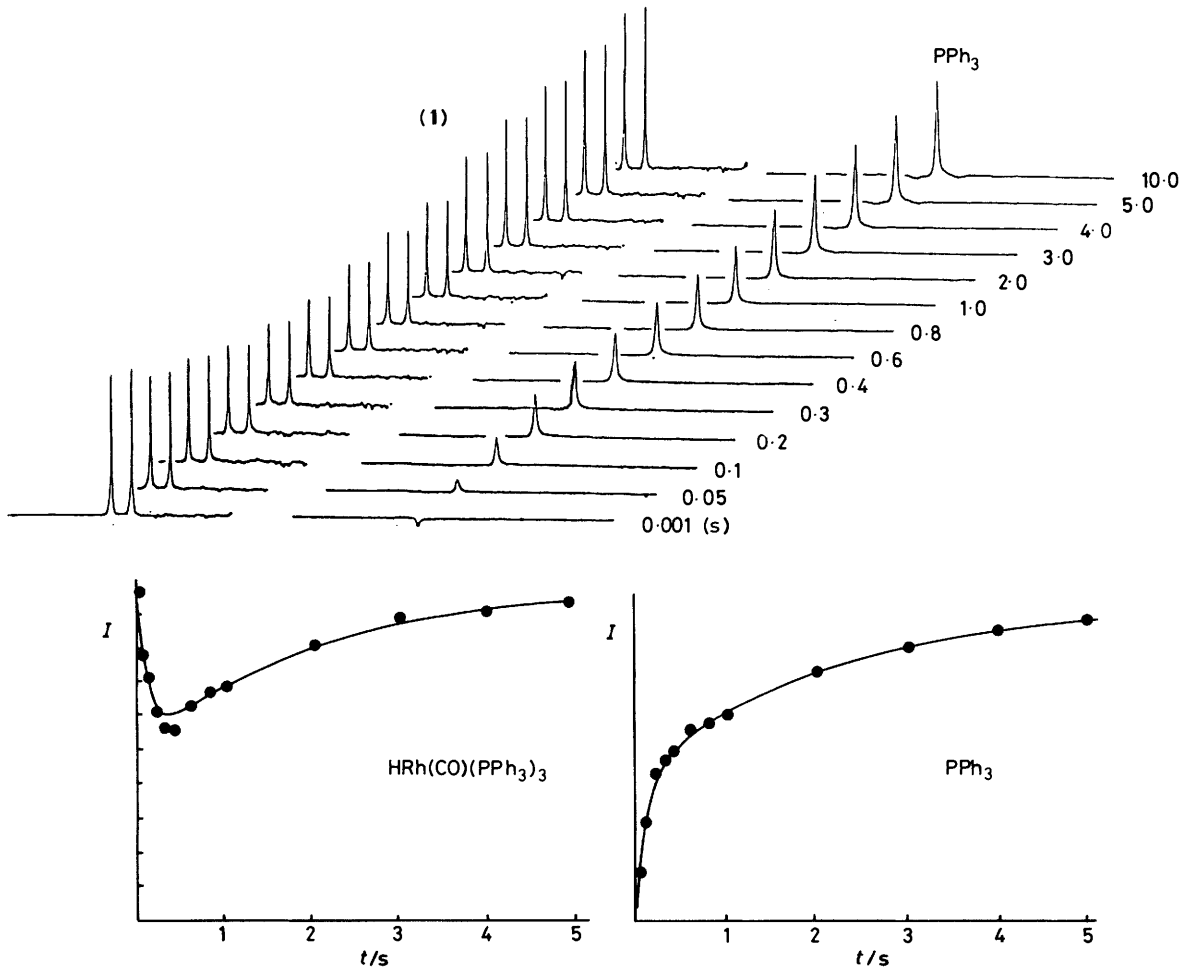


Figure 2. Magnetisation transfer between complex (**1**) and PPh_3 at 280 K in toluene solution, using a DANTE pulse sequence of seventy pulses, flip angle $\pi/70$ radians, of 70 μs total duration. The time axis represents the delay t after selective inversion of the free PPh_3 resonance

isomers.[18] A similar situation ensues in the related complex $HRh(CO)_2[P(OPr^i)_3]_2$ whose low-temperature ^1H n.m.r. spectrum was reported[19] to have the (anomalous) appearance of a doublet of doublets, similar to that observed for complex (**2**). By running the ^1H n.m.r. spectrum of the carbonylated species at very low temperatures a dynamic equilibrium between two trigonal bipyramidal isomers of complex (**2**) can be frozen out and the line-shape at intermediate temperatures can be successfully simulated (Figure 3). The major conformer (**2a**) (85%) has H *trans* to CO and a minor conformer (**2b**) (15%) has H *trans* to PPh_3, this being sterically more encumbered. The predominance of (**2a**) over (**2b**) runs counter to the situation in the otherwise similar iridum compound.[17]

Under ambient CO pressure the ^{31}P n.m.r. spectrum of a solution initially moderately concentrated in complex (**1**) indicates that the dicarbonyl (**2**) is the major component and both PPh_3 and residual (**1**) are present. Below room temperature dimer formation is not a serious side reaction. A DANTE magnetisation transfer experiment (Figure 4) was carried out at 273 K, irradiating the resonance of free PPh_3. It is clear that exchanges between both rhodium complexes and the free ligand are occurring, and the intensity change was plotted as a function of delay time. The data were simulated as described earlier. Spin excitation is transferred from PPh_3 to the phosphorus nuclei of complex (**1**) as expected, and also directly between the two organometallic complexes. This latter observation can readily be explained by dissociation of PPh_3 from complex (**1**) to give the square-planar species[20] $(PPh_3)_2Rh(CO)H$ (**3**) and its competitive interception by CO. In consequence, the build-up of magnetisation in dicarbonyl (**2**) is considerably slower than its build-up in the monocarbonyl (**1**). These processes alone fit the experimental data less well than simulation with a further exchange of excitation (Figure 4) due to direct dissociation of PPh_3 from the dicarbonyl complex (**2**), by which the monophosphine complex $Ph_3PRh(CO)_2H$ (**4**) is formed. This second dissociation is much slower, so that most of the flux of magnetism arises *via* the formation and trapping of complex (**3**). The probable existence of the alternative square-planar transient (**4**) is significant in consideration of hydroformylation mechanisms.

Rhodium complexes of 5-phenyl-5*H*-dibenzophosphole have proved effective as hydroformylation catalysts.[21] Consequently, we examined the reaction of the readily prepared $HRhL_4$ species (**5**) with CO and ^{13}CO by n.m.r., and observed mainly $HRh(CO)L_3$ (**6**)[22] with a small quantity of the dicarbonyl species (**7**), which had not previously been reported. Thus the relative stabilities of di- and tri-phosphinerhodium complexes differ from the PPh_3 series, and favour ligation of the phosphole over ligation of CO. Further, the different complexes are in slow equilibration on the n.m.r. time scale, and simple first-order ^1H spectra are obtained. For the dicarbonyl (**7**), the observed J_{PH} value of 19 Hz is consistent with the *cis*-biphosphine structure

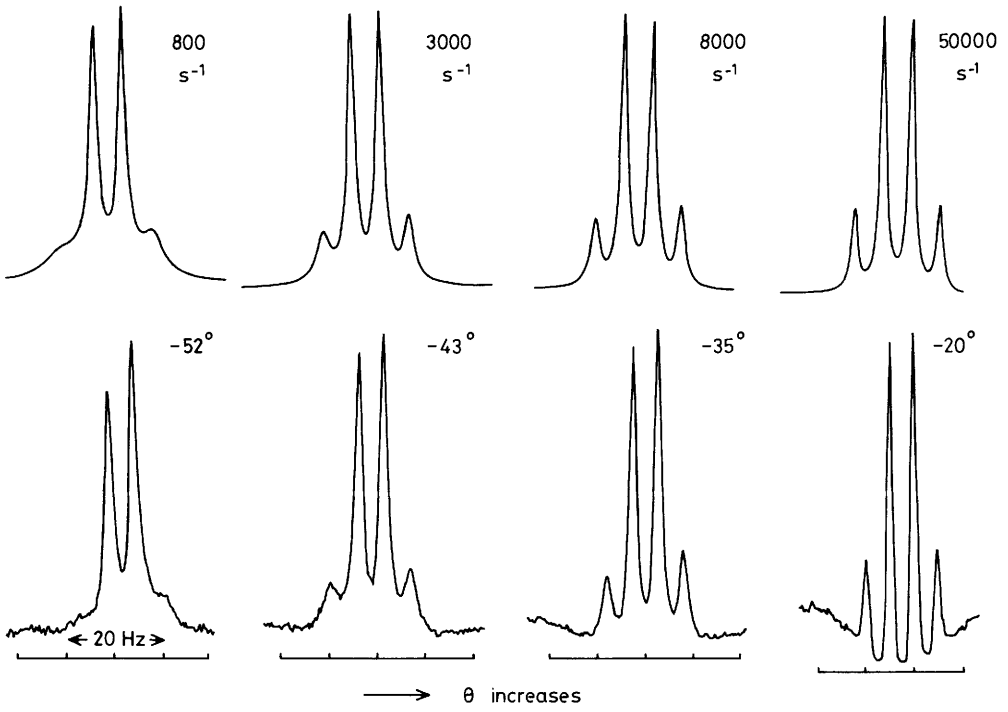


Figure 3. ^{1}H N.m.r. spectra of the rhodium hydride proton (δ −8.9) of complex (**2**) in CD_2Cl_2–$CF_2ClCFCl_2$ (4:1) with simulations by the DNMR3 routine

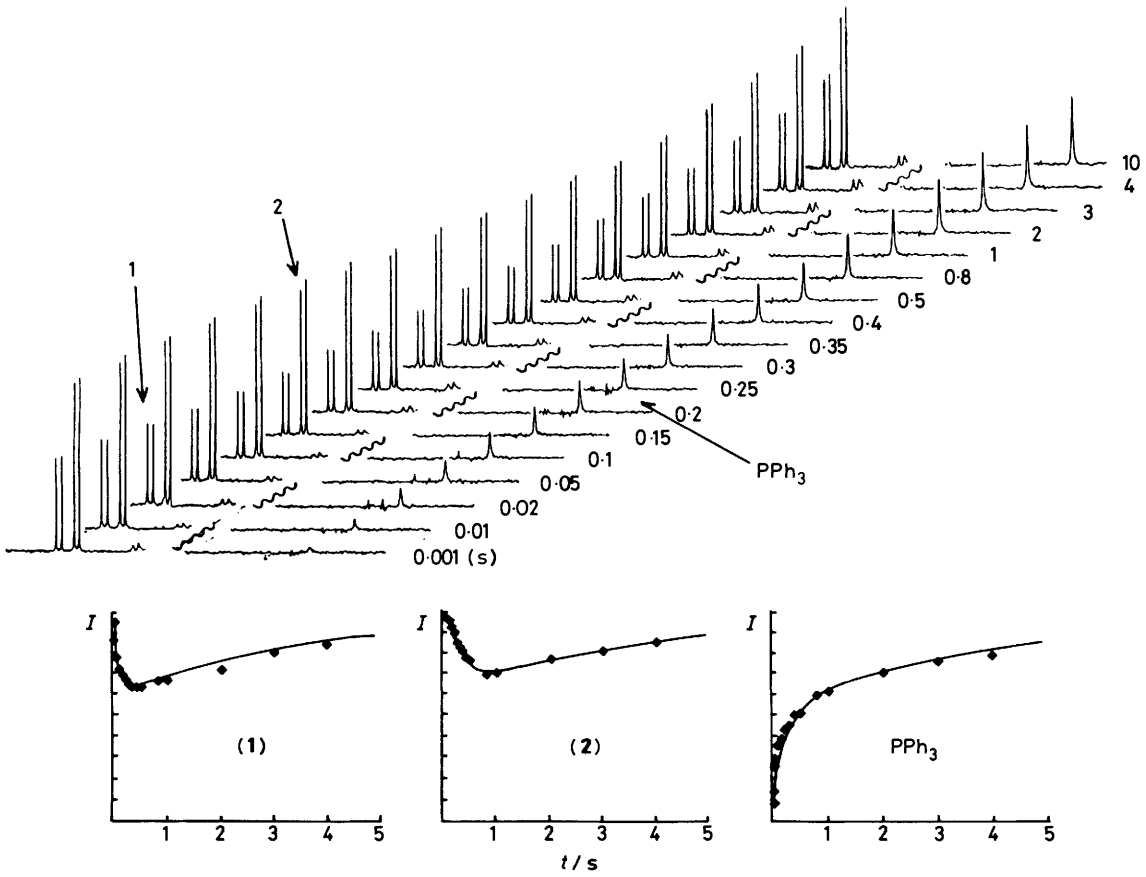


Figure 4. Magnetisation transfer between complexes (**1**) and (**2**) (under an ambient pressure of CO) and free PPh_3 at 280 K in toluene solution, using a DANTE pulse sequence of eighteen pulses, flip angle $\pi/18$ radians, with a total duration of 72 μs. The time axis represents the delay t after selective excitation of the triphenylphosphine resonance. Computer-generated data fitting gives k_{diss} for PPh_3 loss from (**1**) and (**2**), respectively 4.4 and 0.6 s^{-1}

drawn, which is reinforced by the $J_{^{13}CH}$ value of 20 Hz, expected for rapid equilibration between apical CO [*J ca.* 34 Hz, as in complex (**6**)] and equatorial CO [*J ca.* 6 Hz).

On standing the solution in toluene under CO orange crystals were deposited which were characterised as the dimer (**8**), ν_{C-O} 1 760 cm^{-1}, *m/z* 1 302. The characteristic second-order ^{31}P n.m.r. spectrum was simulated successfully only if Rh–Rh coupling was incorporated, $J_{PP'}$ 150, J_{RPh} 138, $J_{P'Rh}$ 18, $J_{RhRh'}$ 8 Hz. A variety of bridged rhodium dimers have been obtained both by carbonylation of phosphinerhodium hydrides and by alternative means[19,23,24] and their existence in equilibrium with the catalytically active complexes was noted in the early studies on rhodium hydroformylation.[1] More commonly, the isolated species are co-ordinatively unsaturated, with each rhodium atom carrying two phosphines and one CO; an unsymmetrical triscarbonyltristriphenylphosphine dimer has been characterised by *X*-ray structural analysis.[4]

The reaction of complex (**1**) with bidentate phosphines was examined under CO, since they are known to influence the rate and regioselectivity of hydroformylation,[25] and chelated analogues of the starting complex have been characterised.[26] With 1,3-bis-(diphenylphosphino)propane at −5 to −30 °C a single new dicarbonyl species was observed in equilibrium with complex (**2**), whose ^1H n.m.r. spectrum [*apparent* double triplet at δ −9.17 (*J ca.* 55, 11 Hz)] is consistent with structure (**9**), where P_a and P_b are in rapid interchange on the n.m.r. time scale. Surprisingly, the equilibrium is much less favourable for the formation of an analogous chelate complex in the case of 1,2-bis(diphenylphosphino)ethane.*

In summary, dicarbonylbisphosphinerhodium hydride complexes may be observed with a range of ligands. For the triphenylphosphine case, two trigonal bipyramidal isomers are in rapid equilibrium. At 273 K and above, dissociative equilibria occur, although the concentrations of square-planar species is low and the recombination rate is consequently rapid. Dissociation of CO to give the 16-electron complex $HRh(CO)(PPh_3)_2$ (of unknown stereochemistry) is the more rapid process, and it is likely that this is accompanied by a slower dissociation of PPh_3 to give $HRh(CO)_2PPh_3$. The time evolution of magnetisation transfer can be satisfactory simulated without recourse to 14-electron intermediates,[27] and all these processes are rapid on the time scale of catalytic hydroformylation under ambient conditions.

The Olefin Addition Step.—The starting complex (**1**) is an effective catalyst for olefin isomerisation under mild conditions[3] in an inert atmosphere. This is likely to involve phosphine dissociation, followed by reversible olefin addition to intermediate (**3**) and intracomplex addition–elimination of Rh–H to the co-ordinated double-bond. In the presence of H_2 the intermediate can be intercepted and catalytic hydrogenation of terminal olefins can be effected.[3]

We studied the reaction of (Z)-[1,2-$^2H_2$]styrene with catalytic quantities of complex (**1**) in C_6D_6. The observations are very clearcut (Figure 5) in that rapid equilibration of H and D occurs at C-2, whilst the transfer of protium to C-1 is a very much slower process. In the first few cycles of turnover Rh–H and one or both of the C–D moieties must equilibrate, and this implies in turn that isomerisation with be accompanied by equilibration of the starting material with $^2H_1$ and $^2H_3$ isotopomers. The observed dominance of isomerisation at C-2 over isotope exchange at C-1 indicates that the addition step is regioselective, favouring rhodium transfer to the benzylic carbon atom (Figure 6). This is in line with the observed preference for hydroformylation at the benzylic site in vinylarenes.[28]

* Five-membered-ring chelates are generally most strongly favoured thermodynamically.

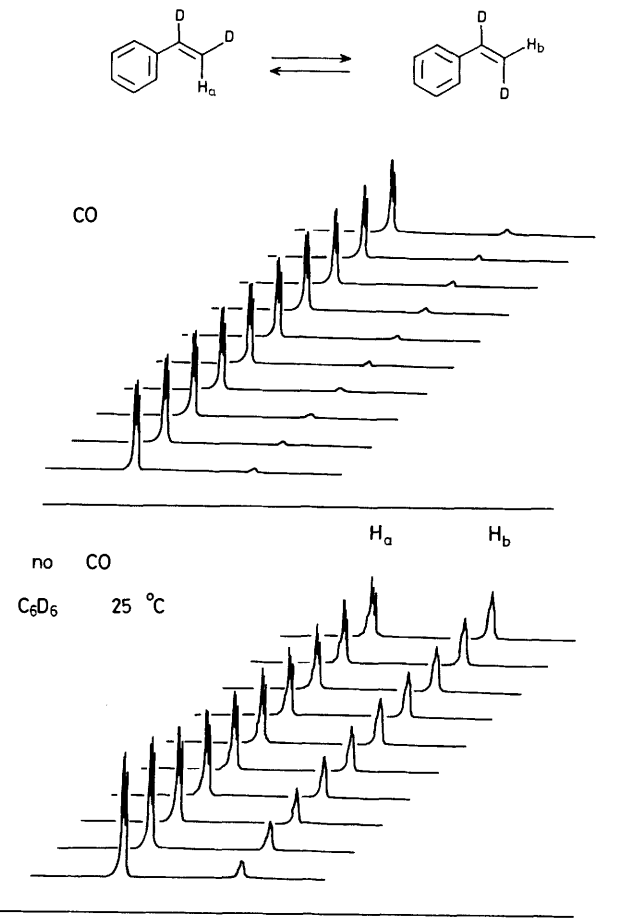


Figure 5. Isomerisation of *cis*-1,2-dideuteriostyrene catalysed by complex (**1**) in C_6D_6, followed by ^1H n.m.r. at 298 K in the presence (upper trace) and absence of CO (lower trace). Stacked spectra were recorded at 3 min intervals

In the presence of 5 equiv. PPh_3, isomerisation is effectively suppressed and the same is true under an atmosphere of CO. A rough calculation suggests that isomerisation under these conditions is slower than hydroformylation (1:1 H_2–CO in C_6H_6, 5 equiv. PPh_3–Rh). This indicates that the alkyl intermediate in hydroformylation is not identical with the alkyl intermediate in olefin isomerisation. A possible explanation for this is that isomerisation involves a 16ε olefinic hydride equilibrating with a 14ε alkyl, for which there is good precedent.[29] In hydroformylation, such 14ε intermediates are inaccessible because CO is an effective trap for the 16ε state, and reaction proceeds irreversibly to the acyl intermediate (Figure 6).

One experiment was conducted to monitor olefin trapping. The mixture of phosphole complexes (**6**) and (**7**) produced from $HRhL_4$ under CO in C_7D_8 at 278 K was treated with methylenecyclopropane. This caused immediate loss of the ^1H resonance due to the dicarbonyl (**7**). In the complex reaction sequence which ensued butadiene was a significant product. Likewise, a mixture of PPh_3 complexes (**1**) and (**2**) was treated with methylenecyclopropane under the same conditions. Again the ^1H resonance of the dicarbonyl (**2**) disappeared although this is a less definitive trapping experiment because exchange between the complexes initially present is rapid on the time scale of chemical transformation.

Characterisation of Rhodium Acyl Derivatives.—In the early studies of rhodium hydroformylation,[1] the presence of acyl

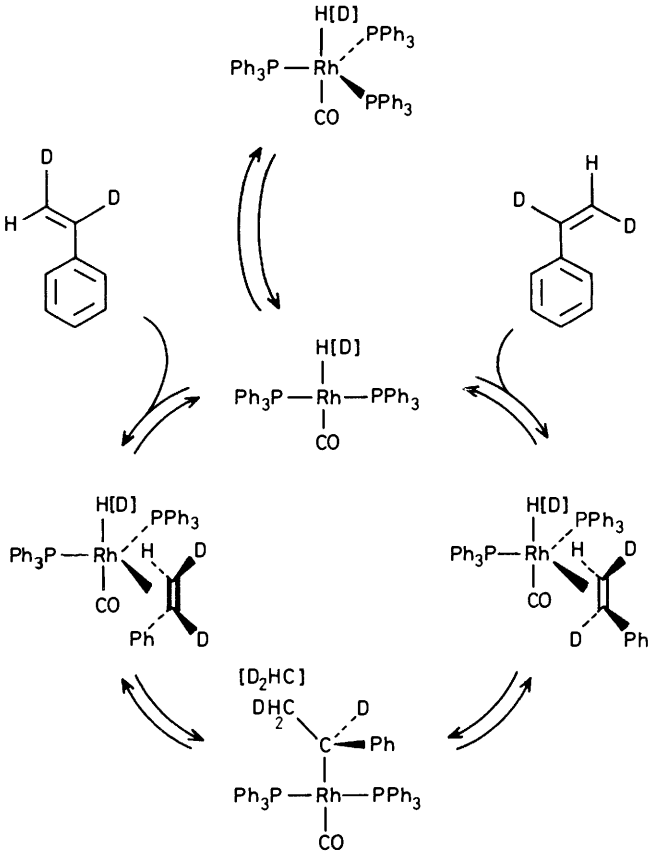


Figure 6. The pathway for isomerisation of *cis*-1,2-dideuteriostyrene catalysed by complex (**1**), involving regioselective addition of rhodium to the benzylic position

species in the reaction of complex (**1**) and styrene under CO was demonstrated by i.r. and n.m.r. but the species was incompletely characterised.

Freshly purified styrene was added to a solution of complex (**1**) in C_6D_6 under CO and the ^1H n.m.r. spectrum monitored immediately and then as a function of time. Initially, the predominant species contained two broad signals at δ 4.50 and 1.27 in 1:3 ratio assigned to the acyl complex (**10**). This was accompanied by a second acyl complex (**11**), and 2-phenylpropionaldehyde (**12**). As time progresses, the major acyl (**10**) is depleted, partly by isomerisation to (**11**) and partly by an increase in the concentration of aldehyde (**12**). The concentration of the linear aldehyde (**13**), apparent in the early stages, increases with time so that after 40 min the two aldehydes comprise the major part of the reaction mixture (Figure 7).

These observations are reinforced by a related sequence conducted in the presence of a five-fold excess of PPh_3. The isoacyl complex is formed very cleanly under these conditions (Figure 8) and rearranges smoothly over 40 min; aldehyde production is much less significant under these conditions. Two independent reactions are occurring. First the skeletal isomerisation is a result of formal reversal of the hydroformylation sequence (acyl $\rightleftharpoons$ alkyl $\rightleftharpoons$ olefin hydride) and reversion with opposite regioselectivity within the co-ordination sphere. There are precedents in acyliridium and acylcobalt chemistry.[30] This isomerisation occurs slowly in the present case ($t_{\frac{1}{2}}$ *ca.* 10 min) so that it is unlikely to contribute to the product isomer distribution observed in hydroformylation;[31] the acyl is converted into aldehyde rapidly. This second process is formation of aromatic aldehydes by acyl reduction and at first sight it is surprising that this occurs in the absence of H_2. The most likely explanation is a binuclear reduction step[32] and since the reaction occurs more readily in the absence of excess of PPh_3, dicarbonyl complex (**2**) is the more likely hydride donor.

Further investigations were carried out employing [$^{13}C_1$]-styrene and ^{13}CO, monitoring the reaction by ^{13}C n.m.r. at 278

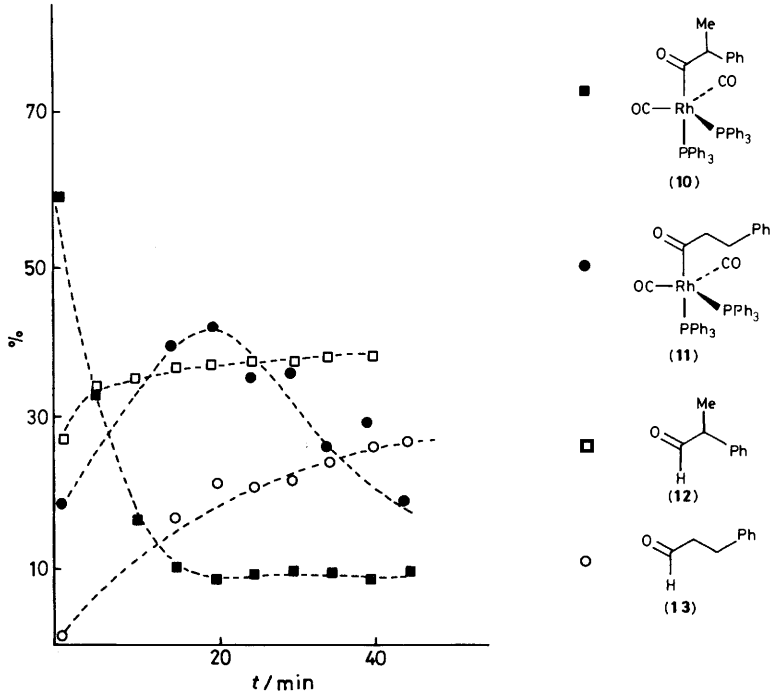


Figure 7. Skeletal interconversion of rhodium acyl complexes (**10**) and (**11**) occurring in competition with aldehyde formation. The sample was prepared from styrene (0.025 mmol) added to a solution of complex (**1**) (0.02 mmol) in C_6D_6 (0.5 ml) under ambient pressure of CO, and monitored by ^1H n.m.r.

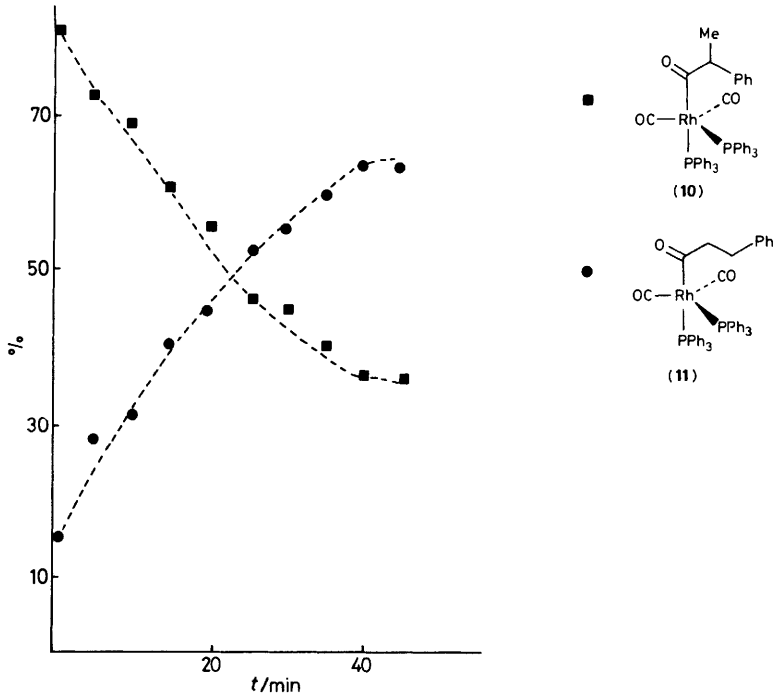


Figure 8. Skeletal interconversion of rhodium acyl complexes (**10**) and (**11**). Conditions as for Figure 7, but now PPh_3 (0.1 mmol) suppresses aldehyde formation

K. For the initially formed branched acyl (**10**), one observes bound ^{13}CO at δ 198 p.p.m. (J_{CRh} 75 Hz) and the acyl carbonyl at δ 235 p.p.m. This slowly isomerises to its equilibrium mixture with acyl (**11**), resonating at δ 199 (J_{CRh} 75 Hz) and 233.5 p.p.m. When [1-^{13}C]styrene was employed and the ^{13}C n.m.r. spectrum monitored at 298 K, then equal amounts of acyls (**10**) and (**11**) were observed initially, together with the branched chain aldehyde (**12**). Over the course of 90 min the intensity of the ^{13}C-enriched site in straight-chain acyl (**11**) resonance at δ 31.8 p.p.m. increased at the expense of that of its isomer (**10**) at δ 75 p.p.m. and at the same time linear aldehyde (**13**) appeared (δ 28.2 p.p.m.) and grew progressively, whilst little change was observed in the signal due to the branched isomer (**12**) (δ 52 p.p.m.). These results are in accord with those obtained from ^1H n.m.r.

A more detailed examination of the structure of rhodium acyls was carried out employing oct-1-ene, where the straight-chain isomer is kinetically favoured and skeletal isomerisation does not occur. The complex (**14**) was prepared as before in a ^{13}CO atmosphere, and the ^{13}C n.m.r. spectrum examined at different temperature temperatures close to room temperature. The acyl resonance at δ 233.6 p.p.m. is very broad, and broadening is also apparent in the terminal CO resonance of (**14**) at δ 198.5 p.p.m. At 243 K the latter is a sharp Rh-coupled doublet (J_{Rh-c} 75 Hz) and the acyl carbon resonance exhibits fine structure consistent with coupling to two equivalent phosphine nuclei and rhodium (Figure 9). At lower temperatures broadening occurs, and further couplings are evident which become resolved at 193 K. The acyl carbon is then coupled to rhodium (J_{CRh} ±20 Hz) and to two inequivalent phosphorus nuclei (J_{CP} 8, 75 Hz). The terminal carbonyls exhibit equal coupling to both phosphorus nuclei (J_{CP} 20 Hz). Thus defines the structure of (**14**) as drawn, with an apical acyl group *trans* to phosphorus. The main dynamic process observed at low temperatures is then a pseudorotation which makes the phosphorus nuclei and their associated coupling equivalent. The *J* values are as expected for a *trans* P–Rh–C arrangement,[33] and the line-

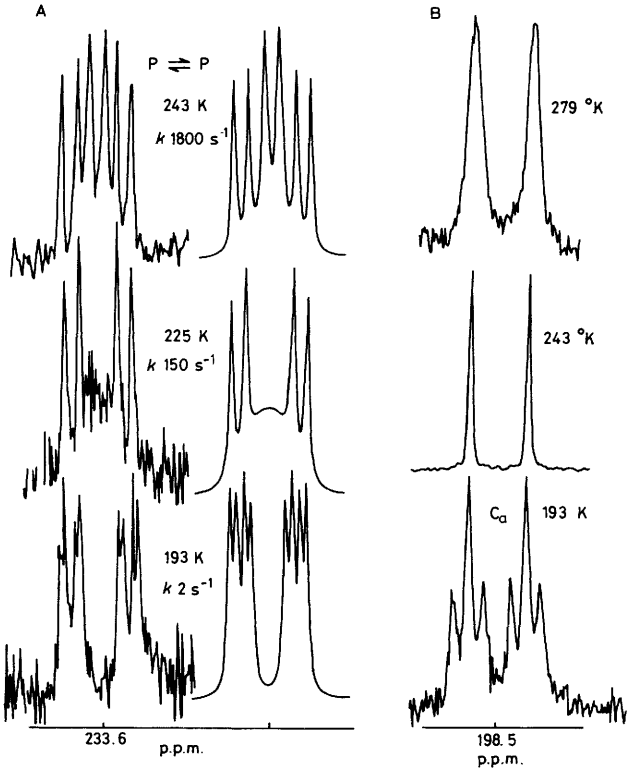


Figure 9. ^{13}C N.m.r. spectra of enriched complex (**14**), prepared in a ^{13}CO (90%) atmosphere from 1-octene and complex (**1**). Spectra A represent the low-field acyl at δ 233.6 p.p.m. and simulations are based on $P_a \rightleftharpoons P_b$ interchange by an intramolecular mechanism; At 279 K a broad featureless envelope is observed. Spectra B represent the Rh–C≡O resonance, with the loss of coupling between 193 and 243 K due to $P_a \rightleftharpoons P_b$ interchange (J_{P-C} +20, −20 Hz) and a further intermolecular exchange apparent at higher temperatures

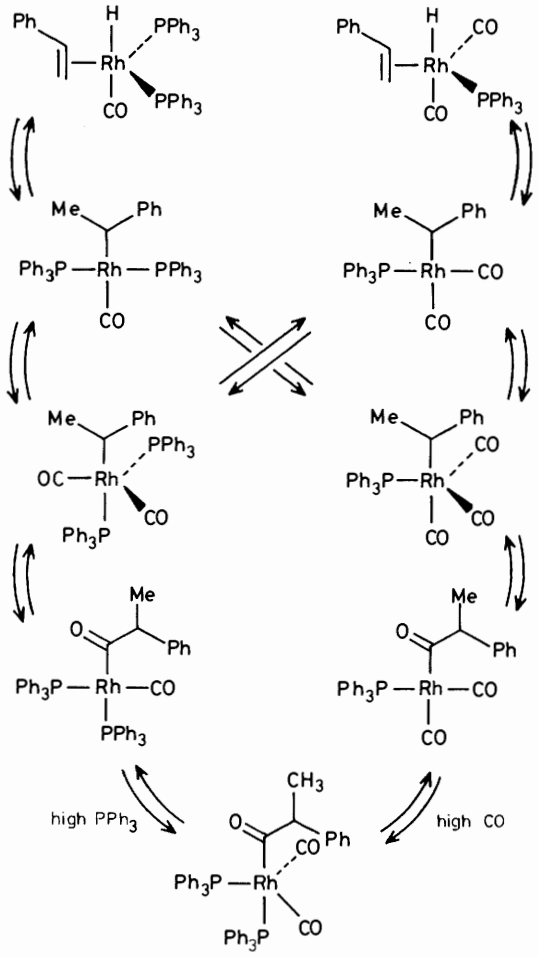


Figure 10. Routes from olefin complex to acyl complex. Reversibility is not likely to be important under the common conditions of catalytic hydroformylation

shape changes at low temperatures may be successfully simulated with DNMR3.* At higher temperatures the situation is more complicated because dissociative exchange processes may be occurring, and broadening of the terminal carbonyl resonance at 278 K reflects reversible CO loss, since J_{CP} couplings are already averaged at lower temperatures. The broadening of the acyl resonance at 278 K is more intriguing. Rapid phosphine loss could cause this, since the average J_{CP} is 34 Hz, and the loss of PRh coupling in the ^{31}P n.m.r. spectrum in this temperature range is supportive evidence. In that case, the limiting spectrum would be a Rh-coupled doublet, J_{PRh} 20 Hz, whereas the appearance of the spectrum (Figure 9) indicates that rhodium coupling is lost as well. This would be consistent with a process (Figure 10) whereby rapid reversible acyl–alkyl interconversion occurs in the co-ordinatively unsaturated intermediate arising from CO or PPh_3 dissociation. There is precedent in ruthenium chemistry for rapid acyl $\rightleftharpoons$ alkyl transformations.[34]

The experiment was repeated using [1-^{13}C]decene in place of octene. The ^{13}C resonance of the acyl carbon in (**15**) revealed an additional coupling of 20 Hz to be compared with values of 32 and 34 Hz observed in a mixture of complexes (**16**) and (**17**) prepared separately from ^{13}C-labelled 2-phenylpropanoic acid.[35] No further information could be obtained from the ^{13}C resonance of C_α in complex (**15**) since this remained broad over the temperature range 193—278 K, presumed to be due to the multiple heteronuclear couplings incurred.

No evidence for acyl complexes with different ligation or different stereochemistry was ever obtained. It seems probable that under hydroformylation conditions acyls of this structure are an important resting state directly coupled to the catalytic cycle. Ligand dissociation (PPh_3 or CO) from the acyl gives rise to a co-ordinatively unsaturated intermediate which is intercepted by hydrogen. Loss of aldehyde by fragmentation[36] then regenerates either (**3**) or (**4**). We think it likely that the reversible isomerisation observed is too slow to compete with this process under catalytic conditions, and thus the regiochemistry of hydroformylation is set early in its catalytic cycle.

Relationship to the Mechanism of Hydroformylation.—The present work provides structural characterisation for intermediates in the catalytic cycle or closely associated with it, and also information on the dynamics of ligand dissociation processes. A major preoccupation in rhodium hydroformylation has been the control of regiochemistry, and maximisation of the proportion of straight-chain aldehyde in the reaction product. It is well known that high phosphine concentrations and low CO pressures enhance the normal:secondary ratio. Aside from the Montedison work[12] much of the detailed kinetic evaluation is subject to the constraints of industrial confidentiality.[37]

Wilkinson's explanation for the variation in regioselectivity[1] still finds a place in current reviews of the topic.[38] It involves competition between 16ε and 18ε rhodium hydrides for olefin with the former exhibiting lower regioselectivity. It suffers from the fact that addition of a co-ordinatively unsaturated metal hydride to an olefin is unprecedented and intrinsically unlikely to compete with alternatives which require only 16ε intermediates. The Montedison group[12] do allude to the fact that they can fit their experimental data completely by competitive trapping of olefinic substrate by the co-ordinatively unsaturated intermediates (**3**) and (**4**), assuming that the monophosphine complex reacts with lower regioselectivity towards terminal olefins. Now that complex (**4**) has been shown to be a kinetically feasible intermediate, we support that mechanism and outline the likely route in Figure 11. This has been tested to a limited extent by computer modelling, using Runge–Kutta numerical integration techniques and applying rate constants k_1—k_4 based on the DANTE experiments described earlier. Conversion into the structurally distinct normal and isoacyl complexes (**18**) and (**19**) then occurs through a sequence of fast steps and the product-determining step is H_2 addition, following ligand loss. As delineated, and with normal:secondary selectivity set at 20:1 for trapping of complex (**3**) and at 4:1 for trapping of complex (**4**), the model reproduces the main experimental features of rhodium hydroformylation. Thus increasing CO pressure with [CO]:[H_2] set at 1.25:1 (CO is more soluble in organic solvents than H_2) reduces regioselectivity whereas increasing [PPh_3] increases it; varying [H_2] has little effect. In a qualitative sense, the changes are reasonable. If intermediate (**4**) is ignored, then it is necessary to assume that the saturated acyls (**18**) and (**19**) react at very different rates and that their fractionation along CO and PPh_3 dissociation pathways is quite distinct. In the absence of firmer experimental evidence this latter possibility seems intrinsically less probable.

The work provides an incentive to identify co-ordinatively unsaturated intermediates in hydroformylation directly and to quantify their olefin-trapping ability.

Experimental

^1H N.m.r. spectra were obtained on either a Perkin-Elmer R24 (60 MHz), a Perkin-Elmer R32 (90 MHz), or a Bruker WH 300

* Obtained from Professor R. K. Harris, Durham University.

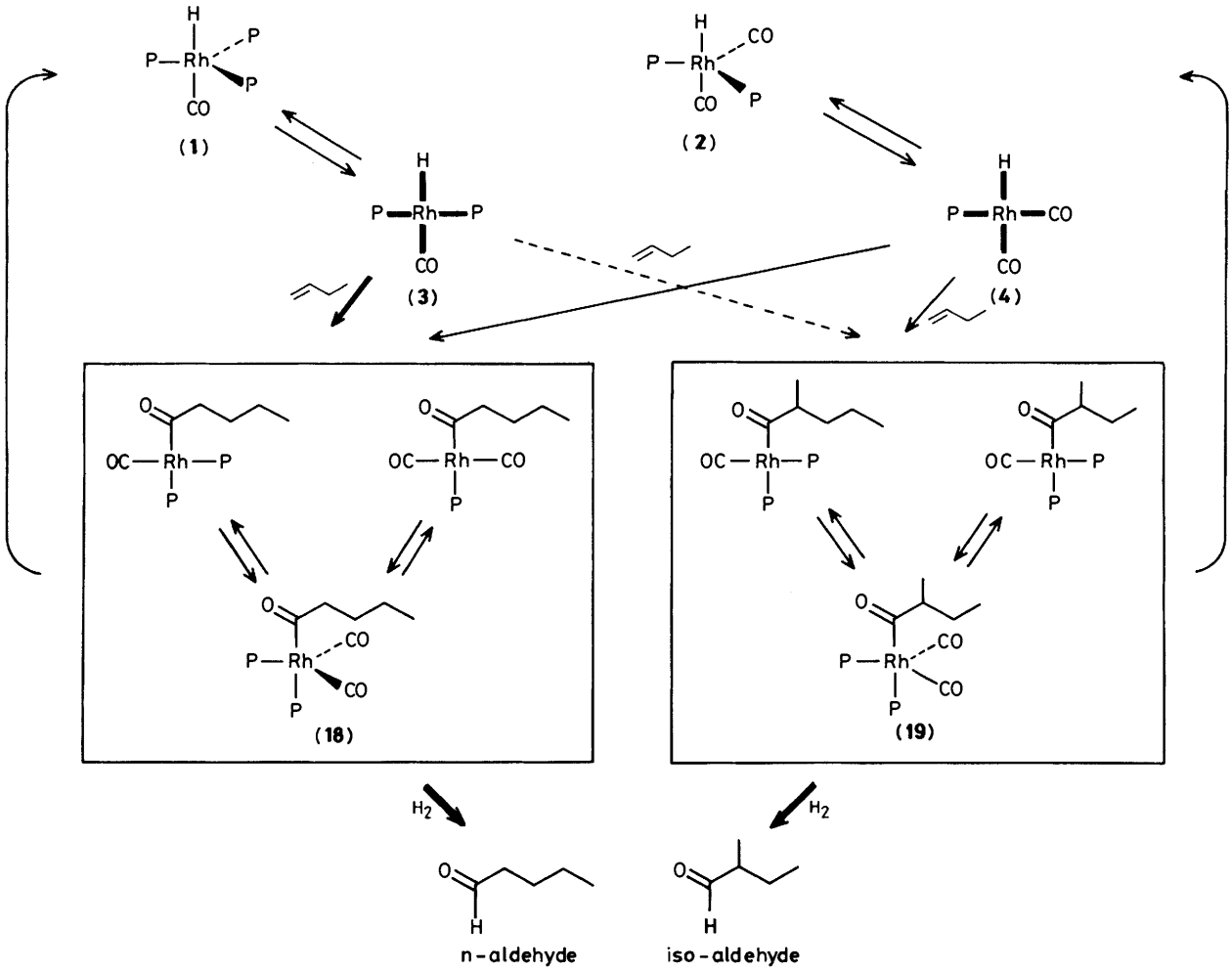


Figure 11. A mechanistic proposal for rhodium-catalysed hydroformylation. The regiochemistry is controlled by competitive interception of complexes (**3**) and (**4**), the former being highly biased towards n-acyl formation

(300.13 MHz) instrument. ^{13}C N.m.r. spectra were recorded on Bruker WH 90 (22.63 MHz), Bruker WH 300 (75.47 MHz), and Bruker WH 400 (100 MHz) pulsed Fourier-transform spectrometers. ^{31}P N.m.r. spectra were also recorded on Bruker WH 90 (36.43 MHz), Bruker WH 300 (121.5 MHz), and Bruker WH 400 (162 MHz) instruments; chemical shifts are quoted relative to external phosphoric acid (85%)

All reactions involving phosphines, organometallic complexes, and other air-sensitive compounds were conducted under argon using standard vacuum-line techniques and Schlenk glassware. All transfers of liquids and solution of air- or moisture-sensitive materials were carried out with dried, inert gas-purged syringes fitted with stainless steel needles or with thin steel tubing.

Hydrogen and carbon monoxide (1:1 mixture) and carbon monoxide gases were obtained from Air Products Ltd. [^{13}C]-Carbon monoxide (5 l cylinder) and barium [^{13}C]carbonate came from Prochem Ltd (now Amersham International plc).

Silica gel for column chromatography was 40—60 μ grade. T.l.c. was performed on 0.2 mm thick Merck silica plates 60F-254; preparative t.l.c. was performed on plates (20 cm × 20 cm × 1 mm) coated with Merck silica gel (60 $PF_{254+366}$) prepared by Mr. R. Prior. Analytical g.l.c. employed a Pye series 104 chromatograph at *ca.* 100 °C, using a 2 m column of 3% Carbowax 20M on Chromasorb W with nitrogen as eluant. Preparative g.l.c. was carried out on a Pye series 104 A chromatograph at *ca.* 150 °C with a 5 mm column of 5% Carbowax on Chromsorb W.

Hydrocarbonyltris(triphenylphosphine)rhodium,[39] 5-phenyl-5*H*-dibenzophosphole,[21] and methylenecyclopropane[40] were prepared by literature methods. Hydro[^{13}C]-carbonyltris(triphenylphosphine)rhodium was prepared from the corresponding [^{13}C]carbonyl-*trans*-bis(triphenylphosphine)chlororhodium by modifying a literature method,[41] $\nu_{max.}$ 2 029 and 1 891 cm^{-1}, m.p. 118—120 °C (lit.,[39] 120—122 °C).

(*Z*)-[1,2-$^2H_2$]*Styrene*.—A solution of phenylacetylene (1.0 g, 9.8 mmol) and bicyclo[2.2.1]hepta-2,5-dienebis(methyldiphenylphosphine)rhodium(I) tetrafluoroborate (0.05 g, 0.073 mmol) in 2-methoxyethanol (10 ml) was thoroughly degassed by three freeze–thaw cycles under argon. The reaction vessel was evacuated, deuterium admitted, and the solution was stirred at 20 °C until the required uptake of gas was achieved (*ca.* 230 ml in 4 h). Water (20 ml) was added and the mixture extracted with 2-methylbutane (3 × 10 ml). The extracts were combined, dried ($MgSO_4$), and warmed (*ca.* 40 °C) to remove solvent. The residue was distilled to give *cis*-[α,β-$^2H_2$]styrene (*ca.* 0.5 ml) as the sole product, b.p. 40—50 °C 10 mmHg; δ($CDCl_3$) 5.70 (1 H, t, CH) and 7.30 (5 H, m, aromatic H).

[1-^{13}C]*Styrene*.—A solution of [^{13}C]benzoic acid (3.35 g, 0.028 mol)[42] in ether (dried; 50 ml) was added dropwise to a

stirred suspension of lithium aluminium hydride (2.0 g, 0.053 mol) in ether (100 ml) at 0 °C. The mixture was then boiled under reflux for 2 h, cooled to 0 °C, and water (5 ml) slowly added, followed by aqueous 4M-sodium hydroxide (5 ml) and water (10 ml). The suspension was filtered and solvent was removed from the filtrate *in vacuo* to leave [α-^{13}C]benzyl alcohol (2.45 g, 82%) as a yellow oil; δ($CDCl_3$) 2.65 (1 H, br s, OH), 4.55 (2 H, d, $J_{C,H}$ 27 Hz, $^{13}CH_2$), 7.25 (5 H, br s, aromatic H). The material was used without further purification.

Nitrogen dioxide[43] (*ca.* 10 g) was added to a solution of [^{13}C]benzyl alcohol (2.45 g, 0.023 mol) in dichloromethane (50 ml) at −15 °C, and the solution allowed to warm to 20 °C during 3 h, and left for 12 h at 20 °C. The solvent was evaporated *in vacuo* and the residue dissolved in ether (50 ml), washed with aqueous sodium hydrogencarbonate (50 ml), and the organic layer separated. Removal of the solvent *in vacuo* and distillation of the residue (bath temperature 70—75 °C at 10 mmHg) gave [α-^{13}C]benzaldehyde (1.50 g, 63%); δ($CDCl_3$) 7.2—7.9 (5 H, m, aromatic H) and 9.9 (1 H, d, $J_{C,H}$ 87 Hz, CHO).

Dimethyl sulphoxide (20 ml) was added to sodium hydride (2.7 g, 50% dispersion in oil; washed three times with light petroleum and dried *in vacuo*) and the mixture heated at 70 °C for 1 h to produce a solution of (methylsulphinyl)methyl sodium (2.8M) in dimethyl sulphoxide.

(Methylsulphinyl)methyl sodium (2.7 ml, 7.5 mmol; solution in dimethyl sulphoxide prepared as above) was added to methyltriphenylphosphonium bromide (3.6 g, 10 mmol) and dimethyl sulphoxide (10 ml) and the mixture left for 5 min. [α-^{13}C]Benzaldehyde (0.5 g, 4.7 mmol) in 2-methylbutane (3 ml) was added and the mixture stirred vigorously for 10 min, then left for 10 min. 2-Methylbutane was separated and the residue extracted further with 2-methylbutane (3 × 5 ml); the extracts were warmed (*ca.* 40 °C) to evaporate solvent and the residue distilled (bath temperature 30—40 °C at 10 mmHg) to give [1-^{13}C]styrene (0.38 g, 80%); δ($CDCl_3$) 5.1—5.9 (2½ H, CH_2 and ½ ^{13}CH), 7.3 (5 H, m, aromatic H), and 7.5—7.7 (½ H, m, ½ ^{13}CH).

[1-^{13}C]*Dec*-1-*ene*.—A mixture of [^{13}C]carbon dioxide {generated in a closed system from barium [^{13}C]carbonate (6.0 g, 0.0303 mol) and concentrated sulphuric acid} and nonylmagnesium bromide [(0.04 mol, 60 ml of 0.65M solution) from nonyl bromide (15 g, 0.072 mol) and magnesium turnings (5 g) in ether (100 ml)] was vigorously stirred at −50 °C. When the uptake of carbon dioxide has ceased, the mixture was stirred for 3 h at 0 °C, and water (6 ml) and concentrated hydrochloric acid (6 ml) added. The organic layer was separated and extracted with 4M-sodium hydroxide (3 × 75 ml); this extract was acidified (concentrated hydrochloric acid) and further extracted with ether (2 × 75 ml). After combining and drying the extracts over magnesium sulphate the solvent was evaporated *in vacuo* to leave [α-^{13}C]decanoic acid (5.05 g, 92%), m.p. 28.5—30 °C (lit.,[44] 30—31 °C); δ($CDCl_3$) 0.5—2.0 (17 H, m, CH_2 and CH_3), 2.35 (2 H, t, *J* Hz, $CH_2{}^{13}CO_2H$), and 10.6 (1 H, s, CO_2H).

A solution of [α-^{13}C]decanoic acid (5.05 g, 0.029 mol) in ether (50 ml) was added dropwise to a suspension of lithium aluminium hydride (2.5 g, 0.065 mol) in ether (50 ml) at 0 °C during 30 min. The mixture was stirred at 0 °C for ½ h then boiled under reflux (3 h), cooled to 0 °C and water (5 ml), 4M-NaOH (10 ml), and water (10 ml) added. After filtration and washing the filter-cake with ether (100 ml) the solvent was evaporated to give [α-^{13}C]decan-1-ol (4.6 g, *ca.* 100%) as a oil; δ($CDCl_3$) 0.8—2.0 (19 H, m, CH_2 and CH_3) 2.35 (1 H, br s, OH) and 3.55 (2 H, doublet t, $J_{^{13}CH}$ 140, $J_{H,H}$ 6 Hz, $^{13}CH_2OH$). The material was used without further purification.

A solution of [α-^{13}C]decan-1-ol (1.6, 0.01 mol) and hexamethylphosphorus triamide (10 ml) was heated and the fraction distilling between 170 and 225 °C was collected. Water (10 ml) and 2-methylbutane (50 ml) were added to the distillate and shaken; the organic layer was separated, dried ($MgSO_4$), and warmed (*ca.* 40°) to remove solvent. The residue was distilled (bath temperature 80—90 °C at 10 mmHg, lit.,[45] 75—78 °C at 30 mmHg) to give [1-^{13}C]dec-1-ene (1.4 g, 60%) as a liquid; δ($CDCl_3$) 0.91 (3 H, t, CH_3), 1.16—1.50 (12 H, m, CH_2), 2.06 (2 H, m, CH_2C=C), 5.00 (2 H, m, $J_{^{13}CH}$ *ca.* 155 Hz, $^{13}CH_2$), and 5.81 (1 H, m, C*H*=$^{13}CH_2$).

[1-^{13}C]-2-*Phenylpropanoic Acid*.—1-Bromo-1-phenylethane (17.5 g, 0.095 mol) was added dropwise to a suspension of magnesium turnings (8.0 g, 0.33 mol) in ether (100 ml) and the mixture then boiled under reflux (1 h). Filtration under argon gave a solution of 1-phenylethylmagnesium bromide in ether (0.7M, estimated by titration).

A mixture of [^{13}C]carbon dioxide [generated in a closed system from barium [^{13}C]carbonate (5.0 g, 25.5 mmol) and concentrated sulphuric acid] and 1-phenylethylmagnesium bromide (50 mg, 0.7M, 35 mmol; solution in ether prepared as above) was vigorously stirred at −50 °C. When the uptake of carbon dioxide had ceased the mixture was allowed to warm to 20 °C and water (6 ml) and concentrated hydrochloric acid (6 ml) were added. The organic layer was separated and extracted with 4M-sodium hydroxide (3 × 75 ml); the extract was acidified (concentrated hydrochloric acid) and the mixture extracted with ether (2 × 75 ml). The organic layer was separated, dried ($MgSO_4$), and solvent removed *in vacuo* to leave a yellow oil. This was distilled giving [α-^{13}C]-2-phenylpropanoic acid, b.p. 80—82 °C at 0.1 mmHg (lit.,[46] 144—147 °C at 11 mmHg); δ($CDCl_3$) 1.50 (3 H, dd, $J_{H,H}$ 6, and $J_{H,C}$ 7 Hz, CH_3), 3.70 (1 H, dq, $J_{H,H}$ 7, $J_{H,C}$ 7 Hz, CH), and 7.2 (5 H, br s, aromatic H).

Isomeric Acylbis(triphenylphosphine)dichlororhodium Derivatives, ^{13}C-*Labelled*.—A solution of [α-^{13}C]-2-phenylpropanoic acid (0.725 g, 4.84 mmol) and oxalyl chloride (0.650 g, 5.12 mmol) in toluene was stirred for 1 h. Solvent was removed by evaporation *in vacuo*, chlorotris(triphenylphosphine)-rhodium(I) (1.50 g, 1.62 mmol) in dichloromethane (20 ml) added and the mixture stirred for 24 h. Addition of ethanol precipitated a golden yellow complex which was collected by filtration and dried *in vacuo*. ^{1}H and ^{13}C n.m.r. showed this to be a 3:1 mixture of bis(triphenylphosphine)dichloro[α-^{13}C]-3-phenylpropanoylrhodium(III), δ_H($CDCl_3$) 2.65 (2 H, m, CH_2) and 3.15 (2 H, m, CH_2); δ_C($CDCl_3$) 33.3 (1 C, s, CH_2), 54.7 (1 C, d, CH_2), and 209.9 p.p.m. (1 C, m, CO) and bis(triphenylphosphine)dichloro-[α-^{13}C]-2-phenylpropanoylrhodium(III), δ_H($CDCl_3$) 1.11 (3 H, m, CH_3) and 4.70 (1 H, m, CH); δ_C($CDCl_3$) 63.5 (1 C, d, CH) and 213.5 p.p.m. (1 C, m, CO).

Preparation of Rhodium–Phosphine Species for N.m.r. Studies.—(A) ^{31}P *N.m.r.* A solution of hydridocarbonyltris-(triphenylphosphine)rhodium(I) (35 mg, 0.038 mmol) in toluene (1.8 ml) in an 8 mm n.m.r. tube was thoroughly degassed by three freeze-thaw cycles under argon. The tube was evacuated, carbon monoxide admitted *via* a septum cap pierced by a fine needle, and then vigorously agitated (*ca.* 1—2 min). The ^{31}P n.m.r. spectrum was obtained by loading the 8 mm tube inserted in a 10 mm tube into the spectrometer. D_2O was used as the external lock signal in the space between the tubes.

(B) ^{1}H *N.m.r.* A solution of hydridocarbonyltris(triphenylphosphine)rhodium(I) (10 mg, 0.011 mmol) in [$^2H_8$]toluene (0.5 ml) in a 5 mm tube was thoroughly degassed by three freeze–thaw cycles under argon. The tube was evacuated, and carbon monoxide admitted *via* a septum cap and fine needle. The sample was then agitated vigorously (*ca.* 1—2 min) before immediate recording the spectrum.

(C) ^{13}C *N.m.r.* A solution of hydridocarbonyltris(triphenylphosphine)rhodium(I) (35 mg, 0.038 mmol) in [$^2H_8$]toluene

(1.8 ml) in an 8 mm n.m.r. tube was prepared for analysis in a manner similar to (A) With the exception that [^{13}C]carbon monoxide was used in place of the ^{12}C-labelled gas. Other samples for ^{31}P, ^{1}H, or ^{13}C n.m.r. analysis were prepared analogously.

Preparation of Rhodium–Phosphine Species for N.m.r. Studies in the Presence of Olefinic Substrates.—(A) ^{31}P *and* ^{13}C *N.m.r.* A solution of hydridocarbonyltris(triphenylphosphine)rhodium(I) (35 mg, 0.038 mmol) in [$^{2}H_8$]toluene (1.8 ml) (lock signal) in an 8 mm n.m.r. tube was degassed by three freeze–thaw cycles under argon. The tube was evacuated and [^{13}C]carbon monoxide admitted *via* a septum cap and fine needle. The tube was agitated vigorously for 3 min and [α-^{13}C]styrene (0.1 g, 0.96 mmol) was introduced into the tube *via* a microsyringe and fine needle. The tube was agitated for a further 1 min, placed inside a 10 mm tube, and the n.m.r. spectrum obtained immediately.

(B) ^{1}H *N.m.r.* A solution of hydridocarbonyltris(triphenylphosphine)rhodium(I) (10 mg, 0.011 mmol) in [$^{2}H_6$]benzene (0.5 ml) (lock signal) in a 5 mm n.m.r. tube was degassed by three freeze–thaw cycles under argon. The tube was evacuated and carbon monoxide admitted *via* a septum cap and fine needle. The tube was agitated (3 min) and styrene (25 mg, 0.24 mmol, freshly obtained by preparative g.l.c. of commercial material) added; the n.m.r. spectrum was recorded immediately.

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