

Observation of Dicarbyldiphosphinerhodium Hydrides and their Olefin-trapping Ability

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The solution structure and reactivity of dicarbonylhydridobis(triphenylphosphine)rhodium and its 5-phenyl-5*H*-dibenzophosphole analogue are defined.

For hydroformylation catalysed by rhodium complexes, the mechanistic concepts proposed in papers published up to 1970¹ continue to be accepted in recent reviews as being essentially correct, and little in the way of detailed mechanistic studies has been published since that time. We report the application of n.m.r. techniques which help to specify the primary catalytic intermediate.

If the tetraphosphole complex² (1) in toluene is sealed under a carbon monoxide atmosphere then the ¹H n.m.r. spectrum shows a mixture of (2) and (3) whose equilibration is slow on the n.m.r. time-scale. The structure of the latter is defined by its ¹³C and ³¹P n.m.r. couplings (Table 1) and when the solution is left to stand the stable dimer (4)³ slowly precipitates. Addition of methylenecyclopropane at 278 K to a solution containing both (2) and (3) and immediate monitoring of the ¹H n.m.r. spectrum demonstrates that the latter compound is selectively trapped.

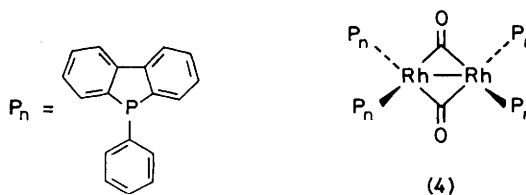
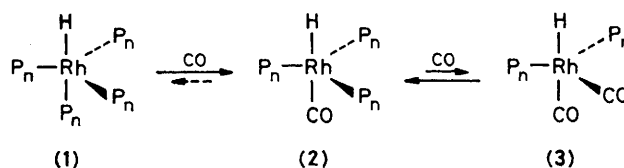
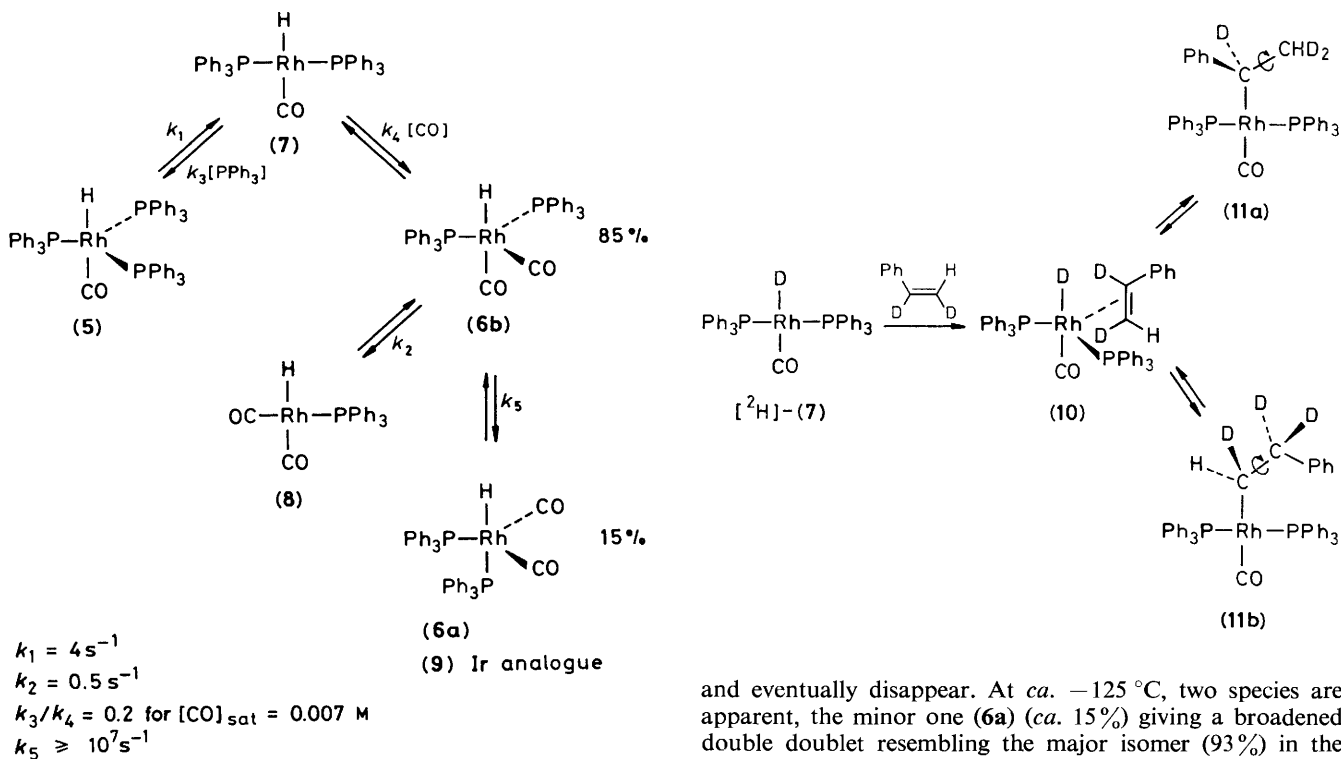


Table 1. Chemical shift (δ /p.p.m. for ^{13}C and ^{31}P) and coupling constant (J /Hz) data for rhodium hydridocarbonyl complexes.

Complex	T/K	^{13}C			^{31}P		^1H			
		δ	$J_{\text{C-Rh}}$	$J_{\text{C-P}}$	δ	$J_{\text{P-Rh}}$	δ	$J_{\text{H-Rh}}$	$J_{\text{H-P}}$	$J_{\text{H-C}}$
(2)	298	205.1	54	10	31.2	149	-9.2	3	∓ 13	34
(3)	298						-8.3	7	∓ 19	<i>ca.</i> 20
(5)	245	206.8	50	10	42.5	155	-9.3	≤ 1	∓ 14	38
(6)	245	200.3	63	11	39.9	138	-8.9	(see text)		15
(6a) ^{a,b}							-9.3	3	99, -13	} 13.5
(6b) ^{a,b}							-9.3	6.5	-14	

Spectra were measured in C_7D_8 using a Bruker WH 300 spectrometer excepting ^a WH 400 (Warwick) for which we thank Dr. E. H. Curzon, spectra recorded in 4:1 CD_2Cl_2 - $\text{CF}_2\text{ClCFCl}_2$, ^b low-temperature limiting spectrum recorded on a WH 90 at *ca.* 150 K.



Related triphenylphosphine complexes exhibit rapid equilibria. Thus carbonylhydridotris(triphenylphosphine)rhodium (5) is in equilibrium with (6) under a CO atmosphere at 273 K in toluene, observed by ^1H , ^{13}C , and ^{31}P spectroscopy (Table 1). At this temperature the formation of dimeric species occurs quite slowly and no other species are present in the initially formed solution. Intermolecular exchange processes are best delineated by ^{31}P n.m.r. studies using the DANTE pulse sequence introduced by Freeman and Morris.⁴ In the absence of CO it may be shown that complex (5) is in equilibrium with free triphenylphosphine *via* dissociation to (7) with $k_1 = 4 \text{ s}^{-1}$ at 273 K in toluene. This is *ca.* 10^3 times faster than dissociation of the iridium analogue.⁵ Under CO the saturation recovery data may be accurately simulated if (6) is in equilibrium with free triphenylphosphine *via* dissociation to (8) with $k_2 = 0.5 \text{ s}^{-1}$ and also if intermediate (7) is formed reversibly from both complexes (5) and (6) and intercepted by CO or PPh_3 with comparable facility under the experimental conditions. All the equilibrations are fast compared with the turnover rate of hydroformylation¹ under ambient conditions.

The ^1H n.m.r. spectrum of (6) is complicated by dissociative exchange near ambient temperature but in CD_2Cl_2 - $\text{CF}_2\text{ClCFCl}_2$ (4:1) this has the appearance of a quartet at -30°C ($J_{\text{app}} 6 \text{ Hz}$). On further cooling the outer lines broaden

and eventually disappear. At *ca.* -125°C , two species are apparent, the minor one (6a) (*ca.* 15%) giving a broadened double doublet resembling the major isomer (93%) in the low-temperature limiting spectrum⁶ of the iridium analogue, complex (9). The latter structure is supported by X-ray crystallographic analysis⁶ of the orthorhombic form of complex (9). The major species in the low-temperature n.m.r. spectrum of complex (6) (*ca.* 85%) appears as a broadened triplet, consistent with structure (6b). Assuming rapid interphosphine site-exchange in (6a) permits the simulation of spectra at intermediate temperatures. Analysis of the spectrum is considerably aided by the fact that the proton resonances of (6a) and (6b) are nearly isochronous; in C_7D_8 a more complex spectrum is observed which approximates to a double doublet ($J_{\text{app}} 4, 1.5 \text{ Hz}$). In the equilibrated mixture of complexes (5) and (6) selective depletion of the latter occurs when methylene-cyclopropane or styrene is added at 278 K.

In the presence of a catalytic quantity of complex (5), *Z*-[1,2- $^2\text{H}_2$]styrene⁷ isomerises rapidly, much faster than scrambling of protium between the 1 and 2 positions. This is because complex (7) is trapped by the olefin giving (10) and (11) sequentially and reversibly. Since the catalyst becomes deuterated in initial cycles of isomerisation, the experiment is not informative on the regioselectivity of addition since either (11a) or (11b) may effect reaction. Addition of CO (760 mm) or PPh_3 [in 5 M excess of (5)] leads to *ca.* 100-fold suppression of the rate of isomerisation. Hydroformylation of styrene under identical conditions of catalyst and substrate concentration

and 1 : 1 CO-H₂ at ambient temperature and pressure is slower than isomerisation of the deuteriated olefin (respective turnover numbers 0.0033 s and 0.027 s at 0.43 M styrene). The reverse is true in the presence of a 5 M excess of PPh₃ over catalyst (turnover numbers now 0.0012 s and <0.0002 s). This means that the square-planar bisphosphine complex (7) cannot mediate on the hydroformylation pathway since it is intercepted by PPh₃ or CO too efficiently for the olefin to compete. The square-planar dicarbonyl complex (8) is a possible intermediate and in the presence of olefins it is trapped to form an acyl complex, stable in the absence of H₂, whose structure and reactivity are described separately.⁸

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