

Structure and Dynamics of the Stable Rhodium–Acyl Complex formed during Hydroformylation

John M. Brown and Alexander G. Kent

Dyson Perrins Laboratory, South Parks Road, Oxford OX1 3QY, U.K.

Terminal olefins react with dicarbonylhydridobis(triphenylphosphine)rhodium to give acyl complexes whose inter- and intra-molecular rearrangements are described.

In the original ^1H n.m.r. studies¹ on hydroformylation catalysed by carbonylhydridotris(triphenylphosphine)rhodium (1), Wilkinson and co-workers reported the formation of a mixture of two isomeric acyl complexes from styrene, mainly the 3-phenylpropanoyl isomer. We have observed similar complexes, formed with high regioselectivity from styrene, oct-1-ene, or dec-1-ene, by ^1H , ^{13}C , and ^{31}P n.m.r. spectroscopy.

Under a ^{13}CO atmosphere at 273 K where complex (2) is the predominant species,^{1,2} oct-1-ene reacts to form a single complex whose ^{13}C n.m.r. spectrum at different temperatures is shown in Figure 1. Structure (3) with two distinct triphenylphosphine environments is supported by the following evidence.

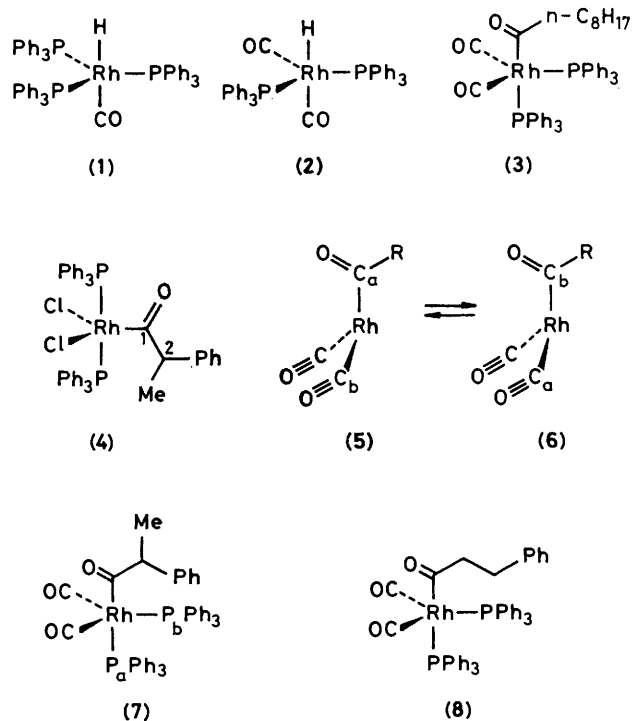
(a) The two ^{13}CO signals are in the ratio 2 : 1 and the higher field resonance has chemical shift and Rh–C coupling consistent with a terminal carbonyl ligand.³

(b) The chemical shift of the low-field signal is comparable with other metal–acyls;³ complex (4)⁴ prepared from $^{13}\text{CO}_2$ -labelled 2-phenylpropanoic acid had $J_{\text{C-Rh}}$ 28 Hz.

(c) The analogue of (3) prepared from $[1-^{13}\text{C}]$ dec-1-ene⁵ and ^{13}CO had $J(\text{C-1-C-2})$ 22 Hz in a broadened spectrum at 193 K; complex (4) has $J(\text{C-1-C-2})$ 32 Hz.

(d) The ^{31}P spectrum of (3) at 178 K shows two inequivalent nuclei at δ 36 ($J_{\text{P-Rh}}$ 140 Hz) and 30 p.p.m. ($J_{\text{P-Rh}}$ 70 Hz); the latter is further split, possibly owing to unequal populations of P–Ph rotamers.

On raising the temperature the phosphorus coupling to the



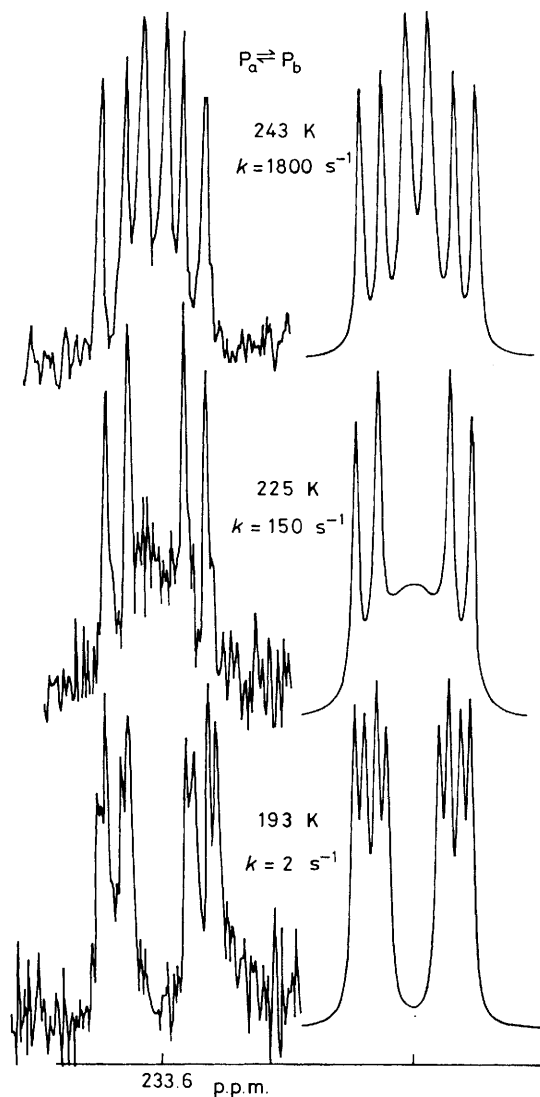


Figure 1. The ^{13}C n.m.r. spectrum of (3) at different temperatures showing the acyl carbon resonance at 233.6 p.p.m.; $J(\text{P}_a\text{-C})$ 77, $J(\text{P}_b\text{-C})$ -9, and $J(\text{C-Rh})$ 20 Hz. Spectra below 243 K were recorded at 100 MHz and those above at 75 MHz. Simulations were carried out by DNMR 3.

terminal carbonyls is lost ($J_+ \rightleftharpoons J_-$) and the acyl carbonyl group demonstrates the effect of a dynamic phosphine interchange which is accurately simulated below 243 K. Above that temperature further broadening of *both* signals occurs. Intermolecular PPh_3 exchange is evident from the ^{31}P spectrum but this could not account for the changes observed at 279 K signifying loss of rhodium coupling to both acyl and terminal CO nuclei. It is highly probable that the exchange process (5) \rightleftharpoons (6) is accompanied by a dissociative equilibrium with free CO; this point is to be tested by ^{17}O n.m.r. spectroscopy.

Complex (7), derived from $[1\text{-}^{13}\text{C}]$ styrene in benzene at 278 K, predominates by 91:9 over its isomer (8), this being very similar to the ratio of 2-phenylpropanal to 3-phenylpropanal formed in hydroformylation of styrene with 1:1 $\text{H}_2\text{-CO}$ under ambient conditions. Over 2 h at 298 K this ratio changes to favour (8) and both aldehydes are formed concomitantly. The same changes may be observed by ^1H n.m.r. spectroscopy with unlabelled styrene when the initially formed

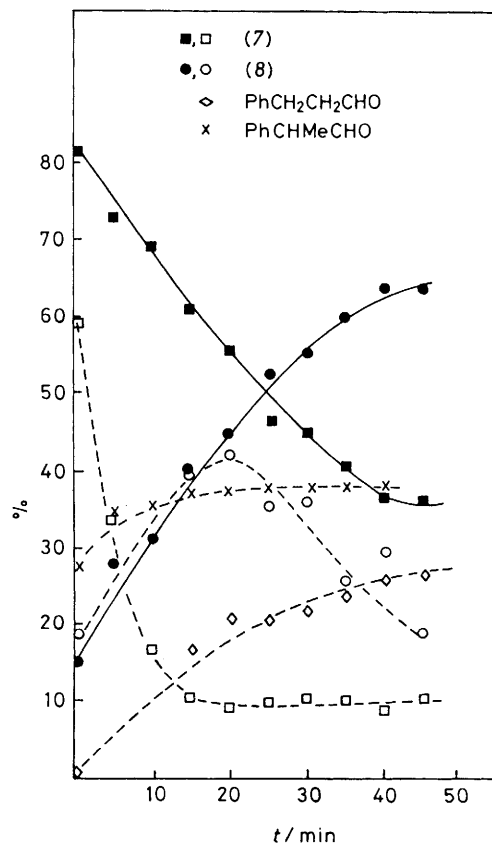


Figure 2. Product proportions in the isomerisation of acyl complex (7) alone (---) and with excess of PPh_3 (—) in $[\text{P}^2\text{H}_6]$ benzene at 298 K.

complex (7) is shown to have a half-life of *ca.* 4 min. The major process is isomerisation to (8) (Figure 2) and over the course of 30 min its intensity grows and decays whilst the proportion of 3-phenylpropanal increases; this may arise by reaction of (8) with a small amount of hydrogen produced by dimer formation, or by its reaction with an organometallic hydride donor [*e.g.* complex (2)] as is observed in cobalt hydroformylation and elsewhere.⁶ In the presence of a 5 M excess of triphenylphosphine, isomerisation is slowed about four-fold and the formation of aldehydes suppressed.

The isomerisation is probably unimportant in hydroformylation at ambient temperature and pressure since the isomer ratio is unchanged even at 1:5 $\text{H}_2\text{-CO}$. It may however be important at higher temperatures where 3-phenylpropanal is the predominant product.

Both the methyl and methine signals of (7) are broadened, particularly in the absence of excess of PPh_3 . This lends support to the suggestion that reversible ligand loss from (7) leads to rapid alkyl-acyl interconversion as has been observed in other cases.⁷ Since acyl complexes (3), and (7) or (8) are observed to accumulate during hydroformylation (*i.e.* when H_2 is present), the catalytic cycle may embody their formation and trapping by H_2 following ligand loss. It then seems quite possible that the much-discussed isomer ratio in hydroformylation is controlled by the kinetic lability of saturated and unsaturated acyl complexes [*e.g.* (7) *versus* (8)] rather than the dual catalytic pathway favoured by most authors.⁸

We thank Johnson-Matthey PLC, for the loan of rhodium salts. Dr. E. Curzon, Dr. L. D. Field, and Lady Eva Richards

gave generous assistance with n.m.r. experiments. Support for A. G. K. through S.E.R.C. and Johnson-Matthey PLC by a CASE award is gratefully acknowledged.

Received, 21st January 1982; Com. 066

References

- 1 C. K. Brown and G. Wilkinson, *J. Chem. Soc. A*, 1970, 2753, and earlier papers.
 - 2 J. M. Brown, L. R. Canning, A. G. Kent, and P. J. Sidebottom, *J. Chem. Soc., Chem. Commun.*, 1982, preceding communication.
 - 3 B. E. Mann and B. R. Taylor, '¹³C NMR of Organometallics,' Academic Press, London, 1981.
 - 4 K. S. Y. Lau, Y. Becker, F. Huang, N. Baezinger, and J. K. Stille, *J. Am. Chem. Soc.*, 1977, **99**, 5664; the product was obtained as a mixture of complex (4) and its 3-phenylpropanoyl isomer in which the latter predominated; cf. M. A. Bennett, R. Charles, and T. R. B. Mitchell, *J. Am. Chem. Soc.*, 1978, **100**, 2737.
 - 5 Using hexamethylphosphoramide at 220 °C to dehydrate [1-¹³C]decan-1-ol; R. S. Monson, *Tetrahedron Lett.*, 1971, 567.
 - 6 W. D. Jones, J. M. Huggins, and R. G. Bergman, *J. Am. Chem. Soc.*, 1981, **103**, 4415.
 - 7 C. F. J. Barnard, J. A. Daniels, and R. J. Mawby, *J. Chem. Soc., Dalton Trans.*, 1979, 1331; M. A. Bennett, J. C. Jeffery, and G. B. Robinson, *Inorg. Chem.*, 1981, **20**, 303.
 - 8 In several recent reviews, for example R. L. Pruett, *Adv. Organomet. Chem.*, 1980, **17**, 1.
-