

Stereochemistry of Formation and Reactions of Carbonyldichloro-(*threo*- α,β -dideuteriophenethyl)bis(triphenylphosphine)-rhodium and -iridium Complexes

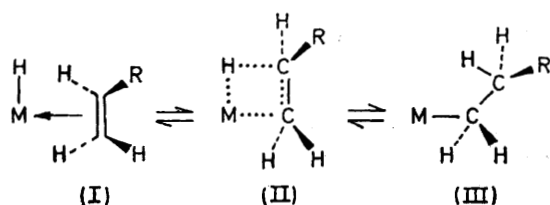
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Treatment of $[\text{RhCl}(\text{PPh}_3)_3]$ and $[\text{IrCl}(\text{N}_2)(\text{PPh}_3)_2]$ with *threo*-PhCHD·CHD·CO·Cl gives the complexes $[(\text{dpp})\text{-MCl}_2(\text{PPh}_3)_2]$ (M = Rh or Ir; dpp = *threo*-2,3-deuterio-3-phenylpropionyl) and $[(\text{dpe})\text{IrCl}_2\text{CO}(\text{PPh}_3)_2]$ (dpe = *threo*- α,β -dideuteriophenethyl); the alkyl migration reaction in this system thus proceeds with retention of configuration. Decomposition of both rhodium and iridium complexes yields all six possible mono- and di-deuteriostyrenes. The product distribution is interpreted in terms of a series of reversible β -elimination reactions.

As organotransition-metal chemistry becomes increasingly systematized, it is becoming apparent that one of the more important and general reactions is transfer of a metal hydride to an olefin to yield a σ -bonded alkylmetal compound. This process and its reverse, the elimination of an olefin from an alkylmetal com-

pound, are recognized as occurring in a variety of catalytic reactions of olefins such as hydrogenation, isomerization, hydroformylation, dimerization, and hydrosilylation;¹ it also provides the probable major route for thermal decomposition of many transition-metal alkyl complexes.²

Reliable mechanistic data are, however, remarkably scarce. General opinion at present favours a sequence in which an intermediate hydrido-olefin complex, (I), rearranges to the alkylmetal product, (III), via a four-centred transition state, (II),³ as in Scheme 1. Compounds of type (I) are rare because of their normally great



SCHEME 1

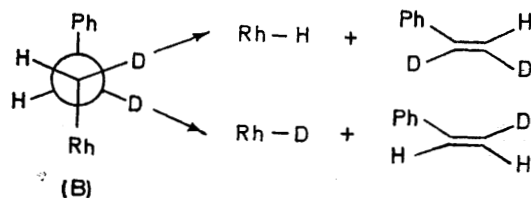
lability, but the complex $\text{trans}[\text{PtH}(\text{C}_2\text{H}_4)(\text{PEt}_3)_2]^+$, for instance, has been isolated and shown to rearrange to a σ -ethylplatinum complex.^{4,5} Stereochemically, the mechanism requires that the hydrido-ligand migrate to the β -carbon atom of the σ -alkyl group (a 1,2-addition) and that the overall addition be *cis*. The former requisite has been demonstrated by the formation of stable metal- $\text{CF}_2\text{CF}_2\text{H}$ complexes from reactions of tetrafluoroethylene with the hydrides $[\text{HMn}(\text{CO})_5]$,⁶ $[\text{HCo}(\text{CO})_4]$,⁷ $[\text{HRhCO}(\text{PPh}_3)_3]$,⁸ and $[\text{HRhCl}_2(\text{PPh}_3)_2]$,⁹ although experiments involving deuterium labelling have usually resulted in scrambling of the hydrogen isotopes because of the reversibility of the process.¹⁰⁻¹²

Experiments demonstrating *cis*-addition are exceptional for the same reasons. Stereochemical studies have demonstrated that the addition of $[(\text{cp})_2\text{MoD}_2]$ ($\text{cp} = \eta$ -cyclopentadienyl) to dimethyl fumarate and maleate yields selectively the *cis*-adducts, *threo*- and *erythro*- $[(\text{cp})_2\text{MoD}\{\text{CH}(\text{CO}_2\text{Me})\text{CHD}(\text{CO}_2\text{Me})\}]$, respectively.¹³ Similarly, the stereospecific palladium(II)-catalysed oxidation of 3,3,6,6-tetradeuteriocyclohexene has been shown to require a mechanism which includes stepwise movement of the palladium(II) around the ring

by *cis* palladium(II) hydride β -eliminations and additions.¹⁴ Although addition of the $[\text{DCo}(\text{CN})_5]^{3-}$ ion occurs non-stereospecifically to the anions of several α,β -unsaturated acids, addition to the fumarate and maleate anions does proceed in a *cis*-fashion.¹⁵ The conclusions to be drawn from the latter observations are uncertain, as kinetic studies suggest that the addition reactions do not involve prior co-ordination of the olefins to the metal.¹⁶

In an effort to learn more about the intricacies of β -elimination reactions, we have studied the thermal-decomposition reactions of $[(\text{dpp})\text{MCl}_2(\text{PPh}_3)_2]$ ($\text{M} = \text{Rh}$ or Ir ; $\text{dpp} = \text{threo-2,3-dideuterio-3-phenylpropionyl}$), and the catalytic decarbonylation of *threo*- $\text{PhCHD}\cdot\text{CHD}\cdot\text{CO}\cdot\text{Cl}$ by $[\text{RhCl}(\text{PPh}_3)_3]$. Reactions of the latter with a variety of acid chlorides, RCOCl , are known^{9,17} to yield first the acyl derivatives $[\text{RhCl}_2(\text{COR})(\text{PPh}_3)_2]$ and then the alkylcarbonyl derivatives $[\text{RhCl}_2\text{R}(\text{CO})(\text{PPh}_3)_2]$. When R does not contain a β -hydrogen atom, the latter can thermally eliminate RCl to yield $[\text{RhCl}(\text{CO})(\text{PPh}_3)_2]$. When R does contain a β hydrogen, olefin and HCl are eliminated to give $[\text{RhCl}(\text{CO})(\text{PPh}_3)_2]$, a process believed to proceed *via* an alkyl intermediate by a mechanism such as Scheme 1; although the alkyl compounds have not been detected in such cases, they have in analogous iridium systems.¹⁸⁻²⁰ At high temperatures the reactions are catalytic,¹⁷ possibly proceeding *via* oxidative addition of RCOCl to $[\text{RhCl}(\text{CO})(\text{PPh}_3)_2]$.

It was anticipated that the compound $[(\text{dpp})\text{RhCl}_2(\text{PPh}_3)_2]$ (A), formed by the oxidative addition of *threo*- $\text{PhCHD}\cdot\text{CHD}\cdot\text{CO}\cdot\text{Cl}$ to $[\text{RhCl}(\text{PPh}_3)_3]$,¹⁷ would rearrange with retention of configuration of the phenethyl group^{21,22} to the unstable intermediate $[(\text{dpe})\text{RhCl}_2(\text{CO})(\text{PPh}_3)_2]$ (B; $\text{dpe} = \alpha,\beta$ -dideuteriophenethyl). Stereospecific *cis*- β -elimination from such an alkyl intermediate would yield only two deuteriated styrenes:



¹ C. A. Tolman in 'Transition Metal Hydrides,' ed. E. L. Muetterties, Marcel Dekker, New York, 1971, p. 271.

² M. C. Baird, *J. Organometallic Chem.*, 1974, **64**, 289.

³ F. A. Cotton and G. Wilkinson, 'Advanced Inorganic Chemistry,' 3rd edn., Interscience, New York, 1972, p. 779.

⁴ H. C. Clark and H. Kurosawa, *Inorg. Chem.*, 1972, **11**, 1275.

⁵ A. J. Deeming, B. F. G. Johnson, and J. Lewis, *J.C.S. Dalton*, 1973, 1848.

⁶ P. M. Treichel, E. Pitcher, and F. G. A. Stone, *Inorg. Chem.*, 1962, **1**, 511.

⁷ J. B. Wilford, A. Forster, and F. G. A. Stone, *J. Chem. Soc.*, 1965, 6519.

⁸ G. Yagupsky, C. K. Brown, and G. Wilkinson, *J. Chem. Soc. (A)*, 1970, 1392.

⁹ M. C. Baird, J. T. Mague, J. A. Osborn, and G. Wilkinson, *J. Chem. Soc. (A)*, 1967, 1347.

¹⁰ J. Chatt, R. S. Coffey, A. Gough, and D. T. Thompson, *J. Chem. Soc. (A)*, 1968, 190.

¹¹ G. M. Whitesides, J. F. Gaasch, and E. R. Stedronsky, *J. Amer. Chem. Soc.*, 1972, **94**, 5258.

¹² B. Hudson, D. E. Webster, and P. B. Wells, *J.C.S. Dalton*, 1972, 1204.

¹³ A. Nakamura and S. Otsuka, *J. Amer. Chem. Soc.*, 1973, **95**, 7262.

¹⁴ P. M. Henry, *J. Amer. Chem. Soc.*, 1972, **94**, 7305.

¹⁵ L. M. Jackman, J. A. Hamilton, and J. M. Lawlor, *J. Amer. Chem. Soc.*, 1968, **90**, 1914.

¹⁶ J. Halpern and L.-Y. Wong, *J. Amer. Chem. Soc.*, 1968, **90**, 6665.

¹⁷ K. Ohno and J. Tsuji, *J. Amer. Chem. Soc.*, 1968, **90**, 99.

¹⁸ M. Kubota and D. Blake, *J. Amer. Chem. Soc.*, 1971, **93**, 1368.

¹⁹ M. A. Bennett and R. Charles, *J. Amer. Chem. Soc.*, 1972, **94**, 666.

²⁰ J. Blum, S. Kraus, and Y. Pickholtz, *J. Organometallic Chem.*, 1971, **33**, 227.

²¹ P. L. Bock, D. J. Boschetto, J. R. Rasmussen, J. P. Demers, and G. M. Whitesides, *J. Amer. Chem. Soc.*, 1974, **96**, 2814.

²² L. F. Hines and J. K. Stille, *J. Amer. Chem. Soc.*, 1972, **94**, 485.

A *trans*-elimination, on the other hand, should give two other deuteriated styrenes. While this work was in progress two relevant publications appeared. Stille *et al.*²³ reported that the decomposition of *erythro*- and *threo*-2,3-diphenylbutyryl chloride by $[\text{RhCl}(\text{PPh}_3)_3]$ does proceed stereospecifically to the products expected for a *cis*- β -elimination, *trans*- and *cis*-methylstilbene, respectively. They interpreted their results, however, in terms of a concerted *cis*-elimination rather than in terms of Scheme 1; no suggestions were made as to the nature of the concerted reaction, although precedents may be provided by reactions of the $[\text{DCo}(\text{CN})_5]^{3-}$ ion with α,β -unsaturated acids^{15,16} (see above). Casey *et al.*,²⁴ on the other hand, found that pentacarbonyl(*threo*- and *erythro*-2,3-dimethylvaleryl)manganese(I) decompose thermally to give identical mixtures of olefins, a result which was interpreted in terms of Scheme 1.

RESULTS AND DISCUSSION

The α,β -dideuteriophenethyl group provides a very convenient means of determining stereochemical changes in chemical reactions of primary alkyl ligands, including migration and elimination reactions. Its usefulness lies in the fact that compounds of the general formula $\text{PhCHD}\cdot\text{CHDX}$ favour the conformation in which the phenyl and X groups are mutually *trans*, although their n.m.r. spectral parameters are actually weighted averages of the parameters of all three staggered conformations. The deuterium-decoupled ^1H n.m.r. spectra, therefore, exhibit well resolved AB quartets in the aliphatic regions of the spectra. As the vicinal hydrogen atoms of the *trans*-conformation of the *threo*- and *erythro*-isomers are mutually *gauche* and *trans* to each other, respectively, the vicinal coupling constants, $J(\text{AB})$, are normally larger for the *erythro*-isomer. A similar group has been introduced by Bock *et al.*,²¹ while the α,β -dideuteriophenethyl group discussed here has previously been applied by Snyder and his co-workers.²⁵

The compound *threo*- $\text{PhCHD}\cdot\text{CHD}\cdot\text{CO}\cdot\text{Cl}$ was prepared *via cis*-addition of D_2 to *trans*-cinnamic acid²⁶ and conversion of the resulting *threo*- $\text{PhCHD}\cdot\text{CHD}\cdot\text{CO}_2\text{H}$ to the acid chloride with oxalyl chloride. The stereospecificity of both reactions was shown by the magnitudes of $^3J(\text{HH})$, 6.6 and 6.4 Hz, for the acid and the acid chloride, respectively, and considerably smaller than the value of 9.1 Hz observed for *erythro*- $\text{PhCHD}\cdot\text{CHD}\cdot\text{CO}_2\text{H}$, prepared from *cis*-cinnamic acid. The results are in themselves significant because they provide further evidence for *cis*-addition in the $[\text{RhCl}(\text{PPh}_3)_3]$ catalytic olefin-hydrogenation system.²⁶

In refluxing chloroform, $[\text{RhCl}(\text{PPh}_3)_3]$ and *threo*- $\text{PhCHD}\cdot\text{CHD}\cdot\text{CO}\cdot\text{Cl}$ reacted rapidly to form the orange

acyl complex $[(\text{dpp})\text{RhCl}_2(\text{PPh}_3)_2]$, (A); the unlabelled^{17,23} and $\text{C}_6\text{D}_5\text{CD}_2\text{CH}_2$ analogues have been reported previously. The i.r. spectrum of the complex exhibited a rather broad acyl band at *ca.* 1710 cm^{-1} and two rhodium-chlorine stretching bands at 347 and 315 cm^{-1} . Besides broad phenyl resonances, the deuterium-decoupled n.m.r. spectrum exhibited a simple AB quartet (that of the perhydro-compound contains a complex AA'BB' multiplet), τ_A , τ_B , and $J(\text{AB})$ being 6.89, 7.40, and 5.6 Hz, respectively. Similar complexes are monomeric;^{9,17} although the stereochemistry about the rhodium (trigonal bipyramidal or square pyramidal) cannot be determined, the two chlorines must be mutually *cis* and, by analogy with the orange isomer of $[\text{RhCl}_2(\text{COMe})(\text{PPh}_3)_2]$,⁹ the two triphenylphosphines are probably in equivalent positions. The stereochemistry of the acyl ligand is readily established by the relatively low value of $^3J(\text{HH})$.

On heating a CDCl_3 solution of the acyl complex at 100 °C in a sealed tube, the only detectable organic product was a mixture of deuteriated 1-chloro-1-phenylethanes, the products of reversible Markownikoff addition of the liberated $\text{HCl}(\text{DCl})$ to the liberated styrenes. In the presence of excess of hexamethyldisiloxane, however, no 1-chloro-1-phenylethanes are formed, but rather all possible styrenes containing zero, one, and two deuterium atoms in the vinyl group.²⁷ Although a very poor ligand towards rhodium, hexamethyldisiloxane reacts very rapidly with HCl to form trimethylsilanol and chlorotrimethylsilane.²⁸ No reaction occurs between styrene and DCl in hexamethyldisiloxane- CDCl_3 at 100 °C, and thus the mixture of deuteriated styrenes obtained from the acyl complex indicates that the styrene elimination reaction is either completely non-stereospecific or that it involves a sequence of stereospecific reversible steps, as in Scheme 2 (only some of the possible products expected from hydrogen migration are shown). Thus the acyl complex, (A), would isomerize to an alkyl intermediate, (B), which would in turn rearrange to give a second intermediate, the hydrido-olefin complex, (C). To explain the observed distribution of deuteriated styrenes, formation of a secondary alkyl derivative ($\text{C} \rightarrow \text{D}$ in Scheme 2) must occur at a rate at least comparable to the rate of dissociation of the olefin from the rhodium.

As the postulated intermediate, $[(\text{dpe})\text{RhCl}_2(\text{CO})(\text{PPh}_3)_2]$, (B), could not be detected by n.m.r. spectroscopy, the stereochemistry of the acyl-alkyl conversion was substantiated by preparing the analogous iridium complexes. The complex $[\text{IrCl}(\text{N}_2)(\text{PPh}_3)_2]$ ¹⁸ reacted with *threo*- $\text{PhCHD}\cdot\text{CHD}\cdot\text{CO}\cdot\text{Cl}$ to form a rather unstable *threo*-acyl complex [$^3J(\text{HH})$ 6.4 Hz], which in turn readily isomerized to $[(\text{dpe})\text{IrCl}_2(\text{CO})(\text{PPh}_3)_2]$ [$^3J(\text{HH})$ 4.8, $^3J(\text{PH})$ 6.1 Hz]; thus the alkyl-migration reaction proceeds with retention of configuration of the alkyl

²³ J. K. Stille, F. Huang, and M. T. Regan, *J. Amer. Chem. Soc.*, 1974, **96**, 1518.

²⁴ C. P. Casey, C. R. Cyr, and J. A. Grant, *Inorg. Chem.*, 1974, **13**, 910.

²⁵ R. G. Weiss and E. I. Snyder, *Chem. Comm.*, 1968, 1358; R. J. Jablonski and E. I. Snyder, *Tetrahedron Letters*, 1968, 1103; *J. Amer. Chem. Soc.*, 1969, **91**, 4445; E. I. Snyder, *ibid.*, p. 5118; W. F. Bayne and E. I. Snyder, *Tetrahedron Letters*, 1971, 571.

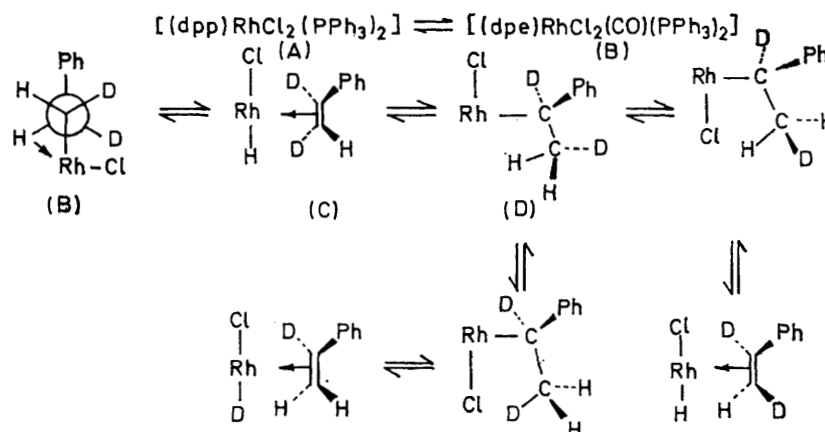
²⁶ J. A. Osborn, F. H. Jardine, J. F. Young, and G. Wilkinson, *J. Chem. Soc. (A)*, 1966, 1711.

²⁷ M. C. Baird, *J. Magnetic Resonance*, 1974, **14**, 117.

²⁸ C. Eaborn, 'Organosilicon Compounds,' Butterworths, London, 1960, p. 264.

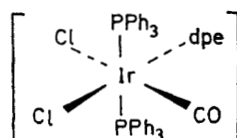
group. The latter complex, as the tetrahydro- and tetradeuterio-species, has been prepared by other routes.^{19,20} Its i.r. spectrum exhibits $\nu(\text{CO})$ at 2018 cm^{-1} and $\nu(\text{IrCl})$ at 310 and 250 cm^{-1} , very similar to other alkyliridium complexes,¹⁸ while the n.m.r. spectrum

inhibiting effect of added triphenylphosphine may be a result of co-ordination to the apparently five-coordinate (A), thus blocking the site required for migration of the alkyl group [although separate n.m.r. experiments suggest that co-ordination of a third triphenylphosphine



SCHEME 2

shows that the triphenylphosphines are equivalent, and therefore the structure is probably:



The stereochemistry about the metal atom is thus the same as that of $[\text{RhCl}_2\text{Me}(\text{CO})(\text{PPh}_3)_2]$.⁹ Thermal decomposition of the iridium complex under similar conditions as above yielded essentially the same mixture of deuteriated styrenes. Similar scrambling was observed in the decarbonylation and dehydrohalogenation of $\text{PhCD}_2\text{CH}_2\text{COCl}$ by $[\text{IrCl}(\text{CO})(\text{PPh}_3)_2]$, although no scrambling of the phenyl hydrogen atoms was observed.²⁰ Thus the chemistry of the rhodium and iridium systems is very similar.

Corroboration of Scheme 2 was found in the product distribution from the catalytic decarbonylation of $\text{PhCH}_2\text{CH}_2\text{COCl}$ (10^{-2} mol) by $[\text{RhCl}(\text{PPh}_3)_3]$ (10^{-4} mol) both in the absence and the presence of added triphenylphosphine (10^{-3} mol). The neat acid chloride was smoothly decarbonylated by $[\text{RhCl}(\text{PPh}_3)_3]$ above 150 °C in the presence of hexamethyldisiloxane to form styrene and small amounts of both 1-chloro-1-phenyl- and 1-chloro-2-phenylethane. In the presence of excess of triphenylphosphine, however, the decarbonylation reaction was considerably slower, requiring higher temperatures for convenient rates, and significant amounts only of 1-chloro-2-phenylethane and styrene were formed.

These observations are readily interpreted in terms of Scheme 2; the two (chloroethyl) benzenes are formed by reductive elimination from species such as (B) and (D), and provide evidence for their existence. The rate-

to (A) does not occur to a significant extent], or it may reflect increased difficulty in the formulation of (C) from (B). Unless the rhodium of (B) were to increase its co-ordination number to seven, the hydrogen-transfer step would require dissociation of one of the other ligands, as has been observed for the elimination of but-1-ene from $[\text{Bu}^n_2\text{Pt}(\text{PPh}_3)_2]$.¹¹ The presence of excess of triphenylphosphine would tend to retard such a dissociation. Furthermore, if the step (B) \rightarrow (D) were retarded, the rate of reductive elimination of primary alkyl chloride from (B) could become competitive, explaining the change in product distribution.

Although the work described here does not, as was hoped, demonstrate unambiguously that the decarbonylation and dehydrohalogenation of the phenylpropionyl-rhodium complexes involve a *cis*- β -elimination step, the results are clearly consistent with such a step; similar conclusions were reached by Casey *et al.*²⁴ for the thermal decomposition of complexes of the type $[(\text{RCO})\text{Mn}(\text{CO})_5]$. Both our observations and our conclusions, however, are in variance with those reached by Stille *et al.* for a very similar rhodium system.²³ As mentioned above, they found that decarbonylation of *erythro*- and *threo*-2,3-diphenylbutyryl chloride with $[\text{RhCl}(\text{PPh}_3)_3]$ gave *trans*- and *cis*- β -methylstilbene, respectively, consistent with a *cis*- β -elimination mechanism. No isomerization was observed in the former case, although some 10% of the *cis*-isomer isomerized to the more stable ²⁹ *trans*-isomer. They rejected the β -elimination mechanism, however, because they could not detect the presence of an alkyl-rhodium intermediate, (B), although kinetic studies of the decarbonylation of $[\text{RhCl}_2(\text{COCH}_2\text{CH}_2\text{Ph})(\text{PPh}_3)_2]$ and $[\text{RhCl}_2(\text{COCH}_2\text{CD}_2\text{Ph})(\text{PPh}_3)_2]$ in toluene at 80 °C suggested that such a species should be detectable.

²⁹ D. H. Hunter and D. J. Cram, *J. Amer. Chem. Soc.*, **1964**, **86**, 5478; A. Zwierzak and H. Pines, *J. Org. Chem.*, **1962**, **27**, 4084.

No details of the i.r. method used in the attempt to detect the alkylrhodium intermediate are given,²³ and we found that indeed no bands were present in the 2 000 cm^{-1} region of the spectrum of $[\text{RhCl}_2(\text{COCH}_2\text{CH}_2\text{Ph})-(\text{PPh}_3)_2]$ at room temperature, either as a Nujol mull or in chloroform solution. On heating a toluene solution at 80–90 °C for 30 min, however, a new band appeared reversibly at 1 996 cm^{-1} , in the region expected for a rhodium(III) carbonyl complex.⁹ On cooling to room temperature, the intensity of the band relative to that at 1 710 cm^{-1} decreased slowly, and thus an endothermic acyl-alkyl equilibrium in the solvent and at the temperature at which the kinetic studies were carried out is clearly established.

Finally, we note that the lack of stereospecificity observed here for the phenethylrhodium system is in direct contrast with, for instance, the stereospecificity of the dimethyl maleato- and fumarato-molybdenum,¹³ cyclohexylpalladium,¹⁴ and diphenylpropylrhodium²³ complexes. The configurational stability of compounds containing the highly electronegative ester groups on the α -carbon atom of the alkyl groups may be a result of relatively high metal-carbon bond strengths,² however, while in the case of the cyclohexylpalladium complexes the type of carbon-carbon bond rotation postulated in Scheme 2 clearly cannot occur. In the case of the diphenylpropylrhodium complexes,²³ the species corresponding to (C) and (D) of Scheme 2 would be much more highly hindered than in the phenethylrhodium system. Complexes of more highly substituted olefins are known to be relatively unstable,³⁰ and it is reasonable to suppose that the rates of dissociation of the methylstilbene complexes could be faster than the rates of reinsertion into the rhodium-hydrogen bond. Thus isomerization of the co-ordinated olefin would occur to a much lesser extent.

EXPERIMENTAL

I.r. spectra were measured on Beckman IR 10 and Perkin-Elmer 180 spectrometers, n.m.r. spectra on a Bruker HX 60 spectrometer.

Threo-2,3-dideuterio-3-phenylpropionic Acid, threo-PhCHD·CHD·CO₂H.—A suspension of *trans*-cinnamic acid (15 g) in D₂O (100 cm^3) was heated under reflux for 1 h in order to exchange the acid protons for deuterium. {When this step was not carried out the subsequent deuteration was not completely stereospecific, presumably because of exchange of the acid proton with the $[\text{RhD}_2(\text{Cl})(\text{PPh}_3)_3]$ catalyst. Similar exchange was observed when the reduction was carried out in 1:1 benzene-ethanol.} The suspension was then cooled, and the solid acid was collected by filtration, air dried, and dissolved in benzene (150 cm^3). The benzene solution was dried further over anhydrous sodium sulphate and then subjected, with $[\text{RhCl}(\text{PPh}_3)_3]$ catalyst (0.5 g), to ca. 3 atm of deuterium gas in a Parr catalytic apparatus for 2 d.* At the end of this period, n.m.r. spectroscopy showed that essentially all of the cinnamic acid had been reduced, and the product was obtained in a reasonably pure form by removing the solvent

* 1 atm = 101 325 Pa.

³⁰ F. R. Hartley, *Chem. Rev.*, 1973, **73**, 163.

³¹ S. Lindensfors, *Arkiv. Kemi*, 1959, **14**, 227.

on an aspirator and extracting the residue with low boiling light petroleum to remove the rhodium catalyst. On removal of the solvent, the solid *threo*-PhCHD·CHD·CO₂D exhibited a well resolved AB quartet in its n.m.r. spectrum [τ_A 7.07, τ_B 7.34, $J(\text{AB})$ 6.6 Hz in CDCl_3 solution]; the downfield doublet was broadened somewhat by long-range coupling to the phenyl protons, and thus may be assigned to the PhCHD group. A sample prepared similarly but with hydrogen had an n.m.r. spectrum identical to that of an authentic sample of 3-phenylpropionic acid, while reduction with deuterium of a mixture of *cis*- and *trans*-cinnamic acid, prepared by u.v. irradiation of a solution of the *trans*-isomer,³¹ gave a material whose deuterium-decoupled n.m.r. spectrum exhibited the pair of overlapping AB quartets expected for a mixture of *threo*- and *erythro*-PhCHD·CHD·CO₂D [for the *erythro*-isomer, τ_A 7.06, τ_B 7.35, $J(\text{AB})$ 9.1 Hz in CDCl_3].

Threo-2,3-dideuterio-3-phenylpropionyl Chloride, threo-PhCHD·CHD·CO·Cl.—Treatment of the *threo*-PhCHD·CHD·CO₂D with oxalyl chloride in benzene gave pure *threo*-PhCHD·CHD·CO·Cl (b.p. 63–66 °C, 0.3 mmHg)³² [τ_A 6.87, τ_B 7.05, $J(\text{AB})$ 6.4 Hz in CDCl_3]. In this case it is the upfield doublet which is broadened by the phenyl protons, and thus may be assigned to the PhCHD group.

Dichloro(3-phenylpropionyl)bis(triphenylphosphine)-rhodium(III), $[\text{RhCl}_2(\text{COCH}_2\text{CH}_2\text{Ph})(\text{PPh}_3)_2]$.—To a refluxing chloroform solution of $[\text{RhCl}(\text{PPh}_3)_3]$ (0.5 g) was added $\text{PhCH}_2\text{CH}_2\text{COCl}$ (1 cm^3). The solution quickly became orange and after 5 min the product was precipitated on addition of diethyl ether. The complex was recrystallized from methylene chloride-methanol as stable orange crystals which turn yellow with evolution of a colourless liquid above 165 °C and melt above 200 °C with decomposition. The n.m.r. spectrum of a CDCl_3 solution exhibited complex AA'BB' multiplets centred at ca. τ 6.83 and 7.40, which may be assigned to the methylene protons.¹⁷

The complex dichloro(*threo*-2,3-dideuterio-3-phenylpropionyl)bis(triphenylphosphine)rhodium(III) was prepared in a similar manner from $[\text{RhCl}(\text{PPh}_3)_3]$ and *threo*-PhCHD·CHD·CO·Cl. Its n.m.r. spectrum exhibited a well resolved AB quartet in the aliphatic region [τ_A 6.89, τ_B 7.40, $J(\text{AB})$ 5.6 Hz]. Again the downfield doublet may be assigned to the PhCHD group on the basis of its greater broadening. The i.r. spectrum in chloroform solution exhibited a broad band at ca. 1 712 cm^{-1} which may be assigned to the acyl stretching mode, while a polyethylene mull spectrum exhibited bands at 347 and 315 cm^{-1} which may be assigned to rhodium-chlorine stretching modes.

Carbonyldichloro(threo- α,β -dideuteriophenethyl)bis(triphenylphosphine)iridium(III), $[\text{IrCl}_2(\text{CO})(\text{dpe})(\text{PPh}_3)_2]$.²⁰—The complex $[\text{IrCl}(\text{CO})(\text{PPh}_3)_2]$ (1.17 g) was converted to $[\text{IrCl}(\text{N}_2)(\text{PPh}_3)_2]$ as described in the literature;³³ a stirred benzene solution of the latter was treated with *threo*-PhCHD·CHD·CO·Cl (0.3 cm^3) at room temperature. Nitrogen was evolved and the solution became orange then pale yellow. After 1.5 h the n.m.r. spectrum showed a weak AB quartet which can probably be assigned to an acyl complex [τ_A 7.15, τ_B 7.37, $J(\text{AB})$ 6.4 Hz]. The solution was warmed for a few minutes and the solvent was removed *in vacuo* to give an off-white solid which recrystallized from methylene chloride to give the product {0.75 g,

³² R. Adams and L. H. Ulich, *J. Amer. Chem. Soc.*, 1920, **42**, 599.

³³ J. P. Collman, N. W. Hoffman, and J. W. Hosking, *Inorg. Synth.*, 1970, **12**, 8.

51% yield from $[\text{IrCl}(\text{CO})(\text{PPh}_3)_2]$. The compound turns yellow above 175 °C, darkens, and slowly melts above 200 °C. The n.m.r. spectrum of the complex exhibited an ABX_2 -type system ($\text{X} = {}^{31}\text{P}$) [τ_{A} 7.64, τ_{B} 8.18, $J(\text{AB})$ 4.8, $J(\text{AX})$ 0, $J(\text{BX})$ 6.1 Hz]; the i.r. spectrum showed a single carbonyl-stretching mode at 2018 cm^{-1} (chloroform solution) and two iridium-chlorine stretching modes at 310 and 250 cm^{-1} (polyethylene disc).

Thermal-decomposition Studies.—Decompositions of $[(\text{dpe})\text{RhCl}_2(\text{PPh}_3)_2]$ were carried out in CDCl_3 solutions in an evacuated sealed tube. The tubes were heated in an oil-bath at 100 °C for several hours. The iridium analogue was much more robust and decomposition was carried out

by flaming an evacuated sealed tube containing the complex and hexamethyldisiloxane. Catalytic-decarbonylation reactions of *threo*- $\text{PhCHD}\cdot\text{CHD}\cdot\text{CO}\cdot\text{Cl}$ by $[\text{RhCl}(\text{PPh}_3)_3]$ were carried out in an open flask under nitrogen. The solutions were heated in an oil-bath above 145 °C, samples being extracted with a syringe and diluted with CDCl_3 . Decarbonylation was very slow below 130 °C, very rapid above 180 °C. All products were identified by n.m.r. spectroscopy.

We thank the National Research Council of Canada for support and Johnson, Matthey Ltd. for a loan of rhodium trichloride.

[4/1297 Received, 28th June, 1974]