The Preparation of Soluble Mixed-ligand Rhodium Hydrogenation Catalysts by Reduction of Dioxygenrhodium Complexes

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The reduction of the dioxygen species $[\{RhCl(O_2)(PPh_3)_2\}_2]$ with ethanol in the presence of 1 equivalent of a phosphine ligand, L, other than PPh_3, gives a catalytically active mixture having a PPh_3 : L ratio of 3 : 1. When the reduction is carried out under hydrogen, this mixture is composed of two species, $[RhClH_2(PPh_3)_2]$ and $[RhClH_2(PPh_3)L]$. A comparison is made of the rate and stereochemical data obtained using these mixtures for the hydrogenation of 1-methylene-4-t-butylcyclohexane with data obtained using the $[RhClL_2]$ complexes as catalysts. This comparison and others have shown that in the mixed-ligand species, $[RhClH_2(PPh_3)L]$, the ligand L is present exclusively at the site *trans* to the position of olefin complexation prior to hydrogen transfer.

IT has been shown previously that the reaction of $[RhCl(PPh_3)_3]$ (1) with oxygen can result in the formation of a number of different rhodium–oxygen complexes with the nature of the product formed being dependent, at least in part, on the solvent in which the oxidation was run.[1,2] It was further established that the reduction of some of these oxides either alone or in the presence of other ligands would produce species capable of catalysing the hydrogenation of double bonds.[1,3,4] Most of the previous work concerned the determination of the catalytic properties of these active reduction products and little direct evidence was obtained of their composition. Since the reduction of the rhodium–oxygen complexes in the presence of additional triphenylphosphine or other ligands apparently resulted in the incorporation of these ligands into the catalytic complex,[1] it was felt that this procedure might be useful for the preparation of mixed-ligand complexes having specific catalytic properties. Thus, work was begun on an investigation of the composition and structure of these reduced species, and this paper describes the results obtained.

EXPERIMENTAL

The i.r. spectra as Nujol mulls on KBr plates were obtained with a Beckman IR 10 double-beam recording spectrophotometer. N.m.r. spectra were recorded on a Varian A-60A spectrometer. *X*-Ray fluorescence data were obtained using a General Electric XRD-5 spectrometer, equipped with an EDT crystal and SPG-4 detector under helium. Rhodium was determined using the $L_{\alpha 1}$ line (62.97°), phosphorus with the $K_{\alpha 1}$ line (88.75°), and chlorine with the K_{α} line (64.98°). The instrument was calibrated using known mixtures of rhodium(III) oxide, PPh_3, and 2-chloroanthraquinone as well as an authentic sample of $[RhCl(PPh_3)_3]$. Gas chromatographic analyses were carried out on a Varian Autoprep model A-100 gas chromatograph with a thermal-conductivity detector and repeated on a Varian Aerograph model 200 gas chromatograph with a flame ionization detector. The column employed was a copper tube (length 45 ft, outside diameter 0.25 in) filled with 10% diethylene glycol succinate on Chromosorb P. The following retention times were recorded at a helium flow rate of 47 $cm^3 min^{-1}$ and a column temperature of 125 °C: *trans*-1-methyl-4-t-butylcyclohexane, 38 min; *cis*-1-methyl-4-t-butylcyclohexane, 44 min; 1-methylene-4-t-butylcyclohexane, 55 min; 1-methyl-4-t-butylcyclohex-1-ene, 60 min. Optical rotations were measured in a Visual High Precision model 80 polarimeter supplied by O. C. Rudolf and Co., Inc., Caldwell, New Jersey. Thin-layer chromatography (t.l.c.) was run on silica gel Eastman Chromatogram Sheet 6060 while preparative t.l.c. was run using 2-mm silica gel plates supplied by Merck Instruments. Visualization was carried out by use of u.v. light. Elemental analyses and molecular-weight determinations were performed by Schwartzkopf Microanalytical Laboratory, Woodside, New York.

The hydrogen used in this work was passed through an Engelhard Deoxo Puridryer before use and only prepurified nitrogen was used. All the solvents were degassed before use by refluxing and subsequent cooling under a steady stream of nitrogen. Thiophene-free benzene and absolute ethanol were used. 1-Methylene-4-t-butylcyclohexane was prepared from methyltriphenylphosphonium bromide and 4-t-butylcyclohexanone by a modified Wittig reaction[5] and was purified by silica gel column chromatography. Chlorotris(triphenylphosphine)rhodium(I), (1), was prepared from triphenylphosphine and rhodium trichloride trihydrate by a method described by Wilkinson and his co-workers.[6] Di-μ-chloro-bis[bis(cyclo-octene)rhodium], (16), was prepared from cyclo-octene and $RhCl_3 \cdot 3H_2O$.[7] All phosphine ligands were recrystallized immediately before use. Trianisyl-, tritolyl-, and triphenyl-phosphines were recrystallized from ethanol, tri-*p*-fluoro- and tri-*p*-chloro-phenylphosphine from methanol.

General Procedure for the Gas–Liquid Reactions.—A specially designed reactor, illustrated elsewhere,[8] was used which permits the observation of the uptake of a small volume of gas. This apparatus consisted of a flat-bottomed flask (125 cm^3) equipped with a 24/40 ground-glass joint. The flask had three side arms connected to its upper portion. One side arm was a U-tube serving as a manometer, the second was sealed by a serum cap allowing addition or sampling, and the third was connected to a hydrogen-filled syringe of desired volume. The benzene level in the manometer was maintained constant during an experiment by moving the plunger of the syringe. The volume of gas absorbed during a reaction was read from the position of the plunger. The 24/40 glass joint was stoppered. The apparatus was totally submerged in a water-bath, maintained at a constant temperature of 25.0 °C. The reaction mixture was agitated by a Teflon-coated magnet driven by a motor positioned beneath the water-bath. The speed of agitation was such that it was not a rate-controlling factor.

Synthesis of Complexes of the Type $[RhClL_3]$.—The complex $[RhCl\{P(C_6H_4OMe\text{-}p)_3\}_3]$ was prepared by heating under reflux a slurry of $[\{RhCl(C_8H_{14})_2\}_2]$ (0.5 g, 1.4 mmol of Rh) and trianisylphosphine (4.2 mmol) in ethanol (40 cm^3) under nitrogen for 30 min. Orange crystals of the product began to separate from the yellow solution minutes after the addition of the solvent. The final reaction mixture was cooled in an ice-bath and the orange solid centrifuged from solution, washed three times with cold ethanol (35 cm^3), and dried *in vacuo*, yield 1.0 g (60%). *X*-Ray fluorescence analysis indicated the correct atomic ratio for Rh : P : Cl of 1 : 3 : 1.

The complex $[RhCl\{P(C_6H_4Cl\text{-}p)_3\}_3]$ was prepared as above using a slurry of $[\{RhCl(C_8H_{14})_2\}_2]$ (0.58 g, 1.62 mmol of Rh) and tri-*p*-chlorophenylphosphine (4.85 mmol) in ethanol (100 cm^3). The solid orange product was centrifuged from solution, washed three times with pentane (35 cm^3), and dried *in vacuo*, yield 1.3 g (65%). *X*-Ray fluorescence spectroscopy indicated a Rh : P ratio of 1 : 3.

Synthesis of Dioxygen Complexes.—The complex $[RhCl(O_2)(PPh_3)_2]$ (2a) was prepared by bubbling dry oxygen for 20 min through a solution of (1) (2.0 g, 2.17 mmol) in benzene (200 cm^3) which had been dried by distillation from sodium immediately before use. The solvent was removed under reduced pressure and the residue was washed four times with 35-cm^3 portions of benzene–ethanol (1 : 1) and once with diethyl ether (35 cm^3). The brick red product was dried *in vacuo* and stored under nitrogen in the dark, yield 0.6 g (40%); i.r. spectrum, 850 cm^{-1} (peroxo) [Found: C, 61.85; H, 4.40; Cl, 5.30; O, 4.95; P, 8.70. Calc. for (2a): C, 62.2; H, 4.30; Cl, 5.10; O, 4.60; P, 8.95%].

When samples were allowed to stand in air for prolonged times, further oxidation occurred to give a phosphine oxide dioxygen complex; i.r. spectrum, 850 and 1 120 cm^{-1} (phosphine oxide) {Found: C, 60.7; H, 4.55; Cl, 5.10; O, 8.40; P, 8.75. Calc. for $[RhCl(O_2)(PPh_3O)_2]$: C, 54.0; H, 4.15; Cl, 4.90; O, 8.80; P, 8.55%}.

The complex $[RhCl(O_2)\{P(C_6H_4OMe\text{-}p)_3\}_2]$ (2b) was prepared as above using a solution of $[RhCl\{P(C_6H_4OMe\text{-}p)_3\}_3]$ (0.96 g, 0.80 mmol) in dry benzene (95 cm^3) at 25.0 °C for 15 min. The orange residue was washed, dried, and stored as before, yield 0.33 g (47%); i.r. spectrum, 860 cm^{-1} (peroxo) [Found: C, 57.6; H, 5.00; Cl, 4.75; O, 13.65; P, 6.35. Calc. for (2b): C, 57.65; H, 4.80; Cl, 4.05; O, 14.65; P, 7.05%].

The complex $[RhCl(O_2)\{P(C_6H_4Cl\text{-}p)_3\}_2]$ (2c) was prepared as above using a solution of $[RhCl\{P(C_6H_4Cl\text{-}p)_3\}_3]$ (1.0 g, 0.81 mmol) in dry benzene (90 cm^3) at 25.0 °C for 30 min. The product was treated as before, yield 0.14 g (19%); i.r. spectrum, 845 cm^{-1} (peroxo). *X*-Ray fluorescence data indicated a Rh : P ratio of 1 : 2.

Preparation, in situ, *and Hydrogenation with Chlorobis(phosphine)rhodium*(I) *Complexes*.—All chlorobis(phosphine)rhodium(I) complexes were prepared *in situ* in the gas–liquid reactor previously described. They were then used immediately in olefin hydrogenation. In general, the preparation involved stirring a 4 : 1 mol ratio of ligand and $[\{RhCl(C_8H_{14})_2\}_2]$ in benzene–ethanol (1 : 1) under nitrogen for 15 min and then under hydrogen for 45 min. 1-Methylene-4-t-butylcyclohexane, (11), was then admitted to the reactor and the rate of hydrogen consumption was measured at a constant temperature of 25.0 °C. The olefin concentration was usually 0.048 mol dm^{-3}. Data for these hydrogenations are presented in Figure 2 and Table 1.

General Procedure for the Reduction of Dioxygen Complexes.—A solution (20 cm^3) consisting of the dioxygen complex (1.8 mmol of Rh) and an added ligand (1.8 mmol) dissolved in benzene–ethanol (1 : 1) was stirred under H_2 or N_2 at 25.0 °C. A 10-cm^3 sample was withdrawn and admitted to a hydrogen-filled gas-liquid reactor and stirred for 15 min before the 1-methylene-4-t-butylcyclohexane (80 μl, 0.048 mol) was injected. Data for those hydrogenations run on the catalysts prepared under H_2 are presented in Figure 2 and Table 2. In cases where an i.r. study of the dioxygen complex at varying times was required a larger volume of solution containing the same concentrations was prepared. Aliquots were withdrawn periodically and the solvent was removed under reduced pressure. The i.r. spectra of the residues were recorded. In cases where trapping of the active species was required, the solution was treated with carbon monoxide, the solvent removed under reduced pressure, and the stable carbonyl complexes studied by *X*-ray fluorescence analysis.

Trapping Acetaldehyde produced in the Reduction of (2a) *in Ethanol–Benzene Solvent*.—A steady stream of hydrogen was passed over a solution consisting of (2a) (0.30 g, 0.43 mmol) and tri-*p*-tolylphosphine, (0.13 g, 0.43 mmol) in benzene–ethanol (1 : 1, 250 cm^3). This hydrogen stream was then passed through a solution of 2,4-dinitrophenylhydrazine for 24 h. The hydrazone produced was isolated and identified as that of acetaldehyde by comparison of its t.l.c. R_F value and its m.p. with those of an authentic sample.

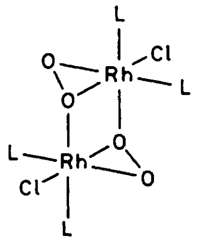
Isolation of the Phosphine Oxides produced in the Reduction of (2a) *in Benzene–Ethanol*.—A mixture of (2a) (0.100 g, 0.144 mmol) and tri-*p*-tolylphosphine (0.044 g, 0.144 mmol) was stirred in benzene–ethanol (1 : 1, 80 cm^3) under hydrogen at 25.0 °C for 24 h. The solvent was removed under reduced pressure and the residue was washed three times with 15-cm^3 portions of diethyl ether to isolate the phosphine oxides. The ether solution was concentrated under reduced pressure and applied to a preparative t.l.c. plate. The chromatogram was developed in 20% ethanol in hexane. The phosphine oxides (R_F *ca.* 0.2) were removed from the plate and subjected to ^1H n.m.r. analysis to determine the relative amount of each oxide. It was found that the oxide mixture was composed of *ca.* 55% triphenylphosphine oxide and 45% tri-*p*-tolylphosphine oxide.

Hydrogenation of α-Acetamidoacrylic Acid.—Solid α-acetamidoacrylic acid (0.5 g, 4.4 mmol) was placed in a gas–liquid reactor, which was then filled with hydrogen. A solution of (2a) (1.88 mmol) and (+)-menthyldiphenylphosphine (1.8 mmol) in benzene–ethanol (1 : 1, 25 cm^3) was added to the reactor and hydrogen absorption was followed volumetrically. Upon completion of hydrogenation, the solution was evaporated to dryness and the saturated acid residue was recrystallized from acetone. Polarimetry studies on an aqueous solution of the acid (0.1 g per 10 cm^3) indicated a specific rotation of 1.6°. Optically pure α-acetamidoalanine has a specific rotation of 45.6°. This indicates an optical purity of the product of *ca.* 3—4%.

RESULTS AND DISCUSSION

While a number of different rhodium–oxygen complexes were available [1] for this reduction study, some preliminary results indicated that the dioxygen species obtained on oxidation of (1) in dry benzene was readily reproducible and, thus, was best suited for use in this investigation. Reaction of oxygen with a solution of (1) in carefully dried benzene resulted in the rapid uptake of 1 equivalent of oxygen and the formation of a product having the formula $[RhCl(O_2)(PPh_3)_2]$ (2a).

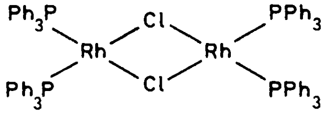
This complex was reasonably stable and could be prepared several days before use, but when the solid was kept, even under nitrogen, for longer than 2 weeks some insertion of the oxygen into the rhodium–phosphorus bond occurred as indicated by the decrease in intensity of the dioxygen ligand band [9] in the i.r. spectrum (850 cm^{-1}) and the formation of a phosphine oxide band [10] at 1 120 cm^{-1}. This reaction occurred more readily in solution but was still sufficiently slow that solutions of (2a) in dry benzene were stable for at least 24 h. Not only was (2a) relatively stable, it was also quite unreactive. It was recovered, unchanged, from attempted reactions in dry benzene solution with various olefins, PPh_3, $P(C_6H_{11})Ph_2$, and hydrogen. This lack of reactivity indicated that (2a) was co-ordinatively saturated and, thus, was probably identical with the rhodium–dioxygen complex prepared by Bennett and Donaldson [11] from a methylene chloride solution of (1). *X*-Ray diffractometry on this oxide showed it to be dimeric with peroxide bridging ligands. Unfortunately (2a) was always obtained as an amorphous solid which could not be induced to crystallize so a direct structure determination was not possible. Comparison with the Bennett oxide was complicated by the fact that the latter was shown to crystallize together with several molecules of methylene chloride while analysis of (2a) indicated the absence of any solvent in the isolated solid. Even with these difficulties, the lack of reactivity of (2a) and some of the reaction data discussed below strongly indicate that (2a) is at least very similar to the Bennett oxide in structure.



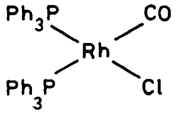
(2a) L = PPh_3
(2b) L = $P(C_6H_4OMe-p)_3$
(2c) L = $P(C_6H_4Cl-p)_3$

While (2a) was stable in dry benzene solutions, the addition of ethanol resulted in the initial orange colour of the solution changing to dark brown in a few hours. The loss of the dioxygen function during this time was shown by the gradual disappearance of the band at 850 cm^{-1} in the i.r. spectrum of the reaction mixture. This change was accompanied by the gradual appearance of a band at 1 960 cm^{-1} indicating the presence of a metal carbonyl complex.[12] This complex was isolated by evaporation of the reaction mixture and thorough washing of the residue. It was shown by *X*-ray fluorescence spectrometry to have a Rh : P : Cl ratio of 2 : 3 : 2. Since (2a) had a Rh : P : Cl ratio of 2 : 4 : 2 the loss of one half of an equivalent of the phosphine has evidently occurred during this reduction. Examination of the material removed from the reaction residue during the washing sequence showed that this phosphine had been converted entirely into the oxide. Thus, in the course of the reduction of (2a) by an alcohol one half of an equivalent of the phosphine present on (2a) is converted into the oxide. Oxidation of the ethanol also occurred since the presence of acetaldehyde was established by trapping it as its 2,4-dinitrophenylhydrazone. The carbonyl complex was apparently formed by the decarbonylation of this acetaldehyde. The rate of loss of the dioxygen ligand, as indicated by i.r. analyses of reaction aliquots, was dependent on the alcohol used in the reduction with the observed order: methanol > ethanol > isopropyl alcohol. Since this parallels the acidities of these alcohols [13] it is possible that proton transfer to the dioxygen group is important in the reduction, but steric and/or electronic factors could also be influential.

When (2a) was reduced in a benzene–ethanol solution containing an additional equivalent of PPh_3 the dioxygen function was again lost but two rhodium-containing products were obtained; the dimer,[6] $[\{RhCl(PPh_3)_2\}_2]$ (3), which precipitated from the solution, and the carbonyl complex [6], $[RhCl(CO)(PPh_3)_2]$ (4), which was isolated after evaporation of the filtered reaction mixture. The identities of both species were confirmed by comparison with authentic samples. Triphenylphosphine oxide was also recovered but no free PPh_3 could be detected by t.l.c. analyses of the various reaction solutions or wash liquids. When 1 equivalent of $P(C_6H_4Me\text{-}p)_3$ was present during the reduction of (2a) the precipitation of a dimeric species such as (3) did not take place and almost all of the rhodium was present as the carbonyl-containing material isolated on evaporation of the reaction mixture. Hydrogen-1 n.m.r. analysis of this material showed it to contain PPh_3 and $P(C_6H_4Me\text{-}p)_3$ in a 3 : 1 ratio. Preparative t.l.c. of the phosphine oxide fraction from this reaction followed by ^1H n.m.r. analysis of the isolated materials showed that the phosphine oxides were a nearly equal mixture of PPh_3O and $P(C_6H_4Me\text{-}p)_3O$. Thus, not only is one of the phosphines present on (2a) converted into the oxide during the reduction of this material but, if another phosphine is present in the reaction mixture, one half of an equivalent of that species is also oxidized.

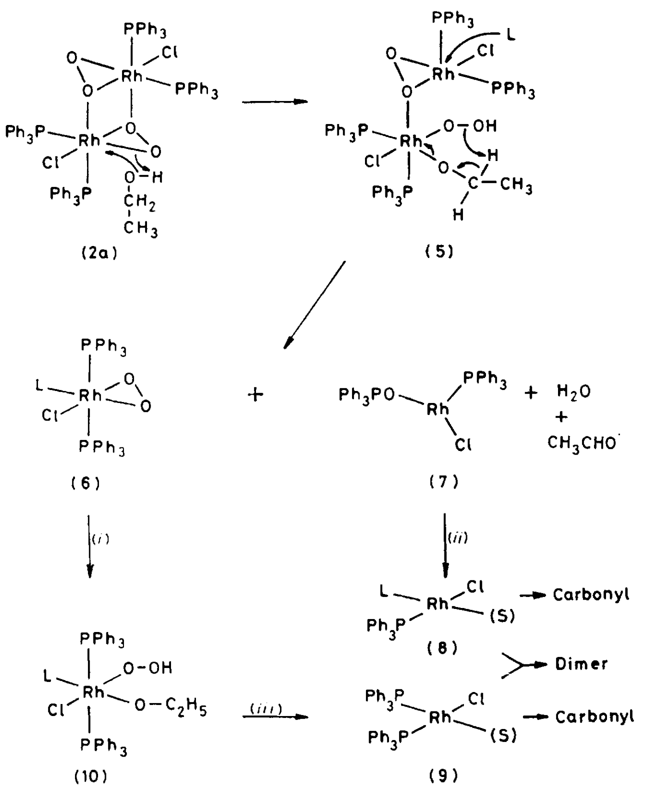


(3)



(4)

A rationale for the reduction of (2a) which accounts for these observations is presented in Scheme 1. By analogy with the addition of carbonyl compounds to dioxygen complexes to form *p*-ozonides,[14,15] it would seem likely that an alcohol could react with the Rh–O bond to give the alkoxide hydroperoxide (5). Reaction of the five-co-ordinate rhodium with one half of an equivalent of the added ligand, L, and rearrangement of alkoxide hydroperoxide as depicted would give two distinct rhodium-containing species: a monomeric dioxygen complex, (6), and a rhodium(I) phosphine oxide complex, (7), which can react with the other half-equivalent of L to displace PPh_3O and give the mixed-ligand species, (8). Further reaction of (6) with ethanol would lead to the formation of the oxide of L and the bis(triphenylphosphine) species, (9). Complexes (8) and (9) can then proceed to form a dimer or mixture of dimers and/or, by decarbonylation of the acetaldehyde, give the corresponding carbonyl complexes. It is not entirely evident at this time why only the L oxide should be formed from the mixed-ligand dioxygen species (6). That the reason was not simply the more ready oxidation of the electron-rich $P(C_6H_4Me\text{-}p)_3$ was shown by the observation of the same incorporation pattern when tri-*p*-chlorophenylphosphine was used as the added ligand, L. In the light of data presented later concerning the stereospecific incorporation of the ligand, L, into the complexes in a hydrogen atmosphere, it could also be anticipated that reaction of L with (5) would lead to the formation of a single monomeric dioxygen complex such as (6). Reaction with an alcohol from the less-hindered side of the dioxygen group would give (10), and oxygen insertion into the more available ligand (L) would lead to predominant formation of the L oxide.



SCHEME 1 L = Added ligand, S = solvent or olefin. (*i*) EtOH; (*ii*) +L, −phosphine oxide; (*iii*) −L oxide

This similarity in behaviour when both electron-withdrawing and electron-donating ligands were used as well as the isolation of nearly equal amounts of the triphenylphosphine oxide and L oxides as mentioned above also rules out the possibility of the formation of these mixed-ligand species by way of an equilibrium-controlled ligand-exchange process. If such a process were operating the similarity in ligand incorporation when both $P(C_6H_4Me\text{-}p)_3$ and $P(C_6H_4Cl\text{-}p)_3$ were used as the added ligand, L, would not be expected.

This procedure, then, appeared to be a reasonably attractive method for the preparation of potentially useful mixed-ligand homogeneous catalysts. Unfortunately, the catalytic activity of these reaction mixtures toward the hydrogenation of double bonds went through a maximum and then decreased as the formation of the catalytically inactive carbonyl complexes progressed as shown in Figure 1. Since rhodium dihydrides do not promote decarbonylations,[16] it was felt that, if the reduction of (2a) with ethanol were run under hydrogen, carbonyl complex formation would be repressed and consistently reactive catalysts could be prepared. When this reduction was carried out it was, indeed, found that the resulting solutions maintained a maximum catalytic activity for up to 48 h. As with the previous reductions, the residue obtained on evaporation of the solvent and washing free from phosphine oxide had a Rh : P : Cl ratio of 2 : 3 : 2 as determined by *X*-ray fluorescence spectrometry. When 1 equivalent of PPh_3 was present in the reaction mixture during the reduction this ratio was found to be 1 : 2 : 1. If 1 equivalent of $P(C_6H_4Me\text{-}p)_3$ were used as the added ligand, L, the reduced products were shown by ^1H n.m.r. and *X*-ray fluorescence spectrometry to have a PPh_3 : L ratio of 3 : 1. It appears, then, that the reduction of (2a) with alcohol in a hydrogen atmosphere follows essentially the same type of reaction path as occurs on reduction of (2a) under nitrogen with the primary difference being a lack of formation of any carbonyl-containing species from the dihydrorhodium intermediates as outlined in Scheme 2.

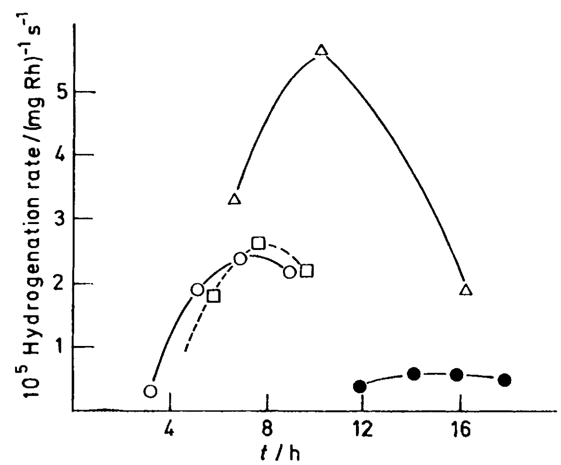
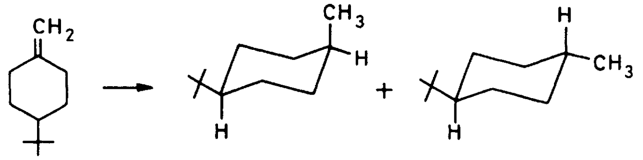


FIGURE 1 Catalytic activity *versus* time for catalysts prepared by the reduction of (2a) under nitrogen in the presence of tri(substituted aryl)phosphines: (△), PPh_3; (○), $P(C_6H_4OMe\text{-}p)_3$; (□), $P(C_6H_4Me\text{-}p)_3$; (●), $P(C_6H_4Cl\text{-}p)_3$

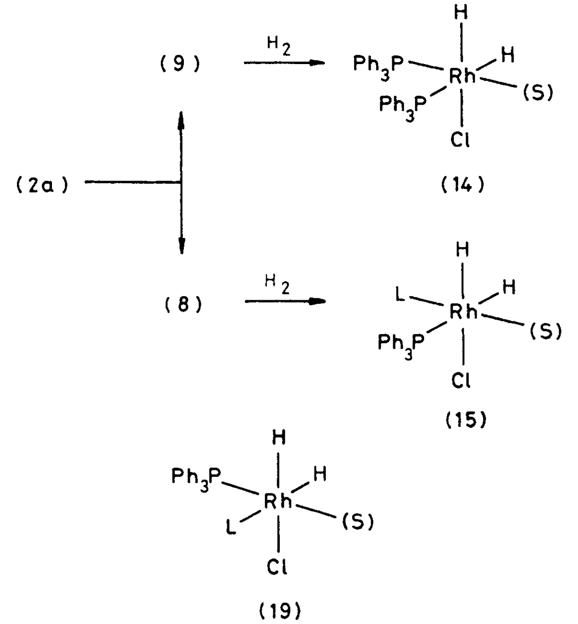
There remained, though, the question of the nature of the catalytically active species which were formed during these reduction procedures. Since the product stereochemistries obtained on hydrogenation of substituted cyclohexenes and methylenecyclohexanes have been found to be a useful probe in the comparison, evaluation, and mechanistic determinations of both heterogeneous[17] and homogeneous catalysis,[4,18] it was felt that examination of the *cis* : *trans* (12) : (13) ratio obtained on hydrogenation of 1-methylene-4-t-butylcyclohexane (11) would provide a valid means of comparing these mixed-ligand catalysts with known materials. Before such a comparison could effectively be made, it was necessary to establish whether or not the composition of the active catalyst or catalysts prepared by the reduction of (2a) remained constant throughout the course of the reaction. To determine this, (2a) was reduced under nitrogen in a benzene–ethanol solution in the presence of 1 equivalent of a number of different *meta*- and *para*-substituted triphenylphosphines and aliquots were withdrawn at varying times and used to catalyze the hydrogenation of (11). In every case, even though the reaction rate reached a maximum and then decreased as shown in Figure 1, the *cis* : *trans* (12) : (13) ratio was found to be independent of the time of sampling, indicating that the active intermediate(s) generated in the reduction of (2a) remained unchanged until destroyed by carbonyl formation. The same observations were made in a similar study on the reduction of (2a) under hydrogen except, as previously noted, the catalytic activity did not decrease appreciably after the rate maximum was reached. Because of the problems associated with the formation of inactive carbonyl complexes during the reduction of (2a) under nitrogen, all further efforts were directed toward determining the nature of the catalyst(s) prepared when (2a) was reduced in a hydrogen atmosphere.



(11) (12) (13)

It has been shown in previous work that the hydrogenation of (11) using hydrogen-presaturated (1) as the catalyst led to a (12) : (13) ratio of *ca.* 1.95—2.0 : 1.[4,8] This ratio appeared to be invariant in all hydrogenations in which the active catalyst was $[RhClH_2(PPh_3)_2]$ (14), proposed as the intermediate in hydrogenations catalyzed by (1),[6] regardless of how (14) was prepared.[8] Thus, this ratio has been used as an indication of whether or not (14) was present in a catalyst preparation.[8] When (2a) was reduced in a hydrogen atmosphere in the presence of 1 equivalent of PPh_3 and the resulting solution used to catalyse the hydrogenation of (11), the ratio (12) : (13) obtained was 1.97 : 1 indicating that the catalytically active species formed during this reaction was, indeed, the bis(phosphine), (14), as depicted in Scheme 2.

While this characterization may be valid for those catalysts prepared in the presence of PPh_3, there do not appear to be any reasonably valid correlations available which would be of use in determining the nature of the catalysts prepared on reduction of (2a) in the presence of a ligand other than PPh_3. Previously it had been shown that the electronic characteristics of the aryl substituent in chloro(triarylphosphine)rhodium complexes could have a marked influence on the rate of olefin hydrogenation catalysed by these complexes.[7,19] Electron-releasing groups lower the effective oxidation state of the metal thus facilitating the oxidative addition of hydrogen to the double bond. Electron-withdrawing groups have the opposite effect. Changes in electron-donating or -withdrawing capability can also affect olefin complexation on these catalysts. Thus, in the hydrogenation of cyclohexene with catalysts prepared by treating di-μ-chloro-bis[bis(cyclo-octene)rhodium] (16) with 3 equivalents of substituted triarylphosphines the rate decreased in the order *p*-anisyl > phenyl > *p*-fluorophenyl,[7] and with catalysts prepared from (16) and 2.2—2.5 equivalents of the phosphine the rate decreased: *p*-anisyl > *p*-tolyl > *p*-chlorophenyl.[19] No data could be found, however, on the relative rate or product stereochemistry obtained using catalysts prepared from (16) and exactly 2 equivalents of added ligands. To remedy this situation and, thus, provide a basis for evaluating and characterizing the mixed-ligand complexes prepared from (2a), the hydrogenation of (11) was studied over a series of catalysts prepared by treating (16) with 2 equivalents of a number of *meta*- and *para*-substituted triarylphosphines. To avoid potentially restrictive steric interactions, *ortho*-sub-



SCHEME 2 L = Added ligand, S = solvent or olefin

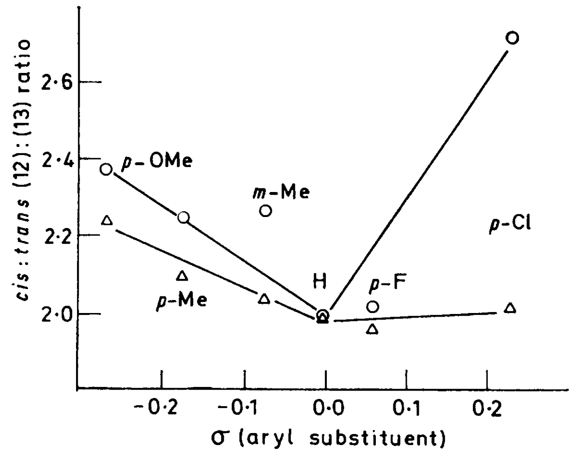


FIGURE 2 Product stereochemistry obtained on hydrogenation of (11) over (substituted arylphosphine)-containing rhodium catalysts: (○), bis(phosphine) complexes, [RhClL$_2$]; (△), catalysts prepared by the reduction of (2a) under hydrogen in the presence of a tri(substituted aryl)phosphine

stituted species were not used. The *cis* : *trans* (12) : (13) ratios and rates of hydrogen uptake obtained with these catalysts are presented in Table 1 and Figure 2. In contrast to previous rate comparisons, in this instance the hydrogenation of (11) over the tri-*p*-anisylphosphine complex was slower than that observed using the tri-*p*-tolylphosphine complex. The reason for this discrepancy is not clear but could be due to differences in solvent composition and/or rhodium : phosphine ratios used in this and the previous work. In any event, it is quite apparent from the (12) : (13) ratios obtained that the product stereochemistry is, indeed, dependent on the electronic character of the phosphine ligand present and, thus, this *cis* : *trans* ratio could be useful in characterizing the catalysts prepared by the reduction of (2a).

TABLE 1

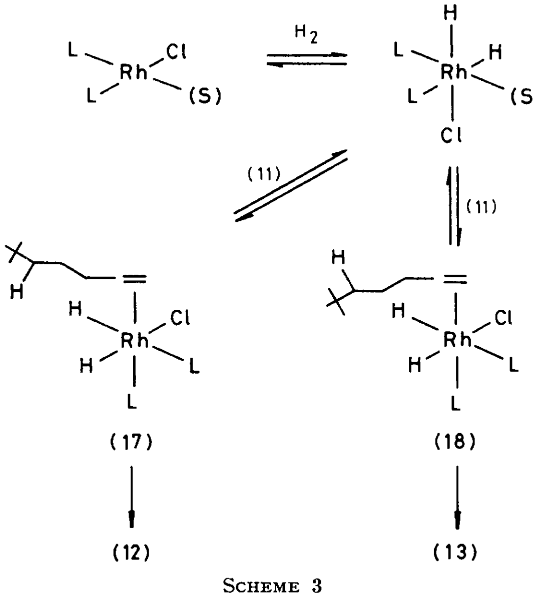
Rate and product stereochemistry data obtained from the hydrogenation of (11) with chlorobis(trisubstituted arylphosphine)rhodium complexes, [RhClL$_2$]

Aryl substituent	10^2 Rate/ s^{-1} $\pm 2\%$	*cis* : *trans* ratio ± 0.05
OMe-*p*	0.168	2.37
Me-*p*	0.210	2.24
Me-*m*	0.160	2.26
H-*p*	0.106	1.97
F-*p*	0.015	2.06
Cl-*p*	0.005 2	2.71

It is of interest that the presence of both electron-donating and electron-withdrawing groups in the arylphosphines results in an increase in the *cis* : *trans* (12) : (13) ratio obtained from the value of 2.0 : 1 observed with the unsubstituted PPh$_3$. As described by the Dewar–Chatt–Duncanson [20] model of the metal-olefin bond, an empty d^2sp^3 orbital of the dihydridorhodium complex (14) can overlap with the filled π orbital of the olefin to form a σ bond while one of the three filled d orbitals on the rhodium can overlap with the empty π^* antibonding orbital of the olefin resulting in π-bond formation. It appears that the electronic properties of PPh$_3$ are such that both these types of bonding are maximized to give a relatively stable rhodium–olefin complex. On the other hand, electron-releasing phosphines would destabilize σ-bond formation but favour the formation of π bonds, while electron-withdrawing phosphines would have the opposite effect. Thus, in either case a less-stable complex could result. If this were the case the olefin complex would be more labile thus permitting more equilibration to take place during the olefin complexation step in the hydrogenation. As depicted in Scheme 3, the complex, (17), which would give the *cis*-alkane, (12) is less hindered than that one, (18), from which the *trans* product, (13), would be formed. Thus, any factors which could affect an increase in the reversiblity of the olefin complexation step would lead to the formation of more of the *cis* product, (12), on hydrogenation of (11). This is apparently what is taking place when the ligands, L, in these complexes are arylphosphines containing either electron-donating or electron-withdrawing substituents as discussed above.

It has been generally reported that the steric effect of a *para* substituent is of little importance in hydrogenations run using substituted phenylphosphine complexes.[7] This is apparently not true for the *meta*-substituted species, although, as the data in Figure 2 show, an unusually high *cis* : *trans* product ratio was obtained with the use of the bis(tri-*m*-tolylphosphine) complex. In this case steric interactions with the olefin could result in the formation of even more of the sterically favoured olefin complex (17) than would be expected from electronic factors alone.

Compound (11) was then hydrogenated over a series of catalysts prepared by the alcohol reduction of (2a) under hydrogen in the presence of this same series of substituted arylphosphines, with the results obtained in Table 2 and Figure 2. As seen from these data the presence of an electron-donating substituent on the added phosphine ligand resulted in an increase in the *cis* : *trans*



SCHEME 3

Table 2

Rate and product stereochemistry data from the hydrogenation of (11) with the catalysts obtained on reduction of (2a) under hydrogen in the presence of a tri(substituted aryl)phosphine

Aryl substituent	10^2 Rate/ s^{-1} ±2%	*cis* : *trans* ratio obs. ±0.05	calc.*
OMe-*p*	0.136	2.24	2.29
Me-*p*	0.159	2.09	2.14
Me-*m*	0.151	2.04	2.12
H-*p*	0.106	1.95	1.97
F-*p*	0.075	1.92	1.92
Cl-*p*	0.032	2.01	1.94

* Using equation (1).

(12) : (13) product ratio similar to, but not as great as, that observed using the bis(substituted phosphine) catalysts. This diminution of the ligand effect on the *cis* : *trans* ratio seemed reasonable since, as stated previously, only one half of an equivalent of the added ligand was incorporated into the reactive species on reduction of (2a) while there are two such ligands per rhodium in the catalysts used as the reaction models. However, a simple comparison such as this is negated by the fact that electron-withdrawing groups in these mixed-ligand species exert very little effect on product stereochemistry in contrast to what is noted with the bis(ligand) complexes. A reasonable explanation of these results lies in the production of two independent species on reduction of (2a) as shown previously in Schemes 1 and 2. For the purpose of simplifying further discussion, the bis(triphenylphosphine) complex (14) will be referred to as the P_2 complex, while the mixed-ligand species (15) will be denoted as the PL material. Since the presence of electron-withdrawing ligands decrease the catalytic activity of rhodium–phosphine catalysts, when a ligand such as L is present, the hydrogenation would take place primarily on the P_2 species and, thus, this entity would make the largest contribution to the overall *cis* : *trans* product ratio. On the other hand, when L is an electron-donating ligand the catalytic activity of the PL complex would increase relative to P_2 and the PL species would make more of a contribution to the observed product ratio.

If the added ligand, L, in the mixed–ligand complex is *trans* to the olefin complexation site it would be expected to exert a maximum influence on the stability of the olefin complex.[21] Under these circumstances it would be expected that the mixed-ligand complex should exhibit essentially the same reactivity as the bis(substituted phosphine) species and, therefore, it should be possible to use the rate and product stereochemistry data obtained using the P_2 and L_2 complexes to calculate the product ratio expected from a competitive reaction between the PL and P_2 species, using equation (1).

$$(cis : trans)_{\text{calc.}} = (cis : trans)_{L_2} \times \frac{\text{Rate}_{L_2}}{\text{Rate}_{L_2} + \text{Rate}_{P_2}} + (cis : trans)_{P_2} \times \left(\frac{\text{Rate}_{P_2}}{\text{Rate}_{L_2} + \text{Rate}_{P_2}}\right) \quad (1)$$

The near identity of the calculated results with those obtained experimentally, as shown in Table 2, strengthens the conclusions arrived at previously, that is that reduction of (2a) in the presence of L gives two independent catalytically active species, (14) and (15), and, further, that the added ligand, L, in (15) is probably *trans* to the olefin complexation sites.

In an attempt to define the stereochemistry of the mixed-ligand species (15) more rigorously, (2a) was reduced in the presence of menthyldiphenylphosphine (mdpp), a chiral ligand known to be able to promote the asymmetric hydrogenation of prochiral olefins.[22] The catalyst mixture from this reduction was first used to hydrogenate (11). The resulting *cis* : *trans* ratio of 2.5 : 1 established both that the mdpp was incorporated into the catalytically active species and that the mixed-ligand entity containing the mdpp was more catalytically active than the P_2 complex, (14). This mixture was then used to hydrogenate the prochiral olefin, α-acetamidoacrylic acid. The hydrogenation took place rapidly but the product formed had an optical purity of, at most, 3—4%. If the mdpp were incorporated into the mixed-ligand catalyst *cis* to the olefin complexation site as in (19), or if this complex were a mixture of (15) and (19), one would have expected a more efficient enantioselective hydrogenation to take place.

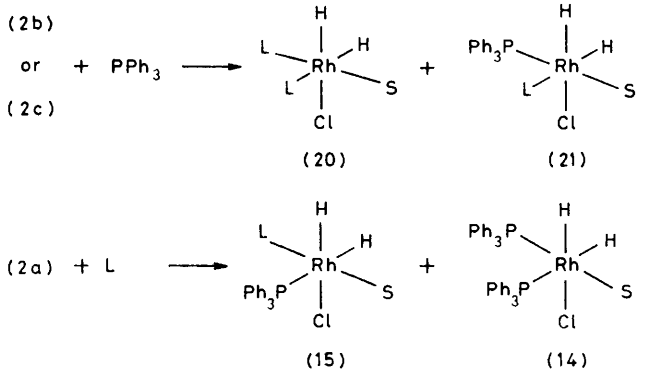
While all of these arguments favour the presence of the *trans*-L species, (15), in the catalyst mixture, they are not unambiguous and do not unequivocally rule out the presence of a mixture of (15) and (19) with the hydrogenation taking place primarily on the *trans*-substituted species, (15). This latter consideration can be removed, however, by examining the results obtained using rhodium–dioxygen complexes having ligands other than PPh_3. The oxide complexes containing both tri-*p*-anisylphosphine (2b) and tri-*p*-chlorophenylphosphine (2c) were readily prepared from the corresponding chlorotris(triarylphosphine)rhodium complexes by oxygenation in dry benzene. Complexes (2b) and (2c) were reduced in benzene–ethanol under a hydrogen atmosphere in the presence of PPh_3 and the resulting mixtures were used for the hydrogenation of (11). The rate of hydrogen uptake and the *cis* : *trans* ratios obtained from these hydrogenations are listed in Table 3 together with the corresponding results found on hydrogenation of (11) using the catalyst mixtures obtained by the reduction of (2a) in the presence of $P(C_6H_4OMe\text{-}p)_3$ and $P(C_6H_4Cl\text{-}p)_3$. As seen from these data, the results found on use of reduced (2b) and PPh_3 are essentially the same as those

Table 3

Rate and product stereochemistry data from the hydrogenation of (11) with catalysts obtained on reduction of complexes (2) under hydrogen

Catalysts prepared from:	10^2 Rate/ s^{-1} ±2%	*cis* : *trans* ratio ±0.05
(2b) $+PPh_3$	0.141	2.19
(2a) $+P(C_6H_4OMe\text{-}p)_3$	0.136	2.24
(2c) $+PPh_3$	0.030	2.01
(2a) $+P(C_6H_4Cl\text{-}p)_3$	0.032	2.01

obtained from reduced (2a) and $P(C_6H_4OMe\text{-}p)_3$. In addition, data from the use of reduced (2c) and PPh_3 were the same as those from reduced (2a) and $P(C_6H_4Cl\text{-}p)_3$. These results are readily explained by the presence in the reduction mixture of only two species; the P_2 (14) or L_2 (20) and the PL (15) or LP (21), with the added ligand in the latter incorporated *trans* to the olefin complexation site as depicted in Scheme 4. The reduction of (2b) in the presence of PPh_3 gives two bis(phosphine) complexes, in one of which [(20)] the phosphine $P(C_6H_4OMe\text{-}p)_3$ is *trans* to the olefin site and in the other [(21)] the phosphine PPh_3 occupies this *trans* position. Since the rate of hydrogen uptake and product stereochemistry should be determined most strongly by the ligand occupying the position *trans* to the olefin,[21] the data obtained from this mixture and that found from the mixture resulting from the reduction of (2a) in the presence of $P(C_6H_4OMe\text{-}p)_3$ should be identical since in both cases one of the bis(phosphines) has $P(C_6H_4OMe\text{-}p)$, as the *trans* ligand [(20) and (15)] while in the other the *trans* ligand is PPh_3 [(21) and (14)]. On the other hand, if (15) and (21) were mixtures of the *cis* and *trans* isomers there would be more of PPh_3 in the *trans* position in the mixture obtained on reduction of (2a) in the presence of $P(C_6H_4OMe\text{-}p)_3$, and there would be more $P(C_6H_4OMe\text{-}p)_3$ in the *trans* position in the reduction mixture from (2b) and PPh_3. Then, while the *cis* : *trans* ratios might still be the same for both mixtures, the latter mixture would react faster than the former resulting in non-identical hydrogenation rates. Since this was not observed, mixtures of the *cis* and *trans* isomers such as (15) and (19) must not be present. The identity of the rate and stereochemistry data obtained from both the reduction of (2c) in the presence of PPh_3 and from (2a) in the presence of $P(C_6H_4Cl\text{-}p)_3$ further substantiates this conclusion.



SCHEME 4 L = $p(C_6H_4OMe\text{-}p)_3$ or $p(C_6H_4Cl\text{-}p)_3$; S = olefin complexation site

It can be said, then, that the alcohol reduction of (2a) in the presence of ligands other than PPh_3 represents a good method for the preparation of mixed-ligand rhodium complexes which are effective homogeneous hydrogenation catalysts. When this reduction is carried out under hydrogen the incorporation of this added ligand occurs stereospecifically at that position *trans* to the site of olefin co-ordination. Unfortunately, the mixed-ligand species is formed together with an equal amount of the bis(triphenylphosphine) complex, (14), a factor which diminishes the general utility of this approach for the preparation of isolated mixed-ligand catalysts.

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