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SOLUTION STUDIES OF THE ASYMMETRIC HYDROGENATION CATALYST SYSTEM DERIVED FROM THE [RHODIUM (1,2-BIS(DIPHENYLPHOSPHINO)-1-CYCLOHEXYLETHANE)] MOIETY

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Summary

A solution ^{31}P NMR study of the asymmetric hydrogenation catalyst derived from the [rhodium(1,2-bis(diphenylphosphino)-1-cyclohexylethane)] system was initiated to gain further insight into the solution chemistry of this catalyst. In polar, weakly coordinating solvents, the solution behavior is similar to that of previously studied hydrogenation catalysts. However, since this ligand imparts enhanced solubilities to the cationic rhodium complexes, it was possible to study the catalytic intermediates in non-donor solvents such as CH_2Cl_2. When the catalyst precursor complex [Rh(norbornadiene)-(Cycphos)] (PF_6) is hydrogenated in CH_2Cl_2, a dimeric structure results. The ^{31}P NMR of this complex formed in CD_2Cl_2 is complex and is interpreted as a mixture of different isomeric dimeric complexes. When the dimeric complex [Rh(Cycphos)]$_2$(PF_6)$_2$ is isolated as a crystalline solid and redissolved in CD_2Cl_2, the resultant ^{31}P NMR spectrum is unusual. The spectrum is interpreted as arising from a single dimeric isomer showing novel long-range, non-bonded Rh—P couplings. This result and its implications to the mechanism of action of these chiral catalysts is discussed.

Introduction

We recently published observations [1] showing the ability of the cationic precursor rhodium complex [Rh(Cycphos)(norbornadiene)]$^+$ derived from the chiral phosphine, (*R*)-1,2-bis(diphenylphosphino)-1-cyclohexylethane (Cycphos, Structure 1b), to function as a superior asymmetric hydrogenation catalyst. A solution NMR study of this catalyst system was initiated to gain futher insight into its solution chemistry and to compare its solution behavior to similar catalysts derived from chelate ring-substituted phosphines derived from 1,2-

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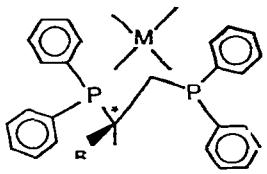


R = CH_3 Ia
R = cyclohexyl Ib
R = phenyl Ic

Fig. 1. Known chelate ring substituted chiral phosphines are shown coordinated to rhodium in their more stable equatorial conformation.

bis(diphenylphosphino)ethane; e.g., (*R*)-Prophos [2] and (*R*)-Phenphos (Fig. 1) [3,4].

The cyclohexyl substituted phosphine (1b) rhodium complexes are particularly well suited for solution study since the cyclohexyl derivative is more soluble than the parent [Rh(diphos)]$^+$ system. In fact, the [Rh(Cycphos)(NBD)]X (where X = PF_6^-, BF_4^-) complexes are even very soluble in such non-polar solvents as ethyl acetate or dichloromethane. Indeed, these solvents were found to be suitable for achieving high optical yields with the [Rh(Cycphos)]$^+$ catalyst system. In many instances, the use of dichloromethane as the solvent gave higher optical yields and faster rates than alcoholic solvents. This trend was observed for the more sterically encumbered olefins that exhibit slow hydrogenation rates in donor solvents. In addition, the tetrasubstituted olefin β,β-dimethyl-α-benzamidoacrylic acid can be reduced in 35—45% enantiomeric excess in donor solvents, but in dichloromethane the optical yield under the same conditions is 70% [1].

When these cationic [Rh(diene)(bidentate phosphine)]$^+$ complexes are exposed to hydrogen in solution, two moles of hydrogen are taken up per mole of rhodium to afford the totally reduced diene [5]. In donor solvents these complexes do not add a third mole of hydrogen, but form the cationic *cis*-[Rh(I) bis(solvated)(diphosphine)]$^+$ complex [5,6]. A material has been isolated from methanolic solutions of the solvated [Rh(diphos)]$^+$ complex. It has been characterized in the solid state as a dimer containing two bridging arenes $[Rh_2(Diphos)_2]^{2+}$ (analogous to the structure in Fig. 3, with the cyclohexyls replaced by hydrogens) [5]. However, it has never been characterized in solution due to its insolubility in non-donor solvents. Thus, a major purpose of this work was to elucidate the solution chemistry of the Rh(Cycphos) based catalyst system both in a non-donor solvent, such as dichloromethane, and in methanol. In particular, we wanted to gain an understanding of the solution chemistry pertinant to the catalytic situation in non-donor solvents; e.g., are hydride intermediates formed in the catalytic reductions using non-donor solvents or are other non-hydridic species present in solution such as π-arene-bridged dimers?

Results and discussion

The ^{31}P NMR spectrum of the starting precursor complex [Rh(Cycphos)-(NBD)]PF_6 was obtained in both dichloromethane and methanol. It was found to be solvent independent and to show the expected eight-line pattern that is consistent with two non-equivalent phosphorus atoms coupled to rhodium (see

TABLE 1

^{31}P NMR PARAMETERS FOR THE Rh(diphosphine) COMPLEXES [a]

Complex	δ Chemical Shifts, (ppm) [coupling constants, J(Rh—P) (Hz)]
[Rh((*R*)-Prophos)(NBD)]$^+$ 6	60.5(172), 41.8(139) [J(P—P) 34]
[Rh((*R*)-Phenphos)(NBD)]$^+$ 7	70.6(158), 43.9(154) [J(P—P) 37]
[Rh((*R*)-Cycphos)(NBD)]$^+$	60.7(156), 43.0(156) [J(P—P) 36]
[Rh((*R*)-Cycphos)(MeOH)$_2$]$^+$	89.0(203), 68.0(203) [J(P—P) 56]
[Rh((*R*)-Cycphos)(η^6-toluene)]$^+$	86.1(203), 66.8(200) [J(P—P) 44]
[Rh((*R*)-Cycphos)]$_2^{2+}$ $(PF_6)_2$	δP_1 = 79.5 [J(Rh$_1$—P$_1$) 199] δP_2 = 65.0 [J(Rh$_1$—P$_2$) 213] δP_3 = 60.9 [J(Rh$_2$—P$_3$) 211] δP_4 = 84.3 [J(Rh$_2$—P$_4$) 191] [J(P$_1$—P$_2$) = J(P$_3$—P$_4$) 44] [J(Rh$_1$—P$_3$) = J(Rh$_2$—P$_2$) 11]
[Rh((*R*)-Cycphos)((*Z*)-ethyl-α-benzamidocinnamate)]$^+$	δP_1 = 43.8(165), δP_4 = 77.8(156) δP_2 = 63.0(153), δP_3 = 67.3 (159) [J(P$_1$—P$_4$) = J(P$_2$—P$_3$) = 47]

[a] Chemical shifts with respect to external H_3PO_4; downfield shifts positive. The spectra of each of these compounds were also determined at 121.5 MHz on a Bruker CXP-300 spectrometer. The higher field supports all the assigned coupling constants.

Table 1). Furthermore, the spectrum was very similar to those reported for the [Rh(phosphine)(NBD)]$^+$ complexes of (*R*)-prophos [6] and (*R*)-phenphos [4, 7]. In fact, comparison to these spectra made it possible to assign the phosphorus atom adjacent to the substituted methylene carbon as the downfield resonance. This assignment appears valid since each complex has one phosphorus resonance near δ 43 ppm that is insensitive to the substituted *R*-group (Table 1).

The subsequent solution studies in both methanol and dichloromethane utilized the air-sensitive yellow product obtained by hydrogenating, in either dichloromethane or methanol, the starting norbornadiene complex, Rh[Cycphos)(NBD)]PF_6. This material, isolated as either the PF_6^- or the BF_4^- salts, contained no solvent or metal hydride (via NMR). Elemental analysis supports the empirical formulation as [Rh(Cycphos)]$^+$ X^-. Based on earlier work done on the diphos system [5], we presume that in the solid state this complex is a dimer in which each rhodium atom is bonded to the two phosphorus atoms of the cycphos ligand and also through symmetrical π-arene coordination to a phenyl ring of the cycphos ligand on the second rhodium atom (Fig. 3).

Of primary importance in this work was the study and characterization of the solution species obtained in non-donor and donor solvents. For example, the active catalyst complex [5] generated by hydrogenating the [Rh(Cycphos)-(NBD)]$^+$ precursor complex in the absence of an olefin substrate exhibits solvent dependent ^{31}P NMR spectra. In dilute methanol solution ([Rh] 0.01 *M*), there is observed a single species as revealed by the eight line pattern in the ^{31}P

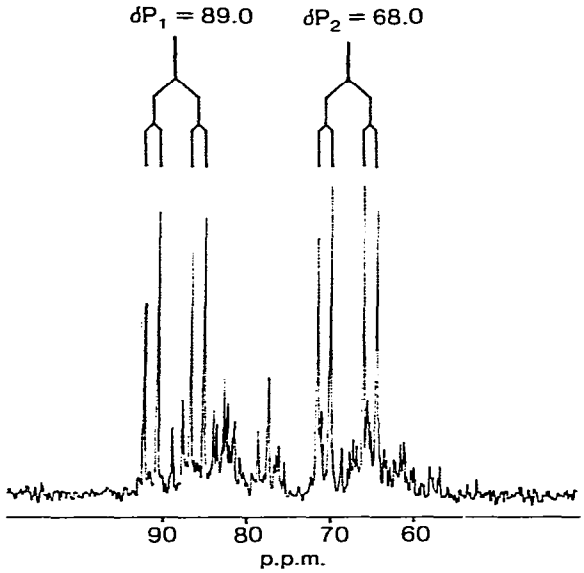


Fig. 2a. ^{31}P NMR spectrum of a 0.1 *M* solution of [Rh(Cycphos)]$_2$(BF$_4$)$_2$ in MeOH-d_4 obtained at 36.2 MHz.

NMR (see Table 1 for assignments). In more concentrated solution ([Rh] 0.1 *M*) other resonances (Fig. 2a) are apparent. This observation is consistent with the presence of a solvated monomeric [Rh(Phosphine)(MeOH)$_2$]$^+$ species at low concentrations, as has been demonstrated previously for [Rh(diphosphine)]$^+$ solutions in alcoholic solvents [4—6]. At higher concentrations, dimeric (oligomeric) complexes (stereoisomers) form, in which the bridging units are either π-arene bridges or solvent molecules as postulated by Brown et al. [4]. Our evidence suggests that the additional resonances, observable in concentrated solutions, are due to π-arene bridged species, and is discussed below.

In contrast, in dichloromethane solution the slow hydrogenation of the [Rh(Cycphos)(NBD)]$^+$ precursor complex results in a very much different solution chemistry than was obtained in methanol. Both the solution ^{31}P NMR spectra (discussion below) and the electronic spectra in dichloromethane (no visible bands) are much different from those observed in methanol. Thus, it was important to determine if dimeric π-arene bridged species (previously observed in the solid state [5]) are generated and present in dichloromethane solution or if monomeric complexes or higher molecular weight oligomeric species are present.

Since these solutions are very air-sensitive, a variable concentration conductance study was carried out in an inert atmosphere glove-box. Dichloromethane solutions of the material isolated previously from methanol [Rh((*R*)-Cycphos)]$_n$(PF$_6$)$_n$ (see Experimental), and of [Rh(Cycphos)(NBD)](PF$_6$) hydrogenated directly in dichloromethane were utilized for these studies. Conductances for both systems are measured at several concentrations. A plot of the equivalent conductance (Λ_e) versus the square root of the equivalent concentration (c_e) was linear over the concentration range of 10^{-4} to 5.0×10^{-3} eq/l

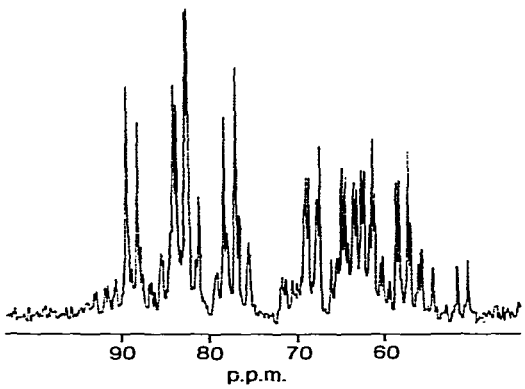


Fig. 2b. ^{31}P NMR spectrum of 0.02 *M* solution of $[Rh(Cycphos)_2(PF_6)_2$ in CD_2Cl_2 obtained at 36.2 MHz.

for both systems. These results indicate that the molecularity of the species is constant in both systems; consequently, there must be only one oligomeric species in solution [9,10]. Further, the slope of the straight-line plot of the equivalent conductance at infinite dilution minus the measured equivalent conductance at a known concentration versus the square root of the equivalent concentration, $(\Lambda_o - \Lambda_e)/\sqrt{c_e}$, gave values very close to those obtained with a standard 2/1 electrolyte in dichloromethane. These conductance studies show that a dimeric two-to-one electrolyte species is indeed present in dichloromethane. This result confirms that dimeric complexes are generated in dichloromethane and are stable in such non-donor solvents.

In dichloromethane ([Rh] 0.02 *M*) the solution ^{31}P spectrum (Fig. 2b) of the dimeric complex (generated in situ from [Rh(NBD)(Cycphos)](PF_6) is dramatically different from that in methanol. It is very complex, showing at least seventy lines (Fig. 2b). This spectrum is virtually identical to that obtained by dissolving the complex $[Rh(R)\text{-Cycphos})]_2$ $(PF_6)_2$, (previously precipitated from methanol with diethyl ether) in CD_2Cl_2. The spectra are unchanged in the range [Rh] 0.01—0.09 *M* indicating, as expected, that no concentration dependent equilibria are present. Further, since no hydride resonances are observed upfield in the ^1H NMR spectrum and since the methanol solvate spectrum is regenerated when methanol is added to the CD_2Cl_2 solution (as monitored by UV-VIS spectra and ^{31}P NMR), an *ortho*-metalated rhodium (III) species or a complex formed by oxidative addition of the dichloromethane solvent can be discounted.

These ^{31}P NMR results and the complex nature of this spectrum are consistent with the π-arene bridged dimer structure being maintained in the non-donor solvent dichloromethane [11]. In fact, the formation of a phenyl bridged dimer of the sort expected from the diphos analogy would generate three basic structural isomers which could give rise to as many as twelve unique diastereomeric complexes. The structural variations arise due to the complexity introduced by the asymmetric substitution on the chelate ring which generates four nonequivalent phenyl rings about each rhodium. If each possible structure were present, several hundred lines would be expected.

Additional support for the presence of the $[Rh(Cycphos)]_2(PF_6)_2$ dimer in dichloromethane is found in the ^1H NMR spectrum of this complex in CD_2Cl_2. At both 60 and 300 MHz a very complex aromatic region is present with phenyl protons shifted upfield to δ 5.25. For comparison, the starting [Rh(Cycphos)(NBD)] (PF_6) complex in CD_2Cl_2 shows a singlet at δ 7.5 corresponding to the phenyl protons. The presence of the very complex aromatic pattern supports the contention that the integrity of the π-phenyl bridged dimeric structure is present in solution in such solvents as dichloromethane [11]. This view is further supported by the fact that the electronic spectrum of the dimeric solid is identical to its dichloromethane solution spectrum; namely, no visible band maxima are present. This is contrary to what is observed for the solvated complex $[Rh(Cycphos)(MeOH)_2]^+$ where a prominent visible band exists at 435 nm (ϵ = 1080).

If the complex $[Rh(R)\text{-Cycphos})]_2(PF_6)_2$ is allowed to crystallize slowly out of methanol over a period of several weeks, a single crystalline dimeric product can be isolated having the same elemental analysis as the starting material. The ^{31}P NMR spectrum (Fig. 2c) obtained when these crystals are dissolved in CD_2Cl_2 is much less complex than the spectra obtained by generating the dimer directly in CD_2Cl_2 or by dissolving in CD_2Cl_2 the dimer bis hexafluorophosphate salt (previously obtained by adding diethyl ether to a methanol solution of the complex, thus precipitating the dimer). This ^{31}P NMR spectrum (Fig. 2c) shows a symmetrical twenty-four line pattern.

Attempts to assign this ^{31}P NMR spectrum assuming a mixture of different dimeric isomers were unsuccessful. Such interpretations require that either two dimeric species are present in a one-to-one ratio (one species gives rise to eight lines and the other to sixteen lines) or three dimeric species are present in a two-one-one ratio. An added constraint is that the dimeric complexes are built-up by π-arene bridges. Further, only three basic structural types would be expected. One symmetric structure could have each cyclohexyl substituent adjacent to the bridging diphenylphosphine, the other symmetric isomer would have each cyclohexyl adjacent to the non-bridging or terminal diphenyl phosphines, and the third structure would have the dissymmetric placement of cyclohexyl substituents shown in Fig. 3.

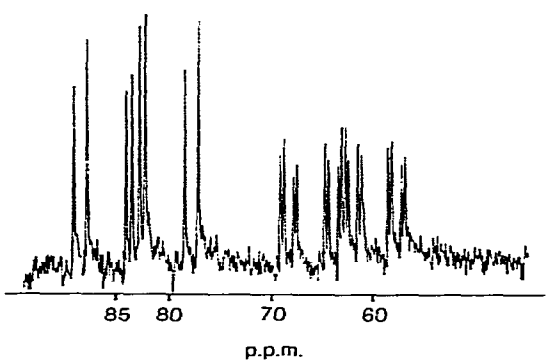


Fig. 2c. ^{31}P NMR spectrum of $[Rh((R)\text{-Cycphos})]_2(PF_6)_2$ in CD_2Cl_2 from the crystalline source obtained at 36.2 MHz.

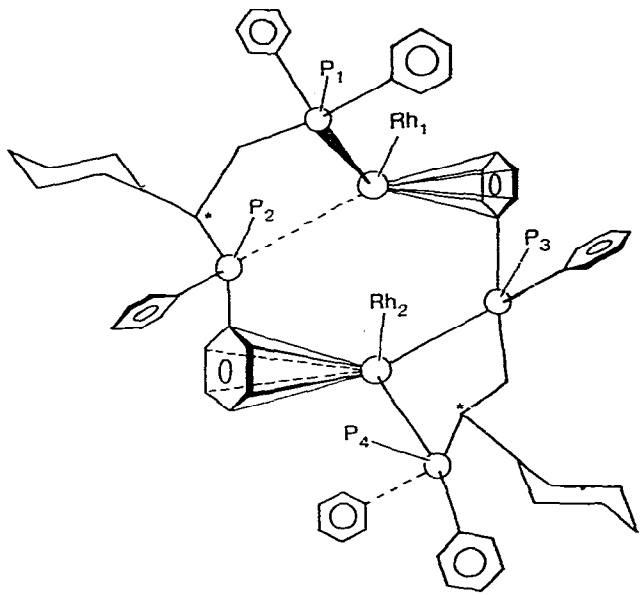


Fig. 3. Proposed structure of the unique dimeric unit $[Rh((R)\text{-Cycphos})]_2(PF_6)_2$ whose ^{31}P NMR spectrum is shown in Fig. 2c.

Each combination of such structures were considered during our attempts to interpret this unusual ^{31}P NMR (Fig. 2c). A mixture of two symmetric isomers was ruled out since only sixteen lines would be predicted. The number of observed lines could still be explained as a mixture of two species, either symmetric dimer giving rise to the eight-line pattern at 80—90 ppm and the dissymmetric dimer (Fig. 3) giving rise to the sixteen line pattern at 60—70 ppm. This interpretation based on a mixture of two species is not consistent with either our knowledge of the chemical shifts of diphenylphosphine groups bonded to rhodium or, even more importantly, the observed intensity pattern and chemical shift positions. Further, since the dissymmetric dimer contains at least one $[Rh((R)\text{-Cycphos})]^+$ unit that would be virtually chemically equivalent to the $[Rh((R)\text{-Cycphos})]^+$ units of each symmetrical dimer, a much simpler spectrum would be expected, certainly not a spectrum in which all the phosphine resonances for the dissymmetric dimer occur at 60—70 ppm and those for a symmetric dimer occur at 80—90 ppm. Finally, a mixture of three species can be ruled out, since either a sixteen or a thirty-two line spectrum would be expected.

Consequently, an attempt was made to interpret this single crystal derived spectrum on the basis of only one isomer. Assuming there is one isomer, a structure such as is shown in Fig. 3 could give the observed spectrum. This structure would give rise to four chemically and magnetically nonequivalent phosphorus atoms owing to the dissymmetric placement of the cyclohexyl substituents. The ^{31}P NMR spectrum is then the ABCD portion of a six-spin ABCDXY system.

The presence of an observable coupling between a rhodium atom and the phosphorus atom bearing the phenyl group π-bonded to that rhodium accounts

for the unusual twenty-four line observed spectrum. Since the phosphorus atoms that contain the bridging π-phenyl group are close to the second nonbonded rhodium atom in the dimer and since there are also only two bonds separating these two $I = 1/2$ nuclei, it seems likely they would couple. From the spectrum this coupling $J(\mathrm{Rh(1)—P(3)}) = J(\mathrm{Rh(2)—P(2)})$ is determined to be 11 Hz. This represents to our knowledge the first observation of such a coupling between a coordinated phosphine and an adjacent nonbonded metal atom in a molecule.

Computer simulations were carried out using the Bruker PANIC program. These studies confirmed that a unique combination of coupling constants and chemical shifts would give the observed pattern complete with the observed subtle intensity differences. As a consequence, they provide strong support for this unique assignment. For a six-spin system using combinations of coupling constants extracted from the spectrum shown in Fig. 2c, one set of unique assignments gave a best fit for the observed spectrum. All other combinations gave either too many lines or incorrect line intensities. This best fit required that a J(Rh—Rh) 5 Hz be included to give the observed intensity pattern. The chemical shifts and coupling constants that gave the best fit spectrum (shown in Fig. 4) are given in Table 1. The chemical shift of the phosphorus atoms bonded to π-arene bridges are further upfield from the chemical shift for the terminal diphenyl-substituted phosphorus atoms. Finally, these assignments require that the resonance due to the phosphorus atom bonded to the cyclohexyl-substituted methylene carbon atom occur further downfield from the signal due to the phosphorus adjacent to the unsubstituted carbon. This was

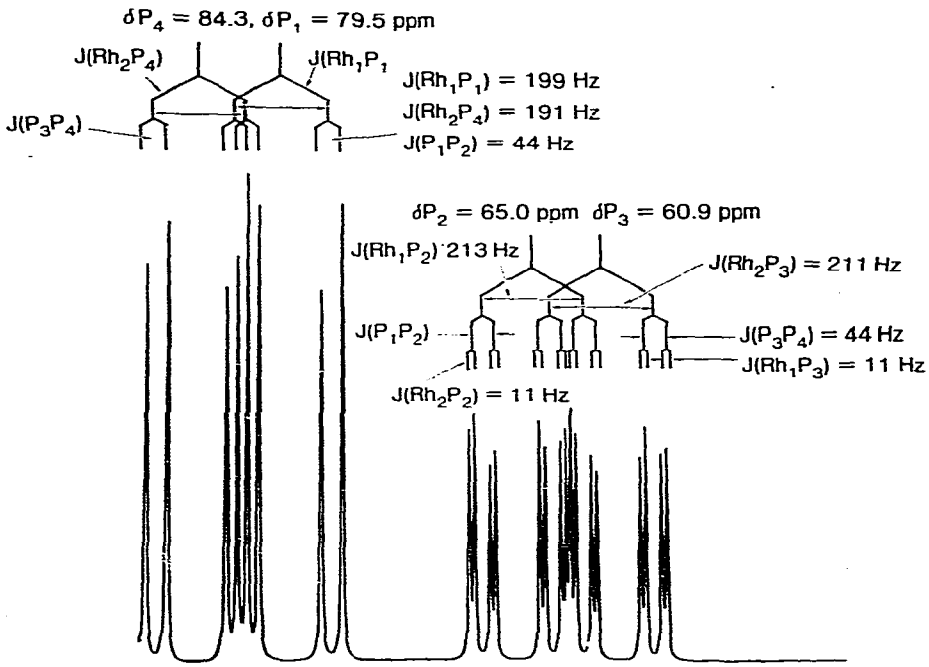


Fig. 4. Best fit computer simulated ^{31}P NMR spectrum for the $[\mathrm{Rh((}R\mathrm{)\text{-}Cycphos)}]_2(PF_6)_2$ dimer.

also stipulated above for the [Rh(*R*)-(Cycphos)(NBD)]$^+$ complex.

There is also one other possible explanation of the observed twenty-four line ^{31}P NMR pattern. This requires that the two symmetric isomers be present in a fortuitous one-to-one ratio. This still requires the existence of an observable coupling of 11 Hz between the rhodium atom and the adjacent π-arene bridged phosphorus atom. Under such circumstances a twenty-four line ^{31}P NMR spectrum would again result. While it is not possible to absolutely preclude this interpretation, the computer simulation studies strongly support the single dissymmetric isomer interpretation. Since the spin simulation program assumed one isomer and gave such excellent agreement with the observed pattern, complete with the observed subtle intensities, it is assumed that the spectrum arises from a single isomer of the type shown in Fig. 3.

The toluene complex [Rh(Cycphos)(toluene)](PF_6) was synthesized as a model for the π-phenyl bridged dimer. It was characterized independently as the η^6-π-bonded complex by analogy to other compounds of this type [12, 13]. The ^{31}P NMR spectra of this complex in CD_2Cl_2 and methanol-d_4 are identical to one another and to the spectra generated when toluene is added to the [Rh(Cycphos)]$_2$(PF_6)$_2$ complex dissolved in methanol-d_4 or CD_2Cl_2. All three show the expected eight line spectrum of a single species (Table 1). The chemical shifts for these two types of phosphorus atoms are similar to those observed for the complex [Rh(Cycphos)]$_2$(PF_6)$_2$ dissolved in CD_2Cl_2. The magnitude of the rhodium—phosphorus coupling constants (200 Hz) agrees well with those proposed for the π-arene bridged dimer. Also, the observed phosphorus—phosphorus coupling constant (44 Hz) is identical to that observed for the dimer. These facts further support the ^{31}P NMR assignments for the π-phenyl bridged dimer in CD_2Cl_2 solution. Since the addition of toluene to the dichloromethane solution of the dimeric complex, [Rh(Cycphos)]$_2$(PF_6)$_2$, slowly generates the π-bonded toluene adduct, it is also again reasonable to conclude that neither *ortho*-metalation nor oxidative addition of solvent to the rhodium center is occurring.

Plausible structures of the compounds that give the new peaks which appear in the ^{31}P NMR spectrum of the concentrated methanol solutions of [Rh(Cycphos)]$_2$(PF_6)$_2$ can now be assigned. The new peaks that appear in methanol correspond very closely with the major peaks observed for the dimers in CD_2Cl_2. This and the fact that crystals of the dimer can be obtained from methanolic solutions of [Rh(Cycphos)]$_2$(PF_6)$_2$ support the assignment of the additional minor species to be simply the dimeric π-arene bridged dimers, not solvent bridged dimers [4].

The addition of *Z*-substituted α-amide acrylic acids (esters), from the class of suitable prochiral asymmetric hydrogenation substrates, to either dichloromethane or methanol solutions of [Rh(Cycphos)]$_2$(PF_6)$_2$ results in the formation of olefinic adducts [14], whose ^{31}P NMR spectra are identical in either solvent. This substitution was done with a number of prochiral olefins and in all cases similar behavior was noted. The ^{31}P NMR spectrum of the complex formed when *Z*-ethyl α-benzamidocinnamate was added to solutions of the [Rh(Cycphos)]$_2$(PF_6)$_2$ is shown in Fig. 5. This sixteen line pattern is consistent with the presence of two regioisomers in the ratio of approximately two to one (see Table 1 for assignments). This spectrum is very similar to that

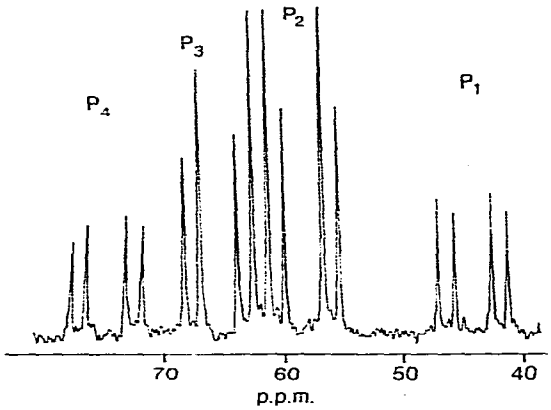
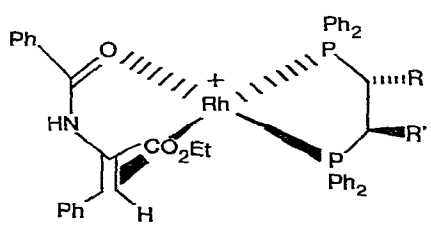


Fig. 5. ^{31}P NMR spectrum (obtained at 36.2 MHz) of the complex [Rh(Cycphos)((Z)-ethyl-α-benzamidocinnamate)] PF_6 in methanol shows the presence of two isomeric complexes.

obtained by Brown et al. [4], for the *Z*-methyl α-acetamido cinnamate complex with the Phenphos (Ib) complex, [Rh(Phenphos)(methyl α-acetamidocinnamate)]$^+$, in methanol. The two stable enamide complexes formed are likely to be the regioisomers shown in Fig. 6, structurally analogous to those reported by Brown et al. [4]. But the structures differ from those of reference 4 in that the opposite stereoisomers are shown. This assignment is based on recent results of Halpern et al., which show that the stable enamide complex detected in solution is the unexpected isomer; namely, the isomer in which *cis* addition of hydrogen from the metal side would yield the opposite isomer product from that actually generated from a hydrogenation [15].

The chemistry of the dimeric π-arene bridged species in a non-donor solvent such as dichloromethane is in many respects strikingly different from that observed for the dissociated [Rh(diphosphine)(Solv.)$_2$]$^+$ complexes in solvents such as methanol. The dimer complex is much more inert to substitution at room temperature with donor olefins and also chemically more inert. For example, the dimer in dichloromethane does not react with an added proton (from a source such as *p*-toluenesulfonic acid or trifluoromethanesulfonic acid).



Major Isomer: R = C_6H_{11}, R' = H
Minor Isomer: R = H, R' = C_6H_{11}

Fig. 6. Structure of the two predicted coordinated enamide complex regioisomers.

This is in marked contrast to the [Rh(diphosphine)(Solv.)$_2$]$^+$ species in alcoholic solvents [10].

The enamide complexes form very rapidly when [Rh(Cycphos)]$_2$(PF$_6$)$_2$ is dissolved in methanol solution containing the olefin, but form slowly when the dimer is dissolved in dichloromethane solutions containing the olefin (reaction times are on the order of hours at room temperature). This is consistent with maintenance of the dimeric unit in dichloromethane, but it also indicates that the dimer would play little role, if any, in the catalytic hydrogenation cycle, where the observed hydrogenation rates are as high in dichloromethane as in methanol. Since the prochiral olefin is usually present in large excess over the catalyst, the enamide complex would form directly in dichloromethane with no competition from either solvent adduct or dimer formation during a catalytic reduction.

Conclusion

This study has shown that the solution chemistry of the [Rh((*R*)-Cycphos)]$^+$ based system is similar to that of other previously reported chelating diphosphine rhodium catalyst systems in a donor solvent, such as methanol. But our extension of such solution studies to the non-donor solvent, dichloromethane, has shown that a different solution chemistry results. Indeed, we have shown that dimeric π-arene bridged complexes exist in the non-donor solvent dichloromethane, and further that such dimers are very likely present in low levels in a donor solvent, such as methanol. An important part of this work is the observation in the solution ^{31}P NMR spectrum of a mixture of diastereomeric π-arene bridged dimers. In addition, the observation of an unusual twenty-four line ^{31}P NMR spectrum is shown to most likely arise from a single π-arene bridged species. A most unique aspect of this spectrum is the presence of an observable coupling of 11 Hz between one rhodium atom and an adjacent non-bonded π-arene bridged phosphorus atom of the dimer.

Experimental

A. Instrumentation

All electronic spectra were recorded on a Cary 14 recording spectrophotometer. All ^{1}H NMR spectra were recorded on a Bruker CXP-300 or Varian T-60 spectrometer and ^{31}P NMR were recorded both on a Jeol FX-90Q and the Bruker CXP-300 spectrometer. All ^{31}P chemical shifts are reported relative to external H_3PO_4, with downfield shifts positive. Electrical conductance was measured with an Industrial Instruments Model RC-16B conductivity bridge using a dip-type cell with a cell conductance of 1.0.

B. Conductance studies

Standard electrolytes were used for the calibration of both 1/1 electrolytes and 2/1 electrolytes in dichloromethane for the conductance studies. For a 1/1 electrolyte tetrabutylammonium tetrafluoroborate was chosen and used as supplied from Aldrich Chem. Co. For a 2/1 electrolyte that would be soluble in CH_2Cl_2, 1,2-Ethylenebis(triphenylphosphonium) bis-tetrafluoroborate was used. The bis-tetrafluoroborate salt was prepared by reacted the dibromide salt

(supplied by Strem Chem. Co.) with two equivalents of $AgBF_4$ in methanol. After filtration of the precipitated AgBr, colorless needles of the bis-tetrafluoroborate crystallized from the cold methanol. This material was then characterized by ^{31}P and ^{1}H NMR and by elemental analysis as the desired diposition cation bis-tetrafluoroborate salt.

Variable concentration conductance studies are necessary to distinguish between a monomeric complex [M(L)]X and the corresponding bi-univalent dimer $[M_2(L)_2]X_2$ [9,10]. According to the Onsager limiting law $\Lambda_o - \Lambda_e = A\sqrt{c_e}$, the equivalent conductance (Λ_e) varies linearly with $\sqrt{c_e}$ (c_e is the equivalent concentration). The slope of this plot (A) can be calculated using an experimentally determined Λ_e and Λ_o. From our studies in dichloromethane, for a 1/1 electrolyte A = 137 and Λ_o = 24 mhos. (a single concentration value was reported for Λ_m = 20 mhos in ref. 17). No variable concentration conductance studies could be found in the literature for dichloromethane solvent. The bi-univalent salt 1,2-ethylenebis(triphenylphosphonium) bis-tetrafluoroborate was soluble and demonstrated linear behavior according to the Onsager Law and was used as the reference. For this bi-univalent salt it was experimentally found that A = 460 and Λ_o = 30. For the complexes $[Rh(Cycphos)]_n(PF_6)_n$ generated in CH_2Cl_2 and isolated from methanol, plots of Λ_e vs. $\sqrt{c_e}$ gave linear agreement to Onsager's Law. For the complex isolated from methanol Λ_o = 29.4 and A = 451 and for the in situ generated complex Λ_o = 31.1 and A = 474.

Materials

[Rh((R)-Cycphos)(norbornadiene)](PF$_6$). This synthesis has been reported elsewhere [1].

[Rh((R)-Cycphos)]$_2$(PF$_6$)$_2$. This air-sensitive complex was prepared by dissolving 1 g of [Rh(Cycphos)(NBD)]PF_6 in 50 ml degassed MeOH. This solution was shaken under hydrogen until all uptake of H_2 ceased (on a manometer reactor two mol H_2 were consumed per mol Rh). The MeOH solvent was then removed by vacuum and the oily yellow residue was dissolved in a minimum volume of hot methanol. While still hot, diethyl ether was added to the cloud point. After cooling and standing undisturbed for 24 h, a yellow precipitate resulted. The precipitate was collected via filtration, washed with Et_2O, and dried in vacuo at 40°C for 40 h. The yield was 0.7 g, 80%, based on the starting complex. Anal. Found: C, 52.34; H, 4.87; P, 12.43. $C_{32}H_{34}F_6P_3Rh$ calcd.: C, 52.76; H, 4.70; P, 12.76%. $^{max}\lambda_{MeOH}$ 435 nm (ϵ = 1080).

[Rh((R)-Cycphos)(toluene)]PF$_6$. To a methanol solution, under N_2, containing 1.0 g of the previously synthesized dimer, $[Rh((R)\text{-Cycphos})]_2(PF_6)_2$, was added one ml of toluene. The solution was evaporated slowly under vacuum until the volume of solution was about 10 ml. The solution was then warmed and diethyl ether added until the solution became cloudy. After cooling for 24 h, a pale yellow precipitate formed and was collected via filtration and dried in vacuo for 24 h at 40° C. The yield was 0.7 g (63%). Anal. Found: C, 57.32; H, 5.29; P, 11.01. $C_{39}H_{42}F_6P_3Rh$ calcd.: C, 57.08; H, 5.16; P, 11.32%. No absorption bands are present in the visible region.

[Rh(R)-Cycphos)(Z-ethyl-benzamidocinnamate)](PF$_6$). A 0.5 g sample of $[Rh_2(R)\text{-Cycphos})_2](PF_6)_2$ and 0.2 g of *Z*-ethyl-benzemidocinnamate were dis-

solved together in 25 ml warm methanol under N_2. To the red solution was added Et_2O until the solution turned cloudy. After cooling and standing for a day, a deep red precipitate formed which was collected via filtration and dried in vacuo for 24 h at 40°C. The yield was 0.45 g (65%). Anal. Found: C, 58.28; H, 5.19; P, 8.81. $C_{50}H_{51}F_6NO_3P_3Rh$ calcd.: C, 58.66; H, 5.02; P, 9.08%. $^{max}\lambda_{MeOH}$ 483 nm (ϵ = 1470).

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