structural types lies only in the position of the projection of the two monodentate ligands (D and E) upon the tridentate ligand plane. In the second case, the projection is parallel to one of the triangular ABC *sides*. This latter structure (Figure 2b) can be considered as a distorted square pyramid with the metal lying above the basal plane and approaching the fifth, apical ligand. Until now, the only monomeric compound with a structure corresponding to this second type was $Cu\{S[C-H_2CON(CH_3)_2]_2\}Cl_2$.[30] The two chlorine atoms in this complex are projected over the O–O edge and one S–O edge of the O–S–O triangle of donor atoms. The copper(II) complex reported here is only the second example to date of a monomeric complex exhibiting the structure represented in Figure 2b.[31]

The ⟨Cu–N⟩ and ⟨Cu–Br⟩ distances are normal for copper(II) complexes. A great deal of variation in axial ligand–copper(II) distances has been noted, and this bond is almost always longer than in-plane bonds.[32] The value here of 2.231 (42) Å for the axial ⟨Cu–N⟩ distance is moderately short and probably reflects both the highly constrained nature of the cyclic triamine and the fact that the "axial" nitrogen does not lie at a purely axial position but is distorted off the axis slightly. The electron density distribution about copper(II) has often been described as a prolate ellipsoid, and any "axial" position off the pure apical position will result in a shortened axial bond distance.[27,32]

Bond distances and angles within the cyclic triamine are quite similar to those found by Zompa and Margulis in the $([9]aneN_3)_2Ni^{2+}$ ion.[9] This suggests that the ligand is rather inflexible as a coordinating group, and perhaps little variation in ligand geometry of this tridentate ligand will be found.

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Registry No. $Cu([9]aneN_3)Br_2$, 70814-02-7.

Supplementary Material Available: A listing of observed and calculated structure factor amplitudes (11 pages). Ordering information is given on any current masthead page.

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^{31}P NMR Studies of Catalytic Systems Containing Rhodium Complexes of Chelating Chiral and Achiral Diphosphines

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^{31}P NMR spectroscopy was utilized to determine the nature of the olefin hydrogenation catalyst species present in solution (a) on treating $[RhCl(C_2H_4)_2]_2$ with chelating diphosphines and (b) on treating the complexes $[(NBD)Rh(diphosphine)]^+$ with hydrogen. In all cases, reaction of the generated species with (*Z*)-α-acetamidocinnamic acid was also studied. A brief investigation of the oxidative addition of hydrogen, hydrogen chloride, and oxygen to bis[1,3-bis(diphenylphosphino)propane]chlororhodium(I) was carried out.

The catalytic, asymmetric reduction of prochiral olefins by rhodium(I) complexes of chiral tertiary phosphines has been an extremely active area of research in recent years.[1-3] Particularly successful catalysts have been those, modeled on the well-known, much studied Wilkinson catalyst,[4-8] $RhCl(PPh_3)_3$, containing chelating, bidentate diphosphine ligands. Thus complexes of rhodium(I) containing (*R,R*)- and (*S,S*)-2,3-*O*-isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)butane ((–)- and (+)-diop, Ia and Ib, respectively),[9] substituted derivatives of (–)-diop (II),[10] similar (*R,R*)- or (*S,S*)-*trans*-1,2-bis((diphenylphosphino)methyl)cycloalkanes (III–VI),[10,11] (*R,R*)-1,2-bis[(*o*-methoxyphenyl)phenylphosphino]ethane (VII),[12] (2*S*,3*S*)-bis(diphenylphosphino)-butane (*S,S*-chiraphos, VIII),[13] and (*R*)-1,2-bis(diphenylphosphino)propane (*R*-prophos, IX)[14] have proven to be extremely effective catalysts for the reduction of a variety of α-*N*-acylaminoacrylic acids to amino acid derivatives in high (60–100%) optical yields.

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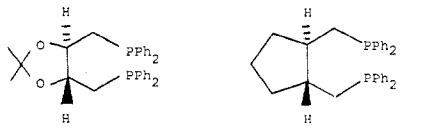
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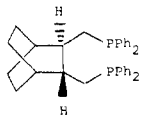
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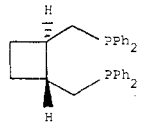
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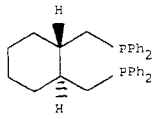
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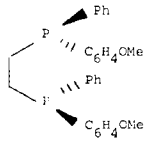
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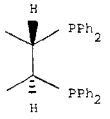
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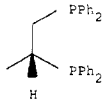

IX

Active catalyst solutions have generally been prepared in two ways, by treating $[RhCl(C_2H_4)_2]_2$ with the diphosphine, as in eq 1, or by hydrogenating a cationic (diene)rhodium(I)

$$[RhCl(C_2H_4)_2]_2 + 2(\text{diphosphine}) \rightarrow 2\text{"RhCl(diphosphine)"} + 4C_2H_4 \quad (1)$$

catalyst precursor, as in eq 2. The identity of the actual

$$[(\text{diene})Rh(\text{diphosphine})]^+ + 2H_2 \rightarrow \text{"Rh(diphosphine)}^+\text{"} + \text{alkane} \quad (2)$$

diene = norbornadiene (NBD), 1,5-cyclooctadiene

catalyst species in eq 1 had not been determined by 1976 but had only been inferred by analogy with the known chemistry of the triphenylphosphine system.[4-8] The identity of the active species in eq 2 was also unknown in 1976, although it was generally thought to involve a solvated rhodium(III) dihydride, analogous to similar cationic hydrogenation catalysts of monodentate phosphines studied by Schrock and Osborn.[15,16]

Prompted by the known utility of ^{31}P NMR spectroscopy in studies of the solution chemistry of tertiary phosphine complexes of rhodium,[5,17-19] we began, in early 1976, an investigation of the solution species of eq 1 and 2. Initially we studied the chemistry of an achiral model diphosphine, 1,3-bis(diphenylphosphino)propane (dppp), and of (-)-diop, both with $[RhCl(C_2H_4)_2]_2$ and as the norbornadiene complexes $[(NBD)Rh(diphosphine)]BF_4$. Later we extended studies to the corresponding norbornadiene complexes of *S,S*-chiraphos and *R*-prophos, as they were announced,[13,14] and two other achiral diphosphines, 1,2-bis(diphenylphosphino)ethane (dppe) and 1,4-bis(diphenylphosphino)butane (dppb). While the work was in progress, Halpern et al.[20] reported complementary studies using dppe, Vilím and Hetflejš[21] reported kinetics studies of the catalytic system using diop, and Brown and Chaloner[22,23] reported ^{31}P NMR spectroscopy data for rhodium(I) complexes of diop, VII, and dppe with α-acylaminoacrylic acids. In addition, several authors have made various proposals concerning the nature of the selective diastereomeric interaction between the chiral metal catalysts and the prochiral olefinic substrates.[12-14,24,25] A preliminary communication of the work described herein has appeared,[26a] while some aspects have been discussed elsewhere.[26b]

Experimental Section

The diphosphines dppe, dppp, and dppb were purchased from Strem Chemicals, while (-)-diop was prepared by the method of Kagan and Dang.[9] The compound $[(NBD)Rh(dppp)]BF_4$ was prepared by the usual methods,[12-15,28] via $[(NBD)RhCl]_2$ and (NBD)Rh(acac); it was obtained in an overall yield of 55% as the orange mono(tetrahydrofuran) adduct. Anal. Calcd for $C_{38}H_{42}BF_4OP_2Rh$: C, 59.55; H, 5.52. Found: C, 58.22; H, 5.39. The compound (NBD)RhCl(dppp) was obtained in 90% yield by treating a solution of $[(NBD)RhCl]_2$ (0.25 g) with dppp (0.45 g) in 20 mL of dry acetone for 15 min. The solvent was then removed at reduced pressure and unreacted dppp was extracted with ethyl ether to give the product as the mono(acetone) adduct. Anal. Calcd for $C_{37}H_{40}ClOP_2Rh$: C, 64.13; H, 5.82. Found: C, 65.86; H, 5.76. The presence of the solvent was in both cases verified by ^1H NMR spectroscopy. The compound $RhCl(dppp)_2$ was prepared in 75% yield by adding dppp (0.6 g) to a suspension of $RhClCO(PPh_3)_2$ (0.5 g) in 25 mL of benzene. The resulting orange solution was refluxed for 30 min, yielding a yellow precipitate of the product. Anal. Calcd for $C_{54}H_{52}ClP_4Rh$: C, 71.92; H, 5.82. Found: C, 71.66; H, 6.13.

Complexes of the other diphosphines considered here have been reported elsewhere and were prepared as described in the literature.[12-15,20,22,23,27,28] Where comparisons are possible, agreement with spectroscopic data presented in the literature was very good.

(*Z*)-α-Acetamidocinnamic acid was prepared by the method of Herbst.[29]

All reactions were carried out, unless specified, under nitrogen in dried, deaerated solvents; analyses were carried out by Microanalysis Laboratories, Toronto. NMR spectra were run on Varian T60, Varian HA100, and Bruker HX60 spectrometers. Samples for ^{31}P NMR spectra were generally made up in a nitrogen atmosphere in a K.S.E. glovebox; samples under a hydrogen atmosphere were prepared on a vacuum line in a 10-mm Wilmad Taperlok tube.

Results and Discussion

The investigation initially involved studying the species obtained in a variety of solvents on treating $[RhCl(C_2H_4)_2]_2$ with dppp and (-)-diop, in varying mole ratios, and thence the nature of the interactions of so-generated species with hydrogen, (*Z*)-α-acetamidocinnamic acid, air and, in one case, anhydrous hydrogen chloride. The second phase of the investigation involved studying the interactions of the compounds $[(NBD)Rh(diphosphine)]BF_4$ (diphosphine: dppe, dppp, dppb, (-)-diop, *S,S*-chiraphos, and *R*-prophos) with hydrogen, and of the thus engendered species with (*Z*)-α-acetamidocinnamic acid; in some cases, oxygenation and further hydrogenation of the species in solution were also carried out.

Attributions of observed resonances to specific species in a study such as this are complicated by the fact that different phosphines generally exhibit quite different ^{31}P chemical shifts in otherwise essentially identical complexes.[30] Assignments were made, therefore, largely on the basis of the two general considerations (a) that for a given tertiary phosphine in a series of rhodium complexes, ^{31}P resonances shift to lower field and values of $J(Rh-P)$ increase as the trans influences of the ligands trans to the phosphine decrease and (b) that ring strain contributions to the ^{31}P chemical shifts of chelating diphosphines vary in a characteristic, albeit as yet not understood, manner as the size of the ring varies.

The former criterion has been utilized with some success by Tolman et al.[5] and ourselves[17-19] in studies of other aspects of organorhodium chemistry. A survey of some of the pertinent literature[5,17-19,31-35] shows that $J(Rh-P)$ normally increases by 30-40% on going from trans P to trans Cl in otherwise similar complexes; carbon monoxide, alkyl groups, and hydride appear to have effects similar to those of phosphines. Similarly, chemical shift differences between P trans to P and P trans to Cl can amount to as much as 20 ppm. Although data comparisons between rhodium(I) and rhodium(III) compounds cannot be made, the same general trends seem to hold true within each oxidation state. Henceforth,

listed coupling constant data will refer to rhodium–phosphorus couplings, unless otherwise specified.

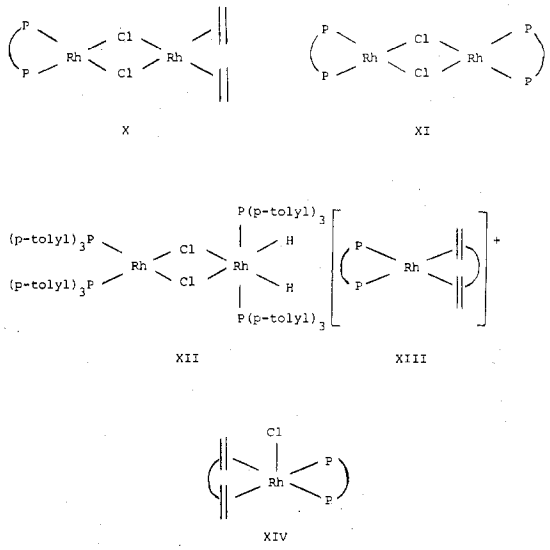
Ring strain contributions to ^{31}P chemical shifts of coordinated diphosphines have been discussed by Garrou,[36] who has defined a ring contribution, Δ_R, as the difference between the coordination shift, Δ,[37] of a cis-disubstituted bis(phosphine) complex and the observed Δ for an approximately equivalent phosphorus in a chelate complex. He was able to show that, in a wide variety of compounds, coordinated phosphorus atoms in five- and six-membered rings are deshielded 24–55 ppm and shielded 2–12 ppm, respectively, relative to similar monodentate complexes. In an extension to Garrou's data compilation we have found[38] that Δ_R values for the five-, six-, and seven-membered rings of platinum(II) compounds of dppe, dppp, and dppb are approximately −25, +13, and +1 ppm, respectively.

Reactions of $[RhCl(C_2H_4)_2]_2$ with dppp and (−)-diop. As outlined in the introductory section, an often used method for the in situ generation of chiral rhodium hydrogenation catalysts is the treatment of $[RhCl(C_2H_4)_2]_2$ with an equimolar amount of a diphosphine. It seemed appropriate, therefore, to study such reactions with ^{31}P NMR spectroscopy. In order to minimize ambiguities in the interpretation of ^{31}P NMR spectra, we investigated initially an achiral model diphosphine, dppp, which is known (see above) to exhibit relatively "normal" chemical shifts (i.e., relatively small values of Δ_R) when complexed; complexes of dppp also seemed more soluble than many analogous complexes of dppb, which would otherwise also be quite suitable. Reactions of (−)-diop were also studied because of the great interest in this ligand.

Treatment of a stirred suspension of $[RhCl(C_2H_4)_2]_2$ in acetone-d_6 with a deficiency of dppp (0.5 mol of dppp/mol of Rh) resulted in evolution of ethylene and the formation of an orange solution. The ^{31}P NMR spectrum of the orange solution (283 K) consisted only of a doublet at δ 32.0 (J = 187 Hz). Addition of a further 0.2 mol of dppp/mol of Rh resulted in a weakening of the doublet at δ 32.0 and the appearance of new doublets at δ 30.3 (J = 184 Hz) (~65% of total) and δ 17.6 (J = 124 Hz) (~5% of total), the latter very weak. Addition of more dppp (up to 1 dppp/Rh) resulted in a new doublet at δ 6.4 (J = 132 Hz). Similar behavior was observed in benzene-d_6 but, in methanol-d_4, as little as 0.6 dppp/Rh yielded predominantly a doublet at δ 6.75 (J = 132 Hz). Excess dppp in all three solvents, as well as in methylene chloride, gave the species exhibiting a doublet at δ ~6.3–6.8 in its ^{31}P NMR spectrum. Isolation and characterization of the latter compound, which was also prepared by treating $RhClCO(PPh_3)_2$ with excess dppp, showed it to be $RhCl(dppp)_2$. Its physical and chemical properties will be discussed below.

The observation of doublets shows that, in each compound formed, the two phosphorus atoms of the dppp either are in equivalent environments or are engaged in an exchange process which is rapid on the NMR time scale. The low-field ^{31}P chemical shifts ($\Delta \approx 48$ ppm) and large rhodium–phosphorus coupling constants of the two major species formed by a deficiency of dppp are reminiscent of the similar parameters of the chloride-bridged compounds $[RhCl(PR_3)_2]_2$ (R = *p*-tolyl (Δ = 47 ppm)[5] and cyclohexyl (Δ = 45 ppm)[39]). The species formed initially also exhibited a resonance at δ 2.88 in its ^1H NMR spectrum, consistent with a coordinated ethylene, and thus the compound is probably $(C_2H_4)_2Rh(\mu\text{-}Cl)_2Rh(dppp)$ (X). Its ^{31}P NMR spectrum did not change significantly on cooling to 213 K, consistent with this formulation, although the compound could not be isolated and characterized satisfactorily.

The compound obtained on adding further dppp clearly also contains chloride trans to the phosphorus atoms and is probably



$[RhCl(dppp)]_2$ (XI). Its ^{31}P spectrum also remains unchanged on cooling to 223 K, consistent with the proposed dimeric structure. In contrast to the tri-*p*-tolylphosphine complex, however, which adds hydrogen to form XII,[5] $[RhCl(dppp)]_2$ does not react noticeably with hydrogen (1 atm) (although the compound is an active hydrogenation catalyst). The ethylene complex, on the other hand, does react with hydrogen to give an uncharacterized precipitate and a dark orange solution containing no new ^{31}P resonances. Possibly hydrogen addition occurs at the rhodium atom bonded to the ethylenes.

Rather surprisingly, $[RhCl(dppp)]_2$ in acetone–methanol (10:1) also does not appear to react noticeably with 1 equiv of (*Z*)-α-acetamidocinnamic acid, no change in the ^{31}P NMR spectrum being evident even down to 223 K. On the other hand, the minor species with δ 17.6 (J = 124 Hz), formed on treating $[RhCl(C_2H_4)_2]_2$ with a deficiency of dppp in acetone, may, on the basis of the ^{31}P NMR parameters, be the bridge-splitting product, $RhCl(C_2H_4)_2dppp$ (see below).

Reactions of $[RhCl(C_2H_4)_2]_2$ with (−)-diop paralleled in part those with dppp. Addition of 0.5 mol of diop/mol of rhodium in acetone-d_6 resulted in ^{31}P resonance doublets at δ 34.1 (J = 194 Hz) and δ 31.8 (J = 191 Hz). Addition of 0.8–0.9 mol of diop/mol of rhodium, on the other hand, led only to the doublet at δ 31.8. The chemical shift and rhodium–phosphorus coupling constant data, as well as the facts that both doublet resonances were essentially invariant down to 223 K, suggest that the downfield doublet is to be attributed to the diop analogue of X and the other to the diop analogue of XI. Similar results were observed in benzene-d_6 and, surprisingly, methanol-d_4 solutions. Whereas a $(dppp)_2$ complex was very readily formed in methanol, the corresponding $(diop)_2$ species was not, although such compounds are known.[28] Also surprising was the observation that the doublet spectrum of a solution of $[RhCl(diop)]_2$ in 1:1 benzene-d_6–methanol at 283 K exhibited little change on addition of excess (*Z*)-α-acetamidocinnamic acid.

The above results demonstrate that, although a species of the oft-proposed type "RhCl(diphosphine)" is probably the active catalyst formed on treating compounds of the type $[RhCl(monoolefin)_2]_2$ with a diphosphine, the mechanism of the hydrogenation of olefins by such species is not completely analogous to that of Wilkinson's catalyst, $RhCl(PPh_3)_3$. Although oxidative addition of hydrogen and olefin coordination undoubtedly occur, neither a dihydridorhodium(III) intermediate nor a complex of (*Z*)-α-acetamidocinnamic acid could be detected for either the dppp or the diop system by using ^{31}P NMR spectroscopy. We had anticipated possibly observing enantioselective coordination of this prochiral olefin to the chiral diop metal complex.

Table I. ^{31}P NMR Parameters for Diphosphine Ligands, L, and Their Rhodium(I) Complexes in CD_3OD

	chemical shifts, ppm (J(Rh–P), Hz)[a]			
L	free L	$[NBDRhL]^+$	$[(MeOH)_2RhL]^+$	$[((Z)$-α-acetamidocinnamic acid)$RhL]^+$
dppe	−12.3	55.6 (157)	80.3 (203)	72 (162), 61 (158)[b] (J(PP) = 39)
S,S-chiraphos	−10.7	56.9 (153)	81.7 (176)	72.9 (159), 60.4 (153) (J(PP) = 51)
R-prophos	1.7, −20.6 (J(PP) = 20.6)	60.5 (172), 41.8 (139) (J(PP) = 34)	86.7 (204), 68.9 (202) (J(PP) = 55)	75.3 (163), 43.5 (157) (J(PP) = 45) 62.9 (158), 59.9 (156) (J(PP) = 45)
VII			80.8 (209)[c]	71(161), 50 (154)[c] (J(PP) = 41)
dppp	−17.0	14.1 (148)	38.9 (190)	19.4 (126), 15.7 (130) (J(PP) = 43)
dppb	−15.0	26.8 (152)	52.7 (196)	
(−)-diop	−24.1	16.2 (153)	42.6 (197)	34.1 (150), 7.8 (150) (J(PP) = 50)

[a] With respect to external H_3PO_4; downfield shifts positive. [b] Reference 22. [c] Reference 23.

Finally, the apparent coexistence of four different dppp rhodium(I) species when dppp is added to $[RhCl(C_2H_4)_2]_2$, the relative concentrations depending on both the dppp:Rh ratio and the solvent, suggests that this method of generating catalyst solutions for the accumulation of, for instance, kinetic data on the hydrogenation of olefins should be avoided. Much better behaved are those hydrogenation systems based on catalyst precursors of the type $[(NBD)Rh(diphosphine)]BF_4$.

Reactions of [(NBD)Rh(diphosphine)]X (X = Cl, BF_4, ClO_4; diphosphine = dppe, dppp, dppb, (−)-diop, *S,S*-chiraphos, *R*-prophos) with Hydrogen. The ^{31}P NMR spectrum of the compound $[(NBD)Rh(dppp)]BF_4$ exhibited a doublet at $\delta \sim 14$ ($J \approx 148$ Hz) in a variety of solvents (see Table I); the spectrum in acetone-d_6 remained unchanged to 213 K. These data are consistent with the expected planar structure of the cationic complex (XIII). Furthermore, inasmuch as both the coordination shift ($\Delta \approx 31$ ppm) and the coupling constant are much lower than those of the chloride-bridged compounds discussed in the previous section, it seems that the chelating diolefin exhibits a rather high trans influence. This conclusion is consistent with the known very high trans effect of the ethylene in Zeise's salt.[40]

Although the ^{31}P NMR spectrum of the chloride complex, (NBD)RhCl(dppp), was essentially the same as that of the fluoroborate complex in methanol, it was significantly different in acetone-d_6 (δ 16.7, J = 129 Hz) and $CDCl_3$ (δ 16.9, J = 131 Hz). Furthermore, addition of 1 molar equiv of $Ph_4As^+Cl^-$ to an acetone solution of $[(NBD)Rh(dppp)]BF_4$ caused diminution of the doublet at $\delta \sim 14$ and growth of the doublet at δ 16.7. Thus, although the fluoroborate ion appears to be ionic in all solvents tried, solvent effects seem to be important in determining the extent of association of chloride with the rhodium. The decrease in J(Rh–P) on going from four-coordinated $[(NBD)Rh(dppp)]^+BF_4^-$ to, apparently, five-coordinated (NBD)RhCl(dppp), is consistent with an increase in coordination number.[30] The ^{31}P NMR spectrum of the chloro compound was unchanged to 220 K in $CDCl_3$ and 233 K in acetone-d_6, suggesting a structure such as XIV. We note in passing the similarity of the spectral parameters of the chloro compound in acetone-d_6 with that of the putative $RhCl(C_2H_4)_2$dppp, discussed in the previous section.

Hydrogenation of $[(NBD)Rh(dppp)]BF_4$ in acetone or methanol resulted in the smooth disappearance of the doublet at $\delta \sim 14$ and the appearance of a new doublet at $\delta \sim 38$ ($J \approx 190$ Hz) but not in the appearance of a hydride resonance in the ^1H NMR spectrum. The large, downfield chemical shift ($\Delta \approx 55$ ppm) and coupling constant suggest a drastically different environment for the phosphorus atoms in the new species, one in which the atoms trans to phosphorus exhibit very low trans influences. The new species has not been isolated, but is quite air-sensitive and is probably a solvent complex, $[dpppRh(solvent)_2]^+$, formed by hydrogenation of the diene.[20] It is clearly not a dihydride, $[RhH_2dppp(solvent)_2]^+$, a conclusion reached by Halpern[20] and Brown[22,23] for similar complexes of other diphosphines. The ^{31}P NMR spectrum of the low-field doublet in acetone-d_6 underwent a series of changes on being cooled to 193 K, consistent with nonequivalence of the phosphorus atoms at low temperature (Figure 1). Although we cannot be certain that the limiting spectrum had been reached, it may be that the fluoroborate coordinates to form the complex $Rh(BF_4)$dppp(solvent). Interestingly, addition of $Ph_4As^+Cl^-$ to an acetone-d_6 solution of $[dpppRh(solvent)_2]^+$ resulted in appearance of a doublet attributable to $[RhCl(dppp)]_2$ (δ 30.3, J = 184 Hz) (see above).

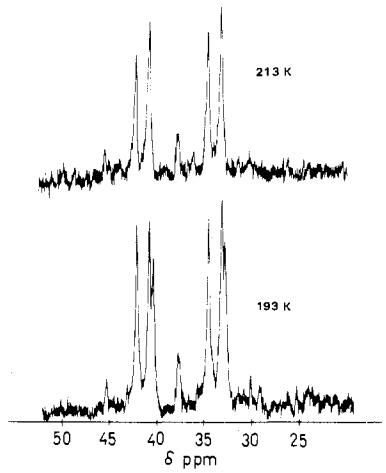


Figure 1. ^{31}P NMR spectrum of "$Rh(dppp)BF_4$" in acetone at 213 and 193 K.

The diop compounds, $[(NBD)Rh(diop)]X$ (X = Cl, BF_4), exhibited very similar physical and chemical properties. Thus hydrogenation of $[(NBD)Rh(diop)]BF_4$ in acetone-d_6 or methanol-d_4 resulted in the smooth disappearance of the doublet at $\delta \sim 16$ ($J \approx 150$ Hz) (Table I) and the appearance of a new doublet of the solvated species at much lower field ($\delta \sim 40$, $J \approx 197$ Hz); the new doublet also broadened asymmetrically on cooling. Reduction of the chloro compound, (NBD)RhCl(diop), in either acetone-d_6 or methanol-d_4 gave the spectrum of $[RhCl(diop)]_2$, showing that the chloride is largely coordinated, even in methanol.

Similar hydrogenation studies were carried out in methanol-d_4 with the complexes of dppe, dppb, *S,S*-chiraphos, and

R-prophos, as the fluoroborate or perchlorate salts. ^{31}P NMR data are presented in Table I. In the first three cases, hydrogenation proceeded smoothly, an upfield doublet ($J \approx 150$ Hz) being replaced by a downfield doublet ($J \approx 175$–195 Hz). In the case of *R*-prophos in which the phosphorus atoms are not equivalent, the ^{31}P NMR spectra comprise the eight-line AB parts of ABX (X = ^{103}Rh) spin systems. Although the two ^{31}P chemical shifts of each *R*-prophos complex, as well as the two rhodium–phosphorus coupling constants of [(NBD)Rh(*R*-prophos)]$^+$, differ considerably, given that the pairs of trans atoms are identical in each case, approximately the same difference is observed for the free ligand. In addition, the averages of each pair of chemical shifts and coupling constants are reasonably consistent with analogous data for the dppe and *S,S*-chiraphos complexes.

The results underline the position, taken above, that while the mechanism of catalysis of olefin hydrogenation by rhodium complexes of chelating diphosphines may be similar to the mechanism of catalysis by complexes of monodentate phosphines, major differences exist. In particular, dihydride complexes of the type [RhH_2(diphosphine)(solvent)$_2$]$^+$ are much less stable than complexes of the type [RhH_2L_2(solvent)$_2$]$^+$ (L = monodentate phosphine).[15]

Reactions of [(diphosphine)Rh(MeOH)$_2$]$^+$ (diphosphine = dppe, dppp, dppb, (−)-diop, *S,S*-chiraphos, *R*-prophos) with (*Z*)-α-Acetamidocinnamic Acid. Solutions of [(NBD)Rh(diphosphine)]BF_4 (diphosphine = dppp, diop) and (*Z*)-α-acetamidocinnamic acid (~1:1) in methanol-d_4 were maintained under ~1 atm of hydrogen for over 2 h; spectral data were accumulated for 20–30-min periods during this time at both 295 and 223 K. Although separate experiments, in the absence of (*Z*)-α-acetamidocinnamic acid, showed that conversion to [(diphosphine)Rh(MeOH)$_2$]$^+$ would be complete during this time, no reasonably resolved resonances other than those of the starting materials could be detected. Only broad bands were observed, suggesting exchange processes of some kind.

Well-resolved ^{31}P NMR spectra of, presumably, the complexes [(diphosphine)Rh((*Z*)-α-acetamidocinnamic acid)]$^+$ were obtained at 220 K by treating degassed solutions of the methanol complexes with a tenfold excess of the olefin. Data are presented in Table I; included are the corresponding data for the complexes of VII.[23] The nature of the species in solution is rather uncertain, as they could contain a η^2-olefin–metal linkage cis to a coordinated solvent molecule, a chelated olefin, in which coordination of the amide oxygen accompanies η^2 coordination of the olefinic group or η^6-arene species. The first possibility is perhaps to be expected and, as olefin and methanol should have very different trans influences, might be expected to result in very different ^{31}P chemical shifts and rhodium–phosphorus coupling constants. An arene complex of the type [(diphosphine)Rh(η^6-arene)]$^+$ would be consistent with the equilibrium constant studies of Halpern et al.[20] but might be expected to contain equivalent phosphorus atoms for all except the *R*-prophos complex.

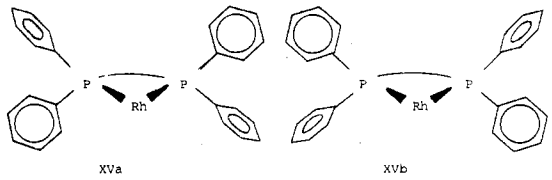
The third alternative, containing a chelated ligand, would be consistent with the work of Knowles et al.,[12] which has demonstrated a general increase in efficiency of hydrogenation when such an amide group is present. Furthermore, a crystal structure of a cationic dppe complex containing the methyl ester of (*Z*)-α-acetamidocinnamic acid demonstrates that simultaneous amide oxygen and η^2-olefin coordination can occur.[41] Again, the two phosphorus atoms might exhibit quite different chemical shifts and rhodium–phosphorus coupling constants.

The data on the olefin complexes in Table I are unfortunately rather inconclusive on the matter. Although the phosphorus atoms of each complex do exhibit quite different chemical shifts, the two rhodium–phosphorus coupling constants are never very different. One cannot even be certain that the same type of complex is formed at each step for all diphosphines, although all samples were generated in essentially the same manner. The fact that most of the ^{31}P chemical shifts of the presumed olefin complexes lie between those of the corresponding norbornadiene and methanol complexes, however, suggests that the same type of species is present in solution in each case and that the assignments are likely to be valid.[42]

Our work to a large extent complements and confirms the assignments in that of Brown and Chaloner,[22,23] who reported the ^{31}P NMR spectra of various complexes of prochiral olefins with catalyst systems involving diop and VII. In some cases, their apparent observations of pairs of diastereomers in solution were related to the published stereoselectivities observed during hydrogenations, consistent with the suggestion that the enantioselectivity arises during the bonding of the olefin to the metal. If this hypothesis is correct, the two species present in the solution of the *R*-prophos olefin complex must be geometrical isomers rather than diastereomers, as very high selectivity is observed during hydrogenation.[14]

Origin of the Enantioselectivity during Coordination of Prochiral Olefins to Catalysts of the Type [(chiral diphosphine)Rh(solvent)$_2$]$^+$. It seems likely[12b,22,23] that a major factor in the induction of asymmetry during olefin hydrogenation reactions involves enantioselectivity during coordination of a prochiral olefin to a chiral catalyst. It also seems to be generally agreed that, since the actual chiral centers of most of the diphosphine ligands discussed here reside in the hydrocarbon backbones of the ligands, and hence are far from the olefin coordination site, the conformations of the phenyl groups must somehow play a critical role.

There have been considered basically two different ways in which the phosphorus–phenyl moieties may generate the functional chirality sensed by the incoming prochiral olefin. For instance, a coordinated diarylphosphorus moiety will assume propeller-like chiral conformations, the difference between the conformations being the sense of twist about the phosphorus–aryl bonds.[43] Consistent with this idea, Knowles et al.[12] have made the proposal, supported by crystal structure data, that the catalysts discussed herein exist in enantiomeric conformations in which the four aryl rings are arranged in an alternating edge–face manner, as in XVa and XVb.

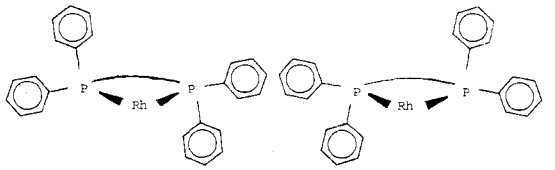


XVa XVb

It was suggested that the orientations of the aryl rings are decided by the dispositions of the vicinal aliphatic CH groups of the puckered rings; in all cases, the face-exposed rings were those closest to the skewed methylene or methyne groups of the aliphatic ligand backbones. The major interaction was believed to be steric in nature, between axial hydrogen atoms and ortho aryl hydrogen atoms. In any case these chiral conformations could be enantioselective, since an incoming prochiral olefin would experience a greater steric interaction with the ortho hydrogen atoms of the edge-exposed rings in the preferred, albeit nonrigid, conformation.

A second type of chirality occurs[13,14] if the phenyl groups occupy axial and equatorial positions, as in the mutually enantiomeric conformations XVIa and XVIb.

Crystal structures of rhodium complexes of *S,S*-chiraphos[44] and *R*-prophos[14] show quite clearly that the phenyl groups on the puckered rings formed in these cyclic compounds can



XVIa XVIb

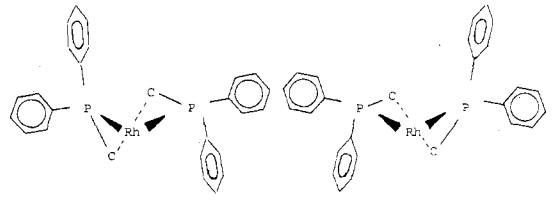
indeed assume such axial and equatorial positions.[45]

Interconversion between enantiomeric conformations such as XVa and XVb by aryl ring flipping is expected to be very facile, since similar ring flipping in relatively crowded complexes of triphenylphosphine is rapid on the NMR time scale.[43,46] If conformations such as XVa,b are important factors in determining the degree of enantioselectivity during olefin coordination, then a rigid, chiral environment about the rhodium prior to olefin coordination cannot be a requirement.

Interconversion between enantiomers such as XVIa and XVIb is probably also normally quite facile.[47] While the two enantiomers would be of equal stability for complexes of the achiral ligands dppe, dppp, and dppb, however, conformations of coordinated *S,S*-chiraphos and *R*-prophos are fixed by the necessarily equatorial dispositions of the methyl groups of the hydrocarbon backbones.[13,14] A prochiral olefin interacting with either fixed conformation would experience two possible diastereomeric relationships, depending on which face of the olefin were to approach the metal atom. Since, in principle, coordination of one prochiral face to, say, XVIa should be more facile than coordination of the other, it would follow that XVIa and XVIb should each exhibit equal but opposite preferences for the two olefin faces.

Noting that *S,S*-chiraphos and *R*-prophos appear to assume conformations XVIa and XVIb, respectively, Bosnich and Fryzuk[13,14] have also pointed out that rhodium(I) complexes of these two diphosphines do indeed each catalyze the hydrogenation of a number of (*Z*)-α-*N*-acylaminoacrylic acids to the two series of enantiomeric amino acids. Thus the *S,S*-chiraphos and *R*-prophos complexes yield almost exclusively the *R* and *S* amino acids, respectively.

It is readily seen, however, that conformations such as XVa,b and XVIa,b are not independent of each other, as it is the puckering of the rings which results in both the apparent axial–equatorial dispositions and the apparent edge–face-exposed dispositions of the aryl rings. Thus, as can be seen in XVIIa and XVIIb, the face- and edge-exposed aryl rings



XVIIa XVIIb

should prefer equatorial and axial orientations, respectively, so that XVa and XVIa depict the same conformation, and the chiral characteristics of both can be represented by XVIIa. Similarly, XVIIb combines the chiral characteristics of XVb and XVIb.

We[26b] and Knowles et al.[12b] have discussed from different points of view the generality of these ideas to all of the catalytic systems mentioned in the introductory section. Thus ligand VII resembles *R*-prophos in that it forms, on coordination, a five-membered ring and assumes conformation XVIIb;[12] as does *R*-prophos, it generates *S* amino acids. The origin of the conformational chirality in this case is not a chiral backbone, but possibly arises from preference of the relatively bulky

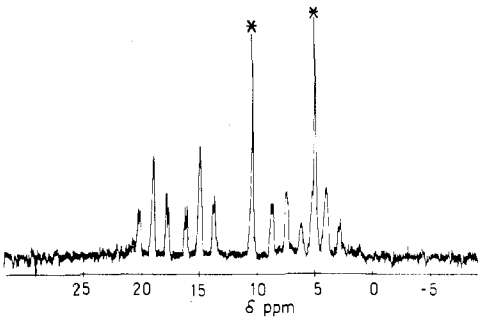


Figure 2. ^{31}P NMR spectrum of $[RhH_2dppp_2]Cl$ and $RhCl(dppp)_2$ (asterisked) in $CDCl_3$.

o-methoxyphenyl groups for equatorial positions on the five-membered ring.

The ligands (−)-diop (and its derivatives II, III, IV, and V) comprise a series of ligands similar to the above, but forming seven-membered rings on coordination. Their coordination complexes are bicyclic and contain 1,4-bis(diphenylphosphino)butane backbones in which the 2- and 3-carbon atoms are chiral with the same handedness. Ligand VI is in this category as well, but with the opposite handedness.

Few suitable crystal structures of complexes of these ligands are available.[48] Space-filling molecular models, however, do suggest that coordination of these chelating ligands does result in puckered rings in which the aryl groups assume axial and equatorial positions. Furthermore, the models suggest that (−)-diop, III, IV, and V all assume conformation XVIIa, while (+)-diop and VI assume conformation XVIIb, a prediction verified for (−)-diop by a crystal structure determination.[12b] The structures would be fixed in solution by the bicyclic nature of the complexes.

Reports concerning hydrogenation of (*Z*)-α-*N*-acylaminoacrylic acids by rhodium(I) complexes of these ligands show that (−)-diop,[1,9] III,[10,11] IV,[10] and V[11] all give *R*-amino acids, as does *S,S*-chiraphos.[13] Thus it seems that complexes containing conformation XVIIa coordinate the *si* olefin face and give *R* amino acids, while those containing conformation XVIIb coordinate the *re* face and give *S* amino acids.[50,53]

While correlation between apparent handedness of the catalysts in solution and handedness of the products seems good, it is probably futile at present to attempt to rationalize in terms of steric effects the differences in activation energies of the diasteromeric pathways of the catalytic reactions. Almost all of the optical yields reported in the literature arise from differences of free energies of activation of less than 2 kcal/mol, significantly less than the barrier to rotation about the carbon–carbon bond of ethane (2.88 kcal/mol).[54] If the differences in $\Delta G^{\ddagger}$ arise totally from differences in steric interactions between diphenylphosphorus moieties and the prochiral olefin faces, the interactions would be more subtle and hence less noticeable than the intramolecular repulsive forces in ethane. Space filling molecular models are far too crude to assess such subtle steric effects.

Oxidative Addition Reactions of $RhCl(dppp)_2$. As has been indicated in a previous section, reactions of $[RhCl(C_2H_4)_2]_2$ with dppp in some cases produced surprising amounts of the bis(dppp) complex. Although this complex is not a hydrogenation catalyst, the possibility of its formation in solution under hydrogenation conditions prompted a brief study of its chemistry, if only to eliminate any confusion between its reaction products and those of the desired mono(dppp) complex.

The compound $RhCl(dppp)_2$ exhibits a doublet in its ^{31}P NMR spectrum at $\delta \sim 6.4$ ($J = 132$ Hz) in a variety of solvents. Although no exchange is observed at room temperature with either free dppp in methylene chloride or

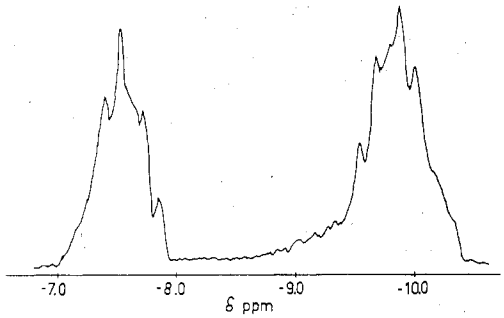
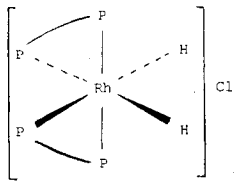


Figure 3. ^{1}H NMR spectrum of $[RhH_2dppp_2]Cl$ in the hydride region.

(*Z*)-α-acetamidocinnamic acid in 1:1 benzene–methanol, the doublet resonance broadens considerably below 223 K in acetone. Although a limiting spectrum was not observed, it is possible that the compound is fluxional with a trigonal-bipyramidal static structure.[58]

Bubbling hydrogen through solutions of $RhCl(dppp)_2$ in methylene chloride or chloroform resulted in partial conversion to the dihydride, $[RhH_2(dppp)_2]Cl$; although the latter was not isolated, it was readily identified as the cis isomer XXI by its ^{1}H and ^{31}P NMR spectra.



XXI

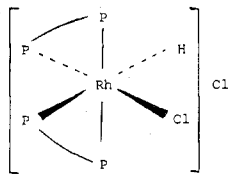
Thus the $^{31}P\{^1H\}$ spectrum, which remains essentially unchanged on cooling of the system to 213 K, is consistent with that expected for an $[AB]_2X$ spin system (A,B = P; X = Rh) (δ 17.0, J = 49 Hz; δ 6.3, J = 80 Hz; J(PP) = 30 Hz) (Figure 2). On the basis that the trans influence of hydride is expected to be greater than that of phosphorus, it seems likely that the downfield ^{31}P resonance, with the larger rhodium–phosphorus coupling constant, is to be assigned to the mutually trans phosphorus atoms.

The ^{1}H NMR spectrum exhibits a complex doublet centered at δ −8.6 and attributable to a hydride resonance (Figure 3). As the hydrogen spins would comprise the MM′ part of an $[ABM]_2X$ spin system, no attempt to analyze the spectrum was made except to note that trans J(P–H) ≈ 141 Hz.

The spectral parameters of the dihydride are comparable with those of similar complexes of monodentate phosphines.[15] None of this family of complexes appears to be fluxional. Our observed addition of hydrogen to $RhCl(dppp)_2$ is interesting in light of the report[55] that $RhCl(dppe)_2$ is inert to hydrogen.

Reactions of $RhCl(dppp)_2$ with anhydrous hydrogen chloride and oxygen were also studied cursorily. Addition of anhydrous hydrogen chloride to a solution of $RhCl(dppp)_2$ in methylene chloride gave, on reduction of the volume of the solution and the addition of ethyl ether, a pale yellow precipitate of $[RhHCl(dppp)_2]Cl$. The IR spectrum (Nujol) exhibited ν(RhH) at 2090 cm^{-1}, while the ^{1}H NMR spectrum (CD_2Cl_2) at room temperature exhibited a sextet at δ −15.0 (J(PH) = J(RhH) = 13.5 Hz), attributable to a hydride resonance. The $^{31}P\{^1H\}$ NMR spectrum exhibited, at room temperature, a doublet at δ 1.9 (J = 90 Hz). On cooling of the system, however, the resonances broadened, split into two broad bands, and then sharpened up at ~203 K into two well-resolved doublet triplets, consistent with the AA′BB′MX spin system of the cis isomer (XXII) (δ 12.3, J = 90 Hz; δ −8.9, J = 93 Hz; J(PP) = 35 Hz).

The spectral changes are very similar to those of the iridium analogue,[56] with the addition of rhodium coupling, and show



XXII

that the molecule is fluxional.[57] In spite of the expected differences in trans influences between hydride and chloride, however, the phosphorus atoms trans to the ligands exhibit the same chemical shifts, even at 203 K. Presumably an exchange process is still occurring between the hydride and chloride coordination sites.

In some of the ^{31}P NMR spectra run during the course of this work, there was present another quartet of triplets. This was eventually identified as the stereochemically rigid oxygen adduct, $[Rh(dppp)_2O_2]Cl$ (δ 15.4, J = 122 Hz; δ −12.7, J = 85 Hz; J(PP) = 30.5 Hz).

Acknowledgment. We thank Queen's University and the National Research Council of Canada for financial support of this research and the latter also for a graduate fellowship to D.A.S. We are very grateful to Johnson Matthey, Ltd., for a loan of rhodium trichloride, to Professor B. Bosnich for samples of *S,S*-chiraphos and *R*-prophos and their complexes, to Professor J. Halpern for information concerning unpublished work, and to Mr. J. Martin for assistance in the laboratory.

Registry No. $[(NBD)Rh(dppp)]BF_4$, 65606-90-8; (NBD)-RhCl(dppp), 71264-66-9; $RhCl(dppp)_2$, 71264-67-0; $[(NBD)RhCl]_2$, 12257-42-0; $RhClCO(PPh_3)_2$, 13938-94-8; $[RhCl(C_2H_4)_2]_2$, 12081-16-2; $(C_2H_4)_2Rh(\mu\text{-}Cl)_2Rh(dppp)$, 65554-22-5; $[RhCl(dppp)]_2$, 65554-24-7; $RhCl(C_2H_4)_2dppp$, 71264-68-1; $(C_2H_4)_2Rh(\mu\text{-}Cl)_2Rh((-)\text{-diop})$, 65554-18-9; $[RhCl((-)\text{-diop})]_2$, 63569-12-0; $[(NBD)Rh(diop)]BF_4$, 60584-05-6; (NBD)RhCl(diop), 71264-69-2; $[(NBD)Rh(dppe)]^+$, 47768-38-7; $[(NBD)Rh(S,S\text{-chiraphos})]^+$, 65012-73-9; $[(NBD)Rh(R\text{-prophos})]^+$, 67881-58-7; $[(NBD)Rh(dppb)]^+$, 71264-70-5; $[(MeOH)_2Rh(dppe)]^+$, 68811-68-7; $[(MeOH)_2Rh(S,S\text{-chiraphos})]^+$, 71264-71-6; $[(MeOH)_2Rh(R\text{-prophos})]^+$, 71264-72-7; $[(MeOH)_2Rh(dppp)]^+$, 71264-73-8; $[(MeOH)_2Rh(dppb)]^+$, 71264-74-9; $[(MeOH)_2Rh((-)\text{-diop})]^+$, 71264-75-0; [((*Z*)-α-acetamidocinnamic acid)Rh(*S,S*-chiraphos)]$^+$, 71302-36-8; [((*Z*)-α-acetamidocinnamic acid)Rh(*R*-prophos)]$^+$, 71264-76-1; [((*Z*)-α-acetamidocinnamic acid)Rh(dppp)]$^+$, 71264-77-2; [((*Z*)-α-acetamidocinnamic acid)Rh((−)-diop)]$^+$, 71301-39-8; *cis*-$[RhH_2(dppp)_2]Cl$, 71264-78-3; *cis*-$[RhHCl(dppp)_2]Cl$, 65849-06-1; $[Rh(dppp)_2O_2]Cl$, 65554-16-7; dppe, 1663-45-2; *S,S*-chiraphos, 64896-28-2; *R*-prophos, 67884-32-6; dppp, 6737-42-4; dppb, 7688-25-7; (−)-diop, 32305-98-9; $PtCl_2dppe$, 14647-25-7; $PtCl_2dppp$, 59329-00-9; $PtEt_2dppe$, 52621-10-0; $PtEt_2dppp$, 65097-97-4; $PtEt_2dppb$, 65097-98-5; (*Z*)-α-acetamidocinnamic acid, 55065-02-6.

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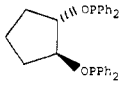
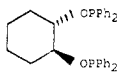


XIX



XX

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Soluble (Chlorosilyl)phosphine and Siloxyphosphine Complexes of Rhodium(I)

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A number of soluble (chlorosilyl)phosphine complexes of rhodium(I) which are capable of being polymerized into poly(siloxyphosphine)–rhodium(I) species have been synthesized and characterized. They are $L_2'Rh(CO)Cl$, L'_3RhCl, L''_3RhCl, and $L'_4Rh_2Cl_2$ (L′ = $Cl_3Si(CH_2)_2P(C_6H_5)_2$, L″ = $Cl_3Si(CH_2)_8P(C_6H_5)_2$). Soluble siloxyphosphine–rhodium(I) complexes $LRh(NBD)Cl$, $L_2Rh(CO)Cl$, L_3RhCl, and $L_4Rh_2Cl_2$ (NBD = norbornadiene, L = $[(CH_3)_3SiO]_2(CH_3)Si(CH_2)_2P(C_6H_5)_2$) have also been synthesized and characterized and their reactions with gaseous H_2, CO, and HCl as well as their catalytic behavior in hydrogenation reactions have been studied. These complexes were prepared to serve as study models for their polymeric counterparts.

Introduction

There is currently a considerable interest in the problem of "heterogenizing" homogeneous catalysts by attaching transition-metal complexes to insoluble supports.[1] These supports are usually polystyrene and related polymers or inert materials such as silica and glass. In our laboratories we are interested in utilizing silicones as supports since these are potentially more inert than traditional organic polymers and also, if necessary, can be modified more easily than other inorganic supports.

Two methods are available for producing metal centers anchored to an insoluble matrix in such a way that there is a good likelihood of multiple attachment. These are exemplified in the present context of our aim of combining silicones with phosphine derivatives of rhodium(I) as follows: a preformed (chlorosilyl)phosphine–rhodium(I) complex could be attached to a polymeric support[2] or it could be hydrolytically polycondensed to a poly(siloxyphosphine)–rhodium(I) macro compound.[3] In the latter case if the starting monomeric complex is well characterized and if the "heterogenization" process does not change appreciably the environment of the metal center, it should be possible to produce a polymer with well-defined catalytic sites.

This work describes the synthesis and characterization of some (chlorosilyl)phosphine complexes of rhodium(I) which

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