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Preliminary communication

INVESTIGATIONS OF OLEFIN HYDROGENATION CATALYSTS. THE MAJOR SPECIES PRESENT IN SOLUTIONS CONTAINING RHODIUM(I) COMPLEXES OF CHELATING DIPHOSPHINES

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Summary

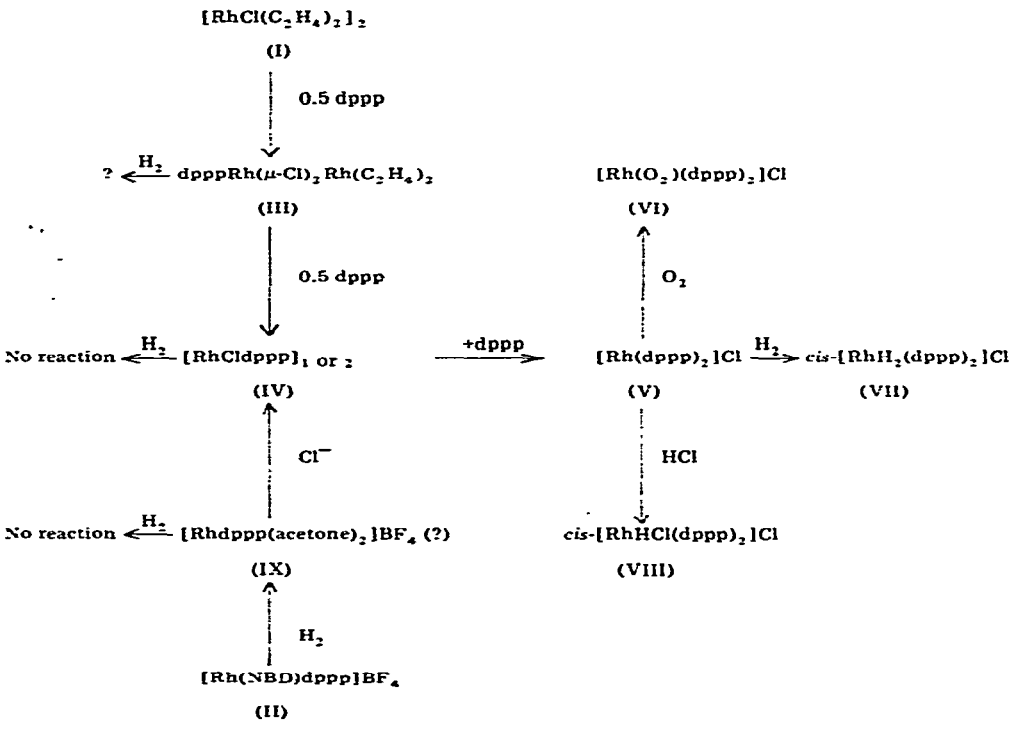
^1H and ^{31}P NMR spectroscopy are used to determine the nature of the species present in catalytically active solutions prepared by treating $[RhCl(C_2H_4)_2]_2$ with diphosphines and [Rh(norbornadiene)diphosphine]BF_4 with hydrogen (diphosphine = 1,3-bis(diphenylphosphino)propane (dppp) and isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)butane (diop)).

Although there has recently been considerable interest in asymmetric catalysis by rhodium complexes containing chiral chelating diphosphines such as isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)butane (diop) [1, 2], little has been done to elucidate the mechanism(s) of the catalytic reactions. Most commonly, the catalyst is generated in situ, either by substitution of the olefin in $[RhCl(olefin)_2]_2$ (olefin = C_2H_4, cyclooctene) by diphosphine [3], or by hydrogenation of the olefin of complexes of the type [Rh(diene)(diphosphine)]X (diene = norbornadiene (NBD), cyclooctadiene; X = ClO_4, BF_4) [4, 5]. In the case of catalytic hydrogenation of prochiral olefins, it has generally been assumed that both the nature of the active species in solution and the mechanism of hydrogen transfer are the same as for the well-studied monodentate phosphine systems [6, 7].

We [8, 9] and others [10—13] have recently drawn attention to the great utility of $^{31}P\{^1H\}$ NMR spectroscopy in the elucidation of the structures of rhodium—phosphine complexes in solution. Both ^{31}P chemical shifts and rhodium—phosphorus coupling constants can provide information concerning stereochemistry, coordination number and the *trans* influences of other ligands. We report here preliminary results of an investigation into the nature of the major species present in catalytically active solutions, of the types described above, with both 1,3-bis(diphenylphosphino)propane (dppp) and diop. The former was chosen as a model diphosphine because previous work [14, 15] has

shown that "ring strain" contributions to the ^{31}P NMR parameters of its complexes are relatively small, allowing correlations with data for monodentate phosphine systems to be made.

The various chemical species generated by treating $[RhCl(C_2H_4)_2]_2$ (I) with dppp and $[Rh(NBD)(dppp)]BF_4$ (II) with hydrogen in $(CD_3)CO$ are shown in Scheme 1.The corresponding $^{31}P\{^1H\}$ NMR data are listed in Table 1.



SCHEME 1

Addition of I to a deficiency of dppp (0.5 mol dppp/mol of I) resulted in the evolution of some ethylene and the formation of an orange solution exhibiting a doublet in the ^{31}P NMR spectrum at very low field (32.0 ppm) and with a relatively large rhodium—phosphorus coupling constant (187 Hz). On the addition of 0.75 mol dppp/mol I, there also appeared a second doublet, at slightly higher field, but with a very similar coupling constant. By analogy with data for compounds of the type $[RhCl(PR_3)_2]_n$ (n = 2 [10], 1 [12]), the ^{31}P NMR parameters are consistent with structures III and IV, in which the phosphorus atoms are *trans* to chloride ions. Lowering the temperature of IV to 223 K indicated no nonequivalence of the phosphorus atoms, suggesting a dimeric structure, but there is precedence for a monomeric structure [12]. Although hydrogen addition to IV (1 atm) did not occur, acetyl chloride does add to form $RhCl_2(COMe)(dppp)$ [16]. Hydrogenation of a solution of III, on the other hand, led to darkening and

TABLE 1

^{31}P CHEMICAL SHIFTS AND COUPLING CONSTANTS

Compound	δ (ppm) [a]	J(Rh—P) (Hz)
[Rh(NBD)dppp]BF_4 (II)	14.2	148
dpppRh(μ-Cl)$_2$Rh(C_2H_4)$_2$ (III) [b]	32.0	187
[RhCldppp]$_{1\ or\ 2}$ (IV)	30.3	184
[Rh(dppp)$_2$]Cl (V)	6.4	132
[RhO_2(dppp)$_2$]Cl (VI) [c]	15.0	122
	−13.8	85
cis-[RhH_2(dppp)$_2$]Cl (VII) [d]	17.0	99
	6.3	80
cis-[RhHCl(dppp)$_2$]Cl (VIII) [e]	1.9	90
[Rhdppp(acetone)$_2$]BF_4 (IX)	37.1	187
diopRh(μ-Cl)$_2$Rh(C_2H_4)$_2$ (X)	34.1	194
[RhCldiop]$_{1\ or\ 2}$ (XI)	31.8	191
[Rh(NBD)diop]BF_4 (XII)	15.3	153
[Rhdiop(acetone)$_2$]BF_4 (XIII)	38.4	195

[a] In $(CD_3)_2CO$ unless otherwise noted; all shifts relative to external 85% H_3PO_4, with positive δ meaning a downfield shift. [b] Proton NMR spectrum in $(CD_3)_2CO$ exhibits ethylene resonance at δ 2.8 ppm. [c] In CH_3OD; the spectrum is first order, consisting of a quartet of triplets at room temperature, with J(PP) 30 Hz. [d] In $CDCl_3$; the spectrum shows a second order A_2B_2X pattern, indicating a *cis*-dihydride with J(PP) 30 Hz. The proton NMR spectrum shows a complicated pattern at δ −8.6 ppm, with J(PH) 141 Hz (*trans* coupling). [e] On cooling to 203 K, an A_2M_2X pattern, consistent with the *cis*-HCl adduct is obtained; δ_A 12.3 ppm, δ_B −9.0 ppm, J(Rh—P_A) 90 Hz, J(Rh—P_B) 93 Hz, J(PP) 35 Hz. The proton NMR spectrum at room temperature is a sextet at δ −15.0 ppm, with J(Rh—H) ~ J(Rh—P) 13.5 Hz, consistent with the averaging of two sets of equivalent phosphorus atoms at ambient temperatures (cf. ref. 20).

precipitation of an ill-defined solid. As no new ^{31}P resonances were observed, the nature of the products of hydrogenation is not known.

Although addition of 1 mol dppp/mol I gives predominantly IV, excess dppp in $(CD_3)_2CO$ gives [Rh(dppp)$_2$]Cl (V), which was also prepared by treating $RhClCO(PPh_3)_2$ with excess dppp in benzene or by treating I with a deficiency of dppp in methanol [17]. The more polar, protic solvent seems to assist the displacement by chloride ion and the formation of the bis-dppp complex. Compound V adds oxygen, hydrogen and hydrogen chloride in solution to form the cationic species $[Rh(O_2)(dppp)_2]^+$ (VI), *cis*-$[RhH_2(dppp)_2]^+$ (VII) and the fluxional *cis*-$[RhHCl(dppp)_2]^+$ (VIII), none of which was successfully isolated pure, but all of which could be identified by their ^{1}H and ^{31}P NMR spectra (see Table 1).

Hydrogenation of II in $(CD_3)_2CO$ resulted in the appearance of a new doublet at very low field, attributable to the species IX, which presumably contains co-ordinated acetone. The low temperature spectrum indicated nonequivalence of the phosphorus atoms, perhaps because of BF_4^- coordination, or because of dimer formation via h^6-arene coordination of an aryl ring of one molecule to the rhodium atom of another [18]. Compound IX does not add a detectable amount of hydrogen, in contrast to the behaviour of similar rhodium complexes of monodentate phosphines [19], but in accord with the behaviour of IV. Addition of tetraphenylarsonium chloride to a solution of IX resulted in formation of IV, confirming the relationship between these compounds.

Results with diop appear to closely resemble those with dppp. For instance, complexes corresponding to III and IV, i.e. [(diop)Rh(μ-Cl)$_2$Rh(C_2H_4)$_2$] (X) and RhCl(diop) (XI) are formed in acetone and benzene, while [Rh(diop)(solvent)$_n$]BF_4

(XIII) is formed on hydrogenation of [(NBD)Rh(diop)]BF_4 (XII) in acetone. The fact that XI and XIII exist as different species in solution is consistent with observed variation of degree of asymmetric induction with anion [5]. In contrast to dppp, reaction of 2 mol of diop/mol of I in methanol does not yield detectable amounts of [$Rh(diop)_2$]Cl.

The nature of the species present when α-acetamidocinnamic acid is added to a hydrogenated solution of [Rh(NBD)(dppp)]BF_4 in methanol are rather ambiguous at present. Broadening of the ^{31}P resonance at 37.1 ppm occurs, consistent with formation of a species of the type [Rh(olefin)(solvent)dppp]$^+$. Clearly complexation occurs, but an understanding of the behaviour of the complex in solution must await further studies.

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References

1 H.B. Kagan, Pure Appl. Chem., 43 (1975) 401.
2 J.W. Scott and D. Valentine, Science, 184 (1974) 943.
3 H.B. Kagan and T.-P. Dang, J. Amer. Chem. Soc., 94 (1972) 6429.
4 R.R. Schrock and J.A. Osborn, J. Amer. Chem. Soc., 98 (1976) 4450.
5 D. Sinou and H.B. Kagan, J. Organometal. Chem., 114 (1976) 325.
6 J.A. Osborn, F.H. Jardine and G. Wilkinson, J. Chem. Soc. A, (1966) 1711.
7 J. Halpern, T. Okamoto and A. Zakhariev, J. Mol. Catal., 2 (1976) 65.
8 D.L. Egglestone and M.C. Baird, J. Organometal. Chem., 113 (1976) C25.
9 D.L. Egglestone, M.C. Baird, C.J.L. Lock and G. Turner, J. Chem. Soc. Dalton, (1977) 1576.
10 C.A. Tolman, P.Z. Meakin, D.L. Lindner and J.P. Jesson, J. Amer. Chem. Soc., 96 (1974) 2762.
11 A.R. Sanger, J. Chem. Soc. Dalton, (1977) 120.
12 H.L.M. Van Gaal and F.L.A. Van Den Bekerom, J. Organometal. Chem., 134 (1977) 237.
13 For a general review, see J.F. Nixon and A. Pidcock, Ann. Rev. NMR Spectrosc., 2 (1969) 346.
14 D.A. Slack and M.C. Baird, Inorg. Chim. Acta, 24 (1977) 275.
15 P.E. Garrou, Inorg. Chem., 14 (1975) 1435 and ref. therein.
16 D.A. Slack, D.L. Egglestone and M.C. Baird, J. Organometal. Chem., in press.
17 J. Chatt and B.L. Shaw, J. Chem. Soc. A, (1966) 1437.
18 J. Halpern, Second C.I.C.-A.C.S. Joint Conference, Montreal, 1977, abstract INOR 2.
19 R.R. Schrock and J.A. Osborn, J. Amer. Chem. Soc., 98 (1976) 2134.
20 J.S. Miller and K.G. Caulton, J. Amer. Chem. Soc., 97 (1975) 1067.