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KINETIC AND MECHANISTIC ASPECTS OF THE BINDING OF DIHYDROGEN BY BIS(DITERTIARYPHOSPHINE)RHODIUM(I) TETRAFLUOROBORATE COMPLEXES, AND ACTIVITY OF THE DIHYDRIDES FOR CATALYTIC ASYMMETRIC HYDROGENATION OF PROCHIRAL OLEFINIC ACIDS *

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Summary

The kinetics of the reversible binding of H_2 by solutions of the cationic bis(ditertiaryphosphine)rhodium(I) complexes $Rh(dppp)_2^+ BF_4^-$ and $Rh[(+)\text{-diop}]_2^+ BF_4^-$, where dppp = 1,3-bis(diphenylphosphino)propane and (+)-diop = 4*S*,5*S*-bis((diphenylphosphino)methyl)-2,2-dimethyl-1,3-dioxolane, are reported. Reversible formation of $RhH_2(dppp)_2^+$, monitored by the stopped-flow method, analyzes for the expected second-order forward reaction opposed by a first-order off-rate. Formation of $RhH_2(diop)_2^+$ proceeds, however, via a two-stage process which is interpreted in terms of intermediate solvated species containing monodentate diphosphine. Kinetic and spectroscopic studies on catalytic hydrogenation of the prochiral olefinic substrate, 2-methylenesuccinic acid, indicate a mechanism involving olefin coordination to the rapidly formed dihydride and subsequent hydrogen transfer; the (+)-diop system shows an unusual increase in optical yield of the *R*-2-methylsuccinic acid with temperature. Hydrogenation of olefinic acids with bis(diop) species is much slower than with comparable mono(diop) systems, but can lead to higher optical yields (e.g. up to 94% e.e. with (*Z*)-*N*-acetamidocinnamic acid).

Introduction

Complexes of rhodium(I) containing two chelating ditertiaryphosphine ligands, $Ph_2P(CH_2)_nPPh_2$, or chiral $n = 4$ analogues such as diop [1], are reactive towards

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the gas molecules H_2, O_2, CO and HCl [2–8], and have been shown to be catalytically active for hydrogenation of olefins [2,9–12] and aromatic nitro compounds [12], hydroformylation of olefins [13], and decarbonylation of aldehydes [5–8,12].

Early reports on very low hydrogenation activity for $Rh(dppe)_2^+$ [14,15] were consistent with the idea that such bis(diphosphine) chelate complexes were unlikely catalysts because of the difficulty in providing a vacant coordination site [16]. However, we have since shown that such complexes with larger ring sizes can have quite high activity and, in the case of $RhH(diop)_2$, kinetic data are consistent with the vacant site being generated by one of the diphosphine ligands becoming monodentate [2,5,11]. There are many cases where such "dangling" diphosphines within complexes have been characterized in the solid state [17,18]; the $[Rh(diop)(diop^\star)(CO)_2]Cl$ species is reasonably substantiated by spectroscopic data [19], although we were unable to isolate this as a pure compound [3].

Preliminary data indicated that the most active hydrogenation catalysts of the $Rh[Ph_2P(CH_2)_nPPh_2]_2^+$ ($n = 1$–4) series were the dppp ($n = 3$) and dppb ($n = 4$) complexes, together with the bis(diop) analogue [2]; these three systems were also the only ones that reacted reversibly with H_2 [3], and thus appeared suitable for kinetic and mechanistic investigations. This paper reports mainly kinetic data on the reactivity of the dppp and diop cations toward H_2 and on the activity of the latter for catalytic hydrogenation of the prochiral substrate 2-methylenesuccinic acid (eq. 1).

$$HO_2CCH_2C(=CH_2)CO_2H \xrightarrow{H_2} HO_2CCH_2\overset{\star}{C}H(CH_3)CO_2H \qquad (1)$$

The studies seem particularly appropriate for a volume dedicated to Professor J. Halpern on the occasion of his 60th birthday, because his very elegant work on the corresponding mono(ditertiaryphosphine) systems $Rh(dppe)S_2^+$ and $Rh(chiraphos)S_2^+$ (S = solvent) has contributed so greatly to an understanding of catalytic asymmetric hydrogenation [20,21].

Experimental

The primary rhodium source was $RhCl_3 \cdot 3H_2O$ (Johnson, Matthey Ltd.), and the tetrafluoroborates of $Rh(dppp)_2^+$ (**1**) and $Rh(diop)_2^+$ (**2**) and their corresponding dihydrides were synthesized as described previously [2,3]. The olefinic acid substrates (CP grade, Eastman or Fluka) were recrystallized before use. *N,N'*-Dimethylacetamide was purified by storing over CaH_2 under N_2 for long periods followed by distillation under reduced pressure. Toluene was refluxed with CaH_2, and n-butanol was refluxed with magnesium metal/iodine to remove traces of water. Matheson prepurified grade H_2 was passed through a Deoxo unit (Fisher) prior to use. The procedures used for following the rate of H_2-uptake at constant pressure and the work-up of the hydrogenation products for determining optical yields have been reported elsewhere [9,10].

The catalytic hydrogenations were usually carried out in a 2/1 volume mixture of ^{n}BuOH and toluene, which was convenient for solubility compatibility of catalyst and substrate. The solubility of H_2 in the mixed solvent at 15 °C was found to be 2.0×10^{-3} M atm^{-1}, Henry's Law being obeyed up to 1 atm; the solubility surprisingly increased with temperature, being 2.2, 2.5, and 2.9×10^{-3} M atm^{-1} at 20, 25 and 30 °C, respectively. The partial pressure of the solvent mixture increased from 5 Torr at 15 °C to 20 Torr at 30 °C. The solubility of H_2 in dma at 30 °C was 1.8×10^{-3} M atm^{-1}, Henry's Law again being obeyed; the vapour pressure of dma is negligible (1.0 Torr at 15 °C, 4.5 Torr at 40 °C [22]).

The reactions of the cations with H_2 to give the dihydrides were fast, and were studied using a thermostatted Durrum 110 stopped-flow apparatus equipped with a 2-cm light path cuvette. The average k_{obs} values were determined by monitoring absorption at the λ_{max} of **1** and **2** (412 nm, $\epsilon = 2.8 \times 10^3$ M^{-1} cm^{-1}, and 442 nm, $\epsilon = 3.6 \times 10^3$ M^{-1} cm^{-1}, respectively [2]; e.g. see Fig. 2 and 3). Pseudo first-order conditions were implemented by using low Rh concentrations (up to 10^{-4} M) with excess H_2 concentrations. The data were analyzed according to the standard first-order rate-law $\log(A_t - A_\infty) = \log(A_0 - A_\infty) - k_{obs}t$, where A_0, A_t and A_∞ are the solution absorbances at $t = 0$, time t, and completion of the reaction, respectively. A linear regression analysis was used to obtain k_{obs} from the $\log(A_t - A_\infty)$ vs. t plot. In the mixing chamber of the stopped-flow instrument, equal volumes of the Rh and H_2 solutions are mixed and thus the actual concentration of both reagents in the reaction solution is one-half that made up and transferred to the storage syringe.

The relatively slow loss of H_2 from $RhH_2(diop)_2^+$ was studied in a thermostatted Cary 15D spectrophotometer using a specially designed cell consisting of a 1-cm path length cell (into which the solid was weighed) attached by a side-arm to a reservoir bulb (containing solvent), fitted with a Teflon stopcock and an O-ring joint for attachment to a vacuum/gas-handling line [23]. Following a degassing of the apparatus by several freeze-pump-thaw cycles, argon was admitted prior to transferring the solvent to dissolve the dihydride. The growth of the $Rh(diop)_2^+$ peak at 442 nm was monitored during intermittent shaking; the low off-rates ($t_{1/2}$ ~ 30 min at 30 °C) were not governed by any diffusion control. The standard log (absorbance difference) vs. time plots (see above) gave linearity over at least three half-lives from which the first-order off-rate constant k_{-1} was readily evaluated. The dehydrogenation rate from $RhH_2(dppp)_2^+$ was much too rapid ($t_{1/2}$ of the order of seconds) to be studied by this technique, and was obtained from equilibrium stopped-flow data (see below).

Studies on the equilibrium constants for binding of H_2 were made in the described special optical cell by measuring the equilibrated spectra at several pressures of H_2. Since the spectrum of both reactant and product were measurable, estimation of K (see eq. 2) is straightforward [23].

Results and discussion

Reversible formation of the dihydrides

The *cis*-dihydride complexes $RhH_2(dppp)_2^+$ and $RhH_2(diop)_2^+$ are well characterized by analytical, conductometric and spectroscopic data [3], and their formation in solution may be represented initially in the simplest way by eq. 2.

$$Rh(P\text{–}P)_2^+ + H_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} cis\text{-}RhH_2(P\text{–}P)_2^+ ; \quad K = k_1/k_{-1} \qquad (2)$$

The forward reaction is accompanied by a fading of the orange solution of the reactant to the very pale yellow of the dihydride. The rate-law for process 2 is given in eq. 3 ($Rh = Rh(P{-}P)_2{}^+$), and a standard integrated form is given in eq. 4.

$$-\frac{d[Rh]}{dt} = \frac{d[RhH_2]}{dt} = k_1[Rh][H_2] - k_{-1}[RhH_2] \qquad (3)$$

$$\ln[A_0 - A_\infty / A_t - A_\infty] = (k_1[H_2] + k_{-1})t \qquad (4)$$

Under the stopped-flow conditions used, the $[H_2]$ is effectively constant and $k_{obs} = k_1' + k_{-1}$, where $k_1' = k_1[H_2]$.

The dppp system

The data for the dppp system gave excellent first-order rate plots (see Experimental) that were linear for at least three half-lives. The k_{obs} values at a fixed $[H_2]$ were independent of the initial [Rh] from $(0.25\text{–}2.0) \times 10^{-4}$ M, confirming the first-order dependence on [Rh]. Figure 1 shows a plot of k_{obs} vs.$[H_2]$ for data in dma at 30 °C. The linearity is in accord with the above analysis; the slope yields a k_1 value of 1.0×10^3 M^{-1} s^{-1}, and the intercept a k_{-1} value of ~ 0.45 s^{-1}. The ratio of these gives a kinetically determined equilibrium constant of ~ 2.2×10^3 M^{-1}. Figure 2 shows a static spectrophotometric titration technique for determining K directly; the $RhH_2(dppp)_2{}^+$ complex is found to be not quite fully formed at 1 atm H_2. A limiting spectrum, taken to be that of the dihydride, was obtained by cooling the solution under 1 atm H_2 to about 0 °C. The three intermediate spectra yield by standard analysis [23] K values of $(5.2 \pm 0.5) \times 10^3$ M^{-1}. The agreement with the kinetic value is considered reasonable; the static value is probably more reliable because of the technique that allows for somewhat better control of the H_2 concentrations. The number implies that the dihydride is about 90% formed under 1 atm H_2. As far as we are aware, the oxidative addition of H_2 to solutions of metal complexes is always favored thermodynamically at lower temperatures, i.e. the processes are invariably exothermic [25,26].

The kinetics were not studied in detail in other solvents, although the k_{obs} value in ^{n}BuOH at 380 Torr and 30 °C was about 20% higher than the value in dma;

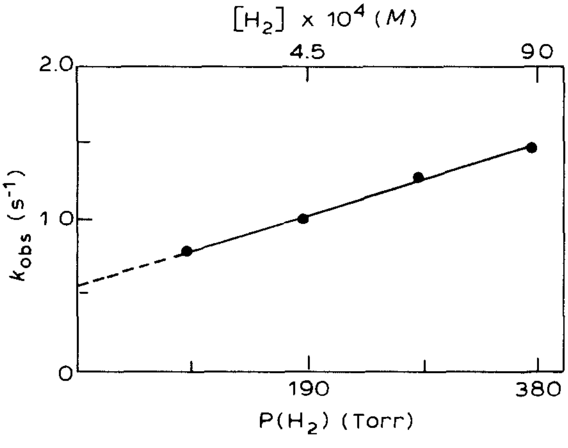


Fig. 1. Plot of observed pseudo-first-order rate constant vs. H_2 concentration (pressure) for reaction of $Rh(dppp)_2{}^+$ with H_2 in dma at 30 °C.

TABLE 1

KINETIC DATA FOR REVERSIBLE BINDING OF H_2 TO SOME d^8 GROUP VIII METAL COMPLEXES [a]

Complex	k_1 (M^{-1} s^{-1})	k_{-1} (s^{-1})	Ref.
Co(P=P)$_2^+$ [b]	1.2×10^5	negl.	28
Rh(P=P)$_2^+$ [b]	no measurable reaction		28
RhCl(PPh$_3$)$_3$ [c]	4.8	2.8×10^{-4}	29
RhCl(PPh$_3$)$_2$S [d]	$>7\times10^4$	–	29
Rh(dppm)$_2^+$ [e]	no measurable reaction		3
Rh(dppe)$_2^+$ [e]	no measurable reaction		3, 26, 30, tw
Rh(dppp)$_2^+$ [e]	1.0×10^3	0.45	tw
Rh(dppe)(olefin) [f]	50–100	see text	21
Rh(chiraphos)(olefin) [f]	1.6–130	see text	21
Rh(diop)$_2^+$ [h]	see text	7.7×10^{-4}	tw
Ir(P=P)$_2^+$ [b]	6.7×10^3	negl.	28
IrCl(CO)(PPh$_3$)$_2$ [i]	0.48–1.4	1.7×10^{-5}	25,31
Rh(dppb)$_2^+$ [g]	20?	$\sim10^{-3}$?	tw

[a] Rate constants refer to oxidative addition of H_2 (k_1), and reductive elimination from the dihydride (k_{-1}) at 25 °C, except for this work (tw) at 30 °C. [b] P=P represents *cis*-1,2-bis(diphenylphosphino)ethylene; in C_6H_5Cl. [c] In C_6H_6. [d] S = benzene solvent. [e] In dma; very similar behavior in ^{n}BuOH, CH_2Cl_2. [f] In MeOH; olefin = 1-hexene, alkyl(*Z*)-α-acetamidocinnamates. [g] In dma; see text. [h] In dma; $k_{-1} = 4.9\times10^{-4}$ s^{-1} in MeOH, CH_2Cl_2. [i] Solvents were C_6H_6, $C_6H_5CH_3$, C_6H_5Cl, dmf. In C_6H_5Cl at 30 °C, k_1 values (M^{-1} s^{-1}) for the *p*-tolyl and *p*-anisole analogs were 1.7 and 2.1, respectively, and for IrX(CO)(PPh$_3$)$_2$ 8.2 (X = Br), 430 (X = I) and 2.2×10^{-2} (X = NCO); k_{-1} values (s^{-1}) for IrH$_2$X(CO)(PPh$_3$)$_2$ were 1.1×10^{-5} (X = I) and 1.4×10^{-5} (X = NCO).

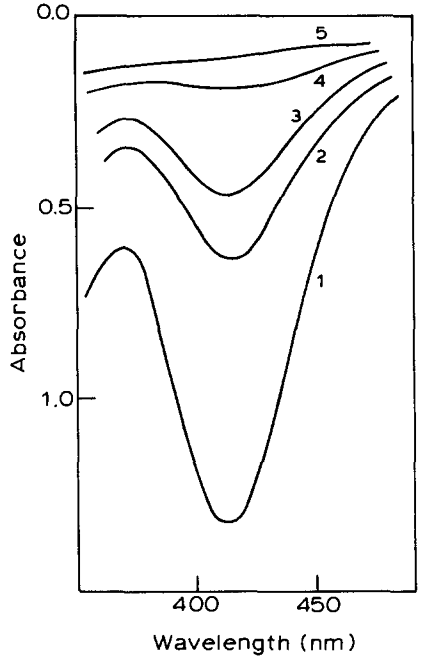


Fig. 2. Spectrophotometric determination of *K* for reversible binding of H_2 by Rh(dppp)$_2^+$ in dma at 30 °C; Curve 1 is spectrum of Rh(dppp)$_2^+$; 2–4 measured at 105, 190, and 760 Torr H_2, respectively; 5 measured at 760 Torr H_2 at 0 °C.

qualitatively, the reversible dihydride formation was similar in dma, ^{n}BuOH and $CHCl_3$, the off-rates all being 'fast'. The kinetics of reversible binding of CO and O_2 to $Rh(dppp)_2{}^+$ [3] are quantitatively very similar in all three solvents [27].

Table 1 lists kinetic data for reversible binding of H_2 to some d^8 transition metal complexes; the forward rates are generally in the stopped-flow regime, but the off-rates, except for $RhH_2(dppp)_2{}^+$, are slow (off-rate data are not available for the $Rh(P{-}P)(olefin)^+$ systems since the hydrides are transferred rapidly to the coordinated olefin within a catalytic hydrogenation cycle [20]). Indeed, to our knowledge, the k_{-1} value for the dppp system may be largest yet recorded for a dihydride complex.

Of interest, of the $Rh[Ph_2P(CH_2)_nPPh_2]_2{}^+$ cations the $n = 2$ and $n = 1$ species show no reactivity toward 1 atm H_2, while the $n = 4$ and diop cations react rapidly (stopped-flow time scale) but unfortunately give a mixture of products [3], some of which may be bi- or poly-nuclear (see below). Qualitatively, it appears that "reactivity" increases with n but, without knowledge of both on- and off-rates, no real conclusions can be drawn. More structural data are required before detailed discussion can be presented; solid state structures are not available for the dihydride cations, but within $Rh[Ph_2P(CH_2)_nPPh_2]_2{}^+$ species there is increasing distortion

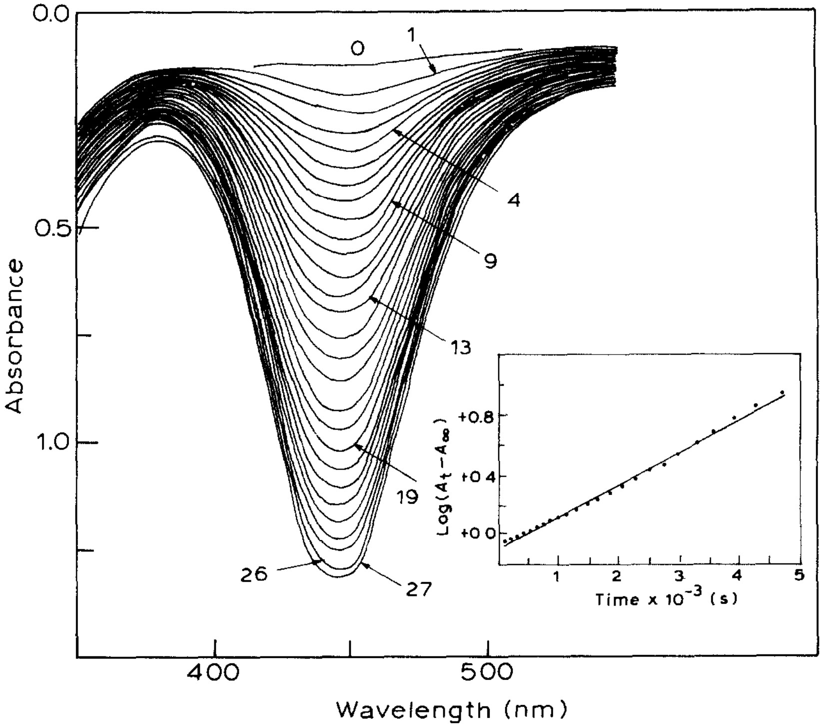
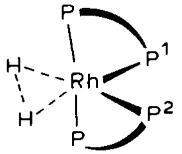


Fig 3. Dehydrogenation of $RhH_2(diop)_2{}^+$ in MeOH at 30 °C; spectrum 1 recorded at 90 s; 4, 9, 13, 19, 26 and 27 recorded at 415, 1020, 1675, 3000, 6100 and 13,500 s, respectively (time refers to monitoring at 442 nm). Spectra 0 and 27 are those of $RhH_2(diop)_2{}^+$ and $Rh(diop)_2{}^+$, respectively. Inset shows 1st order log plot for these data to determine k_{-1}. Reverse reaction $(+H_2)$ gives a spectrum close to 4 (within 50 s) which then slowly gives a spectrum close to 0 (~ 1200 s); compared to the spectra shown, there is a slight general increase in intensity over the 350–400 nm range during dihydride formation.

from close to square planar ($n = 2$ [32]) towards tetrahedral as n increases from 3 [33] to 4 [8]. The $Rh(diop)_2^+$ structure has not been reported, but it is likely to be similar to that of $RhH(diop)_2$ which can be viewed as an approximately tetrahedral $Rh(diop)_2$ unit containing the hydride *trans* to one of the phosphorus atoms [11]. Of more relevance, however, are the solution structures; low temperature ^{31}P NMR data for $Rh(dppp)_2^+$ in acetone have revealed an A_2B_2X pattern consistent with five-coordinate trigonal bipyramidal (tbp) species with solvent in an equatorial position [7], while $Rh(dppe)_2^+$ and $Rh(dppm)_2^+$ reveal equivalent P atoms consistent with essentially square planar or fluxional tbp solvated species [2,3,7]. The $n = 4$ (dppb) and diop cations at low temperature yield complex and as yet unassigned ^{31}P spectra that have been attributed to the presence of solvated and dimeric species, although both cations at room temperature give the simple doublet [2,3,7]. It is possible that as regards on-rates, the solvated tbp species are more reactive because a transition state such as **3** may be more readily attained by replacement of solvent with H_2, since geometry **3** may be viewed as distorted tbp (or distorted square pyramid) on considering H...H to occupy a single coordination site [31,34]. Five-coordinate d^8 complexes are usually considered to be unreactive toward H_2, but Chen and Halpern [35] have reported on higher reactivity of $IrCl(CO)(PMe_2Ph)_3$ (to give $[IrH_2(CO)(PMe_2Ph)_3]Cl$) compared to $IrCl(CO)(PMe_2Ph)_2$.



(3)

cis-Dihydride cations such as $RhH_2(P{-}P)_2^+$ have distorted octahedral geometry in solution [3] and, since hydride ligands prefer not to be in unfavored positions *trans* to a phosphine [36], a quite labile loss of H_2 is to be expected; indeed, this could be the major factor for the non-existence for the dppm and dppe dihydrides. Otsuka, Ibers and coworkers [37] have suggested a possible correlation between lability of H_2 loss from *cis*-$PtH_2[R_2P(CH_2)_nPR_2]$ square planar complexes and the P–Pt–P angle. The P^1–Rh–P^2 angle in a transition state such as **3**, as well as in the ground state dihydride, is also likely to be critical here.

It should be noted that more quantitative data for reactivity of the cationic species toward CO reveal rapid on-and off-rates for $Rh(dppm)_2^+$, no binding by $Rh(dppe)_2^+$, a rapid on-rate and slow off-rate for $Rh(dppp)_2^+$, and formation of a mixture of products, including a dinuclear species with bridging phosphine $[Rh(dppb)(CO)_2]_2(\mu\text{-dppb})$, with $Rh(dppb)_2^+$ [3,5,7,12]; there are no obvious simple reactivity patterns, even allowing for possible differences in solution structures. The rôle played by intermediates containing monodentate diphosphines may be more important. Evidence for such species is given in the Introduction, and findings on reactivity of the $Rh(dppb)_2^+$ and $Rh(diop)_2^+$ with CO, particularly reaction stoichiometry (1.3–1.7 mol CO per Rh) together with isolated dimeric species containing bridging diphosphine [3,5,7], necessarily require their involvement, although ^{31}P NMR reveals no evidence for their presence. It should be noted also that these cations obeys Beer's Law at their visible absorption maximum from 10^{-3}–10^{-4}

M, and there is no evidence (at least at 20 °C) for the presence of other species. Kinetic data on the reaction of H_2 with $Rh(diop)_2^+$ indicate, however, a rôle for solvated species (see below).

The dppb and diop systems

The simple equilibrium of eq. 2 does not account for data obtained for the dppb and diop systems. Thus the dppb system in MeOH or dma shows a gas-uptake H_2/Rh stoichiometry of ~ 0.6 that is essentially independent of H_2 pressure; a simple equilibrium would give a higher stoichiometry with increasing pressure. Further, an isolated BF_4^- salt, although clearly containing $[RhH_2(dppb)_2]^+$, was contaminated with other unidentified species [3]. Limited stopped-flow data for the on-rate analyzed for a first-order dependence on Rh and an approximate first-order dependence on H_2; the off-rate measured spectrophotometrically using an in-situ formed dihydride showed first-order behavior for about one half-life. The rate constants are given in Table 1, but there are clearly other species present in the reactant solutions.

A more detailed study was undertaken with the diop system, since a pure, well characterized dihydride could be isolated and thus an equilibrium such as eq. 2 could be approached from either side. Figure 3 shows typical dehydrogenation data using weighed samples of synthesized $RhH_2(diop)_2^+$; the reactions are strictly first-order (see inset plot) and the k_{-1} rate constants were identical in MeOH and CH_2Cl_2 and about 50% higher in dma (see Table 1). Addition of H_2 to $Rh(diop)_2^+$ at 25 °C (solid sample, or in-situ via $RhH_2(diop)_2^+$) results in rapid decrease in intensity of the 442 nm band (orange → yellow in ~ 50 s), followed by a further relatively slow decrease to give a steady spectrum after ~ 20 min (Fig. 3). The dihydride formation was studied quantitatively in dma at 30 °C using stopped-flow spectrophotometry, and Fig. 4 shows that attempted analysis according to the standard pseudo first-order log plot (eq. 4) is not correct; indeed, the optical density data overall could not be analyzed for any satisfactory (fractional or integral) dependence on Rh; very similar and reproducible data were obtained in CH_2Cl_2, ^nBuOH, and MeOH. Of importance, the spectral changes for the forward and reverse reactions were independent of added diop.

The linear part of Fig. 4 after about 50 s refers to the slower reaction and clearly shows a first-order process which can be defined in terms of a pseudo first-order rate constant k''. Monitoring the first 20 s or so by stopped-flow also yields an essentially linear plot for log $(A_t - A_\infty)$ vs. t (see initial part of Fig. 4), and this can be defined by the rate constant k'. The overall data analyze well for a process involving two pseudo first-order steps. Values of k' and k'' are given in Table 2.

The observed behavior could result from (a) the presence of two species not in rapid equilibrium, with essentially the same spectrum, reacting with different rates (cf. work from this laboratory on binding of CO by ruthenium-substituted myoglobin [38]) or (b) a reaction involving two consecutive first-order processes (reaction of a single species reacting via two different first-order processes gives an overall first-order loss of reactant [24], as does first-order loss for each of two species that are in rapid equilibrium). It seems impossible that situation (a) prevails since the $Rh(diop)_2^+BF_4^-$ salt is very well characterized (except for X-ray analysis) [3] and, if other solvated (with or without dangling diop) or nucleated species (via Rh to phenyl [36] or oxygen interactions) exist, their presence in solution is expected to be

TABLE 2

STOPPED-FLOW KINETIC DATA FOR REACTION OF $Rh(diop)_2^+$ WITH H_2 IN SOLUTION AT 30 °C

Solvent	$P(H_2)$ (Torr)	$k' \times 10^2$ (s^{-1})	$k'' \times 10^3$ (s^{-1})
dma	380	9.2	6.6
dma	280	9.2	4.3
dma	190	7.7	5.4
dma	95	8.3	4.3
MeOH	320	8.2	4.3
MeOH	225	8.1	4.1
MeOH	130	7.4	3.3
MeOH	~ 35	~ 6.6	~ 2.2
^{n}BuOH	375	9.2	5.1
CH_2Cl_2	280	9.9	3.8

governed by rapid equilibria (see below). Situation (b) is thus favored, and as the k' value is essentially independent of H_2 (Table 2), the fast process ($t_{1/2}$ is of the order of seconds) is attributed to reaction via a solvolysis step; the intermediate formed **4** must have an absorption close to that of the dihydride product (i.e. very little absorption at 442 nm, see Fig. 3), and thus the process outlined in eq. 5 provides a reasonable rationale particularly since the processes are independent of free [diop] and none is detected (S = solvent; diop* = monodentate diop):

$$\underset{(\mathbf{2})}{Rh(diop)_2^+} + S \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} Rh(diop)(diop^*)S^+ \overset{H_2,k_3}{\rightleftharpoons} \underset{(\mathbf{4})}{RhH_2(diop)(diop^*)S^+} \qquad (5)$$

$$\mathbf{4} \overset{k''}{\rightleftharpoons} RhH_2(diop)_2^+ + S \qquad (6)$$

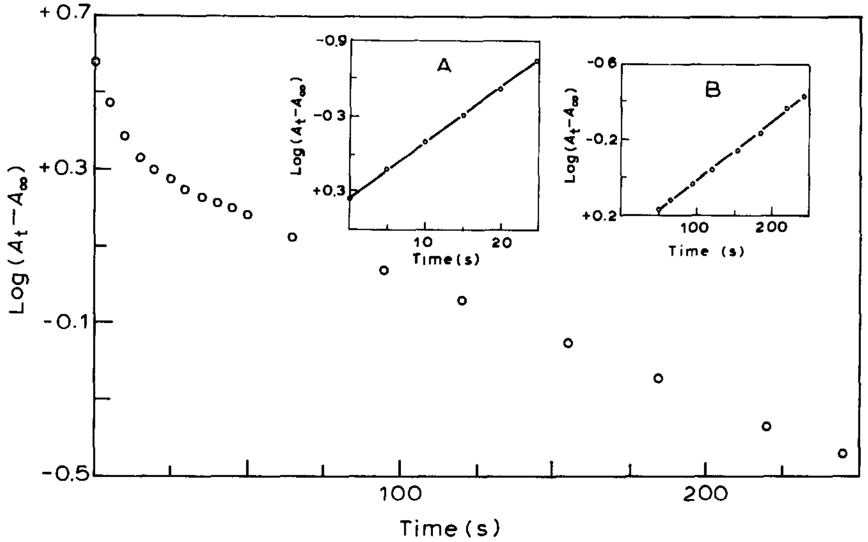


Fig. 4. Attempted 1st-order log plot for reaction of H_2 with $Rh(diop)_2^+$ in dma at 30 °C. Insets A and B show analysis for initial faster (k') and second slower (k'') steps.

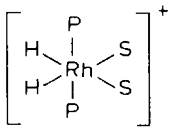
A steady state treatment for the diop* species means that the measured k' equals $k_2k_3[\mathbf{2}][H_2]/(k_{-2}+k_3[H_2])$, while zero-order dependence on $[H_2]$ implies that $k_3[H_2] \gg k_{-2}$ and that $k' \simeq k_2$. The markedly small dependence of k' on solvent (varying from weak to strong donors [39]) suggests that the solvolysis step is governed largely by dissociation of one end of the diphosphine ligand. Formation of five-coordinate tbp solvates, as with $Rh(dppp)_2^+$, is presumably sterically prevented with diop, and indeed this appears to give rise to the more complex kinetics of the latter system.

The slower k'' step then has to be associated with formation of $RhH_2(diop)_2^+$ from **4**, eq.6. As outlined in eqs. 5,6, this step should also be zero order in $[H_2]$; the data in dma are reasonably consistent with this, while the data in methanol (Table 2) indicate about a $\frac{1}{3}$rd order. A slight fractional order could be accounted for, at least qualitatively, if the k_3 step is written reversibly (with $k_3[H_2] \gg k_{-3}$), and indeed this has to be so as well as for the k'' step, since the overall reaction is reversible (law of microscopic reversibility). Nevertheless the off-rate is relatively slow, and the forward process, as written in eqs. 5,6 is a good approximation. The kinetic data are not extensive or accurate enough to allow for analysis incorporating the reversible contributions. The solvent effect on k'' is still very small, again implying a minor role for the solvent in the transition state. The measured k_{-1} off-rate (which as noted shows little solvent dependence) most likely refers to the reverse of the k'' step. The rate constants evaluated at 30 °C imply that within the diop seven-membered chelate rings, the ring opening dissociation (k_2) is faster than the chelate-forming ring closure (k''), which is in constrast to the usual behavior of five-membered rings [40]. That the ring opening for $RhH_2(diop)_2$ ($k_{-1} = 7.7 \times 10^{-4}$ s^{-1}) is slower than for $Rh(diop)_2^+$ ($k_2 \sim 9.2 \times 10^{-2}$ s^{-1}) is consistent with the relative ligand lability properties of rhodium(III) and rhodium(I) complexes [41].

A kinetic role for solvated species in a closely related system has been noted by Brown et al. while using ^{31}P NMR to study hydrogenation of cationic (nbd)(bisphosphine)rhodium(I) complexes [42]. For example, treatment of **5a** with H_2 removes the diene as norbornane and gives only **6a**; removal of H_2 then generates small amounts of **7a**. In contrast, addition of H_2 to **5b** gives initially only **7b** which

$Rh(nbd)P_2^+$

(**5**)



(**6**)

cis-$RhP_2S_2^+$

(**7**)

(a, L = PPh_3, b, L = $P(o\text{-}MeC_6H_4)PhMe$; S = MeOH)

then slowly converts to **6b**. The data demonstrate mainly the sensitivity of the equilibrium between **6** and **7** to the nature of the phosphine but indicate that solvation occurs prior to oxidative addition of H_2, as in eq. 5.

It should be noted that the stoichiometry of the H_2 : Rh rapid gas-uptake for our diop system was consistently measured as 0.80 ± 0.05; this was essentially independent of rhodium concentration and H_2 pressure, and so the somewhat low value, as with the dppb system, is not a function of the equilibrium position of the reaction. Some formation of binuclear species perhaps containing 1.0 H_2 per dimer is indicated from the stoichiometry, and such species containing bridging diphosphine could be readily formed via the diop* species postulated in eq. 5; the kinetic analysis presented would probably be insensitive to their degree of formation at the conditions used. The ^1H and ^{31}P {^1H} NMR spectra at room temperature of the isolated or in situ *cis*-$RhH_2(diop)_2{}^+$ species are quite consistent with the presence of this single compound, as is the room temperature ^{31}P spectrum of $Rh(diop)_2{}^+$ [3]; at lower temperatures, where nucleation might be favored, the ^{31}P NMR of $Rh(diop)_2{}^+$ is extremely complex [2] (cf. Fig. 4 of ref. 8) and it seems almost certain that diphosphine-bridged dimers are present.

Catalytic hydrogenation of prochiral olefinic acids

Despite the non-trivial but interesting solution behavior of the $Rh(diop)_2{}^+/H_2$ system, its use for catalytic hydrogenation of 2-methylenesuccinic acid (MSA) (eq. 1) reveals straightforward kinetics and a good picture of the overall mechanism. The important feature of reaction 2 for the diop system is that the forward reaction is essentially complete within about 200 s using 1 atm H_2 at ambient temperatures, while the dehydrogenation is relatively slow; this means that the dihydride is rapidly and fully formed in solution above ~ 150 Torr.

The hydrogenation was studied in 2 : 1 ^{n}BuOH/toluene from 15–30 °C. Figure 5 shows a typical H_2-uptake plot at the conditions noted; the initial faster uptake slows down somewhat, and the hydrogenation rates were measured in the subsequent linear region during the first 20% of the reaction over the following concentration ranges (*M*): $Rh(diop)_2{}^+$ (**2**), $(0.5–2.5) \times 10^{-3}$; MSA, (0.04–0.2); H_2, $(0.36–2.0) \times 10^{-3}$, i.e. 145–750 Torr. On adding 0.2 *M* MSA (or 1-hexene) to solutions of **2** under Ar, there are essentially no spectral changes in the 450 nm region (cf. Fig. 3) over the time-scale of the catalytic hydrogenation experiments; there is a slight decrease in intensity on leaving the solution for several hours but these changes also occur if succinic acid is used instead of MSA. Thus **2** does not bind the olefinic substrate. Addition of diop to **2** (which obeys Beer's Law, see above) has no effect on the UV/VIS spectrum and indeed also prevents the very slow reaction noted with

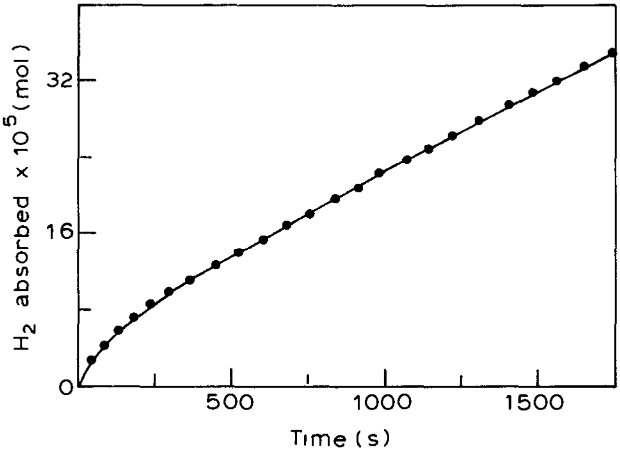


Fig. 5. H_2-uptake plot for hydrogenation of MSA; $[Rh] \approx 1.0 \times 10^{-3}$ *M*, [MSA] = 0.2 *M*, H_2 = 750 Torr, in 5 ml ^{n}BuOH/toluene (2 : 1) at 15 °C.

the carboxylic acids (possibly oxidative addition to give a carboxylato(hydrido)-rhodium(III) species [3]).

The kinetic data from the linear rates are summarized in Fig. 6A, 6B and 7. The rates were strictly first-order in Rh (Fig. 6A), and were zero-order in H_2 over the range studied (Fig. 6B). The dependence on MSA went from first-order at lower concentrations to considerably less than first-order at 0.2 *M* (Fig. 7). A quite remarkable inhibition of rate occurred on addition on diop; on adding 0.2×10^{-4} *M* diop to the systems asterisked in Fig. 7 (added diop/Rh = 1/5), the hydrogenation was completely inhibited. For conditions first-order in MSA, the visible spectrum

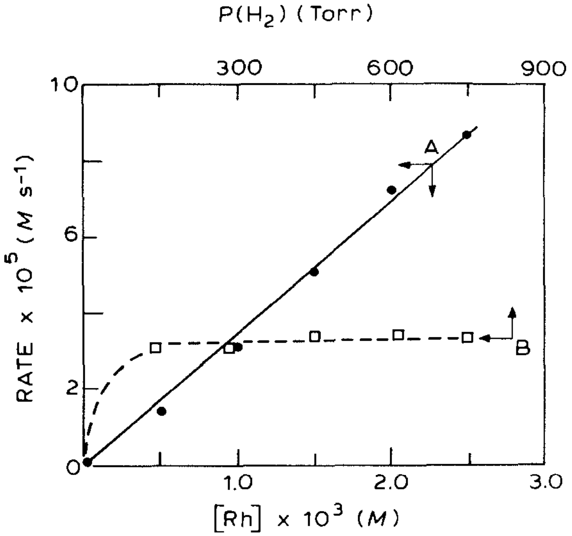


Fig. 6. A. Dependence of hydrogenation rate on [Rh]; [MSA] = 0.1 *M*, H_2 = 750 Torr, 15 °C. B. Dependence on [H_2]; [MSA] = 0.1 *M*, [Rh] = 1.0×10^{-3} *M*, 15 °C.

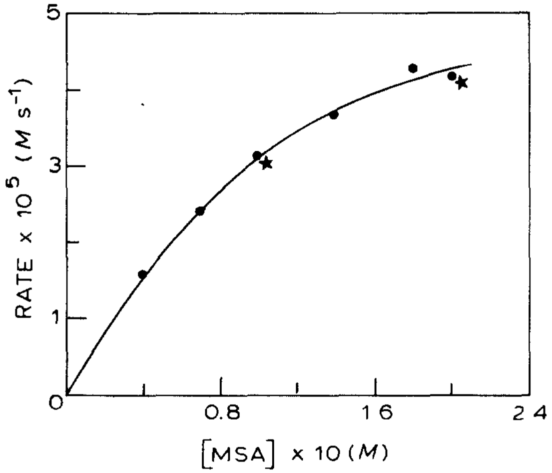
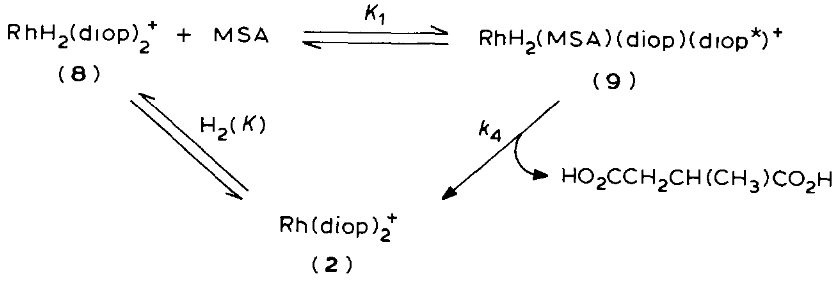


Fig. 7. Dependence of hydrogenation rate on [MSA]; [Rh] = 1.0×10^{-3} *M*, H_2 = 750 Torr, 15 °C.

during hydrogenation corresponded to that of $RhH_2(diop)_2^+$ (Fig. 3), while at higher [substrate] a slight increase in intensity in the 350–400 nm region was evident. Use of the $RhH_2(diop)_2^+ BF_4^-$ salt in place of **2** gave identical kinetic data.

Ignoring the effect of added diop, all the data are consistent with the catalytic "hydride route" [43] outlined in eq. 7.



(7)

Since K, the overall relatively rapid equilibrium for the reactions given in eqs. 5 and 6, is large (i.e. [**8**] ≫ [**2**]), the rate-law is independent of $[H_2]$, and is given by eq. 8, which is consistent with the measured dependences on [MSA] and total rhodium, $[Rh_T]$.

$$\text{Rate, } \frac{-d[H_2]}{dt} = K_1k_4[\mathbf{8}][MSA] = \frac{K_1k_4[Rh_T][MSA]}{1 + K_1[MSA]} \tag{8}$$

The validity of this rate-law is confirmed by an inverse plot of $Rate^{-1}$ vs. $[MSA]^{-1}$, according to eq. 9 (Fig. 8); measurement of the slope and intercept leads to a K_1 value of $\sim 6\ M^{-1}$ and a k_4 value of $\sim 0.08\ s^{-1}$ at 30 °C.

$$\frac{1}{Rate} = \frac{1}{K_1k_4[RhT]} \cdot \frac{1}{[MSA]} + \frac{1}{k_4[Rh_T]} \tag{9}$$

The vacant site necessary for coordination of MSA to **8** is considered to be provided by a diop ligand becoming monodentate. The saturated product would be formed from **9** by consecutive hydride transfers, either one being the rate determining step (eq. 10).

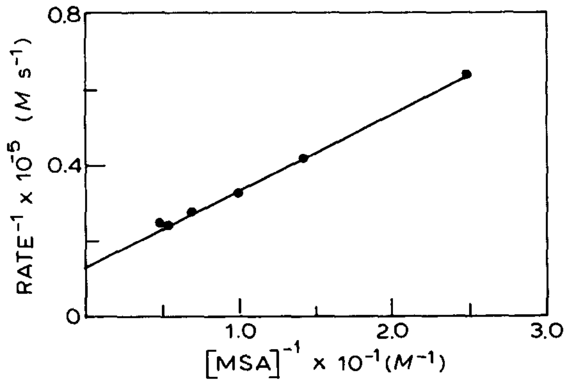


Fig. 8. Plot of $Rate^{-1}$ vs. $[MSA]^{-1}$ for the data of Fig. 7 according to eq. 9.

$$\begin{array}{ll} \mathbf{9} \rightarrow \mathrm{RhH(alkyl)(diop)(diop^{\star})\ or\ RhH(alkyl)(diop)_2} & (10) \\ \qquad\qquad\qquad \Big\downarrow \qquad\qquad \mathbf{(10)} & \\ \qquad \mathrm{Rh(diop)_2^{+} + saturated\ product} & \end{array}$$

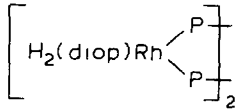
At lower [MSA] (first-order), the rhodium is present entirely as **8**, as required by the mechanism; with increasing [MSA] (becoming < first-order) the concentration of **9** (or **10**) increases. Indeed, if zero-order were reached (cf. Fig. 7), the limiting rate-law $k_4[\mathrm{Rh_T}]$ should hold and all the rhodium should be present as **9** (or a hydridoalkyl such as **10**). The UV/VIS spectral changes at higher [MSA] indicate the presence of some new species and the estimated K_1 value is of the right order of magnitude for such changes; however, attempts to use NMR to study the species have proved fruitless (see above). Halpern's group [20,21] have shown in closely related catalytic $\mathrm{Rh(P{-}P)S_2^{+}}$ systems (P–P = dppe or chiraphos, S = MeOH) that the rate-determining step can become hydride transfer within a hydridoalkyl that is the analog of **10** with one diop (or diop*) replaced by a solvent molecule.

At conditions close to first-order in [MSA], when the rate is given by $K_1k_4[\mathrm{Rh_T}][\mathrm{MSA}]$, the linear rates $(\times 10^5)$ at $[\mathrm{Rh_T}] = 10^{-3}$ M, $[\mathrm{H_2}] = 2 \times 10^{-3}$ M, and $[\mathrm{MSA}] = 0.1$ M, were 3.3, 5.5, 7.5 and 13.6 M s^{-1} at temperatures of 15, 20, 25 and 30 °C, respectively; these data give a good Arrhenius plot which yields the "activation" parameters $\Delta H^{\neq} = 68 \pm 5$ kJ mol^{-1} and $\Delta S^{\neq} = -16 \pm 12$ J mol^{-1} K^{-1}. The values refer to the K_1k_4 term and represent the addition of the thermodynamic and activation parameters for the step incorporated by the K_1 and k_4 constants.

The marked inhibition by added diop is not accounted for by the mechanism (eq. 7). A qualitative explanation might appear to be available by invoking reaction 11 instead of the K_1 equilibrium of 7. However, this leads to the rate-law $K_1k_4[\mathrm{Rh_T}][\mathrm{MSA}]/([\mathrm{diop}] + K_1[\mathrm{MSA}])$ and requires that, at conditions first-order in [MSA], the Rh dependence should become fractional (approaching half-order), since the [diop] term in the above rate-law would increase with increasing $\mathrm{Rh_T}$; this is not the case.

$$\mathrm{RhH_2(diop)_2^{+} + MSA \overset{K_1}{\rightleftharpoons} RhH_2(MSA)(diop)^{+} + diop} \qquad (11)$$

Formation of catalytically inactive $\mathrm{RhH_2(diop)(diop^{\star})_2^{+}}$ is a possibility (cf. eq. 5), but this cannot account for complete inhibition at added diop/Rh = 1/5, since at least $\frac{4}{5}$th of the activity should still remain. A tentative suggestion is the formation of inactive dimeric (or polymeric) species such as **11** containing bridging diop ligands;



(11)

in principle, a very slight excess of added diop could initiate complete dimerization to inactive species via formation of small amounts of $\mathrm{RhH_2(diop)(diop^{\star})_2^{+}}$. It should be recalled that the kinetics of the $\mathrm{Rh(diop)_2^{+}/H_2}$ system were unaffected by addition of diop, but this does not rule out formation of **11**. Spectroscopically and chemically (at least in terms of loss of $\mathrm{H_2}$) **11** could be very similar to **8**.

TABLE 3

ASYMMETRIC HYDROGENATIONS CATALYZED BY Rh[(+)-diop]$_2^+$ BF_4^- [a]

Substrate	Temperature (°C)	Product (% e.e.)	Reaction time [b]
MSA	15	$R(+)$, 19	8 h
MSA	30	$R(+)$, 37	2 h
MSA	60	$R(+)$, 50	20 min
MSA	80	$R(+)$, 52	15 min
MSA [c]	80	$R(+)$, 56	45 min
CA [d]	70	$R(+)$, 6	1.5 d
CA [c,d]	70	$S(-)$, 6	3 d
AAA [d,e]	30	$S(-)$, 70	16 h
AAA [d]	60	$S(-)$, 73	2 h
ACA [d,e]	80	$S(+)$, 94	7 d
ACA [c,f]	80	$S(+)$, 86	6 d
PAA [d]	50	$R(-)$, 41	2 d
MCA [f]	70	[g]	–

[a] At 760 Torr H_2; in 2:1 ^{n}BuOH/toluene with $[Rh] = 10^{-3}$ *M*, and [substrate] = 0.3 *M*, unless stated otherwise; MSA = 2-methylenesuccinic acid, $HO_2CCH_2C(CO_2H)=CH_2$; CA = citraconic acid, *cis*-$CH_3C(CO_2H)=CH(CO_2H)$; AAA = *N*-acetamidoacrylic acid, $H_2C=C(CO_2H)(NHCOCH_3)$; ACA = (*Z*)-*N*-acetamidocinnamic acid, $PhCH=C(CO_2H)(NHCOCH_3)$; PAA = α-phenylacrylic acid, $H_2C=C(CO_2H)Ph$; MCA = *E*-α-methylcinnamic acid, $PhCH=C(CO_2H)CH_3$. [b] Time for > 90% conversion of substrate, unless stated otherwise. [c] In dma. [d] $[Rh] = 2.0 \times 10^{-3}$ *M*. [e] [substrate] = 0.15 *M*. [f] $[Rh] = 6.0 \times 10^{-3}$ *M*. [g] <10% reaction in 5d.

Unfortunately we have been unable to obtain any evidence for such aggregation that we were also forced to invoke for catalytic hydrogenation using $RhH(diop)_2$ [11]. That these larger diphosphines tend to form bridged dimeric complexes is, however, well documented (see above and refs. 5,8,10,44).

The optical purity of the 2-methylsuccinic acid obtained in a reaction under conditions of Fig. 5 was ~ 20% (*R*), although by varying the conditions high optical yields have been obtained with other prochiral olefinic acid substrates. Table 3 summarizes some data for asymmetric hydrogenations catalyzed by Rh[(+)-diop]$_2^+$ BF_4^-; very similar data were obtained for all the substrates using the dihydride as catalyst. The 94% e.e. *S*(+)-*N*-acetylphenylalanine obtained from acetamidocinnamic acid is among the highest recorded for this substrate, and is higher than that obtained with solvated rhodium mono(diop) systems (up to 85% e.e.) [45]. The 73% e.e. recorded for the acetamidoacrylic acid substrate is the same as that sometimes attained with a mono(diop) system (42–73%) [46–48]. However, the mono(diop) systems invariably operate with much faster rates [45]. The chirality induced in the product (*R* or *S*) is the same whether the mono- or bis-(diop) catalysts are used, as long as similar solvent systems (2 : 1 alcohol/aromatic) and the same diop chirality are used [45,49]. This is an important point because the former operate by an unsaturate route (substrate binding prior to reaction with H_2) in contrast to the hydride route of the latter. The data imply that the dihydrido(olefin) intermediates formed by either route lead to the same configuration-determining step. It has been suggested that the two routes could give rise to different enantioselectivity [48,50].

The methylenesuccinic acid hydrogenation gives greater optical induction with increasing temperature, the effect levelling off at ~ 80 °C. Such a trend is unusual [51], and might reflect dissociation of a diop ligand at the higher temperatures to give a more effective mono(diop) catalyst for this substrate. The faster rates were obtained with the least sterically hindered disubstituted olefins containing terminal $=CH_2$ groups.

The marked difference in reactivity toward (Z)-N-acetamidocinnamic acid (effectively hydrogenated with high e.e.) and (E)-α-methylcinnamic acid (essentially unreactive) implies a role for the -$NHCOCH_3$ group; coordination via the amide and olefinic groups in related substrates is well documented [20,48]. While the suggested intermediate such as **9** allows for coordination via the olefinic group only, a RhH(alkyl)(diop)(diop*) species can also accommodate the alkyl as a chelated substrate, and the tendency to chelate could promote the first hydride transfer. It is this step that determines the chirality of the final product, since the final reductive elimination step (eq. 10) occurs with retention of configuration at the metal-bonded carbon [26]. Preferential coordination of one olefinic face of the substrate and/or a kinetically preferred hydrogen transfer to one face within an intermediate such as **9** is required for asymmetric hydrogenation via a catalytic hydride route of the type suggested here. In a study of an unsaturate type of system, Halpern et al. have shown that optical induction can result from a preferential kinetic attack by H_2 on one of a pair of diastereotopic rhodium/chiral phosphine/prochiral substrate species [20].

The hydrogenations were faster in BuOH/toluene than in dma but the optical inductions, ignoring the low values with citraconic acid, were essentially the same, and this seems reasonable in that solvated species are not invoked in the suggested catalytic route; quite marked solvent dependence have been noted, however, using solvated $Rh(diop)^+$ catalysts [49]. Unlike some of these [52,53], the $Rh(diop)_2{}^+$ system under corresponding conditions was completely unreactive toward prochiral (or achiral) saturated ketones ($CH_3COC_2H_5$, CH_3COPh), presumably because the donor carbonyl group is too weak to establish an effective equilibrium such as the K_1, in eq. 7.

Concluding remarks

The reactivities of $Rh[Ph_2P(CH_2)_nPPh_2]_2{}^+$ species ($n = 1$–4) and the diop analog toward H_2 in solution have been studied, and the factors governing both the on- and off-rates considered. Rapid dihydride formation by the $Rh(diop)_2{}^+$ complex is remarkable in that the rate is essentially independent of H_2 concentration, and the behavior is rationalized in terms of the intermediacy of solvated species containing monodentate-bound diphosphine ligand. The $Rh(diop)_2{}^+$ systems are effective for asymmetric hydrogenation of prochiral olefinic acids via a hydride route, in contrast to the unsaturate route commonly followed by corresponding 1 : 1 tertiarydiphosphine/Rh catalysts. Intermediates containing a dangling diop are again invoked. Indirect evidence suggests that solutions of the $n = 4$ and diop cations contain small amounts of nucleated species, possibly diphosphine-bridged dimers.

Acknowledgements

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1 Abbreviations used: dppm = bis(diphenylphosphino)methane, dppe = 1,2-bis(diphenylphosphino)-ethane, dppp = 1,3-bis(diphenylphosphino)propane, dppb = 1,4-bis(diphenylphosphino)butane, (−)-chiraphos = 2*S*,3*S*-bis(diphenylphosphino)butane, (+)-diop = 4*S*,5*S*-bis((diphenylphosphino) methyl)-2,2-dimethyl-1,3-dioxolane, diop* = monodentate, 'dangling' diop, dma = *N*,*N*'-dimethylacetamide, dmf = dimethylformamide, nbd = norbornadiene; for olefinic acid substrates, see Table 3, footnote *a*.
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