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# CATIONIC RHODIUM HYDROGENATION CATALYSTS CONTAINING CHELATING DIPHOSPHINE LIGANDS: EFFECT OF CHELATE RING SIZE

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## Summary

Earlier studies on the [(1,2-bis(diphenylphosphino)ethane)rhodium]$^+$-catalyzed hydrogenation of 1-hexene and methyl-(*Z*)-α-acetamidocinnamate have been extended to catalysts containing larger chelating diphosphine ligands, i.e., $Ph_2P(CH_2)_nPPh_2$, where $n = 3$, 4 and 5. Comparisons include measurements of equilibrium constants for the binding of the olefinic substrates to the catalysts and of the catalytic hydrogenation rates. Some related measurements also are reported for the corresponding catalyst systems containing the chiral ligand, 4R,5R-bis(diphenylphosphinomethyl)-2,2-dimethyldioxalane (DIOP) and non-chelating $PPh_3$ ligands.

## Introduction

We have previously described the hydrogenation of olefinic substrates, including 1-hexene and methyl-(*Z*)-α-acetamidocinnamate (MAC), using cationic rhodium phosphine catalysts, notably containing the chelating diphosphine ligand 1,2-bis(diphenylphosphino)ethane [$Ph_2P(CH_2)_2PPh_2$, abbreviated DIPHOS-2] and chiral derivatives thereof [e.g., $Ph_2PC^*H(CH_3)C^*H(CH_3)PPh_2$, CHIRAPHOS] [1]. Starting with the catalyst precursor [Rh(DIPHOS-2)(NBD)]$^+$ (NBD = norbornadiene) the catalyst generation step in methanol (S) is described by eq. 1 and the essential mechanism of alkene hydrogenation by eq. 2 and 3. At ambient temperatures and $H_2$ pressures, the first step of eq. 3, i.e., the oxidative addition of $H_2$ to [Rh(DIPHOS)(⟩C=C⟨)]$^+$, is rate-determining and the rate-law, accordingly, is described by eq. 4. In the case of [Rh(DIPHOS-2)(MAC)]$^+$ the final reductive elimination step became rate-determining at low temperatures ($< -40°C$) so that the hydridoalkyl intermediate, [RhH(⟩C–C⟨H)(DIPHOS-2)]$^+$ (I), could be intercepted and the rate constant $k_4$ directly determined [1d]. In the case of the substrate MAC the oxygen atom of the amide group also is coordinated to the Rh atom in the

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intermediate olefin and hydridoalkyl complexes (structure I).

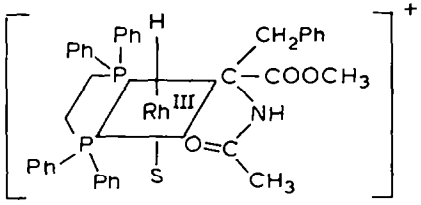
$$[Rh(DIPHOS)(NBD)]^+ + 2H_2 \xrightarrow{fast} [Rh(DIPHOS)S_2]^+ + \text{norbornane} \quad (1)$$

$$[Rh(DIPHOS)S_2]^+ + \rangle C{=}C\langle \overset{K_{eq}}{\rightleftarrows} [Rh(DIPHOS)(\rangle C{=}C\langle)]^+ \text{ (rapid equilibrium)} \quad (2)$$

$$H_2 + [Rh(DIPHOS)(\rangle C{=}C\langle)]^+ \xrightarrow{k_2} [RhH_2(DIPHOS)(\rangle C{=}C\langle)]^+ \xrightarrow{fast}$$

$$[RhH(\rangle C{-}C\langle H)(DIPHOS)]^+ \xrightarrow{k_4} [Rh(DIPHOS)S_2]^+ + H\rangle C{-}C\langle H \quad (3)$$

$$-d[\rangle C{=}C\langle]/dt = k_2[Rh(DIPHOS)(\rangle C{=}C\langle)^+][H_2] \quad (4)$$




(I)

In this paper we describe the extension of these studies to rhodium complexes containing larger chelating diphosphine ligands, notably $Ph_2P(CH_2)_nPPh_2$, where $n = 3$, 4 and 5 (DIPHOS-3, -4 and -5, respectively). Some comparisons also are made with the related catalyst systems containing the chiral ligand 4R,5R-bis(diphenylphosphinomethyl)-2,2-dimethyldioxalane (DIOP) and non-chelating $PPh_3$ ligands. Some recent studies by Brown et al. [2] also are pertinent to the themes of this paper.

## Experimental

All the measurements reported in this paper have previously been described for $[Rh(DIPHOS\text{-}2)]^+$ [1]. Equilibrium binding constants ($K_{eq}$) for MAC were determined spectrophotometrically and for 1-hexene from the kinetic measurements, i.e., from the intercepts and slopes of plots of $rate^{-1}$ vs. $[1\text{-hexene}]^{-1}$. The kinetics of hydrogenation were determined by measuring the rate of uptake of $H_2$ gas volumetrically at constant pressure or by stopped flow spectrophotometry. UV-visible spectra were recorded with a Cary 14 spectrophotometer and NMR spectra with a Bruker HFX-90 spectrometer. The initial concentration ranges encompassed by the kinetic measurements are: $6 \times 10^{-6}$ to $2 \times 10^{-4}$ *M* Rh; 0.3 to 0.9 atm $H_2$, 0.01 to 0.2 *M* MAC and 0.2 to 2.0 *M* 1-hexene.

## Results and discussion

### *DIPHOS-3, DIPHOS-4 and DIOP*

The behavior of these systems was qualitatively similar to that for DIPHOS-2 [1].

In each case, as already reported [2], reaction of $H_2$ with a methanol solution of [Rh(DIPHOS)(NBD)]$^+$ yielded the corresponding [Rh(DIPHOS)$S_2$]$^+$ complex. Only one diastereomer of [Rh(DIOP)(MAC)]$^+$ could be detected in solution by NMR even when [Rh(DIOP)$S_2$]$^+$ and MAC were mixed at $-80°C$.

The results of the equilibrium and kinetic measurements are reported in Table 1 which also includes earlier data for DIPHOS-2 for comparison. For DIPHOS-3 and DIPHOS-4 the rate of hydrogenation of MAC was too fast to measure and only a lower limit for $k_2$ ($> 1.5 \times 10^3\ M^{-1}\ sec^{-1}$) could be defined. In the case of DIPHOS-3, reaction of $H_2$ with [Rh(DIPHOS-3)(MAC)]$^+$ at $-80°C$ yielded a transient intermediate which, by analogy with the corresponding DIPHOS-2 system, is inferred to be the hydridoalkyl complex, [RhH(MACH)(DIPHOS-3)S]$^+$. In this case the reductive elimination step could be monitored directly yielding the value of $k_4$ listed in Table 1. The data in Table 1 warrant the following comments.

1. For 1-hexene, the value of $K_{eq}$ remains relatively constant (1.3 to 2.7 $M^{-1}$) while the catalytic activity, reflected in the rate constant $k_2$, increases significantly (from 48 to $3.7 \times 10^2\ M^{-1}\ sec^{-1}$) with increasing diphosphinerhodium chelate ring size. The values of both $K_{eq}$ and $k_2$ for DIOP are close to those of the corresponding DIPHOS-4 with the same ring size.

2. For MAC the values of $K_{eq}$ decrease significantly with increasing chelate ring size and in going from DIPHOS-4 to DIOP, a trend that may reflect increasing steric interference. At the same time, the limited data available suggest that both $k_2$ and $k_4$ increase significantly with increasing chelate ring size so that the catalytic activities of DIPHOS-3 and DIPHOS-4 become too high to measure. If $\Delta H^{\ddagger}$ for $k_4$ is assumed to be the same as that previously measured for DIPHOS-2 [1d], i.e., 17.0 kcal/mol, extrapolation from the measured value at $-80°C$ yields a value of $k_4$ (i.e., of the limiting catalytic turnover frequency) for [Rh(DIPHOS-3)]$^+$ at 25°C of ca. $10^4\ sec^{-1}$, a remarkably high activity for a hydrogenation catalyst.

It is noteworthy that all the rate constants (i.e., for the C–H reductive elimination step as well as the $H_2$ oxidative addition step) appear to increase with increasing chelate ring size. One possible explanation for this is that the increasing flexibility associated with increasing chelate ring size facilitates attainment of the favored transition state geometries of the various reaction steps. A qualitative trend of increasing overall catalytic rate with increasing diphosphine chelate ring size also has been noted by Poulin, Dang and Kagan [3].

TABLE 1

SUMMARY OF EQUILIBRIUM AND KINETIC MEASUREMENTS [a]

| Ligand | Chelate ring size | 1-hexene | | MAC | | |
|---|---|---|---|---|---|---|
| | | $K_{eq}$ ($M^{-1}$) | $k_2$ ($M^{-1}\ sec^{-1}$) | $K_{eq}$ [b] ($M^{-1}$) | $k_2$ ($M^{-1}\ sec^{-1}$) | $k_4$ [c] ($sec^{-1}$) |
| DIPHOS-2 | 5 | 1.7 | 48 | $2.2 \times 10^4$ | $2.0 \times 10^2$ | $1 \times 10^{-5}$ |
| DIPHOS-3 | 6 | 2.7 | 86 | $4.6 \times 10^2$ | $> 1.5 \times 10^3$ | $5 \times 10^{-3}$ |
| DIPHOS-4 | 7 | 1.3 | $3.6 \times 10^2$ | $3.6 \times 10^2$ | $> 1.5 \times 10^3$ | – |
| DIOP | 7 | 1.8 | $3.7 \times 10^2$ | $1.0 \times 10^2$ | $\sim 2 \times 10^3$ | – |
| $(PPh_3)_2$ | – | – | – | $2.9 \times 10^2$ | – | – |

[a] Measurements at 40°C unless otherwise noted. [b] At 25°C. [c] At $-80°C$.

*DIPHOS-5*

Our observations on the hydrogenation of $[Rh(DIPHOS\text{-}5)(NBD)]^+$ at 25°C are similar to those reported independently by Brown et al. [2]. The rapid reaction with $H_2$ yielded the internally metallated complex, $[RhH(Ph_2PCH_2CH_2CH\text{-}CH_2CH_2PPh_2)S_2]^+$ as the major initial product together with some $[Rh(DIPHOS\text{-}5)S_2]^+$ (both previously characterized [2], approximate ratio by NMR, 4/1). Further very slow reaction with $H_2$ (36 h) resulted in some decomposition together with formation of a new hydride species, exhibiting a complex $^1H$ NMR spectrum in the metal hydride region (ca. −22.5 ppm), which may be the previously reported $[RhH_2(DIPHOS\text{-}5)S_2]^+$ complex [2].

Hydrogenation of $[Rh(DIPHOS\text{-}5)(NBD)]^+$ at −80°C followed a somewhat different course. Reaction with $H_2$ (1 atm) for 3 h resulted in complete conversion to $[Rh(DIPHOS\text{-}5)S_2]^+$ ($^{31}P$ NMR: $\delta$ 43.5, $J$(Rh–P) 119 Hz) which rearranged only slowly to $[RhH(Ph_2PCH_2CH_2CHCH_2CH_2PPh_2)S_2]^+$. Warming the freshly treated solution to −25°C for 2.5 min, followed by cooling again to −80°C, resulted in quantitative formation of a new rhodium species containing two non-equivalent phosphines ($^{31}P$ NMR: $\delta_1$ 46.20, $J(Rh\text{–}P^1)$ 134 Hz; $\delta_2$ 30.76, $J(Rh\text{–}P^2)$ 155 Hz; $J(P^1\text{–}P^2)$ 34.1 Hz) and identified as a $[Rh(DIPHOS\text{-}5)(norbornene)]^+$ adduct (presumably $[Rh(DIPHOS\text{-}5)(norbornene)S]^+$. This was substantiated by independent generation of the same species by addition of authentic norbornene to a solution of $[Rh(DIPHOS\text{-}5)S_2]^+$. These observations demonstrate that $[Rh(DIPHOS\text{-}5)S_2]^+$ is the initial product of hydrogenation of $[Rh(DIPHOS\text{-}5)(NBD)]^+$ and that the hydrogenation of $[Rh(DIPHOS)(NBD)]^+$ proceeds in a stepwise manner with the formation of free norbornene as an intermediate.

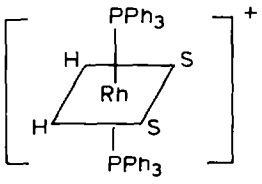
In contrast to the other DIPHOS and DIOP systems examined, the hydrogenation of 1-hexene catalyzed by $[Rh(DIPHOS\text{-}5)(NBD)]^+$ exhibited complex and presently unexplained kinetics, the rate passing through a maximum, rather than levelling off, with increasing 1-hexene concentration and falling off again above ca. 0.8 *M* 1-hexene. The catalytic rate exhibited by this system for the hydrogenation of 0.8 *M* 1-hexene with 0.45 atm $H_2$ at 40°C (ca. 1.2 mol 1-hexene/mol Rh sec) was ca. 4 times that exhibited by $[Rh(DIPHOS\text{-}4)(NBD)]^+$ under comparable conditions. This is consistent with, and extends, the previously noted trend of increasing catalytic activity of $[Rh(DIPHOS)]^+$ complexes with increasing chelate ring size. The facile formation of the metallated complex $[RhH(PPh_2CH_2CH_2CH\text{-}CH_2CH_2PPh_2)S_2]^+$, involving intramolecular oxidative addition of an unactivated saturated C–H bond, further attests to the high reactivity of $[Rh(DIPHOS\text{-}5)S_2]^+$.

*$PPh_3$*

Hydrogenation of a methanol solution of $[Rh(PPh_3)_2(NBD)]^+$ (1 atm $H_2$, 25°C) for 10 min resulted in quantitative conversion to $[RhH_2(PPh_3)_2S_2]^+$ (II) and norbornane in accord with earlier reports [2,3].

Reaction with a stoichiometric amount of $H_2$ ($Rh/H_2$ 1/2) resulted in formation of $[Rh(PPh_3)_2S_2]^+$ in accord with eq. 5, in strict analogy with $[Rh(DIPHOS)(NBD)]^+$ (eq. 1) ($^{31}P$ NMR of $[Rh(PPh_3)_2S_2]^+$ $\delta$ 59.6 ppm; $J$(Rh–P) 205 Hz). The similarity of the $^{31}P$–Rh coupling constant to that of $[Rh(DIPHOS)S_2]^+$ ($J$(Rh–P) 203 Hz) is consistent with an analogous *cis*-structure for $[Rh(PPh_3)_2S_2]^+$ (i.e., III).

Treatment of $[Rh(PPh_3)_2S_2]^+$ with an excess of $H_2$ resulted in formation of the previously identified $[RhH_2(PPh_3)_2S_2]^+$, according to eq. 6 for which the equi-



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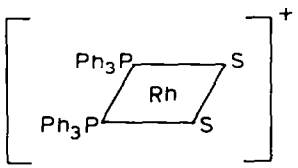


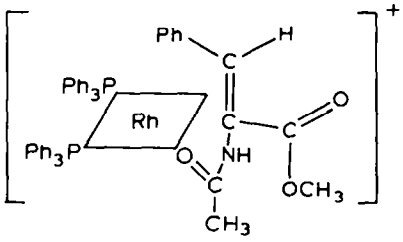
(III)

librium constant was determined (by spectral titration) to be $> 10^5\ M^{-1}$. Additional evidence for the reversibility of reaction 6 recently has been reported [2].

$$[Rh(PPh_3)_2(NBD)]^+ + 2H_2 \rightarrow [Rh(PPh_3)_2S_2]^+ + \text{norbornane} \quad (5)$$

$$[Rh(PPh_3)_2S_2]^+ + H_2 \overset{K'_{eq}}{\rightleftarrows} [RhH_2(PPh_3)_2S_2]^+ \quad (6)$$

Although spectral evidence was obtained for the formation of a 1/1 $[Rh(PPh_3)_2(MAC)]^+$ adduct, attempts to determine the formation equilibrium constant were thwarted by the accompanying formation of other unknown species. The $^{31}P$ NMR spectrum of $[Rh(PPh_3)_2(MAC)]^+$ ($\delta(P^1)$ 48.8, $J(Rh-P^1)$ 168 Hz, $\delta(P^2)$ 28.2, $J(Rh-P^2)$ 157 Hz, $J(P^1-P^2)$ 37 Hz) resembled that of [Rh(DIPHOS)(MAC)]$^+$ [1d], suggesting a similar *cis*-phosphine structure, i.e. IV.



(IV)

Kinetic measurements on the $[Rh(PPh_3)_2(NBD)]^+$-catalyzed hydrogenation of MAC (encompassing the initial concentration ranges 0.01 to 0.2 *M* MAC and 0.3 to 1 atm $H_2$) yielded the second order rate law corresponding to eq. 7, where $[Rh]_{TOT}$ is the total rhodium complex concentration and where $k_7$ (25°C) = 4.0 $M^{-1}$ sec$^{-1}$ (rate independent of $[H_2]$).

$$-d[MAC]/dt = k_7\,[Rh]_{TOT}\,[MAC] \quad (7)$$

In keeping with the fact that $[RhH_2(PPh_3)_2S_2]^+$ is the principal rhodium species in hydrogenated solutions of $[Rh(PPh_3)_2(NBD)]^+$ it has previously been suggested [4] that the $[Rh(PPh_3)_2(NBD)]^+$-catalyzed hydrogenation of olefins proceeds predominantly through the "hydride pathway" described by eq. 8, 9 and 6, rather than the "olefin pathway" that we have identified for cationic rhodium catalysts containing chelating diphosphine ligands (eq. 2-3).

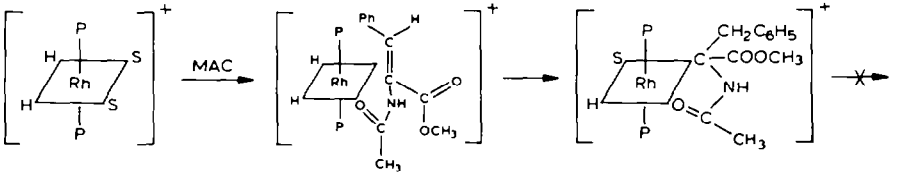
$$[Rh(PPh_3)_2(NBD)]^+ + 3H_2 \overset{\text{fast}}{\rightarrow} [RhH_2(PPh_3)_2S_2]^+ + \text{Norbornane} \quad (8)$$

$$[RhH_2(PPh_3)_2S_2]^+ + \rangle C{=}C\langle \overset{\text{slow}}{\rightarrow} [Rh(PPh_3)_2S_2]^+ + H\rangle C{-}C\langle H \quad (9)$$

$$[Rh(PPh_3)_2S_2]^+ + H_2 \overset{K'_{eq}}{\rightleftarrows} [RhH_2(PPh_3)_2S_2]^+ \quad \text{(fast)} \quad (6)$$

While the rate-law that we have determined (eq. 7) is consistent with this interpretation, i.e., with reaction 9 being rate-determining, it also should be recognized as being consistent with the alternative mechanisms of eq. 2–3. Thus, if the equilibrium of eq. 6 is rapidly established and lies far to the right, the $[Rh(PPh_3)_2S_2]^+$ concentration is given by $K'^{-1}_{eq}[H_2]^{-1}[RhH_2(PPh_3)_2S_2^+] \sim K'^{-1}_{eq}[H_2]^{-1}[Rh]_{TOT}$. The rate-law, eq. 4, corresponding to the mechanism of eq. 2–3, then reduces to $-d[MAC]/dt = k_2 K'^{-1}_{eq} K_{eq}[Rh]_{TOT}[MAC]$, i.e., to a form equivalent to eq. 7 with $k_7 = k_2 K'^{-1}_{eq} K_{eq}$. Thus, the mechanism (eq. 2–3) that we have demonstrated for the hydrogenation of olefins catalyzed by cationic rhodium complexes containing chelating diphosphine ligands also would appear to accommodate the corresponding monophosphine ($PPh_3$)-containing catalysts.

Note added in proof: In support of the last conclusion, a referee has called attention to a possible stereochemical barrier to reaction via the "hydride route", i.e., via reaction of II with MAC. Thus, the stereochemical course of such a reaction pathway, involving coordination of MAC via solvent displacement to form V and followed by hydride migration to the coordinated C=C bond, might be expected to lead to a *trans*-hydridoalkyl complex (VI) from which C–H bond-forming reductive elimination would be disfavored, i.e.:




(II) (V) (VI)

On the other hand, the "olefin route", involving reaction of IV with $H_2$, would be expected to lead, by strict analogy with the corresponding $[Rh(DIPHOS)S_2]^+$-catalyzed reaction [1d], to a *cis*-hydridoalkyl intermediate, analogous to I, from which reductive elimination of the product could readily occur.

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