10548 J. Am. Chem. Soc. **1994,** *116,* 10548–10556

Observation of New Intermediates in Hydrogenation Catalyzed by Wilkinson's Catalyst, $RhCl(PPh_3)_3$, Using Parahydrogen-Induced Polarization

Simon B. Duckett, Connie L. Newell, and Richard Eisenberg*

Contribution from the Departments of Chemistry, University of Rochester, Rochester, New York 14627, and University of York, Heslington, York, England YO1 5DD

Received October 4, 1993. Revised Manuscript Received July 25, 1994®

Abstract: Through the use of parahydrogen-induced polarization, the chemistry of $RhCl(PPh_3)_3$, $[RhCl(PPh_3)_2]_2$, and $RhCl(olefin)(PPh_3)_2$ with H_2 and olefinic substrates has been investigated. The phenomenon of PHIP makes possible the detection of previously unobserved dihydride species in the reaction system. Specifically, the binuclear complex $H_2Rh(PPh_3)_2(\mu\text{-}Cl)_2Rh(PPh_3)(olefin)$ for *cis-* and *trans-*2-hexene, 2-pentene, methyl methacrylate, styrene, and substituted styrenes has been detected and characterized. While readily observable during hydrogenation catalysis under *ca.* 1–2 atm of para-enriched hydrogen, $H_2Rh(PPh_3)_2(\mu\text{-}Cl)_2Rh(PPh_3)(olefin)$ is not directly in the catalytic cycle; in fact, its appearance suggests reduced activity of the system through the formation of less active binuclear species. A second new species observed with styrene, *p*-chlorostyrene, and *p*-methylstyrene as substrates is the mononuclear complex $RhH_2(olefin)(PPh_3)_2(Cl)$, which appears to be an intermediate in hydrogenation catalysis. From PHIP spectra, it is possible to assign this species as having cis phosphines as well as cis hydrides. The study also underscores the crucial role of PPh_3 at low concentration to inhibit formation of binuclear species in the catalytic system. In a separate experiment, strong polarization for $RhH_2Cl(PMe_3)_3$ is observed, consistent with its poor effectiveness as a catalyst.

Introduction

The action of Wilkinson's complex, $RhCl(PPh_3)_3$ (**1**), as a hydrogenation catalyst has been extensively investigated since its discovery in 1965.[1–9] Despite the numerous mechanistic and kinetic studies that have been carried out, the only species that have been observed directly and characterized when **1** is allowed to react with H_2 and/or olefins are the complexes $RhH_2Cl(PPh_3)_3$, $RhCl(PPh_3)_2(olefin)$, $[RhCl(PPh_3)_2]_2$, and $H_2Rh_2Cl_2(PPh_3)_4$. However, based on kinetic investigations carried out on individual stoichiometric stages of the catalysis, Halpern has concluded that none of these species is actually part of the kinetically significant hydrogenation cycle.[6–8] This cycle is outlined in Scheme 1 and, as originally proposed by Osborn and Wilkinson,[2] is based on the "hydride" mechanism for catalytic hydrogenation in which reversible H_2 addition to the active catalyst is followed by olefin binding and transformation. In the specific case of $RhCl(PPh_3)_3$, the active catalyst is the 14-electron bis(phosphine)rhodium species $RhCl(PPh_3)_2$, and the transfer of hydrogen to the olefinic substrate occurs stereoselectively in a cis manner. Based on the kinetics of the stoichiometric hydrogenation of cyclohexene by $RhH_2Cl(PPh_3)_3$, the rate-determining step in the catalysis is proposed to be olefin insertion into the metal–hydride bond.[7]

The catalytic and stoichiometric reactions of **1** have been examined extensively by NMR spectroscopy in order to elucidate the structures of reaction products and catalytic intermediates.[10,11] The stable dihydride $RhH_2Cl(PPh_3)_3$ (**2**) produced upon the oxidative addition of H_2 to **1** possesses a *mer* arrangement of PPh_3 donors and has been shown by Brown to dissociate the phosphine trans to hydride readily with a k_{diss} of 400 s^{-1} at 298 K (Scheme 1).[10] The resultant 16 e^- species $RhH_2Cl(PPh_3)_2$ has effective C_{2v} symmetry consistent with either a trigonal bipyramidal structure having trans axial phosphines and equivalent hydrides or a fluxional square pyramidal arrangement with non-exchanging trans phosphine ligands. In the latter, the hydride ligands must interchange more rapidly than the phosphine exchange process defined by k_{diss}. A slower exchange of PPh_3 from $RhH_2Cl(PPh_3)_3$ has been observed that involves the mutually trans phosphine ligands and has a rate constant of 0.2 s^{-1} at 303 K.[12] This process, while considerably slower than dissociation of PPh_3 trans to hydride in **2**, is fast enough, according to Brown, to play a possible role in hydrogenation catalysis by Wilkinson's catalyst.[10]

In Scheme 1, the 16 e^- species $RhH_2Cl(PPh_3)_2$ generated by either H_2 addition to the 14 e^- complex $RhCl(PPh_3)_2$ or phosphine dissociation from **2** coordinates olefin under catalytic conditions to form a key intermediate in the catalysis. Initially, this species was proposed to have the coordination geometry shown as **I** with trans phosphine ligands.[7] However, alternative arrangements can be envisaged for the olefin dihydride intermediate, and based on molecular modeling and phosphine exchange studies, Brown has postulated that this key species

---

® Abstract published in *Advance ACS Abstracts,* October 1, 1994.

[1] Young, J. F.; Osborn, J. A.; Jardine, F. H.; Wilkinson, G. *Chem. Commun.* **1965**, 131–132.

[2] Osborn, J. A.; Jardine, F. H.; Young, J. F.; Wilkinson, G. *J. Chem Soc. A* **1966**, 1711–1732.

[3] Jardine, F. H. *Prog. Inorg. Chem.* **1981**, *28*, 63–202.

[4] Tolman, C. A.; Meakin, P. Z.; Lindner, D. L.; Jesson, J. P. *J. Am. Chem. Soc.* **1974**, *96*, 2762–2774.

[5] Meakin, P.; Jesson, J. P.; Tolman, C. A. *J. Am. Chem. Soc.* **1972**, *94*, 2140–3142.

[6] Halpern, J.; Wong, C. S. *J. Chem. Soc., Chem. Commun.* **1973**, 629–630.

[7] Halpern, J.; Okamoto, T.; Zakhariev, A. *J. Mol. Catal.* **1976**, *2*, 65–68.

[8] Halpern, J. *Inorg. Chim. Acta* **1981**, *50*, 11–19.

[9] Ohtani, Y.; Yamagishi, A.; Fujimoto, M. *Bull. Chem. Soc. Jpn.* **1979**, *52*, 69–72.

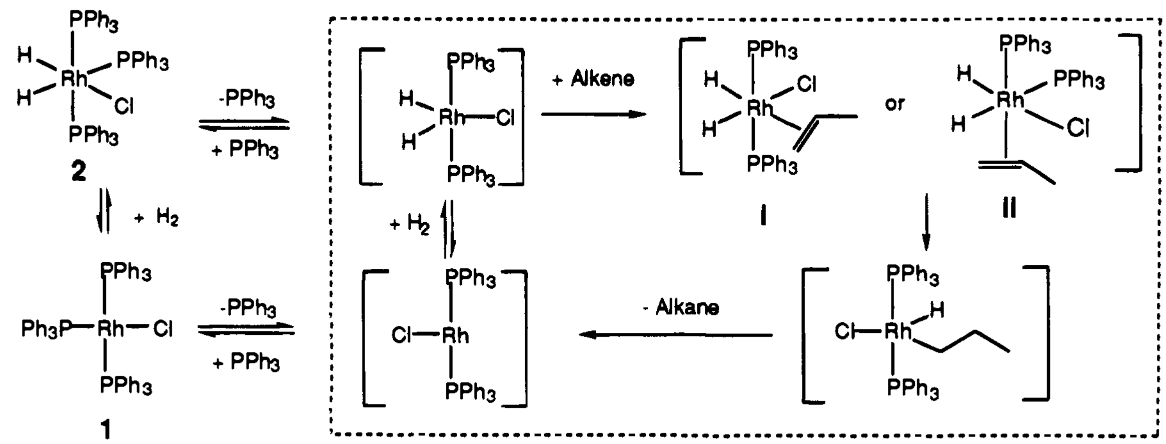
[10] Brown, J. M.; Evans, P. L.; Lucy, A. R. *J. Chem. Soc., Perkin Trans. II* **1987**, 1589–1596.

[11] Brown, J. M. *Chem. Soc. Rev.* **1993**, 25–41.

[12] Brown, J. M.; Kent, A. G. *J. Chem. Soc., Perkin Trans. II* **1987**, 1597–1607.

0002-7863/94/1516-10548$04.50/0

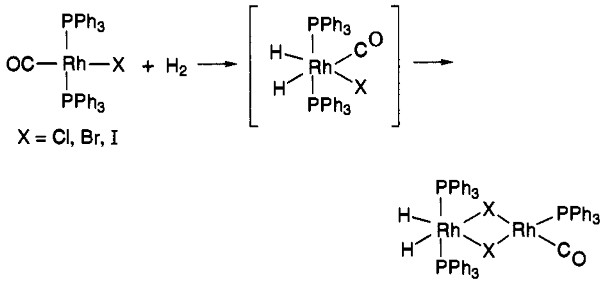
Scheme 1



contains cis phosphines and inequivalent hydrides as in **II**.[12] To date, however, an olefin dihydride intermediate $RhH_2Cl(olefin)(PPh_3)_3$ has not been observed directly by any experimental method capable of providing structural information, and thus a definitive assignment of its geometry has not been possible.[13]

In the present paper, we examine hydrogenation reactions promoted by **1** using parahydrogen-induced polarization (PHIP) which allows us to achieve much greater sensitivity than is available by classical NMR spectroscopic methods. In parahydrogen-induced polarization, enhanced absorptions and emissions occur in product NMR spectra when H_2 enriched in the para spin state is added in a pairwise manner to a metal center or an unsaturated substrate while spin correlation between the two protons is maintained.[14,15] This situation may be illustrated by the addition of H_2 to a metal center M to generate the product MH_aH_b having two magnetically different protons and a four-level ^1H spin system ($\alpha\alpha$, $\alpha\beta$, $\beta\alpha$, $\beta\beta$). If the addition takes place without loss of spin correlation, then the $\alpha\beta$ and $\beta\alpha$ levels of the MH_aH_b spin system become overpopulated relative to $\alpha\alpha$ and $\beta\beta$ leading to enhanced absorption *and* emission for the lines of each hydride doublet with a separation between the transitions of J_{HH}. A key requirement of parahydrogen-induced polarization is that the two protons of the original parahydrogen molecule become magnetically inequivalent in the product.

The phenomenon of PHIP, described initially by Weitekamp as PASADENA,[16] has been used to examine hydrogenation reaction mechanisms[17-22] and, in one study, to determine hydrogenation rate constants.[23] It has also been demonstrated that ^1H polarization achieved with parahydrogen can be transferred to other nuclei such as ^{31}P and ^{13}C through cross-relaxation[24] and that, in conjunction with pulse sequences, the transfer of ^1H polarization can be efficient and impressive.[25] Recently, we demonstrated the utility of PHIP to see species present in small concentration by examining the oxidative addition of H_2 to $RhCl(CO)(PPh_3)_2$ and its PMe_3 analog.[26,27] Prior to our study, the reaction of $RhCl(CO)(PPh_3)_2$ with H_2 had not been observed directly. Through the use of PHIP, we were able to establish that reaction does indeed occur and that, as shown in eq 1, an unexpected binuclear product, $H_2Rh(PPh_3)_2(\mu\text{-}Cl)_2Rh(PPh_3)(CO)$, is generated during the course of the reaction.[26]



(1)

The present study reports that with PHIP several new rhodium species are observed and identified during olefin hydrogenation catalyzed by $RhCl(PPh_3)_3$. The new species include binuclear complexes similar to that shown in eq 1 and a mononuclear species that corresponds to an olefin dihydride intermediate in the catalysis of Scheme 1. In the course of these studies, we have employed the three catalyst precursors $RhCl(PPh_3)_3$ (**1**), the chloro-bridged dimer $Rh(PPh_3)_2(\mu\text{-}Cl)_2Rh(PPh_3)_2$ (**3**) which is generated under phosphine-deficient conditions, and the labile ethylene complex $RhCl(C_2H_4)(PPh_3)_2$ (**4**). Each of these catalyst precursors allows the examination of a different aspect of the hydrogenation reaction.

Results and Discussion

Reactions of $RhCl(PPh_3)_3$ with H_2. The oxidative addition of H_2 to $RhCl(PPh_3)_3$ (**1**) to form the Rh(III) product $RhH_2Cl(PPh_3)_3$ (**2**) was originally reported by Wilkinson in 1965.[1,2] The two hydride ligands in the Rh(III) product are distinct with

---

[13] (a) Daniel, C.; Koga, N.; Han, J.; Fu, X. Y.; Morokuma, K. *J. Am. Chem. Soc.* **1988**, *110*, 3773–3787. (b) Koga, N.; Morokuma, K. *ACS Symp. Ser.* **1989**, *394*, 77–91.

[14] Bowers, C. R.; Weitekamp, D. P. *Phys. Rev. Lett.* **1986**, *57*, 2645–2648.

[15] Eisenschmid, T. C.; Kirss, R. U.; Deutsch, P. P.; Hommeltoft, S. I.; Eisenberg, R.; Bargon, J.; Lawler, R. G.; Balch, A. L. *J. Am. Chem. Soc.* **1987**, *109*, 8089–8091.

[16] Bowers, C. R.; Weitekamp, D. P. *J. Am. Chem. Soc.* **1987**, *109*, 5541.

[17] Kirss, R. U.; Eisenschmid, T. C.; Eisenberg, R. *J. Am. Chem. Soc.* **1988**, *110*, 8564–8566.

[18] Kirss, R. U.; Eisenberg, R. *J. Organomet. Chem.* **1989**, *359*, C22–C26.

[19] Eisenberg, R. *Acc. Chem. Res.* **1991**, *24*, 110–116.

[20] Eisenberg, R.; Eisenschmid, T. C.; Chinn, M. S.; Kirss, R. U. *Adv. Chem. Ser.* **1992**, *230*, 47–74.

[21] Bargon, J.; Kandels, J.; Kating, P.; Thomas, A.; Woelk, K. *Tetrahedron Lett.* **1990**, *31*, 5721–5724.

[22] Bargon, J.; Kandels, J.; Kating, P. *J. Chem. Phys.* **1993**, *98*, 6150–6153.

[23] Chinn, M. S.; Eisenberg, R. *J. Am. Chem. Soc.* **1992**, *114*, 1908–1909.

[24] Eisenschmid, T. C.; McDonald, J.; Eisenberg, R. *J. Am. Chem. Soc.* **1989**, *111*, 7267–7269.

[25] Duckett, S. B.; Newell, C. L.; Eisenberg, R. *J. Am. Chem. Soc.* **1993**, *115*, 1156–1157.

[26] Duckett, S. B.; Eisenberg, R. *J. Am. Chem. Soc.* **1993**, *115*, 5292–5293.

[27] Duckett, S. B.; Eisenberg, R.; Goldman, A. S. *J. Chem. Soc., Chem. Commun.* **1993**, 1185–1187.

Table 1. ^1H NMR Data of Hydride Species Observed from Rhodium Triphenylphosphine Precursors[a]

no.	formula	substrate	chemical shifts δ, ppm (coupling constants J, Hz)
2	$RhH_2Cl(PPh_3)_3$		-9.33 (dt, $J_{PH} = 159, 18$), -16.65 (q, $J_{PH} = ca.\ 15$)
5	$H_2Rh(PPh_3)_2(\mu\text{-}Cl)_2Rh(PPh_3)_2$		-19.4 (dt, $J_{RhH} = 22$, $J_{PH} = 17$)
6a	$H_2Rh(PPh_3)_2(\mu\text{-}Cl)_2Rh(PPh_3)$(olefin)	*cis*-2-hexene	-18.86 (qd, $J_{RhH} = J_{PH} = 22$, $J_{HH} = -9$); -19.66 (qd, $J_{RhH} = J_{PH} = 22$, $J_{HH} = -9$)
6b	$H_2Rh(PPh_3)_2(\mu\text{-}Cl)_2Rh(PPh_3)$(olefin)	*trans*-2-hexene	-18.79; -19.59
6c	$H_2Rh(PPh_3)_2(\mu\text{-}Cl)_2Rh(PPh_3)$(olefin)	*cis*-2-pentene	-18.8 (qd, $J_{RhH} = J_{PH} = 22$, $J_{HH} = -10$); -19.61 (qd, $J_{RhH} = J_{PH} = 22$, $J_{HH} = -10$)
6d	$H_2Rh(PPh_3)_2(\mu\text{-}Cl)_2Rh(PPh_3)$(olefin)	methyl methacrylate	-18.92 (qd, $J_{RhH} = J_{PH} = 16$, $J_{HH} = -10$); -19.64 (qd, $J_{RhH} = J_{PH} = 16$, $J_{HH} = -10$)
6e	$H_2Rh(PPh_3)_2(\mu\text{-}Cl)_2Rh(PPh_3)$(olefin)	styrene	-18.87 ($J_{RhH} = 22$, $J_{HH} = -12$); -19.66 ($J_{RhH} = 23$, $J_{HH} = -12$); -18.45 ($J_{RhH} = 24$, $J_{HH} = -12$); -18.99 ($J_{RhH} = 22$, $J_{HH} = -12$)
6f	$H_2Rh(PPh_3)_2(\mu\text{-}Cl)_2Rh(PPh_3)$(olefin)[b]	pentafluorostyrene	-19.33 ($J_{RhH} = 23$ Hz, $J_{PH} = 15$, $J_{HH} = -11$); -20.27 ($J_{RhH} = 24$, $J_{PH} = 15$, $J_{HH} = -11$)
6g	$H_2Rh(PPh_3)_2(\mu\text{-}Cl)_2Rh(PPh_3)$(olefin)[b]	*p*-chlorostyrene	-19.27 ($J_{RhH} = 24$, $J_{HH} = -10$); -19.76 ($J_{RhH} = 24$, $J_{HH} = -10$)
7a	$RhH_2Cl(PPh_3)_2$(olefin)	styrene	-9.42 ($J_{PH} = 159$); -15.63
7b	$RhH_2Cl(PPh_3)_2$(olefin)	*p*-chlorostyrene	-9.53; -13.85
7c	$RhH_2Cl(PPh_3)_2$(olefin)	*p*-methylstyrene	-9.84; -17.37
8	$RhHCl(PPh_3)_2(\mu\text{-}H)_2RhHCl(PPh_3)_2$[b]		-10.88 (ttt, $J_{PH} = 75, 10$, $J_{RhH} = 21$); -16.49 (q, $J_{RhH} = J_{PH} = 17$)

[a] ^1H NMR chemical shifts reported in C_6D_6 unless otherwise indicated. [b] CD_2Cl_2 as solvent.

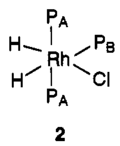
Table 2. ^{31}P NMR Data of Hydride Species Observed from Rhodium Triphenylphosphine Precursors[a]

no.	formula	chemical shifts δ, ppm (coupling constants J, Hz)
2	$RhH_2Cl(PPh_3)_3$	-20.7 ($J_{RhP} = 114$), -40.3 ($J_{RhP} = 90$)
5	$H_2Rh(PPh_3)_2(\mu\text{-}Cl)_2Rh(PPh_3)_2$[b]	52.2 ($J_{RhP} = 196$), 37.6 ($J_{RhP} = 119$)
5	$H_2Rh(PPh_3)_2(\mu\text{-}Cl)_2Rh(PPh_3)_2$	54.3 ($J_{RhP} = 193$), 38.4 ($J_{RhP} = 116$)
6d	$H_2Rh(PPh_3)_2(\mu\text{-}Cl)_2Rh(PPh_3)$(methyl methacrylate)	52.4 ($J_{RhP} = 187$), 39.3 ($J_{RhP} = 118$)
6g	$H_2Rh(PPh_3)_2(\mu\text{-}Cl)_2Rh(PPh_3)$(*p*-chlorostyrene)	52.7 ($J_{RhP} = 188$), 39.7 ($J_{RhP} = 119$)
8	$RhHCl(PPh_3)_2(\mu\text{-}H)_2RhHCl(PPh_3)_2$[b]	30.2 ($J_{RhP} = 126$)

[a] ^{31}P NMR chemical shifts reported in C_6D_6 unless otherwise indicated. [b] CD_2Cl_2 as solvent.

the hydride trans to PPh_3 resonating at δ -9.33 ppm with a large doublet coupling J_{PH} of 159 Hz and the hydride trans to chloride exhibiting a higher filed resonance of δ -16.65 ppm with coupling to three cis phosphine ligands, J_{PH} of *ca.* 15 Hz (see Table 1). When the reaction of **1** with H_2 is examined at 298 K using hydrogen enriched in the para spin state (*i.e.*, para-enriched hydrogen or p-H_2), very weakly polarized hydride resonances are observed for the Rh(III) product. The polarization corresponds to enhanced absorption and emission in transitions separated by J_{HH}. Polarization of the hydrides of **2** using parahydrogen has been reported previously by Bowers and Weitekamp in their initial experiments.[16]

At elevated temperatures (330 K), *no* polarization is seen in the hydride resonances for the reaction of **1** with p-H_2. However, a resonance for the phosphine ligands P_A cis to both hydrides of **2** is clearly seen in the corresponding ^{31}P NMR spectrum, although it has lost is coupling to the phosphine P_B which is trans to one of the hydrides. The resonance for P_B at 330 K is unobserved due to exchange but does appear upon cooling of the sample. These observations indicative of facile phosphine exchange explain the failure to detect **2** by its hydride resonance signature since rapid PPh_3 dissociation ($k_{diss} = 400$ s^{-1}) and subsequent dynamic behavior serve to equilibrate the two hydrides and broaden their resonances into the baseline. Thus, even the resonance amplification provided by PHIP fails to permit detection of the hydrides of **2**. In addition, neither the hydrides of the phosphine loss product, $RhH_2Cl(PPh_3)_2$, nor those of its solvated counterpart, $RhH_2Cl(PPh_3)_2$(sol), are observed at 330 K. Since PHIP is only observed when the two protons of the parahydrogen molecule are transferred into magnetically *inequivalent* positions, we conclude that $RhH_2Cl(PPh_3)_2$ has equivalent hydrides or hydrides that are interchanged rapidly on the NMR timescale. Support for the former is obtained from the structural study of the related complex $RhH_2Cl(P(t\text{-}Bu)_3)_2$ which possesses a distorted trigonal bipyramidal geometry.[28]



2

When the temperature of the reaction of $RhCl(PPh_3)_3$ with p-H_2 is lowered to 283 K in order to slow the rate of phosphine exchange, the hydride resonances of **2** still show only weak polarization. While the rate of phosphine dissociation is slowed, thereby sharpening the corresponding hydride resonances, the lower temperature also serves to reduce the rates of H_2 oxidative addition and reductive elimination involving **1**, resulting in little increase in polarization.

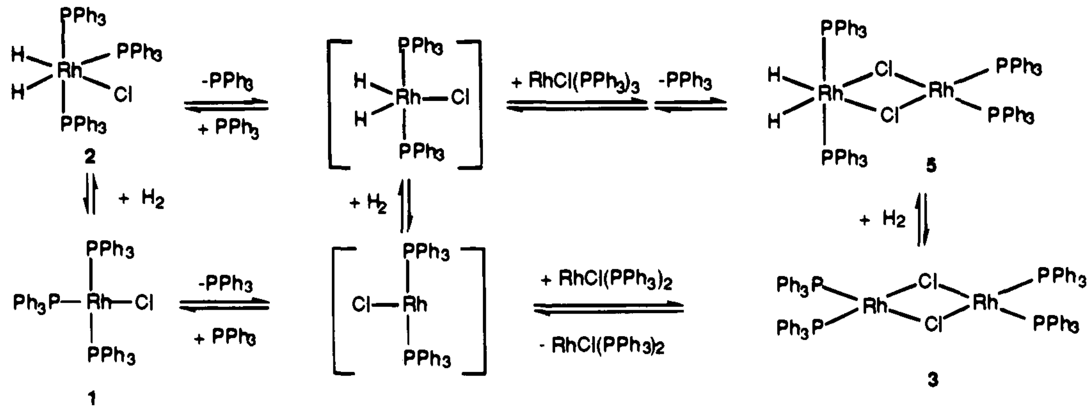
At elevated temperatures, the reaction of $RhCl(PPh_3)_3$ (**1**) with p-H_2 in benzene-d_6 also leads to the formation of the Rh(III)/Rh(I) binuclear complex $H_2Rh(PPh_3)_2(\mu\text{-}Cl)_2Rh(PPh_3)_2$ (**5**) first identified by Tolman *et al.*[4] Product **5** is characterized by a single *un*polarized hydride resonance at δ -19.4 which has a doublet of triplets multiplicity with $J_{RhH} = 22$ Hz and $J_{PH} = 17$ Hz. The presence of both Rh(III) and Rh(I) in **5** was established by Tolman *et al.* through ^{31}P NMR spectroscopy which revealed resonances and J_{RhP} coupling constants characteristic of PPh_3 coordinated to Rh(III) and Rh(I) (see Table 2). When **5** is produced under these conditions, it is in equilibrium with **1**, **2**, and the Rh(I) chloro-bridged dimer **3** as shown in Scheme 2.

At higher temperatures, the binuclear dihydride product **5** is

---

(28) Yoshida, T.; Otsuka, S.; Matsumoto, M.; Nakatsu, K. *Inorg. Chim. Acta* **1978**, *29*, L257–L259.

Scheme 2



favored over the mononuclear dihydride complex $RhH_2Cl(PPh_3)_3$ (**2**), but the presence of PPh_3 liberated from $RhCl(PPh_3)_3$ and $RhH_2Cl(PPh_3)_3$ prevents **5** from becoming the dominant hydride in solution. The facile equilibria shown in Scheme 2 are an important aspect of the reaction chemistry of Wilkinson's catalyst and, in fact, led Halpern in this kinetic studies of hydrogenation catalysis to use excess PPh_3 to suppress formation of binuclear species.[7,8]

The formation of $H_2Rh(PPh_3)_2(\mu\text{-}Cl)_2Rh(PPh_3)_2$ (**5**) is clearly complex with routes involving both mono- and binuclear precursors. Tolman *et al.* showed that the reaction of the chloro-bridged dimer $Rh(P(p\text{-tolyl})_3)_2(\mu\text{-}Cl)_2Rh(P(p\text{-tol})_3)_2$ with H_2 to yield $H_2Rh(P(p\text{-tolyl})_3)_2(\mu\text{-}Cl)_2Rh(P(p\text{-tol})_3)_2$ was first order in dimer concentration, and they were therefore able to conclude that the formation of **5** occurred by direct H_2 oxidative addition to $Rh(PPh_3)_2(\mu\text{-}Cl)_2Rh(PPh_3)_2$ (**3**).[4] A crossover experiment performed by us confirms this view. When a sample containing a mixture of the chloro-bridged dimers $Rh(P(p\text{-tol})_3)_2(\mu\text{-}Cl)_2Rh(P(p\text{-tol})_3)_2$ and $Rh(PPh_3)_2(\mu\text{-}Cl)_2Rh(PPh_3)_2$ (**3**) in a 1:1 ratio reacts with H_2, hydride resonances for **5** and for $H_2Rh(P(p\text{-tolyl})_3)_2(\mu\text{-}Cl)_2Rh(P(p\text{-tolyl})_3)_2$ at δ -19.4 and -17.8 ppm, respectively, are observed immediately at 298 K. After several minutes at 332 K, however, the resonance at δ -17.8 disappears and that at δ -19.4 increases in complexity, indicating phosphine scrambling and the formation of mixed phosphine binuclear dihydride complexes. The observation of no initial crossover indicates that H_2 oxidative addition to one of the Rh(I) centers of the binuclear complexes occurs more readily than dissociation of the dimers into highly reactive $RhCl(PAr_3)_2$ fragments, as suggested by Tolman *et al.*[4]

However, a mononuclear pathway to the formation of $H_2Rh(PPh_3)_2(\mu\text{-}Cl)_2Rh(PPh_3)_2$ (**5**) commencing with $RhCl(PPh_3)_3$ also exists, as seen by its occurrence under conditions in which formation of $Rh(PPh_3)_2(\mu\text{-}Cl)_2Rh(PPh_3)_2$ (**3**) is clearly suppressed. In support of the mononuclear pathway to the formation of **5**, we have recently shown that $RhCl(CO)(PPh_3)_2$ reacts with H_2 to produce the binuclear product $[H_2Rh(PPh_3)_2(\mu\text{-}Cl)_2Rh(PPh_3)(CO)]$, eq 1,[26] and that the corresponding complex $RhCl(CO)(PMe_3)_2$ reacts similarly.[27] Our results indicate that these addition reactions proceed via the formation of $[RhH_2Cl(CO)(PR_3)_2]$ which readily liberates CO to form the unsaturated species $RhH_2Cl(PR_3)_2$. This unsaturated dihydride then reacts with a second molecule of $RhCl(CO)(PR_3)_2$ to form a Cl-bridged species followed by an internal displacement of phosphine at the Rh(I) center leading to the doubly bridged structure experimentally detected. Such a process can also be envisaged to lead from Wilkinson's catalyst (**1**) and H_2 to Tolman's binuclear dihydride **5** via $RhH_2Cl(PPh_3)_2$ with additional $RhCl(PPh_3)_3$ acting to form the chloride bridge.

The addition of a 50-fold excess of PPh_3 to the reaction system of **1** + p-H_2 results in quenching of the polarization in the hydride resonances of $RhH_2Cl(PPh_3)_3$ (**2**) at 298 K. This quenching with excess PPh_3 indicates that oxidative addition and reductive elimination of H_2 to $RhCl(PPh_3)_3$ (H_2 cycling) takes place much more slowly with excess phosphine present than in its absence. This conclusion is consistent with the relative rates of H_2 oxidative addition to $RhCl(PPh_3)_3$ and $RhCl(PPh_3)_2$ determined by Halpern—specifically, the latter reacts *ca.* 10^4 times more rapidly with H_2 than the former.[6,29] With excess phosphine in the reaction system, dissociation of PPh_3 from Wilkinson's catalyst **1** to generate $RhCl(PPh_3)_2$ is suppressed and the formation of $RhH_2Cl(PPh_3)_3$ proceeds mainly via the direct, albeit slower reaction of H_2 with $RhCl(PPh_3)_3$. This result with excess phosphine present underscores the importance of $RhCl(PPh_3)_2$ during hydrogenation catalysis as shown in Scheme 1. At elevated temperatures, the presence of excess phosphine also inhibits the formation of the binuclear dihydride $H_2Rh(PPh_3)_2(\mu\text{-}Cl)_2Rh(PPh_3)_2$ (**5**).

Reactions of $RhCl(PMe_3)_3$ with H_2. The weak polarization of $RhH_2Cl(PPh_3)_3$ (**2**) stands in sharp contrast to the strong polarization seen for the analogous complex $RhH_2Cl(PMe_3)_3$ formed by the oxidative addition of H_2 to $RhCl(PMe_3)_3$. The unpolarized methyl resonances of $RhH_2Cl(PMe_3)_3$ are shown in Figure 1a along with the resonance for orthohydrogen at δ 4.43, while the polarized hydrides are shown in Figure 1b, with the hydride trans to PMe_3 resonating at δ -9.32 and the hydride trans to chloride having a characteristically higher field chemical shift at δ -18.65 ppm. The lower field hydride resonance exhibits a large trans phosphorus coupling, J_{PH}, of 180 Hz with an 18 Hz quartet coupling ($J_{PcisH} = J_{RhH}$) and antiphase coupling due to J_{HH}, while the higher field partner appears as an overlapped doublet of quartets of antiphase doublets due to $J_{PH} = 40$ Hz, $J_{PH} = J_{RhH} = 18$ Hz, and $J_{HH} = -7.5$ Hz. For $RhH_2Cl(PMe_3)_3$, elevated temperatures result in a substantial increase in the polarized hydride resonance intensity, such that at 343 K a 208-fold enhancement is observed. The amplitude setting of the spectrum in Figure 1a is four times *greater* than that in Figure 1b for the sake of comparison. Under these conditions, the hydride resonances are sharp, indicating a lack of dynamic behavior for $RhH_2Cl(PMe_3)_3$. The difference in the magnitudes of polarization for $RhH_2Cl(PPh_3)_3$ and $RhH_2Cl(PMe_3)_3$ relates inversely to the facility of phosphine exchange in these species, which in turn correlates with their efficacy in hydrogenation catalysis. The complex $RhH_2Cl(PPh_3)_3$ exchanges phosphine readily and is an effective homogeneous hydrogenation catalyst, whereas $RhH_2Cl(PMe_3)_3$ does not undergo facile phosphine exchange with free PMe_3 and is a poor hydrogenation catalyst.

---

(29) Wink, D. A.; Ford, P. C. *J. Am. Chem. Soc.* **1987**, *109*, 436–442.

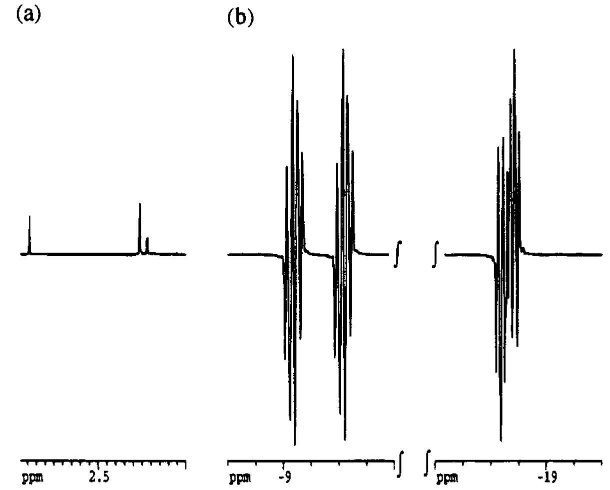


Figure 1. ^{1}H NMR spectrum of $RhH_2Cl(PMe_3)_3$ formed from 1 mg of $RhCl(PMe_3)_3$ with p-H_2 in C_6D_6 at 243 K and obtained after one scan with a 45° observation pulse (each division corresponds to 0.25 ppm): (a) region showing free orthohydrogen and the two inequivalent PMe_3 groups of $RhH_2Cl(PMe_3)_3$; (b) the polarized hydride resonances scaled by one-fourth that of part a for comparison.

Reactions of $RhCl(PPh_3)_3$ (1) with Olefin Substrates and p-H_2. When a benzene solution of **1**, p-H_2, and 2-hexene containing both the cis and trans isomers is monitored at 295 K by NMR spectroscopy, two sets of polarized resonances are observed. The first belongs to the hydrogenation product hexane which shows very modest intensity enhancements for the inequivalent protons transferred pairwise from parahydrogen, in part because similarity in chemical shift of the transferred protons results in overlap and partial cancellation of enhanced absorption and emission lines. The second, showing a weaker degree of polarization, is the metal complex $RhH_2Cl(PPh_3)_3$ (**2**). Repeating this experiment at 303 K leads to the observation of additional unpolarized resonances corresponding to $H_2Rh(PPh_3)_2(\mu\text{-}Cl)_2Rh(PPh_3)_2$ (**5**), in accord with experiments carried out in the absence of substrate. However, when the sample is removed from the spectrometer, shaken to reestablish parahydrogen in solution, and returned to the probe immediately at this temperature, two new polarized resonances are observed as shown in Figure 2a. These resonances are close to those of **5** and occur at δ −18.86 and −19.66 ppm. Each of these hydride resonances is a quartet of antiphase doublets with the doublet coupling corresponding to J_{HH} of the added protons as shown in Figure 2b. The antiphase character of these resonances confirms that their respective protons originate from reactant parahydrogen. The corresponding $^1H\{^{31}P\}$ spectrum exhibits the two hydride resonances as a doublet of antiphase doublets with $J_{RhH} = 22$ Hz and $J_{HH} = -9$ Hz (see Figure 2c).

An INEPT pulse sequence was then used to transfer the parahydrogen-induced polarization into the ^{31}P manifold of the product with the result that a single ^{31}P resonance was observed which showed couplings to rhodium and two hydride ligands. The spectroscopic data for this species require that it contains a rhodium center with two trans phosphine ligands and two inequivalent hydrides. When the reaction was repeated at 332 K, the new polarized species was again detected along with the binuclear complex **5**.

The spectroscopic characteristics of the newly observed rhodium hydride product and hence its identity are very similar to those of $H_2Rh(PPh_3)_2(\mu\text{-}Cl)_2Rh(PPh_3)(CO)$ observed in the reaction of $RhCl(CO(PPh_3)_2$ and p-H_2 described above.[26] In that study, the product was identified through a complex series of PHIP experiments, although subsequently it was possible to observe this species using normal H_2 by monitoring the reaction of a mixture of $RhCl(CO)(PPh_3)_2$ and the dimer $Rh(PPh_3)_2(\mu\text{-}Cl)_2Rh(PPh_3)_2$ (**3**) with H_2 in dichloromethane-d_2 at low temperatures. As with Tolman's study leading to the identification of the dihydride **5**, a key to identifying the binuclear product as $H_2Rh(PPh_3)_2(\mu\text{-}Cl)_2Rh(PPh_3)(CO)$ was the observation of two sets of ^{31}P resonances having J_{RhP} coupling constants characteristic of PPh_3 bound to Rh(III) and Rh(I) centers. In an experiment discussed in the next section with results given in Table 2, a similar approach was used in the present study that led to the successful observation of two ^{31}P resonances for the new hydride product formed in the reaction of Wilkinson's catalyst (**1**) + olefin + n-H_2 indicative of a Rh(III)−Rh(I) binuclear complex. We are thus able to assign the new resonances observed initially with PHIP to the binuclear complex $H_2Rh(PPh_3)_2(\mu\text{-}Cl)_2Rh(PPh_3)$(2-hexene) (**6a**) in which the olefin coordinates to the Rh(I) center in place of CO.

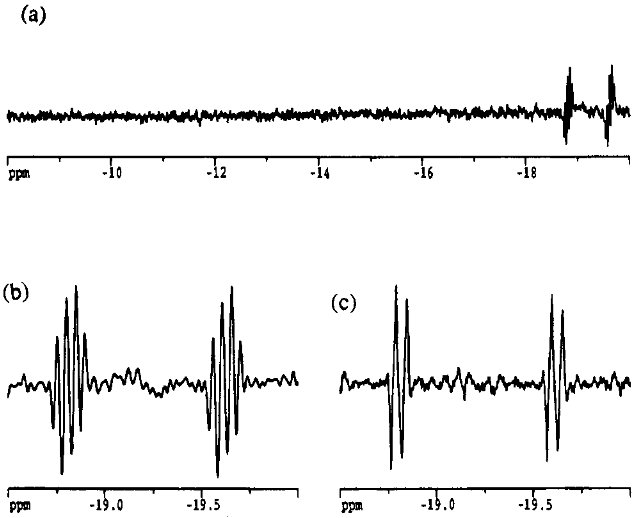
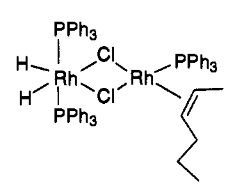


Figure 2. ^{1}H NMR spectra showing enhanced signals obtained for $H_2Rh(PPh_3)_2(\mu\text{-}Cl)_2Rh(PPh_3)$(*cis*-2-hexene) (**6a**) produced in the reaction of **1** with 2-hexene and p-H_2 at 303 K in C_6D_6. The antiphase components are separated by J_{HH} between the protons originally in p-H_2: (a) ^{1}H spectrum of the hydride region showing suppression of polarized resonances for $RhH_2Cl(PPh_3)_3$ (**2**) at 303 K; (b) expansion of the hydride region illustrating the doublet of quartet multiplicity of each resonance of **6a**; and (c) $^1H\{^{31}P\}$ spectrum of **6a**.



6a

Reactions Catalyzed by $Rh(PPh_3)_2(\mu\text{-}Cl)_2Rh(PPh_3)_2$ (3). When dimer **3** is used as the catalyst, hydrogenation proceeds at a much slower rate than with Wilkinson's catalyst **1**. The dimer complex **3** is only sparingly soluble in benzene and hence the utilization of parahydrogen-induced polarization becomes increasingly important in characterizing solution species. When the hydrogenation of 2-hexene catalyzed by **3** was examined, polarized hydride resonances corresponding to $RhH_2Cl(PPh_3)_3$ (**2**) and the binuclear dihydride **6a** were observed. The optimal temperature for observing **6a** proved to be 313 K, and the extent of polarization was greater than that obtained beginning with **1**. Reaction of **3** with pure *cis*-2-hexene and p-H_2 yielded the same hydride resonances, implying that the binuclear product **6a** contains the cis olefin. However, during reaction some alkene isomerization was observed, as indicated by changes in the olefinic region of the ^{1}H NMR spectrum.

The reaction of **3** with *trans*-2-hexene and H_2 was therefore examined. For this substrate, the corresponding product is much harder to detect and PHIP spectra must be acquired within 15 s of placement of the sample in the NMR probe and without spinning. At temperatures between 313 and 333 K, weakly polarized hydride resonances are found at δ −18.79 and −19.59 ppm. These hydride resonances differ slightly in chemical shift from those detected with *cis*-2-hexene, indicating that the binuclear hydride product of this reaction contains trans olefin. This conclusion is supported by the observation that when a small amount of *cis*-2-hexene is added to the sample containing *trans*-2-hexene, the resonances assigned to the *trans*-2-hexene analog **6b** disappear while those characteristic of the cis adduct **6a** are generated. During these experiments, polarized resonances belonging to **2** were always observed until the temperature was reached at which point phosphine dissociation of **2** became significant. Upon changing the substrate to *cis*-2-pentene in the reaction of **3** with p-H_2, similar resonances assignable to the analogous species $H_2Rh(PPh_3)_2(\mu\text{-}Cl)_2Rh(PPh_3)$(2-pentene) (**6c**) were observed (see Table 1), demonstrating that the olefin is indeed coordinated in the binuclear dihydride complex **6**.

When hydrogenation of methyl methacrylate catalyzed by dimer **3** was carried out at 298 K, multiplet polarization was observed in the hydrogenation product. In the first acquisition period within 5 min of commencing reaction, polarized hydride resonances were also observed for the mononuclear dihydride $RhH_2Cl(PPh_3)_3$ (**2**) and the binuclear species $H_2Rh(PPh_3)_2(\mu\text{-}Cl)_2Rh(PPh_3)$(methyl methyacrylate) (**6d**) (see Table 1). The binuclear complex was also observed without polarization in dichloromethane-d_2 at 273 K when 26 mg of dimer **3** was employed as catalyst in the hydrogenation reaction. The hydride chemical shifts for binuclear product **6d** show a slight solvent dependence, moving to δ −19.23 and −19.81 ppm in CD_2Cl_2. Under these conditions, two resonances in the ^{31}P NMR spectrum of this species are observed at δ 39.3 (J_{RhP} = 118) and δ 52.4 (J_{RhP} = 187 Hz) with coupling constants that confirm the structural assignment of **6d** as a dihydride complex containing Rh(III) and Rh(I) centers.

After the initial acquisition in the hydrogenation of methyl methacrylate, a series of spectra were obtained by removing the sample from the probe, shaking vigorously to reestablish a concentration of para-enriched H_2 in solution, reinserting the sample into the spectrometer and commencing data acquisition within 30 s. These spectra showed weaker polarization in the hydrogenation product, as well as the absence of polarized resonances for **2**. It thus appeared that the rate of hydrogenation was decreasing relative to the rate observed in the initial acquisition. At the same time, polarization for the binuclear species $H_2Rh(PPh_3)_2(\mu\text{-}Cl)_2Rh(PPh_3)$(methyl methacrylate) (**6d**) was observed to increase in each spectrum of the series. These observations suggest that the principal species in solution are changing over time and that the binuclear dihydrides **6** are not involved *directly* in the catalytic cycle for hydrogenation.

The hydrogenation of styrene catalyzed by $Rh(PPh_3)_2(\mu\text{-}Cl)_2Rh(PPh_3)_2$ (**3**) in dichloromethane-d_2 was also examined. In this case, hydrogenation at 298 K proved so rapid that the ethylbenzene product showed net polarization in its resonances at δ 2.41 and 1.04 ppm. The occurrence of *net* polarization in PHIP spectra has been discussed previously and arises due to rapid reaction with p-H_2 *prior* to insertion of the sample into the spectrometer. In other words, when net polarization is seen, reaction involving p-H_2 takes place more rapidly than when multiplet polarization is observed for an identically handled sample. In spectra of styrene hydrogenation using dimer **3**, polarized resonances for $RhH_2Cl(PPh_3)_3$ (**2**) were not observed. On lowering the temperature to 222 K, however, resonances for **2** did appear, and polarization in the ethylbenzene resonances changed from net to multiplet, consistent with slower reaction at the lower temperature. On reducing the temperature further to 213 K, an additional hydride species was seen to be present by virtue of a weakly polarized resonances at δ −16.46 ppm.

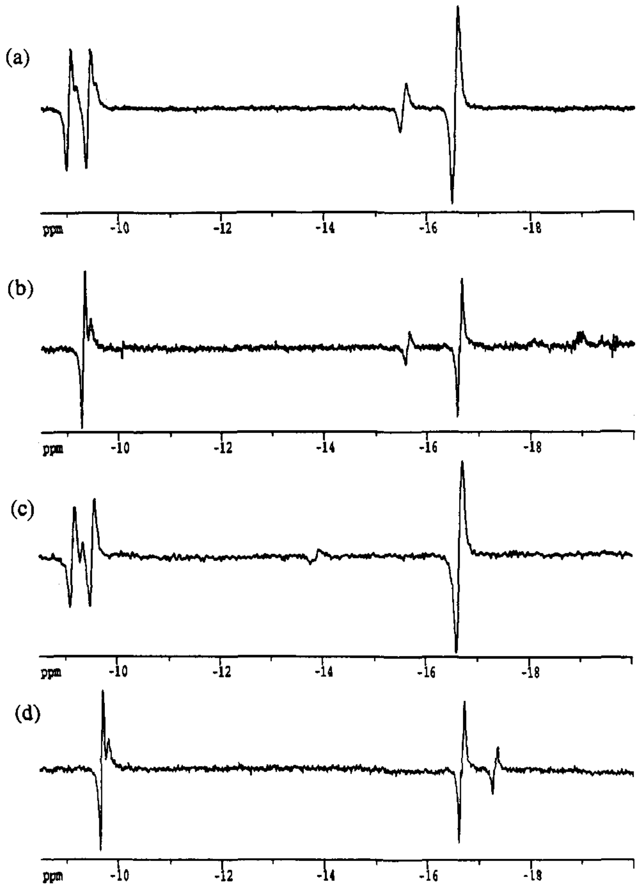


Figure 3. ^{1}H NMR spectra showing enhanced signals obtained in the reaction of p-H_2 with **3** + styrene, *p*-chlorostyrene, and *p*-methylstyrene in C_6D_6: (a) ^{1}H spectrum at 283 K showing polarized resonances for $RhH_2Cl(PPh_3)_3$ (**2**) and $RhH_2Cl(PPh_3)_2$(styrene) (**7a**); (b) $^1H\{^{31}P\}$ spectrum at 283 K of **2** and **7a**; (c) ^{1}H spectrum at 280 K showing polarized resonances for $RhH_2Cl(PPh_3)_3$ (**2**) and $RhH_2Cl(PPh_3)_2$(*p*-chlorostyrene) (**7b**) produced with *p*-chlorostyrene; (d) $^1H\{^{31}P\}$ spectrum at 288 K showing polarized resonances for $RhH_2Cl(PPh_3)_3$ (**2**) and $RhH_2Cl(PPh_3)_2$(*p*-methylstyrene) (**7c**) produced with *p*-methylstyrene.

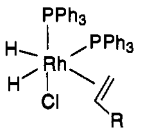
The identity of this new hydride species, denoted **7a**, was probed further by a change in solvent to benzene-d_6 and the use of temperatures between 273 and 283 K that led to PHIP spectra in which the new species was more clearly visible. As shown in Figure 3a, the polarized hydride signature of the new species is partially obscured by the lower field hydride resonance of $RhH_2Cl(PPh_3)_3$ (**2**). The lower field resonances of **7a** occurs at δ −9.42 ppm and corresponds to a hydride that is trans to phosphorus with J_{PH} = 159 Hz, while the higher field component appears at δ −15.63 ppm. A $^1H\{^{31}P\}$ spectrum (Figure 3b) reveals that both of these resonances possess additional *un*resolved coupling from ^{103}Rh as well as antiphase J_{HH} resulting from parahydrogen. When the new hydride is observed, the ratio of detectable H_2 to free olefin in solution is 1:36. Species **7a** can also be detected when **1** is employed as the catalyst in CD_2Cl_2 and the experiment is started at 240 K;

the polarized species is then visible in subsequent runs between 283 and 293 K.

At advanced stages of the hydrogenation, polarized resonances of the binuclear complex $H_2Rh(PPh_3)_2(\mu\text{-}Cl)_2Rh(PPh_3)$(styrene) (**6e**) grow in, while those of **2** and the species denoted **7a** diminish in intensity. After 5 h at 298 K, the sample was placed under fresh p-H_2 and reexamined by NMR spectroscopy at 298 K. The $^1H\{^{31}P\}$ spectrum at this point reveals two sets of resonances (Table 1), both of which are consistent with the binuclear formulation **6e**. The two sets of resonances are present in an approximate 2:1 ratio, and we assign them as belonging to conformers of $H_2Rh(PPh_3)_2(\mu\text{-}Cl)_2Rh(PPh_3)$(styrene) resulting from hindered rotation about the Rh–olefin bond.[30]

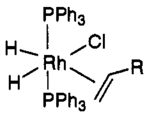
When styrene is replaced by *p*-chlorostyrene and the chloro-bridged dimer **3** is employed as the catalyst, rapid hydrogenation occurs in benzene-d_6 at 280 K and polarized hydride signals for $RhH_2Cl(PPh_3)_3$ (**2**) and an intermediate with resonances at δ −13.85 and −9.53 ppm are seen, as shown in Figure 3c. The intensity of the resonances of the latter intermediate, which we denote as **7b**, is much weaker than that found using styrene. When *p*-methylstyrene is employed as the substrate, new hydride resonances corresponding to **7c** are observed at δ −17.37 and −9.84 ppm with polarization that is slightly stronger than that for **7a**. While the three species **7a**, **7b**, and **7c** exhibit very similar hydride resonances, the differences in their hydride chemical shifts indicate that they possess bound olefin as well as hydrides.

It is noteworthy that parahydrogen signals from **7** parallel in intensity the *rate* of hydrogenation rather than the reversible *binding* of olefin as determined by Halpern.[31] Based on the observations of **7a**, **7b**, and **7c**, the accessibility of these species from different precursors, and their chemical shift sensitivity to particular substrate, we assign their identity as $RhH_2Cl(PPh_3)_2$(olefin), corresponding to one of the intermediates in catalytic hydrogenation by Wilkinson's catalyst (**1**) (Scheme 1). Clearly, the large $^1H-^{31}P$ coupling seen for the more downfield hydride of **7** means that one phosphine is trans to a hydride and that the complex is therefore constrained to have cis phosphines. Additionally, the sensitivity of the other hydride's chemical shift to the particular styrene substrate indicates that the second hydride is trans to the olefin as shown in structure **A**.

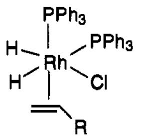


A

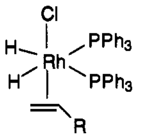
While parahydrogen-induced polarization leads to the structure of **A** for an olefin dihydride species during hydrogenation catalysis, it is not possible at this point to prove its kinetic significance in Scheme 1 through time domain or conventional kinetic experiments. Additionally, other olefin dihydride species shown as **B**–**D** may exist in the system although we have no evidence for them from the experiments reported here. Both structures **B** and **C** should yield parahydrogen-induced polarization if their lifetimes are of similar magnitude to those of **7** (**A**). Structure **D** has apparently equivalent hydrides that may be rendered inequivalent by steric effects of olefin coordination. If the lifetime of any of these olefin dihydride isomers is longer than that of **A**, then it may be possible to observe it by conventional NMR methods—to date, this has not been achieved. If, on the other hand, any of them possesses a significantly shorter lifetime, then the species would represent a more reactive intermediate in hydrogenation catalysis.



B



C



D

An additional consideration in styrene hydrogenation catalysis is the comment by Halpern that for styrene under "commonly employed" conditions, a pathway proceeding via a bis(olefin) mono(phosphine) intermediate becomes dominant.[8] The proposed "bis(olefin)" catalytic cycle, which would be followed in the absence of added phosphine, also contains an olefin dihydride bis(phosphine) intermediate that may have a longer lifetime depending on the equilibrium between mono- and bis(olefin) species. While we cannot rule out the potential importance of the proposed bis(styrene) intermediate under the conditions of the catalysis, we see no evidence for it in the experiments employing parahydrogen.

Reactions of $RhCl(C_2H_4)(PPh_3)_2$ (4) with p-H_2 and Olefin Substrates. The higher solubility of the ethylene complex **4** in benzene-d_6 and dichloromethane-d_2 makes it ideal as a catalyst precursor for following reactions by NMR spectroscopy without the need to utilize parahydrogen-induced polarization. Through the use of **4**, it becomes possible to observe the binuclear species $H_2Rh(PPh_3)_2(\mu\text{-}Cl)_2Rh(PPh_3)$(olefin) (**6**) at low temperatures using conventional NMR spectroscopic methods. In this way, we were able to characterize binuclear species containing a series of substituted styrene ligands and to determine that as the electron withdrawing ability of the olefin increased, the stability of $H_2Rh(PPh_3)_2(\mu\text{-}Cl)_2Rh(PPh_3)$(substituted styrene) increased accordingly.

The most stable of the binuclear complexes $H_2Rh(PPh_3)_2(\mu\text{-}Cl)_2Rh(PPh_3)$(substituted styrene) was found to be that containing pentafluorostyrene, denoted **6f**. Unpolarized resonances for this species (see Table 1) were obtained upon reaction of **4** with pentafluorostyrene and p-H_2 in dichloromethane-d_2 at 243 K. Also seen in the reaction system were resonances for the dihydride complex $RhH_2Cl(PPh_3)_3$ (**2**) and for a small amount of the binuclear complex $H_2Rh(PPh_3)_2(\mu\text{-}Cl)_2Rh(PPh_3)_2$, (**5**). In parahydrogen experiments involving pentafluorostyrene, no polarization was observed, possibly due to rapid equilibration of para- and orthohydrogen via interaction with ^{19}F nuclei in solution. Upon warming the sample to 283 K, resonances for **2** disappeared rapidly while those of the binuclear species remained, suggesting that hydrogenation catalysis involving **2** proceeds more rapidly than that of the binuclear species $H_2Rh(PPh_3)_2(\mu\text{-}Cl)_2Rh(PPh_3)$(pentafluorostyrene) (**6f**). After 12 h at room temperature, however, all of **6f** had been consumed by subsequent reaction.

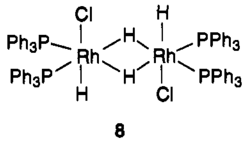
The observation of yet another new hydride was accomplished in a different experiment involving the same reaction system. Specifically, a sample containing 20 mg of **4** and pentafluorostyrene under H_2 in CD_2Cl_2 at 272 K showed after 12 h new hydride resonances that were not attributable to $RhH_2Cl(PPh_3)_3$ (**2**), $H_2Rh(PPh_3)_2(\mu\text{-}Cl)_2Rh(PPh_3)_2$ (**5**), or $H_2Rh(PPh_3)_2(\mu\text{-}Cl)_2Rh(PPh_3)$(pentafluorostyrene) (**6f**). The most prominent of the new hydride resonances were at δ −10.88 and −16.49 with coupling distinctive enough to make possible a reasonable proposal for its structure. The δ −10.88 resonance possesses a triplet of triplets of triplets coupling (J = 75, 21, 10 Hz) which

---

(30) Because of the symmetry of the $H_2Rh(PPh_3)_2(\mu\text{-}Cl)_2Rh(PPh_3)$(styrene) complex, coordination of the *re* and *si* faces of styrene yields the same stereochemistry if rotation about the Rh–olefin bond is rapid and facile.

(31) Halpern, J.; Okamoto, T. *Inorg. Chim. Acta* **1984**, *89*, L53–L54.

simplifies upon ^{31}P decoupling to a triplet with $J = 21$ Hz, while the δ −16.49 resonance is a quartet ($J = 17$ Hz) that simplifies to a doublet upon ^{31}P decoupling. Clearly, this species possesses two different hydrides that are coupled to two and one Rh atoms, respectively. Moreover, the large triplet coupling of the δ −10.88 resonance is consistent with J_{PHtrans} only. A ^{31}P NMR spectrum of the new hydride species shows a lone ^{31}P signal that is split into a doublet-of-doublets-of-doublets pattern with couplings of 126, 76, and 18 Hz (see Table 2); upon ^{1}H decoupling, the resonance simplifies to a single doublet ($J_{\mathrm{Rh-P}} = 126$ Hz). A structure consistent with the spectroscopy assuming an unresolved coupling of 10 Hz in the ^{31}P resonance is shown as **8**. The broadeness of individual lines in the ^{31}P NMR spectrum inhibits observation of the 10 Hz coupling seen in the corresponding ^{1}H NMR spectrum.



8

Complex **8** is also produced, along with $H_2Rh(PPh_3)_2(\mu\text{-}Cl)_2Rh(PPh_3)_2$ (**5**), when the Rh(I) dimer **3** is reacted with H_2 at 298 K for long periods of time (>10 h); other unidentified hydride species are also noted at this point in the reaction but their concentrations are substantially smaller. Bridging hydride complexes similar to **8** have been synthesized and characterized by Fryzuk and co-workers, and the observed coupling patterns for the unsupported hydride bridges are very similar to those noted for **8**.[32−34]

When low concentrations of the ethylene complex **4** are used to catalyze the hydrogenation of *p*-chlorostyrene at 243 K, polarized resonances for $RhH_2Cl(PPh_3)_3$ (**2**), *p*-chloroethylbenzene, and the olefin dihydride catalytic intermediate **7b** are observed. Complex **7b** possesses hydride ligands that resonate at δ −10.19 ($J_{\mathrm{PH}} = 160$ Hz) and −14.54 ppm in CD_2Cl_2. After the addition of fresh p-H_2 to the sample, the $^{1}H\{^{31}P\}$ spectrum at 243 K reveals the binuclear complexes $H_2Rh(PPh_3)_2(\mu\text{-}Cl)_2Rh(PPh_3)$(*p*-chlorostyrene) (**6g**, unpolarized) and $H_2Rh(PPh_3)_2(\mu\text{-}Cl)_2Rh(PPh_3)_2$ (**5**) in a 2:1 ratio and the absence of polarized resonances for **2** and the olefin dihydride species **7b**. A $^{31}P\{^{1}H\}$ spectrum of the sample shows the resonances characteristic of the Rh(III)/Rh(I) binuclear olefin complexes **6g** and **5** as given in Table 2. After the consumption of substrate, the only Rh species that we were able to observe were Tolman's dihydride $H_2Rh(PPh_3)_2(\mu\text{-}Cl)_2Rh(PPh_3)_2$ (**5**), the bridging hydride complex $RhHCl(PPh_3)_2(\mu\text{-}H)_2RhHCl(PPh_3)_2$ (**8**), and minor and as yet unidentified species. Based on the experiments with **4** as the catalyst precursor, it is evident that the binuclear olefin complexes **6** can be readily detected at higher catalyst concentrations without polarization.

Interestingly, when $[RhCl(C_2H_4)_2]_2$ was added as a phosphine sponge to samples containing **4** or **1**, the rate of hydrogenation of *p*-chlorostyrene based on the magnitude of parahydrogen-induced polarization in the product was observed to decrease from one run to the next and no polarized hydride product resonances were observed. However, when a small amount of free PPh_3 was added to the sample, the system returned to full activity and strongly polarized product resonances were again observed. We propose that the rate of hydrogenation drops upon the introduction of $[RhCl(C_2H_4)_2]_2$ because as free PPh_3, generated by dissociation from $RhCl(PPh_3)_3$ (**1**) and $RhH_2Cl(PPh_3)_3$ (**2**) and by olefin substitution of *in situ* generated $Rh(PPh_3)_2(\mu\text{-}Cl)_2Rh(PPh_3)_2$ (**3**), is removed from the reaction system, binuclear complex formation increases, leading to a less reactive catalyst system. In other words, small amounts of free phosphine are needed in the catalyst system to maintain its activity and inhibit transformation to the less reactive binuclear species. Tolman *et al.* have made this point previously,[4] and our results confirm this view.

Conclusions

Studies of the reaction chemistry of $RhCl(PPh_3)_3$ with p-H_2 in the absence and presence of olefin have provided insight into the nature and role of important unsymmetrical dihydride species in hydrogenation catalysis promoted by **1**. Specifically we have found evidence that Rh(III)/Rh(I) dimers of the type $H_2Rh(PPh_3)_2(\mu\text{-}Cl)_2Rh(PPh_3)$(olefin) (**6**) are accessible and that their stability increases as the olefin becomes less electron rich. Under these conditions, we have also been able to detect spectroscopically a $RhH_2Cl(PPh_3)_2$(olefin) complex (**7**) that corresponds to a possible intermediate in hydrogenation catalyzed by **1** and find that it contains phosphines that are arranged in cis fashion. For such hydrogenation reactions, this seems to be the optimum geometry for what is the key olefin dihydride intermediate.[11] Our results also confirm that small amounts of free phosphine inhibit the formation of binuclear complexes **5** and **6**, thereby enhancing the catalytic activity of Wilkinson's complex. The great sensitivity of parahydrogen-induced polarization as a means of detecting *and* characterizing species present in small concentrations also serves to underscore the notion that the potential surface of the $RhCl(PPh_3)_3 + H_2 +$ olefin reaction system contains more local minima than previously recognized, regardless of their kinetic significance.

Experimental Section

The complexes $RhCl(PPh_3)_3$, $RhCl(C_2H_4)(PPh_3)_2$, and $[RhCl(PPh_3)_2]_2$ were prepared according to established procedures.[2] The olefins 2-hexene, *cis*-2-hexene, *trans*-2-hexene, *cis*-2-pentene, styrene, *p*-chlorostyrene, *p*-fluorostyrene, pentafluorostyrene, and cyclohexene were purchased from Aldrich and added by vacuum transfer or syringed addition. NMR samples were prepared in 5 mm tubes which were fitted with a high-vacuum valve (J. Young). NMR solvents benzene-d_6, toluene-d_8, and dichloromethane-d_2 were bought from Cambridge Isotopes, dried using standard methods, and stored under nitrogen prior to use. Spectra were recorded on a Bruker AMX400 spectrometer with a multichannel interface and a rapid switching, power selective X channel amplifier. All ^{1}H spectra were acquired using 45° excitation pulses, and $^{1}H\{^{31}P\}$ spectra were acquired using a modified GARP sequence for large frequency range decoupling at ^{31}P and CW irradiation for selective decoupling.[35] Polarization transfer to ^{31}P was achieved via the INEPT pulse sequence with initial 45° excitation pulses in the ^{1}H channel.

Typically, the rhodium catalyst was placed in an NMR tube under N_2 in a drybox. If the olefin substrate was of low volatility, it was introduced onto the catalyst at this stage. The NMR tube was then connected to a vacuum line where deuterated solvent was added by vacuum transfer. For cases such as aliphatic olefins, substrate addition took place after solvent introduction via similar vacuum transfer methods. The sample was then degassed, and the tube was opened to a 1 L bulb containing H_2 equilibrated at 77 K over a paramagnetic catalyst. Both vessels were immersed in liquid nitrogen. The Young's valve was then closed and the NMR tube was stored in liquid nitrogen until just prior to examination.

---

(32) (a) Fryzuk, M. D. *Can. J. Chem.* **1983**, *61*, 1347−1351. (b) Fryzuk, M. D.; Jang, M.-L. *Can. J. Chem.* **1986**, *64*, 174−179.

(33) Fryzuk, M. D.; Piers, W. E.; Einstein, F. W. B.; Jones, T. *Can. J. Chem.* **1989**, *67*, 883−896.

(34) Fryzuk, M. D.; McConville, D. H.; Rettig, S. J. *Organometallics* **1990**, *9*, 1359−1360.

(35) Shaka, A. J.; Barker, P. B.; Freeman, R. *J. Magn. Reson.* **1985**, *53*, 457.

All of the reaction systems were examined by the same basic procedure. Therefore, we only describe two typical experiments in more detail.

Reaction of 1 with p-H_2 and *cis*-2-pentene. After the sample was prepared according to the procedure described above and stored in liquid nitrogen, it was rapidly warmed by immersion in a flask of cool water, shaken, and introduced into the spectrometer probe within 30 s. The first run showed polarization in the hydrogenation product pentane and the hydride resonances of **2**. Also observed were weak and unpolarized resonances for **5**. In this spectrum the ratio of olefin to catalyst, based on the phenyl region of the spectrum, was 122:1. An additional spectrum was acquired immediately after the first set of scans was finished and it revealed that no hydrogen was left in solution. The sample was then removed from the probe, shaken, and returned to the spectrometer at which point both **2** and **5** could be seen, with the resonances for **5** more intense than in the previous run. After several more spectral acquisitions, the sample was refilled with p-H_2 and spectra were collected at 303 K, revealing that the unpolarized resonances of **5** were larger than the amplified resonances of **2**. As the olefin was consumed in the reaction system, the time period over which polarization remained visible increased, indicating a corresponding reduction in hydrogenation rate.

Reaction of $RhCl(C_2H_4)(PPh_3)_2$ with *p*-chlorostyrene. A CD_2Cl_2 sample was prepared which contained **4** and *p*-chlorostyrene in the ratio 1:20. The sample was introduced into the probe at 243 K and spectra were rapidly recorded. Both **2** and the olefin dihydride intermediate **7b** were observed. In a subsequent run, a $^1H\{^{31}P\}$ spectrum was acquired which simplified the resonances for the two products into doublets of antiphase doublets due to J_{RhH} and J_{HH}. The sample was refilled with p-H_2 and examined between 243 and 277 K. During all these runs, **7b** was visible. Approximately 12 h later, an additional amount of **4** was added to the sample. Under these conditions the binuclear products were now detected at 243 K, but their hydride resonances were not polarized.

Acknowledgment. Financial support of this work from the National Science Foundation (Grant No. CHE 89-06090) and a generous loan of rhodium trichloride from the Johnson-Mathey Aesar/Alfa Company are gratefully recognized.