

- (1989).
- S. Lee and H. Kim, *Arch. Biochem. Biophys.* **271**, 188 (1989).
 - H. Sigrest, C. Kempf, in A. Azzi, V. Brodbeck, and P. Zahler eds. "Membrane Proteins. A Laboratory Manual", Springer-Verlag, 1981.
 - K. Sigrist-Nelson, H. Sigrest, H. Ariano and A. Azzi, *FEBS Letter* **95**, 140-142 (1978).
 - M. E. Dumont and F. M. Richards, *J. Biol. Chem.* **259**, 4147 (1984).
 - A. Rietveld, W. Jordi, and de B. Kruijff, *J. Biol. Chem.* **261**, 3846 (1986).
 - F. J. Szoka and D. Papahadjopoulos, *Proc. Nat. Acad. Sci. U.S.A.* **75**, 4194 (1978).
 - O. H. Lowry, N. J. Rosebrough, A. L. Farr and R. J. Randall, *J. Biol. Chem.* **193**, 265 (1951).
 - R. T. Swank and K. D. Munkres, *Anal. Biochem.* **39**, 462 (1971).
 - D. M. Engelman and T. A. Steitz, *Cell* **23**, 411 (1981).
 - M. Chabre, *Trends in Biochem. Sci.* **12**, 213 (1987).
 - R. W. Dams and A. Helenius, in S. Ohki *et al.* eds. "Molecular Mechanisms of Membrane Fusion" Plenum, 1988.

Synthesis and Solution Chemistry of Metal Hydrides from Cationic Rhodium(I) Catalyst Precursors [(L-L)Rh(NBD)]ClO₄ (L-L = Fe(η^5 -C₅H₄PBu^t)₂, Fe(η^5 -C₅H₄PPhBu^t)₂)

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The hydrogenation catalyst precursors [(L-L)Rh(NBD)]ClO₄ (L-L = Fe(η^5 -C₅H₄PBu^t)₂, Fe(η^5 -C₅H₄PPhBu^t)₂; NBD = norbornadiene) react with H₂ (1 atm, 30 °C, MeOH) to yield [(L-L)HRh(μ -H)₃RhH(L-L)]ClO₄. These hydrido species are fluxional, and variable temperature NMR studies show the existence of a number of equilibria involving both fluxional and non-fluxional species. The synthesis, solution structures, and fluxional behaviors of these hydrides are described.

Introduction

One of characteristic features of cationic rhodium(I) hydrogenation catalyst [(L-L)Rh(diene)]⁺ (L-L = chelating di(tertiaryphosphine)) is that hydrogenation of this complex results initially in the formation of a disolvate [(L-L)Rh(S)₂]⁺ (S = solvent) rather than catalytic hydride(s) commonly found in the case of the monophosphine analogues [(L)₂Rh(diene)]⁺.^{1,2} Brown and coworkers³, however, have recently shown that hydrogen does add reversibly to [(dppe)Rh(S)₂]⁺ (dppe = 1,2-bis(diphenylphosphino)ethane, S = MeOH) to give an undetectable concentration of a dihydride [(dppe)Rh(H)₂(S)₂]⁺. This hydride was formulated as such because Otsuka and coworkers⁴ have suggested that this is the composition of the incompletely characterized solids obtained from the reaction of [(L-L)Rh(NBD)]ClO₄ with H₂ (L-L = (C₆H₁₁)₂P(CH₂)₄P(C₆H₁₁)₂).

More recently, for the first time, we⁵ also reported that metal hydrides are easily obtained from cationic rhodium complexes where L-L is one of a wide range of ferrocenylalkylphosphine [η^5 -C₅H_{5-n}(PR₂)_n]Fe[η^5 -C₅H₃(PR₂)C(H)MeNMe₂-1,2] and Fe(η^5 -C₅H₄PR₂)₂ (R = Bu^t, Pr^t, or Ph; n = 0-2). In two instances hydrides were isolated as stable crystals formulated as [(L-L)HRh(μ -H)₃RhH(L-L)]ClO₄ (**3a**, L-L = Fe(η^5 -C₅H₄PBu^t)₂ (**1a**); **3b**, L-L = Fe(η^5 -C₅H₄PPhBu^t)₂ (**1b**)). As crystals of **3a** were not good enough to allow the number and disposition of hydrogen atoms to be determined with any certainty, the formulation was based on the charge and the similarity of the overall ligand disposition in the two

hydride **3a** and **3b**.

We now provide further evidence for the presence of both terminal and bridging hydrido ligands in **3a** from our NMR studies, along with the description in detail of the synthesis of the two. The NMR spectra of both **3a** and **3b** are complex, and variable temperature studies show the existence of a number of equilibria involving both fluxional and non-fluxional species. These points will also be addressed in this paper.

Experimental

Generals. All manipulations of air-sensitive reagents and products were conducted under an argon atmosphere using a double manifold vacuum system and Schlenk techniques. All commercial reagents were used as received unless otherwise mentioned. Solvents were purified by standard techniques⁶, and were freshly distilled prior to use. Hydrogen was passed through a "deoxo" catalytic purifier before use.

Melting points were determined using a Gallenkamp melting point apparatus and are reported without correction. Micro-analyses were performed by Mr. P. Borda of Department of Chemistry, University of British Columbia, Vancouver, Canada. ¹H NMR spectra were recorded on a Bruker WH-400 spectrometer operating at 400 MHz and ³¹P NMR spectra on Bruker WP-80 or Varian XL-100 spectrometers operating at 32.3 MHz or 40.5 MHz, respectively. All chemical shifts are positive to lower shielding with the following

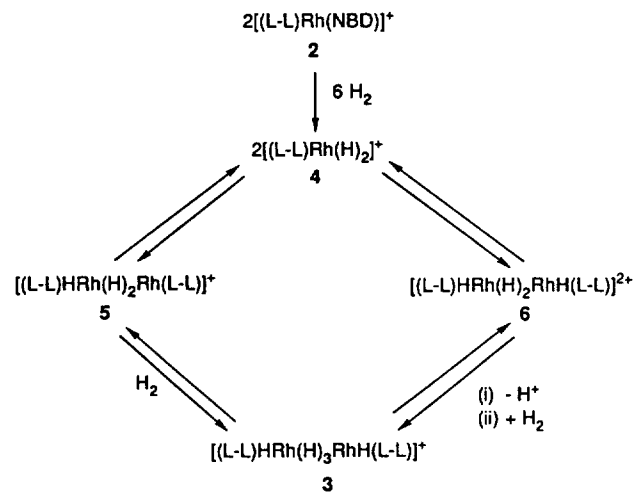
captions for coupling constants: d = doublet, dd = doublet of doublets, dm = doublet of multiplets, dtd = doublet of triplets of doublets, dt = doublet of triplets, tbd = triplet of broad doublets. All coupling constants are in Hz. ^1H shifts are relative to external standard TMS ($\delta = 0$ ppm) and ^{31}P shifts are relative to 85% H_3PO_4 with $\text{P}(\text{OMe})_3$ ($\delta = +141.0$ ppm) used as an external standard. 1,1'-bis(di-*t*-butylphosphino)ferrocene (**1a**), 1,1'-bis(*t*-butylphenylphosphino)ferrocene (**1b**), and their cationic rhodium complexes $[(\text{L}-\text{L})\text{Rh}(\text{NBD})]\text{ClO}_4$ (**2a**, $\text{L}-\text{L} = \mathbf{1a}$; **2b**, $\text{L}-\text{L} = \mathbf{1b}$) were prepared according to the literature procedures.^{7,8}

Synthesis of $[(\text{L}-\text{L})\text{HRh}(\text{u}-\text{H})_3\text{RhH}(\text{L}-\text{L})]\text{ClO}_4$ (3a**, $\text{L}-\text{L} = \mathbf{1a}$; **3b**, $\text{L}-\text{L} = \mathbf{1b}$).** Hydrogenation of the catalyst precursors **2a** and **2b** was carried out using the following three methods.

Method A: with measurement of H_2 up-take. The accurately weighed catalyst precursor (1.2×10^{-4} mol) and an appropriate solvent (3 ml) were placed in a reaction vessel. The typical gas-up-take experiments were followed using the constant gas up-take apparatus described in the literature.^{7,9}

Method B: with crystallization of the product. In order to isolate any product formed, the reaction described in Method A was duplicated as follows. The same amount of catalyst precursor and methanol were placed in a Schlenk tube. This was connected to a double manifold vacuum system which, in turn, was connected to both N_2 and H_2 . The solution was degassed by the freeze-and-thaw method, and hydrogen was introduced to this solution with vigorous stirring at room temperature for 1–1.5 h to ensure that the reaction was complete. The hydride **3a** was isolated as dark red crystals by cooling the final solution to 0°C overnight. Anal. calcd. for $\text{Rh}_2\text{Fe}_2\text{P}_4\text{ClO}_4\text{C}_{52}\text{H}_{93}$: C, 49.60; H, 7.39; Cl, 2.82; O, 5.09. Found: C, 49.23; H, 7.36; Cl, 3.64; O, 6.30. ^1H NMR (400 MHz) in the hydride region at -85°C (CD_2Cl_2): δ -9.96 (d, $J = 120$ Hz, relative intensity (I) = 2); δ -10.77 (d, $J = 120$ Hz, I = 3); δ -22.38 (dtd, $J(\text{t}) = 17.2$ Hz, $J(\text{d}) = 27$ Hz, $J(\text{d}) = 4$ Hz); δ -25.46 (dt, $J(\text{d}) = 32$ Hz, $J(\text{t}) = 32$ Hz); δ -27.66 (dtd, $J(\text{t}) = 16$ Hz, $J(\text{d}) = 39.6$ Hz, $J(\text{d}) = 4$ Hz); δ -26.99 (m, $l = 2$); δ -27.08 (m, $l = 1$). The hydride **3b** was isolated as orange crystals by allowing the final reaction mixture to stand overnight at room temperature. The full crystallographic data and the structure of this compound has been published in our preliminary communication.⁵ ^1H NMR (400 MHz) in the hydride region at -90°C (CD_2Cl_2): δ -8.7 (bd, $l = 3$); δ -23.3 (br, $l = 2$).

Method C: with NMR monitoring of the *in situ* solutions. The catalyst precursor **2b** (40 mg, 5.0×10^{-5} mol) was dissolved in CD_3OD , CD_3CN , or CDCl_3 in an NMR tube which was then connected to the vacuum system described above. The solution was degassed as above, and then hydrogen was introduced to the solution with occasional shaking. As the gas diffused through the solution and reacted with the complex, the color change progressed from the top meniscus to the bottom of the tube. No further color change was observed over a period of 1 h. The variable temperature NMR spectrum of the *in situ* solution was then recorded. ^1H NMR (400 MHz) in the hydride region at -90°C (CD_3OD): δ -12.35 (dm, $J(\text{d}) = 172$ Hz, $l = 2$); δ -13.23 (dm, $J(\text{d}) = 180$ Hz, $l = 2$); δ -18.13 (dd, $J(\text{d}) = 24$ Hz, $J(\text{d}) = 28$ Hz, $l = 1$); δ -18.29 (dd, $J(\text{d}) = 24$ Hz, $J(\text{d}) = 28$ Hz); δ -18.53 (dd, $J(\text{d}) = 24$ Hz, $J(\text{d}) = 28$ Hz); δ -21.82 (tm, $J(\text{t}) = 24$ Hz, $l = 2$); δ -22.45 (tm, $J(\text{t}) =$



Scheme 1

28 Hz, $l = 2$); δ -22.88 (tbd, $J(\text{t}) = 28$, $J(\text{bd}) = 12$ Hz, $l = 1$); δ -23.36 (m, $l = 1$).

Results and Discussion

$[(\text{L}-\text{L})_2\text{HRh}(\text{u}-\text{H})_3\text{RhH}(\text{L}-\text{L})]\text{ClO}_4$ (3a**, $\text{L}-\text{L} = \mathbf{1a}$).** After passage of H_2 to a methanolic solution of **2a** for 30 min deep red crystals deposited on cooling the reaction mixture to 0°C . The partial crystal structure of this product has already appeared in our preliminary communication.⁵ Although the number and disposition of hydrogen atoms could not be determined with certainty because of disorder in the crystal, the formulation of this compound was based on the charge and the similarity of the overall ligand disposition in the two hydrido species **3a** and **3b**. A possible route to this product is as in Scheme 1.

The first step, the formation of the dihydrido Rh(III) species from the precursor (**2**), might have been facilitated by increased nucleophilicity of the rhodium center exerted by more basic alkylphosphinoferrocene toward oxidative addition of hydrogen. A plausible dimerization of **4** yields either cation with a dihydride bridge **5** or **6** or both which may be present in solution. The more stable species **3** can be isolated on cooling either by further oxidative addition or by deprotonation from **6** followed by oxidative addition of hydrogen.

The ^1H NMR spectrum of **3a** is quite complex, and variable temperature studies exhibit the existence of a number of equilibria, thus providing further evidence for the presence of hydrido ligands. These are seen in Figure 1. The hydride NMR pattern at -85°C consists of (i) a set of temperature-independent signals T1, T2, and T3 and (ii) a set of temperature-dependent signals B1, B2, T4, and T5. On warming the solution to -60°C , both bridging and terminal resonances B1/B2 and T4/T5 merge to give broad multiplet B (~ -10.6 ppm) and T (~ -27.5 ppm), respectively. By 0°C both signals B and T have collapsed, and a new averaged signal A appears at -17.23 ppm on further warming to 35°C . The attempted interpretation of all these spectra is as follows. As indicated in Scheme 1, any dimeric Rh(III) species could dissociate reversibly to form $[(\text{L}-\text{L})\text{Rh}(\text{H})_2]^+$ which in turn could produce $[(\text{L}-\text{L})\text{RhH}]$ via deprotonation. Here the perchlorate anion is likely to be coordinating because the solvent

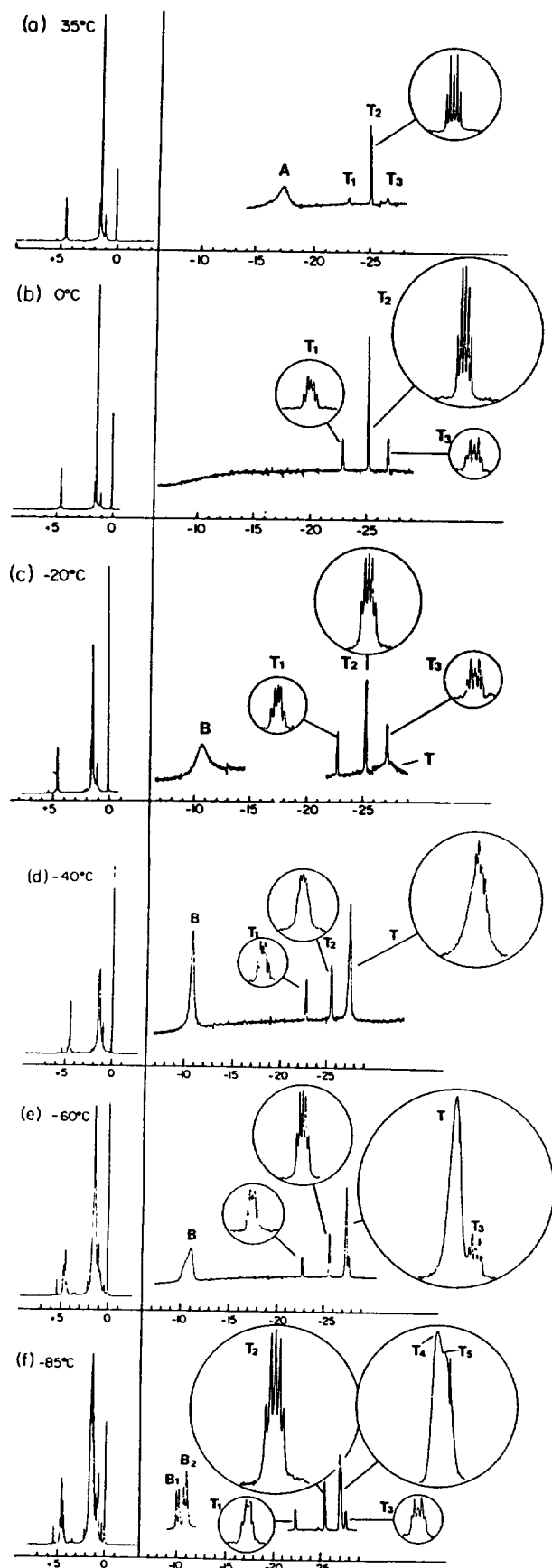


Figure 1. Variable temperature 400 MHz ^1H NMR spectrum (CD_2Cl_2) of the hydrogenation product (**3a**) from MeOH.

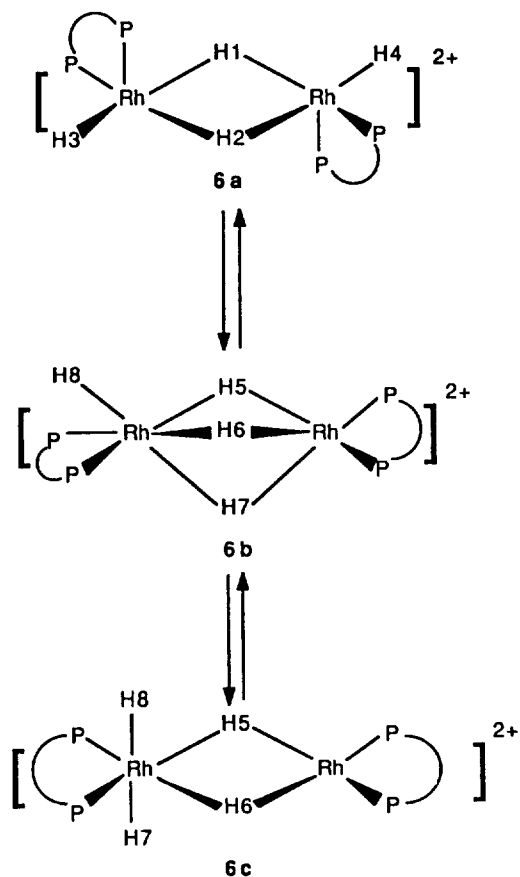
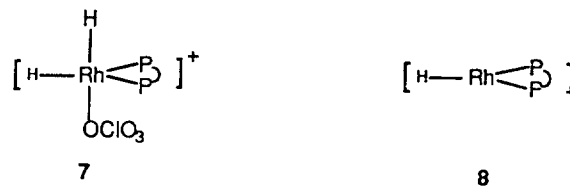
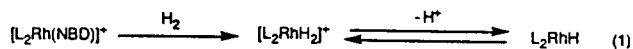


Figure 2. The proposed intramolecular exchange processes in the CD_2Cl_2 solution of the hydrogenation product (**3a**).

in this case is non-coordinating CD_2Cl_2 . The possible structures of these two species are shown below. This reversible



loss of a proton has been well-established for dihydrides obtained in similar systems involving monodentate ligands (equation 1).¹⁰



The pair of signals T1 and T3 can be assigned to the two non-equivalent hydrides in **7**. They appear to be a doublet of triplets of doublets with coupling constants as follows: T1 ($^1J_{\text{RhH}} = 27$ Hz, $^2J_{\text{PH}} = 17.2$ Hz, $^2J_{\text{HH}} = 4$ Hz); T3 ($^1J_{\text{RhH}} = 39.6$ Hz, $^2J_{\text{PH}} = 16$ Hz, $^2J_{\text{HH}} = 4$ Hz). These coupling constants are not unreasonable as compared with reported values for other related species.^{2a,4,11-13} The signal T2 with five lines can be treated as a doublet of triplets with separation of 32 Hz in both patterns. This signal may be assigned to the Rh(I) monohydride **8**. In connection with the structure **7**, it should be mentioned that monitoring the same reaction by ^{31}P NMR in MeOH (~ 30 min) resulted in a broad doublet ($\delta = 83.3$ ppm, $^1J_{\text{RhP}} = 113.5$ Hz). Each signal in the doublet was split into

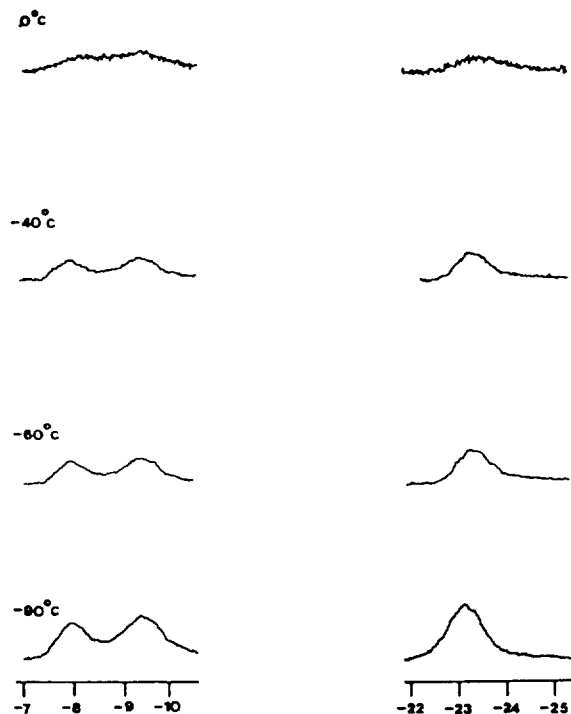


Figure 3. Variable temperature 80 MHz ^1H NMR spectrum of **3b** in CD_2Cl_2 .

four lines ($^2J_{\text{PH}} = 10$ Hz) when hydride coupling was left in. These observations are consistent with the formation of **7** although the coordinated perchlorate ion should be replaced with MeOH in this case. The anticipated disolvate $[(\text{L}-\text{L})\text{Rh}(\text{MeOH})_2]^+$ and the proposed monohydride **8** were not observed in this experiment. A number of other species were formed on leaving the solution overnight.

The temperature-dependent signals (B1, B2, T4, and T5) can be explained in terms of the Rh(III) dimer **6** and its fluxional behavior as proposed in Figure 2.

If, at -85°C , only one exchange process ($\mathbf{6a} \rightleftharpoons \mathbf{6b}$) were occurring slowly on the NMR time scale, the hydride NMR pattern would consist of five distinct signals due to H1/H2, H5/H6, H7, H3/H4, and H8. On these bases the broad doublets B1 and B2 can be assigned to the pair of equivalent bridging hydrides H1/H2 and H5/H6, respectively. The resonance for the unique bridging hydride H7 could be superposed on the higher shielding peak of the doublet B2 since the signal B2 is asymmetric (Note 1 $(\text{B2})/1(\text{B1}) = 3/2$). All the bridging hydrides except H7 have a single *trans* P atom, accounting for large separation (120 Hz) in both doublets B1 and B2. Their chemical shifts and coupling constants are consistent with those previously noted for related bridging hydrides.^{14,15} Other couplings, H-H, Rh-H, and *cis* P-H are too small to be observed. The broad signal T4 and T5 can then be assigned to the terminal hydrides H3/H4 and H8, respectively. On warming the solution ($-85^\circ\text{C} \rightarrow -60^\circ\text{C}$), the exchange $\mathbf{6a} \rightleftharpoons \mathbf{6b}$ should become fast to give the averaged signal B and T for the five bridging hydrides and the three terminal ones, respectively. The exchange is still slow enough for the bridging and terminal hydrides to be distinguished in the range -85°C to -20°C . At higher temperatures ($> -20^\circ\text{C}$) an exchange process such as $\mathbf{6b} \rightleftharpoons \mathbf{6c}$ seems

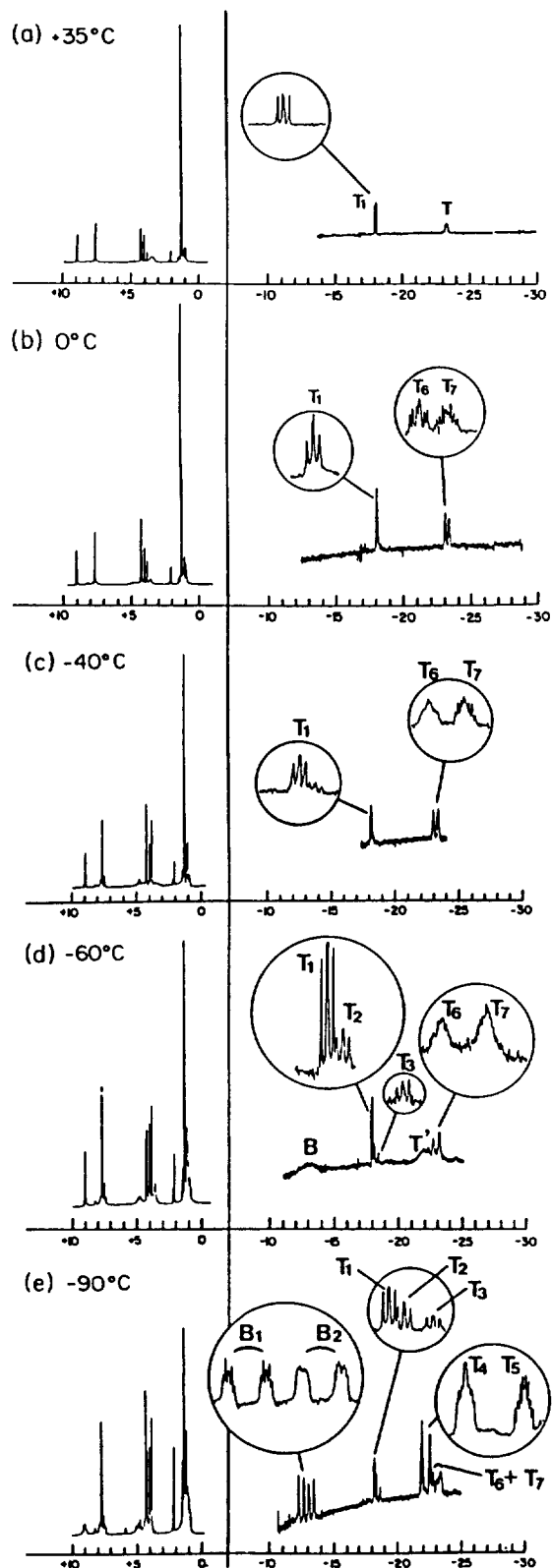


Figure 4. Variable temperature 400 MHz ^1H NMR spectrum of the hydrogenated solution (CD_3OD) of **2b**.

operative and all the hydride ligands become equivalent to give only one signal: signal A.

$[(\text{L}-\text{L})\text{HRh}(\text{u}-\text{H})_3\text{RhH}(\text{L}-\text{L})]\text{ClO}_4$ (**3b**, $\text{L}-\text{L} = \mathbf{1b}$). Af-

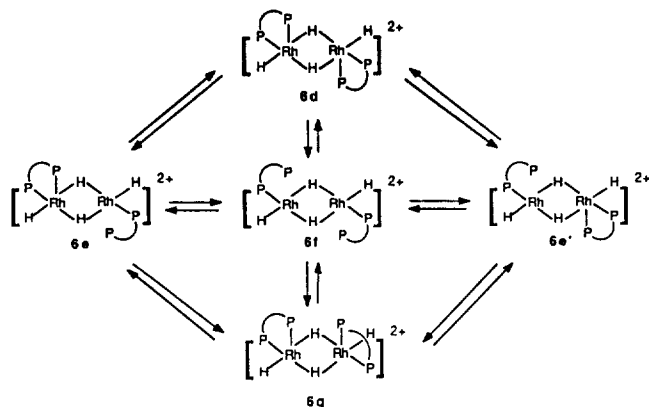


Figure 5. The proposed intramolecular exchange processes in the hydrogenated solution (CD_3OD) of **2b**. The vacant sites of metal may be filled with CD_3OD . $\text{M} = \text{Rh}$, $\text{P-P} = \mathbf{1b}$.

ter passage of H_2 to a methanolic solution of **2b** for about 1 h the resultant yellow solution deposited orange crystals on standing at room temperature. According to the crystal structure described earlier in our preliminary communication,⁵ this molecule should exhibit three hydride resonance signals if it is non-fluxional. Yet no hydride signal was observed at 35°C . Cooling to 0°C resulted in the appearance of (i) a broad terminal resonance at -23.3 ppm ($l = 2$) and (ii) a pair of broad signals of equal intensity at -8.0 ppm and -9.4 ppm ($l = 3$). Both signals are slightly sharpened on further cooling ($-40^\circ\text{C} \rightarrow -90^\circ\text{C}$). The fluxional process in the two regions seem to be independent in the range -90°C to 0°C as seen in Figure 3.

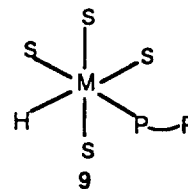
Thus a possible exchange process may involve the structure where all three bridging hydrides are equivalent and *trans* to a single phosphorus atom to give a broad doublet whose separation of 112 Hz is assignable to a *trans* P-H coupling ($^2J_{\text{PH}}$). Similar but better resolved and assignable spectra have been reported for the iridium analogues $[\text{Ir}_n(\text{H})_{2n+1}(\text{dppp})_n](\text{BF}_4)_{n-1}$ ($n = 2, 3$; $\text{dppp} = \text{Ph}_2\text{P}(\text{CH}_2)_3\text{PPh}_2$) and $[\text{Ir}_2(\text{u-H})_3(\text{PPh}_3)_4]\text{PF}_6$.^{14a,15}

Since we set out to garner more information on the solution structures and the fluxional behavior of these hydrido species, we carried out the same reaction in CD_3OD , and the solution monitored by ^1H NMR (-30 min) as described in the Experimental section. The variable temperature ^1H NMR spectra are shown in Figure 4.

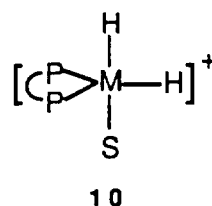
The low temperature (-90°C) hydride NMR pattern consists of (i) a set of temperature-invariant signals T1, T2, and T3 and (ii) a set of temperature-variant signals B1, B2, T4, T5, T6, and T7. As the temperature is raised to -60°C , both pairs of bridging signals B1/B2 and terminal signals T4/T5 merge to give broad multiplets B and T', respectively. By 0°C all the signals except T1, T6, and T7 have disappeared. Further warming (35°C) causes the pair of multiplets T6 and T7 to coalesce to a broad multiplet T, and thus only two signals T1 and T are seen at this temperature. None of the signals associated with the isolated product (**3b**) are present in these spectra. The attempted interpretation of all these spectra is as follows based on Scheme 1 and Figure 5.

The temperature-invariant signal T1 appears to be a doublet of doublets with small coupling constants (24 Hz and 28 Hz). The weaker signals T2 and T3 also give the same pat-

tern which is difficult to account for in terms of chelating ligands. One possibility involving a dangling phosphine is seen below. A possible dissociative process through which **9** can be formed is proposed in Figure 5 based on the equilibria in Scheme 1.



The intensity of T2 and T3 decreases as that of T1 increases on warming ($-90^\circ\text{C} \rightarrow -60^\circ\text{C}$), and then T2/T3 disappear at -40°C . This fluxional behavior is hard to explain although the intramolecular exchange processes in Figure 5 suggest that dissociation of the dimers **6d-6g** become irreversible at higher temperatures ($> -40^\circ\text{C}$) to result in the predominant formation of monomers such as **9**. The remaining aspect of Figure 4 may be discussed as below. If the isolated product **3b** were formed reversibly through the route $2 \rightarrow 4 \rightarrow 6 \rightarrow 3$ as shown in Scheme 1, then the solution could contain a doubly bridged Rh(III) dimer analogous to **6**. Since the ligand (L-L) in this case is *rac*-**1b**, there are two possible combinations to form this dimer: namely, an enantiomeric pair of dimers (S,S,S,S) $-/(R,R,R,R)-$ and an equivalent pair of dimers (S,S,R,R) $-/(R,R,S,S)-$ **1b**. Here S and R refer to the configuration at P atoms of the ligand. Each enantiomer such as (S,S,S,S) possesses two pairs of diastereotopic hydrides H1/H2 and H3/H4 by internal comparison. On the other hand, the (S,S,R,R) $-/(R,R,S,S)-$ diastereomers possess an equivalent pair of bridging and of terminal hydrides by internal comparison. Thus the signals B1, B2, T4, and T5 can be assigned to the structure (S,S,S,S)-**6d**. Either the doublet of multiplets B1 or B2 is associated with H1 or H2 with $^2J_{\text{PH}}(\text{B1}) = 172$ Hz and $^2J_{\text{PH}}(\text{B2}) = 180$ Hz. The terminal hydrides H3 and H4 would appear as a triplet of multiplets with $^2J_{\text{PH}}$ value of 24 Hz and 28 Hz as seen in T4 and T5. Additional small couplings to Rh and H1/H2 are responsible for the multiplicities. Although it is conceivable that the solution contains the equivalent pair of diastereomers (S,S,R,R) $-/(R,R,S,S)-$, the low temperature (-90°C) NMR pattern seems to exclude this possibility, due to the pair of equivalent bridging and terminal hydrides. Another possible intermediate on the same reaction route $2 \rightarrow 4 \rightarrow 6 \rightarrow 3$ could be the five-coordinate dihydride Rh(III) species **10** analogous to **4**. The multiplets T6 and T7 can be assigned to this



species. Thus the axial hydrogen is seen as a triplet of broad doublets T6 ($^2J_{\text{PH}} = 28$ Hz, $^1J_{\text{RhH}} = 12$ Hz). The equatorial hydrogen has essentially the same but more spread-out pattern (signal T7) probably because of a greater $^2J_{\text{PH}}$.

The principal feature of the temperature-dependent spectra is the collapse of the bridging resonances B1 and B2 at

the same rate as the terminal resonances T4 and T5 without the appearance of any new average resonance. This indicates that the fluxional process must be such as the exchange among terminal and bridging hydrogen atoms independently. Such a process is also set out in Figure 5. The most important feature of the equilibria shown is the requirement for phosphine dissociation as suggested above for the structure of **10**. The exchange process could proceed in a stepwise manner (**6a** \rightleftharpoons **6b** \rightleftharpoons **6f** (or **6g**) \rightleftharpoons **6e'** \rightleftharpoons **6d**) or in a simultaneous manner (**6d** \rightleftharpoons **6f** \rightleftharpoons **6g**). If the exchange is fast on the NMR time scale the diastereotopic pair of bridging hydrides H1/H2 and terminal ones H3/H4 become equivalent resulting in the broad signal B and T' at -60°C . As mentioned previously, at higher temperatures ($>-60^\circ\text{C}$), the fluxional dimers **6d-6g** presumably dissociate to the monomers **9** and **10**. The remaining two temperature-dependent signals T6 and T7 are not altered in the temperature range -90°C to 0°C , but the averaged signal T at 35°C suggests that the two distinct hydrides in **10** become equivalent.

Conclusions

The hydrogenation catalyst precursors [(L-L)Rh(NBD)ClO₄ (L-L = ferrocenyl-alkylphosphines) lead to the formation of metal hydrides in various solvents such as alcohol, CH₃CN, CHCl₃. NMR (¹H, ³¹P) monitoring suggests that various hydride species are formed reversibly in any one reaction. The anticipated disolvate [(L-L)Rh(S)₂]⁺ was not observed in MeOH or EtOH. Some hydrides can be isolated as crystalline solids which show fluxional behaviors in solution.

The unique behavior of the present systems (**2a** and **2b**) may be due to the presence of the basic and bulky tert-butyl derivatives although this aspect needs further studies in order to investigate any electronic and/or steric influences on the mechanisms of olefin hydrogenation. These points will be the subjects of our future studies.

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References

1. (a) B. R. James, "Homogeneous Hydrogenation",

- Wiley, New York, 1973; (b) B. R. James, *Adv. Organometal. Chem.*, **17**, 319 (1979).
2. (a) J. Halpern, D. P. Riley, A. S. C. Chan, and J. J. Pluth, *J. Am. Chem. Soc.*, **99**, 8055 (1977); (b) A. S. C. Chan, J. J. Pluth, and J. Halpern, *Inorg. Chim. Acta*, **L** 477 (1979); (c) A. S. C. Chan, J. Halpern, *J. Am. Chem. Soc.*, **102**, 838 (1980); (d) J. M. Brown and P. A. Chaloner, *J. Chem. Soc., Chem. Commun.*, 321 (1978); (e) *idem*, 646 (1978); (f) *idem*, *Tetrahedron Lett.*, **21**, 1877 (1978); (g) *idem*, *J. Am. Chem. Soc.*, **102**, 3040 (1980); (h) *idem*, *Organometallics*, **1**, 950 (1982).
3. J. M. Brown, L. R. Canning, A. J. Down, and A. M. Forster, *J. Organometal. Chem.*, **255**, 103 (1983).
4. (a) K. Tani, K. Suwa, E. Tanigawa, T. Yoshida, T. Okano, and S. Otsuka, *Chem. Lett.*, 261 (1982); (b) K. Tani, K. Suwa, T. Yanagata, and S. Otsuka, *ibid.*, p.265.
5. I. R. Butler, W. R. Cullen, T. J. Kim, F. W. B. Einstein, and T. Jones, *J. Chem. Soc., Chem. Commun.*, 719 (1984).
6. D. D. Perin, W. L. F. Armarego, and D. R. Perrin, "Purification of Laboratory Chemicals", 2nd ed., Pergamon Press, New York, 1980.
7. T. J. Kim, Ph.D. Dissertation, University of British Columbia (1984).
8. I. R. Butler, W. R. Cullen, T. J. Kim, S. J. Rettig, and J. Trotter, *Organometallics*, **4**, 972 (1985).
9. B. R. James and G. Rempel, *Can. J. Chem.*, **44**, 233 (1966).
10. R. R. Schrock and J. A. Osborne, *J. Am. Chem. Soc.*, **98**, 2134 (1976).
11. K. C. Deuherst, W. Keim, and C. A. Reiley, *Inorg. Chem.*, **7**, 546 (1968).
12. (a) A. J. Sivak and E. L. Muetterties, *J. Am. Chem. Soc.*, **101**, 4878 (1979); (b) E. B. Meier, R. R. Burch, E. L. Muetterties, and V. W. Day, *ibid.*, **104**, 2661 (1982).
13. (a) M. D. Fryzuk, *Can. J. Chem.*, **61**, 1347 (1983); (b) *idem*, *Organometallics*, **11**, 408 (1982).
14. (a) H. H. Wang and L. H. Pignolet, *Inorg. Chem.*, **19**, 1470 (1980); (b) H. H. Wang, A. L. Casalnuovo, B. J. Johnson, A. M. Mueting, and L. H. Pignolet, *ibid.*, **27**, 325 (1988).
15. (a) R. H. Crabtree, H. Felkin, G. Morris, T. J. King, and J. A. Richards, *J. Organometal. Chem.*, **113**, C7 (1976); (b) R. H. Crabtree, *Acc. Chem. Res.*, **12**, 331 (1979).