Agostic Interaction and Intramolecular Hydrogen Exchange in Coordinatively Unsaturated Ruthenium Complexes: Effects of Chelate Ring Size on Intramolecular Carbon–Hydrogen Bond Activation of Diphosphine Ligands

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The solution properties of formally five-coordinate ruthenium complexes $[RuH(P\text{-}P)_2]PF_6$ (P-P = 1,4-bis(diphenylphosphino)butane (dppb) (**1a**), 2,3-*O*-isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)butane (diop) (**1b**), 1,3-bis(diphenylphosphino)propane (dppp) (**1c**), 1,2-bis(diphenylphosphino)ethane (dppe) (**1d**)) were examined by various NMR measurements. Variable temperature ^1H NMR measurements suggest that the behaviors of **1a** and **1b** at low temperatures differ significantly from those at high temperature. The agostic interaction between an α-methylene CH moiety of the diphosphine ligand and the ruthenium center was detected in **1a** below −30 °C and in **1b** below −60 °C. In **1c** and **1d** no agostic interaction could be detected. The hydrogen exchanges among the terminal hydride, the agostic hydrogen, and a noncoordinating methylene hydrogen of dppb in **1a** were proved on the basis of spin saturation transfer phenomena in the ^1H NMR measurements. The exchange rate between the agostic hydrogen and the terminal hydride was estimated in the temperature range −55 to −90 °C by spin saturation transfer studies, to reveal that $\Delta G^{\ddagger}$ for the hydrogen exchange is about 11 kcal mol^{-1}. At high temperatures the hydrogen scrambling between *ortho* hydrogens on the phenyl groups, all the methylene hydrogens, and the terminal hydride in **1a** was proved by employing the partially deuterized ligand $Ph_2P(CD_2)_4PPh_2$. Upon the contact of **1a**, **1c**, and **1d** with D_2 gas in solution, deuterium incorporation takes place at *ortho* and all methylene positions of diphosphines in these complexes. In the case of **1a**, the deuterium content of each site is in the order β-CH_2 > α-CH_2 > *o*-CH. In **1b** and **1c**, the H/D exchange at *o*-CH proceeded in preference to those at α-CH_2 or β-CH_2.

Introduction

The activation of the carbon–hydrogen σ bond is one of the most important target reactions in organo-transition metal chemistry.[1] In order to facilitate the cleavage of a chemical bond with a metal complex, the interaction between the bonds and the metal center is necessary either in the transition state or in an intermediate. Organometallic moieties involving the coordination of a σ bond to a transition metal center have attracted considerable attention as possible models for the intermediate of a σ bond dissociation.[2]

It was proposed that M←H–C bonds, i.e. agostic interactions, are similar in bonding character to the η^2-type coordination of a dihydrogen ligand to a transition metal (three-center two-electron bond).[2c] The fact that some coordinatively unsaturated 16-electron complexes, which are the precursors of molecular hydrogen complexes, involve agostic interactions demonstrates the similarity in bonding between the agostic interaction and dihydrogen coordination.[3] Due to the fact that the isolation of such coordinatively unsaturated complexes is often difficult because of their high reactivities, it is required on such occasions to generate them in situ by thermochemical[4] or photochemical[5] ligand dissociation of saturated precursors. Although agostic interactions are regarded as intermediates on the way to oxidative addition of carbon–hydrogen bonds, few cases are known as examples of actual C–H bond activation, especially of aliphatic C–H groups.[6]

We describe herein the solution behavior of the formally five-coordinate ruthenium complexes $[RuH(P\text{-}P)_2]PF_6$ (P-P = dppb (**1a**),[7] diop (**1b**),[8] dppp (**1c**),[7] and dppe (**1d**)[7]). It was disclosed by NMR measurements that, at low temperature, the interaction between an aliphatic C–H

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moiety of the diphosphine ligand and the ruthenium center is detected clearly for complexes **1a** and **1b** and that the agostic hydrogen undergoes exchanges with the terminal hydride (Ru–H) at a considerable rate. Such an agostic interaction could not be detected for analogous complexes **1c** and **1d**. The rate and thermodynamic parameters for the exchange between the terminal hydride and the agostic hydrogen in **1a** were determined in the temperature range −55 to −90 °C. At high temperatures, however, the agostic interaction in **1a** was no longer observed, and instead, rapid hydrogen scrambling including the terminal hydride, all the methylene hydrogens, and the *ortho* hydrogens on the phenyl groups of the ligands could be proved by employing the partially deuterated ligand $Ph_2P(CD_2)_4PPh_2$. It was demonstrated, further, that facile deuterium incorporation takes place at the diphosphines of the five-coordinate complexes (**1a**, **1c**, and **1d**) in solution under a D_2 atmosphere. The mechanism for such H/D exchange, which could be promoted by a deuteride complex as $[RuD(P\text{-}P)_2]^+$, is proposed. The difference of the H/D exchange reactivity between complexes **1a**, **1c**, and **1d** is also discussed. Part of this work has been reported in a preliminary communication.[3]

Results and Discussion

Preparation of [RuH(diphosphine)$_2$]PF$_6$ (1). The formally five-coordinate complexes **1a–d** are prepared from $[RuH(cod)(NH_2NMe_2)_3]PF_6$[9] and 2 equiv of respective diphosphines according to the reported method[7a,8b] with slight modifications.

$$[RuH(cod)(NH_2NMe_2)_3]PF_6 + 2P\text{-}P \rightarrow [RuH(P\text{-}P)_2]PF_6 + COD + 3NH_2NMe_2 \quad (1)$$

In the previous papers,[7a,8b] methanol or ethanol was used as a solvent for the synthesis of **1** (eq 1). These complexes are coordinatively unsaturated and, therefore, tend to react slowly with primary or secondary alcohols to give dihydride complexes (eq 2).[7a,10] The proton thus formed can react with 1,1-dimethylhydrazine, the salt of which remains in a reaction mixture as a byproduct.

$$[RuH(P\text{-}P)_2]^+ + RR'CHOH \rightarrow RuH_2(P\text{-}P)_2 + RR'C{=}O + H^+ \quad (2)$$

It was found that the side reaction with alcoholic solvent can be avoided by employing *tert*-butyl alcohol or acetone as a solvent.

^{1}H and ^{31}P NMR Characteristics of [RuH(dppb)$_2$]PF$_6$ (1a) and [RuH(diop)$_2$]PF$_6$ (1b). The high field region of the variable temperature ^{1}H NMR spectra of **1a** and their spectroscopic features have been given in the preliminary account.[3] The intensity of the broad signal observed in the ^{1}H NMR spectra above 0 °C corresponds to one hydrogen nucleus, and that of each resonance detected below −30 °C also corresponds to one proton, respectively. The $^{31}P\{^1H\}$ NMR spectrum of **1a** at −90 °C showed the presence of four inequivalent phosphorus nuclei (see Table 1).[11] The possibility of the existence of two isomers or the formation of a polynuclear complex at low temperature was entirely denied by the $^{31}P\{^1H\}$ NMR spectrum. Below −30 °C, **1a** seems to have two hydride-like nuclei in a molecule. The signal at δ −10.6, which reveals the couplings with phosphorus nuclei at −90 °C, is ascribed to the terminal hydride (Ru–H), while the other at δ −7.0, showing no coupling with phosphorus at the same temperature, is assigned to the hydrogen in a C–H moiety interacting with the ruthenium center (agostic interaction).[2a,b] All these NMR characteristics were observed for the tetraphenylborate analogue [RuH(dppb)$_2$]BPh_4 (**1a**-BPh_4). This fact indicates that the anions, PF_6^- in **1a** and BPh_4^- in **1a**-BPh_4, have no interaction with the ruthenium center.

Table 1. $^{31}P\{^1H\}$ NMR Data for [RuH(dppb)$_2$]PF$_6$ (1a) and [RuH(diop)$_2$]PF$_6$ (1b) in CD_2Cl_2 at −90 °C[a]

complex	δ_A[b]	δ_B[b]	δ_M[b]	δ_X[b]	$J_{AM} = J_{BM}$[c]	$J_{AX} = J_{BX}$[c]
1a[d]	37.9[e]		−13.4	79.1	30	10
1b[d]	30.4	31.1	−9.5	73.2	20	30

[a] Recorded at 162 MHz. [b] Relative to external 85% D_3PO_4. [c] Coupling constants in hertz. [d] J_{AB} and J_{MX} were not observed clearly. [e] Observed as an unresolved multiplet.

The diop complex **1b** exhibited ^{1}H NMR features similar to those of **1a** (Figure 1). In the case of **1b**, two hydride-like resonances, a broad signal (ca. δ −4.1), and a doublet of quartets (ca. δ −10.2), were detected at and below −60 °C. The highest temperature where the agostic interaction can be observed for **1b** is considerably lower than that for **1a**. As we expected, **1b** shows an ABMX pattern in the $^{31}P\{^1H\}$ NMR spectrum at −90 °C (Table 1).

Assignment of the Agostic Hydrogen. As described in the former communication,[3] it is demonstrated that, on the basis of the ^{1}H–^{1}H COSY measurements, the complexes **1a** and **1b** involve the coordination of an α-methylene C–H moiety, not an *ortho* phenyl proton, of dppb or diop at the sixth coordination site of the ruthenium center to give rise to the agostic interaction at low temperature, respectively.

The ^{13}C NMR spectrum of **1a** at −90 °C (Figure 2) showed eight resonances in the methylene region. This indicates that each methylene carbon in **1a** differs from the remaining carbons, so that the structure of **1a** has no elements of molecular symmetry, in accord with the results of the $^{31}P\{^1H\}$ NMR data. On such an occasion, two hydrogens of each methylene group in dppb are inequivalent. The proton-coupled ^{13}C NMR spectrum of **1a**, however, appeared as eight pseudotriplets, instead of eight doublets of doublets signals, in the methylene region. This is probably due to the broadening of the signals resulting from the coupling with ^{31}P nuclei and/or the similarity between the two geminal J_{CH} values. Among the ^{13}C NMR signals of the CH_2 groups of **1a**, the resonance at δ 27.9 showed a J_{CH} value smaller than the others[3] and was assigned to the signal of the agostic carbon.[2a,b] This is consistent with the coordination of a methylene C–H group in **1a**. Under selective decoupling at the agostic hydrogen (δ −7.0), only the resonance at δ 27.9 turned into a simple doublet. This observation confirms the above-mentioned assignment.

A similar agostic interaction could not be detected for analogous five-coordinate complexes of dppp (**1c**), dppe

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(11) Ashworth, T. V.; Chalmers, A. A.; Singleton, E. *Inorg. Chem.* **1985**, *24*, 2126. In this paper, they reported the ^{31}P NMR spectrum of **1a** in acetone-d_6 at −80 °C as an A_2MX pattern.

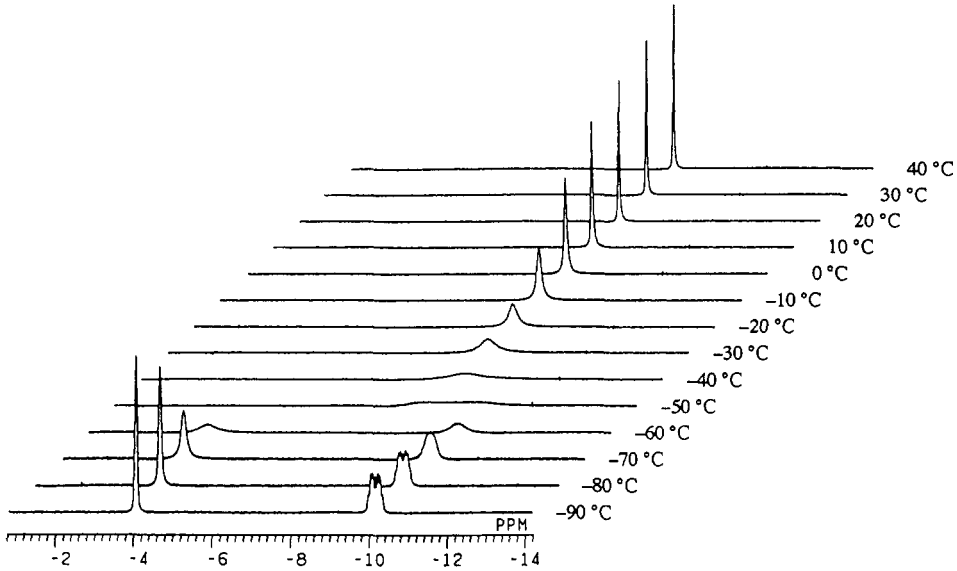


Figure 1. Variable temperature ^1H NMR spectra of $[RuH(diop)_2]PF_6$ (**1b**) in the high field region at 400 MHz in CD_2Cl_2.

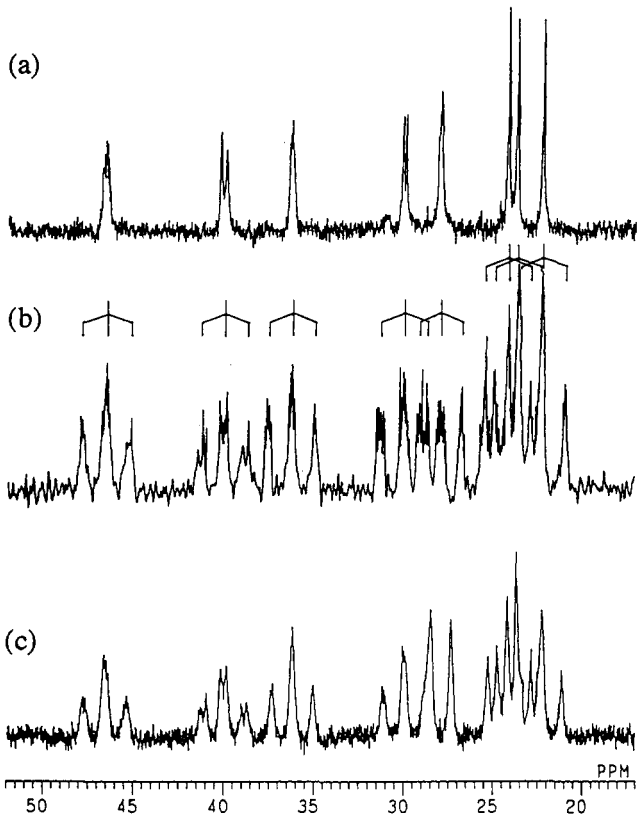
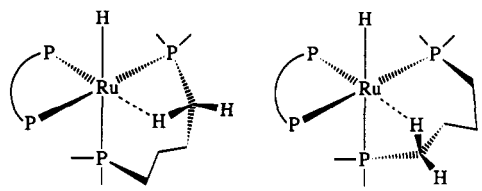


Figure 2. ^{13}C NMR (101-MHz) spectra of $[RuH(dppb)_2]PF_6$ (**1a**) in the methylene region at −90 °C in CD_2Cl_2: (a) proton decoupled; (b) proton coupled (J_{CH} value of each signal is shown in ref 3); (c) selective decoupled with the agostic hydrogen (δ −7.0).

(**1d**), dpbp,[12] and binap.[12b,13] In the case of **1c** and **1d**, the smaller size of the chelate rings prevents a C–H bond in a methylene unit from coordinating to the ruthenium center, whereas dppb and diop ligands provide a flexible seven-membered chelate upon coordination. As to the complexes of dpbp and binap, the ligands have no aliphatic C–H groups in themselves, although these diphosphines form seven-membered chelate rings. The highest temperature, at which the agostic interaction is recognized in the ^1H NMR spectrum, is −30 °C for **1a** and −60 °C for **1b**. The flexibility of the diop chelate ring should be reduced due to the presence of the dioxolane ring, compared to that of the simple four-carbon chain in the dppb chelate. This makes the coordination of an α-methylene hydrogen to the ruthenium center more difficult in **1b** than in **1a**. The difference in the chelate ring flexibility between dppb and diop is reflected in the above-mentioned temperature dependence of the agostic interaction.

MM2 Calculation of 1a. In the ^1H NMR spectra, the coupling patterns (doublet of quartets) of the terminal hydride signals of **1a** and **1b** at low temperature indicate that the two chelating diphosphine ligands adopt a *cis* arrangement in these complexes. The terminal hydride should be located *trans* to one phosphorus nucleus, and *cis* to the other three. There are two candidates for the manner of coordination of an α-methylene hydrogen of dppb to the ruthenium center in **1a** at low temperatures (**I** and **II**), both of which fill the other steric requirements



I **II**

described above. We could not decide on the basis of the spectroscopic data alone which of these two structures is probable for **1a**. The molecular mechanics 2 (MM2) calculations suggest that structure **I** is more stable than **II**, the energy difference between **I** and **II** being about 8.6 kcal mol^{-1}. Although electronic effects are completely ignored in the MM2 calculations, it is reasonable to suppose that the difference in the electronic properties between **I** and **II** is small. Furthermore, the energy difference obtained above is significantly large to suggest that structure **I** is a more possible structure of **1a**.

Intramolecular Hydrogen Exchange at Low Temperatures. As we described previously,[3] the rapid

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Table 2. T_1 Values and Rate Constants, k, for Hydrogen Exchange between the Agostic Hydrogen and the Terminal Hydride in $[RuH(dppb)_2]PF_6$ (1a)

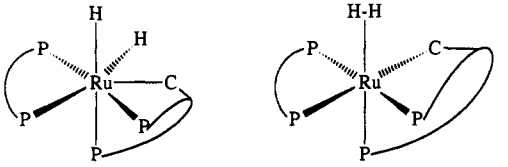
T/°C	T/K	T_1(agostic)/ ms[a]	T_1(hydride)/ ms[a]	k/s^{-1}	$\Delta G^{\ddagger}$/ kcal mol^{-1} [b]
−55	218	102	120	32.6	11.1
−60	213	141	147	17.1	11.1
−65	208	174	171	12.9	11.0
−70	203	242	182	8.9	10.8
−75	198	284	193	4.5	10.8
−80	193	335	287	1.5	11.0
−85	188	395	389	0.6	11.0
−90	183	483	513	0.3	11.0

[a] The T_1 experiments were performed at 400 MHz with a 180°-τ-90° pulse sequence by the inversion-recovery method. [b] Calculated from the rate constants k.

hydrogen exchanges among the Ru–H, agostic C–H, and noncoordinating methylene protons of the dppb ligands in **1a** were demonstrated by the ^{1}H NMR spin saturation transfer phenomena at −45 °C.

The exchange rate, k, between the agostic hydrogen and the terminal hydride was estimated in the temperature range −55 to −90 °C by the spin saturation transfer technique.[14-17] The rate constants and the T_1 values of each signal are summarized in Table 2. The Eyring plot (ln k/T vs $1/T$) is linear, and the thermodynamic parameters for the exchange between the agostic hydrogen and the terminal hydride in **1a** are $\Delta H^{\ddagger} = 10.3 \pm 0.5$ kcal mol^{-1} and $\Delta S^{\ddagger} = -3.6 \pm 0.6$ cal mol^{-1} K^{-1}. Interestingly, these values lie in the range of those reported for the intramolecular hydrogen exchange between the hydride and the dihydrogen ligand in $[RuH(\eta^2\text{-}H_2)(diphosphine)_2]^+$.[18]

Two intermediates are possible for the hydrogen exchange; i.e., (A) a seven-coordinate dihydride, and (B) a six-coordinate η^2-H_2 complex. Albéniz and co-workers recently suggested the formation of the dihydrogen com-



A **B**

plex as the intermediate for intramolecular hydrogen exchange.[19] They also proposed the direct proton transfer as a key step in the hydrogen exchange of the M←H–C system in a transition metal complex.[19] As mentioned above, complex **1a**, which involves the agostic interaction between α-CH and the ruthenium center, exhibits the hydrogen exchange between the agostic hydrogen and the terminal hydride. The result of the ^{1}H–^{1}H COSY measurement demonstrates that this agostic hydrogen has a coupling with the neighboring methylene hydrogens.[3] These observations suggest the possibility that this hydrogen exchange proceeds via direct proton transfer, rather than the successive process of oxidative addition and reductive elimination.[20-23] Recently, Crabtree and co-workers reported either dissociative or nondissociative interaction of a C–H moiety in quinoline derivatives with iridium complexes and suggested the relationship between these hydrogen exchanges and agostic interactions.[24] However, there has been no direct evidence of the agostic interaction participating in C–H activation. Our results are the first example[3] of the observation of the direct intramolecular hydrogen exchange involving the agostic hydrogen.

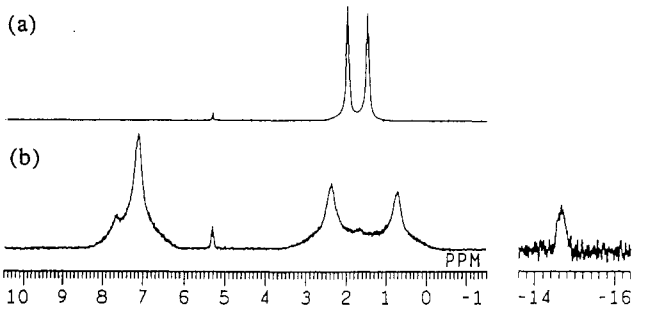


Figure 3. ^{2}D NMR (61-MHz) spectra at 30 °C in CH_2Cl_2: (a) $Ph_2P(CD_2)_4PPh_2$ (dppb-d_8); (b) $[RuH(dppb\text{-}d_8)_2]PF_6$ (**1a**-d_{16}).

Intramolecular Hydrogen Exchange at High Temperatures. At higher temperatures, **1a** (above 0 °C) and **1b** (above −40 °C) are highly fluxional in solution, so that it is impossible to decide whether the hydrogen exchange between α-CH and Ru–H is still taking place or not. Judging from the variable temperature ^{1}H NMR spectra,[3] the high temperature behavior of **1a** differs from the low temperature one. With a view to answer this problem, we prepared partially deuterated dppb $Ph_2P(CD_2)_4PPh_2$ (dppb-d_8). The ^{1}H NMR spectrum of the complex $[RuH(dppb\text{-}d_8)_2]PF_6$ (**1a**-d_{16}), obtained by a reaction of dppb-d_8 and $[RuH(cod)(NH_2NMe_2)_3]PF_6$ in ethanol, displays the signals assignable to the methylene protons of coordinating diphosphines. It should be noted that the resonances not only of α-methylene but also of β-methylene of dppb appear with practically equal intensities. The ^{2}D NMR spectrum of **1a**-d_{16} revealed the resonance assignable to deuteriums incorporated into the phenyl group (δ 7.1) and the Ru–D part (δ −14.7), in addition to the C–D signals of the methylene groups (δ 0.7 and 2.4, Figure 3). Further, a detailed examination of the aromatic region in the ^{1}H NMR spectrum showed that the intensity of the *ortho* hydrogen resonance of **1a**-d_{16} is distinctly smaller than that of the *meta* hydrogens, and that the latter signal broadens considerably as a result of H–D coupling with the *ortho* deuterium (see Figure 4). It is demonstrated, therefore, that the protium source introduced into the

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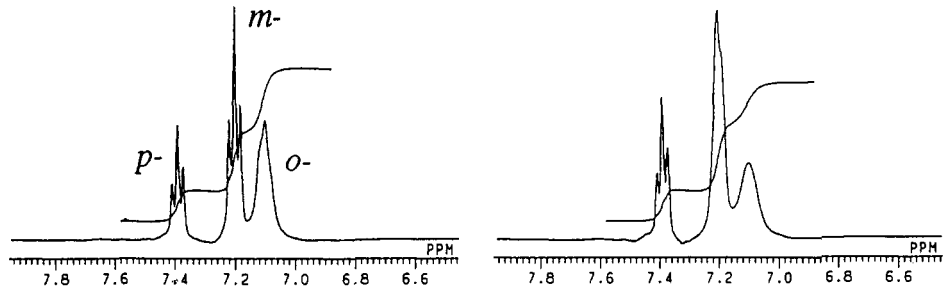
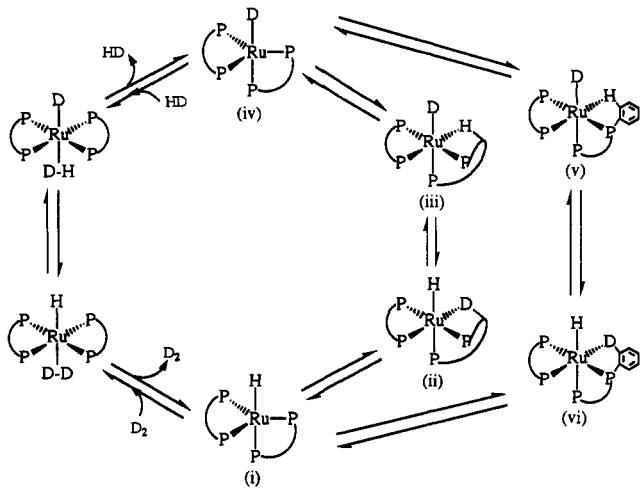


Figure 4. ^{1}H NMR spectra of **1a** (left) and **1a**-d_{16} (right) in the phenyl region at 30 °C in CD_2Cl_2 at 400 MHz.

Scheme 1. Proposed Mechanism of the Deuterium Incorporation and the Hydrogen Scrambling in Complex 1



methylene parts of dppb-d_8 is the *ortho* C–H groups on the phenyl moieties.[1c,20,21] It is certain that the protiums incorporated into the methylene groups do not originate from ethanol employed as a solvent, because the use of C_2D_5OD in place of C_2H_5OH causes no change in the ^{1}H NMR spectrum of **1a**-d_{16}.[25] The total protium amount of *ortho* and α- and β-methylene positions in **1a**-d_{16} estimated from the ^{1}H NMR spectrum corresponds well to the hydrogens that initially exist at the *ortho* positions of dppb-d_8. These results indicate that this hydrogen exchange proceeds via an intramolecular process.

At lower temperatures, only one of the α-methylene hydrogens of dppb exchanges with the terminal hydride via the agostic interaction. In contrast, at higher temperatures, not only the α-CH_2 but also the β-CH_2 and the *ortho* hydrogen on the phenyl groups of coordinating dppb can be sufficiently activated, so that rapid hydrogen scrambling takes place among these hydrogens and the Ru–H in **1a**. The possible pathway of H–D scrambling among α- and β-CH_2 parts and *o*-hydrogens of dppb-d_8 is illustrated in Scheme 1. Thus, according to the reaction sequence (i → ii → iii → iv), a deuterium at the methylene groups, not only of the α- but also of the β-position, is replaced with protium of Ru–H, while the Ru–H is transformed into Ru–D. The deuteration of the *ortho* hydrogen on the phenyl group proceed via the sequence iv → v → vi → i. By uniting these sequences, a complete cycle for H/D scrambling among a coordinating dppb-d_8 was obtained.

We suppose that in the H/D scrambling in **1a**-d_{16} the β-CH and *o*-CH groups also take part in the agostic interaction (ii, iii or v, vi) in a manner similar to that of the α-CH group. Although the agostic interactions involving the β-CH or *o*-CH group have not been detected in the ^{1}H NMR spectra of **1a**, the observed H/D scramblings clearly indicate that these C–H bonds are sufficiently activated in a kinetic sense at higher temperatures.

Deuterium Introduction into Diphosphine Ligands by Treatments of 1 with D_2 Gas. It is noteworthy that all steps in the cycle shown in Scheme 1 are reversible. If the deuteride species $[RuD(dppb)_2]^+$ were once obtained, the deuterium incorporation into the methylene moieties and *o*-CH parts would be achieved via the sequences iv → iii → ii → i and iv → v → vi → i, respectively. Upon contact with D_2 gas, **1a** is spontaneously converted into a mixture of $[RuH(D_2)(dppb)_2]^+$ and $[RuD(HD)(dppb)_2]^+$, and the latter can afford $[RuD(dppb)_2]^+$ by the dissociation of HD.[7b,18a] It has been clarified, however, that under a H_2 atmosphere, **1a** turned almost completely into $[RuH(H_2)(dppb)_2]^+$ and that the NMR measurements showed no detectable amount of the precursor remained.[7b] Despite that, a trace amount of $[RuD(dppb)_2]^+$ could be generated to promote the deuterium incorporation into the diphosphine ligands.

With a view to examine the above possibility, the ^{1}H NMR change of **1a** in tetrahydrofuran was followed under a D_2 atmosphere. Indeed, a clear decrease of signal intensities in the methylene region could be observed after keeping a solution of **1a** for several hours under D_2. It was found to be somewhat difficult to determine the exact intensity ratio of α-CH:β-CH:*o*-CH in the complex itself by the ^{1}H NMR measurements, presumably due to the broadening of the signals resulting from the presence of conformers and isotopomers. Hence, the deuterated complex was decomposed with H_2O_2 and the diphosphine ligands were converted into the diphosphine dioxide. The dioxide of dppb-d_n was separated from the reaction mixture (dppb-d_n refers to a mixture of partially deuterated dppb), and the ^{1}H NMR spectrum was recorded for this dioxide ($dppbO_2$). Fortunately, a complete signal separation was obtained between *meta* and *para* hydrogens and *ortho* hydrogens of $dppbO_2$ in the ^{1}H NMR spectrum. Using the total signal intensity of *meta* and *para* hydrogens as the internal standard, the intensities of *o*-CH, α-CH_2, and β-CH_2 were evaluated with good accuracy. The results of the deuterium replacement after a 72-h treatment were given in Table 3. As shown in entry 1, deuterium substitution occurred at all possible sites of dppb. It is interesting that the D content of each site in dppb is in the order β-CH_2 > α-CH_2 > *o*-CH. The deuterium replacement at β-CH_2 proceeds faster than that at α-CH_2 groups, although β-CH bonds are excluded from the agostic interaction in complex **1a** at lower temperatures.

This strongly suggests that similar H/D exchanges could occur in analogous complexes that exhibit no detectable

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Table 3. Ratio of Deuterium Incorporation into the Diphosphine Ligand[a]

entry	complex	*o*-CD/%	α-CD/%	β-CD/%
1	**1a**[b,c]	18	54	92
2	**1a**-d_{16}	38	57	55
3	**1b**[b]	61	45	<5
4	**1c**[b]	52	8	

[a] Calculated from the signal intensity of the ^{1}H NMR spectra of the diphosphine dioxide obtained by the decomposition of the complexes. [b] Reaction conditions: complex (50 mg), THF (10 mL), under D_2 (1 atm), at 30 °C, 72 h. [c] No deuterium introduction to the dppb ligands was observed for the reaction of **1a** in THF under an argon atmosphere.

agostic interaction in the ^{1}H NMR spectra. Thus, **1c** and **1d** were treated with D_2 gas, and the deuterium incorporation into **1c** and **1d** was estimated in a manner similar to that mentioned above for **1a**. As expected, the deuterium incorporation into the diphosphines was recognized for both **1c** and **1d** (see Table 3). It should be noted that, in **1c** and **1d**, the H/D exchange at *o*-CH proceeded in preference to those at α-CH_2 or β-CH_2.[24,25] It is supposed that, as the chelate ring of $[RuH(P\text{-}P)_2]^+$ becomes smaller, the approach of the methylene parts to the ruthenium center becomes harder, whereas that of *o*-CH is affected by the size of chelate rings to a lesser extent.[22] The experimental results in Table 3 are well in accord with this assumption.

Conclusions

We have discovered the agostic interaction between an α-methylene hydrogen of the diphosphine ligand and the ruthenium center in **1a** and **1b** at low temperatures. The agostic hydrogen undergoes intramolecular hydrogen exchanges between the terminal hydride and a noncoordinating methylene hydrogen of the diphosphine ligand. In **1c** and **1d**, a similar agostic interaction was not recognized. At high temperatures, these complexes become highly fluxional and exhibit hydrogen scrambling between the *ortho* hydrogens on the phenyl groups, all the methylene hydrogens, and the terminal hydride. This hydrogen scrambling is detected not only in **1a** but also in **1c** and **1d** by the H/D exchange under a D_2 atmosphere. Under D_2, deuterium is introduced into the diphosphine ligands via $[RuD(P\text{-}P)_2]^+$. In **1a**, the H/D exchange proceeds at the methylene positions in preference to *o*-CH, while, in **1c** and **1d**, the deuterium introduction occurs faster at the *ortho* positions than at the methylene parts. The differences between **1a**, **1c**, and **1d** are ascribed to the fact that the smaller size of the chelate rings in **1c** and **1d** restricts the access of methylene hydrogens to the ruthenium center, whereas dppb in **1a** forms a sufficiently flexible seven-membered ring.

Experimental Section

General Procedure. Unless otherwise noted, all manipulations were carried out under a dry argon or dinitrogen atmosphere by standard Schlenk-tube techniques. All the solvents were dried over appropriate reagents and distilled under N_2.[26] C_2D_5OD and $DO(CD_2)_4OD$ were purchased from Aldrich Chemical Co. Dppb, dppp, and dppe were purchased from Kanto Chemical Co. and used as received without further purification. Diop[27] and $[RuH(cod)(NH_2NMe_2)_3]PF_6$[9] were prepared as reported. $[RuH(dppb)_2]PF_6$,[7] $[RuH(diop)_2]PF_6$,[8] $[RuH(dppp)_2]PF_6$,[7] and $[RuH(dppe)_2]PF_6$[7] were prepared by literature methods, except that *tert*-butyl alcohol (for **1a**, **1c**, and **1d**) or acetone (for **1b**) was employed as a solvent instead of ethanol. $[RuH(dppb\text{-}d_8)_2]PF_6$ was prepared by using dppb-d_8.

NMR Studies. The preparation of sample solutions of the complexes for NMR measurements was carried out under an argon (not dinitrogen) atmosphere using air free CD_2Cl_2 as a solvent. ^{1}H NMR (400-MHz), ^{2}D NMR (61-MHz), ^{13}C NMR (101-MHz), and ^{31}P NMR (162-MHz) spectra were recorded on a JEOL JNM-GX 400 spectrometer. ^{1}H and ^{13}C NMR chemical shifts are reported in ppm downfield of tetramethylsilane. ^{2}D NMR chemical shifts are relative to the solvent resonance, $CHDCl_2$ (δ 5.3), as an internal standard. ^{31}P NMR chemical shifts are reported in ppm downfield of external 85% D_3PO_4. ^{1}H NMR T_1 determinations were performed with a standard 180°-τ-90° pulse sequence by the inversion-recovery method.

Measurements of the Exchange Rates between the Agostic Hydrogen and the Terminal Hydride in 1a. Determination of the exchange rates between the two resonances was carried out according to the Forsén–Hoffman method.[15,16] Spin saturation transfer experiments were performed by irradiating the ^{1}H resonance of the agostic hydrogen. The exchange rates, k, were calculated from the following equation:

$$I'/I = \tau/(\tau + T_1)$$

where I and I' are the signal intensities of the terminal hydride without and with saturation of the agostic signal, respectively. T_1 is the spin–lattice relaxation time of the hydride resonance and τ (=1/k) is the pre-exchange lifetime of this exchange system. The ratio I'/I was calculated from the difference spectrum recorded by subtracting the spectrum irradiated at the agostic resonance from the reference (nonirradiated) spectrum. The activation parameters, $\Delta H^{\ddagger}$, $\Delta S^{\ddagger}$, and $\Delta G^{\ddagger}$, were obtained from a linear least-squares fit of the Eyring plot (ln k/T versus $1/T$) utilizing the Eyring equation.[16]

1,4-Bis(diphenylphosphino)butane-1,1,2,2,3,3,4,4-d_8 (dppb-d_8). To a pyridine (20-mL) solution of $DO(CD_2)_4OD$ (1.12 g, 11.4 mmol) was added *p*-toluenesulfonyl chloride (4.70 g, 24.6 mmol) at −10 °C. After the mixture was stirred at room temperature for 3 h, the volume of the mixture was reduced to about 5 mL and then the mixture was poured into ice-water. The ditosylate, deposited as a white solid, was filtered, washed with water, and then dried under reduced pressure. This crude ditosylate ($TsO(CD_2)_4OTs$, 2.95 g) was used in the following reaction without further purification. ^{1}H NMR [$CDCl_3$, TMS]: δ 2.46 (s, 6H), 7.35 (d, J = 8 Hz, 4H), 7.76 (d, J = 8 Hz, 4H).

A tetrahydrofuran (5-mL) solution of the crude ditosylate (2.90 g) was added to a solution of $LiPPh_2$ (prepared from PPh_3 (4.53 g, 17.3 mmol) and Li (0.26 g, 37.5 mmol) in THF (15 mL), followed by *tert*-BuCl treatment) at 0 °C. After the addition, the mixture was refluxed for 1 h. After the mixture had been cooled to room temperature, tetrahydrofuran was removed and degassed water (25 mL) was added. The diphosphine was extracted with hot benzene (25 mL × 4), and the benzene extracts were dried with $MgSO_4$. After the removal of the solvent, the title compound was recrystallized from absolute ethanol to give a colorless needle: 2.33 g (47%, as a total yield). ^{1}H NMR [$CDCl_3$, TMS]: δ 7.27–7.32 (m, *m*- and *p*-H), 7.34–7.40 (m, *o*-H). ^{2}D{^{1}H} NMR [CH_2Cl_2, $CHDCl_2$ (δ 5.3) as internal standard]: δ 1.49 (br, β-CD_2), 1.98 (br, α-CD_2). ^{13}C{^{1}H} NMR [$CDCl_3$, TMS]: δ 26.5 (m, α- and β-CH_2), 128.3 (d, $^3J_{PC}$ = 7 Hz, *m*-C), 128.4 (s, *p*-C), 132.6 (d, $^2J_{PC}$ = 18 Hz, *o*-C), 138.8 (d, $^1J_{PC}$ = 13 Hz, *ipso*-C). ^{31}P{^{1}H} NMR [$CDCl_3$, D_3PO_4 (85%) as external standard]: δ −11.8 (s). Anal. Calcd for $C_{28}H_{20}D_8P_2$: C, 77.40; H + D, 8.35. Found: C, 77.79; H + D, 8.01.

Reaction of the Complexes (1a, 1c, and 1d) with D_2 Gas. The complex (50 mg) was dissolved in 10 mL of THF, and the solution was stirred under a D_2 atmosphere at 30 °C for 72 h. After the removal of the solvent, 30% H_2O_2 (about 5 mL) was added to the residue. The produced diphosphine dioxide was extracted with $CHCl_3$ from the mixture, and the chloroform

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solution was dried with $MgSO_4$. After the removal of the solvent, residual diphosphine dioxide was purified by the appropriate methods as follows. The dioxides of dppb and dppe were recrystallized from acetone. Dppp dioxide was purified with a HPLC equipped with a silica gel column (Merck RT 250-10) using isopropyl alcohol–*n*-hexane (3:7) as an eluent. The ratio of deuterium incorporation into the diphosphine was determined by the ^1H NMR measurements of these diphosphine dioxides.

Dppb Dioxide: ^1H NMR [$CDCl_3$, TMS] δ 1.65–1.78 (m, β-CH_2), 2.16–2.29 (m, α-CH_2), 7.40–7.51 (m, *m*- and *p*-H), 7.63–7.73 (m, *o*-H).[28a] Anal. Calcd for $C_{28}H_{20.7}D_{7.3}O_2P_2$: C, 72.20; H + D, 7.64. Found: C, 72.63; H + D, 7.18.[29]

Dppp Dioxide: ^1H NMR [$CDCl_3$, TMS] δ 1.93–2.10 (m, β-CH_2), 2.46–2.59 (m, α-CH_2), 7.39–7.53 (m, *m*- and *p*-H), 7.64–7.74 (m, *o*-H). Anal. Calcd for $C_{27}H_{19.3}D_{6.7}O_2P_2$: C, 71.88; H + D, 7.30. Found: C, 71.22; H + D, 7.63.[29]

Dppe Dioxide: ^1H NMR [$CDCl_3$, TMS] δ 2.53 (s, α-CH_2), 7.41–7.55 (m, *m*- and *p*-H), 7.66–7.77 (m, *o*-H).[28b] Anal. Calcd for $C_{26}H_{19.5}D_{4.5}O_2P_2$: C, 71.80; H + D, 6.60. Found: C, 71.83; H + D, 6.21.[29]

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(29) The disphosphine dioxides obtained here were mixtures of isotopomers partially deuterated at all the methylene and the *ortho* positions. The formulas of the diphosphine dioxides (total amounts of deuterium atoms incorporated into the diphosphine dioxides) were calculated from the results of ^1H NMR measurements (see Table 3).