Effects of chelate ring rigidity on intramolecular hydrogen exchange in hydrido(dihydrogen)bis(diphosphine)ruthenium(II) ions $[RuH(\eta^2\text{-}H_2)(diphosphine)_2]^+$ (diphosphine = binap and dpbp) *

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(Received October 13, 1993; in revised form February 9, 1994)

Abstract

The molecular hydrogen complex $[RuH(\eta^2\text{-}H_2)(dpbp)_2]^+$ (**2f**) was prepared *in situ* by reaction of H_2 gas with five-coordinate complex $[RuH(dpbp)_2]PF_6$ (**1f**) (dpbp = 2,2′-bis(diphenylphosphino)-1,1′-biphenyl). ^1H and $^{31}P\{^1H\}$ NMR behaviour of **2f** was measured in the temperature range 303–183 K, and compared with that of $[RuH(\eta^2\text{-}H_2)(binap)_2]^+$ (**2e**; binap = 2,2′-bis(diphenylphosphino)-1,1′-binaphthyl). In the ^1H NMR spectrum, **2f** showed a single broad signal in the hydride region due to a rapid hydrogen exchange between molecular hydrogen and terminal hydride at 303 K. The signal separated into two peaks at lower temperatures and the characteristic resonances of Ru–(H_2) and Ru–H were detected below 213 K. In contrast, **2e** showed two signals of Ru–(H_2) and Ru–H even at 303 K. The differences in the NMR features between dpbp complexes and binap complexes were discussed on the basis of the flexibility or rigidity of diphosphine chelate rings.

Key words: Ruthenium; Dihydrogen; Diphosphine; Hydride; Hydrogen exchange; Nuclear magnetic resonance

1. Introduction

Since the first confirmation of the coordination of a dihydrogen molecule, without breaking the H–H σ-bond, to a transition metal centre in $W(H_2)(CO)_3(PR_3)_2$ (R = cyclohexyl or isopropyl) [1,2], investigations of molecular hydrogen complexes have made great progress not only from the experimental but also from theoretical angles [3]. Among a variety of dihydrogen complexes, complexes of the type $[MH(H_2)(P_4)]^+$ ($M = Fe^{II}$, Ru^{II}, Os^{II}, (P_4) = two diphosphines or a tetradentate phosphine) [4 **], constitute one of the most representative and best documented families [5–7].

We have reported in previous communications that the introduction of H_2 gas into solutions of five-coordinate complexes $[RuH(P\text{-}P)_2]PF_6$ (**1**) resulted in the spontaneous formation of $[RuH(H_2)(P\text{-}P)_2]^+$ (P-P = diphosphine) (**2**) [8–10] and that, for homologous

$$[RuH(P\text{-}P)_2]PF_6 + H_2 \rightleftharpoons [RuH(\eta^2\text{-}H_2)(P\text{-}P)_2]PF_6$$
1 **2**

a, P-P = dppe **d**, P-P = diop
b, = dppp **e**, = binap
c, = dppb **f**, = dpbp

complexes (P-P = dppe, dppp, dppb), the intramolecular hydrogen exchange between the terminal hydride (Ru–H) and coordinating dihydrogen (Ru–(H_2)) in **2** depends considerably on the size and flexibility of the diphosphine chelate rings [9]. Thus, for $[RuH(H_2)(dppe)_2]^+$ (**2a**), in which the diphosphine forms a five-membered chelate, the hydrogen exchange is so slow as to make the ^1H NMR resonances of Ru–H and Ru–(H_2) observable separately at room temperature with distinct spin couplings between Ru–H and phosphorus atoms [5]. In the case of $[RuH(H_2)(dppp)_2]^+$ (**2b**) having six-membered chelate rings, the resonances of Ru–H and –(H_2) are still observed separately, but the

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* Abbreviations of diposphines: binap = (*R*) or (*S*)-2,2′-bis(diphenylphosphino)-1,1′-binaphthyl; dpbp = 2,2′-bis(diphenylphosphino)-1,1′-biphenyl; dppe = 1,2-bis(diphenylphosphino)ethane; dppp = 1,3-bis(diphenylphosphino)propane; dppb = 1,4-bis(diphenylphosphino)butane; diop = (*R,R*)-4,5-bis[(diphenylphosphino)methyl]-2,2-dimethyl-1,3-dioxolane.

** Reference number with asterisk indicates a note in the list of references.

0022-328X/94/$7.00
SSDI 0022-328X(94)24640-5

hydride–phosphorus couplings are no longer detected at the same temperature [9]. Under the same conditions the signals of dihydrogen and of terminal hydride coalesce into a single broad peak for $[RuH(H_2)(dppb)_2]^+$ (**2c**), where dppb forms a seven-membered chelate ring [9]. This indicates that in **2c** a fast intramolecular hydrogen exchange takes place between Ru–(H_2) and Ru–H [9]. These results suggest that the hydrogen exchange in **2a–c** occurs faster as the diphosphine chelate ring becomes larger and more flexible, due to the easier conformational changes for the larger chelate.

The variable-temperature ^1H NMR spectra, similar to but clearer than those of **2c**, were obtained for the diop analogue $[RuH(H_2)(diop)_2]^+$ (**2d**) [10]. In contrast, the binap complex $[RuH(H_2)(binap)_2]^+$ (**2e**) shows ^1H NMR characteristics similar to those of **2a**, which is typical for the slow exchange region [8]. Although the chelate rings of diop and binap are chiral and are the same size (seven-membered ring), their conformational rigidities differ significantly from each other. Conformational change of binap chelate should be impossible because of the nature of the binaphthyl backbone, but in diop chelate it is probable to some extent, due to the presence of methylene units. With a view to examining further the effects of conformational flexibility of diphosphine chelates on the intramolecular hydrogen exchange in **2**, we prepared the dpbp complex $[RuH(H_2)(dpbp)_2]^+$ (**2f**). Although dpbp itself has an apparent structural resemblance to binap, the dpbp chelate ring, also seven-membered, is flexible enough to undergo conformational changes, in contrast to the case of binap. It is expected, therefore, that the complex **2f** exhibits ^1H NMR features similar to those of **2c** or **2d** and different from those of **2e**. In this paper, we will focus on the differences in dynamic behaviour between **2e** and **2f** and also between their parent complexes, $[RuH(binap)_2]^+$ (**1e**) and $[RuH(dpbp)_2]^+$ (**1f**).

2. Results and discussion

It has been clarified by crystallography that (*R*)- and (*S*)-binap adopt, respectively, λ-skew and δ-skew conformations in the transition metal complexes [11,12]. A simplified structure of (*R*)-binap chelate is illustrated in Fig. 1, where the phenyl rings bonded to phosphorus atoms are shown by Ph. Figure 1 also shows possible structures of dpbp chelate, whose λ-skew conformation is apparently similar to that of (*R*)-binap. It should be noted that the δ-skew form, the antipode of the λ-skew one, is possible for a dpbp chelate, because the biphenyl backbone of dpbp is flexible thus permitting rotation around the C–C bond. Conversely, it is impossible for (*R*)-binap chelate to adopt the antipodal conformation, as mentioned above. These differences in flexibility between binap and dpbp chelate are expected to result in differences in the dynamic behaviour of complexes with these diphosphines.

2.1. Five-coordinate complexes

The deep orange-red complexes $[RuH(binap)_2]PF_6$ (**1e**) and $[RuH(dpbp)_2]PF_6$ (**1f**) were readily prepared by reactions of $[RuH(NH_2NMe_2)_3(cod)]PF_6$ [13] with two equivalents of respective diphosphines with slight modifications to the reported method [14]. As described previously [8], the ^1H NMR spectrum (400 MHz, in CD_2Cl_2) of the binap complex **1e** shows two hydride signals in the high field region at 303 K (see Fig. 2 and Table 1). Although the higher field peak broadens gradually as the temperature is lowered, no intrinsic change was noticed in the spectra at 303–243 K. In the spectra of the dpbp complex **1f**, we similarly observed two hydride resonances in the temperature range 303–243 K (Fig. 3). These findings indicate that there are two isomers for **1e** and **1f** in solution and that they are distinguishable from each other at these temperatures. In other words, the interconversion of two

TABLE 1. ^1H (at 400 MHz) and ^{31}P (at 162 MHz) NMR data of $[RuH(binap)_2]^+$ (**1e**) and $[RuH(dpbp)_2]^+$ (**1f**) in CD_2Cl_2

Complex	Temp./K	^1H NMR		^{31}P NMR	
		cis (J_{PH}/Hz)	*trans* (J_{PH}/Hz)	*cis* (J_{PP}/Hz)	*trans*
1e	303	−6.25 (dq; 27, 73)	−19.75 (br)	29.8 (1P, br), 42.4 (2P, br), 81.9 (1P, br)	44.6 (br)
	273	−6.25 (dq; 21, 68)	−19.80 (br)	29.3 (1P, d; 12), 42.3 (2P, t; 27), 82.8 (1P, dt; 12, 27)	45.7 (br)
	243	−6.26 (dq; 21, 68)	−20.08 (br)	29.6 (1P, d; 12), 42.4 (2P, t; 27), 82.3 (1P, dt; 12, 27)	47.0 (br)
	213	−6.28 (dq; 26, 74)		29.0 (1P, br), 42.3 (2P, br), 83.4 (1P, m)	
	183	−6.29 (dq; 24, 68)		28.4 (1P, br), 42.2 (2P, br), 83.9 (1P, br)	
1f	303	−2.34 (br)	8.07 (quint; 4)	30.7 (1P, br), 37.1 (2P, br), 49.4 (1P, br)	45.9 (br)
	273	−2.45 (br)	−8.08 (br)	30.3 (1P, br), 37.4 (2P, br), 49.3 (1P, br)	45.9 (br)
	243	−2.61 (br)	−8.06 (br)		*ca.* 46 (br)
	213		−8.14 (br)		very broad

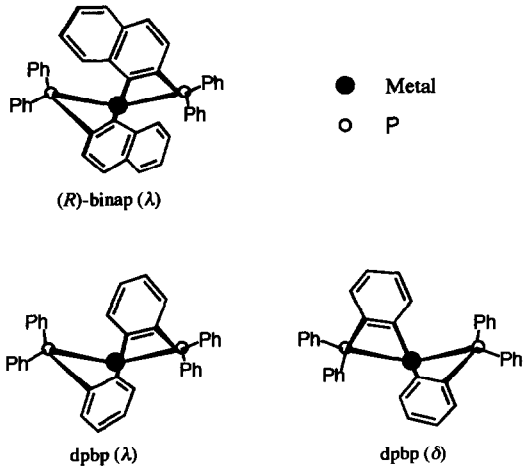

Fig. 1. Chelate ring conformations of (*R*)-binap and dpbp in the complexes.

isomers is very slow on the NMR time scale. When H_2 gas was introduced into a solution of either **1e** or **1f**, a spontaneous colour change took place from deep orange-red to pale yellow. The hydride signals for both isomers of **1e** or **1f** disappeared completely, and those for the molecular hydrogen complex, $[RuH(H_2)(binap)_2]^+$ (**2e**) or $[RuH(H_2)(dpbp)_2]^+$ (**2f**) emerged in the ^1H NMR spectra (*vide infra*). This strongly supports the assignment of the two hydride signals of the five-coordinate complexes **1e** and **1f** to their stereoisomers.

The doublet of quartets at $\delta - 6.25$ in the spectra of **1e**, which showed no appreciable temperature dependence, exhibited a clear spin couplings with phosphorus atoms. The coupling features suggest that one of four phosphorus atoms is located in a very different environment from those of the other three. This signal can be assigned to the hydride (Ru–H) of the "*cis*" isomer, in which the vacant site and the hydride ligand occupy the adjacent coordination sites as illustrated in

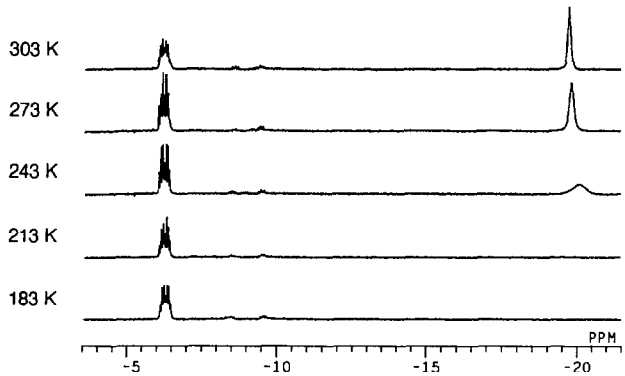

Fig. 2. Variable temperature ^1H NMR spectra (400 MHz) of $[RuH(binap)_2]^+$ (**1e**) in the high field region in CD_2Cl_2.

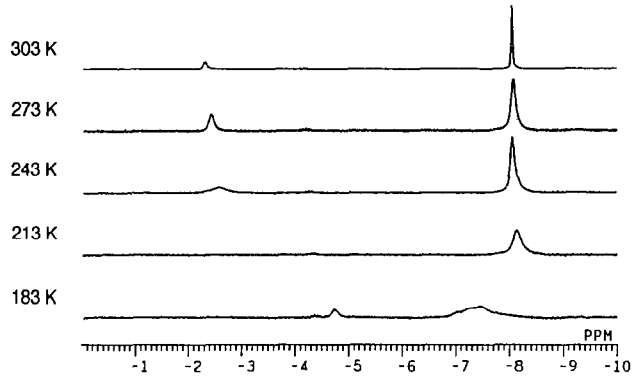

Fig. 3. Variable temperature ^1H NMR spectra (400 MHz) of $[RuH(dpbp)_2]^+$ (**1f**) in the high field region in CD_2Cl_2.

Fig. 4. Here one of the P atoms is situated *trans* to the hydride ligand, while the others are *cis*. In accord with the true molecular symmetry for the "*cis*" isomer (C_1), the $^{31}P\{^1H\}$ NMR spectrum of **1e** showed three resonances assignable to this stereoisomer (Table 1). An alternative interpretation for these ^1H and ^{31}P NMR characteristics is that this isomer takes a trigonal-bipyramidal structure shown as "tbp" in Fig. 4(c). The trigonal-bipyramidal structure requires the binap chelate in the equatorial plane to adopt a bite angle of approximately 120°. In fact, however, the bite angles of binap chelate (∠P–Ru–P) reported so far for some ruthenium complexes are without exception close to 90° [11b,15,16]. Therefore, the *cis* form is more probable than tbp geometry as the structure of the present isomer.

It is natural that the other isomer of **1e** is assigned to the "*trans*" form, where the hydride and the vacant site are located *trans* to each other (Fig. 4). The "*trans*" form of **1e** possesses C_2 molecular symmetry. It was found that typical *trans*-$[RuHX(binap)_2]^{n+}$ complexes, such as *trans*-$RuHCl(binap)_2$ and *trans*-$[RuH(CO)(binap)_2]^+$, gave a triplet of triplets as the Ru–H resonance, and a pair of triplets as the phosphorus resonances [8,16]. These NMR features support the hypothesis that, in the *trans* isomers, phosphorus atoms belonging to the same chelate are magnetically unequal

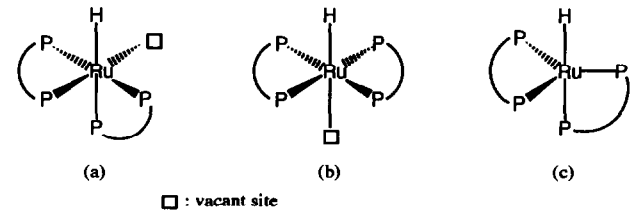

Fig. 4. Three possible structures for **1e** and **1f**: (a) *cis* isomer; (b) *trans* isomer; (c) trigonal-bipyramidal (tbp) isomer.

due to the rigid conformation of binap. However, the second ^{1}H NMR signal of **1e**, observed at δ *ca.* -20 as a broad peak, had no obvious spin couplings with P atoms and was not a typical hydride signal for the *trans*-[RuHX(binap)$_2$]$^{n+}$ complexes. Further, the ^{31}P-{^{1}H} NMR signal assignable to the second isomer of **1e** was noted as a single broad peak (δ 44.6) at 303 K (Table 1). These NMR characteristics do not suggest clearly that the second isomer of **1e** adopts the "*trans*" configuration. However, strong evidence that supports the assignment of this isomer to the "*trans*" geometry was given by the ^{1}H NMR measurements of dpbp complex **1f** (*vide infra*).

The ^{1}H and ^{31}P{^{1}H} NMR signals for the "*trans*" isomer of **1e** broadened gradually at lower temperatures and could no longer be detected below 213 K (Fig. 2). In contrast, the signals for the "*cis*" isomer of the same complex remained almost unchanged even at this temperature. These facts suggest that a fast exchange process occurs only for the "*trans*" isomer. It seems, further, that the rate of exchange decreased as the temperature is lowered and became comparable to the NMR time scale at 213 K. We suggest that the exchange of solvent molecules, interacting weakly at the vacant site, is a candidate for the fast exchange process, which may affect the shape and temperature dependence of the Ru–H signal of the "*trans*" isomer.

We draw attention to evidence suggesting a weak interaction of the solvent molecule at the vacant coordination site of **1e**. It is anticipated that the coordination of different solvents should result in changes in chemical shift of some key NMR resonances. In fact, the Ru–H signal of the "*trans*" isomer of **1e** in acetone-d_6 at 243 K shifted up field by 1.37 ppm compared to that in CD_2Cl_2, while the corresponding signal for the "*cis*" isomer showed no significant dependence on solvent. In addition, **1e** in $CDCl_3$ solution turned gradually into RuHCl(binap)$_2$ after standing for several days [8]. This strongly supports the hypothesis that the solvent molecule interacts with **1e** at the vacant site.

The dpbp complex **1f** shows two hydride signals (δ *ca.* -2.4 and -8.1) in the temperature range 303–243 K, in a similar manner to those of **1e** (Fig. 3 and Table 1). It is noteworthy that the higher field signal for one of the isomers of **1f** appears as a quintet at 303 K. It was revealed, further, that the present isomer gives a slightly broad singlet in the ^{31}P{^{1}H} NMR spectrum. The spectral features are rationalized by taking the couplings among the terminal hydride and four equivalent phosphorus atoms into consideration. The observation that the phosphorus atoms of two dpbp ligands are practically equivalent indicates that the conformation changes of dpbp chelates are very fast when they are in the "*trans*" form. If the interconversion between δ-and λ-conformation is rapid enough for the two chelate rings, all the P atoms in the "*trans*" isomer of **1f** will be regarded as equivalent. Then the Ru–H signal can appear as a quintet, even if the geometry of the isomer is restricted in the "*trans*" form.

Alternatively, it is expected that the Ru–H signal is observed as a quintet and that the phosphorus signal appears as a singlet, when **1f** is highly fluxional as a whole molecule. In such case, however, only one peak will be found as the Ru–H signal in the hydride region. Since we detected the other hydride signal at δ *ca.* -2.4, the higher field signal at δ *ca* -8.1 is unambiguously assigned to the terminal hydride of the "*trans*" isomer of **1f**. In fact, the dppb complex **1c** and diop complex **1d** are fluxional at room temperature, so that a broad single peak is found as the hydride resonance [17]. For these systems, however, no coupling between Ru–H and P atoms was observed.

It is noteworthy that the hydride signal assigned to the "*trans*" isomer of **1f** turns into a broad peak (no spin coupling with ^{31}P) below 273 K. In addition, the spectral changes of this signal at 273–213 K are obviously similar to those of the hydride signal at δ *ca.* -20 of **1e** in the range 303–243 K. The similarity of the temperature dependence of these signals strongly suggests as described previously, that the higher field hydride signal of **1e** can be assigned to the "*trans*" isomer. The temperature dependence also implies that the rate of conformation change of the diphosphine in **1f** is decreased at lower temperatures, although the other exchange process, possibly the exchange of coordinating solvent at the vacant site, should become concomitantly slower.

The other hydride signal of **1f**, which should be ascribed to the "*cis*" isomer, is a broad peak (δ *ca.* -2.4) in the range 303–243 K. No clear coupling with phosphorus atoms was detected even at 303 K, in sharp contrast to the case of the "*cis*" isomer of the binap complex **1e**. The reason for these differences in the ^{1}H NMR features of "*cis*" isomers is uncertain. The ^{31}P{^{1}H} NMR data support the hypothesis that the isomers of **1f** other than the "*trans*" form has no molecular symmetry.

2.2. Molecular hydrogen complexes

2.2.1. Binap complex

As described in our preliminary report [8], contact of the five-coordinate complex **1e** with hydrogen gas in a THF solution afforded white crystals of molecular hydrogen complex [RuH(H_2)(binap)$_2$]PF_6 (**2e**). The ^{1}H NMR spectrum of **2e** at 303 K revealed two high field resonances assignable to Ru–(H_2) and Ru–H groups

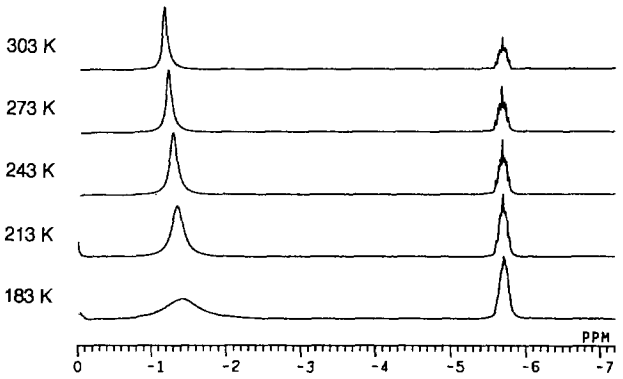

Fig. 5. Variable temperature ^1H NMR spectra (400 MHz) of $[RuH(H_2)(binap)_2]^+$ (**2e**) in the high field region in CD_2Cl_2.

with intensity ratio of 2:1 (Fig. 5 and Table 2). Thus, the broad singlet which appeared at δ −1.17 was ascribed to the dihydrogen ligand, and the triplet of triplets at δ −5.68 (J_{H-P} = 13, 21 Hz) to the terminal hydride in **2e**. The coupling features of the Ru–H signal, which are the same as those of *trans*-RuHCl(binap)$_2$ [12], indicates that **2e** takes the *trans* configuration with regard to the dihydrogen and terminal hydride ligands. These signals showed no significant temperature dependence in the range 303–183 K, except for a gradual broadening of the former at lower temperatures (Fig. 5).

The partially deuterated species $[RuD(HD)(binap)_2]^+$ was readily prepared by introducing D_2 gas into a solution of complex **1e** and subsequent intramolecular hydrogen-deuterium exchange. The ^1H NMR measurement of the deuterated complex showed a triplet of 1:1:1 intensities (J_{H-D} = 30 Hz) at δ − 1.1 [8]. The coupling features and the chemical shift of this signal are diagnostic of the presence of coordinating HD molecule and, consequently, provide strong evidence for the formation of η^2-H_2 complex [2,3].

It has been recognized that the observation of short T_1 values (< 100 ms at 400 MHz) for metal hydride species are also useful in diagnosing the presence of H_2 ligand [3], although a limitation for this simple judgment was proposed recently [18]. In fact, the T_1 criteria for the dihydrogen and hydride ligands, proposed initially by Crabtree and co-workers [3b], could be satisfactorily applied for complex **2e**, where the T_1 values of the signals at δ − 1.17 and −5.68 were found to be, respectively, 21 and 185 ms at 303 K.

The ^1H NMR characteristics of **2e** are, as a whole, similar to those of the dppe analogue $[RuH(H_2)(dppe)_2]^+$ (**2a**) [5a, 5f, 19]. In both instances, the intramolecular exchange between dihydrogen and terminal hydride ligands is sufficiently slow compared with the NMR time scale. In each case, the Ru–H signal exhibits definite couplings with ^{31}P nuclei of diphosphine ligands (Table 2 and ref. 5f), whereas the Ru–(H_2) signal appears as a broad singlet as in most molecular hydrogen complexes. These NMR features are, however, in sharp contrast to those of the molecular hydrogen complexes of dppb and of diop, $[RuH(H_2)(dppb)_2]^+$ (**2c**) and $[RuH(H_2)(diop)_2]^+$ (**2d**). These complexes are found to be highly fluxional at higher temperature, and the signals of Ru–(H_2) and Ru–H coalesce into a single broad peak at 303 K [9,10].

2.2.2. *Dpbp complex*

We consider that the clear difference in patterns of hydrogen exchange between **2e** and **2c** or **2d** is due to the difference in the conformational rigidity between the complexes with binap and dppb or diop ligands, as described in the introduction, because all these diphosphines form seven-membered chelate rings. With a view to examining the effects of flexibility or rigidity of diphosphine chelates on hydrogen exchange in more detail, the NMR properties of the molecular hydrogen complex $[RuH(H_2)(dpbp)_2]^+$ (**2f**) were measured. As mentioned previously, a dpbp chelate also gives rise to a seven-membered ring quite similar to that of binap,

TABLE 2. ^1H (at 400 MHz) and ^{31}P (at 162 MHz) NMR data of $[RuH(H_2)(binap)_2]^+$ (**2e**) and $[RuH(H_2)(dpbp)_2]^+$ (**2f**) in CD_2Cl_2

Complex	Temp./K	^1H NMR		^{31}P NMR
		Ru-H_2	Ru-H (J_{PH}/Hz)	
2e	303	−1.17 (br)	−5.68 (tt; 13, 21)	49.0 (t; 30), 50.5 (t; 30)
	273	−1.23 (br)	−5.68 (tt; 13, 21)	49.1 (t; 30), 50.8 (t; 30)
	243	−1.28 (br)	−5.68 (tt; 13, 21)	49.1 (t; 30), 51.0 (t; 30)
	213	−1.35 (br)	−5.69 (m)	49.1 (t; 30), 51.4 (t; 30)
	183	−1.41 (br)	−5.70 (br)	49.1 (t; 30), 51.8 (t; 30)
2f	303	−4.32 (br)		34.2 (br)
	273	*ca.* −4.2 (br)		*ca.* 34 (br)
	243	*ca.* −2.9 (br)	*ca.* −6.1 (br)	*ca.* 30 (br), *ca.* 37 (br)
	213	−2.90 (br)	−6.38 (m)	30.1 (t; 31), 38.2 (t; 31)
	183	−2.91 (br)	−6.53 (tt; 15, 27)	30.0 (t; 31), 38.2 (t; 31)

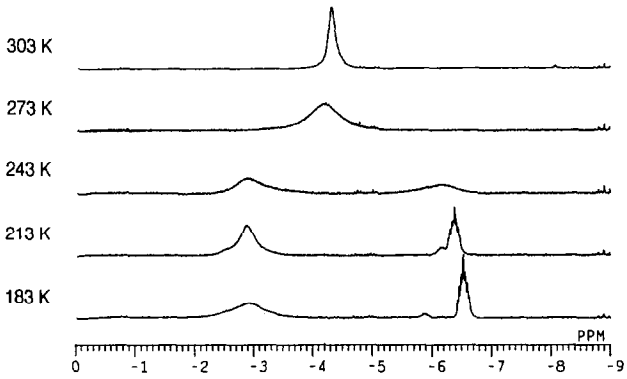

Fig. 6. Variable temperature ^{1}H NMR spectra (400 MHz) of $[RuH(H_2)(dpbp)_2]^+$ (**2f**) in the high field region in CD_2Cl_2.

but the freedom of inversion of conformation for the former ligand is in sharp contrast to the rigidity of the latter. The variable temperature ^{1}H NMR spectra of **2f** are shown in Fig. 6, and the detailed data are collected in Table 2.

The ^{1}H NMR spectra of **2f** exhibited a remarkable temperature dependence (Fig. 6). The observed spectral changes for **2f** are, as a whole, partly similar to those of $[FeH(H_2)(dppe)_2]^+$ reported by Morris and collaborators [5f]. At and below 213 K, two dominant resonances, a broad singlet (δ *ca.* -2.9) assigned to Ru–(H_2) and a triplet of triplets (δ *ca.* -6.5, J_{P-H} = 15, 27 Hz at 183 K) due to Ru–H, were detected. The T_1 values of these resonances obtained at 203 K are as follows: 12 ms for Ru–(H_2) and 240 ms for Ru–H. The values are the indication of slow hydrogen exchange between the dihydrogen and terminal hydride under these conditions. In such a slow exchange region, the complex **2f** should hold the *trans* configuration in the same way as the binap complex **2e**. In accord with this hypothesis, ^{31}P NMR spectra showed a couple of triplets in the same temperature range, reflecting the inequivalence of the two phosphorus atoms of a dpbp chelate (Table 2).

As the temperature is raised, the intramolecular hydrogen exchange becomes faster, so that the signals for Ru–(H_2) and Ru–H broaden significantly at 243 K (Fig. 6). Around this temperature, the spin couplings between Ru–H and P atoms could no longer be detected. In addition, the T_1 values of Ru–(H_2) and Ru–H were found to be 12 and 14 ms, respectively, at 233 K. The fact that the T_1 times for Ru–(H_2) and Ru–H signals are averaged (relaxation coalescence) suggests an increased rate of exchange between the dihydrogen and terminal hydride. We noticed that $[RuH(H_2)(dppp)_2]^+$ (**2b**) showed similar tendencies in T_1 of the hydride signals in the range 273–303 K [9].

It is apparent that the two resonances coalesce completely between 243 and 273 K (line-shape coalescence). The chemical shift of the broad peak (δ *ca.* -4.2 at 273 K), which must have the intensity of three hydrogens, is close to the weighted average (2:1) of $\delta(H_2)$ and δ(Ru–H) at 243 K. This indicates that a fast hydrogen exchange takes place for **2f** above *ca.* 250 K. The coalesced signal becomes narrower at higher temperatures (see the spectrum at 303 K, Fig. 6), but does not show any couplings with phosphorus atoms. The T_1 time of this resonance was as short as 24 ms (303 K), indicating the influence of (H_2) ligand even at higher temperatures.

We estimated the rate of H atom exchange (k^{H_2}) from dihydrogen to hydride for complex **2f** at the line-shape coalescence temperature ($k^{H_2} = \pi\nu_0\{\delta(H_2) - \delta(H)\}/\sqrt{2}$; ν_0 is the spectrometer frequency). Using the chemical shifts $\delta(H_2)$ and δ(H) at 183 K, k^{H_2} = 3200 s^{-1} was obtained. Although the exact coalescence temperature was not determined, the activation free energy, $\Delta G^{\ddagger}$, for the rate of H atom exchange in **2f** was calculated on the basis of the rate constant. Assuming a coalescence temperature of 250 K, a $\Delta G^{\ddagger}$ of 10.5 kcal/mol was approximated [20*]. Similar values were reported by Jessop and Morris for the complex **2f** [3d]. The $\Delta G^{\ddagger}$ for **2f** is comparable to those for **2c** and **2d** but significantly smaller than those for **2a** and **2e** [3d].

Two independent mechanisms have been proposed for the hydrogen exchange process in $[MH(H_2)(P-P)_2]^+$ complexes. Morris and collaborators assumed a dissociative mechanism for H atom exchange that involves homolysis of the H–H bond to produce a fluxional trihydride intermediate (see Fig. 7) [3d, 5f]. It is hypothesized that the dissociative mechanism is more reasonable for $[MH(H_2)(P-P)_2]^+$ having strictly *trans* configuration, such as **2a** and **2e**. Alternatively, an associative mechanism, involving an intermediate with

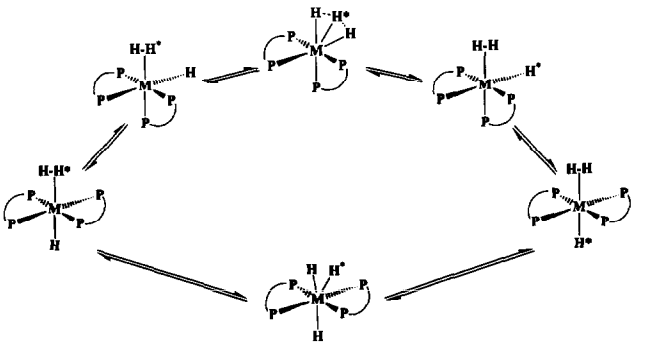

Fig. 7. Two proposed mechanisms for intramolecular hydrogen exchange in $[MH(H_2)(diphosphine)_2]^+$: (above) non-dissociative; (below) dissociative.

a H_3 unit, was proposed on the basis of *ab initio* calculations on the *cis*-$[FeH(H_2)(PH_3)_4]^+$ system (Fig. 7) [21]. This mechanism could be applied for molecular hydrogen complexes that adopt, at least in part, *cis* configuration as **2c** and **2d**. It was reasonably understood that the $\Delta G^{\ddagger}$ values for **2a** and **2e** (> 15 kcal/mol) are significantly larger than those for **2c** and **2d** (< 12 kcal/mol), taking these hypothetical differences in H atom exchange mechanisms into consideration [5f].

The occurrence of the *cis* isomer was suggested for **2d** because a broad resonance other than those of the *trans* isomer is found downfield of the Ru–H signal in the variable temperature ^1H NMR spectrum [9]. However, detailed examination of ^1H NMR charts (Fig. 6) revealed no sign of the formation of the *cis* isomer of **2f**. We can recognize, in fact, a broad peak downfield of the Ru–H resonance of the *trans* form at 213 and 183 K, in a similar manner to what is observed for **2d**. An intrinsic difference between **2d** and **2f** is that the broad $Ru–H_2$ signal is a symmetrical and a smaller broad peak seems to overlap at the lower frequency side in the latter case. These findings are rationalized by hypothesizing the presence of two *trans* isomers of **2f**, which arise from the different combinations of the conformation of dpbp.

Thus, the dominant isomer should have a racemic structure, where both dpbp chelates adopt the same conformation, as (δ, δ) or (λ, λ). We consider that the minor isomer takes a *meso* structure, in which the conformations of dpbp chelates are antipodal to each other, as (δ, λ). Steric congestion in the racemic form is expected to be similar to or smaller than that of **2e**. In the *meso* form, however, steric repulsion between diphosphines should be more severe than in the racemic form. Other examples suggesting the presence of stereoisomers have never been clarified for a variety of *trans*-$[MH(H_2)(P-P)_2]^+$ complexes reported so far [3]. The *meso* form is, of course, regarded as an intermediate in the interconversion between (δ, δ) and (λ, λ) form at elevated temperatures. This strongly supports that a dpbp chelate undergoes facile conformation changes at high temperatures.

2.3. Summary

The reason for the small $\Delta G^{\ddagger}$ value of H atom exchange for **2f** is still uncertain. Whichever mechanism of H atom exchange actually works for **2f**, it is noteworthy that the temperature dependence in the ^1H NMR spectrum of **2f** obviously differs from that of the binap analogue **2e**. The differences in the hydrogen exchange properties in these complexes should be ascribed to the differences in the flexibility of the respective chelate of diphosphines, as mentioned above. We conclude that the NMR behaviour of the binap complex **2e** is rather unusual in relation to its analogues with seven-membered diphosphine chelates.

Remarkable differences between the diop complex **2d** and the binap complex **2e** have been noticed in the asymmetric induction for hydrogenation catalyzed by these complexes [22]. For hydrogenation of several unsaturated carboxylic acids, **2e** revealed sufficiently high selectivities, while **2d** showed only moderate selectivities. This could also be attributed to the differences in the flexibility or rigidity of diphosphines.

3. Experimental details

Unless otherwise noted, all manipulations were carried out under a dry nitrogen atmosphere by standard Schlenk-tube techniques. All the solvents were dried over appropriate reagents and distilled under nitrogen. Binap was presented by Takasago International Corporation. Dpbp [23], $[RuH(NH_2NMe_2)_3(cod)]PF_6$ [13], and $[RuH(binap)_2]PF_6$ [22] were prepared by the reported methods. ^1H NMR (400 MHz) and ^{31}P NMR (162 MHz) spectra were measured with a JEOL JNM-GX 400 spectrometer. ^1H NMR T_1 measurements were carried out by the inversion recovery method using a standard 180°-τ-90° pulse sequence.

3.1. Hydridobis[2,2'-bis(diphenylphosphino)-1,1'-biphenyl]ruthenium(II) hexafluorophosphate [RuH(dpbp)$_2$]PF$_6$ (1f)

A solution of $[RuH(NH_2NMe_2)_3(cod)]PF_6$ (199 mg, 0.37 mmol) and dpbp (402 mg, 0.77 mmol) in acetone was stirred at room temperature for 12 h. During this period the colour of the solution changed to deep red. The solution was filtered and the filtrate was concentrated to about 2 ml under reduced pressure. Diethyl ether was added to this solution to afford an oily product, which solidified on standing for several days at room temperature; yield 373 mg, 78%. Anal. Calcd. for $C_{72}H_{57}F_6P_5Ru$: C, 66.9; H, 4.5. Found: C, 66.1; H, 4.5%.

3.2. Hydrido(dihydrogen)bis[2,2'-bis(diphenylphosphino)-1,1'-binaphthyl]ruthenium(II) hexafluorophosphate [RuH(η^2-H$_2$)(binap)$_2$]PF$_6$ (2e)

$[RuH(binap)_2]PF_6$ (**1e**; 30 mg) was dissolved in CD_2Cl_2 (0.5 ml) in a 5 mm NMR tube. The introduction of dry H_2 gas to this solution resulted in a spontaneous colour change from deep red to pale yellow. $[RuH(binap)_2]PF_6$ was converted into $[RuH(\eta^2-H_2)(binap)_2]PF_6$ quantitatively within 3 min. The resulting sample was used for NMR measurements without further purification.

3.3. *Hydrido(dihydrogen)bis[2,2'-bis(diphenylphosphino)-1,1'-biphenyl]ruthenium(II) hexafluorophosphate* $[RuH(\eta^2\text{-}H_2)(dpbp)_2]PF_6$ (**2f**)

The title complex was prepared from $[RuH(dpbp)_2]PF_6$ (**1f**) as described above for **2e**.

Acknowledgment

This work was supported by a Grant-in Aid for Scientific Research from the Ministry of Education, Science and Culture, Japan (No. 03453098).

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