CHEMISTRY LETTERS, pp. 601-604, 1990.

Chelate Size Dependence of Dihydrogen-Hydride Exchange in Ruthenium(II) Molecular Hydrogen Complexes with Diphosphines $[RuH(\eta^2\text{-}H_2)(P\text{-}P)_2]PF_6$ ($P\text{-}P = Ph_2P(CH_2)_nPPh_2$; $n = 2,3,4$)

Masahiko SABURI,* Ko AOYAGI, Tamotsu TAKAHASHI, and Yasuzo UCHIDA
Department of Industrial Chemistry, Faculty of Engineering, The University of Tokyo,
Hongo, Bunkyo-Ku, Tokyo 113

The introduction of H_2 gas into CD_2Cl_2 solutions of the five-coordinate complexes $[RuH(P\text{-}P)_2]PF_6$ (**1**) resulted in the spontaneous generation of molecular hydrogen complexes $[RuH(\eta^2\text{-}H_2)(P\text{-}P)_2]PF_6$ (**2**) (P-P = 1,3-bis(diphenylphosphino)propane, 1,4-bis(diphenylphosphino)butane). ^1H-NMR measurements revealed that the dihydrogen-hydride exchange for a series of complexes **2** depends significantly on the size of diphosphine chelate.

Since Kubas reported the first confirmation of the transition metal complex coordinating a molecular hydrogen in the side-on fashion,[1a)] a considerable number of η^2-H_2 complexes has been prepared and characterized in detail in these years.[2)] Although sixteen electron five-coordinate complexes have been expected to give rise to η^2-H_2 complexes upon contacted with dihydrogen, a limited number of such coordinatively unsaturated complexes have been applied as precursors for molecular hydrogen complexes.[1,3,4)] We have previously reported that the formally five-coordinate ruthenium complex, $[RuH(binap)_2]PF_6$ (**1a**, binap = (*R*)- or (*S*)-2,2'-bis(diphenylphosphino)-1,1'-binaphthyl[5)]), coordinates dihydrogen to afford a molecular hydrogen complex, *trans*-$[RuH(\eta^2\text{-}H_2)(binap)_2]PF_6$ (**2a**).[6)]

The preparation of the prototypes of complex **1a**, *i.e.* $[RuH(dppp)_2]PF_6$ (**1b**, dppp = 1,3-bis(diphenylphosphino)propane) and $[RuH(dppb)_2]PF_6$ (**1c**, dppb = 1,4-bis(diphenylphosphino)butane) and their treatments with dihydrogen were reported in a preliminary form,[7)] but no further details have been clarified to date. During the course of our study on examining the hydrogenation catalytic activity of **1a**, we required to compare the solution behaviors of the η^2-H_2 complexes $[RuH(H_2)(P\text{-}P)_2]PF_6$ (**2b**, P-P = dppp; **2c**, P-P = dppb; **2d**, P-P = dppe (1,2-bis(diphenylphosphino)ethane)) with those of **2a**. Here we describe the characteristics of **2b** and **2c**, especially the chelate size dependence of the hydrogen exchange between the dihydrogen and terminal hydride established by variable temperature ^1H- and ^{31}P-NMR measurements.

Deep brown **1b** and **1c** were prepared by reactions of $[RuH(NH_2NMe_2)_3(cod)]PF_6$ (cod = 1,5-cyclooctadiene) with respective diphosphines in ethanol.[7)] A distinct color change from brown to pale yellow could be observed spontaneously by introducing H_2 gas into a solution of **1b** in dichloromethane. This strongly suggests the formation of a new Ru(II) species involving a coordinating H_2 molecule, highly probably of the η^2-H_2

$$[RuH(P\text{-}P)_2]^+ \xrightarrow[\text{in } CH_2Cl_2 \text{ or in } CD_2Cl_2]{H_2\ (gas)} [RuH(\eta^2\text{-}H_2)(P\text{-}P)_2]^+$$

a, P-P = binap b, P-P = dppp
c, = dppb d, = dppe

Table 1. ^{1}H- and ^{31}P-NMR data of $[RuH(\eta^2\text{-}H_2)(dppp)_2]PF_6$ (**2b**)

	^{1}H-NMR (400 MHz in CD_2Cl_2)				^{31}P-NMR (162 MHz)
T/K	Ru-H	T_1/ms	Ru-(H_2)	T_1/ms	(in CH_2Cl_2)
303	-8.1 (br s)	14	-3.2 (br s)	14	23.6 (s)
273	-8.1 (qui)$^{a)}$		-3.2 (br s)		23.7 (s)
243	-8.1 (qui)$^{b)}$	239	-3.2 (br s)	6	23.7 (s)
213	-8.1 (qui)$^{c)}$		-3.3 (br)		23.9 (s), 23.6 (s)
183	-8.2 (m)		-3.3 (br)		24.3 (t)$^{d)}$, 23.6 (t)$^{d)}$

a) $^{2}J(H,P)$ = 21 Hz. b) $^{2}J(H,P)$ = 19 Hz. c) $^{2}J(H,P)$ = 18 Hz. d) J(P,P) = 34 Hz.

complex **2b**, in solution, although it was found difficult to isolate the complex as the crystalline product. The complete transformation from **1b** to **2b** under the above conditions could be confirmed by ^{1}H-NMR spectral changes in the hydride region. Thus, two broad singlets appeared at δ -3.2 and -8.1 with 2:1 intensity ratio by the introduction of H_2 gas to a CD_2Cl_2 solution of **1b** at 303 K, at the expense of the broad hydride resonance of the parent complex at δ -10.4. At lower temperatures (213-273 K) the signal at δ -3.2 appeared as a quintet due to the coupling with P atoms of dppp. The variable temperature ^{1}H- and ^{31}P-NMR data for **2b** are summarized in Table 1.

The ^{1}H-NMR features of **2b** in the temperature range 213-273 K are similar to those of previously reported **2d**$^{4,8)}$ and the depe analogue$^{9)}$ (depe = 1,2-bis(diethylphosphino)ethane) in the range 210-300 K. The T_1 values of the high-field resonances for **2b** at 243 K, 6 ms for the signal at δ -3.2 and 239 ms at - 8.1, enable to assign the former to Ru-(η^2-H_2) and the latter to Ru-H resonances.$^{4,8,9)}$ It was found further that the $^{1}J(H,D)$ for the coordinating (HD) at δ -8.1 in an isotopomer $[RuD(HD)(dppp)_2]^+$ was 32 Hz at 243 K, the corresponding values for **2d** and the depe analogue also being 32$^{6)}$ and 32 Hz,$^{8)}$ respectively. These NMR characteristics unambiguously indicate that **2b** assumes the *trans* configuration and that no rapid exchange between Ru-(H_2) and Ru-H occurs below 273 K.

A fluxional process, which can be ascribed to the rapid hydrogen exchange between the dihydrogen and the terminal hydride, was recognized in $MH(\eta^2\text{-}H_2)(L)_4$ species (L = ligand) for M = Fe(II)$^{6,8\text{-}11)}$ and Ir(III).$^{12)}$ For these instances the exchange is so rapid at higher temperatures that the resonances of M-(H_2) and of M-H coalesced to give a broad signal. Interesting is that the Ru(II) complexes so far reported, **2d** and the

Table 2. ^{1}H- and ^{31}P-NMR data of $[RuH(\eta^2\text{-}H_2)(dppb)_2]PF_6$ (**2c**)

T/K	^{1}H-NMR (400 MHz)$^{a)}$	^{31}P-NMR (162 MHz)$^{b)}$
303	-5.8 (br)$^{c)}$	33.9 (s), 34.8 (s)
273	-5.5 (br)	34.6 (b)
243	-6.6 (br)$^{d)}$, -3.9 (br)d)	37$^{e)}$
213	-7.9 (m)$^{f)}$, -3.1 (br)$^{g)}$	17.1 (br), 26.5 (br), 34.4 (br), 38.9 (br), 44.3 (br)
183	-7.9 (m), -3.1 (br)	16.5 (m), 26.0 (m), 34.6 (m), 38.8 (m), 44.7 (m)

a) Obtained in CD_2Cl_2. b) Obtained in CH_2Cl_2. c) T_1 = 23 ms. d) Partly overlapping with each other. e) Very broad peak with a tendency of splitting. f) T_1 = 34 ms. g) T_1 = 10 ms.

depe analogue, showed no tendency of such fluxionality even at 300 K.[4,8] It is worth noting, therefore, that the T_1 values for Ru-(H_2) and Ru-H of **2b** were accidentally the same (14 ms) at this temperature. In accord with this observation, no obvious ^1J(H,D) could be detected for the above mentioned deuterated complex at 303 K. Although the signals of Ru-(H_2) and Ru-H could be observed as the separate peaks up to 323 K, it is apparent that for the dppp complex **2b** an intramolecular hydrogen exchange takes place with a significant rate above 300 K.

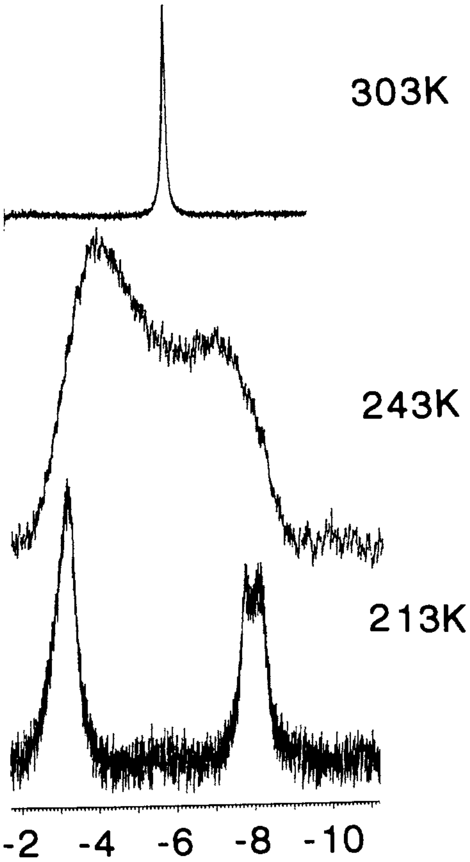

Fig. 1. ^{1}H-NMR spectra of **2c** in the high field region.

It is noteworthy that the chelate size enlargement from five-membered dppe to six-membered dppp by one methylene unit resulted in a marked enhancement of the exchange between dihydrogen and terminal hydride. This suggests a possibility of a faster hydrogen exchange for the corresponding seven-membered dppb complex **2c**. Indeed, the ^{1}H-NMR spectrum of **2c**, prepared by introducing H_2 into a CD_2Cl_2 solution of **1c**, exhibited only one broad singlet in the hydride region at 303 K (Fig. 1). The NMR data of **2c** at variable temperatures are shown in Table 2. On decreasing the temperature, the signal became broader, and at 243 K an evident decoalescence into two peaks was noticed as shown in Fig. 1. A complete separation into two resonances, δ -3.1 and -7.9 with the intensity ratio ca 5:3, could be attained at 213 K. The T_1 values for these resonances were 10 and 34 ms, respectively. These features seem to indicate that the signal at δ -7.9 is ascribed to Ru-H resonance. The fairly short T_1 time (34 ms) and no observation of clear couplings with P atoms can be ascribed to that the hydrogen exchange has not fully frozen out at this stage. However, ^{31}P-NMR spectra of **2c** obtained below 213 K revealed another source of fluxionality to be taken into consideration.

The ^{31}P resonance of **2c** was found as broad singlet at 273 K. This became broader as the temperature lowered, and finally split into five peaks having different intensities. No clear ^2J(P,P) values could be obtained. Besides the dihydrogen-hydride exchange discussed above, the second fluxional process has been recognized for η^2-H_2 complexes, i.e. the broadening of dihydrogen resonance at low temperatures presumably due to a slowing of the rotation of the η^2-H_2 ligand on the square face of a square pyramid defined by the four P atoms and apical hydride.[4] This should be acting in the case of **2c**, because the ^{1}H resonance at δ -3.1 showed further broadening at 183 K. However, the ^{31}P splitting pattern which suggests the existence of a few stereoisomers could not be rationalized by the same reasoning.

The conformational inversion of diphosphine chelate ring is regarded as an alternative source of fluxionality for **2c** which should freeze out below 210 K as well as the rotation of η^2-H_2 moiety. As for Rh(I)-

dppb complexes, possible conformations such as twist-chair and boat were disclosed in the crystalline state by an X-ray study.[13)] Furthermore, the existence of a few diastereomers due to combinations of varied conformations of both chelates was detected for $[Rh(dppb)_2]^+$ ion by NMR measurements at 178 K.[14)] Thus, the observed ^{31}P-NMR features of **2c** in 183-213 K region are reasonably understood based on the presence of conformers, even if the geometry was restricted in the *trans* configuration. The population of such conformers are considered not to be equal to one another. This may reflect on the complicated ^{31}P-NMR spectra of **2c** at low temperatures, although the spectra could not be fully analyzed.

It was thus demonstrated that for $[RuH(\eta^2\text{-}H_2)(P\text{-}P)_2]^+$ series (P-P = dppe, dppp, dppb) the flexibility of the chelate ring affects considerably the intramolecular hydrogen exchange between Ru-H and Ru-(H_2). Further studies on the effects from the size and flexibility of chelate rings on the dynamic behaviors of these complexes are now in progress.

This work was supported by Grant-in Aid for Scientific Research from the Ministry of Education, Science, and Culture (No. 01550661).

References

1) a) G. J. Kubas, R. R. Ryan, B. I. Swanson, P. J. Vergamini, and H. J. Wasserman, *J. Am. Chem. Soc.*, **106**, 451 (1984); b) H. J. Wasserman, G. J. Kubas, and R. R. Ryan, *ibid.*, **108**, 2294 (1986); c) G. J. Kubas, C. J. Unkefer, B. I. Swanson, and E. Fukushima, *ibid.*, **108**, 7000 (1986).
2) Recent reviews. G. J. Kubas, *Acc. Chem. Res.*, **21**, 120 (1988); R. H. Crabtree and D. G. Hamilton, *Adv. Organomet. Chem.*, **28**, 299 (1988).
3) G. J. Kubas, R. R. Ryan, and D. A. Wrobleski, *J. Am. Chem. Soc.*, **108**, 1339 (1986); G. J. Kubas, R. R. Ryan, and C. J. Unkefer, *ibid.*, **109**, 8113 (1987).
4) R. H. Morris,.J. F. Sawyer, M. Shiralian, and J. D. Zubkowski, *J. Am. Chem. Soc.*, **107**, 5581 (1985).
5) A. Miyashita, H. Takaya, T. Souchi, and R. Noyori, *Tetrahedron*, **40**,1245 (1984).
6) T. Tsukahara, H. Kawano, Y. Ishii, T. Takahashi, M. Saburi, Y. Uchida, and S. Akutagawa, *Chem. Lett.*, **1988**, 2055.
7) T. V. Ashworth and E. Singleton, *J. Chem. Soc., Chem. Commun.*, **1976**, 705.
8) M.T. Bautista, K. A. Earl, P. A. Maltby, R. H. Morris, C. T. Schweitzer, and A. Sella, *J. Am. Chem. Soc.*, **110**, 7031 (1988).
9) M. Bautista, K. A. Earl, R. H. Morris, and A. Sella, *J. Am. Chem. Soc.*, **109**, 3780 (1987).
10) M. V. Baker, L. D. Field, and D. J. Young, *J. Chem. Soc., Chem. Commun.*, **1988**, 546; M. V. Baker and L. D. Field, *J. Organomet. Chem.*, **354**, 351 (1988).
11) C. Bianchini, M. Peruzzini, and F. Zanobini, *J. Organomet. Chem.*, **354**, C19, (1988).
12) R. H. Crabtree, M. Lavin, and L. Bonneviot, *J. Am. Chem. Soc.*, **108**, 4032 (1986).
13) M. P. Anderson and L. H. Pignolet, *Inorg. Chem.*, **20**, 4101 (1981).
14) P. A. Chaloner, *J. Organomet. Chem.*, **266**, 191 (1984).

(Received January 23, 1990)