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Characterization of Ruthenium(II) Molecular Hydrogen Complex with (*R,R*)-4,5-Bis (diphenylphosphinomethyl)-2,2-dimethyl-1,3-dioxolane (diop)

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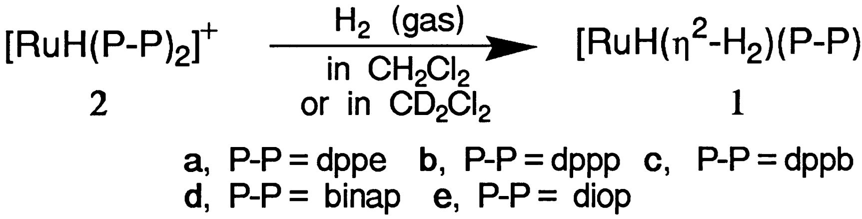
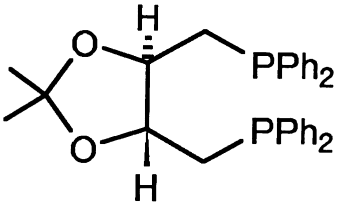
The Ru(II) molecular hydrogen complex $[RuH(\eta^2\text{-}H_2)(diop)_2]^+$ was prepared *in situ* from $[RuH(diop)_2]^+$ and H_2 gas. The low temperature (213-243 K) ^1H and ^{31}P NMR data of this η^2-H_2 complex indicated the coexistence of two isomers (*trans* and *cis*) at equilibrium in solution. At 303 K the coalescence of Ru-H and Ru-(η^2-H_2) resonances due to their rapid exchanges was observed.

Since the first report of transition metal complexes containing a molecular hydrogen (η^2-H_2) ligand,[1] the number of η^2-H_2 complexes has rapidly increased.[2,3] The compounds having the formula $[MH(H_2)(P)_4]X$ (M = Fe, Ru, Os; $(P)_4$ = two diphosphines or a tetraphosphine) are one of the representatives of the η^2-H_2 complexes.[4-8] We previously reported that the Ru(II)-(η^2-H_2) complexes $[RuH(\eta^2\text{-}H_2)(P\text{-}P)_2]^+$ (**1a**-**d**) are readily prepared by introducing H_2 gas into solutions of formally five-coordinate complexes $[RuH(P\text{-}P)_2]^+$ (**2a**-**d**), (**a**, P-P = 1,2-bis(diphenylphosphino)ethane (dppe); **b**, 1,3-bis(diphenylphosphino)propane (dppp); **c**, 1,4-bis(diphenylphosphino)butane (dppb); **d**, 2,2'-bis(diphenylphosphino)-1,1'-binaphthyl (binap); Scheme 1).[7,8]



Scheme 1.

The structures of **1a**, **b**, and **d** were unambiguously determined to be *trans* on the basis of ^{1}H-NMR data.[4a,7,8] In contrast, it was found difficult to assign definitely the structure of **1c** even at lower temperatures because of the conformational flexibility of seven-membered dppb chelate.[8] With a view to obtain further informations on the structure and fluxional behaviors of η^2-H_2 complexes of the type **1**, we employed (*R,R*)-4,5-bis(diphenylphosphinomethyl)-2,2-dimethyl-1,3-dioxolane (diop), a representative chiral seven-membered diphosphine, as a ligand. As a diop chelate has the substituents making up the 1,3-dioxolane part, its flexibility should be considerably reduced in comparison with that of dppb. We



(***R,R***)-diop

describe here that $[RuH(\eta^2\text{-}H_2)(diop)_2]^+$ (**1e**) shows a rapid hydrogen exchange between dihydrogen and terminal hydride at higher temperatures in a similar manner as **1c**, and, further, it substantiates the first example indicating the coexistence of two distinguishable isomers, *trans* and *cis*, in solution at lower temperatures.

The formally five-coordinate complex $[RuH(diop)_2]PF_6$ was prepared according to a general procedure for obtaining PF_6 salts of **2a-d**.[7,8,10] Thus, a reaction of diop (2 equiv.) with $[RuH(NH_2NMe_2)_3(cod)]PF_6$[11] (cod = 1,5-cyclooctadiene) in ethanol at room temperature, followed by usual purification process, afforded the desired complex.[12] The introduction of H_2 gas to a dichloromethane solution of **2e** resulted in a spontaneous color change from brown to pale yellow. This suggests the incorporation of H_2 to the vacant site of **2e** to give the dihydrogen complex **1e** (Scheme 1). However, several attempts to isolate **1e** as the crystalline product (PF_6 salt) were unsuccessful because of difficulties in crystallization.

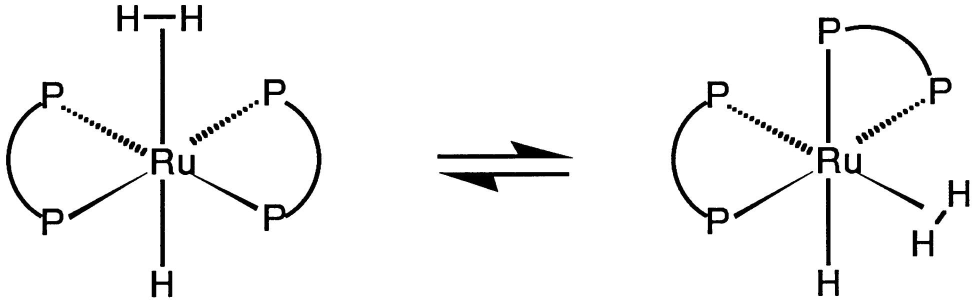
For some $[MH(H_2)(P)_4]^+$ complexes, a fluxional process due to the facile hydrogen exchange between terminal hydride (M-H) and dihydrogen ($M\text{-}(\eta^2\text{-}H_2)$) was evidenced by ^1H NMR measurements.[4-6,9] The spectra revealed the coalescence of M-H and $M\text{-}H_2$ resonances at higher temperatures. We observed that for **1a-d** the facility of such hydrogen exchange depends significantly on the ring size and flexibility of diphosphine chelates.[7,8] It was found that the NMR properties of **1e** at 303 K resemble those of **1c** obtained under the same conditions.[8] Thus the ^1H-NMR spectrum of **1e** showed a very broad signal ($w_{1/2}$ = 170 Hz) at δ -7.4 in the hydride region at 303 K (Fig.1), while the parent five-coordinate complex **2e** exhibited a broad singlet at δ -9.1 under argon at the same temperature. The broad signal of **1e**, like that of **1c**, gave a short T_1 time (31 ms) at this temperature. This sustains that **1e** as well as **1c** is highly fluxional so that the $\eta^2\text{-}H_2$ ligand undergoes a rapid exchange with the terminal hydride under these conditions. It has been established that such short T_1 values are diagnostic to the presence of a $\eta^2\text{-}H_2$ ligand.[13]

On decreasing the temperature, several $\eta^2\text{-}H_2$ complexes, which showed a coalesced hydrogen signal at higher temperatures, turned to exhibit two resonances corresponding to dihydrogen and terminal hydride as distinguishable signals.[4a,b,5,6,9] As for the diop complex **1e**, a trend of decoalecsence of the broad signal could be detected even at 273 K, where the dominant signal shifted to higher field (δ = -8.1) and a bump centered at -3.3 ppm emerged. A full splitting into *three* resonances was recognized at 183-243 K as shown in Fig. 1. The variable temperature NMR data of **1e** are summarized in Table 1. The resonances at δ -3.2 and -8.5 with the intensity ratio of 2:1 can be ascribed respectively to $Ru\text{-}(H_2)$ and Ru-H for one of two $[RuH(H_2)(diop)_2]^+$ species, which will be referred tentatively as (**A**). For (**A**) the hydrogen exchange freezes out partly at 243 K and

Table 1. ^1H and ^{31}P NMR spectral data of $[RuH(\eta^2\text{-}H_2)(diop)_2]^+$ (**1e**)

T/K	^1H NMR (400 MHz)[a]	^{31}P NMR (162 MHz)[b]
303	-7.4 (br)	ca. 32[c]
273	-8.1 (br), ca. -3.3[d]	10.7 (br), 32.4 (br), 34.2 (br), ca 41[e]
243	-8.4 (br), -8.1 (br s), -3.1 (br)	8.1 (br), 10.7 (m)[f], 32.6 (br), 34.0 (m)[f], 41.3 (br)
213	-8.5 (sep)[g], -8.1 (br s), -3.2 (br)	7.6 (s), 10.7 (t)[h], 32.5 (br), 33.9 (t)[h], ca 41 (br)
183	-8.6 (sep)[i], -8.1 (br), -3.2 (br)	7.4(br), 11.0(m), 33.6 (m)[j]

a) Obtained in CD_2Cl_2. b) Obtained in CH_2Cl_2. c) Very broad. d) Very broad. e) Very broad. f) An incomplete splitting into a triplet was observed. g) $^2J(H,P)$ = 13 Hz, 26 Hz. h) $^2J(P,P)$ = 33 Hz. i) $^2J(H,P)$ = 14 Hz, 27 Hz. j) A shoulder was observed at ca. δ 32.



(A); ***trans*** **(B)**; ***cis***

Scheme 2.

entirely at 213 K. Thus both resonances were fairly broad at 243 K, demonstrating that a slow exchange between Ru-H and Ru-H_2 is still taking place. The Ru-H signal at δ -8.5 turned into a septet due to the couplings with P atoms ($^2J(H,P)$ = 13-14 and 26-27 Hz) below 213 K. This shows that the dihydrogen-hydride exchange has frozen out at lower temperatures, although the η^2-H_2 signal at δ -3.2 remains broad. In accord with the above assignments, the T_1 value of the septet was considerably large (199 ms) at 213 K, while that of the broad signal at δ -3.2 was much shorter (< 10 ms). It was found, further, that the ^{31}P NMR spectrum of **1e** at 213-243 K shows a pair of triplets at δ 10.7 and 33.9 ($^2J(P,P)$ = 33 Hz), a characteristic pattern for a six-coordinate bis(diphosphine) complexes taking the *trans* configuration. All these NMR features coincide with that (**A**) adopts the rigid *trans* configuration at lower temperatures.

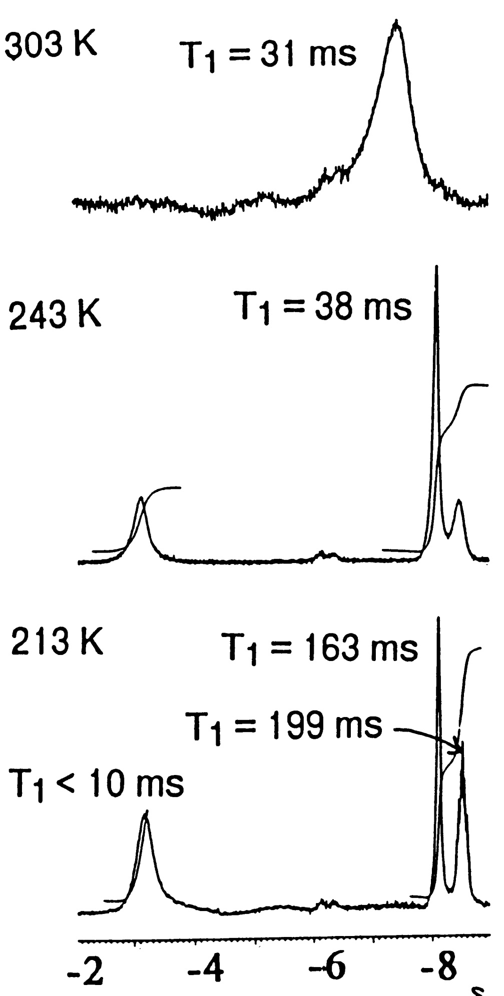


Fig. 1. Variable temperature ^1H NMR spectra of [RuH(η^2-H_2)(diop)$_2$]$^+$ (**1e**) in CD_2Cl_2.

It should be noted that the lower temperature ^1H NMR spectra of **1e** exhibit an unexpected broad singlet as the third signal at δ -8.1 in addition to the resonances for the *trans* isomer (see Fig. 1). Such an extra signal has never been detected for previously reported η^2-H_2 complexes of the type [MH(η^2-H_2)(L)$_4$]$^{n+}$.[4-9] Interesting is that the relative intensities of this signal and those of the *trans* form are temperature dependent. The signals of the *trans* isomer became more intense as the temperature lowered at the expense of the third signal, so that the latter almost disappeared at 183 K. This suggests the existence of the other [RuH(H_2)(diop)$_2$]$^+$ species (**B**), being in equilibrium with the *trans* isomer (**A**).

The most plausible structure for (**B**) should be the *cis* form as indicated in Scheme 2, because ^{31}P spectra at 183-243 K exhibited three resonances (δ 8, 32, 41) assignable to (**B**). Furthermore, the T_1 value for the proton signal at δ -8.1 was found considerably short (38 ms) at 243 K, diagnostic to complexes containing η^2-H_2 ligand. These NMR features are consistent with that (**B**) takes the *cis* configuration in which the

Ru-H_2 undergoes a rapid exchange with Ru-H. There has been no report describing the coexistence of *trans* and *cis* isomers for $[MH(H_2)(L)_4]^{n+}$ complexes.

The validity of the equilibrium between the *trans* and *cis* forms was supported by the saturation transfer technique applied to ^1H NMR of **1e** at 243 K. The irradiation of the η^2-H_2 resonance of the *trans* isomer at δ -3.1 resulted in marked decreases in the intensity of not only the signal at δ -8.4 (Ru-H of the *trans* form) but also the resonance at δ -8.1 of the *cis* form. Alternatively, the irradiation of the signal at δ -8.1 effected a complete disappearance of the signals of the *trans* form. These observations demonstrate that the *trans* and *cis* isomers are in equilibrium and interchanging with each other at a considerable rate under these conditions. At 213 K, however, such saturation transfer did not occur any more, probably due to that the interconversion rate should be significantly reduced at this temperature. In conclusion, it was demonstrated that the diop complex **1e** provides a rare example of $[MH(\eta^2\text{-}H_2)(P)_4]^+$ complexes which can produce an equilibrated mixture of the *trans* and *cis* isomers.

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