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Ruthenium Hydride Complex with 1,1'-Bis(diphenylphosphino)ferrocene (dppf). Characterization and Molecular Structure of $[RuH_3(dppf)_2]PF_6$

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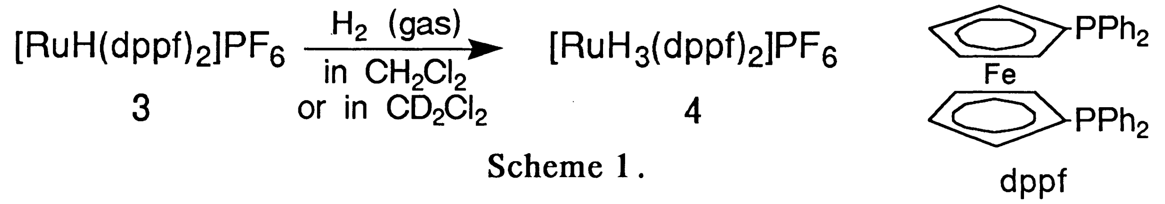
The ruthenium trihydride complex $[RuH_3(dppf)_2]PF_6$ (dppf = 1,1'-bis(diphenylphosphino)ferrocene) was prepared by contacting $[RuH(dppf)_2]PF_6$ with H_2 gas, and its molecular structure was determined by the X-ray crystallography. The four phosphorus atoms were found to adopt a distorted tetrahedral arrangement around the Ru atom. The ^1H and ^{31}P NMR characteristics suggested that the above dppf complex is regarded as a Ru(IV) trihydride complex in the range 243-303 K.

We have recently reported that the five-coordinate complexes $[RuH(P\text{-}P)_2]PF_6$ (**1**) is readily converted into the corresponding molecular hydrogen complexes $[RuH(\eta^2\text{-}H_2)(P\text{-}P)_2]PF_6$ (**2**) (P-P = diphosphine) upon contacted with H_2 gas and that the dynamic properties of **2** in solution depend significantly on the coordinating diphosphine.1-3) Thus, the size and flexibility of diphosphines affected the exchange rates of Ru-(η^2-H_2) with Ru-H for a series of **2** (P-P = 1,2-bis(diphenylphosphino)ethane (dppe), **a**; 1,3-bis(diphenylphosphino)propane (dppp), **b**; 1,4-bis(diphenylphosphino)butane (dppb), **c**; (*R*)- or (*S*)-2,2'-bis(diphenylphosphino)-1,1'-binaphthyl (binap), **d**).1,2) It was found further that the diop complex (**2e**, P-P = (*R,R*)-4,5-bis(diphenylphosphinomethyl)-2,2-dimethyl-1,3-dioxolane; diop) gave rise to the two possible isomers (*trans* and *cis*) in solution at low temperature, while the others such as **2a**, **b**, and **d** took solely the *trans* structure under similar conditions.3) This implies that the solution structure of **2** may be controlled by the diphosphine used.

Recent X-ray crystallographic studies on metal complexes of 1,1'-bis(diphenylphosphino)ferrocene (dppf) demonstrated that the bulkiness of the ligand resulted the expansion of P-M-P bond angles within dppf chelate rings.4-6) These characteristics of dppf complexes prompted us to examine the structure and properties of the ruthenium dppf complex analogous to **2**. We expected that the structure deformations in such Ru complex due to the ligand bulkiness should cause notable changes in its dynamic properties.

The formally five-coordinate complex $[RuH(dppf)_2]PF_6$ (**3**) was obtained as an orange yellow powder in a



Scheme 1.

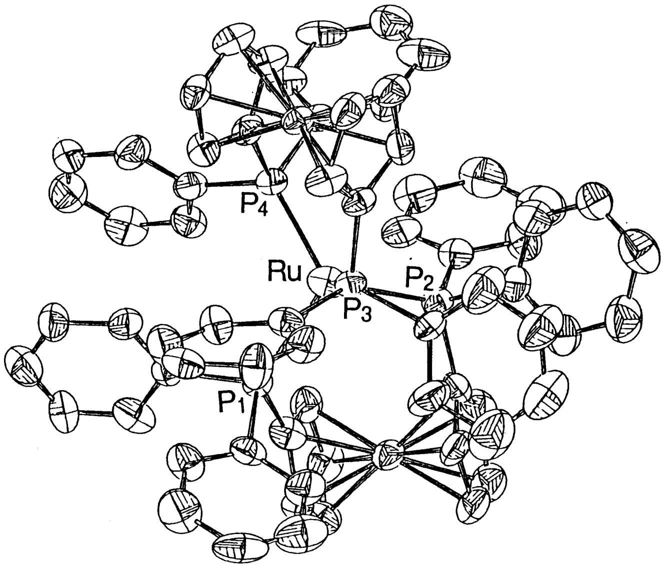


Fig. 1. A perspective view of $[RuH_3(dppf)_2]^+$ ion.

Bond lengths (Å)

Ru-P_1	2.429 (6)	Ru-P_2	2.392 (7)
Ru-P_3	2.428 (7)	Ru-P_4	2.325 (7)

Bond angles (°)

P_1-Ru-P_2	106.0 (2)
P_3-Ru-P_4	106.9 (2)
P_1-Ru-P_3	106.0 (2)
P_1-Ru-P_4	114.1 (2)
P_2-Ru-P_3	105.0 (2)
P_2-Ru-P_4	117.9 (2)

usual manner.[1-3] The novel orange Ru complex having the formula $[RuH_3(dppf)_2]PF_6$ (**4**) was prepared by introducing H_2 gas into a CH_2Cl_2 solution of **3**, followed by the addition of hexane (Scheme 1). Since **4** showed NMR features markedly different from those for η^2-H_2 complexes **2a-e** as will be described later, the structure determination of **4** by the X-ray crystallographic method was undertaken. Although the structure analysis is still at an insufficient stage (R = 0.162) partly due to the disorder of fluorine atoms in PF_6^- anion, the outline of the molecular structure of $[RuH_3(dppf)_2]^+$ ion has been obtained.[7] A perspective view of the complex ion is given in Fig. 1, along with the representative bond lengths and angles.

It is obvious that $[RuH_3(dppf)_2]^+$ ion no longer adopts the ordinary octahedral geometry. The four P atoms of two dppf ligands are arrayed in a slightly distorted tetrahedron around the Ru center. The bond angles P_1-Ru-P_2 and P_3-Ru-P_4, both involved in the dppf chelates, are found to be 106 and 107°, respectively. These values are the largest of the P-M-P angles determined so far for several dppf complexes by the crystallographic method.[4-6] Further, other P-Ru-P angles in **4** such as P_1-Ru-P_3 and P_2-Ru-P_3, in which the P atoms do not belong to the same chelate, take likewise values in the range of 105-118°; the small deviations from 109.5° for all of P-Ru-P angles lead to the distorted tetrahedral arrangement of four P atoms as mentioned above. In contrast, the Ru-P distances in **4**, ranging 2.33-2.43 Å, are regarded normal for M-P bonds in transition metal complexes involving dppf (2.20-2.55 Å[4-6]), and fall within the range of observed Ru-P distances in Ru complexes containing less strained diphosphines.[8]

It should be noted that the structure in Fig. 1 is far different from the *trans* geometry expected for most dihydrogen complexes of the type **2**.[1-3] Although the coordinates of hydrogens bound to the Ru atom have not been specified in the present study, we assume that the space surrounded by P_1, P_2, and P_4 is the most probable one for the hydrogen coordination in this structure. It is difficult, however, to find any other site appropriate for the hydrogen coordination. This implies that three hydrogen ligands in **4** may locate adjacent to one another like those in a *cis* (H/H_2) isomer.

Further informations on the characteristics of coordinating hydrogens in complex **4** were provided by variable temperature ^1H and ^{31}P NMR spectral measurements. The spectral date are summarized in Table 1.

Table 1. ^{1}H and ^{31}P NMR spectral data of $[RuH_3(dppf)_2]PF_6$ (**4**)

T/K	^{1}H NMR (400 MHz)	T_1/ms	^{31}P NMR (162 MHz)
303	-7.89 (qui)$^{a)}$	356	38.2 (br)
273	-7.9 (br s)		ca 35 (br)$^{b)}$
243	-7.9 (br)	227	29.6 (br), 71.4 (br)
213	-7.9 (br)		ca 22$^{c)}$, 24.3 (br), 28.2 (br), 31.2 (br), ca 35$^{d)}$, 69$^{d)}$, 71.2 (br)
183	-8.3 (br m)	240	21.1 (br), 23.1 (br), 24.1 (br), 27.8 (br),
	-7.8 (br)	208	30.9 (br), 36.3 (br), 68.6 (br), 71.3 (br)

a) $^2J(H,P) = 10$ Hz. b) Very broad. c) Very broad. d) Very broad.

It is interesting that the ^{1}H NMR spectrum of **4** at 303 K shows only one quintet ($^2J(H,P) = 10$ Hz) for the signal assignable to the hydrogens bound to the Ru center and that this has a remarkably large T_1 time (356 ms), diagnostic to terminal hydrides rather than a η^2-H_2 ligand.$^{9)}$ Further, the $^{31}P\{^1H\}$ NMR spectrum gave one broad singlet under the same conditions. These NMR characteristics indicate that **4** is highly fluxional so that four P atoms of two dppf ligands and three hydrides become, respectively, magnetically indistinguishable from one another and that **4** can be regarded as a Ru(IV) trihydride species $[RuH_3(dppf)_2]PF_6$ as shown in Scheme 1, presenting the first case where a Ru complex produced by the contact of a five-coordinate $[RuH(P\text{-}P)_2]PF_6$ with H_2 is assigned as a Ru(IV) trihydride. This is in sharp contrast to that the complexes **2a-e**, derived from **1a-e** respectively, were thoroughly the Ru(II)-(η^2-H_2) species.

A similar quintet ($^2J(H,P) = 12$ Hz) was observed in the ^{1}H NMR spectrum of $[OsH(H_2)(\textit{rac}\text{-tetraphos-1})]BF_4$ (**5**; *rac*-tetraphos-1 = *rac*-1,1,4,7,10,10-hexaphenyl-1,4,7,10-tetraphosphadecane).$^{10)}$ For **5** the tetraphosphine ligand, which adopts exclusively *cis*-α configuration upon coordination, forces the hydridic ligands occupy the adjacent two coordination sites around Os center so that an extremely rapid intramolecular hydrogen exchange takes place. Since the minimum T_1 value of the hydridic resonances obtained at 252 K was fairly large (160 ms), it was suggested that the structure of **5** must be close to that of a seven coordinate trihydride, although some degree of H-H bonding is possibly present.$^{10)}$

A series of complexes $Cp^*RuH_3(PR_3)$ (**6**; Cp* = pentamethylcyclopentadienyl anion) provides a well-defined Ru(IV) trihydride species in which three hydride ligands locate adjacent one another in the solid state.$^{11)}$ ^{1}H NMR spectra of **6** simply showed a doublet ($^2J(H,P) = 20$-22.5 Hz) for the hydride resonances at room temperature, indicating the highly fluxional properties of the complexes. The T_1 values of the hydride signal for **6** were found sufficiently large at room temperature (190 and 622 ms, respectively, for $PR_3 = PCy_3$ and $P(i\text{-}Pr)_3$),$^{12)}$ and made it possible to regard the complexes to be Ru(IV) trihydrides in solutions as well. Thus, it is apparent that the above-mentioned ^{1}H NMR features for the hydridic signals of **5** and **6**, *i.e.* (i) the high fluxionality, (ii) the clear coupling with P atoms, and (iii) T_1 time larger than 100 ms, are similar to those of **4** at 303 K. So we feasibly recognized complex **4** in solution at 303 K to be a Ru(IV) trihydride species as described previously.

As the temperature lowered, the coupling between the P atoms and hydrides in complex **4** disappeared. The quintet at δ -7.89 turned into a single broad peak below 273 K, and at 183 K the resonances finally split into two broad signals centered at δ -8.3 and -7.8 (see Table 1). The former is smaller than the latter, the intensity ratio being approximately 2:1. Of interest is that the ^{31}P NMR spectrum of **4** at 183 K displayed eight signals which can be classified to two sets of four resonances, {δ 24.1, 27.8, 30.9, 71.3} and {δ 21.1, 23.1, 36.3, 68.6}, the former being more intense than the latter. The intensities of four signals for each set are practically equal to one another.

The observations of two peaks for the hydride resonances and these two sets in the ^{31}P spectrum strongly suggest the presence of two stereoisomers for **4** at low temperature. Further, the clear differences in the chemical shift of four phosphorous resonances are consistent with that each isomer involves such structural distortions as those found in the crystalline state (Fig.1), although the origin of the isomerism is still uncertain. Whatever the exact structures of these isomers are, the hydrogen ligands seem to maintain the terminal hydride character, because the T_1 values of the hydridic resonances are larger than 200 ms even at 183 K (Table 1).

It is clarified, therefore, that dppf, a diphosphine having an extremely large bite angle in its chelate, causes significant deviations from octahedral geometry and changes in the properties of hydridic ligands for complex **4**. The variable temperature ^{1}H and ^{31}P NMR features indicates that **4** is characterized as a trihydride through the range 183-303 K.

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7) Crystal data for [$RuH_3(dppf)_2]PF_6$: M = 1357.9, triclinic, $P\bar{1}$, a = 14.909(2), b = 20.347(3), c = 11.201(1) Å, α = 89.46(1), β = 98.104(9), γ = 96.75(1)°, Z = 2, Dc = 1.35 g cm^{-3}, μ(Mo Kα) = 8.35 cm^{-1}, R = 0.162 for 7669 independent reflections with $|Fo| > 3\sigma(|Fo|)$ ($2 \le 2\theta < 50°$).
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