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HOMOGENEOUS HYDROGENATION WITH NEW CATIONIC RUTHENIUM(II) COMPLEXES OF [RuH(CO)(NCCH₃)(PPh₃)₂(diphos)]⁺ AND [RuH(CO)(NCCH₃)(PPh₃)(diphos)]⁺. CRYSTAL STRUCTURE OF [RuH(CO)(NCCH₃)(PPh₃) (Fe(η^{5} -C₅H₄PPh₂)₂)][BF₄]

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Abstract—A series of ruthenium(II) complexes [RuH(CO)(NCCH₃)(PPh₃)₂(diphos)][BF₄] (diphos := dppm, Ph₂PCH₂PPh₂ (**2**); dppe = Ph₂PCH₂CH₂PPh₂ (**3**); = dppp, Ph₂PCH₂ CH₂CH₂PPh₂ (**4**); = dppb, Ph₂PCH₂CH₂CH₂CH₂PPh₂ (**5**)) and [RuH(CO)(NCCH₃) (PPh₃)(diphos)][BF₄] (diphos := dppe (**6**); = dppp (**7**); = dppb (**8**); = dppf, Fe(η^{5} -C₅H₄PPh₂)₂ (**9**)) was prepared from the reaction of [RuH(CO)(NCCH₃)₂(PPh₃)₂][BF₄] and diphos ligands by changing the reaction conditions. These complexes have been characterized by analytical and spectroscopic (IR and ¹H NMR) methods. The structure of [RuH(CO)(NCCH₃)(PPh₃)(dppf)][BF₄] (**9**) has been determined by X-ray crystallography. The homogeneous hydrogenations of propanal to propan-1-ol catalyzed by complexes **2**-**9** have been investigated at 90°C and 20 atm hydrogen pressure. The catalytic activities of the chelating diphosphine species **6**-**9** were dependent upon the structure of the complex as well as upon the ring sizes of the chelates. Copyright © 1996 Elsevier Science Ltd

Several different types of Ru^{II} complexes such as $RuCl_2(PPh_3)_3$, $^1RuCl_2(CO)_2(PPh_3)_2$, $^2RuH_2(PPh_3)_4$ and $RuHCl(CO)(PPh_3)_3$, have attracted much attention because of their applications as catalysts in the homogeneous hydrogenation of aldehydes and ketones. Among the above compounds, the carbonyl-hydride-phosphine Ru^{II} complex, $RuHCl(CO)(PPh_3)_3$, is especially useful due to its convenience for preparation, 5 stability in air and facility for further substitution reactions. This com-

plex has also been an efficient catalyst for the reduction of numerous aldehydes and ketones to their corresponding alcohols.^{3,4,6}

Our previous report demonstrated that some chelate diphosphine complexes, [RuHCl(CO) (PPh₃)(L—L)] (L—L = Ph₂PCH₂CH₂PPh₂, dppe; Ph₂PCH₂CH₂CH₂CH₂PPh₂ dppb), have better catalytic activities with larger chelate ring sizes⁷ and also the catalytic reaction rate increased when phosphine ligands were used rather than arsine analogues.⁸ Depending on the synthetic reaction conditions, the diphosphine ligands coordinate monodentately or bidentately. In order to find out

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the difference in the catalytic activity between monodentate and bidentated diphosphine complex derivatives, a series of bidentate diphosphine complexes having different chelate ring size have been prepared since their chelate ring size affects the catalytic activities of the complexes.

[RuH(CO)(NCMe)₂(PPh₃)₂]⁺ (1) was initially prepared by Sanchez-Delgado *et al.* from RuHCl(CO)(PPh₃)₃ and was used in the hydroformylation reaction.⁹ The labile acetonitrile ligand facilitates the substitution reactions with Lewis bases involving the diphosphine ligands to form the corresponding monodentate complex, [RuH(CO)(NCCH₃)(PPh₃)₂(diphos)]⁺, at room temperature. However, in a boiling condition, a PPh₃ ligand rather than the other acetonitrile ligand is also substituted to form the bidentate complex, [RuH(CO)(NCCH₃)(PPh₃)(diphos)]⁺.

In this paper, the synthesis of these two types of cationic complexes is described along with comparison of the catalytic activities of the complexes.

EXPERIMENTAL

General procedures

All solvents were dried and distilled under nitrogen by conventional procedures. $RuCl_3 \cdot 3H_2O$, PPh₃, dppm, dppe, dppp, dppb, dppf and NaBF₄ were purchased from Aldrich and used as received. All other chemicals were used as commercial reagents grade. For the syntheses of 1–9, the starting complex RuHCl(CO)(PPh₃)₃ was prepared according to the literature method.⁵

Instruments

IR spectra were recorded on an Analect FT-6160 FT-IR spectrometer using KBr discs. ¹H NMR spectra were taken with a 300 MHz Varian Gemini-300 NMR spectrometer. Elemental analyses were performed by Micro-Tech Analytical Laboratories, Skokie, Illinois, U.S.A. and Korea Institute of Science and Technology, Seoul, Korea. Hydrogenation reactions were carried out by Parr Series 4560 bench-top mini reactors (100 cm³) connected to a Parr 4842 controller. A Hewlett Packard 5890 Series II gas chromatograph equipped with HP-5 capillary column (cross-linked 5% phenyl methyl silicone phase; $25 \text{ m} \times 0.2 \text{ mm} \times 0.11 \mu \text{m}$ film thickness and HP 3394A integrator was used for the quantitative analysis of the hydrogenation reaction products.

Preparation of [RuH(CO)(NCCH₃)₂(PPh₃)₂][BF₄], (1)

Complex 1 was prepared by the known method.⁹

Preparation of [RuH(CO)(NCCH₃)(PPh₃)₂ (dppm)][BF₄], (**2**)

0.185 g (0.02 mmol) of 1 and 0.085 g (0.22 mmol) of dppm were dissolved in 30 cm³ of dichloromethane and stirred vigorously at room temperature under N₂ for 1 h. The pale yellow solution was filtered and concentrated under reduced pressure to *ca* one-third of its original volume. Addition of n-pentane yielded a white solid, which was filtered in air, washed with freshly distilled n-pentane (30 cm³) and dried *in vacuo* (yield : 0.156 g 67%). Found : C, 65.9; H, 4.9; N, 1.2 Calc. for C₆₄H₅₆NBF₄OP₄Ru : C, 65.8; H, 4.8; N, 1.2%. IR (KBr disc, cm⁻¹): 1950 (vs), 1481 (m), 1436 (s), 1309 (w), 1188 (w), 1066 (vs), 1042 (s), 1001 (w). 806 (w), 747 (s), 696 (vs), 596 (w), 519 (vs).

Preparation of [RuH(CO)(NCCH₃)(PPh₃)₂ (dppe)][BF₄], (**3**)

This complex was prepared according to the method described by Sanchez-Delgado *et al.*⁹ **3** was obtained with 0.200 g (0.22 mmol) of **1** and 0.100 g (0.25 mmol) of dppe (white solid, yield: 0.195 g, 75%) in the same way as the preparation of **2**. Found: C, 65.9; H, 5.0; N, 1.1 Calc. for $C_{65}H_{58}NBF_4OP_4Ru: C, 66.0: H, 4.9: N, 1.2\%$. IR (KBr disc, cm⁻¹): 1952 (vs), 1481 (m), 1433 (s), 1309 (w), 1186 (w), 1161 (w), 1066 (vs), 1059 (s), 999 (w), 804 (w), 747 (s), 696 (vs), 596 (w), 580 (w), 519 (vs).

Preparation of [RuH(CO)(NCCH₃)(PPh₃)₂ (dppp)][BF₄], (4)

4 was prepared by the same method as that used for 2 using 1 (0.185 g, 0.20 mmol) and dppp (0.091 g, 0.22 mmol) in place of dppm (white solid, yield : 0.201 g, 84%). Found : C, 66.0; H, 5.0; N, 1.80. Calc. for C₆₆H₆₀NBF₄OP₄Ru : C, 66.3; H, 5.1; N, 1.2%. IR (KBr disc, cm⁻¹) : 1946 (vs), 1479 (m), 1431 (s), 1308 (w), 1184 (w), 1157 (w), 1066 (vs), 1057 (vs), 999 (w), 800 (w), 749 (s), 696 (vs), 580 (w), 519 (vs).

Preparation of [RuH(CO)(NCCH₃)(PPh₃)₂ (dppb)][BF₄], (5)

5 was prepared by the same method as that used for 2 using 1 (0.222 g, 0.24 mmol) and dppb (0.107 g,

	'H NMR (SiMe₄)"			IR $(cm^{-1})^{h}$	
Complex	δ_{Ru-H} (ppm)	${}^{2}J_{\rm HP}$ (Hz)	v(CO)	v(Ru - P)	v(B —F)
2	-8.0(dtd)	92, 23, 4 ^c	1950	519	1063
3 ^d	-8.1(dt)	91, 23	1952	519	1059
4 ″	-8.1(dt)	89, 23	1956	519	1057
	-8.2(dt)	90, 24			
5"	-8.1(dt)	88, 23	1950	519	1059
	-8.3(dt)	89, 24			
6 °	-6.5(ddd)	92, 19, 15	1960	521	1063
	-13.7(quart)	18			
7	-6.9(ddd)	89, 22, 17	1956	515	1061
8	-7.6(dt)	88, 21	1942	518	1057
9	-8.3(ddd)	93, 27, 21	1952	519	1060

Table 1. ¹H NMR and IR data

"In CDCl₃.

^h In KBr disk.

 $^{c4}J_{\rm H-P}$ (Hz).

 d1 H NMR data are consistent with Sanchez-Delgado's values.⁹

^e Those complexes with structural isomers.

0.25 mmol) in place of dppm (white solid, yield: 0.235 g, 81%). Found; C, 66.3; H, 5.1; N, 1.1 Calc. for $O_{67}H_{62}NBF_4OP_4Ru$: C, 66.6; H, 5.1; N, 1.2%. IR (KBr disc, cm⁻¹): 1950 (vs), 1822 (w), 1586 (w), 1481 (m), 1435 (s), 1388 (s), 1310 (w), 1186 (w), 1059 (vs), 806 (w), 749 (s), 696 (vs), 560 (m), 519 (vs).

Preparation of [RuH(CO)(NCCH₃)(PPh₃) (dppe)][BF₄], (**6**)

0.222 g (0.24 mmol) of **1** and 0.010 g (0.25 mmol) of dppe were dissolved in 30 cm³ of toluene and refluxed under nitrogen stream for *ca* 4 h. The colorless solution was cooled to room temperature and filtered in air to remove crystalline impurities. The solution was concentrated under reduced pressure to *ca* one-fourth of its original volume. Addition of n-pentane yielded a white solid, which was washed with freshly distilled n-pentane and dried *in vacuo* (yield: 0.174 g, 79%). Found : C, 61.4; H, 4.6; N, 1.6. Calc. for C₄₇H₄₃NBF₄OP₃Ru: C, 61.4; H, 4.6; N, 1.5%. IR (KBr disc, cm⁻¹) : 1957 (vs), 1481 (m), 1435 (s), 1312 (w), 1186 (w), 1084 (vs), 1062 (vs), 999 (w). 872 (w), 816 (w), 784 (m), 696 (vs), 521 (vs).

Preparation of [RuH(CO)(NCCH₃)(PPh₃) (dppp)][BF₄], (7)

7 was prepared by the same method as that used for **6** using **1** (0.185 g, 0.20 mmol) and dppp (0.091 g, 0.222 mmol) in place of dppe (white solid, yield : 0.114 g, 61%). Found: C, 62.0; H, 4.8; N, 1.6. Calc. for $C_{48}H_{45}NBF_4OP_3Ru$: C, 61.7; H, 4.9; N, 1.5%. IR (KBr disc, cm⁻¹): 1956 (vs), 1481 (m), 1436 (s), 1310 (w), 1279 (w), 1186 (w), 1159 (w), 1086 (vs), 1061 (vs), 999 (w), 972 (w), 922 (w), 835 (w), 793 (w), 749 (m), 698 (vs), 656 (w), 596 (w), 577 (w), 515 (s).

Preparation of [RuH(CO)(NCCH₃)(PPh₃) (dppb)][BF₄], (8)

0.222 g (0.24 mmol) of 1 and 0.107 g (0.25 mmol) of dppb was dissolved in 30 cm³ of toluene and refluxed for 5 h. After the solution was cooled to room temperature, the insoluble white solid was filtered out and washed with n-pentane (yield : 0.155 g, 68%). Found : C, 62.1 ; H, 4.8 ; N, 1.3. Calc. for $C_{49}H_{47}NBF_4OP_3Ru : C, 62.2 ; H, 5.0 ; N, 1.5\%$. IR (KBr disc, cm⁻¹) : 1942 (vs), 1481 (m), 1435 (s), 1158 (w), 1957 (vs), 752 (s), 698 (vs), 519 (s).

Preparation of [RuH(CO)(NCCH₃)(PPh₃) (dppf)][BF₄], (9)

9 was prepared by the same method as that used for **8** using **1** (0.185 g, 0.20 mmol) and dppf (0.139 g, 0.25 mmol) in place of dppb. The reddish yellow solution was recrystallized with n-pentane and the yellow solid was obtained (yield: 0.137 g, 64%). Found: C, 61.0; H, 4.6; N, 1.2. Calc. for $C_{55}H_{47}NBF_4FeOP_3Ru: C, 61.4; H, 4.4; N, 1.3\%$. IR (KBr disc, cm⁻¹): 1952 (vs), 1481 (m), 1435 (s). 1190 (w), 1183 (w), 1086 (vs), 1061 (vs), 1001 (w), 820 (w), 748 (m), 698 (vs), 519 (vs).

X-ray crystal structure determination for **9** · C₂H₅OH

Complex 9 was dissolved in ethanol and the corresponding supersaturated solution was made by heating. Pale reddish yellow single crystals of $9 \cdot C_2H_5OH$ were obtained by gradually cooling the supersaturated solution.

A crystal $(0.4 \times 0.3 \times 0.2 \text{ mm})$ sealed in Lindemann capillary tube was mounted on Enraf-Nonius CAD4 diffractometer. X-ray data were collected using Mo- K_{α} radiation at room temperature. Cell parameters and orientation matrix for data collection were obtained from least squares refinement, using the setting angles of 25 reflections. The intensities of 3 standard reflections, recorded every 3 h of X-ray exposure, showed no systematic changes. Crystal and refinement data are noted in Table 2. The intensity data were corrected for Lorentz and polarization effects. Empirical absorption corrections were also applied (DIFABS). The structure was solved by a combination of Patterson and difference Fourier methods (SHELXS86).¹⁰ The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in the structure factor calculation in idealized positions ($d_{C-H} = 0.95$ Å) and were assigned an isotropic thermal parameter of 1.2 times that of attached atom. All the calculations except structure solution were carried with the Enraf-Nonius MolEN program package. Selected bond lengths and bond angles are given in Table 3.

Hydrogenation reaction of propanal

Compounds 2–9 and RuHCl(CO)(PPh₃)₃ were used as catalysts in the homogenous hydrogenation of propanal to propan-1-ol. The reactions were run routinely as follows: 2.0×10^{-2} mmol of catalyst,

Formula	$C_{55}H_{47}NOBF_4P_3FeRu \cdot C_2H_6O$
fw	1120.71
Space group	triclinic, P1 (No. 2)
<i>a</i> , Å	13.3312(19)
<i>b</i> , Å	14.565(3)
<i>c</i> , Å	14.706(2)
α, deg	83.757(14)
β , deg	77.483(13)
γ, deg	78.976(14)
V, Å ³	2729.4(8)
Ζ	2
temp, °C	23
d (calcd), g/cm ³	1.366
λ (Mo— K_{α}), Å	0.71073
Monochromator	graphite
Linear abs. coeff., cm^{-1}	6.77
Crystal size, mm	$0.40 \times 0.30 \times 0.20$
Scan mode	$\omega/2 heta$
ω -scan width, deg	$0.80 \pm 0.35 \tan \theta$
2θ limits, deg	46
No. of data collected	7948
No. of unique data	7564
No. of unique data with $I > 3\sigma(I)$	5029
No. of variables	611
R	0.070
R_{w}	0.081
G.O.F.	3.28

Table 2. Crystal and refinement data for $[RuH(CO) (NCCH_3)(PPh_3)(dppf)][BF_4] \cdot C_2H_5OH (9)$

^a $R = \Sigma ||F_o| - |F_o|| / \Sigma |F_o|.$

 ${}^{b} R_{w} = \Sigma \omega (|F_{o}| - |F_{c}|)^{2} / \Sigma \omega |F_{o}|^{2}]^{1/2}; \quad \omega = 4F_{o}^{2} / \sigma^{2}(F_{o}^{2}); \quad \sigma(F_{o}^{22}) = [\sigma^{2}(I) + (p \cdot F_{o}^{22})^{2}]^{1/2}, \quad p = 0.04.$

Ru—P(1)	2.506(3)	RuP(2)	2.367(3)	Ru—P(3)	2.381(3)
Ru—N	2.083(9)	Ru-C(1)	1.83(1)	FeC(16)	2.01(1)
FeC(17)	2.02(1)	FeC(18)	2.06(1)	Fe-C(19)	2.05(1)
Fe—C(20)	2.03(1)	Fe—C(21)	2.00(1)	Fe—C(22)	2.03(1)
Fe-C(23)	2.05(1)	Fe-C(24)	2.04(1)	Fe—C(25)	2.02(1)
P(1) - C(4)	1.85(1)	P(1) - C(10)	1.84(1)	P(1) - C(16)	1.84(1)
P(2) - C(21)	1.81(1)	P(2)—C(26)	1.86(1)	P(2) - C(32)	1.84(1)
P(3)—C(38)	1.84(1)	P(3)—C(44)	1.84(1)	P(3) - C(50)	1.84(1)
O—C(1)	1.15(1)	N—C(2)	1.14(2)	C(2)—C(3)	1.49(2)
C(16)-C(17)	1.41(2)	C(16)—C(20)	1.44(1)	C(17)—C(18)	1.42(2)
C(18)-C(19)	1.41(2)	C(19)-C(20)	1.42(2)	C(21)—C(22)	1.46(2)
C(21)C(25)	1.44(2)	C(22)—C(23)	1.45(1)	C(23) - C(24)	1.35(2)
C(24)—-C(25)	1.40(1)				
P(1) - Ru - P(2)	102.15(9)	P(1)Ru	ı—₽(3)	99.3(1)	
P(1)— Ru — N	87.7(3)	$P(1) - R\iota$	i −−C(1)	101.1(3)	
P(2) - Ru - P(3)	158.6(1)	P(2)— Ru	I-N	90.3(3)	
P(2)— Ru — $C(1)$	86.4(4)	$P(3) - R\iota$	ı—N	91.1(2)	
P(3) - Ru - C(1)	89.0(3)	N—Ru—	-C(1)	171.4(4)	
C(16)—Fe— $C(21)$	113.2(4)	Ru - P(1))—C(4)	114.4(3)	
Ru - P(1) - C(10)	121.9(4)	RuP(1))—C(16)	114.3(4)	
Ru - P(2) - C(21)	118.9(4)	Ru - P(2)	-C(26)	114.7(4)	
Ru - P(2) - C(32)	112.1(4)	Ru - P(3))—C(38)	114.0(4)	
Ru - P(3) - C(44)	114.5(4)	Ru - P(3)	-C(50)	117.2(3)	
Ru - N - C(2)	175.0(1)	RuC(1)—0	178.5(9)	
N-C(2)-C(3)	178.0(2)	Fe—C(10	(b) - P(1)	124.0(6)	
Fe-C(21)-P(2)	124.6(7)	x			

Table 3. Selected bond distances (Å) and bond angles (°) for $[RuH(CO)(NCCH_3)(PPh_3)(dppf)][BF_4] \cdot C_2H_5OH (9)^{a}$

"Numbers in parentheses are estimated standard deviations in the least significant digits.

20.0 mmol of substrate and ca 0.2 g of n-heptane (internal standard material) in 60 cm³ of toluene were introduced to the autoclave equipped with a gas (H₂) inlet valve and a sampling valve. The system was purged twice with nitrogen and then once with hydrogen at room temperature to remove air in the vessel, and was filled with hydrogen to ca 25 atm, which is 5 atm lower than the reaction pressure, 30 atm. At this time the reactor was heated rapidly to 100°C, the reaction temperature. As soon as the heating was completed, the hydrogen pressure was fitted to the exact reaction pressure and stirring was commenced. This point was regarded as zero time and sampling was performed intermittently using a needle attached to the sampling valve. The temperature and pressure were maintained constant throughout the reaction. The extracted sample was induced to an aluminum capped vial (2 cm³) and quenched at -20° C quickly to prevent further reaction. After 5 min the amount of the substrate and the product was determined

using a gas chromatograph equipped with an FID detector using the internal standard method.

RESULTS AND DISCUSSION

Syntheses and characterizations of the cationic monodentate diphosphine ruthenium(II) complexes

The structure of 1 is known by Sanchez-Delgado *et al.* as shown in Scheme 1. Both the *trans* effect¹¹ and *trans* influence¹² of the hydride played a major role in the substitution of the acetonitrile *trans* to the hydride with a diphosphine ligand. Since hydride has a rather strong *trans* effect and *trans* influence, the *trans*-positioned acetonitrile ligand can be readily labilized kinetically and thermodynamically.

At room temperature, the reaction of 1 and diphosphine ligands yielded the corresponding complexes 2, 3, 4 and 5. These diphosphine ligands substitute the *trans*-positioned nitrile mono-



dentately because of the strong *trans* effect of hydride. In general, ${}^{2}J(H - P_{trans})$ is 90–160 Hz and ${}^{2}J(H - P_{cis})$ is 10–30 Hz. These values are consistent with the ¹H NMR data in Table 1.¹³ From ¹H NMR spectra (**a**) and (**b**) type isomers are found to exist together in case of **4** and **5** in solution. IR spectra were not able to distinguish these two types of isomers, while only one conformation was expected to exist in the solid state since the split mode of carbonyl stretching frequency v(CO) could not be observed.

The integrated areas of the hydride peaks of both 4 and 5 show that the ratios of the quantity of isomers are 2:1 in 4 and 1:1 in 5. Since the π -accepting ligand like phosphine is located in the *trans* position to hydride in both cases, the hydride signals of both (a) and (b) have relatively lower frequency resulting from the deshielded *d*-electron circumstances, and the chemical shift difference observed in these isomers becomes very small (-8.1 and -8.2 ppm in 4; -8.1 and -8.3 ppm in 5). Therefore, it was impossible to assign chemical shift

data to those two isomers because of the similarity of the chemical environment on the hydride.

In the case of the complex 2, it is interestingly found that ${}^{4}J_{H--P}$ is 4 Hz. It is noted that the long range coupling occurs when there are more than one multiple bond between the atoms which couple to each other or when the two atoms are in the rigid W-shaped spatial structure.¹⁴ Complex 2 is like the former case now that the ruthenium *d* orbital electrons readily delocalize into the vacant *d* orbital of the phosphorus atom. However, the other complexes 3, 4 and 5, each of which has longer diphosphines than dppm, show no long range couplings.

Syntheses and characterizations of the cationic bidentate diphosphine ruthenium(II) complexes

Complexes 6, 7, 8 and 9 have been synthesized in a somewhat different way from monodentate diphosphine ruthenium(II) complexes. During the refluxing process, a triphenylphosphine ligand which is in a *cis* to hydride is dissociated to make



room for a diphosphine ligand to make a chelate ring as shown in Scheme 2.

From ¹H NMR spectroscopic analyses, only one conformation of the type (c) is shown to exist in all the complexes except for the case of complex 6, which has both (c) and (d) types of isomers in solution. Only in complex 6, one phosphine side of dppe coordinates to ruthenium in both *trans* and *cis* positions to hydride. These two types of isomers can simply be identified from the large difference in their chemical shifts, e.g. -6.5 ppm (*trans*) and -13.7 ppm (*cis*). As pointed out earlier, the π -accepting phosphine located *trans* to the hydride shows less high-field chemical shift. The quartet signal of 6(d) is due to all the three phosphines being in almost the same environment to hydride, and the coupling constant ${}^{2}J_{H-P} = 18$.

Scheme 3 shows the possible isomerization for the complex **6**. The phosphorus donor atom of dppe *trans* to the hydride in the complex $\mathbf{6}(\mathbf{c})$ is labile and thus dissociates to make a TBP intermediate structure, eventually leading to the isomerization to $\mathbf{6}(\mathbf{d})$.

The ratio $\mathbf{6}(\mathbf{c}): \mathbf{6}(\mathbf{d})$ is found to be equal from integration of the hydride resonance. From the IR spectrum of $\mathbf{6}$, v(CO) is slightly larger than that of the other complexes, which suggests that the π accepting phosphine coordinates *trans* to carbonyl in $\mathbf{6}(\mathbf{d})$, thereby strengthening the CO bond.

In complexes of 7, 8 and 9, only one type of complex, (c), has been formed. These facts result from the large chain of dppp and dppb in 7 and 8 and the high rigidity of dppf in 9.

Crystal structure of 9

The structure determined by X-ray crystallography (Fig. 1) shows that dppf is coordinated to ruthenium via P(1) and P(2). P(3) from triphenylphosphine coordinates to Ru meridionally with P(1) and P(2) and N from acetonitrile and C(1) from carbonyl are *trans*-positioned to each other and *cis*-positioned to all three phosphorus atoms. The hydride ligand which has been omitted in the difference Fourier map, is considered to exist *trans* to P(1). In the coordination core diagram of **9** (Fig. 2), the 6-coordinated structure shows a highly distorted octahedral geometry. Due to the relatively small hydride, the equatorial plane containing N, C(1), P(2) and P(3) is located in the plane below the Ru atom. Bond distances Ru-N, 2.083(9) Å and Ru - C(1), 1.83(1) Å, agree well with the data from other related complexes. Bond length Ru-P(1), 2.506(3) Å, is quite large compared to the other two ruthenium-phosphorus distances Ru = P(2), 2.367(3) Å and Ru = P(3), 2.381(3) Å arising from the strong trans influence of the hydride. The structural rigidity of dppf is responsible for the difference between P(1)—Ru—P(2), 102.15(9)^a and P(1)—Ru—P(3), 99.3(1)^a. According to Cullen et al., the dppf ligand coordinates to several metals in different ways. In the M-dppf system, the P—M—P' angle changes from ca 90 to 103° depending upon the geometry e.g. squareplanar, tetrahedral or octahedral as well as the kind of metal.¹⁵ Generally, if the two cyclopentadienyl rings in dppf are nearly eclipsed, the P-M-P' angle increases. Our results, described in Table 4, which shows the comparison of configuration of M—dppf, indicates that dppf has the nearly eclipsed configuration, and the P(1)—Ru—P(2)angle of $102.15(9)^\circ$ satisfies all the requirements discussed by Cullen.

М	MP (Å, mean)	PMP' (degree)	Cp—Cp' conformation
Ru	2.437	102.15	eclipsed
\mathbf{Pd}^{a}	2.284	97.98	staggered
Ni"	2.290	102.5	eclipsed
Mo^a	2.560	95.28	staggered

^a Data from reference 15.





Fig. 1. View of a $[RuH(CO)(NCCH_3)(PPh_3)(dppf)][BF_4] \cdot C_2H_5OH$ (9) molecule with atom numbering. The counter anion BF_4^- and the solvent molecule C_2H_5OH are omitted for clarity. The metal bonded H atom was not detected and is not shown here.

Hydrogenation of propanal

All the reactions were performed at 90°C and 20 atm H₂ pressure. During the reaction period (200 min), the most efficient catalyst among all the complexes used converted *ca* 95% of propanal to propan-1-ol. All the catalytic reactions have been shown to be pseudo-first order, and the observed reaction rates (k_{obs}) are described in Table 5. To compare the reaction rates, the [RuHCl (CO)(PPh₃)₃] complex as a reference catalyst has been used. From the reaction rate constant (k_{obs}) and the relative activity, it is observed that the rates increase remarkably if the diphosphine ligands function as a bidentate ligand in the complex. Among $[RuHCl(CO)(PPh_3)_3]$ and complexes 2–5 used, the catalytic activity decreases in the order $5 \gg 3 \simeq 4 > 2 > [RuHCl(CO)(PPh_3)_3]$. Complexes 2–5, the monodentate diphosphine complexes, have shown better activity than $[RuHCl(CO)(PPh_3)_3]$, the reference catalyst. However, the increase was not linearly proportional to the chain length of the diphosphine ligands. In the cases of 6–9, the bidentate diphosphine complexes, the order of the catalytic activities is $8 \gg 9 > 7 > 6$, and all the complexes have also shown better efficiencies than $[RuHCl(CO)(PPh_3)_3]$.

As observed in our previous work,⁷ such catalytic activity can be accounted for in accordance with the chelating ring size. In the complex **5** which has



Fig. 2. The coordination core diagram of 9.

a five-membered chelate ring and is thus more stable than 7 or 8, the chelate effect¹⁶ is maximized. It is suggested that the chelate ring opening is the rate determining step in these catalytic reactions. Thus it is expected that the larger the catalytic ring size is, the faster the catalytic reaction proceeds. Both 7 and 9 have the same chelating ring size, but 9 catalyzed the reaction about 7 times faster than 7. The difference in the electronic and steric factors between dppe and dppf can be cited to explain such results. The structural rigidity and the electronic conjugation of dppf by its cyclopentadienyl groups is considered to readily confirm the vacant site which is the major conformation in the catalytic cycle.

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Table	5.	Catalytic	hydrogenation	of	propanal	catalyzed	by	29	and
			RuHCl(0	CO)	$(\mathbf{PPh}_3)_3^a$				

Complex	$k_{\rm obs} imes 10^3 ({ m min}^{-1})^b$	Rel. Act. ^c
RuHCl(CO)(PPh ₃) ₃	0.89	1.0
unidentate disphosphine complexes		
$2 [RuH(CO)(NCCH_3)(PPh_3)_2(dmmp)]^+$	1.78	2.0
$3 [RuH(CO))(NCCH_3)(PPh_3)_2(dppe)]^+$	4.15	4.7
$4 [RuH(CO)(NCCH_3)(PPh_3)_2(dppp)]^+$	4.04	4.5
$5 [RuH(CO)(NCCH_3)(PPh_3)_2(dppb)]^+$	16.22	18.2
bidentate disphosphine complexes		
6 [RuH(CO)($NCCH_3$)(PPh_3)(dppe)] ⁺	3.78	7.6
7 $[RuH(CO)(NCCH_3)(PPh_3)(dppp)]^+$	10.02	11.3
8 $[RuH(CO)(NCCH_3)(PPh_3)(dppb)]^+$	128.01	143.8
9 [RuH(CO)(NCCH ₃)(PPh ₃)(dppf)] ⁺	69.99	78.6

"In toluene, 90°C, 20 atm of H_2 , [Catalyst]: [propanal] = 1:1000.

^{*b*} d[propanal]/ $dt = -k_{obs}$ [propanal].

 k_{obs}/k_{obs} for RuHCl(CO)(PPh₃)₃.

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