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PREPARATION AND STEREOCHEMISTRY OF RHODIUM—OLEFIN COMPLEXES CONTAINING ASYMMETRIC PICOLINALDIMINE LIGANDS

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Summary

Some bis(*N*-substituted picolinaldimine)rhodium perchlorates, $[Rh(2\text{-}C_5H_4NCH{=}N{-}R)_2]ClO_4$ (I, R = (*S*)-CHMePh; II, CH_2Ph; III, tert-Bu) and their adducts with fumaronitrile(FN), maleic anhydride(MA), dimethyl fumarate(DF), and dimethyl acetylenedicarboxylate(DAD) were prepared. The stereochemistry of the adducts is discussed in terms of the geometrical isomers and optical isomers due to the chiralities both of the metal center and of the coordinated olefin. A stereoselectivity was found in the formation of the MA and DAD adducts of I, which yielded two diastereomeric complexes. Furthermore, one of diastereomers of the MA and DF adducts was isolated by fractional crystallization. The epimerization of these was observed and the mechanisms are discussed.

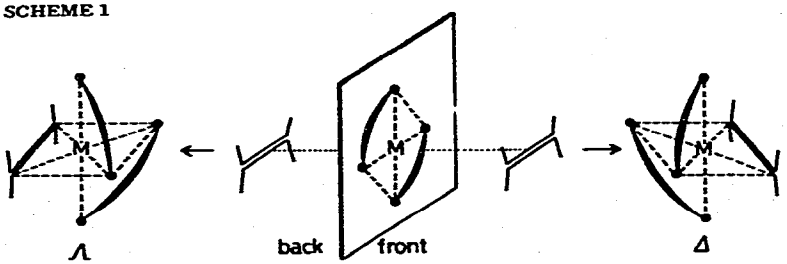
Introduction

Asymmetric homogeneous catalytic reactions by chiral transition metal complexes, such as hydrogenation of prochiral olefins and ketones, have recently been studied by a number of workers [1]. The stereochemical differentiation of these reactions may be governed not only by the coordination face of the prochiral olefin to the chiral catalysts but also by the free energy difference between the resultant diastereomers. In most cases the structure of intermediates in the reactions is inaccessible to direct or reliable observations. For this reason, we have attempted to prepare stable chiral olefin—rhodium complexes, which may be useful model compounds to help understand the mechanism of enantioselective reactions [2].

A nitrogen chelate with chirality was chosen, *N*-(*S*)-phenylethylpicolinaldimine [3], $2\text{-}C_5H_4NCH{=}N\text{-}(S)\text{-}CHMePh$, which can be easily prepared. When an olefin or an acetylene oxidatively adds to a bis-chelated rhodium complex, the

metal center is converted into a chiral moiety (Scheme 1). At the same time, the

SCHEME 1



enantiomeric pair is produced by the coordination of a prochiral olefin to the complex [4]. In addition, a pair of diastereomeric complexes is formed when a chiral chelate such as 2-C_5H_4NCH=N-(*S*)-CHMePh is used. The extent of stereoselectivity in asymmetric rhodium catalysts may be affected by the chiralities both of the metal center and of the coordinated olefin. This paper reports the preparation and stereochemistry of the complexes $[Rh(2\text{-}C_5H_4NCH{=}N\text{-}R)_2]ClO_4$ (R = (*S*)-CHMePh, CH_2Ph, tert-Bu) and their adducts with an olefin or an acetylene.

Experimental

Materials and general procedures

α-Phenylethylamine was resolved using (+)-tartaric acid [5] to give the *S*(—)-enantiomorph, $[\alpha]_D^{24}$ —38.6° (neat) (lit. [6], $[\alpha]_D^{22}$ —40.3°). *N*-Alkylpicolinaldimines were prepared according to the literature [3]. An ethanol solution of (*S*)-α-phenylethylamine and 2-picolinaldehyde was refluxed for about 3 h, followed by distillation to give *N*-(*S*)-α-phenylethylpicolinaldimine; b.p. 141°C/3 mmHg, $[\alpha]_D^{24}$ +42.2° (*c* 5.86, CH_3OH). $[Rh(C_2H_4)_2Cl]_2$ was prepared by the literature method [7].

Preparation of the complexes was carried out at room temperature under nitrogen. Solvents were degassed before use.

Bis(N-substituted picolinaldimine)rhodium perchlorate, $[Rh(2\text{-}C_5H_4NCH{=}N{-}R)_2]ClO_4$ (I, R = (S)-CHMePh; II, CH_2Ph; III, tert-Bu)

A methanol solution (10 ml) of 2-C_5H_4NCH=N-(*S*)-CHMePh (0.36 g, 1.7 mmol) was added slowly to a suspension of $[Rh(C_2H_4)_2Cl]_2$ (0.16 g, 0.4 mmol) in methanol (15 ml) to evolve ethylene immediately. The clear solution obtained was stirred for 1 h, during which time the color of the solution changed from orange to violet. Addition of $NaClO_4 \cdot H_2O$ (0.2 g, 1.4 mmol) in methanol (5 ml) to the solution yielded violet microcrystals of I, which were filtered, washed with methanol three times, and dried in vacuo, yielding 0.40 g (80%); $\Lambda_M = 153\ \Omega^{-1}\ cm^2\ mol^{-1}$. Analysis found: C, 54.00; H, 4.79; N, 8.63. $C_{28}H_{28}N_4O_4ClRh$ calcd.: C, 53.99; H, 4.53; N, 8.99%.

II and III were similarly prepared by using the appropriate picolinaldimine (75 and 70% respectively); the former was solvated with one molecule of methanol. II: $\Lambda_M = 143\ \Omega^{-1}\ cm^2\ mol^{-1}$. Analysis found: C, 51.14; H, 4.19; N, 8.73.

$C_{26}H_{24}N_4O_4ClRh \cdot CH_3OH$ calcd.: C, 51.73; H, 4.50; N, 4.50; N, 8.94%. III: Λ_M = 142 Ω^{-1} cm^2 mol^{-1}. Analysis found: C, 45.80; H, 5.48; N, 9.93. $C_{20}H_{28}N_4O_4$-ClRh calcd.: C, 45.60; H, 5.36; N, 10.63%.

Bis[N-(S)-α-phenylethylpicolinaldimine](olefin)rhodium perchlorate, {Rh[2-C_5H_4NCH=N-(S)-CHMePh]$_2$(L)}ClO_4 (L = FN, MA, DF)

Fumaronitrile (0.05 g, 0.64 mmol) and I (0.4 g, 0.64 mmol) was dissolved in dichloromethane (10 ml), and stirred for 20 min, during which time the color of the solution changed from violet to orange. The solution was evaporated to dryness under reduced pressure to give the crude FN adduct, which was recrystallized from dichloromethane/petroleum ether to yield 0.32 g (71%) of product. The crystals were solvated with 0.25 mol of dichloromethane, $[\alpha]_D^{24}$ −110° (*c* 0.100, CH_3CN); Λ_M = 155 Ω^{-1} cm^2 mol^{-1}; ν(C≡N) 2204 cm^{-1}. Analysis found: C, 53.75; H, 4.25; N, 11.86. $C_{32}H_{30}N_6O_4ClRh \cdot 1/4CH_2Cl_2$ calcd.: C, 53.63; H, 4.26; N, 11.64%.

An equimolar solution of I and MA or DF in dichloromethane was stirred for 10 min, filtered and evaporated to dryness under reduced pressure to give analytically pure MA (83%) or DF adduct (90%) without recrystallization. The MA adduct: Λ_M = 133 Ω^{-1} cm^2 mol^{-1}; ν(C=O) 1792 and 1720 cm^{-1}. Analysis found: C, 53.34; H, 4.22; N, 7.87. $C_{32}H_{30}N_4O_7ClRh$ calcd.: C, 53.31; H, 4.19; N, 7.77%. The DF adduct: Λ_M = 150 Ω^{-1} cm^2 mol^{-1}; ν(C=O) 1691 cm^{-1}. Analysis found: C, 53.06; H, 4.58; N, 7.32. $C_{34}H_{36}N_4O_8ClRh$ calcd.: C, 53.24; H, 4.73; N, 7.30%.

Bis[N-(S)-α-phenylethylpicolinaldimine](dimethyl acetylenedicarboxylate)rhodium perchlorate, {Rh[2-C_5H_4NCH=N-(S)-CHMePh]$_2$(DAD)}ClO_4

An equimolar solution of I and DAD in dichloromethane was stirred for 1 h, followed by evaporation to dryness under reduced pressure. The resulting product was recrystallized from hot methanol to afford orange needles (65%); $[\alpha]_D^{23}$ +43.0° (*c* 0.100, CH_3CN); Λ_M = 190 Ω^{-1} cm^2 mol^{-1}; ν(C≡C) 1802 cm^{-1}; ν(C=O) 1656 cm^{-1}. Analysis found: C, 53.19; H, 4.45; N, 7.38. $C_{34}H_{34}N_4O_8ClRh$ calcd.: C, 53.38; H, 4.48; N, 7.32%.

Bis(N-benzylpicolinaldimine)(dimethyl fumarate)rhodium perchlorate, [Rh(2-C_5H_4NCH=NCH_2Ph)$_2$(DF)]ClO_4

The complex was prepared by the reaction of II with DF as described in the DAD adduct of I. Recrystallization from hot ethanol gave hygroscopic crystals (50%) which contained two molecules of water as confirmed by IR and ^{1}H NMR: Λ_M = 160 Ω^{-1} cm^2 mol^{-1}; ν(O—H) 3550 cm^{-1}; ν(C=O) 1683 cm^{-1}. Analysis found: C, 49.81; H, 4.46; N, 7.30. $C_{32}H_{32}N_4O_8ClRh \cdot 2H_2O$ calcd.: C, 49.59; H, 4.63; N, 7.23%.

Separation of diastereomers

A hot methanol solution of the MA or DF adduct of I was allowed to stand at room temperature for a few hours to give orange needles (the MA adduct); $[\alpha]_D^{24}$ +97.9° (*c* 0.114, CH_3CN), or a red needles (the DF adduct); $[\alpha]_D^{24}$ −419° (*c* 0.100, CH_3CN). The optical rotations of these compounds were constant even after repeated crystallization, indicating the presence of one of the diastereomers. Some attempts to separate the other of the diastereomeric pair from the mother liquor were unsuccessful.

Physical measurements

The electric conductivity was measured in an CH_3CN solution (10^{-4} *M*) by using a Yokogawa F-255A universal bridge. Infrared spectra were recorded in Nujol mulls on a Hitachi 215 spectrophotometer. ^1H NMR spectra were obtained on a Japan Electron Optics JNM-PS-100 spectrometer using tetramethylsilane as the internal standard. Optical rotations were measured on a Perkin—Elmer 241 polarimeter using an 1 dm cell.

Results and discussion

Bis(chelate) complexes

I, II and III are stable under dry nitrogen, but they are gradually decomposed in air.

Variable temperature ^1H NMR spectra of I in C_6H_5CN are depicted in Fig. 1, which shows two doublets of the CH_3 signals at 24°C. With raising the temperature, these signals become broad and coalesce at about 80°C. The spectra were reproducible in the 24—80°C range, while the complex was decomposed on heating up to 90°C. Further, the appearance of spectra at each temperature was little altered, not only by changing the concentration but on addition of 2-C_5H_4NCH=N-(*S*)-CHMePh to the parent solution. There may be three possible explanations for the temperature dependence of the spectra; (i) *cis—trans* isomerization around the rhodium center, (ii) conformational restriction of rotation about the asymmetric carbon—imine nitrogen bond, and (iii) an inversion of the distorted planar configuration at the rhodium center. II and III in C_6H_5CN, however, exhibit only one set of benzyl and tert-Bu proton signals, respectively, which show no change in the same temperature range. This indicates that *cis—trans* isomerization is unlikely. The second possibility is also unlikely, because restricted

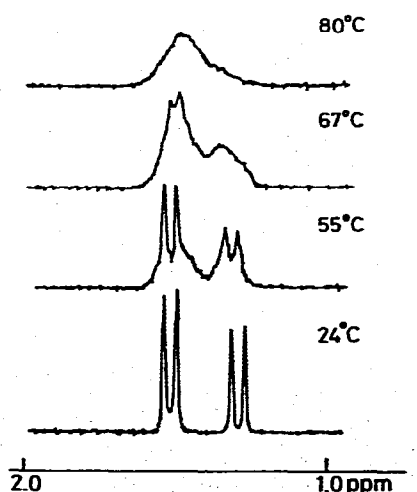


Fig. 1. Variable temperature ^1H NMR spectra of the CH_3 protons of $\{Rh[2\text{-}C_5H_4NCH{=}N\text{-}(S)\text{-}CHMePh]_2\}ClO_4$ in C_6H_5CN.

rotation of this sort has not been observed not only in Mo(II) and W(II) complexes of the chiral ligand used here [3] but also in the olefin or acetylene adducts of I. On the other hand, an X-ray structure analysis has demonstrated that $[Pd(bipy)_2]^{2+}$ (bipy = α,α'-bipyridine) adopts a distorted planar configuration, in which two ligand planes are twisted with respect to each other [8]. A similar distorted structure may be assumed for I which is sterically crowded. It may, therefore, be suggested that I involves two diastereomers due to the right-handed and left-handed helicities, which predicts the appearance of two sets of proton signals. The inversion of helicity in I may cause diastereomeric averaging at elevated temperatures. An analogous inversion has been reported for a series of bis(β-aminothionato)zinc(II) complexes [9]. Thus, the inversion at the rhodium center is most likely to occur.

Although the ^{1}H NMR spectra indicate that I, II and III all exist as a single geometrical isomer, the stereochemistry could not be determined by their infrared and ^{1}H NMR spectra. Molecular models, however, show that steric repulsions are minimized when the imine nitrogen atoms of two ligands are located in *trans* positions with respect to each other.

Adducts of the bis(chelate) complexes

The DF adduct of II exhibits an AB type quartet of the CH_2 proton signals at δ 4.95 and 4.73 ppm (^2J 13 Hz), which indicates that the metal center becomes chiral upon coordination of DF. On the other hand, the DF adduct of I displays two sets of the olefinic and C—CH_3 proton signals with different intensities designated as α and β in Fig. 2, although two DF—CH_3 signals are superimposed. This is suggestive of the existence of two diastereomers, at least in the DF adduct of I. Similar two sets of proton signals are observed in the FN, MA, and DAD adducts of I (Table 1). In addition, the MA adduct shows two AB type quartet signals due to the olefinic protons of diastereomers, and each signal is further split into a doublet owing to coupling with the ^{103}Rh nucleus (Fig. 2). The intensity ratio of two sets of signals (α/β) in these four adducts more or less varies with temperature and solvent.

Stereochemistry

When two unsymmetrical chelates, 2-C_5H_4NCH=N—R, and one molecule of olefin or acetylene occupy six coordination sites of an octahedron as in the DF adduct of II, three geometrical isomers, A, B, and C, are possible, as shown in Fig. 3. In the A and B isomers only one NMR signal is expected to occur for each of the different protons in the 2-C_5H_4NCH=N—R ligand, while C predicts the appearance of two sets of signals with identical intensity. The spectrum of the DF adduct of II showed only one set of resonances. This was also the case with each of the diastereomeric pairs of the FN, DF, and DAD adducts of I. The geometrical isomer would therefore be A or B. The C—CH_3 signals of the MA adduct of I appeared as two kinds of doublets (Fig. 2), because of the diamagnetic anisotropy of the carbonyl groups of MA [10]. This anisotropy, however, hardly affects the chemical shifts of the H(6) proton of the pyridine ring (Table 1). Thus, the MA adduct of I is more likely to assume the structure of the A isomer. Almost unchanged chemical shifts of the H(6) proton in all the adducts predict that the FN, DF, and DAD adducts of I and the DF adduct of II adopt the same configuration as the MA adduct of I.

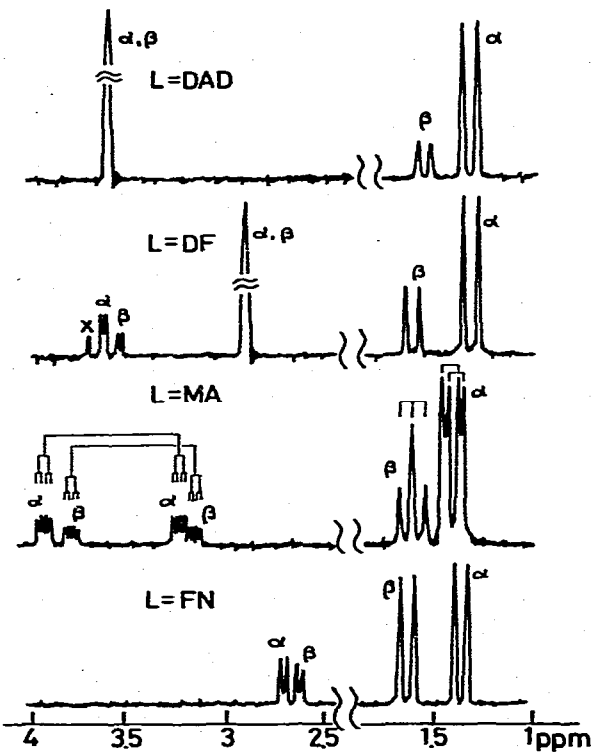


Fig. 2. ^{1}H NMR spectra of $\{Rh[2\text{-}C_5H_4NCH{=}N\text{-}(S)\text{-}CHMePh]_2(L)\}ClO_4$ at equilibrium in CD_3CN at 25°C. The signal indicated by x (L = DF) is due to the CH_3 protons of dissociated DF.

TABLE 1

^{1}H CHEMICAL SHIFTS (δ, ppm) OF $\{Rh[2\text{-}C_5H_4NCH{=}N\text{-}(S)\text{-}CHMePh]_2\}ClO_4$ AND THEIR ADDUCTS WITH OLEFINS OR ACETYLENE AT 25°C

Olefin or acetylene [a]	Solvent	Picolinaldimine [b]		Olefin or acetylene		Isomer ratio [f]
		CH_3 [c]	H(6) [d]	CH [e]	CH_3	
—	C_6H_5CN	1.23, 1.56	8.72, 8.62			
	CD_3CN	1.29, 1.50	8.76, 8.60			
FN	CD_3CN	α 1.35	8.76	2.69		54
		β 1.63	8.76	2.61		46
MA	CD_3CN	α 1.41, 1.37	8.62	3.93, 3.25		64
		β 1.64, 1.56	8.76	3.78, 3.16		36
DF	CD_3CN	α 1.34	8.58	3.63	2.91	55
		β 1.60	8.51	3.55	2.91	45
	$CDCl_3$	α 1.26	8.83	3.59	3.00	60
		β 1.67	8.67	3.53	3.02	40
DAD	CD_3CN	α 1.34	8.72		3.63	74
		β 1.56	8.59		3.63	26

[a] The abbreviations used are as follows: FN = fumaronitrile, MA = maleic anhydride, DF = dimethyl fumarate and DAD = dimethyl acetylenedicarboxylate. [b] α and β correspond to those in Fig. 2. [c] $^3J(CH_3\text{—}CH)$ 6.5 Hz. [d] $^3J(HH)$ 1.5 Hz. [e] $J(^{103}Rh\text{—}H)$ 2 Hz. [f] Determined from the intensity of the CH_3 signals of $2\text{-}C_5H_4NCH{=}N\text{-}(S)\text{-}CHMePh$.

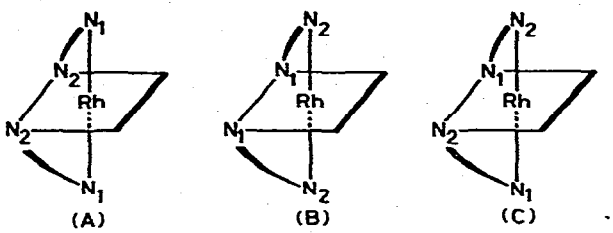


Fig. 3. Possible geometrical isomers of [Rh(2-$C_5H_4NCH{=}N{-}R)_2(L)$]-ClO_4: L = olefin or acetylene; N_1 = imine nitrogen, N_2 = pyridine nitrogen.

The A isomer of the FN and DF adducts of II may theoretically involve four possible optical isomers; two diastereomeric pairs of enantiomers owing to chiralities of the rhodium center (Δ or Λ) defined according to [11] and of the coordinated olefin carbons (*R* or *S*) [4], as seen in Fig. 4. When the chiral ligand, 2-$C_5H_4NCH{=}N$-(*S*)-CHMePh, is used, each optical isomer bears a diastereomeric relation to the others.

The ^1H NMR pattern of the DF adduct of II was little changed in the 60° to −50°C range. Similar rhodium complexes, [Rh(*p*-$CH_3C_6H_4NC)_4$(TCNE)]ClO_4 (TCNE = tetracyanoethylene) and Rh(*p*-$CH_3OC_6H_4NC)_2(PPh_3)$(FN)I, exhibit temperature dependences to give their limiting spectra at −35° and −50°C, respectively [12]. Thus, a fast dynamic process for the present adducts may be excluded on the NMR time scale. The occurrence of one set of the ^1H signals in the DF adduct of II implies either the formation of only one pair of enantiomers or the coincidence of two resonances of the diastereomeric pair. Similarly, two sets of resonances observed in the DF and FN adducts of I suggest either the

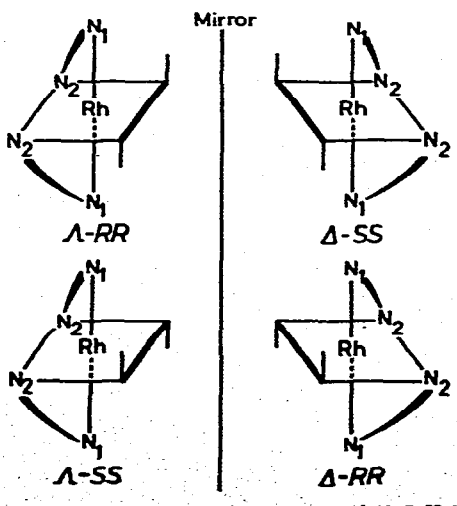


Fig. 4. Possible optical isomers of [Rh(2-$C_5H_4NCH{=}N{-}R)_2$ (*trans*-olefin)]ClO_4 for the geometrical isomer of A.

existence of only two diastereomers or a coincidence of spectra. Attempts to resolve this question by the use of shift reagents were unsuccessful. Thus, the enantiotopic face of prochiral olefins (DF, FN) has not been differentiated because of duplication of chiralities of the metal center and coordinated olefin carbons.

Stereoselectivity

^{1}H NMR measurements indicated that two diastereomers equilibrated in an CD_3CN solution are formed in the ratios of 64 : 36 and 74 : 26 for the MA and DAD adducts of I, respectively. Thus, the stereoselectivity in the two diastereomers, arising from the chirality of the rhodium center, are 28 and 48% respectively. We have carried out an approximate conformational analysis [13] of the asymmetric (*S*)-carbon moiety on the imine nitrogen by considering the bulkiness of phenyl groups. The result indicates that the conformations of D and E being diastereomeric to each other, shown in Fig. 5, are preferable to the other rotational isomers. The stereoselectivity on equilibration may be mainly related to the difference in the steric repulsion between the H(1)-proton or CH_3 group and olefin or acetylene. The repulsion of the H(1)-proton with olefin or acetylene in D would be small. It is therefore suggested that the configuration of the major diastereomer (the α signal in Fig. 2) of the MA and DAD adducts is Δ, and that of the minor diastereomer (the β signal in Fig. 2) Λ. This assignment is consistent with the observation that the splitting of the β signal of the MA adduct is larger than that of the α signal. The large splitting of the former may be expected from the fact that in E the CH_3 protons are located closely to MA, which exerts an anisotropy effect [10].

Epimerization mechanism

The separated MA or DF adduct of I is subject to configurational interconversion in solution, as confirmed by the ^{1}H NMR and optical rotation measurements; the solution immediately after dissolution in CD_3CN exhibits only one set of the α signals in Fig. 2, but the β signals gradually appear in the spectra. A corresponding change in the optical rotation at 589 nm was observed. The rate of epimerization was obtained in an CH_3CN solution at 24°C (1×10^{-3}—10^{-4} *M*). The epimerization of both adducts was found to obey first order kinetics. The rate of epi-

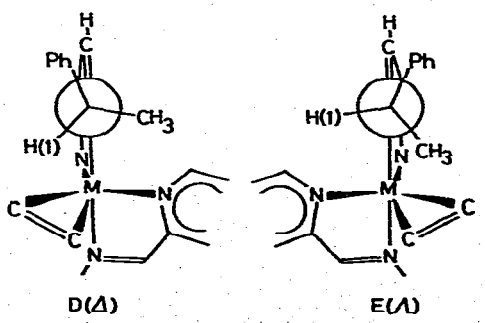


Fig. 5. Preferred conformations of two diastereomers of the MA or DAD adduct of I; the view along one of the asymmetric carbon-imine nitrogen bonds.

merization of the DF adduct ($3.34 \pm 0.20 \times 10^{-2}$ min^{-1}) is faster than that of the MA adduct ($6.90 \pm 0.31 \times 10^{-3}$ min^{-1}). There may be two possible mechanisms, intra- and intermolecular, for the epimerization. When MA or DF was added to the solution of the corresponding adduct, a decreasing rate of epimerization was observed. At the same time, a very weak CH_3 signal of the dissociated DF appear at δ 3.75 ppm in the course of epimerization. These observations do not contradict the intermolecular mechanism of epimerization, which involves the dissociation of olefin. It may be conceivable that the slower epimerization rate in the MA adduct reflects a stronger rhodium—olefin bond than in the DF adduct. Thus, the present interconversion appears to occur via the S_N1 mechanism. This is in contrast to the olefin complexes of platinum(II), such as PtCl(*L*-prolinato) (*trans*-2-butene), whose interconversion was reported to take place through an S_N2 mechanism [14].

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