

NMR conformational studies of (1,2-bis(diarylphosphino)ethane)-(diorgano sulfide)ruthenium complexes

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Abstract

Some (η^5 -cyclopentadienyl)(1,2-bis(diarylphosphino)ethane)(diorgano sulfide)ruthenium complexes, $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)(\text{Ar}_2\text{PCH}_2\text{CH}_2\text{PAr}_2)(\text{R}^1\text{R}^2\text{S})]\text{BF}_4$ ($\text{Ar} = \text{Ph}$, *p*-Tol; $\text{R}^1, \text{R}^2 = \text{Ph}$, Et) were prepared. Variable temperature NMR spectra of these complexes showed the existence of two fluxional processes; inversion at the sulfur atom and δ - λ interconversion of the chelate ring. The former process was slower, and its barriers in these complexes were calculated as *ca.* 7 kcal mol⁻¹. The spectral features of ethyl phenyl sulfide complexes suggested that substantiation of the new chiral center at sulfur induces a significant conformational rigidity at the chelate ring.

Key words: Ruthenium; Sulfide; Nuclear magnetic resonance; Conformation; Diphosphine

1. Introduction

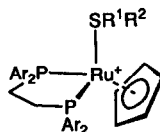
There is a considerable interest in fluxional behavior of coordinated diorgano sulfide ligands, $\text{R}^1\text{R}^2\text{S}$ [1]. For coordination to metal, they utilize one of two lone pairs of electrons, but exchange of coordinated and uncoordinated electron pairs usually occurs rapidly. Also, a chiral center is produced when R^1 and R^2 are different from each other. We wish to describe here preparation of some (η^5 -cyclopentadienyl)(1,2-bis(diarylphosphino)ethane)(diorgano sulfide)ruthenium complexes and their fluxional behaviors studied with the aid of NMR method.

The coexistence of a 1,2-bis(diarylphosphino)ethane ligand, $\text{Ar}_2\text{PCH}_2\text{CH}_2\text{PAr}_2$ ($\text{Ar} = \text{Ph}$, dppe; $\text{Ar} = p\text{-Tol}$, dtpe), would bring about another interesting stereochemical aspect, since another chirality is imposed by coordination of this phosphine, if the chelate ring conformation is fixed in one of enantiomeric configurations (see, *e.g.* eqn. (1)) [2]. Generally, these phosphine ligands generate a chiral environment around the metal center by rigidity of the conformation of the phenyl groups which in turn is brought about by rigidity of the chelate ring [3–6]. Thus, it may well be that in the

present complexes the chelate ring inversion possibly depends on the environment induced by the inversion at sulfur and *vice versa*. It is an interesting problem to see whether two or more different fluxional dynamics can occur complementarily when involved in a single molecule (see, *e.g.* a study of correlated dynamics of (η^6 -arene)tricarbonylchromium involving a metal tripod rotation and a conformational rearrangement of the substituent on the arene ligand) [7].

2. Results and discussion

Treatment of $\text{Ru}(\eta^5\text{-C}_5\text{H}_5)(\text{dppe})\text{Cl}$ or $\text{Ru}(\eta^5\text{-C}_5\text{H}_5)(\text{dtpe})\text{Cl}$ with silver tetrafluoroborate in the presence of sulfides, $\text{R}^1\text{R}^2\text{S}$ ($\text{R}^1, \text{R}^2 = \text{Ph}$, Et), gave the cationic complexes 1–3.



1: $\text{R}^1 = \text{Et}$, $\text{R}^2 = \text{Ph}$; $\text{Ar} = \text{Ph}$ (a), *p*-Tol (b)

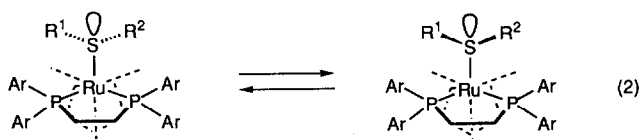
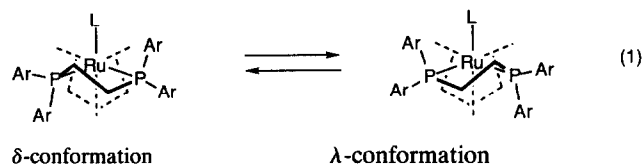
2: $\text{R}^1 = \text{R}^2 = \text{Et}$; $\text{Ar} = \text{Ph}$

3: $\text{R}^1 = \text{R}^2 = \text{Ph}$; $\text{Ar} = \text{Ph}$

For these complexes, two fluxional processes may arise. One is an interconversion between δ and λ

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conformational isomers (eqn. (1)), and the other an inversion at the sulfur center (eqn. (2)). At ambient temperature, the ethyl group of complexes **1** and **2** gave one quartet and one triplet for methylene and methyl protons. In other words, the interconversion between the diastereomers depicted in these equations is fast enough, and the SCH₂ protons are not diastereotopic even in the ethyl phenyl sulfide complex (**1**). Moreover, the ³¹P NMR spectra of **1–3** showed only one phosphorus resonance. For dppe and dtpe ligand protons, the ¹H NMR spectra of **1–3** showed two methylene signals and two sets of aryl ring signals. This non-equivalency is due to the difference of the environments between the upper and the lower sides of the P–Ru–P coordination plane. Above all, there is no net chirality in the molecule and thus both processes depicted in the equations are very rapid at ambient temperature.



The ¹H NMR spectra of **1–3** exhibited different temperature dependency according to the type of the sulfide ligand. Lowering the temperature of a CD₂Cl₂ solution containing the symmetric sulfide complexes, **2** and **3**, led to no spectral change for the hydrogen and phosphorus resonances of the dppe moiety down to –90°C, indicating occurrence of a rapid δ – λ interconversion. Fixation of the chelate ring interconversion might have induced non-equivalency for the four dppe phenyl rings and CH₂CH₂ protons as well as two phosphorus atoms.

In the complexes **1** at lower temperatures, the resonance of the SCH₂ protons appeared as a diastereotopic pair. In **1a** all the phenyl groups and the methylene groups were observed non-equivalent and the two phosphorus atoms of dppe also became non-equivalent. Also in **1b** all the tolyl groups were observed non-equivalent (aryl ring region shown in Fig. 1, and the four methyl signals of the tolyl groups; δ 2.03, 2.24, 2.28, 2.29). These observations are fully consistent with the substantiation of chirality in the molecule at the lower temperature. We presume that this chirality did not originate from the freezing of the chelate ring inversion but from the freezing of the inversion at

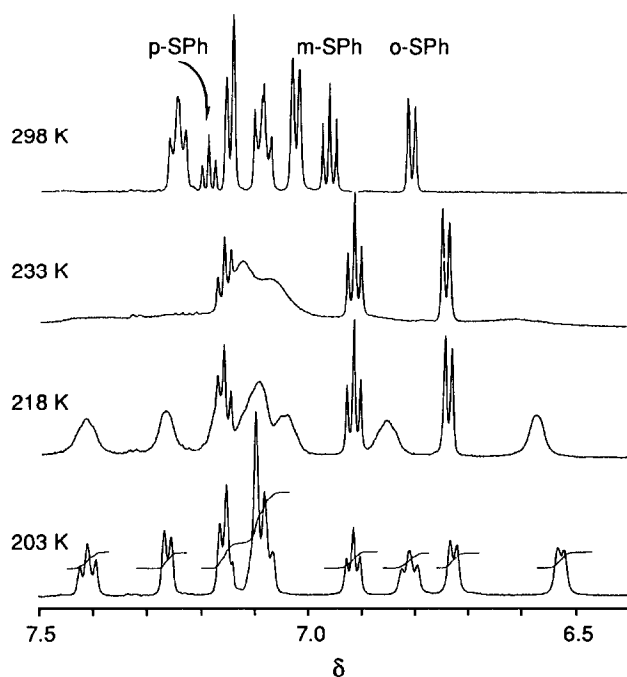
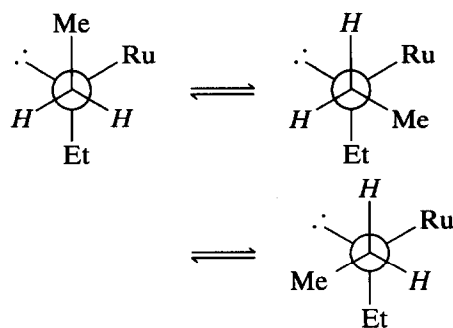


Fig. 1. Variable temperature ¹H NMR spectra of **1b** in CD₂Cl₂ in the aryl proton region.

sulfur. Note, however, an important consequence of the substantiation of one chiral center (at sulfur) brought about onto another unit (chelate ring) within the molecule (*vide infra*).

The observation that in **2** only the methylene group of the sulfide gave two different signals at low temperature is also reasonably explained by the freezing of the sulfide inversion. It is apparent that although there exists no chirality in the molecule, no rotation however rapid about the S–C bond can ever equalize two protons of the SCH₂ group (Scheme 1). Only rapid inversion at sulfur leads to interconversion of these protons.

Different coalescence temperatures for the methylene group of the sulfide in **1a** and **2** were obtained with NMR instruments operating at different frequencies and Arrhenius plots (Fig. 2) were obtained and the



Scheme 1.

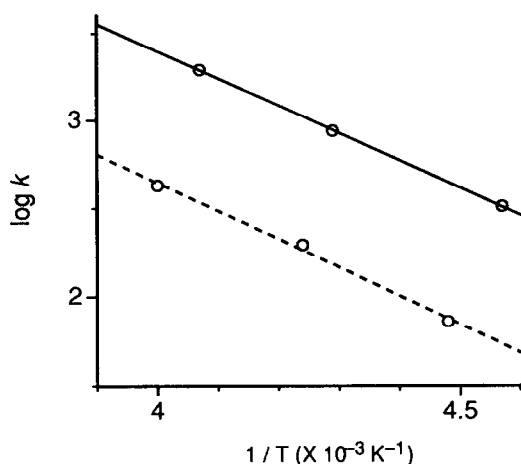


Fig. 2. Arrhenius plots for SCH_2 signals of **1a** (full line) and **2** (dashed line).

barriers to the inversion calculated as $E_a = 7.1$ and $7.4 \text{ kcal mol}^{-1}$, respectively. These values are reasonable for inversions at sulfur atom [1]. Data from variable temperature ^{31}P NMR spectra were not appropriate for the Arrhenius plot because of lack of the convergence of two ^{31}P chemical shift values even down to -90°C .

All the aryl proton signals of dppe and dtpe in **1–3** gathered within a range of 0.30 ppm (**1a**, δ 7.18–7.40; **1b**, δ 7.03–7.25; **2**, δ 7.35–7.58; **3**, δ 7.15–7.44) at ambient temperature (Fig. 1). This feature did not change upon lowering the temperature for **2** and **3**. Remarkably, in **1** in which the four aryl signals were observed non-equivalent, these signals appeared in a relatively wide range as shown in Fig. 1 (**1a**, δ 6.75–7.55; **1b**, δ 6.47–7.41). This suggests that the magnetic environments around the four aryl groups are largely different from each other. That is, the chirality generated on the sulfur forced the diastereomeric equilibrium of the chelate ring to lie predominantly on one side, and more rigid conformation of each aryl group (e.g. edge-face orientation) [3–6] was reflected in the spectra. In the cases of **2** and **3** the δ and λ conformers exist equally, and undergo the rapid interconversion to each other, which might synchronize with a low energy rotation about the Ru–S bond where the configuration at sulfur is rigid and achiral. Then a difference in magnetic environments around each diastereotopic aryl pair would be averaged to a narrower range of resonances.

In conclusion, the δ – λ conformational interconversion of the chelate ring is very rapid at low temperatures even for **3** that is thought to suffer a largest steric hindrance. However, the spectral feature observed in **1** suggests that substantiation of the new chiral center at sulfur induces a significant conformational rigidity at the chelate ring.

3. Experimental details

Most reagents were commercially available and were used without further purification. Silver tetrafluoroborate (purity 90%) was used after drying under vacuum. Preparations of $\text{Ru}(\eta^5\text{-C}_5\text{H}_5)(\text{dppe})\text{Cl}$ and the dtpe analog were carried out according to the literature [8]. 1,2-Bis(di-*p*-tolylphosphino)ethane was prepared from tri-*p*-tolylphosphine and sodium metal in liquid ammonia followed by treatment with 1,2-dichloroethane [9]. ^1H NMR spectra were obtained on JEOL JNM-100, GSX-270, GSX-400, and Bruker AM600 spectrometers. The chemical shifts were referenced to CH_2Cl_2 (δ 5.30) in CD_2Cl_2 . ^{31}P NMR spectra were obtained on GSX-400 and AM600 spectrometers operating at 162 and 243 MHz respectively and the chemical shifts were referenced to external $\text{P}(\text{OMe})_3$ (δ 0.00).

3.1. Preparation of $(\eta^5\text{-cyclopentadienyl})(1,2\text{-bis}(\text{diphenylphosphino})\text{ethane})(\text{ethylphenyl sulfide})\text{ruthenium tetrafluoroborate}$ (**1a**)

To a solution of 600 mg (1.0 mmol) of $\text{Ru}(\eta^5\text{-C}_5\text{H}_5)(\text{dppe})\text{Cl}$ and 410 mg (3.0 mmol) of ethylphenyl sulfide in 10 ml of acetone, 430 mg (2.0 mmol) of silver tetrafluoroborate in 20 ml of acetone was added under an inert atmosphere. The resulting dark red solution was stirred until it turned yellow (ca. 1 h). It was filtered, and the filtrate evaporated under reduced pressure. The residue was extracted with 3 ml of CH_2Cl_2 and purified through a short florisil column. To the eluent was added n-hexane to give a yellow oil which was dried under vacuum. The residue was recrystallized with ethanol–ether to give 410 mg (0.52 mmol, 52%) of yellow microcrystals. These were washed with n-hexane and ether; mp $163\text{--}164^\circ\text{C}$. ^1H NMR (CD_2Cl_2 , 25°C): δ 0.33 (t, 3H, SCH_2CH_3), 1.97 (q, 2H, SCH_2), 2.56 (m, 2H) and 2.83 (m, 2H) (PCH_2), 5.07 (s, 5H, C_5H_5), 6.84 (d, 2H, *o*-SPh), 6.98 (t, 2H, *m*-SPh), 7.16 (t, 1H, *p*-SPh), 7.18–7.40 (20H, PC_6H_5); (CD_2Cl_2 , -90°C): δ 0.20 (t, 3H, SCH_2CH_3), 0.86 (br, 1H) and 2.32 (br, 1H) (SCH_2), 2.32 (br, 1H), 2.40 (br, 1H), 2.75 (br, 1H) and 2.88 (br, 1H) (PCH_2), 5.07 (s, 5H, C_5H_5), 6.73 (d, 2H, *o*-SPh), 6.89 (t, 2H, *m*-SPh), 7.10 (t, 1H, *p*-SPh), 6.75–7.55 (20H, PC_6H_5). ^{31}P NMR (CD_2Cl_2 , 25°C): δ -69.5 (s); (CD_2Cl_2 , -90°C): -67.9 (br) and -73.8 (br). Anal. Calcd for $\text{C}_{39}\text{H}_{39}\text{SP}_2\text{BF}_4\text{Ru}$: C, 59.32; H, 4.98. Found: C, 59.10; H, 5.00%.

3.2. Preparation of $(\eta^5\text{-cyclopentadienyl})(1,2\text{-bis}(\text{di-}p\text{-tolylphosphino})\text{ethane})(\text{ethylphenyl sulfide})\text{ruthenium tetrafluoroborate}$ (**1b**)

In a similar way to the preparation of **1a**, **1b** was prepared from 200 mg (0.30 mmol) of $\text{Ru}(\eta^5\text{-C}_5\text{H}_5)(\text{dtpe})\text{Cl}$ as 156 mg of yellow powder (0.18 mmol,

61%); mp 123–130°C. ^1H NMR (CD_2Cl_2 , 25°C): δ 0.31 (t, 3H, CH_3), 1.93 (q, 2H, SCH_2), 2.29 (s, 6H) and 2.33 (s, 6H) ($\text{PC}_6\text{H}_4\text{CH}_3$), 2.42 (m, 2H) and 2.75 (m, 2H) (PCH_2), 5.03 (s, 5H, C_5H_5), 6.81 (d, 2H, *o*-SPh), 6.97 (t, 2H, *m*-SPh), 7.19 (t, 1H, *p*-SPh), 7.03 (d, 2H), 7.09 (dd, 2H, $J(\text{PH}) = 10$ Hz), 7.15 (d, 2H) and 7.25 (dd, 2H, $J(\text{PH}) = 10$ Hz) ($\text{PC}_6\text{H}_4\text{Me}$); (CD_2Cl_2 , -90°C): δ 0.20 (t, 3H, SCH_2CH_3), 0.85 (br, 1H) and 2.18 (br, 1H) (SCH_2), 2.03 (s, 3H), 2.24 (s, 3H), 2.28 (s, 3H) and 2.29 (s, 3H) ($\text{PC}_6\text{H}_4\text{CH}_3$), 2.18 (br, 1H), 2.32 (br, 1H), 2.74 (br, 1H), and 2.78 (br, 1H) (PCH_2), 5.05 (s, 5H, C_5H_5), 6.72 (br, 2H, *o*-SPh), 6.92 (br, 2H, *m*-SPh), 7.15 (t, 1H, *p*-SPh), 6.47–7.41 (16H, $\text{PC}_6\text{H}_4\text{Me}$). ^{31}P NMR (CD_2Cl_2 , 25°C): δ -72.1 (s); (CD_2Cl_2 , -70°C): -69.5 (br), -75.8 (br). Anal. Calcd for $\text{C}_{43}\text{H}_{47}\text{SP}_2\text{BF}_4\text{Ru}$: C, 61.07; H, 5.60. Found: C, 60.79; H, 5.72%.

3.3. Preparation of $(\eta^5\text{-cyclopentadienyl})(1,2\text{-bis}(\text{diphenylphosphino})\text{ethane})(\text{diethyl sulfide})\text{ruthenium tetrafluoroborate (2)}$

To a yellow eluent through a short florisil column, which was obtained similarly to the preparation of **1a** from 0.25 mmol of $\text{Ru}(\eta^5\text{-C}_5\text{H}_5)(\text{dppe})\text{Cl}$, was added *n*-hexane to give yellow crystals (0.17 mmol, 69%); mp 184°C. ^1H NMR (CD_2Cl_2 , 25°C): δ 0.60 (t, 6H, SCH_2CH_3), 1.68 (q, 4H, SCH_2), 2.38 (m, 2H) and 2.81 (m, 2H) (PCH_2), 5.06 (s, 5H, C_5H_5), 7.35–7.58 (20H, PC_6H_5); (CD_2Cl_2 , -90°C): δ 0.44 (br, 6H, SCH_2CH_3), 1.16 (br, 2H) and 1.49 (br, 2H) (SCH_2), 2.26 (br, 2H) and 2.81 (br, 2H) (PCH_2), 5.05 (s, 5H, C_5H_5), 7.33–7.45 (25H, C_6H_5). ^{31}P NMR (CD_2Cl_2 , 25°C): δ -71.2 (s). Anal. Calcd for $\text{C}_{35}\text{H}_{39}\text{SP}_2\text{BF}_4\text{Ru}$: C, 56.69; H, 5.30. Found: C, 56.54; H, 5.41%.

3.4. Preparation of $(\eta^5\text{-cyclopentadienyl})(1,2\text{-bis}(\text{diphenylphosphino})\text{ethane})(\text{diphenyl sulfide})\text{ruthenium tetrafluoroborate (3)}$

In a similar way to the preparation of **1a**, **3** was prepared from 0.33 mmol of $\text{Ru}(\eta^5\text{-C}_5\text{H}_5)(\text{dppe})\text{Cl}$ as yellow crystals (0.21 mmol, 64%); mp 153–156°C. ^1H NMR (CD_2Cl_2 , 25°C): δ 2.61 (m, 2H) and 2.85 (m, 2H) (PCH_2), 4.97 (s, 5H, C_5H_5), 6.71 (d, 4H, *o*-SPh), 6.96

(t, 4H, *m*-SPh), 7.10 (t, 2H, *p*-SPh), 7.15–7.44 (20H, PC_6H_5). ^{31}P NMR (CD_2Cl_2 , 25°C): δ -78.3 (s). Anal. Calcd for $\text{C}_{43}\text{H}_{39}\text{SP}_2\text{BF}_4\text{Ru}$: C, 61.66; H, 4.69. Found: C, 61.21; H, 4.69%.

3.5. Variable temperature studies of **1a** and **2**

Coalescence temperatures for methylene proton resonances, SCH_2 , in each complex were determined by the use of NMR spectrometers with different frequencies. For the Arrhenius plot (Fig. 2), least-square relationships between the following rate constants (s^{-1}) [10] and the coalescence temperatures were used; for **1a**, 1940 (246 K), 875 (233 K) and 324 (219 K), $r = 1.00$; for **2**, 435 (250 K), 196 (236 K) and 72.6 (223 K), $r = 0.998$.

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