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Optically Active Ortho-Metalated Half-Sandwich Ruthenium Complexes: Solid-State NMR as a Convenient Tool To Analyze Mixtures of Diastereomers

Vincent Ritleng,[†] Philippe Bertani,[‡] Michel Pfeffer,^{*,†} Claude Sirlin,[†] and Jérôme Hirschinger[‡]

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Bulk solid samples of various ratios of the cyclometalated arene ruthenium diastereomers (*S*)_{Ru}- and (*R*)_{Ru}-[(η^6 -C₆H₆)Ru(C₆H₄-2-(*R*)-CH(Me)NMe₂)PMe₂Ph]⁺PF₆⁻ (**3a/3b**), of which the configurational stability at the metal center has been established by classical solution techniques, have been analyzed by the ¹³C cross-polarization magic angle spinning (CP-MAS) and ³¹P MAS NMR. The spectra obtained allowed us to detect both isomers and to estimate their respective proportions by ³¹P spectra. This technique was applied to a bulk solid sample of the diastereomers (*S*)_{Ru}- and (*R*)_{Ru}-[(η^6 -C₆H₆)Ru(C₆H₄-2-(*R*)-CH(Me)NMe₂)NCMe]⁺PF₆⁻ (**1a/1b**), which were shown to be configurationally labile by classical solution experiments. Detection of isomer **1a** only in the resulting ¹³C CP-MAS NMR spectrum demonstrated that there has been epimerization of **1b** to **1a** during crystallization, thus confirming the configurational lability at the metal center.

Introduction

Half-sandwich organometallic complexes, with a three-legged piano stool structure containing a stereogenic metal center, have attracted much interest in recent years. They have been used as catalyst precursors in enantioselective catalysis such as in asymmetric Diels–Alder reactions¹ and asymmetric hydrogen transfer.² To gain optimal enantioselection, it is crucial to understand the factors that render the metallic center configurationally stable or labile, and many investigations of the stereochemistry at the metal center have been undertaken.³

To this end, the organometallic complexes must be studied both in solution and in the solid state. Indeed, a mixture of two diastereomers which are in fast equilibrium might well lead to one single isomer in the solid state depending on the respective rates of crystallization of both isomers. Whereas there are many spectroscopic tools available for solution studies, so far X-ray diffraction studies have been the main technique used to obtain information pertaining to the structure of the compounds in the solid state. However, this technique is very limited in that it does not provide any information on the bulk material, leading to misinterpreted results.⁴ This has been established on several occasions.⁵ We therefore report our recent results concerning

the study of two half-sandwich organoruthenium complexes displaying chirality at the metal center. The use of solid-state NMR⁶ has enabled us to obtain information about the diastereomeric ratios of these complexes in the solid state, and thus, it proved to be a valuable technique for the analysis of mixtures of diastereomers.

Experimental Section

All reactions were performed in Schlenk tubes under argon unless otherwise specified. Solvents were dried and distilled under argon prior to use: diethyl ether and *n*-hexane over sodium/benzophenone, dichloromethane and acetonitrile over calcium hydride, and methanol over magnesium. Solution NMR spectra were recorded at 298 K on FT-Bruker AM 300, DRX 400, and ARX 500 spectrometers operating at 400.13 or 500.14 MHz for ¹H, at 100.61 or 125.77 MHz for ¹³C {¹H}, and at 121.51 MHz for ³¹P {¹H}. The chemical shifts are referenced to the residual deuterated solvent peaks. The assignments of the ¹³C {¹H} NMR spectra were made with the aid of ¹H/¹³C heteronuclear single quantum coherence (HSQC) and ¹H/¹³C heteronuclear multiple-bond correlation (HMBC). Solid-state NMR spectra were recorded at 298 K on a FT-Bruker ASX 200 operating at 50.30 MHz for ¹³C and at 80.98 MHz for ³¹P and equipped with a Bruker 4 mm ¹H/X cross-polarization magic angle spinning (CP-MAS) probe. The spinning speed was set to 10 kHz. For the ¹³C CP-MAS experiments, the contact time was in the range of 1–3 ms and the decoupling rf-field during acquisition was fixed at a strength of ~40 kHz with a recycle delay of 3 s. For the ³¹P MAS experiment, the decoupling rf-field was set to ~40 kHz and the recycle delay to 60 s. Column and preparative chromatography were, respectively, performed under argon using Al₂O₃ as support (aluminum oxide 90, Merck) and performed under air using SiO₂ plates as support (silica gel 60 F₂₅₄, Merck). Elemental analyses were performed by the

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Service Central de Microanalyse du CNRS, Strasbourg. Commercial compounds were used as received.

(*S*)_{Ru}⁻ and (*R*)_{Ru}⁻[(η^6 -C₆H₆)Ru(C₆H₄-2-(*R*)-CH(Me)NMe₂)NCMe]⁺PF₆⁻ (**1a** and **1b**). The diastereomeric mixture was synthesized by C–H activation reaction.⁷ The observed ratio for **1a/1b** was 75/25 in CD₃CN, 70/30 in CD₃OD, 67/33 in CDCl₃, and 65/35 in CD₂Cl₂ at room temperature. Anal. Calcd for C₁₈H₂₃N₂RuPF₆: C, 42.10; H, 4.51; N, 5.46. Found: C, 42.31; H, 4.58; N, 5.49. For **1a**, ¹H NMR (CD₃CN, 500.14 MHz): δ 8.15 (dd, 1H, H₆, ³*J* = 7.4 Hz, ⁴*J* = 1.3 Hz), 7.06 (td, 1H, H₅, ³*J* = 7.4 Hz, ⁴*J* = 1.3 Hz), 7.00 (td, 1H, H₄, ³*J* = 7.4 Hz, ⁴*J* = 1.3 Hz), 6.86 (dt, 1H, H₃, ³*J* = 7.4 Hz, ⁴*J* = 1.3 Hz, ⁵*J* = 1.3 Hz), 5.66 (s, 6H, C₆H₆), 3.71 (q, 1H, CHCH₃, ³*J* = 6.7 Hz), 3.17 and 2.47 (2s, 6H, NMe₂), 2.13 (s, CH₃CN⁸), 1.24 (d, 3H, CHCH₃). For ¹³C {¹H} NMR (CD₃CN, 125.77 MHz) and ¹³C CP-MAS NMR (50.30 MHz) results, see Table 3. For **1b**, ¹H NMR (CD₃CN, 500.14 MHz): δ 7.67 (dd, 1H, H₆, ³*J* = 7.3 Hz, ⁴*J* = 1.4 Hz), 7.09 (td, 1H, H₅, ³*J* = 7.3 Hz, ⁴*J* = 1.4 Hz), 7.01 (td, 1H, H₄, ³*J* = 7.3 Hz, ⁴*J* = 1.4 Hz), 6.85 (dt, 1H, H₃, ³*J* = 7.3 Hz, ⁴*J* = 1.4 Hz, ⁵*J* = 1.4 Hz), 5.58 (s, 6H, C₆H₆), 3.94 (q, 1H, CHCH₃, ³*J* = 6.8 Hz), 3.33 and 1.89 (2s, 6H, NMe₂), 2.13 (s, CH₃CN⁸), 1.28 (d, 3H, CHCH₃). For ¹³C {¹H} NMR (CD₃CN, 125.77 MHz) results, see Table 3.

(*S*)_{Ru}⁻ and (*R*)_{Ru}⁻[(η^6 -C₆H₆)Ru(C₆H₄-2-(*R*)-CH(Me)NMe₂)Cl] (**2a** and **2b**). The diastereomeric mixture was synthesized by transmercuration⁹ or by substitution reaction (see below). The observed ratio for **2a/2b** was 95/5 in CD₃CN, CD₃OD, CDCl₃, and CD₂Cl₂ at room temperature.

Preparation of 2a/2b by Substitution Reaction. A yellow suspension of **1a/1b** (0.1 g, 0.195 mmol) and KCl (0.2 g, 2.7 mmol) in MeOH (30 mL) was stirred at room temperature. After 3 h, an aliquot of the solution was removed by syringe, concentrated in vacuo, and redissolved in CDCl₃ for ¹H NMR measurement. The resulting spectrum indicated complete conversion of **1a/1b** to **2a/2b**. Complete characterization of **2a/2b** can be found in ref 9. For **2a**, ¹³C CP-MAS NMR (50.30 MHz): δ 167.9 (C1), 150.7 (C2), 137.9 (C6), 126.3 (C5), 123.9 (C4), 122.6 (C3), 86.6 (C₆H₆), 66.2 (CHCH₃), 50.5 and 48.0 (NMe₂), 10.4 (CHCH₃).

(*S*)_{Ru}⁻ and (*R*)_{Ru}⁻[(η^6 -C₆H₆)Ru(C₆H₄-2-(*R*)-CH(Me)NMe₂)PMe₂Ph]⁺PF₆⁻ (**3a** and **3b**) **Preparation of the 60/40 Diastereomeric Mixture (Method 1).** An orange suspension of **2a/2b** (0.200 g, 0.55 mmol), PMe₂Ph (0.313 mL, 2.2 mmol), and KPF₆ (0.202 g, 1.1 mmol) was stirred in CH₂Cl₂ (10 mL) for 15 h at room temperature. The resulting reaction mixture was dried in vacuo and washed with *n*-hexane (3 \times 10 mL) to remove excess PMe₂Ph. The yellow residue was then redissolved in CH₂Cl₂ (3 mL) and filtered over Al₂O₃ (10 cm \times 3 cm) using CH₂Cl₂/MeOH (98/2) as eluent. A yellow fraction was collected and concentrated in vacuo to a minimum of solvent (1–2 mL). A yellow solid (0.260 g, **3a/3b** ratio of 60/40 in CD₃CN and CDCl₃, 77% yield) was precipitated by addition of *n*-hexane. Anal. Calcd for C₂₄H₃₁NF₆P₂-Ru: C, 47.22; H, 5.12; N, 2.29. Found: C, 47.34; H, 4.94; N, 2.38. For **3a**, ¹H NMR (CDCl₃, 400.13 MHz): δ 7.71 (dt, 1H, H₆, ³*J* = 7.5 Hz, ⁴*J* = 1.5 Hz, ⁵*J*_{P–H} = 1.5 Hz), 7.33 (ttd, 1H, H₁₆, ³*J* = 7.5 Hz, ⁴*J* = 1.3 Hz, ⁵*J*_{P–H} = 1.8 Hz), 7.21 (tdd, 2H, H₁₅ and H₁₇, ³*J* = 7.5 Hz, ³*J* = 7.1 Hz, ⁴*J*_{P–H} = 2.4 Hz), 7.13 (tdd, 1H, H₅ or H₄, ³*J* = 7.5 Hz, ⁴*J* = 1.5 Hz, *J*_{P–H} = 0.9 Hz), 7.05 (tt, 1H, H₄ or H₅, ³*J* = 7.5 Hz, ⁴*J* = 1.5 Hz, *J*_{P–H} = 1.5 Hz), 6.86 (tdd, 2H, H₁₄ and H₁₈, ³*J* = 7.1 Hz, ⁴*J* = 1.3 Hz, ⁵*J*_{P–H} = 8.4 Hz), 6.61 (dt, 1H, H₃, ³*J* = 7.5 Hz, ⁴*J* = 1.5 Hz, ⁵*J* = 1.5 Hz), 5.71 (d, 6H, C₆H₆, ³*J*_{P–H} = 1.1 Hz), 2.96 and 2.49 (d and s, 6H, NMe₂, ⁴*J*_{P–H} = 1.4 Hz), 2.50 (q, 1H, CHCH₃, ³*J* = 6.6 Hz), 1.98 and 1.61 (2d, 6H, PMe₂, ²*J*_{P–H} = 9.0 and 9.4 Hz), 0.92 (d, 3H, CHCH₃). For ¹³C {¹H} NMR (CDCl₃, 100.61 MHz) and ¹³C CP-MAS NMR (50.30 MHz) results, see Table 2. ³¹P {¹H} NMR (CDCl₃, 121.51 MHz): δ 4.31 (s, PMe₂Ph), –144.29 (sept, PF₆⁻, ¹*J*_{P–F} = 712.1 Hz). ³¹P MAS NMR (80.98 MHz): δ 6.35 (s + m, PMe₂Ph, ¹*J*_{Ru–P} = 197 Hz), –143.99 (sept, PF₆⁻, ¹*J*_{P–F} = 714.4 Hz). For **3b**, ¹H NMR

(CDCl₃, 400.13 MHz): δ 7.78 (tdd, 2H, H₁₄ and H₁₈, ³*J* = 7.1 Hz, ⁴*J* = 1.3 Hz, ⁵*J*_{P–H} = 8.4 Hz), 7.57 (tdd, 2H, H₁₅ and H₁₇, ³*J* = 7.3 Hz, ³*J* = 7.1 Hz, ⁴*J*_{P–H} = 2.0 Hz), 7.50 (ttd, 1H, H₁₆, ³*J* = 7.3 Hz, ⁴*J* = 1.3 Hz, ⁵*J*_{P–H} nr), 7.42 (d, 1H, H₆, ³*J* = 7.5 Hz), 7.13 (t, 1H, H₅ or H₄, ³*J* = 7.5 Hz), 7.06 (td, 1H, H₄ or H₅, ³*J* = 7.5 Hz, ⁴*J* = 1.2 Hz), 6.87 (dd, 1H, H₃, ³*J* = 7.5 Hz, ⁴*J* = 1.2 Hz), 5.76 (d, 6H, C₆H₆, ³*J*_{P–H} = 0.9 Hz), 4.05 (q, 1H, CHCH₃, ³*J* = 6.6 Hz), 3.17 and 1.79 (s and d, 6H, NMe₂, ⁴*J*_{P–H} = 4.0 Hz), 1.75 and 1.31 (2d, 6H, PMe₂, ²*J*_{P–H} = 8.6 and 8.8 Hz), 1.26 (d, 3H, CHCH₃). For ¹³C {¹H} NMR (CDCl₃, 100.61 MHz) and ¹³C CP-MAS NMR (50.30 MHz) results, see Table 2. ³¹P {¹H} NMR (CDCl₃, 121.51 MHz): δ 10.00 (s, PMe₂Ph), –144.29 (sept, PF₆⁻, ¹*J*_{P–F} = 712.1 Hz). ³¹P MAS NMR (80.98 MHz): δ 12.52 (s, PMe₂Ph), –143.99 (sept, PF₆⁻, ¹*J*_{P–F} = 714.4 Hz).

Preparation of the 60/40 Diastereomeric Mixture of 3a/3b (Method 2). A yellow solution of **1a/1b** (0.080 g, 0.156 mmol) and PMe₂Ph (0.088 mL, 0.623 mmol) was stirred in CH₂Cl₂ (10 mL) for 15 h at room temperature. The resulting reaction mixture was dried in vacuo and washed with *n*-hexane (3 \times 5 mL) to remove excess PMe₂Ph. The yellow residue was then redissolved in a minimum of CH₂Cl₂ (1 mL), and a yellow solid (0.090 g, **3a/3b** ratio of 60/40 in CD₃CN and CDCl₃, 95% yield) was precipitated by addition of *n*-hexane.

Preparation of the 60/40 Diastereomeric Mixture of 3a/3b (Method 3). The following experiment was performed in a NMR tube. To a yellow solution of **1a/1b** (0.030 g, 0.058 mmol) in CD₃CN (0.5 mL) was added PMe₂Ph (8.3 μ L, 0.058 mmol). After 20 min, ¹H NMR signal integration of the reaction products **3a/3b** and the starting material **1a/1b** indicated 82% conversion with a ratio of 63/37 for **3a/3b**. After 5 h, ¹H NMR measurement only showed **3a** and free ligands ((*R*)-(+)-*N,N*-dimethyl-1-phenylethylamine, PMe₂Ph, and benzene) in a ratio of 64/36 indicating that **3b** had completely decomposed.

Preparation of Pure 3a. An orange suspension of **2a/2b** (0.363 g, 1.0 mmol), PMe₂Ph (0.285 mL, 2.0 mmol), and KPF₆ (0.368 g, 2.0 mmol) was stirred in CH₃CN (15 mL) for 15 h at room temperature. The resulting greenish reaction mixture was dried in vacuo, redissolved in CH₂Cl₂ (2–3 mL), and subjected to column chromatography over Al₂O₃ using Et₂O/*n*-hexane (1/1) as eluent to remove excess ligands and CH₂Cl₂/MeOH (98/2) to collect a yellow fraction. This latter was then concentrated in vacuo to a minimum of solvent (2 mL) and eluted on a SiO₂ preparative plate with CH₂Cl₂/MeOH (95/5). A yellow band was collected, and the product was desorbed with CH₂Cl₂/MeOH (90/10). After filtration, the resulting yellow solution was concentrated to 1–2 mL of solvent, and a yellow solid (0.3 g, **3a**, 49% yield) was precipitated by addition of *n*-hexane.

Preparation of the 80/20, 90/10, and 95/5 Diastereomeric Mixtures, General Procedure. The required solid amounts of **3a** and of **3a/3b** (60/40) were mixed and dissolved in a minimum of CH₂Cl₂. For instance, 0.037 g of **3a/3b** (60/40) and 0.112 g of **3a** were mixed and dissolved in CH₂Cl₂ (2 mL) to give the (90/10) diastereomeric mixture. The resulting yellow solution was stirred for ca. 5–10 min, and a yellow solid was precipitated by addition of *n*-hexane. The thus obtained **3a/3b** ratio was checked by ¹H NMR in CDCl₃ before submitting the solid to ¹³C CP-MAS NMR and ³¹P MAS NMR.

Experimental Procedure for the X-ray Diffraction Analysis of Compound 3a. Reflections were collected on a KappaCCD diffractometer using Mo K α graphite-monochromated radiation (λ = 0.710 73 Å). The structure was solved using direct methods and refined against $|F|$. Hydrogen atoms were introduced as fixed contributors. The absolute structure was determined by refining Flack's *x* parameter (*x* = 0.01(4)). For all computations, the Nonius OpenMoleN package was used.¹⁰

Results and Discussion

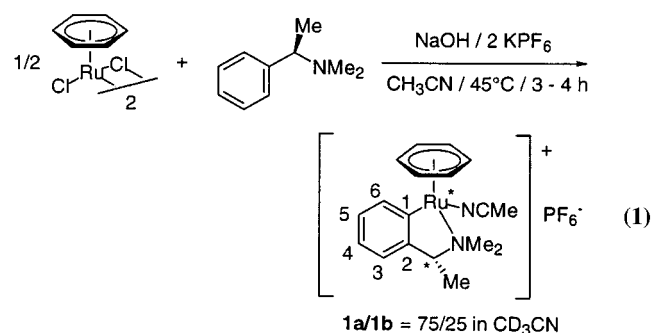
We have recently found that the mixture of diastereomers (*S*)_{Ru}⁻ and (*R*)_{Ru}⁻[(η^6 -C₆H₆)Ru(C₆H₄-2-(*R*)-CH(Me)NMe₂)NCMe]⁺PF₆⁻ (**1a/1b**) could be easily obtained by an intramolecular C–H activation reaction (eq 1). The two diastereomers

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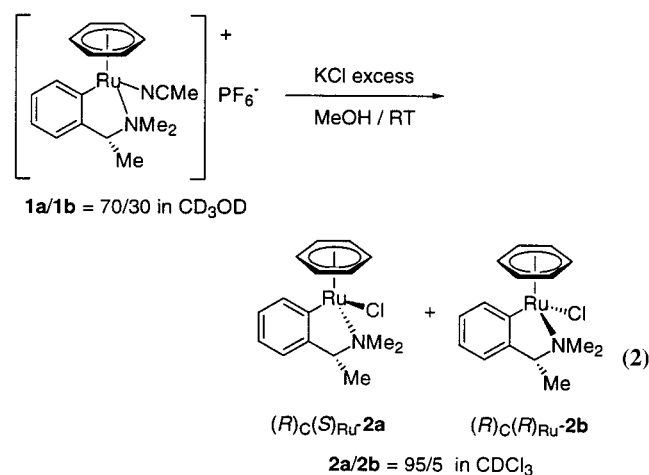
(8) The CH₃CN singlet does not integrate for the expected number of protons because of the CD₃CN/CH₃CN exchange process.

(9) (a) Abbenhuis, H. C. L.; Pfeffer, M.; Sutter, J. P.; de Cian, A.; Fischer, J.; Li Ji, H.; Nelson, J. H. *Organometallics* **1993**, *12*, 4464–4472. (b) Attar, S.; Nelson, J. H.; Fischer, J.; de Cian, A.; Sutter, J. P.; Pfeffer, M. *Organometallics* **1995**, *14*, 4559–4569.

(10) *Open MoleN. Interactive Structure Solution*; Nonius, B. V.: Delft, The Netherlands, 1997.



1a and **1b** were present in CD₃CN solution in a 75/25 ratio.⁷ This mixture, when treated with an excess of KCl in MeOH, afforded the neutral compounds (*S*)_{Ru}- and (*R*)_{Ru}-[(η^6 -C₆H₆)Ru-(C₆H₄-2-(*R*)-CH(Me)NMe₂)Cl] (**2a/2b**) in which the acetonitrile ligand had been substituted by a chloride ion (eq 2). The ob-



served ratio of **2a/2b** in CDCl₃ was the same as previously observed in the same solvent (95/5), this compound being obtained by a completely different route.⁹ Dissolution of **2a/2b** in CD₃CN gave the four diastereomers **2a/2b** and **1a/1b** (in which CH₃CN had been substituted by CD₃CN) in ratios of 95/5 and 75/25, respectively. These results demonstrate a thermodynamic

control of the diastereomeric ratios of both types of complexes. Moreover, the ratio of diastereomers for **1a/1b** was solvent dependent as it dropped to 70/30 in CD₃OD, 67/33 in CDCl₃, and 65/35 in CD₂Cl₂. We have verified that these two diastereomers were in equilibrium in solution via classical ¹H NMR measurements. For instance, 2D ¹H NMR ROESY experiments carried out in CD₃CN showed that, in addition to negative NOE cross-peaks arising from cross-relaxation, the phase sensitive 2D ROESY experiment displayed positive cross-peaks connecting diastereomers **1a** and **1b**. It is noteworthy that one particular *N*-methyl of a given diastereomer interacts only with one *N*-methyl of the corresponding diastereomer. This indicates that no inversion of the N atom is taking place during the process and thus that the NMe₂ unit remains coordinated to the Ru atom during the epimerization of the organoruthenium compound.

The ¹H NMR spectrum of a CD₂Cl₂ solution of a solid sample of **1a/1b** prepared and measured at -80 °C only showed the signals of **1a**. The presence of the second diastereomer **1b** could only be detected when the temperature rose to -40 °C. The epimerization of **1a** to **1b** was studied at -30 °C, following a procedure that was recently described for closely related compounds.^{5c} At this temperature, the following kinetic data were found: $k = 4.2 \times 10^{-5} \text{ s}^{-1}$, $\tau_{1/2} = 276 \text{ min}$, and $\Delta G^\ddagger = 79 \text{ kJ mol}^{-1}$.

It thus appeared that the diastereomeric mixture **1a/1b** consists of only isomer **1a** in the solid state. However, the above-described method used to establish this result proved to be somehow difficult to run and might not be amenable for those species for which the epimerization would be much faster even at low temperature. Therefore, we wondered whether other methods might be available for studying mixtures of two diastereomers in the solid state via a technique that would afford information on the bulk material. In this instance, because infrared or electronic spectra are of little help, we decided to tackle this problem via solid-state NMR techniques. As a starting point, we studied a mixture of diastereomers that are indeed configurationally stable at the metal center.

The phosphine derivatives (*S*)_{Ru}- and (*R*)_{Ru}-[(η^6 -C₆H₆)Ru-(C₆H₄-2-(*R*)-CH(Me)NMe₂)PMe₂Ph]⁺PF₆⁻ (**3a/3b**) were obtained by substitution reactions in different solvents of the acetonitrile or chlorine ligands of diastereomers **1a/1b** or **2a/2b** (eq 3).

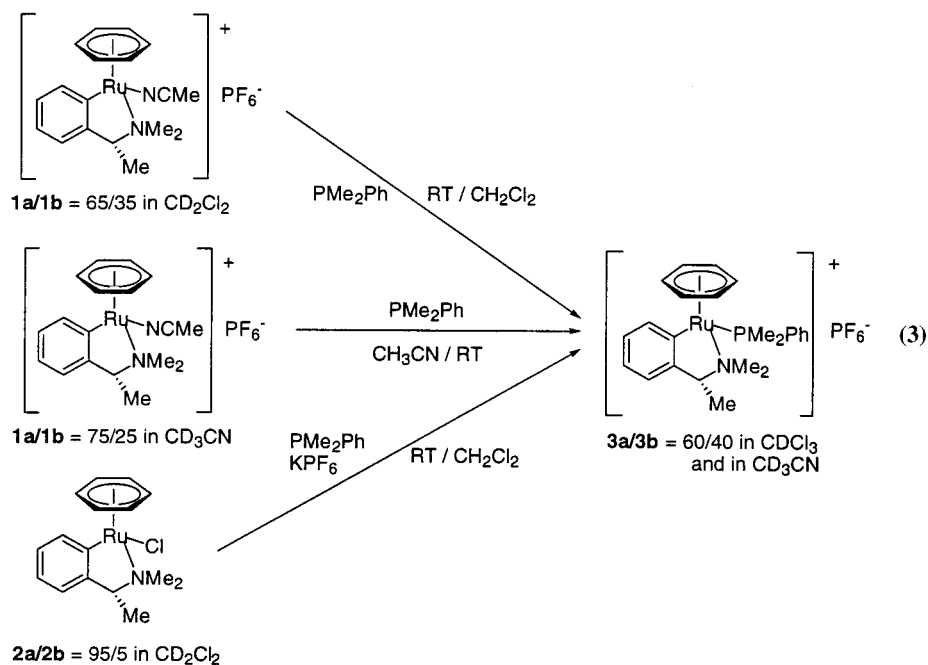
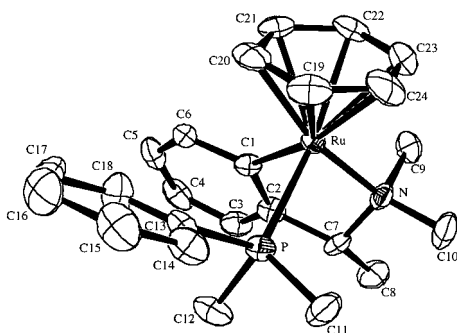


Table 1. Summary of Crystal Data, Data Collection, and Structure Refinement of **3a**

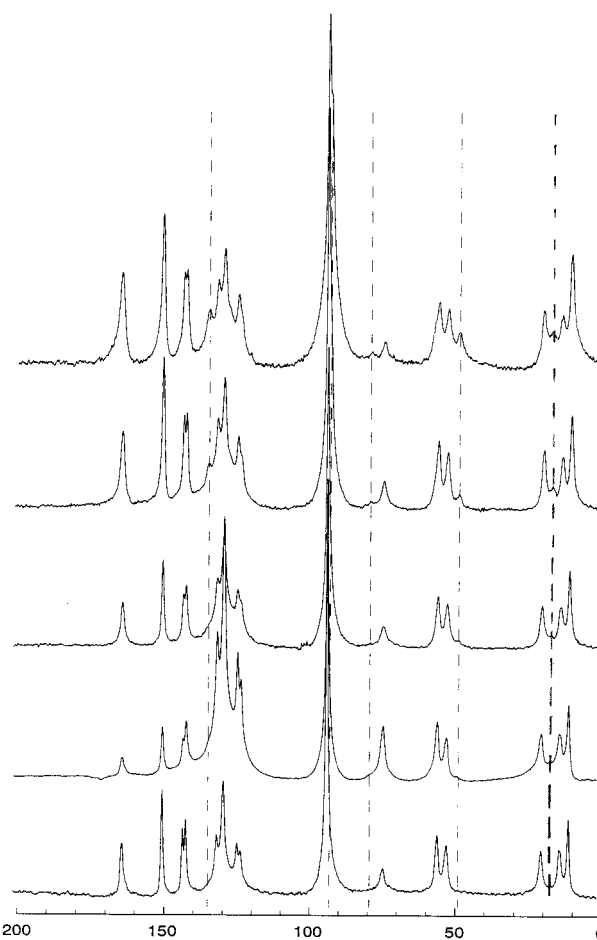
formula	C ₂₄ H ₃₁ NPRu•PF ₆
fw, g mol ⁻¹	610.53
cryst syst	orthorhombic
space group	<i>P</i> 2 ₁ 2 ₁ 2 ₁
<i>a</i> , Å	11.8196(2)
<i>b</i> , Å	13.4161(4)
<i>c</i> , Å	15.8619(5)
<i>V</i> , Å ³	2515.3(2)
<i>Z</i>	4
temp, K	173
λ , Å	0.71073
<i>D</i> _{calcd} , g cm ⁻³	1.61
μ , mm ⁻¹	0.808
final <i>R</i> ^a [<i>I</i> > 3 σ (<i>I</i>)]	<i>R</i> 1 = 0.032, <i>wR</i> 2 = 0.050
<i>R</i> ^a (all data)	<i>R</i> 1 = 0.040, <i>wR</i> 2 = 0.072

$$^a R1 = \sum ||F_o| - |F_c|| / \sum |F_o|. \quad wR2 = [\sum w[(F_o^2 - F_c^2)^2] / \sum w[F_o^2]]^{1/2}.$$

**Figure 1.** ORTEP plot of the crystal structure of **3a** (thermal ellipsoids at 50% probability level). The PF₆ anion and the hydrogen atoms are omitted for clarity. Selected bond distances (Å) and bond angles (deg) are as follows: Ru–P 2.343(1), Ru–N 2.198(4), Ru–C1 2.058(5), N–Ru–P 96.7(1), C1–Ru–P 83.6(1), C1–Ru–N 77.2(2).

Irrespective of the starting complexes and the solvents used, the same diastereomeric ratio of 60/40 was always observed; of note is that this ratio was the same in CDCl₃ and CD₃CN. When the reaction was run in acetonitrile, the minor isomer **3b** which was initially formed started to decompose after ca. 2 h in solution, this decomposition being complete after ca. 5–10 h, thus allowing the isolation of the pure diastereomer **3a** which did not epimerize. Yellow crystals of **3a** suitable for an X-ray structure determination were obtained by slow diffusion of *n*-hexane into a CH₂Cl₂ solution of **3a**. The structure confirmed the *R* configuration of the chiral carbon and established the *S* configuration of the stereogenic ruthenium center assuming the following priority numbers:¹¹ 1 (η^6 -C₆H₆), 2 (PMe₂Ph), 3 (NMe₂), and 4 (C phenyl). Crystallographic data and an ORTEP plot of the crystal structure are given in Table 1 and Figure 1.

As one could well anticipate from the selective decomposition of **3b**, analyses of the mixture **3a/3b** by 1D ¹H NMR NOE showed that **3a** and **3b** were not in equilibrium in solution. Thus, samples of **3a/3b** were good candidates for checking the validity of using solid-state NMR to achieve our goal. We have used the following five solid samples: the pure diastereomer **3a**, the 60/40 **3a/3b** mixture obtained by fast precipitation of the solution resulting from the kinetically controlled substitution of MeCN or Cl⁻ by PMe₂Ph, and three other mixtures whose ratios are 80/20, 90/10, and 95/5. These latter were obtained by mixing

**Figure 2.** Overlap of the ¹³C CP-MAS NMR spectra of **3a/3b** in 60/40, 80/20, 90/10, 95/5, and 100/0 ratios (from top to bottom).

3a with the 60/40 **3a/3b** mixture in the required proportions (see Experimental Section).

We studied these samples by ¹³C CP-MAS NMR¹² and ³¹P MAS NMR. We obtained ¹³C CP-MAS spectra with good resolution for all samples studied. For pure **3a**, most of the signals observed in CDCl₃ solution virtually coincide (maximum difference 5.5 ppm) with those in the solid state (Table 2). The 60/40 **3a/3b** mixture displayed, in the solid state, five signals that were not present in the previous sample. These signals appeared at almost the same chemical shifts as those of the minor isomer in CDCl₃ solution (Table 2). The intensity of these five signals decreased for the 80/20 and 90/10 samples so that only three of these signals were seen at ca. 133.5, 47.7, and 15.8 ppm for the latter (Figure 2). These observations allowed us to conclude that the mixture of the two diastereomers **3a/3b** indeed led to two sets of signals. Thus, ¹³C CP-MAS NMR spectroscopy is a valuable and easy-to-perform technique for detecting mixtures of diastereomers in the solid state. However, the 95/5 sample did not allow clear detection of a signal due to the presence of the minor isomer **3b**, and thus, the lower limit of concentration of the minor isomer that can be detected in this particular case appeared to be close to 10%. One may well anticipate that this limit will be different for other samples and could be lower at higher field.

An important issue in the application of an analytical technique is the quantitative reliability of the data. In the case

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Table 2. ^{13}C $\{^1\text{H}\}$ NMR and ^{13}C CP-MAS NMR Data (δ , ppm) for **3a/3b**

product	^{13}C chemical shift (ppm) and (^{13}C – ^{31}P)J (Hz)				
	aromatics ^a	$\eta^6\text{-C}_6\text{H}_6$	CHCH_3	NMe_2	PMe_2
3a^b	159.6 (C1, $^2J = 24.0$)	92.4 ($^2J = 2.5$)	70.9 (CH)	56.3 ($^3J = 4.1$)	18.7 ($^1J = 36.5$)
	150.0 (C2, $^3J = 2.5$)		9.9 (CH_3)	52.5	18.5 ($^1J = 30.7$)
	140.0 (C6)				
	135.8 (C13, $^1J = 42.3$)				
	130.4 (C16, $^4J = 2.5$)				
	129.8 (C14 and C18, $^2J = 9.9$)				
	128.8 (C15 and C17, $^3J = 9.1$)				
	127.1 (C4 or C5, $J = 2.5$)				
	125.2 (C3, $^4J = 2.5$)				
	124.0 (C5 or C4)				
3a^c	162.7 (C1)	92.6	73.1 (CH)	54.6	19.2
	149.1 (C2)		9.9 (CH_3)	51.5	13.0
	142.1, 141.1, 130.4, 128.2, 122.5				
3b^b	163.3 (C1, $^2J = 20.7$)	91.9 ($^2J = 2.5$)	77.4 (CH)	57.6	21.7 ($^1J = 34.0$)
	149.6 (C2)		10.4 (CH_3)	48.3 ($^3J = 7.4$)	15.5 ($^1J = 31.5$)
	140.0 (C6, $^3J = 8.3$)				
	136.2 (C13, $^1J = 39.8$)				
	131.3 (C16, $^4J = 2.5$)				
	131.0 (C14 and C18, $^2J = 10.7$)				
	130.0 (C15 and C17, $^3J = 7.5$)				
	127.4 (C4 or C5)				
	124.4 (C3)				
	124.1 (C5 or C4, $J = 2.5$)				
3a/3b^{c,d}	163.3, 149.3, 142.2, 141.2,	92.5	77.6 (CH) ^e	54.6	19
	133.5, ^e 130.6, 128.2, 123.4		73.4 (CH)	51.4	15.8 ^e
			9.6 (CH_3)	47.7 ^e	12.4

^a The aryl carbon numbering scheme follows that depicted in the ORTEP plot. ^b ^{13}C $\{^1\text{H}\}$ NMR data recorded at 100.61 MHz in CDCl_3 . ^c ^{13}C CP-MAS NMR data recorded at 50.30 MHz. ^d **3a/3b** ratio equals 60/40. ^e Peaks attributed to **3b**.

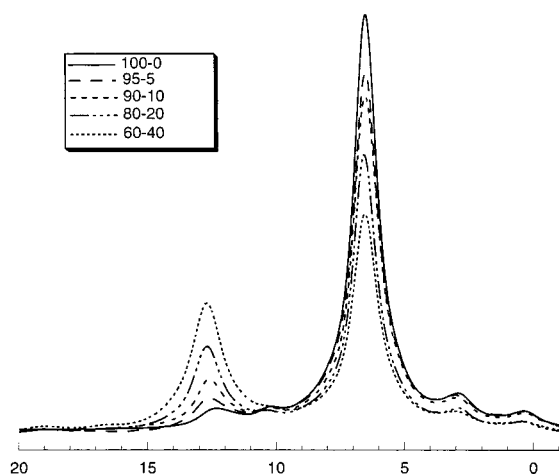


Figure 3. Overlap of the ^{31}P MAS NMR spectra of **3a/3b** in 60/40, 80/20, 90/10, 95/5, and 100/0 ratios. The signal of the PF_6 anion has been omitted for clarity.

of the cross-polarization experiment, the carbon magnetization comes from the proton reservoir. Thus, it has long been recognized that the signal intensities may disagree with the atomic ratios.¹³ On the other hand, the MAS technique gives a quantifiable signal. Indeed, ^{31}P MAS NMR spectroscopy of the same samples as above proved to be much more efficient. Pure **3a** showed two sets of signals at 6.35 and -143.99 ppm for PMe_2Ph and PF_6^- , respectively. The signal of PMe_2Ph was the superimposition of a singlet and a six-line 1:1:1:1:1:1 multiplet due to $^1J(^{99}\text{Ru}-^{31}\text{P})$ coupling.¹⁴ All the other samples (even

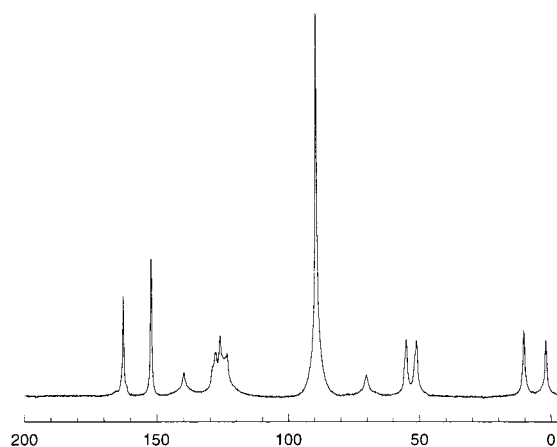


Figure 4. ^{13}C CP-MAS NMR spectrum of **1a**.

with a 95/5 ratio) displayed clearly two signals for the PMe_2Ph unit, thus indicating the presence of the two isomers (Figure 3). Moreover, in these cases, the integration of the signals made it possible to calculate the ratio of the isomers, and this led to results close to those expected.¹⁵

We had thus a new tool for studying the **1a/1b** mixture in the solid state. The required sample was obtained by addition of diethyl ether and *n*-hexane in an acetonitrile solution of **1a/1b**. This resulted in almost instantaneous ($t < 1$ s) precipitation of the organoruthenium species; note that more than 90% of the dissolved **1a/1b** mixture had thus been precipitated. This was done in order to avoid a slow crystallization which might have favored the formation of one isomer only.

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(15) Integration: 60/40 = 58/42; 80/20 = 74/26; 90/10 = 89/11; 95/5 = 92/8 \pm 5%; 100/0 = 100/0 \pm 5%. The intensities of the small spinning sidebands were neglected for integration.

Table 3. ^{13}C $\{^1\text{H}\}$ NMR and ^{13}C CP-MAS NMR Data (δ ppm) of **1a/1b**

product	^{13}C chemical shift				
	aromatics ^a	$\eta^6\text{-C}_6\text{H}_6$	CHCH_3	NMe_2	CH_3CN
1a ^b	162.5 (C1)	89.5	71.3 (CH)	54.5	118.3 (CN)
	150.5 (C2)		11.4 (CH_3)	50.9	1.3 (CH_3)
	139.5 (C6)				
	127.2 (C5)				
	124.8 (C4 and C3)				
1b ^b	168.7 (C1)	88.9	77.3 (CH)	56.6	118.3 (CN)
	150.0 (C2)		11.0 (CH_3)	45.7	1.3 (CH_3)
	139.5 (C6)				
	127.2 (C5)				
	124.8 (C4 and C3)				
1a ^{c,d}	162.4 (C1)	89.2	69.9 (CH)	54.7	130–120 nr (CN)
	151.8 (C2)		10.1 (CH_3)	50.9	1.6 (CH_3)
	139.5 (C6)				
	130.0–120.0 nr (C5, C4, and C3)				

^a The numeration of the aryl carbons follows that depicted in eq 1. ^b ^{13}C $\{^1\text{H}\}$ NMR data recorded at 125.77 MHz in CD_3CN . ^c ^{13}C CP-MAS NMR data recorded at 50.30 MHz. ^d The assignments were made using NQS (nonquaternary suppression) and CP with short contact time and by comparison with the solution spectrum.

The ^{13}C CP-MAS NMR spectrum of the thus obtained solid displayed one set of signals that almost coincide with all signals of the major diastereomer **1a** in CD_3CN solution (Table 3 and Figure 4). The maximum deviation between the signals in solution and in the solid state is 1.4 ppm for identified signals. There was no characteristic signal present that could be assigned to the minor isomer **1b**. This was obvious for the signals of the ruthenated aryl carbon, the benzylic carbon, and the methyl carbon atoms of the NMe_2 unit which resonate at chemical shifts significantly different from those of **1a**. As far as the sensitivity of this technique is concerned and assuming that for this compound the sensitivity is analogous to that found for compounds **3a/3b**, solid-state NMR allows us to conclude that the solid-state structure of **1a/1b** consists of mainly isomer **1a**. With no **1b** being detectable, it demonstrates that the **1a/1b** ratio should be at least greater than 90/10.¹⁶ Hence, it is a valuable technique for demonstrating that there has been epimerization

of **1b** to **1a** during crystallization and that the Ru centers in **1a** and **1b** are configurationally labile.

Conclusion

The application of solid-state NMR has allowed us to identify the presence in the solid state of two very closely related species. Hence, it seems that this technique will prove to be quite useful soon for establishing the composition of the bulk solid materials. One may well anticipate that from this starting point further related examples will be studied by this method. However, we have so far failed to apply it to the problem of related cobalt-containing complexes because of large couplings with the ^{59}Co nuclei ($S = 7/2$) leading to overlapping and broad signals.

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Supporting Information Available: X-ray crystallographic data in CIF format. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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(16) To check the influence of the temperature upon the apparent faster crystallization rate of **1a** as compared to that of **1b**, the precipitation of an epimerized solution of **1a/1b** was performed at $-45\text{ }^\circ\text{C}$ in CH_3CN within a very short period of time ($t < 1\text{ s}$) (as suggested by one of the reviewers). This afforded a good yield (ca. 86%) of a solid material that was dissolved and analyzed by ^1H NMR at $-50\text{ }^\circ\text{C}$ in CD_2Cl_2 . This study revealed that the solid obtained consisted of a **1a/1b** mixture in a 94/6 ratio. This simple experiment thus allows us to conclude that, even at low temperature, the apparent rate of crystallization of **1a** is significantly superior to that of **1b**.