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

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Received February 20, 2001

Bulk solid samples of various ratios of the cyclometalated arene ruthenium diastereomers $(S)_{Ru}$- and $(R)_{Ru}$-$[(\eta^6\text{-}C_6H_6)Ru(C_6H_4\text{-}2\text{-}(R)\text{-}CH(Me)NMe_2)PMe_2Ph]^+PF_6^-$ (**3a**/**3b**), of which the configurational stability at the metal center has been established by classical solution techniques, have been analyzed by the ^{13}C cross-polarization magic angle spinning (CP-MAS) and ^{31}P MAS NMR. The spectra obtained allowed us to detect both isomers and to estimate their respective proportions by ^{31}P spectra. This technique was applied to a bulk solid sample of the diastereomers $(S)_{Ru}$- and $(R)_{Ru}$-$[(\eta^6\text{-}C_6H_6)Ru(C_6H_4\text{-}2\text{-}(R)\text{-}CH(Me)NMe_2)NCMe]^+PF_6^-$ (**1a**/**1b**), which were shown to be configurationally labile by classical solution experiments. Detection of isomer **1a** only in the resulting ^{13}C 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 reactions[1] 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 NMR[6] 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 $^{13}C\ \{^1H\}$, and at 121.51 MHz for $^{31}P\ \{^1H\}$. The chemical shifts are referenced to the residual deuterated solvent peaks. The assignments of the $^{13}C\ \{^1H\}$ NMR spectra were made with the aid of $^1H/^{13}C$ heteronuclear single quantum coherence (HSQC) and $^1H/^{13}C$ 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 ^{13}C and at 80.98 MHz for ^{31}P 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 ^{13}C 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 ^{31}P 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 Al_2O_3 as support (aluminum oxide 90, Merck) and performed under air using SiO_2 plates as support (silica gel 60 F_{254}, Merck). Elemental analyses were performed by the

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10.1021/ic010204w CCC: $20.00

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

$(S)_{Ru}$- and $(R)_{Ru}$-[(η^6-C_6H_6)Ru(C_6H_4-2-(R)-CH(Me)NMe_2)NCMe]$^+$$PF_6^-$ (1a and 1b). The diastereomeric mixture was synthesized by C−H activation reaction.[7] The observed ratio for **1a**/**1b** was 75/25 in CD_3CN, 70/30 in CD_3OD, 67/33 in $CDCl_3$, and 65/35 in CD_2Cl_2 at room temperature. Anal. Calcd for $C_{18}H_{23}N_2RuPF_6$: C, 42.10; H, 4.51; N, 5.46. Found: C, 42.31; H, 4.58; N, 5.49. For **1a**, ^1H NMR (CD_3CN, 500.14 MHz): δ 8.15 (dd, 1H, H6, $^3J = 7.4$ Hz, $^4J = 1.3$ Hz), 7.06 (td, 1H, H5, $^3J = 7.4$ Hz, $^4J = 1.3$ Hz), 7.00 (td, 1H, H4, $^3J = 7.4$ Hz, $^4J = 1.3$ Hz), 6.86 (dt, 1H, H3, $^3J = 7.4$ Hz, $^4J = 1.3$ Hz, $^5J = 1.3$ Hz), 5.66 (s, 6H, C_6H_6), 3.71 (q, 1H, C*H*CH_3, $^3J = 6.7$ Hz), 3.17 and 2.47 (2s, 6H, NMe_2), 2.13 (s, CH_3CN[8]), 1.24 (d, 3H, CHC*H*$_3$). For ^{13}C {^1H} NMR (CD_3CN, 125.77 MHz) and ^{13}C CP-MAS NMR (50.30 MHz) results, see Table 3. For **1b**, ^1H NMR (CD_3CN, 500.14 MHz): δ 7.67 (dd, 1H, H6, $^3J = 7.3$ Hz, $^4J = 1.4$ Hz), 7.09 (td, 1H, H5, $^3J = 7.3$ Hz, $^4J = 1.4$ Hz), 7.01 (td, 1H, H4, $^3J = 7.3$ Hz, $^4J = 1.4$ Hz), 6.85 (dt, 1H, H3, $^3J = 7.3$ Hz, $^4J = 1.4$ Hz, $^5J = 1.4$ Hz), 5.58 (s, 6H, C_6H_6), 3.94 (q, 1H, C*H*CH_3, $^3J = 6.8$ Hz), 3.33 and 1.89 (2s, 6H, NMe_2), 2.13 (s, CH_3CN[8]), 1.28 (d, 3H, CHC*H*$_3$). For ^{13}C {^1H} NMR (CD_3CN, 125.77 MHz) results, see Table 3.

$(S)_{Ru}$- and $(R)_{Ru}$-[(η^6-C_6H_6)Ru(C_6H_4-2-(R)-CH(Me)NMe_2)Cl] (2a and 2b). The diastereomeric mixture was synthesized by transmercuration[9] or by substitution reaction (see below). The observed ratio for **2a**/**2b** was 95/5 in CD_3CN, CD_3OD, $CDCl_3$, and CD_2Cl_2 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 $CDCl_3$ 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**, ^{13}C 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 (C_6H_6), 66.2 (*C*HCH_3), 50.5 and 48.0 (NMe_2), 10.4 (CH*C*H_3).

$(S)_{Ru}$- and $(R)_{Ru}$-[(η^6-C_6H_6)Ru(C_6H_4-2-(R)-CH(Me)NMe_2)PMe_2Ph]$^+$$PF_6^-$ (3a and 3b) Preparation of the 60/40 Diastereomeric Mixture (Method 1). An orange suspension of **2a**/**2b** (0.200 g, 0.55 mmol), PMe_2Ph (0.313 mL, 2.2 mmol), and KPF_6 (0.202 g, 1.1 mmol) was stirred in CH_2Cl_2 (10 mL) for 15 h at room temperature. The resulting reaction mixture was dried in vacuo and washed with *n*-hexane (3 × 10 mL) to remove excess PMe_2Ph. The yellow residue was then redissolved in CH_2Cl_2 (3 mL) and filtered over Al_2O_3 (10 cm × 3 cm) using CH_2Cl_2/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 CD_3CN and $CDCl_3$, 77% yield) was precipitated by addition of *n*-hexane. Anal. Calcd for $C_{24}H_{31}NF_6P_2Ru$: C, 47.22; H, 5.12; N, 2.29. Found: C, 47.34; H, 4.94; N, 2.38. For **3a**, ^1H NMR ($CDCl_3$, 400.13 MHz): δ 7.71 (dt, 1H, H6, $^3J = 7.5$ Hz, $^4J = 1.5$ Hz, $^4J_{P-H} = 1.5$ Hz), 7.33 (ttd, 1H, H16, $^3J = 7.5$ Hz, $^4J = 1.3$ Hz, $^5J_{P-H} = 1.8$ Hz), 7.21 (tdd, 2H, H15 and H17, $^3J = 7.5$ Hz, $^3J = 7.1$ Hz, $^4J_{P-H} = 2.4$ Hz), 7.13 (tdd, 1H, H5 or H4, $^3J = 7.5$ Hz, $^4J = 1.5$ Hz, $J_{P-H} = 0.9$ Hz), 7.05 (tt, 1H, H4 or H5, $^3J = 7.5$ Hz, $^4J = 1.5$ Hz, $J_{P-H} = 1.5$ Hz), 6.86 (tdd, 2H, H14 and H18, $^3J = 7.1$ Hz, $^4J = 1.3$ Hz, $^3J_{P-H} = 8.4$ Hz), 6.61 (dt, 1H, H3, $^3J = 7.5$ Hz, $^4J = 1.5$ Hz, $^5J = 1.5$ Hz), 5.71 (d, 6H, C_6H_6, $^3J_{P-H} = 1.1$ Hz), 2.96 and 2.49 (d and s, 6H, NMe_2, $^4J_{P-H} = 1.4$ Hz), 2.50 (q, 1H, C*H*CH_3, $^3J = 6.6$ Hz), 1.98 and 1.61 (2d, 6H, PMe_2, $^2J_{P-H} = 9.0$ and 9.4 Hz), 0.92 (d, 3H, CHC*H*$_3$). For ^{13}C{^1H} NMR ($CDCl_3$, 100.61 MHz) and ^{13}C CP-MAS NMR (50.30 MHz) results, see Table 2. ^{31}P {^1H} NMR ($CDCl_3$, 121.51 MHz): δ 4.31 (s, PMe_2Ph), −144.29 (sept, PF_6^-, $^1J_{P-F} = 712.1$ Hz). ^{31}P MAS NMR (80.98 MHz): δ 6.35 (s + m, PMe_2Ph, $^1J_{Ru-P} = 197$ Hz), −143.99 (sept, PF_6^-, $^1J_{P-F} = 714.4$ Hz). For **3b**, ^1H NMR ($CDCl_3$, 400.13 MHz): δ 7.78 (tdd, 2H, H14 and H18, $^3J = 7.1$ Hz, $^4J = 1.3$ Hz, $^3J_{P-H} = 8.4$ Hz), 7.57 (tdd, 2H, H15 and H17, $^3J = 7.3$ Hz, $^3J = 7.1$ Hz, $^4J_{P-H} = 2.0$ Hz), 7.50 (ttd, 1H, H16, $^3J = 7.3$ Hz, $^4J = 1.3$ Hz, $^5J_{P-H}$ nr), 7.42 (d, 1H, H6, $^3J = 7.5$ Hz), 7.13 (t, 1H, H5 or H4, $^3J = 7.5$ Hz), 7.06 (td, 1H, H4 or H5, $^3J = 7.5$ Hz, $^4J = 1.2$ Hz), 6.87 (dd, 1H, H3, $^3J = 7.5$ Hz, $^4J = 1.2$ Hz), 5.76 (d, 6H, C_6H_6, $^3J_{P-H} = 0.9$ Hz), 4.05 (q, 1H, C*H*CH_3, $^3J = 6.6$ Hz), 3.17 and 1.79 (s and d, 6H, NMe_2, $^4J_{P-H} = 4.0$ Hz), 1.75 and 1.31 (2d, 6H, PMe_2, $^2J_{P-H} = 8.6$ and 8.8 Hz), 1.26 (d, 3H, CHC*H*$_3$). For ^{13}C {^1H} NMR ($CDCl_3$, 100.61 MHz) and ^{13}C CP-MAS NMR (50.30 MHz) results, see Table 2. ^{31}P {^1H} NMR ($CDCl_3$, 121.51 MHz): δ 10.00 (s, PMe_2Ph), −144.29 (sept, PF_6^-, $^1J_{P-F} = 712.1$ Hz). ^{31}P MAS NMR (80.98 MHz): δ 12.52 (s, PMe_2Ph), −143.99 (sept, PF_6^-, $^1J_{P-F} = 714.4$ 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 PMe_2Ph (0.088 mL, 0.623 mmol) was stirred in CH_2Cl_2 (10 mL) for 15 h at room temperature. The resulting reaction mixture was dried in vacuo and washed with *n*-hexane (3 × 5 mL) to remove excess PMe_2Ph. The yellow residue was then redissolved in a minimum of CH_2Cl_2 (1 mL), and a yellow solid (0.090 g, **3a**/**3b** ratio of 60/40 in CD_3CN and $CDCl_3$, 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 CD_3CN (0.5 mL) was added PMe_2Ph (8.3 μL, 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, PMe_2Ph, 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), PMe_2Ph (0.285 mL, 2.0 mmol), and KPF_6 (0.368 g, 2.0 mmol) was stirred in CH_3CN (15 mL) for 15 h at room temperature. The resulting greenish reaction mixture was dried in vacuo, redissolved in CH_2Cl_2 (2−3 mL), and subjected to column chromatography over Al_2O_3 using Et_2O/*n*-hexane (1/1) as eluent to remove excess ligands and CH_2Cl_2/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 SiO_2 preparative plate with CH_2Cl_2/MeOH (95/5). A yellow band was collected, and the product was desorbed with CH_2Cl_2/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 CH_2Cl_2. For instance, 0.037 g of **3a**/**3b** (60/40) and 0.112 g of **3a** were mixed and dissolved in CH_2Cl_2 (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 $CDCl_3$ before submitting the solid to ^{13}C CP-MAS NMR and ^{31}P MAS NMR.

Experimental Procedure for the X-ray Diffraction Analysis of Compound 3a. Reflections were collected on a KappaCCD diffractometer using Mo Kα graphite-monochromated radiation ($\lambda = 0.710\,73$ 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-C_6H_6)Ru(C_6H_4-2-(R)-CH(Me)NMe_2)-NCMe]$^+$$PF_6^-$ (**1a**/**1b**) could be easily obtained by an intramolecular C−H activation reaction (eq 1). The two diasteromers

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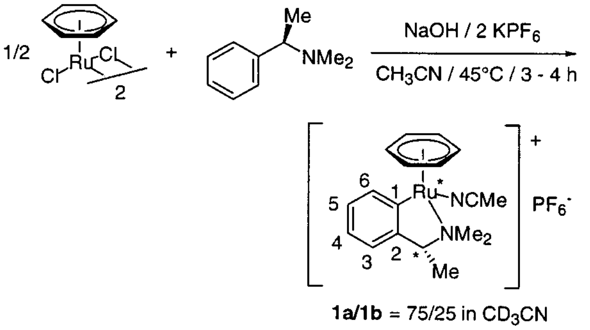
[7] Fernandez, S.; Pfeffer, M.; Ritleng, V.; Sirlin, C. *Organometallics* **1999**, *18*, 2390−2394.

[8] The CH_3CN singlet does not integrate for the expected number of protons because of the CD_3CN/CH_3CN exchange process.

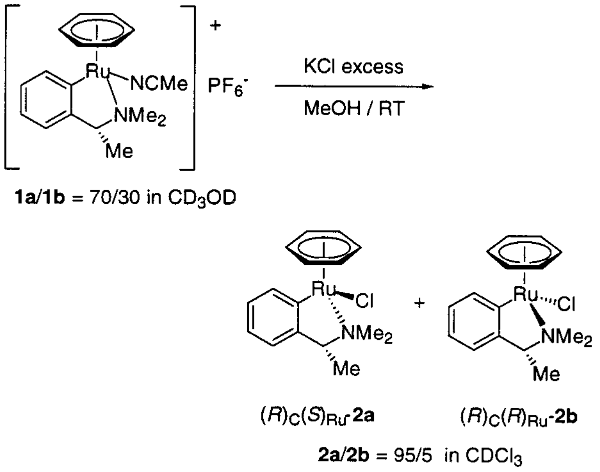
[9] (a) Abbenhuis, H. C. L.; Pfeffer, M.; Sutter, J. P.; de Cian, A.; Fischer, J.; Li Ji, H.; Nelson, J. H. *Organometallics* **1993**, *12*, 4464−4472. (b) Attar, S.; Nelson, J. H.; Fischer, J.; de Cian, A.; Sutter, J. P.; Pfeffer, M. *Organometallics* **1995**, *14*, 4559−4569.

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



(1)

1a and **1b** were present in CD_3CN solution in a 75/25 ratio.[7] This mixture, when treated with an excess of KCl in MeOH, afforded the neutral compounds $(S)_{\text{Ru}}$- and $(R)_{\text{Ru}}$-$[(\eta^6\text{-}C_6H_6)Ru(C_6H_4\text{-}2\text{-}(R)\text{-}CH(Me)NMe_2)Cl]$ (**2a**/**2b**) in which the acetonitrile ligand had been substituted by a chloride ion (eq 2). The observed ratio of **2a**/**2b** in $CDCl_3$ 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 CD_3CN gave the four diastereomers **2a**/**2b** and **1a**/**1b** (in which CH_3CN had been substituted by CD_3CN) 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 CD_3OD, 67/33 in $CDCl_3$, and 65/35 in CD_2Cl_2. 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 CD_3CN 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 NMe_2 unit remains coordinated to the Ru atom during the epimerization of the organoruthenium compound.

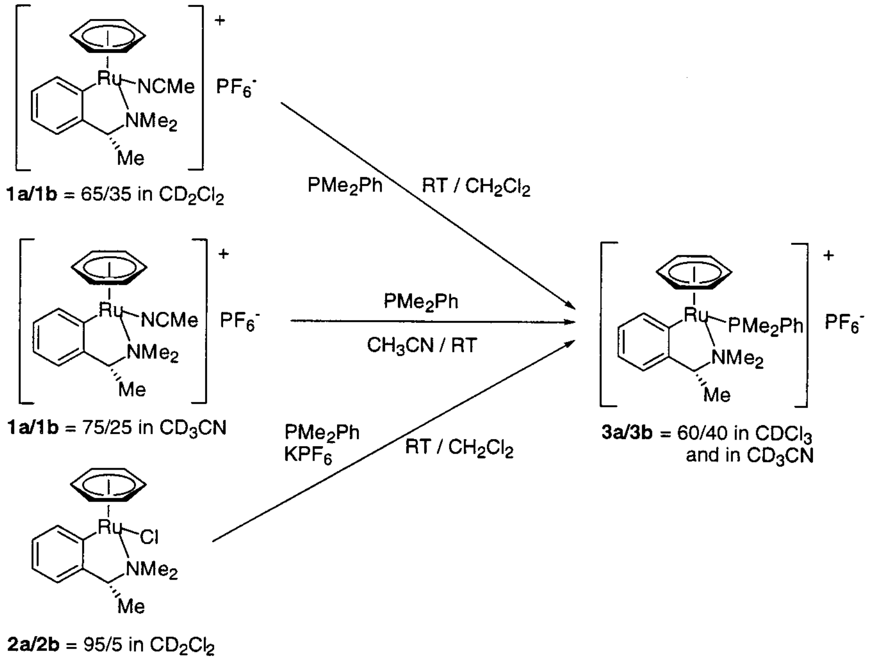


(2)

The ^1H NMR spectrum of a CD_2Cl_2 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: $k = 4.2 \times 10^{-5}\ s^{-1}$, $\tau_{1/2} = 276$ min, and $\Delta G^{\ddagger} = 79\ kJ\ mol^{-1}$.

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 $(S)_{\text{Ru}}$- and $(R)_{\text{Ru}}$-$[(\eta^6\text{-}C_6H_6)Ru(C_6H_4\text{-}2\text{-}(R)\text{-}CH(Me)NMe_2)PMe_2Ph]^+PF_6^-$ (**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).



(3)

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

formula	$C_{24}H_{31}NPRu{\cdot}PF_6$
fw, g mol^{-1}	610.53
cryst syst	orthorhombic
space group	$P2_12_12_1$
a, Å	11.8196(2)
b, Å	13.4161(4)
c, Å	15.8619(5)
V, Å^3	2515.3(2)
Z	4
temp, K	173
λ, Å	0.71073
D_{calcd}, g cm^{-3}	1.61
μ, mm^{-1}	0.808
final R^a [$I > 3\sigma(I)$]	R1 = 0.032, wR2 = 0.050
R^a (all data)	R1 = 0.040, wR2 = 0.672

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

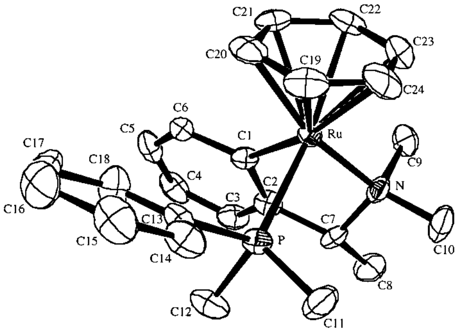


Figure 1. ORTEP plot of the crystal structure of **3a** (thermal ellipsoids at 50% probability level). The PF_6 anion and the hydrogen atoms are omitted for clarity. Selected bond distances (Å) and bond angles (deg) are as follows: Ru−P 2.343(1), Ru−N 2.198(4), Ru−C1 2.058(5), N−Ru−P 96.7(1), C1−Ru−P 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 $CDCl_3$ and CD_3CN. 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 CH_2Cl_2 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-C_6H_6), 2 (PMe_2Ph), 3 (NMe_2), 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 PMe_2Ph, and three other mixtures whose ratios are 80/20, 90/10, and 95/5. These latter were obtained by mixing **3a** with the 60/40 **3a**/**3b** mixture in the required proportions (see Experimental Section).

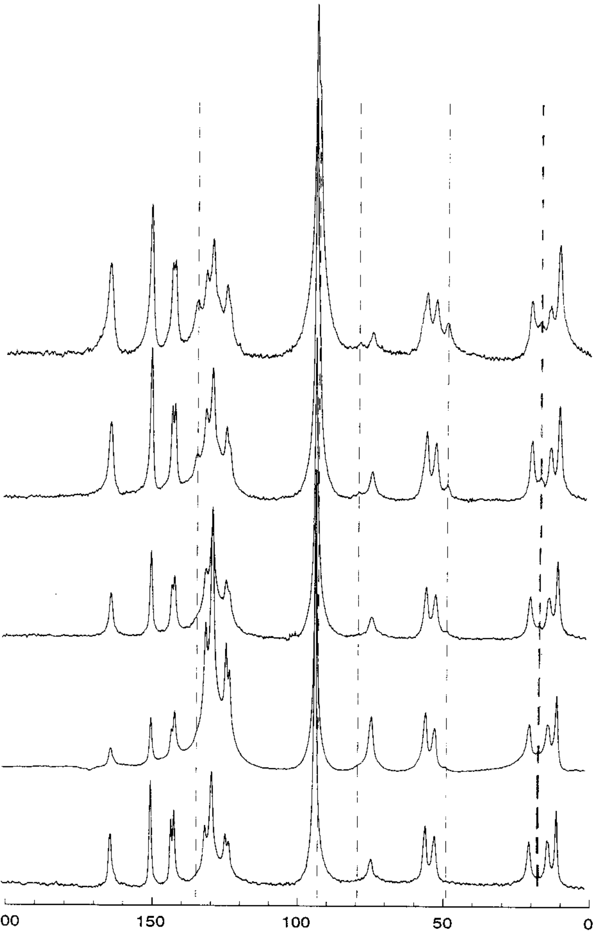


Figure 2. Overlap of the ^{13}C CP-MAS NMR spectra of **3a/3b** in 60/40, 80/20, 90/10, 95/5, and 100/0 ratios (from top to bottom).

We studied these samples by ^{13}C CP-MAS NMR[12] and ^{31}P MAS NMR. We obtained ^{13}C CP-MAS spectra with good resolution for all samples studied. For pure **3a**, most of the signals observed in $CDCl_3$ 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 $CDCl_3$ 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, ^{13}C 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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[11] (a) Lecomte, C.; Dusausoy, Y.; Protas, J.; Tirouflet, J.; Dormond, A. *J. Organomet. Chem.* **1974**, *73*, 67−76. (b) Brunner, H. *Enantiomer*, **1997**, *2*, 133.

[12] Fyfe, C. A. *Solid State NMR for Chemists*; CFC Press: Guelph, Ontario, Canada, 1983.

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

	^{13}C chemical shift (ppm) and ($^{13}C-^{31}P$)J (Hz)				
product	aromatics[a]	η^{6}-C_6H_6	CHCH$_3$	NMe$_2$	PMe$_2$
3a[b]	159.6 (C1, $^{2}J = 24.0$) 150.0 (C2, $^{3}J = 2.5$) 140.0 (C6) 135.8 (C13, $^{1}J = 42.3$) 130.4 (C16, $^{4}J = 2.5$) 129.8 (C14 and C18, $^{2}J = 9.9$) 128.8 (C15 and C17, $^{3}J = 9.1$) 127.1 (C4 or C5, $J = 2.5$) 125.2 (C3, $^{4}J = 2.5$) 124.0 (C5 or C4)	92.4 ($^{2}J = 2.5$)	70.9 (CH) 9.9 (CH$_3$)	56.3 ($^{3}J = 4.1$) 52.5	18.7 ($^{1}J = 36.5$) 18.5 ($^{1}J = 30.7$)
3a[c]	162.7 (C1) 149.1 (C2) 142.1, 141.1, 130.4, 128.2, 122.5	92.6	73.1 (CH) 9.9 (CH$_3$)	54.6 51.5	19.2 13.0
3b[b]	163.3 (C1, $^{2}J = 20.7$) 149.6 (C2) 140.0 (C6, $^{3}J = 8.3$) 136.2 (C13, $^{1}J = 39.8$) 131.3 (C16, $^{4}J = 2.5$) 131.0 (C14 and C18, $^{2}J = 10.7$) 130.0 (C15 and C17, $^{3}J = 7.5$) 127.4 (C4 or C5) 124.4 (C3) 124.1 (C5 or C4, $J = 2.5$)	91.9 ($^{2}J = 2.5$)	77.4 (CH) 10.4 (CH$_3$)	57.6 48.3 ($^{3}J = 7.4$)	21.7 ($^{1}J = 34.0$) 15.5 ($^{1}J = 31.5$)
3a/3b[c,d]	163.3, 149.3, 142.2, 141.2, 133.5,[e] 130.6, 128.2, 123.4	92.5 91.5[e]	77.6 (CH)[e] 73.4 (CH) 9.6 (CH$_3$)	54.6 51.4 47.7[e]	19 15.8[e] 12.4

[a] The aryl carbon numbering scheme follows that depicted in the ORTEP plot. [b] ^{13}C {^{1}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**.

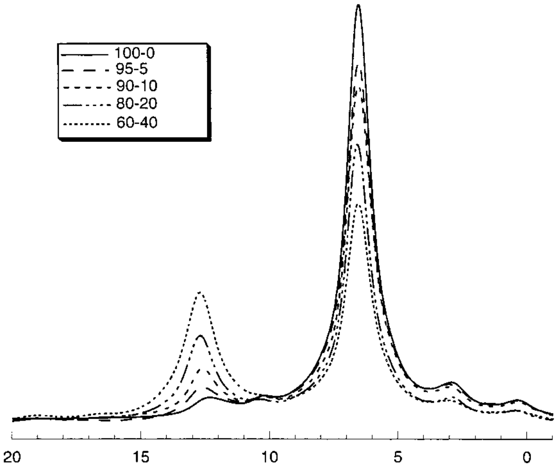

Figure 3. Overlap of the ^{31}P MAS NMR spectra of **3a/3b** in 60/40, 80/20, 90/10, 95/5, and 100/0 ratios. The signal of the PF$_6$ anion has been omitted for clarity.

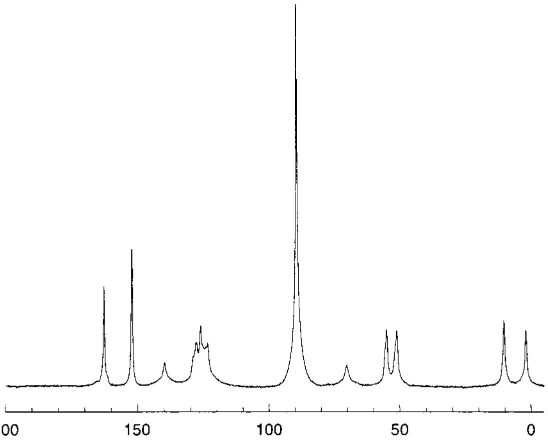

Figure 4. ^{13}C CP-MAS NMR spectrum of **1a**.

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$_2$Ph and PF$_6^-$, respectively. The signal of PMe$_2$Ph was the superimposition of a singlet and a six-line 1:1:1:1:1:1 multiplet due to $^{1}J(^{99}Ru-^{31}P)$ coupling.[14] All the other samples (even with a 95/5 ratio) displayed clearly two signals for the PMe$_2$Ph 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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(13) Alemany, L. B.; Grant, D. M.; Pugmire, R. J.; Alder, T. D.; Zilm, K. W. *J. Am. Chem. Soc.* **1983**, *105*, 2133-2141.

(14) Eichele, K.; Wasylishen, R. E.; Corrigan, J. F.; Doherty, S.; Sun, Y.; Carty, A. J. *Inorg. Chem.* **1993**, *32*, 121−123.

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

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

	^{13}C chemical shift				
product	aromatics[a]	η^6-C_6H_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] $^{13}C\ \{^{1}H\}$ 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.

Acknowledgment. Financial support of this work by the Ministère de l’Education Nationale, de la Recherche et de la Technologie (fellowship for V.R. and P.B.) is acknowledged. Dr. R. Graff and Dr. J.-D. Sauer are gratefully acknowledged for ^{1}H NMR variable temperature and 2D ^{1}H NMR ROESY experiments, Dr. A. de Cian for X-ray diffraction study, and Dr. B. Meurer for allowing use of the ASX 200 spectrometer.

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 °C in CH_3CN within a very short period of time ($t < 1$ 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 ^{1}H NMR at −50 °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**.