Organometallics **2000,** *19,* 2423−2426

Correspondence

Optically Active Transition Metal Complexes. 126.[1] *ortho*-Metalated Chiral-at-Metal Half-Sandwich (η^6-Arene)ruthenium Complexes Are Configurationally More Labile at the Metal Center than Described: Correction of Published Papers

Sir: Half-sandwich (η^6-arene)ruthenium(II) complexes have attracted much interest in the last few years. They have been used as catalyst precursors in organic transformations,[2] and their pseudotetrahedral geometry makes them particularly suitable for investigations of the stereochemistry at the metal center.[3]

In a paper[4] published in 1995 in this journal, entitled "Metallacycles with Stereogenic Metal Centers: Synthesis and Characterization of Diastereomeric Cycloruthenated Chiral Amines", Attar et al. described the diastereomers of the compounds [(η^6-arene)Ru(LL*)Cl], with η^6-arene = benzene, toluene, cymene (1-Me-4-^{i}Pr-C_6H_4) and LL* = *ortho*-metalated (R_C)-(+)- or (S_C)-(−)-*N*,*N*-dimethyl-1-phenylethylamine, which differ only in the metal configuration.

Essential conclusions from their study were as follows. In the reaction of enantiomerically pure (R_C)- or (S_C)-{HgCl[$C_6H_4CH(Me)NMe_2$]} with [(η^6-arene)$RuCl_2$]$_2$ in CH_3CN at ambient temperatures mixtures of two diastereomeric ruthenium half-sandwich complexes are formed in a transmetalation reaction. The complexes were characterized by ^1H and ^{13}C NMR, UV, CD, IR, X-ray, and elemental analysis. These data are in accord with our results. However, because crucial stereochemical experiments have been carried out incorrectly or not carried out at all, the following statements in ref 3 are wrong conclusions or misinterpretations. "The ^1H NMR spectra obtained on $CDCl_3$, acetone-d_6, and CD_3NO_2 solutions of these diastereomeric ruthenacycles are independent of time (days) and temperature (−20 to 50 °C), indicating their configurational stability." Because there is no "observable epimerization in these ruthenacycles in solution over a period of several days at ambient temperatures, hence, their configurational stability has been established." "The ^1H NMR spectra obtained on $CDCl_3$ solutions of the bulk samples from which the X-ray-quality crystals were isolated show the existence of two diastereomers in the same ratio as that observed before crystallization." "Each bulk-crystallized sample is a solid mixture of the two diastereomers in a ratio equal to that observed in their solutions." The crystal structure obtained is assigned to the major diastereomer, because "the crystals of this species have a higher statistical chance of being isolated from a mixture". If the fast epimerization at the metal center described below is taken into account, it is a logical consequence that all attempts "to separate the minor diastereomer by column chromatography and/or fractional crystallization have met with failure." These citations are repeated here, because they have been used in identical or similar form in successive papers.[5−8]

Results. Chloro Complexes 1a,b. We synthesized the chloro complexes **1a**,**b** according to the published procedure,[4] using [(η^6-cymene)$RuCl_2$]$_2$ and (S_C)-{HgCl[$C_6H_4CH(Me)NMe_2$]} as the starting materials.[9] Deep red-orange needles were obtained by slow diffusion of a 1:1 mixture of ether/hexane into a CH_2Cl_2 solution of the chloro complexes **1a**,**b**. The X-ray structure analysis confirmed the S_C configuration of the chiral carbon atom of the chelate ligand and established the R_{Ru} configuration of the stereogenic ruthenium atom, specified with the priority sequence η^6-cymene > Cl > N > C.[10] Solutions of these crystals in $CDCl_3$ exhibited at room temperature in the ^1H NMR spectrum the signals of both diastereomers (R_{Ru},S_C)-**1a** and (S_{Ru},S_C)-**1b** in a ratio of 83:17. These results were in accord with ref 4.

However, the ^1H NMR spectrum of a CD_2Cl_2 solution of a sample of crystals, prepared and measured at −80 °C, showed only the signals of the major diastereomer **1a**. Measurements at −50, −20, 0, and +21 °C revealed that the second diastereomer **1b** was formed only at higher temperatures (Figure 1). For a detailed analysis of the epimerization (Scheme 1), the conversion of **1a** into the equilibrium mixture **1a** $\rightleftarrows$ **1b** was followed in CD_2Cl_2 solution by ^1H NMR spectroscopy at different temperatures. The ratio **1a**:**1b** was determined by integration of the methyl singlets at 2.38/2.05 ppm for **1a** and 1.87/1.69 ppm for **1b**. The evaluation was

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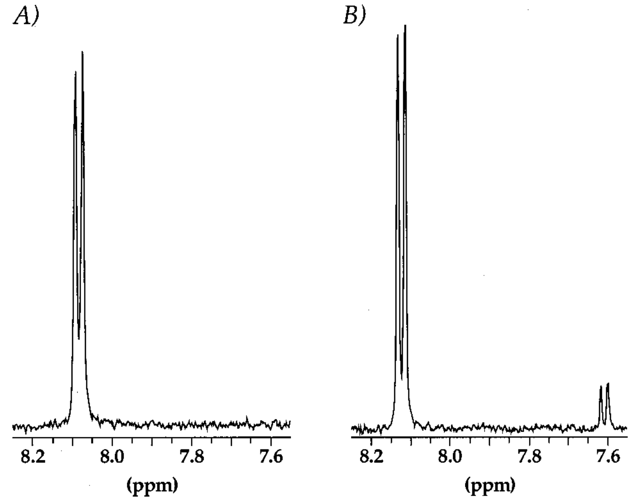


Figure 1. Doublets of the proton in α-position to the ruthenated carbon atom of the chiral ligand in the ^{1}H NMR spectrum (400 MHz, CD_2Cl_2): (A) solution obtained by dissolving crystals of **1a** at −80 °C; (B) same solution after warming to +21 °C.

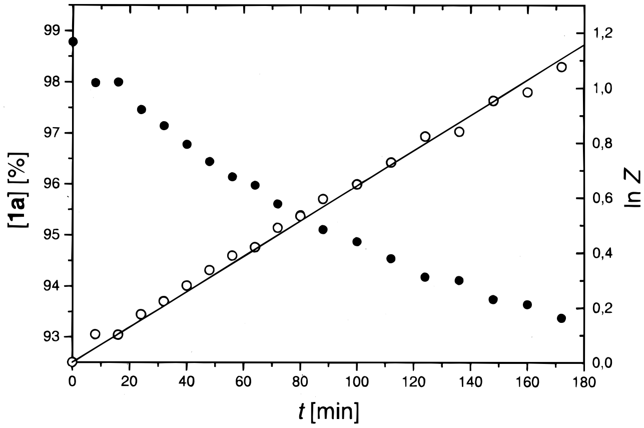
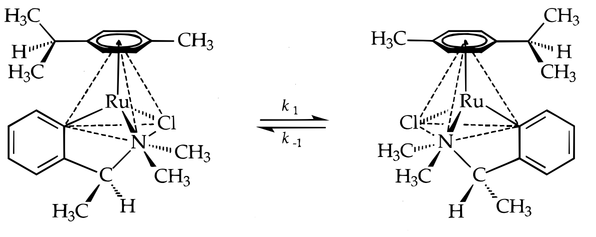


Figure 2. Epimerization of complex **1a** in CD_2Cl_2 at −4 °C (equilibrium ratio **1a**:**1b** = 90:10) and interpretation according to a first-order rate law. $Z = ([\mathbf{1a}]_0 - [\mathbf{1a}]_\infty)/([\mathbf{1a}] - [\mathbf{1a}]_\infty)$.

Scheme 1. Epimerization of the Complexes 1a,b



(R_{Ru},S_C)-**1a** (S_{Ru},S_C)-**1b**

performed with the first-order rate law, using the equilibrium ratios determined after 10 half-lives. A typical plot is shown in Figure 2.

At −4 °C the half-life for approach to the equilibrium **1a** ⇄ **1b** is 107.8 min. The half-life is 50.2 min at +1.5 °C and 33.6 min at +6.6 °C (Table 1). The half-life of 9 min at +11 °C shows that solutions of the complex **1a** cannot be handled at room temperature without a fast change of the metal configuration. Thus, the statement of the authors of ref 4 that “the transmetalation reactions leading to their (the ruthenium complexes) formation are under kinetic, rather than thermodynamic, control” is wrong, as the temperatures and times of the synthesis are very much above the temperatures and times at which epimerization takes place.

Table 1. Kinetic Data of the Approach to the Epimerization Equilibria 1a ⇆ 1b and 2a ⇆ 2b at Various Temperatures Starting from Diastereomerically Pure 1a and 2a, Respectively (CD_2Cl_2 Solution)

T (°C)	k (s^{-1})	$\tau_{1/2}$ (min)	$\Delta G^‡$ (kJ mol^{-1})	$[\mathbf{1a}]_\infty$ or $[\mathbf{2a}]_\infty$ (%)	K_{eq}
		Chloro Complexes **1a**,**b**			
−4.2	1.07×10^{-4}	107.8	86.1	90.6	9.63
+1.5	2.30×10^{-4}	50.2	86.2	88.4	7.64
+6.6	3.44×10^{-4}	33.6	86.9	90.0	9.00
+11.3	1.20×10^{-3}	9.63	85.5	89.4	8.42
		Iodo Complexes **2a**,**b**			
−15.0	1.86×10^{-4}	62.1	81.4	91.6	10.9
−9.6	4.20×10^{-4}	27.5	81.3	91.3	10.5
−4.3	7.60×10^{-4}	15.2	81.7	90.4	9.39

The activation parameters of the epimerization **1a** ⇄ **1b** were derived from the temperature dependence of the rate constants, using the Eyring equation. The enthalpy of activation is 98.1 kJ mol^{-1} and the entropy of activation 43.6 J K^{-1} mol^{-1}.

Iodo Complexes 2a,b. Another paper[5] published 1996 in this journal by the same group, entitled “Diastereoselectivity of Chloride Substitution Reactions of Cycloruthenated (R_C)-(+)- and (S_C)-(−)-Dimethyl(1-phenylethyl)amine”, dealt with the substitution of the chloride ligand in [(η^6-C_6H_6)Ru(LL*)Cl] by iodide to give the corresponding iodo complexes. It was also to these iodo complexes that the authors attributed configurational stability at the metal center.

We synthesized the iodo complexes [(η^6-cymene)Ru(LL*)I] (**2a**,**b**) by adding solid NaI to a solution of **1a**,**b** in methanol. The ^{1}H NMR spectrum of the product showed the two diastereomers in a ratio **2a**:**2b** = 89:11 in CD_2Cl_2 solution at room temperature. The ratio **2a**:**2b** was determined by integration of the methyl singlets at 2.35 and 2.28 ppm for **2a** and **2b**, respectively. Dark red-brown crystals were obtained by slow diffusion of a 1:1 ether/hexane mixture into a CH_2Cl_2 solution of the iodo complexes **2a**,**b**. The ^{1}H NMR spectrum of a solution of these crystals, prepared and measured at −80 °C, exhibited only the signals of the major diastereomer **2a**. The signals of the minor diastereomer **2b** appeared on warming. Table 1 summarizes the results of the epimerization kinetics.

The measured half-lives were 62 min at −15 °C and 27 min at −9.6 °C. The half-life of 15 min at −4 °C shows that the epimerization at room temperature is finished soon after dissolution. Definitely, the iodo complexes **2a**,**b** are not configurationally stable at the metal center. It should be kept in mind that ref 5 dealt with the benzene derivative [(η^6-C_6H_6)Ru(LL*)I], whereas we stayed in the cymene series [(η^6-1-Me-4-^{i}Pr-C_6H_4)-Ru(LL*)I]. We do not expect fundamental differences between the benzene and cymene derivatives as far as the configurational stability/instability at the metal center is concerned.

Discussion. Diastereomers, which differ only in the metal configuration, may be formed under kinetic control or under thermodynamic control.[11] In both cases

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(11) Brunner, H. *Acc. Chem. Res.* **1979**, *12*, 250.

the diastereomer ratios can be close to 1:1 or approach high values.[11] Irrespective of the ratio, the isolation of diastereomerically pure samples or at least diastereomerically enriched samples (compared to the starting composition) should be possible using fractional crystallization or chromatography, including zone cutting, provided the diastereomers are configurationally stable at the metal center. If a diastereomer mixture of whatever composition stubbornly resists separation or enrichment (as in ref 3), the reason may be configurational instability at the metal atom. In this case the configurational stability/instability should be checked with all available techniques, including the dissolution of crystallized samples at low temperatures and the measurement of low-temperature NMR spectra without prior warming. Provided the equilibration between the two diastereoisomers is slow under the conditions of dissolution, this technique shows whether a crystallized sample consists of a pure diastereoisomer or a mixture of the two diastereomers. Depending on the crystallization conditions and the epimerization rate, both situations may be encountered. For the chloro and iodo complexes **1a**,**b** and **2a**,**b** there is a second-order asymmetric transformation.[12] At least under our crystallization conditions pure diastereomers of the chloro and iodo complexes crystallized exclusively. There are many examples known for which an optically pure diastereomer crystallizes, although in solution both diastereomers equilibrate rapidly. It should be mentioned that there are cases in which a major diastereomer dominates the minor diastereomer by more than 90:10 in the diastereomer equilibrium established in solution and, nevertheless, it is the minor diastereomer which crystallizes.[1] The argument that “the bulk-crystallized sample is a solid mixture of the two diastereomers in a ratio equal to that observed in solution”[4] repeated in ref 6 without any further proof implies that there is a relatively high chance to make a misassignment, if a crystal of the minor diastereomer is picked for X-ray structure analysis and the configuration found is ascribed to the major diastereomer, because “the crystals of this species have a higher statistical chance of being isolated”.[4,6]

On the basis of the misinterpreted configurational stability at the metal center in the chloro and iodo complexes **1a,b** and **2a,b**, emphasized throughout refs 4−8, the authors discuss the stereochemistry of the substitution of the chloride ligand by other ligands. They claim “predominant retention of configuration at ruthenium”, which is true only in a strictly formal sense. However, associative, dissociative, and ring slippage mechanisms are presented at length and the authors put forward strange arguments such as total retention of configuration in the reaction of the major diastereomer and partial retention and inversion in the reaction of the minor diastereomer to account for the observed diastereoselectivities. This is unjustified. No conclusions regarding the stereochemistry of the substitution reaction can be drawn, because the diastereoselectivities of the starting material (chloro complexes) and the product (iodo complexes) have nothing to do with it. These diastereoselectivities only reflect the different stabilities of the diastereomers in the respective diastereomer equilibria.

Some years ago we had come across similar misinterpretations in a related series of chiral-at-metal half-sandwich (η^6-arene)ruthenium complexes, the configurational instability of which also had been overlooked. Our correction was coupled with an appeal to be careful with respect to unproved claims of configurational stability at transition-metal centers.[13] The authors of refs 4−6 cited our paper but did not take our warning into account.

In recent papers, entitled “Synthesis, Characterization, and Diastereoselectivity of Chloride Substitution Reactions of Cycloruthenated $(R)_C$-(+)-*N*,*N*-Dimethyl-α-(2-naphthyl) Ethylamine” (Gül and Nelson)[7] and “Chloride Substitution Reactions of Cycloruthenated $(R)_C$-(+)-*N*,*N*-Dimethyl(1-phenylethyl)amine with Pseudohalides: Ruthenium Atom Stereochemistry” (Hansen, Maitra, and Nelson),[8] further chiral-at-metal (η^6-arene)ruthenium complexes were reported to be obtained on substitution of the chloride ligand in compounds of the type **1a**,**b** by azide, nitrite, thiocyanate, cyanate, and other ligands. It will have to be checked whether these compounds really are “configurationally rigid in solution under mild conditions” and whether “these ligand substitution reactions proceed with predominant retention of configuration at ruthenium” or not.

Experimental Section

General Information. All reactions were performed under a nitrogen atmosphere using Schlenk techniques and dried solvents saturated with nitrogen. ^{1}H NMR spectra were measured on Bruker ARX 400 and AC 250 spectrometers. Elemental analyses were performed by the microanalytical laboratory of the University of Regensburg.

Chloro Complexes [(η^6-cymene)Ru(LL*)Cl] (1a,b). The diastereomer mixture [(η^6-cymene)Ru(LL*)Cl] (**1a**,**b**) was synthesized in a slightly different way than was described in ref 4. [(η^6-cymene)RuCl$_2$]$_2$ (1.27 g, 2.07 mmol) and (S_C)-{HgCl-[C$_6$H$_4$CH(Me)NMe$_2$]} (2.39 g, 6.22 mmol) were suspended in CH$_3$CN (50 mL) and stirred at room temperature for 72 h. The solvent was evaporated, and the residue was dissolved in CH$_2$Cl$_2$. The red-orange, transparent solution was filtered through Celite to remove the grayish precipitate (mostly HgCl$_2$). The filtrate was concentrated and purified by filtration chromatography over a short (5 × 1 cm) alumina column which had been packed with ether/hexane (1:1). The excess ligand was eluted with ether/hexane (1:1) and the product with CH$_2$Cl$_2$. The red-orange band was collected and concentrated. The product was obtained as long, red-orange needles by slow diffusion of ether/hexane (1:1) into the CH$_2$Cl$_2$ solution. Yield: 1.33 g (3.17 mmol, 77%). Anal. Calcd for $C_{20}H_{28}ClNRu$: C, 57.34; H, 6.74; N, 3.34. Found: C, 56.88; H, 6.74; N, 3.23. ^{1}H NMR (250 MHz, CD$_2$Cl$_2$, TMS; signals of the minor diastereomer in parentheses): δ 8.12 (7.61) (dd, ^3J(H,H) = 7.3 Hz, ^4J(H,H) = 1.0 Hz, 1 H, *Ar*), 7.11−7.02 (m, 1 H, *Ar*), 6.90 (6.89) (dt, ^3J(H,H) = 7.3 Hz, ^4J(H,H) = 1.0 Hz, 1 H, *Ar*), 6.70 (td, ^3J(H,H) = 7.3 Hz, ^4J(H,H) = 1.0 Hz, 1 H, *Ar*), 5.54 (5.53), 5.40 (5.11), 4.51 (4.52), 4.48 (4.40) (4 d, ^3J(H,H) = 5.9 Hz, 4 × 1 H, *cymene*), 4.31 (3.72) (q, ^3J(H,H) = 6.9 Hz, 1 H, C*H*CH$_3$), 3.27 (s, 3 H, NC*H*$_3$), 2.88 (sept, ^3J(H,H) = 7.0 Hz, 1 H, C*H* ^{i}Pr), 2.38 (1.87) (s, 3 H, NC*H*$_3$), 2.05 (1.69) (s, 3 H, C*H*$_3$ cymene), 1.28 (1.26) (d, ^3J(H,H) = 7.0 Hz, 3 H, C*H*$_3$ ^{i}Pr), 1.17 (1.14) (d, ^3J(H,H) = 6.9 Hz, 3 H, CHC*H*$_3$), 1.08 (d, ^3J(H,H) = 7.0 Hz, 3 H, C*H*$_3$ ^{i}Pr).

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(13) Brunner, H.; Oeschey, R.; Nuber, B. *Inorg. Chem.* **1995**, *34*, 3349.

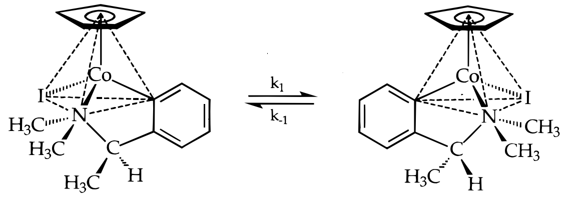
Iodo Complexes [(η^6-cymene)Ru(LL*)I] (2a,b). The Cl/I substitution was performed in a slightly different way than described in ref 5. A sample of **1a**/**1b** (100 mg, 0.24 mmol) was dissolved in MeOH (20 mL). To this solution was added NaI (360 mg, 2.40 mmol), and the mixture was stirred at ambient temperature for 3 h. The solvent was removed, and the residue was extracted with CH_2Cl_2. The CH_2Cl_2 solution was filtered through Celite, and the filtrate was concentrated. The pure product was obtained as dark red needles by slow diffusion of ether/hexane (1:1) into the CH_2Cl_2 solution. Yield: 93 mg (0.18 mmol, 76%). Anal. Calcd for $C_{20}H_{28}INRu$: C, 47.06; H, 5.53; N, 2.74. Found: C, 47.10; H, 5.50; N, 2.71. ^1H NMR (250 MHz, $CDCl_3$, TMS; signals of the minor diastereomer in parentheses): δ 8.01 (7.77) (dd, ^3J(H,H) = 7.5 Hz, ^4J(H,H) = 1.2 Hz, 1 H, *Ar*), 7.14−7.05 (m, 1 H, *Ar*), 6.87 (dt, ^3J(H,H) = 7.5 Hz, ^4J(H,H) = 1.2 Hz, 1 H, *Ar*), 6.76−6.68 (m, 1 H, *Ar*), 5.32 (5.38), 5.12, 4.68, 4.64 (4 d, ^3J(H,H) = 5.9 Hz, 4 × 1 H, *cymene*), 4.38 (3.76) (q, ^3J(H,H) = 6.7 Hz, 1 H, C*H*CH_3), 3.38 (s, 3 H, NCH_3), 3.23 (sept, ^3J(H,H) = 6.7 Hz, 1 H, C*H* ^{i}Pr), 2.40 (2.37) (s, 3 H, NCH_3), 2.20 (1.67) (s, 3 H, CH_3 cymene), 1.35 (d, ^3J(H,H) = 6.7 Hz, 3 H, CH_3 ^{i}Pr), 1.18 (d, ^3J(H,H) = 6.7 Hz, 3 H, CHCH_3), 1.06 (d, ^3J(H,H) = 6.7 Hz, 3 H, CH_3 ^{i}Pr).

Note Added in Proof

During the review procedure of our paper, we came across another paper,[14] containing misinterpretations and wrong conclusions similar to those outlined above. It was published at the end of 1999 in this journal, entitled “Synthesis of Configurationally Stable, Optically Active Organocobalt Compounds”. In the paper Meneghetti et al. reported on a series of cobaltacyclic compounds of the type [(η^5-C_5H_5)Co(LL′)I] differing in the metal configuration. With the optically active ligands LL′H = (R_C)-(+)- and (S_C)-(−)-*N*,*N*-dimethyl-1-phenylethylamine they obtained a mixture of the two diastereomers (R_{Co},R_C),(S_{Co},R_C) and (S_{Co},S_C),(R_{Co},S_C), respectively, in a ratio of 19:1 (91% de). This ratio “could not be improved by fractional crystallization or column chromatography”. “^1H NMR studies indicate that the compounds are configurationally stable at the cobalt center.” “No epimerization could be observed in solution, for instance, over a period of 7 days at room temperature in either $CDCl_3$ or d_6-acetone.” Although the diastereomers “displayed comparable crystallization rates so that the bulk sample from which X-ray-quality crystals were obtained contained the same ratio of both diastereomers as determined above”, they assigned the crystal structure of the R_{Co},R_C complex to the major diastereomer, because “the crystals of this species have a higher statistical chance of being isolated from a mixture of diastereomers.”

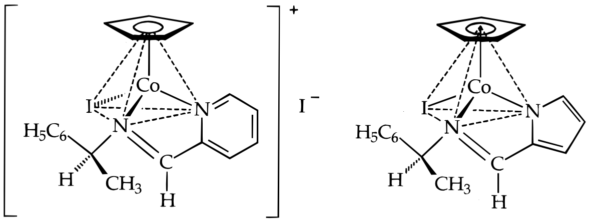
We synthesized the complexes **3a**,**b** according to the published procedure[14] using [(η^5-C_5H_5)CoI_2]$_2$ and *ortho*-lithiated (R_C)-(+)-*N*,*N*-dimethyl-1-phenylethylamine as starting materials. We obtained dark green needles by slow diffusion of hexane into a toluene solution of the complexes **3a**,**b**. The ^1H NMR spectrum of a CD_2Cl_2 solution of these crystals at room temperature exhibited the signals of both diastereomers (R_{Co},R_C)-**3a** and (S_{Co},R_C)-**3b** in a ratio of 96:4 (92% de), in accord with ref 14. However, ^1H NMR studies of a sample of crystals dissolved and measured in CD_2Cl_2 at −40 °C showed only the signals of the major diastereomer. Measurements at −20, 0, and +21 °C revealed that the minor diastereomer **3b** was formed only at higher temperatures. An estimation of the the half-life of the conversion of **3a** into the equilibrium mixture **3a** $\rightleftarrows$ **3b** was obtained by ^1H NMR spectroscopy (Scheme 2).

Scheme 2. Epimerization of the Complexes 3a,b



(R_{Co},R_C)-**3a** (S_{Co},R_C)-**3b**

Chart 1. Complexes 4 and 5[a]



4 **5**

[a] Only one diastereomer, with respect to the cobalt configuration, is shown for each compound.

The ratio **3a**:**3b** was determined by integration of the methyl singlets at 3.49/2.45 ppm for **3a** and 3.24/1.90 ppm for **3b**. Evaluation with the first-order rate law gave a half-life between 20 and 25 min in CD_2Cl_2 solution at +1.4 °C. The accuracy of these measurements is limited by the fact that the equilibration of the major diastereomer involves only a small concentration change to give the equilibrium mixture major diastereomer:minor diastereomer = 96:4. It is obvious that the major diastereomer **3a** cannot be handled at room temperature without a fast change in the metal configuration. Probably, the measurements leading to the postulation of configurational stability at the cobalt center[14] were carried out with epimerized samples. Interestingly, it had been demonstrated before that the cobalt configuration in the compounds **4** and **5** (Chart 1; only one diastereomer shown for each compound) is labile.[15] However, compounds **4** and **5**, which are very similar to compounds **3** and which address the same stereochemical problem of the cobalt configuration, have not been mentioned in ref 14.

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