

OPTICALLY ACTIVE TRANSITION METAL COMPLEXES

LVI[†]. Preparation and Stereochemistry of (+)₅₇₈⁻ and (-)₅₇₈⁻-(η -C₆H₆)RuX(Me)[Ph₂PNHCH(Me)(Ph)], where X = Cl, SnCl₃.

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SUMMARY

The synthesis and resolution of (+)₅₇₈⁻ and (-)₅₇₈⁻-(η -C₆H₆)RuCl(Me)[Ph₂PNHCH(Me)(Ph)] is described. Insertion of anhydrous SnCl₂ into the Ru-Cl bond yielded (+)₅₇₈⁻ and (-)₅₇₈⁻-(η -C₆H₆)RuSnCl₃(Me)-[Ph₂PNHCH(Me)(Ph)], the stereoselectivity of which is dependent on the reaction conditions. All the new complexes were found to be configurationally stable in a wide variety of solvents up to 60°C.

INTRODUCTION

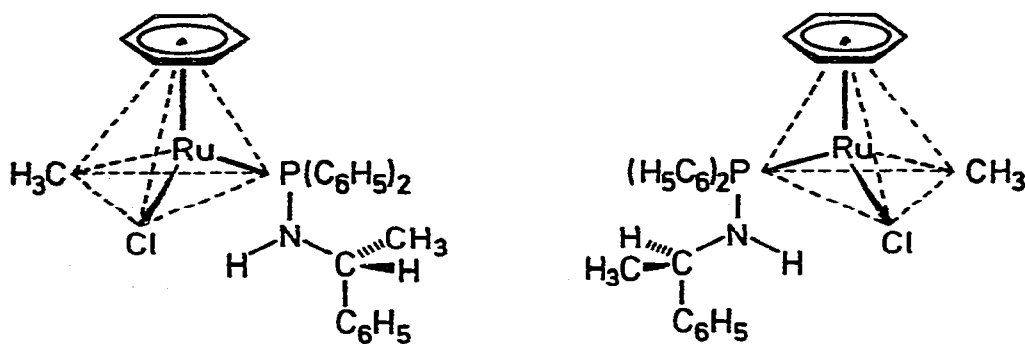
In recent years a broad range of chiral organometallic complexes has been synthesized and resolved¹. The use of such complexes as a monitor of the stereochemical course of reactions has therefore become feasible². Chiral pseudotetrahedral η -arene complexes have previously been resolved only in the case of certain chromium derivatives³. A recent report demonstrated that for η -arene-alanato-ruthenium complexes epimerization at the metal atom was slow on the NMR time scale⁴.

In a short communication we have described the synthesis of (+)- and (-)-(η -C₆H₆)RuCl(Me)[Ph₂PNHCH(Me)(Ph)] (1a,b) which differ only in the configuration at the asymmetric ruthenium atom⁵. We now report in full our investigations into the synthesis, resolution and chemistry of 1a and 1b.

[†]LV. Communication see ref. 18

SYNTHESIS OF (+)₅₇₈- AND (-)₅₇₈-(η -C₆H₆)RuCl(Me)[Ph₂PNHCH(Me)(Ph)]

The reaction of benzenedichlororuthenium dimer with dimethylmercury in acetonitrile followed by addition of the optically active phosphine, R-(+)-Ph₂PNHCH(Me)(Ph), gave (η -C₆H₆)RuCl(Me)[Ph₂PNHCH(Me)(Ph)] 1a,b as the major product as well as (η -C₆H₆)RuCl₂[Ph₂PNHCH(Me)(Ph)] 2 as a minor product ⁵⁻⁷. The separation of 1a and 1b, which was facilitated by the large solubility difference between the diastereomers, was achieved by a combination of column chromatography and fractional crystallization ⁵.



1a,b

The spectroscopy and analytical data of 1a and 1b are in agreement with the proposed structures. Their mass spectra contain the expected molecular ion [M]⁺ and fragmentation pattern (Table 1).

Table 1. Mass Spectral Data for (η -C₆H₆)Ru Complexes (¹⁰²Ru and ³⁵Cl) with PN* = Ph₂PNHCH(Me)(Ph) (Varian MAT CH5, 70 eV)

| assignment | <u>1a</u> | | <u>1b</u> | | <u>2</u> | |
|---|-----------|------------|-----------|------------|----------|------------|
| | m/e | % rel.int. | m/e | % rel.int. | m/e | % rel.int. |
| [M] ⁺ | 535 | 13 | 12 | 555 | 4 | |
| [M-CH ₃] ⁺ | 520 | 6 | 4 | - | - | |
| [M-C ₆ H ₆] ⁺ | 457 | 15 | 13 | 477 | 4 | |
| [RuCl(PN*)] ⁺ | 442 | 92 | 100 | 442 | 3 | |
| [RuCl(PN*)-HCl] ⁺ | 406 | 100 | 98 | 406 | 4 | |
| [Ph ₃ P] ⁺ | - | - | - | 262 | 100 | |

Table 2. ^1H NMR and IR Data for $(\eta\text{-C}_6\text{H}_6)\text{Ru}$ Complexes

| | NMR resonances ^{a,b)} | | | | | IR $\nu_{\text{N-H}}^{\text{c)}$ |
|-----------|----------------------------------|-----------------------------------|------------|--|------------|-------------------------------------|
| | Ru-Me | C-Me | C-H | $\eta\text{-C}_6\text{H}_6$ | Ar | |
| <u>1a</u> | 29.17 $J_{\text{Me-P}}^{6.2}$ | 28.97 $J_{\text{Me-CH}}^{7.2}$ | $m_{6.00}$ | 24.87 $J_{\text{C}_6\text{H}_6\text{-P}}^{0.9}$ | $m_{2.76}$ | 3270 |
| <u>1b</u> | 28.70 $J_{\text{Me-P}}^{6.3}$ | 28.99 $J_{\text{Me-CH}}^{7.2}$ | $m_{6.00}$ | 24.93 $J_{\text{C}_6\text{H}_6\text{-P}}^{0.9}$ | $m_{2.76}$ | 3320 |
| <u>2</u> | - | 28.85 $J_{\text{Me-CH}}^{6.0}$ | $m_{6.20}$ | 24.67 $J_{\text{C}_6\text{H}_6\text{-P}}^{0.8}$ | $m_{2.70}$ | 3330 |
| <u>3a</u> | 29.07 $J_{\text{Me-P}}^{6.0}$ | 29.47 $J_{\text{Me-CH}}^{7.0}$ | $m_{6.32}$ | 24.58 $J_{\text{C}_6\text{H}_6\text{-P}}^{0.9}$ | $m_{2.50}$ | 3380 |
| <u>3b</u> | 28.63 $J_{\text{Me-P}}^{6.0}$ | 29.52 $J_{\text{Me-CH}}^{6.0}$ | $m_{6.22}$ | 24.58 $J_{\text{C}_6\text{H}_6\text{-P}}^{0.9}$ | $m_{2.70}$ | - |

a) CDCl_3 , $i\text{-TMS}$; Varian T-60; τ values in ppm; coupling constants in Hz.

b) Integrals in accord with proposed structures.

c) In cm^{-1} ; KBr pellet.

The N-H stretching frequencies (KBr pellet) of 1a at 3320 cm^{-1} and 1b at 3270 cm^{-1} differ by 50 wavenumbers (Table 2). This difference is indicative of the non-equivalent environments caused by the chiral ruthenium atom. As can be seen from Table 2 the ^1H NMR chemical shift differences between the ruthenium-methyl resonances and, to a lesser extent, the $\eta\text{-C}_6\text{H}_6$ resonances of 1a and 1b are large enough to allow their use as a gauge of optical purity as well as a monitor of epimerization.

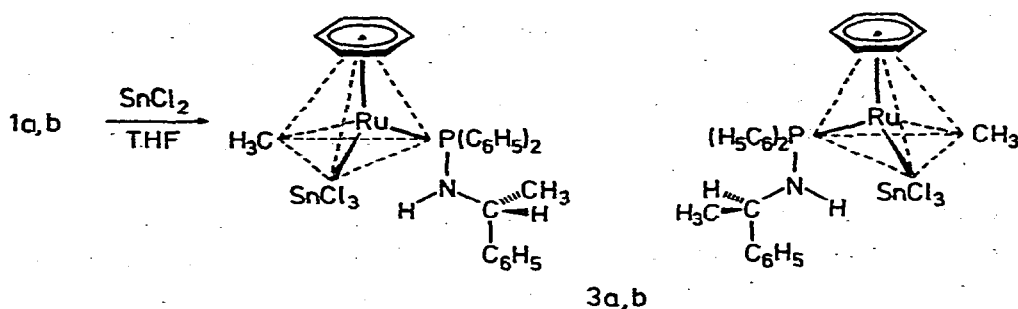
The configurations of both diastereoisomers were found to be stable in the solid state and in solution in a variety of solvents. Solutions of either 1a or 1b in benzene, toluene, chloroform, THF, acetone or acetonitrile showed little or no change in rotational value after 24 h at room temperature. Moreover, solutions of these diastereoisomers in benzene, toluene or chloroform, when kept oxygen

free, showed no epimerization for up to 18 h at 60°C. THF solutions could be heated to 60°C for 1 h without epimerization. When heated to higher temperatures or for longer periods of time epimerization was generally not observed in these solutions but only decomposition of the complexes. At 60 or 70°C acetonitrile solutions were found to show a first order decrease in rotational values. However, NMR studies at these temperatures indicated that the processes observed were actually decomposition with no apparent epimerization involved.

Also, no phosphine exchange was observed in benzene or chloroform solutions of 1a at 60°C containing an excess of free tri(p-tolyl) phosphine.

SYNTHESIS OF $(-)_578-(\eta\text{-C}_6\text{H}_6)\text{Ru}(\text{SnCl}_3)(\text{Me})[\text{Ph}_2\text{PNHCH}(\text{Me})(\text{Ph})]$

The insertion reactions of Sn(II) compounds into metal-metal⁸⁻¹⁰, metal-carbon¹¹⁻¹³, and metal halogen^{8,13-17} bonds have been the subject of much research. We find that the reaction of 1a,b and anhydrous SnCl₂ in THF solution leads to a mixture of the Ru-Cl insertion products 3a,b. The less soluble diastereomer (3a) was isolated optically pure by fractional crystallization. The insertion products, 3a and 3b, differ significantly in their ¹H NMR spectra (Table 2). An adequate mass spectrum was not obtainable due to sample decomposition in the mass spectrometer.



The configurational stability of 3a was found to be similar to that of 1a and 1b. Benzene, chloroform and THF solutions of 3a showed no epimerization after several days at ambient temperature as monitored by NMR spectroscopy. An unusual temperature effect on

the rotational value of 3a was observed. At 25°C a benzene solution of 3a (3.5 mg/ml) has a specific rotation at 436 nm of -212°. If this solution is heated to 60°C and the temperature maintained the specific rotation drops to -84°. Upon cooling to 25°C the value returns to -212°. This heating and cooling process can be repeated at least four times with identical results even with heating periods up to 18.5 h.

STEREOCHEMISTRY OF SnCl₂ INSERTION INTO THE Ru-Cl BOND

The reaction of 1 and SnCl₂ was originally carried out in refluxing THF. It was observed that regardless of the diastereomeric purity of 1 a partially epimerized product was isolated. In order to discover whether such epimerization is a result of pre- or post-reaction configurational instability or an outcome of the mechanism involved, the reaction was carried out in THF-d₈. Periodic measurement of the η-arene resonances of the reactants and products was accomplished using a Bruker WH-90 instrument which was able to ascertain the diastereomeric ratio of both. The low solubility of 1b in THF precluded its use in these experiments and the following results, which are summarized in Table 3, therefore are based on the reaction of 1a and SnCl₂.

As was stated earlier 1a is configurationally stable in THF up to 60°C. It was further observed that 3a shows similar stability even in the presence of excess SnCl₂. It is therefore evident that the formation of epimerized 3 as well as the epimerization of 1a occurs during the reaction.

Table 3. Reaction of 1a (0.07 M) and SnCl₂ in THF-d₈ at 0°C

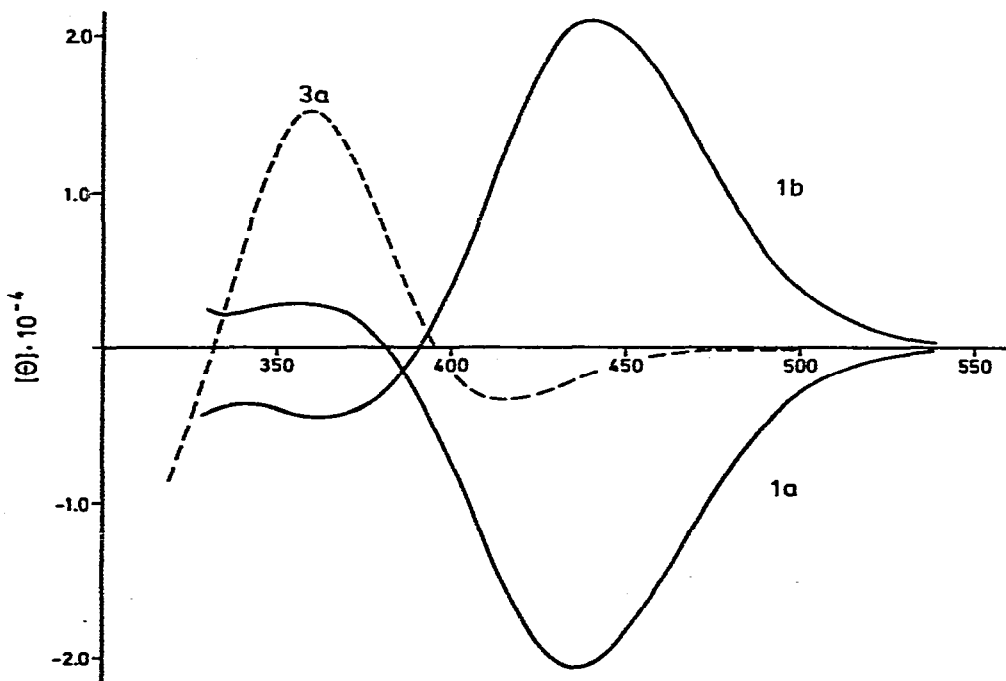
| Initial Ratio SnCl ₂ / <u>1a</u> | Extent of Reaction | time h | Diastereomer Ratio <u>1a/1b</u> | Ratio <u>3b/3a</u> |
|--|-----------------------|-----------|------------------------------------|-----------------------|
| 4/1 | 95 % | 13.8 | 100/72 | 100/24 |
| 1.1/1 | 27 % | 5.7 | 100/16 | 100/4 |
| 1.1/1 | 60 % | 21.7 | 100/32 | 100/6 |
| 1.1/1 | 93 % | 125.0 | 100/45 | 100/18 |

The data from Table 3 indicate that the concentration of SnCl₂ affects both the overall rate of insertion and its stereoselectivity.

At 0°C using a 4/1 ratio of $\text{SnCl}_2/1\text{a}$ the reaction was 95 % completed after 13.8 h while with 1.1/1 ratio 125 h were required for 93 % completion. Moreover, the degree of epimerization of 1a during the reaction increased with increasing concentration of SnCl_2 , but at 0°C the SnCl_2 insertion into the Ru-Cl bond of 1a is greatly favored over epimerization at the metal center. Both diastereomers, 3a and 3b, were formed during the reaction, the ratio 3a/3b decreasing with increasing SnCl_2 concentration. It was noted that throughout these reactions the ratio 3a/3b was always greater than 1a/1b and, especially, that starting with 1a isomer 3b is greatly favored. This suggests a high degree of stereoselectivity in the insertion reaction. As expected, increasing the temperature decreases the stereoselectivity and enhances the epimerization of 1a.

Because of the complexity of the reaction and the inadequate understanding of the exact nature of the tin species involved in the reaction ¹² firm conclusions cannot be made. The insertion process as well as the interconversion of 1a and 1b probably have reaction orders of two or greater. It seems likely that the conversion of 1a into 3b is highly stereoselective and 3a mainly arises from 1b, formed by epimerization of 1a.

Figure: CD spectra of 1a, 1b, and 3a in 0.002 M benzene solution



As described, 1a is transformed predominantly in 3b. In the same way 1b and 3a are interrelated. The observed high stereoselectivity of the SnCl_2 insertion could be the result of overall retention or inversion at the Ru atom. Unfortunately, the CD spectrum of 3a is so different from the CD spectra of either 1a and 1b (figure) that no safe conclusions on the stereochemistry can be drawn on the basis of the CD curves.

EXPERIMENTAL SECTION

All operations were carried out in a nitrogen atmosphere using standard Schlenk techniques. The solvents were dried and distilled before use.

Preparation of 1a and 1b

To a suspension of 1.65 g (3.31 mmol) of benzenedichlororuthenium dimer in 150 ml acetonitrile are added 5.0 ml (15 g, 66 mmol) of dimethylmercury and the mixture is reacted for 60 min at room temperature. After addition of 3.0 g (9.8 mmol) of R-(+)- $\text{Ph}_2\text{PNHCH}(\text{Me})(\text{Ph})$ the mixture is stirred for an additional 30 min. Acetonitrile is then used to dissolve the entire reaction mixture followed by ca. 20 g of alumina (deactivated with 5 % water). The solvent is removed, the residue dried and the coated alumina transferred to an alumina column (2 x 50 cm) packed dry.

Elution of the column with ether followed by 15/1 ether/acetonitrile brought down a yellow band which upon solvent removal yielded 0.83 g (23 %) of a yellow solid which consisted of a mixture of 1a and 1b in the ratio of about 85 to 15, respectively. Pure 1a was obtained by fractional crystallization in acetonitrile at -30°C . The less soluble 1b crystallized initially. Partial evaporation of the mother liquor and cooling to -30°C yielded 1a as yellow needles, mp $143\text{--}145^\circ\text{C}$. (Found: C, 60.78; H, 5.65; N, 3.18. $\text{C}_{27}\text{H}_{29}\text{ClNPRu}$ calc.: C, 60.61; H, 5.46; N, 2.62 %). Optical rotation (Perkin-Elmer polarimeter 241): $[\alpha]_{578}^{25} = -640^\circ$, $[\alpha]_{546}^{25} = -1000^\circ$, $[\alpha]_{436}^{25} = +940^\circ$ (benzene, 1 mg/ml).

Further elution of the column with 1/1 ether/acetonitrile brought down a light yellow band which was collected in fractions. The first several fractions contained mixtures of 1a and 1b but greatly enriched in the latter. The total amount was 0.125 g (3.5 %). The

succeeding fractions consisted of only 1b and yielded 0.086 g (1.9 %). Pure 1b was obtained by crystallization in acetonitrile at -30°C , mp $175-177^{\circ}\text{C}$. (Found: C, 60.63; H, 5.48; N, 2.63. $\text{C}_{27}\text{H}_{29}\text{ClNPRu}$ calc.: C, 60.61; H, 5.46; N, 2.62 %). Optical rotation: $[\alpha]_{578}^{25} = +650^{\circ}$, $[\alpha]_{546}^{25} = +970^{\circ}$, $[\alpha]_{436}^{25} = -1080^{\circ}$ (benzene, 1 mg/ml).

After another small yellow band continued elution with acetonitrile yielded a red band which upon solvent removal and crystallization from acetonitrile at -30°C gave 0.250 g (7 %) of 2, mp $210-212^{\circ}\text{C}$. (Found: C, 56.37; H, 4.70; N, 2.67. $\text{C}_{26}\text{H}_{26}\text{Cl}_2\text{NPRu}$ calc.: C, 56.24; H, 4.69; N, 2.52 %).

Preparation of 3a

To a solution of 0.300 g (0.57 mmol) of 1a,b consisting of 40-60 % 1a, in 15 ml THF are added 0.424 g (2.24 mmol) of anhydrous SnCl_2 and the mixture is refluxed for 30 min. The solvent is then removed and the residue extracted with benzene, filtered and dried. Crystallization from ether gave pure 3a isolated as yellow-orange prisms (0.109 g, 27 %), mp $189-190^{\circ}\text{C}$ with dec. (Found: C, 44.55; H, 4.04; N, 1.74; Cl, 14.67; mol. mass, 735 (osmometrically in benzene). $\text{C}_{27}\text{H}_{29}\text{Cl}_3\text{NPRuSn}$ calc.: C, 44.75; H, 4.03; N, 1.93; Cl, 14.68 %; mol. mass, 724.6). Optical rotation: $[\alpha]_{578}^{25} = -125^{\circ}$, $[\alpha]_{546}^{25} = -135^{\circ}$, $[\alpha]_{436}^{25} = -275^{\circ}$ (benzene, 1 mg/ml).

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