Dynamic stereochemistry of bis-β-diketonato-1,5-cyclooctadiene ruthenium(II) complexes

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Abstract

Tris(chelate)$_2$(diene)ruthenium(II) complexes have been synthesized. All three possible diastereoisomers of Ru(bzac)$_2$(cod) (where cod = 1,5-cyclooctadiene and bzac = benzoylacetonato) have been isolated and diastereoisomerization processes were observed at elevated temperature. The energy barriers were found to be in the range of 35–36 kcal/mol. The DNMR behaviour of Ru(S_2CNMe_2)$_2$(cod) and Ru(S_2PMe_2)$_2$(L) complexes is also discussed. We synthesized a new Ru(*N*-isopropylsalicylaldiminato)$_2$(cod) tris-chelate which was found to clathrate some solvents.

Introduction

In previous works [1–7] we analyzed in some details the dynamic stereochemistry of propeller-like bis-chelate complexes of the Groups IV and II metals with the aim of elucidating the possible stereomerization pathways responsible for the interconversion among the various isomeric forms. In particular, we ascertained that among the possible non-bond rupture rearrangement modes only those occurring with reversal of the helicity of the structure are the preferred ones. Among these, the threshold mechanism involves correlated twisting of the chelate rings [1, 4, 6]; this lowest energy pathway is, in turn, permutationally equivalent to the 'one-ring flip' transition state of diaryl derivatives [1, 8].

During these studies we had the opportunity to synthesize a bis-chelate complex of ruthenium(II), [Ru(acac)$_2$(PPh_3)$_2$] (denoted, hereafter, as **1**) which showed stereochemical rigidity on the NMR timescale even at very high temperatures [1]. From these experimental evidences we concluded that **1** should possess a threshold enantiomerization barrier greater than 24.5 kcal/mol, and therefore it can be regarded as an example of a two-bladed propeller molecule in which separation of the enantiomers could be possible at room temperature [1]. Unfortunately, since any attempt to resolve **1** by chromatography on chiral columns failed [9], information on the energetics of the racemization process and on the chiroptical properties of this class of molecules were precluded. However, literature data indicate that (bzac)$_2$(diene)ruthenium(II) complexes, which can exist as three diastereomeric DL pairs, are also stereochemically rigid at room temperature and thus some of the possible isomers were separated by chromatography on Florisil [10].

Therefore, such input information prompted us to resynthesize some of these ruthenium complexes whose diketonate chelating rings do not possess a C_2 axis of symmetry coincident with the central metal atom, with the aim of gaining the following information:

(i) isolation of all possible diastereoisomers;
(ii) assignment of their structure by NMR techniques;
(iii) estimation of the energy barriers necessary to average the isomeric structures.

Results and discussion

Following literature procedures [10], we synthesized Ru(bzac)$_2$(cod) (denoted, hereafter, as **2**), which possesses the requisites for accomplishing our stereochemical studies. Separation of the crude mixture through chromatography yielded three isomers: **2A**, orange–yellow solid (55%) with m.p. 143–144

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°C; **2B**, purple solid (10%), m.p. 93–95 °C; **2C**, orange solid (35%) m.p. 177–178 °C.

As pointed out previously [1, 10], β-diketonate(cod)tris-chelate complexes, in which the two β-diketonate chelate rings are identical but lack a C_2 axis of symmetry, can exist in six stereoisomeric forms, i.e., three diastereomeric DL pairs, as exemplified in Fig. 1. Looking at the overall symmetry of such structures, it is evident that the isomer **2A** (point group C_1, as well as **2Ā**), should feature two signals (a and b) of equal intensity in the methyl region of the NMR spectrum, whereas in each of the isomers **2B** and **2C** the methyl groups (c and d, respectively) are symmetry related and therefore only one signal for each isomer is expected on the methyl region of the spectrum.

According to this analysis, the isomer with m.p. at 143–144 °C, which in $CDCl_3$ shows two signals

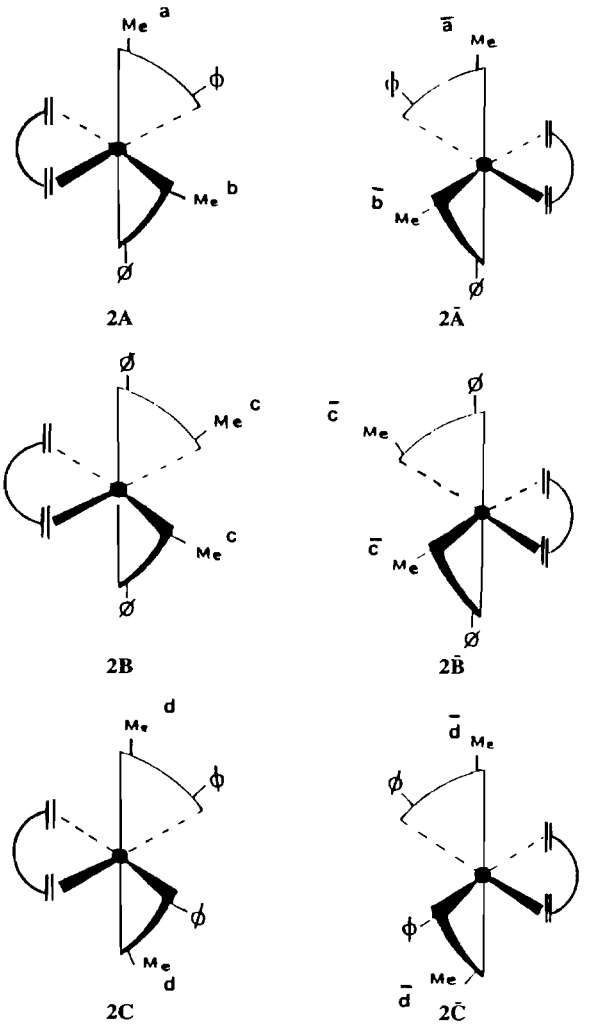


Fig. 1. Schematic representation of the six isomers of **2**. Barred letters denote enantiomeric relationships. Diastereotopic methyl groups are differentiated by letters.

of equal intensity in the methyl region at $\delta = 2.01$ and 2.31 ppm, is safely associated with structure **2A**. Assignments of the other two isomers is less straightforward; however, chemical shifts considerations can help in such a task. In fact, in isomer **2A** one methyl group, which experiences the diamagnetic effect of the β-diketonate chelate ring, resonates at higher fields ($\delta = 2.01$) whereas the other one, experiencing an opposite effect, resonates at $\delta = 2.31$. Since in the isomer with m.p. 95 °C the methyl groups resonate at $\delta = 2.00$, indicating an upfield shift of the signals, it can be associated with structure **2B**; on the other hand, the isomer with m.p. 177–178 °C shows the methyl signal at $\delta = 2.31$, whereby structure **2C** can be assigned to it.

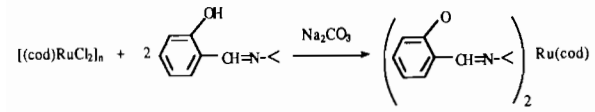
As expected from the information gained on the variable-temperature NMR behaviour of $Ru(acac)_2(PPh_3)_2$, also for compound **2** coalescence of the methyl signals is not observed on the NMR time-scale, even at very high temperatures. Therefore, in order to gain information on the energetic of the processes responsible of the possible isomerizations, we analyzed the kinetics of such rearrangements operating at 170 °C in $C_6D_5NO_2$ as solvent. In $C_6D_5NO_2$ at 170 °C the methyl groups resonate at $\delta = 1.97$ and 2.32 for isomer **2A**, and at $\delta = 2.32$ and 1.99 for isomer **2C** and **2B**, respectively. Hence, by monitoring the relative intensities of the signals and following the intensity at $\delta = 2.32$ of compound **2C** as function of time, it was possible to follow the diastereomerization processes. Unfortunately, because of the complex equilibria involved (see 'Experimental') it was not possible to calculate accurately the diastereomerization barrier. However its crude estimation was still possible and the value was found to be in the range of 35–36 kcal/mol, in agreement with the observation that the diastereoisomers of **2** are separable by fractional recrystallization at room temperature. From such experimental information it can be concluded that complex **1** should also behave similarly and therefore, with such a high barrier to enantiomerization, it can be resolved. Experiments are still in progress in order to achieve such goal.

Beside the isolation of compounds **2(A–C)**, we also synthesized two other (tris-chelate)–Ru complexes, in which benzoylacetone was replaced by different ligands. $Ru(S_2CNMe_2)_2(cod)$ (denoted, hereafter, as **3**), was prepared according to literature procedures [10, 11],

$$[(cod)RuCl_2]_n + 2(CH_3)_2NCS_2Na \longrightarrow Ru(S_2CNMe_2)_2(cod) + 2NaCl,$$

whereas Ru(*N*-isopropylsalicylaldiminato)$_2$(cod) (denoted hereafter as **4**), was synthesized in a similar

way from $[Ru(cod)Cl_2]_n$ and *N*-isopropylsalicylaldimine



At 30 °C the ^1H NMR spectrum of compound **3** shows two distinct signals for the CH_3–N groups, indicating a *cis*-geometry of the complex and thus two enantiomeric structures are possible.

By increasing the temperature, we observed stereochemical fluxionality on the NMR time-scale. In fact, when a $CDCl_3$ solution of **3** was warmed, coalescence of the two diastereotopic *N*-methyl groups was observed at 53 °C, and employing the Gutowsky–Holm approximation [12], a barrier of 16.5 kcal/mol was calculated for the fluxional process which provokes enantiomerization. Interesting enough, this barrier is much lower than the one expected for **1** or found for **2**, and a little higher than the one found by Duffy and Pignolet [13] for the corresponding tris-chelate $Ru(S_2CNMe_2)_3$ complexes. These authors have already pointed out that "it is not fully understood why the $Ru(S_2CNMe_2)_3$ complex rearranges with such a low (as compared with other ruthenium complexes) activation energy"; however, our data confirm this trend and seem to indicate that the coordinating properties of S atoms are much weaker than those of O atoms. This is bolstered by inspection of some literature data which reveal that for *cis*-$Mo(S_2CNMe_2)_2(NO)_2$ and *cis*-$W(S_2CNMe_2)_2(NO)_2$ the barrier for averaging the two diastereotopic methyl dithiocarbamate signals is of the order of 20 kcal/mol [14], whereas for $Ru(S_2CNMe_2)_2(PPh_3)_2$ and $Ru(S_2CNMe_2)_2(PMe_2Ph)_2$ such barrier decreases to *c.* 17 kcal.mol [15].

Interesting enough, in the complex $Ru(S_2PMe_2)(PMe_2Ph)_2$ the presence of the moiety $-PMe_2Ph$ functions as a diastereotopic probe which can monitor changes in the chirality of the structure. The interesting result found by Cole-Hamilton and Stephenson [16] i.e. that the averaging of the methyl signals in the $-S_2PMe_2$ and $-PMe_2Ph$ moieties are occurring with similar activation energies, can be interpreted as an indication that optical isomerization in this complex occurs with concomitant reversal of the helicity of the structure ($\Delta \rightleftharpoons \Lambda$ isomerization).

In fact, among the various possible non-bond rupture twist mechanisms for bis- and tris-chelate complexes [1, 17], isomerization processes which occur without changing the chirality of the structure would average only the $-S_2PMe_2$ methyl signals, leaving unaffected the signals of the prochiral $-PMe_2Ph$ probe.

Therefore, this behaviour seems to be a general trend in chelate complexes where the threshold isomerization pathways always occur with concomitant reversal of the helicity of the structure [1, 17]*.

From the room temperature NMR spectrum of compound **4** the following information can be extracted:

(i) First of all, this compound was found by ^1H NMR analyses to include two mol of Et_2O. Other solvents such as benzene and dioxane were also found to be included by **4**; however, all the guests are released under vacuum at 60 °C. The clathrating ability of **4** is of great interest because, due to the stable chiral structure of the host, such compound can be reasonably used in order to separate enantiomers from racemic mixtures of guests (see below).

(ii) The presence of four lines of equal intensity in the isopropyl region of the spectrum reveals that **4** is chiral at ambient temperature, and that enantiomerization is not occurring, at least on the NMR time-scale; hence, complex **4**, similarly to compound **2**, is stereochemically rigid. Furthermore, the absence of additional lines indicates that the isolated **4** is a single isomer with structure of type **B** or **C**.

Any other effort aimed towards the isolation of the other two possible stereoisomers failed.

Experimental

^1H NMR spectra at room temperature were recorded on a Bruker AC-250 operating at 250 MHz; variable temperature NMR studies were performed on a Bruker WP-80 instrument operating at 80 MHz; TMS was used as an internal standard. Melting points were obtained on a Gallenkamp apparatus. IR spectra were determined with a Perkin-Elmer 1430 spectrophotometer. Materials: $[Ru(cod)Cl_2]_n$ (Johnson Matthey); *N*,*N*-dimethyldithiocarbamic

*For compound **3**, two different processes resulting in an average of diastereotopic dithiocarbamate methyl groups can be envisioned. One is related to the rotation about the C–N bond which should require an activation energy *c.* 14–15 kcal/mol [18]; the other one is concerned with $\Delta \rightleftharpoons \Lambda$ isomerization of the whole complex and its activation energy should strongly depend both on the nature of the metal to which the S_2CNMe_2 moiety is attached and on the steric requirement of the eventual extra ligand present on the complexed metal. Considering that the latter case is supported by the literature data above reported on a large variety of complexes we did not take into consideration in our discussion the first isomerizating process connected with rotation around the C–N bond.

acid sodium salt dihydrate, 1-benzylacetone and salicylaldehyde (Aldrich-Chemie).

Ru(cod)(bzac)$_2$ (2)

(1,5-Cyclooctadiene)ruthenium(II) chloride (0.55 g, 2 mmol) was heated with benzoylacetone (0.65 g) in dimethylformamide (5 ml) in the presence of anhydrous sodium carbonate (1.50 g) until, after about 10 min, it dissolved. The mixture was filtered and water was added to the filtrate to precipitate the compound. Recrystallization from methanol afforded the bis(benzoylacetonate)(1,5-cyclooctadiene)ruthenium(II) (500 mg) mixture of three isomers, as shown by thin-layer chromatography. It was possible to separate them by column chromatography on SiO_2 using chloroform as eluent.

Isomer **A**: orange–yellow solid, m.p. 143–144 °C, δ ($CDCl_3$; 25 °C): 2.02–2.25–2.47 (8H, three m, methylenic protons), 2.01 (3H, s, CH_3), 2.31 (3H, s, CH_3), 4.19 (2H, m, olefinic protons), 4.35 (2H, m, olefinic protons), 6.04 (2H, bs, CH ligand), 7.27 (3H, m, ArH), 7.43 (3H, m, ArH), 7.68 (2H, dd, $J_o = 7.5$ Hz, $J_m = 2.5$ Hz, ArH), 7.95 (2H, dd, $J_o = 7.5$ Hz, $J_m = 2.5$ Hz, ArH). *Anal.* Found: C, 62.95; H, 5.87. Calc for $C_{28}H_{30}O_4Ru$: C, 63.2; H, 5.64%.

Isomer **B**: purple solid, m.p. 93–95 °C, δ ($CDCl_3$; 25 °C): 2.00 (3H, s, CH_3), 2.06–2.22–2.44 (8H, three m, methylenic protons), 4.21 (2H, m, olefinic protons), 4.40 (2H, m, olefinic protons), 5.96 (2H, bs, CH ligand), 7.41 (6H, m, ArH), 7.95 (4H, dd, ArH). *Anal.* Found: C, 62.89; H, 5.72. Calc. for $C_{28}H_{30}O_4Ru$: C, 63.2; H, 5.64%.

Isomer **C**: orange solid, m.p. 177–178 °C, δ ($CDCl_3$; 25 °C): 2.02–2.25–2.42 (8H, three m, methylenic protons), 2.31 (3H, s, CH_3), 4.14 (2H, m, olefinic protons), 4.32 (2H, m, olefinic protons), 6.00 (2H, bs, CH ligand), 7.26 (6H, m, ArH), 7.68 (4H, dd, $J_o = 7.5$ Hz, $J_m = 2.5$ Hz, ArH). *Anal.* Found: C, 63.29; H, 6.01. Calc. for $C_{28}H_{30}O_4Ru$: C, 63.2; H, 5.64%.

Kinetic measurements

As we have already pointed out, non-bond rupture twist mechanisms can interconvert all three diastereomers of **2**; in fact, when a $C_6D_5NO_2$ solution of pure **2C** ($\delta = 2.32$) was placed in a thin-walled NMR tube and the probe temperature was set at 170 °C, additional methyl signals at $\delta = 1.97$ and 1.99, due to isomers **2A** and **2B**, were seen to grow with time. Unfortunately, some peak overlapping due to accidental isochronies and the complex equilibria involved (**A** ⇌ **B** ⇌ **C**, or **A** ⇌ **C** ⇌ **B**, etc.) did not allow us to establish a precise value of the specific rate constants. As a very first approximation we used a simplified kinetic treatment in order to calculate the rate constants for the equilibration of the two diastereoisomers **2A** and **2C**. The equation used, which is adapted from the usual expression for a reversible first-order reaction [19], was

$$K_{kin}t = \ln \frac{h_0 - h_e}{h_t - h_e} \quad (1)$$

where h_0 is the relative peak intensity of the methyl proton absorption at $t = 0$, h_e the peak intensity of isomer **2C** after the equilibration process, and h_t is the peak intensity at time t of isomer **2C**.

The calculated value of K_{kin}, which was found to be of the order of magnitude of 10^{-5} s^{-1} and which is not very precise for what we have previously said*, was used in conjunction with the Eyring equation,

$$\Delta G^{\#} = RT\left(\ln \frac{kT}{h} - \ln K_{kin}\right) \quad (2)$$

in order to estimate the free energy of activation for the diastereomerization processes.

Ru(cod)(S_2CNMe_2)$_2$ (3)

It was synthesized according to the literature [10]. m.p. 226–228 °C, δ ($CDCl_3$; 25 °C): 1.66–2.06–2.54 (8H, three m, methylenic protons), 3.05 (2H, m, olefinic protons), 3.29 (6H, s, CH_3), 3.73 (2H, m, olefinic protons).

Ru(cod)bis(N-isopropylsalicylaldiminato) (4)

It was prepared by treating *N*-isopropylsalicylaldimine (obtained from *N*-isopropylamine and salicylaldehyde) with 0.4 g of (1,5-cyclooctadiene)ruthenium(II)chloride in dimethylformamide in the presence of anhydrous sodium carbonate (1.4 g). The solution was heated for about 30 min. The mixture was filtered and the sodium salts were washed with methanol. Water was added to the filtrate in order to precipitate the complex, which has been purified by chromatography in SiO_2 using chloroform as eluent. Green solid, m.p. 166–168 °C, δ ($CDCl_3$; 25 °C): 0.85 (6H, d, $^3J_{H,H} = 6.6$Hz, CH_3), 1.21 (6H, d, $^3J_{H,H} = 6.6$Hz, CH_3), 1.92–2.07–2.42 (8H, three m, methylenic protons), 4.10 (2H, m, olefinic protons), 4.38 (2H, m, olefinic protons), 4.69 (2H, heptet, $^3J_{H,H} = 6.6$Hz, *CH*–(Me)$_2$), 6.49 (2H, ddd, ArH, $J_o = 8.0$ Hz, $J_m = 6.7$ Hz, $J_p = 2$ Hz), 6.91 (2H, dd, ArH, $J_o = 8.0$ Hz, $J_m = 6.5$ Hz), 7.05 (2H, dd, ArH, $J_0 = 8.5$ Hz, $J_m = 6.7$ Hz), 7.19 (2H, ddd, ArH, $J_o = 8.5$ Hz, $J_m = 6.75$ Hz, $J_p = 2$ Hz) pseudo first-order pattern, 7.99 (2H, s, *CH*=N–). *Anal.* Found:P C, 62.97; H, 6.81; N, 5.30. Calc. for $C_{28}H_{36}N_2O_2Ru$: C, 63.01; H, 6.74; N,

*As can be easily checked through eqn. (2), possible limited discrepancies on the values of K_{kin} do not influence significantly the calculated value of $\Delta G^{\#}$ which is, in turn, extremely sensitive to the much more precisely measured temperature.

5.24%. ν (Nujol mulls) (C=N) 1620, (C–O) 1540 cm^{-1}.

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