Pseudo-tetrahedral semi-sandwich cycloruthenated compounds: ^{1}H NMR data and DFT-calculations about the racemisation process of the ruthenium atom

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This article is dedicated to the memory of J.A. Osborn, with whom we learned a lot about science and life.

Abstract – The partial substitution of the acetonitrile ligand of compound **1a** $[(\eta^6\text{-}C_6H_6)Ru(C_6H_4\text{-}2\text{-}CH_2NMe_2)(NCMe)]^+PF_6^-$ by CD_3OD was observed while running the ^{1}H NMR spectra of **1a** in this solvent, this giving rise to the formation of **1b**. In opposition to **1a**, the ^{1}H NMR spectrum of **1b** is temperature-dependent, as at $T > 40\,°C$ the coalescence of the signals of the $-CH_2NMe_2$ protons was observed, this being an evidence for the fast racemisation of the Ru centre in **1b** at the NMR timescale. DFT-calculations allowed us to envision a likely process for this racemisation. It should take place via the decoordination of the methanol ligand at an early step of the reaction, followed by the inversion of the configuration of the thus-obtained $16\,e^-$ species (**2**). The transition state (**3**) for this latter reaction was identified and the total free energy of the racemisation was thus calculated, affording a value close to the activation energy found experimentally by ^{1}H NMR ($\sim 13\ \text{kcal mol}^{-1}$ vs $\sim 15.5\ \text{kcal mol}^{-1}$, respectively). *To cite this article: M. Robitzer et al., C. R. Chimie 5 (2002) 467–472* © 2002 Académie des sciences / Éditions scientifiques et médicales Elsevier SAS

ruthenium / C–N ligand / configuration stability / DFT-calculations

Résumé – La dissolution du composé **1a** $[(\eta^6\text{-}C_6H_6)Ru(C_6H_4\text{-}2\text{-}CH_2NMe_2)(NCMe)]^+PF_6^-$ dans le méthanol d_4 provoque la substitution partielle de l'acétonitrile par le méthanol, pour former **1b**, ainsi que l'a montré la RMN ^{1}H de ce composé. À l'inverse de **1a**, le spectre RMN ^{1}H de **1b** dépend fortement de la température. À $T > 40\,°C$ les signaux des protons du groupe $-CH_2NMe_2$ coalescent, ce qui indique que le ruthénium de **1b**, qui est un centre asymétrique, se racémise rapidement à l'échelle de temps de la RMN. Des calculs DFT nous ont permis de visualiser le phénomène d'inversion de configuration du métal. Il est provoqué par la décoordination initiale du méthanol, suivie par l'inversion du centre métallique électroniquement insaturé à $16\,e^-$ (**2**). Nous avons identifié un état de transition pour ce dernier phénomène (**3**) et avons ainsi pu calculer l'énergie libre globale de la réaction de racémisation. Cette valeur ($\sim 13\ \text{kcal mol}^{-1}$) est cohérente avec celle déterminé expérimentalement par RMN [1]H ($\sim 15.5\ \text{kcal mol}^{-1}$). *Pour citer cet article : M. Robitzer et al., C. R. Chimie 5 (2002) 467–472* © 2002 Académie des sciences / Éditions scientifiques et médicales Elsevier SAS

ruthénium / ligand C–N / stabilité configurationnelle / calculs DFT

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1. Introduction

Pseudo-tetrahedral organometallic compounds, which display chirality at the metal, have been studied since many decades [1,2]. Important asymmetric hydrogen transfers between isopropanol and acetophenone catalysed by such ruthenium species have recently contributed to intense research in this area [3]. Among them, the η^6-benzene derivatives have played an important role, as spectacular high enantiomeric excesses (> 95%) of 1-phenylethanol have been obtained in some cases [4]. We have been interested in the synthesis of such organometallic compounds as they could be obtained via an intramolecular C–H activation procedure of tertiary amines, leading to cycloruthenated compounds [5]. The configuration of the metal centre of these compounds proved to be rather unstable in solution [6,7], but so far we have not had any clear evidence to support a mechanism for this reaction. In this paper we report about variable temperature ^{1}H NMR spectra that have been collected for one of these compounds and which were a direct evidence of the fast racemisation of the ruthenium centre at the NMR time scale. These data, with the help of theoretical calculations, shed light on this process.

2. Results and discussion

The compound $[(\eta^6\text{-}C_6H_6)Ru(C_6H_4\text{-}2\text{-}CH_2NMe_2)(NCMe)]^+PF_6^-$ (**1a**) has been obtained recently via a classical cyclometallation reaction [5]. As we recorded the ^{1}H NMR spectrum of **1a** in CD$_3$OD, we observed, besides the resonances of **1a**, new signals whose chemical shifts and multiplicity were in accord with the presence of a new species **1b** closely related to **1a** (Fig. 1). Indeed the η^6-benzene resonated at 5.62 for **1b** vs 5.71 for **1a**, whereas the aromatic proton, ortho to the Ru-C bond, was found at 8.43 for **1b** vs 8.05 for **1a**. However, the CH$_2$NMe$_2$ protons of **1b** were difficult to identify, as they gave rise to broad signals. When the ^{1}H NMR spectra of **1a** were run at low

temperature (< –60 °C) the new species **1b** displayed a normal spectrum, showing all characteristics of a species akin to **1a**. Most diagnostic were the diastereotopy of the CH$_2$NMe$_2$ protons that resonated at 3.71 and 3.05 for the CH$_2$ unit (AB system, $^2J_{H-H} = 13.7$ Hz) and at 3.15 and 2.74 for the NMe$_2$ protons (2s). As we could detect non-coordinated MeCN in the ^{1}H NMR spectrum with a concentration consistent to the quantity of **1b**, it was reasonable to state that **1b** is a CD$_3$OD adduct of the cycloruthenated species, in which the acetonitrile has been substituted by the methanol.

The variable temperature-behaviour of the ^{1}H NMR of **1b** is typical of a dynamic process. At temperature above 40 °C, the signals of the CH$_2$NMe$_2$ group completely disappeared, but at 60 °C a broad signal for the NMe$_2$ protons could be detected (Fig. 2). It is now well established that the configuration of the ruthenium atom is not stable in this type of pseudo-tetrahedral compounds [6,7] and hence in solution at this temperature, **1b** should exist as a mixture of enantiomers that are in fast equilibrium with one another.

At low temperatures, the exchange rate is slow as compared to the ^{1}H NMR timescale, but at temperatures above 40 °C, it became sufficiently fast so that the disappearance of the diastereotopicity of the CH$_2$NMe$_2$ protons is visible. The thermodynamic data for the racemisation process ($k_c = 450$ s^{-1}, $\Delta G^{\neq} = 15.5$ kcal mol^{-1}) could be deduced from the latter experiments (Fig. 3).

In order to obtain more details about the Ru–methanol interaction and to better characterise the likely intermediate involved in the exchange process, DFT-calculations were performed on the **1b** non deuterated analog (**1c**) and on the 16 e$^-$ species (**2**) resulting from decoordination of the MeOH. These calculations were also motivated by the fact that only scarce theoretical studies have been performed on Ru(η^6-benzene)-containing species [8], whereas a large number of such studies involving (η^5-Cp)metal are available in the literature [9–13].
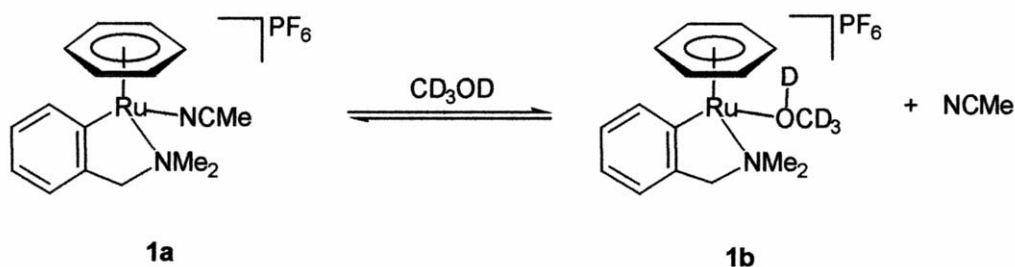

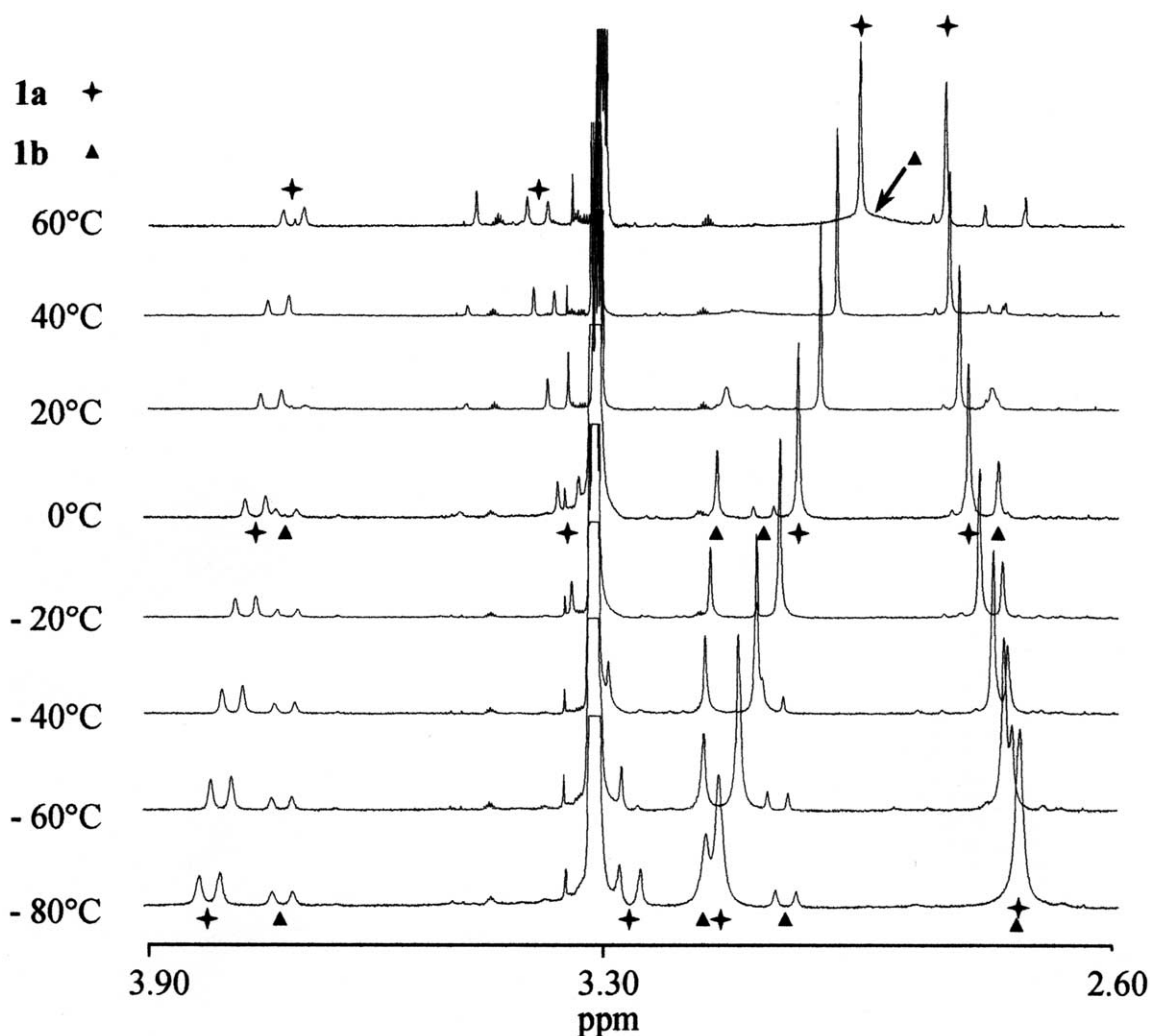Fig. 1. Equilibrium between compounds **1a** and **1b**.

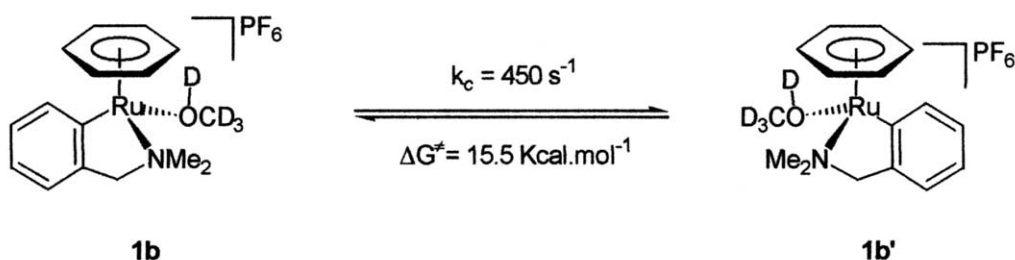Fig. 2. ^{1}H NMR spectra of the acetonitrile complex **1a** at variable temperatures in CD$_3$OD.

Fig. 3. Equilibrium between compounds **1b** and **1b'**.

Calibration of our calculations was performed on **1d** [(η^6-C$_6$H$_6$)RuCl(C$_6$H$_4$-2-CH$_2$NMe$_2$)], whose structure was determined experimentally [14]. Fairly good agreement was found for most bond distances and angles except for the geometry of the Ru(η^6-benzene) unit (see Table 1). Our calculations have led to a lengthening of these Ru–C distances. DFT-B3LYP calculations using valence double zeta basis set may lead

to metal-to-ring distances that are slightly too long as compared to those observed experimentally (see for instance the examples quoted in reference [15]). Moreover, the benzene ligand in **1d** was idealised in the X-ray refining process of the data, and thus the experimental Ru–C distances involving the benzene ligand may be less reliable than the other data. In line with this statement, we note that in several other crys-

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Table 1. Selected bond distances and angles in complexes **1c**, **1d**, **2** and **3**

		$1d_{exp}$[a]	$1d_{calc}$[b]	1c		2	3
				Rotamer 1	Rotamer 2		
Distances	Ru–C	2.080	2.052	2.056	2.056	2.007	1.995
	Ru–C_b[c]	1.668	1.884	1.891	1.895	1.841	1.829
	Ru–N	2.148	2.200	2.194	2.192	2.190	2.205
	Ru–C_a[d]	2.177	2.364	2.369	2.372	2.330	2.321
	Ru–L	2.430	2.491	2.056	2.201	–	–
Angles	C–Ru–N	78.1	79.3	79.1	79.3	80.4	82.9
	C–Ru–C_b	131.3	129.4	129.0	129.6	136.4	138.8
	C–Ru–L	86.0	88.1	86.4	80.5	–	–
	N–Ru–C_b	133.6	133.7	132.6	132.3	137.2	138.2
	L–Ru–C_b	124.3	123.6	128.0	131.5	–	–
	C_b–Ru–C_l[e]	156.8	156.2	155.1	155.2	171.0	179.0
Torsion angle	C_b–Ru–O–Me	–	–	–100.2	13.4	–	–

[a] Experimental X-ray data for the chloride complex (**1c**).

[b] Theoretical data for **1c**.

[c] C_b: C_6H_6 centroid.

[d] C_a: Average of the six Ru–C distances.

[e] C_l: Centroid of the CN orthometallated ligand.

tal structures of closely related compounds [7,16–18], it appeared that the Ru–C distances in this Ru(η^6-benzene) fragment are usually fond in the range 2.20/2.24 Å, i.e. somewhat longer than the 2.18 Å present experimental value. Thus, altogether these DFT-calculations should give a reasonable picture of the system under investigation here.

Two 'rotamers' of **1c**, characterised by their frequency analysis as true intermediates, were found. They correspond to a rotation of about 110° of the methanol molecule around the Ru–O bond (see the values of the torsion angle in Table 1) and are almost equal in energy. The most important structural data are reported in Table 1 and they are in agreement with those obtained for the Cl derivative (**1d**). The unsaturated methanol-free complex **2** was also characterised as a true intermediate (as established by frequency analysis). The energy of [2 + MeOH] is 10.3 kcal mol^{-1} above **1c** (ΔG value for the most stable conformation of [**2** + MeOH]).

It is apparent that in this intermediate the pyramidalisation of the Ru atom has evolved so as to move the cyclometallated ring in a position closer to the plane of symmetry of the hypothetical non-pyramidalised species **3**. This effect is best visualised through the angle between the centroid of the benzene ligand (C_b), the ruthenium centre and the centroid of the CN ligand (C_l). This C_b–Ru–C_l angle is close to 155° for the genuine pseudo-tetrahedral complexes and 180° for a hypothetical species in which the molecule has a pseudo-plane of symmetry (see **3**). If we assume that **2** is the intermediate that should lead to **1c** by coordination of one methanol ligand to ruthenium, then the mirror image of **2**, **2'** should likely be the intermediate to the formation of **1c'**, the enantiomer of **1c**, and **3** be the transition state for the racemisation of **2** to **2'**. This latter has been identified (see Fig. 4) – the imaginary frequency for this TS has a value of 67.43 i cm^{-1}; the associated eigenvector corresponds to the **2**-to-**2'** racemisation.

It lies 2.6 kcal mol^{-1} above **2** ($\Delta G^{\neq}$ value), thus the free activation energy calculated for the inversion of the configuration of **1c** to **1c'** is $\Delta G^{\neq} = 12.9$ kcal mol^{-1}, a value which is in close agreement with that determined experimentally (Fig. 5).

3. Conclusion

This study has allowed us to visualise a likely pathway for the racemisation of cycloruthenated semi-sandwich complexes. Any other process which would have required either the splitting of the Ru–N bond of the cycloruthenated ligand or a slippage of the benzene ring η^6-bound to Ru is expected to be much more higher in energy than the mechanism envisioned (a η^6-to-η^4 slippage of the benzene ring in the Noyori's system, which is quite similar to ours, required an energy of ~ 22 kcal mol^{-1} (B3LYP//B3LYP value) [8]).

4. Experimental part

[(η^6-C_6H_6)Ru(C_6H_4-2-CH_2NMe_2)(NCMe)]$^+PF_6^-$ (**1a**) was synthesised according to the published procedure [5]. The ^1H NMR variable temperature was recorded
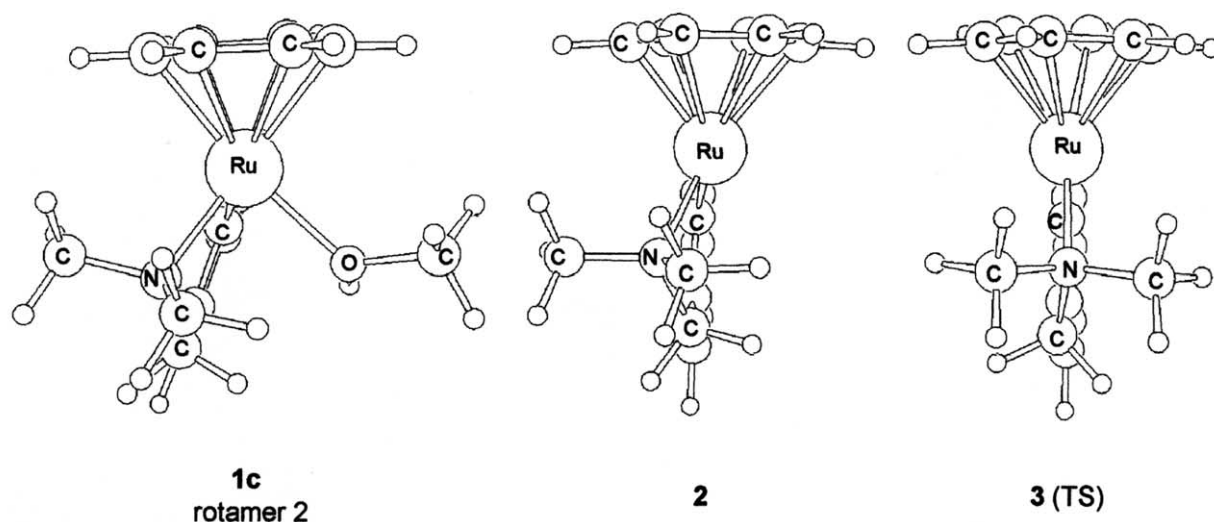
1c
rotamer 2

2

3 (TS)

Fig. 4. Representation of the methanol complex **1b** (rotamer 2), the 16 e⁻ species **2** and the transition state **3**.
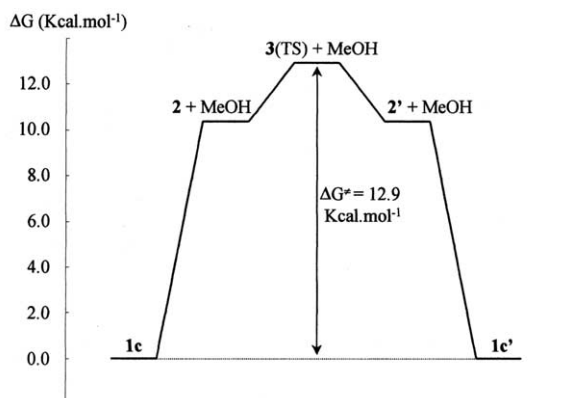

Fig. 5. Schematic representation of the energy variation.

on a Bruker-ft Avance 500 MHz, in deuterated methanol, from –80 to 60 °C. Chemical shifts (δ) and coupling constants (J) are expressed in ppm and Hz respectively and referenced to residual CHD_2OH. The DFT-calculations were carried out using the Gaussian 98 program [19]. The geometries of the intermediates and transition states were optimised using the B3LYP hybrid density functional method [20–22]. The standard LANL2DZ pseudo-potential and basis were used for all atoms [23–25]. Frequency calculations were performed for all points to characterise them either as TS (one imaginary frequency) or as true intermediate (no imaginary frequencies), and to compute Gibbs free energies (at 298.15 K, 1 atm).

$[(\eta^6\text{-}C_6H_6)Ru(C_6H_4\text{-}2\text{-}CH_2NMe_2)(ODCD_3)]^+PF_6^-$ (1b)

1a (0.005 g, 0.01 mmol) was dissolved at room temperature in carefully degassed CD_3OD (0.5 ml). The resulting yellow solution was transferred in a NMR tube that had been carefully dried and degassed. The tube was then put in the spectrometer and cooled to –80 °C. ^1H NMR measurement were made every 20 °C. As the temperature rise went up a peak broadening of the solvated species **1b** was observed and coalescence was reached at +60 °C. ^1H NMR (273 K): δ 8.44 (d, 1H, H_o, $^3J_{H-H} = 7.3$), 7.10 (t, 1H, H_m), 7.00 (t, 1H, H_p), 6.93 (d, 1H, $H_{m'}$), 5.63 (s, 6H, C_6H_6), 3.71 and 3.07 (AB, 2H, CH_2N, $^2J_{H-H} = 13.4$), 3.14 and 2.76 (2s, NMe_2).

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