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THE SYNTHESIS AND THE REACTIVITY OF ARENE RUTHENIUM OXALATO COMPLEXES

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ABSTRACT. This article outlines the reactions of the well known $[RuCl(\eta^6\text{-}p\text{-cymene})]_2(\mu\text{-}\eta^4\text{-}C_2O_4)$ and $[RuCl(\eta^6\text{-}p\text{-cymene})(\eta^2\text{-dppm})][PF_6]$ ruthenium complexes with $C_2O_4(Me_4N)_2$ in the mol ratios 1:1 and 2:1. While the 2:1 ratio reaction led to the sole and expected binuclear product $\{[Ru(\eta^6\text{-}p\text{-cymene})(\eta^2\text{-dppm})]_2(\mu\text{-}\eta^2\text{-}C_2O_4)\}[PF_6]_2$, the reaction also afforded the unexpected mononuclear complex $[RuCl(\eta^2\text{-}C_2O_4)(\eta^6\text{-}p\text{-cymene})][Me_4N]$. This can also be obtained in improved yield by reacting $[RuCl_2(p\text{-cymene})]_2$ with $C_2O_4[Me_4N]_2$ in a 1:1 mol ratio. Surprisingly, when $[RuCl(\eta^6\text{-}p\text{-cymene})]_2(\mu\text{-}\eta^4\text{-}C_2O_4)$ was reacted with an equimolar amount of the ligand dppm, the expected complex $\{[Ru(\eta^6\text{-}p\text{-cymene})]_2(\mu\text{-}\eta^4\text{-}C_2O_4)(\mu\text{-dppm})\}[PF_6]_2$ was accompanied by $[RuCl(\eta^6\text{-}p\text{-cymene})(\eta^2\text{-dppm})][PF_6]$ in an inseparable solid mixture.

KEY WORDS: Ruthenium, Arene, *p*-cymene, Mesitylene, Oxalate, *bis*-(Dipenylphosphino)methane

INTRODUCTION

In earlier publications, we have reported on the reactivity of $[RuCl_2(\eta^6\text{-arene})]_2$ **1** (arene = *p*-cymene **1a** and mesitylene **1b**) complexes toward *bis*-(diphenylphosphino)methane (dppm) [1, 2] and tetramethylammonium oxalate ($C_2O_4TMN_2$, TMN = $(CH_3)_4N^+$) [2]. Recent reports on the synthesis [3] and the reactivity [3, 4] of $[RuCl(\eta^6\text{-}p\text{-cymene})]_2(\mu\text{-}\eta^4\text{-}C_2O_4)$ **2** prompted us to reinvestigate our initial studies in this field.

The chemistry of dimers $[RuCl_2(\eta^6\text{-arene})]_2$ is centred around the cleavage of the bridging chloro ligands and the heterolytic rupture, under the effect of a polar solvent, of one of the two Ru-Cl bonds [5]. Furthermore, the advantage of the facile coordination of numerous varieties of electron donor pair ligands to the metal centre offers useful methods of access to an increasing range of mono-, bi- and polynuclear (η^6-arene) ruthenium(II) complexes [6].

Since the discovery of such reactivity, the chemistry of arene ruthenium derivatives has shown remarkable development in the homogeneous catalysis [7]. Arene ruthenium complexes have proved to be very active for olefin metathesis [8], Diels-Alder activation [9], catalytic hydrogenation of ketones [10], etc. Furthermore, these complexes have recently demonstrated efficient anticancer, antibacterial and antiviral activities, and some complexes are currently making significant progress in clinical trials [11]. In particular, arene ruthenium oxalato complexes are remarkable in cancer chemotherapy and a number of them have exhibited effectiveness in inhibiting cancer cell-growth proliferation [12].

The present paper deals with the reaction of $[RuCl(\eta^6\text{-}p\text{-cymene})]_2(\mu\text{-}\eta^4\text{-}C_2O_4)$ and $[RuCl(\eta^6\text{-}p\text{-cymene})(\eta^2\text{-dppm})][PF_6]$ complexes with oxalato and dppm ligands.

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EXPERIMENTAL

All synthetic reactions were carried out under nitrogen using standard Schlenk techniques. Organic solvents were distilled by conventional practices, kept to dryness over drying agents under nitrogen and degassed before use. NMR spectra were recorded on a Bruker AM300 spectrometer taking TMS as reference. Infrared spectra were determined on a Jasco FT/IR-5300 (Nujol mulls) and on Nicolet 250 (KBr) instruments. Microanalytical data were determined by the Service de Microanalyse du CNRS (Vernaison/France). Dimers $[RuCl_2(\eta^6\text{-}p\text{-cymene})]_2$ (**1a**) [13] and $[RuCl_2(\eta^6\text{-mesitylene})]_2$ (**1b**) [14] were prepared according to published methods from the starting material $RuCl_3.3H_2O$ purchased from Aldrich. Dppm was also obtained from Aldrich. Tetramethylammonium oxalate was a gift from Laboratoire de Chimie Minérale et Analytique (UCAD/Sénégal) prior to being synthesized by ourselves. $[RuCl(\eta^6\text{-}p\text{-cymene})(\eta^2\text{-dppm})][PF_6]$ (**9**) was synthesized as reported by us [1].

$[RuCl(\eta^6\text{-}p\text{-cymene})]_2(\mu\text{-}\eta^4\text{-}C_2O_4)$ (**2**). A solution of $C_2O_4TMN_2$ (0.193 g, 0.817 mmol) in MeOH (10 mL) was added to a red brown solution of $[RuCl_2(\eta^6\text{-}p\text{-cymene})]_2$ (0.500 g, 0.817 mmol) in CH_2Cl_2 (10 mL). The reaction mixture was then stirred upon completion for 24 h at room temperature under N_2. The resulting yellow solution was then evaporated to dryness under reduced pressure. Thereafter, the so obtained residue was taken up in CH_2Cl_2 (20 mL) and the resulting slurry filtered in air and on celite to remove the TMNCl salt. The orange filtrate collected was afterwards evaporated under vacuum to give an air stable solid in a yellow powdered form. The product was then recrystallized in a freeze by slow vapour diffusion of hexane in a saturated solution of the solid in CH_2Cl_2. After removing the solvent and drying the solid, compound **2** was gathered as yellow crystals. Yield: 0.500 g, 97 %. Analysis (%): found (calculated for $C_{22}H_{28}Cl_2O_4Ru_2$, 629.14 g/mol): C 41.83 (41.96), H 4.98 (4.45). IR (Nujol) cm^{-1}: 1616 ($\nu_{as(OCO)}$); (KBr) cm^{-1}: 1615 ($\nu_{as(OCO)}$), 1375 ($\nu_{s(OCO)}$). NMR ^1H [$(CD_3)_2CO$, 300.135 MHz, 297 K] δ (ppm): 5.7, 5.4 (dd , 4H , J_{HH} = 6.07 Hz , Me-$C_6\underline{H}_4$-^{i}Pr), 2.3 (m, 1H, J_{HH} = 6.90 Hz, Me-C_6H_4-C$\underline{H}$Me$_2$), 2.2 (s, 3H, C$\underline{H}_3$-C_6H_4-^{i}Pr), 1.8 (m, 1H, J_{HH} = 6.91 Hz, Me-C_6H_4-C$\underline{H}$Me$_2$), 1.3 (d, 6H, J_{HH} = 6.93 Hz, Me-C_6H_4-CH(C$\underline{H}_3$)$_2$).

$[RuCl(\eta^6\text{-mesitylene})]_2(\mu\text{-}\eta^4\text{-}C_2O_4)$ (**3**, **4**). When a solution of $C_2O_4TMN_2$ (0.404 g, 1.712 mmol) in MeOH (10 mL) was added to a brown solution of $[RuCl_2(\eta^6\text{-mesitylene})]_2$ (1 g, 1.712 mmol) in CH_2Cl_2 (10 mL), at room temperature and under nitrogen, a pale green solid identified to complex **3** suddenly precipitated. The stirring was nevertheless maintained for 4 hours. The precipitate was then filtered off, washed with diethyl ether and dried under vacuum. Complex **3** was obtained in a pale green solid state insoluble in most organic solvents. Yield: 675 mg, 67 %. Analysis (%): found (calculated for $C_{20}H_{24}Cl_2O_4Ru_2$: 603.14 g/mol or for $C_{40}H_{48}Cl_4O_8Ru_4$: 1206.28 g/mol): C 39.41 (39.79), H 3.90 (3.98). IR (in Nujol mulls) cm^{-1}: 1620 ($\nu_{as(OCO)}$). The filtrate was thereafter evaporated to dryness and the solid mixture melted in CH_2Cl_2 (20 mL). Thus, complex **4** was isolated (yield: 0.011 g, 14 %) in the form of a yellow solid after work up as mentioned above for the isolation of compound **2**. Analysis (%): found (calculated for $C_{20}H_{24}Cl_2O_4Ru_2$, 603.14 g/mol): C 39.53 (39.79), H 3.75 (3.98). IR (in Nujol mulls) cm^{-1}: 1624 ($\nu_{as(OCO)}$); (in KBr disc) cm^{-1}: 1618 ($\nu_{as(OCO)}$), 1384 ($\nu_{as(OCO)}$). NMR ^1H [$(CD_3)_2CO$; 300.135 MHz; 297K] δ (ppm): 5.2 (s , 3H , $C_6\underline{H}_3$), 2.2(s, 9H, -C$\underline{H}_3$).

$[RuCl(\eta^2\text{-}C_2O_4)(\eta^6\text{-}p\text{-cymene})]TMN$ (**7**). Two procedures were used for the preparation of complex **7**. *Procedure A*. The ligand $C_2O_4TMN_2$ (0.075 g, 0.305 mmol) in solution in MeOH (10 mL) was added dropwise to a stirred solution of **2** (0.200 g, 0.305 mmol) in CH_2Cl_2 (10 mL) at room temperature under N_2. After 72 h of stirring, the solvents were removed under vacuum. The crude residue was subsequently extracted with CH_2Cl_2 (20 mL) and the extract filtered in air

and on celite. The evaporation of the filtrate gave a pale yellow solid that was purified as above and identified later to complex **7**. Yield: 0.044 g, 17 %. Analysis (%): found (calculated for $C_{16}H_{26}NClO_4Ru.H_2O$, 450.57 g/mol): C 42.39 (42.61), H 6.10 (6.21). IR (Nujol) cm^{-1}: 1701 ($\nu_{(C=O)}$), 1657, 1635 ($\nu_{as(OCO)}$), 951 ($\nu_{(NC4)}$). ^1H NMR [$(CD_3)_2CO$, 300.135 MHz, 297 K] δ (ppm): 5.45, 5.15 (dd, 4H, J_{HH} = 5.97 Hz, Me-$C_6\underline{H}_4$-^{i}Pr), 3.4 (s, $(CH_3)_2N^+$), 2.25 (m, 1H, Me-C_6H_4-C$\underline{H}$Me$_2$), 2.15 (s, 3H, C$\underline{H}_3$-C_6H_4-^{i}Pr), 1.85 (m, 1H, J_{HH} = 6.91 Hz, Me-C_6H_4-C$\underline{H}$Me$_2$), 1.34 (d, 6H, J_{HH} = 6.93 Hz, Me-C_6H_4-CH(C$\underline{H}_3$)$_2$). ^{13}C NMR [$(CD_3)_2CO$, 75.034 MHz, 297 K] δ (ppm): 207, 42 (s, C=O). ***Procedure B***. Complex **7** was obtained in form of a yellow and air stable solid (yield: 0.040 g, 57 %) according to the described procedure for **2** by reacting [$RuCl_2(\eta^6$-*p*-cymene)]$_2$ (0.100 g, 0.165 mmol) with a large excess of $C_2O_4TMN_2$ (0.100 g, 0.423 mmol), with respect to the mol ratio 1:2. Analysis (%): found (calculated for $C_{16}H_{26}NClO_4Ru$, 432.57 g/mol): C 42.66 (42.61), H 6.52 (6.21). IR (Nujol) cm^{-1}: 1700 ($\nu_{(C=O)}$), 1658, 1635 ($\nu_{as(OCO)}$), 951 ($\nu_{(NC4)}$). NMR ^1H [$(CD_3)_2CO$, 300.135 MHz, 297 K] δ (ppm): 5.45, 5.15 (dd, 4H, J_{HH} = 5.80 Hz, Me-$C_6\underline{H}_4$-^{i}Pr), 3.40 (s, $(CH_3)_2N^+$), 2.30 (m, 1H, J_{HH} = 6.89 Hz, Me-C_6H_4-C$\underline{H}$Me$_2$), 2.20 (s, 3H, C$\underline{H}_3$-C_6H_4-^{i}Pr), 1.80 (m, 1H, J_{HH} = 6.91 Hz , Me-C_6H_4-C$\underline{H}$Me$_2$), 1.30 (d, 6H, J_{HH} = 6.93 Hz, Me-C_6H_4-CH(C$\underline{H}_3$)$_2$).

[Ru(η^6-p-cymene)]$_2$(μ-η^4-C_2O_4)(μ-dppm)][PF_6]$_2$ (**8**) *and [RuCl(η^6-p-cymene)(η^2-dppm)][PF_6]* (**9**). A stirred solution of complex **2** (0.100 g, 0.160 mmol) and the ligand dppm (0.063 g, 0.160 mmol), in a mixture of MeOH (10 mL) and CH_2Cl_2 (10 mL), was treated dropwise with NH_4PF_6 (0.052 g, 0.320 mmol) at room temperature under N_2. The resultant yellow solution gradually turned to brown during stirring. After 72 h, the solvents were evaporated to dryness under vacuum. Thus, the solid material was dissolved in CH_2Cl_2 (20 mL). The brown supernatant liquid was next filtered off on celite and evaporated to dryness under reduced pressure. By this means, the obtained brown solid was washed twice with 10 mL portions of diethyl ether. Drying as well as purification led to a brown powder that will be recognized to be a mixture on the whole percentage of 44.5 % of complex **8** and 55.5 % of complex **9**. Analysis (%): found (calculated for a mixture of 44.5 % of $C_{47}H_{50}P_4F_{12}O_4Ru_2$ (**8**) and 54.5 % of $C_{35}H_{36}P_3F_6ClRu.3H_2O$ (**9**)): C 46.53 (46.29), H 4.43 (4.61), P 9.18 (9.85). IR (Nujol) cm^{-1}: 1680, 1660, 1624 ($\nu_{as(OCO)}$), 839 (ν_{PF}). NMR ^{31}P {^1H} [$(CD_3)_2CO$, 121.497 MHz, 297 K] δ (ppm): 25.86 (s, μ-P$\underline{CH}_2$P of (8)), 3.23 (s, η^2-P$\underline{CH}_2$P of (9)), -143,04 (m, PF_6^-). NMR ^1H [$(CD_3)_2CO$, 300.135 MHz, 297K] δ (ppm): 7.5-7.9 (m, $C_6\underline{H}_5$), 6.6, 6.5 (dd, Me-$C_6\underline{H}_4$-^{i}Pr of (**9**)), 5.7, 5.45 ((dd, Me-$C_6\underline{H}_4$-^{i}Pr of (**8**)), 5.60 ((dt, PC$\underline{H}_2$P of (**9**)), 4.7 (dt, PC$\underline{H}_2$P of (**9**)), 4.3 (t, PC$\underline{H}_2$P of (**8**)), 2.4 (m, 1H, Me-C_6H_4-C$\underline{H}$Me$_2$ of (**9**)), 2.3 (m, 1H, Me-C_6H_4-C$\underline{H}$Me$_2$ of (**8**)), 1.9 (s, 3H, C$\underline{H}_3$-C_6H_4-^{i}Pr of (**9**)), 1.55 (s, 3H, C$\underline{H}_3$-C_6H_4-^{i}Pr of (**8**)), 1.25 (d, 6H, Me-C_6H_4-CH(C$\underline{H}_3$)$_2$ of (**9**)), 1.15 (d, 6H, Me-C_6H_4-CH(C$\underline{H}_3$)$_2$ of (**8**)).

{[Ru(η^6-p-cymene)(η^2-dppm)]$_2$.(μ-η^2-C_2O_4)}[PF_6]$_2$ (**10**). A solution of **9** (0.100 g, 0.125 mmol) and $C_2O_4TMN_2$ (0.015 g, 62.5 mmol), in a mixture of MeOH (10 mL) and CH_2Cl_2 (10 mL), was stirred for 72 h. After removal of the solvents, the yellow powdered solid was melted in CH_2Cl_2 (20 mL). After that, the resulting solution was filtered off to remove the salt NH_4Cl and the filtrate evaporated to dryness. Next, the product was washed twice with small portions of diethyl ether. Drying yielded complex (**10**) in a yellow solid form exclusive of further purification. Yield: 0.084 g, 49 %. Analysis (%): found (calculated for $C_{72}H_{72}P_6F_{12}O_4Ru_2$, 1616.14 g/mol): C 53.78 (53.46), H 4.86 (4.63). IR (Nujol) cm^{-1}: 1700.00 ($\nu_{(C=O)}$), 1651, 1625 ($\nu_{as(OCO)}$), 839 (ν_{PF}). NMR ^{31}P {^1H} [$(CD_3)_2CO$, 121.497 MHz, 297 K] δ (ppm): 3.96 (s, η^2-P$\underline{CH}_2$P), -143.04 (m, PF_6^-). NMR ^1H [$(CD_3)_2CO$, 300.135 MHz, 297 K] δ (ppm): 7.9-7.5 (m, -$C_6\underline{H}_5$), 6.6, 6.5 (d, 4H, Me-$C_6\underline{H}_4$-^{i}Pr); 5.8 (m, 2H, PC$\underline{H}_2$P), 4.6 (m, 2H, PC$\underline{H}_2$P), 2.5 (m, 1H, Me-C_6H_4-C$\underline{H}$Me$_2$), 1.5 (s, 3H, C$\underline{H}_3$-C_6H_4-^{i}Pr), 1.15 (d, 6H, Me-C_6H_4-CH(C$\underline{H}_3$)$_2$).

RESULTS AND DISCUSSION

The preparation of $[RuCl(\eta^6\text{-}p\text{-cymene})]_2(\mu\text{-}\eta^4\text{-}C_2O_4)$ **2** was first reported by Yan and co-workers [3]. Four years earlier, as mentioned in that study, we had reacted the oxalato ligand with $[RuCl_2(\eta^6\text{-arene})]_2$ (arene = *p*-cymene **1a**, and mesitylene **1b**). In contrast to the later procedures [3, 4], we used $C_2O_4(TMN)_2$ instead of the commercially available ammonium and sodium oxalate salts. Our choice of reagent was determined by two factors. Firstly, we tried to prevent a possible acidification by the ammonium salt, by employing $C_2O_4(NH_4)_2$, and, secondly, the organometallic complexes are water-sensitive.

The oxalato ligand has long played an important role in coordination chemistry [15]. It is easily isolated in the form of a white hygroscopic solid by acid-base neutralization of oxalic acid ($H_2C_2O_4$) with the tetramethylammonium hydroxide (TMNOH) in absolute ethanol [16].

Once bonded to the Ru(II), the characterization of the oxalato ligand by infrared spectroscopy (IR) is possible and gives information on its mode of coordination by use of group theory calculations [17].

$[RuCl(\eta^6\text{-arene})]_2.(\mu\text{-}\eta^4\text{-}C_2O_4)$ complexes (arene = p-cymene and mesitylene) (**2-4**)

As depicted in Figure 1, **1a** was reacted with $C_2O_4TMN_2$ in a mixture of CH_2Cl_2-MeOH in the mol ratio 1:1 (1 unit of the dimer per 1 unit of the ligand). The reaction led to a single yellow product **2** (97 % yield) soluble in CH_2Cl_2.

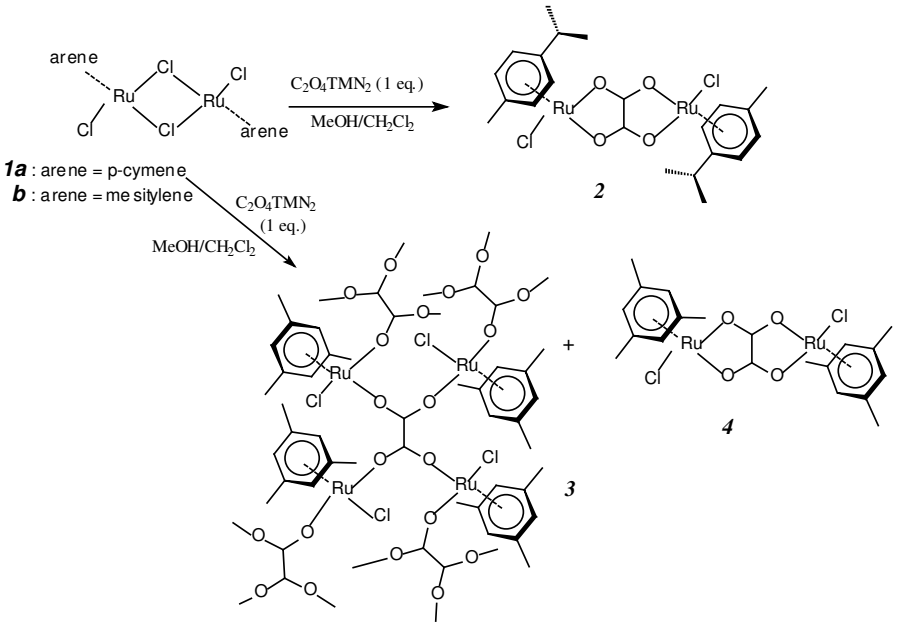
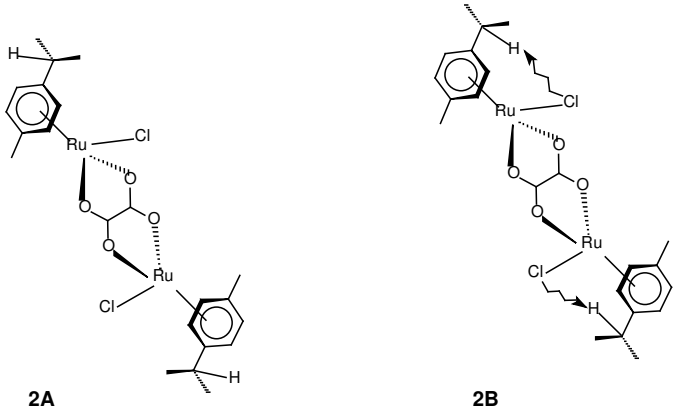


Figure 1. Scheme of formation of complexes (**2**-**4**).

Using identical reaction conditions, dimer **1b** was reacted with $C_2O_4(TMN)_2$ yielding **3** (67 % yield) and **4** (14 % yield). Compound **3** was isolated in the form of a pale green precipitate insoluble in CH_2Cl_2 and other organic solvents, although slightly soluble in DMSO at room temperature. Complex **4** was obtained as a yellow solid soluble in CH_2Cl_2.

Complexes **2** and **4** were characterized by infrared and ^{1}H NMR spectroscopy and **3** only by infrared spectroscopy. The IR spectra (Nujol mulls) shows a strong and unique band between 1646 and 1625 cm^{-1} associated with $\nu_{as(OCO)}$. The infrared spectra of **2** and **4** in KBr show that the related $\nu_{s(OCO)}$ band appears at 1375 and 1384 cm^{-1}, while the $\nu_{as(OCO)}$ band occurs at 1615 and 1618 cm^{-1} [18]. The absence of a third band above 1700 cm^{-1} is consistent with an identical perturbance of the four oxygen atoms corresponding to the D_2h symmetry group of the ligand.

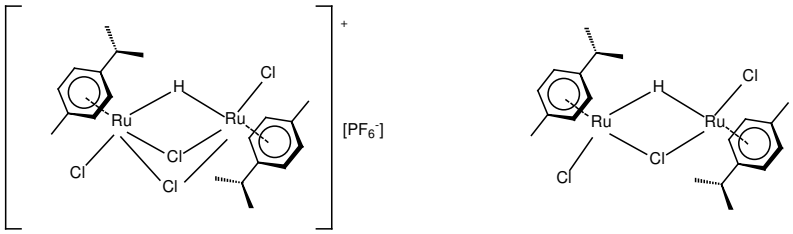
As reported in the Experimental section, the presence of the arene groups is confirmed by ^{1}H NMR spectroscopy. For instance, the aromatic protons of the *p*-cymene group appear in two AB patterns at δ_H 5.7 and 5.4. Surprisingly, in the ^{1}H NMR spectrum of **2**, the isopropylic proton occurs as two multiplets at δ_H 2.3 (J_{HH} = 6.90 Hz) and 1.8 (J_{HH} = 6.91 Hz), for an integration ratio of one proton. The ^{1}H NMR data of Yan and his co-workers [3] show only one peak at δ_H 2.883 for the isopropylic proton. Accordingly, this study gave an account of the existence of two conformational isomers for complex **2**, as well established by these authors for the complex of the identical analytical formula [RuCl(η^6-p-cymene)]$_2$.(μ-η^4-C_2O_4) on the basis of a single-crystal X-ray analysis [3]. The $\delta_{Hisopropyl}$ chemical shift = 1.8 ppm could be due to a pronounced shielding effect of the chloro ligand (Figure 2).



2A **2B**

Figure 2. Two conformational isomers for complex **2**.

Similar observations in ^{1}H NMR spectra were reported by Bennett and Ennett for dinuclear (μ-hydrido)(*p*-cymene)Ru(II) complexes and Brunner *et al*. for chiral-at-metal (η^6-*p*-cymene)Ru(II) and (η^6-*p*-cymene)Os(II) half sandwich complexes [14]. In particular, Bennett and Ennett have found that both the AB patterns of the aromatic proton resonances and the isopropyl-methyl doublets of the *p*-cymene group are doubled in moving from species **I** to **II** (Figure 3).



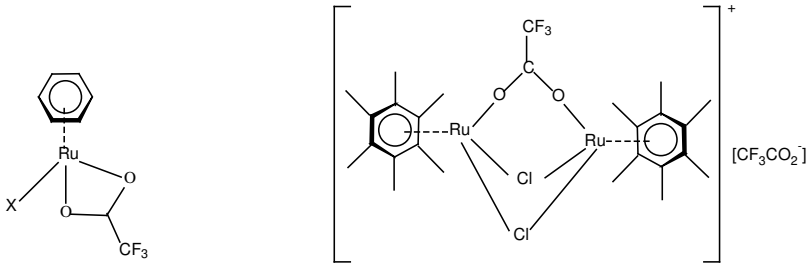
I **II**

Figure 3. Species **I** and **II**.

The reported elemental analysis, IR and ^{1}H NMR spectroscopies data for **4** are in agreement with an arene ruthenium oxalato complex of the formula $[RuCl(\eta^6\text{-mesitylene})]_2(\mu\text{-}\eta^4\text{-}C_2O_4)$. Complex **4** is then structurally analogous to **2**.

The infrared data of **3** are consistent with an oxalato ligand in the D_2h symmetry group. However, the additional microanalysis records and the insolubility of this compound are not sufficient to validate the proposed polymeric structure in Figure 1.

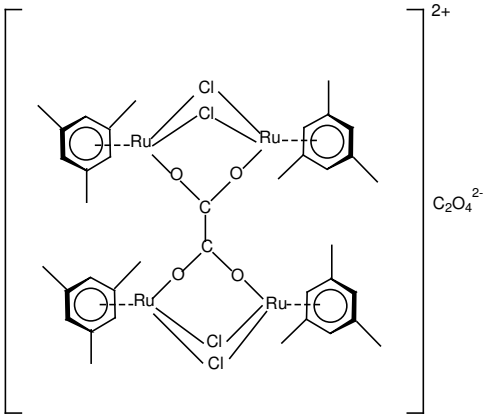
In a similar fashion, the difference in reactivity of dimers *p*-cymene and mesitylene ruthenium toward the oxalato ligand was also previously observed by Tocher and his co-workers when benzene and hexamethylbenzene ruthenium complexes were reacted with trifluoroacetic acid [19]. The reaction of trifluoroacetic acid, with $[RuCl_2(\eta^6\text{-benzene})]_2$ and $[RuCl_2(\eta^6\text{-hexamethylbenzene})]_2$ dimers gave different products **III** and **IV** (Figure 4).



III **IV**

Figure 4. Species **III** and **IV**.

The proposed structure **5** exhibits the same calculated analytical data (for $C_{40}H_{48}Cl_4O_8Ru_4$) as that of **3** (for $C_{20}H_{24}Cl_2O_4Ru_2$). Also, it is expected to show an infrared spectrum like that of **3**. Since, in **5**, the oxalate counter-cation is also in a D_2h symmetry group similar to $C_2O_4(TMN)_2$, its associated $\nu_{as(OCO)}$ band and that of the bonded oxalate ligand could overlap. Thus, **5** would be the dimer of **3** (Figure 5).



5

Figure 5. Complex **5** as a dimmer of **3**.

*Complex [RuCl(η^2-C_2O_4)(η^6-p-cymene)][TMN] (**7**)*

Compound **2** was reacted with an excess of $C_2O_4TMN_2$, in a CH_2Cl_2-MeOH mixture, to give a red-brown solid 7 in a poor yield of 17 % (Figure 6). The identification of the solid as **7** was established by elemental analysis and by infrared and NMR spectroscopies. The expected product **6** was not observed. The low yield of **7** is related to the decomposition of the reaction mixture over 3 days. The reaction was monitored with the aim of reducing its duration.

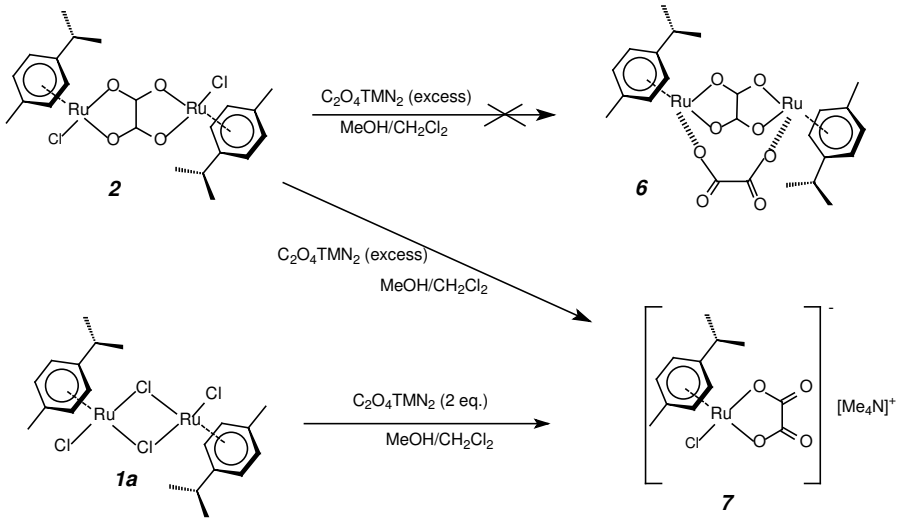


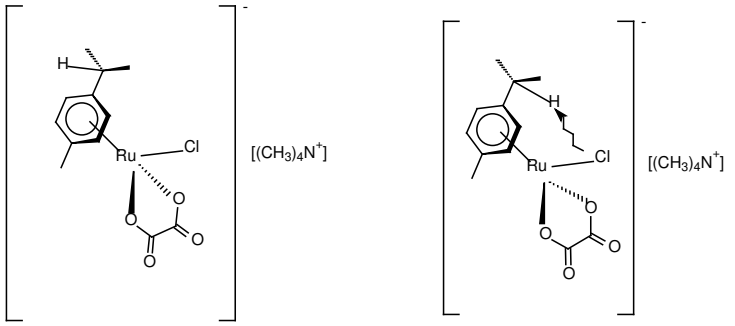
Figure 6. Scheme of formation of complexes (**7**).

An alternative route for the preparation of **7** consisted of treating **1a** with $C_2O_4TMN_2$ with a mol ratio 1:2 (1 equiv. of **1a** per 2 equiv. of $C_2O_4TMN_2$) at room temperature, in a mixture of CH_2Cl_2 and MeOH. A red-brown solid **7** was obtained in a moderate yield of 57 %.

The infrared spectrum of **7** shows two bands at 1657 and 1635 cm^{-1} attributable to $\nu_{as(OCO)}$ stretching vibration. The additional shoulder at 1701 cm^{-1} is assigned to $\nu_{(C=O)}$. Such IR bands are characteristic of an oxalate ligand in a C_2v symmetry group. The presence of the counter-cation $CH_3)_4N^+$ in the structure of **7** is confirmed by the band at 951 cm^{-1} assignable to the stretching vibration $\nu_{(NC4)}$ [20].

The ^1H NMR spectrum shows signals of the aromatic proton resonances at 5.45 and 5.15, similar to the ^1H NMR spectra of compound **2**. Resonances due to the methyl of the arene and those of the isopropyl group give two multiplets at 2.25 and 1.85. This might reflect, as mentioned above, an interaction with the chloro group. The presence of the counter-anion $[(CH_3)_2N]^+$ is revealed by the peak at 3.40 ppm.

In connection with the crystal structures described by Yan and his co-workers [3], the reported spectroscopies and elemental analysis data are consistent with the existence of two conformational isomers **7A** and **7B** for complex **7** (Figure 7a).

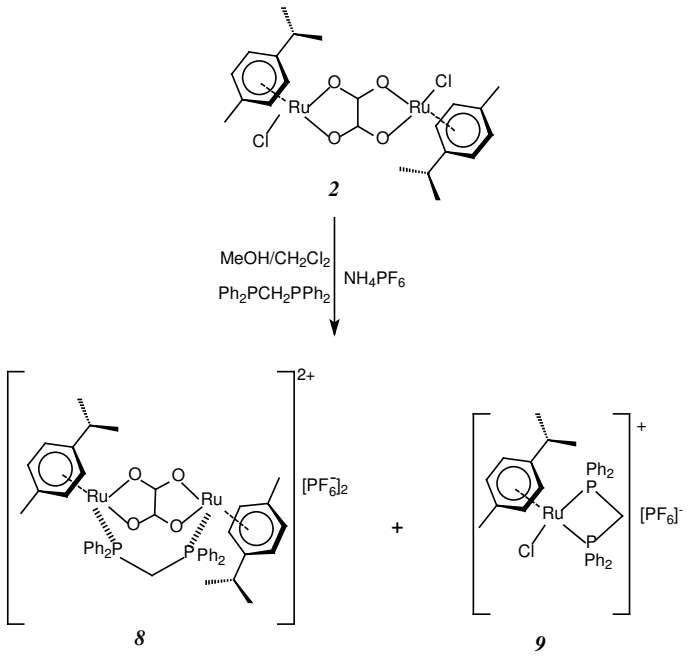


7A **7B**

Figure 7. Two conformational isomers of **7**.

Complex {[Ru(η⁶-p-cymene)]₂.(μ-η⁴-C₂O₄)].(μ-dppm)}[PF₆]₂ (**8** *and* **9**)

To elucidate the reactivity of **2** toward ligands, we determined whether dppm would replace the remaining chloride atoms or displace the oxalate ligand from the complex (Figure 8).



8 *9*

Figure 8. Scheme of formation of complexes (**8** and **9**).

Complex **2** was treated with an equimolar amount of dppm at room temperature, in CH_2Cl_2/MeOH in the presence of two equivalents of NH_4PF_6. The brown solid isolated proved

to be a mixture of the expected complex **8** and **9**. Attempts to separate **8** and **9** by recrystallization in mixed CH_2Cl_2 /hexane failed. **9** can be readily prepared by reacting the dimer $[RuCl_2(\eta^6\text{-}p\text{-cymene})]_2$ at room temperature with an equimolar amount of dppm, in CH_2Cl_2/MeOH in the presence of NH_4PF_6.

The IR spectrum of the solid mixture gives peaks at 1624 ($\nu_{as(OCO)}$) and 839 (ν_{PF} of PF_6^-). A change is observable in the shape of the $\nu_{as(OCO)}$ band. Perfectly symmetrical in the IR spectrum of **2**, it becomes irregular, without being split, with the appearance of two shoulders before 1700 cm^{-1} at 1680 and 1660 cm^{-1}. This connotes the effect of the ligand dppm once bonded to the Ru(II). Hence, we can state that the four oxygen atoms of the oxalate remain bonded to the Ru(II) as in **2**. Only, it is noticeable that the observed asymmetry in the form of the $\nu_{as(OCO)}$ band would indicate an oxalate ligand slightly bent from planarity to minimize interactions, similarly to an umbrella arrangement and owing to the closeness of the PPh_2 groups [21]. Hence, this would induce a difference in the perturbation of the oxygen atoms in the limits of that observable for the ligand in a C_2v symmetry group.

The NMR spectroscopy gives a best account of the mixture of complexes **8** and **9**. After subtraction of the peaks due to the protons of **9**, triplet at δ_H 4.3 (vs. δ_H 5.6 (dt) and 4.7 (dt) of **9**) is attributable to the methylenic protons of the bridged ligand dppm of **8**. The isopropylic proton of **8** appears at δ_H 2.3 (vs. 2.4 of **9**). Therefore, in the case of **8**, this signal does not occur as two peaks as observed for **2** and **7**, despite the presence of the oxalate ligand. This implicates the chloride interaction within the isopropylic proton in **2** and **7** as the source of this peak doubling. The $^{31}P\{^1H\}$ NMR spectrum shows the typical multiplet of the anion PF_6^- at δ_P –143.04 and a signal at δ_P 25.86 due to the phosphorous nuclei of the bridging dppm ligand of **8**. This is in addition to the peak at δ_P 3.23 which is characteristic of the chelating dppm ligand in **9**. The ^{31}P intensity ratios of these two peaks reveal that the mixture is composed of 44.5 % of complex **8** and 55.5 % of **9**.

Complex $\{[Ru(\eta^6\text{-}p\text{-cymene})(\eta^2\text{-}dppm)]_2.(\mu\text{-}\eta^2\text{-}C_2O_4)\}[PF_6]_2$ (**10**)

The reaction of two equivalents of complex **9** with one equivalent of $C_2O_4[TMN]_2$ at room temperature, in CH_2Cl_2/MeOH, resulted in the formation of complex **10** that was isolated as an air-stable yellow solid (49 % yield) (Figure 9). Complex **10** is soluble in the usual organic solvents and was characterized by microanalysis, IR and NMR (^1H, $^{31}P\text{-}\{^1H\}$) spectroscopies (details are given in the Experimental section).

In addition to the expected absorption for the PF_6^- (839 cm^{-1}), the IR spectrum of **10** exhibits a strong band ($\nu_{as(OCO)}$) split into two components at 1651 and 1625 cm^{-1} due to the coordinated oxygen atoms of the oxalate. The shoulder at 1700 cm^{-1} matches the stretching vibrations ($\nu_{(C=O)}$) of non-coordinated C=O bonds. The appearance of this shoulder and the splitting of the $\nu_{as(OCO)}$ vibration are in accordance with the C_2v symmetry group of the oxalate.

The most remarkable feature of the ^1H NMR spectrum is the unresolved two multiplets at δ_H 5.8 and 4.6 that was expected for the characteristic two triplet resonances of the methylenic protons. The resolution of these two signals, compared to those found in the ^1H NMR spectrum of **9**, is related to the electron-withdrawing of the oxalate. In comparison to the NMR data of **2** and **7**, the ^1H NMR spectrum of **10** shows only one unique signal at δ_H 2.5 due to the isopropylic proton. Thus, we conclude that **10** does not possess conformational isomers like derivatives **2** and **7**. Further, **10** displays in its $^{31}P\text{-}\{^1H\}$ NMR spectrum a singlet at δ_P 3.96 that is shifted to lower frequency compared to the peak due to the phosphorus nuclei of the chelating dppm in **9** (3.23 ppm). This is anticipated, given the deshielding effect of the carboxylate groups. The multiplet at δ_P -143.04 is associated with the PF_6^- anion.

The spectroscopic data of **10**, as well as its elemental analysis, are consistent with the proposed structure in Figure 9.

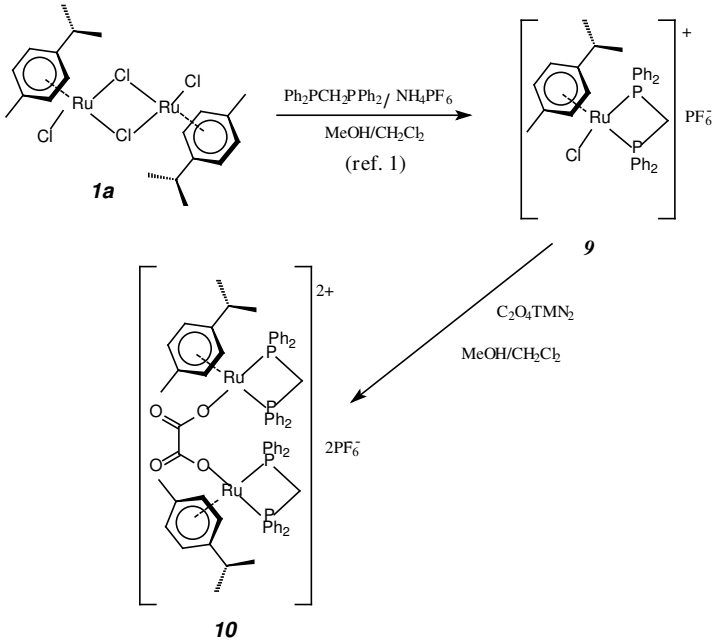


Figure 9. Scheme of formation of complexes (**10**).

CONCLUSIONS

This paper has shed more light on the complex $[RuCl(\eta^6\text{-}p\text{-cymene})]_2.(\mu\text{-}\eta^4\text{-}C_2O_4)$. The ^1H NMR spectra have revealed the existence of two conformational isomers for this and related complexes. Further reaction of dppm, with $[RuCl(\eta^6\text{-}p\text{-cymene})]_2.(\mu\text{-}\eta^4\text{-}C_2O_4)$ generates $[RuCl(\eta^6\text{-p-cymene})(\eta^2\text{-dppm})][PF_6]$, in addition to the expected binuclear $[Ru(\eta^6\text{-p-cymene})]_2(\mu\text{-}\eta^4\text{-}C_2O_4)(\mu\text{-dppm})][PF_6]_2$ complex. Additionally, this study has revealed a difference in the reactivity of $[RuCl_2(\eta^6\text{-}p\text{-cymene})]_2$ and $[RuCl_2(\eta^6\text{-mesitylene})]_2$ toward the oxalate ligand. Investigations on the synthesis and the reactivity of other [η^6-(methyl-substituted)arene] Ru(II) oxalato complexes to further verify the proposed structures are in progress in our laboratory.

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