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# Synthesis, structure, and kinetic studies on $[RuCl_2(NCCH_3)_2(cod)]$

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$[RuCl_2(NCCH_3)_2(cod)]$, an alternative starting material to $[RuCl_2(cod)]_n$ for the preparation of ruthenium(II) complexes, has been prepared from the polymer compound and isolated in yields up to 87% using a new work-up procedure. The compound has been obtained as a yellow solid without water of crystallization. The complexes $[RuCl_2(NCR)_2(cod)]$ spontaneously transform into dimers $[Ru_2Cl(\mu\text{-}Cl)_3(cod)_2(NCR)]$ (R = Me, Ph). $^1$H NMR kinetic experiments for these transformations evidenced first-order behavior. $[RuCl_2(NCPh)_2(cod)]$ dimerizes slower by a factor of ten than $[RuCl_2(NCCH_3)_2(cod)]$. The following activation parameters, $\Delta H^{\#} = 114 \pm 3\,kJ\,mol^{-1}$ and $\Delta S^{\#} = 66 \pm 9\,J\,K^{-1}\,mol^{-1}$ for $R = CH_3CN$ ($\Delta G^{\#} = 94 \pm 5\,kJ\,mol^{-1}$, 298.15 K) and $\Delta H^{\#} = 122 \pm 2\,kJ\,mol^{-1}$ and $\Delta S^{\#} = 75 \pm 6\,J\,K^{-1}\,mol^{-1}$ for R = Ph ($\Delta G^{\#} = 100 \pm 4\,kJ\,mol^{-1}$, 298.15 K), have been calculated from the first-order rate constants in the temperature range 294–323 K. The kinetic parameters are in agreement with a two-step mechanism with dissociation of acetonitrile as the rate-determining step. The molecular structures of $[Ru_2Cl(\mu\text{-}Cl)_3(cod)_2(NCR)]$ (R = Me, Ph) have been determined by X-ray diffraction.

*Keywords*: Ruthenium; Dimerization; Kinetics



## 1. Introduction

The polymer $[RuCl_2(cod)]_n$ is a useful synthetic precursor that has been widely used as an entry into ruthenium chemistry [1]. The easy cleavage of the chloro-bridges by neutral ligands, metathesis with anionic ligands or replacement of the strongly bonded 1,5-cyclooctadiene, has led to preparation of a range of ruthenium(II) complexes [2–5]. In general, syntheses using $[RuCl_2(cod)]_n$ need harsh conditions and long reaction times due to its low solubility. Moreover, a filtration step is generally required to remove the unreacted ruthenium polymer, which very often results in moderate yields.

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Less attention has been paid to the soluble compound $[RuCl_2(NCCH_3)_2(cod)]$ despite its potential as an equivalent precursor for ruthenium chemistry due to lability of the acetonitrile ligands [6–11]. Only a handful of compounds have been synthesized from this mononuclear ruthenium(II) complex with hydridotris(pyrazolyl)borate compound [RuTpCl(cod)] [12], a platform for synthesis of a range of organometallic compounds [13, 14], as the most notable example. $[RuCl_2(NCCH_3)_2(cod)]$ has been recently applied to the synthesis of ruthenium complexes with biological properties and biomedical applications [15–21].

The relatively low yield attained in its preparation and the variable water content of the isolated product are major factors that have discouraged the application of $[RuCl_2(NCCH_3)_2(cod)]$ in synthesis. We have found that this compound dimerizes in solution at room temperature; the dinuclear $[Ru_2Cl(\mu\text{-}Cl)_3(cod)_2(NCCH_3)]$ was observed in the NMR spectrum of $[RuCl_2(NCCH_3)_2(cod)]$ when the spectrum is recorded a few minutes after its dissolution. We report herein a reliable work-up for the synthesis of $[RuCl_2(NCCH_3)_2(cod)]$ that leads to isolated yields over 85% without water of crystallization. In addition, the kinetics of dimerization of $[RuCl_2(NCR)_2(cod)]$ (R = Me, Ph) have been studied by NMR.



## 2. Experimental

### 2.1. *General methods*

All manipulations were performed under a dry argon atmosphere using Schlenk and Cannula techniques. Acetonitrile was distilled over $CaH_2$. Other solvents were obtained from a Solvent Purification System (Innovative Technologies). Standard literature procedures were used to prepare $[RuCl_2(cod)]_n$ and $[RuCl_2(NCPh)_2(cod)]$ [22]. $^1$H NMR spectra were recorded on a Bruker Avance 500 operating at 500.13 MHz. Chemical shifts are reported in parts per million and referenced to $SiMe_4$ using the signal of the deuterated solvent. C, H, and N analyses were performed in a Perkin-Elmer 2400 CHNS/O microanalyzer.

### 2.2. *Synthesis of [RuCl$_2$(NCCH$_3$)$_2$(cod)] (1)*

A 100 mL Schlenk tube was charged with $[RuCl_2(cod)]_n$ (1.00 g, 3.57 mmol), acetonitrile (60 mL), and 1,5-cyclooctadiene (1.0 mL). The suspension was refluxed for 12 h and then filtered while hot through a celite pad to give an orange solution that was brought to dryness under vacuum. The orange-yellow residue was stirred with methanol (3 mL) for 10 min and then diethyl ether (9 mL) was added. The suspension was further stirred for 10 min and then allowed to settle and filtered. The washing procedure to remove the soluble $[RuCl_2(NCCH_3)_4]$ was repeated three more times. The pale-yellow solid was washed with diethyl ether ($3 \times 3$ mL) and dried under vacuum overnight. Yield: 87% (1.13 g). Anal. Calcd for $C_{12}Cl_2H_{18}N_2Ru$ (%): C, 39.79; H, 5.01; N, 7.73. Found: C, 39.68; H, 5.68; N, 7.78. $^1$H NMR ($CDCl_3$): $\delta = 4.31$ (m, 4H, =CH cod), 2.63 (s, 6H, $NCCH_3$), 2.45 (m, 4H, $>CH_2$ cod), 2.06 (m, 4H, $>CH_2$ cod).

### 2.3. *Kinetic measurements*

The rates of dimerization of **1** and **3** were measured by $^1$H NMR spectroscopy. A 5 mm NMR tube containing a $CDCl_3$ solution of [$RuCl_2(NCR)_2(cod)$] (0.030 M) and methoxybenzene (1.2 μL) was introduced into the NMR probe preheated to the desired temperature (294–323 K). After allowing for thermal equilibration and experiment setup, periodic NMR spectra (typically each 10 min) with identical acquisition parameters were recorded over several hours. Disappearance of [$RuCl_2(NCR)_2(cod)$] was monitored by $^1$H NMR (500.13 MHz) spectroscopy by integrating the resonances of the =CH protons of cod (4.31 ppm for **1** and 4.42 ppm for **3**) compared to the internal standard methoxybenzene using automatic integration software. The observed rate constants were obtained from linear least square regression analysis. The activation parameters, $\Delta H^{\#}$ and $\Delta S^{\#}$, were calculated from a linear least squares fit of $\ln(k/T)$ *versus* $1/T$ (Eyring equation) [23].

### 2.4. *Crystal structure determination*

Single crystals for X-ray diffraction study of [$Ru_2Cl(\mu\text{-}Cl)_3(cod)_2(NCCH_3)$] (**2**) and [$Ru_2Cl(\mu\text{-}Cl)_3(cod)_2(NCPh)$] (**4**) were grown by slow diffusion of diethylether into dichloromethane solutions of the complexes. Intensity data for both structures were collected at low temperature (100(2) K) on a Bruker SMART APEX CCD area diffractometer using graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å). Data were processed using SAINT [24] and corrected for absorption using a multi-scan method applied with SADABS [25, 26]. The structures were solved by direct methods with SHELXS-86 [27] and the refinement, by full-matrix least squares on $F^2$, was carried out with SHELXL97 [28] with anisotropic displacement parameters for all non-hydrogen atoms. Hydrogen atoms were included in calculated positions and refined as riding atoms. All residual peaks were lower than 1.03 e Å$^{-3}$ and were situated close to ruthenium. Crystallographic and structure refinement data are given in table 1.

## 3. Results and discussion

### 3.1. *Synthesis of [$RuCl_2(NCCH_3)_2(cod)$]*

The polymer [$RuCl_2(cod)]_n$ was obtained as a brown solid directly from $RuCl_3 \cdot xH_2O$ and cyclooctadiene in refluxing ethanol with excellent yields (91–96%, 0.2 mol scale, equation (1)). [$RuCl_2(NCCH_3)_2(cod)$] (**1**) was prepared by refluxing a suspension of [$RuCl_2(cod)]_n$ in acetonitrile and obtained as orange crystals by crystallization from acetonitrile in moderate yield (38–44%, 5.0 mmol scale, equation (2)) [22].

$$RuCl_3 \times H_2O + 2cod + CH_3CH_2OH \rightarrow [RuCl_2(cod)]_n + 2HCl + CH_3COH \quad (1)$$

$$[RuCl_2(cod)]_n + 2CH_3CN \rightarrow [RuCl_2(NCCH_3)_2(cod)] \quad (2)$$

Crystalline **1** was reported to contain varying amounts of water of crystallization; the X-ray structure showed a *trans* disposition of the acetonitrile ligands (*OC-6*-33 isomer) [29, 30]. In addition, **1** spontaneously transforms in solution at room temperature into

Table 1. Crystal data and structure refinements for **2** and **4**.

| Complex | **2** | **4** |
|---|---|---|
| Empirical formula | $C_{18}H_{27}Cl_4NRu_2$ | $C_{23}H_{29}Cl_4NRu_2$ |
| Formula weight | 601.35 | 663.44 |
| Temperature (K) | 100(2) | 100(2) |
| Wavelength (Å) | 0.71073 | 0.71073 |
| Crystal size ($mm^3$) | $0.073 \times 0.064 \times 0.024$ | $0.106 \times 0.096 \times 0.093$ |
| Crystal system | Monoclinic | Monoclinic |
| Space group | *C2/c* | *C2/c* |
| Unit cell dimensions (Å, °) | | |
| *a* | 21.234(9) | 18.244(4) |
| *b* | 7.152(3) | 16.398(4) |
| *c* | 26.760(11) | 17.930(4) |
| *β* | 92.968(7) | 116.346(4) |
| Volume ($Å^3$), *Z* | 4058(3), 8 | 4807(2), 8 |
| Calculated density ($g\,cm^{-3}$) | 1.968 | 1.834 |
| Absorption coefficient ($mm^{-1}$) | 2.018 | 1.713 |
| *θ* range for data collection (°) | 1.52–28.38 | 1.76–27.05 |
| Reflections collected | 13,030 | 15,199 |
| Independent reflections | 4780 [$R$(int) = 0.0574] | 5225 [$R$(int) = 0.0728] |
| Goodness-of-fit on $F^2$ | 1.013 | 0.975 |
| Final $R$ indices [$I > 2\sigma(I)$][a] | $R_1 = 0.0433$, $wR^2 = 0.0853$ | $R_1 = 0.0459$, $wR^2 = 0.0813$ |
| $R$ indices (all data) | $R_1 = 0.0640$, $wR^2 = 0.0930$ | $R_1 = 0.0763$, $wR^2 = 0.0916$ |
| Largest difference peak and hole ($e\,Å^{-3}$) | 1.027 and −0.833 | 0.929 and −0.705 |

[a] $R_1(F) = \Sigma F_o - F_c / \Sigma F_o$; $wR_2(F^2) = (\Sigma[w(F_o^2 - F_c^2)^2] / \Sigma] w(F_o^2)^2])^{1/2}$.

the dinuclear compound $[Ru_2Cl(\mu\text{-}Cl)_3(cod)_2(NCCH_3)]$ (**2**). Thus, in order to optimize the yield in the synthesis of $[RuCl_2(NCCH_3)_2(cod)]$ (**1**) we have investigated its preparation and chemical behavior further.

We carried out the synthesis of $[RuCl_2(NCCH_3)_2(cod)]$ (**1**) following the reported experimental conditions [22]. Refluxing a suspension of $[RuCl_2(cod)]_n$ (2.76 mmol) in acetonitrile (28 mL) for 5 h in the presence of cod (1 mL), in order to minimize the formation of $[RuCl_2(NCCH_3)_4]$ [31], gave an orange solution after removing an insoluble material. Concentration of the solution to half of the volume and cooling to 258 K gave orange crystals of $\mathbf{1} \cdot x H_2O$ in ≈57% yield (1.57 mmol).

We have investigated both the composition of the resulting solution after isolation of **1** and the unreacted recovered solid. The $^1H$ NMR ($CDCl_3$) of an aliquot of the solution showed mainly **1** and a small amount of $[RuCl_2(NCCH_3)_4]$, apart from acetonitrile and 1,5-cyclooctadiene, which suggests to modify the work-up procedure to increase the isolated yield. In fact, starting from $[RuCl_2(cod)]_n$ (1.00 g, 3.57 mmol), following the same experimental procedure, **1** was isolated in 72% yield (0.937 g, 2.59 mmol) as a yellow–orange solid by crystallization from acetonitrile/diethyl ether; **1** was obtained free of crystallization water as evidenced in the $^1H$ NMR spectrum in dry $Cl_2Cl_2$. However, the 500 MHz $^1H$ NMR spectrum also showed the presence of $[RuCl_2(NCCH_3)_4]$ (≈5%). This by-product is only observable in the 500 MHz $^1H$ NMR spectra as a sharp singlet at 2.51 ppm. This signal is overlapped with the broad resonance at 2.45 ppm corresponding to $>CH_2$ protons of cod of **1** in the 300 MHz spectrum. The recovered solid (0.247 g) was shown to contain unreacted starting material and, in fact, it was possible to obtain a second crop of **1** (0.129 g, 0.356 mmol) by reacting this solid again with $CH_3CN$ under the same conditions giving a combined yield of 82%.

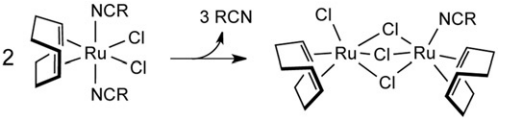


Figure 1. Spontaneous dimerization of $[RuCl_2(NCR)_2(cod)]$.

In order to improve the conversion of $[RuCl_2(cod)]_n$ to $[RuCl_2(NCCH_3)_2(cod)]$ (**1**) we have undertaken the synthesis under more diluted conditions (1.00 g, 3.57 mmol, in 60 mL of $CH_3CN$) increasing the reaction time (12 h). The crude compound was purified by washing several times with methanol/diethyl ether following the procedure described in the Experimental section. This optimized synthesis allows the isolation of anhydrous **1** in 87% yield (1.13 g, 3.12 mmol), free of $[RuCl_2(NCCH_3)_4]$, minimizing the amount of unreacted solid (Supplementary material).

### 3.2. *Kinetic study and mechanism for dimerization of [$RuCl_2(NCR)_2(cod)$] (R = Me, Ph)*

The acetonitrile ligands in $[RuCl_2(NCCH_3)_2(cod)]$ (**1**) are labile. The $^1H$ NMR of **1** in acetonitrile-$d^3$ at room temperature showed a resonance at 1.96 ppm corresponding to free acetonitrile, which steadily increases with time with concomitant decrease of the resonance at 2.60 ppm of the acetonitrile ligands in **1**, due to acetonitrile exchange. In the same way, the $^1H$ NMR of **1** in DMSO-$d^6$ evidenced the formation of $[RuCl_2(DMSO\text{-}d^6)_2(cod)]$ (5.50 ppm, 4H, =CH; 2.50, 2.29, 4H each, $>CH_2$) and free acetonitrile (2.07 ppm).

In addition, **1** spontaneously dimerizes in solution to give $[Ru_2Cl(\mu\text{-}Cl)_3(cod)_2(NCCH_3)]$ (**2**). The $^1H$ NMR of a solution of **1** in $CDCl_3$ (500 MHz) showed in a few minutes four new resonances at 4.69, 4.53, 4.46, and 4.26 ppm corresponding to =CH of the cod ligands of **2**. This spectrum also showed two new resonances in the acetonitrile region at 2.67 and 2.01 ppm that correspond to **2** and free $CH_3CN$, respectively. The dimerization of **1** also gives a second species (<10%), probably an asymmetric isomer of the dinuclear compound. In the same way, the related benzonitrile complex $[RuCl_2(NCPh)_2(cod)]$ (**3**) slowly transforms into $[Ru_2Cl(\mu\text{-}Cl)_3(cod)_2(NCPh)]$ (**4**). The formation of the dimeric species is a consequence of the lability of the nitrile ligands and the stability of triple halide-bridging ruthenium compounds (figure 1) [32–35].

To obtain information for these transformations, the kinetics of the conversion of $[RuCl_2(NCR)_2(cod)]$ (R = Me, **1**; Ph, **3**) into $[Ru_2Cl(\mu\text{-}Cl)_3(cod)_2(NCR)]$ (R = Me, **2**; Ph, **4**) has been studied by NMR spectroscopy in $CDCl_3$. Disappearance of **1** and **3** was monitored by $^1H$ NMR by integration of the olefinic =CH resonances of cod at 4.31 and 4.42 ppm, respectively, compared to the internal standard anisole. A typical plot of [**1**] and [**3**] *versus t*, obtained from NMR measurements at $[Ru]_0 = 0.028$ M and 304.15 K, is shown in figure 2. Dimerization of the acetonitrile complex **1** is much faster than the benzonitrile complex **3**.

Representation of $\ln([Ru]_0/[Ru])$ *versus t* for both complexes gave curves that show a linear fragment which is an indication that the dimerization reactions follow first-order kinetics up to 65% conversion (figure 3).

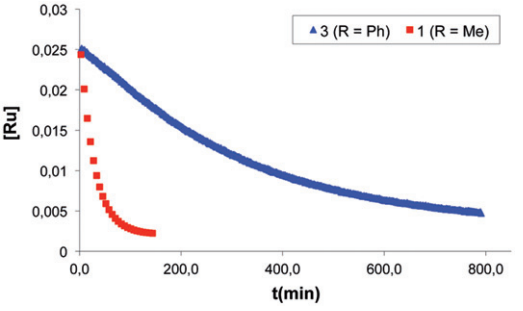


Figure 2. Decay of [**1**] and [**3**] *vs.* time for conversion of $[RuCl_2(NCR)_2(cod)]$ into $[Ru_2Cl(\mu\text{-}Cl)_3(cod)_2(NCR)]$ (R = Me, Ph) in $CDCl_3$ at 304.15 K determined from $^1H$ NMR measurements.

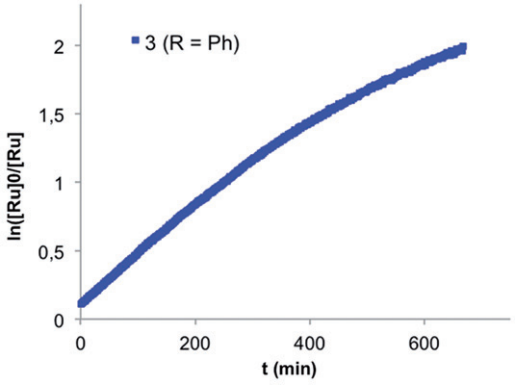


Figure 3. Typical first-order kinetic fit of the data: $\ln([\mathbf{3}]_0/[\mathbf{3}])$ *vs.* time plot for the conversion of **3** into **4** in $CDCl_3$ at 304.15 K.

The kinetic behavior for the dimerization reaction is compatible with the following mechanism:

$$[RuCl_2(NCR)_2(cod)] \underset{k_{1r}}{\overset{k_{1f}}{\rightleftharpoons}} [RuCl_2(NCR)(cod)] + RCN \tag{3}$$

$$2[RuCl_2(NCR)(cod)] \underset{k_{2r}}{\overset{k_{2f}}{\rightleftharpoons}} [Ru_2Cl(\mu\text{-}Cl)_3(cod)_2(NCR)] + RCN \tag{4}$$

The first step is an equilibrium involving dissociation of RCN to give the five-coordinate $[RuCl_2(NCR)(cod)]$ intermediate. In a second equilibrium step, the assembly of two molecules of this unsaturated species results in formation of $[Ru_2Cl(\mu\text{-}Cl)_3(cod)_2(NCR)]$ with extrusion of RCN.

The following rate equation can be written for the first step:

$$-\frac{d[RuCl_2(NCR)_2(cod)]}{dt} = k_{1f}[RuCl_2(NCR)_2(cod)] - k_{1r}[RuCl_2(NCR)(cod)][NCR]$$

Table 2. Temperature dependence of the first-order observed rate constant, $k_{obs}$ ($k_{1f}$), for RCN dissociation in $[RuCl_2(NCR)_2(cod)]$ ($CDCl_3$).

| | **1** (R = $CH_3$) | | **3** (R = Ph) | |
|---|---|---|---|---|
| $T$ (K) | $k_{1f}$ ($s^{-1}$) | $R^{2a}$ | $k_{1f}$ ($s^{-1}$) | $R^{2a}$ |
| 294.15 | $9.64 \pm 0.05 \times 10^{-5}$ | 0.996 | | |
| 299.15 | $2.25 \pm 0.02 \times 10^{-4}$ | 0.996 | $1.90 \pm 0.01 \times 10^{-5}$ | 0.999 |
| 304.15 | $5.02 \pm 0.04 \times 10^{-4}$ | 0.998 | $4.95 \pm 0.01 \times 10^{-5}$ | 0.999 |
| 309.15 | $9.32 \pm 0.1 \times 10^{-3}$ | 0.996 | $1.06 \pm 0.01 \times 10^{-4}$ | 0.996 |
| 314.15 | $2.09 \pm 0.07 \times 10^{-3}$ | 0.994 | $2.24 \pm 0.01 \times 10^{-4}$ | 0.998 |
| 319.15 | | | $5.02 \pm 0.03 \times 10^{-4}$ | 0.999 |
| 323.15 | | | $9.54 \pm 0.09 \times 10^{-4}$ | 0.999 |

[a]Correlation coefficient.

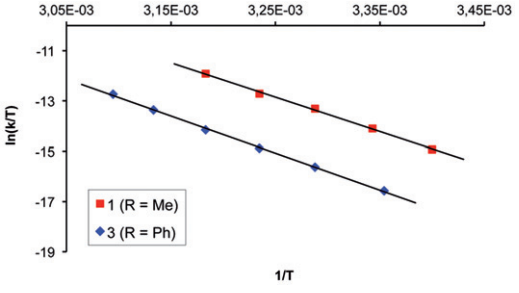


Figure 4. Eyring plot for the dimerization of $[RuCl_2(NCR)_2(cod)]$ into $[Ru_2Cl(\mu\text{-}Cl)_3(cod)_2(NCR)]$ (R = Me, Ph) in $CDCl_3$. The line represents the least squares fit to the data.

Assuming a very small concentration of $[RuCl_2(NCR)(cod)]$ (not observable by NMR) and a low [RCN] at the beginning of the reaction:

$$k_{1f}[RuCl_2(NCR)_2(cod)] > k_{1r}[RuCl_2(NCR)(cod)][NCR]$$

and, under these conditions, the dimerization reaction follows first-order kinetics [23].

$$-\frac{d[RuCl_2(NCR)_2(cod)]}{dt} = k_{1f}[RuCl_2(NCR)_2(cod)]$$

Thus, the first-order constants $k_{obs}$ ($s^{-1}$) determined from the slope of the straight section of the $\ln([Ru]_0/[Ru])$ *versus* $t$ plots correspond to $k_{1f}$, the rate constant for the RCN dissociation in $[RuCl_2(NCR)_2(cod)]$ [23].

The temperature influence on the reaction rate was investigated from 294.15–323.15 K in $CDCl_3$. The first-order observed rate constants, $k_{obs}$ ($k_{1f}$), determined at different temperatures are shown in table 2. The overall activation parameters were determined using the logarithmic form of the Eyring equation. The kinetic parameters obtained from the Eyring plot (figure 4) were: $\Delta H^{\#} = 114 \pm 3\,kJ\,mol^{-1}$ and $\Delta S^{\#} = 66 \pm 9\,J\,K^{-1}\,mol^{-1}$ ($\Delta G^{\#} = 94 \pm 5\,kJ\,mol^{-1}$, 298.15 K) for **1** ($CH_3CN$), and $\Delta H^{\#} = 122 \pm 2\,kJ\,mol^{-1}$ and $\Delta S^{\#} = 75 \pm 6\,J\,K^{-1}\,mol^{-1}$ ($\Delta G^{\#} = 100 \pm 4\,kJ\,mol^{-1}$, 298.15 K) for **3** (PhCN). The positive value of the entropy term in both cases suggests that the rate-determining step is dissociative in agreement with the mechanistic proposal. The higher

activation enthalpy for **3** suggests that the Ru–NCPh bond is stronger than the Ru–$NCCH_3$ bond. In fact, **3** was prepared refluxing **1** in PhCN [29], in agreement with the kinetic observations.

A kinetic analysis of the proposed dimerization mechanism (equations (3) and (4)) using the software Berkeley–Madonna has allowed a rough estimation of the other involved rate constants [36]. Model parameters were estimated by fitting of the [**3**] *versus* *t* plot to the experimental data using numerical integration. The obtained values for dimerization of **3** at 304.15 K were $k_{1f} \approx 0.28\,h^{-1}$, $k_{1r} \approx 1240\,L\,mol^{-1}\,h^{-1}$, $k_{2f} \approx 5.2 \times 10^5\,h^{-1}$ and $k_{2r} \approx 2.4 \times 10^{-5}\,L\,mol^{-1}\,h^{-1}$. These data support the dissociation equilibrium leading to the unsaturated species $[RuCl_2(NCR)(cod)]$ as the rate-determining step (step 1, $k_{1f} < k_{1r}$), and evidence the fast dimerization of $[RuCl_2(NCR)(cod)]$ (step 2, $k_{2f} \gg k_{2r}$).

In principle, the labile character of $[RuCl_2(NCCH_3)_2(cod)]$ (**1**) accounts for its reactivity. However, fast dimerization into $[Ru_2Cl(\mu\text{-}Cl)_3(cod)_2(NCCH_3)]$ (**2**) at the refluxing temperature of most of the standard solvents could be a drawback that limits its synthetic application. Noteworthy, the dimerization process is reversible and the $^1H$ NMR of **2** in acetonitrile-$d^3$ shows clean formation of the mononuclear compound $[RuCl_2(NCCD_3)_2(cod)]$ (**1***). Thus, the trichloro-bridge diruthenium core is easily cleaved even with poor ligands such as acetonitrile, and **2** can also be considered as a precursor of the unsaturated fragment "$RuCl_2(cod)$."

### 3.3. *Molecular structure of [$Ru_2Cl(\mu\text{-}Cl)_3(cod)_2(NCR)$] (2 and 4)*

Suitable crystals for X-ray diffraction analysis of the dinuclear complexes $[Ru_2Cl(\mu\text{-}Cl)_3(cod)_2(NCCH_3)]$ (**2**) and $[Ru_2Cl(\mu\text{-}Cl)_3(cod)_2(NCPh)]$ (**4**) were grown from dichloromethane solutions of the complexes from dimerization of **1** and **3**, respectively. The molecular structure of isostructural **2** and **4** is shown in figure 5. A selection of bond distances and angles is given in table 3. Compound **2** was obtained as a marginal product from reactivity studies on Ru(0) complexes and its crystal structure determined at 295 K [37]. The low temperature crystal structure of **2** (100 K) presented the same space group and very similar unit-cell parameters of the previously determined structure (295 K).

The structures of both complexes consist of a trichloro-bridged diruthenium core with distorted octahedral coordination. Both ruthenium centers are bonded to three bridging chloro ligands and a 1,5-cyclooctadiene molecule, but have different coordination environments as a consequence of the sixth terminal ligand: a chloride in Ru(2) and a nitrile in Ru(1). The structural features are similar to those found in related face-sharing di-octahedral $Ru^{II}$–$Ru^{II}$ complexes [32–35]. In particular, the Ru–$Cl_{term}$ distances, 2.4095(14) Å in **2** and 2.3821(15) Å in **4**, are shorter than the Ru–$Cl_{brid}$ distances that range from 2.4195(13)–2.4990(14) Å in **2** and 2.4081(13)–2.4994(14) Å in **4**, with the Ru–$Cl_{brid}$ *trans* to the nitrile the shortest distance. The Ru–Ru distances, 3.2597(13) Å in **2** and 3.2410(9) Å in **4**, lie in the range expected for non-bonded dinuclear Ru(II) complexes of this type (3.28–3.44 Å) [38]. More importantly, the Ru–N bond distance in **4**, 2.020(4) Å, is shorter than in **2**, 2.039(4), which points to a stronger ruthenium benzonitrile bond that is in full agreement with the kinetic data.

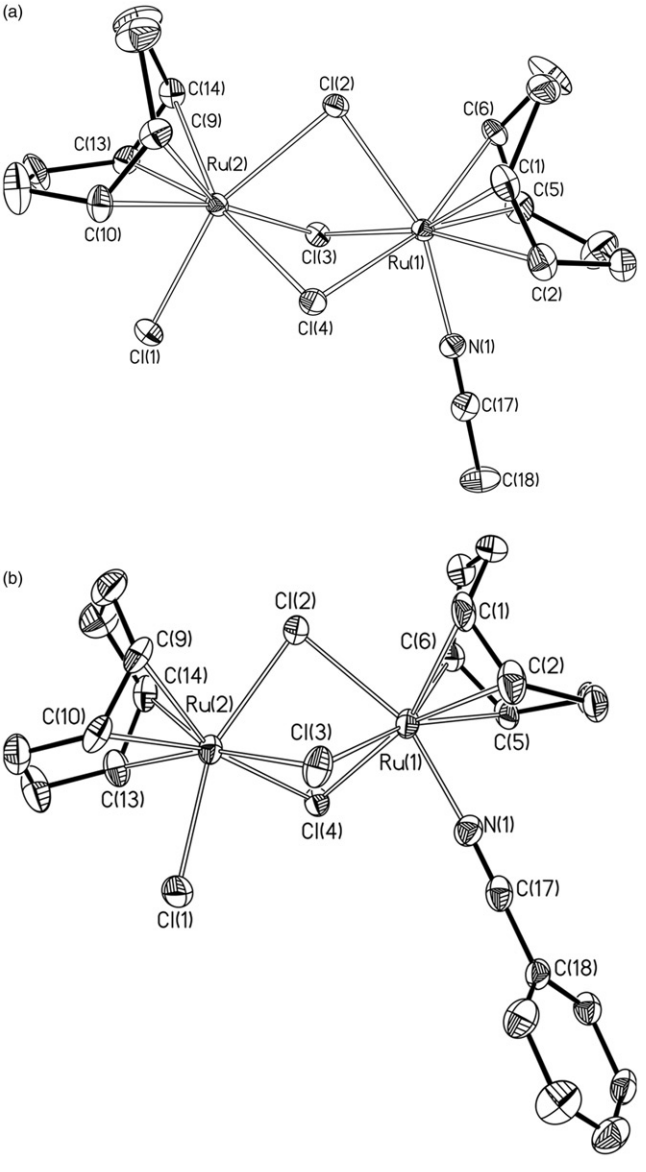


Figure 5. Molecular structures of $[Ru_2Cl(\mu\text{-}Cl)_3(cod)_2(NCCH_3)]$ (**2**) (a) and $[Ru_2Cl(\mu\text{-}Cl)_3(cod)_2(NCPh)]$ (**4**) (b). Hydrogens have been omitted for clarity.

## 4. Conclusions

The synthesis of labile $[RuCl_2(NCCH_3)_2(cod)]$, an alternative starting material to $[RuCl_2(cod)]_n$ for the preparation of ruthenium(II) complexes, has been investigated. The compound has been obtained free of water of crystallization in yields up to 87% using a new work up procedure. We have found that this compound spontaneously transforms into $[Ru_2Cl(\mu\text{-}Cl)_3(cod)_2(NCCH_3)]$ at room temperature with the release of

Table 3. Selected bond distances (Å) and angles (°) for **2** and **4**.

| | **2** | **4** |
|---|---|---|
| Ru(1)–N(1) | 2.039(4) | 2.020(4) |
| Ru(1)–Cl(2) | 2.4357(13) | 2.4081(13) |
| Ru(1)–Cl(3) | 2.4565(13) | 2.4416(14) |
| Ru(1)–Cl(4) | 2.4195(13) | 2.4627(14) |
| Ru(2)–Cl(1) | 2.4095(14) | 2.3821(15) |
| Ru(2)–Cl(2) | 2.4652(14) | 2.4471(14) |
| Ru(2)–Cl(3) | 2.4990(14) | 2.4706(14) |
| Ru(2)–Cl(4) | 2.4445(14) | 2.4994(14) |
| N(1)–C(17) | 1.130(6) | 1.143(6) |
| C(17)–C(18) | 1.456(7) | 1.436(7) |
| Ru(1)–Cl(2)–Ru(2) | 83.38(4) | 83.75(5) |
| Ru(1)–Cl(3)–Ru(2) | 82.26(5) | 82.56(4) |
| Ru(1)–Cl(4)–Ru(2) | 84.16(4) | 81.56(4) |
| C(17)–N(1)–Ru(1) | 175.8(4) | 174.0(5) |
| N(1)–C(17)–C(18) | 177.2(5) | 177.7(6) |
| N(1)–Ru(1)–Cl(2) | 160.02(11) | 159.65(12) |
| N(1)–Ru(1)–Cl(3) | 86.68(11) | 85.15(13) |
| N(1)–Ru(1)–Cl(4) | 85.55(12) | 86.13(12) |
| Cl(1)–Ru(2)–Cl(2) | 158.58(4) | 157.62(5) |
| Cl(1)–Ru(2)–Cl(3) | 84.72(5) | 84.84(5) |
| Cl(1)–Ru(2)–Cl(4) | 87.39(5) | 85.91(5) |

acetonitrile. This transformation, that is reversible in the presence of acetonitrile, follows first-order kinetics. Determination of activation parameters for this process supports a two-step mechanism with dissociation of acetonitrile as the rate-determining step. $[RuCl_2(NCPh)_2(cod)]$ behaves similarly although the dimerization reaction slows by a factor of 10.

## Supplementary material

$^1$H NMR (500 MHz) of compound **1**. CCDC-865062 (**2**) and CCDC-865063 (**4**) contain the supplementary crystallographic data. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif

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