

Organometallic complexes of ruthenium(II) with *N,N*-dialkylcarbamato as the supporting ligand

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Abstract

By using $[\text{RuCl}_2(\eta^4\text{-COD})]_n$, COD = cycloocta-1,5-diene (C_8H_{12}) or $[\text{RuCl}_2(\eta^6\text{-cym})]_2$, cym = *p*-methyl-isopropylbenzene, as precursors, *N,N*-dialkylcarbamato complexes of ruthenium(II) containing the unsaturated hydrocarbon as ligand have been prepared, namely $\text{Ru}(\text{O}_2\text{CN}^i\text{Pr}_2)(\eta^4\text{-COD})$, **1**; $\text{RuCl}(\text{O}_2\text{CNR}_2)(\eta^6\text{-cym})$; R = Et, **2**; R = *i*Pr, **3**; $\text{Ru}(\text{O}_2\text{CNR}_2)_2(\eta^6\text{-cym})$, R = Me, **5**; R = Et, **6**. The crystal and molecular structures of $\text{RuCl}_2(\eta^6\text{-cym})(\text{NHMe}_2)$, **4** and $\text{Ru}(\text{O}_2\text{CNEt}_2)_2(\eta^6\text{-cym})$, **6**, are reported. Compound **6**, which represents the first example of a crystallographically established compound with the η^6 -arene– O_2CNR_2 ligand combination, contains both monodentate and bidentate carbamato ligands. The reaction and structural patterns appear to conform systematically to the 18-electron rule for organometallic derivatives. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Organometallic complexes; Ruthenium(II); *N,N*-dialkylcarbamato

1. Introduction

The extensive use of ruthenium in homogeneous catalysis [1] has stimulated a number of studies on complexes containing labile ligands, free coordination sites on the metal thus becoming readily available. Among them, carboxylato complexes have largely been studied [2]. *N,N*-dialkylcarbamato ligands, R_2NCO_2 , similar to the carboxylato ones as far as composition and geometry of the coordinating fragment are concerned, may undergo a change of hapticity, thus creating a free coordination position and, moreover, they may experience easily accessible reaction patterns involving CO_2 evolution, thus becoming useful intermediates in the preparation of new complexes [3].

Recently, some of us have reported the synthesis and characterisation of *N,N*-dialkylcarbamato complexes of ruthenium(II) containing carbon monoxide and/or trialkylphosphine as ancillary ligands [4a] and further work from these Laboratories [4b] has shown that *N,N*-

dialkylcarbamato complexes can be useful starting materials for the preparation of triflate complexes of ruthenium(II). Some Japanese workers recently described the tricyclohexylphosphine (Pcy_3) derivative of ruthenium(II) $\text{Ru}(\text{O}_2\text{CNEt}_2)\text{H}(\text{CO})(\text{Pcy}_3)_2$ [5], prepared in moderate yields from the $\text{RuCl}_3 \cdot 3\text{H}_2\text{O} - \text{Et}_2\text{NH} - \text{Pcy}_3 - \text{CO}_2$ system and crystallographically shown to contain the bidentate carbamato group. The same paper reports the failure to obtain any carbamato derivative in the absence of Pcy_3 . The Pcy_3 derivative [5] was somewhat anticipated by the similar derivative $\text{Ru}(\text{O}_2\text{CNMe}_2)\text{H}(\text{PPh}_3)_3$ reported years before [6a]. Earlier structural data on *N,N*-dialkylcarbamato derivatives of ruthenium(II) are limited to the cationic compounds $[\text{Ru}(\text{O}_2\text{CNMe}_2)(\text{PMe}_2\text{Ph})_4]^+$ and $[\text{Ru}(\text{CO})(\text{O}_2\text{CNMe}_2)(\text{PMe}_2\text{Ph})_4]^+$ (isolated as their hexafluorophosphate derivatives) [6a,6b].

We were interested in establishing that: (a) *N,N*-dialkylcarbamato complexes of ruthenium(II) do not necessarily require tertiary phosphines to become isolatable; (b) the still largely unexplored (unsaturated hydrocarbon)–dialkylcarbamato ligand combination could exist, depending on the electronic configuration of the central metal atom. As a matter of fact, work

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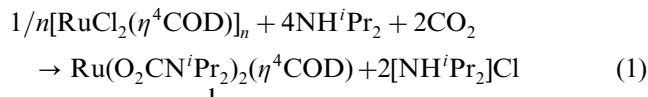
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from these Laboratories has described [6c] the complexes of d³ niobium(II) and tantalum(II) of analytical formula $M(\eta^6\text{-C}_6\text{Me}_6)(\text{O}_2\text{CN}^i\text{Pr}_2)_2$ and the suggestion was made that these compounds could be dinuclear with a single metal–metal bond, and four bidentate carbamate ligands, in order to comply with the 18-e rule for organometallic derivatives. The reason for choosing ruthenium(II) for this project was manifold: (i) complexes of d⁸ ruthenium(II) with both halide and η^6 (or diolefin) ligands are known and therefore could be used as starting materials for introducing the *N,N*-dialkylcarbamato ligand through a metathetical reaction; (ii) complexes of a low molecular complexity could perhaps be obtained in view of the even electronic counting associated with ruthenium(II); (iii) the well-established aptitude of the O_2CNR_2 group to act as a monodentate or a bidentate ligand could drive the systems to adjust to the 18e-requirement for organometallic systems.

In the present paper some new *N,N*-dialkylcarbamato complexes of ruthenium(II) are described, as obtained starting from the organometallic precursors $\text{RuCl}_2(\eta^4\text{-COD})_n$ [6d], and $\text{RuCl}_2(\eta^6\text{-cym})_2$ [6e], which are readily obtained by simple synthetic procedures. The diolefin complex is believed to be a polynuclear chloride-bridged compound, although an X-ray study has shown that also the ruthenium–ruthenium bonded dimer $\text{Ru}_2\text{Cl}_2(\mu\text{-Cl})_2(\text{COD})_2$ [with a Ru–Ru bond distance of 2.791(1) Å] may exist under certain experimental conditions {co-crystallised with $\text{RuH}(\text{C}_8\text{H}_{11})\text{C}_6\text{H}_6$ [6f]}. On the other hand, the η^6 -arene-chloroderivative, based on osmometry in CHCl_3 , is believed to be a chloride-bridged dimer $[\text{Ru}_2\text{Cl}_2(\mu\text{-Cl})_2(\eta^6\text{-cym})_2]$ [6e], analogous to the already established structures for the *p*-cymene bromo- and iodo analogues [6g] and for the hexamethylbenzene chloro derivative [6h] $[\text{Ru}_2\text{Cl}_2(\mu\text{-Cl})_2(\eta^6\text{-C}_6\text{Me}_6)_2]$.

2. Results and discussion

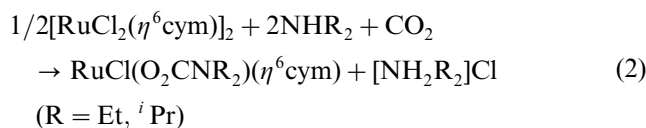
The reaction, see Eq. (1), of the brick-red $[\text{RuCl}_2(\eta^4\text{-COD})]_n$ with NH^iPr_2 and CO_2 affords $\text{Ru}(\text{O}_2\text{CN}^i\text{Pr}_2)_2(\eta^4\text{-COD})$, **1**. Although the reaction is rather slow (the conversion of 4 g of precursor requires several days at room temperature), it goes to completion. Both the low solubility of the precursor and the relative kinetic inertness of ruthenium(II) {the rate constant for the H_2O exchange in $[\text{Ru}(\text{H}_2\text{O})_6]^{2+}$ is $(1.8 \pm 0.2) \times 10^{-2} \text{ s}^{-1}$ at 298 K [7], corresponding to a half-life time of 38 s} are presumably responsible for the observed facts. The reaction is accompanied by a change of colour, the colourless $[\text{NH}_2^i\text{Pr}_2]\text{Cl}$ precipitating within the yellow solution of the ruthenium-containing product.



The yellow ruthenium derivative, soluble in the common organic solvents, is sensitive to moisture. The presence of bidentate carbamate ligands is suggested by IR bands at wavenumbers below 1600 cm^{-1} . Moreover, the ¹H and ¹³C-NMR signals due to the COD moiety of **1** (see Section 4) compared with those of $\text{Ru}(\text{O}_2\text{CMe})_2(\eta^4\text{-COD})$ [8], agree with a similar bonding arrangement of the organometallic fragment in both compounds.

The $\text{Ru}(\text{O}_2\text{CMe})_2(\eta^4\text{-COD})$ complex was suggested to be mononuclear with two bidentate acetato ligands [8] and also the *N,N*-dimethyldithiocarbamate complex $\text{Ru}(\text{S}_2\text{CNMe}_2)_2(\text{COD})$ was reported to be mononuclear in solution [9]. The high solubility of **1** in the usual organic solvents is consistent with a mononuclear structure.

The reaction of $[\text{RuCl}_2(\eta^6\text{-cym})]_2$ with the $\text{NHR}_2\text{-CO}_2$ system ($\text{R} = \text{Et}, ^i\text{Pr}$) yields the products of monosubstitution $\text{RuCl}(\text{O}_2\text{CNR}_2)(\eta^6\text{-cym})$, $\text{R} = \text{Et}$, **2**; $\text{R} = ^i\text{Pr}$, **3**; see Eq. (2).



The reaction is moderately slow at room temperature and the mono-carbamato complexes, which do not appear to suffer in air for a period of at least 40 h in the solid state, are soluble in the common organic solvents. Particularly diagnostic from the point of view of identifying the reaction products are, as expected, the NMR spectra of the aromatic ring protons. Firstly, only one set of resonances was observed for these protons (see Section 4) thus suggesting that we were dealing with the product of monosubstitution rather than with an equimolar mixture of the homoleptic products $\text{RuCl}_2(\eta^6\text{-cym})_2$ and $\text{Ru}(\text{O}_2\text{CNR}_2)_2(\eta^6\text{-cym})$.

Their IR spectra in the region typical of the O_2CN stretching vibrations show the highest energy band at 1536 and 1551 cm^{-1} for the *iso*-propyl- and the ethyl derivative, respectively, which suggests the presence of bidentate carbamate groups. By analogy with the acetates of composition $\text{RuCl}(\text{O}_2\text{CMe})(\eta^6\text{-arene})$ [arene = cym, C_6Me_6 , 1,3,5- $\text{C}_6\text{H}_3\text{Me}_3$] which are mononuclear in acetone or CH_2Cl_2 [10], we suggest our products to be mononuclear with a bidentate carbamate ligand. Additional experiments have been carried out under more severe conditions to force the substitution of the second chloride: (a) by using amine–Ru molar ratios up to 30, (b) by increasing the reaction time to 8 d, (c) by increasing the temperature to 50 °C; (d) by increasing the CO_2 pressure up to 6 atm. In every case, the monosubstitution products only were obtained.

A different reaction course was observed when the *p*-cymene complex of ruthenium(II) $[\text{RuCl}_2(\eta^6\text{-cym})]_2$ was reacted with the $\text{NHMe}_2\text{-CO}_2$ system in toluene, the

sparingly soluble $\text{RuCl}_2(\eta^6\text{-cym})(\text{NHMe}_2)$, **4**, being obtained with no evidence of *N,N*-dimethylcarbamato complexes being formed. This finding is particularly intriguing in view of the long reaction times which would tend to consider kinetic factors unlikely to be involved, also considering that unreacted amine in equilibrium with $[\text{NH}_2\text{R}_2]\text{O}_2\text{CNR}_2$ in the $\text{R}_2\text{NH}-\text{CO}_2$ system is more likely to be present when $\text{R} = i\text{Pr}$ than when $\text{R} = \text{Me}$. We have no plausible explanation for this observation, and an interpretation must require additional experimental data. The amine adduct $\text{RuCl}_2(\eta^6\text{-cym})(\text{NHR}_2)$ is presumably the primary product of the reaction in the $\text{RuCl}_2(\eta^6\text{-cym})_2-(\text{NHR}_2)$ system, which, only in the case of $\text{R} = \text{Et}$, and *iPr* further proceeds under CO_2 to give chloride substitution.

The IR spectrum of $\text{RuCl}_2(\eta^6\text{-cym})(\text{NHMe}_2)$, **4**, shows a band at 3231 cm^{-1} , attributed to the N–H stretching vibration of the coordinated amine. In the $^1\text{H-NMR}$ spectrum the signal due to the nitrogen-bonded methyl groups is a doublet ($\delta\ 2.8\text{ ppm}$, $J = 6.1\text{ Hz}$) due to coupling with the NH proton ($\delta\ 2.4\text{ ppm}$).

Crystals of **4** were obtained and an X-ray diffraction study was performed. The mononuclear species shows hexacoordinate ruthenium (see Fig. 1). The more relevant bond parameters are listed in Table 1. The molecule adopts the usual three-legged piano stool arrangement generally found in $\text{M}(\eta^6\text{-arene})\text{L}_3$ units. The distance between the metal and the arene centroid, 1.666 \AA is very similar to that observed in other ruthenium(II) complexes of the same class, such as $\text{RuCl}_2(p\text{-cymene})(\text{sec-butylamine})$ [11] ($1.663\text{--}1.664\text{ \AA}$) and $\text{RuCl}_2(p\text{-cymene})(p\text{-toluidine})$ [12] (1.637 \AA). Similarly, the angles between the 'legs' of the stool are slightly lower than 90° , due to steric hindrance of the arene ligand.

As observed in $\text{RuCl}_2(p\text{-cymene})(p\text{-toluidine})$, short (1.38 \AA) and long (1.42 \AA) C–C distances, although barely over the significance threshold, appear to alternate in the cymene ring with the longer ones opposing

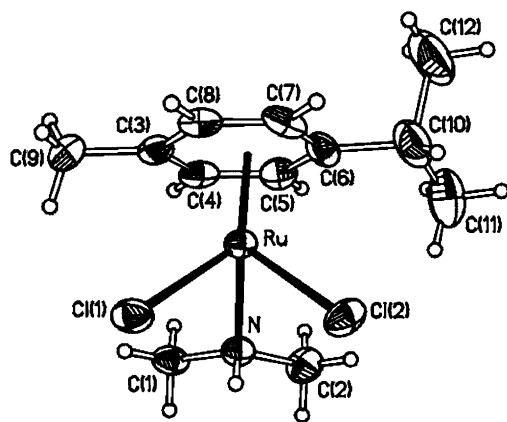


Fig. 1. The molecular structure of $\text{RuCl}_2(\eta^6\text{-cym})(\text{NHMe}_2)$, **4**, with the atom labels. The ellipsoids are at 30% probability.

Table 1

Main bond lengths (\AA) and angles ($^\circ$) for $\text{RuCl}_2(\eta^6\text{-cym})(\text{NHMe}_2)$ (**4**)^a

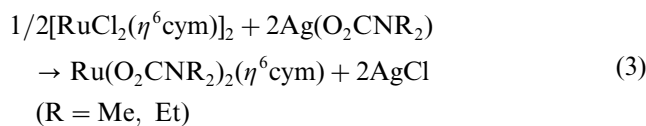
Bond lengths			
Ru–Cl(1)	2.421(2)	N–C(1)	1.473(7)
Ru–Cl(2)	2.414(2)	C(3)–C(4)	1.404(9)
Ru–C(3)	2.185(6)	C(3)–C(8)	1.428(9)
Ru–C(4)	2.162(5)	C(3)–C(9)	1.502(9)
Ru–C(5)	2.180(6)	C(4)–C(5)	1.412(9)
Ru–C(6)	2.188(6)	C(5)–C(6)	1.382(9)
Ru–C(7)	2.178(6)	C(6)–C(7)	1.412(9)
Ru–C(8)	2.165(6)	C(6)–C(10)	1.54(1)
Ru–ar	1.666(9)	C(7)–C(8)	1.365(9)
Ru–N	2.165(5)	C(10)–C(11)	1.44(2)
N–C(2)	1.466(8)	C(10)–C(12)	1.56(1)
Bond angles			
ar–Ru–Cl(1)	126.9(3)	C(8)–C(3)–C(9)	121.3(7)
ar–Ru–Cl(2)	128.9(3)	C(3)–C(4)–C(5)	121.2(5)
ar–Ru–N	131.9(3)	C(6)–C(5)–C(4)	120.3(6)
N–Ru–Cl(1)	83.1(1)	C(5)–C(6)–C(7)	119.0(6)
N–Ru–Cl(2)	81.9(1)	C(5)–C(6)–C(10)	123.7(8)
Cl(2)–Ru–Cl(1)	87.66(6)	C(7)–C(6)–C(10)	117.2(7)
C(2)–N–C(1)	109.8(5)	C(8)–C(7)–C(6)	121.1(6)
C(2)–N–Ru	116.4(4)	C(7)–C(8)–C(3)	121.3(6)
C(1)–N–Ru	115.1(4)	C(11)–C(10)–C(6)	115.9(9)
C(4)–C(3)–C(8)	117.1(6)	C(11)–C(10)–C(12)	112.2(10)
C(4)–C(3)–C(9)	121.5(6)	C(6)–C(10)–C(12)	106.3(8)

^a The abbreviation ar is the centroid of the η^6 -arene ligand.

the Ru–Cl and Ru–N bonds. The Ru–N distance of 2.165 \AA is significantly longer than those found in compounds of the same type [11,12], which may be regarded to indicate a relatively weaker bond in the present case.

The molecules, which pack according to a trigonal structure, may be viewed as pairs, the NH group pointing towards the Cl(1) of the partner. The Cl–H distances of $2.78(5)\text{ \AA}$ are shorter than the sum of the van der Waals radii, if the Pauling [13] or Bondi [14] estimates are considered, and are near the limit, in the Nyburg's [15] estimate. This may be considered as a weak interaction, in agreement with the slightly longer Ru–Cl(1) bond with respect to Ru–Cl(2).

As there was incomplete or no substitution of the chloride in the reaction of $[\text{RuCl}_2(\eta^6\text{-cym})]_2$ with NHR_2 and CO_2 , the ruthenium precursor was treated with silver *N,N*-dialkylcarbamates, $\text{Ag}(\text{O}_2\text{CNR}_2)$ ($\text{R} = \text{Me}$, Et). In both cases, by using a Ag–Ru molar ratio of 2, the reaction afforded the expected products $\text{Ru}(\text{O}_2\text{CNR}_2)_2(\eta^6\text{-cym})$, $\text{R} = \text{Me}$, **5**; $\text{R} = \text{Et}$, **6** (see Eq. (3)).



Absorptions at wavenumbers higher than 1600 cm^{-1} in the IR spectra suggest the presence of at least one monodentate carbamato ligand. The simplest hypothesis

is that we are dealing with mononuclear complexes containing both monodentate and bidentate O_2CN moieties. The equivalence of the carbamate ligands observed in the 1H and ^{13}C -NMR spectra recorded at room temperature in C_6D_6 or C_7D_8 can be related to low-energy paths allowing exchange of the mono and bidentate ligands. In a sequence of 1H -NMR spectra of **6** recorded at variable temperature ($-10 \div -80$ °C), a progressive broadening of the signals due to the protons of the ethyl groups was observed. Fast exchange between terminal and bridging carbamate ligands at room temperature has already been noted with the dinuclear complex $Al_2(O_2CN^iPr)_6$ [16].

An X-ray diffraction study on a single crystal of **6** confirmed our structural hypothesis based on spectroscopic data. Fig. 2 shows the molecular structure, while the more relevant bond distances and angles are listed in Table 2. It is a three-legged piano stool structure reminiscent of **4**, with even less symmetrical legs, due to the geometric requirements of the carbamate ligands. One of the carbamate groups is η^2 coordinated, forming a small $O(1)-Ru-O(2)$ angle of 61.5° . The second carbamate group binds η^1 with $O(1)-Ru-O(3)$ and $O(2)-Ru-O(3)$ angles similar to the $Cl-Ru-Cl$ and $N-Ru-Cl$ ones in **4**.

One of the two angles being smaller, the total hindrance is reduced, so that the cymene ligand can approach somewhat more closely to ruthenium at a distance of 1.640 Å to be compared with 1.666 Å in **4**. The $Ru-O(3)$ distance (2.058 Å) involving the η^1 -coordinated ligand is significantly shorter than the others (2.128 , 2.143 Å), as expected.

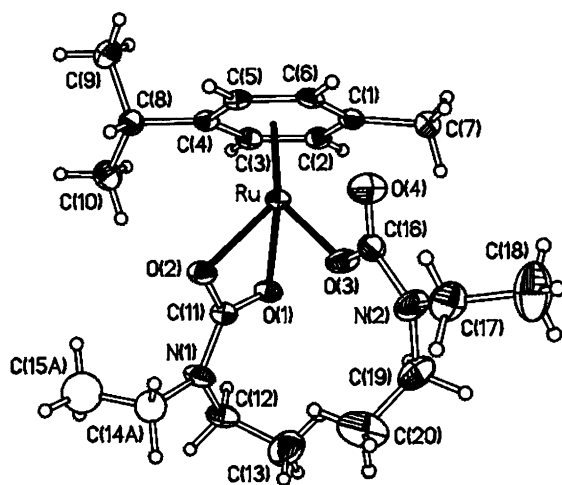


Fig. 2. The molecular structure of $Ru(O_2CNEt_2)_2(\eta^6\text{-cym})$ **6**. The disordered ethyl group $C(14)-C(15)$ is represented only in its more populated position. The ellipsoids are at 30% probability.

Table 2

The more relevant bond lengths (Å) and angles ($^\circ$) for $Ru(O_2CNEt_2)_2(\eta^6\text{-cym})$ (**6**)^a

Bond lengths			
Ru–C(1)	2.170(3)	C(2)–C(3)	1.426(5)
Ru–C(2)	2.145(3)	C(3)–C(4)	1.415(5)
Ru–C(3)	2.168(3)	C(4)–C(5)	1.434(4)
Ru–C(4)	2.189(3)	C(4)–C(8)	1.509(5)
Ru–C(5)	2.162(3)	C(5)–C(6)	1.401(5)
Ru–C(6)	2.168(3)	C(8)–C(9)	1.520(5)
Ru–ar	1.640(4)	C(8)–C(10)	1.523(5)
Ru–O(1)	2.128(2)	O(1)–C(11)	1.278(4)
Ru–O(2)	2.143(2)	O(2)–C(11)	1.278(4)
Ru–O(3)	2.058(2)	C(11)–N(1)	1.340(4)
C(1)–C(2)	1.404(5)	O(3)–C(16)	1.295(4)
C(1)–C(6)	1.419(5)	O(4)–C(16)	1.233(4)
C(1)–C(7)	1.509(5)	C(16)–N(2)	1.364(5)
Bond angles			
ar–Ru–O(1)	134.9(2)	C(6)–C(5)–C(4)	121.2(3)
ar–Ru–O(2)	136.5(2)	C(5)–C(6)–C(1)	121.5(3)
ar–Ru–O(3)	134.1(2)	C(4)–C(8)–C(9)	108.6(3)
O(1)–Ru–O(2)	61.53(9)	C(4)–C(8)–C(10)	114.0(3)
O(1)–Ru–O(3)	80.44(9)	C(9)–C(8)–C(10)	110.6(3)
O(2)–Ru–O(3)	81.4(1)	C(11)–O(1)–Ru	90.7(2)
C(2)–C(1)–C(6)	117.5(3)	C(11)–O(2)–Ru	90.0(2)
C(2)–C(1)–C(7)	121.1(3)	O(2)–C(11)–O(1)	117.4(3)
C(6)–C(1)–C(7)	121.2(3)	O(2)–C(11)–N(1)	121.9(3)
C(1)–C(2)–C(3)	121.8(3)	O(1)–C(11)–N(1)	120.6(3)
C(4)–C(3)–C(2)	120.6(3)	C(16)–O(3)–Ru	127.6(2)
C(3)–C(4)–C(5)	117.3(3)	O(4)–C(16)–O(3)	126.0(3)
C(3)–C(4)–C(8)	123.4(3)	O(4)–C(16)–N(2)	120.3(3)
C(5)–C(4)–C(8)	119.3(3)	O(3)–C(16)–N(2)	113.7(3)

^a The abbreviation ar denotes the centroid of the η^6 -arene ligand.

3. Conclusions

Starting from the well-known chloride derivatives $[RuCl_2(COD)]_n$ and $[RuCl_2(\eta^6\text{-cym})]_2$, some simple syntheses of *N,N*-dialkylcarbamato complexes of ruthenium(II) have been performed and the conditions favourable to the mono- or the disubstitution of the chloride have been established. With the polynuclear $[RuCl_2(COD)]_n$, containing the relatively weaker $Ru-Cl$ bond to the bridging chloride, the NHR_2-CO_2 system affords disubstitution ($R = ^iPr$). Surprisingly, with $[RuCl_2(\eta^6\text{-cym})]_2$ and $NHMe_2-CO_2$, only the product of bridging chloride splitting by the amine, namely $RuCl_2(\eta^6\text{-cym})(NHMe_2)$, was isolated. No further reaction with $[NH_2Me_2][O_2CNMe_2]$ was observed, presumably due to the higher $Ru-Cl$ bond enthalpy in the mononuclear amine adduct with respect to the $Ru-O$ bond to be formed in the carbamate complex. On the other hand, the observed mono-substitution to give $RuCl(O_2CNR_2)(\eta^6\text{-cym})$, $R = Et, ^iPr$, in the $[RuCl_2(\eta^6\text{-cym})]_2-NHR_2-CO_2$ system, is not easy to explain since we are probably dealing with a common intermediate $RuCl_2(\eta^6\text{-cym})(NHR_2)$ in all cases. Disubstitution was never observed even under forcing conditions and, accordingly, the bis-carbamato complexes

$\text{Ru}(\text{O}_2\text{CNR}_2)_2(\eta^6\text{-cym})$ ($\text{R} = \text{Me}, \text{Et}$) had to be obtained by using $\text{Ag}(\text{O}_2\text{CNR}_2)$ as the carbamate transfer reagent from $[\text{RuCl}_2(\eta^6\text{-cym})]_2$. The *N,N*-dialkylcarbamato complexes here described are all well soluble in the common organic solvents and, in view of the facile displacement of the carbamate ligand, appear to be attractive precursors to a variety of other organometallic derivatives of ruthenium(II), including the grafting on silica of ruthenium organometallics, by using a well-established methodology [17] reported earlier based on *N,N*-dialkylcarbamato derivatives.

4. Experimental

4.1. General

All preparations were carried out in standard Schlenk tubes. Solvents were freshly distilled over conventional drying agents under dinitrogen and all manipulations were carried out under an atmosphere of dinitrogen, unless otherwise specified. $[\text{RuCl}_2(\text{COD})]_n$ [6d] and $[\text{RuCl}_2(\eta^6\text{-cym})]_2$ [6e], $\text{Ag}(\text{O}_2\text{CNMe}_2)$ and $\text{Ag}(\text{O}_2\text{CNEt}_2)$ [18] were prepared according to the literature. The NMR data of the starting material $[\text{RuCl}_2(\eta^6\text{-cym})]_2$ have been measured and are reported here, for comparison with those (vide infra) of compounds 2–6. $^1\text{H-NMR}$ (CDCl_3): δ 1.2 [d, cymene $\text{CH}(\text{CH}_3)_2$, 6H]; 2.1 [s, cymene CH_3 , 3H], 2.9 [sept, cymene CH Me_2 1H]; 5.35 and 5.49 [AB system, $J = 6.0$ Hz, aromatic CH , 4H]; $^{13}\text{C-NMR}$: δ 18.7 [cymene CH_3]; 21.8 [cymene $\text{CH}(\text{CH}_3)_2$]; 30.6 [cymene CHMe_2]; 80.1 and 80.8 [aromatic CH]; 93.4 [aromatic CMe]; 98.2 [aromatic C^iPr]. Commercial (Aldrich) or home-made $[\text{NH}_2\text{Me}_2][\text{O}_2\text{CNMe}_2]$ (by saturation of NHMe_2 with CO_2) was used. Elemental analyses (C, H, N) were performed by Laboratorio di Microanalisi della Facoltà di Farmacia, Università di Pisa, with a C. Erba mod. 1106 elemental analyser. Ruthenium contents were determined by AAS by using a Perkin–Elmer Analyst 100 instrument with air acetylene flame $\lambda = 349.9$ nm). Chloride analyses were carried out by the Volhard method, after attack with a boiling 20 N KOH solution, followed by acidification with HNO_3 . Carbon dioxide was determined by gas-volumetric measurements of the gas evolved in the presence of 20% sulphuric acid. IR spectra were measured with a Perkin–Elmer FTIR mod. 1725X spectrophotometer. Nuclear magnetic resonance spectra were recorded using a Varian Gemini 200BB instrument, the data being expressed in ppm from TMS.

4.2. Synthesis of $\text{Ru}(\text{O}_2\text{CN}^i\text{Pr}_2)_2(\text{COD})$ (1)

The chloride complex $[\text{RuCl}_2(\text{COD})]_n$ (4.69 g, 16.75 mmol of ruthenium) was added to 50 ml of NH^iPr_2 (357 mmol). The suspension was saturated with CO_2 and

then toluene (50 ml) was added. After 10 days stirring at room temperature (r.t.) under CO_2 , further toluene (100 ml) was added and the resulting suspension was filtered. The solid was washed with toluene (50 ml) and the filtrate was concentrated to small volume (about 50 ml) and added of heptane (75 ml). The suspension was filtered and the solid was dried in vacuo (2.72 g, 33% yield). Anal. Calc. for $\text{C}_{22}\text{H}_{40}\text{N}_2\text{O}_4\text{Ru}$: CO_2 , 17.7%. Found: CO_2 , 17.4%. IR (Nujol, cm^{-1}): 1525, 1356. $^1\text{H-NMR}$ (C_6D_6): δ 1.2 [d, CH_3 , 24H], 1.8–2.6 [m, COD CH_2 , 8H]; 3.9 [sept, CHMe_2 , 4H], 3.4 and 4.8 [m, COD CH , 4H]; $^{13}\text{C-NMR}$ (C_6D_6): δ 21.1 [CH_3]; 28.3 and 32.3 [COD CH_2]; 44.5 [CHMe_2]; 83.0 and 87.3 [COD CH]; 169.1 [NCO_2]. The NMR spectra [8] of the COD ligand in the acetato complex $\text{Ru}(\text{O}_2\text{CMe})_2(\text{COD})$ compare well with our data. $^1\text{H-NMR}$ (CDCl_3): δ 1.9 [m, COD CH_2 , 8H]; 3.2 and 4.7 [m, COD CH , 4H]; $^{13}\text{C-NMR}$ (CDCl_3): δ 27.0 and 31.3 [COD CH_2]; 84.5 and 89.1 [COD CH].

4.3. Synthesis of $\text{RuCl}(\text{O}_2\text{CNEt}_2)(\eta^6\text{-cym})$ (2)

The arene complex $[\text{RuCl}_2(\eta^6\text{-cym})]_2$ (2.34 g, 3.82 mmol) was added to 10 ml of NH_2Et (97 mmol). The mixture was saturated with CO_2 and stirred for 4 h, toluene (10 ml) being then added. After 50 h stirring at r.t., 100 ml of toluene were added and the suspension was filtered. The colourless solid, $[\text{NH}_2\text{Et}_2]\text{Cl}$, was discarded and the filtrate was evaporated to dryness. The residue was treated with heptane (30 ml). The suspension was filtered and the solid was dried in vacuo (1.98 g, 67% yield). Anal. Calc. for $\text{C}_{15}\text{H}_{24}\text{ClNO}_2\text{Ru}$: CO_2 , 11.4; Cl, 9.2; Ru, 26.3. Found: CO_2 , 10.7; Cl, 8.9; Ru, 27.1%. IR (Nujol, cm^{-1}): 1553, 1338. $^1\text{H-NMR}$ (C_6D_6): δ 0.9[t, CH_2CH_3 , 6H]; 1.1 [d, cymene $\text{CH}(\text{CH}_3)_2$, 6H]; 1.9 [s, cymene CH_3 , 3H], 2.7 [sept, cymene CHMe_2 , 1H]; 3.0 [q, CH_2CH_3 , 4H]; 4.7 and 5.0 [AB system, $J = 6$ Hz, aromatic CH , 4H]; $^{13}\text{C-NMR}$: δ 14.0 [CH_2CH_3]; 18.7 [cymene CH_3]; 22.5 [cymene $\text{CH}(\text{CH}_3)_2$]; 31.7 [cymene CHMe_2]; 39.9 [CH_2CH_3]; 77.4 and 78.6 [aromatic CH]; 93.4 [aromatic CMe]; 98.6 [aromatic C^iPr]; 169.1 [NCO_2]. For sake of comparison, the NMR spectra of *p*-cymene (CDCl_3) are reported. $^1\text{H-NMR}$ (CDCl_3): δ 1.2 [d, cymene $\text{CH}(\text{CH}_3)_2$, 6H]; 2.3 [s, cymene CH_3 , 3H], 2.7 [sept, cymene CH Me_2 , 1H]; 7.1 [m, aromatic CH , 4H]; $^{13}\text{C-NMR}$: δ 18.7 [cymene CH_3]; 22.5 [cymene $\text{CH}(\text{CH}_3)_2$]; 31.7 [cymene CHMe_2]; 77.4 and 78.6 [aromatic CH]; 93.4 [aromatic CMe]; 98.6 [aromatic C^iPr].

The same ruthenium derivative was obtained when the reaction was carried out in a stainless-steel autoclave under CO_2 pressure (6 atm.) at r.t. or at 50 °C at atmospheric pressure. The product gave satisfactory analytical results. The analytical data follow for the product obtained in the experiment under pressure. Anal. Calc. for $\text{C}_{15}\text{H}_{24}\text{ClNO}_2\text{Ru}$: C, 46.6; H, 6.3; Cl,

9.2; N, 3.6; Ru, 26.1. Found: C, 46.0; H, 6.3; Cl, 8.9; N, 4.4; Ru 27.1%.

4.4. Synthesis of $RuCl(O_2CN^iPr_2)(\eta^6-cym)$ (**3**)

The *p*-cymene complex $[RuCl_2(\eta^6-cym)]_2$ (1.70 g, 2.78 mmol of ruthenium) was added to 10 ml of NH^iPr_2 (71.4 mmol). The mixture was saturated with CO_2 and stirred for 4 h, and then added of toluene (25 ml). After 70 h stirring at r.t. under CO_2 , 100 ml of toluene were added and the suspension was filtered. The colourless $[NH^iPr_2]Cl$ was filtered off and the filtrate was evaporated to dryness, the residue being then treated with heptane (30 ml). The suspension was filtered and the solid was dried in vacuo (1.61 g, 69% yield). Anal. Calc. for $C_{17}H_{28}ClNO_2Ru$: CO_2 , 10.5; Cl, 8.5; Ru, 24.2. Found: CO_2 , 10.3; Cl, 8.2; Ru, 24.7%. IR (Nujol, cm^{-1}): 1535, 1358. 1H -NMR (C_6D_6): δ 1.1 [two doublets, partially overlapped, cymene $CH(CH_3)_2$ and $CH(CH_3)_2$ of the carbamato group, 18H]; 1.9 [s, cymene CH_3 , 3H]; 2.7 [sept, cymene $CHMe_2$, 1H], 3.6 [sept, $CHMe_2$ of the carbamato group, 2H]; 4.8 and 5.1 [AB system, $J = 6$ Hz, aromatic CH , 4H]; ^{13}C -NMR: δ 18.6 [cymene CH_3]; 21.1 [cymene $CH(CH_3)_2$]; 22.3 [$CH(CH_3)_2$ of the carbamato group]; 31.6 [cymene $CHMe_2$]; 44.8 [$CH(CH_3)_2$ of the carbamato group]; 77.1 and 78.5 [aromatic CH]; 93.8 [aromatic $C(CH_3)$]; 98.5 [aromatic C^iPr]; 169.4 [NCO_2].

The same ruthenium derivative was obtained under more forcing conditions (6 atm. of CO_2 pressure) in a stainless-steel autoclave.

4.5. Reaction of $RuCl_2(\eta^6-cym)$ with $NHMe_2$ under CO_2 : formation of $RuCl_2(\eta^6-cym)(NHMe_2)$ (**4**)

The *p*-cymene complex $[RuCl_2(\eta^6-cym)]_2$ (2.81 g, 4.59 mmol) was added to 78.2 mmol of $NHMe_2$ under CO_2 maintained at 0 °C. The mixture was stirred for 0.5 h, and then toluene (20 ml) was added. After 70 h stirring at r.t., 200 ml of toluene were added and the suspension was filtered. The colourless solid was dried in vacuo (2.35 g, 73% yield). A further crop of crystalline product was obtained from the filtrate (total yield 83%). Anal. Calc. for $C_{12}H_{21}Cl_2NRu$: C, 41.0; H, 6.0; N, 4.0; Cl, 20.2. Found: C, 41.3; H, 6.0; N, 4.0; Cl, 19.5%. IR (Nujol, cm^{-1}): 3231, 265, 240. 1H -NMR ($CDCl_3$): δ 1.3 [d, cymene $CH(CH_3)_2$, 6H]; 2.2 [s, cymene CH_3 , 3H]; 2.4 [broad, NH , 1H]; 2.8 [d, NCH_3 , 6H]; 2.9 [sept, cymene $CHMe_2$, 1H]; 5.26 and 5.30 [AB system, $J = 8.0$ Hz, aromatic CH , 4H]; ^{13}C -NMR: δ 19.0 [cymene CH_3]; 22.6 [cymene $CH(CH_3)_2$]; 31.5 [cymene $CHMe_2$]; 46.8 [CH_3N]; 78.7 and 83.6 [aromatic CH]; 93.7 [aromatic CMe]; 105.3 [aromatic C^iPr].

4.6. Synthesis of $Ru(O_2CNR_2)_2(\eta^6-cym)$, $R = Me$ **5**, $R = Et$, **6**

The *p*-cymene complex $[RuCl_2(\eta^6-cym)]_2$ (0.37 g, 1.20 mmol of ruthenium) was reacted with $Ag(O_2CNMe_2)$ (0.47 g, 2.40 mmol) in toluene (20 ml) under CO_2 . After 70 h stirring at r.t., 100 ml of toluene were added and the suspension was filtered. The colourless solid ($AgCl$) was discarded and the filtrate was evaporated to small volume and treated with heptane (50 ml). The suspension was filtered and the solid was dried in vacuo (0.15 g, 31% yield). Anal. Calc. for $Ru(O_2CNMe_2)_2(\eta^6-cym)$, $C_{16}H_{26}N_2O_4Ru$: CO_2 , 21.4. Found: CO_2 , 20.8%. IR (Nujol, cm^{-1}): 1660, 1603, 1519. 1H -NMR (C_6D_6): δ 1.1 [d, cymene $CH(CH_3)_2$, 6H]; 1.8 [s, cymene CH_3 , 3H], 2.7 [sept, cymene $CHMe_2$, 1H]; [s, $N(CH_3)_2$, 12H]; 5.2 and 5.6 [AB system, $J = 6$ Hz, aromatic CH , 4H].

The corresponding ethyl derivative $Ru(O_2CNEt_2)_2(\eta^6-cym)$, **6**, was similarly prepared (95% yield). Anal. Calc. for $C_{20}H_{34}N_2O_4Ru$: CO_2 , 18.8; Ru, 21.7. Found: CO_2 , 18.0; Ru, 20.6%. IR (Nujol, cm^{-1}): 1594, 1548, 1408, 1328. 1H -NMR (C_7D_8): δ 1.0 [t, CH_2CH_3 , 12H]; 1.1 [d, cymene $CH(CH_3)_2$, 6H]; 1.8 [s, cymene CH_3 , 3H], 2.6 [sept, cymene $CHMe_2$, 1H]; 3.3 [q, CH_2CH_3 , 8H]; 5.2 and 5.6 [AB system, $J = 6$ Hz, aromatic CH , 4H]; ^{13}C -NMR: δ 14.7 [CH_2CH_3]; 18.4 [cymene CH_3]; 22.8 [cymene $CH(CH_3)_2$]; 31.7 [cymene $CHMe_2$]; 41.1 [CH_2CH_3]; 77.6 and 79.3 [aromatic CH]; 91.1 [aromatic CMe]; 96.3 [aromatic C^iPr]; 166.8 [NCO_2].

4.7. X-ray crystallographic studies

The diffractometric measurements were carried out by using a Bruker P4 diffractometer equipped with graphite-monochromated $Mo-K_\alpha$ radiation ($\lambda = 0.71073$ Å). All data were collected in the $\omega-2\theta$ scan mode, and three standard reflections were monitored every 97 measurements for checking crystal decay and equipment stability. Data reduction was done by the XSCANS programme [19].

Crystals of **4**, prepared as described before, are brown-red needles. A section of one of them of dimensions $0.36 \times 0.12 \times 0.12$ mm was glued at the end of a glass fibre and the unit cell parameters listed in Table 3 were derived from the setting angles of 40 strong reflections. A set of 2781 intensity data were collected between $\theta = 2.2$ and 23.0° and corrected for Lorentz and polarisation effects and for absorption by the ψ -scan method. After merging the equivalent reflections $\{R_{int} = [\sum(F_o^2 - F_o^2(\text{mean})) / \sum(F_o^2)] = 0.0211\}$, 1615 unique reflections satisfying the condition $I > 2\sigma(I)$ were retained for the following calculations. The systematic absences indicated the rhombohedral $R\bar{3}$ or $R\bar{3}$ space groups. The structure solution was found by the automatic direct methods in the centrosymmetric space group $R\bar{3}$. The hydrogen atoms were partly located by

Table 3
Crystal data and structure refinement for compounds **4** and **6**

Compound	4	6
Empirical formula	C ₁₂ H ₂₁ Cl ₂ NRu	C ₂₀ H ₃₄ N ₂ O ₄ Ru
Formula weight	351.27	467.56
Temperature (K)	293(2)	293(2)
Crystal system	Trigonal	Triclinic
Space group	R $\bar{3}$ (No. 148)	P $\bar{1}$ (No. 2)
Unit cell dimensions		
<i>a</i> (Å)	28.459(2)	9.995(1)
<i>b</i> (Å)	28.459(2)	10.051(1)
<i>c</i> (Å)	9.963(1)	13.108(1)
α (°)	90	91.43(1)
β (°)	90	106.79(1)
γ (°)	120	116.07(1)
Volume (Å ³)	6988(1)	1114.6(2)
<i>Z</i>	18	2
ρ_{calc} (Mg m ⁻³)	1.503	1.393
μ (mm ⁻¹)	1.331	0.729
Data/restraints/parameters	2128/0/149	3082/0/235
$R(F_o)[I > 2\sigma(I)]$	0.0344	0.0269
$Rw(F_o^2)[I > 2\sigma(I)]$	0.0726	0.0649

$$R(F_o) = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}; \quad R_w(F_o^2) = \frac{\sum [w(F_o^2 - F_c^2)^2]}{\sum [w(F_o^2)^2]}^{1/2};$$

$$w = 1/[\sigma^2(F_o^2) + (AQ)^2 + BQ] \text{ where } Q = [\max(F_o^2, 0) + 2F_c^2]/3.$$

the difference Fourier map and partly placed in calculated positions. In the final refinement cycles, based on F^2 , anisotropic thermal parameters were used for all non-hydrogen atoms. The final reliability factors are listed in Table 3. The calculations were done by the SHELX-97 program [20].

Crystals of **6** are red prisms. One of them of dimensions 0.80 × 0.50 × 0.31 mm, sealed in a glass capillary under a N₂ atmosphere, showed the cell parameters listed in Table 3. About 3716 intensities were collected between $\theta = 2.2$ and 23.0° and corrected for Lorentz and polarisation effects and for absorption by the ψ -scan method. After merging of equivalent reflections ($R_{\text{int}} = 0.0099$), 3082 independent reflections were obtained, 2755 of which with $I > 2\sigma(I)$. The structure was solved by direct methods and refined by least-squares methods based on F^2 (SHELXTL) [21]. One of the ethyl groups of the bidentate carbamate ligand was found to be disordered and was refined as the superposition of two different conformations with probability 53 and 47%. The hydrogen atoms were placed in calculated positions. The final reliability factors listed in Table 3 refer to the last refinement cycle with anisotropic thermal factors for all the ordered non-hydrogen atoms.

5. Supplementary material

Final atomic parameters, thermal factors and the details of the structure determinations have been deposited in the form of a CIF file with the Cambridge

Crystallographic Data Centre, CCDC, No. CCDC 176779 for **4** and No. 176780 for **6**. Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.com.ac.uk or www: <http://www.ccdc.cam.ac.uk>).

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