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Triphenylphosphine-substituted *N*,*N*-di-*iso*-propylcarbamate of ruthenium(II) and its reactions with carbon monoxide

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Dedicated to Professor Frank Albert Cotton in recognition of his outstanding contributions to inorganic chemistry, on the
occasion of his 70th birthday

Abstract

Chloride displacement from $RuCl_2(PPh_3)_3$ by NH^iPr_2/CO_2 in toluene as medium gave the *N*,*N*-di-*iso*-propylcarbamato derivative $Ru(O_2CN^iPr_2)_2(PPh_3)_2$, (**1**), whose X-ray crystal structure determination showed the mononuclear compound to contain hexacoordinated ruthenium bonded to bidentate carbamato and to *cis*-arranged tertiary phosphine groups in a distorted octahedral geometry. Carbonylation at room temperature rapidly converted **1** to the monocarbonyl derivative $Ru(O_2CN^iPr_2)_2(PPh_3)_2(CO)$ (**2**), presumably containing a monodentate carbamato group, the dicarbonyl compound $Ru(O_2CN^iPr_2)_2(PPh_3)_2(CO)_2$ (**3**) being formed over longer reaction times. X-ray diffraction data showed **3** to contain hexacoordinate ruthenium(II) with monodentate carbamato groups *trans* to the carbonyl groups and with *trans*-arranged triphenylphosphine groups. Controlled hydrolysis of **3** yielded the dicarbonyl-carbonato complex $Ru(O_3C)(PPh_3)_2(CO)_2 \cdot H_2O$ (**4**), crystallographically established to contain a bidentate carbonato group, *trans* triphenylphosphine ligands and water hydrogen-bonded to the carbonato ligand. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Carbamato complexes; Ruthenium; Carbonylation; Structure

1. Introduction

Coordination compounds of ruthenium(II) have attracted considerable interest [1] both for their scientific relevance and for their catalytic properties, especially in connection with hydrogenation of unsaturated substrates [1c]. Halo- [2–5], carboxylato- [6–12] and sulfonato [13] complexes have been studied more extensively, together with their interaction with carbon-based ligands, such as carbon monoxide.

Several years ago we initiated a study of the relatively new area of *N*,*N*-dialkylcarbamato complexes of transition- and non-transition elements of general formula $M(O_2CNR_2)_n$, including late transition metals of the 4d series, such as silver [14] and palladium [15], which require both specific reaction conditions and especially designed precursors for their preparation to be successful. Cotton and Chisholm and their coworkers [16–18], together with Lappert [19], have pioneeered the area of *N*,*N*-dialkylcarbamato complexes of early transition elements (generally in their d^0 electronic configuration), as prepared by carbonatation of the corresponding *N*,*N*-dialkylamide derivatives.

N,*N*-carbamato complexes of ruthenium have been little studied until now, the only known examples being the cationic *N*,*N*-dimethylcarbamates $[Ru(O_2CNMe_2)(PMe_2Ph)_4]^+$ and $[Ru(CO)(O_2CNMe_2)(PMe_2Ph)_4]^+$ (isolated as their hexafluorophosphate derivatives) [20] and a neutral complex of formula $Ru(O_2CNEt_2)_3$ of unknown structure produced [21] in milligram quantities and in low yields (due to secondary reactions) by one of us through the reaction of $RuCl_3 \cdot 3L$ (L = Et_2S) with the $NHEt_2/CO_2$ system.

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We now wish to report that the reaction of $RuCl_2(PPh_3)_3$ with NH^iPr_2/CO_2 produces the corresponding triphenylphosphine-substituted carbamato complex of ruthenium(II) $Ru(O_2CN^iPr_2)_2(PPh_3)_2$ (**1**). We also have carried out the reactions of this compound with carbon monoxide yielding the corresponding mono- (**2**), and dicarbonyl (**3**), adducts, whereas the controlled hydrolysis of **3** under an inert atmosphere gave the dicarbonyl-carbonato derivative **4**, $Ru(O_3C)(CO)_2(PPh_3)_2 \cdot H_2O$. The crystal and molecular structures of **1**, **3** and **4** are reported.
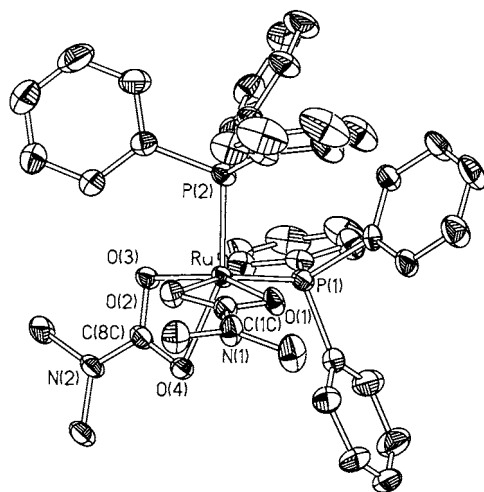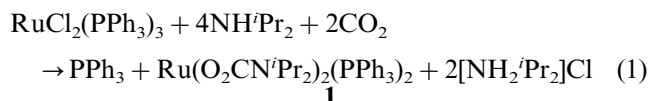

Fig. 1. View of the molecular structure of **1**. Thermal ellipsoids are at 30% probability. All hydrogen atoms and the methyl groups of carbamates are removed for clarity.

Table 1
Bond distances (Å) and angles (°) for compound **1**, $Ru(O_2CN^iPr_2)_2$-$(PPh_3)_2$, with estimated S.D.s in parentheses

Bond distances

Ru–O(1)	2.105(4)	Ru–P(2)	2.2408(18)
Ru–O(2)	2.250(4)	O(1)–C(1C)	1.279(7)
Ru–O(3)	2.112(4)	O(2)–C(1C)	1.281(7)
Ru–O(4)	2.231(4)	O(3)–C(8C)	1.279(6)
Ru–P(1)	2.2465(18)	O(4)–C(8C)	1.270(7)

Bond angles

O(1)–Ru–O(3)	158.01(14)	O(1)–Ru–O(2)	60.72(15)
O(1)–Ru–O(4)	102.29(15)	O(3)–Ru–O(2)	101.78(15)
O(3)–Ru–O(4)	60.75(14)	O(4)–Ru–O(2)	85.39(16)
O(1)–Ru–P(2)	93.37(12)	P(2)–Ru–O(2)	88.53(12)
O(3)–Ru–P(2)	99.72(12)	P(1)–Ru–O(2)	156.02(11)
O(4)–Ru–P(2)	157.63(11)	C(1C)–O(1)–Ru	93.3(3)
O(1)–Ru–P(1)	96.01(12)	C(1C)–O(2)–Ru	86.8(4)
O(3)–Ru–P(1)	99.19(12)	C(8C)–O(3)–Ru	92.2(3)
O(4)–Ru–P(1)	94.91(12)	C(8C)–O(4)–Ru	87.1(3)
P(2)–Ru–P(1)	99.28(6)		

2. Results and discussion

The homoleptic *N,N*-di-*iso*-propylcarbamato derivative of ruthenium(II) **1** was obtained by chloride displacement from $RuCl_2(PPh_3)_3$ with NH^iPr_2/CO_2 in toluene as medium, see Eq. (1):

$$RuCl_2(PPh_3)_3 + 4NH^iPr_2 + 2CO_2$$
$$\rightarrow PPh_3 + Ru(O_2CN^iPr_2)_2(PPh_3)_2 + 2[NH_2{}^iPr_2]Cl \quad (1)$$
$$\mathbf{1}$$

Complete chloride substitution on $RuCl_2(PPh_3)_3$ requires several hours to proceed to completion. Shorter reaction times may lead to partial substitution. The red–orange product is well soluble in common organic solvents; its IR spectrum shows strong bands attributable to the carbamato ligands around 1500 cm^{-1}, which is suggestive of bidentate linkage [22,23]. Moreover, the ^{31}P-NMR spectrum, showing one signal only, suggested the presence of equivalent phosphine ligands. This structural evidence in solution was subsequently confirmed by X-ray diffraction data on a single crystal.

The molecular structure of compound **1** is shown in Fig. 1, the more significant bond distances and angles being listed in Table 1.

Ruthenium is hexacoordinate with *cis*-arranged PPh$_3$ ligands. However, the bite angle of the carbamato ligands is small, giving rise to a very distorted octahedral geometry. Within each carbamato group, the oxygen atoms are connected to ruthenium through a small O–Ru–O angle of 60.7°. The large free space thus available around the metal allows the sterically hindered triphenylphosphines to increase the P–Ru–P angle to 99.3°. A closely resembling geometry was found in Λ–(*S*)–(2,2′-bisdiphenylphosphino-1,1′-binaphthyl-P,P′)-bisbutyratoruthenium(II) [24] and in *cis*-bisacetato[*t*-butyl-bis(2-thienyl)phosphine]ruthenium(II) [25], the latter as the dichloromethane solvate. Two oxygen atoms, O(2) and O(4), occupy approximately *trans* positions with respect to the phosphine ligands, the P–Ru–O angles being 156.0 and 157.6°, respectively. The oxygen atoms O(1) and O(3) are substantially *cis* to both phosphine ligands, see Fig. 1 and bond angles of Table 1. The Ru–O bonds *trans* to phosphine are 0.14 Å longer than the *cis* ones, thus making the bite of the bidentate carbamato ligand an asymmetric one.

Compound **1** was found to undergo carbonylation in two steps; the first rapid step, see Eq. (2), leads to the monocarbonyl derivative **2**, followed by the relatively slow addition of a second CO molecule to give the disubstitution product **3**:

$$Ru(O_2CN^iPr_2)_2(PPh_3)_2 + CO$$
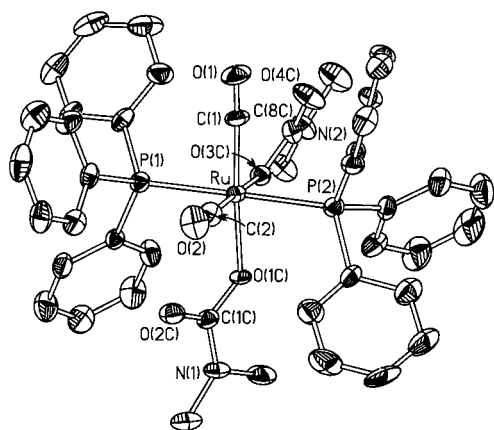$$\rightarrow Ru(O_2CN^iPr_2)_2(PPh_3)_2(CO) \quad (2)$$
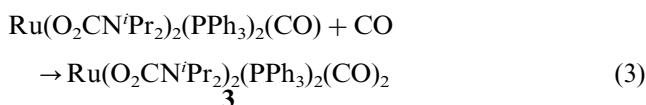$$\mathbf{2}$$
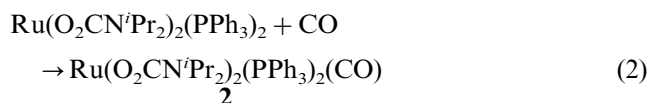
Fig. 2. View of the molecular structure of **3**. Thermal ellipsoids are at 30% probability. All hydrogen atoms and the methyl groups of carbamates are removed for clarity.

Table 2
Bond lengths (Å) and angles (°) for compound **3**, $Ru(O_2CN^iPr_2)_2(PPh_3)_2(CO)_2$, with estimated S.D.s in parentheses

Bond distances			
Ru–C(2)	1.862(9)	C(1)–O(1)	1.117(8)
Ru–C(1)	1.882(8)	C(2)–O(2)	1.148(9)
Ru–O(1C)	2.076(5)	O(1C)–C(1C)	1.313(9)
Ru–O(3C)	2.090(5)	O(2C)–C(1C)	1.231(8)
Ru–P(1)	2.402(2)	O(3C)–C(8C)	1.296(9)
Ru–P(2)	2.411(2)	O(4C)–C(8C)	1.235(9)
Bond angles			
C(2)–Ru–C(1)	86.1(4)	C(2)–Ru–P(2)	91.2(2)
C(2)–Ru–O(1C)	96.3(3)	C(1)–Ru–P(2)	90.6(2)
C(1)–Ru–O(1C)	176.0(3)	O(1C)–Ru–P(2)	86.24(14)
C(2)–Ru–O(3C)	175.7(3)	O(3C)–Ru–P(2)	91.55(14)
C(1)–Ru–O(3C)	97.3(3)	P(1)–Ru–P(2)	177.58(9)
O(1C)–Ru–O(3C)	80.47(19)	O(1)–C(1)–Ru	174.1(8)
C(2)–Ru–P(1)	90.9(3)	O(2)–C(2)–Ru	174.5(8)
C(1)–Ru–P(1)	90.8(2)	C(1C)–O(1C)–Ru	123.2(5)
O(1C)–Ru–P(1)	92.25(14)	C(8C)–O(3C)–Ru	122.5(5)
O(3C)–Ru–P(1)	86.33(14)		

$$Ru(O_2CN^iPr_2)_2(PPh_3)_2(CO) + CO$$

$$\rightarrow \underset{\mathbf{3}}{Ru(O_2CN^iPr_2)_2(PPh_3)_2(CO)_2} \qquad (3)$$

With the molecular parameters of **1** being available, it is quite reasonable to assume that the fast addition of the first CO group corresponds to the conversion of one of the carbamato groups from bidentate to monodentate, thus leaving a free coordination site for the incoming CO. The monocarbonyl derivative is characterized by an IR CO stretching vibration at 1936 cm^{-1}, in agreement with similar findings for the halo-monocarbonyl derivatives of ruthenium(II) [2,5] of formula $RuX_2(CO)(PR_3)_3$, showing a carbonyl absorption around 1950 cm^{-1}. The monocarbonyl derivatives of ruthenium(II) with perfluorinated carboxylato groups [8] of formula $Ru(O_2CR)_2(CO)(PPh_3)_2$ absorb at about

2050 cm^{-1}, corresponding to a shift of about 100 cm^{-1}, with respect to both the halo- and the carbamato substituted derivatives, as one would expect taking into consideration the electron-withdrawing effect of the fluorinated R groups.
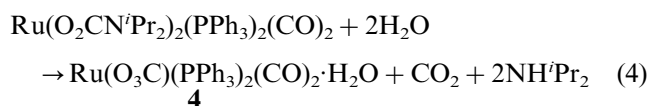
The dicarbonyl derivative **3** has two IR CO stretching vibrations, suggesting the presence of mutually *cis* carbonyl groups. Moreover, intense IR absorptions, due to the O$_2$CN moiety, are present in the region just below 1600 cm^{-1}, corresponding to a shift of about 100 cm^{-1} above the absorptions typical of compound **1**. This is suggestive of the conversion from bidentate carbamato groups to monodentate ones on going from **1** to **3**. In this connection, it is interesting to note that in the silicon derivative $Si(O_2CNR_2)_4$ [26] the monodentate carbamato groups absorb at about 1700 cm^{-1}.

The molecular structure of **3** can be described as the octahedrally arranged disposition of the substituents around ruthenium(II), with mutually *cis* monodentate carbamato and carbonyl groups and with mutually *trans* phosphine ligands. The molecular structure is shown in Fig. 2 and a selected list of bond distances and angles is in Table 2.

The coordination geometry closely approaches that of an ideal octahedron, the residual distortions being due to the different steric hindrance of the ligands. A similar bonding situation has been observed in two dicarbonyl-biscarboxylato triphenylphosphino-substituted derivatives of ruthenium(II) [10,27]. As expected, the monodentate carbamato groups of **3** show a considerable difference of C–O bond lengths (0.06 and 0.08 Å) between the terminal and the bridging oxygen atoms. The ruthenium–CO bonds have the same length (1.87 Å) as in the two just mentioned dicarbonyl derivatives of ruthenium(II) [10,27].

The fact that di-*iso*-propylcarbamato derivative of ruthenium(II) has the same overall geometry as the corresponding dicarboxylato derivatives [10,27] confirms the general observation [23] that carboxylates and carbamates of low nuclearity (mono- or dinuclear) have frequently similar structures. It is interesting to note that the slow addition of the second CO molecule to **2** can be rationalized by taking into consideration the molecular structure of the resulting compound **3** showing that a dramatic structural change has occurred on going from **1** to **3**. The more drastic change concerns the disposition of the phosphine ligands becoming almost exactly *trans* in **3**.

Controlled hydrolysis of the carbamato complex **3** led to the carbonato derivative **4** according to Eq. (4):

$$Ru(O_2CN^iPr_2)_2(PPh_3)_2(CO)_2 + 2H_2O$$

$$\rightarrow \underset{\mathbf{4}}{Ru(O_3C)(PPh_3)_2(CO)_2 \cdot H_2O} + CO_2 + 2NH^iPr_2 \quad (4)$$

Reaction (4) has been carried out with a twofold excess of water, see Section 4, taking into consideration that

the compound crystallizes with one molecule of water per ruthenium. It is important to realize that reaction (4) must be carried out under an inert atmosphere; as a matter of fact, the hydrolysis of **1** or **3** under carbon monoxide leads to reduction forming the carbonyl derivative of ruthenium(0), $Ru(CO)_3(PPh_3)_2$, vide infra.

Compound **4** shows two strong carbonyl stretching vibrations at 2046 and 1982 cm^{-1}, suggestive of a cis arrangement of the CO ligands. Moreover, it displays bands at 1651 and 1626 cm^{-1}, consistent with the presence of a bidentate carbonato group [28], although a contribution from hydrogen-bonded water to the lower wavenumber vibration cannot be excluded. The failure to detect nitrogen analytically in the compound indicated that the starting carbamato derivative had undergone complete hydrolysis. Earlier attempts in these laboratories [14] to prepare the *iso*-propylcarbamato derivative of silver, $Ag(O_2CN^iPr_2)$, through the
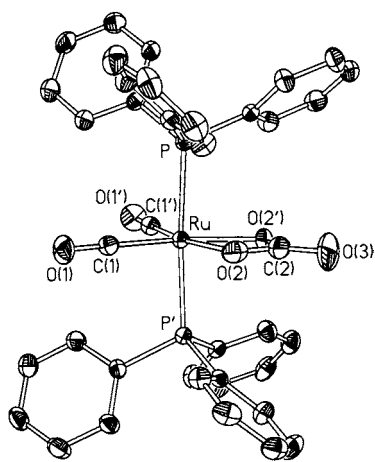

Fig. 3. View of the molecular structure of **4**. Thermal ellipsoids are at 30% probability. Hydrogen atoms and hydrogen-bonded water are removed for clarity.

Table 3
Bond distances (Å) and angles (°) for compound **4**, $Ru(O_3C)(PPh_3)_2(CO)_2 \cdot H_2O$, with estimated S.D.s in parentheses [a]

Bond distances

Ru–C(1′)	1.880(3)	Ru–P	2.4151(7)
Ru–C(1)	1.880(3)	Ru–C(2)	2.518(5)
Ru–O(2′)	2.079(2)	C(1)–O(1)	1.134(4)
Ru–O(2)	2.079(2)	O(2)–C(2)	1.311(4)
Ru–P′	2.4151(7)	C(2)–O(3)	1.207(7)

Bond angles

C(1′)–Ru–C(1)	89.68(18)	O(2)–Ru–P	86.54(7)
C(1)–Ru–O(2′)	166.38(12)	P′–Ru–P	176.05(4)
C(1)–Ru–O(2)	103.86(12)	O(1)–C(1)–Ru	179.3(3)
O(2′)–Ru–O(2)	62.65(16)	C(2)–O(2)–Ru	93.1(2)
C(1)–Ru–P′	91.88(9)	O(3)–C(2)–O(2)	124.5(2)
O(2)–Ru–P′	90.08(6)	O(2′)–C(2)–O(2)	111.1(4)
C(1)–Ru–P	90.92(9)		

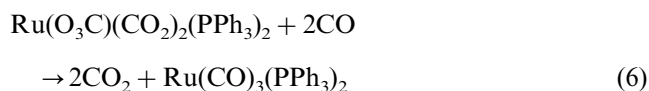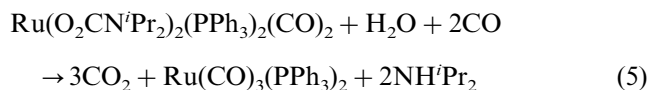[a] Symmetry transformations used to generate equivalent atoms: $-x+1, y, -z+3/2$.

$Ag_2O/NH^iPr_2/CO_2$ system, invariably led to the corresponding carbonate Ag_2CO_3, presumably through the intermediacy of the expected but unstable carbamato derivative.

A projection of the molecular structure of compound **4** is shown in Fig. 3, while Table 3 collects a selection of some relevant bond distances and angles. The carbonato ligand has bidentate coordination. The phosphines are *trans* with a P–Ru–P angle of 176°, to be compared with the corresponding angle of 177.6° for compound **3**. Similar again to compound **3**, the Ru–P bonds are elongated to about 2.4 Å, with respect to the value of about 2.2 Å in compound **1**. Since the steric hindrance of the carbonato ligand of **4** is certainly smaller than that of the oxygen-based anionic ligands of **1** and **3**, this finding suggests the presence of weaker Ru–P bonds in both **3** and **4**, in agreement with the literature data [29] on *trans*-diphosphino derivatives of ruthenium(II). The molecule possesses a twofold axis of symmetry passing through C(2) and O(3). Within the carbonato group, the two C–O bonds involving the ruthenium-bonded oxygens (1.311 Å) are longer than the third one (1.207 Å). The coordination geometry is close to that of an ideal octahedron with the exclusion of the small O(2)–Ru–O(2′) angle of 62.7° obviously due to the short bite of the carbonato ligand.

Mostly interesting is the fact that the coordinated carbonato ligand is involved in a rather strong hydrogen bond with water, the $O \cdots O_w$ distance of 2.602 Å being about 0.4 Å shorter than the double of the oxygen van der Waals radius [30]. A similar example of a water molecule interacting with a carbonato ligand was found [31a] within the $[W(CO)_4(O_3C) \cdot H_2O]^{2-}$ anion, but at a longer $O \cdots O_w$ distance of 2.834 Å.

Compound **4** represents one of the few known examples of mixed carbonato-carbonyl derivatives [31b–f]; as such, it is interesting per se and for its possible intermediacy in the reduction of the ruthenium(II) precursor to ruthenium(0) by carbon monoxide. We have in fact also found that hydrolysis of the carbamato derivative **3** in the presence of carbon monoxide leads to the well established [32] ruthenium(0) complex $Ru(CO)_3(PPh_3)_2$, see Eq. (5), presumably through the intermediacy of the carbonato complex **4**, see Eq. (6).

$$Ru(O_2CN^iPr_2)_2(PPh_3)_2(CO) + H_2O + 2CO$$

$$\rightarrow 3CO_2 + Ru(CO)_3(PPh_3)_2 + 2NH^iPr_2 \qquad (5)$$

$$Ru(O_3C)(CO_2)_2(PPh_3)_2 + 2CO$$

$$\rightarrow 2CO_2 + Ru(CO)_3(PPh_3)_2 \qquad (6)$$

It is easily recognized that release of one of the bites of the sterically constrained carbonato complex followed by addition of CO may lead to carbon dioxide elimination with reduction of the central metal atom to the zerovalent state (see Scheme 1).

$Ru(O_2CN^iPr_2)_2(PPh_3)_2(CO)_2$

3

CO, H₂O ↙   ↘ N₂, H₂O

$Ru(CO)_3(PPh_3)_2$ $Ru(O_3C)(PPh_3)_2(CO)_2 \cdot H_2O$

4
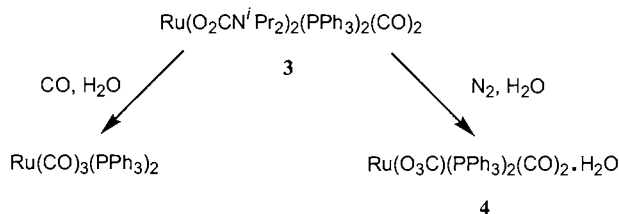
Scheme 1.

In this connection, it is interesting to recall the isolation of an iridium complex [33] having two carbon dioxide moieties linked together to form a five-membered metallacycle: a similar intermediate can possibly be involved in the reduction from ruthenium(II) to ruthenium(0).

It is interesting to note that attempts to oxidatively add N,N-di-isopropylcarbamic acid (HOOCN^{i}Pr$_2$, prepared in situ from CO_2/NH^iPr_2 with carbon dioxide under pressure) to the ruthenium(0) complex $Ru(CO)_3$-$(PPh_3)_2$ were unsuccessful. This contrasts with the behaviour of carboxylic acids; the oxidative addition of RCOOH to $Ru(CO)_3(PPh_3)_2$ is in fact one of the current methods for the preparation of ruthenium(II) carboxylato complexes [6,10,13].

3. Conclusions

This paper reports the first homoleptic (i.e. containing a number of anionic ligands of the same type corresponding to the oxidation state of the central metal atom) N,N-dialkylcarbamato derivatives of ruthenium(II) and a preliminary investigation of their reactivity. Although the study has been until now limited to the di-iso-propyl derivative only, it has been demonstrated for the first time that N,N-dialkylcarbamato complexes of ruthenium(II) can become easily accessible when ruthenium(II) chloride stabilized by triphenylphosphine coordination is used as starting material. As expected, the new complexes are structurally similar to their carboxylato counterparts already reported in the literature. On the other hand, the reactivity is largely different and the new carbamato derivatives have been shown to undergo: (a) addition of carbon monoxide, (b) hydrolysis to the carbonato derivative, (c) reduction by the combined action of carbon monoxide and water. All these reactions occur under mild conditions, i.e. at room temperature and atmospheric pressure. This behaviour can be compared with that of the more robust carboxylato derivatives [12], which normally require more drastic conditions to undergo reduction (by dihydrogen) and, of course, are not attacked by water. The catalytic activity of these new systems is now under investigation and will be reported in a forthcoming paper.

4. Experimental

4.1. General considerations

All preparations were carried out in standard Schlenk tubes. All solvents were freshly distilled over conventional drying agents under dinitrogen and all reactions were carried out under an atmosphere of dinitrogen, or carbon monoxide, or carbon dioxide, as indicated. $RuCl_2(PPh_3)_3$ was synthesized as previously described [34]. Elemental analyses (C, H, N,) were performed by Laboratorio di Microanalisi della Facoltà di Farmacia, Università di Pisa, with a C. Erba model 1106 elemental analyzer. IR spectra were measured with a Perkin–Elmer FT–IR model1725X spectrophotometer. Nuclear magnetic resonance spectra were recorded using a Varian Gemini 200 MHz, the data being expressed in ppm from TMS for ^{1}H and ^{13}C and from H_3PO_4 for ^{31}P.

4.2. Synthesis of $Ru(O_2CN^iPr_2)_2(PPh_3)_2$ (1)

A suspension of $RuCl_2(PPh_3)_3$ (1.83 g, 1.91 mmol) in toluene (50 ml) was treated at room temperature (r.t.) with di-iso-propylamine (3.3 ml, 25.5 mmol) and carbon dioxide at atmospheric pressure. After stirring for 2 days, no further absorption of CO_2 was observed; a ^{31}P-NMR spectrum of the supernatant liquid showed only one signal at 65.6 ppm. The suspension was filtered to eliminate [NH$^i_2$Pr$_2$]Cl and the filtrate was evaporated to dryness under reduced pressure. The resulting dark orange solid was dissolved in toluene (10 ml) and heptane (30 ml) was added to precipitate the title compound. After a few days, dark orange crystals were collected (0.89 g, 51% yield). Triphenylphosphine, a byproduct of the reaction, is soluble under these conditions, as confirmed by separate experiments. Anal. Found: C, 65.6; H, 6.7; N, 2.7%. $C_{50}H_{58}N_2O_4P_2Ru$ requires: C, 65.7; H, 6.4; N, 3.1%. IR (Nujol, cm^{-1}): 1588(w), 1574(w), 1505(vs), 1465(s), 1436(s), 1378(s), 1366(m), 1352(s), 1314(w). NMR (C_6D_6, ppm); ^{1}H: 1.1 (CH$_3$, 24 H), 3.8 (CH, 4 H), 7.0 (m-CH and p-CH, 18 H), 7.6 (o-CH, 12 H); ^{31}P: 65.6; ^{13}C: 21.1 (CH$_3$), 44.2 (CH), 134.8, 137.4 (aromatic carbons), 169.1 (CO$_2$).

4.3. Synthesis of $Ru(O_2CN^iPr_2)_2(PPh_3)_2(CO)$ (2)

An orange solution of $Ru(O_2CN^iPr_2)_2(PPh_3)_2$ (0.1 g, 0.11 mmol) in 20 ml of toluene turned quickly yellow under carbon monoxide at atmospheric pressure at r.t. After 10 min, carbon monoxide uptake slowed down. The IR spectrum in solution showed one carbonyl band only at 1936 cm^{-1}. By removing the volatiles within 30 min, the monocarbonyl derivative was recovered in a substantially quantitative yield. A minor impurity of the dicarbonyl derivative (vide infra) was detected in

the Nujol IR spectrum as evidenced by two bands of low intensity at 2046 and 1984 cm^{-1}, accompanying the intense band of the main product. NMR (C_6D_6, ppm): ^{31}P: 35.0; ^{13}C: 21.5 (CH_3), 21.8 (CH_3), 44.2 (CH), 45.2 (CH), 128.6, 130.0, 132.4, 135.5 (aromatic carbons), 162.9 (CO_2), 208.5 (CO). The compound can be directly recovered by carrying out the carbonylation in a 1:3 toluene–heptane mixture, the monocarbonyl derivative precipitating out from solution, while the dicarbonyl remained in solution. The carbonylation reaction was monitored gas volumetrically: about one equivalent of carbon monoxide was absorbed in toluene solution in 10 min. Compound **1** absorbs CO even in the solid state, the uptake of one equivalent of CO being complete in 2 days.

4.4. Synthesis of Ru(O$_2$CN^{i}Pr$_2$)$_2$(PPh$_3$)$_2$(CO)$_2$ (3)

An orange solution of Ru(O$_2$CN^{i}Pr$_2$)$_2$(PPh$_3$)$_2$ (0.86 g, 0.94 mmol) in 20 ml of toluene turned quickly yellow under carbon monoxide at atmospheric pressure. After 3 days, two CO bands in the IR spectrum of the solution were present at 2046 and 1984 cm^{-1}. By removing the volatiles, a sufficiently pure product was recovered in good yields (79%). Anal. Found: C, 64.9; H, 6.4; N, 2.3%. $C_{52}H_{58}N_2O_6P_2Ru$ requires: C, 64.4; H, 6.0; N, 2.9%. IR (Nujol, cm^{-1}): 2050(s), 1988(s), 1958(m), 1904(w), 1594(s), 1570(s), 1529(w), 1485(s), 1434(s), 1425(s), 1370(s), 1337(s). NMR (C_6D_6, ppm): ^1H: 0.8 (CH_3, d, 12 H), 1.3 (CH_3, d, 12 H), 3.3 (CH, sept, 2 H), 4.5 (CH, sept, 2 H), 7.1 (*m*-CH and *p*-CH, m, 18 H), 8.1 (*o*-CH, m, 12 H); ^{31}P: 28.9; ^{13}C: 21.3 (CH_3), 21.9 (CH_3), 44.2 (CH), 46.7 (CH), 129.9, 132.7, 134.5 (aromatic carbons), 160.5 (CO_2), 196.7 (CO). A sample of Ru(O$_2$CN^{i}Pr$_2$)$_2$(PPh$_3$)$_2$(CO)$_2$ in C_6D_6 was sealed under carbon monoxide in an NMR tube: no modification of the ^{31}P-NMR signals was observed in 3 weeks.

4.5. Synthesis of Ru(O$_3$C)(PPh$_3$)$_2$(CO)$_2$·H$_2$O (4)

By operating under a dinitrogen atmosphere, a solution of Ru(O$_2$CN^{i}Pr$_2$)$_2$(PPh$_3$)$_2$(CO) (0.26 g, 0.27 mmol) in toluene (20 ml) was treated with water (0.02 ml, 1.11 mmol). After a few hours, a colourless solid started to precipitate out. After 2 days, the carbonato complex was filtered and dried in vacuo (0.12 g, 59% yield). Anal. Found: C, 61.9; H, 3.6%. $C_{39}H_{32}O_6P_2Ru$ requires: C, 61.7; H, 4.2%. IR (Nujol, cm^{-1}): 3376(ν_{OH}), 2046(s), 1982(s), 1651(s), 1626(s), 1481(m), 1435(s), 1311(w). NMR (MeOH, ppm): ^{31}P: 28.0. The hydrolysis was monitored by NMR in a tube sealed under dinitrogen: ^1H peaks due to di-*iso*-propylamine were found to progressively grow.

4.6. Hydrolysis of 3 under carbon monoxide

To a solution in toluene (20 ml) of Ru(O$_2$-CN^{i}Pr$_2$)$_2$(PPh$_3$)$_2$(CO)$_2$ (0.33 g, 0.34 mmol) under carbon monoxide at atmospheric pressure, water (0.02 ml, 1.11 mmol) was added. A slow reaction occurred in about 3 days. A ^{31}P-NMR spectrum of the solution showed a major peak at 56.0 ppm due to Ru(PPh$_3$)$_2$-(CO)$_3$, while a minor peak due to Ru(O$_2$CN^{i}Pr$_2$)$_2$-(PPh$_3$)$_2$(CO)$_2$ was still present at 28.9 ppm, together with unidentified products with peaks of low intensity at 47.1 and 24.3 ppm and free PPh$_3$ at -5.1 ppm. The solution showed a strong broad IR band at 1900 cm^{-1} due to Ru(PPh$_3$)$_2$(CO)$_3$. The ruthenium(0) tricarbonyl complex was precipitated by adding heptane to a concentrated toluene solution, collected by filtration and dried in vacuo (0.11 g, 46% yield). It was characterized analytically (C, H) and spectroscopically [32].

4.7. Attempted oxidative addition to Ru(PPh$_3$)$_2$(CO)$_3$

A solution of Ru(PPh$_3$)$_2$(CO)$_3$ (0.6 g, 0.85 mmol) in 20 ml of toluene was treated with diisopropylamine (15 ml) and introduced in a glass autoclave loaded with 5 atm pressure of carbon dioxide. After 2 h at r.t., the suspension was heated at 60°C for 10 h: an IR spectrum of the solution showed only the band at 1900 cm^{-1} due [30] to the starting metal complex.

4.8. X-ray crystallography

All X-ray diffraction measurements were carried out at r.t. ($T = 293$ K) by means of a Siemens P4 diffractometer equipped with graphite-monochromated Mo–K_α radiation ($\lambda = 0.71073$ Å). The samples were sealed in glass capillaries under dinitrogen. The intensity data collection was carried out with an $\omega/2\theta$ scan mode. The intensities of **1** and **3** were corrected for absorption by means of a ψ-scan method; for **4**, an integration method based on crystal shape was used. Data reduction was carried out by means of the SHELXTL package [35] and structure solutions and refinements, based on full-matrix least-squares on F^2, were done by means of the SHELX97 programme [36]. The structure of **3** was solved by the direct methods of the SIR92 programme [37].

Dark orange prismatic crystals of **1**, obtained by layering heptane on a toluene solution, were found to have the lattice parameters listed in Table 4. The cell parameters were calculated from the setting angles of 37 reflections having $5.2° < \theta < 11.7°$. The structure was solved by direct methods and completed by standard Fourier methods. The hydrogen atoms were introduced in calculated positions and were let to ride on the connected carbon atoms. The final refinement cycle gave the reliability factors listed in Table 4.

Table 4
Crystal data and structure refinement

Compound	Ru(O$_2$CN^{i}Pr$_2$)$_2$(PPh$_3$)$_2$ (**1**)	Ru(O$_2$CN^{i}Pr$_2$)$_2$(PPh$_3$)$_2$(CO)$_2$ (**3**)	Ru(O$_3$C)(PPh$_3$)$_2$(CO)$_2$·H$_2$O (**4**)
Empirical formula	C$_{50}$H$_{58}$N$_2$O$_4$P$_2$Ru	C$_{52}$H$_{58}$N$_2$O$_6$P$_2$Ru	C$_{39}$H$_{32}$O$_6$P$_2$Ru
Formula weight	913.99	970.01	759.66
Crystal system	Monoclinic	Monoclinic	Orthorhombic
Space group	$P2_1/n$ (No. 14)	$P2_1/n$ (No. 14)	$Pbcn$ (No. 60)
a (Å)	13.241(3)	11.419(1)	19.218(2)
b (Å)	26.127(7)	20.796(2)	10.919(2)
c (Å)	13.594(3)	21.627(3)	15.814(1)
β (°)	90.05(1)	99.71(1)	–
Volume (Å^3)	4702.8(19)	5062.2(10)	3318.4(7)
Z	4	4	4
D_{calc} (Mg m^{-3})	1.291	1.273	1.521
Absorption coefficient (mm^{-1})	0.446	0.421	0.618
$F(000)$	1912	2024	1552
Crystal size (mm^3)	0.60 × 0.28 × 0.20	0.44 × 0.32 × 0.10	0.29 × 0.27 × 0.18
θ range for data collection (°)	2.15–22.51	2.06–21.25	2.12–25.00
Index ranges	$-14 \leq h \leq 1$, $-1 \leq k \leq 28$, $-14 \leq l \leq 14$	$-11 \leq h \leq 1$, $-1 \leq k \leq 21$, $-21 \leq l \leq 22$	$-22 \leq h \leq 22$, $-12 \leq k \leq 1$, $-1 \leq l \leq 18$
Reflections collected	7483	7132	6850
Independent reflections	6162 [$R_{int} = 0.0417$]	5610 [$R_{int} = 0.0526$]	2920 [$R_{int} = 0.0270$]
Completeness to $\theta = 22.51°$	99.9%	99.7%	100.0%
Data/restraints/parameters	6162/0/532	5610/0/568	2920/0/220
Goodness–of-fit [a] on F^2	1.025	1.000	1.033
Final R indices [a] [$I > 2\sigma(I)$]	$R_1 = 0.0477$, $wR_2 = 0.0938$	$R_1 = 0.0562$, $wR_2 = 0.0831$	$R_1 = 0.0301$, $wR_2 = 0.0681$
R indices [a] (all data)	$R_1 = 0.0917$, $wR_2 = 0.1155$	$R_1 = 0.1268$, $wR_2 = 0.1025$	$R_1 = 0.0452$, $wR_2 = 0.0741$
A; B (w) [a]	0.0350; 8.46	0.0263; 0.00	0.0386; 0.04
Largest difference peak and hole (e Å^{-3})	0.439 and -0.533	0.402 and -0.317	0.319 and -0.478

[a] Goodness-of-fit = $[\Sigma[w(F_o^2 - F_c^2)^2]/(N-P)]^{1/2}$, where N, P are the numbers of observations and parameters, respectively. $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR_2 = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2}$; $w = 1/[\sigma^2(F_o^2) + (AQ)^2 + BQ]$ where $Q = [\max(F_o^2, 0) + 2F_c^2]/3$.

Colourless tabular crystals of **3**, obtained by slow evaporation of a heptane solution, were found to have the lattice parameters listed in Table 4. The cell parameters were calculated from the setting angles of 36 reflections having $5.2 < \theta < 11.1°$. The structure was solved by direct methods. The hydrogen atoms were partly localized in the difference Fourier map and partly introduced in calculated positions. The final refinement cycle, performed with anisotropic thermal factors for all carbon and oxygen atoms, produced the reliability factors listed in Table 4.

Prismatic crystals of **4**, obtained by slowly hydrolysing the precursor **3** in toluene solution, were found to have the lattice parameters listed in Table 4. The cell parameters were calculated from the setting angles of 27 reflections having $2.1 < \theta < 11.3°$. The structure was solved by direct methods and refined by full-matrix least-squares methods after introducing the hydrogen atoms in calculated positions. The final reliability factors are listed in Table 4.

5. Supplementary material

Crystallographic data for the structural analyses have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 133939 for compound **1**, 133940 for compound **3**, and 133941 for compound **4**. 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.cam.ac.uk or http://www.ccdc.cam.ac.uk).

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