

Inorganica Chimica Acta 334 (2002) 411-418



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Trifluoromethanesulfonato derivatives of ruthenium(II)

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Received 31 December 2001; accepted 25 January 2002

Dedicated to Professor Andrew Wojcicki, The Ohio State University, in recognition of his outstanding contributions to Inorganic Chemistry

Abstract

The reactivity of $\text{Ru}(O_2\text{CN}^{i}\text{Pr}_2)_2(\text{CO})_2(\text{PPh}_3)_2$ (1), towards $\text{CF}_3\text{SO}_3\text{H}$ (TfOH, trifloromethanesulfonic acid or triflic acid) has been studied and the products $[\text{Ru}(O_2\text{CN}^{i}\text{Pr}_2)(\text{CO})_2(\text{PPh}_3)_2][\text{OTf}]$ (2), and $\text{Ru}(\text{OTf})_2(\text{CO})_2(\text{PPh}_3)_2$ (3), have been obtained, the former being structurally characterised as one of the few examples of cationic *N*,*N*-dialkylcarbamato complexes. In compound 2, the *N*,*N*-di-*iso*-propylcarbamato group is bidentate. In experiments aimed at obtaining $\text{Ru}(\text{OTf})_2(\text{CO})_2(\text{PPh}_3)_2$ according to the literature method, i.e. from $\text{Ru}(\text{CO})_3(\text{PPh}_3)_2$ and TfOH, the intermediate species $[\text{RuH}(\text{CO})_3(\text{PPh}_3)_2][\text{OTf}]$ (4), corresponding to the oxidative addition of triflic acid, has been intercepted. Treatment of this derivative in refluxing toluene followed by addition of methanol afforded the compound $[\text{RuH}(\text{CO})_2(\text{PPh}_3)_2(\text{CH}_3\text{OH})][\text{OTf}]$ (5), which has been characterised by single-crystal X-ray diffractometry. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Ruthenium(II); Trifluoromethanesulfonato; Triflic acid

1. Introduction

An earlier paper from these laboratories [1] has reported a new valuable ruthenium compound, namely $Ru(O_2CN^1Pr_2)_2(CO)_2(PPh_3)_2$ (1). This stable product contains the substitutionally labile monodentate dialkylcarbamato group, thus proving to be a remarkably good starting material for the preparation of other complexes, difficult to prepare otherwise. Metal comthe trifluoromethanesulfonato plexes containing $(O_3SCF_3, triflato)$ ligand are interesting in view of the low coordinating power of this ligand [2], and this area of inorganic chemistry is growing rapidly. Several ruthenium(II) triflates have been reported: they are generally prepared from chlorides of ruthenium(II) using Ag(OTf) as dehalogenating agent [3], from ruthenium(II) hydrides and TfOH [4] or from ruthenium(0) derivatives and TfOH [5]. X-ray diffractometric studies

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have shown cases of ruthenium-coordinated triflato groups [3a], and examples where the anion is outside the coordination sphere [3].

In this paper, which is in the track of earlier investigations by Wojcicki and coworkers [4], compound 1 has been used for the preparation of triflato derivatives. Also, attempts have been made aimed at preparing new cationic N,N-dialkylcarbamato derivatives based on the higher coordinating power of the O₂CNR₂ ligand with respect to the triflato. Previous literature data about cationic N,N-dialkylcarbamato derivatives were limited to the ruthenium derivatives, $[Ru(O_2CNMe_2)(PMe_2Ph)_4]^+$ and $[Ru(CO)(O_2CNMe_2) (PMe_2Ph)_4$ ⁺, isolated as their hexafluorophosphate derivatives [6]. In addition to the reaction of 1 with both triflic anhydride and triflic acid, this paper reports the room temperature oxidative addition of triflic acid to the ruthenium(0) derivative $Ru(CO)_3(PPh_3)_2$ leading to the corresponding hydrido-triflato complexes, the product of carbonyl substitution by methanol, [RuH(CO)₂(PPh₃)₂(CH₃OH)][OTf], being structurally characterized.

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2. Experimental

2.1. General

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 dinitrogen, unless otherwise stated. The compounds $Ru(O_2CN^iPr_2)_2(CO)_2(PPh_3)_2$ (1) [1], $Ru(CO)_3(PPh_3)_2$ [7] and $RuCl_2(CO)_2(PPh_3)_2$ [7,8] were synthesized according to the literature. Diiso-propylammonium triflate [NH¹₂Pr₂][OTf] was prepared from [NH₂¹Pr₂]Cl (1.26 g, 9.2 mmol) and Ag(OTf) (2.32 g, 9.03 mmol) in CH₂Cl₂. After removal of AgCl by filtration, the product with a satisfactory elemental analysis was recovered from the filtrate upon evaporation of the solvent. IR (most intense bands, cm^{-1}): 3122 (s, br), 2907 (s), 2496 (m, NH), 1605 (m-s), 1407 (s), 1294 (s), 1261 (s, SO₃ [2a]), 1165 (s), 1100 (s), 1089 (s), 1035 (s, SO₃ [2a]), 805 (s), 641 (s), 579 (m), 517 (s). ¹H NMR (CDCl₃, ppm): 1.4 (d, CH₃), 3.5 (sept, CH), 7.6 (br, NH₂). ¹³C NMR (CDCl₃, ppm): 18.9 (CH₃), 47.9 (CH). Elemental analyses (C, H, N) were performed by Laboratorio di Microanalisi, Facoltà di Farmacia, Università di Pisa, with a C. Erba mod. 1106 elemental analyzer. IR spectra were measured with a Perkin-Elmer FT-IR mod. 1725X spectrophotometer. NMR spectra were recorded using a Varian Gemini 200 MHz instrument, the data being expressed in ppm from TMS for ¹H and ¹³C, from H₃PO₄ for ³¹P and from CFCl₃ for ¹⁹F.

2.2. Reaction of 1 with triflic anhydride. Preparation of $[Ru(O_2CN^iPr_2)(CO)_2(PPh_3)_2][OTf]$, (2)

Triflic anhydride (0.07 g, 0.25 mmol) in 5 ml of $C_6H_5CH_3$ was added to a solution of Ru(O₂C- $N^{1}Pr_{2}_{2}(CO)_{2}(PPh_{3})_{2}$ (0.12 g, 0.12 mmol) in 5 ml of $C_6H_5CH_3$. Gas evolution was observed and a colourless solid precipitated out after a few minutes. The solid, recovered by filtration, was dissolved in 5 ml of CH₂Cl₂ and precipitated out by addition of $C_6H_5CH_3$ (10 ml) and cooling at -30 °C. The colourless crystals thus obtained were separated by filtration and dried in vacuo (0.046 g, 39.3% yield). Anal. Calc. for C₄₆H₄₄F₃NO₇-P2RuS: C, 56.7; H, 4.5; N, 1.4. Found: C, 55.8; H, 4.4; N, 1.3%. IR (Nujol mull, most significant bands in the 2300-1000 cm⁻¹ range): 2070 (s), 2010 (s), 1556 (s), 1438 (s), 1274 (sh), 1262 (s), 1141 (m), 1095 (s), 1032 (s). ¹H NMR (CDCl₃): δ 7.7–7.1 (18H); 3.2 (m, J = 7.4 Hz, 1H); 0.4 (d, J = 7.4 Hz, 6H). ³¹P NMR (CDCl₃): δ 28.7 (s). ¹⁹F NMR (CDCl₃): δ -78.6. The product was recrystallized from a C₆H₅CH₃-CH₂Cl₂ mixture, the resulting crystals being used for the X-ray diffractometric experiment.

2.3. Preparation of compound 3

2.3.1. From the reaction of 1 with triflic acid

To a solution of $Ru(O_2CN^{1}Pr_2)_2(CO)_2(PPh_3)_2$ (1) (0.30 g, 0.31 mmol) in C₆H₅CH₃ (10 ml), TfOH (0.19 g, 1.27 mmol) was added at about 20 °C. After 1 h stirring, a ³¹P NMR spectrum showed the starting product 1 to have disappeared, while the formation of the soluble 3 was evidenced by a resonance at 20.2 ppm. After 4 h stirring further C₆H₅CH₃ (20 ml) was added, the suspension was filtered, and the solid (A) was washed with $C_6H_5CH_3$ (10 ml \times 4). The filtered solution was treated with C_7H_{16} (100 ml) and stored at -30 °C for 12 h. The resulting suspension was filtered at low temperature and the colourless solid (B) was recrystallized from a mixture (2:5 by volume) of CH_2Cl_2 and C₆H₅CH₃, recovered by filtration and dried in vacuo (0.10 g, 32.9% yield). Anal. Calc. for Ru(OTf)₂(CO)₂-(PPh₃)₂ (**3**), C₄₀H₃₀F₆O₈P₂RuS₂: C, 49.0; H, 3.1. Found: C, 48.6; H, 3.0%. IR (Nujol mull, most significant bands in the $2300-1000 \text{ cm}^{-1}$ range): 2074 (s), 2012 (s), 1338 (sh), 1328 (m), 1190 (s, br), 1090 (s). ¹H NMR (CDCl₃): δ 7.5 (m). ¹³C NMR (C₆D₆): δ 192.9 (s), 134.7–129.0; 120.1 (q, $J_{C-F} = 256$ Hz). ³¹P NMR (C₆D₆): δ 20.2 (s), with a resonance of low intensity at 23.2 (s). ¹⁹F NMR (C₆D₆): δ -77.1 (s). A portion of the solid A was dissolved in CD₂Cl₂ and NMR spectra showed signals due to 2 (³¹P NMR: δ 28.8) and to [NHⁱ₂Pr₂][OTf], the latter characterized by ¹H NMR with δ 1.4 (d, CH₃); 3.5 (sept, CH) and 7.6 (br, NH_2).

A gas-volumetric monitoring of the reaction was carried out by reacting $Ru(O_2CN^iPr_2)_2(CO)_2(PPh_3)_2$ (0.63 g, 0.65 mmol) in 25 ml of $C_6H_5CH_3$ with triflic acid (0.19 g, 1.27 mmol) under CO_2 at 25.3 °C, evolution of 0.65 mmol of CO_2 being observed in about 10 min, corresponding to a CO_2-Ru molar ratio of 1. When the reaction was repeated with a triflic acid-Ru molar ratio of 6 at 28.1 °C, $Ru(O_2CN^iPr_2)_2(CO)_2$ -(PPh_3)₂ (0.29 g, 0.30 mmol) in 20 ml of $C_6H_5CH_3$ and triflic acid (0.27 g, 1.80 mmol) caused the evolution of 0.57 mmol of CO_2 , corresponding to a CO_2-Ru molar ratio of 1.9 in about 1 h.

2.3.2. From $RuCl_2(CO)_2(PPh_3)_2$ and Ag(OTf)

The chloro-complex RuCl₂(CO)₂(PPh₃)₂ (0.65 g, 0.86 mmol) in 120 ml of C₆H₅CH₃ was treated with Ag(OTf) (0.44 g, 1.71 mmol). The suspension was refluxed for 1 h and a grey suspension was thus obtained. The mixture was cooled down to room temperature (r.t.) and the suspension was filtered. The filtrate was evaporated to about half its original volume, diluted with C₇H₁₆ (100 ml) and cooled down to 0 °C. After 12 h the suspension was filtered, the solid was washed with C₇H₁₆ (3 × 10 ml) and dried in vacuo (0.59 g, 70.0% yield). Spectroscopic data corresponded to those reported for the product described under Section 2.3.1.

Upon exposure to air, a sample of $Ru(OTf)_2(CO)_2(PPh_3)_2$ gave analytical results corresponding to the formation of an aquo complex, presumably $[Ru(H_2O)_2(CO)_2(PPh_3)_2][CF_3SO_3]_2$. Anal. Calc. for $C_{40}H_{34}F_6O_{10}P_2RuS_2$: C, 47.3; H, 3.4. Found: C, 46.9; H, 3.1%. The spectroscopic data (see Section 3) are consistent with such a formulation.

2.3.3. From $Ru(CO)_3(PPh_3)_2$ and TfOH

This preparation was carried out by a modification of the literature method [5]. A suspension of $Ru(CO)_3(PPh_3)_2$ (0.68 g, 0.96 mmol) in $C_6H_5CH_3$ (30 ml) was treated with CF_3SO_3H (0.44 g, 2.93 mmol). The mixture was refluxed for 1 h and then slowly cooled to r.t. The suspension was filtered and the solid was washed with MeOH (25 ml × 3) and dried in vacuo (0.38 g, 40% yield). *Anal*. Calc. for $C_{40}H_{30}F_6O_8P_2RuS_2$: C, 48.4; H, 3.0. Found: 49.0; H, 3.1%. For the spectroscopic data, see Section 2.3.2.

In *sym*-dichloroethane as solvent with an anhydride– **1** molar ratio of 1.7, the ³¹P NMR spectrum of the reaction mixture showed the prevailing presence of $Ru(OTf)_2(CO)_2(PPh_3)_2$ (**3**).

2.4. Preparation of $[RuH(CO)_3(PPh_3)_2](OTf)$, (4)

A suspension of Ru(CO)₃(PPh₃)₂ (0.54 g, 0.76 mmol) in C₆H₅CH₃ (40 ml) was treated with TfOH (0.12 g, 0.80 mmol), which resulted in the immediate formation of a colourless solid. The reaction mixture was stirred for 20 min and then filtered. The solid was washed with C₆H₅CH₃ (10 ml × 3) and dried in vacuo (0.43 g, 66% yield). *Anal*. Calc. for C₄₀H₃₁F₃O₆P₂RuS: C, 55.9; H, 3.6. Found: C, 55.1; H, 3.6. IR (Nujol mull, most significant bands in the 2300–1000 cm⁻¹ range): 2139 (w), 2083 (s), 2069 (s), 1998 (w), 1266 (s), 1162 (m), 1092 (m), 1029 (s). ³¹P NMR (CDCl₃): δ 34.9 (s). ¹H NMR (CDCl₃): δ 7.5 (m); 6.4 (t, *J*_{H-P} = 19.3 Hz). ¹³C NMR (CDCl₃): δ 192.3 (t); 189.8 (t); 134.7–128.5. ¹⁹F NMR (CDCl₃): δ –78.5 (s).

The ³¹P NMR spectrum of a CH_2Cl_2 solution of [RuH(CO)₃(PPh₃)₂](OTf) shows a signal at 34.5 ppm. When an eccess of Et₃N was added this resonance disappeared, and a new signal, due to Ru(CO)₃(PPh₃)₂, appeared at 57.6 ppm.

2.5. Preparation of 5

A suspension of 4 (0.22 g, 0.26 mmol) in C₆H₅CH₃ (20 ml) was refluxed to give a yellow solution. By cooling down to r.t. and adding MeOH (13 mg, 0.41 mmol), colourless crystals precipitated out which were filtered and dried in vacuo (4% yield). *Anal*. Calc. for [RuH(CO)₂(MeOH)(PPh₃)₂][OTf], C₄₀H₃₅F₃O₆P₂RuS: C, 55.6; H, 4.1%. Found: C, 55.7; H, 4.1%. IR (Nujol mull, most significant bands in the 2300–1000 cm⁻¹

range): 2067 (s), 2007 (s), 1918 (w), 1296 (s), 1220 (s), 1160 (s, br), 1091 (s), 1024 (s). ³¹P NMR (CDCl₃): δ 44.1 (s) and a resonance of low intensity at 41.2 (s). ¹H NMR (CDCl₃): δ 7.9–7.4 (m), 5.6 (q), 3.7 (s), 3.5 (s), 1.7 (d), – 3.6 (t, $J_{\rm H-P}$ = 19.3 Hz), -4.3 (t, $J_{\rm H-P}$ = 19.4 Hz). ¹⁹F NMR (CDCl₃): δ -78.3 (s); -78.7 (s). For the NMR spectra in the presence of excess MeOH, see Section 3.

2.6. X-ray crystallographic studies

The X-ray diffraction experiments were carried out at r.t. (T = 293 K) by means of a Bruker P4 diffractometer operating with a graphite-monochromated Mo Ka radiation ($\lambda = 0.71073$ Å). The samples were sealed in glass capillaries under an atmosphere of dinitrogen saturated with the crystallization solvent. The intensity data collection was carried out with the $\omega/2\theta$ -scan mode, collecting a redundant set of data. Three standard reflections were measured every 97 measurements to check sample decay. The intensities were corrected for Lp effects and for absorption by means of a ψ -scan method [9]. The structure solutions, obtained by means of the automatic direct methods, and the refinements, based on full-matrix least-squares on F^2 , were done by means of the SHELX-97 programme [10]. Data reduction of measured intensities was done by the XSCANS package [11]. Some other utilities contained in the WINGX suite [12] were also used.

Crystals of 2 are light yellow prisms. By selecting one of them of dimensions $0.48 \times 0.48 \times 0.25$ mm³ the unit cell parameters listed in Table 1 were obtained. A set of 3576 intensity data were collected in the range $2.01 \leq$ $\theta \leq 22.5^{\circ}$. By merging the equivalent ones, a set of 3027 independent intensities $(R_{int} = [\Sigma|F_o^2 - F_o^2(\text{mean})]/\Sigma(F_o^2)] = 0.0282)$ was obtained, among which 2365 satisfied the condition $I > 2\sigma(I)$. The systematic absences suggested the C2/m, C2 or Cm space groups. The multiplicity of these groups and the cell volume of 5199 $Å^3$ appeared to be appropriate to contain four units of $[Ru(O_2CN^iPr_2)(CO)_2(PPh_3)_2](OSO_2CF_3)$ and four molecules of the solvents $C_6H_5CH_3$ and CH_2Cl_2 . By considering the cell content, a mean atomic volume of 18.3 $Å^3$ per atom, almost identical to that calculated for compound 1, was obtained, see also Table 1. The structure solution was obtained in the space group C2/m, the asymmetric unit consisting of one-half of the $[Ru(O_2CN^iPr_2)(CO)_2(PPh_3)_2]^+$ cation and one-half of the triflate anion, one-third of C₆H₅CH₃ and one CH₂Cl₂. Toluene is placed on the inversion centre at 0, 0, 0, with a random distribution of the methyl groups, which could not be localized, while the CH₂Cl₂ is randomly placed in two positions related by an inversion centre at y=0. A different kind of disorder was observed in the position of the fluorine atoms, which were treated, however, as ordered. The final refinement

Table 1 Crystal data and structure refinement

Compound	$2 \cdot 0.5$ toluene · CH ₂ Cl ₂	5
Empirical formula	C50.5H50Cl2F3NO7P2RuS	C40H35F3O6P2RuS
Formula weight	1105.89	863.75
Temperature (K)	293(2)	293(2)
Crystal system	monoclinic	orthorhombic
Space group	C2/m (No. 12)	Pnma (No. 62)
Unit cell dimensions		
a (Å)	23.635(6)	17.400(2)
b (Å)	16.824(3)	23.222(2)
c (Å)	15.269(3)	9.4255(6)
β (°)	121.10(1)	
V (Å ³)	5199(2)	3808.5(5)
Ζ	4	4
$\rho_{\rm calc} ({\rm Mg}~{\rm m}^{-3})$	1.413	1.506
$\mu ({\rm mm}^{-1})$	0.566	0.612
Data/restraints/para- meters	3027/0/313	2729/0/250
$R(F_{\alpha})$ $[I > 2\sigma(I)]$	0.0933	0.0418
$Rw(F_{o}^{2}) [I > 2\sigma(I)]$	0.2545	0.0952

$$\begin{split} R(F_{\rm o}) &= \Sigma ||F_{\rm o}| - |F_{\rm c}| / \Sigma |F_{\rm o}|; \quad Rw(F_{\rm o}^2) = [\Sigma [w(F_{\rm o}^2 - F_{\rm c}^2)^2] / \Sigma [w - (F_{\rm o}^2)^2]^{1/2}; \quad w = 1 / [\sigma^2(F_{\rm o}^2) + (AQ)^2 + BQ] \quad \text{where} \quad Q = [\max(F_{\rm o}^2, 0) + 2F_{\rm c}^2] / 3. \end{split}$$

cycle was done by using anisotropic thermal parameters for all heavy atoms of the anion, cation and CH_2Cl_2 and isotropic for the others and by placing the hydrogen atoms in calculated positions. The resulting reliability factors are listed in Table 1.

Crystals of 5 are colourless prisms. One of them of dimensions $0.48 \times 0.38 \times 0.26$ mm³ showed the unit cell parameters listed in Table 1. A set of 3430 intensity data was collected in the range $2.3 \le 2\theta \le 23.0^\circ$. By merging the equivalent ones, a set of 2729 independent intensities $(R_{\rm int} = 0.0169)$ was obtained, among which 2060 satisfied the condition $I > 2\sigma(I)$. The systematic absences indicated the *Pnma* or $Pn2_1a$ space groups. The solution was found in the centrosymmetric group by the automatic direct methods, which revealed the location of ruthenium, carbonyl and MeOH ligands on the mirror plane at y = 1/4. The triflato anion was found to be randomly distributed in two mirror-related almost superimposed positions. In order to exclude that the anion disorder can be an artifact resulting from an erroneous assumption of the higher symmetry, the refinement was tried both in the Pnma and in the $Pn2_1a$ space groups. As the anion disorder was not removed, and the R factor was not lowered, the Pnma space group was preferred. The final refinement cycle was done by using anisotropic thermal parameters for all heavy atoms and placing the hydrogen atoms in calculated positions. The resulting reliability factors are listed in Table 1.

3. Results and discussion

Metal N,N-dialkylcarbamato complexes have been extensively studied in these laboratories [13] and results on ruthenium derivatives have recently been reported [1]. In the course of the present work, one of these compounds, namely $Ru(O_2CN^iPr_2)_2(CO)_2(PPh_3)_2$ (1), has been used as a precursor to ruthenium triflates by exploiting the reactivity of the N,N-dialkylcarbamato ligand. In 1 the ruthenium centre is *pseudo*-octahedrally coordinated with the phosphine ligands reciprocally trans and with the carbonyl and the monodentate carbamato ligands in mutual cis positions. The reaction of 1 with triflic anhydride in toluene yields the sparingly soluble $[Ru(O_2CN^1Pr_2)(CO)_2(PPh_3)_2](OTf)$ (2), which has been structurally and spectroscopically characterised. The CO stretching vibrations of 2, 2070 and 2010 cm^{-1} , are at higher wavenumbers with respect to the precursor $Ru(O_2CN^{1}Pr_2)_2(CO)_2(PPh_3)_2$ (1), (2050) and 1988 cm^{-1}), suggesting a positive charge in the ruthenium-containing moiety of the compound. The highest energy band associated with the carbamato group is at 1556 cm^{-1} , to be compared with the value of 1594 cm^{-1} in 1, containing monodentate carbamato ligands. This suggests that the N,N-di-iso-propylcarbamato is bidentate. In the $1400-1000 \text{ cm}^{-1}$ region, bands attributable to the triflato group were observed at 1262 (s) and 1032 (s) cm⁻¹. The ionic OTf⁻ anion has intense bands at 1269 and 1032 cm^{-1} assigned to the asymmetric and symmetric S-O stretching modes, respectively [2a,14a], as confirmed also by our independent data on the di-iso-propylammonium derivative (NH¹₂- Pr_2)(OTf), see Section 2.

The spectroscopic information was completely confirmed by X-ray crystallographic study. The triflato group is outside the coordination sphere of the metal, the mononuclear cation having a distorted octahedral geometry (see Fig. 1) with *trans* phosphines and *cis*



Fig. 1. Structure of the $[Ru(O_2CN^iPr_2)(CO)_2(PPh_3)_2]^+$ cation, with some of the metal-coordinated atoms beeing represented by thermal ellipsoids at 30% probability. The apex of the phosphorous label has the same meaning as in Table 2.

carbonyl groups. The terminal bidentate N,N-di-*iso*-propylcarbamato ligand displays Ru–O(3) and Ru–O(4) distances of 2.088 and 2.157 Å, respectively, and a bite angle of 62.3° (see Fig. 1 and Table 2 for the most significant bond distances and angles).

The two tertiary phosphine groups are equivalent by symmetry and show Ru-P distances of 2.420 Å, the P-Ru-P angle being 174.3°. The Ru-CO distances are 1.87(1) and 1.86(2) Å. In compound 1 the carbamato ligands are monodentate with Ru-O distances of 2.076(5) and 2.090(5) Å and an O-Ru-O angle of 80.5(2)°. The Ru-P [2.402(2) and 2.411(2) Å] and Ru-CO (1.87 Å) distances in 1 are comparable to those observed in 2. In compound Ru(O₂CNⁱPr₂)₂(PPh₃)₂ [1], with terminal bidentate carbamato ligands, the Ru-O distances range from 2.105(4) to 2.250(4) Å, slightly longer than the corresponding distances in the $[Ru(O_2CN^iPr_2)(CO)_2(PPh_3)_2]^+$ cation. In $Ru(CO_3)$ - $(CO)_2(PPh_3)_2$ [1], where the carbonato is terminal bidentate, the Ru–O distance [2.079(2) Å] is shorter than in 2, as expected in view of the double negative charge of the ligand; the O-Ru-O bite angle is $62.7(2)^{\circ}$, comparable to that observed in 2 (60.7°). The Ru–CO distance [1.880(3) Å] is similar to those observed in 2.

In the crystal the cations are disposed with the $P \cdots P$ axis parallel to **b** with the metal and the other ligands lying on the mirrors spanned by **b**/2. The closest interionic approach is between the carbonyl groups and the triflate anion at a Ru \cdots S distance of 5.65 Å. The ion pairs are arranged in rows in the **c** direction, spaced by the solvent molecules.

Although the field of the ruthenium N,N-dialkylcarbamato complexes has been recently enriched with some new contributions [1,15], examples of cationic species are rare [6], as reported in Section 1. In [Ru(O₂CN-Me₂)(PMe₂Ph)₄][PF₆] [6a], obtained from [RuH(P-Me₂Ph)₅][PF₆], CO₂ and NHMe₂, the carbamato ligand is terminal bidentate, as in **2**.

The formation of 2 in toluene, even in the presence of an excess of triflic anhydride, is presumably due to its

Table 2 Bond lengths (Å) and angles (°) for [Ru(O₂CNⁱPr₂)(CO)₂-(PPh₃)₂](OTf)·0.5 toluene·CH₂Cl₂ Bond lengths 2.088(10) Ru-C(1)1.872(17) Ru-O(3)Ru-C(2)1.863(16) Ru-O(4)2.157(9) Ru-P 2.420(2)Bond angles C(1)-Ru-C(2)P-Ru-C(1)92.84(6) 92.4(6) C(1) - Ru - O(3)P-Ru-C(2)89.74(7) 99.4(6) C(2) - Ru - O(4)15.9(5) P-Ru-O(3)89.68(7) O(3)-Ru-O(4) P-Ru-O(4)87.35(6) 62.3(4) C(1)-Ru-O(4) P-Ru-P' 161.6(6) 174.3(1) C(2)-Ru-O(3) 168.2(4)

Symmetry transformations: ' = x, -y, z.

low solubility in the reaction medium. In fact, when the reaction between 1 and excess of triflic anhydride was carried out in 1,2-dichloroethane, the prompt and transient formation of 2 was observed by 31 P NMR spectroscopy, followed by further reaction to produce Ru(OTf)₂(CO)₂(PPh₃)₂, **3**.

When 1 was reacted with 4 or more equiv. of triflic acid in toluene as medium $Ru(OTf)_2(CO)_2(PPh_3)_2$ (3), was obtained as the main product together with variable amounts of 2, depending on time, temperature and excess of triflic acid. A gas-volumetric monitoring of this reaction showed that the addition of the first 2 equiv. of triflic acid produces the fast evolution of 1 equiv. of CO_2 , corresponding to the formation of 2, see Eq. (1).

$$Ru(O_{2}CN^{i}Pr_{2})_{2}(CO)_{2}(PPh_{3})_{2} + 2 \text{ HOTf}$$

$$\rightarrow [Ru(O_{2}CN^{i}Pr_{2})(CO)_{2}(PPh_{3})_{2}][OTf]$$

$$+[NH_{2}^{i}Pr_{2}][OTf] + CO_{2} \qquad (1)$$

$$2 + 2 \text{ HOTf} \rightarrow Ru(OTf)_{2}(CO)_{2}(PPh_{3})_{2}$$

$$+[NH_2^{1}Pr_2](OTf) + CO_2$$
⁽²⁾

By reaction with 2 more equiv. of triflic acid, a second equivalent of CO₂ is slowly released with formation of **3** (see Eq. (2)). The low solubility of **2** in toluene can explain its transient accumulation. Compound **3** is well soluble in toluene, suggesting to be a non-ionic mononuclear complex. The IR spectrum of the product indicates that the carbonyl ligands maintain the relative *cis* position, two stretching vibrations at 2074 and 2012 cm^{-1} being observed. These bands are nearly coincident with those of **2**, which carries a positive charge. A band at 1328 cm^{-1} is typical of terminal monodentate OTf groups [2a,14b]: for instance, Ru(O₃SCF₃)₂(dppe)(CO)₂, containing a monodentate triflato, as confirmed by an X-ray investigation [3a], has an absorption band at 1329 cm^{-1} .

Compound 3, Ru(OTf)₂(CO)₂(PPh₃)₂, has already been described in the literature [5], being obtained by reaction of the ruthenium(0) the complex $Ru(CO)_3(PPh_3)_2$ with triflic acid. The spectroscopic data reported earlier (³¹P NMR: 22.7 ppm; IR: v_{CO} 2080, 2021 cm⁻¹) do not agree with our data (${}^{31}P$ NMR: 20.2 ppm; IR: v_{CO} 2074, 2012 cm⁻¹). As the compound is affected by moisture, we suggest that the discrepancy may be reconciled by the formation of aquo-complexes. As a matter of fact, upon ageing, CH₂Cl₂ solutions of **3** show an additional ³¹P NMR peak at 23.2 ppm beside the main one at 20.2 ppm. In order to confirm our hypothesis, 3 was treated with the stoichiometric amount of water in CDCl₃ and the system was monitored by ³¹P NMR spectroscopy: the intensity of the original signal at 20.2 ppm gradually decreased while that of the new signal at 23.2 ppm increased. A Nujol IR spectrum of the resulting solid

product showed that the original CO stretchings were displaced to 2082 and 2027 cm⁻¹, while the band at 1328 cm⁻¹, assigned to the coordinated triflato group, had disappeared being substituted by two bands at 1260 and 1032 cm⁻¹ attributable to the triflate ion and by a broad absorption at 3250 cm⁻¹ due to water. These data suggest the formation of a cationic aquo-complex through the substitution of the terminal monodentate triflato ligand.

Triflato ligand substitution by water with formation of ionic aquo-complexes of ruthenium(II) has been reported, documented by the structural characterization of the solid products [3]. Moreover, spectroscopic evidence of rapid equilibria in solution involving triflato- and aquo-complexes has been reported [3]. The lability of this family of low-spin hexacoordinated ruthenium(II) derivatives can be exploited for the preparation of a series of ruthenium derivatives, as pointed out by Wojcicki and coworkers [4].

In order to confirm the nature of our product, we have prepared **3** by the already quoted literature method [5], see Eq. (3), at the reflux temperature of toluene. Under these conditions and also by reacting $RuCl_2(CO)_2(PPh_3)_2$ with $Ag(O_3SCF_3)$, and by operating under exclusion of moisture, we obtained a product with spectroscopic features identical to those discussed above.

$$Ru(CO)_{3}(PPh_{3})_{2} + 2 \text{ HOTf} \rightarrow Ru(OTf)_{2}(CO)_{2}(PPh_{3})_{2}$$

+ products (3)

In the hypothesis that reaction (3) is preceded by a primary oxidative addition of TfOH to ruthenium(0), the reaction was carried out at room temperature. The formation of a colourless solid, corresponding to the species $[RuH(CO)_3(PPh_3)_2](OTf)$ (4), was observed, being characterized by a ³¹P NMR signal (CH₂Cl₂ solution) at 34.5 ppm.

$$Ru(CO)_{3}(PPh_{3})_{2} + TfOH$$

$$\rightarrow [RuH(CO)_{3}(PPh_{3})_{2}](OTf)$$
(4)

Product 4 in CDCl₃ does not react with an excess of triflic acid at room temperature in a week time. More than 10 days are necessary to observe, in the ³¹P NMR spectrum of the solution, signals due to small amounts of **3**. On the contrary, **4** reacts quickly with NEt₃ with production of the precursor Ru(CO)₃(PPh₃)₂ (Eq. (5)), this result showing that triethylamine is a sufficiently strong Lewis base to deprotonate ruthenium(II). This is a two-electron process, leading to ruthenium(0). Reaction (5) is reminiscent of the two-electron reductive elimination operated by tertiary amines on CoH(CO)₄ giving the trialkylammonium derivatives (R₃NH)-[Co(CO)₄] [16].

$$[\operatorname{RuH}(\operatorname{CO})_3(\operatorname{PPh}_3)_2](\operatorname{OTf}) + \operatorname{NEt}_3 \to \operatorname{Ru}(\operatorname{CO})_3(\operatorname{PPh}_3)_2 + [\operatorname{NEt}_3\operatorname{H}](\operatorname{OTf})$$
(5)

Spectroscopic evidence of the formation of protonation products by reaction of Ru(CO)₃(PPh₃)₂ with strong protic acids has been reported in the literature, and the derivatives were described to be difficult to isolate in a pure form [17]. In the course of our work, 4 was obtained in good yields and its IR spectrum shows three bands attributable to CO stretching vibrations at 2139 (w), 2083 (s) and 2069 (s) cm^{-1} . These bands compare well with those [at 2138 (m), 2077 (s) and 2055 (s) cm⁻¹] reported for *mer*-[RuI(CO)₃(PPh₃)₂]I containing the mer- $M(CO)_3$ fragment, and the two phosphine ligands reciprocally trans [18]. Bands due to the triflato group are found in the region typical of the ionic derivatives. The ³¹P NMR displays a resonance at 34.9 ppm in CDCl₃, similar to [RuH(CO)₃(PPh₃)₂](O₂CCF₃) [17c] and to [RuH(CO)₃(PPh₃)₂]Cl [17c], both showing a resonance at 34.5 ppm. In the ¹H NMR spectrum, the hydride absorbs at -6.4 ppm, the signal having multiplicity three by coupling with the two equivalent phosphorus nuclei. The hydride resonances for $[RuH(CO)_3(PPh_3)_2](O_2CCF_3)$ and $[RuH(CO)_3(PPh_3)_2]Cl$ are reported at -6.1 and -6.2ppm, respectively [17c]. In the ¹³C NMR spectrum, two triplets are attributable to the CO ligands, the less intense, at 189.8 ppm, being reasonably due to the ligand *trans* to the hydride, the other one, at 192.3 ppm, to the reciprocally *trans* carbonyls.

A suspension of $[RuH(CO)_3(PPh_3)_2][OTf]$ (4), was refluxed in toluene and, after cooling and addition of methanol to the resulting solution, colourless crystals of $[RuH(CO)_2(MeOH)(PPh_3)_2][OTf]$ (5), were obtained. Under these conditions of reduced partial pressure of CO, one of the carbonyl groups is lost and replaced by methanol (Eq. (6)).

$$[\operatorname{RuH}(\operatorname{CO})_{3}(\operatorname{PPh}_{3})_{2}][\operatorname{OTf}] + \operatorname{MeOH}_{4} \rightarrow [\operatorname{RuH}(\operatorname{CO})_{2}(\operatorname{MeOH})(\operatorname{PPh}_{3})_{2}][\operatorname{OTf}] + \operatorname{CO}$$
(6)

Product 5 has been structurally characterized. In the cation, see Fig. 2, ruthenium is hexa-coordinated in a distorted octahedral geometry. The most significant bond distances and angles are reported in Table 3. Ruthenium, carbonyls, hydride and methanol ligands are placed on a plane which is the mirror relating the two phosphines. The presence of four monodentate ligands releases some constraint and allows a coordination geometry close to the ideal octahedron. The CO-Ru-CO', C(1)-Ru-O(3), C(2)-Ru-H(1) and O(3)-Ru-H(1) angles are in fact close to 90°. The Ru-CO distances are significantly different, namely 1.981 and 1.855 Å for the CO ligands opposite to the hydride and to methanol, respectively. Moreover, the P-Ru-P' angle is reduced to 164.9° with the Ru-P bonds leaning



Fig. 2. Structure of the $[RuH(CO)_2(MeOH)(PPh_3)_2]^+$ cation. The Ru, P and some of the C and O atoms are represented by ellipsoids at 30% probability; two hydrogen atoms are represented as spheres of arbitrary radii. The apexes of the labels have the same meaning as in Table 3. The hydrogen interaction of the coordinated methanol with the O(5) atom of the disordered anion is represented by a dashed line.

Table 3 Bond lengths (Å) and angles (°) for [RuH(CO)₂(MeOH)(PPh₃)₂](OTf) (5)

Bond lengths			
Ru-C(1)	1.981(7)	Ru-O(3)	2.141(5)
Ru-C(2)	1.855(7)	Ru-H(1)	1.57(6)
Ru–P	2.389(1)		
Bond angles			
C(1)-Ru-C(2)	94.8(3)	P-Ru-C(2)	89.41(3)
C(1)-Ru-O(3)	89.8(3)	P-Ru-O(3)	89.99(3)
C(2) - Ru - H(1)	93(2)	P-Ru-H(1)	82.53(3)
O(3)-Ru-H(1)	82(2)	P-Ru-P'	164.92(6)
P-Ru-C(1)	97.54(3)		

Symmetry transformations: ' = x, -y + 1/2, z.

towards the less hindered hydride ligand. C_2 symmetry is however, rigorously maintained in the cation. The anion is disordered in the crystal, being placed slightly out of the mirror plane. The *m* operation produces another equally populated position on the opposite side. The two positions of the triflate have an almost coincident oxygen, labelled as O(5) and O(5') in Fig. 2, due to the hydrogen bond [O(3)···O(5), 2.562 Å] with the coordinated methanol.

The Ru–H distance is about 1.6 Å, to be compared with the value of 1.7 Å reported for $[RuH(CO)_2(H_2O)-(PPh_3)_2](BF_4)$ [19], whose cation has a geometric distribution of the ligands analogous to that observed in **5**, with the H₂O ligand replacing MeOH. The Ru–OH₂ distance is 2.15 Å. As in **2**, the coordination around ruthenium is distorted octahedral with the P–Ru–P angle of 165.1°. The Ru–CO bond distances are different, the carbonyl *trans* to H₂O being closer to the metal (1.83 Å) than that trans to the hydride (1.97 Å).

The IR spectrum of 5 displays two bands at 2067 and 2007 cm^{-1} attributed to the CO stretching vibrations.

The NMR spectra of the product in CDCl₃ are relatively complex: the protonic spectrum shows a multiplet centred at about 7.6 ppm due to the aromatic nuclei, one quadruplet (5.6 ppm) and one doublet (1.7 ppm) due to coordinated methanol, two singlets at 3.7 and 3.5 ppm attributed to uncoordinated methanol and two triplets in the hydride region at -3.6 and -4.3 ppm; two ³¹P resonances are observed at 44.1 and 41.2 ppm, the former of higher intensity. Moreover, two ¹⁹F signals are found at -78.3 and -78.7 ppm. The addition of some drops of methanol to the solution causes a simplification of the spectra, single ³¹P and ¹⁹F resonances at 44.1 and -78.7 ppm, respectively being observed together with a single triplet (-4.3 ppm) due to the hydride ligand in the ¹H NMR spectrum. If the solution was evaporated to dryness and treated in vacuo to remove completely the solvents, the residue, dissolved in CDCl₃, shows again the original NMR spectra showing coordinated methanol. This behaviour can be explained by the following equilibrium in solution.



Methanol and OTf⁻ compete for the coordination sphere, the reaction being presumably balanced from a thermodynamic point of view.

It is interesting to note that in compound **2** the presence of a carbamato group, which acts as a bidentate ligand, is sufficient to prevent the triflato group from being coordinated [2]. This is consistent with the expulsion of ruthenium-coordinated triflato groups and with the formation of ionic products observed in the presence of oxygen-, nitrogen-, and phosphorous donors [3,4].

4. Conclusions

Taking the earlier results [1] into additional consideration, the chemistry of these systems of ruthenium(II) appears to be dictated by the requirement for the central metal atom to attain the 18-electron configuration. The hapticity of the potentially mono- or bidentate ligand (R_2NCO_2), as confirmed by the X-ray diffraction structural data, can therefore be predicted on this basis.

5. Supplementary material

Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallo-

graphic Data Centre, CCDC Nos. 176709 and 176710 for compounds **2** and **5**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

Acknowledgements

The authors wish to thank the Ministero dell'Università e della Ricerca Scientifica e Tecnologica (MURST), Programmi di Ricerca Scientifica di Rilevante Interesse Nazionale, Cofinanziamento 2000-1, for financial support. The authors are grateful to Dr Alessandra Merigo [20] for the synthesis and characterization of (NHⁱ₂-Pr₂)(OTf).

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