

Carbonyl and nitrosyl diruthenium compounds: Crystal structure of $[\text{Ru}_2(\text{O}_2\text{CMe})(\text{DPhF})_3(\text{CO})]\text{BF}_4 \cdot \text{CH}_2\text{Cl}_2$ and its isomorphous nitrosyl analogue

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Abstract

The reaction of $[\text{Ru}_2(\text{O}_2\text{CMe})(\text{DPhF})_3(\text{H}_2\text{O})]\text{BF}_4$ (DPhF = *N,N'*-diphenylformamidinate) with CO gas leads to $[\text{Ru}_2(\text{O}_2\text{CMe})(\text{DPhF})_3(\text{CO})]\text{BF}_4$ (**1**), that is the first isolated carbonyl complex containing the Ru_2^{5+} unit. The nitrosyl analogue $[\text{Ru}_2(\text{O}_2\text{CMe})(\text{DPhF})_3(\text{NO})]\text{BF}_4$ (**2**) is prepared by reaction of $\text{Ru}_2\text{Cl}(\text{O}_2\text{CMe})(\text{DPhF})_3$ with NOBF_4 . However, the attempts to obtain the cyanide derivative by reaction of $\text{Ru}_2\text{Cl}(\text{O}_2\text{CMe})(\text{DPhF})_3$ or $[\text{Ru}_2(\text{O}_2\text{CMe})(\text{DPhF})_3(\text{H}_2\text{O})]\text{BF}_4$ with NaCN were unsuccessful. The structure of compounds **1** · CH_2Cl_2 and **2** · CH_2Cl_2 are described. Both compounds are isomorphous. The magnetic measurements at variable temperature demonstrate that **1** is paramagnetic with one unpaired electron in all range of temperature, in contrast to the three unpaired electrons usually present in Ru_2^{5+} complexes. The analogous nitrosyl compound **2** is diamagnetic.

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Keywords: Carbonyl complexes; Nitrosyl complexes; Ruthenium; Magnetism; Metal–metal bond

1. Introduction

The carbon monoxide (CO) has been extensively used as ligand in organometallic chemistry [1]. Due to its σ donor and π acceptor character numerous metal complexes, especially with the metal in low oxidation state have been prepared. The coordination chemistry of the nitrogen monoxide (nitric oxide, NO) [2] has been less studied. However, because of its fundamental role as constituent of air pollution [3] and in biochemical processes [4], the interest of the chemistry of NO has largely increased [5].

Numerous paddlewheel diruthenium complexes with different equatorial and axial ligands showing a large range of basicities have been described [6]. However, it is known that complexes containing Ru_2^{5+} core are sensitive to

cleavage by strong π acceptor ligands [7] and, therefore, reports on diruthenium compounds with NO or CO ligands are very scarce in the literature. The first two structurally characterized nitrosyl complexes $\text{Ru}_2(\text{O}_2\text{CC}_2\text{H}_5)_4(\text{NO})_2$ and $\text{Ru}_2(\text{O}_2\text{CCF}_3)_4(\text{NO})_2$ were prepared from the corresponding tetracarboxylatodiruthenium(II) derivatives and were described as Ru_2^{2+} compounds [8]. A formally diruthenium(II) complex $\text{Ru}_2\text{Cl}(\text{Fap})_4(\text{NO})$ (Fap = 2-(2-fluoroanilino)pyridinate) containing a more basic equatorial ligand has also been published [9]. More recently, two new nitrosyl compounds $\text{Ru}_2(\text{DPhF})_4(\text{NO})$ and $\text{Ru}_2(\text{DPhF})_4(\text{NO})_2$ (DPhF = *N,N'*-diphenylformamidinate) proposed to be Ru_2^{3+} and Ru_2^{2+} , respectively, were also structurally characterized [10]. The reduction of $\text{Ru}_2(\text{DPhF})_4(\text{NO})$ under CO atmosphere gives the anion $[\text{Ru}_2(\text{DPhF})_4(\text{NO})(\text{CO})]^-$. This species contains both CO and NO axial ligands but the complex was not isolated [10]. The number of carbonyl complexes containing

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diruthenium cores reported in the literature is even lower than of nitrosyl compounds. The unstable dicarbonyl complex $\text{Ru}_2(\text{N}_3\text{Ph}_2)_4(\text{CO})_2$ has been briefly described [8] but its crystal structure is unknown. The first stable carbonyl-diruthenium complex $\text{Ru}_2(\text{DPhF})_4(\text{CO})$ containing a Ru_2^{4+} unit has four strongly basic equatorial ligands. This compound can be converted by oxidation in the analogous Ru_2^{5+} derivative but this latter complex was not isolated [11].

In this paper we analyze the reaction of the neutral and the cationic complexes $\text{Ru}_2\text{Cl}(\text{O}_2\text{CMe})(\text{DPhF})_3$ and $[\text{Ru}_2(\text{O}_2\text{CMe})(\text{DPhF})_3(\text{H}_2\text{O})]\text{BF}_4$ with NO^+ , CO , and CN^- species. These reactions allow us to isolate and characterize the new carbonyl and nitrosyl isomorphous complexes $[\text{Ru}_2(\text{O}_2\text{CMe})(\text{DPhF})_3(\text{CO})]\text{BF}_4$ (**1**) and $[\text{Ru}_2(\text{O}_2\text{CMe})(\text{DPhF})_3(\text{NO})]\text{BF}_4$ (**2**). **1** represents the first example of a carbonyl compound containing the Ru_2^{5+} core.

2. Results and discussion

2.1. Synthesis of the complexes

The first neutral low spin complex of Ru_2^{5+} , $\text{Ru}_2(\text{CN})(\text{DPhF})_4$ [12], and the oxidized Ru_2^{6+} derivative $\text{Ru}_2(\text{CN})_2(\text{DPhF})_4$ [13] were isolated from the reaction between $\text{Ru}_2\text{Cl}(\text{DPhF})_4$ and an excess of NaCN . However, the attempts to obtain the same kind of complexes by reaction of $\text{Ru}_2\text{Cl}(\text{O}_2\text{CMe})(\text{DPhF})_3$ or $[\text{Ru}_2(\text{O}_2\text{CMe})(\text{DPhF})_3(\text{H}_2\text{O})]\text{BF}_4$ with NaCN have been unsuccessful. It is reasonable to think that the less donor carboxylate group compare to the formamidinate ligand makes the complexes unstable in the presence of cyanide species. This fact is consistent with the difficulties found by numerous authors to oxidize the $[\text{Ru}_2(\text{O}_2\text{CR})_4]^+$ core and to isolate Ru_2^{6+} carboxylates [6].

The cationic species $[\text{Ru}_2(\text{DPhF})_4(\text{CO})]^+$ was detected in the electrochemical studies carried out on $\text{Ru}_2(\text{DPhF})_4(\text{CO})$ in CH_2Cl_2 solution [11], although the complex was not isolated. However, the easy coordination of CO at the axial position of $[\text{Ru}_2(\text{O}_2\text{CMe})(\text{DPhF})_3(\text{H}_2\text{O})]\text{BF}_4$ in dichloromethane solution allows the isolation of $[\text{Ru}_2(\text{O}_2\text{CMe})(\text{DPhF})_3(\text{CO})]\text{BF}_4$ (**1**) in good yield. In contrast, when CO was bubbled through a dichloromethane solution of $\text{Ru}_2\text{Cl}(\text{O}_2\text{CMe})(\text{DPhF})_3$, only the starting material was recovered, in accordance with the high tendency of the “ $\text{Ru}_2(\text{O}_2\text{CMe})(\text{DPhF})_3$ ” moiety to coordinate only one axial ligand.

The easy isolation of the carbonyl complex **1** contrasts to the difficulties found to obtain the cyanide derivative. The lower basicity of CO with respect to CN^- may be the reason why the fragment “ $\text{Ru}_2(\text{O}_2\text{CMe})(\text{DPhF})_3$ ” endures the coordination of CO . Compound **1** is stable to the air and constitutes the first example of a Ru_2^{5+} carbonyl complex. Crystals of **1** · CH_2Cl_2 and **1** · THF were obtained by crystallization from CH_2Cl_2 /hexane and THF /hexane, respectively. The nitrosyl analogue of com-

plex **1**, $[\text{Ru}_2(\text{O}_2\text{CMe})(\text{DPhF})_3(\text{NO})]\text{BF}_4$ (**2**), was prepared by reaction of $\text{Ru}_2\text{Cl}(\text{O}_2\text{CMe})(\text{DPhF})_3$ with NOBF_4 . Crystals of **2** · CH_2Cl_2 were obtained similarly to **1** · CH_2Cl_2 . Regardless of the formal oxidation state of the diruthenium core, there is one additional electron in **2** with respect to **1**. Presumably, the solvent is involved in this reduction process and it could be related to the stabilization of the π^* orbitals upon coordination of NO^+ , which makes the complex more oxidizing. The reduction of dimetallic compounds in THF has been previously pointed out [14].

A different procedure, bubbling NO gas through a solution of $\text{Ru}_2\text{Cl}(\text{Fap})_4$ ($\text{Fap} = 2$ -(2-fluoroanilino)pyridinate), was employed to obtain the related compound $\text{Ru}_2\text{Cl}(\text{Fap})_4(\text{NO})$ [9].

2.2. IR spectra

The absorptions in the IR spectra of the complexes are consistent with previous data observed for other diphenylformamidinate complexes of Ru_2^{5+} where DPhF^- acts as a bridge between the metal atoms. A detailed study of the IR bands, in related compounds, has been published elsewhere [15]. In compound **1** · CH_2Cl_2 , the C–O normal mode of vibration of the carbonyl group absorbs at 2016 cm^{-1} . This value is very similar to the reported for the electrochemically generated species $[\text{Ru}_2(\text{DPhF})_4(\text{CO})]^+$ in CH_2Cl_2 solution (2019 cm^{-1}). The CO stretching vibration bands for the compound $\text{Ru}_2(\text{DPhF})_4(\text{CO})$ and the electrochemically reduced species $[\text{Ru}_2(\text{DPhF})_4(\text{CO})]^-$ appear at 1929 and 1840 cm^{-1} , respectively. This difference is in agreement with the variation of the electron density in the metal centres and, consequently, with the back-donation to the carbonyl ligand [11].

The $\nu(\text{CO})$ in **1** is sensitive to the solvent of crystallization being higher in **1** · THF (2024 cm^{-1}). In accordance with this behaviour, we have shown, very recently, how small changes in the structure of the solids can modify the electronic configuration of this kind of species [16]. The different population of the orbitals π^* and δ^* may change and affect the retrodonation of the electronic density to the axial ligand.

The most important feature in the IR spectrum of **2** · CH_2Cl_2 is the absorption of the N–O bond that appears at 1771 cm^{-1} , near to that found for $\text{Ru}_2(\text{DPhF})_4(\text{NO})$ (1773 cm^{-1}) despite the assigned oxidation state is lower in this last compound [10]. However, the derivative $\text{Ru}_2\text{Cl}(\text{Fap})_4(\text{NO})$ [9], described as Ru_2^{4+} complex, presents an absorption band at lower wavenumber (1740 cm^{-1}), close to the bands detected for $\text{Ru}_2(\text{DPhF})_4(\text{NO})_2$ at 1747 and 1727 cm^{-1} [10]. It must be taken in consideration that the magnitude of the back-donation from the Ru_2^{n+} unit depends not only on the oxidation state of these units but also on the donor character of the equatorial ligands. Other complexes with formula $\text{Ru}_2(\text{O}_2\text{CR})_4(\text{NO})_2$, $\text{R} = \text{Me}, \text{Et}, \text{Ph}, \text{CF}_3$, present bands between 1722 and 1800 cm^{-1} [8].

2.3. Mass spectra

The stability of the fragment $[\text{Ru}_2(\text{L-L})_4]^+$ has been pointed out in mass-spectrometry studies on carboxylate complexes containing the Ru_2^{5+} core [17]. The mass spectrum of complex **1** also shows a strong signal attributed to the fragment $[\text{Ru}_2(\text{O}_2\text{CMe})(\text{DPhF})_3]^+$, originated by the loss of the axial ligand. This fragment has also been detected for $\text{Ru}_2\text{Cl}(\text{O}_2\text{CMe})(\text{DPhF})_3$ [18], $\text{Ru}_2(\text{N}_3)(\text{O}_2\text{CMe})(\text{DPhF})_3$, $\text{Ru}_2(\text{NCS})(\text{O}_2\text{CMe})(\text{DPhF})_3$ [12], and $[\text{Ru}_2(\text{O}_2\text{CMe})(\text{DPhF})_3(\text{H}_2\text{O})]\text{BF}_4$ [19]. However, in the mass spectrum of **2** only the peak assigned to the $[\text{Ru}_2(\text{O}_2\text{CMe})(\text{DPhF})_3(\text{NO})]^+$ fragment is displayed, which indicates the strength of the Ru–NO bond in this compound. A signal corresponding to $[\text{Ru}_2(\text{Fap})_4(\text{NO})]^+$ was observed for $\text{Ru}_2\text{Cl}(\text{Fap})_4(\text{NO})$ although other fragments as $[\text{Ru}_2(\text{Fap})_4]^+$ and $[\text{Ru}_2(\text{Fap})_3]^+$ were also detected [9]. The only fragment reported from the mass spectra of the complexes $\text{Ru}_2(\text{DPhF})_4(\text{NO})$ and $\text{Ru}_2(\text{DPhF})_4(\text{NO})_2$ was $[\text{Ru}_2(\text{DPhF})_4]^+$ [10].

2.4. Magnetism

Complexes of Ru_2^{5+} have been usually represented with a $(\pi^*\delta^*)^3$ configuration, with three unpaired electrons, due to the accidental degeneration of the π^* and δ^* orbitals [6]. However, for some triazenido [20] and formamidinato [12] complexes a HOMO π^* , with one unpaired electron, have been proposed. In addition, more recently some formamidinate compounds with a magnetic moment intermediate between three and one unpaired electrons have been published [15,16,19,21,22].

Complex **1** · CH_2Cl_2 shows a magnetic moment at room temperature of $2.03 \mu_B$, corresponding to one unpaired electron. The magnetic moment remains constant from room temperature to 2 K as expected for a doublet ground term. This magnetic behaviour contrasts with the three unpaired electrons of the parent compound $\text{Ru}_2\text{Cl}(\text{O}_2\text{CMe})(\text{DPhF})_3$ [18] and the intermediate behaviour of $[\text{Ru}_2(\text{O}_2\text{CMe})(\text{DPhF})_3(\text{H}_2\text{O})]\text{BF}_4$ [19]. Moreover, the magnetic moment for **1** · THF is $2.24 \mu_B$ at room temperature. However, the difference of $0.21 \mu_B$ for the same complex, but crystallized with other solvent, is not a surprise in this class of compounds where small changes, such as additional hydrogen bond interactions, may induce different magnetic behaviour [16].

Complex **2** is diamagnetic. This diamagnetism is compatible with two formulations, $\text{Ru}_2^{4+}(\text{NO}^+)$ and $\text{Ru}_2^{6+}(\text{NO}^-)$, with electronic configurations $\sigma^2\pi^4\delta^2(\pi^*)^4$ and $\sigma^2\pi^4\delta^2(\delta^*)^2$, respectively. Nevertheless, the absorption band of NO at 1771 cm^{-1} rejects the last configuration. Thus, a Ru_2^{4+} core seems to be more probable although a $\text{Ru}_2^{5+}(\text{NO})$ formulation with low spin configuration $\sigma^2\pi^4\delta^2(\pi^*)^3$ and a strong antiferromagnetic coupling between the unpaired electrons of the Ru_2^{5+} unit and the NO radical cannot be discarded.

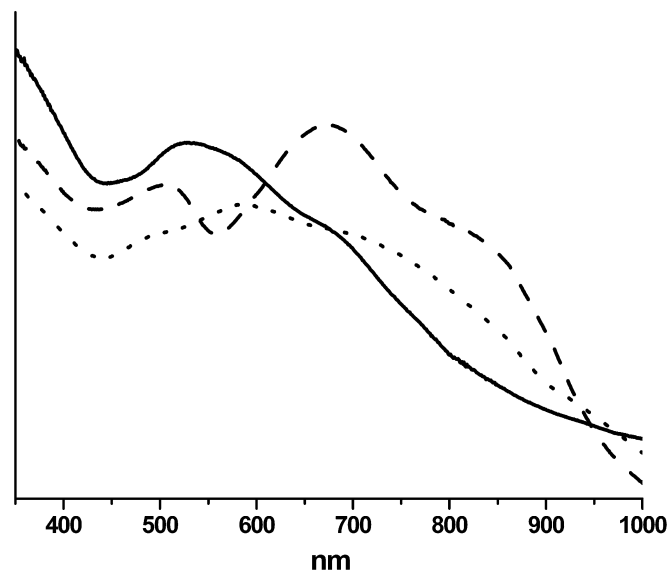


Fig. 1. Electronic spectra in the solid state for $\text{Ru}_2\text{Cl}(\text{O}_2\text{CMe})(\text{DPhF})_3$ (solid), **1** · CH_2Cl_2 (dots), and **2** · CH_2Cl_2 (dashed).

2.5. Electronic properties

In Fig. 1, the visible spectra in the solid state of complexes **1** and **2** are shown. The spectrum of the high spin compound $\text{Ru}_2\text{Cl}(\text{O}_2\text{CMe})(\text{DPhF})_3$ is also included for comparison. The most noticeable differences between the curves of $\text{Ru}_2\text{Cl}(\text{O}_2\text{CMe})(\text{DPhF})_3$ and **1** are the presence, in the latter, of a shoulder at 490 nm and the shift of its maximum to lower energy (587 nm). A possible explanation could be that the absorption at 528 nm for $\text{Ru}_2\text{Cl}(\text{O}_2\text{CMe})(\text{DPhF})_3$ corresponds to the sum of two bands, due to the $\pi \rightarrow \pi^*$ and $\pi^* \rightarrow \delta^*$ transitions [15]. The exchange of Cl^- by CO as axial ligand produces a stabilization of the π^* orbital. This stabilization increases the gap between the π^* and δ^* orbitals and reduces the distance between the π and π^* levels. In that case, for complex **1**, the absorptions at about 490 and 587 nm can be attributed to the $\pi^* \rightarrow \delta^*$ and $\pi \rightarrow \pi^*$ transitions, respectively. The electronic spectrum of complex **2** shows the $\pi^* \rightarrow \delta^*$ band at 504 nm but does not display any absorption near 600 nm, as expected for a completely occupied π^* orbital. The other absorptions in the spectrum of **2** at lower energies should be related to transitions in which the σ^* orbital is involved. This σ^* orbital must be strongly stabilized due to the coordination of the NO ligand at the axial position as evidenced by the elongated metal–metal bond distances observed in this class of complexes [8–10].

2.6. Cyclic voltammetry

The redox behaviour of compounds **1** and **2** has been investigated by cyclic voltammetry.

Complex **1** shows two quasi-reversible cathodic processes and two anodic peaks due to irreversible reductions (Table 1). This voltammogram can be explained consider-

Table 1
Half-wave potentials of diruthenium complexes in CH₂Cl₂ solution under N₂

Compound	Formal OE	1st oxid.	1st red.	2nd red.	Reference
[Ru ₂ (O ₂ CMe)(DPhF) ₃ (CO)]BF ₄	Ru ₂ ⁵⁺	0.93 0.61 ^a	−0.11 −0.64 ^a		This work ^b
Ru ₂ (DPhF) ₄ (CO)	Ru ₂ ⁴⁺	0.28	−1.17		[11]
[Ru ₂ (O ₂ CMe)(DPhF) ₃ (NO)]BF ₄	Ru ₂ ⁴⁺		0.09	−1.16	This work ^b
Ru ₂ (DPhF) ₄ (NO)	Ru ₂ ³⁺		0.06	−1.24	[10]

^a Potentials redox corresponding to the species [Ru₂(O₂CMe)(DPhF)₃(CO)](BF₄).

^b The potential values were corrected to be compared with bibliographic data obtained vs. SCE.

ing the presence of two species in equilibrium, [Ru₂(O₂CMe)(DPhF)₃(CO)]⁺ and [Ru₂(O₂CMe)(DPhF)₃(BF₄)(CO)], as described previously for similar compounds in the presence of BF₄[−] in high concentration [15]. The complex [Ru₂(O₂CMe)(DPhF)₃(CO)]⁺ is expected to be more difficult to oxidize and easier to reduce than [Ru₂(O₂CMe)(DPhF)₃(BF₄)(CO)]. Accordingly, the increase of electrolyte concentration (NBu₄BF₄) reduces the intensity of the cathodic process and the irreversible reduction that appear at higher potentials. The electrochemical data of **1** are also consistent with those described for Ru₂(DPhF)₄(CO) taking into account the different oxidation state of the diruthenium units in these complexes.

Complex **2** shows one quasi-reversible cathodic process and one anodic peak due to an irreversible reduction (Table 1). This behaviour is analogous to that observed for Ru₂Cl(O₂CMe)(DPhF)₃ [18] and Ru₂Cl(O₂CPh)(DPhF)₃ [15]. Surprisingly, the redox potentials of **2** and Ru₂(DPhF)₄(NO) are very similar in spite of the different formal oxidation state proposed for these complexes. These data confirm the difficulties to establish unequivocally the oxidation states in nitrosyl compounds and that the NO⁺–NO[−] formalism seem to be also artificial.

2.7. X-ray crystallography

Crystal data of complexes **1** · CH₂Cl₂ and **2** · CH₂Cl₂ are given in Table 2. Selected geometric parameters of the compounds are provided in Table 3.

1 · CH₂Cl₂ and **2** · CH₂Cl₂ are isomorphous compounds whose only constitutional difference is the atom linked at the axial position of the diruthenium moiety, being carbon in **1** · CH₂Cl₂ and nitrogen in **2** · CH₂Cl₂. Their molecular structures are illustrated in Figs. 2 and 3, respectively. Both complexes are constituted by eclipsed paddlewheel species (Table 3) with three diphenylformamidinate and one acetate ligands occupying the equatorial positions of the dimetallic units. An important feature of these structures is the long Ru–Ru bond distances: 2.4502(9) and 2.4152(7) Å for **1** · CH₂Cl₂ and **2** · CH₂Cl₂, respectively, although several Ru₂⁵⁺ [12,23] and Ru₂⁴⁺ [9,11,24] complexes with *d*(Ru–Ru) > 2.40 Å have been reported. In particular, the related complex Ru₂(DPhF)₄(CO) [11] has a very long Ru–Ru bond distance (2.5544 Å). This diruthenium(II) complex has shorter Ru–CO [1.913(10) Å] and longer C–O

[1.148(11) Å] bonds than **1** · CH₂Cl₂. These significant differences can be attributed to a higher back-donation in Ru₂(DPhF)₄(CO), richer in electron density than **1** · CH₂Cl₂. The same explanation could be inferred in the comparison of Ru₂(DPhF)₄(NO) [10] and **2** · CH₂Cl₂. However, the measurements of **2** · CH₂Cl₂ are quite similar to those of Ru₂(DPhF)₄(NO) [10], despite the latter compound has been claimed as Ru₂³⁺ species and contains a fourth formamidinate group instead of the less donor acetate ligand (Table 3). The Ru–N–O angle in **2** · CH₂Cl₂ is closer to linearity [174.6(6)°] than in Ru₂Cl(Fap)₄(NO), 155.8(6)° [9], that has been formulated as Ru₂⁴⁺(NO⁺) complex.

Table 2
Crystallographic data for **1** · CH₂Cl₂ and **2** · CH₂Cl₂

	1 · CH ₂ Cl ₂	2 · CH ₂ Cl ₂
Empirical formula	C ₄₃ H ₃₈ BCl ₂ F ₄ N ₆ O ₃ Ru ₂	C ₄₂ H ₃₈ BCl ₂ F ₄ N ₇ O ₃ Ru ₂
Formula weight	1046.64	1048.64
Crystal size (mm ³)	0.15 × 0.18 × 0.19	0.17 × 0.23 × 0.26
Crystal system	Triclinic	Triclinic
Space group	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$
<i>a</i> (Å)	11.7603(8)	11.7391(8)
<i>b</i> (Å)	12.2951(8)	12.2741(9)
<i>c</i> (Å)	17.0903(11)	17.0382(12)
α (°)	105.4790(10)	105.4200(10)
β (°)	90.4370(10)	90.2010(10)
γ (°)	111.2650(10)	111.3240(10)
Volume (Å ³)	2204.3(3)	2190.8(3)
<i>Z</i>	2	2
ρ_{calc} (g cm ^{−3})	1.577	1.590
μ (mm ^{−1})	0.869	0.875
<i>F</i> (000)	1050	1052
θ Range (°)	1.86–23.28	1.25–27.00
Index ranges	−13 ≤ <i>h</i> ≤ 10, −13 ≤ <i>k</i> ≤ 13, −18 ≤ <i>l</i> ≤ 17	−14 ≤ <i>h</i> ≤ 14, −15 ≤ <i>k</i> ≤ 10, −20 ≤ <i>l</i> ≤ 21
Collected reflections	9883	13,318
Independent reflections [<i>R</i> _{int}]	6274 [0.0278]	9265 [0.0279]
Completeness (%) to θ max (°)	98.9–23.28	96.9–27.00
Data/restraints/parameters	6274/6/515	9265/4/500
<i>R</i> ₁	0.0722	0.0648
<i>wR</i> ₂ (all data)	0.2213	0.2207
Largest difference in peak/hole (e Å ^{−3})	2.225/−3.473	2.216/−2.481

Table 3
Selected bond distances (Å) and angles (°) for **1** · CH₂Cl₂ and **2** · CH₂Cl₂

	1 · CH ₂ Cl ₂	2 · CH ₂ Cl ₂	Ru ₂ (DPhF) ₄ (CO) [11]	Ru ₂ (DPhF) ₄ (NO) [10]
Ru(1)–Ru(2)	2.4502(9)	2.4152(7)	2.5544(8)	2.4444(13)
Ru(1)–L _{ax.}	2.033(11)	1.834(6)	1.913(10)	1.809(11)
X–O (L _{ax.})	1.105(12)	1.148(8)	1.148(11)	1.142(12)
Ru(1)–O(1)	2.089(6)	2.088(5)		
Ru(2)–O(2)	2.061(6)	2.084(4)		
Ru(1)–N _{eq.} (av.)	2.037(12)	2.062(9)	2.069(3)	2.044
Ru(2)–N _{eq.} (av.)	1.997(12)	1.981(9)	2.028(3)	
Ru(2)–Ru(1)–L _{ax.}	176.0(3)	176.74(18)	180	180
Ru(1)–X _{ax.} –O(3)	177.3(9)	174.6(6)	180	180
O(1)–Ru(1)–Ru(2)–O(2)	–0.7(2)	0.87(17)		

Selected bond distances and angles for Ru₂(DPhF)₄(CO) and Ru₂(DPhF)₄(NO) are given for comparison.

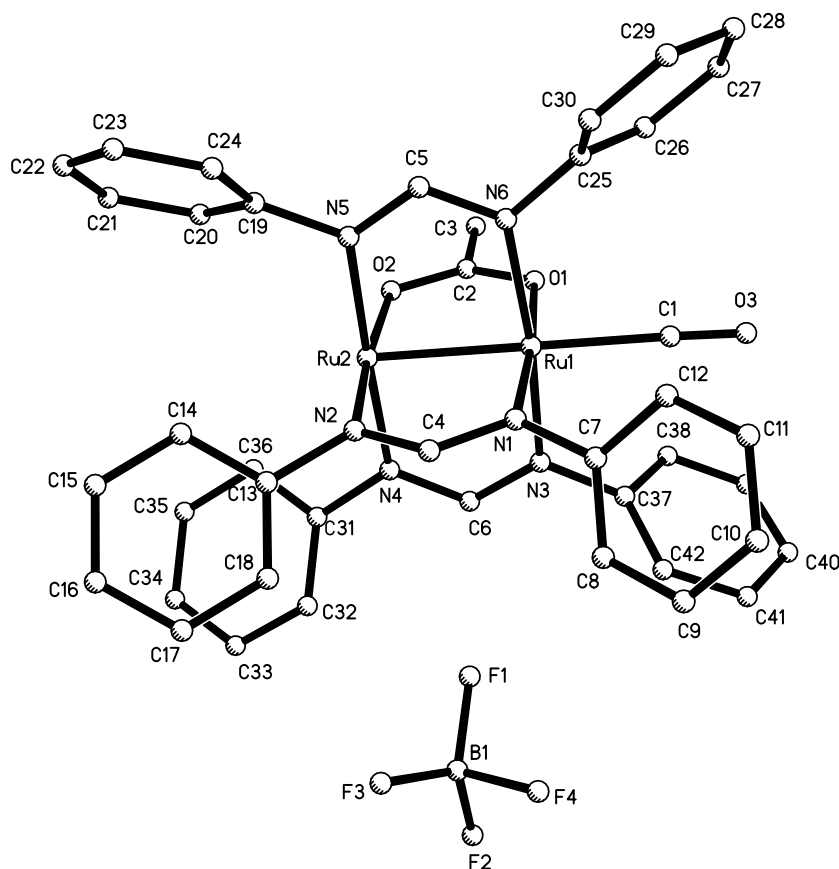


Fig. 2. PLUTO view of [Ru₂(O₂CMe)(DPhF)₃(CO)](BF₄) · CH₂Cl₂ (**1** · CH₂Cl₂). Crystallization solvent molecule and hydrogen atoms are omitted for clarity.

3. Conclusions

In this work, we have presented the first example of a Ru₂⁵⁺ carbonyl complex isolated and structurally characterized, **1** · CH₂Cl₂, which is air stable in the solid state and in solution. This Ru₂⁵⁺ compound completes the series of Ru₂²⁺, Ru₂³⁺, and Ru₂⁴⁺ carbonyl derivatives. The isomorphous compound **2** · CH₂Cl₂ can be described as a Ru₂⁴⁺(NO⁺) low spin complex taking into account its diamagnetism, IR and visible spectra, and its crystal structure. The higher basicity of CN[–] with respect to NO⁺ and CO

combined with the presence of a carboxylate bridging ligand may be the reason why it was not possible to isolate the cyanide derivative.

4. Experimental

4.1. Materials and equipment

All reactions were carried out under nitrogen atmosphere by using conventional Schlenk techniques and dried solvents. Subsequent manipulations were carried out in

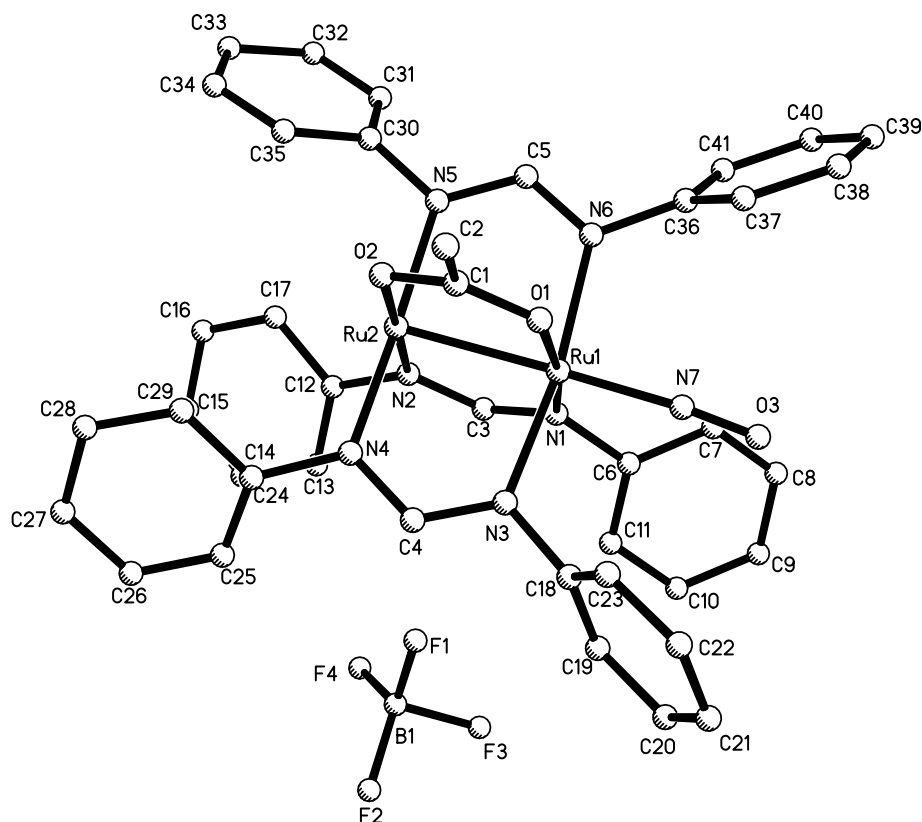


Fig. 3. PLUTO view of $[\text{Ru}_2(\text{O}_2\text{CMe})(\text{DPhF})_3(\text{NO})](\text{BF}_4) \cdot \text{CH}_2\text{Cl}_2$ ($\mathbf{2} \cdot \text{CH}_2\text{Cl}_2$). Crystallization solvent molecule and hydrogen atoms are omitted for clarity.

open air. Chemicals were purchased from commercial sources and used without further purification. $\text{Ru}_2\text{Cl}(\text{O}_2\text{CMe})(\text{DPhF})_3$ [18] and $[\text{Ru}_2(\text{O}_2\text{CMe})(\text{DPhF})_3(\text{H}_2\text{O})]\text{BF}_4 \cdot 0.5\text{CH}_2\text{Cl}_2$ [19] were prepared by following published procedures. Elemental analyses were done by the Microanalytical Service of the Complutense University of Madrid. IR spectra were obtained with a FT Midac prospect spectrophotometer using KBr pellets. Electronic spectra of the complexes in dichloromethane solution ($\sim 10^{-4}$ M) and in the solid state (Nujol mulls) were acquired on a Cary 5G spectrophotometer. Mass spectra were recorded on a Bruker Esquire-LC with Electrospray Ionization. Nominal molecular masses and distribution isotopic of all peaks were calculated with the MASAS [25] computer program, using a polynomial expansion based on natural abundances of the isotopes. Variable-temperature magnetic susceptibility measurements were performed on a Quantum Design MPMSXL SQUID magnetometer. All data were corrected for the diamagnetic contribution to the susceptibility of both the sample holder and the compound. Molar diamagnetic corrections were calculated on the basis of Pascal's constants. The NMR spectra of $\mathbf{2}$ in CD_2Cl_2 solution were acquired on a Bruker Avance DPX 300 MHz in the NMR Service of the Complutense University of Madrid. Electrochemical measurements were done using a MicroAutolab Type III potentiostat, with the general-purpose electrochemical system (GPES) (EcoChemie

B.V.) electrochemical software. A three-electrode system was used and consisted of a glassy carbon disk working electrode, a platinum wire counter electrode, and a Ag/AgCl reference electrode. The experiments were performed at room temperature under a nitrogen atmosphere, in dichloromethane solutions that contained 0.1 M NBu_4BF_4 as the supporting electrolyte, with a scan rate of 100 mV s^{-1} . Under our experimental conditions, the oxidation of ferrocene was located at $E_{1/2} = +0.625 \text{ V}$.

4.2. Synthesis of $[\text{Ru}_2(\text{O}_2\text{CMe})(\text{DPhF})_3(\text{CO})](\text{BF}_4) \cdot \text{CH}_2\text{Cl}_2$ ($\mathbf{1} \cdot \text{CH}_2\text{Cl}_2$) and $[\text{Ru}_2(\text{O}_2\text{CMe})(\text{DPhF})_3(\text{CO})](\text{BF}_4) \cdot \text{THF}$ ($\mathbf{1} \cdot \text{THF}$)

A solution of $[\text{Ru}_2(\text{O}_2\text{CMe})(\text{DPhF})_3(\text{H}_2\text{O})](\text{BF}_4) \cdot 0.5\text{CH}_2\text{Cl}_2$ (0.1040 g, 0.105 mmol) in freshly distilled CH_2Cl_2 (10 mL) was bubbled with CO for 1 h at room temperature until all the solvent was gone and the solid was dried. The yield of $\mathbf{1} \cdot \text{CH}_2\text{Cl}_2$ was quantitative. Anal. Calc. for $\text{C}_{43}\text{H}_{38}\text{BCl}_2\text{F}_4\text{N}_6\text{O}_3\text{Ru}_2$: C, 49.34; H, 3.66; N, 8.03. Found: C, 49.32; H, 3.58; N, 7.90%. IR (KBr): ν (cm^{-1}) (intensity): 3058 (w), 2016 (vs), 1590 (m), 1530 (s), 1486 (vs), 1438 (m), 1316 (m), 1306 (m), 1212 (vs), 1068 (s), 1024 (s), 999 (m), 939 (m), 781 (m), 768 (s), 759 (s), 737 (m), 695 (s), 535 (w), 455 (m), 436 (m). Visible (Nujol): λ (nm) 390sh, 490sh, 587, 710sh, 860sh. Visible (CH_2Cl_2): λ (nm) 390sh, 485sh, 584, 650sh, 815sh. MS-ESI⁺ (CHCl_3):

m/z 848 ($M^+ - CO$, 100%). μ_{eff} at r.t. (μ_{B}): 2.03. Crystals of **1** · CH_2Cl_2 suitable for X-ray analysis were obtained by diffusion of hexane on a solution of the compound in CH_2Cl_2 .

Compound **1** · THF was obtained when THF was used instead of CH_2Cl_2 in the crystallization process. Anal. Calc. for $\text{C}_{46}\text{H}_{44}\text{BF}_4\text{N}_6\text{O}_4\text{Ru}_2$: C, 53.44; H, 4.29; N, 8.13. Found: C, 53.46; H, 4.43; N, 7.92%. IR (KBr): ν (cm^{-1}) (intensity): 3059 (w), 2024 (vs), 1591 (m), 1532 (s), 1487 (vs), 1437 (m), 1316 (s), 1212 (vs), 1065 (vs), 1025 (s), 999 (m), 939 (m), 780 (m), 759 (s), 695 (s), 535 (w), 453 (m), 436 (m). μ_{eff} at r.t. (μ_{B}): 2.24.

4.3. Synthesis of $[\text{Ru}_2(\text{O}_2\text{CMe})(\text{DPhF})_3(\text{NO})](\text{BF}_4) \cdot \text{CH}_2\text{Cl}_2$ (**2** · CH_2Cl_2)

To a solution of $\text{Ru}_2\text{Cl}(\text{O}_2\text{CMe})(\text{DPhF})_3$ (0.2003 g, 0.227 mmol) in freshly distilled THF (15 mL) was added NOBF_4 (0.0265 g, 0.227 mmol) in THF (10 mL). After 2 h of stirring, the volatile components were removed and the solid was recrystallized from CH_2Cl_2 /hexane. Yield: 0.1619 (81%). Anal. Calc. for $\text{C}_{42}\text{H}_{38}\text{BCl}_2\text{F}_4\text{N}_7\text{O}_3\text{Ru}_2$: C, 48.11; H, 3.65; N, 9.35. Found: C, 48.09; H, 3.61; N, 9.32%. IR (KBr): ν (cm^{-1}) (intensity): 3059 (w), 1771 (vs), 1590 (m), 1526 (s), 1487 (vs), 1438 (m), 1309 (m), 1210 (vs), 1083 (s), 1028 (m), 940 (m), 780 (m), 760 (s), 695 (s), 452 (m), 436 (m). Visible (Nujol): λ (nm) 504, 690, 850sh. Visible (CH_2Cl_2): λ (nm) 411, 494, 665. MS-ESI⁺ (CHCl_3): m/z 878 (M^+ , 100%). ¹H NMR (CD_2Cl_2 , 23 °C) δ : 9.22 (s, 2H, NCHN), 8.62 (s, 1H, NCHN), 7.25–7.45 (m, 15H), 7.15 (t, 1H), 7.08 (m, 4H), 7.02 (t, 2H), 6.92 (m, 4H), 6.78 (m, 2H), 6.42 (d, 2H), 2.52 (s, 3H, CH_3). ¹³C{¹H} NMR (CD_2Cl_2 , 24 °C) δ : 190.37 (CO_2), 173.97, 172.85 (NCHN), 154.74, 154.68, 154.47, 153.65, 130.90, 130.23, 129.92, 129.83, 128.32, 128.28, 127.61, 127.14, 123.25, 123.15, 122.83, 122.01 (NPh), 24.14 (CH_3). Crystals of **2** · CH_2Cl_2 suitable for X-ray analysis were collected after a slow diffusion of hexane over a dichloromethane solution of the compound.

4.4. X-ray structure determinations

Data collection for all compounds were carried out at room temperature on a Bruker Smart CCD diffractometer using graphite-monochromated Mo $K\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) operating at 50 kV and 10 mA. In all cases, the data were collected over a hemisphere of the reciprocal space by combination of three exposure sets, each exposure was of 30 and 20 s for **1** and **2**, respectively, and covered 0.3° in ω . The first 50 frames were recollected at the end of the data collection to monitor crystal decay. A summary of the fundamental crystal and refinement data are given in Table 2.

The structures were solved by direct methods and refined by full-matrix least-square procedures on F^2 [26]. All non-hydrogen atoms were refined anisotropically, with some exceptions. Thus, in **1** · CH_2Cl_2 only coordinates

were refined for the fluorine atoms of BF_4 and the chlorine atoms of CH_2Cl_2 . In **2** · CH_2Cl_2 , only coordinates were refined for the fluorine atoms of BF_4 , while the chlorine atoms of CH_2Cl_2 were located in a Fourier synthesis, included and fixed. In all cases, hydrogen atoms were included in calculated positions and refined riding on the respective carbon atoms.

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Appendix A. Supplementary material

CCDC 663295 and 663296 contain the supplementary crystallographic data for **1** · CH_2Cl_2 and **2** · CH_2Cl_2 . These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.jorganchem.2007.11.025](https://doi.org/10.1016/j.jorganchem.2007.11.025).

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