

Dinuclear ruthenium sawhorse-type complexes containing bridging ligands with ferrocenyl substituents in *endo/endo*, *endo/exo* and *exo/exo* orientations

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Abstract

The dinuclear ruthenium complexes $\text{Ru}_2(\text{CO})_4(\text{OCC}_5\text{H}_4\text{FeC}_5\text{H}_5)_2\text{L}_2$ ($\text{L} = \text{NC}_5\text{H}_5$: **1**, $\text{L} = \text{PPh}_3$: **2**) have been synthesized from $\text{Ru}_3(\text{CO})_{12}$, ferrocene carboxylic acid and pyridine or triphenylphosphine, respectively. The single-crystal X-ray structure analysis reveals for **1** and **2** a $\text{Ru}_2(\text{CO})_4$ sawhorse backbone with the two ferrocenyl substituents of the two carboxylato bridges being *endo/exo* with respect to each other in the solid state. With the new pyridine derivative $\text{NC}_5\text{H}_4\text{OCC}_5\text{H}_4\text{FeC}_5\text{H}_5$ (4-ferrocenoyl pyridine) (**3**) as axial ligand, the complex $\text{Ru}_2(\text{CO})_4(\text{OCC}_5\text{H}_4\text{FeC}_5\text{H}_5)_2(\text{NC}_5\text{H}_4\text{OCC}_5\text{H}_4\text{FeC}_5\text{H}_5)_2$ (**4**) was obtained, the single crystal X-ray structure analysis showing an *exo/exo* orientation of the two carboxylato bridges in the solid state. The *endo/endo* orientation is found in the solid-state structure of $\text{Ru}_2(\text{CO})_4(\text{HNOCC}_5\text{H}_4\text{FeC}_5\text{H}_5)_2(\text{PPh}_3)_2$ (**5**), the two OCNH bridges being transoid with respect to each other; this complex is accessible from $\text{Ru}_3(\text{CO})_{12}$, ferrocenamide and triphenylphosphine.

Keywords: Carbonyl ligands; Carboxylato bridges; Carbamido bridges; Ferrocenyl substituents; Dinuclear complexes; Ruthenium

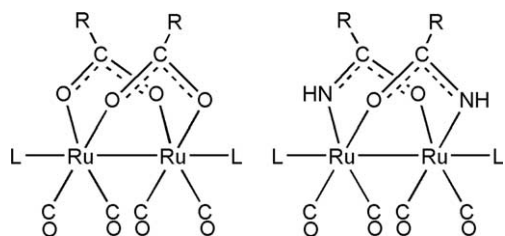
1. Introduction

Sawhorse-type ruthenium complexes are well-known since 1969, when Lewis and co-workers [1] reported the formation of $[\text{Ru}_2(\text{CO})_4(\text{OOCR})_2]_n$ polymers by refluxing $\text{Ru}_3(\text{CO})_{12}$ in the corresponding carboxylic acid and the depolymerization of these materials in coordinating solvents to give dinuclear complexes of the type $\text{Ru}_2(\text{CO})_4(\text{OOCR})_2\text{L}_2$, L being acetonitrile, pyridine or another two-electron donor. These dinuclear complexes have been shown later, by a single-crystal X-ray structure analysis of $\text{Ru}_2(\text{CO})_4(\text{OOCBu}^n)_2(\text{PBu}_3^t)_2$ to have a $\text{Ru}_2(\text{CO})_4$ backbone in a sawhorse-type arrangement with two μ_2 - η^2 -carb-

oxylato bridges and two axial (phosphine) ligands [2]. In the meantime, a considerable number of such sawhorse-type diruthenium complexes with carboxylato [3], carboxamido [4], phosphinato [5], sulfonato [6], pyrazolato [7] or oximato [8] bridges have been synthesized and used in catalysis [8,9] or for the assembly of mesomorphic materials [10] (see Scheme 1).

Herein, we report the synthesis and molecular structure of new $\text{Ru}_2(\text{CO})_4$ sawhorse-type complexes containing ferrocenyl substituents in the carboxylato or carboxamido bridges and in one case also in the axial ligand: $\text{Ru}_2(\text{CO})_4(\text{OCC}_5\text{H}_4\text{FeC}_5\text{H}_5)_2\text{L}_2$ ($\text{L} = \text{NC}_5\text{H}_5$: **1**, $\text{L} = \text{PPh}_3$: **2**, $\text{L} = \text{NC}_5\text{H}_4\text{OCC}_5\text{H}_4\text{FeC}_5\text{H}_5$: **4**) and $\text{Ru}_2(\text{CO})_4(\text{HNOCC}_5\text{H}_4\text{FeC}_5\text{H}_5)_2(\text{PPh}_3)_2$ (**5**), obtained from $\text{Ru}_3(\text{CO})_{12}$, ferrocene carboxylic acid and pyridine, triphenylphosphine or 4-ferrocenoyl pyridine (**3**) and from $\text{Ru}_3(\text{CO})_{12}$, ferrocenamide and triphenylphosphine, respectively.

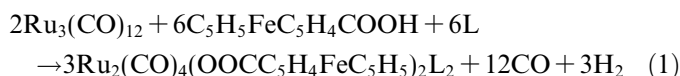
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Scheme 1.

2. Results and discussion

Dodecacarbonyltriruthenium reacts with ferrocene carboxylic acid in refluxing tetrahydrofuran to give, in the presence of pyridine or triphenylphosphine, the dinuclear complexes $\text{Ru}_2(\text{CO})_4(\text{OCC}_5\text{H}_4\text{FeC}_5\text{H}_5)_2\text{L}_2$ ($\text{L} = \text{NC}_5\text{H}_5$: **1**, $\text{L} = \text{PPh}_3$: **2**) in good yields. Compounds **1** and **2** are air-stable brown-yellowish crystalline materials, which have been unambiguously characterized by their IR, NMR and MS data (see Scheme 2).



The single-crystal X-ray structure analyses of **1** and **2** reveal in both cases the typical $\text{Ru}_2(\text{CO})_4$ sawhorse backbone with two ferrocenyl carboxylato bridges, the Ru–Ru distances (**1**: 2.6854(5) Å, **2**: 2.7330(5) Å) being in the range of a ruthenium–ruthenium single bond, as it was also observed in analogous complexes [2,3b,3d,11]. The OCO bond angles of the two carboxylato bridges (**1**: 125.7(4) and 124.6(4)°, **2**: 125.5(3)°) differ only slightly from those observed in other $\text{Ru}_2(\text{CO})_4(\text{OOCR})_2\text{L}_2$ complexes [2,3b,

3d,11]. In the solid state, the two ferrocenyl substituents at the two carboxylato bridges in **1** and **2** adopt an *endo/endo* orientation.

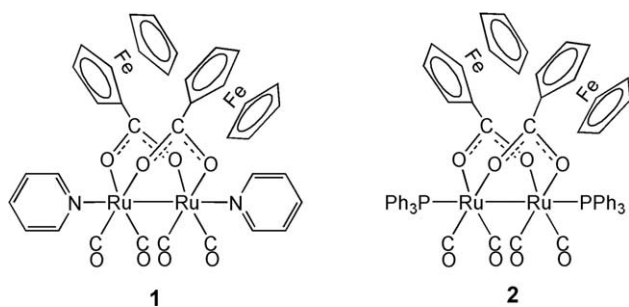
In order to introduce ferrocenyl substituents not only in the carboxylato bridges, but also in the axial ligand positions of these sawhorse-type complexes, we synthesized 4-ferrocenyl pyridine (**3**), a new ligand accessible from ferrocene carboxylic acid and 4-hydroxypyridine in the presence of *N,N'*-dicyclohexylcarbodiimide, 4-pyrrolidino-pyridine and dimethylaminopyridine as condensation auxiliaries [12]. Compound **3** is an orange air-stable crystalline substance, the single-crystal X-ray analysis of which shows the expected molecular structure (see Scheme 3).

The reaction of $\text{Ru}_3(\text{CO})_{12}$ with ferrocene carboxylic acid in refluxing THF gives, in the presence of ligand **3**, according to Eq. (1), the dinuclear complex $\text{Ru}_2(\text{CO})_4(\text{OCC}_5\text{H}_4\text{FeC}_5\text{H}_5)_2(\text{NC}_5\text{H}_4\text{OCC}_5\text{H}_4\text{FeC}_5\text{H}_5)_2$ (**4**), isolated in the same manner as **1** and **2**. The solid state molecular structure of **4** shows the same $\text{Ru}_2(\text{CO})_4$ sawhorse backbone as **1** and **2** (Ru–Ru: 2.6850(7) Å) (see Scheme 4).

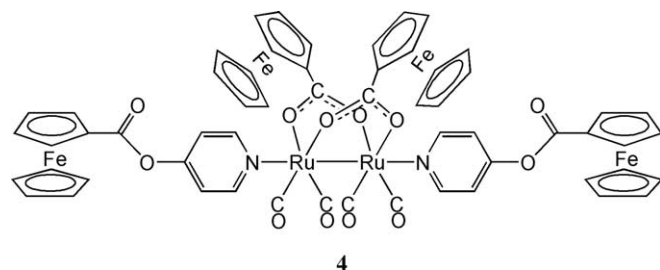
However, while the two ferrocenyl substituents in the two axial pyridine ligands are *transoid* with respect to each other, the orientation of the two ferrocenyl substituents in the two carboxylato bridges is *exo/exo*, both being oriented outwards, in contrast to the *exo/endo* orientation found in **1** and **2**.

Moreover, in the solid state, two molecules of chloroform per molecule of **4** are found in the crystal, one of them being encapsulated between the two ferrocenyl substituents of the bridging ligands, see Fig. 4. The distance between the centroid of the cyclopentadienyl and the hydrogen atom of the chloroform molecule is only 2.47 Å.

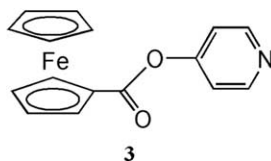
The missing *endo/endo* orientation of the two ferrocenyl substituents in the two bridging ligands was finally found in



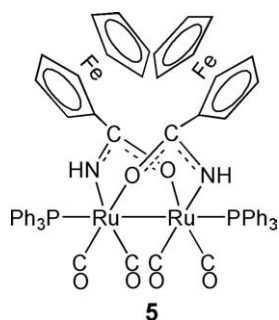
Scheme 2.



Scheme 4.



Scheme 3.



Scheme 5.

the solid state structure of the carboxamido derivative $\text{Ru}_2(\text{CO})_4(\text{HNOCC}_5\text{H}_4\text{FeC}_5\text{H}_5)_2(\text{PPh}_3)_2$ (**5**), accessible from $\text{Ru}_3(\text{CO})_{12}$, ferrocenamide and triphenylphosphine (see Scheme 5). However, **5** is not very stable: although it can be isolated in the solid state, it is very hygroscopic and decomposes quickly in solution, even under inert atmosphere.

In conclusion, we have synthesized and structurally characterized four new $\text{Ru}_2(\text{CO})_4$ sawhorse-type complexes containing μ_2 - η^2 -ferrocene carboxylato or carbamido ligands as well as a new ferrocenyl pyridine derivative. All possible conformations (*endo/endo*, *exo/exo* and *endo/exo*) of the two ferrocenyl substituents in the bridging ligands have been observed in the solid state.

3. Experimental

3.1. General

All manipulations were carried out by routine under nitrogen atmosphere. De-ionized water and organic solvents were degassed and saturated with nitrogen prior to use. All reagents were purchased either from Aldrich or Fluka and used as received. NMR spectra were recorded on a Bruker 400 MHz spectrometer. IR spectra were recorded on a Perkin-Elmer 1720X FT-IR spectrometer (4000 – 400 cm^{-1}). Microanalyses were performed by the Laboratory of Pharmaceutical Chemistry, University of Geneva (Switzerland). Electro-spray mass spectra were obtained in positive-ion mode with an LCQ Finnigan mass spectrometer. Dodecacarbonyltriruthenium [13] and ferrocenamide [14] was prepared according to published methods.

3.2. General method for the preparation of complexes **1**, **2** and **4**

A solution of $\text{Ru}_3(\text{CO})_{12}$ (100 mg, 0.16 mmol) and ferrocene carboxylic acid (108 mg, 0.47 mmol) in dry tetrahydrofuran (25 ml) was heated at 120° C in a pressure Schlenk tube for 12 h. Then the solvent was evaporated to give an orange-brown residue which was dissolved in tetrahydrofuran and the appropriate ligand L (0.47 mmol) was added. The solution was stirred at room temperature

for 2 h, the solution was evaporated and the product isolated from the residue by crystallization from a tetrahydrofuran/hexane mixture. In order to improve the purity, the raw product was subjected to a thin-layer chromatography on silica gel using dichloromethane as eluent and obtained as yellow-brown powder.

$\text{Ru}_2(\text{CO})_4(\text{OCC}_5\text{H}_4\text{FeC}_5\text{H}_5)_2(\text{NC}_5\text{H}_5)_2$ (**1**): Yield: 84% (122 mg, 0.13 mmol). ^1H NMR (400 MHz, CDCl_3): δ = 8.92 (m, 4H), 7.94 (m, 2H), 7.54 (m, 4H), 4.60 (t, 4H), 4.20 (t, 4H), 4.08 (s, 10H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ = 197.32 (2C), 184.0 (4C), 152.40 (4C), 137.75 (2C), 125.10 (4C), 75.84 (2C), 70.62 (4C), 70.55 (4C), 69.96 (10C); IR (CaF_2 , THF): $\nu_{(\text{CO})}$ 2021 vs, 1969 m, 1938 vs, $\nu_{(\text{OCO})}$ 1559 s cm^{-1} ; ESI-MS: 904 $[\text{M} - \text{CO} + \text{H}^+]$, 825 $[\text{M} - \text{CO} - \text{NC}_5\text{H}_5 + \text{H}^+]$, 773 $[\text{M} - 2\{\text{NC}_5\text{H}_5\}]$; Anal. Calc. for $\text{C}_{36}\text{H}_{28}\text{Fe}_2\text{N}_2\text{O}_8\text{Ru}_2$ (930.45), C, 46.47; H, 3.03; N, 3.01. Found: C, 46.87; H, 3.27; N, 2.91%.

$\text{Ru}_2(\text{CO})_4(\text{OCC}_5\text{H}_4\text{FeC}_5\text{H}_5)_2(\text{PPh}_3)_2$ (**2**): Yield: 64% (133 mg, 0.10 mmol). ^1H NMR (400 MHz, CDCl_3): δ = 7.76–7.72 ppm (m, 12H), 7.50–7.48 (m, 18H), 4.14 (t, 4H), 4.08 (t, 4H), 3.94 (s, 10H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ = 206.08 ppm (2C), 186.2 (4C), 134.25 (18C), 128.83 (18C), 75.88 (2C), 70.74 (4C), 70.60 (4C), 69.90 (10C); $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, CDCl_3): δ = 14.70 ppm; IR (CaF_2 , THF): $\nu_{(\text{CO})}$ 2022 vs, 1977 m, 1951 vs, $\nu_{(\text{OCO})}$ 1552 s cm^{-1} ; ESI-MS: 1333 $[\text{M} + 2\text{H}_2\text{O}]$, 1315 $[\text{M} + \text{H}_2\text{O}]$; Anal. Calc. for $\text{C}_{62}\text{H}_{48}\text{Fe}_2\text{O}_8\text{P}_2\text{Ru}_2$ (1296.84), C, 57.42; H, 3.99. Found: C, 57.23; H, 3.99%.

$\text{Ru}_2(\text{CO})_4(\text{OCC}_5\text{H}_4\text{FeC}_5\text{H}_5)_2(\text{NC}_5\text{H}_4\text{OCC}_5\text{H}_4\text{FeC}_5\text{H}_5)_2$ (**4**): Yield: 81% (177 mg, 0.13 mmol). ^1H NMR (400 MHz, CDCl_3): δ = 8.95 ppm (d, 4H), 7.48 (d, 4H), 5.05 (t, 4H), 4.63 (m, 8H), 4.38 (s, 10H), 4.22 (m, 4H), 4.12 (s, 10H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ = 205.00 ppm (2C), 184.11 (4C), 169.50 (2C), 159.16 (2C), 153.89 (4C), 118.15 (4C), 87.8 (2C), 75.5 (2C), 73.12 (4C), 71.24 (4C), 70.60 (18C), 70.01 (10C); IR (CaF_2 , THF): $\nu_{(\text{CO})}$ 2021 vs, 1969 m, 1939 vs, $\nu_{(\text{OCO})}$ 1560 s cm^{-1} ; ESI-MS: 1389 $[\text{M} + 2\text{H}^+]$; 1360 $[\text{M} - \text{CO} + \text{H}^+]$; 1159 $[\text{M} - (\text{C}_5\text{H}_5\text{FeC}_5\text{H}_4\text{-CO}_2)]$; 1104 $[\text{M} - (\text{C}_5\text{H}_5\text{FeC}_5\text{H}_4\text{-CO}_2)\text{-CO}]$; 1080 $[\text{M} - (\text{C}_5\text{H}_5\text{FeC}_5\text{H}_4\text{-CO}_2\text{-C}_5\text{H}_4\text{N})]$; 971 $[\text{M} - (\text{C}_5\text{H}_5\text{FeC}_5\text{H}_4\text{-CO}_2\text{-C}_5\text{H}_4\text{N})\text{-4CO}]$; 773 $[\text{M} - 2(\text{C}_5\text{H}_5\text{FeC}_5\text{H}_4\text{-CO}_2\text{-C}_5\text{H}_4\text{N})]$; Anal. Calc. for $\text{C}_{58}\text{H}_{44}\text{Fe}_4\text{N}_2\text{O}_{12}\text{Ru}_2$ (1386.5), C, 50.24; H, 3.20. Found: C, 49.60; H, 3.04% ($\text{C}_{58}\text{H}_{44}\text{Fe}_4\text{N}_2\text{O}_{12}\text{Ru}_2 \cdot \frac{1}{8}\text{C}_4\text{H}_8\text{O}$).

3.3. Preparation of 4-ferrocenyl pyridine, $\text{NC}_5\text{H}_4\text{OCC}_5\text{H}_4\text{FeC}_5\text{H}_5$ (**3**)

In a pressure Schlenk tube was introduced ferrocene carboxylic acid (500 mg, 2.17 mmol), *N,N'*-dicyclohexylcarbodiimide (688 mg, 3.34 mmol), dimethylaminopyridine (204 mg, 1.67 mmol), 4-pyrrolidinopyridine (124 mg, 0.83 mmol) and hydroxypyridine (159 mg, 1.67 mmol) in anhydrous dichloromethane (30 ml). The solution was stirred under nitrogen at room temperature for 36 h without

Table 1
Crystallographic and selected experimental data of compounds **1**, **2**, **3**, **4**, and **5**

	1 · THF	2	3	4 · 2 CHCl ₃	5
Chemical formula	C ₄₀ H ₃₆ Fe ₂ N ₂ O ₉ Ru ₂	C ₆₂ H ₄₈ Fe ₂ O ₈ P ₂ Ru ₂	C ₁₆ H ₁₃ FeNO ₂	C ₆₀ H ₄₆ Cl ₆ Fe ₄ N ₂ O ₁₂ Ru ₂	C ₆₂ H ₅₀ Fe ₂ N ₂ O ₆ P ₂ Ru ₂
Formula weight	1002.55	1296.78	307.12	1625.23	1294.82
Crystal system	monoclinic	monoclinic	triclinic	triclinic	trigonal
Space group	<i>P</i> 2 ₁	<i>P</i> 2 ₁ / <i>m</i>	<i>P</i> 1	<i>P</i> 1	<i>R</i> 3 <i>c</i>
Crystal colour and shape	orange block	orange block	orange plate	orange block	orange block
Crystal size	0.32 × 0.26 × 0.18	0.40 × 0.30 × 0.30	0.25 × 0.25 × 0.12	0.32 × 0.22 × 0.10	0.38 × 0.34 × 0.15
<i>a</i> (Å)	10.2754(8)	11.8573(8)	5.8020(10)	13.8596(12)	26.434(4)
<i>b</i> (Å)	17.0987(13)	17.8627(9)	10.242(2)	14.2649(12)	26.434(4)
<i>c</i> (Å)	11.1261(8)	12.6909(8)	11.288(2)	17.5106(15)	40.754(8)
α (°)	90	90	93.14(3)	113.829(10)	90
β (°)	106.540(9)	102.862(8)	103.98(3)	91.681(10)	90
γ (°)	90	90	97.93(3)	102.787(10)	120
<i>V</i> (Å ³)	1873.9(2)	2620.5(3)	642.0(2)	3060.8(5)	24662(7)
<i>Z</i>	2	2	2	2	18
<i>T</i> (K)	173(2)	173(2)	173(2)	173(2)	173(2)
<i>D</i> _{calc} (g cm ⁻³)	1.777	1.643	1.589	1.763	1.569
μ (mm ⁻¹)	1.609	1.227	1.173	1.729	1.172
Scan range (°)	3.82 < 2 θ < 51.84	4.0 < 2 θ < 51.88	4.04 < 2 θ < 52.24	4.04 < 2 θ < 52.0	4.3 < 2 θ < 51.96
Unique reflections	7241	5257	2353	11170	5031
Reflections used [<i>I</i> > 2 σ (<i>I</i>)]	6268	3588	1806	6475	3805
<i>R</i> _{int}	0.0483	0.0583	0.0438	0.0394	0.0363
Final <i>R</i> indices [<i>I</i> > 2 σ (<i>I</i>)]	0.0298, <i>wR</i> ₂ 0.0626	0.0268, <i>wR</i> ₂ 0.0520	0.0329, <i>wR</i> ₂ 0.0722	0.0515, <i>wR</i> ₂ 0.1253	0.0307, <i>wR</i> ₂ 0.0736
<i>R</i> indices (all data)	0.0377, <i>wR</i> ₂ 0.0641	0.0517, <i>wR</i> ₂ 0.0549	0.0496, <i>wR</i> ₂ 0.0781	0.0922, <i>wR</i> ₂ 0.1382	0.0468, <i>wR</i> ₂ 0.0812
Goodness-of-fit	0.948	0.839	0.937	0.889	0.918
Maximum, Minimum $\Delta\rho/e$ (Å ⁻³)	0.662, -0.957	0.522, -1.086	0.416, -0.816	1.772, -1.497	0.727, -0.709

light. Then the red solution was slowly filtered on Celite to eliminate the dicyclohexylurea. The product was obtained as an orange powder by column chromatography on silica gel using hexane/acetone (10:1) as eluent (265 mg, 0.86 mmol). Yield: 52%. ¹H NMR (400 MHz, CD₃OD): δ = 8.61 (dd, 2H), 7.40 (dd, 2H), 4.99 (t, 2H), 4.65 (t, 2H), 4.36 (s, 5H); IR (CaF₂, THF): 1742 cm⁻¹; ESI-MS: 308 [M + H⁺]; *Anal.* Calc. for C₁₆H₁₃FeNO₂(307.12) C, 62.57; H, 4.27; N, 4.56. Found: C, 62.52; H, 4.56; N, 4.36%.

3.4. Preparation of

*Ru*₂(CO)₄(HNOCC₅H₄FeC₅H₅)₂(PPh₃)₂ (**5**)

A solution of Ru₃(CO)₁₂ (200 mg, 0.31 mmol) and ferrocenamide (215 mg, 0.94 mmol) in dry tetrahydrofuran (25 ml) was heated at 120 °C in a pressure Schlenk tube for 12 h. Then the solvent was evaporated to give a brown residue which was dissolved in tetrahydrofuran and the triphenylphosphine (250 mg, 0.94 mmol) was added. The

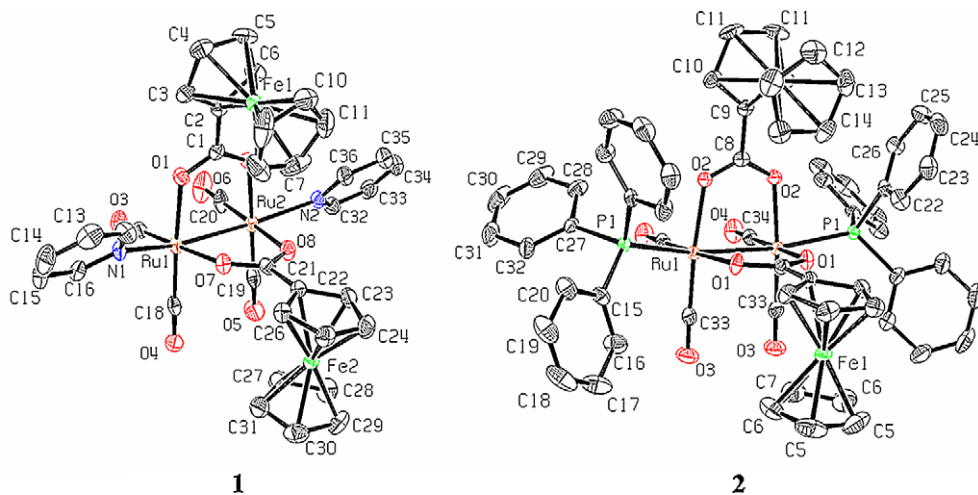


Fig. 1. Molecular structure of Ru₂(CO)₄(OCC₅H₄FeC₅H₅)₂L₂ (L = NC₅H₅: **1**, L = PPh₃: **2**), the hydrogen atoms, and in **1** the THF molecule, are omitted for clarity. Selected bond distances (Å), angles and torsion angles (°): (**1**) Ru1–Ru2 2.6854(5), Ru1–N1 2.221(3), Ru2–N2 2.228(4), Ru1–O1 2.107(3), Ru1–O7 2.143(3), Ru2–O2 2.136(3), Ru2–O8 2.125(3), O1–C1–O2 124.6(4), O7–C21–O8 125.7(4), N1–Ru1–Ru2–N2 12.1(5); (**2**) Ru1–Ru1ⁱ 2.7330(5), Ru1–P1 2.4462(7), Ru1–O1 2.125(2), Ru1–O2 2.124(2), O1–C1–O1ⁱ 125.5(3), O2–C8–O2ⁱ 126.4(4), (i = x, 1.5 – y, z).

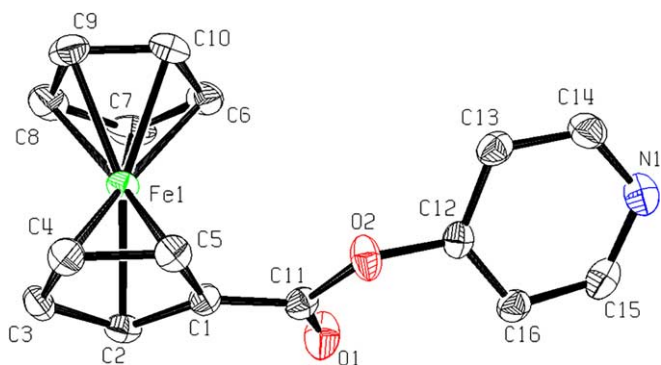


Fig. 2. Molecular structure of $\text{NC}_5\text{H}_4\text{OOC}_5\text{H}_4\text{FeC}_5\text{H}_5$ (**3**), hydrogen atoms are omitted for clarity. Selected bond distances (Å), angles and torsion angles (°): C11–O1 1.196(3), C11–O2 1.374(3), O2–C12 1.383(3), O1–C11–O2 124.0(2), C1–C11–O2–C12 $-170.9(2)$.

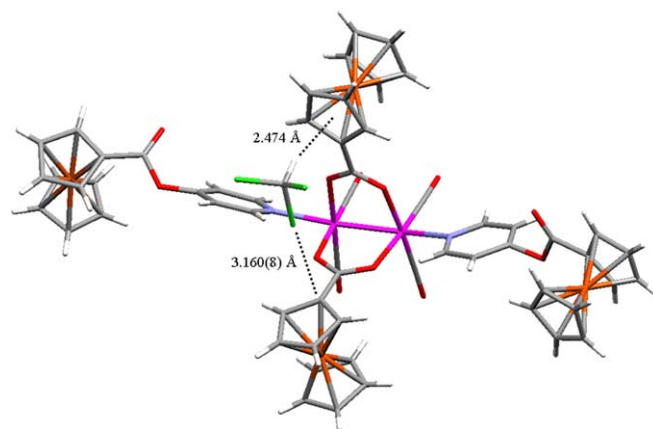


Fig. 4. Encapsulation of a CHCl_3 molecule between the two ferrocenyl substituents of the bridging ligands in **4**.

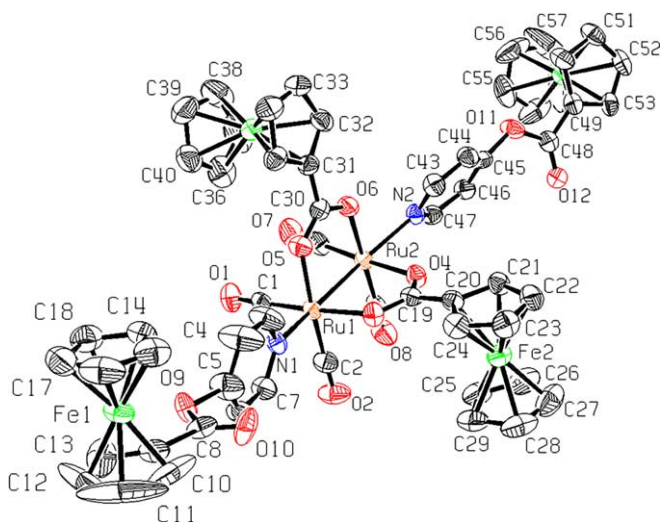


Fig. 3. Molecular structure of $\text{Ru}_2(\text{CO})_4(\text{OOC}_5\text{H}_4\text{FeC}_5\text{H}_5)_2(\text{NC}_5\text{H}_4\text{OOC}_5\text{H}_4\text{FeC}_5\text{H}_5)_2$ (**4**), the chloroform molecules and the hydrogen atoms are omitted for clarity. Selected bond distances (Å), angles and torsion angles: Ru1–Ru2 2.6850(7), Ru1–O3 2.123(4), Ru1–O5 2.120(4), Ru2–O4 2.104(4), Ru2–O6 2.112(4), Ru1–N1 2.253(4), Ru2–N2 2.210(5), O3–C19–O5 125.2(6), O5–C30–O6 125.7(5), N1–Ru1–Ru2–N2 8.9(6).

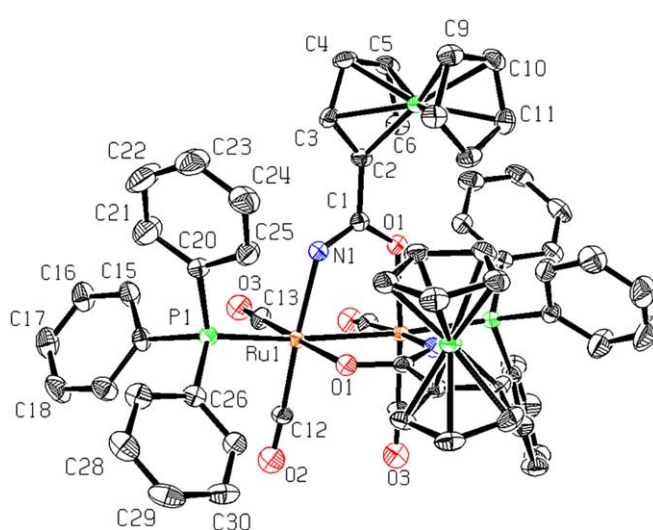


Fig. 5. Molecular structure of $\text{Ru}_2(\text{CO})_4(\text{HNOCC}_5\text{H}_4\text{FeC}_5\text{H}_5)_2(\text{PPh}_3)_2$ (**5**), the hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (°): Ru1–Ru1ⁱ 2.7697(6), Ru1–N1ⁱ 2.128(3), Ru1–O1 2.127(2), Ru1–P1 2.4133(9), O1–C1–N1 122.9(3).

solution was stirred at room temperature for 3 h, the solution was evaporated and the product isolated from the residue by crystallization from a chloroform/hexane mixture. In order to improve the purity, the raw product was subjected to a thin-layer chromatography on silica gel using a dichloromethane/hexane mixture (1:1) as eluent and obtained as yellow powder. Yield: 81% (327 mg, 0.25 mmol). ^1H NMR (400 MHz, CDCl_3): δ = 7.82–7.60 ppm (m, 12H), 7.59–7.43 (m, 18H), 3.97 (t, 4H), 3.88 (s, 10H), 3.83 (d, 2H), 3.66 (d, 2H); $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, CDCl_3): δ = 21.09 ppm; IR (CaF_2 , CH_2Cl_2): ν_{CO} 2011 vs, 1967 m, 1939 vs, ν_{OCNH} 1551 s cm^{-1} ; ESI–MS: 1296 $[\text{M} + \text{H}^+]$; Anal. Calc. for $\text{C}_{62}\text{H}_{50}\text{Fe}_2\text{N}_2\text{O}_6\text{P}_2\text{Ru}_2$ (1294.85), C, 57.51; H, 3.89; N, 2.16. Found: C, 55.73; H, 3.93; N, 1.99% ($\text{C}_{62}\text{H}_{50}\text{Fe}_2\text{N}_2\text{O}_6\text{P}_2\text{Ru}_2 \cdot 2\text{H}_2\text{O}$).

3.5. X-ray crystallography

Single-crystals of **1–5**, obtained by slow diffusion of hexane into a solution of the complex (THF: **1**, **2**; CHCl_3 : **3–5**), were mounted on a Stoe Image Plate Diffraction system equipped with a ϕ circle goniometer, using Mo $K\alpha$ graphite monochromated radiation ($\lambda = 0.71073$ Å) with ϕ range 0–200°, increment varying from 0.7° to 2.0°, $D_{\text{max}} - D_{\text{min}} = 12.45 - 0.81$ Å. The structures were solved by direct methods using the program SHELXS-97 [15]. The refinement and all further calculations were carried out using SHELXL-97 [16]. In all compounds the hydrogen atoms have been included in calculated positions and treated as riding atoms using the SHELXL default parameters. All non-H atoms were refined anisotropically, using weighted full-matrix least-square on F^2 . In **4**, one $-\text{OCO}-$ fragment of a carboxylate was found to be disorder over two positions and the partial

occupancy factor was fixed at 50:50. In **4**, the residual densities greater than $1 \text{ e } \text{\AA}^{-3}$ are located closed to the chloride atoms of the solvent molecules. Crystallographic details are summarized in Table 1. Figs. 1–3 and 5 were drawn with ORTEP [17] and Fig. 4 with MERCURY [18].

4. Supplementary material

CCDC-280633 **1** · THF, 280634 **2**, 280635 **3**, 280636 **4** · 2CHCl₃ and 280637 **5** contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, by e-mail: data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223 336033).

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