

Tetra- and hexanuclear cage molecules based on diruthenium tetracarbonyl sawhorse units: Synthesis and molecular structure of $[\{\text{Ru}_2(\text{CO})_4(\text{PPh}_3)_2\}_2(\text{O}_2\text{CCH}_2\text{CO}_2)_2]$ and $[\{\text{Ru}_2(\text{CO})_4(\text{PMe}_3)_2\}_3(\text{O}_2\text{CC}_6\text{H}_4\text{CO}_2)_3]$

Mathieu Auzias, Bruno Therrien, Georg Süss-Fink *

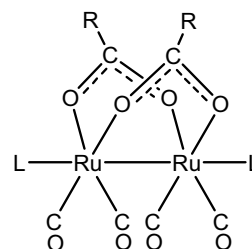
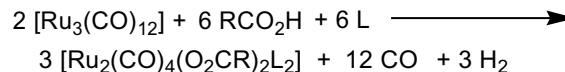
Institut de Chimie, Université de Neuchâtel, Case Postale 158, CH-2009 Neuchâtel, Switzerland

Abstract

The thermal reaction of $\text{Ru}_3(\text{CO})_{12}$ with malonic acid, followed by the addition of the corresponding ligand, yields the tetranuclear ruthenium complexes $[\{\text{Ru}_2(\text{CO})_4\text{L}_2\}_2(\text{O}_2\text{CCH}_2\text{CO}_2)_2]$ ($\text{L} = \text{PPh}_3$: **1**, $\text{L} = 3,5\text{-Me}_2\text{NC}_5\text{H}_3$: **2**), while the reaction of $\text{Ru}_3(\text{CO})_{12}$ with terephthalic acid, followed by the addition of the corresponding ligand, gives rise to the formation of the hexanuclear ruthenium complexes $[\{\text{Ru}_2(\text{CO})_4\text{L}_2\}_3(\text{O}_2\text{CC}_6\text{H}_4\text{CO}_2)_3]$ ($\text{L} = \text{PMe}_3$: **3**, $\text{L} = 3,5\text{-Me}_2\text{NC}_5\text{H}_3$: **4**). The single-crystal X-ray structure analyses for **1** and **3**, reveal both cages to consist of $\text{Ru}_2(\text{CO})_4$ sawhorse units, **1** being a molecular loop, while **3** is a molecular triangle.

Keywords: Cages; Sawhorse-type complexes; Carboxylato bridges; Macromolecular systems; Molecular triangle; Molecular loop

Sawhorse-type ruthenium complexes are well-known since 1969, when Lewis and co-workers reported the reaction of $\text{Ru}_3(\text{CO})_{12}$ with the corresponding carboxylic acid under reflux and the depolymerisation of the polymer obtained in coordinating solvents to give dinuclear complexes of the type $\text{Ru}_2(\text{CO})_4(\text{O}_2\text{CR})_2\text{L}_2$, L being a two-electron donor [1]. These dinuclear complexes have been shown later to have a $\text{Ru}_2(\text{CO})_4$ backbone in a sawhorse-type arrangement with two $\mu_2\text{-}\eta^2\text{-carboxylato}$ bridges and two axial ligands [2] (Eq. (1)).

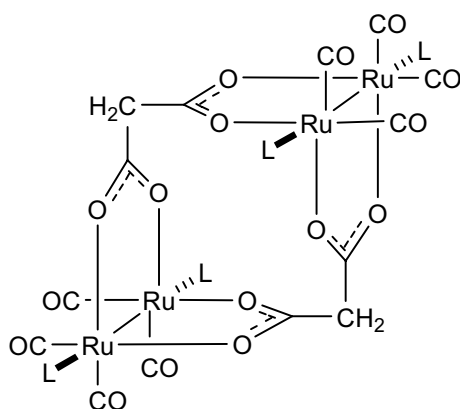


Since their discovery, a considerable number of such sawhorse-type diruthenium complexes with carboxylato bridges have been synthesised and studied [3], used in catalysis [4–6] or for the assembly of mesomorphic materials [7]. These complexes have been also used to build

* Corresponding author. Tel.: +41 32 718 24 00; fax: +41 32 718 25 11.
E-mail address: georg.suess-fink@unine.ch (G. Süss-Fink).

macromolecular structures, by reacting $\text{Ru}_3(\text{CO})_{12}$ with dicarboxylic acid, leading to different types of macromolecular assemblies: a molecular loop has been found for $[\{\text{Ru}_2(\text{CO})_4(\text{PBu}_3)_2\}_2(\text{O}_2\text{CCH}_2\text{CH}_2\text{CH}_2\text{CO}_2)_2]$ [3a] and $[\{\text{Ru}_2(\text{CO})_4(\text{PMe}_3)_2\}_2(\text{O}_2\text{CCH}_2\text{CO}_2)_2]$ [8], a molecular triangle for $[\{\text{Ru}_2(\text{CO})_4(\text{PBu}_3)_2\}_3(\text{O}_2\text{CCHOHCHOHCO}_2)_3]$ [3h], and a molecular square for $[\{\text{Ru}_2(\text{CO})_4(\text{PMe}_3)_2\}_4(\text{O}_2\text{CCO}_2)_4]$ [8]. Noticeably, the complexity of the sawhorse-based macromolecules obtained is not in line with the length of the spacer between the two carboxylic functions of the diacid used.

Herein, we report the synthesis of two tetranuclear ruthenium complexes $[\{\text{Ru}_2(\text{CO})_4(\text{L})_2\}_2(\text{O}_2\text{CCH}_2\text{CO}_2)_2]$ ($\text{L} = \text{PPh}_3$: **1**, $\text{L} = 3,5\text{-Me}_2\text{NC}_5\text{H}_3$: **2**) and two hexanuclear ruthenium complexes $[\{\text{Ru}_2(\text{CO})_4(\text{L})_2\}_3(\text{O}_2\text{CC}_6\text{H}_4\text{CO}_2)_3]$ ($\text{L} = \text{PMe}_3$: **3**, $\text{L} = 3,5\text{-Me}_2\text{NC}_5\text{H}_3$: **4**), which form macro-



Scheme 1. General arrangement of the sawhorse units in tetranuclear ruthenium complexes $[\{\text{Ru}_2(\text{CO})_4(\text{L})_2\}_2(\text{O}_2\text{CCH}_2\text{CO}_2)_2]$ ($\text{L} = \text{PPh}_3$: **1**, $\text{L} = 3,5\text{-Me}_2\text{NC}_5\text{H}_3$: **2**).

molecular cages, as shown by the X-ray single-crystal structure analyses of **1** and **3**.

Dodecarbonyltriruthenium [9] reacts with malonic acid in refluxing thf to give, after the addition of the corresponding ligand, the tetranuclear ruthenium complexes $[\{\text{Ru}_2(\text{CO})_4(\text{L})_2\}_2(\text{O}_2\text{CCH}_2\text{CO}_2)_2]$ ($\text{L} = \text{PPh}_3$: **1**, $\text{L} = 3,5\text{-Me}_2\text{NC}_5\text{H}_3$: **2**) [10]. Compounds **1** and **2** are air-stable colored crystalline powders, which have been characterised by their ^1H , $^{31}\text{P}\{^1\text{H}\}$ NMR, IR and MS data. The IR spectra of **1** and **2** exhibit the characteristic $\nu(\text{CO})$ pattern of the $\text{Ru}_2(\text{CO})_4$ sawhorse backbone, which is confirmed by the single-crystal X-ray structure analysis of **1**. As in the case of the known trimethylphosphine analogue [8], the triphenylphosphine derivative **1** also forms a molecular loop, see Scheme 1.

The single-crystal X-ray structure analysis of **1** reveals a molecular loop containing two symmetrically equivalent $\text{Ru}_2(\text{CO})_4$ sawhorse backbone units connected by two malonato bridges [11]. The four ruthenium atoms are coordinated to an axial triphenylphosphine ligand each. The Ru–Ru distance of 2.7160(7) Å is typical of a ruthenium–ruthenium single bond (see Fig. 1).

A square cage of $4.2 \times 4.2 \times 2.7$ Å, defined by two Ru–Ru midpoint– CH_2 distances (4.167 Å) and the metal–metal distance (2.7159(7) Å), is observed in **1**, see Fig. 2. However, as it was observed in the analogous molecular loop $[\{\text{Ru}_2(\text{CO})_4(\text{PMe}_3)_2\}_2(\text{O}_2\text{CCH}_2\text{CO}_2)_2]$ [8], the diameter of the cage is too small to accommodate guest molecules. Moreover, the phenyl groups of the triphenylphosphine ligands block totally the access to the cavity, see Fig. 2.

By contrast, the thermal reaction between dodecarbonyltriruthenium and terephthalic acid gives, after the addition of the corresponding ligand, the hexanuclear

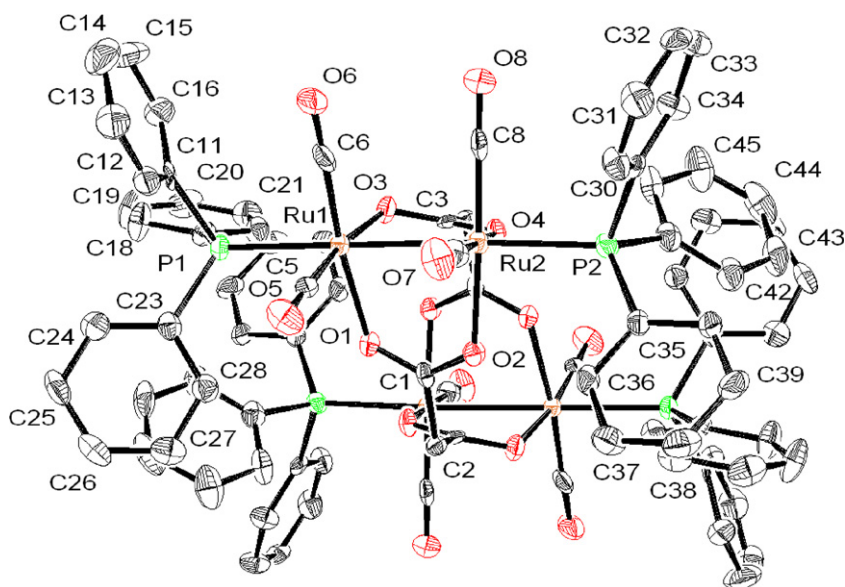


Fig. 1. ORTEP representation [12] of **1** at 50% probability level with H atoms omitted for clarity. Selected bond lengths (Å) and angles (°): Ru(1)–Ru(2) 2.7159(7), Ru(1)–O(1) 2.133(4), Ru(1)–O(3) 2.135(4), Ru(2)–O(2) 2.154(4), Ru(2)–O(4) 2.124(4), Ru(1)–P(1) 2.4720(2), Ru(2)–P(2) 2.416(2); P(1)–Ru(1)–O(1) 95.34(11), P(1)–Ru(1)–O(3) 95.08(12), O(1)–Ru(1)–O(3) 82.07(14), P(2)–Ru(2)–O(2) 94.05(11), P(2)–Ru(2)–O(4) 93.89(12), O(2)–Ru(2)–O(4) 81.02(14). Symmetry code: $1 - x, 1 - y, -z$.

ruthenium complexes $[\{\text{Ru}_2(\text{CO})_4(\text{L})_2\}_3(\text{O}_2\text{CC}_6\text{H}_4\text{CO}_2)_3]$ ($\text{L} = \text{PMe}_3$: **3**, $\text{L} = 3,5\text{-Me}_2\text{NC}_5\text{H}_3$: **4**) [10]. Compounds **3** and **4** are air-stable brownish crystalline powders, which have been characterised by their ^1H , $^{31}\text{P}\{^1\text{H}\}$ NMR, IR and MS data. The IR spectra of **3** and **4** show the characteristic absorption bands of the sawhorse-type complexes: three bands assigned to the CO ligands around 2000 cm^{-1} and the band of the carboxylato bridges around 1580 cm^{-1} . Given the analogous reaction of oxalic acid

with dodecarbonyltriruthenium yielding the octanuclear complex $[\{\text{Ru}_2(\text{CO})_4(\text{PMe}_3)_2\}_4(\text{O}_2\text{CCO}_2)_4]$ [8], the formation of a molecular square could also be expected instead of a molecular triangle. This difference is presumably due to the greater flexibility of the two carboxylato groups in

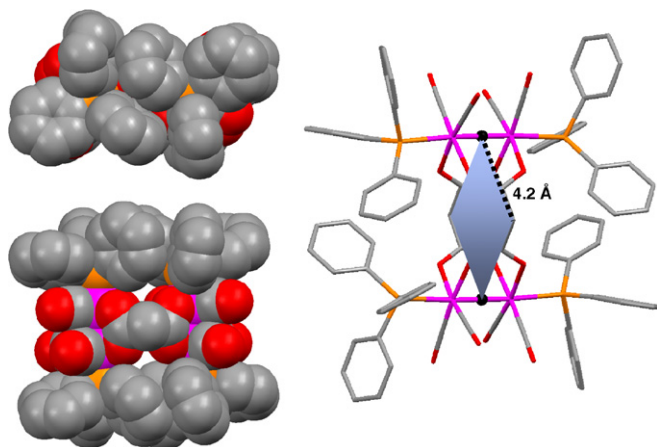
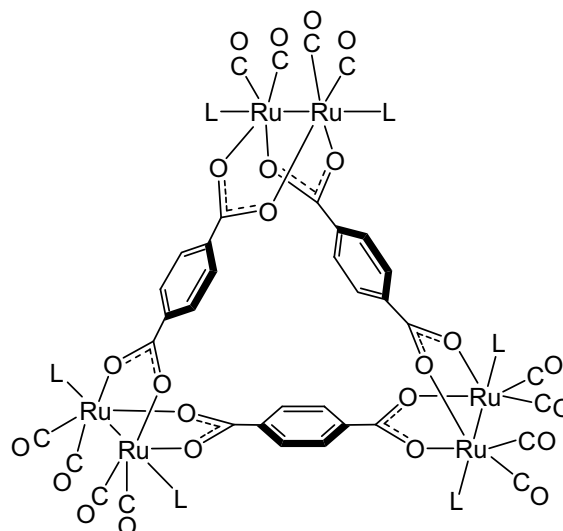


Fig. 2. Space-filling views [13] of the crystal structure of **1**, and the square area of the cage.



Scheme 2. General arrangement of the sawhorse units in the hexanuclear complexes $[\{\text{Ru}_2(\text{CO})_4(\text{L})_2\}_3(\text{O}_2\text{CC}_6\text{H}_4\text{CO}_2)_3]$ ($\text{L} = \text{PMe}_3$: **3**, $\text{L} = 3,5\text{-Me}_2\text{NC}_5\text{H}_3$: **4**).

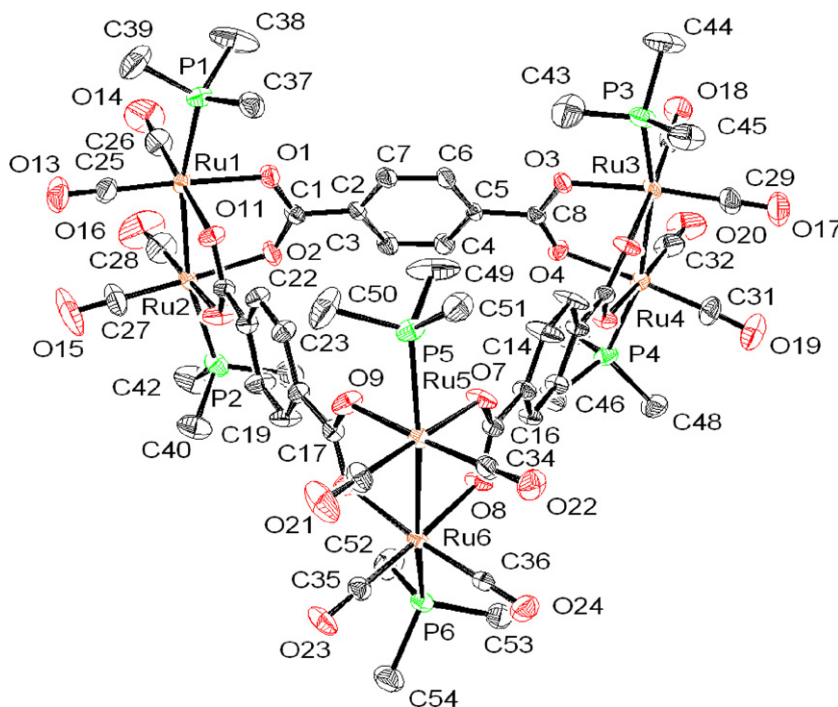


Fig. 3. ORTEP representation [12] of **3** at 35% probability level, H atoms and dichloromethane molecules omitted for clarity. Selected bond lengths (\AA) and angles ($^\circ$): Ru(1)–Ru(2) 2.7196(6), Ru(3)–Ru(4) 2.7252(7), Ru(5)–Ru(6) 2.7316(6), Ru(1)–O(1) 2.129(4), Ru(1)–O(11) 2.148(4), Ru(2)–O(2) 2.132(4), Ru(2)–O(12) 2.112(4), Ru(3)–O(3) 2.128(4), Ru(3)–O(5) 2.117(4), Ru(4)–O(4) 2.122(4), Ru(4)–O(6) 2.142(3), Ru(5)–O(7) 2.134(4), Ru(5)–O(9) 2.125(4), Ru(6)–O(8) 2.119(4), Ru(6)–O(10) 2.148(4); P(1)–Ru(1)–O(1) 84.18(12), P(2)–Ru(2)–O(2) 86.13(13), P(1)–Ru(1)–O(11) 90.15(11), P(2)–Ru(2)–O(12) 85.26(12), P(3)–Ru(3)–O(3) 87.94(11), P(4)–Ru(4)–O(4) 83.28(11), P(3)–Ru(3)–O(5) 81.70(12), P(4)–Ru(4)–O(6) 89.40(11), P(5)–Ru(5)–O(7) 88.21(11), P(5)–Ru(5)–O(9) 83.22(11), P(6)–Ru(6)–O(8) 82.90(11), P(6)–Ru(6)–O(10) 88.22(11).

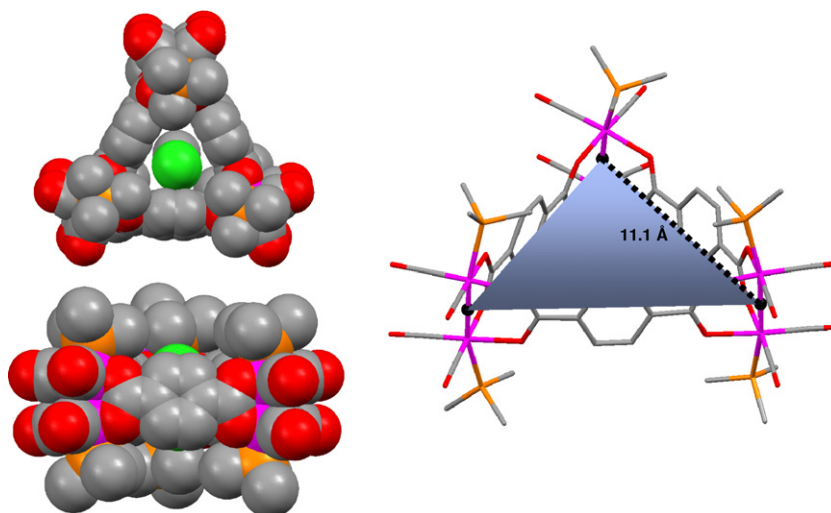


Fig. 4. Space-filling views [13] of the crystal structure of $[\text{CH}_2\text{Cl}_2 \cdot 3]$, and the diameter of the cage.

the terephthalato ligands with respect to those in the oxalato ligands (Scheme 2).

The single-crystal X-ray structure analysis of **3** shows a hexanuclear structure [14], in which three $\text{Ru}_2(\text{CO})_4$ units are coupled by three terephthalato bridging ligands to give a trimeric macrocycle, see Fig. 3. The formation of a triangular structure imposes distortion around the ruthenium atoms. The angles between the oxygen atoms of two adjacent terephthalato ligands are not 90° as expected for an octahedral metal centre, but range from $82.8(2)$ to $84.7(2)^\circ$. Moreover, the trimethylphosphine ligands are far from being co-axial to the Ru–Ru axes, the P–Ru–Ru–P torsion angles are $18.0(3)^\circ$, $29.8(2)^\circ$ and $40.5(2)^\circ$, respectively, with all the trimethylphosphine moieties pointing towards the cavity with the Ru–Ru–P angles ranging from $163.07(5)$ to $166.58(5)^\circ$ (Fig. 4).

In **3**, a triangular hollow space of $11.1 \times 11.1 \times 11.1 \text{ \AA}$ (distances between Ru–Ru axes) is observed, see Fig. 4. This cavity is large enough to accommodate small guest molecules. Indeed, upon crystallisation from dichloromethane, a molecule of CH_2Cl_2 is observed within the cavity of **3** (Fig. 4): The shortest Cl–C distances being 3.5 \AA , and the hydrogen atoms of the dichloromethane guest molecule pointing in direction of the aromatic rings of two adjacent terephthalato ligands.

In conclusion, we have synthesised tetra- and hexanuclear cage molecules formed from $\text{Ru}_2(\text{CO})_4$ sawhorse units and from dicarboxylato bridging ligands. While the hollow space is too small to accommodate guest molecules in the tetranuclear loops, the hexanuclear triangles can crystallise as an inclusion compound with small guest molecules inside the cavity.

Acknowledgements

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ride hydrate from the Johnson Matthey Technology Centre is gratefully acknowledged.

Appendix A. Supplementary materials

CCDC 652978 and 652979 contains the supplementary crystallographic data for **1** and $3 \cdot 3\text{CH}_2\text{Cl}_2$. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.inoche.2007.08.026.

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- [10] All manipulations were carried out by routine under nitrogen atmosphere. Organic solvents were dried, 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 Varian 200 MHz spectrometer. IR spectra were recorded on a Perkin-Elmer 1720X FT-IR spectrometer (4000–400 cm^{-1}). Electro-spray mass spectra were obtained in positive-ion mode with an LCQ Finnigan mass spectrometer. Dodecacarbonyltriruthenium [9] was prepared according to published methods. General synthetic method for **1–4**. A solution of 0.23 mmol of $\text{Ru}_3(\text{CO})_{12}$ (150 mg) and 0.35 mmol of the corresponding diacid (37 mg of malonic acid for **1** and **2**, 59 mg of terephthalic acid for **3** and **4**) in dry tetrahydrofuran (30 ml) was heated at 120 °C in a pressure Schlenk tube for 6–8 h. Then the solvent was evaporated to give an orange-brown residue which was dissolved in tetrahydrofuran and 0.70 mmol of the appropriate ligand L (L = PPh₃; **1**, L = 3,5-Me₂NC₅H₃; **2**, L = PMe₃; **3**, L = 3,5-Me₂NC₅H₃; **4**) was added. The solution was stirred at room temperature for 2 h, the solution was evaporated and the product isolated by crystallisation from a tetrahydrofuran/hexane mixture. The products were obtained as crystalline powders (**1** and **3** yellow, **2**: brown and **4**: purple-brown). [$\text{Ru}_2(\text{CO})_4(\text{PPh}_3)_2$ ($\text{O}_2\text{CCH}_2\text{CO}_2$)₂] (**1**): 83 mg, 0.044 mmol, 25%. ¹H NMR (200 MHz, CDCl₃): δ = 7.66–7.30 (m, 60 H, P(C₆H₅)₃), 3.09 (s, 4 H, O₂CCH₂CO₂). ³¹P{¹H} NMR (81 MHz, CDCl₃): δ = 14.74 (P(C₆H₅)₃). IR (CaF₂, thf): $\nu_{(\text{CO})}$ 2025(s), 1968(m), 1956(s), $\nu_{(\text{OCO})}$ 1586(m) cm^{-1} . ESI-MS (thf/MeOH) m/z = 1619.86 [M-PPh₃]⁺. [$\text{Ru}_2(\text{CO})_4(3,5\text{-Me}_2\text{NC}_5\text{H}_3)_2(\text{O}_2\text{CCH}_2\text{CO}_2)_2$] (**2**): 85 mg, 0.067 mmol, 38%. ¹H NMR (200 MHz, CDCl₃): δ = 8.41 (s, 8H, NC₅H₃), 7.28 (s, 4H, NC₅H₃), 3.49 (s, 4H, O₂CCH₂CO₂), 2.01 (s, 24H, CH₃). IR (CaF₂, CH₂Cl₂): $\nu_{(\text{CO})}$ 2022(s), 1973(m), 1940(s), $\nu_{(\text{OCO})}$ 1587(m) cm^{-1} . [$\text{Ru}_2(\text{CO})_4(\text{PMe}_3)_2(\text{O}_2\text{CC}_6\text{H}_4\text{CO}_2)_2$] (**3**): 105 mg, 0.061 mmol, 52%. ¹H NMR (200 MHz, CDCl₃): δ = 7.63 (s, 12H, C₆H₄), 1.66 (s, 54H, CH₃). ³¹P{¹H} NMR (81 MHz, CDCl₃): δ = -10.30 (PMe₃). IR (CaF₂, CHCl₃): $\nu_{(\text{CO})}$ 2018(s), 1973(m), 1944(s), $\nu_{(\text{OCO})}$ 1577(m) cm^{-1} . ESI-MS (thf/MeOH) m/z = 1815.4 [M-PMe₃]⁺. [$\text{Ru}_2(\text{CO})_4(3,5\text{-Me}_2\text{NC}_5\text{H}_3)_2(\text{O}_2\text{CC}_6\text{H}_4\text{CO}_2)_3$] (**4**): 95 mg, 0.045 mmol, 39%. ¹H NMR (200 MHz, CDCl₃): δ = 8.53 (s, 12 H, NC₅H₃), 7.59 (s, 12H, C₆H₄), 7.51 (s, 6H, NC₅H₃), 2.42 (s, 36H, CH₃). IR (CaF₂, CH₂Cl₂): $\nu_{(\text{CO})}$ 2024(s), 1974(m), 1942(s), $\nu_{(\text{OCO})}$ 1581(m) cm^{-1} .
- [11] Yellow crystals of **1** suitable for X-ray diffraction analysis were grown by slow evaporation of a concentrated solution of **1** in a mixture of CH₂Cl₂/MeOH. *Crystal data for 1*; C₈₆H₆₄O₁₆P₄Ru₄, monoclinic space group *P*2₁/*n* (No. 14), cell parameters *a* = 11.763(1) Å, *b* = 17.553(1) Å, *c* = 19.640(2) Å, β = 106.337(9)°, *V* = 3891.5(7) Å³, *T* = 173(2) K, *Z* = 2, *D_c* = 1.606 g cm⁻³, *F*(000) 1888, λ (Mo K α) = 0.71073 Å, 6889 reflections measured, 3526 unique (*R*_{int} = 0.1141) which were used in all calculations. The structure was solved by direct method (SHELXS-97) and refined (SHELXL-97) by full-matrix least-squares methods on *F*² with 496 parameters. *R*₁ = 0.0412 (*I* > 2 σ (*I*)) and *wR*₂ = 0.0636, GOF = 0.659; max/min residual density 0.499/−0.521 eÅ⁻³.
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- [14] Brown crystals of **3** suitable for X-ray diffraction analysis were grown by slow evaporation of a concentrated solution of **3** in CH₂Cl₂. *Crystal data for 3* · 3CH₂Cl₂; C₅₇H₇₂Cl₆O₂₄P₆Ru₆, orthorhombic space group *P* bca (No. 61), cell parameters *a* = 15.232(1) Å, *b* = 27.266(1) Å, *c* = 40.753(2) Å, *V* = 16926.1(18) Å³, *T* = 173(2) K, *Z* = 8, *D_c* = 1.684 g cm⁻³, *F*(000) 8496, λ (Mo K α) = 0.71073 Å, 15315 reflections measured, 10655 unique (*R*_{int} = 0.0489) which were used in all calculations. The structure was solved by direct method (SHELXS-97) and refined (SHELXL-97) by full-matrix least-squares methods on *F*² with 910 parameters. *R*₁ = 0.0447 (*I* > 2 σ (*I*)) and *wR*₂ = 0.1290, GOF = 0.991; max/min residual density 2.120/−1.076 eÅ⁻³.