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New Dinuclear $Ru_2(CO)_4$ Sawhorse-Type Complexes Containing Bridging Carboxylato Ligands

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Abstract. The thermal reaction of $Ru_3(CO)_{12}$ with ethacrynic acid, 4-[bis(2-chlorethyl)amino]benzenebutanoic acid (chlorambucil), or 4-phenylbutyric acid in refluxing solvents, followed by addition of two-electron donor ligands (L), gives the diruthenium complexes $Ru_2(CO)_4(O_2CR)_2L_2$ (**1**: R = CH_2O-$C_6H_2Cl_2$-$COC(CH_2)C_2H_5$, L = C_5H_5N; **2**: R = CH_2O-$C_6H_2Cl_2$-$COC(CH_2)C_2H_5$, L = PPh_3; **3**: R = C_3H_6-C_6H_4-$N(C_2H_4$-$Cl)_2$, L = C_5H_5N; **4**: R = C_3H_6-C_6H_4-$N(C_2H_4$-$Cl)_2$, L = PPh_3; **5**: R = C_3H_6-C_6H_5, L = C_5H_5N; **6**: R = C_3H_6-C_6H_5, L = PPh_3). The single-crystal structure analyses of **2**, **3**, **5** and **6** reveal a dinuclear $Ru_2(CO)_4$ sawhorse structure, the diruthenium backbone being bridged by the carboxylato ligands, while the two L ligands occupy the axial positions of the diruthenium unit.

Keywords: Carbonyl ligands; Carboxylato bridges; Dinuclear complexes; Ruthenium

Introduction

Sawhorse-type diruthenium complexes are well-known since 1969, when J. Lewis and co-workers reported their formation by refluxing $Ru_3(CO)_{12}$ in the corresponding carboxylic acid and the depolymerisation of the materials obtained in coordinating solvents to give dinuclear complexes of the type $Ru_2(CO)_4(O_2CR)_2L_2$ (R = H, CH_3, C_2H_5, C_9H_{19}; L = C_5H_5N, $AsPh_3$, PPh_3), L being a two-electron donor ligand [1]. Later, by a single-crystal X-ray structure analysis of $Ru_2(CO)_4(O_2CR)_2L_2$ (R = C_4H_9; L = PBu^t_3), these complexes have been shown to have a $Ru_2(CO)_4$ backbone in a sawhorse-type arrangement with two μ_2-η^2-carboxylato bridges and two axial ligands [2]. Since their discovery, a considerable number of such sawhorse-type diruthenium complexes with carboxylato bridges have been synthesized [3], and used in various fields as well as catalysis [4, 5, 6] or to synthesize metallo-mesomorphic materials [7].

Herein, we report the synthesis and characterization of six new $Ru_2(CO)_4$ sawhorse-type complexes containing carboxylato ligands, some of which with biologically active substituents. The single-crystal structure analysis of four representative complexes is presented as well.

Experimental Section

General Remarks

All manipulations were carried out by routine under nitrogen atmosphere. Organic solvents were degassed and saturated with nitrogen prior to use. All reagents were purchased either from Aldrich or Fluka and used as received. Dodecacarbonyltriruthenium was prepared according to published method [8]. The ^1H, $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ NMR spectra were recorded on a Bruker AMX 400 spectrometer using the residual protonated solvent as internal standard. Infrared spectra were recorded on a Perkin-Elmer FT-IR 1720X spectrometer (4000-400 cm^{-1}). Electro-spray mass spectra were obtained in positive-ion mode with an LCQ Finnigan mass spectrometer.

Synthesis of 1−6

A solution of $Ru_3(CO)_{12}$ (200 mg, 0.32 mmol) and the corresponding acid (285 mg, 0.94 mmol for ethacrynic acid **1**−**2**; 288 mg, 0.94 mmol for chlorambucil **3**−**4**; 154 mg, 0.94 mmol for 4-phenyl-1-butyric acid **5**−**6**) in dry tetrahydrofuran (30 mL) was heated to 120 °C in a pressure Schlenk tube for 18 h. Then the solvent was evaporated to give a brown residue which was dissolved in tetrahydrofuran and the appropriate ligand L (0.94 mmol) (**1**, **3**, **5**, L = C_5H_5N; **2**, **4**, **6**, L = PPh_3) was added. The solution was stirred at room temperature for two hours, then the solution was evaporated and the product isolated from the residue by crystallization from a tetrahydrofuran/hexane or dichloromethane/hexane mixture. The products were purified by column chromatography on silica gel using dichloromethane as eluent. Complexes **1**−**6** were obtained as yellow crystalline powders which are stable up to 200 °C.

$Ru_2(CO)_4\{O_2CCH_2O$-$C_6H_2Cl_2$-$COC(CH_2)C_2H_5\}_2(C_5H_5N)_2$ (1). Yield: 68 %, 344 mg, 0.32 mmol.

^1H NMR (400 MHz, $CDCl_3$): δ = 8.34 (m, 4H, CH_{pyr}), 7.81 (t, 2H, CH_{pyr}, ^3J = 7.6 Hz), 7.32 (m, 4H, CH_{pyr}), 7.10 (d, 2H, CH_{aro}, ^3J = 8.6 Hz), 7.04 (d, 2H, CH_{aro}, ^3J = 8.6 Hz), 5.90 (s, 2H, CH_2=C), 5.48 (s, 2H, CH_2=C), 4.72 (s, 4H, CH_2COO), 2.46 (q, 4H, CH_2CH$_3$, ^3J = 7.4 Hz), 1.15 (t, 6H, CH_3, ^3J = 7.4 Hz). **$^{13}C\{^1H\}$ NMR** (100 MHz, $CDCl_3$): δ = 206.44 (*C*O), 195.70 (2C, *C*=O), 185.78 (*C*OO), 157.17, 156.88 (*C*-Cl), 151.06 (*C*-O), 150.22 (C_5H_5N), 137.53 (C_5H_5N), 129.24 (CH_2), 125.34 (C_5H_5N), 111.49 (CH_3), 68.60 (CH_2), 46.54 (*C*H), 26.61 (CH_2). **IR** (CaF_2, CH_2Cl_2): $\nu_{(CO)}$ 2030 vs, 1978 m, 1947 vs, $\nu_{(OCO)}$ 1613 m, 1585 m cm^{-1}. **ESI-MS**: *m*/*z* = 941.79 $[M\text{-}C_5H_5N\text{-}2CO+H]^+$.

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$Ru_2(CO)_4\{O_2CCH_2O\text{-}C_6H_2Cl_2\text{-}COC(CH_2)C_2H_5\}_2(PPh_3)_2$ (2). Yield: 39 %, 260 mg, 0.180 mmol.

^{1}H NMR (400 MHz, $(CD_3)_2CO$): δ = 7.61-7.30 (m, 30H, CH_{aro}), 7.07 (d, 2H, CH_{aro}, ^3J = 8.6 Hz), 7.10 (d, 2H, CH_{aro}, ^3J = 8.6 Hz), 5.95 (s, 2H, CH_2=C), 5.38 (s, 2H, CH_2=C), 4.45 (s, 2H, CH_2COO), 2.43 (q, 4H, CH_2CH$_3$, ^3J = 7.4 Hz), 1.10 (t, 6H, CH$_3$, ^3J = 7.4 Hz). **^{13}C{^{1}H} NMR** (100 MHz, $(CD_3)_2CO$): δ = 205.13 (*C*O), 195.70 (*C*=O), 183.90 (*C*OO), 157.19, 156.79 (*C*-Cl), 151.06 (*C*-O), 144.80, 139.20, 134.71, 134.50, 134.45, 134.39, 133.81, 133.65, 133.60, 131.06, 129.43, 129.38, 129.34 (*C*H$_{aro}$), 129.24 (*C*H$_2$), 123.29, 122.78 (*C*H$_{aro}$), 111.49 (*C*H$_3$), 68.60 (*C*H$_2$), 47.06 (*C*H), 26.61 (*C*H$_2$). **^{31}P{^{1}H} NMR** (161 MHz, $(CD_3)_2CO$): δ = 12.68. **IR** (CaF_2, CH_2Cl_2): $\nu_{(CO)}$ 2028 vs, 1984 m, 1956 vs, $\nu_{(OCO)}$ 1606 m, 1586 cm^{-1}. **ESI-MS**: *m*/*z* = 1443.02 $[M+H]^+$, 1466.99 $[M\text{-}2CO+Na+(CH_3)_2CO]^+$.

$Ru_2(CO)_4\{O_2CC_3H_6\text{-}C_6H_4\text{-}N(C_2H_4\text{-}Cl)_2\}_2(C_5H_5N)_2$ (3). Yield: 81 %, 412 mg, 0.381 mmol.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.81-8.83 (m, 4H, C_5H_5N), 7.87-7.92 (m, 2H, C_5H_5N), 7.44-7.48 (m, 4H, C_5H_5N), 6.98 (d, 4H, C_6H_4, ^3J = 8.7 Hz), 6.58 (d, 4H, C_6H_4, ^3J = 8.7 Hz), 3.63-3.75 (m, 16H, N(CH_2)$_2$Cl), 2.49 (t, 4H, (CH$_2$)$_2$CH_2, ^3J = 7.2 Hz), 2.36 (t, 4H, (CH$_2$)$_2$CH_2, ^3J = 7.2 Hz), 1.81-1.92 (m, 4H, CH$_2$CH_2CH$_2$). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ = 206.64 (*C*O), 187.08 (*C*OO), 152.31 (C_5H_5N), 144.57 (*C*H$_{aro}$), 137.83 (C_5H_5N), 131.67 (*C*H$_{aro}$), 130.08 (*C*H), 125.34 (C_5H_5N), 112.44 (*C*H), 54.01, 40.99, 36.72, 34.39, 28.53 (*C*H$_2$). **IR** (CaF_2, CH_2Cl_2): $\nu_{(CO)}$ 2023 vs, 1971 m, 1939 vs, $\nu_{(OCO)}$ 1582 m, 1568 m cm^{-1}. **ESI-MS**: *m*/*z* = 1082.02 $[M+H]^+$, 1002.89 $[M\text{-}C_5H_5N+H]^+$.

$Ru_2(CO)_4\{O_2CC_3H_6\text{-}C_6H_4\text{-}N(C_2H_4\text{-}Cl)_2\}_2(PPh_3)_2$ (4). Yield: 53 %, 357 mg, 0.247 mmol.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.61-7.57 (m, 12H, CH_{aro}), 7.45-7.36 (m, 18H, CH_{aro}), 6.85 (d, 4H, C_6H_4, ^3J = 8.7 Hz), 6.55 (d, 4H, C_6H_4, ^3J = 8.7 Hz), 3.75-3.62 (m, 16H, N(CH_2)$_2$Cl), 2.22 (t, 4H, (CH$_2$)$_2$CH_2, ^3J = 7.2 Hz), 2.02 (t, 4H, (CH$_2$)$_2$CH_2, ^3J = 7.2 Hz), 1.34-1.50 (m, 4H, CH$_2$CH_2CH$_2$). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ = 205.85 (*C*O), 188.67 (*C*OO), 144.45 (*C*H$_{aro}$), 134.35, 134.29, 134.23, 133.82, 131.72, 130.07, 128.62, 128.59, 128.54 (*C*H$_{aro}$), 133.98, 133.67 (*C*H$_{aro}$), 112.46 (*C*H$_{aro}$), 54.05, 40.98, 36.86, 34.19, 27.99 (*C*H$_2$). **^{31}P{^{1}H} NMR** (161 MHz, $CDCl_3$): δ = 14.79. **IR** (CaF_2, CH_2Cl_2): $\nu_{(CO)}$ 2022 vs, 1974 m, 1943 vs, $\nu_{(OCO)}$ 1614 m, 1585 m cm^{-1}. **ESI-MS**: *m*/*z* = 1469.17 $[M+Na]^+$.

$Ru_2(CO)_4(O_2CC_3H_6\text{-}C_6H_5)_2(C_5H_5N)_2$ (5). Yield: 67 %, 252 mg, 0.316 mmol.

^{1}H NMR (400 MHz $CDCl_3$): δ = 8.76 (m, 4H, C_5H_5N), 7.82 (m, 2H, C_5H_5N), 7.38 (m, 4H, C_5H_5N), 7.13-7.23 (m, 6H, C_6H_5), 7.03 (dd, 4H, C_6H_5, ^5J = 1.53 Hz ^3J = 6.63 Hz), 2.53 (t, 4H, OOCCH_2CH$_2$, ^3J = 7.8 Hz), 2.32 (t, 4H, CH$_2$CH_2C$_6$H$_5$, ^3J = 7.1 Hz), 1.84 (m, 4H, CH$_2$CH_2CH$_2$). **^{13}C{^{1}H} NMR** (100 MHz $CDCl_3$): δ = 204.15 (CO), 186.50 (COO), 151.87 (C_5H_5N), 142.07 (C_6H_4), 137.32 (C_5H_5N), 128.41 (C_6H_4), 128.23 (C_6H_4), 125.72 (C_6H_4), 124.85 (C_5H_5N), 36.29 (CH$_2$), 35.15 (CH$_2$), 27.83 (CH$_2$). **IR** (CaF_2, CH_2Cl_2): $\nu_{(CO)}$ 2023 vs, 1971 m, 1938 vs, $\nu_{(OCO)}$ 1600 w, 1569 m cm^{-1}. **ESI-MS**: *m*/*z* = 821.5 $[M+Na]^+$, 742.7 $[M\text{-}2CO+H]^+$.

$Ru_2(CO)_4(O_2CC_3H_6\text{-}C_6H_5)_2(PPh_3)_2$ (6). Yield: 69 %, 206 mg, 0.177 mmol.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.53 (m, 12H, PPh_3), 7.33 (m, 18H, PPh_3), 7.17 (m, 6H, C_6H_5), 6.89 (m, 4H, C_6H_5), 2.25 (t, 4H, OOCCH_2CH$_2$, ^3J = 7.7 Hz), 1.96 (t, 4H, CH$_2$CH_2C$_6$H$_5$, ^3J = 7.4 Hz), 1.42 (m, 4H, CH$_2$CH_2CH$_2$C$_6$H$_5$). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ = 205.66 (*C*O), 188.30 (*C*OO), 142.24 (C_{aro}), 134.12 (C_{aro}), 134.06 (C_{aro}), 134.00 (C_{aro}), 133.69 (C_{aro}), 133.53 (C_{aro}), 133.37 (C_{aro}), 129.86 (C_{aro}), 128.66 (C_{aro}), 128.41 (C_{aro}), 128.37 (C_{aro}), 128.32 (C_{aro}), 125.82 (C_{aro}), 36.76 (*C*H$_2$), 35.25 (*C*H$_2$), 27.57 (*C*H$_2$). **^{31}P{^{1}H} NMR** (161 MHz, $CDCl_3$): δ = 12.72 ppm. **IR** (CaF_2, CH_2Cl_2): $\nu_{(CO)}$ 2022 vs, 1977 m, 1949 s, $\nu_{(OCO)}$ 1566 s cm^{-1}. **ESI-MS**: *m*/*z* = 1187.6 $[M+Na]^+$, 845.1 $[M\text{-}PPh_3\text{-}3CO+Na+CH_3OH]^+$.

Alternative Synthesis of 5 and 6

A suspension of $Ru_3(CO)_{12}$ (111 mg, 0.174 mmol) and 4-phenyl-1-butyric acid (85 mg, 0.515 mmol) in dry methanol (50 ml) was refluxed (bath temperature 70 °C) under inert atmosphere in a classical Schlenk tube overnight. After filtration of the methanol solution, a CH_2Cl_2 solution (20 mL) of the appropriate ligand L (0.515 mmol) C_5H_5N (**5**) or PPh_3 (**6**) was added. Then the solution was stirred at room temperature for two hours. The volume of the solvent was then reduced and the product was precipitated by addition of hexane. The product was obtained as a yellow powder. Yields: 67 % (**5**) and 69 % (**6**).

X-ray Crystallographic Study

Yellow crystals of **2**, **3**, **5** and **6** were mounted at 203 K on a Stoe Image Plate Diffraction system equipped with a ϕ circle goniometer, using Mo-Kα graphite monochromated radiation (λ = 0.71073 Å) with ϕ range 0-200°. The structures were solved by direct methods using the program SHELXS-97 [9]. Refinement and all further calculations were carried out using SHELXL-97 [10]. The H-atoms were included in calculated positions and treated as riding atoms using the SHELXL default parameters. The non-H atoms were refined anisotropically, using weighted full-matrix least-square on F^2.

Crystal data for **2**; $C_{66}H_{52}Cl_4O_{12}P_2Ru_2$, triclinic space group $P\bar{1}$ (No. 2), cell parameters a = 10.1138(9), b = 15.4929(13), c = 21.1252(17) Å, α = 91.972(10), β = 96.308(10), γ = 108.582(9)°, V = 3110.1(5) Å^3, Z = 2, D_c = 1.541 g cm^{-3}, F(000) 1460, 11372 reflections measured, 8944 unique (R_{int} = 0.0308) which were used in all calculations. R_1 = 0.0524 ($I > 2\sigma(I)$) and wR_2 = 0.1594, GOF = 1.081; max./min. residual density 2.787/−1.592 eÅ^{-3}.

Crystal data for **3**; $C_{42}H_{46}Cl_4N_4O_8Ru_2$, triclinic space group $P\bar{1}$ (No. 2), cell parameters a = 10.2849(12), b = 11.1549(13), c = 20.220(3) Å, α = 95.111(10), β = 94.363(10), γ = 104.394(9)°, V = 2226.4(5) Å^3, Z = 2, D_c = 1.609 g cm^{-3}, F(000) 1092, 7868 reflections measured, 5227 unique (R_{int} = 0.0906) which were used in all calculations. R_1 = 0.0496 ($I > 2\sigma(I)$) and wR_2 = 0.1227, GOF = 0.918; max./min. residual density 0.554/−0.942 eÅ^{-3}.

Crystal data for **5**; $C_{34}H_{32}N_2O_8Ru_2$, triclinic space group $P\bar{1}$ (No. 2), cell parameters a = 9.614(4), b = 10.713(4), c = 17.766(9) Å, α = 73.17(5), β = 88.74(5), γ = 72.71(5)°, V = 1668.3(12) Å^3, Z = 2, D_c = 1.590 g cm^{-3}, F(000) 804, 6070 reflections measured, 4331 unique (R_{int} = 0.0642) which were used in all calculations. R_1 = 0.0403 ($I > 2\sigma(I)$) and wR_2 = 0.1011, GOF = 0.915; max./min. residual density 0.838/−1.007 eÅ^{-3}.

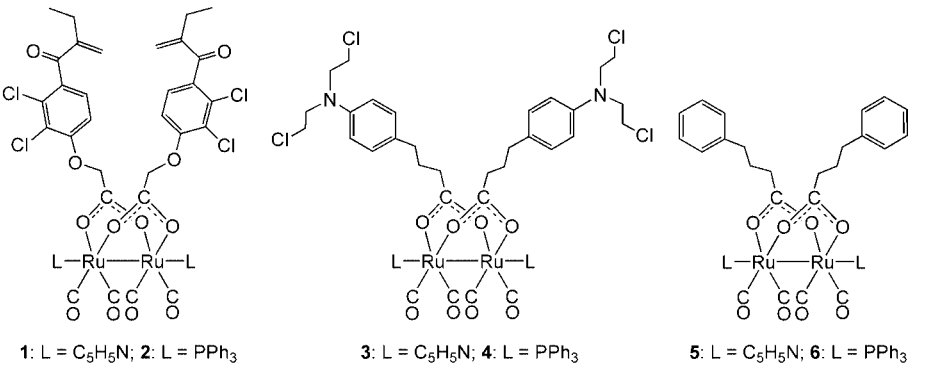
Crystal data for **6**; $C_{60}H_{52}O_8P_2Ru_2$, monoclinic space group $P2_1/n$ (No. 14), cell parameters a = 15.2072(9), b = 39.987(2), c = 17.5163(11) Å, β = 90.797(5)°, V = 10650.4(11) Å^3, Z = 8, D_c = 1.453 g cm^{-3}, F(000) 4752, 18938 reflections measured, 8571 unique (R_{int} = 0.1735) which were used in all calculations. R_1 = 0.0650 ($I > 2\sigma(I)$) and wR_2 = 0.1572, GOF = 0.834; max./min. residual density 0.661/−1.436 eÅ^{-3}. Figures 1 to 4 were drawn with ORTEP [11].

CCDC 698270 (**2**), 698271 (**3**), 698272 (**5**) and 698273 (**6**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via **www.ccdc.cam.ac.uk/data_request/cif**.

Results and Discussion

Synthesis

In a high pressure Schlenk tube, dodecacarbonyltriruthenium reacts first with the appropriate carboxylic acid in



1: L = C_5H_5N; **2**: L = PPh_3 **3**: L = C_5H_5N; **4**: L = PPh_3 **5**: L = C_5H_5N; **6**: L = PPh_3

Scheme 1.

tetrahydrofuran at 120 °C to yield the corresponding thf-intermediates $[Ru_2(CO)_4(O_2CR)_2(thf)_2]$, which react with two-electron donor ligands L such as pyridine or triphenylphosphine to give the complexes $Ru_2(CO)_4(O_2CR)_2L_2$ **1**−**6** in good yields according to Equation (1).

$$^2/_3\ Ru_3(CO)_{12} + 2\ RCOOH + 2\ L \rightarrow Ru_2(CO)_4(O_2CR)_2L_2 + 4\ CO + H_2 \quad (1)$$

Compounds **1**−**6** are air-stable yellow crystalline powders which have been characterized by IR, NMR and mass spectroscopy. All compounds exhibit in the $\nu_{(CO)}$ region of the infrared spectrum the characteristic pattern of the $Ru_2(CO)_4$ sawhorse unit: three bands around 2000 cm^{-1} for the CO terminal ligands and two bands for symmetric and asymmetric vibrations of the carboxylato bridges, around 1500−1600 cm^{-1} [1].

A convenient method for the synthesis of diruthenium sawhorse-type complexes avoiding pressure Schlenk tube heating was reported by *A. H. White* and co-workers [12]. We therefore tried to find out if refluxing conditions are sufficient for the synthesis of our complexes. Indeed, refluxing $Ru_3(CO)_{12}$ and the corresponding carboxylic acid in methanol turned out to be adequate. The yields, however, are not higher: In the case of **5** and **6**, the yields are identical to those obtained in the classical high-temperature synthesis.

Crystal Structures

Crystals suitable for X-ray structural analysis were obtained by slow diffusion of hexane in concentrated solutions of **2**, **3**, **5** and **6** in chloroform. The single-crystal structure analyses of **2**, **3**, **5** and **6** exhibit the $Ru_2(CO)_4$ sawhorse backbone with the two two-electron donor ligands in the axial positions and the carboxylato bridges in the equatorial positions. The molecular structures of **2**, **3**, **5** and **6** are shown in Figures 1, 2, 3 and 4, respectively, and a series of selected geometrical parameters are presented in Table 1.

All Ru−Ru distances are in the range of a ruthenium-ruthenium single bond but they are considerably shorter in the pyridine derivatives **3** and **5** (2.6816(7) and 2.669(1) Å) than those of the triphenylphosphine analogues **2** and **6** (2.7107(9) to 2.7197(6) Å). This difference in the metal−metal separation can be associated to an increase in electron density between the metal atoms as a result of the lack of back-bonding to the NC_5H_5 ligands.

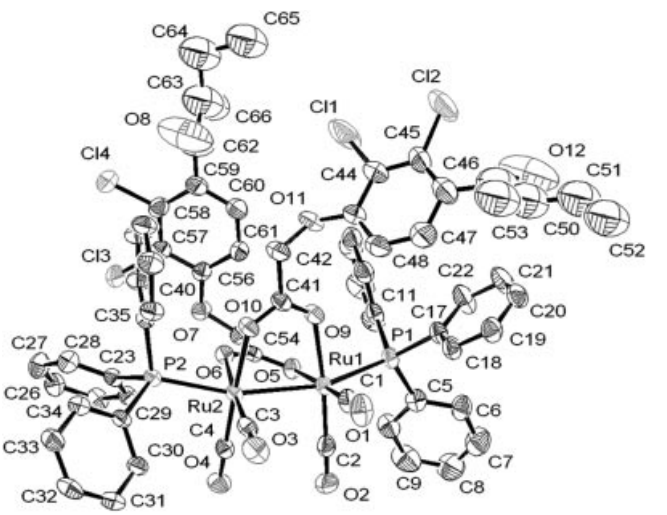


Figure 1. ORTEP drawing of **2**, at 50 % probability level for thermal displacement ellipsoids, with hydrogen atoms being omitted for clarity.

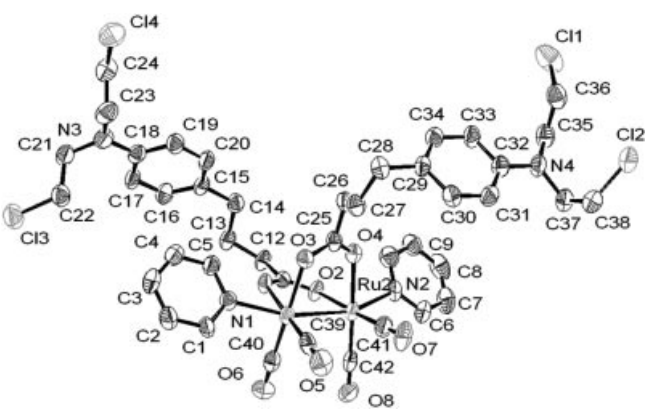


Figure 2. ORTEP drawing of **3**, at 50 % probability level for thermal displacement ellipsoids, with hydrogen atoms being omitted for clarity.

Table 1. Selected bond lengths /Å and angles /° for **2**, **3**, **5** and **6**

L =	**2** PPh_3	**3** NC_5H_5	**5** NC_5H_5	**6A** PPh_3	**6B** PPh_3
Distances					
Ru−Ru	2.7197(6)	2.6816(7)	2.6689(13)	2.7107(9)	2.7156(9)
Ru−L(1)	2.424(1)	2.223(5)	2.221(4)	2.429(2)	2.427(2)
Ru−L(2)	2.454(1)	2.239(5)	2.228(4)	2.435(2)	2.446(2)
$Ru-O_{carboxylato}$	2.128(3)	2.113(4)	2.113(3)	2.129(5)	2.120(6)
$Ru-O_{carboxylato}$	2.143(3)	2.124(3)	2.129(3)	2.164(5)	2.121(6)
$Ru-O_{carboxylato}$	2.122(3)	2.119(4)	2.113(3)	2.120(6)	2.143(5)
$Ru-O_{carboxylato}$	2.147(3)	2.136(4)	2.126(3)	2.127(6)	2.144(5)
Angles					
$O_{carboxylato}$					
O-Ru-O	86.2(1)	85.1(1)	84.9(1)	85.4(2)	84.1(2)
O-Ru-O	85.4(1)	86.2(1)	83.8(1)	82.2(2)	81.7(2)
$C_{carbonyl}$					
C-Ru-C	89.7(2)	89.2(2)	87.7(2)	88.0(4)	89.2(4)
C-Ru-C	88.3(2)	89.2(2)	90.2(2)	90.1(4)	89.7(4)
Torsion angles					
L−Ru−Ru−L	−18.5(2)	−8.2(5)	−3.0(4)	32.5(5)	−40.1(5)

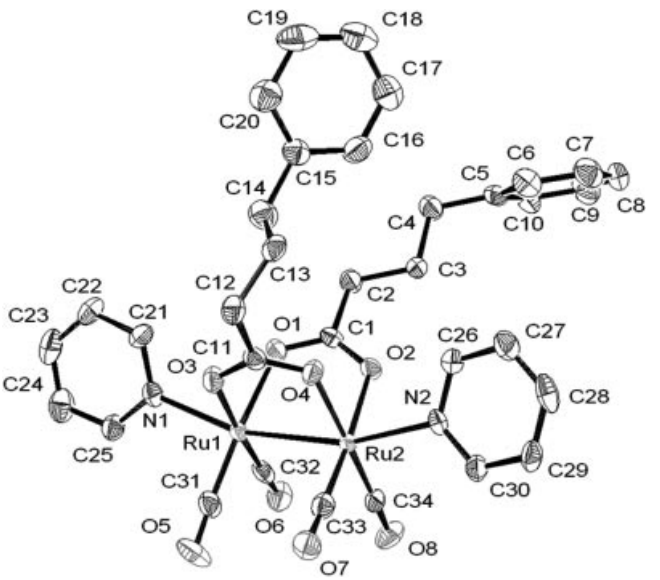


Figure 3. ORTEP drawing of **5**, at 50 % probability level for thermal displacement ellipsoids, with hydrogen atoms omitted for clarity.

The OCO bond angles of the carboxylato bridges [**2**: 126.6(4) and 127.9(4)°, **3**: 125.9(5) and 127.0(5)°, **5**: 124.9(4) and 125.0(4)°, **6A**: 124.2(8) and 125.4(8)°, **6B**: 123.5(8) and 125.1(7)°] differ only slightly from those observed in other $Ru_2(CO)_4(O_2CR)_2L_2$ complexes [2, 3b, 3d].

The unit cell of complex **6** contains two symmetry-independent molecules, identified **6A** and **6B**, respectively. However, the two molecules are almost identical, the main difference being in the relative position of the phenyl rings of the two coordinated phenylbutyl carboxylato bridging ligands.

Diruthenium sawhorse-type complexes containing porphyrin-derived ligands show interesting anti-cancer properties [13]. Ethacrynic acid and chlorambucil are two biologically active acids, ethacrynic acid is a Glutathione S-Transferase inhibitor (an enzyme involved in the process of detoxification of the cell) [14], while chlorambucil is an alkylating agent inducing death cell by apoptosis [15]. According to the X-ray analysis structures of complexes **2** and **3**, the coordination of ethacrynic acid and chlorambucil do not induce any changes in their structure. They are coordinated to the ruthenium atoms by the carboxylato bridge keeping their active parts free, the methylene group and the two chloro-ethyl arms, respectively. However, complexes **1**−**4** showed no cytotoxicity on human ovarian cancer cells, due probably to their very low solubility in water.

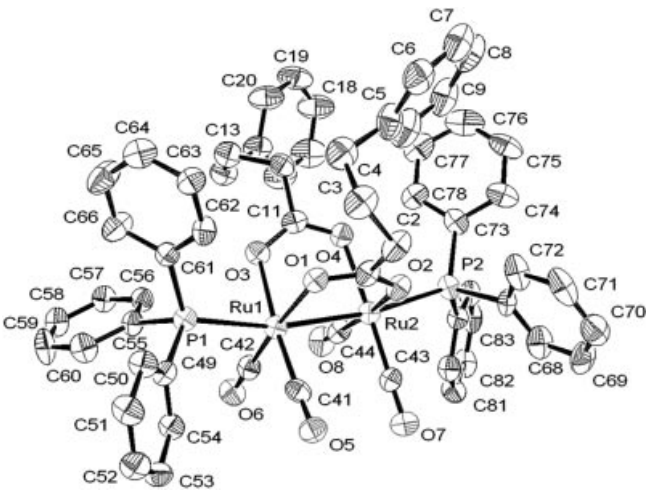


Figure 4. ORTEP drawing of **6A**, at 50 % probability level for thermal displacement ellipsoids, with hydrogen atoms omitted for clarity.

In conclusion we have synthesized and structurally characterized six new sawhorse-type complexes containing various carboxylato bridging ligands. Additionally, we described a method of synthesis using milder conditions as compared to the classical method.

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