



Diruthenium tetracarbonyl complexes of sawhorse-type



Daniel Beck, Peter Mayer, Hans-Christian Böttcher*

Department of Chemistry, Ludwig Maximilian University, Butenandtstraße 5-13, 81377 Munich, Germany

ARTICLE INFO

Article history:

Received 24 April 2014

Received in revised form

26 May 2014

Accepted 27 May 2014

Available online 12 June 2014

Dedicated to Prof. Reinhard Schmutzler on the occasion of his 80th birthday.

Keywords:

Ruthenium

Carbonyl complexes

Carboxylato-bridged

Crystal structure

ABSTRACT

The reaction of $[\text{Ru}_3(\text{CO})_{12}]$ with pivalic acid in acetonitrile afforded the coordinatively unsaturated complex $[\{\text{Ru}_2(\mu\text{-O}_2\text{C}^t\text{Bu})_2(\text{CO})_4\}_n]$ (**1**) for which a so far unknown polymeric structure is assumed. Compound **1** showed in the solid as well as dissolved in non-polar aliphatic solvents and carbon tetrachloride, respectively, a deep violet color. In common organic solvents **1** is readily dissolved resulting in solutions exhibiting a yellow to orange color. On the one hand, in such solutions the polymeric structure of **1** is broken resulting in distinct compounds as the $\text{Ru}_2(\mu\text{-O}_2\text{C}^t\text{Bu})_2(\text{CO})_4$ units coordinate two monodentate solvent molecules, as shown for $[\text{Ru}_2(\mu\text{-O}_2\text{C}^t\text{Bu})_2(\text{CO})_4(\text{py})_2]$ (**3**, py = pyridine), or they coordinate ligands like phosphanes, as shown for $[\text{Ru}_2(\mu\text{-O}_2\text{C}^t\text{Bu})_2(\text{CO})_4(\text{P}^t\text{Bu}_2\text{H})_2]$ (**4**). On the other hand, in solutions of **1** the Ru_2 frameworks are linked by coordination of multidentate solvent molecules resulting in a coordination polymer which was confirmed by the crystal structure determination of $[\{\text{Ru}_2(\mu\text{-O}_2\text{C}^t\text{Bu})_2(\text{CO})_4(\text{HOC}_2\text{H}_4\text{OEt})\}_n]$ (**2**).

© 2014 Elsevier B.V. All rights reserved.

Introduction

Since some years we are interested in studies on the reactivity of coordinatively unsaturated diruthenium complexes [1]. The coordinative unsaturation in the type of compounds $[\text{Ru}_2(\mu\text{-P}^t\text{Bu}_2)(\mu\text{-H})(\mu\text{-PP})(\text{CO})_4]$ (PP = diphosphanes and *N,N*-substituted bis(diphenylphosphanyl)amines respectively) is indicated not last by an intense violet color. During coordinative saturation mostly a typical color change from violet to yellow was observed. In this context we examined compounds of the formula $[\text{Ru}_2(\mu\text{-O}_2\text{CR})_2(\text{CO})_4]$ (R = ^tBu) whereas the corresponding complex with R = 1-adamantyl (Ad) was described recently [2]. Compound $[\text{Ru}_2(\mu\text{-O}_2\text{CAD})_2(\text{CO})_4]$ was reported to be a deep purple solid, however the exact molecular structure in the solid of this material could not be elucidated to date. We used the synthetic protocol for the preparation of the latter compound and investigated the reaction of $[\text{Ru}_3(\text{CO})_{12}]$ with pivalic acid (^tBuCOOH) under similar conditions. It is well documented that reactions of triruthenium dodecacarbonyl with carboxylic acids resulted usually in the formation of so-called sawhorse-type diruthenium tetracarbonyl complexes which exhibit often a distinct polymeric structure [3]. This structure consists of dinuclear units which are combined by strong interactions between an oxygen atom of the carboxylato bridging ligand and a ruthenium atom of a

neighboring dinuclear unit. Relatively few is known on related osmium compounds which result from the reaction of $[\text{Os}_3(\text{CO})_{12}]$ with carboxylic acids. Recently an improved synthesis of similar compounds $[\text{Os}_2(\mu\text{-O}_2\text{CR})_2(\text{CO})_6]$ (R = H, Ph) was described [4] which exhibit also a sawhorse-type dimetal core. Here we report the synthesis and reactions of $[\{\text{Ru}_2(\mu\text{-O}_2\text{C}^t\text{Bu})_2(\text{CO})_4\}_n]$ (**1**) whereas the exact molecular structure of solid **1** remains unknown to date. We found that polyfunctional solvent molecules can act as the bridging ligands between $[\text{Ru}_2(\mu\text{-O}_2\text{C}^t\text{Bu})_2(\text{CO})_4]$ units resulting in a coordination polymer structure which was confirmed by an X-ray diffraction study of the novel compound $[\{\text{Ru}_2(\mu\text{-O}_2\text{C}^t\text{Bu})_2(\text{CO})_4(\text{HOC}_2\text{H}_4\text{OEt})\}_n]$ (**2**).

Experimental

General considerations

All manipulations were performed under a dry nitrogen atmosphere using conventional Schlenk techniques. Solvents were dried over sodium-benzophenone ketyl or molecular sieves and stored under nitrogen. Chemicals were purchased commercially from ABCR and used as received. IR spectra were recorded from solids with a JASCO FT/IR-460 plus spectrometer equipped with an ATR unit. NMR spectra were obtained using a Jeol Eclipse 270 instrument operating at 270 (¹H), 109 MHz (³¹P), and 68 MHz (¹³C), respectively. Chemical shifts are given in ppm from SiMe₄ (¹H, ¹³C), and 85% H₃PO₄ (³¹P). Mass spectra were recorded using a Jeol Mstation JMS-700

* Corresponding author. Tel.: +49 89218077422; fax: +49 89218077407.
E-mail address: hans.boettcher@cup.uni-muenchen.de (H.-C. Böttcher).

spectrometer. Microanalyses (C, H, N) were performed by the Microanalytical Laboratory of the Department of Chemistry, LMU Munich, using a Heraeus Elementar vario EL instrument.

Synthesis of $[\{Ru_2(\mu-O_2C^tBu)_2(CO)_4\}_n]$ (**1**)

A mixture of $[Ru_3(CO)_{12}]$ (225 mg, 0.35 mmol) and pivalic acid (216 mg, 2.12 mmol) in 25 mL of acetonitrile was refluxed for 2 h. During this time the color of the solution changed from dark red-brown to yellow. The resulting solution was cooled to room temperature and evaporated to dryness in vacuo. The dry residue exhibited a deep violet color if all of the solvent was removed. The remaining residue was dissolved in 10 mL of dichloromethane affording an orange solution. The solution was chromatographed on silica gel over a short column using the same solvent as the eluent. The solvent was removed in vacuo to dryness affording a dark violet powder of analytically pure **1**.

1: Yield: 270 mg (98%). Anal. Calcd for $C_{14}H_{18}O_8Ru_2$ (516.43): C, 32.56; H, 3.51. Found: C, 32.41; H, 3.39%. IR (solid, cm^{-1}): $\nu(CO)$: 2035vs, 1993m, 1987s, 1950vs, 1945sh, $\nu(\mu-OOC)$: 1558vs, 1482s. 1H NMR (270 MHz, C_6D_6): δ 1.80 (s, 18H, tBu). $^{13}C\{^1H\}$ NMR (68 MHz, C_6D_6): δ 27.8 (s, CCH_3), 39.9 (s, CCH_3), 199.8 (s, COO), MS (DEI): $m/z = 517 [M^+]$, 1034 $[2M^+]$.

Synthesis of $[\{Ru_2(\mu-O_2C^tBu)_2(CO)_4(HOC_2H_4OEt)\}_n]$ (**2**)

A mixture of $[Ru_3(CO)_{12}]$ (450 mg, 0.70 mmol), pivalic acid (432 mg, 4.24 mmol), and 10 mL of ethoxyethanol was refluxed for 1 h. During this time the color of the solution changed from dark orange-brown to yellow. The resulting solution was cooled to room temperature and evaporated in vacuo. The remaining oily orange residue was dissolved in 5 mL of dichloromethane and layered with 40 mL of *n*-hexane at room temperature affording orange crystals of **2** overnight which were suitable for the X-ray diffraction study.

2: Yield: 500 mg (79%). Anal. Calcd for $C_{18}H_{28}O_{10}Ru_2$ (606.55): C, 35.64; H, 4.65. Found: C, 35.40; H, 4.59%. IR (solid, cm^{-1}): $\nu(CO)$: 2033vs, 1989m, 1972s, 1932vs, $\nu(\mu-OOC)$: 1559s, 1537s, 1481s, 1424s. 1H NMR (270 MHz, C_6D_6): δ 1.14 (s, 18H, tBu), 1.21 (t, 3H, $^3J_{HH} = 7.0$ Hz, OCH_2CH_3), 3.61 (q, 2H, OCH_2CH_3 , $^3J_{HH} = 7.0$ Hz), 3.62 (t, 2H, $HOCH_2CH_2$, $^3J_{HH} = 8.0$ Hz), 3.64 (t, 2H, $HOCH_2CH_2$, $^3J_{HH} = 8.0$ Hz), 3.81 (s, 1H, $HOCH_2CH_2$). $^{13}C\{^1H\}$ NMR (68 MHz, C_6D_6): δ 14.8 (s, CH_2CH_3), 27.9 (s, CCH_3), 39.9 (s, CCH_3), 63.5 (s, CH_2), 66.7 (s, CH_2), 70.7 (s, CH_2), 200.6 (s, COO).

Synthesis of $[Ru_2(\mu-O_2C^tBu)_2(CO)_4(py)_2]$ (**3**)

Compound **1** (259 mg, 0.50 mmol, monomer) was dissolved in 25 mL of pyridine and stirred at room temperature. After few minutes the initially formed suspension changed to a clear yellow solution. After stirring for 30 min the solution was evaporated to dryness in vacuo. The residue was dissolved in 4 mL of dichloromethane and layered with 25 mL of *n*-hexane affording slightly yellow crystal plates of **3** overnight.

3: Yield: 277 mg (82%). Anal. Calcd for $C_{24}H_{28}N_2O_8Ru_2$ (674.63): C, 42.73; H, 4.18; N, 4.15. Found: C, 43.00; H, 4.29; N, 4.02%. IR (solid, cm^{-1}): $\nu(CO)$: 2010vs, 1956m, 1927vs, 1920sh, $\nu(\mu-OOC)$: 1558vs, 1428s. 1H NMR (270 MHz, acetone- d_6): δ 1.04 (s, 18H, tBu), 7.41 (m, 4H, *m*- C_5H_5N), 7.81 (m, 2H, *p*- C_5H_5N), 8.72 (m, 4H, *o*- C_5H_5N). $^{13}C\{^1H\}$ NMR (68 MHz, $CDCl_3$): δ 28.2 (s, CCH_3), 40.0 (s, CCH_3), 125.2 (s, *m*- C_5H_5N), 138.9 (s, *p*- C_5H_5N), 152.7 (s, *o*- C_5H_5N), 204.6 (s, COO).

Synthesis of $[Ru_2(\mu-O_2C^tBu)_2(CO)_4(P^tBu_2H)_2]$ (**4**)

Compound **1** (259 mg, 0.50 mmol, monomer) was suspended in 30 mL of *n*-hexane with stirring at room temperature. By adding

P^tBu_2H (292 mg, 0.37 mL, 1 mmol) immediately a clear yellow solution resulted. After stirring for 30 min the solution was evaporated to dryness in vacuo. The residue was dissolved in 5 mL of *n*-hexane and the solution was filtered. After cooling at -25 °C overnight slightly yellow rods resulted which were suitable for the X-ray diffraction study.

4: Yield: 311 mg (77%). Anal. Calcd for $C_{30}H_{56}O_8P_2Ru_2$ (808.86): C, 44.55; H, 6.98. Found: C, 44.69; H, 6.83%. IR (solid, cm^{-1}): $\nu(CO)$: 2019vs, 1965s, 1936vs, 1907m, $\nu(\mu-OOC)$: 1562vs, 1485s. 1H NMR (270 MHz, C_6D_6): δ 1.12 (s, 18H, tBu), 1.29 (d, $^3J_{PH} = 12.9$ Hz, 36H, P^tBu_2H), 3.99 (d, 2H, $J_{PH} = 303.3$ Hz, PH). $^{31}P\{^1H\}$ NMR (109 MHz, C_6D_6): δ 41.8 (s, P^tBu_2H). $^{13}C\{^1H\}$ NMR (68 MHz, C_6D_6): δ 28.5 (s, CCH_3), 31.2 (s, $PCCH_3$), 34.9 (t, $J_{PC} = 3.5$ Hz, $PCCH_3$), 40.0 (s, CCH_3), 193.3 (t, $J_{PC} = 7.7$ Hz, CO), 206.5 (t, $J_{PC} = 3.8$ Hz, COO).

X-ray structural determination

Suitable single crystals for X-ray diffraction of the compounds **2** and **4** were obtained as described in the experimental section. Crystals were selected by means of a polarization microscope, mounted on the tip of a glass fiber, and investigated on a Bruker D8 Venture (**2**) and on a Bruker D8 Quest diffractometer (**4**), respectively, using Mo-K α radiation ($\lambda = 0.71073$ Å). The structures were solved by direct methods (SHELXS) [5] for **2** and (SIR-97) [6] for **4**, respectively, and refined by full-matrix least-squares calculations on F^2 (SHELXL-97) [7]. Details of the crystal data, data collection, structure solution, and refinement parameters of the new compounds are summarized in Table 1.

Results and discussion

Preparation and characterization of new compounds

Treatment of $[Ru_3(CO)_{12}]$ with pivalic acid in refluxing acetonitrile for 2 h resulted in a yellow solution which afforded after workup by chromatography on silica gel and removing the solvent a deep violet solid. This material was analytically pure and could be identified as a compound having the formula $[\{Ru_2(\mu-$

Table 1
Crystal data and structure refinement details for compounds **2** and **4**.

| Compound | 2 | 4 |
|---|--------------------------|--------------------------|
| Empirical formula | $C_{18}H_{28}O_{10}Ru_2$ | $C_{30}H_{56}O_8P_2Ru_2$ |
| Formula weight | 606.55 | 808.85 |
| Temperature (K) | 100(2) | 200(2) |
| Crystal system | Orthorhombic | Triclinic |
| Space group | <i>Pcca</i> | <i>P</i> 1 |
| <i>a</i> (Å) | 27.1599(10) | 11.5722(3) |
| <i>b</i> (Å) | 9.4077(3) | 11.9100(4) |
| <i>c</i> (Å) | 18.8128(7) | 14.2817(4) |
| α (°) | 90 | 93.294(1) |
| β (°) | 90 | 104.079(1) |
| γ (°) | 90 | 98.269(1) |
| Volume (Å ³) | 4806.9(3) | 1880.61(10) |
| <i>Z</i> | 8 | 2 |
| ρ_{calcd} (g cm ⁻³) | 1.67628(10) | 1.42841(8) |
| μ/mm^{-1} | 1.303 | 0.929 |
| θ range for data collection (°) | 3.12–26.49 | 2.58–27.54 |
| Reflections measured | 119,327 | 31,907 |
| <i>R</i> _{int} | 0.0304 | 0.0316 |
| Observed reflections | 4555 | 7145 |
| Reflections, unique | 4932 | 8600 |
| Parameters/restraints | 282/1 | 405/0 |
| <i>R</i> (<i>F</i> _{obs}) | 0.0211 | 0.0274 |
| <i>R</i> _w (<i>F</i> ²) | 0.0513 | 0.0669 |
| <i>S</i> | 1.079 | 1.048 |
| Max electron density (e Å ⁻³) | 0.719 | 1.511 |
| Min electron density (e Å ⁻³) | −0.354 | −0.581 |

Download English Version:

<https://daneshyari.com/en/article/7757397>

Download Persian Version:

<https://daneshyari.com/article/7757397>

[Daneshyari.com](https://daneshyari.com)