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Highly efficient synthesis of mononuclear Pt-based carboxylic complexes *trans*-[$Py_2Pt(OC(O)R)_2$] (R = Me, Bu^t, Ph)

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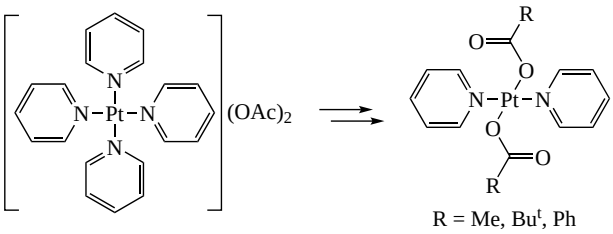
Two novel synthetic routes were suggested for square-planar carboxylic platinum(II) complexes with acetic, pivalic, and benzoic ligands. In the first method, heating ionic complex $[Py_4Pt](OAc)_2$ under reduced pressure gives a molecular compound *trans*-$[Py_2Pt(OAc)_2]$ with a moderate yield. In the second method, the same starting compound $[Py_4Pt](OAc)_2 \cdot 6H_2O$ is melted with pivalic or benzoic acids, which leads to analogous carboxylic *trans*-complexes with almost quantitative yields.



Keywords: platinum, synthesis, carboxylate complexes, pyridine, XRD analysis.

Despite the fact that the first reports on the synthesis and chemical properties of platinum carboxylates appeared in 1965,[1] research in this area continues. Modern research focuses on studying the cytotoxic properties of platinum complexes,[2] the evolution of the coordination environment in solutions[3] and the formation of nanoalloys[4] and metal nanoparticles.[5] Analogously to recently prepared Pd^{II}-based carboxylic complexes, which were used as simple 'building blocks' for the syntheses of polynuclear bimetallic compounds,[6,7] the similar Pt-based complexes may be considered as practical materials for such applications.

The synthesis of mononuclear platinum carboxylate complexes remains a significant challenge. The prevailing method involves the synthesis of platinum chloride derivatives with mono- and bidentate N-donor ligands, which then are subjected to multi-day exchange reactions with silver carboxylates. However, this method does not provide high product yields.[8] Platinum carboxylates in principle could be obtained from platinum acetate $[Pt_4(OAc)_8]$, in analogy to palladium complexes, however, this compound proved difficult to synthesize and possesses low reactivity.[9–11] Platinum acetate blue (PAB)[12] and potassium hexahydroxoplatinate $K_2[Pt(OH)_6]$[13] are often employed for the synthesis of heterometallic complexes[14,15] as alternative platinum sources.

The synthesis of ionic complexes can be one of the methods to access these compounds. Their further chemical transformations may afford both mononuclear platinum complexes and bimetallic structures.[16] Previously, we have obtained several mono- and heterometallic carboxylate complexes of platinum, including ionic ones.[16,17] Herein, we used such a compound for the synthesis of platinum complexes, namely, cation-anionic platinum compound $[Py_4Pt](OAc)_2 \cdot 6H_2O$ **1** was utilized as the starting material for the synthesis of molecular platinum complexes of the formula $[Py_2Pt(OC(O)R)_2]$.

In fact, thermolysis of **1** under reduced pressure proceeds with the elimination of all the water and two pyridine molecules resulting in a rearrangement of the ligands to the form of *trans*-$[Py_2Pt(OAc)_2]$ **2** (Figure 1 and Scheme 1, step i). The preparation of similar starting compounds with other carboxylate ligands is difficult due to the labour-intensive exchange of chloride ligands for carboxylate ones and the low yield of the final product. Therefore, we have proposed an optimized method based on the exchange reaction of carboxylate ligands in the starting complex **1** followed by thermolysis of the reaction mass under different conditions.

The reaction of **1** with boiling pivalic acid leads to compound $[Py_2Pt(OC(O)Bu^t)_2] \cdot 2Bu^tC(O)OH$ **3** (Figure 2 and Scheme 1,

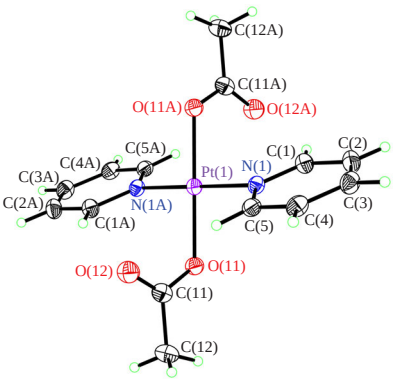
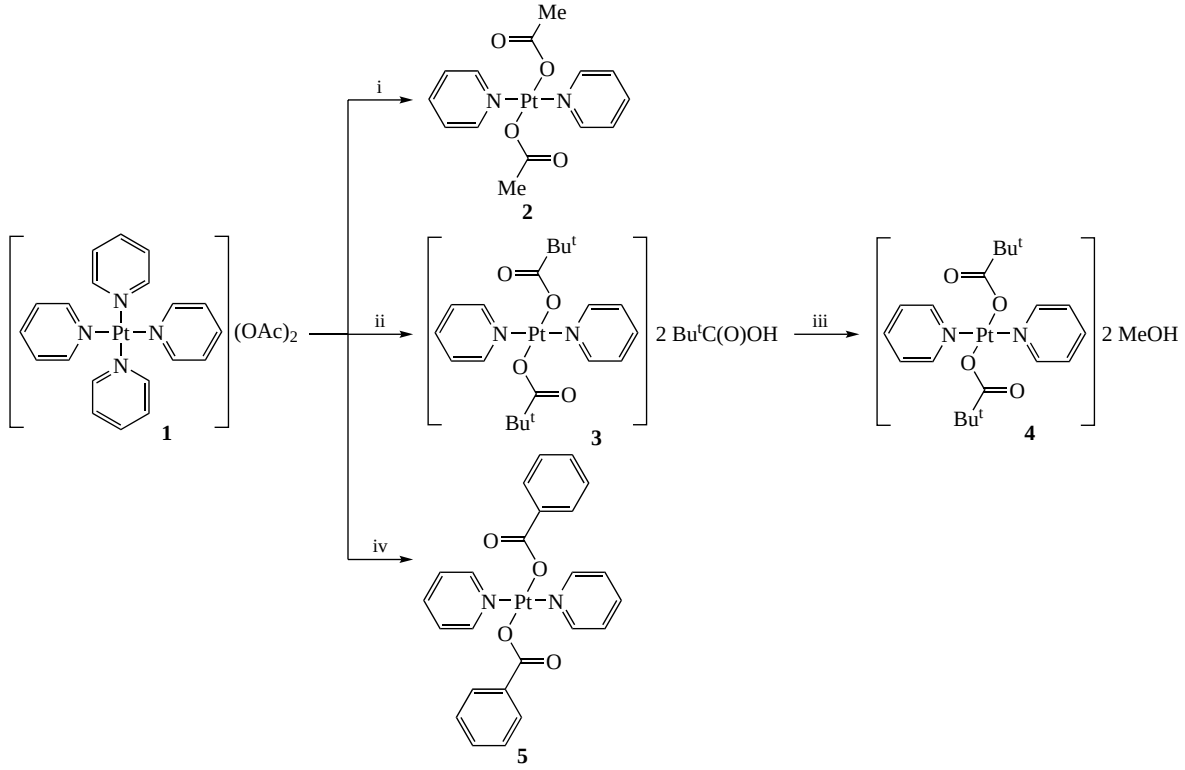


Figure 1 Molecular structure and numbering scheme for compound *trans*-$[Py_2Pt(OAc)_2]$ **2**. Atomic thermal displacement parameters are shown at 30% probability level.



Scheme 1 *Reagents and conditions*: i, reduced pressure, 90 °C; ii, Bu^{t}C(O)OH, 110 °C; iii, MeOH; iv, PhC(O)OH, 165 °C.

step ii). The recrystallization of **3** from methanol allows one to get rid of the excess pivalic acid and to obtain solvate *trans*-[$Py_2Pt(OC(O)Bu^t)_2$]·2MeOH **4** (Figure 3 and Scheme 1, step iii). Complex *trans*-[$Py_2Pt(OC(O)Ph)_2$] **5** was prepared similarly when compound **1** was reacted with melted benzoic acid at *ca*. 165 °C. Excess of benzoic acid was sublimed at 100 °C, and the desired complex **5** was obtained in crystalline form (Figure 4 and Scheme 1, step iv).†

Compound **2** crystallizes in the monoclinic space group $P2_1/c$ without additional solvent molecules (see Figure 1). The central Pt(1) atom is located at the inversion centre and is surrounded by two nitrogen atoms and two oxygen atoms in the *trans*-position, each with typical interatomic distances Pt(1)–N(1) 2.014(2) Å and Pt(1)–O(11) 2.0148(17) Å.‡

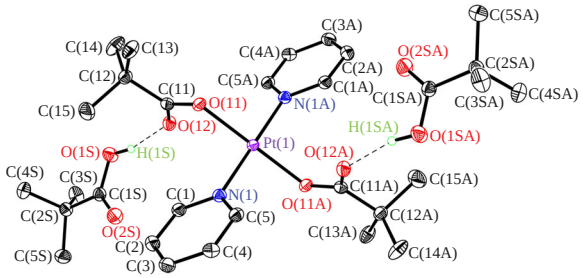


Figure 2 Crystal structure and numbering scheme for *trans*-[$Py_2Pt(OC(O)Bu^t)_2$]·2Bu^{t}C(O)OH **3**. Atomic thermal displacement parameters are shown at 30% probability level. The hydrogen atoms of pyridine and methyl groups are not shown for clarity.

† The starting complex [Py_4Pt]$(OAc)_2$·6H_2O **1** was synthesized by a known procedure.[17]

trans-[$Py_2Pt(OAc)_2$] **2**. [Py_4Pt]$(OAc)_2$·6H_2O (0.60 g, 0.81 mmol) was placed into a round-bottom flask and heated using an oil bath at 90 °C for 6 h under vacuum (*ca*. 0.133 kPa); during this operation the reaction mass was turned into a powder. The collected product was recrystallized from methanol to give colourless crystals. Yield 0.30 g (79%).

trans-[$Py_2Pt(OC(O)Bu^t)_2$]·2Bu^{t}C(O)OH **3**. [Py_4Pt]$(OAc)_2$·6H_2O **1** (0.21 g, 0.29 mmol) was placed into a test tube and excess pivalic acid was added. The reaction mixture was heated using oil bath at 110 °C for 1.5 h. The obtained colourless liquid was dissolved in hexane. As a result of slow drying of the solution colourless crystals were formed. Yield 0.19 g (87%).

trans-[$Py_2Pt(OC(O)Bu^t)_2$]·2MeOH **4**. [$Py_2Pt(OC(O)Bu^t)_2$]·2Bu^{t}C(O)OH **3** (0.19 g, 0.25 mmol) was dissolved in methanol and evaporated under reduced pressure to dryness. This operation was repeated 3 times. The obtained dry substance was dissolved in methanol and left for slow drying, as a result of which colourless crystals were formed. Yield 0.14 g (92%).

trans-[$Py_2Pt(OC(O)Ph)_2$] **5**. [Py_4Pt]$(OAc)_2$·6H_2O **1** (0.10 g, 0.14 mmol) was placed into a test tube and benzoic acid (0.55 g, 4.50 mmol) was added. The reaction mixture was heated on an oil bath at 165 °C for 2 h, a colour change from colourless to dark yellow was observed. The resulting solution was filtered through a paper filter onto a Petri dish and the excess acid was sublimed off for several hours using steam bath.

The collected product was recrystallized from methanol to give light yellow crystals. Yield 0.07 g (84%).

‡ *Crystal data for* **2**. $C_{14}H_{16}N_2O_4Pt$, F_w = 471.38, monoclinic, a = 7.7617(3), b = 11.8014(5) and c = 8.0673(3) Å, α = 90, β = 91.1421(13) and γ = 90°, V = 738.81(5) Å^3, space group $P2_1/c$, Z = 2, d_{calc} = 2.119 g cm^{-3}, $F(000)$ = 448, μ(MoK_α) = 9.513, colourless needle with dimensions *ca*. 0.350 × 0.050 × 0.030. Total of 13066 reflections (2269 unique, R_{int} = 0.0284) were measured with a Bruker D8 Venture diffractometer (graphite monochromatized MoK_α radiation, λ = 0.71073 Å) using ω- and φ-scan modes at 100(2) K. The final residuals were: R_1 = 0.0155 for 1791 reflections with $I > 2\sigma(I)$ and wR_2 = 0.0376 for all data and 98 parameters. GoF = 1.060.

Crystal data for **3**. $C_{30}H_{48}N_2O_8Pt$, F_w = 759.79, triclinic, a = 5.928(2), b = 10.8284(18) and c = 13.3992(14) Å, α = 79.606(5), β = 77.570(6) and γ = 83.998(13)°, V = 824.2(3) Å^3, space group $P\bar{1}$, Z = 1, d_{calc} = 1.531 g cm^{-3}, $F(000)$ = 384, μ(MoK_α) = 4.957, colourless needle with dimensions *ca*. 0.200 × 0.060 × 0.040. Total of 13290 reflections (3616 unique, R_{int} = 0.0599) were collected using Rayonix SX165 CCD one-circle diffractometer at the 'Belok' beamline[18] of the National Research Centre 'Kurchatov Institute' (Moscow, Russian Federation, synchrotron focusing-mirror monochromatized radiation, λ = 0.75268 Å) using φ-scan modes at 100(2) K. The final residuals were: R_1 = 0.0278 for 3616 reflections with $I > 2\sigma(I)$ and wR_2 = 0.0662 for all data and 197 parameters. GoF = 1.027.

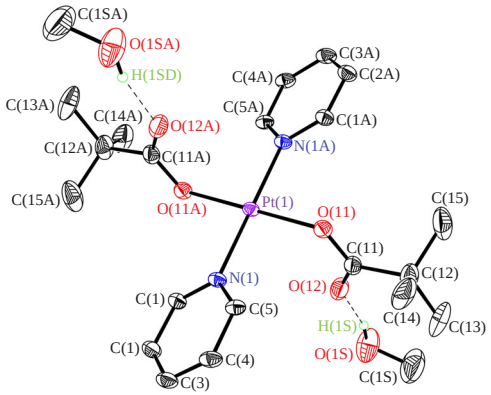


Figure 3 Crystal structure and numbering scheme for *trans*-$[Py_2Pt(OC(O)Bu^t)_2]\cdot 2MeOH$ **4**. Atomic thermal displacement parameters are shown at 30% probability level. The hydrogen atoms of pyridine and methyl groups are not shown for clarity.

According to X-ray diffraction data, compound **3** crystallizes in the triclinic space group $P\bar{1}$ with two neutral pivalic acid molecules forming hydrogen bonds with the oxygen atoms of pivalate anions O(1S)–H(1S)···O(12) with an interatomic distance of 2.638(4) Å between donor and acceptor atoms. The central Pt(1) atom lies at the inversion centre and is surrounded by two nitrogen atoms and two oxygen atoms in the *trans*-position, each with interatomic distances Pt(1)–N(1) of 2.023(3) Å and Pt(1)–O(11) 2.028(2) Å which typical for square-planar platinum and palladium-based complexes.[24]

According to X-ray diffraction data, compound **4** crystallizes in the triclinic space group $P\bar{1}$ with two solvate methanol molecules. These molecules form hydrogen bonds between themselves and the oxygen atoms of pivalate anions O(1S)–H(1S)···O(12) with an interatomic distance of 2.719(5) Å. The central Pt(1) atom is located at the inversion centre and is surrounded by two nitrogen atoms and two oxygen atoms in the *trans*-position, each with typical interatomic distances Pt(1)–N(1) 2.029(2) Å and Pt(1)–O(11) 2.003(2) Å.

Crystal data for **4**. $C_{22}H_{36}N_2O_6Pt$, F_w = 619.62, triclinic, a = 5.8821(3), b = 8.6827(5) and c = 12.9466(7) Å, α = 97.3709(9), β = 96.5006(9) and γ = 104.9594(8)°, V = 626.09(6) Å^3, space group $P\bar{1}$, Z = 1, d_{calc} = 1.643 g cm^{-3}, $F(000)$ = 308, μ(MoK$_\alpha$) = 5.640, colourless plate with dimensions *ca.* 0.130 × 0.110 × 0.020. Total of 18313 reflections (3832 unique, R_{int} = 0.0370) were measured with a Bruker D8 Venture diffractometer (graphite monochromatized MoK$_\alpha$ radiation, λ = 0.71073 Å) using ω- and φ-scan modes at 100(2) K. The final residuals were: R_1 = 0.0227 for 3832 reflections with $I > 2\sigma(I)$ and wR_2 = 0.0560 for all data and 180 parameters. GoF = 1.043.

Crystal data for **5**. $C_{24}H_{20}N_2O_4Pt$, F_w = 595.51, monoclinic, a = 10.930(3), b = 9.2732(10) and c = 11.0814(19) Å, α = 90, β = 109.042(12) and γ = 90°, V = 1061.7(4) Å^3, space group $P2_1$, Z = 2, d_{calc} = 1.863 g cm^{-3}, $F(000)$ = 576, μ = 7.651, colourless plate with dimensions *ca.* 0.230 × 0.150 × 0.070. Total of 17463 reflections (5040 unique, R_{int} = 0.0563) were collected at the 'Belok' beamline[18] of the National Research Centre 'Kurchatov Institute' at 100(2) K. The final residuals were: R_1 = 0.0283 for 4779 reflections with $I > 2\sigma(I)$ and wR_2 = 0.0778 for all data and 281 parameters. GoF = 1.087.

The reflection intensity was corrected for absorption using SADABS[19] (for **2** and **4**) and XDS software[20] (for **3** and **5**). The structures were solved by direct methods[21] and refined by full-matrix least-squares technique[22] on F^2 with anisotropic displacement parameters for non-hydrogen atoms. The hydrogen atoms were placed in calculated positions and refined using a riding model with fixed isotropic displacement parameters [U_{iso}(H) = 1.5U_{eq}(C) for methyl groups and U_{iso}(H) = 1.2U_{eq}(C) for all other H-atoms]. All calculations were carried out using the SHELXTL[19] program and Olex2 X-ray data visualization program package.[23] For details, see Online Supplementary Materials, Table S1.

CCDC 2162275, 2299674, 2162276, 2263470 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* https://www.ccdc.cam.ac.uk.

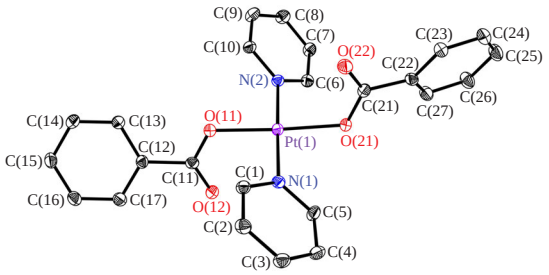


Figure 4 Crystal structure and numbering scheme for *trans*-$[Py_2Pt(OC(O)Ph)_2]$ **5**. Atomic thermal displacement parameters are shown at 30% probability level. The hydrogen atoms of pyridine and methyl groups are not shown for clarity.

Single crystals of compound **5** were obtained upon concentrating from solution as light-yellow crystals. They crystallize in the monoclinic space group $P2_1$ without additional solvent molecules, just as isostructural Pd-based analogue[25] (Figure 4). All atoms of the molecule are located in general positions, which leads to some nonequivalence of the interatomic distances Pt(1)–N(1) 2.022(5) Å, Pt(1)–N(2) 2.014(5) Å, Pt(1)–O(11) 2.016(4) Å and Pt(1)–O(21) 2.026(4) Å, respectively, in contrast to structures **2**, **3** and **4**. The resulting coordination environment of the synthesized platinum complexes is similar to previously described palladium complexes with N-donor ligands.[26,27]

To conclude, the work presents a facile method for the preparation of molecular carboxylate complexes of platinum with pyridine of general formula *trans*-$[Py_2Pt(OC(O)R)_2]$. This method is based on the reaction of starting complex $[Py_4Pt](OAc)_2\cdot 6H_2O$ with an excess of carboxylic acids followed by thermolysis and removal of excess acid. The resulting *trans*-compounds can be proposed as precursors of supported catalysts or for the preparation of heterometallic polynuclear carboxylate-bridged complexes.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2024.10.013.

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