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Bismuth−Palladium Heterometallic Carboxylate as a Single-Source Precursor for the Carbon-Supported Pd−Bi/C Catalysts

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The heterometallic complex $[Bi_2Pd_2(O_2CCF_3)_{10}(HO_2CCF_3)_2]$ (**1**) was obtained by the solid state reaction of Bi^{III} trifluoroacetate/trifluoroacetic acid adduct with unsolvated trinuclear Pd^{II} trifluoroacetate. The crystal structure of **1** consists of discrete tetranuclear molecules, in which two paddlewheel $[BiPd(O_2CCF_3)_4]$ units are connected by two chelating-bridging trifluoroacetate ligands through bismuth ends. There are no metal−metal bonds in the tetrameric structure of **1**, since both Bi···Pd (3.0843(4) Å) and Bi···Bi (4.5074(4) Å) distances are too long to be considered as bonding interactions. A study of the solution behavior revealed that not only the coordinated trifluoroacetic acid in **1** can be effectively replaced by other donor solvent molecules but also the tetranuclear complex can be cleaved in solution into discrete dinuclear Bi−Pd species. Complex **1** was used as precursor for the preparation of a bimetallic Pd−Bi carbon-supported catalyst. The preparation procedure included the modification of the carbon support to increase the number of oxygenated functions at its surface followed by grafting complex **1** via ligand exchange for surface carboxylates and activating thermally. The resulting catalyst, consisting of small supported metallic particles, was found to be more active than the reference materials prepared from multisource homometallic Pd and Bi precursors.

Introduction

The promotion of noble metal-based heterogeneous catalysts by heavy post-transition elements such as Bi, Pb, Sn, and Sb was known for a long time to play a crucial role in the improvement of their overall catalytic performances (activity, sometimes selectivity) and/or their lifetime in a wide series of selective liquid-phase oxidation reactions of functionalized organic substrates.[1−3] The use of such catalysts in the oxidation of carbohydrates is particularly attractive, since these processes provide an environmentally friendly route to convert the renewable resources under mild conditions into many intermediate chemicals that are of primary importance for the synthesis of high added value chemicals in the food, cosmetic, and pharmaceutical industries. In particular, carbon-supported Bi−Pd catalysts were successfully employed in the partial oxidation of alcohols and aldehydes to carboxylic acids using molecular oxygen or air. The selective and almost quantitative aqueous phase conversion of glucose to gluconic acid,[4,5] of glyoxal to glyoxalic acid,[6,7] and of propylene glycol to lactic and pyruvic acids[8] have been actively investigated. Silica-supported Bi−Pd catalysts were also used for the synthesis of benzylacetate by oxyacetoxylation of toluene.[9]

Heterogeneous catalysts are usually finely divided solids in a bulk or supported form. The supported active phase generally consists of an oxide or metal, or even a bimetal. In the latter case, the homogeneity of the surface can be questioned as it is very difficult to disperse two metals while making them intimately mixed on each spot of the support. However, it has been shown that synergetic effects can occur

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with cooperativity between the two metals leading to enhanced catalytic properties. It has also been demonstrated[10] that close contact between the two metals is a prerequisite for such effects. We have shown,[11] in particular for the carbon-supported Pd−Bi catalysts, that the very nature of the alloys formed on the surface could have a drastic influence on the catalytic activity in liquid phase oxidation. Therefore, the use of heterometallic polynuclear complexes as metal precursors should open new venues in this area.

Carboxylate complexes offer additional advantages as catalyst precursors. First, they can be activated thermally under an inert atmosphere and assist in metal reduction without surface contamination by heteroatoms such as sulfur or phosphorus.[12] Second, they allow spectroscopic investigations as (OCO) stretching bands are sensitive to the bonding mode.[13] Third, they are capable of undergoing instant ligand exchange processes under mild conditions.[14] Finally, they are usually soluble in a variety of common solvents, including water.[15]

Several heterometallic carboxylate-bridged palladium compounds are known,[16] none of them contain bismuth. We have recently suggested[17] an effective solid-state approach for the preparation of Bi^{II}-M^{II} (M^{II} = Rh, Ru) heterometallic paddlewheel carboxylates using a unique ability of bismuth(II) trifluoroacetate to act as a metalloligand toward transition metal fragments. Bismuth(III) carboxylates are also promising candidates for the formation of heterometallic species. Metal centers in coordinatively unsaturated Bi^{III} carboxylates are known to be highly Lewis acidic and exhibit high coordination numbers, up to 10.[18] Whitmire et al. developed[19] a successful strategy for the synthesis of heterometallic compounds using bismuth(III) salicylate via direct adduct formation with the second metal complexes bearing basic donor atoms. Bismuth(III) trifluoroacetate is also known to form coordinatively unsaturated fragments. Thus, it has been shown[20] that even its adduct with trifluoroacetic acid crystallizes in the form of polymeric chains in the solid state to accommodate the coordination number of eight for bismuth atoms.

In this paper, we describe the synthesis and detailed characterization of heterometallic $Bi^{III}-Pd^{II}$ carboxylate and its use as a single-source precursor for heterogeneous catalysts. The preparation strategy consists of treating an active carbon support to increase its surface functionality followed by grafting the bimetallic molecules onto it via carboxylate ligand exchange. The obtained immobilized complex was activated thermally and tested in the selective oxidation of D-glucose into D-gluconic acid. This reaction is of interest in an environmentally conscious framework since it is carried out in water and employs renewable feedstock as a raw material. Moreover, the reaction product is a useful chelating agent. Importantly, the occurrence of subtle bimetallic effects[5] in this reaction has been unraveled and requires further investigation.

Experimental Section

General Procedures. All of the manipulations were carried out in a dry, oxygen-free, dinitrogen, or argon atmosphere by employing standard ampule, glovebox, and Schlenk line techniques. All chemicals, unless otherwise described, were purchased from Aldrich and used as received. Anhydrous solvents were kept under the protection of activated molecular sieves. UV−vis spectra were acquired using a Hewlett-Packard 8452A diode array spectrophotometer. The attenuated total reflection (ATR) IR spectra were recorded on a Perkin-Elmer Spectrum 100 FT-IR spectrometer. NMR spectra were obtained using a Bruker Avance 400 spectrometer at 400 MHz for ^1H and at 376.47 MHz for ^{19}F. Chemical shifts (δ) are reported in ppm relative to residual solvent peak for ^1H and to $CFCl_3$ for ^{19}F.

Synthesis. $[Bi(O_2CCF_3)_3(HO_2CCF_3)]$. Bismuth(III) trifluoroacetate adduct with trifluoroacetic acid was prepared following the literature procedure[20] with minor changes. Trifluoroacetic anhydride (5.0 mL, 35.4 mmol) was added to the suspension of bismuth oxide powder (3.0 g, 6.7 mmol) in dichloromethane (10 mL) under nitrogen. After 1 h, a trifluoroacetic acid (10 mL, 139 mmol) was slowly added, and the mixture was stirred overnight at room temperature to afford a clear solution. The solution was then stored in a freezer at 0 °C, and colorless needles started to appear after 48 h at the bottom of the flask. The precipitation was completed after 1 week, and the solvent was removed by cannula. The resulting $[Bi(O_2CCF_3)_3(HO_2CCF_3)]$ crystals were dried under vacuum at room temperature for 1 day. The purity of the bulk product has been confirmed by comparison of the powder diffraction pattern with the theoretical one calculated on the basis of single crystal data[20] analysis. ^1H NMR (d_6-acetone, −20 °C): $\delta = 14.22$ (s); ^{19}F NMR ($CDCl_3$, 22 °C): $\delta = -75.76$ (s, br). ^{19}F NMR (d_6-acetone, −20 °C): $\delta = -75.75$ (s), −76.19 (sh); UV/vis (C_7H_8, 22 °C): λ_{max} (ε, $M^{-1}\cdot cm^{-1}$) = 276 (sh, 740), 290 (1560) nm.

$[Bi_2Pd_2(O_2CCF_3)_{10}(HO_2CCF_3)_2]$ (1). A stoichiometric mixture of $[Bi(O_2CCF_3)_3(HO_2CCF_3)]$ (0.066 g, 0.10 mmol) and $[Pd(O_2CCF_3)_2]_3$ (0.034 g, 0.033 mmol) was sealed in an evacuated glass ampule. The ampule was placed in an electric furnace having a small temperature gradient along the length of the tube. The temperature in the hot zone was kept in different experiments at 120−130 °C for 3 days to allow yellow-brown block crystals to be deposited in the cold section of the container where the temperature was set about 6 °C lower. The purity of the bulk product has been confirmed by comparison of the powder diffraction pattern with the theoretical one calculated on the basis of single crystal data. Yield: about 55% (crystals

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Table 1. Crystallographic Data and Structure Refinement Parameters for $[Bi_2Pd_2(O_2CCF_3)_{10}(HO_2CCF_3)_2]$ (**1**), $[Bi_2Pd_2(O_2CCF_3)_{10}(H_2O)_2]\cdot 2Me_2CO$ (**2**), and $[BiPd(O_2CCF_3)_5(THF)_3]$ (**3**)

	1	2	3
formula	$Bi_2Pd_2O_{24}$-$C_{24}F_{36}H_2$	$Bi_2Pd_2O_{24}$-$C_{26}F_{30}H_{16}$	$BiPdO_{13}C_{22}$-$F_{15}H_{24}$
fw	1989.02	1913.15	1096.79
crystal system	triclinic	triclinic	monoclinic
space group	$P\bar{1}$	$P\bar{1}$	$P2_1$
a (Å)	9.9277(5)	10.141(5)	8.780(2)
b (Å)	11.6374(6)	11.545(7)	19.926(6)
c (Å)	11.6834(6)	12.051(6)	10.043(3)
α (deg)	66.2120(10)	115.962(12)	90
β (deg)	74.7380(10)	95.546(14)	95.018(4)
γ (deg)	81.7510(10)	93.337(15)	90
V (Å^3)	1190.51(11)	1254.6(12)	1750.4(8)
Z	1	1	2
ρ_{calcd} (g·cm^{-3})	2.774	2.532	2.081
μ (mm^{-1})	8.335	7.887	5.670
transm factors	0.3678−0.4895	0.3310−0.5710	0.2997−0.6598
temp (K)	173(2)	173(2)	173(2)
data/restr/params	5292/36/419	3547/352/382	5511/94/496
$R1^a$, $wR2^b$			
$I > 2\sigma(I)$	0.0310, 0.0731	0.0303, 0.0777	0.0297, 0.0660
all data	0.0380, 0.0760	0.0320, 0.0787	0.0355, 0.0680
quality-of-fit^c	1.055	1.004	0.950

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR2 = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$. [c] Quality-of-fit $= [\sum[w(F_o^2 - F_c^2)^2]/(N_{obs} - N_{params})]^{1/2}$, based on all data.

collected). Elemental analysis (%) calcd for $C_{24}H_2O_{24}F_{36}Bi_2Pd_2$: C, 14.48; O, 19.31; F, 34.39; Bi, 21.02; Pd, 10.70; found: C, 14.23; O, 19.78; F, 34.02; Bi, 21.20; Pd, 10.42. ^{19}F NMR ($CDCl_3$, 22 °C): $\delta = -73.05$ (s), -75.63 (s, br); ^1H NMR (d_6-acetone, −50 °C): $\delta = 9.17$ (s); ATR-IR (cm^{-1}): 3400br, 1694s, 1671s, 1602m, 1439w, 1155s, 855m, 788s, 733s, 698m; UV/vis ($CHCl_3$, 22 °C): λ_{max} (ε, M^{-1}·cm^{-1}) = 258 (312), 278 (sh, 1443), 286 (3210) nm.

$[Bi_2Pd_2(O_2CCF_3)_{10}(H_2O)_2]\cdot 2Me_2CO$ (2). Crystals of **1** (20 mg) were dissolved in 1 mL of wet acetone in an NMR tube and kept in a freezer at −10 °C. Red crystals of **2** were collected at the bottom of the tube after few hours.

$[BiPd(O_2CCF_3)_5(THF)_3]$ (3). Crystals of **1** (20 mg) dissolved in 0.5 mL of tetrahydrofuran (THF) were layered with hexanes in an NMR tube and kept in a freezer at −10 °C. Orange crystals of **3** accumulated at the bottom of the tube after 3 days. ^1H NMR ($CDCl_3$, 22 °C): $\delta = 1.91$ (br), 3.83 (br); ^{19}F NMR ($CDCl_3$, 22 °C): $\delta = -73.63$ (s), -76.16 (s); ATR−IR (cm^{-1}): 2984w, 2895w, 1697s, 1640m, 1629m, 1581w, 1440m, 1428w, 1366w, 1185s, 1151s, 1040m, 1014m, 918w, 872m, 849s, 797m, 788s, 731s; UV/vis ($CHCl_3$, 22 °C): λ_{max} (ε, M^{-1}·cm^{-1}) = 216 (2072), 244 (5735) nm.

X-ray Diffraction Procedures. X-ray powder diffraction data were collected using an automated Bruker D8 Advance diffractometer (Cu K_α radiation, focusing Göbel Mirror, LynxEye one-dimensional detector, step 0.01° 2θ, 20 °C). The crystalline samples under investigation were grounded and placed in the dome-like airtight zero-background holders inside the glovebox.

Selected single crystals suitable for X-ray crystallographic analysis were used for structure determination. The X-ray intensity data were measured at 173(2) K (Bruker KRYO-FLEX) on a Bruker SMART APEX CCD-based X-ray diffractometer system. The data collection and refinement procedures have been described elsewhere.[21] In the process of structure solution, it was found that the fluorine atoms of some CF_3 groups in **1**−**3** and the carbon atoms of THF molecules in **3** appeared to be disordered. This disorder was modeled in each individual case. Anisotropic displacement parameters were assigned to all non-hydrogen atoms, except the disordered fluorines and carbons. For **1**, the hydrogen atoms were located and refined independently, while the hydrogen atoms in **2** and **3** were included in idealized positions for structure factor calculations. The crystals of **2** were found to slowly lose crystallinity even during low-temperature data collection. Nevertheless, the short-time data acquisition allows to obtain the crystal structure of satisfactory quality. Relevant crystallographic data are summarized in Table 1. Selected bond lengths for compounds **1**−**3** are given in Table 2.

Table 2. Selected Bond Distances (Å) in Compounds **1**−**3**^{a}

	1	2	3
Pd−O (av.)	1.986(4)	1.988(4)	2.005(6)
Bi−O_b	2.309(4)−2.671(4)	2.317(4)−2.647(4)	2.476(5)−2.528(6)
Bi−O_c	2.296(3)	2.322(4)	2.430(5), 2.463(6)
Bi−$O_{c\text{-}b}$	2.643(4), 2.722(4)	2.574(4), 2.789(4)	
Bi−O_L	2.511(4)	2.321(5)	2.444(5), 2.464(6)
Bi···Pd	3.0843(4)	3.0606(13)	3.2222(9)

[a] b − bridging; c − chelating; c-b − chelating-bridging carboxylate oxygen; L = HO_2CCF_3 (**1**), H_2O (**2**), THF (**3**).

Grafting of 1 onto Functionalized Carbon Support. The support used is an activated carbon SX+ from NORIT (granulometry: 50−100 μm, S_{BET} ~900 m^2/g, 32 mmol acidic groups/100 g_C), which was first treated with HNO_3 to increase the number of surface oxygenated groups, as described previously.[14] The functionalized carbon obtained was characterized by a specific surface area S_{BET} ~ 700 m^2/g and an acidity (determined by Boehm's titration) of 325 mmol acidic groups/100 g_C.

A solution of 0.094 g of complex **1** in 20 mL of degassed acetone was prepared in a Schlenk flask, while 0.270 g functionalized carbon were dried under vacuum at room temperature for 2 h in another Schlenk tube. The carbon was then added to the yellow solution and stirred at room temperature for 24 h. The solid was recuperated by filtration and washed two times with acetone. All these steps were performed under nitrogen, and the solid obtained was kept in a glovebox under argon prior to any further use.

Preparation of Pd(5 wt %)-Bi(5 wt %)/C Reference Materials. Reference materials were obtained by deposition of 0.105 g palladium acetate, $Pd(O_2CCH_3)_2$, (ROCC) and 0.068 g bismuth oxoacetate, ($BiO(O_2CCH_3)$, obtained from Bi_2O_3 (Janssen Chimica) following a procedure reported earlier[12]) onto 0.9 g untreated SX+ carbon or onto 0.9 g functionalized carbon, as follows: in the first step, a mixture of carbon and palladium acetate was sonicated in heptane (100 mL) during 30 min, the solvent was then slowly evaporated under reduced pressure at room temperature, and in the second step, the procedure was repeated with the solid obtained and bismuth oxoacetate.

Thermal Activation. The three supported samples were activated by thermal heating in a CARBOLITE tubular oven under a nitrogen flow at 500 °C for 8 h.

Solid Samples Characterization. ICP-OES analyses were performed by Medac Ltd. (U.K.) after digestion of the solid samples in acid overnight. Atomic absorption analyses were carried out on a PERKIN-ELMER 3110 spectrometer. Calibration curves were established with standard solutions of variable concentrations. X-ray photoelectron spectroscopy (XPS) was carried out on a SSI-X-probe (SSX-100/206) Fisons spectrometer. The samples were fixed to small troughs using double-face adhesive tape and then placed on an insulating homemade ceramic sample holder (Macor, Switzerland). A nickel grid was fixed above the samples, and an electron flood

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gun was set at 8 eV to overcompensate for the positive charging of the samples during analysis. The analyzed area was approximately 1.4 mm^2 and the pass energy was set at 150 eV. Under these conditions, the resolution determined by the full width at half-maximum (fwhm) of the Au4f$_{7/2}$ peak was around 1.6 eV. The energy scale calibration was done with reference to the Au4f$_{7/2}$ peak at 84 eV, and the binding energies were set up by fixing the C1s peak (*C*-(C,H) component) at 284.8 eV. The analyses were carried out with the following experimental parameters: resolution = 4, spot size = 1000 μm. Four photopeaks (C1s, O1s, Pd3d, and Bi4f) were systematically analyzed. The XPS results were decomposed, with the CasaXPS software, using a sum of Gaussian/Lorentzian (85/15) after subtraction of a Shirley-type baseline. The constraints used for decomposition of the Pd3d peak were as follows: imposing an area ratio Pd3d$_{5/2}$/Pd3d$_{3/2}$ of 1.5, a difference in the binding energies (Pd3d$_{3/2}$ − Pd3d$_{5/2}$) of 5.26 eV and a fwhm ratio (for the Pd3d$_{5/2}$/Pd3d$_{3/2}$ peaks) of 1. The constraints used for decomposition of the Bi4f peak were as follows: imposing an area ratio Bi4f$_{5/2}$/Bi4f$_{7/2}$ of 0.75, a difference in the binding energies (Bi4f$_{5/2}$ − Bi4f$_{7/2}$) of 5.31 eV and a fwhm ratio (for the Bi4f$_{7/2}$/Bi4f$_{5/2}$ peaks) of 1. The catalysts were characterized by X-ray powder diffraction on a SIEMENS D-5000 diffractometer using the Cu K$_\alpha$ radiation (Ni filter). The crystalline phases present in the samples were identified by comparison with the JCPDS−ICDD database. SEM (scanning electron microscopy) images were acquired on a FEG digital scanning microscope (DSM 982 Gemini from LEO) equipped with an EDXS detector (Phoenix CDU LEAP). The samples were fixed by double-sided conducting adhesive tape onto 5 mm diameter aluminum specimen stubs from Agar Scientific.

Measurements of the Catalytic Performance. The oxidation of D-glucose into D-gluconic acid was chosen as a test reaction to evaluate the performance of the obtained catalysts. The catalytic tests were performed in a 600 mL double-wall glass reactor. The glucose solution (72 g D-glucose (ACROS, 99+ %) in 375 mL of water) was stirred at 1000 rpm and heated at 50 °C via water circulation in the outer compartment of the reactor. Once the temperature was stabilized, a known amount of catalyst (0.054 g) dispersed in 25 mL of water was added to the solution. The pH of the solution was measured continuously by a combined Ag/AgCl electrode (Beckman, model 39843) coupled with an automatic titration device (METROHM, Stat Titrino 718) to keep the mixture at a constant pH by the addition of a 5 mol·L^{-1} NaOH solution. The pH was adjusted to a value of 9.2, and the oxidation reaction began with the introduction of oxygen, which flow rate was fixed at 0.4 mL·min^{-1}.

After 4 h, the catalyst was removed from the mixture by filtration, washed with ethanol and ether, and dried under vacuum. The filtrate was analyzed by atomic absorption spectrometry (PERKIN-ELMER 3110) to quantify the metal leaching that could have occurred during the catalytic tests. The catalytic performance was determined directly from the amount of NaOH added, given that the main product of the reaction is gluconic acid, which is continuously neutralized by an addition of NaOH to maintain the pH constant during the reaction. The results were expressed as X_{GLU}, the conversion of D-glucose, or as X_{GLU}/m_{Pd}, the conversion of D-glucose normalized with respect to the amount of Pd introduced in the reactor.

Results and Discussion

Synthesis and Characterization of Heterometallic Bi−Pd Complex. The heterometallic complex, $[Bi_2Pd_2(O_2CCF_3)_{10}(HO_2CCF_3)_2]$ (**1**) was obtained by the solid state reaction of Bi^{III} trifluoroacetate/trifluoroacetic acid adduct, $[Bi(O_2CCF_3)_3(HO_2CCF_3)]$, with unsolvated trinuclear Pd^{II} trifluoroacetate:

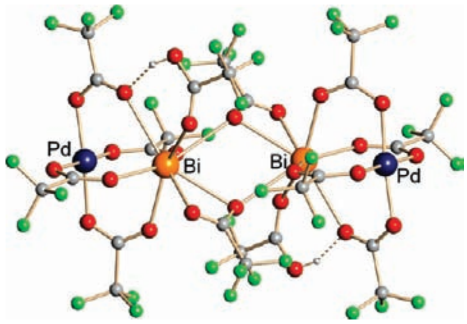

Figure 1. Molecular structure of $[Bi_2Pd_2(O_2CCF_3)_{10}(HO_2CCF_3)_2]$ (**1**).

$$6[Bi(O_2CCF_3)_3(HO_2CCF_3)] + 2[Pd_3(O_2CCF_3)_6] \rightarrow 3[Bi_2Pd_2(O_2CCF_3)_{10}(HO_2CCF_3)_2] \qquad (1)$$

Although a similar bimetallic $[CdPd(CH_3COO)_4(HO_2CCH_3)]_2$ complex was prepared in solution,[16d] our multiple attempts to obtain **1** in common solvents and trifluoroacetic acid all have failed. Shiny orange crystals of **1** quickly become dull, once the reaction vessel is cooled down, but still can be used for X-ray diffraction study. The heterometallic complex shows poor stability toward air and moisture and should be kept in a closed vial or in a glovebox. Compound **1** can be dissolved in a variety of common coordinating and aromatic solvents but exhibits limited solubility in non-coordinating solvents like dichloromethane and chloroform.

The solid state structure of **1** consists of discrete tetranuclear units (Figure 1), in which two bismuth atoms are flanked by two palladium atoms and bridged by carboxylate ligands. Alternatively, the structure can be viewed as built of two paddlewheel $[BiPd(O_2CCF_3)_4]$ units connected by two chelating-bridging trifluoroacetate ligands through bismuth ends. Each palladium atom maintains a square planar coordination of four oxygen atoms, typical for Pd^{II} carboxylates.[22] On the other hand, the coordination environment for the central part of the molecule, where two bismuth atoms reside, resembles that in the chain structure of bismuth(III) trifluoroacetate with comparable Bi−O bond lengths. Bismuth atoms are held together by two carboxylate groups. As it can be reasonably expected for Bi^{III} and Pd^{II} centers, there are no metal−metal bonds in this tetramer, both Bi···Pd (3.0843(4) Å) and Bi···Bi (4.5074(4) Å) distances are too long to be considered as bonding interactions. The axial positions at the palladium sites are empty; intermolecular (axial) Pd···Pd and Pd···O distances are measured at 3.3672(8) and 2.988(4) Å, respectively. Each bismuth atom in **1** is 8-coordinated by seven carboxylate oxygens and one O-atom coming from η^1-trifluoroacetic acid. This dangling trifluoroacetic acid is oriented in such a way that the H atom from the hydroxyl group forms a strong hydrogen bond (O−H···O, 1.788(7) Å, 155.8°) with the oxygen atom from one of the Bi/Pd bridging trifluoroacetate ligands. The presence of such strong hydrogen bonding in **1** is likely a reason why these

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[22] Batsanov, A. S.; Timko, G. A.; Struchkov, Yu. T.; Gerbeleu, N. V.; Indrichan, K. M.; Popovich, G. A. *Koord. Khim* **1989**, *15*, 688–693.

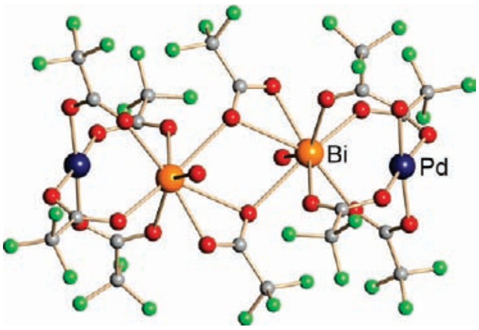

Figure 2. Molecular structure of $[Bi_2Pd_2(O_2CCF_3)_{10}(H_2O)_2]\cdot 2Me_2CO$ (**2**). Acetone molecules and hydrogen atoms of water are omitted for clarity.

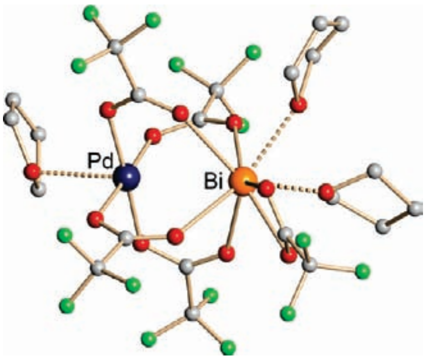

Figure 3. Molecular structure of $[BiPd(O_2CCF_3)_5(THF)_3]$ (**3**). Hydrogen atoms are omitted for clarity.

H-atoms can easily be located from the difference Fourier map in X-ray diffraction experiment. Spectroscopic characterization of compound **1** unambiguously supports the presence of coordinated trifluoroacetic acid in its structure. The IR-spectrum features a broadband centered at 3400 cm^{-1}. While the ^1H NMR spectrum of **1** in acetone is silent at room temperature, a broad signal at 9.17 ppm instantly appears at the cooling of the solution to −50 °C.

The isolation of $[Bi_2Pd_2(O_2CCF_3)_{10}(H_2O)_2]\cdot 2Me_2CO$ (**2**) crystals from the wet acetone solution of **1** provides an additional support for an assignment of oxidation states in the tetranuclear heterometallic complex. Water molecules effectively replace coordinated trifluoroacetic acid in the structure of **1**. Complex **2** (Figure 2) crystallizes in the same space group as **1** with similar cell dimensions. There are only small differences in the corresponding bond distances between two tetrameric structures (Table 2).

An additional study of the solution behavior revealed that not only can the coordinated carboxylic acid in **1** be replaced by other donor solvent molecules but also the tetranulear complex can be cleaved in solution into discrete dinuclear Bi−Pd species. Single crystals of $[BiPd(O_2CCF_3)_5(THF)_3]$ (**3**) were obtained from a saturated solution of **1** in THF. The structure of **3** (Figure 3) consists of heterobimetallic units, in which bismuth and palladium atoms are bridged by four trifluoroacetate groups. The Bi···Pd distance (3.2222(9) Å) is even longer than that in the tetranuclear molecules **1** and **2**. There are additional chelating trifluoroacetate group and two THF molecules residing on the bismuth(III) center, raising its coordination number to eight. In addition, one THF molecule is loosely attached (2.883(6) Å) to the axial position of palladium atom. Importantly, the isolation of complex **3** provides evidence that even when the tetranuclear complex is cleaved in solution, there are still heterobimetallic units present there. This finding allows one to use the solution of **1** in coordinating solvents for deposition of heterometallic complex into solid support with subsequent application as a precursor for catalyst.

Table 3. Determination of Metal Loading

	element analyzed	metal %		
		Pd−Bi/C	ref-SX+	ref-Fonct
theoretical amounts	Pd	3.37	5.00	5.00
	Bi	6.62	5.00	5.00
atomic absorption of the filtrate [a]	Pd	3.15	N/A	N/A
	Bi	6.62	N/A	N/A
ICP-OES [b]	Pd	2.83	5.01	6.07
	Bi	9.47	4.83	6.00

[a] Analysis of the solution obtained by filtration at the end of the grafting process: the amount of metal grafted onto carbon support is obtained by subtraction. [b] Analyzed by MEDAC Ltd., U.K.

Table 4. Results of XPS Analysis for Bimetallic Samples

	O/C (×100)	atomic Pd %	atomic Bi %	Pd/Bi
		Pd−Bi/C		
before activation	22.05	0.28	1.10	0.26
after activation	9.52	0.25	0.74	0.32
after test	18.07	0.30	0.20	1.50
		ref-SX+		
before activation	8.67	0.93	1.40	0.67
after activation	6.94	0.58	0.52	1.10
after test	31.70	0.62	0.22	2.80
		ref-Fonct		
before activation	22.71	0.80	1.14	0.70
after activation	13.80	0.86	1.14	0.75
after test	23.11	1.31	0.54	2.45

Catalysis. To incorporate the heterometallic complex **1** onto a solid support to produce bimetallic heterogeneous catalysts, a grafting procedure was envisaged. This ought to improve the complex/support interaction and lead to optimal dispersion. The carbon support selected in the present study was thus functionalized to increase the number of oxygenated functions at its surface. These can act as anchors for carboxylate metal complexes via a ligand exchange mechanism of the carboxylate ligands for the surface O-groups.[14]

The amount of metal grafted after bringing the functionalized support into contact with the heterometallic complex **1** was determined by ICP-OES analysis of the solid samples (after acid digestion) and by atomic absorption analysis of the synthesis filtrates. These results are shown in Table 3 and compared with calculated values. It appears that the results obtained by atomic absorption are in line with the calculated values. This confirms that the total amount of complex was grafted on the surface prior to activation. On the opposite, the results obtained by ICP-OES after activation were different from the calculated values: Pd percentage was decreased and Bi

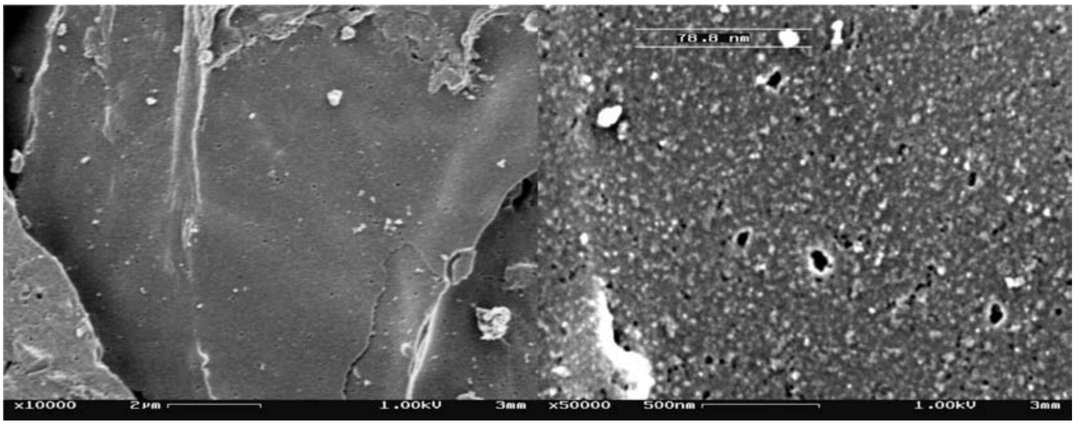

Figure 4. SEM images of the Pd−Bi/C sample prepared from the heterometallic complex **1** and activated thermally (magnification: left ×10000, right ×50000).

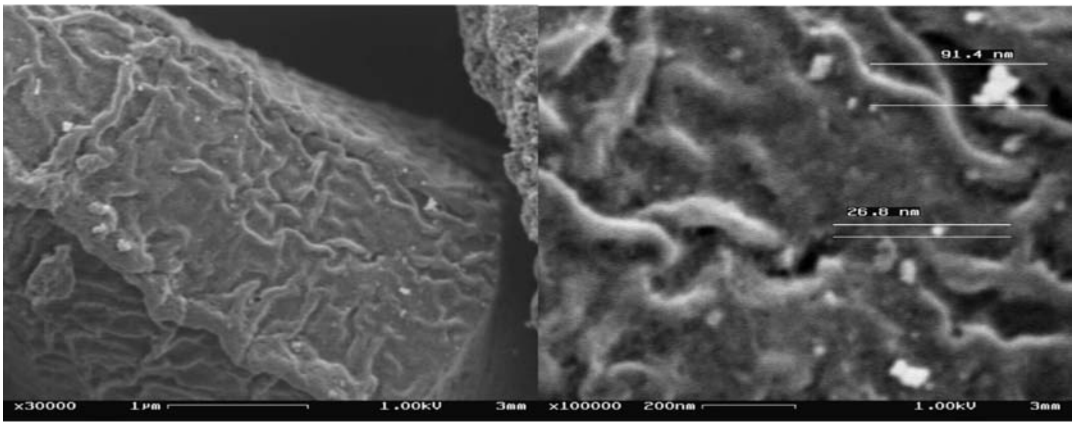

Figure 5. SEM images of the Pd−Bi/C sample prepared from the heterometallic complex **1** after catalytic test (magnification: left ×30000, right ×100000).

percentage increased. Reference Pd−Bi/C catalysts containing 5 wt % in each metal were prepared by a standard deposition method, involving Pd acetate and Bi oxoacetate as precursors.[12] These were prepared on the pristine support (SX+) and on the functionalized carbon, to allow for comparison. Reference materials were also analyzed by ICP-OES after activation to determine the composition of the catalysts. The C_{SX+} based catalyst gave metal percentages close to 5 wt % as expected (5.64% for Bi and 4.83% for Pd), while the functionalized C gave a reference catalyst containing 6 wt % of each metal. It has been shown previously in our laboratory that, during the activation step, a part of the oxygenated functions of the support are removed, which increases artificially the analyzed percentage of Pd and Bi in the resulting solid, especially when using the functionalized support. This could also explain the results obtained with the bimetallic precursor exposed above, and the difference of metal loading before and after activation.

All bimetallic samples were characterized by XPS before and after activation. The obtained atomic ratios and percentages were compared. Table 4 shows that lower surface atomic Pd percentages were obtained when using the heterometallic complex as precursor, while less effect on the atomic Bi percentage was observed.

SEM images of the heterometallic complex-based sample are shown after activation (Figure 4) and after testing (Figure 5) of the catalyst in the oxidation of D-glucose. After activation, small particles homogeneously dispersed are obtained, although some bigger Pd agglomerates are also observed. During catalytic testing, some further agglomeration of the small particles seems to occur. The heterometallic complex-based sample was also analyzed by powder X-ray diffraction (XRD). The absence of lines in the XRD patterns confirms the presence of small particles.

Table 5. Catalytic Results Obtained after 4 h Tests

	X_{GLU}/m_{cata} (%/mg)	X_{GLU}/mPd (%/mg)
ref-SX+ (1)	0.69	14.22
ref-SX+ (2)	0.62	12.73
ref-Fonct (1)	1.46	24.14
ref-Fonct (2)	1.37	22.93
Pd−Bi/C (1)	0.61	24.87
Pd−Bi/C (2)	0.74	30.59
Pd−Bi/C (3)	0.90	31.89
Pd−Bi/C (4)	0.72	25.67
Pd−Bi/C (5)	0.71	25.27

The catalytic performance of the sample prepared by grafting of the heterometallic complex was compared with those obtained with the reference materials (Table 5). Each catalytic test was conducted two times for the reference materials. In the case of the heterometallic complex-based sample, the catalytic test was repeated 5 times, to give an average value of X_{GLU}/mPd = 27.66%/mg, with a standard deviation of 2.96. The sample obtained

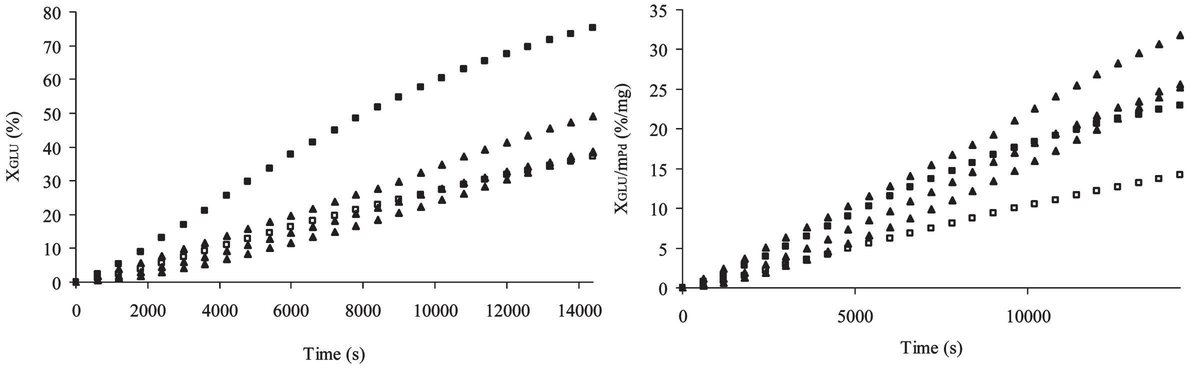

Figure 6. Catalytic results obtained for the oxidation of D-glucose into D-gluconic acid with the Pd−Bi catalysts prepared by grafting or by deposition: (□) ref-SX+, (■) ref-Fonct, (▲) Pd−Bi/C prepared from heterometallic complex **1**; X_{GLU} (left) and X_{GLU}/m_{Pd} (right).

from heterometallic Bi−Pd complex demonstrates similar catalytic performance (Figure 6, left) when compared to the reference sample prepared on untreated SX+ support at exactly the same catalytic testing conditions. The reference sample prepared on the functionalized support seems to give better results. However, the amount of active metal (Pd) in these three catalysts is not identical. When normalizing the catalytic results with respect to the amount of active metal (Pd) introduced in the reactor, the results obtained with the heterometallic complex-based sample are now similar to (or even better than) the reference sample prepared on functionalized support (Figure 6, right). After the reaction, the catalysts were removed by filtration, and the filtrates were analyzed by atomic absorption. Similar losses of metal were found for the catalysts obtained on the functionalized support from the heterometallic complex and for the reference (1 to 3% of Pd lost and about 50% of Bi lost). The reference obtained on the non-modified support exhibits lower Bi loss (about 20%) and similar Pd loss. Such phenomena are common for this type of catalysts and are intimately linked to the reaction mechanism,[5] leading to stable catalysts after a few runs, but this was beyond the scope of the present study.

Conclusions

Herein, we demonstrated that bismuth(III) carboxylates are promising starting materials for the synthesis of heterometallic compounds. Highly Lewis acidic metal centers in bismuth(III) trifluoroacetate are trying to reach high coordination numbers and readily interact with coordinatively unsaturated transition metal species. The bismuth−palladium carboxylate obtained in this work exhibits a rigid heterometallic structure that is retained even in solutions of coordinating solvents. This complex was used as a single-source precursor for the preparation of a carbon-supported catalyst, which proved to be highly active in the selective oxidation of glucose into gluconic acid. Such high catalytic activity reflects the fact that intimate contacts between the two metals must pertain in the activated catalyst, and highlights the interest in this type of compounds as precursors. Moreover, the presence of carboxylate ligands allows for a grafting preparation procedure to be carried out, giving optimized dispersion at the support's surface. This opens up new avenues at the boundary between molecular solution chemistry and surface/materials science to control the structure of solids at the nanoscale level. Similar strategies could be envisaged for other supports and/or for other catalytic applications. Fundamental studies should be carried out in situ to investigate in more detail the grafting and activation procedures.

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Supporting Information Available: IR spectra for **1** and **3**, low-temperature ^{1}H NMR spectrum for **1**, additional crystallographic information for **1**−**3**, X-ray crystallographic files for **1**−**3** in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.