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Bismuth Perfluoroalkylphosphinates: New Catalysts for Application in Organic Syntheses

Sven Solyntjes,[a] Beate Neumann,[a] Hans-Georg Stammler,[a] Nikolai Ignat'ev[b] and Berthold Hoge*[a]

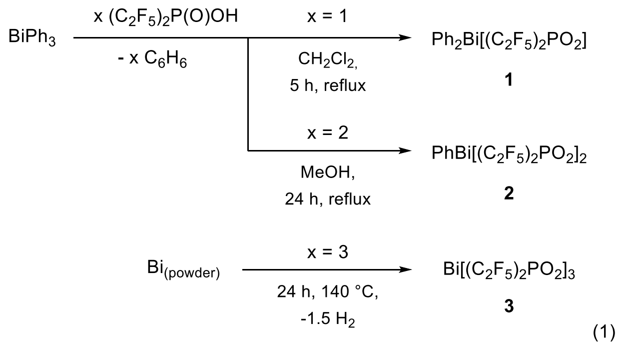
Abstract: Commercially available $BiPh_3$ was treated with perfluoroalkylphosphinic acids [e.g. $(C_2F_5)_2P(O)OH$] to generate novel, highly Lewis acidic bismuth(III) perfluoroalkylphosphinates of the type $Ph_xBi[R^F{}_2PO_2]_{3-x}$ (x = 0, 1, 2) (R^F= $-C_2F_5$, $-C_4F_9$). The first bismuth(V) perfluoroalkylphosphinate, $Ph_3Bi[(C_2F_5)_2PO_2]_2$, was synthesized from Ph_3BiCl_2 and $Ag[(C_2F_5)_2PO_2]$. Examples for the successful application of the catalytically active bismuth(III) and bismuth(V) phosphinates in carbon-carbon bond forming reactions, such as Friedel Crafts acylation and alkylation, Diels-Alder, Strecker and Mannich reaction, are presented.

Introduction

Bismuth represents the heaviest and most metallic group 15 element and is also the heaviest stable element in the periodic table. It combines many interesting properties for industrial and everyday-life applications. It is generally obtained as a byproduct in copper, lead and tin mining and is therefore, although a rare metal, relatively inexpensive. The most important point is the remarkably low toxicity of most bismuth compounds, particularly with respect to many other heavy metals. Most bismuth(III) salts are even less toxic than table salt.[1] These advantages make bismuth(III) salts more attractive as catalysts in industrial organic syntheses than other Lewis acids, which are often corrosive and are responsible for a large amount of waste during the course of the process.[2]
Various bismuth(III) salts like bismuth chloride, $BiCl_3$, bismuth nitrate, $Bi(NO_3)_3$, and bismuth triflate, $Bi(OTf)_3$, have been tested as Lewis acidic catalysts in diverse organic reactions, whereby $Bi(OTf)_3$ proved to be the superior one.[3,4]
Treating triphenylbismuth, $BiPh_3$, at room temperature with one, two or three equivalents of triflic acid selectively leads to the corresponding mono-, di- and trisubstituted bismuth triflates.[5] $Bi(OTf)_3$ is moisture sensitive and also reacts with alcohols and amines releasing triflic acid, CF_3SO_2OH.[6,7]
The less toxic and less corrosive bis(pentafluoroethyl)phosphinic acid, $(C_2F_5)_2P(O)OH$, is of similar acidity and should represent an excellent alternative to triflic acid.[8] $(C_2F_5)_2P(O)OH$ was first synthesized by Shreeve at al. via hydrolysis of $(C_2F_5)_2P(O)Cl$.[9] A more convenient protocol for large quantities of the acid is based upon the hydrolysis of $(C_2F_5)_3PF_2$[10] or $[H(OH_2)_5][(C_2F_5)_3PF_3]$.[11]

Results and Discussion

In keeping with previous methods[5], $BiPh_3$ reacted with one equivalent of $(C_2F_5)_2P(O)OH$ in dichloromethane to yield $Ph_2Bi[(C_2F_5)_2PO_2]$, **1**, as a colourless precipitate. The bisphosphinate $PhBi[(C_2F_5)_2PO_2]_2$, **2**, was prepared by prolonged heating of a methanol solution of $BiPh_3$ and two equivalents of $(C_2F_5)_2P(O)OH$. This protocol, however, failed with the cleavage of the third phenyl substituent, presumably due to the decreased reactivity of $PhBi[(C_2F_5)_2PO_2]_2$, **2**. An effective synthesis of $Bi[(C_2F_5)_2PO_2]_3$, **3**, makes use of stirring bismuth powder in a large excess of the phosphinic acid for 24 h. From the reaction mixture the bismuth(III) trisphosphinate **3** was isolated in moderate yield (Eq. 1).



(1)

The bismuth(III) phosphinates **1**, **2**, and **3** are colourless solids. Their stability is highlighted by the fact that these compounds are air and moisture stable, showing no change in colour or weight stored open on the benchtop for more than one day. The monophosphinate **1** melts at 270 °C, whereas compounds **2** and **3** slowly decompose without melting above 550 °C and 490 °C, respectively. The compounds **1**, **2**, and **3** are soluble without decomposition in dry ethanol, methanol, DMSO, DMF and only moderately soluble in acetone and acetonitrile. On the other hand in aqueous solutions of phosphinates **1**, **2**, and **3** a voluminous precipitate is formed within 1 h.
Single crystals of **2** suitable for X-ray diffraction analysis were obtained by slowly concentrating an ethanolic solution. The compound crystallizes in the monoclinic space group $P2_1/n$. The X-ray diffraction analysis shows the picture of endless chains of eight-membered rings. Each ring consists of two PhBi fragments bridged by two phosphinate groups in a κO:κO' mode. The coordination geometry around the bismuth is that of a pseudo-octahedron, with an apical phenyl group and four oxygen atoms in the

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square plane. The sixth position at the metal atom is occupied by a lone pair (Figure 1). The Bi-O bond lengths range from 232 to 236 pm and are thus shorter than the shortest Bi-O distance in $Ph_2Bi(OTf)$ [253(1) pm][12] or in $Bi(OTf)_3{\cdot}(H_2O)_4$ [254(5) pm][13], indicating a stronger Bi-O bonding in bismuth perfluoroalkylphosphinates than in triflates.

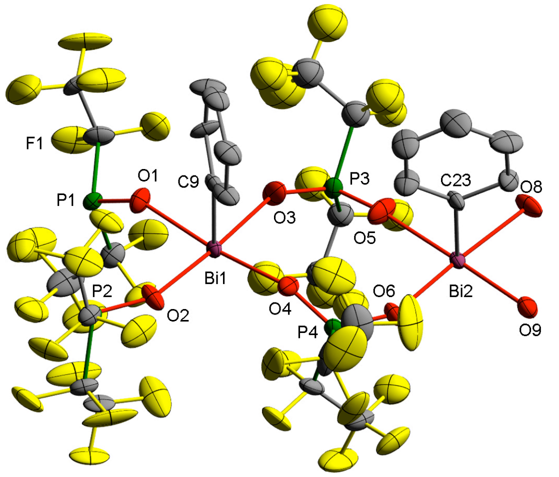


Figure 1. Molecular structure of $PhBi[(C_2F_5)_2PO_2]_2$, (**2**); 50 % probability amplitude displacement ellipsoids are shown; H atoms omitted for clarity; selected bond lengths [pm] and angles [°]: Bi1–O1-4 232.2(7)-235.7(7), Bi1–C9 219.6(8), Bi2–O5-9 233.7(7)-236.3(7), Bi2–C23 219.3(8), P1–O1/9 150.7(7)/145.1(7), P2–O2/8 149.8(7)/146.8(7), P3–O3/5 148.0(8)/146.8(7), P4–O4/6 148.6(7)/148.8(7); O1–Bi1–O2 92.4(3), O1–Bi1–O3 86.2(3), O2–Bi1–O4 86.7(3), O4–Bi1–O3 93.8(3), C9–Bi1–O1-4 84.8(5)-87.7(4), O5–Bi2–O6 90.3(3), O5–Bi2–O8 96.0(3), O6–Bi2–O9 83.9(2), O8–Bi2–O9 89.1(3), C23–Bi2–O5-9 85.9(3)-88.4(3), O9–P1–O1 120.4(4), O8–P2–O2 120.3(5), O5–P3–O3 121.9(5), O4–P4–O6 121.7(4).

Crystals of **3** were only obtained in a poor quality from a methanol solution, probably due to the high bridging tendency of the phosphinate units which was also observed for $PhBi[(C_2F_5)_2PO_2]_2$ (see Figure 1). However, single crystals suitable for the X-ray diffraction analysis were grown by adding one equivalent of [18]crown-6 to the methanol solution of **3**, forming a salt consisting of a $[Bi\{(C_2F_5)_2PO_2\}_2([18]crown\text{-}6)(CH_3OH)]^+$ cation and a bis-(pentafluoroethyl)phosphinate anion, $[(C_2F_5)_2PO_2]^-$. In the cation the bismuth(III) centre is coordinated by nine oxygen atoms (Figure 2).

In order to increase the stability of bismuth perfluoroalkylphosphinates against water the introduction of longer perfluoroalkyl chains was envisaged. Bis(nonafluorobutyl)phosphinic acid, $(C_4F_9)_2P(O)OH$ was chosen as a reactant.[14] Following the reaction conditions yielding compound **2** $PhBi[(C_4F_9)_2PO_2]_2$, **4**, is obtained as an air stable, colourless, hydrophobic powder (Eq. 2).

$$BiPh_3 \xrightarrow[\text{MeOH, 20 h, reflux} \atop -2\ C_6H_6]{2\ (C_4F_9)_2P(O)OH} \underset{\mathbf{4}}{PhBi[(C_4F_9)_2PO_2]_2} \qquad (2)$$

Product **4** is well soluble in alcohols and decomposes at temperatures above 490 °C. As expected $PhBi[(C_4F_9)_2PO_2]_2$ is less moisture sensitive than $PhBi[(C_2F_5)_2PO_2]_2$. The solubility of **4** in organic solvents, however, decreases in comparison to that of **2**.

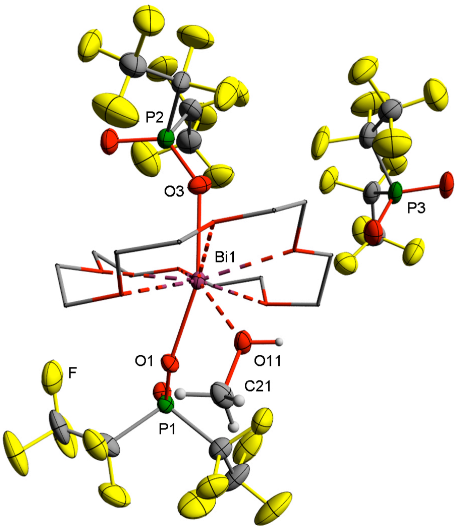


Figure 2. Molecular structure of $[Bi\{(C_2F_5)_2PO_2\}_2([18]crown\text{-}6)(OHCH_3)]$ $[(C_2F_5)_2PO_2]$; 50 % probability amplitude displacement ellipsoids are shown; [18]crown-6 ether pictured in *wires/sticks* mode with H atoms omitted for clarity; selected bond lengths [pm] and angles [°]: Bi1–O1 230.2(4), Bi1–O3 248.0(5), Bi1–O11 239.8(4), Bi1–O([18]crown-6) 253.5(4)-270.2(4), O11-C21 144.6(8); O1-Bi1-O3 151.0(2).

Most triarylbismuth(V) compounds of the Ar_3BiX_2 type are crystalline, non-hygroscopic solids which are soluble in many organic solvents. The preparation, properties and applications of a large number of these compounds have been summarized in several reviews. Typically their oxidizing and arylating abilities are highlighted.[15] A frequently observed decomposition reaction is the reductive elimination giving Ar_2BiX and ArX. The thermal stability of these Ar_3BiX_2 derivatives depends on the ancillary substituents X.[1]

The introduction of perfluoroalkylphosphinate substituents was carried out via a metathesis. Treating a solution of Ph_3BiCl_2 with two equivalents of $Ag[(C_2F_5)_2PO_2]$, **5**, made from Ag_2O and $(C_2F_5)_2P(O)OH$, leads to the first bismuth(V) perfluoroalkylphosphinate $Ph_3Bi[(C_2F_5)_2PO_2]_2$, **6** (Eq. 3). This compound is obtained as an air stable, colourless, hydrophobic, crystalline solid melting at 132 °C. Product **6** is well soluble in various organic solvents and solutions of **6** in water/ethanol mixtures are surprisingly stable.

$$\begin{aligned}&\mathrm{Ag_2O} \xrightarrow[\substack{\mathrm{CH_3CN,}\\ \text{3 h, reflux}\\ \mathrm{-\ H_2O}}]{2\ (\mathrm{C_2F_5})_2\mathrm{P(O)OH}} \underset{\mathbf{5}}{2\ \mathrm{Ag[(C_2F_5)_2PO_2]}} \\ &\mathrm{Ph_3BiCl_2} \xrightarrow[\substack{\mathrm{CH_2Cl_2,\ rt}\\ \mathrm{-\ 2\ AgCl}}]{2\ \mathrm{Ag[(C_2F_5)_2PO_2]}} \underset{\mathbf{6}}{\mathrm{Ph_3Bi[(C_2F_5)_2PO_2]_2}}\end{aligned} \qquad (3)$$

Single crystals of $Ph_3Bi[(C_2F_5)_2PO_2]_2$ suitable for X-ray diffraction analysis were obtained by slowly evaporating a solution of the compound in ethanol. Product **6** crystallizes in the orthorhombic space group *Pbca*. The bismuth centre resides in a trigonal-bipyramidal environment, with three phenyl groups in equatorial and the oxygen atoms of the monodentate phosphinates in axial positions. The Bi-C distances fall in the range of 217(1)-220(1) pm as observed in $Ph_3Bi(OSO_2Ph)_2$[16] or in $Ph_3Bi(OTf)_2$ (218(1) pm)[17]. As already observed for compound **2** the Bi-O distances of $Ph_3Bi[(C_2F_5)_2PO_2]_2$ are slightly shorter than for those of analogous $Ph_3Bi(OTf)_2$ (232.5 pm)[17].

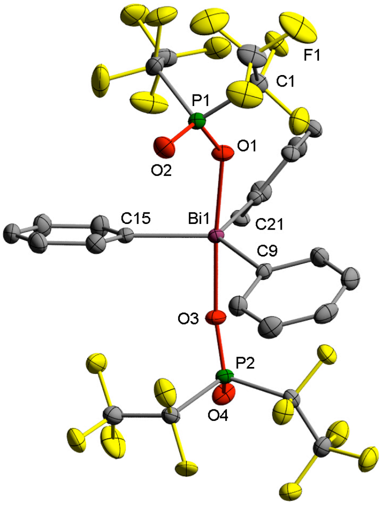
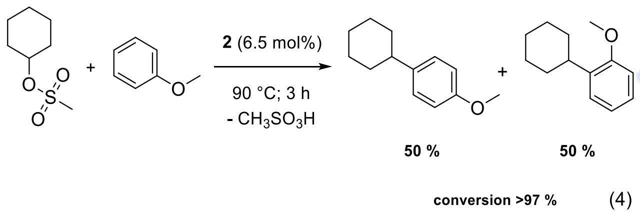


Figure 3. Molecular structure of $Ph_3Bi[(C_2F_5)_2PO_2]_2$, (**6**); 50 % probability amplitude displacement ellipsoids are shown; H atoms omitted for clarity; selected bond lengths [pm] and angles [°]: Bi1-O1 226.0(2), Bi1-O3 225.4(2), Bi1-C9 219.3(2), Bi1-C15 218.3(2), Bi1-C21 218.4(2), P1-O1 150.5(2), P1-O2 146.4(2), P2-O3 149.5(2), P2-O4 145.8(2); O3-Bi1-O1 175.7(1), C9-Bi1-O1 88.6(1), C9-Bi1-O3 88.7(1), C9-Bi1-C15 114.7(1), C9-Bi1-C21 122.4(1), C15-Bi1-C21 122.9(1), O2-P1-O1 122.6(1).

Bismuth perfluoroalkylphosphinates in carbon-carbon bond forming reactions

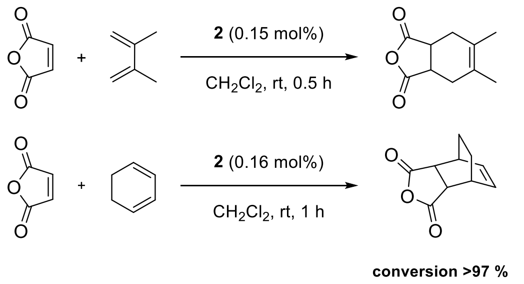
To elucidate the catalytic activity of the bismuth phosphinate **2** a number of common organic transformations were selected. The focus was rather on a broad and versatile applicability of the catalyst than on optimisation of conditions or yields of a particular process.

While there are recent examples for the benzylation of arenes with phenylethyl alcohols[4,18], examples for bismuth(III) catalysed Friedel-Crafts alkylations with alkyl mesylates are hardly known. For an alkylation reaction cyclohexyl methane sulfonate and anisole were treated with 6.5 mol% of compound **2** at 90 °C without solvent. After 3 h no more cyclohexyl methane sulfonate was observed by ^1H and ^{13}C NMR spectroscopy. The alkylated products were identified by comparison with literature NMR data (Eq. 4). The same Friedel-Crafts alkylation with $Sc(OTf)_3$[19] and $Cu(OTf)_2$[20] as catalysts show comparable results, however, with higher catalyst loadings (10 mol%). In the absence of a catalyst no reaction occurs under the given conditions.



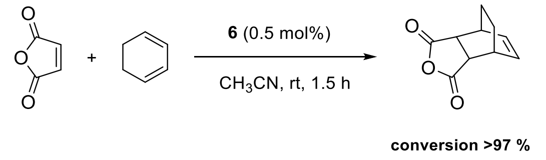
(4)

The Diels-Alder reaction is a powerful method for the construction of cyclic or polycyclic systems. For the synthesis of natural products this [4+2] cycloaddition requires mild conditions which these bismuth catalysts can provide. Despite the numerous examples of Diels-Alder and hetero Diels-Alder reactions compiled in review articles[2] we focussed our interest on the basic reaction of maleic anhydride with 2,3-dimethyl-1,3-butadiene or 1,3-cyclohexadiene in dichloromethane (Eq. 5). The transformations were carried out in dry dichloromethane under nitrogen atmosphere.



(5)

The reaction was monitored by ^1H and ^{13}C NMR spectroscopy and the products were identified by comparison with NMR data from the literature. The conversions are quantitative after 0.5 or 1 h, respectively. Thereby the Diels-Alder reaction is impressively accelerated by only small amounts of bismuth phosphinate **2** (0.15 mol%). Without the catalyst the reaction of maleic anhydride with 1,3-cyclohexadiene takes 6.5 h under the same conditions. Unexpectedly, the catalytic activity of the bismuth(V) compound **6** in the Diels-Alder reaction of maleic anhydride with 1,3-cyclohexadiene (Eq. 6) is inferior to the one catalysed with the bismuth(III) compound **2**. Thereby the complete conversion of maleic anhydride was only achieved after a reaction time of 1.5 h and with the threefold amount of catalyst loading.



(6)

In order to get an impression of the degree of moisture sensitivity, freshly prepared samples of the synthesized phosphinates **2**, **3**, **6** and $Bi(OTf)_3$ were exposed to ambient air for 24 h. A sample of $Bi(OTf)_3$ (250 mg), synthesized under inert conditions[5], was placed on a watch glass. Within 24 h a crumbly, clay-coloured solid was formed, showing an increase of weight of 66 mg. This amounts to 9.6 equivalents of water. However, for compounds **2**, **3** and **6** no colour change and only an insignificant increase of weight was observed (Figure 4).

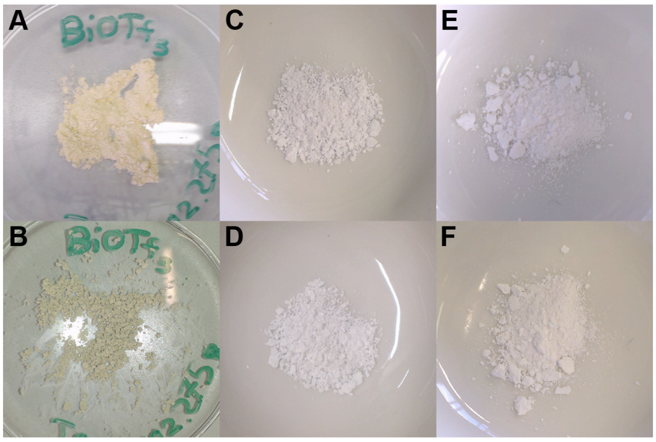
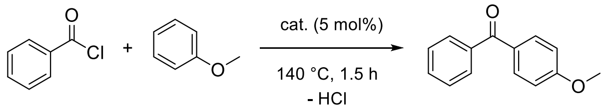


Figure 4. Illustrations of the 24 h hygroscopicity studies of $Bi(OTf)_3$ and bismuth(III) compounds **2** and **3**; **A** $Bi(OTf)_3$ before, **B** after storing at ambient air; **C** $PhBi[(C_2F_5)_2PO_2]_2$ before, **D** after storing at ambient air; **E** $Bi[(C_2F_5)_2PO_2]_3$ before, **F** after storing at ambient air.

In order to test the influence of moisture on the catalytic activity of the compounds listed in Table 1 we chose the Friedel-Crafts acylation between anisole and benzoyl chloride as a model reaction (Eq. 7). The Friedel-Crafts acylation was performed under a N_2 atmosphere with the air exposed bismuth catalyst as well as with $(C_2F_5)_2P(O)OH$. The degree of conversion of anisole and formation of 4-methoxybenzophenone was ascertained by ^1H and ^{13}C NMR spectroscopy. Typical procedures are given in the experimental section.



(7)

Table 1 illustrates that moisture and partial hydrolysis of the new catalysts have a small retarding effect on the process. This effect is stronger for $Bi(OTf)_3$ than for the bismuth phosphinates.[21]

In addition the catalytic activity of pure phosphinic acid is very low, confirming that the here performed reactions are not promoted by free acid (Entry 3).

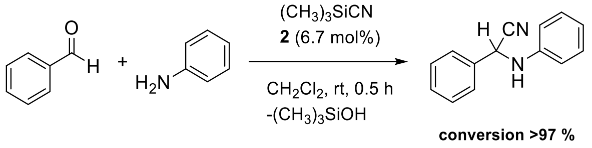
Table 1. Friedel-Crafts acylation of anisole and benzoyl chloride by various bismuth catalysts under identical conditions.[a]

Entry	Catalyst	Conditions	Conversion[b] (%)
1	$Bi(OTf)_3$	Inert atmosphere	80
2	$Bi(OTf)_3 \cdot n\ H_2O$	24 h exp. to air	72
3	$(C_2F_5)_2P(O)OH$	Inert atmosphere	29
4	$Ph_2Bi[(C_2F_5)_2PO_2]$ (**1**)	Inert atmosphere	63
5	$PhBi[(C_4F_9)_2PO_2]_2$ (**4**)	Inert atmosphere	72
6	$PhBi[(C_2F_5)_2PO_2]_2$ (**2**)	Inert atmosphere	81
7	$PhBi[(C_2F_5)_2PO_2]_2$ (**2**)	24 h exp. to air	83
8	$Ph_3Bi[(C_2F_5)_2PO_2]_2$ (**6**)	Inert atmosphere	86
9	$Ph_3Bi[(C_2F_5)_2PO_2]_2$ (**6**)	24 h exp. to air	88
10	$Bi[(C_2F_5)_2PO_2]_3$ (**3**)	Inert atmosphere	90
11	$Bi[(C_2F_5)_2PO_2]_3$ (**3**)	24 h exp. to air	85
12	no catalyst	Inert atmosphere	0

[a] Time: 1.5 h; temperature: 140 °C; amount of catalyst: 5 mol%; [b] Conversion followed by ^1H and ^{13}C NMR spectroscopy.

As expected a multiple substitution of phenyl groups by perfluoroalkylphosphinate units at the bismuth(III) centre leads to a higher conversion in the Friedel-Crafts reaction. Longer perfluoroalkyl chains, like e.g. the nonafluorobutyl substituent, give lower conversions probably due to steric effects (Entry 5). Unlike the $Ph_3Bi[(C_2F_5)_2PO_2]_2$ catalysed Diels-Alder reaction, the Friedel-Crafts acylation also proceeds very efficiently under the selected conditions.

Up to this point of our studies we investigated only the catalytic activity of bismuth(III) and bismuth(V) compounds in bimolecular reactions. One of the most important one-pot multi-component condensation reactions is the synthesis of α-aminonitriles, which are useful precursors for the synthesis of α-amino acids and can efficiently be realised by the Strecker reaction. These reactions are often characterised by their high atom economy, by mild and simplified conditions and environmental friendliness.[22] Few bismuth(III) catalysed examples with $Bi(NO_3)_3$ and $BiCl_3$ are known to date.[23] We studied the one-pot reaction of benzaldehyde, aniline and trimethylsilyl cyanide in dichloromethane at room temperature in the presence of phosphinate **2** as a catalyst (Eq. 8).

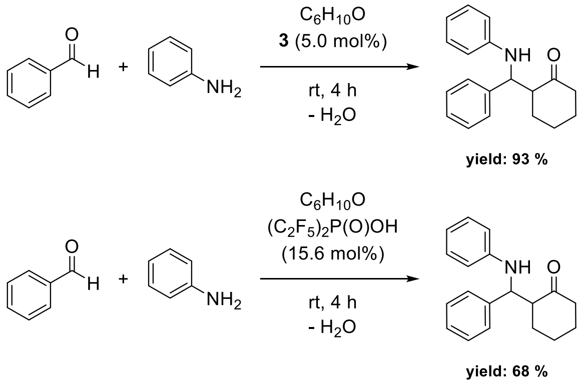


(8)

The selective and quantitative conversion to the α-aminonitrile was confirmed by ^1H and ^{13}C NMR spectroscopy after 30 minutes, which is four times faster than the non-catalysed one-pot Strecker reaction under identical conditions (2 h).

Another important multi-component C-C bond forming reaction is the Mannich reaction, which is a classical method for the preparation of β-amino ketones and aldehydes. These β-amino carbonyls are of pharmaceutical interest because of their wide use as biologically active molecules.[24] A few articles of bismuth catalysed direct Mannich reactions are available in particular with air-stable cationic bismuth containing heterocyclic complexes.[25] A smooth Mannich type reaction occurred with various silyl enolates and silyl ketene acetals when assisted by $Bi(OTf)_3{\cdot}(H_2O)_4$ as a catalyst.[26] Here the formation of trimethylsilyl triflate as the true catalytic system is conceivable, as it is also discussed for the Mukaiyama-aldol reaction.[7,27]

However, we performed a multi component reaction with a stoichiometric mixture of benzaldehyde and aniline. Cyclohexanone was used in excess and acted as reagent and the solvent, while compound **3** (5 mol%) was used as the catalyst. The reaction mixture was stirred at room temperature for 4 h, whereby the poorly soluble β-amino ketone precipitated (Eq. 9). The crude product was collected in water, stirred for 10 minutes and was then filtered off via a glass frit. After washing with small amounts of water and *n*-hexane the pure β-amino ketone was obtained as a colourless solid with an isolated yield of 93 %. The product was identified by ^1H and ^{13}C NMR spectroscopy and mass spectrometry. The Mannich reaction in the absence of a catalyst showed only a 50 % conversion after 24 h under identical conditions.



(9)

Performing this reaction with $(C_2F_5)_2P(O)OH$ as Brønsted acidic catalyst under the same conditions and workup showed a significant decrease in the isolated yield of 68 % after 4 h (Eq. 9). The employed amount of 15 mol% phosphinic acid represents a very high catalyst loading, but is equal to the theoretically obtained amount of acid after complete hydrolysis of $Bi[(C_2F_5)_2PO_2]_3$ (5.0 mol%). These experiments indicate again that the high catalytic activity is not primarily caused by phosphinic acid, resulting from hydrolysis, but rather by the bismuth(III) phosphinate derivative itself.

Conclusions

We reported that previously unknown bismuth perfluoroalkylphosphinate compounds, $Ph_xBi[R^F_2PO_2]_{3-x}$ (x = 0, 1, 2) ($R^F = -C_2F_5$), $PhBi[(C_4F_9)_2PO_2]_2$ and $Ph_3Bi[(C_2F_5)_2PO_2]_2$ are very active catalysts for a whole series of organic transformations.[21] The presented bismuth(III) phosphinates were successfully applied in Friedel-Crafts alkylations and acylations, as well as in Diels-Alder, Strecker and Mannich reactions. As an improvement over other catalytic systems the complexes are easily available, non-hygroscopic, soluble in a few organic solvents and they are stable towards moisture, air oxidation and heat. This allows their use of theses new catalysts working under air without protection from moisture.[21]

Experimental Section

Bis(pentafluoroethyl)phosphinic acid and bis(nonafluorobutyl)phosphinic acid (Tivida® TM FL 2100) were provided by Merck KGaA (Darmstadt, Germany). Benzaldehyde, aniline, anisole and cyclohexanone were freshly distilled prior to use. Other reagents and solvents were obtained from commercial sources and were used without further purification. Standard high-vacuum techniques were employed throughout all experiments with nitrogen as the inert gas.

The NMR spectra were recorded on a Bruker Model Avance III 300 spectrometer (^{31}P 111.92 MHz; ^{19}F 282.40 MHz; ^{13}C 75.47 MHz; ^1H 300.13 MHz) with positive shifts being downfield from the external standards (85 % orthophosphoric acid (^{31}P), CCl_3F (^{19}F) and TMS (^1H)).

IR spectra were recorded on an ALPHA-FT-IR spectrometer (Bruker). Determination of melting points was carried out with a Mettler Toledo MP70. ESI mass spectra were recorded using an Esquire 3000 ion-trap mass spectrometer (Bruker Daltonik GmbH, Bremen, Germany) equipped with a standard ESI/APCI source. Samples were introduced by direct infusion with a syringe pump. Nitrogen served both as the nebulizer gas and the dry gas and was generated by a Bruker nitrogen generator NGM 11. Helium served as the cooling gas for the ion trap and collision gas for MS experiments. The spectra were recorded with Bruker Daltonik esquireNT 5.2 esquireControl software by the accumulation and averaging of several single spectra. Data analysis software 3.4 was used for processing the spectra. C, H, and N analyses were carried out with a HEKAtech Euro EA 3000.

The crystal data for compounds **2**, **3** and **6** were collected on an Agilent SuperNova diffractometer at 100.0(1) K. Radiation used was $Mo_{K\alpha}$ radiation (λ = 71.073 pm). Suitable crystals were selected, coated with paratone oil and mounted onto the diffractometer. Using Olex2[28] the structures were solved with the SHELXS[29] structure solution program using direct methods and refined with the SHELXL[29] refinement package using least-squares minimization. Details of the X-ray investigation are given in Table **2**. CCDC-1433863 (**2**), CCDC-1433864 (**3**) and CCDC-1433865 (**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.

Synthesis of $Ph_2Bi[(C_2F_5)_2PO_2]$ (1): A sample of $(C_2F_5)_2P(O)OH$ (0.82 g, 2.72 mmol) was added dropwise to a solution of $BiPh_3$ (1.25 g, 2.84 mmol) in dichloromethane (30 mL) at room temperature. The reaction mixture was heated under reflux for 5 h. The supernatant liquid was decanted and the resulting solid was washed twice with dichloromethane (10 mL) and dried in vacuo yielding **1** (1.41 g, 2.13 mmol, 78 %) as a colourless solid. m. p. 270 °C; ^1H NMR ([D$_4$]methanol, RT): δ = 7.5 (m, 2H; H_{para}), 7.9 (m, 4H; H_{meta}), 8.4 ppm (m, 4H; H_{ortho}); $^{13}C\{^1H\}$ NMR ([D$_4$]methanol, RT): δ = 129.1 (s; C_{para}), 132.1 (s; C_{meta}), 136.8 (s; C_{ortho}); 194.3 ppm (s; C_{quart}); $^{13}C\{^{19}F\}$ NMR ([D$_4$]methanol, RT): δ = 111.8 (d, $^1J(C,P)$=137 Hz; CF_2), 119.0 ppm (d, ^2J(C,P)=17 Hz; CF_3); ^{19}F NMR ([D$_4$]methanol, RT): δ = -126.7 (d, ^2J(P,F)=74 Hz, 4F; CF_2), -82.0 ppm (m, 6F; CF_3); ^{31}P NMR ([D$_4$]methanol, RT): δ = -0.2 ppm (quint, ^2J(P,F)=74 Hz); IR (solid): $\tilde{\nu}$ = 435 (m), 447 (m), 502 (s), 567 (m), 597 (m), 638 (m), 690 (s), 721 (s), 750 (w), 909 (w), 964 (s), 996 (m), 1069 (s), 1112 (s), 1126 (s), 1163 (m), 1205 (vs), 1311 (m), 1432 (w), 1477 (w), 1572 (w), 3071 (w) cm^{-1}; MS (ESI, pos.): *m/z* (%): 665 (20) $[M]^+$, 363 $[Ph_2Bi]^+$, 209 (50) $[Bi]^+$.

Synthesis of $PhBi[(C_2F_5)_2PO_2]_2$ (2): A sample of $(C_2F_5)_2P(O)OH$ (3.09 g, 10.23 mmol) was added dropwise to a solution of $BiPh_3$ (1.49 g, 3.38 mmol) in methanol (15 mL) at room temperature. The reaction mixture was heated under reflux for 24 h. After removal of all volatile compounds under reduced pressure, the crude product was washed twice with water (20 mL) and diethyl ether (20 mL) and dried in vacuo at 90 °C yielding **2** (2.70 g, 3.04 mmol, 89 %) as a colourless powder. dec. p. >550 °C; ^{1}H NMR ([D$_6$]acetone, RT): δ = 7.4 (t, ^3J(H,H)=7 Hz, 1H; H_{para}), 8.3 (t, ^3J(H,H)=8 Hz, 2H; H_{meta}), 9.2 ppm (d, ^3J(H,H)=7 Hz, 2H; H_{ortho}); ^{13}C{^{1}H} NMR ([D$_6$]acetone, RT): δ = 130.4 (s; C_{para}), 134.3 (s; C_{meta}), 138.2 (s; C_{ortho}), 230.9 ppm (s; C_{quart}); ^{13}C{^{19}F} NMR ([D$_6$]acetone, RT): δ = 112.1 (d, ^1J(C,P)=141 Hz; CF_2), 119.4 ppm (d, ^2J(C,P)=18 Hz; CF_3); ^{19}F NMR ([D$_6$]acetone, RT): δ = -126.0 (d, ^2J(P,F)=77 Hz, 8F; CF_2), -81.2 ppm (m, 12F; CF_3); ^{31}P NMR ([D$_6$]acetone, RT): δ = 0.6 ppm (quint, ^2J(P,F)=77 Hz); IR (solid): $\tilde{\nu}$ = 428 (w), 442 (w), 498 (s), 569 (s), 599 (w), 634 (w), 689 (w), 728 (w), 750 (w), 963 (s), 999 (s), 1070 (s), 1113 (s), 1135 (s), 1164 (s), 1205 (vs), 1309 (m), 1434 (w), 3074 (w) cm^{-1}; MS (ESI, pos.): *m/z* (%): 889 (50) $[M]^+$, 587 (60) $[PhBi(C_2F_5)_2PO_2]^+$, 209 (75) $[Bi]^+$; MS (ESI, neg.): *m/z* (%): 1189 (100) $[M+(C_2F_5)_2PO_2]^-$, 965 (90) $[Ph_2Bi\{(C_2F_5)_2PO_2\}_2]^-$, 301 (40) $[(C_2F_5)_2PO_2]^-$; elemental analysis calcd (%) for $C_{14}H_5BiF_{20}O_4P_2$: C 18.93, H 0.57; found: C 18.11. H 0.45. Crystals were obtained by slowly concentrating a solution of compound **2** in ethanol.

Synthesis of $Bi[(C_2F_5)_2PO_2]_3$ (3): A sample of $(C_2F_5)_2P(O)OH$ (24.02 g, 79.55 mmol) was added dropwise to freshly pestled bismuth powder (3.43 g, 16.39 mmol) at room temperature. The reaction mixture was heated at 140 °C for 24 h, cooled to room temperature and was then solved in methanol (25 mL). Unreacted bismuth powder was filtered off and the solvent was removed under reduced pressure. After adding diethyl ether (50 mL) to the residue, the resulting precipitate was filtered off. The residue was washed four times with diethyl ether (20 mL) and dried in vacuo yielding **3** (5.98 g, 5.38 mmol, 33 %) as a colourless solid. dec. p. >490 °C; ^{13}C{^{19}F} NMR (methanol/[D$_6$]acetone, RT): δ = 112.4 (d, ^1J(C,P)=138 Hz; CF_2), 119.6 ppm (d, ^2J(C,P)=17 Hz; CF_3); ^{19}F NMR methanol/[D$_6$]acetone, RT): δ = -126.2 (d, ^2J(P,F)=74 Hz, 12F; CF_2), -81.5 ppm (s, 18F; CF_3); ^{31}P NMR (methanol/ [D$_6$]acetone, RT): δ = 0.6 ppm (quint, ^2J(P,F)=74 Hz); IR (solid): $\tilde{\nu}$ = 429 (m), 473 (w), 496 (m), 519 (m), 571 (m), 601 (m), 641 (w), 752 (w), 958 (s), 1003 (m), 1056 (m), 1083 (m), 1160 (m), 1122 (s), 1174 (m), 1213 (s), 1314 (w) cm^{-1}; elemental analysis calcd (%) for $C_{12}BiF_{30}O_6P_3$: C 12.96; found: C 13.01. Crystals were obtained by adding one equivalent of [18]crown-6 to a methanol solution of **3**, forming $[Bi\{(C_2F_5)_2PO_2\}_2$([18]crown-6)$(OHCH_3)][(C_2F_5)_2PO_2]$.

Synthesis of $PhBi[(C_4F_9)_2PO_2]_2$ (4): An aqueous solution of $(C_4F_9)_2P(O)OH$ was evaporated to dryness for 24 h yielding the phosphinic acid (7.63 g, 15.21 mmol) as a colourless solid. The obtained solid was then added to a solution of $BiPh_3$ (2.20 g, 5.00 mmol) in methanol (50 mL) and the reaction mixture was heated under reflux for 20 h. Non-soluble components were filtered off and the solvent was removed under reduced pressure. After adding diethyl ether (50 mL) to the residue, the resulting precipitate was filtered off, washed four times with diethyl ether (20 mL) and dried in vacuo to yield **4** (4.35 g, 3.37 mmol, 68 %) as a colourless solid. dec. p. >490 °C; ^{1}H NMR ([D$_4$]methanol, RT): δ = 7.6 (m, 1H; H_{para}), 8.3 (m, 2H; H_{meta}), 8.8 ppm (m, 2H; H_{ortho}); ^{13}C{^{1}H} NMR ([D$_4$]methanol, RT): δ = 129.9 (s; C_{para}), 134.2 (s; C_{meta}), 137.1 (s; C_{ortho}), 230.9 ppm (s; C_{quart}); ^{13}C{^{19}F} NMR ([D$_4$]methanol, RT): δ = 109.0 (d, ^3J(C,P)=3 Hz; $CF_3\boldsymbol{C}F_2CF_2CF_2$), 111.3 (d, ^2J(C,P)=10 Hz; $CF_3CF_2\boldsymbol{C}F_2CF_2$), 114.5 (d, ^1J(C,P)=134 Hz; $CF_3CF_2CF_2\boldsymbol{C}F_2$), 117.5 ppm (s; CF_3); ^{19}F NMR ([D$_4$]methanol, RT): δ = -127.1 (m, 8F; $CF_3C\boldsymbol{F}_2CF_2CF_2$), -122.9 (dm, ^2J(P,F)=75 Hz, 8F; $CF_3CF_2CF_2C\boldsymbol{F}_2$), -121.9 (m, 8F; $CF_3CF_2C\boldsymbol{F}_2CF_2$), -82.6 ppm (m, 12F; CF_3); ^{31}P NMR ([D$_4$]methanol, RT): δ = 1.1 ppm (quint, ^2J(P,F)=75 Hz); IR (solid): $\tilde{\nu}$ = 400 (w), 454 (m), 489 (w), 533 (w), 558 (w), 575 (w), 693 (m), 729 (s), 750 (w), 792 (w), 815 (w), 849 (w), 1009 (m), 1031 (s), 1069 (s), 1095 (m), 1133 (vs), 1210 (vs), 1349 (w), 3061 (vw) cm^{-1}; elemental analysis calcd (%) for $C_{22}H_5BiF_{36}O_4P_2$: C 20.51, H 0.39; found: C 20.13.

Synthesis of $Ag[(C_2F_5)_2PO_2]$ (5): A sample of Ag_2O (6.17 g, 26.63 mmol) was added portionwise to a solution of $(C_2F_5)_2P(O)OH$ (15.03 g, 49.77 mmol) in acetonitrile (50 mL) at room temperature. The reaction mixture was heated under reflux for 3 h, not soluble components were filtered off, the solvent was removed under reduced pressure and the residue was dried in vacuo overnight. After adding diethyl ether (50 mL) the solution was stirred over charcoal and filtered. Removing the solvent under reduced pressure and drying in vacuo yielded silver phosphinate **5** (15.50 g, 38.01 mmol, 76 %) as an off-white solid. ^{13}C NMR ([D$_3$]acetonitrile, RT): δ = 112.5 (d, ^1J(C,P)=127 Hz; CF_2), 119.5 ppm (d, ^2J(C,P)=16 Hz; CF_3); ^{19}F NMR ([D$_3$]acetonitrile, RT): δ = -125.7 (d, ^2J(P,F)=69 Hz, 4F; CF_2), -81.1 ppm (s, 6F; CF_3); ^{31}P NMR ([D$_3$]acetonitrile, RT): δ = -0.2 ppm (quint, ^2J(P,F)=69 Hz); IR (solid): $\tilde{\nu}$ = 430 (w), 497 (s), 559 (m), 631 (vw), 753 (w), 966 (m), 983 (m), 1078 (s), 1118 (m), 1147 (m), 1159 (m), 1204 (w), 1267 (m), 1292 (w), 1373 (w), 1661 (vw), 2285 (vw), 2951 (vw) cm^{-1}; MS (ESI, pos.): *m/z* (%): 599 (50) $[Ag_2(C_2F_5)_2PO_2(CH_3CN)_2]^+$, 301 (10) $[(C_2F_5)_2PO_2H_2]^+$, 189 (100) $[Ag(CH_3CN)_2]^+$, 150 (10) $[Ag(CH_3CN)]^+$, 107/109 (5) $[Ag]^+$; MS (ESI, neg.): *m/z* (%): 303 (100) $[(C_2F_5)_2PO_2]^-$, 201 (20) $[(C_2F_5)PFO_2]^-$; elemental analysis calcd (%) for $C_4AgF_{10}O_2P$ + 0.06 CH_3CN: C 12.04, N 0.21; found: C 12.41, N 0.21.

Synthesis of $Ph_3Bi[(C_2F_5)_2PO_2]_2$ (6): A sample of SO_2Cl_2 (0.68 g, 5.0 mmol) was condensed onto a solution of $BiPh_3$ (1.58 g, 3.59 mmol) in dichloromethane (20 mL) and stirred at room temperature for 1 h. All volatile compounds were removed in vacuo leaving Ph_3BiCl_2 as an off-white solid in quantitative yield. A solution of Ph_3BiCl_2 in dichloromethane (20 mL) was combined with $Ag[(C_2F_5)_2PO_2]$ (3.24 g, 7.20 mmol) and the reaction mixture was stirred at room temperature for 1 h. The resulting precipitate was filtered off and the filtrate was freed from all volatile compounds under reduced pressure. Recrystallization of the crude product from cyclohexane yields **6** (2.61 g, 2.50 mmol, 70 % yield related to $BiPh_3$) as colourless needles. m. p. 130-133 °C; dec. >170 °C; ^{1}H NMR ([D$_6$]acetone, RT): δ = 7.7 (t, ^3J(H,H)=7 Hz, 3H; H_{para}), 7.9 (t, ^3J(H,H)=8 Hz, 6H; H_{meta}), 8.1 ppm (d, ^3J(H,H)=8 Hz, 6H; H_{ortho}); ^{13}C{^{1}H} NMR ([D$_6$]acetone, RT): δ = 133.0 (s; C_{para}), 133.6 (s; C_{meta}), 134.1 (s; C_{ortho}), 155.2 ppm (s; C_{quart}); ^{13}C{^{19}F} NMR ([D$_6$]acetone, RT): δ = 110.9 (d, ^1J(C,P)=145 Hz; CF_2), 118.1 ppm (d, ^2J(C,P)=20 Hz; CF_3); ^{19}F NMR ([D$_6$]acetone, RT): δ = -124.3 (d, ^2J(P,F)=83 Hz, 8F; CF_2), -80.7 ppm (m, 12F; CF_3); ^{31}P NMR ([D$_6$]acetone, RT): δ = 0.6 ppm (quint, ^2J(P,F)=83 Hz); IR (solid): $\tilde{\nu}$ = 408 (w), 445 (s), 501 (s), 512 (s), 547 (w), 567 (s), 597 (m), 636 (w), 651 (w), 677 (m), 727 (m), 750 (w), 962 (s), 985 (s), 992 (s), 1047 (s), 1069 (m), 1105 (s), 1128 (s), 1147 (s), 1205 (vs), 1289 (s), 1442 (w), 1472 (w), 1561 (w), 3070 (vw) cm^{-1}; MS (ESI, pos.): *m/z* (%): 741 (100) $[Ph_3Bi(C_2F_5)_2PO_2]^+$ 587 (10) $[PhBi(C_2F_5)_2PO_2]^+$, 363 (50) $[Ph_2Bi]^+$, 286 (90) $[BiPh]^+$, 209 (30) $[Bi]^+$; MS (ESI, neg.): *m/z* (%): 301 (100) $[(C_2F_5)_2PO_2]^-$, 201 (20) $[(C_2F_5)PFO_2]^-$; elemental analysis calcd (%) for $C_{26}H_{15}BiF_{20}O_4P_2$: C 29.96, H 1.45; found: C 29.80, H 1.53, N 0.13. Crystals were obtained by slowly evaporating a solution of compound **6** in ethanol.

Bi phosphinate catalysed C-C bond forming reactions:

Typical procedure for a Bi phosphinate catalysed Friedel Crafts alkylation: Cyclohexyl methane sulfonate (1.036 g, 5.812 mmol) was added

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to PhBi[$(C_2F_5)_2PO_2$]$_2$ (335 mg, 0.377 mmol, 6.49 mol%) in a 25 mL Schlenk tube. Anisole (1.295 g, 11.974 mmol) was added and the reaction mixture was stirred at 90 °C for 3 h. The conversion of cyclohexyl methane sulfonate and formation of cyclohexyl anisole were followed by ^{1}H and ^{13}C NMR spectroscopy.

Typical procedure for a Bi phosphinate catalysed Diels-Alder reaction: Maleic anhydride (993 mg, 10.127 mmol) was added to PhBi[$(C_2F_5)_2PO_2$]$_2$ (13 mg, 0.015 mmol, 0.15 mol%) in a 25 mL Schlenk tube. 2,3-Dimethyl-1,3-butadiene (2.468 g, 30.050 mmol) was added and the reaction mixture was stirred at room temperature for 30 min. The conversion to the Diels-Alder adduct was followed by ^{1}H and ^{13}C NMR spectroscopy.

Typical procedure for a Bi phosphinate catalysed Friedel Crafts acylation: Benzoyl chloride (441 mg, 3.14 mmol) was added to Bi[$(C_2F_5)_2PO_2$]$_3$ (149 mg, 0.134 mmol, 4.95 mol%) in a 25 mL Schlenk tube under a nitrogen atmosphere. Anisole (293 mg, 2.71 mmol) was added and the reaction mixture was stirred at 140 °C for 1.5 h. The colour changes rapidly to pale yellow and then to dark red. The conversion to 4-methoxybenzophenone was followed by ^{1}H and ^{13}C NMR spectroscopy. For reactions under ambient atmosphere a weighted amount of catalysts was stored for 24 h on a watch glass in air. Catalyst loadings and substrate stoichiometry were calculated with the originally determined weights.
The pure product was obtained by extracting the reaction mixture with diethyl ether. This extract was washed twice with water and concentrated $NaHCO_3$ solution. After drying the organic phase over $MgSO_4$ and removing the solvent under reduced pressure the orange residue was crystallised from *n*-hexane/diethyl ether (2:1) yielding 4-methoxybenzophenone as a colourless solid identified by ^{1}H and ^{13}C NMR spectroscopy and mass spectrometry.

Typical procedure for a Bi phosphinate catalysed Strecker reaction: Benzaldehyde (distilled) (210 mg, 1.978 mmol) and aniline (distilled) (184 mg, 1.972 mmol) were added to PhBi[$(C_2F_5)_2PO_2$]$_2$ (117 mg, 0.132 mmol, 6.67 mol%) in a 25 mL Schlenk tube. Trimethylsilyl cyanide (292 mg, 2.946 mmol) was added and the reaction mixture was stirred at room temperature for 30 min. The conversion to the α-aminonitrile was followed by ^{1}H and ^{13}C NMR spectroscopy.

Typical procedure for a Bi phosphinate catalysed Mannich type reaction: A sample of Bi[$(C_2F_5)_2PO_2$]$_3$ (364 mg, 0.327 mmol, 5.00 mol%) was combined with a mixture of benzaldehyde (694 mg, 6.540 mmol), aniline (606 mg, 6.507 mmol) and cyclohexanone (2.584 g, 26.329 mmol) in a 50 mL Schlenk flask. The reaction mixture was stirred for 4 h at room temperature, whereby a colourless solid precipitated. Water (10 mL) was added and the mixture was stirred for 10 min. The crude product was filtered off via a frit, and the filter cake was washed four times with water (5 mL) as well as *n*-hexane (5 mL). The residue was dried in vacuo yielding the β-aminoketone as a colourless solid (1.697 g, 6.074 mmol, 93 %). The product was identified according to literature known NMR spectroscopic and mass spectrometric data.

Typical procedure for a $(C_2F_5)_2P(O)OH$ catalysed Mannich type reaction: A sample of $(C_2F_5)_2P(O)OH$ (336 mg, 1.113 mmol, 15.6 mol%) was added to a mixture of benzaldehyde (760 mg, 7.162 mmol), aniline (665 mg, 7.140 mmol) and cyclohexanone (2.051 g, 20.898 mmol) in a 50 mL Schlenk flask. The reaction mixture was stirred at room temperature for 4 h while a colourless solid precipitated. Water (10 mL) was added, the supernatant was removed and the residue was collected in diethyl ether. The crude product was filtered off via a frit and the filter cake was washed four times with water (5 mL) as well as *n*-hexane (5 mL). The residue was dried in vacuo yielding the β-aminoketone as a colourless solid (1.352 g, 4.839 mmol, 68 %). The product was identified according to literature known NMR spectroscopic data.

Table 2. Structure and refinement data of PhBi[$(C_2F_5)_2PO_2$]$_2$, **2**; Bi[$(C_2F_5)_2PO_2$]$_3$, **3** and $Ph_3Bi[(C_2F_5)_2PO_2]_2$, **6**.

	2	3	6
Crystallographic Section			
empirical formula	$C_{14}H_5BiF_{20}O_4P_2$	$C_{25}H_{28}BiF_{30}O_{13}P_3$	$C_{26}H_{15}BiF_{20}O_4P_2$
a / pm	1544.7(4)	1200.30(2)	1589.07(3)
b / pm	2058.4(2)	1555.70(2)	1716.37(4)
c / pm	1543.9(3)	2408.83(4)	2408.96(4)
α / °	90	89.1804(12)	90
β / °	96.37(3)	88.0205(12)	90
γ /°	90	88.9555(12)	90
V / 10^6 Å^3	4878.5(18)	4494.19(12)	6570.3(2)
Z	8	4	8
ρ_{calc} / mg·mm^{-3}	2.418	2.081	2.107
crystal system	monoclinic	triclinic	orthorhombic
space group	$P2_1/n$	$P\bar{1}$	*P*bca
shape / color	colourless fragment	colourless fragment	colourless block
crystal size / mm$^{-3.}$	0.36 x 0.14 x 0.09	0.31 x 0.28 x 0.16	0.35 x 0.29 x 0.23
Data Collection			
μ / mm^{-1}	5.550	4.210	5.612
F(000)	3312.0	2720.0	3968.0
2θ range for data collection	3.31 to 59.998°	4876 to 59.998°	3.382 to 60.162°
index ranges	$-21 \le h \le 21$ $-28 \le k \le 28$ $-21 \le l \le 21$	$-16\le h \le 16$ $-21 \le k \le 21$ $-33 \le l \le 33$	$-15 \le h \le 22$ $-24 \le k \le 22$ $-33 \le l \le 33$
reflections collected	284807	261486	59963
independent reflections	14223 [R(int) = 0.0868]	26174 [R(int) = 0.0878]	9634 [R(int) = 0.0332]
data/restraints/parameters	14223/0/648	26174/4/1305	9634/23/503
goodness-of-fit on F^2	1.109	0.991	1.038
R_1 / wR_2 [$I\le2\sigma(I)$]	0.0535 / 0.1305	0.0557 / 0.1424	0.0227 / 0.0485
R_1 / wR_2 (all data)	0.0573 / 0.1342	0.0669 / 0.1513	0.0325 / 0.0516

$\Delta\rho_{max/min}$ / e Å^{-3}	9.22 / −2.52	5.05 / −2.26	1.02 / -0.94
CCDC number	1433863	1433864	1433865

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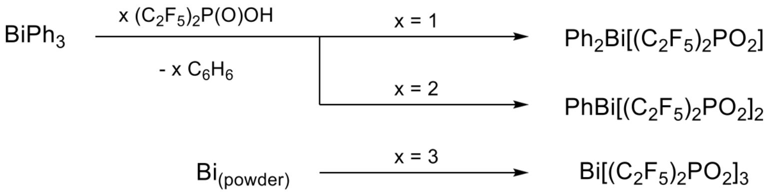

Bismuth perfluoroalkylphosphinate compounds, $Ph_xBi[R^F{}_2PO_2]_{3-x}$ (x = 0, 1, 2) (R^F= $-C_2F_5$, $-C_4F_8$), and $Ph_3Bi[(C_2F_5)_2PO_2]_2$ are very active catalysts for a whole series of organic transformations, such as Friedel-Crafts alkylations and acylations, as well as Diels-Alder, Strecker and Mannich type reactions. As an improvement over other catalytic systems the complexes are easily available, non-hygroscopic, soluble in a few organic solvents and they are stable towards moisture, air oxidation and heat.

*Sven Solyntjes, Beate Neumann, Hans-Georg Stammler, Nikolai Ignat'ev and Berthold Hoge**

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Bismuth Perfluoroalkylphosphinates: New Catalysts for Application in Organic Syntheses