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Bismuth

Bismuthanes as Hemilabile Donors in an O_2-Activating Palladium(0) Complex

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Dedicated to Professor Dieter Fenske on occasion of his 75th birthday

Abstract: A xanthene-based bismuthane/phosphane chelating ligand has been accessed that has enabled the synthesis of a palladium(0) bismuthane complex. The bismuthane donor proved to be hemilabile as it switched to a dangling position upon addition of O_2 that gave a palladium(II) peroxide complex. Unlike the corresponding 4,5-bis(diphenylphosphino)-9,9-dimethylxanthene (Xantphos) palladium peroxide, the bismuth analogue could be employed for catalytic phosphane oxidation and oxidative phenol coupling.

A lively area of current research is concerned with the directed construction of compounds, in which two different metals interact. Such investigations are motivated to uncover new properties, emerging through the M⋯M′ contact or to develop new modes of cooperative reactivity.[1] Focusing on bismuth(III) as part of such heterometallic entities, it is noted that only few complexes exist, in which a transition metal neighbors Bi directly, and most of them feature a covalent bonding situation, that is, a metal–metal bond.[2] Some compounds have been isolated, which showed that bismuthanes principally can act as donor ligands;[3] however, their number is rather limited, and because of their reduced donor abilities, bismuthanes were called the Cinderellas among Group 15/16 ligands.[3b] Those bismuthane complexes, which are known, mainly contain Group 6–8 central atoms,[2] and until recently, closed-shell M⋯Bi interactions, for M representing a late-transition metal, remained virtually unexplored.[4] In 2012, we and concomitantly Gabbaï and co-workers established bismuth–late-metal bonds through a different kind of metallophilic interaction. The Lewis acidity of Bi^{III} in an ambiphilic PBiP ligand system (Ph_2P-C_6H_4-Bi(Cl)-C_6H_4-PPh_2), employed as such[5] or generated in situ,[6] was exploited to bind Au^{I}, Pt^{II} and Pd^{II} centers, which acted as σ donors. It was further shown that upon replacement of the Cl residue at Bi against less electronegative ligands, the character of the bismuthane changed from acceptor to predominantly donor.[7]

The insights gained tethering bismuthane functions with phosphane units as in the PBiP ligand mentioned above for the complexation of late transition metals, led us to pursue further promising bismuthane/phosphane combinations. The xanthene backbone has been used for the construction of a variety of potent bidentate ligands and complexes that exhibit interesting reactivity.[8] Mostly, these ligands contain two aryl phosphane units (rarely also mixed P/N donors), the most prominent representative being 4,5-bis(diphenylphosphino)-9,9-dimethylxanthene (Xantphos; Figure 1, left).

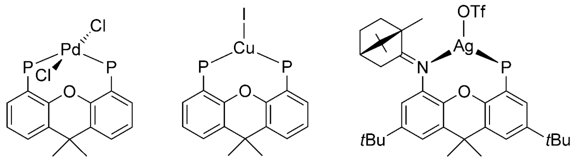

Figure 1. Selected complexes with xanthene-based phosphane ligands ($P=PPh_2$).[8a–c]

Hence, we were interested to replace (formally) one of the phosphane functions in Xantphos by a bismuthane unit ($BiPh_2$) and to then investigate the coordination properties of the new potential ligand Xan(PPh_2)($BiPh_2$) towards a Group 10 metal in the oxidation state 0. Herein, we present the synthesis of Xan(PPh_2)($BiPh_2$), its reactivity towards a Pd^0 precursor, and the activation of O_2 by the resulting complex.

The synthesis of Xan(PPh_2)($BiPh_2$) started with the introduction of the phosphane fragment to the xanthene backbone according to a modified literature procedure.[9] For this, $XanBr_2$ was lithiated with one equivalent of phenyllithium and then treated with one equivalent of Ph_2PCl in tetrahydrofuran. The bismuthane unit was then introduced through a second lithiation and a subsequent reaction with Ph_2BiCl (Scheme 1). After work-up, a white solid was isolated, which was identified as Xan(PPh_2)($BiPh_2$) by NMR spectroscopy, elemental analysis, and ESI MS data. Single-crystals of Xan(PPh_2)($BiPh_2$) that were suitable for an X-ray diffraction analysis were obtained by diffusion of hexane into a saturated solution of Xan(PPh_2)($BiPh_2$) in toluene (Figure 2).

The bismuth atom exhibits the typical structural features of triply arylated bismuthanes, so that the sum of the angles

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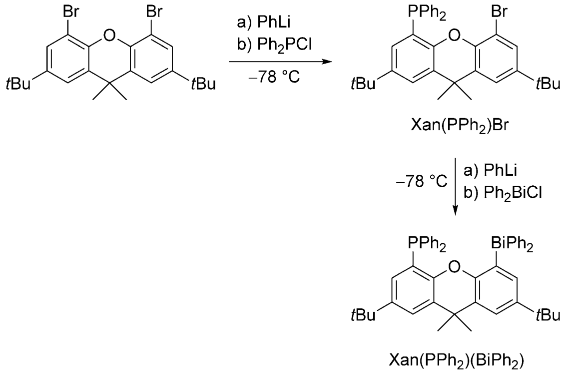


Scheme 1. Synthesis of the potential ligand Xan(PPh_2)($BiPh_2$).

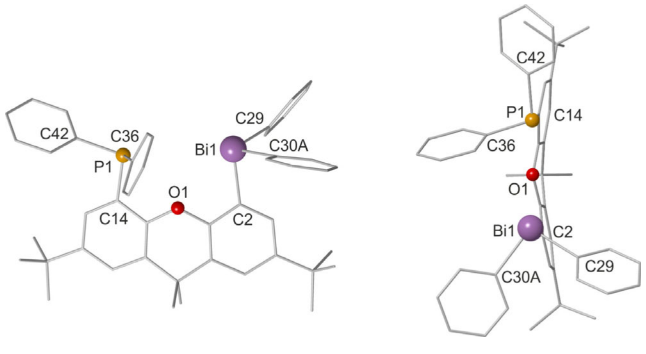
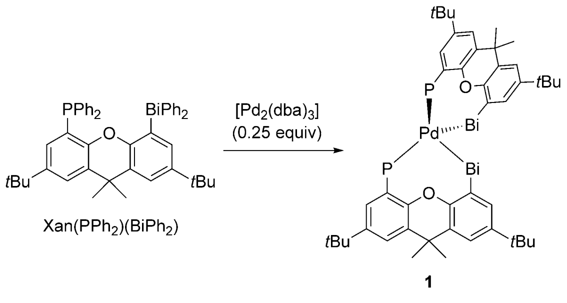


Figure 2. Molecular structure of Xan(PPh_2)($BiPh_2$): (left) front view, (right) top view. All hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: C2–Bi1 2.273(2), C29–Bi1 2.223(3), Bi1–C30A 2.256(4), C36–P1 1.865(3), C42–P1 1.886(3), C14–P1 1.832(3), P1···Bi1 4.2096(15); C29-Bi1-C2 91.53(10), C30A-Bi1-C2 93.38(12), C14-P1-C36 103.59(14), C14-P1-C42 102.11(13), C29-Bi1-C30A 94.90(13).

around the Bi^{III} atom amounts to only 279.81°.[10] The phenyl residues at the P and Bi atoms are pointing away from each other, and the $Bi^{III}\cdots P^{III}$ distance is 4.2096(15) Å.

Bearing in mind the scarcity of complexes with Pd···Bi interactions (apart from a cluster[11] and a complex[10a] containing Pd–Bi metal bonds, only a $Pd^{II}\rightarrow Bi$ complex of the above-mentioned ambiphilic pincer ligand is known[6]) the potential of Xan(PPh_2)($BiPh_2$) to bind Pd^0 was investigated. Therefore, a mixture of Xan(PPh_2)($BiPh_2$) and 0.25 equivalents of [$Pd_2(dba)_3$] (dba = bis(dibenzylideneacetone)) was dissolved in tetrahydrofuran, and a color change from dark red to yellow was observed within a few minutes (Scheme 2).



Scheme 2. Synthesis of a Pd^0 complex **1** (P = PPh_2, Bi = $BiPh_2$).

In the $^{31}P\{^1H\}$ NMR spectrum of a solution in C_6D_6, the phosphane donor gave rise to a signal at $\delta = 20.8$ ppm, shifted by 37 ppm in comparison to unbound Xan(PPh_2)($BiPh_2$). The proton NMR spectrum displayed two new singlet signals for the methyl groups ($\delta = 1.56$ and 1.71 ppm) of the xanthene backbone. Suitable crystals for an X-ray diffraction analysis could be grown by diffusion of diethylether into a saturated solution of the product in acetonitrile at room temperature and the corresponding molecular structure determined is shown in Figure 3.

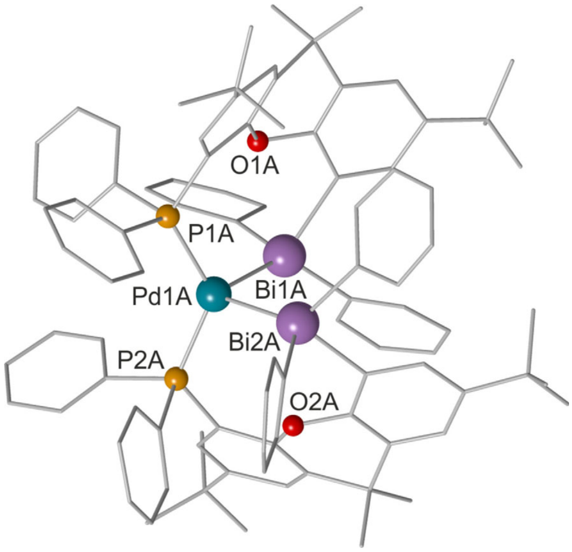
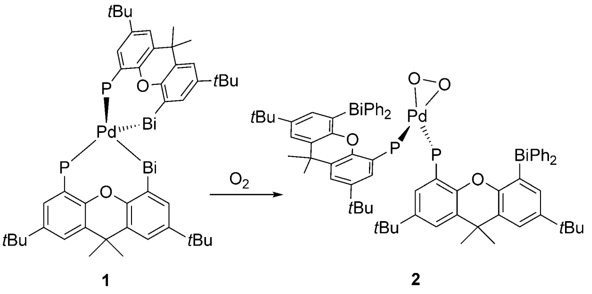


Figure 3. Molecular structure of **1**·MeCN. The co-crystallized MeCN solvent molecule and hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: P1A–Pd1A 2.290(3), P2A–Pd1A 2.297(3), Bi1A–Pd1A 2.7342(11), Bi2A–Pd1A 2.7845 (11); P1A-Pd1A-P2A 129.07(12), P1A-Pd1A-Bi1A 105.67(9), P2A-Pd1A-Bi1A 106.86(8), P1A-Pd1A-Bi2A 105.97(8), P2A-Pd1A-Bi2A 107.51(8), Bi1A-Pd1A-Bi2A 97.27(3).

The complex was identified as [(Xan(PPh_2)($BiPh_2$))$_2$Pd] (**1**), that is, the Pd^0 center is surrounded by two ligand molecules. Both phosphorus and bismuth donors are bound, so that a tetrahedral coordination sphere results. The distances of Bi1A···Pd1A 2.7342(11) Å and Bi2A···Pd1A 2.7845(11) Å indicate a significant interaction between these atoms, because the values are significantly smaller than the sum of the corresponding van der Waals radii (3.70 Å).[12] To clarify the nature of the metallophilic Bi···Pd interactions present, DFT calculations (B3LYP) were carried out for **1**, and a natural bond orbital (NBO) analysis revealed one dominating donor–acceptor interaction between the filled atomic orbital of bismuth (6s) and the empty atomic orbital of palladium (5s), and thus, an unprecedented to date $Bi\rightarrow Pd$ ligation. The corresponding average NBO deletion energy amounts to 61.9 $kcal\,mol^{-1}$ ($Bi1A\rightarrow Pd1A$ 67.1 and $Bi2A\rightarrow Pd1A$ 56.8 $kcal\,mol^{-1}$).

Because a series of different P-ligand-based Pd^0 complexes are known, which are able to react with dioxygen forming palladium(II) peroxido complexes,[13] the reaction behavior of complex **1** towards the activation of O_2 was tested.



Scheme 3. Synthesis of a Pd^{II} peroxido complex **2** (P = PPh$_2$, Bi = BiPh$_2$).

After treatment of complex **1** with dioxygen in *n*-hexane, a light yellow precipitate was formed within a few minutes, which was analyzed by infrared spectroscopy (Scheme 3). The solid-state IR spectrum (ATR) showed one characteristic absorption band at $\tilde{\nu} = 920\,\mathrm{cm}^{-1}$, which can be assigned to a O–O stretching vibration of a η^2-peroxido ligand.[13] For the ^{18}O isotopically labeled complex a shift of $\Delta\tilde{\nu} = 52\,\mathrm{cm}^{-1}$ to higher wavelengths could be observed (Figure 4).

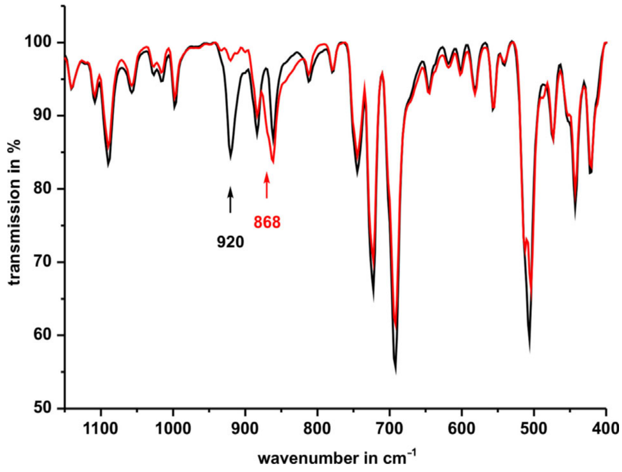


Figure 4. ATR-FTIR spectra of ^{16}O-**2** (black) and ^{18}O-**2** (red) between 1150 and 400 cm^{-1}.

Upon cooling of a saturated solution of the product in toluene/*n*-hexane (1:2) to −30 °C for 16 hours, crystals were grown, and an X-ray diffraction analysis revealed the molecular structure of [(Xan(PPh$_2$)(BiPh$_2$))$_2$PdO$_2$] (**2**; Figure 5).

The Pd^{II} center is coordinated in a distorted square-planar coordination sphere by the phosphane units and the peroxide ligand, whereas the bismuthane units remain dangling. Accordingly, these bismuthane donors in **1** can be considered as hemilabile[14]: they readily give way to an external substrate, such as O$_2$, but in **1**, they serve to fill the otherwise vacant coordination sites. The crystallographically determined O2–O2′ bond length of 1.433(5) Å is within the typical range of known Pd^{II}(η^2-O$_2$) complexes,[13] and also the Pd1–O2/O2′ distances are with 2.015(3) Å characteristic.[13]

Compound **2** decomposes rapidly in solution, but as a solid **2** is stable for months at room temperature. Dissolving **2** in a solvent leads to the loss of the peroxido unit with regeneration of the Pd^0 complex **1**. The hemilabile behavior of the bismuthanes triggered investigations on the potential of **2** as an oxidant, because some of the known Pd–O$_2$ complexes have been reported to perform oxidations.[15]

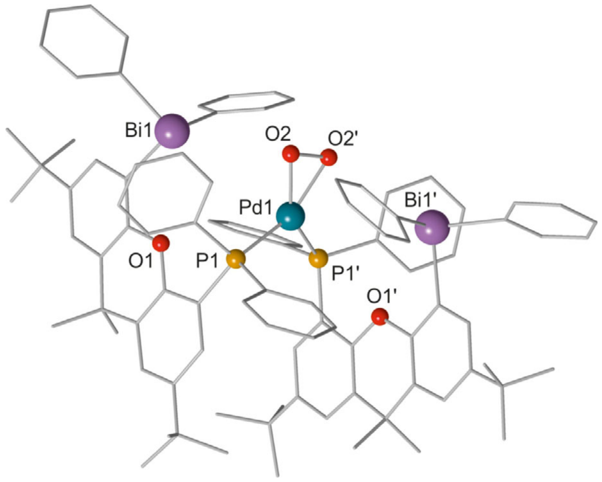
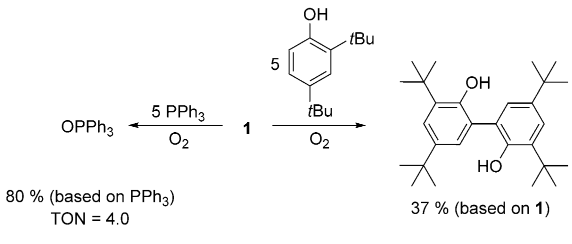


Figure 5. Molecular structure of **2**. All hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Pd1–O2 2.015(3), Pd1–P1 2.3175(9), O2–O2′ 1.433(5), Bi1⋯P1 4.4507(12), Bi1⋯Pd1 4.2233(16); O2-Pd1-O2′ 41.65(15), O2-Pd1-P1 104.14(8), O2′-Pd1-P1 144.76(8), P1-Pd1-P1′ 110.84(5).

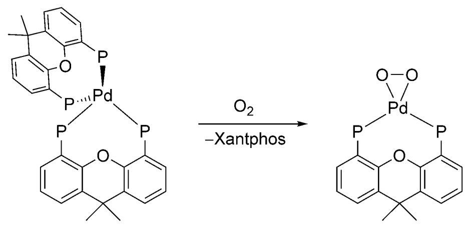
Due to the low stability of **2** in solution, dioxygen was added to a mixture of complex **1** and five equivalents of PPh$_3$ in tetrahydrofuran.[17] A discoloration of the solution was observed immediately. By using ^{31}P{^{1}H} NMR spectroscopy, the formation of OPPh$_3$ (80 %, TON = 4.0; based on PPh$_3$) was detected (Scheme 4). Although we could not obtain evidence for any intermediate of the catalytic cycle, a conceivable mechanism could include a bis(μ-oxido) species generated after the first O atom transfer or the insertion of phosphane into the Pd–O$_2$ bonds.[16]



Scheme 4. Reactions of complex **1** with PPh$_3$ and 2,4-di-*tert*-butylphenol in the presence of dioxygen.

Employing 2,4-di-*tert*-butylphenol as a substrate (5 equiv in THF) led to the formation of the coupling product 3,3′,5,5′-tetra-*tert*-butyl-2,4-bisphenol (37 %; based on complex **1**). For the analogous reaction with 9,10-dihydroanthracene, no reactivity was observed.

To investigate the influence of the bismuthane units in **1** for O$_2$ activation and subsequent substrate oxidation, the analo-



Scheme 5. Synthesis of a Pd^{II} peroxido complex **4** (P = PPh_2).

gous bis-ligated Pd^0 complex [(Xantphos)$_2$Pd] (**3**) based on the Xantphos ligand[8e] was prepared in situ and also reacted with molecular dioxygen in THF to generate a Pd^{II} peroxido complex (Scheme 5).

Formation of a crystalline, yellow green solid was observed, which was analyzed by infrared spectroscopy. A characteristic absorption band at $\tilde{\nu} = 907\ cm^{-1}$, shifting by $67\ cm^{-1}$ upon usage of $^{18}O_2$ was observed again, suggestive of a O–O stretching vibration and formation of a peroxide complex.[13]

Upon cooling a saturated solution of the product in tetrahydrofuran to −30 °C for 16 hours, crystals could be grown, and an X-ray diffraction analysis identified the product as [(Xantphos)$_2$PdO$_2$] (**4**; Figure 6). In comparison to **2**, complex **4** contains only one ligand molecule, coordinating to the metal center by both phosphane donors. The palladium(II) center is found in a square planar coordination sphere, and the O2–O2′ distance of 1.422(5) Å, as well as the Pd1–O2 distance of 2.015(3) Å (Pd1–O2′ is the same) are similar to those found for compound **2**.

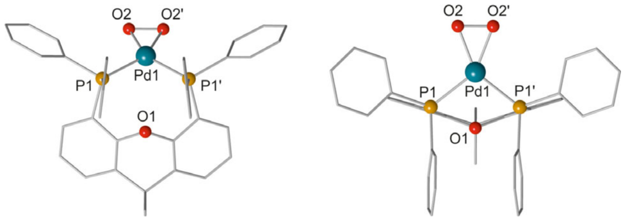


Figure 6. Molecular structure of **4**. Left: front view; Right: top view. All hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Pd1–O2 2.015(3), Pd1–P1 2.3100(10), O2–O2′ 1.422(5), P1···P1′ 3.5883(14); O2-Pd1-O2′ 41.33(14), O2-Pd1-P1 108.30(8), O2′-Pd1-P1 149.54(8), P1-Pd1-P1′ 101.91(5).

Compound **4** proved to be stable in solution, that is, neither elimination of O_2 nor reformation of **3** was observed. Once isolated, **4** showed a rather low solubility in common aprotic solvents. Because the precursor **3** showed the same behavior, the reactivity of **4** was studied best by preparing first **3** and then **4** in situ.[17]

The reaction with PPh_3 led to the formation of $OPPh_3$ with yields of 31 % (based on complex **3**); hence, unlike **2**, **4** does not even achieve one oxygen-atom transfer (OAT) turnover. In the presence of 2,4-di-*tert*-butylphenol as a substrate, no oxidation or coupling product was observed. Also attempts to perform C–H bond activations failed.

In conclusion, first reactivity studies exhibit a higher reactivity for the bismuthane based complex **2** in comparison to **4** concerning the tested substrates PPh_3 and 2,4-di-*tert*-butylphenol. Apparently, the hemilabile character of the bismuth groups exerts a positive effect on the reactivity of the palladium peroxide complex **2** and restricts decomposition under turnover conditions. Further studies, especially with regard to the complexation behavior of the new bismuth-based ligand Xan(PPh_2)($BiPh_2$) towards other late transition metals and their reactivity towards small molecules are ongoing.

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Conflict of interest

The authors declare no conflict of interest.

Keywords: bismuth · hemilabile · metallophilic interactions · palladium · peroxido ligands

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[17] To confirm that indeed the peroxide is responsible for the observations made proceeding this way, all reactions with PPh_3 and 2,4-di-*tert*-butylphenol were also carried out in a different order (first the palladium peroxo complex **2** or **4** were generated, and afterwards the substrate was added). In these cases, the formation of $OPPh_3$ and the bisphenol, respectively, was observed, too, proving that the Pd^{II} peroxo compounds do in fact react this way. However, when using **2** directly, in the reactions with PPh_3 and the phenol, the yields were significantly lower compared to those observed after its generation in situ already in the presence of the substrate. This is probably due to the fact, that the palladium peroxo complex decomposes rapidly in solution. Therefore, the described procedure was preferred.

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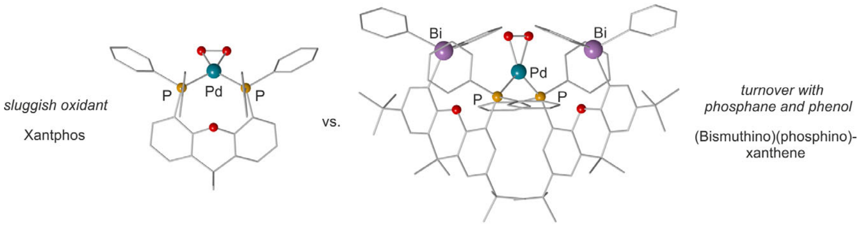
Bismuthanes as Hemilabile Donors in an O_2-Activating Palladium(0) Complex



New character trait of bismuthanes: Pd^0 chelated by a phosphino/bismuthino ligand reacted with dioxygen to form a palladium(II) peroxido complex (see scheme). In this reaction, the bismuthane donor acts as a hemilabile ligand that leaves when O_2 enters and comes back, upon O_2 elimination. This feature proved to be favorable for the properties of the peroxide as an oxidant.