DOI: 10.1002/anie.201200848

Metallophilic Interactions

Gold– and Platinum–Bismuth Donor–Acceptor Interactions Supported by an Ambiphilic PBiP Pincer Ligand**

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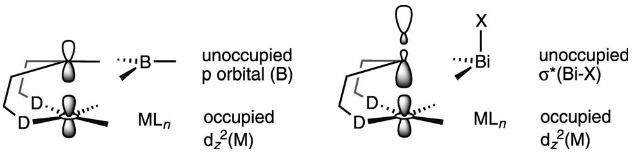
Dedicated to Professor Karl Wieghardt on the occasion of his 70th birthday

Compared to the other pnictogens, bismuth, the heaviest of all stable elements, certainly has a unique character. Correspondingly, also its chemistry in the oxidation state +III frequently differs greatly from that of its lighter homologues. Although some compounds have been isolated that show that bismuthanes can principally act as donor ligands for transition-metal ions,[1] their number is rather limited. This is likely due to the inert character of the $6s^2$ lone pair, which, because it is stabilized by pronounced relativistic effects, does not possess a donor strength comparable to that of phosphane lone pairs for example. In contrast, Bi^{III} compounds often show distinct Lewis acidic properties, especially if electronegative ligands X are bound. This can be rationalized by the fact that binding of X to Bi^{III} generates an antibonding σ*(Bi−X) orbital directed towards the position *trans* to X, which acts as an acceptor orbital for external ligands ("secondary bonding").[2] Lewis acidity combined with the large ionic radius of Bi^{3+} and the low toxicity of its complexes has led to an increasing popularity of Bi compounds, including as catalysts in organic chemistry.[3]

The σ-donor behavior of electron-rich transition-metal ions towards electron deficient, Lewis acidic main-group elements (for example of Group 13) was demonstrated some time ago.[4] A general framework of systems that have allowed for the successful establishment of metal–boron interactions through tethering even in the absence of a *trans*-positioned σ-donor[4i] is shown in Scheme 1 on the left hand side. Very recently, compounds were reported in which transition-metal complex fragments act as donors even for *saturated* Lewis acidic units containing Si^{IV} and Sn^{IV},[5a,b] as well as Sb^{V} centers.[5c]

In the past we have been concerned with Bi−M bonds,[6] and the background outlined above made us wonder whether the concepts that have allowed for the synthesis of stable metal→boron complexes may also be utilized to access complexes in which bismuth(III) presents its Lewis acidic nature in a bond to a late transition metal (Scheme 1, right). The abovementioned properties of bismuth particularly encourage corresponding investigations, both to gain fundamental insights and also with respect to potential applications: The possibility of influencing the reactivity and catalytic activity (selectivity) of a late transition-metal complex entity by Lewis acidic bismuth moieties, the properties of which in turn can be tuned by the electronegativity of the connected coligands, appears highly attractive. Nevertheless, closed-shell M−Bi interactions, with M representing a late transition metal, are still virtually unexplored: Bismuthane complexes are known mainly for the Groups 6–8,[1] and with regard to the noble metals, only one precedent case of a metallophilic M−Bi interaction has been reported: in $[Au(C_6F_5)_2]^-[Bi(2\text{-}CH_2NMe_2C_6H_4)_2]^+$ electrostatic effects lead to a $Au^I\cdots Bi^{III}$ contact.[7]



Scheme 1. Frameworks enabling electronic interactions of Lewis acidic boron (left) and bismuth centers (right) with electron-rich transition-metal fragments d^8 ML_n ($D=PR_2$, X = electronegative ligand).

To stabilize complexes displaying such metallic contacts with pronounced M→Bi character, we have now developed an ambiphilic ligand system in which a Lewis acidic Bi−X unit is combined with two Lewis basic phosphane donor functions that may serve to place the Bi−X unit close to a transition-metal center. Obvious choices for suitable complex metal fragments are those containing metals with a d^8 configuration and thus a filled Lewis basic d_{z^2} orbital (see Scheme 1). An interesting candidate is also Au^I, as it can be expected to lead to large relativistic effects.[7] Having tailored a PBiP pincer ligand for this purpose, we have therefore tested its potential to establish M−Bi interactions for Au^I and d^8-configurated Pt^{II}. Herein we describe the results of our efforts that led to complexes incorporating strong Au→Bi and Pt→Bi interactions.

To synthesize the envisaged ambiphilic ligand, two equivalents of 1-bromo-2-diphenylphosphinobenzene were reacted with *n*BuLi for a subsequent salt metathesis reaction

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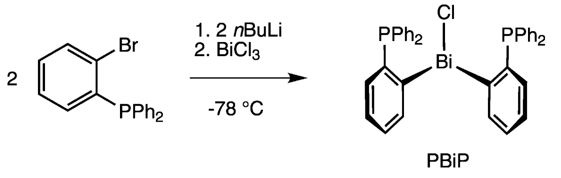
[**] We are grateful to the Deutsche Forschungsgemeinschaft, the Fonds der Chemischen Industrie, and the Humboldt-Universität zu Berlin for financial support. We also would like to thank Martin Quick for support in femtosecond spectroscopy studies and Prof. Martin Kaupp for helpful discussions.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201200848.



Scheme 2. Synthesis of ambiphilic Bi(o-PPh_2-C_6H_4)$_2$Cl (PBiP).

with $BiCl_3$ (Scheme 2). After purification, Bi(*o*-PPh_2-C_6H_4)$_2$Cl (PBiP) was isolated as a creamy white solid.

Single crystals of PBiP suitable for X-ray diffraction were obtained by slow evaporation of the solvent from a saturated solution in *p*-xylene, and Figure 1 shows the molecular structure.[8] The Bi–C and Bi–Cl distances in PBiP do not significantly differ from those in other Bi(aryl)$_2$Cl compounds,[9] and the sum of angles around the bismuth atom (276.29°) is also characteristic for this metal in its oxidation state +III.[10] The two Bi–P/P′ distances in the molecule differ from each other (3.1695(18) and 3.4071(18) Å), both being shorter than the sum of the Bi and P van der Waals radii (3.87 Å).[11]

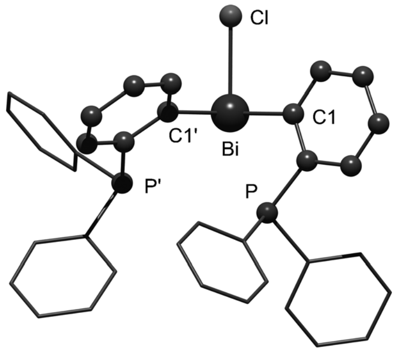
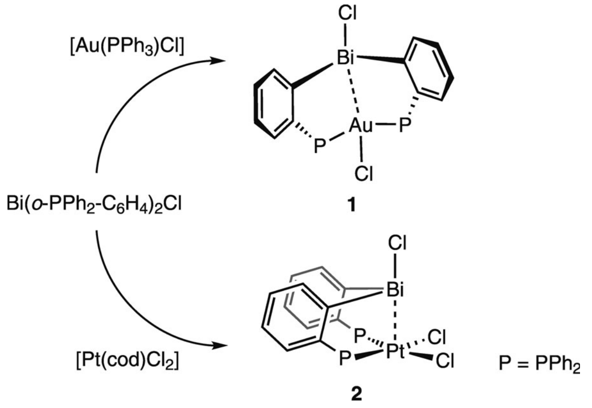


Figure 1. Molecular structure of Bi(*o*-PPh_2-C_6H_4)$_2$Cl (PBiP). Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Bi–Cl 2.5639(17); Cl-Bi-C1 90.91(18), Cl-Bi-C1′ 89.98(17), C1-Bi-C1′ 95.4(2).

For the complexation of Au^I, a mixture of the two colorless compounds [Au(PPh_3)Cl] and PBiP was dissolved in dichloromethane, which led to an immediate coloration to yellow. The $^{31}P\{^1H\}$ NMR spectrum of the corresponding yellow solid dissolved in CD_2Cl_2 showed a single resonance at $\delta = 25.8$ ppm, which a chemical shift typical for aryl phosphane units coordinated to Au^I,[5c,12] thus suggesting the complex [Au(PBiP)Cl] (**1**) as the product (Scheme 3).

By diffusion of hexane into a saturated solution of **1** in acetone, crystals could be grown that where suitable for an X-ray diffraction analysis;[8] the corresponding molecular structure is depicted in Figure 2. The Au^I center in **1** is located in a distorted square-planar coordination sphere composed of the bismuth(III) atom, the two phosphane moieties, and the chloride ligand. This is noteworthy, as a four-coordinate gold(I) atom should favor a tetrahedral surrounding.[13] However, the same observation has been made by Bourissou et al. in case of the gold–boron system [Au{B(*o*-PPh_2-C_6H_4)$_2$Ph}Cl][4c] and it documents the unusual character of these ligand systems. The Bi/B-Au-Cl and P-Au-P′ angles are quite similar for both complexes. Obviously, the most important structural parameter of [Au(PBiP)Cl] is the Au–Bi distance. To our knowledge, only one compound so far exists in the literature that may be compared with **1** in this respect: In 2007, Fernández et al. reported a Au–Bi interaction in $[Au(C_6F_5)_2]^-[Bi(2\text{-}CH_2NMe_2C_6H_4)_2]^+$.[7a] In this complex, the Au^I–Bi^{III} distance of 3.7284(5) Å is still as long as the sum of the corresponding van der Waals radii that can formally be assigned (3.728 Å),[11] but naturally in case of such large atoms the latter are somewhat ill-defined, as even the homometallic element–element distances vary substantially in different compounds. DFT and ab initio calculations have revealed that in $[Au(C_6F_5)_2]^-[Bi(2\text{-}CH_2NMe_2C_6H_4)_2]^+$, the Au–Bi contact mainly arises from electrostatic interactions (80%), complemented by some dispersion-type interactions (20%).



Scheme 3. Synthesis of heterometallic complexes **1** and **2**. cod = 1,5-cyclooctadiene.

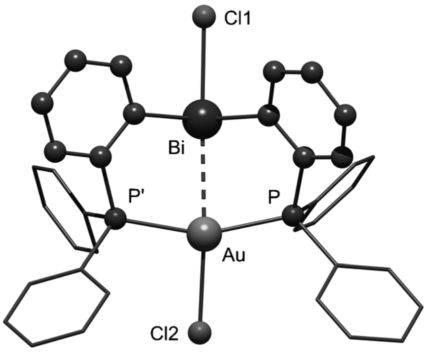


Figure 2. Molecular structure of [Au(PBiP)Cl] (**1**). One co-crystallized acetone solvent molecule and hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Bi–Au 2.9979(3), Bi–Cl1 2.6183(16), Au–Cl2 2.5185(16), Au–P 2.3061(14), Au–P′ 2.3044(14); Au-Bi-Cl1 171.42(4), Bi-Au-Cl2 162.25(4), P-Au-P′ 157.90(5), Bi-Au-P 79.26(4), Bi-Au-P′ 80.55(4), P-Au-Cl2 104.37(5), P′-Au-Cl2 97.60(5).

The Au–Bi distance is much shorter in **1** (2.9979(3) Å). To clarify which kind of orbitals are involved in bonding, density functional calculations were performed (B3LYP/Def2-TZVP), and an NBO analysis revealed one dominating donor–acceptor interaction between atomic orbitals of the two metal atoms: Au($5d_{x^2-y^2}$)→Bi($6p_y$), which stabilizes the Lewis structure by an energy of 12.3 kcal mol^{-1}. Some back-donation Bi(6s)→Au(6s) does occur, but comparison of the corresponding stabilizing energy of 4.9 kcal mol^{-1} shows that its contribution to the bonding is minor (see the Supporting Information). The orbitals mainly contributing to the donor–acceptor interactions are shown in Figure 3.

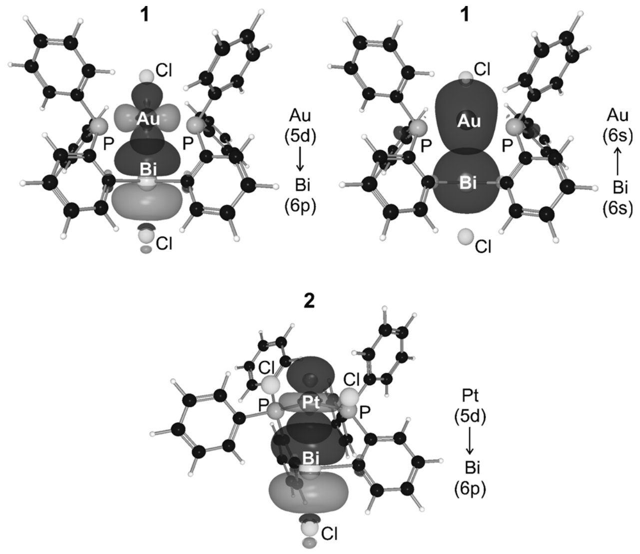


Figure 3. Superposition of the donor and acceptor orbitals according to NBO analysis, which contribute mainly to the metal–bismuth interactions in **1** (above) and **2** (below); s character Bi 6s 87%, Au 6s 96%.

Metallophilic interactions involving gold are of interest not only principally and theoretically but also for photophysical chemistry: Luminescence of gold(I) complexes has been observed depending on the nature and geometry of the chosen ligands and on the strength of intermolecular aurophilic interactions.[14] A new development in this area is the synthesis of complexes, which contain a second metal component through heterometallic interactions.[14] The latter can modify the frontier orbital situation of gold and thus influence the photophysical properties.

Indeed, the combination of [Au(PPh_3)Cl] and PBiP results in a new absorption band for **1** that is not inherent to the starting materials. The optical absorption of [Au(PBiP)Cl] in dichloromethane has its maximum at 377 nm. As static fluorescence measurements did not show emission, the fate of photoexcited complex **1** was investigated in more detail by femtosecond transient absorption spectroscopy.[15] Excitation was performed with short pulses at 403 nm, which is on the red flank of the absorption band. After a variable time delay, induced absorption spectra were measured (90 fs time resolution) with white-light continuum pulses. Characteristic spectral changes at early times, between 430–630 nm, can be attributed to stimulated emission (SE). The initial SE band at around 460 nm mirrors the absorption band and also its oscillator strength is similar. It is assigned to the Franck–Condon region on the excited-state potential energy surface. With a 0.43 ps time constant, the emission shifts to the red region and broadens significantly. This process could reflect the reorganization of the structure and solvent shell. Thereafter, the emission disappears with 1.76 ps time constant. All spectra and their analysis are reported in the Supporting Information.

The complexation behavior of PBiP with regard to Lewis basic d^8 transition-metal complex fragments was investigated in the reaction of PBiP with [Pt(cod)Cl_2] in dichloromethane, which led to the formation of [Pt(PBiP)Cl_2] (**2**; Scheme 3). Compound **2** was isolated as a light-yellow solid, and crystals that were suitable for X-ray diffraction analysis could be obtained by the same procedure as described above for **1**; the molecular structure of **2** is shown in Figure 4.[8] The platinum(II) center is found in a square-pyramidal coordination sphere, where the two phosphane donor functions of the ambiphilic ligand are in *cis* configuration to each other. The two chloride ligands complement the square base, and owing to the geometry of the PBiP ligand, the bismuth atom forms the top of the pyramid. In this position, the Lewis acidic σ*(Bi−Cl) orbital is ideally oriented for an interaction with the filled d_{z^2} orbital of the Pt^{II} ion (Scheme 1), and to maximize this interaction the Pt-Bi-Cl unit adopts an almost linear arrangement (Pt-Bi-Cl angle 178°), as often found in case of efficient secondary bonding.[1,2] The Pt−Bi distance in **2** amounts to 2.9009(5) Å; therefore, the ratio between the metal–metal distance and the sum of the van der Waals radii is even smaller (0.76) than in the case of the gold–bismuth complex **1** (0.80).[10] If the structure of **2** is divided by the plane including the Pt−Bi axis and the P-Pt-P angle bisector, it becomes obvious that the two P atoms of **2** experience somewhat different environments (Figure 4 b), and if this structure was preserved in solution, different resonances should be expected for the two P donor functions in the NMR spectra of the complex. Indeed at −80 °C, the $^{31}P\{^1H\}$ NMR spectrum of **2** dissolved in [D_8]THF displays two doublets

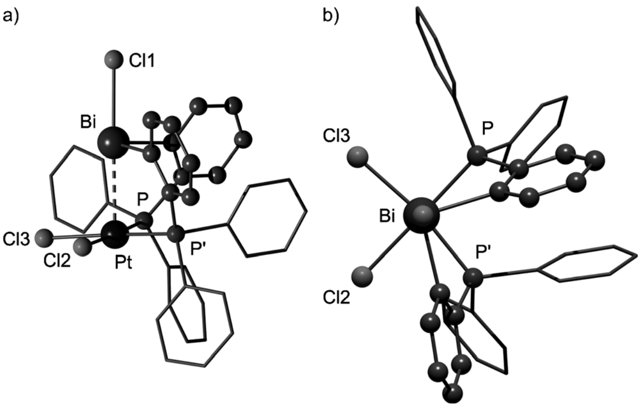


Figure 4. a) Molecular structure of [Pt(PBiP)Cl_2] (**2**). One co-crystallized acetone solvent molecule and hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Bi–Pt 2.9009(5), Bi–Cl1 2.6197(19), Pt–Cl2 2.4195(17), Pt–Cl3 2.4193(17), Pt–P′ 2.268(2), Pt–P 2.266(2); Pt-Bi-Cl1 178.67(6), Bi-Pt-Cl3 93.95(4), Bi-Pt-P′ 87.46(6), Cl2-Pt-Cl3 87.54(6), P-Pt-P′ 97.96(9); b) View onto Cl1 along the Bi−Pt axis.

($\delta = 23.8$ and 16.8 ppm with ^{195}Pt satellites), which at room temperature are broadened into the baseline, presumably through a dynamic process. At low temperatures, the two donor moities of the ligand can also be distinguished by ^{1}H and ^{13}C{^{1}H} NMR spectroscopic analysis.

Calculations were also carried out for **2**, and an NBO analysis revealed again one dominating metal–metal interaction, namely Pt(5d)→Bi(6p) with a stabilizing energy of 24.4 kcal mol^{-1} (see Figure 3 and Supporting Information). No significant contribution of a Bi→Pt back-donation was found, so the situation depicted in Scheme 1 is realized in **2** in an ideal way. This explains how the Pt→Bi stabilization energy is almost twice as high as the Au→Bi stabilization energy in **1**, indicating a stronger interaction between the metal atoms in **2**, which is consistent with the above findings regarding the Pt–Bi distance.

These results clearly indicate the feasibility of the concept illustrated in an idealized way in Scheme 1 and the potential of $Bi(o\text{-}PPh_2\text{-}C_6H_4)_2Cl$ in the establishment of metallophilic interactions involving bismuth and M→Bi bonds. In future work, the influence of the Bi functions and their modification (by variation of X) on the reactivity/selectivity of platinum and also palladium complex fragments, for instance in catalytic applications, will be investigated. A cooperative reactivity of late-metal and bismuth centers in substrate activation is also conceivable.

Received: January 31, 2012

Keywords: ambiphilic ligands · bismuth · gold · metallophilic interactions · platinum

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