A trigonal coordination of Au(I) phosphane complexes stabilized by O–H⋯X (X = Cl−, Br−, I−) interactions

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Abstract
In this work, we show that intramolecular hydrogen bonding can be used to stabilize tri-coordinated phosphane-gold(I) complexes. Two molecular structures of 2-(diphenylphosphino)benzoic acid (L) coordinated to a gold(I) atom were determined by single-crystal X-ray diffraction. The linear L–Au–Br shows a standard linear coordination and dimerizes via hydrogen bonds of the carboxylic acid. Upon addition of two additional phosphane ligands the complex [L3Au]X is formed which is stabilized by three intramolecular –C(O)O–H⋯X hydrogen bonds as proven by the X-ray structure of the respective chlorido-complex. X-ray powder diffractograms suggest the same structure also for X− = Br− and I−.

Keywords Gold complexes · Crystal structure · Tri-coordinate gold(I) · Hydrogen bonds

Introduction
The structural chemistry of gold(I) complexes is dominated by a linear coordination, although higher coordination numbers are not particularly rare [1–4]. Interestingly, for isoelectronic cations like Ag(I), Pt(0), or Hg(II) the preference for a linear coordination is much weaker and they usually form complexes with coordination numbers higher than two. Due to a possible formation of aurophilic interactions a huge structural diversity is observed for various types of ligands in their gold(I) complexes. Especially well investigated are phosphane complexes of gold(I) for a variety of reasons: (i) they are easy to prepare, (ii) a wide variety of structural diverse phosphanes are commercial available, (iii) they are relatively stable under ambient condition, although sometimes light sensitive, (iv) with 31P NMR spectroscopy, a very convenient and sensitive method for a fast and efficient characterisation is available, (v) gold(I) phosphane complexes have been proven to be very useful in many different applications and can be found as luminescent material, catalyst, or pharmaceutical active agent [5–14].

However, there are surprising few systematic structural studies on the extension of the coordination sphere of
mononuclear gold(I) complexes beyond the linear geometry. By adding additional phosphane ligands R3P to complexes of the type R3P–Au–X (X = mostly anionic ligand, e.g. halides or pseudohalides), different coordination environments are conceivable and have been reported. For a P:Au ratio of 2:1, either the distorted trigonal-planar and neutral form (R3P)2AuX or the ionic form [(R3P)2Au]X are known. In the latter case, the gold atom is often in a linear, sometimes more or less distorted environment with the halide non- or weakly bonded [15–22]. The neutral form is often found for rigid bidentate phosphanes like 1,2-bis(diphenylphosphino)carbólane or 1,2-bis(diphenylphosphino)benzene and have the form (P3P)AuCl [23–27].

The ratios 3:1 and 4:1 is often but not exclusively found for X = weakly coordinating anions and these compounds contain a trigonal-planar [(R3P)2Au] + or tetrahedral [(R3P)2Au] + coordinated cation, respectively [12, 28–30]. The latter is also the highest coordination number found for phosphane-gold(I) complexes but very rare for monodentate phosphanes [31–33]. Seldom, neutral tetrahedral species are found (R3P)2AuX (X = halide) [34–37]. Again, rigid bidentate phosphanes facilitate higher coordination numbers. In these cases, several complex cations of the form [(P3P)AuL]+ (L = phosphane or carbene ligand) and [(P3P)2Au]+ have been reported [38–43].

Mononuclear, tri-coordinated gold(I) cations are interesting as they often feature phosphorescence based on mainly ligand field excited states [44–46]. Due to Jahn–Teller distortion, these complexes feature T-shape geometries in the excited state [47]. This strong distortion is also the reason for the huge Stokes shift, broad and unstructured emission band and the fact that luminescence is often relatively weak in solution or only observed at cryogenic temperature [48]. It should be mentioned that there are also several examples of bidentate phosphine ligands which form dinuclear gold(I) complexes with short Au–Au distances. However, such phosphorescence is based on aurophilic interactions and also observable at room temperature [49].

For monodentate phosphanes steric and electronic properties seem to subtly influence the stability of gold(I) complexes with higher coordination numbers [50]. In the literature, the complete series of (Ph3P)2AuX complexes (with n = 1–3, X = anion) is described whereas there are no reports on the existence of other, even very similar phosphanes which would form the whole set of possible complexes [45, 51]. Taking the dynamic behaviour of gold(I) complexes in solution into account, the polarity of the solvent might also play a crucial role as the formation of ionic or neutral complexes are sometimes determined by the polarity of the solvent [52, 53]. Besides sterics, it had been reasoned that higher coordination numbers could be established with (moderate) electron-poor ligands and indeed several gold(I) complexes bearing such phosphane ligands have been reported [29, 31, 36, 37]. This observation is conform with the fact that the less electron-donating Ph3E (E = As, Sb) readily form the respective gold complexes [(Ph3E)2Au]BF4 [54]. However, there are also examples of electron-donating phosphorus forming highly coordinated gold(I) atoms [28].

In this contribution, we would like to introduce a concept to stabilize mononuclear, tri-coordinate gold(I) complexes via E–H···X (E = O, N) interactions. A previously reported example is a complex, where an amide N–H functions as hydrogen-bond donor to the coordinated chloride facilitating tri-coordination of the form (Ph3RP)2AuCl (R = O-trifluoroacetanilide) [55]. An extensive hydrogen-bond network was also found in the tetrahedral gold(I) complex bearing 1,3,5-triaza-7-phosphaadamantane [31]. Similar, the tri-coordinated gold(I) complex bearing the trisulfonated triphenylphosphate is stabilized via an excessive network between the sulfonate groups and Cs+ counterions [29].

Results and discussion

Synthesis

Reaction of 2-(diphenylphosphino)benzoic acid, Ph2(o-BzOH)P, with equimolar amounts of (tht)AuCl (tht = tetrahydrothiophene) leads to the formation of 2-(diphenylphosphino)benzoic acid gold(I) chloride, Ph2(o-BzOH)PAuCl, 1-Cl. It should be mentioned that various gold(I) complexes bearing a diphenylphosphino-benzoic acid—both ortho and para—have been reported, among them also 1-Cl [56–59]. Through metathesis with KBr and KI the bromido and iodo congener 1-Br and 1-I are easily accessible. Upon addition of two further equivalents of the phosphane ligand, [Au(PPh2(o-BzOH))3]X (X = Cl, Br, I), 2-X, is formed (Fig. 1).

NMR spectroscopy

Due to the low solubility of the tri-coordinate gold(I) complexes 2-X, a thorough characterization by NMR spectroscopy was only possible for 1-X. Nevertheless, we conducted 31P(1H) NMR studies to get some basic information by adding different equivalents of the phosphate ligand to solutions of 1-X in CDCl3 (see Supporting Information, Fig. S1). The 31P NMR shift of the free ligand is at 72−4.1 ppm. Upon adding (tht)AuCl in equimolar amounts, the peak is shifted to 36.1 ppm for 1-Cl. For 1-Br and 1-I the peaks can be found at 38.3 and 42.5 ppm, respectively. An additional equivalent of the phosphate ligand gives a very broad signals at 745 ppm, the respective peaks of for the bromide (742.5 ppm) and iodide (739 ppm) are slightly sharper. These observations are indicative for a dynamic behaviour of the present
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Gold(I) species, presumably due to an equilibrium between the neutral tri- and ionic di-coordinated form according to $[\text{AuL}_3\text{X}] \rightleftharpoons [\text{AuL}_2]^+ \text{X}^- [L = \text{PPh}_2(o\text{-BzOH})]$. After the addition of the third equivalent of the ligand, the $^{31}\text{P}$ NMR signals either almost vanish (for 2-Br and 2-I, both at ~ 41 ppm) or have a low intensity (2-Cl, ~ 43 ppm) reflecting the low solubility of the complexes. Indeed, already with the addition of the second equivalent, some white precipitate forms. These observations are indicative for a lower solubility of the 2-Br/2-I compared to 2-Cl, which might be the reason for the unsuccessful attempts of growing single crystals of all prepared complexes (vide infra). Interestingly, upon addition of an excess of the ligand to 2-Cl, not only the peak of the complex, but also the free ligands are broad possible due to an exchange between bound and free phosphane ligands.

**Structural studies**

Crystals suitable for single-crystal X-ray diffraction analysis of 2-(diphenylphosphino)benzoic acid gold(I) bromide, 1-Br, could be obtained by slow gas diffusion of n-pentane into a concentrated solution of 1-Br in DCM (Fig. 2). The compound crystallizes in the monoclinic space group $\text{P}_{21}/n$. Crystals of chlorido-complex contains one molecule of CHCl$_3$ [59], hence 1-Cl and 1-Br are not isostructural. However, the arrangement of the molecules is very similar in both crystals: in their crystals the complexes dimerize via hydrogen bonds between the carboxylic groups (Fig. 2). The O⋯O distance of two adjacent gold complexes is 2.686(3) Å, which is typical for O–H⋯O of hydrogen bonded carboxylic acid groups [60, 61]. The gold atom is linearly coordinated with an angle Br1–Au1–P1 of 175.38(2)$^\circ$. The distance between the bonds and angles in Å and $^\circ$: Au1–Br1 2.3957(4), Au1–P1 2.247(1), P1–C1 1.825(3), P1–C8 1.817(3), P1–C14 1.815(3), Br1–Au1–P1 175.38(2), Au1–P1–C8 108.7(1), Au1–P1–C14 110.9(1), O1–C13–O2 124.7(3)

![Fig. 1](image1.png)

**Fig. 1** Reaction scheme for the synthesis of mono (a) and trifold (b) coordinate Au(I) complexes bearing the diphenylphosphino-benzoic acid ligand (X = Cl, Br, I).

![Fig. 2](image2.png)

**Fig. 2** Left: molecular structure of 2-(diphenylphosphino)benzoic acid gold(I) bromide, 1-Br (H omitted for clarity); right: dimerization of 1-Br in the solid state via hydrogen bonds. Selected bond lengths in Å and angles in $^\circ$: Au1–Br1 2.3957(4), Au1–P1 2.247(1), P1–C1 1.825(3), P1–C8 1.817(3), P1–C14 1.815(3), Br1–Au1–P1 175.38(2), Au1–P1–C8 108.7(1), Au1–P1–C14 110.9(1), O1–C13–O2 124.7(3)
Au1–P1 is 2.247(1) Å and only slightly shorter than that of
the chlorido congener [2.26(1) Å [59]]. The Au1–Br1 bond
length is 2.3957(4) Å and typical for R3P–Au–Br complexes
[62, 63]. Contrary to the para-substituted homologue, there
are no aurophilic interactions present [64]. The shortest
Au–Au distance of 7.431(1) Å is far beyond the aurophilic-
ity limit of ~ 3.5 Å [65].

In the course of the synthetic work, also a few crystals
of the complex [Au(PPh2(o-BzOH))2I] could be isolated,
however, we were not able to synthesis this compound in
pure form. This is somewhat surprising as the homologue
chlorido-complex is known [56]. Unfortunately, the crystals
contain solvent molecules which could not be modelled sat-
isfactorily and thus lead to poor structural refinement data.
For the sake of completeness, we have added this structure
to the supporting information but will not further discuss it
here (Fig. S2 + Table S1).

Complex 2-Cl crystallizes in the cubic space group Pa3.
The asymmetric unit consist of one third of the molecule.
The gold atom is coordinated by three phosphorus atoms
of the phosphane ligands in trigonal-planar arrangement
with a C3-axis passing through the gold and chlorine atoms.
Therefore, there is only one Au1–P1 distance with 2.412(2)
Å, which is considerably longer than those of 1-Br. The
angle P1–Au1–P1 is 119.57(1)° and sums up to 358.71°.
The carboxylic acid groups are oriented towards the C3-axis.
This arrangement leads to intense hydrogen bonding of the
carboxylic acid proton towards the chloride anion locking it
in their center (Fig. 3). The O–Cl distance of the O–H⋯Cl
group is 3.108 Å indicative for moderate hydrogen bonds
[60, 61]. The previously reported complex of the form
(Ph3RP)2AuCl (with R = o-trifluoracetanilide) feature com-
parable N–H⋯Cl hydrogen bonds (N–Cl ~ 3.2 Å), which sta-
bilize the trigonal-planar coordination environment around
the Au(I) atom [55]. Thus, the utilization of hydrogen bonds
might be regarded as a general synthetic strategy to stabilize
otherwise not isolable, tri-coordinated Au(I) complexes.

Unfortunately, single crystals suitable for structural
analysis could only be obtained for the chlorido compound.
Although numerous attempts to grow crystals for the bro-
mido and iodido congeners were undertaken, only pow-
ders could be isolated. The reason is their general very low
solubility in common organic solvents. Immediately after
addition of the third equivalent of the phosphane ligand, the
complexes precipitate out of solution. Various attempts with
different solvents, concentrations, and crystallization condi-
tions always lead to micro-crystalline samples. Hence, pow-
der X-ray diffractograms were recorded for comparing the
samples and ascertain whether they crystalize isostructural.
The single-crystal structure data of 2-Cl are used to simu-
late its powder pattern. As depicted in Fig. 4, the diffraction
patterns are similar for all three compounds and also match
the simulated pattern of 2-Cl. The most intense peaks are
generated from the (200), (210), and (211) planes. Another
characteristic pattern arises from the (510) and (520) planes.
Therefore, it can be inferred that the bromido and iodido
complexes are isostructural to the chlorido congener featur-
ing a tri-coordinated Au(I) atom.

Although tri-coordinate phosphane-gold(I) complexes
often feature photo-luminescence, we could not detect any
light emission upon excitation with UV-light.
Table 1 Crystal data and data collection and structure refinement details for 1-Br and 2-Cl

|     | 1-Br          | 2-Cl          |
|-----|---------------|---------------|
|     | C_{19}H_{15}AuBrO_{2}P | C_{19}H_{15}AuClO_{2}P |
| M/ g mol⁻¹ | 583.16       | 1151.26      |
| Crystal size/mm³ | 0.29 x 0.10 x 0.05 | 0.46 x 0.34 x 0.08 |
| Crystal system | monoclinic    | cubic         |
| Space group | P_{2}₁/n     | P_{\overline{3}} |
| a/Å       | 15.3001(10)  | 21.4601(4)   |
| b/Å       | 7.4332(4)    | 21.4601(4)   |
| c/Å       | 17.4332(10)  | 21.4601(4)   |
| α/°       | 90           | 90           |
| β/°       | 114.829(1)   | 90           |
| γ/°       | 90           | 90           |
| V/Å³      | 1800.60(18)  | 9883.1(6)    |
| \(\rho_{\text{calc}}\)/g cm⁻³ | 2.151         | 1.547        |
| Z         | 4            | 8            |
| \(\mu\)/(mm⁻¹) | 10.49         | 3.18         |
| T/K       | 296          | 296          |
| Θ Range/° | 2.9–26.3     | 2.7–23.4     |
| Reflections collected | 57,743       | 67,167       |
| Unique reflections | 3644         | 2409         |
| Observed reflections I > 2σ(I) | 3181         | 1447         |
| Absorption correction | Multi-scan   | Multi-scan   |
| \(T_{\text{min}}/T_{\text{max}}\) | 0.15/0.60    | 0.32/0.78    |
| \(Δρ_{\text{max}}\)/(e Å⁻³) | 0.46, 0 – 0.49 | 1.31, – 0.69 |
| R1 [I ≥ 2σ(I)] | 0.020        | 0.048        |
| wR2      | 0.042        | 0.131        |
| CCDC     | 2094495      | 2094497      |

Conclusion

In this work, we suggest a new concept to stabilize coordination numbers larger than two of gold(I) in its phosphane complexes beyond the dominating standard linear coordination. Using intramolecular hydrogen bonds, it is possible to stabilize a complex of the form [L₃Au]X (L = 2-(diphenylphosphino)benzoic acid, X = Cl, Br, I). The molecular structure of [L₃Au]Cl could be determined by single-crystal X-ray diffraction, whereas those of X = Br and I are deduced by a similar pattern of powder-diffractograms. This information can be obtained free of charge via https://www.ccdc.cam.ac.uk/structures/

Experimental

All commercially available solvents and starting materials were used without further purification. 2-(Diphenylphosphino)benzoic acid was purchased from abcr. (tht)AuCl (tht = tetrahydrothiophene) was prepared according to a reported procedure [66].

NMR spectra were recorded on a Bruker 300 MHz Avance III spectrometer. For all measurements, deuterated solvents were used. Chemical shifts are related to the residual solvent signal and are stated to the δ-convention in ppm. HR-MS measurements were carried out on an Agilent 6520 QTOF mass spectrometer with an ESI source. X-ray powder diffraction was recorded on a Philips X′pert Pro diffractometer operated in Bragg–Brentano geometry and employing CuKα radiation (\(λ = 1.541874\) Å). The patterns were acquired using a step size of 0.008° with a counting time of 60 s per step; the samples were rotated with 15 rotations per min.

Single-crystal structure analysis was carried out at room temperature on a Bruker D8 Quest ECO diffractometer with graphite-monochromated MoKα radiation (\(λ = 0.71073\) Å). The structures were solved by direct methods (SHELXS-97 [67]) and refined by full-matrix least-squares on \(F^2\) [SHELXL-2014/7 [68]]. The H atoms were calculated geometrically, and a riding model was applied in the refinement process. Crystallographic details can be found in Table 1 and S1. CCDC 2094495 (1-Br), 2094497 (2-Cl), 2094497 ([Au(PhP₂(α-BzOH))I]), contain supplementary crystallographic data for this paper. This information can be obtained free of charge via https://www.ccdc.cam.ac.uk/structures/

Chlorido-[2-(diphenylphosphino)benzoic acid]gold(I), (1-Cl, C_{19}H_{15}AuClO_{2}P) 1-Cl was prepared according to a modified literature method [56, 57]: (tht)AuCl (98.8 mg, 0.308 mmol) was dissolved in 20 cm³ DCM and 2-(diphenylphosphino)benzoic acid (91 mg, 0.30 mmol) was added and the mixture was stirred for 2 h at r.t.. Pentane was added until a white precipitate formed. Yield: 118 mg (71%); ^1H NMR (300.13 MHz, CDCl₃): \(δ = 8.31\) (m, 1H), 7.66 (m, 1H), 7.51 (m, 11H), 6.96 (m, 1H) ppm; ^31P{¹H} NMR (75.47 MHz, CDCl₃): \(δ = 168.55\) (s), 134.85 (d, \(J = 7.24\) Hz), 134.07 (d, \(J = 15.13\) Hz), 133.11 (d, \(J = 8.18\) Hz), 132.89 (d, \(J = 9.54\) Hz), 132.83 (d, \(J = 7.08\) Hz), 131.84 (s), 131.64 (d, \(J = 1.76\) Hz), 130.42 (s), 129.57 (s), 129.19 (d, \(J = 12.13\) Hz) ppm; ^13C{¹H} (121.49 MHz, CDCl₃): \(δ = 35.97\) (s) ppm; HRMS(ESI): m/z for [M+Na]^⁺ calculated 561.0056, found 561.0094.

Bromido-[2-(diphenylphosphino)benzoic acid]gold(I), (1-Br, C_{19}H_{15}AuBrO_{2}P) 1-Cl (17.6 mg, 32.7 µmol) was dissolved in 5 cm³ DCM. KBr (16.7 mg, 0.140 mmol) was...
dissolved in 5 cm³ water. After combining both solutions, the reaction mixture was stirred for 2 h at r.t. Phases were separated and the organic phase was dried over anhydrous Na₂SO₄. Evaporation of the solvent resulted in a white solid. Yield: 17.4 mg (91%); ¹H NMR (300.13 MHz, CDCl₃): δ = 8.30 (m, 1H), 7.56 (t, J₃₁₂₂ = 7.56 Hz, 1H), 7.51 (m, 11H), 6.96 (m, 1H) ppm; ¹³C{¹H} NMR (75.47 MHz, CDCl₃): δ = 169.36 (s), 135.10 (d, J = 7.73 Hz), 132.47 (s), 131.67 (s), 131.12 (s), 130.32 (s), 129.38 (d, J = 12.12 Hz) ppm; HRMS(ESI): m/z for [M + Na]⁺ calculated 604.9593, found 604.9593. Crystals suitable for single-crystal X-ray diffraction were obtained by slow gas-phase diffusion of pentane into a diluted DCM solution.

**Iodido-tris[2-(diphenylphosphino)benzoic acid]gold(I), (2-I, C₅₇H₄₅AuIO₆P₃) 1-I** (95 mg, 0.15 mmol) was dissolved in chloroform and 2-(diphenylphosphino)benzoic acid (94 mg, 0.30 mmol) was added. After stirring for a few minutes, the product began to precipitate directly from the reaction solution. Excess solution was decanted and the white solid was washed with chloroform. The product was dried in vacuum. Yield: 175 mg (93%). Due to the low solubility of the compound, no NMR and MS spectra could be recorded.

**Chlorido-tris[2-(diphenylphosphino)benzoic acid]gold(I), (2-Cl, C₅₇H₄₅AuClO₆P₃) 1-Cl** (118 mg, 0.219 mmol) was dissolved in dry DCM and cooled and 2-(diphenylphosphino)benzoic acid (134 mg, 0.437 mmol) was added to the solution and stirred for 2 h at r.t. The product directly precipitated from the reaction solution. Filtration of the product resulted in a white solid. The product was dried in vacuum. Yield: 217 mg (86%). Due to the low solubility of the compound, no NMR and MS spectra could be recorded. Crystals suitable for single-crystal XRD were obtained by addition of excess amounts of the respective ligand to a slurry of 2-Cl in chloroform.

**Bromido-tris[2-(diphenylphosphino)benzoic acid]gold(I), (2-Br, C₅₇H₄₅AuBrO₆P₃) 1-Br** (98 mg, 0.17 mmol) was dissolved in chloroform and 2-(diphenylphosphino)benzoic acid (104 mg, 0.340 mmol) was added. After a few minutes of stirring at r.t. the product precipitated directly from the reaction solution. Excess solution was decanted and the white powder was washed with chloroform. The product was dried in vacuum. Yield: 191 mg (95%). Due to the low solubility of the compound, no NMR and MS spectra could be recorded.

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