

# Tetrakis(triphenylphosphine oxide)lithium Di(iodo)aurate(I)

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Z. Naturforsch. **61b**, 956–960 (2006); received April 13, 2006

The title compound,  $[(\text{Ph}_3\text{PO})_4\text{Li}]^+ \text{AuI}_2^-$ , crystallized from a reaction mixture obtained from  $\text{Ph}_3\text{PAuC}\equiv\text{CPh}$ ,  $\text{LiMe}$  and  $\text{MeI}$  (molar ratio 1:1:2) in diethylether upon subsequent oxidation in air. The triclinic crystals, space group  $P\bar{1}$ , are isomorphous with those of the corresponding di(bromo)cuprate(I). The gold atoms of the two independent  $[\text{AuI}_2]^-$  anions reside on centers of inversion and have no close interanionic contacts. The structure of the complete  $[(\text{Ph}_3\text{PO})_4\text{Li}]^+$  cation does not approach any standard symmetry (*e. g.*,  $S_4$  or  $D_{2d}$ ). Its conformation is similar to that reported for the isomorphous reference compound with the anion  $\text{CuBr}_2^-$ , but different from that in the bromide·acetonitrile, Li-phthalocyaninate or iodide·triphenylphosphine oxide salts, suggesting that the relative orientation of the four  $\text{Ph}_3\text{PO}$  molecules at the  $\text{Li}^+$  center is flexible and co-determined by the packing in the crystals. Even the  $\text{O}_4\text{Li}$  core units are affected by the variations in the mode of attachment of the  $\text{Ph}_3\text{PO}$  ligands, and their distortions are significant as shown by the ranges of Li–O distances and O–Li–O angles, which are small in the title compound, but spread from 1.886(5) to 1.953(9) Å and from 105.1(4) to 111.8(4)°, respectively, when taking into account all known salts with the  $[(\text{Ph}_3\text{PO})_4\text{Li}]^+$  cation.

**Key words:** Lithium Coordination, Triphenylphosphine Oxide Ligand, Di(iodo)aurate(I) Anion, Conformation

## Introduction

Tertiary phosphines  $\text{R}_3\text{P}$  have been widely used as powerful “soft” ligands mainly to low-valent main group and transition metals (M) [1–3]. By contrast, the corresponding tertiary phosphine *oxides*  $\text{R}_3\text{PO}$  have been employed as the “hard” counterparts for metals in higher oxidation states or with a high volume concentration of positive charge (*i. e.* high charge/radius ratio) [4]. While tertiary phosphines are to be considered as “bulky”, with three organic substituents in  $\alpha$ -position relative to the metal atom M, in tertiary phosphine oxide complexes the bulky  $\text{R}_3\text{P}$  groups are moved away from the metal center formally by inserting the electronegative oxygen atom into the P–M bond. For three identical substituents R, the local symmetry of a ligand  $\text{R}_3\text{P}$  attached to the metal atom M is that of point group  $C_3$  or  $C_{3v}$ , while in the corresponding  $\text{R}_3\text{PO}$  ligand the local symmetry is reduced to that of point group  $C_s$  because the oxygen bridge M–O–PR<sub>3</sub> established between M and P appears to be invariably bent. The angle P–O–M for metal complexes with a strictly terminal phosphine oxide ligand

is generally larger than 120° and may approach 180°, but confirmed cases of linearity are rare [4–7].

In the course of extended studies of aurophilicity effects [8] in ionic crystals of complex gold(I) anions with halide or pseudohalide ligands,  $[\text{AuX}_2]^-$  [9], we have obtained by accident a compound  $[(\text{Ph}_3\text{PO})_4\text{Li}]^+ [\text{AuI}_2]^-$  and studied its crystal structure. The structure of this 1:1 array of complex cations and anions was of interest for two reasons: 1) The cation contains one of the smallest cations,  $\text{Li}^+$ , as the coordination center of the most common tertiary phosphine oxide,  $\text{Ph}_3\text{PO}$ . This cation has been investigated in very different contexts but its configuration and conformation have not been analyzed in detail [10–13]. An additional independent set of data may shed light on the intrinsic organization of the four dipolar ligands at this small cation which almost can be taken as a point charge, and with its  $1s^2$  electronic ground state has no directional orbital preference. 2) There are scattered observations of aurophilic (counter-Coulomb!) attractions between  $[\text{X–Au–X}]^-$  anions [14]. This is in contrast to a growing number of cases with evidence for attraction between the related  $[\text{NC–Au–CN}]^-$  an-

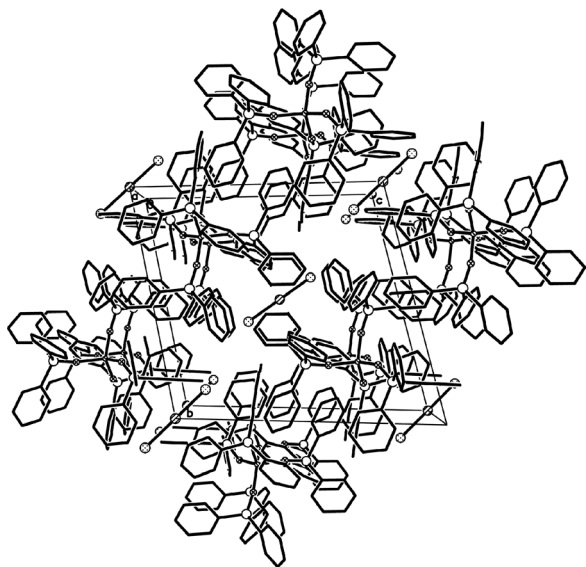


Fig. 1. Unit cell of  $[(\text{Ph}_3\text{PO})_4\text{Li}]^+ [\text{AuI}_2]^-$  (arbitrary radii).

ions [15]. Theoretical calculations have predicted that soft (pseudo)halides should enhance aurophilic bonding [16], but some of the experimental data gave no support to this assumption [17].

## Results and Discussion

### Preparation

In attempts to prepare mixed alkyl/alkenyl/alkynyl-gold(I) and -gold(III) complexes [18–20] various synthetic pathways have been probed including the reaction of complexes  $(\text{Ph}_3\text{P})\text{AuR}$  with  $\text{R}'\text{Li}$  reagents in the molar ratio 1:1 in diethylether. This reaction is known to afford a solution of  $\text{Li}[\text{R}'\text{AuR}]$  containing liberated  $\text{Ph}_3\text{P}$ . In order to accomplish an oxidative addition of haloalkanes, -alkenes or -alkynes to give the corresponding gold(III) complexes, this solution was treated with a selection of  $\text{R}''\text{X}$  substrates [20]. It was observed, however, that these additions proceed only very slowly and product mixtures were formed. In order to identify the compounds produced, attempts were made to separate the components by fractional crystallization from  $\text{CH}_2\text{Cl}_2$ /pentane at r. t. The specimens obtained were analyzed by single crystal X-ray diffraction. From a flask with a mixture obtained for  $\text{R} = \text{PhC}\equiv\text{C}$  and  $\text{R}' = \text{R}'' = \text{Me}$ , which was not completely sealed against the atmosphere, large transparent blocks of the title compound were formed after several days. As we discovered later in the literature, similar observations were made *e. g.* in anal-

ogous copper systems where  $[(\text{Ph}_3\text{PO})_4\text{Li}]^+ \text{CuBr}_2^-$  was obtained serendipitously from solutions containing  $\text{Ph}_3\text{PO}$ ,  $\text{MeLi}$ ,  $\text{Br}^-$ , and  $\text{Cu}^{2+}$  [10]. Note that if iodine is produced in the oxidation of iodide, no oxidation of  $\text{Au}^+$  is to be expected as neither  $\text{R}_3\text{PAuI}_3$  complexes nor  $\text{AuI}_4^-$  salts are stable at r. t. [21–23].

The ease of formation of triphenylphosphine oxide from triphenylphosphine in air at r. t. is remarkable and suggests a catalytic effect of the gold component. However, there is precedent for this phenomenon: 1:1 complexes of gold(I) or gold(III) with *ditertiary* phosphines  $\text{R}_2\text{P}(\text{CH}_2)_n\text{PR}_2$  are readily converted to complexes of the *monoxides*  $\text{R}_2\text{P}(\text{CH}_2)_n\text{PR}_2\text{O}$  even with traces of oxygen [24]. As another parallel, the tertiary phosphine ligands  $\text{R}_3\text{P}$  in the copper(I) cluster complex  $(\text{R}_3\text{P})_4[\text{Cu}_4\text{OCl}_6]$  were found to be readily oxidized even by traces of oxygen to give the cluster complex  $(\text{R}_3\text{PO})_4[\text{Cu}_4\text{OCl}_6]$  [7].

### Description of the structure

In the triclinic unit cell (space group  $P\bar{1}$ ) the two independent  $[\text{AuI}_2]^-$  anions have their gold atoms in special positions at (000) and  $(\frac{1}{2} \frac{1}{2} \frac{1}{2})$ , respectively. The anions are thus linear by inversion symmetry with distances  $\text{Au1-I1}$  2.5346(3) and  $\text{Au2-I2}$  2.5437(3) Å, respectively. These data are in good agreement with literature data [25]. The anions are embedded between the extremely bulky cations without any special inter-ionic contacts (Fig. 1).

The cations have no crystallographically imposed symmetry and are not discernibly approaching the point groups of maximum symmetry (point groups  $S_4$  or  $D_{2d}$ ) [26] that are possible for the homoleptic tetra-coordination of four substituents ( $\text{Ph}_3\text{PO}$ ) which have local mirror symmetry (point group  $C_s$ ) owing to the bending of the  $\text{Li-O-P}$  linkages. The four  $\text{Li-O}$  distances are very similar with individual values in the narrow range from 1.886(5) to 1.895(5) Å. Together with the six  $\text{O-Li-O}$  angles in a similarly narrow range from 108.2(3) to 110.8(2)°, these data suggest a co-ordination of the four  $\text{Ph}_3\text{PO}$  dipole ligands at the  $\text{Li}^+$  cation which is largely strain-free in the  $\text{LiO}_4$  core unit. Upon coordination, the  $\text{P-O}$  distances of the free ligands are not altered significantly: The values are in the range from 1.481(2) to 1.488(2) Å as compared to 1.483(4) Å in crystals of pure  $\text{Ph}_3\text{PO}$  [27].

More significant variations are found in the more peripheral coordination sphere as indicated by large differences among the  $\text{Li-O-P}$  angles with individual

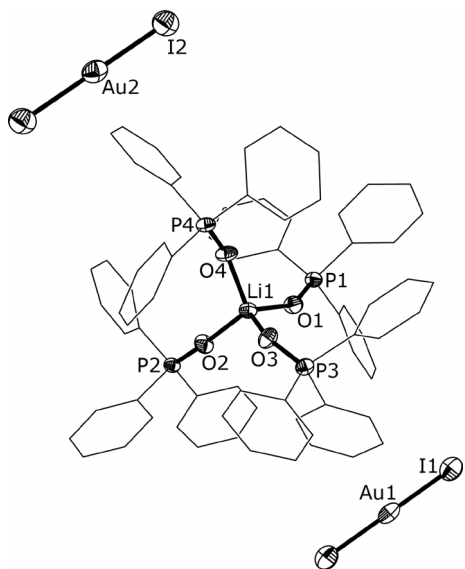


Fig. 2. Cation and anion in the crystal of  $[(\text{Ph}_3\text{PO})_4\text{Li}]^+ [\text{AuI}_2]^-$  with atomic numbering. (ORTEP with 50% probability ellipsoids for the core atoms.) Selected bond lengths [Å] and angles [°]: Au1-I1 2.5345(3), Au2-I2 2.5437(3), Li1-O1 1.895(5), Li1-O2 1.886(5), Li1-O3 1.886(5), Li1-O4 1.887(5), P1-O1 1.486(2), P2-O2 1.481(2), P3-O3 1.486(2), P4-O4 1.488(2); I1-Au1-I1' 180, I2-Au2-I2' 180; O1-Li1-O2 109.5(2), O2-Li1-O3 108.7(3), O3-Li1-O4 109.9(2), O1-Li1-O3 110.8(3), O1-Li1-O4 108.28(3), O2-Li1-O4 109.8(3), Li1-O1-P1 148.7(29), Li1-O2-P2 169.8(2), Li1-O3-P3 143.5(2), Li1-O4-P4 143.2(2).

values of Li1-O1-P1 148.7(2), Li1-O2-P2 169.8(2), Li1-O3-P3 143.5(2), and Li1-O4-P4 143.2(2)°. (It should be noted that the angle Li1-O2-P2 fails linearity by only 10°). It therefore appears that strain out of repulsive inter-ligand forces becomes effective only in the outer realm of the complex where it is relieved through the bending of the Li-O-P linkages which seems to have a flat energy profile for the bending motion. In addition, the intracationic repulsive forces are minimized by adjustments of the Li-O-P-C dihedral angles. For idealized  $S_4$  or  $D_{2d}$  symmetry these dihedral angles would have to approach 0°/180° or be  $\neq$  0°/180° but equal, respectively. According to the set of twelve Li-O-P-C dihedral angles, those involving P1, P3 and P4 show a similar distribution of data (including relative signs), while the values for the ligand with P2 are very different, and it is probably no coincidence that this ligand also has the largest Li-O-P angle (*v. s.*). Therefore the structure of the cation may be described as based on a  $\text{Li}^+$ -centered tetrahedron of four oxygen atoms, three  $\text{Ph}_3\text{PO}$  dipole ligands be-

ing placed with an almost equivalent conformation at three vertices, while the fourth ligand occupies the remaining "apical" position with a distinctly different configuration (Li-O2-P2 angle) and conformation (Li-O2-P2-C torsion angles).

It appears that this structure of the cation is typical for compounds where the cation is associated with symmetrical, rod-like anions, because the corresponding dibromocuprate is isomorphous and has almost identical geometrical characteristics [10]. The distribution of Li-O-P angles is still similar in crystals of  $[(\text{Ph}_3\text{PO})_4\text{Li}]^+ [\text{Li}(\text{Pc})]^-$  where (Pc) is the flat, plate-like phthalocyaninate dianion, including one angle again at 170°, but another one also large at 166.2(3)°, and the remainder at 138.4(4) and 139.7(3)° [13]. Finally, with the spherical bromide anion and a polar, rod-like acetonitrile solvate molecule, as in  $[(\text{Ph}_3\text{PO})_4\text{Li}]^+ \text{Br}^- \cdot \text{MeCN}$ , the values of the Li-O-P angles are closer together at 145.7(3), 148.8(3), 151.6(3), and 163.7(3)°, but large variations are found for the Li-O-P-C torsional angles which are not discussed here in any further detail [11]. For the iodide with a large interstitial  $\text{Ph}_3\text{PO}$  molecule,  $[(\text{Ph}_3\text{PO})_4\text{Li}]^+ \text{I}^- \cdot \text{Ph}_3\text{PO}$ , no details are available [12].

## Conclusions

The new results, in a comparison with existing data [10–13], suggest that the structure of the  $[(\text{Ph}_3\text{PO})_4\text{Li}]^+$  cation is rather flexible and easily adjusted to different environments in the crystal. No dominance of an intrinsic ground-state configuration or conformation is discernible. There is also no evidence for  $\pi$ - $\pi$  stacking or other arene-arene interactions which may co-determine significantly the organization of the components. The title cation may therefore be an interesting alternative to established species like the bis(triphenylphosphoranylidene)ammonium cation  $[\text{Ph}_3\text{PNPPh}_3]^+$  or the "carbodiphosphorane"  $\text{Ph}_3\text{PCPPh}_3$  which are known to have particularly flexible P-N-P and P-C-P units, respectively, with angles spreading from 130° to as much as 180° depending on the environment [28, 29].

Obviously, many salts with the cation  $[(\text{Ph}_3\text{PO})_4\text{Li}]^+$  are readily precipitated. Note that none of the compounds mentioned as "reference salts" above was prepared deliberately [10–13]. By contrast, all salts were obtained by accident. The oxidation, hydrolysis or decomposition products crystallized preferentially from the reaction mixtures intended to be pools

Table 1: Crystal and structure solution data for  $[(\text{Ph}_3\text{PO})_4\text{Li}]^+ [\text{AuI}_2]^-$ .

	$[(\text{Ph}_3\text{PO})_4\text{Li}]^+ [\text{AuI}_2]^-$
Empirical formula	$\text{C}_{72}\text{H}_{60}\text{AuI}_2\text{LiO}_4\text{P}_4$
$M_r$	1570.79
Crystal system	triclinic
Space group	$P\bar{1}$
$a$ [Å]	14.4368(1)
$b$ [Å]	16.2794(1)
$c$ [Å]	16.9054(2)
$\alpha$ [°]	70.1902(4)
$\beta$ [°]	69.3900(4)
$\gamma$ [°]	64.7750(3)
$V$ [Å <sup>3</sup> ]	3279.46(5)
$\rho_{\text{calc}}$ [g cm <sup>-3</sup> ]	1.591
$Z$	2
$F(000)$	1544
$\mu$ (Mo-K $\alpha$ ) [cm <sup>-1</sup> ]	33.30
$T$ [K]	143
Refls. measured	77008
Refls. unique	11364 [ $R_{\text{int}} = 0.033$ ]
Refined parameters	760
Restraints	0
$R1[I \geq 2\sigma(I)]$	0.0330
$wR2^a$	0.0848
Weighting scheme	$a = 0.0364, b = 5.1649$
$\sigma_{\text{fin}}$ (max/min) [eÅ <sup>-3</sup> ]	0.793 / -1.259

<sup>a</sup>  $wR2 = \{\Sigma[w(F_o^2 - F_c^2)^2] / \Sigma[w(F_o^2)^2]\}^{1/2}$ ;  $w = 1/[\sigma^2(F_o^2) + (ap)^2 + bp]$ ;  $p = (F_o^2 + 2F_c^2)/3$ .

of entirely different products.

The findings confirm previous observations that gold(I) salts catalyze the oxidation of tertiary phosphines to the corresponding phosphine oxides [24]. It is also again obvious [30] that large, innocent cations do not support aggregation of di[(pseudo)halo]aurate(I) anions  $[\text{X-Au-X}]^-$  in the solid state. It appears that cations with higher concentrations of positive charge per volume element (including hydrogen bonding) are required to reduce the Coulomb repulsion between the anions and thus allow the mutual approach which is necessary to establish discrete aurophilic contacts [8d, 8e, 15, 31].

## Experimental Section

### General

All experiments were carried out in an atmosphere of dry and pure nitrogen. Solvents were dried, distilled and

saturated with nitrogen, and glassware was oven-dried and filled with nitrogen. Standard equipment was used throughout. NMR: Jeol JNM-GX 270 and 400; chemical shifts in  $\delta$  values rel. residual <sup>1</sup>H and <sup>13</sup>C resonances of the CD<sub>2</sub>Cl<sub>2</sub> solvent converted to int. TMS, and ext. 85% aqueous H<sub>3</sub>PO<sub>4</sub> for <sup>31</sup>P, respectively. <sup>13</sup>C and <sup>31</sup>P were hydrogen-decoupled. (Ph<sub>3</sub>P)AuC≡CPh [18] was prepared as described in the literature, all other reagents are commercially available.

### $[(\text{Ph}_3\text{PO})_4\text{Li}]^+ [\text{AuI}_2]^-$

(Ph<sub>3</sub>P)AuC≡CPh (90 mg, 0.16 mmol) was dissolved in 20 ml of diethylether and 0.1 ml of a 1.6 M solution of MeLi in diethylether (0.16 mmol) was added with stirring at 25 °C. After addition of an excess of MeI (45 mg, 0.32 mmol) the reaction mixture was stirred over night. In a flask not tightly sealed, this mixture developed large colourless crystals of the title compound after several weeks. Alternatively, immediate removal of the solvent and residual MeI under reduced pressure and crystallisation of the residue from CH<sub>2</sub>Cl<sub>2</sub>/pentane under atmospheric conditions gave a large crop of the same type of crystals.  $\text{C}_{72}\text{H}_{60}\text{AuI}_2\text{LiO}_4\text{P}_4$  (1570.79): found C 55.55 H 3.91; calcd. C 55.05, H 3.85. NMR (CD<sub>2</sub>Cl<sub>2</sub>, 25 °C):  $\delta_P = 26.9$ , s.  $\delta_H = 7.27 - 7.71$ , m, Ph.  $\delta_C = 128.4$  (d, <sup>3</sup>J<sub>P,C</sub> = 12.6), 131.8 (d, <sup>4</sup>J<sub>P,C</sub> = 3.0), 132.0 (d, <sup>2</sup>J<sub>P,C</sub> = 10.4) and 132.8 (d, <sup>1</sup>J<sub>P,C</sub> = 103.3) for *m*-, *p*-, *o*- and *i*-Ph.

### Crystal structure determinations

The single crystals were placed in inert oil on the top of a glass pin and transferred to the cold gas stream of the diffractometer. Crystal data were collected using a Nonius DIP2020 system with monochromated Mo-K $\alpha$  ( $\lambda = 0.71073$  Å) radiation at -130 °C. The structure was solved by direct methods (SHELXS-97) and refined by full matrix least-squares calculations on  $F^2$  (SHELXL-97) [32]. Non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were placed in idealized positions and refined using a riding model with fixed isotropic contributions. Further information on crystal data, data collection and structure refinement are summarized in Table 1. Important interatomic distances and angles are given in the figure captions. Complete lists of displacement parameters and tables of interatomic distances and angles have been deposited with the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK. The data are available on request on quoting CCDS-606391.

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