Ligand Properties of Tri(2-thienyl)- and Tri(2-furyl)phosphine and -arsine $(2-C_4H_3E)_3P/As$ (E = O, S) in Gold(I) Complexes

Uwe Monkowius, Stefan Nogai, and Hubert Schmidbaur

Anorganisch-chemisches Institut der Technischen Universität München, Lichtenbergstraße 4, D-85747 Garching, Germany

Reprint requests to Prof. Dr. Schmidbaur. E-mail: H.Schmidbaur@lrz.tum.de

Z. Naturforsch. 58b, 751-758 (2003); received May 7, 2003

Tri(2-thienyl)- and tri(2-furyl)phosphine and -arsine (L) have been introduced as ligands to gold(I) chloride and acetate (AuX). Structural studies have shown that in the 1:1 complexes of the type L-Au-X the gold atoms are bound exclusively to the phosphorus/arsenic centers without any intraor intermolecular approach of the donor atoms of the three heterocycles towards the metal atoms. Intermolecular aurophilic bonding is found in the crystals of the [tri(thienyl)phosphine]gold acetate complex, but is absent in crystals of the chloride complexes. The phosphines L have been quaternized with methyl iodide and the resulting phosphonium salts [LMe]I structurally characterized to provide reference data as to the preferred configurational and conformational motifs. The mass spectra of the gold complexes indicate a high stability of the dinuclear cationic species [(LAu)₂X]⁺ with X = Cl, OAc for all ligands L.

Key words: Gold Complexes, Heteroarylphosphines/arsines, Furylphosphines/arsines, Thienylphosphines/arsine, Phosphines, Arsines

Introduction

Tertiary phosphines R₃P with heterocyclic substituents R have attracted considerable interest at different stages of the development of "tailor-made" ligands for Transition and Main Group Elements [1,2] or as auxiliary components in organic synthesis [3-6]. Tri(2-thienyl)phosphine was among the first prototypes to be synthesized in the late 1950ies in studies by Issleib and Brack [7], preceded only by early work on 2-thienyl-dichlorophosphine and its hydrolysis and oxidation products [8]. Tri(2-furyl)phosphine was prepared by Japanese workers for the first time in 1966 [9]. The results of the preparative studies [4, 7, 10-12], and of extensive kinetic [2, 5, 6, 13-16] and spectroscopic investigations [17-23] suggested differences of the inductive and electronic effects of the phenyl, 2-thienyl and 2-furyl substituents [7, 10, 11] ascribed intermittently to the $d(\pi)$ -p(π) interactions between the (hetero)arene systems and central phosphorus atom [11, 14, 17, 20]. However, straightforward steric and electronegativity effects appear to be sufficient to account for most experimental observations [20]. The 2-furyl group appears to act as the most electron-withdrawing substituent among the tri-(hetero)arylphosphines [5, 12, 14, 15].

With one phosphorus and three sulfur atoms, tri(2thienyl)phosphine is a potential tetradentate ligand with all donor centers in close proximity. However, very little is known about the structural chemistry of its metal complexes [7, 10-12, 20, 24-26] and of the products obtained in its simple nucleophilic substitution reactions [7, 10]. For tri(2-furyl)phosphine the ligand properties are more predictable owing to the larger differences between the soft phosphorus and the hard oxygen donor functions. With gold(I) as an acceptor, the former will clearly be the donor center of choice.

The present report is an account of preparative and structural studies of four gold(I) complexes of the type $(2-C_4H_3E)_3P$ -Au-X with a) E = S and X = chloride (1), b) E = S and X = acetate (2), c) E = O and X = chloride (4), and d) E = O and X = acetate (5). In all cases the gold atom is two-coordinate and bound solely to the phosphorus atom showing the superior donor properties of the phosphorus center for soft acceptor centers of low (+1) charge. As a reference for the geometry of fully quaternized compounds, the structures of the methylation products, the phosphonium salts $[(2-C_4H_3S)_3PMe]^+I^-$, **3**, and $[(2-C_4H_3O)_3PMe]^+I^-$, **6**, have been determined. Also for comparison, tri(2-furyl)- and tri(2-thienyl)arsine have been prepared and used as ligands for AuCl. These arsines were first syn-

0932-0776 / 03 / 0800-0751 \$ 06.00 © 2003 Verlag der Zeitschrift für Naturforschung, Tübingen · http://znaturforsch.com



Scheme 1.

thesized in 1935 and 1948, respectively, from 2-furyl and 2-thienyl mercury chloride and arsenic trichloride [27-30]. Nothing is known about their reactivity and donor properties towards Transition and Main Group Elements.

Preparative Results

Tri(2-*thienyl*)*phosphine* $(2-C_4H_3S)_3P$ is readily obtained in good yield via the Grignard route employing 2-bromothiophene, magnesium and phosphorus trichloride in diethylether at -20 °C [7]. It is also commercially available. Its 1:1 complexes with *gold*(*I*) *chloride* can be prepared using (tetrahydrothiophene)gold(I) chloride in tetrahydrofuran. The cyclic thioether is liberated in the reaction, which gives high yields of a colorless, crystalline product (1, 95.4% yield, m. p. 192 °C). This complex can be converted into the corresponding *acetate* (2) by metathesis with silver acetate in dichloromethane (84.5% yield, m.p. 100 °C, decomposition) (Scheme 1).

Upon coordination to gold(I) salts, the ³¹P NMR signal of the ligand $[(2-C_4H_3S)_3P, -45.61 \text{ ppm in} dichloromethane at 25 °C] is shifted downfield very significantly [1: -6.39 ppm, 2: -12.32 ppm, in the same solvent]. For 1 and 2 the shift differences are thus as much as 39.22 and 33.29 ppm, respectively, indicating ligation to the phosphorus atom.$

Quantitative *quaternization* of $(2-C_4H_3S)_3P$ was achieved with an excess of methyl iodide in tetrahydrofuran at room temperature (94.4% yield) (Scheme 1) [14,19,22]. The colorless product (**3**) crystallizes from acetone. The ³¹P NMR spectrum of **3** also shows a large downfield shift of no less than 50.14 ppm to 4.53 ppm as compared to the free ligand.

Tri(2-furyl)phosphine $(2-C_4H_3O)_3P$ is commercially available. Its reaction with (tetrahydrothiophene)gold(I) chloride in tetrahydrofuran afforded complex **4** in good yields (95.0%). The product was crystallized from dichloromethane/pentane. The chloride **4** can be converted into the acetate **5** by metathesis with silver acetate in dichloromethane at -32 °C (56.5% yield) (Scheme 1). However, this product is unstable both as a solid and in solution and could not be crystallized.

Quaternization of $(2-C_4H_3O)_3P$ with excess methyl iodide in toluene at reflux temperature gives the phosphonium salt [MeP(2-C_4H_3O)_3]⁺ I⁻, **6**, in good yield (76.1%) (Scheme 1) [19]. The single crystals grown from acetonitrile/diethylether were light-brown and contained some excess iodine, as also confirmed by disorder phenomena in the crystal structure determination.

As observed for the tri(2-thienyl)phosphine derivatives (1-3, above), the ³¹P NMR signals of the tri(2furyl)phosphine compounds 4-6 are shifted downfield very considerably as compared to the resonance of the free ligand [-77.39 ppm in CD₂Cl₂ at 25 °C]. The shift difference is 49.37 ppm for 4, 42.63 ppm for 5, and 61.62 ppm for 6. This leaves no doubt that all derivatives are products of the reaction at the phosphorus center.

Tri(2-thienyl)arsine and tris(2-furyl)arsine are obtained in low yield (28.4 and 47%, respectively) from three equivalents of mono-lithiated thiophene or furan and arsenic(III) chloride in tetrahydrofuran as paleyellow viscous liquids [eq. (1)]. The thienyl compound solidifies as a glass on cooling, while the furyl analogue can be crystallized from diethylether at -78 °C.

$$\underbrace{ \begin{pmatrix} 1 \end{pmatrix}_{\text{PBULi}}}_{\text{E}} \underbrace{ 1 \end{pmatrix}_{\text{ASCI}_3}}_{\text{E}} \underbrace{ \left(\begin{pmatrix} 1 \end{pmatrix}_{\text{E}} \\ - \end{pmatrix}_{\text{ASCI}_3}}_{\text{E}} As$$
(1)

 $(2-C_4H_3S)_3$ As reacts with (tetrahydrothiophene) gold chloride in dichloromethane at -78 °C to give the product $(C_4H_3S)_3AsAuCl$, **7**, which crystallizes from dichloromethane/pentane in high yield (94.3%, m.p. 144 °C).

Mass spectrometry

The mass spectra (FAB mode) of the gold complexes show similar patterns which confirm the proposed composition of the products through the appearance of the molecular ions. Interestingly however, the chloride complexes 1, 4 and 7 show the di(gold)chloronium cations [(LAu)₂Cl]⁺ as the ions of highest mass in high abundance. This result is in agreement with the high stability of cationic elementcentered gold clusters of the general type $[E(AuL)_n]^+$ [31]. In the present case with E = Cl, $L = (2-C_4H_3S)_3P$, $(2-C_4H_3O)_3P$ or $(2-C_4H_3S)_3As$, and n = 2, species with narrow angles Au-Cl-Au and short aurophilic Au-Au contacts are characteristic for species formed from LAuCl molecules and LAu⁺ cations. The results suggest that the arsines can also function as the stabilizing ligand in these cations. Salts of this type have not yet been isolated in crystalline form. Other cations of high abundance are $[L_2Au]^+$ and $[LAu]^+$. Dinuclear, acetate-bridged cations are also observed for complexes **2** and **5**.

In the mass spectra of the phosphonium salts **3** and **6**, the cations are by far the most prominent parent peaks.

Structural Studies

[Tri(2-thienyl)phosphine]gold(I) chloride, $[(C_4H_3)$ S)₃P-Au-Cl], **1**, crystallizes in the triclinic space group $P\bar{1}$ with two formula units in the unit cell. The asymmetric unit contains one molecule which has no subvan-der-Waals contacts with neighboring units (Fig. 1). The gold atom is attached solely to the phosphorus atom with an Au-P distance of 2.2315(12) Å, and to the chlorine atom with an Au-Cl distance of 2.2894(12) Å. The coordination is linear with the angle Cl-Au-P at $177.89(4)^{\circ}$. With the three sulfur atoms oriented away from the gold atom and with the three C-P-Au angles all larger than the tetrahedral standard $[111.10(16) - 115.13(15)^{\circ}]$, there is no evidence for gold-sulfur coordination. There is also no indication for dimerization via aurophilic contacts. This result is in agreement with the crystal structure of (triphenylphosphine)gold(I) chloride [32], which also features monomeric units, and suggests similar steric and electronic effects of phenyl and thienyl substituents (in combination with a trans chloride ligand).

Complementary to the three large Au-P-C angles (above), the three C-P-C angles are consistently smaller than the tetrahedral standard $[104.3(2) - 108.5(2)^{\circ}]$ showing that the complexation has not induced a perfect tetrahedral arrangement of the atoms at the phosphorus atom. One of the three thiophene rings in complex 1 is disordered over two positions with equal occupation factors (in Fig. 1 only one orientation is shown). The overall conformation of the phosphine is neither close to mirror symmetry nor to propeller symmetry, which are the two conformations



Fig. 1. Molecular structure of **1** (ORTEP [36] drawing with 50% probability ellipsoids). Selected bond lengths [Å] and angles [°]: Au1-Cl1 2.2894(12), Au1-P1 2.2315(12), P1-Cl1 1.796(4), P1-Au1-Cl1 177.89(4), Cl1-P1-Au1 115.13(15), C21-P1-Au1 111.10(16), C31-P1-Au1 111.94(15), C21-P1-Cl1 105.4(2), C31-P1-Cl1 104.3(2), C21-P1-C31 108.5(2).



Fig. 2. Structure of dimeric complex **2** (ORTEP drawing with 50% probability ellipsoids, H-atoms omitted for clarity). Only one orientation of the disordered thienyl substituent is shown. Selected bond lengths [Å], angles and torsion angles [°]: Au1-Au1' 2.2170(8), Au1-P1 2.2170(8), Au1-O1 2.072(3), Au1-Au1' 3.0136(2), P1-Au1-O1 174.86(8), C11-P1-Au1 111.14(12), C21-P1-Au1 108.66(11), C31-P1-Au1 118.28(12), P1-Au1-Au1'-P1' 100.6, O1-Au1-Au1'-O1' 102.1.

with maximum attainable symmetry, and – taking also into account the disorder phenomenon – may be considered virtually random or co-determined by packing forces.

[*Tri*(2-*thienyl*)*phosphine*]*gold*(*I*) *acetate*, [(2-*C*₄*H*₃ *S*)₃*P*-*Au*-*OC*(*O*)*CH*₃], **2**, crystallizes in the monoclinic space group *C*2/*c* with Z = 8 formula units in the unit cell. The asymmetric unit contains one molecule with a linear coordination of the gold atom [Au-P 2.2170(8), Au-O1 2.072(3) Å; P-Au-O1 174.86(8)°]. However, these monomers are clearly associated into



Fig. 3. Molecular structure of **4** (ORTEP drawing with 50% probability ellipsoids). Selected bond lengths [Å], angles and torsion angles [°]: Au1-Cl1 2.2864(11), Au1-P1 2.2159(11), P1-Cl1 1.787(5), P1-Au1-Cl1 178.12(4), Cl1-P1-Au1 112.88, C21-P1-Au1 111.90(16), C31-P1-Au1 114.56(15), C11-P1-C31 103.3(2), C21-P1-Cl1 107.3(2), C21-P1-C31 106.2(2), Au1-P1-Cl1-Cl2 -6.2(6), Au1-P1-C21-C22 0.6(6), Au1-P1-C31-O3 1.9(4).

pairs via aurophilic bonding [Au-Au' 3.0136(2) Å, dihedral angles P-Au-Au'-P' 100.6°, O1-Au-Au'-O1' 102.1°] (Fig. 2). With one thienyl substituent also disordered, the configuration of the phosphine ligand in **2** is very similar to that in **1**, and yet only complex **2** shows dimerization. This result shows that the electronic influence of the anion X is a very significant factor in establishing aurophilic bonding between L-Au-X molecules. With the influence of L constant in **1** and **2**, X is determining the building (or not building) of dimers.

This result is confirmed by the structure of the furyl analogue of complex 1: [Tri(2-furyl)phosphine]gold(I) chloride, $[(C_4H_3O)_3P]AuCl, 4$, crystallizes in the monoclinic space group $P2_1/n$ with Z = 4 molecules in the unit cell. Although the ligand L in 4 with oxygen instead of sulfur as the heteroatom can be considered smaller than that in 1, the crystals are also built of monomeric units which show no tendency to aggregate (Fig. 3). The gold atom is in a standard linear coordination [P-Au-Cl 178.12(4)°; Au-P 2.2159(11), Au-Cl 2.2864(11) Å] and entertains no oxygen contacts. The phosphine ligand of 4 shows no disorder of furyl substituents, and the overall conformation approaches mirror symmetry (the mirror plane containing Cl, Au and P and bisecting the C11-Au-C21 angle). The dihedral angles Au-P-C11-C12 and Au-P-C21-C22 are -6.2(6) and $+0.6(6)^{\circ}$, respectively, and Au-P-C31-O3 is 1.9(4)°. All Au-P-C angles are larger than the tetrahedral standard $[111.90(16) - 114.56(15)^{\circ}]$, and all C-P-C angles are smaller $[103.3(2) - 107.3(2)^{\circ}]$.



Fig. 4. Asymmetric unit in the structure of **3** (ORTEP drawing with 50% probability ellipsoids, H-atoms omitted for clarity). Selected bond lengths [Å], angles and torsion angles [°]: P1-C1 1.784(3), P1-C11 1.764(4), P1-C21 1.770(3), P1-C31 1.770(3), C11-P1-C1 108.36(17), C21-P1-C1 109.53, C31-P1-C1 111.60(16).

Compared with the data for the thienyl analogue 1, this result suggests slightly poorer donor properties of the tri(2-furyl)phosphine ligand in 4. The corresponding acetate 5 could not be crystallized.

In order to obtain structural data of genuinely quaternized tri(2-thienyl)- and tri(2-furyl)phosphine compounds for comparison, the derivatives 3 and 6 were also investigated.

Methyl-tri(2-thienyl)phosphonium iodide, 3, crystallizes in the triclinic space group $P\bar{1}$ with Z = 4formula units in the unit cell. The asymmetric unit thus contains two independent cations and anions (Fig. 4). Bond lengths and angles of the two cations are very similar. The P-C(methyl) bonds are significantly longer than the P-C(thienyl) bonds as expected for carbon atoms with different hybridization. The valence angles at the phosphorus atoms are all close to the tetrahedral standard indicating virtually complete hybridization (sp³ for P) as a reaction to quaternization. By contrast, complexation by AuCl or AuOC(O)CH₃ (in **1** and **2**) left the C-P-C angles well below 109° . The orientation of the thienyl rings of the cations does not approach any symmetrical arrangement and appears to be largely random.

Methyl-tri(2-furyl)phosphonium iodide, **6**, crystallizes in the tetragonal space group P4/ncc with Z = 16 formula units in the unit cell. The configuration of the phosphonium center of the cation is distorted tetrahedral with C-P-C angles spreading over the broad range between 105.60(14) and as much as 116.11(15)° for C1-P1-C11 (Fig. 5). All of these angles are larger



Fig. 5. Structure of the cation in crystals of **6** (ORTEP drawing with 50% probability ellipsoids). Selected bond lengths [Å] and angles [°]: P1-C1 1.779(3), P1-C11 1.763(3), P1-C21 1.771(3), P1-C31 1.762(3), C11-P1-C1 116.11(15), C21-P1-C1 107.55(14), C31-P1-C1 109.60(14), C1-P1-C21-O22 176.8(2), C11-P1-C21-O22 51.2(3), C31-P1-C21-O22 -63.5(2).

than those in the AuCl complex (above) suggesting a much stronger acceptor character of Me⁺ as compared to AuCl. The four P-C bond lengths are all very similar [1.762(3)-1.779(3) Å]. The dihedral angles C1-P1-C21-O22 176.8(2)°, C11-P1-C21-O22 +51.2(3)° and C31-P1-C21-O22 -63.5(2)° indicate an approach to mirror symmetry, but the deviations are larger than found in the AuCl complex of the same phosphine (4). The iodide anions are disordered over three different sites and the total occupancy indicates a non-stoichiometric cation/anion ratio of 1/1.1. This result explains the light brown color of the crystals, which also indicates the contents of iodine, probably as triiodide anions.

Crystals of [*Tri*(2-*thienyl*)*arsine*]gold chloride, **7** are monoclinic, space group $P2_1/c$, with Z = 4molecules in the unit cell, and thus not isomorphous with the phosphine analogue **1**. Two of the three thienyl substituents are disordered over two rotatory orientations each (Fig. 6). The Au-As and Au-Cl distances are not anomalous, and the configuration at the arsenic atom is close to tetrahedral with all C-As-C angles smaller (average 104.12°) and all Au-As-C angles larger than the tetrahedral standard (average 114.42°).

Discussion and Conclusions

Tri(2-thienyl)- and tri(2-furyl)*phosphine* (L) were employed as ligands for gold(I) chloride and acetate. From the ³¹P NMR data it is immediately obvious that in the resulting heteroleptic 1:1 complexes L-Au-



Fig. 6. Molecular structure of **7** (ORTEP drawing with 50% probability ellipsoids, H-atoms omitted for clarity). Selected bond lengths [Å] and angles [°]: Au1-Cl1 2.2834(10), Au1-As1 2.3284(4), As1-Cl1 1.901(4), Cl1-Au1-As1 176.93(3), Cl1-As1-Au1 110.95(13), C21-As1-Au1 113.82(12), C31-As1-Au1 118.48(12), C11-As1-C21 105.94(19), C11-As1-C31104.03(18), C21-As1-C31 102.39(16).

X the gold atoms are attached exclusively to the phosphorus centers. There is no evidence for homoleptic structures $[L_2Au]^+[AuX_2]^-$ in solution or in the solid state. While the two chloride complexes (1 and 4) are monomers in the crystal, the acetate 2 is present as a dimer with significant intermolecular aurophilic bonding.

The FAB mass spectra of the complexes show the dinuclear cations $[(LAu)_2X]^+$ (X = Cl, OAc) in high abundance suggesting extra stability of these compact species due to efficient intra-ionic aurophilic interactions. This structural motif has already been confirmed for several other examples with standard trialkyl- and triarylphosphine ligands [31].

Tri(2-thienyl)- and tri(2-furyl)*arsine* have been prepared successfully *via* an organolithium route, but yields were found to be low owing to side-reactions. Both arsines were used as ligands for AuCl, but only the tri(2-thienyl)arsine complex was found to be a sufficiently robust compound to allow analytical, spectroscopic and structural characterization. The data show no anomalies. The mass spectrum of $(C_4H_3S)_3AsAuCl$, **7**, is again dominated by the dinuclear cation [(LAu)₂Cl]⁺ indicating that the arsine ligand L is also an efficient donor to stabilize this chloronium species.

In model quaternization reactions, tri(2-thienyl)and tri(2-furyl)phosphine were converted into the methylphosphonium salts (**3** and **6**) using an excess of

	1	2	3	4	5	6
Empirical formula	C12H9AuClPS3	C14H12AuO2PS3	C ₁₃ H ₁₂ IPS ₃	C12H9AuClO3P	$C_{13}H_{12}IO_{3}P \cdot I_{0.10}$	C12H9AsAuClS3
М	512.76	536.35	422.28	464.58	387.02	556.71
Crystal system	Triclinic	Monoclinic	Triclinic	Monoclinic	Tetragonal	Monoclinic
Space group	$P\overline{1}$	C2/c	$P\bar{1}$	$P2_1/n$	P4/ncc	$P2_1/c$
a/Å	9.0833(1)	23.3435(3)	9.4955(1)	9.7253(1)	20.4104(1)	9.4214(1)
b/Å	9.0939(1)	10.0027(2)	12.1118(2)	12.4449(2)	20.4104	13.2064(2)
c/Å	10.4493(2)	17.6489(2)	14.3116(2)	11.1625(2)	14.2572(2)	14.7627(2)
$\alpha/^{\circ}$	112.8596(8)	90	81.4286(8)	90	90	90
$\beta/^{\circ}$	102.7816(7)	126.7145(8)	88.0477(9)	92.4088(6)	90	124.6795(6)
$\gamma/^{\circ}$	98.1767(7)	90	80.5240(6)	90	90	90
$V/Å^3$	750.220(19)	3303.48(9)	1606.27(4)	1349.81(4)	6939.33(9)	1510.50(3)
$ ho_{\rm calc}/{\rm g}~{\rm cm}^{-3}$	2.270	2.157	1.747	2.286	1.731	2.448
Z	2	8	4	4	16	4
F(000)	480	2032	824	864	2998	1032
μ (Mo-K _{α}) (cm ⁻¹)	104.84	93.82	24.65	112.10	24.74	124.83
T/K	143	143	143	143	143	143
Refls. measured	20784	47908	42192	37499	155893	42159
Refls. unique	3241	3053	6982	3090	3265	3442
R _{int}	0.034	0.057	0.033	0.050	0.043	0.046
Refined parameters	189	209	325	199	172	201
Restraints	12	0	0	0	0	0
$R1[I \ge 2\sigma(I)]$	0.0257	0.0216	0.0359	0.0267	0.0310	0.0245
wR2 ^a	0.0674	0.0560	0.1030	0.0637	0.0724	0.0596
Weighting scheme	a = 0.0315	<i>a</i> = 0.0166	a = 0.0488	a = 0.0037	a = 0.0157	a = 0.0127
-	b = 1.7801	<i>b</i> = 8.1973	b = 2.2327	b = 6.0070	b = 11.5911	b = 3.0870
$\sigma_{\rm fin}({\rm max/min})/{\rm e}{\rm \AA}^{-3}$	1.326 / -1.275	0.769 /-0.888	1.323 / -1.015	$1.031 \ / \ -0.981$	0.754 / -0.381	1.1145 / -1.189

Table 1. Crystal data, data collection, and structure refinement of 1-6.

 ${}^{a}wR2 = \{\Sigma[w(F_{o}^{2} - F_{c}^{2})^{2}]/\Sigma[w(F_{o}^{2})^{2}]\}^{1/2}; w = 1/[\sigma^{2}(F_{o}^{2}) + (ap)^{2} + bp]; p = (F_{o}^{2} + 2F_{c}^{2})/3.$

methyl iodide. The structures of **3** and **6** have been determined. In the phosphonium cations, the central atom reaches an almost perfect tetrahedral configuration. By contrast, in the gold(I) complexes the ligands still have much smaller C-P-C angles as compared to the tetrahedral standard, indicating the rather low acceptor character. This result is in agreement with the ³¹P NMR data, where the largest downfield shifts are observed for both phosphines upon quaternization with MeI (50.14 ppm for **3** and 61.62 ppm for **6**). The shift differences for **1** and **4** are only 39.22 and 49.37 ppm, respectively.

Experimental Section

All experiments were carried out routinely in an atmosphere of dry nitrogen. Glassware was oven-dried and filled with nitrogen, and solvents were dried and saturated with nitrogen. Standard equipment was used throughout. Reactions with silver salts were carried out in flasks covered with aluminium foil. Tri(2-thienyl)- and tri(2-furyl)phosphine are commercially available (Aldrich). (Tetrahydrothiophene)gold chloride was prepared following a literature procedure [33].

[*Tri*(2-*thienyl*)*phosphine*]*gold chloride* (1): Tri(2-*thienyl*)*phosphine* (0.200 g, 6.20 mmol) is added to a

solution of $(C_4H_8S)AuCl$ (0.175 g, 6.20 mmol) in tetrahydrofuran (15 ml) at -78 °C with stirring. After 2 h the solvent is removed in a vacuum at room temperature. The residue is crystallized from CH₂Cl₂/n-pentane; colorless crystals, m.p. 192 °C, 0.303 g (95.4% yield), soluble in CH₂Cl₂, CHCl₃, C₄H₈O, sparingly soluble in diethylether. NMR (CD₂Cl₂, 20 °C) ³¹P{¹H} -6.39, s; ¹H 7.26-7.85 (ABCX); ¹³C{¹H}: 129.35, 131.09, 135.66, and 138.69, all d (J 14.3, 74.2, 5.2, and 14.8 Hz). MS(FAB): *m*/z 984.8 (19.1) [(LAu)₂Cl]⁺; 757.0 (4.9) [L₂Au]⁺; 511.9 (5.4) [M]⁺; 477.0 (100) [LAu]⁺. Analysis found C 31.13, H 2.24, P 6.59, Cl 7.54; calcd. C 31.02, H 1.95, P 6.67, Cl 7.63.

[*Tri*(2-*thienyl*)*phosphine*]*gold acetate* (2): Compound 1 (0.200 g, 0.620 mmol) is reacted with a slurry of silver acetate (0.103 g, 0.620 mmol) in dichloromethane (15 ml) at -78 °C for 2 h with stirring. The reaction mixture is filtered and the filtrate concentrated in a vacuum. The product is finally precipitated from a small volume of the solution by the addition of pentane. Colorless needles, m.p. 100 °C (decomposition), 0.282 g (84.8% yield). NMR (CD₂Cl₂, 20 °C) ³¹P{¹H}: -12.32, s; ¹H: 7.26-7.85, m, ABCX; 1.97, s, Me; ¹³C{¹H}: 176.71, s, CO₂; 129.30, 131.04, 135.61, and 138.73, all d (J 13.84, 77.64, 5.38, and 15.37 Hz); 23.61, s, Me. MS(FAB): 756.6 (5.6) [L₂Au]⁺; 476.8 (57.7) [LAu]⁺. Analysis found C 31.61, H 2.27, P 5.73, Au 37.60; calcd. C 31.29, H 2.44, P 5.76, Au 36.65.

Methyl-tri(2-*thienyl*)*phosphonium iodide* (**3**): This compound was prepared previously from the phosphine and methyl iodide in benzene [14, 19, 22]. m.p. 183 °C. Complementary data: NMR (CDCl₃, 20 °C), ³¹P{¹H}: 4.53, s. ¹H: 3.34, d, J 13.9 Hz, Me; 7.45, 8.12, 8.22, m, ABCX. ¹³C{¹H}: 16.43, d, J 62.3, Me; 119.43, 130.87, 139.52, and 142.36, all d (J 112.1, 16.1, 5.7, and 12.5 Hz). MS(FAB) *m/z* 294.7 (100) [M]⁺.

[*Tri*(2-*furyl*)*phosphine*]*gold chloride* (**4**): As described for complex **1**, compound **4** is prepared from (tht)AuCl (0.200 g, 0.620 mmol) and the ligand (0.144 g, 0.620 mmol) in thf (15 ml) at -78 °C. Work-up after 2 h gives 0.273 g of **4** (95.0% yield), colorless crystals, m.p. 175 °C (decomposition). ³¹P{¹H} NMR (thf, 20 °C): -28.52, s. ¹H (CD₂Cl₂): 6.58, 7.18, 7.82, m, ABCX. ¹³C{¹H} (CD₂Cl₂): 112.04, 125.54, 141.55, and 150.53, all d (J 6.2, 17.7, 67.6, and 4.7 Hz). MS(FAB) *m*/z 893.1 (32) [(LAu)₂Cl]⁺; 464.0 (2) [M]⁺; 429.0 (92) [LAu]⁺; 164.9 (100) [R₂P]⁺. Analysis found C 28.24, H 1.83, Au 38.1, Cl 6.78; calcd. C 28.11, H 1.77, Au 38.41, Cl 6.91.

[Tri(2-furyl)phosphine]gold acetate (5): As described for complex 2, compound 4 (0.273 g, 0.588 mmol) is converted into compound 5 using silver acetate (0.103 g, 0.620 mmol) in dichloromethane (15 ml) at -78 °C. The mixture is kept at -32 °C for 1 week and filtered. Evaporation of the filtrate leaves a frozen foam, which is taken up in dichloromethane and reprecipitated as a siroup by addition of pentane. Drying in a vacuum leaves again a frozen foam of the product, which cannot be crystallized. The product decomposes at room temperature and must be kept below -32 °C for prolonged storage; 0.162 g (56.5% yield). NMR (CD₂Cl₂, 20 °C), ³¹P{¹H}: -35.26, s. ¹H: 1.97, s, Me; 6.57, 7.21, 7.82, ABCX, m. ¹³C{¹H}: 23.41, s, Me; 111.99, 125.64, 141.33, all d, (J 9.34, 25.95, 1.73 Hz); 150.48, s; 176.48, s, CO₂. MS(FAB) m/z 916.0 (15.6) [(LAu)₂OAc]⁺; 660.4 (39.3) [L₂Au]⁺; 488.6 (1.6) $[M]^+$; 428.7 (97.6) $[LAu]^+$; 165.0 (100) $[R_2P]^+$. The compound was too unstable for a reliable microanalysis.

Methyl-tri(2-*furyl*)*phosphonium iodide* (6): As described for compound **3**, the salt is obtained from the phosphine (0.085 g, 0.380 mmol) and an excess of methyl iodide (0.5 ml, 1.14 g, 8.1 mmol) in toluene (5 ml) under reflux for 2 h [19]. Recrystallization from acetonitrile/diethylether gives light brown rods, m. p. 138 °C; 0.108 g (76.1% yield). NMR (CDCl₃, 20 °C), ${}^{31}P{}^{1}H{}$: -16.27, s. ¹H: 3.09, d, J 15.1 Hz, Me; 7.73, 7.78, 7.99, br. m, ABCX; ${}^{13}C{}^{1}H{}$: 9.35, d, J 62.80 Hz, Me; 113.27, 130.82, 130.84, and 153.38, all d (J 10.4, 23.4, 144.3, 8.8 Hz). MS(FAB) *m*/z 247.1 (100) [M]⁺; 180.1 (2.1) [R₂MeP]⁺; 165.1 (3.6) [R₂P]⁺. Analysis found C 40.23, H 3.19, I 35.38; calcd. C 41.74, H 3.23, I 33.92.

Tri(2-thienyl)arsine: Thiophene (12 g, 0.14 mol) is dissolved in tetrahydrofuran (50 ml) and treated with a 1.6 M solution of n-butyllithium in n-hexane (75 ml, 0.12 mol) at 0 °C with stirring. The mixture is allowed to warm to 20 °C and stirring is continued for 30 min. before a solution of arsenic trichloride (5.0 g, 28 mmol) in tetrahydrofuran (20 ml) is added dropwise with stirring. After 12 h the reaction mixture is quenched with water (50 ml). The lower layer is separated and the solvent evaporated to leave a residue which is taken up in chloroform (10 ml) and washed with the same volume of water. The aqueous phase is extracted with chloroform and the combined organic phase is dried over Na₂SO₄. Evaporation of the solvent and kugelrohr distillation (220 °C/0.9 mbar) gives a yellow oil, which solidifies to a glass upon cooling; 3.41 g (28.4% yield). NMR (CDCl₃, 20 °C), ¹H: 7.16, 7.35, 7.59, ABC. ¹³C{¹H}: 127.82, 131.13, 134.46, and 138.28, all s. MS(FAB) m/z 324 [M]⁺.

Tri(2-*furyl*)*arsine*: As described for (2-C₄H₃S)₃As, the compound is prepared from furan (10 g, 0.15 mol), nbutyllithium (75 ml, 1.6 m, 0.12 mol) and AsCl₃ (5.0 g, 28 mmol) in a total of 75 ml of tetrahydrofuran. Kugelrohr distillation at 160 °C/0.9 mbar gives 3.58 g of an oily product (47% yield), which crystallizes from diethylether at -78 °C. NMR (CDCl₃, 20 °C), ¹H: 6.44, 6.71, 7.66, ABC. ¹³C{¹H}: 110.52, 120.05, 146.86, and 150.50, all s. MS(FAB) *m/z* 276 [M]⁺.

[*Tri*(2-thienyl)arsine]gold chloride (**7**): As described for **1**, the compound is prepared from (tht)AuCl (0.20 g, 0.62 mmol) and the arsine (0.20 g, 0.62 mmol) in dichloromethane (7 ml). Colorless crystals, m.p. 144 °C; 0.326 g (94.3% yield). NMR (CDCl₃, 20 °C) ¹H: 7.20, 7.52, 7.73, ABC. ¹³C{¹H}: 128.56, 130.36, 133.92, and 136.76, all s. MS(FAB) *m*/z 1075.7 (40.6) [(LAu)₂Cl]⁺; 844.1 (9.4) [L₂Au]⁺; 520.5 (100) [LAu]⁺.

Crystal structure determinations: Specimens of suitable quality and size of 1, 2, 3, 4, 6 and 7 were mounted on the ends of quartz fibres in inert perfluoropolyalkylether and used for intensity data collection on a Nonius DIP2020 diffractometer, employing graphite-monochromated Mo-K $_{\alpha}$ radiation. The structures were solved by a combination of direct methods (SHELXS-97) and difference-Fourier syntheses and refined by full matrix least-squares calculations on F^2 (SHELXL-97) [34]. The thermal motion was treated anisotropically for all non-hydrogen atoms. The hydrogen atoms were calculated in ideal positions and allowed to ride on their parent atoms with fixed isotropic contributions except for those of 4 which were located and refined with isotropic displacement parameters. Further information on crystal data, data collection and structure refinement are summarized in Table 1. One thienyl group each in 1 and 2 and two in 7 are disordered over two sites by a rotation of the ring of 180° about the C-P axis. The occupation factors for the predominantly occupied positions are 0.5, 0.560, 0.62 (S22) and 0.68 (S32), respectively. One of the iodide positions of 6 is disordered over two sites with occupation factors of 0.20 and 0.16, respectively. Referring the full occupancy for this speVolkswagenstiftung, and Heraeus GmbH.

Acknowledgements

cial position (0.5), there is an occupational deficit. Absorption corrections for all structures were carried out using DE-LABS, as part of the PLATON suite of programs [35]. 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 CCDC 210532 – 210537 [37].

- [1] D. Redmore, Chem. Rev. **71**, 315 (1971).
- [2] N.G. Andersen, B.A. Keay, Chem. Rev. 101, 997 (2001).
- [3] U. Schröder, S. Berger, Eur. J. Org. Chem. 2601 (2000).
- [4] M. Appel, S. Blaurock, S. Berger, Eur. J. Org. Chem. 1143 (2002).
- [5] D. W. Allen, H. Ward, Z. Naturforsch. 35b, 754 (1980).
- [6] B. Schaub, S. Jeganathan, M. Schlosser, Chimia **40**, 246 (1986).
- [7] K. Issleib, A. Brack, Z. Anorg. Allg. Chem. 292, 245 (1957).
- [8] a) H. Sachs, Chem. Ber. dtsch. chem. Ges. 25, 1514 (1892); b) G. M. Kosolapoff, J. Amer. Chem. Soc. 69, 2248 (1947).
- [9] E. Niwa, H. Aoki, H. Tanaka, K. Munakata, Chem. Ber. 99, 712 (1966).
- [10] Ya. L. Gol'dfarb, A. A. Dudikov, V. P. Litvinov, D. S. Yurit, Yu. T. Struchkov, Khim. Geterotsikl. Soed. 1326 (1982).
- [11] S. S. Moore, G. M. Whitesides, J. Org. Chem. 47, 1489 (1982).
- [12] D. W. Allen, N. A. Bell, S. T. Fong, L. A. March, I. W. Nowell, Inorg. Chim. Acta 99, 157 (1985).
- [13] L. Horner, J. Röder, Phosphorus 6, 147 (1976).
- [14] D. W. Allen, J. Chem. Soc. B 1490 (1970).
- [15] D. W. Allen, L. Ebdon, Phosphorus 7, 161 (1979).
- [16] Y. Uchida, Y. Takaya, S. Oae, Heterocycles 30, 347 (1990).
- [17] R. H. Kemp, W. A. Thomas, M. Gordon, C. E. Griffin, J. Chem. Soc. B 527 (1969).
- [18] H. J. Jakobsen, O. Manscher, Acta Chem. Scand. 25, 680 (1971).
- [19] D. W. Allen, B. G. Hutley, M. T. J. Mellor, J. Chem. Soc. Perkin II 63, (1972).
- [20] D. W. Allen, B. F. Taylor, J. Chem. Soc., Dalton Trans. 51 (1982).
- [21] H. J. Jakobsen, J. A. Nielsen, J. Mol. Spectr. 33, 474 (1970).

[22] P. Dembach, G. Seconi, P. Vivarelli, F. Taddei, Org.

This work was generously supported by Deutsche

Forschungsgemeinschaft, Fonds der Chemischen Industrie,

- Magn. Reson. **4**, 185 (1972). [23] D. W. Allen, I. W. Nowell, B. F. Taylor, J. Chem. Soc., Dalton Trans. 2505 (1985).
- [24] T.M. Räsänen, S. Jääskeläinen, T.A. Pakkanen, J. Organomet. Chem. 553, 453 (1998).
- [25] U. Bodensieck, H. Vahrenkamp, G. Rheinwald, H. Stoeckli-Evans, J. Organomet. Chem. 488, 85 (1995).
- [26] Ya. L. Gol'dfarb, A. A. Dudinov, V. S. Bogdanov, Bull. Acad. Sci. USSR, Chem. Sci. 35, 1919 (1986).
- [27] L.J. Goldsworthy, W.H. Hook, J.A. John, S.G.P. Plant, J. Rushton, L.M. Smith, J. Chem. Soc. 2208 (1948).
- [28] W.G. Lowe, C.S. Hamilton, J. Am. Chem. Soc. 57, 1081 (1935).
- [29] J. F. Morgan, E. J. Cragoe, Jr., B. Elpern, C. S. Hamilton, J. Am. Chem. Soc. 69, 932 (1947).
- [30] A. Étienne, Bull. Soc. Chim. France 13, 669 (1946).
- [31] H. Schmidbaur, A. Hamel, N.W. Mitzel, A. Schier, S. Nogai, Proc. Natl. Acad. Sci. USA 99, 4916 (2002).
- [32] N.C. Baenziger, W.E. Bennett, D.M. Soboroff, Acta Crystallogr. 32 B, 962 (1976).
- [33] R. Usón, A. Laguna, J. Vincente, J. Organomet. Chem. 131, 471 (1977).
- [34] G. M. Sheldrick, SHELX-97, Programs for crystal structure analysis, University of Göttingen, Germany, 1997.
- [35] A.L. Spek, Acta Crystallogr. 46 A, 194 (1990).
- [36] M. N. Burnett, C. K. Johnson, ORTEP-3: Oak Ridge Thermal Ellipsoid Plot Program for Crystal Structures Illustrations, Report ORNL-6895, Oak Ridge National Laboratory, Oak Ridge, TN, USA (1996).
- [37] The structure of 4 has recently been published: S. Y. Ho, E. R. T. Tiekink, Z. Kristallogr. NCS 217, 591 (2002). The results are in agreement.