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Abstract. Three different arsonium salts were prepared by a solventfree method from Ph<sub>3</sub>As and the respective 2-bromoacetophenones. These salts were deprotonated by NaOH to form keto-stabilized arse-

nic ylides. The ylids react with [AuCl(tht)] affording gold(I) complexes containing the C-bound ylide. The compounds were characterized by NMR spectroscopy, IR spectroscopy, and X-ray diffraction.

### Introduction

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Keto-stabilized phosphorus-derived ylides of the type Ph<sub>2</sub>PCHC(O)R are a well-studied class of compounds, exhibiting both diverse organic reactivity as well as rich coordination chemistry with a variety of metals.<sup>[1]</sup> In contrast, not much is known about the metal chemistry of the corresponding ketostabilized arsenic-ylides Ph<sub>3</sub>AsCHC(O)R, despite the fact that the vlides themselves are quite old compounds. The formation of arsonium salts from the reaction of triphenylarsine with chloroacetone or 2-bromoacetophenone and their subsequent deprotonation was first reported by Michaelis in two papers from 1899 and 1902.<sup>[2]</sup> More than half a century later Nesmeyanov and Frøven independently studied the reactivity as well as physical and spectroscopic properties of these stabilized arsenic ylides in more detail.<sup>[3]</sup> It was also Nesmeyanov who showed that Ph<sub>3</sub>AsCHC(O)Ph formed a stable salt with HgCl<sub>2</sub>, which was formulated as [HgCl{Ph<sub>3</sub>AsCHC(O)Ph}]Cl.<sup>[4]</sup> Later, Buckle and Harrison reported that keto-stabilized Asylids act as C-bound ligands in a family of organotin(IV) complexes. Their assignment was based on the IR-stretching frequency of the carbonyl group.<sup>[5]</sup>

Palladium(II) and platinum(II) complexes of the type [MCl<sub>2</sub>(ylide)<sub>2</sub>], prepared by two different methods, were reported by the groups of Burmeister and Bravo in the mid-1970's. Based on IR- and NMR spectroscopy, the ylids were assigned to bind to the metal through the carbon atom.<sup>[6]</sup> Furthermore, Bravo observed a mixture of two stereoisomers in solution by NMR spectroscopy, resulting from the chirality at the ylide-carbon-atom upon coordination to the metal.<sup>[6a]</sup>

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Burmeister showed that keto-stabilized phosphorus ylides coordinated to Pd<sup>II</sup> readily undergo orthometallation at either a phenyl ring of the Ph<sub>3</sub>P moiety or the phenyl ring adjacent to the carbonyl group.<sup>[7]</sup> In case of their arsenic counterparts. orthometallation was only observed with MeC(O)CHAsPh<sub>3</sub> but not with PhC(O)CHAsPh<sub>3</sub>.<sup>[7]</sup> Around the same time Tanaka reported a detailed NMR spectroscopic study of some PtII and PdII-phosphine complexes of the type  $[MX_2(PR_3)(ylide)]$   $[M = Pd, Pd; X = Cl, Br, I; PR_3 = PPhMe_2,$ PMe<sub>3</sub>] with various keto-stabilized phosphorus-, arsenic- and sulfur-ylides.<sup>[8]</sup> Platinum(II) ethylene complexes containing Cbound keto-stabilized phosphorus- and arsenic ylides of the type *trans*-[PtCl<sub>2</sub>( $\eta^2$ -C<sub>2</sub>H<sub>4</sub>)(ylide)] are accessible from the reaction of the respective ylides with K[PtCl<sub>3</sub>( $\eta^2$ -C<sub>2</sub>H<sub>4</sub>)].<sup>[9]</sup> There is also a more recent publication on palladium complexes containing bis(chelating) ylides derived from 1,3-dibromoacetone.[10]

Whilst in all these compounds the ylides are bound to the metal through the ylide-carbon atom, there is one report showing that the reaction of keto-stabilized phosphorus- or arsenic ylides with  $[PtCl(dppe)]_2[BF_4]_2$  at low temperature affords the cationic species [PtCl(dppe)(ylide)]BF<sub>4</sub>, in which the ylide is O-bound to the metal.<sup>[11]</sup> In solution however, these compounds transform to the C-bound isomer in a first-order process, the kinetics of which were studied by IR spectroscopy in solution. Thus the coordination chemistry of keto-stabilized arsenic ylides is to date restricted to compounds containing Sn<sup>IV</sup>, Hg<sup>II</sup>, Pd<sup>II</sup>, and Pt<sup>II</sup> and none of these derivatives have been studied by X-ray diffraction (Chart 1).



arsenic ylides.

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Given our interest in gold compounds containing *C*-bound ligands,<sup>[12]</sup> we wished to examine the behavior of keto-stabilized arsenic ylides towards gold and to investigate the compounds with modern spectroscopic methods and X-ray diffraction. The first results of this endeavor are reported herein.

### **Results and Discussion**

Ylides are typically synthesized by deprotonation of an appropriate arsonium salt. In the case of Ph<sub>3</sub>As, the classical procedure in a solvent typically requires long reaction times due to the weak nucleophilicity of Ph<sub>3</sub>As. We therefore used a solvent-free method, which involved melting together Ph<sub>3</sub>As with the appropriate 2-bromoacetophenone at 100 °C.<sup>[13]</sup> This procedure afforded the desired arsonium salts in high yields and purity with simple workup in a short amount of time. Subsequently, the arsonium salts **1a–1c** were readily deprotonated in EtOH using 2.5 M aqueous NaOH as base (Scheme 1).

The resulting keto-stabilized arsenic ylides 2a-2c were characterized by various spectroscopic methods including NMR spectroscopy, IR spectroscopy and mass spectrometry. In addition, 2a and 2b were also characterized by single-crystal X-ray diffraction (see below). The proton NMR spectra of the compounds readily confirm the formation of the ylides. In particular, the resonance of the ylidic proton can be observed as a broad signal at around 4.8 ppm, shifted by about 1.5 ppm when compared to that of the arsonium salts. Similarly, in the <sup>13</sup>C-NMR spectra the resonance of the ylidic carbon atom is found at around 58 ppm in the ylides and at approximately 42 ppm in the arsonium salts. A further diagnostic feature of these compounds is the wavenumber of the carbonyl stretching frequency. In the ylides this band is shifted by about 100 cm<sup>-1</sup> to a lower wavenumber than that in the arsonium salts, where the CO stretching frequency falls in the range of 1660 to 1670 cm<sup>-1</sup>. For the chloro- and nitro-derivatives (2a and 2b) we obtained single crystals suitable for X-ray diffrac-



Figure 1. Molecular structures of 2a (top) and 2b (below) Ellipsoids are drawn at the 30% level. Hydrogen atoms as well as the solvated CH<sub>2</sub>Cl<sub>2</sub> (in 2b) are omitted for clarity.

tion, which allowed us to determine their molecular structures (Figure 1).

Compounds **2a** and **2b** crystallize in the monoclinic space groups C2/c and  $P2_1/c$ , respectively. The As- $C_{ylide}$  bond lengths of 1.826(2) Å and 1.842(3) Å are slightly longer than an arsenic-carbon double bond (1.78 Å) but considerably shorter than an As-C single bond (1.98 Å). Furthermore, the



#### Scheme 1.

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two carbon atoms adjacent to arsenic (C1 and C2) are 1.375(3) Å and 1.370(5) Å apart, clearly indicative of considerable double bond character. The C–O bond lengths of 1.253(2) Å and 1.255(4) Å are also slightly longer than a carbon–oxygen double bond. Thus, these parameters show considerable bond delocalization along the As–C–C–O unit. A keto-stabilized arsenic ylide may be represented by the three tautomeric forms a-c illustrated in Figure 2. Tautomer a, the ylene form, can however be neglected, since the d-orbitals are too high in energy to be involved in bonding of main group elements.

Figure 2. Tautomeric forms of a keto-stabilized arsenic ylide.

The bond lengths observed in the solid-state structures therefore result from an averaging of all three tautomers. Surprisingly, there are only two other crystal structures of keto-stabilized arsenic ylides deposited in the CCSD: PhC(O)CHAsPh<sub>3</sub> and CF<sub>3</sub>C(O)CHAsPh<sub>3</sub>.<sup>[14]</sup> In the former, which is structurally most similar to 2a and 2b, the bond lengths are close to those discussed above. Since, the original dataset was recorded at room temperature,<sup>[14a]</sup> we wished to have high-quality 150 K data for better comparison. We therefore also synthesized and crystallized PhC(O)CHAsPh<sub>3</sub>. The molecular structure (Figure S1) and spectroscopic details are included in the Supporting low-temperature Information. In our structure of PhC(O)CHAsPh<sub>3</sub> the As-C<sub>vlide</sub> bond length is with 1.846(2) Å slightly longer than that in 2a and 2b and similarly, the C-C and C-O bond lengths are slightly longer, being 1.389(3) Å and 1.268(2) Å, respectively. In all four compounds, the conjugated As-C-C-O unit is planar and the ylidic carbon is close to being sp<sup>2</sup> hybridized, as evidenced by an As-C-C bond angle of approximately 119° in 2a, 114° in 2b and 113° in PhC(O)CHAsPh<sub>3</sub>.

The ylides 2a-2c reacted with [AuCl(tht)] [tht = tetrahydrothiophene] in CH<sub>2</sub>Cl<sub>2</sub> to give colorless complexes 3a-3cin varying yields (Scheme 1). Spectroscopically, the wavenumber of the carbonyl stretching frequency as well as the chemical shift of the ylidic proton resonance are most diagnostic. We managed to obtain X-ray quality crystals of the nitroderivative **3b** to confirm the molecular structure (Figure 3).

The compound crystallizes in the orthorhombic centrosymmetric space group *Pbcn*. Although the compound has a chiral center at C(1), the crystals are racemic. In the crystal packing both *S*- and *R*-configured molecules can be observed. The molecule consists of the ylide bound through the carbon atom to gold. The coordination about the gold is completed by a chloride ligand. As expected for a gold(I) compound, its coordination arrangement is linear with a C–Au–Cl angle of 179.5°. The bond lengths in the ylide ligand involving the As–C–C–O unit are quite different when compared to those of the ylide **2b** discussed above (Table 1).

As can be seen, the As–C and the C–C bonds in **3b** are now much closer to a single bond and the C–O bond length is



Figure 3. Molecular structure of 3b. Ellipsoids are drawn at the 30% level. Hydrogen atoms are omitted for clarity. Only one part of the disordered Au–Cl unit is shown.

**Table 1.** Comparison of selected bond lengths /Å, angles  $/^{\circ}$ , and carbonyl stretching frequencies  $/\text{cm}^{-1}$  in complexes **2b** and **3b**.

	2b	3b	
As(1)–C(1)	1.842(3)	1.905(5)	
C(1)-C(2)	1.370(5)	1.473(8)	
C(2)–O(1)	1.255(4)	1.226(7)	
As(1)-C(1)-C(2)	113.5(3)	108.4(3)	
v(CO)	1519	1627	

consistent with the presence of a double bond. Thus, it is the tautomeric form c (Figure 2) of the ylide which is dominant: The lone pair at the ylidic carbon coordinates to the metal center as shown in Figure 4.



Figure 4. Schematic illustration of the coordination mode of the ylide to the AuCl unit.

This structure represents the first reported structure of a metal complex containing a keto-stabilized arsenic ylide. Therefore, we have no related structures to compare our data to, however in the gold(I) complex containing the keto-stabilized phosphorus-ylide [Ph<sub>3</sub>PCHC(O)CH<sub>2</sub>C(O)OEt], the Au–C<sub>ylide</sub> bond length of 2.079(3) Å is similar to that observed in **3b** [2.041(6) Å].<sup>[15]</sup> As can be seen from the angles about the ylidic carbon atom (ranging from 107.9° to 109.7°), its geometry is consistent with sp<sup>3</sup>-hybridized tetrahedral.

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Gold(I) complexes with carbon-based ligands often show luminescence in the solid-state and/or in solution. Examination of the gold complexes 3a-3c under a UV-light unfortunately revealed that the solid compounds were not luminescent at room temperature and also at liquid nitrogen temperature. To access a wider range of gold complexes, we attempted to remove or exchange the chloride-ligand in 3a-3c. Unfortunately, the complexes proved to be rather unstable and we only observed cleavage of the gold–carbon bond accompanied by formation of decomposition products and metallic gold.

In summary, we prepared a series of keto-stabilized arsenic ylides and their corresponding gold(I) chloride complexes. The *C*-coordination of the ylide to the metal was studied by various spectroscopic methods and confirmed by X-ray diffraction. Further studies of this class of compounds are being continued in our group.

## **Experimental Section**

**General:** Unless specified otherwise, reactions were carried out under dinitrogen gas using HPLC grade solvents dried with 3 Å molecular sieves. [AuCl(tht)] (tht = tetrahydrothiophene) was prepared by a published method.<sup>[16]</sup> All other chemicals and solvents were commercial products and were used as received. NMR spectra were recorded on Bruker Avance 400 or Bruker Avance III 600 instruments. Spectra were referenced externally to Me<sub>4</sub>Si. IR spectra were measured on a Nicolet iS5 spectrometer equipped with an iD5 diamond ATR unit. High-resolution electrospray mass spectra were measured on a Bruker Daltonics micrOTOF instrument.

**Preparation of the Arsonium Salts:** Ph<sub>3</sub>As (0.500 g, 1.64 mmol) was heated to 100 °C (heating block temperature) in an open vessel. Once the material had completely melted, the 2-bromoacetophenone derivative (1.2 equiv.) was added. After ca. 30 min the melt was left to cool to room temperature. The resulting solid was dissolved in CH<sub>2</sub>Cl<sub>2</sub> (5 mL) and Et<sub>2</sub>O (50 mL) was added causing precipitation of the product. The solid was isolated by filtration and was washed with Et<sub>2</sub>O (3 × 10 mL) and subsequently dried in vacuo.

**[4-ClC<sub>6</sub>H<sub>4</sub>C(O)CH<sub>2</sub>AsPh<sub>3</sub>]Br (1a):** The product was isolated in 96% yield as a colorless solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 6.47 (s, 2 H, CH<sub>2</sub>), 7.51 (d, *J* = 8.7 Hz, 2 H, C<sub>6</sub>H<sub>4</sub>), 7.68 (t, *J* = 7.5 Hz, 6 H, *m*-Ph<sub>3</sub>As), 7.72–7.76 (m, 3 H, *p*-Ph<sub>3</sub>As), 7.92 (dd, *J* = 8.6, 1.1 Hz, 6 H, *o*-Ph<sub>3</sub>As), 8.41 (d, *J* = 8.7 Hz, 2 H, C<sub>6</sub>H<sub>4</sub>). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>):  $\delta$  = 42.76 (CH<sub>2</sub>), 122.23 (*ipso*-Ph<sub>3</sub>As), 129.39 (C<sub>6</sub>H<sub>4</sub>), 130.66 (*m*-Ph<sub>3</sub>As), 131.75 (C<sub>6</sub>H<sub>4</sub>), 132.87 (C<sub>6</sub>H<sub>4</sub>), 133.11 (*o*-Ph<sub>3</sub>As), 133.85 (*p*-Ph<sub>3</sub>As), 141.81 (C<sub>6</sub>H<sub>4</sub>), 192.07 (CO). **HR ES-MS**: Calcd. for [C<sub>26</sub>H<sub>21</sub>ClOAs]<sup>+</sup> 459.0497; found 459.0449. **IR** (ATR):  $\tilde{v}$  = 1663 cm<sup>-1</sup> v(CO).

**[4-O<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>C(O)CH<sub>2</sub>AsPh<sub>3</sub>]Br (1b):** The product was isolated in 95% yield as a pale yellow solid. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>):  $\delta$  = 6.63 (s, 2 H, CH<sub>2</sub>), 7.65 (t, *J* = 7.6 Hz, 6 H, *m*-Ph<sub>3</sub>As), 7.72 (t, *J* = 7.5 Hz, 3 H, *p*-Ph<sub>3</sub>As), 7.92 (d, *J* = 7.1 Hz, 6 H, *o*-Ph<sub>3</sub>As), 8.22 (d, *J* = 8.9 Hz, 2 H, C<sub>6</sub>H<sub>4</sub>), 8.63 (d, *J* = 8.9 Hz, 2 H, C<sub>6</sub>H<sub>4</sub>), <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>):  $\delta$  = 42.61 (CH<sub>2</sub>), 121.80 (*ipso*-Ph<sub>3</sub>As), 123.84 (C<sub>6</sub>H<sub>4</sub>), 130.66 (*m*-Ph<sub>3</sub>As), 131.48 (C<sub>6</sub>H<sub>4</sub>), 130.20 (*o*-Ph<sub>3</sub>As), 133.91 (*p*-Ph<sub>3</sub>As), 138.80 (C<sub>6</sub>H<sub>4</sub>), 150.99 (C<sub>6</sub>H<sub>4</sub>), 192.18 (CO). **HR ES-MS**: Calcd. for [C<sub>26</sub>H<sub>21</sub>NO<sub>3</sub>As]<sup>+</sup> 470.0737; found 470.0733. **IR** (ATR):  $\tilde{v}$  = 1671 cm<sup>-1</sup> v(CO).

[4-PhC<sub>6</sub>H<sub>4</sub>C(O)CH<sub>2</sub>AsPh<sub>3</sub>]Br (1c): The product was isolated in 66% yield as a yellow solid. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>):  $\delta = 6.47$  (s, 2

H, CH<sub>2</sub>), 7.39–7.43 (m, 1 H, *p*-Ph), 7.48 (t, J = 7.5 Hz, 2 H, *m*-Ph), 7.63 (dd, J = 8.3, 1.3 Hz, 2 H, *o*-Ph), 7.68 (t, J = 7.5 Hz, 6 H, *m*-Ph<sub>3</sub>As), 7.71–7.75 (m, 3 H, *p*-Ph<sub>3</sub>As), 7.77 (d, J = 8.6 Hz, 2 H, C<sub>6</sub>H<sub>4</sub>), 7.93 (dd, J = 8.2, 1.3 Hz, 6 H, *o*-Ph<sub>3</sub>As), 8.50 (d, J = 8.5 Hz, 2 H, C<sub>6</sub>H<sub>4</sub>). <sup>13</sup>C **NMR** (151 MHz, CDCl<sub>3</sub>):  $\delta = 42.86$  (CH<sub>2</sub>), 122.37 (*ipso*-Ph<sub>3</sub>As), 127.31 (*o*-Ph), 127.57 (C<sub>6</sub>H<sub>4</sub>), 128.50 (*p*-Ph), 128.96 (*m*-Ph), 130.61 (*m*-Ph<sub>3</sub>As), 130.87 (C<sub>6</sub>H<sub>4</sub>), 133.11 (*o*-Ph<sub>3</sub>As), 133.16 (C<sub>6</sub>H<sub>4</sub>), 133.77 (*p*-Ph<sub>3</sub>As), 139.49 (*ipso*-Ph), 147.57 (C<sub>6</sub>H<sub>4</sub>), 192.51 (CO). **HR ES-MS**: Calcd. for [C<sub>32</sub>H<sub>26</sub>OAs]<sup>+</sup> 501.1200; found 501.1197. **IR** (ATR):  $\tilde{v} = 1659$  cm<sup>-1</sup> v(CO).

**Preparation of the Ylides:** To a solution of the arsonium salt in EtOH (10 mL) was added NaOH (2.5 M aqueous solution) causing immediate precipitation of a solid. The solid was isolated by filtration and was washed well with water and subsequently dried in vacuo.

**4-CIC<sub>6</sub>H<sub>4</sub>C(O)CHAsPh<sub>3</sub> (2a):** This was prepared as described above from **1a** (0.840 g, 1.55 mmol). The product was isolated as a beige solid in 60 % yield. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>):  $\delta$  = 4.72 (br. s, 1 H, CH), 7.33 (d, *J* = 8.5 Hz, 2 H, C<sub>6</sub>H<sub>4</sub>), 7.52 (t, *J* = 7.3 Hz, 6 H, *m*-Ph<sub>3</sub>As), 7.58 (t, *J* = 7.3 Hz, 3 H, *p*-Ph<sub>3</sub>As), 7.72 (d, *J* = 7.1 Hz, 6 H, *o*-Ph<sub>3</sub>As), 7.91 (d, *J* = 8.5 Hz, 2 H, C<sub>6</sub>H<sub>4</sub>). <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>):  $\delta$  = 58.16 (CH), 127.47 (C<sub>6</sub>H<sub>4</sub>), 128.83 (*ipso*-Ph<sub>3</sub>As), 128.96 (C<sub>6</sub>H<sub>4</sub>), 129.49 (*o*-Ph<sub>3</sub>As), 131.73 (*p*-Ph<sub>3</sub>As), 132.53 (*m*-Ph<sub>3</sub>As), 133.19 (C<sub>6</sub>H<sub>4</sub>), 137.64 (C<sub>6</sub>H<sub>4</sub>), 181.61 (CO). HR ES-MS: Calcd. for [C<sub>26</sub>H<sub>20</sub>ClOAs + H]<sup>+</sup> 459.0497; found 459.0449. IR (ATR):  $\tilde{v}$  = 1576 cm<sup>-1</sup> v(CO). X-ray quality crystals were obtained by vapor diffusion using a combination of CH<sub>2</sub>Cl<sub>2</sub> and cyclopentane.

**4-O<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>C(O)CHAsPh<sub>3</sub> (2b):** This was prepared as described above from **1b** (0.845 g, 1.54 mmol). The product was isolated as a bright yellow solid in 80% yield. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>):  $\delta$  = 4.80 (br. s, 1 H, CH), 7.55 (t, *J* = 7.5 Hz, 6 H, *m*-Ph<sub>3</sub>As), 7.59–7.63 (m, 3 H, *p*-Ph<sub>3</sub>As), 7.71–7.75 (m, 6 H, *o*-Ph<sub>3</sub>As), 8.11 (d, *J* = 8.9 Hz, 2 H, C<sub>6</sub>H<sub>4</sub>), 8.22 (d, *J* = 8.9 Hz, 2 H, C<sub>6</sub>H<sub>4</sub>). <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>):  $\delta$  = 59.79 (CH), 123.10 (C<sub>6</sub>H<sub>4</sub>), 127.78 (C<sub>6</sub>H<sub>4</sub>), 128.05 (*ipso*-Ph<sub>3</sub>As), 129.63 (*o*-Ph<sub>3</sub>As), 132.01 (*p*-Ph<sub>3</sub>As), 132.42 (*m*-Ph<sub>3</sub>As), 146.58 (C<sub>6</sub>H<sub>4</sub>), 148.13 (C<sub>6</sub>H<sub>4</sub>), 178.98 (CO). HR ES-MS: Calcd. for [C<sub>26</sub>H<sub>20</sub>NO<sub>3</sub>As + H]<sup>+</sup> 470.0737; found 470.0735. IR (ATR):  $\tilde{v}$  = 1519 cm<sup>-1</sup> v(CO). Large yellow crystals for X-ray diffraction were obtained by crystallization from a mixture of CH<sub>2</sub>Cl<sub>2</sub> and Et<sub>2</sub>O.

**4-PhC<sub>6</sub>H<sub>4</sub>C(O)CHAsPh<sub>3</sub> (2c):** This was prepared as described above from **1c** (0.375 g, 0.64 mmol). The product was isolated as a pale red solid in 64% yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 4.81 (s, 1 H, CH), 7.36 (t, *J* = 7.8 Hz, 1 H, *p*-Ph), 7.46 (t, *J* = 7.7 Hz, 2 H, *m*-Ph), 7.53 (t, *J* = 7.5 Hz, 6 H, *m*-Ph<sub>3</sub>As), 7.59 (t, *J* = 7.4 Hz, 3 H, *p*-Ph<sub>3</sub>As), 7.63 (d, *J* = 8.1 Hz, 2 H, C<sub>6</sub>H<sub>4</sub>), 7.66 (dd, *J* = 8.3, 1.1 Hz, 2 H, *o*-Ph), 7.77 (dd, *J* = 8.0, 1.6 Hz, 6 H, *o*-Ph<sub>3</sub>As), 8.08 (d, *J* = 8.1 Hz, 2 H, C<sub>6</sub>H<sub>4</sub>). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>):  $\delta$  = 57.33 (CH), 126.50 (C<sub>6</sub>H<sub>4</sub>), 127.15 (*o*-Ph), 127.20 (*p*-Ph), 127.46 (C<sub>6</sub>H<sub>4</sub>), 128.68 (*ipso*-Ph<sub>3</sub>As), 128.89 (*m*-Ph), 129.46 (*m*-Ph<sub>3</sub>As), 131.68 (*p*-Ph<sub>3</sub>As), 132.52 (*o*-Ph<sub>3</sub>As), 139.30 (*ipso*-Ph), 141.12 (C<sub>6</sub>H<sub>4</sub>), 141.79 (C<sub>6</sub>H<sub>4</sub>), 181.40 (CO). HR ES-MS: Calcd. for [C<sub>32</sub>H<sub>25</sub>OAs + H]<sup>+</sup> 501.1200; found 501.1207. **IR** (ATR):  $\tilde{v}$  = 1567 cm<sup>-1</sup> v(CO).

**Preparation of the Gold(I) Complexes:** To an ice-cooled solution of the respective ylide (0.5 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (10 mL) was added [AuCl(tht)] (0.160 g, 0.5 mmol). The mixture was left to stir at room temperature protected from light for ca. 24 h. Addition of Et<sub>2</sub>O (50 mL) caused precipitation of the product. The solid was isolated by filtration and was washed with Et<sub>2</sub>O ( $3 \times 10$  mL) and subsequently dried in vacuo.

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Table 2. Crystallographic and refinement details for compounds 2a, 2b and 3b.

	2a	2b	3b
Empirical formula	C <sub>26</sub> H <sub>20</sub> AsClO	C <sub>27</sub> H <sub>22</sub> AsCl <sub>2</sub> NO <sub>3</sub>	C <sub>26</sub> H <sub>20</sub> AsAuClNO <sub>3</sub>
Color	colorless	yellow	colorless
Formula weight /g·mol <sup>-1</sup>	458.79	554.27	701.77 g/mol
Wavelength /Å	0.71073	0.71073	0.71073
Crystal system	monoclinic	monoclinic	orthorhombic
Space group	C2/c	$P2_{1}/c$	Pbcn
Unit cell dimensions		-	
a /Å	16.8053(5)	8.9714(3)	24.5525(12)
b /Å	11.0627(4)	18.6537(6)	10.6633(3)
c /Å	23.7443(7)	15.0625(4)	18.8241(5)
a /°	90.0	103.97(3)	90.0
βΙ°	100.286(3)	103.907(3)	90.0
y /°	90.0	90.0	90.0
Volume /Å <sup>3</sup>	4343.4(2)	2446.82(13)	4928.3(3)
Z	8	4	8
$\rho_{\rm calc}/{\rm g}\cdot{\rm cm}^{-3}$	1.403	1.505	1.892
$\mu$ /mm <sup>-1</sup>	1.702	1.638	7.439
F(000)	1872.0	1128.0	2688.0
Crystal size /mm	$0.05 \times 0.10 \times 0.13$	$0.05 \times 0.07 \times 0.12$	$0.02 \times 0.04 \times 0.07$
$2\theta$ range for data collection /°	4.92 to 59.286	5.18 to 59.05	4.694 to 58.968
Reflections collected	11726	13437	18053
Independent reflections	$5051 [R_{int} = 0.0209]$	$5805 [R_{int} = 0.0307]$	$5844 [R_{int} = 0.0550]$
Data/restraints/parameters	5051/0/262	5805/0/307	5844/0/316
Goodness-of-fit on $F^2$	1.034	1.075	1.040
Final <i>R</i> indices $[I > 2\sigma(I)]$	$R_1 = 0.0320, wR_2 = 0.0676$	$R_1 = 0.0492, wR_2 = 0.1224$	$R_1 = 0.0452, wR_2 = 0.0700$
Final <i>R</i> indices [all data]	$R_1 = 0.0471, wR_2 = 0.0742$	$R_1 = 0.0678, wR_2 = 0.1327$	$R_1 = 0.0850, wR_2 = 0.0802$
Largest difference peak/hole /e·Å <sup>-3</sup>	0.28/-0.36	1.46/-1.21	0.79/-0.96

[AuCl{4-ClC<sub>6</sub>H<sub>4</sub>C(O)CHAsPh<sub>3</sub>]] (3a): The product was isolated in 28% yield as a colorless solid. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>):  $\delta$  = 5.17 (s, 1 H, CH), 7.40 (d, *J* = 8.6 Hz, 2 H, C<sub>6</sub>H<sub>4</sub>), 7.57 (t, *J* = 7.5 Hz, 6 H, *m*-Ph<sub>3</sub>As), 7.64–7.69 (m, 3 H, *p*-Ph<sub>3</sub>As), 7.79 (dd, *J* = 8.2, 1.1 Hz, 6 H, *o*-Ph<sub>3</sub>As), 8.12 (d, *J* = 8.6 Hz, 2 H, C<sub>6</sub>H<sub>4</sub>). The material was not soluble enough to obtain a meaningful <sup>13</sup>C NMR spectrum. **IR** (ATR):  $\tilde{\nu} = 1622 \text{ cm}^{-1} \text{ v}(\text{CO}).$ 

[AuCl{4-O<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>C(O)CHAsPh<sub>3</sub>]] (3b): The product was isolated in 64% yield as a colorless solid. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>):  $\delta$  = 5.08 (s, 1 H, CH), 7.55–7.62 (m, 6 H, *m*-Ph<sub>3</sub>As), 7.69–7.75 (m, 3 H, *p*-Ph<sub>3</sub>As), 7.78–7.90 (m, 6 H, *o*-Ph<sub>3</sub>As), 8.25 (d, *J* = 8.8 Hz, 2 H, C<sub>6</sub>H<sub>4</sub>), 8.32 (d, *J* = 8.8 Hz, 2 H, C<sub>6</sub>H<sub>4</sub>). <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>):  $\delta$  = 59.94 (CH), 123.12 (C<sub>6</sub>H<sub>4</sub>), 127.78 (C<sub>6</sub>H<sub>4</sub>), 128.04 (*ipso*-Ph<sub>3</sub>As), 129.64 (*m*-Ph<sub>3</sub>As), 132.03 (*p*-Ph<sub>3</sub>As), 132.43 (*o*-Ph<sub>3</sub>As), 146.56 (C<sub>6</sub>H<sub>4</sub>), 147.96 (C<sub>6</sub>H<sub>4</sub>), 179.01 (CO). **IR** (ATR):  $\tilde{v}$  = 1627 cm<sup>-1</sup> v(CO). X-ray quality crystals were obtained by vapor diffusion using a combination of CH<sub>2</sub>Cl<sub>2</sub> and cyclopentane.

[AuCl{4-PhC<sub>6</sub>H<sub>4</sub>C(O)CHAsPh<sub>3</sub>]] (3c): The product was isolated in 74% yield as a colorless solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 5.30 (s, 1 H, CH), 7.41 (t, *J* = 7.3 Hz, 1 H, *p*-Ph), 7.48 (t, *J* = 7.5 Hz, 2 H, *m*-Ph), 7.57 (t, *J* = 7.5 Hz, 6 H, *m*-Ph<sub>3</sub>As), 7.60–7.70 (m,7 H, *o*-Ph, *p*-Ph<sub>3</sub>As, C<sub>6</sub>H<sub>4</sub>), 7.82 (d, *J* = 7.1 Hz, 6 H, *o*-Ph<sub>3</sub>As), 8.25 (d, *J* = 8.4 Hz, 2 H, C<sub>6</sub>H<sub>4</sub>). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>):  $\delta$  = 39.88 (CH), 126.53 (*ipso*-Ph<sub>3</sub>As), 127.10 (*o*-Ph), 127.28 (C<sub>6</sub>H<sub>4</sub>), 128.13 (*p*-Ph), 128.90 (*m*-Ph), 129.22 (C<sub>6</sub>H<sub>4</sub>), 130.01 (*m*-Ph<sub>3</sub>As), 132.76 (*p*-Ph<sub>3</sub>As), 132.85 (*o*-Ph<sub>3</sub>As), 134.72 (*ipso*-Ph), 139.99 (C<sub>6</sub>H<sub>4</sub>), 145.70 (C<sub>6</sub>H<sub>4</sub>), 195.69 (CO). **IR** (ATR):  $\tilde{v}$  = 1615 cm<sup>-1</sup> v(CO).

X-ray Crystallography: Diffraction data was collected at 150 K (2b, 3b) or room temperature (2a) using a Rigaku Oxford Diffraction Gemini Ultra diffractometer, equipped with an EOS CCD area detector and a four-circle kappa goniometer. Data integration, scaling and empirical absorption correction was carried out using the CrysAlis Pro program package.<sup>[17]</sup> The structures were solved using SHELXT<sup>[18]</sup> and refined with SHELXL<sup>[19]</sup> operated through the Olex2 interface.<sup>[20]</sup> Crystallographic and refinement details are collected in Table 2. During refinement of the structure **3b** it became apparent that the Au–Cl unit is disordered over two positions, which was best modeled with a 50:50 occupancy for each gold and chloride atom. In addition, there was evidence for highly disordered residual solvent molecules, for which we were unable to develop a suitable model. The data was therefore subjected to the Solvent Mask procedure implemented in Olex2.<sup>[20]</sup>

Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC, 12 Union Road, Cambridge CB21EZ, UK. Copies of the data can be obtained free of charge on quoting the depository numbers CCDC-1964292 (2a), CCDC-1971090 (2b), and CCDC-1964291 (3b) (Fax: +44-1223-336-033; E-Mail: deposit@ccdc.cam.ac.uk, http://www.ccdc.cam.ac.uk)

**Supporting Information** (see footnote on the first page of this article): Crystallographic details and copies of NMR spectra.

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