Crystal Structures of the Gold(I) Phosphinine Complexes $[AuCl(C_5H_2P\text{-}2,6\text{-}Me_2\text{-}4\text{-}Ph)]$ and $[AuCl(C_5H_2P\text{-}2,4,6\text{-}Ph_3)]$

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The gold(I) phosphinine complexes $[AuCl(C_5H_2P\text{-}2,6\text{-}Me_2\text{-}4\text{-}Ph)]$ and $[AuCl(C_5H_2P\text{-}2,4,6\text{-}Ph_3)]$ were prepared and structurally characterised by single-crystal X-ray diffraction studies. In the former case, individual molecules are aggregated in the crystal as crossed dimers with an Au···Au distance of 3.60 Å, compatible with a weak aurophilic interaction. In the latter case, intermolecular Au···π interactions involving the phosphinine ring are observed with Au···C distances in the range from *ca.* 3.32 to 3.44 Å, which make $[AuCl(C_5H_2P\text{-}2,4,6\text{-}Ph_3)]$ the first structurally characterised example of intermolecular Au···π interactions involving a heteroarene.

Key words: Aurophilicity, Crystal Structure, Gold, Gold-π Interaction, Phosphinine

Introduction

λ^3-Phosphinines (phosphabenzenes) were introduced more than four decades ago by Märkl [1] and Ashe [2]. Their recent rapid development from laboratory curiosities to important ligands in homogeneous transition metal catalysis [3 – 7] was triggered by seminal work published by the group of Zenneck [8] and by Breit [9] in 1996. The first transition metal complexes containing phosphinine ligands were already described in the early 1970s by the groups of Nöth [10 – 13], Fraser [14], Schmidbaur [15], and Dimroth [16]. Single-crystal X-ray diffraction studies performed by Vahrenkamp and Nöth for the metal carbonyl complexes $[Cr(\kappa P\text{-}C_5H_2P\text{-}2,4,6\text{-}Ph_3)(CO)_5]$ [11] and $[Cr(\eta^6\text{-}C_5H_2P\text{-}2,4,6\text{-}Ph_3)(CO)_3]$ [12] revealed that phosphinines can coordinate *via* their P lone pair and also *via* their π system. Homologous molybdenum and tungsten pentacarbonyl complexes were structurally characterised by the groups of Ashe [17] and Mathey [18]. This development culminated in the synthesis and structural characterisation of $[M(\kappa P\text{-}C_5H_5P)_6]$ (M = Cr, Mo, W), the phosphinine analogue of the group 6 metal hexacarbonyl complexes, by Elschenbroich and coworkers [19, 20]. The first structurally characterised κP-phosphinine complexes with transition metals not belonging to group 6 were published in the early 1990s [21, 22]. However, in these cases phosphinine analogues of 2,2′-biypridine were used instead of simple monodentate ligands. It was only in 1999 that the groups of Elschenbroich and of Mathey and Le Floch, respectively, reported *cis*-$[PtCl_2(C_5H_2P\text{-}2,6\text{-}Me_2\text{-}4\text{-}Ph)_2]$ [23] and $[AuCl\{C_5H_2P\text{-}2,6\text{-}(SiMe_3)_2\text{-}4\text{-}Ph\}]$ [24] as the first examples of structurally characterised non-group 6 metal complexes containing a simple, unfunctionalised κP-phosphinine ligand. Note that even the first structurally characterised *f*-block metal η^6-phosphinine complex was published earlier [25]. We here report the crystal structures of the phosphinine gold complexes $[AuCl(C_5H_2P\text{-}2,6\text{-}Me_2\text{-}4\text{-}Ph)]$ and $[AuCl(C_5H_2P\text{-}2,4,6\text{-}Ph_3)]$. While the latter compound was already described by Schmidbaur and coworkers four decades ago [15], the former one has not been reported before. We are aware of only three structurally characterised complexes of the type [AuX(phos)] (X = halogenido ligand, phos = κP-phosphinine ligand) to date, *viz.* $[AuCl\{C_5H_2P\text{-}2,6\text{-}(SiMe_3)_2\text{-}4\text{-}Ph\}]$ [24], $[AuCl\{C_5H_2P\text{-}2,4\text{-}Ph_2\text{-}6\text{-}[C_6H_3\text{-}3,4\text{-}(OMe)_2]\}]$ [26] and $[AuCl(C_5H_2P\text{-}2,4,6\text{-}t\text{Bu})]$ [27].

Results and Discussion

Schmidbaur and coworkers obtained [AuCl(C_5H_2P-2,4,6-Ph_3)] from the very labile carbonyl complex [AuCl(CO)] and C_5H_2P-2,4,6-Ph_3 in benzene solvent. We have modified this procedure by using the readily available tetrahydrothiophene (THT) complex [AuCl(THT)] in dichloromethane. The new compound [AuCl(C_5H_2P-2,6-Me_2-4-Ph)] was prepared analogously. Single crystals suitable for an X-ray diffraction study were obtained in each case by layering a dichloromethane solution of the complex with hexane. The molecular structures are shown in Figs. 1 and 2.

The Au atom of [AuCl(C_5H_2P-2,6-Me_2-4-Ph)] is in the quasilinear environment typically observed for dicoordinate complexes of the type [AuX(L)]. The Cl–Au–P angle has a value of 175.70(10)°. The Au–Cl and Au–P bond lengths of 2.298(3) and 2.234(3) Å, respectively, are marginally longer than those reported by Mathey [24], Gudat [26] and Nixon [27] for the three structurally investigated complexes of the type [AuCl(phos)], where Au-Cl Au–P bond lengths in the narrow range from 2.27 to 2.28 Å and 2.21 to 2.22 Å, respectively, have been determined. The P–C bond lengths of 1.681(12) and 1.723(10) Å are indistinguishable within experimental error and very similar to the corresponding bond lengths reported for the three previously investigated cases. Neighbouring molecules in the crystal exhibit intermolecular Au···Au distances of 3.60 Å, compatible with weak aurophilic interactions [28–32]. This distance is identical with the traditional contact limit for significant aurophilic interactions [33]. However, recent experimental work has demonstrated that aurophilic interactions may be structurally relevant up to Au···Au distances of 4.0 Å [34], which is in accord with earlier theoretical predictions [35]. The aurophilic aggregation usually observed in the solid state for linear dicoordinate gold(I) complexes can give rise to three principal structural motifs, *viz.* a parallel, an antiparallel, and a crossed arrangement of neighbouring molecules. A recent CSD analysis [36] confirmed the result of an earlier study [37] that Au···Au distances are on average shortest for the crossed arrangement. This is perfectly plausible, since at a given Au···Au distance steric repulsions between the ligands of neighbouring molecules will be least for a staggered orientation, which corresponds to a crossed arrangement with a torsion angle of 90°. In the present case, a crossed arrangement is indeed observed, with a Cl–Au–Au–Cl torsion angle of *ca.* 101.3°. This is strongly reminiscent of the structures of the gold phosphane complexes [AuX(PMe_2Ph)] (X=Cl, Br, I), where X–Au–Au–X torsion angles between *ca.* 105.9° and 115.9° were found for the dimeric aggregates in the crystal [38]. In the same vein, a Cl–Au–Au–Cl torsion angle of *ca.* 103.1° was reported for [AuCl{P($CH=CH_2$)$_3$}] [39]. In the case of [AuCl{C_5H_2P-2,6-($SiMe_3$)$_2$-4-Ph}], however, neighbouring molecules are paired in an antiparallel fashion, resulting in Au···Au distances of only 3.37 Å [24]. An antiparallel arrangement of

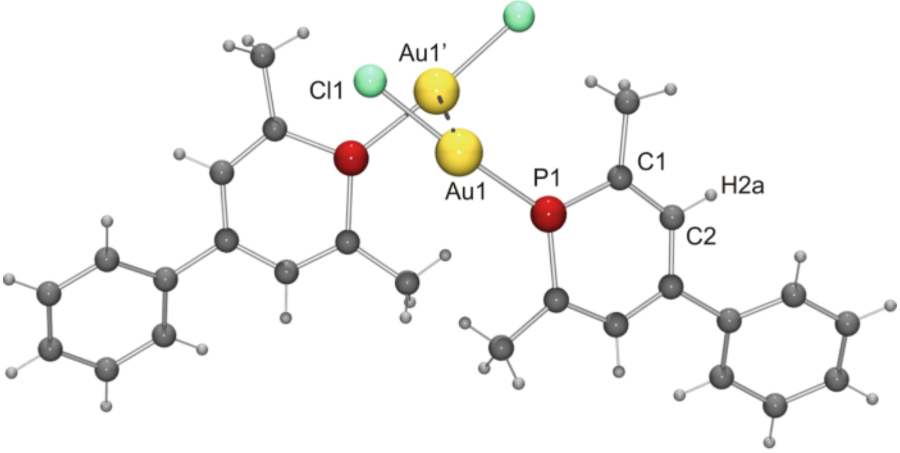

Fig. 1 (color online). Molecular structure and aggregation of [AuCl(C_5H_2P-2,6-Me_2-4-Ph)] in the crystal. The Au···Au contact (3.60 Å) is indicated by a dotted line.

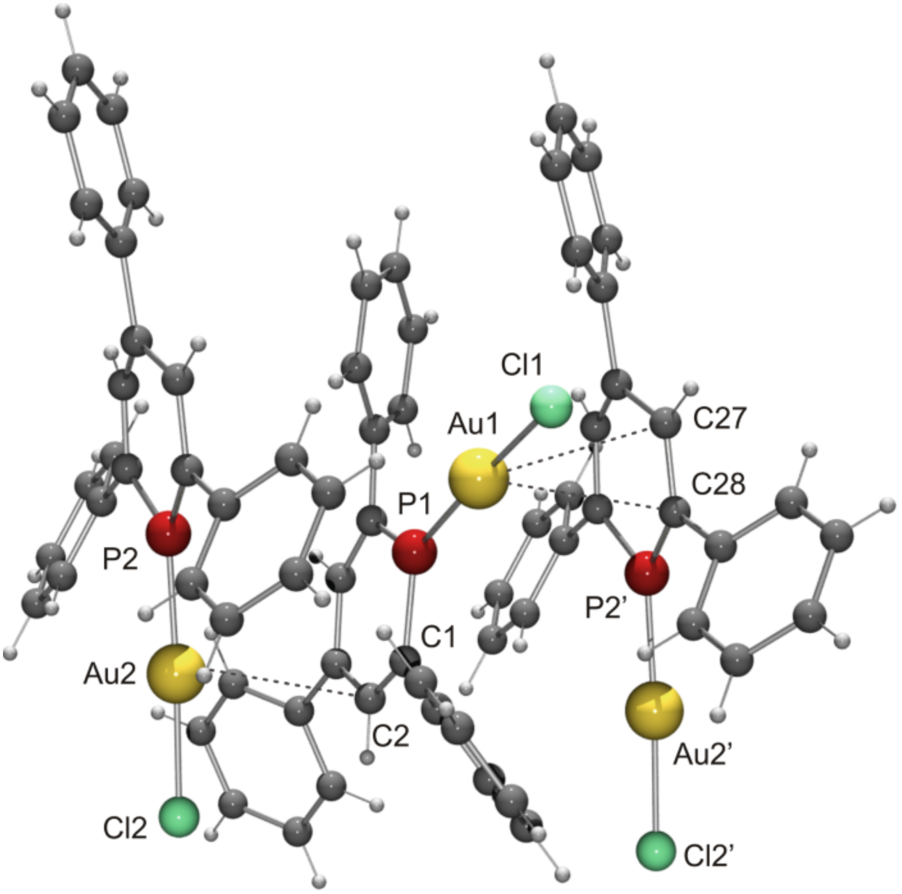

Fig. 2 (color online). Molecular structure and aggregation of [AuCl(C_5H_2P-2,4,6-Ph_3)] (two independent molecules) in the crystal. Intermolecular Au···π interactions are indicated by dotted lines.

[AuX(L)] units is commonly observed with lean rigid rod-type ligands L such as isocyanides, where the aggregational motif was shown to originate principally from the dipole-dipole interaction [40]. In the case of phosphane ligands only primary [41] and secondary phosphanes [42] appear to be sufficiently lean for this antiparallel arrangement.

Due to the low resolution of the data for [AuCl(C_5H_2P-2,4,6-Ph_3)], a detailed discussion of structural parameters is meaningful only for the heavy atoms. The asymmetric unit contains two crystallographically independent molecules, whose bond parameters are indistinguishable within experimental error. The Au atom is in a quasilinear dicoordinate environment (Cl–Au–P *ca.* 177°) with Au–Cl and Au–P bond lengths of *ca.* 2.28 and 2.22 Å, respectively. Not unexpectedly, these values are very similar to those reported by Gudat and coworkers for the closely related [AuCl{C_5H_2P-2,4-Ph_2-6-[C_6H_3-3,4-$(OMe)_2$]}] [26], which differs from [AuCl(C_5H_2P-2,4,6-Ph_3)] just by the presence of two OMe substituents in one of the three phenyl groups. However, the intermolecular Au···Cl interactions reported for the methoxy-substituted compound are absent in the present case. Instead, we note intermolecular Au···π interactions with the phosphinine ring. Au···arene interactions are of enormous current interest [43 – 45], especially with a view to the highly dynamic field of gold catalysis [46 – 62]. Previous work has mainly focussed on intramolecular Au···arene interactions supported by tailor-made aryl-substituted phosphane ligands in complexes of the type [AuX(PR_3)] [43, 45, 63 – 67]. Au···C_{arene} distances as low as 2.96 Å [66] have been realised with such systems. In passing we

Table 1. Crystal structure data for $[AuCl(C_5H_2P\text{-}2,6\text{-}Me_2\text{-}4\text{-}Ph)]$ and $[AuCl(C_5H_2P\text{-}2,4,6\text{-}Ph_3)]$.

	$[AuCl(C_5H_2P\text{-}2,6\text{-}Me_2\text{-}4\text{-}Ph)]$	$[AuCl(C_5H_2P\text{-}2,4,6\text{-}Ph_3)]$
Crystal habit	yellow plate	yellow needle
Crystal size, mm^3	$0.20 \times 0.16 \times 0.02$	$0.07 \times 0.04 \times 0.02$
Empirical formula	$C_{13}H_{13}AuClP$	$C_{23}H_{17}AuClP$
M_r	432.62	556.75
Crystal system	orthorhombic	orthorhombic
Space group (no.)	*Pbca* (no. 61)	$P2_12_12_1$ (no. 19)
a, Å	7.1884(4)	7.8440(9)
b, Å	15.5674(10)	20.317(3)
c, Å	22.725(2)	24.843(4)
V, Å^3	2543.0(3)	3959.3(9)
Z	8	8
$D_{calcd.}$, g cm^{-3}	2.26	1.87
μ, mm^{-1}	11.9	7.7
$F(000)$, e	1616	2128
No. of frames measured	98	116
θ range, deg	2.77 to 25.00	1.29 to 25.00
hkl range	$-8 \le h \le +8$ $-16 \le k \le +18$ $-23 \le l \le 26$	$-9 \le h \le +8$ $-24 \le k \le +21$ $-28 \le l \le +29$
Refl. measured / unique / R_{int}	8262 / 2240 / 0.0955	16040 / 6976 / 0.2275
Refl. observed $[I > 2\sigma(I)]$	1550	2416
Data / restraints / parameters	2240 / 0 / 147	6976 / 0 / 237
Final $R/Rw[I > 2\sigma(I)]$	0.0453 / 0.1305	0.0783 / 0.1277
Flack parameter x	–	$-0.04(3)$
$\Delta\rho_{fin}$ (max / min), e Å^{-3}	2.62 / -2.47	1.14 / -2.49

note that much shorter such distances of only *ca.* 2.33 Å were observed by Bertrand and coworkers for the cation of $[Au(CAAC)(\eta^2\text{-toluene})]$ $[B(C_6F_5)_4]$, which contains a bulky cyclic (alkyl)(amino)carbene (CAAC) ligand [44]. However, this is not particularly surprising, since in this case the metal-ligand fragment which interacts with the arene π system contains *mono*coordinate Au^I and is cationic, while in the other cases this interaction occurs with a *di*coordinate, and electroneutral, fragment. As mentioned above, $[AuCl(C_5H_2P\text{-}2,4,6\text{-}Ph_3)]$ exhibits intermolecular, instead of intramolecular, Au···arene interactions, giving rise to an η^1-type motif for Au2 and C2 with an interatomic distance of 3.32(3) Å and to an η^2-type motif for Au1 and C27/C28 with interatomic distances of 3.39(3) and 3.44(3) Å, respectively. These distances are shorter than the sum of the estimated van der Waals radii of C and Au. For the former, the value of 1.70 Å given already by Bondi [68] is still commonly accepted [69], although in his very recent cartography of the van der Waals territories Alvarez comes to the slightly higher value of 1.77 Å [70]. The van der Waals radius of gold has been a notoriously difficult and contentious issue. In 2007 Datta and coworkers [71] confirmed the value of 2.1 Å given earlier by Batsanov [72]. An almost identical value of 2.14 Å was published in 2009 by Hu *et al.* [73]. In 2010, Flower and coworkers proposed a value of 2.0 Å [34]. The most recent values, published by Batsanov in 2011 [74] and by Alvarez in 2013 [70], differ considerably: 1.97 Å *vs.* 2.32 Å. We conclude that the sum of the van der Waals radii of carbon and gold can be safely assumed to be ≥ 3.7 Å.

The first crystallographically authenticated case of intermolecular Au···arene interactions was published in 1998 by Churakov *et al.*, who found Au···C_{arene} distances of *ca.* 3.35 and 3.56 Å in the crystal structure of $[AuX(PPh_3)]$ ($X = \kappa N$-2,3-dioxoindolinido) [75]. We are aware of only a single closely related report since then. Zhang and coworkers described the complex $[Au(py)\{PPh_2[N\textit{n}Pr(CH_2Anth)]\}](ClO_4)$ (py=pyridine, Anth=9-anthracenyl), whose tailor-made phosphane ligand gives rise to an intramolecular η^2-type interaction of the Au atom with the anthracenyl π system (Au···C_{arene} 3.02 and 3.16 Å). The cationic units are connected to stacks in the crystal by an additional intermolecular η^1-type interaction with an Au···C_{arene} distance of *ca.* 3.35 Å, similar to what we observe for the Au2···C2 interaction in the case of $[AuCl(C_5H_2P\text{-}2,4,6\text{-}Ph_3)]$. Finally, we note that this

λ^3-phosphinine complex is the first structurally characterised example of intermolecular Au···π interactions involving a heteroarene.

Experimental Section

NMR spectra were recorded with the following Varian spectrometers: NMRS-500 (500 MHz) and MR-400 (400 MHz). ^{31}P NMR data were collected by proton-decoupled methods. Chemical shifts (δ) are given in ppm and are referenced to the signal due to the residual protio impurities of the solvent used relative to tetramethylsilane for ^{1}H. ^{31}P chemical shifts were referenced to external Ph_3PO ($\delta = 23.7$ ppm) [76]. Coupling constants are given as absolute values in Hz. All preparations involving air-sensitive compounds were carried out under an atmosphere of dry nitrogen by using standard Schlenk techniques or in a conventional argon-filled glove box. Solvents and reagents were appropriately dried and purified by conventional methods and stored under inert gas atmosphere. Gold complexes were handled with exclusion of light. [AuCl(THT)] [77] and the phosphinines C_5H_2P-2,6-Me_2-4-Ph [78] and C_5H_2P-2,4,6-Ph_3 [78] were prepared according to published procedures. X-Ray crystal structure analyses: For each data collection a single crystal was mounted on a glass fibre, and all geometric and intensity data were taken from this sample. Diffraction experiments were carried out at $T = 123\,(2)$ K using MoK_α radiation ($\lambda = 0.71073$ Å) on a Stoe IPDS2 diffractometer equipped with a 2-circle goniometer and an area detector. Absorption correction was done by integration using X-RED [79]. The data sets were corrected for Lorentz and polarisation effects. The structures were solved by Direct Methods (SHELXS-97 [80, 81]) and refined using alternating cycles of least-squares refinements against F^2 (SHELXL-97 [82, 83]). All non-H atoms of [AuCl(C_5H_2P-2,6-Me_2-4-Ph)] were found in difference Fourier maps and were refined with anisotropic displacement parameters. Due to a very low data / parameter ratio many carbon atoms of [AuCl(C_5H_2P-2,4,6-Ph_3)] could not be refined anisotropically. All H atoms were placed in constrained positions according to the riding model with the 1.2 fold isotropic displacement parameters. Pertinent crystallographic data are collected in Table 1. Graphical representations were made using ORTEP-3 WIN [84, 85].

CCDC 943924-943925 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

[AuCl(C_5H_2P-2,6-Me_2-4-Ph)]

A solution of [AuCl(THT)] (16 mg, 50 μmol) in dichloromethane (2 mL) was added to a stirred solution of C_5H_2P-2,6-Me_2-4-Ph (10 mg, 50 μmol) in dichloromethane (3 mL) at -40 °C. The stirred mixture was allowed to warm to room temperature over the course of 1 h. The volume of the solution was reduced to *ca.* 1 mL *in vacuo*. Layering of the concentrated solution with hexane afforded the product as pale-yellow crystals. Yield 12 mg (55 %). – ^{1}H NMR (CD_2Cl_2): $\delta = 2.75$ (d, $^3J_{PH} = 22.6$ Hz, 6 H, Me), 7.50 – 7.60 (m, 5 H, Ph), 8.15 (d, $^3J_{PH} = 24.3$ Hz, 2 H, C_5H_2P). – ^{31}P NMR (CD_2Cl_2): $\delta = 165.1$.

[AuCl(C_5H_2P-2,4,6-Ph_3)]

The preparation of this compound was performed in analogy to [AuCl(C_5H_2P-2,6-Me_2-4-Ph)], affording the product in 59 % yield. – ^{1}H NMR (CD_2Cl_2): $\delta = 7.50$ – 7.60 (m, 10 H, Ph), 7.70 – 7.80 (m, 5 H, Ph), 8.50 (d, $^3J_{PH} = 22.8$ Hz, 2 H, C_5H_2P). – ^{31}P NMR (CD_2Cl_2): $\delta = 154.0$.

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