Gold(I) Complexes of Ketiminophosphanes and -phosphane Sulfides

Wolfgang Schneider, Andreas Bauer, Annette Schier, and Hubert Schmidbaur*

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

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The reactions of chloro(dimethyl sulfide)gold(I) with equivalent quantities of the ketiminophosphane diphenyl(diphenylmethyleneamino)phosphane (**1a**) or its sulfide (**1aS**) lead to high yields of stable, crystalline 1:1 complexes with AuCl units attached to the phosphorus and sulfur atom, respectively. Tris(diphenylmethyleneamino)phosphane (**1c**) gives the related complex $(Ph_2C{=}N)_3PAuCl$ with the gold atom also selectively *P*-bound. Bis(diphenylmethyleneamino)phenylphosphane (**1b**) could not be used because of its limited stability. Single-crystal X-ray diffraction studies have shown that there is no auxiliary coordination of the metal center by the imino functions of the ligands. The geometry of the P/S–Au–Cl moieties deviates only very slightly from linearity. The angle at the sulfur atom in $(Ph_2C{=}N)Ph_2PSAuCl$ is very small [94.30(3)°], but despite of the resulting rather open coordination there are no discernible intra- or intermolecular contacts in the lattice. Such contacts are also absent with $(Ph_2C{=}N)Ph_2PAuCl$ and $(Ph_2C{=}N)_3PAuCl$ owing to the bulk of the ligands. The 1:1 complexes do not react with an excess of $(Me_2S)AuCl$. This finding, and the molecular structures of the 1:1 complexes, show very consistently that both phosphane and sulfide donors are far superior as ligands for gold(I) as compared to ketimine donor molecules.

Introduction

In a few very recent studies it has been demonstrated that simple ketimines can function as independent ligands for gold(I) even in homoleptic complexes.[1][2] For the products the reduced shielding of the metal centers at three-coordinate nitrogen atoms gives rise to interesting supramolecular chemistry, in favourable cases with concerted auriophilic and hydrogen bonding. Polynuclear aggregates arise from the intimate metal-metal interactions at short Au–Au distances as the underlying principle of supramolecular bonding.[3][4]

In this context information was required on the role of the imino group in mixed donor ligands also containing other donor sites. Because of the paramount importance of phosphane ligands in gold chemistry, a study of ketiminophosphanes was therefore initiated, where phosphane and ketimine donor centers are competing for gold(I) centers. (Diphenylmethyleneamino)diphenylphosphane (**1a**)[5] and tris(diphenylmethyleneamino)phosphane (**1c**)[6] were chosen as prototype ligands in this study. All attempts to employ the missing link in this series, bis(diphenylmethyleneamino)phenylphosphane (**1b**), were unsuccessful because of the limited stability of this compound. The investigations were extended to include the phosphane sulfide **1aS**.

$Ph_2PN{=}CPh_2$ **1a** $Ph_2P(S)N{=}CPh_2$ **1aS**

$PhP(N{=}CPh_2)_2$ **1b**

$P(N{=}CPh_2)_3$ **1c**

Synthesis, Properties and Spectroscopic Data of the Complexes

The reactions of equimolar quantities of the ligands **1a**, **1c**, and **1aS** with chloro(dimethyl sulfide)gold(I) in dichloromethane at ambient temperature afford high yields of the corresponding 1:1 complexes (**1aAuCl**, **1cAuCl**, and **1aSAuCl**). Dimethyl sulfide is liberated in the process.

$$Ph_2PN{=}CPh_2 + (Me_2S)AuCl \longrightarrow Me_2S + (ClAu)Ph_2PN{=}CPh_2$$

1aAuCl

$$P(N{=}PPh_2)_3 + (Me_2S)AuCl \longrightarrow Me_2S + (ClAu)P(N{=}CPh_2)_3$$

1cAuCl

$$Ph_2P(S)N{=}CPh_2 + (Me_2S)AuCl \longrightarrow Me_2S + (ClAu)SPPh_2(N{=}CPh_2)$$

1aSAuCl

Reactions with more than one equivalent of $(Me_2S)AuCl$ did not lead to di- or trinuclear complexes. Only the 1:1 addition compounds could be isolated and the excess of $(Me_2S)AuCl$ was recovered or detected unchanged in the reaction mixtures by analytical methods.

The products are colourless (**1aAuCl**, **1aSAuCl**) to pale yellow (**1cAuCl**), crystalline solids with high melting points [**1aAuCl**: 272°C; **1cAuCl**: 264°C; **1aSAuCl**: 174°C]. Contrary to the free ligands, all three complexes are stable to air and moisture. The composition has been confirmed by elemental analysis. The IR spectra (KBr) show imino stretching frequencies at $\tilde{\nu}$ = 1601 (**1aAuCl**), 1608 (**1aSAuCl**), and 1608 cm^{-1} (**1cAuCl**), indicating little

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change in the bonding characteristics of the $Ph_2C{=}N-$ units upon complexation.

The ^{31}P NMR spectra (in $CDCl_3$) are indicative of a regioselective coordination of the AuCl units to the phosphorus (**1a**, **1c**) and sulfur atoms (**1aS**), respectively. For the former, the ^{31}P resonances appear as low as $\delta = 55.4$ (**1aAuCl**) and $\delta = 70.3$ (**1cAuCl**), corresponding to differences $\Delta\delta = 18.9$ and 15.2 as compared to the data for the free ligands. For **1aSAuCl** ($\delta = 45.2$) the $\Delta\delta$ value is smaller (2.4) but still significant in combination with the IR spectra.

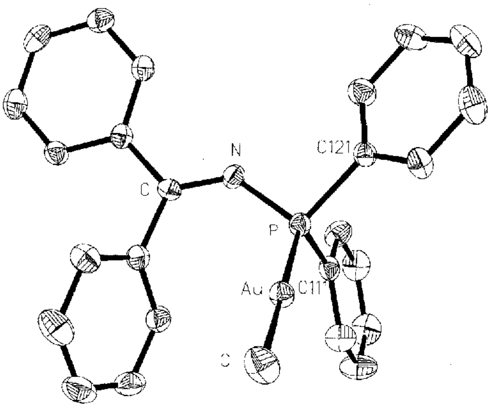
The ^{1}H and ^{13}C resonances of the phenyl and ketimino groups are less affected by the gold coordination. Details are given in the Experimental Section.

Molecular Structures

Crystals of compound **1aAuCl** are monoclinic with $Z = 4$ formula units in the unit cell. The lattice contains monomeric units with no sub-van-der-Waals contacts. Intermolecular interactions of the metal atoms are clearly prevented by the bulky substituents of the ligand.

The AuCl component is coordinated to the phosphorus atom of the ligand to give a quasi-linear unit P−Au−Cl [173.85(4)°]. The short Au−P distance [2.231(1) Å] indicates strong metal-to-ligand bonding. There is no evidence even for distant internal coordination of the imino group to the gold atom; on the contrary, the nitrogen donor site of the $Ph_2C{=}N-$ unit is in fact oriented away from the metal center (Figure 1).

Figure 1. Molecular structure of **1aAuCl** (ORTEP, 50% probability ellipsoids, phenyl hydrogen atoms are omitted)[a]

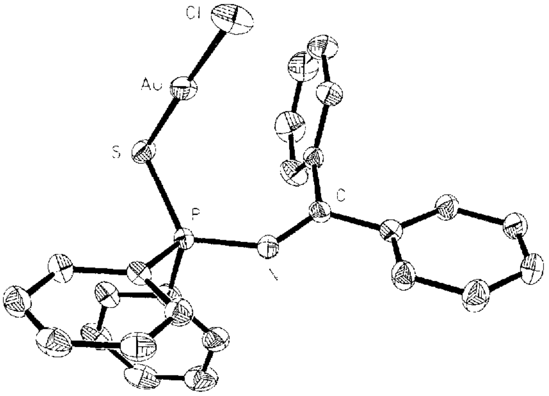


[a] Selected bond lengths [Å] and angles [°]: Au−P 2.2308(10), Au−Cl 2.2879(10), P−N 1.694(3), N−C 1.270(5); P−Au−Cl 173.85(4), N−P−Au 118.10(12), C−N−P 126.5(3).

The angle at the nitrogen atom of the ligand P−N=C [126.5(3)°] is slightly larger than the 120° standard for sp^2 nitrogen, and the C=N and N−P bond lengths indicate multiple-bond character for both bonds (Caption to Figure 1).

The structure of the corresponding phosphane sulfide complex **1aSAuCl** (monoclinic, $Z = 2$) has a similar ligand geometry, except for the insertion of the sulfur atom into the gold−phosphorus bond. This sulfur atom is becoming the sole donor center for the gold atom in this compound, with an Au−S−P angle of only 94.30(3)°. The S−Au−Cl angle is close to linear [178.14(3)°], the C=N−P angle is widened to 131.2(2)°, and the P−N bond shortened to 1.647(2) Å as compared to **1aAuCl**. Both changes are associated with the oxydation of the phosphorus atom by the strongly electronegative sulfur atom. The P−S and Au−S distances compare well with those of other phosphane sulfide complexes of gold(I)[7] (Figure 2).

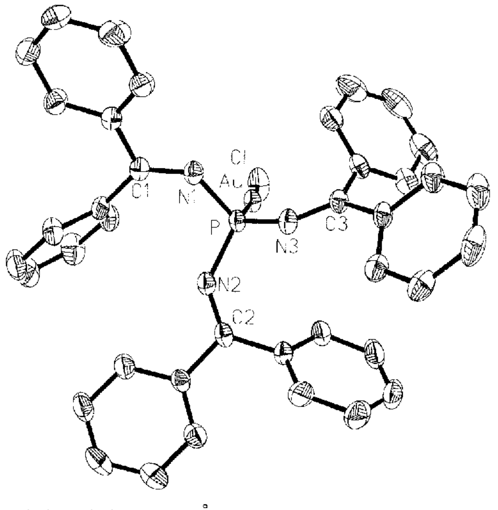
Figure 2. Molecular structure of **1aSAuCl** (ORTEP, 50% probability ellipsoids, phenyl hydrogen atoms are omitted)[a]



[a] Selected bond lengths [Å] and angles [°]: Au−Cl 2.2707(8), Au−S 2.2784(8), S−P 2.0137(10), P−N 1.647(2), N−C 1.293(3); Cl−Au−S 178.14(3), P−S−Au 94.30(3), N−P−S 121.39(9), C−N−P 131.2(2).

Compound **1cAuCl** also crystallizes monoclinically with $Z = 2$ formula units in the unit cell. In the lattice the molecules are monomeric. The AuCl unit is attached to the phosphorus center of the ligand (Figure 3). The P−Au−Cl moiety is almost linear [174.39(3)°] with a P−Au bond length of 2.2226(7) Å, very similar to the data for **1aAuCl** (above).

Figure 3. Molecular structure of **1cAuCl** (ORTEP, 50% probability ellipsoids, phenyl hydrogen atoms are omitted)[a]



[a] Selected bond lenghts [Å] and angles [°]: Au−P 2.2226(7), Au−Cl 2.2846(7), P−N1 1.671(2), P−N2 1.662(2), P−N3 1.681(2), N1−C1 1.284(3), N2−C2 1.275(3), N3−C3 1.286(3); P−Au−Cl 174.39(3), N2−P−N1 107.38(11), N2−P−N3 104.95(11), N1−P−N3 98.95(11), N2−P−Au 109.87(8), N1−P−Au 110.12(8), N3−P−Au 124.18(8).

The geometry of the ligand **1c** in **1cAuCl** is very distorted and far from the maximum possible threefold symmetry. The N–P–N angles vary between 98.9(1) and 107.4(1)° and the C=N–P angles between 128.7(2) and 134.3(2)°. The latter are thus not very different from those in **1aAuCl** and **1aSAuCl** (above).

It appears that the C=N–P units are rather flexible and that their geometry responds quite noticeably even to minor changes within the molecule and in the packing. None of the imino nitrogen atoms directs its lone pair of electrons towards the metal atom which indicates that there is no affinity for further coordination of the gold atom.

Conclusions

The experiments carried out in this study have shown that the phosphorus atoms of ketiminophosphanes and the sulfur atoms of the corresponding ketiminophosphane sulfides are superior donors for gold(I) as compared to the nitrogen atoms of neighbouring ketimino groups. The prototype ligands employed (**1a**, **1c**, **1aS**) and AuCl afford only 1:1 complexes with linearly two-coordinate metal atoms. The ketimino groups have a flexible geometry which is readily adjusted to changes in the substitution pattern or to the packing of the molecules. No 1:2 or 1:3 complexes are formed with an excess of the (Me_2S)AuCl reagent, and in the 1:1 complexes there is no conspicuous approach of the imino group towards the metal center which would indicate weak chelation. In all three lattices no sub-van-der-Waals intermolecular contacts are observed. Au–Au contacts are prevented by the bulk of the ligands.

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Experimental Section

All experiments were carried out under dry, purified nitrogen. Glassware was dried and filled with nitrogen, solvents were distilled and kept under nitrogen. – NMR: Jeol GX 400, TMS as internal standard. – IR: Perkin-Elmer (type 1600 series FT-IR). – Microanalyses: In-house analyzers (by combustion and atomic absorption spectroscopy). Starting materials were either commercially available or were prepared according to literature procedures: ($Ph_2C{=}N$)Ph_2P[5], ($Ph_2C{=}N$)$Ph_2P{=}S$[5], ($Ph_2C{=}N$)$_3P$[6], (Me_2S)AuCl[8].

[(Diphenylmethyleneamino)diphenylphosphane]gold(I) Chloride (**1aAuCl**): To a solution of (diphenylmethyleneamino)diphenylphosphane (280 mg, 0.77 mmol) in dichloromethane (5 ml) was added (Me_2S)AuCl (226 mg, 0.77 mmol). After stirring for 1 h, the solvent was removed and the yellow solid taken up again in dichloromethane. By cautious layering with pentane, 412 mg of colourless crystals were obtained after several days (90%), m. p. 272°C. – ^1H NMR ($CDCl_3$, room temp.): δ = 7.37–7.55 (m, Ph_2C), 7.78–7.86 (m, Ph_2P). – $^{13}C\{^1H\}$ NMR ($CDCl_3$, room

Table 1. Crystallographic data of compounds **1aAuCl**, **1aSAuCl** and **1cAuCl**

Compound	**1aAuCl**	**1aSAuCl**	**1cAuCl**
empirical formula	$C_{25}H_{20}AuClNP$	$C_{25}H_{20}AuClNPS$	$C_{39}H_{30}AuClN_3P$
formula weight	597.81	629.87	804.05
crystal system	monoclinic	monoclinic	monoclinic
space group (No.)	$P2_1/n$ (14)	$P2_1$ (4)	$P2_1$ (4)
a [Å]	12.610(1)	7.741(1)	11.691(1)
b [Å]	11.307(1)	16.020(1)	12.566(1)
c [Å]	15.272(2)	9.344(1)	11.947(1)
β [°]	101.23(1)	101.83(1)	110.86(1)
V [Å^3]	2135.8(4)	1134.1(2)	1640.1(2)
$\rho_{calcd.}$ [gcm^{-3}]	1.859	1.844	1.628
Z	4	2	2
$F(000)$ [c]	1152	608	792
λ(Mo-K_α) [Å]	0.71073	0.71073	0.71073
T [°C]	−75	−80	−74
diffractometer	Enraf Nonius CAD4	Enraf Nonius CAD4	Enraf Nonius CAD4
scan	$\omega/2\theta$	ω	ω/θ
hkl range	$-16 \leq h \leq 15, 0 \leq k \leq 14, 0 \leq l \leq 19$	$0 \leq h \leq 9, -20 \leq k \leq 20, -11 \leq l \leq 11$	$-14 \leq h \leq 13, -16 \leq k \leq 16, 0 \leq l \leq 15$
measured reflections	4794	5270	7336
unique reflections	4626	4917	7006
observed reflections [with $I \geq 2\sigma(I)$]	4604	4911	7002
R_{int}	0.0184	0.0136	0.0165
refined parameters	262	270	405
H atoms (found/calcd.)	0/20	0/20	0/30
absorption corr.	semi empirical	semi empirical	semi empirical
T_{min}/T_{max}	0.80/0.99	0.70/0.99	0.57/0.99
R based on (OMIT 4)[a]	0.0243	0.0144	0.0157
$wR2$[a]	0.0559	0.0346	0.0390
weighting scheme (l/k)[a]	0.0270/4.30	0.0173/0.65	0.0252/0.29
ρ_{fin}(max/min)[b] [eÅ^{-3}]	+0.517/−1.092	+0.301/−0.609	+0.986/−1.049

[a] $R = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$. – $wR2 = \{[\Sigma w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$. – $w = 1/2\sigma^2(F_o^2) + (lp)^2 + kp$, $p = (F_o^2 + 2F_c^2)/3$. – [b] Residual electron densities located at the gold atoms.

temp.): δ = 184.0 [d, ^{2}J(CP) = 2.8 Hz, N=C], 138.2 and 138.0 [s each, *ipso*-C (Ph_2C)], 131.8 [s, *para*-C (Ph_2C)], 128.9 [s, *ortho*-C (Ph_2C)], 128.6 [s, *meta*-C (Ph_2C)], 134.5 [d, ^{1}J(CP) = 72.7 Hz, *ipso*-C (Ph_2P)], 132.4 [d, ^{2}J(CP) = 15.4 Hz, *ortho*-C (Ph_2P)], 128.7 [d, ^{3}J(CP) = 12.1 Hz, *meta*-C (Ph_2P)], 131.7 [br. s, *para*-C (Ph_2P)]. – $^{31}P\{^{1}H\}$ NMR ($CDCl_3$, room temp.): δ = 55.4 (s, PAu). – IR (KBr): ṽ = 1601 cm^{-1} [ν(C=N)]. – $C_{25}H_{20}AuClNP$ (597.81): calcd. C 50.23, H 3.37, N 2.34; found C 50.12, H 3.36, N 2.27.

[(Diphenylmethyleneamino)diphenylphosphane sulfide]gold(I) Chloride (**1aSAuCl**): To a solution of (diphenylmethyleneamino)diphenylphosphane sulfide (195 mg, 0.49 mmol) in dichloromethane (5 ml) was added (Me_2S)AuCl (145 mg, 0.49 mmol) at room temp. After 1 h, the solvent was removed in vacuo and the pale yellow residue was taken up again in dichloromethane. The filtered solution was layered with pentane. After 24 h, colourless crystals (253 mg, 82%) were obtained, m. p. 174°C. – ^{1}H NMR ($CDCl_3$, room temp.): δ = 7.23–7.56 (m, Ph_2C), 7.88–7.96 (m, Ph_2P). – $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, room temp.): δ = 196.7 [d, ^{2}J(CP) = 9.9 Hz, N=C], 146.8 and 146.1 [s each, *ipso*-C (Ph_2C)], 142.6 [s, *para*-C (Ph_2C)], 140.0 [s, *ortho*-C (Ph_2C)], 138.4 [s, *meta*-C (Ph_2C)], 142.5 [d, ^{1}J(CP) = 106.9 Hz, *ipso*-C (Ph_2P)], 139.0 [d, ^{2}J(CP) = 13.2 Hz, *ortho*-C (Ph_2P)], 141.4 [d, ^{3}J(CP) = 11.0 Hz, *meta*-C (Ph_2P)], 142.8 [d, ^{4}J(CP) = 11.0 Hz, *para*-C (Ph_2P)]. – $^{31}P\{^{1}H\}$ NMR ($CDCl_3$, room temp.): δ = 45.2 (s, PAu). – IR (KBr): ṽ = 1608 cm^{-1} [ν(C=N)]. – $C_{25}H_{20}AuClNPS$ (629.87): calcd. C 47.67, H 3.20, N 2.22, S 5.09; found C 47.62, H 3.11, N 2.20, S 5.43.

[Tris(diphenylmethyleneamino)phosphane]gold(I) Chloride (**1cAuCl**): To a solution of (Me_2S)AuCl (291 mg, 0.51 mmol) in dichloromethane (15 ml) was slowly added a solution of $(Ph_2C=N)_3P$ (150 mg, 0.51 mmol) in dichloromethane (5 ml). The red colour of the solution changed to yellow. After 30 min, the solvent was removed in vacuo and the yellow residue taken up again in dichloromethane and layered with pentane (1:5). During one week, pale yellow crystals separated (410 mg, 95%), m. p. 264°C. – ^{1}H NMR ($CDCl_3$, room temp.): δ = 7.28–7.52 (m, Ph). – $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, room temp.): δ = 178.8 [d, ^{2}J(CP) = 2.8 Hz, N=C], 138.7 and 138.5 (s each, *ipso*-C), 131.3 (s, *para*-C), 129.7 (s, *ortho*-C), 128.2 (s, *meta*-C). – $^{31}P\{^{1}H\}$ NMR ($CDCl_3$, room temp.): δ = 70.3 (s, PAu). – IR (KBr): ṽ = 1608 cm^{-1} [ν(C=N)]. – $C_{39}H_{30}AuClN_3P$ (804.05): calcd. C 58.25, H 3.73, N 5.23; found C 56.49, H 3.73, N 4.93.

Crystal-Structure Determinations: Suitable crystals of compounds **1aAuCl**, **1cAuCl** and **1aSAuCl** were sealed into glass capillaries and used for the measurement of precise cell constants and intensity data collection. During data collection, three standard reflections were measured periodically as a general check of crystal and instrument stability. No significant changes were observed for the compounds. Diffraction intensities were corrected for Lp and absorption effects. The structures were solved by direct methods and refined by full-matrix least-squares calculations against F^2[9]. The thermal motion of all non-hydrogen atoms was treated anisotropically. All hydrogen atoms were calculated in idealized positions and allowed to ride on their corresponding carbon or nitrogen atom. Their isotropic thermal parameters were tied to that of the adjacent atom by a factor of 1.5 (Table 1). Selected interatomic distances and angles are given in the figure captions. Crystal and structure-solution data are summarized in Table 1. Further information may be obtained from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen, on quoting the depository numbers CSD-407212 (**1aAuCl**), -407211 (**1aSAuCl**) and -407213 (**1cAuCl**), the names of the authors, and the journal citation.

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