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Organogold Chemistry. XVI.[1,2]
Trimethylgold Trimethylphosphonium-methylid and Related Compounds

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A series of methylgold complexes of trimethylphosphonium-methylid has been synthesized and characterized by analytical and spectroscopic methods. These novel compounds contain Au–CH_2–P^+ bonds as part of the square planar coordination sphere of gold(III), which are very stable both thermally and in some selective cleavage and substitution reactions. The thermal decomposition of a $[(CH_3)_2Au\{(CH_2P(CH_3)_3\}_2]Br$ *salt leads to a reductive elimination of ethane with formation of the gold(I) ylid complex. Oxydative addition of halogen to the latter yielded the corresponding gold(III) halide ylid compounds, that are found to exist as trans and cis isomers.*

Introduction

Recent work on the main group and transition metal chemistry of ylids[2,3] has shown that ylids of phosphorus and sulfur are able to form exceptionally strong carbon to metal bonds, exceeding in most cases even those found in the closely related silylmethyl compounds[4,5]:

$$M–CH_2–\overset{\oplus}{P}R_3 \qquad M–CH_2–SiR_3$$

$$M–CH_2–\overset{\oplus}{S}(O)R_2$$

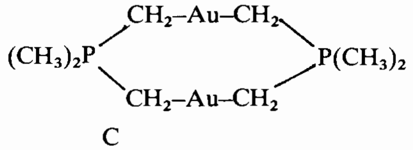
This is also true for the ylid complexes of the coinage metals copper and silver, as described in a series of previous papers[6–8]. Finally gold has been shown to form a large variety of stable ylid derivatives of the metal in its +1 oxydation state, including simple molecular and ionic species[1,9] (A or B, *e.g.*), but also a novel type of heterocyclic compounds (C):[1,10]

$$CH_3–Au–CH_2–P(CH_3)_3$$

A

$$[(CH_3)_3P–CH_2–Au–CH_2–P(CH_3)_3]Cl$$

B



C

These investigations have now been extended to the gold(III) derivatives of phosphorus ylids and again a number of related organometallics could be isolated and characterized, which contain the Au–CH_2–P^+ moieties as part of the square planar coordination sphere of the d^8 metal center. There is only one earlier reference on related studies in the literature, covering preliminary work on the interaction of gold halides with a carbonyl stabilized ylid[11].

Experimental

All compounds were prepared under an atmosphere of nitrogen using anhydrous solvents that were degassed by bubbling pure nitrogen through them. The starting materials were available via standard literature procedures or from commercial sources. Microchemical analyses were performed in the Würzburg laboratories by Mrs. E. Ullrich.

Trimethyl-trimethylphosphoniummethylid-gold(III), 1

349 mg of trimethylphosphonium-methylid (3.87 mmol) are added to a solution of 1.310 mg trimethyl-trimethylphosphinegold(III) (4.12 mmol) in a mixture of 25 ml n-pentane and 10 ml diethylether at –10°C with stirring. After 24 h at 20°C about half of the solvent is removed in vacuo, the solution cooled to –30°C and the colourless crystalline precipitate collected and dried *in vacuo.* 1.221 mg (95%), mp. 111–112°C. *Anal.* Calcd. for $C_7H_{20}AuP$ (322.2): C, 25.31; H, 6.07. Found: C, 25.08; H, 5.75. Mass spectrum: M^+ at m/e 332(1.1).

cis-Dimethyl-chloro-trimethylphosphoniummethylid-gold(III), **2**

Addition of 1.06 mmol of ethereal HCl to a solution of 352 mg **1** (1.06 mmol) in 15 ml ether leads to the precipitation of colourless crystalline **2** at 20° C. Filtration after 12 h yields 356 mg (95.2%), mp. 107–110° C (dec.). *Anal.* Calcd. for $C_6H_{17}AuClP$ (352.6): C, 20.44; H, 4.86. Found: C, 20.30; H, 4.75. MS: M^+ at m/e 352 (0.9).

cis-Dimethyl-trimethylphosphine-trimethylphosphoniummethylid-gold(III) Chloride, **3**

242 mg **1** (0.728 mmol), in 20 ml of ether, are converted into **2** by addition of an equivalent of ethereal HCl. After 2 h, an equivalent of trimethylphosphine is added (56 mg). The suspension obtained may be contaminated by elementary gold, which is removed by dissolving in CH_2Cl_2 and filtration after addition of active coal. The solution is concentrated *in vacuo;* 252 mg (80.7%), mp. 111° C (dec), very hygroscopic. *Anal.* Calcd. for $C_9H_{26}AuClP_2$ (428.7): C, 25.21; H, 6.11. Fond: C, 24.23; H, 6.20.

cis-Dimethyl-bis-trimethylphosphoniummethylid-gold(III) Bromide, **4**

216 mg $(CH_3)_3PCH_2$ (240 mmol) are added with stirring to a solution of 369 mg $[(CH_3)_2AuBr]_2$ (0.60 mmol) in 25 ml of n-pentane. After 1 h 347 mg (59.4%) of a colourless precipitate are obtained, mp. 205° C. Soluble in water: Λ_M 95 mhos at 25° C. *Anal.* Calcd. for $C_{10}H_{28}AuBrP_2$ (487.2): C, 24.65; H, 5.79. Found: C, 24.50; H, 5.97.

Thermal decomposition of **4** is accompahied by evolution of ethane gas. The melt resolidifies and melts again at 246° C. An authentical sample of **5** has the same mp and DTA graph. Ir and nmr spectra are also identical.

cis-and trans-Chloro-methyl-bis-trimethylphosphoniummethylid-gold(III) Bromide, **6** *and* **7**

An equivalent of ethereal HCl is added to a solution of 260 mg **3** (0.535 mmol) in 25 ml of ether. Filtration after 48 h yields 265 mg (97.6%), mp. 188–191° C (dec.). **5** is quickly isomerized in boiling water solution (nmr). **6** was not isolated from the aqueous medium. *Anal.* Calcd. for $C_9H_{25}AuBrClP_2$ (507.6): C, 21.30; H, 4.96. Found: C, 21.53; H, 5.06.

trans- and cis-Bis-trimethylphosphoniummethylid-dihalogold(III) Halides, **8–11**

229 mg of bis-trimethylphosphoniummethylid-gold (I) bromide **5**[1] are dissolved in 20 ml CH_2Cl_2 and 80 mg bromine (0.5 mmol each) added with stirring. A pale-yellow precipitate is formed immediately. Filtration after 30 min yields 254 mg **8** (82.3%), mp. 245–246° C (dec.). **8** is isomerized to the *cis*-product **10** after stirring for 24 h in water at 20° C (nmr). *Anal.* Calcd. for $C_8H_{22}AuBr_3P_2$ (616.9): C, 15.57; H, 3.59. Found: C, 15.74; H, 3.77.

Similarly from 351 mg of the same starting material and 195 mg I_2 (0.768 mmol each), 427 mg **9** (78.2%), red-brown, mp. 165° C, are obtained.

9 is also isomerized in water/ethanol or water/acetonitrile mixtures to the orange-red *cis*-complex **11**. *Anal.* Calcd. for $C_8H_{22}AuBrI_2P_2$ (710.9): C, 13.52; H, 3.12, Found: C, 13.76; H, 3.36.

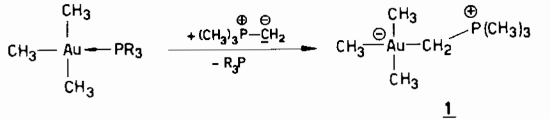
Oxidative Addition

Attempts for an oxydative addition of bromine or iodine to methyl-trimethylphosphoniummethylid-gold (I) in n-pentane/CH_2Cl_2 at –45° C led only to decomposition products.

Results and Discussion

An Ylid Complex of Trimethylgold

Trimethylgold is known to form stable complexes of a square planar configuration with a variety of ligands, primarily with trialkyl- and triarylphosphines[12]. Trimethylphosphonium-methylide[13] has now been shown to be able to replace these phosphine donors even under very mild conditions with formation of a very stable gold(III) ylid complex.



$$(CH_3)_3Au \leftarrow PR_3 \xrightarrow[- R_3P]{+ (CH_3)_3\overset{\oplus}{P}-\overset{\ominus}{\underline{C}}H_2} (CH_3)_3\overset{\ominus}{Au}-CH_2-\overset{\oplus}{P}(CH_3)_3$$

1

The trimethyl-trimethylphosphoniummethylid-gold (III) product, **1**, mp. 111–112° C, is decomposed only above 185° C in an inert atmosphere, and is volatile in a vacuum, showing the molecular ion in the mass spectrum. Its square planar molecular structure is easily confirmed by nmr spectra, which provide evidence for the presence of *cis-* and *trans*-methyl groups[14] in the ratio 2:1, for a methylene bridge with a PCH_2-coupling characteristic of ylid complexes,[15,16] and for a ^{31}P-resonance in the usual range of phosphonium centers[17]. Typically, the *trans*-CH_3Au resonance is split into a doublet by a $^1HCAuC^{31}P$ coupling (Table I).

The thermal stability of **1** is unusual, because the only other organogold compounds containing four Au–C σ-bonds known to-date[12], the AuR_4^- anions, are not existent above room temperature in solution, and they can only be isolated as pure solids in special cases.[18] Obviously the presence of the onium center has a pronounced stabilizing effect on the Au–C bonds in **1**.

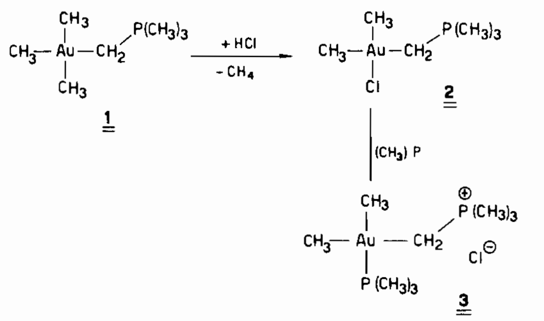
TABLE I. ^1H– and ^{31}P-nmr Data in ppm Relative to TMS and H_3PO_4.

Nr. Solvent	**1** CH_2Cl_2	**2** CH_2Cl_2	**3** CH_2Cl_2	**4** CH_2Cl_2	**6**[b] H_2O	**7**[c] H_2O	**8**[b] H_2O	**10**[c] H_2O	**11**[d] $D_2O + D_3CCN$
^1H									
$\delta H_3C_{cis}Au$	–0.05, s	1.07, s	1.00, d	0.41, d	0.70, s br	1.50, s	–	–	–
$\delta H_3C_{trans}Au$	0.39, d	0.63, d	0.67, d						
δCH_2	0.96, d	0.85, d	1.45, dd	1.39, d	0.99, d 2.37, d	1.57, d	2.13, d	2.49, d	2.63, d
δCH_3P	1.72, d	1.87, d	2.09, d	1.91, d	1.75, d 1.84, d	1.88, d	1.98, d	2.16, d	1.92, d
δCH_3P_{Au}	–	–	1.83, d	–	–	–	–	–	–
$^4J(H_3CAuCP)^a$	0.7	0.4	–	0.7	small	–	–	–	–
$^3J(H_3CAuP)_{trans}$	–	–	8.8	–	–	–	–	–	–
$^3J(H_3CAuP)_{cis}$	–	–	8.2	–	–	–	–	–	–
$^3J(H_2CAuP)_{cis}$	–	–	8.2	–	–	–	–	–	–
$^2J(H_2CP)$	14.4	14.2	16.0	16.5	14.8 12.5	14.6	13.3	11.6	14.2
$^2J(H_3CP)$	13.0	13.4	13.6	13.4	13.5 13.5	13.7	13.8	13.8	14.2
$^2J(H_3CP)_{Au}$	–	–	10.2	–	–	–	–	–	–
^{31}P									
P(Ylid)	+24.0	+26.0	+29.0	+26.8	–	–	–	–	–
P(Au)			–9.1						

[a] *trans*. [b] Immediately after the compound has been dissolved in cold water. [c] These signals increase with time in a solution of **6** or **8**, respectively, while those of the original compound disappear. [d] **9** is too sparingly soluble in water. In the D_2O/D_3CCN mixture complete isomerisation to **11** has occured, as taken from the low field shift of δCH_2 (*trans*-influence of halogen).

Reactions of Trialkylgold Ylid Complexes and Derivatives

Dry hydrogen chloride is a selective cleaving agent for the title complexes, and in a fast reaction one of the *cis*-methyl groups is substituted by chlorine.



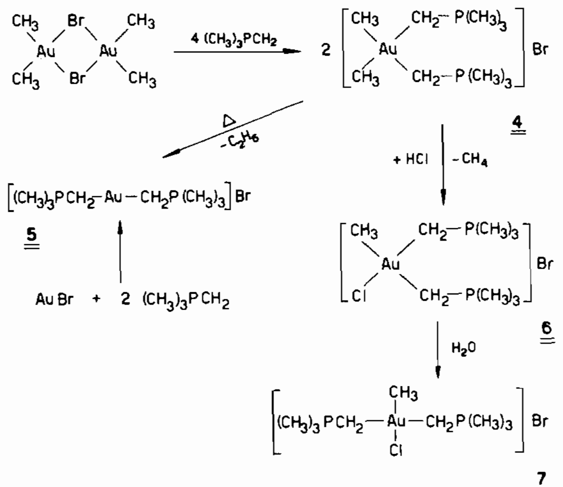
The resulting ylid complex of dimethylgold chloride therefore has the *cis*-structure, as it can be easily demonstrated again by nmr studies: two separate ^1H-signals for the CH_3Au hydrogens, one of which is a $^1HCAuC^{31}P$ doublet, along with the ^1H- and ^{31}P-resonances of the coordinated ylid, are in agreement with formula **2**, but would be at variance with a *trans* configuration (Table I).

It is significant, that in reaction (2) it is exclusively the CH_3–Au bond that is attacked by HCl, whereas the $(CH_3)_3PCH_2$–Au linkage remains unchanged. This result is indicative of a stabilizing effect of the onium center on the metal–carbon bond in chemical reactions as well.

Trimethylphosphine, which has no effect on **1**, transforms **2** into a cationic species **3** through substitution of the chlorine atom. The *cis*-structure is retained in this reaction according to similar nmr arguments as with **2** (Table I).

A complex, **4**, *with two ylid molecules* attached to gold(III), is obtained through the reaction of dimethylgold bromide and $(CH_3)_3PCH_2$ in the ratio 1:2. In this case the original $(CH_3)_2AuBr$ dimer is cleaved with substitution at all Au–Br bonds, but the methyl groups and the ylids are still found in a *cis*-position to each other in the product.

Compound **4** is dissolved by water without decomposition and the conductivity of the solution corresponds to a 1 : 1 electrolyte.



4 is stable to the melting point of 205° C, whereafter it is decomposed with reductive elimination of ethane and resolidification of the melt. The decomposition product, mp. 246° C, is easily identified as bis-trimethylphosphonium-methylid-gold(I) bromide, because it has been prepared independently from gold(I) bromide and two ylid equivalents.[1]

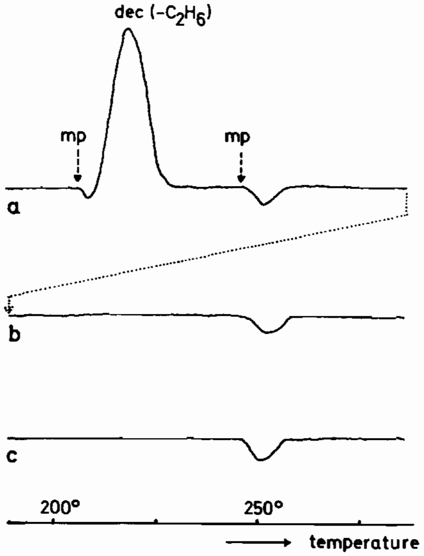


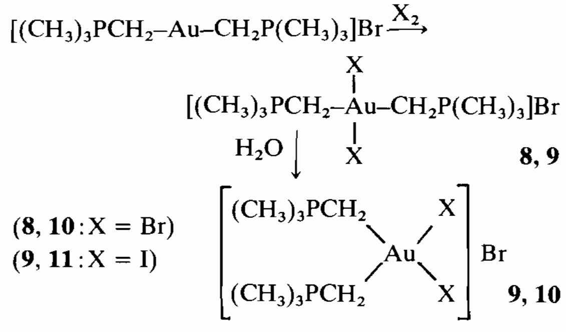
Figure 1. Differential thermal analysis diagrams of a) compound **4**, b) compound **4** after decomposition and cooling, and c) of compound **5**, prepared from AuBr and $(CH_3)_3PCH_2$ (1 : 2).

Clearly the gold bonds to the ylids remain intact and only those to the methyl groups are cleaved in the thermal decomposition.

The reductive elimination of ethane (**4**→**5**) has been followed by differential thermal analysis and found to be strongly exothermic, preceded and followed by endothermic melting of **4** and **5**, respectively (Figure 1).

Compound **4**, like **1**, reacts with HCl and thereby yields the methyl-chloro-bis-ylid complex **6**, having the ylids in a *cis*-position. This primary product was found to isomerize, however, in aqueous solution to the *trans* complex **7**. This process was followed by pmr, but **7** was not isolated, because it turned out to be extremely difficult to remove the solvent without at least partial decomposition. The pmr data of **6** and **7** are summarized in Table I.

In order to provide additional evidence for similar processes with gold(III) ylid complexes, compound **5** was subjected to oxydative addition reactions with bromide and iodine.



The primary products **8** and **9** cannot be assigned a *cis*- or *trans*-configuration only on the basis of nmr, but a study of their infrared spectra suggests a *cis*-structure in both cases. In aqueous solution again isomerization has been observed by pmr, which is supposed to lead to the *trans*-products.

The successful attempt of oxydative addition of elementary halogen to **5** in itself illustrates the stability of the gold–ylid bonds, which remain intact even in experiments, where no special precautions have been taken. The relative stabilities of the two possible configurations are not obvious from our experiments and seem to vary with the nature of the ligands (as in **6**/**7** as compared with **8**/**9**), and of the solvent employed. Further studies are required for this problem.

Infrared Spectra

All compounds containing CH_3Au groups are found to show bands in the region 1234–1174 cm^{-1}, which is characteristic for δCH_3 of these units[14, 19, 20]. In addition, **1** has three bands at 541, 510 and 496 cm^{-1}, very similar to those reported[20] for Au–C stretching modes of $(CH_3)_3AuP(CH_3)_3$. **2** has only one such line at

519, but also a ν(AuCl) band at 271 cm^{-1}, whereas **3** exhibits ν(AuP) at 363 cm^{-1}. The isomerization **6**→**7** is accompanied by a ν(AuC) band shift from 515 to 531 and a ν(AuCl) displacement from 296 to 274 cm^{-1}, probably due to the different *trans*-influence of methyl and chlorine ligands[21].

The dibromo compound **8** shows ν($AuBr_2$) at 256 cm^{-1}, as typical for the *trans* configuration of two bromine atoms at square planar gold(III)[22–24]. This band is shifted beyond the experimental limit (of 250 cm^{-1}) upon isomerization, as it is expected for a *cis*-arrangement. ν(AuC) on the other hand was observed to increase in wave-numbers for **8**→**10** and **9**→**11** from 549 to 560 and from 543 to 556 cm^{-1}, respectively, which is also evidence for this rearrangement. ν(AuI) has not been observed. Bands of the ylid ligands are subject to slight alterations, that cannot be explained in a straightforeward manner.

Acknowledgement

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