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Synthesis and Reactions of the Gold(I)-dimethylphosphonium-bis-methylid Dimer

H. SCHMIDBAUR* and R. FRANKE

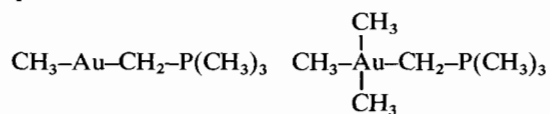
Institute of Inorganic Chemistry, University of Würzburg, and Inorganic Chemistry Laboratory, Technical University of Munich*, West Germany

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From the reaction of $(\text{CH}_3)_3\text{PCH}_2$ and $(\text{CH}_3)_3\text{PAuCl}$ in the ratio 2:1 a cyclic dimer of the formula $[(\text{CH}_3)_2\text{P}(\text{CH}_2)_2\text{Au}]_2$ is obtained, containing two linear CAuC and two tetrahedral PC_4 units as components of an eight-membered ring. Oxidative addition of one or two moles of halogen leads to products, for which structures with a transannular metal–metal bond in the first case and with two halogen atoms at both gold atoms in a trans configuration in the second case are proposed. Methyl iodide was found to add to the title compound only in a 1:1 ratio across the heterocycle. Methylation of the halogen adducts with CH_3Li exclusively yields the trans-dimethyl derivative with one of the gold atoms solely being in the +III oxidation state. Thermally induced reductive elimination of ethane converts this material to the title compound in the original configuration.

Introduction

In two previous papers it has been shown that phosphorus ylids form stable organometallic compounds with both gold(I) and gold(III) alkyls. In these species the ylid ligands are part of the linear and square planar coordination sphere of gold, respectively, as demonstrated for the following two most simple examples^{1,3}:



In all cases the ylid molecule is functioning as a *monodentate* carbanionic donor. This mode of interaction is now known to be a wide-spread structural unit in stable ylid complexes of many metals.⁴

In the presence of excess ylid as a transylidation reagent, or through previous metalation, ylids are known, however, to be also potential *bidentate* ligands. Thus trimethylphosphonium-methylid is forming both chelating and bridging $(\text{CH}_3)_2\text{P}(\text{CH}_2)_2^-$ units for

complexes of copper⁵, nickel⁶, cobalt⁷, chromium⁸, silver⁵, palladium⁴, and platinum⁴. The present paper describes analogous compounds of gold(I) and gold(III). A preliminary communication has already appeared⁹.

Experimental

Dimeric Gold(I)-dimethylphosphonium-bis-methylid, **1**

To a suspension of 647 mg $(\text{CH}_3)_3\text{PAuCl}$ (2.10 mmol) in 25 ml of benzene or toluene 566 mg $(\text{CH}_3)_3\text{PCH}_2$ (an excess of 6.30 mmol) are added and the mixture stirred in a closed flask for one week. The insoluble material is filtered, dried in vacuo and extracted with two 5 ml portions of methanol to remove the $[(\text{CH}_3)_4\text{P}]\text{Cl}$. After filtration and drying *in vacuo* 520 mg are obtained (86.6%), mp. 216–218°C. White crystals, stable to air and water, soluble in CH_2Cl_2 and CHCl_3 , from which it can be crystallized. *Anal.* Calcd. for $\text{C}_8\text{H}_{20}\text{Au}_2\text{P}_2$ (572.2): C, 16.79; H, 3.52. Found: C, 17.03; H, 3.84. MS (70 eV, 30°C): M^+ at m/e 572 (100.0).

Dihalo-digold-bis-[dimethylphosphonium-bis-methylid] Compounds, **2–4**

To a suspension of 404 mg of **1** (0.707 mmol) in 10 ml CH_2Cl_2 , 170 mg I_2 , dissolved in 20 ml CH_2Cl_2 , are added with stirring. The solution turns dark red and a karmine red precipitate is formed. After 1 h of stirring 515 mg of **4** (93%) are isolated by filtration; dec. 216°C. *Anal.* Calcd. for $\text{C}_8\text{H}_{20}\text{Au}_2\text{I}_2\text{P}_2$ (826.0): C, 11.63; H, 2.44.

Found: C, 11.31; H, 2.66.

580 mg **3** were obtained similarly from 557 mg **1** and 156 mg Br_2 (0.975 mmol each) (81.3% yield). Orange-red powder, dec. 224°C.

Anal. Calcd. for $\text{C}_8\text{H}_{20}\text{Au}_2\text{Br}_2\text{P}_2$ (732.0): C, 13.13; H, 2.75.

Found: C, 12.73; H, 2.89. MS: M^+ at m/e 732.

572 mg **1** was converted into 613 mg of **2** through addition of an equimolar amount of a standardized

solution of Cl_2 in CCl_4 (1.00 mmol each); yield 95.3%. Yellow powder, dec. 197°C .

Anal. Calcd. for $\text{C}_8\text{H}_{20}\text{Au}_2\text{Cl}_2\text{P}_2$ (643.1): C, 14.94; H, 3.13.

Found: C, 14.46; H, 3.52.

Tetrahalo-digold-bis-[dimethylphosphonium-bis-methylid], 5 and 6

As described for **2–4**, 669 mg **1** are found to add 2.34 mmol of Br_2 ; yield 1.007 g (96.5%) of orange-red **6**, mp. $163\text{--}165^\circ\text{C}$ (dec.).

Anal. Calcd. for $\text{C}_8\text{H}_{20}\text{Au}_2\text{Br}_4\text{P}_2$ (891.8): C, 10.78; H, 2.26.

Found: C, 10.81; H, 2.35.

189 mg **5** (90.7% yield) were isolated from 167 mg **1** and 0.584 mmol of Cl_2 (molar ratio 1:2). Yellow solid, dec. 183°C .

Anal. Calcd. for $\text{C}_8\text{H}_{20}\text{Au}_2\text{Cl}_4\text{P}_2$ (714.0): C, 13.46; H, 2.82.

Found: C, 13.34; H, 2.87.

Au-Methyl-, Au'-iodo-digold-bis-[dimethylphosphonium-bis-methylid], 7

1 ml of CH_3I (16.0 mmol) are added to a suspension of 491 mg **1** (0.86 mmol) in 50 ml ether. After 36 h of stirring the red product is filtered; 613 mg (100% yield), dec. 143°C .

Anal. Calcd. for $\text{C}_9\text{H}_{23}\text{Au}_2\text{IP}_2$ (714.1): C, 15.13; H, 3.25.

Found: C, 15.17; H, 3.17. MS: m/e 572 ($\text{M}^+ - \text{CH}_3\text{I}$), 100%.

Gold(I)-dimethylgold(III)-bis-[dimethylphosphonium-bis-methylid], 8

1.34 mmol of ethereal CH_3Li are added to a suspension of 490 mg **3** (0.67 mmol) in 25 ml THF, at -60°C . After 30 min the mixture is allowed to warm to room temperature. The product becomes colourless. The solvent is removed after 24 h in a vacuum and **8** extracted with *n*-pentane. 247 mg **8** (61.2%), dec. 153°C .

Similarly 611 mg **6** (0.685 mmol) react with 2.74 mmol of LiCH_3 to yield 312 mg **8** (75.6%).

A reaction of 476 mg **7** with LiCH_3 (0.67 mmol each) in ether failed to give **8** after 3d.

Anal. Calcd. for $\text{C}_{10}\text{H}_{26}\text{Au}_2\text{P}_2$ (602.3): C, 19.94; H, 4.35.

Found: C, 19.91; H, 4.51. MS: M^+ at m/e 602.

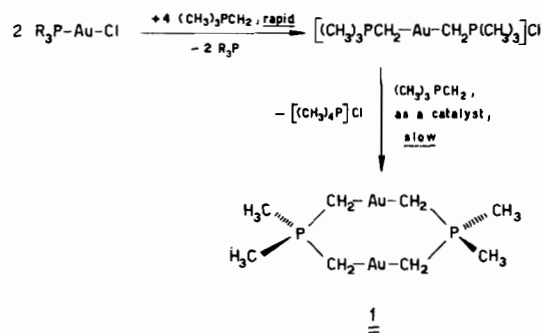
Results and Discussion

Preparation and Properties of the Gold(I)-dimethylphosphonium-bis-methylid Dimer

Gold(I) halides have been shown¹ to form 1:2 addition compounds with $(\text{CH}_3)_3\text{PCH}_2$. These products are most easily obtained from the phosphine

complexes of the halides with substitution of the triorganophosphine ligands, because the R_3PAuX starting materials are soluble in inert solvents and can be prepared in a very pure state, *i.e.* free of traces of metallic gold, whereas this is not true for the gold(I) halides themselves. This process is a rapid, largely homogeneous reaction.

If the reaction is carried out with excess ylid, in benzene or toluene as a solvent, and over a period of about seven days at room temperature, this initial reaction product is slowly converted into a mixture of tetramethylphosphonium halide and a corresponding dehydrohalogenated species **1** of the composition $(\text{C}_4\text{H}_{10}\text{PAu})_n$. In accordance with the related copper and silver compounds, this substance has to be formulated as a dimer (*v.i.*) and therefore the reaction scheme can be represented as follows:



After about one week the yields are quite satisfactory (80–90%). Compound **1** is a colourless crystalline material, that melts reversibly (without decomposition) at $216\text{--}218^\circ\text{C}$, and is stable to air and moisture. It may be stored unchanged at 20°C for a long time and is not sensitive to light. It is very slightly volatile in a vacuum and shows a strong parent ion peak in the mass spectrum.

These properties are unusual, because the analytical and spectroscopic data require the molecule to have four gold-to-carbon σ -bonds as part of an eight-membered heterocycle. Again⁴ the presence of onium centers adjacent to the metal-carbon bonds seems to lead to a dramatic stabilization of otherwise quite labile M-C moieties.

Formula **1** is inferred predominantly from the nmr spectra, which prove structural equivalence of the two ylidic groups by the observation of only one ^{31}P signal in the typical "phosphonium" shift region¹⁰, and by only one ^1H doublet resonance each for both the CH_3 - and CH_2 - groups (Table I). ^{31}P decoupling causes these doublets to collapse to singlets and detailed $\{^{31}\text{P}\}^1\text{H}$ experiments provided unequivocal evidence that $^2\text{J}(\text{H}_3\text{CP})$ and $^2\text{J}(\text{H}_2\text{CP})$ are of the same sign. This result is characteristic of $(\text{CH}_3)_2\text{P}(\text{CH}_2)_2$ groups with both carbanions engaged in bonding to metals¹¹.

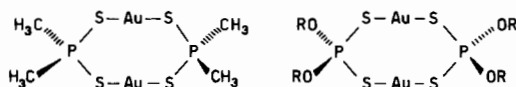
TABLE I. ^1H and ^{31}P nmr Data in ppm Relative to TMS and H_3PO_4 .^a

| Nr. | 1 | 6 | 7 | 8 | |
|-----------------------------------|--------------------------|-----------------|--------------------------|--------------------------|------------------------|
| Solvent | CH_2Cl_2 | CHCl_3 | CH_2Cl_2 | CH_2Cl_2 | C_6H_6 |
| ^1H | | | | | |
| $\delta\text{H}_3\text{CP}$ | 1.57, d | 2.17, d | 1.79, d | 1.54, d | 0.36, d |
| $\delta\text{H}_2\text{CP}$ | 0.79, d | 2.11, d | 1.13, d | 1.18, d | 0.63, d |
| | | | 1.53, d | 0.62, d | 0.11, d |
| $\delta\text{H}_3\text{CAu}$ | — | — | 1.67, s | 0.20, s | 0.15, s |
| $^2\text{J}(\text{H}_3\text{CP})$ | -11.9 ^c | 12.6 | 12.1 | 12.0 | 12.0 |
| $^2\text{J}(\text{H}_2\text{CP})$ | -12.4 ^c | 10.8 | 12.0 | 12.8 | 12.8 |
| | | | 11.6 | 12.0 | 12.0 |
| $^{31}\text{P}^b$ | | | | | |
| δp | 32.4, s | — | — | — | 29.2, s |

^a External standards, negative δ values for higher fields, 30 °C. ^b Hydrogen decoupling. ^c Relative signs determined by $^1\text{H}\{^{31}\text{P}\}$ experiments.

These data suggest an eight-membered ring structure **1** comprising two linear CAuC and two tetrahedral PC_4 units. An analogous configuration has been demonstrated for the copper homologue⁵ by an x-ray diffraction study¹³.

A similar structure has also been detected for the gold(I) dimethyldithiophosphinate¹⁴ and dialkyldithiophosphate^{15,16} dimers



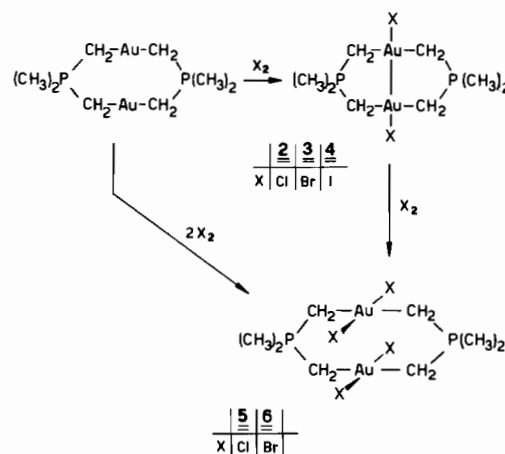
Oxidative Addition Reactions

The title compound contains two gold(I) centers in a transannular proximity of about 3.0 Å. Therefore various ways of oxidative addition are possible and should lead to products in the formal oxidation states +I/+III, +III/+III or, possibly, +II/+II of the gold atoms, if a transannular Au–Au bond is formed.

Addition of equimolar amounts of halogen indeed was found to yield 1:1 oxidation products, the properties of which seem to indicate the presence of such a metal–metal bond. Molecular chlorine, bromine and iodine are quickly taken up by **1** even under very mild conditions and pale yellow, orange red, and karmine red insoluble precipitates are formed in high yields (**2–4**). These compounds have decomposition temperatures as high as 197, 224 and 216 °C, and gave correct elemental analyses. The dibromide **3** was sufficiently volatile to show the parent ion in the mass spectrum, but due to the low solubility no nmr spectra could be obtained for any of the three compounds. The infrared spectra of **1** and **2–4** are almost identical in the region of 4000–250 cm^{-1} and point to similar and highly symmetrical structures. Of the AuX stretching vibrations only $\nu(\text{AuCl})$ has been observed at

260 cm^{-1} . $\nu(\text{AuC}_2)$ bands appear at 558 to 552, and 530 cm^{-1} (ν_{as} and ν_{s} , resp.) for **2–4** and therefore are very similar to that of the starting material (**1**: 551 cm^{-1}).

On the basis of these data a formula with two gold atoms in the formal oxidation state +II is proposed, invoking a transannular Au–Au bond. The fragmentation pattern in the mass spectrum of **3** includes $\text{M}^+ - \text{Br}$ and $\text{M}^+ - 2\text{Br}$, which is the molecular ion of **1**. This is also indicative of closely related structures. An unsymmetrical configuration ($\text{Au}^{\text{I}}, \text{Au}^{\text{III}}$) was discarded, because more pronounced changes would be expected in the vibrational spectra. The poor crystallinity of all samples precluded an x-ray diffraction study to date.



Addition of a second mole of halogen in fact led finally to compounds (**5, 6**) with more significant changes in the infrared spectra, as expected for $\text{Au}^{\text{III}}/\text{Au}^{\text{III}}$ species. This second oxidative addition was only successful with Cl_2 and Br_2 , but not with I_2 . Deeply yellow and orange red materials are obtained, which

decompose at 183 and 163–165°C, respectively. The solubility is again very low and only for **6** in chloroform nmr spectra could be obtained. This pmr spectrum shows two 1:1 doublets in the ratio 3:2, indicating that both ylid ligands in the compound are still equivalent as in **1**. The coupling constants are slightly different as are the chemical shift values (Table I). The infrared spectra of both species are very similar and differ significantly only in the low frequency region. Very strong bands for **5** at 357 cm⁻¹ and for **6** at 249 cm⁻¹ are assigned to $\nu(\text{Au}-\text{X}_2)$ and are important evidence for a *trans*-structure of the halogens at the gold atoms.

Formulae **5**, **6** were therefore drawn accordingly. This structural proposal could explain the non-existence of the corresponding iodine compound, because in such a *trans* arrangement the bulky iodine atoms would certainly give rise to severe steric hindrance.

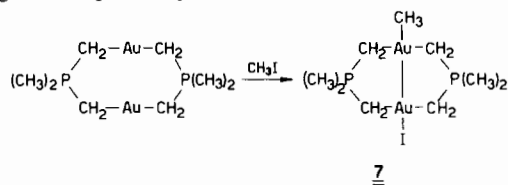
The *trans* formula also has the closer relation with **1**, **2** and **4**, inferred from the preparation and the infrared characteristics in the high frequency region.

The mass spectrum of **5** also shows this relation of **1**, **2** and **5**. Ions of this molecule and those of M⁺-Cl, M⁺-2Cl, M⁺-3Cl, and M⁺-4Cl can be detected, the latter being of strongest intensity.

Addition of methyl iodide

With equimolar amounts of **1** and methyl iodide, or with excess CH₃I, an orange red 1:1 addition compound **7** is obtained from a mixture of ether and CHCl₃ at room temperature. This product is stable to air and moisture and decomposes at 143°C. The yields are quantitative, corresponding to an uptake of only one mol of CH₃I.

Due to a satisfactory solubility of the compound in CH₂Cl₂ registration of the pmr spectrum was possible. This spectrum showed equivalence of four methyl groups and a two by two equivalence of the four methylene groups. This pattern suggests a structure analogous to that of **2**–**4**, invoking a transannular oxidative addition with formation of an Au^{III}–Au^{III} bond. *Cis*- and *trans*-addition to only one gold atom should lead to more complicated nmr spectra with AB characteristics in the CH₂ resonances or with four different CH₂ signals, respectively.

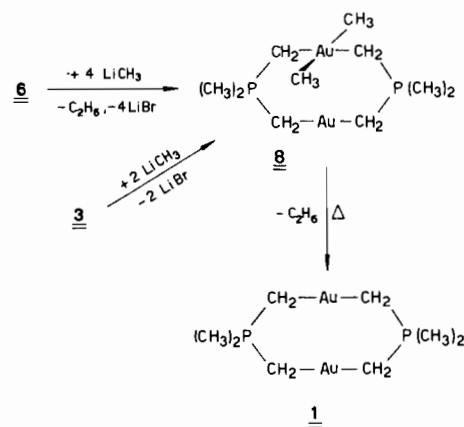


The mass spectrum of **7** does not show the molecular ion, but the ion of **1** is observed as the base peak. In addition the ions CH₃I⁺ and I⁺ are of high intensity. This result shows, that oxidative addition is easily reversed under these conditions.

There are many similarities in the ir spectra of **7** and **1**, but none of the special features would indicate structural peculiarities.

Dimethylgold-bis-dimethylphosphonium-bis-methylide, **8**

All attempts to prepare a dimethylgold-dimethylphosphonium-bis-methylide $[(\text{CH}_3)_2\text{Au}(\text{CH}_2)_2\text{P}(\text{CH}_3)_2]_n$, $n = 1$ or 2 , were unsuccessful. While the reactions of $(\text{CH}_3)_2\text{AuX}$ compounds with excess ylide yield only the salt-like primary products¹ of the type $[(\text{CH}_3)_2\text{Au}\{\text{CH}_2\text{P}(\text{CH}_3)_3\}_2]X$, the methylation of the halides **5** and **6** by LiCH₃ gave only a *dimethyl* derivative **8**. The same substance is available from **3** and LiCH₃:



8 decomposes at 153–155°C with evolution of ethane and formation of **1**. This process was followed by differential thermal analysis and the enthalpy of the decomposition determined to be of the order of $\Delta H = -9$ kcal/mol. The residue of the decomposition is almost pure **1**.

The pmr spectra of the compound (in CH₂Cl₂ and in C₆H₆) allow us to rule out a symmetrical structure as proposed for **2**–**5**, but a decision as to a *cis*- or *trans*-arrangement of the two methyl groups at one of the two gold atoms is not unambiguous. Both configurations are in agreement with the observed pattern of two equivalent methyl groups at gold atoms, four equivalent methyl groups at phosphorus atoms and two pairs of equivalent methylene units, as found in both solvents. The absence of any $H_3\text{CAuCP}$ coupling, which has been observed in other related systems, favours a *trans*-structure, as does the strong shielding of the CH₃Au protons, however. An intense ir band at 490 cm⁻¹ is also indicating such a *trans*-structure, but this assignment is again a tentative one, as the complete spectrum is exceedingly complicated.

The mass spectrum, though showing the molecular ion in low intensity, has M⁺-15 and M⁺-30 (= **1**⁺) as the most intense peaks. This parallels the observations.

The non-existence of a tetramethyl derivative of **1** may be due to significant steric hindrance and has a parallel in the findings with the corresponding tetraiodo compound (v.s.).

Acknowledgement

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