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Au(I)–Au(II) and Au(I)–Au(III) Oxidation in Ylide Complexes with Chlorinating Agents

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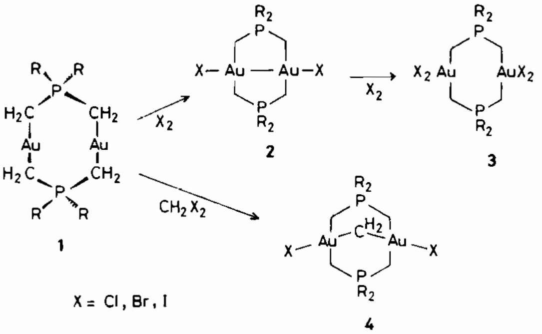
The gold(I) dimethylphosphonium-bis-methylide dimer 1a *is converted into the Au–Au-bonded gold (II) complexes* 2a, 2b *on addition of 1,2-dichloro- or 1,2-dibromo-ethane respectively. Ethylene is eliminated in this oxidative addition process. With oxalyl or thionyl chloride the gold(III) complex* 3a *is obtained and no gold(II) intermediate can be observed.* ortho-*Dichlorobenzene and* sym-*tetrachloroethane give no reaction with* 1a. *Oxidative addition of dichloromethane to the gold(I)-di-t-butylphosphonium-bis-methylide dimer* 1c *yields the Au–CH_2–Au-bridged Au(III) complex* 4c, *analogous to the (P,P)-tetramethyl homologues (*4*) described previously.*

Introduction

Compounds of gold in its oxidation state +2 are rare [1–3] and the existence of the gold–gold bonded version $Au_2^{4\oplus}$ has only been demonstrated in cyclic ylide complexes [4–8] and some related materials [9]. These compounds (*2*) were obtained through oxidative addition of halogen or, in one case, of an alkyl halide [5, 8] to the gold(I) heterocycles *1*. Certain disulfides also give this reaction [6]. Excess halogen is known to convert either *1* or *2* directly into the Au(III) complexes 3.



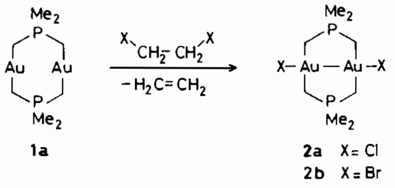
Dihalomethanes CH_2X_2 (X = Cl, Br, I) give methylene-bridged addition products (*4*) [10] with no Au–Au-bonded intermediate being observed. The structures of compounds *1*, *2*, and *4* have been confirmed by single crystal X-ray diffraction [4] and the oxidation state of their gold atoms verified by Mössbauer and ESCA data [1, 4].

In a continuing study of related oxidative addition reactions, attempts were made to use reagents other than elemental halogen for oxidation and to possibly introduce other bridging moieties between the gold atoms, and this paper presents some of the results.

Results and Discussion

Oxydation with 1,2-Dichloro- and 1,2-Dibromoethane

When solutions of the gold(I)-dimethylphosphoniumbis(methylide) dimer (*1a*) in $ClCH_2CH_2Cl$ are kept at room temperature for several weeks or heated to reflux temperature for two days a deep-yellow precipitate is formed in good yield, easily identified as the Au(II) complex *2a* [5]. The analogous bromo-compound (*2b*) is obtained similarly as bright orange crystals from $BrCH_2CH_2Br$ solutions.



It appears therefore that ethylene is lost in these reactions, and no (Au–CH_2CH_2–Au)-bridged intermediate or product can be detected. Both reactions are quite clean and represent new and convenient routes to the Au(II) compounds *2a, b.*

Oxidation with Oxalylchloride and Thionyl Chloride

Treatment of pyridine solutions of *1a* with *oxalyl chloride* at 0 °C yields a yellow solid, the tetrachlorodigold(III) complex *3a*. The reaction is not without by-products and yields of *3a* are unsatisfactory (52%).

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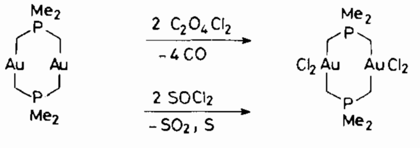


1a 3a

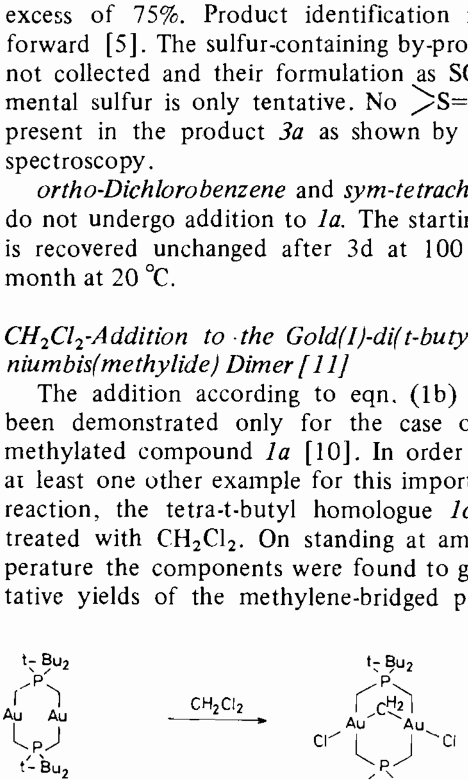
Carbon monoxide is evolved in the process and no carbonyl-bridged species appears to be formed.

With *thionyl chloride* in toluene as a solvent the same product *3a* is generated, but yields are now in excess of 75%. Product identification is straightforward [5]. The sulfur-containing by-products were not collected and their formulation as SO_2 and elemental sulfur is only tentative. No $>S=O$ group is present in the product *3a* as shown by vibrational spectroscopy.

ortho-Dichlorobenzene and *sym-tetrachloroethane* do not undergo addition to *1a*. The starting material is recovered unchanged after 3d at 100 °C or one month at 20 °C.

CH_2Cl_2-Addition to the Gold(I)-di(t-butyl)phosphoniumbis(methylide) Dimer [11]

The addition according to eqn. (1b) has so far been demonstrated only for the case of the permethylated compound *1a* [10]. In order to provide at least one other example for this important model reaction, the tetra-t-butyl homologue *1c* was also treated with CH_2Cl_2. On standing at ambient temperature the components were found to give quantitative yields of the methylene-bridged product *4c*.



1c 4c

4c was identified by elemental analysis, mass spectrum and NMR spectra. As in *4a, b** the two substitutents are non-equivalent at each phosphorus atom due to the ligand array at the square planar d^8 Au(III) centers. On the same grounds the CH_2 hydrogens at the $Au-CH_2-P$ bridges display ABX multiplets, as demonstrated by $\{^{31}P\}$ decoupling (X). The structure of *4c* is thus clearly analogous to that of *4a* [10].

Some of the above reactions are reminiscent of results obtained by other workers in the area of 'A-frame' complexes, where both oxidative addition and oxidation with elimination may occur depending on the nature of the reagents [12].

Experimental

The reactions were carried out in an atmosphere of dry nitrogen. Solvents were dried and saturated with nitrogen, and all glass apparatus was filled with nitrogen after heat-drying *in vacuo.*

Bis[µ-dimethylphosphonium-bis-methylido]-Au,Au'-dichloro- and -dibromodigold(II) (Au–Au), 2a, b

90 mg *1a* (0.16 mmol) was dissolved in 45 ml of 1,2-dichloroethane and the solution heated under reflux for 2d. A yellow precipitate was formed, which was filtered, washed with fresh $C_2H_4Cl_2$ and dried *in vacuo*, yield 76 mg (74%), m.p. 193 °C (dec.), *2a.*

IR-spectrum (Nujol): 1297, 1287, 1047, 1043, 942, 850, 804, 757, 723, 558, 533, 260 cm^{-1}; virtually identical with the spectrum of an authentical sample [5]. *Anal.* $C_8H_{20}Au_2Cl_2P_2$ (643.03) Calc. (Found): C, 14.94 (15.46); H, 3.14 (3.13); Au, 61.26 (59.40).

2b was obtained similarly from 70 mg *1a* (0.12 mmol) in 35 ml $BrCH_2CH_2Br$, yield 76 mg (85%) after 10 d at 20 °C, m.p. 201 °C (dec.).

IR-spectrum (Nujol): 1291, 1282, 1052, 1029, 1000, 940, 922, 851, 804, 755, 555, 532 cm^{-1}; virtually identical with the spectrum of an authentical sample [5]. *Anal.* $C_8H_{20}Au_2Br_2P_2$ (731.94) Calc. (Found): C, 13.13 (12.56); H, 2.75 (2.90); Au, 53.82 (53.50).

Bis[µ-dimethylphosphonium-bis-methylido]-Au, Au, Au', Au'-tetrachloro-digold(III), 3a

0.6 ml of freshly distilled oxalyl chloride was added at 0 °C to a solution of 70 mg *1a* (0.12 mmol) in 50 ml of pyridine. The reaction mixture was allowed to warm to room temperature and was stirred for 2 d. The precipitate was filtered off and the product isolated from the filtrate after evaporation of the solvent, treating the residue with methanol and drying *in vacuo*; yield 46 mg (52%), m.p. 178 °C (dec.).

Anal. $C_8H_{20}Au_2Cl_4P_2$ (713.93) Calc. (Found): Au, 55.18 (54.80). The same material was obtained from 90 mg *1a* (0.16 mmol) dissolved in 30 ml toluene on addition of 10 ml freshly distilled $SOCl_2$. After 3d at 20 °C the precipitate was filtered and dried *in vacuo*; yield 85 mg (75%), m.p. 181 °C (dec.) IR-spectrum (Nujol): 1425, 1414, 1305, 1289, 1286, 1089, 1058, 1013, 958, 934, 855, 802, 773, 744, 656, 642, 547, 531, 357, 334 cm^{-1} (see ref. [5]).

Anal. (above): Au, 55.18 (54.90); Cl, 19.80 (19.70).

trans, trans-Bis[µ-(di-t-butyl)phosphonium-bis-methylido]-Au, Au'-dichloro-µ-methylene-digold(III), 4c

90 mg *1c* (0.12 mmol) [11] were dissolved in 12.5 ml CH_2Cl_2. After 7 d at room temperature all volatiles were removed *in vacuo*. An off-white solid remained, m.p. 180 °C (dec.).

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*4a: Formula 4, R = CH_3, X = Cl. 4b: Formula 4, X = CH_3, X = Br.

^{1}H-NMR spectrum (CD_2Cl_2): $\delta = 1.90$ ppm, d, and 2.20, d, $^3J(PH) = 13.5$ Hz, CH_3; 2.15, ABX, $^2J(PH)$ *ca.* 14, $^2J(HH)$ *ca.* 13, PCH_2; 2.40, s. CH_2Au_2. ^{31}P-NMR spectrum (CD_2Cl_2): 69.4 ppm, s $\{^1H\}$. Mass spectrum (70 eV, EI): m/e = 824, M^+ (1%); 789, M^+-Cl (80); 775, M^+-CH_2Cl (40); 740, $M^+-CH_2Cl_2$ (100). *Anal.* $C_{21}H_{46}Au_2Cl_2P_2$ (825.38) Calc. (Found): C, 30.56 (32.10); H, 5.62 (6.40); Cl, 8.59 (8.00); Au, 47.73 (47.61).

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