PHOSPHINE COMPLEXES OF (1-CARBOMETHOXY-2-PHENYLVINYL)GOLD

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Previously [1] we had reported that the configuration is retained when mercury is replaced by gold in trans, trans-distyrylmercury. trans, trans-Di-(1-carbomethoxy-2-phenylvinyl)mercury (I) was studied in the present paper.

The triphenylphosphine (II) and triferrocenylphosphine (III) complexes of trans(1-carbomethoxy-2-phenylvinyl)gold were obtained from (I) and the corresponding complexes of methylgold in the presence of HBF4:

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The configuration of complexes (II) and (III) was established indirectly, via a number of chemical transformations. It was shown on a few examples that the protolysis of organomercury compounds goes with a retention of the configuration [2]. We used conc. HCl for the protolysis of the starting (I) and isolated trans-cinnamic acid (IV) in high yield, which was identical with that described in [3, 4]. The protolysis of (II) and (III) under the same conditions also led to the isolation of trans-cinnamic acid (IV) and the corresponding gold chloride complexes in high yields. As a result, it may be assumed that the formed organogold compound has the same configuration as the starting organomercury compound.

Previously [5] the reaction of (I) with the triphenylphosphine complex of methylgold gave only the monoorganogold compound, while the binuclear cationic complex, due to its extreme instability, could not be isolated:



When the triferrocenylphosphine complex of methylgold was used in this reaction we obtained various products, depending on the ratio of the starting organomercury and -gold compounds. Thus, the monoorganogold compound (III) is formed when the ratio is 1:2, and the binuclear cationic complex (V) when the ratio is 1:3.

The reaction of (V) with triferrocenylphosphine gave the monoorganogold compound, which was identical with the trans-(l-carbomethoxy-2-phenylvinyl)(triferrocenylphosphine)gold (III) that was obtained by the same reaction using a different ratio of the reactants.

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As a result, replacing triphenylphosphine by triferrocenylphosphine affects the direction of the reaction of (I) with methylgold complexes, but the stereochemical result of the reaction is the same in all cases.

EXPERIMENTAL

(1-Carbomethoxy-2-phenylvinyl)(triphenylphosphine) gold (II). To a solution of 0.39 g of (I) [6] and 0.71 g of methyl(triphenylphosphine)gold [7] in 200 ml of ether was added 11 ml of an 0.23 N ether solution of HBF4. After stirring for 3 h the precipitate was separated, washed with ether, and dried *in vacuo*. We obtained 0.12 g of bis(triphenylphosphine)gold fluoborate, mp 233-235° [8]. The ether filtrate was washed with water and dried over K₂CO₃. After removal of the solvent *in vacuo* we obtained 0.73 g (79%) of (II), mp 148-149° [from a tetrahydrofuran (THF)-heptane mixture] [5]. Found (%): C 54.10, H 3.95, Au 31.50. C₂₈H₂₄AuPO₂. Calculated (%): C 54.20, H 3.89, Au 31.74.

(1-Carbomethoxy-2-phenylvinyl)(triferrocenylphosphine)gold (III). To a solution of 0.26 g of (I) and 0.83 g of methyl(triferrocenylphosphine)gold [9] in 250 ml of ether was added 4 ml of an 0.23 N ether solution of HBF4. After stirring for 1 h the reaction mixture was filtered, and the ether solution was washed with water and dried over K₂CO₃. After removal of the solvent *in vacuo* we obtained 0.75 g (80%) of (III), mp 205-208° (in a sealed capillary) (from an ether-benzene-petroleum ether mixture). Found (%): C 50.81, H 3.90. C₄₀H₃₆Fe₃PAuO₂. Calculated (%): C 50.88, H 3.84.

(1-Carbomethoxy-2-phenylvinyl)-bis(triferrocenylphosphinegold) fluoborate (V). To a solution of 0.10 g of (I) and 0.48 g of methyl(triferrocenylphosphine)gold in 100 ml of ether was added 8 ml of an 0.2 N ether solution of HBF4.* After stirring for 1 h the precipitate was separated, washed with ether, and dried. We obtained 0.33 g (95%) of (V), which decomposes above 186°. Found (%): C 47.20, H 3.85. C₇₀H₆₃Fe₆Au₂O₂P₂BF4. Calculated (%): C 47.07, H 3.89.

Reaction of (V) and triferrocenylphosphine. To a stirred solution of 0.11 g of triferrocenylphosphine in 50 ml of benzene were added in drops a solution of 0.33 g of (V) in 15 ml of CHCl₃ and then 75 ml of ether. The obtained suspension was stirred for 2 h, after which the precipitate was filtered and washed with ether to give 0.25 g (94%) of bis)triferrocenylphosphine)gold fluoborate, which decomposes above 270° (from methanol). Found (%): C 49.09, H 3.74. $C_{60}H_{54}Fe_6P_2AuBF_4$. Calculated (%): C 49.49, H 3.73. After removal of the solvent from the combined filtrate *in vacuo* and reprecipitation from an ether-benzene-petroleum ether mixture we obtained 0.16 g (93%) of (III), mp 205-207°. The IR spectrum of the sample was identical with that of the product obtained by direct synthesis.

Protodemercuration of trans,trans-Di(1-carbomethoxy-2-phenylvinyl)mercury (I). A stirred mixture of 0.52 g of (I) and 30 ml of conc. HCl was refluxed for 1 h. The precipitate obtained on cooling was separated, washed with water, dried, and dissolved in CC14. The aqueous layer was extracted with CC14. The combined organic extracts were washed with water, dried, and dissolved in CaC12. After removal of the solvent *in vacuo* we obtained 0.24 g (81%) of (IV), mp 133-134° [3, 4].

Protodeauration of (1-Carbomethoxy-2-phenylvinyl) (triphenylphosphine)gold (II) and (1-Carbomethoxy-2-phenylvinyl)(triferrocenylphosphine)gold (III). A stirred mixture of 0.62 g of (II) and 30 ml of conc. HCl was refluxed for 1 h. Using the above described method we obtained 0.12 g (81%) of (IV), mp 133-134°. From the precipitate we obtained 0.41 g (83%) of triphenylphosphinegold chloride, mp 242-245° [10].

Using the above described procedure, from 0.73 g of (III) we obtained 0.10 g (88%) of (IV) and 0.55 g (87%) of the triferrocenylphosphinegold chloride solvate with one molecule of benzene, mp.251-252° (in a sealed capillary) (from benzene). Found (%): C 48.42, H 3.70, Cl 4.06. C₃₆H₃₃Fe₃AuClP. Calculated (%): C 48.21, H 3.70, Cl 3.95. After drying the sample *in vacuo* at 140° for 10 h we obtained triferrocenylphosphinegold chloride. Found (%): C 44.25, H 3.22, Cl 4.44. C₃₀H₂₇Fe₃AuPCl. Calculated (%): C 44.01, H 3.32, Cl 4.33.

CONCLUSIONS

1. The replacement of mercury by gold in trans, trans-di(l-carbomethoxy-2-phenylvinyl)mercury goes with a retention of the configuration.

^{*}The amount of HBF4 has little effect on the direction of the reaction and the yield of products.

2. The replacement of triphenylphosphine by triferrocenylphosphine in an organogold complex affects the direction of the reaction, but does not change its stereochemical result.

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SYNTHESIS OF A NEW PHOSPHORUS-CONTAINING MACROCYCLE

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Heterocyclic compounds that contain at least two P atoms in the ring [1-3], especially macrocyclic structures [4-7], are available only with difficulty, and have received little study. At the same time, a large number of quite readily available macrocyclic polyethers (crown ethers), which possess complexing properties, is known [8].

The synthesis of a 15-membered macrocyclic compound, which contains both phosphine oxide groupings and polyether units, is described in the present paper. The complexing properties of such systems are of definite interest [9].

The scheme for the synthesis of the macrocycle includes obtaining a phosphorus-containing diphenol, which then can be used in the cyclization step with the dihalo derivatives of polyglycols via the method for the synthesis of crown ethers.

From o-bromo(methoxymethoxy)benzene (I), which was obtained from o-bromophenol, we prepared the Grignard reagent, which when reacted with ethylenebis(phenylphosphinic chloride) [10] gives ethylenebis[phenyl(o-methoxymethoxyphenyl)phosphine oxide] (II). The basic properties of this dioxide were studied by the method of potentiometric titration with HClO4 in nitromethane solution [11]; the found value was pK_{q} (CH₃NO₂) = 6.57. Treatment of dioxide (II) with alcoholic HCl solution gives ethylenebis[phenyl(o-hydroxyphenyl)phosphine oxide] (III), which is insoluble in water and most organic solvents. The IR spectrum of (III) has a very broad absorption band in the 2300-3200-cm⁻¹ region that corresponds to the stretching vibration of phenolic OH groups, which take part in strong H bonding. The stretching vibra-tions of the P=O group gives a quite broad band around 1140-1150 cm⁻¹. The treatment of (III) with sodium ethoxide, and then with β,β '-dichlorodiethyl ether in dimethylformamide (DMF) at high dilution gives 1,2,7,8-dibenzo-3,6-diphospha-3,6-dioxo-3,6-dipheny1-15-crown-5 (IV). This compound is readily soluble in alcohol or chloroform, and less readily soluble in benzene. The molecular weight of macrocycle (IV), determined in an analytical ultracentrifuge, is 540; the calculated mol.wt. is 532.5. The IR spectrum of (IV) lacks absorption in the vibration region of phenolic OH groups, while the $v_{P=0}$ (shoulder at 1170 cm⁻¹). The basicity of dioxide (IV) is pK_{α} (CH₃NO₂) = 6.84. The ³¹P-{¹H} NMR spectrum of (IV) represents a narnow singlet line, which, relative to the signal of 85% H₃PO₄, is shifted downfield by 35.7 ppm.

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