

Oxidative Addition of Methyl Iodide to Dinuclear Gold(I) Amidinate Complex: Schmidbaur's Breakthrough Reaction Revisited with Amidinates

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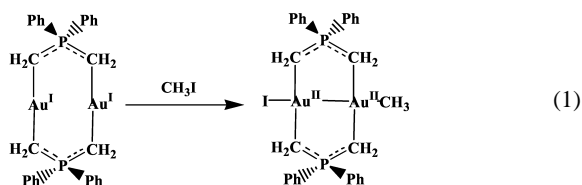
Gold chemistry was stimulated nearly 30 years ago by the addition of methyl iodide to a dinuclear Au(I) ylide complex by Schmidbaur. Congratulations Hubert on the occasion of your 70th birthday. God speed for many more.

Oxidative-addition of methyl iodide, CH₃I, to the dinuclear gold amidinate [Au₂(*o*-Me₂-form)₂] in THF generates a metal-metal bonded Au(II) product, formulated as [Au₂(*o*-Me₂-form)₂CH₃I], in quantitative yield under nitrogen at 0 °C and in absence of light. The product is characterized by ¹H NMR, elemental analysis and preliminary X-ray crystallography.

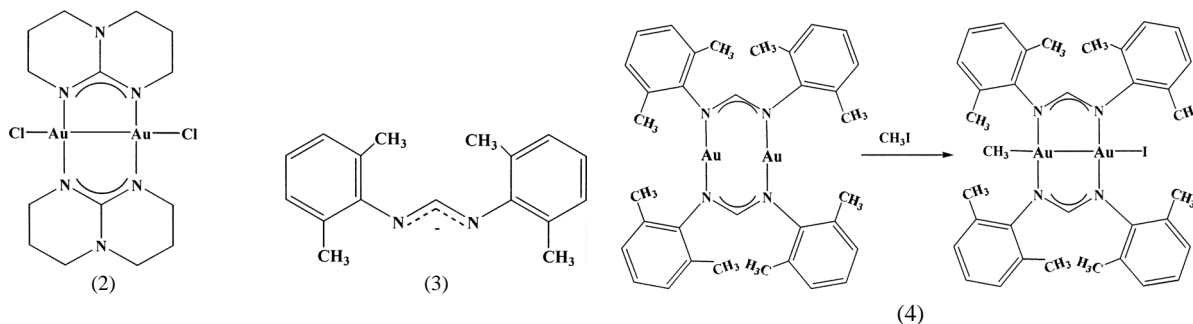
Key words: Oxidative-Addition, Gold, Amidinate Complexes, Methyl Iodide

Introduction

The report by Schmidbaur and Franke [1] that CH₃I adds to a dinuclear gold(I) ylide complex to form a metal-metal bonded Au(II) product (1) similar to results that had been obtained with halogen addition was novel in dinuclear Au(I) organometallic chemistry at the time. In fact, no crystallographic data became available to substantiate formation of this product until seven years later when Fackler and Basil [2] reported the structure of the CH₃I addition to [Au(CH₂)₂P(CH₃)₂]₂. The sensitivity of the compound to UV light had hampered reproduction of the Schmidbaur synthesis. Since this time much new chemistry has developed with dinuclear Au(I) species but no stable alkyl halide addition products have been characterized with other (non ylide) ligands which support formation of dinuclear Au(I) precursors. Indeed relatively few examples exist in general in dinuclear chemistry in which two such widely different ligands bond to the metal-metal bonded [M-M]²⁺ unit [3]. An extensive review of this chemistry with gold has been described by Grohmann and Schmidbaur [4] and Laguna [5]. Our own contributions to the formation of the oxidative addition products also have been reviewed [6, 7].



Oxidative addition of halogens is known with ligands other than those of ylides coordinated to the Au(I). The ligands methylenethiophosphonate, [CH₂P(S)Ph₂][−], *i*-MNT, [S₂CC(CN)₂]^{2−}, diethyldithiocarbamate, [S₂CNEt₂][−], along with the mixed ligand complex {Au₂[S₂P(OPh)₂][(CH₂)₂PPh₂]} have produced well characterized metal-metal bonded Au(II) products. *However, none of these materials has produced a stable alkyl halide oxidative addition product.* Recently we reported that the guanidinate-type ligand **Hhpp**, (1,3,4,6,7,8-hexahydro-2H-pyrimido[1,2-*a*]pyrimidine), forms a dinuclear Au(II) product with terminal chlorides with a remarkably short Au(II)-Au(II) bond of 2.46 Å (2) [8]. This remarkably stable product with such an exceptionally short metal-metal bond suggested that an extensive Au(II) chemistry may exist with amidinates. Hence we have been examining the ability of hpp[−] and related amidinates such as the dimethylformamidinate (3) to form stable



dinuclear Au(I) products which might undergo oxidative addition reactions.

When 1 mol of Cl_2 , Br_2 , or I_2 is added to 1 mol of the $[\text{Au}_2(o\text{-Me}_2\text{-form})_2]$ dinuclear in THF at room temperature, an immediate color change occurs, from colorless or light yellow to a very deep, dark green or brown. X-ray structures of the dark orange or brown crystals show formation of oxidative addition products [9] containing short (~ 2.51 Å) Au(II)-Au(II) bonds with solvent (THF or hexane) in the structure. Thermal gravimetric analysis and differential thermal analysis indicate that the solvent is released before loss of the halogen. In this paper we report the formation and characterization of the CH_3I addition product (4).

Experimental Section

Synthesis

To 230 mg (0.25 mmol) of the dinuclear gold amidinate [10] $[\text{Au}_2(o\text{-Me}_2\text{-form})_2]$ in 20 ml freshly distilled ether in round bottom flask a 0.5 ml (excess) of CH_3I was added. After stirring for 2 h under N_2 stream in ice bath in absence of light the brown product was filtered (85% yield). ^1H NMR (400 MHz, CDCl_3): δ = s, 1.37 (Au- CH_3). $-\text{C}_{35}\text{H}_{41}\text{Au}_2\text{IN}_4$ (1038.56): calcd. C 40.47, H 3.97; found C 39.91, H 4.05.

Results and Discussion

The dinuclear $[\text{Au}_2(2,6\text{-Me}_2\text{-form})_2]$ is isolated in quantitative yield by the reaction of $\text{Au}(\text{THT})\text{Cl}$ and sodium salt of 2,6- $\text{Me}_2\text{-form}$ in 1:1 stoichiometric ratio. The Au-Au distance is 2.711(3) Å and N-Au-N is $170.2(3)^\circ$ [10]. To our knowledge, there is only one example of symmetrical dinuclear gold(I) nitro complex, $\{\text{Au}_2[(\text{Me}_3\text{SiN})_2\text{C}(\text{Ph})_2]\}$ of Au-Au = 2.646 Å [11]. The dropwise addition of methyl iodide, CH_3I , to a solution of $[\text{Au}_2(o\text{-Me}_2\text{-form})_2]$ in ether generates $[\text{Au}_2(o\text{-Me}_2\text{-form})_2\text{CH}_3\text{I}]$ in quantitative yield under nitrogen at 0°C and in absence of light.

The dark orange brown crystals which form as large blocks are stable at room temperature after growing. A gold metal forms around the wall of the reaction vessel if the reaction carried in the open air at room temperature. Growing crystals was successful at 0°C after one week. Although well shaped, brown-black crystals were grown from ether which diffracted well, the spatial volume occupied by CH_3 and I is approximately identical. This leads to a disorder in the positions of the CH_3 and iodide atoms. While the Au(II) atoms and the amidinate ligand atoms refine well, the CH_3 and I atom positions remain somewhat uncertain regarding their distances from the Au(II) atoms. The Au(II)-Au(II) distance is ~ 2.52 Å, is typical of the Au(II)-Au(II) distances observed for the halogen adducts.

Although few details are known at present regarding the chemistry of the methyl iodide addition product reported here, this work demonstrates that the amidinate system supports the formation of unsymmetrical alkylhalide addition products similar to the addition product first observed by Schmidbaur for a dinuclear ylide complex. The reaction of methyl iodide appears similar to that of the halogen oxidants in forming a metal-metal bonded product rather than a mixed valent Au(III)/Au(I) species. The solution changes to dark brown after mixing and forms a brown product. ^1H NMR characterization in CDCl_3 shows the characteristic singlet peak for the methyl group at 1.37 ppm.

Oxidative addition reactions using alkyl halides containing fluorinated alkyl groups, as well as nitroalkanes, reactions which successfully produced unsymmetrical oxidative addition products with the ylides [4], are under investigation in our laboratory.

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