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The Reactivity of Bromoform with $[Au(CH_2)_2PPh_2]_2$. The Completion of the Halomethane Series CH_yX_{4-y} (y = 3,2,1,0; X = Cl, Br, I) and Reactivity with $[Au(CH_2)_2PPh_2]_2$

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Abstract

The reaction of $[Au(CH_2)_2PPh_2]_2$ with excess $CHBr_3$ in benzene initially gives $[Au(CH_2)_2PPh_2]_2(CHBr_2)Br$. This observation establishes that halomethanes, CH_yX_{4-y} (y = 3,2,1,0; X = Cl, Br, I), react with $[Au(CH_2)_2PPh_2]_2$ to initially give Au(II) adducts of the general form $[Au(CH_2)_2PPh_2]_2(CH_yX_{3-y})X$ (y = 3,2,1,0) via oxidative addition across the carbon–halogen bond. The order of reactivity inversely follows the order of carbon–halogen bond dissociation energies of haloalkanes. Methyl chloride is the only halomethane of the series that does not give a Au(II) adduct under similar reaction conditions.

Oxidative-addition [1] is the predominant reaction [2] found with the gold ylide dimer $[Au(CH_2)_2PPh_2]_2$ (**1**). A Au(II) diamagnetic complex containing a Au–Au bond is formed in two-center two-electron oxidative-addition of halogens [3], pseudohalogens [4] and alkyl halides [5]. Attention was drawn to these complexes because of the stabilization of the unusual [6] oxidation state of gold (Au(II)) as well as the formation of a Au–Au bond. Additional interest in the reaction of alkyl halides with **1** results from stability of the Au–C bond formed.

Our interest in the reaction chemistry of halomethanes with **1** began several years ago with the complete structural characterization [7] of $[Au(CH_2)_2PMe_2]_2(Me)I$. In addition to the discovery of a greatly enhanced structural *trans* effect caused by the methyl group, an effect enhanced by the Au–Au bond [7], it was also recognized that $[Au(CH_2)_2PMe_2]_2(Me)I$ is in equilibrium [8] with the gold(I) dimer $[Au(CH_2)_2PMe_2]_2$, and MeI. Continuing the study of halomethanes, the reaction of **1** and $CHBr_3$ was examined. With the spectroscopic characterization of $[Au(CH_2)_2PPh_2]_2(CHBr_2)Br$ a general pattern of reactivity of **1** with halomethanes has been recognized.

Due to the reported photosensitivity [6–8] of $[Au(CH_2)_2PPh_2]_2(Me)I$, MeBr and MeCl were reacted* with **1**. The former yielded $[Au(CH_2)_2PPh_2]_2(Me)Br$ (**2**); no oxidative-addition occured in the case of MeCl even after several days of reaction time. In the series of halomethanes, the order of reactivity (I > Br > Cl) follows inversely the order of carbon–halogen bond dissociation energies [9], C–Cl > C–Br > C–I.

In 1982 Schmidbaur and coworkers [10] characterized the reaction product between the gold(I) dimer and CH_2Cl_2. A bridging methylene Au(III) A-frame complex was obtained. Furthermore, they later reported [11] that no intermediate was observed in this remarkable two-center four-electron oxidative-addition reaction.

Taking advantage of the different reactivity of the halogens, separate experiments showed that **1** reacted with neat CH_2ClBr [12] and CH_2ClI [13]. In both cases, the initial product is a Au(II) alkyl halide adduct, $[Au(CH_2)_2PPh_2]_2(CH_2Cl)X$, (X = Br, **3**; X = I, **4**). Both of these intermediates have been characterized structurally. As in the case of the reaction of **1** with CH_2X_2 (X = I, Br, Cl), when **3** and **4** are allowed to react further with CH_2ClBr and CH_2ClI respectively, bridging methylene gold(III) A-frame products result. In these reactions the order of reactivity** for CH_2ClX or CH_2X_2 with **1** is I > Br > Cl.

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*MeI and **1** react in benzene in the time of mixing, MeBr and **1** require 18 h of reaction time to generate the Au(II)-MeBr adduct. After 4 days of reaction between excess MeCl and **1** in benzene only the parent Au(I) dimer was recovered with no observation of $[Au(CH_2)_2PPh_2]_2(Me)Cl$ adduct or $[Au(CH_2)_2PPh_2]_2Cl_2$.

The reaction of **1 with neat CH_2I_2 to give the bridging methylene Au(III) A-frame complex occurs in the time of mixing. The analogous reaction with CH_2Br_2 takes approximately 2 h at 25 °C. Complex **1** and CH_2Cl_2 must be refluxed (40 °C) for 4 days in order to generate the Au(III) A-frame product.

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The reactivity of CHX_3 with **1** is of considerable interest if, for no other reason, than many ^1H NMR spectra had been obtained in $CDCl_3$. Iodoform and **1** give $[Au(CH_2)_2PPh_2]_2I_2$ in the time of mixing. However, the reaction of **1** in benzene with excess $CHBr_3$ produced the new complex $[Au(CH_2)_2PPh_2]_2(CHBr_2)Br$ (**5**) which has been isolated and characterized spectroscopically.

The ^1H NMR spectrum of **5** is that of a asymmetrically substituted Au(II) complex (Fig. 1(a)). The assignment of the ^1H NMR spectra is based on a variety of analogous complexes for which the structure has been obtained (Fig. 1(b)). The doublet (J_{HP} = 10.5 Hz) at 1.90 ppm is assigned to the ring methylene protons proximal to the Br, the doublet (J_{HP} = 10.5 Hz) at 1.71 ppm is assigned to the methylene protons proximal to the $CHBr_2$ moiety.

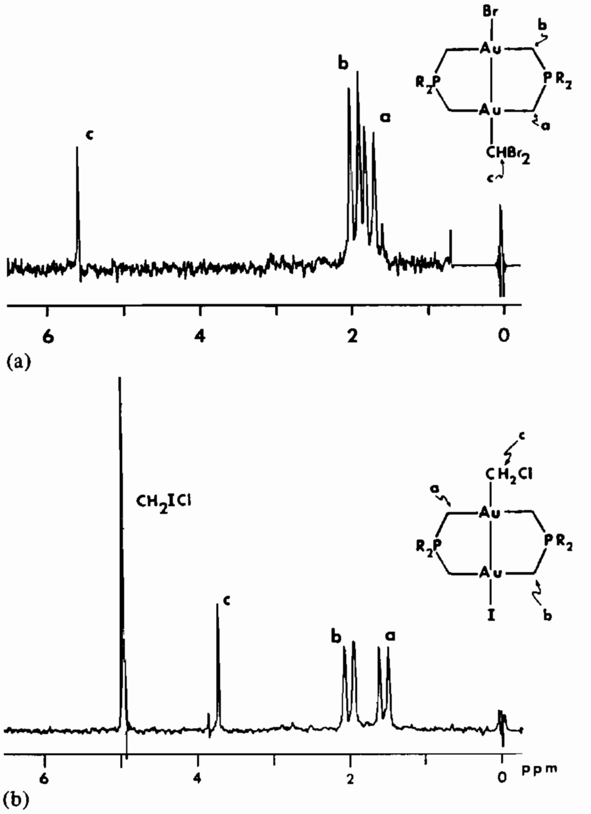
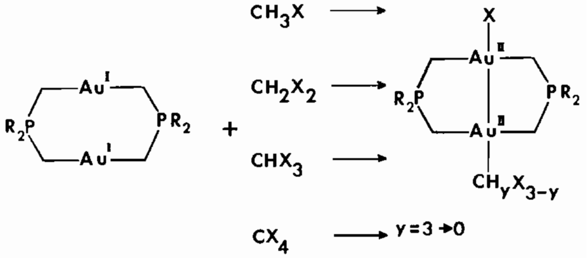


Fig. 1. (a) The methylene region from the ^1H NMR spectrum (90 MHz, 35 ℃, $CDCl_3$, reference TMS) of $[Au(CH_2)_2PPh_2]_2(CHBr_2)Br$ (**5**), δ = 1.90 and 1.71 (d, J_{HP} = 10.5 and 10.5 Hz respectively, $AuCH_2P$), 5.56 (s, $AuCHBr_2$). (b) The methylene region of the the ^1H NMR spectrum (90 MHz, 35 ℃, $CDCl_3$, reference TMS) of $[Au(CH_2)_2PPh_2]_2(CH_2Cl)I$ (**4**), δ = 1.55 and 2.00 (d, J_{HP} = 11.4 and 11.1 Hz respectively, $AuCH_2P$), 3.72 (s, $AuCH_2Cl$). Complex **4** has been structurally characterized [13].

The reactivity of **1** with the $y = 0$ member of the CH_yX_{y-4} series, CCl_4, yielded some very interesting chemistry [14]. One product is the Au(II) perhalogenated alkyl halide adduct $[Au(CH_2)_2PPh_2]_2(CCl_3)Cl$ (**6**), formed from the reaction of **1** and neat carbon tetrachloride. This adduct has also been structurally characterized [14].

Taken together, the results of this extensive investigation clearly demonstrate three important things. First and foremost, $[Au(CH_2)_2PPh_2]_2$ reacts with all the halomethanes via oxidative-addition across a carbon–halogen bond to give Au(II) alkyl halide products, see Scheme 1. Second, the order of reactivity of **1** with CH_yX_{y-4} (y = 3,2,1,0; X = I, Br, Cl) inversely follows the order of carbon–halogen bond dissociation energies of haloalkanes. Third, and perhaps the reason this pattern in reactivity has gone unobserved until now, it is the further reactivity of the Au(II) alkyl halide adduct $[Au(CH_2)_2PPh_2]_2(CH_yX_{y-3})X$ that governs or dictates the 'final product' observed in these reactions.



Scheme 1.

Specifically, note the observation [10] of the bridging methylene Au(III) adducts $(\mu\text{-}CH_2)[Au(CH_2)_2PPh_2]_2X_2$ formed from the reaction of $[Au(CH_2)_2PPh_2]_2$ and CH_2X_2 (X = Br, Cl, I). Note also that the reaction of CCl_4 and **1** was first reported [8] to give $[Au(CH_2)_2PPh_2]_2Cl_2$, not the perhalogenated alkyl halide adduct.

With the initial step in the oxidative-addition reaction of alkyl halides with **1** now better understood, further reactions of $[Au(CH_2)_2PPh_2]_2(CH_yX_{y-3})X$ with other alkyl halides and small molecules are being investigated.

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