Inorganica Chimica Acta, 126 (1987) 7–10

Symmetrical Ring Cleavage of the Gold(I) Phosphorus Ylide Dimer $[Au(CH_2)_2PPh_2]_2$ by Hydrogen Halides in Toluene

HOWARD C. KNACHEL*, COLLEEN A. DETTORRE, HENRY J. GALASKA, TERESE A. SALUPO
Department of Chemistry, University of Dayton, Dayton, Ohio 45469, U.S.A.
JOHN P. FACKLER, Jr. and H. H. MURRAY
Department of Chemistry, Texas A&M University, College Station, Tex. 77843, U.S.A.

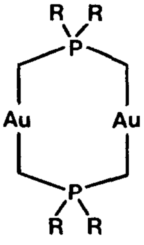
(Received May 26, 1986)

Abstract

The reaction of the cyclic, 8-membered gold(I) ylide dimer, bis[μ-(dimethylenediphenylphosphoranyl-C,C)]-digold(I), $[Au(CH_2)_2PPh_2]_2$, with two moles of HX (X = Cl, Br) in toluene yields the symmetric cleavage product halo(methylmethylenediphenylphosphoranyl)-gold(I), $X-Au-CH_2PPh_2(CH_3)$, as the only isolable gold containing product. Further addition of HX affords a dimethyldiphenylphosphonium dihaloaurate(I) salt.

Introduction

The chemistry of gold phosphorus ylide dimers, first synthesized by Schmidbaur [1], has received attention recently due to their interesting oxidative addition and reductive elimination reactions [2]. The gold(I) dimers, **1**, react with halogens [3], alkyl halides [4], peroxides [5], disulfides [6], and other reagents [7], to yield gold(II) species, **2**, possessing a Au–Au bond. Dimeric gold(III) species, with and without a bridging ligand (**3** and **4**), have also been recently characterized [5, 7, 8].



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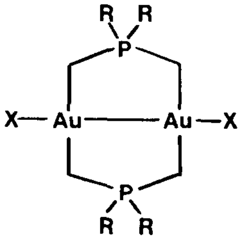

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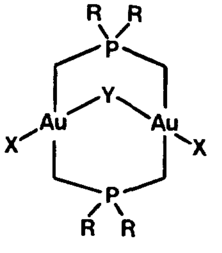

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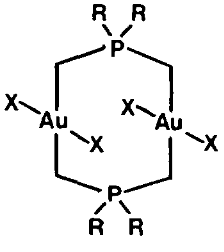

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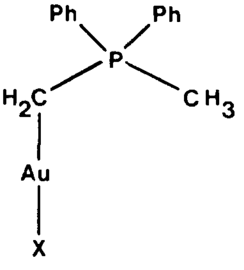
Continuing our investigations involving oxidative addition of small molecules to the Au(I) dimer species, bis[μ-dimethylenediphenylphosphoranyl-C, C)]digold(I) (**1**) with ($R = C_6H_5$), we have undertaken its reaction with hydrogen halides under conditions of controlled addition of HX(g). The possibility that a stable species containing the H–Au–Au–X unit could be isolated, was not realized. Rather, symmetrical cleavage of the 8-membered ring occurs by protonation of two transannular methylene groups and formation of Au–X bonds, **5**.



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Experimental

The gold(I) dimer, **1**, was prepared as described elsewhere [3, 4c]. The recrystallized material melted at 237 °C [3, 9].

Hydrogen chloride (Matheson) and hydrogen bromide (Airco) were used after several fractionations through a −96 °C U-trap. The purity was checked by gas phase infrared spectroscopy using a 10 cm cell fitted with NaCl windows. Deuterium chloride was prepared by reaction of freshly sublimed PCl_5 with

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*Author to whom correspondence should be addressed.

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99.96 atom% D_2O (Aldrich). The vacuum system was flamed prior to generation of DCl to eliminate traces of H_2O. The product was fractionated several times, as above, to remove traces of $POCl_3$, the product of incomplete hydrolysis. Difficulty was encountered in obtaining a clean infrared spectrum of DCl, free of HCl. It was determined that the major source of HCl was H-D exchange from moisture in the salt windows of the IR cell. Heating the windows to 400 °C, under vacuum, reduced significantly the amount of H-D exchange. In addition, the vacuum line and the IR cell were exposed to D_2O vapors for several hours after the heat treatments. Thereafter, additional flaming of the vacuum system followed by pumping was used to insure minimal availability of adsorbed H_2O in the system.

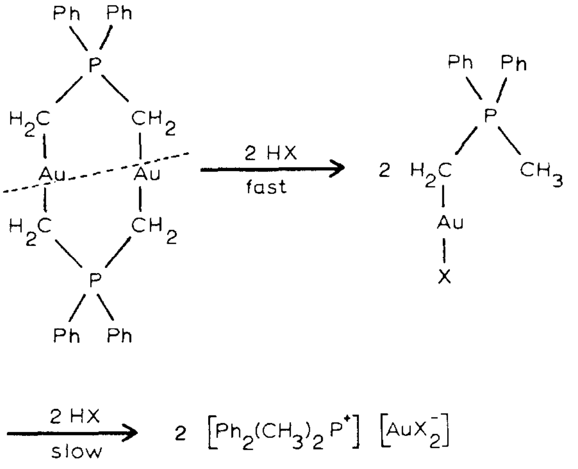
Reactions of the gold(I) dimer, **1**, with measured amounts of HCl(g), DCl(g), and HBr(g) were performed in freshly distilled toluene, utilizing a calibrated vacuum line [10] employing a mercury diffusion pump. In a typical reaction, 0.200 mmol of **1** was accurately weighed and placed into a reaction vessel with 5 ml of toluene. The mixture was degassed by 3 freeze-pump-thaw cycles, and stirred via a internal, solenoid-activated stirrer. Gases were added from the calibrated vacuum line by vapor transfer utilizing liquid nitrogen coolant. Optimum conditions for the production of **5** are: HCl and DCl, 80 °C for 3 h; HBr, room temperature for 3 h. A mole ratio, not exceeding 2:1, HX:**1**, avoids the occurrence of a secondary, much slower, reaction that generates the fully cleaved and protonated $[Me_2Ph_2P^+][AuX_2^-]$ salt.

A tensimetric titration of **1** with HBr(g) was performed by addition of small increments of HBr(g) to 0.163 mmol of **1** in toluene. After each addition of HBr(g), the stirred sample was heated to 40 °C for 30 min, cooled to 0 °C, and the pressure within the tensimeter [10] was measured after equilibration (15 to 30 min).

Proton NMR spectra were recorded on a Perkin-Elmer R24A spectrometer utilizing TMS as an internal standard. NMR solvents, $CDCl_3$ (Norell) and $C_6H_5NO_2$ (Fisher), were used without further purification. Infrared spectra were recorded on a Perkin-Elmer 283 Infrared Spectrophotometer. Solid samples were prepared as CsI (Alfa) pellets.

Single crystal X-ray photographs were obtained using Enraf-Nonius precession and Weissenberg cameras with Cu radiation. Analysis of cone axis and zero and first layer diffraction patterns yielded the space group and cell parameters of **5**.

Results and Discussion



Two consecutive reactions were found to take place between **1** and HX. The stoichiometry of the 2:1 reaction was determined via a tensimetric titration (Fig. 1) and by recovering unreacted HCl and weighing it as $(CH_3)_3NHCl$. *Anal.* Calc. for **5**, $Cl{-}Au{-}CH_2P(C_6H_5)_2(CH_3)$: C, 37.65; H, 3.39. Found: C, 37.53; H, 3.56%. Melting point = 159 °C. Evidence for the structure of **5** is derived from X-ray diffraction, ^1H NMR, and infrared spectroscopy.

X-ray Diffraction

X-ray quality crystals of **5** (X = Cl) were obtained from a 2:1, HCl:**1**, reaction by recrystallization from toluene and benzene. The clear, thin plates, mounted with the fiber axis parallel to b, yielded the results

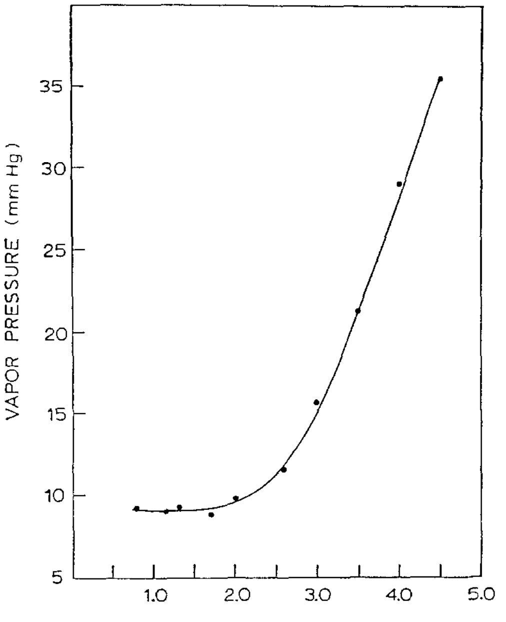


Fig. 1. Tensimetric titration of 1 with HBr(g) in toluene dispersing medium.

TABLE I. Unit Cell Parameters for the Chloro and Bromo Derivatives of 5

	$ClAuCH_2P(C_6H_5)_2(CH_3)$	$BrAuCH_2P(C_6H_5)_2(CH_3)$[a]
Space group	$P2_1/n$	$P2_1/n$
a (Å)	15.26	15.746(4)
b (Å)	11.80	11.930(4)
c (Å)	16.82	16.564(5)
β (°)	103.7	105.10(2)
V (Å^3)	2943	3004
D_{calc} (g cm^{-3})	2.02	2.17

[a] Ref. 11.

shown in Table I. The crystal is isomorphous with the analogous bromine derivative which has been structured recently by X-ray crystallography [11].

NMR Spectrum

The ^1H NMR spectrum of **5** has two doublets in the methylene/methyl region at 1.85 ppm and 2.27 ppm, $J = 13$ Hz, in the intensity ratio of 2:3. The product obtained from a reaction of deuterium chloride with **1** yields a NMR spectrum with the same chemical shifts and coupling constants, but the intensity ratio of the two doublets is 1:1 (Fig. 2). We conclude that deuterium is incorporated into the methyl group of chemical shift 2.27 ppm with slight broadening of the resonance. The fact that the methylene protons are upfield from the methyl protons of **5** suggests increased shielding by gold(I) compared to hydrogen. It is also instructive to note the position of the methylene chemical shift in **5** (1.85 ppm) compared to the methylene chemical shift in **1** (1.38 ppm). The halogen, *trans* to methylene in **5**, reduces the shielding effect of gold upon methylene.

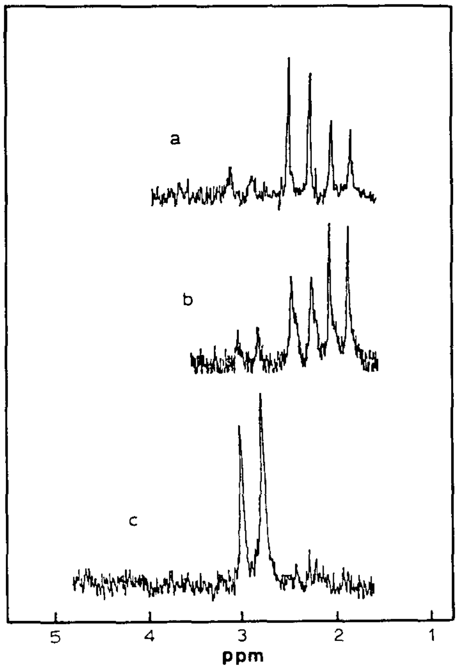


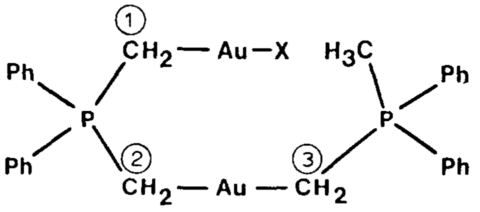
Fig. 2. ^1H NMR spectra of the products of reactions: (a) 3:1, HBr:**1**, 3 h at room temperature; (b) 3:1, DCl:**1**, 3 1/2 h at 82 °C; (c) 4:1, HBr:**1**, 40 h at 45 °C.

Infrared Spectrum

The infrared spectrum of **5** (X = Cl), and its deuterated analog, has a strong band at 290 cm^{-1}. The molecule **5** (X = Br) has a band at 210 cm^{-1}. We attribute these absorptions to Au–X, based on assignments made by McAuliffe [12], Westland [13], Schmidbaur [3], and Niera [14], for the compounds: $Ph_3P–Au–Cl$ [12, 13] (325, 330 cm^{-1}), $[Au(CH_2)_2PEt_2Cl]_2$ [3] (255 cm^{-1}), $[Au(CH_2)_2PPh_2Cl]_2$ [14] (288 cm^{-1}) and $[Au(CH_2)_2PPh_2Br]_2$ [14] (215 cm^{-1}). In addition, a simple reduced-mass calculation of the expected Au–Br frequency, using 290 cm^{-1} for Au–Cl, predicts a band at 200 cm^{-1} for Au–Br. Force constants of 2.07 mdyn/Å for Au–Cl and 1.86 mdyn/Å for Au–Br, published by Clark [15, 16] for the ions AuX_2^-, were used in this calculation.

The specificity of the reaction for production of the symmetrical cleavage product, **5**, may reflect the stabilizing influence of toluene on the molecular product – all other possible cleavage products being ionic. Inductive influences, on the other hand, may also play a role. Initial attack of HX may yield the intermediate **6**, although this species has not been observed. The second mole of HX must cleave one of the three remaining Au–C bonds. Positions 2 and 3 are more likely candidates for protonation than position 1 from an inductive argument and from the greater *trans*-labilizing ability of ylide *vs.* chlorine [17]. The formal ylidic ligand at position 3 might be expected to be more electron donating than the gold-halide containing ylide at position 2. The resulting negative charge on carbon atom 2 compared to carbon atom 3 presents a more electrophylic center for protonation leading to the observed product.

When mole ratios greater than 2:1, HX:**1**, are used, a second reaction takes place. The NMR spectra



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of Fig. 2 each contain evidence of the presence of the dimethyldiphenylphosphonium ion at ~2.9 ppm. This reaction is much slower than the initial cleavage reaction, presumably because the ionic product is not stabilized by the hydrocarbon medium, toluene.

Acknowledgements

The National Science Foundation, CHE8408414, the donors of the Petroleum Research Fund and The Welch Foundation have supported the work at Texas A&M University. H.C.K. wishes to thank D. W. Johnson for comments on the text, and the University of Dayton for research support.

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