Communications

Bridging (Methylene)gold(III) Ylide Dimers: The Reactivity of and a Possible Intermediate Involved in Its Generation

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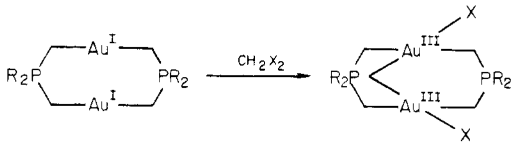
Summary: The reaction of neat $CH_2X'X$ (X = Cl, X′ = Br, I) with $[Au(CH_2)_2PPh_2]_2$ initially gives the dinuclear Au(II) alkyl halide $[Au(CH_2)_2PPh_2]_2(CH_2X)X'$ that has been characterized in solution and by X-ray crystallography. Upon standing in this solvent the Au(II) alkyl halide adduct gives the bridging (methylene)gold(III) ylide dimer. The bridging (methylene)gold(III) complex undergoes a halogen substitution reaction with AgE (1:2) (E = CN, SCN, OOCPh). Diazomethane addition to $[Au(CH_2)_2PPh_2]_2Br_2$ gives $(\mu\text{-}CH_2)[Au(CH_2)_2PPh_2]_2Br_2$.

The addition of dihalomethanes to dinuclear metal complexes can be a useful entry into the chemistry of bridging methylene complexes (eq 1).[1,2] This is certainly



(1)

the case regarding the dinuclear gold(I) ylide complexes $[Au(CH_2)_2PR_2]_2$ (R = Ph,[3] Me,[4] and *t*-Bu[5]). We have found nothing in the literature suggesting possible intermediates involved in this overall four-electron, two-center oxidative addition reaction of $[Au(CH_2)_2PR_2]_2$ and CH_2X_2. There is also no reported chemistry of these remarkably stable[4] (μ-methylene)gold(III) dinuclear ylide dimers. We report now the formation of a dinuclear gold(II) ylide complex that appears to be an intermediate in this overall four-electron, two-center oxidative addition reaction. We also describe some of the chemistry of the (μ-methylene)gold(III) dinuclear ylide dimer as well as the synthesis of the (μ-methylene)gold(III) dimer with diazomethane.

The reaction of neat $CH_2X'X$ (X = Cl, X′ = Br, I) with $[Au(CH_2)_2PPh_2]_2$, 1, appears to give $(\mu\text{-}CH_2)[Au(CH_2)_2PPh_2]_2X'X$ (X = Cl, X′ = I, 3) and (X = Cl, X′ = Br, 4) in quantitative yield in less than 16 h[6] at 22 °C.

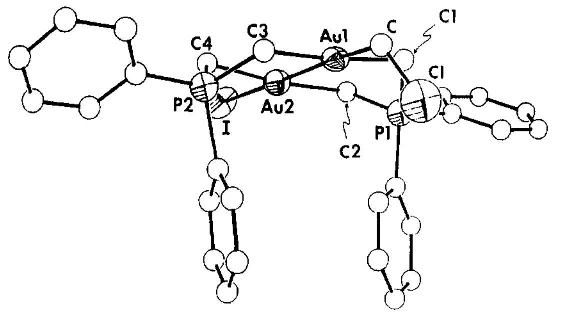
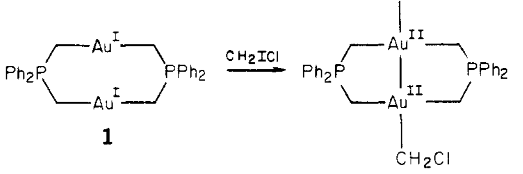


Figure 1. Molecular structure of 2, $[Au(CH_2)_2PPh_2]_2(CH_2Cl)(I)$, hydrogen atoms are omitted for clarity (50% probability thermal ellipsoids). Selected bond lengths: Au(1)–Au(2) = 2.681 (3) Å, Au(2)–I = 2.858 (4) Å, Au(1)–C = 2.00 (4) Å, C–Cl = 1.75 (4) Å, Au(1)–C(1) = 2.03 (5) Å. Selected bond angles: Au(1)–Au(2)–I = 179.1 (1)°, Au(2)–Au(1)–C = 177.6 (1.3)°, C(2)–Au(2)–C(4) = 177.3 (1.7)°, C(1)–Au(1)–C(3) = 174.5 (1.7)°, Au(1)–C–Cl = 115.6 (2.1)°, C(1)–Au(1)–Au(2) = 93.0 (1.0)°.

Furthermore, when CH_2ClI and 1 are combined, the stable gold(II) intermediate $[Au(CH_2)_2PPh_2]_2(CH_2Cl)I$, 2, can be isolated[7] in near quantitative yield as a yellow-orange powder by immediately reducing the volume and precipitation of the intermediate with hexane (eq 2).



1

2

(2)

Initial characterization of 2 came from the comparison of the ^1H NMR spectrum of 2 with the ^1H NMR spectrum of the well-characterized[8] Au(II) alkyl halide $[Au(CH_2)_2PPh_2]_2(CH_3)I$, 5 (average C_{2v} symmetry), and the spectrum of the product from the reaction (1 h) of 1 with CH_2ClBr. The chemical shift difference between the ^1H NMR resonances of the $Au{-}CH_2X$ moiety in each is 0.04 ppm. As the nature of the halide X will dominate the chemical shift of these methylene portons, X in both intermediates is concluded to be Cl. Confirmation of our interpretation of the ^1H NMR spectrum of the intermediate 2 was obtained from the X-ray crystal structure[9] of

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(1) Herrmann, W. A. *Adv. Organomet. Chem.* **1982**, *20.*

(2) (a) Summer, C. E., Jr.; Riley, P. E.; Davis, R. E.; Pettit, R. *J. Am. Chem. Soc.* **1980**, *102*, 1752. (b) Pettit, R. Int. Symp. Homogeneous Catal. 2nd Dusseldorf 1980. (c) Theopold, K. H.; Bergman, R. G. *J. Am. Chem. Soc.* **1980**, *102*, 5694. (d) King, R. B.; Saran, M. S. *Ibid.* **1973**, *95*, 1811. (e) Balch, A. L.; Hunt, C. T.; Lee, C.-L.; Olmstead, M. M.; Farr, J. P. *J. Am. Chem. Soc.* **1981**, *103*, 3764.

(3) This work (vida infra).

(4) (a) Jandik, P.; Schubert, U.; Schmidbaur, H. *Angew. Chem.* **1982**, *94*, 74. (b) Schmidbaur, H. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 907.

(5) Jandik, P.; Schmidbaur, H. *Inorg. Chim. Acta* **1975**, *13*, 84.

(6) Schmidbaur reports[4] the reaction of CH_2Cl_2 with $[Au(CH_2)_2P(CH_3)_2]_2$ to give the bridging methylene complexes takes 3 days at room temperature, 65% yield.

(7) **2**: ^1H NMR ($CDCl_3$, Me_4Si internal, 90 MHz, 36 °C) δ 1.55 and 2.00 (d, J_{HP} = 11.4 and 11.1 Hz, respectively, $AuCH_2P$), 3.72 (s, $AuCH_2Cl$), 7.8–7.6 (m, Ph).

(8) Fackler, J. P., Jr.; Basil, J. D. *Organometallics* **1982**, *1*, 871.

(9) A crystal of intermediate **2** was obtained by layering a CH_2Cl_2 solution of the complex with hexanes. Complex **2** crystallized with a methylene chloride molecule in the lattice. Loss of this solvent molecule during data collection (Wyckoff scan) resulted in a decay (ca. 43%) of intensity of the check reflections. Crystallographic data: $C_{29}H_{30}Au_2IClP_2$, triclinic of space group $P\bar{1}$ (No. 2); a = 13.003 (3) Å, b = 13.370 (4) Å, c = 10.0605 (21) Å, α = 103.401 (19)°, β = 100.954 (19)°, γ = 90.263 (22)°, V = 1668.3 (7) Å^3; ρ_{calcd} = 1.98 g/cm^3; Z = 2, Mo K_α = 98.76 cm^{-1}. Intensity data (2287 reflections $3 \leq 2\theta \leq 35$, $\pm h,k,\pm l$) were recorded on a Nicolet P3/F diffractiometer at ambient temperature with graphite-monochromated Mo K_α radiation. The 1246 independent reflections with $I > 3.0^\sigma (I)$ were corrected for Lorentz, decay, polarization, and absorption effects. With 145 parameters, R = 0.057, R_w = 0.048, and goodness-of-fit = 1.427. Maximum shift/esd = 0.004. All calculations were performed by using the SHELXTL crystallographic computational package (version 4.1) installed on a Data General Eclipse S140 minicomputer.

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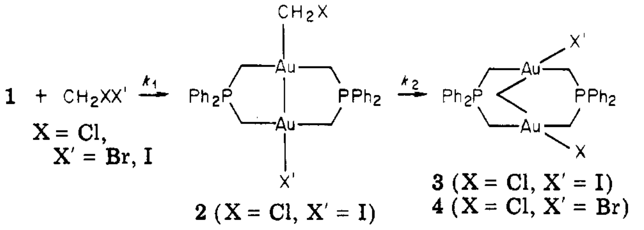
this gold(II) alkyl halide complex. The molecular structure of $[Au(CH_2)_2PPh_2]_2(CH_2Cl)I$, **2**, which was determined in this study, is shown in Figure 1.

We suggest that CH_2X_2 (X = Cl, Br, I) and $CH_2X'X$ (X = Cl, X' = Br, I) react in a similar fashion as both react with **1** to give $(\mu\text{-}CH_2)[Au(CH_2)_2PPh_2]_2X'X$ (X = X' or X ≠ X') (eq 3). The formulation of the final product in these reactions as the mixed halogenated species **3** and **4** is tentative as further rearrangement probably occurs. The final product could be equal molar mixtures of the dichloride and the diiodide in the CH_2ClI reaction and equal molar mixtures of the dichloride and dibromide in the CH_2ClBr reaction. Preliminary low-temperature ^1H NMR investigations reveal only two doublets of doublets, suggesting rapid exchange of the halides.



2 (X = Cl, X' = I)
3 (X = Cl, X' = I)
4 (X = Cl, X' = Br)

(3)

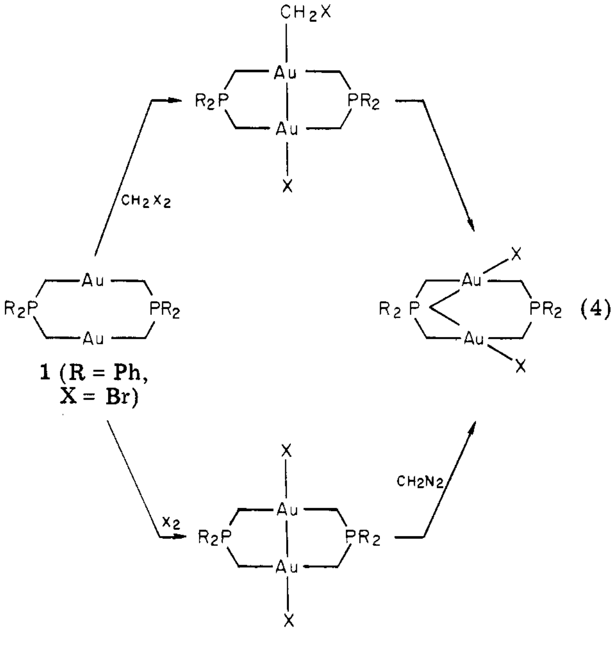
A qualitative interpretation of the kinetics governing this reaction suggests that for the reaction of **1** with CH_2ClI, the rate-limiting step is the formation of **3** from **2**. The reaction of CH_2X_2 (X = Cl, Br, and I) with **1** could proceed via this same pathway and yet be consistent with reported[5] observations if the observed rate of formation of the bridging (methylene)gold(III) ylide dimer is sufficiently fast that no appreciable concentration of the dinuclear gold(II) alkyl halide intermediate ever builds up and consequently is not observed.[10]

The substitution of the halides in **4** for other anions was carried out by the facile reaction of $(\mu\text{-}CH_2)[Au(CH_2)_2PPh_2]_2Cl(Br)$, **4**, with AgE (1:2) (E = CN, SCN, O_2CPh). The new complexes obtained possess characteristic ^1H NMR and IR spectra and were readily identified. A crystal structure of the cyanide adduct conclusively characterized the product.[11]

The bridging methylene complex derived from the reaction of **1** and CH_2Cl_2 does not undergo[12] facile hydrogen exchange when dissolved in CF_3COOD (by ^1H NMR spectroscopy).

The reaction of **4** with the anionic nucleophile KI results in halogen exchange and not nucleophilic addition of I^- to the bridging methylene unit.[13] The addition of KCN to $(\mu\text{-}CH_2)[Au(CH_2)_2PPh_2]_2Cl_2$ in THF produced no reaction. In view of the facile oxidative addition of bromoacetonitrile to the gold(I) dimer **1** to give the gold(II) methylene cyanide bromide adduct,[11,16] this observation was unexpected.

The addition of diazomethane to $[Au(CH_2)_2PPh_2]_2Br_2$ in THF at −78 °C gives the bridging (methylene)gold(III) complex $(\mu\text{-}CH_2)[Au(CH_2)_2PPh_2]_2Br_2$.[17] This reaction offers an alternate synthetic route to bridging methylene complexes (eq 4). The diazomethane reaction again demonstrates the achievement of an overall two-center, four-electron oxidative addition reaction in two-electron steps.



1 (R = Ph, X = Br)

5

(4)

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Registry No. **1**, 81457-56-9; **2**, 90742-62-4; **3**, 90762-78-0; **4**, 90762-79-1; **4** (X = X' = CN), 90914-55-9; **4** (X = X' = SCN), 90914-54-8; **4** (X = X' = O_2CPh), 90941-99-4; $(\mu\text{-}CH_2)[Au(CH_2)_2PPh_2]_2Cl_2$, 90742-63-5; $(\mu\text{-}CH_2)[Au(CH_2)_2PPh_2]_2Br_2$, 90742-64-6; $[Au(CH_2)_2PPh_2]_2(CH_2CN)(Br)$, 90742-65-7; CH_2ClBr, 74-97-5; CH_2ClI, 593-71-5; $[Au(CH_2)_2PPh_2]_2Br_2$, 89462-50-0.

Supplementary Material Available: Tables of atomic coordinates, anisotropic temperature factors, hydrogen coordinates, and structure factors (11 pages). Ordering information is given on any current masthead page.

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[10] Schmidbaur and Jandik[5] report that no Au–Au bonded intermediates was observed in the reaction of CH_2X_2 (X = Cl, Br, I) with the dinuclear gold(I) ylide.

[11] Murray, H. H.; Fackler, J. P., Jr.; Mazany, A. M., submitted for publication.

[12] In the original[4] report of these bridging methylene complexes by Schmidbaur some of the ^1H NMR spectra were obtained in CF_3COOH.

[13] Another related observation we have made comes from the reaction of **1** with excess Cl_2CO in benzene. In this reaction dinuclear gold(II) dichloride complex is obtained. No bridging CO complex analogous to the dinuclear bridging CO complexes of Balch et al.[14] with Pd diphos dimers or Puddephatt et al.[15] with the Pt diphos dimers is obtained. The CO addition reaction to gold(II) dimers in under study.

[14] (a) Pignolet, L. H. "Homogeneous Catalysis with Metal Phosphine complexes" Modern Inorganic Chemistry Series, Plenum Press: 1983% see Chapter 5 (Alan L. Balch), p 167. (b) Balch, A. L.; Hunt, C. T.; Lee, C.-L.; Olmstead, M. M.; Farr, J. P. *J. Am. Chem. Soc.* **1981**, *103*, 3764.

[15] (a) Brown, M. P.; Puddephatt, R. J.; Rashidi,: Seddon, K. R. *J. Chem. Soc., Dalton Trans.* **1978**, 1540. (b) Brown, M. P.; Keith, A. N.; Manojlovi-Muir, Lj.; Muir, K. W.; Puddephatt, R. J.; Seddon, K. R. *Inorg. Chim. Acta* **1979**, *34*, 1223.

[16] The addition of excess $BrCH_2CN$ to a CH_2Cl_2 solution of $[Au(CH_2)_2PPh_2]_2$ gives the dinuclear Au(II) ylide adduct $[Au(CH_2)_2PPh_2]_2(CH_2CN(Br)$ as a yellow powder upon workup (reduce volume then precipitate and wash product with hexane). ^1H NMR ($CDCl_3$, 90 MHz, 36 °C) δ 1.54 and 1.89 (d, J_{HP} = 9.0 and 10.5 Hz, respectively, $AuCH_2P$), 2.12 (s, $AuCH_2CN$); 7.8–7.2 (m Ph). The X-ray crystal structure of the product[11] conclusively characterized the complex as a dinuclear Au(II) ylide adduct.

[17] The ^1H NMR spectrum of the crude reaction mixture obtained from the diazomethane reaction clearly showed the pair of doublets of doublets (J_{HP} about equal to J_{HH}) for the methylene resonances of $(\mu\text{-}CH_2)[Au(CH_2)_2PPh_2]_2Br_2$ to be the major component. ^1H NMR ($CDCl_3$, 36 °C, 90 MHz): δ 2.60 and 1.68 (dd, 12.7 Hz and 11.2 Hz, respectively, $AuCH_2P$, 2.58 (s, $\mu\text{-}CH_2$), 7.8–7.6 (m, Ph). As this reaction was carried out to qualitatively demonstrate the two-electron oxidative addition of $[Au(CH_2)_2PPh_2]_2Br_2$ by CH_2N_2, the isolated yield was not measured.