Characterization of the Gold(II) Dimer $[Au(CH_2)_2PPh_2]_2(CH_2Cl)Br$: Structural Evidence suggesting the Formation of a Carbene Intermediate preceeding A-frame (Bridging Methylene) Formation

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$[Au(CH_2)_2PPh_2]_2$, (**1**), reacts with neat CH_2ClBr to give $[Au(CH_2)_2PPh_2]_2(CH_2Cl)Br$, (**2**), and the *X*-ray structure of (**2**) shows a close contact between one Au centre and the Cl of the co-ordinated CH_2Cl [2.895(16) Å]; this interaction is consistent with the observed further oxidative addition of the CH_2Cl to form the bridging methylene A-frame complex, and suggests that a carbene intermediate may be involved.

Further elaboration of the mechanism of oxidative addition of dinuclear complexes by alkyl halides is very desirable. The role of the second metal centre is not fully understood.[1] Of particular interest to us has been the reaction of dihalogenomethanes with $[Au(CH_2)_2PPh_2]_2$, (**1**). This reaction gives a gold(III) bridging methylene complex in near-quantitative yields (>95%).[2] Overall the four-electron oxidation (oxidative-addition) involves both metal centres. Significant electronic and structural reorganization accompanies this process. Other than recent papers by Fackler and co-workers,[3a] Espenson,[3b], and Eisenberg[3c] there is no information regarding the species involved or mechanistic aspects of this chemistry.

$[Au(CH_2)_2PPh_2]_2$
(**1**)

$[Au(CH_2)_2PPh_2]_2(CH_2Cl)Br$
(**2**)

The addition of 10—20 mg of (**1**) to approximately 5 ml of neat CH_2ClBr at 20 °C produces $[Au(CH_2)_2PPh_2]_2(CH_2Cl)Br$, (**2**), nearly quantitatively after about one hour (^1H n.m.r. spectroscopy). However, after *ca.* 45 minutes, the gold(III) bridging methylene complex, $(\mu\text{-}CH_2)[Au(CH_2)_2PPh_2]_2Br_2$, can be detected in the solution [δ 2.58 (s, μ-CH_2)] as (**2**) begins to disappear. Orange crystals of (**2**) for *X*-ray diffraction[†] are obtained by dissolving (**1**) in about 5 ml CH_2ClBr in a vial and immediately placing the vial into a closed larger vial with diethyl ether which can slowly vapour diffuse into the sample at room temperature. The *X*-ray structure of (**2**), Figure 1, shows three significant features that are consistent with an interaction between one Au centre and the Cl of the co-ordinated CH_2Cl.

In (**2**), the Au $\cdots$ Cl distance is observed to be 2.895(16) Å. This is only 17% greater than the sum of the covalent radii[4] of Au and Cl (1.50 and 0.99 Å respectively). Other structures not

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[†] *Crystal data:* for $[Au(CH_2)_2PPh_2]_2(CH_2Cl)Br$, (**2**), $C_{29}H_{30}P_2ClBrAu_2$, $M = 949.53$, monoclinic, space group $C2/c$, $a = 13.422(3)$, $b = 12.370(2)$, $c = 17.686(4)$ Å, $\beta = 103.25(14)°$, $U = 2858.3(8)$ Å^3, $D_c = 2.20$ g cm^{-3}, $\mu(\text{Mo-}K_\alpha) = 122.2$ cm^{-1}, $Z = 4$, $\lambda = 0.71073$ Å, crystal dimensions $0.3 \times 0.25 \times 0.20$ mm^3, $R = 0.057$ and $R_w = 0.056$ for 1601 reflections with $F > 3\sigma(F)$, 157 parameters refined, collected at 22 °C on a Nicolet P3F four-circle diffractometer, crystallographic computations, SHELXTL. The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road. Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

showing any connectivity between the Au centre and a halogen or pseudo halogen on the carbon of the alkyl moiety in the dinuclear gold(II) complex have been observed in our laboratory. The Au $\cdots$ E distances are given in Table 1 for four[5] gold(II) complexes (**3**)—(**6**) of the type $[Au(CH_2)_2PPh_2]_2(CH_2E)X$, where E = CN, CF_3, or Cl and X = halide. In each case note that there is approximately a 30% increase in the Au–halide distance beyond the sum of the covalent radii. These distances are roughly 45% greater than the anomalously short Au $\cdots$ Cl distance observed in (**2**). The C–Cl distance in (**2**) is comparable with analogous distances in (**5**) and (**6**).[5b]

A second significant structural feature observed in (**2**) is the small Au–C–Cl angle of 96.2(14)°. This is 13.3° smaller than the 109.5° angle for an sp^3 carbon centre (see Figure 1). The analogous angles in the complexes referred to in Table 1 are all greater than 109.5°, additional evidence for the unique structural feature observed in (**2**).

Finally, the Au–Au–C angle is only 166.7°. This is 10° smaller than the angle found in other Au^{II} complexes.[5,6]

The structural features of (**2**) are like those expected for an intermediate in a intramolecular process which leads to the bridging methylene gold(III) product (Scheme 1). The 'agostic' halide present is reminiscent of (but not electronically like) agostic hydrides often[7] associated with C–H insertion

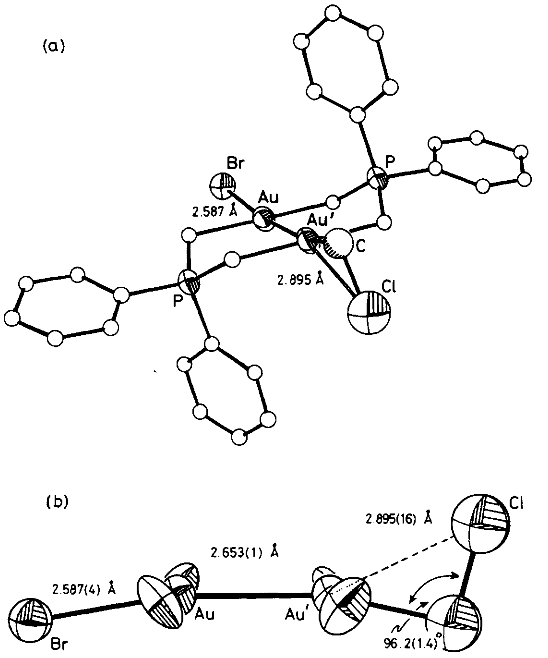
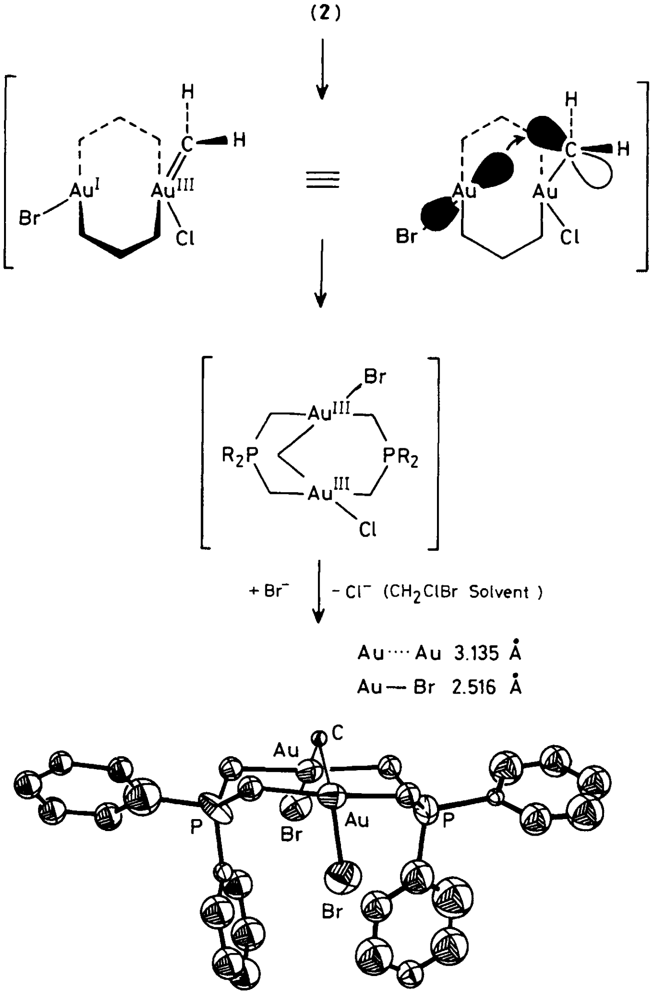


Figure 1. (a) Molecular structure of (**2**). Hydrogen atoms omitted for clarity (50% probability thermal ellipsoids). Selected bond lengths: Au–Au' 2.653(1), Au–Br 2.587(4), Au'$\cdots$Cl 2.895(16), Au–C 2.10(3), C–Cl 1.78(4) Å. Selected bond angles: Br–Au–Au' 171.1(1), Au–Au'–C 166.7(9), Au'–C–Cl 96.2(14)°. (b) Br–Au–Au'–CH_2Cl backbone of (**2**) (with ring methylene carbon atoms present) showing significant distances and angles (50% probability thermal ellipsoids).



Scheme 1

Table 1. Angles and distances of complexes related to (**2**).

Formula	Au $\cdots\cdot$ E	(Å)[a]	% Increase above sum covalent radii	Ref.	Au–C–E (°)	Au–Au–C (°)
$[Au(CH_2)_2PPh_2]_2(CH_2CF_3)I$ (**3**)	Au $\cdots\cdot$ C	3.000(1)	32	5a	115(1)	173.2(3)
$[Au(CH_2)_2PPh_2]_2(CH_2CN)Br$ (**4**)	Au $\cdots\cdot$ C	2.950(2)	30	5b	111(1)	176.8(4)
$[Au(CH_2)_2PPh_2]_2(CCl_3)Cl$ (**5**)	Au $\cdots\cdot$ Cl	3.310(1)	31	5b	114(1)	175.0(5)
$[Au(CH_2)_2PPh_2]_2(CH_2Cl)I$ (**6**)	Au $\cdots\cdot$ Cl	3.185(1)	28	3a	116(2)	178(1)

[a] Ref. 9.

processes. A gold(I)–gold(III) carbene[1c,8] (Fischer type) intermediate is postulated to form along with the Au–Cl at the Au^{III} centre prior to the rearrangement to the final A-frame product. The resulting *trans* configuration about Au^{III} is consistent with nucleophilic attack by the Au^{I} centre on the carbene carbon, leading to the product.

In the proposed intermediate the co-ordinated CH_2 moiety is formulated to be neutral with each ylide methylene on Au^{III} and the chloride having a formal -1 charge. The second gold centre therefore formally contains 3-co-ordinate Au^{I}. This formulation of the carbene as a planar 3-co-ordinate sp^2 centre is consistent with present knowledge[8] of Au-carbene species. In stabilized Au-carbene complexes, lone pairs from adjacent N and or O atoms allow for electron delocalization onto the carbene carbon.

A Fischer-type carbene formulation also appears to be consistent with the properties of the bridging methylene gold(III) product. H/D exchange on the (μ-CH_2) moiety of the bridging A-frame is not observed[3] in neat CF_3CO_2D. However, the A-frame can be reduced to (**1**) with lithium aluminium hydride. The mechanism of this reduction and other studies of the reactivity of the bridging methylene species are in progress.

Clearly, complex (**2**) possesses structural features suggestive of formation of the bridging methylene gold(III) product. The proposed mechanism of A-frame formation involves a two electron oxidation at the second metal centre. This work therefore addresses the role of the second metal atom centre in bimetallic oxidative addition.

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