Organometallics 1982, 1, 871-873

$(\eta^5\text{-}C_5H_5)_2(Cl)Zr[(OCCH)P(C_6H_5)_3]$,[14] which has been chemically but not structurally characterized would seem to be a close analogue of **2**. The second is an incompletely characterized product formed from the reaction of $(\eta^5\text{-}C_5H_5)_2(Cl)Ta{=}CH(C(CH_3)_3)$ with CO.[15] Since a structure of this molecule is not available, we can not yet compare our product with those from analogous reactions with alkylidenes.

Registry No. **1a**, 77357-86-9; **1b**, 77357-85-8; **2a**, 81388-97-8; **2b**, 81388-96-7.

Supplementary Material Available: Crystal and data collection data (Table I), nongroup atom positional and thermal parameters with standard deviations for $(\eta^5\text{-}C_5H_5)_3U(OCCH)P(CH_3)_2(C_6H_5)$ (Table III), positional and thermal parameters for group atoms (Table IV), and observed and calculated structure factors (Table V) (10 pages). Ordering information is given on any current masthead page.

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Oxidative Addition of Methyl Iodide to a Dinuclear Gold(I) Complex. The X-ray Crystal Structure of Bis[μ-(dimethyldimethylenephosphoranyl-*C*,*C*)]-iodomethyldigold(II)(*Au*-*Au*), $Au_2[(CH_2)_2P(CH_3)_2]_2(CH_3)I$

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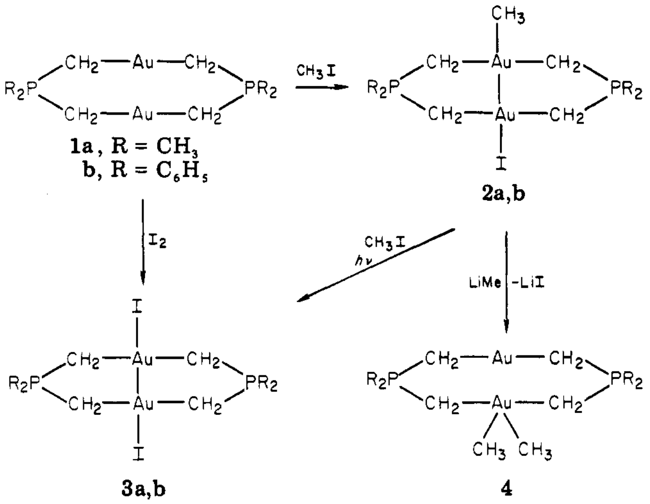
Summary: The oxidative addition of alkyl halides to dinuclear species may produce two-electron oxidation at a single center or one-electron oxidation at each of the two centers. X-ray crystallographic structural studies show that the product of CH_3I addition to dinuclear gold(I) ylide complexes occurs with the formation of one-electron oxidation at each center and a Au-Au band (2.695 (4) Å).

The oxidative addition of alkyl halides and related species to transition-metal complexes plays an important role in many M-C bond-forming reactions and transition-metal-mediated catalytic processes.[1] While oxidative addition has been studied in detail for reactions which occur at a single metal center,[1] few well defined examples involving two or more metal atom centers can be found. Gray and co-workers[2] have reported the oxidative addition of CH_3I to $Rh_2(bridge)_4^{2+}$, but only spectroscopic data exist concerning the nature of the product. Similarly Schmidbaur and co-workers[3] have reported that CH_3I adds to **1a** to produce **2a**. Due to the photosensitivity of the product, our initial attempts to reproduce these results (to obtain a crystalline product) failed. Instead **3a** was obtained along with **1a** and methylated products. The structures of both **1a** and **3a** have been determined previously in our laboratory.[4]

Scheme I



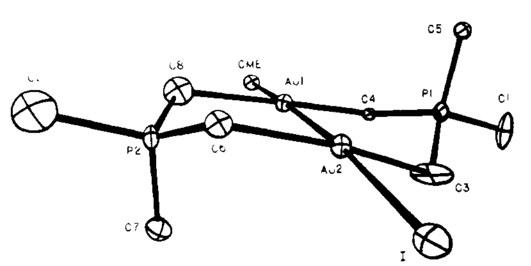


Figure 1. ORTEP drawing (50% probability) of bis[μ-(dimethyldimethylenephosphoranyl-*c*,*c*)]-iodomethyldigold(II)(Au-Au). Important distances (in Å): Au(1)-Au(2) = 2.695 (4); Au(1)-CMe = 2.13 (5); Au(2)-I = 2.894 (5); Au-CH_2(av) = 2.14; P-CH_2(av) = 1.70; P-CH_3(av) = 1.79. Some angles (in deg): CMe-Au(1)-Au(2) = 177.5 (1.9); Au(1)-Au(2)-I = 175.1 (2); C(4)-Au(1)-Au(2) = 90.4 (1.7); C(6)-Au(2)-Au(1) = 91.0 (2.0); C(6)-P(2)-C(8) = 112 (3).

Added incentive for a detailed structural characterization of **2** stems from the reported observation[19] that **2** reacts with $LiCH_3$ to produce the asymmetric mixed-valent species **4**.

Synthesis. The dimer **1a** was prepared by established methods.[3,5] Using the same procedure with Ph_2PMe (Strem), **1b** was also synthesized. The synthesis of **2a** and **2b** proceeded essentially as described,[3] except that rigorous precautions were taken to prevent solutions of the products from being exposed to light. Dry 1,2-dichloroethane (stored over P_4O_{10}) was used as the solvent. Products were isolated by first filtering, adding a twofold excess of dry ($CaCl_2$) heptane, and cooling the solution to −18 °C overnight. The resulting yellow crystalline products were washed (in air) with a few milliliters of cold toluene and then with diethyl ether: yield 60–70%; for **2a** mp 142–145 °C (lit.[3] 143 °C); for **2b** mp 172 °C dec. Anal. Calcd for

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0276-7333/82/2301-0871$01.25/0

2b, $C_{29}H_{31}P_2IAu_2$ (fw 962.35): C, 36.19; H, 3.25. Found: C, 35.97; H, 3.28.

FT ^1H NMR spectra were obtained on Varian XL-100 and HA-100 spectrometers. For monitoring the decomposition of **2b**, the solvent $CDCl_3$ (99.8%, Norell) was rigorously dried (refluxed over P_4O_{10}) and freeze–pump–thaw degassed. Samples were prepared and maintained in a N_2 atmosphere. For all other NMR spectra, $CDCl_3$ was dried over 4A molecular sieves.

X-ray Studies. Crystals of **2a** appear to be air and light stable. A clear yellow rectangular crystal 0.13 × 0.11 × 0.04 mm was attached to a glass fiber and centered optically on a Syntex $P2_1$ diffractometer. The structure, Figure 1, was determined by using 1567 reflections, $\theta \leq 25.0°$, $I/\sigma(I) > 3.0$, in a monoclinic cell[6] by standard crystallographic methods.[10]

Although initial phasing proceeded normally, convergence occurred with 1313 data, $\theta < 22.5$, not corrected for absorption, at $R = 0.146$ (aniostropic Au, I, and P). While no residuals greater than 2.0 e/A^3 appeared in the difference Fourier, the C atoms refined poorly. Some conformational disorder was suspected. Absorption corrections were applied to the data,[21] additional reflections to $\theta = 25.0°$ were added, and 118 axial or near axial reflections were removed which appeared to suffer from secondary extinction. With anomalous scattering corrections for Au and I and anisotropic thermal parameters for all 14 atoms, convergence occurred at $R = 0.109$ and $R_w = 0.106$. Unfortunately large thermal motions and/or disorder appear present in the refinement of many of the C positions, a rather common occurrence with gold structures.[23] Various models which included disorder, large anisotropic thermal motion, and even disorder within an acentric cell produced no improvement in the refinement statistics. More importantly, the basic coordination geometry of the Au_2C_5I fragment did not change by more than two standard deviations from the positions found with the original model using isotropic thermal parameters for the C atoms and anisotropic parameters for the Au, I, and P atoms. Thus we are confident that the bond lengths and angles for the core reported here are correct. A full description of the crystallographic treatment will be reported elsewhere.

The X-ray structure of **2a** confirms the formulation of the CH_3I oxidative addition product to **1a** as an iodomethyldigold(II) complex. The coordination geometry about each gold atom is square planar with a twist of ~8.9° between planes. No crystallographic symmetry is required but the molecular symmetry is approximately C_2. The Au(1)–Au(2) distance of 2.695 (4) Å is much shorter than the Au–Au distance[4] of 3.005 (3) Å in **1a** or in other[7] gold(I) bis(phosphonium ylide) dimers, 2.962–3.023 Å. It is similar in length[4] to the observed distance of 2.654 (4) Å in **3a** and the distance[8] of 2.597 Å in $Au_2Cl_2[(CH_2)_2P(C_2H_5)_2]_2$.

The Au–I bond length in **2a** is 0.20 Å longer than in **3a** where it is[4] 2.699 (8) Å. Surprisingly the structural trans effect due to the methyl group is not significantly attenuated by the Au–Au bond. A STE of similar magnitude is observed[9] in $Br_2Au(\mu\text{-}Br)_2AuMe_2$ where the bridging Au–Br bonds trans to methyl are ~0.15 Å longer than those trans to Br. The Au–CH_3 bond[10] in Me_3AuPPh_3 trans to CH_3 also is ~0.13 Å longer than the bond trans to PPh_3. The Au–CH_3 bond length in **2a** is normal (1.92–2.16 Å).[10-13]

The only other structurally characterized halomethyldimetal complexes are bromomethylbis$[(\mu\text{-}CO)(\eta^5\text{-}C_5H_5)Rh](Rh\text{-}Rh)$[14] and $[Pd_2(dpm)_2(\mu\text{-}I)I(CH_3)]BF_4$.[15] Both were prepared by protonation of a μ-CH_2 bridge rather than by direct oxidative addition of CH_3X. The addition of 2 equiv of CH_3I to the dinuclear complexes $Pd_2(dpm)_2$[15] and $[RhCl(CO)PR_3]_2$[16] produces a two-electron oxidation of each metal. One equivalent of CH_3I oxidatively adds to a single metal center of $Rh_2(\mu\text{-}S\text{-}t\text{-}Bu)_2(CO)_2(PMe_2Ph)_2$.[17,20]

When the formation of **2b** in $CDCl_3$ at −20 and +35 °C is monitored by ^1H NMR, no signals other than those due to **1a**, **2a**, and CH_3I are detected. We have failed by this technique to detect any intermediate Au^{III}–Au^{I} species which might be formed by initial oxidative addition at one metal center. Both metal centers in **1** appear to be involved intimately in the process. The importance of the digold(II) metal–metal (single) bonded species is demonstrated by the observation that when equimolar (~0.02 M) amounts of $Ph(Me)P(CH_2Au^{III}(Br)_2CH_2)_2P(Me)Ph$ and $Ph(Me)P(CH_2Au^{I}CH_2)_2P(Me)Ph$ are combined in $CDCl_3$, complete (by NMR) conversion to $Ph(Me)P(CH_2Au^{II}(Br)CH_2)_2P(Me)Ph$ occurs within a few minutes.

Photodecomposition is observed for **2a** in solution upon exposure to light. In toluene, THF or halocarbon solutions, light converts **2** to **3** or mixtures of **3** and **1** (identified by ^1H NMR, IR, and TLC), depending on the amount of excess CH_3I present. Near-UV photolysis (3500 Å, 1 h) of a dry, O_2-free $CDCl_3$ solution of **2b** results in complete disappearance of the Au–CH_3 ^1H-NMR signal and appearance of a new peak (at 3.02 ppm) assigned to CH_3Cl. This result is consistent with a photogeneration of methyl radicals and subsequent halide abstraction from $CDCl_3$. Methyl radicals also have been observed as the initial product of UV photodecompsition of CH_3AuPPh_3.[18]

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(6) Crystal data for $Au_2IP_2C_9H_{23}$: mol wt 712.08, monoclinic, space group $P2_1/n$, $a = 12.221$ (2) Å, $b = 12.144$ (2) Å, $c = 11.462$ (1) Å, $\beta = 100.81$ (1)°, $Z = 4$, ρ(calcd) = 2.855 g cm^{-3}, ρ(obsd) = 2.875 g cm^{-3} (CH_2I_2/C_6H_5Br solution), $\mu = 202.7$ cm^{-1}.

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Table I. Atomic Positions and Thermal Parameters for $[Au(CH_2)_2P(CH_3)_2]_2(CH_3)(I)$

(1) Atomic Positions

atom	*x*	*y*	*z*	atom	*x*	*y*	*z*
Au(1)	0.3227 (2)	0.3876 (2)	0.5180 (2)	C(1)	0.1293 (58)	0.3920 (54)	0.8538 (62)
Au(2)	0.2025 (2)	0.5749 (2)	0.5022 (2)	C(2)	0.3897 (50)	0.5789 (41)	0.1690 (51)
I	0.0637 (3)	0.7695 (4)	0.4656 (4)	C(6)	0.2816 (46)	0.6343 (48)	0.3610 (46)
P(1)	0.2032 (11)	0.4429 (13)	0.7380 (12)	C(5)	0.3133 (51)	0.5208 (50)	0.8178 (50)
P(2)	0.3154 (12)	0.5248 (16)	0.2801 (14)	C(4)	0.2544 (35)	0.3371 (40)	0.6638 (41)
CME	0.4127 (41)	0.2365 (38)	0.5240 (51)	C(7)	0.1915 (45)	0.4626 (56)	0.2157 (52)
C(3)	0.1129 (46)	0.5090 (63)	0.6240 (54)	C(8)	0.3925 (55)	0.4352 (57)	0.3619 (43)

(2) Thermal Parameters[a]

atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Au(1)	45 (2)	73 (2)	51 (2)	3 (2)	13 (2)	−10 (2)
Au(2)	53 (2)	69 (2)	49 (2)	2 (2)	18 (2)	−5 (2)
I	71 (4)	81 (4)	75 (5)	3 (3)	3 (3)	−10 (3)
P(1)	53 (12)	69 (16)	18 (12)	5 (10)	20 (11)	15 (11)
P(2)	55 (13)	107 (19)	34 (15)	6 (12)	22 (12)	12 (13)
CME	80 (48)	12 (36)	139 (72)	−85 (35)	103 (51)	−94 (42)
C(3)	84 (55)	182 (96)	70 (71)	−26 (58)	−61 (51)	177 (74)
C(1)	174 (76)	52 (61)	129 (80)	52 (54)	111 (69)	27 (55)
C(2)	153 (65)	15 (42)	86 (61)	47 (41)	101 (57)	44 (40)
C(6)	114 (56)	67 (55)	44 (54)	−85 (46)	56 (48)	−21 (43)
C(5)	118 (60)	67 (55)	58 (59)	−70 (49)	−4 (50)	−59 (45)
C(4)	33 (36)	30 (43)	30 (45)	−11 (32)	−26 (34)	19 (33)
C(7)	70 (51)	118 (73)	58 (64)	−30 (48)	0 (50)	−15 (51)
C(8)	148 (71)	158 (78)	−11 (42)	39 (59)	−15 (46)	−63 (45)

[a] Anisotropic thermal parameters are ×10^4; the temperature factor equation is $\exp(-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23}))$.

Table II. Selected Bond Lengths (Å) and Angles (Deg) for **2a**[a]

Bond Lengths

Au(1)-Au(2)	2.695 (4)	P(1)-C(3)	1.74 (6)
Au(1)-CME	2.13 (5)	P(1)-C(1)	1.85 (8)
Au(1)-C(4)	2.10 (5)	P(1)-C(5)	1.75 (6)
Au(1)-C(8)	2.20 (5)	P(1)-C(4)	1.72 (5)
Au(2)-I	2.894 (5)	P(2)-C(2)	1.82 (7)
Au(2)-C(3)	2.09 (7)	P(2)-C(6)	1.71 (6)
Au(2)-C(6)	2.16 (6)	P(2)-C(7)	1.73 (6)
		P(2)-C(8)	1.62 (6)

Bond Angles

Au(1)-Au(2)-I	175.1 (2)	Au(1)-C(4)-P(1)	114.3 (2.6)
Au(2)-Au(1)-CME	177.5 (1.9)	Au(2)-C(3)-P(1)	109.9 (3.6)
C(3)-Au(2)-C(6)	173.6 (2.9)	Au(2)-C(6)-P(2)	109.5 (3.1)
C(4)-Au(1)-C(8)	178.0 (2.6)	Au(1)-C(8)-P(2)	112.0 (3.5)
Au(1)-Au(2)-C(3)	88.8 (2.5)	C(3)-P(1)-C(1)	111.6 (3.3)
Au(1)-Au(2)-C(6)	91.0 (2.1)	C(3)-P(1)-C(5)	117.3 (3.0)
Au(2)-Au(1)-C(4)	90.4 (1.7)	C(1)-P(1)-C(5)	103.7 (3.1)
Au(2)-Au(1)-C(8)	90.8 (2.3)	C(3)-P(1)-C(4)	102.2 (2.8)
CME-Au(1)-C(4)	90.2 (2.3)	C(1)-P(1)-C(4)	112.2 (2.8)
CME-Au(1)-C(8)	88.6 (2.7)	C(5)-P(1)-C(4)	110.2 (2.6)
I-Au(2)-C(3)	92.5 (2.6)	C(2)-P(2)-C(6)	107.5 (2.8)
I-Au(2)-C(6)	87.2 (2.1)	C(2)-P(2)-C(7)	111.8 (2.9)
		C(6)-P(2)-C(7)	106.8 (2.9)
		C(2)-P(2)-C(8)	109.6 (3.0)
		C(6)-P(2)-C(8)	112.4 (2.9)
		C(7)-P(2)-C(8)	108.8 (3.0)

[a] Esd's in parentheses.

We are currently investigating further the mechanism of formation and decomposition of **2a**, characterizing similar complexes with a variety of other alkyl halides, and examining the reaction chemistry of these haloalkyldigold(II) complexes.

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Registry No. 1a, 50449-81-5; **1b**, 81457-56-9; **2a**, 55927-69-0; **2b**, 81457-57-0; **3a**, 55744-31-5; **3b**, 81457-58-1.

Supplementary Material Available: A listing of structure factor amplitudes for compound **2a** (6 pages). Ordering information is given on any current masthead page.

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(21) A local version of the Gaussian integration method of Busing and Levy[22] has been used by assuming the crystal shape to approximate a flattened cube with dimensions 0.04 × 0.12 × 0.12 mm. Transmission factors ranged from 0.136 to 0.517.

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