Testing β-Hydrogen Activity toward Dinuclear Gold(I). The Reactivity of the Gold(I) Ylide Dimer $[Au(CH_2)_2PPh_2]_2$ with Ethyl Iodide and Trifluoroethyl Iodide. Crystal and Molecular Structures of $[Au(CH_2)_2PPh_2]_2(CH_2CF_3)I$ and $[Au(CH_2)_2PPh_2]_2(CH_2CH_3)I$

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The gold(I) ylide dimer $[Au(CH_2)_2PPh_2]_2$, **1**, reacts with neat CH_3CH_2I to give $[Au(CH_2)_2PPh_2]_2(CH_3CH_2)I$, **2**. The gold(II) adduct **2** has been characterized structurally. The gold(I) ylide dimer **1** reacts with CF_3CH_2I in benzene to give the gold(II)–alkyl halide adduct $[Au(CH_2)_2PPh_2]_2(CH_2CF_3)I$, **3**, in good yield. The gold(II) adduct **3** has also been structurally characterized by X-ray diffraction methods. Complex **2**: triclinic, $P\bar{1}$, $a = 10.1669$ (28) Å, $b = 12.5923$ (24) Å, $c = 12.9374$ (24) Å, $\alpha = 93.281$ (15)°, $\beta = 97.9261$ (19)°, $\gamma = 93.864$ (19)°, $Z = 2$. Complex **3**: triclinic, $P\bar{1}$, $a = 10.0928$ (22) Å, $b = 12.7083$ (27) Å, $c = 14.2173$ (28) Å, $\alpha = 112.589$ (16)°, $\beta = 110.267$ (16)°, $\gamma = 94.084$ (18)°, $V = 1534.85$ (56) Å^3, $Z = 2$.

Introduction

The chemistry of metal hydride complexes has received considerable attention in the last decade.[1] Several groups have demonstrated that metal hydrides are key species in a number of catalytic[2] and stoichiometric[3] processes. The obvious relationship of metal hydrides to carbon–hydrogen activation via β-hydrogen elimination or carbon–hydrogen insertion has encouraged vigorous research in the field.

Despite these extensive and significant developments, no documented nonbridging organometallic gold hydride compounds have been reported in the literature. Mononuclear gold(III) hydride intermediates have been postulated by Puddephatt[4] and Kochi[5] in the reaction of alkylgold complexes with proton sources. But such gold hydride intermediates apparently are too short-lived to be fully characterized. The best examples of gold hydride compounds appear to be the mixed-metal cation complexes of L. Venanzi and co-workers[6] and the group 6[15]–gold dimers of Stone et al.[7] Venanzi reports the X-ray structure of $[PPh_3Au(\mu\text{-}H)Ir(PPh_3)_3H_3][BF_4]$ to be an octahedral *mer*-$[IrH_3(PPh_3)_3]$ unit coordinated through the bridging hydride to the $[AuPPh_3]$ unit. The neutral gold–group 6 dimer, characterized structurally by Stone,[7] $(CO)_5Cr(\mu\text{-}H)AuPPh_3$ has a bent $Au(\mu\text{-}H)Cr$ geometry (111 (5)°). The Au–H and Cr–H bond distances are reported to be 1.72 (11) and 1.64 (12) Å, respectively.

In a preliminary investigation of β-hydrogen elimination, $[Au(CH_2)_2PPh_2]_2$, **1**, was reacted with neat ethyl iodide.[8] The ^1H NMR spectrum of this product, **2**, indicated it was a asymmetrically substituted gold(II) complex involving an ethyl substituent. Demonstrating the existence of this complex is important. *This is the first example of a gold(II) ylide dimer containing an alkyl group with β-hydrogens*; hence the first opportunity to investigate what effects, if any, β-hydrogens have on the dimeric gold system. The X-ray structure of the complex unfortunately suffers from problems associated with decomposition.

Recently[9] we have observed that an electron-withdrawing substituent on the alkyl moiety of the Au(II) ylide dimer stabilizes the adduct over dissociation to **1** and the alkyl halide. With this in mind **1** was reacted with excess CF_3CH_2I in benzene. The asymmetrically substituted gold(II) ylide dimer **3** was obtained. The ^1H NMR spectrum of **3** shows no unreacted starting material or free alkyl halide. The X-ray structural characterization of **3** gave none of the problems observed with **2**.

Experimental Section

All reactions were carried out in oven dried Schlenk ware under dry, oxygen free argon using standard inert atmosphere techniques. All solvents were dried before use according to standard methods. ^1H NMR spectra were obtained by using a Varian EM-390 spectrometer operating at 90 MHz at 35 °C. The complex $[Au(CH_2)_2PPh_2]_2$, **1**, was prepared very similarly to previously published methods.[10,11] In the synthesis of **1**, $[Ph_2PMe_2]Br$ was deprotonated with KH in THF giving the corresponding ylide which was then used in the subsequent synthesis of **1**.

Synthesis. $[Au(CH_2)_2PPh_2]_2(CH_2CH_3)I$. To 27 mg (0.03 mmol) of $[Au(CH_2)_2PPh_2]_2$ is added approximately 3 mL of ethyl iodide (Aldrich, used as received, bp 69–73 °C, fw 155.97). The solution turns yellow then orange in color (similar to the color changes observed in the reaction of CF_3CH_2I with **1**). After 5 min

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Table I. Crystal Data for Complexes 2 and 3

	2	**3**
formula	$C_{30}H_{33}P_2IAu_2$	$C_{30}H_{30}P_2F_3IAu_2$
fw	977.08	1030.05
space group	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)
systematic absences	none	none
a, Å	10.1669 (28)	10.0928 (22)
b, Å	12.5923 (24)	12.7083 (27)
c, Å	12.9374 (24)	14.2173 (28)
α, deg	93.281 (15)	112.589 (16)
β, deg	96.926 (19)	110.267 (16)
γ, deg	93.864 (19)	94.084 (18)
V, Å^3	1631.33	1534.85 (56)
Z	2	2
d_{calcd}, g/cm^3	1.97	2.23
cryst size, mm	0.075 × 0.075 × 0.15	0.3 × 0.3 × 0.23
$F(000)$, e	941.78	956.0
μ(Mo Kα), cm^{-1}	101.01	109.5
radiatn (monochromated in Mo Kα ($\lambda_\alpha = 0.71073$ Å) incident beam)		
orientatn reflctns, no., range (2θ)	25, $20 \le \theta \le 30$	25, $14 \le 2\theta \le 25$
temp, °C	20	20
scan method	Wyckoff ω	ω
data colln range, 2θ, deg	3–50	3–50
total reflectns measd	6299	5628
no. of unique data, total with $F_0^2 > 3\sigma(F_0^2)$	5739, 1751	5388, 3571
check reflctns	3 every 97	3 every 97
no. of parameters refined	89	343
trans factors, max, min	0.964, 0.615	0.078, 0.040
R^a	0.1098	0.0370
$R_w{}^b$	0.1171	0.0372
goodness-of-fit indicator^c	0.686	1.398
largest shift/esd, final cycle	0.004	0.09
largest peak, e/Å^3	6.6	1.1
g	0.00417	0.00036

[a] $R = \sum||F_0| - |F_c||/\sum|F_0|$. [b] $R_w = [\sum w^{1/2}(|F_0| - |F_c|)]/\sum w^{1/2}|F_0|$; $w^{-1} = [\sigma^2(|F_0|) + g|F_0|^2]$. [c] Goodness-of-fit $= [\sum w(|F_0| - |F_c|)^2/N_0 - N_p]^{1/2}$.

of stirring at 25 °C the solvent is removed in vacuo maintaining a temperature of 25 °C or less. The dry solid left behind, **2**, is taken up in $CDCl_3$ and the ^1H NMR spectrum obtained. ^1H NMR characterization of $[Au(CH_2)_2PPh_2]_2(CH_2CH_3)I$ (90 MHz, $CDCl_3$, 35 °C, Me_4Si internal standard): δ 7.7–7.2 (m, Ph), 2.16 (q, J_{HH} = 7.5 Hz, Au–C*H$_2$CH$_3$), 1.95 (d, J_{PH} = 11.3 Hz. Au–CH$_2$–PPh$_2$), 1.30 (d, J_{PH} = 9.7 Hz, Au–CH$_2$–PPh$_2$), 0.78 (t, J_{HH} = 7.5 Hz, Au–CH$_2$C*H$_3$). Also present in the methylene region is the quartet and triplet of the ethyl iodide (δ 3.17 (q, J_{HH} = 7.4 Hz), 1.83 (t, J_{HH} = 7.4 Hz)) and the characteristic doublet for the Au(I) starting material at 1.36 ppm (J_{HH} = 12.75 Hz). Orange-yellow crystals of **2** suitable for diffraction were obtained via diffusion of ether into a CH_2Cl_2 solution of **2** containing excess CH_3CH_2I.

$[Au(CH_2)_2PPh_2]_2(CH_2CF_3)I$. To 35 mg (0.04 mmol) of $[Au(CH_2)_2PPh_2]_2$ in 3 mL of dry benzene is added excess CF_3CH_2I (Fluka, used as received). As the reaction proceeds, the white starting material is seen to go into solution. At the same time the solution turns an orange color. After 10 min of reaction at 25 °C, the solvent is removed in vacuo. The product is isolated as a yellow orange air stable powder in approximately 75% yield (30 mg). Orange crystals of **3** suitable for X-ray structural investigation are obtained by diffusing diethyl ether into a CH_2Cl_2 solution of **3**. ^1H NMR (90 MHz, $CDCl_3$, 35 °C, Me_4Si internal standard): δ 7.7–7.2 (m, Ph), 2.30 (q, J_{HF} = 14.3 Hz, Au–CH$_2$–CF$_3$), 1.99 and 1.51 (d, J_{PH} = 10.5 Hz, Au–CH$_2$–PPh$_2$).

Equilibrium Constants. The estimation of the upper and lower limits for K in $[1 + RI = Au^{II}(R)I]$ ($R = CH_2CH_3, CH_2CF_3$; $K = [Au(R)I]/[1][RI]$) was carried out in the same manner for both **2** and **3** from ^1H NMR data ($CDCl_3$, 35 °C, 90 MHz, $\sim 1 \times 10^{-2}$ M). Approximately 10–15 mg of the Au(II) adduct **2** or **3** was dissolved in 1–1.5 mL of $CDCl_3$ in a 5-mm NMR tube. Several ^1H NMR spectra of the complexes were taken until no change could be detected. Equilibrium was assumed to have then been reached. In the case of **2**, *only* uncoordinated CH_3CH_2I and **1** were observed at equilibrium. For **3**, *neither* **1** or uncoordinated CF_3CH_2I were detected. In both cases it was assumed that 10% was the level of detection of the minor component. Therefore, a lower limit for K for **3** was determined to be $\simeq 9.0 \times 10^3$ M^{-1}. Similarly, a upper limit for K for **2** was determined to be $\simeq 12$ M^{-1}.

X-ray Diffraction Data Collection. Crystal data for **2** and **3** are provided in Table I. Intensity data were collected at ambient temperature on a Nicolet P3F four-circle diffractometer controlled by a Data General Nova 4 minicomputer. All crystallographic computations were performed by using the SHELXTL (Revision 4.1; Eclipse 32K version, August 1983) crystallographic computational package installed on a Data General Eclipse S/140 minicomputer. All data were corrected for Lorentz and polarization. An empirical absorption correction to **2** was applied after the data was corrected for decay (17%) as measured by the three check reflections. Due to loss of solvent, photosensitivity and decay the refinement was limited. In **3**, an empirical absorption correction was applied after the data was corrected for decay (2%) as measured by the check reflections (three every 97 reflections) during data collection.

Structure Determination and Refinement. Axial photographs and a Delaunay reduction confirmed the cell parameters of **2** as triclinic. The space group of **2** was determined to be $P\bar{1}$. The initial positional parameters for the gold atoms in **2** were obtained from the Patterson function listing. Subsequent difference Fourier maps revealed large peaks in the vicinity of the heavy atoms; therefore further refinement of the positional parameters for C(3), C(5), and C(6) was impossible. Thus, the positional and thermal parameters of C(5) and C(6) (carbons of ethyl moiety) were fixed and not refined. Carbon C(3) had the positional parameters fixed but the thermal parameter was refined. The phenyl rings were refined as rigid bodies with a C–C distance of 1.395 Å, the C–C–C angle fixed at 120°. A molecule of methylene chloride was present at the inversion center. The disorder made it possible to locate only the chloride atom. The final refinement with 89 parameters gave $R = 0.109$ and $R_w = 0.117$. Atomic coordinates and isotropic thermal parameters are given in Table II.

The initial positional parameters for the gold atoms in **3** were determined from the Patterson function listing. The space group for **3** (triclinic) was determined to be $P\bar{1}$. All remaining nonhydrogen atoms were located by using different Fourier techniques and refined anisotropically. Structure **3** refined to $R = 0.0362$ and $R_w = 0.0351$ for 3571 reflections with $I > 3.0\sigma(I)$. Atomic coordinates and isotropic thermal parameters are given in Table

Table II. Atom Coordinates (×10⁴) and Isotropic Thermal Parameters (Å² × 10³) for 2

	x	y	z	U, Å²
Au(1)	584 (3)	553 (2)	3271 (2)	58 (1)[a]
Au(2)	−1621 (3)	1458 (2)	3681 (2)	57 (1)[a]
I(1)	3067 (5)	−453 (4)	3013 (4)	68 (2)[a]
P(1)	−2012 (17)	−1051 (13)	3260 (12)	50 (6)[a]
P(2)	450 (19)	3081 (13)	2773 (15)	60 (7)[a]
C(1)	−369 (57)	−1019 (46)	3677 (49)	54 (17)
C(2)	−2795 (77)	−59 (56)	3798 (65)	96 (27)
C(3)	1580	1877	2825	108 (29)
C(4)	−551 (73)	3017 (56)	3707 (56)	83 (23)
C(5)	−4388	2169	2990	90
C(6)	−3309	2189	3924	90
Cl	4207 (43)	4113 (34)	−76 (34)	231 (18)
C(11)	−3537 (51)	−2427 (36)	4362 (40)	94 (5)
C(12)	−3947	−3422	4681	94 (5)
C(13)	−3555	−4354	4213	94 (5)
C(14)	−2752	−4293	3427	94 (5)
C(15)	−2342	−3298	3108	94 (5)
C(16)	−2734	−2366	3575	94 (5)
C(21)	859 (42)	5249 (46)	3323 (39)	94 (5)
C(22)	1661	6205	3478	94 (5)
C(23)	2883	6274	3105	94 (5)
C(24)	3303	5387	2578	94 (5)
C(25)	2500	4431	2423	94 (5)
C(26)	1278	4362	2796	94 (5)
C(31)	−3726 (49)	−1132 (40)	1400 (40)	94 (5)
C(32)	−4065	−1105	321	94 (5)
C(33)	−3068	−1019	−314	94 (5)
C(34)	−1732	−961	131	94 (5)
C(35)	−1393	−988	1211	94 (5)
C(36)	−2390	−1074	1845	94 (5)
C(41)	−1317 (53)	2022 (39)	1110 (40)	94 (5)
C(42)	−1878	1876	60	94 (5)
C(43)	−1499	2583	−654	94 (5)
C(44)	−559	3437	−319	94 (5)
C(45)	2	3582	731	94 (5)
C(46)	−377	2875	1445	94 (5)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Table III. Atom Coordinates (×10⁴) and Isotropic Thermal Parameters (Å² × 10³) for 3

	x	y	z	U,[a] Å²
Au(1)	4350 (1)	1880 (1)	1449 (1)	32 (1)
Au(2)	6943 (1)	1338 (1)	1806 (1)	33 (1)
P(1)	4617 (3)	−378 (2)	1910 (2)	32 (1)
P(2)	7037 (4)	4065 (3)	2500 (3)	42 (1)
I	1579 (1)	2382 (1)	830 (1)	53 (1)
C(1)	8003 (12)	3008 (10)	2081 (10)	44 (6)
C(2)	5208 (14)	3504 (10)	1556 (10)	51 (6)
C(3)	3326 (13)	249 (10)	1227 (10)	47 (6)
C(4)	6087 (12)	−377 (10)	1465 (9)	41 (5)
C(5)	8883 (13)	805 (11)	1879 (10)	49 (6)
C(6)	9872 (1)	998 (8)	2968 (9)	33 (5)
F(1)	9351 (9)	489 (9)	3472 (7)	90 (5)
F(2)	10416 (11)	2113 (8)	3728 (7)	109 (6)
F(3)	11087 (9)	598 (10)	2993 (8)	100 (6)
C(11)	2274 (13)	−2212 (10)	1230 (10)	48 (6)
C(12)	1656 (14)	−3320 (11)	1058 (11)	55 (7)
C(13)	2469 (17)	−4073 (11)	1280 (11)	60 (7)
C(14)	4004 (16)	−3709 (11)	1645 (12)	65 (8)
C(15)	4650 (14)	−2603 (11)	1803 (11)	56 (7)
C(16)	3793 (12)	−1838 (8)	1625 (8)	33 (5)
C(21)	6478 (15)	155 (13)	4061 (10)	61 (7)
C(22)	7053 (19)	784 (17)	5250 (12)	101 (10)
C(23)	6430 (19)	1713 (15)	5744 (12)	86 (9)
C(24)	5318 (22)	1929 (14)	5084 (12)	94 (10)
C(25)	4712 (18)	1333 (12)	3891 (11)	66 (8)
C(26)	5305 (12)	459 (10)	3402 (8)	41 (5)
C(31)	6539 (21)	5278 (14)	4389 (14)	85 (11)
C(32)	6763 (25)	5651 (16)	5504 (15)	105 (13)
C(33)	7576 (21)	5135 (15)	6103 (12)	96 (10)
C(34)	8235 (18)	4234 (16)	5625 (13)	78 (9)
C(35)	8077 (17)	3883 (15)	4514 (10)	74 (8)
C(36)	7228 (14)	4433 (10)	3917 (10)	46 (6)
C(41)	7538 (17)	5401 (11)	1464 (12)	65 (8)
C(42)	8027 (18)	6399 (13)	1388 (13)	75 (9)
C(43)	8760 (15)	7424 (12)	2348 (14)	70 (9)
C(44)	8912 (17)	7481 (12)	3373 (13)	76 (9)
C(45)	8457 (16)	6473 (11)	3462 (11)	68 (7)
C(46)	7735 (14)	5427 (10)	2497 (10)	50 (6)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

III with anisotropic thermal parameters in the supplementary material.

Results

The gold(I) ylide dimer $[Au(CH_2)_2PPh_2]_2$ reacts with CF_3CH_2I in benzene to give the gold(II)–alkyl halide $[Au(CH_2)_2PPh_2]_2(CH_2CF_3)I$, **3**, in 75% yield as a yellow-orange air-stable complex. The ^1H NMR spectrum of **3** (ca. 0.01 M, $CDCl_3$ 35 °C) shows no resonances for **1** or the free CF_3CH_2I.

The gold(I) dimer **1** reacts with neat ethyl iodide at 25 °C to give $[Au(CH_2)_2PPh_2]_2(CH_2CH_3)I$, **2**. The ^1H NMR spectrum of this yellow-orange product unambigiously demonstrates the existence of **2** in solution (^1H NMR data of **2** and **3** in the Experimental Section). The ^1H NMR spectrum (ca. 0.01 M, $CDCl_3$, 35 °C) of **2** as a function of time indicates that the equilibrium for this complex heavily favors the gold(I) ylide dimer and free alkyl halide. No evidence for the generation of ethylene is observed as equilibrium is achieved.

Molecular Structure of $[Au(CH_2)_2PPh_2]_2(CH_2CH_3)I$, 2. A diagram of the ethyl iodide complex **2** is shown in perspective in Figure 1. The eight-membered ring containing the two gold centers is in the boat conformation. Each Au(II) d^9 center is square planar with a twist of ca. 13° between planes. The Au–Au distance is 2.684 (4) Å. The complex is diamagnetic.

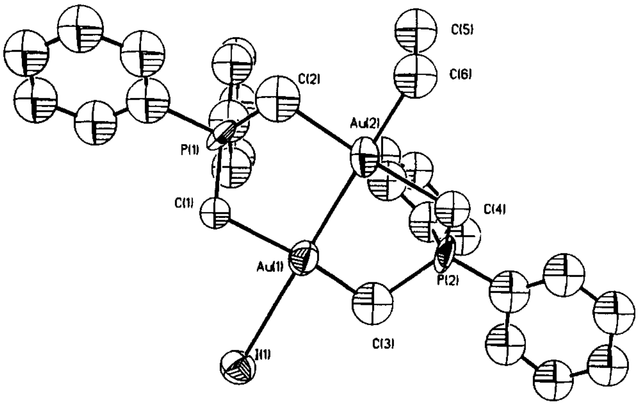

Figure 1. Molecular structure and labeling scheme (50% probability thermal ellipsoids, hydrogen atoms omitted for clarity) of **2**, $[Au(CH_2)_2PPh_2]_2(CH_2CH_3)I$. Selected bond lengths (in Å): Au(1)–Au(2) = 2.684 (4); Au(1)–I(1) = 2.950 (6); Au(1)–C(6) = 2.054 (3); C(5)–C(6) = 1.512; Au(1)–C(1) = 2.262 (59). Selected bond angles (in deg): Au(2)–Au(1)–I(1) = 175.2 (2); Au(2)–Au(1)–C(1) = 87.7 (15); Au(2)–C(6)–C(5) = 116.0 (1); Au(1)–Au(2)–C(6) = 177.1 (2).

The Au–I distance is 2.950 (6) Å. Compared with the gold(II) diiodide adduct **4**,[12] $[Au(CH_2)PPh_2]_2I_2$, this bond distance is 0.26 Å longer. The structural trans effect observed with **2** is the largest yet observed in complexes of this type.[14] The Au–I distance in **2** when compared to the methyl iodide adduct is 0.056 Å longer. Despite the large difference in the Au–I bond distances, the Au–Au distances remain fairly constant. The Au–Au bond distance in **2** is only 0.034 Å greater than in **4**.

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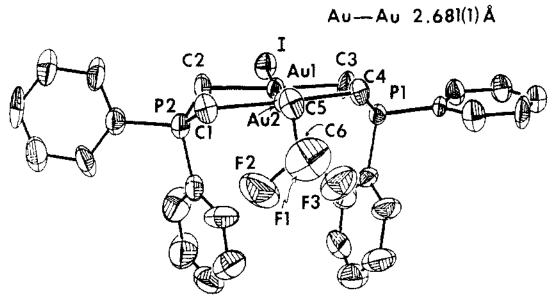

Figure 2. Molecular structure and labeling scheme (50% probability thermal ellipsoids, Hydrogen atoms omitted for clarity) of 3, $[Au(CH_2)_2PPh_2]_2(CH_2CF_3)I$. Selected bond lengths (in Å): Au(1)–Au(2) = 2.681 (1); Au(1)–I = 2.826 (1); Au(2)–C(5) = 2.082 (14); C(5)–C(6) = 1.439 (17); Au(1)–C(2) = 2.109 (14); C(2)–P(2) = 1.754 (12). Selected bond angles (in deg): Au(2)–Au(1)–I = 173.7 (1); C(1)–Au(2)–C(4) = 173.0 (5); C(2)–Au(1)–C(3) = 174.9 (5); Au(1)–Au(2)–C(5) = 173.1 (3); Au(1)–Au(2)–C(1) = 93.5 (3); Au(2)–C(5)–C(6) = 115.0 (10); Au(2)–C(1)–P(2) = 110.5 (7).

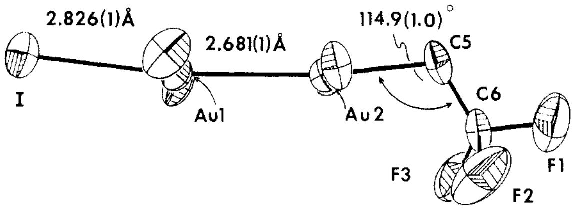

Figure 3. CF_3CH_2–Au–Au–I backbone of 3, 50% probability thermal ellipsoids, Hydrogen atoms omitted for clarity.

A comparison of the structural parameters of 2 and 3 (vida infra) clearly indicates the biggest difference between the two structures is the Au–I distance. In 2, the Au–I distance is 0.124 Å greater than in 3. This observation appears to be related to the differences in the estimated equilibrium constants. Taken together, these parameters suggest a lability of the Au–I bond and the formation of a cationic intermediate,[8] $[[Au(CH_2)_2PPh_2]_2(CH_2R)]^+$.

Considering the differences in the Au–I bond distances between 2 and 3, it is important to note that the Au–Au distances in 2 and 3 are not statistically different (2.684 (4) Å vs. 2.681 (1) Å).

Molecular Structure of $[Au(CH_2)_2PPh_2]_2(CH_2CF_3)I$, 3. A perspective view of complex 3, along with selected bond lengths and angles, is given in Figure 2. The I–Au–Au–CH_2–CF_3 backbone of complex 3 is shown in perspective in Figure 3. The heteronuclear eight-membered ring of 3 adopts a boat configuration. The four methylene carbons and two gold atoms of the ring are not rigorously planar as the C(1)–Au(2)–C(4) angle is 173.0 (5)° and the C(2)–Au(1)–C(3) angle is 174.9 (5)°. The coordination geometry about each Au(II) d^9 center is square planar with a twist of ca. 6.3° between planes. The Au(1)–Au(2) distance is 2.681 (1) Å. This distance is typical for compounds containing a Au–Au bond. The complex is diamagnetic.

The Au–I bond length of 3 (2.826 (1) Å) is *only* 0.133 Å longer than the Au–I distance (2.693 Å)[12] in $[Au(CH_2)_2PPh_2]_2I_2$, 4. This bond length change is much smaller than the 0.21-Å difference[13] between Au–I bond lengths of the methyl iodide adduct $[Au(CH_2)_2PPh_2]_2(Me)I$, 5 (where the Au–I bond length is 2.894 (5) Å), and the diiodide adduct 4.

The structural trans effect as seen in these dimer Au(II) d^9 systems has been previously recognized.[13] The significant observation made here is that the magnitude of the structural trans effect (STE) decreases with the presence of an electronegative substituent on the alkyl moiety. This is consistent with orbital interpretations[14] of the origin of the effect.

The observed *decrease* in the STE can be understood qualitatively by examining the *differences* in polarization of R–Au(II)–Au(II)–I σ-bonded backbone complexes 2 and 3 and the methyl iodide adduct 5. In 3, where R is CH_2CF_3 the extent of polarization is expected to be less than in 2 or 5 where the alkyl moiety is ethyl or methyl, respectively. Clearly, the polarization of the R–Au–Au–I σ-bond (HOMO) follows the order $2 > 5 > 3 \gg 4$.

The orientation of the CH_2CF_3 unit in the solid state such that it is in a seemingly sterically hindered position appears to be due to the relative orientation of the dimers in the cell.

Discussion

The reaction of $[Au(CH_2)_2PPh_2]_2$ with excess ethyl iodide to give $[Au(CH_2)_2PPh_2]_2(CH_2CH_3)I$, 2, demonstrates that alkyl groups containing β-hydrogens are not rapidly eliminated from this gold ylide dimer. In $CDCl_3$, 2 reaches equilibrium quickly with 1 and ethyl iodide. A clean reductive elimination reaction is observed giving 1 and the noncoordinated alkyl halide as the only products. The presence of ethylene is not detected from the ^1H NMR spectrum during equilibration of 2. The X-ray crystal structure, although not of high quality, shows no evidence of β-hydride–Au interactions.

Complex 2, as do other alkyl halide–gold (II) ylide dimer adducts, ($[Au(CH_2)_2PPh_2](Me)X$, X = Br, I), reductively eliminates the alkyl halide upon heating in the solid state.[14] The reductively eliminated ethyl iodide was identified from its gas-phase infrared spectrum. Complex 3, $[Au(CH_2)_2PPh_2]_2(CH_2CF_3)I$, does not undergo such a solid-state reductive elimination reaction; it decomposes at ~ 130 °C. This appears to be related to the considerable difference observed in the equilibrium constants for 2 and 3 in $CDCl_3$ and the ease of formation of free halide.

The reason complex 2 has gone unobserved and hence uncharacterized until now correlates with the thermodynamics which govern its formation in solution. Although the gold(I) ylide dimer 1 is converted to 2 in neat ethyl iodide, once isolated and dissolved in $CDCl_3$, 2 readily eliminates C_2H_5I. The rate of this reductive elimination reaction, however, is sufficiently slow to allow detection by ^1H NMR and the estimate of the upper limit for the formation constant of $K \simeq 12\ M^{-1}$.

The 1,1,1-trifluoro analogue of 2 $[Au(CH_2)_2PPh_2]_2(CH_2CF_3)I$, 3, is much more stable thermodynamically. In $CDCl_3$ the lower limit for the formation constant ($K \simeq 9 \times 10^3\ M^{-1}$) shows that 3 is greatly favored. Therefore, the ^1H NMR spectrum of 3 was unambigiously assigned and used to help characterize 2.

The ^1H NMR spectra of 2 and 3 have many similar features. In solution, the time-averaged spectrum of the ensemble of interconverting conformations of 2 and 3 (boat to chair interconversion; rotation about the Au–C bond of the Au–R (R = CH_2CF_3, CH_2CH_3) gives rise to a ^1H NMR spectrum with average C_{2v} symmetry. The static molecular

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[13] Fackler, J. P., Jr.; Basil, J. D. *Organometallics* **1982**, *1*, 871.

[14] Basil, J. D.; Murray, H. H.; Fackler, J. P., Jr.; Mazany, A. M.; Trzcinska-Bancroft, B.; Dudis, D. S.; Tocher, J.; Knachel, H., submitted for publication. This paper gives a detailed molecular orbital description of the structural trans effect for these dinuclear compounds.

[15] In this paper the periodic group notation is in accord with recent actions by IUPAC and ACS nomenclature committees. A and B notation is eliminated because of wide confusion. Groups IA and IIA become groups 1 and 2. The d-transition elements comprise groups 3 through 12, and the p-block elements comprise groups 13 through 18. (Note that the former Roman number designation is preserved in the last digit of the new numbering: e.g., III → 3 and 13.)

structure as determined via X-ray crystallography has no symmetry. The ^1H NMR spectra of the ring methylenes of both **2** and **3** appear as two A_4X doublets (J_{HP}). The chemical shift difference between these doublets is dictated by the substituents coordinated to the Au centers. A comparison of the ^1H NMR spectra of symmetrically substituted dihalogold(II) adducts[11,14] of **1** allows for a tentative assignment of the spectra. The downfield doublet is assigned to the methylenes proximal to the halide coordinated to the Au(II) center, and the upfield A_4X doublet arises from the methylenes nearest to the coordinated alkyl. The resonance of the methylenes in the alkyl moieties in **2** and **3** are further upfield (**2**, δ 2.16; **3** δ 2.30) than the methylene resonances in the noncoordinated alkyl iodides (CF_3CH_2I, δ 3.61 (q, $J_{HF} = 9.9$ Hz); CH_3CH_2I, δ 3.24 (q), 1.85 (t, $J_{HH} = 7.4$ Hz). In both complexes these methylenes appear as quartets with coupling to the three nearby spin $^1/_2$ nuclei.

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Registry No. **1**, 81457-56-9; **2**, 97374-16-8; **3**, 97374-17-9; CH_3CH_2I, 75-03-6; CF_3CH_2I, 353-83-3.

Supplementary Material Available: Tables of bond lengths and bond angels as well as anisotropic thermal parameters and structure factors (36 pages). Ordering information is given on any current masthead paper.

Hydroxy- and Hydrido-Bridged Binuclear Complexes of Iridium: Synthesis, Characterization, and Attempts To Model Binuclear Water-Gas Shift Catalysts. Structure of $[Ir_2(CO)_2(\mu\text{-}OH{\cdot}Cl)(Ph_2PCH_2PPh_2)_2]$

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The reaction of *trans*-$[IrCl(CO)(DPM)]_2$ with excess NaOH yields $[Ir_2(CO)_2(\mu\text{-}OH{\cdot}Cl)(DPM)_2]$ which upon treatment with $HBF_4{\cdot}Et_2O$ gives $[Ir_2(CO)_2(\mu\text{-}OH)(DPM)_2][BF_4]$. Reaction of the former product with CO produces the binuclear Ir(0) complex $[Ir_2(CO)_4(DPM)_2]$ which after flushing with N_2 yields $[Ir_2(CO)_3(DPM)_2]$. Reaction of $[Ir_2(CO)_2(\mu\text{-}OH)(DPM)_2][BF_4]$ with CO produces $[Ir_2(CO)_2(\mu\text{-}H)(\mu\text{-}CO)(DPM)_2][BF_4]$. This latter complex reacts with $HBF_4{\cdot}Et_2O$ to give $[Ir_2(H)(CO)_2(\mu\text{-}H)(\mu\text{-}CO)(DPM)_2][BF_4]_2$ which rearranges with time yielding the isomeric complex $[Ir_2(H)_2(CO)_3(DPM)_2][BF_4]_2$. Reaction of either of these dihydrides with CO produces $[Ir_2(CO)_4(\mu\text{-}H)_2(DPM)_2][BF_4]_2$ and $[Ir_2(CO)_4(\mu\text{-}CO)(DPM)_2][BF_4]_2$ in the ratio 9:1, the latter product resulting from reductive elimination of H_2. Refluxing $[Ir_2(H)_2(CO)_3(DPM)_2][BF_4]_2$ in CH_3CN also produces some H_2 elimination and the formation of $[Ir_2(CO)_2(CH_3CN)_2(\mu\text{-}CO)(DPM)_2][BF_4]_2$. Reaction of $[Ir_2(CO)_4(\mu\text{-}CO)(DPM)_2][BF_4]_2$ with OH^- yields $[Ir_2(CO)_2(\mu\text{-}H)(\mu\text{-}CO)(DPM)_2][BF_4]$ whereas reaction of $[Ir_2(CO)_2(CH_3CN)_2(\mu\text{-}CO)(DPM)_2][BF_4]_2$ with OH^- gives a mixture of this hydride and the bridging hydroxide complex $[Ir_2(CO)_2(\mu\text{-}OH)(DPM)_2][BF_4]$. This chemistry is discussed and related to a model water-gas shift cycle. The related rhodium complex $[Rh_2(CO)_2(\mu\text{-}OH)(DPM)_2]^+$ is shown to be a WGS catalyst precursor under mild conditions, although it seems that metal hydrides and not hydroxides are the catalytically important species. The complex $[Ir_2(CO)_2(\mu\text{-}OH{\cdot}Cl)(DPM)_2]$ crystallizes in the space group $P2_12_12_1$ with $a = 14.762$ (2) Å, $b = 25.583$ (4) Å, $c = 13.770$ (3) Å, and $Z = 4$ and was refined to $R = 0.043$ and $R_w = 0.065$ based on 2650 unique observed reflections and 223 variables.

Introduction

The water-gas shift (WGS) reaction, shown in eq 1, is an industrially important process for increasing the H_2/CO ratio of synthesis gas.[1,2] At the present time this reaction

$$CO + H_2O \rightleftarrows CO_2 + H_2 \qquad (1)$$

utilizes heterogeneous catalysts (usually metal oxides) at high temperatures.[1] However, there has been increasing interest of late in the use of homogeneous catalysts which are active at lower temperatures[3-15] where the above equilibrium is more favorable.[16,17] One such study by Yoshida and co-workers, utilizing mononuclear rhodium

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