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Decarboxylation of (Triphenylphosphine)gold(I) Carboxylates

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(Triphenylphosphine)gold(I) carboxylates $Ph_3PAuOC(O)CH(CH_3)_2$ (1) and $Ph_3PAuOC(O)CH(OH)CH_3$ (2) have been synthesized and structurally characterized by single-crystal X-ray diffraction studies. Decarboxylation of these complexes is observed at temperatures under 100 °C with the formation of carbon dioxide, metallic gold (mirror), triphenylphosphine, and organic products. The nature of the organic products that are formed depends on the type of carboxylate and the reaction conditions. Decarboxylation of a carboxylate copolymer of polyethylene and acrylic acid (EAA), Dow Chemical PRIMACOR 5980, with $[Ph_3PAu]^+$ bound to the carboxylate, is observed to give CO_2, triphenylphosphine, metallic gold, and unsaturated polymer. Structural results: complex 1 triclinic, $P\bar{1}$, $a = 6.845$ (1) Å, $b = 11.968$ (3) Å, $c = 13.413$ (3) Å, $\alpha = 77.45$ (2)°, $\beta = 84.80$ (2)°, $\gamma = 77.66$ (2)°, $V = 1046.6$ (4) Å^3, $Z = 2$, $R = 0.0306$, and $R_w = 0.0315$; complex 2 triclinic, $P\bar{1}$, $a = 8.681$ (3) Å, $b = 11.342$ (4) Å, $c = 12.619$ (5) Å, $\alpha = 111.74$ (3)°, $\beta = 104.37$ (3)°, $\gamma = 95.34$ (3)°, $V = 1094.1$ (7) Å^3, $Z = 2$, $R = 0.060$, and $R_w = 0.060$.

Introduction

The oxidative decarboxylation of organic carboxylic acids is known to be catalyzed by the presence of certain high-valent metals, e.g. Pb(IV),[1] Ag(II),[2,3] and Co(III).[4] Such reactions have been shown to proceed via a radical pathway. In published studies, suitable metal complexes, e.g. lead tetraacetate, have been added to solutions of the organic acid to achieve the desired result.

Decarboxylation of $R-COO^-$ by Ph_3PAu^+ (R = polyethylene polymer backbone) was observed at 100 °C during the attempted synthesis of a gold-containing organic polymer.[5] The oxygen-bound complex, $R-COOAuPPh_3$, dissolved in *p*-xylene at 100 °C, readily gives CO_2 and purple complexes (clusters) followed by the formation of metallic gold (film), triphenylphosphine, and unsaturated organic polymer. The IR spectrum provides evidence for the formation of unsaturated polymer in these reactions. This observation led us to prepare and isolate some Ph_3PAu(carboxylate) complexes containing short-chain organic acids in order to further investigate the decarboxylation. Efforts were made to identify the organic products formed in the decarboxylation reaction.

(Triphenylphosphine)gold carboxylates are comparatively rare. In addition to one amino acid complex,[6] only the acetate[7] and benzoate[8] have been structurally characterized. These carboxylates, including two newly characterized Au^I carboxylates reported here, readily lose carbon dioxide at 100 °C with the formation of a gold mirror, organic products, and triphenylphosphine. Unlike the situation with other high-valent metal catalysts, coordination of Au^I to the carboxylate was found to be essential. No decarboxylation was observed for $[(Ph_3P)_2Au]O_2CR$ [R = $-CH_3$, $-CH(OH)CH_3$, and $-CH(CH_3)_2$], wherein only weak ionic interaction between the gold center and the carboxylate anion exists. In this paper, we report the X-ray structural characterizations of Ph_3PAu(isobutyrate) (1) and Ph_3PAu(lactate) (2) and decarboxylations of $R-COOAuPPh_3$ (R = polyethylene polymer backbone), Ph_3PAu(isobutyrate), Ph_3PAu(lactate), and Ph_3PAu(benzoate).

Experimental Section

Silver lactate was purchased from Alfa Chemicals and used without further purification. (Triphenylphosphine)gold(I) acetate[7] and benzoate[8] were prepared by literature procedures. All solvents were dried and distilled prior to use, and syntheses were carried out by using standard Schlenk methods at room temperature. ^1H NMR spectra were recorded on a Varian XL-200 spectrometer. IR spectra were recorded on a Perkin-Elmer 783 spectrophotometer. GC-MS spectra were recorded on a Hewlett-Packard 5790A series gas chromatograph.

Synthesis of Silver Isobutyrate. Silver oxide (2.63 g, 11.4 mmol) was added to isobutyric acid (2 g, 22.7 mmol) in 5:1 H_2O/MeOH (60 mL). The resultant mixture was stirred overnight. A colorless solid was isolated by filtration and dried in vacuo. IR: ν(CO) 1520 cm^{-1} (s, br).

Synthesis of (Triphenylphosphine)gold(I) Isobutyrate (1). (Triphenylphosphine)gold(I) chloride (0.5 g, 1.01 mmol) was suspended in benzene (15 mL) in a brown Schlenk tube. Silver isobutyrate (0.2 g, 1.01 mmol) was added in one portion, and the resultant mixture was stirred under N_2, in the dark for 3 days. A colorless solid (AgCl) formed, and this was removed by filtration. The solution was then evaporated to dryness under reduced pressure to give a colorless oil. This was recrystallized by slow diffusion at -20 °C of petroleum ether into a CH_2Cl_2 solution of the oil. Colorless needle-shaped crystals were isolated after 1 day to give 0.44 g (80%) of Ph_3PAu(isobutyrate). Anal. Calcd for $C_{22}H_{22}O_2PAu$: C, 48.26; H, 4.02. Found: C, 47.76; H, 3.82. ^1H NMR ($CDCl_3$): δ 1.2 (d, $J_{H-H} = 10.3$ Hz, CH_3), 2.52 (septet, $J_{H-H} = 10.5$ Hz, CH), and 7.3-7.6 (multiplet, aromatic protons).

Synthesis of (Triphenylphosphine)gold(I) Lactate (2). A 0.5-g (1.01 mmol) sample of Ph_3AuCl was dissolved in 3:2 benzene/CH_2Cl_2 (25 mL) in a brown Schlenk tube. To this stirred solution was added silver lactate (0.2 g, 1.01 mmol) in one portion, and the resulting solution mixture was stirred under N_2, in the dark for 3 days. A colorless solid (AgCl) formed, which was removed by filtration. The solution was evaporated to dryness under reduced pressure to give a colorless residue. This residue was redissolved in benzene (5 mL), and a colorless solid was precipitated upon addition of pentane to give 0.50 g (90%) of Ph_3PAu(lactate). Anal. Calcd for $C_{21}H_{20}O_3PAu$: C, 45.90; H, 3.64. Found: C, 46.83; H, 3.59. IR: ν(OH) 3390 cm^{-1} (m, br). ^1H NMR (C_6D_6): δ 1.85 (d, $J_{H-H} = 10.3$ Hz, CH_3), 4.20 (broad singlet, OH), 4.75 (quartet, $J_{H-H} = 10.5$ Hz, CH), and 6.9, 7.2 (multiplet, aromatic protons).

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Decarboxylations. A 100-mg sample of the complex (either isobutyrate (1), lactate (2), or benzoate) was dissolved in benzene (10 mL). The solution was refluxed overnight, during which time a purple solid and a metallic gold film formed. The purple solid is due to colloid gold formation. The solution was cooled to room temperature and filtered. The filtrate was examined by GC–MS. In all cases, three bands were seen: the first contained biphenylbenzene (*m*/*z* 154), the second triphenylphosphine (*m*/*z*, 262), and the third benzaldehyde (*m*/*z* 106).

Decarboxylation with Mixed Carboxylates. A 100-mg (0.18 mmol) sample of Ph_3PAu(lactate) and 105.8 mg (0.18 mmol) of Ph_3PAu(benzoate) were dissolved in toluene (10 mL). The mixture was refluxed overnight under a N_2 atmosphere, during which time a metallic gold film formed along with a colorless solution. The colorless solution was examined by GC–MS. It gave bands for $C_6H_5CH(OH)CH_3$ [(±)-2-phenethyl alcohol) (*m*/*z* 122) and triphenylphosphine (*m*/*z* 262)]. The solution was removed from the reaction vessel and evaporated to dryness to yield a colorless residue. The residue was extracted with diethyl ether and was filtered to remove any solid present. The diethyl ether was evaporated to dryness by rotavapor and then dried under vacuo. This sample was also examined by GC–MS, which shows the same two bands that are indicated above. ^1H NMR ($CDCl_3$): δ 1.45 (doublet, J_{H-H} = 10.5 Hz, CH_3), 3.8 (broad singlet for OH), 4.8 (quartet, J_{H-H} = 10.5 Hz, CH), 7.5 (multiplet, aromatic protons, PPh_3 and (±)-2-phenethyl alcohol).

Decarboxylation of Polyethylene Acrylic Acid Copolymer (Dow Chemical PRIMACOR 5980, P5980 containing 20% acrylic acid). A 2.5-g sample of the polyethylene acrylic acid copolymer was dissolved in 5:2 *p*-xylene/*n*-butanol or *p*-xylene/THF (50 mL) at 90 °C. To this stirred solution was added 1.0 g of Ph_3PAuNO_3 in one portion. The solid disappeared within 5 min to give a clear colorless solution. The resultant solution was stirred for 2 h, during which time a purple solution formed followed by observation of a metallic gold film. The solution was cooled to room temperature to give the solid polymer. The IR spectrum of the polymer shows bands at 1700 and 1590 cm^{-1} associated with the carboxylic acid and olefin formation.

Carbon dioxide was detected in all reactions involving decarboxylation by passing the liberated gas into a saturated solution of $Ba(OH)_2$. Colorless, solid $BaCO_3$ formed in each case.

X-ray Crystallographic Analysis. Colorless crystals of 1 and 2 were grown by slow diffusion of petroleum ether into dichloromethane for 2 and into benzene for 1. Crystals were mounted on glass fibers with epoxy resin.

The diffractometer and procedures (Nicolet R3m/E diffractometer, SHELXTL 5.1) used have been previously described.[9] Unit cells were determined from 25 machine-centered reflections. Data were collected by using graphite-monochromated Mo Kα radiation at 293 K. Crystals of both compounds belonged to the triclinic crystal system. Neither crystal showed any significant decay during data collection. All data were corrected for Lorentz and polarization effects and for absorption by empirical methods based on azimuthal data.

Both structures were solved in $P\bar{1}$ by the heavy-atom method, which in each case revealed the position of the Au atom. All non-hydrogen atoms, except for the disordered methyl groups in 1, were located by subsequent difference Fourier syntheses and refined anisotropically. The phenyl groups were refined as rigid bodies with fixed C–C distances of 1.395 Å and angles of 120°. The positions of the hydrogen atoms attached to the phenyl ring were calculated by using a fixed C–H bond length of 0.96 Å and $U(H) = 1.2U_{eq}(C)$. The hydrogen atoms of the carboxylate ligands were neither located nor included in the refinement. In 1 the methyl atoms C(21) and C(22) were disordered over two positions, with refined site occupancies of 6:4. In both cases refinement was also attempted in the acentric space group, with a marked increase in disorder resulting.

Table I. Crystallographic Data for 1 and 2

	1	2
formula	$C_{22}H_{22}AuO_2P$	$C_{21}H_{20}AuO_3P{\cdot}C_6H_6$
fw	546.30	626.38
space group	$P\bar{1}$	$P\bar{1}$
a, Å	6.845 (2)	8.681 (3)
b, Å	11.968 (3)	11.342 (4)
c, Å	13.413 (3)	12.619 (5)
α, deg	77.45 (2)	111.74 (3)
β, deg	84.80 (2)	104.37 (3)
γ, deg	77.66 (2)	95.34 (3)
V, Å^3	1046.6 (4)	1094.1 (7)
Z	2	2
ρ(calc), gcm^{-3}	1.74	1.91
μ(Mo Kα), cm^{-1}	71.13	68.03
λ(Mo Kα), Å	0.710 69 (graphite monochromated)	
data collcn range, 2θ, deg	$2 \le 2\theta \le 45$	$2 \le 2\theta \le 45$
no. of unique reflns, $F_o > 3\sigma(F_o)$	2317	2122
no. of params refined	191	262
transm factors, % (max, min)	80.8, 71.5	91.1, 59.1
R^a	0.0306	0.060
$R_w{}^b$	0.0315	0.060
largest shift/esd, final cycle	0.004	0.006
largest residual peak, e Å^{-3}	1.23 (0.4 Å from C20)	3.33 (1.1 Å from Au)

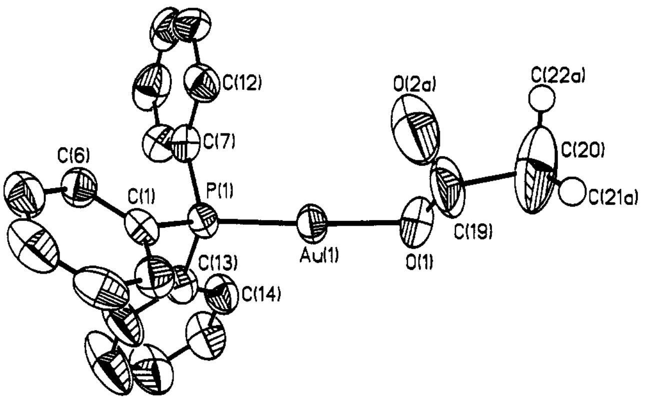

Figure 1. Structure of $Ph_3PAuO_2CCH(CH_3)_2$ (1). The thermal ellipsoids have been drawn at the 50% probability level.

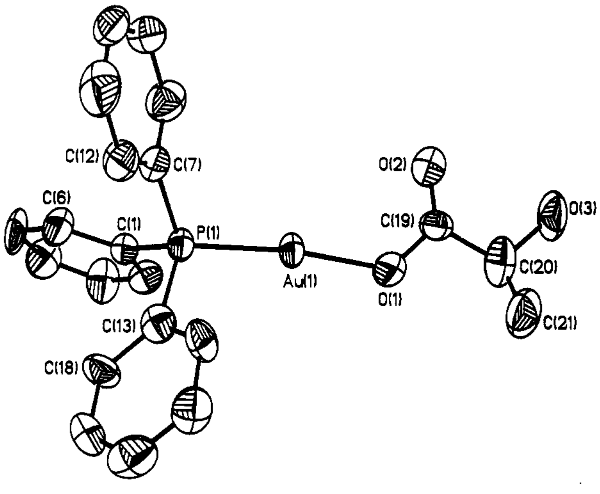

Figure 2. Structure of $Ph_3PAuO_2CCH(OH)CH_3$ (2). The thermal ellipsoids have been drawn at the 50% probability level.

Results

(a) Structural Studies. Crystallographic data for Ph_3PAu(isobutyrate) (1) and Ph_3PAu(lactate) (2) are recorded in Table I. Atomic positional and thermal parameters for 1 and 2 are given in Tables II and IV, and bond lengths and angles are given in Tables III and V. The structures of 1 and 2 are shown in Figures 1 and 2, respectively. The structures (Figures 1 and 2) are unremarkable except for illustrating the advantage of hydrogen

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[9] Porter, L. C.; Khan, Md. N. I.; King, C.; Fackler, J. P., Jr. *Acta Crystallogr., Sect. C* **1989**, *45*, 947.

Table II. Atomic Coordinates (×10^4) and Isotropic Thermal Parameters (Å^2 × 10^3)[a] for $Ph_3PAu[O_2CCH(CH_3)_2]$ (1)

atom	*x*	*y*	*z*	U_{iso}[b]
Au(1)	−873 (1)	−73 (1)	−2585 (1)	51 (1)*
O(1)	1411 (10)	−1453 (7)	−2116 (6)	77 (3)*
O(2a)	−588 (18)	−2704 (10)	−2078 (12)	144 (8)*
C(19)	1212 (17)	−2489 (10)	−2197 (5)	105 (7)*
C(20)	2928 (1)	−3565 (1)	−1378 (1)	184 (12)*
P(1)	−3359 (3)	1457 (2)	−2916 (2)	45 (1)*
C(1)	−4713 (8)	1549 (5)	−4032 (3)	46 (3)*
C(2)	−6784 (8)	1938 (5)	−4049 (3)	55 (4)*
C(3)	−7773 (8)	2044 (5)	−4939 (3)	68 (4)*
C(4)	−6692 (8)	1760 (5)	−5813 (3)	78 (5)*
C(5)	−4621 (8)	1371 (5)	−5797 (3)	73 (5)*
C(6)	−3632 (8)	1265 (5)	−4907 (3)	57 (4)*
C(7)	−5179 (8)	1413 (5)	−1852 (4)	50 (3)*
C(8)	−5754 (8)	2324 (5)	−1325 (4)	61 (4)*
C(9)	−7120 (8)	2225 (5)	−489 (4)	84 (5)*
C(10)	−7910 (8)	1215 (5)	−180 (4)	79 (5)*
C(11)	−7335 (8)	304 (5)	−708 (4)	70 (4)*
C(12)	−5969 (8)	403 (5)	−1544 (4)	58 (4)*
C(13)	−2538 (7)	2842 (4)	−3081 (4)	55 (4)*
C(14)	−1220 (7)	2943 (4)	−2387 (4)	66 (4)*
C(15)	−611 (7)	4000 (4)	−2461 (4)	85 (5)*
C(16)	−1320 (7)	4954 (4)	−3230 (4)	119 (8)*
C(17)	−2636 (7)	4853 (4)	−3925 (4)	145 (9)*
C(18)	−3245 (7)	3796 (4)	−3851 (4)	104 (6)*
C(21a)	3674 (7)	−4227 (4)	−2132 (4)	162 (13)
C(22a)	1787 (7)	−4167 (4)	−650 (4)	224 (20)
C(21b)	4630 (7)	−3130 (4)	−1340 (4)	99 (14)
C(22b)	2503 (7)	−3644 (4)	−305 (4)	127 (17)
O(2b)	498 (7)	−2487 (4)	−3064 (4)	37 (14)

[a] Estimated standard deviations in the least significant digits are given in parentheses. [b] For values with asterisks, the equivalent isotropic *U* is defined as one-third of the trace of the U_{ij} tensor.

Table III. Bond Lengths (Å) and Angles (deg)[a] for $Ph_3PAu[O_2CCH(CH_3)_2]$ (1)

	Bond Lengths		
Au(1)–O(1)	2.047 (6)	Au(1)–P(1)	2.213 (2)
O(1)–C(19)	1.305 (15)	O(2a)–C(19)	1.300 (18)
C(19)–C(20)	1.794 (9)	C(19)–O(2b)	1.300 (10)
C(20)–C(21a)	1.412 (5)	C(20)–C(22a)	1.371 (5)
C(20)–C(21b)	1.383 (5)	C(20)–C(22b)	1.429 (5)
P(1)–C(1)	1.802 (6)	P(1)–C(7)	1.807 (5)
P(1)–C(13)	1.825 (5)		
	Bond Angles		
O(1)–Au(1)–P(1)	173.6 (2)	Au(1)–O(1)–C(19)	117.8 (7)
O(1)–C(19)–O(2a)	117.2 (10)	O(1)–C(19)–C(20)	108.7 (7)
O(2a)–C(19)–C(20)	112.1 (8)	O(1)–C(19)–O(2b)	112.7 (7)
C(20)–C(19)–O(2b)	132.1 (8)	C(19)–C(20)–C(21a)	94.7 (3)
C(19)–C(20)–C(22a)	106.5 (4)	C(21a)–C(20)–C(22a)	109.8 (3)
C(19)–C(20)–C(21b)	108.7 (4)	C(19)–C(20)–C(22b)	115.8 (3)
C(21b)–C(20)–C(22b)	91.7 (3)	Au(1)–P(1)–C(1)	115.3 (2)
Au(1)–P(1)–C(7)	109.3 (2)	C(1)–P(1)–C(7)	106.2 (3)
Au(1)–P(1)–C(13)	112.7 (2)	C(1)–P(1)–C(13)	106.3 (3)
C(7)–P(1)–C(13)	106.5 (3)	P(1)–C(1)–C(2)	121.5 (2)
P(1)–C(1)–C(6)	118.4 (2)	P(1)–C(7)–C(8)	122.6 (2)
P(1)–C(7)–C(12)	117.4 (2)	P(1)–C(13)–C(14)	118.0 (2)
P(1)–C(13)–C(18)	121.9 (2)		

[a] Estimated standard deviations in the least significant digits are given in parentheses.

Table IV. Atomic Coordinates (×10^4) and Isotropic Thermal Parameters (Å^2 × 10^3)[a] for (Triphenylphosphine)gold Lactate (2)

atom	*x*	*y*	*z*	U_{iso}[b]
Au	−835 (1)	2371 (1)	−3954 (1)	42 (1)
O(1)	−1837 (18)	2932 (14)	−5285 (11)	76 (7)
O(2)	−3274 (17)	4266 (13)	−4437 (12)	75 (7)
C(19)	−2762 (18)	3764 (15)	−5245 (13)	45 (6)
O(3)	−4174 (16)	4880 (15)	−6401 (13)	81 (7)
C(21)	−1888 (33)	4218 (28)	−6792 (25)	109 (17)
C(20)	−3205 (31)	3955 (25)	−6409 (22)	93 (13)
P	522 (4)	1681 (3)	−2637 (3)	36 (1)
C(1)	−422 (16)	139 (13)	−2753 (12)	39 (6)
C(2)	−1543 (17)	−761 (14)	−3828 (13)	48 (6)
C(3)	−2193 (22)	−1989 (16)	−3905 (16)	64 (8)
C(4)	−1789 (23)	−2285 (15)	−2963 (15)	61 (8)
C(5)	−671 (23)	−1448 (16)	−1875 (15)	63 (8)
C(6)	19 (20)	−214 (16)	−1789 (14)	54 (7)
C(7)	914 (18)	2776 (14)	−1083 (12)	46 (7)
C(8)	−423 (23)	3037 (16)	−687 (15)	62 (8)
C(9)	−186 (28)	3863 (18)	477 (16)	72 (9)
C(10)	1318 (35)	4367 (18)	1268 (16)	80 (11)
C(11)	2628 (30)	4174 (18)	906 (17)	81 (10)
C(12)	2428 (20)	3318 (16)	−275 (13)	55 (7)
C(13)	2484 (17)	1474 (14)	−2887 (13)	47 (6)
C(14)	3409 (17)	2474 (14)	−2944 (14)	47 (7)
C(15)	4877 (18)	2363 (17)	−3221 (16)	59 (8)
C(16)	5336 (20)	1179 (19)	−3425 (15)	67 (8)
C(17)	4416 (19)	167 (16)	−3326 (15)	56 (7)
C(18)	3001 (17)	281 (15)	−3080 (15)	51 (7)
C(23)	4406 (38)	1001 (29)	659 (28)	128 (17)
C(24)	3833 (33)	−216 (40)	446 (23)	133 (19)
C(22)	5584 (35)	1220 (30)	213 (28)	136 (18)

[a] Estimated standard deviations in the least significant digits are given in parentheses. [b] The equivalent isotropic *U* is defined as one-third of the trace of the U_{ij} tensor.

bonding in producing an ordered crystal structure. In (triphenylphosphine)gold lactate (**2**), there is a strong intermolecular hydrogen bond between O(2) and O(3′) (Figure 3), which prevents free rotation about the C(19)–C(20) bond. In (triphenylphosphine)gold isobutyrate (**1**), no such bond can be formed. Thus, the methyl groups attached to C(20) are disordered over two equal occupancy sites.

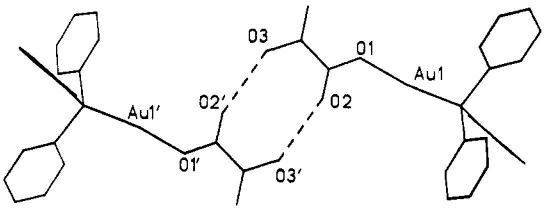


Figure 3. H-bonding interaction between the two molecules of $Ph_3PAuO_2CCH(OH)CH_3$ (**2**).

The bond lengths to Au for **1** and **2** are closer to those reported for the benzoate derivative[2] than for the acetate[1] with Au–O(1) = 2.041 (5) in **1** and 2.038 (16) Å in **2**; cf. 2.033 (6) and 2.063 (6) Å in the benzoate and acetate complexes, respectively. The Au–P distance is also more like that in the benzoate than in the acetate, though the significance of these observations is marginal.

(b) Decarboxylation Studies. Heating any of the three carboxylates or the mixed carboxylate compounds and the P5980 in refluxing benzene/toluene or *p*-xylene/THF under an atmosphere of either air or argon leads to the formation of a gold mirror with the evolution of CO_2. If the bis(triphenylphosphine)gold carboxylates (salts) of nonpolymeric and polymeric compounds are similarly treated, neither gas nor gold mirror are observed. This implies that the decarboxylation requires coordination of the Ph_3PAu^+ unit to the carboxylate.

1. Gold Carboxylate Polymer Studies. The first product obtained in the reaction of Ph_3PAuNO_3 with P5980 contains the Ph_3PAu bound covalently to the oxygens of the carboxylates of the polymer, as indicated in Scheme I. HNO_3 is formed and washed out with H_2O from the polymer solution. Acid removal was confirmed with pH paper. At higher temperatures the oxygen-bound Ph_3PAu^+ was reduced to the metallic gold with the liberation of CO_2 and H_2. An unsaturated polymer is formed, as is shown in Scheme I.

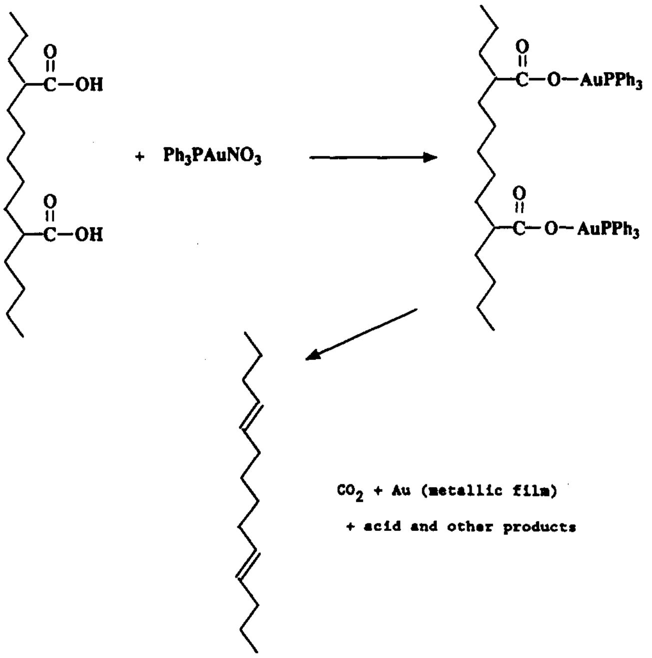
The IR spectrum clearly demonstrates the presence of double bonds as well as residual carboxylate groups. Only

Table V. Bond Lengths (Å) and Angles (deg)[a] for (Triphenylphosphine)gold Lactate (2)

Bond Lengths			
Au-O(1)	2.038 (16)	Au-P	2.219 (4)
O(1)-C(19)	1.290 (24)	O(2)–C(19)	1.184 (22)
C(19)–C(20)	1.525 (35)	O(3)–C(20)	1.403 (34)
C(21)–C(20)	1.395 (45)	P–C(1)	1.799 (16)
P–C(7)	1.814 (13)	P–C(13)	1.828 (17)
C(1)–C(2)	1.401 (16)	C(1)–C(6)	1.394 (26)
C(2)–C(3)	1.412 (26)	C(3)–C(4)	1.326 (30)
C(4)–C(5)	1.389 (20)	C(5)–C(6)	1.425 (27)
C(7)–C(8)	1.388 (27)	C(7)–C(12)	1.366 (19)
C(8)–C(9)	1.368 (24)	C(9)–C(10)	1.349 (31)
C(10)–C(11)	1.334 (41)	C(11)–C(12)	1.401 (23)
C(13)–C(14)	1.363 (24)	C(13)–C(18)	1.419 (24)
C(14)–C(15)	1.407 (24)	C(15)–C(16)	1.387 (29)
C(16)–C(17)	1.399 (30)	C(17)–C(18)	1.346 (25)
C(23)–C(24)	1.325 (55)	C(23)–C(22)	1.328 (53)
C(24)–C(22a)	1.363 (47)	C(22)–C(24a)	1.363 (47)
Bond Angles			
O(1)–Au–P	171.8 (5)	Au–O(1)–C(19)	127.2 (12)
O(1)–C(19)–O(2)	124.7 (18)	O(1)–C(19)–C(20)	111.2 (16)
O(2)–C(19)–C(20)	124.0 (19)	C(19)–C(20)–O(3)	113.6 (20)
C(19)–C(20)–C(21)	114.8 (22)	O(3)–C(20)–C(21)	109.7 (27)
Au–P–C(1)	115.3 (5)	Au–P–C(7)	114.5 (6)
C(1)–P–C(7)	104.9 (8)	Au–P–C(13)	108.1 (6)
C(1)–P–C(13)	105.9 (7)	C(7)–P–C(13)	107.7 (6)
P–C(1)–C(2)	121.0 (14)	P–C(1)–C(6)	120.4 (9)
C(2)–C(1)–C(6)	118.5 (15)	C(1)–C(2)–C(3)	119.4 (16)
C(2)–C(3)–C(4)	120.8 (13)	C(3)–C(4)–C(5)	122.9 (17)
C(4)–C(5)–C(6)	117.0 (18)	C(1)–C(6)–C(5)	121.3 (12)
P–C(7)–C(8)	117.3 (10)	P–C(7)–C(12)	124.3 (13)
C(8)–C(7)–C(12)	118.3 (13)	C(7)–C(8)–C(9)	119.4 (16)
C(8)–C(9)–C(10)	121.4 (23)	C(9)–C(10)–C(11)	120.5 (18)
C(10)–C(11)–C(12)	119.2 (18)	C(7)–C(12)–C(11)	120.8 (18)
P–C(13)–C(14)	118.3 (12)	P–C(13)–C(18)	121.1 (13)
C(14)–C(13)–C(18)	120.5 (15)	C(13)–C(14)–C(15)	122.0 (16)
C(14)–C(15)–C(16)	116.2 (18)	C(15)–C(16)–C(17)	121.8 (18)
C(16)–C(17)–C(18)	121.2 (17)	C(13)–C(18)–C(17)	118.3 (17)
C(24)–C(23)–C(22)	117.8 (31)	C(23)–C(24)–C(22a)	121.6 (34)
C(23)–C(22)–C(24a)	120.5 (33)		

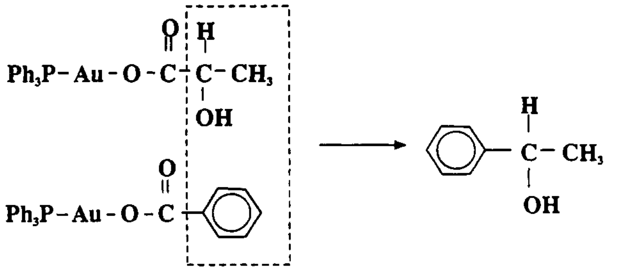
[a] Estimated standard deviations in the least significant digits are given in parentheses.

Scheme I



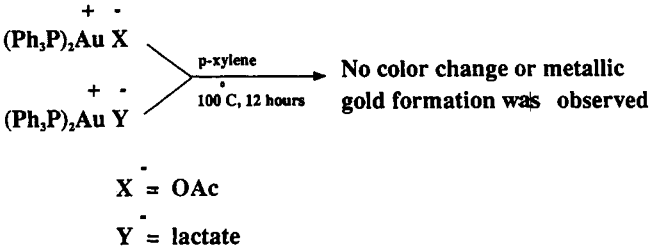
the carboxylate sites that contain gold are assumed to lose CO_2 and produce unsaturation. The IR spectrum of the P5980 (pure) shows a broad peak at 1700 cm^{-1}, which is assigned to the -COOH group. This peak splits into two peaks at 1700 and 1590 cm^{-1} (strong) upon reaction with Ph_3PAuNO_3. The peak at 1590 cm^{-1} is assigned to the double-bond stretch of the polymer. When $(Ph_3P)_2AuCl$ is reacted with the P5980 polymer in the presence of base, no color change, CO_2 liberation, or metallic gold formation is observed.

Scheme II



(±)-2-phenethyl alcohol

Scheme III



2. Decarboxylation Reactions of Ph_3PAu(isobutyrate), Ph_3PAu(lactate), and Ph_3PAu(benzoate). When any one of these three compounds is dissolved in distilled/degassed benzene under an inert atmosphere and refluxed overnight, formation of metallic gold, CO_2, triphenylphosphine, biphenyl, and a trace amount of benzaldehyde is observed. The organic products were identified by GC–MS with peaks at m/z 154 assigned to biphenyl, m/z 262 assigned to triphenylphosphine, and m/z 106 for benzaldehyde. Formation of biphenyl from PH_3PAu(benzoate) could be expected, but the formation of biphenyl in the other decarboxylations and the formation of benzaldehyde implicates the incorporation of the solvent benzene into these reactions.

3. Decarboxylation Reactions of the Mixed Compounds, Ph_3PAu(lactate) and Ph_3PAu(benzoate). This reaction was carried out in toluene with the hope that we could determine the fate of the organic radical species. Decarboxylation of this mixed-acid system gives metallic gold, CO_2, triphenylphosphine, and (±)-2-phenethyl alcohol as the primary organic component. The (±)-2-phenethyl alcohol formation apparently occurs by coupling organic radical components from the two acids, as indicated in Scheme II. The alcohol has been characterized by GC–MS and ^{1}H NMR studies. GC–MS studies show two major peaks at m/z 122 and 262 (triphenylphosphine). The peak at m/z 122 and its fragmentation pattern (m/z 105, 77, 51, and 28) clearly demonstrate the presence of (±)-2-phenethyl alcohol. The ^{1}H NMR spectrum of this material provides further identification. The spectrum shows a doublet at δ 1.35 and quartet at δ 4.8 assigned for CH_3 and -CH protons, respectively. In addition, GC–MS and ^{1}H NMR studies were carried out on an authentic sample of (±)-2-phenethyl alcohol.

The compounds, $(Ph_3P)_2Au^{+}\,{}^{-}(OAc)$ and $(Ph_3P)_2Au^{+}\,{}^{-}$(lactate) were prepared to make sure that the covalent-bonding interaction between Ph_3PAu^+ and the oxygen of carboxylate is essential for the decarboxylation reaction to occur. These types of gold compounds possess a linear AuP_2 geometry,[10] and the interaction between the Au^+ center and the carboxylate is largely ionic. The reaction given in Scheme III was attempted. The failure of these ionic complexes to decarboxylate demonstrates that covalent bonding between Ph_3PAu and the oxygen of the carboxylate is essential for this reaction to occur. With two (or more) phosphines on the gold(I), reduction to the metal does not occur.

Discussion

The decarboxylation of organic acids by high-valent metal ions is thought to be driven by a one-electron reduction of the metal ion followed by elimination of CO_2 (exothermic) from the carboxylate radical.[1,3] A discrete two-step, one-electron reduction of the metal ions has been suggested.[1,2] For example, with Ag(II) formed by oxidation of Ag(I) with peroxydisulfate, oxidation of the carboxylate group by Ag(II) occurs, followed by further oxidation of the alkyl radical to R^+ by a second Ag(II). The CO_2 elimination from RCO_2 gives the alkyl free radical.

In our gold(I) systems the chemistry superficially appears similar to the chemistry previously reported for Ag(II) and other high-valent metal ions.[1-3] Reduction of the Au(I) species to Au(0) occurs, but this can be controlled thermally and by addition of phosphine. Since the Au(I) reduction is stoichiometric and the Au(0) not readily reoxidized, the reaction is not catalytic. The formation of an alkyl (R^+) cation (as observed for the Ag(II) systems) by further oxidation with Au(I) is not expected, since uncoordinated Au(I) is not present.

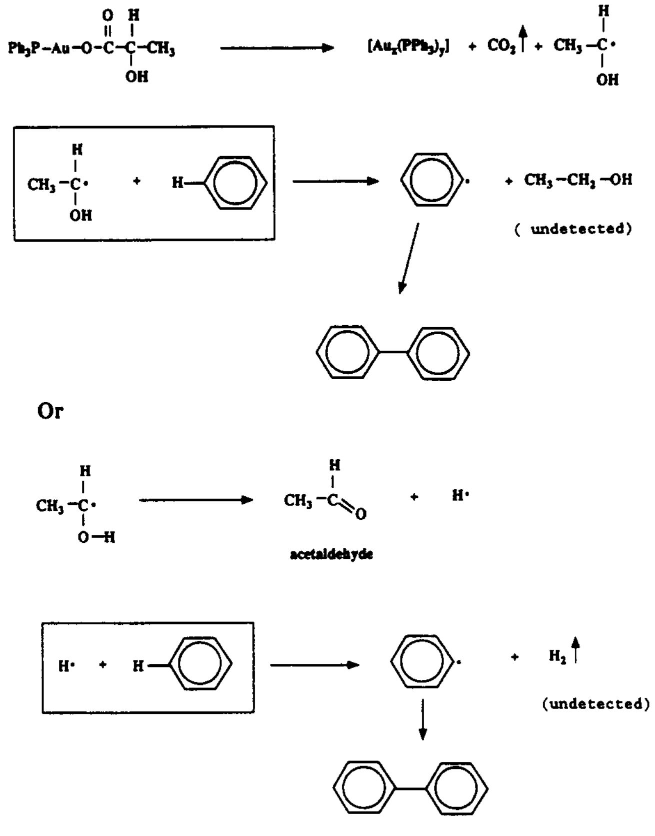
In the gold(I) systems, homolytic cleavage of the Au–O bond leads first to the formation of purple $[Au_x(PPh_3)_y]^0$ clusters followed by the formation of metallic gold, uncoordinated PPh_3, and the carboxylate radical. Homolytic cleavage of the carboxylate C–C bond gives an organic radical and CO_2. In the polymeric carboxylic acid system, further reaction with air, phosphine, or nitrate may lead to the observed unsaturation, although the details of the origin of this unsaturation remains to be established. With the nonpolymeric gold(I) carboxylates, radical coupling reactions are observed and no unsaturated products have been detected. The formation of biphenyl in the decarboxylation of Ph_3PAu(isobutyrate) and Ph_3PAu(lactate) in benzene can be achieved on the basis of a free radical mechanism involving the solvent. Homolytic cleavages of Au–O and C–C bonds lead to the formation of Au(0), CO_2, and an alkyl radical. Radical coupling reactions such as those illustrated in Scheme IV may then follow. Carboxylate radical coupling reactions are not observed due to the instability of the carboxylate radicals.[1]

Since no direct coupling between $CH_3(OH)CH$ radicals (leading to the formation of (±)-1,2-butanediol) was observed, the formation of acetaldehyde or ethanol (Scheme IV) is a possible alternative. The ethanolate radical may give acetaldehyde simply by the loss of H or ethanol by capture of an H atom from the solvent. The failure to detect ethanol in GC–MS studies tentatively suggests that the formation of acetaldehyde is the most likely reaction pathway. In either case, reaction with the benzene solvent is essential and leads to the formation of the observed biphenyl. A similar reaction scheme is applicable for the decarboxylation of Ph_3PAu(isobutyrate).

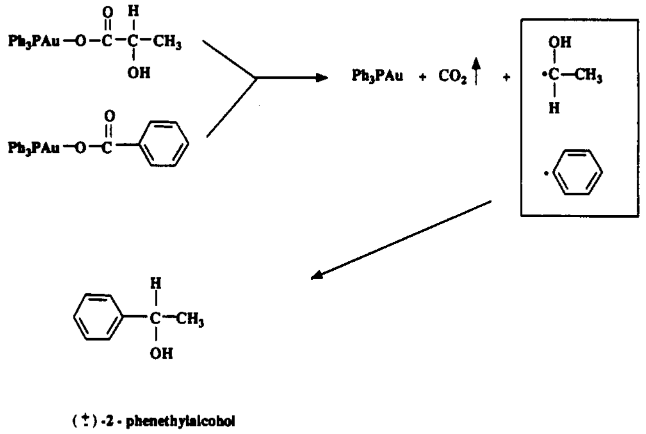
The formation of (±)-2-phenethyl alcohol, Scheme II, in the decarboxylation in toluene of mixed compounds Ph_3PAu(lactate) and Ph_3PAu(benzoate) also may be explained on the basis of free radical reaction pathways. The (±)-2-phenethyl alcohol results from the direct coupling of ethanolate and phenyl radicals. No biphenyl or (±)-1,2-butanediol was detected.

From these results we conclude that the decarboxylation of carboxylate by Ph_3Au^+ occurs via a free radical reaction pathway. Covalent bonding between Ph_3PAu^+ and the carboxylate is essential. Decarboxylation by Au(I) always gives metallic gold film. This method may have potential in the formation of gold film for various applications. However, we have not determined the residual carbon or phosphorus content present. Pure gold (metallic film) is usually conventionally prepared[11] by vapor deposition of volatile organogold(I) and -gold(II) compounds at decomposition temperatures or by laser-induced chemical vapor deposition methods.[12,13]

Scheme IV



Scheme V



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(10) Structural characterizations by X-ray diffraction have been carried out for $(Ph_3P)_2Au^+X^-$ ($X^- = NO_3$ and PF_6) in our laboratories. These studies show that gold(I) has a linear coordination. These structural results will be submitted elsewhere for publication.

(11) Puddephatt, R. J.; Treurnicht, I. *J. Organomet. Chem.* **1987**, *319*, 129.

The preparation of Ph_3PAu carboxylates is relatively simple compared to that of other organogold(I) complexes. The preparation of the Ph_3PAu(carboxylate) can be done in the presence of air and moisture. In addition, formation of a gold film occurs at lower temperatures than in conventional CVD methods.

Acknowledgment. This work has been supported by the National Science Foundation, the Robert A. Welch Foundation, and the Texas Engineering Experiment Station. We thank Steve P. Chum, Dow Chemical Co., for suggesting the problem.

Supplementary Material Available: Full tables of anisotropic thermal parameters and hydrogen atom coordinates for the two compounds reported (5 pages); listings of structure factors (33 pages). Ordering information is given on any current masthead page.

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(13) Baum, T. H. *J. Electrochem. Soc.: Solid State Sci. Technol.* **1987**, *134* (10), 2616.

Reactions of $(\eta\text{-C}_5\text{Me}_5)\text{Ta}(\text{PMe}_3)(\text{H})_2(\eta^2\text{-CHPMe}_2)$ and the Nature of the $\eta^2\text{-CHPMe}_2$ Ligand

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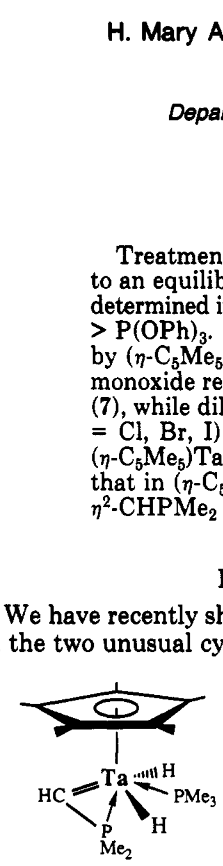
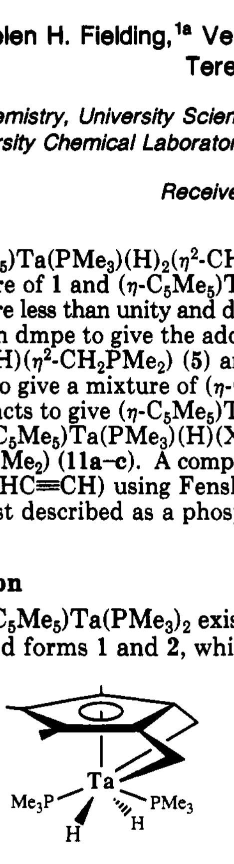
Treatment of $(\eta\text{-C}_5\text{Me}_5)\text{Ta}(\text{PMe}_3)(\text{H})_2(\eta^2\text{-CHPMe}_2)$ (1) with tertiary phosphines and phosphites leads to an equilibrium mixture of 1 and $(\eta\text{-C}_5\text{Me}_5)\text{Ta}(\text{PR}_3)(\text{H})_2(\eta^2\text{-CHPMe}_2)$ (**3a–d**). Equilibrium constants, determined in benzene, are less than unity and decrease in the order $\text{PMe}_2\text{Ph} \approx \text{P(OMe)}_3 > \text{PEt}_3 > \text{PMePh}_2 > \text{P(OPh)}_3$. 1 reacts with dmpe to give the adduct $(\eta\text{-C}_5\text{Me}_5)\text{Ta}(\eta^1\text{-dmpe})(\text{H})_2(\eta^2\text{-CHPMe}_2)$ (4) followed by $(\eta\text{-C}_5\text{Me}_5)\text{Ta}(\text{dmpe})(\text{H})(\eta^2\text{-CH}_2\text{PMe}_2)$ (5) arising by a metal → carbon hydrogen migration. Carbon monoxide reacts with 1 to give a mixture of $(\eta\text{-C}_5\text{Me}_5)\text{Ta}(\text{CO})_2(\text{PMe}_3)_2$ (6) and $(\eta\text{-C}_5\text{Me}_5)\text{Ta}(\text{CO})_3(\text{PMe}_3)$ (7), while dihydrogen reacts to give $(\eta\text{-C}_5\text{Me}_5)\text{Ta}(\text{PMe}_3)_2\text{H}_4$ (8). Treatment of 1 with 1 equiv of MeX (X = Cl, Br, I) affords $(\eta\text{-C}_5\text{Me}_5)\text{Ta}(\text{PMe}_3)(\text{H})(\text{X})(\eta^2\text{-CHPMe}_2)$ (**9a–c**) and treatment with excess MeX, $(\eta\text{-C}_5\text{Me}_5)\text{Ta}(\text{X})_2(\eta^2\text{-CHPMe}_2)$ (**11a–c**). A comparison of the bonding in $(\eta\text{-C}_5\text{Me}_5)\text{NbCl}_2(\eta^2\text{-CHPMe}_2)$ with that in $(\eta\text{-C}_5\text{Me}_5)\text{NbCl}_2(\text{HC}{\equiv}\text{CH})$ using Fenske–Hall quantum chemical calculations suggests that the $\eta^2\text{-CHPMe}_2$ ligand is best described as a phosphinocarbene rather than a phosphaalkyne.

Introduction

We have recently shown that $(\text{C}_5\text{Me}_5)\text{Ta}(\text{PMe}_3)_2$ exists in the two unusual cyclometalated forms 1 and 2, which do not readily interconvert.[2c] A potentially useful feature of these compounds is the retention of the abstracted hydrogens within the metal coordination sphere allowing an opportunity to exploit the reverse metal → carbon hydrogen migrations to generate coordinatively unsaturated, highly reactive tantalum species.

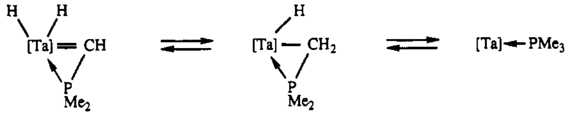


(1)



(2)

This paper presents the results of some of our investigations into the first of these isomers, the phosphine-metalated form 1. We were particularly interested to establish the viability of the reverse hydrogen migrations to give first $[\text{Ta}(\text{H})(\eta^2\text{-CH}_2\text{PMe}_2)]$ and thence regenerate the classical PMe_3 ligand (eq 1) and also to explore the derivative chemistry of 1 in which the $\eta^2\text{-CHPMe}_2$ ligand is retained. Fenske–Hall quantum chemical calculations have been employed to probe the nature of the 4-electron $(\eta^2\text{-CHPMe}_2)$ ligand and allow a comparison with 4-electron acetylene ligands.



(1)

Results and Discussion

1. Reactions of 1 with Tertiary Phosphines and Phosphites. 1 reacts with phosphines and phosphites by displacement of the PMe_3 ligand to give adducts of the type $(\eta\text{-C}_5\text{Me}_5)\text{Ta}(\text{PR}_3)(\text{H})_2(\eta^2\text{-CHPMe}_2)$ (Scheme I). The adducts are readily characterized by ^{1}H NMR spectroscopy (Table I) but have not been isolated. Equilibrium was reached within 6 days at room temperature, and there was no evidence for the formation of $\text{Cp*Ta}(\text{H})(\eta^2\text{-CH}_2\text{PMe}_2)(\text{PR}_3)_2$ or $\text{Cp*Ta}(\text{PMe}_3)_2(\text{PR}_3)_2$. The equilibrium mixture is stable over several months at room temperature for the tertiary phosphine derivatives, but with

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