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FORMATION AND DECOMPOSITION OF ALKYL–GOLD(I) COMPLEXES

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SUMMARY

The syntheses of new primary, secondary and tertiary alkyl(triphenylphosphine)gold(I) complexes are described. Isolation of the thermally stable tert-butyl, isopropyl and sec-butylgold(I) complexes is unusual among organotransition metal complexes. All of these alkyl(triphenylphosphine)gold(I) complexes are monomeric in benzene solution. Methyl and primary alkyl derivatives undergo reductive coupling in high yields on thermolysis of the solid or in solution. The more highly branched isopropyl and tert-butyl analogs afford disproportionation products. The decomposition of methyl(triphenylphosphine)gold(I) in decalin follows first-order kinetics and is retarded by added triphenylphosphine. A mechanism for reductive coupling to ethane is proposed, in which a rate-limiting loss of phosphine is followed by a rapid association with an additional methyl(triphenylphosphine)gold(I).

INTRODUCTION

Organogold chemistry has been largely restricted to those compounds containing aryl, alkenyl, alkynyl or other unsaturated hydrocarbon ligands[1]. Alkyl–gold complexes are generally unstable thermally, but stabilization by nitrogen and phosphorus donors can be sufficiently effective to enable isolation of crystalline adducts. Thus, among alkyl derivatives a variety of methylgold(I, III) complexes are known[2–6], and far outnumber those of any other group. The greater stability of methyl–gold complexes compared to those containing other alkyl groups is consistent with the general trend observed for other organometallics[7]. Organogold(I) complexes containing more highly branched alkyl groups have not been reported, with the exception of a very few examples of some primary alkyl analogs[2,4].

We wish to report the synthesis of a variety of alkyl–gold complexes with triphenylphosphine, including the tert-butyl, isopropyl and sec-butyl derivatives. The latter contrasts with an earlier attempt by Gregory and Ingold[4], who reported that sec-butyl(triphenylphosphine)gold(I) was unstable at room temperature. Furthermore, the preparation of the homologous series of alkyl derivatives also allowed the examination of the thermal decomposition of these alkylgold(I) compounds.

RESULTS

Synthesis of alkylgold(I) complexes

Methyl(triphenylphosphine)gold(I) was prepared from chloro(triphenylphosphine)gold(I) and methylmagnesium iodide according to the procedure similar to that described by Gregory and Ingold[4]. It was isolated as a colorless crystalline

$$CH_3MgI + ClAu^IL \rightarrow CH_3Au^IL + IMgCl \quad (1)^*$$
$$L = (C_6H_5)_3P$$

compound melting at 167–168° [3a]. The methyl groups appeared in the PMR spectrum as a doublet [δ 1.10 ppm, external TMS, J 8.0 Hz ($CDCl_3$)] due to $^1HCAu^{31}P$ coupling[5]. Molecular weight determinations in benzene by vapor pressure osmometry (VPO) indicated that methyl(triphenylphosphine)gold(I) existed as monomeric species.

Ethyl-, n-propyl-, n-butyl- and neopentyl-(triphenylphosphine)gold(I) complexes were prepared from ethylmagnesium bromide, n-propylmagnesium bromide, n-butyllithium and neopentylmagnesium chloride, respectively, by a procedure similar to that used for the methyl analog. These primary alkylgold complexes were crystalline, with the exception of the n-butyl derivative which was a low melting solid. The molecular weight of neopentyl(triphenylphosphine)gold(I) was also determined in diethyl ether, using the isothermal distillation method, and the compound was shown to be monomeric.

tert-Butyl- and isopropyl- and sec-butyl(triphenylphosphine)gold(I) were prepared from the appropriate Grignard reagent and $ClAuPPh_3$ in the presence of excess triphenylphosphine and isolated as colorless crystalline compounds. The tert-butyl derivative melted at 139–142° with decomposition, and VPO indicated it to be monomeric in benzene. The PMR spectrum in dioxane showed a broad unresolved methyl doublet (δ 1.35 ppm) consisting of 9 protons relative to the phenyl multiplet (δ 7.48 ppm) taken as 15 protons, but the methyl resonances (δ 1.97 ppm, J 6.5 Hz), were well-resolved in benzene. The isopropyl analog melted at 150–151° (dec.) and was also a monomeric species in benzene by VPO measurements. The PMR in methylene chloride consisted of a broad unresolved singlet (δ 1.54) with 6 protons relative to those (15) of the phenyl groups. The sec-butylgold complex was isolated as a colorless viscous oil which crystallized on cooling. The compound showed an apparent molecular weight of 426 (calcd. 516.4) at 37° in benzene by VPO, probably due to partial decomposition.

Thermal decomposition of alkyl(triphenylphosphine)gold(I) complexes-solid samples

Methyltriphenylphosphine)gold(I) was placed in a round bottom flask which was sealed with a gas-tight rubber septum, flushed with helium and then placed in a constant temperature bath (118°). The colorless solid darkened as the flask was heated, and evolved ethane quantitatively according to eqn. (2).

$$2CH_3AuL \rightarrow CH_3\text{-}CH_3 + 2Au + 2L \quad (2)$$

Only a trace of methane was detected by gas chromatography. When the thermolysis was complete, the reduced gold appeared as a black solid admixed with triphenylphosphine.

The rate of decomposition was followed by removing samples (< 0.01 %) of the gas phase periodically and analyzing the ethane by gas chromatography

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[*] Coordination around gold will not be included unless necessary for the discussion.

using propane as an internal standard. Figure 1 shows the presence of a sizable induction period prior to the commencement of ethane evolution.

Ethyl(triphenylphosphine)gold(I) decomposed at slightly faster rates than the methyl–gold(I) complex, but showed the same induction period. n-Butane was formed in high yield (90%) together with only small amounts of ethane (1.4%) and ethylene (0.7%).

$$2CH_3CH_2\text{–}Au(PPh_3) \rightarrow CH_3CH_2CH_2CH_3 + 2Au + 2L \qquad (3)$$

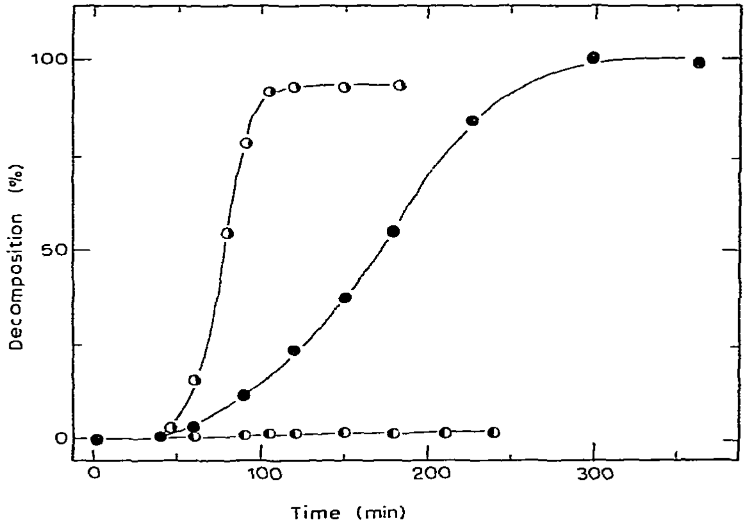

Fig. 1. Thermal decomposition of alkyl(triphenylphosphine)gold(I) in the solid state. ● ethane from methylgold(I); ◑ n-butane and ◐ ethane plus ethylene from ethylgold(I) at 100°.

Isopropyl(triphenylphosphine)gold(I) was heated at 100°, and afforded mainly the disproportionation products, propane (28%) and propylene (34%) and only traces of 2,3-dimethylbutane, if at all. The liquid products were examined further by

$$(CH_3)_2CH\text{–}Au(PPh_3) \rightarrow [C_3H_8, C_3H_6, C_6H_{14}] + 2Au + 2L \qquad (4)$$

heating a sample of the isopropylgold complex in a sealed capillary tube. Gas chromatographic analysis indicated (tentatively) the presence of 2,3-dimethylbutane, 2-methylpentane and at least three unidentified components. The 2-methylpentane may have arisen by addition to propylene, since the decomposition of isopropyl(triphenylphosphine)gold in the presence of isobutylene at 100° (sealed capillary) afforded 2,4-dimethylpentane in addition to those products obtained in the absence added isobutylene.

tert-Butyl(triphenylphosphine)gold(I) did not decompose during a 150 min period at 70°, the flask was then placed in a bath at 118°. After an additional induction period lasting 30 min, isobutylene (47%) and isobutane (13%) were rapidly liberated. Qualitative tests using sealed capillary tubes indicated the presence of C_8-hydrocarbons, the gas chromatography of which showed components corresponding to 2,4,4-trimethylpentane and 2,4,4-trimethylpentene(-1,-2) and at least two other components.

However, no 2,2,3,3-tetramethylbutane could be found by comparison with an authentic sample.

Decomposition of alkyl(triphenylphosphine)gold(I) complexes in solution

Methyl(triphenylphosphine)gold(I) was decomposed in decalin solution smoothly at 100°. The reaction mixture initially turned purple on heating, and as the thermolysis progressed a shiny film of metallic gold was deposited on the sides of the vessel. The reaction mixture of completion was colorless and a quantitative yield of ethane was liberated [eqn. (1)]. We tentatively attribute the transient purple color to the formation of colloidal gold, somewhat analogous to some gold clusters reported recently[8].

The products from the thermal decomposition of other alkyl(triphenylphosphine)gold(I) complexes in solution are also described in Table 1. In general, the complexion of the products obtained in solution was similar to that obtained from the thermolysis of the solid material (*vide supra*).

TABLE 1

THERMAL DECOMPOSITION OF ALKYL(TRIPHENYLPHOSPHINE)GOLD(I) COMPLEXES IN SOLUTION

Alkylgold(I) complex		*Conc. (M)*	*Solvent*	*Temp. (°C)*	*Products (mol %)*			
					RH	*R(−H)*	*R–R*[a]	*ΣR*
CH_3AuPPh_3		0.043	Decalin	100	0		93	93
		0.023	Decalin	100	0		>97	>97
	(O_2)	0.016[b]	Decalin	100	0		95	95
		0.012	Tetralin	100	0		99	99
		0.040	Ethylbenzene	98	0		100	100
$CH_3CH_2AuPPh_3$		0.022	Tetralin	69	2	3	69	74
		0.022	Tetralin	79	2	2	67	71
	 (PPh_3)	0.020 0.040	Tetralin	124	7	5	73	85
$CH_3CH_2CH_2AuPPh_3$		0.021	Toluene	69	4	10	70	84
$(CH_3)_2CHAuPPh_3$		0.021	Tetralin	100	28	16	[c]	
$(CH_3)_3CAuPPh_3$		0.017	Tetralin	99	23	19	20[d]	

[a] Multiplied by 2. [b] Run in air. [c] Liquid products not analyzed. [d] Tentatively identified as 2,4,4-trimethylpentane, not 2,2,3,3-tetramethylbutane.

The kinetics of the decomposition of methyl(triphenylphosphine)gold(I) was followed in decalin solution by the procedure described earlier. Unlike the thermolysis carried out on the solid, methyl(triphenylphosphine)gold(I) in solution evolved ethane at 100° without any apparent induction period as shown in Fig. 2. The formation of ethane followed first-order kinetics for approximately two half-lives, and the first-order rate constant $k = 3.7 \times 10^{-4}$ sec^{-1} was independent of the concentration of methyl(triphenylphosphine)gold(I) in the range, 0.01–0.04 *M*. On the other hand, a second-order plot was linear only up to about 50 % decomposition and curved upward thereafter, clearly indicating a reaction of lower kinetic order. Further, the second-order rate constant obtained from the linear portion, decreased at lower initial

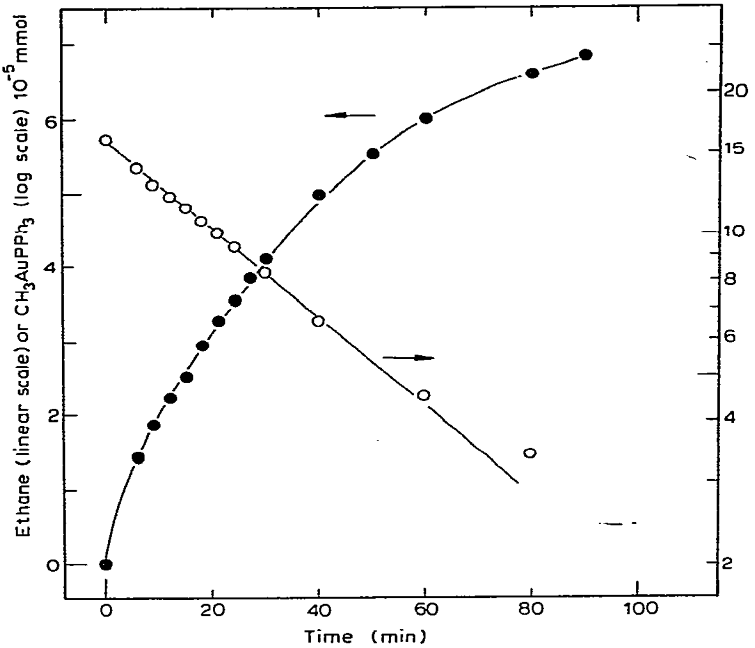

Fig. 2. Decomposition of 0.033 *M* methyl(triphenylphosphine)gold(I) in decalin at 100°. Evolution of ethane ● on linear scale (left). ○ Disappearance of methylgold(I) on log scale (right).

concentrations of methyl(triphenylphosphine)gold(I). The first-order rate constant was the same whether the reaction was carried out in air or under an helium atmosphere. The decomposition was retarded by the addition of triphenylphosphine, but proceeded approximately 5 times faster in tetralin solutions.

The kinetics of the decomposition of ethyl(triphenylphosphine)gold(I) at 69° were much more difficult to reproduce than that of the methyl analog examined at a higher temperature. The evolution of butane appeared to show an induction period, and the rate of decomposition was strongly retarded by triphenylphosphine.

DISCUSSION

Alkyl derivatives of (triphenylphosphine)gold(I) are among the most stable organo-transition metal complexes, since even the rather highly branched tertiary and secondary alkyl analogs can be readily isolated. For example, there are as yet, only a limited number of examples of readily isolable tert-alkylmetal derivatives[9].

The decomposition of these alkyl(triphenylphosphine)gold(I) complexes proceeds by at least two routes: reductive coupling and disproportionation which we formulate in the following manner:

$$2\,\text{R–AuL} \left\{ \begin{array}{ll} \rightarrow \text{RH}+\text{R}(-\text{H})+2\text{Au}+2\text{L} & (5)\\ \rightarrow \text{R–R}+2\text{Au}+2\text{L} & (6) \end{array}\right.$$

These paths are not fundamentally altered whether the thermolysis is carried out on the solid or in solution.

Disproportionation [eqn. (5)] is the dominant reaction with secondary and tertiary alkylgold(I) complexes, since no significant amounts of coupled alkyl dimers were derived from the decomposition of the tert-butyl or isopropyl complexes. In contrast, primary alkyl derivatives such as those containing ethyl and n-propyl groups gave good yields of alkyl dimers [eqn. (6)] and only very small yields of disproportionation products.

The latter observations rule out alkyl radicals as transient intermediates in significant amounts, since hydrogen abstraction from the solvent and disproportionation/combination ratios are known for alkyl radicals. Thus, little ethane was observed even when the decomposition of ethyl(triphenylphosphine)gold(I) was carried out in such good donor solvents as decalin, ethylbenzene and tetralin[10]. Furthermore, if ethyl radicals were formed during the thermolysis of ethyl(triphenylphosphine)gold(I), ethylene (and ethane) would have been formed in 15% yield each relative to n-butane; since the bimolecular rate constant k_c for combination is about 5 times larger than that (k_d) for disproportionation.

$$2\,CH_3CH_2^{\bullet} \xrightarrow{k_d} CH_3CH_3 + CH_2{=}CH_2 \qquad (7)$$

$$2\,CH_3CH_2^{\bullet} \xrightarrow[k_c]{} CH_3CH_2CH_2CH_3 \qquad (8)$$

The ratio k_d/k_c is largely independent of whether the reaction is carried out in the gas phase or in solution[11]. However, the data at hand are insufficient to exclude completely the participation of *any* homolytic processes.

The formation of ethane in very high yields as the sole hydrocarbon product derived from methyl(triphenylphosphine)gold(I) even in the presence of hydrogen donor solvents and molecular oxygen also strongly indicates that methyl coupling involves a molecular process. The monomeric nature of alkyl(triphenylphosphine)gold(I) in solution, the first-order thermolysis and the retardation by added triphenylphosphine suggest a rate-limiting loss of ligand [eqn. (9)].

SCHEME 1

$$CH_3AuL \overset{k_1}{\rightleftharpoons} CH_3Au + L \qquad (9)$$

$$CH_3Au + CH_3AuL \rightarrow CH_3CH_3 + 2Au + L \qquad (10)$$

Rapid reaction of the coordinatively unsaturated alkylgold(I) species with an additional alkyl(triphenylphosphine)gold in a subsequent step (10) would then account for all the known facts about this coupling.

The rate-limiting loss of the phosphine ligand in eqn. (9) contrasts with the rapid *associative* exchange [eqn. (11)] observed in a NMR study of the related methyl(trimethylphosphine)gold(I) complex[12].

$$CH_3AuP(CH_3)_3 + P(CH_3)_3 \rightleftharpoons CH_3Au[P(CH_3)_3]_2 \qquad (11)$$

An association of this type (depending on the equilibrium constant) could be responsible for the fall-off in the rate of decomposition of methyl(triphenylphosphine)gold(I) observed at high conversions (see Fig. 2). It may also contribute to the retardation in the rate by added triphenylphosphine.

The present studies do not allow a further description of the coupling process formulated in eqn. (10). It is likely that one or several intermediates are formed, in contrast to a bimolecular extrusion of ethane. We suggest speculatively that a dialkylaurate(I) species, such as $(CH_3)_2Au^-AuL^+$, may be one such possibility.

The applicability of the mechanism presented in Scheme 1 to other alkyl derivatives is not yet clear. For example, the observation of induction periods during the decomposition of ethyl(triphenylphosphine)gold(I), is not readily accommodated. Induction periods have been observed previously in the reductive disproportionation of alkylcopper(I) and dialkylmanganese(II) species and attributed to autocatalytic processes[13]. Whether similar mechanisms are operative in the decomposition of alkylgold(I) complexes is unknown, and the resolution of this question is made difficult by the quasi-heterogeneous nature of the reaction due to the deposition of gold during the course of the decomposition. Finally, several mechanisms[13b,14] are available to account for the reductive disproportionation [eqn. (5)] observed with the higher alkylgold(I) derivatives, but the variety of products obtained from the thermolysis and the poor material balances, discourage further discussion until more information is available.

EXPERIMENTAL

Materials

Hydrogen tetrachloroaurate(III). $[HAuCl_4 \cdot 3H_2O]$ was prepared from 99.95% gold by dissolution in aqua regia[15] and converted in 96% yield to *chlorotriphenylphosphinegold(I)* according to the procedure described by Gregory and Ingold[4] m.p. 242–243°C (lit.[4] 248–249°C).

Methyl(triphenylphosphine)gold(I). A Grignard reagent prepared from methyl iodide (2.5 ml, 40 mmol) and magnesium (1.0 g, 43 mmol) in 15 ml ether was added dropwise to a suspension of $ClAuPPh_3$ (3.00 g, 6.06 mmol) in 25 ml ether under nitrogen at $-5°$ during 15 min. The mixture was refluxed for an hour, and then added to 150 ml ice-cold 0.5% H_2SO_4. Ether 20 ml was added and the mixture filtered. The solid was washed three times with benzene (100 ml each). The ether layer and the benzene washings were combined, washed with water, dried with Na_2SO_4 and evaporated to about 80 ml. Pentane (200 ml) was then added and the mixture chilled at $-20°$. Colorless find crystals were obtained, 2.23 g (78% yield). A crystallized sample had a melting point 167–168° (lit. 175°)[3a], 173–175°[4], 172–174°[5a]. Mol. wt. (VPO), 475: theor., 474. (Found: Au, 40.9, 40.5, 40.8. Calcd.: Au, 41.5%.) NMR (in $CDCl_3$): δ 1.10 ppm, J 8.0 Hz (room temp.) [lit. δ 0.67 ppm, 8.0 Hz (35°)[5a]].

$C_2H_5AuPPh_3$. A Grignard reagent prepared from 3.0 ml ethyl bromide (40 mmol) and 1.15 g Mg (47 mmol) in 50 ml ether was added dropwise to a suspension of $ClAuPPh_3$ (2.66 g, 5.4 mmol) in 20 ml ether under nitrogen at $-10°$. The mixture was stirred for two hours at room temperature, and then added to 800 ml 0.5% aqueous H_2SO_4 at 0°. The ether layer was separated and the aqueous layer extracted with 200 ml ether. The combined ether solution was dried with Na_2SO_4, treated with active carbon, concentrated to about 150 ml, added to 100 ml pentane and chilled to $-20°$. Crystals separated, which were filtered and dried in vacuum, 1.30 g (49% yield). M.p., 134.5–135.5° (dec.) [lit. 150–152° (dec.)][4]. Ca. 130° (dec.)[3a]. (Analysis: Found, C, 49.3; H, 4.2. $C_{20}H_{20}PAu$ calcd.: C, 49.2; H, 4.1%.)

n-$C_3H_7AuPPh_3$. A Grignard reagent prepared from 4.0 ml n-propyl bromide

(44 mmol) and 1.12 g Mg (46 mmol) in 30 mol ether was added to a suspension of $ClAuPPh_3$ (3.02 g, 6.1 mmol) in 20 ml ether between −11 and −5° during 20 min. The mixture was stirred at room temperature for an hour and added to 400 ml 0.5% H_2SO_4 at 0°. Ether 100 ml was added and the ether layer was separated. It was washed with water, dried with Na_2SO_4, treated with active carbon and evaporated until almost dry. The residue was recrystallized with a 1/1 mixture of ether and pentane, and afforded almost colorless crystals, 1.91 g (62%). M.p. 77.5–79.0° (dec.).

neo-$C_6H_{11}AuPPh_3$. A Grignard reagent prepared from neopentyl chloride and Mg 1.2 g (49 mmol) in 50 ml ether was added dropwise to a suspension of $ClAuPPh_3$ (3.00 g, 6.1 mmol) at −10° during 25 min. The mixture was stirred at room temperature for 95 min and added to 400 ml 5% H_2SO_4 at 0°. The ether layer was separated, dried with Na_2SO_4, treated with active carbon, concentrated to about 30 ml and cooled to −20°. Colorless crystals were obtained: 1.93 g (59%). M.p. 129–133° (dec.). The molecular weight was determined in diethyl ether solution with a benzophenone reference by the Signer method[16]. Mol. wt.: found, 529, calcd.: 530.4. (Analysis: Found, C, 52.3; H, 4.9. $C_{23}H_{26}PAu$ calcd.: C, 52.1; H, 5.0%.)

s-$C_4H_9AuPPh_3$. A Grignard reagent prepared from sec-butyl bromide (4.0 ml., 36 mmol) and magnesium (1.0 g, 43 mmol) in 50 ml ether was added dropwise to a suspension of $ClAuPPh_3$ (3.02 g, 6.11 mmol) in 50 mol ether at −10° under nitrogen during 20 min. Triphenylphosphine (1.61 g, 6.12 mmol) was then added and the mixture was warmed to room temperature, and poured into a solution prepared from 2.2 ml H_2SO_4 and 400 ml water at 0°. The ether layer was dried over Na_2SO_4 and concentrated to a viscous liquid, which was cooled to −20°. Colorless solid (2.67 g) was obtained in 84% yield.

i-$C_3H_7AuPPh_3$. A Grignard reagent, prepared from isopropyl bromide (3.5 ml) and Mg (1.0 g) in 30 ml ether in an atmosphere of He, was added dropwise to a suspension of $ClAuPPh_3$ (3.013 g, 6.09 mmol) in 100 ml ether at −10° during 15 min. Triphenylphosphine (1.610 g, 5.91 mmol) was then added. The mixture was added to 400 ml 0.5% H_2SO_4 at 0°. The ether layer was separated. The aqueous layer was twice extracted with 150 ml ether each time. The combined ether extracts were then dried over Na_2SO_4, treated with a active carbon, filtered and concentrated to about 5 ml. Pentane (5 ml) was added and the solution was chilled to −26°, whereupon 2.623 g slightly brown crystals were obtained. Crude yield: 86%. Molecular weight in benzene solution (VPO): 487, 493; calcd.: 502. M.p.: 150–151° (dec.). NMR (in CH_2Cl_2): δ 1.54, broad singlet, 6 H (taking the phenyl signal as 15 H).(Analysis: Found, C, 49.9; H, 4.0; Au, 37.3. $C_{21}H_{22}PAu$ calcd.: C, 503; H, 4.4; Au, 39.9%.)

t-$C_4H_9AuPPh_3$. A Grignard reagent prepared from tert-butyl chloride (4.0 ml) and Mg 1.0 g in 30 ml ether was added dropwise to a suspension of $ClAuPPh_3$ (2.005 g, 4.05 mmol) in 50 ml ether at −20° during 25 min. Triphenylphosphine (1.070 Hg) was then added, and the mixture stirred for 1.5 h at −10° and 1.5 h at room temperature. The mixture was added to 400 ml 0.5% H_2SO_4 at 0°. The ether layer was separated and the aqueous layer was extracted with 150 ml ether. The combined ether solution was dried, treated with active carbon and concentrated at reduced pressure to about 20 ml. It was then chilled to −26° overnight. Colorless crystals (618 mg) were obtained (30%) which melted at 139–142° (dec.). Molecular weight (VPO): 494, 516; calcd., 516. The NMR spectrum in dioxane solution showed a broad doublet at δ 1.35 ppm which had 9 protons, taking phenyl signal (δ 7.48 ppm) as 15 protons. In benzene solution, it showed a sharp doublet (δ 1.97 ppm, J 6.5 Hz). (Analysis: Found, C, 51.6; H, 5.1; Au, 39.2. $C_{22}H_{24}PAu$ calcd.: C, 51.2; H, 4.7; Au, 38.1).

Thermolysis of alkyl(triphenylphosphine)gold(I)

Solid samples. A 100 ml round bottom flask containing 0.05–0.20 g of the alkylgold(I) complex was swept with helium and capped with a gas-tight rubber septum cap. It was placed in a thermostatted oil bath controlled to ±0.5°. In those runs in which the course of decomposition was followed, a known amount of marker gas was quantitatively added with a hypodermic syringe before the vessel was placed in the bath. A small amount (10 μl) of the gas phase was removed periodically and analyzed by gas chromatography.

In solution. A two-neck round bottom flask was equipped with a rubber septum cap and a glass spoon which could be rotated in the ground glass joint without exposing the constants to air. Solvent (5 ml) was added and a weighed amount of alkylgold complex placed on the spoon. The sealed vessel was swept with helium and a known amount of marker gas added via a hypodermic syringe. The vessel was placed in the bath and the reaction started by rotating the spoon in the ground glass joint so that the contents dropped into the magnetically stirred solvent. When it was determined that air had no large effect on the decomposition of methyl(triphenylphosphine)gold(I), the procedure was simplified. The one-neck vessel containing solvent was swept with helium and the sample quickly added to the preequilibrated solvent as the rubber septum was put in place.

Analysis. The gold content was determined gravimetrically by digesting the sample in concentrated sulfuric acid[17]. Other methods involving iodometry or complete thermolysis followed by gravimetry did not afford accurate analyses.

The hydrocarbon gases were analyzed by gas chromatography (hydrogen flame. Aerograph 500, 50 cm Porapak Q column at 90° or a 20 ft ODPN column). Quantitative analysis was effected by the internal standard method after calibration under reaction conditions. The latter was especially important when solvent was present due to differential solubility of gases. The analyses were reproducible to ±2%. The liquid hydrocarbons were also analyzed by gas chromatography and were only identified (tentatively) by comparison of the retention times with authentic samples. More extensive analyses to prove structure were not carried out.

The molecular weights in benzene solutions were usually carried out with a Mechrochrom 301A vapor pressure osmometer at 37° using benzil or ferrocene as calibrant. The PMR spectra were obtained on a Varian HA 100 spectrometer.

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REFERENCES

1 (a) For a review see: B. Armer and H. Schmidbaur, *Angew. Chem., Int. Ed. Engl.*, 9 (1970) 101;
(b) L. G. Vaughan and W. A. Sheppard, *J. Organometal. Chem.*, 22 (1970) 739; L. G. Vaughan, *J. Amer. Chem. Soc.*, 92 (1970) 730;

(c) K. S. Liddle and C. Parkin, *J. Chem. Soc., Chem. Commun.*, (1972) 26.

2 (a) C. Calvin, G. E. Coates and P. S. Dixon, *Chem. Ind. (London)*, (1959) 1628;
(b) C. S. Gibson and W. T. Weller, *J. Chem. Soc.* (1941) 102 and related papers.

3 (a) G. E. Coates and C. Parkin, *J. Chem. Soc.*, (1962) 3220;
(b) G. E. Coates and C. Parkin, *ibid.*, (1963) 421.

4 B. J. Gregory and C. K. Ingold, *J. Chem. Soc. B*, (1969) 276.

5 (a) H. Schmidbaur and A. Shiotani, *Chem. Ber.*, 104 (1971) 2821;
(b) A. Shiotani and H. Schmidbaur, *ibid.*, 104 (1971) 2838;
(c) M. Bergfeld and H. Schmidbaur, *ibid.*, 12 (1969) 2406;
(d) H. Schmidbaur and R. Franke, *ibid.*, 105 (1972) 2985;
(e) H. Schmidbaur and K. C. Dash, *ibid.*, 105 (1972) 3662.

6 (a) G. C. Stocco and R. S. Tobias, *J. Amer. Chem. Soc.*, 93 (1971) 5057;
(b) F. Stocco, G. C. Stocco, W. M. Scovel and R. S. Tobias, *Inorg. Chem.*, 10 (1971) 2639;
(c) S. W. Krauhs, G. C. Stocco, and R. S. Tobias, *ibid.*, 10 (1971) 1365;
(d) W. M. Scovell, G. C. Stocco and R. S. Tobias, *ibid.*, 9 (1970) 2682;
(e) E. Rivarola, G. C. Stocco, B. L. Pepe and R. Barbieri, *J. Organometal. Chem.*, 14 (1968) 467;
(f) S. J. Harris and R. S. Tobias, *Inorg. Chem.*, 8 (1969) 2259;
(g) W. M. Scovell and R. S. Tobias, *ibid.*, 9 (1970) 945.

7 (a) *Cf.* W. Mowat, A. Shortland, G. Yagupsky, N J. Hill, M. Yagupsky and G. Wilkinson, *J. Chem. Soc., Dalton Trans.*, (1972) 533;
(b) G. W. Parshall and J. J. Mwroca, *Advan. Organometal. Chem.*, 7 (1968) 157.

8 (a) F. Cariati and L. Naldini, *Inorg. Chim. Acta*, 5 (1971) 172;
(b) P. L. Bellon, F. Cariati, M. Manessero, L. Naldini and M. Sansoni, *Chem. Commun.*, (1971) 1423:
(c) L. Malatesta, L. Naldini, G. Simonetta and F. Cariati, *ibid.*, (1965) 212.

9 (a) W. Kruse, *J. Organometal. Chem.*, 42 (1972) C39;
(b) W. P. Giering and M. Rosenblum, *ibid.*, 25 (1970) C71;
(c) B. K. Bower and H. G. Tennent, *J. Amer. Chem. Soc.*, 94 (1972) 2512;
(d) *Cf.* also R. P. A. Sneeden and H. H. Zeiss, J. Thomson and M. C. Baird, *Can. J. Chem.*, 48 (1970) 3443; R. B. King, *Advan. Organometal. Chem.*, 2 (1964) 207.

10 (a) E. S. Huyser, "*Free-Radical Chain Reactions*", Wiley Interscience, New York, N.Y., 1970 p. 90 *ff.*;
(b) G. A. Russell, "*Free Radicals*", Vol. I, Wiley Interscience, New York, N.Y., 1973, Chapter 7.

11 (a) A. P. Stefani, *J. Amer. Chem. Soc.*, 90 (1968) 1694;
(b) R. A. Sheldon and J. K. Kochi, *ibid.*, 92 (1970) 4395.

12 (a) A. Shiotani, H.-F. Klein and H. Schmidbaur, *J. Amer. Chem. Soc.*, 93 (1971) 1555;
(b) H. Schmidbaur, A. Shiotani and H. F. Klein, *Chem. Ber.*, 104 (1971) 2831.

13 (a) M. Tamura and J. K. Kochi, *J. Organometal. Chem.*, 29 (1971) 111;
(b) K. Wada, M. Tamura and J. K. Kochi, *J. Amer. Chem. Soc.*, 92 (1970) 6656; *J. Organometal. Chem.*, 42 (1972) 205.

14 (a) G. M. Whitesides, E. R. Stedronsky, C. P. Casey and J. San Filippo, *J. Amer. Chem. Soc.*, 92 (1970) 1426;
(b) M. Tamura and J. K. Kochi, *ibid.*, 93 (1971) 1485; M. Tamura and J. K. Kochi, *J. Organometal. Chem.*, 31 (1971) 289.

15 O. Glemser and H. Sauer, in G. Bauer (Ed.), "*Handbook of Preparative Inorganic Chemistry*," Vol. II, Academic Press, New York, N.Y., 2nd ed., 1965, p. 1057.

16 A. Steyermark, "*Quantitative Organic Microanalysis*", Academic Press, New York, N.Y., 2nd ed., 1961, p. 535 *ff.*

17 C. L. Wilson and D. W. Wilson, "*Comprehensive Analytical Chemistry*," Vol. IC, Elsevier Pub. Co., Amsterdam, 1961, p. 390.