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COMPLEX BIS(TERTIARYPHOSPHINE)DIMETHYLGOLD(III) CATIONS: PHOSPHINE EXCHANGE AND REDUCTIVE ELIMINATION OF ETHANE*

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SUMMARY

The syntheses and reactivity of cationic dimethylgold(III) complexes $[(CH_3)_2AuL_2]^+$, $L=P(CH_3)_3$, $P(CH_3)_2(C_6H_5)$, $P(CH_3)(C_6H_5)_2$, and $P(C_6H_5)_3$, have been examined. With the exception of $P(C_6H_5)_3$, the ligands react directly with $[(CH_3)_2AuX]_2$, X=Cl, I, giving the bis(tertiaryphosphine) complex. The cationic bis(triphenylphosphine) complex can be produced only with a weakly coordinating ligand, *e.g.*, ClO_4^-. PMR spectra indicate that phosphine exchange is rapid at 40° for all of the chlorides and iodides. The rates increase with increasing phenyl substitution on the phosphine, and non-bonded interactions are postulated as being responsible for the variation in exchange rate. Vibrational spectra indicate only minor electronic changes in the dimethylgold moiety with increasing phenyl substitution of the phosphine. Exchange is faster with I^- than Cl^-, suggesting that reaction occurs by a nucleophilic attack of halide ion on the cation. With ClO_4^- as the anion, exchange is slow even with $\{(CH_3)_2Au[P(C_6H_5)_3]_2^+\}$ at room temperature; however, in solution this cation undergoes a rapid reductive elimination of ethane yielding $\{Au[P(C_6H_5)_3]_2^+\}ClO_4^-$. There is evidence that analogous facile reductive eliminations occur with $[(CH_3)_2AuL_2^+]ClO_4^-$, $L=As(C_6H_5)_3$, $Sb(C_6H_5)_3$ suggesting steric crowding at gold contributes to the ease with which ethane is eliminated from these cations.

INTRODUCTION

The syntheses of stable cationic complexes of the type $[cis\text{-}(CH_3)_2AuL_2^+]$, $L=P(C_6H_5)_3$, $As(C_6H_5)_3$, $Sb(C_6H_5)_3$ and $\{(CH_3)_2Au[P(C_6H_5)_2CH_2]_2^+\}$ have been described previously[1]. It was reported that $\{cis\text{-}(CH_3)_2Au[P(C_6H_5)_3]_2\}ClO_4$ exhibited rapid phosphine exchange in chloroform solution at 40° on the PMR time scale, while the Diphos complex $\{(CH_3)_2Au[P(C_6H_5)_2CH_2]_2\}Cl$ did not. Moreover, it has been reported that the corresponding bis(trimethylphosphine) cation $\{(CH_3)_2Au[P(CH_3)_3]_2^+\}$ does not undergo rapid exchange in aqueous solution on the PMR time scale[2]. In order to determine whether the nature of the phosphine affects the rate of exchange, we have examined the NMR and vibrational

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spectra of complexes with the formulas $[(CH_3)_2AuL_2^+]$, L=$P(CH_3)_3$, $P(CH_3)_2(C_6H_5)$, $P(CH_3)(C_6H_5)_2$, and $P(C_6H_5)_3$. Spectra of $\{(CH_3)_2Au[P(CH_3)_3]_2\}X$, X=$Cl^-$, I^-, were obtained with aqueous and chloroform solutions to determine the effect of solvent and of the anion.

The PMR parameters reported earlier for the ions $[(CH_3)_2AuL_2^+]$, L=$P(C_6H_5)_3$, $As(C_6H_5)_3$, and $Sb(C_6H_5)_3$, also exhibited some apparent inconsistencies. The methyl resonances were at rather high field, apparently accidentally the same for all three compounds at τ 9.14 ppm. Rapid phosphine exchange appeared to be indicated by the absence of coupling with ^{31}P. With these same ligands in compounds of the type $[(CH_3)_2AuClL]$, slightly different methyl chemical shifts were observed as L was varied, and the protons were coupled to ^{31}P in the phosphine complex. This apparently anomalous behavior of the cations was accepted, because the Raman spectrum of a freshly prepared solution of $\{(CH_3)_2Au[P(C_6H_5)_3]_2^+\}ClO_4^-$ showed that no appreciable decomposition had occurred.

Recently $CH_3AuP(C_6H_5)_3$ has been shown to undergo oxidative addition in methyl iodide followed by rapid exchange of methide for iodide between $CH_3AuP(C_6H_5)_3$ and $(CH_3)_2AuIP(C_6H_5)_3$ yielding $(CH_3)_3AuP(C_6H_5)_3$ and $IAuP(C_6H_5)_3$[3]. The resulting trimethylgold product reacts rapidly at room temperature with methyl iodide to produce two moles of ethane and $IAuP(C_6H_5)_3$. It now appears that such reductive eliminations may be much more facile with organogold(III) compounds than previously believed.

EXPERIMENTAL

Microanalyses were performed by the Purdue Microanalytical Laboratory.

Compounds

$\{cis\text{-}(CH_3)_2Au[P(CH_3)_3]_2\}I$. Trimethylphosphine (1.5 ml) was syringed directly into a solution of $[(CH_3)_2AuI]_2$ (0.561 g) in 15 ml of benzene. The solvent and excess phosphine were decanted from the white precipitate which was dissolved in a large quantity of benzene and recrystallized by slowly adding petroleum ether (b.p. 30–60°). A second recrystallization was effected from chloroform by adding hexane. m.p. 126–130°. (Found: C, 18.7; H, 5.04; Au, 38.7; P, 12.5. $C_8H_{24}AuIP_2$ calcd.: C, 19.0; H, 4.78; Au, 38.9; P, 12.2%.)

$\{cis\text{-}(CH_3)_2Au[P(CH_3)_3]_2\}Cl$. This was prepared as described above from $[(CH_3)_2AuCl]_2$. m.p. 128–131°, lit.[2] 128–131°. (Found: C, 22.1; H, 6.10; Au, 45.4; P, 14.5. $C_8H_{24}AuClP_2$ calcd.: C, 23.1; H, 5.83; Au, 47.5; P, 14.9%.)

$\{cis\text{-}(CH_3)_2Au[P(CH_3)_3]_2\}ClO_4$. A solution of $[(CH_3)_2AuI]_2$ (1.0 g) in benzene (10 ml) was stirred with $NaClO_4$ (0.342 g) dissolved in methanol (10 ml). The solution turned yellow and was filtered to remove precipitated sodium iodide. To the remaining solution was added neat trimethylphosphine which caused an immediate white precipitate. The product was washed with hexane and dried over P_4O_{10}. (Found: C, 20.0; H, 5.18; Au, 41.3; P, 12.7; $C_8H_{24}AuClO_4P_2$ calcd.: C, 20.1; H, 5.05; Au, 41.2; P, 12.9%.)

$\{cis\text{-}(CH_3)_2Au[P(CH_3)_2(C_6H_5)]I$. To 0.5 g of $[(CH_3)_2AuI]_2$ in petroleum ether (b.p. 30–60°) was added dropwise neat dimethylphenylphosphine until no further precipitate was formed. Benzene (20 ml) was added, and the solution was

stirred until the precipitate was broken into fine particles. The mixture was filtered, and the fluffy white powder was washed with hexane and dried over P_4O_{10}. m.p. 124–126°. (Found: C, 44.5; H, 4.28; Au, 26.1; P, 8.21. $C_{28}H_{32}AuIP_2$ calcd.: C, 44.6; H, 4.44; Au, 26.3; P, 8.41%.)

Attempted syntheses of $\{cis\text{-}(CH_3)_2Au[P(C_6H_5)_3]_2\}X$ ($X = Cl^-$ *and* I^-). To 0.248 g of *cis*-chlorodimethyl(triphenylphosphine)gold(III)[1] in benzene (10 ml) was added an equimolar amount of triphenylphosphine in benzene (10 ml). Addition of ethyl ether did not induce precipitation, so the ether was removed on a Rotovac and methylcyclopentane added. After cooling to 0°, a precipitate did form which was shown by infrared spectroscopy to be chlorodimethyl(triphenylphosphine)gold(III). Similar results were obtained with the analogous iodide.

$\{cis\text{-}(CH_3)_2Au[P(C_6H_5)_3]_2\}ClO_4$. Synthesis was by the method of Stocco and Tobias[1] (Found: C, 53.4; H, 4.39; Cl, 4.06; Au, 23.5; P, 7.10. $C_{38}H_{36}AuClO_4P_2$ calcd.: C, 53.5; H, 4.23; Cl, 4.17; Au, 23.2; P, 7.28%.)

$\{Au[P(C_6H_5)_3]_2\}ClO_4$. This compound was prepared by the method of Malatesta *et al.*[4]: m.p. 209–210°; lit.[5] 203° (Found: C, 52.5; H, 3.57; Au, 23.9; P, 7.29. $C_{36}H_{30}AuClO_4P_2$ calcd.: C, 52.7; H, 3.67; Au, 24.0; P, 7.56%.)

Solution decomposition of $\{cis\text{-}(CH_3)_2Au[P(C_6H_5)_3]_2\}ClO_4$

An almost saturated solution of $\{(CH_3)_2Au[P(C_6H_5)_3]_2\}ClO_4$ (0.06 g) in $CDCl_3$ was prepared and allowed to stand at room temperature for ca. 72 h in a 10 ml glass bulb. The clear, colorless solution was cooled to dry ice temperature and a sample transferred into the mass spectrometer. A blank was obtained with the $CDCl_3$ solvent.

Pyrolysis of $\{cis\text{-}(CH_3)_2Au[P(C_6H_5)_3]_2\}ClO_4$ *and* $\{cis\text{-}(CH_3)_2Au[As(C_6H_5)_3]_2\}ClO_4$

A sample of the phosphine complex (0.62 g) was placed in a 20 ml glass bulb, and the bulb was evacuated. The sample was placed in an oil bath, and the temperature was raised slowly. At 165°, rapid decomposition was observed. The evolved gas was analyzed by mass spectrometry. The residue contained metallic gold. A sample of the arsine complex (0.31 g) decomposed slowly at ca. 160°, and the gaseous products also were analyzed.

Nuclear magnetic resonance spectra

Routine spectra were obtained with a Varian A60A with the probe maintained at ca. 40°. Low temperature spectra (30° to −65°) were determined with a Varian A60 fitted with a variable temperature probe. For ^{31}P spectra, a Varian XL-100 spectrometer operating at 40.5 MHz was used.

Mass spectra

A Hitachi RMU-6A spectrometer operating with an ion current of 4.5×10^{-9} amp and an ion voltage of 75 eV was used.

Infrared spectra

A Beckman IR-12 spectrometer calibrated *vs.* indene and polystyrene was used to obtain spectra in the range 250–4000 cm^{-1}.

TABLE 1

NUCLEAR MAGNETIC RESONANCE SPECTRA[a] OF $[(CH_3)_2AuL_2^+]$ COMPLEXES

Compound	*Solvent*	*Temp.* (°C)	*CH_3–Au*		*CH_3–P*		*$\tau(C_6H_5P)$*[d] *(ppm)*
			τ(ppm)	*$^3J(^{31}P–^1H)$(Hz)*[b]	*τ(ppm)*	*$^2J(^{31}P–^1H)$(Hz)*[c]	
$\{(CH_3)_2Au[P(CH_3)_3]_2\}I$	$CDCl_3$	−10	8.92	±6.8, ±8.1	8.18	10.4	
$\{(CH_3)_2Au[P(CH_3)_2C_6H_5]_2\}I$	$CDCl_3$	−30	8.70	±6.7, ±8.0	8.12	10.2	2.58
$\{(CH_3)_2Au[P(CH_3)(C_6H_5)_2]_2\}I$	$CDCl_3$	−40	8.83	±9.3, ±9.3	8.08	10.4	2.63
$\{(CH_3)_2Au[P(C_6H_5)_3]_2\}ClO_4$	$CDCl_3$	30	8.82	±6.9, ±8.4			2.63
$\{(CH_3)_2Au[P(CH_3)_3]_2\}Cl$	$CDCl_3$	0	9.04	±6.2, ±7.8	8.14	10.8	
$\{(CH_3)_2Au[P(C_6H_5)_2CH_2]_2\}Cl$	$CDCl_3$	40	8.77	±7.4, ±7.4	6.68[e]	17.0[e]	2.45
$\{(CH_3)_2Au[P(CH_3)_3]_2\}I$	D_2O	40	9.01	±6.2, ±7.6	8.31	10.9	
$\{(CH_3)_2Au[P(CH_3)_3]_2\}Cl$	D_2O	40	9.01	±6.8, ±8.2	8.31	10.7	
$\{Au[P(C_6H_5)_3]_2\}ClO_4$	$CDCl_3$	40					2.40

[a] ^1H Chemical shifts are relative to TMS, τ 10 ppm ($CDCl_3$) or $(CH_3)_3Si(CH_2)_3SO_3^-Na^+$ (D_2O). Estimated errors in chemical shifts, ±0.02 ppm; in coupling constants, ±0.2 Hz. [b] All $^2J(^{31}P–^{31}P')$ in the range 0 to 2 Hz. [c] Actually $^2J(^{31}P–H) + {}^4J(^{31}P–Au–P–C–H)$. [d] Chemical shift of the maximum in the phenyl resonance. [e] CH_2 protons of Diphos ligand.

Raman spectra

Spectra of microcrystalline powders were excited with a Spectra-Physics 125 He/Ne laser and obtained with a Jarrell Ash 25-300 spectrophotometer. Calibration was effected with background plasma lines.

DATA AND RESULTS

Proton magnetic resonance data for the compounds are collected in Table 1. The effect of temperature on the spectrum of {*cis*-$(CH_3)_2Au[P(CH_3)_2(C_6H_5)]_2$}I is illustrated in Fig. 1. The gold methyl resonances under conditions where exchange is slow all are characteristic $A_3XX'A'_3$ spectra with small $^2J(^{31}P–^{31}P')$. The spectrum of {$(CH_3)_2Au[P(C_6H_5)_3]_2$}$ClO_4$, which previously had been reported to exhibit rapid phosphine exchange at 40°, exhibits initially a similar triplet resonance for the gold methyls at room temperature. The spectrum undergoes time dependent changes, and these are illustrated for a $CDCl_3$ solution in Fig. 2. The initial spectrum is very similar to that of the isoelectronic, isostructural {*cis*-$(CH_3)_2Pt[P(C_6H_5)_3]_2$}[5]. Similarly, the parameters for the cation in {$(CH_3)_2Au[P(CH_3)_2(C_6H_5)]_2$}I are very similar to those reported for the isoelectronic {$(CH_3)_2Pt[P(CH_3)_2(C_6H_5)]_2$}[6]: $^2J(^{31}P–C–^1H)$ 10.2, 7.7; $^2J(^{31}P–M–^{31}P')$ ca. 2, 0.5; $^3J(^{31}P–M–C–^1H)_{trans}$ 8.0, 8.2; $^3J(^{31}P–M–C–^1H)_{cis}$ 6.7, 6.3 Hz; respectively. The $^3J(^{31}P–Au–C–^1H)$ and $^2J(^{31}P–^{31}P')$ coupling constants were estimated by comparison of the observed spectra with those

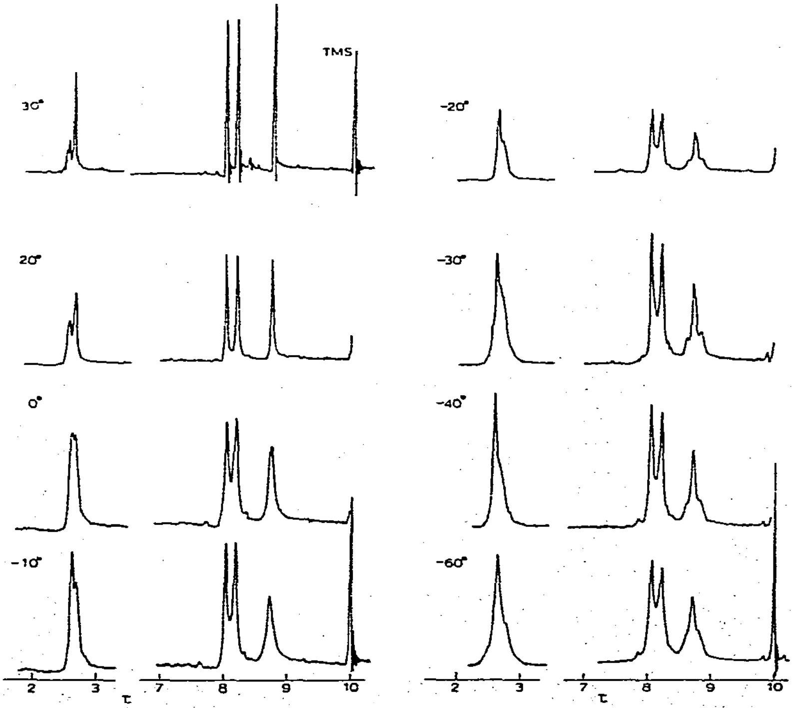
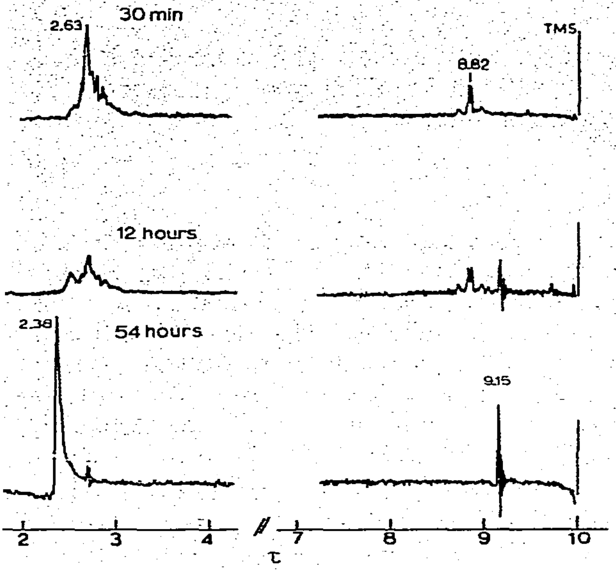


Fig. 1. Effect of temperature on the proton magnetic resonance spectrum of {$(CH_3)_2Au[P(CH_3)_2(C_6H_5)]_2$}I in $CDCl_3$ solution.



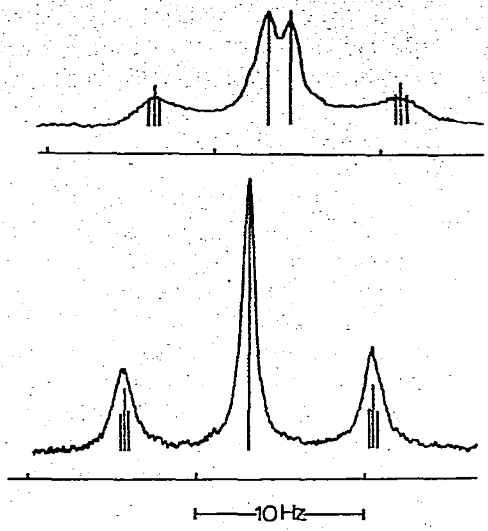


Fig. 2. Changes with time in the proton magnetic resonance spectrum of $\{(CH_3)_2Au[P(C_6H_5)_3]_2\}ClO_4$ in $CDCl_3$ solution at room temperature.

Fig. 3. Observed and calculated PMR spectra for (a) $\{(CH_3)_2Au[P(CH_3)_3]_2\}I$, −40°: $^3J(^{31}P–^1H)$ ±8.4, ±6.8, $^2J(^{31}P–^{31}P')$ 0.5 Hz; (b) $\{(CH_3)_2Au[P(C_6H_5)_2CH_2]_2\}Cl$: $^3J(^{31}P–^1H)$ ±7.4, ±7.4, $^2J(^{31}P–^{31}P')$ 0.5 Hz.

TABLE 2

RAMAN AND INFRARED DATA (cm^{-1}) FOR CRYSTALLINE $[(CH_3)_2AuL_2^+]$ COMPLEXES

Compound	$\delta_s(CH_3)$		$\nu_{as}(Au\text{-}C_2)$		$\nu_s(Au\text{-}C_2)$	
	R	*IR*	*R*	*IR*	*R*	*IR*
$\{(CH_3)_2Au[P(CH_3)_3]_2\}I$[a]	1186w	1185m	513s	513s	522vs	524w
	1194w	1194m				
	1213w	1214w				
	1223w	1222w				
$\{(CH_3)_2Au[P(CH_3)_2(C_6H_5)]_2\}I$[a]	1183w	1180m	521s	522m	526vs	526 (sh)
	1214w	1212w				
$\{(CH_3)_2Au[P(CH_3)(C_6H_5)_2]_2\}I$[a]	1180w–m	1183m	523s		528vs	528 w
	1212w	1217w				
$\{(CH_3)_2Au[P(C_6H_5)_3]_2\}ClO_4$[b]	1190m	1190s	530vs	530m	536vs	539m
	1220s	1223m				
$\{(CH_3)_2Au[P(C_6H_5)_2CH_2]_2\}Cl$[b]	1175m	1175w	530vs	—	524vs	
	1203m	1204m				

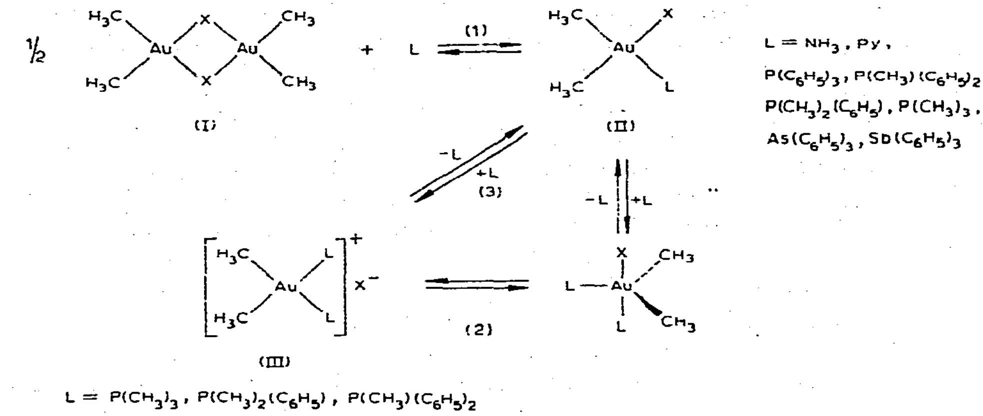
[a] Sampled as microcrystalline powders in capillaries. [b] Data from ref. 1.

calculated using the program UEAITR[7]. Initial values were estimated using the approximate equations of Harris[8]. Calculated and observed spectra for $\{(CH_3)_2Au[P(CH_3)_3]_2\}I$ and $\{(CH_3)_2Au[P(C_6H_5)_2(CH_2)]_2\}Cl$, which are typical, are given in Fig. 3. With the exception of the Diphos chelate, all of the compounds in chloroform solution exhibit resonances which are slightly broadened in comparison to TMS. The ^{31}P NMR spectrum of $\{(CH_3)_2Au[P(CH_3)_3]_2\}I$ at $-30°$ in $CDCl_3$ with proton decoupling in the methyl region exhibits a single resonance at δ 15.45 ppm relative to 85% H_3PO_4.

Infrared and particularly Raman spectra, where the gold–carbon stretching vibrations have very high intensity, were recorded to probe electronic changes at the gold atom caused by varying the phosphine ligands. Data are collected in Table 2 for (AuC_2) stretching and for the symmetric CH_3 deformations.

DISCUSSION

The course of the simple bridge splitting reactions[1,2] of dimethylgold halides is illustrated below. In chloroform solution, the cations, (III), should exist as intimate ion pairs with the counter ions. This gives rise to slightly different chemical shifts for the gold methyl protons with $X=Cl^-$ and I^-. The difference vanishes when the spectra are obtained with aqueous solutions.



The two nitrogen donors are poorer ligands than the phosphines for the dimethylgold moiety, and the bis complexes are not formed. For example, $[(CH_3)_2AuCl]_2$ and $[(CH_3)_2AuI]_2$ dissolve in neat pyridine to yield only (II)[9]. Although $[(CH_3)_2Au(NH_3)_2^+]$ is present when $[(CH_3)_2AuCl]_2$ or $[(CH_3)_2AuI]_2$ dissolves in liquid ammonia[9], crystallization yields a product which loses ammonia very readily yielding (II). In the presence of excess pyridine, the two resonances for the non-equivalent methyls of (II) collapse, and the process is first order in pyridine[9]. The same effect was observed here with excess triphenyl phosphine and $(CH_3)_2AuIP(C_6H_5)_3$ during efforts to synthesize $\{(CH_3)_2Au[P(C_6H_5)_3]_2\}I$.

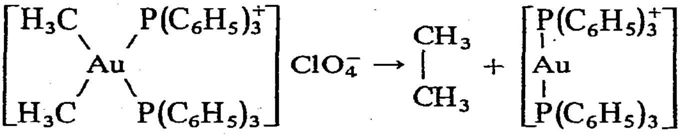
When L contains one or more methyl groups bound to phosphorus, the cationic bis(phosphine) complexes, (III), are produced. When the tertiary phosphine is varied with constant counter ion, the temperature at which the $A_3XX'A'_3$ multiplet collapses decreases with increasing phenyl substitution. In the series $[(CH_3)_2AuL_2]I$, $L=(CH_3)_3P$, $(CH_3)_2(C_6H_5)P$, $(CH_3)(C_6H_5)_2P$, the temperatures are $>0°$, ca.

$-10°$, and ca. $-30°$, respectively, for $CDCl_3$ solutions. The most reasonable explanation for this order is that nonbonded interactions between the *cis* phosphines increase as methyl groups are replaced successively by the bulkier phenyl groups. This shifts equilibrium (3) in favor of the neutral complex and free phosphine. Consistent with this hypothesis is the observation that $\{(CH_3)_2Au[P(C_6H_5)_3]_2^+\}$ could not be prepared as the chloride or iodide[1,2], but with a weakly coordinating ligand such as ClO_4^-, stable salts can be obtained[2].

While an earlier report[1] indicated that phosphine exchange with $\{(CH_3)_2Au[P(C_6H_5)_3]_2^+\}ClO_4$ in chloroform solution was fast on the PMR time scale, this was not observed to be the case. Freshly prepared solutions in $CDCl_3$ gave the same $A_3XX'A_3'$ spectrum. In this case, the slow exchange is a consequence of the presence of perchlorate as the counter ion. Exchange appears to proceed via a nucleophilic attack of the anion on gold. In order to obtain comparable exchange rates with $[(CH_3)_2AuL_2]X, X=Cl, I$, the iodide solution must be ca. 10° lower in temperature, consistent with a higher nucleophilicity of iodide for gold. In addition the solvent is important. The absence of exchange observed by Shiotani and Schmidbaur[2] for $\{(CH_3)_2Au[P(CH_3)_3]_2\}Cl$ in D_2O is a consequence of the poor nucleophilicity of water and the high fugacity of the phosphine in this solvent.

The chloroform solutions of $\{(CH_3)_2Au[P(C_6H_5)_3]_2\}ClO_4$ do undergo a time dependent change as illustrated in Fig. 2. The resonance of τ 9.15 ppm, which previously was the only signal observed, was identified as ethane by the mass spectrum and by comparison of the PMR chemical shift with that of the ethane resonance in a saturated $CDCl_3$ solution. No methane was observed, and a simple reductive elimination reaction appears to occur. The phenyl resonance shifts to τ 2.40 ppm as ethane is eliminated. After the triplet signal characteristic of the *cis*-bis(phosphine) complex had disappeared, the clear solution was evaporated, and the residue was recrystallized from a chloroform–hexane mixture. This compound gave both PMR and infrared spectra identical to an authentic sample of $\{Au[P(C_6H_5)_3]_2\}ClO_4$.

This reductive elimination reaction, (4), appears to have proceeded considerably more rapidly in our previous investigation[1] using $CHCl_3$ freshly distilled



(IV) (V) (4)

from sulfuric acid as the solvent, and spectra obtained shortly after solution preparation showed only the ethane resonance. On the other hand, the solution Raman spectrum[1] recorded at ca. 22° rather than 40° as in the PMR measurements correctly indicated the presence of (IV) although the analysis reported for the sample recovered after the spectrum was obtained corresponds to $\{Au[P(C_6H_5)_3]_2\}ClO_4$. We are at a loss to explain this difference in reaction rate, although it is possible that impurities in the chloroform solution, *e.g.*, CCl_3^-, catalyze the reaction.

Crystalline $\{(CH_3)_2Au[P(C_6H_5)_3]_2^+\}ClO_4$ shows no detectable decomposition after storage for over two years at 2°. A solution of $\{(CH_2)_2Au[P(C_6H_5)_3]_2\}ClO_4$ in dried and degassed $CDCl_3$ was prepared on a vacuum line. This solution underwent the same reductive elimination indicating that oxygen or other environmental contaminants are not involved in this reaction.

Both $\{(CH_3)_2Au[As(C_6H_5)_3]_2\}ClO_4$ and $\{(CH_3)_2Au[Sb(C_6H_5)_3]_2\}ClO_4$ also were observed previously to give only the τ 9.14 ppm resonance now identified as due to ethane, and so these ions also undergo facile reductive eliminations at room temperature. Pyrolyses of the solid bis-triphenylphosphine and triphenylarsine compounds gave ethane as the principal gaseous product as identified by its mass spectrum. Neither the solution decomposition nor the pyrolysis experiments yielded measurable amounts of methane.

The condition required for the facile reductive elimination appears to be coordination of two bulky ligands to the *cis*-dimethylgold(III) moiety. For example, the cation $\{cis\text{-}(CH_3)_2Au[P(CH_3)(C_6H_5)_2]_2^+\}$ was stable under the same conditions which led to elimination of ethane from $\{cis\text{-}(CH_3)_2Au[P(C_6H_5)_3]_2\}^+$. The tertiary phosphines also exert a rather high *trans* influence on the gold methyls and this may be a necessary but not sufficient condition. The order of *trans* influence of several ligands can be estimated from values of $\nu_s(AuC_2)$* obtained from Raman spectra of compounds of the $[cis\text{-}(CH_3)_2AuL_2]$ type: H_2O, 590[9]; OH^-, 586[10]; NH_3, 579[9]; Cl^-, 572[10]; Br^-, 558[10]; $S(CH_3)_2$, 555[10]; $As(C_6H_5)_3$, 529[1]; $P(CH_3)_3$, 522 cm^{-1} [1]. If the phosphines are examined, the order is $P(C_6H_5)_3$, 536; $P(CH_3)(C_6H_5)_2$, 528; $P(CH_3)_2(C_6H_5)$, 526; $P(CH_3)_3$, 522 cm^{-1}; however, this may not reflect increasing *trans*-influence, because the Raman and infrared intensities of the $P(C_6H_5)_3$ compound clearly show that there is mixing of the (Au–C) and phenyl coordinates in the normal mode[11]. Consequently, the variation among the phosphines may only reflect the effect of increasing vibrational mixing with increasing phenyl substitution.

Reductive elimination of ethane has been observed to occur with $(CH_3)_3$-$AuP(C_6H_5)_3$ upon pyrolysis of the solid at 120°, or upon warming of xylene solutions to 120° and biphenyl solutions to 175° [12]. The trimethylgold compounds, however, are quite stable in chloroform solution at room temperature[13] or in the case of $(CH_3)_3AuP(CH_3)_3$ as the neat liquid[14]. The facile elimination of ethane from the $[(CH_3)_2AuL_2^+]ClO_4^-$ compounds in solution certainly involves a concerted cleavage facilitated by steric effects involving these bulky ligands which also exert a large *trans* influence on the gold methyls.

As defined by Woodward and Hoffmann, these eliminations are cheletropic reactions[15]. If the two electrons from the breaking σ bonds are derived from the molecular orbital antisymmetric with respect to the plane normal to the C_2AuP_2 plane, they can be transferred to $d_{x^2-y^2}$ of the $\{Au[P(C_6H_5)_3]_2^+\}$ product with conservation of orbital symmetry completing the d^{10} configuration of the gold(I) complex.

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* The same series is obtained using 1/2 $(\nu_s + \nu_{as})$, since the separations of these modes are all about the same and of the order of 5–10 cm^{-1}.

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