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Bonding in Methylgold(I) and Trimethylgold(III) Compounds. Nuclear Magnetic Resonance, Raman, and Infrared Spectra and Normal Coordinates[1]

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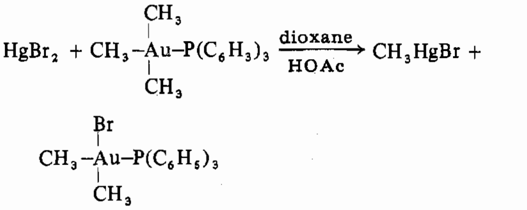
Reaction of *cis*-$(CH_3)_2AuIP(CH_3)_3$ with CD_3Li gives only *cis*-$(CH_3)_2(CD_3)AuP(CH_3)_3$. There is no evidence for intramolecular exchange of methyl groups between positions cis and trans to the phosphine or of intermolecular exchange between $(CH_3)_2(CD_3)AuP(CH_3)_3$ molecules or between $(CH_3)_2(CD_3)AuP(CH_3)_3$ and CD_3Li. Raman, infrared, and pmr data are reported for $(CH_3)_3AuP(CH_3)_3$, *cis*-$(CH_3)_2(CD_3)AuP(CH_3)_3$, $(CD_3)_3AuP(CH_3)_3$, $(CH_3)_3AuAs(CH_3)_3$, $CH_3AuP(CH_3)_3$, and $CD_3AuP(CH_3)_3$. For $(CH_3)_3AuPR_3$ compounds ($R = CH_3, C_2H_5, C_6H_5$) $|{}^3J(P\text{-}H)_{\text{trans P}}| / |{}^3J(P\text{-}H)_{\text{cis P}}| = 1.3 \pm 0.1$. Vibrational analyses were carried out for these molecules as well as for $XAuP(CH_3)_3$ ($X = Cl, Br, I$). In all of the compounds, there is extensive vibrational coupling between the symmetric deformation of the PC_3 ligand skeleton and the Au–P coordinate in the two totally symmetric vibrations at *ca.* 200 and 350 cm^{-1}. Exchange of L between $(CH_3)_3AuL$ is faster when $L = As(CH_3)_3$ than $P(CH_3)_3$, and the stretching force constant of Au–As is smaller than that of Au–P. The trimethylgold(III) compounds have two distinctly different kinds of gold–carbon bonds, and the Au–C stretching force constants differ by *ca.* 0.2 mdyn/Å. The difference in bond lengths is estimated from the force constants to be *ca.* 0.03 Å. The signs of the f(Au–C, Au–P) interaction force constants in the $(CH_3)_3AuP(CH_3)_3$ and $(CH_3)AuP(CH_3)_3$ compounds are consistent with the stabilization of these compounds by tertiary phosphines. The sign of the interaction force constant $f(\text{Au–C,Au–C})_{\text{trans}}$ indicates a strengthening of one bond as the other methyl group is removed, consistent with chemical data. The force constants are discussed with respect to the oxidative addition of saturated molecules to CH_3AuPR_3 and the reductive cleavage of $(CH_3)_3AuPR_3$ compounds. With the $XAuP(CH_3)_3$ compounds, the Au–P stretching force constant decreases in the sequence $Cl > Br > I \simeq CH_3$. This is consistent with increasing trans influence from chloride to iodide and methide.

Introduction

The organometallic chemistry of gold involves primarily σ-bonded alkyl derivatives of gold(I) and gold(III) and has been reviewed recently.[2] Trimethyl(trimethylphosphine)gold(III) and methyl(trimethylphosphine)gold(I) were originally prepared by Coates and Parkin,[3] and the ^1H nuclear magnetic resonance spectra have appeared in several recent reports.[4-6] In benzene solution, free trimethylphosphine exchanges rapidly on the proton nmr time scale with the coordinated phosphine of the gold(I) complex;[4-6] however, exchange between trimethylphosphine and trimethyl(trimethylphosphine)gold(III) is slow up to 60°,[4] at which temperature decomposition of the gold compound begins. Differences in δ and ^3J(P-H) for the two kinds of methyls bound to gold in trimethyl(trimethylphosphine)gold(III) were attributed to different trans influences of the ligands.[4]

Mercuric salts cleave one methyl group rapidly from trimethyl(triphenylphosphine)gold(III) and methyl(triphenylphosphine)gold(I) in a variety of solvents.[7] For both substrates, the reaction order and relative reactivities of mercuric salts are consistent with an SE2 mechanism. The gold(III) reaction involves stereospecific cleavage of a methyl group trans to methyl, reaction 1. The second-order constants for



$$HgBr_2 + CH_3\text{-}\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{Au}}\text{-}P(C_6H_5)_3 \xrightarrow[\text{HOAc}]{\text{dioxane}} CH_3HgBr + CH_3\text{-}\underset{\displaystyle CH_3}{\overset{\displaystyle Br}{Au}}\text{-}P(C_6H_5)_3 \qquad (1)$$

mercuric bromide reacting with trimethyl(triphenylphosphine)gold(III) and methyl(triphenylphosphine)gold(I) in dioxane at 24.7° are 130 and 144 l. mol^{-1} sec^{-1}, respectively; in acetone at 0.0° the rates are 2000 and 1320 l. mol^{-1} sec^{-1}, respectively. Gregory and Ingold[7] noted the similarity in reaction rates of the gold(I) and gold(III) compounds but offered no explanation for it.

Recently Tamaki and Kochi[8] have observed oxidative addition of methyl iodide to methyl(triphenylphosphine)gold(I) to yield iododimethyl(triphenylphosphine)gold(III) which

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reacts rapidly with additional gold(I) complex producing trimethyl(triphenylphosphine)gold(III). These reactions are quite sensitive to the experimental conditions, and Shiotani and Schmidbaur obtained only C_2H_6 and $IAuP(CH_3)_3$ by reaction of the analogous $P(CH_3)_3$ complex in benzene at 20°.[9]

In order to obtain information on the strengths of the bonds in trimethylgold(III) compounds and to compare these with the corresponding bonds in methylgold(I) compounds, we have collected Raman and infrared data for $(CH_3)_3AuP(CH_3)_3$, $(CH_3)AuP(CH_3)_3$, some deuterated molecules, and $(CH_3)_3AuAs(CH_3)_3$. Normal-coordinate analyses have been made for both the gold(III) and gold(I) compounds.

Coates and Parkin[3] and Schmidbaur and Shiotani[5] have reported partial infrared data for trimethyl(trimethylphosphine)gold(III) and methyl(trimethylphosphine)gold(I) with tentative assignments. While our work was in progress, Duddell, *et. al.*,[10] reported vibrational spectra of trimethylphosphine- and trimethylarsinegold(I) halides, commenting that they were unable to obtain satisfactory normal coordinates and force constants for the molecules. Since these have a simple structure insofar as coordination compounds are concerned, this observation seemed to have disturbing implications for all normal-coordinate analyses of metal complexes. Consequently, problems of assignments and coupling in these gold(I) complexes are examined too, and normal-coordinate analyses were carried out.

Experimental Section

Syntheses. Standard techniques[11] for preparation and handling of air-sensitive compounds were employed where necessary. Diethyl ether was stored over $LiAlH_4$ and distilled under nitrogen immediately before use. Pyridine was refluxed over KOH and distilled before use. Other solvents were dried over activated molecular sieves (Linde 4A). Methyllithium (1.72 *M*) was purchased from Foote Mineral Co., lithium (30% dispersion in mineral oil) from Lithcoa, and CD_3I (99.5% isotopic purity) from Stohler Isotope Co.

CD_3Li. Lithium metal was washed repeatedly with ether under argon to remove the dispersing agent. A solution of CD_3I in ether was added to this and reaction was initiated by gentle warming. When refluxing ceased after complete addition, the mixture was syringed into a serum cap stoppered tube and centrifuged to settle the lithium iodide and float lithium metal. The clear CD_3Li–ether solution was syringed out and transferred directly to a reaction vessel.

$(CH_3)_3AuP(CH_3)_3$. This compound was prepared by the method of Krauhs, Stocco, and Tobias.[12] To $[(CH_3)_2AuI]_2$ (6.0 mmol) disolved in 25 ml of dry cyclopentane was added trimethylphosphine (7 mmol). Ether to dissolve the white precipitate and then methyllithium (15 mmol) were added at 0°. The mixture was stirred for several hours and warmed to room temperature, excess methyllithium was destroyed with water, the organic phase was separated and dried over molecular sieves (4A), and excess solvent was removed on a Roto-Vac. The oily residue was sublimed several times to produce a white waxy crystalline material, mp 26° (lit.[3] mp 23°). *Anal.* Calcd for $C_6H_{18}PAu$: C, 22.6; H, 5.70; P, 9.73; Au, 61.9. Found: C, 22.5; H, 5.60; P, 9.81; Au, 61.7.

***cis*-$(CH_3)_2(CD_3)AuP(CH_3)_3$.** This was prepared in the same manner as the parent compound, except that CD_3Li was utilized. *Anal.* Calcd for $C_6H_{15}D_3PAu$: C, 22.4; H and D, 6.58; P, 9.64; Au, 61.3. Found: C, 22.6; H and D, 6.50; P, 9.52; Au, 61.6.

$(CD_3)_3AuP(CH_3)_3$. Methyllithium-d_3 (29 mmol) was added dropwise under an argon atmosphere at 0° to a slurry of trichloropyridinegold(III) (4 mmol) in dry ether. When about two-thirds of the CD_3Li had been added, 1.5 ml of trimethylphosphine was syringed into the mixture and the CD_3Li addition was continued. The work-up was the same as for $(CH_3)_3AuP(CH_3)_3$. The proton nmr spectrum showed no traces of any CH_3–Au resonances. (The same procedure with CH_3Li produces a product identical with that prepared from $[(CH_3)_2AuI]_2$ above.)

$CH_3AuP(CH_3)_3$. The method of Coates and Parkin[3] was used to prepare this compound, mp 75–75.5°. *Anal.* Calcd for $C_4H_{12}PAu$: C, 16.7; H, 4.20; P, 10.7; Au, 68.4. Found: C, 16.6; H, 4.09; P, 10.7; Au, 68.2.

$CD_3AuP(CH_3)_3$. This compound was prepared by the method of Coates and Parkin[3] using CD_3Li. *Anal.* Calcd for $C_4H_9D_3PAu$: C, 16.5; H and D, 5.19; P, 10.6; Au, 67.7. Found: C, 16.7; H and D, 5.20; P, 10.6; Au, 67.4.

$(CH_3)_3AuAs(CH_3)_3$. Preparation was by the same method as for $(CH_3)_3AuP(CH_3)_3$, using trimethylarsine in place of the phosphine. The product is a liquid at room temperature, and it freezes at about 0°. [After subliming the product from the reaction mixture, a gray solid remained which showed proton magnetic resonance absorptions at τ 8.70, 8.55, and 8.42 in approximately 1:1:3 ratio, infrared absorptions (Nujol mull) at 530, 540, 592 and 621 cm^{-1}, and which reacts with aqueous silver nitrate to form a yellow precipitate. It is undoubtedly iododimethyl(trimethylarsine)gold(III) but was not characterized further.] *Anal.* Calcd for $C_6H_{18}AuAs$: C, 19.9; H, 5.01; Au, 54.4. Found: C, 19.8; H, 4.95; Au, 54.1.

Raman Spectra. The spectra of $(CH_3)_3AuP(CH_3)_3$, its isotopically substituted analogs, and $(CH_3)_3AuAs(CH_3)_3$ were obtained with neat liquid samples in capillary tubes with the Purdue Mark II laser Raman spectrophotometer[13] using both He–Ne and Ar^+ laser excitation and on a Jarrell-Ash 25-300 spectrophotometer using He–Ne excitation. Spectra of $CH_3AuP(CH_3)_3$ were obtained with microcrystalline powders and solutions. In benzene or carbon disulfide, $CH_3AuP(CH_3)_3$ tended to decompose in the laser beam, but spectra were obtained by scanning until decomposition began and then substituting a new solution.

The invariants of the Raman polarizability tensor, $\bar{\alpha}'^2$ and γ'^2, were calculated on a point by point basis from spectra obtained with the exciting electrical vector oriented parallel and perpendicular to the monochromator axis. In these measurements, no analyzer was employed (ρ(depolarized bands) = $^6/_7$).

Infrared Spectra. Over the 200–4000-cm^{-1} range a Beckman IR-12 spectrometer calibrated *vs.* indene and polystyrene was used. Far-infrared spectra for $(CH_3)_3AuP(CH_3)_3$ and $(CH_3)_3AuAs(CH_3)_3$ were obtained in the region 100–600 cm^{-1} using a Beckman IR-11 spectrometer calibrated with water vapor.

Proton Magnetic Resonance Spectra. Spectra were obtained on a Varian A-60A spectrometer in which the probe temperature is *ca.* 40°. TMS was used as an internal reference. Coupling constants are accurate to ±0.5 cps and chemical shifts to 0.01 ppm.

Data and Results

Proton Magnetic Resonance. Chemical shifts and coupling constants for methylgold compounds are collected in Table I. In chloroform and carbon tetrachloride, the order of chemical shifts for $(CH_3)_3AuP(CH_3)_3$ and $(CH_3)_3AuAs(CH_3)_3$ is $\tau_{CH_3Au(cis\ P)} > \tau_{CH_3Au(trans\ P)} > \tau_{CH_3P}$ but in benzene the order inverts to $\tau_{CH_3Au(cis\ P)} > \tau_{CH_3P} > \tau_{CH_3Au(trans\ P)}$. The coupling constants show little solvent dependence, and the absolute magnitudes are $^2J(P\text{-}H) \simeq {}^3J(P\text{-}H)_{trans} > {}^3J(P\text{-}H)_{cis}$. The τ values for $CH_3AuP(CH_3)_3$ show the same reversal from $CDCl_3$ to C_6H_6 solution. To determine if benzene might be acting as a weakly bound ligand, gold–carbon stretching frequencies, which should be sensitive to a change in coordination, were measured for benzene and chloroform solutions (0.9 *M*) of $CH_3AuP(CH_3)_3$. The measured values were 539.3 and 539.5 cm^{-1}, respectively, suggesting that benzene is not bound to gold in any manner. A more probable explanation is that the solvent cage is structured so that on the average the methyls bound to gold are deshielded, while methyls bound to phosphorus are shielded by the ring currents of the benzene molecules. Mixtures of $(CH_3)_3As$ and $(CH_3)_3AuAs(CH_3)_3$ did not undergo rapid exchange on the pmr time scale at 40°, but the signals for both free and bound ligand broadened. Addition of $(CH_3)_3P$ to $(CH_3)_3AuAs(CH_3)_3$ caused disappearance of the bound arsine signal

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Table I. Nmr Spectral Parameters

	Solvent					
	CCl_4		$CDCl_3$		C_6H_6	
Compd	τ_{CH_3}, ppm	*J*(P-H), Hz[a]	τ_{CH_3}, ppm	*J*(P-H), Hz[a]	τ_{CH_3}, ppm	*J*(P-H), Hz[a]
$(CH_3)_3AuP(C_6H_5)_3$	10.09 (2.0 ± 0.2)[b]	7.1[b]			9.50 (1.98 ± 0.07)[b]	7.1[b]
	8.97 (1)[b]	9.4[b]			8.36 (1)[b]	9.5[b]
$(CH_3)_3AuP(C_2H_5)_3$	10.06 (1.99 ± 0.05)[b]	6.7[b]			9.95[c]	6.7[c]
	9.32 (1)[b]	9.2[b]			9.13[c]	9.1[c]
$(CH_3)_3AuP(CH_3)_3$	10.03 (2)	8.0	9.92 (2.00 ± 0.05)	7.7	9.96[c]	7.8[c]
	9.28 (1)	9.8	9.20 (1)	9.5	9.11[c]	9.7[c]
	8.52 (3)	9.8[d]	8.53 (3.05 ± 0.5)	9.5[d]	9.57[c]	10.1[c,d]
cis-$(CH_3)_2(CD_3)AuP(CH_3)_3$	10.01 (1)	7.5	9.93 (1.01 ± 0.03)	7.5		
	9.26 (1)	9.5	9.21 (1)	9.0		
	8.50 (3)	9.7[d]	8.52 (3.02 ± 0.04)	9.7[d]		
$(CH_3)_3AuAs(CH_3)_3$	10.04 (2)		9.96 (2.04 ± 0.02)		9.55 (2)	
	9.07 (1)		9.04 (1)		8.45 (1)	
	8.59 (3)		8.61 (2.95 ± 0.04)		9.29 (3)	
$CH_3AuP(CH_3)_3$			9.91 (1)	8.6	9.43 (1)[b]	8.7
			8.62 (3.04 ± 0.06)	8.6[d]	9.79 (3)	8.9[d]

[a] Unless otherwise noted, these are couplings through bonds P-Au-C-H. [b] Reference 12. [c] Reference 5. [d] Coupling through two bonds P-C-H.

Table II. Vibrational Spectra (cm^{-1}) of $CH_3AuP(CH_3)_3$ and $CD_3AuP(CH_3)_3$[a]

	$CH_3AuP(CH_3)_3$				$CD_3AuP(CH_3)_3$	
	Raman		Infrared		Infrared	
Qualitative assignment	Powder[b]	Benzene soln[c]	Mull	$CDCl_3$, CS_2 soln	Mull	$CDCl_3$, CS_2 soln
$\delta(CAuP)$	115 w					
$\rho(C_3P-Au)$	188 sh					
$\nu(AuP) + \delta_s(C_3P)$	200 m 210 sh	200 m, p				
$\delta_{as}(C_3P)$	217 m	266 s, dp			265 w	268 w
$\delta_s(C_3P) + \nu(AuP)$	359 w	353 w, p	356 w		359 w	356 m
$\nu(Au-CD_3)$					479 m 485 m	489 s
$\rho(CD_3Au)$					537 m, b	543 m, b
$\nu(AuCH_3)$	531 s 536 s	539 s, p	528 m 534 m	539 m		
$\nu_s(C_3P)$	681 m	678 w, p	681 w 696 w	678 m	681 m	679 w
$\rho(CH_3Au)$		710 w		710 m, b		
$\nu_{as}(C_3P)$	743 m	742 m, dp	722 w 745 m	741 m	724 sh 743 s	741 m
$\rho(CH_3P)$			845 w 854 w	849 m	845 w 852 w	851 m
$\rho(CH_3P)$			938 s 960 s	949 sh 962 s	940 s 963 s	950 sh 962 s
$\delta_{as}(CD_3Au)$					1025 w	1030 w, b
$\delta_s(CH_3Au)$	1159 m 1170 m	1172 m				
$\delta_s(CH_3P)$			1283 m	1292 m	1284 m 1287 m	1293 m
$\delta_s(CH_3P)$			1308 w	1311 w	1308 w	1312 s
$\delta_{as}(CH_3P)$	1418 sh 1426 w		1419 s, b	1423 s 1434 s		1423 s 1434 s
$2\delta_{as}(CD_3)$					2028 w	2037 m
$\nu_s(CD_3)$					2073 w 2103 w	2088 s
$\nu_{as}(CD_3)$					2185 w	2192 s
$2\delta_{as}(CH_3)$			2818 sh	2811 w 2815 w	2810 w	2810 w 2815 w
$\nu_s(CH_3Au)$		2855 w	2850 m	2865 m		
$\nu_s(CH_3P)$		2907 m, p	2907 s	2914 m		2913 m
$\nu_{as}(CH_3Au)$				2930 sh, m		2931 w
$\nu_{as}(CH_3P)$		2975 s, dp	2975 m	2981 m		2979 m
$\nu_{as}(CH_3P)$		2987 sh, dp				

[a] Key: s, strong; m, medium; w, weak; b, broad; p, polarized; sh, shoulder. [b] 632.8-nm excitation. [c] 488.0- and 501.7-nm excitation.

and appearance of trimethyl(trimethylphosphine)gold(III) signals clearly identified by the P-H coupling.

Vibrational Spectra. The infrared and Raman data for $CH_3AuP(CH_3)_3$ and $CD_3AuP(CH_3)_3$ are collected in Table II, and those for $(CH_3)_3AuAs(CH_3)_3$, $(CH_3)_3AuP(CH_3)_3$, and its deuterated analog are collected in Table III. The infrared (mull and solution) and Raman (powder) spectra of $(CH_3)_3AuP(CH_3)_3$ are shown in Figure 1. Figure 2 shows the infrared spectra of $(CH_3)_3AuP(CH_3)_3$ and $(CH_3)_3AuAs(CH_3)_3$, while Figure 3 shows the effect of deuteration in the

Table III. Vibrational Spectra of Trimethylgold(III) Compounds Recorded with Neat Liquids

	$(CH_3)_3AuP(CH_3)_3$		$(CH_3)_2(CD_3)AuP(CH_3)_3$		$(CD_3)_3AuP(CH_3)_3$		$(CH_3)_3AuAs(CH_3)_3$	
Qualitative assignment	Ir	R[a]	Ir	R[b]	Ir	R[c]	Ir	R[a]
$\delta(CAuY)$[d]		103 w				96 w		92 m, dp
$\rho(C_3Y\text{-}Au)$		190 sh, dp				190 sh	160 w	158 w, dp
$\nu(AuY) + \delta_s(C_3Y)$	200 m	197 m, p		196 m		197 m, p		162 m, p
$\delta_{as}(CAuC)$		208 sh				180?		
$\delta_{as}(C_3Y)$	268 w	267 m, dp	273 w	267 w, dp	269.5 w	271 w, dp		219 w, dp
$\delta_{as}(CAuC)$	290 sh	286 dp	286? vw	286 w, sh		252 w, dp	285?	270 w, dp
$\delta_s(C_3P) + \nu(AuY)$	351 w	351 w, p	353 w	349 w, p	352 vw	349 w, p	254 w	257.5 w, p
$\nu_{as}(AuC)_{cis}$	498 s		465 m	463 m, p	457 s		499 m	
$\nu_s(AuC)_{cis}$		512 s, p	506 s	506 s, p		471 s, p		516 s, p
$\nu(AuC)_{trans}$	541 m	540 s, p	544 s	541 s, p	495.5 m	494 s, p	546 m	546 s, p
$\rho(CD_3Au)$					587 w, b 605 w, sh			
$\nu_s(YC_3)$	677 w	678 w, p	678 w	677 w, p	678.5 w	677 m, p	591 m	591 s, p
$\nu_{as}(YC_3)$	742 s	742 w, dp	744 m	745 w, dp	746 s	743 w, dp	616 s	616 m, dp
$\rho(CH_3Au)$	767 w, b						774 m, b	
$\rho(CH_3Y)$	852 m 950 sh 960 s	957 vw	852 s 950 sh 960 vs	956 w	852 m 951 sh 962 s	956 vw	825 m 903 vs, b	819 w, dp 902 vw
$\delta_s(CH_3Au)$	1176 m 1189 m 1209 w	1176 s, p 1209 s, p	1184 m 1206 m	911, 914 m, p 1182 m, p 1203 m, p		900 m 925 m	1176 m 1189 w 1210 m	1176 m, dp
$\delta_{as}(CD)_3$					1042 vw			
$\delta_s(CH_3Y)$	1292 s 1308 w	1287 vw 1310 vw	1292 s 1310 w		1293 m 1311 w	1292 w 1309 w, p	1260 m 1281 w	1258 w, dp 1278 w, p
$\delta_{as}(CH_3Y)$	1421 s 1434 sh	1411.5 w, dp			1423 s 1433 m	1411 w, dp	1420 s, b	1413 w, b, dp
$\delta_{as}(CH_3Au)$		1438 sh, dp						
$2\delta_{as}(CD_3)$			2065 m	2053 w	2057 m	2054 w, p		
$\nu_s(CD_3Au)$			2108 m	2095 w, p	2111 s	2108 s, p		
$\nu_{as}(CD_3Au)$			2210 m	2208 w, dp	2202 m, b 2221 sh			
$2\delta_{as}(CH_3)$	2805 sh	2802 w	2810 w		2811 w	2802 w	2812 w	2810 w, p
$\nu_s(CH_3Au)$	2895 s	2894 sh, p	2898 s	2895 sh, p 2897 sh, p			2893 2903? s, sh	2891 sh, p 2900 sh, p
$\nu_s(CH_3Y)$		2911 s, p		2909 s, p		2909 s, p		2918 s, p
$\nu_s(CH_3Y)$	2913 sh		2914 sh		2915.5 m		2922 s	
$\nu_{as}(CH_3Au)$	2960 s		2958 s				2956 s	
$\nu_{as}(CH_3Y)$	2973 s 2991 sh	2978 m, dp 2990 m, dp	2975 s	2976 s 2987 sh	2982 m	2974 m, dp 2985? sh, dp 2989? sh, dp	2990 sh	2996 s, dp

[a] 488.0-nm excitation. [b] 501.7-nm excitation. [c] 514.5 nm excitation. [d] Y = P or As.

Raman spectra of trimethyl(trimethylphosphine)gold(III).

Assignments of the Spectra. A detailed and reliable normal-coordinate analysis of trimethylphosphine would have been helpful in the assignments and calculations reported here for the gold complexes, but previous calculations are based on Raman spectra only[14-18] or treat only the skeletal modes using a methyl mass or effective methyl mass approximations.[14,15,17,18] Trimethylarsine was also considered in several reports.[14,16,18] Several fundamentals can be observed only in the infrared spectrum. Complete normal-coordinate analyses of trimethylphosphine oxide and trimethylarsine oxide have been published recently,[19] but the reported potential energy distributions appear unrealistic. For example, modes at 1450 and 1285 cm^{-1} were calculated to be methyl rocking, and vibrations at 945 and 860 cm^{-1} were calculated as asymmetric methyl deformations.

One particular problem with compounds of this type has been the assignment of metal-phosphorus stretching frequencies. Assignments in the literature[3,18,20-22] range from 150 to 400 cm^{-1}, and the proper assignment often is in doubt. Coates and Parkin[3] assigned a weak band at 391 cm^{-1} to the Au-P stretch in trimethyl(trimethylphosphine)gold(III). Raman spectroscopy has identified clearly the polarized A_1 modes of $(CH_3)_3PAuX$ and $(CH_3)_3PNi(CO)_3$ and has narrowed the choice to bands in the regions 350-400 or 210-230 cm^{-1} for the gold(I) halides[10] and 348 or 221 cm^{-1} for the nickel complex.[20] By elimination, the other band must be assigned to the symmetric bending mode of the MPC_3 grouping. Loutellier and Bigorgne were able to obtain good agreement between observed and calculated frequencies using a methyl mass approximation for $(CH_3)_3PNi(CO)_3$.[21] On that basis they assigned the Ni-P stretch at 221 and the PC_3 symmetric deformation at 348 cm^{-1} but did not indicate how closely the normal modes resembled symmetry coordinates or give a potential energy distribution. The most definitive evidence for either assignment is the metal isotope study by Shobatake and Nakamoto,[22] who prepared *trans*-$\{[(C_2H_5)_3P]_2MX_2\}$ (X = Cl, Br) using M = ^{58}Ni, ^{62}Ni and ^{104}Pd, ^{110}Pd. The asymmetric metal-phosphorus stretch of dichlorobis(triethylphosphine)palladium(II) occurs at 234 cm^{-1} and for dichloro- and dibromobis(triethylphosphine)nickel(II) at 273 and 265 cm^{-1}, respectively. In dichlorobis(triphenylphos-

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(15) R. K. Sheline, *J. Chem. Phys.*, **18**, 602 (1950).

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(17) D. A. Long and R. B. Gravenor, *Spectrochim. Acta*, **19**, 961 (1963).

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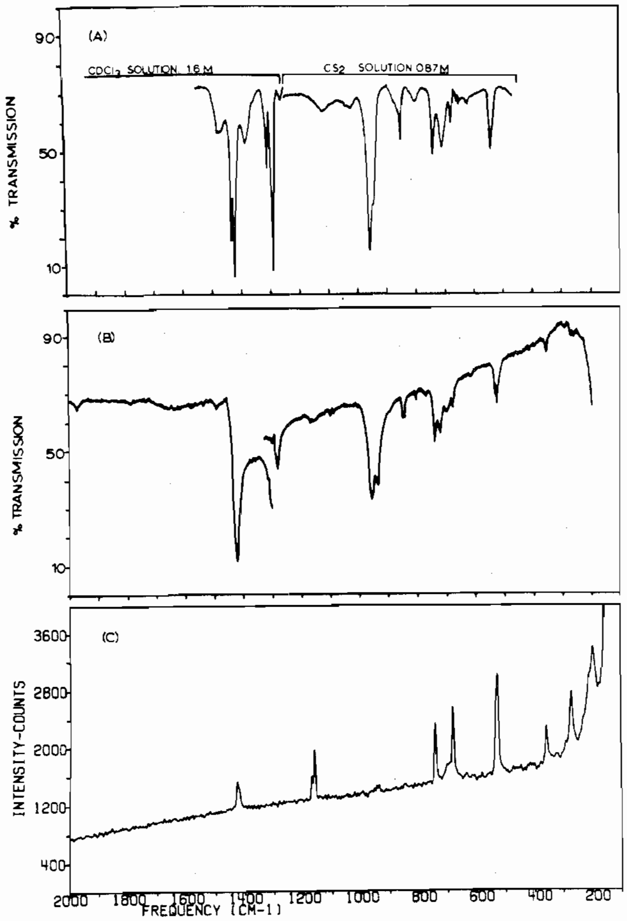

Figure 1. Raman and infrared spectra of $CH_3AuP(CH_3)_3$: A, infrared spectrum of $CDCl_3$ and CS_2 solutions; B, mull infrared spectrum; C, Raman spectrum of microcrystalline powder.

phine)nickel(II) and- palladium(II), the bands shift to 189 and 191 cm^{-1}. These results indicate that the band position is sensitive to both the mass of the metal atom and the mass of the phosphine.

In the discussions which follow, the values quoted are from solution or neat liquid spectra, unless the vibration only could be observed with a solid sample or is otherwise noted. In general Raman frequencies can be determined more accurately than infrared, and normally the Raman values are quoted. When the bands are comparable in intensity and accuracy, frequencies are averaged.

Local Vibrations of Coordinated $P(CH_3)_3$. The modes associated with the methyl groups on phosphorus are well-documented for trimethylphosphine,[14,16] trimethylphosphine oxide,[19] trimethylphosphinegold(I) halides,[10] and some trimethylphosphine complexes of platinum.[23] Qualitative assignments can readily be made by comparison and are presented in Tables II and III. In the discussions which follow, C_{3v} symmetry was used, although the symmetry of $P(CH_3)_3$ can vary from C_{3v} to C_1 depending upon the orientations of the methyl groups. A rigorous treatment would require a group of order 162[24] rather than the 6 of C_{3v}, since the barrier to methyl group rotation is probably quite small.

$CH_3AuP(CH_3)_3$. Vibrations of the skeleton will conform approximately to the selection rules for the trans conformer with C_{3v} symmetry. Since this molecule probably has a low barrier to rotation about the Au-C bond, the skeletal symmetry group should contain 9 elements.[24] A rigorous treatment of the entire molecule would require a group with 486 elements.[24] In C_{3v} symmetry, the representation of the skeletal vibrations (methyl groups taken as point masses) is $\Gamma_{vib} = 4\ A_1 + 4\ E$. Examination of Table II indicates that nine modes below 800 cm^{-1} are observed in the vibrational spectra of $CH_3AuP(CH_3)_3$ solutions and powder. The broad band at 710 cm^{-1} in the infrared spectra, which is very weak in the Raman spectra, is assigned to the nonskeletal methylgold rocking frequency. Of the remaining bands, those at 200, 353, 539, and 678 cm^{-1} are polarized and those at 115, 188, 266 and 742 cm^{-1} are not. The assignments $\delta(CAuP)$ 115, $\rho(C_3PAu)$ 188, $\delta_{as}(PC_3)$ 266, $\nu(AuC)$ 539, $\nu_s(PC_3)$ 678, and $\nu_{as}(PC_3)$ 742 cm^{-1} are straightforward, but the assignment of $\delta_s(PC_3)$ and $\nu(AuP)$ requires some comment. The intensity of a stretching mode in the Raman effect is generally much greater than that of a bending mode; and indeed, the band at 200 cm^{-1} is more intense than that at 353 cm^{-1}. However, anomalous Raman intensities for the angle deformation modes of free trimethylphosphine have been observed; $\delta_s(PC_3)$ is less than the $\delta_{as}(PC_3)$, a fact which led to early misassignments. Accurate measurements of depolarization ratios using a laser Raman spectrophotometer made possible the correct assignment.[18] The difficulty in making qualitative assignments for $\delta_s(PC_3)$ and $\nu(AuP)$ results from severe mixing of these coordinates in the normal modes. Metal-phosphorus bonding will be more fully discussed with the normal-coordinate analyses, since those results are crucial to the arguments.

The bands attributed to the methyl bound to gold are $\rho(CH_3Au)$ 710 (ir), $\delta_s(CH_3Au)$ 1172 (R), $\nu_s(CH_3Au)$ 2865, and $\nu_{as}(CH_3Au)$ 2928 cm^{-1}; however, $\delta_{as}(CH_3Au)$ was obscured by the intense $\delta_{as}(CH_3P)$ bands of the trimethylphosphine moiety. The Au-C stretch at 539 cm^{-1} is the most intense feature of the Raman spectrum.

$CD_3AuP(CH_3)_3$. The internal CD_3 modes of $CD_3AuP(CH_3)_3$, except the symmetric deformation, all are observed in the solution infrared spectrum as follows: ν_s 2088, ν_{as} 2192, δ_{as} 1030, ρ 543 cm^{-1}. Because of photodecomposition, no Raman spectrum was obtained. The Au-C stretching frequency is 489 cm^{-1}, and the ratio of 1.102 for the frequencies of protium and deuterium compounds is very close to the value of 1.095 calculated assuming simple masses of 15 and 18.

Monomethylgold(I) Solid-State Spectra. The Raman powder and infrared mull spectra of $CH_3AuP(CH_3)_3$, Figure 1, and $CD_3AuP(CH_3)_3$ show doubling of $\nu(Au\text{-}CH_3)$, $\delta_s(CH_3Au)$, $\rho(CH_3P)$ (A_2 mode), and $\delta_s(CH_3P)$ (A_1 and E modes). These must be correlation multiplets caused by solid-state coupling of two or more molecules per unit cell; the crystal structure is unknown. Small but significant shifts are observed for the change from solid to solution spectra, but they follow no pattern or trend.

Trimethyl(trimethylphosphine)gold(III). The point group for the most symmetric conformer of this molecule, considering the methyl groups as point masses, is C_s; and the vibrational representation is $\Gamma_{vib} = 11\ A' + 7A''$. For the ligand, three P-C stretches and three C-P-C bending vibrations are predicted in C_s symmetry. Only two stretching modes, ν_s 678 (p) and ν_{as} 742 cm^{-1} (dp), and two bending modes, δ_{as} 267 cm^{-1}, (dp) and δ_s which couples strongly with ν_{AuP} to give bands at 351 (p) and 197 cm^{-1} (p), are observed. The similarity of the phosphine bands with those of the monomethylgold(I) compound and the retention of degeneracy indicate that the effective symmetry of the phosphine moiety remains C_{3v}.

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(24) H. C. Longuet-Higgins, *Mol. Phys.*, 6, 445 (1963).

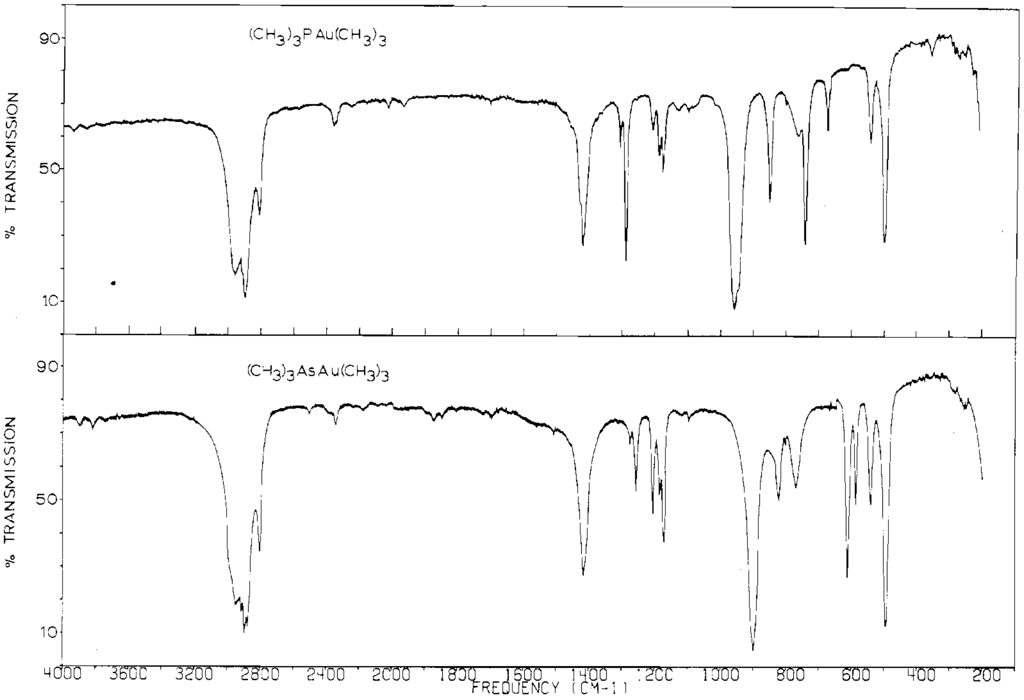

Figure 2. Infrared spectra of $(CH_3)_3AuP(CH_3)_3$ and $(CH_3)_3AuAs(CH_3)_3$.

Two gold-carbon stretches are observed in the Raman spectrum and two in the infrared spectrum. Considering the relative trans influence of methide and phosphine, we assign the polarized band at 540 cm^{-1}, which is also infrared active, to a vibration which involves predominantly stretching of the unique Au-C bond trans to phosphorus. The remaining bands, 512 (R, p) and 498 cm^{-1} (ir), are assigned to modes involving mainly symmetric and asymmetric stretching of the linear C-Au-C unit with methyls cis to phosphorus. The in-plane deformations of the $PAuC_3$ skeleton are assigned to bands at 290 (ir) (and 286 (R)), 208 (R), and 103 cm^{-1} (R). (A simple valence force field treatment considering only in-plane deformations suggests that this set of assignments is reasonable: F(CAuC) and F(CAuP) were calculated using the bands at 290 and 103 cm^{-1}, and the third band using the values of F(CAuC) and F(CAuP) was calculated to be 215 cm^{-1}, which is close to the assigned value of 208 cm^{-1}. These force constants were used as trial values in the more complete calculation described below.)

Only one rocking mode was observed at 767 cm^{-1} in the infrared spectrum. Attempts to resolve this into components were unsuccessful. This may be due, in part, to the broadness of the band. Three infrared bands are found in the region for symmetric methyl-gold deformations, two of which are observed in the Raman spectrum (1176, 1209 cm^{-1}) as polarized bands. The third band in the infrared spectrum (1189 cm^{-1}) is assigned to the out-of-phase combination for the methyls cis to phosphorus. On the basis of correlations between $\nu(M-CH_3)$ and $\delta_s(CH_3M)$ for platinum(II)[25] and gold(III)[26] complexes, we assign the 1209-cm^{-1} band to the symmetric deformation of the unique methyl and the 1176-cm^{-1} band to the in-phase mode of the methyls cis to phosphorus. Again the asymmetric methyl deformations are obscured in the infrared spectrum by the intense bands of the trimethylphosphine group. The Raman spectrum has a band at 1411 cm^{-1}, with a high-frequency shoulder. The 1411-cm^{-1} band is the in-phase (A_1) mode of the $(CH_3)_3P$ group, and the 1417-cm^{-1} shoulder is due to the methyl groups on gold. This is close to the value of 1421 cm^{-1} observed for $\delta_{as}(CH_3Au)$ in dichlorodimethylaurate(III)[27] where the complication of the trimethylphosphine group is not present. The CH stretching vibrations $\nu_s(CH_3Au)$ and $\nu_{as}(CH_3Au)$ are all assigned to the bands at 2895 and 2960 cm^{-1}.

***cis*-Dimethylmethyl-d_3-(trimethylphosphine)gold(III).** The bands of the deuterated methyl group are obvious from comparison to the spectrum of $(CH_3)_3AuP(CH_3)_3$. Raman bands arise at 2209 (average R, ir), 2108, 914, and 463 cm^{-1} which can be attributed to ν_{as}, ν_s, $\delta_s(CD_3)$, and $\nu(Au-CD_3)$. Except for δ_s which is obscured by the intense $\rho(CH_3P)$ bands, all are observed in the infrared spectrum as well. The symmetric and asymmetric carbon-hydrogen stretching frequencies of the nondeuterated methyls are not significantly shifted, but the symmetric deformations shift slightly to 1183 and 1204 cm^{-1}, the latter being polarized in the Raman spectrum. The frequency of Au-C stretching for CH_3 cis to phosphorus is 506 cm^{-1}, and the trans methyl frequency is 543 cm^{-1}. The skeletal modes attributed to the trimethylphosphine moiety are unshifted from the parent compound.

Trimethyl-d_9-(trimethylphosphine)gold(III). The vibrations of this molecule have a pattern identical with that of the protium parent compound except for the lower frequency values of the modes involving the methyls on gold. Three gold-methyl-d_3 stretching vibrations (one in both infrared and Raman, one only in Raman, and one only in infrared) are assigned as the unique Au-C stretching vibration (495 cm^{-1}) and the in-phase (471 cm^{-1}) and out-of-phase (457 cm^{-1}) modes of the Au-C coordinates cis to phosphorus. A broad band at 1042 cm^{-1} in the infrared spectrum is the asymmetric deformation of the deuterated methyl groups. Bands assigned in the protium compound as ν_{as}, ν_s, $\delta_s(AuCH_3)$, and $\rho(AuCH_3)$ are no longer present. The rocking mode, ρ-$(AuCD_3)$, appears at 587 cm^{-1} in the infrared spectrum. Two strong Raman bands at 900 and 925 cm^{-1} are assigned to $\delta_s(AuCD_3)$; but again the very intense $\rho(PCH_3)$ modes ob-

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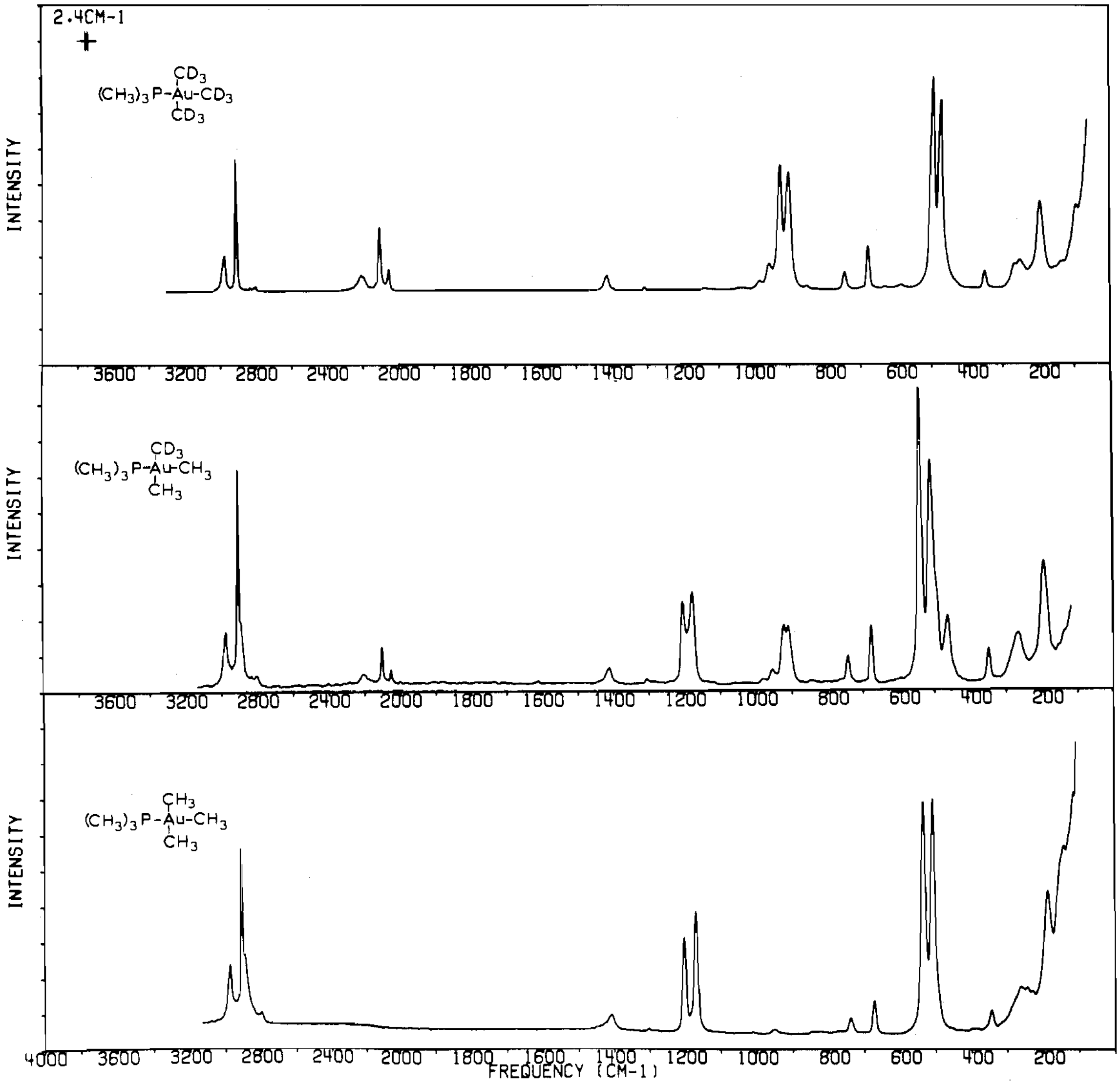

Figure 3. Raman spectra of $(CH_3)_3AuP(CH_3)_3$, $CD_3(CH_3)_2AuP(CH_3)_3$, and $(CD_3)_3AuP(CH_3)_3$.

scure the weak infrared absorptions expected for $\delta_s(AuCD_3)$. The skeletal modes of the trimethylphosphine ligand and the modes assigned to mixed ν(Au-P) and $\delta_s(PC_3)$ are essentially unshifted. Two in-plane deformations are clearly shifted to lower frequencies, from 290 to 252 cm^{-1} and from 103 to 96 cm^{-1}, but the third such band at 208 cm^{-1} in the parent compound has apparently moved under the 200- and 188-cm^{-1} bands where it is no longer discernible.

Trimethyl(trimethylarsine)gold(III). The bands due to the trimethylarsine portion of the molecule are readily assigned by comparison with reported spectra for halo(trimethylarsine)gold(I) complexes[10] and trimethylarsine[14,15,18] and by elimination of bands attributable to the trimethylgold moiety. These are presented in Table III. It is noteworthy that complexity of these bands is less than that of analogous bands of the trimethylphosphine ligand, a fact expected because of the heavier mass and larger size of the arsenic atom. The assignments of the asymmetric methyl deformation to methyls bound to gold and to arsenic are less obvious, since the infrared band at 1420 cm^{-1} and the Raman band at 1413 cm^{-1} have no structure. It can only be assumed that the frequency differences are too small to give rise to resolved bands. Ligand modes are assigned as follows (cm^{-1}): 616 (R, dp, ir), $\nu_{as}(AsC_3)$; 591 (R, ir), $\nu_s(AsC_3)$; 219 (R, dp, ir), $\delta_{as}(AsC_3)$; 158 (R, dp), ρ(Au-AsC$_3$). Significant mixing of ν(Au-As) and $\delta_s(AsC_3)$ is expected in the modes at 162 (R, p, ir) and 257.5 cm^{-1} (R, p, ir). Modes attributable to the trimethylgold portion of the molecule are obvious by comparison with the phosphine complex and are shifted by fewer than ten wave numbers. The Au-CH$_3$ stretching frequencies are only slightly higher for the arsine compared to the phosphine complex and show the same intensity pattern. Bands at 93 and 270 cm^{-1} are assigned to asymmetric in-plane (C_3AuAs plane) bending vibrations, but no mode was observed which can be attributed to the symmetric in-plane deformation.

Normal-Coordinate Calculations. The internal coordinates used to express the potential energy for the molecules $XAuP(CH_3)_3$ (X = Cl, Br, I), $CH_3AuP(CH_3)_3$, and $(CH_3)_3AuY(CH_3)_3$ (Y = P, As) are illustrated in Figure 4. For clarity, only representative coordinates of each type are shown. A modified Urey-Bradley force field, in which trans stretch-stretch interaction force constants were included for the gold-ligand bonds, was used for the alkylgold compounds. Inclusion of analogous interaction force constants for the $XAuP(CH_3)_3$ molecules was not warranted by the data. Only vibrations in the C_3AuY plane of the Au(III) compounds were considered, and torsional modes were neglected in all cases. Harmonic vibrations were assumed.

For the $(CH_3)_3YAu$ group (Y = P or As), which is common

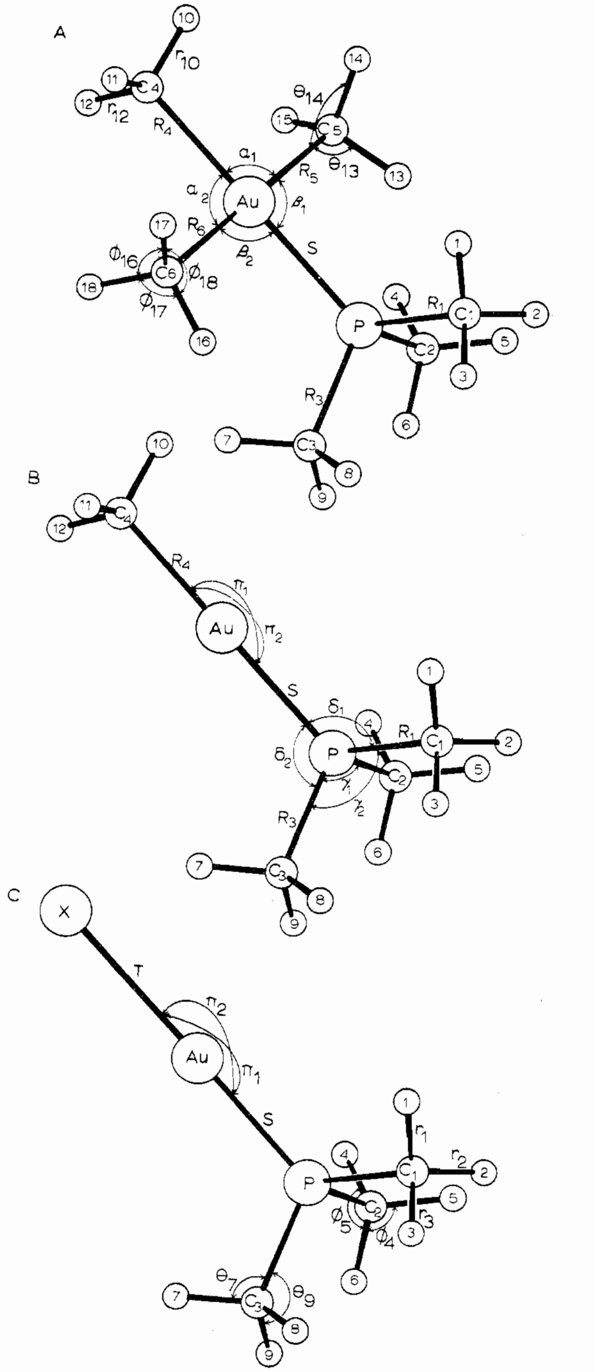

Figure 4. Internal coordinates of the gold compounds: A, $(CH_3)_3AuP(CH_3)_3$; B, $CH_3AuP(CH_3)_3$; C, $XAuP(CH_3)_3$.

to all of the molecules treated here, the potential energy, assuming axial symmetry, is given by

$$
\begin{aligned}
2V_{\mathrm{Me_3YAu}} = {} & [2SK_s'(\Delta s) + K_s(\Delta s)^2] + \sum_{i=1}^{3}\{[2R_iK_R'(\Delta R_i) + \\
& K_R(\Delta R_i)^2] + [2H_\gamma'(\Delta\gamma_i) + H_\gamma(\Delta\gamma_i)^2] + \\
& [2H_\delta'(\Delta\delta_i) + H_\delta(\Delta\delta_i)^2] + [2q_i^{\mathrm{CAu}}F_q'(\Delta q_i^{\mathrm{CAu}}) + \\
& F_q(\Delta q_i^{\mathrm{CAu}})^2] + [2q_i^{\mathrm{CC}}F_q'(\Delta q_i^{\mathrm{CC}}) + F_q(\Delta q_i^{\mathrm{CC}})^2]\} + \\
& \sum_{i=i}^{9}\{[2r_iK_r'(\Delta r_i) + K_r(\Delta r_i)^2] + [2H_\phi'(\Delta\phi_i) + \\
& H_\phi(\Delta\phi_i)^2] + [2H_\theta'(\Delta\theta_i) + H_\theta(\Delta\theta_i)^2] + \\
& [2q_i^{\mathrm{HY}}F_q'(\Delta q_i^{\mathrm{HY}}) + F_q(\Delta q_i^{\mathrm{HY}})^2] + \\
& [2q_i^{\mathrm{HH}}F_q{}^{\mathrm{HH}}(\Delta q_i^{\mathrm{HH}} + F_q{}^{\mathrm{HH}}(\Delta q_i^{\mathrm{HH}})^2]\}
\end{aligned}
\qquad (2)
$$

Using the above expression, the full potential energy expressions for the three types of molecules are given by the following equations: for $XAuP(CH_3)_3$

$$
\begin{aligned}
2V = {} & 2V_{\mathrm{(CH_3)_3PAu}} + [2TK_T'(\Delta T) + K_T(\Delta T)^2] + \\
& \sum_{i=1}^{2}[2H_\pi'(\Delta\pi) + H_\pi(\Delta\pi_i)^2]
\end{aligned}
\qquad (3)
$$

for $CH_3AuP(CH_3)_3$

$$
\begin{aligned}
2V = {} & 2V_{\mathrm{(CH_3)_3PAu}} + [2R_4K'(\Delta R_4) + K_{R_4}(\Delta R_4)^2] + \\
& \sum_{i=1}^{2}[2H_\pi'(\Delta\pi) + H_\pi(\Delta\pi_i)^2] + \sum_{i=10}^{12}\{[2r_iK'(\Delta r_i) + \\
& K_{r_i}(\Delta r_i)^2] + [2H_{\phi_i}'(\Delta\phi_i) + H_{\phi_i}(\Delta\phi_i)^2] + [2H_{\theta i}'(\Delta\theta_i) + \\
& H_{\theta_i}(\Delta\theta_i)^2] + [2q_i^{\mathrm{HAu}}F_{\mathrm{HAu}}'(\Delta q_i^{\mathrm{HAu}}) + \\
& F_{\mathrm{HAu}}(\Delta q_i^{\mathrm{HAu}})^2] + [2q_i^{\mathrm{HH}}F_{\mathrm{HH}}'(\Delta q_i^{\mathrm{HH}}) + \\
& F_{\mathrm{HH}}(\Delta q_i^{\mathrm{HH}})^2]\} + f_{\mathrm{R_4S}}(\Delta R_4)(\Delta S)
\end{aligned}
\qquad (4)
$$

and for $(CH_3)_3AuP(CH_3)_3$ and $(CH_3)_3AuAs(CH_3)_3$, motion in the C_3AuY plane

$$
\begin{aligned}
2V = {} & 2V_{\mathrm{(CH_3)_3YAu}} + \sum_{i=4}^{6}[2R_iK_{R_i}'(\Delta R_i) + K_{R_i}(\Delta R_i)^2] + \\
& \sum_{i=1}^{2}\{[2H_\alpha'(\Delta\alpha_i) + H_\alpha(\Delta\alpha_i)^2] + [2H_\beta'(\Delta\beta_i) + \\
& H_\beta(\Delta\beta_i)^2] + [2q_i^{\mathrm{CP}}F_{\mathrm{CP}}'(\Delta q_i^{\mathrm{CP}}) + F_{\mathrm{CP}}(\Delta q_i^{\mathrm{CP}})^2] + \\
& [2q_i^{\mathrm{CC}}F_{\mathrm{CC}}'(\Delta q_i^{\mathrm{CC}}) + F_{\mathrm{CC}}(\Delta q_i^{\mathrm{CC}})^2]\} + \\
& \sum_{i=10}^{18}\{[2r_iK_{r_i}'(\Delta r_i) + K_{r_i}(\Delta r_i)^2] + [2H_{\phi_i}'(\Delta\phi_i) + \\
& H_{\phi_i}(\Delta\phi_i)^2] + [2H_{\theta i}'(\Delta\theta_i) + H_{\theta i}(\Delta\theta_i)^2] + \\
& [2q_i^{\mathrm{HAu}}F_{\mathrm{HAu}}'(\Delta q_i^{\mathrm{HAu}}) + F_{\mathrm{HAu}}(\Delta q_i^{\mathrm{HAu}})^2] + \\
& [2q_i^{\mathrm{HH}}F_{\mathrm{HH}}'(\Delta q_i^{\mathrm{HH}}) + F_{\mathrm{HH}}(\Delta q_i^{\mathrm{HH}})^2]\} + \\
& [f_{R_4S}(\Delta R_4)(\Delta S) + f_{R_5R_6}(\Delta R_5)(\Delta R_6)]
\end{aligned}
\qquad (5)
$$

f_{R_4S} and $f_{R_5R_6}$ refer to the non-Urey–Bradley stretch–stretch interaction constants. With these force fields, the potential energy is independent of the orientation of $P(CH_3)_3$ or $As(CH_3)_3$ with respect to rotation about the Au–P or Au–As bond.

The computations were performed with the Purdue University CDC-6500 computer using the programs ZMAT, WMAT, and OVEREND.[28,29] Initial values of the force constants for the methylgold moieties were transferred from the $[(CH_3)_2AuX_2^-]$ ions.[26] For $P(CH_3)_3$, initial values were taken from the corresponding constants of $(CH_3)_4Si$.[30] As usual the linear terms in the potential energy were taken as −0.1 of the quadratic terms.

The molecular parameters used in the calculations are collected in Table IV.[31-37] In the absence of crystallo-

Table IV. Molecular Parameters Used in the Normal-Coordinate Analyses[a]

Parameter	Value	Ref	Parameter	Value	Ref
d(Au-C)	2.05 Å	33	*d*(As-C)	1.95 Å	32
d(Au-Cl)	2.35 Å	34	*d*(C-H)	1.112 Å	37
d(Au-Br)	2.50 Å	35	∠(AuPC)	116°	31
d(Au-I)	2.65 Å	36	∠(CPC)	102°	31
d(Au-P)	2.25 Å	31	∠(AuAsC)	113°	32
d(P-C)	1.83 Å	31	∠(CAsC)	107°	32
d(Au-As)	2.30 Å	32	∠XAu$^{\mathrm{I}}$P	180°	

[a] Tetrahedral values were assumed for ∠(HCH), ∠(HCAu), ∠(HCP), and ∠(HCAs). Right angles were assumed for ∠(CAu$^{\mathrm{III}}$C), ∠(CAu$^{\mathrm{III}}$P), and ∠(CAu$^{\mathrm{III}}$As).

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(28) J. Overend and J. R. Scherer, *J. Chem. Phys.*, **32**, 1289 (1960).

(29) C. D. Needham, Ph.D. Thesis, University of Minnesota, 1965.

(30) J. Overend and J. R. Scherer, *J. Opt. Soc. Amer.*, **50**, 1203 (1960).

Table V. Urey-Bradley Force Constants[a] (Errors[b]) for $CH_3AuP(CH_3)_3$ and $(CH_3)_3AuY(CH_3)_3$ (Y = P, As)

Force constant	$CH_3AuP(CH_3)_3$ $CD_3AuP(CH_3)_3$	$(CH_3)_3AuP(CH_3)_3$ $(CD_3)_3AuP(CH_3)_3$	$(CH_3)_3AuAs(CH_3)_3$
	Skeletal		
$K(AuC)_{cis}$[c]		1.03 (6)	1.08 (14)
$K(AuC)_{trans}$	1.33 (12)	1.24 (10)	1.36 (10)
$K(AuY)$	1.56 (31)	1.17 (28)	1.18 (54)
$H(CAuC)$		0.99 (11)	0.84 (15)
$H(CAuY)$		0.34 (15)	0.14 (21)
$H(PAuC)$	0.50 (15)		
$F(C\cdots C)_{Au}$		0.05	0.05
$F(C\cdots Y)_{Au}$		0.075	0.100
$K(YC)$	2.26 (7)	2.22 (6)	1.79 (9)
$H(CYC)$	0.79 (6)	0.77 (6)	0.53 (8)
$H(CYAu)$	0.33 (11)	0.34 (6)	0.34 (11)
$F(C\cdots Au)_Y$	0.14	0.21	0.18
$F(C\cdots C)_Y$	0.056	0.084	0.09
	Trans $AuCH_3$		
$K(CH)$	4.49 (3)	4.57 (2)	4.52 (4)
$H(HCH)$	0.53 (1)	0.54 (1)	0.53 (1)
$H(HCAu)$	0.04 (1)	0.06 (1)	0.06 (1)
$F(H\cdots Au)$	0.40	0.46	0.46
$F(H\cdots H)$	0.02	0.02	0.02
	Cis $AuCH_3$		
$K(CH)$		4.52 (1)	4.52 (2)
$H(HCH)$		0.53 (1)	0.53 (1)
$H(HCAu)$		0.05 (1)	0.05 (1)
$F(H\cdots Au)$		0.47	0.47
$F(H\cdots H)$		0.02	0.02
	YCH_3		
$K(CH)$	4.60 (1)	4.62 (1)	4.65 (2)
$H(HCH)$	0.52 (1)	0.50 (1)	0.50 (1)
$H(HCY)$	0.38 (1)	0.36 (1)	0.29 (1)
$F(H\cdots Y)$	0.30	0.31	0.32
$F(H\cdots H)$	0.025	0.038	0.038
	Non-UB Interactions		
$f(AuC,AuC)_{trans}$		0.20	0.20
$f(AuC,AuY)_{trans}$	−0.29	−0.16	−0.16

[a] K and F in mdyn/Å; H in mdyn Å/radian^2. The internal tension parameters, κ, for the C_3PAu, H_3CAu, and H_3CP tetrahedra were all constrained to 0. [b] The so-called standard errors from the least-squares frequency fit are appended to give some idea of how the overall frequency fit depends upon a particular force constant. It should be recognized that the residuals in the frequency parameters will not follow the gaussian error law, and consequently the errors do not have the statistical significance of true standard errors. For example, a force constant which is determined primarily by a single frequency will tend to have a relatively large error. [c] Cis and trans refer to the orientation with respect to phosphine or arsine.

graphic information, bond distances and valence angles were transferred from analogous d^8 complexes; *e.g.*, for the phosphine and arsine ligands, values were taken from *cis*-dichlorobis(trimethylphosphine)platinum(II)[31] and di-μ-chloro-*trans*-dichlorobis(trimethylarsine)diplatinum(II).[32]

The Urey-Bradley force constants together with standard errors from the last cycle of the least-squares refinement are listed in Tables V and VI. In an effort to give some idea of the significance of the force constants, the last cycle of least-squares refinement was carried out with the nonbonded force constants constrained to the best values estimated from various trial refinements. In this case, the force constants are considerably overdetermined, since rather extensive vibrational data are available. For the compounds $XAuP(CH_3)_3$ (X = Cl, Br, I), the frequency data of Dudell, *et al.*,[10] were used in the computations. Selected diagonal elements of the force constant matrix in terms of internal coordinates are listed in Table VII, since these are comparable with the results of GVFF calculations on other related coordination compounds. The average errors of the calculated frequencies were in the range of 1-2% for all compounds.

Assumptions about the force constants and details of the fit of the force constants to the spectroscopic data are discussed below for each molecule. There are, however, certain general comments which pertain to these calculations. First, all molecules involve coordination about a massive gold atom, and this minimizes coupling between the various ligands. The lack of coupling in the square-planar Au(III) compounds also is due, in part, to the orthogonal nature of the bond vectors which minimizes coupling through the *G* matrix. Second, the Urey-Bradley force field does a satisfactory job in describing the internal vibrations of methyl groups coordinated to heavy metals.[27,38-40]

One deficiency of the Urey-Bradley field is that it does not reproduce perfectly splittings due to vibrational coupling

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Table VI. Observed and Calculated Frequencies (cm^{-1}) of $CH_3AuP(CH_3)_3$ and the Principal Contributions to the Potential Energy (%)

	$CH_3AuP(CH_3)_3$			$CD_3AuP(CH_3)_3$	
	ν_{obsd}	ν_{calcd}	PED	ν_{obsd}	ν_{calcd}
A_1	2975	2983	$K(CH)_P$, 97	2975	2983
	2907	2885	$K(CH)_P$, 96	2907	2885
	2865	2851	$K(CH)_{Au}$, 95	2088	2043
	1423	1417	$H(HCH)_P$, 91	1434	1418
	1311	1343	$H(HCH)_P$, 47; $H(HCP)$, 34; $F(PH)$, 13	1311	1344
	1172	1171	$H(HCH)_{Au}$, 63; $F(HAu)$, 27		956
		956	$H(HCP)$, 55; $F(PH)$, 33		880
	678	686	$K(PC)$, 63; $F(PH)$, 31	678	686
	539	531	$K(AuC)$, 59; $F(HAu)$, 30	489	499
	353	354	$K(AuP)$, 36; $H(CPC)$, 35; $H(CPAu)$, 10	356	352
	200	198	$K(AuP)$, 43; $H(CPC)$, 24; $F(CAu)$, 23	200	198
A_2		3000	$K(CH)_P$, 96		3000
		1418	$H(HCH)_P$, 92		1418
		908	$H(HCP)$, 59; $F(PH)$, 34		908
E	2987	3001	$K(CH)_P$, 96	2975	3001
	2975	2981	$K(CH)_P$, 97	2975	2981
	2930	2951	$K(CH)_{Au}$, 96	2192	2192
	2907	2885	$K(CH)_P$, 94	2907	2885
		1423	$H(HCH)_{Au}$, 96	1030	1030
	1434	1419	$H(HCH)_P$, 91	1434	1420
	1423	1417	$H(HCH)_P$, 92	1423	1417
	1292	1342	$H(HCH)_P$, 47; $H(HCP)$, 34; $F(HP)$, 13	1293	1343
	962	939	$H(HCP)$, 54; $F(HP)$, 32	962	939
	950	919	$H(HCP)$, 58; $F(HP)$, 35	950	919
	742	735	$K(PC)$, 68; $F(HP)$, 23	741	734
	710	716	$H(HCAu)$, 12; $F(AuH)$, 84	543	535
	268	268	$H(CPC)$, 85; $F(CC)$, 10	268	269
	188	182	$H(CPAu)$, 48; $F(CAu)$, 30; $H(CAuP)$, 20		180
	115	114	$H(CPAu)$, 12; $H(CAuP)$, 78		104
	Av error = 1.2%			Av error = 1.2%	

Table VII. Urey-Bradley Force Constants[a] (Errors) for $XAuP(CH_3)_3$ (X = Cl, Br, I)

	Compound		
Force constant	$ClAuP(CH_3)_3$	$BrAuP(CH_3)_3$	$IAuP(CH_3)_3$
	Skeletal		
$K(AuX)$	1.85 (22)	1.58 (35)	1.46 (32)
$K(AuP)$	1.86 (42)	1.78 (36)	1.47 (31)
$H(PAuX)$	0.62 (22)	0.36 (15)	0.27 (12)
$K(PC)$	2.24 (10)	2.08 (8)	2.25 (7)
$H(CPC)$	0.89 (9)	0.77 (7)	0.78 (6)
$H(CPAu)$	0.29 (9)	0.33 (8)	0.33 (7)
$F(C\cdots Au)_P$	0.20	0.19	0.19
$F(C\cdots C)_P$	0.064	0.070	0.077
	PCH_3		
$K(CH)$	4.61 (2)	4.59 (2)	4.60 (2)
$H(HCH)$	0.51 (1)	0.51 (1)	0.51 (1)
$H(HCP)$	0.36 (1)	0.31 (1)	0.32 (1)
$F(H\cdots P)$	0.33	0.41	0.34
$F(H\cdots H)$	0.029	0.028	0.026

[a] K and F in mdyn/Å; H in mdyn Å/radian^2. The internal tension parameter κ for the $AuPC_3$ tetrahedron was constrained to 0.

between the three methyl groups of $P(CH_3)_3$ or $As(CH_3)_3$. As noted earlier, all previous normal-coordinate analyses for these molecules and their complexes have been based on methyl mass or effective mass approximations.[14-18] The inadequacy is most severe for the methyl rocking modes which for $P(CH_3)_3$ span the range from 850 to 960 cm^{-1}. The calculated frequencies vary only over a 60-cm^{-1} range. The data for $\delta_s(CH_3)$ of $P(CH_3)_3$ and $As(CH_3)_3$ also are rather poorly fitted. Overend and Scherer[28] in calculations on tetramethyl compounds of C, Si, Ge, Sn, and Pb also were unable to reproduce exactly the rocking and symmetric deformation frequencies. These large splittings are probably caused by nonbonded methyl interactions which are not reproduced adequately by the UBFF. Support for this comes from the observation that the range of rocking frequencies with $As(CH_3)_3$ is only *ca.* 80 cm^{-1} as a consequence of the larger, more massive arsenic atom. The average rocking frequency is reproduced well for the phosphine complexes. For example, the average value for $CH_3AuP(CH_3)_3$ is 935 cm^{-1}; calculated, 930 cm^{-1}. This deficiency of the UBFF may have a small effect on the HCH bending force constants. The ligand methyl frequencies are essentially independent of the remainder of the molecule; *i.e.*, almost the same values are observed for $CH_3AuP(CH_3)_3$, $XAuP(CH_3)_3$, and $(CH_3)_3AuP(CH_3)_3$.

In all of the calculations, the internal tension parameters, κ, for the tetrahedral structures were constrained at 0. They correlate strongly with $F(H\cdots H)$, and both cannot be refined simultaneously.

$H_3CAuP(CH_3)_3$ and $D_3CAuP(CH_3)_3$. The computation is relatively straightforward, since the effective molecular symmetry is C_{3v}. Forty-nine internal coordinates including five redundancies distributed among 12 symmetrically equivalent sets were used to express the potential energy. For the calculation 25 frequencies from $H_3CAuP(CH_3)_3$ and 22 from $D_3CAuP(CH_3)_3$ were used; however, only five frequencies for the deuterated molecule differed significantly from those of the non-deuterated compound. From these 30 data items, 21 nonzero force constants were calculated; and 13 were adjusted in the last least-squares cycle. The Urey-Bradley constants are given in Table V.

Although, as noted above, the $P(CH_3)_3$ methyl modes are not fitted especially well, the phosphine modes do not mix with skeletal or Au-CH_3 modes with the single exception of extensive mixing between $\delta_s(PC_3)$ and ν(Au-P). The invariance of the $P(CH_3)_3$ modes upon deuteration of the methyl bound to gold substantiates the absence of coupling between the two ligands. A comparison of the observed and calculated frequencies is given in Table VI.

In the final stages of the refinement, $F(H\cdots H)_{Au}$ and $F(H\cdots H)_P$ were constrained to 0.020 and 0.025, respectively. The former value corresponds to that obtained by Scovell and Tobias for $[(CH_3)_2AuCl_2^-]$.[26] The value 0.40 for $F(Au\cdots H)$ is slightly smaller than that for $[(CH_3)_2AuCl_2^-]$, 0.50. The values of K(Au-P), H(AuPC), and $F(Au\cdots C)$ are strongly correlated because of mixing between $\delta_s(AuPC_3)$ and ν(Au-P). This mixing is evidenced by the decrease in the two A_1 modes in the sequence $XAuP(CH_3)_3$, X = Br, I, and CH_3: 378, 371, 353 and 230, 213, 200 cm^{-1}. This is the order of increasing trans influence of these X ligands. The potential energy indicates 42:24:23% contributions of K(Au-P), H(CPC), and $F(C\cdots Au)$ in the 353-cm^{-1} mode of $H_3CAuP(CH_3)_3$, and this mixing coupled with the fact that it is related to only two frequencies is responsible for the rather large standard error in K(Au-P).

$XAuP(CH_3)_3$ (X = Cl, Br, I). These molecules all have C_{3v} symmetry. The potential energy is described in terms of 40 internal coordinates distributed among 9 symmetrically equivalent sets. From 21 frequencies, 13 force constants were calculated; and 9 were varied in the last least-squares cycle. Trial values for the force constants associated with the $P(CH_3)_3$ ligand were transferred from $CH_3AuP(CH_3)_3$, while those for the Au-X bond were taken from the corresponding CH_3HgX molecules.[41] Because of the limited frequency data obtained with these molecules, the standard

Table VIII. Observed and Calculated Frequencies (cm^{-1}) and Potential Energy Distributions (%) for $XAuP(CH_3)_3$ (X = Cl, Br, I)

	$ClAuP(CH_3)_3$			$BrAuP(CH_3)_3$			$IAuP(CH_3)_3$		
	ν_{obs}	ν_{calc}	P.E.D.	ν_{obs}	ν_{calc}	P.E.D.	ν_{obs}	ν_{calc}	P.E.D.
A_1	2975	2992	K(CH), 97	2974	2990	K(CH), 96	2971	2987	K(CH), 96
	2904	2897	K(CH), 95	2903	2896	K(CH), 95	2900	2890	K(CH), 95
	1409	1409	H(HCH), 90	1406	1412	H(HCH), 91	1406	1409	H(HCH), 92
	1283	1344	H(HCH), 46; H(HCP), 34 F(HP), 14	1283	1328	H(HCH), 47; H(HCP), 29; F(HP), 19	1284	1320	H(HCH), 48; H(HCP), 31; F(HP), 15
	970	969	H(HCP), 52; F(HP), 35	965	964	H(HCP), 44; F(HP), 43	-	940	H(HCP), 49; F(HP), 39
	687	695	K(PC), 61; F(HP), 23	683	692	K(PC), 60; F(HP), 26	681	694	K(PC), 62; F(HP), 24
	383	387	K(AuP), 42; H(CPC), 26	378	375	K(AuP), 44; H(CPC), 28	371	363	K(AuP), 37; H(CPC), 33; H(CPAu), 10
	327[a]	326[a]	K(AuCl), 88; H(CPC), 7	230	241	K(AuBr), 46; K(AuP), 12; H(CPC), 21; F(AuC), 13	213	224	K(AuI), 25; K(AuP), 25; H(CPC), 19; F(AuC), 21
	211	215	K(AuP), 34; H(CPC), 27; F(AuC), 25	202	186	K(AuBr), 53; K(AuP), 19; H(CPC), 11; F(AuC), 13	164	157	K(AuI), 74; K(AuP), 13
A_2	-	2991	K(CH), 97	-	2989	K(CH), 96	-	2986	K(CH), 97
	-	1407	H(HCH), 97	-	1410	H(HCH), 91	-	1408	H(HCH), 92
	-	924	H(HCP), 56; F(HP), 37	-	920	H(HCP), 48; F(HP), 46	-	896	H(HCP), 53; F(HP), 41
E	2990	2993	K(CH), 97	2989	2991	K(CH), 96	2983	2987	K(CH), 97
	2990	2992	K(CH), 97	2989	2989	K(CH), 96	2983	2986	K(CH), 97
	2904	2897	K(CH), 95	2903	2986	K(CH), 95	2900	2890	K(CH), 95
	1435	1409	H(HCH), 91	1434	1412	H(HCH), 91	1420	1410	H(HCH), 92
	1413	1408	H(HCH), 91	1413	1411	H(HCH), 91	1416	1409	H(HCH), 92
	1305	1342	H(HCH), 46; H(HCP), 34 F(HP), 14	1307	1328	H(HCH), 47; H(HCP), 29; F(HP), 19	1304	1318	H(HCH), 48; H(HCP), 31; F(HP), 16
	970	957	H(HCP), 52; F(HP), 35	965	952	H(HCP), 44; F(HP), 44	958	929	H(HCP), 48; F(HP), 39
	952	930	H(HCP), 56; F(HP), 37	952	926	H(HCP), 47; F(HP), 45	-	902	H(HCP), 53; F(HP), 13
	750	742	K(PC), 67; F(HP), 37	750	744	K(PC), 64; F(HP), 27	750	743	K(PC), 66; F(HP), 25
	284	284	H(CPC), 85; F(CC), 10	267	268	H(CPC), 90	267	270	H(CPC), 83; F(CC), 13
	188	188	H(CPAu), 42; F(AuC), 42; H(PAuCl), 14	187	188	H(CPAu), 51; F(AuC), 43	188	189	H(CPAu), 63; F(AuC), 42
	94	93	H(PAuCl), 84	59	59	H(PAuBr), 93	47	47	H(PAuI), 95
	Average Error = 1.1%			Average Error = 1.2%			Average Error = 1.2%		

a - ($\nu_{^{35}Cl} - \nu_{^{37}Cl}$) 6.0 obs and 6.7 cm^{-1} calc.

errors are quite large. The Urey-Bradley constants are given in Table VII, and a comparison of calculated and observed frequencies is made in Table VIII.

The fit to the two lowest frequencies in the A_1 block, which are primarily Au-P and Au-X stretching, is very good for X = Cl, somewhat poorer for X = I, and poorest with X = Br. In this series, there appears to be progressive vibrational mixing, and *K*(Au-P) and *K*(Au-Br) are strongly correlated. Figure 5 shows the variation of *K*(Au-P) obtained when *K*(Au-Br) is constrained to different values and both *K*(Au-P) and *H*(CPC) are allowed to refine. Over the entire range of *K*(Au-Br) from 1.3 to 1.9 mdyn/Å, *H*(CPC) varies only from 0.773 to 0.764 mdyn Å/radian^2. The average error in the two lowest frequencies varies from 14.7 to 14.5% over this range with a minimum error of 12.2% for the parameters listed in Table VII.

$(CH_3)_3AuP(CH_3)_3$ and $(CH_3)_3AuAs(CH_3)_3$. The most symmetric conformations of these molecules have only a single plane of symmetry, and this may be either horizontal or vertical with respect to the AuC_3Y plane. Nevertheless, the spectra indicate that the effective symmetry for the C_3AuY skeleton is C_{2v}; and as in the other molecules, the $Y(CH_3)_3$ ligands (Y = P, As) have effective C_{3v} symmetry. In this case, the molecular symmetry group as described by Longuet-Higgins[24] for molecules with free rotation would contain 4×3^7 elements. This result is not practically helpful, and consequently the normal-coordinate analysis was carried out with C_s molecular symmetry. Symmetry coordinates for the $(CH_3)_3Au^{III}$ moiety were constructed for C_{2v} symmetry and correlated to A′ and A″ modes of C_s, while the C_{3v} symmetry coordinates of $P(CH_3)_3$ and $As(CH_3)_3$ also were correlated to C_s. In this way, the C_{2v} and C_{3v} descriptions of the trimethylgold and tertiary phosphine or arsine, respectively, are retained in constructing the C_s symmetry coordinates.

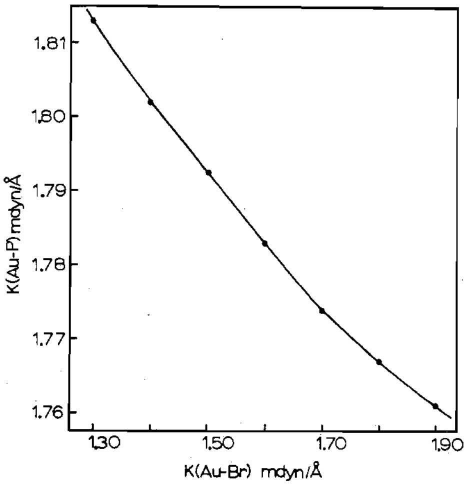


Figure 5. Variation of *K*(Au-P) with *K*(Au-Br) for $Br-Au-P(CH_3)_3$.

(41) C. F. Shaw and R. S. Tobias, unpublished results.

Table IX. Observed and Calculated Frequencies (cm^{-1}) and Potential Energy Distribution (%) of Trimethylgold(III) Compounds

	$(CH_3)_3AuP(CH_3)_3$			$(CD_3)_3AuP(CH_3)_3$		$(CH_3)_3AuAs(CH_3)_3$		
	ν_{obsd}	ν_{calcd}	PED	ν_{obsd}	ν_{calcd}	ν_{obsd}	ν_{calcd}	PED
A′	2909	2900	$K(\mathrm{CH})_{\mathrm{P}}$, 95	2909	2900	2918	2908	$K(\mathrm{CH})_{\mathrm{As}}$, 95
	2883	2882	$K(\mathrm{CH})_{\mathrm{Au}}$, 95	2109	2067	2900	2870	$K(\mathrm{CH})_{\mathrm{Au}}$, 95
	1308	1334	$H(\mathrm{HCH})_{\mathrm{P}}$, 47; $H(\mathrm{HCAu})$, 34	1309	1335	1278	1290	$H(\mathrm{HCH})$, 50; $H(\mathrm{HCAs})$, 28; $F(\mathrm{H}\cdots\mathrm{As})$, 16
	1209	1207	$H(\mathrm{HCH})_{\mathrm{Au}}$, 61; $F(\mathrm{H}\cdots\mathrm{Au})$, 30	957	941	1210	1203	$H(\mathrm{HCH})_{\mathrm{Au}}$, 59; $F(\mathrm{H}\cdots\mathrm{Au})$, 30
	1176	1200	$H(\mathrm{HCH})_{\mathrm{Au}}$, 60; $F(\mathrm{H}\cdots\mathrm{Au})$, 30	925	904	1176	1195	$H(\mathrm{HCH})_{\mathrm{Au}}$, 60; $F(\mathrm{H}\cdots\mathrm{Au})$, 31
	957	949	$H(\mathrm{HCP})$, 53; $F(\mathrm{H}\cdots\mathrm{P})$, 35	900	897	903	871	$H(\mathrm{HCAs})$, 51; $F(\mathrm{H}\cdots\mathrm{Au})$, 43
	767	772	$F(\mathrm{H}\cdots\mathrm{Au})$, 83, $H(\mathrm{HCAu})$, 11	677	686	774	773	$H(\mathrm{HCAu})$, 14; $F(\mathrm{H}\cdots\mathrm{Au})$, 78
	677	686	$K(\mathrm{PC})$, 63; $F(\mathrm{H}\cdots\mathrm{P})$, 23	587	583	591	593	$K(\mathrm{AsC})$, 63
	540	533	$K(\mathrm{AuC})$, 56; $F(\mathrm{H}\cdots\mathrm{Au})$, 32	494	501	546	546	$K(\mathrm{AuC})$, 59; $F(\mathrm{H}\cdots\mathrm{Au})$, 31
	512	509	$K(\mathrm{AuC})$, 48; $F(\mathrm{H}\cdots\mathrm{Au})$, 33; $f'(\mathrm{AuC,AuC'})$, 9	471	475	516	516	$K(\mathrm{AuC})$, 48; $F(\mathrm{H}\cdots\mathrm{Au})$, 32; $f'(\mathrm{AuC,AuC})$, 9
	351	350	$H(\mathrm{CPC})$, 38; $H(\mathrm{CPAu})$, 11; $K(\mathrm{AuP})$, 28	350	349	257	246	$H(\mathrm{CAsC})$, 33; $H(\mathrm{CAsAu})$, 12; $K(\mathrm{AsAu})$, 37; $F(\mathrm{C}\cdots\mathrm{C})_{\mathrm{As}}$, 10
	208	217	$H(\mathrm{CAuC})$, 75; $H(\mathrm{CAuP})$, 10		207	270	267	$H(\mathrm{CAuC})$, 79; $F(\mathrm{C}\cdots)_{\mathrm{Au}}$, 12
	197	196	$K(\mathrm{AuP})$, 23; $F(\mathrm{C}\cdots\mathrm{P})$, 20 $H(\mathrm{CAuC})$, 22; $F(\mathrm{C}\cdots\mathrm{P})$, 10	197	186		195	$H(\mathrm{CAuC})$, 45; $K(\mathrm{AsAu})$, 11; $H(\mathrm{CAuAs})$, 11; $F(\mathrm{C}\cdots\mathrm{As})$, 10
A″	1189	1198	$H(\mathrm{HCH})$, 60; $F(\mathrm{H}\cdots\mathrm{Au})$, 30	930	908	1189	1193	$H(\mathrm{HCH})$, 60; $F(\mathrm{H}\cdots\mathrm{Au})$, 31
	767	765		851	908	825	857	$H(\mathrm{HCAs})$, 51; $F(\mathrm{H}\cdots\mathrm{As})$, 43
	851	908	$H(\mathrm{HCP})$, 57; $F(\mathrm{H}\cdots\mathrm{P})$, 37	587	593	774	781	$H(\mathrm{HCAu})$, 14; $F(\mathrm{H}\cdots\mathrm{Au})$, 78
	498	489	$K(\mathrm{AuC})$, 62; $F(\mathrm{H}\cdots\mathrm{Au})$, 39; $f'(\mathrm{AuC,AuC})$, −12	456	465	499	498	$K(\mathrm{AuC})$, 63; $F(\mathrm{H}\cdots\mathrm{Au})$, 38; $f'(\mathrm{AuC,AuC})$, −12
	288	289	$H(\mathrm{CAuC})$, 75; $H(\mathrm{CAuP})$, 10	252	249	270	267	$H(\mathrm{CAuC})$, 79; $F(\mathrm{C}\cdots\mathrm{C})$, 14
	103	102	$H(\mathrm{CAuP})$, 49; $F(\mathrm{C}\cdots\mathrm{P})$, 27; $H(\mathrm{CPAu})$, 10	96	94	93	90	$H(\mathrm{CAuAs})$, 28; $F(\mathrm{C}\cdots\mathrm{As})$, 55
A′ + A″	2990	2990	$K(\mathrm{CH})_{\mathrm{P}}$, 97	2987	2991	2996	2999	$K(\mathrm{CH})_{\mathrm{As}}$, 97
	2990	2989	$K(\mathrm{CH})_{\mathrm{P}}$, 97	2987	2990	2990	2999	$K(\mathrm{CH})_{\mathrm{As}}$, 97
	2979	2989	$K(\mathrm{CH})_{\mathrm{P}}$, 97	2974	2989	2990	2998	$K(\mathrm{CH})_{\mathrm{As}}$, 97
	2960	2984	$K(\mathrm{CH})_{\mathrm{Au}}$, 96	2221	2216	2956	2971	$K(\mathrm{CH})_{\mathrm{Au}}$, 96
	2960	2975	$K(\mathrm{CH})_{\mathrm{Au}}$, 96	2202	2221	2956	2970	$K(\mathrm{CH})_{\mathrm{Au}}$, 96
	2960	2975	$K(\mathrm{CH})_{\mathrm{Au}}$, 96	2202	2209	2956	2970	$K(\mathrm{CH})_{\mathrm{Au}}$, 96
	2913	2900	$K(\mathrm{CH})_{\mathrm{P}}$, 95	2915	2900	2922	2908	$K(\mathrm{CH})_{\mathrm{As}}$, 95
	2895	2876	$K(\mathrm{CH})_{\mathrm{Au}}$, 95	2109	2061	2900	2870	$K(\mathrm{CH})_{\mathrm{Au}}$, 95
	1438	1438	$H(\mathrm{HCH})_{\mathrm{Au}}$, 95	1042	1041	1420	1421	$H(\mathrm{HCH})_{\mathrm{Au}}$, 95
	1432	1429	$H(\mathrm{HCH})_{\mathrm{Au}}$, 95	1042	1034	1420	1420	$H(\mathrm{HCH})_{\mathrm{Au}}$, 95
	1431	1428	$H(\mathrm{HCH})_{\mathrm{Au}}$, 95	1042	1032	1420	1416	$H(\mathrm{HCH})_{\mathrm{Au}}$, 95
	1420	1411	$H(\mathrm{HCH})_{\mathrm{P}}$, 90	1433	1411	1413	1408	$H(\mathrm{HCH})_{\mathrm{As}}$, 92
	1420	1410	$H(\mathrm{HCH})_{\mathrm{P}}$, 91	1422	1411	1413	1408	$H(\mathrm{HCH})_{\mathrm{As}}$, 92
	1411	1410	$H(\mathrm{HCH})_{\mathrm{P}}$, 91	1411	1411	1413	1407	$H(\mathrm{HCH})_{\mathrm{As}}$, 92
	1290	1335	$H(\mathrm{HCH})_{\mathrm{P}}$, 47	1292	1333	1258	1288	$H(\mathrm{HCH})_{\mathrm{As}}$, 50; $H(\mathrm{HCAs})$, 28; $F(\mathrm{H}\cdots\mathrm{As})$, 16
	960	939	$H(\mathrm{HCP})$, 53; $F(\mathrm{P}\cdots\mathrm{H})$, 35	962	939	903	867	$H(\mathrm{HCAs})$, 51; $F(\mathrm{H}\cdots\mathrm{As})$, 43
	950	913	$H(\mathrm{HCP})$, 57; $F(\mathrm{P}\cdots\mathrm{H})$, 36	950	913	903	861	$H(\mathrm{HCAs})$, 51; $F(\mathrm{H}\cdots\mathrm{As})$, 43
	767	778	$F(\mathrm{H}\cdots\mathrm{Au})$, 83; $H(\mathrm{HCAu})$, 11	587	584	774	771	$H(\mathrm{HCAu})$, 11; $F(\mathrm{H}\cdots\mathrm{Au})$, 84
	767		$F(\mathrm{H}\cdots\mathrm{Au})$, 84; $H(\mathrm{HCAu})$, 12	587	571	774	767	$H(\mathrm{HCAu})$, 11; $F(\mathrm{H}\cdots\mathrm{Au})$, 81
	742	755	$K(\mathrm{PC})$, 63; $F(\mathrm{H}\cdots\mathrm{P})$, 24	743	735	616	613	$K(\mathrm{AsC})$, 68
	267	272	$H(\mathrm{CPC})$, 75; $F(\mathrm{C}\cdots\mathrm{C})$, 12	271	272	219	222	$H(\mathrm{CAsC})$, 75; $F(\mathrm{C}\cdots\mathrm{C})_{\mathrm{As}}$, 22
	190	186, 200	$H(\mathrm{CPAu})$, 52; $F(\mathrm{C}\cdots\mathrm{Au})$, 47	190	173, 189	158	156, 162	$H(\mathrm{CAsAu})$, 42; $F(\mathrm{C}\cdots\mathrm{Au})$, 56
	Av error = 1.00%			Av error = 1.42%		Av error = 1.14%		

The potential energy for vibrations symmetric with respect to the AuC_3P plane is described in terms of 71 internal coordinates. On the basis of the local symmetry, they are distributed among 17 symmetrically equivalent sets; *i.e.*, all C-H coordinates of the $P(CH_3)_3$ or $As(CH_3)_3$ ligand are considered equivalent, the C-H coordinates of the mutually trans methyl groups are taken to be equivalent, etc. From the 49 distinct frequencies observed with $(CH_3)_3AuP(CH_3)_3$ and $(CD_3)_3AuP(CH_3)_3$, 30 nonzero force constants were computed, and 17 were adjusted in the last least-squares cycle. The nature of the force field employed is such that the accidental degeneracy expected because of the local symmetry is introduced into the calculation.

The value of $F(\mathrm{C}\cdots\mathrm{C})_{\mathrm{Au}}$ was from the $[(CH_3)_2AuX_2^-]$ ions and constrained at 0.05 mdyn/Å. The nonbonded interactions $F(\mathrm{C}\cdots\mathrm{P})_{\mathrm{Au}}$ and $F(\mathrm{C}\cdots\mathrm{As})_{\mathrm{Au}}$ were constrained at 0.075 and 0.100 mdyn/Å. Rather than constrain $F(\mathrm{Au}\cdots\mathrm{H})$ as done by Scovell and Tobias,[26] the value of $F(\mathrm{H}\cdots\mathrm{H})$ which should be more nearly invariant for cis and trans methyls was fixed at 0.02 mdyn/Å, the value found for $[(CH_3)_2AuCl_2^-]$.[26] Trial values of $H(\mathrm{CAuC})$ and $H(\mathrm{CAuP})$ were taken from a SVFF calculation using only the four in-plane bending frequencies. Initial values of all other force constants were transferred from $CH_3AuP(CH_3)_3$. The Urey-Bradley field was modified by the introduction of the interaction constants $f(\mathrm{AuC,AuC})_{\mathrm{trans}}$ and $f(\mathrm{AuC,AuP})_{\mathrm{trans}}$ only after a reasonable frequency fit was obtained. The standard errors in the force constants are in general smallest for $(CH_3)_3AuP(CH_3)_3$ for which the experimental data are the most extensive.

The trial values of the force constants for $(CH_3)_3AuAs(CH_3)_3$ were transferred from the phosphine complex. The change from $P(CH_3)_3$ to $As(CH_3)_3$, insofar as the $(CH_3)_3Au^{III}$ moiety is concerned, is almost like an isotopic substitution, since the principal changes in the spectrum result from the increased mass of the group V donor atom. The following constants were constrained to have the same values as in $(CH_3)_3AuP(CH_3)_3$: $F(\mathrm{H}\cdots\mathrm{H})\mathrm{Au}$, $F(\mathrm{C}\cdots\mathrm{C})\mathrm{Au}$,

Table X. Selected Valence Force Constants[a] (Errors) for $(CH_3)_3AuY(CH_3)_3$ (Y = P, As), $CH_3AuP(CH_3)_3$, and $XAuP(CH_3)_3$ (X = Cl, Br, I)

	Compound					
Force constant	$(CH_3)_3AuAs(CH_3)_3$	$(CH_3)_3AuP(CH_3)_3$	$CH_3AuP(CH_3)_3$	$ClAuP(CH_3)_3$	$BrAuP(CH_3)_3$	$IAuP(CH_3)_3$
			Skeletal			
f(Au-C)$_{trans}$	2.55 (16)	2.42 (14)	2.30 (12)			
f(Au-C)$_{cis}$	2.31 (10)	2.25 (9)				
f(Au-X)				1.85 (25)	1.57 (35)	1.46 (32)
f(Au-Y)	1.77 (54)	2.00 (38)	1.96 (30)	2.30 (53)	2.22 (36)	1.90 (31)
f(XAuY)			0.49 (15)	0.62 (22)	0.36 (14)	0.27 (11)
f(CAuC)	0.96 (15)	1.07 (11)				
f(CAuY)	0.42 (4)	0.64 (15)				
			$Y(CH_3)_3$			
f(Y-C)	2.77 (34)	3.18 (9)	3.19 (7)	3.23 (17)	3.24 (9)	3.27 (7)
f(CYC)	0.69 (8)	0.92 (6)	0.88 (6)	0.98 (10)	0.88 (8)	0.89 (6)
f(CYAu)	0.69 (12)	0.64 (12)	0.48 (11)	0.58 (18)	0.61 (8)	0.63 (7)

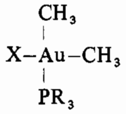
[a] Stretching constants, mdyn/Å; bending constants, mdyn Å/radian^2.

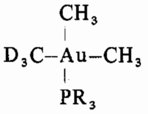
f(AuC,AuC)$_{trans}$, and f(AuC,AuAs)$_{trans}$. The Urey-Bradley force constants are given in Table V. Calculated and observed frequencies are compared in Table IX.

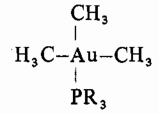
Discussion

For the discussion of bond strengths in terms of force constants, valence force field constants have been obtained by transformation; and selected constants are listed in Table X. These will be used exclusively in the discussions which follow unless otherwise noted.

Reaction of $(CH_3)_2AuIP(CH_3)_3$, I, with CD_3Li is stereospecific, and the perdeuteriomethyl group is found only cis to the phosphine, II. This is similar to the reaction of $(CH_3)_2AuIP(C_6H_5)_3$ with C_5H_5Na which gives only *cis*-(σ-C_5H_5)$(CH_3)_2AuP(C_6H_5)_3$. The pmr spectra show that there is no alkyl group exchange between positions cis and trans to the phosphine. It might be expected that intermolecular exchange involving the mutually trans methyls would be more facile, but none was observed either with CD_3Li during the synthesis or between molecules of II upon standing for several days. A statistical distribution of methyl groups should yield measurable concentrations of *trans*-$(CH_3)(CD_3)_2AuP(CH_3)_3$. Because of the rather narrow Au-C stretching bands in the Raman spectra ($\Delta\nu_{\text{half-intensity}} = 14.4$ cm^{-1}) and their high intensity, there should be little difficulty in detecting the bis(deuteriomethyl) compound. The analogous exchange in the $(CD_3)_2Hg$-$(CH_3)_2Hg$ system also is slow and was only observed after heating for 78 hr at 65°.[42]


$$\begin{array}{c} \mathrm{CH_3} \\ | \\ \mathrm{X{-}Au{-}CH_3} \\ | \\ \mathrm{PR_3} \end{array}$$
I


$$\begin{array}{c} \mathrm{CH_3} \\ | \\ \mathrm{D_3C{-}Au{-}CH_3} \\ | \\ \mathrm{PR_3} \end{array}$$
II


$$\begin{array}{c} \mathrm{CH_3} \\ | \\ \mathrm{H_3C{-}Au{-}CH_3} \\ | \\ \mathrm{PR_3} \end{array}$$
III

The nmr spectra indicate that exchange of $As(CH_3)_3$ between free ligand and $(CH_3)_3AuAs(CH_3)_3$ is faster than for the corresponding reaction of $P(CH_3)_3$ and III. The spectra also show that $P(CH_3)_3$ displaces coordinated $As(CH_3)_3$. These results are consistent with the relative values of the Au-P and Au-As force constants, f(Au-P) = 2.0 and f(Au-As) = 1.7$_7$ mdyn/Å, although these undoubtedly are associative rather than simple dissociative processes.

In the pmr spectra of the trimethyl compounds with different tertiary phosphines, III, $|^3J(\text{P-H})_{\text{trans P}}|/|^3J(\text{P-H})_{\text{cis P}}| = 1.3 \pm 0.1$. It has been suggested that the sign of the cis and trans coupling constants differs with $(CH_3)_2Pt(PR_3)_2$ compounds.[43]

With the univalent gold X-Au-PR$_3$ compounds, f(Au^{I}-X) values decrease in the sequence Cl > Br > I, similar to the trend in the $[(CH_3)_2AuX_2^-]$ anions.[26] The values of f(Au^{I}-P) are similar for the chloride and bromide and are considerably larger than the values for X = I and CH_3, consistent with a larger trans influence for the latter two ligands. The large trans influence for iodide is unusual but consistent with observations on $(CH_3)_2AuXP(C_6H_5)_3$ compounds. With X = I, the two Raman bands for Au-C stretching are observed at 518 and 532 cm^{-1}, while with the X = CH_3 they occur at 511 (two, almost accidentally degenerate) and 544 cm^{-1}.[12] All other X ligands give higher frequencies: X = Cl, 552, 544; CN, 555, 538; NCO, 569, 541.[44]

As can be seen in the potential energy distributions in Tables VI and VIII, there is marked coupling between the Au-P stretching coordinate and the symmetric deformation of the PC_3 group. This contributes to making the Au-P stretching force constants the most poorly defined parameters in the computations. Coupling becomes especially troublesome in the Au(I) compounds with X = halide where isotopic substitution is not a useful adjunct to the study. In the totally symmetric modes, mixing tends to occur among Au-X, Au-P, and CPC coordinates. This is particularly pronounced in the case of $BrAuP(CH_3)_3$ and presumably was responsible for the difficulties encountered by Duddell, *et al.*,[10] in trying to obtain meaningful force constants for the $XAuP(CH_3)_3$ molecules. In this work, least-squares refinement gave a reasonable set of parameters for the five molecules with X = CH_3, CD_3, Cl, Br, and I.

With $CH_3AuP(CH_3)_3$, the interaction force constant f'(Au-P,Au-C) refined to −0.285 mdyn/Å indicating that an extension of the Au-P bond results in a lengthening of the Au-C bond, consistent with the observation that a tertiary phosphine or arsine is necessary to stabilize a Au^{I}-C bond.

The trimethylgold(III) compounds have two distinctly different kinds of Au-C bonds because of the appreciably greater trans influence of methide compared to tertiary phosphine or arsine. This difference is reflected in the course of the reaction of the electrophile $HgBr_2$ with III. Stereospecific cleavage of one of the mutually trans methyl Au-C bonds occurs, and there is no further attack on the $(CH_3)_2AuBrPR_3$ product.[7] In this and several other cases, III reacts as $(CH_3)_2Hg$ and I as CH_3HgX. The bond stretching force constants for III are f(Au-C)$_{\text{trans to phosphine}}$ = 2.42 and f(Au-C)$_{\text{trans to CH}_3}$ = 2.25 mdyn/Å. Assuming applicability of the empirical relation between force constant and bond

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length of Herschbach and Laurie[45] and their parameters for atoms in rows 1 and 5 of the periodic table, the difference in the lengths[46] of the two Au-C bonds can be estimated to be $d(\text{Au-C})_{\text{trans CH}_3} - d(\text{Au-C})_{\text{trans P}} = 0.03$ Å. The Au-C bond lengths also can be calculated using the Herschbach-Laurie parameters as a check on the internal consistency of the calculations. For the shorter Au-C bond of $(CH_3)_3AuP(CH_3)_3$ ($f = 2.42$ mdyn/Å), the value $d(\text{Au-C}) = 2.11$ Å is calculated, close to that used in the normal-coordinate analyses, 2.05 Å. Since the calculated values of the force constants are insensitive to small changes in bond length, essentially the same set of force constants would be obtained using 2.11 Å as input for the computation. The interaction constant $f(\text{Au-C,Au-P})_{\text{trans}}$ also has a negative value as in the case of $CH_3AuP(CH_3)_3$. In the case of the trimethylgold(III) compounds, a tertiary phosphine or arsine again is needed to stabilize the compound. The interaction constant $f(\text{Au-C,Au-C})_{\text{trans}}$ is positive. This indicates a shortening of the Au-C bond as the trans Au-C bond is lengthened, and all of the available experimental evidence indicates that the Au-C bonds are stronger in the dimethyl than in the trimethylgold compounds.

The trimethylarsine analog, $(CH_3)_3AuAs(CH_3)_3$, has very similar parameters for the trimethylgold moiety, although the force constant for Au-As stretching is considerably less than for Au-P bond stretching. The difference $f(\text{Au-C})_{\text{trans CH}_3} - f(\text{Au-C})_{\text{trans P}}$ is 0.24 mdyn/Å, corresponding to a difference of 0.03_7 Å in bond lengths.

The values of the force constants for Au-C stretching of the mutually trans bonds in $(CH_3)_3AuP(CH_3)_3$ and $(CH_3)_3AuAs(CH_3)_3$ and the single bond in $CH_3AuP(CH_3)_3$ all are the same within the experimental error 2.2_5, 2.3_1, and 2.3_0 mdyn/Å, respectively. This suggests that these bonds are nearly identical, and this correlates well with the similarity in the rates of electrophilic attack by $HgBr_2$ on them in the gold(I)- and gold(III)-phosphine complexes.[7]

Although comparisons of force constants for molecules of appreciably different structures is considerably less accurate than for related structures, it may be noted that the force constants for Au-C bond stretching of the mutually trans Au-C bonds are essentially the same as the value for Hg-C stretching, $f(\text{Hg-C}) = 2.3_3$ mdyn/Å, calculated[40] with data for both $(CH_3)_2Hg$ and $(CD_3)_2Hg$. The interaction constant $f(\text{HgC,HgC}) = 0.06$ mdyn/Å is of the same sign but smaller than the corresponding constants in the gold(III) complexes. Both Au-C force constants are smaller than the values for $[(CH_3)_2AuCl_2^-]$, $f(\text{Au-C}) = 2.8_1$ (06) mdyn/Å, or $[(CH_3)_2AuBr_2^-]$, $f(\text{Au-C}) = 2.7_2$ (09) mdyn/Å.[26]

The Au-P valence force constants are essentially the same for the organogold(I) and -gold(III) compounds. The Urey-Bradley Au-P constant is smaller with Au(III), since these square-planar complexes have two P· · ·C nonbonded constants which correlate highly with $K(\text{Au-P})$. This suggests that the small value used for $F(\text{P}\cdots\text{C})$, 0.075 mdyn/Å, is still too large.

Oxidative addition of RX to CH_3AuPR_3 should be energetically favorable in many instances, since the $Au\text{-}PR_3$ bond strength will be altered little. Since the Au-C bond of CH_3AuPR_3 is similar to the weaker trans bonds in $(CH_3)_2AuP(CH_3)_3$, the exchange reaction (eq 6) observed by Tamaki

$$(CH_3)_2AuXPR_3 + CH_3AuPR_3 \rightleftarrows (CH_3)_3AuPR_3 + XAuPR_3 \qquad (6)$$

and Kochi for X = I[8] would be expected to involve little enthalpy change.

Registry No. *cis*-$(CH_3)_2(CD_3)AuP(CH_3)_3$, 38386-64-0; $(CD_3)_3AuP(CH_3)_3$, 38386-65-1; $(CH_3)_3AuAs(CH_3)_3$, 38386-66-2; $CH_3AuP(CH_3)_3$, 32407-79-7; $CD_3AuP(CH_3)_3$, 38386-67-3; $(CH_3)_3AuP(CH_3)_3$, 33012-33-8; $ClAuP(CH_3)_3$, 15278-97-4; $BrAuP(CH_3)_3$, 25884-75-7; $IAuP(CH_3)_3$, 25892-35-7.

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Two Magnetically Subnormal Copper Halide Complexes with 1,8-Naphthyridine

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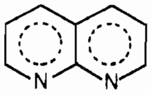
The compounds (1,8-naphthyridine)copper(II) chloride and the corresponding bromide have been prepared and characterized using magnetic properties and ir and visible spectra. The compounds are dimeric in the solid state and probably have square-pyramidal coordination at the metal atom.

Introduction

These laboratories have been concerned for some years with ligands having two basic groups separated by only a single atom (*e.g.*, acetate ion) which have the capability of forming a strained four-membered ring chelate or of bidentately bridging two metal atoms as in a wide variety of copper carboxylates. Among the more readily available ligands in this class are the negatively charged ions acetate, amidinate, and the anions of 2-pyridone and 1,3-diphenyltriazene. 1,8-Naphthyridine (I) is one of the rare neutral molecules in this class. Hendricker[1-5] and coworkers have recently done a great deal of work on coordination of 1,8-naphthyridine and



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