Syntheses of Organogold(III) Compounds Containing Pyridine and Tertiary Phosphines, Arsines, and Stibines. Application of Laser-Raman and Proton Magnetic Resonance Spectroscopy in the Elucidation of Their Structures and Reactions[1]

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Abstract: The new square-planar organogold compounds $[(CH_3)_2AuCl(py)]$, $[(CH_3)_2AuClPPh_3]$, $[(CH_3)_2AuClAsPh_3]$, $[(CH_3)_2AuClSbPh_3]$, $[(CH_3)_2Au(SCN)py]$, $[(CH_3)_2Au(SCN)PPh_3]$, $[(CH_3)_2Au(SCN)AsPh_3]$, $[(CH_3)_2Au(PPh_3)_2]ClO_4$, $[(CH_3)_2Au(AsPh_3)_2]ClO_4$, $[(CH_3)_2Au(SbPh_3)_2]ClO_4$, $[(CH_3)_2Au(PPh_2CH_2)_2]Cl$, and $[(CH_3)_2Au(PPh_2CH_2)_2][(CH_3)_2AuCl_2]$ have been synthesized. All compounds have been characterized by Raman, infrared, and pmr spectroscopy. The pyridine complexes $[(CH_3)_2AuCl(py)]$ and $[(CH_3)_2Au(SCN)(py)]$ undergo rapid exchange of pyridine at room temperature as determined from the proton resonance line shapes. The triphenylarsine complex $[(CH_3)_2Au(SCN)AsPh_3]$ also undergoes rapid exchange at room temperature. In contrast, $[(CH_3)_2AuClPPh_3]$, $[(CH_3)_2AuClAsPh_3]$, $[(CH_3)_2AuClSbPh_3]$, and $[(CH_3)_2Au(SCN)PPh_3]$ show no significant line broadening at room temperature. The $SbPh_3$ complex is very unstable thermally. The vibrational and pmr spectra of $[(CH_3)_2Au(SCN)py]$ and $[(CH_3)_2Au(SCN)AsPh_3]$ indicate that the neutral ligands tend to dissociate in solution with the formation of some $[(CH_3)_2Au(NCS)]_2$. The complexes $[(CH_3)_2Au(PPh_3)_2]ClO_4$, $[(CH_3)_2Au(AsPh_3)_2]ClO_4$, and $[(CH_3)_2Au(SbPh_3)_2]ClO_4$ which have cations that are isoelectronic with well-known organoplatinum(II) compounds undergo very rapid exchange in chloroform solution. In contrast, the chelated cations in $[(CH_3)_2Au(PPh_2CH_2)_2]Cl$ and $[(CH_3)_2Au(PPh_2CH_2)_2][(CH_3)_2]AuCl_2]$ show no evidence of dissociation. Laser-Raman spectra are particularly useful in assigning the structures of these labile organometallic compounds which all contain cis methyl groups. Both Ar^+ and He–Ne excitation have been used with crystalline and solution samples.

In contrast to the plethora of platinum(II) complexes, the number of known gold(III) compounds is minuscule. Also, considerably more is known about the square-planar complexes of Rh(I), Ir(I), and Pd(II) than about the related gold(III) compounds. In a large part this is a result of the strong oxidizing character of Au(III). Reaction of, *e.g.*, $AuCl_4^-$ with ligands such as triphenylphosphine,[4] triphenylarsine, thiourea,[5] or olefins[6] leads to reduction to gold(I) or gold metal.

The standard procedure which has been developed for the synthesis of diorganogold(III) compounds has involved the alkylation of $AuCl_3 \cdot py$ and the eventual isolation of the water insoluble $[R_2AuI]_2$. The organogold(III) products readily lose the molecule of pyridine. In general, the known organogold compounds do not have high thermal stability, and they decompose at elevated temperatures, yielding metallic gold and hydrocarbons. Armer and Schmidbaur[7] recently have reviewed their chemistry.

In this communication, we describe the synthesis of a series of new compounds of the type $[(CH_3)_2AuClL]$ by reactions of dimethylgold chloride with pyridine, triphenylphosphine, triphenylarsine, and triphenylstibine. Related cations $[(CH_3)_2AuL_2]^+$ have been prepared, as has the cation with the chelating 1,2-bis(diphenylphosphino)ethane (hereafter referred to as diphos). These ions are isoelectronic with well-known dimethylplatinum(II) compounds. Structures have been established for the compounds by the use of a combination of pmr, laser-Raman, and infrared spectroscopy.

Cleavage reactions of the binuclear thiocyanate $[(CH_3)_2AuNCS]_2$[8] also have been studied, since Gent and Gibson[9] reported that nitrogen bases did not cleave the thiocyanate bridge. Recently we observed that pyridine, triphenylphosphine, and triphenylarsine all will cleave some of the thiocyanate bridges in tetrakis(trimethylplatinum thiocyanate).[10,11]

Experimental Section

General Data. All compounds were handled under a dry nitrogen atmosphere and stored at *ca.* 5°. Benzene, carbon tetrachloride, and cyclopentane used as solvents were dried over 3A molecular sieves. Chloroform used as an nmr solvent was treated with sulfuric acid and distilled just before use. Microanalyses were performed by the Schwarzkopf Microanalytical Laboratory or by the microanalytical laboratory in this department. Molecular weights were determined osmometrically. Melting points were obtained with a Thomas-Hoover capillary melting point apparatus. Bis(dimethylgold chloride) was prepared using a modification of the procedure of Scovell, *et al.*[8] Tetrakis(dimethylgold hydroxide), synthesized by the method of Miles, *et al.*,[12] was dissolved in methanol and allowed to react with an aqueous $HCl-HNO_3$ mixture; the precipitate of $[(CH_3)_2AuCl]_2$ was collected on a frit and washed. Recrystallization was from *n*-hexane. Bis(dimethylgold thiocyanate) was prepared as described by Scovell, *et al.*[8]

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Compounds of the Type $[(CH_3)_2AuXL]$, X = Halide or Pseudohalide. Chlorodimethyl(pyridine)gold. To a solution of $[(CH_3)_2AuCl]_2$ (0.098 g, 0.00037 monomol) in cyclopentane was added the stoichiometric amount of pyridine using an ultramicroburet. The white precipitate which appeared immediately was collected on a frit, washed with cyclopentane, and dried over P_4O_{10} under vacuum at *ca.* 5°; mp 57–58°. The product is soluble in most organic solvents. *Anal.* Calcd for $C_7H_{11}NClAu$: C, 24.6; H, 3.23; N, 4.10; Cl, 10.4; Au, 57.8. Found: C, 24.7; H, 3.28; N, 3.92; Cl, 9.78; Au, 57.4.

Chlorodimethyl(triphenylphosphine)gold and Chlorodimethyl(triphenylarsine)gold. Both compounds were prepared using the same procedure. In a typical synthesis, a solution of $[(CH_3)_2AuCl]_2$ (0.196 g, 0.00075 monomol) in 1 ml of cyclopentane was added to a solution of the stoichiometric amount of $AsPh_3$ dissolved in 3 ml of cyclopentane. The crystalline precipitate which appeared immediately was collected on a frit, washed with cyclopentane, and dried under vacuum over P_4O_{10} at *ca.* 5°. These compounds are soluble in acetone, methanol, chloroform, carbon tetrachloride, and benzene. The PPh_3 derivative had mp 155–158° dec. *Anal.* Calcd for $C_{20}H_{21}ClPAu$: C, 45.7; H, 4.00; Cl, 6.76; P, 5.91; Au, 37.5. Found: C, 45.8; H, 4.10; Cl, 7.15; P, 5.87; Au, 37.6. The $AsPh_3$ derivative had mp 188° dec. *Anal.* Calcd for $C_{20}H_{21}ClAsAu$: C, 42.3; H, 3.69; Cl, 6.24; Au, 34.6. Found: C, 42.8; H, 3.86; Cl, 6.24; Au, 34.9.

Chlorodimethyl(triphenylstibine)gold. A solution of $[(CH_3)_2AuCl]_2$ (0.180 g, 0.00068 monomol) in cyclopentane was added to the stoichiometric amount of $SbPh_3$ dissolved in a cyclopentane–ether mixture. A white precipitate similar to that obtained in the reactions with PPh_3 and $AsPh_3$ appeared immediately, and this was collected on a frit. The compound was very unstable and decomposed within a few hours in a nitrogen atmosphere at 5°. No analyses could be obtained, but the nmr spectrum in $CDCl_3$ solution indicated that the compound was pure.

Thiocyanatodimethyl(pyridine)gold. To a solution of $[(CH_3)_2AuNCS]_2$ (0.15 g, 0.00053 monomol) in 3 ml of cyclopentane was added the stoichiometric amount of pyridine using an ultramicroburet. Initially, a white precipitate appeared, but after shaking an oil was present at the bottom of the flask. The supernatant liquid was removed and the oil was washed with CCl_4, cooled to 0°, washed with dry ether, and dried with a stream of nitrogen, giving a crystalline product, mp 48°. *Anal.* Calcd for $C_8H_{11}N_2SAu$: C, 26.4; H, 3.02; N, 7.69; S, 8.79; Au, 54.1; mol wt (for monomer), 364. Found: C, 26.2; H, 3.31; N, 7.54; S, 8.56; Au, 54.4; mol wt (benzene), 402.

Thiocyanatodimethyl(triphenylphosphine)gold and Thiocyanatodimethyl(triphenylarsine)gold. These compounds also were prepared similarly. For example, to a solution of $[(CH_3)_2AuNCS]_2$ (0.228 g, 0.008 monomol) in 8 ml of cyclopentane was added the stoichiometric amount of PPh_3 dissolved in 2 ml of anhydrous ether. The white precipitate which appeared instantly was collected on a frit, washed three times with ether, and stored under vacuum over P_4O_{10} at 5°. The PPh_3 complex had mp 123–125°. *Anal.* Calcd for $C_{21}H_{21}NSPAu$: C, 46.0; H, 3.86; N, 2.56; S, 5.86; P, 5.67; Au, 36.0. Found: C, 45.9; H, 3.81; N, 2.51; S, 6.15; P, 5.50; Au, 35.9. The $AsPh_3$ complex had mp 100–101°. *Anal.* Calcd for $C_{21}H_{21}NSAsAu$: C, 42.6; H, 3.55; N, 2.37; S, 5.41; Au, 33.3. Found: C, 42.4; H, 3.76; N, 2.49; S, 5.68; Au, 33.4.

Compounds Containing Complex Organogold Cations. Dimethylbis(triphenylphosphine)gold(III) Perchlorate, Dimethylbis(triphenylarsine)gold(III) Perchlorate, and Dimethylbis(triphenylstibine)gold(III) Perchlorate. These three compounds were prepared in the same way. To a suspension of $[(CH_3)_2AuOH]_4$ prepared according to the method of Miles, *et al.*,[12] in methanol was added at 0° an aqueous solution of $HClO_4$ (concentrated acid diluted with an equal volume of water) to give a slightly acid solution. To this was added a solution containing 2 equiv of PPh_3, $AsPh_3$, or $SbPh_3$ dissolved in the minimum volume of diethyl ether (<1 ml). The white crystalline precipitate which appeared was washed with ether and dried under vacuum over P_4O_{10}. The PPh_3 complex had mp 200–201° dec, with minor explosions beginning at *ca.* 139°. *Anal.* Calcd for $C_{38}H_{36}ClP_2O_4Au$: C, 53.6; H, 4.23; Cl, 4.17; P, 7.28; Au, 23.2. Found: C, 53.4; H, 4.39; Cl, 4.06; P, 7.10; Au, 23.5. The $AsPh_3$ complex had mp 180–185° dec. *Anal.* Calcd for $C_{38}H_{36}ClAs_2O_4Au$: C, 48.6; H, 3.83; Cl, 3.78; Au, 21.0. Found: C, 48.2; H, 4.01; Cl, 3.97; Au, 21.3. The $SbPh_3$ complex had mp 77–80° dec. *Anal.* Calcd for $C_{38}H_{36}ClSb_2O_4Au$: C, 44.2; H, 3.48; Cl, 3.44; Au, 19.1. Found: C, 44.3; H, 3.66; Cl, 3.47; Au, 19.3.

Dimethyl-1,2-bis(diphenylphosphino)ethanegold(III) Chloride. To a solution of bis(diphenylphosphino)ethane (diphos) in benzene (0.185 g, 0.00047 mol) was added a solution of $[(CH_3)_2AuCl]_2$ (0.118 g, 0.00045 monomol) in benzene. The white precipitate which appeared was collected on a frit and washed with benzene; mp 190°. *Anal.* Calcd for $C_{28}H_{30}ClP_2Au$: C, 50.9; H, 4.54; Cl, 5.37; P, 9.38; Au, 29.8. Found: C, 50.6; H, 4.56; Cl, 5.60; P, 9.10; Au, 30.0.

Dimethyl-1,2-bis(diphenylphosphino)ethanegold(III) Dimethyldichloroaurate(III). To a solution of $[(CH_3)_2AuCl]_2$ (0.145 g, (0.00055 monomol) in benzene was added diphos (0.111 g, 0.00022 mol). The solvent was removed in a stream of nitrogen, and the oil which remained was stored at 5° in a vacuum desiccator over P_4O_{10}, giving an opalescent white solid, mp 60–62°. *Anal.* Calcd for $C_{15}H_{18}ClPAu$: C, 39.0; H, 3.90; Cl, 7.70; P, 6.72; Au, 42.7; mol wt (for $C_{30}H_{36}Cl_2P_2Au_2$), 923. Found: C, 38.8; H, 4.19; Cl, 7.72; P, 6.92; Au, 43.0; mol wt (benzene), 1010 (0.0125 *M* solution).

The two diphos compounds bind CCl_4 very strongly, giving solvates, and it cannot be used in their syntheses or recrystallization.

Raman Spectra. These were obtained using He–Ne or Ar^+ excitation and an instrument which has been described briefly elsewhere.[13] Detection was by photon counting. The crystalline compounds were sealed in glass capillaries and the transillumination technique was employed. Solutions were run either in capillaries or in 2.5-ml Perkin-Elmer multireflection cells coated for maximum reflectance at 4880 (Ar^+) or 6328 Å (He–Ne). Calibration of the monochromator was effected with the exciting line, background plasma lines, and neat indene as recommended by Hendra.[14] Frequencies are corrected to vacuum at 15° and for sharp lines are accurate to within $\pm 2\ cm^{-1}$.

Infrared Spectra. These were recorded with a Beckman IR-12 spectrometer using Nujol–halocarbon oil split mulls, KBr disks, or standard liquid cells. In all cases, disk spectra were checked with mull spectra to be certain no reaction with KBr occurred. Exchange even has been observed between dimethylgold(III) pseudohalides and KBr or CsI mull plates. The instrument was calibrated with polystyrene film and neat indene. The frequencies for sharp bands are accurate to $\pm 2\ cm^{-1}$, while those for broad bands should be within $\pm 5\ cm^{-1}$.

Proton Magnetic Resonance Spectra. Varian A-60 and XL-100 spectrometers were used for pmr spectra. The ambient probe temperature was *ca.* 40°. Coupling constants are believed to be accurate to ±0.5 Hz. Chemical shifts were measured relative to an internal TMS reference and are accurate to ±0.01 ppm. Variable-temperature measurements were made with A-60 and A-60D as well as the XL-100 spectrometers.

Conductivity Measurements. Conductances were determined with nitrobenzene solutions thermostated at *ca.* 25° using a simple bridge designed in the department electronics laboratory. The cell constant was obtained by measuring the conductance of 0.2 *M* KCl.

Data and Results

Proton Magnetic Resonance Spectra. Preliminary observations with organogold(III) compounds indicated that exchange processes often occur with very low activation energies. For example, a moderately concentrated, equimolar mixture of $[(CH_3)_2AuCl]_2$ and $[(CH_3)_2AuI]_2$ in CCl_4 (each 0.21 *M*) gives only one proton resonance at 40° with τ 8.60 ppm ($\tau[(CH_3)_2AuCl]_2$ 8.72, $\tau[(CH_3)_2AuI]_2$ 8.49 ppm). Scovell[15] found that the addition of $[(CH_3)_2AuCl]_2$ to a solution of $[(CH_3)_2AuI]_2$ led to a broadening and reduction in intensity of the proton resonance of the iodide dimer at τ 8.49 ppm. A very broad and low-intensity resonance was observed at τ 8.71, about the value for the chloride dimer resonance. In addition, a very broad new band appeared at τ 8.59 which must result from a mixed chloride–iodide dimer. The total stoichiometric concentrations in the solution were 20 m*M* in the iodide dimer and 7.4 m*M* in the chloride dimer. The very

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[15] W. M. Scovell, Ph.D. Thesis, University of Minnesota, 1969.

Table I. Methyl Proton Resonances for Some Dimethylgold(III) Compounds at 40°

Compound	Solvent	$\tau(CH_3)$, ppm[a]
$[(CH_3)_2AuNCS]_2$	$CHCl_3$	9.05 (1), 8.70 (1)[b]
$[(CH_3)_2Au(acac)]$	$CHCl_3$	8.86[c]
$[(CH_3)_2AuN_3]_2$	$CDCl_3$	8.8[d]
$[(CH_3)_2AuCl]_2$	CCl_4	8.72[b]
	C_6H_6	9.00
$[(CH_3)_2AuBr]_2$	CCl_4	8.62[b]
$[(CH_3)_2AuI]_2$	CCl_4	8.49[b]
	$CHCl_3$	8.46[c]
$[(CH_3)_2Au(SCN)py]$[e]	$CHCl_3$	9.02 (1) bd, 8.85 (5) bd
	$CDCl_3$	(−5°) 9.02 (3) bd, 8.93 (1) bd, 8.82 (12), 8.75 (12), 8.67 (4) bd
$[(CH_3)_2Au(SCN)PPh_3]$[e]	$CDCl_3$	8.94 (1) ($^3J_{^{31}P-H}$ = 8.8 Hz), 8.57 (1) ($^3J_{^{31}P-H}$ = 8.1 Hz)
$[(CH_3)_2Au(SCN)AsPh_3]$[e]	$CDCl_3$	8.87, (−15°) 8.81 (1), 8.40 (1)
$[(CH_3)_2AuCl(py)]$[e]	$CHCl_3$	(−38°) 8.80 (1), 8.66 (1)
$[(CH_3)_2AuClPPh_3]$[e]	$CHCl_3$	9.12 (1) ($^3J_{^{31}P-H}$ = 8.5 Hz), 8.62 (1) ($^3J_{^{31}P-H}$ = 9.3 Hz)
	CCl_4	9.28 (1) ($^3J_{^{31}P-H}$ = 8.5 Hz), 8.67 (1) ($^3J_{^{31}P-H}$ = 9.3 Hz)
$[(CH_3)_2AuClAsPh_3]$	$CHCl_3$	9.05 (1), 8.47 (1)
$[(CH_3)_2AuClSbPh_3]$	$CDCl_3$	8.85 (1), 8.44 (1)
$[(CH_3)_3AuPPh_3]$	$CHCl_3$	9.50 (2) ($^3J_{^{31}P-H}$ = 7.1 Hz), 8.36 (1) ($^3J_{^{31}P-H}$ = 9.5 Hz)
$[(CH_3)_2Au(PPh_3)_2]ClO_4$[e]	$CHCl_3$	9.14
$[(CH_3)_2Au(AsPh_3)_2]ClO_4$[e]	$CDCl_3$	9.14
$[(CH_3)_2Au(SbPh_3)_2]ClO_4$[f]	$CDCl_3$	9.14
$[(CH_3)_2Au(PPh_2CH_2)_2]Cl$	$CHCl_3$	8.77 ($^3J_{^{31}P-H}$ = 7.4 Hz)
$[(CH_3)_2Au(PPh_2CH_2][(CH_3)_2AuCl_2]$	$CHCl_3$	8.87 (1), 8.77 (1) ($^3J_{^{31}P-H}$ = 7.4 Hz)
$[AsPh_4][(CH_3)_2AuCl_2]$	$CHCl_3$	8.90[g]
$[AsPh_4][(CH_3)_2AuBr_2]$	$CHCl_3$	8.79[g]
$[AsPh_4][(CH_3)_2AuI_2]$	$CHCl_3$	8.55[g]

[a] Relative intensities in parentheses. [b] Data from ref 8. [c] Data from ref 12. [d] Data from ref 16. [e] Determined at both 60 and 100 MHz. [f] Run at 0° because of the thermal instability of the compound. [g] Data from ref 13.

broad resonances prevented an accurate estimate of the equilibrium concentrations.

On the basis of these observations, it is to be expected that many organogold(III) compounds will undergo inter- or intramolecular exchange processes which at room temperature are fast on the pmr time scale. This must be borne in mind when using pmr spectroscopy to establish the structures of new compounds.

The Molecules $[(CH_3)_2AuClpy]$, $[(CH_3)_2AuClPPh_3]$, $[(CH_3)_2AuClAsPh_3]$, $[(Cu_3)_2AuClSbPh_3]$, $[(CH_3)_2Au(SCN)py]$, $[(CH_3)_2Au(SCN)PPh_3]$, and $[(CH_3)_2Au(SCN)AsPh_3]$. Data for the pmr spectra of these molecules are collected in Table I, together with chemical shifts and, in some cases, coupling constants for a number of other known dimethylgold(III) compounds. The spectra indicate that only the cis isomers are obtained. Conductance data are given in Table II.

Table II. Equivalent Conductance of Dimethylgold(III) Compounds in Nitrobenzene at 24.85°

Compound	Concn, m*M*	Λ,[a] ohm^{-1} cm^{-1}
$[(CH_3)_2Au(PPh_3)_2]ClO_4$	1.05	27.5
	0.418	28.2
$[(CH_3)_2Au(AsPh_3)_2]ClO_4$	1.08	26.1
	0.433	27.1
$[(CH_3)_2Au(PPh_2CH_2)_2]Cl$	1.27	27.3
	0.508	27.7
$[(CH_3)_2Au(PPh_2CH_2)_2][(CH_3)_2AuCl_2]$	1.31	18.4
	0.68	24.8

[a] Equivalent conductance.

At 25°, $[(CH_3)_2AuCl(py)]$ in $CHCl_3$ solution exhibits two slightly broadened resonances of equal intensity at τ 8.64 and 8.88 ppm. As the solution temperature is lowered, the bands sharpen and two signals of equal intensity are observed, τ 8.66 and 8.80 at −38°. The addition of pyridine to the solution increases the exchange rate, and coalescence can be made to occur at room temperature. Log $(1/\tau_e)$, where τ_e is the exchange lifetime, varies linearly with the logarithm of the pyridine concentration.[17]

Addition of 1 equiv of PPh_3 to a CCl_4 solution of $[(CH_3)_2AuCl(py)]$ causes the disappearance of the broad resonances characteristic of the pyridine complex. In their place appear two new resonances at τ 9.28 and 8.67 ppm, each of which is split by coupling with phosphorus-31, $^3J_{^{31}P-H}$ = 8.5 and 9.3 Hz, respectively. The same spectrum is exhibited by an authentic sample of $[(CH_3)_2AuClPPh_3]$. Consequently, PPh_3 will displace py quantitively in solution, and the phosphine complex is much more inert to substitution than the pyridine complex. Solutions of $[(CH_3)_2AuClAsPh_3]$ and $[(CH_3)_2AuClSbPh_3]$ also show two methyl proton resonances of equal intensity in $CHCl_3$ solution. Again exchange is slow at 40° on the pmr time scale. Addition of the excess PPh_3 or $AsPh_3$ to the solution of the corresponding complexes leads to broadening of the methyl proton resonances, indicating that exchange processes also take place in these systems, albeit more slowly than with pyridine.

The compound $[(CH_3)_2Au(SCN)py]$ also undergoes a rather rapid process which leads to collapse of the nonequivalent methyl proton resonances. In benzene solution at 40°, a single broad resonance is observed at τ 9.00 ppm, while in $CHCl_3$ two broad resonances with relative intensities of *ca.* 5:1 are observed at τ 8.85 (full width at half intensity = 0.13 ppm) and 9.02 ppm, respectively. Upon cooling, two signals of equal intensity appear at τ 8.75 and 8.82 ppm. There are signals approximately one-third as intense at 8.67 and

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(16) W. Beck, W. F. Fehlhammer, P. Pöllmann, and R. S. Tobias, *Inorg. Chim. Acta*, **2**, 467 (1968).

(17) G. C. Stocco and R. S. Tobias, manuscript in preparation.

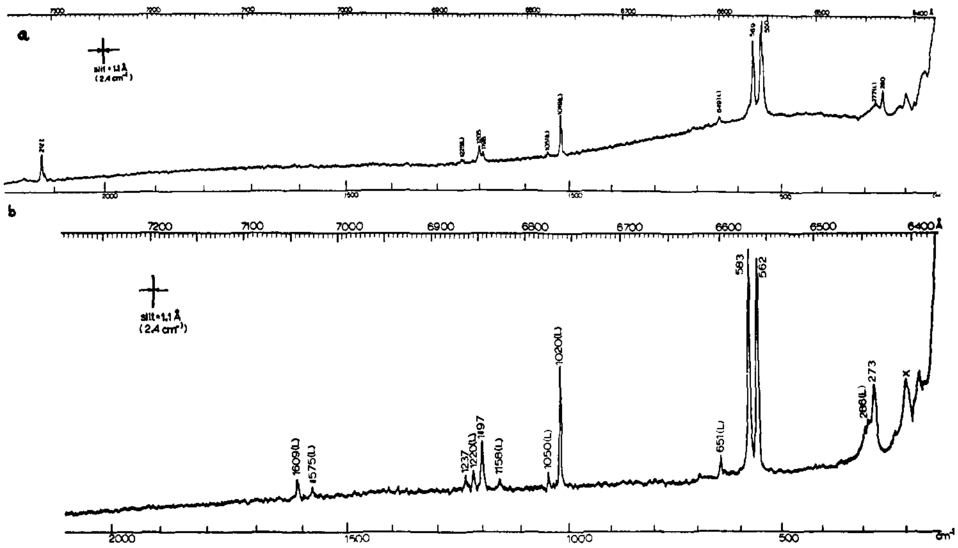

Figure 1. He–Ne laser-Raman spectra of crystalline (a) $[(CH_3)_2Au(SCN)py]$ and (b) $[(CH_3)_2AuCl(py)]$. Pyridine bands are marked with L.

9.02 ppm, which are similar to those of $[(CH_3)_2AuNCS]_2$ plus a very weak resonance at 8.93 ppm. The spectra appear to be concentration as well as temperature dependent. The line broadening and multiplicity of signals indicate substantial dissociation of pyridine occurs in solution. The complexity of the spectra may also result from the presence of both nitrogen- and sulfur-bonded isomers in solution.

As is the case with the chloro derivative, $[(CH_3)_2Au(SCN)PPh_3]$ does not undergo rapid exchange at room temperature. Two resonances are observed at τ 8.57 and 8.94 ppm with well-defined ^{31}P coupling. In contrast, $[(CH_3)_2Au(SCN)AsPh_3]$ does undergo rapid exchange at 40°, and only one methyl resonance is observed.

Cationic Complexes. Dissolution in $CHCl_3$ or $CDCl_3$ of $[(CH_3)_2AuL_2]ClO_4$, L = PPh_3, $AsPh_3$, and $SbPh_3$, gives solutions each of which exhibits a single proton resonance at τ 9.14 ppm. Although the methyl protons should be equivalent in the cations, the absence of any coupling with phosphorus-31 in $[(CH_3)_2Au(PPh_3)_2]ClO_4$ indicates that rapid exchange is taking place. The similarity of the chemical shifts for the three different complexes suggests that very similar species are present in the $CHCl_3$ solutions. Although one possibility is complete dissociation of the phosphine, arsine, and stibine ligands with coordination of the perchlorate ion, the vibrational spectra, as described below, do not indicate strong binding of the perchlorate. Chloroform was the only solvent found in which the solubilities were adequate, with no extensive displacement of the neutral ligands. As the solutions were cooled to $-30°$ with the complexes for which L = PPh_3 or $SbPh_3$, weak new signals appeared in addition to the main resonance at τ 9.14 ppm. With L = $AsPh_3$, an intense signal appeared at 8.57 ppm, and only a weak signal remained at τ 9.14 ppm.

The cation with the chelating 1,2-bis(diphenylphosphino)ethane does not undergo dissociation at 40°. The methyl protons of $[(CH_3)_2Au(PPh_2CH_2)_2]Cl$ give a single resonance in $CHCl_3$ solution which is split into a *ca.* 1:2:1 triplet by coupling with the two phosphorus atoms. The ligand methylene protons give a doublet centered at τ 6.71 ppm with a splitting of 17 Hz, similar to $Mo(CO)_4$diphos. The product obtained by the reaction of 1 mol of diphos with 1 mol of $[(CH_3)_2AuCl]_2$ shows the same triplet resonance as $[(CH_3)_2Au(PPh_2CH_2)_2]Cl$ in $CHCl_3$ solution plus another resonance at τ 8.87 ppm of comparable intensity to the cation methyl proton triplet. This signal corresponds closely to the value observed for $[Ph_4As][(CH_3)_2AuCl_2]$, τ 8.90 ppm.[13]

Raman and Infrared Spectra. As we have pointed out in other recent communications dealing with organogold(III)[18] and organoplatinum(IV)[10] compounds stabilized with ligands like py, PPh_3, $AsPh_3$, and $SbPh_3$, Raman spectra are of considerably more use than infrared for determiming the molecular structure. Because the infrared intensities of the (AuC_2) vibrations are too low to be measured with most dimethylgold(III) compounds and because the ligand bands are so complex, the infrared spectra are not reproduced. Most of the qualitative assignments were made first from the Raman data, and then this information made it possible to assign some of the infrared bands. Figure 1 illustrates Raman spectra for $[(CH_3)_2Au(SCN)py]$ and $[(CH_3)_2AuCl(py)]$, Figure 2 for $[(CH_3)_2Au(SCN)PPh_3$, $[(CH_3)_2AuClPPh_3]$, and $[(CH_3)_2Au(PPh_3)_2]ClO_4$, Figure 3 for $[(CH_3)_2Au(SCN)AsPh_3]$, $[(CH_3)_2AuClAsPh_3]$, and $[(CH_3)_2Au(AsPh_3)_2]ClO_4$, and Figure 4 for $[(CH_3)_2AuPPh_2(CH_2)_2]Cl$ and $[(CH_3)_2Au(PPh_2CH_2)_2][(CH_3)_2AuCl_2]$. Table III gives data for the (AuC_2) stretching frequencies, the symmetric methyl deformation frequencies, and other characteristic vibrations of all of the complexes synthesized. The vibrations of the coordinated PPh_3 and $AsPh_3$ are very consistent in these heavy-metal methyl derivatives, and this has been discussed earlier with respect to Au(III)[18] and Pt(IV)[10] compounds. The appearance of two (AuC_2) stretching vibrations of similar intensity in all of the compounds except $[(CH_3)_2Au(PPh_2CH_2)_2][(CH_3)_2AuCl_2]$, where the resolution was poorer, indicates that the cis isomers were obtained.

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(18) S. W. Krauhs, G. C. Stocco, and R. S. Tobias, *Inorg. Chem.*, 10, 1365 (1971).

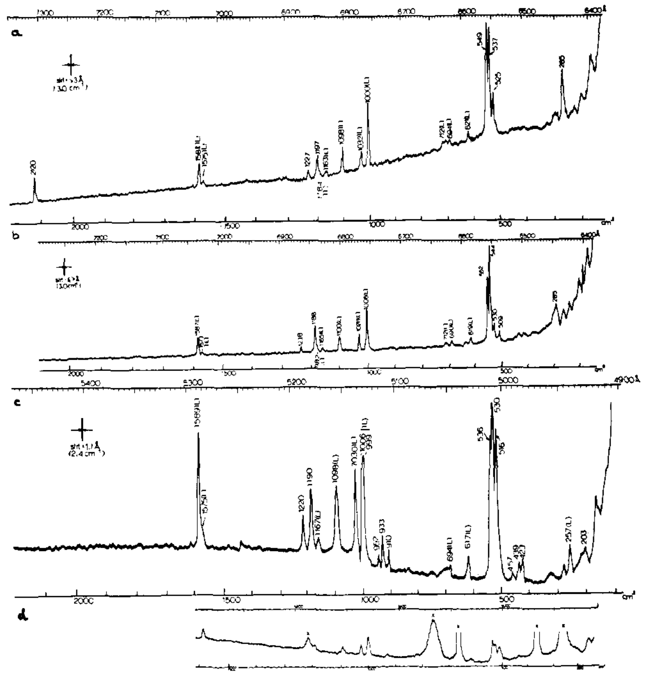

Figure 2. Laser-Raman spectra of crystalline (a) $[(CH_3)_2Au(SCN)PPh_3]$, He–Ne excitation, (b) $[(CH_3)_2AuClPPh_3]$, He–Ne excitation, (c) $[(CH_3)_2Au(PPh_3)_2]ClO_4$, Ar^+ excitation, (d) same compound in CS_2 solution, Ar^+ excitation, solvent bands marked with X. PPh_3 bands are marked with L.

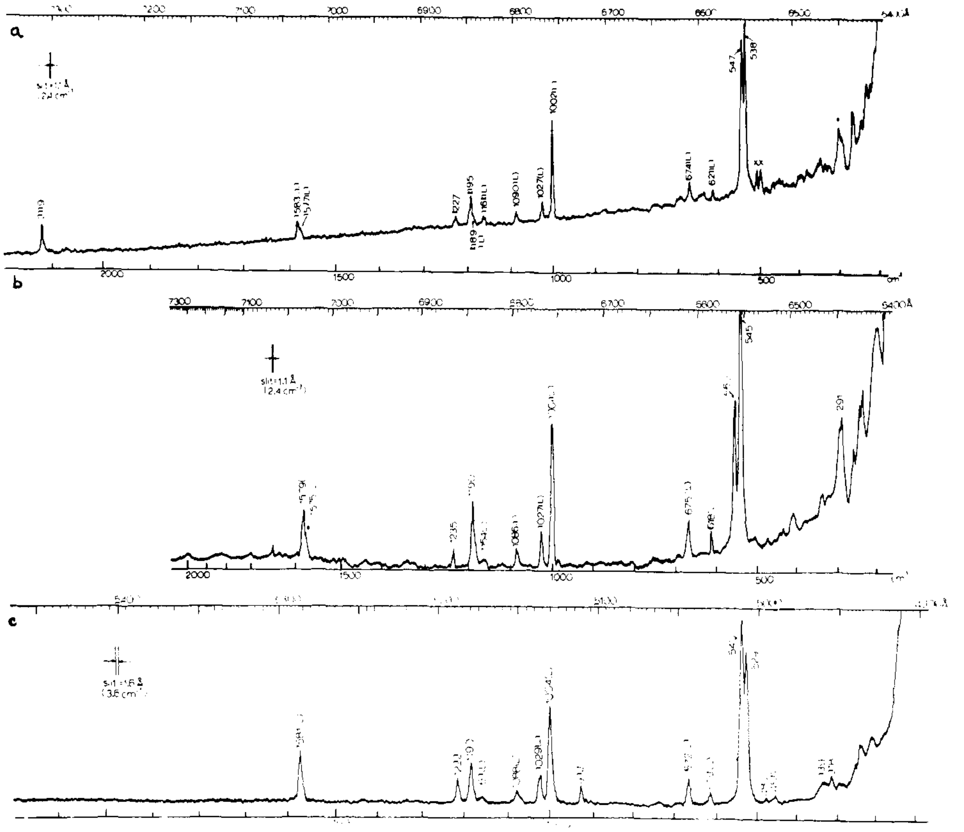

Figure 3. Laser-Raman spectra of crystalline (a) $[(CH_3)_2Au(SCN)AsPh_3]$, He–Ne excitation, (b) $[(CH_3)_2AuClAsPh_3]$, He–Ne excitation, (c) $[(CH_3)_2Au(AsPh_3)_2]ClO_4$, Ar^+ excitation. $AsPh_3$ bands are marked with L.

Crystalline $[(CH_3)_2Au(SCN)py]$ gives a Raman spectrum which is consistent with a monomeric complex which has a terminal, sulfur-bonded thiocyanate. By comparison, $[(CH_3)_2Au(SCN)(SC(NH_2)_2)]$ has $\nu_{C\equiv N} = 2217$ cm^{-1} in the Raman spectrum,[8] while this frequency is observed at 2123 cm^{-1} with $[(CH_3)_2Au(SCN)py]$. The bending mode δ_{NCS} was found at 430 for the thiourea complex, but the pyridine obscures this region. The ν_{AuC_2} values are 569 and 550 for py and 554 and 546 cm^{-1} for thiourea. The infrared spectrum of $[(CH_3)_2Au(SCN)py]$ shows the characteristic frequencies for coordinated pyridine,[19] as can be seen from the data in Table IV. For (C≡N) stretching, an intense band is observed at 2120 cm^{-1}, corresponding to the Raman band found at 2123 cm^{-1}. Raman and infrared spectra of solutions of this compound in $CHCl_3$ show the characteristic vibrations of $[(CH_3)_2AuNCS]_2$, especially the (C≡N) stretch, which appears as a broad band at 2156 cm^{-1}. Both the infrared and Raman spectra of $[(CH_3)_2Au(SCN)PPh_3]$ show only a single (C≡N) stretch at 2120 cm^{-1} again suggesting the presence of a terminal, sulfur-bonded thiocyanate. This compound shows, in addition to the intense (Au–C) stretches at 549 and 537 cm^{-1}, a medium band at 525 cm^{-1} which is coincident with an intense infrared band due to the PPh_3. The spectrum of $[(CH_3)_2Au(SCN)AsPh_3]$ is very similar, except only two bands are observed in the 500–550-cm^{-1} region.

The complex $[(CH_3)_2AuCl(py)]$ shows the two (Au–C) stretching frequencies at 583 and 562 cm^{-1}. An in-

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[19] See, for example, the discussion in K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," 2nd ed, Wiley, New York, N. Y., 1970, p 212.

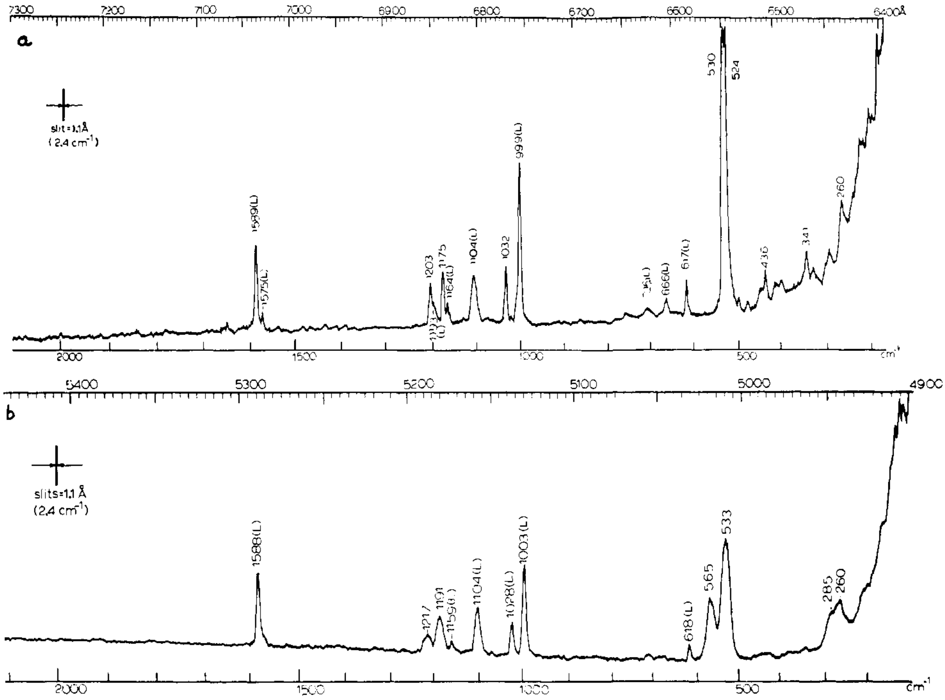

Figure 4. Laser-Raman spectra of crystalline (a) $[(CH_3)_2Au(diphos)]Cl$, He-Ne excitation, (b) $[(CH_3)_2Au(diphos)][(CH_3)_2AuCl_2]$, Ar^+ excitation. The diphos bands are marked with L.

tense band assigned to ν_{Au-Cl} is observed in the infrared spectrum at 277 cm^{-1} and in the Raman at 273 cm^{-1}. The two molecules $[(CH_3)_2AuClPPh_3]$ and $[(CH_3)_2AuClAsPh_3]$ are quite stable and give very similar infrared and Raman spectra. Each exhibits a single, intense Au–Cl stretching band at 285 (Raman, ir), 291 (Raman),

Table III. Infrared and Laser-Raman Spectra of Dimethylgold(III) Compounds

Compound	ν_{Au-C_2}, cm^{-1} Raman	Ir	δ_{s,CH_3}, cm^{-1} Raman	Ir	Other vibrations, cm^{-1} Raman	Ir	Assignment
$[(CH_3)_2Au(SCN)py]_s$[e]	569 vs	570 w	1205 w	1210 w	2123 m	2120 vs	$\nu_{C\equiv N}$
	550 vs	553 w	1198 w	1197 m			
$[(CH_3)_2Au(SCN)PPh_3]_s$[e]	549 vs		1227 w	1226 w	2120 m	2120 vs	$\nu_{C\equiv N}$
	537 vs	*b*	1197 m	1192 w			
$[(CH_3)_2Au(SCN)AsPh_3]_s$[e]	547 vs		1227 w	1126 m	2119 m	2120 vs	$\nu_{C\equiv N}$
	538 vs	540	1195 m	1195 m			
$[(CH_3)_2AuCl(py)]_s$[e]	583 vs	*a*	1237 w, bd	1235 w			
	562 vs		1197 m	1194 m	273 s	277 vs	ν_{Au-Cl}
$[(CH_3)_2AuClPPh]_3$[e]	552 vs	*b*	1238 w	1236 w	285 m	285 vs	ν_{Au-Cl}
	544 vs		1188 m	1185 m			
$[(CH_3)_2AuClAsPh_3]_s$[e]	560 vs		1235 w	1235 w	291 m	290 s	ν_{Au-Cl}
	545 vs	546 vw	1190 m	1190 m			
$[(CH_3)_2Au(PPh_3)_2]ClO_{4s}$[e,f]	536 vs	539 m	1220 s	1223 m	952 w, 933 m,		
					910 w		$\nu_1(ClO_4)$
	530 vs	530 m	1190 m	1190 s		1092 vvs, vbd,	$\nu_3(ClO_4)$
						625 m	$\nu_4(ClO_4)$
$CHCl_3$[e,f]	536 s		*h*	*g*	932 w		$\nu_1(ClO_4)$
Solution	528 s	*b*	1194 m	*g*		1100 vs, vbd	$\nu_3(ClO_4)$
						628 m	$\nu_4(ClO_4)$
$[(CH_3)_2Au(AsPh_3)_2]ClO_{4s}$[e,f]	540 vs	543 vw	1222 m	1221 w	932 w		$\nu_1(ClO_4)$
	529 vs	532 vw	1190 m	1188 m	456 w		$\nu_2(ClO_4)$
						1090, 1077 ws	$\nu_3(ClO_4)$
					619 w[i]	624 s	$\nu_4(ClO_4)$
$[(CH_3)_2Au(Ph_2CH_2)_2]Cl_s$[e]	530 vs	*d*	1203 m	1204 w			
	524 vs		1175 m	1175 m			
$[(CH_3)_2Au(Ph_2CH_2)_2]^+$	533 vs	*d*	1217 bd	1220 w, bd			
			1191 bd	1186, m, bd			
$[(CH_3)_2AuCl_2]^-{}_s$[e,f]	565 vs	*d*			285 m	280 s	$\nu_s(AuCl_2)$
					260 m	268 s	$\nu_{as}(AuCl_2)$

[a] Obscured by pyridine vibrations. [b] Obscured by PPh_3. [c] Intensity too low to be measured. [d] Obscured by diphos ligand. [e] He-Ne excitation. [f] Ar^+ (4880 Å) excitation. [g] Obscured by $CHCl_3$ solvent. [h] Superimposed on solvent band. [i] Coincident with ligand band.

Table IV. Metal-Sensitive Ligand Vibrations from Infrared and Laser-Raman Spectra of the Crystalline Compounds

Raman	Ir[a]	Raman	Ir	Raman	Ir	Raman	Ir
Pyridine		$[(CH_3)_2Au(SCN)py]$[e]		$[(CH_3)_2AuCl(py)]$[e]			
1033 s	1033 s	1051 vw	1047	1050 vw	1046		
994 s	993 s	1019 s	1019	1020 s	1016		
606 w	604 s	649 w	645 s	651 w	643 m		
	405 s		435 m		438 w		
PPh_3[b]		$[(CH_3)_2Au(SCN)PPh_3]$[e]		$[(CH_3)_2AuClPPh_3$[e]$]$		$[(CH_3)_2Au(PPh_3)_2]ClO_4$[e,f]	
1096 s	1091 m	1098 m	1100, 1097 s	1100 m	1101 vs	1107	*d*
698 w		712, 694 w		712, 690 w		702, 694 bd	
500 w	514, 499, 491 s	525 m	525, 514, 495 vs	530, 509 w	530, 509, 496, vs	516, vs, 509 w, sh	516, 508, 496 vs
	433 m		449 m		456 m		454 w
	423 m		430 m		435 m		424 w
$AsPh_3$[c]		$(CH_3)_2Au(SCN)AsPh_3$[e]		$[(CH_3)_2AuClAsPh_3]$[e]		$[(CH_3)_2Au(AsPh_3)_2]ClO_4$[e,f]	
1079 s	1086 w, 1077 s, 1069 m	1090 w	1077 m	1086	1080 m	1088 w	*d*
312 m	315 s		345 w, 335 m, 325 m	337, 327 w, bd	332 s	339, 318, 291 w	350, 339, 331, 320 s
236 m	242 sh			236 m		243	

[a] The ligand vibrations are discussed in ref 19. [b] Ligand vibrations are discussed in ref 20. [c] Ligand vibrations are discussed in ref 21. [d] Obscured by ν_3 of ClO_4. [e] He–Ne excitation. [f] Ar^+ (4880 Å) excitation.

and 290 (ir), respectively. Both show the two ($Au-C_2$) stretches in the Raman spectra expected for cis methyl groups at 552, 544 and 560, 545 cm^{-1}, respectively.

Five of the complexes contain cationic gold species. The perchlorate vibrations of crystalline $[(CH_3)_2Au(PPh_3)_2]ClO_4$, $[(CH_3)_2Au(AsPh_3)_2]ClO_4$, and $[(CH_3)_2Au(SbPh_3)_2]ClO_4$ indicate that there is only a slight perturbation of the tetrahedral ion. In the infrared spectra, the triply degenerate vibration ν_3 appears as a very intense broad band at 1092 cm^{-1} with L = PPh_3, as an intense doublet 1090, 1077 cm^{-1} with L = $AsPh_3$, and as a doublet 1097, 1082 cm^{-1} with L = $SbPh_3$. The Ar^+-excited Raman spectrum of $[(CH_3)_2Au(PPh_3)_2]ClO_4$ shows three bands in the perchlorate ν_1 region at 952, 933, and 910 cm^{-1}, suggesting that the anions sit in different environments. This may also result in part from Fermi resonance between ν_1 and $2\nu_2$. Both Raman and infrared spectra were run on $[(CH_3)_2Au(PPh_3)_2]ClO_4$ dissolved in $CHCl_3$, and there are no significant changes in the spectra upon dissolution of the compound. The compound used for the Raman spectrum was isolated from solution and resubmitted for analysis. There was no change in composition.

The metal-sensitive ligand vibrations of PPh_3 and $AsPh_3$ are very similar in these bis complexes to those of the $[(CH_3)_2AuClL]$ molecules, indicating that the tertiary phosphine and arsine molecules are bound to gold. The vibrations of PPh_3 have been discussed by Deacon and Green.[20] Green, *et al.*,[21] have presented similar data for $AsPh_3$. The ($Au-C_2$) stretches of the bis PPh_3 and $AsPh_3$ cations shift to lower frequencies than found for any of the other complexes studied, indicating that both ligands are coordinated. These very intense bands were the same in the Raman spectra of the crystalline sample and the $CHCl_3$ solution.

The intensities of these cations are rather different from any of the $[(CH_3)_2AuX]_2$ or $[(CH_3)_2AuXL]$ molecules which have been studied. First, the ($Au-C_2$) stretches are moderately intense in the infrared, which is unusual. Secondly, the triphenylphosphine vibrations at *ca.* 500 cm^{-1} have rather high Raman intensity. In the other compounds, these have very high infrared and low Raman intensities. Thus there is an unusually intense band at 516 and a weaker one at 509 cm^{-1} in the Raman spectrum of $[(CH_3)_2Au(PPh_3)_2]ClO_4$, and these correspond exactly to the intense ligand infrared bands. These particular PPh_3 vibrations are assigned to ($C-P$) stretching.[18] It has been observed[22] in a series of five dimethylgold compounds that as the lowest frequency ($Au-C_2$) stretch drops below 545 cm^{-1}, Raman bands appear which correspond exactly in frequency to the very intense infrared bands assigned to ($P-C_3$) stretching vibrations. The closer the ($Au-C_2$) frequency approaches to the ($P-C_3$) frequencies, the greater the relative intensity of these new Raman bands. Consequently, it seems likely that there is mixing of these coordinates in the normal modes. A similar but much less pronounced effect is observed with $[(CH_3)_2Au(SCN)PPh_3]$. Because of thermal instability, no Raman spectrum could be recorded for $[(CH_3)_2Au(SbPh_3)_2]ClO_4$.

The Raman spectrum of $[(CH_3)_2Au(PPh_2CH_2)_2]Cl$ exhibits two ($Au-C_2$) stretches at 530 and 524 cm^{-1} similar to the two (AuC_2) stretching bands of $[(CH_3)_2Au(PPh_3)_2]ClO_4$ and two symmetric methyl deformations at 1203 and 1174 cm^{-1} as would be expected for the chelate complex. Neither the infrared nor the Raman spectrum shows any band attributable to an ($Au-Cl$) stretching vibration consistent with the ionic formulation.

The product of the 1:1 reaction of $[(CH_3)_2AuCl]_2$ and 1,2-bis(diphenylphosphino)ethane gave a poorer quality He-Ne Raman spectrum, and it was necessary to use 10-cm^{-1} slits to record it. A much better spectrum was obtained with Ar^+ excitation (2.5-cm^{-1} slits). Two ($Au-C$) stretching bands were observed. The one at 531 cm^{-1} is assigned to the $[(CH_3)_2Au(PPh_2CH_2)]^+$ cation and would appear to include both of the bands observed under high resolution at 530 and 524 cm^{-1} with $[(CH_3)_2Au(PPh_2CH_2)_2]Cl$. The other band at 564 cm^{-1} is assigned to the anion $[(CH_3)_2AuCl_2]^-$, ν_{AuC_2} of $[AsPh_4][(CH_3)_2AuCl_2]$ = 572 cm^{-1}.[12] The pres-

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(20) G. B. Deacon and J. H. S. Green, *Spectrochim. Acta, Part A*, **24**, 845 (1968).

(21) J. H. S. Green, W. Kynaston, and G. A. Rodley, *ibid.*, *Part A*, **24**, 853 (1968).

(22) G. C. Stocco and R. S. Tobias, *Inorg. Chem.*, submitted for publication.

ence of two $AuCl_2$ stretches [280, 268 (ir) and 285, 260 (Raman)] confirms the ionic formulation, since these vibrations were observed with $Ph_4As[(CH_3)_2AuCl_2]$ at 281 and 268 cm^{-1} in the infrared.[13]

Discussion

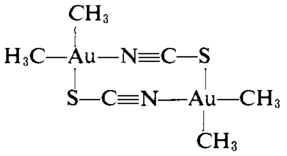
Many organogold(III) complexes exchange ligands other than the organo groups rapidly. With the dimethyl derivatives, this is true for halide, pseudohalide, and nitrogen-base ligands. In contrast, the complexes with phosphine or arsine ligands are considerably more inert.

Halide exchange, reaction 1, occurs rapidly, and in

$$[(CH_3)_2AuCl]_2 + [(CH_3)_2AuI]_2 \rightleftharpoons 2[((CH_3)_2Au)_2ClI] \qquad (1)$$

chloroform solution exchange occurs between all species at room temperature. This behavior is very similar to that of the methylmercury(II) halides.[23–25] With the dimethylgold(III) halides, we assume that bridge dissociation occurs, while it is generally presumed that a bridged structure is an intermediate in the exchange of the organomercury halides.

The rather appreciable value of the equilibrium constant for the formation of the mixed dimer has precedent in the corresponding reaction between methylallylpalladium(II) chloride and iodide dimers in $CHCl_3$–CH_2Cl_2 solution.[26] For that reaction, the equilibrium constant was estimated to be 1.0. Clearly the $[(CH_3)_2AuX]_2$ and $[CH_3C_3H_4PdX]_2$ systems are much alike. The main difference appears to be that the gold compounds undergo exchange somewhat more slowly. For example, $[(CH_3)_2AuNCS]_2$ (I)[8] shows unbroadened pmr signals for the two kinds of methyl protons at 40°, while $[(CH_3C_3H_4)PdNCS]_2$ shows line broadening above −60°, as a result of a bimolecular process which makes the allyl protons equivalent.[23]



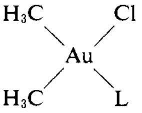
I

Most bases, L, cleave the dimethylgold(III) halides and pseudohalides according to reaction 2. Again

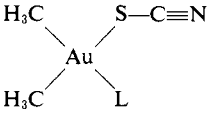
$$[(CH_3)_2AuX]_2 + 2L \rightleftharpoons 2[(CH_3)_2AuXL] \qquad (2)$$

the dimethylgold(III) compounds behave very much like the allylpalladium(II) analogs.[27] The reactions and exchange processes observed with the nmr spectra appear to be very similar to those of allylpalladium compounds.[25–35]

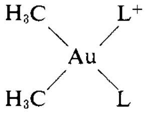
Gibson and Simonsen first described an organogold compound of this type, $[(C_2H_5)_2AuBr(py)]$.[36] It was reported to be colorless when first prepared but to decompose rapidly upon exposure to light. In comparison, $[(CH_3)_2AuCl(py)]$ seems to be more stable, and $[(CH_3)_2AuClPPh_3]$ and $[(CH_3)_2AuClAsPh_3]$ are very much more so. A related compound, *cis*-$[(C_6F_5)_2AuClPPh_3]$, has been prepared recently[37] and the structure determined.[38] The synthesis of $[(CH_3)_2AuBrPPh_3]$ by reaction of $(CH_3)_3AuPPh_3$ and Br_2 also has been described.[39] The complex $[(CH_3)_2AuClSbPh_3]$ was found to be very unstable thermally. The structures assigned to the new square planar gold complexes are illustrated as II–V.



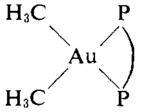
II



III



IV



V

At room temperature, $[(CH_3)_2AuCl(py)]$ gives broadened methyl proton resonances because of an exchange process (3), presumably involving dissociation of pyri-

$$[(CH_3)_2AuCl(py)] \rightleftharpoons [(CH_3)_2AuCl] + py \qquad (3)$$

dine. The addition of pyridine lowers the coalescence temperature, and the exchange rate is first order in pyridine. This process (4) may involve as an inter-

$$[(CH_3)_2AuCl(py^*)] + py \rightleftharpoons [(CH_3)_2AuCl(py)] + py^* \qquad (4)$$

mediate a symmetric, five-coordinate $[(CH_3)_2AuCl(py)_2]$ or an ion pair, $[(CH_3)_2Au(py)_2]Cl$. The low-temperature spectra show no indication of appreciable concentrations of these intermediates.

The displacement of coordinated pyridine by triphenylphosphine, reaction 5, is rapid and quantita-

$$[(CH_3)_2AuCl(py)] + PPh_3 \rightleftharpoons [(CH_3)_2AuClPPh_3] + py \qquad (5)$$

tive. The PPh_3, $AsPh_3$, and $SbPh_3$ complexes, structure II, do not exhibit exchange at room temperature on the nmr time scale, although the addition of excess ligand leads to line broadening. The Au–N bond appears to be substantially weaker in these organogold compounds than the bonds to the heavier group V donors. Very similar exchange processes are observed for the π-allylpalladium(II) chloride complexes with PPh_3, $AsPh_3$, and $SbPh_3$, although these sometimes have been described as "rotations" of the π-allyl ligand, π–σ conversions, etc. Tibbetts and Brown[35] have summarized the possibilities. Again the dimethylgold(III) complexes undergo exchange at a considerably slower rate.

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Similar to the $[(CH_3)_2AuClL]$ compounds, $[(CH_3)_2Au(SCN)py]$ obtained by reaction 6 undergoes rapid exchange at room temperature, while $[(CH_3)_2Au(SCN)PPh_3]$ does not. The appearance of signals characteristic of $[(CH_3)_2AuNCS]_2$ at low temperature when L = py supports the Raman and infrared evidence for some dissociation of pyridine in solution. The triphenylarsine derivative undergoes rapid exchange of the nonequivalent methyl proton sites at 40°. Allylpalladium(II) complexes with triphenylarsine also were found to undergo more rapid exchange than their triphenylphine counterparts.[33] This was attributed to the lower Pd–As bond energy compared to the energy of the Pd–P bond.

$$[(CH_3)_2AuNCS]_2 + 2L \rightleftharpoons 2[(CH_3)_2Au(SCN)L] \qquad (6)$$

Although Gent and Gibson[9] were incorrect in believing that nitrogen bases would not cleave the binuclear thiocyanate, it is true that the $[(CH_3)_2Au(SCN)L]$ complexes are appreciably less stable than the $[(CH_3)_2AuClL]$ analogs. Reaction 6 probably provides one mechanism for the exchange of the nonequivalent methyl proton sites which was observed to be faster with the thiocyanate than with the analogous chloride complexes.

The ionic compounds $[(CH_3)_2Au(PPh_3)_2]ClO_4$, $[(CH_3)_2Au(AsPh_3)_2]ClO_4$, $[(CH_3)_2Au(PPh_2CH_2)_2]Cl$, and $[(CH_3)_2Au(PPh_2CH_2)][(CH_3)_2AuCl_2]$ all gave conductivities typical of 1:1 electrolytes; *cf.* the molar conductivity of $[Au(dipy)Cl_2]ClO_4$ at 25° in nitrobenzene solution = 33.7 ohm^{-1} cm^{-1}.[40] This is consistent with the vibrational spectra which indicated ionic structures in the crystalline state.

The bis(phosphine) complex undergoes a rapid dissociation (7) in solution as indicated by the collapse of the ^{31}P–proton coupling. Undoubtedly the bis(arsine) and bis(stibine) complexes behave similarly. The molecule $[(CH_3)_2Pt(PPh_3)_2]$ which is isoelectronic with $[(CH_3)_2Au(PPh_3)_2]^+$ does not show any exchange broadening at room temperature in $CDCl_3$–CH_2Cl_2 solution and gives an $AA'MX_3X_3'$ type of nmr spectrum.[41] The other platinum analogs also have been prepared recently.[42] The three complexes $[(CH_3)_2Au(PPh_3)_2]ClO_4$, $[(CH_3)_2Au(AsPh_3)_2]ClO_4$, and $[(CH_3)_2Au(SbPh_3)_2]ClO_4$ all have the same methyl proton chemical shifts at 40°, although they differ at low temperature. In the case of the bis(phosphine) complex, solution Raman and infrared spectra were obtained and were found to be the same as for the crystalline compound. In particular, the intensely infrared-active triply degenerate perchlorate vibrational frequencies were not altered, which tends to exclude a strong ion pair with perchlorate in the first coordination sphere formed by dissociation of the phosphine, arsine, and stibine in solution. The phenyl proton resonance signal for $[(CH_3)_2Au(PPh_3)_2]ClO_4$ in $CHCl_3$ solution was shifted *ca.* 0.27 ppm downfield from the resonance of PPh_3, also ruling out complete dissociation of the phosphine.

$$[(CH_3)_2Au(PPh_3)_2]ClO_4 \rightleftharpoons [(CH_3)_2AuPPh_3]ClO_4 + PPh_3 \qquad (7)$$

The cation with the chelating diphos ligand, on the other hand, gives an nmr spectrum which is very similar to the isoelectronic $[(CH_3)_2Pt(diphos)]$.[43] The methyl proton resonances are split into triplets in both cases, with $^3J_{^{31}P-H} = 7.4$ Hz for both the platinum and gold complexes. In this case, two gold–phosphine bonds would have to be broken to uncouple the ^{31}P and ^1H spins, and this would account for the difference in behavior compared to $[(CH_3)_2Au(PPh_3)_2]^+$.

In summary, it is clear that the reactions of these dimethylgold(III) compounds are very similar to those of the allylpalladium(II) analogs. The main difference appears to be that the gold compounds react somewhat more slowly. The complexes with tertiary phosphine ligands are particularly stable. In comparison with the isoelectronic platinum(II) complexes, the gold(III) complexes with tertiary phosphines and arsines dissociate more readily.

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