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# Dimethylgold(III) Pseudohalides and Their Reactions with Triphenylphosphine and Triphenylarsine[1]

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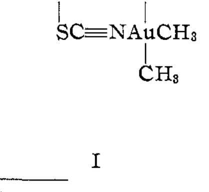
The new dimethylgold pseudohalides $[(CH_3)_2AuNCSe]_2$ and $[(CH_3)_2AuNCO]_2$ have been synthesized and found to be dimeric from molecular weight measurements. The selenocyanate is assigned a centric $C_{2h}$ structure analogous to that of $[(CH_3)_2AuNCS]_2$ on the basis of laser Raman, infrared, and proton magnetic resonance spectra. On similar grounds, the cyanate is assigned a nitrogen-bridged $D_{2h}$ structure which is closely related to that of $[(CH_3)_2AuN_3]_2$. For comparison, the Raman spectrum of KNCO was determined. Dimethylgold cyanide is tetrameric in solution as are the diethyl and di-*n*-propyl derivatives which have long been known. The proton resonance spectra are inconsistent with the simple $C_{4h}$ skeletal structure which is generally accepted, and it is suggested that the cyanides are disordered in some of the molecules. All three compounds undergo bridge-splitting reactions with bases, and the cis complexes $(CH_3)_2Au(NCO)P(C_6H_5)_3$, $(CH_3)_2Au(NCO)As(C_6H_5)_3$, and $(CH_3)_2Au(CN)P(C_6H_5)_3$ have been isolated and characterized. The selenocyanate reacts quantitatively with $P(C_6H_5)_3$ in solution to yield *cis*-$(CH_3)_2Au(SeCN)P(C_6H_5)_3$, but a pure product could not be isolated. The reactions of the dimethylgold halides and pseudohalides are summarized and compared with those of the related $\pi$-allylpalladium(II) and dicarbonylrhodium(I) compounds.

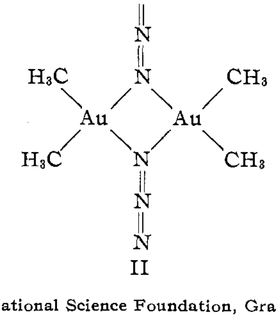
## Introduction

In a previous communication,[4] the synthesis of dimethylgold thiocyanate was reported, and the compound was assigned a centric $C_{2h}$ structure, I, on the basis of molecular weight data; Raman, infrared, and proton magnetic resonance spectra; and its reaction with thiourea.

Dimethylgold azide,[5] which also is dimeric, was assigned $D_{2h}$ symmetry, II, on the basis of its infrared and proton magnetic resonance spectra. The bridge using only one nitrogen of each azide ion is assigned by analogy with the known structure of the azide-bridged palladium(II) complex $[As(C_6H_5)_4]_2[Pd_2(N_3)_6]$ which has been studied by X-ray diffraction.[6]

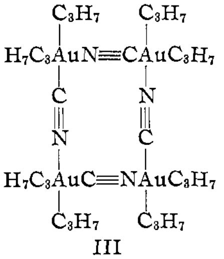


I



II

Dialkylgold cyanides have been known for many years, and the diethyl and di-*n*-propyl compounds were found to be tetrameric by cryoscopy in bromoform.[7] On the basis of an early X-ray study[8] which determined the gold positions, the centric structure III with a fourfold axis normally is written, although there was no experimental evidence for this. In fact, the dipole moment was determined to be 1.47 D.[9]



III

In order to investigate additional compounds where a pseudohalide ion is forced to bridge two atoms, we have synthesized dimethylgold(III) cyanate and selenocyanate. Dimethylgold cyanide also was prepared for comparison.

In a recent communication,[10] it was reported that the chloro bridges of $[(CH_3)_2AuCl]_2$ and the thiocyanato bridges of I could be cleaved readily with pyridine, tertiary phosphines, and tertiary arsines. Analogous

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[1] Supported, in part, by the National Science Foundation, Grants GP-15083 and -23208.

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[4] W. M. Scovell, G. C. Stocco, and R. S. Tobias, *Inorg. Chem.*, **9**, 2682 (1970).

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

[6] W. P. Fehlhammer and L. F. Dahl, *J. Amer. Chem. Soc.*, in press.

[7] A. Buraway, C. S. Gibson, and S. Holt, *J. Chem. Soc.*, 1024 (1935).

[8] R. F. Phillips and H. M. Powell, *Proc. Roy. Soc., Ser. A*, **173**, 147 (1939).

[9] A. Buraway, C. S. Gibson, G. C. Hampson, and H. M. Powell, *J. Chem. Soc.*, 1690 (1937).

[10] G. C. Stocco and R. S. Tobias, *J. Amer. Chem. Soc.*, **93**, 5057 (1971).

bridge-splitting reactions have been examined with the cyanate, selenocyanate, and cyanide.

## Experimental Section

**General Data.**—The starting material for the preparation of the organogold compounds, di-$\mu$-iodo-tetramethyldigold(III), was synthesized by the method of Brain and Gibson.[11] All preparations were carried out under an atmosphere of nitrogen. Molecular weights were determined by osmometry in the Purdue Microanalytical Laboratory or with a Hewlett-Packard Model 302 osmometer. Elemental analyses were performed by this department or by Schwarzkopf Microanalytical Laboratory. Melting points were determined with a Thomas-Hoover capillary melting point apparatus. Chloroform used as an nmr solvent was distilled from sulfuric acid just prior to use.

**Dimethylgold Cyanate, Dimethylgold Selenocyanate, and Dimethylgold Cyanide.**—These three compounds were synthesized by a procedure similar to that employed by Scovell, *et al.*,[4] for $[(CH_3)_2AuNCS]_2$. For the cyanate, $[(CH_3)_2AuI]_2$ (0.713 g, 0.002 monomol) (monomol refers to moles computed on the basis of the monomer weight) was dissolved in 20 ml of petroleum ether (bp 30–60°) and allowed to react under continuous stirring with a slight excess of $AgNO_3$ in 30 ml of water. The petroleum ether was evaporated in a stream of nitrogen, the AgI was removed by filtration, and the colorless aqueous solution was cooled to 0°. The stoichiometric quantity of KNCO (KNCSe, KCN) dissolved in 5 ml of water was added, and the white precipitate which resulted was collected on a frit, washed with water and methanol, and dried under vacuum over $P_4O_{10}$. Recrystallization from cyclopentane gave long colorless needles. Data for the **cyanate** are as follows: mp 75° dec; mol wt found (benzene), 549; mol wt calcd for $[(CH_3)_2AuNCO]_2$, 538. *Anal.* Calcd for $C_3H_6NOAu$: C, 13.4; H, 2.38; N, 5.20; Au, 73.2. Found: C, 13.2; H, 2.32; N, 4.99; Au, 73.1. Data for the **selenocyanate** are as follows: mp 92° dec; mol wt found (benzene), 625; mol wt calcd for $[(CH_3)_2AuNCSe]_2$, 664. *Anal.* Calcd for $C_3H_6NSeAu$: C, 10.8; H, 1.82; N, 4.21; Au, 59.3. Found: C, 11.0; H, 1.74; N, 4.29; Au, 59.1. Data for the **cyanide** follow. *Caution! This compound is very shock sensitive and explodes readily.* It was synthesized from both $[(CH_3)_2AuI]_2$ and $[(CH_3)_2AuCl]_2$.[4] In some cases, to minimize the explosion hazard, the product was extracted from the aqueous phase with $CCl_4$. Slow evaporation of the $CCl_4$ gave well-defined crystals which were much less shock sensitive than the compound precipitated from aqueous solution. Recrystallization was from $CHCl_3$; mp 140° dec; mol wt found (benzene) 1030, ($CCl_4$) 1060; mol wt calcd for $[(CH_3)AuCN]_4$, 1013. *Anal.* Calcd for $C_3H_6NAu$: C, 14.2; H, 2.59; N, 5.53; Au, 77.9. Found: C, 14.5; H, 2.59; N, 5.67; Au, 77.6.

**Isocyanatotriphenylphosphinedimethylgold(III), Cyanotriphenylphosphinedimethylgold(III), and Isocyanatotriphenylarsinedimethylgold(III).**—These compounds were synthesized by a procedure similar to that employed in the bridge-splitting reactions of $[(CH_3)_2AuCl]_2$ and $[(CH_3)_2AuNCS]_2$.[10] To a solution of $[(CH_3)_2AuNCO]_2$ (0.485 g, 0.7 × $10^{-3}$ monomol) dissolved in 5 ml of cyclopentane was added the stoichiometric amount of $P(C_6H_5)_3$ dissolved in the minimum volume of anhydrous ether (3 ml). The white, crystalline precipitate which appeared immediately was collected on a frit, washed with anhydrous ether, and stored under vacuum over $P_4O_{10}$. Data for $\mathbf{(CH_3)_2Au(NCO)P(C_6H_5)_3}$ are as follows: mp 135–136° dec. *Anal.* Calcd for $C_{21}H_{21}NOPAu$: C, 47.4; H, 3.98; N, 2.63; P, 5.84; Au, 37.1. Found: C, 47.2; H, 4.13; N, 2.84; P, 5.59; Au, 37.0. For $\mathbf{(CH_3)_2Au(CN)P(C_6H_5)_3}$, the same procedure was used taking $[(CH_3)_2AuCN]_4$ (0.088 g, 0.34 × $10^{-3}$ monomol) in 8 ml of cyclopentane and allowing it to react with the stoichiometric amount of $P(C_6H_5)_3$ in 5 ml of ether; mp 155–158° dec. *Anal.* Calcd for $C_{21}H_{21}NPAu$: C, 48.8; H, 4.10; N, 2.72; P, 6.02; Au, 38.2. Found: C, 49.0; H, 4.46; N, 2.65; P, 6.00; Au, 38.6. For $\mathbf{(CH_3)_2Au(NCO)As(C_6H_5)_3}$, to a solution of $[(CH_3)_2AuNCO]_2$ (0.138 g, 0.51 × $10^{-3}$ monomol) in 8 ml of cyclopentane was added the stoichiometric amount of $As(C_6H_5)_3$ dissolved in anhydrous ether. The solution was concentrated in a stream of nitrogen. The white crystals which formed were collected on a frit, washed with ether and cyclopentane, and dried under vacuum over $P_4O_{10}$; mp 100–101°. *Anal.* Calcd for $C_{21}H_{21}NOAsAu$: C, 43.8; H, 3.65; N, 2.43; Au, 34.3. Found: C, 44.1; H, 3.78; N, 2.49; Au, 34.4.

**Raman Spectra.**—These were obtained with an instrument built around a Spex Model 1400 double monochromator. A Spectra Physics Model 112 He–Ne laser (6328 Å) or a Coherent Radiation Model 52 $Ar^+$ laser (4880 Å) was used to excite the spectra. The signal from a cooled EMI 9558 A photomultiplier (−25°, Products for Research thermoelectric cooler) was detected with Canberra pulse-counting equipment. Calibration was effected with the laser lines, background plasma lines, $CCl_4$, and neat indene. Spectra were run with the samples sealed in melting point capillaries using the transillumination technique. The Raman shifts are the differences between the exciting frequency and the scattered frequencies each corrected to vacuum at 15°, and for sharp lines they are accurate to ±2 $cm^{-1}$.

**Infrared Spectra.**—These were recorded with a Beckman IR-12 spectrometer using the split Nujol–Halocarbon mull technique. Instrument calibration was effected with polystyrene film and neat indene. The frequencies of sharp bands are accurate to ±2 $cm^{-1}$, while those for broad bands should be within 5 $cm^{-1}$.

**Proton Magnetic Resonance Spectra.**—Spectra were recorded with Varian A-60 (40°), A-60D (40°), and XL-100 (35°) spectrometers (probe temperatures in parentheses). Coupling constants are believed to be accurate to ±0.5 Hz and chemical shifts to 0.01 ppm. In some cases, the signal to noise ratio was enhanced for dilute solutions with a Varian C1024 CAT. An internal TMS reference was used in all cases. Signals were integrated with a Gelman planimeter. Errors were estimated from four integrations.

## Data and Results

**Proton Magnetic Resonance Spectra.**—The chemical shifts and coupling constants for these compounds are collected in Table I. The cyanate gave a single, sharp resonance at 40° comparable in line width to the TMS reference, and this was unchanged upon cooling the solution to −15°. The selenocyanate spectrum exhibited two methyl resonances at almost the same $\tau$ values as

TABLE I

PROTON MAGNETIC RESONANCE DATA ON DIMETHYLGOLD PSEUDOHALIDE COMPOUNDS

| Compound | Solvent | $\tau$,[a] ppm [$^2J(^{31}P\text{–}H)$, Hz] |
|---|---|---|
| $[(CH_3)_2Au(NCS)]_2$ | $CHCl_3$ | 9.05 (1)[b] |
| | | 8.70 (1) |
| $(CH_3)_2Au(SCN)P(C_6H_5)_3$ | $CDCl_3$ | 8.94 (1) [8.8][c] |
| | | 8.57 (1) [8.1] |
| $[(CH_3)_2Au(NCSe)]_2$ | $CDCl_3$ | 9.07 (1) |
| | | 8.67 (1) |
| | $C_6H_6$ | 9.43 (1) |
| | | 9.00 (1) |
| $(CH_3)_2Au(SeCN)P(C_6H_5)_3$[e] | $CDCl_3$ | 8.90 (1) [8.6] |
| | | 8.57 (1) [8.4] |
| $[(CH_3)_2Au(NCO)]_2$ | $CCl_4$ | 8.85 |
| $(CH_3)_2Au(NCO)P(C_6H_5)_3$ | $CDCl_3$ | 9.28 (1) [8.8] |
| | | 8.71 (1) [9.3] |
| $(CH_3)_2Au(NCO)As(C_6H_5)_3$ | $CDCl_3$ | 9.19 (1) |
| | | 8.57 (1) |
| $[(CH_3)_2Au(N_3)]_2$ | $CDCl_3$ | 8.8[d] |
| $[(CH_3)_2Au(CN)]_4$ | $CDCl_3$, $CHCl_3$[f,g] | 9.17 (1.3 ± 0.1) |
| | | 9.09 (2.8 ± 0.2) |
| | | 8.93 (3.0 ± 0.2) |
| | | 8.85 (1 ± 0.04) |
| | $CCl_4$ | 9.18 (0.7 ± 0.2) |
| | | 9.11 (2.2 ± 0.2) |
| | | 8.97 (2.2 ± 0.2) |
| | | 8.88 (1 ± 0.03) |
| | $CS_2$ | 9.20 (1.2 ± 0.1) |
| | | 9.13 (2.8 ± 0.2) |
| | | 8.95 (2.9 ± 0.2) |
| | | 8.88 (1 ± 0.03) |
| $(CH_3)_2Au(CN)P(C_6H_5)_3$ | $CDCl_3$[f] | 9.48 (1) [8.7] |
| | | 8.55 (1) [8.9] |
| | $CCl_4$ | 9.62 (1) [9] |
| | | 8.58 (1) [9] |

[a] Relative intensities within parentheses. [b] Reference 4. [c] Reference 10. [d] Reference 5. [e] Prepared *in situ*. [f] Examined at both 60 and 100 MHz. [g] The 60-MHz $CHCl_3$ spectrum was improved by accumulating 15 scans with the CAT.

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[11] F. H. Brain and C. S. Gibson, *J. Chem. Soc.*, 762 (1939).

the thiocyanate.[4] These signals were significantly broader than the TMS reference (full width at half-intensity 2.5 Hz). Spectra of solutions of a number of different samples of the cyanide in $CDCl_3$, $CCl_4$, and $CS_2$ all exhibited *ca.* 1:3:3:1 quartets, and these are illustrated in Figure 1. They were recorded at both 60 and 100 MHz. Spectra obtained at −15, −5, and +35° were essentially identical. At 47°, the two outer components of the quartet had broadened slightly without change in the τ values. At 59° they were very broad and had shifted toward the more intense inner pair of peaks. At this temperature, there was very slight broadening of the two more intense signals.

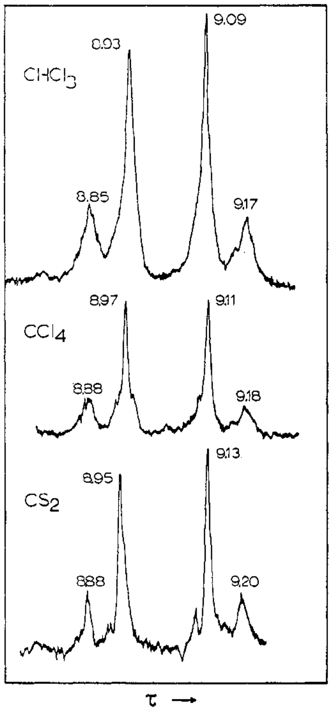

Figure 1.—Proton magnetic resonance spectra of $[(CH_3)_2AuCN]_4$ in $CHCl_3$, $CCl_4$, and $CS_2$ solution at 40°.

TABLE II

INFRARED AND LASER RAMAN (He–Ne) SPECTRA ($CM^{-1}$) OF $[(CH_3)_2AuNCSe]_2$ AND $[(CH_3)_2AuNCS]_2$[4]

| $[(CH_3)_2AuNCSe]_2$ | | | $[(CH_3)_2AuNCS]_2$[a] | | |
|---|---|---|---|---|---|
| Ir | | | | | |
| Mull | CCl₄ soln | Raman[c] Powder | Ir Mull | Raman Powder | Qualitative assignment |
| 2998 w | 3010 vw | . . . | 3000 w | . . . | $\nu_{as}(CH_3)$ |
| 2916 m | 2924 w | 2915 (1) | 2914 m | 2920 m | $\nu_s(CH_3)$ |
| 2169 vs | 2169 vs | 2158 (3) | 2163 m | 2148 s | $\nu(C\equiv N)$ |
| 1411 w, b | . . . | . . . | 1412 w | . . . | $\delta_{as}(CH_3)$ |
| 1243<br>1220 m | 1250 m | 1245 (0) | 1239 s | 1239 w | $\delta_s(CH_3)$ |
| 1196<br>1190 s | 1201 m | 1186 (3) | 1195 vs | 1195 m | |
| 845 w | *b* | | 816 w | | $\rho_r(CH_3)$ |
| 805 w | | | 775 m | | |
| 724 m | | | | | |
| 620 m | *b* | 621 (0) | | | $\nu$(C–Se) |
| . . . | 576 vw | 576 (3) | | 577 m | $\nu(AuC_2)$ |
| 540 w | 536 vw | 542 (10) | 548 w | 548 vs | |
| . . . | . . . | 427 (1) | | 444 w | δ(NCS), δ(NCSe) |
| | | | | 430 vw, sh | |
| . . . | . . . | 279 (2) vb | | 276 m | δ(CAuC) |
| | | 199 (1) | | 239 s | $\nu$(Au–S), $\nu$(Au–Se) ring modes |
| | | 172 (3) | | 194 m | |

[a] Reference 4. [b] Region obscured by solvent. [c] Relative Raman intensities in parentheses.

TABLE III

INFRARED AND LASER RAMAN (He–Ne) SPECTRA OF $[(CH_3)_2AuNCO]_2$ WITH THE INFRARED SPECTRUM OF $[(CH_3)_2AuN_3]$ FOR COMPARISON ($CM^{-1}$)

| $[(CH_3)_2AuNCO]_2$ | | | $[(CH_3)_2AuN_3]_2$[a] | |
|---|---|---|---|---|
| Ir | | | | |
| Mull | CCl₄ soln | Raman[c] Powder | Ir Mull | Qualitative assignments |
| 3014 w | 3016 w, b | . . . | 2993 vw | $\nu_{as}(CH_3)$ |
| 2914 m | 2924 m | 2922 (1) b | 2921 vw | $\nu_s(CH_3)$ |
| 2806 w | 2820 w | . . . | | $2\delta_{as}(CH_3)$ |
| 2192 vs | 2185 vs | 2193 (0) | 2087 vs | $\nu_{as}(N_3)$, pseudoasym NCO |
| 1415 w, b | 1426 w, b | . . . . . . | 1419 w | $\delta_{as}(CH_3)$ |
| 1323 w | 1324 w | 1328 (1) | 1279 w–m | $\nu_s(N_3)$, pseudosym NCO |
| 1248<br>1240 w | 1248 m | 1250 (0) | 1255 s | $\delta_s(CH_3)$ |
| 1216<br>1207 m | 1215 s | 1218 (1) | 1213 s | |
| 820 m, b | *b* | | 805 m, b | $\rho_r(CH_3)$ |
| 723 m | | | 719 m | |
| 711 m | | | 709 m | $\delta(N_3)$, δ(NCO) |
| 606 m | 608 m | | 632 m | $\gamma(N_3)$, γ(NCO) |
| | | 584 (6) | | $\nu(AuC_2)$ |
| . . . | . . . | 578 (10) | | |
| | | 570 (5) | 572 m | |
| 470 m, b | 470 m, b | | | $\nu_{ring}(Au_2N_2)$ |
| | *b* | | 420 s | |
| 373 vs, b | | | 396 sh | |
| | | 280 (6) vb | 284 w | δ(CAuC) |

[a] Reference 5. [b] Region obscured by solvent.

TABLE IV

INFRARED AND LASER RAMAN ($Ar^+$, He–Ne) SPECTRA ($CM^{-1}$) OF $[(CH_3)_2AuCN]_4$

| Ir (mull) | Raman[a] | Qualitative assignments |
|---|---|---|
| 2998 w, b | . . . | $\nu_{as}(CH_3)$ |
| 2919 m | 2917 (0) | $\nu_s(CH_3)$ |
| 2820 w | | $2\delta_{as}(CH_3)$ |
| 2202 vs | 2202 (7) vb | $\nu(C\equiv N)$ |
| 1411 w, b | . . . | $\delta_{as}(CH_3)$ |
| 1248<br>1240 w | 1250 (1) | $\delta_s(CH_3)$ |
| 1219<br>1211 m | 1212 (2) | |
| 805 w | | $\rho_r(CH_3)$ |
| 725 m–s | | |
| 580 w | 583 (10) | $\nu(Au(CH_3)_2)$ |
| 560 w | 565 (9) | |
| 473 vvs, vb | . . . | Ring modes |
| 396 m | | |
| 370<br>358 m | 354 (1) | |
| | 282 (4) b | δ(CAuC) |

[a] Raman frequencies are the average of values obtained with $Ar^+$ and He–Ne excitation. The quality of the He–Ne spectrum was unusually bad.

The products of the bridge-splitting reactions gave two methyl proton resonances comparable in line width to the internal TMS standard indicating that these compounds all are stereochemically rigid and that only the cis isomers were produced.

**Infrared and Raman Spectra.**—The data[12] for $[(CH_3)_2AuNCSe]_2$, $[(CH_3)_2AuNCO]_2$, and $[(CH_3)_2AuCN]_4$ are collected in Tables II–IV, respectively, together with frequencies of $[(CH_3)_2AuNCS]_2$[4] and $[(CH_3)_2AuN_3]_2$[5] for comparison. Raman spectra for the new $(CH_3)_2AuXL$ compounds are given in Figure 2 and Table V. As noted previously,[10] the infrared spectra of these adducts with tertiary arsines and phosphines are so complex that they are of little value in assigning structures. When the frequencies involving the $(CH_3)_2AuX$ portion of the molecule have been deter-

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[12] Photographic reproductions of the spectra are available from the author.

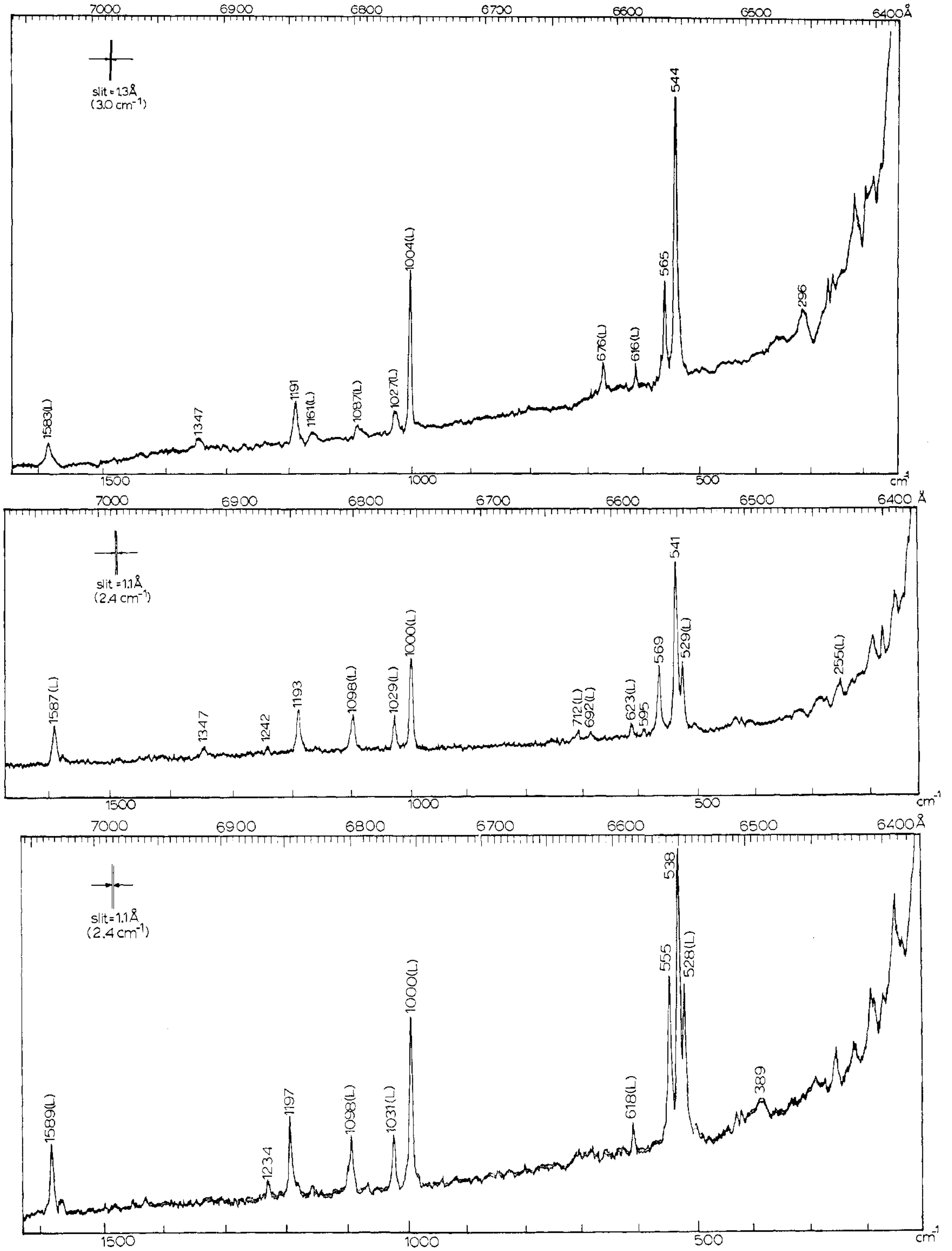

Figure 2.—Raman spectra (He–Ne) of (top) $(CH_3)_2Au(NCO)As(C_6H_5)_3$, (middle) $(CH_3)_2Au(NCO)P(C_6H_5)_3$, and (bottom) $(CH_3)_2Au(CN)P(C_6H_5)_3$.

mined from the Raman spectra, it often is possible to assign the corresponding vibrations in the infrared spectrum.

## Discussion

The proton magnetic resonance spectra of $[(CH_3)_2AuNCSe]_2$ and $[(CH_3)_2AuNCS]_2$ can be seen to be almost identical from the data in Table I. The lower field signal is assigned to the methyls trans to selenium by analogy with $[(CH_3)_2AuNCS]_2$[4] and $[(CH_3)_3PtNCS]_4$.[13,14] The resonances of the methyl protons trans to nitrogen are slightly broader, perhaps because of slight coupling to nitrogen, nuclear spin $I = 1$. Comparing the thiocyanate and selenocyanate in $CHCl_3$ solution, it is seen that the $\tau$ values differ by only 0.02 ppm for the methyls trans to nitrogen and by only 0.03 ppm for the methyls trans to the group VI donor atom.

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[13] G. C. Stocco, and R. S. Tobias, *J. Coord. Chem.*, in press.

[14] J. M. Homan, J. M. Kawamoto, and G. L. Morgan, *Inorg. Chem.*, **9**, 2533 (1970).

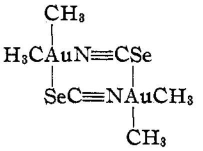
TABLE V

INFRARED AND LASER RAMAN (He–Ne) SPECTRA ($cm^{-1}$) OF $(CH_3)_2AuXL$ COMPOUNDS ($X$ = PSEUDOHALIDE; $L = P(C_6H_5)_3$, $As(C_6H_5)_3$)

| Compd | ν(AuC₂) |  | δ(CH₃) |  | Other ν vibrations |  | Qualitative assignments |
|---|---|---|---|---|---|---|---|
|  | Raman | Ir | Raman | Ir | Raman | Ir |  |
| $(CH_3)_2Au(SCN)P(C_6H_5)_3$[a] | 549 vs | 547 w | 1227 w | 1226 w | 2120 m | 2120 vs | ν(C≡N) |
|  | 537 vs | . . . | 1197 m | 1192 w |  |  |  |
| $(CH_3)_2Au(NCO)P(C_6H_5)_3$ | 569 vs | 570 vw | 1242 w | 1245 w | . . . | 2210 vvs | Pseudoasym NCO str |
|  | 541 vvs | . . . | 1193 m | 1194 m | 1347 w | 1349 w | Pseudosym NCO str |
|  |  |  |  |  | 595 vw | 597 m | π(NCO) |
|  |  |  |  |  | . . . | 327 s | ν(Au—N) |
| $(CH_3)_2Au(NCO)As(C_6H_5)_3$ | 565 vvs | 565 vw | 1242 vw | 1240 w | . . . | 2190 vvs | Pseudoasym NCO str |
|  | 544 vs | 545 w | 1191 m | 1192 m | 1347 w | . . . | Pseudosym NCO str |
|  |  |  |  |  |  | 331 s[b] | ν(Au—N) |
| $(CH_3)_2Au(CN)P(C_6H_5)_3$ | 555 s | 555 w | 1234 w | 1235 w | 2153 w | 2156 vw | ν(C≡N) |
|  | 538 vs | . . . | 1197 vm | 1197 m |  |  |  |
|  |  |  |  |  | 389 w, b | 394<br>385 } s | ν(Au—CN) |

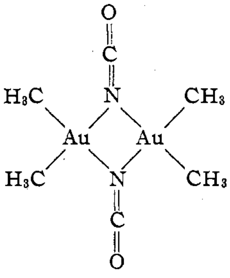
[a] Reference 10. [b] Overlaps with bands of $As(C_6H_5)_3$.

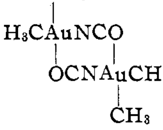
The selenocyanate gives only one C≡N stretch in the Raman and one in the infrared spectrum suggesting a centric structure. The Raman and infrared frequencies and intensities, Table II, are very similar for $[(CH_3)_2AuNCSe]_2$ and $[(CH_3)_2AuNCS]_2$, and consequently they are assigned the same structure. The dimer IV, with $C_{2h}$ symmetry is in accord with all of the spectra, and the selection rules have been discussed previously.[4]

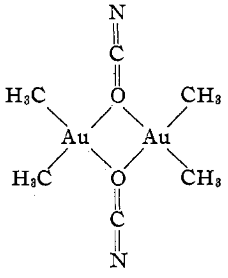

IV

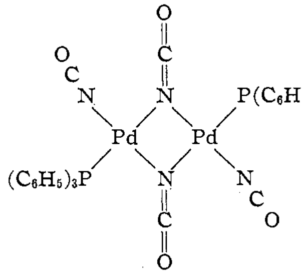
Both $[(CH_3)_2AuNCSe]_2$ and $[(CH_3)_2AuNCS]_2$ are stereochemically rigid molecules at room temperature. This mode of bridging is common for thiocyanate and presumably for selenocyanate complexes of the transition metals. Recently, the crystal structures of the two isomers of dichlorodi-μ-thiocyanato-bis(tri-*n*-propylphosphine)diplatinum(II) which have this kind of bridge were refined.[15] In contrast to the dimethylgold compound, (π-methylallyl)palladium thiocyanate which is dimeric and undoubtedly involves this same kind of bridge gives an nmr spectrum at 6° which indicates that a rapid exchange process is taking place.[16] A mechanism involving an association to a tetramer was suggested on the basis of the kinetic data.

Dimethylgold cyanate also is dimeric in solution, but it exhibits only one pmr signal at τ 8.85 ppm essentially the same as found for the azide, 8.8 ppm.[5] This could result from a symmetric structure where all 12 methyl protons are magnetically equivalent, or it could be caused by a rapid exchange process, *e.g.*, involving bridge dissociation. Various structures, among them V–VII, can be suggested for this compound in solution.


V


VI


VII


VIII

The infrared spectra of $[(CH_3)_2AuNCO]_2$ and $[(CH_3)_2AuN_3]_2$ are very similar, suggesting that they have similar structures. The frequencies involving the bridging cyanate ligands also are almost the same as those of $[P(C_6H_5)_3Pd(NCO)_2]_2$ which has been assigned structure VIII.[17] The frequencies assigned to vibrations of the bridging cyanates of the palladium compound are pseudoasymmetric stretch, 2173 $cm^{-1}$, and pseudosymmetric stretch, 1334 $cm^{-1}$. The corresponding values for $[(CH_3)_2AuNCO]_2$ are 2185 and 1324 $cm^{-1}$. The frequencies assigned to the bridging cyanates in the gold compound also are very similar to those reported recently for $[(CO)_2Rh(NCO)]_2$,[18] 2185 and 1336 $cm^{-1}$, although no structure was proposed for this rhodium(I) complex. It is very likely that the Rh(I), Pd(II), and Au(III) compounds all have the same kind of bridge.

Dimethylgold cyanate is assigned structure V by analogy with the azide and the cyanate-bridged palladium(II) compounds. In addition, as discussed below, there is an increase of *ca.* 20 $cm^{-1}$ in the pseudoasymmetric stretch as the cyanate bridge is cleaved by $P(C_6H_5)_3$ giving a unidentate isocyanate. This suggests a structure involving bridging by only one atom of the cyanate, *e.g.*, V.

The selection rules for the skeletal vibrations of this $D_{2h}$ structure have been discussed earlier with respect to the azide.[5] The Au–C coordinates transform as $A_g + B_{3g} + B_{1u} + B_{2u}$ ($\sigma_{yz}$ = molecular plane). In addition to the Raman powder spectra of $[(CH_3)_2AuNCO]_2$ reported in Table III, spectra were also obtained with $CS_2$ and $CHCl_3$ solutions. Only two bands were observed

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(15) U. A. Gregory, J. A. J. Jarvis, B. T. Kilbourn, and P. G. Owston, *J. Chem. Soc. A*, 2770 (1970).

(16) D. L. Tibbetts and T. L. Brown, *J. Amer. Chem. Soc.*, **91**, 1108 (1969).

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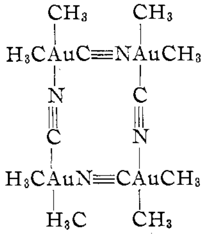
in the 500–600-cm$^{-1}$ region: $CS_2$, 579 (vs, p), 572 (m, dp) cm$^{-1}$; $CHCl_3$, 579 (vs, p), 568 (m, dp) cm$^{-1}$. This is in accord with the $D_{2h}$ structue. The CO and CN coordinates transform as $A_g + B_{1u}$. The observation of only one infrared-active pseudoasymmetric NCO stretch and of only one Raman pseudosymmetric stretch and one in the infrared spectrum is in accord with structure V, although the same would be expected for VI and VII as well. The large separation of the two frequencies 606 and 711 cm$^{-1}$ observed in the NCO bending region is consistent with the behavior observed by Nelson and Nelson for bridging cyanates of the type in V,[19] and these authors have summarized the evidence for single-atom (nitrogen) bridging in binuclear cyanates.

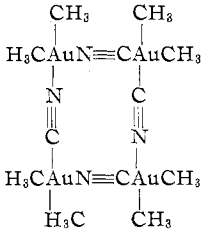
The Raman spectrum of a *crystalline* sample of $[(CH_3)_2AuNCO]_2$ has three bands in the $AuC_2$ stretching region at 569, 577, and 586 cm$^{-1}$. The two lower frequency bands correspond approximately to those observed with the $CHCl_3$ solution, 568 and 579 cm$^{-1}$. Since no trace of the high-frequency band could be observed with $CHCl_3$ and $CS_2$ solutions, it seems that this is a lattice effect. Surprisingly, this is the first of over 30 dimethylgold(III) compounds for which we have observed such behavior. It is possible that the crystal does not contain dimeric molecules such as are indicated for the solution by vapor pressure osmometry. Nitrogen is a small atom to bridge two golds giving a four-membered ring. For example, the crystal dimethylgold(III) hydroxide[20] has an eight-membered ring structure, and $AuF_3$[21] has a helix structure with two cis bridging and two cis terminal fluorines per gold atom.

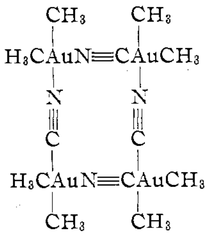
As often is the case, the Raman and infrared intensities of the coordinated cyanato group are complementary. A Raman spectrum (He–Ne) was recorded with a crystalline powder sample of KNCO, and the pseudoasymmetric stretch was observed as a very weak, very broad band at 2167 cm$^{-1}$, the pseudosymmetric stretch appeared at 1302 (m) and 1208 (s) cm$^{-1}$ (Fermi resonance), and the deformation appeared as a medium-intensity, broad band at 641 cm$^{-1}$. These values correspond closely to those reported by Decius, *et al.*,[22,23] on the basis of infrared spectra: 2165, 1301.5, and 1207.3 cm$^{-1}$ (Fermi resonance); 636.9 and 628.0 cm$^{-1}$ (lattice splitting). In $[(CH_3)_2AuNCO]_2$, the pseudoasymmetric stretch was barely detectable above the noise level in the Raman spectrum, while it was exceedingly intense in the infrared spectrum at 2185 cm$^{-1}$ ($CCl_4$ solution).

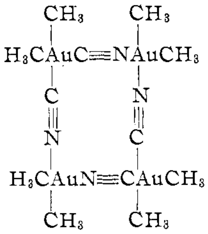
Dimethylgold cyanide gave osmometric molecular weights in both chloroform and benzene which corresponded closely to a tetramer as found cryoscopically by Buraway, Gibson, and Holt[7] for the diethyl and di-*n*-propyl compounds. The planar tetrameric structure with $C_{4h}$ skeletal symmetry, III, which was suggested on the basis of the original X-ray structure determination[8] should give a first-order nmr spectrum with only two methyl proton resonances. In $CHCl_3$, $CCl_4$, and $CS_2$ solution, the observed spectrum consists of four resonances, Figure 1. Spectra obtained at both 60 and 100 MHz confirm the presence of four chemically nonequivalent kinds of protons. If cyanide disordering occurs, isomers will result. If IX with the fourfold axis is described as (1,1,1,1) using 1 and 2 to represent the two possible cyanide orientations, isomers may be obtained by rotation of one cyanide, *e.g.*, (1,2,1,1), and by rotation of two cyanides. In the latter case, two kinds of structures result depending upon whether the rotated cyanides are adjacent, *e.g.*, (1,1,2,2), or across the ring, (1,2,1,2). The statistical weights are 2:8:4:2, respectively, and the structures are illustrated by IX–XII.

With these structurally similar compounds, the methyl proton chemical shifts should be determined primarily by the other two atoms bound to gold and also by the specific trans influence.[10] Consequently four signals might be expected: one for $(CH_3)_2Au(CN)_2$, two for $(CH_3)_2Au(NC)(CN)$, and one for $(CH_3)_2Au(NC)_2$. If complete disordering of the cyanides occurred, this would lead to four signals with relative intensities 28:36:36:28. Since the high- and low-field resonances would be expected to result from dimethylgold moieties with only cyano or isocyano coordination, the observed 1:3:3:1 intensities indicate that structure IX is favored. As the solution temperature is raised, extensive broadening of the high- and low-field signal is observed suggesting that reorientation of cyanides is occurring.


IX


X


XI


XII

Other possible explanations for the spectra appeared to be ruled out by the experimental data. Since the osmometric molecular weights in both benzene and $CCl_4$ are very close to the value expected for the tetramer, it seems unlikely that a mixture of molecules with different degrees of polymerization exists. Buraway, Gibson, and Holt[7] observed that diethylgold cyanide lost ethyl groups upon heating, but the analyses of a number of different samples of dimethylgold cyanide prepared by slightly different methods and recrystallized from different solvents all gave carbon determinations very close to the theoretical values. In addition, the products described by Buraway, *et al.*,[7] remaining after some of the alkyl groups had been lost were reported to be only very slightly soluble.

Disordering of the cyanides might be expected to manifest itself in the vibrational spectra. Unfortunately this is of little help because of the complexity of

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[23] A. Maki and J. C. Decius, *ibid.*, **31**, 772 (1959).

the molecule and the lack of coupling through the gold atom. With $C_{4h}$ symmetry the Au–C coordinates trans to the cyanide carbon transform as $A_g + B_g + E_u$ as does the set of Au–C coordinates trans to the cyanide nitrogen. It is likely that the $A_g$ and $B_g$ modes in each representation are accidentally degenerate, and the two rather broad bands in the Raman spectrum represent the stretching of bonds trans to carbon and trans to nitrogen. The C≡N coordinates also transform as $A_g + B_g + E_u$. Only a single, broad C≡N stretching band ($A_g + B_g$) is observed in the Raman spectrum. Only one band is observed in the infrared spectrum as predicted ($E_u$), although it is asymmetric.

In the Raman spectrum, only a weak, broad band at 354 cm$^{-1}$ could be assigned to modes involving Au—NC and Au—CN bond stretching. This suggests that the bonds between the $(CH_3)_2Au^{III}$ moieties and the bridging cyanides are highly polar. In contrast, (Au—C≡N) stretching vibrations of $Cl_2Au(CN)_2^-$ [24,25] give a moderately intense Raman band at 461 cm$^{-1}$. The very broad intense infrared band of $[(CH_3)_2AuCN]_4$ at 473 cm$^{-1}$ and the less intense band at 396 cm$^{-1}$ undoubtedly involve Au—N and Au—C stretching in ring modes.

With predominantly electrostatic interactions between gold and cyanide, some disordering of the cyanides along the Au–Au axis would not be unexpected. For example, $(CH_3)_3SnCN$[26] involves similar bridges, and complete disordering of the cyanides was observed for that compound. Comparable bridges exist in $AgCN \cdot 2AgNO_3$,[27] AgCN,[28] and AuCN,[28] and the cyanides are apparently disordered in all three compounds.

**Bridge-Splitting Reactions.**—Reactions of $[(CH_3)_2AuCl]_2$ and $[(CH_3)_2AuNCS]_2$ with pyridine, triphenylphosphine, and triphenylarsine previously have been observed to give isolable products.[10] The nmr spectrum of a $CDCl_3$ solution containing equimolar amounts of $[(CH_3)_2Au(NCSe)]_2$ and $P(C_6H_5)_3$ was almost identical with that of a solution of $(CH_3)_2Au(SCN)P(C_6H_5)_3$[8] indicating that the reaction was virtually quantitative. Although numerous attempts were made, a pure product could not be crystallized from the solutions. By analogy with the thiocyanato complex, a selenocyanato structure is assigned.

Dimethylgold cyanate reacted readily with $P(C_6H_5)_3$ and $As(C_6H_5)_3$ to yield isolable adducts. The metal-sensitive modes of $P(C_6H_5)_3$[29] and $As(C_6H_5)_3$[30] are very similar in these adducts to those of the corresponding products obtained from $[(CH_3)_2AuCl]_2$ and $[(CH_3)_2AuNCS]_2$.[10] The Raman intensity of the NCO pseudoasymmetric stretch was too low for these frequencies to be determined from the Raman spectra. In the infrared spectra, extremely intense bands were observed at 2210 and 2190 cm$^{-1}$ for $P(C_6H_5)_3$ and $As(C_6H_5)_3$ adducts, respectively, compared to 2185 cm$^{-1}$ for $[(CH_3)_2AuNCO]_2$. The pseudosymmetric stretch is observed in the Raman spectrum of both adducts at 1347 compared to 1328 cm$^{-1}$ for $[(CH_3)_2AuNCO]_2$.

The cyanate deformation could be measured only in the spectrum of $(CH_3)_2Au(NCO)P(C_6H_5)_3$ where it appeared at 595 cm$^{-1}$ (Raman) and 597 cm$^{-1}$ (ir). The frequencies for the coordinated cyanate are very similar to the values observed in the infrared spectrum (cm$^{-1}$) of $Pd(P(C_6H_5)_3)_2(NCO)_2$: $\nu$(C≡N) 2212–2218 (s), $\nu$(C—O) 1350 (m), $\delta$(NCO) 615 (w), 610 (w), 590 (m).[31] The very low Raman and high infrared intensity of the C≡N stretch supports the assignment of the isocyanato structure to both of the gold adducts. The $AuC_2$ stretching vibrations (cm$^{-1}$) also are very similar in these cyanate adducts: 569, 541 ($P(C_6H_5)_3$); 565, 544 ($As(C_6H_5)_3$). The large frequency difference for the two modes is a result of the appreciably different trans influence of $NCO^-$ on the one hand and $P(C_6H_5)_3$ or $As(C_6H_5)_3$ on the other.

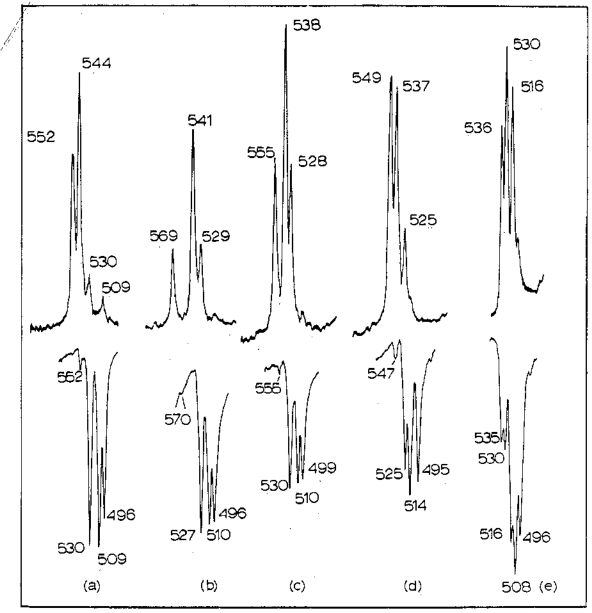

Figure 3.—Raman and infrared spectra of $(CH_3)_2AuXP(C_6H_5)_3$ compounds in the Au–$C_2$ stretching region illustrating the mixing of Au–C and P–C internal coordinates. X: (a) $Cl^-$, (b) $NCO^-$, (c) $CN^-$, (d) $SCN^-$, (e) $P(C_6H_5)_3$.

Dimethylgold cyanide also reacts readily with $P(C_6H_5)_3$, to produce a stereochemically rigid *cis*-$(CH_3)_2Au(CN)P(C_6H_5)_3$ complex. In the adducts, the C≡N stretch is observed at 2153 cm$^{-1}$ in the Raman and 2156 cm$^{-1}$ in the infrared spectra. These values correspond to decreases of *ca.* 50 cm$^{-1}$ from the values for $[(CH_3)_2AuCN]_4$. This frequency decrease would be expected to accompany the change from bridging to terminal cyanide. The bands in 385–394-cm$^{-1}$ region undoubtedly arise from Au–CN stretching and bending modes, and these frequencies are somewhat lower than in the inorganic gold(III) complexes, *e.g.*, $AuCl_2(CN)_2$.[24,25]

With this work, five compounds of the type $(CH_3)_2AuXP(C_6H_5)_3$ have been synthesized with X = $Cl^-$, $NCO^-$, $NCS^-$, $CN^-$, and $P(C_6H_5)_3$. These illustrate an interesting intensity effect observed with dimethylgold(III) compounds. In general, the $AuC_2$ stretching modes in the 500–600-cm$^{-1}$ region have very high Raman and very low infrared intensities. Conversely, the modes of $P(C_6H_5)_3$ in the 490–530-cm$^{-1}$ region have very low Raman and very high infrared intensities. These are complex modes involving both P–C stretching and ring folding.[29] As the Au–$C_2$ stretching frequencies

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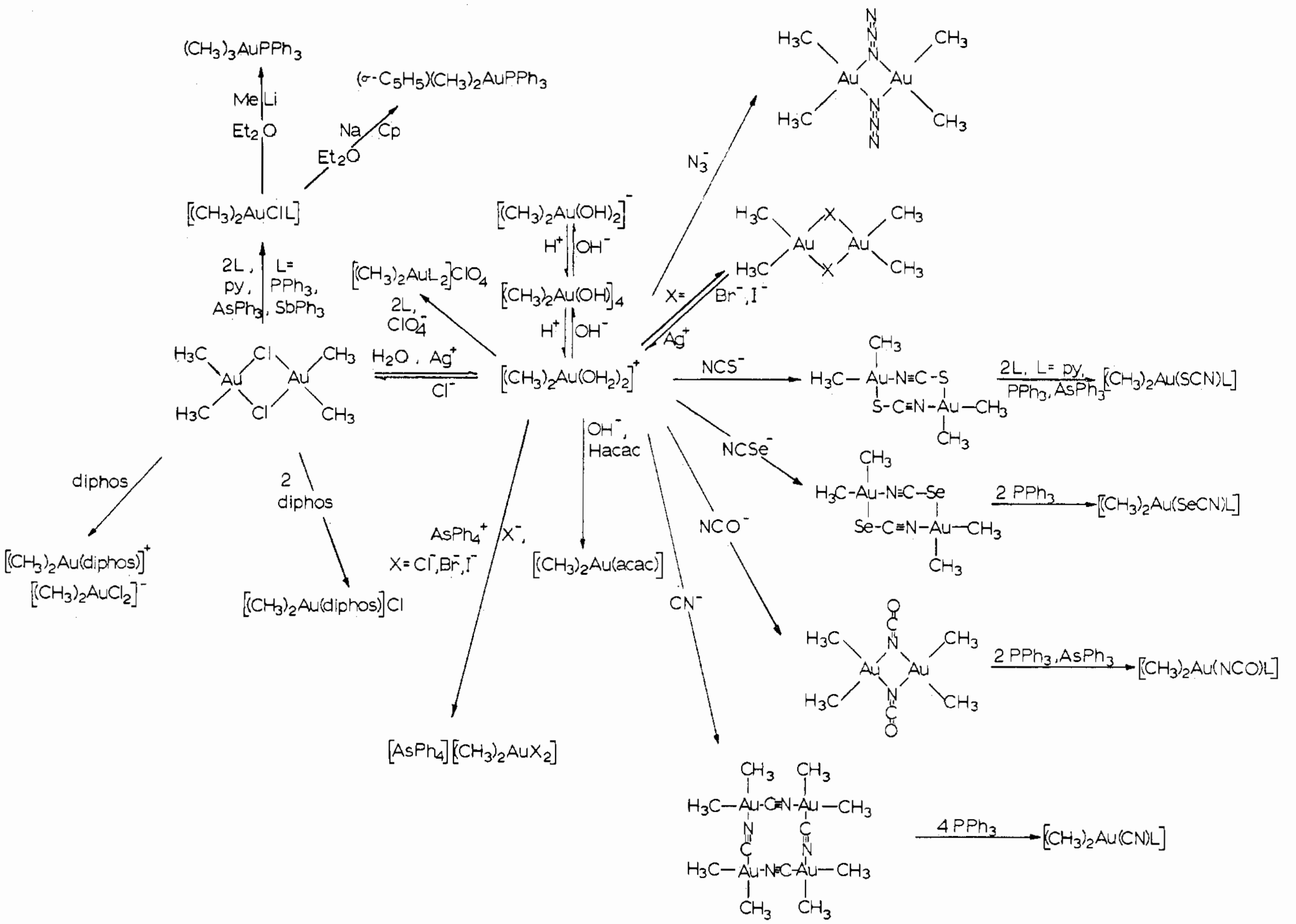
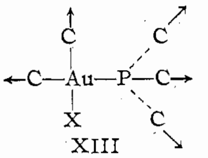


Figure 4.—Reactions of dimethylgold(III) halides and pseudohalides.

drop to lower values approaching the $P(C_6H_5)_3$ frequencies because of the substitution of ligands with higher trans influences, the Raman intensity of the $P(C_6H_5)_3$ modes increases, while the infrared intensity of the $AuC_2$ modes also increases. This effect is illustrated in Figure 3. It is completely absent in the chemically very similar $As(C_6H_5)_3$ complexes, since there is no ligand mode of frequency comparable to the $AuC_2$ stretches. It seems likely, as suggested earlier,[10] that mixing of Au–C and P–C internal coordinates occurs to some extent as illustrated in XIII. If this effect is not recognized, it can lead to confusion in the assignment of structures. The appearance of three strong bands in the Au–$C_2$ stretching region normally would indicate the presence of two different structures, *e.g.*, both cis and trans isomers.


XIII

$\Gamma(\text{Au–C}) = 2A'$

$\Gamma(\text{P–C}) = 2A' + A''$

This contribution completes a survey of the synthesis and reactions of the dimethylgold halides and pseudohalides. A number of these are illustrated in Figure 4. These bridge-cleavage reactions parallel those of the electronically analogous organometallic π-allylpalladium(II) moiety closely.[32] Many are similar to the reactions of the dicarbonylrhodium(I) moiety too.[33] The similarity in gold–pseudohalide bonding in $(CH_3)_2Au^{III}XL$ and $LAu^{I}X$ compounds may be seen by comparing the vibrational frequencies given here and in ref 10 with those of DeStefano and Burmeister[34] for the gold(I) analogs.

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