J. Am. Chem. Soc. 1981, 103, 2192-2198

Structure and Properties of Transition-Metal Ylide Complexes.[24] 2. Organometallic Complexes of Gold(III)

Judith Stein, John P. Fackler, Jr.,* C. Paparizos, and H.-W. Chen

Contribution from the Department of Chemistry, Case Western Reserve University, Cleveland, Ohio 44106.

Received September 22, 1980

Abstract: The syntheses, properties, and structures of ylide complexes of trimethylgold(III) are reported. The X-ray structures of $Me_3AuCH_2S(O)Me_2$ and $Me_3AuCH_2PPh_3$ ($Me = CH_3$ and $Ph = C_6H_5$) are compared with the phosphine precursor, Me_3AuPPh_3. The ylide complexes structurally are tetracoordinated σ-bonded alkyls. They are surprisingly stable, a result of several important factors which are discussed. Displacement of the sulfoxonium ylide from the gold(III) complex has been accomplished with alkyl phosphines. The phosphonium ylides are displaced much less readily. The complexes all react with acids to form CH_4 and cis-substituted derivatives. The ESCA and NMR spectra of the trimethylgold(III) complexes show that the charge on metal ion is effectively reduced by the ylide. The UV photoelectron spectra also indicate a lowering of the ionization potential when compared with the phosphine complex.

The field of organometallic chemistry has undergone an explosive development in recent years. Much of this interest has arisen from the fact that many organometallic complexes function as catalysts for a wide variety of organic reactions.[1] Recently attention has turned to understanding the mechanistic role of the metal and the nature of the actual catalytic species. Intermediates in these reactions often are assumed to contain carbon-to-metal σ bonds. Ylides readily form metal–carbon σ "alkyl" bonds with transition metals. Since the compounds formed with ylides generally are more robust than transition-metal alkyls, they form interesting models for comparison with more reactive organometallic catalysts and catalyst precursors.

Since the 1955 review by Cotton,[2] much progress has been made in characterizing the carbon-to-transition metal σ-bond. Wilkinson states in his Nobel lecture[3] that his own "knowledge of the instability of transition-metal alkyls and aryls" was important in formulating the correct structural description of dicyclopentadienyliron. By 1968 it was generally recognized[4] that certain ligands could lend stability to the metal–carbon bond. Chatt had expounded[5] this thought about a decade earlier in his Rome lectures. Chatt focused on the difference in energy between highest energy occupied orbitals (HOMO) and lowest energy vacant orbitals (LUMO). Various coligands with the alkyls increase the HOMO–LUMO separation to produce metal–carbon bond stability. Promotion of electrons from filled d orbitals or from carbon-to-metal bonding orbitals into vacant orbitals weakens the metal-to-carbon bond. Rupture of this bond generally leads to an unstable hydrocarbon species. Other processes effectively compete with metal–ligand recombination. Thus the lack of stability of the dissociated organic ligand contributes[7] to the observed instability of the complexes, also.

There is now substantial evidence that carbon-to-transition metal σ bonds can be abundant[7,8] when carbon ligands such as ylides[9] are used which themselves are relatively stable under the special conditions of solvent and temperature of the reaction. Kinetic (not thermodynamic) instability[7,8] of the metal–carbon bond appears to be associated with the decomposition of transition-metal alkyls.

One of the best established ways[10] in which alkyls decompose is through β-hydride elimination to form an olefin and a metal hydride, the latter further decomposing to the metal and hydrogen. Wilkinson,[6] Lappert,[8] and many others[7] have utilized the fact that ligands such as $-CH_2Si(CH_3)_3$ do not readily β-eliminate to prepare many stable complexes containing transition metal-to-carbon bonds. Wilkinson[3] says that "the main purpose of additional ligands, π-acid or otherwise, in stabilizing compounds with metal-to-carbon σ-bonds is merely to firmly block off the coordination sites required for decomposition reactions to proceed". Thus electronic factors such as those suggested[5] by Chatt may be of little or no consequence. To substantiate his conclusions, Wilkinson points to the thermal stability of homoleptic complexes of neopentyl and (trimethylsilyl)methyl ligands in forming tetrahedral paramagnetic complexes[11] of Cr(III) and Cr(IV).

Ylides have been regarded as highly versatile and useful synthetic reagents.[12,13] Recently phosphorus ylides have also been employed as ligands in transition-metal complexes.[9] Ylides contain a heteroatom coordinated to a carbanion and are generally represented by the resonance forms I, where X = P, As, S, N, S(O), etc.

$$\underset{\substack{\text{ylide}\\ \text{Ia}}}{{}^{-}CR_2{-}{}^{+}XR_n} \leftrightarrow \underset{\substack{\text{ylidene}\\ \text{Ib}}}{CR_2{=}XR_n}$$

etc. The ylide resonance form Ia emphasizes the zwitterionic nature of the ylide whereas in the ylidene resonance form Ib the ylide is described as containing a double bond between the heteroatom and ylidic carbon.

Although a patent[14] to Cities Service Corp. in the early 1960s suggested the use of ylides with transition-metal halides and oxohalides as polymerization catalysts and Hieber et al.[15] in the 1960s had displaced carbonyls with phosphorus ylides, little concerted effort was made to study reactions with transition element compounds until the early 1970s. Early in the 1960s,

---

(1) Kochi, J. K. "Organometallic Mechanisms and Catalysts"; Academic Press: New York, 1978. Boor, J. "Ziegler-Natta Catalysts and Polymerization"; Academic Press: New York, 1979. Parshall, G. W. *Science (Washington, D.C.)* **1980**, *208*, 1221–1229.

(2) Cotton, F. A. *Chem. Rev.* **1955**, *55*, 551–594.

(3) Wilkinson, G. *Science (Washington, D.C.)* **1974**, *185*, 109–112.

(4) Parshall, G. W.; Mrowen, J. J. *Adv. Organomet. Chem.* **1968**, *7*, 157–209.

(5) Chatt, J., Accademia Nazionale Dei Lincei, IV Corso Estivo di Chimica, Oct 7, 1959.

(6) Wilkinson, G. *Pure Appl. Chem.* **1972**, *30*, 627–635.

(7) Schrock, R. R.; Parshall, G. W. *Chem. Rev.* **1976**, *76*, 243–268.

(8) Davidson, P. J.; Lappert, M. F.; Pearce, R. *Chem. Rev.* **1976**, *76*, 219–242; *Acc. Chem. Res.* **1974**, *7*, 209–217.

(9) Schmidbaur, H. *Acc. Chem. Res.* **1975**, *8*, 62–76; *Adv. Organomet. Chem.* **1976**, *14*, 205–243; *Pure Appl. Chem.* **1978**, *50*, 19–25.

(10) Purcell, K. F.; Kotz, U. C. "Inorganic Chemistry"; W. B. Saunders Co.: Philadelphia, 1977.

(11) Kruse, W. M. U.S. patent 3 875 132, April 1, 1975 to Hercules, Inc. See also: Kruse, W. M. *J. Organomet. Chem.* **1972**, *42*, C39–C42.

(12) Wittig, G.; Geissler, G. *Justus Liebigs Ann. Chem.* **1953**, *580*, 44. Wittig, G.; Schollkopf, U. *Chem. Ber.* **1954**, *87*, 1318–1330.

(13) Corey, E. J.; Chaykowsky, M. *J. Am. Chem. Soc.* **1965**, *87*, 1353–1364. Trost, B. M.; Melvin, L. S. "Sulfur Ylides"; Academic Press: New York, 1975.

(14) Mendel, A. *Chem. Abstr.* **1960** *56*, 587*g*; U.S. Patent 2 998 416, June 23, 1960.

(15) Hieber, W.; Winter, E.; Schubert, E. *Chem. Ber.* **1962**, *95*, 3070–3076.

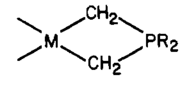
0002-7863/81/1503-2192$01.25/0 © 1981 American Chemical Society

Seyferth and Grim applied[16] the Wittig reaction to organometallic halides of various group 4 elements. In the late 1960s and early 1970s, two German theses[17] were followed by papers from Greco,[18] Kurras,[19] Schmidbaur and co-workers,[20,57] and others.[21-23]

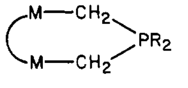
Ylides are observed to coordinate to metals in one of the three ways illustrated II, III, and IV for phosphorus ylides.[9]

$-M—CH_2PR_3$

II



III



IV

The mode of coordination is a function of the oxidation state of the metal, the ylide, and the reaction conditions. Type II compounds are typically formed by substitution reactions of ylides on metal phosphine or metal carbonyls, using a one-to-one stoichiometry.[9] Type III complexes can be formed by reaction of a metal complex with ylide anions such as $Li(CH_2)_2PR_2$.[22] Type IV complexes are formed by transylidation reactions[9] or by reaction of dinuclear octamethyl complexes with phosphonium salts.[19]

We have communicated previously the synthesis and preliminary X-ray structural results of the novel trimethylgold(III) dimethyloxosulfonium methylide complex.[24] This example of a type II complex displays remarkable air and thermal stability. Our continued interest in factors leading to the stabilization of various oxidation states of transition-metal ions has led to further investigations of the aforementioned complex and other related trimethylgold(III) species.

Experimental Section

All manipulations were performed under an atmosphere of dry argon either in a Vacuum Atmosphere drybox or by conventional Schlenk techniques.

Reagents. Metallic gold(99.99% pure) was purchased from I. Miller Co. (Cleveland). Triphenylphosphine (PPh_3) was purchased from Fisher Scientific and recrystallized from ethanol before use. Tricyclohexylphosphine, obtained from Orgmet, Inc., was used without further purification. Dimethyl sulfoxide (Me_2SO), purchased from Fisher, was purified by repeated fractional crystallizations followed by flash distillation from calcium hydride. Reagent grade acetone, chloroform, and hexane were obtained from Fisher and dried over activated molecular sieves (3A or 4A) before use. Methyl iodide (MeI) obtained from Aldrich was distilled under argon and stored in a dark bottle over a bead of mercury. Low halide methyllithium (MeLi) was obtained from Ventron. Phosphorus tribromide (PBr_3) and methyltriphenylphosphonium bromide ($MePPh_3Br$) were purchased from Aldrich. Trimethylsulfonium chloride (Me_3SCl) was obtained from Pfaltz and Bauer Chemical Co. Sodium hydride (NaH) was purchased as a 57% mineral oil dispersion from Alfa Chemicals. Tetrahydrofuran (THF) and diethyl ether (Et_2O) were distilled from sodium benzophenone ketyl before use.

Preparation of Ligands and Complexes. Trimethyl oxosulfonium chloride,[13] dimethylsulfoxonium methylide,[13] sodium amide,[25] triphenylmethylenephosphorane,[26] and dimethylsulfonium methylide[13] were prepared by literature methods. (Triphenylphosphine)gold(I) chloride (Ph_3PAuCl), prepared by literature methods,[27] was recrystallized from benzene before use. Trimethyl(tricyclohexylphosphine)gold(III) was prepared by a modification of the procedure[28] for the preparation of trimethyl(triphenylphosphine)gold(III). Lithium peralkylgold was synthesized according to literature methods.[28]

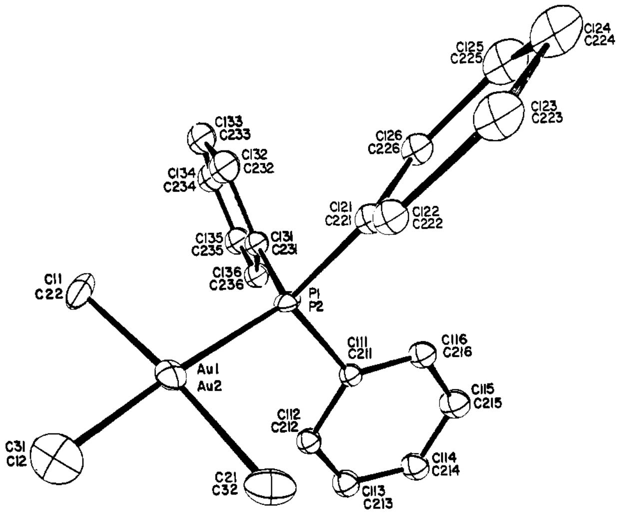


Figure 1. An ORTEP drawing (50% probability) of the structure of $(CH_3)_3AuP(C_6H_5)_3$.

Synthesis of Trimethyl(trimethylphosphine)gold(III), Me_3AuPMe_3.[29] To a Schlenk flask containing 7.0 g (0.014 mol) of Ph_3PAuCl in 50 mL of Et_2O at -78 °C was added 17.5 mL (0.028 mol, 1.6 M) of low halide MeLi dropwise. To the resultant solution was added 1.24 mL (0.020 mol) of MeI. With continued stirring, the solution was allowed to slowly warm to room temperature, and water was added to destroy any residual MeLi. The ether layer was separated and evaporated to approximately 15 mL. Twenty milliliters of pentane was added, and the white precipitate was collected and dried in vacuo; mp 120 °C.

Synthesis of Trimethylmethylenephosphorane.[30,31] A 2-L three-neck flask equipped with a 500-mL dropping funnel, dry ice condenser, gas inlet, and magnetic stir bar was charged with 560 mL (0.73 mol, 1.3 M) of MeLi solution. The solution was cooled to -20 °C. PBr_3 (22.8 mL, 0.24 mol) was added to the dropping funnel via syringe, and 125 mL of anhydrous Et_2O was added to the dropping funnel. The PBr_3 solution was added dropwise to the MeLi at -20 °C. After addition, the flask was allowed to warm to room temperature and then held at reflux for 0.5 h. The PMe_3 and Et_2O were then flash distilled, while maintaining a vigorous stirring rate, into a 1-L flask equipped with a dry ice condenser and a water condenser and containing 23 mL of MeBr (0.25 mol) in Et_2O. The resulting solution was stirred for 3 h, whereupon a white precipitate, Me_4PBr, was formed. The Me_4PBr was collected, washed with ether, recrystallized from a water/ethanol mixture and dried at 100 °C in vacuo.

A 200-mL Schlenk flask containing 6.4 g (0.038 mol) of Me_4PBr and 1.5 g (0.038 mol) of $NaNH_2$ in 100 mL of THF was fitted with a reflux condenser and allowed to reflux overnight under argon. The Et_2O and Me_3PCH_2 (bp 122 °C) were then distilled into a 200-mL Schlenk flask. Aliquots were transferred by syringe. The concentration of the stock solution was determined by titration with phenolphthalein as indicator.

Preparation of Trimethylgold(III) Ylide Complexes. In a typical preparation, the ylide in Et_2O was added dropwise to an equimolar amount of Ph_3PAuMe_3 in ether at -78 °C with stirring. The mixture was allowed to warm to ambient temperature, and stirring was continued overnight. The mixture was then evaporated to yield a white residue which was recrystallized from a chloroform/pentane mixture.

Synthesis of Trimethyl(dimethylsulfonium methylide)gold(III), $Me_3AuCH_2SMe_2$. Sodium hydride (0.3 g) as a 57% mineral oil dispersion was placed in a 100-mL Schlenk flask and washed three times with 10-mL portions of ether to remove the mineral oil. The flask was then evacuated to remove the last traces of ether. The vacuum was broken, and 0.4 g of trimethylsulfonium chloride, 0.5 g of trimethyl(triphenylphosphine)gold(III), and 50 mL of the THF were introduced into the flask. The mixture was stirred at 0 °C for 3 days under argon. Stirring was interrupted, the solution filtered, and the filtrate evaporated to yield

---

[16] Seyferth, D.; Grim, S. O. *J. Am. Chem. Soc.* **1961**, *83*, 1610–1616.

[17] Zuckgraf, K. Dissertation, University of Heidelberg, 1968. Heydenreich, F. Dissertation, University of Ruhr, 1971 (see reference 8).

[18] Greco, A. *J. Organomet. Chem.* **1972**, *43*, 351–356.

[19] Kurras, E.; Rosenthal, U.; Mennenga, H.; Oehme, G. *Angew. Chem.* **1973**, *85*, 913; *Angew. Chem. Int. Ed. Engl.* **1973**, *12*, 854.

[20] Schmidbaur, H.; Franke, R. *Inorg. Chim. Acta* **1975**, *13*, 85–89. Schmidbaur, H. *Acc. Chem. Res.* **1975**, *8*, 62–69. Grey, R. A.; Anderson, L. R. *Inorg. Chem.* **1977**, *16*, 3187–3190.

[21] Heydenreich, F.; Mollbach, A.; Wilke, G.; Dreeskamp, H.; Hoffman, E. G.; Schroth, G.; Seevogel, K.; Stempfle, W. *Isr. J. Chem.* **1972**, *10*, 293.

[22] Manzer, L. *Inorg. Chem.* **1976**, *15*, 2567–2569.

[23] Kaska, W. C.; Richelderfer, R. F. *J. Organomet. Chem.* **1974**, *78*, C47–C50.

[24] Fackler, J. P., Jr.; Paparizos, C. *J. Am. Chem. Soc.* **1977**, *99*, 2363–2364 (first paper of this series).

[25] Brauer, G. "Handbook of Preparative Inorganic Chemistry"; *Academic Press*: New York, 1965.

[26] Koster, R.; Simic, D.; Grassberger, M. *Justus Liebigs Ann. Chem.* **1970**, *739*, 211–219.

[27] Roulet, R.; Lan, W.; Mason, W.; Fenske, A. *Helv. Chim. Acta* **1973**, *56*, 2405.

[28] Rice, G. W.; Tobias, R. S. *Inorg. Chem.* **1975**, *14*, 2402–2407.

[29] (a) Tamaki, A.; Kochi, J. K. *J. organomet. Chem.* **1973**, *51*, C39–C42. (b) *J. Chem. Soc., Dalton Trans.* **1973**, 2620–2626.

[30] Markham, R. T.; Dietz, E. A., Jr.; Martin, D. R. *Inorg. Synth.* **1976**, *16*, 153–155.

[31] Schmidbaur, H. *Inorg. Synth.* **1978**, *18*, 135–143.

[32] MacGillaury, C., Reich, O., Eds. "International Tables for X-ray Crystallography"; Kynoch Press: England, 1962.

Table I. Crystallographic Information

	Me_3AuPPh_3	$Me_3AuCH_2S(O)Me_2$	$Me_3AuCH_2PPh_3$
atomic formula	$AuC_{21}H_{24}P$	$AuC_6H_{17}SO$	$AuC_{22}H_{26}P$
fw	504.36	334.23	518.42
cryst dimens, mm^3	0.47 × 0.31 × 0.21	0.20 × 0.23 × 0.33	0.18 × 0.18 × 0.25
linear abs coeff μ,[a] cm^{-1}	77.0	155	76.1
radiation (Mo Kα)	0.710^{69}	0.710 69	0.710 73
cell constants			
a, Å	15.569 (8)	5.297 (1)	9.679 (2)
b, Å	12.652 (4)	10.953 (3)	19.477 (7)
c, Å	10.676 (9)	17.065 (5)	10.713 (3)
α, deg	103.70 (6)	90.00	90.00
β, deg	99.10 (6)	90.00	92.71 (2)
γ, deg	99.76 (4)	90.00	90.00
vol, Å^3	1969.9 (9)	990.6 (4)	2017.4 (9)
d_{calcd},[b] g/cm^3	1.69	2.24	1.706
Z	4	4	4
space group[32]	triclinic, $P\bar{1}$	orthorhombic,[c] $P2_12_12_1$	monoclinic, $P2_1/c$
unique data ($I/\sigma(I) > 3$)	3979	824	2838
R	0.074	0.089	0.044
R_w (statistical)	0.085	0.10	0.044
anisotropic atoms	Au, P (CH_3)	Au, S	Au

[a] No absorption corrections were applied. Although some improvement in refinement might be expected, the expense to information ratio was deemed too high. [b] Observed densities by flotation were very near the calculated value. [c] Refinement insufficient to determine absolute configuration.

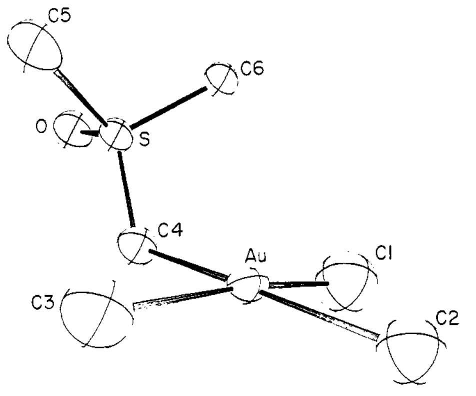


Figure 2. An ORTEP drawing (50% probability) of the structure of $(CH_3)_3AuCH_2S(O)(CH_3)_2$.

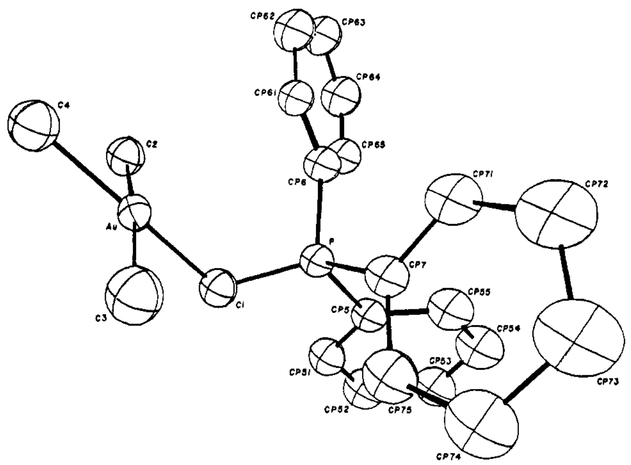


Figure 3. An ORTEP drawing (50% probability) of the structure of $(CH_3)_3AuCH_2P(C_6H_5)_3$.

a white residue. The precipitate was recrystallized from $CHCl_3$ to yield colorless crystals, mp 83–85 °C.

Structure Determinations. Crystallographic information is contained in Table I. Although the materials have not been studied sufficiently well to produce a truly satisfactory crystallographic result, a final difference Fourier showed no unexpected residuals, and none of these were larger than 1 e/Å^3. Also we did not refine $Me_3AuCH_2S(O)Me_2$ with inverted phasing in view of the crystal quality and the dominance of the scattering by gold. Absorption corrections could be expected to improve residuals but their expense, the overall quality of the crystals, and specific information to be gained from further refinement deemed additional study unwarranted.

Data for these crystallographic studies were obtained on a Syntex P2$_1$ diffractometer. Procedures followed for data handling and computer programs have been described previously.[33] Positional parameters for the three structures are given in Tables II–IV. Temperature factors are placed in appendix tables. Significant bond lengths and angles are recorded in Tables V–VII. Figures 1–3 are ORTEP drawings of the structures.

Physical Measurements and Instrumentation. Melting points were determined by using a Meltemp melting point apparatus and are reported uncorrected. Mass spectra were recorded on a Finnegan mass spectrometer using electron-impact ionization. Photoelectron spectra (ESCA) were obtained by using a Varian ICC spectrophotometer equipped with a high intensity anode and 620/L computer. Samples were prepared as finely ground powders dusted onto cellophane tape which was wrapped around gold cylinders. The binding energy for the Au ($4f_{7/2}$) level of the complex was calibrated vs. the Au ($4f_{7/2}$) line of a metallic gold dot vapor deposited onto the surface of the sample. For the binding energy of the Au ($4f_{7/2}$) line in the metal, a value of 84.00 eV relative to the Fermi level was used. Phosphorus ($2p_{3/2}$) and sulfur ($2p_{3/2}$) binding energies also were calibrated with the Au ($4f_{7/2}$) line of the vapor-deposited gold. Error is estimated at 0.15 eV. Ultraviolet photoelectron spectra (UPS) were recorded on a Perkin-Elmer Model PS18 spectrometer, using Xe (12.13 eV) as an internal calibrant. Error is estimated at 0.03 eV. ^1H NMR spectra were recorded on a Varian A-60A spectrometer using 1% Me_4Si as internal standard. ^{13}C and ^{31}P NMR spectra were recorded on a Varian XL-100 spectrometer with 1% Me_4Si and 85% H_3PO_4 as internal and external calibrants, respectively. All spectra were recorded by using deuterochloroform as the solvent, and all resonances are reported in the δ scale.

Results

Crystal and Molecular Structures. The molecular structures of Me_3AuPPh_3, $Me_3AuCH_2S(O)Me_2$, and $Me_3AuCH_2PPh_3$ are shown in Figures 1–3, respectively. For each molecule, the Au(III) atom is coordinated to three methyl groups and the base. The coordination about the gold in each complex is essentially square planar. Both ylide complexes contain average AuC_{sp^3} bond lengths of ~2.137 (13) Å, which is longer than the average 2.065 (15) Å AuC_{sp^3} bond length in Me_3AuPPh_3. In Me_3AuY (Y = PPh_3, CH_2PPh_3, $CH_2S(O)Me_2$) complexes, the Au–C_{sp^3} bond length of the methyl groups trans to Y is smaller than the Au–C_{sp^3} bond lengths for the methyl groups cis to Y.

In $MeAuPPh_3$[47] the Au–P distance [2.279 (8) Å] is, rather surprisingly, significantly shorter than the Au–P distance in the gold(III) complex. The long Au–P distance in Me_3AuPPh_3 undoubtedly is attributable to steric interactions between the phenyl

---

(33) Chen, H.-W.; Fackler, J. P., Jr. *Inorg. Chem.* **1978**, *17*, 22–26.

Table II. Atomic Coordinates[a, b] for $(CH_3)_3AuP(C_6H_5)_3$

atom	x/a	y/b	z/c
		Molecule 1	
Au$_1$	0.3871 (6)	0.5231 (1)	0.2652 (9)
P$_1$	0.2369 (4)	0.5287 (4)	0.2639 (5)
C$_{11}$	0.3599 (16)	0.4126 (19)	0.0759 (20)
C$_{21}$	0.4233 (16)	0.6338 (19)	0.4636 (23)
C$_{31}$	0.5084 (21)	0.5134 (23)	0.2706 (20)
C$_{111}$	0.2236 (12)	0.6714 (15)	0.3148 (17)
C$_{112}$	0.2704 (16)	0.7492 (21)	0.2628 (23)
C$_{113}$	0.2636 (18)	0.8622 (24)	0.2972 (26)
C$_{114}$	0.2100 (17)	0.8948 (22)	0.3860 (25)
C$_{115}$	0.1596 (15)	0.8190 (19)	0.4359 (21)
C$_{116}$	0.1688 (16)	0.7046 (18)	0.4024 (20)
C$_{121}$	0.1895 (13)	0.4537 (16)	0.3747 (18)
C$_{122}$	0.12494 (13)	0.4204 (16)	0.4662 (18)
C$_{123}$	0.2116 (15)	0.3595 (18)	0.5448 (21)
C$_{124}$	0.1221 (16)	0.3371 (20)	0.5343 (23)
C$_{125}$	0.0621 (16)	0.3678 (21)	0.4495 (24)
C$_{126}$	0.0984 (15)	0.4288 (19)	0.3645 (21)
C$_{131}$	0.1605 (15)	0.4698 (19)	0.1054 (20)
C$_{132}$	0.1360 (15)	0.5337 (19)	0.0269 (22)
C$_{133}$	0.0778 (22)	0.4819 (29)	−0.1022 (31)
C$_{134}$	0.0516 (20)	0.3706 (29)	−0.1362 (31)
C$_{135}$	0.0733 (19)	0.3032 (25)	−0.0620 (29)
C$_{136}$	0.1297 (18)	0.3508 (23)	0.0675 (26)
		Molecule 2	
Au$_2$	0.1297 (18)	0.3508 (23)	0.0675 (26)
P$_2$	0.2648 (4)	0.9800 (4)	0.8830 (5)
C$_{12}$	−0.0148 (19)	0.9731 (25)	0.7334 (25)
C$_{22}$	0.0683 (17)	0.8693 (20)	0.9017 (26)
C$_{32}$	0.1491 (19)	1.0871 (20)	0.6844 (23)
C$_{211}$	0.3502 (14)	1.0340 (18)	0.8065 (20)
C$_{212}$	0.3851 (16)	0.9616 (20)	0.7170 (22)
C$_{213}$	0.4521 (20)	1.0027 (26)	0.6521 (28)
C$_{214}$	0.4746 (20)	1.1215 (28)	0.6722 (30)
C$_{215}$	0.4384 (19)	1.1919 (26)	0.7508 (28)
C$_{216}$	0.3729 (17)	1.1512 (23)	0.8245 (25)
C$_{221}$	0.2829 (12)	0.8391 (15)	0.8790 (17)
C$_{222}$	0.2265 (14)	0.7546 (17)	0.7707 (19)
C$_{223}$	0.2421 (16)	0.6461 (21)	0.7553 (23)
C$_{224}$	0.3088 (17)	0.6256 (22)	0.8451 (25)
C$_{225}$	0.3678 (18)	0.7116 (23)	0.9461 (25)
C$_{226}$	0.3514 (15)	0.8220 (20)	0.9609 (21)
C$_{231}$	0.3003 (13)	1.0640 (16)	1.0545 (18)
C$_{232}$	0.2354 (13)	1.0880 (17)	1.1243 (19)
C$_{233}$	0.2600 (14)	1.1520 (18)	1.2599 (20)
C$_{234}$	0.3481 (16)	1.1915 (20)	1.3154 (23)
C$_{235}$	0.4132 (17)	1.1709 (22)	1.2467 (25)
C$_{236}$	0.3918 (14)	1.1074 (17)	1.1095 (19)

[a] Numbers in the parentheses are the standard deviations estimated for the final least-squares refinement cycle. (See ref 52.) [b] Thermal parameters are obtainable in the Ph.D. Thesis of P. Paparizos, Cas Western Reserve University 1977.

Table III. Atomic Coordinates[a, b] for $(CH_3)_3AuCH_2S(O)(CH_3)_2$

atom	x/a	y/b	z/c
Au	0.1507 (3)	0.1371 (1)	0.1834 (1)
S	−0.0632 (22)	−0.0764 (10)	0.066 (6)
O	−0.2762 (66)	−0.1470 (28)	0.0330 (17)
C$_1$	0.103 (11)	0.028 (5)	0.287 (3)
C$_2$	0.438 (12)	0.230 (5)	0.246 (3)
C$_3$	0.228 (10)	0.262 (4)	0.088 (2)
C$_4$	−0.145 (10)	0.045 (7)	0.122 (2)
C$_5$	0.137 (10)	−0.027 (4)	−0.009 (3)
C$_6$	0.147 (9)	−0.174 (10)	0.124 (2)

[a] Numbers in parentheses are standard deviations estimated from the final least-squares refinement. [b] Thermal parameters are available in the Ph.D. Theses of J. Stein, CAse Western Reserve University, 1979.

rings and the cis methyl groups in Me_3AuPPh_3. The Au–C distance[47] in $MeAuPPh_3$ [2.124 (28) Å] is slightly longer than the Au–C distances in Me_3AuPPh_3, as expected for gold(I) compared[48] with those for gold(III).

Table IV. Atomic Coordinates[a, b] for $(CH_3)_3AuCH_2P(C_6H_5)_3$

atom	x/a	y/b	z/c
Au	0.07401 (4)	0.15242 (2)	0.32002 (4)
P	0.3213 (3)	0.1388 (2)	0.1201 (3)
C$_1$	0.2376 (13)	0.1964 (6)	0.2174 (11)
C$_2$	0.2145 (15)	0.1337 (7)	0.4768 (12)
C$_3$	−0.0775 (16)	0.1746 (7)	0.1728 (14)
C$_4$	−0.0832 (15)	0.1112 (7)	0.4286 (12)
CP$_5$	0.4654 (12)	0.1770 (6)	0.0436 (11)
CP$_{51}$	0.5089 (14)	0.2429 (7)	0.0815 (12)
CP$_{52}$	0.6232 (16)	0.2713 (8)	0.0207 (14)
CP$_{53}$	0.6886 (15)	0.2359 (7)	−0.0746 (13)
CP$_{54}$	0.6438 (16)	0.1709 (8)	−0.1057 (14)
CP$_{55}$	0.5269 (14)	0.1403 (7)	−0.0507 (12)
CP$_6$	0.3877 (12)	0.0657 (6)	0.2084 (11)
CP$_{61}$	0.2944 (12)	0.0202 (6)	0.2594 (10)
CP$_{62}$	0.3408 (14)	−0.0333 (7)	0.3346 (12)
CP$_{63}$	0.4872 (14)	−0.0434 (7)	0.3573 (12)
CP$_{64}$	0.5782 (16)	0.0032 (7)	0.3065 (14)
CP$_{65}$	0.5306 (13)	0.0566 (7)	0.2326 (12)
CP$_7$	0.2079 (12)	0.1088 (6)	−0.0076 (10)
CP$_{71}$	0.1901 (13)	0.0394 (7)	−0.0350 (12)
CP$_{72}$	0.1064 (14)	0.0209 (7)	−0.1422 (12)
CP$_{73}$	0.0417 (14)	0.0712 (7)	−0.2149 (13)
CP$_{74}$	0.0568 (14)	0.1398 (6)	−0.1881 (12)
CP$_{75}$	0.1428 (12)	0.1607 (6)	−0.0811 (11)

[a] Numbers in parentheses are standard deviations estimated from the final least-squares refinement. [b] Thermal parameters are available in the Ph.D. Thesis of J. Stein, Case Western Reserve University, 1977.

Table V. Significant Bond Lengths and Angles in Me_3AuPPh_3[a]

		Lengths, Å		
AuI–P$_1$	2.350 (6)	Au$_2$–P$_2$	2.347 (6)	2.35[b]
–C$_{31}$(trans)	1.923 (33)	–C$_{12}$(trans)	2.029 (28)	1.98[b]
–C$_{11}$	2.100 (19)	–C$_{22}$	2.111 (27)	2.11[b]
–C$_{21}$	2.168 (22)	–C$_{32}$	2.057 (27)	2.11[b]
average C–C in phenyl groups = 1.40				
average P–C to phenyl groups = 1.82				
		Angles, Deg		
P$_1$–Au$_1$–C$_{11}$	94.0	P$_2$–Au$_2$–C$_{22}$	91.5	92.8[b]
P$_1$–Au$_1$–C$_{31}$	177.7	P$_2$–Au$_2$–C$_{12}$	174.2	176.0[b]
P$_1$–Au$_1$–C$_{21}$	89.4	P$_2$–Au$_2$–C$_{32}$	94.7	92.1[b]
average Au–P–C(phenyl) = 113.8				

[a] Estimated standard deviations are shown in parentheses. [b] Average values.

Table VI. Significant Lengths and Angles of $Me_3AuCH_2S(O)Me_2$[a]

	Lengths, Å		
Au–C$_3$	2.16 (4)	S–O	1.48 (3)
Au–C$_2$(trans)	2.13 (5)	S–C$_5$	1.75 (4)
Au–C$_1$	2.14 (5)	S–C$_4$	1.68 (6)
Au–C$_4$(ylide)	2.12 (6)	S–C$_6$	1.82 (4)
	Angles, Deg		
C$_3$–Au–C$_2$	93.8 (25)	O–S–C$_5$	109.7 (19)
Au–C$_4$–S	117.2 (34)	O–S–C$_4$	115.5 (22)
C$_3$–Au–C$_1$	172.7 (25)	C$_5$–S–C$_4$	108.8 (25)
C$_2$–Au–C$_1$	93.1 (27)	O–S–C$_6$	111.3 (18)
C$_3$–Au–C$_4$	86.8 (26)	C$_5$–S–C$_6$	102.0 (21)
C$_2$–Au–C$_4$	178.6 (28)	C$_4$–S–C$_6$	108.6 (25)
C$_1$–Au–C$_4$	86.1 (27)		

[a] Estimated standard deviations are shown in parentheses.

The geometries around the phosphorus atom in Me_3AuPPh_3 and $Me_3AuCH_2PPh_3$ are approximately tetrahedral. In Ph_3PCH_2, the C_{Ph}–P–C_{Ph} bond angle is 105.0° and the C_{Ph}–P–C_{CH_2} bond angles is 113.5°.[34] Phosphonium salts also contain a tetrahedral phosphorus atom. In $Me_3AuCH_2S(O)Me_2$, the geometry around the sulfur atom is tetrahedral.

---

(34) Bart, J. C. J. *J. Chem. Soc. B* **1969**, 350–365.

(35) Pauling, L. "Nature of the Chemical Bond", 2nd ed.; Cornell University Press: Ithaca, N.Y. 1948; p 164.

Table VII. Significant Bond Lengths and Angles in $Me_3AuCH_2PPh_3$

	Lengths, Å		
Au–C_1(ylide)	2.149 (13)	P–C_1	1.755 (13)
Au–C_2	2.142 (13)	P–CP_5	1.811 (12)
Au–C_3	2.146 (15)	P–CP_6	1.811 (12)
Au–C_4(trans)	2.117 (14)	P–CP_7	1.811 (11)
average C–C(phenyl) = 1.40 (2)			
	Angles, Deg		
C_1–Au–C_2	90.79 (61)	C_1–P–CP_5	113.17 (59)
C_1–Au–C_3	92.20 (63)	C_1–P–CP_6	110.81 (59)
C_1–Au–C_4	177.40 (62)	C_1–P–CP_7	111.99 (58)
Au–C_1–P	114.89 (71)	CP_6–P–CP_7	109.17 (56)

Table VIII. Electron-Binding Energies of Organogold Complexes (eV)

compd	Au ($4f_{7/2}$)[c]	P ($2p_{3/2}$)	S ($2p_{3/2}$)
$Me_3AuCH_2PMe_3$	85.15	132.3	
$(Me_3)_3AuCH_2SMe_2$	85.30		165.8
$(Me_3)_3AuCH_2S(O)Me_2$	85.50		168.2
$(CH_3)_3AuPPh_3$	85.95	131.6	
$(CH_3)_3AuCH_2PPh_3$	85.25	132.4	
$KAuCl_4$	87.60[a]		
$[Au(CH_2)_2PEt_2Br]_2$	86.20[a]		
$[Au(CH_2)_2PEt_2]_2$	84.70[a]		
RbAu, CsAu	82.70[b]		
Au^0	84.00		

[a] References 28, 37, and 38. [b] Knecht, J.; Fischer, R.; Overhof, H.; Hensel, F. *J. Chem. Soc., Chem. Commun.* 1978, 905–906. [c] Au ($4f_{7/2}$) energies referred to Au^0 at 84.00 eV. See also ref 36.

The bond lengths and bond angles of the phenyl rings in Me_3AuPPh_3 and $Me_3AuCH_2PPh_3$ are normal. All phenyl rings are planar within experimental error.

In $Me_3AuCH_2PPh_3$, the C_{CH_2}–P bond length is 1.755 (13) Å which is shorter than the 1.811 (12)-Å bond length for the average P–C_{Ph} bond. Thus, the C_{CH_2}–P bond length is slightly shorter than expected for a single bond but longer than expected for a double bond (1.67 Å). The P—$C_{CH(CH_3)}$ bond lengths in $(CO)_3NiCH(CH_3)P(C_6H_{11})_3$[21] is identical with that in $Me_3AuCH_2PPh_3$. The P–C_{CH_2} bond lengths in $(Cu(CH_2)_2PMe_2)_2$[9] are also similar. In Ph_3PCH_2,[34] the P–C_{CH_2} bond length is 1.661 (8) Å, which clearly indicates that the methylene carbon is sp^2 hybridized. Thus, the increased bond length of the P–C_{CH_2} bond in the ylide complexes indicates that these methylene carbons are best described as sp^3 hybridized. In $Me_3AuCH_2S(O)Me_2$, the S–C_{CH_2} bond length of 1.68 Å is shorter than the S–C_{CH_3} single bond in Me_2S (1.81 Å) but greater than the sum of the double-bond radii of carbon and sulfur,[36] 1.605 Å.

ESCA Results. In Table VIII are presented the results of ESCA studies on organogold complexes. It is evident that upon increasing the oxidation state of the gold, the binding energy also increases as anticipated. It is also apparent that gold(III) ylide complexes have smaller Au ($4f_{7/2}$) binding energies than do gold(III) phosphine complexes. Thus ylides more effectively reduce the charge on gold than do phosphines. The lower binding energies of gold in gold(III) phosphoranes compared with trimethylgold(III) dimethyloxosulfonium methylide may be attributed to the fact that oxosulfuranes contain the electronegative oxygen atom which contributes to making them somewhat less effective than the phosphoranes and sulfuranes in reducing the charge on gold(III).

UPS Results. The ultraviolet photoelectron spectroscopy results are presented in Table IX for a series of gold complexes. It is seen that the first ionization potential for the gold(III) complexes is lower than for the gold(I) complexes. This may be attributed to the destabilizing effect of two mutually trans methyl groups in the gold(III) complexes which causes the σ(Au–C) ionization potential to be lowered.[40] There is little difference between the 5d ionization potentials of gold(III) and gold(I) complexes. As expected, the 5d ionization potential of the gold(III) ylide complex is slightly lower than it is in the gold(III) phosphine complexes.

Table IX. Vertical Ionization Potentials of Gold Complexes (eV)

compd	σ(Au–C)	π(Ph)	5d
$MeAuPMe_3$[a]	8.27		9.34
			9.95
			10.63
			10.45
Me_3AuPMe_3[a]	7.80		10.18
	8.63		10.70
			11.06
$Me_3AuPMePh_2$[a]	7.64	9.48	9.98
	8.34		10.56
			10.98
$Me_3AuCH_2S(O)Me_2$	7.77		9.93
	8.66		10.56
			10.91

[a] From ref 40.

NMR Results. Tables X and XI present the results of ^1H NMR and ^{13}C NMR studies of organogold complexes. It is apparent that the proton resonance for the methylene group in ylides is shifted downfield upon complexation (becomes more like terminal CH_3 groups). These chemical shifts suggest that the phosphorus atom is more positively charged in the metal-bound ylide than in the uncomplexed ligand. Analogously, the ^{13}C NMR spectra also indicates that the methylene carbon in complexed ylides relative to uncomplexed ylides is shifted downfield (less shielded).

Discussion

Organogold(III) ylide complexes can be synthesized[20] according to the substitution reaction eq 1, where Y = $CH_2S(O)Me_2$,

$$Y + Me_3AuPPh_3 \xrightarrow[THF]{} Me_3AuY + PPh_3 \qquad (1)$$

CH_2PPh_3, CH_2PMe_3, or CH_2SMe_2. The square-planar structures of these complexes have been confirmed here (Y = $CH_2S(O)Me_2$, CH_2PPh_3) by X-ray crystallography. The ^1H and ^{13}C NMR results are consistent with the presence of three different environments for the carbon atoms bound to the metal.

Acids such as acetic, HOAc, cleave a methyl group to produce primarily cis product according to eq 2. The rate of acetolysis

$$Me_3AuY + HOAc \rightarrow \textit{cis}\text{-}Me_2AuY(OAc) + CH_4 \qquad (2)$$

of gold(III) ylide complexes is increased relative to gold(III) phosphine complexes. Kochi[43] has suggested that "ease of oxidation of the alkyl metal apparently is a factor in ... hydrogen transfers." He suggests that the observed trend Me_3AuPMe_3 > $Me_3AuPMePh_2$ > Me_3AuPPh_3 can be accommodated by a chain process proceeding via "either the formation of a five-coordinate intermediate or one involving electron transfer." The trends we have observed in acetolysis rates and electronic structures are consistent with the observations of Kochi. The presence of the positively charged onium center on the ligand with the concommitant increase in electron density at the metal also may contribute to the initial protonation at the metal center. The onium center and the resultant dipole product furthermore can influence the overall thermal stability (to loss of methane, ethane, etc.) of the ylide complexes. (Because of the basicity of the ylide ligands, the thermal stability of the organometallic ylide complexes initially appeared to be inconsistent with the Kochi electron-transfer

---

(36) Basch, H. *Chem. Phys. Lett.* **1970**, *5*, 337–339.

(37) McNeillie, A.; Brown, D.; Smith, W. E.; Gibson, M.; Watson, L. *J. Chem. Soc., Dalton Trans.* **1980**, 767–770.

(38) Van de Vonde, D. F.; Van der Kelen, G. P.; Schmidbaur, H.; Wolleben, A.; Wagner, F. E. *Phys. Scr.* **1977**, *16*, 364–366.

(39) Swartz, W.; Hercules, D. *Anal. Chem.* **1971**, *43*, 1066.

(40) Puddephatt, R. "The Chemistry of Gold"; Elsevier: New York, 1978.

(41) Albright, T.; Freeman, W.; Schweizer, E. *J. Am. Chem. Soc.* **1975**, *97*, 940–942.

(42) Schmidbaur, H.; Buchner, W.; Scheutzow, D. *Chem. Ber.* **1973**, *106*, 1251–1255.

(43) Kochi, J. K., 1, p 361.

Table X. ^1H NMR of Ylides and Organogold Complexes

complex	$\delta_{cis}(CH_3)$	$\delta_{trans}(CH_3)$	$\delta(CH_2)$	other
$Me_3AuCH_2SOMe_2$	−0.01	0.57	2.84	$\delta(SCH_3)$ 3.38
CH_2SOMe_2[a]			1.92	δ(Me) 2.95
$Me_3AuCH_2SMe_2$	−0.11	0.35	1.90	δ(SMe) 2.49
$Me_3AuCH_2PPh_3$	−0.41	0.47	1.73 (^2J = 14 Hz)	$\delta(PPh_3)$ 7.55
CH_2PPh_3[b]			0.13 (^2J = 8 Hz)	δ(Ph) 7.6
Me_3AuPPh_3	0.04	1.11		δ(Ph) 7.55
$Me_3AuP(C_6H_{11})_3$	0.05	0.77		$\delta(P(C_6H_{11})_3)$ ~2
$Me_3AuCH_2PMe_3$	−0.13	0.31	0.88 (^2J = 14.3 Hz)	$\delta(PMe_3)$ 1.63
CH_2PMe_3[c]			−0.40 (^2J = 6.5 Hz)	δ(Me) 1.36 (^2J = 12.5 Hz)

[a] Reference 53. [b] Reference 26. [c] Reference 42.

Table XI. ^{13}C NMR of Ylides and Organogold Complexes

complex	$\delta_{cis}(CH_3)$	$\delta_{trans}(CH_3)$	CH_2	other
Me_4Au	5.1			
$Me_3AuCH_2SOMe_2$	7.1	13.1	44.3	$\delta(SCH_3)$ 45.2
$CH_2S(O)Me_2$[a]			32.8	δ(Me) 44.7
$Me_3AuCH_2SMe_2$	4.5	9.0	31.6	$\delta(SCH_3)$ 33.4
$Me_3AuCH_2PPh_3$	4.06	9.2	5.45 (^1J = 30 Hz)	$\delta(PPh_3)$ 128–133
CH_2PPh_3[b]			−4.1 (^1J = 51.9 Hz)	$\delta(PPh_3)$ 128–132
$Me_3AuCH_2PMe_3$	5.5	9.1	10.1 (^1J = 4 Hz)	$\delta(PMe_3)$ 14.8 (^1J = 5.6 Hz)
CH_2PMe_3[c]			−1.5 (^1J = 90 Hz)	$\delta(PMe_3)$ 19.7 (^1J = 56 Hz)
Me_3AuPPh_3	11.9	16.0		$\delta(PPh_3)$

[a] Reference 53. [b] Reference 41. [c] Reference 42.

mechanism for their decomposition).

With ylide complexes of the type described here a large permanent dipole moment is produced due to the presence of the positively charged heteroatom (the onium center). Hence although the metal atom is effectively reduced in the gold(III) ylide complexes compared with the phosphines and the electron binding energy is lowered, there are bound electron states available. This must happen whenever[44] the dipole moment exceeds 1.60 D. Consequently, the electron-loss mechanism for organometallic decomposition probably becomes less effective as a decomposition pathway in these charge-separated species than in the neutral compounds.

The structural trans effect, STE,[54] observed in this series of Me_3AuX complexes, wherein the Au–C_{sp^3} distance decreases in the order cis > trans (ylide) > trans (phosphine), appears to reflect both the electron-donating ability of carbon relative to phosphorus and the presence of the positively charge onium center. The methylene group of the ylide, as a result of its proximity to the charge center, does not exert as strong a σ STE as the CH_3^- group. This STE or trans influence also appears in the NMR spectra

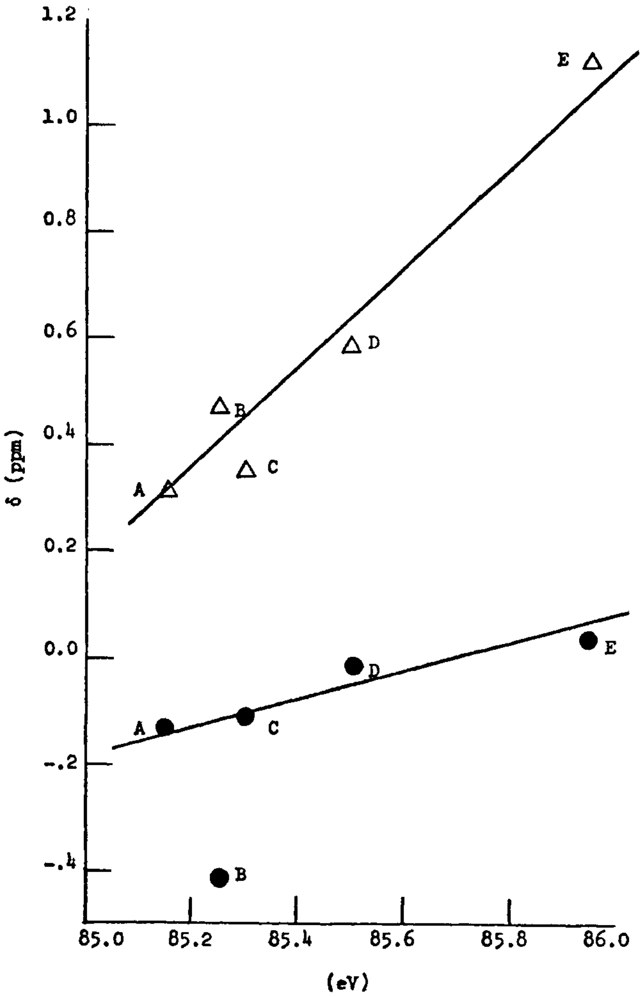


Figure 4. A plot of ^1H NMR chemical shifts (δ) of CH_3Au vs. Au ($4f_{7/2}$) binding energies: trans, △, cis, ○; A, $(CH_3)_3AuCH_2PMe_3$; B, $(CH_3)_3AuCH_2PPh_3$; C, $(CH_3)_3AuCH_2SMe_2$; D, $(CH_3)_3AuCH_2S(O)Me_2$; E, $(CH_3)_3AuPPh_3$.

---

(44) Garrett, W. R. *J. Chem. Phys.* **1978**, *68*, 2621. Landau, L. D.; Lifschitz, E. M. "Quantum Mechanics", 2nd ed.; Pergamon Press: London, 1965; p 113.

(45) Ostoga-Starzewski, K.; Bock, H. *J. Am. Chem. Soc.* **1976**, *98*, 8486–8499. See also ref 46.

(46) Mason, J. *Adv. Inorg. Chem. Radiochem.* **1979**, *22*, 199–237.

(47) Gavens, P. D.; Guy, J. J.; Mays, M. J.; Sheldrick, G. M. *Acta Crystallogr., Sect. B* **1977**, *B33*, 137–139.

(48) The Au–CH_2 distances observed here for the gold(III) complexes are somewhat shorter than the Au–CH_2 distances found in the gold(I) and gold(II) complexes $Au_2[(CH_2)_2PMe_2]_2$,[49] $Au_2[(CH_2)_2PEt_2]_2$,[50] $Au_2Cl_2[(CH_2)_2P(Et)_2]_2$,[51] and $Au_2I_2[(CH_2)_2P(Me)_2]_2$.[49]

(49) Fackler, J. P., Jr.; Chen. H.-W., unpublished results.

(50) Schmidbaur, H.; Mandl, J. E.; Richter, W.; Bejenke, V.; Frank, A.; Huttner, G. *Chem. Ber.* **1977**, *110*, 2236–2237.

(51) Schmidbaur, H.; Mandl, J. E.; Frank, A.; Huttner, G. *Chem. Ber.* **1976**, *109*, 466–469. The published values of the signs for several of the coordinates are incorrect in this paper. Professor George Sheldrick has corrected them as follows: Au, +++; Cl, +++; P, ++−; Cl, ++−; C2, ++−; C3, ++−; C4 −+−; C5, ++−; C6, −+−.

(52) The structural results are not entirely satisfactory for this compound due in part to poor crystal quality. The average bond lengths and angles appear consistent with normal values, however. There is a distinct possibility that better crystals might show an expected higher symmetry. We were unable to obtain such crystals.

(53) Schmidbaur, H.; Richter, W. *Z. Anorg. Allg. Chem.* **1977**, *429*, 222–224.

(54) Elder, R. C.; Kennard, G. J.; Payne, M. D.; Deutsch, E. *Inorg. Chem.* **1978**, *17*, 1296–1303. Unfortunately the STE differences between the two ylide complexes studied here cannot be assessed from the X-ray data due to the high standard deviations in Au–C distances. The NMR data suggests, however, CH_3^- > CH_2PMe_3 > CH_2SME_2 > CH_2PPh_3 > $CH_2S(O)Me_2$ > $P(C_6H_{11})_3$ > PPh_3.

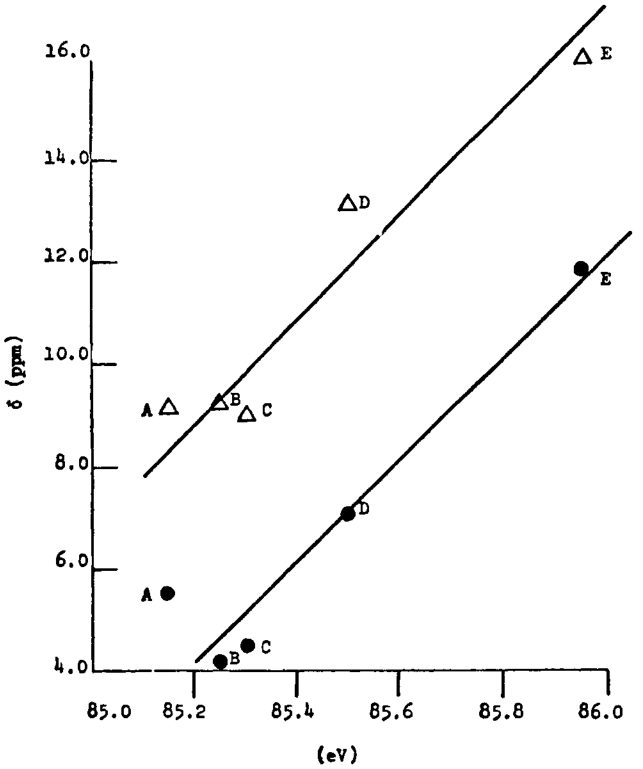
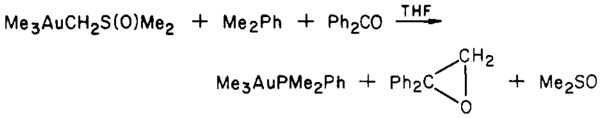


Figure 5. A plot of ^{13}C NMR chemical shifts (δ) of CH_3Au vs. Au ($4f_{7/2}$) binding energies: trans, △, cis, ○; A, $(CH_3)_3AuCH_2PMe_3$; B, $(CH_3)_3AuCH_2PPh_3$; C, $(CH_3)_3AuCH_2SMe_2$; D, $(CH_3)_3AuCH_2S(O)Me_2$; E, $(CH_3)_3AuPPh_3$.

of the complexes wherein the ^1H and ^{13}C resonances for the trans CH_3 groups are downfield (less shielded) relative to the position of the cis CH_3 resonances.

Strongly basic phosphines displace[55] the ylide in trialkylgold(III) sulfur ylide complexes. The displaced ylide can undergo reactions with carbonyls and other functional groups via typical ylide reaction, 3. In the absence of the methylene scavenger (Ph_2CO), ethylene and Me_2SO are the products of the above sulfur ylide



(3)

reaction. Trialkylgold(III) phosphoranes appear to be less reactive to substitution by phosphines.

The organogold(III) ylide complexes show remarkable air and thermal stability. They may be stored in the dark at 0 °C in the solid state for several months without noticeable decomposition. In addition to the fact that β-elimination cannot occur and electron loss may be prevented by the charge separation, the stability of organogold(III) ylide complexes relative to species such as trimethylgold(III) triphenylphosphine arises from the small extent the ylide is dissociated from the metal complex in the absence of strong bases. There appears to be no readily accessible pathway for reductive elimination, a process thought to involve[43] the three-coordinate Me_3Au species.

It has been stated[45] that "nuclear magnetic resonance and ESCA may be considered analogous in that NMR measures the magnetic shielding of the nucleus by the electrons from an external field while ESCA measures the electrostatic shielding of a photoelectron as it is removed from the atom." Basch[36] has proposed that the diamagnetic contribution to the nuclear shielding can be related to the difference in potential felt by an atom in chemically different environments. This prediction has been borne out in the linear correlation of $P(2p_{3/2})$ binding energies with ^{31}P NMR chemical shifts for phosphonium salts.[39]

We have observed that the Au ($4f_{7/2}$) binding energies correlate well with the ^1H and ^{13}C NMR chemical shifts of the cis and trans methyl groups of trimethylgold(III) complexes (Figures 4 and 5). Larger binding energies are expected when the electron density on the gold atom is lowered. This also results in less shielding of the methyl groups. Paramagnetic terms, however, can interfere with this correlation between ESCA and NMR spectra. The good correlation observed here suggests that paramagnetic effects are unimportant in these complexes. However, the cis methyl groups of $Me_3AuCH_2PPh_3$ do behave anomalously. This exception is likely a consequence of the short intramolecular contact (3.42 Å) between the cis methyl and phenyl carbon atoms and the shielding effects of the rings.

Acknowledgment. This work was supported by the National Science Foundation Grant CHE76-18709. We also thank Professor Alan Cowley, University of Texas, Austin, for obtaining the UV photoelectron spectra reported here. We wish to thank Professor George Nazaroff, Indiana University at South Bend, for pointing out what theoretical work exists on the critical binding of an electron to a electric dipole.

Supplementary Material Available: Thermal parameters for each of the structures along with observed and calculated factors (23 pages). Ordering information is given on any current masthead page.

---

(55) Phosphines also may induce the cleavage of S–C or P–C bonds to produce an alkylidene species Me_3AuCH_2 which then reacts with the carbonyl group to form products. Schrock[56] has observed alkylidene formation with Ta using ylides. We have no solid evidence to support or reject this possibility with gold. The reaction chemistry does appear to mimic the chemistry of the free ylide, however. We have not successfully displaced a phosphorus ylide to date. A free phosphorus ylide will produce a Wittig product not the epoxide. A common alkylidene intermediate might be expected to give the same products for both $Me_3AuCH_2S(O)Me_2$ and $Me_3AuCH_2PPh_3$.

(56) Schrock, R. R. *Acc. Chem. Res.* **1979**, *12*, 98–104.

(57) Blaschke, G.; Schmidbaur, H.; Kaska, W. C. *J. Organomet. Chem.* **1979**, *182*, 251–255.