Organometallics **1990**, *9*, 1973–1975

Organosilver Complexes. Synthesis and Crystal Structure of the Ylide Disilver Complex $[AgCH_2P(S)Ph_2]_2$

Suning Wang, John P. Fackler, Jr.,* and Thomas F. Carlson

Department of Chemistry and Laboratory for Molecular Structure and Bonding, Texas A&M University, College Station, Texas 77843

Received May 31, 1989

Summary: A dimeric silver(I) complex, $[Ag(CH_2PPh_2S)]_2$ (**1**), was obtained by the reaction of $Li(CH_2PPh_2S)$ with $AgNO_3$ in THF solution at −78 °C. The X-ray crystal structure of **1** shows that the ylide ligand CH_2PPh_2S bridges two Ag^I atoms with a Ag^I–Ag^I separation of 2.990 (2) Å. **1** has a one-dimensional chain structure in the solid with an intermolecular Ag–Ag separation of 3.227 (2) Å.

Organometallic complexes of coinage metals have attracted much attention due to their special roles in medicine and industry. Dimeric and polymeric coinage metal complexes are of special interest to us. A variety of dimeric and polymeric organogold compounds and their unusual redox reactions have been reported.[1] Compared with the rich chemistry of organogold complexes, very little is known about organosilver compounds.[2] One of the major difficulties encountered in organosilver chemistry is the poor stability of the compounds.[2] The ability of ylide ligands to stabilize organometallic compounds was recognized a decade ago.[1] Schmidbaur reported[3] the first stable ylide-bridged Ag^I dimer, $[(CH_3)_2P(CH_2)_2]_2Ag_2$, in 1973. This compound was characterized by ^1H NMR and ^{31}P NMR spectroscopies. However, the first crystal structure of a dinuclear silver complex with an ylide (stabilized) ligand, $[CH(COOC_2H_5)]_2PPh_2$, was not reported until recently.[4] We describe here the synthesis, crystal structure, and spectroscopic studies of a new silver ylide dimer, $[Ag(MTP)]_2$ (MTP = $[CH_2P(S)Ph_2]^-$), 1. It has a one-dimensional chain structure in the solid.

Results and Discussion

Reaction of[5] LiMTP with $AgNO_3$ in a 1:1 ratio in THF solution at −78 °C with the exclusion of light under a N_2 atmosphere produced the colorless compound $[AgMTP]_2$ (1) in 44% yield. 1 is stable for a few hours in solution at 22 °C. The crystals[6] of 1 are stable for about 3 days at 22 °C in air and decompose at 115 °C. Crystals of 1 luminesce with a yellow color at 77 K when subjected to UV irradiation. Single crystals of 1 suitable for X-ray diffraction analysis were obtained by recrystallization of 1 from CH_2Cl_2/diethyl ether at 0 °C.

Table I. Crystallographic Data for $[Ag(CH_2PPh_2S)]_2$ (1)

formula	$C_{26}H_{24}Ag_2S_2P_2$
fw	678.3
space group	*C*2/*c*
a, Å	24.20 (1)
b, Å	9.067 (4)
c, Å	12.101 (6)
β, deg	105.79 (1)
V, $Å^3$	2555 (2)
Z	4
d_{calc}, g cm^{-3}	1.76
cryst size, mm	0.10 × 0.20 × 0.40
F(000), e	1344
μ(Mo Kα), cm^{-1}	17.9
radiation (Mo Kα), α	0.71069
temp, °C	22
scan method	Wyckoff
2θ range, deg	2–45
total no. of reflns measd	1735
o of reflns, $F^2 \geq 3\sigma(F^2)$	1001
no. of params refined	121
transmissn factor: max, min	0.875, 0.748
R^a	0.0397
$R_w{}^b$	0.0439
goodness-of-fit indicator[c]	1.214
largest shift/esd, final cycle	0.000
largest peak, e $Å^{-3}$	0.64

[a] $R = \sum \| |F_o| - |F_c| \| / \sum |F_o|$. [b] $R_w = [\sum w(|F_o| - |F_c|)] / \sum w |F_o|$; $w^{-1} = \sigma^2(|F_o|) + |g|F_o{}^2$; $g = 0.00038$. [c] Goodness of fit $= [\sum w(|F_o| - |F_c|)^2 / (N_o - N_p)]^{1/2}$.

Table II. Atomic Coordinates (×10^4) and Isotropic Thermal Parameters ($Å^2$ × 10^3)[a]

atom	*x*	*y*	*z*	$U_{iso}{}^b$
Ag	124 (1)	4682 (1)	3879 (1)	41 (1)
S	545 (1)	7045 (3)	3818 (2)	52 (1)
P	764 (1)	7676 (3)	5469 (2)	30 (1)
C	211 (4)	7562 (10)	6199 (8)	30 (4)
C(11)	1421 (3)	5954 (8)	7312 (6)	48 (5)
C(12)	1923 (3)	5252 (8)	7930 (6)	58 (5)
C(13)	2412 (3)	5285 (8)	7530 (6)	64 (5)
C(14)	2398 (3)	6021 (8)	6510 (6)	64 (6)
C(15)	1896 (3)	6723 (8)	5891 (6)	49 (5)
C(16)	1408 (3)	6689 (8)	6292 (6)	31 (4)
C(21)	1281 (3)	10050 (7)	4634 (5)	44 (4)
C(22)	1484 (3)	11493 (7)	4654 (5)	53 (5)
C(23)	1412 (3)	12477 (7)	5490 (5)	54 (5)
C(24)	1137 (3)	12018 (7)	6306 (5)	49 (5)
C(25)	934 (3)	10575 (7)	6285 (5)	41 (4)
C(26)	1007 (3)	9591 (7)	5449 (5)	30 (3)

[a] Estimated standard deviations in the least significant digits are given in parentheses. [b] The equivalent isotropic *U* is defined as one-third of the trace of the U_{ij} tensor.

Table III. Bond Lengths (Å)[a]

Ag–S	2.382 (3)	Ag–Ag′	2.990 (2)
Ag–Ag″	3.227 (2)	Ag–C′	2.183 (9)
S–P	2.007 (4)	P–C	1.795 (11)
P–C(16)	1.836 (7)	P–C(26)	1.835 (7)

[a] Estimated standard deviations in the least significant digits are given in parentheses.

The molecular structure of 1 is shown in Figure 1. Crystallographic data are given in Table I. Atomic positional and thermal parameters are given in Table II. The

---

[1] (a) Basil, J. D.; Murray, H. H.; Fackler, J. P., Jr.; Tocher, J.; Mazany, A. M.; Bancroft, B. T.; Knachel, H.; Dudis, D.; Delord, T. J.; Marler, D. O. *J. Am. Chem. Soc.* **1985**, *107*, 6908. (b) Murray, H. H.; Briggs, D. A.; Garzon, G.; Raptis, R. G.; Porter, L. C.; Fackler, J. P., Jr. *Organometallics* **1987**, *6*, 1992. (c) Schmidbaur, H. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 907. (d) Schmidbaur, H.; Slawisch, A. *Gmelin Handbuch der Anorganischen Chemie*, 8th ed.; Springer-Verlag: Berlin, 1980; Organogold Compounds.

[2] (a) *Gmelin Handbuch der Anorganischen Chemie*; Springer-Verlag: Berlin, 1975; Vol. 61, Part B5. (b) *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Eds.; Pergamon Press: Oxford, England, 1982; Vol. 2.

[3] Schmidbaur, H.; Adlkofer, J.; Büchner, W. *Angew. Chem., Int. Ed. Engl.* **1973**, *12*, 415.

[4] Vicente, J.; Chicote, M. T.; Saura-Llamas, I. *Organometallics* **1989**, *8*, 767.

[5] (a) Seyferth, D.; Welch, D. E. *J. Organomet. Chem.* **1964**, *2*, 1. (b) Seyferth, D.; Welch, D. E.; Heeren, J. K. *J. Am. Chem. Soc.* **1963**, *85*, 642.

[6] Elemental analysis for 1 was unsuccessful due to decomposition.

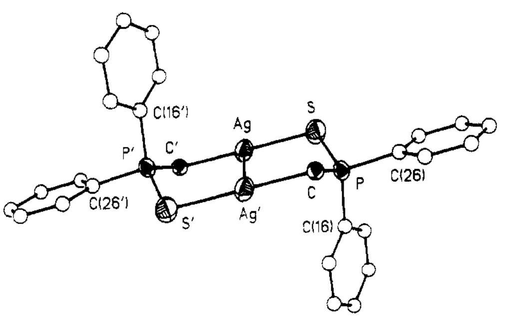

Figure 1. Molecular structure of 1 showing 50% thermal ellipsoids. Selected bond lengths (Å) and angles (deg) are as follows: Ag-Ag' = 2.990 (2), Ag-S = 2.382 (3), Ag-C' = 2.183 (9), S-P = 2.007 (4), P-C = 1.795 (11); S-Ag-C' = 173.7 (3), Ag-S-P = 103.0 (2), S-P-C = 116.3 (3), P-C-Ag' = 110.5 (5).

Table IV. Bond Angles (deg)[a]

S-Ag-Ag'	92.8 (1)	S-Ag-Ag''	85.9 (1)
Ag'-Ag-Ag''	155.7 (1)	S-Ag-C'	173.7 (3)
Ag'-Ag-C'	93.2 (3)	Ag-Ag-C'	89.6 (3)
Ag-S-P	103.0 (2)	S-P-C	116.3 (3)
S-P-C(16)	110.9 (3)	C-P-C(16)	109.9 (4)
S-P-C(26)	104.8 (2)	C-P-C(26)	110.1 (4)
C(16)-P-C(26)	103.9 (3)	P-C-Ag'	110.5 (5)
P-C(16)-C(11)	121.6 (3)	P-C(16)-C(15)	118.3 (3)
P-C(26)-C(25)	119.5 (2)	P-C(26)-C(21)	120.5 (2)

[a] Estimated standard deviations in the least significant digits are given in parentheses.

two Ag atoms are bridged by the MTP ligand. Each Ag atom is coordinated linearly to one carbon atom and one sulfur atom; S-Ag-C' = 173.7 (3)°. The Ag-S and Ag-C bond lengths are similar to previously reported values.[2,4] Half of the molecule is related to the other half by a center of symmetry. The intramolecular Ag-Ag' separation is 2.990 (2) Å, similar to the distances found in[4,7a,b] $Ag_2\{[CH(COOC_2H_5)]_2PPh_2\}_2$ (2.953 (1) Å), $Ag_2(O_2CC_6H_5)_2$ (2.902 (3) Å), and $Ag_2(p\text{-}HO\text{-}C_6H_4COO)_2$ (2.915 (8) Å) but much longer than those found in[7c,d] $Ag_2[o\text{-}(Me_3Si)_2CC_5H_4N]_2$ (2.654 (1) Å), $Ag_2(PhNNNPh)_2$ (2.669 (1) Å), and[7e] $Ag_2(p\text{-}CH_3C_6H_4NCHNC_6H_4\text{-}p\text{-}CH_3)_2$ (2.705 (1) Å). The sum of the metallic radii of two Ag atoms is 2.884 Å;[8] hence, 1 has no formal metal-metal bond. However, the yellow luminescence of 1 at 77 K suggests that some Ag-Ag interaction may be present.[9]

Interestingly, 1 forms a one-dimensional chain in the solid with intermolecular Ag-Ag'' separations of 3.227 (2) Å and a Ag'-Ag-Ag'' angle of 155.7 (1)° as shown in Figure 2. Such one-dimensional chain structures have been well established for dimeric Au^I complexes[1b,10] but have not been reported for dimeric Ag^I compounds. Surprisingly, 1 is isomorphous with the analogous compound $[Au(MTP)]_2$. The short intermolecular metal-metal distance was expected for the Au^I species but not the Ag^I complex.

^1H NMR spectroscopic studies indicate that silver-ligand bonds in 1 are labile (Figure 3). At 22 °C a doublet at $\delta = 1.63$ ppm with a $^2J_{P-H}$ coupling constant of 12 Hz, typical for a CH_2 group in ylide complexes, is observed. However, no Ag-H coupling is detected. When the solution is cooled to −60 °C, a "triplet" at $\delta = 1.69$ ppm is observed (Figure 3). This "triplet" is attributed to the coupling of the protons on the CH_2 group with the ^{107}Ag, ^{109}Ag, and ^{31}P nuclei. Since the difference of magnetogyric ratios[11] of ^{107}Ag and ^{109}Ag is small $(\gamma(^{107}Ag)/\gamma(^{109}Ag) =$

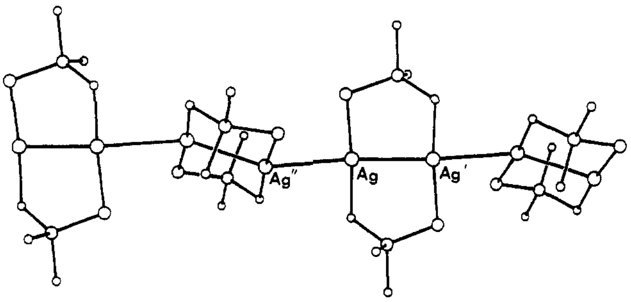

Figure 2. Diagram showing the one-dimensional chain structure of 1. Phenyl groups are omitted from the drawing for clarity.

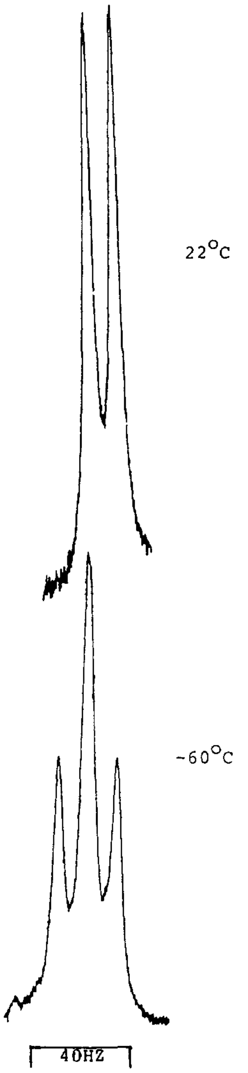

Figure 3. ^1H NMR spectra of 1 in $CDCl_3$. The resonances are centered at $\delta = 1.63$ ppm for the doublet and $\delta = 1.69$ ppm for the "triplet".

---

(7) (a) Griffin, R. G.; Ellett, J. D., Jr.; Mehring, M.; Bullitt, J. G.; Waugh, J. S. *J. Chem. Phys.* **1972**, *57*, 2147. (b) Usubaliev, B. T.; Movsumov, E. M.; Amiraslanov, I. R.; Akhmedov, A. I.; Musaev, A. A.; Mamedov, K. H. S. *Zh. Strukt. Khim.* **1981**, *22*, 98. (c) Papasergio, R. I.; Raston, C. L.; White, A. H. *J. Chem. Soc., Dalton Trans.* **1987**, 3085. (d) Beck, J.; Strähle, J. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1986**, *41B*, 4. (e) Cotton, F. A.; Feng, X. J.; Matusz, M.; Poli, R. *J. Am. Chem. Soc.* **1988**, *110*, 7077.

(8) Pauling, L. *The Nature of the Chemical Bond*, 3rd ed.; Cornell University Press: Ithaca, NY, 1960.

(9) King, C.; Wang, J. C.; Khan, M. N. I.; Fackler, J. P., Jr. *Inorg. Chem.* **1989**, *28*, 2145.

(10) (a) Jones, P. G. *Gold Bull.* **1981**, *14*, 102. (b) Mazany, A. M.; Fackler, J. P., Jr. *J. Am. Chem. Soc.* **1984**, *106*, 801.

(11) (a) *NMR and the Periodic Table*; Harris, R. K., Mann, B. E., Eds.; Academic Press: London, 1978. (b) Brevard, C.; Granger, P. *Handbook of High Resolution Multinuclear NMR*; Wiley: New York, 1981.

0.87), it is assumed that ${}^2J({}^{107}\text{Ag–H}) \simeq {}^2J({}^{109}\text{Ag–H}) \simeq {}^2J_{\text{P–H}} = 12$ Hz. Similar coupling constants of ${}^2J_{\text{Ag–H}}$ were reported previously by Schmidbaur.[12] The ^{31}P NMR spectrum of 1 at −40 °C in $CDCl_3$ ($\delta = 51.44$ ppm) shows a pattern of a doublet with satellites that is consistent with the molecular structure in the solid, i.e. a AA′XX′ system.[13] The coupling constant of 15 Hz, therefore, is assigned as ${}^2J_{\text{Ag–P}} + {}^2J_{\text{Ag′–P}}$.

Oxidation of 1 by 1 equiv of $PhICl_2$ in CH_2Cl_2 at −78 °C yields a yellow-orange compound that decomposes rapidly upon warming to 0 °C. AgCl was obtained as the final isolable product. The yellow-orange compound may be a Ag^{II} species. Efforts to characterize this compound have been unsuccessful to date.

Experimental Section

LiMTP was prepared according to published procedures.[5] All solvents were freshly dried and distilled prior to use. All reactions were carried out in darkness and under a nitrogen atmosphere. ^{1}H NMR spectra were recorded on a Varian XL-200 NMR spectrometer at 200 MHz. ^{31}P NMR spectra were taken on a Varian XL-400 spectrometer at 81 MHz.

Synthesis of $[AgMTP]_2$. A THF solution (7 mL) containing 1.7 mmol of LiMTP was cooled to −78 °C in a dry-ice bath. $AgNO_3$ (0.30 g, 1.7 mmol) was added to this solution. After it was stirred for 1.5 h, the solution was warmed to room temperature. A white solid precipitated. The solution was filtered, and the white solid was washed with ~10 mL of THF and then 5 mL of diethyl ether. The product was dried under vacuum for a few hours (0.26 g, yield 44%). $[AgMTP]_2$ was recrystallized from CH_2Cl_2/diethyl ether at 0 °C. Elemental analysis was unsuccessful due to the rapid decomposition of 1.

Reaction of 1 with $PhICl_2$. $[AgMTP]_2$ (20 mg, 0.029 mmol) was dissolved in 3 mL of CH_2Cl_2. The solution was cooled to −78 °C. To this solution was added $PhICl_2$ (8 mg, 0.029 mmol). The light yellow solution became orange with some white powder precipitation. After it was stirred for 1 h, the solution was warmed to ~0 °C. The color of the solution was lost rapidly, and a large quantity of white solid (AgCl) precipitated.

X-ray Crystallography. The single-crystal X-ray analysis of 1 was performed by procedures (Nicolet R3m/E diffractometer, SHELXTL (Version 5.1) software) described in detail elsewhere.[14] Crystallographic data are presented in Table I. Colorless crystals of 1 suitable for X-ray diffraction analysis were grown from CH_2Cl_2/diethyl ether at 0 °C. The crystal was mounted on a glass fiber with epoxy. The lattice parameters were determined by using 22 reflections ($16° < 2\theta < 33°$). The data were collected by the Wyckoff technique and were corrected for Lorentz and polarization effects and for intensity fluctuations in the standards. Only random fluctuations were observed. Absorption corrections were made empirically on the basis of azimuthal scans. The crystal structure was determined by using direct methods and difference Fourier techniques. The final cycles of refinement were performed with hydrogen atoms placed in idealized positions (C–H = 0.96 Å). Phenyl rings were refined as rigid bodies (C–C = 1.395 Å). All non-hydrogen atoms were refined anisotropically.

The crystal of 1 belongs to the monoclinic system. The space group $C2/c$ was determined by systematic absences and the successful refinement of the structure.

Acknowledgment. We thank the Welch Foundation and the Available Fund of Texas A&M University for financial support. The National Science Foundation (Grant No. CHE8708625) also has supported this work.

Registry No. 1, 126752-85-0; $PhICl_2$, 932-72-9; LiMTP, 52101-86-7.

Supplementary Material Available: A table of anisotropic thermal parameters for 1 (1 page); a listing of structure factors for 1 (9 pages). Ordering information is given on any current masthead page.

---

(12) (a) Yamamoto, Y.; Schmidbaur, H. *J. Organomet. Chem.* **1975**, *96*, 133. (b) Schmidbaur, H.; Adlkofer, J.; Heimann, M. *Chem. Ber.* **1974**, *107*, 3697.

(13) Becker, E. D. *High Resolution NMR*, 2nd ed.; Academic Press: New York, 1980.

(14) Porter, L. C.; Fackler, J. P. *Acta Crystallogr.* **1987**, *C43*, 587.