*Organometallics* **1989**, *8*, 767–770

# Synthesis of $[Ag_2\{\mu\text{-}\{\{CH(COOR)\}_2PPh_2\}\}_2]$ (R = Me, Et). The First Crystal Structure of a Dinuclear Silver Diylide Complex (R = Et). One-Pot Synthesis of the Phosphonium Salts $[Ph_2P(CH_2COOR)_2]Cl$ (R = Me, Et)

José Vicente,* M. Teresa Chicote, and Isabel Saura-Llamas

*Departamento de Quimica Inorganica, Facultad de Ciencias Quimicas, Universidad de Murcia, Campus de Espinardo, 30.171 Espinardo, Murcia, Spain*

Peter G. Jones*,†

*Institut für Anorganische Chemie der Universität, Tammannstrasse 4, 3400 Göttingen, West Germany*

*Received August 1, 1988*

$[Ph_2P(CH_2COOR)_2]Cl$ [R = Me (**1a**), Et (**1b**)] can be obtained by refluxing $ClCH_2COOR$ and $Ph_2PH$ (3:1) in chloroform. The corresponding perchlorate salts **2a** and **2b** have been synthesized by reacting **1a** or **1b** with $NaClO_4\cdot H_2O$. When the phosphonium chlorides react with $Ag_2CO_3$ (1:1) in acetone, the complexes $[Ag_2\{\mu\text{-}\{\{CH(COOR)\}_2PPh_2\}\}_2]$ [R = Me (**3a**), Et (**3b**)] are obtained. The crystal and molecular structure of complex **3b** has been determined. It crystallizes in the space group $P\bar{1}$, with one centrosymmetric molecule in the cell; across the eight-membered ring, the Ag–Ag contact is 2.953 (1) Å. The coordination of both Ag atoms is almost linear [178.2 (1)°] with C–Ag distances of 2.183 (2) and 2.169 (2) Å.

## Introduction

Four types of ylide complexes of silver(I) have been reported so far: (i) mononuclear neutral [Ag(R)Y] [R = Cl, Y = $Ph_3PCH_2$,[1] $(Ph_3P)_2C$;[2] R = $C_6F_5$, Y = $Ph_3PCH_2$, $MePh_2PCH_2$, $Me_2PhPCH_2$, $Ph_3AsCH_2$, $Ph_3PCHCOOCH_3$[3]], (ii) mononuclear cationic $[AgY_2]X$ [X = Cl, Y = $Ph_3PCH_2$, $Ph_3PCHMe$, $Ph_3PCHPr$,[4] $Me_3PCH(SiMe_3)$;[5] X = $ClO_4$, Y = $Ph_3PCH_2$,[3] $Ph_3PCHCOR$ (R = OMe, OEt, Me, Ph);[6] X = $NO_3$, Y = $Ph_3PCHCOR$ (R = OMe, OEt, Me, Ph)[6]], (iii) dinuclear neutral $[Ag_2\{(CH_2)_2ERR'\}_2]$ [E = P, R = R′ = Me,[7] Ph;[5] R = Me, R′ = Ph,[5] R + R′ = $(CH_2)_5$;[8] E = As, R = R′ = Me[9]], and (iv) dinuclear dicationic $[Ag_2\{\mu\text{-}\{\{CH(PPh_3)\}_2CO\}\}_2](ClO_4)_2$.[10] As far as we know only three of these complexes have been characterized by X-ray crystallography, namely, $[Ag(C_6F_5)(CH_2PPh_3)]$[3] and $[AgY_2]X$[6] [Y = $Ph_3PCHCOR$, R = OEt, X = $ClO_4$; R = Ph, X = $NO_3$]. In this paper we report the first X-ray crystal structure of a dinuclear ylide complex of silver.

In spite of the low nucleophilicity of the carbonyl-stabilized phosphorus ylides, we have previously shown[6,10–12] that (i) they can coordinate to gold(I), gold(III), and silver(I) to give stable complexes and (ii) the silver(I) complexes are useful ylide transfer reagents in the preparation of ylide complexes of other metals.

These considerations prompted us to attempt the synthesis of the title complexes, which would be the first dinuclear neutral complexes, i.e. type iii, containing a carbonyl-stabilized phosphorus ylide; furthermore, neither the ylides nor any of their metal complexes had been described.

One of the synthetic procedures we have followed for preparing ylide complexes involves the use of the parent phosphonium salts,[10–12] which in turn are prepared from the corresponding phosphine and alkyl halide. Given that the phosphines $Ph_2PCH_2COOR$ are not commercially available and their reported preparations are not straightforward,[13] we have developed a one-pot synthesis for the phosphonium salts.

## Results and Discussion

When $ClCH_2COOR$ (R = Me, Et) and $Ph_2PH$ are refluxed (3:1) in chloroform, evolution of HCl takes place and the corresponding phosphonium chlorides $[Ph_2P(CH_2COOR)_2]Cl$ [R = Me (**1a**), Et (**1b**)] precipitate. The IR spectra of **1a**,**b** show the band corresponding to $\nu_{asym}(CO_2)$ at 1715 (vs, br) $cm^{-1}$. This value is very similar to those found in other phosphonium salts of the type $[Ph_3PCH_2COR]^+$ [R = OMe (1720 $cm^{-1}$), OEt (1715 $cm^{-1}$), Me (1710 $cm^{-1}$)].[11]

The molar conductivities of these compounds, measured in ca. $10^{-4}$ M solutions in acetone, are lower than expected for 1:1 electrolytes [58 (**1a**) and 78 (**1b**) $\Omega^{-1}\ mol^{-1}\ cm^2$], which must be explained in terms of some ion association.

When the phosphonium chlorides **1a** or **1b** are reacted with excess $NaClO_4\cdot H_2O$, the corresponding perchlorates $[Ph_2P(CH_2COOR)_2]ClO_4$ [R = Me (**2a**), Et (**2b**)] are obtained, with normal molar conductivities in acetone [124 (**2a**) and 112 (**2b**) $\Omega^{-1}\ mol^{-1}\ cm^2$].

The IR spectra of **2a**,**b** show bands at 1100 (vs, br) and

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† Present address: Institut für Anorganische und Analytische Chemie der Technischen Universität, Hagenring 30, 3300 Braunschweig, Federal Republic of Germany.

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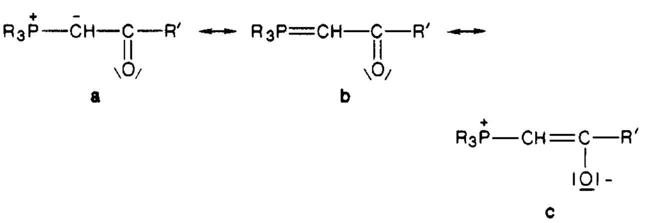
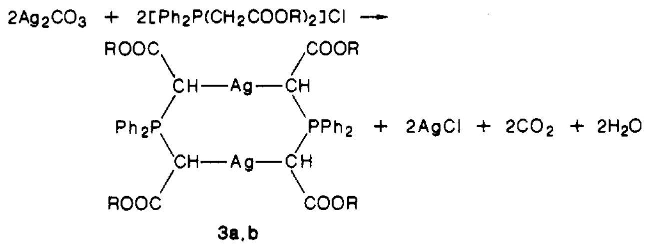
0276-7333/89/2308-0767\$01.50/0

620 (s) cm$^{-1}$ assigned to $ClO_4^-$ and the band corresponding to $\nu_{asym}(CO_2)$ at 1725 (vs) (**2a**) cm$^{-1}$ and at 1715 (vs) and 1745 (vs) (**2b**) cm$^{-1}$. When the $^1H$ and $^{31}P\{^1H\}$ NMR spectra of **2a,b** are compared with those of the chlorides **1a,b**, the only significant difference is the position of the resonances from the P–$CH_2$ protons. In **1** they are shifted downfield by 0.9 ppm with respect to the corresponding perchlorates. This is evidence that the interaction, responsible for the low conductivity of **1a,b**, takes place through these methylene protons. It is, possibly, a C–H···Cl hydrogen bonding.

The basic character of the ylides is due to the partial localization of an electron pair on the α-carbon atom (resonance forms **a** and **b**). The presence of a C=O group in β-position allows a delocalization over the C—C=O moiety (resonance form **c**) which decreases the basic nature and increases the stability of these carbonyl ylides. Therefore, their corresponding phosphonium salts, which are their conjugate acids, ought to be acids of a moderate strength.



In fact, when $Ag_2CO_3$ and $[Ph_2P(CH_2COOR)_2]Cl$ react (1:1) in acetone, complexes **3a,b** are obtained along with AgCl and $CO_2$. Therefore, **1a,b** behave as diprotic acids leading, by reaction with the base $Ag_2CO_3$, to the silver complexes of the corresponding symmetric anionic diylides which, as far as we know, have neither been isolated nor described in metal complexes.



3a,b

R = Me (**3a**), Et (**3b**)

The precipitation of AgCl could be the driving force of these reactions, since we have proved that $Ag_2CO_3$ and the corresponding phosphonium perchlorates do not react under the same conditions. Nevertheless, the anion–cation association in **1a,b**, which should increase their acidic character, could also be an additional factor in this different behavior.

In contrast with the procedures described for other silver ylide complexes,[5,7–9] it should be noted that this reaction takes place even in the presence of laboratory air. The insolubility of **3a** in all common organic solvents prevented us from measuring its molar conductivity; by the contrary, **3b** is very soluble in organic solvents, being even slightly soluble in diethyl ether. Replacing methyl by ethyl also affects the stability (or lability) of the complexes, **3a** being more stable (or inert) than **3b**. However, the different solubilities of **3a,b** affect neither the reaction rates nor the yield.

The IR spectra of **3a,b** show $\nu_{asym}(CO_2)$ as a very strong band at 1660 cm$^{-1}$, 55 cm$^{-1}$ lower than the corresponding phosphonium salts. This lowering is a well-established effect in silver and gold complexes containing other carbonyl-stabilized phosphorus ylides[10–12] and shows that the ligand coordinates through the carbon atom and not through the oxygen. In general, the value of $\nu_{asym}(CO_2)$ is lowered as a consequence of the substitution of the hydrogen atom of the phosphonium salt by a less electronegative group.

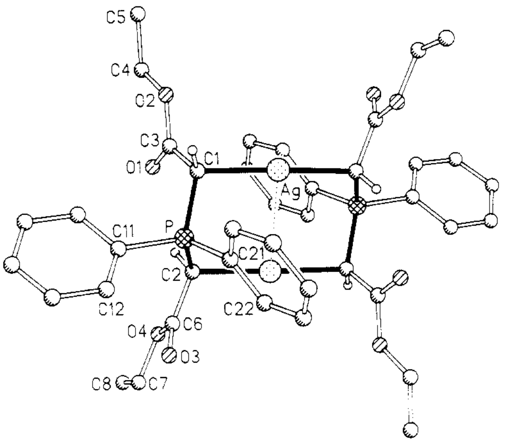


**Figure 1.** The molecule of complex **3b** in the crystal, showing the numbering scheme of the asymmetric unit. Radii are arbitrary. The short transannular Ag···Ag contact is indicated by a dotted line. Ethyl and phenyl H are omitted for clarity.

Two bands appear in the 550–450 cm$^{-1}$ region [**3a**, 528 (m), 500 (m); **3b**, 528 (m), 490 (m) cm$^{-1}$]; these could be tentatively assigned[7–9] to $C_2Ag$ stretching vibrations.

Complexes **3a,b** have four chiral carbon atoms, which, even assuming that in solution a rapid chair–boat conversion occurs, makes up to three meso forms and two pairs of enantiomers possible. Assuming a planar averaged structure for the $\overline{\text{PCAgCPCAgC}}$ ring, both phosphorus atoms and the protons of the four methyl, methylene, and methyne groups are equivalent for all the stereoisomers, except for the pair of enantiomers which have three protons and one COOEt group on the same side of the plane [*SRSS* and *RSRR* for C(1)C(2a)C(1a)C(2), according to the atom numbering in Figure 1], which should give one resonance for each of these groups in the molecule.

$^1H$ NMR spectrum of **3a** in $CD_2Cl_2$ shows two singlets ($CH_3$, 3.42, 3.46 ppm) and an apparent doublet (CH, 3.71 ppm, $^2J_{PH}$ = 11 Hz). The $^{31}P\{^1H\}$ NMR spectrum shows two 1:1 triplets (27.54 ppm, $^2J_{PAg}$ = 16 Hz; 27.46 ppm, $^2J_{PAg}$ = 17 Hz).

Although the $CH_2$–$CH_3$ groups are strictly $ABX_3$ systems, the $^1H$ NMR spectrum of **3b** in $CDCl_3$ is deceptively simple because it shows two 1:1 triplets [$CH_3$, 1.03, 1.05 ppm, $^3J_{HH}$ = 7.1 Hz], an apparent quartet ($CH_2$, 3.9 ppm), and a doublet (CH, 3.7 ppm, $^2J_{PH}$ = 11 Hz). The $^{31}P\{^1H\}$ NMR spectrum shows two 1:1 triplets (25.68, 25.65 ppm, $^2J_{PAg}$ = 16 Hz). Therefore, in **3a** or **3b** solution there exists a ca. 1:1 mixture of two of the meso forms or one of them and the pair of enantiomers *RRRR* and *SSSS*.

The crystal structure of **3b** (see Figure 1) shows an eight-membered ring with two silver atoms bridged by the two ylide ligands as had been previously suggested by Schmidbaur for some of the related complexes of the type $[Ag_2\{(CH_2)_2ERR'\}_2]$.[5,7–9] It corresponds to one of the meso forms with a chair conformation; crystallographic inversion symmetry is imposed. The chirality of the C(1)C(2a)C(1a)C(2) ring is *SRRS*. The coordination at silver is almost linear [178.2 (1)°]. The transannular Ag–Ag contact [2.953 (1) Å] is longer than that in the metal [2.8894 Å].[14] The

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[14] West, R. C. Editor. *CRC Handbook of Chemistry and Physics*, 62nd ed.; CRC Press: Boca Raton, FL, 1981–1982; p F-177.

tendency of silver(I) atoms to aggregate has been discussed by Jansen;[15] the presence of short metal···metal contacts across eight-membered rings is a common feature of gold(I) chemistry.[16]

The C–Ag distances [2.183 (2), 2.169 (2) Å] are similar to those found in the complex $[Ag\{CH(PPh_3)COOEt\}_2]ClO_4$[6] [2.184 (14), 2.181 (16) Å] but shorter than those in $[Ag\{CH(PPh_3)C(O)Ph\}_2]NO_3$[6] [2.219 (9), 2.210 (9) Å in one of the two independent molecules and 2.256 (8), 2.253 (9) Å in the other]. However, they are all longer than those found in $[Ag(C_6F_5)(CH_2PPh_3)]$[3] [2.144 (5), and 2.131 (6) Å] probably because $CH_2PPh_3$ is a better $\sigma$-donor ligand than the carbonyl-stabilized ylides or/and, as suggested by one of the reviewers, because the strong electron-withdrawing effect of the $C_6F_5$ group increases the acceptor capacity of the $Ag^+$ ion.

The HC–P bond distances [1.774 (3), 1.767 (3) Å] are similar to those in the above mentioned complexes $[Ag\{CH(PPh_3)C(O)R\}_2]X$[6] but longer than those in $[Ag(C_6F_5)(CH_2PPh_3)]$ [1.738 (4), 1.739 (6) Å].[3]

## Experimental Section

Recording of the infrared spectra, the C and H analyses, conductance measurements, melting point determinations, and NMR spectra (at 80 MHz; **3a** at 200 MHz) was performed as described elsewhere.[10] Reactions were carried out at room temperature with magnetic stirring and without special precautions against light or atmospheric moisture, unless otherwise stated. $^1H$ and $^{31}P\{^1H\}$ NMR data in $CDCl_3$ or $CD_2Cl_2$ (**3a**) ($\delta$ in ppm) refer to TMS or $H_3PO_4$, respectively.

**Preparation of $[Ph_2P(CH_2COOR)_2]Cl$ [R = Me (1a), Et (1b)].** To a solution of $ClCH_2COOR$ (R = Me, 7 cm$^3$, 80 mmol; R = Et, 4 cm$^3$, 38 mmol) in chloroform (5 cm$^3$) was added $Ph_2PH$ (5 cm$^3$, 30 mmol; or 2 cm$^3$, 11 mmol, respectively) under $N_2$. The reaction mixture was refluxed, and after 1 h a white precipitate appeared. During the reaction, evolution of HCl was detected. After 3 h of refluxing, the suspension was allowed to cool to room temperature, diethyl ether (30 cm$^3$) added to complete precipitation, and the suspension filtered. The white solid [R = Me (**1a**), 9.35 g, 85%; R = Et (**1b**), 3.70 g, 85%] was washed with diethyl ether (3 × 10 cm$^3$) to remove the excess of alkyl chloride and air-dried. [**1a**: mp 150 °C; $\Lambda_M = 58\ \Omega^{-1}\ mol^{-1}\ cm^2$ ($7.52 \times 10^{-4}$ mol dm$^{-3}$ acetone); IR $\nu_{asym}(CO_2)$ 1715 (vs) cm$^{-1}$. NMR data: $^1H$ 3.55 (s, $CH_3$), 5.36 (d, $CH_2$, $^2J_{PH}$ = 14 Hz), 7.6–8.2 (m, Ph); $^{31}P\{^1H\}$ 20.8 (s). Anal. Calcd for $C_{18}H_{20}ClO_4P$: C, 58.94; H, 5.50. Found: C, 59.77; H, 5.70. **1b**: mp 108 °C; $\Lambda_M = 78\ \Omega^{-1}\ mol^{-1}\ cm^2$ ($5.87 \times 10^{-4}$ mol dm$^{-3}$ acetone); IR $\nu_{asym}(CO_2)$ 1715 (vs) cm$^{-1}$. NMR data: $^1H$ 1.05 (t, $CH_3$, $^3J_{HH}$ = 7 Hz), 4.00 (q, $CH_2CH_3$), 5.2 (d, $CH_2P$, $^2J_{PH}$ = 14 Hz), 7.6–8.2 (m, Ph); $^{31}P\{^1H\}$ 20.5 (s). Anal. Calcd for $C_{20}H_{24}ClO_4P$: C, 60.84; H, 6.13. Found: C, 60.41; H, 5.86.]

**Preparation of $[Ph_2P(CH_2COOR)_2]ClO_4$ [R = Me (2a), Et (2b)].** To a solution of **1a** (500 mg, 1.36 mmol) or **1b** (500 mg, 1.27 mmol) in water (30 cm$^3$) was added $NaClO_4{\cdot}H_2O$ (388 mg, 2.72 mmol; or 355 mg, 2.52 mmol, respectively). **2a** (R = Me) or **2b** (R = Et) precipitated as a white solid (**2a**, 394 mg, 67%; **2b**, 290 mg, 50%), which was filtered off, air-dried, and recrystallized from dichloromethane/diethyl ether. [**2a**: mp 137 °C; $\Lambda_M = 124\ \Omega^{-1}\ mol^{-1}\ cm^2$ ($4.55 \times 10^{-4}$ mol dm$^{-3}$ acetone); IR $\nu_{asym}(CO_2)$ 1725 (vs) cm$^{-1}$. NMR data: $^1H$ 3.64 (s, $CH_3$), 4.48 (d, $CH_2$, $^2J_{PH}$ = 13.5 Hz); $^{31}P\{^1H\}$ 20.2 (s). Anal. Calcd for $C_{18}H_{20}ClO_8P$: C, 50.19; H, 4.68. Found: C, 50.37; H, 4.92. **2b**: mp 104 °C; $\Lambda_M = 112\ \Omega^{-1}\ mol^{-1}\ cm^2$ ($8.72 \times 10^{-4}$ mol dm$^{-3}$ acetone); IR $\nu_{asym}(CO_2)$ 1715 (vs), 1745 (vs) cm$^{-1}$. NMR data: $^1H$ 1.02 (t, $CH_3$, $^3J_{HH}$ = 7.1 Hz), 3.99 (q, $CH_2CH_3$), 4.34 (d, $CH_2P$, $^2J_{PH}$ = 13.6 Hz); $^{31}P\{^1H\}$ 19.8 (s). Anal. Calcd for $C_{20}H_{24}ClO_8P$: C, 52.35; H, 5.27. Found: C, 53.10; H, 5.80.]

**Preparation of $[Ag_2\{\mu\text{-}\{\{CH(COOR)\}_2PPh_2\}\}_2]$ [R = Me (3a), Et (3b)].** To a suspension of **1a** (500 mg, 1.36 mmol) or a solution of **1b** (500 mg, 1.26 mmol) in acetone (30 cm$^3$) was added $Ag_2CO_3$ in molar ratio 1:1. The reaction mixture was stirred in the dark. After 3 h, the solvent was evaporated, the residues were extracted with dichloromethane (3 × 30 cm$^3$ or 30 cm$^3$, respectively), and the resulting suspensions were filtered over $MgSO_4$. The solutions were concentrated (3 cm$^3$), and diethyl ether (25 cm$^3$) or *n*-hexane (25 cm$^3$), respectively, was added to complete precipitation of **3a** or **3b** as white solids (**3a**, 535 mg, 90%; **3b**, 484 mg, 83%). [**3a**: mp 197 °C dec; **3a** is too insoluble for its conductivity to be measured; IR $\nu$(CO) 1660 (vs) cm$^{-1}$. NMR data ($CD_2Cl_2$): $^1H$ 3.42, 3.46 (s, $CH_3$), 3.71 (d, CH, $^2J_{PH}$ = 11 Hz), 7.4–7.8 (m, Ph); $^{31}P\{^1H\}$ 27.54 (t, $^2J_{PAg}$ = 17 Hz), 27.46 (t, $^2J_{PAg}$ = 16 Hz). Anal. Calcd for $C_{36}H_{36}Ag_2O_8P_2$: C, 49.45; H, 4.15. Found: C, 49.35; H, 4.12. **3b**: mp 180 °C dec; $\Lambda_M = 2\ \Omega^{-1}\ mol^{-1}\ cm^2$ ($4.3 \times 10^{-4}$ mol dm$^{-3}$ acetone); IR $\nu$(CO) 1650 (vs), 1660 (vs) cm$^{-1}$. NMR data: $^1H$ 1.03 (t, $CH_3$, $^3J_{HH}$ = 7 Hz), 1.05 (t, $CH_3$, $^3J_{HH}$ = 7 Hz), 3.7 (d, CH, $^2J_{PH}$ = 11 Hz), 3.91 (q, $CH_2$); $^{31}P\{^1H\}$ 25.68 (t, $^2J_{PAg}$ = 16 Hz), 25.65 (t, $^2J_{PAg}$ = 16 Hz). Anal. Calcd for $C_{40}H_{44}Ag_2O_8P_2$: C, 51.63; H, 4.77. Found: C, 52.26, H, 5.01.]

**Table I. Atomic Coordinates (×10$^4$) and Equivalent Isotropic Displacement Parameters (Å$^2$ × 10$^3$) for Complex 3b**

| | *x* | *y* | *z* | *U*(eq)[a] |
|---|---|---|---|---|
| Ag | 4860.9 (2) | 9359.7 (2) | 3917.0 (2) | 45 (1) |
| P | 5275.0 (7) | 7367.6 (6) | 6290.6 (6) | 40 (1) |
| O(1) | 8396 (2) | 6862 (3) | 4874 (2) | 74 (1) |
| O(2) | 7705 (2) | 6098 (2) | 3318 (2) | 67 (1) |
| O (3) | 5063 (2) | 8256 (2) | 8859 (2) | 61 (1) |
| O(4) | 7217 (2) | 8694 (2) | 8510 (2) | 57 (1) |
| C(1) | 5823 (3) | 7203 (3) | 4739 (2) | 44 (1) |
| C(2) | 6107 (3) | 8472 (3) | 6845 (2) | 41 (1) |
| C(3) | 7418 (3) | 6722 (3) | 4364 (2) | 49 (1) |
| C(4) | 9262 (4) | 5643 (4) | 2858 (3) | 87 (2) |
| C(5) | 9361 (5) | 4877 (5) | 1737 (4) | 114 (2) |
| C(6) | 6033 (3) | 8450 (3) | 8152 (2) | 44 (1) |
| C(7) | 7282 (4) | 8705 (4) | 9776 (3) | 71 (1) |
| C(8) | 8705 (5) | 8857 (5) | 9969 (4) | 101 (2) |
| C(11) | 5704 (3) | 5636 (3) | 7128 (3) | 49 (1) |
| C(12) | 4789 (5) | 5358 (4) | 8070 (4) | 95 (2) |
| C(13) | 5119 (6) | 4028 (5) | 8683 (4) | 105 (2) |
| C(14) | 6343 (6) | 2978 (4) | 8379 (4) | 104 (2) |
| C(15) | 7247 (5) | 3190 (4) | 7400 (5) | 119 (2) |
| C(16) | 6936 (4) | 4527 (4) | 6772 (4) | 85 (2) |
| C(21) | 3264 (3) | 8070 (3) | 6394 (2) | 48 (1) |
| C(22) | 2461 (3) | 9276 (4) | 6970 (3) | 66 (1) |
| C(23) | 928 (3) | 9786 (4) | 6980 (4) | 82 (2) |
| C(24) | 204 (3) | 9109 (4) | 6434 (3) | 77 (2) |
| C(25) | 977 (4) | 7906 (4) | 5871 (4) | 83 (2) |
| C(26) | 2522 (3) | 7378 (3) | 5848 (4) | 71 (1) |

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

**Table II. Bond Lengths (Å) for Complex 3b[a]**

| | | | |
|---|---|---|---|
| Ag–C(1) | 2.183 (2) | Ag···Ag(a) | 2.953 (1) |
| Ag–C(2a) | 2.169 (2) | P–C(1) | 1.774 (3) |
| P–C(2) | 1.767 (3) | P–C(11) | 1.819 (3) |
| P–C(21) | 1.811 (2) | O(1)–C(3) | 1.210 (4) |
| O(2)–C(3) | 1.349 (4) | O(2)–C(4) | 1.457 (4) |
| O(3)–C(6) | 1.208 (3) | O(4)–C(6) | 1.355 (4) |
| O(4)–C(7) | 1.434 (4) | C(1)–C(3) | 1.466 (4) |
| C(2)–C(6) | 1.462 (4) | C(4)–C(5) | 1.523 (6) |
| C(7)–C(8) | 1.470 (7) | C(11)–C(12) | 1.365 (5) |
| C(11)–C(16) | 1.373 (4) | C(12)–C(13) | 1.382 (6) |
| C(13)–C(14) | 1.321 (6) | C(14)–C(15) | 1.367 (7) |
| C(15)–C(16) | 1.396 (6) | C(21)–C(22) | 1.376 (4) |
| C(21)–C(26) | 1.378 (5) | C(22)–C(23) | 1.383 (4) |
| C(23)–C(24) | 1.353 (6) | C(24)–C(25) | 1.360 (5) |
| C(25)–C(26) | 1.393 (5) | | |

[a] Symmetry operator: (a) $1 - x$, $2 - y$, $1 - z$.

**Crystal Structure Determination of 3b.** Colorless prisms and tablets were obtained by liquid diffusion of *n*-hexane into a solution in dichloromethane.

**Crystal data**: $C_{40}H_{44}Ag_2O_4P_2$; $M_r$ 930.5, triclinic, space group $P\bar{1}$; $a$ = 9.611 (2), $b$ = 10.010 (2), $c$ = 11.253 (2) Å; $\alpha$ = 83.74 (2), $\beta$ = 83.42 (2), $\gamma$ = 69.99 (2)°; $V$ = 1007.8 Å$^3$; $Z$ = 1; $D_{calcd}$ = 1.53

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**Table III. Bond Angles (deg) for Complex 3b**[a]

| | | | |
|---|---|---|---|
| C(1)–Ag···Ag(a) | 91.9 (1) | C(1)–Ag–C(2a) | 178.2 (1) |
| Ag(a)···Ag–C(2a) | 86.4 (1) | C(1)–P–C(2) | 109.4 (1) |
| C(1)–P–C(11) | 111.7 (1) | C(2)–P–C(11) | 112.1 (1) |
| C(1)–P–C(21) | 105.2 (1) | C(2)–P–C(21) | 114.0 (1) |
| C(11)–P–C(21) | 104.3 (1) | C(3)–O(2)–C(4) | 114.7 (3) |
| C(6)–O(4)–C(7) | 117.1 (2) | Ag–C(1)–P | 104.2 (1) |
| Ag–C(1)–C(3) | 107.3 (2) | P–C(1)–C(3) | 117.9 (2) |
| P–C(2)–C(6) | 115.4 (2) | P–C(2)–Ag(a) | 109.2 (1) |
| C(6)–C(2)–Ag(a) | 110.1 (2) | O(1)–C(3)–O(2) | 121.6 (2) |
| O(1)–C(3)–C(1) | 127.1 (3) | O(2)–C(3)–C(1) | 111.3 (3) |
| O(2)–C(4)–C(5) | 106.3 (4) | O(3)–C(6)–O(4) | 122.0 (2) |
| O(3)–C(6)–C(2) | 126.7 (3) | O(4)–C(6)–C(2) | 111.3 (2) |
| O(4)–C(7)–C(8) | 108.1 (3) | P–C(11)–C(12) | 122.3 (2) |
| P–C(11)–C(16) | 119.9 (2) | C(12)–C(11)–C(16) | 117.6 (3) |
| C(11)–C(12)–C(13) | 121.5 (3) | C(12)–C(13)–C(14) | 120.9 (4) |
| C(13)–C(14)–C(15) | 119.3 (4) | C(14)–C(15)–C(16) | 120.5 (4) |
| C(11)–C(16)–C(15) | 119.9 (4) | P–C(21)–C(22) | 122.7 (2) |
| P–C(21)–C(26) | 118.2 (2) | C(22)–C(21)–C(26) | 119.2 (3) |
| C(21)–C(22)–C(23) | 119.8 (4) | C(22)–C(23)–C(24) | 120.9 (3) |
| C(23)–C(24)–C(25) | 120.3 (3) | C(24)–C(25)–C(26) | 119.7 (4) |
| C(21)–C(26)–C(25) | 120.2 (3) | | |

[a] Symmetry operator: (a) $1 - x$, $2 - y$, $1 - z$.

Mg m$^{-3}$; $F(000) = 472$; $\lambda(\mathrm{Mo\ K}\alpha) = 0.71069$ Å; $\mu = 1.1$ mm$^{-1}$.

**Data Collection and Reduction.** A crystal, 0.55 × 0.3 × 0.15 mm, was mounted in a glass capillary. A total 4929 profile-fitted intensities[17] were registered on a Stoe-Siemens four-circle diffractometer using monochromated Mo K$\alpha$ radiation ($2\theta_{\max} = 50°$). An absorption correction based on $\psi$ scans was applied, with transmission factors of 0.78–0.99. Merging equivalents gave 3526 unique reflections ($R_{\mathrm{int}} = 0.012$), of which 3307 with $F > 4\sigma(F)$ were used for all calculations (program system SHELX, locally modified by its author, Prof. G.M. Sheldrick). Cell constants were refined from $2\theta$ values of 54 reflections in the range 20–23°.

**Structure Solution and Refinement.** The structure was solved by the heavy-atom method and refined anisotropically on $F$ to $R = 0.025$ and $R_w = 0.027$. H atoms were included by using a riding model. The weighting scheme was $w^{-1} = \sigma^2(F) + 0.00017F^2$ (235 parameters; $S = 1.8$; maximum $\Delta/\sigma = 0.002$; maximum $\Delta\rho = 0.7$ e Å$^{-3}$). Final atomic coordinates are given in Table I, with derived bond lengths and angles in Tables II and III, respectively.

**Acknowledgment.** We thank the Fonds der Chemischen Industrie and Comision Asesora de Investigacion Cientifica y Tecnica (PB85-0295) for financial support and the Ministerio de Educacion y Ciencia (Spain) for a grant to I.S.-L.

**Supplementary Material Available:** Tables of anisotropic displacement parameters and H-atom coordinates (2 pages); a listing of observed and calculated structure factors (12 pages). Ordering information is given on any current masthead page.

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# Synthesis and Solid-State Structures of Some Sterically Hindered Cyclopropenylsilanes

Dhananjay B. Puranik, M. Pontier Johnson, and Mark J. Fink*

*Department of Chemistry, Tulane University, New Orleans, Louisiana 70118*

*Received August 1, 1988*

The reaction of tri-*tert*-butylcyclopropenium tetrafluoroborate with the polysilyllithium reagents LiSiR(SiMe$_3$)$_2$ [R = SiMe$_3$, Ph, 2,4,6-trimethylphenyl (Mes), 2,4,6-triisopropylphenyl] affords covalent 3-cyclopropenylsilanes, Cyp*SiR(SiMe$_3$)$_2$, in high yields (Cyp* = tri-*tert*-butylcyclopropenyl). The compounds display remarkable thermal and chemical stability. The spectroscopic properties are compared, and two X-ray crystal structures are reported. The compound Cyp*SiPh(SiMe$_3$)$_2$ crystallizes in the monoclinic system: Si$_3$C$_{27}$H$_{50}$, space group $P2_1/c$, $Z = 4$, $a = 16.382$ (5) Å, $b = 11.990$ (2) Å, $c = 15.199$ (3) Å, $\beta = 96.70$ (2)°. The compound Cyp*SiMes(SiMe$_3$)$_2$ also crystallizes in the monoclinic system: Si$_3$C$_{30}$H$_{56}$, space group $P2_1/c$, $Z = 4$, $a = 16.412$ (4) Å, $b = 10.403$ (2) Å, $c = 15.566$ (5) Å, $\beta = 104.69$ (2)°. The two structures reveal unusually long bond lengths to the central silicon atom due to strong steric interactions.

## Introduction

The chemistry of 3-cyclopropenylsilanes is largely unexplored despite the potential for these compounds to serve as sources of cyclopropenyl anions[1,2] and of high energy organosilicon intermediates.[3,4] Only a few examples of 3-cyclopropenylsilanes are known. The compound 3-(trimethylsilyl)-1,2,3-triphenylcyclopropene (**1**) has been shown to undergo fluorodesilylation in both solution and the gas phase to yield the triphenylcyclopropenyl anion.[1] A similar compound, 3-(trimethylsilyl)-3-phenyl-1,2-dimethylcyclopropene (**2**), also undergoes gas-phase fluorodesilylation. Additionally, compound **2** and several closely related analogues have been demonstrated to undergo [1,5]-sigmatropic migrations of the trimethylsilyl group about the cyclopropene ring.[5]

All of the forementioned cyclopropenylsilanes have been prepared by the reaction of acetylenes with sources of $\alpha$-silylcarbenes. Distressing limitations are encountered with this type of synthesis, however: the general nonavailibility of $\alpha$-silylcarbene precursors[6] and the tendency of the $\alpha$-silylcarbenes to undergo facile intramolecular rearrangements.[7] Our interest in highly hindered cyclo-

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