

## ORGANOMETALLIC ACETYLENE CHEMISTRY III\*. DISUBSTITUTED ACETYLENES OF THE TYPE $\text{Ph}_2\text{PC}\equiv\text{CMR}_3$

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### SUMMARY

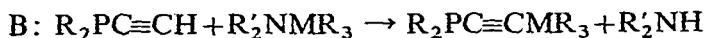
A series of organometallic acetylenes has been prepared containing as substituents both diphenylphosphino and  $\text{R}_3\text{M}$  moieties, where R is either methyl or phenyl, and M is one of the Group IVb metals. These phosphinoacetylenes have been oxidized with both hydrogen peroxide and sulfur to give the corresponding phosphinyl and phosphinothioyl-acetylenes, respectively.

### INTRODUCTION

A number of acetylenic based compounds having organometallic substituents have been reported during the past decade<sup>1</sup>. In a recent publication<sup>2</sup> we have prepared acetylenic derivatives having two different Group IVb metal atom based moieties,  $\text{R}_3\text{MC}\equiv\text{CMR}_3$ . In this paper we report the synthesis and characterization of (diphenylphosphino)acetylenic based compounds with Group IVb atom moieties of the generalized formula,  $\text{Ph}_2\text{PC}\equiv\text{CMR}_3$ .

### RESULTS AND DISCUSSION

Compounds of the type  $\text{Ph}_2\text{PC}\equiv\text{CMR}_3$  can be synthesized by several methods shown below:



Method A is the most convenient and is generally applicable. Method B is

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useful in synthesizing the hydrolytically unstable organotin and organolead derivatives of (diphenylphosphino)acetylene. The secondary aliphatic amine, formed in the reaction usually diethylamine, can be easily removed under vacuum. By this method, for example, we have obtained pure  $\text{Ph}_2\text{PC}\equiv\text{CSnPh}_3$  from the reaction of (diethylamino)triphenylstannane and diphenyl(ethynyl)phosphine in a smooth reaction.

Method C is limited to compounds containing tin or lead, since the corresponding aminosilicon and germanium compounds are not sufficiently reactive toward the acetylenic proton. Due to their general instability, difficulties in the preparation of mono-organotin and organolead derivatives of acetylene, limits Method D to silicon and germanium acetylene derivatives. Thus the transformation of trimethyl(ethynyl)silane into its lithium salt, followed by reaction with diphenylchlorophosphine produced the disubstituted acetylene  $\text{Ph}_2\text{PC}\equiv\text{CSiMe}_3$  in yields corresponding to those obtained using Method A.

The compounds synthesized, their physical properties, yields and analytical data are presented in Table 1.

TABLE 1

DATA AND ANALYSIS OF ORGANOMETALLIC "MIXED" ACETYLENES

Compounds No.	Yield M (%)	M.p. (°C)	B.p. [°C(mm)]	$\nu(\text{C}\equiv\text{C})$ ( $\text{cm}^{-1}$ )	Mol. wt.		C(%)		H(%)		
					Calcd.	Found	Calcd.	Found	Calcd.	Found	
$(\text{C}_6\text{H}_5)_2\text{PC}\equiv\text{CM}(\text{CH}_3)_3$											
(I)	Si	81; 77	17-18	114-5(0.05)	2105 m-s	282.1	278	72.34	72.45	6.73	6.82
(II)	Ge	70	35	126-7(0.05)	2115 m	326.6	324	62.46	62.70	5.81	5.77
(III)	Sn	62	35-36	146-7(0.05)	2078 w	372.7	383	54.73	54.60	5.09	4.94
(IV)	Pb	43	58-60			461.2	423	44.23	44.45	4.11	4.50
$(\text{C}_6\text{H}_5)_2\text{PC}\equiv\text{CM}(\text{C}_6\text{H}_5)_3$											
(V)	Si	85	100-101		2101 w-m	468.1	458	82.03	82.30	5.34	5.48
(VI)	Ge	56	102-103		2105 w	512.6	518	74.91	75.10	4.87	5.14
(VII)	Sn	68	89-90.5		2084 w	558.7	545	68.73	68.40	4.47	4.55
(VIII)	Pb	64	83-84.5			647.2	629	59.33	58.95	3.86	3.93
$(\text{C}_6\text{H}_5)_2\text{P}(\text{O})\text{C}\equiv\text{CM}(\text{C}_6\text{H}_5)_3$											
(IX)	Si	74	138-9		2126 w	484.1	492	79.32	79.40	5.16	5.32
(X)	Ge	81	136-7		2123 w	528.6	505	72.64	72.75	4.72	4.70
$(\text{C}_6\text{H}_5)_2\text{P}(\text{S})\text{C}\equiv\text{CM}(\text{CH}_3)_3$											
(XI)	Si	76	161-162		2120 w	314.1	307	64.94	64.85	6.05	6.32
(XII)	Ge	65	173		2115 w	358.7	354	56.87	57.30	5.29	5.02
(XIII) <sup>a</sup>	Sn	49	168-170		2098 w	404.8	401	50.39	51.10	4.69	4.81
$(\text{C}_6\text{H}_5)_2\text{P}(\text{S})\text{C}\equiv\text{CM}(\text{C}_6\text{H}_5)_3$											
(XIV)	Si	70	153		2124 w	500.2	494	76.76	76.75	5.00	4.72
(XV)	Ge	55	155		2122 w	544.7	568	70.49	70.80	4.58	4.32
(XVI) <sup>a</sup>	Sn	43	133-4		2103 w	590.7	633	64.99	64.00	4.23	4.58

<sup>a</sup> Satisfactory elemental analyses for these types of compounds could not be obtained.

## REACTIONS AND PROPERTIES

### Oxidation of the diphenylphosphino group

The phosphorus atom in some of the acetylenes under consideration can be

readily oxidized with 30% hydrogen peroxide in acetone at 0°. The tin and lead containing acetylenes were not studied since these compounds are very sensitive toward both hydrolytic attack and cleavage of the metal-acetylene bond. In a similar fashion treatment of the "mixed" acetylenes with sulfur in carbon disulfide resulted in the formation of the corresponding phosphine sulfides. Analytical data for the foregoing compounds are listed in Table 1.

### Properties

With the exception of the liquid trimethylsilicon derivative,  $\text{Me}_3\text{SiC}\equiv\text{CPh}_2$ , all acetylene derivatives of the type  $\text{R}_3\text{MC}\equiv\text{CPh}_2$  are colorless crystalline substances. The trimethyl Group IVb metal derivatives slowly turn brown upon standing at room temperature. In contrast, the corresponding triphenyl derivatives, with the exception of the lead compound, remain colorless. The decomposition temperatures of the Group IV metal analogs of the (trimethylsilyl)(diphenylphosphino)acetylene were obtained by observing the onset of decomposition through blackening when they were subjected to incremental increases of temperature in a capillary tube. The following approximate decomposition temperatures in this series indicated that the stability of these acetylenes decreased as the metal atom progressed from silicon to lead: Si, 320–330°; Ge, 280–300°; Sn, 190–210° and Pb, 130–140°.

The  $^1\text{H}$  NMR data of the methyl derivatives of  $\text{Ph}_2\text{PC}\equiv\text{CMR}_3$  are given in Table 2. No unusual chemical shift of the methyl protons was observed. The  $\delta$  and  $J$  values are similar to those reported for Group IVb compounds of the type  $(\text{CH}_3)_3\text{MCl}^4$ . The aromatic multiplett of the compounds listed in Table 2 appeared between –470 and –410 cps and showed the calculated ratio to the methyl protons 10:9.

TABLE 2

$^1\text{H}$  NMR DATA<sup>a</sup> OF  $(\text{CH}_3)_3\text{MC}\equiv\text{CP}(\text{C}_6\text{H}_5)_2$

M	$\delta(\text{CH}_3)$ (cps)	$J(^{13}\text{C}-\text{H})$ (cps)	$J(\text{M}-\text{C}-\text{H})$ (cps)
Si	–12	121	7 ( $^{29}\text{Si}$ )
Ge	–21	129	
Sn	–21	131	56.0, 58.5 ( $^{117/119}\text{Sn}$ )
Pb	–64	138	75.0 ( $^{207}\text{Pb}$ )

<sup>a</sup> TMS int. standard, appr. 10%  $\text{CCl}_4$  solution; Varian A60 spectrometer

### Mass spectra of the compounds

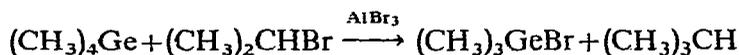
In the case of the silicon and tin compounds the parent ions are in high abundance, whereas the parent ions of the germanium compounds show lower intensities. Relatively intense  $\text{R}_3\text{M}$  isotopic clusters are observed in all spectra, indicating a favored splitting of the acetylene metal bond in the molecular ions. The stepwise loss of  $\text{CH}_3$ -fragments from the molecular ion of  $\text{Ph}_2\text{PC}\equiv\text{CSn}(\text{CH}_3)_3$  (III) is indicated by peaks at 374, 359, 344, 329 and a similar loss from the  $\text{Me}_3\text{Sn}$ -ion by the peaks at 165, 150, 135 and 120. The observed abundance of the tin isotopes is in good agreement with the natural distribution. In contrast to this, however, the spectra of (I) and (II) did not contain the pattern of silicon (28–30) and germanium (70, 72, 73, 74, 76). The isotopic cluster of the triphenylgermyl-ion in compound (XIII) has the highest relative intensity. The pattern shows also the loss of sulfur as well as phenyl from the molecular

ions. In this case the cluster of the  $C_6H_5-Ge$  fragment represents the smallest germanium containing particle.

#### EXPERIMENTAL

A Mechrolab Vapor Pressure Osmometer Model 301A was used to determine molecular weights. IR spectra were recorded on a Beckman IR-12. NMR data were obtained on a Varian A-60 spectrometer; the mass spectra on a CEC-110B spectrometer. Melting points were observed on a Thomas Hoover melting point apparatus and are not corrected. All reactions were carried out under argon and anhydrous conditions. Diethyl ether and tetrahydrofuran were distilled over lithium aluminium hydride.

Group IV organometallic halides were obtained from commercial sources. Trimethylgermanium bromide was prepared according to the following procedure<sup>5</sup>:



The method of Charrier<sup>3</sup> for the preparation of diphenyl(ethynyl)phosphine using diphenylchlorophosphine and sodium acetylide was slightly changed. Instead of treating the reaction mixture with water, the solvent (THF) was evaporated and the black residue extracted with dry hexane to separate the desired  $Ph_2PC\equiv CH$  from NaCl and any excess of unreacted sodium acetylide.

#### (1). (Trimethylsilyl)(diphenylphosphino)acetylene, $(CH_3)_3SiC\equiv CP(C_6H_5)_2$

(a). *Synthesis by method A.* A solution of 30 mmoles n-butyllithium in 20 ml hexane was added dropwise to 6.3 g (30 mmoles) of diphenyl(ethynyl)phosphine dissolved in 80 ml diethyl ether at  $-78^\circ$ , and the mixture was stirred for one h. A solution of 3.26 g (30 mmoles) trimethylchlorosilane in 20 ml of diethyl ether was then added and the mixture was allowed to come to room temperature. The reactants were stirred for 3 h. After treating the mixture with 20 ml water the organic layer was separated, dried over magnesium sulfate, filtered, and the solvent removed under vacuum. The remaining yellow brown liquid distilled at  $117-118^\circ/0.05$  mm. A colorless low melting substance was obtained, m.p.  $17-18^\circ$ . The yield was 6.5 g (77%).

(b). *Synthesis by method D.* A solution of 67 mmoles n-butyllithium in 45 ml hexane was added to 6.6 g (67 mmoles) of trimethyl(ethynyl)silane dissolved in 100 ml tetrahydrofuran, at  $-78^\circ$  and the mixture was stirred for one h. After addition of 14.8 g (67 mmoles) diphenylchlorophosphine the reaction mixture was treated in the same manner as described in (1a). The product had a b.p.  $120^\circ/0.05$  mm and the yield was 15.3 g (81%).

#### (2). (Trimethylgermyl)(diphenylphosphino)acetylene, $(CH_3)_3GeC\equiv CP(C_6H_5)_2$

This compound was synthesized in a manner similar to (1a). Starting with a solution of 4.2 g (20 mmoles) of diphenyl(ethynyl)phosphine in 80 ml diethyl ether, 20 mmoles n-butyllithium and 4 g (20 mmoles) of trimethylgermanium bromide the completed reaction yielded 4.6 g (70%) of  $(CH_3)_3GeC\equiv CP(C_6H_5)_2$ , b.p.  $126-127^\circ/0.05$  mm; m.p.  $35^\circ$ .

(3). *(Trimethylstannyl)(diphenylphosphino)acetylene*,  $(\text{CH}_3)_3\text{SnC}\equiv\text{CP}(\text{C}_6\text{H}_5)_2$

(a). *Synthesis by method A.* A solution of 6.3 g (30 mmoles) diphenyl(ethynyl)phosphine dissolved in 100 ml of tetrahydrofuran was cooled to  $-78^\circ$  and a solution of 30 mmoles of n-butyllithium in 19 ml of hexane was added dropwise. The reaction mixture was kept one h at  $-30^\circ$ . Trimethyltin chloride, 6.0 g (30 mmoles), dissolved in 25 ml of tetrahydrofuran was added and stirred for 3 h at room temperature. At the end of this period the solvent was removed in vacuum. The dark residue was extracted with dry hexane, filtered and the solvent was removed. The resulting product was distilled under reduced pressure; yield 6.9 g (62%), b.p.  $146\text{--}147^\circ/0.05$  mm; m.p.  $35\text{--}36^\circ$ . A small amount of a white crystalline material sublimed during the distillation on the cool finger of the distilling head, it was identified as bis(trimethylstannyl)acetylene by its melting point,  $58^\circ$ , and its IR spectrum.

(b). *Synthesis by method B.* To a solution of 4.2 g (20 mmoles) of  $(\text{C}_6\text{H}_5)_2\text{PC}\equiv\text{CH}$  in 30 ml of hexane, 4.7 g (20 mmoles) of  $(\text{CH}_3)_3\text{SnNEt}_2$  were added slowly at room temperature. After standing overnight the "mixed" acetylene was isolated by distillation, b.p.  $142\text{--}144^\circ/0.02$  mm. The yield was 6.7 g (90%). In contrast to (3a), no bis(trimethylstannyl)acetylene was formed.

(4). *Reaction of bis(trimethylstannyl)acetylene with diphenylchlorophosphine*

Bis(trimethylstannyl)acetylene (3.5 g, 10 mmoles) and diphenylchlorophosphine (2.2 g, 10 mmoles) were mixed without a solvent. An exothermic reaction took place within a short time. The mixture was subjected to a fractional sublimation at 0.05 mm. The following products were isolated: trimethyltin chloride (1.7 g, 85%), bis(trimethylstannyl)acetylene (0.2 g) and bis(diphenylphosphino)acetylene. The latter product was recrystallized from methanol/chloroform to yield 1 g (50%) of the pure substance. No evidence was found for the formation of (trimethylstannyl)(diphenylphosphino)acetylene. The reaction of diphenylchlorophosphine with bis(trimethylstannyl)acetylene in a ratio of 2:1 (10 mmoles:5 mmoles) gave 1.1 g, 55% bis(diphenylphosphino)acetylene and trimethyltin chloride. No reaction occurred between bis(triphenylstannyl)acetylene and diphenylchlorophosphine at room temperature.

(5). *(Trimethylplumbyl)(diphenylphosphino)acetylene*,  $(\text{CH}_3)_3\text{PbC}\equiv\text{CP}(\text{C}_6\text{H}_5)_2$

A solution of 2.1 g (10 mmoles) diphenyl(ethynyl)phosphine in 100 ml of tetrahydrofuran was treated with 10 mmoles n-butyllithium in 6.5 ml hexane at  $-78^\circ$ , followed by the addition of 2.88 g (10 mmoles) trimethyllead chloride dissolved in 40 ml of tetrahydrofuran. The reaction mixture was allowed to come to room temperature and was stirred for 24 h. A sample of the solution still showed an alkaline reaction after hydrolysis, indicating the presence of unreacted organolithium reagent. The mixture was therefore heated for 4 more hours. The yellow residue, which remained in the flask after removal of the solvent, was extracted with benzene and a semicrystalline material was isolated. The substance became crystalline upon treatment with dry ligroin and cooling, (yield 2.0 g; 43%). The compound was recrystallized from diethyl ether; m.p.  $58\text{--}60^\circ$ . Purification by distillation was not attempted.

(6). *(Triphenylsilyl)(diphenylphosphino)acetylene*,  $(\text{C}_6\text{H}_5)_3\text{SiC}\equiv\text{CP}(\text{C}_6\text{H}_5)_2$

The method of preparation is the same as described under (1a). Starting with

10 mmoles of diphenyl(ethynyl)phosphine, n-butyllithium and triphenylchlorosilane, a white crystalline compound was obtained, which melted at 100–101° after recrystallization from methanol/acetone. The yield was 4.0 g; 85%.

(7). (Triphenylgermyl)(diphenylphosphino)acetylene,  $(C_6H_5)_3GeC\equiv CP(C_6H_5)_2$

The reaction was conducted in a manner similar to (1a). Starting with 3.8 g (10 mmoles) of triphenylbromogermane, there was formed, after recrystallization from methanol/acetone, 2.9 g (56%) of compound (VI); m.p. 102–103°

(8). (Triphenylstannyl)(diphenylphosphino)acetylene,  $(C_6H_5)_3SnC\equiv CP(C_6H_5)_2$

(a). *Synthesis of method A.* The reaction conditions and the isolation procedure were similar to (3). Ten mmoles of the reactants yielded 3.1 g (55%) of compound (VII); m.p. 89–90.5°. This compound was recrystallized from ether.

(b). *Synthesis by method B.* To a solution of 2.1 g (5 mmoles) triphenyl(diethyl-amino)stannane in 30 ml of diethyl ether were added 1.05 g (5 mmoles) of diphenyl(ethynyl)phosphine. The solution was kept 24 h at room temperature, filtered (from a small quantity of triphenyltin hydroxide) and the solvent partially evaporated. Cooling of the concentrated solution resulted in the crystallization of 1.9 g (68%) of the product, m.p. 88–90°.

(9). (Triphenylplumbyl)(diphenylphosphino)acetylene,  $(C_6H_5)_3PbC\equiv CP(C_6H_5)_2$

Diphenyl(ethynyl)phosphine (7.5 mmoles) in 100 ml of tetrahydrofuran were converted into its lithium salt with n-butyllithium at –78°. A solution of 3.5 g (7.5 mmoles) triphenyllead chloride in 200 ml tetrahydrofuran was added, the mixture was stirred for 24 h at room temperature, and then refluxed for 5 h. The solvent was removed, and the residue extracted with hexane. Evaporation of the solvent left a yellow viscous liquid which crystallized when triturated with a small quantity of pentane; the yield was 3.1 g (64%); m.p. 79–81°. Recrystallization from diethyl ether gave a colorless crystalline product; m.p. 83–84.5°. No band corresponding to the  $C\equiv C$  stretching frequency could be detected in the IR spectrum of this compound.

(10). (Triphenylsilyl)(diphenylphosphino)acetylene,  $(C_6H_5)_3SiC\equiv CP(O)(C_6H_5)_2$

A solution of 0.23 g (0.5 mmoles) (triphenylsilyl)(diphenylphosphino)acetylene in 10 ml acetone was treated with 0.5 ml 30% hydrogen peroxide solution at 0°. The reaction was exothermic. After completion of the reaction the solvent was removed and the crude product recrystallized from methanol. The yield was 0.18 g (74%); m.p. 140–141°.

(11). (Triphenylgermyl)(diphenylphosphino)acetylene,  $(C_6H_5)_3GeC\equiv CP(O)(C_6H_5)_2$

The oxidation of 0.5 g (1 mmole) (triphenylgermyl)(diphenylphosphino)acetylene was carried out in a similar manner to that described above. The yield was 0.43 g (81%) of colorless crystals; m.p. 136–137°.

(12). (Trimethylsilyl)(diphenylphosphinothioyl)acetylene,  $(CH_3)_3SiC\equiv CP(C_6H_5)_2$

A solution of 1.9 g (6.7 mmoles) of (trimethylsilyl)(diphenylphosphino)acetylene and 0.64 g (20 mmoles) of sulfur in 30 ml carbon disulfide was heated for 6 h. The reaction mixture turned red. The solvent was evaporated until crystals started to

appear. Cooling of this solution with an ice bath yielded 1.6 g (76%) of a crystalline substance. The compound was washed with cold carbon disulfide to remove traces of sulfur and recrystallized from a small amount of acetone to give colorless needles, m.p. 161–162°.

(13). *Oxidation of compounds (II), (III), (V)–(VII) with sulfur*

The oxidation of compounds (II), (III), (V), (VI), and (VII) with sulfur was conducted in a manner similar to (12). The physical data of the resulting phosphinothioylacetylenes are recorded in Table 1.

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