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ORGANOMETALLIC ACETYLENE CHEMISTRY
IV. DISUBSTITUTED ACETYLENES OF THE TYPE $PhP(C{\equiv}CMR_3)_2$ AND $P(C{\equiv}CMR_3)_3$*

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SUMMARY

A series of organometallic acetylenes has been prepared of the type $PhP(C{\equiv}CMR_3)_2$ and $P(C{\equiv}CMR_3)_3$, where R is methyl and M is one of the Group IVb metals. These phosphinoacetylenes have been oxidized with hydrogen peroxide to give the corresponding phosphinyl acetylenes.

INTRODUCTION

In a previous paper we reported the synthesis of substituted diphenylphosphinoacetylenes of the type $Ph_2PC{\equiv}CMR_3$, where R is methyl or phenyl and M is Si, Ge, Sn or Pb[1]. This work has been extended with the preparation of a number of compounds of the types $PhP(C{\equiv}CMR_3)_2$ and $P(C{\equiv}CMR_3)_3$.

RESULTS AND DISCUSSION

Group IVb organometal-substituted phenyldialkynylphosphines were obtained in good yields by the reaction of the dilithio derivative of phenyldiethynylphosphine and Group IVb organometallic halides as follows:

$$PhP(C{\equiv}CH)_2 + 2\,BuLi \xrightarrow{2(CH_3)_3MX} PhP[C{\equiv}CM(CH_3)_3]_2$$

An alternate synthetic route to this compound where M = Si, which was attempted by reacting the lithium salt of trimethylethynylsilane and phenyldichlorosilane, as indicated below, gave a poor yield.

$$2\,(CH_3)_3SiC{\equiv}CH \xrightarrow{2BuLi} 2\,(CH_3)_3SiC{\equiv}CLi \xrightarrow{PhPCl_2} PhP[C{\equiv}CSi(CH_3)_3]_2$$

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Attempts to carry out an exchange reaction between bis(trimethyltin)acetylene and phenyldichlorophosphine to obtain $PhP[C{\equiv}CM(CH_3)_3]_2$ were unsuccessful. A black insoluble product, the infrared spectrum of which indicated the presence of phenylphosphorus and acetylene moieties, was not further characterized.

The Group IVb phenyldialkynylphosphines, $PhP[C{\equiv}CM(CH_3)_3]_2$, thus far prepared have limited stability since they all turn brown on standing, even under inert, anhydrous conditions. Decomposition temperatures are comparable to those of the previously reported diphenylphosphine derivatives[1]. The lead derivative, $PhP[C{\equiv}CPb(CH_3)_3]_2$, explodes above 130° and cannot be distilled.

In order to complete this series of organometallic alkynylphosphines, we synthesized two trialkynylphosphines of the type $P[C{\equiv}CM(CH_3)_3]_3$, where $M = Si$ or Ge. Two independent routes were used described by the following reactions:

$$3\,(CH_3)_3SiC{\equiv}CLi + PBr_3 \rightarrow [(CH_3)_3SiC{\equiv}C]_3P + 3\,LiBr \qquad (1)$$

$$3\,(CH_3)_3SiC{\equiv}CSn(CH_3)_3 + PCl_3 \rightarrow [(CH_3)_3SiC{\equiv}C]_3P + 3\,(CH_3)_3SnCl \qquad (2)$$

Reaction (2), an exchange reaction, proceeds smoothly and in high yields. It is interesting to note that the silicon–carbon bond adjacent to the triple bond does not react with phosphorus halides as indicated by the absence of trimethylchlorosilane. We have found that in the reaction of (trimethylgermyl)(trimethyltin)acetylene with phosphorus halide the corresponding germaniun–carbon bond is cleaved as indicated by the isolation of approximately 5% trimethylgermanium chloride.

The attempted synthesis of $P[C{\equiv}CSn(CH_3)_3]_3$ from bis(trimethyltin)acetylene and phosphorus trichloride resulted in the formation of black infusible products. The structure of these products is at present unknown. Exchange reactions of organometallic acetylenes with Group V halides are the subject of a recent publication[2]

The two compounds of the type $P[C{\equiv}CM(CH_3)_3]_3$, where $M = Ge$ and Si, are quite stable at room temperature. The infrared spectra show absorption bands at frequencies characteristic for trimethyl Group IVb metal moieties. Only in the case of the $P[C{\equiv}CSi(CH_3)_3]_3$ derivative there was an observable absorption in the $C{\equiv}C$ stretching region.

Polarization of the π-electron system in the phosphine oxides is increased over the corresponding parent compounds of the type $P[C{\equiv}CM(CH_3)_3]_3$, as indicated by the increased intensity of the $C{\equiv}C$ stretching vibration in the case of the silicon

TABLE 1

NMR DATA OF THE COMPOUNDS [a]

Compound	δ (ppm)	J(M–C–H) (Hz)
$PhP[C{\equiv}C\text{-}Si(CH_3)_3]_2$	0.11	7 (^{29}Si)
$PhP[C{\equiv}C\text{-}Ge(CH_3)_3]_2$	0.35	
$PhP[C{\equiv}C\text{-}Sn(CH_3)_3]_2$	0.30	51.4/60.6 ($^{117/119}Sn$)
$PhP[C{\equiv}C\text{-}Pb(CH_3)_3]_2$	1.08	65 (^{207}Pb)
$P[C{\equiv}C\text{-}Si(CH_3)_3]_3$	0.21	7 (^{29}Si)
$P[C{\equiv}C\text{-}Ge(CH_3)_3]_3$	0.40	

[a] Downfield from TMS int. standard, approx. 10% CCl_4 solution; Varian A60.

compounds as well as the appearance of this vibration in the spectrum of the analagous germanium compound. NMR data are listed in Table 1 and are in consonance with expected values. The physical data are tabulated in Table 2.

EXPERIMENTAL

A Mechrolab Osmometer Model 301A was used to determine the molecular weights. Infrared spectra were recorded on a Beckmann IR 12 Spectrophotometer. NMR data were obtained on a Varian A 60 Spectrometer. Melting points were observed on a Thomas Hoover melting point apparatus and are not corrected. All reactions were carried out in an argon atmosphere under anhydrous conditions. Tetrahydrofuran (THF) was distilled from lithium aluminum hydride. Organometallic halides were obtained from commercial sources. Trimethylethynylsilane[3], trimethylethynylgermane[3], phenyldiethynylphosphine, (trimethyltin)(trimethylsilyl)-acetylene[4] and (trimethyltin)(trimethylgermyl)acetylene[4] were prepared according to described literature procedures.

(1) *Synthesis of* $PhP[C{\equiv}CSi(CH_3)_3]_2$

(*a*) *From phenyldiethynylphosphine,* $PhP(C{\equiv}CH)_2$. A solution of 40 mmoles of n-butyllithium in 26 ml of hexane was added dropwise to 3.15 g (20 mmoles) of phenyldiethynylphosphine dissolved in 160 ml of THF at −78°. The solution was stirred for 1 h during which time it turned yellow-brown. Trimethylchlorosilane, 3.34 g, 40 mmoles), dissolved in 20 ml THF, was slowly added and stirred for 1 h. The solution was allowed to come to room temperature and stirred for an additional 3 h. The solvent was evaporated under vacuum and the residue extracted with dry hexane and filtered. The brown liquid that remained after evaporation of the hexane extracts was distilled at 103–105° (0.02 mm). The yield was 4.1 g (67.5%).

(*b*) *From trimethylethynylsilane,* $(CH_3)_3SiC{\equiv}CH$. A solution of 53 mmoles of n-butyllithium in 38 ml of hexane was added dropwise at −78° to a solution of 5.4 g (54 mmoles) of trimethylethynylsilane in 100 ml of THF. The solution was stirred for 1 h after which was added a solution of 3.83 g (27 mmoles) of phenyldichlorophosphine in 20 ml of THF. $PhP[C{\equiv}CSi(CH_3)_3]_2$ was isolated from the mixture as described under (*a*). The yield was 0.6 g (7.5%); b.p. 100°/0.02 mm.

(2) *Synthesis of* $PhP[C{\equiv}CGe(CH_3)_3]_2$

The procedure was the same as described under (1*a*). The following reactants were used: 1.58 g (10 mmoles) of phenyldiethynylphosphine in 100 ml of THF, 14 ml (20 mmoles) of n-butyllithium/hexane solution and 4 g (20 mmoles) of trimethylgermanium bromide. The yield was 2.4 g (61%); b.p. 120–122°/0.02 mm.

(3) *Synthesis of* $PhP[C{\equiv}CSn(CH_3)_3]_2$

(*a*) *From phenyldiethynylphosphine,* $PhP(C{\equiv}CH)_2$. The procedure was the same as described under (1*a*). The reactants, 2.4 g (15 mmoles) of phenyldiethynylphosphine in 100 ml of THF, 21 ml (30 mmoles) of n-butyllithium/hexane solution, and 6 g (30 mmoles) of trimethyltin chloride, were reacted in a similar manner to that described in (1*a*). The yield of product was 5.1 g (70.4%), b.p. 146–148°/0.02 mm. After recrystallization from hexane the product had a melting point of 72–74°.

TABLE 2

DATA AND ANALYSIS OF THE PHOSPHINE ACETYLENES

Compound	Yield (%)	M.p. (°C)	B.p. (°C/mm)	ν(C≡C) (cm⁻¹)	C(%) found (calcd.)	H(%) found (calcd.)	Mol.wt. found (calcd.)
$PhP[C{\equiv}CSi(CH_3)_3]_2$	67.5 7.5		103–105/0.02	2105 m	63.65 (63.54)	8.00 (7.61)	302 (302.2)
$PhP[C{\equiv}CGe(CH_3)_3]_2$	61		120–122/0.02	2096 w	48.30 (49.08)	6.10 (5.87)	372 (391.2)
$PhP[C{\equiv}CSn(CH_3)_3]_2$	59 70.4	72–74	146–148/0.02		39.50 (39.71)	4.90 (4.75)	471 (483.4)
$PhP[C{\equiv}CPb(CH_3)_3]_2$	50	94–95 dec. 130°C			29.00 (29.07)	3.24 (3.48)	605 (660.4)
$P[C{\equiv}CSi(CH_3)_3]_3$	73.6 44.2	49–50	90–92/0.02	2112 m	56.10 (55.84)	8.00 (8.37)	333 (322.3)
$P[C{\equiv}CGe(CH_3)_3]_3$	56.6	81–82	112–114/0.02		39.50 (39.49)	6.17 (5.92)	451 (455.8)
$O{=}P[C{\equiv}CSi(CH_3)_3]_3$	85	137–138.5		2133 m	53.20 (53.25)	7.97 (7.98)	320 (338.0)
$O{=}P[C{\equiv}CGe(CH_3)_3]_3$	64	172–173		2122	38.00 (38.15)	5.70 (5.72)	451 (471.8)

(*b*) *Attempted exchange reaction.* Phenyldichlorophosphine (1.8 g; 10 mmoles) in 10 ml of THF was slowly added to a 50 ml THF solution containing 7 g (20 mmoles) of bis(trimethyltin)acetylene. After standing for 16 h a black solid had formed. The mixture was filtered and the solid dried under vacuum. It melted slightly above 150° and showed a C≡C stretching vibration in the infrared spectrum. The only other product isolated from this reaction mixture was trimethyltin chloride, indicating that the exchange reaction had taken place but had not stopped after releasing the initial trimethyltin group.

(4) *Synthesis of* $PhP[C{\equiv}CPb(CH_3)_3]_2$

The procedure was the same as described in (1*a*) with the exception that the reaction mixture was refluxed for 5 h. The reactants, 7 ml (10 mmoles) of n-butyllithium/hexane, 0.8 g (5 mmoles) of phenyldiethynylphosphine in 150 ml of THF, and 2.88 g (10 mmoles) of trimethyllead chloride, yielded 1.65 g (50%) of product with m.p. 94–95° after two crystallizations from hexane. The compound melts to a colorless liquid, turns rapidly brown above 110° and detonates above 130°.

(5) *Synthesis of* $P[C{\equiv}CSi(CH_3)_3]_3$

(*a*) *From trimethylethynylsilane,* $(CH_3)_3SiC{\equiv}CH$. The procedure was the same as that described under (1*a*). Thus, from 5.5 g (55 mmoles) of trimethylethynylsilane in 150 ml of THF, 38 ml (55 mmoles) of n-butyllithium/hexane solution and 4.9 g (18 mmoles) of phosphorus tribromide in 20 ml of hexane there was obtained 2.9 g (49%) of product with b.p. 90–92°/0.02 mm and m.p. 49–50° (hexane).

(*b*) *Exchange reaction.* A solution of 1.1 g (0.8 mmoles) of phosphorus trichloride in 2 ml hexane was added to 6.4 g (25 mmoles) of (trimethylsilyl)(trimethyltin)-acetylene and the mixture heated for 5 h. The solution turned brown. The trimethyltin chloride formed during the reaction, as well as some starting material, were removed under vacuum and the residue vacuum distilled. The yield was 1.9 g (73.6%) with b.p. 90–92°/0.2 mm; m.p. 49° (hexane).

(6) *Synthesis of* $P[C{\equiv}CGe(CH_3)_3]_3$

A solution of 6.1 g (20 mmoles) of (trimethylgermyl)(trimethyltin)acetylene and 0.9 g (6.6 moles) of phosphorus trichloride in THF was allowed to stand for approximately 16 h at room temperature. The solvent was removed by distillation and the residue vacuum distilled. The NMR spectrum of the more volatile fraction containing the trimethyltin chloride indicated the presence of about 5% trimethylchlorogermane but no starting material. $P[C{\equiv}CGe(CH_3)_3]_3$ was obtained in 56% yield (1.7 g) b.p. 112–114°/0.02 mm; m.p. 81–82° (hexane).

(7) *Synthesis of* $OP[C{\equiv}CSi(CH_3)_3]_3$ *and* $OP[C{\equiv}CGe(CH_3)_3]_2$

A solution of 0.45 g (1.4 mmoles) of tris[(trimethylsilyl)ethynyl]phosphine in 5 ml of acetone was heated with 0.5 ml of 30% hydrogen peroxide solution for 30 minutes. The solvent was evaporated and the residue recrystallized twice from hexane. The yield was 0.4 g (85%); m.p. 137–138°.

Via the same method described above, the phosphine oxide was obtained from tris[(trimethylgermyl)ethynyl]phosphine in 64% yield; m.p. 172–173°.

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