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## SYNTHESIS AND PROPERTIES OF A NEW KIND OF ONE-DIMENSIONAL CONDUCTOR

### VIII \*. SYNTHESIS AND CHARACTERIZATION OF *trans*-BIS-1-ALKYNYL SUBSTITUTED SILICON, GERMANIUM, TIN PHTHALOCYANINES AND GERMANIUM HEMIPORPHYRAZINES

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#### Summary

The preparation of several new *trans*-bis-1-alkynyl(phthalocyaninato)silicon (VIc–f), -germanium (VIIc–f) and -tin (VIII d, f) compounds as well as *trans*-bis-1-alkynyl(hemiporphyrizinato)germanium (XIc, e, f) derivatives is described. The products were obtained in high yields by treating the corresponding dichlorides (I, II, IV, X; X = Cl) with 1-alkynyl Grignard reagents (Vc–f) in tetrahydrofuran (THF) and were characterized spectroscopically. The compounds obtained are considered as models for a new kind of one-dimensional conductor.

#### Introduction

The phenomenon of electrical conductivity in organic and inorganic compounds in the solid state has attracted considerable attention among solid state chemists and physicists [2]. Currently there is increasing interest in the study of efficient charge transport in such compounds [3]. Our concept for the development of conducting organic material was presented recently [4]. The proposed compounds consist of tetradentate, bivalent, planar, highly polarizable macrocycles e.g. phthalocyaninate ( $Pc^{2-}$ ) or hemiporphyrizinate ( $Hp^{2-}$ ) (Figure 1), which are complexed with quadrivalent metals, e.g.  $SiCl_2^{2+}$ ,  $GeCl_2^{2+}$  and  $SnCl_2^{2+}$ . By displacement of the chloride and simultaneous polymerization

\* For part VII see Ref. 1.

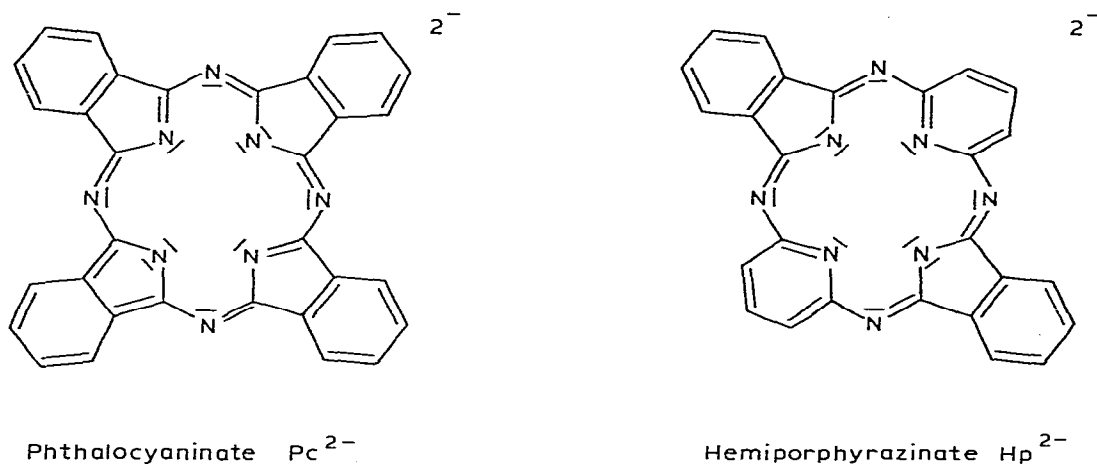
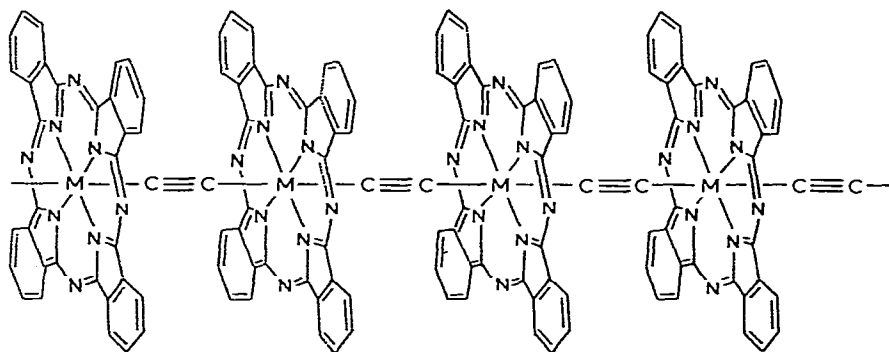


Fig. 1. Basic structures of the phthalocyanine and hemiporphyrizine ligands.

of the metal phthalocyanines and hemiporphyrizines by a bidentate, linear bridging ligand, e.g.  $C_2^{2-}$ , one should obtain a polymeric backbone structure with stacked macrocycle arrangement (Figure 2). MO calculations have shown that these compounds have energy band structure which should give rise to electronic charge transport in the molecule [5].

Only a little work had been done on the preparation of metal-IVb phthalocyanines and related compounds with bisaxial metal-carbon bonds [6]. Although monoaxial metal-carbon bonded phthalocyanines (III) were prepared directly by reacting appropriate alkyl- or aryltrichlorosilanes with 1,3-diiminoisoindoline [7], only two compounds with bisaxial metal-carbon bonds in the phthalocyanine series have been reported (briefly) in the literature [8,9]. Thus we have made a general study of the preparation of metal-IVb phthalocyanines and hemiporphyrizines containing bisaxial metal-carbon



M = Si, Ge, (Sn)

Fig. 2. Drawing of the polymer phthalocyanine-metal-acetylide as a model for a new type of one-dimensional conductor.

bonds, and have examined the chemical and physical properties of such compounds.

In this paper we describe the preparation and characterization of *trans*-bis-1-alkynyl(phthalocyaninato)silicon (VIc–f), -germanium (VIIc–f), -tin (VIIIc, f) and -hemiporphyrinatogermanium (XIc, e, f) with bisaxial metal–carbon (*sp*) bonds, which we consider as monomeric models for the proposed new polymeric structure (Figure 2). Furthermore we examined the stabilities of the metal–carbon bonds by varying the metal and the macrocycle, as well as the effect of substituents on the alkynyl  $C_{sp}$  atoms of the bisaxial ligands e.g. with respect to the influence of the size of these substituents on the solubilities of compounds VIc–f, VIIc–f and VIIIc, f.

## Results and discussion

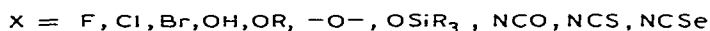
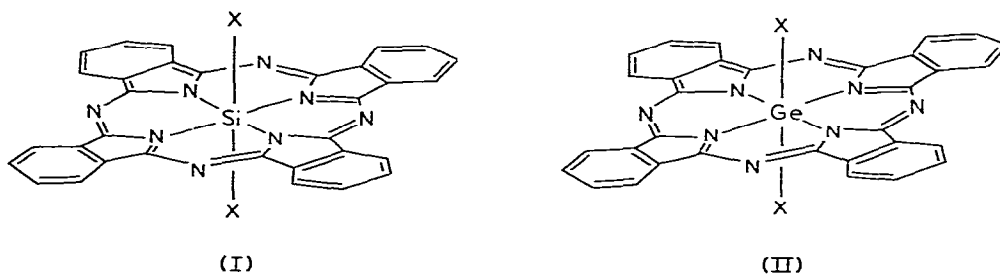
Among the Group-IVb-metal phthalocyanines studied, the tin phthalocyanines exhibited properties different from those of the silicon and germanium analogues. In agreement with earlier work [10], dichloro(phthalocyaninato)tin (IV, X = Cl) and its derivatives showed the lowest stability in the reaction with Grignard reagents, and so the reactions of IV, X = Cl, with organometallic reagents are discussed separately.

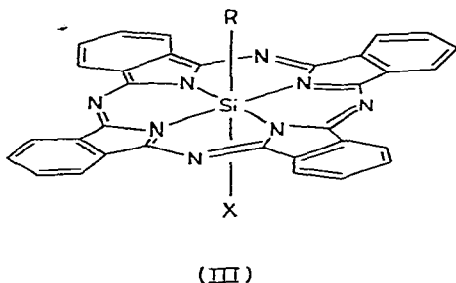
### a. *trans*-Bis-1-alkynyl(phthalocyaninato)silicon (VIc–f) and -germanium (VIIc–f)

Most metal phthalocyanines are formed with elements that are considerably more metallic than either silicon or germanium. With these elements, the formation of hexacoordinated octahedral complexes is unusual and deviates from the behaviour generally associated with these two semi-metals. Thus the silicon and germanium in the phthalocyanine derivatives are bound to four planar nitrogen atoms and to two other atoms, one above and the other below the planar macrocycle.

Dichloro(phthalocyaninato)silicon and -germanium (I, II, X = Cl) were prepared and characterized in 1960 [11a,b]. It was found, that the two axial substituents X on the central metal atom could be varied over a wide range and several derivatives were thus prepared [11c].

A new class of substituted silicon phthalocyanines (III) in which one of the axial substituents is replaced by an organic group with a direct metal–carbon bond was also prepared. The synthetic route to these compounds is based on the reaction of alkyl- or phenyltrichlorosilanes with 1,3-diiminoisoindoline [7].



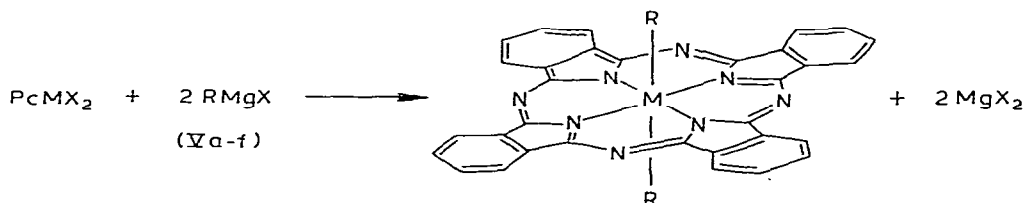


R = CH<sub>3</sub>, C<sub>2</sub>H<sub>5</sub>, C<sub>6</sub>H<sub>5</sub>

X = Cl, OH, OR

With tetracoordinated metal-IVb compounds the usual method of converting a metal-halogen bond to a metal-carbon bond is to treat the metal halide with metal organic compounds, e.g. with lithium, sodium or magnesium derivatives.

Preliminary studies on the reaction of dichloro(phthalocyaninato)silicon and -germanium (I, II, X = Cl) with simple alkyl and aryl Grignard compounds, e.g. methyl- or phenylmagnesium bromide (Va, b) gave the expected *trans*-bis-alkyl- and -phenyl(phthalocyaninato)metal derivatives (VIa, b, VIIa, b) in excellent yields. In this reaction the Grignard reagents were far more effective and gave purer products VIa, b and VIIa, b than the corresponding organolithium or -sodium compounds. In accord with these results, we obtained the *trans*-bis-1-alkynyl(phthalocyaninato)silicon (VIc-f) and -germanium (VIIc-f) compounds in about 90% yield by treating highly purified dichloro(phthalocyaninato)silicon and -germanium (I, II, X = Cl) with a 2-3 fold excess of 1-alkynyl Grignard compounds (Vc-f) in tetrahydrofuran.



(I, M = Si, X = Cl;

II, M = Ge, X = Cl;

IV, M = Sn, X = Cl)

(VI, M = Si, R = a-f;

VII, M = Ge, R = a-f;

VIII, M = Sn, R = d, f)

a = CH<sub>3</sub>

b = C<sub>6</sub>H<sub>5</sub>

c = C≡CH

d = C≡C-CH<sub>3</sub>

e = C≡C-C(CH<sub>3</sub>)<sub>3</sub>

f = C≡C-C<sub>6</sub>H<sub>5</sub>

Due to the low solubility of dichloro(phthalocyaninato)silicon and -germanium (I, II, X = Cl) in the usual organic solvents and also to the fact that the attack of the Grignard reagents Vc-f on the octahedral starting materials I and II, X = Cl, might be hindered, the reaction was continued under reflux for

several hours. The use of solvents other than THF, e.g. ether or glyme, gave a complex mixture of starting material and products, and sometimes did not give any of the expected products. The products (VIc-f, VIIc-f) were obtained in a fairly pure form under the reaction conditions described. They were further purified by the usual extraction methods. It should be noted, that our experimental conditions differ markedly from earlier investigations on related solvent-soluble analogues e.g. porphine or tetraphenylporphine [12,13]. It was not possible to achieve successful results in our systems using the cited conditions [12].

In the pure state the microcrystalline blue-greenish powders VIc-f and VIIc-f are stable towards moisture and light for several months without decomposition. Different thermoanalysis (DTA) of VIc, d showed no significant changes up to 250°C; at more elevated temperatures the metal-carbon bond breaks and the macrocycle is partially destroyed. In solution, however, the compounds VIc-f and VIIc-f are less stable in the presence of UV and visible light. It was difficult to purify the products VIc-f and VIIc-f by recrystallisation from high boiling solvents such as DMF, HMPT or 1-chloronaphthalene. The metal-carbon bond was found to be cleaved, and a mixture of dihydroxy compounds (I, X = OH, II, X = OH) and polymers (I, X = -O- and II, X = -O-) was formed due to the presence of trace amounts of water in the solvent. The cleavage of the metal-carbon bond depends mostly on the solvent temperature used. The compounds VIc-f and VIIc-f, are convertible into the corresponding dihydroxy(phthalocyaninato)silicon and -germanium (I, X = OH, II, X = OH) by hydrolysis in aqueous acidic medium and to the chlorides (I, X = Cl, II, X = Cl) in conc. HCl. Phenylacetylene was detected by GLC as the other product of the reaction from VI f and VII f.

Compounds VIc-f and VIIc-f obtained were characterized by spectroscopic

TABLE 1  
(PHthalocyaninato)SILICON, -GERMANIUM AND -TIN DERIVATIVES WITH METAL-CARBON BONDS <sup>a</sup>

Compound	R	IR(Nujol) $\nu(\text{C}\equiv\text{C})$ ( $\nu(\text{C}\equiv\text{C}-\text{H})$ ) ( $\text{cm}^{-1}$ )	<sup>1</sup> H NMR(CDCl <sub>3</sub> ) $\delta$ (ppm)	$M^+(m/e)$ <sup>b</sup>
VIa	CH <sub>3</sub>			570
VIb	C <sub>6</sub> H <sub>5</sub>			694
VIc	C≡CH	2017(3262)		590
VId	C≡CMe	2164		618
VIe	C≡Ct-Bu	2132, 2140	9.6(m, arom.), 8.3(m, arom.) -0.82(s, CH <sub>3</sub> )	702
VI f	C≡CPh	2148		742
VIIa	CH <sub>3</sub>			616
VIIb	C <sub>6</sub> H <sub>5</sub>			740
VIIc	C≡CH	2013(3273)		636
VIIe	C≡Ct-Bu	2128, 2137	9.62(m, arom.), 8.36(m, arom.) -0.78(s, CH <sub>3</sub> )	748
VII f	C≡CPh	2145		788
VIII d	C≡CMe	2125 <sup>c</sup>		710
VIII f	C≡CPh	2120 <sup>c</sup>		834

<sup>a</sup> The compounds prepared gave satisfactory microanalytical data except for the tin derivatives VIII d and VIII f (see text). <sup>b</sup>  $M^+$  with <sup>28</sup>Si, <sup>74</sup>Ge, <sup>120</sup>Sn. <sup>c</sup> Not analytical pure.

methods and the spectral data are listed in Table 1. It has been reported [14] that bulkier substituents on the phthalocyanine ring periphery increase the solubility of phthalocyanines in common organic solvents. In agreement with this we observed that the compounds VIe and VIIe are more soluble in organic solvents than the other related compounds and this permits observation of the NMR spectra. The tertiary-butyl groups in these compounds give rise to a singlet at high field in the NMR spectra at  $-0.82$  and  $-0.78$  ppm, respectively [15]. This effect is due to the shielding of the bisaxial group by the ring current of the phthalocyanine moiety. At the same time the peripheral protons of the benzene ring appear at lower field (see Table 1).

The IR spectra (Nujol) of VIc-f and VIIc-f, showed the absorption band due to the C=C bond (Table 1). The acetylenic compounds VIc and VIIc showed also the  $\equiv\text{C}-\text{H}$  stretching absorption at  $3260\text{ cm}^{-1}$  in a region where phthalocyanines do not absorb.

The electronic absorption spectra (in 1-chloronaphthalene) of VIc-f and VIIc-f show an intense absorption around  $690\text{ nm}$  in addition to the so-called Soret band around  $350\text{ nm}$  [16]. The spectra are similar to those of the starting materials I, X = Cl, and II, X = Cl. This is because the alkynyl groups are perpendicular to the plane of the ring and the conjugated  $\pi$ -system is not affected. The effect of irradiation on phthalocyanines was demonstrated for  $\text{PcSi}(\text{C}\equiv\text{CtBu})_2$  (VIe). Upon irradiation of this compound in THF with a high pressure mercury lamp without filter, the absorption at  $690\text{ nm}$  was found to decrease rapidly in intensity and to disappear in 10 min. However, upon irradiation in  $\text{CHCl}_3$  at  $332\text{ nm}$  the absorption at  $690\text{ nm}$  disappeared only slowly.

The mass spectra of phthalocyanines VIc-f and VIIc-f show the molecule peak as the base peak in all cases (Table 1). The consecutive loss of both alkynyl substituents was also observed. The appearance of the doubly charged molecule ion is characteristic of these compounds [17].

#### *b. trans-Bis-1-alkynyl(phthalocyaninato)tin (VIII d, f)*

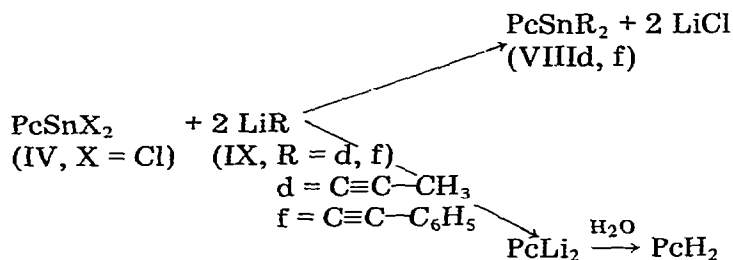
Earlier investigations on the phthalocyaninetin derivatives  $\text{PcSnX}_2$  (IV, X = Cl, Br, I, OH, OR,  $-\text{O}-$ ), led to the conclusion that these compounds differ markedly in their stability and reactivity from the corresponding dichloro-(phthalocyaninato)silicon and -germanium (I, X = Cl, II, X = Cl). This is not surprising because tin is significantly larger than either silicon or germanium and does not fit without distortion into the hole of the phthalocyanine macrocycle. Moreover tin is stable in both the +II and +IV oxidation states and is easily convertible from one state into the other.

The preparation of tin phthalocyanines was first reported in the 1930's [18], and the existence of  $\text{PcSn}$ ,  $\text{PcSnCl}_2$  and  $\text{Pc}_2\text{Sn}$  was established. Later the ease of changing the oxidation states of tin complexed by phthalocyanine was demonstrated [19]. Several X-ray studies [20] demonstrated the nonpolarity of the phthalocyanine ring when complexed with tin, the tin atom lying out of the plane of the macrocycle. The structure as well as the low redox-potential give rise to a lower stability of the tin phthalocyanines towards heat, oxidizing and reducing agents, and acids [10b,21,22].

Due to the different reactivity of the dichloro(phthalocyaninato)tin (IV, X = Cl) it was not possible to isolate the *trans-bis-1-alkynyl(phthalocyaninato)tin*

(VIIIId, f) from reactions under the conditions used for the silicon and germanium analogues. The use of milder conditions (room temperature) and longer reaction times (72 h) yielded the expected products VIIIId, f ( $M = \text{Sn}$ ), but it was not possible to isolate them in a pure state, because the usual chromatographic or recrystallization methods could not be used. The reaction of  $\text{PcSnCl}_2$  with a large excess of the alkynyl Grignard reagents Vd, f did not give purer products VIIIId, f, but mainly  $\text{PcMg}$ , which is evidently formed by transmetallation. The same result was obtained when longer reaction times were used. Heating IV,  $X = \text{Cl}$ , and Vd, f in THF to reflux led to the formation of a mixture of mainly  $\text{PcSn}$  and  $\text{PcMg}$ . From one experiment in THF in an autoclave at  $100^\circ\text{C}$   $\text{PcMg}$  was formed in 100% yield.

The difficulty of obtaining pure VIIIId, f led us to try other organometallic reagents; however, when sodium alkynes in liquid ammonia or aluminium alkynes in THF were used, only the starting material IV,  $X = \text{Cl}$ , was recovered and no reaction had occurred. Lithium alkynes, IXd, f, on the other hand, gave the desired products VIIIId, f contaminated with  $\text{PcH}_2$  and  $\text{PcSnCl}_2$ .  $\text{PcH}_2$  is formed by initial transmetallation to give  $\text{PcLi}_2$  and subsequent hydrolysis.



Earlier investigations [19] have shown that dibromo- and diiodo(phthalocyaninato)tin (IV,  $X = \text{Br}, \text{I}$ ) are more reactive towards hydrolysis than the dichloride IV,  $X = \text{Cl}$ . Use of IV,  $X = \text{Br}, \text{I}$ , in reactions with the Grignard reagents Vd, f gave no advantage over use of the dichloride IV,  $X = \text{Cl}$ .

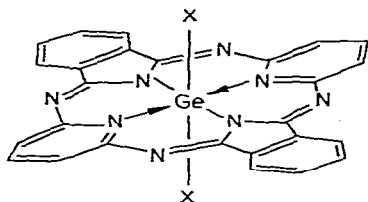
The products VIIIId, f are greenish-blue amorphous powders, relatively stable towards heat and light. When hydrolysed in alkaline media the hydroxide (IV,  $X = \text{OH}$ ) is formed, while acidic hydrolysis with dilute  $\text{HCl}$  gives  $\text{PcSnCl}_2$ . Treatment of VIIIId, f with concentrated sulfuric acid caused immediate demetallation and considerable amounts of phthalimide were detected by infrared spectroscopy.

Like those of the silicon and germanium analogues, the IR spectra of VIIIId, f differ from those of the starting material. The  $\nu(\text{C}=\text{C})$  vibration appears at about  $2120 \text{ cm}^{-1}$  (Table 1). The  $\text{Sn}-\text{C}$  vibrations could be assigned only partly on the basis of data in the literature [23]. The mass spectra show the parent molecular peak, as do the silicon and germanium analogues.

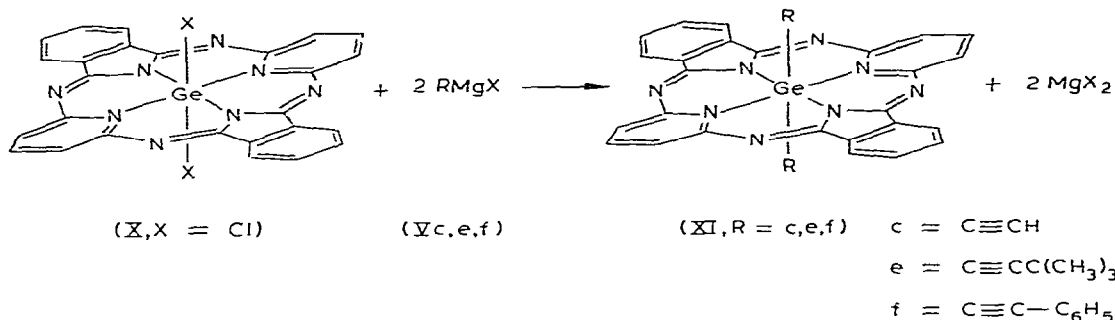
### c. *trans-Bis-1-alkynyl(hemiporphyrizinato)germanium (XIc, e, f)*

The nearly planar [24] hemiporphyrazine system was first prepared in 1952 [25]. The metal-free macrocycle was found to react with several metal salts to yield stable metal complexes [25,26], but it was impossible to prepare the silicon complex [17b].

However, several bisaxial (hemiporphyrizinato)germanium compounds (X) are known [25,26]. For the preparation of hemiporphyrizinato analogues XI a method similar to that used for the phthalocyanines was used, invoking reaction of  $\text{HpGeX}_2$  (X, X = Cl) with alkynyl Grignard compounds, Vc, e, f, in THF. However, it was necessary to use dichlorobis(triphenylphosphine)nickel [27] as a catalyst to force the reaction to completion.



(X, X = Cl, Br, F, OH, OR)



The compounds XIc, e, f were characterized spectroscopically. The methyl protons of the t-butyl group in XIe give a singlet at  $\delta = 0.95$  ppm, compared with values of  $-0.82$  and  $-0.78$  ppm for the phthalocyanines VIe and VIIe. This can be ascribed to the fact that the hemiporphyrizine ring system has a weaker ring current [24] than the phthalocyanine system.

Differential thermoanalysis of XIe in a helium atmosphere showed an endothermic decomposition around  $300^\circ\text{C}$ ; this is probably due to the splitting off of the *trans* bisaxial substituents. An exothermic decomposition observed at  $330^\circ\text{C}$  is due to the decomposition of the hemiporphyrizine ring [17b].

The hemiporphyrizine XIe could be sublimed at  $280^\circ\text{C}/2$  Torr under nitrogen. Details of an X-ray study of the violet crystals thus obtained have been published elsewhere [28].

The IR spectra of the hemiporphyrizines [17b,26] were found to have more absorption bands than their phthalocyanine analogues due to their lower symmetry ( $D_{2h}$  against  $D_{4h}$  of phthalocyanines). The IR spectra were valuable in interpreting the structure of the products as can be seen from Table 2.

The mass spectra of the hemiporphyrizines XIc, e, f in all cases showed the molecular ion (Table 2), and characteristic fragmentation ions analogous to those from the phthalocyanines [17b].



TABLE 2  
(HEMIPORPHYRAZINATO)GERMANIUM DERIVATIVES WITH METAL—CARBON BONDS <sup>a</sup>

Compound	R	IR(Nujol) $\nu(\text{C}\equiv\text{C})(\nu(\equiv\text{C}-\text{H}))(\text{cm}^{-1})$	<sup>1</sup> H NMR(CDCl <sub>3</sub> ) $\delta(\text{ppm})$	<i>M</i> <sup>+</sup> ( <i>m/e</i> , <sup>74</sup> Ge)
XIc	C≡CH	2017(3227)	—	562
XIe	C≡Ct-Bu	2142, 2171	7.4—7.8(m) 0.95(s, CH <sub>3</sub> )	684
XIf	C≡CPh	2151	7.75—8.0(m)	714

<sup>a</sup> All compounds gave satisfactory microanalytical data.

In the electronic spectra of XIc, e, f the most intense bands occur at about 390 and 415 nm (Table 2). A less intense band appears at a higher wave length, 580 nm. As for the phthalocyanines, a change in the *trans* bisaxial substituents did not have any appreciable effect in the electronic absorption spectra.

In summary a general method has been devised for forming (phthalocyaninosilicon, -germanium and -tin—carbon bonds and (hemiporphyrinato)-germanium—carbon bonds. The model experiments have been extended to the preparation of one-dimensional polymers (Fig. 2) [1].

## Experimental

The IR spectra were recorded on Philips Unicam Sp 1000 IR spectrometer and the electronic absorption spectra on Beckman Spectrometer Acta M-VII. NMR spectra were recorded on Bruker WP 80 and mass spectra on Varian MAT 711. Differential thermoanalyses were done on the Netzsch-Simultan-Thermo-Analysegerät STA 429.

All organometallic reactions were conducted with exclusion of moisture and air under dry nitrogen using anhydrous solvents. PcSiCl<sub>2</sub>, PcGeCl<sub>2</sub>, PcSnCl<sub>2</sub> and HpGeCl<sub>2</sub> (I, II, IV and X, X = Cl) were prepared as described in the literature [11a,b,19,26]. The alkynyl Grignard reagents Vc—f were prepared by reacting the appropriate alkynes with ethylmagnesium bromide in THF.

### *trans-Bis-1-alkynyl(phthalocyaninato)silicon and -germanium (VIc—f, VIIc—f)*

**General procedure.** Dichloro(phthalocyaninato)silicon or germanium (I, II, X = Cl, 1 mmol) was added under nitrogen to the appropriate Grignard reagent (V, 5 mmol) in THF (50 ml) at room temperature. The mixture was refluxed for 15 h, cooled, hydrolyzed with 5% HCl (10 ml), and filtered. The collected solid was washed thoroughly with water and dried. Insoluble products VIc, d, f and VIIc, d, f were extracted with methanol and acetone successively and dried at 100°C. The THF soluble products VIe and VIIe were extracted with THF and the deep blue solution was evaporated to give pure VIe and VIIe. Yield 90%. The spectral properties of the compounds (VIc—f, VIIc—f) are given in Table 1. Sublimation of VIe and VIIe under high vacuum did not yield any crystals suitable for X-ray analysis.

PcM(CH<sub>3</sub>)<sub>2</sub> and PcM(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub> (VIa, b; VIIa, b, M = Si, Ge) were prepared analogously by reacting the corresponding PcMCl<sub>2</sub> (I, II, M = Si, Ge, X = Cl) with CH<sub>3</sub>MgBr (Va) and C<sub>6</sub>H<sub>5</sub>MgBr (Vb), respectively.

*trans-Bis-1-alkynyl(phthalocyaninato)tin (VIII d, f)*

*General procedure.* Compounds VIII d, f were prepared as described above, but the reaction mixture was stirred at room temperature for 72 h.

The reaction of  $\text{PcSnCl}_2$  (IV) with lithium alkynides was carried out as described for that with the alkynyl Grignards except that ether was used as solvent.

*trans-Bis-1-alkynyl(hemiporphyrizinato)germanium (XI c, e, f)*

*General procedure.* The solid dichloro(hemiporphyrizinato)germanium (XI, X = Cl, 1 mmol) was added to the appropriate Grignard reagents (Vc, e, f, 5 mmol) in THF (50 ml) in presence of dichloro-bis(triphenylphosphine)-nickel(II) (0.02 mmol) as catalyst, and the mixture was refluxed for 10 h. The products were worked up as described for the preparation of VIIc–f. The bis-axial t-butyl substituted product XIe, was sublimed under vacuum (2 Torr, 300°C) and the crystals obtained were analysed by X-ray diffraction [28].

*Hydrolysis of VI f and VII f*

The compounds VI f and VII f (650 mg) were treated with conc. HCl (0.2 ml) in 8 ml THF in a sealed tube for 48 h at room temperature. After filtration, the filtrate was extracted with  $\text{CH}_2\text{Cl}_2$  and the extract analysed by GLC. Phenylacetylene was identified by comparison with an authentic sample.

**Acknowledgements**

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