

# Synthesis, characterization and comparison of group 14 pyrrolides and indolides $\text{Ph}_3\text{MX}$ ( $\text{M} = \text{Si}, \text{Ge}, \text{Sn}$ ; $\text{X} = \text{C}_4\text{H}_4\text{N}, \text{C}_8\text{H}_6\text{N}$ )<sup>☆</sup>

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## ARTICLE INFO

### Article history:

Received 17 May 2010

Received in revised form

28 July 2010

Accepted 29 July 2010

Available online 6 August 2010

### Keywords:

Pyrrolides

Indolides

Multinuclear NMR

X-Ray diffraction

Raman spectroscopy

## ABSTRACT

The biologically important heterocycles pyrrole,  $\text{C}_4\text{H}_4\text{N}$ , and indole,  $\text{C}_8\text{H}_6\text{N}$ , ought to be useful as reagents in organic synthesis. Unfortunately, working with them has proved to be difficult because they tend to self-polymerize in solution, especially in the presence of acid catalysts. When the self-polymerization can be controlled, however, the pyrrole and indole units should provide an important route to selective N-metal binding, particularly when these ligands are activated by alkyl-lithium reagents. Using this approach, a general synthesis of the group 14 pyrrolides and indolides,  $\text{Ph}_3\text{MX}$  ( $\text{M} = \text{Si}, \text{Ge}, \text{Sn}$ ;  $\text{X} = \text{C}_4\text{H}_4\text{N}, \text{C}_8\text{H}_6\text{N}$ ), has been developed and the results are reported here. The compounds are formed as high-melting, white crystalline solids and have been characterized by  $^{13}\text{C}$ -,  $^{29}\text{Si}$ - and  $^{119}\text{Sn}$ -NMR, Raman and electron-impact mass spectroscopy as well as elemental analysis. A single-crystal X-ray study of  $\text{Ph}_3\text{Si}(\text{C}_4\text{H}_4\text{N})$  has shown that the compound is disordered in the tetragonal lattice, even at low temperature (100 K).

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## 1. Introduction

The chemistry of transition metals coupled to organic moieties has been explored for many years. This major research area is still continuing to develop today, as evidenced by the ever-increasing number of journals dedicated solely to transition metal-organic chemistry [1]. One class of main group compounds, which is of considerable practical interest, is that of organotin [2]. These compounds have many important uses, most notably as biocides and in the development of novel treatments for various diseases [3]. There are only a few compounds known in which a tin atom is bonded to the hetero-atom of a heterocycle. Two heterocycles of particular biological significance are pyrrole,  $\text{C}_4\text{H}_4\text{N}$ , and indole,  $\text{C}_8\text{H}_6\text{N}$ , the synthetic organic chemistry of which has been studied since the early 20th century [4,5]. These heterocycles play important roles in nature, e.g., in chlorophyll, the green pigment of plant leaves and algae, and in tryptophan,  $(\text{C}_8\text{H}_6\text{N})\text{CH}_2\text{CH}(\text{NH}_2)(\text{COOH})$ , the essential amino acid that is released from proteins by proteolytic cleavage during digestion. Linkage of a metal centre to the heterocycles can be achieved exclusively at the nitrogen atoms in

both cases by using an alkyl-lithium or alkyl-sodium reagent, and it has already proven possible to attach various metal atoms to them, usually with the formation of only one major product [6].

There are several instances of syntheses of pyrrolides and indolides using the group 14 elements in the literature [7–11]. These studies have usually focused on the reactivity of only one particular group 14 metal with pyrrole and indole. The number of comparative experiments employing several of the group 14 elements is, however, limited [12,13]. There is also no instance of a comparative study contrasting the unsubstituted group 14 pyrrolides with the corresponding indolides. The group 14 triphenylchlorides,  $\text{Ph}_3\text{MCl}$  ( $\text{M} = \text{Si}, \text{Ge}, \text{Sn}$ ), are ideal precursors for the controlled coupling of pyrrole and indole to main group metal centres to facilitate such a comparison. While the synthesis of triphenylgermanium(IV) pyrrolide [14,15], and triphenyltin(IV) pyrrolide [16,17], and the use of triphenyllead(IV) pyrrole and indole derivatives [18] in mass spectrometric studies have been reported previously, the synthesis of the analogous pyrrolides and indolides of the other group 14 elements have apparently not been attempted. It is possible that the best synthetic conditions for these compounds had not been found previously because of the facile self-polymerization of the heterocyclic reagents, which would hinder this type of product formation [19] by competing with chloride substitution on the metal centre. We report here the first successful synthesis and characterization of the complete series of group 14 triphenylmetal(IV) pyrrolides and indolides (Fig. 1),  $\text{Ph}_3\text{MX}$  ( $\text{M} = \text{Si}, \text{Ge}, \text{Sn}$ ;  $\text{X} = \text{C}_4\text{H}_4\text{N}, \text{C}_8\text{H}_6\text{N}$ ).

Abbreviations: Ind,  $\text{C}_8\text{H}_6\text{N}$ ; Pyr,  $\text{C}_4\text{H}_4\text{N}$ .

<sup>☆</sup> Presented, in part, at the 92nd Canadian Chemistry Conference and Exhibition, Hamilton, Ontario, Canada, May–June 2009.

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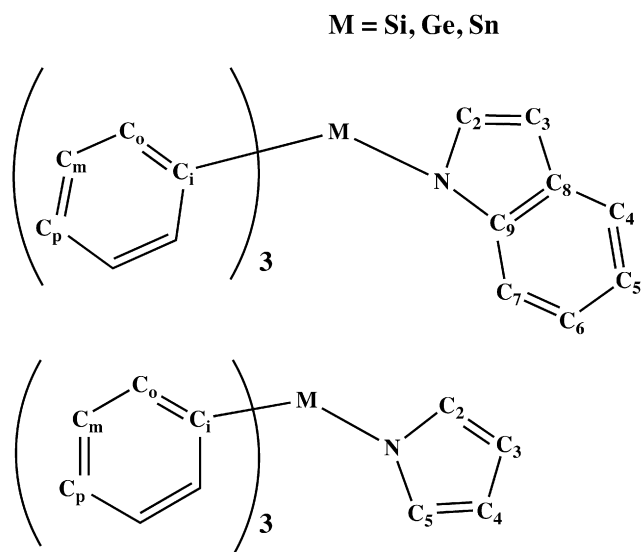


Fig. 1. General structure of indolides and pyrrolides.

## 2. Experimental

### 2.1. Materials and methods

Triphenyltin(IV) chloride, pyrrole and *n*-butyllithium were obtained from Aldrich Chemical Co., while triphenylsilicon(IV) chloride and indole were purchased from Alfa Aesar. Triphenylgermanium(IV) chloride was provided by Strem Chemical Co. All solvents were dried over sodium ribbon prior to use. Solid reagents were used as received and pyrrole was distilled under vacuum and stored under  $N_2$  prior to use.

Raman spectra (band position accuracy,  $\pm 1 \text{ cm}^{-1}$ ) were measured on a Renishaw InVia spectrometer using an argon-ion (514.5-nm) laser. The proprietary Renishaw WiRE 2.0 software was used for data acquisition and processing. NMR spectra ( $CDCl_3$ ) were obtained using JEOL 270-MHz or Varian 300-MHz [ $^{13}C$  (SiMe<sub>4</sub>, int.),  $^1H$  (SiMe<sub>4</sub>, int.)] and Unity 500-MHz [ $^{119}Sn$  (SnMe<sub>4</sub>, ext.),  $^{29}Si$  (SiMe<sub>4</sub>, int.)] spectrometers. Electron-impact (70 eV) spectra were recorded on a Kratos MS25RFA instrument. Elemental analyses were performed using a Costech ECS4010 combustion system.

The single-crystal X-ray diffraction study of  $Ph_3Si(C_4H_4N)$  was undertaken at 100 K on a BRUKER SMART CCD diffractometer, using graphite-monochromated Mo  $K\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ). The structure was solved by direct methods (using SHELX 97 software) on an absorption-corrected model generated by SADABS (SAINT-V7 software). Refinement was achieved by a full-matrix least-squares procedure based on  $F^2$ . The phenyl ring was modeled with a site occupancy factor of 0.75 with the *meta* and *para* carbon atoms being modeled anisotropically, while the *ipso* and *ortho* carbons could only be modeled isotropically because of the overlap of electron density with the pyrrole ring. The pyrrole ring was modeled with a site occupancy of 0.25 with isotropic carbons. The hydrogen atoms were located at calculated positions.

The X-ray data for compound **5** are:  $C_{22}H_{19}NSi$ , colourless, plates, tetragonal, space group  $P4_21/c$ ,  $a = b = 11.331(2)$ ,  $c = 6.561(2) \text{ \AA}$ ,  $\alpha = \beta = \gamma = 90.00^\circ$ ,  $V = 842.3(4) \text{ \AA}^3$ ,  $T = 100 \text{ K}$ ,  $Z = 2$ , 963 reflections measured, 753 observed ( $I > 2\sigma(I)$ ), parameters = 62,  $R(\text{obs}) = 0.0822$ ,  $R(\text{total}) = 0.1098$

#### 2.1.1. $Ph_3Ge(C_8H_6N)$ (**1**)

Dropwise addition of *n*-butyllithium (36 mmol, 1.6 M solution in hexane) to indole (33 mmol) in dried hexane (100 mL) under inert

conditions followed by stirring for 24 h afforded the lithiated indole as a white precipitate. Triphenylgermanium(IV) chloride (31 mmol) in toluene (50 mL) was added dropwise to the solution and a pink colour was observed to develop. The mixture was stirred overnight at room temperature. Filtering over silica yielded the crude reaction product, which was then crystallized from toluene. Yield: 6.32 g, 54.7% (based on  $Ph_3GeCl$ ). M.p. 145–147 °C. Anal. Calcd for  $C_{26}H_{21}NGe$ : C, 74.34%; H, 5.04%; N, 3.01%. Found: C, 74.35%; H, 4.99%; N, 3.26%.  $^{13}C$ -NMR (ppm): 141.3 (C-9), 134.8 (C-o), 133.2 (C-i), 131.8 (C-2), 131.2 (C-p), 130.4 (C-m), 128.8 (C-8), 121.0 (C-5), 120.5 (C-4), 119.4 (C-6), 113.8 (C-7), 103.9 (C-3). Raman ( $cm^{-1}$ ): 130w,  $\nu$  (Ge–Ind); 171w,  $\nu$  [Ge–Ph(x)]; 203vw,  $\delta$  [Ge–Ph( $\mu$ )]; 226mw,  $\nu$  [ $\delta$ Ge–Ph( $t'$ )]; 1337m,  $\nu$  (C–N).

#### 2.1.2. $Ph_3Si(C_8H_6N)$ (**2**)

Compound **2** was prepared as a white crystalline solid using the same procedure as for compound **1**:  $C_8H_7N$  (21.6 mmol), *n*- $C_4H_9Li$  (24.0 mmol) and  $Ph_3SiCl$  (22.3 mmol). Yield: 3.04 g, 37.5%, based on  $Ph_3SiCl$ . M.p. 153.3–153.6 °C. Anal. Calcd for  $C_{26}H_{21}NSi$ : C, 83.15%; H, 5.64%; N, 3.73%. Found: C, 82.76%; H, 5.57%; N, 3.58%.  $^{29}Si$ -NMR (ppm): –14.6.  $^{13}C$ -NMR (ppm), [ $^{119}Si$ – $^{13}C$ , Hz]: 141.0 (C-9), 135.9 (C-o), [2], 11], 132.2 (C-i), 131.8 (C-2), 131.7 (C-p), 130.6 (C-m), 128.2 (C-8), 121.5 (C-5), 120.6 (C-4), 120.3 (C-6), 114.7 (C-7), 105.5 (C-3). Raman ( $cm^{-1}$ ): 146w,  $\nu$  (Si–Ind); 172vw,  $\nu$  [Si–Ph(x)]; 212vw,  $\nu$  [ $\delta$ Si–Ph( $\mu$ )]; 237w,  $\nu$  [ $\delta$ Si–Ph( $t'$ )]; 1334m,  $\nu$  (C–N).

#### 2.1.3. $Ph_3Sn(C_8H_6N)$ (**3**)

Compound **3** was prepared by the same method as compound **1**, using  $C_8H_7N$  (24 mmol), *n*- $C_4H_9Li$  (24 mmol) and  $Ph_3SnCl$  (25 mmol) to give white crystals. Yield: 4.22 g, 38.0%, based on  $C_4H_9Li$ . M.p. 144.7–145.1 °C.  $^{119}Sn$ -NMR (ppm): –109.9.  $^{13}C$ -NMR (ppm), [ $^{119}Sn$ – $^{13}C$ , Hz]: 143.0 (C-9), 137.0 (C-o), [2], 45], 135.9 (C-i), [1], 627], 133.2 (C-2), 130.6 (C-p), [4], 13], 129.5 (C-m), [3], 60], 121.0 (C-5), 120.6 (C-4), 119.3 (C-6), 113.6 (C-7), 104.2 (C-3), [3], 18]. Raman ( $cm^{-1}$ ): 124vw,  $\nu$  (Sn–Ind); 152vw,  $\nu$  [Sn–Ph(x)]; 206 mw,  $\delta$  [Sn–Ph( $\mu$ )]; 215  $\delta$  [Sn–Ph( $t'$ )]; 263vw,  $\nu$  [Sn–Ph( $t$ )]; 277vw,  $\nu$  [Sn–Ph( $t$ )]; 1294m,  $\nu$  (C–N).

#### 2.1.4. $Ph_3Ge(C_4H_4N)$ (**4**)

Compound **4** was prepared by the same method as compound **1**, using 33 mmol  $C_4H_5N$ , 36.0 mmol *n*- $C_4H_9Li$  and 31.0 mmol  $Ph_3GeCl$  to give white crystals. Yield: 3.40 g, 20.9%, based on  $Ph_3GeCl$ . M.p. 203–204 °C. Anal. Calcd for  $C_{22}H_{19}NGe$ : C, 71.42%; H, 5.18%; N, 3.79%. Found: C, 71.0%; H, 5.16%; N, 3.67%.  $^1H$ -NMR (ppm): 6.7 (H-2, H-5), 6.3 (H-3, H-4).  $^{13}C$ -NMR (ppm): 134.7 (C-o), 133.0 (C-i), 130.4 (C-p), 128.6 (C-m), 124.9 (C-2, C-5), 110.1 (C-3, C-4). Raman ( $cm^{-1}$ ): 162sh,  $\nu$  (Ge–Pyr); 174mw,  $\delta$  [GePh(x)]; 215vw,  $\delta$  [GePh(x)]; 234m,  $\nu$  [Ge–Ph( $t'$ )]; 247vw, Ge–Ph( $t$ ); 263vw,  $\nu$  (Ge–N); 1385m,  $\nu$  (C–N).

#### 2.1.5. $Ph_3Si(C_4H_4N)$ (**5**)

Compound **5** was prepared by the same method as compound **1**, using 29.0 mmol  $C_4H_5N$ , 32.0 mmol *n*- $C_4H_9Li$  and 26.0 mmol  $Ph_3SiCl$  to give white crystals. Yield: 1.15 g, 13.6% based on  $Ph_3SiCl$ . M.p. 202–203 °C. Anal. Calcd for  $C_{22}H_{19}NSi \cdot nH_2O$ ;  $n = 0$ : C, 81.18%; H, 5.88%; N, 4.30%;  $n = 1$ : C, 76.93%; H, 6.16%; N, 4.08%. Found: C, 77.02%; H, 5.64%; N, 4.05%.  $^{29}Si$ -NMR (ppm): –21.6.  $^1H$ -NMR (ppm): 6.7 (H-2, H-5), 6.3 (H-3, H-4).  $^{13}C$ -NMR (ppm): 135.9 (C-o), 132.1 (C-i), 130.6 (C-p), 128.2 (C-m), 125.8 (C-2, C-5), 111.5 (C-3, C-4). Raman ( $cm^{-1}$ ): 176mw,  $\delta$  [Si–Ph( $\mu$ )]; 227vw,  $\nu$  [SiPh( $t'$ )]; 244m,  $\nu$  [Si–Ph( $t'$ )]; 247w,  $\nu$  [SiPh( $t$ )]; 263vw,  $\nu$  (Si–N), 1385  $\nu$  (C–N).

#### 2.1.6. $Ph_3Sn(C_4H_4N)$ (**6**)

Compound **6** was prepared by the same method as compound **1**, using 38 mmol  $C_4H_5N$ , 36.0 mmol *n*- $C_4H_9Li$  and 33.0 mmol  $Ph_3SnCl$  to give white crystals. Yield: 1.15 g, 8.2% based on  $Ph_3SnCl$ . M.p.

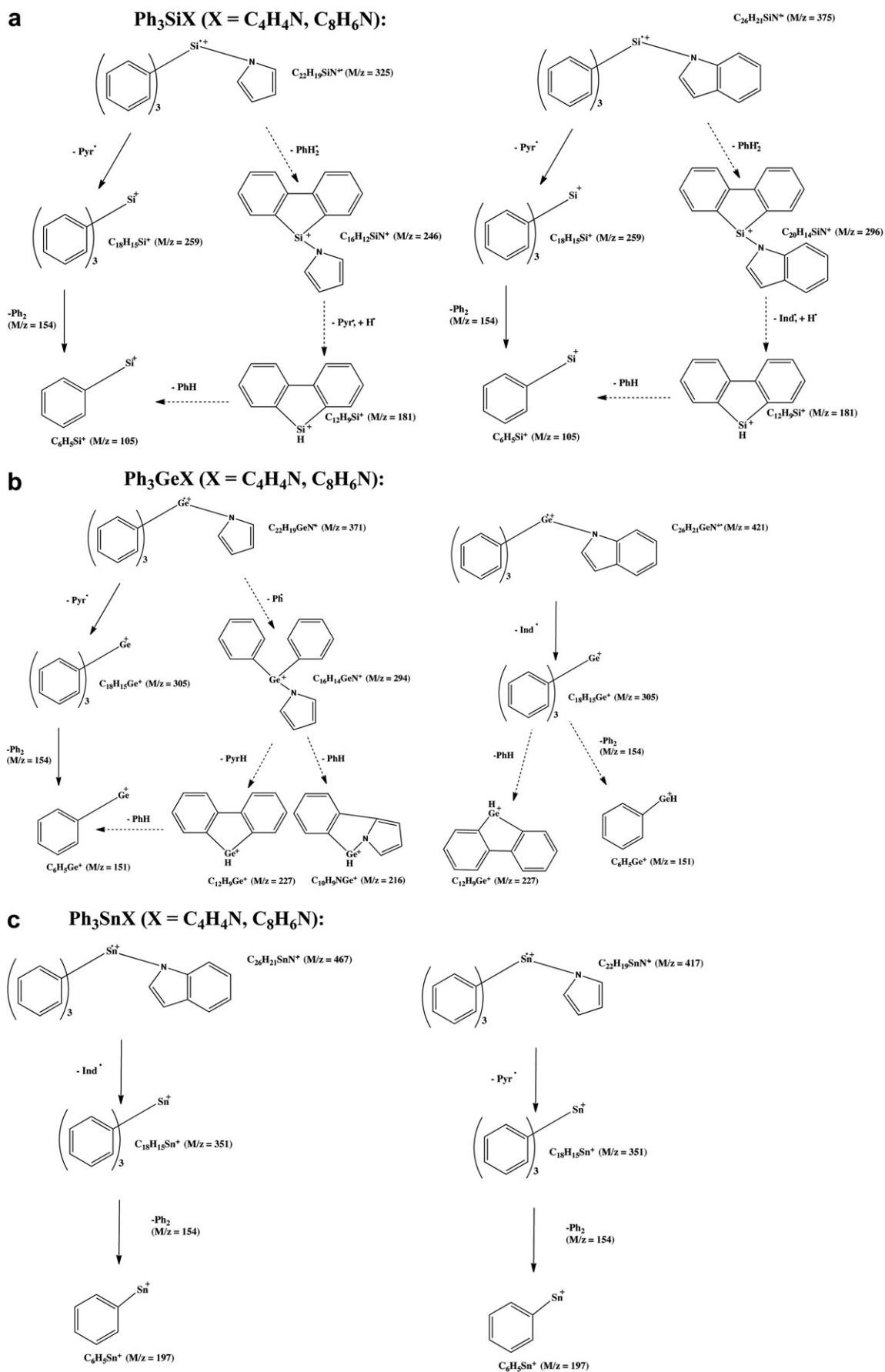


Fig. 2. Mass spectrum decomposition of group 14 pyrrolides and indolides.

204–205 °C. Anal. Calcd for C<sub>22</sub>H<sub>19</sub>NSn: C, 63.51%; H, 4.60%; N, 3.37% Found: C, 63.18%; H, 4.68%; N, 3.08%. <sup>119</sup>Sn-NMR (ppm): –104.8. <sup>1</sup>H-NMR (ppm): 6.7 (H-2, H-5), 6.3 (H-3, H-4). <sup>13</sup>C-NMR (ppm), [<sup>n</sup>J(<sup>119</sup>Sn–<sup>13</sup>C), Hz]: 136.9 (C-o), [2], 44], 135.9 (C-i), 130.6 (C-p), [4], 13], 129.3 (C-m), [3], 60] 126.1 (C-2, C-5), [2], 15] 110.1 (C-3, C-4), [3], 21]. Raman (cm<sup>-1</sup>): 158mw, δ[SnPh(x)]; 188vw, δ[SnPh(x)]; 218s, ν[Sn–Ph(t’)]; 270w, ν[SnPh(t)]; 295w, ν(Sn–N); 1383mw, ν(C–N).

### 3. Results and discussion

#### 3.1. Synthesis of compounds 1–6

The reactions of the group 14 triphenylchlorides, Ph<sub>3</sub>MCl (M = Si, Ge, Sn), with lithiated pyrrole and indole were all successful and resulted in the formation of a single product in each case. Most products gave the appropriate microanalyses but for compound **5**, carbon results were consistently low (~77%) for several samples, even after drying. These data are consistent with **5** being a monohydrate at room temperature. In contrast, <sup>1</sup>H-NMR (CDCl<sub>3</sub>) suggests that **5** has about 1/2H<sub>2</sub>O per pyrrolyl unit. This presumed hydrate is now under further investigation. All white crystalline solids obtained are stable over a period of several days in air and light but eventually darken due to hydrolysis of the heterocyclic moiety. Relatively low temperatures had to be used in the syntheses in order to minimize the possibility of self-polymerization of the heterocycles and, presumably for this reason, the product yields were quite low, with the best yields being obtained for the germanium compounds in both cases: Ph<sub>3</sub>M(C<sub>4</sub>H<sub>4</sub>N) [Sn (8.2%); Si (13.6%); Ge (20.9%)]; Ph<sub>3</sub>M(C<sub>8</sub>H<sub>6</sub>N): [Si (37.5%); Sn (38.0%); Ge (54.7%)]. The melting points for the pyrrole compounds (**4–6**) range between 202 and 205 °C and are significantly higher than are those for the corresponding indole compounds (**1–3**) (144.7–153.6 °C). This trend parallels that observed earlier for the related tetraphenyl derivatives, Ph<sub>4</sub>M, which upon replacement of one of the phenyl groups with another substituent results in a lowering of the overall spherical geometry of the molecules. For example, tetraphenyltin(IV) (m.p. = 225 °C) melts at a much higher temperature than does triphenyltin(IV) acetate (m.p. = 122–124 °C). The similarity in the shapes of the pyrrole and phenyl groups allows an energetically favorable arrangement of substituents around the metal centre. The more bulky nature of the indole group, however, hinders the packing in the crystal lattices and, consequently, the indolides melt at lower temperatures than do the analogous pyrrolides. The sizes of the central atoms can also be correlated with the stabilities in this series of complexes. Upon going from Si to Ge and then to Sn, the melting points of the triphenylmetal(IV) pyrrolides increase. Conversely, the melting points decrease for the same central atom replacement in the indolides. This difference can be attributed to lengthening of the N-metal linkage as the main group element becomes larger.

#### 3.2. NMR spectra

The <sup>13</sup>C-NMR chemical shifts for the four new group 14 metal compounds (**1**, **2**, **3** and **5**) are consistent with the literature values for the trimethyltin(IV) indolide and triphenyltin(IV) pyrrolide (**4**), and the observed chemical shifts are similar. The deshielding effect on the *ortho*, *para* and *ipso* aromatic carbons in both the pyrrolides and indolides follows the order Ge < Si < Sn. This inversion of Ge and Si from the expected periodic trend may be one more example of the tendency of germanium to resemble carbon more than silicon [20]. NMR data are not available for Ph<sub>3</sub>C(Pyr) [21] or Ph<sub>3</sub>C(Ind) [22].

#### 3.3. Mass spectra

From the mass spectral data, it was evident that the parent molecular ions were present in each case and several reasonable fragmentation pathways can be postulated (Fig. 2). The fragments containing group 14 elements were readily identified from their isotope abundance patterns [23]. Mass peaks corresponding to the formation of biphenyl-silicon fragments, for which there is precedent in the literature [24], were observed. Similar behavior was noted for the germanium species, but not for the tin compounds. This is contrary to what has been observed previously for triphenylgermanium(IV) pyrrolide. The isotopic patterns obtained experimentally for the molecular ions were in excellent agreement with the theoretically calculated values (see Table S1 in the electronic supplementary information).

#### 3.4. Raman spectra

Raman spectroscopy provided key information in support of the formation of the metal indolides and pyrrolides. Two linkages of interest, which are broken and formed, respectively, are the N–H bond of the free heterocycle and the N-metal bond of the resulting complex. There are a number of weak vibrational modes, associated with the metal-indole and metal-pyrrole motions, observed in the 500–100 cm<sup>-1</sup> region. In addition, a peak at approx. 3480 cm<sup>-1</sup>, which is attributed to the N–H stretching motion in free indole and pyrrole, disappears upon reaction with the triphenylmetal(IV) chlorides. These observations provide further evidence that the heterocycles are attached to the metal centres *via* the N atom in these reactions. Moreover, the Raman spectra of the indolides and pyrrolides reveal the presence of both the triphenylmetal(IV) and the heterocycles, and are quite similar to those of the tetraphenylmetal(IV) derivatives, Ph<sub>4</sub>M (M = Si, Ge, Sn). There are characteristic stretching and bending modes appearing at low wavenumbers accompanied by the well-known C–N aromatic stretch in the 1290–1390 cm<sup>-1</sup> region.

#### 3.5. Single-crystal X-ray diffraction study of compound 5

In addition to the spectroscopic measurements for **5**, single-crystal X-ray diffraction data were obtained. While a satisfactory solution at ambient temperature was not possible, the low temperature data set (100 K) allowed for a good, albeit disordered, model for the structure. Fig. 3 depicts the asymmetric unit for

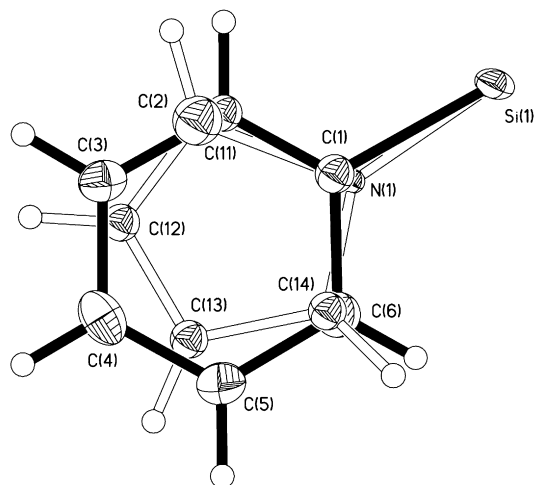


Fig. 3. Asymmetric unit for Ph<sub>3</sub>Si(C<sub>4</sub>H<sub>4</sub>N).

**Table 1**  
Comparison of arylsilane unit cell dimensions.

| Compound             | T (K)    | a, b (Å)   | c (Å)     | V (Å <sup>3</sup> ) | d <sub>calc</sub> (g/mL) | d <sub>exp</sub> (g/mL) | Reference  |
|----------------------|----------|------------|-----------|---------------------|--------------------------|-------------------------|------------|
| SiPh <sub>4</sub>    |          |            |           |                     |                          |                         |            |
| <b>5</b>             | 100 (2)  | 11.331 (2) | 6.561 (2) | 842.3 (4)           | 1.283                    |                         | This work. |
| Si(pyr) <sub>4</sub> | 153      | 10.918 (2) | 6.046 (1) | 720.7 (2)           | 1.348                    |                         | [13]       |
| SiPh <sub>4</sub>    | 293 (10) | 11.440 (2) | 7.060 (4) | 924 (1)             | 1.207                    |                         | [25]       |
| <b>5</b>             | 295 (1)  | 11.334 (6) | 6.882 (8) | 883 (1)             | 1.223(2)                 | 1.23(2)                 | This work. |
| Si(pyr) <sub>4</sub> | 293 (10) | 10.924 (6) | 6.238 (4) | 744.4 (7)           | 1.30                     |                         | [7]        |

compound **5**, which is otherwise isostructural with both tetraphenylsilane [25] and tetrapyrrol-1-ylsilane [7] and all three crystallize in the same  $P\bar{4}2_1/c$  space group. The pyrrole ring is disordered among the four coordination sites of the central Si atom with the other sites being occupied by phenyl rings. The disorder increases the uncertainty of specific molecular dimensions and the geometry. Consequently, we will not discuss specific metric parameters. However, the values for the crystal unit cell of **5** can be reliably compared with those of tetraphenylsilane and tetrapyrrol-1-ylsilane (Table 1). Systematic differences in unit cell dimensions, and densities, correlate with a single phenyl/Pyr substitution. Moreover, the experimental density determined for **5** mirrors the calculated density and independently confirms the structure as having only one phenyl/Pyr substitution (Table 1).

#### 4. Conclusions

The coupling of lithiated N-heterocycles to the group 14 elements (Si, Ge, Sn) under inert atmosphere conditions is an efficient method for the synthesis of novel compounds. While the yields are relatively low, the reactions seem unquestionably to work when completed over long periods under moderate reaction conditions. These conditions provide adequate samples to perform spectroscopic studies and are a convenient way to expand the knowledge base in this relatively unexplored field of chemistry. Gentle heating may be useful in obtaining even better yields, however, great care must be taken to avoid any self-polymerization of the heterocycles. In future work, it is planned to examine the possibility of coupling the triphenylmetal(IV) pyrrolides and indolides to a Cr(CO)<sub>3</sub> fragment. These reactions could lead to new heterocyclic organometallic complexes and these bimetallic compounds may well have some interesting biocidal properties. The thermal lability of the N-metal bond might also be worth investigating, leading to novel catalytic agents.

#### Acknowledgements

The research was generously supported by a Discovery grant from the NSERC (Canada). The authors would like to thank the *Laboratoire d'analyse élémentaire de l'Université de Montréal* for the elemental analyses.

#### Appendix A. Supplementary material

Full details of the structure determination have been deposited with the Cambridge Crystallographic Data Centre as CCDC 775301. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223 336 033; www: <http://www.ccdc.cam.ac.uk>).

Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.jorgchem.2010.07.029.

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