

## THE SYNTHESIS AND PROPERTIES OF SOME ORGANOMETALLIC COMPOUNDS CONTAINING GROUP IV (Ge, Sn)–GROUP II (Zn, Cd) METAL–METAL BONDS

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### SUMMARY

The reactions of triphenylgermane and triphenyltin hydride with coordinatively saturated organozinc or organocadmium compounds give organometallic complexes containing Group IV (Ge, Sn)–Group II (Zn, Cd) metal–metal bonds. The 2,2'-bipyridine complexes show solvent-dependent charge-transfer absorptions in the visible region. The occurrence of charge transfer may account for the observation that the metal–metal stretching frequencies of the Bipy complexes are consistently lower than those of the corresponding TMED complexes.

### INTRODUCTION

In recent years there has been considerable interest in the chemistry of organometallic compounds containing bonds between metals of Groups IIB (Zn, Cd, Hg) and IVA (Si, Ge, Sn) of the periodic system. Emphasis has been on compounds containing Si–Hg, Ge–Cd and Ge–Hg bonds (for recent review articles, see refs. 1 and 2), but isolated examples of compounds containing Ge–Zn<sup>3,4</sup>, Sn–Zn<sup>5</sup>, Sn–Cd<sup>3,5</sup> and Sn–Hg<sup>6,7</sup> bonds have also been reported.

For the preparation of compounds containing tin–metal bonds the reaction of organotin hydrides with reactive metal–carbon or metal–element bonds ("hydrostannolysis"<sup>3</sup>) has been a particularly versatile method. In the past years a variety of organometallic compounds containing tin bound to main- and sub-group elements (e.g. Li<sup>8</sup>, Mg<sup>9,10</sup>, Zn<sup>5</sup>, Cd<sup>3,5</sup>, Hg<sup>6,7</sup>, Ge<sup>11</sup>, Sn<sup>12,13</sup>, Sb<sup>14</sup>, Bi<sup>14</sup>, Te<sup>15</sup>) have been prepared in this way. Organogermanium hydrides, although considerably less reactive than organotin hydrides<sup>11</sup>, have successfully been used, mainly by Vyazankin *et al.*<sup>1,2</sup>, for the synthesis of compounds containing germanium–metal bonds.

In the present paper we wish to report on the synthesis and spectroscopic properties of some donor–acceptor complexes containing Group IV (Ge, Sn)–Group II (Zn, Cd) metal–metal bonds<sup>5</sup>.

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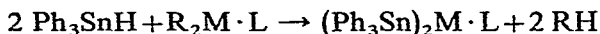
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## RESULTS AND DISCUSSION

*Synthesis*

Mechanistic studies have revealed that hydrostannolysis reactions of metal–nitrogen and metal–oxygen bonds involve electrophilic attack by the hydrogen of the organotin hydride<sup>3,16</sup>. In view of the well-known susceptibility of organozinc and -cadmium compounds towards electrophilic attack, the hydrostannolysis of Zn–C or Cd–C bonds would seem to be the method of choice for preparing compounds with a Sn–Zn or Sn–Cd bond. Triphenyltin hydride, which is considerably more reactive than trialkyltin hydrides in protonolysis-type reactions<sup>16</sup>, is the preferred reagent.

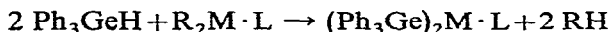
As reported by Vyazankin *et al.*<sup>17</sup> the reaction of triethyltin hydride with diethylzinc does not lead to the formation of tin–zinc bonds, only decomposition products, including zinc metal, being obtained. Likewise, we found that the reaction of triphenyltin hydride with diethylzinc or dimethylcadmium in hydrocarbon solvents results in the deposition of zinc or cadmium. However, when the latter reactions were carried out either in a solvating solvent such as tetrahydrofuran (THF) or 1,2-dimethoxyethane (DME), or by using a pre-formed coordination complex of diethylzinc or dimethylcadmium with *N,N,N',N'*-tetramethylethylenediamine (TMED) or 2,2'-bipyridine (Bipy), the expected bis(triphenyltin)metal complexes were obtained in virtually quantitative yields under mild conditions (–20° to 0°):



R = Et, M = Zn; R = Me, M = Cd; L = THF, DME, TMED or Bipy

Coordination saturation of the zinc or cadmium atom not only promotes this reaction as a result of the enhanced nucleophilicity of the group R (*cf.* ref. 18), but also contributes to the stability of the reaction products. Attempts to remove THF from the bis(triphenyltin)zinc·THF complex at 50°/10<sup>–3</sup> mmHg resulted in gradual decomposition with metal deposition, whereas the TMED complex melts at 172.5–174° without any metal being deposited.

Triphenylgermane is a weaker electrophilic reagent than triphenyltin hydride<sup>11</sup>. Indeed, the corresponding reactions of triphenylgermane proceed much more slowly, and require temperatures up to 80–130° to give satisfactory yields:



R = Et, M = Zn; R = Me, M = Cd; L = TMED or Bipy

All the triphenyltin and triphenylgermyl complexes have been obtained as crystalline solids which slowly decompose upon exposure to air. The complexes prepared are listed in Table 1.

*Spectral properties*

Whereas the TMED and DME complexes are colourless, the Bipy complexes are strongly coloured. Unlike the TMED complexes the Bipy complexes display a pronounced charge-transfer absorption in the visible spectrum (see Table 2). Similar charge-transfer bands in the 350–550 nm region have been observed in the spectra of a series of dialkylzinc–Bipy complexes<sup>19</sup>, and these have been explained in terms of a transition of zinc 3*d* electrons into the lowest unoccupied  $\pi$ -orbital of the Bipy ring system<sup>19,20</sup>. However, an explanation based on the occurrence of charge-transfer

TABLE 1

## COMPLEXES CONTAINING GROUP IV (Ge, Sn)–GROUP II (Zn, Cd) METAL–METAL BONDS

Complex	Colour	Yield (%)	M.p. (°C)	Analysis found (calcd.) (%)		
				C	H	N
(Ph <sub>3</sub> Ge) <sub>2</sub> Zn · TMED	White	35	166 (dec.)	63.61 (63.90)	6.32 (5.87)	4.15 (3.55)
(Ph <sub>3</sub> Ge) <sub>2</sub> Zn · Bipy	Orange	81	205 (dec.)	64.78 (66.62)	4.08 (4.61)	3.38 (3.38)
(Ph <sub>3</sub> Ge) <sub>2</sub> Cd · TMED	White	48	188 (dec.)	60.14 (60.31)	5.69 (5.54)	3.41 (3.35)
(Ph <sub>3</sub> Ge) <sub>2</sub> Cd · Bipy	Ochre	53	> 200	62.93 (63.04)	4.63 (4.37)	3.42 (3.19)
(Ph <sub>3</sub> Sn) <sub>2</sub> Zn · TMED	White	84	172.5–174	56.98 (57.22)	5.52 (5.26)	3.17 (3.18)
(Ph <sub>3</sub> Sn) <sub>2</sub> Zn · Bipy	Red	85	141.5–144	59.58 (59.95)	4.22 (4.16)	3.03 (3.04)
(Ph <sub>3</sub> Sn) <sub>2</sub> Zn · DME	White	48	103.5–104	55.94 (56.16)	4.57 (4.71)	
(Ph <sub>3</sub> Sn) <sub>2</sub> Cd · TMED	White	85	175 (dec.)	53.14 (54.32)	4.29 (4.99)	3.01 (3.24)
(Ph <sub>3</sub> Sn) <sub>2</sub> Cd · Bipy	Orange	87	154 (dec.)	56.21 (57.04)	4.03 (3.95)	2.91 (2.89)
(Ph <sub>3</sub> Sn) <sub>2</sub> Cd · DME	White	30	110 (dec.)	52.53 (53.23)	4.36 (4.46)	

from the zinc–carbon bonds [the antisymmetric combination of the two Zn–C  $\sigma$ -orbitals  $\Psi(\text{Zn}-\text{C}_1) - \Psi(\text{Zn}-\text{C}_2)$  has  $\pi$ -symmetry] into the lowest unoccupied Bipy  $\pi$ -orbital has also been considered<sup>21</sup> (cf. ref. 22). A  $\pi$ -type interaction of this kind in Bipy complexes accounts for the, at first sight, unexpected stability sequence of a series of TMED and Bipy complexes of dialkylzinc compounds<sup>20</sup>.

The charge-transfer band present in the spectra of the  $(\text{Ph}_3\text{M}^{\text{IV}})_2\text{M}^{\text{II}} \cdot \text{Bipy}$  complexes most probably arises from a similar  $\pi$ -type interaction between the  $(\text{Ph}_3\text{M}^{\text{IV}})_2\text{M}^{\text{II}}$  moiety and the Bipy ligand. Since it seems reasonable to assume that such a transfer of electronic density would affect the  $\text{M}^{\text{IV}}-\text{M}^{\text{II}}$  bond, we have examined the far IR spectra of the various Bipy and TMED complexes with emphasis on observing metal–metal stretching frequencies. Examination of the spectra of  $(\text{Ph}_3\text{Ge})_2\text{Zn} \cdot \text{Bipy}$  and  $(\text{Ph}_3\text{Sn})_2\text{Zn} \cdot \text{Bipy}$  reveals only one absorption common to both compounds. This absorption occurring at 241 and 237  $\text{cm}^{-1}$ , respectively, is assigned to a vibration due mainly to zinc–nitrogen stretching. Bands at 212 and 195  $\text{cm}^{-1}$  are assigned to the antisymmetric  $\nu_{\text{as}}(\text{Ge}_2-\text{Zn})$  and  $\nu_{\text{as}}(\text{Sn}_2-\text{Zn})$ , respectively. These assignments are consistent in terms of mass differences, assuming the force constants to be the same. Similarly, the assignment of bands in the spectra of  $(\text{Ph}_3\text{Ge})_2\text{Cd} \cdot \text{Bipy}$  and  $(\text{Ph}_3\text{Sn})_2\text{Cd} \cdot \text{Bipy}$  at 182 and 168  $\text{cm}^{-1}$  mainly to  $\nu_{\text{as}}(\text{Ge}_2-\text{Cd})$  and  $\nu_{\text{as}}(\text{Sn}_2-\text{Cd})$  is consistent in terms of mass differences. The absorptions at 225 and 213  $\text{cm}^{-1}$  in the spectra of these complexes are attributed to modes containing main contributions of cadmium–nitrogen stretching. The band at 168  $\text{cm}^{-1}$  occurring in the spectrum of both  $(\text{Ph}_3\text{Ge})_2\text{Zn} \cdot \text{TMED}$  and  $(\text{Ph}_3\text{Sn})_2\text{Zn} \cdot \text{TMED}$ , and the absorptions at 148 and

144  $\text{cm}^{-1}$  in the spectra of  $(\text{Ph}_3\text{Ge})_2\text{Cd} \cdot \text{TMED}$  and  $(\text{Ph}_3\text{Sn})_2\text{Cd} \cdot \text{TMED}$  are assigned to metal–nitrogen modes as they are the only bands common to both sets of complexes. The absorptions at 221, 211, 192 and 178  $\text{cm}^{-1}$  in the spectra of the four TMED complexes are assigned mainly to antisymmetric metal–metal stretching.

Table 2 presents the wavelength of the absorption maxima of the charge-transfer bands and the frequencies of the metal–metal absorptions for the various complexes studied. It is perhaps significant that in all cases studied the frequency observed for  $\nu_{\text{as}}(\text{M}_2^{\text{IV}}-\text{M}^{\text{II}})$  in the Bipy complexes which do display a charge-transfer absorption is about 10  $\text{cm}^{-1}$  lower than that for the corresponding TMED complexes which do not show this phenomenon. Although care must be exercised in relating shifts in metal–metal stretching frequencies to the relative strengths of the metal–metal bonds, the lowering of the metal–metal stretching frequency in the Bipy complexes can be nicely explained in terms of transfer of electron density from the metal–metal bond into the Bipy ligand. The difference in  $\nu_{\text{as}}(\text{M}_2^{\text{IV}}-\text{M}^{\text{II}})$  observed for Bipy and TMED complexes is greatest for bis(triphenyltin)zinc, which displays the lowest-energy  $\pi$ -interaction (highest-wavelength charge-transfer absorption, *cf.* Table 2).

TABLE 2

METAL–METAL STRETCHING FREQUENCIES AND  $\lambda_{\text{max}}$  OF CHARGE TRANSFER ABSORPTIONS OF  $(\text{Ph}_3\text{M}^{\text{IV}})_2\text{M}^{\text{II}}$  COMPLEXES AND OF TWO  $\text{R}_2\text{Zn} \cdot \text{Bipy}$  REFERENCE COMPOUNDS

Complex	$\nu_{\text{as}}[\text{M}_2^{\text{IV}}-\text{M}^{\text{II}}]$ ( $\text{cm}^{-1}$ )	$\lambda_{\text{max}}$ (nm) in		
		$\text{C}_6\text{H}_6$	THF	DME
$(\text{Ph}_3\text{Ge})_2\text{Zn} \cdot \text{Bipy}$	212	478	458	452
$(\text{Ph}_3\text{Ge})_2\text{Zn} \cdot \text{TMED}$	221			
$(\text{Ph}_3\text{Ge})_2\text{Cd} \cdot \text{Bipy}$	182	434	418	416
$(\text{Ph}_3\text{Ge})_2\text{Cd} \cdot \text{TMED}$	192			
$(\text{Ph}_3\text{Sn})_2\text{Zn} \cdot \text{Bipy}$	195	490	466	455
$(\text{Ph}_3\text{Sn})_2\text{Zn} \cdot \text{TMED}$	211			
$(\text{Ph}_3\text{Sn})_2\text{Cd} \cdot \text{Bipy}$	168	437	421	417
$(\text{Ph}_3\text{Sn})_2\text{Cd} \cdot \text{TMED}$	178			
$\text{Et}_2\text{Zn} \cdot \text{Bipy}$		420 <sup>a</sup>	<sup>b</sup>	400
$\text{t-Bu}_2\text{Zn} \cdot \text{Bipy}$		551 <sup>c</sup>	502	490

<sup>a</sup> Ref. 19. <sup>b</sup> A broad shoulder between 380 and 420 nm is observed. <sup>c</sup> Ref. 21.

The charge-transfer absorption wavelengths are solvent dependent: the excitation energy increases with the solvating power of the medium. Burgess<sup>23</sup> observed a comparable solvent shift of  $\lambda_{\text{max}}$  in the electronic spectra of  $(\text{OC})_4\text{Mo} \cdot \text{Bipy}$  and  $(\text{OC})_4\text{W} \cdot \text{Bipy}$  which was accounted for in terms of solvent interaction with the carbonyl groups. Dialkylzinc Bipy complexes such as  $\text{Et}_2\text{Zn} \cdot \text{Bipy}$  and  $\text{t-Bu}_2\text{Zn} \cdot \text{Bipy}$  also display solvent-dependency of the charge-transfer absorption (*cf.* Table 2). Since the energy of a molecule is lowered by solvation, the transition energy increases when the solvation of the molecule in the ground state is more effective than in the excited state<sup>24</sup>. In the Bipy complexes under study, charge-transfer away from the organo-metal moiety upon excitation will result in a decrease, or maybe even a change of direction of the dipole moment of the molecule in the excited state as compared with that in the ground state. Therefore, solvation of the molecule would be expected to

be more effective in the ground state than in the excited state, and the excitation energy should increase with increasing solvating power of the medium, leading to the observed hypsochromic shift.

## EXPERIMENTAL

### General

All reactions were carried out under dry nitrogen. Elemental analyses were carried out at the Micro Analytical Department of the Institute for Organic Chemistry TNO, Utrecht. The far IR spectra (Nujol mulls) were recorded at the Laboratory for Inorganic Chemistry of the University of Amsterdam, and at the Department of Chemistry of the University of Western Ontario (Prof. H. C. Clark), in both cases on a Beckman IR-11 spectrometer. The electronic spectra were run on a Cary-15 spectrometer.

### Purification of solvents and starting materials

THF and DME were distilled from  $\text{LiAlH}_4$  prior to use. *N,N*-Dimethylacetamide (DMA) was dried over barium oxide, and subsequently distilled *in vacuo*. Diethylzinc, dimethylcadmium, triphenylgermane and triphenyltin hydride were prepared according to published procedures.  $\text{t-Bu}_2\text{Zn}$  was obtained from Dr. J. Boersma, Laboratory for Organic Chemistry, State University, Utrecht.

### Synthesis of bis(triphenylgermyl)zinc and -cadmium complexes

As an example of the preparation of these complexes the synthesis of  $(\text{Ph}_3\text{Ge})_2\text{-Cd}\cdot\text{Bipy}$  will be described in detail.

Solutions of 0.83 g (5.8 mmol) of  $\text{Me}_2\text{Cd}$  in 3 ml of THF and of 0.91 g (5.8 mmol) of Bipy in 2 ml of THF were mixed at room temperature. To the yellow mixture 3.55 g (11 mmol) of  $\text{Ph}_3\text{GeH}$  were added. No evolution of gas was observed so the solvent was removed and the residual viscous yellow oil was heated to 80–90°. At this temperature the evolution of gas started, and after 45 min the reaction was complete (final temperature 127°). The residue was taken up in 25 ml of THF, the slightly turbid solution was filtered, and the clear red filtrate was evaporated to 25% of the original volume. Upon addition of 20 ml of pentane, an ochre-coloured solid precipitated, and was filtered off and dried. Yield 2.7 g (53%). The same procedure was followed for the preparation of  $(\text{Ph}_3\text{Ge})_2\text{Zn}\cdot\text{Bipy}$ , in which reaction started at about 100°, and of  $(\text{Ph}_3\text{Ge})_2\text{Cd}\cdot\text{TMED}$  (100–112°). The preparation of  $(\text{Ph}_3\text{Ge})_2\text{-Zn}\cdot\text{TMED}$  differed in that after evaporation of the original solvent, the addition of 4 ml of DMA ( $\epsilon$  37.6) was necessary to give a sufficient rate of reaction at 110–115°.

### Synthesis of bis(triphenyltin)zinc and -cadmium complexes

As an example for the preparation of this type of complex, the synthesis of  $(\text{Ph}_3\text{Sn})_2\text{Zn}\cdot\text{TMED}$  will be described in detail.

To a solution of 0.55 ml (5.3 mmol) of  $\text{Et}_2\text{Zn}$  in 5 ml of DME 0.62 g (5.3 mmol) of TMED was added. After cooling to –35°, 3.37 g (10.6 mmol) of  $\text{Ph}_3\text{SnH}$  was added. The temperature was allowed to rise to room temperature. Gas was evolved and a white solid gradually precipitated. After 4 h 240 ml of gas had been collected (92%). The gas was identified as ethane by GLC. The flask was then cooled in ice and 10 ml

of pentane was added. The precipitated white solid was filtered off and dried. Yield 4.67 g (84%). In a similar way were prepared:  $(\text{Ph}_3\text{Sn})_2\text{Zn} \cdot \text{Bipy}$  (85%),  $(\text{Ph}_3\text{Sn})_2\text{Zn} \cdot \text{DME}$  (48.5%),  $(\text{Ph}_3\text{Sn})_2\text{Cd} \cdot \text{TMED}$  (82%) and  $(\text{Ph}_3\text{Sn})_2\text{Cd} \cdot \text{Bipy}$  (87%). The gas evolved in the formation reactions of the latter two complexes was identified as methane (GLC). The formation of  $(\text{Ph}_3\text{Sn})_2\text{Cd} \cdot \text{DME}$  was accompanied by cadmium deposition. Therefore, after addition of 5 ml of DME the insoluble materials (cadmium metal and  $\text{Ph}_3\text{SnSnPh}_3$ ) were filtered off. Upon addition of 1.5 ml of pentane, a white solid was precipitated, and this was filtered off and dried. Yield 30%.

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