First characterization of a compound with a tin–germanium double bond: the dimesityl(diisitylstanna)germene $(Is)_2Sn{=}Ge(Mes)_2$

Marie-Anne Chaubon, Jean Escudié,* Henri Ranaivonjatovo and Jacques Satgé

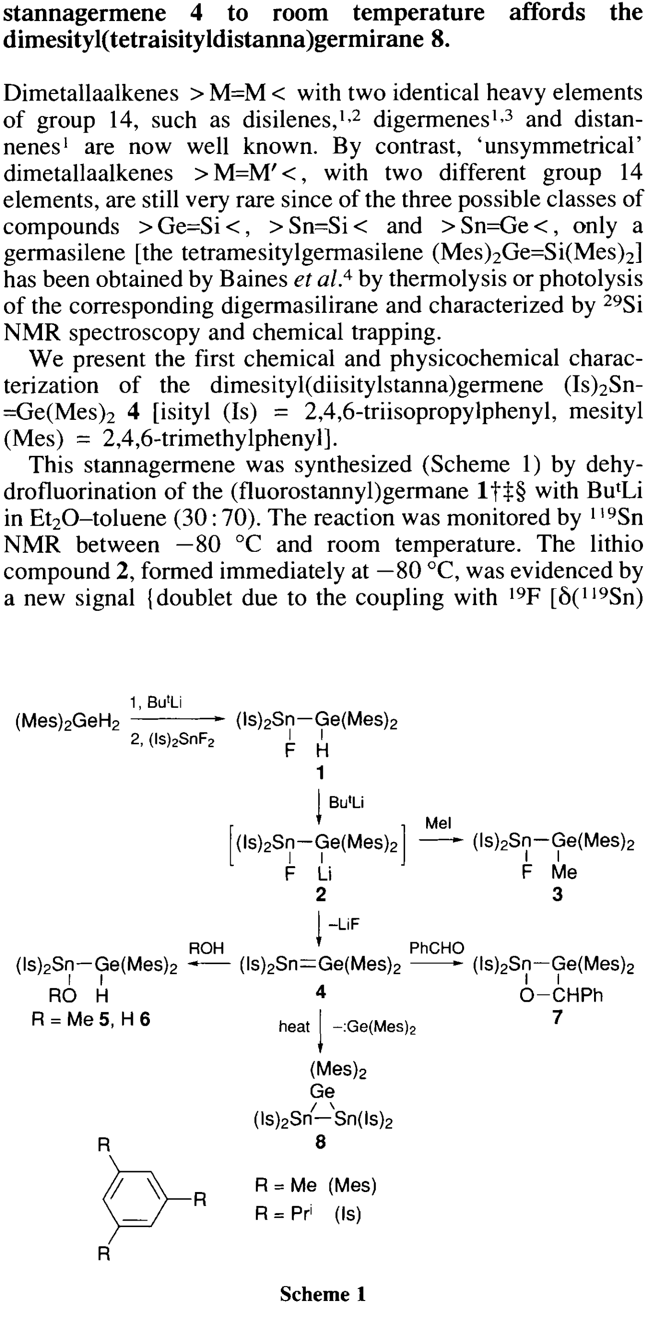
Hétérochimie Fondamentale et Appliquée, UPRES A associée au CNRS n° 5069, Université Paul Sabatier, 118 route de Narbonne, 31062 Toulouse Cedex, France

The dimesityl(diisitylstanna)germene 4 [isityl (Is) = 2,4,6-triisopropylphenyl] is synthesized by dehydrofluorination of the corresponding (fluorostannyl)germane 1 by *tert*-butyllithium at low temperature; its structure is evidenced at −20 °C by ^{119}Sn NMR spectroscopy (δ + 360), by addition of water and methanol to the tin–germanium double bond and by a [2 + 2] cycloaddition with benzaldehyde; warming the stannagermene 4 to room temperature affords the dimesityl(tetraisityldistanna)germirane 8.

Dimetallaalkenes >M=M< with two identical heavy elements of group 14, such as disilenes,[1,2] digermenes[1,3] and distannenes[1] are now well known. By contrast, 'unsymmetrical' dimetallaalkenes >M=M′<, with two different group 14 elements, are still very rare since of the three possible classes of compounds >Ge=Si<, >Sn=Si< and >Sn=Ge<, only a germasilene [the tetramesitylgermasilene $(Mes)_2Ge{=}Si(Mes)_2$] has been obtained by Baines *et al.*[4] by thermolysis or photolysis of the corresponding digermasilirane and characterized by ^{29}Si NMR spectroscopy and chemical trapping.

We present the first chemical and physicochemical characterization of the dimesityl(diisitylstanna)germene $(Is)_2Sn{=}Ge(Mes)_2$ **4** [isityl (Is) = 2,4,6-triisopropylphenyl, mesityl (Mes) = 2,4,6-trimethylphenyl].

This stannagermene was synthesized (Scheme 1) by dehydrofluorination of the (fluorostannyl)germane **1**†‡§ with Bu^tLi in Et_2O–toluene (30 : 70). The reaction was monitored by ^{119}Sn NMR between −80 °C and room temperature. The lithio compound **2**, formed immediately at −80 °C, was evidenced by a new signal {doublet due to the coupling with ^{19}F [δ(^{119}Sn) 124.9, $^1J_{^{119}SnF}$ 1650.5 Hz] whereas a doublet of doublets was observed for **1** (coupling with F and H)} and by quenching with methyl iodide to afford **3**.†‡ Addition of water regenerates **1** quantitatively.



Scheme 1

When the reaction mixture was warmed to −20 °C, a new signal appeared at δ +360 in the ^{119}Sn NMR spectrum attributed to the stannagermene **4**. The chemical shift lies, as expected, at low-field as in other doubly bonded tin derivatives substituted by two isityl groups on tin [*e.g.* $(Is)_2Sn{=}Sn(Is)_2$, δ + 427;[6] $(Is)_2Sn{=}PAr$ (Ar = 2,4,6-tri-*tert*-butylphenyl), δ +499.5;[8] $(Is)_2Sn{=}CR_2$ (CR_2 = fluorenylidene), δ + 288;[5] $(Is)_2Sn{=}CR'_2$ (CR'_2 = 1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene), δ + 710;[9] see also ref 1(*a*) and 10 for δ(^{119}Sn) of other doubly bonded tin compounds]. Orange–red solutions of **4** are air- and moisture-sensitive.

Compound **4** has been characterized by trapping reactions; thus, addition of methanol or water to an orange solution of **4** at −20 °C caused immediate decoloration, with the formation of the (methoxystannyl)- or the (hydroxystannyl)-germanes **5**† and **6** respectively†‡ [**5**, δ(^{119}Sn) −39.3; **5** is moisture-sensitive and gives **6** upon hydrolysis], [**6**, δ(^{119}Sn) −65.4, δ(^1H) 5.71 (s, GeH); ν(GeH) 2024 cm^{-1}]. Only **5** and **6** were obtained and not the reverse regioisomers; one of the reasons for this regiospecific reaction is the polarity $Sn^{\delta+}Ge^{\delta-}$ of the tin–germanium double bond, although this polarity is probably very low.

Addition of benzaldehyde affords the (3-oxa-2-stanna)germetane **7**†¶ in good yield (65%) by a [2 + 2] cycloaddition. A regiospecific reaction was observed with the sole formation of the four-membered heterocycle containing an Sn–O bond. This regiochemistry was established by the presence of an Is_2Sn–O fragment in the mass spectrum and by ^{13}C NMR which revealed an ^{119}Sn–O–C coupling constant of 26.6 Hz characteristic of $^2J_{SnC}$.[11]

Warming a solution of **4** at room temperature afforded the distannagermirane **8**‖ along with other unidentified products. Owing to its low solubility, **8** was easily isolated from the reaction mixture by crystallization from pentane. The mechanism of the formation of **8** from the stannagermene **4** has not yet been elucidated: a disproportionation of **4** into stannylene $:Sn(Is)_2$ and germylene $:Ge(Mes)_2$ can be postulated (*i*) with further addition of stannylene to the Sn=Ge double bond, (*ii*) or with dimerisation of two stannylenes and addition of germylene to the Sn=Sn double bond. However head-to-head or head-to-tail dimerisations of **4** to the corresponding distannadigermetanes Ge–Ge–Sn–Sn or Ge–Sn–Ge–Sn followed by extrusion of germylene to give a three-membered ring cannot be excluded; of course such elimination would be more probable from the strained head-to-head dimer. Attempts to trap germylene: $Ge(Mes)_2$ failed, probably owing to the low temperature of the experiment. Mass spectrometry of **8** revealed two possible [2 + 1] decomposition routes of the three-membered ring: (*a*) $(Is)_2Sn{=}Sn(Is)_2$ + $:Ge(Mes)_2$ and (*b*) $(Is)_2Sn{=}Ge(Mes)_2$ + $:Sn(Is)_2$. Route (*b*) is by far the most important, suggesting that the distannagermirane should, upon thermolysis, be a good precursor of stannagermene **4**.

The study of the reactivity of this new tin–germanium double bond, which is of importance, is now under active investigation.

Footnotes

† Detailed physicochemical data [^{1}H, ^{13}C, ^{19}F and ^{119}Sn NMR, mass spectrometry (^{74}Ge, ^{120}Sn), IR, elemental analysis, mp] and experimental procedures for compounds **1**, **3**, **5–8** are available from the authors upon request.

‡ **1** was synthesized by reaction of 8.5 mmol of $(\mathrm{Is})_2\mathrm{SnF}_2$[5] [obtained from $(\mathrm{Is_2SnO})_3$[6] and HF] with 1 equiv. of $(\mathrm{Mes})_2\mathrm{Ge(H)Li}$[7] prepared from $(\mathrm{Mes})_2\mathrm{GeH}_2$ and Bu^{t}Li in thf at −40 °C. **1** was separated from by-products, such as $(\mathrm{Mes})_2\mathrm{GeH}_2$ and $(\mathrm{Mes})_2\mathrm{Ge(H)Ge(H)(Mes)}_2$, by fractional crystallization from pentane (mp 171 °C, yield = 31%). δ(^{119}Sn) (ref. $\mathrm{SnMe_4}$) −24.4 (dd, $^{1}J_{^{119}\mathrm{SnF}}$ 2430.7, $^{2}J_{^{119}\mathrm{SnH}}$ 217.2 Hz); δ(^{19}F) (ref. $\mathrm{CF_3CO_2H}$) −121.4; δ(^{1}H) 5.79 [d, $^{3}J_{\mathrm{FH}}$ 20.8 Hz, GeH); IR 2018.3 cm^{-1} [ν(GeH)]; MS (EI), *m/z* 837 (M − F, < 1), 645 [$(\mathrm{Is})_2\mathrm{Sn(Mes)}$, 1], 545 [$(\mathrm{Is})_2\mathrm{SnF}$, 4], 526 [$(\mathrm{Is})_2\mathrm{Sn}$, 22], 322 [(Is)Sn−H, 100], 313 [$(\mathrm{Mes})_2\mathrm{GeH}$, 10]; Anal. Calc. for $\mathrm{C_{48}H_{69}FGeSn}$: C, 67.32, H, 8.12. Found: C, 67.24; H, 8.53%.

3: δ(^{119}Sn) −29.9 (d, $^{1}J_{^{119}\mathrm{SnF}}$ 2411.4 Hz); δ(^{1}H) 1.33 (d, $^{4}J_{\mathrm{FH}}$ 2.6 Hz, Me); δ(^{13}C) 7.00 (d, $^{3}J_{\mathrm{FC}}$ 6.4 Hz, Me); δ(^{19}F) −118.9; MS (DCI–$\mathrm{CH_4}$, ^{74}Ge, ^{120}Sn): 526 [$(\mathrm{Is})_2\mathrm{Sn}$, 1]; 346 [$(\mathrm{Mes})_2\mathrm{Ge(Me)F}$, 9], 327 [$(\mathrm{Mes})_2\mathrm{GeMe}$, 47], 227 [(Mes)Ge(Me)F, 100]. Anal. Calc. for $\mathrm{C_{49}H_{71}FGeSn}$: C, 67.62, H, 8.22. Found: C, 67.32; H, 8.27% **6**: δ(^{119}Sn) −65.4; δ(^{1}H) 5.71 (s, GeH); IR 2024 cm^{-1} [υ(GeH)]; MS (EI); *m/z* 854 (M, 1); 837 (M − OH, 1), 645[$(\mathrm{Is})_2\mathrm{Sn(Mes)}$, 2], 543[$(\mathrm{Is})_2\mathrm{Sn(OH)}$, 28], 526 [$(\mathrm{Is})_2\mathrm{Sn}$, 50], 322 [(Is)Sn − H, 100].

§ Mass spectrometry of **1**, **6** and **7** displays $(\mathrm{Is})_2\mathrm{Sn(Mes)}$ fragments due to migration of a mesityl group from germanium to tin. Similar migrations of mesityls from germanium to silicium[4] or to germanium[12] have been reported. In **7**, migration of isityl from tin to germanium is also observed.

¶ **7**: mp 92 °C; δ(^{119}Sn) 69.7; δ(^{1}H) 6.53 (s, OCH); δ(^{13}C) 91.68 ($^{2}J_{^{119}\mathrm{SnC}}$ 26.6 Hz, OCH). The two methyls of each Pr^{i} group, as well as the two isityl groups, are diastereotopic; thus four doublets (6 H each) are observed for the methyls of the *o*-Pr^{i} groups. For the methyls of *p*-Pr^{i} groups only two doublets (instead of the four expected) are observed due to their large distance from the chiral centre. The two mesityl groups are also diastereotopic: thus four singlets are observed for the methyls. MS (EI), *m/z* 645 [$(\mathrm{Is})_2\mathrm{Sn(Mes)}$, 1], 598 [$(\mathrm{Is})_2\mathrm{SnGe}$, 4], 555 [$(\mathrm{Is})_2\mathrm{Sn(OCH)}$, 3], 542 [$(\mathrm{Is})_2\mathrm{SnO}$, 1], 524 [$(\mathrm{Is})_2\mathrm{Sn}$ − 2H, 5], 514 [(Is)SnGe(Mes), 6], 478 [$(\mathrm{Is})_2\mathrm{Ge}$ − 2H, 9], 396 [(Is)SnGe + H, 49], 353[(Is)Sn(OCH) + H, 7], 322 [(Is)Sn−H, 50], 277 [(Is)Ge, 100].

‖ **8**: mp 142 °C; δ(^{119}Sn) −361.6 ($^{1}J_{^{119}\mathrm{Sn}^{117}\mathrm{Sn}}$ 1440 Hz) {a similar high field chemical shift was observed for the tristannirane [$(\mathrm{Is})_2\mathrm{Sn}]_3$[6]}. Because of the significant steric congestion, hindered rotation is observed for the Is groups; thus eight doublets (6 H each) are observed for the *o*-methyls of the Pr^{i} groups and two doublets (12 H each) for the *p*-methyls. MS (FAB), *m/z* 1050 [$(\mathrm{Is})_2\mathrm{SnSn(Is)}_2$, 1], 836 [$(\mathrm{Is})_2\mathrm{SnGe(Mes)}_2$, 45], 644 [(Is)SnSn(Is), 11], 525 [$(\mathrm{Is})_2\mathrm{Sn}$ − H, 100].

References

1 For reviews on stable >M=M< compounds, see (*a*) M. A. Chaubon, H. Ranaivonjatovo, J. Escudié and J. Satgé, *Main Group Met. Chem.*, 1996, **19**, 145; (*b*) T. Tsumuraya, S. A. Batcheller and S. Masamune, *Angew. Chem., Int. Ed. Engl.*, 1991, **30**, 902.

2 R. West, *Angew. Chem., Int. Ed. Engl.*, 1987, **26**, 1201; M. Weidenbruch, *Coord. Chem. Rev.*, 1994, **130**, 275; G. Raabe and J. Michl, in *The Chemistry of Organic Silicon Compounds*, ed. S. Patai and Z. Rappoport, Wiley, 1989, ch. 17, p. 1015.

3 J. Escudié, C. Couret, H. Ranaivonjatovo and J. Satgé, *Coord. Chem. Rev.*, 1994, **130**, 427.

4 K. M. Baines and J. A. Cooke, *Organometallics*, 1991, **10**, 3419; 1992, **11**, 3487; K. M. Baines, J. A. Cooke, C. E. Dixon, H. W. Liu and M. R. Netherton, *Organometallics*, 1994, **13**, 631; K. M. Baines, J. A. Cooke and J. J. Vittal, *Heteroatom Chem.*, 1994, **5**, 293.

5 G. Anselme, H. Ranaivonjatovo, J. Escudié, C. Couret and J. Satgé, *Organometallics*, 1992, **11**, 2748.

6 S. Masamune and L. R. Sita, *J. Am. Chem. Soc.*, 1985, **107**, 6390.

7 A. Castel, P. Rivière, J. Satgé and Y. H. Ko, *J. Organomet. Chem.*, 1988, **342**, C1.

8 H. Ranaivonjatovo, J. Escudié, C. Couret and J. Satgé, *J. Chem. Soc., Chem. Commun.*, 1992, 1047.

9 A. Schäfer, M. Weidenbruch, W. Saak and S. Pohl, *J. Chem. Soc., Chem. Commun.*, 1995, 1157.

10 A. Kandri Rodi, H. Ranaivonjatovo, J. Escudié and A. Kerbal, *Main Group Met. Chem.*, 1996, 19, 199.

11 B. Wrackmeyer, *Ann. Rep. NMR Spectrosc.*, 1985, **16**, 73.

12 T. Tsumuraya, Y. Kabe and W. Ando, *J. Organomet. Chem.*, 1994, **482**, 131.

Received, 18th July 1996; Com. 6/05037I