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Articles

Synthesis and Characterization of the Monomeric Terphenyl−Metal Halides Ge(Cl){C_6H_3-2,6-$Trip_2$} (Trip = C_6H_2-2,4,6-*i*-Pr_3) and Sn(I){C_6H_3-2,6-$Trip_2$} and the Terphenyl−Metal Amide Sn{$N(SiMe_3)_2$}{C_6H_3-2,6-$Trip_2$}[†]

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The reaction of 1 equiv of $(Et_2O)LiC_6H_3$-2,6-$Trip_2$ (Trip = C_6H_2-2,4,6-*i*-Pr_3) with either $GeCl_2$−dioxane or SnI_2 in ether affords the synthetically useful monomeric aryl−metal halides Ge(Cl){C_6H_3-2,6-$Trip_2$} **(1)** and Sn(I){C_6H_3-2,6-$Trip_2$} **(2)**. The compounds have monomeric structures with two-coordination and v-shaped geometries at the group 14 element in the solid state. Treatment of the amide Sn{$N(SiMe_3)_2$}$_2$ with $(Et_2O)LiC_6H_3$-2,6-$Trip_2$ results in displacement of an amide group to afford the mixed aryl/amide species Sn{$N(SiMe_3)_2$}{C_6H_3-2,6-$Trip_2$} **(3)**, which also has a monomeric v-shaped geometry in the solid state.

Introduction

The chemistry of stable, divalent heavier main group 14 element compounds of formula $(MR_2)_{1 or 2}$ (R = organic group or closely related group) has been the subject of intensive investigation for over 2 decades.[1] For germanium, tin, and lead derivatives, the compounds are usually formed by the reaction of the element dihalide with 2 equivs of an organolithium or Grignard reagent. In contrast, the monosubstituted compounds, e.g. $(M(Cl)R)_n$, which in some cases can be obtained as stable entities, have received much less attention, and only a handful of compounds have been isolated and characterized. These include species such as Sn(Cl)Cp [2] (Cp = cyclopentadienyl, X-ray structurally characterized[3]), Sn(Cl)C_6H_2-2,4,6-R_3 [4] (e.g. R = OMe or NMe_2, characterized by Mössbauer spectroscopy), Sn(Cl){$C(SiMe_3)_2$-C_5H_4N-2},[5] Sn(Cl){C_6H_3-2,6(CH_2NMe_2)$_2$} (X-ray),[6] Sn(Cl){C_6H_3-2,6(NMe_2)$_2$},[7] the chloro bridged amides {Sn(Cl){$N(SiMe_3)_2$}}$_2$ [8] and {Sn(Cl)TMP}$_2$ [8] (TMP = 2,2,6,6,-tetramethylpiperdino), germanium derivatives such as Ge(Cl)Cp* [9] (Cp* = pentamethylcyclopentadienyl) and Ge(Cl)Mes* [10] (Mes* = C_6H_2-2,4,6-*t*-Bu_3), and the recently reported complexes [Pb(Cl){$C(SiMe_2Ph)_3$}]$_2$,[11] [Sn(Cl){$C(SiMe_2Ph)_3$}]$_2$,[11] [Pb(Cl){$C(SiMe_3)_3$}]$_3$,[12] [M(Cl)-{$C(SiMe_3)_2SiMe_2OMe$}]$_2$ (M = Sn or Pb), and [M(Cl){C_6H_3-2,6-Mes_2}]$_2$ [13] (M = Ge or Sn). The −$C(SiMe_3)_3$, −$C(SiMe_2Ph)_3$, and −C_6H_3-2,6-Mes_2 compounds, Ge(Cl)-Mes*, and the two amides are the only species in which an organo (or closely related) ligand is of the monohapto

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[†] Dedicated to Professor P. Jutzi on the occasion of his 60th birthday.

(1) (a) West, R. *Science* **1984**, *225*, 1108. (b) Raabe, G.; Michl, J. *Chem. Rev.* **1985**, *85*, 419. (c) Brook, A. G.; Baines, K. M. *Adv. Organomet. Chem.* **1986**, *25*, 1. (d) West, R. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 1201. (e) *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappaport, Z., Eds.; Wiley: New York, 1989. (f) Barrau, J.; Escudié, J.; Satgé, J. *Chem. Rev.* **1990**, *90*, 283. (g) Lappert, M. F.; Rowe, R. S. *Coord. Chem. Rev.* **1990**, *100*, 267. (h) Brook, A. G.; Brook, M. A. *Adv. Organomet. Chem.* **1996**, *39*, 71. (i) Tsumuraya, T.; Batcheller, S. A.; Masamune, S. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 902. (j) Escudié, J.; Couret, C.; Ranaivonjatovo, H.; Satgé, J. *Coord. Chem. Rev.* **1994**, *130*, 427. (k) Okazaki, R.; West, R. *Adv. Organomet. Chem.* **1996**, *39*, 232. (l) Baines, K. M.; Stibbs, W. G. *Adv. Organomet. Chem.* **1996**, *39*, 275. (m) Power, P. P. *J. Chem. Soc., Dalton Trans.* **1998**, 2939.

(2) Bos, K. D.; Bulten, E. J.; Noltes, J. G. *J. Organomet. Chem.* **1972**, *39*, C52.

(3) Bos, K. D.; Bulten, E. J.; Noltes, J. G. *J. Organomet. Chem.* **1975**, *99*, 71.

(4) Bigwood, M. P.; Corvan, P. J.; Zuckerman, J. J. *J. Am. Chem. Soc.* **1981**, *103*, 7643.

(5) Engelhardt, L. M.; Jolly, B. S.; Lappert, M. F.; Raston, C. L.; White, A. L. *J. Chem. Soc., Chem. Commun.* **1988**, 336.

(6) Jastrzebski, J. T. B. H.; van der Schaaf, P. A.; Boersma, J.; van Koten, G.; Zoutberg, M. C.; Heijenrijk, D. *Organometallics* **1989**, *8*, 1373.

(7) Drost, K.; Hitchcock, P. B.; Lappert, M. F.; Pierssens, L. J.-M. *J. Chem. Soc., Chem. Commun.* **1997**, 1141.

(8) Chorley, R. W.; Hitchcock, P. B.; Jolly, B. S.; Lappert, M. F.; Lawless, G. A. *J. Chem. Soc., Chem. Commun.* **1991**, 1303.

(9) Kohl, F. X.; Jutzi, P. *J. Organomet. Chem.* **1987**, *329*, C17.

(10) Jutzi, P.; Leue, C. *Organometallics* **1994**, *13*, 2898.

(11) Eaborn, C.; Izod, K.; Hitchcock, P. B.; Sözerli, S. E.; Smith, J. D. *J. Chem. Soc., Chem. Commun.* **1995**, 1829.

(12) Eaborn, C.; Hitchcock, P. B.; Smith, J. D.; Sözerli, S. E. *Organometallics* **1997**, *16*, 5653.

(13) Simons, R. S.; Pu, L.; Olmstead, M. M.; Power, P. P. *Organometallics* **1997**, *16*, 1920.

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type. Monohapticity is often a desirable characteristic in the stabilizing ligand, especially when a multiply bonded product, e.g. a "dimetallyne", RMMR, is among the synthetic objectives of further reduction of the M(Cl)R derivative. Recent work has shown that the reduction of the aryltin halide $Sn(Cl)\{C_6H_3\text{-}2,6\text{-}Trip_2\}$ leads to the unusual radical species $[K(THF)_6][\{Sn(C_6H_3\text{-}2,6\text{-}Trip_2)\}_2]$,[14] which was thought to have an Sn−Sn bond order of 1.5. In this paper the synthesis and spectroscopic and structural characterization of the terphenyl element halide precursor compounds $Ge(Cl)\{C_6H_3\text{-}2,6\text{-}Trip_2\}$ **(1)** and $Sn(I)\{C_6H_3\text{-}2,6\text{-}Trip_2\}$ **(2)** and the amide derivative $Sn\{N(SiMe_3)_2\}\{C_6H_3\text{-}2,6\text{-}Trip_2\}$ are now described.

Experimental Section

General Procedures. All manipulations were carried out using modified Schlenk techniques under an atmosphere of N_2 or in a Vacuum Atmospheres HE-43 drybox. All solvents were distilled from Na/K alloy and degassed immediately before use. The compounds $(Et_2O)LiC_6H_3\text{-}2,6\text{-}Trip_2$,[15] $Sn\{N(SiMe_3)_2\}_2$,[16] and $GeCl_2$−dioxane[17] were prepared by literature procedures. Anhydrous SnI_2 was purchased commercially and used as received. ^1H, ^{13}C, and ^{119}Sn NMR spectra were recorded on a Bruker 300 MHz instrument and referenced to the deuterated solvent in the case of the ^1H and ^{13}C NMR spectra. ^{119}Sn NMR spectra were referenced to $SnMe_4$. Infrared data were recorded on a Perkin-Elmer PE-1430 instrument. UV−vis data were recorded on a Hitachi-1200 instrument.

$Ge(Cl)\{C_6H_3\text{-}2,6\text{-}Trip_2\}$ (1). $(Et_2O)LiC_6H_3\text{-}2,6\text{-}Trip_2$ (0.99 g, 1.76 mmol) in Et_2O (15 mL) was added to a stirred solution of $GeCl_2$−dioxane (0.407 g, 1.76 mmol) in Et_2O (10 mL) with cooling in a dry ice/acetone bath. Stirring was continued as the reaction mixture was allowed to warm to room temperature. The solution was then stirred for an additional 16 h, whereupon the volatile materials were removed under reduced pressure. The orange residue was extracted with hexane (40 mL), and, after filtration through Celite, the solution was reduced to incipient crystallization and stored in a ca. −20 °C freezer to give product **1** as orange crystals: yield, 0.60 g, 57.6%; mp, 230−232 °C. Anal. Calcd for $C_{36}H_{49}ClGe$: C, 73.29; H, 8.37. Found: C, 74.1; H, 8.51. ^1H NMR (C_6D_6): δ 1.10 (d, 12H, $p\text{-}CH(CH_3)_2$, $^3J_{HH} = 6.6$ Hz), 1.164 (d, 12H, $o\text{-}CH(CH_3)_2$, $^3J_{HH} = 6.9$ Hz), 1.41 (d, 12H, $o\text{-}CH(CH_3)_2$, $^3J_{HH} = 6.9$ Hz), 2.76 (sept, 2H, $p\text{-}CH(CH_3)_2$, $^3J_{HH} = 6.9$ Hz), 3.18 (sept, 4H, $o\text{-}CH(CH_3)_2$, $^3J_{HH} = 6.9$ Hz), 7.20 (s, 4H, m-Trip). $^{13}C\{H\}$ NMR (C_6D_6): δ 22.78 ($o\text{-}CH(CH_3)_2$), 24.10 ($p\text{-}CH(CH_3)_2$), 26.45 ($o\text{-}CH(CH_3)_2$), 31.30 ($o\text{-}CH(CH_3)_2$), 34.70 ($p\text{-}CH(CH_3)_2$), 121.83 (*m*-Trip), 128.84 ($p\text{-}C_6H_3$), 129.42 ($m\text{-}C_6H_3$), 132.06 (*i*-Trip), 142.75 (*p*-Trip), 147.96 (*o*-Trip), 150.34 ($o\text{-}C_6H_3$), 164.57 ($i\text{-}C_6H_3$). UV−vis (hexane): $\lambda_{max} = 393$ nm, $\epsilon = 950$ L mol^{-1} cm^{-1}.

$Sn(I)\{C_6H_3\text{-}2,6\text{-}Trip_2\}$ (2). Method a. $(Et_2O)LiC_6H_3\text{-}2,6\text{-}Trip_2$ (0.91 g, 1.34 mmol) in Et_2O (10 mL) was added dropwise to a stirred suspension of SnI_2 (0.50 g, 1.34 mmol) in Et_2O (108 mL) with cooling in an ice bath. The solution was allowed to come to room temperature, and stirring was continued for ca. 12 h. The solvent was removed under reduced pressure, and the residue was extracted with hexane (40 mL). Filtration through Celite, reduction in the volume to incipient crystallization, and storage in a −20 °C freezer afforded the product **2** as red crystals: yield, 0.48 g, 49%.

Method b. $LiC_6H_3\text{-}2,6\text{-}Trip_2/LiI$ (2.00 mmol synthesized in situ by the addition of 2 equivs of *n*-BuLi to $IC_6H_3\text{-}2,6\text{-}Trip_2$) in toluene (20 mL) was added to $SnCl_2$ (0.38 g, 2.00 mmol) in toluene (10 mL) at room temperature with stirring. The reaction mixture was stirred for an additional 16 h at room temperature. The green solution (red in transmitted light) was filtered through Celite, and then the solution was reduced to incipient crystallization and stored in a ca. −20 °C freezer to give red crystals: yield, 0.56 g, 38.4%; mp, 225−227 °C dec. Anal. Calcd for $C_{36}H_{49}ISn$: C, 59.44; H, 6.79. Found: C, 60.11; H, 6.88. ^1H NMR (C_6D_6): δ 1.10 (d, 12H, $p\text{-}CH(CH_3)_2$, $^3J_{HH} = 6.9$ Hz), 1.22 (d, 12H, $o\text{-}CH(CH_3)_2$, $^3J_{HH} = 6.9$ Hz), 1.38 (d, 12H, $o\text{-}CH(CH_3)_2$, $^3J_{HH} = 6.9$ Hz), 2.81 (sept, 2H, $p\text{-}CH(CH_3)_2$, $^3J_{HH} = 6.9$ Hz), 3.15 (sept, 4H, $o\text{-}CH(CH_3)_2$, $^3J_{HH} = 6.9$ Hz), 7.19 (s, 4H, *m*-Trip). ^{13}C NMR (C_6H_6): δ 23.39 ($o\text{-}CH(CH_3)_2$), 24.26 ($p\text{-}CH(CH_3)_2$), 26.61 ($o\text{-}CH(CH_3)_2$), 31.00 ($o\text{-}CH(CH_3)_2$), 34.74 ($p\text{-}CH(CH_3)_2$), 121.19 (*m*-Trip), 127.75 ($p\text{-}C_6H_3$), 130.68 ($m\text{-}C_6H_3$), 134.85 (*i*-Trip), 145.38 (*p*-Trip), 147.02 (*o*-Trip), 149.53 ($o\text{-}C_6H_3$), 177.60 ($i\text{-}C_6H_3$). $^{119}Sn\{^1H\}$ NMR (C_6D_6): δ 1140. UV−vis (benzene): $\lambda_{max} = 428$ nm, $\epsilon = 3000$ L mol^{-1} cm^{-1}.

$Sn(N(SiMe_3)_2\}_2\{C_6H_3\text{-}2,6\text{-}Trip_2\}$ (3). A solution of $(Et_2O)LiC_6H_3\text{-}2,6\text{-}Trip_2$ (1.85 g, 3.3 mmol) in toluene (20 mL) was added to a solution of $Sn\{N(SiMe_3)_2\}_2$ (1.45 g, 3.3 mmol) in toluene (40 mL), with cooling in an ice bath. The mixture turned deep red upon stirring at ambient temperature for 3 h. After filtration the solution was concentrated to ca. 8 mL under reduced pressure (0.1 mmHg) and cooled in a −20 °C freezer for 24 h. The product **3** crystallizes as red-orange blocks: yield, 1.9 g, 76%. Anal. Calcd for $C_{42}H_{67}N_2Si_2Sn$: C, 66.30; H, 8.88. Found: C, 66.49; H, 8.85. ^1H NMR (C_6D_6): δ 0.004 (s, 18H, $Si{-}CH_3$), 1.127 (d, 12H, $p\text{-}CH(CH_3)_2$, $^3J_{HH} = 6.7$ Hz), 1.25 (d, 12H, $o\text{-}CH(CH_3)_2$, $^3J_{HH} = 6.7$ Hz), 3.35 (sept, 4H, $o\text{-}CH(CH_3)_2$, $^3J_{HH} = 6.7$ Hz), 7.25 (s, 4H, *m*-Trip), 7.31 (d, 2H, $m\text{-}C_6H_3$, $^3J_{HH} = 6.8$ Hz), 7.34 (t, 1H, $p\text{-}C_6H_3$, $^3J_{HH} = 6.8$ Hz). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 6.16 ($Si{-}CH_3$), 22.83 ($o\text{-}CH(CH_3)_2$), 24.26 ($p\text{-}CH(CH_3)_2$), 27.24 ($o\text{-}CH(CH_3)_2$), 30.87 ($o\text{-}CH(CH_3)_2$), 34.81 ($p\text{-}CH(CH_3)_2$), 122.17 (*m*-Trip), 126.78 ($m\text{-}C_6H_3$), 131.74 ($p\text{-}C_6H_3$), 135.14 (*i*-Trip), 144.89 (*o*-Trip), 147.53 (*p*-Trip), 149.67 ($o\text{-}C_6H_3$), 185.58 ($i\text{-}C_6H_3$). $^{119}Sn\{^1H\}$ NMR (C_6D_6): δ 1196.8.

X-ray Crystallography. Crystals of **1**−**3** were coated with hydrocarbon oil, mounted on a glass fiber and quickly placed in the N_2 cold stream on the diffractometer.[18] Data for **1**−**3** were obtained on Siemens R3 m/v diffractometer at 140 **(1)**, 130 **(2)**, or 198 K **(3)** using Mo Kα ($\lambda = 0.710\ 73$ Å) radiation. The diffractometer was equipped with a low-temperature device and a graphite monochromator. Calculations were carried out with SHELXTL-PLUS programs.[19] Scattering factors and the correction for anomalous scattering were taken from common sources.[20] The structures were solved by direct methods and refined by full-matrix least squares refinement. An absorption correction was applied using the program XABS2.[21] Crystal data for **1**−**3** are provided in Table 1.

Results and Discussion

Recent work in the heavier group 14 elements has shown that the use of sterically encumbering terphenyl substituents can effect the stabilization of some unusual and interesting molecules. For example, the use of the $-C_6H_3\text{-}2,6\text{-}Mes_2$ ligand at germanium has resulted in

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(14) Olmstead, M. M.; Simons, R. S.; Power, P. P. *J. Am. Chem. Soc.* **1997**, *119*, 11705.

(15) Schiemenz, B.; Power, P. P. *Organometallics* **1996**, *15*, 958.

(16) Harris, D. H.; Lappert, M. F. *J. Chem. Soc., Chem. Commun.* **1974**, 895.

(17) Fjelberg, T.; Haaland, A.; Schilling, B. E. R.; Lappert, M. F.; Thorne, A. J. *J. Chem Soc., Dalton Trans.* **1986**, 1551.

(18) This method is described by: Hope, H. A Practicum in Synthesis and Characterization. In *Experimental Organometallic Chemistry*; Wayda, A. L., Darensbourg, M. Y., Eds.; ACS Symposium Series 357; American Chemical Society: Washington, DC, 1987; Chapter 10.

(19) *SHELXTL, A Program for Crystal Structure Determinations*, Version 5.03; Siemens Analytical Instruments: Madison, WI, 1994.

(20) *International Tables for X-ray Crystallography*; Reidel; Dordrecht, The Netherlands, 1993; Vol. C.

(21) Parkin, S. R.; Moezzi, B.; Hope, H. *J. Appl. Crystallogr.* **1995**, *28*, 53.

Table 1. Crystallographic Data for Compounds 1−3

	1	2	3
formula	$C_{36}H_{49}ClGe$	$C_{36}H_{49}ISn$	$C_{42}H_{67}NSi_2Sn$
fw	589.79	727.34	760.84
color, habit	orange, parallellpiped	orange, parallellpiped	red block
cryst syst	orthorhombic	orthorhombic	triclinic
space group	*Pnma*	*Pbcm*	$P\bar{1}$
a, Å	8.059(2)	11.044(2)	8.926(6)
b, Å	25.350(5)	12.099(2)	13.223(7)
c, Å	10.230(4)	25.452(5)	19.244(14)
α, deg			96.48(2)
β, deg			93.00(5)
γ, deg			109.13(2)
V, $Å^3$	3316(1)	3401(1)	2123(2)
Z	4	4	2
d, g cm^{-3}	1.181	1.420	1.190
cryst dimens, mm	0.32 × 0.22 × 0.18	0.25 × 0.10 × 0.10	0.50 × 0.40 × 0.25
2Θ range, deg	3−50	3.7−55	3.3−45
μ, cm^{-1}	1.026	1.680	0.685
no. of unique data	2995	4001	6052
no. of data with $I > 2(\sigma)I$	1913	2025	5556
no. of params	184	169	433
R_1 ($I > 2(\sigma)I$)	0.052	0.091	0.053
R_{w2}, all data	0.112	0.249	0.144

the isolation of $Cp(CO)_2MoGeC_6H_3$-2,6-Mes_2,[22] having a Mo−Ge triple bond, and the characterization of the trigermyl radical species $[\{Ge(C_6H_3\text{-}2,6\text{-}Mes_2)\}^{\bullet}]_3$.[23] In addition, it has been shown that the aryl−germanium−halide precursor $[Ge(Cl)\{C_6H_3\text{-}2,6\text{-}Mes_2\}]_2$ has a dimeric, bis(germanediyl) structure featuring a Ge−Ge bond length of 2.443(2) Å.[13] In contrast, the corresponding tin compound $[Sn(\mu\text{-}Cl)\{C_6H_3\text{-}2,6\text{-}Mes_2\}]_2$ has a chloro bridged dimeric structure with no tin−tin bond.[13] As already mentioned, the use of the more crowding $-C_6H_3$-2,6-$Trip_2$, ligand has resulted in the isolation of Sn(Cl)-C_6H_3-$Trip_2$ which, upon reduction, affords the new radical species $[K(THF)_6][\{Sn(C_6H_3\text{-}2,6\text{-}Trip_2)\}_2]$.[14] The apparently rich potential of the $-C_6H_3$-2,6-$Trip_2$ ligand in heavier group 14 elements thus warrants further investigation of the spectroscopic and structural properties of the key halide precursors.

Syntheses and Spectroscopy. Compounds **1** and **2** were obtained in moderate yield by the reaction of 1 equiv of the lithium reagent with either $GeCl_2$−dioxane or SnI_2. The addition of 2 equivs of the lithium aryl did not give the germanium or tin diaryls, most probably for steric reasons. Initially, $Sn(I)\{C_6H_3\text{-}2,6\text{-}Trip_2\}$ **(2)** was isolated in a fortuitous manner as follows. The synthesis of the lithium reagent $(Et_2O)LiC_6H_3$-2,6-$Trip_2$ involves the addition of 2 equivs of Li(*n*-Bu) to the aryl iodide 1-IC_6H_3-2,6-$Trip_2$ during which LiI is produced as one of the products.[15] Unless this is carefully separated from $(Et_2O)LiC_6H_3$-2,6-$Trip_2$, or if the (Et_2O)-LiC_6H_3-2,6-$Trip_2$ is generated in solution by the addition of Li(n-Bu) to the iodide, LiI will be available for further reaction and I^- may undergo exchange with an available metal halide. Thus, treatment of $SnCl_2$ with an LiI containing solution of $(Et_2O)LiC_6H_3$-2,6-$Trip_2$ results in a product that consists mainly of $Sn(I)\{C_6H_3\text{-}2,6\text{-}Trip_2\}$ instead of the expected $Sn(Cl)\{C_6H_3\text{-}2,6\text{-}Trip_2\}$ **(4)**. The latter compound can be obtained as an orange crystalline material if pure $(Et_2O)LiC_6H_3$-2,6-$Trip_2$ is employed under the same conditions.[14] However, crystals of **4** did not prove suitable for X-ray crystal diffraction studies, whereas crystals of **2** permitted an X-ray data set of sufficient quality to be obtained to afford an acceptable structure of **2**. The synthesis of the mixed amido/aryl species **3** was accomplished by the addition of the lithium aryl to the bis amide $Sn\{N(SiMe_3)_2\}_2$. The use of heavier group 14 bivalent amides as starting materials for the synthesis of the corresponding alkyls has been known for some time and originated with the use of $Pb\{N(SiMe_3)_2\}_2$ to synthesize the first stable lead(II) dialkyl $Pb\{CH(SiMe_3)_2\}_2$.[24] Compound **3** was obtained in quite a good yield (76%) by this route. However, attempts to displace both amide groups with the $-C_6H_3$-2,6-$Trip_2$ substituent were unsuccessful.

The ^1H and ^{13}C NMR spectra of **1**−**3** display no unusual features. The *ipso*-C_6H_3 ^{13}C chemical shift of the terphenyl ligand is characterized by low-field signals which are in the range $\delta = 164.57-185.58$. No dynamic behavior was observed, although the $SiMe_3$ signals in **3** showed broadening at low (ca. −70 °C) temperature. The ^{119}Sn NMR chemical shift of **3** at 1197 ppm appears at slightly lower field than those seen for the monomers $Sn\{N(SiMe_3)_2\}_2$ ($\delta = 776$)[25] and $SnMes^*_2$ ($\delta = 980$).[26] These values are consistent with the low coordination numbers of these compounds.

The UV−vis spectroscopy of **1** and **2** displayed absorption maxima at 393 **(1)** and 428 nm **(2)**. These absorptions may be attributed to n−p transitions. However, these appear at considerably shorter wavelengths (ca. 130−150 nm) than those recently reported for $M(C_6H_3\text{-}2,6\text{-}Mes_2)_2$.[13] The higher energy absorptions in **1** and **2** are consistent with the narrower angles at germanium and tin and the presence of a more electronegative halide substituent.

X-ray Crystal Structures. The thermal ellipsoid plots of **1**−**3** are presented in Figures 1−3. The structures are all monomers with no short intramolecular interactions. Both **1** and **2** are characterized by the presence of a crystallographically required plane of symmetry incorporating the halide, group 14, C(*ipso*) and C(*para*) atoms. The monomeric nature of the organometal halide structures **1** and **2** is unique to the extent that the organic ligand is monohapto. The only prior examples of published monomeric structures involve the multihapto ligand species Ge(Cl)Cp*,[9] Sn-$(Cl)\{C(SiMe_3)_2C_6H_4N\text{-}2\}$,[5] and $Sn(Cl)\{C_6H_3\text{-}2,6(NMe_2)_2\}$.[7] The structure of Ge(Cl)Mes* was also reported to be monomeric, although full details have not been disclosed.[10] In **1** and **2** the angles at germanium and tin, 101.31(15) and 102.31(15)°, are almost equal. The latter value is similar to the C−Sn−C angle of 103.6(1)° in $SnMes^*_2$ [26] but somewhat wider than the 98.3(1)° angle in $Sn\{C_6H_2\text{-}2,4,6\text{-}(CF_3)_3\}_2$.[27] However, the I−Sn−C angle is much narrower than the very wide (114.7(2)°) C−Sn−C angle in $Sn(C_6H_3\text{-}2,6\text{-}Mes_2)_2$.[13] Similarly, the Cl−Ge−C angle in **1** is several degrees narrower than the 108.0-

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[22] Simons, R. S.; Power, P. P. *J. Am. Chem. Soc.* **1996**, *118*, 11966.

[23] Olmstead, M. M.; Pu, L.; Simons, R. S.; Power, P. P. *J. Chem. Soc., Chem. Commun.* **1997**, *1595.*

[24] Goldberg, D. E.; Harris, D. H.; Lappert, M. F.; Thomas, K. M. *J. Chem. Soc., Chem. Commun.* **1976**, 261.

[25] Wrackmeyer, B. *J. Magn. Reson.* **1985**, *61*, 536.

[26] Weidenbruch, M.; Schlaefke, J.; Shäfer, A.; Peters, K.; von Schnering, H. G.; Marsmann, H. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1846.

[27] Grützmacher, H.-G.; Pritzkow, H.; Edelmann, F. T. *Organometallics* **1991**, *10*, 23.

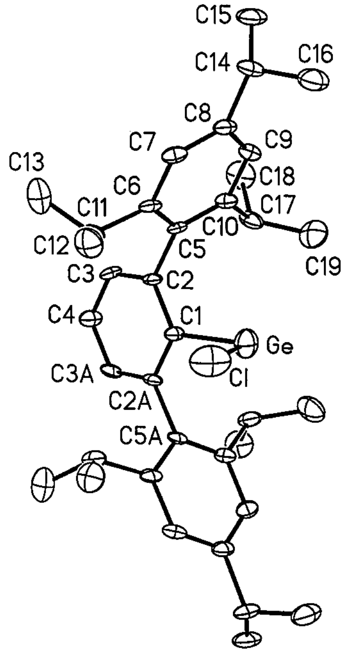

Figure 1. Thermal ellipsoid plot (50%) of **1**. H atoms are not shown. Important structural data are given in Table 1.

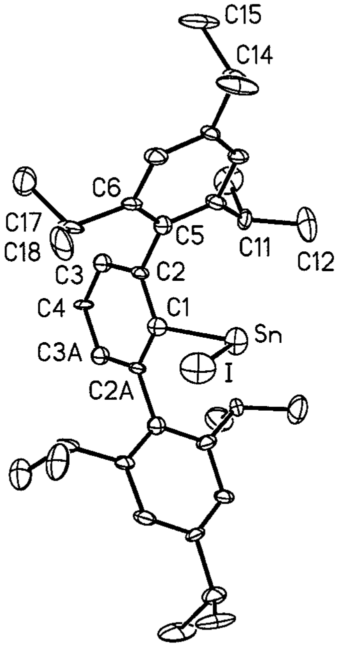

Figure 2. Thermal ellipsoid plot (50%) of **2**. H atoms are not shown. Important structural data are given in Table 1.

(2)° and 114.4(2)° angles at germanium in GeMes*$_2$ [28] and Ge(C$_6$H$_3$-2,6-Mes$_2$)$_2$,[13] where the large size of Mes* and −C$_6$H$_3$-2,6-Mes$_2$ substituents results in considerable steric crowding and wider angle at germanium.

The structures of **1** and **2** may also be compared with those of the dimers [Ge(Cl){C$_6$H$_3$-2,6-Mes$_2$}]$_2$,[13] [Sn(μ^2-Cl){C$_6$H$_3$-2,6-Mes$_2$}]$_2$,[13] and [Sn(μ^2-Cl){C(SiMe$_2$Ph)$_3$}]$_2$.[11] The former compound has a Ge−Ge bonded, bis(germanediyl), dimeric structure in the solid state with a relatively weak Ge−Ge interaction of 2.443(2) Å, whereas both of the tin species[11,13] have a halide bridged structure.[13] In hydrocarbon solution the germanium species is dissociated to monomers which, presumably, have a structure similar to that of **1**. The Cl−Ge−C angle in [Ge(Cl){C$_6$H$_3$-2,6-Mes$_2$}]$_2$ is 109.1(2)°, which is ca. 7° wider than that in **1**. This difference is probably a result of changes in steric crowding and orbital hybridization at germanium. The Ge−C distance, 2.000(8) Å, in the dimer is also close to the 1.989(5) Å seen in **1**, but the Ge−Cl bond length 2.120(2) Å in the dimer is 0.08 Å shorter than the corresponding one of 2.2026(10) Å in the monomer **1**. The Sn−C distance in **2**, 2.213(13) Å, is close to the 2.226(7) Å observed in SnMes*$_2$ [26] or the 2.222(5) Å in [Sn(μ^2-Cl){C$_6$H$_3$-2,6-Mes$_2$}]$_2$ but is somewhat shorter than the 2.296(10) Å in [Sn(μ^2-Cl){C(SiMe$_2$Ph)$_3$}]$_2$.[13] The Sn−I bond length in **2**, 2.766(2) Å, is slightly longer than the 2.73 Å in SnI$_2$.[29]

The mixed amido/aryl species **3** has a wider angle (N−Sn−C = 108.4(2)° at the group 14 element) than those seen in **1** and **2**. The widening of this angle can be attributed to steric effects. It may be noted that it is

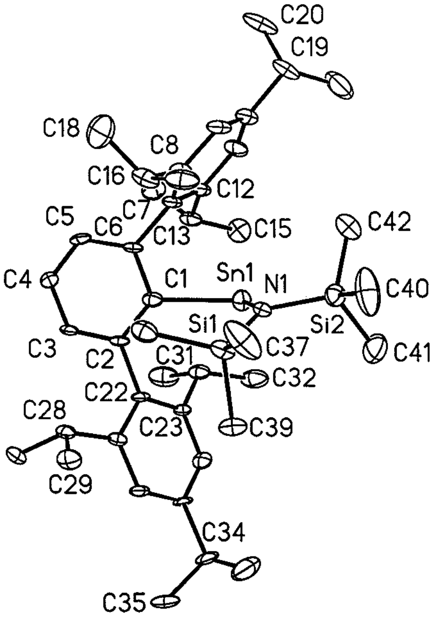

Figure 3. Thermal ellipsoid plot (50%) of **3**. H atoms are not shown. Important structural data are given in Table 1.

Table 2. Selected Bond Distances (Å) and Angles (deg) for 1−3

	Compound **1**		
Ge−C(1)	1.989(5)	C(1)−Ge−Cl	101.31(15)
Ge−Cl	2.2026(19)	C(2)−C(1)−C(2)	120.4(4)
C(1)−C(2)	1.397(4)		
	Compound **2**		
Sn−C(1)	2.213(13)	C(1)−Sn−I	102.6(3)
Sn−I	2.766(2)	C(2)−C(1)−C(2)	119.5(12)
C(1)−C(2)	1.348(11)		
	Compound **3**		
Sn−C(1)	2.225(5)	N(1)−Sn(1)−C(1)	108.4(2)
Sn−N(1)	2.094(5)	S(1)−N(1)−Si(2)	125.7(3)
N(1)−Si(1)	1.736(5)	Sn(1)−N(1)−Si(1)	123.9(2)
N(1)−Si(2)	1.756(4)	Sn(1)−N(1)−Si(2)	106.1(2)
C(1)−C(2)	1.407(7)	C(2)−C(1)−C(6)	113.4(5)
C(1)−C(6)	1.404(7)	C(2)−C(1)−Sn(1)	128.2(4)
		C(6)−C(1)−Sn(1)	111.0(4)

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(28) Jutzi, P.; Schmidt, H.; Neumann, B.; Stammler, H.-G. *Organometallics* **1996**, *15*, 741.

(29) Lister, M. W.; Sutton, L. E. *Trans. Faraday Soc.* **1941**, *37*, 406.

wider than the 104.7(2)° in the amide Sn{N(SiMe$_3$)$_2$}$_2$ [30] or the 103.6(1)° in the previously mentioned SnMes*$_2$ species.[26] The Sn−N bond length in **3** is essentially identical to the 2.09(1) Å in Sn{N(SiMe$_3$)$_2$}$_2$,[30] and the Sn−C distance 2.225(5) Å is very close to the distances discussed for **2**.

A further interesting feature of the structures of **1**−**3** is that some of the structural parameters show deviation from idealized values. For **1** and **2**, the most notable distortion involves the Ge−C(1) and Sn−C(1) vectors which are displaced by 8.3 and 15.5° from the C(1) aryl ring planes, whereas no such deviation is observed between the C(2)−C(5) vector and the plane of the C(1) or C(5) rings. The planes of the Trip rings in **1** and **2** subtend large angles of 85.5 and 82.8° with respect to the C(1) ring plane. In the more crowded structure of **3** the Sn(1)−C(1) vector is an impressive 26.3° out of the plane of the C(1) ring. Also, the C(6)−C(7) vector to the C(7) Trip ring is 11.3° out of the C(1) ring plane, whereas the C(2)−C(22) vector connecting the C(2) Trip ring shows only ca.. 1° deviation. Inspection of Figure 3 and the data in Table 2 also shows that the two Sn−C(*ipso*)−C(*ortho*) angles have a substantial ca.. 17° difference. Similarly, a ca.. 17° difference is observed between the two Sn−N−Si angles. Clearly, the increased steric crowding in **3** causes much greater structural distortions than those observed in **1** and **2**.

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Supporting Information Available: Figures showing ORTEP diagrams of **1** and tables giving full details of the crystallographic data and data collection parameters, atom coordinates, bond distances, bond angles, anisotropic thermal parameters, and hydrogen coordinates for **1**−**3** (26 pages). Ordering information is given on any current masthead page.

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(30) Fjelberg, T.; Hope, H.; Lappert, M. F.; Power, P. P.; Thomas, A. J. *J. Chem. Soc., Chem. Commun.* **1983**, 639.