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Synthesis, Structure, and Spectroscopic Properties of Germanium and Tin Compounds Containing Aryloxide Ligation: Comparison of Aryloxide Bonding to Group 4 and Group 14 Metal Centers

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The mononuclear, four-coordinate germanium compounds Ge(OAr)$_2$Cl$_2$ (**1a**), Ge(OAr)$_3$Cl (**1b**), and Ge(OAr)$_2$(NMe$_2$)$_2$ (**2**) (OAr = 2,6-diphenylphenoxide) are obtained when GeCl$_4$ and Ge(NMe$_2$)$_4$ are treated with LiOAr and HOAr, respectively. In contrast to the case for the corresponding tin compounds, facile cyclometalation of the 2,6-diphenylphenoxide ligands does not occur. Both compounds **1** and **2** are thermally stable at 120 °C for extended periods of time. Similarly, the tin compound Sn(OAr′)$_2$(NMe$_2$)$_2$ (**3**) (OAr′ = 2,6-di-*tert*-butylphenoxide) is obtained from Sn(NMe$_2$)$_4$ and HOAr′. Thermolysis of **3** leads only to decomposition products with no evidence for cyclometalation. The three compounds **1b**, **2**, and **3** have been structurally characterized and shown to contain an almost regular tetrahedral environment about the Ge and Sn metal centers. Despite the steric congestion within the coordination sphere, the M–O–Ar angles all lie in the 120–125° range. A comparison of aryloxide binding to group 14 and group 4 metal centers is made, showing the dramatic structural effect of π-bonding to the d-block metals. Crystal data are as follows: for GeClO$_3$C$_{57}$H$_{45}$ (**1b**) at 20 °C, $a = 41.568$ (6) Å, $b = 10.759$ (3) Å, $c = 21.675$ (3) Å, $\beta = 110.04$ (1)°, $Z = 8$, $d_{\mathrm{calcd}} = 1.288$ g cm^{-3} in space group $C2/c$; for GeO$_2$N$_2$C$_{40}$H$_{38}$ (**2**) at 20 °C, $a = 10.378$ (1) Å, $b = 17.094$ (3) Å, $c = 19.076$ (2) Å, $Z = 4$, $d_{\mathrm{calcd}} = 1.278$ g cm^{-3} in space group $P2_12_12_1$, for SnO$_2$N$_2$C$_{34}$H$_{50}$ (**3**) at 20 °C: $a = 8.446$ (4) Å, $b = 23.589$ (2) Å, $c = 17.300$ (5) Å, $\beta = 94.05$ (2)°, $Z = 4$, $d_{\mathrm{calcd}} = 1.247$ g cm^{-3} space group $P2_1/n$.

Introduction

During recent years there has been a resurgence of interest in the chemistry of main-group metal alkoxide and aryloxide compounds.[1-3] Attention has mainly been focused on the reactivity of these compounds, especially their potential use as precursors to metal oxide derivatives.[4] However, more recently theoretical aspects of the bonding of alkoxide and aryloxide ligands to p-block metal centers have been investigated.[5] During our studies of the inorganic and organometallic chemistry supported by bulky aryloxide ligation[6,7] we have demonstrated the ability of Sn(IV) metal centers to intramolecularly activate the aromatic CH bonds of a number of alkoxide and aryloxide ligands.[8] Treatment of SnCl$_4$ or Sn(NMe$_2$)$_4$ with LiOAr or HOAr, respectively, (OAr = 2,6-diphenylphenoxide) has been shown to lead to a number of cyclometalation products.[8] The formation of five-membered metallacycle rings by the cyclometalation of aryl–methoxide ligation by Sn–NMe$_2$ bonds has also been observed.[9] As an extension of this study, we have synthesized a number of germanium derivatives of 2,6-diphenylphenoxide in order to compare the reactivity with that found for tin. Furthermore, we have also obtained 2,6-di-*tert*-butylphenoxide derivatives of Sn(IV) to evaluate the potential for aliphatic CH bond activation by this metal center. In this paper we wish to report on the lack of cyclometalation observed for these particular systems as well as to carry out a comparison based upon structural data of the bonding characteristics of aryloxide ligands to group 4 and group 14 metal centers.

Results and Discussions

The reaction of SnCl$_4$ with LiOAr (OAr = 2,6-diphenylphenoxide) in hydrocarbon solvents has been shown to lead to a dimeric material containing cyclometalated 2,6-diphenylphenoxide ligation.[8] In contrast the reaction of GeCl$_4$ with LiOAr was found to lead to the simple substitution products Ge(OAr)$_2$Cl$_2$ (**1a**) and Ge(OAr)$_3$Cl (**1b**) in good yield. The spectroscopic properties of **1a** and **1b** clearly show the presence of nonmetalated 2,6-diphenylphenoxide ligands. The complexity in the aromatic region of the ^{1}H NMR spectrum associated with the formation of a six-membered metallacycle is completely missing.[6-8] Thermolysis of **1a** in toluene solution was not found to lead to cyclometalation. Instead **1a** was found to convert slowly to **1b** via ligand-exchange reactions along with other unidentified germanium compounds. The formation of M(OAr)$_3$X type species from M(OAr)$_2$X$_2$ compounds has been observed previously for group 4 metal derivatives of these aryloxide ligands.[10] Compound **1b** was found to be stable at 120 °C for periods of days.

The treatment of Sn(NMe$_2$)$_4$ with HOAr has been shown to lead to the cyclometalated compounds Sn(OC$_6$H$_3$Ph-C$_6$H$_4$)$_2$(HNMe$_2$)$_2$ (2 HOAr per Sn)[8] and Sn(OC$_6$H$_3$Ph-C$_6$H$_4$)(OAr)$_2$(HNMe$_2$) (3 HOAr per Sn).[11] In contrast treatment of Ge(NMe$_2$)$_4$ with HOAr (≥2 equiv) was found to yield the simple bis(amido) derivative (Ge(OAr)$_2$(NMe$_2$)$_2$ (**2**). In the ^{1}H NMR spectrum of **2** the NCH_3 protons resonate as a sharp single at δ 1.51 ppm, while a simple set of aromatic multiplets can be assigned to the nonmetalated 2,6-diphenylphenoxide ligation. Thermolysis of NMR solutions of **2** at 120 °C was found to lead to little change over a period of hours except for the generation of a small amount of dimethylamine. This behavior contrasts markedly with the rapid, room-temperature cyclometalation of OAr ligands by Sn–NMe$_2$ groups.[8]

Previous work by our group has shown that cyclometalation of both 2,6-diphenylphenoxide and 2,6-di-*tert*-butylphenoxide ligands can readily occur at early d-block metal centers.[6,12] In

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Table I. Fractional Coordinates and Isotropic Thermal Parameters for Ge(OAr)$_3$Cl (**1b**)

atom	*x*	*y*	*z*	*B*,[a] Å^2
Ge	0.12486 (2)	0.17284 (9)	0.00124 (4)	3.00 (2)
Cl(1)	0.08652 (6)	0.0848 (2)	-0.0759 (1)	4.31 (6)
O(20)	0.1203 (1)	0.3347 (5)	-0.0065 (2)	3.3 (1)
O(30)	0.1660 (1)	0.1359 (4)	0.0034 (2)	3.4 (1)
O(40)	0.1236 (1)	0.1367 (5)	0.0788 (2)	3.3 (1)
C(21)	0.1172 (2)	0.3972 (8)	-0.0647 (3)	3.2 (2)
C(22)	0.1473 (2)	0.4453 (8)	-0.0708 (4)	3.7 (2)
C(23)	0.1440 (2)	0.5057 (9)	-0.1305 (4)	4.7 (2)
C(24)	0.1130 (2)	0.518 (1)	-0.1799 (4)	5.5 (3)
C(25)	0.0840 (2)	0.470 (1)	-0.1711 (4)	5.2 (3)
C(26)	0.0847 (2)	0.4107 (7)	-0.1124 (3)	3.5 (2)
C(31)	0.1781 (2)	0.0161 (8)	0.0026 (4)	3.8 (2)
C(32)	0.1731 (2)	-0.0425 (8)	-0.0576 (4)	4.2 (2)
C(33)	0.1875 (2)	-0.1623 (9)	-0.0569 (4)	5.5 (3)
C(34)	0.2063 (2)	-0.2178 (9)	0.0011 (5)	6.9 (3)
C(35)	0.2119 (2)	-0.1567 (9)	0.0607 (5)	6.2 (3)
C(36)	0.1980 (2)	-0.0395 (9)	0.0615 (4)	4.6 (2)
C(41)	0.0934 (2)	0.1377 (7)	0.0938 (3)	3.1 (2)
C(42)	0.0864 (2)	0.2434 (8)	0.1252 (3)	4.1 (2)
C(43)	0.0560 (2)	0.2402 (9)	0.1389 (4)	4.8 (2)
C(44)	0.0340 (2)	0.139 (1)	0.1230 (4)	5.1 (3)
C(45)	0.0424 (2)	0.0358 (9)	0.0943 (4)	4.8 (2)
C(46)	0.0725 (2)	0.0322 (9)	0.0790 (3)	3.7 (2)
C(221)	0.1804 (2)	0.4403 (8)	-0.0180 (4)	3.6 (2)
C(222)	0.1844 (2)	0.4716 (8)	0.0468 (4)	4.0 (2)
C(223)	0.2162 (2)	0.4758 (9)	0.0945 (4)	5.1 (3)
C(224)	0.2453 (2)	0.448 (1)	0.0801 (4)	5.8 (3)
C(225)	0.2418 (2)	0.414 (1)	0.0167 (5)	5.7 (3)
C(226)	0.2098 (2)	0.4111 (9)	-0.0321 (4)	4.9 (2)
C(261)	0.0521 (2)	0.3759 (8)	-0.1040 (4)	3.9 (2)
C(262)	0.0256 (2)	0.330 (1)	-0.1559 (4)	6.0 (3)
C(263)	-0.0058 (3)	0.301 (1)	-0.1499 (5)	6.8 (3)
C(264)	-0.0108 (2)	0.321 (1)	-0.0912 (5)	6.1 (3)
C(265)	0.0157 (2)	0.3657 (9)	-0.0387 (4)	5.6 (3)
C(266)	0.0472 (2)	0.3927 (9)	-0.0449 (4)	4.6 (2)
C(321)	0.1535 (2)	0.0119 (8)	-0.1235 (4)	4.2 (2)
C(322)	0.1579 (2)	0.1353 (9)	-0.1374 (4)	4.7 (2)
C(323)	0.1402 (3)	0.186 (1)	-0.1981 (4)	6.4 (3)
C(324)	0.1177 (3)	0.110 (1)	-0.2454 (5)	7.2 (3)
C(325)	0.1137 (3)	-0.012 (1)	-0.2330 (4)	7.1 (3)
C(326)	0.1313 (2)	-0.0620 (9)	-0.1722 (4)	5.7 (3)
C(361)	0.2051 (2)	0.0222 (9)	0.1253 (5)	5.6 (3)
C(362)	0.2196 (2)	0.139 (1)	0.1370 (4)	5.9 (3)
C(363)	0.2293 (3)	0.192 (1)	0.2002 (5)	7.5 (3)
C(364)	0.2225 (3)	0.128 (1)	0.2505 (5)	8.9 (4)
C(365)	0.2072 (3)	0.015 (1)	0.2393 (5)	8.8 (4)
C(366)	0.1996 (3)	-0.040 (1)	0.1780 (5)	7.5 (3)
C(421)	0.1106 (2)	0.3491 (8)	0.1465 (3)	4.7 (2)
C(422)	0.1446 (2)	0.332 (1)	0.1819 (4)	5.6 (2)
C(423)	0.1659 (3)	0.433 (1)	0.2050 (5)	8.1 (3)
C(424)	0.1523 (3)	0.554 (1)	0.1904 (5)	9.6 (3)
C(425)	0.1182 (3)	0.568 (1)	0.1562 (5)	9.5 (4)
C(426)	0.0971 (3)	0.4686 (9)	0.1331 (4)	6.9 (3)
C(461)	0.0795 (2)	-0.0806 (8)	0.0467 (4)	3.8 (2)
C(462)	0.0534 (2)	-0.1429 (8)	-0.0005 (4)	4.7 (2)
C(463)	0.0603 (2)	-0.247 (1)	-0.0322 (4)	5.7 (3)
C(464)	0.0930 (2)	-0.2883 (9)	-0.0180 (5)	6.0 (3)
C(465)	0.1192 (2)	-0.2297 (9)	0.0294 (5)	5.6 (3)
C(466)	0.1128 (2)	-0.1264 (8)	0.0630 (4)	4.2 (2)
C(801)	0	0.270 (3)	$^1/_4$	15.6 (9)*
C(802)	0.0307 (3)	0.207 (1)	0.2890 (6)	9.7 (4)*
C(803)	0.0272 (3)	0.092 (1)	0.2840 (7)	10.9 (4)*
C(804)	0	-0.002 (2)	$^1/_4$	12.8 (7)*

[a] Asterisk indicates *B* values for anisotropically refined atoms given in the form of the isotropic equivalent thermal parameter defined as $(4/3)[a^2\beta(1,1) + b^2\beta(2,2) + c^2\beta(3,3) + ab(\cos\gamma)\beta(1,2) + ac(\cos\beta)\beta(1,3) + bc(\cos\alpha)\beta(2,3)]$.

Table II. Selected Bond Distances (Å) and Angles (deg) for Ge(OAr)$_3$Cl (**1b**)

Ge–Cl	2.099 (2)	Ge–O(20)	1.754 (5)
Ge–O(30)	1.739 (5)	Ge–O(40)	1.744 (5)
Cl–Ge–O(20)	110.1 (2)	Cl–Ge–O(30)	112.9 (2)
Cl–Ge–O(40)	113.7 (2)	O(20)–Ge–O(30)	107.6 (2)
O(20)–Ge–O(40)	106.0 (2)	O(30)–Ge–O(40)	106.0 (2)
Ge–O(20)–C(21)	122.6 (5)	Ge–O(30)–C(31)	124.9 (5)
Ge–O(40)–C(41)	123.1 (4)		

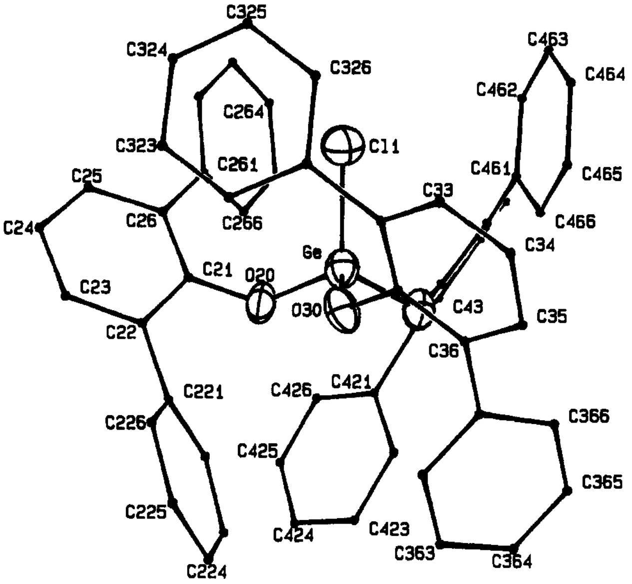

Figure 1. ORTEP view of Ge(OAr)$_3$Cl (**1b**).

the latter case the six-membered metallacycle ring is formed by activation of an aliphatic CH bond.[12] In order to evaluate the potential for aliphatic CH bond activation by Sn(IV) metal centers, we have investigated the reaction of 4-methyl-2,6-di-*tert*-butylphenol (HOAr′) with Sn(NMe$_2$)$_4$. The tin(II) compound Sn(OAr′)$_2$ has been previously reported.[13] Reaction of Sn(NMe$_2$)$_4$ with HOAr′ leads to the formation of Sn(OAr′)$_2$(NMe$_2$)$_2$ (**3**) in high yield. The ^{1}H NMR spectrum of **3** is highly informative. Three sharp singlets are observed in the aliphatic region of the spectrum in the intensity ratio of 6:1:2, leading to their assignments as being due to the C*Me*$_3$, 4-*CH*$_3$, and N*Me*$_2$ methyl groups. In the case of the dimethylamido groups two clearly resolved sets of satellite peaks are also observed due to 3-bond coupling of the protons to ^{117}Sn and ^{119}Sn nuclei. A singlet in the aromatic region due to the meta proton in the OAr′ ligand is also observed. Thermolysis of **3** at 120 °C for days does not lead to any noticeable change in the ^{1}H NMR spectrum. At elevated temperatures (>250 °C) decomposition of **3** slowly occurs, leading to HNMe$_2$ and HOAr′ as the only identifiable products. Hence, if cyclometalation is occurring in this compound, it requires temperatures that also lead to extensive decomposition.

Structural Studies. Despite the large number of structural studies dealing with group 4 metal (Ti, Zr, Hf) compounds containing bulky aryloxide ligands,[6,7,10] there is little previous work dealing with group 14 metal analogues for direct comparison. We have hence carried out single-crystal X-ray diffraction analyses of compounds **1b**, **2**, and **3** in order to compare their structural parameters with known d-block metal analogues. The fractional coordinates and isotropic thermal parameters for compounds **1b**, **2**, and **3** are given in Tables I, III, and V, respectively, while selected bond distances and angles are collected in Tables II, IV, and VI. All three molecules can be seen to adopt an almost regular tetrahedral environment about the central metal atom (Figures 1–3). In **1b** slight distortions occur due to an opening up of the three Cl–Ge–O angles (110–114°) compared to the three O–Ge–O angles (106–108°). In the bis(amido) compound **2** the O–Ge–O angles is compressed (99.8 (2)°) compared to the N–Ge–N angle of 111.9 (3)°, but this effect is nowhere near as pronounced in compound **3** (O–Sn–O = 104.5 (1)°, N–Sn–N = 109.6 (2)°).

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Table III. Fractional Coordinates and Isotropic Thermal Parameters for $Ge(OAr)_2(NMe_2)$ (**2**)

atom	x	y	z	B,[a] Å^2
Ge	0.25363 (6)	0.94928 (3)	0.36203 (2)	3.082 (8)
O(10)	0.2375 (3)	1.0071 (2)	0.4401 (1)	2.99 (6)
O(20)	0.4079 (3)	0.9076 (2)	0.3772 (2)	2.89 (7)
N(30)	0.1385 (4)	0.8720 (3)	0.3565 (3)	4.7 (1)
N(40)	0.2506 (6)	1.0100 (2)	0.2866 (2)	4.64 (9)
C(11)	0.1188 (5)	1.0233 (3)	0.4694 (3)	3.0 (1)
C(12)	0.0621 (5)	0.9696 (3)	0.5159 (3)	3.2 (1)
C(13)	−0.0584 (5)	0.9893 (3)	0.5447 (3)	4.1 (1)
C(14)	−0.1195 (5)	1.0588 (3)	0.5286 (3)	4.2 (1)
C(15)	−0.0604 (5)	1.1100 (3)	0.4834 (3)	3.9 (1)
C(16)	0.0578 (5)	1.0949 (3)	0.4543 (2)	3.1 (1)
C(21)	0.5150 (5)	0.9366 (3)	0.3434 (2)	3.1 (1)
C(22)	0.5398 (5)	0.9168 (3)	0.2727 (3)	3.2 (1)
C(23)	0.6441 (5)	0.9519 (3)	0.2400 (3)	3.9 (1)
C(24)	0.7243 (5)	1.0024 (3)	0.2747 (3)	4.5 (1)
C(25)	0.7034 (5)	1.0193 (3)	0.3449 (3)	4.2 (1)
C(26)	0.5971 (5)	0.9876 (3)	0.3793 (3)	3.3 (1)
C(31)	0.1696 (7)	0.7911 (3)	0.3710 (4)	6.6 (2)
C(32)	0.0015 (6)	0.8912 (4)	0.3533 (4)	6.5 (2)
C(41)	0.1621 (7)	0.9983 (5)	0.2290 (3)	7.3 (2)
C(42)	0.3333 (7)	1.0774 (3)	0.2787 (3)	5.6 (2)
C(121)	0.1199 (5)	0.8940 (3)	0.5361 (3)	3.6 (1)
C(122)	0.2493 (7)	0.8855 (3)	0.5496 (3)	4.7 (1)
C(123)	0.2997 (6)	0.8147 (4)	0.5717 (4)	6.6 (2)
C(124)	0.2184 (7)	0.7510 (3)	0.5810 (4)	7.1 (2)
C(125)	0.0894 (7)	0.7575 (3)	0.5675 (4)	6.2 (2)
C(126)	0.0395 (6)	0.8288 (3)	0.5451 (3)	4.9 (1)
C(161)	0.1153 (5)	1.1532 (3)	0.4056 (3)	3.7 (1)
C(162)	0.2334 (6)	1.1881 (3)	0.4181 (3)	4.5 (1)
C(163)	0.2775 (6)	1.2477 (3)	0.3745 (3)	6.2 (2)
C(164)	0.2045 (7)	1.2709 (3)	0.3183 (4)	7.0 (2)
C(165)	0.0869 (7)	1.2381 (4)	0.3056 (4)	6.9 (2)
C(166)	0.0435 (6)	1.1800 (3)	0.3489 (3)	5.2 (1)
C(221)	0.4579 (5)	0.8604 (3)	0.2329 (3)	3.8 (1)
C(222)	0.4042 (6)	0.8826 (4)	0.1700 (3)	5.3 (1)
C(223)	0.3324 (7)	0.8296 (5)	0.1313 (4)	7.7 (2)
C(224)	0.3156 (7)	0.7551 (4)	0.1544 (4)	7.9 (2)
C(225)	0.3694 (8)	0.7318 (4)	0.2168 (4)	7.5 (2)
C(226)	0.4417 (6)	0.7843 (3)	0.2560 (3)	5.4 (1)
C(261)	0.5715 (5)	1.0111 (3)	0.4536 (3)	3.6 (1)
C(262)	0.5759 (6)	0.9590 (4)	0.5080 (3)	5.2 (1)
C(263)	0.5593 (7)	0.9828 (4)	0.5757 (3)	6.9 (2)
C(264)	0.5399 (6)	1.0609 (5)	0.5905 (3)	6.8 (2)
C(265)	0.5341 (6)	1.1149 (4)	0.5372 (3)	6.1 (2)
C(266)	0.5499 (5)	1.0895 (4)	0.4688 (3)	5.2 (1)

[a] B values for anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $(4/3)[a^2\beta(1,1) + b^2\beta(2,2) + c^2\beta(3,3) + ab(\cos\gamma)\beta(1,2) + ac(\cos\beta)\beta(1,3) + bc(\cos\alpha)\beta(2,3)]$.

Table IV. Selected Bond Distances (Å) and Angles (deg) for $Ge(OAr')_2(NMe_2)_2$ (**2**)

Ge–O(10)	1.795 (3)	Ge–O(20)	1.777 (3)
Ge–N(30)	1.785 (4)	Ge–N(40)	1.774 (4)
O(10)–Ge–O(20)	99.8 (2)	O(10)–Ge–N(30)	113.2 (2)
O(10)–Ge–N(40)	110.5 (2)	O(20)–Ge–N(30)	108.4 (2)
O(20)–Ge–N(40)	112.5 (2)	N(30)–Ge–N(40)	111.9 (3)
Ge–O(10)–C(11)	122.0 (3)	Ge–O(20)–C(21)	120.5 (3)

Table V. Fractional Coordinates and Isotropic Thermal Parameters for $Sn(OAr')_2(NMe_2)_2$ (**3**)

atom	x	y	z	B,[a] Å^2
Sn	0.48902 (3)	0.19695 (1)	0.37551 (2)	2.970 (6)
O(1)	0.4407 (3)	0.2671 (1)	0.3156 (2)	3.25 (6)
O(2)	0.5532 (3)	0.1411 (1)	0.2968 (2)	3.15 (6)
N(10)	0.6601 (5)	0.2143 (2)	0.4563 (2)	4.21 (9)
N(20)	0.3035 (5)	0.1637 (2)	0.4249 (2)	4.7 (1)
C(11)	0.5180 (5)	0.3190 (2)	0.3267 (2)	2.87 (9)
C(12)	0.4633 (5)	0.3591 (2)	0.3796 (2)	3.3 (1)
C(13)	0.5581 (6)	0.4068 (2)	0.3945 (3)	4.0 (1)
C(14)	0.6948 (6)	0.4174 (2)	0.3586 (3)	4.1 (1)
C(15)	0.7333 (5)	0.3805 (2)	0.3003 (3)	3.6 (1)
C(16)	0.6452 (5)	0.3322 (2)	0.2811 (2)	3.05 (9)
C(21)	0.4963 (5)	0.0862 (2)	0.2925 (2)	3.05 (9)
C(22)	0.5810 (5)	0.0424 (2)	0.3321 (2)	3.2 (1)
C(23)	0.5005 (5)	−0.0093 (2)	0.3397 (3)	3.5 (1)
C(24)	0.3500 (6)	−0.0190 (2)	0.3058 (3)	3.6 (1)
C(25)	0.2850 (5)	0.0217 (2)	0.2560 (3)	3.6 (1)
C(26)	0.3558 (5)	0.0738 (2)	0.2454 (2)	3.2 (1)
C(101)	0.6356 (7)	0.2003 (3)	0.5362 (3)	5.7 (1)
C(102)	0.7811 (6)	0.2570 (3)	0.4489 (3)	5.6 (1)
C(121)	0.3065 (6)	0.3538 (2)	0.4199 (3)	4.2 (1)
C(122)	0.3232 (6)	0.3110 (2)	0.4870 (3)	4.8 (1)
C(123)	0.1694 (6)	0.3386 (3)	0.3604 (3)	5.4 (1)
C(124)	0.2598 (7)	0.4103 (3)	0.4570 (4)	6.8 (2)
C(141)	0.7983 (7)	0.4690 (2)	0.3796 (4)	6.4 (2)
C(161)	0.6879 (5)	0.2971 (2)	0.2106 (3)	3.6 (1)
C(162)	0.5381 (7)	0.2876 (3)	0.1570 (3)	5.8 (1)
C(163)	0.7690 (7)	0.2411 (2)	0.2326 (3)	5.0 (1)
C(164)	0.8053 (7)	0.3289 (3)	0.1614 (3)	6.1 (1)
C(201)	0.1447 (7)	0.1848 (3)	0.4130 (4)	6.4 (2)
C(202)	0.3116 (7)	0.1060 (2)	0.4529 (3)	5.7 (1)
C(221)	0.7562 (5)	0.0476 (2)	0.3634 (3)	3.9 (1)
C(222)	0.8351 (7)	−0.0111 (2)	0.3676 (4)	6.5 (2)
C(223)	0.8493 (7)	0.0811 (3)	0.3063 (4)	7.8 (2)
C(224)	0.7719 (7)	0.0736 (3)	0.4426 (4)	7.5 (2)
C(241)	0.2618 (6)	−0.0733 (2)	0.3217 (3)	4.9 (1)
C(261)	0.2935 (6)	0.1135 (2)	0.1794 (3)	4.2 (1)
C(262)	0.4299 (8)	0.1274 (3)	0.1289 (3)	6.0 (1)
C(263)	0.2181 (7)	0.1675 (2)	0.2085 (3)	5.2 (1)
C(264)	0.1626 (7)	0.0845 (3)	0.1263 (3)	6.4 (1)

[a] B values for anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $(4/3)[a^2\beta(1,1) + b^2\beta(2,2) + c^2\beta(3,3) + ab(\cos\gamma)\beta(1,2) + ac(\cos\beta)\beta(1,3) + bc(\cos\alpha)\beta(2,3)]$.

Table VI. Selected Bond Distances (Å) and Angles (deg) for $Sn(OAr')_2(NMe_2)_2$ (**3**)

Sn–O(1)	1.980 (3)	Sn–O(2)	1.996 (3)
Sn–N(10)	1.980 (4)	Sn–N(20)	1.997 (4)
O(1)–Sn–O(2)	104.5 (1)	O(1)–Sn–N(10)	108.0 (1)
O(1)–Sn–N(20)	114.4 (1)	O(2)–Sn–N(10)	113.4 (1)
O(2)–Sn–N(20)	106.9 (1)	N(10)–Sn–N(20)	109.6 (2)
Sn–O(1)–C(11)	125.8 (2)	Sn–O(2)–C(21)	123.0 (2)

Of particular interest to this study are the bonding characteristics of the aryloxide ligands and how they compare to those found for d-block (group 4) metal analogues. In the case of high-valent, early d-block metal derivatives of aryloxide ligands, important characteristics often mentioned are the short M–O distances and large M–O–Ar angles typically found.[6,12,14,15] Both of these parameters have been attributed to the presence of considerable oxygen-p to metal-d π-bonding. A number of studies have clearly shown that there is a definite correlation between the M–O–Ar distance and the electron configuration at the metal center.[16,17] For the group 5 and 6 metals Nb and W it was found that a dramatic contraction of the metal–aryloxide distance occurred on going from saturated, 18-electron compounds to highly electron-deficient derivatives in which the metal has a formal d^0

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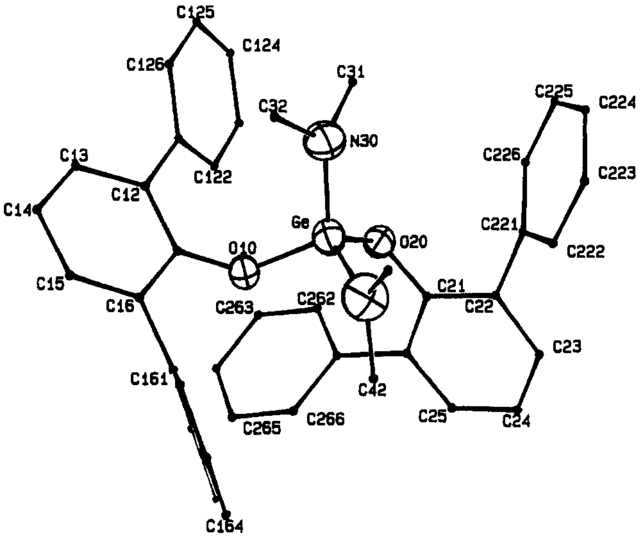

Figure 2. ORTEP view of Ge(OAr)$_2$(NMe$_2$)$_3$ (2).

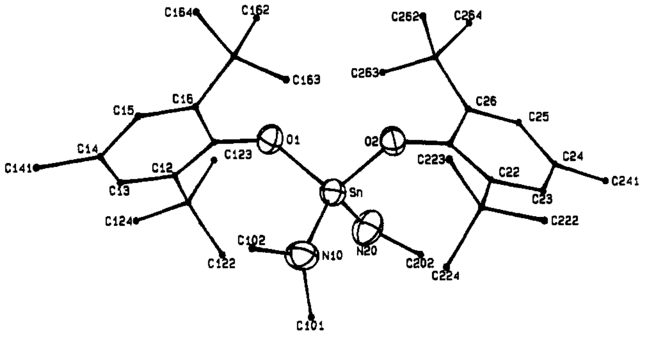

Figure 3. ORTEP view of Sn(OAr′)$_2$(NMe$_2$)$_2$ (3).

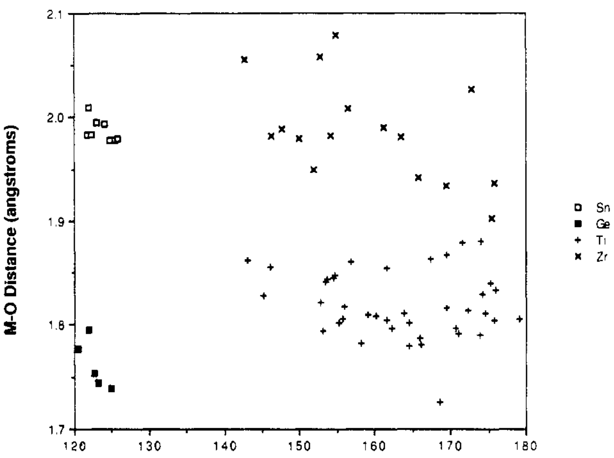

Figure 4. Plot of M–OAr distances versus M–O–Ar angles for the terminal, nonmetalated aryloxide ligands within the compounds listed in Table VII. For clarity, the esd's have been omitted.

configuration.[16,17] However, a recent study of niobium(V) and tantalum(V) aryloxide compounds has shown that there is no apparent correlation between M–OAr distances and M–O–Ar angles.[18] The latter parameter appears to be extremely flexible. Hence, in discussing the differences in the bonding of aryloxide ligands to group 4 and group 14 metal centers, it is best to discuss these two parameters separately.

1. M–OAr Distances. In Table VII are collected M–OAr distances and M–O–Ar angles for various aryloxide derivatives of Ge, Sn, Ti, and Zr. In order to maintain the steric demands

Table VII. M–OAr Distances and M–O–Ar Angles for Selected Aryloxide Derivatives of Ge, Sn, Ti, and Zr

compd	M–OAr, Å	M–O–Ar, deg	ref
Ge(OAr-2,6Ph$_2$)$_3$Cl	1.754 (5)	122.6 (5)	*a*
	1.739 (5)	124.9 (5)	
	1.744 (5)	123.1 (4)	
Ge(OAr-2,6Ph$_2$)$_2$(NMe$_2$)$_2$	1.795 (3)	122.0 (3)	*a*
	1.777 (3)	120.5 (3)	
Sn(OAr-2,6Bu$^t_2$-4Me)$_2$(NMe$_2$)$_2$	1.980 (3)	125.8 (2)	*a*
	1.996 (3)	123.0 (2)	
Sn(OC$_6$H$_2$Ph$_2$-C$_6$H$_4$)(OAr-2,4,6Ph$_2$)$_2$-(HNMe$_2$)	2.063 (9)	123.6 (9)	9
	1.99 (1)	126.1 (8)	
Ti(OAr-2,6Pr$^i_2$)$_4$	1.781 (3)	166.1 (3)	19
	1.780 (3)	164.5 (3)	
Ti(OAr-2,6Bu$^t_2$)$_3$I	1.810 (9)	159.1 (9)	20
	1.802 (7)	155.2 (9)	
	1.782 (8)	158.2 (9)	
Ti(OAr-2,6Ph$_2$)$_2$Cl$_2$	1.726 (2)	168.5 (2)	21
Ti(OAr-2,6Ph$_2$)$_2$Cl[N(SnMe$_3$)$_2$]	1.805 (1)	161.50 (8)	21
	1.808 (1)	160.15 (8)	
Ti(OAr-2,4Ph$_2$-6Bu^t)$_2$(NMe$_2$)$_2$	1.862 (5)	143.0 (5)	22
	1.844 (6)	153.6 (5)	
Ti(OAr-2,4,6Bu$^t_3$)$_2$(NMe$_2$)$_2$	1.813 (4)	171.0 (3)	23
	1.860 (3)	152.0 (3)	
Ti(OAr-2,6Ph$_2$)$_3$(CH$_2$SiMe$_3$)	1.797 (2)	170.7 (2)	24
	1.806 (2)	179.1 (2)	
	1.802 (2)	164.6 (2)	
Ti(OAr-2,6Ph$_2$)$_2$(C$_6$H$_5$)$_2$	1.794 (3)	153.0 (3)	24
	1.792 (3)	186.2 (3)	
Ti(OAr-2,6Ph$_2$)$_2$(C$_4$Et$_4$)	1.806 (6)	155.8 (6)	25
	1.804 (6)	175.7 (6)	
	1.788 (6)	165.9 (6)	
	1.828 (6)	145.1 (6)	
Ti(OAr-2,6Pr$^i_2$)$_2$[xyNC(R)=C(R)NBu^t)]	1.854 (4)	154.5 (5)	26
	1.790 (4)	173.9 (4)	
Ti(OAr-2,6Pr$^i_2$)$_2$[OCC(R)=C(R)NBu^t]	1.814 (2)	172.3 (3)	26
	1.792 (3)	171.0 (3)	
Ti(OAr-2,6Pr$^i_2$)$_2$(O)(py-4pd)$_2$	1.879 (6)	171.5 (6)	27
	1.863 (6)	167.3 (6)	
Ti(OAr-2,6Pr$^i_2$)$_2$(EtCCEt)(py-4Ph)$_2$	1.867 (2)	169.4 (2)	25
	1.880 (2)	174.1 (2)	
Ti(OAr-2,6Pr$^i_2$)$_2$(η^2-Bu^{t}NCR)(R)	1.811 (3)	163.8 (3)	27
	1.816 (3)	169.5 (3)	
Ti(OAr-2,6Ph$_2$)$_2$(η^2-PhNCR)(R)	1.821 (4)	152.7 (3)	27
	1.850 (4)	140.3 (3)	
Ti(OAr-2,6Pr$^i_2$)$_2$(η^2-Bu^{t}NCR$_2$)(py-4Ph)	1.848 (3)	154.6 (3)	28
	1.829 (4)	174.2 (3)	
Ti(OAr-2,6Pr$^i_2$)$_2$(η^2-Bu^{t}NCR$_2$)(Ph-4Et)	1.854 (2)	161.6 (1)	28
	1.840 (2)	175.3 (2)	
Zr(OAr-2,6Bu$^t_2$)(CH$_2$Ph)$_3$	1.942 (8)	165.7 (5)	10
Zr(OAr-2,6Bu$^t_2$)(CH$_2$Ph-4F)$_3$	1.934 (3)	169.4 (3)	10
Zr(OAr-2,6Bu$^t_2$)(OAr-2,6Bu$^t_2$-4OMe)-(CH$_2$Ph)$_2$	1.903 (4)	175.4 (4)	10
	1.936 (4)	175.7 (4)	
Zr(OAr-2,6Bu$^t_2$)(Me)$_2$(bpy)	1.983 (3)	154.2 (3)	29
	1.990 (3)	161.1 (3)	
Zr(OAr-2,6Bu$^t_2$)$_2$(η^2-Bu^{t}NCCH$_2$Ph)$_2$	2.027 (2)	172.7 (2)	27
Zr(OAr-2,6$^t_2$)(η^2-Bu^{t}NCCH$_2$Ph)$_3$	2.058 (2)	152.8 (2)	27
Zr(OAr-2,6Bu$^t_2$)$_2$(OCHR-py-CHRO)	1.982 (3)	146.2 (3)	26
	1.989 (3)	147.7 (3)	
Zr(OAr-2,6Bu$^t_2$)$_2$(OCHR-py-CHRO)(py)	2.015 (6)	178.8 (5)	26
	2.006 (5)	172.8 (5)	

[a] This work.

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of the ligands somewhat constant, only derivatives of 2,6-di-isopropyl- (OAr-2,6Pr$^i_2$), 2,6-diphenyl- (OAr-2,6Ph$_2$), and 2,6-di-*tert*-butylphenoxide (OAr-2,6Bu$^t_2$) and closely related ligands have been considered. On the pure basis of covalent radii and bond lengths reported for organic molecules, one would predict that a metal alkoxide or aryloxide σ-bond length would be 0.10–0.15 Å shorter than a metal–alkyl bond. If we define a parameter ΔO,C as [d(M–O) – d(M–C)] for aryloxide and alkyl ligands bound to the same metal center, then in the absence of π-bonding effects ΔO,C should lie close to the values of –0.12 to –0.15 Å. This parameter can, therefore, be used as a probe of the possible magnitude of π-bonding between aryloxide oxygen atoms and electron-deficient metal centers. In the case of the group 14 metals Ge and Sn one would expect π-donation to the metal centers to be minimal due to the high energy of the vacant d orbitals. In organo derivatives of these metals M–C distances of 1.94 Å ($GeEt_4$) and 2.16 Å ($SnEt_4$) are typical.[31] In tin(IV) compounds containing cyclometalated 2,6-diphenylphenoxide ligands we find the Sn–C(aryl) bonds to lie in the very narrow range of 2.102 (5)–2.13 (1) Å.[8] From the data obtained in this study and others (Table VII, Figure 4) the corresponding terminal metal–aryloxide distances vary from 1.739 (5) to 1.795 (3) Å for germanium and 1.99 (1) to 2.097 (4) Å for tin. Hence, for these metals the value of ΔO,C can be quoted as –0.17 (3) Å for Ge and –0.15 (3) Å for Sn. These numbers are hence entirely consistent with an absence of π-bonding between the aryloxide oxygen atom and the metal center. In the case of the group 4 metals titanium and zirconium we and others have reported compounds containing both aryloxide and alkyl ligands (Table VII). Some representative compounds are $Ti(OAr)_2(C_6H_5)_2$, $Ti(OAr)_3(CH_2SiMe_3)$,[24] and $Zr(OAr')_2(CH_2Ph)_2$.[10] For titanium(IV) the Ti–C(alkyl or aryl) distances typically lie in the 2.05–2.13-Å range, while for zirconium(IV) the corresponding distances are 2.22–2.29 Å.[6,10,24] The metal–aryloxide bond distances are considerably shorter (Table VII, Figure 4). In the case of Ti–OAr bonds, distances as low as 1.79 Å are possible with most lying in the 1.80–1.89-Å range. Similarly for zirconium the distances to aryloxide ligands are much shorter than to alkyl or aryl groups, averaging 1.90–2.00 Å. Hence, values of ΔO,C for these metals are much more negative than for group 14 metals, averaging –0.28 (5) Å for Ti and –0.29 (5) Å for Zr.

Two overall conclusions can be drawn from this analysis. The first is that the M–OAr distances are much more variable for the group 4 metals (Table VII, Figure 4). Second, the metal–aryloxide distances are contracted for the d-block metals below the values expected on the basis of purely σ-bonding. Both of these observations are totally explainable if one recognizes that oxygen-p to metal-d π-donation is an important part of the bonding characteristics for the d-block metals Ti and Zr. The extent of π-bonding is going to be very sensitive to the coordination number and symmetry of the molecules, factors that will determine which metal-based d orbitals will be available for π-donation.[16,17]

2. M–O–Ar Angles. Figure 4 contains a plot of M–OAr distance versus M–O–Ar angles. In the interests of clarity the esd's have not been added as error bars. There is clearly a dramatic difference in the bonding of aryloxide ligands to the group 14 metals versus their group 4 counterparts. For germanium and tin the M–O–Ar angles lie in the very narrow range 120–126°. This is the value one would expect on the basis of purely σ-bonding to the group 14 metal with the oxygen atom being sp^2-hybridized in order to interact with the aromatic π-cloud. It should be noted that the corresponding angles for silicon aryloxide compounds are larger,[30] and the reasons for the large angles at oxygen in silyl ethers have recently been discussed.[31] The CH_3–O–Ar angles in aryl ethers lie in the 120–123° range.[10] For the group 4 metals titanium and zirconium the corresponding M–O–Ar angles are much larger and cover a more extensive range of 140–180° (Figure 4). The size of these angles can in no way reflect steric pressure at the metal center, as the aryloxide ligands used in the study have identical steric demands, cf. Sn(OAr'-2,6Bu$^t_2$)$_2$(NMe$_2$)$_2$ with angles of 123.0 (2) and 125.8 (2)° versus Ti(OAr-2,4,6Bu$^t_3$)$_2$(NMe$_2$)$_2$ with angles of 153.0 (3) and 171.9 (3)°. We can hence conclude that the presence of oxygen-p to metal-d π-donation to the d-block metals Ti and Zr allows the M–O–Ar angles to be dramatically increased over values found for the purely σ-bound p-block metals Ge and Sn. However, another important conclusion is that for the group 4 metals the M–O–Ar angle is a very flexible parameter. There is no apparent correlation between the M–O–Ar angle and the M–OAr distance (Figure 4). It would, therefore, be erroneous to assume that the degree of π-donation to the metal center can be estimated by the size of the M–O–Ar angle. Identical conclusions have been drawn previously for aryloxide derivatives of the group 5 metals Nb and Ta and the group 6 metal W.[16-18]

Table VIII. Crystallographic Data

	1b
$GeClO_3C_{57}H_{42}$	space group $C2/c$ (No. 15)
a = 41.568 (6) Å	T = 20 °C
b = 10.759 (3) Å	λ = 0.71073 Å
c = 21.675 (3) Å	ρ_{calc} = 1.288 g cm^{-3}
β = 110.04 (1)°	μ = 7.64 cm^{-1}
V = 9107 (6) Å^3	transm coeff = 1.000–0.947
Z = 8	$R(F_o)$ = 0.050
fw 883.01	$R_w(F_o)$ = 0.056
	2
$GeO_2N_2C_{40}H_{38}$	space group $P2_12_12_1$ (No. 19)
a = 10.378 (1) Å	T = 20 °C
b = 17.094 Å	λ = 0.71073 Å
c = 19.076 (2) Å	ρ_{calc} = 1.278 g cm^{-3}
V = 3384 (1) Å^3	μ = 9.26 cm^{-1}
Z = 4	transm coeff = 1.000–0.738
fw 651.35	$R(F_o)$ = 0.030
	$R_w(F_o)$ = 0.036
	3
$SnO_2N_2C_{34}H_{58}$	space group $P2_1/n$ (No. 14)
a = 8.446 (4) Å	T = 20 °C
b = 23.589 (2) Å	λ = 0.71073 Å
c = 17.300 (5) Å	ρ_{calc} = 1.247 g cm^{-3}
β = 94.05 (2)°	μ = 7.73 cm^{-1}
V = 3438 (3) Å^3	transm coeff = 1.000–0.629
Z = 4	$R(F_o)$ = 0.031
fw 645.54	$R_w(F_o)$ = 0.038

Experimental Section

All operations were carried out under a dry nitrogen atmosphere either in a Vacuum Atmospheres dri-lab or by standard Schlenk techniques. Hydrocarbon solvents were dried by distillation from sodium benzophenone under a nitrogen atmosphere. The compounds $Ge(NMe_2)_4$ and $Sn(NMe_2)_4$ were synthesized by published procedures. ^{1}H and ^{13}C NMR spectra were recorded on a Varian Associates Gemini-200 spectrometer.

Ge(OAr)$_2$Cl$_2$ (1a) and Ge(OAr)$_3$Cl (1b). To a slurry of LiOAr (4.03 g, 16.0 mmol) in benzene (25 cm^3) was added $GeCl_4$ (1.163 g, 7.6 mmol) by syringe. The resulting mixture was stirred at room temperature for 12 h. Removal of the solvent in vacuuo followed by extraction of the residue with hexane (2 × 10 cm^3) yielded a colorless extract from which $Ge(OAr)_2Cl_2$ (**1a**) was obtained as clear, platelike crystals upon concentration and cooling. Extraction of the residue with hot toluene (3 × 10 cm^3) followed by slow cooling yielded $Ge(OAr)_3Cl$ (**1b**) as colorless crystals. Anal. Calcd for $GeC_{36}H_{26}O_2Cl_2$ (**1a**): C, 68.16; H, 4.13; Cl, 11.18. Found: C, 68.05; H, 4.26; Cl, 11.06. Calcd for $GeC_{54}H_{39}ClO_3$ (**1b**): C, 76.83; H, 4.66; Cl, 4.20. Found: C, 74.36; H, 4.64; Cl, 4.38. The ^{1}H NMR spectra of **1a** and **1b** are uniformative, showing a series of multiplets in the δ 6.8–7.8 ppm region. In the case of **1b** the resonances are broad at room temperature presently due to restricted notation about the Ge–O–Ar bond.

Ge(OAr)$_2$(NMe$_2$)$_2$ (2). To a stirred solution of $Ge(NMe_2)_4$ (0.5 g, 2.84 mmol) in benzene (10 cm^3) was slowly added a slurry of HOAr (1.47 g, 6.0 mmol) in benzene (10 cm^3). The resulting reaction mixture

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was stirred for 12 h and the solvent removed in vacuuo to yield the crude product. Clear crystals of pure **2** were obtained by slow cooling of a hot saturated toluene solution. Anal. Calcd for $GeC_{40}H_{38}N_2O_2$ (**2**): C, 73.72; H, 5.87; N, 4.29 Found: C, 71.60; H, 5.78; N, 3.62. ^1H NMR (C_6D_6, 30 °C): δ 1.51 (s, N*Me*$_2$), 6.8-7.5 (aromatics).

$Sn(OAr')_2(NMe_2)_2$ (3). To a stirred solution of $Sn(NMe_2)_4$ (0.50 g, 1.70 mmol) in benzene (10 cm^3) was added dropwise a solution of 2,6-di-*tert*-butyl-4-methylphenol (HOAr′, 0.75 g, 3.4 mmol) in benzene (10 cm^3). The resulting clear, bright yellow solution was stirred for 12 h before the solvent was removed in vacuuo. The crude yellow product was taken up in the minimum amount of hot hexane and the solution slowly cooled to yield large yellow crystals. Anal. Calcd for $SnC_{34}H_{58}N_2O_2$ (**3**): C, 63.26; H, 9.05; N, 4.34. Found: C, 59.67; H, 9.41; N, 3.89. ^1H NMR (C_6D_6, 30 °C): δ 1.47 (s, *Bu*^{t}), 2.25 (s, 4-*Me*), 2.36 (s, SnN*Me*$_2$, $^2J(^{119}Sn-^1H)$ = 74 Hz), 6.91 (s, *m*-H).

Crystallographic Studies. Selected crystallographic data are collected in Table VIII. The data collection and refinement were carried out by using the routine procedures adopted by the Purdue Chemistry Department Crystallographic Center. A suitable crystal of each of the three compounds was examined under deoxygenated Nujol and mounted in an appropriately sized glass capillary surrounded by epoxy resin. In the case of **3** a 10% loss of intensity of standards was observed during data collection and a linear correction was applied. For the germanium compounds **1b** and **2** no decay was observed and no correction for estimation was applied. For the tin compound **1** an empirical absorption correction was applied. The positions of the hydrogen atoms were calculated by assuming idealized geometry and a carbon-hydrogen bond distance of 0.95 Å. For the methyl groups, one hydrogen was located in a difference Fourier map. This position was idealized, and the remaining positions were calculated. No hydrogen atoms were refined. For compound **2** the other enantiomorph yielded $R = 0.044$ and $R_w = 0.055$ with GOF = 1.788 so that the enantiomorph reported here is correct.

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Supplementary Material Available: Tables of crystallographic data, thermal parameters, full bond distances and angles, and hydrogen positional and thermal parameters (34 pages); listings of observed and calculated structure factors (57 pages). Ordering information is given on any current masthead page.

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Polymeric Xenon Materials: $(-Xe-O-TeF_4-O-)_n$. Crystal Structure of $HF\cdot HO-TeF_4-O-Xe^+AsF_6^-$

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XeF_2 reacts with *cis*-$(HO)_2TeF_4$ to form a yellow, insoluble polymer $(XeO_2TeF_4)_n$ that is stable to about 80 °C. Reaction of *cis*-$(HO)_2TeF_4$ with $Xe_2F_3^+AsF_6^-$ affords a material of the composition $FXe-O-TeF_4-O-Xe^+AsF_6^-$. Recrystallization of this in anhydrous HF affords a crystalline material $HF\cdot HO-TeF_4-O-Xe^+AsF_6^-$. According to its crystal structure (a = 504.74 (4), b = 758.93 (5), c = 1387.25 (7) pm; α = 90.14 (5), β = 95.74 (5), γ = 99.67 (6)°; $P\bar{1}$; Z = 2) the coordination number of xenon is closer to 1 than in any other known xenon compound.

Introduction

Substitution chemistry on xenon fluorides, even on the most stable xenon difluoride, is limited to ligands with high electronegativity. Greatest stability has been observed with the oxygen ligands $-OTeF_5$ and $-OSeF_5$, less so with $-O-SO_2F$ and others.[1] Nitrogen ligands are so far limited to the $-N(SO_2F)_2$ and $-N(SO_2CF_3)_2$ groupings and a few members of the *S*-triazine family.[2-4] Compounds that have nitrogen donor functions to xenon such as $[FXe-NCH]^+$ or $[FXe-NC-CH_3]^+$ have been prepared recently also.[5] The bonding to carbon is even more limited. While $Xe(CF_3)_2$ has never been fully characterized,[6] there is now clear evidence for the existence of the $^+Xe-C_6F_5$ cation including a crystal structure.[7,8]

Reaction of XeF_2 with bidentate ligands poses a challenge, since bidentate ligands having enough electronegativity are very limited. The most stabilizing ligand in xenon-oxygen chemistry, $-OTeF_5$, is derived from $HOTeF_5$, which in turn is a member of a series $(HO)_nTeF_{6-n}$. All these compounds $(HO)_nTeF_{6-n}$ for n = 1-5 have been shown to exist,[9-11] but only $HO-TeF_5$ and *cis*- and *trans*-$(HO)_2TeF_4$ have been isolated in pure form.[12,13] Of these, *cis*- and *trans*-$(HO)_2TeF_4$ are here of special interest. *cis*-$(HO)_2TeF_4$ is somewhat more acidic than *trans*-$(HO)_2TeF_4$,[14] and a number of covalent derivatives such as $(ClO)_2TeF_4$, $(BrO)_2TeF_4$, and $[(CH_3)_3SiO]_2TeF_4$ have already been described with both cis and trans configurations.[12] The intermolecular anhydride $F_4TeO_2TeF_4$ and the anion *cis*-$O_2TeF_4^{2-}$ in $Na_2O_2TeF_4$ are also known.[15]

Results

We reported in a short communication that *cis*-$(HO)_2TeF_4$ reacts with XeF_2 with the formation of HF, whereas *trans*-$(HO)_2TeF_4$ does not react under the same conditions, possibly a consequence of its somewhat lower acidity. The product between

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