

Attempted Isolation of Heavier Group 14 Element Ketone Analogues: Effect of O–H··· π -Ar Hydrogen Bonding on Geometry

Lihung Pu, Ned J. Hardman, and Philip P. Power*

Department of Chemistry, University of California, Davis, One Shields Avenue, Davis, California 95616

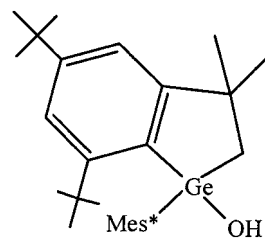
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The terphenyl group 14 element *gem*-dihydroxy (*gem*-diol) derivatives Ar₂M(OH)₂ (Ar = C₆H₃-2,6-Mes₂; Mes = C₆H₂-2,4,6-Me₃, M = Ge (**1**); Sn (**2**), were synthesized and characterized by X-ray crystallography, NMR, IR spectroscopy, and combustion analysis. The synthetic route involved treatment of the divalent MAr₂ compounds with N₂O or Me₃NO in hydrocarbon solution. The objective was the isolation of the heavier group 14 element ketone analogues Ar₂MO. Despite stringent precautions to exclude moisture and oxygen during the synthesis, the products **1** and **2** were isolated in ca. 30–50% yield. These results are in contrast to the recently reported stabilization of the terphenyl-protected, essentially strain-free, species (bisap)₂GeO (bisap = 2,6-di(1'-naphthyl)phenyl). Seemingly, **1** and **2** represent the addition of H₂O to Ar₂MO. The identity of the other products is currently unknown. Compound **1** represents the second example of a germanium *gem*-diol to be structurally characterized, and it features the expected distorted tetrahedral germanium environment. Compound **2** is the first instance of a monomeric *gem*-dihydroxy derivative of tin. Surprisingly, the C–Sn–C angle is ca. 20° wider than the corresponding angle in **1** even though the larger size of tin is expected to reduce steric congestion and so afford a narrower C–Sn–C angle. This unanticipated result was attributed to the nonclassical hydrogen-bonding interaction of the O–H groups with the mesityl ring substituents, which for geometric reasons is more favorable in the tin compound.

Introduction

Compounds of the formula R₂ME (R = organo group; M = Si, Ge, Sn, or Pb; E = O, S, Se, or Te) are heavier element analogues of ketones.¹ Over the past several years a number of stable examples of these compounds, e.g., R₂SiE (E = S^{2,3} or Se³), R₂GeE (E = S,^{4–6} Se,^{4,7} and Te^{6,8,9}), R₂SnE (E = S^{6,10} or Se¹¹), have been reported. They were isolated through the use of large R groups to protect the >M=E moiety. However, despite the considerable progress that has been made, there is very little information available for the lightest chalcogenide derivatives in which E is oxygen. Attempts to synthesize R₂GeO (germanones) by using the bulky amide precursor Ge{N(SiMe₃)₂}₂ afforded the dimer [(Me₃Si)₂N]₂GeO]₂.¹² In addition, the attempted generation of Mes*₂-

GeO (Mes* = –C₆H₂-2,4,6-t-Bu₃) led to isolation of the germaindanol.¹³



Nonetheless, the use of more crowded aryl ligands enabled the germanone (Trip)(Tbt)GeO (Trip = C₆H₂-2,4,6-*i*-Pr₃; Tbt = C₆H₂-2,4,6-{CH(SiMe₃)₂}₃) to be generated in solution.¹⁴ This compound was obtained by the reaction of Ge(Trip)(Tbt) with (PhCH₂)₃NO. It rearranges over a period of hours by –SiMe₃ transfer to oxygen and formation of a Ge–C bond to an ortho substituent of the Tbt group. Ge(Trip)(Tbt) can also be trapped by a 2 + 3 cycloaddition reaction with MeCNO. More recently, the reaction of the ligand-protected, strain-free, Ge(bisap)₂ (bisap = 2,6-di(1'-naphthyl)phenyl) with Me₃NO was reported to give the germanone (bisap)₂GeO as a white solid, which was characterized by ¹³C NMR spectroscopy, C, H analysis, and mass spectrometry.¹⁵ Unfortunately, no structural details of this compound are available to confirm these

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findings. The more crowded, and strained, diaryl germanium and tin species $M(C_6H_3-2,6-Mes_2)_2$ (i.e., MAr_2 ; $M = Ge$ or Sn), which were reported some time ago,¹⁶ are plausible candidates for oxidation reactions with either Me_3NO or N_2O . In this paper it is shown that the reaction of MAr_2 ($M = Ge$ or Sn) with Me_3NO or N_2O affords the *gem*-dihydroxy compounds $(2,6-Mes_2H_3C_6)_2M(OH)_2$ as colorless crystals.

Experimental Section

General Procedures. All manipulations were carried out by 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 $Ge(C_6H_3-2,6-Mes_2)_2$ and $Sn(C_6H_3-2,6-Mes_2)_2$ were synthesized according to literature procedures.¹⁶ Me_3NO (Aldrich) was purified by sublimation prior to use. The IR spectrum of Me_3NO in a Nujol mull displayed no observable O–H absorptions. N_2O (AGG) was of the highest available purity—99.998%. 1H , ^{13}C , and ^{119}Sn NMR spectra were recorded on a Bruker 300 MHz instrument and referenced to the deuterated solvent. Infrared data were recorded as Nujol mulls on a Perkin-Elmer PE-1430 instrument.

(2,6-Mes₂H₃C₆)₂Ge(OH)₂, (1). A violet solution of $Ge\{C_6H_3-2,6-Mes_2\}_2$ (0.72 g, 1.03 mmol) in Et_2O (70 mL) was added to Me_3NO (0.076 g, 1.01 mmol) in Et_2O (5 mL) at ca. 25 °C with rapid stirring. The reaction mixture was stirred for 16 h and became colorless. After filtration through Celite, the colorless solution was concentrated under reduced pressure to incipient crystallization (ca. 15 mL) and stored in a ca. –20 °C freezer for 30 h to give **1** as colorless crystals. Yield: 0.30 g, 33.5%. Mp: 253–255 °C. 1H NMR (400 MHz, 298 K, C_6D_6): 1.11 (t, 6H, $(CH_3CH_2)_2O$), $^3J_{HH} = 7.2$ Hz, 1.96 (s, 12H, *o*-CH₃), 2.13 (s, 6H, *p*-CH₃), 2.42 (s, 2H, OH), 3.25 (q, 4H, $(CH_3CH_2)_2O$), $^3J_{HH} = 6.9$ Hz, 6.68 (d, 2H, *m*-C₆H₃), $^3J_{HH} = 7.8$ Hz, 6.76 (s, 4H, *m*-Mes), 7.01 (tr, 1H, *p*-C₆H₃), $J_{HH} = 7.8$ Hz. $^{13}C\{^1H\}$ NMR (298 K, C_6D_6): 21.00 (*p*-CH₃), 22.42 (*o*-CH₃), 48.20 ($(CH_3CH_2)_2O$), 65.87 ($(CH_3CH_2)_2O$), 129.03 (*m*-Mes), 129.82 (*p*-C₆H₃), 130.66 (*m*-C₆H₃), 137.14 (*p*-Mes), 137.82 (*o*-Mes), 140.43 (*i*-Mes), 148.37 (*o*-C₆H₃). IR (Nujol, cm^{-1}): (O–H) 3560 (s).

Method 2. A violet solution of $Ge\{C_6H_3-2,6-Mes_2\}_2$ (1.35 g, 1.93 mmol) in toluene (30 mL) was treated with N_2O gas (45 mL, ca. 2.0 mmol) at room temperature. The solution was stirred for 16 h, during which time it became almost colorless. The solvent toluene was removed under reduced pressure, and the residue was extracted with warm hexane (50 mL). The colorless solution was decanted to separate a small quantity of starting violet solid. The volume of solution was reduced to incipient crystallization and stored in a ca. –20 °C freezer for 30 h to give **1** as colorless crystals. Yield: 0.70 g, 49%.

(2,6-Mes₂H₃C₆)₂Sn(OH)₂, (2). Compound **2** was synthesized in a manner similar to **1** by adding $Sn\{C_6H_3-2,6-Mes_2\}_2$ (0.91 g, 1.21 mmol) in Et_2O (60 mL) to Me_3NO (0.091 g, 1.21 mmol) in Et_2O (20 mL) at ca. 25 °C with rapid stirring. A similar workup procedure afforded **2** as colorless crystals. Yield: 0.35 g, 37.2%. Mp: 243–245 °C. 1H NMR (298 K, C_6D_6): 1.13 (t, 6H, $(CH_3CH_2)_2O$), $^3J_{HH} = 7.2$ Hz, 1.95 (s, 12H, *o*-CH₃), 2.13 (s, 6H, *p*-CH₃), 2.495 (s, 2H, OH), 3.25 (q, 4H, $(CH_3CH_2)_2O$), $^3J_{HH} = 6.9$ Hz, 6.78 (d, 2H, *m*-C₆H₃), $^3J_{HH} = 7.8$ Hz, 6.75 (s, 4H, *m*-Mes), 7.02 (tr, 1H, *p*-C₆H₃), $^3J_{HH} = 7.2$ Hz. $^{13}C\{^1H\}$ NMR ($CDCl_3$): 21.26 (*p*-CH₃), 21.63 (*o*-CH₃), 128.49 (*m*-Mes), 129.12 (*p*-C₆H₃), 130.00 (*m*-C₆H₃), 137.21 (*p*-Mes), 137.44 (*o*-Mes), 140.10 (*i*-Mes), 147.75 (*o*-C₆H₃). IR (Nujol, cm^{-1}): 3600 (s), 3580 (s). $^{119}Sn\{^1H\}$ (C_6D_6): –38.1.

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Table 1. Selected Details of Data Collection, Reduction, and Refinement for 1 and 2

	1 ·0.33C ₆ H ₁₄	2
formula	C ₅₀ H _{56.62} GeO ₂	C ₄₈ H ₅₂ SnO ₂
fw	762.16	779.59
color habit	colorless block	colorless parallelepiped
cryst dimens, mm	0.32 × 0.20 × 0.14	0.20 × 0.16 × 0.12
cryst syst	monoclinic	monoclinic
space group	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>n</i>
<i>a</i> (Å)	11.1655(7)	15.623(5)
<i>b</i> (Å)	16.2224(14)	16.131(5)
<i>c</i> (Å)	22.8545(15)	16.230(4)
β, deg	96.811(3) ^o	100.44(2) ^o
<i>V</i> (Å ³)	4110.5(5)	4022(2)
<i>Z</i>	4	4
<i>d</i> _{calc} (Mg/m ³)	1.232	1.287
μ (mm ^{−1})	0.784	0.672
θ range	1.79–31.50	1.66–25.01
obsd data (<i>I</i> > 2σ(<i>I</i>))	8482	4921
<i>R</i> ₁	0.0531	0.0540
<i>wR</i> ₂	0.1574	0.1270

Method 2. A purple solution of $Sn\{C_6H_3-2,6-Mes_2\}_2$ (1.62 g, 2.18 mmol) was treated with N_2O gas (50 mL, ca. 2.23 mmol) at room temperature. The solution was stirred for 16 h and became a pale yellow color. Toluene was removed under reduced pressure, and the residue was extracted with hexane (60 mL). The solution was decanted from a small amount of purple residue and was concentrated to incipient crystallization storage in a ca. –20 °C freezer for 30 h to give **2** as colorless crystals. Yield: 0.90 g, 51%.

Crystallographic Studies. Crystals of **1** and **2** were coated with hydrocarbon oil, mounted on a glass fiber, and placed in a N_2 cold stream on the diffractometer.¹⁷ X-ray data for **1** were collected on a Bruker Smart AXS 1000, and the data for **2** were obtained on a Siemens *R3m/v* diffractometer. Data were acquired with Mo Kα radiation ($\lambda = 0.71073$ Å) at 90(2) and 130(2) K for compounds **1** and **2**, respectively. SHELXTL programs were used for structure refinement.¹⁸ The hydrogens attached to the oxygen atoms were found on a difference map and then refined as an idealized OH group. The hydrogen atoms were allowed to ride on the attached oxygen atom and rotate around the Ge–O bond. The thermal parameter was tied to the oxygen and allowed to increase by 20%. The solvent molecule in **1** synthesized by method 2 could not be fully modeled and is present at a level of at least 33%.¹⁹ An absorption correction was applied using the program XABS2.²⁰ All compounds were refined to convergence by using anisotropic thermal parameters for all non-hydrogen atoms. Additional experimental details for all compounds are given in Table 1. Selected bond distances and angles are given in Table 2.

Results and Discussion

Synthesis. The reaction of MAr_2 ($M = Ge$ or Sn)¹⁶ with Me_3NO or N_2O in accordance with the equation

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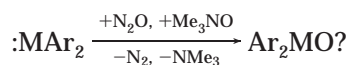
(18) SHELXTL version 5.03; Bruker AXS: Madison, WI, 1998.

(19) At the request of a reviewer, the SQUEEZE subroutine in PLATON^{19a} was used to check the solvent occupancy. The solvent void is large enough for a whole hexane molecule (233 Å³), and the number of electrons occupying the void is 34 (ca. two-thirds of a hexane molecule). However, the subroutine also yielded over 30 difference map peaks ranging from 0.50 to 3.67 e/Å³ in the void. Refinement of the structure showed that assignment of the major residual electron density peaks corresponding to an occupancy of ca. one-third (33%) decreased *R*₁, but resulted in no differences in the geometry of the germanium bishydroxide. Therefore, the occupancy of the hexane molecule in the structure is given as 33%, but is probably closer to 66%. Spek, A. L. *Acta Crystallogr.* **1990**, *A46*, C34.

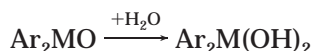
(20) SADABS is an empirical absorption correction program that is part of the SAINT Plus NT version 5.0 package: Bruker AXS: Madison, WI, 1998.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for **1 and **2****

parameter	1 (M = Ge)	2 (M = Sn)
M–O(1)	1.802(2)	1.974(4)
M–O(2)	1.782(2)	1.977(4)
M–C(1)	1.978(2)	2.164(5)
M–C(25)	1.976(2)	2.176(5)
O(1)–M–C(1)	104.19(9)	89.7(2)
O(1)–M–O(2)	105.31(8)	102.4(2)
O(1)–M–C(25)	112.05(9)	113.6(2)
O(2)–M–C(1)	110.95(8)	110.9(2)
O(2)–M–C(25)	101.08(9)	94.7(2)
C(1)–M–C(25)	122.3(1)	141.1(2)



did not afford the intended product Ar_2MO . Instead, the compounds $\text{Ar}_2\text{M}(\text{OH})_2$ (M = Ge, **1**; Sn, **2**) were obtained in ca. 30–50% yield, with higher yields being obtained for the reaction with N_2O . The compounds are very rare examples of monomeric, gem-dihydroxy (gem-diol) derivatives of germanium or tin. For germanium, there is only one structurally characterized example of such a species: the monomer $t\text{-Bu}_2\text{Ge}(\text{OH})_2$.^{21,22} A handful of gem-dihydroxy tin derivatives have been characterized, but these exist as associated species in which the –OH groups bridge the tin centers, and form aggregates that range from dimeric to polymeric.^{23–26} The generation of the gem-dihydroxy products instead of the Ar_2MO compounds is most easily accounted for by the generation of an Ar_2MO intermediate in the first instance. This may then react with adventitious moisture in accordance with



However, stringent measures were taken to exclude moisture contamination of the reaction system and to ensure reagent purity. For example, no contamination of the SnAr_2 solution was observed by ¹¹⁹Sn NMR spectroscopy prior to its reaction with Me_3NO or N_2O . The latter reagents were added in stoichiometric, or slightly less than stoichiometric, amounts. The addition of Me_3NO as a solid or solution produced identical results in each case. The reactions with N_2O were performed without adding further quantities of solvent to the MAr_2 solution. Therefore, it is doubtful that sufficient new moisture could have been introduced to produce the observed yields of **1** and **2** by a stoichiometric process. Furthermore, simultaneous experiments under almost identical conditions, involving the reaction of the electronically related and highly reactive species GaL (L = {N(C₆H₃-2,6-*i*-Pr₂)CMe}CH, i.e., Dipp₂nacnac)

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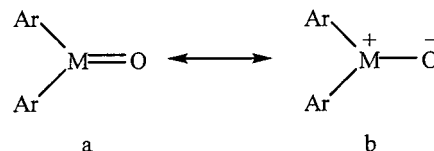
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with N_2O in hexane or toluene, afforded the μ -oxo dimer $\{\text{LGa}(\mu\text{-O})_2\}$ in virtually quantitative yield.²⁷ No hydroxide product was detected. In this case, the Dipp₂nacnac ligand is apparently of insufficient size to prevent dimerization of the reactive LGaO intermediate. This result is similar to that already obtained in the case of $\{(\text{Me}_3\text{Si})_2\text{N}\}_2\text{GeO}$, which associates to afford the dimer $\{[(\text{Me}_3\text{Si})_2\text{N}]_2\text{GeO}\}_2$.¹² In contrast, it seems probable that the putative Ar_2MO intermediate would be prevented from dimerizing by the large size of the Ar ligands. In addition, Ar_2MO is expected to be a very reactive species as a result of the low coordination number of germanium and the polar character of the polar resonance form b.



The three-coordinate M^+ center is expected to be a powerful Lewis acid and the O^- end of the dipole should be a powerful nucleophile. As a result, it is possible that, instead of dimerizing, the polar $\text{R}_2\text{M}^+\text{-O}^-$ species reacts rapidly with a further equivalent of N_2O or Me_3NO to generate a metal bound to two oxygens, and it is also possible that these oxygens attack the solvent or the ligand to generate the hydroxide moiety. It is notable that the hydroxy isomer of H_2GeO , i.e., HGeOH , has been calculated to be 18 kcal mol⁻¹ more stable than the germanone H_2GeO ,²⁸ which suggests a preference for the Ge–OH moiety under certain circumstances. The Ar_2MO might also react in a manner similar to $\text{Mes}^*_2\text{-GeO}^{13}$ (see Introduction) to generate a cyclic product involving a ligand mesityl group, although such a product has not yet been isolated. The contrasting behavior of the strain-free $\text{Ge}(\text{bisap})_2^{15}$ and the strained $\text{Mes}^*_2\text{GeO}^{13}$ and “ Ar_2GeO ” species is therefore quite remarkable and cannot be fully explained with currently available data. It has been suggested that geometric strain within these molecules could account for the reactivity of the group 14 element center.¹⁵ Possibly, the wider C–Ge–C angle in the strained GeAr_2^{16} species, 114.2(2)°, cf. 102.72(9)° in $\text{Ge}(\text{bisap})_2^{15}$ results in a smaller HOMO (lone pair)–LUMO (4p) energy gap, which could account for increased reactivity. The existence of a smaller HOMO–LUMO gap in GeAr_2 receives support from the relatively high wavelength (528 nm)¹⁶ of the n–p absorption in its electronic spectrum. It should be borne in mind, however, that the mass spectrum of $(\text{bisap})_2\text{GeO}$, on which its monomeric formulation is based, provides information only for the gas-phase species. No data have been presented on the degree of aggregation in solution. Ideally, molecular weight data, and suitable ligand modification in order to produce X-ray quality crystals, will allow important structural parameters of the germanone to be determined.

Structures. The structures of **1** and **2** consist of well-separated monomers with no short intermolecular con-

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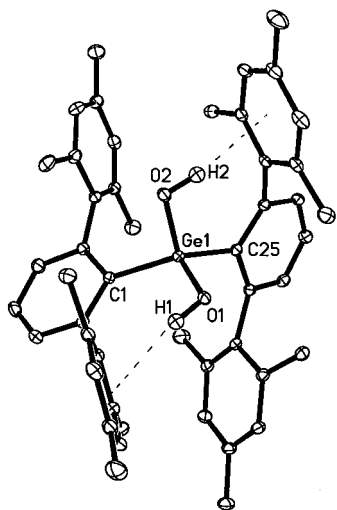


Figure 1. Thermal ellipsoid (30%) plot of **1**. Selected bond distances and angles are given in Table 2.

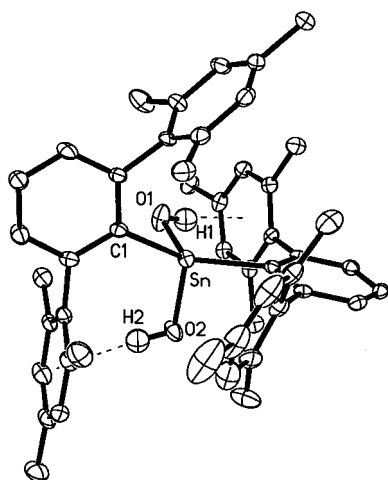


Figure 2. Thermal ellipsoid (30%) plot of **2**. Selected bond distances and angles are given in Table 2.

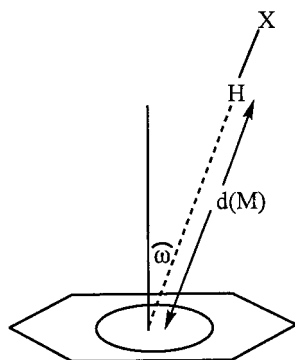


Figure 3. Schematic drawing of the interaction of an X-H group with an aryl ring as defined by the parameters $d(M)$ (Å) and ω (deg).

tacts. The germanium and tin atoms are coordinated in a distorted tetrahedral manner. The Ge–C distances in **1** (Table 2) are close to the sum of the radii²⁹ of germanium (1.22 Å) and carbon (0.77 Å) and to the average Ge–C distances observed in *t*-Bu₂Ge(OH)₂.²² Likewise, the Sn–C bond lengths in **2** are also close to the sum of the covalent radii of Sn (1.4 Å) and C (0.77

Table 3. Parameters $d(M)$ (Å) and ω (deg) for the O–H $\cdots\pi$ -aryl Interactions in **1 and **2****

	1	2
$d(M)$ (Å)	2.484, 2.374	2.094, 2.258
ω (deg)	32.5, 24.9	7.8, 20.6

Å). The Ge–O and Sn–O distances, however, are significantly shorter than the 1.88 and 2.06 Å predicted by the sum of the covalent radii of germanium or tin and oxygen (0.66 Å).³⁰ This is probably a result of the increased ionic character in the M–O bonds. The O(1)–E–O(2) angles in compounds **1** (105.31(8)°) and **2** (102.5(2)°) differ by only 2.8° and are similar to the O–Ge–O angle observed in *t*-Bu₂Ge(OH)₂ (102.4(1)°).²² In sharp contrast, the C(1)–M–C(25) angles in **1** (122.26(10)°) and **2** (141.1(2)°) differ by almost 20°. The angle in **1** is very similar to the C–Ge–C angle (122.5(3)°) observed in *t*-Bu₂Ge(OH)₂. The anomalously large C–Sn–C angle in **2** is the opposite of what is expected on steric grounds since a narrower angle could be anticipated on the basis of the larger size of tin. The most plausible explanation for the wide C–Sn–C angle lies in the interactions between the O–H groups and ortho mesityl rings. These O–H \cdots aryl interactions have been previously observed in heavier group 14 element aryl hydroxy compounds, and hydrogen bonding of this general type has been reviewed.³¹

The classical hydrogen bond is generally thought of as a three-center four-electron bond such as O–H \cdots O. However, there are nonclassical hydrogen bonds that can be described in terms of X–H interactions with the π -electron cloud of various aryl rings. A typical O–H \cdots aryl ring bond energy has been calculated to be between –2 and –4 kcal/mol, and the strength of the interaction depends on how close the O–H hydrogen atom approaches the center of the phenyl ring ($d(M)$) and the angle (ω) between a line drawn to the center of the phenyl ring and the C₆ axis of the phenyl ring. The strongest interactions occur with short H approaches ($d(M)$) and when the X–H moiety is perpendicular to the plane of the aryl ring (i.e., $\omega = 0^\circ$). An illustration of this interaction is provided in Figure 3, and a listing of the values of the parameters for **1** and **2** is given in Table 3. From these data it is clear that such interactions are more favored in the tin compound **2** than in its germanium analogue **1** and is probable that they cause the very distorted geometry observed in **2**. It seems that the longer E–O and E–C distances in **2** as well as the more ionic and less directional nature of binding to electropositive tin allow the molecule to maximize the O–H \cdots Ar π interactions by widening the C(1)–M–C(25) angle. In the germanium species **1** a weaker O–H \cdots Mes interaction is observed owing to the inability of the mesityl rings to assume the optimum geometry. This occurs as a result of the lower flexibility of the germanium coordination angles and the shorter distances to the oxygens and ipso carbons.

The $d(M)$ distances in **1** and **2** are at the lower end of the distance scale.³² The shortness of the interaction

(30) Ref 28, p 498.

(31) (a) Desiraju, G. R.; Steiner, T. *The Weak Hydrogen Bond*; OUP, Oxford, 1999; Chapter 3, p 122. (b) Nishio, M.; Hirota, M.; Umezawa, Y. *The CH/ π Interaction: Evidence, Nature and Consequences*; Wiley-VCH: New York, 1998. (Deals with CH/ π interactions only.)

(32) Braga, D.; Grepioni, F.; Tedesco, E. *Organometallics* **1998**, *17*, 2669.

(29) Wells, A. F. *Structural Inorganic Chemistry*, 5th ed.; Clarendon: Oxford, 1984; pp 913, 1280.

may stem from the acidity of the O–H bonds, which afford protic character to the hydrogen. This increases the strength of H $\cdots\pi$ -aryl interaction, which gives rise to the short distances observed. Calculations on model compounds to investigate the strength of these interactions are in hand.

Conclusions

The reaction of N₂O or Me₃NO with :MAr₂ (M = Ge or Sn; Ar = C₆H₃-2,6-Mes₂) produced the *gem*-dihydroxides Ar₂M(OH)₂. Although stringent precautions were taken to exclude moisture during the synthesis, reaction of the putative intermediate Ar₂MO with H₂O cannot

be completely discounted. The use of ¹⁸O-labeled oxidants may narrow the range of possible mechanisms in future work on this system.

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Supporting Information Available: 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** and **2**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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