

achieved by use of the same buffer composition throughout.¹⁴ Substrate concentrations were initially 47.5–73.1 μM . $\text{H}_2\text{O}/\text{D}_2\text{O}$ mixtures were made up by weight from buffer stock solutions in the pure isotopic solvents.

Runs were conducted by, first, thermal equilibration of 3.00 mL of buffer in a quartz cuvette in the Cary 16 cell compartment, as monitored by a thermistor probe. Then 100 μL of substrate stock solution was added, the solution was manually mixed, and data acquisition (400 nm) begun. Rate constants were calculated from the computer-stored data by a nonlinear least-squares method.

(c) **Methyl Acetate.** Rates were determined by the same pH Stat technique as above. Enzyme concentration was 5 $\mu\text{g mL}^{-1}$ (0.10 M NaCl, 0.04 M MgCl_2). Substrates were introduced neat by Eppendorf pipet (50 μL into 10.00 \pm 0.02 mL) with the final concentrations calculated using an appropriate correction for the densities of $\text{CH}_3\text{CO}_2\text{CH}_3$ (0.965 \pm 0.005 g mL^{-1}) and $\text{CD}_3\text{CO}_2\text{CH}_3$ (1.014 \pm 0.007 g mL^{-1}). The resulting substrate concentrations were 0.0651 M ($\text{CH}_3\text{CO}_2\text{CH}_3$) and 0.0658 M ($\text{CD}_3\text{CO}_2\text{CH}_3$). A 2.5-mL buret with 0.01 M sodium hydroxide titrant was employed, the reactions being followed to less than 2% completion. A linear least-squares fit to the initial-rate data was made.

Nonenzymic Kinetics. The rates of basic hydrolysis of ACh perchlorates were measured by pH Stat methods and of *p*-nitrophenyl acetate by automated spectrophotometry in ways very similar to those used for the enzymic reactions. The only unusual procedures were those denoted methods A and B in the Results section. These differed only in the wavelength of spectrophotometric observation. In both, a quartz cuvette in the Cary 16 cell compartment was charged with 3.00 mL of a solution 5×10^{-2} M in diethylamine and in diethylamine hydrobromide and 10^{-3} M in alizarine yellow GG. After thermal equilibration of this solution was complete, either 50, 100, or 200 μL of a 0.3 M solution of ACh was added by Eppendorf pipet, and data collection was initiated. Thereafter, the procedures were the same as for the *p*-nitrophenyl acetate experiments.

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Communications to the Editor

Lithium and Sodium 2,6-Di-*tert*-butylphenoxides and the Crystal and Molecular Structure of $[\text{Li}(\text{OC}_6\text{H}_2\text{Me}-4\text{-Bu}^t\text{-2,6})(\text{OEt}_2)_2]$

Sir:

A family of alkali metal di-*tert*-butylphenoxides, $(\text{MOAr} \cdot \text{L})_n$, has been prepared (selected examples and data are in Table I; M = Li or Na, L = OEt_2 or THF). These compounds are versatile phenoxide-transfer reagents for preparing corresponding complexes of other metals, which in turn are already showing promise of structural and chemical interest.^{1–5} The present paper is our first (but see also notes 1–5) dealing with the chemistry and structure of the 2,6-di-*tert*-butylphenoxides of the elements and the studies are complementary to researches on bulky amides⁶ and alkyls⁷ (see also note 8), e.g., on metal complexes having $\text{Me}_3\text{SiCH}_2^-$, $(\text{Me}_3\text{Si})_2\text{CH}^-$, $(\text{Me}_3\text{Si})_2\text{N}^-$, $\text{Me}_2\text{C}(\text{CH}_2)_3\text{CMe}_2\text{N}^-$, or ArO^- as ligands.⁹

The crystal and molecular structure of $(\text{LiOAr} \cdot \text{OEt}_2)_2$ ($\text{Ar}^t = 2,6\text{-di-}t\text{-butyl-4-methylphenyl}$) (**1**), illustrated in Figure 1, shows the compound to be the di- μ -phenoxo-dilithium dietherate having three-coordinate lithium atoms and an overall pseudospherical shape with pendant alkyl groups at the periphery, which accounts for its unexpected solubility in hydrocarbon solvents.

Compound **1** is a rare binuclear lithium compound to be

stable under ambient conditions in the crystalline state. The previously reported small lithium clusters include the dimer of bicyclo[1.1.0]butan-1-yl lithium tetramethylethylenediamine,¹⁰ trimers,¹¹ or tetramers;¹² hexamers (as in cyclohexyllithium¹³ or trimethylsilyllithium¹⁴) or chain polymers are also a feature with organic ligands.⁸ Mass spectra led to the suggestion that $\text{LiCH}_2\text{SiMe}_3$ is the tetramer and LiOBu^t the hexamer;¹⁵ the corresponding sodium alkoxide has a more complicated crystal and molecular structure, $(\text{NaOBu}^t)_9$ (NaOBu^t).¹⁶ In general, alkylolithiums are covalent rather than ionic;¹⁷ however, when stabilization of the carbanion is possible and the ligand ceases to be monohapto, solvated ion pairs are found, e.g., in LiCPh_3 (TMEDA).¹⁸

The lithium and sodium phenoxides are obtained according to the equations



In one preparative experiment, 15.3 g of predried 2,6-di-*tert*-butyl-4-methylphenol was dissolved in 50 mL of dry, degassed OEt_2 and cooled to 0 °C; 43.25 mL (49.6 mmol in *n*- C_6H_{14}) of *n*-butyllithium was slowly added with stirring and cooling during 0.5 h. A white precipitate was separated by filtration, and solvent was removed from the filtrate at 20 °C (10^{-2} mmHg). Recrystallization of the residue from *n*-

Table I. Some Data for Lithium and Sodium 2,6-Di-*tert*-butylphenoxides

| compd ^a | yield, % | ¹ H NMR chemical shifts, τ in C ₆ D ₆ ^b | | | solvents at 20 °C | mp, °C | mol wt ^c (calcd for dimer) |
|--|-------------|---|------|------|---|---------|--|
| | | Bu ^t | Me | Ar | | | |
| [LiOAr'.OEt ₂] ₂ , 1 | 97 | 8.23 | 7.57 | 2.67 | C ₆ H ₆ or THF ^d | 172–174 | 555 (601) |
| [LiOAr''.OEt ₂] ₂ | 92 | 8.40 | | | C ₆ H ₆ or THF ^d | 296–298 | 529 (573) |
| [LiOAr'''.OEt ₂] ₂ | 66 | 8.23 (2) | | 2.5 | C ₆ H ₆ or THF ^d | 294–296 | 647 (685) |
| | | 8.53 (1) | | | | | |
| [LiOAr'.THF] ₂ ^e | 15 | 8.20 | 7.50 | 2.6 | C ₆ H ₆ or THF ^d | 264–266 | |
| [NaOAr'''.OEt ₂] _n ^f | 70 | | | | | | |

^a Ar' = 2,6-Bu^t-4-MeC₆H₂, Ar'' = 2,6-Bu^t-2-C₆H₃, and Ar''' = 2,4,6-Bu^t-3-C₆H₂; these are white, air-sensitive crystals all of which gave satisfactory microanalytical results. ^b OEt₂ or THF protons omitted. ^c By cryoscopy in cyclohexane. ^d Sparingly soluble in *n*-C₆H₁₄ at 20 °C, but freely soluble at ~60 °C. ^e This was prepared by heating compound **1** to 150 °C (10⁻² mmHg) and crystallization from THF-*n*-C₆H₁₄ and no attempt was made to optimize yields; see note 1. ^f Insoluble in C₆H₆, PhMe, or *n*-C₆H₁₄, but soluble in THF or C₅H₅N.

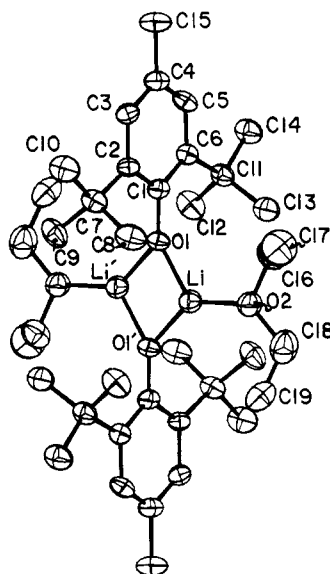


Figure 1. Molecular structure [Li(OC₆H₂Me-4-Bu^t-2,6)(OEt₂)₂]₂ (**1**) with the atoms represented by their 50% probability ellipsoids for thermal motion.

C₆H₁₄-OEt₂ gave 20.27 g (97%) of analytically pure compound **1**.

In another preparation, 9.80 g of 2,6-di-*tert*-butylphenol in 10 mL of OEt₂ was slowly added during 0.5 h to small pieces of Na (1.09 g) in 10 mL of OEt₂ with vigorous stirring at 20 °C, using a few small crystals of I₂ as initiator. The mixture was heated under reflux for 12 h. The white, analytically pure NaOAr'''.OEt₂ was filtered off (6.89 g, 70%).

Compound **1** crystallizes in the monoclinic space group *P*2₁/*n* with unit cell parameters *a* = 11.745 (4), *b* = 13.973 (5), *c* = 11.949 (4) Å; β = 98.45 (3)°; and ρ_{calcd} = 1.03 g cm⁻³ for *Z* = two dimers. The final *R* value was 0.040 for 1138 observed reflections. Hydrogen atoms were refined and all nonhydrogen atoms were refined with anisotropic thermal parameters.

The bulky phenoxide ligand allows the lithium atom to attain a coordination number of only three. This in turn produces two interesting structural effects. First, the lithium atom and its three bonded oxygen atoms are planar to within 0.01 Å. Second, the Li–O bonds to the OAr' ligands are the shortest yet reported, 1.849 (11) and 1.867 (10) Å. For lithium in a tetrahedral environment values as low as 1.883 (10) Å have been observed with peptide ligands.¹⁹ The Li–O bond to the diethyl ether moiety, 1.961 (11) Å, compares favorably with distances found in diethyl ether or THF containing complexes such as Li₄Cr₂(C₄H₈)₄·4C₄H₁₀O²⁰ or [Li(C₄H₈O)₄][Yb{CH(SiMe₃)₂Cl}].²¹

This is the first example of the OAr⁻ ligand in a bridging environment, but the parameters are comparable with those

for Ge(OAr')₂,⁵ Sn(OAr')₂,⁵ and [Ti(η-C₅H₅)₂OAr'].⁴ The only significant difference is the short O(1)–C(1) length, 1.345 (6) Å, in **1**. In the well-determined structure of Sn(OAr')₂ the corresponding value is 1.367 (6) Å.⁵

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**Bivalent Germanium, Tin, and Lead
 2,6-Di-*tert*-butylphenoxides and the Crystal
 and Molecular Structures of $M(\text{OC}_6\text{H}_2\text{Me}-4\text{-Bu}^t\text{-2,6})_2$
 ($M = \text{Ge}$ or Sn)**

Sir:

A series of colored bivalent group 4 metal di-*tert*-butylphenoxides, $M(\text{OAr})_2$, has been prepared (selected data are in Table I; $M = \text{Ge}$, Sn , or Pb). These are the first bivalent two-coordinate compounds of these elements to exist as discrete monomers in the crystalline state at ambient temperature.¹

The crystal and molecular structures of the compounds $M(\text{OAr}')_2$ [$\text{Ar}' = 2,6\text{-di-}t\text{-butyl-4-methylphenyl}$; $M = \text{Ge}$ (**1**) or Sn (**2**)] are illustrated in Figure 1 and significant molecular parameters are listed in Table II. It is evident that, despite the bulk of the $\text{Ar}'\text{O}^-$ ligand, a V-shaped MO_2 arrangement, corresponding to a singlet electronic ground state (sp^2 to p^2 hybridization), is preferred to a linear OMO arrangement (sp hybridization) expected for a triplet. This is consistent with the diamagnetism observed for the bulk compounds and the sharp ^1H NMR spectra of solutions in C_6D_6 . There appears to be only an isolated previous diffraction result for a simple tetravalent alkoxide or aryloxy of Ge , Sn , or Pb .^{2,3} Bivalent analogues are ill-characterized, unless derived from a bidentate ligand; e.g., $\text{Sn}(\text{PhCOCHCOMe})_2$ is monomeric with a pseudo-*trigonal bipyramidal* arrangement at Sn , the stereochemically active lone pair being held to occupy an equatorial position.⁴ Monomeric (in C_6H_6) $\text{Be}(\text{OAr}'')_2$ ($\text{Ar}'' = 2,6\text{-Bu}^t\text{C}_6\text{H}_3$) probably has a linear OBeO structure;⁵ $\text{Mg}(\text{OAr}')_2$ is a monomer in tetrahydrofuran.⁶

It is interesting to compare the structural chemistry of the new M^{II} compounds obtained from the bulky oxygen-centered

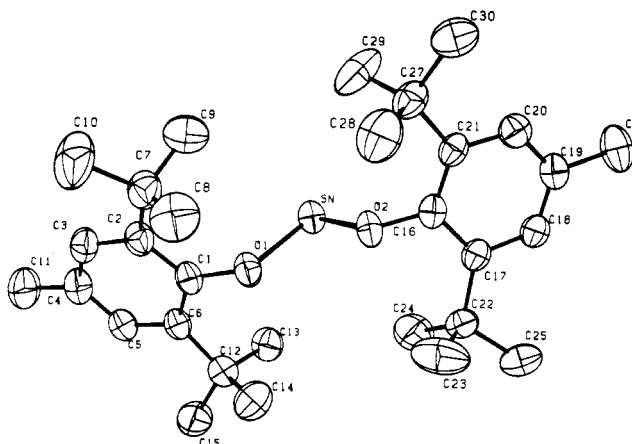


Figure 1. Molecular structure of $\text{Sn}(\text{OC}_6\text{H}_2\text{Me}-4\text{-Bu}^t\text{-2,6})_2$ (**2**) with the atoms represented by their 40% probability ellipsoids for thermal motion. The germanium analogue (**1**) is isostructural.

Table I. Some Data for Bivalent Germanium, Tin, and Lead 2,6-Di-*tert*-butylphenoxides

| compd ^a | color | yield, % | ¹ H NMR shifts, τ in C ₆ D ₆ | | | mp, °C |
|------------------------|---------|-------------|--|------|------|---------|
| | | | Bu ^t | Me | Ar | |
| Ge(OAr') ₂ | yellow | 66 | 9.14 | 8.35 | 3.75 | 189–192 |
| Sn(OAr') ₂ | yellow | 96 | 8.37 | 7.67 | 2.80 | 219–222 |
| Sn(OAr'') ₂ | yellow. | 91 | { 8.30 (2) 8.53 (1) | | 2.43 | 205–207 |
| Pb(OAr') ₂ | red | 85 | 8.60 | 7.47 | 2.67 | 170–172 |

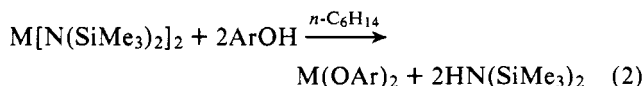
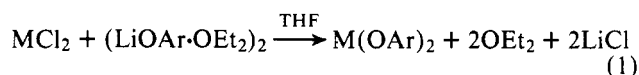
^a $\text{Ar}' = 2,6\text{-Bu}^t\text{-4-MeC}_6\text{H}_2$, $\text{Ar}'' = 2,4,6\text{-Bu}^t\text{C}_6\text{H}_2$; these are air-sensitive compounds, all of which gave satisfactory microanalytical results; they are monomeric in the vapor as judged by parent ions in their mass spectra; they are soluble in C_6H_6 , PhMe , or THF at 20 °C.

Table II. Important Bond Lengths (Ångstroms) and Angles (Degrees) for $M(\text{OAr}')_2$ ($M = \text{Ge}$ or Sn)

| | Ge | Sn |
|---|-----------|-----------|
| Bond Lengths | | |
| $\text{M-O}(1)$ | 1.802 (8) | 1.995 (4) |
| $\text{M-O}(2)$ | 1.812 (7) | 2.022 (4) |
| $\text{D}(1)\text{-C}(1)$ | 1.39 (1) | 1.375 (6) |
| $\text{O}(2)\text{-C}(16)$ | 1.41 (1) | 1.367 (6) |
| Angles | | |
| $\text{O}(1)\text{-M-O}(2)$ | 92.0 (4) | 88.8 (2) |
| $\text{M-O}(1)\text{-C}(1)$ | 128.6 (7) | 128.6 (4) |
| $\text{M-O}(2)\text{-C}(16)$ | 120.7 (6) | 121.8 (3) |
| $\text{O}(1)\text{-C}(1)\text{-C}(2)$ | 120 (1) | 118.7 (5) |
| $\text{O}(1)\text{-C}(1)\text{-C}(6)$ | 120 (1) | 120.4 (5) |
| $\text{O}(2)\text{-C}(16)\text{-C}(17)$ | 118 (1) | 118.6 (5) |
| $\text{O}(2)\text{-C}(16)\text{-C}(21)$ | 121 (1) | 120.5 (5) |

ligands with their isoelectronic N- and C-centered analogues. The alkyls $M[\text{CH}(\text{SiMe}_3)_2]_2$ were described in detail in 1976,⁷ but X-ray data are available only for the tin compound. In the crystal it is a diamagnetic Sn-Sn -bonded dimer, having three-coordinate Sn atoms with a C-Sn-C angle of 112° ; although the Sn-Sn bond is relatively short, 2.764 (2) Å, it is very weak as evidenced by the diamagnetic monomeric character of the compound in cyclohexane solution. This feature is found also in the Ge and Pb analogues and in the amides⁸ $M(\text{NRR}')_2$ [(i) $\text{R} = \text{SiMe}_3$, $\text{R}' = \text{Bu}^t$, $M = \text{Ge}$, or Sn , or Pb ; (ii) $\text{R} = \text{R}' = \text{SiMe}_3$, $M = \text{Ge}$, Sn ,⁹ or Pb ; and (iii) $\text{R} = \text{R}' = \text{GeMe}_3$, SiEt_3 , or GePh_3 ; $M = \text{Ge}$ or Sn]. Electron diffraction on gaseous $\text{Sn}[\text{N}(\text{SiMe}_3)_2]_2$ shows that at 100 °C (10^{-2} atm) this is the C_{2v} monomer with $\text{N-Sn-N} = 96.0^\circ$;¹⁰ crystals proved to be unsuitable for X-ray study.

The group 4 metal phenoxides are obtained according to either of the equations



In one preparative experiment, 3.24 g of solid $(\text{LiOAr}\cdot\text{OEt}_2)_2$ ¹¹ was slowly added to a stirred solution of 1.59 g of GeCl_2 -dioxane in 25 mL of THF at 20 °C. The yellow solution with white precipitate was heated under reflux for 2 h. The solvent was removed at 20 °C (10^{-3} mmHg). Recrystallization of the residue from 20 mL of PhMe with 10 mL of $n\text{-C}_6\text{H}_{14}$ gave 1.82 g of the yellow analytically pure, air-sensitive compound **1**.

In another experiment, slow addition of predried 4.84 g of 2,6- $\text{Bu}^t\text{-4-MeC}_6\text{H}_2\text{OH}$ in 15 mL of $n\text{-C}_6\text{H}_{14}$ to 6.02 g of