(20) Krausse, J.; Schödl, G. *J. Organomet. Chem.* **1971**, *27*, 59.
(21) Atwood, J. L.; Hunter, W. E.; Rogers, R. D.; Holton, J.; McMeeking, J.; Pearce, R.; Lappert, M. F. *J. Chem. Soc., Chem. Commun.* **1978**, 140.

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Bivalent Germanium, Tin, and Lead 2,6-Di-*tert*-butylphenoxides and the Crystal and Molecular Structures of $M(OC_6H_2Me\text{-}4\text{-}\mathrm{Bu}^t{}_2\text{-}2,6)_2$ (M = Ge or Sn)

Sir:

A series of colored bivalent group 4 metal di-*tert*-butylphenoxides, $M(OAr)_2$, has been prepared (selected data are in Table I; M = 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 $M(OAr')_2$ [Ar′ = 2,6-di-*tert*-butyl-4-methylphenyl; M = 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 $Ar'O^-$ 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 aryloxide of Ge, Sn, or Pb.[2,3] Bivalent analogues are ill-characterized, unless derived from a bidentate ligand; e.g., $Sn(PhCOCHCOMe)_2$ is monomeric with a pseudo-tbp (trigonal bipyramidal) arrangement at Sn, the stereochemically active lone pair being held to occupy an equatorial position.[4] Monomeric (in C_6H_6) $Be(OAr''')_2$ (Ar‴ = $2,6\text{-}\mathrm{Bu}^t{}_2C_6H_3$) probably has a linear OBeO structure;[5] $Mg(OAr')_2$ 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 ligands with their isoelectronic N- and C-centered analogues. The alkyls $M[CH(SiMe_3)_2]_2$ 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 amides[8] $M(NRR')_2$ [(i) R = $SiMe_3$, R′ = Bu^t, M = Ge, or Sn, or Pb; (ii) R = R′ = $SiMe_3$, M = Ge, Sn,[9] or Pb; and (iii) R = R′ = $GeMe_3$, $SiEt_3$, or $GePh_3$; M = Ge or Sn]. Electron diffraction on gaseous $Sn[N(SiMe_3)_2]_2$ shows that at 100 °C (10^{-2} atm) this is the C_{2v} monomer with N-Sn-N = 96.0°;[10] crystals proved to be unsuitable for X-ray study.

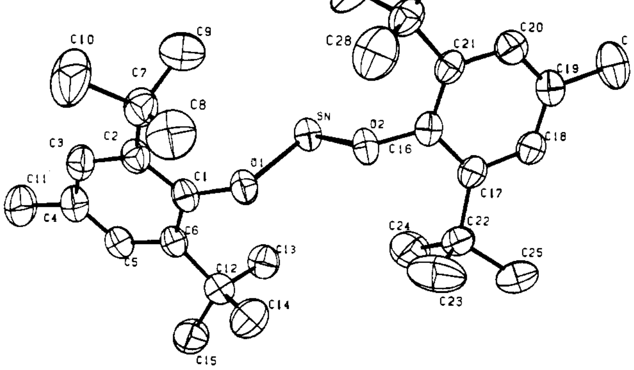

Figure 1. Molecular structure of $Sn(OC_6H_2Me\text{-}4\text{-}\mathrm{Bu}^t{}_2\text{-}2,6)_2$ (**2**) with the atoms represented by their 40% probability ellipsoids for thermal motion. The germanium analogue (**1**) is isostructural.

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

compd[a]	color	yield, %	^1H NMR shifts, τ in C_6D_6: Bu^t	Me	Ar	mp, °C
$Ge(OAr')_2$	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] Ar′ = $2,6\text{-}\mathrm{Bu}^t{}_2\text{-}4\text{-}MeC_6H_2$, Ar″ = $2,4,6\text{-}\mathrm{Bu}^t{}_2C_6H_2$; 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 $M(OAr')_2$ (M = Ge or Sn)

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

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

$$MCl_2 + (LiOAr{\cdot}OEt_2)_2 \xrightarrow{THF} M(OAr)_2 + 2OEt_2 + 2LiCl \quad (1)$$

$$M[N(SiMe_3)_2]_2 + 2ArOH \xrightarrow{n\text{-}C_6H_{14}} M(OAr)_2 + 2HN(SiMe_3)_2 \quad (2)$$

In one preparative experiment, 3.24 g of solid $(LiOAr'{\cdot}OEt_2)_2$[11] was slowly added to a stirred solution of 1.59 g of $GeCl_2{\cdot}$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 $n\text{-}C_6H_{14}$ gave 1.82 g of the yellow analytically pure, air-sensitive compound **1**.

In another experiment, slow addition of predried 4.84 g of $2,6\text{-}\mathrm{Bu}^t{}_2\text{-}4\text{-}MeC_6H_2OH$ in 15 mL of $n\text{-}C_6H_{14}$ to 6.02 g of

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$Pb[N(SiMe_3)_2]_2$ in 5 mL of n-C_6H_{14} at 20 °C gave a red precipitate. The mixture was stirred at this temperature for 2 h. Filtration afforded the red, analytically pure, air-sensitive $Pb(OC_6H_2Me\text{-}4\text{-}Bu^t{}_2\text{-}2,6)_2$.

Compound **1** crystallizes in the monoclinic space group $P2_1/n$ with lattice constants $a = 13.853\ (5)$, $b = 14.289\ (5)$, $c = 14.830\ (6)$ Å; $\beta = 92.90\ (4)°$; and $\rho_{calcd} = 1.16$ g cm^{-3} for $Z = 4$. Least-squares refinement based on 1681 observed reflections led to a final R value of 0.060. The tin analogue **2** is isostructural and possesses unit cell parameters $a = 13.882\ (3)$, $b = 14.164\ (4)$, $c = 15.064\ (4)$ Å; $\beta = 93.95\ (2)°$; and $\rho_{calcd} = 1.25$ g cm^{-3}. The final R value was 0.040 for 3262 observed reflections. For both structures hydrogen atoms were included and all nonhydrogen atoms were refined with anisotropic thermal parameters.

Scrutiny of Table II reveals that there are only two significant differences between the $M(OAr')_2$ structures. The shorter Ge–O bond apparently causes an increase in ligand–ligand repulsion which in turn produces a larger O–Ge–O bond angle, 92.0 (4)°, compared with the O–Sn–O angle, 88.7 (2)°. There are no crystal structures of two-coordinate M^{II} (M = Ge, Sn) complexes in the literature, but the M–O distances in **1** and **2** are near the short end of the reported range for other Ge–O or Sn–O bonds: 1.730 (1) Å for M = Ge[12] in $[(PhCH_2)_3M]_2O$ and 1.919 (1) Å for the Sn analogue.[12]

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References and Notes

(1) The amide $Ge[\overline{NCMe_2(CH_2)_3CMe_2}]_2$ also exists as the monomer in the crystalline state, with N–Ge–N = 111.4°, as shown by Atwood, J. L.; Slade, M. J.; Lappert. M. F.; Zaworotko, M. J., unpublished results.

(2) Cf. Bradley, D. C.; Mehrotra, R. C.; Gaur, D. P. "Metal Alkoxides"; Academic Press: New York, 1978; pp 83–86.

(3) Domingos, A. M.; Sheldrick, G. M., *Acta Crystallogr., Sect. B* **1974,** *30,* 519. Me_3SnOMe is an infinite polymer with trigonal-bipyramidal Sn and bridging MeO groups.

(4) Ewings, P. F. R.; Harrison, P. G.; King, T. G. *J. Chem. Soc., Dalton Trans.* **1975,** 1455.

(5) Andersen, R. A.; Coates, G. E. *J. Chem. Soc., Dalton Trans.* **1972,** 2153.

(6) Goel, A. G.; Mehrotra, R. C. *Indian J. Chem., Sect. A* **1978,** *16,* 428.

(7) Davidson, P. J.; Harris, D. H.; Lappert, M. F. *J. Chem. Soc., Dalton Trans.* **1976,** 2268.

(8) Gynane, M. J. S.; Harris, D. H.; Lappert, M. F.; Power, P. P.; Rivière, P.; Rivière-Baudet, M., *J. Chem. Soc., Dalton Trans.* **1977,** 2004.

(9) See also Harris, D. H.; Lappert. M. F., *J. Chem. Soc., Chem. Commun.* **1974,** 895. Schaeffer, C. D.; Zuckerman, J. J. *J. Am. Chem. Soc.* **1974,** *96,* 7160.

(10) Lappert, M. F.; Power, P. P.; Slade, M. J.; Hedberg, L.; Hedberg, K.; Schomaker, V. *J. Chem. Soc., Chem. Commun.,* **1979,** 369.

(11) Çetinkaya, B.; Gümrükçü, I.; Lappert, M. F.; Atwood. J. L.; Shakir, R., *J. Am. Chem. Soc.,* preceding paper in this issue.

(12) Glidewell, C.; Liles, D. C. *J. Chem. Commun.* **1979,** 93.

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β-Elimination from 6-Alkylmercaptopurine Ribonucleosides

Sir:

In a nonenzymatic process that could serve as a model for the biogenesis of thiolated bases in tRNA, 6-chloropurine ribonucleoside reacts with glutathione to yield a thioether, from which 6-mercaptopurine ribonucleoside is generated by treatment with alkali.[1] Recent evidence from this laboratory seemed to support a hydrolytic mechanism for the second step, offering an apparent method for converting cysteine into serine residues in glutathione and other peptides.[2] Further analysis shows that this evidence was misleading.

Thioethers derived from glutathione and *N*-acetylcysteine, after alkaline degradation as described earlier[2] followed by mild acid hydrolysis (2 M HCl, 100 °C, 2 h), yielded ~0.4 equiv of dehydroalanine as determined by the procedure of Patchornik et al.[3,4] The thioether derived from glutathione, after acid hydrolysis (6 M HCl, 155 °C, 20 min) and analysis with a Technicon single-column analyzer, was found to contain equimolar amounts of glycine and glutamic acid, with no trace of serine or cysteine. Ethanol, detected in earlier experiments in which 6-ethylmercaptopurine ribonucleoside was treated with alkali, was found to have resulted from traces of ethanol in the commercial alcohol dehydrogenase that had been used for analysis. Changes in ultraviolet spectrum, associated with the slow alkaline decomposition of 6-ethylmercaptopurine ribonucleoside,[2] are found to have been the result of degradation of the purine ring.

We conclude that sulfur transfer from glutathione to purine ribonucleoside, in alkaline solution, does not occur by hydrolysis. Instead, thioethers of 6-mercaptopurine ribonucleoside undergo β-elimination to yield 6-mercaptopurine ribonucleoside and an olefin, at a rate that is strongly dependent on the nature of the thioether.[2] In cases where elimination is slow, degradation of the purine ring system becomes significant as a competing reaction.

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References and Notes

(1) B. T. Walsh and R. Wolfenden, *J. Am. Chem. Soc.,* **89,** 6221 (1967).

(2) S. Kirkman and R. Wolfenden, *J. Am. Chem. Soc.,* **100,** 5943 (1978).

(3) A. Patchornik and M. Sokolovsky, *J. Am. Chem. Soc.,* **86,** 1206 (1964).

(4) M. Sokolovsky, T. Sadeh, and A. Patchornik, *J. Am. Chem. Soc.,* **86,** 1212 (1964).

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Synthesis and Molecular Structure of $Pd_4[P(C_6H_5)_2(CH_3)]_4(CO)_5$: A New Tetranuclear Carbonyl Cluster

Sir:

We are systematically investigating the reactions of the nitrite ligand with carbon monoxide. Square planar $Ni(NO_2)_2$ complexes of tertiary phosphines have previously been shown to react with CO forming $\{NiNO\}^{10}$ complexes and CO_2 nearly quantitatively.[1-4] Reaction 1 proceeds by formation of a five-coordinate carbon monoxide complex followed by transfer of an oxygen atom from an adjacent $-NO_2$ ligand to produce carbon dioxide and the nickel nitrosyl complex. To assess the role of the metal in the oxidation of CO by $-NO_2$, we have now examined the reaction of CO with $-NO_2$ complexes of Pd(II). In contrast to reaction 1, carbon monoxide reacts with $Pd(NO_2)_2L_2$ to form the previously unknown tetranuclear palladium(0) clusters, $Pd_4(CO)_5L_4$ (reaction 2). The molecular structure of one of these palladium clusters has been determined and is the subject of this report.