$Pb[N(SiMe_3)_2]_2$ 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 $Pb(OC_6H_2Me$-4-$Bu^t{}_2$-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]

Acknowledgment. We are grateful to the National Science Foundation for partial support (to J.L.A.).

References and Notes

(1) The amide $Ge[\overline{NCMe_2(CH_2)_3C}Me_2]_2$ 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the crystalline state, with N–Ge–N = 111.4°, as shown by Atwood, J. L.; Slade, M. J.; Lappert, M. F.; Zaworotko, M. J., unpublished results.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.

B. Çetinkaya, I. Gümrükçü, M. F. Lappert*
School of Molecular Sciences, University of Sussex
Brighton BN1 9QJ, England

J. L. Atwood,* R. D. Rogers, M. J. Zaworotko
Department of Chemistry, University of Alabama
University, Alabama 35486

Received September 4, 1979

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.

Acknowledgment. This work was generously supported by the National Institutes of Health, Grant No. GM-18325.

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).

Paul Cullis, Sue Kirkman, Richard Wolfenden*
Department of Biochemistry
University of North Carolina
Chapel Hill, North Carolina 27514

Received November 26, 1979

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.