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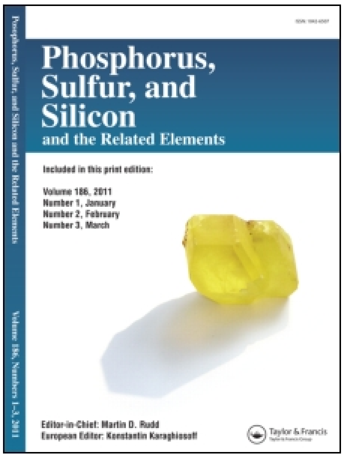

Phosphorus, Sulfur, and Silicon and the Related Elements

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Michael Veith; Charu Mathur; Volker Hugh

To cite this Article Veith, Michael , Mathur, Charu and Hugh, Volker(1997) 'Reactivity of a Cyclopentadienyl Containing Heterobimetallic Alkoxide', Phosphorus, Sulfur, and Silicon and the Related Elements, 124: 1, 489 — 492

To link to this Article: DOI: 10.1080/10426509708545666

URL: http://dx.doi.org/10.1080/10426509708545666

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Phosphorus, Sulfur, and Silicon, 1997, Vol. 124 & 125, pp. 489–492
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REACTIVITY OF A CYCLOPENTADIENYL CONTAINING HETEROBIMETALLIC ALKOXIDE

MICHAEL VEITH,* CHARU MATHUR, and VOLKER HUCH
Institute of Inorganic Chemistry, University of Saarland, PO 151150,
D-66041 Saarbrücken, Germany

The synthesis of the new heteroleptic heterotrimetallic cluster, $[(C_5H_5)Sn(\mu\text{-}OBu^t)_2Ge(OBu^t)Mo(CO)_5]$ (1) has been achieved by a thermally induced CO substitution of the transition metal derivative, $Mo(CO)_6$, by the basic germanium atom of the cyclopentadienyl heterobimetallic alkoxide, $[(C_5H_5)Sn(\mu\text{-}OBu^t)_2Ge(OBu^t)]$. The microanalysis, molecular weight (monomer in benzene), IR and multinuclear NMR data and X-ray diffraction study is consistent with the formulation of **1**. The Sn atom has a trigonal pyramidal coordination environment formed by a aysmmterically π-bonded terminal C_5H_5 ring and two symmetrically bridged tert-butoxy groups. The four-coordinate Ge atom lies at the centre of a distorted tetrahedron and is terminally attached to a tert-butoxy group and a $Mo(CO)_5^-$ fragment.

Keywords: cyclopentadienyl alkoxide; molybednum; group 14 elements

INTRODUCTION

We have recently reported on the synthesis and structural characterisation of a new class of half-sandwich compounds, $[(C_5H_5)Sn(\mu\text{-}OBu^t)_2Ge(OBu^t)]$[1], $[(C_5H_5)Pb(\mu\text{-}OBu^t)_2Sn(OBu^t)]$[2] and $[(C_5H_5)Sn\{Zr_2(OPr^i)_9\}]$[2] resulting from our ongoing investigations on heterometallic derivatives containing both cyclopentadienyl ($C_5H_5^-$) and alkoxide (OR^-) ligands. The heteroleptic ($C_5H_5^-$ / OR^-) heterometallic compounds have been obtained by two synthetic strategies involving the equimolar reactions of cyclopentadienyl tin chloride ($(C_5H_5)SnCl$) with alkali metal alkoxide reagents ($KM(OBu^t)_3$; M = Ge^{II}, Sn^{II} and Pb^{II} and $KM_2(OPr^i)_9$; M = Zr^{IV}, Hf^{IV}) and / or chloride heterobimetallic alkoxides ($[ClSn\{M_2(OPr^i)_9\}]_2$; M = Zr, Hf). The introduction of $C_5H_5^-$ unit as a coligand in heterometal derivatives offered more tractable systems since in contrast to the extraordinary bridging ability of alkoxy groups, a cyclopentadienyl bridging was thermodynamically disfavoured. We report here the reactivity of $[(C_5H_5)Sn(\mu\text{-}OBu^t)_2Ge(OBu^t)]$, possessing two potential basic sites, against $Mo(CO)_6$ which afforded a heterotrimetallic cluster.

RESULTS AND DISCUSSION

The reaction of $[(C_5H_5)Sn(\mu\text{-}OBu^t)_2Ge(OBu^t)]$ with an equimolar amount of $Mo(CO)_6$ in refuxing toluene (48 h) affords $(C_5H_5)Sn(\mu\text{-}OBu^t)_2Ge(OBu^t)Mo(CO)_5$ (1), after crystallisation from toluene, in 50% yield. The X-ray crystallographic study[3] reveals a planar rhombic SnO_2Ge metallacycle in which the two group 14 elements are bridged by two slightly non-planar oxygens (O(1) and O(1c)) of two tert-butoxy groups (Fig. 1). Although the molecule as a whole is asymmetric, a mirror plane can be identified comprising the Sn, Ge, Mo atoms as well as the C(10) atom of the cyclopentadienyl ring. The Sn atom possessing a stereochemically active lone pair lies at the centre of a trigonal pyramid and interacts with the planar cyclopentadienyl ring at a closest distance of 2.45 Å (Sn-C(9) and Sn-C(9c)) suggesting a dihapto (η^2)

coordination mode of the cyclopentadienyl ring. However, the alternation of ring C-C bond distances in **1** is not so distinct as observed in the precursor molecule where a peripherally bonded $(\eta^{1/3})$ cyclopentadienyl ring with diene character has been proposed[1]. The four coordinate Ge atom exhibits a distorted tetrahedral geometry. Mo present in an environment of five terminal CO ligands and a Mo-Ge bond displays a slightly distorted octahedron.

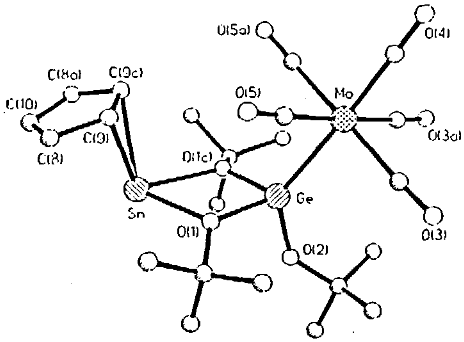

FIGURE 1 Molecular structure of 1. Selected bond distances (Å) and angles (°): Sn-O(1), 2.280(3); Sn-C(9), 2.454(5); Ge-O(1), 1.891(3); Ge-O(2), 1.776(4); Ge-Mo, 2.613(3); O(1)-Sn-O(1c), 65.86(14); O(1)-Ge-O(1c), 81.9(2); Sn-O(1)-Ge, 106.11(13).

The Sn-O(1) (Sn-O(1c)) distances at 2.280(3) Å is marginally longer than that observed in the edduct (2.210 Å). The Mo-Ge distance (2.610 Å) is also slightly longer but comparable with the values reported for other analogous crystallographically characterised complexes containing a bond between a pentacarbonyl fragment and Ge (e.g., $(CO)_5Mo\text{-}In(OBu^t)_3Ge\text{-}Mo(CO)_5$ = 2.567(4) Å)[4] allowing the formulation of the Ge-Mo contact as a donor-acceptor bond. Consistent with this view is the observation of shorter Mo-C distance of the axial carbonyl group (1.985(7) Å) than the equatorial carbonyl ligands (av. Mo-C_{eq} = 2.037 Å) as the Ge-O bonds have higher σ donor to π acceptor ratio when compared to corresponding ratio of a carbonyl group.[4] The formation of Ge-Mo bond causes a considerable shortening in the Ge-O bond lengths, in **1**, which is possibly due to an increase in the electrophilicity of Ge(II) centre in comparison to the precursor molecule.

The ^1H and ^{13}C NMR spectra[5] show a single resonance for one time averaged tert-butoxy groups and cyclopentadienyl ring at room temperature indicating the molecule to be fluxional in the solution. In the IR spectra, **1** shows the three carbonyl stretching bands (2071, 1948,1938 cms^{-1}) as expected for an idealized C_{4v} symmetry of $Mo(CO)_5$ entity. The formation of the Ge-Mo bond, in **1**, shifts the ^{119}Sn NMR signal[5] to higher field (δ -184.6) with respect to the value observed for the precursor molecule (δ -286.4). Interestingly, the addition of the transition metal fragment to **1**, is selective and despite two potential basic sites, a $Mo(CO)_5^-$ unit could not be attached at the tin(II) centre (cf. $[(CO)_5Cr\text{-}In(OBu^t)_3Sn\text{-}Mo(CO)_5]$[4]).

References

[1.] M. Veith, C. Mathur and V. Huch, *Organometallics,* **15**, 2528 (1996).

[2.] M. Veith, C. Mathur, S. Mathur and V. Huch, *Organometallics,* **16,** 1292 (1997).

[3.] Crystal data for **1** $C_{22}H_{32}GeMoO_8Sn$, M = 710.69, orthorhombic, space group Pnma, a = 12.552(14) Å, b = 14.044(14) Å, c = 16.06(2) Å, V = 2831(5) $Å^3$, Z = 2, Dcal = 1.668, F(000) = 1404, $\lambda(MoK\alpha)$ = 0.71073 Å, T = 293(2) K , μ = 2.405 mm^{-1} R1 = 0.0258, wR2 = 0.0612. The structure solution (direct methods) and refinement (by full-matrix least squares on F^2) were carried out using SHELXS program package.

[4.] M. Veith, *Coord. Chem. Rev.*, **137**, 297 (1994).

[5.] Spectral data of **1** : ^1H NMR (C_6D_6, 20 °C) δ 1.40 (s, 27H, $OC(CH_3)_3$), 6.33 (s, 5H, C_5H_5). ^{13}C NMR (C_6D_6, 20 °C) δ 32.43 ($OC(CH_3)_3$), 77.12 ($OC(CH_3)_3$),111.11(C_5H_5), 207.32 (CO). ^{119}Sn NMR (C_6D_6, 20 °C) δ -184.6.