

Since the same yields were obtained with pyridine alone as base (without addition of $\text{BF}_3 \cdot \text{Et}_2\text{O}$) we replaced the pyridine by a cross-linked polyvinylpyridine^[10]; the reaction was accelerated without any loss of selectivity.

Hydrolysis with 10% methanolic KOH and chromatography on Dowex 50 WX (50–100 mesh, H^+ form/ H_2O) led to the glucuronic acids (4a), (4b), and (4c) (see Table 1). The $^1\text{H-NMR}$ data again confirm that the compounds belong to the α -series.

That the acids (4) do not undergo any change under the acidic conditions of ion exchange was demonstrated in the following way: Reaction of (3a) with $\text{NH}_3/\text{CH}_3\text{OH}$ gave the same amide (5a) (m. p. 128°C) as was obtained on treatment of the glucuronic acid (4a) with an ethereal solution of diazomethane and subsequently with $\text{NH}_3/\text{CH}_3\text{OH}$.

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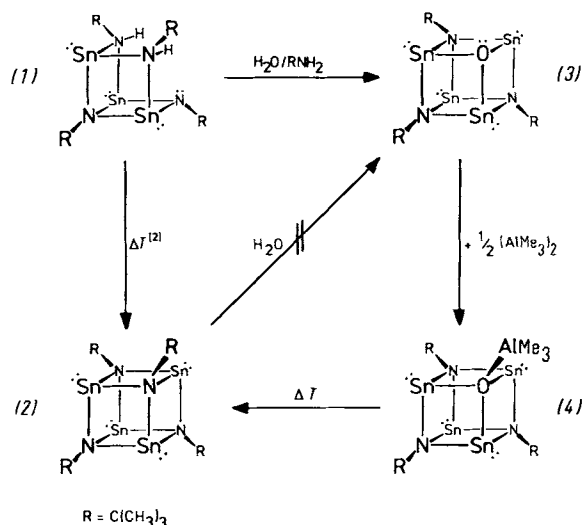
(1a), 73558-95-9; (1b), 73558-96-0; (1c), 53198-40-6; (2), 72692-06-9; (3a), 73558-97-1; (3b), 73558-98-2; (3c), 73558-99-3; (4a), 73559-00-9; (4b), 73559-01-0; (4c), 73559-02-1; (5a), 73559-03-2

- [1] E. C. Miller, *Cancer Res.* 38, 1479 (1978); R. E. Lyle, H. M. Fribush, S. Singh, F. E. Saavedra, G. G. Lyle, R. Barton, S. Yoder, M. K. Jacobson, *ACS Symp. Ser. 101*, 39 (1979).
[2] K. W. Bock, *Arch. Toxikol.* 39, 77 (1977); see also W. Forth, D. Henschler, W. Rummel: *Allgemeine und spezielle Pharmakologie und Toxikologie*. Wissenschaftsverlag B. I., Mannheim 1977.
[3] H. Druckrey, R. Preussmann, S. Ivankovic, D. Schmähl, *Z. Krebsforsch.* 69, 103 (1967).
[4] M. Wiessler, *Angew. Chem.* 86, 817 (1974); *Angew. Chem. Int. Ed. Engl.* 13, 743 (1974); *ACS Symp. Ser. 101*, 57 (1979); see also J. E. Baldwin, A. Scott, S. E. Branz, S. R. Tannenbaum, L. Green, *J. Org. Chem.* 43, 2457 (1978).
[5] Cf. R. Brossmer, V. Eschenfelder, *Justus Liebigs Ann. Chem.* 1974, 967.
[6] N. Pravidic, K. Keglevic, *J. Chem. Soc.* 1964, 4633; W. D. S. Bowering, T. E. Timell, *J. Am. Chem. Soc.* 82, 2827 (1960).
[7] $^1\text{H-NMR}$ (CDCl_3): $\delta = 5.50$, $J = 2$ Hz; $^{13}\text{C-NMR}$ (CDCl_3): $\delta = 95.3$. The C-1 atom can also be unequivocally assigned in the $^{13}\text{C-NMR}$ Spectrum, for the ^{13}C signal for C-1 of the glucuronic acids is shifted by about 3 ppm upfield in the β series; methyl 2,3,4-tri-O-acetyl-1-O-benzyl- β -D-glucuronate: $^{13}\text{C-NMR}$ (CDCl_3): $\delta = 99.4$.

A Cubane-Type $\text{Sn}_4\text{N}_3\text{O}$ Cage^[1]

By Michael Veith and Holger Lange^[2]

Having already synthesized the oligomeric "iminostannyl-enes" (1) and (2)^[2] we have now succeeded in incorporating both tin(II) and nitrogen atoms as well as an oxygen atom into such cage molecules. As shown by the reaction scheme



it is surprisingly only the open cage (1), and not the closed cage (2), which can be transformed by incomplete hydrolysis into the oxa derivative (3). The cubane-type structure of (3) is revealed by the $^1\text{H-NMR}$ spectrum (Table 1), which shows only one signal for the three *tert*-butyl groups. Proof of this structure is provided by the quantitative reaction of (3) with trimethylaluminum to form the Lewis acid-base adduct (4), whose X-ray structure characterization showed it to crystallize isotypically to (2)^[2] (Table 1).

Table 1. Physical data and lattice constants of the compounds (3) and (4); those of compound (2) are also given for the sake of comparison [2].

M.p. [$^\circ\text{C}$]	(3) orange-yellow crystals 180 (dec.)	(4) colorless crystals 196 (dec.)	(2) pale yellow crystals 260 [a]
$^1\text{H-NMR}$ (in benzene; δ values, integration in parentheses)	-1.43	0.2 (1.0); -1.29 (3.0)	-1.52
High-resolution mass spectrum	$^{120}\text{Sn}_2^{118}\text{Sn}_2\text{ON}_3\text{C}_{12}\text{H}_{27}$ exp. 704.8277 calc. 704.8230	$^{119}\text{Sn}^{118}\text{Sn}_3\text{AlON}_3\text{C}_{14}\text{H}_{13}(M-15)$ exp. 758.8516 calc. 758.8520	
Space group	P1 (P1)	P2 ₁ /c	P2 ₁ /c
Lattice constants [pm. $^\circ$]			
<i>a</i>	1275(2)	1015(1)	1033(2)
<i>b</i>	1017(2)	1488(2)	1458(8)
<i>c</i>	1701(2)	1741(2)	1707(8)
α	90.9(1)	90	90
β	102.4(1)	91.4(1)	91.8(1)
γ	106.6(1)	90	90
<i>V</i> (10^6 pm ³)	2057	2630	2570
<i>Z</i>	4	4	4
ρ_{calc} [g/cm ³]	2.27	1.96	1.96

[a] Solid/plastic phase transition at 228°C .

- [8] Cf. M. Kühn, A. v. Wartburg, *Helv. Chim. Acta* 51, 1631 (1968).
[9] The same behavior is observed on reaction of (1a) to (1f) with 2,3,4,6-tetra-O-acetyl- β -D-glucose. Once again, only the glucosides corresponding to (3a), (3b), and (3c) could be isolated, which likewise belong to the α series. In contrast, the more nucleophilic 3,4-dichlorothiophenolate reacts with (1a) to (1f) to give the thioethers in yields of 50 to 60%.
[10] M. L. Hallensleben, M. Wurm, *Angew. Chem.* 88, 192 (1976); *Angew. Chem. Int. Ed. Engl.* 15, 163 (1976).

That (2) and (4) are isotypic is hardly surprising in view of the "isosteric character" of the two molecules. If a nitrogen

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atom of (2) is replaced by an oxygen then the tertiary carbon atom must be replaced by a Group 3 element (by a boron atom for true isosteric character^[3]) in order to preserve the electron balance.

The smooth reaction (3) → (4) shows that the oxygen atom still exhibits Lewis basicity in spite of threefold coordination in the polycycle (3) (cf. also ^[4]); the reason for this reactivity possibly lies in the close proximity of four lone pairs owing to bonding to three Sn^{II} atoms. On addition of the acid AlMe₃ one of the electron pairs is coordinated, thus reducing the electronic interaction; the O atom becomes tetracoordinate.

Under conditions of thermolysis (200 °C), the cage (4) affords the cage (2); the expected fragment (SnOAlMe₃) has not yet been intercepted.

The new compounds (3) and (4) are intermediate members in the series of cubane-type cages (SnX)₄ (X = N or O) of (1) and (2)^[2] on the one hand and the cation Sn₄O₃OH⁺ in Sn₂₁Cl₁₆(OH)₁₄O₆ on the other^[5]. Owing to the *tert*-butyl groups on the nitrogen atoms, compound (3) differs from related SnNO polycycles of lower symmetry and with weaker steric shielding^[6] by being soluble in nonpolar solvents.

Procedure

H₂O (0.049 ml, 2.7 mmol) in *tert*-butylamine (5 ml) is slowly added dropwise to (1)^[2] (7.0 g, 10.9 mmol) in *tert*-butylamine (50 ml). The light yellow solution turns orange and a precipitate appears. After refluxing for 1.5 h the reaction mixture is filtered, *tert*-butylamine is distilled off, and the residue is crystallized from anhydrous benzene. On repeated recrystallization, orange crystals of (3) first grow which can thus be separated from (1); yield 2.5 g (44%).

AlMe₃ (0.2 ml, 2.1 mmol) is added to (3) (1 g, 1.4 mmol) in benzene (10 ml). On concentration, 0.88 g (81%) of the adduct (4) crystallizes.

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(1), 71330-79-5; (3), 73574-68-2; (4), 73587-38-9

[1] Cyclic Diazastannylenes. Part 9. This work was supported by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie.—Part 8: M. Veith, Z. Naturforsch. B 35, 20 (1980).

[2] M. Veith, M.-L. Sommer, D. Jäger, Chem. Ber. 112, 2581 (1979).

[3] The cage is destroyed by substitution of the tin on reaction of (3) with (BMe₃).

[4] M. Veith, Chem. Ber. 111, 2536 (1978).

[5] R. Nesper, H. G. von Schnering, Acta Crystallogr. A 34, 158 (1978).

[6] M. Veith, O. Recktenwald, Z. Anorg. Allg. Chem. 459, 208 (1979).

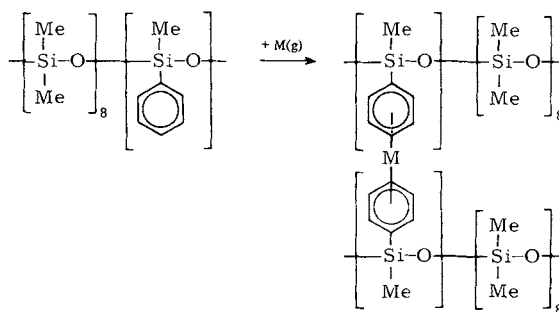
Synthesis of Organotrimetal Polymers Using Trimetal Vapor-Fluid Matrix Techniques^[**]

By Colin G. Francis, Helmut X. Huber, and Geoffrey A. Ozin^[*]

Supported trimetallic particle catalysts have been shown to exhibit certain advantages over their respective bimetallic counterparts, noteworthy features being enhanced stability towards segregation, sintering, and poisoning in hydrocar-

bon reforming processes^[1]. These trimetallic compositions are usually prepared by salt impregnation techniques^[2] although an attractive alternative would be to attach well-defined, organometallic clusters such as FeRuOs₂H₂(CO)₁₃^[3] to functionalized polymers or oxide supports in a manner similar to that currently being developed for bimetallic catalyst systems^[4]. However, as far as we are aware, neither polymer-anchored, three-component mononuclear nor trimetallic cluster systems have been reported previously in the open literature, although a number of two-component and bimetallic cluster analogues are known^[5]. We wish to report that "organotrimetal polymers" containing three different mononuclear metal sites can be readily generated by the metal vapor-fluid matrix technique^[6,10,11].

The fluid polymer chosen for this feasibility study was a poly(methylphenylsiloxane), Dow Corning DC510. This fluid was originally shown to react with the metal vapors of Ti, V, Cr, Mo, and W (in a metal vapor rotatory reactor) to give a liquid bisarene-organometallic polymer^[9], as shown in Scheme 1.



Scheme 1.

We subsequently demonstrated^[6,10,11] that the metal vapor-liquid polymer encounters that occur in such a reactor system (where one envisages both microscopic and macroscopic mobility in the polymer film) can be adequately simulated in a thin, static film experiment.

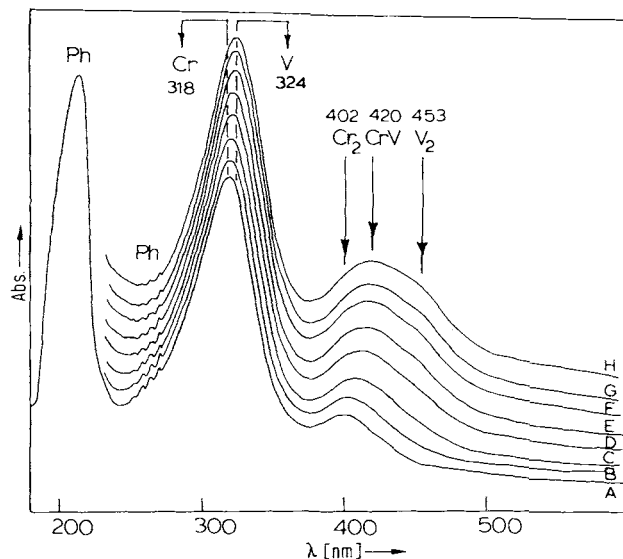


Fig. 1. UV/VIS spectra of the products of (A) a Cr vapor deposition into a thin, static film (ca. 10⁻⁶ m) of DC510 poly(methylphenylsiloxane) at 250 K, followed by (B–H) roughly equal increments of V vapor. The spectra initially show the growth of polymer-attached bis(arene)chromium and polymer-stabilized dichromium, which is followed by the appearance of polymer-attached bis(arene)vanadium and polymer-stabilized divanadium and chromium-vanadium (see [10, 11]).

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