in 10 mL of Et₂O. After warming to room temperature and addition of MeOH, the solution contained—according to the ¹H NMR spectrum—90% 5 (E=Sn), 5% 10a and 5% 10b in case (A) and 60% 5 (E=Sn), 10% 7, 5% 10a, and 25% 10b in case (B). The products were separated by preparative HPLC (retention times: 10a < 10b < 7 < 5).

5 (E = Sn): Colorless crystals, characterized by comparison with an authentic sample [13]. 7: Colorless crystals, correct elemental analysis (C, H). ¹H NMR (C₆H₆): $\delta = 0.125$ (2SiMe₃), 0.234 (SnMe₂), 1.400 (CH₃Sn), 1.696 (2CH₃), 2.453 (CH₂). ¹³C{¹H} NMR (C₆D₆): $\delta = -5.780$ (SnMe₂), 2.015 (2SiMe₃), 9.719 (CSi₂), 17.11 (CH₂Sn), 22.83 (2CH₃), 36.09 (CH₂), 127.2/129.2 (C=C). ²⁹Si NMR (C₆D₆): $\delta = 3.358$. ¹¹⁹Sn NMR (C₆D₆): $\delta = 5.271$. MS (70 eV): *m/z* 390 (*M*⁶).

10a: Colorless liquid. ¹H NMR (C_6D_6): $\delta = -0.458$ (CH), 0.084 (2SiMe₃), 0.364 (SnMe₂), phenyl multiplet. ¹³C[¹H} NMR (C_6D_6): $\delta = -6.064$ (SnMe₂), 0.215 (CH), 3.349 (2SiMe₃), 136.2/143.8 (Ph). ²⁹Si NMR (C_6D_6): $\delta = 1.575$. ¹¹⁹Sn NMR (C_6D_6): $\delta = -23.67$. MS (70 eV): m/z 371 (M^{\oplus} - Me). **10b**: Colorless, liquid, correct elemental analysis (C, H). ¹H NMR (C_6D_6): $\delta = 0.137$ (2SiMe₃), 0.459 (SnMe₂), phenyl multiplet. ¹³C {¹H} NMR (C_6D_6): $\delta = -5.485$ (SnMe₂), 1.587 (2SiMe₃), 30.58 (CBr), 136.8/142.8 (Ph). ²⁹Si NMR (C_6D_6): $\delta = 5.909$. ¹¹⁹Sn NMR (C_6D_6): $\delta = -21.46$. MS (70 eV): m/z464 (M^{\oplus}).

8: PhLi (4.36 mmol) in 2 mL of C_6H_6 and 10 mL of Et_2O was added dropwise over 3 h to a solution of 6(E = Sn) (2.04 g, 4.36 mmol) and $tBu_2MeSiN_3 (3.60 \text{ g}, 17.6 \text{ mmol})$ in 15 mL of Et_2O at -78 °C. The reaction mixture was allowed to warm to room temperature and the LiBr and solvent were removed. Recrystallization of the reaction mixture from pentane afforded 1.80 g (3.50 mmol) 80%) of colorless, crystalline 8. M.p. 116 °C. Correct elemental analysis (C, H). ¹H NMR (C_6D_6): $\delta = 0.068$ (SiMe), 0.112 (2SiMe₃), 0.359 (SnMe₂), 1.142 (Si tBu_2). ¹³C{¹H} NMR (C_6D_6): $\delta = -5.78$ (SnMe₂), -0.843 (SiMe), 1.140 (2SiMe₃), 15.54 (CSi₂), 21.11 (2CMe₃), 28.80 (2CMe₃). ²⁹Si NMR (C_6D_6): $\delta = 0.012$ (2SiMe₃), 12.77 (SiMetBu₂). ¹¹⁹Sn NMR (C_6D_6): $\delta = 64.88$. MS (70 eV): m/z 450 ($M^{\oplus} - tBu$).

12, 13, 14: Compound 8 (0.25 g, 0.50 mmol) was heated in 0.5 mL of C_6D_6 (A), in 0.5 mL of C₆D₆ containing 5 mmol (0.6 mL) of DMB (B), or in 0.5 mL of C_6D_6 containing 0.63 g (3.36 mmol) of tBu_2MeSiN_3 (C) for 20 h at 60 °C. According to the 'H NMR spectrum of the reaction solution, 100% 12 (A), 100 % 13 (B), or 60 % 14/40 % 12 (C) were present in addition to (Me₃Si)₂CN₂ (¹H NMR: $\delta = 0.074$) [14]. Compounds 12, 13, and 14/12 remain as residue after distillative removal of solvent and (Me₃Si)₂CN₂ under high vacuum. Compounds 14 and 12 can be separated by fractional crystallization from Et₂O (1st fraction: 14). 12: Colorless solid. ¹H NMR (C_6D_6): $\delta = -0.100$ (2SiMe), 0.545 (2SnMe₂), 1.040 (2SitBu₂). ¹³C{¹H} NMR (C₆D₆): $\delta = -3.141$ $(2 \text{ SiMe}), 5.018 (2 \text{ SnMe}_2), 21.01 (4 CMe_3), 29.12 (4 CMe_3). ²⁹Si NMR (C_6D_6):$ $\delta = 5.113$. ¹¹⁹Sn NMR (C₆D₆): $\delta = 140.1$. MS (70 eV): m/z 583 ($M^{\oplus} - tBu$). 13: Colorless oil. ¹H NMR (C_6D_6): $\delta = 0.011$ (SiMe), 0.199 (SnMe₂), 1.055 $(SitBu_2)$, 1.823 (CH₃), 2.054 (CH₂Sn), 4.900 (2H₂C=). ¹³C{¹H} NMR (C_6D_6) ; $\delta = -5.969$ (SiMe), -4.824 (SnMe₂), 20.74 (CH₃), 22.94 (CMe₃), $(C_6 D_6)^{-5/1}$ (CH₂Sn), 28.60 (CM₂s), 109.7/113.4 (2H₂C=), 143.7/146.4 (2C=). ²⁹Si NMR (C₆D₆): δ = 10.71. ¹¹⁹Sn NMR (C₆D₆): δ = 42.60. MS (70 eV): m/z 503 (*M*[⊕]).

14: Colorless crystals, decomposition at 160 °C. ¹H NMR (C₆D₆): $\delta = -0.021$ (2SiMe), 0.337 (SnMe₂), 1.121 (2SirBu₂). ¹³C{¹H} NMR (C₆D₆): $\delta = -4.938$ (2SiMe), 0.001 (SnMe₂), 21.05 (4CMe₃), 28.70 (4CMe₃). ²⁹Si NMR (C₆D₆): $\delta = 11.75$. ¹¹Sn NMR (C₆D₆): $\delta = 41.50$. MS (70 eV): *m/z* 520 (M^{\oplus}).

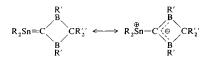
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CAS Registry numbers:

3, 130984-20-2; 5 (E = Sn), 54008-66-1; 6 (E = Sn), 130984-22-4; 7, 130984-23-5; 8, 130984-24-6; 10a, 130984-25-7; 10b, 130984-26-8; 11, 130984-27-9; 12, 130984-28-0; 13, 130984-29-1; 14, 130984-30-4; DMB, 513-81-5; rBu_2MeSiN_3 , 103457-88-1; $(Me_3Si)_2CBr_2$, 29955-10-0; Me_3SnCl , 1066-45-1; $(Me_3Si)_2$ -($Me_3Sn)CBr$, 130984-21-3.

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On the Differing Lewis Basicity of In¹ Compared with Sn¹¹ in Molecular Indium-Tin and Thallium-Tin Alkoxides**

By Michael Veith* and Klaus Kunze

In the thallium-tin alkoxide 1,^[1] which we synthesized for the first time some years ago, each of the two metal atoms has a lone pair. Therefore, 1 could act as a double Lewis base toward electrophilic metal centers, whereby both Sn and Tl



can engage in bonding. When 1 is allowed to react thermally or photochemically with chromium or molybdenum hexacarbonyl in excess, however, only the monoadduct 2 or 3, respectively, is obtained, as shown in Equation (a).

$$[\operatorname{Sn}(\operatorname{OtBu})_{3}\operatorname{Tl}] + [\operatorname{M}(\operatorname{CO})_{6}] \xrightarrow{\Delta I \text{ or } hv} [(\operatorname{CO})_{5}\operatorname{M} - \operatorname{Sn}(\operatorname{OtBu})_{3}\operatorname{Tl}] \quad (a)$$

$$1 \qquad \qquad 2, \ M = \operatorname{Cr}$$

$$3, \ M = \operatorname{Mo}$$

An X-ray structure analysis (Fig. 1 and Table 1) confirms that the tin atom in 3 is bonded to the molybdenum atom.

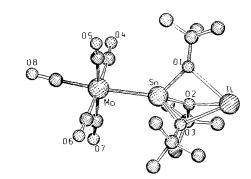


Fig. 1. Molecular structure of 3 [8] determined by X-ray analysis [2, 9]. The unlabeled spheres are carbon atoms; hydrogen atoms are omitted. The Mo-Sn \cdots Tl angle is 178.9(1)°.

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Table 1. Results of the X-ray structure analyses of 3, 4, 8, and 10 [2].

	4	3	8	10
Crystal system	hexagonal	monoclinic	orthorhombi	monoclinic
Space group	$P6_3/m$	$P2_1/n$	Pnma	P2,/n
Ζ	2	4	4	4
a [Å]	9.867(9)	9.952(8)	15.11(1)	10.51(1)
b [Å]	9.867(9)	17.59(1)	14.17(1)	30.30(2)
c [Å]	11.21(1)	15.11(1)	15.76(1)	10.748(7)
Angle [°]	$\gamma = 120$	$\beta = 100.20(7)$	-	$\beta = 107.36(7)$
In-O [Å] (TI-O)	2.413(4)	2.557(15)	2.141(6)	2.21(1)
Sn-O [A°]	2.032(4)	2.017(9)	2.122(9)	2.07(1)
Sn-Mo [Å]	-	2.770(2)	2.761(1)	-
Sn-Cr [Å]		_	-	2.636(3)
In-Mo [Å]	-	-	2.742(1)	2.734(2)
O-In-O [°]	66.7(1)	63.9(8)	73.2(3)	70.6(5)
(O-TI-O)				
O-Sn-O [°]	81.5(1)	84.2(9)	74.0(3)	76.6(5)
In · · · Sn [Å] (Tl)	3.200(3)	3.298(1)	3.078(1)	3.087(2)
R value	0.037	0.062	0.058	0.068

Compared with the starting compound 1 (Sn-O = 2.023(9), TI-O = 2.595(7), and $TI \cdots Sn = 3.306(2) Å^{[1]}$, all metal-oxygen distances are slightly shortened; the distance between thallium and tin is decreased. Characteristic of the monoadducts 2 and 3 are the high CO wave numbers ($v(A_1^{1b})$ bands) and a strong downfield shift of the ¹¹⁹Sn NMR signals relative to those of compound 1 ($\Delta \delta = 97.04$; Table 2). Even under drastic conditions (large excess of metal carbonyl, higher temperature, longer reaction time), no complex fragment becomes bonded to the thallium atom of 2 or 3.

We therefore attempted to replace thallium by its homologue indium. The desired compound 4 may be obtained starting either from 1 or from the sodium salt $[{Na(OtBu)_3Sn}_2]^{[3]}$ in a heterogeneous reaction with InBr [Eq. (b)].

 $[Tl(OtBu)_3Sn]$ $\xrightarrow{+ \text{ In Br}} [\text{In}(\text{O}t\text{Bu})_3\text{Sn}]$ (b) $1/2[{Na(OtBu)_3Sn}_3]$

Toluene, used as solvent, apparently causes partial dissolution of InBr via formation of an arene complex.^[4] The monomeric product 4, like 1, is soluble in nonpolar solvents, exhibits a similar ¹¹⁹Sn absorption (Table 2), and forms isotypic crystals (Table 1). According to an X-ray structure analysis, 4 has a distorted bipyramidal InO₃Sn structure with In and Sn in apical positions and the three oxygens in equatorial positions. Compared with 1, the indium atom is closer to the O_3 plane than the thallium atom, as expected; the distances to the oxygen atoms lie in the normal range (see also indium 2,4,6-tris(trifluoromethyl)phenoxide^[5]).

Reaction of 4 with $[Cr(CO)_6]$ or $[Mo(CO)_6]$ in THF either thermally or photochemically in analogy to Equation (a) likewise results in formation of monoadducts 5 and 6, respectively. Use of an excess of the metal carbonyl or longer reaction times results in further reaction to give the diadducts 7 and 8, respectively [Eq. (c)].

 $[M(CO)_6]$ $(\Delta T \text{ or } hv)$ \rightarrow [Sn(OtBu)₃In - M(CO)₅] -[In(OtBu)₃Sn] THE 5. M = Cr6, M = Mo(c) $[(CO)_5 M - Sn(OtBu)_3 In - M(CO)_5]$ 7. M = Cr8, M = Mo

In contrast to 2 and 3, the transition-metal atoms in 5 and 6 are not coordinated to the tin atom but rather to the indium atom. This is revealed by the upfield shift of the ¹¹⁹Sn NMR signal (6: $\Delta \delta = -95.96$) compared with that of 4 and by the wave numbers of the $v(A_1^{1b})$ stretching band, which indicate a different electron density trans to the CO group (see Table 2).

This is shown especially clearly on going from the monoadducts 5 and 6 to the diadducts 7 and 8. The second $v(A_1^{1b})$ bands due to the M(CO)₅ units on tin lie in the absorption region observed for compounds 2 and 3 (Table 2).

The result of an X-ray structure analysis of 8 is shown in Figure 2. The four metal atoms Mo, Sn, In, and Mo are

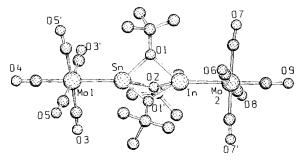


Fig. 2. Molecular structure of 8 [2] (atoms labeled as in Fig. 1). The stacked arrangement of the Mo(CO), groups is clearly shown.

arranged nearly linearly (Mo-Sn-In = 174.2° , Mo-In-Sn = 178.8°), with metal single bonds between Mo and In and between Mo and Sn (distances in Table 1); as found in the starting compound 4, In and Sn are bridged by three tert-butoxy groups. The coordination of Mo(CO), units on indium and tin results in withdrawal of electron density from indium, so that the In-O distance is significantly less than that in 4. The electron density on Sn is increased to a comparable extent; that is, the Sn-O distances are longer than those in free 4. If the whole molecule is considered, however, 4 acts as an electron donor toward the Mo(CO), units, since the In \cdots Sn distance in 8 is less than that in 4 by 0.122 Å (Table 1).

The preferential coordination of the fragments $[Cr(CO)_5]$ and [Mo(CO)₅] to indium in the monoadducts can be ex-

Table 2. ¹H and ¹¹⁹Sn NMR data (δ values in benzene) and CO wave numbers [cm⁻¹] for compounds 1-10.

	$\delta(^{1}H)$	$\delta(^{119}\text{Sn})$	v(A ^{1b} ₁)	v (other CO)
[T](O/Bu) ₃ Sn] 1	1.32	- 78.72 [a]	_	_
$[In(OtBu)_3Sn]$ 4	1.37	- 77.27	-	-
[Tl(OtBu) ₃ Sn-Cr(CO) ₅] 2	1.31	-	2060 (m)	1970 (sh)
				1920 (vs)
$[TI(OtBu)_3Sn-Mo(CO)_5]$ 3	1.31	+18.32	2070 (m)	1980 (sh)
				1930 (vs)
$[Sn(OtBu)_3In-Cr(CO)_5]$ 5	1.23	-	2033 (m)	1968 (w)
				1913 (vs)
$[Sn(OtBu)_3In-Mo(CO)_5] 6$	1.23	-173.23	2051 (m)	1925 (vs)
[(CO) ₅ Cr-Sn(OtBu)In-Cr(CO) ₅] 7	1.27	-	2058 (m)	1975 (sh)
			2041 (m)	1925 (vs, br)
[(CO) ₅ Mo-Sn(OtBu) ₃ In-Mo(CO) ₅] 8	1.28	-	2069 (m)	1965 (s)
			2050 (m)	1915 (vs, br)
$[(CO)_5Cr-In(OtBu)_3Sn-Mo(CO)_5]$ 9	1.28	-	2069 (m)	1978 (sh)
			2033 (m)	1950 (vs)
				1930 (vs)
				1912 (vs)
[(CO) ₅ Mo-In(OtBu) ₃ Sn-Cr(CO) ₅] 10	1.28	-	2059 (m)	1975 (sh)
			2051 (m)	1930 (vs)
				1912 (vs)

 $[a] J(^{205, 203}\text{Tl-Sn}) = 1293 \text{Hz}.$

ploited chemically. As shown in Equations (d) and (e) reaction of 5 and 6 with the THF adduct of the corresponding metal pentacarbonyl affords the positional isomers 9 and 10, respectively, which contain four different metal atoms.

$$[(CO)_{5}Cr - In(OtBu)_{3}Sn] + [Mo(CO)_{5}(thf)] \xrightarrow{-THF} (d)$$
5
$$[(CO)_{5}Cr - In(OtBu)_{3}Sn - Mo(CO)_{5}]$$

$$[(CO)_{5}Mo - In(OtBu)_{3}Sn] + [Cr(CO)_{5}(thf)] \xrightarrow{-THF} (e)$$

$$6 \qquad [(CO)_{5}Mo - In(OtBu)_{3}Sn - Cr(CO)_{5}]$$

$$10$$

Compounds 9 and 10 are clearly distinguished by their CO wave numbers (Table 2) and crystal data (Table 1).^[6] The X-ray structure analysis of 10 (Fig. 3, Table 1) again reveals

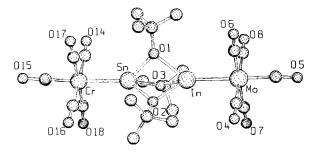


Fig. 3. Molecular structure of 10 [2]. In contrast to 8, the $M(CO)_5$ groups are arranged in an eclipsed fashion.

an almost linear arrangement of the metal atoms (Mo-In...Sn = 178.1(1)°, Cr-Sn...In = 179.7(1)°). Interchange of the Sn and In positions in the structure analysis leads here and for **8** to poorer U values. As found for **8**, addition of [M(CO)₅] fragments to **4** results in a decrease in the separation of the main-group metals ($\Delta d = 0.113$ Å) and a charge shift from indium to tin. However, owing to the shorter Cr-Sn bond compared with the Mo-Sn bond in **8**, the charge shift is less pronounced.

Experimental Procedure

4: [Tl(OtBu)₃Sn] (1.0 mmol) [1] or [{Na(OtBu)₃Sn}₂] (0.5 mmol) [3] was stirred with indium(1) bromide (1.4 mmol) in 15 mL of toluene at 110 °C for 5 or 40 h, respectively. The insoluble material, which may contain some indium, was removed by filtration and the filtrate was concentrated. Sublimation of the residue at $30 \,^{\circ}C/10^{-2}$ Torr afforded 0.42 g (92%) or 0.41 g (90%), respectively, of 4; m.p. 41 °C.

2, 3, and 5-10: A stirred solution of 1 or 4 and $[Cr(CO)_6]$ or $[Mo(CO)_6]$ in toluene was heated to reflux. Alternatively, the metal carbonyl was first photolyzed in THF and then allowed to react with 1 or 4 in toluene. Preparation of 9 and 10 starts with 5 and 6, respectively, whose synthesis must be carried out with exact molar ratios of starting materials. All of the compounds were purified by sublimation or recrystallization and gave correct elemental analyses (C, H, metal).

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1, 83437-08-5; 2, 131010-15-6; 3, 131010-16-7; 4, 131010-17-8; 5, 131010-18-9;

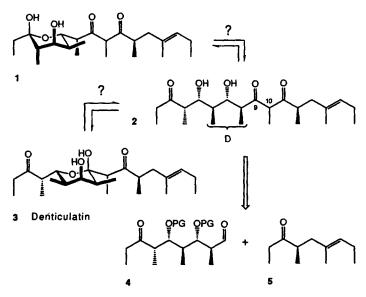
6, 131010-19-0; **7**, 131010-20-3; **8**, 131010-21-4; **9**, 131010-22-5; **10**, 131010-23-6; [Cr(CO)₆], 13007-92-6; [Mo(CO)₆], 13939-06-5; [Na(OtBu)₃Sn], 105803-03-0; [Cr(CO)₅(thf)], 15038-41-2; [Mo(CO)₅(thf)], 53248-43-4; In, 7440-74-6; Mo, 7439-98-7; Cr, 7440-47-3; Sn, 7440-31-5.

- [2] Further details of the crystal structure investigations of 3. 4, 8, and 10 may be obtained from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, W-7514 Eggenstein-Leopoldshafen 2 (FRG), on quoting the depository number CSD-54897, the names of the authors, and the journal citation.
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- [6] Compound 9 forms orthorhombic crystals, space group Pnma, a = 14.93(2), b = 14.33(2), c = 15.46(2) Å.
- [7] M.p., b.p., yield: 2, 104°C, 40°C/10⁻³ Torr, 50%; 3, 107°C, 45°C/10⁻³ Torr, 70%; 5, 101°C, 44°C/10⁻³ Torr, 50%; 6, 103°C, 50°C/10⁻³ Torr, 25%; 7, 148°C (dec.), -, 80%; 8, 150°C (dec.), -, 64%; 9, 143°C (dec.), -, 58%; 10, 145°C (dec.), -, 75%.
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Efficient Stereoselective Total Synthesis of Denticulatins A and B**

By Marc W. Andersen, Bernhard Hildebrandt, and Reinhard W. Hoffmann*

The stereoselective synthesis of natural products of polyketide origin, particularly those which contain the stereotriad D, remains a challenge to the preparative chemist.^[11] Among such substances are the denticulatins 3,^[21] two polypropionates isolated from *Siphonaria*, whose biological significance remains unclear. Denticulatin is a polyhydroxy-polyketo compound and exists in the form of a semiacetal. For the synthesis of the denticulatins it is of interest whether open-chain precursors such as 2 cyclize to the correct denticulatin isomer 3, as well as whether other semiacetals such as 1 isomerize to the desired product (Scheme 1).



Scheme 1. Possible synthetic routes to denticulatin. PG = protecting group.

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M. Veith, R. Rösler, Angew. Chem. 94 (1982) 867; Angew. Chem. Int. Ed. Engl. 21 (1982) 858.

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