Communications to the Editor

Decaphenylstannocene, [η^5-(C_6H_5)$_5$$C_5$]$_2$Sn^{II}: The First Symmetrical Main-Group Sandwich Compound

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The lone-pair electrons in subvalent fourth main-group compounds reveal their VSEPR-expected stereochemical activity in distortions from high-symmetry geometries to give voids in the central-atom coordination sphere[1] and bent, two-coordinated species. Certain rare exceptions, e.g., $CsSnBr_3$,[2] form perfect polyhedra in highly colored, conducting solids.

We have synthesized[3] penta- and decaphenylstannocene (Scheme I). The latter, [η^5-(C_6H_5)$_5$]$_2$Sn^{II},[4] is the first example of a molecular, main-group subvalent species in which the lone pair is stereochemically inert. Here the tin atom sits on an inversion center between symmetry-related, equidistant {2.401 (6) Å to the ring center; d[Sn–C_{ring}(av) = 2.692 (8) Å]} cyclopentadienes that are planar, staggered, and exactly parallel (Figure 1, Table I). The attached phenyl groups are canted to each cyclopentadienyl ring oppositely in a double-opposed paddlewheel fashion to give molecules of S_{10} symmetry (Figure 2). There are no short intermolecular contacts (Figure 3).

Phase changes to give the high-dielectric, intensely colored solids in which tin(II) atoms are at sites of cubic symmetry are accompanied by isotropic lattice expansion.[1] The lone pairs are said to be delocalized in a conduction band. Where, then, are the 5s² electrons in our bright-yellow decaphenylstannocene? Comparison solid-state data are available for the (η^5-R_5C_5)$_2$E derivatives for E = Sn, R = H[5] and CH_3,[6] as well as for E = Ge, R = H,[7] and E = Pb, R = H[8] and CH_3.[5] In addition, gas-phase data are available for E = Sn, Pb, R = H,[9] and for the 1,1'-(CH_3)$_2$ derivatives[10] of E = Ge, Sn. All are severely bent, e.g., the tin–center
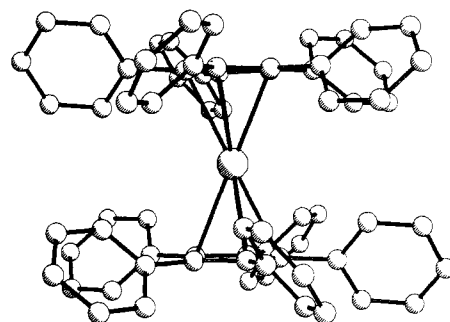

Figure 1. Decaphenylstannocene, [η^5-(C_6H_5)$_5$$C_5$]$_2$Sn^{II}, viewed parallel to the plane of the cyclopentadiene rings.
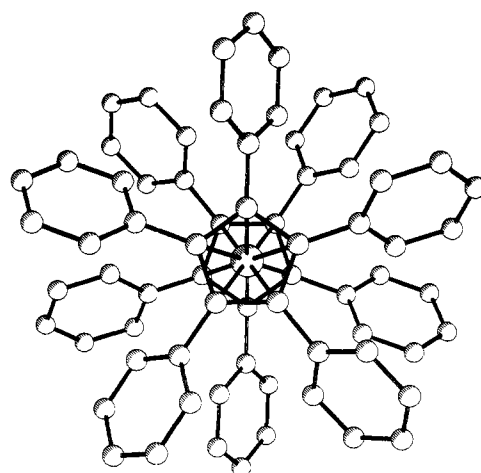

Figure 2. Decaphenylstannocene, [η^5-(C_6H_5)$_5$$C_5$]$_2$Sn^{II}, viewed perpendicular to the plane of the cyclopentadienyl ring.

Table I. Interatomic Distances (Å)^a for Decaphenylstannocene, [η^5-(C_6H_5)$_5$$C_5$]$_2Sn^{II\,b}$

Sn–C1	2.686 (6)	C3–C4	1.424 (9)
Sn–C2	2.687 (7)	C4–C5	1.414 (10)
Sn–C3	2.689 (7)	C1–C5	1.425 (9)
Sn–C4	2.705 (7)	C1–C11	1.506 (8)
Sn–C5	2.688 (7)	C2–C21	1.489 (8)
Sn–Cp^c	2.401 (6)	C3–C31	1.485 (8)
C1–C2	1.426 (9)	C4–C41	1.497 (8)
C2–C3	1.450 (10)	C5–C51	1.494 (7)

^{a} All phenyl carbon atoms were refined as a part of rigid bodies with d(C–C) = 1.395 (7) Å. ^{b} Estimated standard deviations are in parentheses. ^{c} Cp refers to the centroid of the cyclopentadienyl ring.

Table II. Interatomic Angles (Deg) for Decaphenylstannocene, [η^5-(C_6H_5)$_5$$C_5$]$_2Sn^{II\,a}$

C1–C2–C3	108.2 (5)	C4–C5–C1	107.5 (5)
C1–C2–C21	127.7 (6)	C4–C5–C51	124.4 (5)
C2–C3–C4	106.1 (6)	C41–C4–C5	128.4 (5)
C2–C3–C31	125.8 (5)	C5–C1–C2	108.2 (6)
C21–C2–C3	124.0 (6)	C5–C1–C11	128.2 (5)
C3–C4–C5	109.9 (6)	C51–C5–C1	128.0 (5)
C3–C4–C41	121.7 (6)	C11–C1–C2	123.6 (5)
C31–C3–C4	128.1 (6)		

^{a} Estimated standard deviations for the last digit are in parentheses.

of the ring angles for the R = H, CH_3, and C_6H_5 solids is 143.7° and 148.0°, 143.6° and 144.6°[6] (two independent molecules in each), and 180° (Table II). Thus our structure represents a sharp discontinuity from previous results.[11,12] However, our R = C_6H_5

(1) Our review of these structures is in preparation (Ng, S.-W.; Zuckerman, J. J.).

(2) Donaldson, J. D.; Silver, J.; Hadjiminolis, S.; Ross, S. D. *J. Chem. Soc., Dalton Trans.* **1975**, 1500.

(3) Pentaphenylcyclopentadiene and its bromide have been known for nearly 60 years (Ziegler, K.; Schnell, B. *Justus Liebigs Ann. Chem.* **1925**, *445*, 266). See also: Braye, E. H.; Hübel, W.; Caplier, I. *J. Am. Chem. Soc.* **1961**, *83*, 4406.

(4) Decaphenylstannocene, [η^5-(C_6H_5)$_5$$C_5$]$_2$Sn^{II}, $C_{70}H_{50}$Sn, forms bright-yellow parallelepipeds, mp >300 °C dec, in the monoclinic space group $P2_1/n$ with a = 10.458 (2) Å, b = 13.462 (3) Å, c = 18.130 (3) Å, β = 97.81 (1)°, V = 2529 (1) Å³, Z = 2, ρ_{calcd} = 1.326 g cm⁻³. The structure was determined by difference Fourier techniques from 4779 reflections measured at 138 ± 2 K on an Enraf-Nonius CAD/4 automatic diffractometer with monochromatized Mo Kα radiation to a final conventional R value of 0.058 and R_w of 0.053 for the 2560 reflections included in the least-squares sums. Computations were performed by using local modifications of SHELX-76 programs (Sheldrick, G. M. University Chemical Laboratory: Cambridge, U.K., 1976). Scattering factors are from: "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, U.K., 1974; Vol. IV, p 72.

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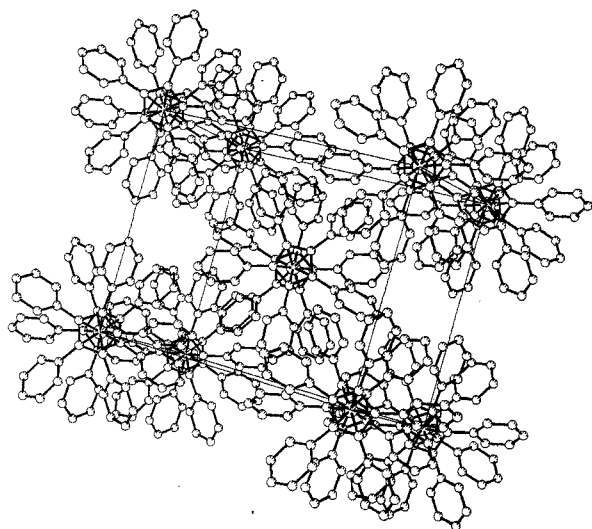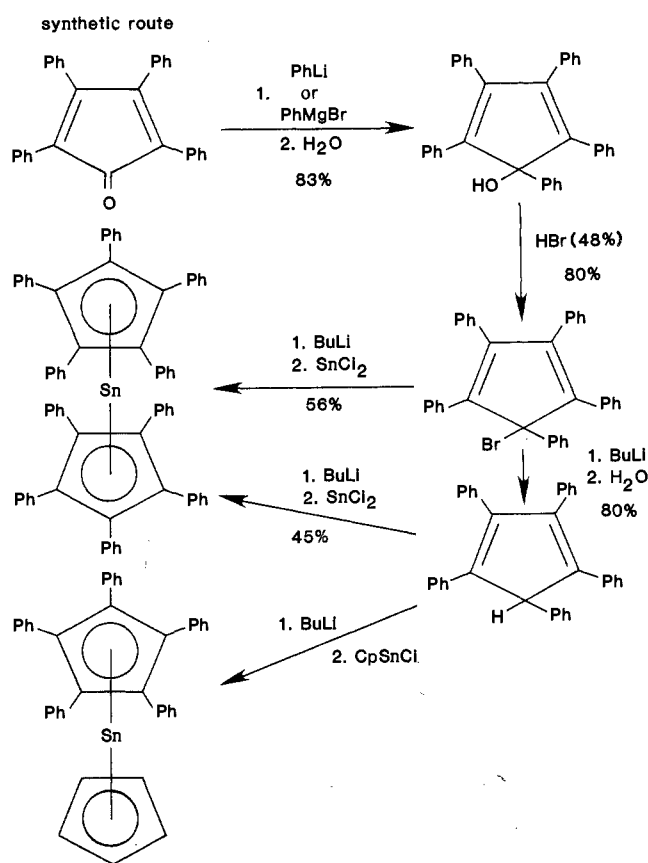
Figure 3. Packing Diagram of decaphenylstannocene, $[\eta^5\text{-}(C_6H_5)_5C_2]_2Sn^{II}$.

Scheme I

synthetic route

tin–ring centroid distance [2.401 (6) Å] is greater than that in the R = CH₃ [av 2.396 (5) Å; range 2.388–2.400 Å], but not the

R = H [av 2.422 (13) Å; range 2.410–2.436 Å][6] homologues.

The fortuitous formation of η^5-pentaphenylcyclopentadiene derivatives of the transition metals is evidence for the stabilizing power of this ligand. The η^5-$(C_6H_5)_5C_5M$ system first unexpectedly turned up from diphenylacetylene with $Mo(CO)_6$,[17] diglyme[18]-$Mo(CO)_3$, or $W(CO)_5$ and subsequently with $Pd(O_2$-$CCH_3)_2$,[19] but pentaphenylaluminole, $(C_6H_5)_5C_4Al$, also irrationally yields an M = Ni derivative from lithium metal and $NiBr_2$.[20] Other, directed syntheses yield the alkali-metal salts[21,22] and derivatives in which M = Fe,[22,23] Ni,[24] Cr,[22] Mo,[22] W,[22] Co,[22] Ru,[22] Ti,[22] Zr,[22] Lu,[25] and Pd.[26]

Aside from imparting high kinetic stability through its large volume, the η^5-$(C_6H_5)_5C_5$ system is also less basic. Electron withdrawal by the phenyl groups makes low-oxidation transition-metal states more accessible as measured by increased potentials of the redox couples,[27] an effect opposite to that wrought by methyl substitution, which makes reduction more difficult.[28] Since the tin $5s^2$ electrons are not occupying a nonbonding orbital and all of the bonding orbitals are filled, then these electrons must occupy an orbital with antibonding character. The phenyl groups, which are not antiparallel to the cyclopentadiene rings, can help delocalize these electrons.

For stannocene itself, initial, semiempirical MO calculations assigning the lone-pair electrons to the HOMO[6] have been replaced by SCF X_α-SW results[29,30] placing the lone pair in a strongly directional, fifth-occupied orbital, ca. 2 eV more stable than the HOMO. However, MNDO calculations on the hypothetical E = Si and $[\eta^5$-$(C_5H_5)_2P]^+$ homologues predict D_{5h} ground-state geometries with the lone pairs distributed among the third and fifth MO's.[30] An ab initio SCF-MO calculation on the E = Ge analogue gives a D_{5d} ground state (the D_{5h} form is less than 0.2 kJ/mol higher) with the lone pair in the HOMO.[10] In solid $(\eta^5$-$C_5H_5)_2Sn$ there are eclipsed and staggered molecules.[5] In $[\eta^5$-$(CH_3)_5C_5]_2Sn$ both independent molecules are staggered.[6] For E = Ge a rather flat well makes large amplitude ring–metal–ring bending with slippage of E away from the ring centroid accessible, but the bent form is more stable at shorter E-ring distances.[10] Bending our decaphenylstannocene, as studied using space-filling models and nonbonded contact radii sums, may require further separating the cyclopentadienyls and slipping the tin vectors from the ring centroids. Rotation about the linear tin vectors, on the other hand, seems easier. Assessing the severity of the intramolecular n,n'-phenyl steric interference is difficult since the rings approach perpendicularly in an H atom···π-system contact. We note that the alternative isomeric η^1- or spiro-stannacyclohexatriene or stannacyclohexatrienyl cation–cyclopentadienyl anion combination structures are not adopted.

Other internuclear distances and angles in decaphenylstannocene are unexceptional. The range of $d(C–C)$ values, 1.414 (10)–1.450 (10) Å and their average, 1.428 (13) Å, resemble those

(11) The germanium (Molloy, K. C.; Zuckerman, J. J. *Adv. Inorg. Chem. Radiochem.* **1983**, *27*, 113) and tin (Zubieta, J. A.; Zuckerman, J. J. *Prog. Inorg. Chem.* **1978**, *24*, 251. Smith, P. J. *J. Organomet. Chem. Libr.* **1981**, *12*, 97) structures have been reviewed, as well as those of bivalent germanium, tin, and lead (Harrison, P. G. *Coord. Chem. Rev.* **1976**, *20*, 1).

(12) Other related structures also show severe bending at the tin(II) atom, e.g., in $\{\eta^5$-$[(i$-$C_3H_7)_2N]_2PC_5H_4\}_2Sn$,[13] $\{\eta^5$-$C_5H_5Co[4,5$-$(C_2H_5)_2$-1,3-$(CH_3)_2C_2BC$-1,3]-$\eta^5\}_2Sn$,[14] $\{[BF_4]^-(\mu$-η^5-$C_5H_5)_2Sn[\mu$-η^5-$C_5H_5Sn]^+THF\}_m$[15] and $(\eta^5$-$C_5H_5)SnCl$.[16]

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in $[\eta^5-(C_6H_5)_5C_5)Ni-(\eta^3-C_3(C_6H_5)_3)-Ni(C_4(C_6H_5)_4-\eta^4)$ (1.41–1.48 and 1.44 Å).[20] The average d(Sn–C) values are 2.67 and 2.70 Å for R = H[5] and 2.675 and 2.678 Å for R = CH₃[6] (two independent molecules in each) vs. 2.692 (8) Å for decaphenylstannocene.

We are now attacking the opposite problem, that of producing a severely bent angle so that the lone-pair electrons will be both chemically (as a base) as well as stereochemically active. Our recent metallocenophane syntheses[31,32] are steps in this direction.

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(32) Molloy, K. C.; Nasser, F. A. K.; Zuckerman, J. J., unpublished results.

New Asymmetric Diels–Alder Cycloaddition Reactions. Chiral α,β-Unsaturated Carboximides as Practical Chiral Acrylate and Crotonate Dienophile Synthons

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The achievement of absolute stereochemical control in the Diels–Alder reaction has been the focus of numerous of investigations spanning a period of more than 20 years. Recently, several examples of highly diastereoselective cycloadditions employing chiral dienophilic esters,[1,2] ketones,[3] and chiral dienes[4] have been reported. Nonetheless, issues associated with absolute stereochemical control in this reaction continue to pose an important challenge in the area of reaction design. The purpose of this communication is to describe our own studies directed at the development of the α,β-unsaturated carboximides **1–3** as practical chiral dienophiles in the Diels–Alder process.

The requisite dienophiles **1–3** were prepared by N-acylation of the illustrated chiral 2-oxazolidones derived from (S)-valinol, (S)-phenylalanol, or (1S,2R)-norephedrine.[5] Specifically, the

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Table I. Et₂AlCl-Promoted Diels–Alder Reactions of Dienophiles 1–3 and Cyclopentadiene (Scheme I)[6]

en-try	dienophile	diastereoselection[a] endo:exo	endo (4:5)	purified ratio (4:5)	isolated yield, %[b]	mp, °C
A	**1a**, R₁ = H	>100:1	93:7	>99:1	81	59.2–61
B	**2a**, R₁ = H	>100:1	95:5	97:3	78	120–121
C	**3a**, R₁ = H	100:1	5:95	<1:99	82	91–92
D	**1b**, R₁ = Me	48:1	95:5	>99:1	82	96–98
E	**2b**, R₁ = Me	55:1	97:3	99:1	83	oil
F	**3b**, R₁ = Me	60:1	2:98	<1:99	88	oil

[a] Reference 10; reaction temperature, –100 °C. [b] Yield refers to isolated material with the indicated diastereomer purity.

crystalline crotonate imides **1b–3b** were obtained in 80–90% yields from the lithiated 2-oxazolidones and (E)-2-butenoyl chloride in direct analogy with previously reported N-acylation procedures:[5] **1b**, mp 56–56.5 °C; **2b**, mp 85–86 °C; **3b**, mp 66–66.5 °C.[6] The more sensitive acrylate carboximides **1a**, mp 44–45 °C; **2a**, 73.5–74.5 °C, and **3a** (oil) were prepared in 50–60% yields from the respective N-bromomagnesium 2-oxazolidones and propenoyl chloride (THF, 0 °C, 5 min) under carefully defined conditions.[6,7] Our preliminary evaluation of the synthetic utility of these dienophiles was made in conjunction with the Lewis acid promoted Diels–Alder process with cyclopentadiene (Scheme I). After an extensive survey of Lewis acid addends, we discovered that diethylaluminum chloride (DEAC) or dimethylaluminum chloride (DMAC), employed in excess of 1 equiv relative to dienophile, is *essential* to the realization of high reaction diastereoselectivity. In a typical experiment, a solution of crotonate imide **1b** in CH₂Cl₂ (0.5 M) and cyclopentadiene (20 equiv) was cooled to –100 °C and 1.4 equiv of precooled DEAC (1.8 M in toluene) was added via cannula.[8] After a reaction time of approximately 2 min, the reaction was quenched via transfer to an aqueous ammonium chloride solution. Conventional product isolation afforded adduct **4b** ($X_C = X_V$)[9] along with minor amounts of other product diastereomers in 99% yield. Recrystallization provided the diastereomerically pure adduct in 82% yield as colorless prisms, mp 96–98 °C (Table I, entry D). The data included in Table I indicate that both chiral acrylates **1a–3a** and crotonates **1b–3b** are excellent chiral dienophiles which undergo exceptionally high-yield cycloaddition reactions. Most significantly, the levels of asymmetric induction in these systems are consistantly good. From the standpoint of practicality, we have found that purification of the major Diels–Alder cycloadduct to high diastereomeric purity may be *routinely* achieved by either recrystallization or chromatography.[10] In this study (see Tables I and II), as in earlier investigations,[5,11] the high incidence of product crystallinity associated with these carboximide systems greatly enhances the practical utility of these dienophiles. The nondestructive removal of the 2-oxazolidone auxiliaries through lithium benzyloxide transesterification (1.5 equiv ROLi, THF, 0 °C 3 h) proceeds in excellent yields (85–95%) and is currently the method of choice for auxiliary cleavage.[11] Accordingly, transesterification of cy-

(6) Satisfactory elemental analysis and spectral data were obtained for all compounds reported herein.
(7) Specific experimental conditions for the synthesis of **1a–3a** are provided in the supplementary material. It is recommended that these conditions be followed precisely.
(8) The general cyclopentadiene cycloaddition procedure for the acrylate imides **1a–3a** requires the addition of DEAC to a solution at –100 °C of dienophile prior to the addition of diene. A detailed experimental is provided in the supplementary material.
(9) For the purpose of brevity, the chiral auxiliaries derived from (S)-valinol, (S)-phenylalanol, and (1S,2R)-norephedrine will be abbreviated as X_V, X_P, and X_N, respectively.
(10) All product diastereomer analyses were carried out by either capillary gas chromatography or high-pressure liquid chromatography. The diastereomerically pure (≥99%) adducts were obtained either by recrystallization or medium-pressure liquid chromatography using Merck Lobar silica gel columns.
(11) For racemization control experiments for these transesterification conditions, see: Evans, D. A.; Ennis, M. D.; Mathre, D. J. *J. Am. Chem. Soc.* **1982**, *104*, 1737.