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**Decaphenylgermanocene, -stannocene and -plumbocene,
[η^5 -(C₆H₅)₅C₅]₂E^{II} (E = Ge, Sn, Pb) and the X-ray crystal
and molecular structure of pentaphenylstannocene,
 η^5 -(C₆H₅)₅C₅SnC₅H₅- η^5**

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Abstract

The [(C₆H₅)₅C₅]⁻ anion reacts with GeI₂, SnCl₂ or Pb(O₂CCH₃)₂ in ethereal solvents to form the sandwich compounds [η^5 -(C₆H₅)₅C₅]₂E^{II} (E = Ge (III), Sn (I) and Pb (IV)) in 60, 73 and 54% yields, respectively. The infusible air- and water-stable products (off-white, bright-yellow and deep-red colored, respectively) exhibit a weak parent ion in the mass spectrum plus the [(C₆H₅)₅C₅E]⁺ cation (100%) and [(C₆H₅)₅C₅H]⁺ and [(C₆H₅)₅C₅]⁺. The E = Pb derivative (IV) is thermochromic. The A_{1u} ν_{asym} ring-metal stretch is observed in the infrared at 164, 149 and 135 and the corresponding A_{1g} ν_{sym} stretch at 153, 138 and 134 cm⁻¹ in the Raman for III, I and IV, respectively. Pentaphenylstannocene (II) is formed in 23%

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yield from η^5 -cyclopentadienyltin(II) chloride as light-yellow, monoclinic platelets which are moderately air-stable, decomposing at 150 °C. The mass spectrum exhibits a weak parent ion plus the equally abundant $[(C_6H_5)_5C_5Sn]^+$ and $[H_5C_5Sn]^+$ cations. The ^{119m}Sn Mössbauer spectra at 78 K of deca- (I) and pentaphenylstannocene (II) ($IS = 3.75, 3.67$; $QS = 0.583, 0.868$ mm s $^{-1}$, respectively) are similar to other stannocenes. Pentaphenylstannocene (II), $C_{40}H_{30}Sn$, crystallizes with a molecule of toluene in the space group $P2_1/c$ with a 13.357(5), b 10.139(3), c 26.967(5) Å, β 100.96(2)°, V 3585(2) Å 3 , $Z = 4$, ρ_{calc} 1.336 g cm $^{-3}$. The structure was determined at 138(2) K using Mo- K_α radiation to a final conventional R value of 0.038 and R_w of 0.045 for 5220 observed reflections. The molecule is bent through 151.1(2)° between the tin vectors to the pentaphenylcyclopentadienyl (2.487(5) Å) and cyclopentadienyl (2.391(5) Å) ring centroids. The phenyl groups are not antiparallel to their cyclopentadienyl ring.

Decaphenylstannocene (I) [1], possibly the first molecule to occupy the S_{10} -symmetry class, violates decisively the valence-shell, electron-pair repulsion (VSEPR) model. The lone-pair electrons are completely inert stereochemically in this bright-yellow metallocene. We now report details of the synthesis of I and its E = Ge II , (III) and Pb II (IV) analogues, and describe the synthesis and structure of pentaphenylstannocene (II) $\eta^5-C_5H_5SnC_5(C_6H_5)_5-\eta^5$.

The decaphenyl group-IV metallocenes were prepared by the reaction of the E II halide (the Pb II acetate was substituted for better solubility) with the $[(C_6H_5)_5C_5]^-$ anion in an ethereal solvent [2*]. The corresponding germanocene [9], its 1,1'-dimethyl [10] and decabenzyl [11] derivatives, decamethyl- [12] and decabenzyl- [11] stannocene and -plumbocene [13,14] are similarly prepared and have been described previously.

Decaphenylgermanocene (III) (60% yield) is an air-stable, off-white powder thermally stable to ca. 370 °C (Found: C, 87.04; H, 5.20; Ge, 7.98. $C_{70}H_{50}Ge$ calc: C, 87.24; H, 5.23; Ge, 7.53%). Sublimation at 250 °C/ 4×10^{-4} torr gives only the purple $[(C_6H_5)_5C_5]^\cdot$ radical on the coldfinger (-20 °C) and a germanium mirror. Steam distillation using deoxygenated water yields only pentaphenylcyclopentadiene. The mass spectrum at 70 eV exhibits $m/e = 964 (< 1)$ $[(C_6H_5)_5C_5]_2^-$, Ge^+ , 519(100) $[(C_6H_5)_5C_5Ge]^+$, 446(16) $[(C_6H_5)_5C_5H]^+$ and 445(48%) $[(C_6H_5)_5C_5]^+$.

Decaphenylstannocene (I) [1] could be recrystallized from 1-methylnaphthalene to yield (56%) bright-yellow, air-stable, monoclinic parallelepipeds, m.p. > 370 °C (decomp). (Found: C, 83.13; H, 5.05; Sn, 11.45. $C_{70}H_{50}Sn$ calc: C, 83.26; H, 4.99; Sn, 11.75%). Its mass spectrum exhibits $m/e = 1010 (< 1)$ $[(C_6H_5)_5C_5]_2Sn^+$, 565(100) $[(C_6H_5)_5C_5Sn]^+$, 446(48) $[(C_6H_5)_5C_5H]^+$ and 445(60%) $[(C_6H_5)_5C_5]^+$.

Decaphenylplumbocene (IV) could be recrystallized from toluene to yield (54%) a deep-red, air- and water-stable powder (Found: C, 76.68; H, 4.90; Pb, 18.79. $C_{70}H_{50}Pb$ calc: C, 76.55; H, 4.59; Pb, 18.86%) which is thermochromic similar to the parent plumbocene [14]. Reversible darkening occurs on heating to ca. 370 °C (melt.). Sublimation at ca. 270 °C/ 3×10^{-5} torr yielded the purple $[(C_6H_5)_5C_5]^\cdot$

* Reference number with asterisk indicates a note in the list of references.

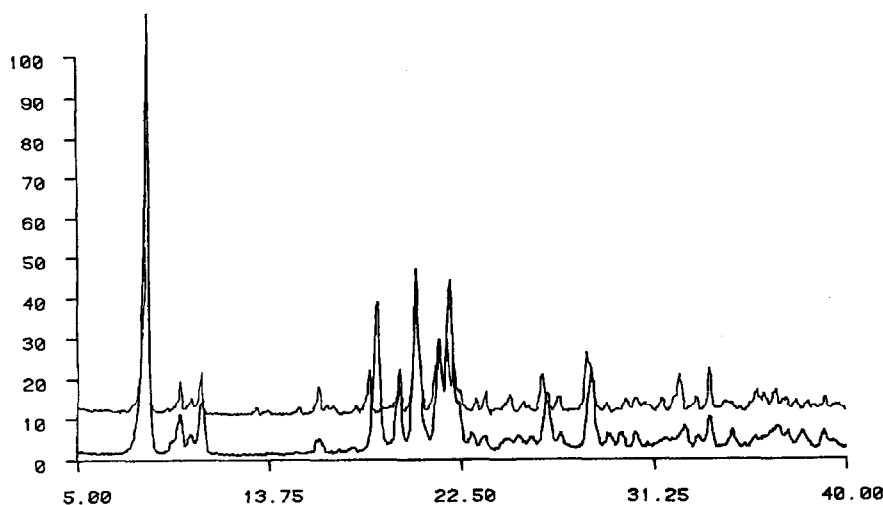


Fig. 1. Superposed X-ray powder patterns for decaphenylstannocene (I) (upper) and decaphenylgermanocene (III) (lower).

radical and a lead mirror. Its mass spectrum exhibits $m/e = 1098 (< 1)$ $[(C_6H_5)_5C_5]_2Pb]^+$, 653(100) $[(C_6H_5)_5C_5Pb]^+$, 446(48) $[(C_6H_5)_5C_5H]^+$ and 445(45) $[(C_6H_5)_5C_5]^+$.

The S_{10} symmetry of I demands 16 Raman and 12 infrared fundamentals (A_{1g} , E_{1g} , E_{2g} , and A_{1u} , E_{1u} , respectively (the phenyl groups being treated as rigid bodies)), and the center of symmetry at the metal site permits invoking the mutual-exclusion rule. However, owing to overlapping phenyl absorptions and the poorer quality Raman data for the colored compounds, a complete assignment of all the vibrational modes could not be made. Far infrared spectroscopy (400–50) yields bands that, as for $E = Fe, Ru$ and Ni [15], can be assigned to the A_{1u} ν_{asym} ring–metal–ring stretch (164, 149 and 135 for $E = Ge$ (III), Sn (I) and Pb (IV) derivatives, respectively) which undergo a much larger shift on change of E than the A_{1g} ν_{sym} (153, 138 and 134, respectively) in the Raman (2000–100 cm^{-1}). We do not regard this evidence as being conclusive for the three compounds being isostructural.

X-Ray powder diffraction patterns of the $E = Ge$ (III) and Sn (I) ($Cu-K_{\alpha_1}$, $E = Pb$ (IV) failed to diffract) derivatives each show prominent peaks at similar positions, but the patterns are not rich enough to establish isomorphism unequivocally (see Fig. 1).

Pentaphenylstannocene (II) from η^5 -cyclopentadienyltin(II) chloride [16] could be recrystallized from toluene to yield (23%) light-yellow, monoclinic plates which are moderately air-sensitive, m.p. 150°C (decomp). (Found: C, 77.45; H, 5.22; Sn, 16.62. $C_{47}H_{38}Sn$ calc: C, 78.24; H, 5.31; Sn, 16.45%). Its mass spectrum exhibits $m/e = 630 (< 1)$ $[(C_6H_5)_5C_5SnC_5H_5]^+$, 565(88) $[(C_6H_5)_5C_5Sn]^+$, 446(100) $[(C_6H_5)_5C_5H]^+$, 185(81) $[C_5H_5Sn]^+$ and 120(8%) Sn^+ .

The ^{119m}Sn Mössbauer spectra at 78 K of I and II (isomer shift (IS) 3.75, 3.67 $mm\ s^{-1}$; quadrupole splitting (QS) 0.583, 0.868 $mm\ s^{-1}$) are unremarkable in the sense that these parameters are very similar to those reported for the parent stannocene and are notable only for the small QS value for formally tin(II) species.

Decabenzylstannocene, $[\eta^5-(C_6H_5CH_2)_5C_5]_2Sn(II)$ (V) which is bent ($< 155.9(1)^\circ$) also exhibits conventional Mössbauer parameters (IS 3.96; QS 0.60 mm s $^{-1}$) [11]. Examining the data [17,18] for structurally authenticated [19–23] stannocene derivatives, there seems to be no correlation between the QS and the angle of bending or nature of the attached groups, except when the substituent group contains a donor atom which can coordinate directly to a neighboring tin as in $\eta^5-C_5H_5SnC_5H_4C(O)R-\eta^5$, (QS 1.92–2.21 mm s $^{-1}$) [24] or in stannocenophanes such as *ortho*- (1.85) and *para*- (1.29) $C_6H_4(CH_2C_5H_4-\eta^5)_2Sn(II)$ and in *meta*- $C_6H_4(CH_2C_5H_4-\eta^5-SnC_5H_5-\eta^5)_2$ (2.08 mm s $^{-1}$) [25]. The IS determined from the Mulliken populations from a recent Fenske–Hall MO calculation gave a value of 3.56 (3.60 without d -functions) for stannocene [26], in fair agreement with the experimental value of 3.74 mm s $^{-1}$ [27], but the computed value for I of 4.09 (4.48 without d -functions) [26] signals a much higher electron density at the tin(II) center than that corresponding to the experimentally observed IS value (3.75 mm s $^{-1}$).

The slopes of the temperature-dependence of the areas of the ^{119m}Sn resonances [18], $\ln A/dT$, are 1.704, 1.677 and 1.405 K $^{-1} \times 10^2$ for I, II and V, respectively. These relatively large values are consistent with large mean amplitudes of vibration of the tin atoms which are not very tightly bound [18]. However, the area ratios of the two components of the doublets are also temperature-dependent and thus the motion of the tin atoms is not isotropic in these stannocenes. Assuming that the charge distribution is elongated along the axes perpendicular to the cyclopentadienyl ring planes, i.e. prolate, then $x_{\parallel}^2 > x_{\perp}^2$, i.e., the excursions of the tin atom have greater amplitudes parallel to the rings which apparently squeeze the metal atoms which then squirt in a direction orthogonal to the ring normals.

A structure determination by X-ray diffraction (Tables 1 and 2) indicates that pentaphenylstannocene (II) [28*] is bent (see Fig. 2). It is less open (smaller β - or α -angles at tin) than I [1] or decamethylstannocene [12], but more than stannocene [29,30] itself or its 1,1-dimethyl derivative [31] (see Table 3). Increasing the steric volume of the cyclopentadienyl ring widens the angle in stannocenes, but then so

Table 1

Experimental crystallographic data ^a for pentaphenylstannocene, $\eta^5-(C_6H_5)_5C_5Sn^{II}C_5H_5-\eta^5 \cdot C_6H_5CH_3$

Formula: $Sn_1C_{47}H_{38}$	2θ range: 3–53°
Mol. wt.: 721.52 dalton	Max. scan time: 60 s
Cryst. dims: 0.10 × 0.38 × 0.50 mm	Scan angle: 0.80 + 0.20 tan θ
Cryst. syst.: monoclinic	Monitor reflections: 3 measured for orientation
Space group: $P2_1/c$	check every 200 reflections; 3 measured for
Cell dims ^b : a 13.357(5), b 10.139(3), c 26.967(5) Å, β 100.96(2)°	intensity check every 2 h
V 3585(2) Å ³	Variation in monitors: 2.4%
$Z = 4$	Total data collected: 7240
Density(calc) 1.336 g cm $^{-3}$	Unique data: 6961
Radiation: Mo- K_{α} (λ 0.71069 Å)	Observed data with $I_0 \geq 3\sigma(I)$: 5220
Temperature: 138(2) K	$\mu(Mo-K_{\alpha})$ 6.7 cm $^{-1}$
Monochromator: graphite crystal	$F(000)$: 1480 e
	$R = 0.038$
	$R_w = 0.045$
	$w = (\sigma_F)^{-2}$

^a Estimated standard deviations for the last digit are in parentheses. ^b Lattice constants calculated from 24 high angle reflections.

Table 2

Atomic positional parameters ^a for pentaphenylstannocene, $\eta^5\text{-}(\text{C}_6\text{H}_5)_5\text{C}_5\text{Sn}^{\text{II}}\text{C}_5\text{H}_5\text{-}\eta^5$

Atom	x	y	z
Sn(1)	0.77523(2)	0.52706(3)	0.35899(1)
C(1)	0.6959(2)	0.2851(3)	0.3515(1)
C(2)	0.7961(2)	0.2554(4)	0.3413(1)
C(3)	0.8046(2)	0.3083(3)	0.2927(1)
C(4)	0.7115(2)	0.3732(3)	0.2709(1)
C(5)	0.6449(2)	0.3595(3)	0.3079(1)
C(11)	0.6534(3)	0.2381(4)	0.3966(1)
C(12)	0.6775(3)	0.1121(4)	0.4180(2)
C(13)	0.6389(3)	0.0690(4)	0.4608(2)
C(14)	0.5743(3)	0.1478(5)	0.4835(2)
C(15)	0.5480(3)	0.2714(4)	0.4619(2)
C(16)	0.5871(3)	0.3159(4)	0.4196(1)
C(21)	0.8793(2)	0.1819(4)	0.3760(1)
C(22)	0.9333(3)	0.0855(4)	0.3543(1)
C(23)	1.0158(3)	0.0207(4)	0.3851(2)
C(24)	1.0439(3)	0.0506(4)	0.4371(2)
C(25)	0.9893(3)	0.1439(4)	0.4597(2)
C(26)	0.9079(3)	0.2091(4)	0.4290(2)
C(31)	0.8962(3)	0.3002(4)	0.2683(1)
C(32)	0.8946(3)	0.2372(4)	0.2208(1)
C(33)	0.9821(3)	0.2262(4)	0.1997(2)
C(34)	1.0726(3)	0.2792(4)	0.2261(2)
C(35)	1.0763(3)	0.3429(4)	0.2735(2)
C(36)	0.9885(3)	0.3537(4)	0.2949(1)
C(41)	0.6893(2)	0.4328(3)	0.2179(1)
C(42)	0.7595(3)	0.5156(4)	0.2007(1)
C(43)	0.7401(3)	0.5681(4)	0.1506(2)
C(44)	0.6499(3)	0.5405(4)	0.1169(2)
C(45)	0.5794(3)	0.4584(4)	0.1335(1)
C(46)	0.5990(3)	0.4043(4)	0.1830(1)
C(51)	0.5354(2)	0.3988(4)	0.2959(1)
C(52)	0.4587(3)	0.3084(4)	0.3007(1)
C(53)	0.3575(3)	0.3421(4)	0.2844(2)
C(54)	0.3304(3)	0.4640(4)	0.2627(2)
C(55)	0.4051(3)	0.5559(4)	0.2588(2)
C(56)	0.5065(3)	0.5236(4)	0.2754(1)
C(6)	0.7026(4)	0.7664(4)	0.3679(2)
C(7)	0.7993(3)	0.7793(4)	0.4001(2)
C(8)	0.8042(4)	0.6949(5)	0.4426(2)
C(9)	0.7100(3)	0.6275(4)	0.4374(2)
C(10)	0.6471(3)	0.6725(4)	0.3917(2)
C(00)	0.3781(4)	0.5975(5)	0.3998(2)
C(01)	0.2757(3)	0.5656(4)	0.4128(2)
C(02)	0.2153(4)	0.6642(5)	0.4281(2)
C(03)	0.1212(4)	0.6329(6)	0.4395(2)
C(04)	0.0853(4)	0.5037(5)	0.4365(2)
C(05)	0.1451(4)	0.4076(5)	0.4212(2)
C(06)	0.2392(3)	0.4369(4)	0.4097(2)

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

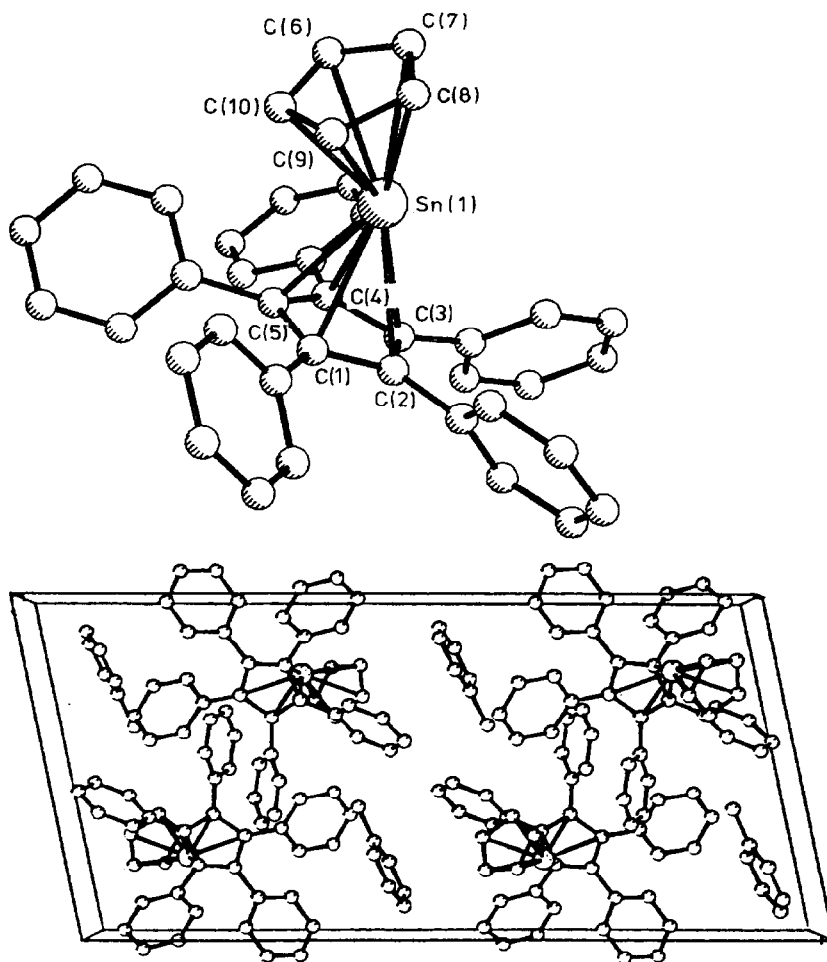


Fig. 2. (a) Pentaphenylstannocene (II), $\eta^5\text{-(C}_6\text{H}_5)_5\text{C}_5\text{Sn}^{\text{II}}\text{C}_5\text{H}_5\text{-}\eta^5$, showing the atomic numberings. (b) The unit cell of II·toluene, $\eta^5\text{-(C}_6\text{H}_5)_5\text{C}_5\text{Sn}^{\text{II}}\text{C}_5\text{H}_5\text{-}\eta^5\cdot\text{C}_6\text{H}_5\text{CH}_3$ viewed down the y -crystallographic axis.

does electron withdrawal. Both effects operate in the same direction in the phenyl-substituted systems. Charge delocalization into the phenyl rings is possible since these groups are not antiparallel to their attached cyclopentadienyl ring (torsion angles between the ring planes are $37.3(2)$ – $59.6(1)^\circ$). The tin distance from the pentaphenylcyclopentadienyl ring is longer (by 0.086 \AA) than in the decaphenyl analogue [1]; and from the cyclopentadienyl ring is shorter (by 0.030 \AA) than in stannocene [29,30]. The situation is reversed in the recently solved structure of $\eta^5\text{-(C}_6\text{H}_5)_5\text{C}_5\text{FeC}_5\text{H}_5\text{-}\eta^5$ where the iron distance from the pentaphenylcyclopentadienyl ring plane is shorter (by 0.017 \AA) than to the plane of the unsubstituted C_5H_5 ring [38].

Other distances and angles in II are unexceptional. The range of $d(\text{C}-\text{C})$ values, $1.416(6)$ – $1.433(6)$ and their average, 1.424 , in the cyclopentadienyl ring are like those seen before, while the $1.430(5)$ – $1.463(4)$ and their average, 1.447 in the

Table 3
Angular parameters for stannocenes^a

Compound	Technique	d, d' (Å) ^b	α (°) ^c	β (°) ^d	γ (°) ^e	b, b' (Å) ^f	c, c' (Å) ^g	Ref.
$(\eta^5\text{-C}_5\text{H}_5)_2\text{Sn}^{\text{II}}$	<i>h</i>	0.0 ⁱ	~ 55	~ 125	$\beta = \gamma$ ⁱ	2.42 ^j	$b = c$	29
	<i>k, l</i>	<i>m</i> 0.21(4), 0.21(4) <i>m</i> 0.34(3), 0.40(3)	46(1) 47(1)	134(1) ⁿ 133(1) ⁿ	143(2) ^o 147(1) ^o	2.401(1), 2.401(1) 2.356(2), 2.417(2)	2.41(4), 2.41(4) 2.38(3), 2.45(3)	30 30
$(\eta^5\text{-CH}_3\text{C}_2\text{H}_4)_2\text{Sn}^{\text{II}}$	<i>h</i>	0.0 ⁱ	50(6)	130(6) ⁿ	$\beta = \gamma$	2.400(6)	$b = c$	31
	<i>k, l</i>	<i>p</i> 0.208(8), 0.277(8) <i>p</i> 0.195(8), 0.240(8)	36.4(6) 35.4(4)	143.6 144.6	154.9(2) 154.8(2)	2.391(2), 2.383(2) 2.380(2), 2.387(2)	2.400(6), 2.399(5) 2.388(6), 2.399(6)	12 12
$\eta^5\text{-}(\text{C}_6\text{H}_5)_3\text{C}_5\text{Sn}^{\text{II}}\text{C}_5\text{H}_5\text{-}\eta^5$ (II)	<i>k</i>	0.352(4) ^q , 0.298(5) ^r	43.9(3)	136.1(3) ⁿ	151.1(1)	2.4620(3) ^q , 2.3724(3) ^r	2.487(4) ^q , 2.391(5) ^r	^s
$[\eta^5\text{-}(\text{C}_5\text{H}_5)_5\text{C}_5]_2\text{Sn}^{\text{II}}$ (I)	<i>k</i>	0.0	0	180	$\beta = \gamma$	2.401(6), 2.401(6)	$b = c$	1
	<i>k, l</i>	0.21(6), [0.00(8)]	16(4)	164(4) ⁿ	162(2)	2.27(1), 2.68(1)	2.28(5), 2.68(7)	32
	<i>k</i>	0.29(1), 0.34(1)	46.6(5)	133.4(5) ⁿ	148.6(6)	2.3618(8), 2.3655(7)	2.38(1), 2.39(1)	33
$[\eta^5\text{-C}_2\text{H}_5\text{Co-4,5-(C}_2\text{H}_5)_2\text{-1,3-(CH}_3)_2\text{-C}_2\text{B}_2\text{C-1,3-}\eta^5]_2\text{Sn}^{\text{II}}$	<i>k, l</i>	0.566(5), 0.584(5)	66.4(1)	114	141.5(2)	2.3044(3), 2.3125(2)	2.373(5), 2.385(5)	34
	<i>k</i>	0.657(5), 0.610(6)	68.1(2)	112	142.2(3)	2.3260(3), 2.3057(3)	2.417(5), 2.385(6)	34
$\eta^5\text{-C}_3\text{H}_5\text{Sn}^{\text{II}}\text{Cl}$	<i>k</i>	0.44	—	106.6	117.4	2.30	2.34	35
	<i>k</i>	0.48	46.5	133.5				36

^a α , γ , b , b' , c and c' were calculated by us from atomic positional parameters using our TANGLE program. The estimated standard deviations are given in parentheses. ^b Distance between the ring centroid and the normal to the tin atom, calculated according to $d = (c^2 - b^2)^{1/2}$ and $d' = (c'^2 - b'^2)^{1/2}$, respectively (Pythagorus). ^c Angle made by the two ring planes at their intersection. ^d Angle made by the two projections, normals b, b' , of the tin atom onto the ring planes. ^e Angle made by the two projections, c, c' , of the tin atom onto the ring centroids. ^f The projections of the tin atom onto the ring plane; the ring normals to the tin atom. ^g The lines joining the ring centroids to the tin atom. ^h Gas-phase electron diffraction. ⁱ Assumed. ^j From ref. 31. ^k X-ray diffraction. ^l Two independent molecules in the unit cell. ^m Eclipsed rings. ⁿ Calculated according to $\beta = 180^\circ - \alpha$. ^o These values were reversed in ref. 30. ^p Staggered rings. ^q η^5 -Pentaphenylcyclopentadienyl ring. ^r η^5 -Cyclopentadienyl ring. ^s This work. ^t Ref. 32 states that the crystals were of poor quality, and hence the geometric parameters are not very accurate; $R = 0.132$.

pentaphenylcyclopentadienyl ring are longer than in I (1.414–1.450; 1.428 (av.)), similar in $[\eta^5-(C_6H_5)_5C_5Ni[\eta^3-C_3(C_6H_5)_3]Ni(C_6H_5)_4C_4-\eta^4]$ (1.41–1.48; 1.44 (av.)) [37], or in the ferrocene analogue (1.423–1.450; 1.434 (av.)) [38]. The range of $d(Sn-C)$ values, 2.541(5)–2.792(5) and their average, 2.679, to the cyclopentadienyl ring are also like those seen before, while the 2.627(3)–2.921(4) and their average, 2.773, to the pentaphenylcyclopentadienyl ring are longer (by 0.08 Å (av)) than in I [1].

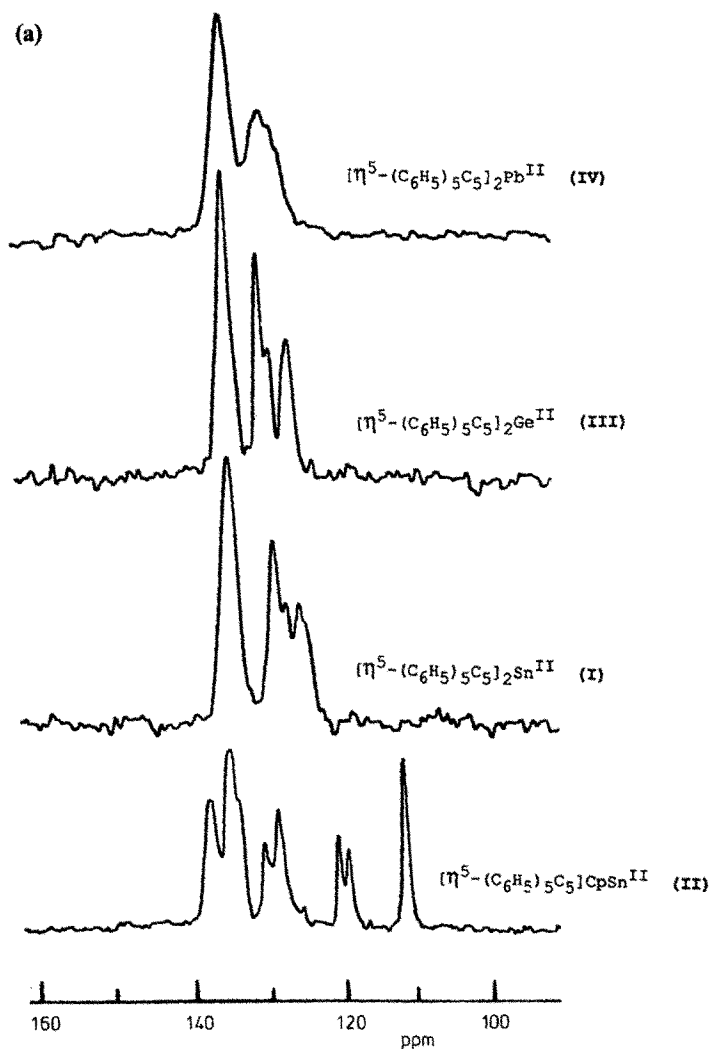


Fig. 3. Delay-decoupled ^{13}C CPMAS spectra of penta- and decaphenylmetallocenes. (a) Carbons without directly bonded hydrogens at low field (60 MHz for 1H) where resonance areas are quantitative. (b) Carbons with directly bonded hydrogens at low field (60 MHz for 1H). (c) Carbons without directly bonded hydrogens at high field (200 MHz for 1H) with improved resolution. (d) Carbons with directly bonded hydrogens at high field (200 MHz for 1H).

One solid-state measurement that does not depend on growing a single crystal is ^{13}C cross-polarization magic angle (C-13 CPMAS) NMR. Delay-decoupled spectra of I–IV contain only the cyclopentadienyl and C_1 -phenyl resonances, i.e., those of carbons without directly bonded hydrogens. These resonances, which are obscured by the remaining phenyl carbons in the fully decoupled spectrum, are expected to be diagnostic of the cyclopentadienyl-ring orientation. A comparison (Fig. 3) of I–IV at low ($\text{H}-1$ equivalent of 60 MHz) field, where the resonance intensities are

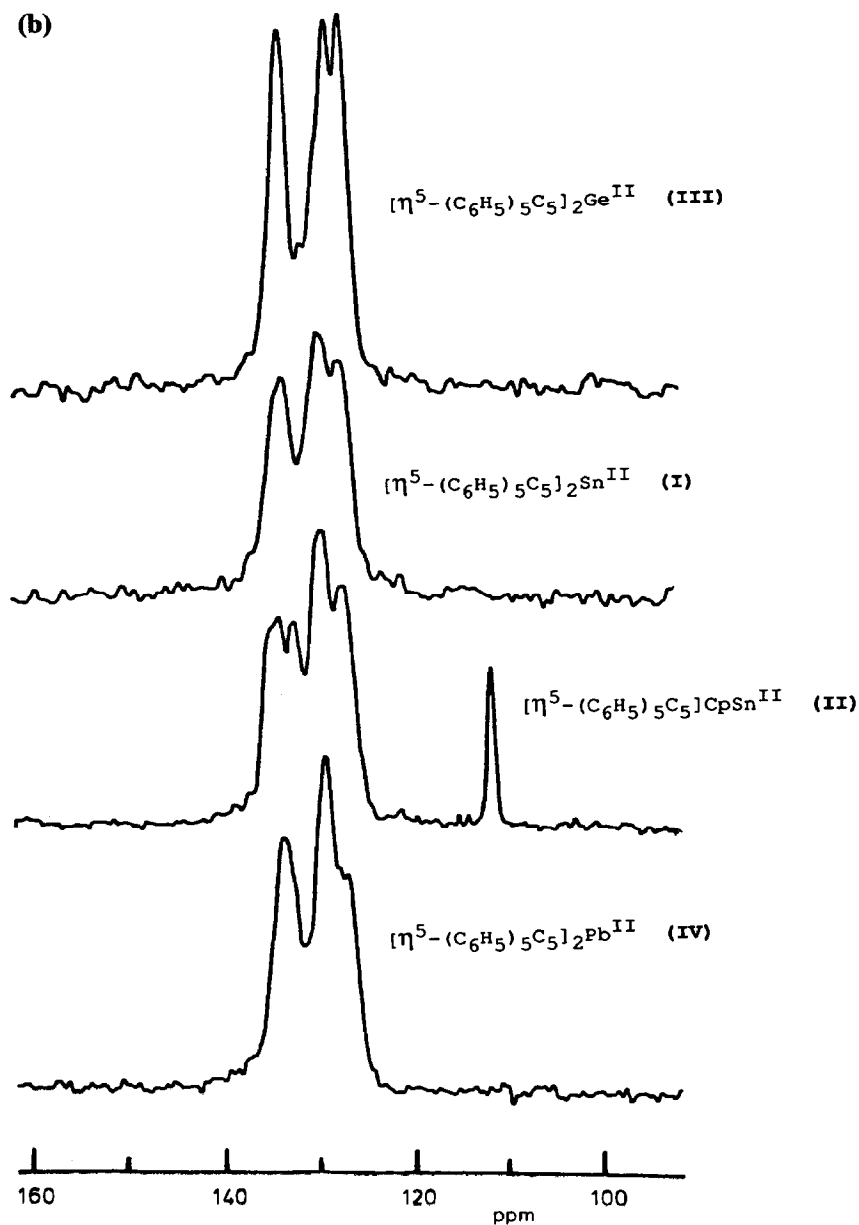


Fig. 3 (continued).

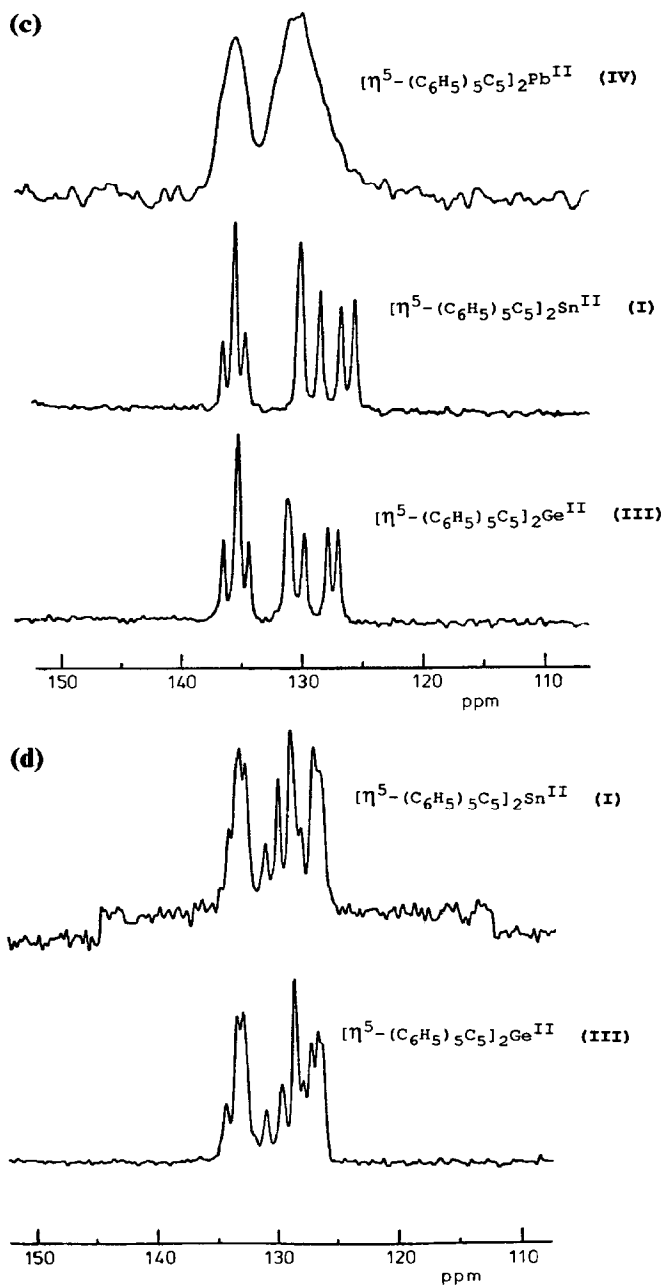


Fig. 3 (continued).

quantitative, and at high (H-1 equivalent of 200 MHz) field, with improved resolution, reveals strong similarities for the decaphenyl compounds (the amorphous lead derivative produces broader lines) [39]. Together with the X-ray powder patterns, these results suggest that all three decaphenylmetallocenes are isostructural, with parallel cyclopentadienyl rings.

Decamethylsilicocene, $[\eta^5\text{-(CH}_3)_5\text{C}_5]_2\text{Si}$, has recently been synthesized. Its crystals contain two structurally distinct molecules in the unit cell in a 2/1 ratio, one bent and one with the rings staggered and perfectly parallel [41]. We conclude from this example of co-existing forms that the energy difference between variously bent fourth main-group metallocenes is small.

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References

- 1 M.J. Heeg, C. Janiak, and J.J. Zuckerman, *J. Am. Chem. Soc.*, 106 (1984) 4259.
- 2 Decaphenyl transition-metal [3–6], lanthanide [7], and actinide [8] cyclopentadienyl sandwich compounds fail to form from this route.
- 3 P.L. Pauson, *J. Am. Chem. Soc.*, 76 (1954) 2187.
- 4 S. McVey and P.L. Pauson, *J. Chem. Soc.*, (1965) 4312.
- 5 J. Powell and N.I. Dowling, *Organometallics*, 2 (1983) 1742.
- 6 D.W. Slocum, S. Duraj, J.L. Cmarik, K.M. Simpson, and D.A. Owen, in C. Carraher, C.U. Pittman and J. Sheats (Eds.), *Met.-Containing Polym. Syst.*, Plenum Press, New York, 1985, pp. 59–68.
- 7 C. Janiak and H. Schumann, unpublished results.
- 8 R.T. Paine, private communication, 1985.
- 9 J.V. Scibelli and M.D. Curtis, *J. Am. Chem. Soc.*, 95 (1973) 924.
- 10 A. Bonny, A.D. McMaster and S.R. Stobart, *Inorg. Chem.*, 17 (1978) 935.
- 11 H. Schumann, C. Janiak, E. Hahn, C. Kolax, J. Loebel, M.D. Rausch, J.J. Zuckerman and M.J. Heeg, *Chem. Ber.*, 119 (1986) 2656.
- 12 P. Jutzi, F. Kohl, P. Hofmann, C. Krüger and Y.-H. Tsay, *Chem. Ber.*, 113 (1980) 757.
- 13 L.D. Dave, D.F. Evans and G. Wilkinson, *J. Chem. Soc.*, (1959) 3684.
- 14 E.O. Fischer and H. Grubert, *Z. Naturforsch. B*, 11 (1956) 423. *Z. Anorg. Allg. Chem.*, 286 (1956) 237.
- 15 E.R. Lippincott and R.D. Nelson, *Spectrochim. Acta*, 10 (1958) 307.
- 16 P.G. Harrison and J.J. Zuckerman, *J. Am. Chem. Soc.*, 91 (1969) 6885.
- 17 J.J. Zuckerman, *Adv. Organomet. Chem.*, 9 (1970) 21.
- 18 J.J. Zuckerman, in R.H. Herber (Ed.), *Chemical Mössbauer Spectroscopy*, Plenum Press, New York, 1984, p. 267.
- 19 P.G. Harrison, *Coord. Chem. Rev.*, 20 (1976) 1.
- 20 J.A. Zubietta and J.J. Zuckerman, *Prog. Inorg. Chem.*, 24 (1978) 251.
- 21 P.J. Smith, *J. Organomet. Chem. Libr.*, 12 (1981) 251.
- 22 J.D. Donaldson and S.M. Grimes, *Rev. Silicon, Germanium, Tin, Lead Compd.*, 8 (1984) 1.
- 23 S.-W. Ng and J.J. Zuckerman, *Adv. Inorg. Chem. Radiochem.*, 29 (1985) 297.
- 24 T.S. Dory, J.J. Zuckerman and M.D. Rausch, *J. Organomet. Chem.*, 281 (1985) C8.
- 25 T.S. Dory and J.J. Zuckerman, *J. Organomet. Chem.*, 264 (1984) 295.
- 26 R.L. Williamson and M.B. Hall, *Organometallics*, 5 (1986) 2142.
- 27 P.G. Harrison and J.J. Zuckerman, *J. Am. Chem. Soc.*, 92 (1970) 2577.
- 28 Pentaphenylstannocene (II), $\eta^5\text{-(C}_6\text{H}_5)_5\text{C}_5\text{SnC}_5\text{H}_5\text{-}\eta^5$, $\text{C}_{40}\text{H}_{30}\text{Sn}$, crystallizes from toluene with one molecule of solvent in yellow monoclinic platelets, m.p. 150 °C (decomp), in the space group $P2_1/c$.

with a 13.357(5), b 10.139(3), c 26.967(5) Å, β 100.96(2)°, V 3585(2) Å³, $Z = 4$, ρ_{calcd} 1.336 g cm⁻³. The structure was determined by difference-Fourier techniques from 6961 unique reflections measured at 138(2) K on an Enraf-Nonius CAD/4 automatic diffractometer with monochromatized Mo-K α radiation to a final conventional R value of 0.038 and R_w of 0.045 for the 5220 reflections included in the least-squares sums. Computations were performed by using local modifications of SHELX-76 programs (G.M. Sheldrick, 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. 75. Atomic coordinates are given in Table 2. Tables of interatomic distances and angles, least-squares planes and dihedral angles, thermal parameters and hydrogen atomic parameters are available on request from H.S.

- 29 A. Almenningen, A. Haaland and T. Motzfeldt, *J. Organomet. Chem.*, 7 (1967) 97.
- 30 J.L. Atwood, W.E. Hunter, A.H. Cowley, R.A. Jones and C.A. Stewart, *J. Chem. Soc., Chem. Commun.*, (1981) 925.
- 31 J. Almlöf, L. Fernholt, K. Faegri, A. Haaland, B.E.R. Schilling, R. Seip and K. Taugbøl, *Acta Chem. Scand., Sect. A*, 37 (1983) 131.
- 32 A.H. Cowley, P. Jutzi, F.X. Kohl, J.G. Lasch, N.C. Norman and E. Schlüter, *Angew. Chem., Int. Ed. Engl.*, 23 (1984) 616.
- 33 A.H. Cowley, J.G. Lasch, N.C. Norman, C.A. Stewart and T.C. Wright, *Organometallics*, 2 (1983) 1691.
- 34 H. Wadepohl, H. Pritzkow and W. Siebert, *Organometallics*, 2 (1983) 1899.
- 35 K.D. Bos, E.J. Bulten, J.G. Noltes and A.L. Spek, *J. Organomet. Chem.*, 99 (1975) 71.
- 36 G. Schmid, D. Zaika and R. Boese, *Angew. Chem., Int. Ed. Engl.*, 24 (1985) 602.
- 37 H. Hoberg, R. Krause-Göing, C. Krüger and J.C. Sekutowski, *Angew. Chem., Int. Ed. Engl.*, 16 (1977) 183.
- 38 F.B. McCormick, private communication.
- 39 Solid-state ¹³C nuclear resonance spectra were acquired at resonant frequencies of 15.1 and 50.3 MHz with cross polarization and magic-angle spinning at 2300 and 3000 Hz, respectively. Delayed proton decoupling was begun 45 μ s after the conclusion of the cross-polarization interval [40]. Chemical shift assignments in the decaphenylmetallocene spectra for the cyclopentadienyl and phenyl carbons were not possible with the available data, although the resonances in the low-field spectra divide at 130 ppm into two groups of equal intensity. These intensities vary in the high-field case because of inequivalent losses to spinning sidebands, but the intra-group profiles remained constant. Sidebands were significant only in the high-field spectra owing to our inability to increase spinning rates in proportion to the increase in field strength.
- 40 S.J. Opella and M.H. Frey, *J. Am. Chem. Soc.*, 101 (1979) 5854.
- 41 P. Jutzi, D. Kanne and C. Krüger, *Angew. Chem., Int. Ed. Engl.*, 25 (1986) 164.