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Preliminary communication

FUNCTIONALLY-SUBSTITUTED STANNOCENES. η^5-ACETYL- AND ALKOXYCARBONYL-CYCLOPENTADIENYLTIN(II) DERIVATIVES*

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Summary

η^5-Acetyl- and alkoxycarbonyl-cyclopentadienyltin(II) compounds, η^5-$RC(=O)C_5H_4SnC_5H_5$-η^5 where $R = CH_3, OCH_3$ and OC_2H_5, are synthesized from the substituted cyclopentadienylsodium salts with η^5-cyclopentadienyltin(II) chloride and characterized by physical properties, analytical data, IR, mass, NMR and tin-119m Mössbauer spectroscopies.

We are interested in perturbing the stereochemistry of stannocenes through substitution of the cyclopentadienyl rings in order to enhance the Lewis basicity of the tin(II) center. Our original claim that the lone pair of electrons at tin engages in donor activity [1] toward BF_3 has had to be withdrawn since the solid product of the reaction of stannocene in THF with the BF_3 etherate [2] is $\{[BF_4]^-(\mu\text{-}\eta^5\text{-}C_5H_5)_2Sn[\mu\text{-}\eta^5\text{-}C_5H_5Sn]^+THF\}_n$, in which the lone pairs play no role in bonding.

At one end of the scale lies the perphenylated decaphenylstannocene with perfectly parallel, staggered cyclopentadienyl rings (S_{10} symmetry) [3], the first molecule to violate decisively the Valence-Shell Electron-Pair Repulsion (VSEPR) model. Pentaphenylstannocene, η^5-$C_5H_5SnC_5(C_6H_5)_5$-η^5, is, on the other hand, bent through 151° at tin [4]. The stannocenophanes based on α,α'-dicyclopentadienyl-*ortho*-, *-meta*- and *-para*-xylene [5] are designed to be bent through larger angles, but no structural data are yet available, In stannocene [6] and deca-

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methylstannocene [7] the angles are 148.0° and 143.7° for the former and 144° and 143.6° for the latter (two independent molecules in each).

Another approach is to utilize strongly polarizing functional groups and depart from the strictly hydrocarbon tin derivatives [8]. The recent recipes of Rausch [12] open new avenues in this regard, and we communicate here our first results using acetyl- and alkoxycarbonyl-containing ligands.

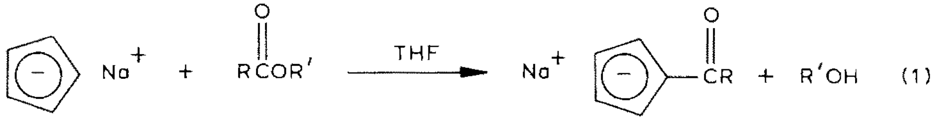
Acetyl-[13,14], methoxycarbonyl- [13,14] and ethoxycarbonyl-cyclopentadienylsodium were prepared from cyclopentadienylsodium with methyl acetate and dimethyl and diethyl carbonate, respectively, in refluxing THF (eq. 1)

TABLE 1

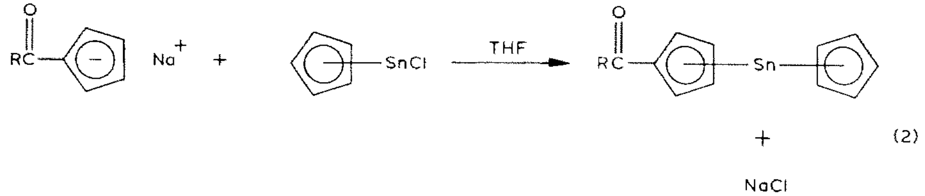
PROPERTIES OF η^5-$C_5H_5SnC_5H_4C(=O)R$-η^5

	R = CH_3	R = OCH_3	R = OC_2H_5
M.p.	>260°C	>260°C	>260°C
Color	light brown	off-white	light brown
Yield	100%	94%	89%
Sn (calcd/found)	40.90/41.57	38.67/40.57	36.52/35.87
tin-119m Mössbauer[a] IS	2.98±0.03 mm s^{-1}	2.84±0.03 mm s^{-1}	2.87±0.03 mm s^{-1}
QS	2.21±0.06 mm s^{-1}	2.21±0.06 mm s^{-1}	1.92±0.06 mm s^{-1}
^{1}H NMR[b] (H(5),s,C_5H_5-η^5)	5.8 ppm	5.8 ppm	5.8 ppm
(H(4),m,C_5H_4-η^5)	5.7, 5.9 ppm	5.7, 5.9 ppm	5.6, 6.0 ppm
(H(3),s,R)	0.3 ppm	0.9 ppm	—
(H(3),t,CH_3)	—	—	1.68 ppm
(H(2),q,CH_2)	—	—	4.15 ppm
ν(C=O)[c]	1650 cm^{-1}	1615 cm^{-1}	1658 cm^{-1}
ν(C—O)[c]	—	1340 cm^{-1}	
Mass spec at 12 eV[d]			
Assignment, *m/e* (abundance)			
$[\eta\text{-}C_5H_5SnC_5H_4C(=O)R]^{+\cdot}$	292 (2.5)	—	
$[\eta^5\text{-}C_5H_5SnC_5H_4C(=O)\text{-}\eta^5]^+$	—	277 (27.1)	
$[\eta^5\text{-}C_5H_5SnC_5H_4C]^+$	—	261 (7.4)	
$[SnC_5H_4C(=O)CH_3]$	227 (0.3)	—	
$[SnC_2H_3C(=O)OCH_3]^{+\cdot}$	—	206 (11.6)	
$[\eta^5\text{-}C_5H_5Sn]^+$	185 (37.7)	—	
$[SnC(=O)OCH_3]^+$	—	179 (8.0)	
$[SnO_2CH_3]^+$	—	167 (76.4)	
$[SnO_2]^{+\cdot}$	—	152 (7.0)	
$[SnO]^{+\cdot}$	—	136 (13.1)	
$[C_5H_4C(=O)OCH_3+H]^{+\cdot}$	—	124 (100.0)	
$[Sn]^{+\cdot}$	120 (16.4)	—	
$[C_5H_4C(=O)OH]^+$		109 (7.5)	
$[C_5H_4C(=O)CH_3+H]^{+\cdot}$	108 (5.7)	—	
$[C_5H_4C(=O)CH_3]^+$	107 (4.7)	—	
$[C_5H_4C(=O)CH]^+$	105 (4.8)	—	
$[C_5H_4OCH_3+H]^{+\cdot}$	—	96 (22.6)	
$[C_5H_4CO]^{+\cdot}$	92 (5.0)	—	
$[C_5H_5OH]^{+\cdot}$	—	82 (12.1)	
$[C_5H_4CH]^+$	77 (8.6)	—	
$[C_5H_4C]^{+\cdot}$	76 (1.5)	—	
$[CHC(=O)OCH_3]^{+\cdot}$	66 (100.0)	—	
$[C_5H_6]^{+\cdot}$	—	72 (4.3)	
$[C_5H_5]^+$	65 (80.5)	—	
$[C_5H_4]^{+\cdot}$	64 (2.8)	—	

[a] Recorded at 77 K vs. $Ca^{119m}SnO_3$ on a Ranger Engineering spectrometer. [b] Recorded on an IBM NR-80 spectrometer in benzene-d_6. Satisfactory integrations of the η^5-C_5H_5/η^5-C_5H_4/R resonances were achieved. [c] Recorded as KBr pellets for R = CH_3 and OCH_3 and as a saturated THF solution for R = OC_2H_5 on a Beckman 4250 spectrometer calibrated with polystyrene. [d] Recorded on a Hewlett—Packard 5985B GC/MS system. The *m/e* values are based on ^{1}H, ^{12}C, ^{16}O and ^{120}Sn.



where R = CH_3, CH_3O, R′ = CH_3, and R = C_2H_5O, R′ = C_2H_5. Addition of η^5-cyclopentadienyltin(II) chloride [15] prepared according to Bos, Bulten and Noltes [16] gave off-white, infusible precipitates whose tin-119m Mössbauer isomer shift (IS) values confirm the tin(II) oxidation state [17,18] and whose mass spectra (parent ion for R = CH_3) confirm their formulation as acetyl- and alkoxycarbonyl-cyclopentadienyltin(II) derivatives (see Table 1):



Attempts to produce the symmetrically-substituted stannocenes using tin(II) chloride yielded in our hands only tin(IV) oxide, and attempts to make the trimethyl- and triphenyl-tin(IV) derivatives from the corresponding chlorides gave only bis(trimethyl)- and bis(triphenyl)tin(IV) oxide. This implies that the negative charge of these anions may reside predominantly on the carbonyl oxygen, making this site the point of attack for the above tin reagents.

The magnitudes of the quadrupole splitting (QS) values would be expected to be enhanced in the unsymmetrical title compounds, but the Mössbauer data are characterized by very large increases in QS and much smaller IS values compared with stannocene itself [15] or its 1,1′-dimethyl analogue [19] (IS = 3.74, 3.83; QS = 0.86, 0.78 mm s^{-1}, respectively). This behavior is characteristic of higher coordination at tin [17,18], and the rather low carbonyl IR stretching frequencies observed along with the infusibility and low solubility of these products argue for an associated solid bound through oxygen—tin(II) bridges. Many examples of such associated tin(II)-oxygen solids are known [20,21]. The mass spectral fragments containing both tin and carbonyl groups in Table 1 may also be bound through direct Sn—O bonds as are the products of the attempted syntheses from tin(II) and organotin(IV) chlorides (see above).

Recently the pentakis(methoxycarbonyl)cyclopentadienyl ligand has been attached to tin(II) in η^5-$(CH_3)_5C_5SnC_5(C(O)CH_3)_5$ and $Sn[C_5(C(O)CH_3)_5]_2$ [22], which contain the $C_5[C(O)OCH_3]_5$ anion with the $[\eta^5\text{-}(CH_3)_5C_5Sn]^+$ cation. In $\{[CH_3OC(O)]_5C_5\}_2Sn$ the tin(II) atom is coordinated by four carbonyl oxygen atoms of two adjacent methoxycarbonyl groups on each of two ligands [23].

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